

# VOGEL's

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## TEXTBOOK OF PRACTICAL ORGANIC CHEMISTRY

FIFTH EDITION

Revised by former and current members of  
The School of Chemistry,  
Thames Polytechnic, London

**Brian S. Furniss**

**Antony J. Hannaford**

**Peter W. G. Smith**

**Austin R. Tatchell**

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## SEPARATION OF LIQUIDS AND SOLIDS

On occasions it is necessary to separate a liquid and a solid in an inert atmosphere. If the liquid and solid separate easily and distinctly with the solid settling to the bottom of the flask, the process of separation can be accomplished by careful use of a syringe or cannula to remove the supernatant liquid. The liquid may be discarded, stored or transferred to another reaction set-up for further reaction as appropriate. The solid remaining in the flask can be washed if necessary by the addition and subsequent removal of further quantities of dry, oxygen-free solvent through the septum. If the solid is desired solvent-free, residual solvent can be removed by connecting the flask to the vacuum line and condensing the solvent in a suitable trap. If the solid and liquid do not separate easily and the solid remains in suspension, filtration will be necessary. The simplest way of achieving this is with the gas dispersion or filter tube with a sintered glass end (Fig. 2.59). The technique is similar to that described in Section 2.20 (Fig. 2.81) for recrystallisation at low temperature. The filter tube can be fitted to the flask at the start of the reaction or subsequently inserted (after thorough drying) with a rapid stream of nitrogen flowing through the neck of the flask into which the tube is to be inserted. If the solid is required it remains in the flask after further washing. If the liquid is required for further reaction it can be led directly to a second reaction flask.

## ISOLATION AND PURIFICATION TECHNIQUES

### 2.18 GENERAL CONSIDERATIONS

At the conclusion of a reaction the pure product must be isolated from the reaction mixture by a sequence of operations collectively termed the 'work-up'. As well as the required product the reaction mixture may contain, for example, solvent which has been used as the reaction medium, excess reactants or reagents, unwanted reaction products (by-products) arising from alternative reaction pathways and so on. The planning of the isolation operations and application to such complex mixtures is therefore an exacting test of the expertise of the chemist. Frequently a student fails to bring a successful reaction to a fruitful conclusion by using an ill-considered work-up procedure, which results in loss of the required product either by decomposition during attempted isolation, or from a premature discard of product because of lack of appreciation of its physical or chemical properties. It should be emphasised that even when a detailed published procedure is being followed it is unwise to discard any liquid or solid fractions separated during work-up until the final product has been isolated and adequately characterised.

Because of the length of time that a complete isolation process often takes, it is wise practice, particularly with new syntheses carried out for the first time, to monitor the progress of the reaction. Thus the disappearance from a reaction mixture of one of the reactants or the build-up of the reaction product, measured on small aliquot portions removed at convenient time intervals from the bulk reaction mixture, can yield valuable information on the progress of a reaction. Usually the former is to be preferred since the physical properties (e.g. spectroscopic information, Chapter 3), chemical reactivity (e.g. characteristic tests of functional groups, Section 9.5) and chromatographic behaviour (Section 2.31) of

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the reactant, and the influence of solvents or other reactants on the reliability of the chosen monitoring processes may be readily checked before the reaction is commenced.

The adoption of a particular isolation procedure will depend to a large extent upon the physical and chemical properties of the product. Some guidelines for useful general approaches may however be given with regard to the physical state at ambient temperature of the crude mixture resulting from the reaction, i.e. whether it is a *one-phase* (either *solid* or *liquid*) or a *two-phase* (*solid/liquid* or *liquid/liquid*) system.

In the case of the *one-phase solid system* if the organic product is neutral and insoluble in water, washing with water may be used to remove soluble impurities such as inorganic salts. Alternatively the crude solid may be extracted with a suitable organic solvent (Section 2.22), filtered, and the extract washed with water. Further washing successively with dilute aqueous acid and dilute aqueous alkali removes basic and acidic impurities. Removal of solvent after drying (Sections 2.23 and 2.24) leads to the recovery of the purified solid for recrystallisation from a suitable solvent (Section 2.20). Continuous extraction of the solid (e.g. in a Soxhlet apparatus) may be necessary if the required product is only sparingly soluble in convenient organic solvents.

If the crude solid product contains the required product in the form of a salt (e.g. the alkali metal salt of a phenol) and is therefore water soluble, acidification of the aqueous solution (or basification in the case, for example, of amine salts) liberates the free acidic compound (or base) which may be recovered by filtration or solvent extraction as appropriate.

The *one-phase liquid system* is more frequently encountered since many organic reactions are carried out in solution. Direct fractional distillation may separate the product, if it is a liquid, from the solvent and other liquid reagents, or concentration or cooling may lead to direct crystallisation of the product if this is a solid. However, it is often more appropriate, whether the required product is a liquid or solid, to subject the solution to the acid/base extraction procedure outlined above and considered in detail on p. 162. This acid/base extraction procedure can be done directly if the product is in solution in a water-immiscible solvent. A knowledge of the acid-base nature of the product and of its water solubility is necessary to ensure that the appropriate fraction is retained for product recovery. In those cases where the reaction solvent is water miscible (e.g. methanol, ethanol, dimethylsulphoxide, etc.) it is necessary to remove all or most of the solvent by distillation and to dissolve the residue in an excess of a water-immiscible solvent before commencing the extraction procedure. The removal of solvent from fractions obtained by these extraction procedures is these days readily effected by the use of a rotary evaporator (p. 185) and this obviates the tedium of removal of large volumes of solvent by conventional distillation.

