LOUIS F. FIESER

ORGANIC EXPERIMENTS

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PREFACE

The previous editions of this book appeared in 1935, 1941, and 1957 under the title *Experiments in Organic Chemistry*. The present edition is given a new title partly for brevity but chiefly because of substantial changes from the 3rd edition.

One departure is the recommendation and photographic illustration of assemblies constructed with standard taper ground glassware for the conduct of simple and fractional distillation, steam distillation, and refluxing. This equipment is not essential and the experiments can all be done without it, but in my opinion this sturdy and quickly assembled apparatus not only speeds up experimentation but also adds to the pleasure of laboratory work and improves technique. The specific designs recommended were selected after careful study and trial of alternative models and are identified by citation in footnotes of the catalog number of a primary supplier. However, identical or equivalent equipment probably will be available from one or more other suppliers. Wilkens-Anderson Co.[1] stocks all the equipment and supplies described in the book and issues a separate circular listing the items.

For modernization of the manual I have worked out the new experiments listed below.

New Synthetic Preparations

Azobenzene, Hydrazobenzene, and Benzidine
Bis-adduct of *cis,cis*-1,5-Cyclooctadiene with Dichlorocarbene
p-Di-*t*-butylbenzene
1,4-Di-*t*-butyl-2,6-dimethoxybenzene
2,7-Dimethyl-3,5-octadiyne-2,7-diol
Dimethyl tetraphenylphthalate
trans,trans-1,4-Diphenylbutadiene
Hexaphenylbenzene
endo-Norbornane-*cis*-5,6-dicarboxylic Acid
endo-Norbornene-*cis*-5,6-dicarboxylic Anhydride, as well as the Acid and its Lactone ("Unknown" X)
p-Terphenyl
Tetraphenylcyclopentadienone
1,2,3,4-Tetraphenylnaphthalene
Tetraphenylthiophene
Triptycene

Additional Natural Products

β-Carotene from Strained Carrots
Guaiazulene by Dehydrogenation of Guaiene
Lycopene from Tomato Paste
Oleic Acid from Olive Oil via the Urea Inclusion Complex

Modern Techniques

Catalytic Hydrogenation ($NaBH_4$–Balloon Technique)
Catalytic Oxidative Acetylene Coupling (Balloon Technique)
Diels-Alder Reactions at Temperatures from 0° to 400°
Generation and Synthetic Uses of Dichlorocarbene and of Benzyne (2 methods)
Oxidative Decarboxylation
Reduction with Diimide
Separations with Urea and Thiourea Inclusion Complexes
Thin Layer Chromatography
Wittig Reaction, Phosphonate Modification

The new experiments are intended to supplement those from earlier editions, some of which have been shortened or otherwise improved in the course of adjusting the procedures to ground glass equipment. Hence, for a beginning course, a selection will be necessary; in some cases it may be stimu-

[1] 4525 West Division St., Chicago 51, Illinois

lating to leave a choice to the student. The procedures also may be useful as guides to new applications of the basic reactions, and I venture to think that they are comparable in reliability to *Organic Syntheses* procedures. In some cases they have the advantage that I have searched for and found a means for shortening the reaction period.

Suggestions to instructors are included in footnotes and I have dispensed with an *Instructor's Manual*. Included, however, are lists of low-cost chemicals suitable for use as unknowns; use of technical-grade products saves in cost and increases the challenge. To save time and library space, I have included properties of the compounds and of characteristic derivatives.

In addition to numerous unknowns to be identified by qualitative analysis, or by paper or thin layer chromatography, I have included projects in which the student is given a brief steer and then left to his own devices. For example, having followed the author's procedure for separation of β-naphthylamine and naphthalene by extraction, the student is to plan and execute a scheme for separation of benzoic acid, β-naphthol, and hydroquinone dimethyl ether. He is to devise tests for establishing the structure of a beautifully crystalline product formed on reaction of *endo*-norbornene-*cis*-5,6-dicarboxylic acid with sulfuric acid. Given the literature procedures for reaction of azulene with $(CF_3CO)_2O$ and hydrolysis of the product, he is to explore the corresponding reactions of guaiazulene. He is to predict the number of moles of urea or of thiourea bound by oleic acid, *p*-di-*t*-butylbenzene or its 2,6-dimethoxy derivative, and check the prediction by experiment.

