(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]

Fausto Ramirez,[2] A. V. Patwardhan, H. J. Kugler, and C. P. Smith

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook New York 11790. *Received June 21, 1967*

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.

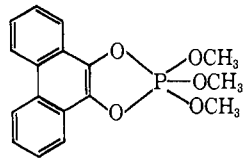
The purpose of this investigation was to compare the behavior of the tris(dialkylamino)phosphines, $(R_2N)_3P$, and of the trialkyl phosphites, $(RO)_3P$, toward *o*-quinones, vicinal triketones, and α-keto esters. We showed that the phosphorus of the phosphites attacked the oxygen of *o*-quinones[3]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

(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).

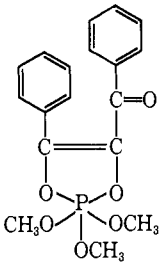
(2) This work was supported by National Science Foundation Grant GP-3341 and by Public Health Service Grant CA-04769-06-08 from the National Cancer Institute.

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

ketones[4] forming stable 2,2-dihydro-2,2,2-trialkoxy-1,3,2-dioxaphospholenes, I and II.



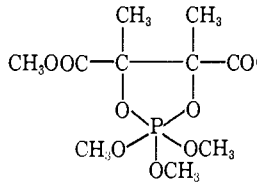
I, δP^{31} = +44.7 ppm *vs.* H_3PO_4



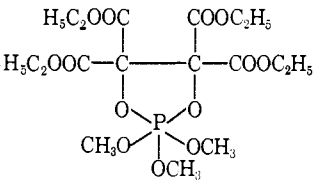
II, δP^{31} = +49.3 ppm

Related spirooxyphosphoranes were made from cyclic phosphite esters.[5] The molecular structure of a phospholene of type I was determined by X-ray analysis.[6]

Information is available on the course of the reactions of trialkyl phosphites with α-keto esters such as methyl pyruvate[7] and diethyl oxomalonate.[3a] Again, the phosphorus added to the carbonyl oxygen but the products were 2:1 adducts with the structures of 2,2-dihydro-2,2,2-trialkoxy-1,3,2-dioxaphospholanes, III and IV.



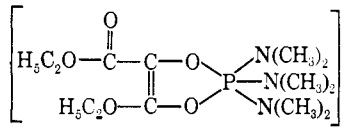
IIIa, *cis* CH_3/CH_3; δP^{31} = +52.2 ppm
b, *trans* CH_3/CH_3; δP^{31} = +50.4 ppm



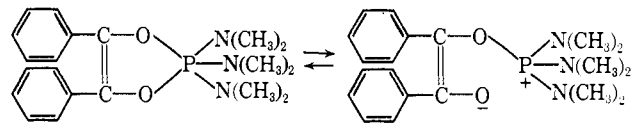
IV, δP^{31} = +50.1 ppm

Attention has been devoted in the recent literature[8,9] to the reactions of tris(dialkylamino)phosphines; however, the available experimental evidence on this subject is rather limited. Burgada,[8] in a paper which appeared while this investigation was in progress,[1] proposed the structure of a 2,2,2-triamino-1,3,2-dioxaphospholene, V, for the product of the reaction of diethyl oxomalonate with tris(dimethylamino)phosphine. It will be shown in the present paper that this formulation is incorrect.

Burgada[8] also assigned the structure of a triaminodioxyphosphorane, VI, to the 1:1 adduct made from benzil and tris(dimethylamino)phosphine. Our investigations of that system showed[10] that the resulting 1:1 adduct can, in fact, be isolated in two crystalline forms, one with pentavalent phosphorus, VI, and the other with tetravalent phosphorus, VII. In solutions, the two forms were in rapid equilibrium with each other. The P^{31} nmr shift associated with the quintuply connected phosphorus of VI was positive, relative to H_3PO_4, while the shift associated with the quadruply connected phosphorus of VII was negative. Consequently, the actual value of the P^{31} shift observed in a given solvent reflected the position of the equilibrium between the two forms, VI and VII, in that solvent.



