

minutes, and the well-stirred mixture should finally be neutral to litmus-paper. Now heat the mixture on a water-bath, using a thermometer as a stirrer, until the temperature reaches 60°, and then filter at the pump through a wide Buchner funnel: at this temperature, filtration should be rapid. Finally wash the residue of calcium sulphate on the filter with a small quantity of hot water, adding the wash-water to the main filtrate. In order to convert the calcium ethyl sulphate to potassium ethyl sulphate, add a concentrated aqueous solution of potassium carbonate cautiously *drop by drop* to the well-stirred filtrate until a drop of the latter withdrawn on a glass rod is *just* sufficiently alkaline to turn red litmus-paper blue. Then filter the solution at the pump, and wash the residual calcium carbonate again with a small quantity of water. Evaporate the filtrate on a water-bath until a drop withdrawn on a rod crystallises on cooling: then allow the solution to stand until almost cold, and finally chill it thoroughly in ice-water. (If the ice-water cooling is omitted, large well-developed colourless crystals of potassium ethyl sulphate will finally separate.) Filter off the crystals at the pump, drain, and dry over calcium chloride in a desiccator.

Yield, about 6g. To obtain a second (but necessarily less pure) crop of the sulphate, evaporate the filtrate further on the water-bath, and cool as before.

Hydrolysis of Potassium Ethyl Sulphate. Dissolve about 1 g. of the crystals in about 4 ml. of cold distilled water, and divide the solution into two portions. (a) To one portion, add barium chloride solution. If *pure* potassium ethyl sulphate were used, no precipitate should now form, as barium ethyl sulphate is soluble in water. Actually however, almost all samples of potassium ethyl sulphate contain traces of potassium hydrogen sulphate formed by slight hydrolysis of the ethyl compound during the evaporation of its solution, and barium chloride almost invariably gives a faint precipitate of barium sulphate. (b) To the second portion, add 2-3 drops of concentrated hydrochloric acid, and boil the mixture *gently* for about one minute. Cool, add distilled water if necessary until the solution has its former volume, and then add barium chloride as before. A markedly heavier precipitate of barium sulphate separates. The hydrolysis of the potassium ethyl sulphate is hastened considerably by the presence of the free acid: caustic alkalis have a similar, but not quite so rapid an effect.

Diethyl Ether.* $(C_2H_5)_2O$.

Required: Rectified spirit or ethanol, 95 ml.; sulphuric acid, 40 ml.

Assemble the apparatus shown in Fig. 54. Into the neck of

* The preparation of ether is described here because this is chemically its logical position. It is advisable, however, for students to defer its preparation

the distilling-flask **A** (of about 450 ml. capacity) are fitted a thistle-funnel **F** and a thermometer **T**, both reaching down to the bottom of **A**. The dropping-funnel **D** is then securely fitted by a cork into the mouth of the thistle-funnel as shown, so that the ethanol subsequently dropping from **D** can be clearly seen. To the flask **A** is fitted a *double-surface* condenser **C**, and to the latter is turned a Buchner flask **B** to act as receiver. To the side-arm of **B** is fitted a length of rubber tubing leading well below the level of the bench, so that any ether vapour escaping condensation cannot return to the neighbourhood of **A**. (Alternatively, use a ground-glass flask (Fig. 22(A), p. 43) carrying a three-necked adaptor (Fig. 22(J)). The thermometer can then be fitted through the central neck, the dropping-funnel through the left-hand neck, and the condenser joined through an adaptor (Fig. 22(E)) to the right-hand neck.)

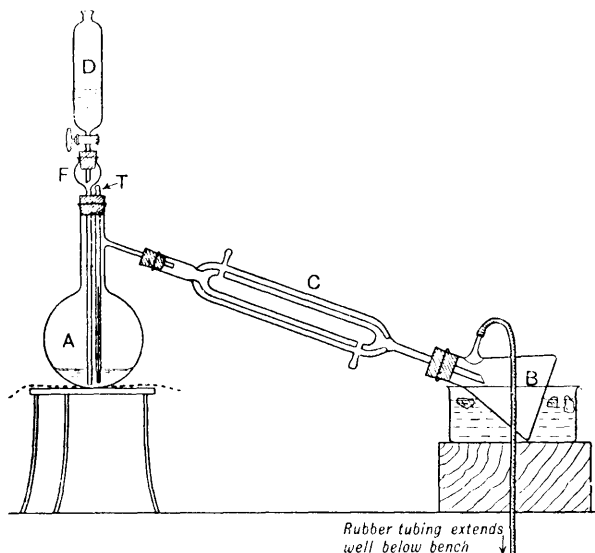


FIG. 54.

