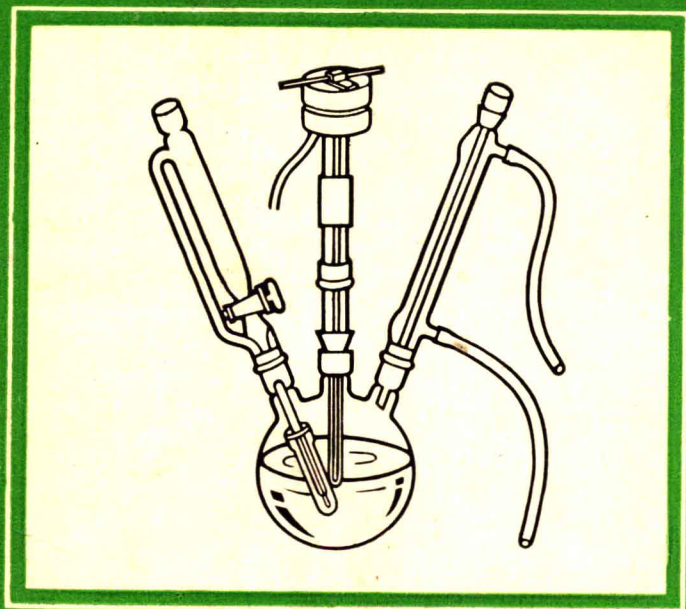


Laboratory Manual in Organic Chemistry



RAJ K BANSAL

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Indian Institute of Technology
New Delhi*



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To my parents
for their unfailing love and encouragement

Preface

A laboratory course in chemistry is essential at all levels for chemistry students. Such a course in laboratory work should be correlated, to a considerable extent, with the lecture material and based on the more modern approach to organic chemistry. Books presently available do not offer much in the way of choice. This manual is an attempt to provide a course of education to the students of organic chemistry which meets the requisite standard of various universities.

The manual consists of seven chapters. It is important that the students become acquainted with the laboratory techniques and apparatus in the beginning itself. With this in mind a brief outline of the basic techniques and apparatus is presented in the introductory first chapter. The subsequent four chapters deal with the qualitative identification of organic compounds. The chemical tests have been designed to illustrate the application of the most familiar chemical means of identifying the unknown compounds. Only selected tests for common functional groups have been given. No attempt has been made to list all the tests for all the functional groups. Pertinent chemical reactions are given wherever possible for a better understanding of a particular test. The derivatives selected are those obtained by simple reactions and their melting points have been listed in tabular forms. Guidelines for the separation of a mixture containing two components have been given.

Chapter 6 describes the laboratory experiments which are concerned with estimations, organic syntheses, polymerization, isolation of products from natural sources and chromatographic methods of separations. The experiments have been carefully selected to give to the students a wide range of experience in an organic chemistry laboratory. A large majority of these experiments is class tested. Several syntheses are selected from the literature to illustrate the major points emphasized in modern texts. Certain exercises offer a choice among several experiments of varying degree of difficulty. The sequence with which the experiments are carried out depends on individual taste and requirements. The organic chemist must know the field of spectroscopy. The applications of the recently developed methods have become necessary components in structure determination. These methods (NMR and IR) generally available to most students have been described in an introductory manner in the last chapter.

Selected references are given for the benefit of those who wish to consult the original literature. The questions appended in a separate section will help the students develop a better understanding of the concepts involved.

The manual is intended for use on the laboratory bench and is designed to suit the needs of both undergraduate and postgraduate students. In addition, it is hoped that it will be of value to pre-medical, pre-engineering and other biologically oriented students.

I would like to thank Drs. K.S. Sharma, R. Varadarajan, B.K. Puri, K.K. Singhal and J.M. Aggarwal who read portions of the book. I also wish to acknowledge the help and encouragement received from Professors G.V. Jere, V.K. Ahluwalia, O.P. Vig and A.C. Jain during the preparation of this book. I am particularly grateful to Professor R.P. Gandhi, head of the department, for providing the necessary facilities. Finally, I would like to put on record my gratitude to Professor O.P. Jain, Director, Indian Institute of Technology, Delhi for financial support in the writing of this manual.