V, not formed



VI, δP^{31} = +30.2 ppm in 0.8 *M* hexane
δP^{31} = +13.1 ppm in 1.0 *M* CH_2Cl_2 VII

Mark[11] studied the reactions of aliphatic and aromatic aldehydes with tris(dimethylamino)phosphine. He isolated epoxides from some of the aldehydes, and suggested that in all of these reactions the phosphorus of the aminophosphines attacked the carbonyl carbon of the aldehydes. While there is no doubt that epoxides[12] can be obtained from certain aldehydes in this type of reaction, the mechanism of their formation is not clear.[13]

Mark[14] claimed the preparation of tris(dimethylamino)difluoromethylenephosphorane, $[(CH_3)_2N]_3P{=}CF_2$, from the reaction of trifluoroacetophenone with tris(dimethylamino)phosphine. We showed subsequently[15] that the major product of this reaction was not the ylide but difluorotris(dimethylamino)phosphorane, $[(CH_3)_2N]_3PF_2$. We proposed a mechanism involving initial attack by the phosphorus of the aminophosphine on the carbonyl oxygen of the perfluoro ketone.

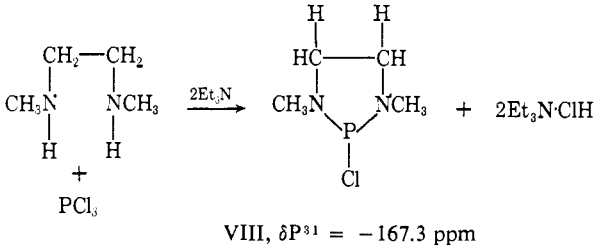
A comparison of the reactions of α,β-unsaturated ketones with tris(dialkylamino)phosphines, tertiary phosphines, and trialkyl phosphites has been published.[16] It was shown that in all cases the phosphorus of the trivalent phosphorus compound performed a 1,4 addition to the carbon of the unsaturated ketone. The structures of the products isolated from these reactions varied a great deal depending on the nature of the ketone.

Results

Preparation of Five-Membered Cyclic Triaminophosphines and Diaminoalkoxyphosphines. 2-Chloro-1,3-dimethyl-1,3,2-diazaphospholane,[17] VIII, was pre-

(4) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **30**, 2575 (1965).
(5) F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, in press.
(6) (a) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965); (b) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967); (c) R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).
(7) F. Ramirez, N. B. Desai, and N. Ramanathan, *Tetrahedron, Letters*, 232 (1963).
(8) (a) R. Burgada, *Bull. Soc. Chim. France*, 347 (1967); (b) R. Burgada, *Compt. Rend.*, **258**, 4789 (1964); (c) D. Houalla, M. Sanchez, and R. Wolf, *Bull. Soc. Chim. France*, 2368 (1965).
(9) (a) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapters 4 and 5; (b) R. F. Hudson, *Chimia*, **16**, 173 (1962); (c) R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967). This paper contains an extensive discussion of the concept of hard and soft bases and acids in nucleophilic reactions in general.
(10) A preliminary communication has appeared: F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, 3053 (1966).
(11) V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963).
(12) M. S. Newman and S. Blum, *ibid.*, **86**, 5598 (1964).
(13) This problem will be discussed in a subsequent paper: F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Org. Chem.*, in press.
(14) V. Mark, *Tetrahedron Letters*, 3139 (1964).
(15) F. Ramirez, C. P. Smith, and S. Meyerson, *ibid.*, 3651 (1966).
(16) (a) F. Ramirez, O. P. Madan, and C. P. Smith, *J. Am. Chem. Soc.*, **86**, 5339 (1964); (b) F. Ramirez, O. P. Madan, and S. R. Heller, *ibid.*, **87**, 731 (1965); (c) F. Ramirez, O. P. Madan, and C. P. Smith, *J. Org. Chem.*, **30**, 2284 (1965); (d) F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, **22**, 567 (1966).

pared from phosphorus trichloride and N,N′-dimethylethylenediamine in dry ether at −70°.

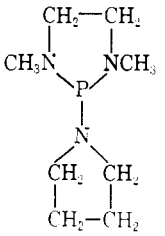


VIII, δP^{31} = −167.3 ppm

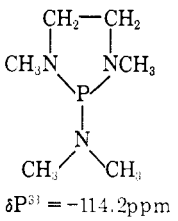
2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, IX, was obtained in 85% yield when 2 mole equiv of pyrrolidine was added to an ether solution of the chlorophosphine VIII at −70°.

