

[CONTRIBUTION NO. 967 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

gem-Bis-(disubstituted-phosphinyl)-alkanes. I. Synthesis and Properties of Bis-(di-*n*-hexylphosphinyl)-methane and Related Compounds^{1a,1b}

By JOHN J. RICHARD, KEITH E. BURKE, JEROME W. O'LAUGHLIN AND CHARLES V. BANKS

RECEIVED NOVEMBER 2, 1960

A general method is described for the preparation of a new class of compounds, bis-(disubstituted-phosphinyl)-methanes, $R_2P(O)CH_2P(O)R_2$. The method has been used for the preparation of bis-(dimethylphosphinyl)-methane, bis-(di-*n*-hexylphosphinyl)-methane, bis-(di-2-ethylbutylphosphinyl)-methane and bis-(diphenylphosphinyl)-methane. It is a comparatively simple synthesis which requires four steps from commercially available chemicals to the product. An improved variation of the Nylen reaction is used to form the intermediate, bis-(dialkoxyphosphinyl)-methane, which is subsequently hydrolyzed to its acid, bis-(dihydroxyphosphinyl)-methane. Chlorination of the acid yields bis-(dichlorophosphinyl)-methane which is caused to react with a Grignard reagent to produce the desired product. Attempts to reduce bis-(di-*n*-hexylphosphinyl)-methane results in partial decomposition into di-*n*-hexylphosphine and di-*n*-hexylmethylphosphine oxide. The possibility of tautomerism is discussed and two compounds, 1,1-bis-(di-*n*-hexylphosphinyl)-butane and 4,4-bis-(di-*n*-hexylphosphinyl)-heptane, are prepared to illustrate the reactivity of the methylene hydrogen atoms. Infrared, nuclear magnetic resonance and dipole moment data are given for bis-(di-*n*-hexylphosphinyl)-methane. Initial studies show that compounds of this type may be useful as extracting agents.

Introduction

Organophosphorus compounds have been extensively studied because of their properties as metal extractants. It has been shown that phosphine oxides are more powerful extractants for uranium than the analogous phosphinates, phosphonates or phosphates. On the basis of these studies and of the formal analogy between β -diketones and bis-(disubstituted-phosphinyl)-methanes, compounds of the type $R_2P(O)CH_2P(O)R_2$ have been synthesized as potential analytical reagents.

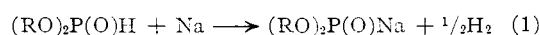
The *gem*-bis-(disubstituted-phosphinyl)-alkanes discussed herein have been named systematically on the basis of the phosphinyl radical $-P(O)H_2$.³ These compounds could also be named by the "oxa-aza" system or as tetrasubstituted-methylenediphosphine dioxides.

At the time this work was initiated, no method had been reported for the preparation of *gem*-bis-(disubstituted-phosphinyl)-alkanes. However, the preparation of similar compounds, having more than one methylene group between the phosphorus atoms, had been reported. For instance 1,6-bis-(dibutylphosphinyl)-hexane,³ 1,3-bis-(dimethylphosphinyl)-propane,⁴ 1,2-bis-(diphenylphosphinyl)-ethane,⁵ as well as a series of compounds of the general formula $[R_2P(O)]_2(CH_2)_x$, where $x = 4, 5$ or 6 and R is phenyl, butyl, ethyl or methyl, have been prepared.⁶

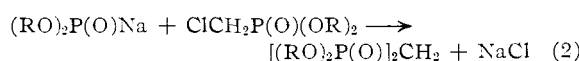
Several approaches to the synthesis of bis-(disubstituted-phosphinyl)-methanes were considered. It has been shown⁶ that α,ω -di-Grignard reagents combine with two moles of $R_2P(O)Cl$ to give bis-(disubstituted-phosphinyl)-alkanes, wherein the number of carbon atoms between the phosphorus nuclei is greater than three. However, this method did not seem promising for the bis-(disubstituted-

phosphinyl)-methanes because the methylene-di-Grignard reagent is difficult to obtain⁷ and is exceptionally unreactive.⁸ It might also be possible to prepare bis-(disubstituted-phosphinyl)-methanes by oxidation of the corresponding *gem*-diphosphines. Similar compounds have been prepared^{4,5,9,10} by this method; but this approach is beset with the difficulty of obtaining the starting materials.