July 1980
New Delhi

RAJ K. BANSAL

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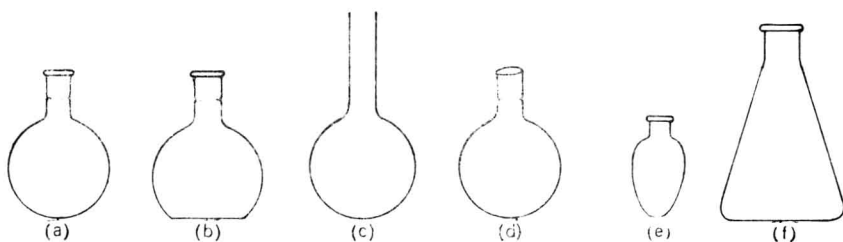
1. Laboratory Equipments and Techniques

In an organic chemistry laboratory a variety of glasswares and techniques are used for separation and purification of compounds as well as for routine work. The apparatus, however, becomes more sophisticated in a research laboratory. It is highly desirable that a student be familiar with the use and handling of apparatus. The laboratory techniques described here are basic to almost all experimentation in organic chemistry.

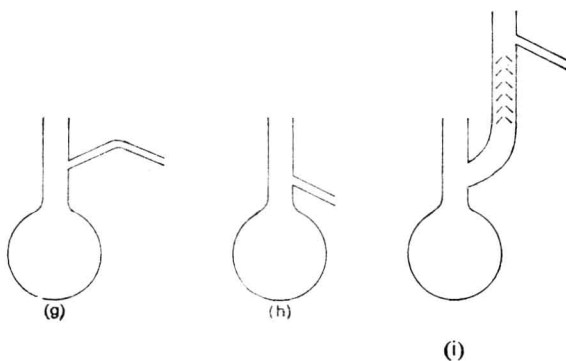
1.1 Glass Apparatus

A brief discussion of the common types of glass apparatus will be made here.

(a) FLASKS



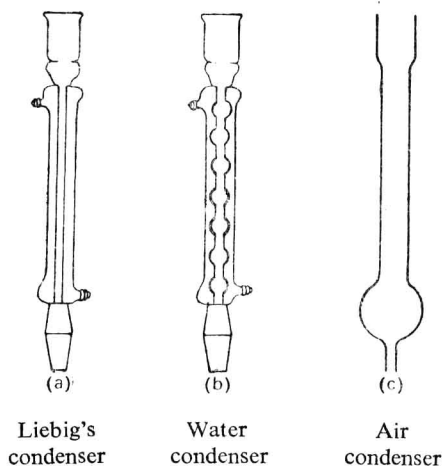
Round-bottom Flat-bottom Long-necked Bolt-head Pear-shaped Erlenmeyer



These are the common types of flasks used for a variety of purposes. Flasks (a) to (e) are employed for refluxing and distillation. The Erlenmeyer flask (f) is used for mixing and titration. Figs. (g) to (i) represent different distillation flasks with condensers attached. The first two are the ordinary

distillation flasks but (i) is called the Claisen flask with a fractionating column.

(b) CONDENSERS



The condensers are used for refluxing and ordinary distillation. The air condenser (c) is employed if the liquid distilling has a very high boiling point.

