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19. DIETHYL PHOSPHITE

$$3C_2H_5OH + PCl_3 \rightarrow (C_2H_5O)_2POH + C_2H_5Cl + 2HCl$$

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Diethyl phosphite was probably first prepared in 1854 by the reaction between alcohol and phosphorus(III) chloride.[1] It can also be prepared from phosphorus(III) oxide and alcohol,[2] from phosphorous acid and diazoethane,[3] or from lead phosphite and ethyl iodide.[4]

Diethyl phosphite is generally produced by the reaction of phosphorus(III) chloride with absolute alcohol. Good yields are difficult to obtain unless special precautions are taken. The by-product hydrogen chloride tends to react with the diethyl phosphite to form additional ethyl chloride and phosphorous acid:

$$(C_2H_5O)_2POH + 2HCl \rightarrow 2C_2H_5Cl + H_3PO_3$$

Various methods have been proposed to prevent this secondary reaction from occurring by removing the hydrogen chloride rapidly, either by applying a vacuum to the reactor, by bubbling a dry inert gas through the mixture, by adding pyridine to combine with the hydrogen chloride, or

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by adding low-boiling solvents like pentane, carbon tetrachloride, or ether to the mixture. Yields are often below 80% and may be as low as 40%. The method of Heider and Gann,[5] which is recommended here, provides an alternative procedure. It depends on the use of refluxing hexane to remove the hydrogen chloride.

Procedure

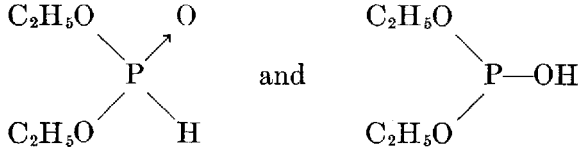
Two hundred seventy-five grams of phosphorus(III) chloride (2.0 mols) and 275 g. of hexane (3.2 mols) are placed in a 2-l. three-necked, round-bottomed flask. The flask is equipped with a stirrer, a dropping funnel, and a reflux condenser protected by a drying tube at the upper end. The contents of the flask are heated to refluxing, and a mixture of 276 g. of alcohol (6.0 mols) with an equal amount of hexane is added slowly over a period of 2 to 3 hours, with constant stirring and refluxing. After all the alcohol has been added, the refluxing is continued for an additional 30 minutes. The reaction mixture is then cooled rapidly and transferred to a distilling flask equipped with a short fractionating column, a thermometer, and a glass capillary. Diethyl phosphite has a tendency to bump or boil over during distillation; this difficulty is alleviated by admitting a slow current of air through the capillary.

A distilling head with a thermometer (to show the vapor temperature), a condenser, and a receiver are connected to the fractionating column, and vacuum is applied. Vigorous boiling of the flask contents begins, caused by the escape of the remaining hydrogen chloride and ethyl chloride. After these substances have been expelled, the pressure falls. At 25 mm. the vapor temperature of the distilling diethyl phosphite is about 90°. The temperature in the flask increases slowly to about 100°, then rapidly to about 130° toward the end of the distillation, with an accompanying increase in pressure to 50 to 60 mm., which indicates the beginning of decomposition. The distillation is stopped

when this occurs. The yield is 75 to 90% based on phosphorus(III) chloride. *Anal.** Calcd. for $C_4H_{11}O_3P$: P, 22.5. Found: P, 21.8, 22.0. The residue has a deep yellow to orange color and consists of phosphorous acid and the lower phosphorus oxides.

Properties

Diethyl phosphite is a colorless liquid with a slight odor; Nylen[6] reports it to be odorless if purified by two distillations. It has the following properties: b.p., 187 to 188° at 760 mm., 77.0 to 77.5° at 13 mm.; sp. gr., 1.0961_4^0; $n_\gamma^{18.4}$, 1.4164 or 1.4165.[7] Diethyl phosphite is miscible with most organic solvents. It is rapidly hydrolyzed by water or moist air, forming phosphorous acid and alcohol. It is decomposed by heating, with the evolution of some phosphine. Since it is a very good solvent for oxidized oils and varnishes, it may be used for removal of old paints. The compound behaves as though it exists in two tautomeric forms:



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* Analytical data are provided by the checkers.