3-Oxa-, Aza-, and Thioorganophosphonium Heterocyclics *via* α-Alkoxy, α-Dialkylamino, and α-Thioalkoxy Tertiary Phosphines

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A new, convenient method of making α-substituted tertiary phosphines has been discovered in the reaction of lithium diphenylphosphide with α-chloro ethers, tertiary amines, and thio ethers. The preparation of bis(diphenylphosphinomethyl) ether (I) and its reaction with dibromomethane and 1,2-dibromoethane to give six- and seven-membered cyclic 3-oxa-1,5-diphosphonium salts is described. Conductance measurements on methanolic solutions of these compounds have been used to establish their structure and degree of ionic association. The reaction of ethylene dibromide with methylthiomethyl- and dimethylaminomethyldiphenylphosphine is also described.

Although numerous organophosphorus heterocycles containing oxygen in the ring are well known, most of them are esters of various phosphorus acids containing phosphorus–oxygen bonds.[2] There are relatively few such tertiary phosphines or phosphine oxides and even fewer phosphonium salts.[3] No examples of cyclic diphosphonium salts containing oxygen, nitrogen, or sulfur in the ring are known.[3]

Cyclic 1,4-diphosphoniacyclohexane dibromides are easily prepared from 1,2-dibromoethane and diphosphines.[3–5] Extension of this method to the synthesis of cyclic 1,4-diphosphonium salts containing oxygen, nitrogen, or sulfur in the ring requires diphosphines containing oxygen, nitrogen, or sulfur in the chain of carbons connecting the two phosphorus atoms. These were not available at the commencement of this work.

It has been found that lithium diphenylphosphide[6] reacts with α-chloro ethers, α-chloro-*t*-amines, and α-chloro thio ethers to produce α-alkoxy, α-dialkylamino-, and α-thioalkoxymethyldiphenylphosphines (eq 1).

$$(C_6H_5)_2PLi + ClCH_2ZCH_3 \xrightarrow{\text{THF}} (C_6H_5)_2PCH_2ZCH_3 + LiCl \quad (1)$$

$$Z = O,\ NCH_3,\ S$$

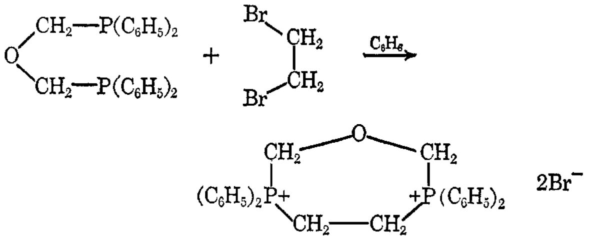
Bis(diphenylphosphinomethyl) ether (I) was synthesized employing bis(chloromethyl) ether (eq 2). Reaction of I with excess, hot 1,2-dibromoethane produced a phosphonium salt (IIa), whose elemental analysis was that expected for a 1:1 adduct of I and 1,2-dibromoethane. Addition of a methanolic solution of IIa to an aqueous solution of sodium picrate caused immediate precipitation of a yellow picrate (IIb) containing no detectable bromine, demonstrating that all of the bromine in IIa was present as bromide ion. Elemental analysis of IIb showed it to contain one picrate moiety for every bromine in IIa. A linear polymeric phosphonium salt would contain some covalently bound bromine. The proton magnetic resonance spectrum of a trifluoroacetic acid solution of IIa is that expected for a cyclic polyphosphonium salt showing only three types of protons (see Table I). A linear polymer would have another type of proton at the end which would give a detectable signal, unless the polymer were very large. It is highly unlikely that IIa has a large polymeric structure, since it melts at 292–93°. Therefore, IIa is a cyclic phosphonium salt of $7n$ atoms, where n = 1, 2, etc.

$$2(C_6H_5)_2PLi + (ClCH_2)_2O \xrightarrow{\text{THF}} \underset{\text{I}}{[(C_6H_5)_2PCH_2]_2O} + 2LiCl \quad (2)$$

The molecular weight of the 1:1 adduct, *i.e.*, $\{[(C_6H_5)_2PCH_2]_2O\cdot(CH_2Br)_2\}_n$, would be $602n$. Complete dissociation of any such cyclic adduct would produce $2n + 1$ ions. Molecular weight determinations based upon colligative properties (*e.g.*, osmotic pressure depression of a solution) would lead to an effective molecular weight of $602n/(2n + 1)$ or 200.7 for the seven-membered ring (where $n = 1$) and 240.8 for the 14-membered ring (where $n = 2$), approaching 301 as a limit. Complete association of one anion with the polycation leads to an effective molecular weight given by the expression $602n/2n$ and a value of 301, regardless of the size of the ring.

