A New Type of Stable Tetrapolar Phosphorus Ylide

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Abstract: The reaction of 2 moles of triphenylphosphine with 1 mole of methylene bromide at 150° gave methylenebis(triphenylphosphonium bromide), $[(C_6H_5)_3PCH_2P(C_6H_5)_3]^{2+}2Br^-$. This was converted into methylidebis(triphenylphosphonium) bromide, $[(C_6H_5)_3P{=}CHP(C_6H_5)_3]^+Br^-$, by aqueous sodium carbonate. Treatment of this ylide with potassium in boiling diglyme gave hexaphenylcarbodiphosphorane, $(C_6H_5)_3PCP(C_6H_5)_3$, a new type of stable cumulated bis ylide. Hexaphenylcarbodiphosphorane formed stable 1:1 adducts with diphenylcarbodiimide, di-*p*-tolylcarbodiimide, phenyl isocyanate, *p*-tolyl isocyanate, *p*-cyanophenyl isocyanate, and *p*-nitrophenyl isocyanate. These new types of phosphorus compounds can be written as dipolar phosphoranium amidines and amides, $[(C_6H_5)_3P]_2{}^+CC[XY]^-$, or as tetrapolar ethylenebis(phosphonium diamides) or oxyamides, $[(C_6H_5)_3P]_2{}^{2+}C{=}C[XY]^{2-}$, where X = Y = NAr or X = NAr and Y = O, respectively. The P^{31} nmr shifts were measured at 40.5 Mcps.

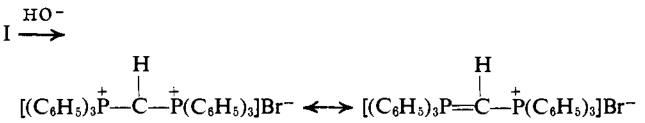
The preparation of the stable, cumulated phosphorus bis ylide hexaphenylcarbodiphosphorane, $(C_6H_5)_3PCP(C_6H_5)_3$, was first reported in 1961.[2] This paper gives the details of that preparation and describes the results of a study of the nucleophilic additions of hexaphenylcarbodiphosphorane to the carbodiimides, ArN=C=NAr, and the aryl isocyanates, ArN=C=O. In 1962, a second group of investigators also reported the preparation of hexaphenylcarbodiphosphorane.[3] Subsequently, this group described the reaction of the carbodiphosphorane with carbon dioxide, carbon disulfide, and carbonyl sulfide.[4]

Results

Preparation of Hexaphenylcarbodiphosphorane. The reaction of 2 moles of triphenylphosphine with 1 mole of methylene bromide at 150° afforded the colorless, high-melting methylenebis(triphenylphosphonium bromide), I. This sparingly soluble bisphosphonium salt, I, was readily converted into methylidebis(triphenylphosphonium) bromide, II, by aqueous sodium carbonate at 20°.

$$2(C_6H_5)_3P + BrCH_2Br \longrightarrow \overset{-}{Br}(C_6H_5)_3\overset{+}{P}CH_2\overset{+}{P}(C_6H_5)_3Br^-$$

I

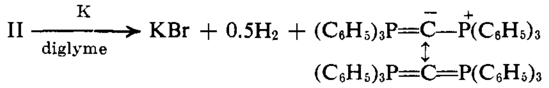


$$I \xrightarrow{HO^-} [(C_6H_5)_3\overset{+}{P}-\underset{-}{\overset{H}{\overset{|}{C}}}-\overset{+}{P}(C_6H_5)_3]Br^- \longleftrightarrow [(C_6H_5)_3P{=}\overset{H}{\overset{|}{C}}-\overset{+}{P}(C_6H_5)_3]Br^-$$

II, $\delta P^{31} = -20.4$ ppm

The phosphoranylidenemethyl(triphenyl phosphonium) bromide, II, is a new type of phosphorus ylide which can be conveniently designated by the term *phosphoranium salt*. The P^{31} nmr shift had one signal for the two equivalent phosphorus nuclei at −20.4 ppm *vs.* 85% phosphoric acid. The H^1 nmr spectrum in $CDCl_3$ at 20° had a triplet at τ 7.98, $J_{HP} = 5.5$ cps, attributed to the methine proton coupled with the two equivalent phosphonium groups. The phosphoranium salt had characteristic infrared bands at 8.15 and 12.40 μ in Nujol mull.

