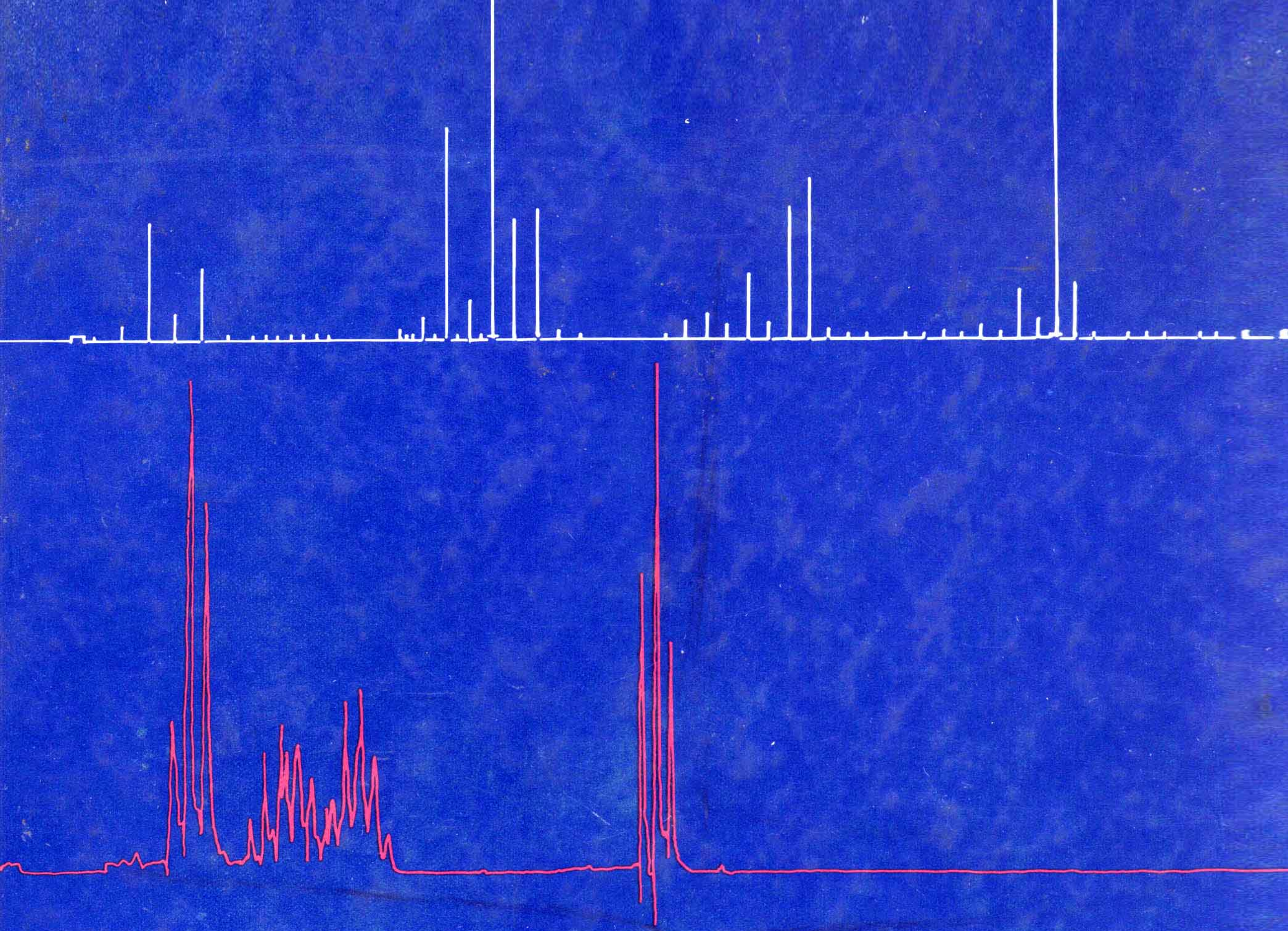

organic chemistry in the Laboratory

Mei Tak Yip / David R. Dalton

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Mei Tak Yip
State University of New York at Binghamton

