1222. *Methods of Formation of Phosphorus–Carbon Bonds: Tertiary Phosphine Oxides*

By Gennady M. Kosolapoff

Some years ago Hamilton and his co-workers reported [1] that the reaction of the potassium derivative of di-n-octylphosphine oxide with β-chloropropionitrile yielded an unidentified product, which melted at 149·5—150·5° and was devoid of nitrogen, chlorine, and potassium. Since the formation of such a substance in this reaction is curious, we prepared it by the method of Hamilton *et al.* It was probably tetra-n-octyl-1,2-ethylenediphosphine dioxide, as was confirmed by an alternative synthesis of this dioxide from n-octylmagnesium bromide and esters of 1,2-ethylenediphosphonic acid.

Formation of this dioxide in the reaction described by Hamilton *et al.* was rather unexpected, for its generation might be explained by either an elimination of the elements of hydrogen cyanide from the normally expected product 2-cyanoethyldi-n-octylphosphine oxide, followed by an addition of the potassium derivative of di-n-octylphosphine oxide to the vinyl group, or a displacement of the cyano-group from 2-cyanoethyl-di-n-octylphosphine oxide by the anion of di-n-octylphosphine oxide. Neither type of reaction has been reported for phosphine oxides.

While we were not concerned with the elucidation of the mechanism by which this product (I) might have been formed, we were interested in its identity as an example of an apparently novel type of formation of the carbon–phosphorus bond in phosphine oxides. Accordingly, the Grignard reaction was used to convert two esters of 1,2,-ethylenediphosphonic acid into (I), which proved to be identical with the substance prepared by the route of Hamilton *et al.* This gave us a good opportunity to test the validity of the claim of superiority of phenyl esters of phosphorus acids, reported by Berlin *et al.*,[2] in such a reaction over alkyl esters. The scheme is as follows:

$$(PhO)_2P(O)CH_2{\cdot}CH_2{\cdot}P(O)(OPh) + C_8H_{17}MgBr\ (excess) \longrightarrow (I)$$

The removal of phenol from the reaction mixture was rather troublesome and the yield of neutral reaction products was disappointing. However, some 15% yield of (I) was obtained and the product was identical with the material of Hamilton *et al.* A similar reaction but with the tetramethyl ester of ethylenediphosphonic acid gave a yield of some 50% of (I) and the product, again identical with the previously prepared (I), was purified much more readily.

(I) was also prepared, but in very disappointing yields, by the schemes ($R = C_8H_{17}$):

$$R_2P(O)OH + PCl_5 \longrightarrow R_2P(O)Cl$$

$$R_2P(O)Cl + BrCH_2{\cdot}CH_2Br + Mg\ or\ Na \longrightarrow (I)$$

Continuing our examination of routes to dioxides of organic diphosphines, we re-examined the product reported [3] as tetra-n-butylmethylenediphosphine dioxide (II) from the reaction of chloromethyldi-n-butylphosphine oxide with lithium or bromomagnesium derivatives of di-n-butylphosphine oxide. The product described as (II) was obtained only in the very low yield of 0·12% among many others.[3] A further examination of this substance, m. p. 170—172°, showed that it was indeed tetraethylenediphosphine dioxide, rather than (II), confirmed by mixed m. p.

---

[1] R. C. Miller, J. S. Bradley, and L. A. Hamilton, *J. Amer. Chem. Soc.*, 1956, **78**, 5299.

[2] K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushanam, "Topics in Phosphorus Chemistry," Interscience Publishers, Inc., New York, 1964, p. 40—41.

[3] G. M. Kosolapoff and R. F. Struck, *J.*, 1961, 2423.

Evidently, the chloromethyl group of chloromethyl-dialkylphosphine oxides is quite prone to metalation, as this appears to be a rational route to the formation of the ethylene bridge, as shown (M = Li or MgBr):

$$2Bu_2P(O)CH_2Cl \longrightarrow Bu_2P(O)CH_2M + Bu_2P(O)CH_2Cl \longrightarrow Bu_2P(O)CH_2{\cdot}CH_2P(O)Bu_2$$

Experimental.—Diphenyl phosphorochloridite, b. p. 145—147°/3·5 mm., was prepared according to Kabachnik *et al.*[4] and converted by ethylene oxide in 68% yield into 2-chloroethyl diphenyl phosphite, b. p. 156—159°/2 mm.[4] This was converted into 55% tetraphenyl ethylenediphosphonate, m. p. 155—156° (lit.,[4] m. p. 155—155·5°) by heating to 250—255°.

The ester (12·8 g.) was added, under helium, to the ethereal solution of n-octylmagnesium bromide (6 mol.) and the mixture refluxed for 16 hr., then poured on ice–hydrochloric acid, steam-distilled to remove much of the phenol, concentrated *in vacuo* to 200 ml., refluxed for 16 hr. with 500 ml. of concentrated hydrochloric acid, and extracted with ether. The concentrated extract was washed with 1% sodium hydroxide and evaporated to dryness. The residue was recrystallised four times from benzene–ligroin and yielded 15% of (I), m. p. 152—152·5°, alone or mixed with the product prepared according to Hamilton *et al.*[1] (Found: C, 70·82, 71·05; H, 12·76, 12·97; P, 10·64, 10·77. Calc. for $C_{34}H_{72}O_2P_2$: C, 71·11; H, 12·55; P, 10·79%) (Microanalyses by Galbraith Laboratories, Knoxville, Tenn.).

A mixture of 3 moles of trimethyl phosphite (372 g.) and 1 mole of ethylene bromide (188 g.) was refluxed for 10 hr. until the b. p. had slowly risen to a constant value of about 170°; distillation gave much dimethyl methylphosphonate, b. p. 75°/18 mm., and 17—20 g. of tetramethyl ethylenediphosphonate, b. p. 142—145°/5 mm., n_D^{25} 1·4345. This was treated with n-octylmagnesium bromide, as described above, and gave 52% of (I), identical with the product prepared from the tetraphenyl ester.

THE FRANK J. SEILER RESEARCH LABORATORY, U.S.A.F. ACADEMY, COLORADO.
[Present address: AUBURN UNIVERSITY, ALABAMA.]

[*Received, March 22nd,* 1965.]

---

[4] M. I. Kabachnik and P. A. Rossiiskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk,* 1947, 631.