ELEMENTARY LABORATORY EXPERIMENTS IN ORGANIC CHEMISTRY

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PREFACE

This laboratory manual is designed for first semester students in organic chemistry whether they are specializing in chemistry or are merely seeking a knowledge of the subject for use in medicine, agriculture, home economics, biology or related fields.

The authors believe that it is very desirable for the beginning student to acquire an understanding of the more important manipulations and procedures in the organic chemical laboratory before any attempt is made to prepare organic compounds or study organic chemical reactions. As a consequence a number of preliminary experiments have been set apart to be carried out first and are designed to give an opportunity to teach the student not only technic but also the important principles involved in the common laboratory procedures. This gives the student laboratory work while the introductory part of the theoretical considerations is being covered in the lectures, and at the same time makes it possible for the student later to devote all his time and energy to a better understanding of the reactions involved in the experiments.

Opinions differ as to whether or not first semester students should be offered numerous test-tube experiments covering an extensive number of reactions, or should be offered comparatively few experiments carried out so that the products are isolated and purified. The authors feel the latter plan is distinctly the more instructive and interesting to the student and it is the one followed in this manual.

The choice of experiments has been made to include the following types of preparations: (1) those representing some of the more important reactions, (2) those involving the preparation of substances readily obtained in good yields, (3) those using the cheapest reagents coincident with the best results, (4) those presenting series of reactions so that a student may use previously prepared materials, such as the series butyl bromide—butyl cyanide—valeric acid or nitrobenzene—aniline—acetanilide—p-bromoacetanilide, etc. In a number of cases two or three experiments involving the same type reaction are included, so that all of the students in a class need not necessarily do the same experiment to illustrate the same general reaction. This duplication of type experiments serves the further purpose of emphasizing to the student the fact that each of such experiments merely represents a specific example of a general reaction. Moreover, a certain variation which may be desired from one year to another is thus made possible. No attempt is made to include certain important reactions such as the acetoacetic ester synthesis of ketones, or the malonic ester synthesis of acids. These preparations certainly fall into a second semester laboratory course, even though one or more of these subjects may be discussed from a theoretical standpoint in the lectures in the first semester course.

Particular care has been taken to describe each experiment in great detail even to specifying the amount of washing or drying reagent to be used in each instance and the exact strength of any reagents used which do not appear on the side-shelf. This has not been the practice in previous manuals and the criticism may be offered that the present method may lead the student to too much of a routine point of view. There are so many details to be learned, however, in beginning the study of organic chemistry, that the procedure suggested is believed to be the better one, particularly if the experiments are accompanied by questions concerning the principles involved. The student is then prepared in the second semester to undertake experiments where such details are not included and is able to use the proper judgment in setting up apparatus and in the use of reagents.

The questions at the end of each experiment are designed to determine whether the student understands the principles and the significance of the experiment performed. Such questions form an important part of the laboratory instruction. The teacher must designate to the class whether part or all of the questions must be answered, since this will depend upon the extent of the theoretical organic chemistry which has been presented.

The order and number of experiments to be carried out must be determined by the individual teacher for any particular class in organic chemistry. The experiments must necessarily be accompanied by an occasional lecture quiz, general instructions and general discussions of the reaction in various experiments.

In order to indicate the amount of work that may be expected, but in no way to attempt to select the best experiments to be chosen, a few outlines of courses follow:

For a one semester course for students majoring in chemistry or chemical engineering which involves six hours' laboratory work per week (including any necessary laboratory instruction by the teacher), the following experiments are suggested: Experiments 1, 2, 3, 4, 5, 6, 8, 9, 10b, 11, 15a or 15b, 16, 25, 26, 17, 18, 19, 32, 33a or 33b or 33c, 34a or 34b, 38, 44.

For a pre-medical, home economics or agricultural course for students taking six hours' laboratory per week (including any necessary laboratory instruction by the teacher), experiments 1, 2, 3, 4, 5, 9, 10a or 11, 12, 15a or 15b, 16, 24, 25, 19, 20, 28, 29, 30, 31, 32, 34a or 34b, 38, 44.

For a short course with only three hours per week in the laboratory, experiments 1, 2, 3, 4, 9, 10a, 15a or 15b, 24, 19 (first half), 20, 40, 28, 34a.