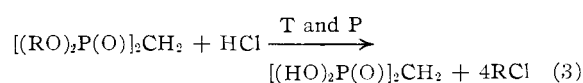
The synthesis described herein is based on the availability of synthetic methods for bis-(dialkoxyphosphinyl)-methanes.^{11,12} Equation 1 shows the reaction for the preparation of the necessary intermediate. A variation,¹² eq. 2, on the Nylen re-



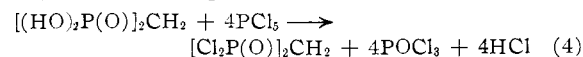
action was used to form the required bis-(dialkoxy-



phosphinyl)-methane, which then was hydrolyzed as shown in eq. 3. Bis-(dichlorophosphinyl)-



methane was formed by chlorination of bis-(dihydroxyphosphinyl)-methane with phosphorus(V) chloride; eq. 4. Direct chlorination of the



bis-(dialkoxyphosphinyl)-methane yielded mixtures from which it was difficult to separate the product. The insolubility of bis-(dihydroxyphosphinyl)-methane in the common inert solvents precludes their use as chlorination media. When an equimolar mixture of bis-(dihydroxyphosphinyl)-methane and its ethyl or butyl ester was heated and caused to react with phosphorus(V) chloride, a crystalline product was formed. The yield of this re-

(7) G. Emschwiller, *Compt. rend.*, **183**, 665 (1926).

(8) D. A. Fidler, J. R. Jones, S. L. Clark and H. Strange, *J. Am. Chem. Soc.*, **77**, 6634 (1955).

(9) C. E. Wymore, Ph.D. Thesis, University of Illinois, 1956.

(10) C. H. S. Hitchcock and F. G. Mann, *J. Chem. Soc.*, 2081 (1958).

(11) J. A. Cade, *ibid.*, 2266 (1959).

(12) G. Schwarzenbach and J. Zurc, *Monatsh.*, **81**, 202 (1950).

(1) (a) Presented before the Division of Analytical Chemistry, 138th Meeting, A.C.S., New York, N. Y., September, 1960; *Chem. Eng. News*, September 19, 1960, p. 57. (b) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) Subject Index, C. A., **51**, 7R (1957).

(3) R. C. Morris and J. L. Van Winkle, U. S. Patent 2,642,461, June 16, 1953.

(4) M. Grayson, P. T. Keough and G. A. Johnson, *J. Am. Chem. Soc.*, **81**, 4803 (1959).

(5) K. Issleib and D. W. Müller, *Chem. Ber.*, **92**, 3175 (1959).

(6) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3950 (1959).

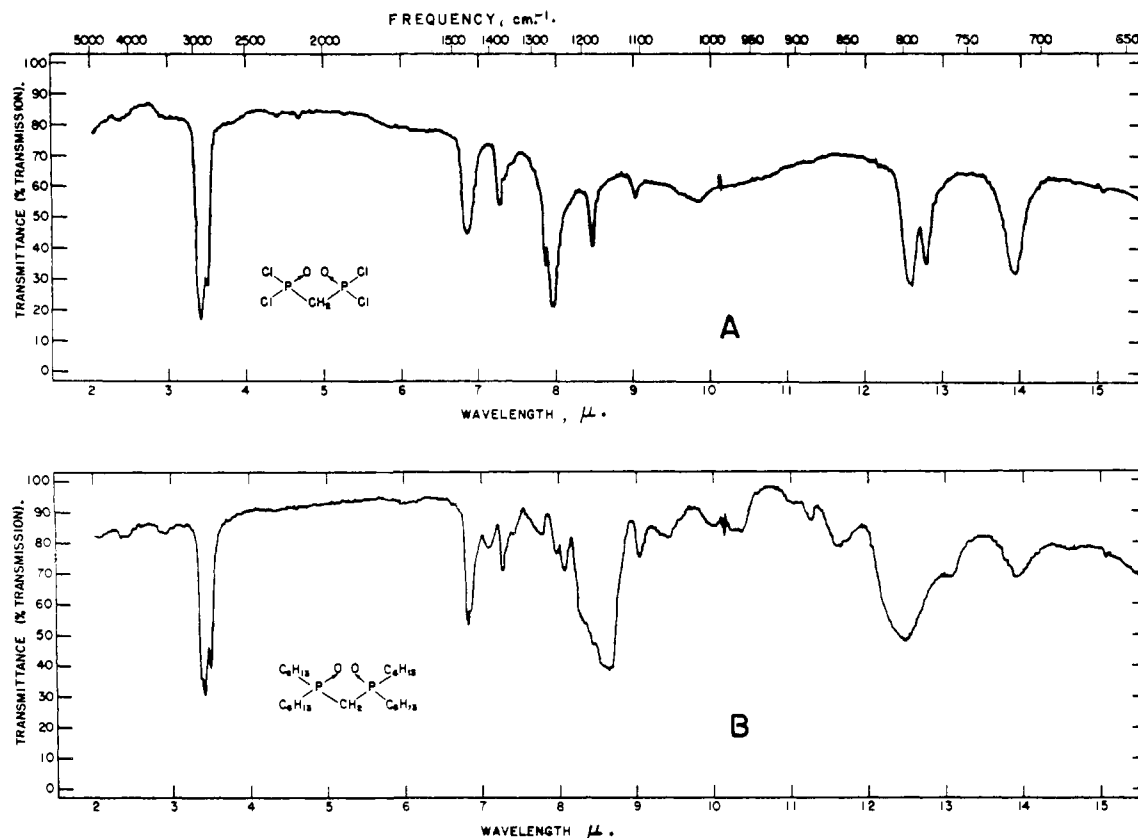
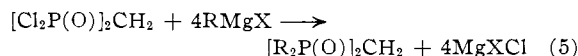


