794. *Diphosphine Dioxides. Part I. Some Representative Diphosphine Dioxides with a Tetra-, Penta-, and Hexa-methylene Bridge.*

By GENNADY M. KOSOLAPOFF and ROBERT F. STRUCK.

Ten members of the novel class of organophosphorus compound $[R_2P(O)]_2[CH_2]_x$, where $x = 4$, 5, or 6, have been synthesized from di-Grignard reagents. The preparation of dialkylphosphinic acids has been improved.

IN our synthetic studies of organophosphorus compounds it appeared advisable to examine the possible series of organic diphosphine dioxides, *i.e.*, compounds of the general class, $[R_2P(O)]_2[CH_2]_x$, with a variety of radicals R and various values of x. These compounds are the closest phosphorus-bearing analogues of diketones and it was obviously interesting to examine the variation of the properties of such compounds with changes in the structural factors R and x.

The present paper deals with the synthesis of several compounds of this class with x values of 4, 5, and 6.

Probably the most satisfactory route to these substances appeared to be the reaction of di-Grignard reagents with appropriate phosphinyl chlorides:

$$2R_2P(O)Cl + [CH_2]_x(MgX_2)_2 \longrightarrow [R_2P(O)]_2[CH_2]_x + 2MgXCl$$

This route is suitable for the preparation of these substances with values of $x = 4$ and higher. It was felt that the separation of the two PO groups by more than six methylene bridge units probably would not produce any further interesting changes in the properties of these compounds.

Accordingly nine substances were prepared in this category with R = methyl, n-butyl, or phenyl; one compound with R = ethyl was also synthesized for reasons which appear below.

The syntheses proceeded satisfactorily but it was noted that the conventional aqueous treatment of the reaction mixtures resulted in the precipitation of the desired compounds in the form of complexes or addition compounds with the magnesium halides. This had not been reported in the analogous Grignard syntheses of the simple tertiary phosphine oxides. After the removal of the inorganic addend in the usual manner, the compounds with R = ethyl, n-butyl, and phenyl were readily purified and isolated as solvent-free substances. The dioxides with R = methyl, however, retained crystallization solvents or moisture most tenaciously. These solvent-bearing products possessed rather sharp melting points and were convertible into the solvent-free form only by rather drastic heating *in vacuo*. The solvent-retention progressed quite evidently with decrease in the size of the methylene bridge. The methyl members of the group also proved to be resistant to the nitric acid–permanganate method of oxidative decomposition for phosphorus analysis, a method which was satisfactory for the other members of the group, including the ethyl derivative, which was prepared at this juncture in order to verify the unusual resistance of the methyl members specifically.

The synthetic route used by us required the preparation of phosphinic acids. Some minor improvements were introduced into the previously described procedure.

EXPERIMENTAL

Synthesis of Phosphinic Acids and Phosphinyl Chlorides.—The previously reported[1] Grignard synthesis of phosphinic acids was changed as indicated below. A Grignard reagent, prepared from 3·0 moles of bromobenzene and 3·0 g.-atoms of magnesium in 1 l. of absolute ethyl ether, was treated during 6 hr. with 135 g. (slightly under one mole) of diethyl hydrogen

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[1] Kosolapoff and Watson, *Amer. Chem. J.*, 1951, **73**, 4101, 5466.

phosphonate with good stirring, then the mixture was refluxed overnight. The product was dropped into ice-water and the mixture was acidified with *ca.* 170 ml. of concentrated hydrochloric acid. The ether evaporated in the course of this operation and its residues were removed by gentle warming. Bromine was added dropwise with stirring until a faint permanent color remained. The precipitated diphenylphosphinic acid was collected, dissolved in aqueous potassium hydroxide, and reprecipitated by acidification. After drying by means of benzene–water azeotropic distillation, there were obtained 161 g. (75%) of diphenylphosphinic acid, m. p. 194—195°. A 78% yield was obtained when the bromine was added to a dioxan solution of the oily layer which had separated after the acidification of the original reaction miture. If a small amount of an alkali-insoluble material is obtained after the oxidation with bromine, as described above, this material (evidently diphenylphosphine oxide) may be readily oxidized to the desired acid by treatment with a small volume of potassium permanganate solution.

