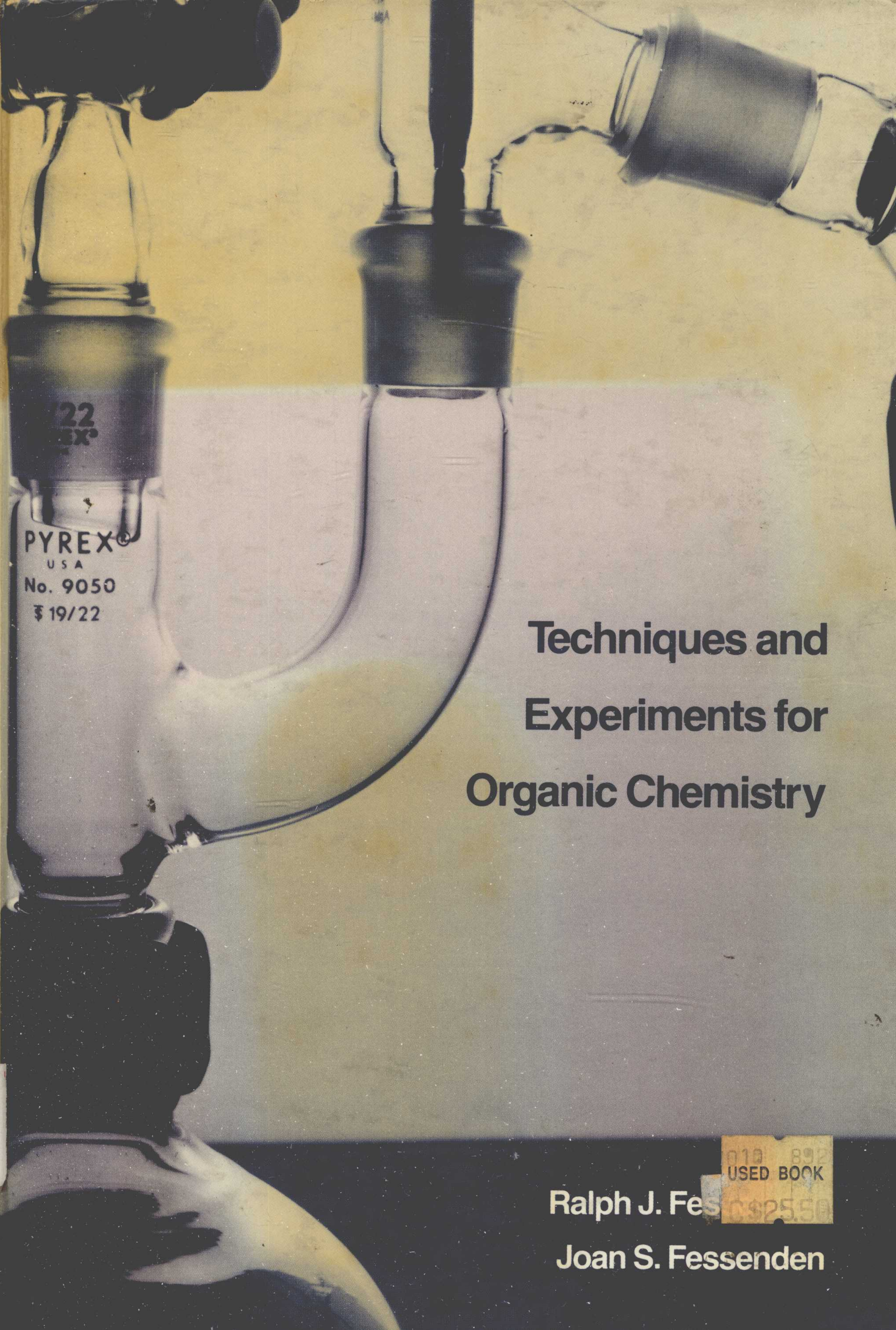

Techniques and Experiments for Organic Chemistry

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PREFACE

Two general approaches often used in teaching the one-year introductory organic laboratory are the *investigative approach*, a tutorial method that prepares the student for research, and what we call the "*techniques approach*," a more structured method in which the student is generally first taught manipulative techniques, then synthesis, and finally organic qualitative analysis. We have chosen the techniques approach because we feel it is more efficient of time and energy (both the student's and the instructor's) in our own chemistry sequence, in which students take lecture and laboratory courses concurrently.

