Chapter

1

SAFETY FIRST, LAST, AND ALWAYS

- *Wear your goggles over your eyes.*
- *If you don't know where a waste product goes—ASK!*
- *Careful reading can prevent failure.*

The organic chemistry laboratory is potentially one of the most dangerous of undergraduate laboratories. That is why you must have a set of safety guidelines. It is a very good idea to pay close attention to these rules, for one very good reason:

The penalties are only too real.

Disobeying safety rules is not at all like flouting many other rules. *You can get seriously hurt.* No appeal. No bargaining for another 12 points so you can get into medical school. Perhaps as a patient, but certainly not as a student. So, go ahead. Ignore these guidelines. But remember—

You have been warned!

1. ***Wear your goggles.*** Eye injuries are extremely serious but can be mitigated or eliminated if you keep your goggles on *at all times*. And I mean *over your eyes,* not on top of your head or around your neck. There are several types of eye protection available, some of them acceptable, some not, according to local, state, and federal laws. I like the clear plastic goggles that leave an unbroken red line on your face when you remove them. Sure, they fog up a bit, but the protection is superb. Also, think about getting chemicals or chemical fumes trapped under your contact lenses before you wear them to lab. Then don't wear them to lab. Ever.

2. ***Touch not thyself.*** Not a Biblical injunction, but a bit of advice. You may have just gotten chemicals on your hands in a concentration that is not noticeable, and, sure enough, up go the goggles for an eye wipe with the fingers. Enough said.
3. ***There is no "away."*** Getting rid of chemicals is a very big problem. You throw them out from here, and they wind up poisoning someone else. Now there are some laws to stop that from happening. The rules were really designed for industrial waste, where there are hundreds of gallons of waste that all has the same composition. In a semester of organic lab, there will be much smaller amounts of different materials. Waste containers could be provided for everything, but this is not practical. If you don't see the waste can you need, ask your instructor. When in doubt, *ask*.
4. ***Bring a friend.*** *You must never work alone*. If you have a serious accident and you are all by yourself, you might not be able to get help before you die. Don't work alone, and don't work at unauthorized times.
5. ***Don't fool around.*** Chemistry is serious business. Don't be careless or clown around in lab. You can hurt yourself or other people. You don't have to be somber about it—just serious.
6. ***Drive defensively.*** Work in the lab as if someone else were going to have an accident that might affect you. Keep the goggles on because *someone else* is going to point a loaded, boiling test tube at you. *Someone else* is going to spill hot, concentrated acid on your body. Get the idea?
7. ***Eating, drinking, or smoking in lab.*** Are you kidding? Eat in a chem lab?? Drink in a chem lab??? Smoke, and blow yourself up????
8. ***The iceman stayeth, alone.*** No food in the ice machine. "It's in a plastic bag, and besides, nobody's spilled their product onto the ice yet." No products cooling in the ice machine, all ready to tip over, either. Use the scoop, and nothing but the scoop, to take ice out of the machine. And don't put the scoop in the machine for storage, either.
9. ***Keep it clean.*** Work neatly. You don't have to make a fetish out of it, but try to be *neat*. Clean up spills. Turn off burners or water or electrical equipment when you're through with them. Close all chemical containers after you use them. Don't leave a mess for someone else.
10. ***Where it's at.*** Learn the locations and proper use of the fire extinguishers, fire blankets, safety showers, and eyewash stations.
11. ***Making the best-dressed list.*** Keep yourself covered from the neck to the toes—no matter what the weather. That might include long-sleeved tops that also cover the midsection. Is that too uncomfortable for you? How about a chemical burn to accompany your belly button, or an oddly shaped scar on your arm in lieu of a tattoo? Pants that come down to the shoes and cover any exposed ankles are probably a good idea as well. No open-toed shoes, sandals, or canvas-covered footwear. No loose-fitting cuffs on the pants or the shirts. Nor are dresses appropriate for lab. Keep the midsection covered. Tie back

that long hair. And a small investment in a lab coat can pay off, projecting that extra professional touch. It gives a lot of protection, too. Consider wearing disposable gloves. Clear polyethylene ones are inexpensive, but the smooth plastic is slippery, and there's a tendency for the seams to rip open when you least expect it. Latex examination gloves keep their grip and don't have seams, but they cost more. Gloves are not perfect protectors. Reagents like bromine can get through and cause severe burns. They'll buy you some time, though, and can help mitigate or prevent severe burns. Oh, yes—laboratory aprons: They only cover the *front,* so your exposed legs are still at risk from behind.