David R. Dalton
Temple University

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To My Parents and Lin-Wah—M. T. Yip

To Aaron, Nathaniel, and Rachel—D. R. Dalton

preface

Some years ago, we began to develop an Organic Chemistry Laboratory course which might aspire to high quality experimental work while providing an environment as safe as possible for our sophomore students. Our efforts have resulted in this text, in which we have avoided the use of known carcinogenic, teratogenic, and mutagenic chemicals. Although governmental bodies have not yet set minimum exposure limits for many of these compounds in an academic environment, we believe enlightened responsibility dictates these materials be avoided. Other safety precautions are emphasized throughout the book and serve as added incentive to the requirement for careful reading of the experiment before coming to the laboratory.

In addition to our concern for safety, we have long held that a good grounding in technique is important before chemical reactions are run. Thus, following our discussion of safety, we have provided a series of experiments to help the student develop manipulative skill. Although these experiments may be omitted, or referred to when the techniques are needed later, their use in the order provided fulfills the intended need and also postpones the study of organic reactions in the laboratory until their classroom discussion may be underway. The experiments themselves are graded in complexity, with the simplest early and the more difficult later. Further, we have found that for solvents such as petroleum ether and diethyl ether, which have been used routinely with large, closely supervised classes for several years, proper disposal in clearly labelled solvent waste containers (for example, "RECOVERED DIETHYL ETHER ONLY") has enabled us to recycle them from day to day in multiple laboratory section classes. This procedure has aided in reducing environmental pollution and continually escalating costs—with no noticeable loss in laboratory effectiveness.

The last decade has seen a dramatic increase in analytical instrumentation that can be profitably applied at the sophomore level. While many schools run a traditional organic laboratory without such equipment, some routinely utilize low cost GLPC, IR, UV, and ^{1}H NMR for all or a selected portion of their sophomore class, and others now go so far as to include ^{13}C NMR and MS. We have included all of these techniques here in the following way: first, we present the experiment without using the analytical tools; then, after a discussion of the analysis techniques, the *same* experiment is used again and various analyses are carried out. The actual spectra of GLPC tracings that have been obtained in the experiment are presented. Thus, even if the tools are unavailable to a particular class, the results may be discussed, spectra analyzed beyond what is given, and "use" of analytical techniques included as a portion of the laboratory.

Finally, we have insisted that students sign a safety acknowledgement sheet on check-in; knowledge that a laboratory safety quiz must be passed prior to commencement of actual work has also helped students locate eyewash fountains, emergency showers, fire extinguishers, etc., before they might have occasion to use them. We believe that our insistence on careful laboratory planning and work, coupled to firm knowledge of emergency procedures, will well serve students who take organic chemistry no matter what their future plans.

ACKNOWLEDGEMENTS

That this book came into being is due in no small measure to the intellectual honesty and perseverance of Dr. E. T. Cutler. He, more than others, catalyzed our thinking along paths which could lead to a practical, safe course for Sophomore Organic Chemistry students.

We also believe that without the willing cooperation of the laboratory instructors and the many students over the several years during which various draft copies of this book were used at Temple University, our efforts could not have reached fruition.

We also must express our gratitude for the uncounted hours that were spent by Dr. S.-L. Huang in checking and rechecking our procedures, and obtaining infrared, ultraviolet, ^{1}H nuclear magnetic resonance spectra, and gas-liquid partition chromatography data, by Mr. M. Frey for the ^{13}C nuclear magnetic resonance and mass spectra, and by Mrs. F. D'Alessandro, Ms. C. Haines, Ms. J. Lawrence, Ms. P. Littles, and Mrs. R. Venable for typing manuscript which at times seemed endless.

Drs. Cecile Dalton, Clelia Mallory, Frank Mallory, Charles C. Price, and Kin Fai Yip were kind enough to read significant portions of early manuscript drafts and comment unreservedly. The work is better for their aid.

Jack Leonard of Texas A.&M. University, Guilford Jones of Boston University, Edward Compere of Eastern Michigan University, and Donald K. Brundage of the University of Toledo are also thanked for their many helpful insights and suggestions for the book.