2-(N-Dimethylamino)-1,3-dimethyl-1,3,2-diazaphospholane, X, was prepared by addition of an ether solution of the chlorophosphine VIII to 2 mole equiv of dimethylamine at −70°.

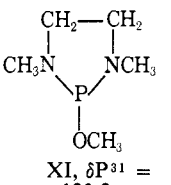
2-Methoxy-1,3-dimethyl-1,3,2-diazaphospholane, XI, was prepared by addition of an equimolar mixture of methanol and triethylamine to an ether solution of the chlorophosphine VIII at −70°.



IX, δP^{31} = −104.8 ppm



X, δP^{31} = −114.2 ppm



XI, δP^{31} = −123.2 ppm

The five-membered cyclic aminophosphines VIII–XI should be handled with extreme care. Complete toxicity data are not available; exposure to vapors may result in acute nausea and vomiting.

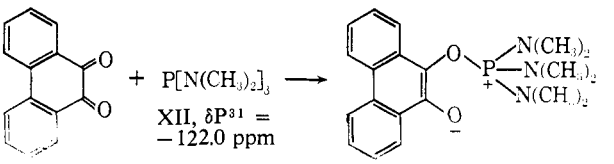
Reactions of Phenanthrenequinone and Diphenylpropanetrione with Tris(dialkylamino)phosphines. Phenanthrenequinone reacted with tris(dimethylamino)-phosphine in methylene chloride at 0°. The crystalline product of this reaction was formulated as the triaminooxyphosphonium dipolar ion XIII from the following evidence.

(1) The P^{31} nmr shift was strongly negative, in contrast to the shift of the phenanthrenequinone–trimethyl phosphite adduct I which is known to have quintuply connected phosphorus,[3,5,6]

(2) The phosphine adduct XIII had strong bands at 6.37 and 6.80 μ (1570 and 1471 cm^{-1}) which could be due to the enolate–carbonyl function. The phosphite adduct I had a weak band at 6.08 μ (1645 cm^{-1}) which has been associated with the C=C function in the phospholene[6] I. Both types of adducts, XIII and I, had absorptions at 6.63 μ (1510 cm^{-1}).

(3) The six methyl groups attached to the nitrogen gave one doublet at τ 7.42, J_{HP} = 10.2 cps; *i.e.*, the three dimethylamino groups were magnetically equivalent.

The reaction of phenanthrenequinone with the cyclic aminophosphine IX, made from pyrrolidine, was violent; when the reagents were mixed at −70° in methylene chloride solution, a stable, crystalline 1:1 adduct was isolated. This substance was formulated as the spirotriaminodioxyphosphorane XIV since it gave a strongly positive P^{31} nmr shift. The infrared spectrum of the phosphorane XIV had a weak band at 6.08 μ assumed to be associated with the C=C of the dioxaphospholene ring.

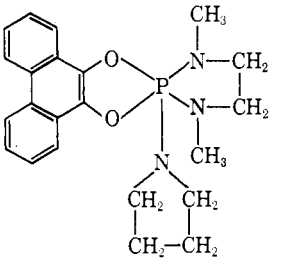


XII, δP^{31} = −122.0 ppm

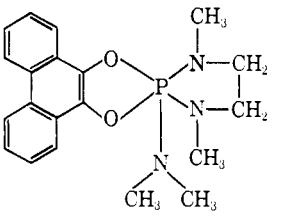
XIII, δP^{31} = −38.5 ppm

An entirely analogous spirotriaminodioxyphosphorane, XV, was prepared from the reaction of phenanthrenequinone with the cyclic aminophosphine X derived from dimethylamine.

The aminophosphine IX was significantly more reactive than X toward phenanthrenequinone.



XIV, δP^{31} = +35.1 ppm

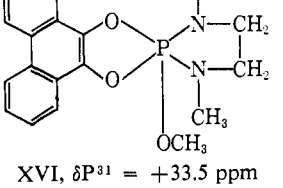


XV, δP^{31} = +29.8 ppm

The infrared spectrum of methylene chloride solutions of the dipolar ion XIII had a very weak band at 6.08 μ. It is possible that, in solution, the dipolar ion XIII might exist in equilibrium with a small amount of a phosphorane structure analogous to XIV, in which case the very weak band at 6.08 μ might be associated with the C=C function. There was no proof of this, but it should be emphasized that an equilibrium of this type has been observed in other adducts derived from carbonyl compounds and tris(dimethylamino)phosphine.[18] This type of equilibrium should be established rapidly relative to the time scale of nmr phenomena; therefore, the value of the P^{31} nmr shift would correspond to the weighed average of the values associated with the structures having quadruply and quintuply connected phosphorus.