Molecular weight determinations carried out at a series of concentrations by the osmometric method on methanolic solutions of IIa led to values below 301 which decreased upon dilution (Table II). The lowest value which could be obtained within the limits of the equipment used corresponds to that for a completely dissociated 14-membered ring ($n = 2$). It is unlikely that at this concentration no association should occur between a tetrapositive cation and four bromide ions.

A graph of conductance measurements carried out on more dilute methanolic solutions of this material (from 3 to 0.01 mg/ml) (<0.01 M, assuming $n = 1$) shows that its behavior closely parallels that of $CoBr_2$, $CaCl_2$, and 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexene-2 dibromide,[5] while deviating from that of dibenzyldiphenylphosphonium bromide over the same concentration range (see Figure 1). It is therefore concluded that IIa is 3,3,6,6-tetraphenyl-3,6-diphosphonia-1-oxacycloheptane dibromide and is formed as depicted in eq 3.



(3)

IIa

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[1] National Aeronautics and Space Administration Fellow, 1964–1967.

[2] F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); *J. Am. Chem. Soc.*, **87**, 731 (1965).

[3] G. Markl, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1023 (1965).

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[5] A. M. Aguiar and H. J. Aguiar, *ibid.*, **88**, 4090 (1966).

[6] A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, **27**, 1001 (1962).

TABLE I

PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA AT 60 MC USING TETRAMETHYLSILANE AS INTERNAL STANDARD

Compound	Proton(s)	Area ratio	Multiplicity	τ	J_{PH}, cps	Solvent
Benzyl(methoxymethyl)diphenylphosphonium bromide	OCH_3	3	1	6.5		$CDCl_3$
	$PCH_2C_6H_5$	2	2	5.01	15.5	
	PCH_2O	2	2	4.63	4	
	Benzyl aromatic	5	1	2.8		
	Aromatic	10	Complex	2.2		
(Methoxymethyl)diphenylphosphine oxide	OCH_3	3	1	6.6		$CDCl_3$
	PCH_2O	2	2	5.8	6	
	Aromatic	10	Complex	2.5		
Bis(diphenylphosphinomethyl) ether (I)	PCH_2O	1	2	5.68	5	$CDCl_3$
	Aromatic	5	Complex	2.7		
Dibenzyl bromide salt of I	$PhCH_2P$	2	2	5.72	15	TFA[a]
	PCH_2O	2	2	4.65	5	
	Aromatic	15	Complex	2.5		
IIa	PCH_2CH_2P	1	2	5.0	11	TFA
	PCH_2O	1	1	4.0		
	Aromatic	5	Complex	2.2		
IIIa	PCH_2P	1	3	4.7	15	TFA
	PCH_2O	2	1	4.1		
	Aromatic	10	Complex	2.2		
IIIb	PCH_2P	1	3	4.5	15	TFA
	PCH_2O	2	1	3.95		
	Aromatic	10	Complex	2.2		
(Methylthiomethyl)diphenylphosphine (IV)	SCH_3	3	1	8.02		Neat
	PCH_2S	2	2	6.95	4	
	Aromatic	10	Complex	2.7		
(Methylthiomethyl)diphenylphosphine oxide (IVa)	SCH_3	3	1	7.82		$CDCl_3$
	PCH_2S	2	2	6.82	7	
	Aromatic	10	Complex	2.5		
Methyl(methylthiomethyl)diphenylphosphonium iodide (IVb)	$-SCH_3$	3	2	7.9	1	$CDCl_3$
	$-PCH_3$	3	2	7.1	14	
	PCH_2S	2	2	5.32	8	
	Aromatic	10	Complex	2.2		
VIa	$-CH_3$	3	1	8.13		TFA
	$-CH_2-$	2	2	6.55	5	
	$-CH_2CH_2-$	2	3	5.73	4	
	Aromatic	10	Complex	2.2		
VIb	$-CH_3$	3	1	8.13		TFA
	$-CH_2-$	2	2	6.63	5	
	$-CH_2CH_2-$	2	1 (broad)	5.8		
	Aromatic	10	Complex	2.2		
Dimethylaminomethyldiphenylphosphine (VII)	NCH_3	3	1	8.0		Neat
	PCH_2N	1	2	7.25	4	
	Aromatic	5	Complex	3.0		
Dimethylaminomethyldiphenylphosphine oxide (VIIa)	NCH_3	3	1	7.1		$CDCl_3$
	PCH_2N	1	2	6.75	6.5	
	Aromatic	5	Complex	2.5		
Tetraphenylboron salts of IIIa and IIIb	PCH_2P	1	3	4.51	13	
	PCH_2O		1	4.25		
	Aromatic	10	Complex	2.5		Acetone-d_6
	Aromatic		Complex	3.1		

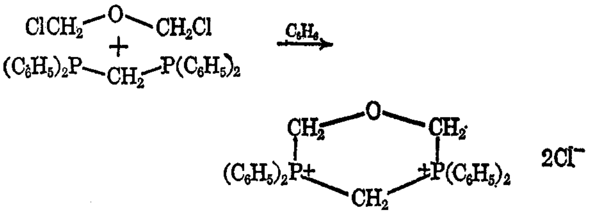
[a] TFA, trifluoroacetic acid.