When the phosphoranium salt was added to a stirred suspension of potassium in boiling diglyme, hydrogen gas was evolved. This reaction afforded the bright yellow crystalline hexaphenylcarbodiphosphorane, III, in 63% yield.



$$II \xrightarrow[\text{diglyme}]{K} KBr + 0.5H_2 + (C_6H_5)_3P{=}\overset{-}{C}-\overset{+}{P}(C_6H_5)_3 \updownarrow (C_6H_5)_3P{=}C{=}P(C_6H_5)_3$$

III, $\delta P^{31} = +3.5$ ppm

The structure of the carbodiphosphorane was based on the following evidence: (1) elemental analysis and molecular weight determination. (2) The P^{31} nmr shift, +3.5 ppm in anhydrous methylene chloride, suggested the presence of a relatively shielded phosphorus nucleus of an ylide.[5] The two phosphorus nuclei were equivalent. (3) The presence of absorption in the region 275–379 mμ with λ_{max} 325 mμ suggested a degree of conjugation consistent with the carbodiphosphorane structure. The absorption maximum disappeared when a solution of the substance in cyclohexane came in contact with moisture. (4) The characteristic bands in the infrared spectrum appeared to be at 7.6 μ with a shoulder at 7.8 μ, in a Nujol mull. (5) Pure hexaphenylcarbodiphosphorane dissolved completely in water. The titration of the colorless solution with 0.10 *N* HCl revealed the presence of a diacidic base. The strength of one of the basic functions was comparable to that of NaOH, indicating the hydrolysis shown in eq A and the neutralization in eq B.

The pK_a for the equilibrium shown in eq C is 5.4 ± 0.1 extrapolated to infinite dilution. The aqueous solutions are moderately stable and eventually undergo irreversible decompositions.

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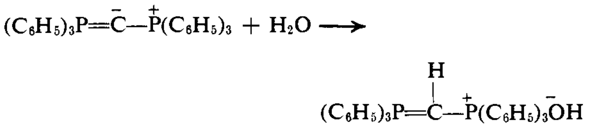
(2) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

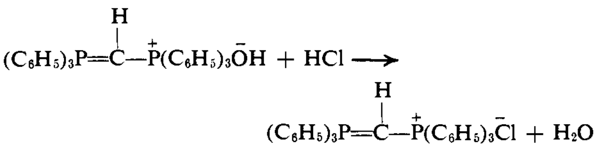
(3) (a) C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *ibid.*, **84**, 4349 (1962); (b) J. S. Driscoll, D. W. Grisley, Jr., J. E. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, **29**, 2427 (1964).

(4) (a) C. N. Matthews, J. S. Driscoll, and G. H. Birum, *Chem. Commun.*, 736 (1966); (b) C. N. Matthews and G. H. Birum, *Tetrahedron Letters*, 5707 (1966).

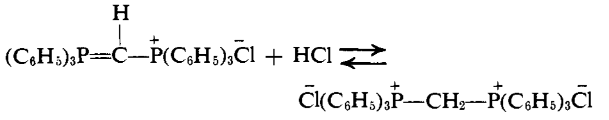
(5) Values of the P^{31} nmr shifts of a number of phosphorus ylides and references to the previous literature will be found in: (a) F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, **22**, 567 (1966); (b) F. Ramirez, D. Rhum, and C. P. Smith, *ibid.*, **21**, 1941 (1965).



$$(C_6H_5)_3P{=}\overset{-}{C}{-}\overset{+}{P}(C_6H_5)_3 + H_2O \longrightarrow (C_6H_5)_3P{=}\overset{\overset{H}{|}}{C}{-}\overset{+}{P}(C_6H_5)_3\overset{-}{O}H \quad (A)$$