The diphenylphosphinic acid, in dry benzene, was treated with an equimolar amount of phosphorus pentachloride at the b. p. with stirring overnight. Distillation gave consistent 88% yields of diphenylphosphinyl chloride, b. p. 227—230°/10 mm.

Di-n-butylphosphinic Acid and Its Chloride.—The acid was prepared in 78—87% yields by the technique described above. Treatment of this with phosphorus pentachloride gave up to 92% of the corresponding chloride, b. p. 163—166°/22 mm.

Diethylphosphinic Acid and Its Chloride.—While the synthesis of the acid was as described above, its isolation had to be performed differently, owing to the solubility of the acid in aqueous media. The original reaction mixture solidified after addition of the phosphonate, and the whole was refluxed overnight without stirring. After the aqueous treatment and addition of bromine, the entire mixture was evaporated under water-pump vacuum at 50° in a rotating glass evaporator. The residue was treated with a solution of 330 g. of potassium hydroxide in aqueous ethanol, the resulting precipitate of magnesium hydroxide was filtered off, and the filtrate was strongly acidified with hydrochloric acid and evaporated to dryness under water-pump vacuum. The residue was triturated with ethanol, and the alcoholic extract was evaporated to dryness and treated with an aqueous slurry of lead oxide until the mixture became slightly basic. The solids were filtered off and the filtrate was freed from lead by treatment with hydrogen sulphide. The viscous residue, after the evaporation of the solvent, was distilled *in vacuo*, yielding diethylphosphinic acid (22%), b. p. 194—195°/21 mm. This was converted into the chloride, as described above, the yield being 86% of a product, b. p. 134—135°/52 mm.

The working time required for this procedure is considerably less than for the previous procedure which employed thiophosphoryl chloride and a Grignard reagent.

The bromination–oxidation technique used in these preparations is more convenient than the previously used hydrogen peroxide oxidation, especially for relatively large runs which become hazardous under the other procedure.

Dimethylphosphinic Acid and Its Chloride.—These were prepared as described recently by Reinhardt *et al.*[2] We found that while a substantially quantitative yield of the acid is obtained if the mixture is stirred overnight (Reinhardt and his co-workers failed to specify the duration of the reaction), the yield fell to *ca.* 50% if the reaction is run at the b. p. for only 6 hr. A similar yield (*ca.* 50%) resulted when the reactants were kept for 15 days at room temperature. The acid was converted in nearly quantitative yield into the chloride, b. p. 202—206°.

The Diphosphine Dioxides.—In a typical preparation, diphenylphosphinic chloride (22·0 g.) in dry ether (50 ml.) was added dropwise to the Grignard reagent prepared from tetramethylene bromide (12·1 g.) and magnesium (2·7 g.) in ether (100 ml.). The mixture was refluxed with stirring for 20 hr., then poured on ice (50 g.), and the precipitated complex of the diphosphine dioxide and magnesium halide was treated *in situ* with a solution of potassium hydroxide (20 g.) in ethanol (200 ml.). Magnesium hydroxide was filtered off and the filtrate adjusted to pH 6 with hydrochloric acid, filtered again, and evaporated to dryness *in vacuo*. The residue was rubbed with 10% aqueous potassium hydroxide (50 ml.) to remove any diphenylphosphinic acid. The oily layer was separated and the aqueous layer was extracted with benzene (50 ml.) to recover a small amount of emulsified product. The combined organic material was evaporated *in vacuo* and the residue was chilled overnight in a refrigerator, yielding 19·3 g. (94%) of the crude product. After recrystallization from dry benzene (100 ml.), this gave the first crop of 7·5 g. (39%) of pure $[Ph_2P(O)]_2[CH_2]_4$. Alternatively, the crude product may be

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[2] Reinhardt, Bianchi, and Möller, *Chem. Ber.*, 1957, **90**, 1658.

vacuum-distilled, boiling without decomposition at 290—291°/1·6 mm. and melting at ~110°. After recrystallization from dry benzene, *tetramethylenebis(diphenylphosphine oxide)* melted at 154—155° (Found: P, 13·2, 13·3. $C_{28}H_{28}O_2P_2$ requires P, 13·5%).