TABLE II

MOLECULAR WEIGHT DETERMINATIONS OF METHANOL SOLUTIONS OF IIa

Concentration		
Mg/ml	Moles/l.	Mol wt
1.915	0.008	239.4
2.480	0.0093	267
4.417	0.0163	271
8.639	0.0315	274

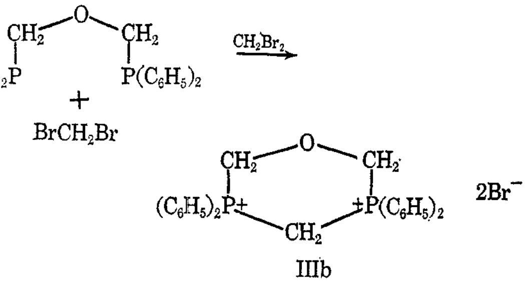
Synthesis of the six-membered analog of II, namely, 3,3,5,5-tetraphenyl-3,5-diphosphonia-1-oxacyclohexane dichloride (IIIa, X = Cl), was accomplished by reaction of methylenebis(diphenylphosphine) with bischloromethyl ether (eq 4). Both the yield (61%) and



(4)

IIIa

the hygroscopic nature of IIIa made it desirable to employ the dibromoalkane method. Reaction of I with dibromomethane in excess of the latter at reflux gives a 91% yield of the nonhygroscopic IIIb (X = Br) (eq 5).



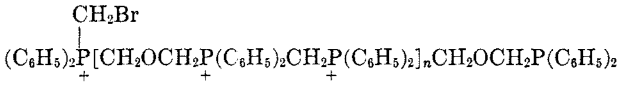
(5)

IIIb

The structure assignments to IIIa and IIIb are based upon elemental analysis of IIIb showing it to be a 1:1 adduct of I and CH_2Br_2, metathetical preparation of the tetraphenylboron salts and analysis of these materials showing that all of the halogen in IIIa and IIIb is ionic and infrared and 60-Mc proton nmr spectra of both IIIa and IIIb, as well as of the corresponding tetraphenylboron salts, showing them to have the same cyclic structure. This structure assignment is further confirmed by molecular weight measurements carried out on IIIb (*vide infra*).

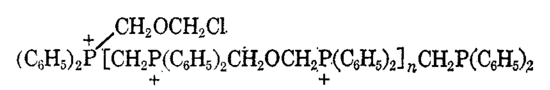
A linear polymer would have more than three types of protons and thus give a proton nmr spectrum containing at least four signals, unless the polymer were very large. This is unlikely in view of the melting point of IIIb (235–241°). The chemical shift of protons α to quaternary phosphorus has been shown to be quite dependent upon concentration.[7] The slight difference in the proton nmr spectra of IIIa and IIIb (Table I) is, therefore, entirely expected and shows that the same cation is present in both IIIa and IIIb.

An open mono- or polymeric phosphonium salt structure for IIIa and IIIb is ruled out by the essentially identical nmr spectra showing only three sets of absorptions. If either one or both were open, the nmr spectra would be different and exhibit at least four sets of peaks in the case of the noncyclic salts. This is seen by comparing compounds 1 and 2. Attempts at



$$(C_6H_5)_2\underset{+}{\overset{CH_2Br}{P}}[CH_2OCH_2\underset{+}{P}(C_6H_5)_2CH_2P(C_6H_5)_2]_nCH_2OCH_2\underset{+}{P}(C_6H_5)_2$$

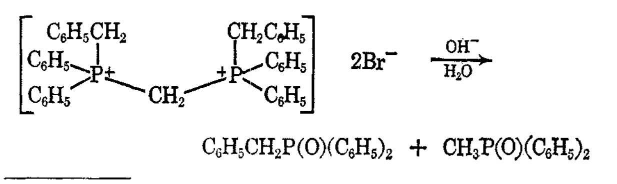
1



$$(C_6H_5)_2\overset{+\ CH_2OCH_2Cl}{P}[CH_2\underset{+}{P}(C_6H_5)_2CH_2OCH_2\underset{+}{P}(C_6H_5)_2]_nCH_2P(C_6H_5)_2$$

