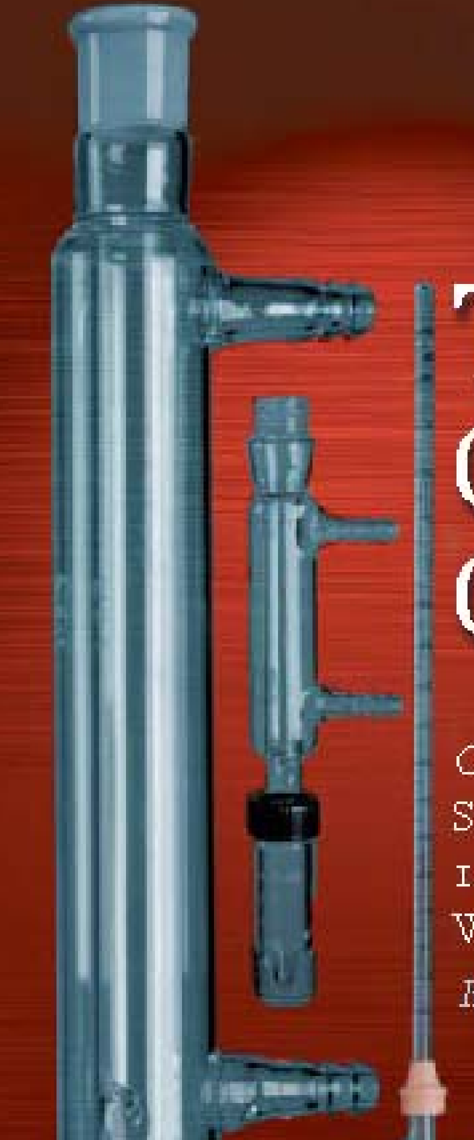


Techniques in Organic Chemistry

Third Edition

Compatible with

Standard Taper Miniscale

14/10 Standard Taper Microscale

Williamson Microscale.

Includes Modern Spectroscopy

Jerry R. Mohrig

Christina Noring Hammond

Paul F. Schatz

Chemical resistance of common types of gloves to various compounds

Compound	Glove type: Neoprene	Nitrile	Latex
Acetone	good	fair	good
Chloroform	good	poor	poor
Dichloromethane	fair	poor	poor
Diethyl ether	very good	good	poor
Ethanol	very good	excellent	excellent
Ethyl acetate	good	poor	fair
Hexane	excellent	excellent	poor
Methanol	very good	fair	fair
Nitric acid (conc.)	good	poor	poor
Sodium hydroxide	very good	excellent	excellent
Sulfuric acid (conc.)	good	poor	poor
Toluene	fair	fair	poor

Common organic solvents

Name	Boiling point (°C)	Density ($g \cdot ml^{-1}$)	Dielectric constant	Miscible with H_2O
Acetone (2-propanone)	56.5	0.792	21	yes
Dichloromethane	40	1.326	9.1	no
Diethyl ether	35	0.713	4.3	no
Ethanol (95% aq. azeotrope)	78	0.816	27	yes
Ethanol (anhydrous)	78.5	0.789	25	yes
Ethyl acetate	77	0.902	6.0	slightly
Hexane	69	0.660	1.9	no
Methanol	65	0.792	33	yes
Pentane	36	0.626	1.8	no
2-Propanol (Isopropyl alcohol)	82.5	0.785	18	yes
Toluene	111	0.866	2.4	no

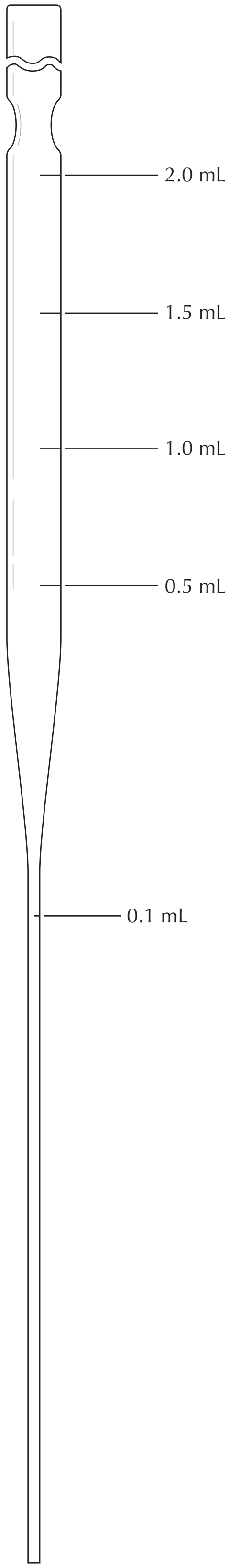
Selected data on common acid and base solutions