Finally, our families have suffered the neglect resulting from the hours we devoted to this work rather than to them, and their forbearance made its eventual production possible.

M. T. Yip
D. R. Dalton

REQUIRED READING
SAFETY INSTRUCTIONS

What are Carcinogenic, Teratogenic, and Mutagenic Materials?

Carcinogens are substances which are known to induce cancer; teratogens are substances which are known to cause developmental malformations in the fetus; and mutagens are substances which are known to cause an increase in the frequency or extent of gene mutation.

Flammable Liquids—Why not use a Bunsen burner all of the time?

Flammable liquids are defined by the National Fire Protection Association as "those with a *flash point* below 60°C and a vapor pressure not exceeding forty pounds per square inch absolute at 38°C."

The *flash point* of a liquid is the temperature at which it gives off sufficient vapors to form an ignitable mixture with the air near the surface of the liquid. Since the *ignition temperature* of a substance is the minimum temperature required to initiate self-sustained combustion, some substances can burn and cause fire without external ignition simply by heating above their ignition temperature.

The following table lists some flammable liquids commonly encountered in Organic Chemistry laboratories:

LIQUID	*FLASH POINT (°C)*	*IGNITION TEMPERATURE (°C)*
2-propanone(acetone)	−18	538
carbon disulfide*	−30	100
cyclohexane	−17	—
ethanol	+13	371
diethyl ether	−45	180
petroleum ether	−56	246

* Carbon disulfide is not used in this laboratory manual. However, it is one compound which can (and has been!) ignited even by a hot steam pipe or steam bath.

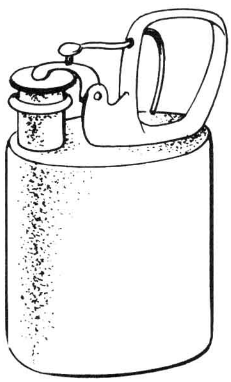
For a fire to "happen," therefore, a flammable liquid, an oxidizing atmosphere (e.g., air), and an ignition source are commonly required. You will be working with flammable liquids and, under most laboratory conditions you will encounter here, air will be present. Flammable vapors, therefore, should be kept as far away as possible from any ignition source, the most readily adjusted parameter. It is safer to use a steam bath or heating mantle as the heat source than a Bunsen burner.

Flammable liquids must never be manipulated near an open flame! A student must check the area for a lighted Bunsen burner *before* working with flammable liquids and vice-versa.

When distilling a flammable liquid, a flask with a ground-glass joint and which has been cooled in an ice-water bath should be used in order to minimize the escape of the flammable vapor into the air. The open part of the system at the receiving adapter must be properly vented. Finally, illuminating gas which fires burners is also flammable and toxic. Thus, gas jets must be completely turned off when you have finished.

How to Store Flammable Liquids.

The amount of flammable liquid present in any laboratory should be kept to a minimum. No more than one gallon of any such material should be present in the laboratory and available to the students. Approved safety metal cans (see illustration) should be used to store the flammable liquid. It is good practice to measure flammable liquids under the hood where the ventilation is known to be suitable.



Safety metal can for flammable liquids.

Safety Equipment

Clothing: Clothing should be comfortable, nonexpensive and should cover most of the body. A laboratory coat or a rubber apron is highly recommended. Shoes should be comfortable and should cover the whole foot. Sandals (with exposed toes, etc.) and high-heeled shoes should not be worn in the laboratory. When handling concentrated acid or corrosive liquids, rubber gloves should be worn.

Eye Safety Goggles: The importance of eye protection cannot be overemphasized. SAFETY GLASSES OR GOGGLES MUST BE WORN AT ALL TIMES IN THE LABORATORY BY STUDENTS AND INSTRUCTORS. THERE ARE NO EXCEPTIONS. Individuals who choose to disregard this rule may not work in the laboratory. Contact lenses *should not* be worn in the laboratory because of the added difficulty in eye irrigation should it be necessary.