The extensive expansion of the part of the book directed to student experimentation dictated deletion of the material of Part II of primary interest at the research level. Mary Fieser and I plan to extend and expand the sections on reagents, solvents, and special techniques and to present a separate book directed to advanced students and research workers.

Louis F. Fieser

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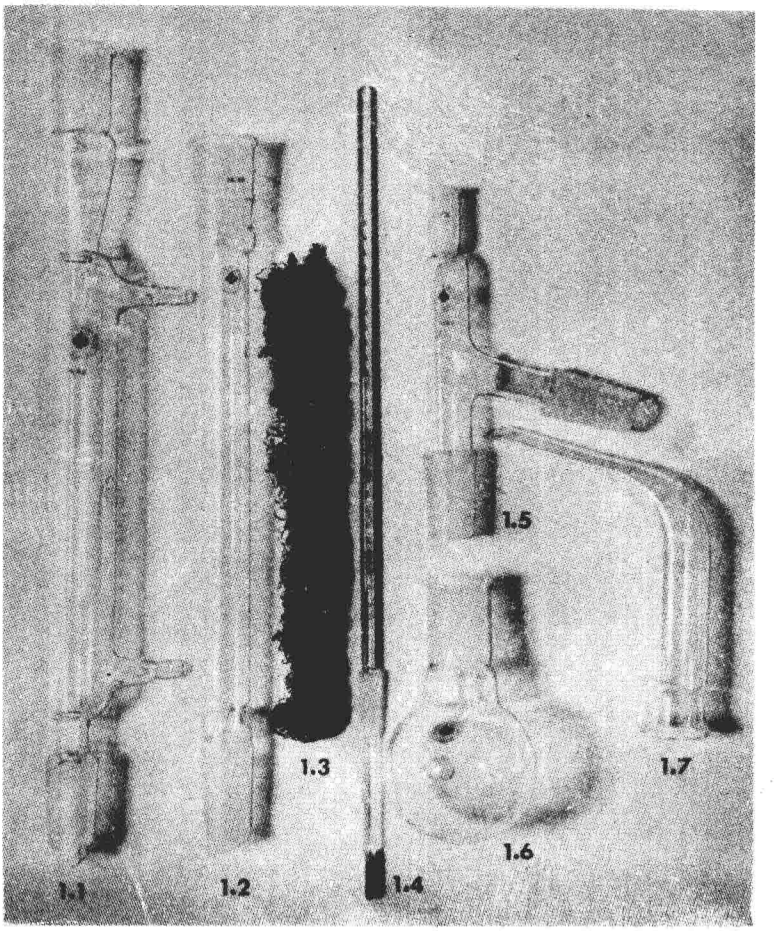


FIGS. 1.1–1.7 Standard-taper ground glass equipment 1.1 Liebig condenser, 200 mm.[1] 1.2 Hempel distilling column[2] 1.3 Stainless steel packing for 1.2[3] 1.4 Thermometer[4] 1.5 Still-head[5] 1.6 Round-bottomed flask, 125 ml.[6] 1.7 Bent adapter[7]

CHAPTER 1

Apparatus

For the convenience of the student in checking out his equipment, I have included in Chapters 1–2 photographs or drawings of apparatus which may not be recognizable easily by name alone. Notes identifying sources of the different items are directed to the instructor.

I recommend standard-taper ($\frac{24}{40}$) ground glass equipment of the types shown in the photograph. These pieces all fit together; the bent adapter (1.7), although not ground, fits snugly onto the condenser (1.1). This equipment makes for rapid and pleasurable experimentation and it is practically unbreakable except by intent, but it is expensive. Do not leave pieces joined together, and if a joint should become stuck consult your supervisor

In case ground glass equipment is not available in your laboratory, follow local instructions for use of cork-stopper or other

Notes for the instructor

[1] Ace Glass condensers 5919, 200 and 300 mm. This model, modified on my recommendation, has tapered tubulators and is much to be preferred to regular model 5920 in which the side tubes are untapered and unduly large.