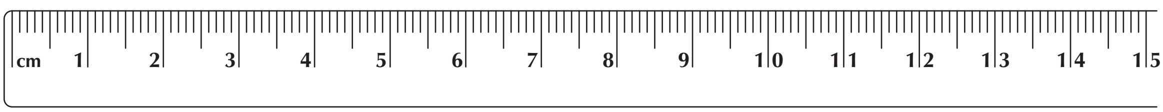
Compound	Molarity	Density ($g \cdot ml^{-1}$)	% by weight
Acetic acid (glacial)	17	1.05	100
Ammonia (concentrated)	15.3	0.90	28.4
Hydrobromic acid (concentrated)	8.9	1.49	48
Hydrochloric acid (concentrated)	12	1.18	37
Nitric acid (concentrated)	16	1.42	71
Phosphoric acid (concentrated)	14.7	1.70	85
Sodium hydroxide	6	1.22	20
Sulfuric acid (concentrated)	18	1.84	95–98

Quick reference for other important tables

Quick reference for other important figures

Quick reference for sections on sources of confusion





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Techniques in Organic Chemistry

Miniscale, Standard Taper Microscale, and Williamson Microscale

Third Edition

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Contents

Preface

The major focus of the Third Edition of *Techniques in Organic Chemistry* is the same as the focus of the earlier editions: the fundamental techniques that students encounter in the organic chemistry laboratory. However, we have also expanded our emphasis on the areas that students need to develop their skills in the critical interpretation of their experimental data and to successfully carry out guided-inquiry experiments.

Organic chemistry is an experimental science, and students learn its process in the laboratory. Our primary goal should be to teach students how to carry out well-designed experiments and draw reasonable conclusions from their results—a process at the heart of science. We should work to find opportunities that engage students in addressing questions whose answers come from their experiments, in an environment where they can succeed. These opportunities should be designed to catch students' interest, transporting them from passive spectators to active participants. A well-written and comprehensive textbook on the techniques of experimental organic chemistry is an important asset in reaching these goals.

Changes in the Third Edition

The Third Edition of *Techniques in Organic Chemistry* includes a number of new features. Entirely new sections have been added on planning a chemical reaction, computational chemistry, and ^{13}C nuclear magnetic resonance spectroscopy. A new chapter on UV-visible spectroscopy has been added. Many sections concerning basic techniques have been brought up to date and reorganized to better meet the practical needs of students as they encounter laboratory work.

A short essay introduces each of the five major parts of the Third Edition, on topics from the role of the laboratory to the spectroscopic revolution. Perhaps most important, the essay Intermolecular Forces in Organic Chemistry provides the basis for subsequent discussions on organic separation and purification techniques.

Many important features of earlier editions have been retained in the Third Edition. Subsections on sources of confusion again walk students through the pitfalls that could easily discourage them if they did not have this practical support. For easy reference, commonly used data on solvents and acids and bases, as well as quick references to frequently used techniques, are located inside the front cover. Data tables for IR and NMR spectroscopy appear inside the back cover and on the back foldout. We believe that these features will assist active learning as students encounter the need for this information during their laboratory work.

Who Should Use This Book?

The book is intended to serve as a laboratory textbook of experimental techniques for all students of organic chemistry. It can be used in conjunction with any lab experiments to provide the background and skills necessary for mastering the organic chemistry laboratory. The book is written to provide effective support for guided-inquiry and design-based experiments and projects. It can also serve as a useful reference for laboratory practitioners and instructors.

Flexibility

Techniques in Organic Chemistry offers a great deal of flexibility. It can be used in any organic laboratory with any glassware. The basic techniques for using standard taper miniscale glassware as well as 14/10 standard taper microscale and Williamson microscale glassware are all covered. The miniscale glassware that is described is appropriate with virtually any 14/20 or 19/22 standard taper glassware kit.

Modern Instrumentation

Modern instrumental methods play a crucial role in supporting guided-inquiry experiments, which provide the active learning opportunities many instructors seek for their students. We feature instrumental methods that offer quick, reliable, quantitative data. NMR spectroscopy and gas chromatography are particularly important. Our emphasis is on how to acquire good data and how to read spectra efficiently and with real understanding. Chapters on ^{1}H and ^{13}C NMR, IR, and mass spectrometry stress the practical interpretation of spectra and how they can be used to answer questions posed in an experimental context. They describe how to deal with real laboratory samples and include case studies of analyzed spectra.