A crude reaction mixture consisting of *two phases* is very common. In the case of a *solid/liquid* system, it will of course be necessary to make certain in which phase the required product resides. A simple example is where the product may have crystallised out from the reaction solvent; the mixture therefore only requires to be cooled and filtered for the bulk of the product to be isolated. The filtrate should then routinely be subjected to suitable concentration or extraction procedures to obtain the maximum yield of product.

Direct filtration would also be employed when the solid consists of unwanted reaction products, in which case the filtrate would be treated as the single-phase

liquid system above. When admixed with contaminants, the mixture is reheated and

*Liquid/liquid two-phase* result from the frequent procedure of pouring it on a liquid system arises from a preliminary isolation procedure. A relatively high-boiling liquid containing contaminants, which presents no additional problems and can be treated in a number of ways, is the product of the required procedure.

All these preliminary procedures rarely yield products of high purity; the products are purified by spectroscopic methods and spectroscopic methods by recrystallisation or sublimation or distillation under atmospheric pressure (Sections 2.26 and 2.28). In those cases where the yield product of adequate purity is obtained by graphic procedures (p. 162), the behaviour obtained from the product is valuable.

The final assessment of its physical constants (Sections 2.26 and 2.28) and those cited in the literature is assessed and the structure is assessed and the structure and spectroscopic methods

## 2.19 FILTRATION TECHNIQUES

Filtration of a mixture either to isolate a solid or to remove impurities or reactants, is considered in this section. The filtration techniques is considered in Section 2.19.

When substantial quantities of a liquid, a Buchner funnel (Fig. 2.43(a)) consisting of a flat, perforated porcelain cone or flat rubber ring, termed a filter flask, Buchner funnel, connected by means of this similar flask or safety flask, is connected by tubing to a filter pump; water pressure may result in the filtrate. The use of suction filtration for more complete removal of the



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liquid system above. Where it is evident that the product has crystallised out admixed with contaminating solid material a separation might be effected if the mixture is reheated and filtered hot (p. 139).

*Liquid/liquid two-phase systems* are often encountered; for example, they result from the frequent practice of quenching a reaction carried out in an organic solvent by pouring it on to ice or into dilute acid. A further instance of a liquid/liquid system arises from the use of steam distillation (Section 2.25) as a preliminary isolation procedure. This is particularly suitable for the separation of relatively high-boiling liquids and steam volatile solids from inorganic contaminants, involatile tars, etc. The subsequent work-up procedure normally presents no additional problems since the phases are usually readily separable and can be treated in a manner appropriate to the chemical or physical properties of the required product by procedures already outlined.

All these preliminary procedures give solid or liquid products which are rarely of high purity; the degree of purity may be checked by chromatographic and spectroscopic methods. Purification may often be successfully accomplished by recrystallisation or sublimation for solids (Sections 2.20 and 2.21); fractional distillation under atmospheric or reduced pressure for liquids or low melting solids (Sections 2.26 and 2.27); molecular distillation for high-boiling liquids (Section 2.28). In those cases where the use of these traditional methods does not yield product of adequate purity, resort must be made to preparative chromatographic procedures (p. 199). Here a knowledge of the chromatographic behaviour obtained from small-scale trial experiments will be particularly valuable.

The final assessment of the purity of a known product is made on the basis of its physical constants (Sections 2.33 to 2.37 and Chapter 3) in comparison with those cited in the literature. In the case of a new compound the purity should be assessed and the structural identity established by appropriate chromatographic and spectroscopic methods.

## 2.19 FILTRATION TECHNIQUES

Filtration of a mixture after completion of a reaction will often be necessary either to isolate a solid product which has separated out or to remove insoluble impurities or reactants, in which case the desired product remains in solution. In this section the filtration of cold solutions is described; the filtration of hot solutions is considered in Section 2.20.

When substantial quantities of a solid are to be filtered from suspension in a liquid, a Buchner funnel of convenient size is employed. The ordinary Buchner funnel (Fig. 2.43(a)) consists of a cylindrical porcelain funnel carrying a fixed, flat, perforated porcelain plate. It is fitted by means of a rubber stopper, rubber cone or flat rubber ring into the neck of a thick-walled filtering flask (also termed a filter flask, Buchner flask or suction flask) (Fig. 2.43(c)), which is connected by means of thick-walled rubber tubing (rubber 'pressure' tubing) to a similar flask or safety bottle, and the latter is attached by rubber 'pressure' tubing to a filter pump; the safety bottle or trap is essential since a sudden fall in water pressure may result in the water being sucked back and contaminating the filtrate. The use of suction renders rapid filtration possible and also results in a more complete removal of the mother-liquor than filtration under atmospheric