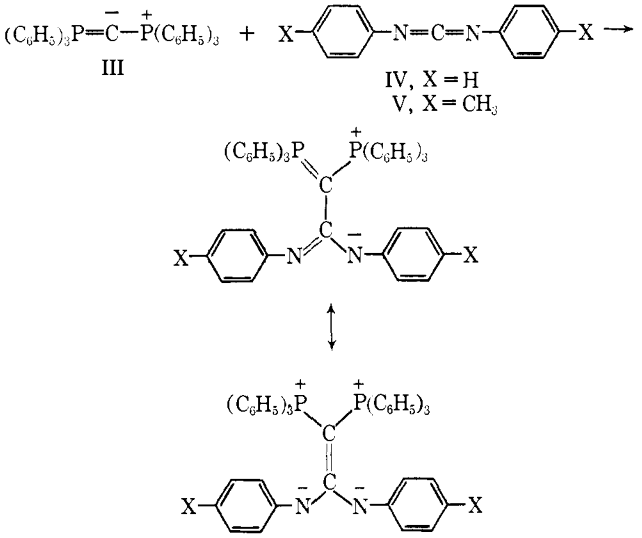


$$(C_6H_5)_3P{=}\overset{\overset{H}{|}}{C}{-}\overset{+}{P}(C_6H_5)_3\overset{-}{O}H + HCl \longrightarrow (C_6H_5)_3P{=}\overset{\overset{H}{|}}{C}{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Cl} + H_2O \quad (B)$$



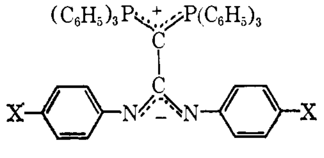
$$(C_6H_5)_3P{=}\overset{\overset{H}{|}}{C}{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Cl} + HCl \rightleftarrows \overset{-}{Cl}(C_6H_5)_3\overset{+}{P}{-}CH_2{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Cl} \quad (C)$$

Reactions of Hexaphenylcarbodiphosphorane with Diarylcarbodiimides. Hexaphenylcarbodiphosphorane reacted with diphenylcarbodiimide at 20° in methylene chloride or in benzene solution. The product of this reaction remained in solution in the methylene chloride, but separated in the form of yellow crystals from the benzene solution. This substance is formulated as a dipolar ion, VI, having in the same molecule a phosphoranium cation and an amidine anion. Another electronic distribution for this new type of phosphorus compound is that of a tetrapolar structure which leads to the convenient nomenclature of ethylene-1,1-bis(triphenylphosphonium)-2,2-bis(phenylamide), VI.



VI, X = H; $\delta P^{31} = -10.2$ ppm
VII, X = CH$_3$; $\delta P^{31} = -8.6$ ppm

Evidently, other resonance structures can be written for the carbodiphosphorane–carbodiimide adduct, a situation that can be summarized in the schematic representation shown in formulas VIa and VIIa.



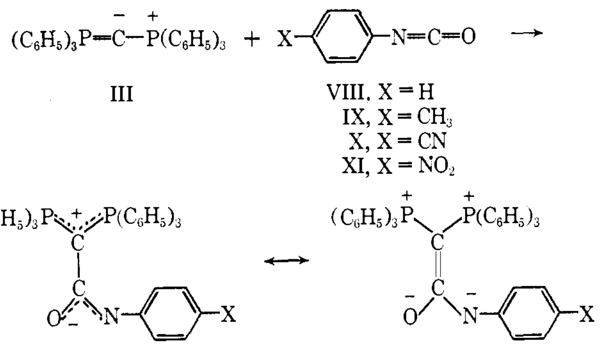
VIa, X = H
VIIa, X = CH$_3$

The carbodiphosphorane–carbodiimide adduct, VI, could be recrystallized from benzene, and in this solvent it gave a molecular weight which corresponded to a monomeric structure. The P^{31} nmr spectrum of VI in methylene chloride solution disclosed that the two phosphorus nuclei were equivalent. The signal appeared at considerably higher magnetic field than the signal of the related methylidebis(triphenylphosphonium) bromide, II, but at a much lower field than the signal of the carbodiphosphorane, III. In other words, the phosphorus nuclei of VI are more shielded than those of II, but less shielded than those of III. The characteristic infrared band of VI was at 6.73 μ.

