469. *Diphosphine Dioxides. Part II.*[1] *Some Diphosphine Dioxides with Mono-, Di-, and Tri-methylene Bridges.*

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Various routes for possible synthesis of compounds of type $[R_2P(O)]_2[CH_2]_x$ with $x = 1$—3 were examined and several representative members of the group were prepared.

The present paper continues the report of our work on synthetic routes to diphosphine dioxides containing polymethylene bridges of varying lengths.[1]

The synthesis of such dioxides with fewer than four methylene groups in the bridge cannot be accomplished by the di-Grignard reagent route used by us previously. Accordingly, we examined a number of other routes, most of which were found to be unworkable or otherwise unattractive.

One of the more fruitful approaches was the reaction of glycol ditoluene-*p*-sulphonates with the Grignard reagents based on secondary phosphine oxides:

$$2R_2P(O)\cdot MgX + (p\text{-}Me\cdot C_6H_4\cdot SO_3)_2[CH_2]_x \longrightarrow R_2P(O)\cdot[CH_2]_x\cdot P(O)R_2 + 2p\text{-}Me\cdot C_6H_4\cdot SO_3\cdot MgX$$

This reaction gave acceptable yields of several dioxides with the ethylene and the trimethylene bridge, but failed for the monomethylene member. A similar reaction employing ethylene bromide in place of the ethylene disulphonate also gave a modest yield of the expected dioxide; this is not surprising in view of the rather high reactivity of ethylene halides.

The second route which was productive, but to a much more limited degree, was that passing through the tetrachlorides of the respective diphosphonic acids:

$$(RO)_2P(O)\cdot[CH_2]_x\cdot P(O)(OR)_2 \longrightarrow Cl_2P(O)\cdot[CH_2]_x\cdot P(O)Cl_2 \longrightarrow R_2P(O)\cdot[CH_2]_x\cdot P(O)R_2$$

This route, which appears superficially attractive, proved much less so in performance. We had explored it rather earnestly before publication [2] of its use for the synthesis of some diphosphine dioxides with a monomethylene bridge; it is this publication that prompted us to report our work at this time.

The conversion of esters of phosphonic acids into phosphonic dichlorides is an old reaction which may be represented simply as follows:

$$R\cdot P(O)(OR)_2 + 2PCl_5 \longrightarrow R\cdot P(O)Cl_2 + 2RCl + 2POCl_3$$

It appeared logical to expect that a similar reaction applied to the esters of diphosphonic acids should lead to formation of the corresponding bisdichlorides $Cl_2P(O)\cdot[CH_2]_x\cdot P(O)Cl_2$. However, the reaction proved to be much more complex than might have been expected; treatment of tetra-alkyl diphosphonates with the theoretically required four-molar quantity of phosphorus pentachloride, under a variety of conditions, yielded products which had a

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[1] Part I, *J.*, 1959, 3950.

[2] Burke, Richard, Sakurai, O'Laughlin, and Banks, Amer. Chem. Soc. 138th Meeting, Abs., p. 13B.

behaviour pattern unexpected of the phosphonic chlorides. The substances were generally insoluble in common organic solvents and usually contained far smaller amounts of chlorine than necessary for the indicated tetrachlorides. Sublimation of such products under a high vacuum did result in volatilization of very small portions of material that had the expected chlorine content, but the bulk of the residual material contained little or no chlorine. It is our opinion, therefore, that the reaction of phosphorus pentachloride with esters of diphosphonic acids is very prone to afford anhydrides, probably of intermolecular type; such reactions are common among organophosphorus compounds:

$$>\mathrm{P(O)Cl} + \mathrm{RO{\cdot}P(O)}< \longrightarrow \mathrm{RCl} + >\mathrm{P(O){-}O{-}P(O)}<$$