[2] Ace Glass 8-in. distilling column, Hempel, 6616.

[3] A large stainless steel sponge (No. 750) which weighs 39 g. and makes three packings is obtainable in dozen or gross lots from the Metal Sponge Sales Corp., 3650 North Tenth St., Philadelphia 40, Pa. Pull out the sponge to a circle about 2 ft. in diameter, cut it in three or four parts with scissors, and push a section into a column with a small dowel. The smaller No. 725 sponge (18 g.) sold at five-and-ten-cent stores makes two packings. Save excess ends and pieces for conversion of a distilling flask into a fractionating flask.

[4] Ace Glass thermometer, 8315.

[5] Ace Glass adapter, 5091.

[6] Ace Glass $\frac{24}{40}$ round-bottomed flasks, 50, 125, 250, and 500 ml. (capacity of bulb proper). The 125-ml. flask has the same capacity as Corning's "100-ml." flask 4320, which is equally satisfactory (but Corning does not offer a 50-ml. flask). Flasks of the same specification and design are available also from Macalaster Scientific Co.

[7] Kimble Glass Co. 180 × 25 mm. bent adapter 10005.

assemblies [8] equivalent to those illustrated and fully adequate.

Fig. 1.8 shows an assembly used for column chromatography. The chromatograph tube [9] is supported on a ring stand [10] by an extension clamp [11] and clamp holder.[12] The flow of liquid is controlled by a screw pinchclamp.[13]

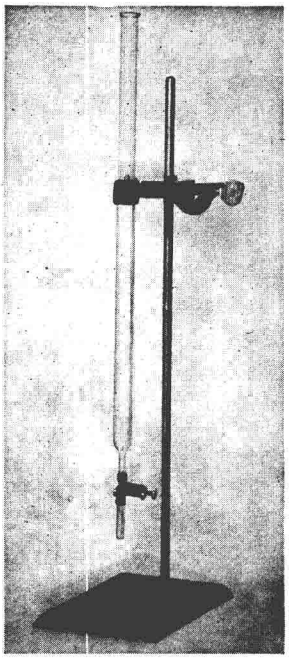
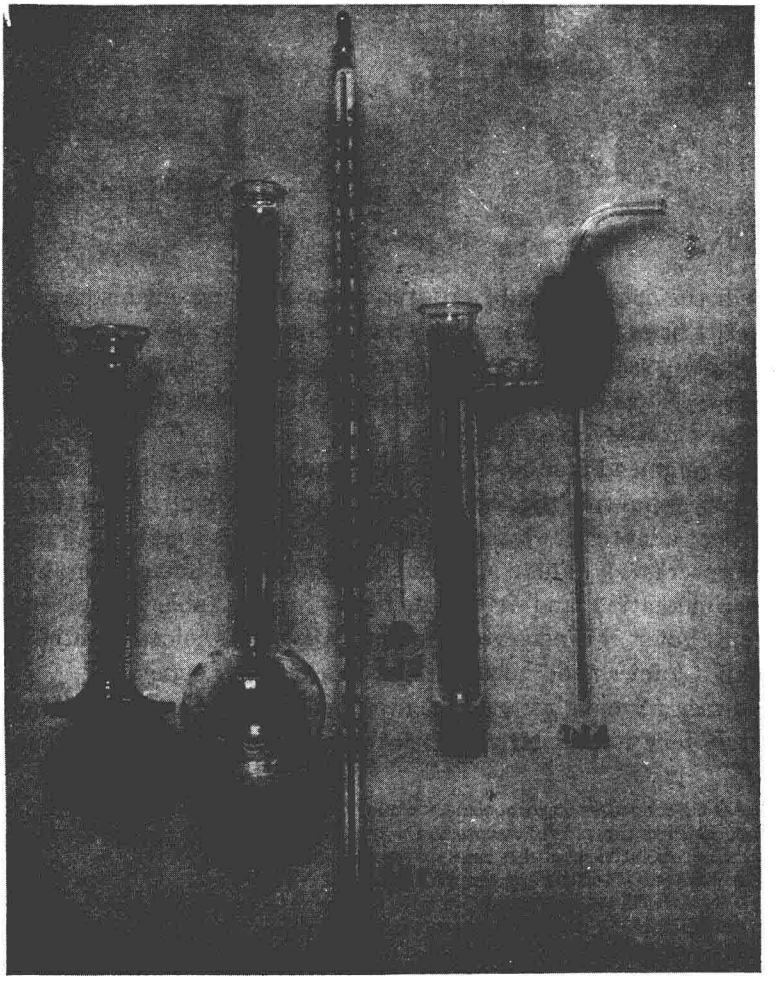