(c) FUNNELS

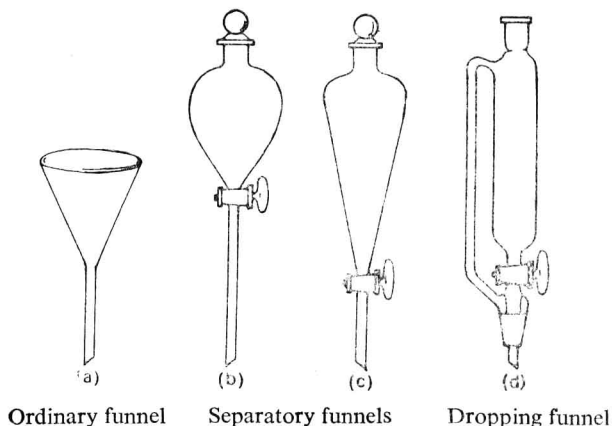
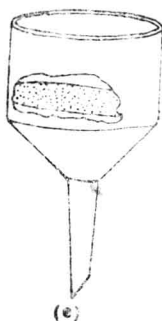


Figure (a) shows an ordinary funnel, whereas (b) and (c) are the separatory funnels used for the extraction of a product from a reaction mixture; (d) is a dropping funnel employed for the addition of a reactant to a reaction mixture.

During the extraction of a product while working with alkaline solutions an emulsion is usually formed which prevents the separation of two layers. This emulsion can be broken up by one of the following methods:

- (i) Gently swirling the funnel while holding it in an upright position.
- (ii) Saturating the aqueous layer with a salt such as sodium chloride.

The second technique decreases the solubility of inert organic solutes and the extraction solvents such as ether in the water layer. This process is referred to as the *salting-out effect*.

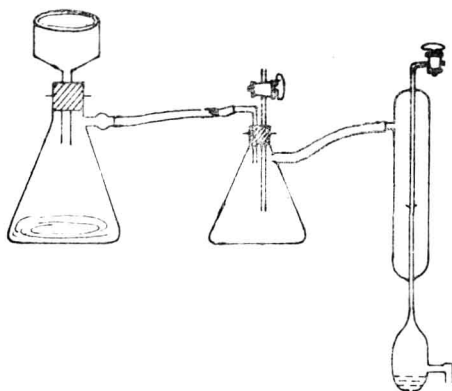


Buchner funnel



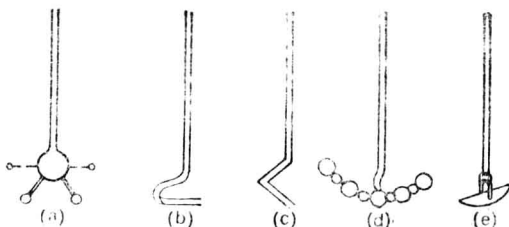
Buchner flask

The Buchner funnel and the Buchner flask are used extensively in synthesis for filtration of a solid product. The arrangement for filtration using a water pump is shown in the following figure:



(g)

(d) STIRRERS

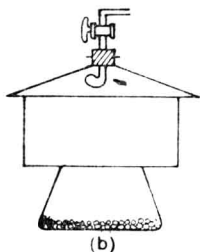
Stirrer with a
teflon blade

These figures represent various types used for stirring purposes. These are usually made of glass but those made of stainless steel or teflon are also in common use. The stirrer is attached directly to a small electric motor with the aid of a small pressure tubing and mechanical agitation is achieved.

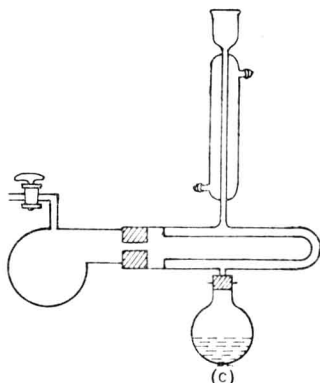
(c) DRYING APPARATUS



Drying tube



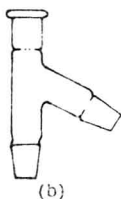
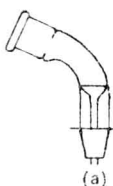
Vacuum desiccator



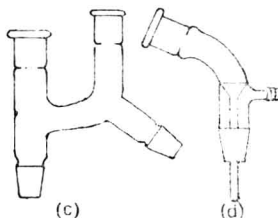
Abderhalden drying apparatus

Tube (a) is usually packed with anhydrous calcium chloride and is used to exclude moisture from a reaction vessel. The vacuum desiccator finds application for drying a compound at low pressure. The bottom may be filled either with anhydrous calcium chloride or conc. sulfuric acid. Sometimes, it is difficult to remove the moisture completely from a wet solid in a vacuum desiccator, complete removal of moisture can be achieved using the Abderhalden drying apparatus. In this the solid preparation is enclosed in a glass-stoppered evacuated tube surrounded by the hot vapours of a suitably chosen refluxing liquid (for instance, toluene). The water vapours from the solid are captured by an efficient chemical drying agent such as phosphorus pentoxide.