12. ***Hot under the collar.*** Many times you'll be asked or told to heat something. Don't just automatically go for the Bunsen burner. That way lies *fire.* Usually—

No flames!

Try a hot plate, try a heating mantle (see Chapter 17, "Sources of Heat"), but try to stay away from flames. Most of the fires I've had to put out started when some bozo decided to heat some flammable solvent in an open beaker. Sure, there are times when you'll *have* to use a flame, but use it away from all flammables and in a hood (Fig. 1.1), and only with the permission of your instructor.

13. ***Work in the hood.*** A hood is a specially constructed workplace that has, at the least, a powered vent to suck noxious fumes outside. There's also a safety glass or plastic panel you can pull down as protection from exploding apparatus (Fig. 1.1). If it is at all possible, treat every chemical (even solids) as if toxic or bad-smelling fumes can come from it, and carry out as many of the operations in the organic lab as you can *inside a hood,* unless told otherwise.

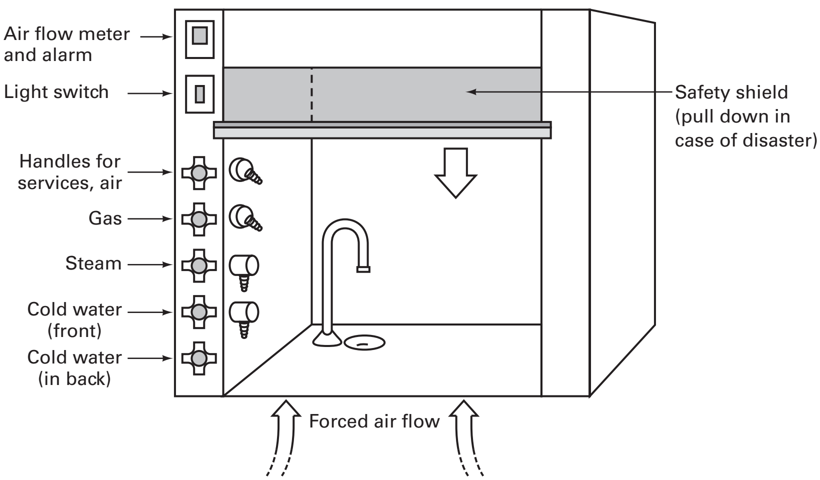

FIGURE 1.1 A typical hood.

14. ***Keep your fingers to yourself.*** Ever practiced "finger chemistry"? You're unprepared so you have a lab book out, and your finger points to the start of a sentence. You move your finger to the end of the first line and do that operation—

    "Add this solution to the beaker containing the ice-water mixture"

    And WHOOSH! Clouds of smoke. What happened? The next line reads—

    "very carefully as the reaction is highly exothermic."

    But you didn't read that line, or the next, or the next. So you are a danger to yourself and everyone else. Read and take notes on any experiment before you come to the lab (see Chapter 2, "Keeping a Notebook").
15. ***Let your eyes roam.*** Not over to another person's exam paper, but all over the entire label of any reagent bottle. You might have both calcium carbonate and calcium chloride in the laboratory, and if your eyes stop reading after the word "calcium," you have a good chance of picking up and using the wrong reagent. At the very least, your experiment fails quietly. You don't really want to have a more exciting exothermic outcome. Read the entire label and be sure you've got the right stuff.
16. ***What you don't know can hurt you.*** If you are not sure about an operation, or you have any question about handling anything, *please* ask your instructor before you go on. Get rid of the notion that asking questions will make you look foolish. Following this safety rule may be the most difficult of all. Grow up. Be responsible for yourself and your own education.
17. ***Blue Cross or Blue Shield?*** Find out how you can get medical help if you need it. Sometimes, during a summer session, the school infirmary is closed, and you would have to be transported to the nearest hospital.
18. ***What's made in Vegas, stays in Vegas.*** You're preparing a compound, and you have a question about what to do next. Perhaps your instructor is in the instrument room, or getting materials from the stockroom, or even just at the next bench with another student. Don't carry your intermediate products around; go *a capella* (without accompaniment of beakers, flasks, or separatory funnels filled with substances) to your instructor and ask that she come over and see what you're talking about. Do not ever carry this stuff out of the main lab, or across or down a hallway—ever. A small vial of purified product to be analyzed in the instrument room, sure. But nothing else.
19. ***A-a-a-a-a-a-c-h-o-o-o-o-o-o! Allergies.*** Let your instructor know if you have any allergies to specific compounds or classes of compounds before you start the lab. It's a bit difficult to bring these things up while you're scratching a rash. Or worse.
20. ***Do you know where the benchtops have been?*** You put your backpack down on the benchtop for a while. Then, you pick it up and put it somewhere else. Did you just transfer some substance from the benchtop with your backpack? Perhaps your pens were rolling around on the benchtop and picked up a substance

themselves and you didn't know it? Often wearing protection doesn't help; gloves can transfer chemicals to your pen (and you can't tell because your hands are covered), and that pen might go where? Behind the ear? In the mouth?