It is also conceivable that the phosphorane structure XIV might be in equilibrium with very small amounts of the corresponding open dipolar structure analogous to XIII; however, there is no proof of this.

The reaction of phenanthrenequinone with the cyclic diaminoalkoxyphosphine XI gave a spirodiaminotrioxyphosphorane, XVI.



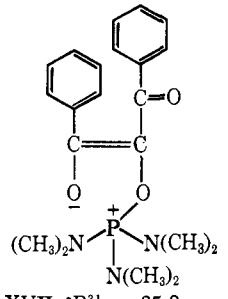
XVI, δP^{31} = +33.5 ppm

(17) A preliminary report of the cyclic chlorophosphine appeared while this investigation was in progress: K. Utvary, V. Gutman, and C. Kemanater, *Inorg. Nucl. Chem. Letters*, 1, 75 (1965).

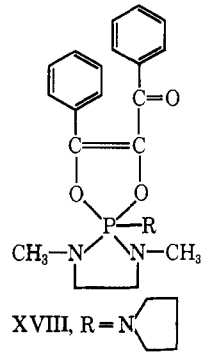
(18) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron*, in press.

The reaction of diphenylpropanetrione with tris(dimethylamino)phosphine gave an open dipolar adduct, XVII. This adduct was similar to, although somewhat more stable than, the adduct XIII made from phenanthrenequinone. The P^{31} nmr shift was strongly negative. The three dimethylamino groups were magnetically equivalent and gave a doublet at τ 7.08, J_{HP} = 10.0 cps. The strong infrared band at 6.76 μ (1479 cm^{-1}) found in methylene chloride solutions of XVII is attributed to the enolate–carbonyl function; formula XVII is one of two equivalent resonance structures, and the two carbonyl groups are equivalent. The methylene chloride solution of XVII had also a very weak band at 6.45 μ (1550 cm^{-1}) which might be due to small amounts of a phosphorane analogous to the adduct II, made from diphenylpropanetrione and trimethyl phosphite. Adduct II had strong absorption[4] at 6.45 μ.

The products of the reactions of diphenylpropanetrione with the cyclic aminophosphines IX and X were formulated as the corresponding triaminodioxyphosphoranes XVIII and XIX, respectively, on the basis of spectral data. The triketone was somewhat less reactive than the *o*-quinone toward the cyclic aminophosphines IX and X.



XVII, δP^{31} = −35.9ppm



XVIII, R = N

δP^{31} = +37.5ppm

XIX, R = $N(CH_3)_2$

δP^{31} = +31.9ppm

The P^{31} nmr spectrum of the phosphorane XIX, derived from the triketone and the aminophospine X, was examined in several solvents. The results were: +31.9 ppm in methylene chloride, +33.8 ppm in benzene, +33.6 ppm in perfluorobenzene, and +33.1 in nitrobenzene. These changes were relatively small and suggest that the phosphorane XIX is not in equilibrium with significant amounts of the corresponding open dipolar structure.[18]

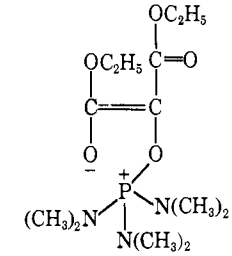
In solutions, the triketone phosphorane XIX appeared to be less stable than the corresponding quinone phosphorane XV. No such difference in the stability for the pair of phosphoranes, XVIII and XIV, could be observed. The triketone dipolar ion XVII was significantly more stable in solutions than the quinone dipolar ion XIII.