FIG. 1.8 Chromatograph tube



FIGS. 1.9–1.14

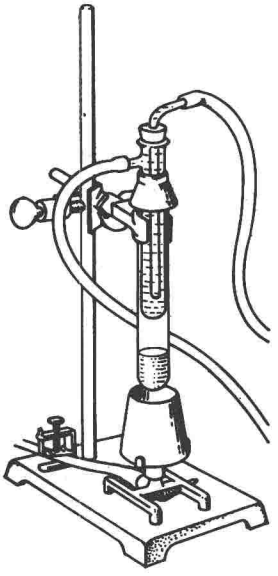


FIG. 1.15 Cold finger condenser

[8] The 100-ml. round-bottomed flask with a flared neck recommended in the 3rd edition is still available from Wilkens-Anderson Co., No. 34894.
[9] Wilkens-Anderson 17425.
[10] Ring stands recommended: 20″ and 24″.
[11] Fisher extension clamp 5–731 without sleeves or vinylized jaws.
[12] Fisher clamp holder 5–755.
[13] Hoffman's clamp, Wilkens-Anderson 18005.

The next photograph shows the following items of glassware:

1.9 10-ml. Graduate with flared mouth.[14]
1.10 Melting point flask.[15]
1.11 Thermometer with enclosed scale.[16]
1.12 Melting point capillary and rubber band.[17]
1.13 Test tube with side tube.[18]
1.14 Right-angle tube,[19] used in a cold finger condenser (Fig. 1.15) and as an aspirator tube (Fig. 2.11).

Items 1.13 and 1.14 are for construction of a cold finger condenser (Fig. 1.15), which is useful for refluxing a small volume of reaction mixture. The water-cooled tube is thrust through an inverted No. 3 neoprene filter adapter[20] and rested in the test tube at a convenient height.

Fig. 1.16 shows a filter block, so named because it has a grooved section for holding thick-walled suction tubing and so supporting

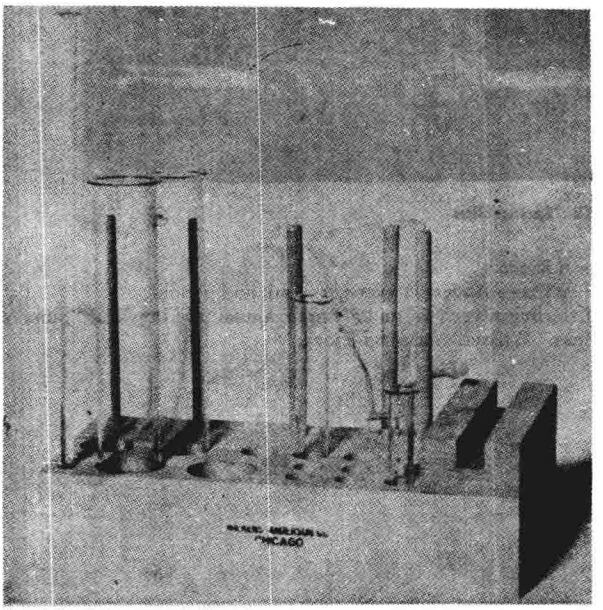


FIG. 1.16 Filter block[21]

Test tubes:
25 × 150 mm. 13 × 100 mm
20 × 150 mm. 10 × 75 mm.