An entirely analogous compound, VII, was made from hexaphenylcarbodiphosphorane and di-*p*-tolylcarbodiimide. The two methyl groups on the benzene rings gave rise to a H^1 nmr singlet at τ 8.09. Again, the two phosphorus nuclei were equivalent, and were somewhat more shielded than the corresponding phenylcarbodiimide adduct, VI.

Reaction of Hexaphenylcarbodiphosphorane with Aryl Isocyanates. Hexaphenylcarbodiphosphorane reacted rapidly and exothermically with phenyl isocyanate at 20° in methylene chloride solution. The yellow crystalline material was formulated as a resonance hybrid to which dipolar structures and tetrapolar structures, XII, make contributions. The two phosphorus nuclei were equivalent and gave one signal in the P^{31} nmr spectrum. This suggested that there was sufficient single-bond character in the bond joining the carbodiphosphorane and the phenyl isocyanate to permit free rotation and magnetic equivalency of the two phosphorus nuclei at 20°. The shielding of the phosphorus nucleus in XII was very similar to that in the carbodiimide adduct, VI.

Three other analogous carbodiphosphorane–isocyanate adducts, XIII, XIV, and XV, were prepared.

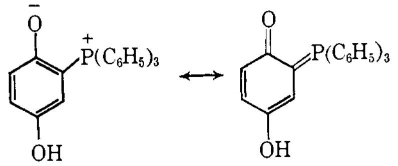


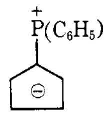
XII, X = H; $\delta P^{31} = -10.5$ ppm
XIII, X = CH$_3$; $\delta P^{31} = -9.2$ ppm
XIV, X = CN; $\delta P^{31} = -13.7$ ppm
XV, X = NO$_2$; $\delta P^{31} = -15.0$ ppm

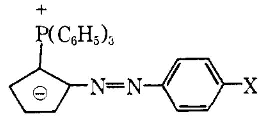
The molecular weight determinations of the carbodiphosphorane–isocyanate adducts, XII–XV, in solvents like dioxane and acetonitrile confirmed the monomeric character of these substances. The infrared spectra in methylene chloride solution had a characteristic band at 6.6 μ, as expected for the carboxamide anion.

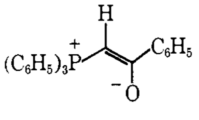
Discussion

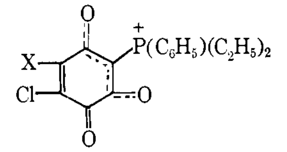
The phosphoranium salt II, hexaphenylcarbodiphosphorane, III, the ethylenebis(phosphonium diamides) VI and VII, and the ethylenebis(phosphonium) oxyamides XII–XV, represent new members of the class of stable phosphorus ylides which have been investigated in this laboratory since 1956. Other examples are the *p*-benzoquinone–triphenylphosphine adduct XVI,[6] triphenylphosphonium cyclopentadienylide XVII,[7] the diazo derivative of the latter, XVIII,[8] β-keto ylides XIX,[5a,9] the quinoneoxyphosphonium betaines XX and XXI,[5b] and the quinonebis(oxyphosphonium betaines) XXII.[5b] A comparison of the P^{31} nmr shifts of these ylides gives a measure of the relative shielding of the phosphorus nucleus in them.