However, such reactions do not usually obtrude on the formation of phosphonic dichlorides from esters of monophosphonic acids. Owing to the general intractability of the presumably intermolecular anhydrides, we were unable to secure any further ideas about their probable structures. It is of interest also that specimens of diphosphonic tetrachlorides, specifically the ethylene member, which had been purified by crystallization from phosphorus oxychloride as described by Petrov *et al.*[3] and contained the expected amount of chlorine, nevertheless gave only minute yields of the expected diphosphine dioxides in prolonged reactions with Grignard reagents. This appears to be a further argument against the acceptance of the substances as true diphosphonic tetrachlorides. It is very likely that a large part of the chlorine content of such specimens is located on the bridge between the phosphorus atoms, rather than at the latter. Certainly, recent work by Petrov *et al.*[3] indicates the ready substitution of bridge-hydrogen atoms by chlorine of phosphorus pentachloride, which would lead to such substances. We conclude, therefore, that the reaction

$$\mathrm{(RO)_2P(O){\cdot}[CH_2]_{\mathit{x}}{\cdot}P(O)(OR)_2} + 4\mathrm{PCl_5} \longrightarrow \mathrm{Cl_2P(O){\cdot}[CH_2]_{\mathit{x}}{\cdot}P(O)Cl_2} + 4\mathrm{RCl} + 4\mathrm{POCl_3}$$

takes place only to a minor degree, being overshadowed by the anhydride formation which evidently occurs between further ester and the initially formed partial chlorides.

Synthesis of diphosphine dioxides with $x = 1$ or 2 may be projected through a variety of routes involving an intermediate of the general formula $\mathrm{R_2P(O){\cdot}CH_2Cl}$. Thus, coupling of two such units by the action of an active metal should form diphosphine dioxides with $x = 2$, whilst an Arbuzov reaction with a trialkyl phosphite should yield an ester readily convertible into the desired dioxide:

$$\begin{tikzcd}
\mathrm{R_2P(O){\cdot}CH_2Cl} \arrow[r, "\mathrm{M}"] \arrow[d, "\mathrm{P(OR)_3}"] & \mathrm{R_2P(O){\cdot}CH_2{\cdot}CH_2{\cdot}P(O)R_2} & \\
\mathrm{R_2P(O){\cdot}CH_2{\cdot}P(O)(OR)_2} \arrow[r] & \mathrm{R_2P(O){\cdot}CH_2{\cdot}POCl_2} \arrow[r] & \mathrm{R_2P(O){\cdot}CH_2{\cdot}P(O)R_2}
\end{tikzcd}$$

For a synthesis of the necessary tertiary phosphine oxides with one chloromethyl group, we first turned to the reaction of diazomethane with phosphinyl chlorides:

$$\mathrm{R_2P(O)Cl} + \mathrm{CH_2N_2} \longrightarrow \mathrm{R_2P(O){\cdot}CH_2Cl} + \mathrm{N_2}$$

This reaction had been reported some time ago by Saunders *et al.*[4] in case of a structurally similar dialkyl phosphorofluoridate:

$$\mathrm{(RO)_2P(O)F} + \mathrm{CH_2N_2} \longrightarrow \mathrm{(RO)_2P(O){\cdot}CH_2F}$$

However, many attempts to carry out this reaction with phosphinyl chlorides, both at low temperatures and at the boiling point of ether (the highest temperature which we felt

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[3] Petrov, Maklyaev, and Bliznyuk, *Zhur. obshchei Khim.*, 1960, **30**, 1608.
[4] Saunders, Stacey, Wild, and Wilding, *J.*, 1948, 699.

would be safe for the reagent used) failed to yield any of the expected chloromethyl compound: only unchanged starting material and varying amounts of evidently polymeric solids or semisolids were isolated. Evidently the phosphinyl group prevents the expected reaction of diazomethane with compounds of this group. Accordingly, we attempted to circumvent this problem by treating the tervalent phosphorus compound (phosphorus trichloride) with diazomethane, after which the resulting dichlorochloromethylphosphine was subjected to alkylation with various organometallic reagents (magnesium or lithium); again, none of the desired dialkylchloromethylphosphine oxides was isolated and only semi-solid polymeric materials were formed, along with some tertiary phosphine oxides resulting from alkylation at all three sites of possible reaction.