[14] Kimble 20025.
[15] Wilkens-Anderson 34902.
[16] Wilkens-Anderson 90380, 0 to 110°, −5 to 250°, −5 to 360°.
[17] Wilkens-Anderson 48930 (tubes are 1.5 × 2.0 mm. × 90 mm. long); rubber bands, 48955.
[18] Kimble 46225, 19 × 150 mm.
[19] These tubes can be prepared by the local glassblower from 6-mm. Pyrex tubing; dimensions: 3 cm. × 18 cm. It is convenient for the student to keep the cold finger condenser assembled and to have a second tube for aspiration.
[20] Wilkens-Anderson 255.
[21] Wilkens-Anderson 88055.

Notes for the instructor

FIG. 1.17 Dowel stand [22]

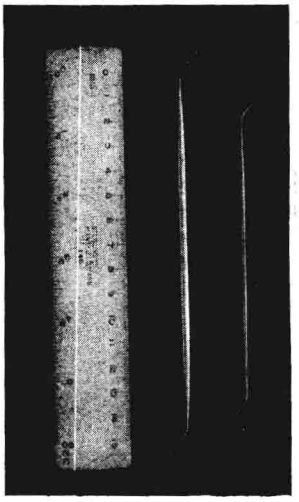


FIG 1.19 Silver spatulas

small filter flasks. It also has holes for supporting Pyrex test tubes of the four sizes noted and stirring rods, as well as pegs for drying and storing apparatus, such as the 25-ml. Erlenmeyer filter flask shown.

A dowel stand (Fig. 1.17) provides a convenient support for a separatory funnel.[23] Spring clips mounted on hardwood clothespins (Fig. 1.18) serve also as useful handles for hot flasks.

Silver spatulas [24] (Fig. 1.19) have many uses. A spatula can be kept clean and shiny by rubbing it with steel wool. A spatula will be ruined if held in a flame.

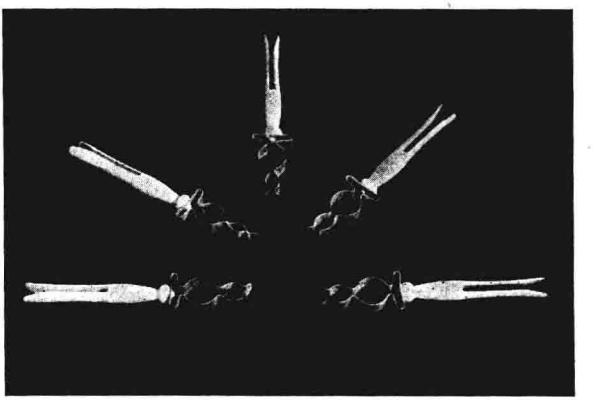


FIG. 1.18 Spring clips

[22] Wilkens-Anderson 88050.
[23] Recommended: Wilkens-Anderson 35995, 125 ml. and 250 ml.
[24] The spatulas of sterling silver ($5\frac{1}{2}$" and 7") are manufactured by R. F. Simmons Co., Attleboro, Mass. Wilkens-Anderson 83025.

CHAPTER 2

Operations

This chapter includes notes for later reference on incidental but important operations of organic laboratory work. While inspecting the illustrations for identification of apparatus, make mental notes of the headings so that you can read the sections when the need arises.

1. Washing and Drying Apparatus

Clean up as you go

Considerable time can be saved by cleaning each piece of equipment soon after it has been used, for you will know then what type of contaminant is present and you will be able to remove it more easily than after it has dried and hardened. Cleaning up after an operation often can be carried out during the period in which another one is in progress. A small amount of organic tar may be removable with a few milliliters of an appropriate organic solvent. If the amount of tar is large it may be best to first try warm water and a detergent; let the vessel soak for a time and then see if the material can be dislodged with a test tube brush. Acetone (b.p. 56.1°) has high solvent power, is miscible with water, and vaporizes readily.