Reaction of Diethyl Oxomalonate with Tris(dimethylamino)phosphine. The reaction of diethyl oxomalonate with tris(dimethylamino)phosphine was investigated in the absence of solvents and in a variety of solvents using various mole ratios of the reactants at various temperatures. When 1 mole of the malonate was added to an excess of the aminophosphine at 0° in the absence of solvent, an exothermic reaction was observed, and a nearly colorless crystalline material was produced. This material was formulated as the open dipolar ion XX since it gave a strongly negative P^{31} nmr shift. The values in various solvents were: −38.8 ppm in benzene, −38.2 ppm in methylene chloride, and −38.8 ppm in tetrahydrofuran. The infrared spectrum in methylene chloride had a strong absorption at 6.30 μ attributed to the enolate ester carbonyl. The three dimethylamino groups were magnetically equivalent and gave a doublet at τ 7.17, J_{HP} = 9.7 cps.

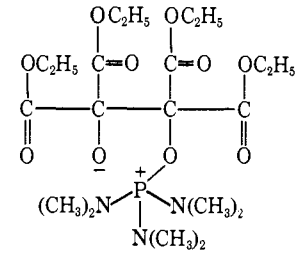
When the malonate was added to an excess of the aminophosphine in hexane, the 1:1 adduct, XX, separated out of the solution. When the reaction was carried out in benzene, and in methylene chloride, the adducts remained in solution. Analyses of these solutions by infrared and by P^{31} nmr revealed the formation of small amounts of what is assumed to be the 2:1 adduct, XXI, in addition to much larger amounts of the 1:1 adduct, XX. The 2:1 adduct, XXI, could not be isolated in pure form and fully characterized. Its structure is postulated on the following evidence. (1) A P^{31} nmr signal at −22.1 ppm was attributed to the 2:1 adduct, XXI; however, this signal was close to that of hexamethylphosphoroamidate, −23.3 ppm, which was always formed as a by-product in this reaction. (2) A band at 5.70 μ was attributed to the normal carbethoxy groups present in XXI. (3) A doublet at τ 7.32, J_{HP} = 10.2 cps, could be due to the three dimethylamino groups of XXI. This doublet was very close to the doublet τ 7.36, J_{HP} = 9.3 cps, due to hexamethylphosphoroamidate.

The addition of tris(dimethylamino)phosphine to an equivalent amount of diethyl oxomalonate in tetrahydrofuran at 20° as described by Burgada[8] gave a complex mixture containing at least five different phosphorus nuclei: (1) δP^{31} = −38.8 ppm due to the 1:1 adduct, XX; (2) δP^{31} = −22.1 ppm tentatively attributed to the 2:1 adduct, XXI; (3) δP^{31} = −23.3 ppm due to hexamethylphosphoroamideate; (4) δP^{31} = −20.2 ppm, which is relatively weak and is of unknown origin; and (5) δP^{31} = −121.9 ppm due to tris(dimethylamino)phosphine, XII. The infrared spectrum confirmed the formation of relatively large amounts of the 2:1 adduct, in addition to the 1:1 adduct.

The formation of an open dipolar adduct, XXI, from the reaction of the oxomalonate with tris(dimethylamino)phosphine stands in contrast to the formation of cyclic 2:1 adducts, III and IV, from the reactions of α-keto esters with trialkyl phosphites.



XX, δP^{31} = −38.8 ppm



XXI, probable δP^{31} = −22 ppm (not fully characterized)

Discussion

This investigation showed that the phosphorus of tris(dialkylamino)phosphines added to the carbonyl oxygen of vicinal polycarbonyl compounds. In this respect, the aminophosphines resembled the trialkyl

