432. *Esters containing Phosphorus. Part XI.* Ethylphosphonic Dichloride containing* ^{32}P.

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Radioactive ethylphosphonic dichloride has been prepared, on a small scale in an enclosed system, by reactions not involving filtrations.

OF convenient methods for preparing non-radioactive ethylphosphonic dichloride (ethyldichlorophosphine oxide; valuable for obtaining esters of ethylphosphonic acid) two may be considered: (1) Phosphorus trichloride, ethyl chloride, and aluminium chloride form the complex $EtCl,PCl_3,AlCl_3$ which is then decomposed by hydrochloric acid (Clay, *J. Org. Chem.*, 1951, **16**, 1892; Kinnear and Perren, *J.*, 1952, 343). (2) Tetraethyl-lead converts phosphorus trichloride into ethylphosphonous dichloride (ethyldichlorophosphine) (Kharasch, Jenson, and Weinhouse, *J. Org. Chem.*, 1949, **14**, 429), which is then oxidized by sulphuryl chloride to the phosphonic dichloride (American workers, personal communication).

The first method is quicker, but the filtration entailed in this reaction presents a hazard because of the danger of inhalation when volatile radioactive materials are employed. Further this method involves some danger because of the pressure developed in an enclosed reaction vessel containing ethyl chloride. It is considered essential that work with the more volatile radioactive compounds (b. p. <150°/760 mm.), should be in a completely enclosed system. This is possible with the second method and the extra time of operation involves a decrease in the radioactivity of only 15% compared with method (1).

The volatility of phosphorus trichloride, ethylphosphonous dichloride, and sulphuryl chloride permit of their quantitative transfer in a high-vacuum system. The conversion of the phosphonous into the phosphonic dichloride was also carried out in an enclosed system.

Phosphorus trichloride was supplied by Radiochemical Centre, Amersham. The

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probable impurities in it are hydrogen chloride and phosphorous acid; the trichloride was obtained analytically pure by fractional evaporation and fractional condensation in the high-vacuum system. Pure ethylphosphonous dichloride was prepared according to the equation : $PbEt_4 + 3PCl_3 = 3EtPCl_2 + EtCl + PbCl_2$. The reaction vessel was attached to the high-vacuum system, and the phosphorus trichloride transferred to it without loss and without risk. Further to reduce the hazards, a powerful magnetic stirrer was employed. The ethylphosphonous dichloride was oxidized in benzene solution in a vessel (Fig. 3) connected to the vacuum system.

Since ethylphosphonic dichloride is not sufficiently volatile to allow its transfer under a high vacuum, the reaction vessel was also designed for distillation.

EXPERIMENTAL

Apparatus.—A high-vacuum system (Fig. 1) was used : additional apparatus could be attached to the main system by sockets J_1 and J_2. Dry air could be let into the system through T_{10}. The system of traps C, D, E was used in the fractionation of phosphorus trichloride. D was graduated and could be used for measuring the volume of a volatile liquid in the system. The main system could be evacuated *via* T_2 and T_3 (volatile materials collecting in traps A and B) or *via* T_1.

FIG. 1.

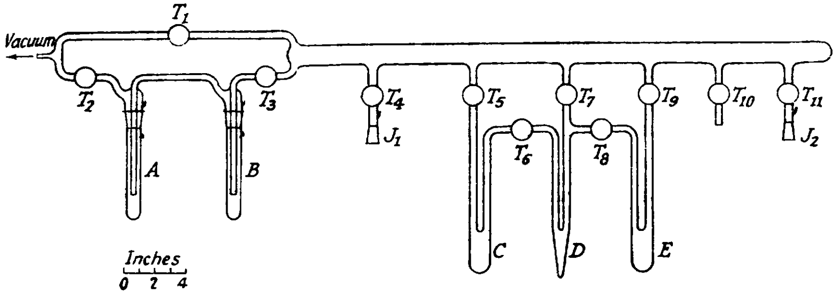


FIG. 2.