Acetone wash bottles

An empty Ronsonol lighter-fuel can with a switch-spout serves as a convenient wash bottle for acetone. The plastic cap can be removed for filling by prying it carefully with a large coin and it can be replaced by pressing down on the two shoulders of the cap. Another convenient acetone dispenser is a 50-ml. Calcutta wash bottle [1] (Fig. 2.1). It is operated by pointing the tip downward and allowing the base of the flask to be warmed

[1] The device was suggested by Dr. Bidyut K. Bhattacharyya, a co-worker from Calcutta, and was unknown to visitors from other parts of India, hence the name.

CHAPTER 2

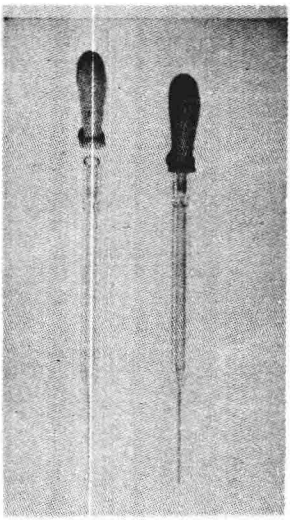


FIG. 2.2 Capillary dropping tubes[2]

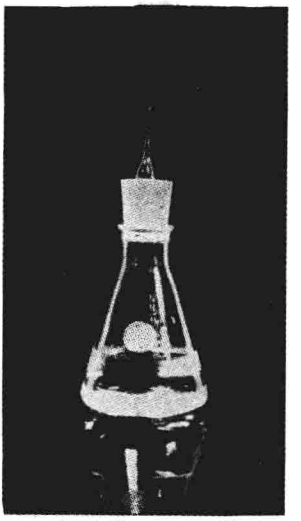
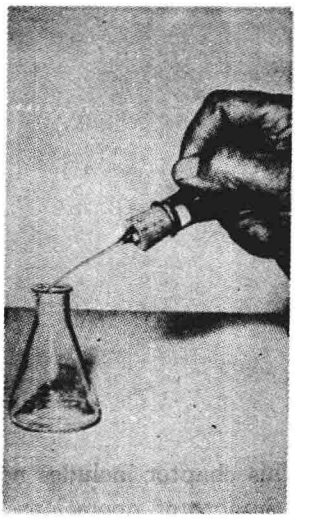


FIG. 2.1 Calcutta wash bottle (50-ml. Erlenmeyer flask)



by the heat of the hand. It is made by cutting a capillary dropping tube (2.2) to an appropriate length and inserting it into a cork. A Calcutta wash bottle containing ether is very useful in extractions and filtrations involving ether solutions.

It sometimes happens that a reaction flask washed repeatedly with water and a detergent and with acetone still retains one or more black spots. If so, rinse the flask with water and let it drain, add about 5 ml. of concentrated sulfuric acid and 1 ml. of concentrated nitric acid, let the mixture stand for a time in the event of a vigorous reaction, and then heat the flask on the steam bath. Usually brown nitrous fumes are evolved for a time and on subsequent decantation of the acid and washing with water the flask will be clean.

To dry a condenser containing moisture or droplets of water, clamp it upright over a beaker and run in a little acetone around the lip at the top; drying takes only a few minutes. *Do not use compressed air for drying*, since it is liable to contain moisture. It is permissible to draw air through the apparatus at the suction of the water pump.

2. Working Glass

To cut a glass tube (Pyrex or soft glass) the first operation is to make a fine, straight scratch extending about a quarter of the

[2] Arthur H. Thomas No. 82116-D, 146 mm. long, 7 mm. OD. Will Corp. 23266 white rubber bulb.

way around the tube. A triangular file becomes worn after brief use and then produces too wide a scratch. Inexpensive, expendable Fisher glass tubing scorers (2.3) are recommended. The scratch is best made by pressing the edge of the scorer firmly against the tube and slightly rotating the tube away from the body while filing in the same direction. Only one stroke should be made; a fine scratch gives a much better opportunity for a clean break than a wide groove. The tube is then grasped with the scratch away from the body and the thumbs pressed together at the near side of the tube just opposite the scratch. Slight pressure is exerted outward with the thumbs and at the same time the tube is forcefully pulled apart. A straight, clean break should result.

