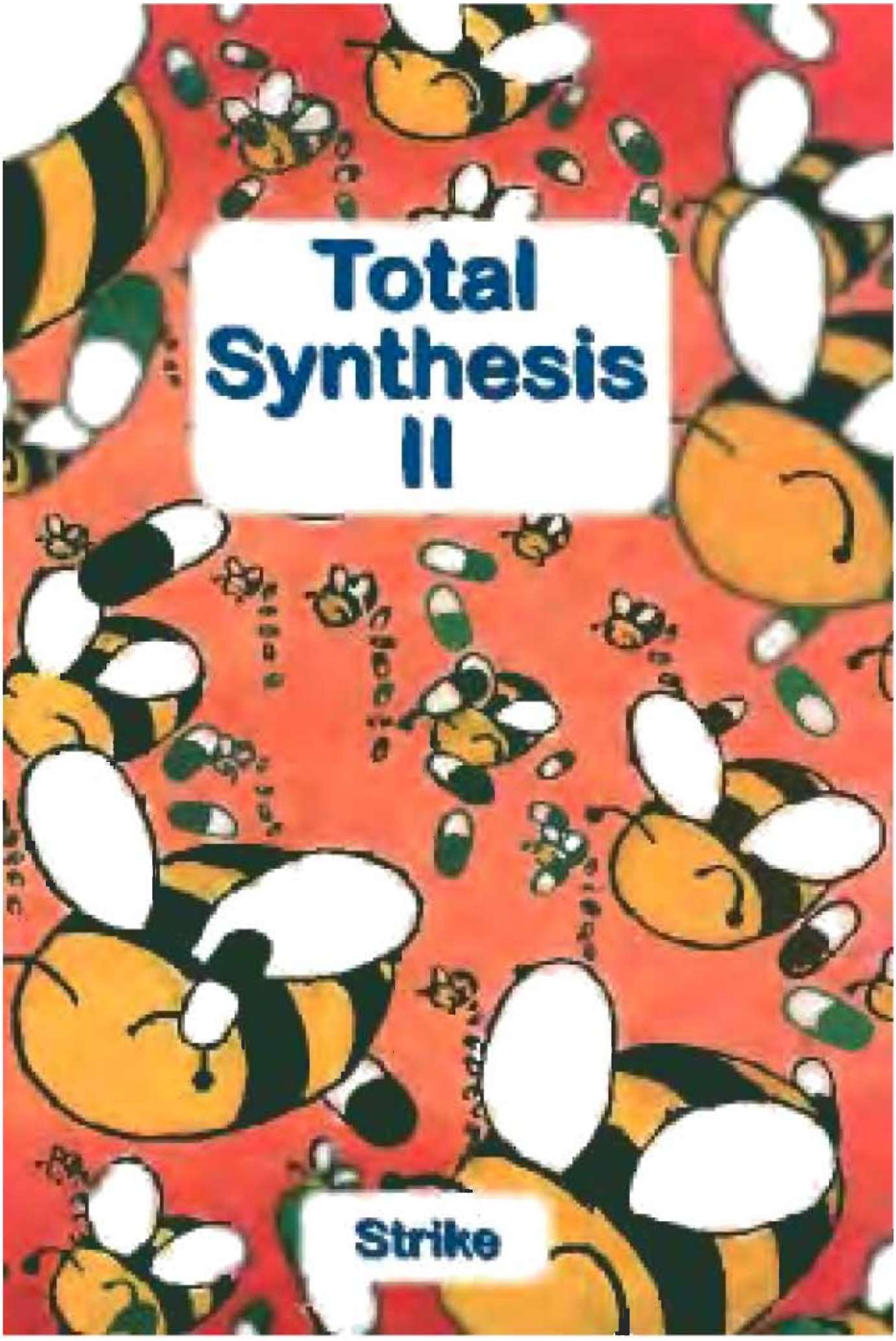
Total
Synthesis
II
Strike

DISCLAIMER

WARNING! This book is intended for informational purposes only! It is currently illegal to attempt almost any procedure depicted in this book. This book does not condone nor imply that any procedure listed herein be used by the reader or anyone else for that matter. Even if the chemistry were legal Strike would not advise anyone to try these procedures unless they have a thorough understanding of chemistry, chemical reactions and methodology. Even the most basic chemical or reaction has the potential to do great harm.

Panda Ink
2211 NW Military Hwy, Ste. 116
PMB# 115
San Antonio, TX 78213

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INTRODUCTION

You have just purchased or stolen the most comprehensive and detailed book on the underground production of ecstasy, methamphetamine and psychedelic amphetamines ever published. Strike (your host) is an ecstasy and amphetamine chemist from Texas who used to be very frustrated with the lack of common-sense information about the production of amphetamines. Strike remedied this for Strike and now Strike is gonna remedy it for you, too. This book is packed with the latest street methods for making amphetamines - written in plain English with the detail that no other book can offer.

Plus, this edition of Total Synthesis marks the first ever collaboration of the chemical underground. Throughout the book you will find recipes, secrets and discussions contributed by the worlds leading underground chemists. They have shared their knowledge so that you may get the best education available. So enjoy!

DISCLAIMER

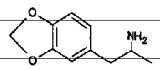
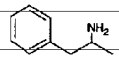
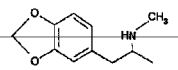
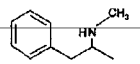
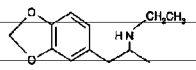
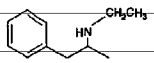
WARNING! This book is intended for informational purposes only! It is currently illegal to attempt almost any procedure depicted in this book. This book does not condone nor imply that any procedure listed herein be used by the reader or anyone else for that matter. Even if the chemistry were legal Strike would not advise anyone to try these procedures unless they have a thorough understanding of chemistry, chemical reactions and methodology. Even the most basic chemical or reaction has the potential to do great harm.

ECSTASY & AMPHETAMINES

The reasons Strike wrote this book. The reasons you're reading this book. Ecstasy is the most benign drug Strike has ever encountered. It is passive yet powerful. By powerful Strike does not mean that it incapacitates or makes one dangerous. It is, in fact, quite the opposite. Its power is in its ability to evoke a total sensory bath of tactile, visual and mental enhancement. One's perception is perfectly clear. Hallucinations are nonexistent. The feeling one has is, literally, ecstasy. Plus, it is one of the few narcotics in the world that is not physically addictive. Why this substance was taken away from the people is a question that only government-funded scientists can answer.

And let's not forget Meth (speed, crank, crystal). Then again...why don't we just forget about them. Momma said if you can't say anything nice...etc., etc.

Final Products

Ecstasy Class	Amphetamine Class
	
MDA 3,4-MethyleneDioxyAmphetamine	Amphetamine (Benzedrine)
	
MDMA 3,4-MethyleneDioxyMethAmphetamine	Methamphetamine (Speed)
	
MDEA 3,4-MethyleneDioxyEthylAmphetamine	PEA Ethylamphetamine

The ecstasy molecule itself is just an amphetamine with a couple of extra things attached to it. The chemical structures of the major ecstasy class drugs and speed class drugs can be seen in the preceding schematic:

MDA and its brother, amphetamine, are the easiest to make, involve the least watched chemicals and are the strongest. MDMA and speed, although less strong and shorter lasting, are perceived by many as 'better' because the highs they produce are smoother and more pleasant. This is not necessarily true as the degrees of differences between MDA and MDMA or amphetamine and speed are very subjective. They are equally fine in their effect except that MDA is better. The sooner the chemist accepts this, the easier her journey through underground synthesis will be in many respects. So, when Strike uses the blanket term of 'ecstasy' or 'X' throughout this book Strike may be referring to either MDA or MDMA (mostly MDA). Strike will let you know when a specific difference is required. Anyway, if one were to look at that nitrogen atom stuck on the MDA or amphetamine core one can see that as more carbon groups are added on, the weaker the drug becomes. So MDEA and PEA are even weaker than MDMA and speed, but they do retain some pretty fair activity. And a few pages away you are going to actually learn every excruciating detail of how underground chemists make every single one of these compounds!

WHERE TO BUY

So how does one go about beginning an underground laboratory? The answer is: "they don't". You see that would be illegal. Hypothetically though, one would need 3 things: a combination heating-magnetic stirring plate, chemicals and glassware. The stirplate is no problem. The chemicals and glassware are sort of a problem. But Strike is going to go over how all of these things can be bought, substituted for or made. Good production can be had with crude, makeshift equipment. But believe Strike, the most effective chemistry possible is achieved with a good heating stirplate and a ground glass distillation kit. So let's see how the good stuff can be had before we discuss the back-up plans. There are basically four types of businesses out there that cater to people needing scientific stuff.

(1) Little, local walk-up type stores
These kinds of stores carry hobby/craft supplies, gimmicky science fair projects, ant farms and a low assortment of basic scienceware products such as beakers, thermometers, scales, rubber stoppers and most of the basic chemicals such as acids, bases and solvents. These places are listed in the chemicals section of any big city's yellow pages and are relatively safe places to get most of the basic lab necessities. The drawback is that they are really expensive and don't sell very large quantities of any chemical. It is possible to have these places special order a needed chemical as long as it's not a controlled chemical.

(2) Local middlemen companies
These places are also local businesses that can be found in the chemicals section of any big city's yellow pages except that these places have some big connections. By this Strike means that they are licensed distributors for some of the biggest chemical and scienceware companies and manufacturers. Those big companies would never sell a thing to a punk like you or Strike. Even if a punk like you or Strike was to present a fake business front or

something they would scrutinize it very closely and would require proofs of clientele etc., etc.

It's needless to say that this is too much to ask of a street punk. That is where these distributors can help. They have the license and authority to sell anything (both chemical and glassware) that the chemist needs and are not subject to the same policies that the companies they sell for employ. This is not meant as a put-down but these distributors are like car salesmen. The only way they make money is through the commission on sales. This means that they tend not to care about whom they sell these other companies' products to. They just want to sell stuff. A chemist calls one of these companies and orders something simple like a thermometer or water and then pays for it promptly. Having then established an account (a foot in the door) the chemist will have gained that company's trust in knowing that she (the chemist) is a good customer. Then, next time, a little catalyst, ether or, perhaps, a distillation kit can be ordered. Having already established that the chemist is a good customer they tend not to ask for the required permit to buy glassware or as to the purpose that some chemical is needed for. And so the charade goes on.

These types of businesses are the prime choice a chemist will use to get that specialty chemical or piece of glassware. There are thousands of such places around the nation, Canada and Mexico.

(3) National distributors
If a chemist were to go down to her local university or graduate research school she could find science company catalogues in the library and in the divisional labs and offices of the research center. Representatives of every conceivable scienceware company and manufacturer like to drop off tons of their catalogues in the hope that someone will order some of their products. If the library has none, then the chemist goes up to one of the labs and asks someone if she could take a look at some of their catalogues. This is not a problem because the labs are full of graduate students who are dying for attention. Some have so many catalogues they don't use that, if asked, they would probably give the chemist some.

What the chemist is looking for are product companies that sell everything but glassware and chemicals. The reason for this is that if they know they don't sell anything that is watched then they have no reason to care who buys their stuff. In fact, they want to sell the chemist stuff very badly. The other types of catalogues to look for are those that accept credit cards and money orders as payment. These companies obviously sell to individuals. All of these companies are excellent places to stock up on everything the chemist needs, especially low priced magnetic stirplates, vacuum pumps, plasticware (great alternatives to some glassware), electronic scales and, in some instances, chemicals and glassware. These companies are just like local distributors only bigger.

(4) Big name science houses and chemical manufacturers
These include such names as Fisher, Baxter, VWR, Cole-Parmer, Alltech, Aldrich and Sigma. It is very hard to get a fledgling account with these giants, but if one can then the sky's the limit. Most chemists should be happy getting these companies' products through the distributors.

No matter what type of company the chemist chooses to purchase from it is a good idea to have some of the actual catalogues from the big name science houses and glassware manufacturers. This is because it will help to have the company's actual product catalogue number whether one is ordering from a distributor or from the company itself (looks professional, bubba!). These really big catalogues are down at the university or the chemist can request one from the company itself. They also make excellent reference books and are just plain interesting to read and daydream of the day when one can order such-and-such an apparatus as is depicted on page whatever.

So with catalogue or list of items needed in hand it is time for the chemist to order. The following is an example of how a typical call will proceed and how it will be handled by a chemist no matter what business she calls:

--Ring!Ring!--

Customer rep: "Good morning, Blah Blah Inc."
Evil chemist: "Uh, yes, this is Fake Name calling for Fake Company Name and I need to order some items or possibly open an account."
Rep: "Does your company currently have an existing account with us?"

[They always ask this whether or not they were just told that a customer is a new one]

Evil: "No, we used to have an account with Rival Scientific Company but they couldn't seem to get our orders on time."
Rep: "And what is your company's name and address?"

[They ask this first because they want to bag the chemist as customer or at least get them on a mailing list so that they can hound the chemist later to buy more of their stuff]

Evil: "Fake Company Name, at Address Of A Friend's House."

[Delivery to an apartment address is unwise and there are very few companies that will deliver science products to a P.O. box]

Rep: "O.K. Mr. Fake Name, what can we do for you today?"

Now the chemist rattles off the catalogue numbers of the things she wants and the quantity of each. After the order is confirmed the chemist asks that the entire order be shipped by overnight express and has this added to the total bill. The chemist then asks for the purchase order number of the purchase she just made so that she can include this on the payment she's going to send. The chemist uses a reputable money order and sends this money order to the company via priority overnight mail. All this rushing accomplishes two things: it shows that the chemist's company is a professional, goal- oriented company, and it also gives no one any time to second guess a thing or establish a stakeout of the delivery site.

At times it may seem that Strike is implying that buying from these companies is a cat-and-mouse affair that leaves suspicions high and traces put on one's phone line. This cannot be further from the truth. These companies want to sell their products. If they had to file notice to the DEA or demand documentation every time someone called then they would be broke in a week. This does not mean that a chemist should be careless. It's just that if a chemist is polite, friendly and smart then almost anything can be had. And since, as this book will point out, most everything the chemist needs will be unwatched, there will not be a great deal of suspicion no matter what the chemist orders. Just remember one thing: the chemist never orders anything to the same place she cooks at.

Science dealerships aren't the only places to get the stuff one needs. At those mega hardware stores one can find pure acetone, methanol, ethanol, toluene, methyl ethyl ketone, DCM(as a constituent of some stripping agents), sodium hydroxide in the form of lye, and some acids such as sulfuric and hydrochloric. These precious tools can be bought there cheaply and in great quantity.

Then there are other places such as chemical waste exchanges, pool supply companies, electroplating companies, photography supply shops, agriculture companies, specialty gas canister companies and just about any place where a chemical can be sold.

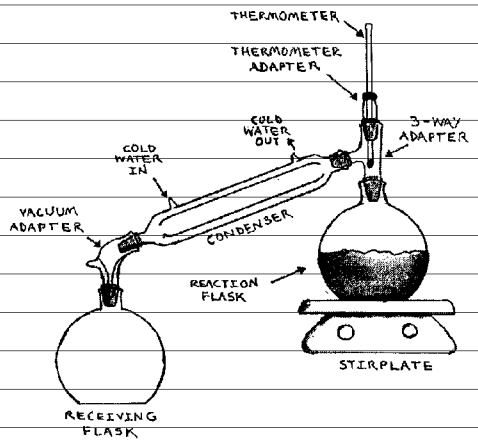
Finally, if one simply cannot find the thing one needs then it's time to hit the bibles of industrial and commercial sources: "Chemical Buyers Weekly", "Chemsource U.S.A." and the massive "Thomas Register". These three source books can be found at most libraries and contain the listings and services of just about every business in the country. No matter what the chemist needs, it can be found in these books. Even if it takes going one-by-one through the listings, Strike can assure you that the chemist will find what she needs and someone that will sell it to her.

The one source Strike does not condone is theft. If you steal then you are a weasel and a coward.

WHAT TO BUY

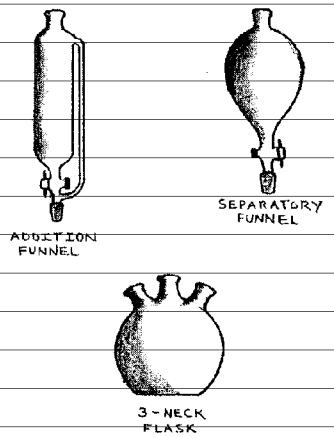
GLASSWARE

Ideally, the chemist wants a distillation kit with joints that are of the size 24/40(don't ask). This is the most versatile joint size for accommodating both large and small flasks. Speaking of flasks, the type one wants these days are flat bottomed flasks, not round bottomed flasks. Flat-bottomed flasks allow one to heat on flat surfaces such as a heating stir plate. In the first of many beautiful, hand-drawn sketches that will appear throughout this fine book one can see the components and proper configuration of a regular distillation set up in figure 1. Other pieces of glassware that are highly desirable but can be lived without or made (as shown later) are shown in figure 2.



[Figure 1]

Now, one is going to see most of the older chemical recipes calling for all reactions, solvents, acids and bases to be held in Pyrex (borosilicate) type glassware because anything else will melt or degrade when exposed to all these harsh chemicals and conditions. This is no longer true! Any reaction, addition or mixing in this book that does not require direct heating can be done in a polypropylene (PP) or polyethylene (PE) container. This is regardless of the chemicals involved. Polypropylene (PP) and polyethylene (PE) are very inert and chemically resistant to almost anything this book describes. Buckets, tubs, funnels, and all sorts of containers of this whitish, opaque, pliable plastic can be found for pennies at any discount or grocery store. These containers are stackable, easy to clean, never break and will save a chemist a fortune in glassware. As was mentioned earlier, plastic ware is starting to make its mark in biological and chemical labs. Buchner funnels, side arm flasks, graduated cylinders and even separatory funnels come in PP and PE. These glassware substitutes are the absolute choice for today's chemists as they are unwatched, versatile and 1/10 the cost of glass. If the chemist is unsure what plastic a container is then she can look for the letters PP or PE somewhere on the product.



[Figure 2]

VACUUM

The chemist is going to need a source of vacuum. When distilling high boiling stuff like valuable ecstasy free base oil, a vacuum is

applied at the nipple (tee hee!) of the vacuum adaptor so that the pressure inside the entire distillation apparatus is reduced well below the normal atmospheric pressure outside. This causes everything to boil at a much lower temperature. If high boiling oils are allowed to distill/boil at their normal temperatures and atmospheric pressure then a considerable amount of product could be lost due to scorching. The other purpose for a vacuum is for vacuum filtration, which is a very useful process and is described later on.

Any commercially available vacuum pump is perfectly fine for the underground chemist's needs; but the best kind to buy is a diaphragm pump, which is more resistant to the often-harsh chemical vapors that are sucked through it. Most vacuum pumps cost about $100-$200. However, the stronger the vacuum the better. If a chemist is looking to pull 1mm of Hg (don't ask) like the girls in the chemistry papers do then she can be looking at a turbovac that can run well over $5000.

The other vacuum option is a simple little aspirator that attaches to ones faucet or hose. This $15 device pulls a decent vacuum; however, it is not an option at all in Strike's book. Running one of these babies 10-12 hrs a day is a despicable waste of a community's water supply.

WATER PUMP

This is going to supply the cold water that courses through the condenser whether that condenser is set up for reflux or is part of a distillation configuration. The pump need not be very strong. In fact, the perfect example is one of those little, submergible fish tank pumps that one can find at any pet store for about $10. All the chemist does is attach a hose to the outlet, chunks the little pump into a bucket of ice water, attaches the hose to the condenser and there it is. An alternative source is that little pump that's attached to the windshield washing fluid reservoir of any car in a junk yard. The chemist removes the reservoir (pump still attached), applies an adapted power source to the pump and uses the plastic reservoir to hold the ice water.

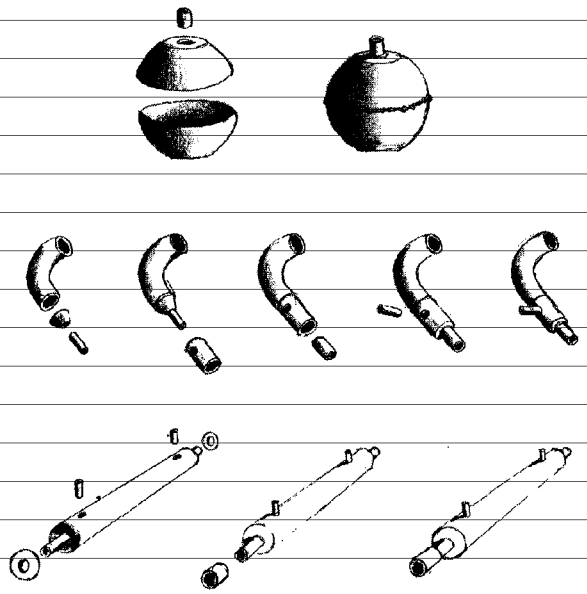
HEATING AND STIRRING

There really is no good substitute for a combination heating and magnetic stirring plate, nor is there any reasonable excuse not to get one. These are perfectly legal to buy and can be found at any science outlet for about 200-400 dollars. Here's one area that the chemist should not skimp on. This piece is going to be the center of every action in the laboratory so a really good one with as large a surface area as possible is a definite plus.

Let's just suppose, hypothetically, that the underground chemist is too stupid or unwilling to get a stir plate. In this case a single unit portable hotplate can work, but controlled heat using these is best accomplished by water or oil baths. Stirring can be accomplished by attaching a shaft and paddle to a power drill or any gear driven motor.

HOW TO MAKE

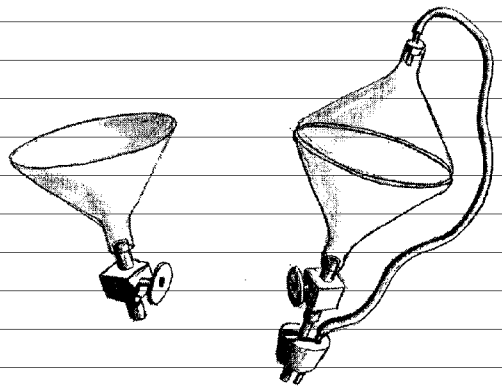
Strike is sure that an imaginative person can look around her everyday surroundings and think of something that can act as a replacement for some of those hard to get glassware items and other gizmos. As it so happens Strike has thought about this too. Here are some of the more likely ways that these things can be made.



[Fig 3]

The best replacement for borosilicate glassware is stainless steel. Stainless steel takes the heat, won't break, and, most importantly, is about as resistant to chemical degradation as the chemist can hope to find. For those items that won't be subjected to direct heat there can be some steel/metal or steel/plastic hybrids. In figure 3 is shown how flasks of any size can be made with two stainless steel mixing bowls welded together. Also shown is the vacuum adaptor and condenser. For the condenser only the inner pipe need be steel. The outside pipe can be copper or something. As for the other components of a distillation set up, well, they are made just as they look.

In figure 4 is shown how a separatory funnel and a pressure equalized addition funnel are made. The funnel part is just a PP funnel from the grocery store and what it is attached to is a stainless steel ball valve. See how the addition funnel is made by using a rubber stopper and an extra extension of tubing to the top of the funnel? Well, that's how one can make a sealed addition funnel out of the ordinary glass separatory funnel that one gets with a distillation kit or from wherever.



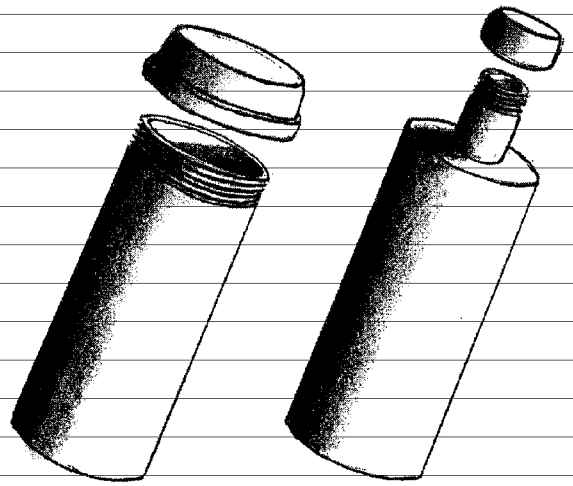
[Fig 4]

All of the pieces pictured here are not going to fit perfectly into each other and that's going to cause all sorts of leaks. The answer is teflon tape. Strike loves teflon tape! This inexpensive product is found in the plumbing department of any hardware store and is the duct tape of the next century. Teflon tape is chemically and thermally indestructible. This stuff is wrapped around any piece of pipe or joint, said part then jammed into its appropriate receptacle and the tape will mold to form a perfect fit. Hell, it can mummify a whole joint complex to make it absolutely impregnable.

So what's the downside of using a stainless steel distillation kit? The chemist can't see shit! There is a definite advantage of being able to see a reaction as it takes place and to see when something starts to distill over. All Strike can say is that the chemist must rely much more heavily on the readings of her thermometer and have a greater faith in the chemistry she is doing. By this Strike means that since there is probably going to be no more than 2-3 different chemicals in the reaction flask, then all the chemist need be aware of is what thing comes over first , second and last. Strike knows. Strike knows. It's a little more complex than that. But if a chemist gets the hang of distillation it really can be as simple as that.

PIPE BOMBS

A pipe bomb is not a bomb. It is just a device to hold high boiling or high-pressure reactions in an enclosed cell. The bomb should be made from a stainless steel pipe that has as big of an inner diameter as possible (width, bubba!). There are two good configurations which can be seen in figure 5. One end is permanently sealed by welding. The other end, no matter which configuration is used, should have as much and as fine a threading as possible. Also, when sealing up the pipe bomb, it is a great idea to wrap a lot of teflon tape around the threads then screw on the cap. This will form an absolutely air tight seal. It is also possible to substitute a stainless steel pressure cooker for some sealed, pressured reactions.

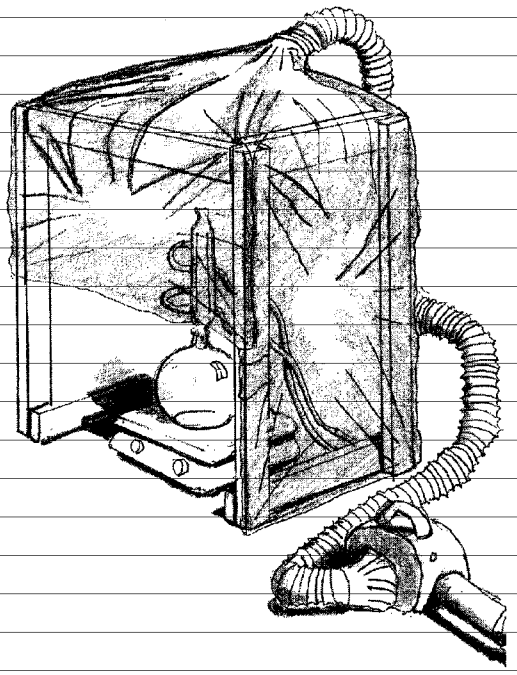


[Fig5]

GIRLS IN DA HOOD

Some of the reactions that the chemist may use will just naturally smell bad. Usually if something smells bad then it's probably bad for the chemist to smell it. Some reactions are, by design, supposed to vent bad things that , when unchanneled, have nowhere to go but into the living room of the chemist. Sometimes there is no guarantee that a method will go as planned. There may be a mistake or unforseen side reaction and some of the most deadly shit imaginable can be evolved. That is why the chemist will construct the one thing that may end up saving her life: a fume hood.

In professional laboratories fume hoods are big metal boxes resting on counter tops and are connected by ducts to blower motors on the roof of the facility. The blower motor is constantly sucking the air from the hoods to the outside so that chemists will not be exposed to the vapors of chemicals they are working with inside the hood. The same precautions are taken by non-dead underground chemists.



[Fig 6]

A fume hood is constructed in the manner shown in figure 6. Strike drew the frame as being made of lumber but it can be made of rebar or, preferably, from PVC pipes and joints so that it can be assembled and disassembled with ease. The frame is enclosed with plastic drop cloths or any semiclear plastic sheeting. The front face of the hood is halfway covered with plastic while the bottom half is exposed to allow one to move objects in or out and to manipulate things. On top of the chamber is attached some clothes dryer duct or some such crap which is led to a leaf blower or blower motor. The exhaust from the blower is led away to the outside.

Although a leaf blower is probably way too strong it may still be adequate at its lowest setting. To insure that a correct airflow is being pulled the chemist holds a lit cigarette about a foot in front of the hood's opening and looks to see if the smoke trail is being pulled into the hood. If so, then the hood works just fine.

Many houses have outside-venting blowers over their stoves. Chemists in these situations can actually drape some plastic around their stovetop to make a perfectly adequate hood. However, chemists who live in apartments never, ever attempt any chemistry at all in their pads. Why? Well, not only do apartment stoves lack an outside vent; but to vent a constructed hood through a chimney or out a window with so many close neighbors living about is just plain stupid. It is also stupid in another very important way. If a chemist fucks up and blows herself up or starts a fire then she is not only harming herself but is also going to put a lot of her neighbors out on the street, in the hospital or in the morgue. No one making drugs has the right to jeopardize others in this manner. That is why drug making is always done in a house, barn, mobile home (watch out for tornados), submarine or cave.

METHodology

Just in case you are not familiar with basic laboratory procedures, this chapter will explain them to you. These are the most basic lab techniques and almost every method in this entire book will require many, if not all, of the protocols to follow. So pay attention!

DISTILLATION

You see that distillation setup in fig. 1? Well, when one puts something into the reaction flask and heats it, low boiling stuff like organic solvents (acetone, ether, DCM etc.) vaporize and then condense inside the condenser. They then drip down into the receiving flask. Next (usually) comes water, then finally (as far as drug chemistry is concerned) comes high boiling drug oils. Distillation is the most preferred and reliable way to purify substances from one another.

There are three basic forms of distillation: simple, vacuum and fractional distillation, which can be an extension of the first two. Simple distillation is just plain old distillation with no vacuum and is used for purification of low boiling mixes or for removing solvents such as ether. For vacuum distillation a thick walled or reinforced hose is connected from a vacuum pump to the nipple (tee hee!) of the vacuum adaptor. Application of a vacuum greatly reduces the temperature of boiling and is a must for most of the distillation in this book. Fractional distillation is merely vacuum distillation except an added glassware component such as a small Vigreux column or a Claisen adaptor packed with shards of glass is placed between the reaction flask and the 3-way joint of a normal setup. Either of these additions create a gauntlet of extra surface area elements that distilling liquids must pass through in order to condense. This affords a greater degree of separation between mixes of oils that have similar boiling points. However, it has been Strike's observation that most of the bulk separation in this book using distillation can be achieved with regular old vacuum distillation.

If the chemist has done the appropriate thing and bought a heating stirplate then a magnetic stir bar is always stirring in the reaction flask. If the chemist only has a hotplate then the chemist is going to have to add some boiling stones to the flask. Boiling stones can be either little chips of teflon, little wadded up balls of teflon tape or little pieces of a shattered porcelain counter top tile. All of these things have lots of microscopic pockets of air in them that help to facilitate the start of boiling. Many of the solutions in this book, especially organic solvent solutions, need these boiling stones in them if they are going to be heated. If there are no boiling stones, then a phenomenon called superheating may occur whereby the solution will start to get hotter than its actual boiling point temperature. Eventually it will burst into boiling but a lot of it will have gone sploosh! into the condenser. Not good.

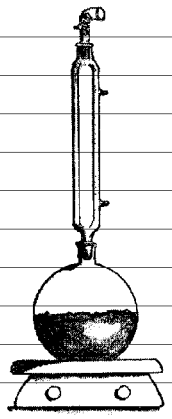
Another thing or two to remember when distilling is to wrap aluminum foil around the reaction flask. This will help stop heat loss so that things will distill quicker and at lower temperatures. Sometimes, if one is going to distill a solution that is just solvent and product, all that pure solvent that comes over first is perfectly reusable and should be saved for future extractions.

The last thing about distillation that needs mentioning is the swapping out of collection flasks. When distilling under vacuum it will be necessary to remove the flask that has collected all the solvent or crap and replace it with a clean one to collect all the product that will be coming over shortly. This swapping of flasks needs to be done quickly as soon as the vacuum hose is disconnected. By quick Strike does not mean lightning fast. Just quick enough so that the hot solution in the reaction flask does not get too much hotter from the heat source it is sitting on, because if it does, and the vacuum is reapplied, it may pull a little form of that superheating stunt and go sploosh! into the condenser.

REFLUXING

Refluxing is all over this book and the proper apparatus to use is pictured in figure 7a. The most general thing that can be said

about refluxing is that it's just plain old boiling except that there is a condenser attached to the flask so that nothing escapes. The condenser must be supplied with really cold water, especially when refluxing high boiling solutions.



[Fig 7a]

[Fig 7b]

You see that vacuum adapter stuck to the top of the condenser in fig. 7a? Well, a closer look at it in fig. 7b will show that it has some drying agent sandwiched between two cotton balls and the nipple (tee heel) sealed with plastic wrap or foil. The drying agent can be either a commercial product called Drierite or calcium chloride. This attachment is placed on top of a condenser when refluxing solutions that have no water in them and must remain that way during the time they are refluxed. All this is to prevent moisture in the outside air from coming into contact with the cold surface of the of the inside walls of the condenser. This will surely happen and the condensed outside-air water will drip down into the reaction flask and ruin the experiment. This is not so much a

concern when refluxing large aqueous solutions such as acid or base hydrolysis seen later in this book.

One side note about the drying attachment is that it need not be a vacuum adapter. Anything, such as a funnel, that can hold a plug of drying material and fit snugly into the condenser will work.

EXTRACTION

In this book extraction is almost always about using an organic solvent such as benzene, DCM, ethyl ether (a.k.a. ether) and hexane to remove (extract) product (almost always in oil form) from an aqueous solution. The most basic way to extract is to pour the water solution into a PP container, add some solvent and stir the two as fast as possible for a few minutes. Most equipped labs use a large separatory funnel to shake the two liquids. When using a separatory funnel it is very important to vent the funnel as soon as the stopper is smacked into the top. This is done by immediately inverting the funnel so that the stopcock end is facing upward, opening the stopcock to release the pressure then closing the stopcock. The sep funnel is given a quick shake then vented again. This is repeated a couple more times after which the pressure production will have pretty much ceased. The rule is to then shake for 2 minutes and allow the layers to separate for 10 minutes. And which layer is going to which? Ether and benzene are always on top of water and DCM and hexane are always on the bottom.

Most science papers call for things to be extracted 3 times (3X) with a solvent. Strike feels that this is overkill and that one or two times is usually sufficient. Sometimes one has so much product oil that it forms its own heavy layer (usually at the bottom). There is no need to extract such a large amount with solvent. In such a case one would merely drain the oil from the water or, if using a PP container, decant the water from the oil. The water itself can then be extracted once with solvent and the solvent added to the oil.

WASHING

Washing is almost always the act of taking an organic solvent layer (most likely the one that was obtained from the extraction of some previous aqueous solution) which usually contains product oil and mixing (washing) it with clean water then discarding the water. A solvent layer is often washed with a dilute acid or base salt solution to neutralize anything the solvent may have absorbed from previous extractions. These salt solution washings are then followed by clean water washings.

Since we're on the subject of clean water, this is as good a time as any to discuss what kind of water is used in all this chemistry. By clean water Strike means distilled water (dH_2O). All reactions are to use distilled water (dH_2O) only. All solutions and dilutions are to be made with dH_2O as well. Distilled water sells for about $1 a gallon down at the supermarket. Tap water is an absolute no-no in chemistry except for cleaning the glassware.

DRYING

Just as it is with laundry, drying often follows washing and is used to rid the solvent of any water that it absorbed. All solvents absorb some water although you can't see it. It is a good idea to rid the solvent/product of any water, especially before distillation, because it's one less thing to worry about and because there is an off-chance that water may form a slight amount of byproduct when heated with product oil under distillation conditions.

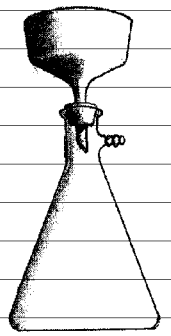
All one has to do to dry something is to take a sheet of filter paper or paper towel, fold it into a cone and place it into a funnel. About a shot glass full of sodium sulfate (Na_2SO_4) or magnesium sulfate is dumped into the filter and the solvent poured through it. It is also a good idea to follow up by rinsing the Na_2SO_4 with a little extra, clean solvent to insure that everything gets washed out of the drying agent. The Na_2SO_4 is a white crystalline salt that tastes like table salt. It binds water molecules without readily dissolving and leaves the solvent water free. This way of drying is also an option for making some solvents and pure liquids anhydrous (water free, bubba!) for some of the recipes in this book that call for such things.

Drying isn't absolutely necessary, but it is a good bet that if a recipe stresses its use then an evil underground chemist will do so.

VACUUM FILTRATION

This procedure is used to separate crystallized product from solvent or to remove crap and solids from a liquid. Figure 8 shows the proper apparatus to use. The collecting flask is called a side arm flask and to that extended nipple (tee hee!) is attached a vacuum source. The thing that is shoved through the rubber stopper is called a Buchner funnel and is usually made of white porcelain or, preferably, PP. The Buchner funnel, when viewed from above, can be seen to have lots of pin holes in the bottom surface of its reservoir. Over this surface is layered a single sheet of rounded filter paper or paper towel.

To filter a solution one attaches a vacuum and pours the solution into the Buchner funnel. All the solution will go whoosh! into the flask leaving what is called a filter cake in the funnel. The liquid that has collected in the flask is now called the filtrate. Usually, the filter cake is then washed with a little bit of clean whatever-kind-of-solvent-it-was-just-filtered-from. That extra washing is then combined with the other filtrate. The most action this procedure is going to see in a clandestine chemistry lab is at the very end of the drug-making process where the chemist will have crystallized her freebase oil into a final, marketable form and then needs to separate those crystals from the solvent they are in.



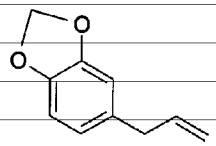
[Fig 8]

PRECURSORS

SAFROLE

Where to begin! Where to begin! Well, starting with this chapter is a good idea! Every amphetamine is a chemical. And since your government doesn't allow one to own or buy the chemical itself, one has to go about making the amphetamine from legal (or sometimes illegal) chemicals that are as close to the final drug as possible. For ecstasy, that starting chemical is almost always Safrole.

Safrole is the #1 starting material for making X today. As a pure chemical it is a schedule I controlled substance and, obviously, is illegal to own or buy without a permit. But, safrole is the major component of the essential oil of sassafras which is still quite legal to obtain. Sassafras oil has a strong licorice smell which is imparted to it from the safrole molecule. Commercially, there are two kinds of sassafras oil being sold today: American sassafras (Sassafras albidum) and Brazilian sassafras (Ocotea cymbarum). Plain old American sassafras contains about 80% safrole but the Brazilian sassafras oil is almost 90-95% safrole and can pretty much be used as is.



So where does one go to get sassafras oil? Well, if one were to go down to one of those sickening hippie health food stores or incense shops there, on the shelves, will be small bottles of 80-90% ecstacy starting material labeled as sassafras oil. Larger quantities are ordered rather cheaply from fragrance or perfume supply companies that one can find in any big city yellow pages. Now the people at these companies aren't stupid. They have a general idea of what some of their essential oils can be used for so they might ask. But they still have no legal reason not to sell these things to the chemist. After all, the same stuff is being sold over the counter to hippies just down the street. Just to make everything easier for all involved the chemist informs the company of the fake name of her business and that she makes soaps, incense, potpourri or is an aromatherapist (no kidding). Other places to order essential oils would be home care products houses, toiletry base companies, soap companies, flavoring companies, aromatherapy stores and organic foodstuff companies.

As of the year 1998, small quantities of sassafras oil are still being sold on retail shelves without any scrutiny. Usually in 1-4oz sizes. Anything larger is usually sold only through distributors and manufacturers. And as of 1998, the DEA has informed most of these distributors that they (the DEA) want lists kept or sales reported of most, if not all, sassafras oil purchases. Mind you it is not illegal to buy the oil. It's just that you will be put on a list if you do. The operative term here is 'Watched Substance'. Solution: have someone else buy it for you.

Strike has also been poking around the DEA and is getting the distinct impression that they will very soon reschedule sassafras oil as schedule I. Then one won't be able to get it at all without a permit or some serious deception.

All of the above safrole/sassafras oil sources are the more standard avenues to get these commodities. There are some rather exotic sources of safrole for the desperate, governmentally-challenged citizens of the future. Certain kinds of Asian camphor oils, especially brown camphor oil, can contain 40-90% safrole (another term to look for is 'Camphor 1070'). Sources selling 'artificial sassafras oil' are actually selling a mix of 50% camphor and 50% safrole, which can of course be used. Appreciable amounts of safrole can be found in star anise oil, and smaller amounts can found in the oils of cinnamon, mace, betel leaf and nutmeg (lots of fun things in nutmeg). Also, there is a spice bush that grows in India called Betel. Betel leaf oil can be found commercially and can contain up to 40% safrole depending on the region it was cultivated in.

The sassafras tree itself grows like a weed in the wilds and along disturbed fence lines throughout the south, southeast, eastern

seaboard, and Appalachian mountain regions of the United States. The trunk and root bark of older, mature sassafras trees can be steam distilled to afford the safrole-containing oil. Another source of safrole would have to the be leaf oil of a little shrub that grows down in the low woods and swamps throughout the coastal plains from Florida to Georgia. The oil is more than 90% safrole [61]. The plant is known as Illicium parviflorum michx and Strike has no idea what the hell it looks like.

A new source of safrole that Strike has just stumbled upon is in Strike's back yard. Momma comes home from the local nursery with two plants that have these enormous leaves. They are succulents and grow like crazy. Strike: "What ya got there Momma?" Momma: "Don't think I haven't noticed those filthy drug books you write, you sick little monkey!" Strike: "Aw c'mon, Mom. Let's not get into this again. Strike doesn't..." Momma: "Well I needed some new ground cover plants, and...sigh...I know you're into this twisted licorice thing...so I bought these weeds that are called 'Licorice Plants'."

Strike breaks off a piece of the plant and smells it. Oh Yeah! That's the bomb! The plant is called *Piper auritum*. Its common name is Hojo Santa. Strike loves Strike's mother.

Suffice to say that anything that remotely smells like sassafras oil or licorice or any of those strong rustic spices is going to have some amphetamine precursor, maybe not safrole exactly, but definitely something. There is just no other substitute in nature for the aroma these unique compounds give.

The sassafras oil that one gets these days is not only going to have the safrole but is usually going to have some amount of each of the compounds seen in Table 1 [6].

Usual Components of Sassafras Oil

Component	range of content	boilingpoint@1atm(oC)
pinene	2-10%	154
phellandrene	2-10%	175
d-camphor	0-5%	204
safrole	80-90%	234
eugenol	0-10%	252

[Table 1]

No matter what the safrole content is, even that of the Brazilian sassafras oil, it is always a good idea to try to get rid of as much of the other components as possible. The most basic way to do this is to throw all of the crude sassafras oil into a PP container and stir it with an equal amount of 3-5% sodium hydroxide (NaOH) solution. Little white crystals of eugenol anion will form in the water layer. The water layer is poured off and saved. That eugenol is valuable. Eugenol is usually the main contaminant in safrole in more ways than one. It is the only molecule in sassafras oil that will react the same way as safrole so if it hangs around with the safrole it will compete with safrole in the conversion reactions. Also, eugenol is about the closest to safrole in both structure and boiling point so that trying to get rid of it by fractional distillation will be very tough indeed. Anyway, after the eugenol/water is poured off the oil that remains is stirred with 3 washings of clean water. The cleaned oil will look a little cloudy now. Strike still does not know why. But it never seems to hurt anything. After the third washing is poured away from the oil, the oil is transferred to an ordinary cooking pot and boiled at 100°C for a few minutes to boil off all the water. What would you think of french fries cooked in that oil, huh?

Strike wrote the above paragraph relying on the few accounts of sassafras oil content that Strike had at the time. Since then, Strike has come across more substantial data showing that Brazilian sassafras has NO eugenol in it. This agrees with the claims of many bees who have stated that no appreciable recovery of

eugenol is observed when washed with the dilute NaOH. Strike has also had commercial samples of both sassafras and brown camphor analyzed for components and the results showed that there was no eugenol in either. So give it a shot with NaOH or don't. Strike no longer feels that it matters.

The above procedure was a good step towards purity and may be all that one can hope for without a distillation apparatus. For those that have a distillation kit its time to get rid of the rest of the stuff by fractional distillation. This still isn't going to be easy because even with a packed Claisen adapter or Vigreux column the entire mass of oil is going to distill over with barely a 5 degree difference between the first drop of oil to come over to the last (this usually occurs at around 170-180°C under normal vacuum). The best strategy is to distill the oil at least 2 times; discarding the first few mLs (milliliters) of distillate and leaving the darker last few mLs behind in the reaction flask (discarding them as well).

It will be a little tricky but one can also try to purify by freezing! The sassafras oil is thrown into the freezer to chill. Safrole itself freezes at -14°C so anything that starts to freeze prior to that can be cold filtered in a prechilled vacuum filtration setup. The filtrate goes back in the freezer until -14°C is reached and the mother lode of safrole freezes up. This again is filtered cold but this time the frozen mass of safrole crystals are washed with some ice cold methanol or ethanol (preferably at -14°C) to wash away the unfrozen high-boiling constituents.

If one is absolutely serious about ultra pure safrole then it can be separated from the eugenol-free sassafras oil by treatment with mercuric acetate [1,2,3,4] which likes that terminal double bond that only safrole has. The $Hg(AcO)_2$ latches on to safrole at that double bond bringing it into solution as a solid; sort of like the way that eugenol was. The safrole can then be separated from its still oily buddies by vacuum filtration. Safrole is then regenerated to its normal oily form by treatment with hydrochloric acid (HCl) which flicks the $Hg(AcO)_2$ off the safrole and the safrole double bond reforms. As it so happens, the mercuric acetate also reforms intact so that it can be reused again such as in one of those

top 10 recipes discussed later. The one problem with this method is that, having been disturbed, some of the safrole molecules' double bonds will tend to migrate or reform in the more energetically favorable position between the alpha and beta carbons. What was all that egghead shit Strike just said? Strike said that not only will safrole reform but there may also be a small amount of isosafrole that forms as well. Also, some very intuitive Bees have suggested that it may be possible to connect the isolating of the safrole with mercuric acetate and proceed directly with the complex into one of the oxidation reactions found later in this book. Could be. Could be.

After Strike wrote the first edition and started up the old web site, a lot of new theories came in. The most promising was a proposition from our founding father of cyber chemistry: Eleusis. This was his proposal:

"*Purification of Sassafras Oil v2.0*

The Sassafras plant is an excellent source of Safrole, a highly useful compound. The plant yields up to 9% oil by weight, which is an exceptionally good yield. Sassafras is indigenous to Virginia, the Carolina's, Tennessee and parts of Canada. The preferred method of extracting oil out of the plant is by Steam Distillation. The most common method of obtaining Sassafras Oil, though, is by purchasing it ;-).

According to the Merck, and "Essential Oils" by Guenther, Sassafras Oil is composed of the following:

80% Safrole

10% Phellandrene

7% Camphor

3% Eugenol & various Sesquiterpenes (Cadinene et al.)

I have derived a process for preferentially separating the Safrole out of Sassafras Oil. This process is based on the physical properties of the various components listed above combined with a little chemistry knowledge. The normal means of purifying Sassa-

fras Oil is through packed column vacuum fractional distillation. This is an expensive, messy, and difficult process - in short, impractical. My process that I am proposing takes advantage of differential solubility among the various oils in acetic acid to separate the mixture down to only two components. The two remaining oils have sufficiently different boiling points to make simple distillation, with or without vacuum, a feasible separation method. To wit: Safrole and Phellandrene are left, Safrole boils at 232C while Phellandrene boils at 171C. The difference of 61C is large enough to permit excellent separation of the two, though some texts feel that there should be 80C difference between distillants (see Vogel), it is generally accepted that fractional distillation is necessary only when the boiling points approach 25C of each other (see Zubrick). However, with information newly acquired, you now don't even have to do the distillation, since Safrole is soluble in ethanol, while phellandrene isn't!

Enough of the arguments, let's take a look at what is going on here.

Materials -------- Separatory funnel (2x volume to contain) Simple Distillation setup or pot on stove ;-)

1) First wash with a volume of Glacial Acetic Acid equal to the amount of Sassafras Oil being processed. This will remove Eugenol, Pinene and Camphor from the oil.

2) Wash with water to remove any salts made from other contaminants and to crash out any partially dissolved Safrole (it might emulsify from the shaking, if so, add common table salt to help it crash).

3) Wash with rectified spirits (azeotrope of Ethanol + water, also known as "grain alcohol") to dissolve the Safrole, leaving the Phellandrene behind. Of course, one should use only the amount of alcohol necessary to dissolve the expected yield of Safrole. 1:1 seems to work, but could be an excessive amount.

4) Setup for simple distillation, on the water bath, or if you don't wish to recover the alcohol (shame on you) just heat gently with a

double boiler setup (especially since this will take quite a while depending on how much you have to distill/evaporate).

5) After distillation terminates (Ethanol boils at 78.4C), test your Safrole using the physical properties data below to confirm purity. Theoretically, your product should be better than 99% pure now.

The entry for Safrole in Lange's indicates the following properties:

Safrole 3,4-methylenedioxyallylbenzene - Bielstein ref. # XIX-39

Molecular Weight: 162.19

Specific Gravity: 1.100@20C

Melting Point: 11C

Boiling Point: 233-234C

Insoluble in water, Soluble in Ethanol, Miscible with Ether and Chloroform

Note that this procedure has been modified from the earlier version in that we no longer distill off the Phellandrene, rather, we target it's insolubility in ethanol as a means to separate it from safrole. I think we can all agree that this is a much better way, eh?

This procedure, Strike believes, was not tried by Eleusis. But his theory on the use of partial solubility is very old and founded. Taken, as we all are, by Eleusis' unique genius, our beloved Bee 'TDK' contracted a Philippine research laboratory to apply this proposal. Here is what they said:

Posted by TDK on December 28, 1997 at 01:28:34:

Sassafras Oil separation/purification

This was pretty simple and is well suited for someone without any distillation equipment!

Starting weight: 112 grams sassafras oil.

Placed 454 grams of 28% acetic acid in 2 liter separatory funnel.

Using 28% acetic acid allows the eugenol, d-camphor and pinene to form its own top layer. There was no separation using 99.5% acetic acid.

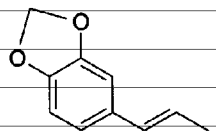
Added 112 grams sassafras oil. Shake for a couple of minutes. You get an orangish emulsion. Clears within 15 minutes forming two layers, bottom layer oil, top layer acetic acid, eugenol + the other solubles. Separated the oil from the others, washed the oil layer 2x with fresh dH_2O. Weight after acetic acid & water washes: 101.5 (-10.5 grams).

Added 100 grams denatured alcohol, no layer formed as the oily product is miscible in ethanol. Added 20 grams of dH_2O. This pulled the ethanol and other product into the top layer, bottom layer containing some ethanol and safrole. Separated layers, placed the oily bottom layer into a 2-liter breaker. Took the temp right to 234 C. The ethanol and water came off <=100 C... The safrole started to boil @ 232C, then came to a full boil and maintained @ 234 C. Product was yellow orange in color, suitable for whatever purpose one has in mind! BTW, after the safrole cooled, she checked it with a 5% NaOH solution to see if any eugenol was left behind, no participate formed.

Beautiful, TDK! Beautiful. Strike suspects we will be seeing more from this gifted chemist later on in the book.

ISOSAFROLE

At this point the chemist has what can be loosely considered as pure safrole. She can use this for some methods or can convert it to isosafrole for others. Isosafrole is the runner-up precursor for making X. It cannot be found in nature but rather is made from almost exclusively safrole.



Strike had previously written that about the best recipe for making isosafrole was from boiling safrole with concentrated KOH (Potassium Hydroxide) in ethanol. This was actually the only

recipe Strike knew of at the time. There are numerous basic references for it in the literature and a couple of very convincing examples in the landmark book "PIHKAL" by Alexander and Ann Shulgin. Pioneers in the research of amphetamines they are. Sounds good enough for Strike so someone other than Strike gave it a few shots.

What happens when isomerization is performed is that the double bond of the allylbenzene safrole migrates to the more energetically favorable position between the alpha and beta carbons of the propyl side chain. Thus isosafrole, a propenylbenzene, is born.

To isomerize safrole to isosafrole one would like to have pure safrole to start with. This, usually, is not the case. Quasi-pure safrole from sassafras oil is ok. Straight-up sassafras oil is probably ok too, though not recommended. The safrole is then refluxed (boiled under a condenser) in a saturated KOH/ethanol solution for about a day and that's it. The temperature of reflux is about 120-140°C owing to the fact that the ethanol (usually boiling around 65-70°C) is saturated with the halide salt.

Now, the ethanol used is almost always anhydrous, meaning it has no water. The closest one can get commercially to anhydrous ethanol is Everclear which is 95% ethanol and 5% water (190 proof). A lot of chemical supply stores will not carry 100% (200 proof) ethanol because it is a potable (drinkable) product. This means that they would have to get a liquor license or some other state permit to sell the stuff and that is a hassle that many don't want to bother with.

The 95% ethanol of Everclear is not an arbitrary concentration that the producer decided to stop at, mind you. It so happens that 95% ethanol and 5% water is a constant boiling mix that no more ethanol can be purified from. That 5% water is there to stay! There are ways to remove that water such as producing a ternary azeotrope by the addition of benzene, but they are kind of a hassle and may

not be necessary. Why? Because an alternative reaction for isomerization would be to use a saturated aqueous (water, Zak) KOH solution instead of an alcoholic one. This will raise the temperature of reflux to over 200°C but is not too bad an can be used if desired. So, if it is ok to isomerize in pure water, then the little bit of water (say 5%) in Everclear shouldn't effect things too greatly except raise the reflux temperature a tad.

What are some of the alternatives for this procedure? Well, one can use NaOH (lye) in place of KOH but the yields will go down. Also, what about using denatured alcohol instead of pure ethanol? Denatured alcohol is ethanol contaminated with 5-10% methanol. The methanol is there because it is poisonous and prevents people from using the ethanol for drinking. This means that places like the giant hardware stores can carry gallons of cheap contaminated ethanol as many of you have discovered. This product CAN be used.

So now that we have all the reagents out of the way let's see how the reaction proceeds. There's the clear- yellow "safrole" sitting in the bottom if the flask and the clear saturated KOH solution is dumped in. The solution is heated to reflux etc. and yes, some brown byproducts and destruction artifacts will appear. Especially if the safrole is not pure. These byproducts should be expected to some extent because concentrated basic (OH) solutions can be as nasty as concentrated acidic solutions. One is mindful that KOH is less intrusive towards the delicate methylenedioxy ring structure of the safrole/isosafrole molecule.

After 12-24 hours of reflux the reaction is, for the most part, complete. The reaction mix will be a dark brown. So what does one do about all those brown particles and junk. Well, usually there aren't any. The solution should be uniformly dark. If any solids can be seen it means that they are insoluble in ethanol and can be removed from solution by gravity or vacuum filtration through a coffee filter or some paper towels. If it takes a day to drip through the filter then so-be-it. The ethanol with its payload of isosafrole will

still be dark regardless and washing this ethanol with water at this point cannot be done because water is infinitely soluble in ethanol (and visa versa) so two layers will not form.

Filtered or not, the ethanol/isosafrole/(sometimes junk) is relieved of its ethanol by openly boiling it on the stove or by distillation. Any ethanol removed by distillation is saved because it is clean and perfectly reusable (remember, it will still have that 5% water). One should not remove all of the solvent this way because things can get really hot really fast as the last of the ethanol boils away.

Most likely one will end up with a dark oily layer at the bottom of the flask which is perfectly normal. Any solvent that remains will be negligible because in the next step the chemist is going to overwhelm it by adding a buttload of water. If there is about 100-200mL of dark oily layer then a liter or more of water is pored in and mixed really well. After things settle one will see a nice little layer of clear isosafrole form at the bottom, a murky brown !yikes! emulsion layer in the middle and a blackish water layer on top. The oil is separated and the emulsion is dealt with in any way that is best from the below mentioned strategies for emulsion fighting. This particular emulsion is of very fine particulates and has a lot of isosafrole in it. If one is patient then one can add solvent (DCM is good) to the remaining water/emulsion layer, shake then vacuum filter. The crud remaining in the filter is the junk that was causing all the trouble. With it gone one can now extract the remaining water layer a couple more times with solvent, add the solvent to the isosafrole oil then remove the solvent by boiling or distillation to get pure isosafrole (70-80% trans, 20-30% cis).

