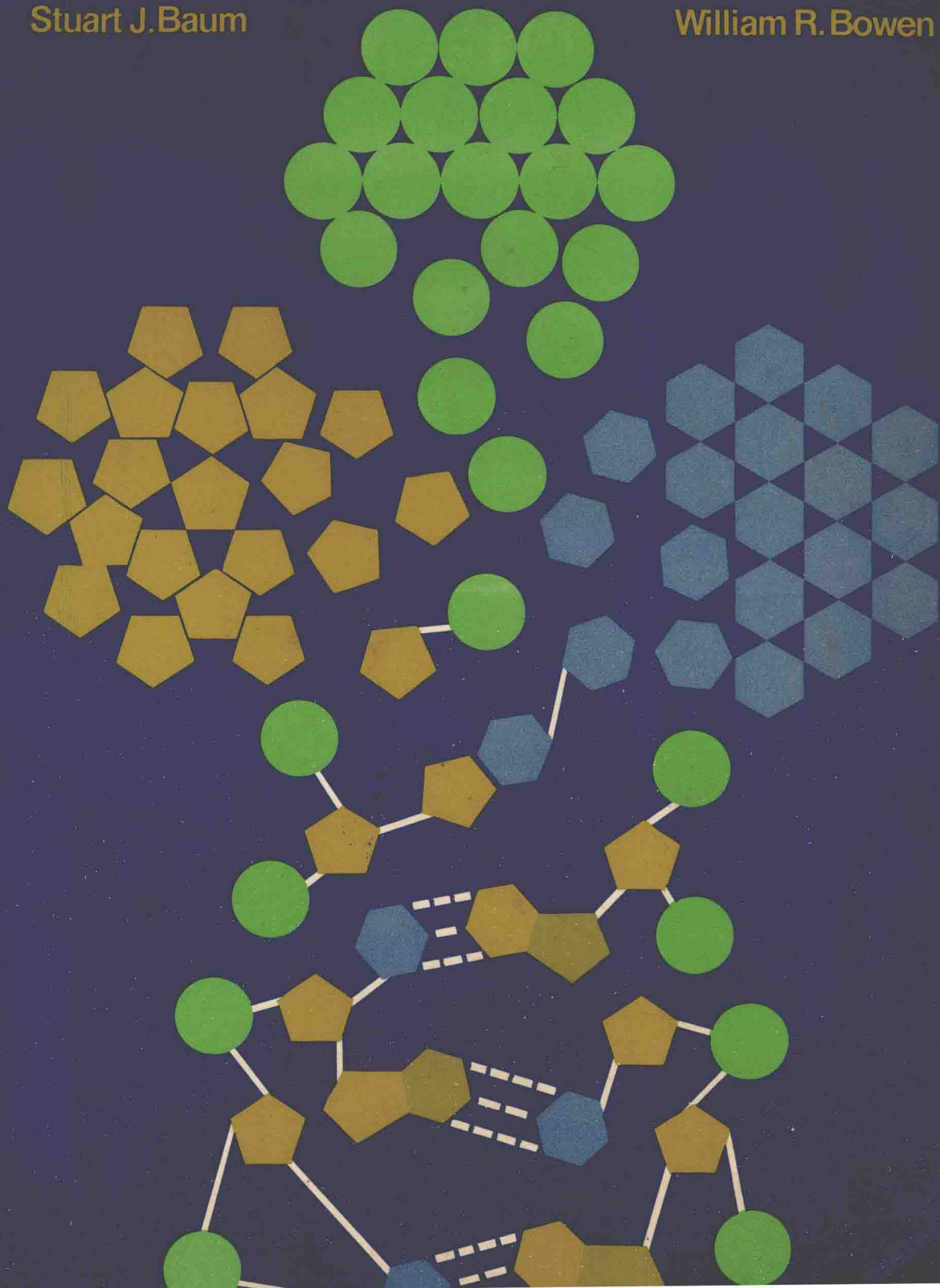


Exercises in Organic and Biological Chemistry

Stuart J. Baum

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MACMILLAN PUBLISHING CO., INC.
NEW YORK

COLLIER MACMILLAN PUBLISHERS
LONDON

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Printed in the United States of America

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Macmillan Publishing Co., Inc.
866 Third Avenue, New York, New York 10022
Collier-Macmillan Canada, Ltd., Toronto, Ontario

Printing	89	Year	90
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Preface

Within the past few years one-semester courses in the concepts of organic and biological chemistry have been designed to serve the nonscience liberal arts major as well as students in nursing, home economics, agriculture, and veterinary science. The diversity of students enrolled in such a course necessitates as dynamic an approach to the subject as is practical and feasible. The purpose of this book is to attempt to fulfill this need.