Ventilation Hoods: Sufficient ventilation hood space must be present in each laboratory. The hoods should be inspected annually for a minimum flow rate of 100 ft./min. Experiments involving very toxic substances, corrosive gasses, or gasses with unpleasant odors should be carried out under the hood. The hoods should be equipped with safety glass windows and controls on the outside.

Fire Extinguishers: Fire extinguishers with carbon dioxide (CO_2) under pressure should be used instead of liquid (tetrachloromethane, carbon tetrachloride, CCl_4) extinguishers because CO_2 gas is more effective and CCl_4 may result in phosgene formation when used to put out a fire. Water should not be used. The fire extinguisher should be easily accessible (at least two in a small laboratory and three in a large one) and in good operating condition. It should be inspected at least annually. A used fire extinguisher cannot be relied upon to have any value in putting out a fire. It should be reported and refilled, immediately. A fire blanket should be readily available.

Safety Showers and Eye Fountains: There should be at least one safety shower (deluge type) and one safety (elbow operated) eye fountain in every laboratory. They should be tested at least annually.

Medical Kit: Every laboratory should have one first-aid box or kit which should contain (at least): adsorbent cotton, adhesive tape, aromatic spirits (ampules), band-aids, gauze bandage (1", 1½", and 2"), sterile gauze pads, anesthetic ointment, antiseptic, and cotton tipped wooden applicators (e.g., Q-tips). Minor cuts and burns can then be treated with the first-aid equipment in the laboratory by the instructor. When a student requires special medical attention, he or she should be treated promptly by a physician. Every laboratory should have the telephone number and address of the safety office, student health center, or emergency center prominently posted. The instructor has the responsibility of staying with the injured student at all times until help arrives.

Fire Alarm Boxes: Fire alarm boxes may alert department, university, or municipal fire fighting bodies. Unless their locations are known, however, they are of little use. Thus, students should be required to locate the nearest alarm box. The box should be clearly marked and easily accessible.

A SUPERVISED DEMONSTRATION OF THE LOCATION AND USE OF SAFETY EQUIPMENT IS SUGGESTED BEFORE THE FIRST EXPERIMENT IS DONE. The added time and expense (e.g., refilling extinguishers, etc.) is trivial compared to the cost and danger of misuse or nonuse because of ignorance. An announced examination question on the location of the equipment in the laboratory is an effective incentive to learning their locations.

Emergency Instructions

Fire: Any fire is dangerous. If there is a fire, report it to the instructor immediately. In putting out a fire, the extinguisher should be aimed at the *base* of the flame and a "back-up" extinguisher held ready. Students should not overestimate their ability to put out a fire. It may spread more rapidly than imagined. Individuals not involved in fire fighting should quickly, but calmly, leave the area for a safe place.

If Your Clothing Is on Fire: Get under a safety (deluge) shower. Avoid running. Running will intensify the flame and cause you to inhale more deeply. If a shower is unavailable or if the safety blanket is closer, wrap yourself in a safety blanket to smother the flame. If neither is available, roll on the floor and smother the fire with a coat or use a fire extinguisher. *To treat a minor burn,* immerse the burned area as quickly as possible in ice water. Keep it there for several minutes. If the burn area cannot be immersed in ice water, cover the area with crushed ice. This treatment will relieve the pain and reduce the severity of the burn. Then, apply ointment and a sterile gauze pad. *For an extensive burn,* get medical help at once and keep the victim as calm and warm as possible while waiting for help. DO NOT LEAVE A BURN VICTIM . . . SEND FOR HELP.

Acid and Alkali Burns: Wash the burned area immediately with copious quantities of running water. Do not try to neutralize the area. If the burn area is on the face or head, DO NOT remove eye goggles until the face and head have been thoroughly flushed. Cover the area with sterile gauze and contact a physician.

Bromine Burns: Wash the burned area with large amounts of running water. Next soak the burned area in 10% sodium thiosulfate solution pads for a few hours. Wash the area again with water and apply a sterile pad. If the burned area is extensive, seek the aid of a physician.