Organization

The book is divided into five parts:

- Part 1 has chapters on safety, green chemistry, and the lab notebook.
- Part 2 discusses glassware, measurements, heating methods, computational chemistry, and planning a chemical reaction.
- Part 3 introduces filtration, extraction, drying organic liquids, distillation, melting points, recrystallization, and a chapter on specialized techniques—sublimation, refractometry, measurement of optical activity, and inert atmosphere techniques.
- Part 4 presents the three chromatographic techniques widely used in the organic laboratory—thin-layer, liquid, and gas chromatography.
- Part 5 discusses IR, ^{1}H and ^{13}C NMR, MS, and UV-visible spectra in some detail.

Traditional organic qualitative analysis is available on our Web site: www.whfreeman.com/mohrig.

Modern Projects and Experiments in Organic Chemistry

The accompanying laboratory manual, *Modern Projects and Experiments in Organic Chemistry*, comes in two complete versions:

- *Modern Projects and Experiments in Organic Chemistry: Miniscale and Standard Taper Microscale* (ISBN 0-7167-9779-8)
- *Modern Projects and Experiments in Organic Chemistry: Miniscale and Williamson Microscale* (ISBN 0-7167-3921-6)

Modern Projects and Experiments is a combination of inquiry-based and traditional experiments, plus multiweek inquiry-based projects. It is designed to provide quality content, student accessibility, and instructor flexibility. This laboratory manual introduces students to the way the contemporary organic lab actually functions and allows them to experience the process of science.

Custom Publishing

All experiments and projects are available through LabPartner for Chemistry, Freeman Custom Publishing's newest offering. LabPartner provides instructors with a diverse database of experiments, selected from the extensive array published by W. H. Freeman and Hayden-McNeil Publishing. Instructors can use LabPartner to create their own customized lab manual by selecting specific experiments from *Modern Projects and Experiments,* adding experiments from other WHF or H-M titles, and incorporating their own original material so that the manual is organized to suit their course. Visit http://www.whfreeman.com/labpartner to learn more.

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We hope that teachers and students of organic chemistry find our approach to laboratory techniques effective, and we would be pleased to hear from those who use our book. Please write to us in care of the Chemistry Acquisitions Editor at W. H. Freeman and Company, 41 Madison Avenue, New York, NY 10010, or e-mail us at chemistry@whfreeman.com.

PART

1

Introduction to the Organic Laboratory

Essay — The Role of the Laboratory

Organic chemistry is an experimental science, and the laboratory is where you learn about "how we know what we know about it." The laboratory deals with the processes of scientific inquiry that organic chemists use. It demonstrates the experimental basis of what your textbook presents as fact. The primary goal of the laboratory is to help you understand how organic chemistry is done by actually doing it. Learning how to obtain and interpret experimental results and draw reasonable conclusions from them is at the heart of doing science. Your laboratory work will give you the opportunity to exercise your critical thinking abilities, to join in the process of science—to observe, to think, and to act.

To learn to do experimental organic chemistry, you need to master an array of techniques for carrying out and interpreting chemical reactions, separating products from their reaction mixtures, purifying products, and analyzing the results. *Techniques in Organic Chemistry* is designed to provide you with a sound fundamental understanding of the techniques that organic chemists use and the chemical principles they are based on. Mastering these techniques involves attention to detail and careful observations that will enable you to obtain accurate results and reach reasonable conclusions in your investigations of chemical phenomena.

While you are in the laboratory, you will have a variety of experiences—from learning basic techniques to running chemical reactions. Interpretation of your experimental results will involve consideration of the relationship between theory and experiment and provide reinforcement of what you are learning in the classroom. You may have the opportunity to do guided-inquiry experiments that ask you to answer a question or solve a problem by drawing conclusions from your experiments. You may also have the opportunity to synthesize an interesting organic compound by adapting a generic experimental procedure from the chemical literature.

Science is often done by teams of people working together on problems, and your experiments may involve teamwork with other students in your lab section. Some of your lab work may involve multiweek related experiments, which have a flexibility that may allow you to repeat a reaction procedure successfully if it didn't work well the first time. In fact, virtually all experimental results that are reported in chemical journals have been repeated many times before they are published.

Part of learning how to do organic chemistry in the laboratory includes learning how to do it safely. Technique 1 discusses laboratory safety and safe handling practices for the chemicals you will use. We urge you to read it carefully before you begin laboratory work.

TECHNIQUE

1 SAFETY IN THE LABORATORY

As you begin your study of experimental organic chemistry, you need a basic understanding of safety principles for handling chemicals and equipment in the laboratory. Consider this chapter to be required reading before you perform any experiments.