Fig. 1.—Infrared spectra of bis-(dichlorophosphinyl)-methane and bis-(di-*n*-hexylphosphinyl)-methane.

action was about 60%, based on the total amount of acid and ester added.

The synthesis was completed by causing bis-(dichlorophosphinyl)-methane to react with a Grignard reagent to give the desired bis-(disubstituted-phosphinyl)-methane; eq. 5. Bis-(di-*n*-hexylphosphinyl)-methane was the first compound



of this class to be prepared and studied. Table I lists some of its physical properties. It was purified by vacuum distillation and crystallization. The high temperature of the distillation causes the yields to be reduced by at least one-third, because the compound partially decomposes to di-*n*-hexylphosphinic acid and di-*n*-hexylmethylphosphine oxide.

TABLE I
PHYSICAL PROPERTIES OF BIS-(DI-*n*-HEXYLPHOSPHINYL)-METHANE

Physical form	White, amorphous solid
M.p., °C.	33–35
B.p., °C. (mm.)	221 (0.2)
Density at 25°	0.952 g./ml.
n_D^{25}	1.4735
Dipole moment, D.	3.6
Mol. wt. (m.p. depression)	445 (theor. 448.6)
Solubility in water at 25°	15.4 mg./l.
Solubility in common organic solvents	Readily soluble

In order to illustrate the applicability of this method to compounds other than bis-(di-*n*-

hexylphosphinyl)-methane, the following compounds were prepared and characterized: bis-(dimethylphosphinyl)-methane, bis-(di-2-ethylbutylphosphinyl)-methane and bis-(diphenylphosphinyl)-methane. Preliminary studies show that bis-(dicyclohexylphosphinyl)-methane, bis-(di-2-ethylhexylphosphinyl)-methane and 1,2-bis-(di-*n*-hexylphosphinyl)-ethane also can be prepared by this method. Bis-(di-*n*-octylphosphinyl)-methane could not be isolated due to difficulties in purifying the product, *i.e.*, the compound could not be crystallized and the high distillation temperature caused extensive decomposition. The reaction between bis-(dichlorophosphinyl)-methane and the various Grignard reagents proceeds satisfactorily with all substituents thus far tried; however, sterically hindered substituents give lower yields. Details concerning separation and purification techniques (see Experimental) are important because of the wide range of solubilities encountered in this class of compounds, *i.e.*, bis-(dimethylphosphinyl)-methane is water soluble and bis-(diphenylphosphinyl)-methane is insoluble in water and only slightly soluble in the organic solvents, whereas bis-(di-*n*-hexylphosphinyl)-methane is soluble in common organic solvents and insoluble in water.

Reactions.—Even though the semi-polar nature of the P–O bond seems to preclude the possibility of enolization, Kosolapoff¹³ has shown that bis-(diethoxyphosphinyl)-methane reacts exothermically with potassium. The resulting salt can be monoalkylated. Enhanced reactivity of the methylene

(13) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 1500 (1953).