It is our belief that the laboratory in such courses should function as the primary learning experience. If such an experience arouses enthusiasm and leads students to enjoy learning, they may gain a lasting insight into chemistry and its relevance. Therefore a discussion of the organic and biological concepts always precedes any experimentation. The integration of textual material with laboratory procedures is intended to eliminate much of the cookbook aspects that are normally associated with laboratory courses in chemistry. Our approach thus has a twofold function: (1) to provoke and stimulate the student's interest and (2) to make the student aware of what he is doing and why he is doing it. The student is encouraged to use the scientific method, i.e., to obtain data and then develop his own conclusions. Wherever applicable, the determination of an "unknown" has been included to stimulate greater interest. Several experiments require quantitative techniques and simple calculations. Pertinent questions within the textual material and at the end of some of the chapters are intended to emphasize particular facts and principles and to test the student's understanding of the experimentation. A stepwise procedure for the laboratory

directions has been utilized to allow the student to accomplish more of the experimental work with less confusion and in less time.

The experiments in each of the chapters can be completed within a three-hour laboratory period with the students working in pairs, except for Experiment 8-3, which requires a separate period. Because this course will have a fairly large enrollment, it is not practical to use highly specialized, expensive apparatus. All of the experiments in this book can be carried out with the standard equipment found in the introductory organic chemistry laboratory. The appendix contains details for the preparation of necessary reagents, equipment needed, and suppliers of certain chemicals and biological materials.

Although this manual is intended to accompany Professor Baum's *Introduction to Organic and Biological Chemistry*, it is not keyed to specific chapters in that book and therefore can be used with any text in this area. We have purposely included more experiments than can be covered in one semester, thus permitting the instructor to select those that are best suited to the purposes of his particular course. In order to have the laboratory work coincide with the lecture material, several of the functional group reactions in Appendix I might be performed in addition to, or instead of, the experiments in the initial chapters. For example, Experiments A-1 through B-3 might be included with Chapter 1, Experiments C-1 through D-4 with Chapter 2, and so on. Alternatively, one laboratory period can be devoted entirely to functional group reactions.

The authors would like to thank Professor Irwin E. Liener for his very thorough review of the manuscript and for allowing us to use Experiments 9-1 and 9-2. We wish to express our gratitude to Jan Bowen and Valerie Wilson for typing the manuscript and to Kathryn Knoche and Judy Russell for testing the experiments.

S. J. B.
W. R. B.

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CHAPTER 1

Purification of Solids by Recrystallization

The solubility of a solute in a particular solvent largely depends upon the temperature of the solvent (see Table 1.1). The majority of organic compounds are more soluble in hot solvents than in cold solvents. A solid that dissolves in a solvent at an elevated temperature will crystallize out of solution when the solvent is cooled. If the original solid were contaminated by some foreign substance, the latter could be removed by a simple purification procedure using an appropriate solvent. The impure solid is dissolved in hot solvent; on cooling, the pure solid crystallizes out, leaving the impurities behind in the solution. This process is called *recrystallization* and is the one most commonly used for the purification of solid organic compounds.

Contaminants usually constitute a relatively small proportion of the impure compound. In some cases the impurity may remain insoluble in the hot solvent and can be removed by filtering the hot solution. If the impurities are soluble in the hot solvent, they will pass through the filter paper along with the desired compound. The filtrate, upon cooling, will become saturated with respect to the desired substance which precipitates out of solution. As long as the contaminants do not reach their respective solubility limits, they will remain in solution. The crystallized solid is recovered, theoretically free of impurities, by filtration.

In many instances the product is colored because of the presence of colored impurities. These contaminants are removed by selective adsorption on activated charcoal. It is believed that the colored substances are adsorbed on the charcoal

because the chromatophoric groups (the functional groups responsible for the color of the molecules) have a strong affinity for the surface of carbon. A small amount of charcoal is therefore added to the hot solution prior to the filtration step. Because charcoal will also adsorb some of the desired compound, it is essential that only a small amount be used (a micro-spatula measure).