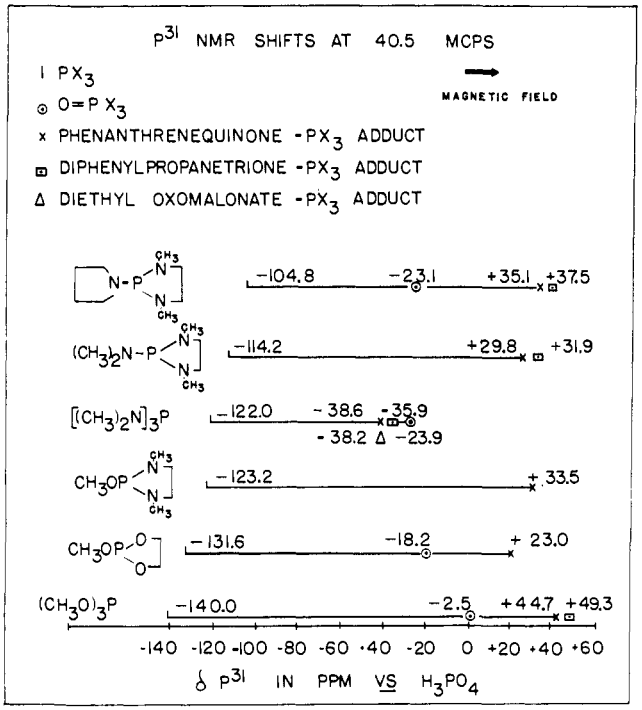
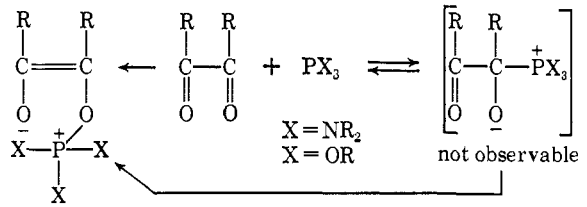


Figure 1. Variations in P^{31} nmr shifts of noncyclic and of five-membered cyclic triaminophosphines, trialkyl phosphites, and diaminophosphoroamidites, upon conversion into oxides, X_3PO, and into *1:1 adducts* with polycarbonyl compounds.

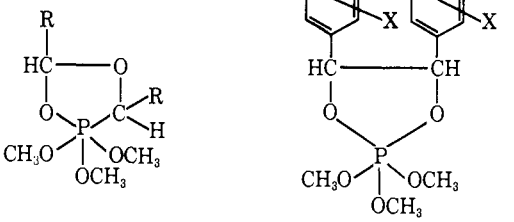
phosphites, but the former were much more reactive than the latter. If the phosphorus of triaminophosphines is a "softer base" than the phosphorus of trialkyl phosphites, and if the oxygen of a carbonyl function is a "softer acid" than the carbon of the carbonyl function, then the site of attack of these two types of trivalent phosphorus compounds and their relative reactivity conformed to the concepts of hard and soft bases discussed by Pearson[9c] and by Hudson.[9a,b]

Our experiments do not rule out the possibility that in these reactions the initial step is actually an addition of phosphorus to carbonyl carbon. This attack could be reversible and would then be followed by addition of the phosphorus to carbonyl oxygen. Alternatively, the 1:1 adduct with P–C–O bonds could rearrange to the adduct with P–O–C bonds through an intermediate or transitions state involving a three-membered ring and five-coordinated phosphorus.



So far, no evidence has been uncovered favoring the initial attack by phosphorus on carbon *in vicinal polycarbonyl compounds*. On the other hand, initial attack on carbon has been observed in the reactions of trialkyl phosphites with unsubstituted aliphatic monoaldehydes,[19] where the products were 2,2-dihydro-2,2,2-trialkoxy-1,4,2-dioxaphospholanes, XXII. The reactions of trialkyl phosphites with aromatic aldehydes having electron-withdrawing substituents led to 2,2-dihydro-2,2,2-trialkoxy-1,3,2-dioxaphospholanes, XXIII; *i.e.*, the attack was on carbonyl oxygen.

It seems quite possible that in the particular case of negatively substituted benzaldehydes the transient intermediate with P–C–O bonds may be involved, but there is no experimental proof on this question.[20]



XXII, δP^{31} = +34 ppm XXIII, X = electron withdrawing, δP^{31} = +48 to +52 ppm

A second finding of the present study was the demonstration that tris(dialkylamino)phosphines had less tendency to form adducts with pentavalent phosphorus than the trialkyl phosphites. This may be due to the lower electronegativity[21] of nitrogen *vs.* oxygen (3.0 *vs.* 3.5).

Finally, this work showed that a given vicinal polycarbonyl compound displayed a greater tendency to form adducts having pentavalent phosphorus with five-membered cyclic tris(dialkylamino)phosphines than with related *acyclic* aminophosphines. This effect may be associated with steric factors in trigonal bipyramids involving pentavalent phosphorus.[6]

The P^{31} nmr shifts of a number of 1:1 adduct derived from the reactions of trialkyl phosphites and of tris(dialkylamino)phosphines with vicinal polycarbonyl compounds are summarized in Figure 1.