These are a few of the safety guidelines for an organic chemistry laboratory. You may have others particular to your own situation.

ACCIDENTS WILL NOT HAPPEN

That's an attitude you might hold while working in the laboratory. You are *not* going to do anything or get anything done to you that will require medical attention. If you do get cut, and the cut is not serious, wash the area with water. If there's serious bleeding, apply direct pressure with a clean, preferably sterile, dressing. For a minor burn, let cold water run over the burned area. For chemical burns to the eyes or skin, flush the area with lots of water. In every case, get to a physician if at all possible.

If you have an accident, *tell your instructor immediately. Get help!* This is no time to worry about your grade in lab. If you put grades ahead of your personal safety, be sure to see a psychiatrist after the internist finishes.

DISPOSING OF WASTE

Once you do your reaction, since your mother probably doesn't take organic lab with you, you'll have to clean up after yourself. I hesitated to write this section for a very long time because the rules for cleaning up vary greatly according to, but not limited to, federal, state, and local laws, as well as individual practices at individual colleges. There are even differences—legally—if you or your instructor do the cleaning up. And, as always, things do seem to run to money—the more money you have to spend, the more you can throw away. So there's not much point in even trying to be authoritative about waste disposal in this little manual, but there are a few things I have picked up that you should pay attention to. Remember, my classification scheme may not be the same as the one you'll be using. When in doubt, *ask! Don't just throw everything into the sink. Think.*

Note to the picky: The word nonhazardous, as applied here, means relatively benign, as far as organic laboratory chemicals go. After all, even pure water, carelessly handled, can kill you.

How you handle laboratory waste will depend upon what it is. Here are some classifications you might find useful:

1. ***Nonhazardous insoluble waste.*** Paper, corks, sand, alumina, silica gel, sodium sulfate, magnesium sulfate, and so on can probably go into the ordinary wastebaskets in the lab. Unfortunately, these things can be contaminated with hazardous waste (see the following items), and then they need special handling.

2. ***Nonhazardous soluble solid waste.*** Some organics, such as benzoic acid, are relatively benign and can be dissolved with a lot of tap water and flushed down the drains. But if the solid is that benign, it might just as well go out with the nonhazardous insoluble solid waste, no? Check with your instructor; watch out for contamination with more hazardous materials.
3. ***Nonhazardous soluble liquid waste.*** Plain water can go down the drains, as well as water-soluble substances not otherwise covered below. Ethanol can probably be sent down the drains, but butanol? It's not that water soluble, so it probably should go into the general organic waste container. Check with your instructor; watch out for contamination with more hazardous materials.
4. ***Nonhazardous insoluble liquid waste.*** These are compounds such as 1-butanol (previously discussed), diethyl ether, and most other solvents and compounds not covered otherwise. In short, this is the traditional "organic waste" category.
5. ***Generic hazardous waste.*** This includes pretty much all else not listed separately. Hydrocarbon solvents (hexane, toluene), amines (aniline, triethylamine), amides, esters, acid chlorides, and on and on. Again, traditional "organic waste." Watch out for incompatibilities, though, before you throw just anything in any waste bucket. If the first substance in the waste bucket was acetyl chloride and the second is diethylamine (both hazardous liquid wastes), the reaction may be quite spectacular. You may have to use separate hazardous waste containers for these special circumstances.
6. ***Halogenated organic compounds.*** 1-Bromobutane and *tert*-butyl chloride, undergraduate laboratory favorites, should go into their own waste containers as "halogenated hydrocarbons." There's a lot of agreement on this procedure for these simple compounds. But what about your organic unknown, 4-bromobenzoic acid? I'd have you put it and any other organic with a halogen in the "halogenated hydrocarbon" container and not flush it down the drain as a harmless organic acid, as you might do with benzoic acid.
7. ***Strong inorganic acids and bases.*** Neutralize them, dilute them, and flush them down the sink. At least as of this writing.
8. ***Oxidizing and reducing agents.*** Reduce the oxidants and oxidize the reductants before disposal. Be careful! Such reactions can be highly exothermic. Check with your instructor before proceeding.
9. ***Toxic heavy metals.*** Convert to a more benign form, minimize the bulk, and put in a separate container. If you do a chromic acid oxidation, you might reduce the more hazardous C^{6+} to Cr^{3+} in solution and then precipitate the Cr^{3+} as the hydroxide, making lots of expensive-to-dispose-of chromium solution into a tiny amount of solid precipitate. There are some gray areas, though. Solid manganese dioxide waste from a permanganate oxidation should probably be considered a hazardous waste. It can be converted to a soluble Mn^{2+} form, but should Mn^{2+} go down the sewer system? I don't know the effect of Mn^{2+} (if any) on the environment. But do we want it out there?