The remaining *diphosphine dioxides* (see Table) were prepared similarly. The synthesis of the methyl members required the addition of the dimethylphosphinic chloride in benzene solution owing to the low solubility of this chloride in ether.

					P, %		C, %		H, %	
R	x	B. p./mm.	M. p.	Yield	found	calc.	found	calc.	found	calc.
Ph	5	326—327°/0·27	119—120°	55%	13·00	13·12				
Ph	6	292—294°/0·20	196—198°	79	12·66	12·73				
Bu	4	270—271°/2·0	116—118°	65	16·38	16·36				
Bu	5	259°/0·75	106—107°	57	15·75	15·75				
Bu	6	279—281°/0·9	110—111°	61	15·29	15·23				
Et	4	181—182°/0·25	111—112°	41	23·26	23·30				
Me	4	219—222°/0·35	204—205°	36	29·03	29·48	45·5	45·7	9·4	9·6
Me	5	249—252/1·3	167—168°	67	27·11	27·59	48·0	48·2	9·6	9·9
Me	6	217°/0·35	179—180°	50	26·43	25·98	49·9	50·1	10·1	10·2

The tetramethyl members differed from the others in their very limited solubility in hydrocarbons, such as benzene. For this reason it was impossible to determine their apparent molecular weight in this solvent. Tetramethylenebis(dimethylphosphine oxide) was obtained directly after the vacuum-distillation or recrystallization from a large volume of dry benzene. Crystallization of this substance from benzene–ethanol gave a crystalline product which contained ethanol (Found: P, 21·1. Calc. for $C_8H_{20}O_2P_2$,2EtOH: P, 20·5%). The product gave an enhanced molecular weight (413) determined ebullioscopically in acetone, which was much higher than that calculated (302) for the dialcoholate. In view of the numerous enhanced molecular weights found ebullioscopically in this group, it appears that considerable association of the dioxides occurs in solution. It was necessary to sublime this particular dioxide in a high vacuum at ~190° in order to remove the alcohol of crystallization. This gave a product identical with that obtained by the direct distillation. Pentamethylenebis(dimethylphosphine oxide) behaved similarly, yielding an adduct with ethanol (Found: P, 20·3. Calc. for $C_9H_{22}O_2P_2$,2EtOH: P, 19·6%). The tetramethylene member was most prone to form such adducts, since the hexamethylene member, which melted at 152—155° after recrystallization from ethanol, required but a single recrystallization from dry benzene to raise its m. p. to a constant value of 177—178°, before distillation. The ebullioscopic molecular weight of this substance in acetone was nearly normal (Found: 261. Calc.: 238), indicating relatively little association.

The tendency to association among these substances may be illustrated by some ebullioscopic molecular-weight data. The tetrabutyl members gave the following values which appear to indicate relatively little intermolecular association for $x = 4$, but considerable association for higher values: $x = 4$, M in benzene = 384 (calc., 378); $x = 5$, M in benzene = 461, in acetone = 831 (calc., 392·5); $x = 6$, M in benzene = 650, in acetone = 628, in camphor (Rast) = 504 (Calc., 406·5).

Except for the tetramethyl members, the compounds of this group were not appreciably hygroscopic in normal air. The solvent-free members of the tetramethyl group, and particularly the tetra- and the penta-methylene member, were hygroscopic and required drastic drying for the removal of moisture after an exposure; this appeared to be similar to the ethanol retention cited above.

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Ross Chemical Laboratory, Alabama Polytechnic Institute,
Auburn, Alabama, U.S.A.

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