(f) ADAPTERS



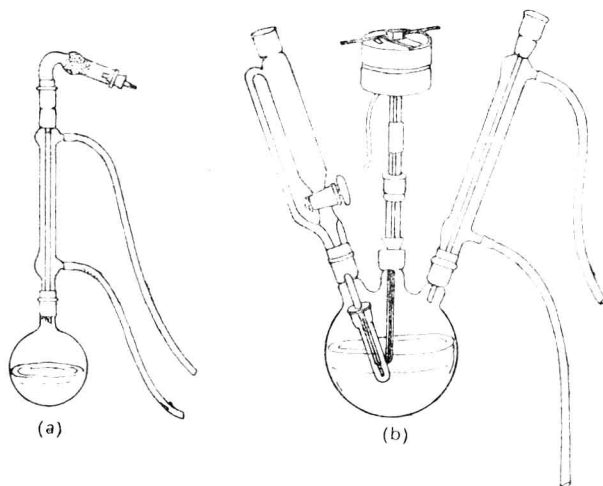
Claisen distillation head



Stillhead

Adapters (a) and (d) are normally used to facilitate the delivery of a distillate from the condenser to a receiver. A vacuum can also be applied to adapter (d) if needed. Fig. (b) represents a simple distillation head while (c) is the widely used Claisen distillation head.

1.2 Assemblies for Reactions



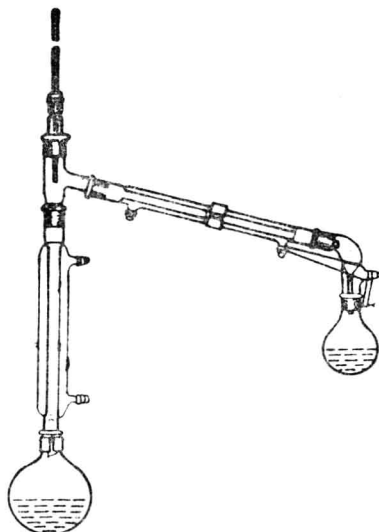
In Fig. (a) a round bottomed-flask is fitted with a water condenser. The joints could be either standard or instead a cork can be used to fix the condenser to the flask. This type of setup is employed for refluxing a reaction mixture. Boiling stones are always used to ensure smooth refluxing. A three-necked flask (b) equipped with a water condenser, dropping funnel and a mechanical stirrer with a mercury seal is the most common type of assembly used in synthesis. Mercury seal prevents the escape of gases during stirring. A drying tube can be fixed on the water condenser to exclude atmospheric moisture.

1.3 Distillation Assemblies

Distillation is a classical technique to purify or separate a mixture of liquids. It may be described as the partial vaporization of a liquid and carrying over and condensation of these vapours in a different part of the distillation apparatus. Depending on the boiling point of the liquid to be distilled different methods of distillation are used.

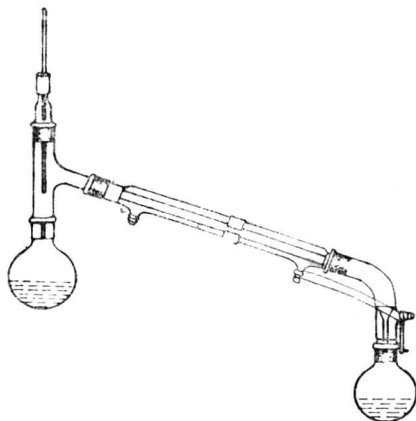
(a) SIMPLE DISTILLATION

This figure illustrates an apparatus if a sample is known to contain only one volatile component. The presence of impurities lowers the vapour pressure (a measure of the ease with which molecules escape the surface of a liquid) and thus increases the boiling point of the liquid. The liquid is vaporized by heating which is then condensed and collected as a liquid in a receiver. The distillation should be carried out slowly to prevent the