Experimental Section

The analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. All P^{31} nmr shifts are given in parts per million from 85% H_3PO_4 as zero; they were determined at 40.5 Mcps. All H^1 nmr are given in parts per million *vs.* TMS as 10 (τ values); they were determined at 60 Mcps.

Preparation of 2-Chloro-1,3-dimethyl-1,3,2-diazaphospholane, VIII. A solution of 83 g of phosphorus trichloride in 600 ml of dry ether at −70° was treated with a solution of 53 g of symmetric dimethylethylenediamine in 800 ml of ether over a period of 15 min. Two mole equiv of triethylamine was added at once and the reaction mixture was allowed to warm to room temperature. The amine hydrochloride was filtered off after 1.5 hr and was washed with 500 ml of dry ether. Evaporation left a residue which was distilled at 70° (0.2 mm) and afforded the chlorophosphine VIII in 52% yield.

Anal. Calcd for $C_4H_{10}N_2PCl$: C, 31.3; H, 6.6; Cl, 23.2. Found: C, 30.9; H, 6.7; Cl, 23.3.

The H^1 nmr of the pure liquid had the following signals: a doublet at τ 7.29 with J_{HP} = 14.9 cps (6 H, $-NCH_3-$), and a multiplet at τ 6.75 [δP^{31} = −167.3 ppm (neat)].

Preparation of 2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, IX. The preparation of chlorophosphine VIII was carried out as described using 1.010 moles of PCl_3. The ether solution of the crude chlorophosphine VIII was cooled to −70° and was treated with 145 g (2.020 moles) of pyrrolidine in 600 ml of dry ether over a period of 5 min. The reaction mixture was allowed to warm to room temperature and kept there for 1 hr, and the amine

(19) F. Ramirez, A. V. Patwardhan, and S. R. Heller, *J. Am. Chem. Soc.*, **86**, 514 (1964).

(20) (a) F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967); (b) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **32**, 2194 (1967).

(21) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948, p 58.

hydrochloride that precipitated was filtered off. The filtrate was distilled at 55° (0.2 mm) affording 100 g of 2-N-pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, IX, in 55% yield, $n^{20}D$ 1.5065.

Anal. Calcd for $C_8H_{16}N_3P$: C, 51.2; H, 9.6; P, 16.7; N, 22.3. Found: C, 51.1; H, 9.9; P, 16.6; N, 21.6.

The H^1 nmr of the pure liquid had the following signals: a multiplet at τ 6.94 (8 H, due to two types of NCH_2– groups), a doublet at τ 7.46 with J_{HP} = 12.6 cps (6 H, NCH_3), and a multiplet at τ 8.34 (4 H, CCH_2–) [δP^{31} = −104.8 ppm (neat)].

The infrared spectrum had bands at (μ): 6.8–7.0 (m), 8.25 (m), 8.7 (ms), 9.72 (s), and 10.75 (ms).

When the pure chlorophosphine VIII was used as starting material instead of the crude chlorophosphine, the yield of the pyrrolidinophosphine IX was 85%.

Preparation of 2-(N-Dimethylamino)-1,3-dimethyl-1,3,2-diazaphospholane, X. The chlorophosphine VIII was prepared as described using 0.33 mole of PCl_3. The ether solution (600 ml) of crude VIII was added to an ether solution (600 ml) containing 30 g (0.67 mole) of dimethylamine at −70° over a period of 15 min. The reaction mixture was allowed to warm to room temperature, the precipitated amine hydrochloride was filtered off, and the ether was evaporated at 20° (20 mm). The residue was distilled at 36° (0.5 mm) and afforded 22 g (42%) of X.

Anal. Calcd for $C_6H_{16}N_3P$: C, 44.7; H, 9.93; N, 26.0; P, 19.2. Found: C, 44.4; H, 9.9; N, 25.8; P, 19.2.

The H^1 nmr spectrum of the pure liquid had the following signals: a multiplet at τ 6.90 (4 H, NCH_2–), a doublet at τ 7.45 with J_{HP} = 8.7 cps (6 H, –NCH_3–), and a doublet at τ 7.50 with J_{HP} = 10.8 cps [6 H, –$N(CH_3)_2$] [δP^{31} = −114.2 ppm (neat)].

