

4. An oil possessing some toxicity to goldfish has been isolated and described.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

A REACTION BETWEEN DIETHYL ETHER AND PHOSPHORUS PENTACHLORIDE

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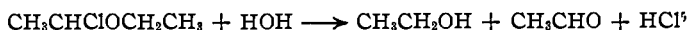
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In the course of some work on molecular rearrangements in the triphenylmethylhydroxylamine series, it was found necessary to reflux ether solutions of the materials being studied with phosphorus pentachloride for several days. At the end of this time water was added to the reaction mixture, and a very considerable and unexpected evolution of acetaldehyde was observed. This led to the investigation reported here.

Liebermann and Landshoff² report the formation of a crystalline compound of the probable formula $C_8H_{14}O_2P_3Cl_{15}$, when ether is treated with phosphorus pentachloride, and show that it is not a direct addition product with the formula $(C_4H_{10}O)_2 \cdot 3PCl_5$. No mention is made, however, of the evolution of acetaldehyde upon addition of water to the above compound.

Reactions of phosphorus pentachloride with aliphatic-aromatic ethers have been reported.³ In these cases only the aromatic portion of the molecule is oxidized.

It has been found that halogens, at ordinary temperatures, will react with ether to form α -halogen ethyl ethers which are easily hydrolyzed by water:⁴



It is well known that phosphorus pentachloride may be used as a chlorinating agent, and this fact might well account for the reaction described below, except that some organic phosphorus derivatives are formed at the

¹ A portion of the dissertation submitted to the graduate faculty of the University of Chicago, by W. S. Guthmann, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Liebermann and Landshoff, *Ber.*, **13**, 690 (1880).

³ Henri, *ibid.*, **2**, 710 (1869); Colson, *Compt. rend.*, **99**, 975 (1884).

⁴ Richter, "Organic Chemistry," P. Blakiston's Son and Co., Philadelphia, 1922, Vol. I, p. 129.

⁵ Since this paper was written, Henze and Murchison [*THIS JOURNAL*, **53**, 4077 (1931)], have reported the preparation of α -chloroethyl *n*-alkyl ethers by saturating equimolar quantities of paraldehyde, and the alcohol which contains the desired alkyl group, with hydrogen chloride, in the cold. The products hydrolyze very readily to re-form the original materials; on long standing they polymerize and leave a dark tarry residue.

same time (see experimental part). We might accept the point of view of Bergmann and Bondi,⁶ who advance evidence that one of the five chlorine atoms in phosphorus pentachloride is differently and less firmly linked than the others, which causes this compound to react as Cl-PCl_4 ; this would account for a C-P linkage in the product of reaction of phosphorus pentachloride with an organic compound.

The ultimate reaction product of phosphorus pentachloride with ether is an oil, not completely miscible with ether, and perfectly stable, at room temperatures, in the absence of moisture. All attempts to crystallize it have failed. On treatment with water the oil yields acetaldehyde, hydrochloric, phosphoric and phosphorous acids, and an unidentified organic residue which contains trivalent phosphorus. In view of the fact that the oil is most probably a mixture, no elementary analysis has been attempted. It is possible that this reaction provides an additional method for the preparation of the type of phosphoric and phosphorous esters prepared by Milobdendzki and Sachnowski⁷ and by Arbuzov and Arbuzuva.⁸

Further work in this field should yield valuable information on organic phosphorus compounds, and conceivably serve to develop a method for the determination of the relative ease of oxidation of the groups in mixed ethers.

Experimental Part

A mixture of pulverized phosphorus pentachloride (7 g.) and ether (30 cc.), carefully dried and purified, was boiled under reflux⁹ on the steam-bath for forty-eight hours, the reaction mixture being protected from moisture by means of a calcium chloride tube. At the end of this time a clear, almost colorless, mobile solution resulted. The reaction flask was well cooled and agitated while water (75 cc.) was slowly added to its contents. After separation from the aqueous layer, the ether layer was repeatedly washed with water. The washings were added to the original aqueous part. The presence of some organic phosphorous compound in the ether layer was shown as follows: the solution was dried over calcium chloride (or potassium carbonate), the solvent evaporated, and the residue oxidized with concentrated nitric acid; addition of molybdcic acid then gave a precipitate, although no such precipitate was obtained prior to the oxidation.¹⁰

⁶ Bergmann and Bondi, *Ber.*, **64B**, 1455-80(1931).

⁷ Milobdendzki and Sachnowski, *Chem. Polski*, **15**, 34 (1917); *cf. Chem. Abs.*, **13**, 2865 (1919).

⁸ Arbuzov and Arbuzuva, *J. Russ. Phys.-Chem. Soc.*, **62**, 1533 (1930); *cf. Chem. Abs.*, **25**, 2414 (1931).

⁹ The flasks used here were of 150-cc. capacity, and were joined to the condenser by means of a ground-glass joint in such a way that the condensed liquid washed the solid material (which otherwise tends to cake on the walls just above the surface of the reaction mixture) back into the bottom of the flask. These flasks also have the great advantage that contamination of the reaction mixture from stoppers is prevented.

¹⁰ Evaporation of the ether, prior to the hydrolysis, left an oil which did not crystallize on standing. Hydrolysis of this oil yielded the same products that were obtained from the ethereal solution.

The aqueous portion was fractionated; the fraction boiling below 35° contained all the acetaldehyde, which was identified by one of its many color reactions, and also by the preparation of the aldehyde semicarbazone¹¹ (melting point 162°). A mixture of the latter material with acetaldehyde semicarbazone from a known source had the same melting point (162°).

The distillation of the aqueous layer was continued until the volume of the material in the flask was reduced one-half; this residue was used for the following tests. (1) A portion allowed to stand exposed to air acquired a brown coloration, but no other change in properties was noted. (2) The presence of phosphate ion was shown by the molybdic acid reaction and confirmed by the precipitation of magnesium ammonium phosphate. When bromine was added to the filtrate obtained in the molybdic acid test, the yellow liquid became colorless, and some of the phosphorus was oxidized to phosphate ion, as was shown by the formation of more precipitate, an excess of molybdic acid having previously been used. (3) Ferric chloride was added to another portion, and the resulting mixture was made slightly alkaline and filtered. Addition of molybdic acid to a portion of the filtrate now gave no precipitate; but when another portion of the filtrate was oxidized with bromine or with concentrated nitric acid, the test for phosphate ion was positive.

The phosphate-free solution mentioned above has strong reducing properties when alkaline. It also gives the various tests for phosphorous acid, and we have the following indications of an organo-phosphorus compound: when the neutralized solution was evaporated a brown sirup resulted, encrusted with sodium chloride (formed in the neutralization of the hydrochloric acid originally present). This brown sirup was further heated, and first gave phosphine (identified in the usual way), and later became charred with the production of a distinct carbylamine odor, although no nitrogen was present. The residue which remained after the heating, when extracted with water, gave the usual phosphate tests; much carbon remained.

I wish to take this opportunity to express my sincere gratitude to Professor Stieglitz for his kind help and guidance.

Summary

1. A new reaction of diethyl ether and phosphorus pentachloride is described.
2. Organo-phosphorus compounds are formed in the course of the reaction. These are easily hydrolyzed by water alone.
3. The products of hydrolysis of the compounds mentioned in (2) include acetaldehyde, hydrogen chloride, phosphoric and phosphorous acids, and some unidentified stable organo-phosphorus compounds.

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¹¹ Thiele and Bailey, *Ann.*, **303**, 79 (1898).