Mixed Waste

Mixed waste has its own special problems and raises even more questions. Here are some examples:

1. ***Preparation of acetaminophen (Tylenol): a multistep synthesis.*** You've just recrystallized 4-nitroaniline on the way to acetaminophen, and washed and collected the product on your Buchner funnel. So you have about 30–40 mL of this really orange solution of 4-nitroaniline and by-products. The nitroaniline is very highly colored, the by-products probably more so, so there isn't really a lot of solid organic waste in this solution, not more than perhaps 100 mg or so. Does this go down the sink, or is it treated as organic waste? Remember, you have to package, label, and transport to a secure disposal facility what amounts to 99.9% perfectly safe water. Check with your instructor.
2. ***Preparation of 1-bromobutane.*** You've just finished the experiment and you're going to clean out your distillation apparatus. There is a residue of 1-bromobutane coating the three-way adapter, the thermometer, the inside of the condenser, and the adapter at the end. Do you wash the equipment in the sink and let this minuscule amount of a halogenated hydrocarbon go down the drain? Or do you rinse everything with a little acetone into yet another beaker and pour that residue into the "halogenated hydrocarbon" bucket, fully aware that most of the liquid is acetone and doesn't need special halide treatment? Check with your instructor.
3. ***The isolation and purification of caffeine.*** You've dried a methylene chloride extract of caffeine and are left with methylene chloride–saturated drying agent. Normally a nonhazardous solid waste, no? Yes. But where do you put this waste while the methylene chloride is on it? Some would have you put it in a bucket in a hood and let the methylene chloride evaporate into the atmosphere. Then the drying agent is nonhazardous solid waste. But you've merely transferred the problem somewhere else. Why not just put the whole mess in with the "halogenated hydrocarbons"? Usually, halogenated hydrocarbons go to a special incinerator equipped with traps to remove HCl or HBr produced by burning. Drying agents don't burn very well, and the cost of shipping the drying agent part of this waste is very high. What should you do? Again, ask your instructor.

In these cases, as in many other questionable situations, I tend to err on the side of caution and consider that the bulk of the waste has the attributes of its most hazardous component. This is, unfortunately, the most expensive way to look at the matter. In the absence of guidelines,

1. Don't make a lot of waste in the first place.
2. Make it as benign as possible. (Remember, though, that such reactions can be highly exothermic, so proceed with caution.)
3. Reduce the volume as much as possible.

Oh: Try to remember that sink drains can be tied together, and if you pour a sodium sulfide solution down one sink while someone else is diluting an acid in another sink, toxic, gagging, rotten-egg-smelling hydrogen sulfide can back up the drains in your entire lab, and maybe even the whole building.

MATERIAL SAFETY DATA SHEET (MSDS)

The MSDS for any substance is chock-full of information, including but not limited to the manufacturer, composition (for mixtures), permissible exposure limit (PEL), threshold limit value (TLV) boiling point, melting point, vapor pressure, flash point, and on and on and on. These data sheets are very complete, very thorough, and very irrelevant to working in the undergraduate organic chemistry laboratory Period.

Don't take my word for it. One outfit, Interactive Learning Paradigms Incorporated (http://www.ilpi.com/msds/faq/parta.html), clearly states: "An MSDS reflects the hazards of working with the material in an occupational fashion. For example, an MSDS for paint is not highly pertinent to someone who uses a can of paint once a year, but is extremely important to someone who does this in a confined space 40 hours a week."

And probably less pertinent, if that's even possible, to someone who will work with 1-bromobutane once in a lifetime.

So if you're teaching organic lab, that's one thing. If you're taking organic lab, well, stick to hazard data and references in the other handbooks and you'll be knowledgeable enough.