NOTE: a really good procedure for busting up the emulsion caused by introducing the water is to slowly acidify the water layer with HCl. As the water layer acidifies one will see the emulsion vanish. As this occurs the water layer will lighten as particulates and stuff start to exit the water layer and go into the DCM layer. Works every time.

If one is still having trouble then there is the old failsafe: just throw the whole mess into a distillation set up and fractionally distill. Solvent comes first, water second and (eventually) isosafrole will come as well.

Sound easy? Well, procedurally it is. But the yield can really suck sometimes and it can get really messy. Lots of people have not been pleased with it. Strike wasn't. But what can you do?

Well, someone named Osmium sent Strike a journal reference about doing the exact procedure above but carrying it out in a microwave [5]! A group of Brazilian folks tried both conventional and microwave heating. They had strangely high yields (all above 90%) using both ways. Both 2M and 4M KOH concentrations were used in ethanol, propanol and butanol. They also found that adding 2M KCl along with the KOH helped things. The really cool things were that when they used butanol and 4M KOH they only had to apply 15min of boiling to get a yield of 99%! Still the other reactions in propanol and ethanol only needed 2-5hrs for 90+% conversion. Strike would assume that the reduced reaction times afforded by the larger alcohols and such may very well help reduce tar and destruction and make for a better procedure.

Using the microwave just decreased the reaction time to 3-30minutes. The dudes in the article used a household, 500W Brazilian microwave (Yikes!). They cut a whole in the top of the microwave to allow the condenser apparatus to pass through the oven. They then killed themselves most likely. But not before they were able to scratch down this procedure as they slowly burned to death:

"*GENERAL PROCEDURE: The Alcoholic alkaline solution is prepared by prolonged stirring of 8.8g (or 4.4g) of KOH pellets in 30mL of alcohol. The alkaline solution is placed in a round-bottom flask provided with a reflux condenser (microwave or conventional systems). Then 4.0g of Safrole (or eugenol) is added and the solution heated.*"

Gee, that all sounds fine and dandy. But Strike saved the best for last. Without a doubt, the cleanest, fastest and easiest method for isomerizing safrole and other allylbenzenes is to use CaOH. Someone who is 'Not Tim' (Strike's name for her) emailed Strike the Chemical Abstracts entry for the procedure:

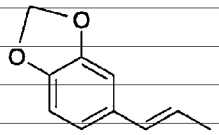
"*CA 47:9360.* ***Isosafrole from safrole.*** *Yoshiharu Ogata (Regeneration Camphor Co.).* ***Japan. 5331 ('51)****, Sept. 15. Safrole, b.132-4°, 100, CaO 15, and KOH 1 g. are heated 15 min. at 243.5°, the CaO and KOH filtered off and the filtrate distd. to obtain 95% isosafrole, b.240-8°. K. Kitsuta*"

'Not-Tim' said Strike was wasting everybody's time with the ethanol/KOH recipe and you wanna know what? He was kinda right (But, those Brazilian improvements above aren't here just to take up space!). This method is sooooo easy!

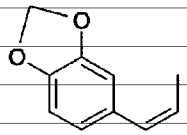
All one does is follow that CA recipe to the letter. In a small flat-bottom flask place 100g safrole, 15g CaO and 1g KOH. Now the flask is heated directly on a stirring hotplate (stirring is nice but not necessary). If one has a round-bottom flask or a low output heating source, a shallow oil bath can be employed to get even heating. The really neat thing about this method is the proof-positive heat gradations that will occur. The mixture will rise to the boiling point of safrole (232-234°C). And it will hold there for just a brief second. Then it will start to bubble and the temperature will rise! Sure enough, after only 15min of this the temperature will reach the near boiling point of isosafrole (~243-250°C). And that, as they say, is it.

The oil that remains is only slightly dark. Definitely translucent which is always lovely. One can then add some water to take up the unreacted salts and separate the oil from this. If an emulsion forms it can be busted up with some 10% HCl. That isosafrole is clean enough to proceed with but it can of course be distilled for ultra purity.

All of the above isomerization recipes can, in theory, produce almost 100% yields of isosafrole. But about 20-30% of that isosafrole is in a screwed up configuration called 'cis'. This cis isomer does not react the same way as trans and the drug that will be made from it will not be recognized in the same way as trans in the brain cells of users. Tsk.



trans-Isosafrole



cis-Isosafrole

The chemist can try to separate the two isomers by careful fractional distillation but it will be next to impossible to do because both the cis and the trans have practically the same boiling point. There are a few things that the chemist can do or hope for to get rid of that cis isomer. The cis configuration is less stable than the trans and may switch over to the trans configuration with a little help. The chemist can gently heat the isosafrole oil to about 150°C for an hour or so. She can also try the same heating except have the oil mixed with some acetic acid. Also, the isosafrole can be fractionally distilled to ultra purity and then be allowed to simply sit for a couple of days. Trans isosafrole 'may' spontaneously crystalize out while the cis form remains as an oil. They can then be separated by filtration.

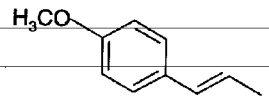
When all is said and done, the chemist may just wish to leave the damn cis isomer in with the trans. It's not really going to hurt anything and if it goes unreacted in some of the conversion steps it will be lost in the process long before X is made. It might even correct itself during some of the conversion steps.

OTHER PRECURSORS

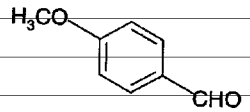
You people won't believe the potential amphetamine precursors just sitting around in naturally occurring oils and essential oils [6, 7

(Strike can't believe Strike can actually quote Strike's own book. That is so freaky!)]. Most of these things will make amphetamines that are much more potent than X. It is also possible to play around with some of the little side groups on these to eventually make X or some other interesting psychotomimetics. With few exceptions these precursors are all substituted allylbenzenes just like safrole. They are all found in the same kind of legal oils and sold in the same kinds of places as sassafras. Finally, these precursors are turned into their own respective amphetamines using the exact same conversion recipes used for safrole.

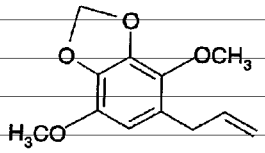
ANETHOLE: Up to 90+% in anise seed oil, 70+% in fennel and star anise oils, and in varying amounts in betel leaf, dill seed, carrot seed and coriander oils.



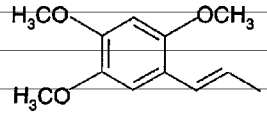
ANISALDEHYDE: In small amounts (less than 5%) in anise, cumin, fennel and star anise oils.



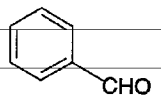
APIOLE: 23% of celery leaf oil, up to 30% in parsley leaf and seed oils, and in small amounts in cubeb, dill and fennel oils.



ASARONE: 70-80% of calamus oil. In trace amounts in Asian carrot seed and clove bud oils.

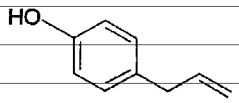


BENZALDEHYDE: The precursor for speed. It makes up nearly 100% of bitter almond oil. Not a very popular oil with the DEA. Some hints: Benzaldehyde is indispensable for the flavoring industry. It is the flavor in almond extract and synthetic benzaldehyde is used in all cherry flavorings. Also, there is currently a little loophole in the system when it comes to a product called 'Roasted Cassia Oil'. Apparently, some manufacturers take cassia oil and run it through some sort of industrial process to change it into benzaldehyde. No one wanted to tell Strike the particulars of how this was done. But one company chemist gave me some hints (You can get really chatty with some of these guys).

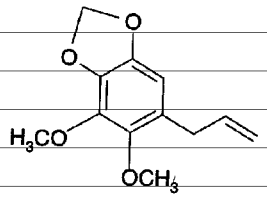


Apparently, these guys are taking regular old cassia oil and simply running it through a series of distillations. This even happens in the Asian fields when the oil is harvested so it obviously is not a complicated process. Cassia oil is made up almost exclusively of cinnamaldehyde. Any of you girls have any idea what these companies are doing to turn cheap cinnamaldehyde into benzaldehyde? Might be beneficial for you if you do.

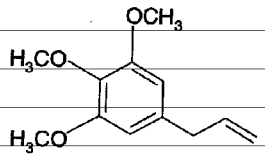
CHAVICOL: Up to 20% in West Indian bay oil.



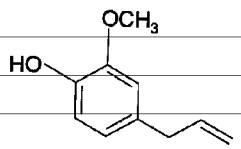
DILL APIOLE: Up to 60% in Indian dill seed oil and in varying amounts in other parts and other species of dill. In various small amounts in fennel and carrot seed oils.



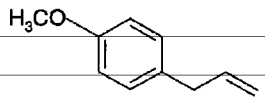
ELEMICIN: In varying amounts in citronella, elemi, mace, nutmeg, parsley snakeroot and tarragon.



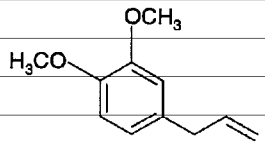
EUGENOL: In very large amounts in bay, cinnamon, clove and pimento oils. In goodly amounts in basil, eucalyptus and tejpat. Lots of trace amounts in many other oils.



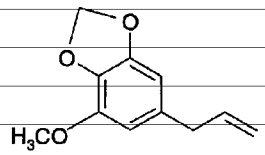
METHYLCHAVICOL: Up to 80+% in most basil, chervil and fennel oils. In small amounts in star anise and wormwood.



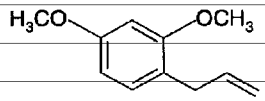
METHYLEUGENOL: Up to 60% in various parts of the basil plant. Around 45% in snakeroot oil. In decent amounts in calamus, cassie, myrtle, pimento, pistacia, pteronia and some forms of tarragon.



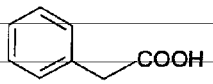
MYRISTICIN: In moderate amounts in dill, carrot, celery, fennel, mace and nutmeg (no more than 10% tops). Makes up about 40% of the oil of parsnip and can reach up to 50-60% of the oil of parsley leaves and seeds. Give nutmeg a rest folks! It just don't have it when compared to parsley and parsnip.



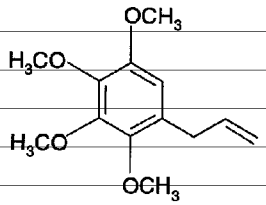
OSMORHIZOLE: Makes up 25% of the essential oil of chervil. Very hard to find this oil though.



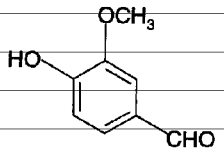
PHENYLACETIC ACID: Very important fragrance chemical. Only recently was it banned by the DEA. Fragrance companies still can't believe they cannot openly sell it. It makes up 15% of jasmine oil (very expensive).



2,3,4,5-TETRAMETHOXYALLYLBENZENE: In varying amounts in some parsley oils (hell, just throw parsley oil in a pot to get a grab bag of psychedelic amphetamines!).



VANILLIN: In vanilla beans of course. But never more than 2%. This stuff is bought as a synthetic and is cheap and legal.



The standard way that scientists get these allylbenzenes and other goodies out of these oils is by careful, fractional distillation. You can see from above that some of the more desirable allylbenzenes do not occur in high concentrations in the oils they are found in. So that means there is a lot of crap one has to get rid of to isolate the goods. This is not as big of a concern as one might think.

Essential oils from plants are technically known as 'volatile' oils. This means, among other things, that most every component of them will eventually evaporate if left to stand. So there is a definite boiling range for these oils which, compared to other things in nature, is relatively low. Strike means to say that when these oils were extracted from the plants they come from, they were taken by steam distillation where steam was the carrier. This leaves you with compounds that have relatively low boiling points with 300°C being close to the max. And Strike can tell you right now that in oils that carry allylbenzenes, those same allylbenzenes are almost always going to be the highest boiling compounds. Usually the bulk of the oil is constituted with compounds that boil well below the allylbenzenes.

People with or without distillation apparatuses can take advantage of this fact. Just boil or distill off most of the oil up to the temperature of your preferred allylbenzene and stop. There is a very good chance that what is left will be a majority of what is wanted.

The above suggestion is, of course, rather broad. Most people would prefer a more specific solution. Unfortunately Strike has one. For over half a year preceding this second edition Strike was pouring money and time into the realization of making an isopropyl intermediate out of safrole using sulfuric acid (please don't ask). So Strike hires this Korean research lab to work out the synthesis. Well, things didn't work out for the isopropyl intermediate, but it did confirm the following procedure as a nifty way of isolating allylbenzenes (sort of) chemically.

The literature states that if one uses ice cold, concentrated sulfuric acid on a terminal alkene (a.k.a. allylbenzene) an alcohol (OH) intermediate will form 'Markovnikovly' on the secondary carbon (don't ask). What does this mean? Let's take an example. Say one has some elemi oil and wants that elemicin that is in it. What one can do is chill, say, 500mLs of the oil to freezing and do the same for about 100-200mLs of concentrated sulfuric acid (at least 90% conc.). Next, one just mixes the two together for about 5 min. What will happen is that the cold H_2SO_4 will make a hydrogen

sulfate intermediate with the elemicin causing it to migrate out of the oil layer and go into the sulfuric acid layer. And since elemicin is going to be about the only thing in elemi oil that has a terminal alkene, it is going to be about the only thing that goes into the acid layer. Presto! Alkene isolated. Well, almost. What the chemist does next is separate the acid layer (still cold mind you!), place it in some vessel and pour in a big old excess of water. The temperature will go up and the hydrogen sulfate will be instantly hydrolyzed by the water to form an OH. One can also heat for 5 minutes to insure conversion.

What happens during hydrolysis is that the OH forms and the 'elemicin propyl alcohol' drops out of solution and forms its own oil layer. Of course one won't see this because the solution is a big old brown mess, lousy with emulsion particles. Emulsions suck! But can be dealt with effectively by adding a little acid or base, or filtration and the like. Anyway, after a little work up one gets some really pure phenylpropyl compound. And if Strike had Strike's way, Strike would have that OH stuck right on the middle (beta) carbon of the species. Work could then progress on using that OH to get an amphetamine (Sob! Strike had so much about that subject that Strike was prepared to put in this book!).

But that is not the case. What the Korean lab found out was that when this procedure is performed, the OH stabilizes on the alpha carbon. That is the carbon right next to the phenyl ring. If one has any use for it as is then that is fine. But what is most preferable is to reduce the OH to get the propenylbenzene (say isoelemicin for our example). Using the simple potassium bisulfate reduction recipe, one can get rid of the OH with no problems at all.

Hey! That really wasn't a lot of work. Just a lot of talk on Strike's part. All one did was mix an oil with some acid, added water and isolated. One gets some pure propenylbenzene without distillation. Done on a massive scale, this is a cheap method for getting lots of small concentration allylbenzene compounds out of complex oil mixes. And since Strike blew so much dough on this glorified extraction protocol, someone better damn well use it! (In an academic lab of course).

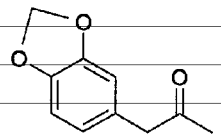
A much more forgiving yet limited extraction method can be used to isolate phenol species such as eugenol and chavicol. You see farther back in this chapter where one can use dilute NaOH to remove eugenol from sassafras oil? Well, why not use it to isolate the damn things for further research. It works like a charm!

There are probably other methods for purifying the products one wants. But as this book makes clear, Strike is no chemist in the real sense of the word. Strike has no real idea of the true application of chemistry and takes a lot of guesses (why is Strike telling you this?). But on the Hive, Strike gave it a few stabs. Things like recrystallization (don't ask), partial solubilities like what our friend Eleusis proposed above, freezing, heating, freezing-and-heating in a two solvent system, solid phase extraction and alternative forms of chemical purification. Or one can use any of the above in combination. All of these are ways that an industrious chemist may wish to further study and apply. So hit the library, Bra'!

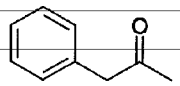
And now for the hardcore chemistry you've been waiting for...

PHENYLACETONES

So let's say, for instance, that some deranged lunatic did the exact opposite of what this book says, and went ahead and got some equipment, a couple of chemicals and some safrole, isosafrole and/or the precursor of their choice. They may very well decide to do something to it to get it farther along the path to final product. Well, currently on the place called Earth, the most widely made precursor for X and amphetamine production is the phenylacetone. For crystal meth the precursor is called just that: phenylacetone (a.k.a. phenyl-2-propanone, a.k.a. P2P). For X the precursor would be called 3,4-Methylenedioxyphenylacetone (a.k.a 3,4-Methylenedioxy-phenyl-2-propanone, a.k.a. MD-P2P). Strike knows it should technically be written as MDP-2-P, but Strike has always written it incorrectly as MD-P2P and that is just how stupid-ass Strike is always gonna refer to it.



MD-P2P

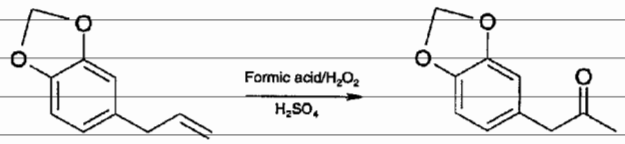


P2P

That double bonded oxygen (a.k.a. ketone) is very amenable to attack and replacement and is the ideal stepping stone to final product. There are a variety of methods to accomplish this intermediate. Many of which Strike is now gonna lay on you!

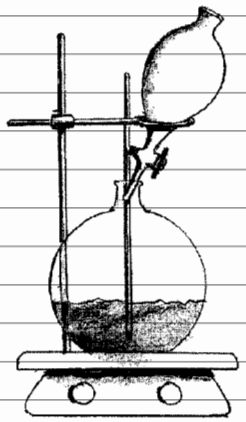
METHOD #1: Strike's sentimental favorite. The one Strike has dreamt about so very often. This method involves taking hydrogen peroxide and formic acid to form a temporary intermediate which is subsequently hydrolyzed with sulfuric acid to give the everlovely ketone.

This method is a little labor-intensive because it involves a lot of distilling, but it is so easy to do and the results are absolutely predictable! The production of MD-P2P or P2P using this method has been previously described [8,9] except that Strike is going to describe the little things. You know, those little bullshit things that never seem to work their way into official accounts but always cause a lot of stress to the novice chemist.



Safrole MD-P2P

A large flask or glass tea jug is placed in a tray of ice on top a magnetic stir plate. Into the flask is poured 340g of 30% hydrogen peroxide (H_2O_2, always store this chemical in the fridge or it will degrade over time) and 1500g of 88% formic acid. The formic acid fumes are immensely overpowering when the stuff is being transferred to the flask but as the solution starts to chill the formic won't evaporate so much and will barely be noticed. 324g isosafrole (or 236g propenylbenzene for meth) and 1000mL acetone are mixed in a PP container and then poured into a separatory funnel which is situated as shown in figure 9. The acetone solution is added drop by drop into the cold formic solution so that the temperature stays between 10-20°C. The temperature will start to rise a little but the ice bath is well stocked and the dripping is controlled so that the temperature stays below 20°C



[Figure 9]

The color of the solution will start off clear to pale yellow, then will turn orangy as the dripping continues. After about 200mLs of addition the chemist will notice that the temperature won't rise so much if the dripping is increased. When addition is complete, the thermometer and separatory funnel are removed. A piece of foil is placed over the opening of the flask and the solution is allowed to stir overnight. The solution is reddish orange after the addition. No more ice is added to the ice tray and the solution, as it stirs overnight, will eventually come to room temperature as the last of the ice melts away.

The next day comes and the hung-over chemist wakens to see a dark red solution stirring away. In some cases where the chemist had made an enormous batch of this stuff, there may be seen a small mass of crystalline precipitate at the bottom of the flask. This is no big deal and will go away in the next step. If the chemist had made this in a flat-bottomed flask (which she really should have for convenience) then the ice tray is removed, the flask returned to the stir plate, a distillation setup attached, and the acetone is vacuum distilled from the flask. After all the acetone has come over the chemist can proceed in two different ways. One way is to just keep on distilling the solution until all of the formic acid has been removed. The chemist knows that just about all the formic has been removed when there is about 300mL of thick black liquid remaining in the reaction flask and hardly any clear formic acid is dripping over into the collection flask. If one were to swirl the reaction flask, the liquid will appear syrupy and kind of coat the sides of the flask. This is more evident when the flask cools. A quick sniff of the flask may indicate that some formic is still in there, but it should be too minimal to be of any concern.

The problem with removing large amounts of formic acid by distillation is that it takes a long time to do so. Really big batches can take an entire day to distill. So a second option [10] after removal of the acetone would be to cool the formic acid solution then extract the whole thing with ether. The black ether layer is then washed with an ice cold 5% sodium carbonate (Na_2CO_3) solution to neutralize any formic acid that was carried over, then washed

once with clean water. The ether is distilled off to give a black heavy mass just as would have been attained by removal of formic acid by distillation except that it was done in a fraction of the time. One thing to add about this alternative is that it does not always work for everybody. There can be some heavy emulsions and, sometimes, the product forms some weird, heavy ball of tar. This is best tried under strict adult supervision. But it may not all be bad. The following is a Hive post by 'Quirks' letting people know what the goods are regarding a successful (Strike guesses) ether extract:

"*If you netralize the formic acid mix with 25% NaOH the layers separate out nicely. It takes ~.75 l of 25% NaOH to neutralize the soln for 150grm 88% formic, so you'll need a big sepatory funnel. After you hit ph 4.5 add it very carefully cause it'll run away to 9+ real quick. You can then back extract the water with DCM, or I guess preferably ether. If you use too much DCM when extracting it sinks to the bottom and some product floats on the top, so you end up with three layers... But then my lab tech SUXS!! (not that I'd partake in illegal activities ;p*"

Either way, the chemist is going to be staring at a black syrup in the bottom of her flask. Into it she pours 500mL methanol and 2500mL 15% sulfuric acid solution. If the chemist does not have a big enough flask the stuff will need to be halved or thirded and processed in batches. As soon as the sulfuric solution hits the methanol/product (oxime) layer the heavy black oil will form beads and sink to the bottom. The solution itself will get kind of milky and hazy. Now all the chemist does is slap a condenser into the flask just like fig. 7a and reflux for three hours. After such time, the solution is allowed to cool down to room temperature. Now, in large batches like this and those that are even larger than this one, its just not feasible to extract all that liquid with solvent to remove all the oil. Just about all the oil is sitting at the bottom of the flask. So the chemist decants (pours off) as much of the water as possible, adds fresh water, stirs, decants the water, adds new fresh water, etc.. Three washings of water should remove any traces of H_2SO_4 left in the oil.

Technically, if the chemist wanted to do things by the book, she would extract the whole H_2SO_4/oil solution with ether, then wash the ether with water. So the oil (which is now MD-P2P, by the way) is transferred to a small flask using ether and vacuum distilled (The oil is still very black with contaminants which need to be removed). After all the ether and water have come over and the receiving flask has been exchanged with a clean, new one, it may seem like an eternity for the oil to get hot enough to come over. But, eventually, the clear yellow oil front will start creeping up the glassware and into the condenser. About 250g (60%-70%) of MD-P2P will come over. The chemist knows its time to stop distilling when the oil flow starts to get a little orangy.

The MD-P2P produced here is very pure and is suitable for use in any of the final product conversion recipes.

*****HOT TIP #1*****

Distillation is always the most reliable way of separating things from complex mixtures such as relieving our P2P from its annoying black contaminants just like what was done above. But wouldn't it be nice if there was another way to do it for those without a distillation apparatus or who just didn't have the time to distill? Well, there actually is such a way, and it works fabulously!

For years chemists have been using sodium bisulfite (that is BISULFITE not BISULFATE) to actually crystallize a ketone out of solution in order to separate it. As it so happens, our happy little MD-P2P is a ketone. And when an oil mixture containing it is mixed with a saturated solution of sodium bisulfite ($NaHSO_3$) the MD-P2P crystallizes out as a 'bisulfite addition product'. It can then be easily separated by filtration. Here's how it goes...

When the MD-P2P/crap oil has been isolated and is at the point where one would normally apply distillation, this is the point where the chemist will use the bisulfite. One should not try this method unless the oil is rid of most solvent. In the Method #1 above, one would apply it after the ether from the final extraction has been removed by boiling or distillation (Yes, some distillation still ap-

plies!). In the methods to come, Strike will let you know when it can be done.

Anyway, one has the P2P/crap oil, right? Right. Next one makes a saturated sodium bisulfite solution by dissolving as much sodium bisulfite as will dissolve in a given amount of water (say, 1000mL). Now one adds the MD-P2P oil into some of the saturated solution and stirs for 30 minutes. The temperature of the reaction will rise and a big old mass of P2P crystals will form. People often say that the crystals look like chicken fat. Those crystals formed because the bisulfite from the sodium bisulfite latched onto the ketone of the P2P to form a precipitate. And since the P2P is probably the only oil component with a ketone, it is gonna be the only thing of any consequence that crystallizes.

The solution is allowed to cool and the crystals of the P2P-bisulfite addition compound are then separated by vacuum filtration, washed with a little clean dH2O then washed with a couple hundred mLs of ether, DCM or benzene. The filter cake of MD-P2P-bisulfate is processed by scraping the crystals into a flask and then 300mL of either 20% sodium carbonate solution or 10% HCl solution are added (HCl works best). The solution is stirred for another 30 minutes during which time the MD-P2P-bisulfite complex will be busted up and the P2P will return to its happy oil form. The P2P is then taken up with ether, dried and removed of the solvent to give pure MD-P2P. Whaddya think of that?!

This procedure can be applied to most P2P mixes but is especially effective on the methods to follow. However, in super clean methods, such as the $PdCl_2$ below, where lots of isosafrole is produced, the iso byproduct can interfere with crystal formation. Someone-Who-Is-Not-Strike once found that when an appreciable amount of isosafrole was formed to the detriment of MD-P2P, the oil screwed up the crystal matrix disallowing it to form. Confused, the chemist tried to rescue the uncrystallized oil from the aqueous solution by extracting out the oil to try other things. But when the solvent hit the solution, the P2P crystallized out. Go figure? The

chemist felt that it may have been due to the solvent solvating out the isosafrole which gave the P2P a chance to form more crystals.

Strike sees a point to this in Vogel's text 'Practical Organic Chemistry' (3rd ed.)[37]. In it, Vogel crystallizes his ketones using a saturated sodium bisulfite solution that *also* contains a little solvent. This is in contrast to the straight up aqueous (only water) solution that Strike described above. Here is what Vogel said on page 342:

'Prepare a saturated solution of sodium bisulfite at the laboratory temperature from 40g of finely powdered sodium bisulphite: about 70ml. of water are required. Measure the volume of the resulting solution and treat it with 70 per cent. of its volume of rectified spirit (or methylated spirit) [ethanol or methanol or both, dude] *; add sufficient water (about 45mL.) to just dissolve the precipitate which separates.'*

Either pure aqueous or aqueous/solvent solutions work. It is entirely up to the preference of the chemist as to which one they use. Just to make one feel more secure, there is a little test one can do with the bisulfite solution to see if they got it right. Just put a little of that ketone known as acetone into the saturated solution and watch the crystals grow. Isn't it nice how chemistry works?!

Now then, there are some chemists that rely on bisulfite as a tool to physically separate all of their ketone from an oil mix. But some chemists, using some methods, are rightfully sure enough that their ketones were produced in such high yields, and so cleanly, that separation isn't necessary at all. But even they, like anyone else, would still like to know for sure that what they made was P2P. This bisulfite procedure works in this regard as well. If one wants to know if what they made is P2P all one has to do is just drop a mL or so into the saturated bisulfite solution and see what happens. If crystals form, one has ketone. If not, one has fucked up.

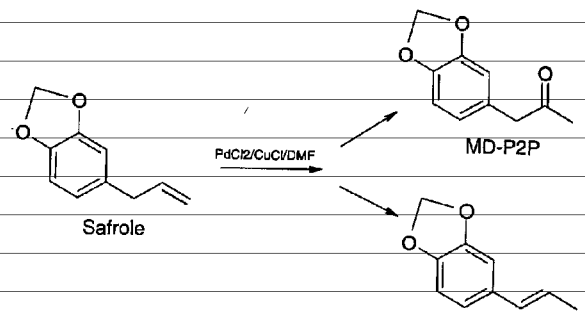
One can even use this test as a quantitative measure. The chemist can weigh 5g or so of their P2P product, crystallize it and weigh

the subsequent P2P oil that results to get an idea of how much of their product is honey, and how much is not. Get it?! As Strike hopes you can see, this simple sodium bisulfite tool has an enormous amount of potential for helping the evil chemist out.

One final thought. Strike found that there are a lot of companies that do not sell sodium bisulfite ($NaHSO_3$). In fact, a lot of companies list 'sodium bisulfite' in their catalogs but tell the reader to see 'sodium metabisulfite' instead because that is the only form of this compound they carry. In other words, a lot of companies sell sodium metabisulfite ($Na_2S_2O_5$) as an acceptable alternative to the other. The Merck Index even says about sodium bisulfite that "*the [sodium] bisulfite of commerce consists chiefly of sodium metabisulfite, $Na_2S_2O_5$, and for all practical purposes possesses the same properties as the true bisulfite*". What this meant to Strike was that metabisulfite would work just as well. So some was purchased and tried. And it really does work just the same!

METHOD #2: Without a doubt, this is the current world favorite for making P2Ps. This method is known as the Wacker oxidation and involves mixing safrole (or any other allylbenzene), palladium chloride, cuprous chloride and dimethylformamide in an oxygen atmosphere to get MD-P2P very quickly and in a totally clean manner [11, 12]. There's also a very nice review in ref. #13.

Strike ranked it #3 in the Top Ten from the first edition because Strike didn't think people would bite at the idea of using such an expensive catalyst as $PdCl_2$. Street chemists are often tightassed when that is the last thing they should be when it comes to production. But this has not been the case with this procedure as Strike has happily found out. At \$7.00-\$9.00/g, $PdCl_2$ is still pretty pricey but this has not been a deterrent as many chemists have found. Nor should it be. This procedure works so well that it would, in fact, be stupid not to do it should one happen to work in an accredited, licensed research lab. The following is what Strike first wrote about it.

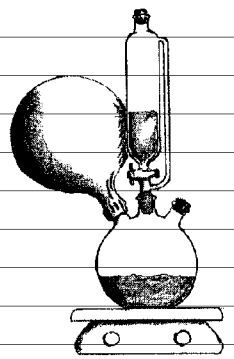


The reaction proceeds via the above schematic. And as one can see in the above schematic, the major side product of the reaction is not tar or junk but is the very useable isosafrole. This is just another illustration of the desire of the safrole double bond to migrate to the isosafrole position when given the chance. The cuprous chloride (CuCl) and oxygen are there to promote and keep the $PdCl_2$ in a +2 state (don't ask). There are two different apparatus setups that a chemist can use to complete this recipe depending on the equipment available. Figure 10a shows a setup using a three-neck flask and figure 10b shows how the same system can be attained using a single neck flask. Also, one can use the single neck flask by placing the Claisen adapter from one's distillation set into the flask's neck.

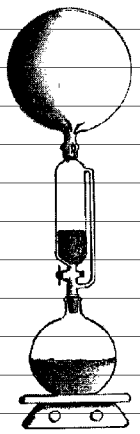
No matter which flask is used, an addition funnel is required. An addition funnel is just like a separatory funnel except there is an extra side arm that allows for addition into a system that has pressure (which this one is going to have). Strike knows! Strike knows! Pressure sounds complicated but this one isn't. You'll see. The addition funnel can be bought, made from a separatory funnel as explained in the **How to Make** section of this book, or

can be made entirely from scratch as suggested in the same section.

The pressure is going to come from oxygen that is applied to the system using a balloon. Pure oxygen is easy to get. The chemist can get it from the neighborhood specialty gas cylinder company or she can plow through the grannies down at the local pharmacy and get a small, personal use bottle there. The oxygen is then used to fill up one of those thick walled carnival balloons that can be bought at any toy store.



[Fig 10a]



[Fig 10b]

The idea is to have everything in place before the oxygen is applied. So, 100g of safrole is in the addition funnel and stirring around in the reaction flask are 10.6g of $PdCl_2$, 60g CuCl and 500mL of aqueous dimethylformamide (made by mixing 62.5mL dH_2O and 437.5mL DMF). Dimethylformamide (DMF) is not the same as the watched chemical known as N-methylformamide.

DMF is a common, legal solvent. If a three-neck flask is being used then the openings on top of the addition funnel and the unused neck of the flask are plugged with stoppers and the stoppers secured in place with wire or strong tape. With everything all set the chemist fills up a balloon with oxygen, pinches it closed with her fingers, wraps the end over whichever opening is appropriate and releases. This setup can look pretty cool depending on what kind of balloon the chemist chose. Maybe one of the three foot elliptical kind or one with a ducky printed on it.

Anyway, all that pure oxygen has infiltrated every part of the enclosed system and the solution in the reaction flask is allowed to stir, exposed to all that oxygen for 1 hour. At first the solution is brownish black, but as it absorbs the oxygen over that hour's time it will turn an olive green. After 1hr it's time for the chemist to add the safrole slowly over a 30min period. As the safrole is being added it will start to take up all that oxygen causing the palladium to turn black again (shows that things are working) but after the addition is complete and the safrole has been converted to MD-P2P the palladium will again start to soak up the remaining oxygen and turn green once again. The solution remains stirring at room temperature for 16-24 hours. If the balloon loses significant volume during the reaction, one just fills it up again. Nothing bad will happen.

The next day the chemist takes a PP container of 1500mL cold 3N HCl out of the fridge and pours the contents of the reaction flask into it. The mixture is stirred a little and extracted 3 times with 100mL portions of either DCM or ether. The one thing that needs to be added here is that the DCM extract needs to be washed 2 to 3 times with water. Many bees have reported that this reduces/prevents an emulsion from happening in the next step. The solvent is then washed with 200mL saturated sodium bicarbonate ($Na(CO_3)_2$) solution then with 200mL saturated NaCl solution. Technically the washings can be skipped, but either way the solvent is going to be dried through sodium sulfate in filter paper and the sodium sulfate washed with a little extra solvent just as is described in the methodology section of this fine book. The solvent is then removed by distillation leaving what should amount to

about 70-80% MD-P2P and 20-30% isosafrole oils still left in the distilling flask.

Oh boy! Here's another case where there is a couple of similar boiling oils that the poor chemist is going to want to separate. Again Strike is going to say that the best way to do this without fancy separation columns is going to be to allow that the first 5-10mLs of oil that distills over is going to be mostly isosafrole and the rest of the clear oil that comes over is going to be the MD-P2P. Strike has never been a believer in predicting the precise temperatures that something comes over at relative to the pull of vacuum or the size of the distillation apparatus. It varies too much and is never applicable to any given circumstance. Strike knows three things in instances like this: 1) solvent always comes over first at low temperatures and in a very rapid manner, 2) the isosafrole starts to slowly roll over at about 170°C at regular vacuum (who the hell knows what that is?), 3) after about a 3-5 degree increase in temperature (usually no increase is noticeable) or, more importantly, after about 5-10mLs of oil has collected then it's time to switch flasks and start to collect what is assumed to be the MD-P2P. In the end, the chemist should just follow her nose. Does the first few mLs of oil smell strongly of licorice? Does all the rest of the oil not? Strike cannot answer this either. The isosafrole fraction will smell like licorice but MD-P2P always smells different relative to the type of reaction it is borne from. Pure MD-P2P doesn't have that strong a smell and can usually be overpowered by impurities that will always carry over with it from the reaction it came from. So MD-P2P that comes from a reaction using formic acid or mercury compounds is going to smell a little differently than one that came from a reaction using palladium. However, the distinction between isosafrole/safrole and MD-P2P is quite evident. In the end, a little of one in the other is not going to hurt things much.

Of course the chemist may wish to forego purification and separation of the two remaining oils by distillation and opt for the sodium bisulfite procedure described earlier. That particular method is perfectly suited for this situation. Perfectly.

If using oxygen balloons is not one's cup of tea, then there are ways to supply the oxygen without it. It has been demonstrated that using quinone (benzoquinone) can accomplish the same thing [12]. To do this one has all the ingredients, including the safrole and quinone, stirring in the reaction flask except for the water that was mixed with the DMF. That water is going to be the thing that is placed in the addition funnel and added to the reaction mix. Another oxygen source can be that of 30% hydrogen peroxide [14]. This procedure is done exactly as the regular method except that the aqueous DMF is made with 30% hydrogen peroxide instead of plain dH_2O.

Other alternatives for this procedure can make it even more versatile. To decrease that 24hr span of incubation/stirring one can run the entire reaction at 60-70°C from the beginning of addition. The reaction need only proceed for about 3 hours. The downside is that a three neck will have to be used to accommodate a thermometer and reflux condenser. Another switch can be made by using cupric chloride ($CuCl_2$) instead of cuprous chloride (CuCl). Both work equally well except that $CuCl_2$ has a tendency to chlorinate the product slightly. Strike has since learned that any and all of these alternatives work well! Keep reading farther down the chapter for all the goods on it!

So anyway, that was what Strike told everybody in the first edition. People then ran with the idea and came up with some very interesting observations of their own since then. The following is an account of the $PdCl_2$ method contributed by our good friend TDK. From what Strike knows of TDK she seems to be a very accomplished, careful and intuitive chemist in her own right. Nothing illegal of course. But she always seems to be coming across evil methodologies that others produce.

"I contacted my sister's friend and went over to her compound for a complete run down on what she dreamt... Her dream was of an educational nature and so should the following be construed as just that...

The Wacker Oxidation a.k.a. #3 of 10 (most fool proof of the lot)

The following is her interpretation, simplified to its MOST BASIC FORM, for the layman with little experience:

First she lists the equipment, next the reagents.. Also, noted are the book's quantity and her dream of a 5x scale up:

Equipment for 5x scale:

Phase One - Equipment
6-liter flat bottom flask (single 24/40 neck)
1 claisen head adapter (24/40)
1 1-liter addition funnel (24/40)
1 Teflon stir bar
1 heavy duty balloon
1 roll of electrical tape
Magnetic stirrer
Support stand and clamps
Ohaus triple beam scale
1 plastic funnel

Phase One – Chems	***5x scale-up***	***Total Synthesis***
Safrole	*500 grams*	*100 grams*
Palladium Chloride	*53 grams*	*10.6 grams*
Cuprous Chloride	*300 grams*	*60 grams*
DMF	*2187.5 mLs*	*437.5 mLs*
Distilled H_2O	*312.5 mLs*	*62.5 mLs*

1 cylinder of pure O_2

The above reagents (ok the safrole and H_2O aren't reagent) are weighed or measured accordingly. The flask is securely clamped into place on the magnetic stirrer. Add the DMF and H_2O. Start stirring, and then slowly add the palladium chloride and cuprous chloride. If you add the powders first then the liquids you'll have problems with the stir bar finding a place to spin.

Now you have the DMF and H_2O stirring away with the $PdCl_2$ and

CuCl added. Insert the claisen head adapter into the flask. Be sure to apply some vac-grease to the joints. Place the addition funnel in the center hole. Add the 500 grams of safrole to the funnel, but don't start adding it to the stirring solution. Next fill the balloon up with O_2. She said that she filled it up pretty tight, but don't blow it up. Carefully attach the balloon to the remaining open hole on the claisen adapter and then TAPE or wire it to prevent any leakage. For those of you that don't have access to various pieces of glassware, placing the balloon on the addition funnel will work as well. This was described in the book, Total Synthesis, pages 52 to 55.

You let the solution stir for 1-1/2 hours so it absorbs as much O_2 as possible before you start adding the safrole. Everything is kept at room temperature for this procedure. The stirring solution looks very dark, almost black in color. Now slowly add the safrole from the addition funnel so that it takes about 60 minutes for the 500 grams to drip in. There is no noticeable reaction as the safrole is dripped into the stirring solution. Once this is completed let it stir away for the next 24 hours. Note: In her dream, she checks the balloon at the 12-hour mark. It has gone down in size as O_2 is being absorbed by the stirring solution. She inflated another balloon, removed the one that had been on there for the past 12 hours and placed the new, full balloon on the open hole. Tape or wire it so there's no leakage. This ensures an adequate O_2 atmosphere while the process finishes (excessive, yes, but cheap and simply). She noted that after 3-4 hours of stirring the solution changes from a dark almost black color to a dark sea green or dark olive green in color.

After 24 hours, the stirring is stopped. Now it's time to filter out the Cuprous Chloride, which is one of the two slight nuisances regarding this procedure. Note: forget about Palladium Chloride recovery. It's too complex for the simplicity of this procedure and purchased from a photo supplier it shouldn't cost more than $6.50 per gram. We'll call this next process Phase Two.

Phase Two - Equipment (Vac filtering)
Vacuum pump

Vacuum-Trap set-up
Buchner funnel
Whatman filter paper
1 4-liter filtering flask (Heavy Walled)
Support stands and clamps

Phase Two - Chems
3N HCl Book calls for 1500 mLs, on the 5x scale up she used 3000 mLs
Silica sand (white, sterilized and washed) or
Celite
Methylene Chloride

There are two ways one can try to filter this solution before acidification. First, set-up your vac-filter flask with vac-trap, Buchner funnel & vac source and start the filtering process. A 5x scale up will take about 6-8 hours to filter. The cuprous chloride is in suspension and it almost completely clogs the filter paper making the process painfully slow. She found a method that works fairly well and reduces the filter time to about an hour. Set-up your vac-filtering as usual, moisten the filter paper with a little H_2O, then pour a ½ inch thick layer of sterilized and washed white silica sand on the filter paper. Moisten the sand with a small amount of H_2O. Apply the vacuum to the set-up and then start pouring the solution right into the sand. The sand will keep the cuprous chloride from totally clogging the paper up. Celite can be used in place of the sand. Celite is a 'filter aid' is available wherever fine chemicals are sold. It's a standard and unwatched laboratory item. Celite works in a similar fashion as the sand. White silica sand is readily available without having to deal with a chem/lab supplier. Place the filtered liquid into a PP container and add the appropriate amount of 3N HCl. She stirred it with a wooden paddle for a few minutes.

The solution is ready for extraction. In her first dream she used DCM and broke it into 4 extractions of about 1500 mLs each (she had a 2-liter separatory funnel). Since DCM goes to the bottom, a separatory funnel is a must. Buy or make one. The extractions should go without any problems, as there isn't any emulsions to contend with. She used 100 mLs of DCM for each extraction.

The extracts are pooled. Wash once with a saturated solution of sodium bicarbonate. This washing is absolutely necessary (the book says it can be skipped - DON'T!). The problem with it (and this is the other nuisance of this process) is that a scum and emulsion develop from the wash neutralizing the acidic nature of the extraction. The easiest way to deal with is to vac-filter the mess. Your rid yourself of the scum and breakup the emulsion into a fairly easy to separate liquid. One washing with sodium bicarbonate is sufficient, then wash once with a saturated solution of sodium chloride, then once with fresh H_2O. Now the extract is dried with sodium sulfate. Your are ready for vacuum distillation. The DCM extraction should be golden to dark brown in color.

Phase Three - Equipment (Vac distillation)
Vacuum pump
Vacuum-Trap set-up
Heat Mantle with heat controller
Or hot plate with oil bath
1 3-liter boiling flask (round or flat bottom)
3-way adapter (still head) 24/40
1 West condenser
Vacuum adapter; condenser to receiving flask (24/40)
1 1-liter round or flat flask (used for receiving ketone)
1 thermometer adapter (24/40)
1 thermometer -10 to 400 C
Tubing for water in/out
Misc fittings to hook water lines up
Aluminum foil (to wrap flask & still head-insulation)
Support stands & clamps

****

Phase Two – Chems
Washed & dried DCM extractions

Set-up for vac-distillation. She wraps the flask and still head with aluminum foil to act as an insulator. Speeds up the distillation process. Begin to heat the DCM extraction slowly under maximum

*vacuum. Her vac-pump would only pull 100mm Hg, so the temp at which product first started coming over was 198-200 C (approx 60 grams of isosafrole - 12%), then again at 204 C. (*yield of ketone was 308 grams 61.6% +). The plus being residue that could not be distilled as there was not a small enough flask to finish the distillation. DO NOT run the larger flask close to dry. If you do, upon cooling the residue will carbonize and push black crap through the condenser and into your clean, yellow ketone. Or worst yet, it will expand so rapidly that the carbonized mass will cause the flask to push away from the condenser and possibly break a valuable piece of glassware. When you get to 1/4" of material to be distilled, it's time to stop. Either save to pool with other similar materials for future distillations or use the bisulfite procedure to separate and purify. This was explained from experience; she ran it close to dry and had the worse happen. Black crap shooting through the condenser into 330 grams of clean ketone. Two distillations did completely rid it of the discoloration or smell.*

**Yield; isosafrole, 60 grams (12%) TOTAL-MDP2P, 338 grams (57.6%) The smaller portion was distilled in a 500 mL flask and yielded another 30 grams. Total yield 79.6% / 67.6% (MDP2P) + 12% (ISOSAFROLE).*

The above dream was scaled up in exact portions, as it was her first. Her next dream had some variations to weights and measures, plus a longer reaction time...

Noted are the changes to the above dream:
Phase One - Chems
Safrole: 500 grams (same)
Palladium Chloride: 26.5 grams (50% less & big saving in $$)
Cuprous Chloride: 300 grams (could have cut this to 200 g)
DMF (n,n-dimethylformamide): 1500 mLs (31% reduction)
Distilled H_2O: 300 mLs
1 cylinder of pure O_2

Do everything else the same except; let the solution stir in the O_2 atmosphere for 72 hours. You'll need to check the balloon every 12 hours or so. Replace as needed (when it starts to sag). The color of the reaction after 72 hours was a richer, darker green and the final yield was 362 grams ketone 72.4%, 51 grams isosafrole 10.2%). Not bad for very little work and it is very difficult to screw this up! Once the safrole is added, you can forget about it until it's time to check the balloon."

Note TDK's appalling pronoun use. Actually, niether TDK nor Strike can be held accountable because this was written by someone else who addresses the audience in a normal way. That aside, look what happened in that account. Seems like the traditional reagent proportions of $PdCl_2$ and others may have been overkill. Given enough time to react, very small amounts of $PdCl_2$ can do the job just fine. That certainly makes a difference in one's wallet!

The next example was a post on the Hive by a bee named TaRa (Could be an alias of TDK. Strike ain't sure.). It is essentially the same old song except this girl proved that $CuCl_2$ (cupric chloride) can indeed be used in place of CuCl (cuprous chloride). It also gives you more examples of technique. The more of this one has the more confident they will be in their 'understanding' of the method.

"Interesting results for something that was thought to be a lost cause [Lost Cause?!]. *Dreamt about using CuCl2 for process #3 as follows:*

In this dream the book writer's chapter began like this - It took 800 g saf, 44 g $PdCl_2$, 240 g $CuCl_2$, 3500 mls DMF + 500 mls H_20, stirred in O_2 atmosphere with balloon for 96 hours in a 3-neck 12 liter flask; yield was 69-71%, (distilled, did bisulfite and then re-distilled the oil from the bisulfite procedure).. Note better lab techniques would get better yield. Materials lost in washing and filtration, purification distilling, etc... This chapter followed the book's (TS) outline, but a few simple variations were applied. To eliminate the nasty emulsion from the sodium bicarbonate wash they washed the initial solvent extracts (right after acidification) 3x with H_2O. Used DCM as extract solvent. Removed a good deal of $CuCl_2$+ some $PdCl_2$ with those H_2O washes. Note, don't know if

this helped but they dissolved the catalysts in 400 mls of DMF + 100 mls of H_2O before they were added to the vessel. The catalysts remained dissolved for the complete rxn' Maintained as much pressure as the balloon would hold as they feed the flask directly from the O_2 cylinders putting the balloon on the top opening of the addition funnel. Used a ground glass 3-way joint with a hose from the regulator to feed O_2 into the system. Was easily able to keep flask as full as possible with O_2. BTW, balloons will burst when filled beyond capacity and it will give you a rush that's not forgotten easily'.(makes you think you blew you rxn up)"

Interesting note, using $CuCl_2$ for the first time.. NO OLIVE GREEN color appeared. Stayed slightly yellow -dark brown... All the way through the rxn. Never came close to Green (light, dark or olive). When rxn finished solution was very dark reddish-brown, even when acid washed it stayed dark reddish brown.

The reduction of catalysts warranted the additional stir time. 96 hours maybe excessive, I believe they were hoping it would turn green and the longerthey waited the more they thought it was a lost cause. Fortunately it worked out on the +++ side ;) "

To read more about the use of $CuCl_2$ read ref #15.

Now here is a post from a very influential chemist named Spiceboy who has contributed quite a bit to this science (hypothetically of course). She decided to go ahead and apply the idea of using benzoquinone as the oxygen source. If this works it would mean that one would not have to use a balloon of O_2 at all, thus making the entire apparatus much more simpler and causing an increase in the efficiency of oxygen uptake and transfer by the system. So let's see what Spiceboy dreamt might happen if this were actually applied:

'Holy Ketone! What a dream.....

Dream setup; 100 ml of DMF stirring in a flask equipped w/ a sidearm 34 g of safrole was added in 4 portions of about 8 g each. Mixed intimately. Next, 11g of p-benzoquinone was added. Stir rate was upped. Finally, 7 g of pdcl2 was added. A dry addition

funnel was coupled to the flask, and 5ml of dh2o was measured into it. Thermometer was attached to side tube. At midnite, one ml of h2o was added, temp went to 70c.Brisk stir rate.15 min et and another ml of h2o added. External heat, if needed is used. At 1:00 another ml was added, and temp held at 70c.at 2:30 the final ml was added, and there should be a trace left, but ok if it aint.....held at 70 c for 30 more minutes, allowed to cool to room temp, flooded w/ chilled h2o, and extracted w/ starting fluid(nod to Q)....BOOOOOMI yield; over 70% "

That looks great, Spiceboy. Thanks, Bra'! And to show you that Spiceboy isn't making this up, the following experimental will prove it. This was taken from the review [13] written by the same doctor that authored the progenitor $PdCl_2$ article that Strike drew from to formulate this recipe. And just as Spiceboy says above, there is no need for any copper compound or balloon. Also, the reaction time is seriously shorter and the amount of PdCl2 catalyst needed is drastically reduced:

*" In a 100mL round-bottomed flask fitted with a magnetic stirrer is placed a mixture of palladium (II) chloride (89mg, 0.5mmol), p-benzoquinone (5.94g, 55mmol) and 7:1 dimethylformamide/water (20mL). To the solution, 1-*decene [substitute safrole for this compound*] (7.0g, 50mmol) is added in 10 min and the mixture is stirred at room temperature for 7h. The solution is poured into cold 3 normal hydrochloric acid (100mL) and extracted with 5 portions of ether. The extracts are combined and washed with three portions of 10% aqueous sodium hydroxide solution and a portion of brine, and then dried After removal of the solvent, the residue is distilled to give 2-decanone [P2P]; yield 6.1g (78%).*

The last variation we should discuss is about the use of solvent. Ever-bitching about the rarity and price of chemicals, the bees have thrust their anger at the DMF used in this method. TDK sent Strike an article that gives some credence to this [16]. In it the alcohols methanol, ethanol, 1-propanol, ethanediol and others were used in place of DMF with beautifully high yields. Below is the sample experimental from the article (just picture using safrole or allylbenzene in place of the 1-hexene):

*"**2- and 3-Hexanone.**---A 50-ml portion of 0.665 M 1-hexene, 0.020 M $PdCl_2$ and 0.100 M $CuCl_2 \cdot 2H_2O$ in 1-propanol was shaken for 120 min at 50C under 3 atm oxygen. The reaction mixture contained 2.0% water from all sources (salt hydration, impurity in the alcohol and water of oxidation). Of the hexene charged, 13% (by gc area) remained unreacted and 86% was converted into hexanone and 1% into side products. Resolution of the hexanone peak showed 75-76% 2-hexanone* [or MD-P2P for the likes of us] *and 24-25% 3-hexanone, both identified by means of residence times and infrared spectra in comparison with authentic samples."*

Whaddya mean it won't work for things like safrole just because the substrate used was 1-hexene?! The only thing Strike had to go on years ago was one article [11] which had as its star 1-decene. And yet the method translates! This last contribution (by Spiceboy again), shows that using methanol as a solvent works just fine and, as has been suggested by others, can lead to a reduction in the amount catalyst needed. Strike doesn't know what the hell is up with the bicycle pump, but to each her own:

"Welcome back...now, before I give up dream details, I want to thank Osmium for his inspiration. You got me to thinkin' man. I want to say that this is another offshoot, I guess , of #3,but with some twists. Such as....process ONE HUNDRED GRAMS of olefin with 2 g of pdcl2, and 8 g of cucl2. There will be no oxygen tank. FUCK THAT SHIT! The reference I based this on indicated that air will work Whaddya know? Theyre right. The air comes from a 14.95 piece of shit tire pump from walmart. It will pressurize the SRV in about 10-20 seconds. Here we go:

Dissolve 8 g CuCl2 in 80 ml MeOH.Dissolve 2 g PdCl2 in40 ml MeoH. Dissolve 100g of safrole in 200 ml MeOH . Pour it all in and add MeOH to make 500 ml MeOH total. Swirl and gently shake. Pressurize the SRV to 37 psi. A tire gauge works great. After one hour, release the pressure and immerse in warm water for 2-3 mins. Shake. Re-pressurize. Repeat process hourly. At night, before bed, pressurize again, allow to stand overnight. My time elapsed; 13 hours at bedtime + 8 hr sleep = 21 hours reaction time. Hit it w/ 3N HCL and extract per usual. KA-FUCKIN' BOOM! 80% + !!!!!!! "

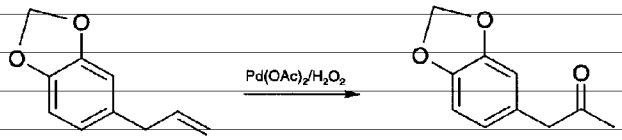
Whatever!!! This person needs some serious psychological help! But Strike would not dismiss the chemistry. No way!

Well, that should be enough examples to give you a good idea of how this Wacker oxidation method works. There are a lot more interesting variations that bees have been posting on the Hive if you wish to read more.

Finally, it must be restated that the biggest plus of this method is that it produces 70-80% MD-P2P or P2P, and 20-30% isosafrole or propenylbenzene as a side product. So if the chemist were to turn around and process that isosafrole using, say, the formic acid method #1, then the potential P2P production from this method could climb to well over 90%!

METHOD #3: As of the printing of this book, this method is still in the experimental stage. But it represents the next generation of the Wacker oxidation and should, if properly realized, scorch the old one in both yield, cost and time. This is entirely due to the work of Osmium, TDK and an aggressively active European chemist named Sunlight. They, and maybe others, found the journal reference, contemplated it and started dreaming about its application. All Strike is doing is filling you in on what Strike has seen and been told.

The method is basically an application of the Wacker oxidation except that the catalyst used is palladium acetate ($Pd(AcO)_2$ or $Pd(O_2CCH_3)_2$), the solvent is acetic acid or tert-butyl alcohol and the oxygen source is the previously suggested hydrogen peroxide (H_2O_2) [17].



Safrole MD-P2P

This article was written by a French group. Strike has mixed feelings about French science. On the one hand they are usually quite correct in their chemistry. On the other hand they are always too lazy to write up the details in a comprehensive and detailed manner. It's like they want to tell you how great they are, but they don't want you to share in it. Strike can say this with confidence because Strike has yet to have anyone from France buy any of Strike's books, so Strike knows they won't see this one either (tee hee!).