TABLE II
 P-O STRETCHING FREQUENCIES

Compound	Formula	Wave number cm. ⁻¹
Bis-(diphenylphosphinyl)-methane	$[(C_6H_5)_2P(O)]_2CH_2$	1190
Bis-(diphenylphosphinyl) ¹⁶	$[(C_6H_5)_2P(O)]_2$	1180
Bis-(2-ethyl- <i>n</i> -butylphosphinyl)-methane	$[(CH_3CH_2CH(C_2H_5)CH_2)_2P(O)]_2CH_2$	1170
Bis-(di- <i>n</i> -hexylphosphinyl)-methane	$[(C_6H_{13})_2P(O)]_2CH_2$	1164
Bis-(dimethylphosphinyl)-methane	$[(CH_3)_2P(O)]_2CH_2$	1170
Bis-(dicyclohexylphosphinyl)-methane	$[(C_6H_{11})_2P(O)]_2CH_2$	1157
1,1-Bis-(di- <i>n</i> -hexylphosphinyl)-butane	$[(C_6H_{13})_2P(O)]_2C_4H_8$	1160
4,4-Bis-(di- <i>n</i> -hexylphosphinyl)-heptane	$[(C_6H_{13})_2P(O)]_2C_7H_{14}$	1163
1,3-Bis-(dimethylphosphinyl)-propane ¹⁷	$[(CH_3)_2P(O)]_2(CH_2)_3$	1160
Bis-(diethoxyphosphinyl)-methane	$[(C_2H_5O)_2P(O)]_2CH_2$	1265
Bis-(di- <i>n</i> -butoxyphosphinyl)-methane	$[(C_4H_9O)_2P(O)]_2CH_2$	1265
1,2-Bis-(di- <i>n</i> -butoxyphosphinyl)-ethane ¹⁸	$[(C_4H_9O)_2P(O)]_2(CH_2)_2$	1250
1,3-Bis-(di- <i>n</i> -butoxyphosphinyl)-propane ¹⁸	$[(C_4H_9O)_2P(O)]_2(CH_2)_3$	1235
1,6-Bis-(di- <i>n</i> -butoxyphosphinyl)-hexane ¹⁹	$[(C_4H_9O)_2P(O)]_2(CH_2)_6$	1190
Bis-(dichlorophosphinyl)-methane	$[Cl_2P(O)]_2CH_2$	1255
Bis-(dihydroxyphosphinyl)-methane	$[(HO)_2P(O)]_2CH_2$	1205
Di- <i>n</i> -hexylmethylphosphine oxide	$(C_6H_{13})_2P(O)CH_3$	1150
Di- <i>n</i> -hexylphosphine oxide	$(C_6H_{13})_2(H)P(O)$	1157
Di- <i>n</i> -hexylphosphinic acid	$(C_6H_{13})_2P(O)OH$	1150

hydrogens was cited as possible evidence for a "keto-enol" type of tautomerism. Similarly, it has been shown that bis-(di-*n*-hexylphosphinyl)-methane can be alkylated to give both the mono- and di-alkylated derivatives. Both 1,1-bis-(di-*n*-hexylphosphinyl)-butane and 4,4-bis-(di-*n*-hexylphosphinyl)-heptane have been characterized. These reactions indicate that the methylene hydrogens have some degree of acidity which may be due either to the ability of the compound to "enolize" or to the labilizing effect of the two P-O groups on the methylene hydrogens. The hydrogens are not acidic enough, however, to react with the Grignard reagent or to be titrated with a base such as tetraalkylammonium hydroxide.

Attempts to isolate the "enol" form by causing hydrogen chloride to react with the potassium salt of bis-(di-*n*-hexylphosphinyl)-methane were unsuccessful. Instead of an "enol," the starting material was recovered along with some di-*n*-hexylphosphinic acid and di-*n*-hexylmethylphosphine oxide.

The infrared spectrum of bis-(di-*n*-hexylphosphinyl)-methane, Fig. 1B, shows the following important features which are consistent with a "keto" structure for the ground state: lack of absorption in the region near 2700 cm.⁻¹ where the hydroxyl group absorbs, the presence of the P-O band at 1164 cm.⁻¹ which is the position expected for a P-O group of a phosphine oxide not associated through hydrogen bonding, and the absence of any infrared band which could be attributed to a P-C double bond.