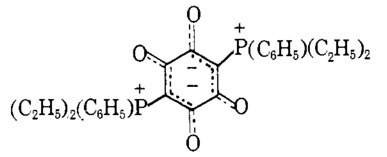

XVI, $\delta P^{31} = -19.7$ ppm


XVII, $\delta P^{31} = -12.9$ ppm


XVIII


XIX, $\delta P^{31} = -16.7$ ppm


XX, X = Cl; $\delta P^{31} = -25.6$ ppm
XXI, X = OH; $\delta P^{31} = -23$ ppm


XXII, $\delta P^{31} = -25.7$ ppm

Nucleophilic additions by hexaphenylcarbodiphosphorane to other electrophiles are being studied in this laboratory. Likewise, experiments directed to an understanding of the pyrolytic behavior of the ethylenebis(phosphoniumdiamides) and oxyamides, VI and VII, and XII–XV, are in progress, and will be reported in subsequent papers.

Experimental Section

The analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The instrumentation was previously given.[10]

Preparation of Starting Materials. Methylenebis(triphenylphosphonium bromide), I, methylidebis(triphenylphosphonium) bromide, II, and hexaphenylcarbodiphosphorane, III, were prepared by the procedures of Ramirez, Desai, Hansen, and McKelvie.[2] In addition to the properties given for these compounds in ref 2, the following ones were obtained: for II, $\delta P^{31} = -20.4$ ppm in CH_2Cl_2, triplet at τ 7.98, $J_{HP} = 5.5$ cps due to the methylide proton; for III, $\delta P^{31} = +3.5$ ppm in CH_2Cl_2.

Reactions of Hexaphenylcarbodiphosphorane, III, with Diphenylcarbodiimide. Preparation of Ethylene-1,1-bis(triphenylphosphonium)-2,2-bis(phenylamide), VI. a. In Benzene Solution. A solution of diphenylcarbodiimide[11] (2.99 g, 15.4 mmoles) in 10 ml of dry benzene was added dropwise over a period of 10 min to a solution of III (8.25 g, 15.4 mmoles) in 110 ml of benzene at 25°. A yellow suspension formed immediately, and then changed into a clear yellow-orange solution within 45 min. The solution was red-orange after 1.5 hr. A yellow suspension formed within 6 hr; this was stirred at 25° for an additional 3 days. An additional 25 ml of benzene was added and the suspension was brought to the boiling point at which time 100 ml of hexane was slowly added. The yellow suspension was allowed to cool to 25° and was filtered to obtain the ethylenebis(phosphonium amide) VI in 92% yield (10.4 g). This substance changed to yellowish tan solid at 178–183°, and melted to a red-brown liquid at 222–225°. Recrystallization from benzene afforded pure VI with the same behavior at the melting point.

Anal. Calcd for $C_{50}H_{40}N_2P_2$: C, 82.2; H, 5.5; N, 3.8; P, 8.5; mol wt, 730. Found: C, 82.3; H, 5.7; N, 4.1; P, 8.2; mol wt, 717 (thermoelectric microdetermination[12] of molecular weight in benzene).

The infrared spectrum in CH_2Cl_2 had the following bands (in μ): *6.73* (*s*), 7.33 (s), 8.18 (m), 8.83 (ms), and 9.05 (ms). In KBr disk, the bands were at (μ): *6.71* (*s*), 7.31 (s), 8.16 (m), 8.73, 8.90 (broad), and 9.05 (ms).

The H^1 nmr spectrum in C_6D_6 had only aromatic protons at τ 2.0–3.40; $\delta P^{31} = -10.2$ ppm, a singlet in CH_2Cl_2 solution.

b. In Methylene Chloride Solution. When equimolar amounts of the carbodiphosphorane and the carbodiimide were mixed at 20°, a clear orange solution was obtained. The reaction was mildly exothermic. The infrared spectrum taken within 5 min showed the complete disappearance of the reagents. Although this procedure is faster than the previous one, the ethylenebis(phosphonium amide) was obtained in lower yield after the recrystallization from benzene–hexane.