Anyway, the details are a little hard to process but the results are very clear:

"*This paper describes a very efficient catalytic procedure for the oxidation of terminal olefins* [ie safrole] *to methyl ketones* [ie MD-P2P] *by hydrogen peroxide using a palladium catalyst and operating in the absence of halogens and co-metals* [ie no CuCl or $CuCl_2$ needed]... *This reaction is carried out either in biphasic medium, using solvents such as ethyl acetate or dichloroethane, or in homogeneous solution, using* tert-*butyl alcohol or acetic acid...a quite complete conversion of 1-octene (90-95%) was obtained after ~3h or reaction time...Under these conditions, 1 mol of palladium was found to transform ~400 mol of 1-octene into 2-octanone per hour.*"

That, folks, is an incredible reaction rate! They are essentially saying that less than a gram of Pd catalyst will turn 100+g of safrole into MD-P2P in less than 3 hours! The cryptic optimal reaction conditions and procedures are as follows:

" *temp = 80C; H_2O_2 (30%): 1-octene = 5; 1-octene:Pd = 1500; reaction time* = 6h. [or in other words] *$0.5x10^{-3}$ M $Pd(AcO)_2$; 0.75 M 1-octene; 3.75 M H_2O_2 (30%); solvent AcOH; temp 80C.*"

The experimental procedure:

"The olefins were oxidized in a three-necked 1L thermostated glass reactor equipped with a magnetic stirrer, a condenser, and a 100mL glass funnel (for introduction of H_2O_2) and connected through a gas counter (for the evaluation of O_2 evolution) to the atmosphere. H_2O_2 solution was introduced dropwise into the mixture of olefin, solvent, and catalyst during 30 min at the reaction temperature. When the reaction was complete, the mixture was cooled and water was added. The yellow upper layer containing the catalyst was separated and passed through a column of alumina in order to eliminate the catalyst and reduced under reduced pressure."

Yeesh! What the hell did all that mean? Well, let's see what Sunlight's preliminary interpretations are as were secreted to Strike via encrypted messages. It is interestingly voyeuristic to see the first machinations of a recipe come to life:

"Well, I've started to work a few days ago with palladium acetate. Normally I start with quantities of 10 - 20 cc of safrol, but this time, animated becuase you [not Strike!] *said there's someone who said this way is good, I make a direct production test with 150 grams of safrol. Well, at 80 C, and after 1 hour or so, I go out from home 10 minutes, and when I came back, rxn was no controllable, a exhotermic rxn started with a lot of evaporation of acid, I did another mistake when trying to stop rxn and a lot of acid whas in the atmosphere. It was hard, near intoxication. Other test with small quantitie shows me 80 C it's too much.The product obtained was only a clear brown tar with no ketone. The problem was the temp, it's too high. I've started again with my classic tests. I put yesterday 10 cc of safrol with 50 mg of $Pd(OAc)_2$ and 35 cc of H_2O_2 30 % and 70 cc of acetic acid at room temp (30 C). After 16 hours, this morning before go to work, rxn was not complete, (in the night temp goes down), and I think in 24 hours it will be done. I put a piece of glass in the flask and wait to acetic acid is evaporated,*

then I smell, if there's safrol, I smell first safrol but like safrol is more volatile than ketone, after 5 minutes (or more depending ratio safrol:ketone) start the ketone smell. I can now smell the ketone in my fingers. I don't know how yield can be achieved. Other probelms are if temp is not used, it's necessary more solvent, may be 1 liter for 100 cc of safrol, what is too much, it will complicate extraction, although in my test there are 70 cc and it seems to work, but it is not an homogeneus solution. In JOC they say the reaction can be done in dual phase, this will be my next try, if it runs, it will be the best, just stir safrol with H_2O_2 and solvent (I'll try with toluene), when done, add some $NaHCO_3$ and stir, and then separate layers, distill. Perfect simplicity, will it work ? It seems best temp will be 40-50 C, it will increase reaction speed."

A few days later:

"I' m working now. Best results were obtained with dual phase with toluene at 50-60 C 24 hours stiring. The isolated oil smelled a lot to ketone, and when two drops were added to a saturated solution of sodium metabisulphite and stired, practically all reacted forming the addition product that precipited to the bottom. I think it's about 80 % yield, but it's only an impression, may be less. Now I'm repeating the experiment to determine conditions and then, I'll do a >100 grams batch, so I'll determine yield. The problem has been is needed a good stirer, and I was working with a motor cassette with two magnets, I realised only 300-400 rpm. Then I bought a more potent one, but now my problem is the noise of it, because it must run 24 hours...

The recipe will be somethlng like :
100 grams of safrol
150 cc of toluene.
100 cc H_2O_2 30 % added dropwise
100 cc H_2O_2 30 % added dropwise at 6 hours
100 cc at 12 hours
100 cc at 18 hours...
2.5 cc of acetic acid
0.5 - 1 gram of $Pd(AcO)_2$ stir about 24 hours.... thats all.

Then add a bit of $NaHCO_3$ (4 grams) and salt to saturate solution. Stir a bit more. Separate layers, Extract one more time and distill. Time depends on reaction speed. Reaction speed depends on the amount of catalyst and temperature. 60 C seems to be good, more catalyst, less time. More temperature ? May be more by-products, this is what happen when acetic acid is the solvent. Probably a good way will be also acetic acid and 40-50 C, but dual phase is easy to extract ans uses less chemicals.

I hope my reaction success and I can run the 100 grams batch tomorow. Another difficultie is now water tap is at about 29 C (to distill) , may be I'll use a refrigerator compressor, I think it will be enough to distill ketone at about 180 C.

Couple of questions for me:

?>Add the toluene + safrol into rxn vessel, then add acetic acid + >$Pd(AcO)_2$, then start stirring, then start dripping in H_2O_2?

Well, I think it's better to add a bit of H_2O_2 to the toluene + safrol + catalyst to prevent catalyst decomposition, for example, with 100 cc of safrol, 10 cc of H_2O_2, and then add the rest dropwise.

?>Also, is the amount of acetic acid exact, for example would 5 cc hurt
>the rxn or help it (in your opinion).... I don't think more >temperature would help, probably create more by-products! ?

Well, I thought previosly a bit of acetic acid can help reaction to prevent decomposition of catalyst. Now I'm thinking after re-read JOC article 1425 times, acetic acid is not needed at all, because if catalyst degrades to Pd metal, is not more dissolved, so why add acetic acid ? My last test with 10 cc of safrol had 0'4 cc of acetic acid, but I'll omit it in next rxn.

I've found that unfortunately, there is a hyper oxydation of oleofin as side reaction, and gives organic acids, probably MDPhenylacetic acid and may be a bit of piperonylic acid. It's easy to realise it,

just measuring ph after reaction. I suppose this side reaction is more important when temperature is high. My last try was dual phase, 10 cc safrol, 0.7 $Pd(AcO_2)$, 20 of toluene and about 45 cc H_2O_2 in three times and at 60 C, may it's too much high. So if we decrease temp reaction, we must increase time or catalyst. If we increase time, H_2O_2 degrades in time, so we must add more, and H_2O_2 concentration decrease, so reactivity decrease also a bit (I think). Best solution will be increase a bit catalyst. BTW, in my next try I'll use $PdCl_2$, as I said you in the first samples I saw $PdCl_2$ yilds also ketone. So I'll do a sample with exact conditions to $Pd(AcO)_2$, and I'll compare results. It' would be better to work with $PdCl_2$. Now, when I come back to home, I'll extract my last 10 cc reaction, and I'll see the lose of material in carboxylic acids, because they will go out in basic wash. I'm afraid my last yield will be about 50-60 % only, far from desired 80 %, but not bad having the nature of chemicals (toluene and H_2O_2, OTC) and the little effort that supposes. But I would prefer 70 +. So try to send me the information of your friend's friend, may be there is some key in it important for me. I'll hope improve this method to make a simple, elegant, cheap, OTC, high yielding procedure. I have only a bit more than 100 cc of safrol. I'll do one or two tests more and then I'll process the rest. And Ketone research will finish for me. May be I'll have your post tomorrow ?
Thanks"

See how things happen when a competent, energized chemist gets ahold of a new recipe? Well as it so happened, Sunlight was getting a little uncomfortable with the results (as was communicated in later emails) and decided to contemplate the alternative use of tert-butyl alcohol and other solvents as was discussed in the French journal article. But just days before this book went to print came the news that will change the production of phenylacetones forever. TDK, bolstered by the reassurances from a secret group of chemists that have apparently been using this recipe for years but forgot to tell everyone else, came through again. The following is the proof positive definitive application of this recipe:

"200 g safrol + 1 g $Pd(AcO)_2$ + 500 mls tert butyl alcohol + 400 mls 35% H_2O_2. Added everything but H_2O_2 to a 5 liter two neck flask equipped with a reflux condenser, thermometer, and dropping funnel, mounted in an oil bath on a good magnetic stirrer. Started stirring while bringing the temp to 80C. At 78-80C start to add the H_2O_2. It was added over a 30 minute time frame. As this was added, they noticed an evolution of bubbles coming from the rxn (O_2 from the H_2O_2). Monitored stirring and temp with no unusal occurrances until hour 4... Initially solution was a light orange brown, after 4 hours in started to turn a very deep orange, almost reddish color. Also the smell of safrol was completely gone and was replaced with a unique aroma of ketone. One that is attributable to this rxn as it differs from the smell of the wacker oxidation ketone. Continued rxn for a total of 6 hours, maintained temp at 79 to 82C. Color at the end of rxn was deep orange- reddish, pH of solution was 2.

To separate the oil added an equal volume of fresh cool water (note: waited until solution cooled before adding the water). The oil started to drop out perfectly, used DCM to extract all traces of the oil. This work up is by far the cleanest, easiest and simplest to date... (This dreamer was tried all method of ketone synthesis)... Once the oil was extracted, the extracts were pooled washed with sodium bicarbonate 1x, saturated solution of NaCl 1x, and two washes with fresh dH_2O... Some time was required for the work up as there was a little emulsion from the use of the base wash and then with the first water wash. The JOC ref suggested using an alumina column to remove the catalyst (could be a better way to go).

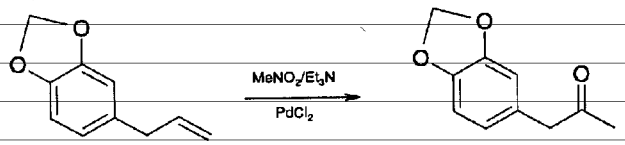
So now we have this solvent containing ketone, dried with $MgSO_4$... Not being able to vac-distill today, took about 50 mls of solvent/ketone and placed in beaker on stir plate and boiled off the solvent. The resulting oil was a nice reddish-orange color. Had a very unique smell too. Took about 2 grams worth of this oil, added to a test tube containing a saturated solution of sodium bisulfite... In less than 60 seconds the oil precipitated into a whitish yellow mass (very similar to what acetone would do if added to a bisulfite solution). Never had this quick of a crystallization. Not

having access to HPLC or other more accurate method of analysis, I would say the purity of this ketone is >90% and the yield will be minimum 78% and probably as high as 86%. No isosafrol either, as this rxn is highly selective.

This is the best method, easiest and most fool proof process to date!"

Strike wants to believe that, but right up til the last day this book had to go to press, the ball was still up in the air on this one. Conflicting, odd results have been seen from many different groups. This method has a lot of advocates and proof of its efficacy. But it seems to be a little fickle at times; the causes of which are still being debated to this day.

METHOD #4: This is a P2P recipe that Strike has no hand in. Strike never even knew about it until Strike saw everybody talking about it on the net. But it seems to be extremely popular. Shulgin has written about it. Uncle Fester, Strike understands, has written about it. And there seems to be a lot of posts regarding its high success rates. Most people get started from the method description in the patent literature where they were first published. The following are some representative examples from the U.S. Patent #4,638,094 "Process for Producing Phenylacetones":



Safrole MD-P2P

"Example 24: Add .1 mole of 3-(3,4-methylenedioxyphenyl) propylene, .25 mole of methyl nitrite, .008 mole palladium bromide as a catalyst, .5L of methanol and 36g of water to a flask. Stir magnetically for 2 hoursat 25C. Yield of 3,4-methylenedioxyphenylacetone (also known as 3,4-

methylenedioxyphenyl-2-propanone/MDP-2-P) is 95% with 100%of the reactants consumed.

Example 51: Add .1 mole of 3-(3,4-methylenedioxyphenyl) propylene, .25 mole of methyl nitrite, .5L of methanol, 36g of water, .00025 mole of trimethylamine, and .0005 mole of palladium chloride as a catalyst to a flask. Stir magnetically for 1.5 hours at 25C. The conversion of the starting material was 92%, the yield of MDP-2-P was 83% and the Pd Turnover Number was 166.

Example 68: Add .1 mole of 3-(3,4-methylenedioxyphenyl) propylene, .25 mole of methyl nitrite, .5L of methanol, 36g of water, .006 mole of bis(benzonitrile) palladium (II) chloride as a catalyst to a flask.Stir magnetically for 1.5 hours at 25C. The conversion of the starting material was 100%, the yield of MDP-2-P was 88%.

Example 86: A 0.10 mole amount of the starting 3-(4-hydroxyphenyl) propylene, 0.25 mole of methyl nitrite, 0.5 liter of methyl alcohol, and 0.006 mole of a palladium chloride catalyst were charged into a reaction vessel. Then,the reaction was carried out at a temperature of 20.degree. C. for 1.5hours."

Those 'propylene' species that the authors were using are no different than safrole or allylbenzene. In fact, safrole is a perfect substitute. Yowza! Those recipes look awesome! Now as Strike understands it, there has already been a detailed writeup of the by-the-numbers application of the above patent as written. This, Strike believes, can be found in Uncle Fester's "Secrets of LSD Manufacture" and/or "Secrets of Methamphetamine Manufacture"[18]. But our adventurous chemist Sunlight came thru again and submitted a new, hybrid form of this method which she seems to have formulated after a lot of 'thought' on the matter. So here again is Sunlight:

"*This is a new post in the Hive, I've performed a new reaction* [she's just kidding folks!] *with the new experience, with is much better than the other. Darkness part is extraction (yes, a lot of dark*

brown product), so may be it's better to do it as your procedure top #3 , sometimes is really hard to make the two layers different in colour. I hope we are in time to include in your bood, if you want.

This is real.

The present post is an adaptation to kitchen chemistry of Japanese patent #4,638,094, process for producing phenylacetones, and is the result of a large battery of dreams. In SOMM (Uncle Fester), we have three versions of this patent, one uses $PdBr_2$, other $PdCl_2$ and the "prefered" uses PdCl2 and CuCl2. Last one doesn't run. Also SOMM version be dangerous because in the scheme of rxn, Fester lets 6 mols of NO and nitrites to go out free of rxn vessel (see Eleusis vs. Fester, Rhodium's page, eleusis it's right). Well, both gases are very toxic, good ventilation is not enough and these gases must by carried out of the window through a tube (use a two hole rubber stop or a two necked flask). Also in this sample a precipitate that is taken out, these are undesirable byproducts, also washes must be done when rxn is done to liberate as Pd as possible. Two explosions have been reported when distilling, may be because this reason. Also in this procedure we spend much less solvent, minimizing evaporation time, less catalyst and less $NaNO_2$. Otherwise, I agree Uncle Fester his work because he have shown me a lot of things, I recognize also the good part of his work.

Interest of this reaction is that uses OTC chemicals or non suspicious, as $NaNO_2$ (it's used in food industry as a conserver) , and it's really easy. Methanol used is drugstore methanol, $PdCl_2$ is from photografy supplier in the net or elsewhere...

Procedure is as follow :

A solution of chilled dilute H_2SO_4 (C) is dropped in a solution af methanol, water and $NaNO_2$ (B), then methyl nitrite is generated,

and bubbled in a solution of safrol in methanol containing $PdCl_2$ catalyst (A).

This example has been done with good yields :

A. 50 cc of safrol, 300 cc of methanol, 2,5 grams of $PdCl_2$

B. 100 grams of $NaNO_2$, 60 cc of methanol and 200 cc of H_20

C. Chilled solution of 38 cc of H_2SO_4 and 85 cc of H_2O

C or a part of C is put in a sep. funnel wich is connected to flask containing B (wich can be a bottle), and a tube connect this flask to the bubbler into flask containing A, wich have other tube to redirect No and nitrite gases. Flask A is in water bath to keep rxn temp between 20 - 30 C /reaction is slightly exothermic) and stired magnetically. MeONO is bubbled in A with a bubbler that provides little bubbles (not necessary a gas difusor, but a single tube is not enough, you must increase then B and C). Bubbler is all deep as it is possible.

We start rxn, one drop / second or so C in B. Sometimes we close sep funnel and shake flask B to ensure a constant rate of MeONO generation. Addition speed is limited by equilibrium of pressure between flasks. If it is too much quick, then MeONO gas go through sep. funnel, then we close the sep funnel and wait a bit till generation is low. The addition of C in B takes 1 hour, we close sep funnel and shake a bit B to finish reaction. If rxn (A) climbs temp too much, we can add ice in the water bath. I've monitorized temp touching a part of solution that was out of water bath. At the final part may be water is to much cool, so we can take it out. After the addition of C in B we wait one more hour.

Now we open flask A. We can put a piece of glass and smell it once methanol is evaporated. There is no safrol smell, it's different, it's the dialkoxy derivative of safrol, rxn is completed perfectly. We add now 75 cc of water and stir 45 minutes more. There's a precipitate. We filter the reaction. I don't know what is this, may be also black tar, I thought this may be palladium complexes, this is a

organic compound that burns easily and may be contains Pd. This will forme tar later, now we don't have it. We can now smell another time rxn. This smell is ketone, we have more than 80 % of MDP2P (patent says 91 %). Good extraction procedures will give better yields.

This is my version, but may be better done. First one, evaporate methanol, better with vacuum. Then we have two layers similar in volume, we add 100 of solvent and 50 cc of basic solution (sodium carbonate, bicarbonate or 10 % NaOH). We shake it and may be we will have little more precipitate or tar. Also may be we can't see separation, then we add a bit more solvent without shaking to see separation. We make two more extractions with 50 cc of solvent. Even if we can't see separation, we can add enough HCl and shake, this will forme some tar and layers will be distincts, so we can separate and make a basic wash. Sometimes I've done first an acid wash, but I can't sure it's better. I'm thinking now may be is better to do all extraction as Strike's top #3. Add acid solution, like 250 cc (less $PdCl_2$ and no CuCl) 15 % HCl, extract and make a basic wash.

This procedure has been tested for a lot of bees and conditions are similar. Distill solvent and distill ketone with a water pump. My yield, 41 grams, about 75 %. Scaling. Of course. This procedure have been done with 150 cc of safrol, but with 1'75 l of methanol with simialr yields, so I've prefered to present this version wich is better (less solvent, less time) Addition of nitrite was done in 2,5 hours. When scaling, water in B can be decreased if we have problems with our volume flasks, but this means a lot of $NaNO_2$ is not dissolved, so each 15 minutes, we close sep. funnel, and shake B a bit, and when there is no foam, we can open sep. funnel again (1 drop or abit more /second). My opinion is 150 is ok, but theorically you can scale more. More time rxn is not a problem for product.

Bubbler. I've done it widening the end of a glass tube, then puting in the hole with pression a piece of glass sponge (for feet) and

welding it with a flame (Bunsen). When done, you can blow through it in water to see there are many bubbles. It's enough.

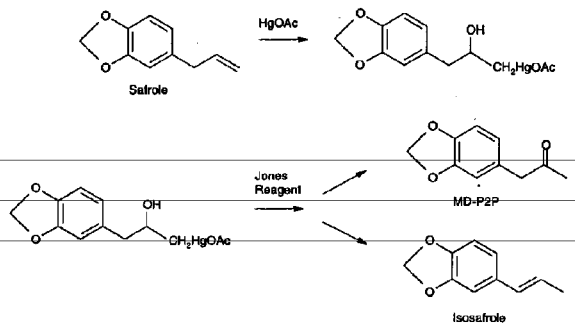
Flasks. Flask containing B can be a bottle. A is a round bottom flask, it's better because in a bottle or a flat bottom flask, $PdCl_2$, wich is not dissolved in methanol until it reacts, could be in the corner of flask without reacting.

Hazards. If you add two much quickly C in B, MeONO goes through sep. funnel. So close the key, but if there was too much addition or you shake immediatly then generation is higher than the possibilities of bubbler, and rubber on flask B can jump with a lot of foam and solution. For this reason it's better to have $NaNO_2$ dissolved , to prevent surprises, but it's not necessary. Be patient and shake. Don't forget redirect NO and MeONO fumes out to the window.

Cleaning flasks. Flasks, specially distilling flask are really dirty, with a brown black semisolid tar. It's easy to clean them. Make a 25 % or stronger NaOH solution (from drugstore, of course), put it in the flask and heat, till boiling if necessary, all tar go out easy. Use gloves, please.

Bisulphite. My personal nightmare. I use metabisulphite, what I think it's the same. Sometimes product is unfilterable, other one couldn't be recovered with NaOH solution. Investigate, I'm not a great chemist. Solvent, $NaNO_2$ or $PdCl_2$ may be can be reduced, but I think the quantities in this sample are really good. Solvent is easily evaporated, NaNO2 could be only slightly reduced and $PdCl_2$ is about 4,5 % versus 6 % in patent, but it's enough because all safrol reacts. Well, I think it's all..."

METHOD #5: Could something this easy really work? Actually, yes! Well, ya wanna know something? Actually Strike doesn't know if this really works or not (We'll discuss this in a bit. But first read the following which was what Strike wrote in the first edition of TS). Safrole is converted to MD-P-2-P in about 8 hours with no watched chemicals and a yield of 70%-80% [19]. The reaction is shown in the accompanying diagram.



This will work for conversion of allylbenzene to P2P. And the bonus is that the major side product is isosafrole. The mercury (II) salts that one can use are mercuric acetate (HgOAc), which can be made quantitatively (100% bubba) from mercuric oxide (HgO) and acetic acid (why anyone would do that is beyond Strike since the stuff is easily purchased), or mercuric propionate made from HgO and propionic acid. The oxidation of the intermediate alcohol is achieved by using Jones reagent [153]. An 8M solution of Jones reagent is made mixing 267g of cold chromic acid (CrO_3) 230mL cold H_2SO_4 and 400mL cold dH_2O then the solution is brought up to a final volume of 1L with dH_2O (or can be purchased). The working concentration that one wants is 2M, so the chemist mixes 125mL 8M stock with 375mL dH_2O.

The chemist now gives her knuckles a crack and begins. An appropriate sized flask or PP container is placed in a tray of water on the stirplate. Into the flask is dumped 800mL acetone, 25mL

dH_2O and 32g HgOAc. This is stirred a little, then 82g of safrole is slowly poured in. The solution should be bright yellow. Now, 375mL of 2M Jones reagent is added drop by excruciating drop over a period of 4hrs. The chemist will keep chunking pieces of ice in the tray to keep the temperature at 25°C +/- 5°C, and the solution will turn dark greenish brown. After addition is complete the solution stirs for 4hrs more.

When completed, the solution is merely dumped into 1L of dH_2O and extracted 3 x 100mL Et_2O or DCM or benzene. BUT when that solution hits the solvent, the biggest, ugliest emulsion Strike has ever hypothesized occurs. It is wicked! The chemists can try all the usual tricks to get rid of that bitch, but when it comes down to it, there is only one way that works. The chemist is going to have to extract with hundreds upon hundreds of mLs of solvent. The idea here is to saturate both the aqueous and emulsion layer with so much solvent that a separate solvent layer can form. Once saturated, the entire mix can then be properly extracted.

The solvent is then washed 3 x 50mL dH_2O and, if desired, can be washed once with 100mL saturated NaCl solution. Finally, the solvent is dried through Na_2SO_4, removed by vacuum distillation, and the first 5 to 10mL of oil that distills over is saved because it is isomerized safrole (isosafrole), which is suitable for reuse. The rest of the oil that comes over will be the ever lovely MD-P2P, which is perfectly suitable for amination by any method given in this book.

What you have just read is what Strike wrote in the first edition. Strike laid down one day just before publishing and had this bad ass premonition regarding the recipe. But most people since then have not. Let's see what the problem is.

Strike got the journal article for this recipe as literature citation used in the original Wacker oxidation Strike used for Method #2. In it both mercuric acetate, and to an extent, lead acetate produced ketones as described. Someone-Who-Is-Not-Strike also got a certain ketone. But maybe they were lucky or just plain wrong. Most people on Strike's site say this mercuric acetate thing

just ain't happening. But some say that it does. Funny how Strike only happened to save those positive posts...

"Posted by Dr. Quack on March 08, 1998 at 16:53:53:

Quack, Quack!!!!!!!!!!!!!!!

So there's this little duck and round and round she struggled with this method. But here is the report for all to benefit from, Quack, Quack...

So for all you book owners out there, boy did you get your money's worth. Check this out (btw, Dr. Quack has NO idea how this came about, but Quack!, Quack! it what the pigeons told Dr. Quack - promise):

For top ten #2 (Mercuric Acetate method) use the following in place of reagent grade materials:

1. Ether - Starting fluid (works great - Quaaaaack!) 2. Home made mercuric acetate (Now this stuff can be special ordered from ones chem supplier but there's a delay, may look funny - Quaaaaack!, and is more expensive. So what is the solution to this? Make it yourself!!! Its easy, quantitative, and cheaper. Strike mentions this in the book and points ducks to a reference. Follow the EXACT same procedure for Mercuric Propionate except use glacial acetic acid...quack!). You'll need to use 20 to 25% more of the home brew mercuric acetate since it is a little contaminated with acetic (ducks can't get it totally dry without a vacuum oven). 3. NaOH washed Brazillian is fine!!! Quack!!!! No need to purify further for starting material!

Now here is the secret(s):
A. Ducke/Bees/ Whatever MUST keep the temperature in the range of 20 to 30 C during the dripping of the Jones Reagent. Either add tepid OR cool ice to the water bath to keep it in this range. Maintain drip at 1 large drop every 4 to 5 seconds...Quack!!! This is imperative since the mecanism of chromic oxidation requires NO excess to be present during the oxidation. That's why one has to drip in over a four hour period. Also, after the drip, the full 4 hours following of stirring IS required but the temp should remain stable...QuaaaaaacK.

B. Big secret...Quack!!!!!, Use approximately a total of 600 ml (twice the amount prescribed) for the three extractions. Don't quack at me...its starting fluid. It's cheap!!!! Quack! Here it is: Let the first extraction sit for several hours (or overnight) and the seperation will be VERY clean. However, there will still be an emulsion present in the ether layer. Now, the Quackload of product will be in the first extraction, so the emulsion and settling of the following two will be much quacker (faster). Combine ALL three ether extracts and note that there will be a little water that will separate out from them.

C. Big secret #2...Quack!!!!!...One MUST filter this 600+ ml of ether...but a duck can't do this all at once...so one must filter in vacuum filter in 200 ml portions...changing the duck paper every time and wash the filter cake with ether...Dr. Quack thinks a vacuum filter (apirator) at this stage is a must...Quack!!!!!!!

D. Now the ether will be a deep reddish yellow. Distill off the ether...quack...and take the temp up to 170 C to drive off any other volatiles. Should recover 90%+ of the original weight of oil. Now add 500 ml of saturated bisulfite and stir for 1.5 hours...Quack!!!!!!! Vacuum Filter, the duck fat crystals!!! Wash with water and ether, yield dull fine ppt in the filter cake...stable bisulfite addition product...can be stored forever...Quack!!! Yield ~50 to 80% depending on a ducks technique!!!!

Dr. Quack thought ole Strike had a screw loose at first, but after continual quacking and persistence, Dr. Quack is convinced...this method is great as well!!!! Quaaaaaaaaaaaaaaack!!!!!!!!!!!!!! Hope the pigeons cleared some things up for some of you bees and ducks. Quack, Quack."

Now as you can see, Dr. Quack is half nuts! And his description of things and outcomes are right in line with what Someone-Who-Is-

Not-Strike may have seen. But what Dr. Quack did that SWINS did not was use the bisulfite test with positive results. What does that mean? It means that some doublebonded oxygen was formed, unless Dr. Quack was fibbing to us. It cannot have been a propiophenone (don't ask) because propiophenones cannot form the bisulfite addition product. Could an aldehyde have formed (don't ask)? Maybe. But highly unlikely considering the mechanism of the reaction.

Later on Strike noticed a few posts from Dr. Quack grumbling about how things did not, in the end, work out with the products of this procedure. Is Dr. Quack cwazy? Yes! Is she a bad chemist? NO! So what gives? Well, the following is a personal communique from Merlin: a chemist that all of you will thank when you see the stuff she wrote later on in this book...

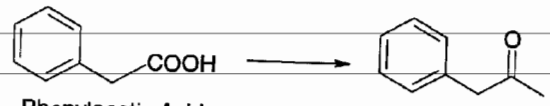
"#2 without water - proceed as follows. After the 4 hours stirring is complete extract direct with Ether. A normal amount of Ether will do nothing so add more till a layer forms. This is due to the need to drag the acetone out from the water. Water and Acetone mix, the Ether needs a hell of a pull to drag it out. The layer will be huge as it includes the Acetone. This will leave the mush which wants to form an emulsion in the water layer which can now be discarded. The ether/acetone layer is now washed with water which will extract the acetone from the ether, leaving a small ether layer which contains the product. This layer will be deep red in colour. After three washings (leaving the boogers in the lower water layer each time) dry with sodium sulfate. Only a tiny amount of isosaffy will come over beforehand (a couple of mils) which will float on top of the product (which I hope is MDP2P as this method is so fucking quick and easy compared to Isosaffy bastards and that palladium chloride method). This extraction method would take 3 hours in total including purification, no need to fuck about with nasty emulsions, and the yield seemed to be nearer 60% (rather than 50%) giving just less than 60g product from 82g of saffy."

And a later email said this:

"Well the gospel according to Sodium Bisulfate confirms it is a ketone. Whether that's all it is I'll know tomorrow."

See?! There it is again! But even when this person sat down and contemplated the use of the P2P nothing but misery followed. This method has to work because its potential is massive. But it needs further study! Yeesh!!!

METHOD #6: This one is for meth cooks only as it is only practical for making P2P, not MD-P2P because Strike don't know where one can get 'piperonylic acid'. It has been around awhile and works really well [20]. Therefore the chemicals needed have been restricted for quite some time. But if one can get them then what the hell.



Phenylacetic Acid P2P

This is a way to do this procedure without having to use one of those crazy tube furnaces stuffed with thorium oxide or manganous oxide catalyst [21]. The key here is to use an excess of acetic anhydride. Using even more than the amount specified will insure that the reaction proceeds in the right direction and the bad side reaction formation of dibenzylketone will be minimalized (don't ask). 18g piperonylic acid or 13.6g phenylacetic acid, 50mL acetic anhydride and 50mL pyridine are refluxed for 6 hours and the solvent removed by vacuum distillation. The remaining residue is taken up in benzene or ether, washed with 10% NaOH solution (discard the water layer), and vacuum distilled to get ~ 8g P2P (56%).

METHOD #7: Another piperonylic acid method for your perusal [22, 23]. 70g piperonylic acid or 65g phenylacetic acid in 250mL DCM is stirred in a flask and 64g $SOCl_2$ is added dropwise. The solution is heated to reflux until no more HCl gas is released from the solution. The chemist should have a tube leading from the top of the reflux condenser to a glass of water to catch all that HCl

gas. What the chemist now has is a chloro-intermediate oil that is fractionally distilled to purify. 65g of this oil is added to 100mL toluene and then this toluene mixture is added dropwise to a solution of toluene containing 210g of methyl zinc iodide (MeZnI). The solution is stirred overnight at room temperature, poured into ice water, acidified with H_2SO_4 and the toluene layer distilled to give P2P in yields of about 40-50%.

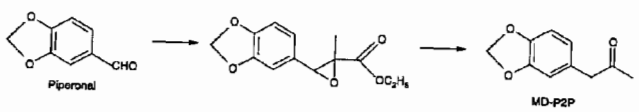
METHOD #8: Check this out! This uses benzene or 1,3-benzodioxole (for X) as the starting material [24]. This method is better suited for speed makers because the $AlCl_3$ catalyst can tear up that methylenedioxy ring structure of the X molecule precursor. Chloroacetone can be easily purchased.

Benzene P2P

41.3g $AlCl_3$ and 100mL anhydrous benzene are stirred in a 500mL flask fitted with an addition funnel and reflux condenser. A tube is attached from the drying tube atop the reflux condenser to a water trap to catch the noxious HCl gas that is going to be evolved. The solution is heated to reflux and 14g of chloroacetone is added dropwise from the addition funnel over a period of 30 minutes. After addition the solution is continued to reflux for 5 hours to give a black solution. While everything is in the same position, water is added from the addition funnel to destroy any remaining $AlCl_3$. This will cause more HCl gas to be evolved until all the catalyst is gone. After such a time 20mL dH_2O and 20mL concentrated HCl are added, the benzene layer separated and the aqueous layer is extracted once with benzene. Both benzene portions are combined, vacuum filtered, dried through Na_2SO_4 and vacuum distilled. The first thing to distill over is benzene, then about 9g of a low boiling oil which will be the P2P and then 10g or so of black, high boiling crap that the chemist leaves behind in the reaction flask. The P2P can also be purified by making a sodium bisulfite addition product out of it which is outlined in this reference and

also discussed in this book. This procedure can be scaled up to massive proportions.

METHOD #9: -This is a little, oddball method that will transforms piperonal or benzaldehyde into a quasi-cyclic intermediate that will lead directly to MD-P2P or P2P [25].



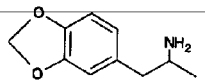
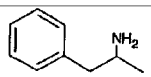
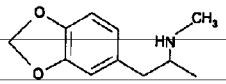
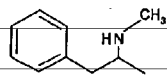
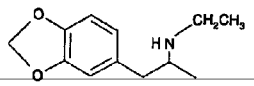
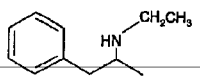
Over a 4 hour period 23g of powdered sodium ethoxide is added to a stirred solution of 50g piperonal (40g benzaldehyde) and 61g bromoproprionate which is being chilled to below 0°C with a bath of ice and rock salt. After addition the solution is stirred for 12 hours at room temperature, then for an additional 6 hours at reflux. Ice water is added and the solution acidified with dilute acetic acid. The solution is extracted with ether, the ether washed with dilute sodium carbonate solution and dried through Na_2SO_4. Distillation affords about 50% glycide ester intermediate (don't ask). 35g of this intermediate is refluxed for 5 hours in 150mL 10% NaOH in ethanol. The ethanol is then removed by distillation, 500mL dH_2O is added to the residue and acidified with HCl. This acidified solution is extracted with ether and the ether layer separated. Remember, this is not an MDA or amphetamine we are talking about so acidifying is not going to bring this into the water. The ether is removed by simple distillation to give a residual oil. This oil remains alone in its flask and about 0.2g of copper powder is added. A condenser is placed on the flask and the oil is heated to 180°C for 18 hours. The procedure claims reflux occurs but Strike is doubtful that reflux as we know it will happen. After 18 hours the MD-P2P or P2P is vacuum distilled directly from the flask it just spent the last 18 hours in to give ~ 45% yield from the intermediate.

Well, that's the end of Strike's section on MD-P2P/P2P synthesis. But that's not all this book has on the subject. For the goods on advanced, cutting-edge recipes, including more P2P synths, just go and check out **Rhodium's Chapter**. You won't regret it!

AMPHETAMINES AND METHAMPHETAMINES FROM PHENYLACETONES

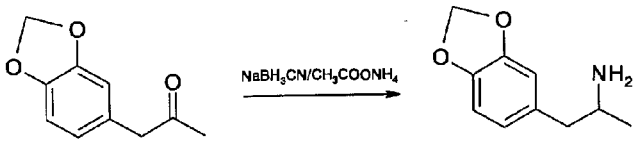
With all of that MD-P2P and/or P2P lying around, there's a good possibility that an evil underground chemist might turn it into final product. Dear God! The thought of it just sickens Strike! But what can ya do? And what again were those final products? Why it's these suckers right below:

Final Products

Ecstasy Class	Amphetamine Class
	
MDA 3,4-MethyleneDioxyAmphetamine	Amphetamine (Benzedrine)
	
MDMA 3,4-MethyleneDioxyMethAmphetamine	Methamphetamine (Speed)
	
MDEA 3,4-MethyleneDioxyEthylAmphetamine	PEA Ethylamphetamine

So without further ado, here's the recipes you've been looking for!

METHOD #1: Strike's extra special, blue ribbon favorite. Guaranteed to put the starch in your socks! This is the cleanest, highest yielding procedure for making MDA from MD-P2P that Strike has ever known. It is absolutely impossible to fuck up.



MD-P2P MDA

The catalyst needed is called sodium cyanoborohydride ($NaBH_3CN$). It is not very common but there are few 'places' that still sell it. It is very prone to take up water out of the air so the chemist makes sure that she doesn't leave it sitting out all night. The method is simplicity itself.

Into a large flask or glass tea jug is dumped 200g MD-P2P (or 150g P2P) oil, 920g ammonium acetate, 2000ml methanol (MeOH) and then 73g of powdery sodium cyanoborohydride ($NaBH_3CN$). Rapid stirring is started, and some nitrogen from a baby nitrogen tank is blown into the airspace of the flask to dispel the air and the flask is immediately covered with foil. The clear, light yellow solution stirs at room temperature for 24hrs.

That's it! The MDA has now been made. The solution is completely clear with not one iota of tar produced, and all of this achieved at room temperature with no pressure needed. Strike told you this was good. The solution is now cleaned up a little and the MDA isolated.

The methanol is vacuum distilled from the flask (this occurs between the temperature of 50-60°C), then allowed to cool. Sometimes upon cooling the concentrated mixture will polymerize into a big, white gummy mass. This will go away in the next step. To the concentrate is added 2000mL 3N HCl solution which will dissolve any polymerized mass (No, Strike still ain't gonna tell you how to calculate '3N'. You really need to learn to calculate Normality & Molarity. Sigh! But in this case 3N = 3M which is approximately a 10% HCl solution). The entire solution can, if desired, be poured into a PP container. Here is where the chemist comes to a slight variation in what is normally considered washing and extracting. The MDA is , at this point, an acid loving species and is actually going to stay in all that HCl solution even if that solution is mixed with an organic solvent. This gives the chemist an excellent chance to recover all of the valuable, unreacted MD-P2P which is not acid loving and will go into the solvent. So the chemist extracts the HCl/MDA solution with a few hundred mLs of DCM (a.k.a. methylene chloride, or dichloromethane) and saves the DCM to recover the MD-P2P for later use. Technically, the concentrate is supposed to be dissolved in DCM and then 'extracted ' three times with about 500mL of 3N HCl each. Strike's way works just as well.

After the DCM is separated from the HCl/MDA, it's time to release the MDA from the water. To do this the chemist has to make some saturated sodium hydroxide solution. A saturated solution is made by dissolving as much sodium hydroxide as possible in an amount of water (say, 500mL). This NaOH solution should be chilled in the freezer. So, the chemist is going to place her MDA/HCl solution in a PP container and chill it in an ice bath tray with stirring. Next she starts adding the cold NaOH solution in small increments so that bubbling wont get out of hand. The solution will start to get warm and slowly turn basic. At around pH 9 beautiful, clear-amber beads of MDA freebase oil will appear all about the solution (most of it settling at the bottom) and the chemist adds a little more base to insure an excess so that all MDA will separate out. This is one of the more pleasant events of drug chemistry.

Now the chemist need only extract the MDA oil from the water with some DCM. Yes, this time the MDA will go into the DCM. The chemist merely pours about 400mLs of DCM into the container and stirs it really well for a few minutes while she watches TV. As much of the water as possible is poured off or separated

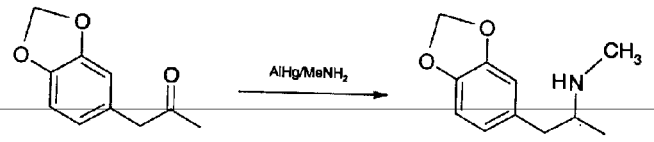
in a separatory funnel and then the DCM layer is dried through 100g of sodium sulfate (see methodology chapter). The DCM is then removed by simple or vacuum distillation to afford a clear, light-amber MDA freebase. This oil is so clean as is that it can be crystallized without distillation. If one wanted to, they could distill it to get rid of the color impurities, but there is so little contamination and, besides, what little there is will separate out in the process of crystallizing the product for consumer usage (see **Crystallization** chapter).

The yield here is 80-90%. No, that is not bullshit! This method has not been given the proper credit it deserves and sometimes has been dismissed without due process. Does Strike sound defensive? You bet! Strike has been in the science game for a long time and knows that bitterness, doubt and contempt abound. But that's ok, because those who do not use this method simply get hammered by those who do!

For those chemists that prefer MDMA or meth, this method can work for them too [27]. Everything about the catalytic reduction remains the same except that instead of using ammonium acetate as the amine source, one is going to use 1000g methylamine hydrochloride (see the **Chemicals** section on how to make). The screwier thing about this procedure is that someone is going to have to babysit that stupid flask for 24-36 hours checking the pH every now and then. The reaction has to remain neutral (pH 6-8, bubba!) the entire time, but that ain't going to happen because the dissociation products from the methylamine are going to start to turn things basic. So someone has to keep it neutral by checking the pH with pH paper and adding a couple of drops of straight-from-the-bottle concentrated HCl. Aside of the two changes, the reaction, cleanup and yield remain exactly the same.

METHOD #2: By far the most popular method currently available. This is a really convenient way to convert P2P or MD-P2P into meth and MDMA ('ecstacy'). It is a very clean procedure, akin to that of the $NaBH_3CN$ method, using amalgamated aluminum catalyst made from ordinary household foil [26, 28]. When Strike was reading all the underground literature on the use of household

aluminum foil to reduce ketones, Strike thought that it was probably a bunch of baloney because this procedure was always dumped in the backwash of conversion examples so it didn't look as if it merited much consideration. In fact, this procedure works very well and is super easy but the yield is a little low (50-60%). But since the catalyst is plain old aluminum this procedure will prove to be the perfect 'foil' (ha ha!) for those who can't get their hands on other high-powered catalysts. Strike did say that this method will produce methamphetamines, but the trade-off for those spoiled babies that just have to have this kind of drug is that they are going to have to use a watched chemical: the dreaded methylamine. It's pretty groovy that this book has gone this far without having to rely on any controlled substances except for precursors. As one of the most watched chemicals of all, methylamine is going to have to be made. In the chemicals section of this book is an easy method for making the form of methylamine that is required for this method which is methylamine hydrochloride ($CH_3NH_2.HCl$).



MD-P2P MDMA

Here's how the chemist proceeds. Next to the cheetos, the pathetically unemptied ashtray full of cigarette and joint butts, the rave fliers and the decomposing cat carcass the budding chemist may find her roll of aluminum foil. 50g of the foil is cut up into 1in x 1in squares and chunked into a big flask or glass sun tea jug. Older methods suggest that those pieces of aluminum foil be washed with some dilute aqueous NaOH, drained, then washed three more times with fresh dH_2O. This is meant to 'clean' the surface of the aluminum before it is amalgamated. This really isn't necessary but can be done if desired.

Either way, the happy little foil pieces end up lying at the bottom of the flask ready to be turned into a catalyst. To do this the chemist

pours a solution of 1.3g mercuric chloride ($HgCl_2$) dissolved in 1700mL dH_2O and stirring is started. The Hg starts to immediately react with the aluminum. Effervescent bubbling will be fierce and the solution will start to get really hot. This is allowed to continue for 15-30 minutes during which time the stirring solution will get cloudy grey with metal particles from the degradation of the aluminum.

There are a couple of notes to consider here. Just about all of that powdered dust is amalgamated catalyst, which is great except that almost all of it will be lost in the next cleanup step. One can make up for the loss of catalyst by increasing the aluminum batch size, but care is necessary in doing this. There is a danger point in making too big a batch of AlHg. Beyond the size of a 150g of Al, the reaction may overwhelm the water it is in and a boiling, volcanic steam cloud may erupt. It can get freaky! Also, the amount of $HgCl_2$ should not be increased beyond the ratio given here because it will pulverize all the aluminum very quickly leaving nothing but dust.

After 15-30 minutes the water is decanted from the catalyst leaving just enough to cover the metal chunks. If the catalyst is exposed to air it quickly degrades. The aluminum is then washed 4 times with fresh dH_2O decanting each washing so that a little water remains to cover. In the clean water the catalyst looks to be frosted with grey dust and is now ready for the big reaction. After the last decanting the chemist, in rapid fire succession, dumps the following ingredients into the flask holding the catalyst in the exact order as follows:

(1) 76g methylamine-HCl in 76mL dH_2O
(2) 230mL isopropyl alcohol
(3) 183 mL 25% aqueous NaOH solution
(4) 67g MD-P2P or 50g P2P
(5) 440mL isopropyl alcohol

The flask is placed in a plastic tray because an ice bath may be necessary and stirring is again started. Ice is added as necessary so that the temperature stays below 50°C and the solution stirs

this way for 3 hours. Usually, the temperature never seems to rise over 30°C no matter what one does. Some folks say that heat is necessary. Strike does not think it is. The solution looks very heterogenous. By this Strike means that all sorts of junk is swirling around in the flask. Amber beads of P2P go flying by as do chunks of foil, grey dust, and frosted beads of oil.

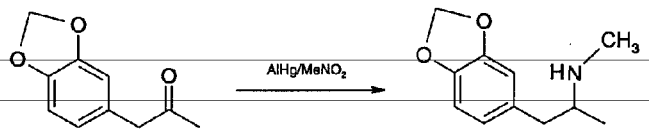
After 3 hours the stirring is stopped and the solution allowed to settle. By this time just about all the foil will have turned to dust, which is going to make the next step of vacuum filtration very difficult because it will plug up the filter paper in a second. So the chemist lets it settle, then pours off the liquid through the vacuum filtration setup (see methodology section). The flask is rinsed with 100mL methanol, the methanol poured through the grey filter cake and the filter cake discarded. All of the filtrate is placed in a flask and vacuum distilled to remove all the methanol, isopropyl alcohol and water which will leave the chemist with oil and junk in the bottom of the flask.

The cleanup of this oil is exactly like that which was done in Method #1. The oil is dissolved in about 500mL of 3N HCl and the solution extracted with 100mL of DCM. The chemist remembers that in this particular case the MDMA or meth is going to stay in the HCl/water but that unreacted, valuable MD-P2P or P2P is going to be in that DCM so it, of course, is saved. The HCl/MDMA solution is then basified with concentrated NaOH so that at around pH 9 the happy little beads of final, freebase product will appear in the solution. As usual, the oil is extracted with DCM, dried through Na_2SO_4 and the DCM removed by distillation. The final product here is usually a little darker in color than the product achieved in Method #1, but it is still remarkably clean and may be crystallized as is with the crystallization process removing most of the color impurities. Of course the chemist may wish to vacuum distill to afford clear product. The average yield with this method is 60-70%.

METHOD #3: This is a simple one pot version of Method #3 except that ammonia is used instead of the watched methylamine.HCl so one can make MDA instead of MDMA [29]. This is

pretty low yielding and can get messy. It is strongly suggested that one consider doing #2 above before trying this method. 54g (0.3M) MD-P2P or 40g P2P, 200mL ethanol, 200mL 25% aqueous ammonia solution (ammonium hydroxide), 40g aluminum grit (a.k.a. powdered aluminum or finely minced aluminum foil) and 0.3g $HgCl_2$ are stirred together. The mixture will heat itself up pretty good so an ice bath can be applied to insure that the reaction doesn't get too violent. When the reaction has simmered down, the solution is refluxed for 2 hours; then the solution is vacuum distilled to remove all the ammonia and methanol. What's left is water, MDA and particulates. This solution is basified with 120g KOH or NaOH to release the freebase oil which is then extracted with ether. This ether is then itself extracted with 3N HCl, the ether discarded and the freebase liberated from the HCl by basifying again with NaOH to give clean freebase with a yield of approximately 30%.

METHOD #4: This here method was contributed by a scholar named Ritter. She is adamant about this method and considers it a major breakthrough. Ritter wants to do what was done in Method #2 except without the insidious methylamine.



MD-P2P MDMA

"Who Needs Methylamine Anyway?
by: Ritter, edited by The Professor
Dedicated to Eleusis

The following procedure may prove to be one of the largest advances in the field of MDMA chemistry since the perfection and dissemination of the Wacker oxidation procedure for producing MDP2P. This reaction is based on a published process that somehow has escaped discovery by underground chemistry until

now. Methylamine is no longer a stumbling block in the aluminum amalgam reductive alkylation method of producing MDMA as this procedure produces this impossible to obtain and fickle to make material, in situ, during the reductive alkylation of MDP2P to MDMA from very common nitromethane. Nitromethane when subjected to the simplest of reductions forms methylamine, so why not make methylamine at the same time MDMA is being produced instead of going through the hassle of making it separately?

Nitromethane is a very common material. Just go down to your local drag strip and pick up a gallon or two for doping your high performance cars fuel. It's also available up to 40% pure in RC model fuels. Simply fractionally distill the nitromethane (bp 101°C) out of the model fuel mixture and you're ready to go. If methanol is present in the fuel formulation, some will azeotropically distill over with the nitromethane lowering its boiling point slightly, but this does not present a problem.

So, how does this whole thing work? It's as simple as it sounds. An alcoholic solution of nitromethane and MDP2P is dripped into a mass of amalgamated aluminum immersed in alcohol first reducing the nitromethane to methylamine, allowing the Schiff base of the amine and ketone to form which is then further reduced to the desired MDMA.

Set up a 2 liter two or three-neck flask with an addition funnel and a reflux condenser and provide with a heat source. Not much heat is needed here so anything from a water bath on a buffet range to a heating mantle is fine. Stuff 55 grams of one-inch squares of aluminum foil into the flask. An important topic must be addressed here which has been formerly neglected to a confusing degree - the proper type and thickness of foil. The problem with aluminum amalgam reductions is that their reaction rate is dependent on three major factors, and depending how you play these factors you may either have a complete failure or an explosion, or better yet if you follow this advice a perfect yield! These factors are the mentioned foil type, the degree of amalgamation allowed by $HgCl_2$

solution before ketone and amine are reacted, and finally, the temp the reaction runs at. Thick foil tends to react slowly at a low temp and very thin foil, such as generic food grade aluminum foil, tends to react so fast and exothermically you can literally shit your pants! The aluminum, which produced the best results, is widely available to the industrial biological community in the form of 4" x 4" sheets .04mm thick neatly separated from each other with a sheet of tissue paper. It is used for sealing flasks and the like before they are autoclaved. For those of you who can't get this, don't worry. Heavy Duty Reynolds Wrap will work fine, only a more careful eye must be kept on the reaction rate. Others have reported success using cut up pie tins. The main idea is don't use real thin foil.

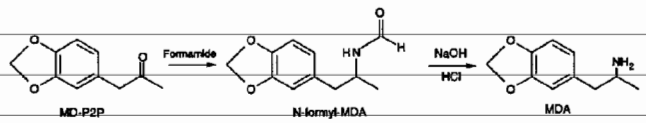
Fill the seperatory funnel with 50 grams of MDP2P and 50grams or 39ml nitromethane dissolved in 200ml methanol. In another 1 liter vessel add 1.5g $HgCl_2$ (mercuric chloride) to a liter of methanol and allow all solids to dissolve. Very carefully ($HgCl_2$ is deadly poisonous!) pour the methanolic solution of $HgCl_2$ onto the aluminum foil pieces in the flask and stand back and watch the magic begin. If all of the foil isn't covered by the methanol just add more until it is. In a few minutes effervescence will begin and the reaction may be started. After about 5-10 minutes the bubbling should be sufficient and you may start adding the methanolic mixture of nitromethane and MDP2P drop by drop from the seperatory funnel. As time progresses the reaction may heat up to the point of boiling and refluxing of the alcohol will occur. This is no problem as the 65°C boiling point of methanol is perfect for this reaction (I know many disagree, but dream about this and you'll see!) The addition should take roughly one hour and the mixture should be allowed to react for at least 4-6 hours after or until all pieces of aluminum are reacted into a gray suspension. Temperature control needs to be addressed here. If the reaction proceeds under ideal conditions, it will run exactly as described above. In less than ideal and more commonly, the reaction will start to slow down halfway through requiring external heating to maintain a good reaction rate. If the Greater Powers really are against you, an addition of another gram of $HgCl_2$ in methanol solution added to the mix will kick it back in.

Now the easy part -isolating your product. One of the most attractive features of this new synthesis is that the standard Al/(Hg) amination mixture must be tediously filtered to separate the product from the spent aluminum hydroxide sludge at this point. The following remedies this most frustrating step and will probably give many a new outlook on the potential of the Al(Hg) reduction.

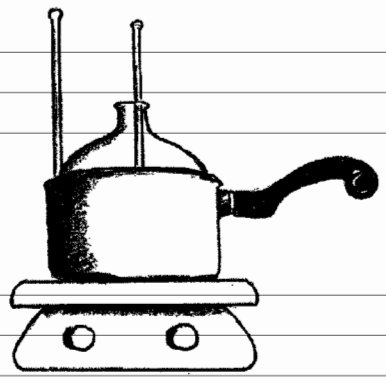
Mix up about 1.5 or 2 liters of 35% NaOH solution and allow to cool. Slowly add the gray aluminum gook produced in the first reaction to the NaOH solution and pour into a large seperatory funnel. Two distinct layers will appear after sitting for maybe an hour, the top being a reddish alcoholic solution of product and the bottom garbage $NaOH/Al(OH)_3$. Simply separate off the garbage bottom layer and discard. Don't worry, there's no product tied up in it, and remember that no filtration is needed anywhere in this recovery process compared to other synths out there! Take the top layer and evaporate off the methanol to give an amazing yield of impure amine and a little bit of water. Unscrupulous souls not worth their weight in shit can take this product and crystallize it directly but there is a lurking deadly poison in it at this point--- solvated mercury salts! These can be easily removed by dissolving the crude product in about a liter of toluene and washing it with several portions of water in aseperatory funnel and finally with a saturated NaCl solution. Dry the toluene with about 50g anhydrous $MgSO_4$ made by heating drug store epsom salts in the oven at 400'F for an hour, cooling then powdering. After sitting for an hour or until the toluene is no longer cloudy, chill the dried toluene solution of freebase in the freezer and bubble away with HCl gas to produce beautifully pure MDMA hydrochloride crystals. If they are a little discolored they can be easily cleaned up with an acetone rinse to pristine purity WITH NO MERCURY CONTAMINATION!

[see ref. CA, 51 11278 (1957)]'

METHOD #5: This method is extremely easy to do but can be messy. One needs to read everything Strike says in this section to get things straight, though. This method is called the Leuckart reaction and it converts P2Ps into amphetamines or methamphetamines as shown below. This method is very simple to do but has been grossly misreported, especially where its applicability to X production is concerned. The method that's been floating around the longest for X is the one found in Chemical Abstracts [9]. This method works but it is very messy and the yields suck (about 20%). Strike is going to detail how this method works, but a few paragraphs away Strike is going to lay down lots of ways that this method can be better for both X and speed production.



23g of MD-P2P or 17g of P2P that was made by any method and 65g formamide ($HCONH_2$) is poured int a small Pyrex flask (sorry, glass is a no-no here). If one wanted to make meth or MDMA then one would use 60g of a chemical called N-methylformamide instead of formamide. However, this chemical is extremely watched because of its use in this recipe so it is not something Strike would expect an underground chemist would use. This flask is placed in an oil bath which



[Figure 11]

is merely an aluminum sauce pan with enough corn oil in it to equal the height of the liquid in the flask. A thermometer is placed in the flask and another one placed in the oil so that the whole setup looks like figure 11.

Stirring is started and heat is applied so that the oil and reaction mix achieve a temperature of about 120°C in about an hours time. It is at this point that CO_2 bubbles will begin to emerge signaling that the reaction has begun. Some amount of ammonia will start to be given off at this point so the apparatus, if not already in a hood, should be placed in one. It is from this point that the solution will start to turn from its clear yellow color to that of a more orangy hue. The temperature of the solution is allowed to slowly climb until it reaches the blistering temperature of 190°C. It is held at this temperature for 5 hours then allowed to cool. What the chemist will have at this point is a thick, gooey mass of black tar that has probably gotten so thick from polymerization and evaporation that even the magnetic stirbar has been halted.

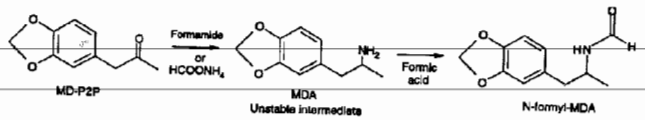
When cool, 100mL ether is added to the flask to dissolve all the tar and then the black tar/ether is poured into a separatory funnel. The ether is washed once with 100mL dH_2O, the upper ether layer separated away and the water extracted once with 100mL fresh ether. The two batches of ether are combined and the solvent removed by simple distillation leaving the chemist with a black mass of oil in the bottom of the flask. Next, the chemist pours 8mL of methanol into the flask, swirls to mix the tar with the MeOH then adds 75mL of 15% HCl. This solution is refluxed for three hours during which time the whole solution becomes black. The chemist is using HCl to hydrolyze the formyl intermediate. The solution is allowed to cool then is basified with concentrated NaOH solution until pH 9 is reached. The chemist won't really need to check the pH with litmus paper because, as usual, dark drops of MDA oil will appear all about the surface of the solution as a pleasant indication. All that is left is for the chemist to extract the MDA with ether or DCM and distill away the solvent. However, separating the solvent layer from the water layer is a bit tricky in this case because the two layers are so equally black that it may require a lot of squinting and a flashlight to spot the inter-

face between the two. Needless to say, the oil obtained is way to filthy to use and must be vacuum distilled to afford clean yellow MDA freebase. The distilled freebase is really pure, but to Strike, the effort to get this sorry yield is not worth it, especially if this is tried in large batch amounts. By large Strike means an attempt at conversion of at least 200g MD-P2P or P2P.