Attempts to prepare bis-(di-*n*-hexylphosphino)-methane by reduction with lithium aluminum hydride were unsuccessful, due to decomposition of bis-(di-*n*-hexylphosphinyl)-methane. See Experimental section.

Structure.—Infrared studies were used to obtain supporting evidence of structure as well as to ascertain the purity of the products and their intermediates. Most spectra were obtained by the

capillary cell method because a majority of compounds were liquids or solids with low melting points.

The spectra of organophosphorus compounds were examined for bands due to P-O, H-C-P, P-C-P and P-C. and from these studies it has been possible to make tentative assignments. The P-O vibration occurs in a rather wide frequency range, from 1350 to 1250 cm.⁻¹.¹⁴ The variation in position of the band depends mainly on the electro-negativity of the substituents.¹⁵ Table II shows the position of the P-O band in various compounds and Fig. 1 shows the spectra of bis-(dichlorophosphinyl)-methane and bis-(di-*n*-hexylphosphinyl)-methane. A change of frequency of the P-O band may be interpreted as implying a change in the bond force constant and a corresponding change in bond order. At one extreme, *i.e.*, phosphine oxides, the P-O bond is primarily sigma in character, while at the other extreme, *i.e.*, phosphorus oxyfluoride, the bond takes on considerable pi character. Thus the P-O stretching frequency shifts toward longer wave lengths on going from an organic phosphate, to a phosphonate, to a phosphinate, to a phosphine oxide. The frequency of the P-O band decreases by about 15 cm.⁻¹ for each methylene group inserted between the P-O groups in the case of bis-(dialkoxyphosphinyl)-alkanes and about 25 cm.⁻¹ for bis-(dialkylphosphinyl)-alkanes.

No useful correlations for the P-C vibration have been established. However, Daasch and

(14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen Co., Ltd., 2nd Ed., 1958, p. 312.

(15) J. U. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *J. Am. Chem. Soc.*, **76**, 5185 (1954).

(16) W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2871 (1958).

(17) Infrared spectra obtained through the courtesy of Martin Grayson of American Cyanamid Co., Stamford, Conn. (see ref. 4).

(18) Samples obtained through the courtesy of C. L. Harowitz of Virginia-Carolina Chemical Corp., Richmond, Va.

(19) Infrared spectra obtained through the courtesy of C. W. Smith of Shell Development Co., Emeryville, Calif.

TABLE III
PREPARATION AND PROPERTIES OF *gem*-BIS-(DISUBSTITUTED-PHOSPHINYL)-ALKANES AND RELATED COMPOUNDS

Compound	Yield, %	B.p., °C.		M.p., °C.	Carbon, %		Hydrogen, %		Phosphorus, %	
		°C.	mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found
Bis-(di- <i>n</i> -butoxyphosphinyl)-methane	61	176	0.5	50.99	51.15	9.56	9.76	15.47	15.73
Bis-(dichlorophosphinyl)-methane ^a	60	101-102	4.81	4.97	0.81	1.00	24.80	24.58
Bis-(di- <i>n</i> -hexylphosphinyl)-methane	35	218-223	0.2	33-35	66.93	66.98	12.13	12.44	13.82	13.87
Bis-(di-2-ethylbutylphosphinyl)-methane	39	215-218	1.2	35-37	66.93	66.38	12.13	12.12	13.82	13.71
Bis-(diphenylphosphinyl)-methane	43	181-182	72.11	71.46	5.33	5.73	14.95	15.00
Bis-(dimethylphosphinyl)-methane	10	132-134						
1,1-Bis-(di- <i>n</i> -hexylphosphinyl)-butane	75	223	0.2	27-28	68.57	68.07	12.33	12.54	12.63	12.55
4,4-Bis-(di- <i>n</i> -hexylphosphinyl)-heptane	40	220-221	0.13	27-28	69.87	69.76	12.49	12.66	11.63	11.71
Di- <i>n</i> -hexylmethylphosphine oxide	..	116-118	0.8	27-28	67.20	67.21	12.58	12.86	13.23	13.13
Tri- <i>n</i> -hexylphosphine oxide	..	146-150	0.8	34-35	71.47	71.04	13.00	13.00	10.20	10.17
Di- <i>n</i> -hexylphosphinic acid ^b	75-76						

^a Calcd.: Cl, 56.77. Found: Cl, 56.63. ^b Calcd.: equiv. wt., 234. Found: equiv. wt., 234.