Cutting glass tubing

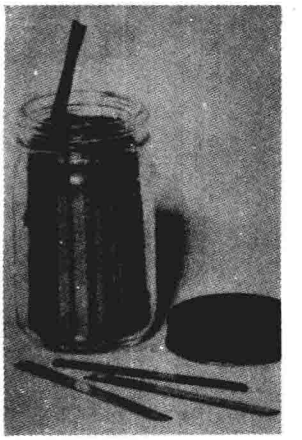


FIG. 2.3 Scorers [3]

A glass tube or rod that has been cut has dangerous sharp edges which should be eliminated by fire polishing. For soft glass use a Bunsen burner (Fig. 2.4) set for the maximum delivery of gas and with the air-inlet orifice adjusted to produce a sharp, nonluminous inner cone of flame. Hold the tube or rod in a slanting position so that the sharp inner cone of the flame impinges on the end to be smoothed and rotate the piece until the sharp edges melt and disappear. A stirring rod with a flattened head, useful for crushing lumps of solid against the bottom of a flask, is made by heating a rod in the same way but continuing until a short section at the end is fluid, and quickly pressing this onto a smooth metal surface. Pyrex glass is worked in the same way but with a gas-oxygen or gas-oxygen-air blast lamp, since the softening point (820°) is higher than that of soft glass (425°).

Fire polishing

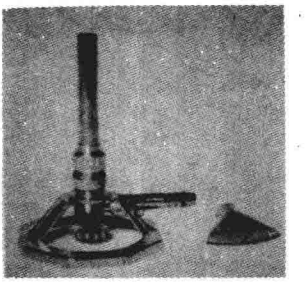


FIG. 2.4 Bunsen burner and wing top [4]

For the production of a successful bend it is important to apply heat uniformly to the entire section of the tubing necessary for the bend. The tube is stoppered at the left-hand end and grasped in the left hand with the palm down and in the right hand with the palm up, for these positions make it possible to swing the right-hand end of the tube into a position for blowing without interruption of the synchronous rotation of the two ends. The rotating is best done in the direction in which the top of the tubing moves away from the body. With soft glass, heating is done with a Bunsen burner fitted with a wing top and adjusted to produce a hot nonluminous flame. Heating is continued until the tube begins to sag of its own weight and the flame has become tinged with yellow (sodium light). When the heated section has become thoroughly plastic, the tube is removed and bent in a

Bends

[3] Fisher Scientific Co. 11–348–15 (in jars of 250).
[4] Wilkens-Anderson burner 8700.

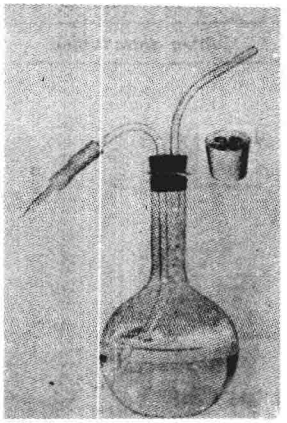


FIG. 2.5 Wash bottle (Florence flask, fusiform stopper)

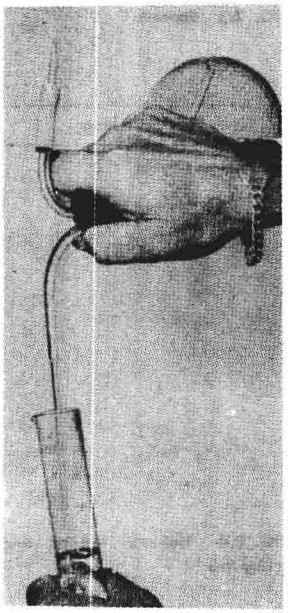


FIG. 2.5a Water wash bottle

vertical plane, with the ends upward and the bend at the bottom. If the tube becomes constricted at the bend, pressure is applied by mouth to the open end immediately on completion of the bend to expand the tube to its full size and eliminate irregularities. To bend Pyrex glass, the section to be bent is rotated evenly in a long, bushy oxygen flame and the tube is held at a slight angle to the flame.