The organic chemistry laboratory is a place where accidents can and do occur and where safety is everyone's business. While working in the laboratory, you are protected by the instructions in an experiment and by the laboratory itself, which is designed to safeguard you from most routine hazards. However, neither the experimental directions nor the laboratory facilities can protect you from the worst hazard—your own or your neighbors' carelessness.

In addition to knowledge of basic laboratory safety, you need to learn how to work safely with organic chemicals. Many organic compounds are flammable or toxic. Some can be absorbed through the skin; others are volatile and vaporize easily into the air in the laboratory. Despite the hazards, organic compounds can be handled with a minimum of risk if you are adequately informed about the hazards and necessary safe handling procedures and if you use common sense while you are in the laboratory.

At the first meeting of your lab class, local safety issues will be discussed—the chemistry department's policies on safety goggles and protective gloves, the location of safety showers and eye wash stations, and the procedures to be followed in emergency situations. The information in this chapter is intended to complement your instructor's safety rules and instructions.

1.1 Causes of Laboratory Accidents

Laboratory accidents are of three general types: accidents involving fires and explosions, accidents producing cuts or burns, and accidents occurring from inhalation, absorption through the skin, or ingestion of toxic materials.

Fires and Explosions

Fire is the chemical union of a fuel with an oxidizing agent, usually molecular oxygen, and is accompanied by the evolution of heat and flame. Most fires involve ordinary combustible materials—hydrocarbons or their derivatives. Such fires are *extinguished* by removing oxygen or the combustible material or by decreasing the heat of the fire. Fires are *prevented* by keeping flammable materials away from a flame source or from oxygen (obviously, the former is easier).

Four sources of ignition are present in the organic laboratory: *open flames*, *hot surfaces* such as hot plates or heating mantles, *faulty electrical equipment*, and *chemicals.* The most obvious way to prevent a fire is to prevent ignition.

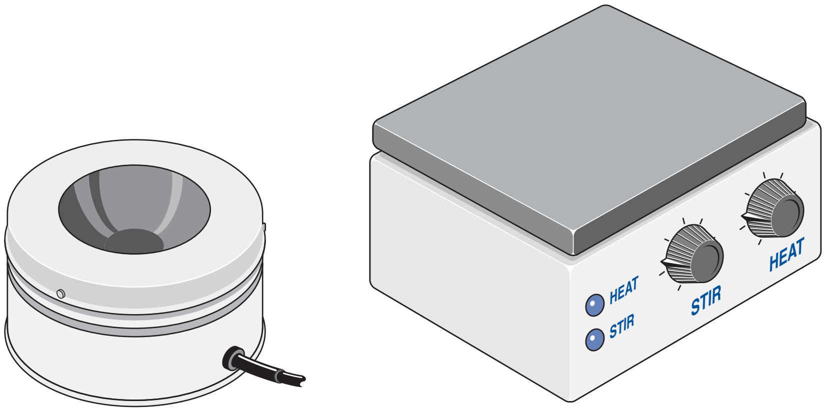

FIGURE 1.1
Heating devices.

Ceramic heating mantle

Hot plate/stirrer

Open flames. Open-flame ignition of organic vapors or liquids is easily prevented: **Never bring a lighted Bunsen burner or a match near a low-boiling-point flammable liquid.** Furthermore, because vapors from organic liquids can travel over long distances at bench or floor level (they are heavier than air), an open flame within 10 ft of diethyl ether, pentane, or other low-boiling organic solvents is an unsafe practice. In fact, the use of a Bunsen burner or any other flame in an organic laboratory should be a rare occurrence and done only with the permission of your instructor.

Hot surfaces. A hot surface, such as a hot plate or heating mantle, presents a trickier problem (Figure 1.1). An organic solvent spilled or heated recklessly on a hot plate surface may burst into flames. The thermostat on most hot plates is not sealed and can spark when it cycles on and off. The spark can ignite flammable vapors from an open container such as a beaker. Remove any hot heating mantle or hot plate from the vicinity before pouring a volatile organic liquid because the vapors from the solvent can be ignited by the hot surface of a hot plate or a heating mantle.

Faulty electrical equipment. Do not use appliances with frayed or damaged electrical cords as their use could lead to an electrical fire.

Chemical fires. Chemical reactions sometimes produce enough heat to cause a fire and explosion. For example, in the reaction of metallic sodium with water, the hydrogen gas that forms in the reaction can explode and ignite a volatile solvent that happens to be nearby.

Cuts and Injuries

Cuts and mechanical injuries are hazards anywhere, including the laboratory.

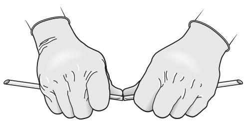

FIGURE 1.2
Breaking a glass rod properly.