Smith²⁰ have associated vibrations in the region 1450-35 and 1005-995 cm.⁻¹ with the P-phenyl link. Bis-(diphenylphosphinyl)-methane shows bands at 1438 and 995 cm.⁻¹. The position of P-C (alkyl) vibrations has been reported at 1300,²¹ 1228²² and between 655-765 cm.⁻¹,^{19,23} The compounds examined here show bands at 1292, 1207 and 718 cm.⁻¹ which have been attributed to P-C vibrations.

In addition to the 718 cm.⁻¹ band attributed to P-C, another band is found in the CH₂ rocking region. The band is broad and occurs at 800 cm.⁻¹. It is tentatively assigned as P-C-P and is present only in those compounds having this linkage.

The H-C-P vibrations have been assigned⁹ and are usually found at 1255-75 and 1245-55 cm.⁻¹. These are weak, usually well defined bands which occur at 1258 and 1240 cm.⁻¹ for the bis-(dialkylphosphinyl)-methanes.

The proton spectra of bis-(di-*n*-hexylphosphinyl)-methane have been determined using high resolution nuclear magnetic spectroscopy.²⁴ The spectra indicate the presence of three types of protons: terminal methyl, long chain methylene and the unique methylene protons between the two phosphorus nuclei. No evidence of a tautomeric equilibrium was adduced from these studies, *i.e.*, neither olefinic nor "enol" protons were observed.

Experimental

All temperature measurements are uncorrected. The method of Lysyj and Zaremba²⁵ was found to be well suited for the determination of carbon in these compounds. Table III lists some properties and the analytical data for the compounds discussed in this paper.

Bis-(di-*n*-butoxyphosphinyl)-methane was prepared by the reaction of the sodium salt of dibutyl hydrogen phosphite¹⁸ with dibutylchloromethyl phosphonate²⁶ by a method quite similar to that of Schwarzenbach and Zurc.¹² A longer reflux period of 12 hours was used to complete the reaction and water extraction was used to remove the sodium chloride. This method gave a higher yield than was reported by Cade¹¹ for the preparation of this compound by a method based on the Michaelis-Arbuzov reaction.

(20) L. W. Daesch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(21) G. Costa and R. Calcinaro, *Univ. Studi Trieste, Fac. sci. Ist. Chim.*, **20**, 15 (1957).

(22) R. A. Melvor, G. A. Grant and C. E. Hubley, *Can. J. Chem.*, **34**, 1611 (1956).

(23) H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, **360** (1959).

(24) Courtesy of James N. Shoolery of Varian Associates, Palo Alto, Calif.

(25) I. Lysyj and J. E. Zaremba, *Microchem. J.*, **2**, 245 (1958).

(26) Supplied by Victor Chemical, Chicago, Ill.

Bis-(dichlorophosphinyl)-methane.—A mixture of 35.2 g. (0.2 mole) of bis-(dihydroxyphosphinyl)-methane, prepared from bis-(di-*n*-butoxyphosphinyl)-methane by the method of Schwarzenbach and Zurc,¹² and 80.0 g. (0.2 mole) of bis-(di-*n*-butoxyphosphinyl)-methane was strongly heated to effect dissolution. Phosphorus(V) chloride (332 g., 1.6 moles) was added, with stirring, over a period of about half an hour to a cooled solution of the acid. During most of the addition of the PCl₅ an ice-bath was used to remove the heat of the reaction. The mixture was heated several minutes to dissolve the last traces of phosphorus(V) chloride, transferred to a larger vessel and 800 ml. of petroleum ether, b.p. 65-110°, was added and crystallization was induced. The product was cooled in an ice-bath, filtered, and washed with 200 ml. of petroleum ether, b.p. 30-60°, to remove the phosphorus oxychloride. Needle-like crystals were obtained by slowly cooling a hot saturated solution of the product in anhydrous benzene. The product was insoluble in ether, readily soluble in hot benzene, and easily hydrolyzed (infrared spectra, Fig. 1A).

Bis-(diethoxyphosphinyl)-methane, prepared by the method of Schwarzenbach and Zurc,¹² can be substituted for bis-(di-*n*-butoxyphosphinyl)-methane in the above reactions. Yields are approximately equivalent for the two esters, but the butyl ester was more easily prepared.