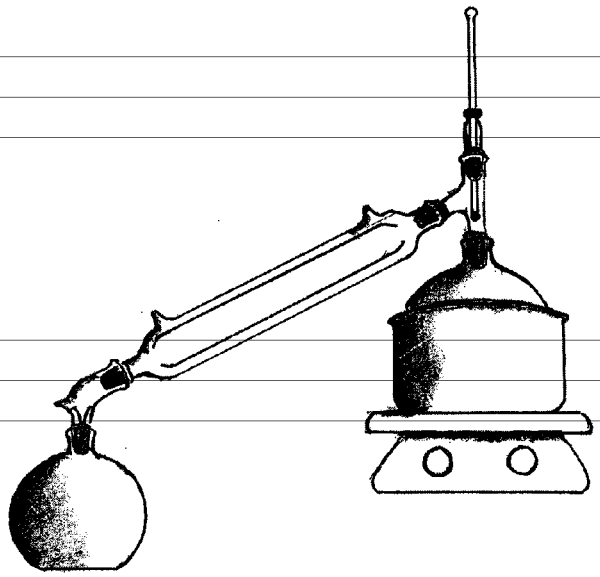
If ever there was a reaction that was batch size independent then it has to be this one. A chemist can try to process 200, 500 or even 1000g of P2P using this version of Leuckart and never recover more than 100g no matter how careful she is. This procedure is more in line with those who wish to make steady reasonable supplies of X and should not be used to process more than 100g of P2P at a time. In fact, it shouldn't be used to make any drugs at all. You see that would be illegal.

Strike's mission with this book is to provide as many methods for a conversion as possible. Slight corrections to a recipe can make a great difference; and to become a truly great chemist one should be aware of both the good ways and the bad ways and what it was that made one recipe a poor one and another a good one. Then, when a chemist comes across other or future experiments, she can make a more educated assessment as to its worthiness. This whole Leuckart business is a good example. The Chemical Abstracts article has been around so long and its merits so few when there have been so many blatantly better recipes staring illegal chemists in the face. Not until very recently has some correction been made in some of the underground literature. Folks interested in speed manufacture should read this closely. It all relates in every way to the betterment of methamphetamine synthesis.

The Leuckart reaction was originally conceived using a chemical called ammonium formate ($HCOONH_4$) which is very similar to formamide ($HCONH_2$) [30]. It is pretty much believed that this molecule donates its ammonium part to the P2P and then the formate part turns into formic acid (HCOOH) which then acts to reduce the intermediate into its stable formyl derivative (don't ask).



If one is using formamide or N-methylformamide then one is not going to have the advantage of creating formic acid as a breakdown product, so the idea is to have formic acid already in the reaction mix. To do this one takes the 65g of formamide and mixes it with 30g of 88% formic acid, places this flask in the oil bath and attaches a simple distillation set up to it as shown in figure 12. Since the formic acid has some water in it the chemist is going to remove that water by heating the oil bath to 160-170°C and allowing the water to distill over with no vacuum. When no more water distills over the chemist allows the reaction flask to cool, adds the 23g of MD-P2P, reattaches that distillation setup and allows the mix to slowly rise in temperature to 160-170°C. The reaction stays at this temperature for 5 hours, any longer makes little difference. Also, if the temperature rises above 170°C then destruction, not production, will occur. The distillation setup is there to condense any product that happens to exit the reaction flask. This distillate is returned to reaction while things are still hot. Using formic acid effectively doubles the yield.



[Fig 12]

Other ways to do this reaction would be to use what the dudes did in the old days: ammonium formate [25]. This way uses 60g of ammonium formate, no formic acid, and a distillation setup. Another combination that works equally well is 1:1 formic acid and ammonia in place of formamide. It is also perfectly fine to remove the water under the distillation setup, then replace it with a reflux condenser and conduct the reaction under reflux for the 5 hours [10]. In fact, reflux is a good way to do any of these Leuckart reactions.

These strategies reduce the amount of tar immensely and keeps the reactants together a lot longer under reaction conditions that

are more amenable to production. Whichever way was used, the chemist is going to have a cooled solution of formyl intermediate, and formamide etc. There are a couple of ways to process this stuff from here that are better and more convenient than the original way [22,31].

Instead of washing the reactants with water, extracting the product with ether, removing the ether then hydrolyzing, why couldn't one just hydrolyze right off the bat in the original reaction pot? As it so happens this can be done. The chemist can put 200mL of 30% aqueous NaOH or 200mL 30% HCl right into the flask and reflux for 5 hours. Using NaOH to hydrolyze has two advantages: it is gentler on the methylenedioxy ring structure of the X molecule and it is faster to process. After hydrolysis is over and the solution has cooled all one needs to do is extract with ether to obtain the MDA oil because using NaOH means that the MDA stays as an oil throughout. A really frugal chemist can do one extra thing to help herself out. She can take that ether/MDA layer and mix it with a few hundred mLs of 3N HCl. This, as usual, will cause the MDA to go into the water layer but what is going to be left behind in the ether besides tar is going to be a lot of unreacted, valuable P2P. The chemist saves that layer to deal with its P2P payload at another time. Meanwhile, all that remains is for the chemist to release the MDA from the water/HCl by basifying and extracting with ether.

Of course, there are a couple advantages to using HCl as the hydrolyzer. Since using hydrochloric acid means that all that fat MDA or amphetamine is in the water solution, the chemist can vacuum filter the solution to get rid of all the tar and crap which will give a remarkably clean water solution. The X is released by basifying and extracting with solvent.

Since the formamide reaction solution is going to be a lot cleaner than the tarry mess of the original recipe, the chemist has yet another option to explore. Instead of hydrolyzing in the reaction pot, the chemist can add 500mL of clean dH_2O and stir just like in the crappy original method except that this time the chemist is going to look for a heavy oil layer that will settle at the bottom. The up-

per water layer is decanted from the oil layer. That water, by the way, can be acidified with HCl to form crystals of formamide that can be isolated for reuse. The heavy oil layer, alone at the bottom of the flask can be hydrolyzed as is with either 10% HCl or 10% NaOH. The chemist, by now, should know the general differences and outcomes of hydrolyzing with either of these two compounds.

By utilizing the improvements stated above in any combination preferable to the chemist, convenience will be enhanced and yield will jump from around 20% to that of 50%. Not bad, but there is one more oddball form of the Leuckart reaction that was devised specifically for X production and produces a yield of 70%! This little procedure [32] has been around for 40 years and has, until recently, failed to be reported as a superior Leuckart conversion method by underground sources. This sort of thing really frustrates Strike.

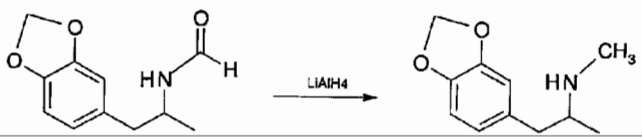
This procedure works equally well for both X and speed production. The set up used is the same as fig. 12 (remember, no vacuum) and into the reaction flask is placed 275 mL formamide, 80g MD-P2P or 70g P2P, and 55mL of 9% glacial acetic acid (50mL dH_2O and 5mL glacial acetic acid, bubbal). This is slowly heated to 140-150°C in the oil bath and kept there for 5 hours. The lower the temperature at which a sustained reaction (bubbling) can occur the better. Suffice to say that 150°C should not be passed. Very early on the water and glacial acetic acid will have distilled over and can be discarded.

After 5 hours the reaction is stopped and the flask cooled. The formyl-MDA can be isolated and hydrolyzed by any of the ways Strike just mentioned a few paragraphs back, but this method offers a third, very convenient way which should be tried. What the chemist does is forget about letting the flask and its contents cool. Instead, she removes the oil bath, places the flask back on the stirplate (distillation setup still attached), attaches a vacuum and distills off all the formamide. What remains is a dark, heavy formyl-MDA precipitate that is allowed to cool down while the chemist makes up a solution of 150g potassium hydroxide (KOH), 500mL ethanol and 125mL dH_2O. This solution is poured into the

flask with the formyl-MDA residue, the condenser from the distillation set is plopped in vertically and the solution refluxed for a mere 30 minutes. The solution is then acidified with concentrated HCl solution, the distillation setup reattached and all the ethanol distilled off under vacuum. What is left is MDA and aqueous HCl and from this the MDA is liberated, as usual, by basifying with NaOH, extracting with solvent, drying the solvent and distilling to get MDA in 70% yield.

Dear readers please take notice: Not once has the flask left the stirplate since the formamide and P2P reaction started up to the last point where MDA freebase was liberated. That's pretty damn convenient. Technically, the Leuckart reaction can continue as a one pot synthesis from the last part of P2P cleanup right up to final product.

The last thing that Strike has to say about the Leuckart reaction is the use of $LiAlH_4$ as a method of making the final freebase out of the formyl intermediate. What we have gone over so far is the method of boiling the formyl intermediate one gets from the formamide reaction with HCl to hydrolyze the species. What happens when one does that is that the bond between the nitrogen and the N-carbon gets ripped apart allowing the amine to form. But if one uses $LiAlH_4$ instead of HCl, what happens is that the double bonded oxygen of the formyl species gets stripped away without any carbon-nitrogen cleavage [26, 27]. The result is that one gets MDMA instead of MDA! And without having to use the restricted N-Methylformamide to do it.



N-Formyl-MDA MDMA

To make MDMA from the formyl intermediate obtained by the Leuckart reaction the chemist is going to have to distill it to get the clean-yellow oil first. That black crap one gets from the formamide

reaction is too dirty. 50g of cleanish N-formyl-MDA or amphetamine is dissolved into 300mL anhydrous (dry, bubba!) ether. This mixture is slowly dripped into a flask containing 38g $LiAlH_4$ in 200mL anhydrous ether and the reaction mix refluxed hard for 4 hours. The chemist makes sure that there is really cold water coursing through the condenser and that there is a drying tube placed on top of that condenser. After four hours have passed 100mL of dH_2O is poured into the flask to destroy any remaining $LiAlH_4$. The ether layer is separated, vacuum filtered and extracted with 3N HCl. The MDMA or meth is, of course, now in the HCl water, not in the ether. That water layer with product is separated from the ether and the MDMA is liberated with NaOH to give MDMA or meth (90%).

Well, that's about as rounded an education on Leuckart reactions as Strike can give. Strike feels that after reading all of those similar, repetitious steps, one can start to get a good feel for where a product is at any given moment. Stuff like what happens to MDA when it's mixed with acid or base, or what happens to ketones (P2P) under the same circumstances. One can see now that it is possible to not only isolate safrole and P2Ps chemically but that the same can be true for the final MDA or meth freebase oil. Repeated washings with acid or base and solvent can effectively clean up a compound to an almost presentable state without the use of vacuum distillation. It can happen, one only needs have confidence in the chemistry.

METHOD #6: [33]--17.8g MD-P2P and 300mL 40% aqueous methylamine is stirred at reflux for 30 minutes then 15g $NaBH_4$ is added over a 10 minute period and refluxed for 1 hour longer (an even longer reflux time than that would be better). The reaction mix is cooled on an ice bath and carefully acidified with concentrated HCl yielding a thick white precipitate. The aqueous acid layer is washed with DCM or chloroform (discard the solvent) and basified with NaOH to release the freebase, which is taken up with ether and distilled to give MDA (yield =30%). Are you starting to see how all this chemistry is just the same bullshit over and over again, with the only differences being an odd chemical here or there?

METHOD #7: [34]--This turns a P2P into an intermediate called a ketoxime which is then reduced to give MDA or benzedrine. To a solution of 25g MD-P2P or 18g P2P in 40mL ethanol, 10g hydroxylamine hydrochloride and 20mL dH_2O is added a solution of 6g NaOH in 20mL dH_2O. This mix is then refluxed for 2 hours, diluted with 100mL dH_2O, acidified with HCl and extracted with ether to give a thick, red oil upon removal of the solvent. 10g of this ketoxime intermediate, 100g acetic acid and 50mL dH_2O are stirred together, then 300mL of 3% sodium amalgam catalyst (see chemicals section) is slowly added, then the solution stirred for 6 hours. The solution is basified with NaOH, extracted with ether and then the ether is extracted with 3N HCl. The free base is released from the acid water, extracted with ether, blah, blah blah. The yields from this type of procedure have been reported as high as 90% [35]. However, these results are from a group in the Netherlands which happens to be right next to Belgium. And from Belgium there came a punk that did Strike dirty. Yeah, you know who you are you piece of shit! If Strike doesn't catch up with you before Strike dies then Strike will definitely be waiting for you in hell, you coward! Anyway, there has also been proposed a way to reduce that ketoxime intermediate using $NaBH_4$ instead of the harsher sodium amalgam [36].

METHOD #8: A very promising and tasty looking method contributed by some person named Feck. Don't know who or where this guy came from. But one day a care package with some very startling research articles appears in Strike's mailbox from this Feck character. This one was the best because it actually used P2P as an experimental subject [54]. So you already know the method works on our favorite ketone species!

The article was a complex read for such a simple process. Strike has done Strike's best to interpret this article correctly for you. First off, even though the reaction is fairly simple, the authors have a lot of caveats about the materials needed. Important is the finding that the pH must remain between pH 7-9 or nothing will happen. Next, the granulation of the magnesium was found to be critical as well. Chunky old magnesium turnings were found to

give much higher yields than the finer powdered magnesium. The purity of the particular Mg used was 99.5%. The last note is that an excess of amine produces max yields.

The versatility of this reaction is quite apparent. One can use ammonium acetate to make MDA or amphetamine, or methylamine in methanol for MDMA. But methylamine is optimal because it gives higher yield and less byproducts. Also, if ammonium acetate is used, one must use either ammonia (NH_3) or a primary amine (any of one's choosing, Strike supposes) in place of the triethylamine in the reaction.

In articles like this one, the scientists don't have the time nor the space to write out the details and amounts of reactants used for every single substrate they tried things on. So they pick just a few of the precursors they tried and use their numbers as an example of how the reaction typically goes. All one does is just substitute an equal amount of their favorite phenylacetone for the one in the example while keeping everything else the same. This will not be too big of a stretch of the old imagination with the first example below. The example ketone is just phenylbutanone. One little carbon more than phenylacetone, but a methyl ketone nonetheless (don't ask). They react exactly the same. As it so happens this first example is also the one using ammonium acetate to make MDA. Sweet!

"*1-Methyl-3-phenylpropylamine----In a 250 cm^3, single-necked flask were combined 4-phenylbutan-2-one (7.41g, 50mmol), $AcONH_4$* [ammonium acetate] *(38.54g, 500mmol), Mg (6.08g, 250mmol) and 70% aqueous MeOH (100 cm^3). The flask was capped with a mercury filled bubbler* [feel free to substitute this one], *to reduce escape of NH_3, and the mixture was stirred at 20-25°C, for 12h. If the reaction was not complete (TLC), additional AcOH (6.0g, 5.7cm^3, 100mmol) and Mg (2.43g, 100mmol) were added and the stirring continued for an additional 12h. The mixture was poured into water (600 cm^3) to which $NaHCO_3$ (50g) was then added: the whole was then internally steam distilled until 500 cm^3 of the distillate collected. It was made alkaline (pH > 12) with 50% aq. NaOH and extracted with CH_2Cl_2 (3 x 50 cm^3). The combined extracts were dried (K_2CO_3), filtered and evaporated on a rotatory evaporator.*"

Strike is stopping the quotation here because the chemist is a point where she can exercise here own options. What the chemist has left after evaporation (or distillation) is freebase residue with some contaminants. The chemist can work this up as usual which would be to do a little more acid/base clean up like has been done with all freebase recipes. Or crystallize the final product for recreational use. The authors continue by making an oxalate salt out of their freebase. One can make whatever salt they want out of an amine freebase. Making an HCl, like what naughty chemists normally do, is just one way of doing things. Here is the rest of the experimental. We're continuing right where the last sentence above ends.

"*The residue was dissolved in MeOH (20 cm^3) and added slowly, with stirring, to a solution of anh. Oxalic acid (5.40g, 60mmol) in MeOH. Complete precipitation was effected by adding Et_2O (50 cm^3) to the mixture and cooling it to -20°C.*"

They are actually using crystallization to purify the amine from any non-amine contaminants. They later freebased the crystals and fractional distilled to get pure amphetamine with a yield of 50%.

Wow! That looked pretty good, huh?! The following example is one of the paper's experimental examples of using Methylamine as the amine source. This allows one to get MDMA or Meth. The authors used methylamine in methanol. That means they are using the $MeNH_2$ freebase, not $MeNH_2$·HCl . The authors explain that they made their methylamine/MeOH solution by dripping (Strike thinks) aq. 40% methylamine onto solid KOH and bubbling the liberated $MeNH_2$ into ice cold methanol. One can do this, or buy a gas cylinder of $MeNH_2$ gas which can be bubbled into the methanol or whatever.

"*N-Methyl-1,5-diphenylpentan-3-ylamine --- Into a 250 cm^3, singlenecked flask, were combined 1,5-diphenylpentan-3-one (7.15g, 30mmol)* [<-insert said P2P here!], *a solution of $MeNH_2$ in MeOH*

(5.4mol dm^{-3}, 44.5 cm^3, 240mmol), and Mg (3.28g, 135mmol). AcOH (14.4g, 13.75 cm^3, 240mmol) was added with a pipette below the surface of the liquid and the flask capped with a mercury-filled bubbler, to reduce escape of $MeNH_2$. The mixture was stirred vigorously, at 20-25°C, for 12h. If the reaction was incomplete (TLC), additional Mg (0.73g, 30mmol), $MeNH_2$ solution (11.1 cm^3, 60mmol) and AcOH (3.6g, 3.4 cm^3, 60mmol) were added and the stirring continued until completion (3-6h). Work-up afforded the monooxalate salt (6.72g, 65%)."

METHOD #9: This method is not '#9' because it is bad. It's just that it, and #8 above, are still in the experimental stage as far as underground chemists are concerned. So Strike placed the less tested methods down here so as not to confuse people too much.

But this method has been generating more rabid attention than any other in the underground. Feck sent Strike some articles on it. Osmium emailed Strike some of the same references [56, 57]. Everyone is talking about it. And for good reason. It is essentially the second generation of reductive amination using superclean, gentle catalysts. Just think of it as Method #1 - except that the $NaBH_3CN$ has been replaced by a more workable catalyst: Sodium Triacetoxyborohydride [$NaBH(OAc)_3$].

This catalyst works in a similar manner to $NaBH_3CN$ except that it does not suffer from the same potential toxicity that $NaBH_3CN$ does. It is also different in that one can synthesize the damn stuff rather easily in one's own garage, as opposed to $NaBH_3CN$ which will require a very complicated and dangerous cyanide generation apparatus as is shown in the **Chem**icals section of this book. The following is about all Strike has on the making of the catalyst $NaBH(OAc)_3$ [55]:

"*Treating a benzene suspension of sodium borohydride (4 equiv.) With glacial acetic acid (3.25 equiv.) And refluxing the mixture for 15 min under nitrogen, after the initial rapid gas evolution subsided (ca. 3 mol of H_2 liberated)* [No Smoking!], *gave a clear solution of $NaBH(OAc)_3$.*"

As you are about to see, the standard methods for using the $NaBH(OAc)_3$ catalyst call for it to be in a dried, powder form. Strike supposes the benzene in the above reaction can be distilled off to leave dry catalyst. But don't quote Strike on that! Maybe it could be made *in situ* in the DCE solvent of the reaction to come (don't ask). Aw hell! Just go and buy the shit!

Anyway, with catalyst in hand it is time to proceed with the reductive amination [56]. As far as Strike can see, this method will not work well in making MDA. It will not use ammonium acetate in the same way as $NaBH_3CN$. So one is stuck with making MDMA or meth using this method. And without further ado, here's your recipe:

"*General Notes:*
(a) The amine [methylamine] and carbonyl compound [P2P] *are mixed in 1,2-dichloroethane and treated with $NaBH(OAc)_3$. THF, CH_2Cl_2, or CH_3CN may also be used as solvents* [but a longer reaction time will be necessary].
(b) Acetic acid (1 - 2 mol equiv) may be used in reactions of ketones [the paper says that AcOH acts as an accelerator to speed up the reaction with the P2P. But without it, the reaction will still go to completion. It will just take longer to do.]
(c) Reactions are normally carried out using the free amines [ie methylamine freebase. One can saturate the reaction solvent with $MeNH_2$ before starting in order to achieve this]*: <u>however</u>, the amine salt* [$MeNH_2$·HCl] *may be used. In this case, 1-2 equiv of Et_3N* [triethylamine] *is added to the reaction mixture. The Et_3N must be removed from basified product prior to salt formation.*"

And here's the two representative methods one would use. Just imagine the carbonyl precursor as a P2P and the amine as methylamine. Visualize....man!

"*<u>Method I</u>. This procedure is used for most ketone reactions. A representative example is the reductive amination of cyclopentanone* [P2P] *with hexamethyleneimine* [$MeNH_2$]*: Hexamethyleneamine (1.0g, 10mmol) and cylclopentanone (0.84g, 10mmol) were mixed in 1,2-dichloroethane (35mL) and then treated with*

sodium triacetoxyborohydride (3.0g, 14mmol) and AcOH (0.6g, 10mmol). The mixture was stirred at room temperature for under a N_2 atmosphere for 24 h until the reactants were consumed as determined by GC analysis. The reaction mixture was quenched by adding 1N NaOH and the product was extracted with ether. The ether extract was washed with brine [NaCl solution] *and dried ($MgSO_4$). The solvent was evaporated to give the crude freebase (1.6g, 96%).*

Method II. The above procedure is followed without the addition of glacial acetic acid. The reaction mixture remains cloudy throughout the reaction. This procedure is more appropriate with most aldehydes and unhindered aliphatic ketones [which P2Ps happen to be]. *A representative example is the reductive amination of 4-pyridinecarboxaldehyde* [P2P] *with ethyl 2-piperidinecarboxylate* [$MeNH_2$]: *Ethyl 2-piperidinecarboxylate (1.57g, 10mmol) and 4-pyridinecarboxaldehyde (1.07g, 10mmol) were mixed in 1,2-dichloroethane (35mL) and then treated with sodium triacetoxyborohydride (3.0g, 14mmol). The mixture was stirred at room temperature under N_2 atmosphere for 24-30 h. The reaction mixture was quenched by adding aqueous saturated $NaHCO_3$, and the product was extracted with EtOAc* [ethyl acetate]. *The EtOAc extract was dried ($MgSO_4$), and the solvent was evaporated to give the crude freebase (2.4g, 96.7%)."*

Both those methods look pretty equal to Strike. Still, Strike tends to think that the Method I looks like it's the best of the two. There are some definite advantages that this method has over the $NaBH_3CN$ one. But all in all, they look about even to Strike. It's great to have options though. Isn't it?!

METHOD #10: You girls need to know that Strike is not just listing every method that produces a precursor or makes a final product. There are hundreds out there. Many make the product but are too hard, too expensive or too low yielding. Many are a combination of both. There are special criteria that makes a method worthy of inclusion in this book. Often, a method has been reviewed by many people before it makes it for consideration. When there is no one person that has actually tried a particular method on our special

precursors, then that method had better have a lot of merit and unique potential.

This really crazy looking method is one of them. There are a lot of things about it that make it very attractive. The first is the author of the article: Rajender S. Varma. You will see in the **Nitropropene** section of this book (and in references from many other parts of the book) that this guy has been making a lot of strangely applicable advances in catalysis, amination, and reduction of amphetamines and related compounds. It is uncanny how often Strike has come across this person's work. It is like he is the Shulgin of basic precursor and amphetamine progress. Go figure!

The other attraction is the method itself: clay, a Sears microwave oven and the most lightning-quick results ever imagined! Someone sent Strike this method via fax, but dumbass Strike did not get the person's 'name'. But you know who you are, Bra'!

Anyway, there have been two very hot topics in chemistry lately: clay & microwaves. Both have been shown to do remarkable things in preparative organic chemistry. And this article Strike has [58], has combined both to produce some stunning reductive aminations of ketones to final amine products. The procedure involves mixing naked ketone, the amine, some clay and some $NaBH_4$ in a beaker and zapping it in the microwave for only a couple of minutes. That's it. The general procedure is as follows:

"*Typical Procedure. The synthesis of N-phenyl-p-chlorobenzylamine is representaive of the general procedure employed. A mixture of p-chlorobenzaldehyde (0.7g, 5mmol), aniline (0.455g, 5mmol) and montmorillonite K10 clay (0.1g) contained in a 25mL beaker was placed in an alumina bath inside the microwave oven and irradiated for two min. The in situ generated Schiff's base was mixed thoroughly with freshly prepared $NaBH_4$-clay (5.0mmol of $NaBH_4$ on 1.72g of reagent) and water (1mL). The reaction mixture was again irradiated for 30 sec (65°C). Upon completion of the reaction, monitored on TLC, the product was extracted into methylene chloride (3x15mL). The removal of solvent under reduced pressure provided pure N-phenyl-p-*

chlorobenzylamine in 90% yield."

This next one is a power pulse modification for using lower boiling point amines (read why later on below):

"*N-(1-Propyl)aminocycloheptane: A mixture of cylcloheptanone (0.56g, 5mmol), n-propylamine (0.46g, 7.5mmol) and K10 clay (0.1g) contained in a small beaker was placed in an alumina bath (heat sink) and irradiated for 6 min in a MW oven at its 20% power using pulsed method (one min cooling between two successive irradiation of 2 min each). The in situ generated Schiff's base was mixed with sodium borohydride (0.19g, 5mmol) and K10 clay (1.53g) to which water (1mL) was added and the reaction mixture was irradiated in MW for 45 sec at its full power. Upon completion of the reaction, as monitored on TLC, the product was extracted into methylene chloride (3x15mL). The removal of solvent under reduced pressure gave the free base in 79% yield. HCl salt (EtOAc-MeOH).*"

Can you see what happened there? Ketone and amine react to give final freebase. Very nice. The authors even suggest that simpler matrices such as alumina or silica might work in place of clay. But, regardless, there is one small problem. The authors did not use any of the amines that an underground chemist would. As a solventless system, the authors had to use amines that were liquid or solid at or above room temperature. The lowest boiling amine they used was propylamine. And it was a borderline case causing them to use a modified pulse method so that it would not get too hot and escape the reaction matrix.

So you can see that to make MDA or MDMA using either NH_3 or $MeNH_2$ one is going to have to think of a way to keep them in the fray. Strike's first impulse is to dissolve the amine in a solvent. But what solvent? And would the reaction even work in any solvent? Rhodium thinks that maybe an aqueous amine solution would work considering the clay is moistened with water anyway.

Well, when in doubt ask the guys who wrote the article. And that is just what Strike did. The co-author of the method was a very kind

and helpful man. When asked how he would modify his method to involve either NH_3, $MeNH_2$, or $EtNH_2$, he said that DMF (Dimethylformamide) would be the first choice for solvent. DMSO would be the second choice. He indicated that water *may* work, but that experimentation would need to be done to be sure.

So now we have a modified method where one has ammonia, methylamine or ethylamine freebase saturated in a small amount of DMF. The author next suggested that a power pulse protocol would not necessarily be needed, but that the power output from the microwave should be between 20-40% of full power. Also, the water in the clay would still be needed for the reaction.

Lastly, Strike asked what he thought about the scalability of this process. Can it be upped to 1 mol or more? He said he was up to 50mmol and said no decrease in yield was apparent. The time of irradiation also did not need to be any longer than the written protocols.

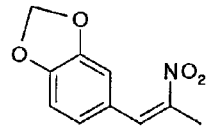
So what the hell are all of you waiting for?! Nuke it!

That is about all Strike has for this section. But Strike is well aware of all the ways that P2Ps can be converted to amphetamines or methamphetamines using catalysts such as palladium black, Raney-nickel and platinum in complex pressure apparatuses often using injections of hydrogen gas. These ways of conversion are relatively clean, with good yields, but they are not what this book is about. Strike feels these ways to be too involved for those looking to make a decent profit while avoiding overly-complex setups or expensive catalysts. These ways of conversion are meant for those who are intent on enormous yields, founding an empire and being placed in a correctional facility for a good part of their lives. Don't get Strike wrong, there's absolutely nothing wrong with these methods; and if one is interested in this sort of thing and wishes to become a professional drug lord, then they would definitely want to invest in the chemicals and proper construction of the type of apparatus necessary to do these pressure reactions.

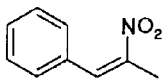
Apart from the academic literature, one should read the book "Secrets of Methamphetamine Manufacture" by Uncle Fester [18]. This book explains all about the in-home applications of these pressure methods. Strike, however, emphasizes reactions that are purely chemical.

β-NITROPROPENES

The next major category of precursors, apart from the phenylacetones, are the β-Nitropropenes. One can see the two representative examples for X and meth in the little drawing below:



MD-Phenyl-beta-Nitropropene

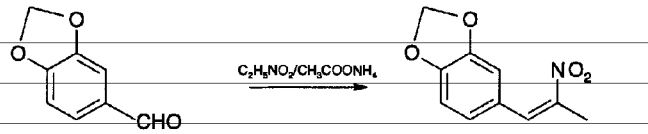


Phenyl-beta-Nitropropene

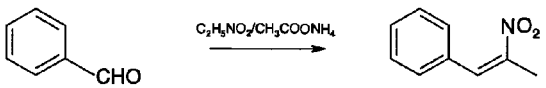
As you can see, there is a nitrogen right in the exact place where one wants it. That is definitely a step in the right direction. But Strike was not very keen on these intermediates because there was really only one decent way to make them that Strike favored and the ways to make final product out of them were not too hot as well. But a lot of things have changed for Strike in a year's time and there are a lot of new promises for this route.

So read what Strike has for ya here, then go to **Rhodium's Chapter** where some inventive new β-Nitropropene recipes can be found. Let's start things off with the basic recipe for this precursor.

METHOD #1: This section is going to be as thoroughly helpful to those interested in X production as it will be to those interested in amphetamine production. The process is known as the Knoevenagel-Walter condensation which can turn a substituted benzaldehyde such as piperonal (X) or plain old benzaldehyde (speed) into an intermediate called a β-nitropropene. This intermediate can then be transformed into MDA (Benzedrine for speed) or MD-P2P (P2P for speed) depending on the capabilities of the chemist.



Piperonal MD-Phenyl-beta-Nitropropene



Benzaldehyde Phenyl-beta-Nitropropene

Both piperonal and benzaldehyde are List I controlled substances just as safrole and isosafrole are, but the speed maker has the advantage here because benzaldehyde makes up over 95% of the quasi-legal bitter almond oil whereas there is no natural source of piperonal. Piperonal, also known as Heliotropin, can be made from sassafras oil. It is also a very important chemical in the fragrance industry. But there are so many ways to make both it and benzaldehyde in the **Build from Scratch** section of this book that the Knoevenagel synthesis has a potential for resurrection from the heavy restrictions that the government has put on it. By heavy strike means that not only are the precursors controlled but so is the main processing chemical: nitroethane. This substance does have a wide use in industry such that the chemist may come across some in daily life (yeah, right) or the stuff can be made as described in the **Chemicals** section. In fact, we have quite a few more recipes for making nitroethane than before!

This procedure has been performed in a variety of ways [28 p714, 38-42] with variations in solvent, base and time of reaction. For piperonal conversion, the consensus is toward the use of acetic acid as the solvent, ammonium acetate as the base and 4 hours of reflux time. Dr. Alexander Shulgin, a giant in this field, prefers the use of cyclohexylamine as the base. Strike would not tend to doubt this man's choice, especially since Strike is also getting the

feeling that ammonium acetate is heading towards the schedule I graveyard.

In a flask the chemist mixes 50g piperonal into 200mL glacial acetic acid, then adds 45mL nitroethane and 17g ammonium acetate. The solution is then refluxed 4 hours and takes on the color of yellow to yellow-orange. After 4 hours and cooling, yellowish crystals of β-nitropropene will spontaneously form. If not, the solution can be diluted with 50ml of dH_2O and chilled in an ice bath for an hour to form the crystals with some slushy glacial acetic acid and water intermixed. The mass of crystals is broken up and plopped into a Buchner funnel to be vacuum filtered. The filter cake is washed with a little extra acetic acid or water. All of the filtrate is saved.

These β-nitropropene crystals the chemist now has can be air-dried and used as is, but that is not advisable. What they need is a little more cleaning up, and one does this by performing recrystallization. To do this the chemist is going to use a solvent that everything in the reaction that the crystals came from is soluble in but that the crystals are not. Get it? No? Well, to demonstrate, the chemist will boil 200mL of methanol in a beaker and start knocking chunks of the impure β-nitropropene filter cake into the hot solvent. If all of the crystals will not dissolve in the 200mL of methanol then more is added and heated to accommodate. As soon as all the crystals are added and have dissolved, then the chemist turns off the heat and chills the mixture to 0-5°C. What is going to happen is that everything the chemist doesn't want will remain dissolved in the now cold methanol, but all of the β-nitropropene crystals will 'recrystallize' when cold. This solution is now vacuum filtered and the now clean crystal filter cake is washed with a little bit of extra, cold methanol just to make sure. That extra methanol washing and the filtrate can be reduced in volume by distillation and chilled to retrieve a second crop of β-nitropropene crystals (total conversion is around 70%). The final thing to add is that the chemist has a choice of recrystallization solvents other than methanol. These include hexane, isopropyl alcohol and ethanol.

You know how just a couple of paragraphs ago where the chemist first filtered the crude crystals from the chilled reaction mixture, then washed them with water or acetic acid? Well, all that liquid filtrate has a lot of valuable, unreacted piperonal or benzaldehyde in it. To rescue the stuff the chemist dilutes the mixture with 500ml dH_2O and extracts it with DCM. The DCM is washed with 100mL 5% NaOH solution then vacuum distilled to give a dark oil which is unreacted aldehyde. Hey! That's a lot of good material that can be put through the process again.

There are some slight alternatives to this process that, for educational reasons only, Strike is going to lay out for you now.

(1) It has been shown that by doubling the amount of nitroethane respective to that of the aldehyde in a ratio of 2 to 1, then the amount of ammonium acetate used can be reduced considerably [28 p703].
(2) The cooled reaction mixture can be induced to crystallize its β-nitropropene payload by simply dumping the whole thing in a large volume of ice water [40].
(3) Once the reaction mix has cooled after reflux, 500mL of room temperature dH_2O can be added and the whole solution extracted with DCM. The DCM layer is separated and the solvent removed by distillation to give the ß-nitropropene as an oil of all things. This oil can then be recrystallized in hot methanol just like the crystalline form was [38].
(4) Russian articles make some outrageous claims and this one is no different [43]. These mothers claim that piperonal or benzaldehyde will react with nitroethane by sitting in the dark at 10°C with only a couple of drops of ethylenediamine. Almost 100% yield no less! Strike has never tried this nor does Strike fall for Russian science, but if anyone is interested...

Once one has the β-Nitropropene, there are two ways one can progress. One can take the β-nitropropene and convert it into final, pleasure-inducing product. Which you can read about in the next section. But the other option for processing β-nitropropenes is to turn them into P2Ps. The chemist has to do something with the stuff because if it sits around too long it's going to degrade. This

procedure is really easy and has high yields [28 p734-735]. 32g elemental (electrolytic) iron (Fe) and 140mL glacial acetic acid are heated in a flask or beaker to around 60°C or, in more vague terms, to the temperature that is as hot as possible without the formation of white precipitates. One might want to do a couple of dry runs to determine the correct temperature. Into the hot mixture is slowly dripped a solution of 10g MD-nitropropene (that's the β-nitropropene made from piperonal) and 75mL glacial acetic acid. The dripping is adjusted so that the reaction does not become too violent or foamy. The color of the reaction will progress from orange to a deep red with the formation of white salt precipitates. After addition the solution is heated for an additional 1.5 hours at 70°C "during which time the body of the reaction mixture become(s) quite white with the product appear(ing) as a black oil climbing the sides of the beaker"[28, thanks Dr. Shulgin]. When cool, the reaction mix is added to 2L of dH_2O, extracted 2 times with 100mL DCM and the DCM extract washed with 1N NaOH solution. The DCM layer is vacuum distilled to give ~8g of pale yellow MD-P2P. Strike must say that that was a pretty easy one-pot procedure using 2-3 simple chemicals with an 80-90% yield.

METHOD #2: This may work on safrole but Strike has never tried it on the molecule. This should make good use of isosafrole and its cis isomer [44]. 76g silver nitrate ($AgNO_2$) and 254g iodine (find this at some pharmacies) are stirred in 600mL ether for 30 minutes, then 82g isosafrole in 100mL ether is dripped in while a gentle breeze of nitrogen from a baby nitrogen tank is blown into the air space of the flask. The nitrogen displaces atmospheric oxygen from the flask so that it won't mess with the reaction mix. The solution is stirred at room temperature for 4 hours, vacuum filtered, washed with a solution of dilute $NaHSO_3$ then washed with saturated sodium chloride solution. The ether is separated, dried through Na_2SO_4 and removed by simple distillation to afford a dark oil residue which is an iodo-nitro intermediate (don't ask). Now, Strike could be wrong (and often is) but the way this article reads gives Strike the distinct impression that the conversion of this intermediate to the final β-nitropropene can occur in two different ways. The implied way is to add 300mL ether and 300mL pyridine to all of the intermediate oil sitting by itself in the flask and

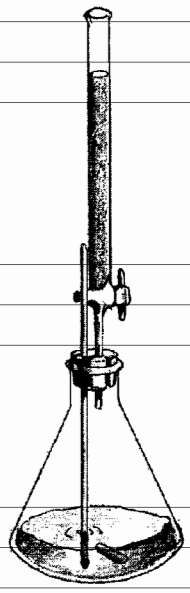
stir it at room temperature for 2 hours. The nitrogen in pyridine plucks the iodine off of the intermediate causing an elimination (don't ask). The solution is extracted with a large volume of pentane and water. The pentane layer is washed repeatedly with fresh dH_2O, dried through Na_2SO_4 and vacuum distilled to give product at +50% yield. The other way this may be done is listed a couple of paragraphs up in the article in the section titled 'Preparation of 3-Nitro-2-cholestene'. To the intermediate oil is added 11g silver oxide powder and 500mL methanol and then refluxed for 4 hours. After cooling, the solution is vacuum filtered and the methanol removed by distillation to give product (99%?). There is also an interesting, simple zinc reduction of the nitro product to ketone. Could this be another way to make P2Ps from β-nitropropenes instead of using Fe that is detailed in Method #1? Eleusis seemed to think so when asked. So here is the experimental as written in the journal article. Just imagine an equal amount of β-Nitropropene in place of the '3-Nitro-2-cholestene' and P2P as the product:

"*Reduction of 3-Nitro-2-cholestene . - Zinc dust (800mg) was added in portions during 1 hr to a stirred warm (40°C) suspension of 250 mg of 3-nitro-2-cholestene in 15mL of acetic acid and 0.5 ml of water. After 4 hr reflux, the mixture was filtered hot and the zinc washed well with hot HOAc. Addition of water and extraction with ether gave 116mg of product.*"

METHOD #3:[45-47]--Do not try this method! Strike repeats, do not try this method! This is the method popularized by Dr. Shulgin and reported in some of the underground literature [8] which uses the most dangerous compound in drug conversion chemistry that Strike is aware of: tetranitromethane. The reason this method keeps hanging around is because one can get clean, hyper yields of β-nitropropenes in less than 5 minutes. But the ultimate method can exact the ultimate price (death, bubba!). Rave rats are very idealistic and figure they can tangle with this method if they are careful. And since Strike cannot undo the presence of this procedure in the literature or the determination of enthusiastic chemist to try this, no matter how much they are told not to, then Strike will at least lay down the proper way it is accomplished.

There is an incredible amount of energy in the carbon-nitro bond. TNT (trinitrotoluene) has three such bonds. Tetranitromethane has four! Starting to get the picture?

Tetranitromethane was used as a double bond detector and for the detection of tyrosine in protein sequences. As you can guess, isosafrole's double bond is the point of attack. The problem is that there is not any accessible chemical company today that makes this compound anymore. So the rave rat is going to have to make it herself, and that's where the trouble begins. The best method for making tetranitromethane is in Organic Synthesis [48] using fuming nitric acid and acetic anhydride. All the glassware is cleaned with soap and hot water, rinsed thoroughly with distilled water, rinsed with acetone then rinsed once more with distilled water. The glassware is placed upside down on a sheet of foil in an oven and baked at 425°F for 1 hour. Baking destroys any remaining organics which can set off the tetranitromethane to explode. This glassware washing procedure, by the way, is the preferred way to wash up all of one's glassware after a long day's experimenting. It is the same procedure used by all the organics labs that Strike has been fired from.



[Figure 13]

The apparatus to use is seen in figure 13 which consists of a burette, thermometer, Erlenmeyer flask and a two-holed rubber stopper that has a small V-shaped wedge cut out of one side of the rubber stopper to allow the inside contents to vent. 31.5g of orangy-red fuming nitric acid (see chemicals section) is poured into the Erlenmeyer flask and the rubber stopper with its burette and thermometer is placed on to the

flask. The HNO_3 is cooled to below 10°C with an external ice bath and is never allowed to go above 10°C for the entire addition. 51g of acetic anhydride is poured into the burette and a big pane of clear acrylic that the chemist buys at the home improvement store is placed between the chemist and the apparatus to act as a blast shield. The acetic anhydride is added in small little squirts or slow dripping to the cold, stirred HNO_3. The solution will not change color throughout the addition. When the addition is complete, the burette is removed from the stopper but the solution continues to stir in the ice for another 4-6 hours then it is slowly allowed to come to room temperature by allowing the ice to melt. Once at room temperature the flask is removed from the stirplate and the solution should be monitored closely for at least 3-5 more hours. If the temperature of the solution starts to rise above room temperature during this time, then the ice bath must be reapplied. If the temperature starts to skyrocket then run. After monitoring, the stopper and thermometer are removed, the flask covered with an inverted beaker and stored behind the blast shield in a dry, dark place for 7 days.

After 7 days the solution is poured into 300mL cool dH_2O in a 500mL flask and slowly distilled with no vacuum. The first 20mL of distillate that comes over will be clear heavy tetranitromethane. The chemist will know that all has distilled over when the last clear drops that come over will be water that will start to form a layer on top of the tetranitromethane. The product is washed with dilute NaOH, then water and dried through a very small amount of Na_2SO_4 to give 16g pure tetranitromethane.

With tetranitromethane in hand, the chemist proceeds to convert isosafrole to β-nitropropene at an astonishing speed. 41g isosafrole, 300mL anhydrous acetone and 24g pyridine are well stirred in a flask and cooled to 0°C by means of an external ice bath (everything behind a blast shield of course). 54g of tetranitromethane is cooled to 0°C and then quickly poured into the reaction flask. The solution is allowed to react for exactly 2 minutes and then the reaction is immediately stopped by adding a mixture of 16.8g KOH in 300mL dH_2O. The temperature will have risen during the 2 minutes of reaction and the stoppage, so it is allowed to stir and

chill back to around 0°C. As the solution chills, β-nitropropene crystals will form and can be removed by filtration. The filtrate can be extracted with DCM and the DCM removed by distillation to yield an additional crop of crystals. The yield is about 50g (90%). These crystals are clean enough to convert into MDA or MD-P2P.

Now Strike is going to tell you a story. Once upon a time there was a beautiful kingdom of wealth and good will because God, in his infinite wisdom, had seen fit to bless the land with an abundance of bee pollen. It was the want of 49% of the citizenry to partake of this bee pollen because it made them happy. One day an army called The Majority invaded the kingdom and took seize of the bee pollen. You see, The Majority did not like bee pollen. In fact, the majority disliked bee pollen so much that not only would they not eat bee pollen themselves, they could not tolerate the idea of others eating bee pollen as well. There was much despair in the kingdom among those who liked bee pollen and many lamented their own fate. Some citizens became angry that those with might would impose their will on others. So those angry citizens took to tending bees in their cellars. It was of great expense to conduct such an undertaking and it forced many a citizen to forfeit a week's wage to obtain what they had once had for free. The Majority soon discovered that not only did many of the citizens have a distaste for the law against bee pollen, but that many citizens would break the law just to ingest bee pollen even though they were forbidden to do so. This affront angered The Majority so much that they decided to actually imprison citizens who ate bee pollen. The enormity of such a task soon became apparent as millions upon millions of citizens were sent to languish in dungeons for eating bee pollen. Confident in their cause, The Majority continued the inquisition unabated.

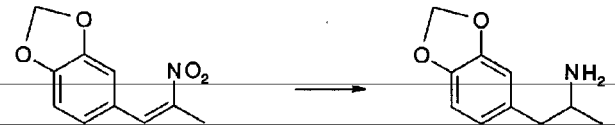
Meanwhile, in a stately laboratory atop a hill, the second finest alchemist in the land cast her sight beyond her potions and upon the landscape below. The troubles in her land prompted her to speak aloud, "How have things come to this? Although I am pleased for the good fortune that has come to my friends who contract and build dungeons, and who enforce the bee pollen laws, I cannot help but feel that...that...aw fucketh it!". And for no

reason at all, the chemist decided to make tetranitromethane. The chemist made a 5X batch of the stuff and had just set the flask to incubate for 7 days behind a blast shield in a bathroom of the house. Being the second greatest chemist in the land meant that the procedure had been performed perfectly under the strictest of conditions. And then, without any warning, the unattended solution decided to spontaneously get hot. The resulting explosion produced a shock wave so powerful that the tiles were ripped from their foundation as the blast plowed through the bathroom door, down hallways, around corners and shattering its way through half the windows of the house.

Strike thinks you get the picture now. Do not try this method. How did the story end you ask? Strike doesn't remember exactly. Strike thinks the kingdom was re-invaded by the forces of the neighboring Bee Keeper Empire.

AMPHETAMINES FROM β-NITROPROPENES

One cannot directly make a methamphetamine from a β-Nitropropene. But who needs 'em anyway when MDA and Benzedrine will do very nicely, thank you. Below is the no-brainer schematic for the conversion:



MD-Phenyl-beta-Nitropropene → MDA

Phenyl-beta-Nitropropene → Amphetamine

What goes on in this conversion is that the β-Nitropropene undergoes a catalytic reduction whereby it loses its propene double bond, and the nitro's oxygens get replaced with hydrogens. All this happens in one pot with, usually, just one reaction.

When Strike wrote the first edition Strike considered there to be only one, decent reduction method for the β-Nitropropene. But since then Strike has come across quite a few new ways that make this conversion very, very easy and varied. A lot of the ways were conjured up by one, industrious lab from Tennessee. We'll get to those in a minute. But first let's start off with the basic, default recipe for the reduction of β-Nitropropenes.

METHOD #1: [155, 28 p715]Using the setup in fig. 9, the chemist stirs 55g of $LiAlH_4$ in 200mL THF and adds dropwise to this a mixture of 50g β-nitropropene and 100mL THF from the separatory funnel. After addition the solution is refluxed for 24 hours during which time there will be the formation of a lot of white aluminum salt precipitates and the solution will also start to darken. The solution is cooled, 50mL dH_2O is added, and the solution is vacuum-filtered. The chemist washes the filter cake with a little extra THF and discards the filter cake. The filtrate is placed in a distillation setup, the THF removed under vacuum and, if desired, the dark MDA/amphetamine oil in the bottom can be distilled over as well to give clear yellow freebase. An alternative cleanup would be to forget about removing the THF and instead adding the solution to 200mL 0.5M H_2SO_4, extracting it with DCM then removing the DCM to get the freebase. Reduction using $LiAlH_4$ gives yields from 60-80%.

The following methods are all the result of one group of scientists: Rajender S. Varma, Laila H. M. Guindi and George W. Kabalka etal. They produced a series of papers in the 1980's that blew the fuck out of nitro compound science. Their methods for reducing β-Nitropropenes are novel and easy. And the best part is that they almost always used our exact precursor (Phenyl-β-nitropropene) as an experimental example. So there ain't gonna be no guessing as to whether their methods are applicable to our precursors. They are!

Although Strike found most of these articles on Strike's own, our good friend and learned scholar Osmium emailed Strike some of the above group's articles and quite a few more that we will get at in just a bit. The following methods can be read about in the original articles in which they were published [49-51]. But there is a nice review by the same authors in which a representative example of each of their methods is included [52]. The following were taken from that review. X and speed chemists just substitute an equimolar amount of their respective β-Nitropropene for the one in the methods below. Also, it should be obvious that these reduction methods will work just fine on 2CB and other phenethylamine intermediates.

METHOD #2: "*Synthesis of Alkylamines. General Procedures. Method (A). The synthesis of β-phenethylamine is representative. A flame dried, nitrogen-flushed, 100 ml flask, equipped with a septum inlet, magnetic stirring bar and reflux condenser was cooled to 0°C. A BH_3-THF solution (16 mmol, 9.5 ml of 1.7 M) was injected into the reaction flask via a syringe, followed by the slow addition of a solution of β-nitrostyrene in THF (4 mmol, 0.6g in 6 ml THF). After the addition, the ice-bath was removed and a catalytic amount (~40 mg) of $NaBH_4$ was added to the stirred reaction mixture by means of a spatula. A moderately exothermic reaction ensued. The reaction was then allowed to proceed for 6 days at 25°C . The reaction mixture was poured on to ice-water mixture (50 ml), acidified with 10% HCl (~20 ml) and then stirred at 60-65°C for 2 h. After cooling to room temperature, the acidic layer was washed with ether (2x50 ml), and then the β-phenylethylamine was liberated via the addition of aqueous sodium hydroxide. Solid NaCl was added and the product extracted into ether (3x50 ml). The combined ethereal extracts were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to yield 0.43 g (88%) of β-phenylethylamine.*"

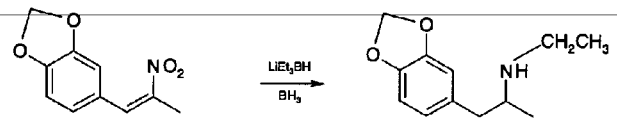
The authors say that the 6 day reaction time at room temp can be accelerated by raising the temperature of the reaction. But they did not specify how much heat or how much time would be reduced.

METHOD #3: The authors next stepped back and considered the cosmic imbalance caused by that 6-day reaction time. The next recipe was what they came up with.

"*Synthesis of Alkylamines. General Procedures. Method (A). The synthesis of β-phenethylamine is representative. A flame dried, nitrogen-flushed, 100 ml flask, equipped with a septum inlet, magnetic stirring bar and reflux condenser was cooled to 0°C. Sodium borohydride (9.5 mmol, 0.36 g) was placed in the flask followed by sequential addition of THF (13-15 ml) and BF_3-Et_2O (12 mmol, 1.5 ml) at 0°C. After the addition, the ice bath was removed and the contents were stirred at room temperature for 15 min. The solution*

of β-nitrostyrene in THF (2 mmol, 0.3g in 5 ml THF) was then injected dropwise into the reaction flask via a syringe and the reaction mixture refluxed on an oil bath for 5.5 h. After cooling to room temperature, the reaction was quenched by careful addition of water (25 ml), the mixture acidified (1N HCl, 25 ml), and then heated at 80-85°C (oil bath) for 2 h. After cooling to room temperature, the product was isolated (75%) as described in method A [from above, folks]."

METHOD #4: The last one from this review [52]. The authors found that reduction occurred using some spacey sounding catalyst called lithium triethylborohydride. But something interesting occurred in the process. The catalyst reduced the nitro group and all to give only a small amount of the predicted amphetamine. But it also stuck one its ethyls on the nitrogen to give a majority product of N-ethylamphetamine!



MD-Phenyl-beta-Nitropropene MDEA

That means that this method is a neat little way one can get the ever lovely MDEA (Methylenedioxyethyl amphetamine, the softer cousin of X). Strike hears you asking "So if one uses lithium trimethylborohydride can one get methamphetamine out of that nitro group?". Good question. Unfortunately the answer is no. The authors say "*Interestingly, N-alkylated products were not produced when other alkylborohydrides were used.*" Fair enough. Here's the recipe:

"*Reduction of Nitroalkene with Lithium Triethylborohydride (Superhydride) and borane. General Procedure. The reduction of β-methyl-β-nitrostyrene* [a.k.a. Phenyl-β-nitropropene, folks] *with superhydride ($LiEt_3BH$) and borane (BH_3) is representative. Into a flame dried, nitrogen-flushed, 100 ml flask, equipped with a septum inlet, magnetic stirring bar and reflux condenser was added a solution of $LiEt_3BH$ (10.5 mmol, , 10.5 ml) via a syringe, followed*

by the addition of a solution of β-methyl-β-nitrostyrene (7mmol, 1.4 g in 5 ml of THF). After the addition, the reaction mixture was stirred at room temperature for 1h. Excess BH_3-THF (23 mmol, 28 ml) was then added and heated at 60-70°C for 15 h. The mixture was poured into ice water and acidified to pH 2. The mixture was stirred and heated at 60-65°C for 2 h and then cooled to room temperature. The acidic water layer was washed with ether (3x30 ml) to remove N-hydroxylamphetamine. The pH was then adjusted to 10 and the product extracted into ether (3x30 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure to yield 0.73 g (64%) of N-ethylamphetamine. The hydrochloride salt was prepared and recrystallized from an ether/ethanol (20:1) mixture."

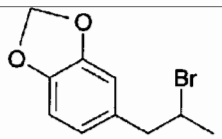
METHOD #5: Contributed by Osmium [53]. The paper reads (at least to Strike) that this reduction method can work to reduce the formyl intermediate made in the Leuckart reaction directly into MDMA instead of needing to hydrolyze to MDA with HCl (don't ask). For this reaction one substitutes an equimolar amount of β-Nitropropene for the 3,4-dimethoxybenzylcyanide in the representative experimental below:

"*$NaBH_4$ (4.56g, 120mmol) was added to a solution of Me_3SiCl (26.04g, 240mmol) in THF (100mL) and the mixture refluxed for three hours under argon. A solution of 3,4-dimethoxybenzylcyanide (10g, 56.4mmol) in THF (50mL) was then added over the course of 10min. The solution was refluxed for a further 10h. After cooling, 100mL MeOH were cautiously added and the volatiles removed in vacuo. The residue was taken up in dilute HCl and washed with ether. The aqueous solution was treated with excess dilute NaOH and then repeatedly extracted CH_2Cl_2. The organic extracts were combined, dried over Na_2SO_4, and the solvent evaporated to afford 2-(3,4-dimethoxyphenyl)ethylamine. Yield = 9.16g (90%).*"

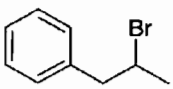
The authors caution that "*MeSiH is formed. It should therefore be ensured that this volatile silane (b.p. ~10°C) can escape from the reaction vessel.*"

BROMOSAFROLE & PHENYLISOPROPYLBROMIDE

The third, and last, major category of X precursor is the halogen species. In the world of chemistry, scientists look to add things or change things with a molecule by exploiting 'functional groups'. So far we have been exploring the possibilities of the ketone functional group (P2P) and the nitro group (β-Nitropropene). And although there are lots of different things that can be considered functional groups, the only one left that really has any broad utility for the underground chemist is the halogen called Bromine. When one introduces a bromine into that magic beta carbon of safrole or allylbenzene (or however one can arrive at that point) one will get the following species:



Bromosafrole

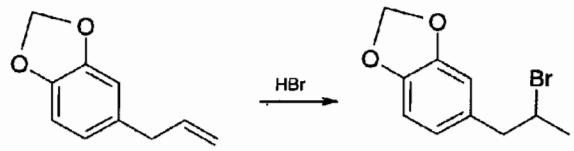


Phenylisopropylbromide

Bromosafrole is a great stepping stone to final product and was, in fact, the exact precursor used by Merck who was the first person to synthesize MDMA. Until very recently it was the defacto method that most underground chemists started out with (Someone-Who-Is-Not-Strike included) because, at first glance, it seems so simple and uses basic chemicals and equipment. Once someone has the bromosafrole, all one has to do is just swap out that Br with simple ammonia or methylamine and the deed is done.