Techniques and Experiments for Organic Chemistry begins with the common laboratory techniques. Actual syntheses are postponed until the student has gained sufficient knowledge of organic chemistry from the lecture portion of the course to understand the experiments being performed. Synthetic work follows the technique chapters of the text and begins with alkyl halide chemistry (Williamson ether synthesis and a Grignard reaction), followed by alcohol chemistry. Spectral techniques (infrared and nmr) are placed after alcohol chemistry, approximately halfway through the text. The remaining chapters are devoted to additional synthetic procedures. The text ends with a chapter on the literature of organic chemistry, an introduction to organic qualitative analysis, and a chapter of supplemental techniques. Four appendices of assorted tables and laboratory calculations conclude the text.

Each chapter begins with a theoretical discussion of the chemistry or techniques contained in the chapter. In addition, each experiment in the chapter is preceded by a discussion of the practical aspects of the experiment, along with explanations of why each reaction or manipulation is performed as it is. Emphasis is placed on understanding *and* doing instead of just doing.

The amount of procedural detail in the experiments is reduced as the text progresses. At the start of the book, the steps to be followed are spelled out in detail. The detail provided is gradually diminished as the student proceeds through the course and gains laboratory experience. Toward the end of the text, the experimental detail is similar to that found in research journals. Therefore, the experiments in the chapters toward the end of the text call for more student ingenuity: for example, Experiment 16.4 (Synthesis of an Acetate Ester by a General Reaction Procedure) and Experiment 21.1 (Qualitative Organic Analysis: Selected Procedures).

Because the student gradually acquires more independence as the experiments progress, this text could also be used for the first part of a course in which the final few weeks consist of independent laboratory work or of a full qualitative organic analysis scheme.

It has been the authors' experience that not all experiments found in standard laboratory texts work for many students. The reasons for these failures are varied but can often be traced to the student's inexperience. Therefore, each experiment in this text has been author-tested, student-tested, and/or class-tested to ensure a high probability of student success and learning.

The cost of chemicals has become quite high in recent years. For this reason, we have tried to include only experiments that require relatively inexpensive, readily available compounds. In addition, we have tried to "recycle" as many of the student products as feasible. In some cases, products prepared or purified by students can be used in later experiments. In other cases, the student products can be used in next year's laboratory course.

Flexibility. For the most part, each technique is presented in more than one experiment or section of an experiment, with one section generally involving an unknown compound. It is not expected that the student will carry out every experiment. In many cases, the instructor may, at his or her discretion, assign the unknown compound experiment in addition to, or in place of, the principal experiment. (See the discussion of *supplemental experiments* that follows.)

To avoid delays because of equipment shortages (such as of melting-point apparatus, gas chromatographs, etc.), the instructor may want to assign different experiments to different groups of students (for example, while one group performs a melting-point experiment, another group performs the crystallization experiment), or to rearrange the order of the experiments for a portion of the class. The instructor's guide outlines various options in more detail.

Supplemental experiments. Almost all chapters in this text contain a main experiment and one or more supplemental experiments. The supplemental experiments are of several types. Some may be used *instead of* the main experiment. A few of the experiments involving unknowns are of this type. Some of the supplemental experiments are *extensions* of the principal experiment. These are included strictly for interest value and are *not* alternative to the principal experiment. We strongly urge that at least a few of these be assigned. For example, the liquid-crystal experiment (Experiment 2.3) is not time-consuming, yet it is quite fascinating. Finally, some of the supplemental experiments are included to offer *variety* in the selection of laboratory work. The instructor's guide discusses these supplemental experiments in more detail.

Chapter 22 contains three supplemental techniques (sublimation, vacuum distillation, and elution chromatography) for those instructors interested and having the proper equipment available. An instructor may wish to assign one or more of these techniques at an appropriate time during the laboratory course.