GREEN CHEMISTRY AND PLANNING AN ORGANIC SYNTHESIS

While it is always good to "reduce, reuse, recycle," unless you're developing new experiments you don't really have any control over these things. But if you have to plan an organic synthesis from the ground up, might as well do it right.

1. ***Eschew the older literature!*** 'Fraid so. Many places will initially steer you to *Organic Syntheses,* which runs from 1932 to the present, as the syntheses there have been checked and will work as advertised. Unfortunately, for the early work there, and in many other places, being green just wasn't even thought about. So be careful. A historical collection of techniques in a reference with a current copyright date can detail reactions that would not be considered green today.
2. ***Teaching over research.*** A better place to look is *The Journal of Chemical Education,* rather than the traditional research resources. While a large research

group at a large university can have the resources (read *money*) to have toxic materials disposed of properly, "one-man shops" at community colleges are under greater pressure to reduce the costs of waste disposal, and, while they may not be the ones to originally develop a greener method from the high-powered research lab, they certainly exploit it, often in an inspired fashion.

3. ***Make what you want, but use what you make.*** You'll have to decide on just how much product you'll need to synthesize. And it depends upon the scale of your apparatus.
   - **Microscale.** For a **solid product**, target at least 200 mg. This should be enough for a melting point, an IR, and an NMR, plus some to hand in to show you made it. If you have to, you can easily recover your product from the NMR solvent; IR might be too problematic to bother about. For a **liquid product**, besides the tests, there might be drying and distillation, so about 2 mL might be your target. Don't forget to use the density of the liquid to calculate the mass you'll need to use for your stoichiometric calculations.
   - **Miniscale.** About 5 g for a solid; about 10 mL of a liquid. Just guidelines, now. The consequences of losing product at any stage are greatly reduced. Doesn't mean you should be sloppy with your technique, though.

4. ***Plan to lose.*** Now that you know how much you're planning to make, assume you won't be making it in a perfect yield. For first-time-this-has-ever-been-done reactions, you might get 40%; if the reaction has been done before, and you have a published procedure with a posted yield, but *you've* never done this before, add a 10% penalty. Then calculate back to get the amount of starting materials you'll need based on this lower yield.

5. ***Timing is everything.*** Generally, the reaction times shouldn't be reduced. Paradoxically, if you have the time, you can take the time to find out by running the experiment over and over again using different reaction times to find the best time. If the published procedure uses half-molar quantities (large-scale equipment), and you rework this for microscale, you might reduce the reaction time since the smaller quantity will have lower thermal mass and not need to be heated for as long a time. Maybe.

6. ***Use less-toxic materials.*** Easy to say; a bit more difficult to do. Some suggestions in no particular order:
   - Do you even need a reaction solvent? Consider direct combination of reagents.
   - Can you replace chlorinated solvents, especially in extraction? You might consider diethyl ether or ethyl acetate.
   - Can you eliminate toxic metals? A shift from a chromium-based to a manganese-based oxidizer in a reaction may help. Organic catalysts can substitute for those based on heavy metals. That sort of thing.

AN iBAG FOR YOUR iTHING

The Survival Manual is available on a Kindle, and along with iPads, Androids, and Nooks, it looks like electronic hardware might be on your benchtop along with everything else. Warrantees aside, though, if somebody's cooling hose pops off and it gets soaked, you might be at quite a loss for quite a while. There is, however, a high-tech remedy: Ziploc bags.

Once inside a bag, the nasty elements of the laboratory can't get to your Kindle, but you can still use your fingers to manipulate the screen. We put 10 in. diagonal screen tablet computers in large Ziploc bags, and not only did they survive water spills and such, we could still write on the screen through the bag with the stylus. They were a bit slipperier than the tablet screen, and we had to stretch the plastic bag a bit to flatten it out, but they worked out.

EXERCISES

1. Make a rough sketch of your lab. Mark where the fire extinguishers, fire blanket, eye wash station, and other safety equipment are, as well as where you'll be working.
2. Why shouldn't you work in a laboratory by yourself?
3. Might there be any problems wearing contact lenses in the laboratory?
4. Biology laboratories often have stools. Why might this be foolish in the organic chemistry laboratory?
5. What the heck are the PEL, TLV, and flash point of substances?
6. Google the MSDS for 2-naphthol. Try to select one from Thermo Fisher and another from J. T. Baker/Mallinckrodt. Speculate as to why one says this compound will cause death on inhalation, and the other, well, not so much. Google the MSDS for sugar, also.