Having been able to prepare the desired dioxides with $x = 2$ by other routes, we explored further the possibilities of a synthesis of a dialkylchloromethylphosphine oxide as a precursor for the dioxides with $x = 1$. Chlorination of trimethylphosphine oxide under controlled conditions could be expected to yield this substance; however, chlorination under ultraviolet illumination at a variety of temperatures, with or without an activating catalyst (antimony chloride), failed to yield the expected product. Curiously, this treatment was quite effective in a progressive cleavage of the methyl groups from the phosphorus atom and such reactions yielded varying amounts of dimethylphosphinyl chloride, methylphosphonic dichloride, and phosphorus oxychloride. This dealkylation appears to be a novel reaction of trimethylphosphine oxide.

Further, we treated trimethylphosphine oxide with metallic sodium, in the hope of forming a sodium derivative by hydrogen displacement, as such reactivity might have been expected at the α-carbon of a phosphine oxide. This reaction, however, failed to take place.

In a search for other routes to the dioxides with $x = 1$ we were able to obtain a modest yield of the desired material by the following reaction:

$$2R_2P(O)\cdot MgX + CH_2I_2 \longrightarrow R_2P(O)\cdot CH_2\cdot P(O)R_2 + 2MgXI$$

but an attempt at a similar reaction with the sodium derivative of secondary phosphine oxides proved fruitless.

Finally, it was felt that our previous failures to isolate dialkylchloromethylphosphine oxides from the reactions shown above might have been caused by unusual sensitivity of the product to temperature. Accordingly we allowed a deficient amount of organometallic reagents (lithium or magnesium) to react with chloromethylphosphonic dichloride, so that the reaction mixtures could have been expected to contain some $R_2P(O)\cdot CH_2Cl$, after the reaction of the expectedly more reactive acid chloride units. Treatment of such a reaction mixture with the Grignard reagent from a secondary phosphine oxide, *viz.*, $R_2P(O)\cdot MgX$, indeed afforded a low yield of the desired diphosphine dioxide with $x = 1$. Again, the use of the sodium salt of the secondary phosphine oxide had a negative conclusion.

Two final negative results might be mentioned from our search for routes to the dioxides with $x = 1$. Oxidative chlorophosphonation of trimethylphosphine oxide, with oxygen and phosphorus trichloride, failed to take place after many trials. An Arbuzov reaction between methylene iodide and butyl dibutylphosphinite also failed to take place.

The seven diphosphine dioxides prepared in this group were then examined as to their tendency to form associated aggregates. Molecular-weight determinations, made ebullioscopically in benzene or in acetone (the latter being necessitated by insolubility of some members in the hydrocarbon solvent), showed that all but two of the phosphine dioxides were substantially monomeric in solution. Methylated members with $x = 2$ and 3 were dimeric and trimeric, respectively. It appeared therefore that the nature of the radicals at the phosphorus atom is of a greater influence on the association of these compounds than is the length of the polymethylene bridge between the phosphorus atoms.

EXPERIMENTAL

The details of numerous unsuccessful trials are omitted, as these experiments employed conventional techniques.