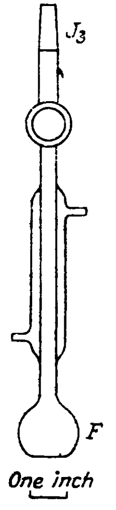
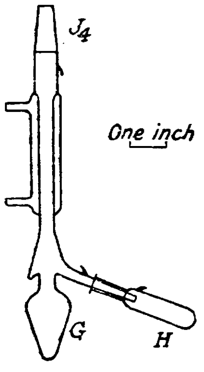


FIG 3.



The reaction vessel (Fig. 2) had a partially flattened base to ensure efficient magnetic stirring by a small piece of soft iron sealed in glass. It could be attached to the main system by J_3. The distillation vessel (Fig. 3) had a 15-ml. tapered flask G, and could be attached to the main system by J_4.

Purification of Phosphorus Trichloride.—Radioactive phosphorus trichloride (*ca.* 1 ml.; activity, 10 mc), contained in tube attached to J_2, was transferred to E under a high vacuum.

C and *E* were cooled in liquid oxygen and *D* in acetone–carbon dioxide. After pumping to a high vacuum, T_5, T_7, and T_9 were closed, T_6 and T_8 being open. The cooling-bath round *E* was removed and the contents allowed to warm slowly to room temperature. T_6 was closed, the bath round *D* removed, and *E* cooled in liquid oxygen. The fractionation was repeated three times. Pure phosphorus trichloride (1·0 ml.) was thus collected in *D*. A sample for analysis was transferred under a high vacuum to a weighed tube attached at J_1. The lower part of the tube containing the sample was then sealed off and finally broken inside the sealed Carius tube (Found : Cl, 77·4. Calc. for PCl_3 : Cl, 77·4%).

Ethylphosphonous Dichloride.—Tetraethyl-lead (twice distilled in nitrogen; b. p. 80°/12 mm.; 1·25 g., 3·9 mmoles) was placed in *F* (Fig. 2). After evacuation, pure phosphorus trichloride (1·0 ml., 11·4 mmoles) was transferred to *F*. Dry nitrogen was admitted to the system through T_{10}, and *F* heated to 110° by an electric heating-coil. The mixture was stirred magnetically for 72 hr. in dry nitrogen. After cooling, the ethylphosphonous dichloride was transferred under a high vacuum to *D*, a small portion being removed under anhydrous conditions as for phosphorus trichloride (above) (Found : Cl, 54·0. Calc. for $C_2H_5Cl_2P$: Cl, 54·1%) (yield, 1·15 ml., 1·5 g., 99%; n_D^{25} 1·4900).

Ethylphosphonic Dichloride.—The distillation vessel (Fig. 3) which contained dry "AnalaR" benzene (5 ml.) was attached by J_4 to J_2. A tube containing sulphuryl chloride (redistilled through a Fenske column; b. p. 68·8°; 1·5 ml.) was attached at J_1. After evacuation, about one-third of the sulphuryl chloride was allowed to evaporate, thus removing volatile impurities, which were collected in the cooled traps *A* and *B*. The pure compound thus obtained (1·0 ml., 1·67 g., 12·3 mmoles) was then transferred to *G*. Ethylphosphonous dichloride (1·15 ml., 1·48 g., 11·0 mmoles) was then transferred in three portions to *G*, the contents of which were allowed to melt slowly after each addition. Benzene and other volatile materials were removed by continous evacuation with a water pump *via* traps *A* and *B*. The liquid in *G* was electrically heated and distilled while the pressure in the system was maintained at 20 mm. Pure ethylphosphonic dichloride (1·35 g., 80%; activity 6 mc) collected in *H*; it had n_D^{20} 1·4670.

Since the b. p. of the phosphonic dichloride (70°/15 mm.) is too high for easy transfer in a high-vacuum system, a specimen for analysis was obtained by using, instead of the tube *H*, an adaptor to which were attached a tube similar to *H* in which the main fraction was collected, and a small weighed tube in which the sample could be collected and sealed off under anhydrous conditions (Found : Cl, 48·2. Calc. for $C_2H_5OCl_2P$: Cl, 48·3%).

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