For a laboratory course to accompany J. B. Conant's *Organic Chemistry* with six hours per week in the laboratory, the following experiments in the following order may be acceptable: Experiments 1, 2, 3, 8, 4, 16, 14 or 15a, 9, 10b or 11, 17, 18, 19, 22 or 31, 25, 26, 28 or 30, 33a or 33c, 34a, 38, 40, 43, 44. If only four hours a week are available, the list might be shortened by omitting experiments 10b or 11, 17, 18, 40, 43 and 44.

Other experiments have been included suitable for any superior students who have extra time.

A convenient and successful procedure for keeping notes and determining a student's ability is described. This happens to be the one used at the University of Illinois and at Cornell University laboratories, but there are many other methods which may be preferable in meeting other conditions. The pages of the manual have been perforated so that, if desired, the experiment sheet may be removed and attached directly into the notebook.

The introductory chapters attempt to explain merely the more important facts and theories concerning the general procedures in organic chemistry. It is better for the beginning student to get just the facts which he can remember and use, and to acquire more and more details later as he becomes advanced. This principle differs from many of the texts in which so many details about various procedures are given that the student does not learn them all readily.

For the convenience of the student, the strength of all the reagents commonly used on the side-shelf and the precautions in the use of certain materials are included. For the aid of the teacher the amounts of chemicals necessary for ten students for each experiment are listed, though no mention is made of the amount of reagents which commonly appear on the student's desk, such as dilute acids and alkalies and the common concentrated acids. The time required by an average student for each experiment is also given, with an indication of the period devoted to refluxing or standing, during which time the student may be working on other experiments. As the beginning student is usually unfamiliar with the common apparatus used in organic chemistry a page of diagrams is inserted. A graphic description of the method for making a fluted filter and a copy of a convenient card upon which the student may report his experiments are included.

Certain special solutions such as ammoniacal cuprous chloride, ammoniacal silver nitrate, Fehling's solution or phenylhydrazine reagent, are described under the particular experiments in which they are to be used, and each student is expected to prepare them, or to be familiar with the method of preparation of such solutions.

The authors wish to acknowledge here their indebtedness for suggestions and advice given by Drs. James B. Conant, C. S. Marvel, H. T. Clarke, W. H. Carothers, and others, for aid in assembling the manual by Letha A. Davies, and for the help obtained from "Organic Syntheses" and a few of the other outstanding laboratory manuals in organic chemistry.

R. A.
J. R. J.

AUGUST, 1928.

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PART ONE

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INTRODUCTION

FOREWORD

The fundamental aim of laboratory work in elementary organic chemistry is to teach the methods which are used in this field and to acquaint the student with the most common organic materials. A student should get first-hand experience of the fact that organic chemistry deals not only with formulas and names but with substances having definite, distinct and characteristic properties. The student should learn especially to regard the preparation of any specific compound by a general method not only as a means of preparing this specific compound but also as an illustration of a general method applicable to an entire class of compounds.

Two factors which contribute to excellence in laboratory work are accuracy and neatness. Accuracy involves performing of experiments in a careful manner and in accordance with the laboratory directions, making careful observations and drawing logical conclusions, and thoroughly understanding the experiment. Promptness in recording experimental observations in the notebook is necessary for accuracy. Neatness applies to the manipulation of reagents and apparatus, the cleanness of equipment, and the appearance of the notebook.

Although each student is required to perform a certain number of experiments, the object is not the mere mechanical performance of experiments or the preparation of a few organic compounds, but is to acquire a knowledge of the basic principles involved in the experiment.

LABORATORY NOTES[1]

In order to do good laboratory work, it is essential to have a suitable notebook in which to record directly the observations made during experiments, and in which to assemble information which will aid in the performance of the experiment. For this

[1] The following specific directions for the preparation of notebooks and the general laboratory procedure are those which are used in the elementary courses in organic chemistry at the University of Illinois and at Cornell University. For the particular conditions which obtain in other laboratories, the instructor in charge of the laboratory work may wish to alter these directions or substitute others.

purpose the student should procure a stiff-covered *bound* notebook, about 7 x 8½ inches, provided preferably with cross-sectioned paper (for facilitating the preparation of tables of physical constants which are required in the later experiments). The use of loose-leaf notebooks for laboratory records is not satisfactory, and the recording of experimental observations on loose sheets or scraps of paper is not permissible. It is preferable to record notes in ink, and if corrections are necessary these should be made by additional notes rather than by erasures.

For the preliminary experiments the student is expected to proceed in the following way:

1. Read the descriptive paragraphs concerning the laboratory operation which is to be carried out (these are found immediately preceding each experiment).