Safety considerations. Experiments in organic chemistry can be dangerous. We believe one of the purposes of the introductory organic laboratory course is to teach students how to handle hazardous chemicals in a safe and prudent manner. With this thought in mind, we have done our utmost to point out the hazards in each experiment. We have included *Safety Notes* before each experiment and precautionary phrases within the experimental instructions. Beginning with Chapter 13, we have cut back the number and detail of these precautions. Therefore, in the latter half of the book, routine hazards that the student has already encountered many times are accompanied by only brief reminders. Of course, safety notes are always included when unfamiliar or especially hazardous operations are to be performed.

Although organic experiments are inherently dangerous, we have attempted to minimize the hazards both by the choice of experiments and by the reagents that have been selected. We have attempted to avoid the use of known or suspected carcinogens, such as benzene. In some experiments, we have pointed out where alternative reagents or solvents can be used. For example, 95% ethanol can often replace methanol as a solvent. In Experiment 10.4, we give two procedures for oxidizing an alcohol: the classic procedure using a dichromate as the oxidizing agent and an alternative procedure using the less toxic hypochlorous acid.

Study problems. The study problems in this text are not as extensive as they would be in a lecture text. The problems included are intended to (1) check the student on his or her theoretical knowledge of the experiments to be performed, and (2) help the student appreciate the practical aspects of laboratory work. The answers are in the instructor's guide that accompanies this text.

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»»» CHAPTER 1 «««

The Organic Laboratory

1.1 Safety in the Laboratory

The organic chemistry laboratory can be a dangerous place. Many organic compounds are volatile and flammable. Many are toxic. Some organic chemicals can cause lung damage, some can give chemical burns, some can lead to cirrhosis of the liver, and some are carcinogenic (cancer causing). Yet, organic chemists generally live as long as the rest of the population because they have learned to be careful. When you work in an organic laboratory, you must always think in terms of safety.

A. Using Common Sense

Most laboratory safety precautions are nothing more than common sense. The laboratory is not the place for horseplay. Do not work alone in the laboratory. Do not perform unauthorized experiments. Do not sniff, inhale, or taste organic compounds, and do not pipet them by mouth. Wipe up any spilled chemicals, using copious amounts of water to wash up spilled acids and bases. (Neutralize any residual spilled acid or base with sodium bicarbonate or dilute acetic acid, respectively.) Do not put dangerous chemicals in the waste crock—the janitor may become injured. Instead, use the jugs provided for chemical disposal.

When working in the laboratory, wear suitable clothing. Jeans and a shirt with rolled-up sleeves, plus a rubber lab apron or cotton lab coat, are ideal. Do not wear your best clothing— laboratory attire usually acquires many small holes from acid splatters, and may also develop a distinctive aroma. Loose sleeves can sweep flasks from the laboratory bench, and such sleeves present the added hazard of easily catching fire. Long hair should be tied back. Broken glass sometimes litters the floor of a laboratory; therefore, shoes should always be worn. Sandals are inadequate because they do not protect the feet from spills. Wash your hands frequently, and always wash them before leaving the laboratory, even to go to the rest room.

Because of the danger of fires, smoking is prohibited in laboratories. Because of the danger of chemical contamination, food and drink also have no place in the laboratory. On the first day of class, familiarize yourself with the locations of the fire extinguishers, fire blanket, eye-wash fountain, and shower.

B. Safety Glasses

Chemicals splashed in the eyes can lead to blindness; therefore, it is imperative that **safety glasses** be worn. They must be worn *at all times*, even if you are merely adding notes to your laboratory notebook or washing dishes. You could be an innocent victim of your lab partner's mistake, who might inadvertently splash a corrosive chemical in your direction. In the case of particularly hazardous manipulations, a **full-face shield** (similar to a welder's face shield) should be worn.

Contact lenses should not be worn, even under safety glasses. The reason for this rule is that contact lenses cannot always be removed quickly if a chemical gets into the eye. A person administering first aid by washing your eye might not even realize that you are wearing contact lenses. In addition, "soft" contact lenses can absorb harmful vapors. If contact lenses are absolutely necessary, then properly fitted **goggles** should also be worn. Also, inform your laboratory instructor and neighbors that you are wearing contact lenses.