Reaction of Di-*p*-tolylcarbodiimide with Hexaphenylcarbodiphosphorane, III. Preparation of Ethylene-1,1-bis(triphenylphosphonium)-2,2-bis(*p*-tolylamide), VII. A solution of di-*p*-tolylcarbodiimide (4.25 g, 18.9 mmoles) in 20 ml of dry benzene was added dropwise over 5 min to a solution of III (10.0 g, 1 mole equiv) in 150 ml of benzene at 25°. Addition of the first drop resulted in the formation of a yellow suspension which became clear within 2.5 hr. Stirring of the red-orange solution was continued for an additional 19 hr. The solution was heated to reflux, was diluted with 300 ml of hexane, and was cooled to 20°. The ethylenebis(phosphonium amide) VII was obtained in 94% yield (13.4 g). The analytical sample was obtained from benzene–hexane and was dried at 80° (0.2 mm) for 4 hr. The yellow crystals changed to a tan solid at 157–161°; this solid melted to a red-brown liquid at 220–230°.

Anal. Calcd for $C_{52}H_{44}N_2P_2$: C, 82.3; H, 5.8; P, 8.2; N, 3.7; mol wt, 758. Found: C, 82.5; H, 5.8; P, 8.0; N, 3.5; mol wt, 750 (thermoelectric method in benzene).

The infrared spectrum in CH_2Cl_2 had bands at (μ): *6.64*, *6.67*, *6.73*, (three strong bands), 7.35 (ms), 8.20 (w), 8.82 (mw), 9.05 (m), and 9.77 (mw); in KBr disk: 6.72 (broad, strong), 7.33 (ms), 8.23 (mw), 8.81 (m), 9.09 (ms), and 9.85 (m).

The H^1 spectrum in CCl_4 had a 12-H^1 multiplet at τ 2.42, an 18-H^1 multiplet at τ 2.80, and an 8-H^1 multiplet at τ 4.04 (aromatic); there was a 6-H^1 singlet at τ 8.09 (CH_3); $\delta P^{31} = -8.6$ ppm, a singlet in CH_2Cl_2 solution.

Reaction of Phenyl Isocyanate with Hexaphenylcarbodiphosphorane, III. Preparation of Ethylene-1,1-bis(triphenylphosphonium)-2-oxy-2-phenylamide, XII. Phenyl isocyanate (0.973 g, 8.17 mmoles) was added all at once to the yellow solution of III (4.38 g, 1 mole equiv) in 25 ml of methylene chloride (dried by distillation from molecular sieves, type 4A) at 25°. The exothermic reaction raised the temperature of the solution to its boiling point. The infrared spectrum of a sample of the deep yellow solution was taken within 5 min and showed that the reaction was complete. Anhydrous ether (100 ml) was added after 15 min, and the light yellow solid was filtered. The ethylenebis(phosphonium) oxyamide XII was obtained in 86% yield (4.57 g, mp 176–177°, with decomposition to a red-brown liquid). The analytical sample was obtained from methylene chloride–benzene and was dried at 40° (0.1 mm) for 15 hr. This substance decomposed without previous changes at 184–186° to a red-brown melt.

Anal. Calcd for $C_{44}H_{35}NOP_2$: C, 80.6; H, 5.3; N, 2.9; P, 9.4; mol wt, 655. Found: C, 80.1; H, 5.7; N, 2.8; P, 9.3; mol wt, 657 (thermoelectric method in dioxane).

The infrared spectrum in CH_2Cl_2 had bands at (μ): 6.57 (s), 6.74 (s), 7.43 (s), 8.22 (mw), 9.07 (ms), 9.81 (m), 9.85 (ms), and 10.1

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[6] F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956).

[7] (a) F. Ramirez and S. Levy, *J. Org. Chem.*, **21**, 488 (1956); (b) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 67 (1957).

[8] (a) F. Ramirez and S. Levy, *J. Org. Chem.*, **21**, 1333 (1956); (b) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 6167 (1957).

[9] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

[10] (a) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *ibid.*, **30**, 2575 (1965); (b) *ibid.*, **31**, 474 (1966); (c) *ibid.*, **31**, 3159 (1966).

[11] S. Hunig, H. Lehmann, and G. Grimmer, *Ann.*, **579**, 77 (1953).