superheating of vapours (rise of temperature above the boiling point). This stage when excessive amounts of vapours are ejected alternatively is referred to as *bumping*. The distillation can be effected either at atmospheric or reduced pressure. In general, if the boiling point of the sample is above 180° , a reduced pressure distillation should be employed.

(b) FRACTIONAL DISTILLATION



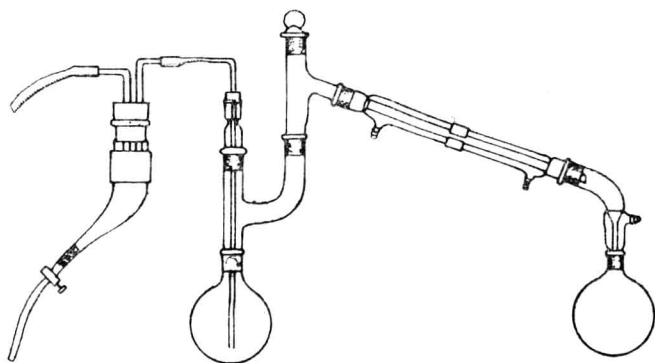
The above apparatus illustrates the separation of two miscible liquids of sufficiently different boiling points. A fractionating column is attached to the flask. The principle of fractional distillation is based on the establishment of a large number of theoretical vaporization plates achieved by a fractionating column. There are a large number of fractional distillation columns available. Glass beads, glass helices or metal gauze may be used as packing in an ordinary column. Indentations in the side of the column (Vigreux column) serves the same purpose. The column provides a large

surface area. On heating, the more volatile part of the liquid vaporizes while the less volatile part gets condensed. Equilibrations occur in all parts of the column and the vapours that eventually pass into the receiver are highly enriched in the more volatile component, the condensate continuously drops back into the flask.

It should be pointed out that there are certain mixtures of organic compounds that form azeotropes and cannot be separated under any circumstances by distillation. An *azeotrope* is a mixture of liquids of certain definite composition that distils at a constant temperature without change in composition. A familiar example is that of ethanol-water mixed in the ratio of 95 : 5.

Many organic compounds tend to decompose when heated even below their melting points. To make the purification of such compounds from the dissolved impurities possible, they are distilled at reduced pressure. An aspirator or a mechanical pump is generally used to create vacuum. When the pressure is reduced the boiling takes place at a lower temperature. This is known as *distillation at reduced pressure*.

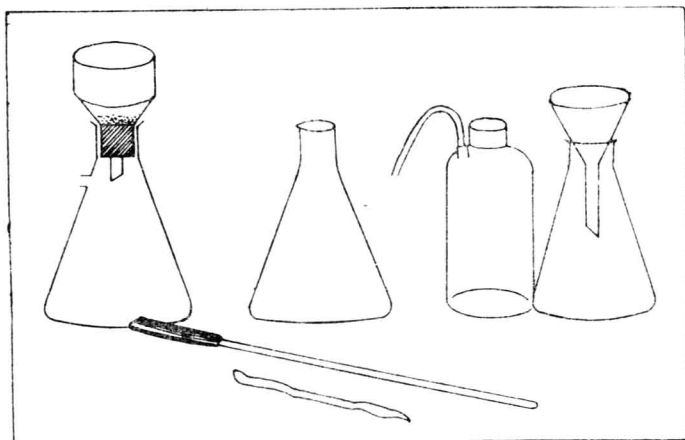
(c) STEAM DISTILLATION



The assembly consists of a steam generator whereby the steam is carried *via* a water trap to a flask containing the substance to be distilled. This flask is also heated directly by a Bunsen burner. A mixture of the compound and water collects in the receiver, the former is separated in a separatory funnel. Steam distillation is very useful for separating volatile from relatively non-volatile components, specially when the more volatile component possesses a very high boiling point and is liable to be decomposed if a direct distillation is undertaken.

