CXXIX.—*Reactions of Triethylphosphine.*

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THE triethylphosphine was made by Hofmann's method of adding phosphorus trichloride to an ethereal solution of zinc ethyl. After adding the sodium hydroxide and distilling off the triethylphosphine, more solid sodium hydroxide was added; an oil separated which, on boiling, dissolved with evolution of hydrogen. The residue was made acid with hydrochloric acid, evaporated to dryness, and extracted with alcohol. From the alcoholic extract diethylphosphinic acid was obtained. $PCl_3 + ZnEt_2 = ZnCl_2 + PEt_2Cl \longrightarrow PEt_2{\cdot}OH \longrightarrow PEt_2O{\cdot}OH$. This acid boiled at about 320° without decomposition. It solidified in a freezing mixture to a mass of long needles radiating from a centre. Boiled with silver hydroxide, it gave a soluble silver salt which was stable and not decomposed by boiling. After evaporation, the concentrated solution was precipitated with alcohol, the silver salt coming down in long, anhydrous, silky needles (Found: Ag = 46·6, 46·1. Calc. for $C_4H_{10}O_2PAg$, Ag = 47·0 %).

The reaction of triethylphosphine with chlorides of the non-metals is quite anomalous. If added to either phosphorus trichloride or phosphorus oxychloride, it reacts with great violence with the formation of free phosphorus. If the oxychloride be dissolved in dry ether, triethylphosphine gives a white precipitate, but this compound soon decomposes, yielding yellow phosphorus. Silicon tetrachloride and sulphur monochloride react in an exactly similar manner, silicon and sulphur being produced. It is curious that metallic chlorides do not behave in the same way. Tin tetrachloride does not react at all violently and gives a white double salt. Zinc chloride behaves also in the same manner; whilst some halogen derivatives of hydrocarbons will not react at all. Chloro- and bromobenzene may be boiled with triethylphosphine, or left for weeks with it without any reaction. Iodobenzene reacts very slowly, and four-sided plates are produced [Found: I = 39·8. $P(C_2H_5)_3(C_6H_5I)$ requires I = 39·4 %]. Trimethylene dibromide also reacts very

slowly, small, white crystals being deposited [Found : Br = 24·8. $P(C_2H_5)_3(CH_2)_3Br_2$ requires for one bromine atom, Br = 25·0 %].

Aldehydes also react with triethylphosphine. With chloral there is a powerful reaction, the chief product being metachloral, in fact if a trace only of triethylphosphine be added to chloral, after a short time the whole becomes nearly solid. When triethylphosphine is added to a solution of chloral hydrate in dry ether, an oil separates which is soluble in water and gives a chloroplatinate (Found : Pt = 21·3. $[P(C_2H_5)_3C_2H_3Cl_3O_2]_2PtCl_4$ requires Pt = 21·5 %).

When a solution of formalin is shaken with triethylphosphine, the latter dissolves, the mixture becomes warm, and all smell of the phosphine disappears, also the solution becomes alkaline, owing to the formation of the quaternary phosphonium hydroxide. On the addition of hydrochloric acid and platinum tetrachloride a crystalline salt is obtained (Found : Pt = 27·4. $[P(C_2H_5)_3CH_3OCl]_2PtCl_4$ requires Pt = 27·6 %).

A similar compound is obtained with acetaldehyde (Found : Pt = 26·5. $[P(C_2H_5)_3C_2H_5OCl]_2PtCl_4$ requires Pt = 26·6 %).

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