2. Read the laboratory directions for the entire experiment, note particularly the cautions for handling materials, and try to understand the reasons for the procedure which is followed.

3. In the notebook, write a statement of the process which is to be carried out, and attach the laboratory direction sheet. All laboratory directions in the manual are on perforated sheets which can be detached and pasted in the notebook. In experiments where chemical tests are made, write equations for the reactions.

In order to save time for laboratory work, the student should carry out the instructions in the above paragraphs before coming to the laboratory. The schedule of experiments will be announced beforehand, so that the student will have an opportunity to prepare his notebook and be ready to start laboratory work at the beginning of the laboratory period.

4. After completing the instructions in the above paragraphs, arrange the apparatus for the experiment and secure the approval of the laboratory instructor for the set-up.

5. Perform the experiment according to the laboratory directions and record your observations directly in your notebook. When you have finished the experiment, dismantle the set-up and clean the glassware and apparatus at once.[1]

6. Draw the conclusions from your results, and write answers

[1] It is advantageous to clean glassware and apparatus immediately, since it is usually easier to remove tarry and gummy substances while they are fresh. Furthermore, considerable time is saved by having the equipment clean and ready for use at all times.

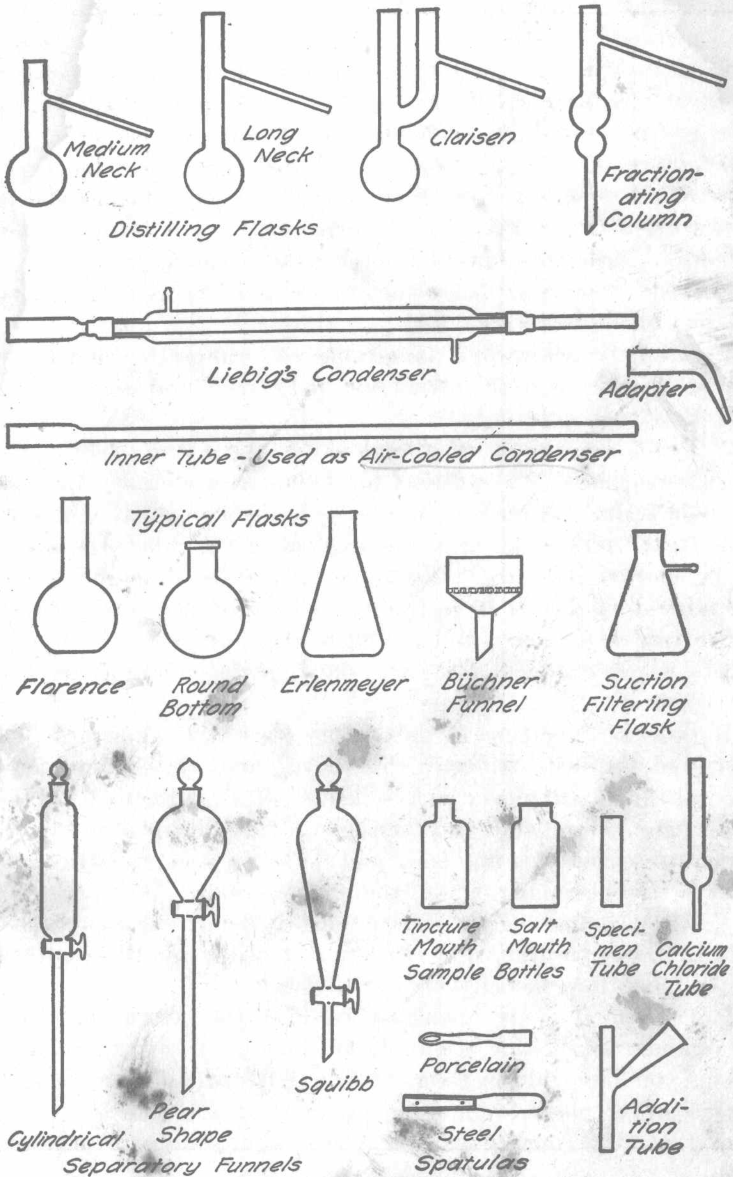

FIG. 1.—Common Organic Laboratory Apparatus.