Bis-(di-*n*-hexylphosphinyl)-methane.—A hot solution of bis-(dichlorophosphinyl)-methane in anhydrous benzene was added to a threefold excess of *n*-hexylmagnesium bromide in ether at a rate which maintains steady reflux. The reaction was completed by refluxing the mixture for an additional 6-8 hours, the excess Grignard reagent was hydrolyzed, and the magnesium hydroxide was dissolved with dilute (1:1) hydrochloric acid. Three layers usually formed. The aqueous layer was discarded. The middle layer, being the hydrochloric acid adduct of the compound, was decomposed by washing with water. Acid impurities, mainly di-*n*-hexylphosphinic acid, were removed from the organic layer by two extractions with a 5% solution of sodium hydroxide, followed in each case by two extractions with water. The solvents were removed by evaporation on the steam-bath and the remaining liquid was vacuum distilled. The fraction boiling from 210-235° at 0.2 mm. was collected and redistilled, saving the fraction between 218-223° at 0.2 mm. The lower boiling fractions contained di-*n*-hexylmethylphosphine oxide, tri-*n*-hexylphosphine oxide and a fraction boiling from 165-210° at 0.2 mm. containing a mixture of acidic by-products that were not identified.

The product was dissolved in diethyl ether and again extracted with a 5% solution of sodium hydroxide to remove remaining acidic impurities. The diethyl ether solution was partially dried with anhydrous sodium sulfate and cooled to Dry Ice-acetone temperature. A hydrate crystallized and was removed by filtration. Approximately one-fourth of the product remained in the mother liquor. The ether was evaporated from the mother liquor and the impure product was added to the 210-235° fraction of the next preparation of bis-(di-*n*-hexylphosphinyl)-methane. The hydrate was heated for 2 hours at approximately 50° under vacuum to remove the water. The product contained less than 0.2% acidic impurity (infrared spectrum, Fig. 1B).

Bis-(di-2-ethylbutylphosphinyl)-methane was prepared using the 2-ethylbutyl Grignard and isolated in the same manner as the *n*-hexyl derivative.

Bis-(diphenylphosphinyl)-methane.—The preparation of this compound was the same as described for the *n*-hexyl derivative, substituting the phenyl Grignard. Isolation was different due to its low solubility in organic solvents and the stability of its hydrochloric acid adduct. The excess Grignard reagent was hydrolyzed and the magnesium hydroxide was dissolved with (1:1) hydrochloric acid. The aqueous and ether layers were decanted from the residue which contains the hydrochloric acid adduct. The hydrochloric acid adduct was recrystallized several times by the addition of a large volume of water to the residue dissolved in hot ethanol. A methanol solution of the adduct was then eluted through an anion exchange (Dowex-1-X8) column (1.5" × 12") in the hydroxide form. After evaporation of the methanol, the product was dissolved in hot acetone, which gave white needle-like crystals upon cooling.

Recently Issleib and Baldauf²⁷ have shown that bis-(diphenylphosphinyl)-methane, m.p. 183°, was obtained when the product, [(C₆H₅)₂P(O)CH₂P(C₆H₅)₂], from the reaction between diphenylchlorophosphine and moist diazomethane was oxidized. The usefulness of this reaction for the preparation of the bis-(dialkylphosphinyl)-methanes is doubtful.

Bis-(dimethylphosphinyl)-methane.—Aside from using the methyl Grignard, this preparation was the same as described for the *n*-hexyl derivative; however, because the product is water soluble, different separation techniques were necessary. After hydrolysis of the excess Grignard reagent, the ether layer was discarded and the magnesium salts in the aqueous phase were precipitated by the addition of a 10% sodium hydroxide solution. The magnesium hydroxide was removed by centrifugation and the resulting solution was acidified with 6 *N* hydrochloric acid prior to removing the water by vacuum distillation at 50°. During the distillation, it was occasionally necessary to filter off the magnesium halides. The desired compound was obtained either by subliming the residue or extracting it into hot benzene and then crystallizing by the addition of petroleum ether, b.p. 30–60°, as white hygroscopic needles. It was not possible to remove all of the water from this compound; therefore, complete analytical determinations

were not attempted. Additional identification was obtained by infrared analysis.