[12] C. Tomlinson, *Mikrochim. Acta*, 457 (1961).

(ms). In a KBr disk, the bands were at (μ): 6.60 (s), 6.78 (m), 7.39 (ms), 8.18 (mw), 8.74 (m), 9.08 (m), 9.85 (mw), and 10.2 (m); $\delta P^{31} = -10.5$ ppm, singlet in CH_2Cl_2.

Reaction of *p*-Tolyl Isocyanate with Hexaphenylcarbodiphosphorane, III. Preparation of Ethylene-1,1-bis(triphenylphosphonium)-2-oxy-2-*p*-tolylamide, XIII. *p*-Tolyl isocyanate (0.992 g, 7.47 mmoles) was added all at once to a stirred solution of III (4.00 g, 1 mole equiv) in 25 ml of dry methylene chloride at 25°. The solution became hot and turned a deeper shade of yellow orange. An infrared spectrum of a sample of the mixture showed complete reaction within 5 min. The solution was allowed to stir at 25° for an additional 16.5 hr, at which time 25 ml of benzene followed by 100 ml of ether were added. The yellow ethylenebis(phosphonium) oxyamide XIII was obtained in 85% yield (4.22 g, mp 160–163°, decomposition to a red-brown melt). Analytical XIII was obtained as yellow crystals from methylene chloride–benzene, mp 167–169° with decomposition after drying at 80° (0.1 mm) for 10 hr.

Anal. Calcd for $C_{45}H_{37}NOP_2$: C, 80.7; H, 5.5; N, 2.1; P, 9.3; mol wt, 669. Found: C, 80.9; H, 5.7; N, 1.9; P, 8.5; mol wt, 697 (thermoelectric method in acetonitrile).

The infrared spectrum in CH_2Cl_2 had bands at (μ): 6.56 (s), 6.65 (s), 7.44 (s), 8.17 (mw), 8.75 (mw), 9.05 (ms), and 9.85 (m). In KBr pellet, the bands were found at (μ): 6.55 (s), 6.67 (ms), 7.45 (s), 8.22 (w), 8.68 (m), 9.06 (m), and 9.93 (m).

The H^1 nmr spectrum in CH_2Cl_2 had 30 aromatic protons at τ 2.2–3.0; four aromatic H^1 at τ 3.44; and a 3-H^1 singlet at τ 7.97 (CH_3); $\delta P^{31} = -9.2$ ppm, a singlet in CH_2Cl_2.

Reaction of *p*-Cyanophenyl Isocyanate with Hexaphenylcarbodiphosphorane, III. Preparation of Ethylene-1,1-bis(triphenylphosphonium)-2-oxy-2-*p*-cyanophenylamide, XIV. A solution of *p*-cyanophenyl isocyanate (1.09 g, 7.58 mmoles) in 10 ml of purified tetrahydrofuran was added over a period of 3 min to a solution of III (4.06 g, 1 mole equiv) in 25 ml of dry methylene chloride at 25°. The reaction was exothermic and gave a clear dark amber solution in 20 min. Dry ether (100 ml) was added, and the resultant light yellow suspension was partially evaporated (20 mm). The ethylenebis(phosphonium) oxyamide XIV was obtained as pale green-yellow crystals from methylene chloride–benzene (mp 196–197° dec, dried at 80° (0.5 mm) for 4 hr).

Anal. Calcd for $C_{45}H_{34}N_2OP_2$: C, 79.4; H, 5.0; N, 4.1; P, 9.1; mol wt, 680. Found: C, 79.5; H, 5.1; N, 4.3; P, 8.9; mol wt, 687 (thermoelectric method in acetonitrile).

The infrared spectrum in CH_2Cl_2 had bands at (μ): 4.52 (w), 6.68 (s), 7.39 (s), 8.11 (mw), 8.83 (w), 9.05 (m), 9.80 (m), and 10.00 (mw). In a KBr pellet, the bands were found at (μ): 4.55 (w), 6.72 (ms), 7.46 (s), 8.10 (mw), 8.74 (m), 9.09 (m), 9.86 (m), and 10.05 (m).