Chemicals in the EYE: Flush the eye or eyes immediately (eye fountain) and continue flushing for at least 15 minutes while a physician is notified. During the flushing, eye lids should be forcibly held up so that the entire eye can be thoroughly irrigated. A physician should be notified immediately. Tell the physician the names of the chemicals involved.

Cuts: After washing the wound area with soap and water, cover with a sterile bandage. If deep and freely bleeding, cleanse the wound as above to remove foreign bodies and apply pressure at the wound with sterile gauze until the bleeding stops. For deep cuts and cuts in which glass or other foreign bodies are lodged, professional medical help should be sought at once. The victim should not be permitted to seek such help alone. Shock may set in at any time after trauma.

Disposal of Chemicals

Improper disposal of chemicals is not only very hazardous to the person involved and housekeeping personnel, but also can result in environmental pollution.

Organic liquid waste should be disposed of in a metal safety container labelled "Organic Liquid Waste ONLY" or labelled specifically for the material, e.g., "Recovered Ether ONLY." Proper ventilation, e.g., a good hood, is necessary. Large amounts of organic liquid waste should not be accumulated at any time in the laboratory.

Organic liquid waste containing corrosive acid should be disposed of in a clearly labelled *glass bottle,* housed within a safety container, because metal containers would be damaged by the acid. Organic waste containing mercury should be disposed of in a clearly labelled metal container. Mercury is a highly toxic cumulative poison. Aqueous waste should be discarded in the sink and washed down with water. Solid waste should be placed in a solid waste container.

How to cut glass tubing and how to pass glass tubing and thermometers through a stopper.

Put Your Goggles on: Flying glass chips are dangerous.

To cut glass tubing, make a straight deep mark with a sharp triangular file or glass cutter at the desired place. Moisten the cut. Place the fingers around the glass tube with both thumbs together, opposite the cut, and bend toward you while pulling the tubing apart.

There are numerous occasions when a glass tube or thermometer must be inserted into a hole of a stopper. Since glass is fragile, the following precautions should always be observed: Fire polish both ends of the tube and wet the tube, as well as the inner walls of the hole in the stopper, with glycerine. Wrap a towel around your hand and grasp the tube near the stopper. Apply a gentle twisting motion to the tube while pushing it through the hole.

Removal of a glass tube or thermometer from a stopper also presents a problem. The glass and rubber stopper may have become "frozen" together. They can occasionally be separated by rolling the stopper with a hard wood block under enough pressure to flex the stopper, or by cutting the stopper with a cork borer to free the glass tubing. A knife can also be used to cut the stopper away from the tube or thermometer.

ADDITIONAL BASIC SAFETY RULES

Work in the laboratory is prohibited unless an instructor is present.

Students must study each laboratory assignment before coming to class and may not perform experiments that have not been assigned.

Arrange apparatus neatly and compactly, with the taller objects at the rear of the work area. Assemblies consisting of several pieces of apparatus must be approved by the instructor. Keep all books except the laboratory manual and your notebook off the laboratory workbench.

Read the labels on bottles carefully. Do not take reagent bottles from the shelves to the workbench. Remove only enough material from the bottle to do the experiment. Any excess reagent should not be returned to the bottle, but placed in the trash can (solid) or in the appropriate waste bottle (liquid).

Do not throw filter paper or solid materials into the water troughs or sinks.

Do not throw organic waste into the water troughs or sinks.

When heating a substance in a test tube, do not point it at anyone. The hot contents may "bump" and be thrown from the tube. "Bumping" or sudden boiling is due to localized heating and formation of a large vapor bubble beneath the surface of the liquid.

When testing for the odor of gases being generated in test tubes, fan the gas toward the nostrils with the hand. Do not breathe deeply.

Do not accumulate flammable or other hazardous substances at the workbench. All chemicals are dangerous if inhaled or ingested in quantity.

DO NOT EAT OR DRINK IN THE LABORATORY. Wash your hands with soap and water if they come in contact with any chemical. Clean up spills promptly.

At the end of the laboratory period, clean off your work space with a sponge or wet paper towel. Check to see that the gas and water have been turned off. You are responsible for keeping the area neat. Repeated failure to do so may result in loss of credit.