2

preparation of the picrates of either material led to pasty solids which could not be crystallized. Perhaps the sodium picrate leads to cleavage of the carbon–phosphorus bond. This has been shown to occur in the basic hydrolysis of the dibenzyl salt of methylenebis-(diphenylphosphine) (eq 6).[8]



(6)

The demonstrated reactivity of 1,2-dibromoethane in salt formation with phosphines, coupled with the known nucleophilicity of sulfides, suggested use of the now available (methylthiomethyl)diphenylphosphine (IV) in the formation of 3-thiaphosphoniacyclopentanes (V) (eq 7). Reaction of IV and 1,2-dibromoethane in ben-

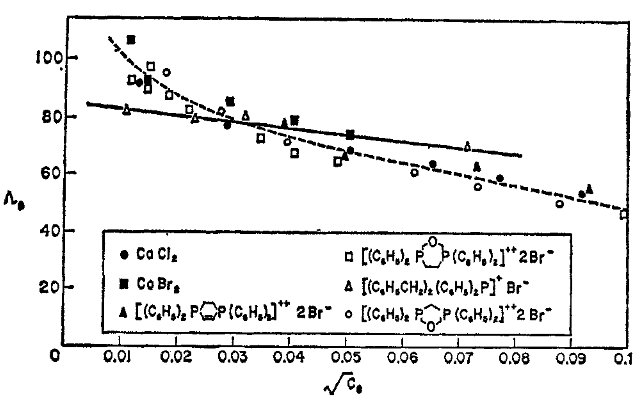


Figure 1.—Equivalent conductances of methanolic solutions of electrolytes over a range of equivalent concentrations at 25°.

Reaction of methanol solutions of IIIa and IIIb with a methanolic solution of sodium tetraphenylboron gave the same precipitate. Both the proton nmr and infrared spectra were identical. The nmr spectra showed three absorptions with the chemical shifts expected for a cyclic cation. These absorptions also were in the ratio expected for this cation. No halogen (detectable by quantitative analysis) was found in the tetraphenylboron salts, showing that all of the halogen in IIIa and IIIb is ionically bonded. Again, this supports a cyclic structure.

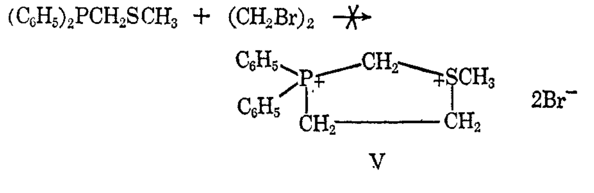
The molecular weight of a 1:1 adduct of I and methylene bromide, *i.e.*, $\{[(C_6H_5)_2PCH_2]_2O{\cdot}CH_2Br_2\}_n$, is 588*n*. Complete dissociation of any such cyclic adduct would produce $2n + 1$ ions. Therefore, the effective molecular weight would be given by the expression $588n/(2n + 1)$ or 196 for a completely dissociated six-membered ring ($n = 1$). Complete association of one bromide ion with the diphosphonium ion leads to a value of 294, independent of the value of *n*. Values larger than 1 for *n* lead to weights of 236 or higher, even if complete dissociation is assumed.

Molecular weight determinations carried out at a series of concentrations by the osmometric method on methanolic solutions of IIIb give values below 236 and approaching 196 upon dilution (Table III). Conductance measurements on this compound are also in accord with the structure assignment (Figure 1).

Table III

Molecular Weight Determinations of Methanol Solutions of IIIb

Concentration		
Mg/ml	Moles/l.	Mol wt
4.975	0.0225	221
3.200	0.0148	216
2.030	0.0095	214



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V

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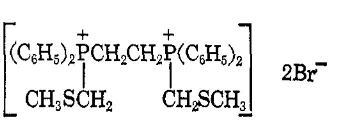
[7] C. E. Griffin and M. Gordon, *J. Organometal. Chem.*, **3**, 414 (1965).

[8] A. M. Aguiar, H. J. Aguiar, and T. G. Archibald, *Tetrahedron Letters*, 3187 (1966).

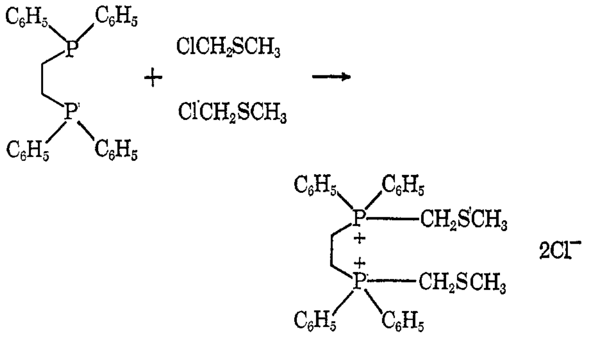
zene or in excess 1,2-dibromoethane did not lead to ring closure, but to a phosphonium salt (VIa) whose elemental analysis disclosed a composition consistent with a 2:1 adduct of IV to 1,2-dibromoethane, respectively. Proton nmr further supported the structure assignment of ethylenebis(methylthiomethyldiphenylphosphonium) dibromide (VIa). The same material was



$$\left[(C_6H_5)_2\underset{CH_3SCH_2}{\overset{+}{P}}CH_2CH_2\underset{CH_2SCH_3}{\overset{+}{P}}(C_6H_5)_2\right]2Br^-$$