Table 1.1 Solubility as a Function of Temperature

<i>Solute</i>	<i>Solvent</i>	<i>Temperature</i> °C	<i>Solubility</i> (g/100ml)
Acetamide	Ethanol	20°	25.0
		60°	257.0
Acetanilide	Water	25°	0.56
		100°	5.0
Benzoic acid	Water	18°	0.27
		75°	2.2
Cholesterol	Ethanol	17°	1.0
		78°	11.0
Iodoform	Ethanol	18°	1.3
		78°	7.8
Succinic acid	Water	20°	6.8
		100°	121.0

The most important consideration in performing a recrystallization is the choice of a suitable solvent. Ideally, a good solvent for purification should have the following characteristics:

- (1) It does not react with the solute.
- (2) It dissolves considerably more of the desired product at high temperatures (usually the boiling point of the solvent) than at low temperatures (usually room temperature or ice temperature).
- (3) It dissolves contaminants at low temperatures and/or it does not dissolve them at high temperatures.
- (4) It has a relatively low boiling point to facilitate its evaporation from the wet crystals.

Solvents commonly used for recrystallization purposes include water, methanol, ethanol, acetone, ethyl acetate, chloroform, carbon tetrachloride, benzene, hexane, and petroleum ether. These solvents are listed in a general order of decreasing polarity.

Experiment 1-1 Recrystallization of Acetanilide

1. Weigh out a 2.0 g sample of impure acetanilide and place it in a 100-ml round-bottom flask (or a 125-ml Erlenmeyer flask).
2. Add 50 ml of water and a small amount of decolorizing charcoal to the flask.
3. Assemble the apparatus with a reflux condenser as illustrated in Figure 1.1.

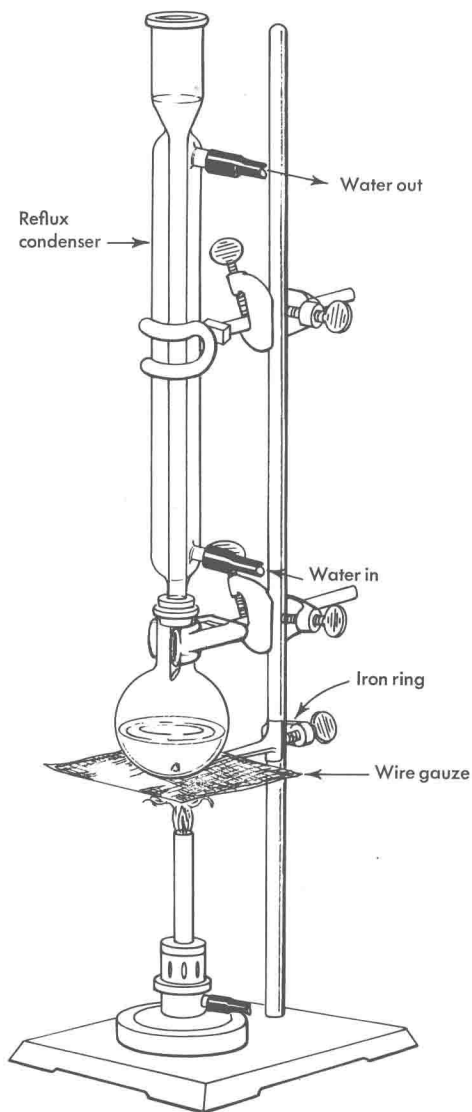


Fig. 1.1 A reflux apparatus.

Refluxing allows a volatile solvent to be heated for long periods of time without boiling away the solvent. When hot solvent vapors come in contact with the cold condenser, they will condense and return, as a liquid, to the boiling flask. Refluxing is also advisable from the point of view of safety because most volatile solvents are flammable and their vapors are toxic.

4. Circulate the water through the condenser in a slow, steady stream.
5. Heat the water in the flask to boiling, adjusting the burner flame so that the water refluxes in a steady drip from the bottom of the condenser.
6. Continue to heat the flask for about 10 min or until no more solid dissolves. While the mixture is being heated prepare a fluted filter paper (Figure 1.2).