*Tetra-*P*-phenyltrimethylenediphosphine Dioxide.*—Trimethylene ditoluene-*p*-sulphonate, m. p. 91—93° (15 g., 0·039 mole), in dry benzene (300 ml.) was added to the Grignard reagent from bromobenzene and magnesium (36·4 g.) and diethyl hydrogen phosphonate acid (69 g.) in ether. The ether component of the solvent mixture was replaced by benzene, and the mixture was refluxed for 44 hr., after which a solution of potassium hydroxide (180 g.) in ethanol (1 l.) was added and the precipitated magnesium hydroxide was separated. The filtrate was combined with ethanolic washings of the filter-cake, and the total filtrate was concentrated *in vacuo*. The residue was taken up in benzene and washed with aqueous potassium hydroxide. Distillation of the organic solution gave the desired *dioxide* (5 g., 36%), b. p. 295—300°/0·1 mm. After several weeks in ethanol–hexane solution, the product crystallized in plates, m. p. 195—196° after two recrystallizations from the same solvent [Found: P, 13·9, 14·1%; *M* (in benzene), 453. $C_{27}H_{26}O_2P_2$ requires P, 13·9%; *M*, 444].

The same dioxide was formed in a somewhat lower yield when trimethylene bromide was used instead of the disulphonate. The crude product contained bromine, evidently owing to a partial reaction; after treatment with alcoholic potassium hydroxide, the product was purified as shown above.

*Tetra-*P*-phenylethylenediphosphine Dioxide.*—The above procedure with ethylene ditoluene-*p*-sulphonate gave 41% of the desired *dioxide*, which formed plates, m. p. 276—278°, from benzene [Found: P, 14·2%; *M* (in acetone), 415. $C_{26}H_{24}O_2P_2$ requires P, 14·4%; *M*, 430].

*Tetra-*P*-butyltrimethylenediphosphine Dioxide.*—The above procedure with trimethylene ditoluene-*p*-sulphonate gave 43% of this *dioxide*, which formed needles, m. p. 128—129°, from hexane [Found: P, 16·9, 17·0%; *M* (in benzene), 356. $C_{19}H_{42}O_2P_2$ requires 17·0%; *M*, 364]. Only a trace of this material was formed after a 24-hr. reaction of an excess of butylmagnesium bromide and tetraethyl trimethylenediphosphonate in boiling dipentyl ether.

In an alternate procedure, tetraethyl trimethylenediphosphonate (91 g.) in dry benzene (50 ml.) was added to phosphorus pentachloride (240 g., 4 mol.) in refluxing benzene, and the mixture was boiled overnight during which ~50% of the theoretical volume of ethyl chloride was collected in a chilled trap connected to the reflux condenser. The volatile materials were removed under water-pump vacuum and the viscous dark residue was suspended in benzene (300 ml.) and added to a Grignard reagent prepared from butyl bromide (192 g.). The whole was refluxed overnight and worked up as described above; some 20 g. of crude neutral product were obtained. This distilled mainly at 193—195°/0·07 mm. (the distillation was stopped before completion by incipient decomposition). In all, only 4·0 g. of the dioxide were obtained pure by this procedure.

*Tetra-*P*-butylethylenediphosphine Dioxide.*—(*a*) The above procedure, with ethylene ditoluene-*p*-sulphonate and the Grignard reagent from butylmagnesium bromide and diethyl hydrogen phosphonate gave 40% of this *dioxide*, b. p. 222—224°/0·8 mm., m. p. 174—175° (from benzene–ether) [Found: P, 17·6%; *M* (in benzene), 351. $C_{18}H_{40}O_2P_2$ requires P, 17·7%; *M*, 350]. This dioxide showed a tendency to dissociate or disproportionate: vacuum-sublimation of a sample gave a series of fractions in which the m. p. dropped progressively with time, beginning with the m. p. shown above. The residual material after several hours' heating in the sublimation apparatus was a semisolid, apparently polymeric mass, while the sublimate contained detectable amounts of tributylphosphine oxide.