Write legibly in ink

ORGANIC CHEMISTRY

COURSE No. ________ SECTION ________ EXPERIMENT No. ________

NAME ________________ DATE ________
Last Name *First Name*

PROCESS OR REACTION STUDIED ________________

____

PRODUCT PREPARED ________________

PHYSICAL CONSTANTS

	Observed in Laboratory	Found in Literature
B. P.		
M.P.		
Color		

YIELD

Based upon ________________

Theoretical Yield (in g.) ________

Actual Yield (in g.) ________

Percentage Yield ________ per cent

Preliminary Approval ________

GRADE: Manipulation ________

Oral Quiz ________

REMARKS:

FINAL GRADE ________

INSTRUCTOR ________

Sample Report Card.
(Actual Size 4 x 6 inches)

to the questions given on the direction sheets. Make complete statements for your answers.

7. Submit the completed notes and the report card (see page 6), together with any substance prepared, to the laboratory instructor for approval, as soon as possible after the completion of the experiment. At this time the instructor will examine the notes and may ask questions pertaining to both the theoretical and practical parts of the experiment.

The grade for the experiment is based upon the student's neatness and skill in carrying out the experiment, and upon his knowledge of the underlying principles and generalizations. No credit is given for the performance of experiments if the notes are not submitted for approval.

NOTES ON REAGENTS

In performing laboratory experiments it is important to weigh or measure the amounts of materials carefully and to use the exact quantities which are called for in the directions. When reagents need not be accurately measured (as for certain tests), the laboratory directions indicate certain approximate quantities.

TABLE I

DESK REAGENTS

Reagent	Sp. G.	Grams of Reagent		Moles per Liter (approx.)
		per 100 g.	per 100 cc.	
Acetic Acid (glacial)	1.06	99.5 g.	105.5 g.	17.5
Hydrochloric Acid (concd.)	1.18	35.4 g.	42 g.	12
Hydrochloric Acid (dil.)	1.08	15 g.	17.5 g.	5
Nitric Acid (concd.)	1.42	70 g.	100 g.	17
Sulfuric Acid (concd.)	1.84	96 g.	176 g.	18
Sodium Hydroxide Solution (dil.)	1.15	10 g.	11.5 g.	3
Ammonia Solution (concd.)	0.90	29 g.	26 g.	15

When an approximate quantity is indicated, as 1–2 cc., the student should use a quantity within the specified limits. At first it will be advisable actually to measure the quantity used, in order to learn to judge such quantities, but after some experience the student should be able to estimate approximate quantities.

It is never permissible to estimate or guess at quantities of starting materials which are to be used in carrying out a preparation. In many cases the success of an operation depends not only upon the starting materials but also upon the use of certain reagents in definite amounts. It is usually advantageous and sometimes absolutely necessary to know at least fairly accurately the amount of each reagent which is present. A careful laboratory worker will acquire the habit of using solutions of known strength, and of weighing or measuring the reagents and solutions used. The strengths of the most common laboratory reagents are listed above.

INTERCONVERSION OF WEIGHTS AND VOLUMES

In laboratory practice it is often necessary or desirable to convert weight measures into volume measures, and vice versa. These conversions may be made by use of the following relationships:

$$\underset{\text{(in g.)}}{\text{Weight}} = \underset{\text{(in cc.)}}{\text{Volume at t}^\circ} \times \underset{\text{(in g. per cc.)}}{\text{Density at t}^\circ}$$

$$\underset{\text{(in cc.)}}{\text{Volume at t}^\circ} = \frac{\text{Weight (in g.)}}{\text{Density at t}^\circ \text{ (in g. per cc.)}}$$

The numerical values of the density and the specific gravity of a particular liquid (at a given temperature) are usually so nearly equal that they may be used interchangeably for approximate calculations. Nevertheless, the student should bear in mind the following accurate definitions:

The density of a liquid is equal to the mass of a unit volume of the substance. An accurate density value includes a statement of the temperature and the units; for example, the density of water at 20° is 0.9982 g. per cc. Since the unit of mass (the gram) is equal to the mass of 1 cc. of water at 4°, the following notation is often used: $d_{4^\circ}^{20^\circ} = 0.9982$.

The specific gravity of a liquid is the ratio of the weight of any volume of the liquid to the weight of an equal volume of water *at some stated temperature.* If the specific gravity of a liquid at a temperature t° is referred to a volume of water at 4°, the specific gravity is numerically exactly equal to the density at t°. Often the specific gravity at a given temperature is determined with reference to water at a given temperature; the following notations may be used for such values: sp. g. $\frac{20^\circ}{20^\circ}$ or $d_{20^\circ}^{20^\circ}$. Obviously the latter values are not numerically equal to the density at 20°. The values may be interconverted by the follow-