1,1-Bis-(di-*n*-hexylphosphinyl)-butane.—The potassium salt of bis-(di-*n*-hexylphosphinyl)-methane was alkylated with *n*-propyl bromide by the procedure of Kosolapoff.¹³ Two fractions were obtained, 120–127° and 223° at 0.2 mm.

Infrared analysis of the lower boiling neutral fraction indicated a mixture of di-*n*-hexylmethylphosphine oxide with an ester. The mixture was heated for 8 hours with concentrated hydrochloric acid to hydrolyze the ester. The acid thus obtained was isolated and identified as di-*n*-hexylphosphinic acid. The ester presumably was propyl di-*n*-hexylphosphinate.

The higher boiling fraction was characterized as the monoalkylated compound. Due to an acidic contaminant, it was further purified by dissolving in diethyl ether and twice extracting with 5% NaOH, then with water. The ether was evaporated and the compound dried; *n*_D²⁰ 1.4781.

4,4-Bis-(di-*n*-hexylphosphinyl)-heptane.—The potassium salt of 1,1-bis-(di-*n*-hexylphosphinyl)-butane was alkylated with *n*-propyl bromide by the same procedure mentioned above. Complete dissolution of the potassium required about 24 hours. The redistilled fraction boiling between 220–221° at 0.13 mm. was collected; *n*_D²⁰ 1.4810.

Attempted Preparation of Bis-(di-*n*-hexylphosphino)-methane.—Reduction of bis-(di-*n*-hexylphosphinyl)-methane with lithium aluminum hydride gave two fractions boiling at 77–84° and 132–134° at 1 mm. The lower boiling fraction upon oxidation with air or neutral potassium permanganate gave di-*n*-hexylphosphine oxide,²⁸ m.p. 73–74°. The same fraction upon oxidation with acidic potassium permanganate gave di-*n*-hexylphosphinic acid. The lower boiling fraction was therefore identified as di-*n*-hexylphosphine.

The 132–134° fraction was di-*n*-hexylmethylphosphine oxide.

Acknowledgment.—The authors are indebted to Hiroshi Sakurai, a visiting research chemist from Mitsubishi Metal Mining Co., Tokyo, Japan, for his assistance in the determination of certain physical constants.

(28) R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74**, 5418 (1952).

(27) K. Issleib and L. Baldauf, *Pharm. Zentr.*, **99**, 329 (1960).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

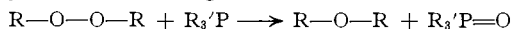
A Study of the Mechanism of the Reaction of *t*-Alkyl Peresters with Trisubstituted Phosphines¹

BY DONALD B. DENNEY, WILLIAM F. GOODYEAR² AND BERNARD GOLDSTEIN

RECEIVED SEPTEMBER 9, 1960

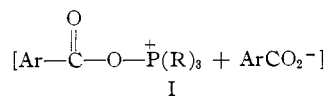
The formation of *t*-alkyl esters and trisubstituted phosphine oxides from *t*-alkyl peresters and trisubstituted phosphines has been studied. A mechanism is proposed using data from oxygen-18 tracer studies, the kinetics of the reaction, the effect of additives, and some stereochemical results. The proposed mechanism involves initial formation of a pentacoordinate phosphorus intermediate which decomposes by ion pair processes to the products.

Recently Horner and Jurgeleit³ have presented the results of an extensive study of the reactions of organic peroxides with trisubstituted phosphines. They found that the general reaction is



The mechanism of the reaction of diaryl peroxides with trisubstituted phosphines has been studied.⁴ It was suggested that the reaction pro-

ceeds by initial displacement by the phosphine on one of the oxygens of the peroxidic link to give an ion pair (I). Decomposition of I most probably



occurs by addition of the carboxylate ion to the carbonyl carbon atom of the phosphonium salt followed by loss of the phosphine oxide and formation of an aromatic anhydride.

It was also shown by the use of suitably substituted peroxides that the phosphine displaces on the most electropositive oxygen of the aryl per-

(1) Support of part of this work by Research Corporation is gratefully acknowledged.

(2) National Science Foundation Predoctoral Fellow, 1957–1959.

(3) L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

(4) (a) M. A. Greenbaum, D. B. Denney and A. K. Hoffman, *J. Am. Chem. Soc.*, **78**, 2563 (1956); (b) D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957).