C. Chemicals in the Eye

If a chemical does get into the eye, the eye should be flushed with gently flowing water for 15 minutes. Do not try to neutralize an acid or base in the eye. Because of the natural tendency for the eyelids to shut when something is in the eye, *they must be held open during the washing*. If there is no eye-wash fountain in the laboratory, a piece of rubber tubing attached to a faucet is a good substitute. Do not take time to put together a fountain if you have something in your eye, however! Either splash your eye (held open) with water from the faucet immediately or lie down on the floor and have someone else pour a gentle stream of water into your eye. *Time* is important. The sooner you can wash a chemical out of your eye, the less the damage.

After the eye has been flushed, medical treatment is strongly advised. For any corrosive chemical, such as sodium hydroxide, prompt medical attention is imperative!

D. Acids and Bases

To prevent acid splatters, *always add concentrated acids to water* (*never add water to acids*). Concentrated sulfuric acid (H_2SO_4) should be added to ice water or crushed ice because of the heat generated by the mixing. Do not pour acids down the drain without first diluting them (by adding them to large amounts of water) and/or neutralizing them. Strong bases should also be diluted before discarding. If you splash an acid or strong base on your skin, wash with copious amounts of water as described in Section 1.1E. Concentrated hydrochloric acid (HCl) and glacial acetic acid (CH_3CO_2H) present the added hazard of extremely irritating vapors. These two acids should be used only in the fume hood.

Sodium hydroxide ("lye," NaOH) is caustic. In the solid form (usually as pellets), it is deliquescent; a pellet that is dropped and ignored will form a dangerous pool of concentrated NaOH. For this reason, solid NaOH should be handled with care. Spilled pellets should be picked up (with plastic gloves or a piece of paper) and flushed down the drain with a large amount of water.

Aqueous ammonia ("ammonium hydroxide") emits ammonia (NH_3) vapors and thus should be used in the fume hood.

E. Chemical Burns

Any chemical (whether water-soluble or not) spilled onto the skin should be washed off immediately with soap and water. The detergent action of the soap and the mechanical action of washing remove most substances, even insoluble ones. If the chemical is a strong acid or base, rinse the splashed area of the skin with *copious amounts of cool water*. Strong acids on the skin usually cause a painful stinging. Strong bases usually do not cause pain, but they are extremely harmful to tissue. Always wash carefully after using a strong base.

If chemicals are spilled on a large area of the body, they should be washed off in the safety shower. If the chemicals are corrosive or can be absorbed through the skin, contaminated clothing should be removed so that the skin can be flushed thoroughly.

F. Heat Burns

Minor burns from hot flasks, glass tubing, and the like are not uncommon occurrences in the laboratory. The only treatment needed for a very minor burn is holding it under cold water for 5–10 minutes. A pain-killing lotion may then be applied. To prevent minor burns, keep a pair of inexpensive, loose-fitting cotton gloves in your laboratory locker to use when you must handle hot beakers, tubing, or flasks.

A person with a serious burn, as from burned clothing, is likely to go into shock. He or she should be made to lie down on the floor and kept warm with the fire blanket or with a coat. Then, an ambulance should be called. Except to extinguish flames or to remove harmful chemicals, do not wash a serious burn and do not apply any ointments. However, cold compresses on a burned area will help dissipate heat.

G. Cuts

Minor cuts from broken glassware are another common occurrence in the laboratory. These cuts should be flushed thoroughly with cold water to remove any chemicals or slivers of glass. A pressure bandage can be used to stop any bleeding.

Major cuts and heavy bleeding are a more serious matter. The injured person should lie down and be kept warm in case of shock. A pressure bandage (such as a folded clean dish towel) should be applied over the wound and the injured area elevated slightly, if possible. An ambulance should be called immediately.

The use of a tourniquet is no longer advised. Experience has shown that cutting off all circulation to a limb may result in gangrene.

H. Inhalation of Toxic Substances

A person who has inhaled vapors of an irritating or toxic substance should be removed immediately to fresh air. If breathing stops, artificial respiration should be administered and an emergency medical vehicle called.

I. Avoiding Fires

Most fires in the laboratory can be prevented by the use of common sense. Before a match or burner is lit, the area should be checked for flammable solvents. Solvent fumes are heavier than air and can travel along a benchtop or a drainage trough in the bench. Hot matches (even if they have been extinguished) or any other hot substance should not be thrown into wastebaskets because some solvents have very low flash points. Conversely, do not put solvents (or filter paper soaked with solvents) in the wastebasket. The heavy solvent fumes can remain there for days.