First place about 5 g. of clean *dry* sand in **A**, and then 45 ml. (36 g.) of rectified spirit: cool the flask in ice-water and *cautiously* add 40 ml. (74 g.) of concentrated sulphuric acid, shaking the mixture thoroughly during the addition to ensure a

until they have had some experience in the manipulation, and particularly the distillation, of ether, such as its use for the extraction of aniline (p. 163), where full details and precautions are given.

homogeneous product. Then reassemble the apparatus with care that the lower end of the thistle-funnel reaches to the bottom of the liquid in the flask. The thermometer is completely immersed in the liquid. Add rectified spirit in the funnel **D**, and cool the flask in ice-water. Heat the flask **A** over a gas flame or Bunsen flame until the temperature of the liquid in the flask owing to the presence of the sand steadily rises and ether begins to distil over. Now allow the ethanol to drop by drop into the thistle-funnel at the same speed as that at which the crude ether is being added. In 1 hour the total addition of the ethanol should be about 100 ml. Then continue heating **A** (still in ice-water) until no more ether distils over (temperature at 140–145°) until no more ether distils over a further 15 minutes. Turn out the distillate into a separating-funnel and wash it with 10% of 10% aqueous sodium hydroxide solution, then with 10% sulphur dioxide and some of the undistilled ether. Run off and reject the lower aqueous layer. Repeat the extraction with a fresh quantity of 10% solution. Again run off the alkaline layer into a small conical flask and dry it with anhydrous calcium chloride for at least 30 minutes. The calcium chloride removes both water and any residual ether.

Now filter the ether through a fluted filter into a 100 ml. distilling-flask, and then equip it with a thermometer and a double-surface condenser. Then attach a receiver with a rubber stopper. Place the flask cautiously in a water-bath of which have previously been heated. Place the flask at a distance from the apparatus: arrange the water-bath so that the ether distils over at a fraction boiling between 34–39°. Yield about 100 ml. more than a very small residue of ether in the flask.

Diethyl ether is a mobile, colourless liquid, d_4^{20} 0.720. It has a characteristic odour, and is used chiefly as a solvent, and was formerly used as an anaesthetic; owing to its chemical non-reactivity it is used actually as a reagent, except in the case of reagents (p. 280) where probably its chemical action is its solvent action.

Very great care should always be

homogeneous product. Then reassemble the apparatus, taking care that the lower end of the thistle-funnel **F** now reaches down to the bottom of the liquid in the flask and that the bulb of the thermometer is completely immersed. Place 50 ml. (40 g.) of rectified spirit in the funnel **D**, and cool the receiver **B** in a pan of ice-water. Heat the flask **A** over a gauze by means of a *small* Bunsen flame until the temperature of the liquid reaches 140–145°: owing to the presence of the sand steady boiling now occurs, and ether begins to distil over. Now allow the ethanol in **D** to fall drop by drop into the thistle-funnel **F** at approximately the same speed as that at which the crude ether distils over: in this way the total addition of the ethanol from **D** should take about 1 hour. Then continue heating **A** (still maintaining the temperature at 140–145°) until no more ether distils over, *i.e.*, for about a further 15 minutes. Turn out the gas, and then pour the distillate into a separating-funnel and shake it with about 25 ml. of 10% aqueous sodium hydroxide solution: this removes both sulphur dioxide and some of the unchanged ethanol from the ether. Run off and reject the lower aqueous layer, and then repeat the extraction with a fresh quantity of sodium hydroxide solution. Again run off the alkaline layer, transfer the ether to a small conical flask and dry it with an ample quantity of granular calcium chloride for at least 30 minutes. (The calcium chloride removes both water and any residual ethanol.)