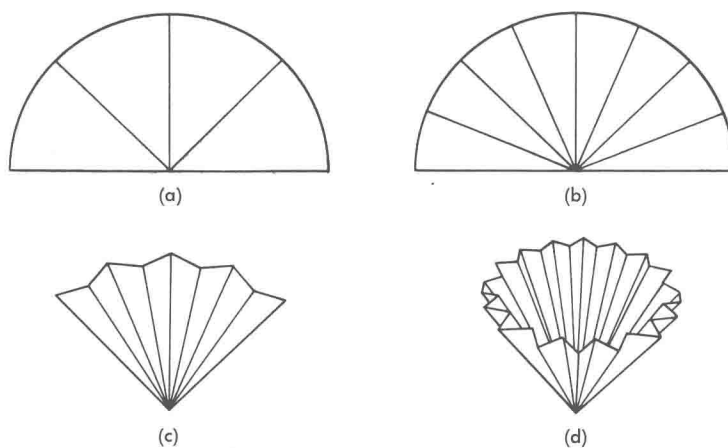


Fig. 1.2 Preparing a fluted filter. (a) Fold the paper in half and then in half again. Bring each edge into the center fold, making two additional creases in the same direction. This divides the paper into four equal sections. (b) Then divide each section by a crease still in the same direction. This gives eight equal sections. (c) Divide each section in two by a crease in the opposite direction, thus making sixteen sections and thirty-two sections when the filter paper is opened (d).

A stemless funnel and fluted filter paper are commonly used to speed up the *gravity filtration* of a hot solution. A fluted filter paper provides a maximum filter surface and a minimum of cooling and crystallization at the glass-paper interface. A stemless funnel prevents the filtrate from cooling in the stem accompanied by premature crystallization of the product.

7. Place the stemless funnel containing the fluted filter paper in a beaker of appropriate size. The lower tip of the paper should project through the opening at the bottom of the funnel.
8. Preheat the filter and funnel just prior to use by pouring a little boiling water through it.
9. Carefully remove the reflux condenser from the flask.

10. Using the flask clamp as a handle, pour the hot suspension through the filter paper. *Note:* It is essential that this operation be completed as quickly as possible in order that cooling be minimized. If all of the solution cannot be placed into the funnel at once, the remainder should be kept hot, by heating over the bunsen flame, until it can be transferred to the funnel. The charcoal and other insoluble impurities collect on the filter paper; the filtrate should be a clear solution.
11. Allow the filtrate to cool to room temperature and then place it in an ice bath.
12. Prepare a *suction filtration* apparatus using a Büchner funnel (Figure 1.3).

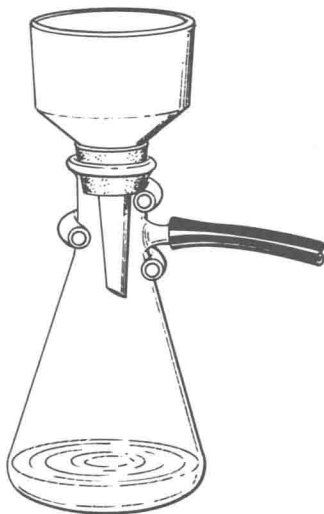


Fig. 1.3 Büchner funnel and filter flask for suction filtration.

After crystallization is completed the crystals are separated from the mother liquor by suction filtration. This affords a rapid means of filtration and, at the same time, aids in removing as much of the liquid from the crystals as possible.

13. Place the proper size filter paper in the funnel. Then attach the funnel to an aspirator with heavy-walled tubing. Turn on the aspirator and pour some distilled water through the funnel. This serves to moisten the filter paper, making it fit snugly to the funnel.
14. Decant, through the funnel, most of the mother liquor and then pour in the bulk of the crystalline acetanilide. Use a wash bottle containing cold distilled water to rinse out the remaining crystals from the beaker.
15. The residual liquid can be pressed out of the mat of crystals with a clean rubber stopper.

16. Disconnect the suction flask and transfer the crystals to a clean watch glass or a large piece of filter paper to air-dry.
17. Weigh your dried crystals and calculate the percentage recovery of purified acetanilide.

Weight of impure acetanilide _____

Weight of recrystallized acetanilide _____

Percentage recovery of acetanilide _____

Questions

1. Would it be wrong to dissolve the original impure material in a large excess of solvent? Why?
2. Why did you preheat the stemless funnel and filter paper with some boiling water just prior to using it for filtering the impure acetanilide suspension?
3. Why is it necessary to use thick-walled tubing in connecting the filter flask to the aspirator?
4. What problems would arise if you filtered a hot solution containing a volatile solvent by suction filtration?
5. At what steps in the recrystallization procedure did you lose some of your product? What can you do in the future to avoid these losses?