But one has to get the bromine on the safrole in the first place, right? And that has proven more difficult than most people thought. Not because it is procedurally difficult, but because people have been misinformed on the subject for a long time.

The basic premise for making bromosafrole has been to mix safrole with Hydrobromic Acid (a.k.a. hydrogen bromide, HBr). That's it. The HBr does what is called a Markovnikov addition reaction whereby the HBr sees the allyl double bond of safrole and preferentially attaches its hydrogen to the gamma carbon and its bromine to the middle beta carbon (don't ask).



Safrole Bromosafrole

But the key to success is getting the right form of HBr for the reaction. A lot of people start off with the CA abstract that uses aqueous 70% HBr as the reagent (this abstract is essentially a rewrite of Merck's original patent) [59]. The following is the write up:

"*Safrole (5.3g) added dropwise at 0°C to 21g. 70%HBr, the mixt. left 14 hrs. at 0°C, poured on ice, extd. with Et_2O, and the ext. Distilled in vacuo yielded 97% 3,4-$CH_2O_2C_6H_3CH_2CHBrMe$.*"

97% yield sounds great. But where the hell can one get 70% HBr? Certainly no place that Strike is aware of. It does not exist in other words. Nor does Strike know how any of these folks were able to make a supersaturated aqueous solution of HBr. All commercially available hydrobromic acid solutions are 48% HBr which happens to be the constant boiling point percent for that species in water (please don't ask).

Some people think that 48% aq. HBr is good enough and, until recently, some underground chemistry texts agreed. But it is not! The 48% is only strong enough to promote what is called acid catalyzed hydration (don't ask) when the medium it is in is water. That means that a water molecule (an OH) will add instead of a Br.

The problem really isn't the concentration of the HBr, but rather is the result of the HBr being in water. As long as there is a significant amount of water present in the reaction mix with safrole, that water is going to compete with bromine for that juicy beta carbon on safrole. And it's gonna win, too. The answer is to use non-aqueous HBr solutions.

For the past year Strike had been in consultation with contract labs over the making of phenylisopropyl alcohols using sulfuric acid and allylbenzenes (don't ask). The lab owners would listen patiently as Strike primitively described how and why an OH should go on the beta carbon. And without exception, the lab owners would point out to Strike that the best way to get an OH on the beta carbon would be to put a Br there first. "But Strike don't wanna put a Br there first" Strike would say, "Strike wants the OH put on directly using sulfuric acid!" The lab guys had to do what Strike said because Strike was holding all the money (...a fool and her money etc.). But out of curiosity Strike asked how they would get that Br on the beta carbon. Every one of them said it was simply a matter of using the 48% HBr in acetic acid. They even showed Strike their stock solutions (usually from Aldrich or Fisher).

Currently, there are commercially available 48% or higher HBr solutions in acetic acid. These work just fine. They really do! The acetic acid is usually used more as a solvent than an acid. It allows the water-loving HBr and the water phobic safrole to mingle with each other in a very positive way. If one cannot get a ready-made solution of HBr in acetic acid then one can make one quite easily.

To make her own HBr solution the chemist needs to go down to the local specialty gas supplier. These sorts of businesses sell tanks of oxygen to hospitals, acetylene tanks to welding shops and, yes, HBr to underground chemists. The chemist places 200g of acetic acid in a small PP container or flask and then weighs the flask with its contents. Next, the flask is stirred in an ice bath tray that has just a small amount of ice to keep the contents cool and

HBr from the tank is slowly bubbled into the acetic acid. Ever so often the chemist will stop the bubbling and reweigh the flask to see how much weight in HBr it has gained. Ideally, the chemist would like to have around 150g of HBr in that acetic acid which is now quite orangy in color.

Another way would be to generate ones own HBr gas. If you were to take a look in the **Crystallization** section of this book one would see that the apparatus used is essentially an HCl gas generator. Substituting the commercially available 48% aq. HBr instead of HCl will give one dry HBr gas instead! That gas can be channeled directly into acetic acid just like above.

The last thing to remember is that the more HBr one packs into that acetic acid, the greater and quicker the yield will be. 70% HBr is still the paragon and should be strived for always. So with the proper HBr solution in hand the evil chemist can proceed with the conversion of safrole.

Safrole Bromosafrole

METHOD #1: To proceed, the chemist uses her concentrated homemade solution that she made above or uses ~350g of any concentrated HBr reagent, places it in an appropriately sized flask and places the flask in an ice bath [60, 154]. The setup is going to look exactly like the one seen in fig. 9. In the separatory funnel is placed 137g of safrole or 100g allylbenzene. The HBr/acetic acid solution is stirring in the ice bath til it is between 5-10°C (if it gets too cold the acetic acid will turn to ice) then the safrole is slowly dripped in. The oil will bead up on the surface for just a bit but will dissolve quickly into the cold acid mix. Good, constant stirring assures that everything comes in contact with everything else. After addition is complete the solution is a dark orange and is allowed to

come to room temperature slowly by letting the ice melt away. Then the solution is covered with foil and stirred at room temperature for 24 hours. After such time the solution will be a single layered burgundy solution. The chemist pours this solution into a container of 300mL cold water and 500g crushed ice made earlier from dH_2O. Things will look lavender in color with the heavy bromo-safrole sitting at the bottom. The bromo-safrole is separated from the water and the water extracted once with 100mL ether or benzene which is then added to the bromo compound. The bromosafrole/solvent is washed once with clean dH_2O, once with 3% sodium carbonate, then dried through Na_2SO_4. What the chemist has now is a dark red bromo-safrole compound in some solvent. The chemist removes the solvent by distillation then vacuum distills the bromo compound over to get a clear, slightly orange bromo-safrole (yield=90%). Actually, the bromo compound is pretty clean as is and can be, if desired, used as is. A chemist who is mindful of the potential of this bromo-safrole would make far bigger batches than the amounts given above. This bromination procedure is perfectly suited for large reactions.

If the chemist wants to know whether her final product is bromosafrole and not just a bunch of unreacted safrole there is a simple little test she can do. Safrole is soluble (will dissolve in) cold concentrated sulfuric acid. But bromosafrole is insoluble in it. So the chemist can take a shot glass full of straight-from-the-bottle 96% H_2SO_4 and place it in the freezer until it's ice cold. Then she takes it out and drops a few drops of mystery product into it. If the oil dissolves then the stuff is unreacted safrole. If the oil drops to the bottom and does not dissolve it's the goods.

METHOD #2: Speed chemists have used hydroiodic acid (HI) for years to reduce ephedrine to meth. So when the government placed HI on the restricted list, speed chemists took to making the HI themselves. One of the ways they used was to make HI in DMSO (dimethylsulfoxide, a common solvent) by reacting NaI or KI with sulfuric acid. This a standard way to make both HBr or HI in water (see the **Chemicals** section of this book) except these speed chemists were using the non-aqueous solvent DMSO instead of water.

When Strike first started the Hive web site Strike was sent a newsgroup post by a very famous underground chemist called Pugsley. Pugsley had apparently been toying with the idea of *in situ* (in the pot) production of HBr for making bromosafrole. The following is her recipe. Strike knows it works because Strike's friend in Houston tried it out in her accredited and licensed university lab and gave it the old thumbs-up!

"Subject: Pugsley's bromosafrole prep > From: nobody@zifi.genetics.utah.edu (Anonymous) > Date: 1996/06/28 > Message-Id: Newsgroups: alt.drugs.chemistry > [More Headers]

Here is the only bromosafrole (or bromo propenylbenzene) synthesis you will ever need. It proceeds totally anhydrous with pure reagents, and generates no obnoxious fumes to give you away. More than likely, this will spur DEA to add new watched chemicals (like what isn't watched already- air, water, ?) To 100 ml of chilled DMSO add 7.8ml conc. H_2SO_4 (i.e. drain cleaner). To this add 30g of NaBr. Stir well and repeatedly. Solution will turn orange as all the NaBr is turned into Na_2SO_4. Do not filter, leave crystals alone in case there is some unreacted NaBr left. If the H_2SO_4 and DMSO is anhydrous, so will the HBr be anhydrous. Add 5 ml of sassafrass oil. Or scale qty of everything up for more sassafrass. Let sit at room temp. Don't bother to filter out crystals, in case there is unreacted NaBr. In 1 or 2 days solution will proceed as in Fester's turning green, then purple, then gradually burgundy. To understand why this works so well, see Fieser and Fieser "Reagents in Organic Synthesis" under DMSO monograph. Note that there are two pathways for HBr to react. Via an ionic mechanism gene rates the desirable compound. Via a free-radical route forms terminal bromo compound, which cannot be used (you can try for interesting analogue, but who cares now that all mind altering chemicals are illegal under the Analoges Act, including all those in everyone's brains- imagine, even Jesse Helmes committing felony if he has any brain cells left). The crude sassafrass oil contains eugenol, a phenolic compound which inhibits free radical reaction. Thus you will get better product if you don't purify out safrole. Also keep reaction mixture away from air and UV light, both generate

free radicals. The final mixture gets 500-1000ml of water added. The crude bromosafrole which settles to the bottom is seperated without adding any organic solvent. If you cool it it gets pretty sticky and syrupy so the water layer can be just poured off."

One need not inhibit oneself by using HBr. One can use NaI or KI to make HI which is even better than HBr in any of these recipes. Iodine adds much better and swaps out with the amines much better. Yield are much higher! The other thing to notice is that reaction carries itself out in DMSO. Seems logical to believe that one could bubble their HBr gasses into this solvent instead of acetic acid.

METHOD #3: This is not really a method. It is more of an idea Strike and others have been toying with. Eleusis had been supporting the idea that one could make use of the common 48% aq HBr if one employed the technique of 'dehydration'. We remember that the water was competing with the Br in the normal 48% solution. But the literature demonstrates that in conditions such as this, a competing acid can strip away the water (dehydrate) from the beta carbon allowing the Br a second chance to pop in.

Fester [18] has made this modification to his recipe by promoting the idea that bubbling HCl gas into the safrole/48% aq HBr reaction mix one can affect dehydration allowing dominant bromination to occur. Strike does not know if that actually works. Could be. But what Strike and Eleusis draw on are the examples given by Vogel [37 p277].

When Vogel wants to brominate something using regular old 48% aq. HBr, he has sulfuric acid already present in the pot. The following is a representative recipe from his book. Just read it. Strike does not expect you to get the inference right away. Strike will explain Strike's interpretation afterwards.

*"**III,35. Sec-Butyl Bromide** (HBr-H_2SO_4 Method)*

To 250g. of 48 per cent. hydrobromic acid contained in a 500ml. round-bottomed flask add 75g. (41 ml.) of concentrated sulphuric acid in portions with shaking (1); some hydrogen bromide may be evolved. Add 88g. (110ml.) of sec-butyl alcohol, followed by 60g. (32.5ml.) of concentrated sulphuric acid in several portions with shaking, and finally a few chips of broken glass. Attach a reflux condensor to the flask and reflux the mixture gently on a wire gauze for 2-3 hours; during this period the formation of sec-butyl bromide is almost complete and a layer separates above the acid. If the preparation is carried out in the open laboratory, fit an absorption device (compare Fig. II,13,8 and Fig.III,28,1) to the top of the condenser i order to absorb any hydrogen bromide and sulfur dioxide which may have evolved. Allow the contents of the flask to cool, remove the condensor and set it for downward distillation; connect the condenser to the flask by means of a wide (7-8mm. diameter bent glass tube. Distil the mixture until no more oily drops of sec-butyl bromide to pass over (30-40 minutes). Transfer the distillate to a separatory funnel and remove the halide which forms the lower layer. Wash it successively with water, an equal volume of concentrated hydrochloric acid (2), water, 5 per cent. sodium bicarbonate or sodium carbonate solution, and water. Separate the water as completely as possible and dry with 2-3g. of anhydrous calcium chloride or anhydrous magnesium sulphate; the desiccant should be left in contact with the bromide for at least 30 minutes and shaken occasionally. Filter the dried product through a small funnel supporting a fluted filter paper or small cotton wool plug into a 200ml. distilling flask, add a few chips of porous porcelain and distill either from an air bath (Fig.II,5,3) or on an asbestos-centered wire gauze. Collect the portion boiling at 100-103°. The yield is 155g.

***Notes.** (1) the acid mixture may be prepared (compare Section **II,49,1**) by placing 120g. (37.5ml) of bromine and 130g. of crushed ice in a 500ml. flask , cooling the latter in ice, and passing sulphur dioxide (from a siphon of the liquified gas) into the bromine layer at such a rate that the gas is completely absorbed. The flask is shaken occasionally, and the flow of gas is stopped immediately the red colour due to free bromine has disappeared; the mixture*

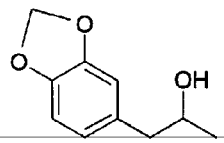
will then have a yellow colour. The resulting mixture is equivalent to 250g. of 48 per cent. hydrobromic acid to which 75g. of concentrated sulphuric acid have been added; it need not be distilled for preparation of sec-butyl bromide.

Owing to the comparatively negligible difference in the cost of bromine and the equivalent quantity of constant boiling point hydrobromic acid, there is little to be gained--apart from the instructional value-- in preparing the hydrobromic acid from bromine in the preparation of alkyl bromides.

CAUTION. Bromine must be handled with great care and in the fume cupboard. The liquid produces painful burns and the vapour is unpleasant. Bromine burns should be treated immediately with a liberal quantity of glycerine. If the vapour is inhaled, relief may be obtained by soaking handkerchief in alcohol,holding it near the nose.

(2) The crude bromide contains a little unchanged alcohol and is said to contain some n-butyl ether (b.p. 141°). The former is removed by washing the concentrated hydrochloric acid and this purification process is satisfactory for most purposes. Both the alcohol and the ether are removed by washing with 11-12ml. of concentrated sulphuric acid; the butyl bromide is not affected by this reagent."

You see that substrate they were using: "sec-butyl alcohol"? Well to Strike that looks just like MD-P2Pol:



MD-Phenyl-2-Propanol

And in the recipe above, Vogel want's to get rid of a secondary alcohol just like the one on MD-P2Pol and replace it with a bromine. "Wait a minute!" you may say, "That isn't a double bond like

safrole he is starting with. It is an OH alcohol!". That's true. But in this instance it does not make a difference. We know that at 48% aq concentration an OH is going to end up on the beta carbon anyway. So starting with an alcohol will make no difference. The clincher is the presence of the H_2SO_4. It is there not only to strip off the existing OH, but to keep it off so that bromination becomes dominant.

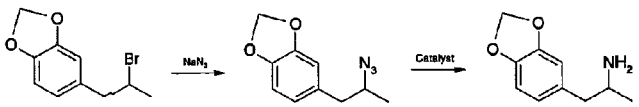
So if one were to replace sec-butyl alcohol in the recipe above with an equimolar amount of safrole in the above reaction, Strike will wager that a positive bromination experience will occur. And all this using the very common 48% aq. HBr! The only difference being that once the reaction mix had cooled, one should do either of two things: (1) distill as described except the bromosafrole will be the last thing to come over (not the first), or (2) flood the reaction mix with water to bring the product out of solution after which it can be physically separated by decanting or sep funnel or some such shit.

Anyway, this is just an idea. But in case one feels inclined to use it or make HBr gas from 48% aq. HBr, Strike has provided quite a few recipes for the manufacture of the 48% in the **Chemicals** section.

AMPHETAMINES & METHAMPHETAMINES FROM BROMOSAFROLE & PHENYLISOPROPYLBROMIDE

With bromo or iodo compound in hand it is time to quit and turn one's self over to the proper authorities. Wait! There are a few who would continue. Most likely in the following manner.

METHOD #1: The bromine on the safrole or allylbenzene is in what is called a secondary position. To chemists this means that if one were to try and screw around with that bromine where it is and replace it with something like ammonia (which would give MDA right off the bat) then more bad things than good would occur. Ammonia is a so-so nucleophile and if it tries to muscle the bromine from its spot then the most likely thing that would happen is that an elimination reaction will occur and the double bond will reform (giving safrole and isosafrole as products) or unwanted inappropriate additions may occur (please don't ask). As it so happens, an azide (N_3) is as good a nucleophile as bromine and will fill its position quite nicely. Having a nitrogen where it's supposed to be on the safrole or allylbenzene molecule is certainly a step in the right direction even though it happens to have a couple of extra nitrogens attached to it. This is not going to be too big an obstacle as you will see.



Bromosafrole Safrole-Azide MDA

The best azide to use these days is sodium azide (NaN_3). It is inexpensive and unwatched. All azides have the potential to explode upon degradation and are toxic to breathe. The methods

given here are designed to insure that this will not occur. Even handled carelessly the potential for harm is not as dire as it may seem. Nevertheless, these procedures should be done in the hood and, if possible, performed behind a clear pane of acrylic that the chemist can find down at the home improvement store. Relax. Trust in the science and read the articles provided [62-67].

The setup used is the one pictured in fig. 9 except there is no ice bath tray. In the reaction flask is stirred a solution of 30g NaN_3 in 400mL ethanol (Everclear is perfectly ok) or propanol (chemist's choice) and 80mL dH_2O. 120g of bromo-safrole or 80g bromo-allylbenzene is dripped into the solution from the separatory funnel over a period of 20 minutes. After addition the thermometer and separatory funnel are removed, a condenser is attached and the solution slowly brought to reflux over an hour's time. The solution is refluxed for 24 hours, cooled, 100mL ether is added and the entire solution slowly poured into 1000mL of dH_2O. The upper ether layer is separated, the bottom water layer extracted once with 100mL more ether and the two ether fractions combined and dried through Na_2SO_4. The chemist now vacuum distills the ether/azide fraction to get what is now safrole-azide (yield=50%).

A much greater yield can be had if the chemist uses carbitol as a solvent instead of propanol [62]. Carbitol is a really hazardous solvent and should not be breathed or placed on one's skin. The reaction proceeds exactly as before except that after 24 hours of reflux and cooling the mixture is slowly poured into 1500mL ice cold dH_2O. The upper solvent layer is separated and the aqueous layer extracted with 200mL ether which is then combined with that upper solvent layer. The combined solvent portions are vacuum distilled to afford safrole-azide (or phenylisopropyl-azide for amphetamine) with the yield rising to 70%.

A newer and equally effective way of swapping azides with halides (bromines or iodines) is in the use of phase transfer catalysts [68]. Strike wouldn't expect an underground chemist to purchase the exotic catalyst Aliquat 336 which the investigators in this reference used to get yields approaching 100% but an alternative catalyst of

butylamine is offered as an effective alternate with yields approaching 75%. The figure 9 set up is again used with 100g bromo-safrole (80g phenylisopropyl-bromide), 30mL dH_2O and 50g sodium azide are stirred in the reaction flask. 5g of butylamine is dripped in, a condenser is attached, the solution slowly brought to reflux and kept there for 6 hours. After cooling, the solution is extracted with ether, dried through Na_2SO_4 and distilled to provide the azide product. The chemist should keep in mind that here, as with the previous two azide procedures, will be a significant amount of salvageable isosafrole formed as a byproduct.

One of the ways that this azide method is going to make it resistant to intervention by law enforcement is that the azide species comes in so many forms aside of plain old sodium azide such as potassium azide, phenyl azide, trimethylsilyl azide [69] etc. However, what makes this method so stellar is the number of ways this azide can be reduced to the final amine of MDA or amphetamine. When most underground methods introduce that precious nitrogen there is always a catch. Usually there is a formyl or acetyl group attached that has to removed in sloppy, destructive ways. Sometimes the amino group is introduced through expensive high-pressure catalysts and equipment usually using that hyper-watched chemical called methylamine. The chemists using azides are in a unique position because the mechanism by which those two extra nitrogens can be flicked off and replaced with hydrogen are varied, easy and successful in producing almost 100% yields.

The chemist can use older methods to reduce such as pressure reactions using Raney-nickle, PtO_2 and Na amalgam. Until recently the most popular way was to use $LiAlH_4$ [70]. To do this, the chemist mixes 50g of safrole-azide with 200mL anhydrous ether and slowly drips this solution into a stirring mix of 40g $LiAlH_4$ in 200mL anhydrous ether. After addition, the solution is refluxed for 4 hours, during which time the chemist will notice profuse bubbling which is harmless nitrogen gas (N_2) being evolved. After 4 hours and cooling, 100mL dH_2O is added to destroy the catalyst, the ether layer separated and distilled to give MDA at yields of 70%.

The following two reductions are, hands down, the ways to go for reducing azides [71, 72]. 200g safrole-azide or 160g phenylisopropyl-azide and 1000mL methanol are chilled in a well-stocked ice bath with stirring. All the chemist needs now is 34g magnesium (Mg) powder or 60g calcium (Ca), which can be purchased in pure form down at the pharmacy or in the vitamin section of the local hippie health food store (you know, Strike thinks Strike should stop bad mouthing the hippie health food stores). This powder is scraped into the cold solution in small increments. Almost immediately, heavy bubbling and heat will evolve. The bubbling is released N_2 gas which lets the chemist know that things are working. The solution stirs in the ice bath for 15 minutes more and that's it. The methanol is removed by vacuum distillation, cooled and 500mL ice cold dH_2O added to the residual oil left in the flask. The solution's pH is adjusted to between 9-10 with dilute NaOH solution and saturated with NaCl. This solution is extracted with ether, the ether washed with dilute NaCl solution then dried through Na_2SO_4. Removal of the solvent by distillation will give MDA or amphetamine in yields of 98%!

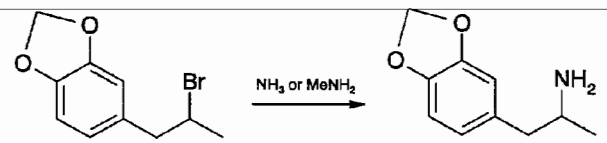
A cousin to this reduction is one using stannous chloride (a.k.a. $SnCl_2$, a.k.a. Tin chloride) which is done exactly as the calcium one except that about 100g of $SnCl_2$ is used in place of the Mg or Ca and the addition occurs at room temperature and the solution is stirred for one hour rather than 15 minutes. Some very good reductions that operate almost exclusively at room temperature with no pressure and give almost 100% yields are to follow. The only reason Strike did not detail these methods is that some of the chemicals involved are a little less common than Strike is used to but all are available to the public. These alternatives include: acetylacetone and triethylamine [73], propanedithiol and triethylamine [74], triphenylphosphine [75], $NaBH_4$ with phase transfer catalyst [76], H_2S and pyridine [77], and palladium hydroxide/carbon with hydrazine [78], stannous chloride dihydrate [85].

Recently, a nice bee named Quirks submitted an article from our new, favorite patron researcher: Rajender S. Varma. This time the good doctor is tackling our azide problem with another novel use of his clay phase transfer catalyst system. This is just going to be

quote from the journal article [86]. If you like the looks of this experimental, then go and read the entire article for more detail.

"*Alkyl Azides from Alkyl Bromides and Sodium Azide : General procedure for the synthesis of alkyl azides. In a typical experiment, benzyl bromide (360 mg, 2.1 mmol) in petroleum ether (3 mL) and sodium azide (180 mg, 2.76 mmol) in water (3 mL) are admixed in a round-bottomed flask. To this stirred solution, pillared clay (100 mg) is added and the reaction mixture is refluxed with constant stirring at 90-100 'C until all the starting material is consumed, as observed by thin layer chromatographv using pure hexane as solvent. The reaction is quenched with water and the product extracted into ether. The ether extracts are washed with water and the organic layer dried over sodium sulfate. The removal of solvent under reduced pressure affords the pure alkyl azides as confirmed by the spectral analysis.*"

METHOD #2: This method is a backup use for all that bromo-safrole or phenylisopropyl-bromide that the chemist made. It is the simplest method in the entire book, uses the cheapest most basic ingredients and happens to be the first method that Strike ever 'studied' [59]. Strike does not have many fond reminiscences about this method because it kind of sucks but the chemistry is so basic that it may well serve the most pathetic chemist. The reaction proceeds as follows which uses ammonia to replace the bromine giving MDA or amphetamine directly:



Bromosafrole MDA

All this business of swapping out bromine would be a lot easier if that bromine were at the end of that aliphatic chain which would make it a primary bromine (don't ask). As it so happens, the bromine in bromo-safrole is at a secondary position which means that

one is going to need a good nucleophile (like N_3) to swap out at such a position. Ammonia is not a very good nucleophile, so in order to do this the chemist is going to need a lot of it. Strike is talking a lot of it! This will not only push the reaction towards substitution, but will help prevent elimination and competing reactions (don't ask). The most basic ammonia available to the chemist is ammonium hydroxide which is ammonia (NH_4) dissolved in water. What the chemist needs is as concentrated a solution of ammonium hydroxide as possible. A desirous term for a good solution would be one that has a specific gravity of 0.9. An even better option would be to buy a solution of ammonia in methanol or ethanol. A good concentration of ammonia in such a solution would be 18-25%. Using methanol or alcohol means that the bromo-safrole or phenylisopropyl-bromide oils can dissolve into the medium so that they can come in greater contact with the ammonia. What may prove to be the best choice for the chemist would be that of going down to the specialty gas cannister company and buying a tank of ammonia gas. The chemist will bubble that gas into ice cold methanol or ethanol until that solution can gain no more weight in ammonia. All of this work with ammonia is going to stink like crazy so good ventilation is a must.

Now, contrary to popular opinions, this method need not be conducted in a sealed pipe bomb. Secondary amination by substitution is as much a reaction of opportunity as it is of brute force and heat. In fact, heating can tend to cause the reformation of safrole and isosafrole. So the simplest way to do this would be to use 500mL of ammonium hydroxide or alcoholic ammonia or, for those wishing to make MDMA or meth, 40% aqueous methylamine or alcoholic methylamine (to tell you the truth, methylamine is preferable in this method because it is more reactive that ammonia so yield will increase). This 500mL is placed in a flask and into it is poured a solution of 35g bromosafrole (30g phenylisopropyl-bromide) mixed with 50mL methanol. The flask is stoppered and stirred at room temperature for anywhere from 3 to 7 days. The chemist could also reflux the same mixture for 6-12 hours or she could throw the whole mix into a sealed pipe bomb (see **How to Make** section) and cook it for 5 hours in a 120-130°C oil bath.

When whichever reaction is complete, the excess ammonia and alcohol is distilled off. The exhaust coming from the vacuum or distillation apparatus must be channeled to the out of doors or bubbled into a container of NaOH solution because all that ammonia discharge will become devastating. The remaining liquid is acidified with 500ml 10% HCl solution and extracted with 100mL ether. By now you readers realize that the MDA product will remain in that acid water and extracting with ether will remove valuable unreacted safrole, isosafrole and bromo compound. The ether is separated and the water layer, which is normally brownish gray at this point, is basified with concentrated NaOH solution and then will appear dark brown droplets of you-know-what. You-know-what is extracted from the solution with ether or some other solvent, dried through Na_2SO_4 and removed of solvent by distillation to afford you-know-what.

Right about now the chemist is probably screaming, "Hey, where the hell is my big yield of you-know-what?!". Sorry, Charlie. This way of aminating is easy but chemically it's a crap shoot with yields anywhere from 10-50%. The theoretical odds are against the reaction but if it is done as outlined here, the chances of success are better. Actually, Strike thinks the yields could be higher because half the problem was probably caused by low bromosafrole yield which we have hopefully corrected in the preceding section!

METHAMPHETAMINES FROM AMPHETAMINES

METHOD #1: [26]-- 8g of perfectly fine, shouldn't-be-messed with MDA or benzedrine freebase is mixed with 100mL methylformate in a small pipe bomb. The sealed bomb is placed in boiling water or a 100°C oven for 12 hours, cooled and the solvent removed by distillation to give approximately 8g of N-formyl intermediate. Yes, that's the same kind of intermediate that one gets from the Leuckart reaction, and this recipe is going to employ the $LiAlH_4$ way of stripping the double bonded oxygen of the formyl side group to give methamphetamine. The 8g of formyl intermediate is dissolved in 50mL ether and added dropwise into a solution of 6g $LiAlH_4$ in 100mL ether and refluxed 4 hours. The solution is allowed to cool, 50mL dH_2O is added, the solution vacuum filtered then extracted with 3N HCl . The MDMA/meth freebase is liberated from the acid with NaOH extracted with DCM and removed of solvent to give ~8g.

METHOD #2: [89]--1M MDA or benzedrine and 1M benzaldehyde is dissolved in 95% ethanol (Everclear), stirred, the solvent removed by distillation then the oil vacuum distilled to give 95% yellow oil which is a Schiff base intermediate. 1M of this intermediate, plus 1M Iodomethane, is sealed in a pipe bomb that's dumped in boiling water for 5 hours giving an orangy-red heavy oil. The oil is taken up in methanol, 1/8 its volume of dH_2O is added and the solution refluxed for 30 minutes. Next, an equal volume of water is added and the whole solution boiled openly until no more odor of benzaldehyde is detected (smells like almond extract). The solution is acidified with acetic acid, washed with ether (discard ether), the MDMA or meth freebase liberated with NaOH and extracted with ether to afford a yield of 90% for meth and 65% for MDMA. That's not a bad conversion but what's with having to use benzaldehyde (a List chemical)? Strike wonders if another aldehyde can substitute.

METHOD #3: [90]--The folks in this article made an acetyl intermediate out of an amphetamine to act as a form of protection group so that they could screw around with the molecule without anything happening to that precious amine group. This method will end up yielding MDEA or PEA and will use the very watched acetic anhydride. This method is only for the weird. 80mL acetic anhydride is added to a solution of 10g MDA freebase, 50g sodium acetate and 300mL dH_2O, which is then shaken until the exothermic reaction ceases. The cooled solution is filtered and extracted with ether to give n-acetyl-MDA, which can be stripped of its oxygen with $LiAlH_4$ just like was done in the Leuckart method.

ADVANCED SHRIMP PREPARATION TECHNOLOGY

Strike has been very disappointed in the lack of responses regarding the shrimp recipes from the last edition. Only two people contacted Strike saying they had tried them. Naturally it was the best food they had ever had. Strike can't understand what was wrong. Was it a problem with translation for the Europeans (hint: 'shrimp' in European is 'prawn', possibly 'langoustine')? Was it that all of you can't afford shrimp? Can't cook? If you can't cook then this book is of no use to you.

Actually, the problem is clear. If all of you would stop taking amphetamines you would regain your fucking appetites! Here's the recipes for when you get out of detox.

Shrimp Diablo

Jumbo shrimp
Jalapeno peppers (seeded and halved)
Bacon strips (blanched 1 min in boiling water)
Teriyaki sauce

-Cut the blanched bacon strips in half. Place one jalapeno half against 1 shrimp, wrap with a bacon piece and secure with a toothpick. Place all of the shrimp 'brochettes' into a bowl and marinated at least 30 minutes covered with teriyaki sauce. Broil 5 minutes and serve. Yum!

Shrimp ala Strike

Jumbo shrimp
Thinly sliced prosciuto or pancetta
Gruyere cheese

-Cut the cheese into french fries-sized pieces, place one piece

with a shrimp and wrap with a slice of prosciuto. Broil this for five minutes and serve as is or with a dipping sauce of butter and lemon. Double yum!!

The following is the tastiest shrimp dish ever! It is complex. But the reward is heaven.

Shrimp Acapulco

Jumbo shrimp
Beef sirloin or tenderloin, cut into 1" pieces
1/3 cup peanut oil
2 tablespoons soy sauce
the juice of 3-4 limes (or lemons)

1 large shallot, minced
2 sticks unsalted butter, cut into tiny pieces and put in freezer
½ tablespoon vinegar
1-2 ounces Grande Marnier (or any orange-flavored liqueur)
1-2 tablespoons of crushed pineapple with juice (canned is fine)
½ tablespoon soy sauce

Alternate beef and shrimp on skewers. Mix the peanut oil, soy sauce and lime juice in a bowl to use a basting sauce. On a nice, hot coal or wood grill, cook the k-bobs until medium rare (or to taste) brushing them often with the basting liquid. Put aside and keep warm.

In a skillet or shallow sauce pan heat 1 tablespoon butter, the vinegar and the orange liqueur, add the shallots and saute them lightly for about a minute or until soft. Now the tough part. You're going to make a tricky butter sauce. Luckily for you, Strike is a trained professional chef (true!). You're gonna take the butter pieces out of the freezer and grab a whisk. Now, while the pan and its contents are still warm (but NOT too hot) start adding the butter piece by piece while whisking vigorously. Keep moving the pan off and on the heat source so that enough heat gets through to melt the butter and warm the sauce. But not so much heat as to cause the butter to break.

After all the butter has been whisked in the sauce will be creamy and warm. If pools of clear butter oil have started pooling up all over the place the sauce has broken. You failed. Actually, the sauce will still taste fine, it just won't be creamy like a snooty Frenchman would like. The sauce can be kept warm over a hot water bath or by stirring over low heat. Anyway, at this point one stirs in the soy sauce and pineapple into the sauce and drapes it over the k-bobs. Oh God is it the best flavor in the world. You have been warned!

RHODIUM'S CHAPTER

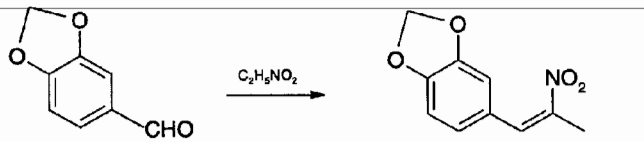
[This is a chapter written entirely by a chemist named Rhodium (with guest speaker Osmium!). Rhodium is, as far as Strike is concerned, the world's leading underground scientist. Knowledgeable in nearly every aspect of drug chemistry, this chemist has been the savior for many a person that was lost. Here he has contributed some new reactions for your reading pleasure. Radical stuff that you can bet will become the next wave of synthesis protocol. The rest of this chapter is Rhodium's voice.]

Syntheses for Total Synthesis II

by Rhodium 980620

Preparation of 3,4-methylenedioxyphenyl-2-nitropropene (from piperonal)

In Pihkal, Alexander Shulgin mentions that the preparation of MDP-nitropropene can be carried out in cold methanol with aqueous sodium hydroxide as the base. In fact, this method is even more reliable, and gives higher yields than the other method advocated by the dear doctor in his book.



Piperonal MD-Phenyl-2-Nitropropene

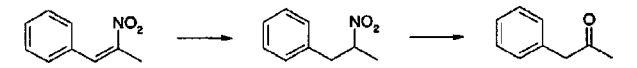
15g of piperonal was dissolved in 40ml of methanol under stirring in a 250ml Erlenmeyer flask. When all of the piperonal had dissolved, 7.1g nitroethane was added to the solution. The flask was put in a ice/salt-bath with magnetic stirring, and when the temperature of the solution had dropped to 0°C, an ice-cold solution of 4g of NaOH in 20ml dH_2O was added at such a rate that temperature never rose above 10°C. A white precipitate formed at the bottom of the flask during this addition, which was broken up with a glass rod. The stirring was continued for another hour, while the temperature of the solution was never allowed to rise above 5°C, and at the end of this time, 100 ml of ice-cold dH_2O was added to the solution, which caused even more precipitation of white solid. The whole slurry was poured into 100 ml of ice-cold 2M HCl solution in a 500ml Erlenmeyer flask, which was gently swirled, and there was a slight bubbling and fizzing, with the color of the solution shifting from white to blue to green to yellow in under a minute. Quite spectacular! When the fizzing had subsided, the solution was once again placed in an ice-bath with magnetic stirring. When the temperature had dropped to about 5°C, the solution was clear with yellow granules of crude product at the bottom. The granules were filtered with suction, and recrystallized from IPA. After air-drying, the canary-yellow crystals amounted to a yield of 65-70% of theory.

This nitropropene should be used within a week, or stored in the cold, as the color fades to a slight orange over a couple of weeks in room temperature, which is a sign of decomposition.

Ref: A.T. Shulgin, Pihkal, #100,
A.I. Vogel, Practical Organic Chemistry, 5th Ed.

Preparation of Phenyl-2-Propanone (P2P)

In this preparation, phenyl-2-nitropropene is reduced to phenyl-2-nitropropane with sodium borohydride in methanol, followed by hydrolysis of the nitro group with hydrogen peroxide and potassium carbonate, a variety of the Nef reaction. The preparation is a one-pot synthesis, without isolation of the intermediate.



Phenyl-2-Nitropropene Phenyl-2-Nitropropane Phenyl-2-Propanone

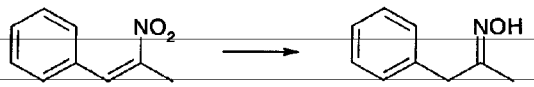
Efforts directed to prepare MDP2P via this method results in good yields of a ketone with properties completely dissimilar to MDP2P, and is probably the propiophenone, formed by migration of the nitro group during the hydrolysis.

16.3g (0.1 mole) phenyl-2-nitropropene was dissolved in 200ml methanol in a 250ml Erlenmeyer flask situated on a magnetic stirrer, and chilled to 0oC with an ice/salt bath. Then, with good stirring, 7.6g (0.2 mole) of $NaBH_4$ was added a little at the time, and the temperature was not allowed to rise above 15°C. When the generation of heat had subsided, the ice/salt-bath was removed and the solution was stirred at room temperature for two hours. At the end of this period, the flask was once again placed in an ice/salt bath and the solution was allowed to cool to 0°C again. 100 ml of 30% H_2O_2 was then added, together with 30 grams of anhydrous potassium carbonate, and the solution was left to stir for 18-24 hours at room temp. During the addition of H_2O_2/K_2CO_3 a white, sticky precipitate forms, which can be a bit too thick for a weak magnetic stirrer to handle, so the mass can be stirred with a glass rod now and then during the first two hours, after which the precipitate will be much looser and no match for any mag-stirrer. The next day, the solution is slowly acidified with 2M HCl with good stirring, care being taken for the evolution of heat and CO_2. About 300 ml of acid is needed. When the pH of the solution turned acid, the color became significantly more yellow, but the acidity was confirmed with pH paper. All of the precipitate was also be gone at this point. The solution was extracted with 3x100ml CH_2Cl_2, and the pooled organic extracts washed with 100ml 2M NaOH and 200ml H_2O. The organic phase was dried over $MgSO_4$, filtered with suction, and the solvent removed under vacuum to give a clear yellow oil. After distillation of said oil at aspirator vacuum, the yield was around 60-70% of phenyl-2-propanone (P2P) as a light yellow oil.

Ref: R. Ballini, Synthesis 723-726 (1994)

Preparation of Phenyl-2-Propanone oxime

Internal nitroalkenes can be reduced to the corresponding ketoximes by $SnCl_2$. The second method is a modification of the first, also allowing terminal nitroalkenes (such as nitrostyrenes) to be reduced to aldoximes. The oximes, in turn, can either be reduced to the corresponding amines, or cleaved to form the carbonyl compound.



Phenyl-2-Nitropropene Phenyl-2-Propanone Oxime

Method 1

A sodium stannite solution was prepared by addition of aqueous sodium hydroxide (2.5 mol, 100g) to aqueous stannous chloride (0.25 mol, 56g). The initially formed precipitate redissolved to form a clear solution. This solution was gradually added to a solution of 16.3g (0.1 mol) phenyl-2-nitropropene in THF at room temperature. A slightly exothermic reaction ensued, and the reaction mixture was stirred for 30 min, a saturated sodium chloride solution was added, and the solution was extracted with ether and the pooled extracts were evaporated under vacuum to give essentially pure P2P oxime in 80% yield.

Ref: G. Kabalka, Tet Lett 26(49) 6011-6014 (1985)

Method 2

16.3g (0.1 mol) Phenyl-2-nitropropene and 45g (0.2 mol) of stannous chloride dihydrate ($SnCl_2$*2H2O) was dissolved under stirring in 200ml ethyl acetate in a 250ml beaker, and the slightly exo-

thermic reaction was allowed to run its course. When the reaction mixture again had cooled to room temperature, it was poured on 200g of an ice/water mix, and was made slightly basic (pH 7-8) with 5% $NaHCO_3$. The product was extracted into ether, washed with a saturated NaCl solution, dried over Na_2SO_4 and the solvent removed under vacuum to give almost pure P2P oxime in 90-95% yield.

Ref: G. Kabalka, Synth Comm 18(7), 693-697 (1988)

Cleavage of Oximes The classic way of cleaving an oxime to the corresponding carbonyl compound is through acid hydrolysis, or an acid catalyzed exchange reaction with excess formaldehyde. This is a crude method, and has often non-satisfactory yields. Below is a very good alternative method, using sodium bisulfite. Alkaline H_2O_2 can also be used, as in Synth Comm 10(6), 465-468 (1980).

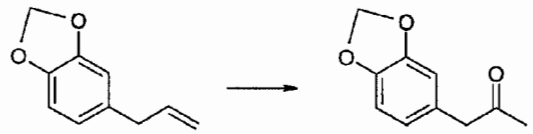
Phenyl-2-Propanone Oxime — Phenyl-2-Propanone

Oxime Cleavage with Sodium Bisulfite

14.9 grams of P2P oxime (0.1 mol) is dissolved in 150ml 50% alcohol and is refluxed with grams 36.4 grams (0.35 mol) sodium bisulfite for 6 hours, when the reaction had gone to completion. The ethanol was removed under vacuum, and the residue mixed with 25ml DCM and the mixture was treated with an excess of 2M HCl and stirred until two clear layers formed. The layers were separated, and the aqueous layer was extracted with 2x25 ml DCM, and the organic extracts were combined and the solvent evaporated to give a near quantitative yield of P2P, which, if it has an orangish tinge, can be vacuum distilled to yield a light yellow oil.

Preparation of MDP2P from safrole

Safrole can be oxidized to safrole epoxide with H_2O_2 in a two-phase system, using a quaternary phosphotungstic PTC. The formed safrole epoxide is then isomerized to MDP2P with LiI.



Safrole — MD-P2P

Preparation of the catalyst

A suspension of tungstic acid (2.50g, 10 mmol) in 7 ml of 30% aqueous H_2O_2 was stirred and heated to 60°C until a colorless solution was obtained. To this solution, filtered and cooled to room temperature, was added 40% w/v H_3PO_4 (0.62ml, ca 2.5 mmol), and the whole was diluted to 30 ml with water. To the resultant soluton, 2.09g of methyltrioctylammonium chloride (97% pure, equiuvalent to 2.027g, 5 mmol) in DCM (40 ml) was added dropwise with stirring over about 2 min. Stirring was continued for an additional 15 min. The organic phase was then separated, dried over Na_2SO_4, filtered, and gently evaporated on a rotary evaporated under reduced pressure at 40-50°C (bath) to give 3.70 g (98.4%, based on the quaternary ammonium salt charged) of an almost colorless syrup.

Ref: C. Venturello, J. Org. Chem. 53, 1553-1557 (1988)

Oxidation of safrole to MDP2P

In a 100ml three-necked, round-bottomed flask equipped with mechanical stirrer, thermometer and a reflux condenser, a vigorously stirred mixture of the above catalyst (0.7g, 0.31 mmol), safrole (13.24g, 80mmol), benzene (35 ml) and 40% w/v H_2O_2 (5.10ml, 60

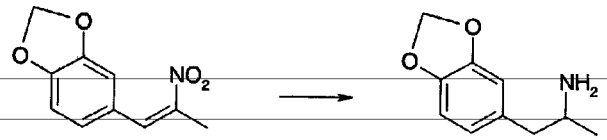
mmol) was heated to 60°C and kept at this temperature for 60 min (External cooling is needed!). The mixture was cooled to room temp, the organic phase was separated and diluted with 30 ml Et_2O. In order to remove the catalyst, the organic solution was first stirred with a solution of Na_2CO_3 (0.75g) and Na_2SO_3 (0.75g) in water (10 ml) for a few minutes, then separated, dried over Na_2SO_4 and passed through a short column (2.5 cm diam) of silica gel (50g), and ~300ml anhydrous Et_2O was passed through the column to ensure complete elution of the products. The solvent was evaporated and the residue dissolved in 18 ml of tetraglyme and treated with anhydrous LiI (0.130g, 0.97 mmol) at 130□C for 5h. After cooling, the products were distilled under vacuum, recovering 5.17 grams safrole (saved for the next run) and collecting 6.25 grams of MDP2P.

Ref: C. Venturello, US Pat 4,731,482

C. Venturello, Synthesis, 1229-1231 (1992)

Reduction of nitroalkenes to primary amines

$NaBH_4$ in methanol, catalyzed by nickel boride, can be used to reduce nitroalkenes to aminoalkanes in about 70% yields in 15 min at room temp. The nickel boride is prepared in situ from $NiCl_2*6H_2O$ (nickel chloride hexahydrate) and $NaBH_4$. The method is general, and can be applied to many conjugated nitroalkenes. Other novel promising methods are catalytic transfer hydrogenation with Pd/C (Tet Lett 29(45), 5733-5734 (1988)), $NaBH_4$ in methanol, followed by Al/Hg (Tet Lett, 1317-1320 (1977)), $NaBH_4$ and $CuSO_4$ (Synlett 419-420 (1990)), and finally $NaBH_4$ and trimethylsilylchloride in THF (Angew Chem Int Ed Engl 28, 218-220 (1989))



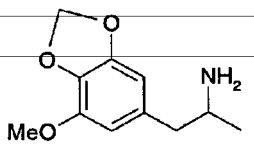
MD-Phenyl-2-Nitropropene MDA

Reduction with $NaBH_4/NiCl_2$

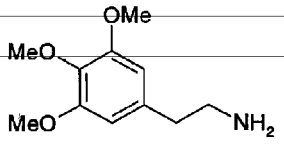
3.68 grams $NiCl_2*6H_2O$ (15.5 mmol) was dissolved in 300 ml MeOH, and 1.76g $NaBH_4$ (46.5 mmol) was added portionwise (Caution, frothing!) with stirring to the wonderfully light green solution, and the solution immediately turned black and hydrogen was evolved. The solution was left to stir at room temp for 30 minutes, and 5.0 grams (31 mmol) phenyl-2-nitropropene was added all at once, followed by 4.1 grams $NaBH_4$ in small portions over a period of 5 minutes, care being taken for the frothing. After 15 minutes, the reaction mixture was filtered through celite to remove the boride and the filter cake was washed with 50 ml MeOH. The solvent was removed under vacuum, and the residue taken up in 100ml dilute H_2SO_4, washed with 3x25 ml CH_2Cl_2, basified with 25% NaOH, and extracted with 3x50 ml CH_2Cl_2. The pooled extracts were dried over $MgSO_4$, filtered and the solvent was evaporated in vacuum, the residue dissolved in a little IPA, and 37% HCl was added until acid. The solution was then diluted with diethyl ether until turbid, and left in the freezer until all product had precipitated. The white crystals of amphetamine hydrochloride was filtered off and air dried. MDA can be produced in exactly the same fashion, just use 6.4 grams of 3,4-methylenedioxyphenyl-2-nitropropene instead of the phenyl-2-nitropropene.

Ref: Osby & Ganem, Tet Lett 26(52), 6413-6416 (1985

Proposed Synthesis of MMDA and Mescaline
by Rhodium and Osmium 980519



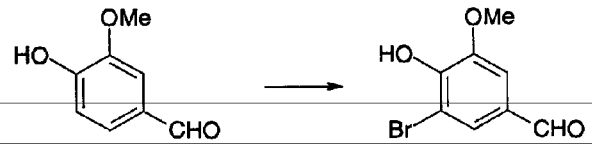
MMDA



Mescaline

[Rhodium's voice:]

The synthesis of MMDA in Pihkal is one of the longest and most tedious in the book. If one is going the route via myristicin, the Sisifos work of isolating the tiny amount of essential oil present in nutmeg, followed by fractional distillation to purify the myristicin fraction is also added to the labor of the poor chemist. Therefore I propose a new route to this "essential amphetamine".



Vanillin 5-Bromovanillin

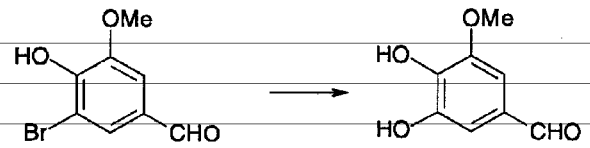
5-Bromovanillin

To a stirred, cooled (0°C) solution of 152.15g (1.0 mol) of vanillin in 1000ml of methanol was added during 20 min 176.0g (1.1 mol) of bromine at such a rate that the temperature was kept below 20°C. The mixture was stirred at room temperature for 1h, cooled to 0°C, and treated during 30 min with 500 ml of cold (5°C) water. Stirring was continued for 15 min and the product was collected by filtration. It was washed with water (4x500 ml), then with 500 ml of

cold (0°C), 70% methanol, and dried in vacuo at 50°C overnight to give 218.5 grams (95%) of 5-bromovanillin as pale yellow crystals, mp 163-164°C.

5-Bromovanillin (alternative) [2]

To vanillin (15.2g, 0.1 mol) in glacial acetic acid (75 ml) is added bromine (17.6g, 0.11 mol). After stirring for 1h, the reaction mixture is diluted with ice/water (200ml), the precipitated solid is filtered, washed with water, and dried to give 5-bromovanillin, yield 22.0g (95%)

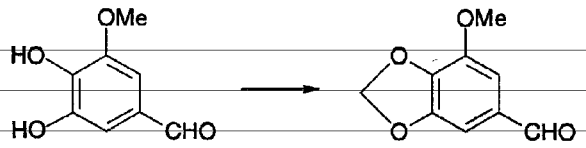


5-Bromovanillin 5-Hydroxyvanillin

5-Hydroxyvanillin [3]

Sodium hydroxide, 61.2 grams (1.53 mol), was dissolved in 750 ml of water in a 2000ml round-bottomed flask. To the still-warm solution was added 50.0g (0.217 mol) of 5-bromovanillin and 0.5 g of Cu powder. A white solid precipitated. The reaction mixture was refluxed vigorously under N_2 and with magnetic stirring. The color changed gradually from yellow to green to dark green and, after ca 6 hours, all solid material was dissolved. After 27 hours of refluxing, the reaction was over, and the solution was acidified with 113ml conc HCl to pH ~2, and was extracted*) with ether (or other suitable organic solvent), and precipitated as the bisulfite adduct through shaking the organic phase with an excess of saturated aqueous sodium bisulfite. The adduct was washed sparingly with cold water, and dissolved in an excess of 10% sodium carbonate solution to release the aldehyde again. The solution was extracted with DCM and evaporated to yield the title compound.

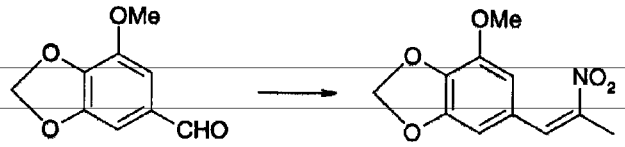
*) [Osmium's voice: In the original patent a continuous, 27 hours extraction with hot toluene was used. This is very impractical. I recommend the following: after extraction and removal of the extraction solvent, dissolve the crude product in 400 - 450 ml hot toluene, put that solution in a beaker and cool it for at least 2 hours in an ice bath. Filter the precipitated product, wash with about 100 ml ice-cold toluene and dry at 70°C or in a desiccator to constant weight. Mp. 132.5-134.0°C.]



5-Hydroxyvanillin Myristicinaldehyde

Myristicinaldehyde [4, 5]

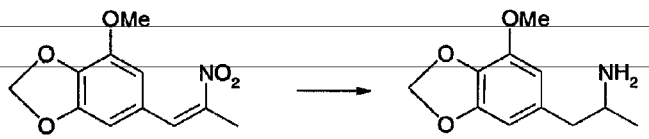
58g KF (0.5 mol) was shaken together with a solution of 16.8g (0.1 mol) 5-hydroxyvanillin in 300ml DMF and the solution warmed up a bit. 19.1g (0.11 mol) of methylene bromide (or 9.35g methylene chloride) was added to the cooled solution, and the mixture was heated to 110-120°C for 1.5 hours. The cooled reaction mixture was then separated by ether extraction followed by washing the ethereal extracts with water to remove DMF and with cold 10% Na_2CO_3. Drying and evaporation followed by recrystallization from hexane afforded myristicinaldehyde in high yields (mp 133-134°C).



Myristicinaldehyde 2-Nitro-isomyristicin

2-Nitro-isomyristicin [6]

A solution of 9.8 grams myristicinaldehyde in 35 ml glacial acetic acid was treated with 5.3 ml nitroethane and 3.2 grams of anhydrous ammonium acetate, and heated on the steam bath for 1.5h. It was removed, treated with H_2O with good stirring, to just short of turbidity, seeded with product nitropropene, and allowed to come slowly to room temperature. The bright yellow solids that formed were removed by filtration, washed with a small amount of aqueous acetic acid, and sucked as free of solvent as possible. After recrystallization from 60ml boiling EtOH, gave, after filtering and air drying, 5.1 grams of 2-nitro-isomyristicin as light yellow solids with a mp of 109-110°C.



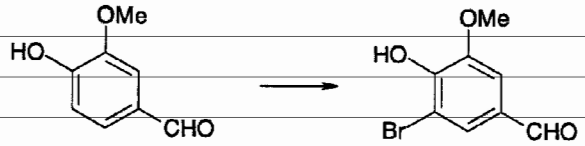
2-Nitro-isomyristicin MMDA

MMDA [6]

A suspension of 7.5 grams LAH in 500ml anhydrous Et_2O was magnetically stirred, and heated in an inert atmosphere to a gentle reflux. The condensing Et_2O leached out a total of 9.8 g 2-nitro-

isomyristicin from a Soxhlet thimble in a shunted reflux condenser. This, in effect, added the nitropropene to the reaction medium as a warm saturated Et_2O solution. When the addition was complete, the solution were refluxed for an additional 5 hours, then the solution was cooled, and the excess hydride destroyed by the addition of 400 ml of 0.75M H_2SO_4. The phases were separated and sufficient saturated aqueous Na_2CO_3 was added to the aqueous phase to bring the pH up to about 6.0. This was heated to 80°C and filtered through a coarse sintered glass funnel to remove some insoluble fines. The clear filtrate was brought up almost to a boil, and treated with a solution of 10.2 grams of 90% picric acid in 110 ml of boiling EtOH. Crystals of the picrate formed immediately at the edges, and as the reaction flask was cooled in an ice tub, the entire reaction set to a yellow mass of crystals. These were removed by filtration, washed sparingly with 80% EtOH, and air dried to give 14.0 grams of the picrate salt of MMDA, with a mp of 182-184°C. This salt was treated with 30 ml 5% NaOH, and the red solution decanted from some insolubles. Additional H_2O and NaOH effectively dissolved everything, and the resulting basic aqueous phase was extracted with 3x50ml CH_2Cl_2. The pooled extracts were stripped of solvent under vacuum, and the residue dissolved in 200ml Et_2O saturated with HCl gas. There was a heavy precipitation of white crystals, which were removed by filtration, Et_2O washed and air dried to give 6.37 grams of MMDA HCl, with a mp of 190-191°C.

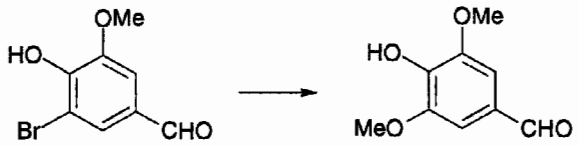
[Osmium's voice:]



Vanillin 5-Bromovanillin

5-Bromovanillin: (another alternative) [3]

A 2-l. 3-necked flask, equipped with a mechanical stirrer, thermometer and 500 ml dropping funnel was charged with 115.7g (0.722 mol, 37.4 ml) Br_2. In the meantime, a soln. of 100 g (0.658 mol) of vanillin in 705 g (470 ml) of 48% HBr was prepared in the dropping funnel. While the reaction flask was immersed in an ice bath, the soln. of vanillin was dropped into the bromine with stirring over a period of 1 hr., keeping the temperature at about 5°C. The bromovanillin precipitated as light yellow crystals. The slurry was stirred for an additional hour in the ice bath, diluted with 940 ml of water and kept for 1 hr. 0-5°C with stirring. The crystals were collected on a sintered glass funnel and washed thoroughly with a total of 1000 ml of water. The material was dried at room temperature to constant weight. Yield: 150.9 g (99.4%), m.p. 163-164°C, VPC purity 98%.