Now filter the ether through a fluted filter-paper directly into a 100 ml. distilling-flask, and then equip the latter with a 100° thermometer and a double-surface condenser: to the end of the latter attach a receiver with a rubber delivery-tube *precisely as before*. Place the flask cautiously in a water-bath, the contents of which have previously been heated to about 60° at some distance from the apparatus: arrange the depth of the flask in the water-bath so that the ether distils slowly over. Collect the fraction boiling between 34–39°. Yield, 25 g. (35 ml.). Not more than a very small residue of ethanol should remain in the flask.

Diethyl ether is a mobile, colourless liquid having b.p. 35° and *d*, 0.720. It has a characteristic odour, and a burning taste. It is used chiefly as a solvent, and was formerly widely used as an anaesthetic; owing to its chemical non-reactivity, it is very seldom used actually as a reagent, except in the preparation of Grignard reagents (p. 280) where probably its chemical properties reinforce its solvent action.

Very great care should always be taken when manipulating

ether, particularly when it is being distilled. The liquid itself is very readily inflammable, and in addition the vapour forms with air a heavy and highly explosive mixture, which may roll along the laboratory bench for surprising distances, and still be capable of exploding when it comes in contact with a flame, the explosion at once travelling back towards the origin of the vapour.

For Williamson's Method for the preparation of ethers, see p. 103.

Pure Ether. Pure ether (entirely free in particular from water) is frequently required in the laboratory, and especially for the preparation and use of Grignard reagents. It is best prepared in quantity for classes by adding an ample quantity of granular calcium chloride to a "Winchester" bottle of technical ether, and allowing the mixture to stand for at least 24 hours, preferably with occasional shaking. The

greater part of the water and ethanol present in the ether is thus removed. The ether should now be filtered through a large fluted filter-paper into another clean dry Winchester bottle. About 25 g. of sodium are now pressed as fine wire directly into the ether. For this purpose, a sodium press is used (Fig. 55). This consists essentially of a heavy iron stand **S** carrying a plunger **P**, which can be screwed down so that its end fits snugly into an iron cup **C**, which has a small hole at its base. (A number of cups, having holes of different diameters, is usually available for alternative use.) The cup **C** is nearly filled with lumps of sodium, and the plunger is then screwed steadily down, while (in this case) the Winchester bottle of ether is held immediately below **C**: the sodium is thus forced as fine wire directly into the ether, and exposure to the air reduced to a minimum.

The Winchester bottle should then be closed by a rubber stopper carrying a calcium chloride tube (to allow escape of hydrogen) and the ether allowed to stand for a further 24 hours. It should then be decanted into a large distilling-flask, a few small pieces of freshly cut sodium preferably added, and the flask connected with a double-surface water-condenser having a receiver cooled in ice-water. Ether in these quantities should always be distilled in a fume-cupboard having an efficient draught, so that there is no possibility of any uncondensed vapour escaping into the laboratory. The flask itself should be heated

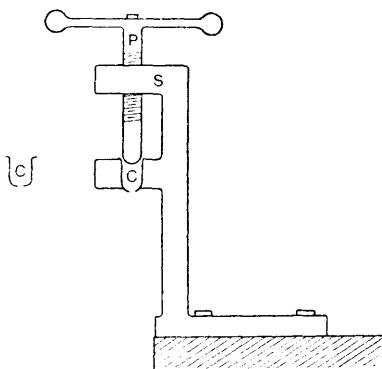


FIG. 55.

PREPARATION

by steam. If steam is not laid on in the laboratory, steam is generated *outside* the cupboard in the boiler and then led into the cupboard through a delivery tube and tubing. The flask is supported on a tripod stand over an empty water-bath: a hole is punched in the water-bath and then the compound tubing is led down into the water-bath and the extreme end of the tubing turns upwards and strikes directly upwards on to the bottom of the fume-cupboard. The fume-cupboard has a vigorous draught induced by a fan. Large quantities of the ether can thus be prepared. A 250 ml. bottle can be used as a receiver, the neck of the bottle is inserted into the neck of the bottle and held fast by a plug of cotton-wool. If a large Buchner flask is used, a rubber delivery tube (as shown in Fig. 56) is of course required.