VIa

also obtained from the reaction of ethylenebis(diphenylphosphine) and chloromethyl methyl sulfide, followed by ionic exchange (eq 8). Unlike the methylthiomethyldiphenylphosphine, dimethylaminomethyldiphenylphosphine (VII) reacts with 1,2-dibromoethane to give a mixture of products whose structure and mode of formation are now being investigated.



(8)

VIb

Experimental Section

Methoxymethyldiphenylphosphine.—A solution of 7.95 g (0.1 mole) of chloromethyl methyl ether in 50 ml of tetrahydrofuran was added dropwise to a refluxing solution of lithium diphenylphosphide (made from 0.1 mole of triphenylphosphine[6]) in 150 ml of tetrahydrofuran. Most of the tetrahydrofuran was distilled off under reduced pressure and the residue poured into 400 ml of water. This mixture was extracted twice with chloroform and the chloroform solution was dried over anhydrous sodium sulfate. After stripping off of solvent, the residue was distilled, giving 14.0 g (63%) of methoxymethyldiphenylphosphine, bp 126–136° (0.65 mm), lit.[9] bp 138–139° (0.1 mm). This was characterized as the methiodide, mp 153–155° dec (from chloroform–ethyl acetate), lit.[9] mp 144–146°, and as the benzylphosphonium bromide, mp 171–175° (from methanol–ethyl acetate), lit.[9] mp 173–175°.

Proton Nmr of Benzylmethoxymethyldiphenylphosphonium Bromide.—The proton nmr spectrum of a deuteriochloroform solution of the benzylphosphonium bromide showed a singlet at τ 6.5, a doublet at τ 5.01 with coupling constant J_{PH} = 15.5 cps, a doublet at τ 4.63 with coupling constant J_{PH} = 4 cps, a singlet at τ 2.8, and a complex centered at τ 2.2 in the ratio of 3:2:2:5:10, respectively. These were assigned to the methyl protons, the methylene protons on the benzyl group, the protons on the methylene group bonded to the oxygen, the phenyl protons on the benzyl group, and the phenyl protons on the phosphorus, respectively.

Methoxymethyldiphenylphosphine Oxide.—The distillation residue from the preparation of methoxymethyldiphenylphosphine yielded 5.2 g (21%) of methoxymethyldiphenylphosphine oxide, mp 114–116° (from cyclohexane). The infrared spectrum of a potassium bromide disk of this material was that expected of a phosphine oxide. The 60-Mc proton nmr spectrum of a deuteriochloroform solution of this solid showed a singlet at τ 6.6, a doublet at τ 5.8 with coupling constant J_{PH} = 6 cps, and a phenyl proton complex centered at τ 2.5 in the ratio of 3:2:10, respectively. These were assigned to the methyl, methylene, and phenyl protons, respectively.

(Methylthiomethyl)diphenylphosphine (IV).—A solution of 0.1 mole of lithium diphenylphosphide (made from 0.1 mole of chlorodiphenylphosphine) in 100 ml of tetrahydrofuran was added slowly to a refluxing tetrahydrofuran solution of 9.0 g (0.095 mole) of chloromethyl methyl sulfide. Reaction was immediate and mildly exothermic. Most of the tetrahydrofuran was stripped off and the residue poured into degassed water. The mixture was extracted twice with chloroform and the chloroform phase dried over anhydrous calcium chloride. After stripping off of solvent, the residual liquid was then vacuum distilled, yielding 14.5 g (62.5%) of IV, bp 152–160° (1.0 mm). The infrared spectrum of IV in chloroform was that expected for a phosphine with no major absorption between 8 and 9 μ,[10] indicating the absence of a phosphoryl function. The 60-Mc proton nmr spectrum of the liquid (neat) showed a singlet at τ 8.02, a doublet at τ 6.95 with a coupling constant J_{PH} = 4 cps, and a complex at τ 2.7 in the ratio of 3:2:10, respectively. These were assigned to the methyl, methylene, and phenyl protons, respectively.