5-Bromovanillin Syringaldehyde

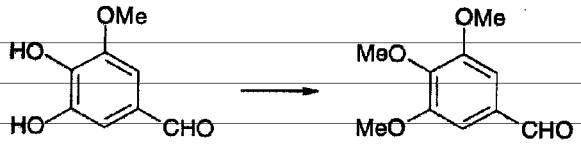
Syringaldehyde: (3,5-dimethoxy-4-hydroxybenzaldehyde): [7]

5-bromovanilline (5mmol) is refluxed with EtOAc (3mmol) and CuBr (1mmol) in 5 M NaOMe/MeOH (10 ml) for 14 hours. Classical work-up (addition of water and acidification followed by extraction of the phenol) leads to pure syringaldehyde (95%). When starting from the more soluble 5-bromovanilline dimethyl acetal, reaction is achieved within 2 hours (yield 98%). Preparation of this acetal is probably not worth the extra work. Substituting EtONa for MeONa seems to work, too, producing 2-ethoxy-3-OH-4-methoxybenzaldehyde, useful for ethoxy-derivatives of Mescaline.

The above synthesis, although performed on a small scale, is easily scaled up to industrial size (French Pat. 2,669,922, CA 118; P6734u). It is a general procedure for substituting aryl-Br with -OMe or -OEt, giving us the possibility to produce other compounds from already known substances, e.g bromination of MDA yields 6-Br-MDA. This is converted by the above procedure to MMDA-2, #133, active at 25-50mg, 8-12 hrs.

Asaronealdehyde (2,4,5-trimethoxy-benzaldehyde) can be produced in the following way: Methylate resorcinol. Product is 1,3-di-MeO-benzene. Do a Vilsmeyer aldehyde synthesis with $POCl_3$/N-methylformanilide to obtain 2,4-di-MeO-benzaldehyde. Brominate and treat as described above to obtain asaronaldehyde.

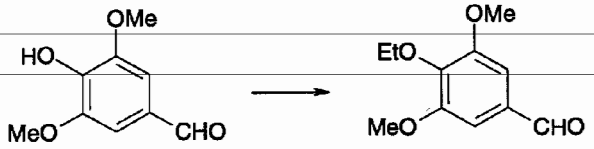
Syringaldehyde is easily methylated or ethylated with the known procedures in high yields forming the highly-desirable 3,4,5-trimethoxybenzaldehyde or the 3,5-di-MeO-4-EtO-benzaldehyde (Escaline, #72, 40-60 mg, 8-12 hrs.).



5-Hydroxyvanillin 3,4,5-Trimethoxybenzaldehyde

3,4,5-Trimethoxybenzaldehyde [3] from 5-hydroxyvanillin:

Into a 1-l. round-bottomed flask equipped with a magnetic stirrer and a reflux condenser were placed: 50 g (0.298 mol) 5-hydroxyvanillin, 500 ml acetone, 91.0 g (0.716 mol) dimethylsulfate, 100 g (0.806 mol) finely ground $Na_2CO_3.H_2O$, 10 ml of 10% KOH in methanol. Of course equimolar amounts of anhydrous Na_2CO_3 or K_2CO_3 can be used. The heterogenous mixture was stirred under vigorous reflux for 24 hours, after which the reflux condenser was replaced with a descending condenser. The solvent was distilled at a bath temp. of ca. 100° until the distillation ceased. To the solid residue was added 400 ml of water and the heterogenous mixture was stirred VIGOROUSLY for 2 hours at room temperature followed by one hour at 0-5° (ice-cooling). The light brown crystals were filtered by suction, washed with 3*150 ml of ice water and air dried to constant weight. Yield 55.1g (94%), m.p. 72.5-74°. After distillation at 0.5mm/130°, there was obtained a 90% yield of 3,4,5-trimethoxybenzaldehyde, m.p. 73.5-75, VPC purity 99.3%. (This distillation is probably unnecessary, because the aldehyde is already quite pure).



Syringaldehyde

3,5-Dimethoxy-
4-ethoxybenzaldehyde

3,5-Dimethoxy-4-ethoxybenzaldehyde [8] from syringaldehyde:

A well-stirred suspension of 21.9 g syringaldehyde in 45 mL H_2O was heated to reflux in a heating mantle. There was then added a solution of 15 g NaOH in 60 mL H_2O. The heating and stirring was continued until the generated solids redissolved. Over a period of 10 min, there was added 23 g diethyl sulfate, then refluxing was continued for 1 h. Four additional portions each of 5 g diethyl sulfate and of 6 mL 20% NaOH were alternately added to the boiling solution over the course of 2 h. The cooled reaction mixture was extracted with Et_2O, the extracts pooled and dried over anhydrous $MgSO_4$, decolorized with Norite, and stripped of solvent. The crude 3,5-dimethoxy-4-ethoxy-benzaldehyde weighed 21.8 g and melted at 51-52°C.

See the same reference in Pihkal for details on how to use ethyl iodide instead of diethyl sulfate.

[1] Syn Comm 20(17), 2659-2666 (1990)
[2] Synthesis, 308 (1983)
[3] US Pat 3,855,306
[4] Tet Lett 38, 3361-3364 (1976)
[5] JACS 99(2), 498-504 (1977)
[6] Pihkal, #132 (p. 787)

[7] Tetrahedron Letters, Vol. 34, No. 6, pp.1007-1010, (1993)
[8] Pihkal, #72 Online - Pihkal can be found at http://www.hyperreal.org/drugs/pihkal/

PROMISING THEORETICAL METHODS

Strike and others' favorite pastime is to comb the library for new methods. Even though we have so many proven, high-yielding methods available (see this entire book), there is always room for more. Relentlessness drives us to find even cheaper, higher yielding methods. But the biggest reason is to make a buffer zone of so many options that governmental restriction is rendered useless. That is our power. So many committed, dangerously-intelligent people around the world with far more motivation than any bureaucratic agency will ever hope to have.

You're not going to find journal articles with new syntheses written especially for X or speed anymore. The scientists of the world already have recipes that work and the access to the restricted chemicals necessary to make them work. So why should they look for anything new? They don't. There is no reason for them to do so.

But we have many reasons. That is why the people of the underground are actually progressing the fields of carbonyl, amine and amphetamine science. Believe it or not, the novel applications of journal methods on precursors such as ours are on equal par with published research work. Half of the stuff in this book is publishable, proper science done by people with no funding. It is actually amazing when you think about it.

So like Strike was saying, without any new, direct literature synthesis of amphetamines, we are forced to take ideas from work on molecules that are similar to our own. Often molecules that one would not think have any relationship at all.

For molecules similar to safrole or allylbenzene we take the work done on any terminal alkene such as 1-heptene, 1 octene. Another term to look for is 'olefin' which is a term for a doublebond containing species. What we then look for are articles about these olefins where the functional groups we are looking for are formed. Articles with terminology like 'methyl ketones from' (P2P), 'ketones from', 'amines from' etc. Or when we want to see about new ways to aminate a ketone (make final product from P2P) we look for any article about ketones where amines are formed. Sound like science fiction to you? Well, how do you think we came up with half the recipes in this book!? It works!

Every article such as these may have the potential to be useful. But it takes a lot of looking, a keen eye and a sense for what is real. The contributions in this section are just that (real). These have gone through the right channels and are contributed by the same chemists that brought you the rest of this book. These are considered to have the greatest potential and are here for your consideration to use in legal research of your choice. Be warned, though. The chemistry here is a little hairy and, for the sake of time and Strike's sanity, is not explained as simply as the other recipes in this book.

SEMI-DIRECT AMINATION OF SAFROLE

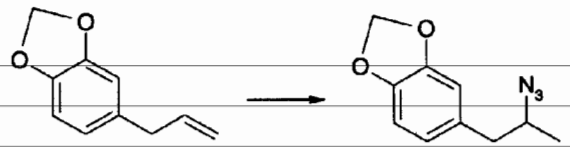
The dream of every X chemist is to get that amine function directly on the safrole molecule without having to go thru any intermediate such as the ketone of MD-P2P or the bromine of bromosafrole. But Strike can tell you right now that that is very, very tough (that is why there ain't no methods for it). About the only article Strike has ever found for the actual placement of an amine directly on a terminal alkene (a.k.a. safrole) is the following [79]:

"***Amination of propylene:*** *The conversion of ammonia and propylene to isopropylamine and diisopropylamine was shown to take place over a sodium catalyst at ca. 250°C and 850-1000 atm pressure (ref. 7). In contrast, we have found that these reagents*

can react in the presence of cesium amide containing catalysts, under far milder reaction conditions to give mostly isopropylamine. In a specific example, NH_3 (112 mmol) and C_3H_6 (142 mmol) were reacted in a reactor of 40 cm^3 total capacity containing $CsNH_2$ (18.5 mmol) and $NaNH_2$ (6.4 mmol), for 17.5 hours at 139°C. Isopropylamine (13 mmol), n-propylamine (0.7 mmol) as well as propane (2 mmol) and non-condensible gasses (0.8 mmol) were produced."

Man, that recipe is WEAK! But hey! That's 10% final product in one pot. Yeesh! Why bother? Don't take this first method seriously folks. It was just Strike's way of illustrating the futility of easy answers. All the rest of the stuff in this section is much, much better.

So without direct amination we are confined to 'semi-direct' amination (Strike's terminology). In Strike's opinion, the direct addition of an azide (N_3) counts. Once on the beta carbon, that azide is as good as an amine. But can we get an azide directly onto safrole without having to go thru the bromosafrole intermediate as was discussed earlier? Maybe we can!



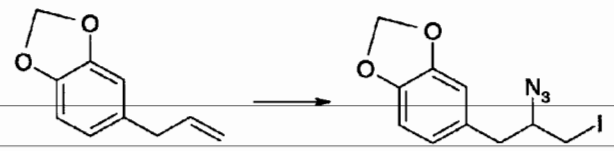
Safrole Safrole-Azide

This following article was sent to Strike by Osmium and Feck (are they the same person?). It involves the direct addition of azide to a terminal alkene (you-know-who) by the *in situ* production of the reactant mercury (II) azide from mercuric acetate and sodium azide (please don't ask) [80].

"General Procedure - To a solution of 0.3 moles of sodium azide and 0.1 mole of mercuric acetate in 200mL of 50% aqueous tetra-

hydrofuran is added 0.1 mol of alkene. After stirring at 50 to 90°C for an appropriate period (17-24 h), the two-phase mixture is diluted with 100 ml of 15% aqueous potassium hydroxide and treated with a solution of 2 g sodium borohydride in 100 ml of 15% potassium hydroxide solution. The alkyl azide is isolated by ether extraction followed by distillation at reduced pressure."(% yield for the representative terminal alkenes 1-heptene and 1-octene were 88% and 55% respectively)

That looks simple and direct don't it?! If safrole was used as the alkene one would get safrole-azide as product. Just one teensy little reduction away from MDA. Strike also found some azide papers that, with a little work, will get safrole-azide in a totally different way. Strike came across a lot of work where groups were using dinucleophilic addition to get an azide and a halogen added across a double bond. The azide would always go to the 'beta' secondary carbon and the halogen to the primary carbon (just what one would want if safrole was the substrate).



Safrole 3,4-Methylenedioxyphenyl -2-azido-3-iodopropane

The first was from a CA article [81]. Various alkenes, styrene and cycloalkenes were tried. But a more followable method is the following [82]. The 'supported salt' of NaN_3-Al_2O_3 was made by mixing the NaN_3 with the alumina in water then evaporating the mixture under vacuum in a water bath until dry:

"Reaction with I_2 (1.5 mmol) [or Br_2], *supported salt (1.5 mmol), alkene (0.625 mmol), in 5 ml of ethanol-free $CHCl_3$ at room tem-*

perature for 30-48 h. Work up with aq. $Na_2S_2O_3$ wash, CH_2Cl_2 extraction, drying ($MgSO_4$) and solvent evaporation."

So, theoretically, one would have a safrole with an azide in the right place and a halogen sticking out the end. So what?! Well, Strike was thinking that since the easiest Grignard reagent to make is the one at a primary carbon (which the I or Br will be in this species), one could just make the Grignard reagent out of the intermediate then destroy it by pouring water into the solution which would immediately remove the halogen. Just a thought.

The next method Strike has for semi-direct amination is really weird. Strike is really exposing Strike's ignorance of chemistry with this dog. But if one looks hard at the articles cited, the potential is there. The authors came up with this little procedure that produced vicinal diamines out of alkenes [83]. Later they found that if they did a couple of things different, they would end up with a 'monoamine' with the majority product being at the 'beta' carbon. The following is a conjoining of the two paper's experimentals:

"*The addition of N-bromosuccinimide (1.1equiv) to a dichloromethane solution containing the alkene (1 equiv) and cyanamide (4 equiv). The solution was maintained at room temperature (3 days) and then washed with water, dried, and concentrated in vacuo. Treatment of the bromocyanamide* [intermediate] *with 1% palladium on charcoal in methanol (1h) led to reduction of the formadine. Addition of base to the reaction mixture (50% aqueous KOH, reflux 6h) followed by extraction with ether gave monoamine.*" (Yield is 48-64% final amine from alkenes analogous to safrole)

PHENYLACETONES

Our trusted friend Osmium has been stressing this following recipe as a breakthrough P2P synthesis for speed from a very unlikely precursor. It is apparently a novel rearrangement of a

thoroughly unwatched chemical called 2-phenylpropanal (a.k.a. methyl-phenyl-acetaldehyde, a.k.a. hydratropic aldehyde). Osmium was kind enough to translate the German article from which it comes [87]. The following is all Osmium's translations and comments:

2-Phenylpropanal P2P

"*With H2SO4:*

9g 2-phenylpropanal (called Methyl-phenyl-acetaldehyd in the ref) are added during 40 minutes to 40ml conc. $H2SO_4$ which is cooled to –16°C. Let react for further 15 mins at –15°C. The mixture is poured on ice. An oily liquid and a gummy/rubbery/sticky mess are evident. All is extracted with ether and distilled (91-96°C/11 torr). Yield: 5.6g P2P (62%).

With HgCl2:

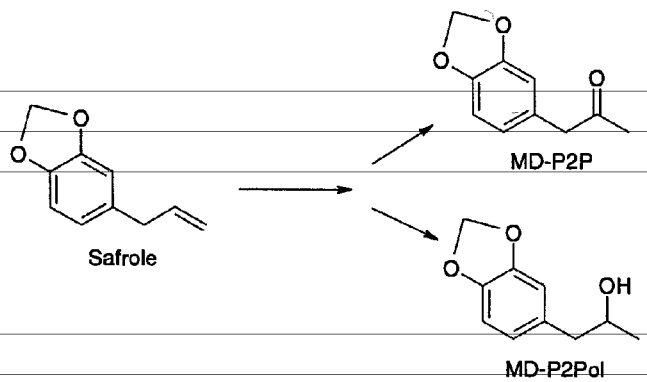
3g 2-phenylpropanal are heated with a solution of $HgCl_2$ (6g, equimolar amount) in 45ml 75% EtOH in a sealed glass container for 4.5 hours. Temp 100°C. A precipitate is formed, which dissolves in the following steam-distillation. The oily layer resulting from this steam-distillation is separated and fractionated. Yield more than 80%.

They isolated their products after conversion into the solid semicarbazone, which included recrystallizations (more losses). This and the fact that they distilled those tiny amounts make me believe that yield will be even higher (at least with the $HgCl_2$ route).

I also found a patent dealing with phenylpropanal rearrangement:

USPat. 4,694,107 They react 2-phenylpropanal in the gas phase at 300-400°C with zeolithes (silicate) to yield 86% P2P. Quite hot, yes, but otherwise not too difficult, I think."

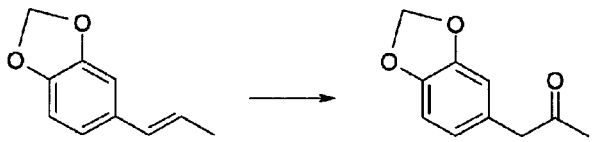
Strike found this next thing doing an all-nighter Chemical Abstracts search. Strike does not even want to try to explain it. Just read it. If you understand it, great! If not, don't sweat it. Hell if Strike will ever try the damn thing [88] (Note the P2Pol production):



*"113: 151836e **Preparation of ketones by oxidation of olefins using cobalt diketone catalysts.** Mukoyama, Mitsuaki: Isayama, Shigeru: Kato, Koji: Inoki, Satoru: Yamada, Toru: Takai, Toshiniro (Mitsui Petrochemical Industries, Ltd.) **Jpn. Kokai Tokkyo Koho JP** 02,121,944 [90,121,944] (Cl. C07C49/04) 09 May 1990, Appl. 88/272,450, 28 Oct 1988; 19pp. $R^1COCH_2R^2$ and $R^1CH_2COR^2$ [I ; R^1 = (un)substituted (cyclo)alkyl or aryl(alkyl); R^2 = H, (un)substituted, alkyl or aryl(alkyl)] are prepd. By reaction of $R^1CH:CHR^2$ with O-contg. Gas in the presence of a secondary alc. And a Co (II) catalyst [II; R^3, R^5, R^6, R^8 = H, straight-chain, branched or cyclic C1-10 alkyl, (un)substituted aryl or $CONH_2$, etc.; R^4, R^7 = H, alkyl, halo, CO_2H, alkoxycarbonyl: excluding R^3 =*

R^5 = R^6 = R^8 = CF_3 and R^4 = R^7 = H]. II may be prepd. By reaction of diketone ligands $R^3COCHR^4COR^5$ with $CoCl_2$ in the presence of KOH in H_2O. Thus, 2 mmol $PhCH_2CH_2CH:CH_2$ was oxidized 2 h at 76° and atom O in the presence of 20 mol% II (R^3 = R^5 = R^6 = R^8 = tert-Bu, R^4 = R^7 = H) in 10 mL Me_2CHOH to give 29% $PhCH_2CH_2COMe$ and 71% $PhCH_2CH_2CH(OH)Me$. Addnl. 39 catalysts were evaluated for the above oxidn. And 18 other olefins were oxidized; alcs. were obtained as byproducts."

This next method for making P2Ps was posted anonymously on the a.d.c. quite awhile ago. Strike is sure most everyone knows who did this, but Strike doesn't to this day. So whoever you are---Thanks! Although Strike has an original paper copy of this post, Strike had no copy on disc. So Strike snagged the text from an archived example saved on Rhodium's home page. So if you want to see more about this method go and visit the site where it rests among many other chemical goodies.



"Subject: Phenyl acetones by electrolytic oxidation
From: "guest" <guest@webshack-cafe.com>
Date: 1997/11/08

Appendix - Phenyl acetones by electrolytic oxidation. Process for 3,4-dimethoxyphenyl-acetone preparation. European Patent Application 0247526, Filed: 02.12.87; to LARK S.p.a. Milan.

Example 1.

6.27 g of NaBr is dissolved in 25 ml of H_2O and 125 ml of CH_3CN, the mixture is then strongly stirred by means of magnetic stirring, and to it 3.76 g of isoeugenol-methylether (I) is then added. The obtained mixture is then electrolysed in a 250-ml not-partitioned electro chemical cell, with a constant current of 850 mA, with two graphite anodes with a total surface of about 17 cm2, and a central stainless-steel cathode having a surface of about 25 cm^2 being used, with a distance between electrodes of about 1 cm. 5,200 Coulombs are passed, with the reaction mixture being kept at a temperature of 20° C. From the reaction mixture, discharged from the electrochemical cell, two phases, i.e., the aqueous phase, containing Br- ions, and the organic phase, containing acetonitrile and the reaction product, are separated. From the organic phase acetonitrile is evaporated off under reduced pressure, and to the resulting reaction product 40 ml of ethyl acetate is added. The gas-chromatographic analysis of the organic phase shows the presence of epoxide (II) with a >90% purity.

The reaction mixture in ethyl acetate is then transferred to a 100-ml reactor, purged under a nitrogen atmosphere, 340 mg of LiI is added, and the whole mass is then heated, with mechanical stirring, on an oil bath, up to ethyl acetate reflux temperature. The heating is continued for 5 hours, until the disappearance of the epoxide (II), as evidenced by the thin-layer chromatography.

The reaction product is cooled to room temperature, is washed with 10 ml of H_2O to the purpose of removing lithium iodide and is then dehydrated over Na_2SO_4. 3.57 g is obtained of dimethoxy-phenylacetone (III), as determined by gas-chromatographic analysis with an inner standard of 4,4'-dimethoxybenzophenone. The yield of ketone (III) relative to the olefin (I) used as the starting material is of 87.1%.

Example 2

Example 1 is repeated in exactly the same way, with the exception that in the isomerization step 250 mg of LiBr instead of 340 mg of LiI is used, and that the reaction time results to be of 10 hours,

instead of 5 hours. In this way, a yield of ketone (III) of 86% relatively to the olefin (I) used as the starting material is obtained.

Example 3

To a 250-ml not-partitioned electro chemical cell, 125 ml of CH_3CN, 25 ml of H_2O, 6.47 g of NaBr and 2.78 g of isoeugenol-methylether (I) is added. The mixture is electrolysed at a constant current of 350 mA, with a titanium anode coated with a mixed Ru-Ti oxide (50:50 by weight), with a total surface of about 7 cm^2, and a central stainless-steel cathode having a surface of about 15 cm2 being used, with a distance between electrodes of about 1 cm. Through the cell 4,000 Coulombs are passed, with the reaction mixture being kept at the temperature of 20° C. The reaction mixture is then processed according to such modalities as reported in Example 1, until the solution of the reaction product in ethylacetate is obtained; to such solution, 337 mg of LiI is added. The mixture is then refluxed (at ethyl acetate refluxing temperature) for 5 hours, and the process is continued as described in Example 1, until 2.795g is obtained of ketone (III), with a yield of 92.2% relatively to the olefin (I) used as the starting material.

Example 4

To a 250-ml not-partitioned electrochemical cell, 125 ml of CH_3CN, 25 ml of H_2O, 6.40 g of NaBr and 2.675 g of isoeugenol-methylether (I) is added. The mixture, kept at 20° C, is electrolysed, with the same constant current density and the same set of electrodes as of Example 1 being used, through the cell 3,625 Coulombs, equalling 2.5 Faradays/mol, being passed. The reaction mixture is then transferred to a rotary evaporator, for CH_3CN tobe stripped under vacuum. The resulting reaction product is then extracted three times with 30 ml of ethyl acetate, and is then dried over Na_2SO_4. The organic extract, concentrated to a volume of 25 ml, and with 160 mg of added LiI, is refluxed (at ethyl acetate refluxing temperature) for 6 hours. The process is continued as described in Example 1, and 2.54 g is obtained of ketone (III), with a yield of 86.5% relatively to the olefin (I) used as the starting material.

Example 5

To a 250-ml not-partitioned electrochemical cell, 135 ml of CH_3CN, 15 ml ofH_2O, 6.20 g of NaBr and 2.82 g of olefin (I) is added.The mixture, kept at 20° C, is electrolysed by using the same electrodes as of Example 1, but with a constant current density of 1.7 A being used,until through the cell 4,000 Coulombs have been passed. The reaction mixture is then processed as described in Example 4.2.56 g is obtained of ketone (III), with a yield of 83.2%, as computed relatively to the olefin (I) used as the starting material.

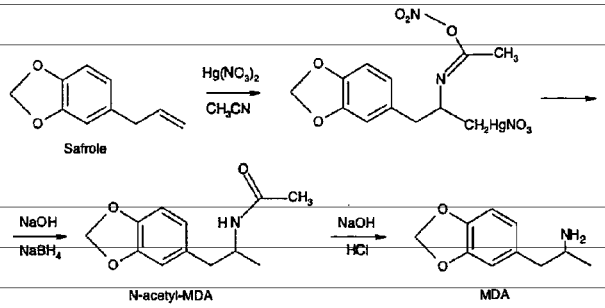
Examples 6-9

To a 250-ml not-partitioned electrochemical cell, 100 ml of DMF, 50 ml of H_2O, 6.72 g of NaBr and 4.25 g of isoeugenol-methylether (I) is charged.The mixture is then electrolysed under the same conditions, and by using the same set of electrodes as used in Example 1, with a total of 5,670 Coulombs being passed. At reaction end, the mixture is discharged, to it 250 ml is added of 20% aqueous NaCl solution, and it is then extracted four times with 50 ml of ethyl acetate. The extract is washed twice with 50 ml of 20% aqueous NaCl solution, and is then dried.The organic extract is concentrated to a volume of 100 ml by the solvent being evaporated off. On three aliquots, of 20 ml each, of said extract, the isomerization reactions are carried out at the ethyl acetate reflux temperature, by using the same lithium salts and reaction times as shown in Table 1. From the fourth aliquot of 20 ml of above said extract, ethyl acetate is evaporated off and replaced with the same amount of acetonitrile.The isomerization of the reaction product is then carried out at acetonitrile refluxing temperature, with the lithium salt and the reaction time being used as shown in Table 1(Table not shown)."

STUFF THAT DEFIES CLASSIFICATION

These last three theoretical methods have no real kinship to any of the major categories or precursors. The first is the one that has caused Strike more despair than any other. It was once a Top Ten recipe in the first edition. But it was a reckless gamble on Strike's part and Strike paid for it. Here is what Strike wrote last year...

If you read the excellent book called "Recreational Drugs" by Professor Buzz [8] you may come across a little recipe in the amphetamine section for something called N-acetyl-phenethylamine. So what the hell is that? Well, actually it happens to be one step away from being an amphetamine but no one makes this clear to all the novices reading the book. Strike means to say that even novices just reading for pleasure need a little help here and there. It's a pity because this is a really good recipe using unwatched chemicals and is a more direct way of aminating safrole or allylbenzene without having to go through the making of an intermediate such as MD-P2P or P2P. Actually, Strike is under the distinct impression that Professor Buzz got this recipe from the progenitor of underground chemistry books: "Psychedelic Chemistry" by Michael Valentine Smith. Unfortunately, both these authors simply copied commentary from the actual scientific article [91] without any elaboration towards the final outcome.



This is almost a one-pot production and uses a simpler borohydride catalyst ($NaBH_4$) than others that are out there. These catalysts are very clean in their action yet very gentle on the molecule as a whole. Before this method is started, there is one bit of preparatory work that needs to be done by the evil underground chemist. The method calls for the use of anhydrous mercuric nitrate ($Hg(NO_3)_2$) but the only commercially available form is a monohydrate (has one molecule of water attached, bubba!). So the chemist buys (or makes) the white, crystalline monohydrate. Next, if the chemist feels she is going to get really attached to this method then she's going to want to invest in a little toaster oven that she will never, ever put food in again. This toaster is placed in the hood or in the backyard because any possibility of vaporized Hg would be bad. In a beaker or mom's Pyrex meatloaf dish is weighed 100g of $Hg(NO_3)_2.H_2O$ then the beaker is placed in the toaster oven which is set at approximately 220°F and remains there for about an hour. The beaker is cooled and reweighed. If the stuff is 5% lighter (95g) then the water is gone. The mercuric nitrate is then ground up with a spoon (spoon thrown away) and used right away because if it sits around its going to gain water from the air.

To do the reaction the chemist places a flask in an ice bath on top of the stirplate and into it is added 100mL acetonitrile (CH_3CN) and 65g anhydrous mercuric nitrate. A small separatory funnel that has 33g of safrole or 24g allylbenzene is placed over the flask so that everything looks just like that of fig. 9. The safrole is then slowly dripped in so that the temperature stays between 20-28°C. A yellow precipitate will form as the mercuric nitrate latches on to the safrole. After the addition is finished, the ice bath is removed and the solution stirred at room temperature for 1 hour.

After 1 hour 200mL of 3M NaOH is slowly poured in followed by 200mL of 0.5M $NaBH_4$ in 3M NaOH (a stock solution of this is made by mixing 120g of NaOH into enough water to make an even 1000mL, then 19g of $NaBH_4$ is mixed in). At first things will grey then blacken slightly as elemental mercury is released and starts to fall to the bottom of the flask, and the droplets of product oil will appear. The solution is stirred for 1 hour and a slight

amount of heat can be applied to hasten the reaction. After 1 hour, 200mL saturated NaCl solution is stirred in, the whole thing extracted twice with 50mL of ether and the ether removed by simple distillation to afford the intermediate 'N-acetyl-MDA' or 'N-acetyl-amphetamine'. Phooey!

This happy acetyl intermediate is just one hydrolysis away from being MDA or benzedrine. By hydrolysis Strike means that by using simple acid or base one can chop off that acetyl group that is stuck to the nitrogen and replace it with a hydrogen thus giving the chemist her final freebase. Hydrolysis is going to show up a lot in this book so lets discuss the two ways to do it. To that acetyl oil sitting alone in the bottom of the flask is added either 500mL of 15% aqueous HCl solution (HCl in water, bubba!) or 500mL of 20% aqueous NaOH with 100mL ethanol and the solution refluxed for 5 hours. MDA is now in the pot. If the chemist hydrolyzed with HCl then she basifies the solution with concentrated NaOH solution until the pH is 9 and all the little droplets of freebase oil have been released. She then extracts the oil with either benzene, ether or DCM (chemists choice), dries the solvent through Na_2SO_4 and distills away the solvent to get product. If NaOH was used to hydrolyze then solution is cooled, extracted with ether, dried and distilled to give product. Either way the yield is ~80%.

The method Strike just described was an extension of an earlier published report [92] in which things were produced a little differently but bear description here because it has applicability as an alternative for those unwilling or unable to do the previous, unbelievably easy process. Besides, it's good to see how science progresses.

The acetonitrile and mercuric nitrate amounts remain the same except they are to be accompanied by 12.6g of fuming nitric acid (see chemicals section) in the reaction flask. Then, with cooling, the safrole or allylbenzene is added just like before. The reaction is immediate and takes no more than 20 minutes of stirring after which 100mL ice cold dH_2O is slowly added. Next, with vigorous stirring, saturated sodium chloride solution is slowly added until a pronounced precipitate forms. This yellowish mass is the chloride,

not hydrochloride, of the acetamino-safrole intermediate (don't ask). The chemist wants to keep these crystals so the solution is vacuum filtrated and the filter cake washed with a little clean dH_2O. 40g of the filter cake is scrapped into a flask containing 160mL dH_2O, 14 mL 6M NaOH and 0.4M of 2% sodium amalgam (a catalyst, see chemicals section) and the solution stirred for 3 hours. Again, the precipitate will grey and elemental mercury will fall to the bottom of the flask. After 3 hours the solution is decanted into a filter (the mercury stays behind in the flask), and the flask with mercury is washed with 100mL ether which is also decanted into the afore mentioned filter. The ether drips through the filter cake then the filter is washed through once more with 100mL fresh ether. Both ether washings are combined and distilled to give N-acetyl-MDA which can be hydrolyzed in the same manner as before.

The acetyl intermediate formed by the reaction is another species that one could use $LiAlH_4$ on to strip the oxygen rather that hydrolyze [26, 27]. To reduce the intermediate one can use the exact method as was used in the Leuckart reaction or one can substitute tetrahydrofuran (THF) in place of ether as the solvent. In using THF the reflux goes for 24 hours instead of 4. After refluxing and cooling, 50mL dH_2O in 100mL THF is added, then 50mL 15% NaOH, and finally 100mL more dH_2O forming a white precipitate. The solution is vacuum filtered, the filter cake washed with 50mL THF and both the filtrate (the liquid stuff) and the THF washing are combined and removed by vacuum distillation to give freebase MDEA (~80-85%).

Yeesh! That was what Strike wrote last year. And the sad truth is that it did not work! The reason why is the way Strike proposed getting 'anhydrous' mercuric nitrate. The baking of commercially available mercuric nitrate monohydrate was actually destroying most of the compound. Aside of that this recipe works! It really does.

So what can be done about the mercuric nitrate problem? The authors in the original paper from which this recipe came from, clearly call for an amount of mercuric nitrate that is exactly equal

to an anhydrous form. Had they used the available monohydrate they would have used an increased amount of the salt to compensate for the added water in order to get an exact molar ratio. But the article just don't read that way! Strike, nor anyone Strike has talked to, has any clue on how to make anhydrous mercuric nitrate. Does that make this method impossible?

Surely one would hope not. What if one just used the mercuric nitrate monohydrate that is at hand. One's only real concern would be if the monohydrate water would interfere with the acetonitrile in a competing oxymercuration reaction. But could it really considering the massive excess of acetonitrile present? All Strike can say is that someone, somewhere is gonna try it. And Strike would really, really like to hear about it.

The next weirdo method is a contribution by Ritter. This one is Ritter's combo contribution whereby she gives all of you a novel synthesis for making the valuable nitroethane (this is also included in the **Chemicals** section). Then Ritter gives you something to think about by hypothesizing how this nitromethane synthesis can be applied in a similar manner to make a beta-Nitropropane (*not* propene) from bromosafrole. From there one can reduce using methods Strike isn't even gonna get into here!

**Ref: JACS 79, 2507 (1957)*

Tetrahedron Vol 46. No.21 pp7443-57, 1990

Nitro Compounds

By Ritter

Nitroethane and 1-(3,4 methylenedioxy) 2- nitropropane This method of producing the above mentioned nitro compounds is by far the best Ritter has come across yet. The problem with standard nitroethane synthesis is that the -NO_2 source most commonly used is silver nitrite (al la Merck Index citing). Needless to say, this is going to be an expensive compound to make as it is not available commercially but must be synthesized from costly silver nitrate. The other methods mentioned in Vogels 5th masterpiece

which use DMSO and sodium nitrite produce low yields of the desired product because other nitrous compounds that are formed compete with formation of the desired product. This improvement prevents those unwanted nitrous compounds from ever forming leaving you with a 80% or higher yield of the desired nitro compound. In the case of 1-(3,4 methylenedioxy) 2- nitropropane existing methods for its production in the literature usually start with the nitropropene and reduce it to the desired nitropropane which can be easily reduced to the desired amine. There is no need to try to make this intermediate nitropropene which uses watched chemicals (piperonal and nitroethane) anymore. Bromosafrole will react in the following synthesis to yield 80% or greater of the 2-nitro compound which can be reduced a bazillion different ways to MDA.

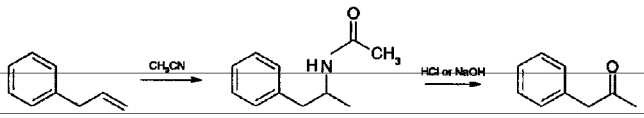
Now the goodies: Nitroethane

Ethyl bromide 32g, 26.0 ml (.3mol) or Ethyl iodide 46g, 24ml (.3mol) is poured into a solution of 250 ml Dimethylsulfoxide (DMSO) or N,N Dimethylformamide or N-methylpyrolidone (DMSO preferred), 36 grams sodium nitrite (that's $NaNO_2$ pyromaniacs, not sodium nitrate) and 52 grams phloroglucinol dihydrate. This stuff is expensive but it can be recycled. Stopper all this in a flask with a good magnetic stirring bar and stir it in a room temp. water bath for 2 hours or until an emulsion forms. At this point dump all into 600ml ice water and extract w/ two portions of 200ml methylene chloride. The $MeCl_2$ extracts are washed w/water three times then dried w/ anhydrous magnesium sulfate then evaporated off in a fractional distillation setup, collecting the fraction that boils at 113-116'C at atmospheric pressure as pure nitroethane. Expected yield about 20 grams. That's not a ton of product but this reaction can be scaled to any size you can dream of and yields will stay in the 80% range.

Synth for: 1-(3,4 methylenedioxy) 2- nitropropane

This compound is made the exact same way as above only .3 mol (72 grams) bromosafrole is substituted for the bromoethane. Some extra DMSO may need to be added to facilitate stirring. Except for this the reaction proceeds as stated above. When the reaction is completed and MeCl2 extracts are evaporated, the raw product is suitable for reduction, no vacuum distillation is needed to purify the nitro compound. Just subject it to one of the many reductions out there that will reduce an aliphatic nitro group (note this is NOT a nitroalkene). Al/(Hg) in IPA should work fine. There are also many exotic $NaBH_4$/transition metal salt combinations that will easily reduce the nitro group, not to mention straight catalytic hydrogenation. One mistake not to make would be to try a dissolving metal reduction such as tin/HCl. The boiling acid will destroy the methylenedioxy bridge and leave you with a frustrating mess of tar. Also don't forget to check out the new Ammonium Formate Catalytic Hydrogen Transfer Reduction detailed in Synthesis Feb. 1988, pp 91-95.

The last recipe deserves to be last: The Ritter Reaction [not affiliated with the above Ritter]....



Allylbenzene N-acetyl-Amphetamine Amphetamine

This method was designed to produce an acetyl intermediate just like that in the failed recipe a few paragraphs above using only sulfuric acid and acetonitrile [93]. This reaction works, in theory, in a so-so manner on allylbenzene but not on safrole. This method will not make X for many reasons. So why does underground literature and DEA forensic scientists keep claiming that it does? Strike doesn't know either. Let's see what the man who invented this, Dr. Ritter, had to say back in 1952: "several attempts to obtain amides from...safrol (sic) were fruitless."[94]. What makes all these people think that this will work unless no one did their homework. This is another sore spot of Strike's and

now Strike is going to bitch for one entire paragraph and will then rejoin you for the recipe at the beginning of the subsequent paragraph.

Concentrated sulfuric acid, which is called for in this experiment, will break the ether bonds of methylenedioxy ring structure on safrole. This allows the resultant phenols to dimerize and polymerize with other injured safrole molecules. If one included this with the natural protic destruction that H_2SO_4 is going to cause on the rest of the molecule then this method becomes very untenable for X. Another contention Strike has is with the idea that cyanide procedures meant as a Ritter reaction nitrile source for the conversion of tertiary alcohols and t-butyl primary alcohols [95] will work on a straight-up allylbenzene as has been suggested. This, in fact, does not work well at all on both allylbenzene and safrole. Let say, for example, that there was a group of 'scientists' that, upon the suggestions from certain sources, invested in some expensive and elaborate equipment to safely perform the Ritter reaction using cyanide (a way that supposedly produces higher yields than acetonitrile). Let's suppose that both allylbenzene and safrole were tried with not one active compound being produced. Next, let's suppose that these scientists were so pissed off that they had every oil fraction from the beginning of the procedure to the very end analyzed by mass spectrometer and found that all one ends up with is crap, crap, crap, and some unreacted precursor. Maybe someone has a way to use these cyanide procedures that work. But as far as Strike is concerned, they are not worth the hassle and/or risk.

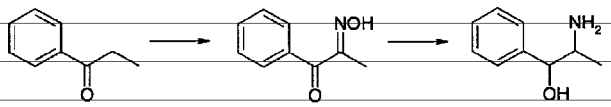
Hey, Strike is back. Anyway, the only people this procedure is going to help are those interested in speed, and the only applicable version is going to be the one using acetonitrile. It's pretty simple though, and the chemicals needed are very basic. 59g allylbenzene in 200mL acetonitrile is stirred in an ice bath to a temperature of 10°C then 270mL H_2SO_4 is slowly dripped in so that the temperature remains at around 10°C. An alternative to this would be to mix the acetonitrile and H_2SO_4 together and then drip the allylbenzene in. Either way, after addition is complete, the ice bath is removed to allow the temperature to rise. The temperature

will rise slowly to around 50°C, then start to rapidly climb towards 80°C. Most methods give the impression that this solution is going to stop getting hotter at 80°C, but it won't. At around 60-70°C the chemist should plunge the reaction flask back into the ice bath. If the chemist does not keep this in mind then the reaction will go super-critical and the chemist will have a horrible sulfuric acid vapor cloud in the house. The reaction color progresses from a light orange to black after the temperature rise. The reaction mix is poured into 400mL ice cold 15% NaOH solution in a PP container. If more NaOH is needed to make the solution basic then so be it. The N-acetyl-amphetamine is removed by extracting with ether then removing the solvent, or by decanting the oil which will form a layer on top. The oil, dirty as it is, is hydrolyzed with 15% HCL for 10 hours just as was done above and in the Leuckart reaction. The freebase isolated in the same way.

OUR FIRST EVER EPHEDRINE SECTION!

Why did it take Strike so long to get with the program? Because Strike does not do speed and Strike has never worked on ephedrine. But for some crazy reason there are a few people out there that do. Since Strike has nothing to say about it, Strike bows to the superior knowledge of those that do.

Naturally there are a trillion reduction methods for ephedrine, pseudoephedrine and phenylpropanolamine to final product. These methods have been used and abused ad nauseam. So as to not tread on the banal work of yesterday's chemist, the advanced underground chemists associated with this book are here to give you the next cutting edge methods for your reading pleasure. Osmium emailed Strike the journal references. She and others discovered them Strike believes. The first recipe here is a nifty little way to actually make phenylpropanolamine from the very safe propiophenone [96-98]. The intermediate made from propiophenone is called isonitrosopropiophenone. It is then subsequently reduced with palladium. Although Strike would imagine that a zillion different reducing agents could be employed:

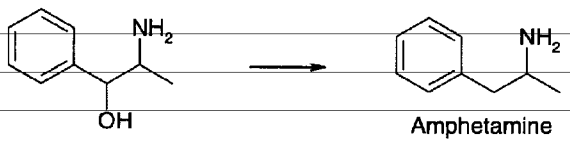


Propiophenone Isonitrosopropiophenone Phenylpropanolamine

"***Isonitrosopropiophenone*** *was prepared from propiophenone and butyl nitrite. Slater[11] used methyl nitrite, a gas: butyl nitrite, a liquid, was found more convenient. In a 1-liter 3-necked, round-bottomed flask, fitted with stirrer, reflux and delivery tube for hydrogen chloride, was placed a solution of 80 g. of propiophenone (0.6 mol) in 400 cc. of ether; hydrogen chloride gas was passed through the stirred solution at the rate of 2-3 bubbles per second, stirring and addition of acid being continued throughout the reaction; then freshly distilled butyl nitrite, b.p. 75-81°, was added through the reflux condenser in 2-3 cc. portions until a total of 61.8 g. (0.6 mol) was added. After addition of the first portion the reaction mixture slowly became a yellow-brown and after several more minutes a light yellow color, after which a second portion was added; now the color change took place more rapidly, whereupon a third portion was added, etc. The mixture gradually warmed up and the ether began to reflux gently. The total time required for the addition of the nitrite was about ninety minutes. Stirring and bubbling of hydrogen chloride were continued for another fifteen minutes and the mixture then was allowed to stand overnight, during which time it became quite dark. The next day the ethereal solution was slowly stirred into dilute sodium hydroxide containing pieces of ice and the ethereal layer was repeatedly extracted with cold alkali until no more product was obtained. The alkaline extracts were slowly stirred into concentrated hydrochloric acid containing sufficient ice to keep the reaction mixture cold. In this manner white crystals of isonitrosopropiophenone were obtained: these were recrystallized from toluene and melted at 106.0-106.5°; [21] yield, 71 g., or 72.5% of the theoretical. When treated with hydroxylamine (hydrochloride) in alkaline solution for several hours it formed, on acidifying, a voluminous precipitate which was recrystallized from alcohol and melted at 230.5-231.0°.*

Phenylpropanolamine. - *With catalyst prepared as previously described[13] from 0.5g of palladium chloride and 3g of charcoal, it was possible to reduce two portions of 9.8g of isonitrosopropiophenone (0.06 mol), dissolved in 150 cc. of absolute alcohol containing 7.0g of hydrogen chloride, to phenylpropanolamine in from 145 - 190 minutes with yields of the isolated chloride from 9.4g to 11.0g, or 84 to 98% of the theoretical. After recrystallization from absolute alcohol the salt melted at 191°. The free base was obtained by treating an aqueous solution of the hydrochloride with alkali; on cooling, the liberated amino alcohol solidified and after recrystallization from water melted at 103°."*

With Phenylpropanolamine at hand (or ephedrine and pseudo-ephedrine) one would next need to reduce that alpha carbon OH group to get the final amine. Strike understands that the current favorite methods for doing this involve lithium and amine, HI and red P or other iodine related protocols. So when you meth heads ruin every aspect of those methods as well, what will you do then? The following are a couple of OH reduction methods (Strike thinks) that have applicable use [99-100].



Phenylpropanolamine Amphetamine

"**Direct Borohydride Reduction of Alcohols to Alkanes with Phosphonium Anhydride Activation:** *N-Propylbenzene.: To a solution of 5.56 g (20 mmol) of triphenylphosphine oxide in 30mL of dry methylene chloride at 0°C was added dropwise a solution of 1.57 mL (10 mmol) of triflic anhydride in 30mL of dry methylene chloride. After 15 min when the precipitate appeared, a solution of 1.36g (10 mmol) of 3-phenyl-1-propanol in 10 mL of dry methylene chloride was added and the precipitate vanished in 5 min. An amount of 1.5g (40 mmol) of sodium borohydride was added as a solid all at once and the slurry was stirred at room temperature for*

4.5 h. The mixture was washed twice with 1N HCl [may want to skip the HCl or wash with ~5% NaOH afterwards when using this on an amine such as PPA etc.] *and then water and brine, dried over $MgSO_4$, and passed thru a short plug of silica to remove triphenylphosphine oxide. Evaporation afforded 1.07g (89%) of phenylpropane as a colorless liquid.*"

Second method:

"***Me_3SiCl - NaI - CH_3CN as an Efficient and Practical Reducing Agent for Benzylic Alcohols.*** *A typical procedure for the present reduction is as follows: To a mixture of Me_3SiCl (1.54 ml, 12 mmol), NaI (1.8 g, 12 mmol), and acetonitrile (0.6 ml, 12 mmol) was added a solution of 1-phenylethanol (244 mg, 2 mmol) in hexane (2 ml). The mixture was stirred for 24 h at room temperature. Dilution with water, extraction with ether and subsequent isolation process gave ethylbenzene (158 mg) with sufficient purity in 75% yield.*"

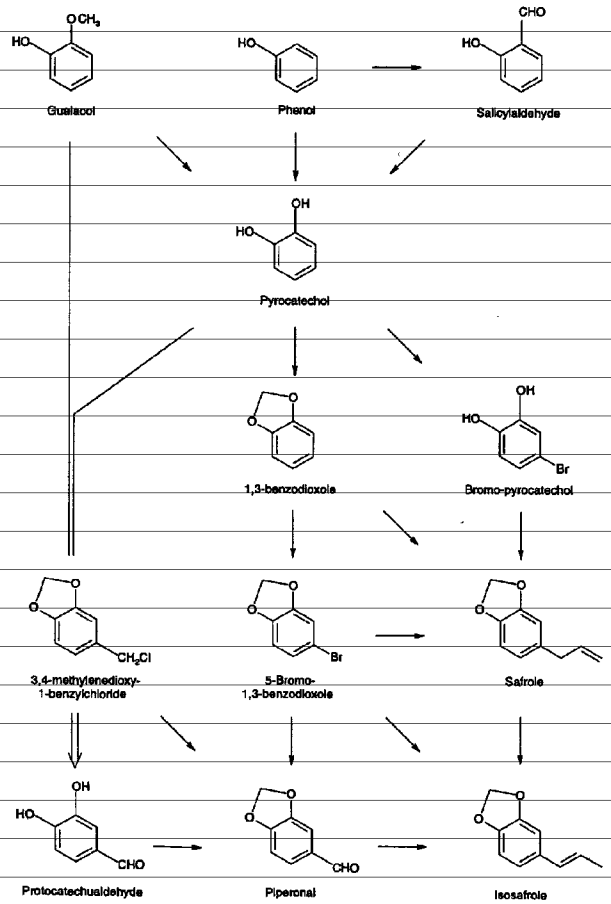
Wow! Strike ought to consider taking up speed as a second habit. Those reductions looked freaking easy!

BUILD FROM SCRATCH

The methods in this book have thus far been presented under the assumption that precursors such as safrole, sassafras oil, benzaldehyde etc. are still available. We know that safrole, isosafrole, piperonal, ephedrine, P2P and the like are currently schedule I controlled substances. Strike has no doubt that natural oils such as sassafras and nutmeg are going to eventually be banned as well. In anticipation of such an outcome, Strike is going to launch a preliminary strike against it. The following is the culmination of a lot of research on how to build X and meth precursors essentially from scratch. In fact, there are so many ways to do this that a whole other book could be written on the subject and still not cover the merest fraction of possibilities. So Strike has narrowed things down to the most direct methods which produce the greatest yields using the least restrictive chemicals and procedures. In some instances the science may be a little squirrelly, but one should keep in mind that, as far as Strike knows, all of the following procedures are legal to perform except for those that actually end up making the precursor. The next drawing shows the general pathway of synthesis that Strike is talking about.

Speed manufacturers need only look at the molecules and imagine them without those extra OHs or methylenedioxy ring structures attached to the benzene core. These particular pathways are, however, more uniquely suited for X precursor production because they take advantage of the hindrance that methylenedioxy ring structures and OHs provide on one side of the benzene core. This helps to better assure that mono chloromethylations or brominations will occur whereas di- and tri-substitutions are possible on a naked benzene molecule which speed chemists are going to be using (please don't ask).

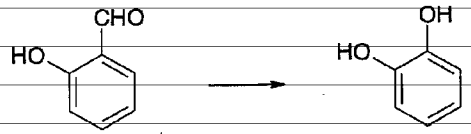
It would be pretty pathetic if one had to start the synthesis of a complex molecule such as X from something like phenol but it can be done. However, since all of the intermediates listed here are legal, there is no excuse not to start as far up the ladder as



possible. This is especially true of pyrocatechol (a.k.a. catechol). One can get a ton of pyrocatechol and play with it ad nauseam. Using some of the techniques mentioned here, and others mentioned God-knows-where-else, just about anything can be done to these pre-precursors. An OH or methyl group can be added here. A methoxy group can be stropped away or added there. Brominations. Alkylations. Believe Strike, if you can imagine it then someone has already done it or the methodology is in place for it to be done.

And wouldn't you know it....someone already has. Without a doubt Strike is most proud of the new testimonials that have been placed in this section for this edition. Strike had little faith that someone would actually apply the (legal) recipes here from the first edition, but one person named Merlin did! Not only is Merlin the handsomest chemist around (seen a picture) but she/he has provided some experimentals for which every one of you ingrates will be thankful for years to come. Maybe not now. But someday soon.

PYROCATECHOL, GUAIACOL, PHENOL & SALICYLALDEHYDE

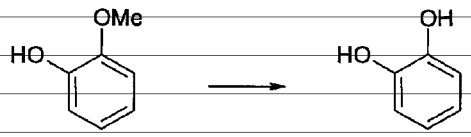


Salicylaldehyde Pyrocatechol

PYROCATECHOL FROM SALICYLALDEHYDE

METHOD #1: [101]--122g salicylaldehyde is stirred into 1L of 1N NaOH solution at room temperature then 1420g of 3% hydrogen peroxide solution (H_2O_2, the exact % solution one finds at the grocery store) is added. The solution darkens and the temperature rises to 45-50°C. An ice bath is applied if the temperature starts to rise above 50°C. The mixture then stands for 15-20 hours, neutralized to pH 7 with acetic acid and the solution vacuum distilled of all its water so that all of the stuff that remains in the flask is completely dry. 500mL toluene is poured into the flask and slowly heated to near boiling, all the while being stirred to break up the crystalline mass. The pyrocatechol will dissolve into the hot toluene but all of the crap and salts will not. The hot mix is vacuum filtered and the stuff in the filter cup can be washed with a little fresh hot toluene which is combined with the original filtrate. The toluene/pyrocatechol is allowed to cool causing the pyrocatechol to crystallize out; which can then be separated by filtration. The remaining toluene can be reduced in volume by distillation and allowed to cool again in order to afford a second crop of pyrocatechol. If desired the catechol crystals can be placed in fresh hot toluene and processed as before to give even cleaner product (yield=70%)

METHOD #2: [102]--Sodium bicarbonate and dH_2O are stirred in a 3-neck flask with two addition funnels attached. One funnel has salicylaldehyde and the other has concentrated H_2O_2 (at least 30%). Both salicylaldehyde and the H_2O_2 are dripped in simultaneously causing a vigorous reaction to occur and who's temperature needs to be kept at 48-55°C with external cooling for 30 minutes. After addition the solution stirs for 1 hour at 20°C to give a yield of catechol at 95%. Looks pretty good don't it?

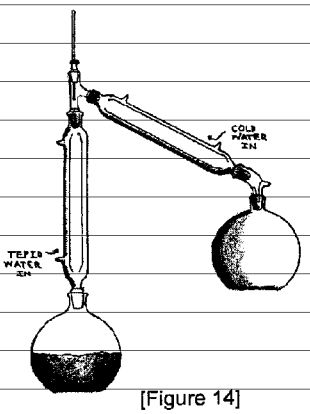


Guaiacol Pyrocatechol

PYROCATECHOL FROM GUAIACOL

METHOD #1: [101, 103]--Before a chemist attempts this procedure she should read both of the referenced articles to understand why Strike has included a hybrid apparatus like the one shown in figure 14.

Into the reaction flask is added 912g crystalline guaiacol and 1500g regular 48% HBr which is then slowly heated to reflux. The tepid water condenser is there to allow the bromomethane that is formed to leave the reaction flask but is still 'cold' enough to keep the other reactants in the reaction flask. The noxious bromoethane condenses in the cold water condenser and drips into the chilled methanol in the collection flask. This will keep this bromoethane trapped so that the chemist will not die



[Figure 14]

from breathing said gas. The reaction refluxes for 4 hours during which time the temperature that registers directly above the warm condenser should be about 95°C. When the temperature starts to climb beyond 95-97°C then it is time to stop the reaction. Some water and a little guaiacol will be lost during the reaction but that is ok because guaiacol is so cheap that the chemist couldn't care less. The reaction flask contents should take on a slightly pink color. The reaction mix is extracted hot with 2X 1L toluene and both the toluene and water layers saved. The toluene layer is distilled to remove any water that it may have absorbed and, upon cooling, will afford a crop pyrocatechol crystals which can be separated by vacuum filtration. Reduction of the toluene volume by distillation will afford a second crop of catechol.

That aqueous layer that was saved can be removed of most of its water by vacuum distillation, allowed to cool slightly then extracted with hot toluene. When the toluene cools, a few hundred more grams of catechol will crystallize out but will be contaminated with some heavy red bromo compounds. The crystals are filtered and vacuum distilled such that the pyrocatechol will distill over first, leaving the higher boiling bromo compounds behind. Yield is about 80% or 600g of catechol.

Technically, the chemist could avoid the complex glassware apparatus of this procedure for a more crude approach [104]. This report shows some dudes de-methylating an amphetamine with concentrated HCl in a pressure cooker. A similar approach with good yields was also employed in ref. 83 and should work as well or better on guaiacol. Hydroiodic acid or hydrobromic acid will work better than hydrochloric acid but, you know, whatever floats the chemist's boat. To do this the chemist can just plain reflux HI or HBr with the guaiacol for a few hours and process as before or she can use HI, HBr or HCl and place the reactants in a pipe bomb for a few hours.

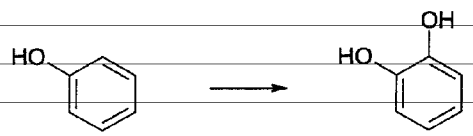
METHOD #2: [105 p725, 106-108]--This is super easy and uses aluminum chloride ($AlCl_3$) for which there are many uses in underground chemistry. The original reference is in German but the master here has translated it for you. There's something about

nuclear winter or body parts at the beginning of the article. Strike is not exactly sure. But later on comes the procedure.

The apparatus to use is the reflux apparatus with drying tube seen in fig. 7a. A tube needs to be led from the top of the apparatus to a water trap because HCl gas will be evolved. 50g of guaiacol is placed in the reaction flask and heated slightly to make it liquid. Then, with stirring, 50g of anhydrous $AlCl_3$ is gradually added causing a vigorous reaction to begin. When the addition is complete the reflux configuration is attached and placed into a 210°C oil bath atop the stirplate. After two hours of reflux, the flask is allowed to cool down which will cause the catechol to crystallize. It is a good idea to dilute this solution with some 0.5M HCl and then stir or shake the flask so as to break up the crystalline mass. Next, some toluene or benzene is poured into the flask and heated so that the catechol dissolves into the hot solvent. The solvent layer is separated, cooled and processed as usual to yield catechol (70%).

METHOD #3: [109]--1 part guaiacol and 2.5 parts Me_3SiSNa in 1,3-dimethyl-2-imidazoline heated at 185°C in a sealed pipe bomb gives 80-96% catechol.

METHOD #4: [110, 111] -- guaiacol and cupric perchlorate ($Cu(ClO_4)_2$)-ascorbic acid (that's vitamin C, bubba!) are mixed in an appropriate solvent under oxygen atmosphere in a flask to give about 30% catechol.