Whenever a flammable solvent is used, all flames in the vicinity should be extinguished beforehand. Solvent bottles should always be capped when not actually in use. Flammable solvents should not be boiled away from a mixture except in the fume hood. Solvent-soaked filter paper should be placed in the fume hood to dry before it is discarded in a waste container. Spilled solvent should not be allowed simply to evaporate—if a solvent is spilled, all flames should be extinguished and the solvent cleaned up immediately with paper towels, which should be placed in the hood to dry.

Solvents should never be poured into a drainage trough (which is for water only). Highly flammable solvents should not be poured into the sink, nor should large amounts of any solvent. Small amounts of relatively harmless solvents that are miscible with water (for example, ethanol) may be flushed down the sink with water. Other solvents should be disposed of in jugs provided for solvent-disposal.

J. Extinguishing Fires

In case of even a small fire, tell your neighbors to leave the area and notify the instructor. A fire confined to a flask or beaker can be smothered with a watch glass or large beaker placed over the flaming vessel. (Try not to drop a flaming flask—this will splatter burning liquid and glass over the area.) All burners in the vicinity of a fire should be extinguished, and all containers of flammable materials should be removed to a safe place in case the fire spreads.

For all but the smallest fire, the laboratory should be cleared of people. It is better to say loudly, "Clear the room," than to scream "Fire!" in a panicky voice. If you *hear* such a shout, do not stand around to see what is happening, but stop whatever you are doing and walk immediately and purposefully toward the nearest clear exit.

Many organic solvents float on water; therefore, water may serve only to spread a chemical fire. Some substances, like sodium metal, explode on contact with water. For these reasons, water should not be used to extinguish a laboratory fire; instead, a *carbon dioxide* or *powder fire extinguisher* should be used.

If a fire extinguisher is needed, it is best to clear the laboratory and allow the instructor to handle the extinguisher. Even so, you should acquaint yourself with the location, classification, and operation of the fire extinguishers on the first day of class. Inspect the fire extinguishers. Find the sealing wire (indicating that the extinguisher is fully charged) and the pin that is used to break this sealing wire when the extinguisher is needed.

Fire extinguishers usually spray their contents with great force. To avoid blowing flaming liquid and broken glass around the room, aim toward the base and to the side of any burning equipment, not directly toward the fire. Once a fire extinguisher has been used, it will need recharging before it is again operable. Therefore, any use of a fire extinguisher must be reported to the instructor.

K. Extinguishing Burning Clothing

If your clothing catches fire, walk (do not run) to the shower if it is close by. If the shower is not near, lie down, roll to extinguish the flames, and call for help.

A clothing fire may be extinguished by having the person roll in a fire blanket. The rolling motion is important because a fire can still burn under the blanket. Wet towels can also be used to extinguish burning clothing. A burned person should be treated for shock (kept quiet and warm). Medical attention should be sought.

L. Handling Solvents

Organic solvents present the double hazard of flammability and toxicity (both short-term and cumulative). (Table III.1, page 422, in Appendix III lists the toxic levels and allowable limits of some common solvents.) *Diethyl ether* ($CH_3CH_2OCH_2CH_3$) and *petroleum ether* (a mixture of alkanes) are both very volatile (have low boiling points) and extremely flammable. These two solvents should never be used in the vicinity of a flame, and should be boiled only in the hood. *Carbon disulfide* (CS_2), which is now rarely used in the organic laboratory, is uniquely hazardous. Its ignition temperature is under 100°, the boiling point of water; therefore, fires can result even from its contact with a steam pipe. *Benzene* (C_6H_6) is flammable and also extremely toxic. It can be absorbed through the skin, and long-term exposure is thought to cause cancer. Benzene should be used as a solvent only when absolutely necessary (and then handled with great care to avoid inhalation, splashes on the skin, or fire).

Most halogenated hydrocarbons, such as *carbon tetrachloride* (CCl_4) and *chloroform* ($CHCl_3$), are toxic, and some are carcinogenic. Halogenated hydrocarbons tend to accumulate in the fatty tissues of living systems instead of being detoxified and excreted as most poisons are. In repeated small doses, they are