3. Rubber Stoppers

On insertion of a glass tube into a rubber stopper the hole should be lubricated by moistening it with a drop of glycerol withdrawn from a bottle on a stirring rod. Grasp the tube very close to the end to be inserted, for if the tube is grasped at a distance the pressure applied for insertion may break the tube and result in a serious cut to the hand. A stopper frozen to a glass tube is easily loosened by painting glycerol around the tube on both sides, inserting the small end of a 7″ spatula between the rubber and glass, and working it around the circumference of the tube on one side and then on the other. Another method is to select a cork borer that fits snugly over the glass tube, moisten it with glycerol, and slowly work it through the stopper. A stopper with the fusiform openings shown in the insert of Fig. 2.5 [5] facilitates insertion and removal of tubes, since it fits tightly at the ends of the hole but not in the middle.

4. Wash Bottles

A wash bottle of distilled water is indispensable, and the classical design shown in Fig. 2.5 is recommended over a variety of others.[6] It is easily constructed from a 500-ml. Pyrex Florence flask, 7 mm. tubing, and a 2-hole No. 5 rubber stopper, preferably of the fusiform type. One can direct the stream of water forced out by pressure from the lips by guiding the flexible tip with the forefinger. After an initial delivery, the few drops of water remaining in the tip can be forced out separately by a quick breath of air. A large volume of water, for example 25, 50, or 100 ml. can be measured rapidly into a graduate by inverting the wash bottle and delivering the liquid into the container through the mouthpiece (Fig. 2.5a). Cut off the flow a little short of the mark and complete the addition by using the wash bottle in the normal fashion.

[5] A. H. Thomas Co., No. HR-108.
[6] Wilkens-Anderson 6965.

Since methanol is required frequently for crystallization, a methanol wash bottle made from a 125-ml. Florence flask [6] is very useful.

5. Boring Corks

Select a cork that initially fits only 4–5 mm. into the opening of the flask and soften it with a cork roller or by rolling it under a wooden block, such as the wooden member of a filter trap (Fig. 2.9); this treatment reduces the size and diminishes the chance of the cork splitting when bored. Select a borer that will give a hole slightly smaller than required, hold it in the right hand and work it into the cork held in the left hand. After each twist grasp the cork at a new place and check the alignment. When the cork has been cut halfway through, withdraw the borer, push out a plug if present, and cut the remainder of the hole from the other side. Test the fit of the tube to be inserted and, with frequent further testing, ream the hole with a round file applied from both sides until the tube can be inserted without undue force but still fits tightly. Grasp the tube or thermometer close to the end to be inserted and work it carefully into the cork by twisting. If it is held very far from the cork it is liable to break and cause a severe cut.

6. Suction Filtration

The classical apparatus for the collection of a crystalline product or a precipitate is a Büchner funnel fitted with a rubber stopper to a filter flask (Fig. 2.6) connected to a water suction pump. A circular filter paper of appropriate size is centered in the funnel and moistened with solvent, suction is applied, and the liquid or solid mixture is poured in. The apparatus has the disadvantage that the rubber stopper has to be bored out to the appropriate size, a tedious operation. I recommend the much neater neoprene filter adapters shown in Fig. 2.7.[7] Suitable assemblies and the proper sizes of filter paper are shown in Fig. 2.7. The small porcelain funnel on the right is a Hirsch funnel and the two other porcelain funnels are Büchner funnels. The glass funnel has the advantage that the inside, where residues often lodge, is visible.

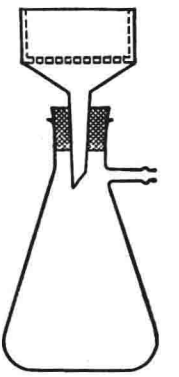


FIG. 2.6 Büchner funnel and filter flask

Neoprene filter adapters

[7] Neoprene filter adapters are available from Arthur H. Thomas Co.; a set of Nos. 2(2), 3, and 4 is recommended. Wilkens-Anderson 255.