Breaking glass rods or tubing. When you purposely break a glass rod or a glass tube, do it correctly. Score (scratch) a small line on one side of the tube with a file. Wet the scored line with a drop of water. Then, holding the tube on both sides with a paper towel and with the scored part away from you, quickly snap it by pulling the ends toward you (Figure 1.2).

Inserting glass into stoppers. Insert thermometers or glass tubes into corks, rubber stoppers, and thermometer adapters carefully and correctly. First, lubricate the end of the glass tube with a drop of water or glycerol. Then, while holding the tube with a towel **close** to the lubricated end, insert it slowly by firmly rotating it into the stopper. Never hold the thermometer by the end away from the stopper—it may break and the shattered end may be driven into your hand.

Chipped glassware. Check the rims of beakers, flasks, and other glassware for chips. Discard any piece of glassware that is chipped because you could be cut very easily by the sharp edge.

Inhalation, Ingestion, and Skin Absorption

Inhalation. The hoods in the laboratory protect you from inhalation of noxious fumes, toxic vapors, or dust from finely powdered materials. A hood is an enclosed space with a continuous flow of air that sweeps over the bench top, removing vapors or fumes from the area.

Because many compounds used in the organic laboratory are at least potentially dangerous, the best practice is to run every experiment in a hood, if possible. Your instructor will tell you when an experiment *must* be carried out in a hood. **Make sure that the hood is turned on before you use it.** Position the sash for the optimal airflow through the hood. If the optimum sash position is not indicated on the hoods in your laboratory, consult your instructor about how far to open the sash.

Ingestion. Ingestion of chemicals by mouth is easily prevented. **Never taste any substance or pipet any liquid by mouth.** Wash your hands with soap and water before you leave the laboratory. **No food or drink of any sort should be brought into a laboratory or eaten there.**

Absorption through the skin. Many organic compounds are absorbed through the skin. Wear the appropriate gloves while handling reagents and reaction mixtures. If you spill any substance on your skin, notify your instructor immediately, and wash the affected area thoroughly with water for 10–15 min.

1.2 Safety Features in the Laboratory

Organic laboratories contain many safety features for the protection and comfort of the people who work in them. It is unlikely that you will have to use the safety features in your lab, but in the event that you do, you must know what and where they are and how they operate.

Fire Extinguishers

Colleges and universities all have standard policies regarding the handling of fires. Your instructor will inform you whether evacuation of the lab or the use of a fire extinguisher takes priority at your institution. **Learn where the exits from your laboratory are located.**

Fire extinguishers are strategically located in your laboratory. There may be several types, and your instructor may demonstrate their use. Your lab is probably equipped with either class BC or class ABC dry chemical fire extinguishers suitable for solvent or electrical fires.

Fire Blankets

Fire blankets are used for one thing and one thing only—to smother a fire involving a person's clothing. Fire blankets are available in most labs.

Safety Showers

Safety showers are for acid burns and other spills of corrosive, irritating, or toxic chemicals on the skin or clothing. If a safety shower is nearby, it can also be used when a person's clothing or hair is ablaze. The typical safety shower dumps a huge volume of water in a short period of time and thus is effective for both fire and acid spills, when speed is of the essence. **Do not use the safety shower routinely, but do not hesitate to use it in an emergency.**

Eye Wash Stations

You should always wear safety goggles while working in a laboratory, but if you accidentally splash something in your eyes, *immediately* use the eye wash station to rinse them with copious quantities of slightly warm water for 10–15 min. Learn the location of the eye wash stations in your laboratory and examine the instructions on them during the first (check-in) lab session.

First Aid Kits

Your laboratory or a nearby stockroom may contain a basic first aid kit consisting of such items as adhesive bandages, sterile pads, and adhesive tape for treating a small cut or burn. **All injuries, no matter how slight, should be reported to your instructor immediately.** Your instructor will indicate the location of the first aid station and instruct you in its use.

1.3 Preventing Accidents

Accidents can largely be prevented by common sense and knowledge of simple safety rules.

Personal Safety

1. Think about what you are doing while you are in the laboratory. Read the experiment before the laboratory session starts and perform laboratory operations with careful forethought.
2. It is a law in many states and common sense in the remainder to **wear safety glasses or goggles at all times in the laboratory.** Your institution may have a policy regarding wearing contact lenses in the laboratory; learn what it is and follow it. Wear clothing that covers and protects your body. **Shorts, tank tops, and sandals (or bare feet) are not suitable attire for the lab.** Avoid loose clothing and loose long hair, which are fire hazards or could become entangled in an apparatus. Laboratory aprons or lab coats may be required by your instructor. Always wash