Clean-up starts fifteen (15) minutes before the official end of the class period.

When the time is up, you are supposed to be out of the laboratory. Failure to properly budget your time is presumptive evidence of poor planning and your grade may suffer.

ACKNOWLEDGEMENT

(1) I have been informed that I am required to wear eye protection at all times in this laboratory and I agree to do so.

(2) I have read and I understand the basic rules for laboratory safety as described in my laboratory manual.

(3) I understand the location and the use of the laboratory emergency equipment, such as fire alarms, fire extinguishers, safety showers, and eye fountains.

______________________________ ______________________________

signature date

Chem ____________________ Lab Day ______ Time __________ Room _________

Lab Section ____________________

Lab Instructor ____________________

Locker No. ____________________

IMPORTANT LABORATORY GRADING CRITERIA

A. *Set-up:* Because of grading and safety, each student's set-up must be checked by the instructor at the beginning and during the laboratory period. The following points must be considered:
   a. Proper lubrication of ground-glass joints when necessary.
   b. Sufficient support for all equipment. Books or other such objects must not be used to support apparatus.
   c. Efficient utilization of space.
   d. Correct source of heat (Bunsen burner, heating mantle, or steam bath). When a Bunsen burner is used, the flame must be adjusted to give the desired rate of heating.

B. ***Technique:*** Creativity and correct manipulation of chemicals and equipment are two important considerations in good laboratory technique. Students should be able to think and work independently, make intelligent observations, and use their time and resources efficiently. Students should handle all the chemicals and equipment with special emphasis on *safety* and *neatness.* Reagent bottles should not be removed from the shelves or the hoods to the bench or anywhere else. *ONLY* enough material from the bottle should be used to do the experiment. Cap all the reagent bottles after use. The utility areas and balances must be kept clean. *SAFETY GOGGLES OR OTHER APPROVED EYE PROTECTION MUST BE WORN AT ALL TIMES DURING THE LABORATORY.*

C. ***Product:*** Purity and percentage are considered.

D. *Notebook:* A preliminary write-up is required for each experiment. The important information that must be included is described on the following pages.

SUGGESTED LABORATORY NOTE-BOOK (for Experiments 1–4)

1. Title of the experiment and date.

2. Physical constants of all the reagents.

Compd.	*formula*	*molecular weight*	*gm or ml used*	*density*	*m.p.*	*b.p.*	*solubility*		
							water	*alcohol*	*ether*

3. A sketch of the set-up involved in the experiment.

4. Procedure and observations:

procedure	*observations*
1. 2. 3. so on	

5. Data and calculations (if any)

6. Discussion

SUGGESTED LABORATORY NOTE-BOOK (Experiment 5 . . .)

1. Title of the experiment and date.

2. Write balanced equations for the main reaction or sequence of reactions involved in converting the starting materials to the final products.

3. Equations for side reactions (if any).

4. Physical constants of all reagents and products.

				mole used					*solubility*		
compd.	*formula*	*mol. wt.*	*gm(ml) used*	*theoretical*	*actual*	*density*	*m.p.*	*b.p.*	*water*	*alcohol*	*ether*

Which one is the limiting reagent?

5. A sketch of the set-up involved in the experiment.

6. Procedure and results/observations:

procedure	*results and observations*
1. 2. 3. etc.	

7. Flow-chart for the procedure of purification of the product (optional).

8. Yield calculation: theoretical yield (calculated from balanced equation and limiting reagent).

$$\text{yield } \% = \frac{\text{actual yield in gm}}{\text{theoretical yield in gm}} \times 100\%$$

9. Physical properties of the product (color, shape, odor, etc.).

10. Discussion.

contents

The numbers in parentheses following the title of the experiment indicate suggested time allotment in three-hour laboratory sessions. The letters in brackets following the title of the experiment indicate supplementary experiments are provided in the appropriate section according to the following code: ir = infrared spectroscopy; n = NMR spectroscopy; g = gas-liquid partition chromatography; c = ^{13}C NMR spectroscopy; u = ultraviolet spectroscopy; m = mass spectroscopy.