(*b*) Tetraethyl ethylenediphosphonate (70 g., 0·232 mole) was added during 1 hr. to phosphorus pentachloride (222 g., 1·065 moles) in benzene (500 ml.), and the mixture was refluxed overnight, during which ~60% of the calculated volume of ethyl chloride was collected. The cooled mixture was treated with sulphur dioxide to destroy the residual pentachloride, and the whole was concentrated *in vacuo*. The residual viscous liquid failed to crystallize, and was treated with additional phosphorus pentachloride (29·2 g., 0·14 mole) in chlorobenzene (150 ml.). After treatment with sulphur dioxide and concentration, the mixture gave a product which melted at 195—205° with much decomposition. This material contained Cl, 54·3% and P, 23·6% (calc. for ethylenebisphosphonic tetrachloride 53·7 and 23·5%, respectively). It was added to butylmagnesium bromide prepared from magnesium (33 g., 46% excess), and the whole was refluxed in dipropyl ether for 12 hr. The usual working-up gave 36 g. of a crude product, which after a vacuum-distillation and purification gave only 1 g. of the above dioxide.

Tetra-P-*butylmethylenediphosphine Dioxide*.—Chloromethylphosphonic dichloride (41·9 g., 0·25 mole) was treated at −5° with butylmagnesium bromide (from 12·2 g. of magnesium). After having been stirred overnight, the crude mixture was added during 1·5 hr. to a mixture prepared from magnesium (24·3 g.), butyl bromide (142 g.), and diethyl hydrogen phosphonate (46 g.) in ethyl ether. The whole was refluxed with stirring for 24 hr. after which it was worked up as described above. Only 120 mg. of the above *dioxide* were isolated; they formed needles, m. p. 172—174° from hexane [Found: P, 19·5%; *M* (in benzene), 340. $C_{17}H_{38}O_2P_2$ requires P, 19·7%; *M*, 336].

In a similar reaction the necessary Grignard reagent of dibutylphosphine oxide was prepared from an isolated phosphine oxide by treatment of it with ethylmagnesium bromide. The reaction run with 0·2-molar amounts of reactants gave 170 mg. (0·25%) of the dioxide, m. p. 167—170°. After sublimation under a high vacuum and recrystallization, ~77 mg. of the dioxide, m. p. 174—176°, were isolated.

Tetra-P-*methyltrimethylenediphosphine Dioxide*.—The above scheme with trimethylene ditoluene-*p*-sulphonate, methylmagnesium iodide, and diethyl hydrogen phosphonate gave 23·5% of this *dioxide*, m. p. 211—212° after vacuum-sublimation [Found: P, 31·5, 31·5%; *M* (in acetone), 337. $C_7H_{18}O_2P_2$ requires P, 31·6%; *M*, 196]. This dioxide was reported earlier [5] to be a semiliquid substance.

Tetra-P-*methylethylenediphosphine Dioxide*.—To phosphorus pentachloride (117 g., 0·56 mole) was added phosphorus oxychloride (450 g.) and the mixture was treated during 30 min. with tetraisopropyl ethylenediphosphonate (50 g., 0·14 mole). After 10 hours' refluxing during which only 23 ml. of isopropyl chloride were evolved, the mass was treated with sulphur dioxide and was cooled overnight, yielding a precipitate. This was stirred with warm toluene, part of which was then distilled off along with residual phosphorus oxychloride, and the residue was chilled, yielding an apparent tetrachloride (33 g., 89%), decomp. 155—165° (see ref. 3). This material was refluxed for 42 hr. with methylmagnesium iodide (8 moles) in ether and after the usual working-up gave 2·6 g. of neutral product. Sublimation at 190°/0·1 mm. gave a product (2·3 g.), m. p. 275—280°. This material was acidic and was, accordingly, made strongly alkaline with potassium hydroxide solution, evaporated, and sublimed *in vacuo*, yielding but 20 mg. of *dioxide*, m. p. 232—233° [Found: P, 34·0, 34·2%; *M* (in acetone), 532. $C_6H_{16}O_2P_2$ requires P, 34·0%; *M*, 182].

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[5] Grayson, Keough, and Johnson, *J. Amer. Chem. Soc.*, 1958, **81**, 4803.