Phenol Pyrocatechol

PYROCATECHOL FROM PHENOL

There are a lot of bad conversion recipes for phenol and a few so-so ones. This doesn't matter because phenol is about as cheap and common as dirt. This means that the chemist can experiment with it at her leisure.

METHOD #1: [112]--5g phenol in dH_2O is stirred 5 hours at 20°C with some ferric sulfate ($Fe_2(SO_4)_3$, an additional 7mLs dH_2O, 13mLs 6% H_2O_2 and a 'pinch' of aluminum oxide (Al_2O_3). Yield of catechol is 2.5g (50%).

METHOD #2: [113]--Phenol can be oxidized with either performic, formic or acetic acids to catechol. For example: phenol, formic acid, concentrated H_2O_2 and polyphosphoric acid are heated 2 hours at 80°C to give 53% catechol. Addition of phosphorus pentoxide (P_2O_5) is said to increase the yield.

METHOD #3: [114]--Phenol and 30% H_2O_2 in molar ratios of 10:3 to 10:8 is heated at 70°C for 8-10 hours to give ~15% catechol. Addition of tert-butyl alcohol increases the yield.

METHOD #4: [115]--80% phenol in aqueous H_2SO_4 solution of pH 3 is brought to 50°C. 30% H_2O_2 is then added causing an exothermic reaction and a temperature of 15°C over 3-4 minutes time. 6% aqueous H_2SO_3? is added after 4.5 minutes, the solution quickly cooled and extracted with isopropyl acetone (Strike would think that another solvent like methyl ethyl ketone could be used) to give 60% catechol.

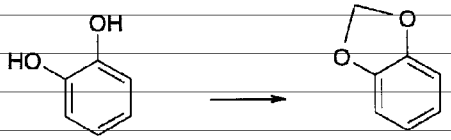
One of the problems with all the current phenol conversions is that a certain amount of other phenols, such as resorcinol and hydroquinone, will be formed along with the catechol (don't ask). These species are very hard to separate from the catechol because they are all so similar. Aside of carefully monitored fractional distillation there are some vague strategies which can be found in the Chemical Abstract references 116-118.

Wow! How did Strike go from such detailed articles to this load of crap about phenol conversion? Well, it's probably because Strike has never had to stoop so low as to need these methods nor

should anyone else these days. These recipes are for the desperate peoples of the future to ponder. Although by then they will have starfleet replicators to do their bidding.

Future drug user: "MDA!! 100mgs"
Computer voice : "Affirmative."

METHYLENATION



Pyrocatechol 1,3-Benzodioxole

With catechol in hand there are many ways to proceed as one can see from the genealogy chart. Strike feels it's best just to dive right in and discuss the most pivotal point of all that makes X what it is: that little bridged ring structure stuck on the benzene core. When the two OH groups of catechol are bridged, the species that is borne can be named either methylenedioxy benzene or, as the Chemical Abstracts call it, 1,3-benzodioxole. Why '1,3-'? Well, the carbon that bridges the two oxygens is now counted as the #2 carbon. Later, when the chemist adds something to the 1,3-benzodioxole, all the numbers change again and the #2 carbon will no longer count. Isn't chemistry confusing? There is one very important thing that there should be no confusion about. That is that if one were to demethylate eugenol to get allylpyrocatechol, demethylate vanillin to protocatechualaldehyde, or acquire any species that has those two adjacent OH groups then those molecules can be methylenated just like catechol with similar yields. One needs to remember to adjust for the weight differences of the different species one wants to methylenate.

The reaction itself works by the action of Na or K from NaOH or KOH which form what is called a catechoxide dianion with the two OHs of the catechol species. This makes the two ripe for an attack by a methylene halide which can be either DCM (methylene chloride, or dichloromethane), DBM (methylene bromide, or dibromomethane) or DIM (methylene iodide, or diiodomethane). DCM is cheap and works pretty well, but DBM and DIM work better yet are more expensive.

METHOD #1: Methylenation started out in the first part of the century using a process pretty much like the following [119]. 55g pyrocatechol, 200mL dH_2O, 40g KOH, 140g DCM and 125mL ethanol are heated in a sealed pipe bomb at 120°C for 24 hours. The solvent is then distilled off and the 1,3-benzodioxole can be extracted from the remaining water solution using benzene or ether and the solvent layer fractionally distilled to afford 1,3-benzodioxole (yield=20%).

There are other articles that have shown that this sort of reaction mix will work just as well under simple reflux rather than a pipe bomb [120]. A mixture of 220g catechol, 272g DCM (or a proportional amount of DBM or DIM), 220g potassium hydroxide and 1L ethanol is refluxed in the hood for 72 hours, cooled and the brown-colored solution vacuum filtered. The filter cake is washed with a little ether, which is combined with the other filtrate, and the solution is distilled to remove all the solvent. The residue that is left will have 500mL ether, 1L dH_2O and 200mL 20% aq. NaOH solution added to it and the whole thing stirred really well for a few minutes. You may or may not recognize what's going on here but it is the exact sort of thing that one uses to get the eugenol out of sassafras oil. Any exposed OH groups (catechols) will form those anions with the Na from the NaOH and bring the catechol into the water as a solid. Any converted 1,3-benzodioxole or methylenated compound will not have any such exposed OHs because they will have been tied up by the successful conversion. This means that such molecules will remain in the solvent layer. This is an excellent way to purify any of the methylenated compounds produced by any of the following methods. The ether layer is separated, washed with water and distilled to give 1,3-benzodioxole in about 26-32% yields.

METHOD #2: Later versions of methylenation get the yield up to 50% by employing the use of a catalytic metal called Tobin bronze [121]. The chemist can buy this or make it herself (yeah, right) by mixing or smelting or whatevering 60% Cu, 38% Zn, 1.5% Sn, 0.3% Pb, and 0.2% Fe (that all adds up to 100% by the way). 0.1M of any catechol (for pyrocatechol that's 11g), 3g of Tobin

bronze shavings and 10.2g DCM are placed in a pipe bomb which is positioned vertically in a bucket of crushed ice with the permanently sealed end on the bottom. The DCM mix is allowed to get cold, then 40mL of cold methanol is poured as gingerly as possible down the inner wall of the bomb so that as little mixing as possible between the two liquids occurs. Then a cold solution of 11g KOH (or 8g NaOH) in 15mL dH_2O is added in the same manner as was the methanol so that as little mixing as possible occurs. The bomb is immediately sealed after the final addition.

All of this careful addition is to keep the reaction from starting before the bomb is sealed. It is also important to note that the chemist must scale up or scale down the amount of reactants so that the total amount of all the ingredients consumes no less than 90 of the volume space of her particular pipe bomb. Too much head space with its atmospheric air will lower the yield. The bomb is heated in an oil bath or oven at 105-115°C for 18-24 hours and the contents are then distilled with the 1,3 benzodioxole coming over at about 170-175°C with no vacuum. Alternatively, the chemist can only distill off the methanol, wash with dilute NaOH solution and extract with ether, etc.

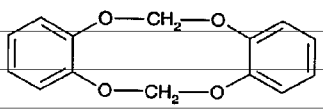
METHOD #3: Things start to look easier and the yields higher when the following method is employed [122]. This method uses a solvent called DMSO (dimethylsulfoxide). Maybe you've never heard of this solvent but Strike has. It is a common solvent used in all fields of science; and although Strike is not 100% sure, Strike believes that one can substitute DMF (dimethylformanilide) for DMSO.

110g catechol, 500mL DMSO, 100mL DCM and 83g NaOH are stirred in a flask with a condenser just like fig. 7a. The temperature is brought up to 120°C either by direct heat or by an oil bath. A violent reaction will start when the temperature is approached and will last for only 10 minutes. That's it! The solution is stirred for another 30 minutes and then allowed to cool. The 1,3-benzodioxole can be removed by methods similar to those of the previous two methylenation methods or one can do the superior method of separation employed by the scientists of this article.

They found that by adding water (about 500mL) to the reaction mix and then distilling it with no vacuum, that the benzodioxole will distill over with the water at the same time as an azeotrope (an azeotrope is a term for when two things are stuck together when they distill over). The azeotrope will separate out in the collection flask to give a clear upper layer of water and a clear lower layer of oily benzodioxole. If one has made heavier oil species such as piperonal or safrole using this, then it is preferable to just straight up distill the stuff without the addition of water. The yield of 1,3-benzodioxole is 70%.

When doing this method the scientists confirmed something that has long been theorized by those who study these sorts of things. That is, they determined that if one tries to convert all of the catechol at once like was done in the above method then it tends to form a dimer side product like that shown below [120].

You see, if there is as much activated catechol swimming around as there is DCM to react with it then there is a greater chance that the activated catechol will react with itself and form a dimer before the DCM has a chance at it. This accounts for about 20% of the loss in yield. This was avoided by adding the NaOH and catechol in small batches to the already hot (120°C) solution of DMSO and DCM. The DCM was allowed to have its way with substrates, then another small addition was introduced, etc., until all the catechol and NaOH were added. This gradual addition strategy raised the yield to 91%! Strike is not about to explain the weird apparatus used to allow simultaneous addition of two dry products to a hot, sealed system. If a chemist wants to try gradual addition then her best bet would be to drop the stuff down through the condenser and wash down anything that sticks to the inner wall of the condenser with a few squirts of DMSO.



You do believe Strike when Strike tells you these things, don't you? No? Well neither does Strike. But fortunately for us, some-

one did. And now that person, Merlin, has schooled us all. Check out Merlin's adaptation of #3:

"***Methylenation for Beginners***

By far the best method I have tried to produce benzodioxole in terms of yields and simplicity. In comparison to other processes, this is in fact quite fun and I'll explain it in a fashion that can be followed by a complete novice, like I was when I started a while ago. What we do is react and reflux the ingredients first, then use a simple distillation procedure to extract the product with water as an azeotrope. Once extracted we wash until the product is clear, and then separate. From start to finish it will take about six hours.

Stage one - the reaction happens in the form of a reflux with a dry set-up. You will need a 2000ml reaction flask, a condenser and a drying tube packed with calcium chloride or other drying agent. The reaction needs to be stirred in a big way, so before we add the ingredients make sure you have a clean stirrer bar ready, I prefer the eggy shape bars as they tend to be less noisy.

Ingredients

Catechol - 110g

DCM (AR Grade) - 100ml

DMSO (AR Grade) - 500ml

Sodium Hydroxide (AR Grade) - 83g

DMSO - Dimethylsulphoxide is a very common solvent with a freezing point of 20 degrees. When you buy this stuff it will be crystallised in the bottle. To melt, all you need to do is place the bottle in a bowl of hot water for 30 minutes - simple. If you're lucky enough to live somewhere warm it may already be liquid, where I live, no chance. When you open the bottle you will notice that this stuff smells a bit farty, don't worry too much, it doesn't get that bad. 500ml straight into the reaction flask and start the stirrer.

DCM - Dichloromethane 100ml pour into the reaction flask with the DMSO.

On one occasion I dried the two solvents with Sodium sulphate, I'm not sure if this affected my yields, but if it's very humid where you live then this would be a good idea. It certainly wouldn't harm if you want to be thorough.

Catechol - 110g, smells like hospital toilets from where I'm sitting. Easy and cheap to purchase. Use a funnel to get this into the flask and don't try to dissolve it first as it just sticks to everything, a dry funnel and add slowly so as not to stop the stirrer bar. When this is added the solution will start to change to a dark greeny colour. It is important that the stirrer keeps spinning, if it all stops moving in there, some bits can get left out of the reaction, and your yield will suffer.

Sodium Hydroxide - 83g of AR grade is added in the same way as the catechol. This will slow the stirrer down loads so add slowly, now the reaction flask will start to get warm as the magic starts.

Now connect the condenser and the drying tube. An important point here for beginners is to make sure the drying agent is not clumped in a big lump which can allow moisture to pass by, smash it all up with a pestle and mortar, so it completely covers the cotton wool in the drying tube. When this reaction starts in anger it is quite "happening", so if the drying tube isn't firmly placed it will blow off and shoot across the kitchen and smash. You can hold it in place for a few minutes or clamp it, or even tape it. If you're using a vacuum adapter make sure the vacuum port is blocked off properly too, once a piece of foil I'd blocked mine off with shot out in front of my very eyes, and my dog nearly ate it, so now I tape it in place.

With everything secured, start the heating gently. The reaction will already be going so things don't normally take long. After ten minutes or so the reaction will start in earnest, gases fizz out of the drying tube and the contents of the flask will be a lovely emerald green colour, this will last for three to four minutes and then gradually slow down. You may notice the smelly DMSO, a good opportunity to fart and blame it on the chemistry, if you don't have a dog to blame, like I do. Once things die down take note of the time and leave for half an hour. The next thing we will do is add 500ml of distilled water, so we need it all to cool down.

Remove the condenser, then with the aid of a funnel add the water slowly, keep stirring. If the solution is too hot the water will evaporate and make a big mess. As the water is added you will notice that loads of stodgy crapp will form, this is normal, connect the condenser for the distillation with a receiving flask at least 500ml in capacity.

We now have a big flask with lots of water in it, which we need to heat lots and lots. This will take a long time, and if you're impatient like me, it's best to sit down and expect to wait at least 30 - 45 minutes before anything starts to happen. What we're doing here is removing the water and our product benzodioxole together as azeotropes. Compared to other distillations I've done this is relatively easy and very satisfying. At about 85 degrees the distillate will start to come over, as it drops into your collection flask a blob of oil will appear in the middle of the water. The oil appears clearer than the water, which will be milky in appearance. Now all we need to do is wait, adjust the heat so the temperature doesn't go above 100 degrees, and sit down and watch TV, or have a cigarette.

After a couple of hours you may notice that what's coming over contains less oil, and eventually no oil at all, just water. That's it, you've done it. The benzodioxole will form a layer underneath the water. We just need to separate the oil with a sep funnel, wash with water twice, to remove any traces of milkiness, which I think

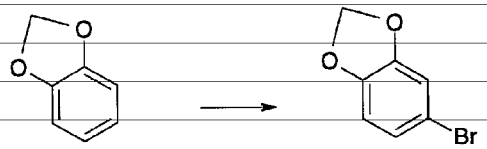
could be sodium hydroxide, and we're sorted. Your product should be crystal clear, slightly more viscous than water, with a very strong odour, similar togasoline or benzene (petrol if you're from the UK).

The best yield I've achieved is 84g of benzodioxole from 110 of catechol. And to progress from here you'll probably need to do this reaction twice to get enough benzodioxole for the bromination."

METHOD #4: In this synthesis everything needs to be as dry as possible [123]. The potassium fluoride (KF) should be heated at 100°C for an hour, all glassware baked at 425°F for an hour and any solvents used need to be dried through Na_2SO_4. 152g KF, 22g catechol and 500g DMF are stirred at room temperature for a few minutes. The solution will get warm during this time and will be allowed to return to room temperature before proceeding further. 19g of DCM is added and the solution refluxed in a 110-120°C oil bath for 1.5 hours. After cooling, the solution is extracted with ether, the ether washed with water to remove any absorbed DMF, the ether dried through Na_2SO_4 and distilled to give 1,3-benzodioxole at a yield of 98%! Using cesium fluoride instead KF reduces the reaction time and gives higher yields on the methylenation of larger molecules.

METHOD #5: This last method gives super high yields and the reaction progresses at room temperature [124]. To a stirred suspension of 12.5g sodium hydride (NaH) in 200mL hexamethylphosphoric triamide (HMPT) is added a solution of 28.6g catechol in 100mL HMPT over a 10 minute period. A lot of bubbling will occur, and when it dies down 80g of DIM or 52g DBM or 25.2g DCM is added and the solution stirred for 20 minutes. After 20 minutes about 500mL cold dH_2O is added and the whole thing extracted with ether. The solvent layer is dried through Na_2SO_4 and distilled to give 1,3-benzodioxole (yield=93%).

BROMINATION OF 1,3-BENZODIOXOLE



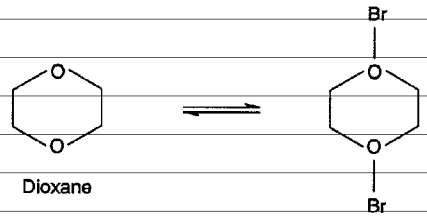
1,3-Benzodioxole 5-Bromo-1,3-benzodioxole

Hey, folks! We're halfway there. One can see throughout this book that bromine plays a key role in a lot of reactions. This is because it is a good nucleophile that adds well to things and helps in getting other things added. As usual, if the chemist wishes to use iodine instead of bromine that is perfectly okay. Since we are talking about bromine here, let's discuss what the bromine one needs is going to be like. What is needed here is bromine (Br_2) not hydrobromic acid (HBr). Br_2 is just heavy enough to be an orangy red liquid at room temperature. If one were to take the lid off a bottle of liquid bromine then lots of red, evaporated Br_2 smoke will come flying out. It isn't advisable to breathe so transfer of this stuff should be quick or in the hood. It would be best if the liquid bromine were kept cold at all times. If one cannot get liquid bromine then they can assuredly get it from the specialty gas cannister supplier. The product of this bromination can be called 1,2-methylenedioxy-4-bromobenzene or 3,4-methylenedioxybromobenzene but Strike is lazy and is going to refer to it simply as bromobenzodioxole.

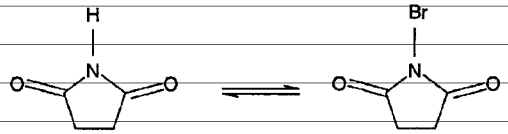
METHOD #1: [125]--143g 1,3-benzodioxole in 600mL chloroform is stirred in a flask and Br_2 from a little tank is slowly bubbled through the solution over a period of 4 hours at room temperature. Ideally one wants to introduce about 190g of bromine into the flask so the chemist may wish to stop the bubbling and check the weight gain of the flask periodically. After 4 hours the solution is vacuum distilled from the flask. The first thing to come over is the chloroform, then a small amount of higher boiling, unreacted

1,3-benzodioxole, and at about 30-40°C higher should come the mother lode of yellowish bromobenzodioxole oil (yield=91%). If one has liquid bromine then one might consider pulling the vapors that come off it into the solution using a very low vacuum pull as described in the article. The chemist may consider using acetic acid as the solvent instead of chloroform and drip liquid bromine into it as previously described [126, 127] to give about 90% yield as well.

The next two bromination recipes use recyclable bromine donors that can be used over and over again. They are called dioxane and succinimide and are more common than you think. No, dioxane is not the same as the notorious dioxin but it is still pretty toxic.



Dioxane



Succinimide

These little beauties are like bromine quarterbacks in that they take the ball (Br) and hand it off to the receiver (1,3-benzodioxole). The great thing about these two species is that they are so bulky that the only place on the benzene ring that they can hand off their Br atom with any efficiency is at the least hindered #5 carbon

which is the exact one one wants the Br to be on. Once brominated, the Br acts as a final deterrent to the possibility of a second bromination. As you can surmise, multiple brominations can be a problem with some methods. After releasing their bromine, both dioxane and succinimide are reformed and can be separated for reuse.

METHOD #2: [128, 129]--To make dibromodioxane one stirs 500g dioxane in a flask which is in an ice bath, all of which is in the hood. 990g of liquid Br_2 is rapidly added, causing the solution to get hot (one can also bubble in an approximate amount of bromine from a gas canister). The solution is dumped into a bucket containing 2L of ice water, causing the immediate formation of a large mass of orange dibromodioxane crystals which are separated by vacuum filtration and dried.

In an ice bath a flask containing 100g 1,3-benzodioxole or catechol or guaiacol and 200mL ether is stirred and then 200g dibromodioxane is slowly added so that the heat and reaction won't get out of control. After stirring for 1 hour the solution is poured into some water and the ether layer is separated. The aqueous layer is extracted once with some more ether and the two ether fractions combined, dried through Na_2SO_4 and distilled to give bromobenzodioxole (90%).

METHOD #3: [130]--This method was perfectly tailored for the bromination of 1,3-benzodioxole. The bromosuccinimide can be purchased or made from succinimide in a way that is pretty much the same as the way dibromodioxane was made (see Ziegler, Ann., vol 551, p109 (1942)). To do this method one mixes 122g 1,3-benzodioxole, 188g N-bromosuccinimide and 500mL chloroform in a flask and refluxes for 3 hours. The solution is then vacuum filtered from the solids and the filter cake washed with a little extra chloroform. The chloroform wash is combined with the original filtrate and vacuum distilled to give about 180g (91%) bromobenzodioxole.

Now the *real* goods on BOTH of the reactions in #2 and #3. Again, courtesy of Merlin:

"Bromination for Beginners

This process will add a bromine atom onto the benzodioxole molecule which is important for the next step of the process. This is a very simple operation, and the yields are easy to achieve. There is however a downside. Brominated chemicals have a phenomenally high boiling point, which in the case of Bromo-Benzodioxole is higher than the temperature at which it will fry. Distillation will just cook your product unless you have a serious vacuum available, and by serious I mean down to at least 10mm. It took me about six attempts until I discovered what was going wrong and once I had a good vacuum pump it was an easy operation. With a vacuum of 2mm I distil this stuff at about 100°C, and it starts to turn black at about 120°C – 130°C without vacuum.

For those without a fume cupboard, proceed as below. For those with a fume cupboard, the second bromination method is recommended.

The Reaction

The Ingredients are placed in a reflux set-up and left for three hours. They are then vacuum filtered from the solids and then distilled with vacuum, it's quite simple.

Ingredients

Benzodioxole - 122g

Bromosuccinimide - 188g

Chloroform - 500ml

Benzodioxole - from the previous reaction, usually you will need to do twice to get the correct amounts. Washed and dried.

Bromosuccinimide - easily purchased but I could only find one grade. It's a very fluffy light orangy crystalline powder - use gloves and a mask, because bromine is VERY nasty.

Chloroform - a very common solvent which has a rather unpleasant smell. Try not to get too close to this stuff as it has anaesthetic properties which you don't really want to find out about.

There's no real order needed to get the stuff into the reaction flask. Use a 1000ml flask with a stirrer bar and it's easier if the chloroform goes in last so you can wash down the solids if you have any stuck in the funnel. Set up the condenser and drying tube as we did with the methylenation.

Start the heat and wait. It will take about 20 minutes to get going and there usually isn't much to see. The flask will be a nice orange colour from the bromine and it won't change much until just before the end. Make sure the water is running, everything is secure and leave for three hours - have a sleep or something to eat maybe.

After three hours the flask will have turned slightly darker in colour and the contents will look slightly more transparent. If so then everything is good, if not I doubt that you have anything to worry about. Allow to cool enough for the vacuum filtration, usually about 30 minutes.

Vacuum filtering can be a bit tricky, as the filter paper clogs up very quickly and stalls the process. With this stuff it is particularly important to get rid of as much of the solids as possible or your distillation be will very messy. A way round that I have found (that isn't in any book) was to use loads of filter papers, throw them all into a big beaker and then rinse them with solvent, then filter the solvent. Filter tiny amounts at a time, as soon as the paper blocks - stop and change the paper. I normally run the filtrate through at least twice. Any way you can make sure that you have done two

things very thoroughly. Remove the solids from the filtrate and wash the solids with fresh solvent to get any product off the solids and back into the solvent. Save the solids that you have filtered as they can be dried and reused.

Place the filtered solvent into a reaction flask with your vacuum distillation gear ready. If you have a vacuum pump capable of getting down to the pressure needed here it will be powerful enough to strip off the chloroform without adding too much heat. If you just turn the vacuum on the evaporating solvent will cool the reaction flask until it freezes and the distillation stalls. So what you need to do is add just enough heat to get the solvent off without the temperature getting above about 20C. The solvent can be removed without vacuum, no problem with that, so long as the temperature never goes above 100°C (or else your product will turn black). Either way sometimes the solvent will come off orange, that Bromosuccinimide gets everywhere and the condenser will start to get really dirty and blocked.

It's obvious when the chloroform has finished coming over. If you're using heat with out vacuum the temperature will start to rise so make sure you stop before it gets too hot. If you are using vacuum it's time to stop anyway.

However well you filtered before it's time to stop the distillation and clean everything up before you distil your product. The condenser will be full of shite. Clean all your bits and replace the flask with stirring and begin to heat. As I said before if you haven't got a vacuum available that's 10mm or less don't bother.

The first few millilitres of distillate is likely to be unreacted benzodioxole. This will come over at about 80°C. The best thing to do here is wait for the temperature to get to about 90°C and then stop everything, change flasks and start again. Don't allow the reaction flask to heat up while you change flasks, in fact let it cool down a bit - if you don't, you'll know why I said this.

With a new flask in place start your heating again. At around 100oc the product will start to appear. There should be loads of it, it will look very clean and clear, and could best be described as slightly yellowish in colour. If you're lucky you'll have about 180g and it will smell similar to Benzodioxole with a hint of bromine (yuck!). The bromine atom is a heavy bastard, so the molecules here weigh much more than the benzodioxole molecules, so expect a higher weight from a similar looking volume in comparison. Stop your distilling when the colour of the distillate starts to get darker in colour. What's left in the flask is shite, and can be thrown away.

The receiving flask contents should contain a very pure product. There is no need to clean up any further. For the next stage however they will need to be dried over sodium sulphate. This can either be done now or later. Now is better, dry your product before you weigh it and place it in a screw capped bottle ready for the Grignard reaction.

Bromination with Dibromodioxane

This method is by far the easiest of the two methods I describe, but because it uses bromine liquid as a precursor to the dibromodioxane crystals a fume cupboard (or a fucking good method of fume extraction) is absolutely essential. Surgically removing ones gonads with a blunt knife would be a much less painful way of harming yourself than messing with this stuff in the kitchen.

The procedure is similar to the reaction described above except that dibromodioxane crystals are used instead of Bromosuccinimide and refluxing isn't necessary as the reaction is much easier. The dibromodioxane crystals are made quite easily and as far as I know can not be purchased.

An ice bath is needed technically but I've never had any problems with heat getting out of control. So use one anyway.

We need:

Dioxane - 500g

Bromine liquid - 990g

Dioxane - is a very common and cheap solvent.

Bromine liquid - a very nasty red liquid with a heavy vapour that shoots out of the bottle as soon as you open it, that will make your skin and eyes sting like you've never known.

Use a PP beaker, on a stir plate, in the ice bath. Slowly add the bromine which will cause the solution to get hot. The crystals will form immediately and before the whole thing gets solid pour the contents of the beaker into 2 litres of cold water. The whole thing goes whoosh! and forms a huge lump of really nice looking orange mass. There will be crystals all over the place including in the reaction beaker, and these should be carefully scraped into the water.

What's left in the water now needs to be vacuum filtered and dried. This should be done carefully and under the fume hood. Up to this point the chemistry will have taken around 30 minutes, the drying might take a day or so. Often bromine liquid stays hanging around the crystals which makes them nasty, leave in the buchner funnel of your vacuum filter overnight to get rid of all that bromine. Unless all the bromine has gone, don't go near them without a fume cupboard or a mask.

The dibromodioxane crystals are now ready for the reaction. Using the same ice bath as before we have a PP beaker containing 100g of benzodioxole and 200ml of ether, which is being stirred. We gently add 200g of dibromodioxane crystals and watch the

solution turn a gorgeous orangy red. We leave to stir for one hour.

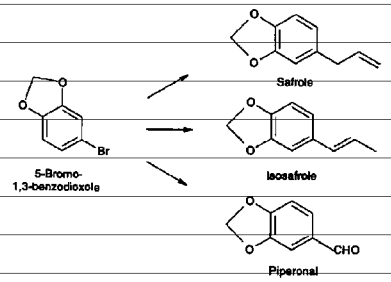
After an hour we pour the contents into 500ml of water. We then separate with a sep funnel and extract the water layer with 50ml of clean ether. We combine these two ether layers and dry over sodium sulphate.

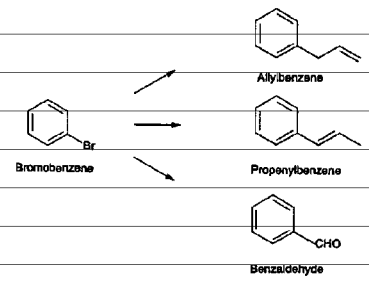
The distillation is the same as in the previous reaction, except there is no need to clean the condenser after the solvent is removed, as there are no solids left over from the reaction. No vacuum filtration is needed prior to the distillation either. However a vacuum of at least 10mm is still required to distil the product.

Although the clean up is much easier the yield is about the same. For those with the correct equipment this has to be the preferred method."

THE BIG CHAPTER

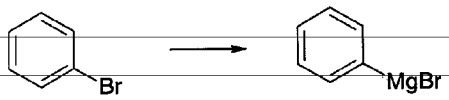
Now comes the mother of all chapters. Three different controlled ecstasy precursors from 1 compound: bromobenzodioxole. This is also the point that speed makers should begin to pay more attention. In the chemicals section of this book Strike has provided the recipe for making bromobenzene so that the speed chemist can make all of the analogous precursors.





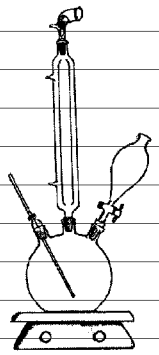
PREPARATION of the GRIGNARD REAGENT

The preparation of the bromobenzodioxole or bromobenzene is going to be the same no matter which one is used and no matter which precursor the chemist wishes to make. This means that this first part needs to be done correctly. This first part of preparation that Strike is talking about is the creation of a Grignard reagent out of the bromo compound starting material [125,131-134]. Mr. Grignard earned a Nobel prize for this in 1912 so you can bet that it's a pretty good procedure.



Bromobenzene Grignard Reagent

The procedure calls for the chemist to place a magnesium atom onto the bromine of the bromobenzodioxole which makes the complex amenable to exchange which you are going to learn about in just a bit. This means that the chemist is going to buy either magnesium powder or magnesium turnings which are thin curly-Qs of Mg that look like they came from a scouring pad. The procedure can be done in either tetrahydrofuran (THF) or ether, but THF is preferable. All the components need to be as dry as possible, which means that the solvent is dried through Na_2SO_4 or distilled, the Mg is dried in an oven at 100°C for an hour and the glassware is baked in an oven at 425°C for at least 20 minutes. The apparatus to use is seen in figure 15.



[Figure 15]

In the three neck flask is stirred 12g Mg and 200mL THF. In the little separatory funnel is placed a mixture of either 100g anhydrous bromobenzodioxole or 78g bromobenzene (for speed) in 200mL THF. What is not pictured is a plastic tray that the apparatus will be resting in on top of the stirplate because the chemist may need to throw some ice water in it during the reaction. Although not entirely necessary, it is probably a good idea to squirt a little nitrogen into the head space of the three neck flask before the reaction begins. Another thing to consider before beginning is whether or not to place a catalyst into the reaction flask. What this means is that it is sometimes difficult to get a reaction going between the magnesium and the bromo compound and chemists often add a little insurance policy in the form of a tiny crystal of iodine or, as in ref 110, exactly 2 drops of dibromoethane into the reaction flask liquid. Like Strike said, it is not always done but it is best that the chemist does so anyway.

The reaction is started by dripping the bromo/THF mix from the separatory funnel into the stirred reaction flask. A vigorous reaction will begin to occur after a little addition. This will give off heat so the chemist adds ice to the ice tray and/or controls the dripping so that the temperature of the reaction stays below 55°C. After addition, the solution is stirred for another hour, during which time it will take on a dark, yellow-green color and just about all the Mg will have dissolved into the solution. That's it. The chemist now has her Grignard reagent which is the entire solution in the reaction flask. She needs to process this into the final product soon because the reagent won't keep forever.

SAFROLE or ALLYLBENZENE FROM GRIGNARD REAGENT

All the glassware from the making of the Grignard reagent remains exactly the same with the Grignard reagent still resting in the reaction flask. The only change is that the ice bath tray is re-

moved. Into the separatory funnel is placed 60g of anhydrous allylbromide (Br-CH_2-CH=CH_2, see chemicals section for how to make) and this is then slowly dripped into the Grignard solution. Another vigorous reaction will start and the addition is regulated so that things do not get out of control. After addition the solution is refluxed for 3 hours, cooled and then hydrolyzed by pouring the reaction mix into 300mL ice cold saturated ammonium chloride solution in a PP container.

What the chemist will see is two layers: a solvent layer (THF or Et_2O) and a water layer with a lot of suspended solids. The chemist can remove and discard the aqueous layer now or, preferably, the chemist can vacuum filter the entire two-layered solution to get rid of all the solids, then remove the water layer. Of course it is always a good idea to extract that water layer once with fresh solvent before it is discarded. The solvent/safrole layer is washed with a little dilute HCl and then with some fresh dH_2O. The solvent layer is then dried through Na_2SO_4 and vacuum distilled. The first thing to distill over is, of course, the solvent. The next thing to come over will be a few mLs of a low boiling oil which is going to be 1,3-benzodioxole and will be saved for reuse. At a much higher temperature comes all the safrole. The chemist will have no trouble knowing that the procedure worked because all of that high-boiling oil is going to smell just like licorice (yield=87%).

Can you believe that? A chemist just recreated a wondrously complex substance that, before now, was only a gift from God to man via plants. Man took this gift away from her fellow man but now, through the unbelievable power of chemistry, man can reclaim her right to self determination. Albeit illegally of course.

And it would certainly be illegal if Merlin had actually done the procedure she next describes. Aside of the unsatisfactory pronoun use, Merlin's accounting is astonishing:

"The Grignard Reaction

Since completing my synthesis of safrole using the methods described here, I have learnt that I am the first person in the world to do so. There may be areas in my procedures that can be improved. What I am doing here is giving you my best shot as well as a fairly detailed account of my experiences.

The Grignard reaction is well documented in many areas of chemistry literature and it would be wise to read as much as possible before attempting this reaction. The apparatus required includes: - 1000ml three neck flask, 1000ml sep funnel, a condenser and a drying tube. This apparatus needs to be set on a magnetic stir plate. For reasons which I would prefer not to go into, the presence of any water during the reaction will severely screw up yields, so everything needs to be dried including the ingredients. The best way to dry the glassware is to cook it in your oven for half an hour at 150°C (300°F). The solvent (THF or ether) and the bromobenzodioxole need to be dried over sodium sulphate, and the magnesium should be cooked in the oven along with the glassware. Atmospheric moisture must be kept out of the reaction by using the drying tube.

Summary

A dry reflux set-up is used with a three neck flask allowing a thermometer and sep funnel to be attached to the reaction flask. The thermometer is placed well below the surface of the flask contents. If the temperature rises above 55°C ice will need to be used to cool things down a bit. So the three neck flask will be sitting in an ice bath on the stir plate before we begin. If ether is used instead of THF the ether will boil well before 50°C is reached giving a better indication of how hot things are getting.

The Reaction

Place 12g of magnesium into the flask along with 200ml of THF and stir. Place 100g of bromobenzodioxole along with 200ml of

THF into the sep funnel. It is recommended that an iodine crystal is placed in the reaction flask and before the condenser is attached, nitrogen should be blown into the receiving flask to remove any air. As I didn't have any nitrogen available I skipped this step but I did place one small crystal of iodine into the reaction flask. When the iodine is added the solvent will begin to turn brown. Although this looks like the iodine is just dissolving it would appear from what I have read that this is also caused by the reaction.

The contents of the sep funnel are now added with care to the reaction flask. Begin by dripping small amounts of the bromobenzodioxole into the reaction flask and keep a close eye on the thermometer, remembering that the temperature should not be allowed to go above 55°C. If the temperature does begin to climb too fast, stop the addition and wait until it reduces to at least 40°C. Addition of the bromobenzodioxole should take about 30 mins. Although the reaction was described as being vigorous, in my experience there wasn't much to see except a rapid rise in temperature. Once all the bromobenzodioxole has been added the solution should be dark brown in colour. The solution should now be left to stir for a further 60 mins., after which it will become a dark greeny-brown with only tiny particles of magnesium that will be swirling around as the solution stirs. What's left in the flask is the Grignard reagent. Anyone getting to this stage should feel happy in the knowledge that very few (only me up until now) have seen this bromobenzodioxole - Grignard reagent.

Safrole from the Grignard reagent Keeping the apparatus from the above reaction, pour 60g of allylbromide into the sep funnel. As with the ingredients of the last procedure the allylbromide must be dried over sodium sulphate. This stuff is really nasty, use a mask at least or a fume cupboard if you can get access to one or fill the sep funnel outdoors. The fumes are invisible and pretty lethal - please be warned.

The allylbromide is slowly added to the Grignard reagent. It should be added as carefully, if not even more so than the bromobenzodioxole, because when it hits the Grignard reagent things really start to get going. There is no need to keep the reaction under any particular temperature, but if it gets too hot in there your solvent boils, a sure sign telling you to slow things down. This reaction was much more vigorous than the first, which was fun as I realised it must be working.

After all the allylbromide has been added, the solution is heated and allowed to reflux for three hours, and subsequently left to cool for thirty minutes.

Prepare a 300ml saturated ammonium chloride solution in a 2000ml PP container by adding 225g of ammonium chloride to 180ml of water. Carefully pour the contents of your reaction flask into the ammonium chloride solution. Two layers will form which contain a big load of suspended solids - which are removed by vacuum filtration. These two layers are then poured into a (clean) sep funnel and allowed to settle. The water layer is discarded, leaving the organic layer which is washed once with 50ml of 5M HCL and then once with 50ml of water. Any remaining water must then be removed by drying over sodium sulphate. Now all we need to do is distil, and we have safrole.

Using a standard vacuum distillation the solvent is distilled off. This shouldn't take too long. The first thing to come over after the solvent was the safrole, which with my vacuum (2mm) started at around 90°C. The safrole will be a clear liquid, slightly viscous and will smell of liquorice. With the above measurements one can expect a yield of around 85g. No further cleaning up is necessary, and the safrole can be used as is for any further reactions."

You can see now why Strike is so proud of this chemist's hypothetical work. It is the most professionally written and applied experimentals of this entire book. It is made all the more remarkable when Strike tells you that these three contributions were the first

chemical experiments Merlin had ever done. Here is this rookie applying some of the most advanced, and often difficult, organic syntheses processes around!

Is this a testament to Strike's masterful book writing abilities? Maybe. Or is it a testament to the fact that anyone can do these methods? Maybe. Strike likes to think that it is a testament to the intelligence and and persistence of one very good looking chemist (no, Strike is not gay!).

PIPERONAL or BENZALDEHYDE FROM GRIGNARD REAGENT

To make piperonal or benzaldehyde the chemist uses the same Grignard solution and the same apparatus except that the Grignard solution is poured from the three-neck flask into the separatory funnel. The three-neck flask is then cleaned and dried and put back in place or, if the chemist has a spare, swapped with a second flask. Into the flask is poured 30g of N-methylformanilide (no, that's not the same as N-methylformamide) and the ice bath tray is put back into place. The chemist is going to need to cool the N-methylformanilide down to -20°C so the chemist is going to have to stock the ice bath with dry ice and ethanol. The Grignard solution is dripped in so that the temperature of the reaction flask contents never rises far from -20°C. After addition, the solution is allowed to come to room temperature and stirred at that temperature for 12 hours. From here the solution is processed exactly like what was done for safrole except that 300mL cold 30% H_2SO_4 solution is used for hydrolysis instead of ammonium chloride (yield=67%). Get it? Good.

ISOSAFROLE or PROPENYLBENZENE FROM GRIGNARD REAGENT

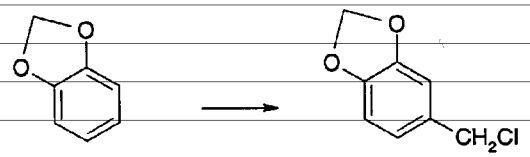
To make isosafrole or propenylbenzene the chemist will do exactly what was done for piperonal except that the chemical in three-neck flask is going to be 30g of propanal chilled to -15°C. The addition is the same except that after the solution reaches room temperature, the ice tray is removed, heat is applied and the

solution is refluxed for 30 minutes. The solution is hydrolyzed with ammonium chloride just like safrole was and then isolated just the same to give an -hydroxy intermediate (please don't ask, but the yield is 81%).

What the chemist has is an alcohol intermediate which is not what she wants. If she were to flick off that OH group then a double bond will form in its place and isosafrole or propenylbenzene will be borne [26]. So what the evil chemist does is place 60g of the alcohol intermediate oil and 1g potassium bisulfate ($KHSO_4$) into a really small flask, attach the flask to a distillation apparatus and start heating with vacuum. As the OH group is being kicked out it will form water, which the chemist will see distilling over. When no more water can be seen evolving then the reaction is finished. However, the chemist continues to heat to distill over all of the isosafrole which will smell just like licorice (yield=91% from the intermediate). If the chemist wanted to she could perform the same bisulfate procedure in a beaker or flask without the distillation setup and stop the reaction when a temperature of 170°C has been reached [28 p698]. The oil is still going to have to be distilled to purify it though.

THANK YOU SIR MAY I HAVE ANOTHER?

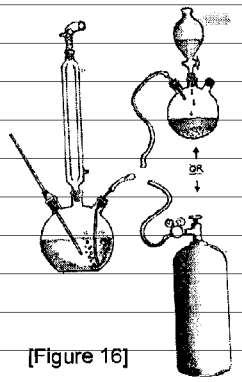
Why sure you can. Here are all the anothers to make that genealogy map of total precursor synthesis complete.



1,3-Benzodioxole Piperonyl chloride

CHLOROMETHYLATION

This procedure is called chloromethylation and will not only turn 1,3-benzodioxole into a methyl chloride but will work equally well in converting plain old benzene into benzyl chloride. Both are important stepping stones towards the production of X and meth. For example, benzyl chloride is a schedule I controlled substance because it will beget benzaldehyde and phenylacetonitrile (a precursor for phenylacetic acid).



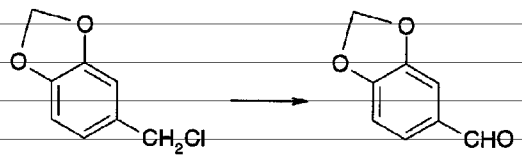
[Figure 16]

The best method Strike found for this [135] does not use ZnCl which is usually included in this procedure as a facilitator to the addition of the chloromethyl group [37 p539, 136]. Strike does not feel that mistake of omission had occurred so Strike will proceed as such. 366g 1,3-benzodioxole, 99g paraformaldehyde and 500mL toluene are placed in the reaction

flask of the apparatus shown in figure 16. This whole setup looks a little involved but it really isn't. The flask has all the components and HCl gas comes from either a gas cylinder or an HCl gas generator using H_2SO_4 and HCl/NaCl which happens to be the exact same generator that the chemist is going to have anyway so that she can crystallize her freebase product (see crystallization section). Either sulfuric acid is dripped into the HCl/NaCl or the valve on the cannister is opened so that a gentle, steady little stream of HCl gas starts bubbling into the reaction fluid. The temperature needs to remain between 25-35°C as the bubbling continues for 3-4 hours. The solution is washed twice with cold water, twice with dilute sodium carbonate solution and once again with water. The solvent is dried through Na_2SO_4 and distilled to give what is essentially called piperonyl chloride or benzyl chloride (yield= 70-90%). Now, if this procedure does not work as described then one should blame the Japanese, who said it would and then proceed to try it over again except this time one is going to add 30g of zinc chloride.

PIPERONAL or BENZALDEHYDE FROM CHLOROMETHYL INTERMEDIATE

The benzylchloride compound made in the previous recipe can be converted to piperonal or benzaldehyde using a chemical called hexamine [137 p817, 37 p700, 136]. Hexamine, also known as methenamine or hexamethylenetetramine, is a weird looking chemical that is easily made from formaldehyde but is better off being purchased.



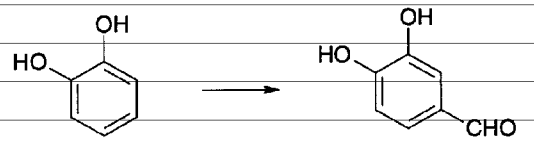
Piperonyl chloride Piperonal

In a flask with stirring is added 158g piperonyl chloride or 126g

benzyl chloride, 140g hexamine and either 500mL 50% aqueous acetic acid or 500mL 60% aqueous ethanol. The solution is refluxed for 2 hours, then 200mL 3N HCl is added and refluxing is continued for 15 minutes more. When cool, the solution is extracted with ether, the ether washed 3 times with water, dried through Na_2SO_4 and vacuum distilled to afford piperonal or benzaldehyde (yield=70%). The two products are quite fragrant which will give the chemist an idea of the success of the procedure. Did you know that a lot of methylamine is produced as a side product of this reaction? How it can be salvaged Strike has no idea.

PROTOCATECHUALDEHYDE FROM PYROCATECHOL

This is a nifty little way to turn catechol or guaiacol into protocatechualdehyde or vanillin using what is called the Riemer-Tiemann reaction [137 p824, 138]. It is a really ancient reaction and only works on benzene molecules that have an OH group. One needs to use KOH instead of NaOH because it is better at promoting para substitutions (don't ask). And if one is going to make vanillin from guaiacol then there needs to be a little ethanol in the reaction as well.



Pyrocatechol Protocatechualdehyde

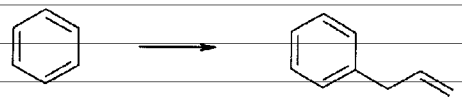
To proceed one can merely throw all the ingredients into a reaction flask and reflux for 5 hours or one can do the more prudent way as follows. Using the same apparatus in fig. 15 one places 400g KOH and 400mL dH_2O and heats it slightly with stirring to dissolve the salt. Next, 110g of catechol or 125g guaiacol is added and slightly heated to dissolve. The condenser and addition are attached and the temperature of the reaction flask is brought to 70°C in an oil bath. 240g (160mL) chloroform is slowly

dripped from the separatory funnel into the reaction mix over a period of 3 hours during which time the solution will blacken and a thick brown sludge will form. After addition, the stuff is poured into 500mL hot water, cooled and carefully acidified with concentrated H_2SO_4 or HCl. The whole mix is vacuum filtered from the tarry resin, extracted with ether, the ether washed with water, dried and vacuum distilled to give protocatechualdehyde or vanillin (yield=70%).

When making vanillin from guaiacol the chemist can smell success because the product will have an intense vanilla odor. One can even flavor cookies with the stuff (true!). This Riemer-Tiemann method is also an excellent way to get salicylaldehyde from phenol in yields of up to 50%. The chemist does everything the same except uses NaOH instead of KOH.

ALLYLBENZENE FROM BENZENE

This is the infamous Friedel-Crafts method and works in a manner similar to the previously mentioned method where P2P was made by merging benzene and chloroacetone using $AlCl_3$. This method is for speed makers only and is not recommended for conversion of 1,3-benzodioxole. However, this should work in a limited way on catechol. The conversion factor is very low but that isn't a major concern of speed chemists because cheap old benzene is the precursor and all of that benzene that isn't converted can be run back through this simple little process over and over again. Before she knows it, the chemist will have amassed an enormous amount of allylbenzene [139, 140].



Benzene Allylbenzene

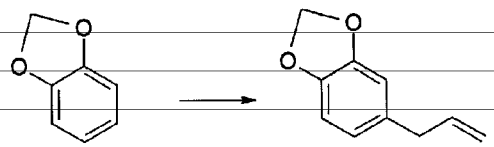
Aside of benzene the chemist has a choice in which allyl she can use. Allyl alcohol, allyl bromide or allyl chloride can be used with equal success but allyl alcohol is a nice bonus because it is easier

to make than the other two. All three of these are really cheap to purchase but Strike is going to tell how all three are made in the **Chemicals** section.

Everything needs to be anhydrous and the procedure begins by chilling 500g benzene, and 80g allyl alcohol to 0°C in a single-neck flask. 90g of powdered, anhydrous $AlCl_3$ is added which will cause a violent reaction and heat. A condenser is immediately attached with a tube leading to a water trap and the solution is allowed to come back down to room temperature. The reaction stirs for 6 more hours at room temperature, poured into ice cold dilute HCl solution and the benzene layer separated. When the benzene layer is distilled the first things to come over are perfectly reusable unreacted allyl alcohol and benzene and finally will come the high boiling allylbenzene.

There are a great many aspects to the Friedel-Crafts method that Strike does not have the space to go into. Friedel-Crafts works better if chloro or bromobenzene and their X counterparts are used in place of plain old benzene. Also, there is a significant amount of unwanted byproducts and molecular rearrangements that accompany this sort of reaction. Strike strongly suggests that people read more about this method before they attempt any such reaction.

SAFROLE FROM 1,3-BENZODIOXOLE



1,3-Benzodioxole Safrole

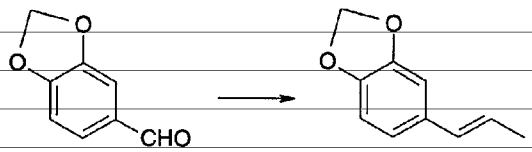
[141, 142]--This is similar to the Friedel-Crafts method but is less harsh and has been proven successful at producing safrole. In a very small flask is added 7.2g of allyl chloride, 34.3g 1,3-benzodioxole and 0.15g powdered Cu (which can be made by

reducing a solution of $CuSO_4$ with zinc dust). The solution is slowly heated to a mild boil for 10 hours with the temperature kept below 125°C. Some ring scission will have occurred so that phenolic compounds are mixed with the tar, safrole and unreacted benzodioxole. These phenols are removed by shaking the mix with 5% NaOH solution, extracting with ether and fractionally distilling under vacuum to give unreacted 1,3-benzodioxole and Safrole (yield=30%)

There is one other benzene to allylbenzene method that you should take a look at. Osmium sent in the article in which that magical clay and other similar catalyst add the allyl to aryl in record fashion. To read more check out ref #143.

ISOSAFROLE FROM PIPERONAL

[26]--This will work just as well in converting benzaldehyde to propenylbenzene as it will in converting piperonal. This is like the millionth method Strike has pulled from the reference 19. This was the most street-applicable article Strike has ever come across, but the greatest thing about this article's recipes is that THEY WORK! Strike means to say they work big time! A lot of this has to do, no doubt, with the fact that the most accomplished amphetamine chemists co-authored the work: Drs. Shulgin and Nichols.



Piperonal Isosafrole

This method is merely an application of the Grignard reaction but is a lot less troublesome because it uses really common chemicals. This method can be done as it was done in the reference where a phenylbutene was made using a bromopropane (bromopropane and bromoethane are cheap to purchase or can be made

from propanol or ethanol). These phenylbutenes will produce a perfectly respectable amphetamine that make an excellent substitute for X, but for confusion's sake Strike is going to describe the isosafrole synthesis as well.

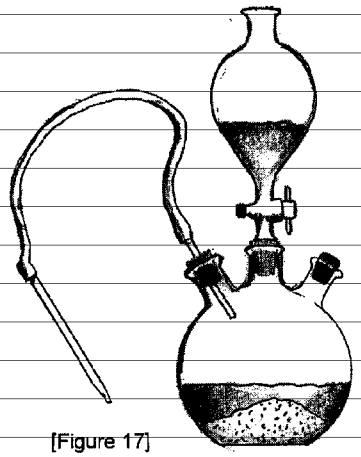
The apparatus to use is the same as fig.15. 52g of 1-bromopropane for the phenylbutene or 46g bromoethane for isosafrole or propenylbenzene is placed in the separatory funnel. In the flask is stirring a solution of 14g Mg turnings and 50mL anhydrous ether and the bromine compound is dripped into the flask over a 20 minute period of time then the solution stirred for an extra 10 minutes. Next, a solution of 50g piperonal (or 35g benzaldehyde) and 200mL anhydrous ether is placed in the separatory funnel and added drop wise to the Grignard reagent over 30 minutes time. The reaction mix is then refluxed for 8 hours, hydrolyzed by the addition of 75 mL ice cold saturated ammonium chloride solution and vacuum filtered to remove the crud. The etherial filtrate is washed with ice cold 1.5N HCl solution, dried through Na_2SO_4 and the ether removed by distillation to afford a residue of 62g of crude alcohol intermediate (almost 96% yield!).

The alcohol intermediate happens to be the exact kind of intermediate that was produced by the Grignard reagent reaction with propanal to produce isosafrole back-a-ways in the big chapter. So what the chemist does is apply the 1g of $KHSO_4$ to that crude alcohol intermediate and process it just as was done before to give isosafrole ,or propenylbenzene or 3,4-methylenedioxyphenyl -1-butene or phenylbutene (yield=91%!). This is a great little procedure.

CRYSTALLIZATION

All of the recipes in this book give ecstasy freebase oil as the final product. Although this can be used as is, it is much more preferable to crystallize it into a distributable, usable form. To do this one is going to place a hydrochloride (HCl) onto the NH_2 group of the MDA (or amphetamine) molecule. This is easy to do and does not affect the drug in any way. In fact, if one were to look at the active ingredients label on almost any pill bottle in the pharmacy one can see that the drug therein is referred to as 'whatever-drug.HCl'. The drug companies crystallize their freebases with HCl and so will the underground chemist.

To do this, one is going to generate a dry HCl gas by using the setup in figure 17. In the reaction flask is placed about 100g non-iodized table salt (NaCl) and 200mL straight-from-the-bottle 30-35% HCl (again, Strike is stressing that that $2.00/gal pool cleaner 30% HCl stuff works great!). These amounts do not have to be exact. All the chemist is doing is using enough salt to bind the water from the HCl solution. In the separatory funnel is placed an arbitrary amount of concentrated (96-98%) H_2SO_4 (let's say 100mLs). The HCl/salt mix doesn't need to be stirred but a little swirling at the beginning, to



[Figure 17]

mix the salt and acid, and occasionally during the addition is preferable.

In a plastic container the chemist dissolves her golden yellow freebase oil into some DCM, ether or ethanol. The chemist then starts a steady dripping of the sulfuric acid into the HCl/salt and white, puffy HCl gas will start to exit the glass rod or pipette which is at the end of the hose. That tip is then plunged into the solvent/freebase solution to bubble the gas through the solvent.

There's a few things to note about what happens next. If the freebase that the chemist has is not 100% pure (which it usually isn't) then there is going to be a little pre-crystallization crap that will crystallize first. This stuff is usually orange or pink and has a crumbly, nugget-like appearance. If this stuff is going to come out it will usually occur after about 30 seconds or so of steady bubbling. When the chemist sees this she stops the bubbling and vacuum filters this stuff from the solution. Every time the chemist vacuum filters during crystallization she must always wash the filter cake with a little extra solvent. Before she discards the filter with the crap in it she washes it with a little extra ether because there will always be some valuable freebase oil coating the filter . And no, that colored crap is not 'dirty X'. If one were to try it they would end up getting sick.

After the crap is removed, the bubbling is resumed and in about 30-60 seconds white, wispy crystals will start spewing from the tip of the pipette. Crystals will start forming everywhere and, if enough freebase is present, the whole solution will become a thick sludge of beautiful, white MDA.HCl crystals. It is the most satisfying sight to behold. These crystals are removed by filtration, washed with a little solvent and spread out to dry on a plate beneath a warming lamp. The remaining solvent still has more freebase and it will be bubbled as many times as necessary to crystallize all of it out. At the end of the run, sadly, no more white X will appear but there will be another small formation of colored crap. This is also discarded.

There is a very important point to stress about the above procedure. Strike listed ether, DCM and ethanol as crystallization solvents. But the one chemists should use is DCM. That's right...DCM! Strike is telling all of you right now that DCM is an absolutely superior solvent for crystallization. In fact it is so good that one need not purify the freebases acquired from the ends of half of the recipes in this book.

Most of the final product producing recipes in this book will provide for the chemist to take up the final free base product in DCM. Usually the freebase oil in the DCM is dark. Used to be that Someone-Who-Is-Not-Strike (SWINS) would have to distill the freebase to get clear yellow oil before crystallizing because when SWINS used ether or ethanol as a crystallization solvent, the colored crap would contaminate the final product. But not with DCM. Even with the grungiest (well...not too grungy) freebase, the crystals that come out are pure snow. The DCM so strongly solvates the contaminants that none remain in the mass of crystalled final product. The filter cake is sooooo clean even in the darkest solvent!

The other amazing thing about DCM is that the crystals produced in it are weird. Crystals produced by ether are little and powder-puffy. Nothing wrong with that per se. But the crystals produced in DCM are large, crystalline and sparkly. And although there shouldn't be a difference, SWINS swears the effects are more powerful.

There are some alternatives to this HCl generator type of crystallization. There are, of course, canisters of HCl gas that can be purchased. Also, one can crystallize with very concentrated (fuming) HCl by pouring the stuff directly into the ether/freebase [26]. Regular 35% HCl can do this too, but the water content may dissolve the MDA.HCl or make the crystals sticky which means that the chemist will have to dry the solution by removing the water.