(Methylthiomethyl)diphenylphosphine Oxide (IVa).—The above liquid (IV) was air sensitive, yielding methylthiomethyldiphenylphosphine oxide, mp 134–135° (from cyclohexane), lit.[11] mp 139–140°.

Anal. Calcd for $C_{14}H_{15}OPS$: C, 64.12; H, 5.73; P, 11.83; S, 12.21. Found: C, 64.01; H, 5.75; P, 12.00; S, 12.39.

The infrared spectrum of this oxide was that expected, with strong absorption at 8.5 μ assigned to the phosphoryl function. The 60-Mc proton nmr spectrum of a deuteriochloroform solution of this solid showed a singlet at τ 7.82, a doublet at τ 6.82 with coupling constant J_{PH} = 7 cps, and complex centered at τ 2.5 in the ratio of 3:2:10, respectively. There were assigned to the methyl, methylene, and phenyl protons, respectively.

Methyl(methylthiomethyl)diphenylphosphonium Iodide (IVb).—The phosphine IV was also characterized as the methiodide by reaction with excess methyl iodide in benzene. The immediate precipitate which formed was recrystallized from ethyl acetate–methanol, mp 157–160° dec. This compound decomposes slowly upon standing in air. The 60-Mc proton nmr spectrum of a deuteriochloroform solution of this salt showed three doublets: one at τ 7.9 with coupling constant J_{PH} = 1 cps assigned to the protons of the methyl group bonded to the sulfur, at τ 7.1 with a coupling constant of J_{PH} = 14 cps assigned to the protons of the methyl group on the phosphorus, and at τ 5.32 with a coupling constant of J_{PH} = 8 cps assigned to the methylene hydrogens. A phenyl proton complex was centered at τ 2.2. The ratio of the area of these signals was 3:3:2:10, respectively.

Bis(diphenylphosphinomethyl) Ether (I).—A solution of 5.8 g (0.05 mole) of bischloromethyl ether in 50 ml of tetrahydrofuran was added slowly to a solution of lithium diphenylphosphide (made from 0.1 mole of chlorodiphenylphosphine) in 200 ml of tetrahydrofuran. An immediate, exothermic reaction ensued. The tetrahydrofuran was stripped off and the residue poured into 300 ml of water. The solid which formed was recrystallized from methanol, yielding 16.8 g (80.5%), mp 86–88°.

Anal. Calcd for $C_{26}H_{24}OP_2$: C, 75.4; H, 5.8; P, 14.98. Found: C, 75.53; H, 5.93; P, 15.18.

The infrared spectrum of a potassium bromide disk of I showed principal absorptions at 3.29 (w), 6.34 (m), 6.80 (s), 7.00 (s), 7.82 (m), 8.10 (m), 9.15 (w), 9.55 (s), 9.80 (w), 10.25 (m), 11.52 (s), and 13.5 (s) μ. The 60-Mc proton nmr spectrum of a deuteriochloroform solution of I showed a doublet centered at τ 5.68 with a coupling constant J_{PH} = 5 cps and a phenyl hydrogen signal centered at τ 2.7 in the ratio of 1:5, respectively.

Bis(benzyldiphenylphosphoniamethyl) Ether Dibromide.—The phosphine I was further characterized as the dibenzylphosphonium dibromide by reaction with excess benzyl bromide in refluxing benzene, mp 286–288° dec (from ethyl acetate–methanol).

Anal. Calcd for $C_{40}H_{38}Br_2OP_2$: C, 63.49; H, 5.03; Br, 21.16; P, 8.20. Found: C, 63.19; H, 5.10; Br, 21.34; P, 7.99.

The 60-Mc proton nmr spectrum showed a doublet at τ 5.72 with a coupling constant J_{PH} = 15 cps, another doublet at τ 4.65 with a coupling constant J_{PH} = 5 cps, and a complex ab-

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(9) S. Trippett, *J. Chem. Soc.*, 2813 (1961).

(10) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 312.

(11) H. Hellman and J. Bader, *Tetrahedron Letters*, 724 (1961).

sorption at τ 2.5 in the ratio of 2:2:15, respectively. These were assigned to the methylene protons on the benzyl groups, to the protons on the methylene groups bonded to the oxygen, and the phenyl protons, respectively.

Reaction of Bis(diphenylphosphinomethyl) Ether (I) with 1,2-Dibromoethane.—Bis(diphenylphosphinomethyl) ether (I) (5.5 g, 0.0133 mole) and 2.5 g (0.0133 mole) of 1,2-dibromoethane were dissolved in 75 ml of benzene (dried over $CaCl_2$) and allowed to reflux under nitrogen for 24 hr. The precipitate was filtered and recrystallized from acetonitrile–methanol to give 4.2 g (52.5%) of IIa, mp 292–293° dec.