1.4 Recrystallization

Products of organic reactions are seldom pure they may be contaminated either with the starting material or some side product with the result that the m.p. or b.p. will not be sharp. Therefore, to obtain satisfactory physical constants the substance needs to be purified. To accomplish this various techniques have been employed depending on the physical state of



the compound. Distillation methods have been described in the previous section for liquids. Recrystallization is used for solids. It depends on the differential solubility of a substance in a hot and a cold solvent. It is desirable that the solubility be high in the hot solvent. The equipment shown in the above figure is usually employed.

A solid substance is dissolved in a suitable solvent at its boiling point and then precipitated in a crystalline form on cooling. The substance is said to be crystallized and the process is referred to as *recrystallization*. Purification by this method requires much skill and patience. A solvent is generally chosen in which the impurities are more soluble than the solid being purified. Selection of a solvent is not an easy matter. Sometimes a mixture of two solvents may have to be employed. Samples to be purified frequently contain soluble extraneous coloring matter. Thus a small amount of active carbon (Norite) should be added. Norite adsorbs the material that gives rise to color. The solution is then filtered hot in an Erlenmeyer flask and the filtrate is cooled slowly at first and then in an ice bath, if necessary. The crystals should separate out at this stage. However, if this does not happen the sides of the container may be scratched with a glass rod to induce crystallization. Crystals usually appear if one proceeds in the above manner. But if this fails then probably there is too much solvent which should be removed by boiling and the remaining solution cooled again. After the recrystallization is complete, the crystals are filtered off in a small Buchner funnel and may be dried in a vacuum desiccator. The melting point is then determined. Two or more recrystallizations may be necessary in some cases, if a satisfactory melting point is not obtained.

1.5 Drying Agents

It is necessary to dry organic reaction products before further analysis is undertaken. Presence of moisture not only affects the melting point and boiling point but also the success of the subsequent reactions. Solids are normally dried either in air or in a vacuum desiccator, but for drying

liquids different types of drying agents are employed. These agents either react with water or form a hydrate with it. An ideal drying agent should not react with the organic liquid and be easily separated by filtration from the dried liquid. The agents most often used are anhydrous salts which form hydrates with water and some of these are described below:

CALCIUM SULFATE (CaSO_4): It is also known as Drierite. It is extremely fast and very efficient. However, it has a low capacity as two molecules of calcium sulfate combine with only one molecule of water ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) to form the hydrate.

MAGNESIUM SULFATE (MgSO_4): It is a good drying agent and forms heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). This is probably the most satisfactory reagent for general drying purposes. Besides, it is cheap also.

SODIUM SULFATE (Na_2SO_4): It is a high capacity reagent but possesses low action and efficiency. It combines with seven and ten molecules of water, and is recommended for removal of water, especially from ether.

CALCIUM CHLORIDE (CaCl_2): It is good in terms of both intensity and capacity. And though, it cannot be used to dry amines, alcohols, phenols, acids and esters, it is good for halides and hydrocarbons.

POTASSIUM CARBONATE (K_2CO_3): It is a basic drying agent and is fairly good. It reacts with two molecules of water.

PHOSPHORUS PENTOXIDE (P_2O_5): It is an acidic reagent. The dried solution can be distilled from the drying agent.

1.6 Cleaning of Apparatus

It is very essential that clean glassware be used for carrying out a reaction. Presence of impurities may have an adverse effect on the desired reaction as well as the purity of the final products. Normally any kind of washing powder (Vim, Ajax or any other brand) may be used. But if the apparatus is soiled with a tarry material, then it can be dislodged with a small quantity of commercial acetone or special washing solutions such as chromic acid. After this the apparatus should be rinsed with water and washed with soap solution.