The H^1 nmr spectrum in $CDCl_3$ had 30 aromatic protons at τ 2.2–3.0, and four aromatic protons at τ 3.12; $\delta P^{31} = -13.7$p pm, singlet in CH_2Cl_2.

Reaction of *p*-Nitrophenyl Isocyanate with Hexaphenylcarbodiphosphorane, III. Preparation of Ethylene-1,1-bis(triphenylphosphonium)-2-oxy-2-*p*-nitrophenylamide, XV. *p*-Nitrophenyl isocyanate (1.29 g, 7.87 mmoles) was added all at once to a solution of III (4.12 g, 1 mole equiv) in 25 ml of dry methylene chloride at 25°. The solution evolved heat and turned a clear deep red brown. The infrared spectrum of a sample of the mixture showed that the reaction was over within 3 hr. Benzene (20 ml), ether (100 ml), and hexane (50 ml) were added in succession. The ethylenebis(phosphonium) oxyamide XV was obtained as a yellowish olive green solid in 99% yield (5.45 g, mp 180.182° dec). Pure XV was obtained from methylene chloride–benzene as greenish orange crystals (mp 187–188° dec, dried at 80° (0.1 mm) for 3.5 hr).

Anal. Calcd for $C_{44}H_{34}N_2O_3P_2$: C, 75.4; H, 4.8; N, 4.0; P, 8.8; mol wt, 700. Found: C, 75.3; H, 4.9; N, 3.6; P, 8.3; mol wt, 659 (thermoelectric method in acetonitrile).

The infrared spectrum in CH_2Cl_2 had bands at (μ): 6.64 (m), 6.74 (m), 7.32 (mw), 7.75 (m), 8.20 (w), 8.88 (w), 9.14 (ms), 9.84 (m), and 10.10 (m).

The H^1 nmr spectrum in $CDCl_3$ had aromatic protons at τ 2.2–2.9 and 3.27; $\delta P^{31} = -15.0$ ppm, singlet in CH_2Cl_2.

The Formation of Phosphorus–Oxygen Bonds in the Reactions of Triaminophosphines with *o*-Quinones, Vicinal Triketones, and Oxomalonic Esters. Triaminooxyphosphonium Dipolar Ions and Triaminodioxaphosphoranes. Phosphorus-31 Nuclear Magnetic Resonance Spectra[1]

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Abstract: The phosphorus of tris(dialkylamino)phosphines added to the oxygen of the carbonyl functions of phenanthrenequinone, diphenylpropanetrione, and diethyl oxomalonate. The 1:1 adducts derived from these reactions had quadruply connected or quintuply connected phosphorus, depending on the structure of the triaminophosphine. The adducts made from trisdimethylaminophosphine, $[(CH_3)_2N]_3P$, had the structure of triaminooxyphosphonium dipolar ions in the crystalline state and in solutions. The P^{31} nmr shifts were strongly negative relative to phosphoric acid. All the 1:1 adducts made from the reactions of the five-membered cyclic aminophosphines, 2-N-pyrrolidino-, 2-dimethylamino-, and 2-methoxy-1,3-dimethyl-1,3,2-diazaphospholanes with the polycarbonyl compounds had the structures of triaminodioxaphosphoranes with pentavalent phosphorus. These gave strongly positive P^{31} nmr shifts.

The purpose of this investigation was to compare the behavior of the tris(dialkylamino)phosphines, $(R_2N)_3P$, and of the trialkyl phosphites, $(RO)_3P$, toward *o*-quinones, vicinal triketones, and α-keto esters. We showed that the phosphorus of the phosphites attacked the oxygen of *o*-quinones[3] and of tri-

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[1] A preliminary account of this work has appeared: F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Am. Chem. Soc.*, **87**, 4973 (1965).

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[3] For reviews, see: (a) F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966); (b) F. Ramirez, *Pure. Appl. Chem.*, **9**, 337 (1964).