In very hot weather, the condenser is cooled by passing it through a tall spiral of soft iron wire in a bucket of ice-water.

Ether so obtained is anhydrous, and free from impurities. On standing, however, it may undergo slow oxidation, with the formation of traces of peroxide. The formation of this peroxide can be avoided by storing the distilled ether over fresh sodium.

Ethylene. C_2H_4 .

Required: Rectified spirit, 20 ml.

Assemble the apparatus shown in Fig. 57. A flat-bottomed flask supported on a tripod stand is connected by a glass delivery-tube to the wash-bottle. The wash-bottle is two-thirds full of 10% aqueous sodium hydroxide solution. The delivery-tube leads from **B** into a beaker containing water. The beaker is placed on earthenware tiles placed side by side.

Place 20 ml. (16 g.) of rectified spirit in the flask with cooling and shaking, 40 ml. of concentrated sulphuric acid. Then add about 2 g. of potassium dichromate. Ensure a steady evolution of ethylene gas by heating up the apparatus and heat **F** over a Bunsen burner.

* Consequently traces of these unstable peroxides are present in all the lower aliphatic ethers unless the ether is distilled. If these ethers when being distilled are heated in a water-bath, the final residue of peroxide may be removed violently. The use of a water-bath for heating the flask is considerably both the risk of the ether exploding.

Peroxides can usually be completely removed by shaking with aqueous potassium permanganate.

by steam. If steam is not laid on in the fume-cupboard, it should be generated *outside* the cupboard in the usual steam-can (Fig. 15, p. 33) and then led into the cupboard through a length of soft metal "compo" tubing. The flask is supported on the usual concentric metal rings over an empty water-bath: a hole is punched in one of the outer rings, and then the compo tubing is led down through this hole into the bath, and the extreme end of the tubing turned up so that the jet of steam strikes directly upwards on to the base of the flask. If the fume-cupboard has a vigorous draught induced by an electric motor, large quantities of the ether can thus be safely distilled, and an ordinary bottle can be used as a receiver, the end of the condenser being fitted into the neck of the bottle and held firmly in position by a plug of cotton-wool. If a large Buchner flask is used as a receiver, the rubber delivery tube (as shown in Fig. 54, p. 80, and in Fig. 23(E), p. 45) is of course required.

In very hot weather, the condenser water should first be chilled by passing it through a tall spiral of soft metal "compo" tubing immersed in a bucket of ice-water.

Ether so obtained is anhydrous, and almost entirely free from other impurities. On standing, however, it undergoes slight atmospheric oxidation, with the formation of traces of diethyl peroxide, $(C_2H_5)_2O_2$.^{*} The formation of this peroxide can be largely checked, however, by storing the distilled ether over fresh sodium wire, preferably in the dark.

Ethylene. C_2H_4 .

Required: Rectified spirit, 20 ml.; sulphuric acid, 40 ml.

Assemble the apparatus shown in Fig. 56. **F** is a 200 ml. flat-bottomed flask supported on a sand-bath and connected by a glass delivery-tube to the wash-bottle **B**, which is about two-thirds full of 10% aqueous sodium hydroxide solution. A second delivery-tube leads from **B** into a beehive stand (or between two earthenware tiles placed side by side) in a pneumatic trough **T** containing water.

Place 20 ml. (16 g.) of rectified spirit in **F**, and add slowly, with cooling and shaking, 40 ml. (74 g.) of concentrated sulphuric acid. Then add about 2-3 g. of clean dry sand, to ensure a steady evolution of ethylene subsequently. Connect up the apparatus and heat **F** over the sand-bath as shown.

^{*} Consequently traces of these unstable peroxides are present in samples of all the lower aliphatic ethers unless the samples have been freshly distilled. If these ethers when being distilled are heated on, for example, an electric heater, the final residue of peroxide may become sufficiently hot to explode violently. The use of a water-bath for heating, as described above, decreases considerably both the risk of the ether catching fire and of the peroxide exploding.

Peroxides can usually be completely removed from a sample of ether by thorough shaking with aqueous potassium permanganate solution.