Anal. Calcd for $C_{28}H_{28}Br_2OP_2$: C, 55.81; H, 4.65; Br, 26.58. Found: C, 55.91; H, 4.81; Br, 26.35.

The 60-Mc proton nmr of a trifluoroacetic acid solution of IIa showed a doublet at τ 6.0 with coupling constant J_{PH} = 11 cps assigned to ethylene hydrogens, a broad singlet at τ 4.0 assigned to methylene hydrogens, and a phenyl hydrogen complex at τ 2.2 in the ratio of 1:1:5, respectively.

Picrate of IIa.—A small amount of the phosphonium salt IIa in methanol was added to an aqueous sodium bicarbonate solution of picric acid. An orange solid (IIb), mp 223–225° dec (from acetonitrile), precipitated.

Anal. Calcd for $C_{40}H_{32}N_6O_{15}P_2$: N, 9.35; Br, 0.00. Found: N, 9.23; Br, 0.00.

Reaction of Methylenebis(diphenylphosphine) with Bis(chloromethyl) Ether.—Methylenebis(diphenylphosphine) (3.5 g, 0.0091 mole) and 2.6 g (0.023 mole) of bis(chloromethyl) ether were dissolved in 75 ml of benzene (dried over $CaCl_2$) and allowed to reflux for 24 hr. IIIa (2.8 g, 61%) precipitated and was recrystallized from acetonitrile–methanol. The compound was hygroscopic. The proton nmr of a trifluoroacetic acid solution of IIIa showed a triplet at τ 4.7 with a coupling constant J_{PH} = 15 cps, a singlet at τ 4.1 and a complex centered at τ 2.2 in the ratio of 1:2:10, respectively.[8] These were assigned to the methylene protons between the two phosphorus atoms, to the methylene protons between the oxygen and phosphorus atoms, and to the phenyl protons, respectively.[8]

Reaction of Bis(diphenylphosphinomethyl) Ether (I) with Excess Dibromomethane.—Bis(diphenylphosphinomethyl) ether (1.0 g, 0.0024 mole) was dissolved in 50 ml of dibromomethane and allowed to reflux for 24 hr. The solid precipitate was recrystallized from ethyl acetate–methanol, yielding 1.3 g (91%) of IIIb, mp 235–241°.

Anal. Calcd for $C_{27}H_{26}Br_2OP_2$: C, 55.10; H, 4.42; Br, 27.21. Found: C, 54.89; H, 4.60; Br, 27.15.

The proton nmr spectrum of a trifluoroacetic acid solution of IIIb showed a triplet at τ 4.5 with a coupling constant J_{PH} = 15 cps, a singlet at τ 3.95, and a complex at τ 2.2 in the ratio of 1:2:10, respectively.[8] These were assigned to the methylene protons between the two phosphorus atoms, to the methylene protons between the oxygen and phosphorus atoms, and to the phenyl protons, respectively.[8]

Tetraphenylboron Salts of IIIa and IIIb.—Methanolic solutions of IIIa and IIIb were separatedly mixed with solutions of sodium tetraphenylboron in methanol with the immediate precipitation of white solids. The solids were washed with methanol and water and dried under vacuum at 90°. The salt from IIIa had mp 135–137° and the salt from IIIb had mp 137–140°, mmp 135–137°.

The infrared spectrum of a potassium bromide disk of the salt prepared from IIIa and IIIb was identical with major absorptions at 6.37, 6.81, 7.00, 7.08, 9.02, 9.47, 10.08, 11.22, and 11.84 μ. The 60-Mc nmr spectra of acetone-d_6 solutions of both solids were identical. They showed a singlet at τ 4.25 overlapping a triplet centered at τ 4.51 with coupling constant J_{PH} = 13 cps and two aromatic complexes at τ 2.5 and 3.1. The ratio of aliphatic protons to aromatic protons was 1:10. Analysis of both salts showed 0.00 halogen.

Reaction of (Methylthiomethyl)diphenylphosphine with 1,2-Dibromoethane.—(Methylthiomethyl)diphenylphosphine (4.1 g, 0.0166 mole) and 3.1 g (0.0166 mole) of 1,2-dibromoethane were dissolved in 100 ml of benzene and refluxed under nitrogen for 24 hr. The precipitated solid was recrystallized from methanol, yielding 2.2 g (40%) of VIa, mp 310–320° (slow decomposition).

Anal. Calcd for $C_{30}H_{34}Br_2P_2S_2$: C, 52.94; H, 5.00; Br, 23.53; P, 9.12; S, 9.41. Found: C, 52.63; H, 5.06; Br, 23.25; P, 9.27; S, 9.52.