One idea that Strike thinks is handy would be to set up the HCl generator and bubble as much HCl as possible into as much sol-

vent as can be spared by the chemist. What the chemist now has is a reagent of super-saturated HCl/solvent. This solvent can be stored indefinitely and be brought out for use when it's time to crystallize. All the chemist has to do is dissolve her freebase in as little solvent as possible, then pour in some HCl/solvent reagent. All of the freebase will instantly go poof! into crystals. All this means that the chemist won't have to keep setting up the generator apparatus all the time.

ANTIDOTE

With all that X lying around someone could conceivably OD on the stuff (an average dose is 100mg). This has never been reported to have happened in more than 40 years of medical documentation. Strike knows because Strike researched this fact very thoroughly. About the closest the government forensic scientists come to attributing a death to X is by stretching the facts of a case so irresponsibly that it can be at times quite amusing. Usually, the title of a medical case reads something like "A reported case of death attributed to the drug ecstasy". But if one reads the case report it is always about how the subject had been mainlining speed for a week or had seventeen existing mental and physical abnormalities prior to taking the X. Such people are ripe for an adverse reaction. Attributing such deaths to X is about the only way scientists or doctors can further whatever agenda they are being paid to further.

It is almost impossible to OD on X. A lethal dose is 70 hits for God's sake! Because of this, and the fact that there is rarely an adverse reaction to a normal dose, hospital personnel are not going to be very familiar with the proper treatment. So, if such a thing occurs it should be related to the doctor what drug it is and how it is treated [155]. The most immediate concern for any amphetamine overdose is fatality caused by hyperthermia (body gets too hot, bubba!). MDA and MDMA have a wide range of effects on the human body, but any of the following drugs, alone or in combination, will help: 5-HT uptake inhibitors such as Fluoxetine and Citalopram, 5-HT antagonists such as Ritanserin and Methiothepin, dopamine antagonists such as Haloperidol and

-butyrolactone, dopamine neurotoxic lesion compounds such as 6-hydroxydopamine, drugs enhancing GABA function such as Chlormethiazole and Pentobarbitone, and excitatory amino acid antagonists such as Dizocilpine and Dextromethorpan. Let Strike tell you this: if you had a buzz you would not have it very long if you were given any one of these drugs.

CHEMICALS

ALLYL ALCOHOL

[37 p459, 146 p42]--This chemical is not only useful in Friedel-Crafts reactions but is the major stepping stone for making allyl bromide which has wide uses. The set up to use is a simple distillation apparatus (no vacuum,bubba!) with a tube leading away from the vacuum adapter to a NaOH solution trap. 400g glycerol and 175g 88% formic acid are placed in the reaction flask and rapidly heated so that it reaches 195°C in about 30-45 minutes during which time CO_2 and a little distillate will evolve. At this time the receiving flask is exchanged with a clean one and heating is continued until a second wave of distillation occurs between the temperatures 225-260°C. After 260°C is reached the reaction flask is allowed to cool to about 115°C, 125g more formic acid is added and the solution heated again to 260°C collecting all the distillate that comes over between 195-260°C into the same receiving flask. A third formic acid addition is done to insure that as much allyl alcohol as possible is obtained. What the chemist has collected is neutralized with a little potassium carbonate and the allyl alcohol is distilled collecting the fraction comes over below 99°C. What the chemist is going to have now is about 210g of an aqueous solution that is 70% allyl alcohol. This can be made anhydrous by refluxing it with potassium carbonate, distilling and collecting the fraction that comes over between 94-97°C. What the chemist should really do is use the 70% solution directly in the production of the more preferable allyl bromide in the next recipe.

ALLYL BROMIDE

[146 p42]--This stuff is cheap and legal to buy. However, Strike has a premonition about the future security of this chemical. In a three-neck flask is stirred 1000g 48% HBr and 300g 98% (concentrated) H_2SO_4. After a few minutes of stirring 385mL of the 70% allyl alcohol made from above or 233g pure allyl alcohol is added. The chemist now attaches a separatory funnel into the

middle neck of the flask, a stopper in one of the side necks and in the final neck attaches a simple distillation setup. 300g of sulfuric acid is then dripped from the separatory funnel into the warm solution. The heat of the reaction alone will allow for the distillation of the allyl bromide as it is formed during the addition. This should take no more than 30 minutes. The crude allyl bromide that is collected is washed with dilute sodium carbonate solution, dried through Na_2SO_4 and simple distilled to give product which boils at 69-72°C (yield=92-96%). Allyl chloride is made using HCl instead of HBr.

BROMOBENZENE

[37 p535]--A flask is placed in an ice bath and in it is stirred 50g benzene and 0.5mL pyridine (slightly watched chemical). A condenser is attached and a drying tube made from a vacuum adaptor is prepared so that it has a hose extending to a glass of water (this will allow for the collection of HBr gas that will form during the reaction). The drying tube with its hose is not yet attached to the condenser. 125g (40mL) of liquid bromine is poured down into the reaction flask through the condenser and the drying tube is immediately attached. A vigorous reaction will occur and when it has died down the reaction is allowed to warm up to 25-30°C by removal of the ice bath and stir there for 1 hour. After 1 hour the solution is brought up to 65-70°C and kept there for 45 minutes or until no more red bromine vapors can be seen. Remember, all of that HBr vapor that bubbled into the glass of water can be salvaged as perfectly usable 48% HBr solution by distilling that water and collecting what comes over at 126°C.

The reaction solution is washed once with water, three times with 5% NaOH and once more with water. The benzene layer is dried through Na_2SO_4 and distilled with no vacuum collecting the fraction between 150-170°C. This fraction is then redistilled and the fraction coming over at 154-157°C is the pure bromobenzene.

ETHYL ETHER

Ethyl Ether--this is a condensed and modified version take from

"Practical Organic Chemistry" by Vogel (3rd ed., 1966 [37]). A simple distillation set up is used with a magnetic heating stir plate. Use of an open flame is absolutely forbidden because of the potential to ignite and explode any stray ether vapors. The distillation set up is used except that a two holed stopper is placed in the top opening of the three-way adapter to accommodate a thermometer and a small separatory funnel. the collecting flask is packed in ice and ice cold water is coursing through the condenser.

With brisk stirring 75mL Everclear (ethanol) is poured into the reaction flask then 75mL concentrated sulfuric acid is slowly added until incorporated. The rest of the distillation apparatus is connected and the solution slowly heated to about 140°C. Next, 150mL Everclear is dripped in slowly so as to match the approximate distillation output that one can see condensing over into the collection flask. The temperature must remain between 140-150°C. After all the ethanol has been added (which should have taken approximately 90 min) the distillate that has collected is washed with 5% NaOH solution then with water (remember that the ether will form the top layer here). The ether can then be dried through sodium sulfate and used or can be distilled to purify.

FUMING NITRIC ACID

This stuff is way too expensive to buy especially since it can be made so easily. 500mL regular nitric acid (HNO_2) and 500mL concentrated H_2SO_4 are mixed together in a flask and distilled with no vacuum. A reddish haze will appear over the reaction liquid which will distill over to give an orangy-red fuming nitric acid distillate. This stuff needs to be stored in the dark.

48% aq. HYDROBROMIC ACID

Recipes for making HBr (from Vogel's "Practical Organic Chemistry"[37])

"Hydrobromic acid. Method 1 (from bromine and sulphur dioxide). A mixture of 600g. (or 188.5ml.) of bromine, 250ml. of water and

750g. of crushed ice is placed in a 1.5 litre round-botomted flask and a rapid stream of sulphur dioxide (from a siphon of the liquified gas) is passed into the flask, care being taken that the outlet of the gas-delivery tube id below the surface of the bromine layer. The rate of flow of the gas is adjusted so that it is completely adsorbed. It is advisable to cool the flask in ice and also to shake the contents from time to time. The reduction is complete when the mixture assumes uniform yellowish-brown or yellowish colour, which is unaffected by further introduction of sulphur dioxide; excess of the latter gas should be avoided as it will be evolved during the subsequent distillation The flask is then connected with a short stilll head and condenser, and the mixture is distilled. The main product will pass over at 125-126° / 760mm., but the temperature may rise to 130°; the distillation is then stopped. The residue is sulphuric acid. The distillate is redistilled from a little barium bromide in order to remove traces of sulphuric acid, and the fraction, b.p. 125-126°--constant boiling point hydrobromic acid containing 48 per cent. HBr-- collected. The yield is about 1150g. or 90 per cent. of the theoretical.

$Br_2 + SO_2 + 2H_2O = H_2SO4 + 2HBr$.

Method 2 (from potassium bromide and sulphuric acid). Potassium bromide (240g.) is dissoleved in water (400ml.) in a litre flask, and the latter is cooled in ice or in a bath of cold water. Concentrated sulphuric acid (180ml.) is then slowly added. Care must be taken that the temperature does not rise above 75° otherwise a little bromine may be formed. The solution is cooled to room temperature and the potassium bisulphate, which has separated, is removed by filtration through a hardened filter paper in a Buchner funnel or through a sintered glass funnel. The filtrate is distilled from a litre distilling flask, and the fraction b.p 124-127° is collected; this contains traces of sulphate. Pure constant boiling point hydrobromic acid is obtained by redistillation from a little barium bromide. The yield is about 285g. or 85 per cent. of the theoretical.

Method 3 (from bromine and sulphur). (1). A 1-litre three necked flask is charged with 27g. of flowers of sulphur and 550 ml. of

water. The flask is equipped with a dropping funnel (with tip below the surface of the water), a water sealed mechanical stirrer and an Allihn reflux condenser; Ground glass joints are preferable, but used rubber stoppers are generally satisfactory. The flask is immersed in a bath of water at 60°, the mixture stirred vigorously and, when the temperature inside the flask is about 50°, 400g. (125.5ml) of bromine are introduced from the dropping funnel during about 20 minutes. The temperature of the reaction mixture rises rapidly as the reaction proceeds; the flask is cooled momentarily in a bath of cold water if the condensed bromine vapour is near the top of the condensor. When all the bromine has been added, the mixture is heated on a boiling water bath for 15 minutes. The reaction product is cooled, and filtered from residual sulphur and other solid matter through a sintered glass funnel. The filtrate is distilled and the constant b.p. hydrobromic acid collected at 125-126° / 760mm. The yield is 805g.

Note. (1) The reaction between bromine and sulphur in the presence of water may be represented by the equation:

$3Br_2 + S + H_2O = 6HBr + H_2SO_4$

It is rather slow at moderate temperatures and the hydrobromic acid formed in the initial stages of the reaction inhibits its further progress. By carrying out the reaction at 50-70° or above in the presence of a large excess of water, the inhibition observed at lower temperatures does not occur.

Cognate preparation taken as one intended for HI (hydroiodic acid, Hey! If it works for HI, it probably works for HBr).

Hydroiodic acid. A 1.5L three-necked flask is charged with a mixture of 480g. of iodine and 600mL water. The central aperature is fitted with a stopper carrying an efficient mechanical stirrer leading almost to the bottom of the flask, and the smaller apperatures respectively with a lead-in tube for hydrogen sulfide extending well below the surface of the liquid and with an exit tube attached to an inverted funnel just dipping into 5% sodium hydroxide solution. The mixture is vigorously stirred and a stream of hydrogen sulphide (either form a freshly charged Kipp's apparatus or from a cylinder of the gas) passed in as rapidly as it can be absorbed. After several hours the liquid assumes a yellow colour (sometimes it is almost colourless) and most of the sulphur sticks together in the form of a hard lump. The sulpur is removed by filtration through a funnel plugged with glass wool (or through a sintered glass funnel), and the filtrate is boiled until the lead acetate paper test for hydrogen sulphide is negative. The solution is filtered again, if necessary. The hydriodic acid is then distilled from a 500ml. Claisen flask, and the fraction b.p. 125.5- 126.5° / 760mm. is collected. This is the constant boiling point hydriodic acid and contains 57% of hydrogen iodide. The yield of the constant boiling acid is 785g. or 90% of the theoretical.

$H_2S + I_2 \rightarrow 2HI + S$

Note. The hard lump of sulphur remaining in the flask is best removed by boiling with concentrated nitric acid in the fume cupboard."

LITHIUM ALUMINUM HYDRIDE ($LiAlH_4$, LAH)

[147]--Everything here must be performed in the hood and everything must be as absolutely water-free as possible. The apparatus to use is the one in fig. 15. In the reaction flask is placed 30mL Et_2O (ether) and 23.5g lithium hydride which is stirred for a few minutes. In the separatory funnel is placed a mixture of 71.2g anhydrous aluminum chloride ($AlCl_3$) and 300mL ether which is dripped in at such a rate that the reaction produces enough generated heat to cause a sustained reflux but not so much that the reaction gets out of control. When the reaction has visibly ceased, the chemist filters the white particulates from the solution by vacuum filtration (the $LiAlH_4$ is in the filtrate solution). The ethereal filtrate is distilled with no vacuum until the residue that remains is syrupy then the rest of the ether is removed under vacuum to give a residue in the flask that is $LiAlH_4$ (86%).

There are a few points to remember about making this catalyst. When scientists were first synthesizing $LiAlH_4$ they found that it

was necessary to have a tiny piece of $LiAlH_4$ already in the reaction vessel to facilitate the start of the reaction between the LiH and $AlCl_3$. If the $LiAlH_4$ was not present then the $AlCl_3$ would keep being added and added until the solution would suddenly burst into an uncontrolled reaction. It was determined later that what caused this 'induction' period of no activity was the time it was taking for the protective coating of lithium hydroxide to dissolve away from the lithium hydride. Apparently all commercial lithium hydride has such a coating. Some people found that a drop of iodine would negate such a phenomenon but it was finally shown that if absolutely, 100% dry ether was used then everything went smoothly. This means that the chemist needs to dry her ether through Na_2SO_4 and distill it before use. The last thing to say is that it is probably a good idea to order lithium hydride and aluminum chloride separately.

METHYLAMINE

[144, 145]--No one should be buying this stuff because it is extremely watched and extremely easy to make. It's best to make this chemical in large batches. In the reaction flask of a simple distillation apparatus is placed 2000g of 40% formaldehyde and 1000g of ammonium chloride. The mixture is slowly heated to 104°C during which time all of the ammonium chloride will dissolve and the solution will be a bright, clear golden color. Lots of sparkly CO_2 bubbles will be evolved and as the solution approaches 100°C a steady run of distillate will commence. After 4-5 hours of maintaining the temperature at 104°C nothing more will distill over and the heating is stopped. If the solution is allowed to heat over 104-105°C then there will be product loss.

As the solution cools a big old mass of unreacted ammonium chloride will form. The chemist removes this by vacuum filtration and saves the crystals for reuse at another time. The golden colored filtrate is placed back in the flask and distilled (with vacuum now!) to reduce its volume by about a third. Temperature is not so much a problem now as the chemist will let the stuff distill over at whatever temperature is necessary. Sometimes the reducing solution is so concentrated that the remaining ammonium chloride crystals

will form in the hot solution as the flask is being heated. No harm done. Either the second batch of crystals form on their own or the chemist, after removing a third of the liquid, allows the flask to cool which will readily bring out a second crop. This second crop of ammonium chloride crystals is separated, saved and the filtrate is once again returned to the reaction flask to be reduced in volume by distillation.

The chemist may have to do one, or possibly two more volume reductions before all of the excess ammonium chloride is removed (usually just one more). Now, what the chemist will be looking at after the last removal of ammonium chloride is a light yellow, slightly viscous solution that is about 1/3 the volume of the original filtrate. The chemist puts this to distill once more. What often happens next is that while the chemist goes off to watch TV the solution will distill off just a little bit of volume and poof! the hot solution will become an instant mass of methylamine hydrochloride. If this doesn't happen for the chemist then she will just reduce a little bit and chill. Either way, what the chemist is going to have is a nice mass of methylamine hydrochloride crystals that she separates by vacuum filtration.

The way the chemist knows that she has methylamine and not ammonium chloride is that she compares the look of the two types of crystals. Ammonium chloride crystals that come from this reaction are white, tiny and fuzzy. The methylamine hydrochloride crystals are longer, more crystalline in nature and are a lot more sparkly. The chemist leaves the methylamine crystals in the Buchner funnel of the vacuum filtration apparatus and returns the filtrate to the distillation set up so it can be reduced one last time to afford a second crop. The combined methylamine hydrochloride filter cake is washed with a little chloroform, scraped into a beaker of hot ethanol and chilled. The methylamine hydrochloride that recrystallizes in the cold ethanol is vacuum filtered to afford clean, happy product (yield=50%).

There is no way this section would be complete without Eleusis' classic "Methylamine FAQ". It was Strike's first-ever introduction to this person's work and it is still Strike's favorite:

"Synthesis of Methylamine/Methylamine HCl via Hofmann Rearrangement

*There are two approaches to producing an amine from an amide using the Hofmann rearrangement reaction. One way is to react the primary amide with an alkaline-halide solution (eg - Sodium Hydroxide and Bromine). The other method is to use an alkaline-hypohalite solution (eg - Sodium Hydroxide and Calcium Hypochlorite). The astute observer will notice that there is *no* chemical difference in the two processes. One produces the Hypohalite in situ, the other uses the Hypohalite itself. Substitution of various halogens/ halides/ hypohalites/ hydroxides is acceptable, but I feel I have picked the best combination of maximal yield and ease of availability. Feel free to prove me wrong ;-). Also, at least one text specifies that Sodium Hypochlorite produces much higher yields than Sodium Hypobromite. This delicious vindication is expected since Chlorine is a more reactive halogen than Bromine. Now, we are going to use Calcium Hypochlorite, in the form of powdered pool shock, because concentrated Sodium Hypochlorite is a rare, unstable creature indeed. Our yield will not suffer in the slightest because of this.*

The main example presented will be the alkaline-hypohalite method as it is the easiest to acquire the necessary chemicals. It is of interest to note that the alkaline-halide method is much easier to perform, process- wise, in that it is more forgiving of sloppy technique.

The general theory behind the process is that the hypohalite will convert the amide to a haloamide. This then spontaneously changes to the isocyanate when heated and decomposes to the amine from the water present. In effect, all that happens is that a Carbonyl (CO) group is stripped off the starting amide to yield the corresponding amine. Yields pre- purification are around 80%, post-purification average around 65%. Certain uses of the resulting amine will not require purification, though, so it will be left up to you whether or not to perform those steps.

To make methylamine we start with Acetamide. The general, unbalanced reaction process is thus:

$CH_3CONH_2 + Ca(OCl)_2 \longrightarrow (CH_3CONCl)_2Ca^{++} + H_2O$

then

$(CH_3CONCl)_2Ca^{++} + NaOH \longrightarrow CH_3NH_2 + Na_2CO_3$

**CAUTION* Methylamine is a poisonous, noxious inflammable gas. It has a strong ammonia/rotting fish-like odor. It's not as bad as Chlorine gas, though, which can be produced if one is careless in the beginning!*

One reference to keep in mind (Thanks to J.W. Smith for sending this one) concerns the first step of the reaction.

Whitmore and Thorpe, J. of the Amer. Chemical Society, Vol 63, April 1941, p1118

"It was necessary to allow several hours for the formation of the N-chloroamide before heating to degradation temperature. With this modification it was possible to prepare methylamine...consistently in 78% yield."

*In my experience, this is a *true* statement. Please remember to keep the reactants well iced, though. Now, to begin:*

In a large mixing bowl which can contain a smaller stainless steel mixing bowl, prepare an ice bath with water and salt to bring the temperature down to -10C or so. Setup your glassware for simple distillation with magnetic stirring beforehand because certain steps need to be performed quickly. Use a vacuum adapter to connect to the receiver flask, and attach some rubber or polypropylene tubing to the vaccum nipple to connect to a bubbler setup (a funnel inverted in a beaker, or a plastic aquarium aerator tube). The distilling flask should be sitting in a stainless steel bowl with nothing in it (you will add pre-heated oil to the bowl).

**NOTE* In order to make this as painless as possible, please observe the following recommendations: 1) Keep the mixing bowl temperature as close to 0C or less as possible; 2) Keep the Hypochlorite solution as it is being added as close to 0C or less as possible; 3) After half the Hypochlorite solution has been added, place a plastic bag with 50-100g ice/salt/water mix into the bowl to help keep temperatures low (use this instead of directly adding ice to the reactants, which adds a considerable volume of water making the process less volumetrically efficient); 4) Purchase an 8lb bag of ice ahead of time!*

Next you will prepare three solutions.

10g of Acetamide in 20mL of distilled water. 16.4g of Calcium Hypochlorite (Pool shock) in 50mL of hot distilled water 24g of Sodium Hydroxide (Lye) in 40mL of cold distilled water

This last solution should be prepared slowly as it is quite exothermic. Set all three aside in a freezer. Now prepare the mixing apparatus which will be a stainless steel "mixing bowl" suspended in the ice/salt bath made earlier. We use a stainless steel bowl here so that heat transfer will be maximal, while preventing any corrosive interaction. A glass bowl will not be sufficient for larger scale preparations as it will not conduct heat fast enough to prevent the reactants from going over 10C (at which point the Haloamide will decompose and you'll have to start over). Take the Sodium Hydroxide solution out of the freezer once it is cool, but not cold.

*After the bowl has been sitting in the ice bath for a few minutes, add the Acetamide solution. Stir well until the solution has cooled to -10C. Now, *slowly* add the Hypochlorite solution to the mixing bowl in bursts of no more than a couple mL while stirring vigorously. If you do this perfectly, there will be no fizzing or bubbling at all. This depends on how cold you keep the mixture, and how slowly you add the pool shock! Realistically, the considerable heat evolution of the reaction will make adding the last few mL a trying task! Keep an additional 50g of ice on hand to throw directly into the mixture if necessary. This solution *may* evolve Chlorine gas so you should obviously perform this step under a fume hood or outside). Keep stirring until it has calmed down and turned a turbid colorless to light green Let it sit for 2 hours, stirring occasionally and making sure that it never gets warmer than 5C.*

After the 2 hours is up, add the Sodium Hydroxide solution quickly with stirring. The solution should immediately turn a chalky, milk white. That's because a lot of Sodium Carbonate just got generated. You no longer need be concerned over it's temperature, so you can leave the solution in this state overnight if perhaps the hours have passed by too quickly and you've suddenly realized it's 2:00am.

Preheat a water bath on the stove (or wherever) to about 80C and place the stainless steel mixing bowl in it. Once the temperature of the solution hits about 65C, take the bowl out and set aside while stirring all the while. This is where it rearranges, and the reaction is exothermic enough to sustain it's temperature nicely. If you find the temperature climbing past 80C, immerse the bowl into some cold water briefly. After about 15 minutes the temperature will start to fall, at which point you should transfer the whole mess to the distilling flask. Before you continue you need to choose whether you want to make the hydrochloride salt or the aqueous solution of Methylamine, though.

*Heat the flask using an oil bath to 100C after adding this solution to effect gentle boiling which will drive off the Methylamine as a gas. In my experience, misbehavior is likely to occur at this point. One particular problem to watch out for is the sucking back of bubbler solution (be it plain water or 6N HCl) into the receiver flask. I don't know why the pressure in the distilling flask would go below atmospheric, and therefore cause this to happen, but it has several times with me. Needless to say, this results in a serious mess and *botches* the whole process (I have found a cure for this by using an automotive one-way vacuum valve, like a PCV).*

Continue heating the flask contents until you have collected around 100mL of distillate in the receiver.

*For the aqueous solution: Place 18mL of cool distilled water into your bubbler setup. The *expected*, not theoretical, yield of Methylamine from this amount of reactants is 7 grams. I have used a plastic aquarium aerator tube as the bubbler with excellent results. Sure beats using an inverted funnel.*

For the HCl salt: Do exactly as above except use 6N Hydrochloric Acid. 6N HCl may be produced by diluting 60.4mL of "Muriatic Acid" to 100mL with distilled water. Evaporate the bubbler solution to dryness then add 15ml of water, 10mL 10% NaOH soln. and heat gently to a boil with constant motion until dense white fumes appear. This will remove the Ammonium Chloride. Remove from heat while stirring as it cools down. Pulverize the dry residue, then reflux with absolute Ethanol for several minutes. Filter the refluxed soln. on a heated Buchner or Hirsch funnel, then distill the alcohol off the filtrate until crystals just begin to form. Allow the soln. to cool naturally to room temperature, then cool further in an ice bath. Filter the solution on a chilled Buchner funnel with suction. The yield of Methylamine Hydrochloride should be around 55% of the theoretical.

To clean the white residue off of your glassware, dump some muriatic acid straight from the jug onto them and swirl.

References: Journal of Chemical Education, v14, pg542 Organic Reactions volume 3 Vogels Elementary Practical Organic Chemistry, pg574

Methylamine/Methylamine HCl via Schmidt Rearrangement

This reaction is quite similar to the Hofmann Rearrangement, but it reacts a Carboxylic Acid with Hydrazoic Acid to generate the desired amine. Like the Hofmann, it has wide application and versatility, yet also has excellent yields in many cases. It will also preserve the chirality of the starting Acid/Anhydride, which is not of interest to us, but an important fact to note. The restrictions on this process are that the starting Carboxylic Acid must not adversely react with either Sulfuric Acid or Hydrazoic Acid. It would be a crime if I didn't also mention that the Schmidt Rearrangement has much greater application than just making amines from carboxylics, but that is well beyond the scope of this FAQ. See Organic Reactions v3 for more details.

*To make Methylamine or the HCl salt using the Schmidt Rearrangement, you start off with glacial Acetic Acid. You might be saying to yourself, "Damn, why bother with the Hofmann!" since glacial Acetic Acid is so easy to get, but, there is a drawback... And that is Hydrazoic Acid, which is *not* easy to get. As well, Hydrazoic Acid is extrememly poisonous and should not be handled without a fume hood under *any* circumstances. Really. This is coming from a guy who has no problem distilling Ether solutions in his kitchen, so take it seriously. Why bother, then? Well, because you *can* generate the Hydrazoic Acid in situ using Sodium Azide and conc. Sulfuric Acid. I have not personally tried this because I don't have a powder addition funnel. Anyway, Sodium Azide is not too hard to come by through chemical supply houses and Sulfuric Acid is easy to acquire in the form of Instant Power*

Drain Opener. This reaction MUST be performed in an area of adequate upward ventilation, or at least with the air flowing away from you.

NOTE In the initial testing of any undesireable interaction between Sodium Azide, Acetic Acid and Sulfuric Acid, I mixed 5mL of each into a small cup underneath my "fume hood". Though I smelled *nothing*, within seconds my head felt like it was expanding, my heart started racing, and I felt more weak and confused than normal. I just barely escaped and recovered in 15 minutes, but, Needless to say, this procedure is a *tad* on the dangerous side. You have been *warned*.

Theory behind this reaction is:

$R\text{-}COOH + NaN_3 \text{ ---}H_2SO_4\text{---> intermediates ---}H_2O\text{---> } R\text{-}NH_2 + CO_2$

The intermediates in making amines are isocyanates (O==C==N) just like the Hofmann Rearrangement. The isocyanates are decomposed with water, just like the Hofmann. In fact, there is a lot of similarity between the Hofmann and the Schmidt reactions. Before I detail the synthesis steps, I should note that if you wish to generate the Hydrazoic Acid in the flask by adding Sodium Azide, you might need a powder addition funnel. This bit of equipment is quite pricey and it's likely you won't have one, so the first part of the synthesis details how to make the Hydrazoic Acid separately.

There are three variations on this process you may choose from:

1) Add Hydrazoic Acid to a Carboxylic Acid/Benzene or Chloroform mixture (O.React. claims this is the preferred method). 2) Add Sulfuric Acid to Carboxylic Acid/Hydrazoic Acid/Benzene or Chloroform mixture (this is my prefered method). 3) Add Carboxylic Acid/Hydrazoic Acid/Benzene or Chloroform mixture to Sulfuric Acid or Sulfuric Acid/Benzene or Chloroform mixture.

a) Preparation of Hydrazoic Acid

CAUTION This compound is EXTREMELY EXPLOSIVE and HIGHLY TOXIC! I am not exaggerating! Do not, under ANY circumstances, allow the acid to heat above room temperature (bp: 37C). Use latex gloves to handle, and dispose of small quantities using plenty of water followed by dilute baking soda/water.

Prepare a paste out of 65g Sodium Azide (1m NaN_3) and 65mL of water in a beaker. Add 400mL of either Chloroform or Benzene to this paste (depending on what you have available, but be consistent later on) and stir well. Dump this mixture into a round bottom flask situated in an ice/salt bath, drop in a stirrer magnet, attach a Claisen adapter, addition funnel, and thermometer. Let this mixture cool to 0C.

Place 49g of cold concentrated Sulfuric Acid into the addition funnel, but only after you make sure the stopcock is turned OFF. Ever so slowly add the acid to the flask, dropwise, such that the flask contents stay around 1C, and never go over 5C. This might take a while, be patient. After all is added, pour the flask contents into a separatory funnel (ventilation is absolutely required here) and separate out the aqueous layer. Your HN_3 is dissolved in the Chloroform/Benzene layer. If you wish to determine the exact concentration of the acid, you may titrate it, but the reaction generally goes to completion with no secondary hydrazides forming as long as you kept the temperature where I told you to. Some HN_3 might have gone to the aqueous layer, but mostly the resulting Sodium Sulfate will crowd it out. The resulting concentration, then, is the moles of Hydrazoic Acid over the the total moles of HN_3 and your solvent (Chloroform = 117g/m, Benzene = 78g/m).

b) Making the Amine (All Variations)

Setup your glassware for simple distillation with a claisen adapter, three way adapter, pressure-equalized addition funnel, water cooled condenser, vacuum adapter and receiver flask to catch any condensed solvent vapors.

c) Specifics for Variation 2

Drop your stirrer magnet into the flask and add 250mL of Benzene or Chloroform (take your pick), Next, add .25 moles glacial Acetic Acid (15g) then .5 moles Hydrazoic Acid with stirring. Warm this solution to about 40C using a water bath. Make sure all joints are air tight. Add 20mL concentrated Sulfuric Acid very slowly. The reaction is mildly exothermic, so take care and watch the temperature. The reaction finishes within 2 hours. The amine is in the sulfate salt form. To convert to the hydrochloride salt form, first add an equinormal amount of 10% NaOH solution and stir well. Next, extract the free amine with ether and bubble HCl gas through it to precipitate out the crystals. Filter to recover.

Methylamine HCl from Formaldehyde and Ammonium Chloride

This is the least desirable of all three processes [What do you mean by that? This is really easy to do! And the yield are fine!]. The yields are lower than the two rearrangements, and it requires substantial labor to get a decently pure product. Not "labor" as in difficult but "labor" as in a lot of it. I would suggest this only for those who have a large supply of Formaldehyde available to them (note - N. Coffey found formaldehyde at Home Depot - look for "Mildewcide" and dissolve it in enough water to make a 37% solution to depolymerize the paraformaldehyde).

Place 250g of Ammonium Chloride and 500g of technical Formaldehyde (37%, Formalin). Rig the flask for simple distillation such that a thermometer extends into the reaction mixture, and a Liebig

or West condenser. Heat the mixture on the steam bath until no more distillate comes over, then turn up the heat and hold the reaction temperature at 104C until, once again, nothing else comes over. This should take from 4 to 5 hours. The distillate may contain interesting things, so check out footnote 1 for details on what to do with it. Next, the reaction flask should be cooled rapidly to room temperature by immersion into first a warm water bath (60C) swirled, and then an ice bath. Filter the solution on the vacuum Buchner funnel to recover ~62g of Ammonium Chloride crystals. Concentrate the filtrate using moderate vacuum and gentle heat until the volume is reduced to half. Filter the mother liquor once again after cooling quickly to yield a second batch of Ammonium Chloride, ~19g.

Transfer the filtrate to a ceramic evaporating dish and heat on a water bath until a crystalline scum forms on the top. Cool the dish quickly then filter the mess on the vacuum Buchner to yield ~96g of Methylamine Hydrochloride. Concentrate the filtrate once again to obtain a second crop of crystals, ~18g. Concentrate the filtrate a third time as far as possible using the water bath, then store the dish in a vacuum dessicator loaded with Sodium Hydroxide in the bottom for 24 hours. Add Chloroform to the residue left in the crucible to dissolve out Dimethylamine Hydrochloride (distill off the Chloroform to recover - good stuff) then filter on the venerable old vacuum Buchner funnel to yield an additional ~20g of Methylamine Hydrochloride, washing the crystals in the funnel with a small portion of Chloroform (~10mL).

Purification of the Methylamine HCl is in order now, so transfer all of the crude product to a 500mL flask and add either 250mL of absolute Ethanol (see end of FAQ for preparing this) or, ideally, n-Butyl Alcohol (see Footnote 4). Heat at reflux with a Calcium Chloride guard tube for 30 minutes. Allow the undissolved solids to settle (Ammonium Chloride) then decant the clear solution and cool quickly to precipitate out Methylamine HCl. Filter rapidly on the vacuum Buchner funnel and transfer crystals to a dessicator (see Footnote 3). Repeat the reflux-settle-cool-filter process four

more times if using absolute Ethanol, or two more times if using n-Butyl Alcohol. The yield of Methylamine HCl should be 100g.

Footnote 1 - The byproducts of the first step are Dimethoxymethane and Sodium Formate.

Footnote 2 - The Methylamine solutions in all steps should be cooled rapidly to promote smaller crystal formation.

Footnote 3 - According to the original document, centrifuging is the most satisfactory method of drying products because of their hygroscopic nature. I suggest warming in an oven on a glass dish then transfering to a vacuum dessicator loaded with either concentrated Sulfuric Acid or Sodium Hydroxide in the bottom. It is not normally necessary to have absolutely dry Methylamine HCl anyway.

Footnote 4 - The solubility of Ammonium Chloride in absolute Ethanol is 0.6g/100g at 15C. The solubility in n-Butyl Alcohol is neglible, even at its boiling point. If you use n-Butyl Alcohol, you will only need to perform 3 reflux/filter operations to obtain sufficiently pure Methylamine Hydrochloride.

References to this section: Sharp & Solomon, J. Chem. Soc. 1477 (1931) Werner, J. Chem. Soc. 850 (1917) Sommelet, Compt. rend. 178, 217 (1924) Hofmann, Ann. 79, 16 (1851)

Synthesis of Acetamide from Acetic Acid and Urea

Urea is conveniently obtained as a constituent of many fertilizers and so it is easily obtained. Sources have indicated that a 50lb bag can be purchased for $15 in the US. It is of less than ideal purity from this source, so some washing will be in order (with what?). Glacial Acetic Acid is easily obtained from photographic supply stores in high purity and for cheap as well. This reaction produces Acetamide with such purity that the product does not

even need to be recrystallized (the reaction goes to completion with no side products). The reaction is:

$CH_3COOH + NH_2CONH_2 \longrightarrow CH_3CONH_2 + CO_2 + 2NH_3$

Place 125g Urea and 125g of Acetic Acid in a 500mL round bottom flask in preparation for simple refluxing with magnetic stirring and without cooling water (or use cooling water heated to about 80C). Attach condenser, claisen adapter and place thermometer so that the bulb is around 1cm from the bottom, fully immersed. Heat on the mantle gently to bring the temperature of the mixture to 150C in 20 minutes. The mixture should be refluxing in the condenser, and probably subliming in it as well unless heated "cooling" weter is used. Push any crystals back down as necessary. Hold at reflux until the temperature rises to 195-200C (approximately 1.5 hours) Allow to cool, then rearrange the condenser for distilling (its really preferable to use 80C water in the condenser). Heat to collect nearly pure Acetamide starting at 200C with most coming over from 214-216C. If the product smells strongly of mice (as in the rodents), then recrystallization from warm methanol is in order. To recrystallize, take 50g of Acetamide, dissolve in 40mL warm Methanol, add 100mL Ether to crash it out and allow to stand. If no crystals have formed after an hour or so, gently scratch the inside of the beaker with a glass rod. If your product is only faintly odorous and is colourless to white, then it is considered pure. Melting point is 80.5C.

Synthesis of Acetamide from Ethyl Acetate and Ammonia

Ethyl Acetate is allowed to mix with concentrated Ammonia solution for several days to make Acetamide. This is a very attractive method because all the reagents involved are easy to acquire and cheap.

a) Preparation of Ethyl Acetate from Ethanol and glacial Acetic Acid

Dehydrate at least 100mL of grain alcohol to yield absolute Ethanol. 74mL (58g) will be required. Add this quantity of Ethanol to a round bottom flask with 225g glacial Acetic Acid and 3g of concentrated Sulfuric Acid. Heat at reflux on an electric heating mantle for 12 hours then attach a Vigreaux or Hempel fractionating column to distill off the crude ester at 76-77C. Change receiver flasks and recover the excess of Acetic Acid, bp 118C. Wash the first receiver contents with a half volume of saturated Sodium Bicarbonate solution then add 50g of anhydrous Sodium Sulfate (the salt of Sulfuric Acid and Sodium Hydroxide, dried in an oven at >100C for several hours) and distill the pure dry ester once again. Yield should be greater than 70g.

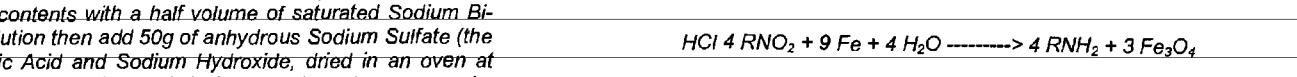
b) Reaction of Ethyl Acetate and Ammonia to make Acetamide

Add 44g of Ethyl Acetate and 90mL of concentrated Ammonia solution (~28%) to a 500mL round bottom flask with a stirrer magnet. Plug the neck with a thermometer in a thermometer adapter and stir gently for 48 hours or until the mixture becomes homogenous (stop the stirrer occasionally to check). Attach standard distillation apparatus but leave off the receiver flask at first, connecting a short piece of rubber tubing to the receiver adapter which is submerged in a beaker of dilute HCl (10-20%). Heat gently on a mantle to drive off the excess ammonia into the beaker. When no more bubbles come over then attach the receiver flask and commence distilling acetamide from 170C up, rapidly. Run 80C water though the condenser to prevent clogging. Once distillation slows to a crawl, remove the receiver flask and set aside in a hot water bath (80-90C). Clean up the glassware used for the distillation then use the receiver flask as the distilling flask and a glass container with screw-lid top as a receiver. Run 80C water through the condenser as before, and redistill the Acetamide,

which should come over completely at 216C using the heating mantle. Yield should be greater than 24g.

Reduction of Nitromethane

The lower nitroalkanes (sometimes refered to as nitroparaffins) are easily reduced by a multitude of systems, but by far the easiest, and also the highest yielding, is the Iron/Hydrochloric acid system. The reaction is:



*First, your Nitromethane *may* require purification, especially if it was for "fuel" use. In this case, it needs to be vacuum distilled at a vacuum of better than 100mm Hg. At that pressure, it will come off at ~47C. Distillation at atmospheric pressure is possible, but I do not recommend it due to the highly flammable nature of the compound and because it's flash point is 42C. It's your choice.*

**CAUTION* - The lower nitroalkanes form shock and/or temperature sensitive EXPLOSIVE compounds with amines and hydroxides. BE CAREFUL, DAMNIT! You have been warned.*

Heat the reaction mixture to 100C and hold for 14 hours. A temperature regulator is necessary if using a heating mantle, else use a large boiling water bath (if you will be doing it overnight, so it doesn't run out).

At the end of this time, allow to cool then add enough 25% Sodium Hydroxide solution to to get the pH above 11. Heat on a water bath or with gentle electric heat to drive the Methylamine off as a gas into the same beaker of Hydrochloric acid used as a trap during the reaction.

Evaporate the beaker contents to dryness on a glass plate in the oven to collect the crystals of Methylamine HCl (hygroscopic!). The yield should be approximately 15g (95%).

NOTE: Alternately, you may want to try using a Tin/HCl system which will give an equivalent yield in a much shorter time with the disadvantage that Tin is a much more expensive metal. The balanced equation for the reduction follows:

$2CH_3NO_2 + 6Sn + 12H+ \text{---> } 2CH_3NH_2 + 3Sn(IV) + 4H_2O$

Cognate procedure: Setup a flask with reflux condenser in which .25 mol of nitromethane, .38 mol of granulated tin metal and a stirrer magnet have been added. Carefully pour 115mL of 31.45% hydrochloric acid (muriatic acid) down the reflux condenser in 10-15mL increments, waiting for the reaction to settle down before pouring the next aliquot. If the reaction seems to get out of hand (excessive frothing, vapor escaping the reflux condenser, etc...) then quickly slide an ice bath in place until it slackens back down. Once all the HCl has been added, heat the mixture to reflux with an electric mantle for 1hr. At the end of this time, allow to cool, preferably in an ice bath, then add, carefully, a chilled solution of 75g sodium hydroxide in 125mL of water. If the flask contents start to bubble violently you will watch your yield go out the window, so add slowly! Since methylamine readily dissolves in water, you will need to distill the reaction contents carefully to first liberate the 40% constant boiling solution (bp: 53) and then the gas itself. The product is best captured by bubbling the distillation vapor into a beaker of hydrochloric acid (use a slight molar excess of HCl to insure no loss). Proceed as above by evaporating the bubbler solution to yield the crystals (take care when evaporating HCl solutions, as the excess acid will vaporize into the air, corroding ovens, lungs, etc...). [Vogel's, pg 892]

Additional notes - Nitromethane is found in high performance RC model fuel, usually as a mixture with methanol and various strange lubricants. One particular brand, found at a local hobby shop, was 55% nitromethane.

Johnson & Degering, J. Am. Chem. Soc., v61, 1939, pp3194-3195

Hydrolysis of Hexamine

Hexamine, more formally known as Hexamethylenetetramine, is easily and conveniently produced from Formaldehyde and Ammonia solutions. Formaldehyde may be easily produced by depolymerizing, with heat, Paraformaldehyde (the only ingredient in OTC MildewCide). Hexamine is then reacted with Hydrochloric Acid and heated to yield Methylamine HCl in near quantitative yield.

The pertinent equations are thus:

$6\ HCOH + 4\ NH_3 \text{---> } 1\ C_6H_{12}N_4 + 6\ H_2O\ 1\ C_6H_{12}N_4 + 4\ HCl + 4\ H_2O \text{---> } 4\ CH_2NH_3{*}HCl + 2\ CO_2$

a) Preparation of Formaldehyde

Place 3 3oz packets of Mildewcide into a 1L flask with an electric heating mantle and cork in the neck connected to a gas bubbler immersed in at least 550mL of distilled water. Heat the paraformaldehyde (what is in the Mildewcide) to between 180-200C (a temp. regulator is absolutely necessary for this step or use a silicone oil bath). The paraformaldehyde will depolymerize making formaldehyde gas in about 91% yield. Alternatively, the gas can be bubbled through the Ammonia solution directly (only for the brave!!!). If the Formaldehyde solution will not be used immedi-

ately, 55mL of methanol should be added to it to prevent flocculation (repolymerization).

b) Preparation of Hexamine

**CAUTION* - Formaldehyde and ammonia solutions are extremely poisonous and quite noxious. Perform this step in a well-ventilated area (outside or with direct exhaust of the fumes)!*

*454mL of 40% Formaldehyde solution (Formalin) or 490mL of 37% technical grade solution is *slowly* poured into a tall beaker containing 250mL of 28% Ammonia solution. Stir vigorously the entire time. The solution will get hot as the reaction occurs, take care that the Formaldehyde solution is not added too rapidly otherwise it will boil over.*

Allow this mixture to react, with stirring, overnight.

Evaporate off the water by heating the beaker in a hot water bath. (CAUTION: excess ammonia will be liberated!)

The yield of Hexamine should be 140g, white crystals.

c) Hydrolysis of Hexamine

140g of Hexamine is carefully dissolved in 400mL of Muriatic Acid (31.45% HCl) with vigorous stirring. After all is added, heat on the water bath. This will drive off the formed Carbon Dioxide and then the excess water. The yield of Methylamine HCl is 270g, colourless to just barely white deliquescent crystals.

If the crystals are opaque white and do not deliquesce quickly in air of average humidity (65% rh), they may be contaminated with some Hexamine. Washing 100g of the crude product with 100mL of Chloroform by stirring in a beaker then filtering, repeated as many times as necessary, will remove Hexamine. Methylamine HCl is insoluble in Chloroform whereas Hexamine is at the rate of 1g to 10mL.

Synthesis, March 1979, Blazevic, "Hexamethylenetetramine, A Versatile Reagent in Organic Synthesis", pp161-176"

NITROETHANE

[148, 149]-Strike couldn't find any decent nitroethane synths except for a couple of Chemical Abstract articles. One suggestion is to treat 1.5 moles of Na_2CO_2 with 1 mole of sodium ethylsulfite and 0.0645 moles of K_2CO_3 at 125-130°C. Another route would be to use silver nitrate and ethyl iodide [8 p119]. This type of reaction has been used to nitrate other paraffins and would probably work.

Luckily for all of you there were a lot of people who contributed some very nice protocols for this extremely important chemical. The first recipe below was sent to Strike unsolicited in the mail by someone named Don Antoine (a very nice person) [150] (Note: Strike was not given a complete citation with the article and so can only give a partial reference for this article. Sorry):

"Initial Run. - Into each of seven stoppered bottles was placed a mixture of ethyl sulphate [EtO-SO_2-OEt] (120 g.) and sodium nitrite [$NaNO_2$] solution (120 g. in 160 c.c. of water.) The bottles were shaken mechanically for 20 hours, the pressure being released at intervals. The contents were then poured into a separating funnel, and the upper layer separated, dried over calcium chloride and distilled at 14mm., the distillate up to 60° being col-

lected (the residue, ca 230 g., consisted of ethyl sulphate and was used again). The distillate was fractionated at atmospheric pressure, and the fraction of b.p. 114-116° collected. This was shaken with water, dried over calcium chloride, run through charcoal and redistilled ; b.p. 114-115.5°. Yield, 124 g. (31% or allowing for recovered ethyl sulphate, 43.5%).

Routine Run. - A second experiment was then carried out using the same quantities of ethyl sulphate as above. The recovered nitrite solution (lower layer) from the first run was concentrated by adding approximately 16 g. of sodium nitrite per 160 c.c. of solution . Yield, 185 g. (46%, or allowing for recovered ethyl sulphate, 65%)."

This next method was included with a submission by Ritter that appeared in the **Theoretical** section of this book.

"*Ethyl bromide 32g, 26.0 ml (.3mol) or Ethyl iodide 46g, 24ml (.3mol) is poured into a solution of 250 ml Dimethylsulfoxide (DMSO) or N,N Dimethylformamide or N-methylpyrolidone (DMSO preferred), 36 grams sodium nitrite (that's $NaNO_2$ pyromaniacs, not sodium nitrate) and 52 grams phloroglucinol dihydrate. This stuff is expensive but it can be recycled. Stopper all this in a flask with a good magnetic stirring bar and stir it in a room temp. water bath for 2 hours or until an emulsion forms. At this point dump all into 600ml ice water and extract w/ two portions of 200ml methylene chloride. The MeCl2 extracts are washed w/water three times then dried w/ anhydrous magnesium sulfate then evaporated off in a fractional distillation setup, collecting the fraction that boils at 113-116'C at atmospheric pressure as pure nitroethane. Expected yield about 20 grams. That's not a ton of product but this reaction can be scaled to any size you can dream of and yields will stay in the 80% range.*"

The only other thing Strike has to say is that some have hinted that all of those β-nitropropene reduction methods (or at least

some of them) and others like them (which did not include) can be used to reduce species such as nitroethene to nitroethane. That certainly sounds reasonable. Now where the hell can one find nitroethene?

SODIUM AMALGAM

[37 p194]--This is done in the hood because it has the potential to generate poisonous vaporized mercury. In a small flask is placed 15.2g of pure sodium metal with no stirbar. Sodium metal is explosive when put in contact with water. The sodium is immediately covered with about 100ml of toluene and slowly heated on the hotplate. Near a temperature of around 50°C the metal will melt in the hot toluene and at this point 750g of mercury are added drop by drop. The first few drops will cause violent bubbling of the toluene but this will diminish as the addition continues. When addition is complete, the chemist decants most of the toluene leaving just enough to cover the molten catalyst so that it will not degrade by exposure to the air. Now, while still hot, the toluene/amalgam mix is poured into the container the chemist wishes to store it in, the rest of the toluene is decanted and the air space flushed with nitrogen before sealing the container. The amalgam the chemist made is one of 2% strength.

SODIUM BOROHYDRIDE ($NaBH_4$)

[151]--This catalyst should really be purchased rather than made because its use in underground chemistry is limited and is hardly watched at all if not ever. This may change considering its potential as a precursor to the $NaBH_3CN$ in Strike's #1 method of choice. There are a lot of ways to make this catalyst, but the least involved is the one using boron trifluoride. What the method calls for is an apparatus called an autoclave. You know how using a vacuum causes the absence of pressure to make things boil at a lower temperature? Well, an autoclave is a device that causes an

increase in pressure so that things will get to a higher temperature without boiling. Yeesh! This is already starting to sound complicated and, yeah, Strike guesses it kind of is. But there is a little price to pay for total independence from government scrutiny.

All biology labs and hospitals have autoclaves for sterilizing their equipment so if the chemist has access to one then all she needs to do is place the reactants in a flask, cover the flask with foil and blast them in an autoclave for a few hours. This, however, is probably not feasible so about the best thing Strike can think of for home use would be as follows. Still, Strike is not entirely sure if this apparatus is a correct one, and if the chemist also has some doubts then she would probably want to ask a professional research chemist who has used autoclaving as a synthetic tool. Strike's idea is to use a pipe bomb with a special fitting so that pressure from a pump can be introduced into the bomb. Most vacuum pumps are reversible so that they will produce pressure as well as vacuum. How much pressure? Well, that is something the chemist is going to have to look up because it was not provided, and Strike does not want to look it up either. It is suffice to say that one is going to use as much pressure as is necessary to bring an ether solution to 120-130°C without it boiling.

7.9g sodium hydride (NaH) and 100mL of a 0.05M solution of boron trifluoride etherate (0.4g BF_3 in 100mL ether, this usually must be purchased as a commercially made product)is placed in a pipe bomb. Pressure is applied and the bomb is placed in a 120-130° oil bath for 2 hours. The ether is removed under vacuum and the $NaBH_4$ is isolated by recrystallization from water. To do this the chemist adds water to the residue which causes the $NaBH_4$ to crystallize out as a dihydrate precipitate. This white precipitate is separated as a filter cake, washed with a little water and the filter cake is vacuum distilled to remove the dihydrate water molecules that are attached the catalyst. This dry $NaBH_4$ is now suitable for use. Although Strike is again not sure, Strike thinks it might be possible to attempt this in a plain old sealed pipe bomb without the pressure addition.

SODIUM CYANOBOROHYDRIDE ($NaBH_3CN$)

[152]--This catalyst has not been given a fair shake in underground literature and, as of this book's printing, is still relatively safe to purchase. A prudent chemist will most likely stock up on this chemical because the eventuality of more intense scrutiny is inevitable. The best way to make this product is to start with $NaBH_4$ which is much more safe to buy. However, the way to go about making this catalyst is not very safe unless strict adherence to safety is used.

The 'cyano' part of cyanoborohydride is going to come from cyanide of course, and cyanide is lethal. Cyanide has no odor and will kill you instantly if a single whiff of it is inhaled. Everything must be done in a hood and study or investigation of the literature beyond what is published here is strongly urged. To acquire a stabilized source of cyanide one is going to need to introduce hydrogen cyanide (HCN) into tetrahydrofuran (THF) solvent. Ideally one would want to use a cannister of cyanide gas and bubble it into the THF but Strike seriously doubts such a thing will be sold to a street punk. This is because such an item, in the wrong hands, could be a terrible terrorist weapon. The best way a home chemist could 'safely' produce HCN is by generating it herself.

To make a cyanide/THF solution one is going to have to create HCN from sodium or potassium cyanide. To do this one is going to need to use the apparatus seen in fig. 14. There are going to be some minor changes though. The reaction flask is not going to be a simple single-neck flask but, instead, is going to be a single-neck with a sidearm inlet tube or a three neck flask with one of the necks stoppered and the other one plugged with a rubber stopper that has a wide glass tube extending all the way from the outside of the flask down to the bottom of the flask. At the other end of the apparatus is the vacuum adapter connected to the re-

ceiving flask. If one were to look up into the vacuum adapter one will see that it has a little drip tube that extends down its neck where liquids normally drips from into the receiving flask. Right? Now, what one wants to do is attach an extension of tubing or glass to the end of that drip tube so that it will extend all the way to the bottom of the receiving flask. The chemist does this because she wants the cyanide to bubble through the THF that she is going to place in the receiving flask. The receiving flask itself must be sitting in a an ice bath.

In professional laboratories, scientists use things called gas dispersion tubes at the ends of their 'drip tubes'. These kinds of 'drip tubes' are commercially made pieces of glass that have a tip made out of porous ceramic. When a gas is pulled through the end of a gas disperser it is busted up into a bunch of tiny, fizzy bubbles which greatly enhances the absorption of the HCN gas into the solvent. What the chemist has is a bubbling tip that is going to produce big bubbles. This works, but not as efficiently. The best way a chemist can approximate a phase separator is by wrapping a bunch of netting or some such shit around the tip. But one should simply buy the proper gas dispersion tube from any glassware maker.

To make the HCN/THF the chemist is going to have the setup as described in place, under the hood and the vent from the vacuum source must be channeled way, way outside (the vacuum is not on at this point mind you). In the preweighed receiving flask is placed a 300g of THF. In the reaction flask is placed 113g sodium cyanide (NaCN) and 500mL water and the stoppers are immediately put back in place. The vacuum hose, which is connected to the vacuum adapter is going to have a hose clamp on it so that vacuum flow can be regulated. With the hose pinched shut by the clamp, the vacuum is turned on and the flow is slowly started by adjusting the clamp. What the chemist wants to see is a slow bubbling coming from the inlet tube in the reaction flask and also from the bubbling tube in the receiving flask. The vacuum flow should not be any stronger than what is needed to cause this

bubbling. The solution in the reaction flask should be stirring during all this so that the NaCN dissolves into the water. No HCN gas should be evolving at this point.

To release the HCN gas one is going to acidify the solution with concentrated H_2SO_4. To do this one is going to gradually add 30mL of H_2SO_4 through the inlet tube. Each addition aliquot will cause the bubbling to temporarily stop, which is normal. The pull of the vacuum will get things going again. After addition the solution is brought to a boil and kept there for 1 hour. The chemist can now remove the receiving flask, weigh it and hope that it has gained approximately 60g in weight. That gain in weight will be due to the absorption of HCN.

With the HCN solution in hand, the rest of the procedure goes pretty quickly. 80g NaBH3 in 1L THF is stirred at 25°C and then the HCN/THF solution is gradually added. Bubbling caused by the release of hydrogen will occur (no smoking!) as the solution stirs for 1 hour at 25°C. The solution is then heated at reflux until no more hydrogen can be seen evolving. The solution is then vacuum filtered and the filtrate removed of THF by vacuum distillation to give $NaBH_3CN$ (91%). Whew! All catalysts, including this one, must be stored immediately so that they have no prolonged exposure to air and moisture. This is especially true for $NaBH_3CN$.

The following is the current list of DEA List I and List II chemicals. List I chemicals can only be bought or owned if one has a DEA or state permit. List II chemicals can be purchased in any amount below the given threshold. If one requires an amount of List II chemical above the threshold amount, then will need the same DEA permit for List I chemicals.

LIST I CHEMICALS

Anthranilic Acid	Piperonal	Nitroethane
Isosafrole	Ephedrine	Safrole
Phenylpropanolamine	N-Methylephedrine	Ethylamine
Benzaldehyde	Propionic Anhydride	N-pseudoephedrine
Methylamine	Ergonovine	MD-P2P
Piperidine	N-Methyl-Pfed	HI (57%)
Benzyl Cyanide	Pseudoephedrine	Phenylacetic Acid
N-Acetylanthranilic Acid	Ergotomine	

LIST II CHEMICALS	**Threshold by Vol.**	**Threshold by Wt.**
Acetic Anhydride	250 gal	1,023kg
Acetone	50 gal	150kg
Benzyl Chloride	N/A	1kg
Ethyl Ether	50 gal	135.8kg
HCl (Gas)	Not yet known	
Iodine	Not yet known	
Methyl Ethyl Ketone	50 gal	145kg
KMnO4	N/A	55kg
Toluene	50 gal	159kg

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