The 60-Mc proton nmr spectrum of a trifluoroacetic acid solution of VIa showed a singlet at τ 8.13 assigned to the methyl hydrogens, a doublet at τ 6.55 with coupling constant J_{PH} = 5 cps assigned to methylene hydrogens, and a triplet at τ 5.73 with coupling constant J_{PH} = 4 cps assigned to ethylene hydrogens. A phenyl hydrogen complex was centered at τ 2.2. The ratio of the areas was 3:2:2:10, respectively.

Reaction of Ethylenebis(diphenylphosphine) with Chloromethyl Methyl Sulfide.—Ethylenebis(diphenylphosphine) (1 g, 0.0025 mole) and excess chloromethyl methyl sulfide were dissolved in 75 ml of benzene and allowed to reflux for 24 hr. The precipitate was recrystallized from ethyl acetate–methanol, yielding 1.3 g (88%) of VIb. The infrared spectrum of VIb was identical with that of VIa. The 60-Mc proton nmr spectrum of a trifluoroacetic acid solution of VIb showed a singlet at τ 8.13, a doublet at τ 6.63 with coupling constant J_{PH} = 5 cps, a broad singlet at τ 5.8, and a complex at τ 2.2 in the ratio of 3:2:2:10. These were assigned to methyl protons, methylene protons, ethylene protons, and phenyl protons, respectively.

Preparation of Chloromethyldimethylamine.[12]—A solution of 13.4 g (0.095 mole) of benzoyl chloride (dried over anhydrous calcium chloride) in 50 ml of anhydrous ether was added slowly with stirring to a solution of 10.2 g (0.1 mole) of methylenebis(dimethylamine) (dried over potassium hydroxide pellets) in 100 ml of anhydrous ether. An immediate reaction ensued with the formation of a white precipitate of chloromethyldimethylamine. The solid (very hygroscopic) was filtered in a dry nitrogen atmosphere, washed with 50 ml of anhydrous ether, and dried. The compound was used as such with no further purification.

Preparation of Dimethylaminomethyldiphenylphosphine (VII).—A solution of lithium diphenylphosphide (made from 0.1 mole of chlorodiphenylphosphine and excess lithium) in 100 ml of tetrahydrofuran was added slowly to a tetrahydrofuran suspension of 0.095 mole of chloromethyldimethylamine. An immediate, mildly exothermic reaction occurred with slow dissolution of the amine. The tetrahydrofuran was stripped off and the residue was vacuum distilled, yielding 15.3 g (66.2%) of VII, bp 130° (0.2 mm). The proton nmr spectrum of the neat liquid showed a singlet at τ 8.0, a doublet at τ 7.25 with a coupling constant J_{PH} = 4 cps, and a complex centered at τ 3.0 in the ratio of 3:1:5, respectively. These were assigned to the methyl protons, to the methylene protons, and to the phenyl protons, respectively.

Dimethylaminomethyldiphenylphosphine Oxide (VIIa).—The phosphine VII formed a crystalline phosphine oxide upon standing in the air, mp 185–187° (from acetone), lit.[13] mp 189–190°.

Anal. Calcd for $C_{15}H_{18}NOP$: C, 69.50; H, 6.95; N, 5.41; P, 11.97. Found: C, 69.38; H, 7.10; N, 5.80; P, 11.63.

The proton nmr of a deuteriochloroform solution of the phosphine oxide showed a singlet at τ 7.1, a doublet at τ 6.75 with a coupling constant J_{PH} = 6.5 cps, and a complex centered at τ 2.5 in the ratio of 3:1:5, respectively. These were assigned to the methyl protons, to the methylene protons, and to the phenyl protons, respectively.

Conductance Measurements.—Conductance measurements were made at 25° using a conventional Serfass bridge and a Freas-type cell with platinized electrodes. The cell was calibrated with aqueous potassium chloride. All solutions were made using Matheson anhydrous methanol. The methanol had a conductivity of 5×10^{-6} ohm^{-1}. Measurements were made on solutions in the range from 10^{-2} to 10^{-4} *M* and plots were made of the equivalent conductance (Λ_e) *vs.* the square root of the equivalent concentration C_e. The marked nonlinearity of the curves (Figure 1) indicates that association occurs.

Registry No.—I, 13119-09-0; I (dibenzyl bromide salt), 13119-10-3; IIa, 13119-11-4; IIb, 13143-83-4; IIIa, 13119-12-5; IIIb, 13119-13-6; IV, 13119-14-7; IVa, 13119-15-8; IVb, 10428-59-8; VIa, 13119-17-0; VIb, 13119-18-1; VII, 13119-19-2; VIIa, 13119-20-5; benzyl(methoxymethyl)diphenylphosphonium bromide, 13119-21-6; (methoxymethyl)diphenylphosphine oxide, 4455-77-0.

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