The infrared spectrum in CH_2Cl_2 had bands at (μ): 6.85 (m), 6.94 (m), 8.40 (ms), 8.72 (s), 9.75 (m), 10.5 (s), and 10.82 (s).

Preparation of 2-Methoxy-1,3-dimethyl-1,3,2-diazaphospholane, XI. The chlorophosphine VIII was prepared from 0.33 mole of PCl_3. The ether solution of the crude VIII, cooled to −70°, was treated with a mixture of 10.5 g (0.33 mole) of methanol and 33 g (0.33 mole) of triethylamine over a period of 15 min. The reaction mixture was warmed to room temperature over a period of 1.5 hr, the amine hydrochloride was filtered off, and the ether was evaporated at 20° (20 mm). The residue was distilled at 56° (20 mm) and afforded XI in 58% yield, $n^{20}D$ 1.4721.

Anal. Calcd for $C_5H_{13}N_2OP$: C, 40.5; H, 8.8; N, 18.9; P, 20.9. Found: C, 40.3; H, 8.9; N, 19.1; P, 20.7.

The H^1 nmr had the following signals: a doublet at τ 6.88 with J_{HP} = 8.0 cps (3 H, CH_3O), a doublet at τ 7.42 with J_{HP} = 11.5 cps (6 H, –NCH_3–), and a multiplet at τ 6.86 (4 H, NCH_2–) (δP^{31} = −123.2 ppm).

The infrared spectrum in CH_2Cl_2 had bands at (μ): 8.69 (ms), 9.96 (s), and 10.71 (ms).

Reaction of Tris(dimethylamino)phosphine with Phenanthrenequinone. The aminophosphine XII (1.63 g) was added dropwise over a 20-min period to a mixture of phenanthrenequinone (2.08 g, 1 mole equiv) and CH_2Cl_2 (70 ml) at 0° with stirring under N_2. The color of the mixture changed from orange to yellow. After 6 hr at 20°, the solvent was removed first at 20 mm and then at 1 mm. The crude yellow adduct, XIII, had mp 97–103°. One crystallization from benzene–hexane gave the analytical sample of XIII, mp 100–101°, in 85% yield.

Anal. Calcd for $C_{20}H_{26}O_2N_3P$: C, 64.7; H, 7.0; N, 11.3; P, 8.4; mol wt, 371. Found: C, 66.4; H, 7.3; N, 9.0; P, 7.6. mol wt, 346 (thermoelectric method in benzene).

The P^{31} nmr spectrum of a fresh solution in methylene chloride had a signal at +38.5 ppm. The infrared spectrum of the same solution had the following bands (μ): 6.22 (w), *6.33* (*s*), 6.66 (ms), *6.80* (*s*), 7.32 (w), 7.67 (m), 8.40 (m), 9.50 (m), 9.90 (s), and 11.7 (vs).

The H^1 nmr of a fresh solution in $CDCl_3$ had a doublet at τ 7.42, J_{HP} = 10.2 cps.

Methylene chloride solutions of adduct XIII underwent decompositions after several days at 20°. One of the products of the decomposition was hexamethylphosphoroamidate, δP^{31} = −24.6 ppm.

Reaction of 2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, IX, with Phenanthrenequinone. A solution containing 3.9 g (0.018 mole) of phenanthrenequinone in 40 ml of methylene chloride at −70° was treated with a solution of 3.5 g (0.018 mole) of phospholane IX in 30 ml of methylene chloride over a period of 30 sec. The mixture was allowed to warm to 20° and kept there for 1.5 hr. Concentration and dilution with pentane led to crystallization at −15°, giving 6.7 g of the adduct XIV, mp 139–141° (90% yield).

Anal. Calcd for $C_{22}H_{26}N_3O_2P$: C, 66.9; H, 6.6; P, 7.8; N, 13.0. Found: C, 66.8; H, 6.8; P, 7.7; N, 14.0.

The H^1 nmr in $CDCl_3$ had the following signals: multiplet centered at τ 2.0 (8 H, aromatic), two multiplets at τ 7.00 and τ 7.10 (8 H, two kinds of NCH_2–), a doublet at τ 7.25 with J_{HP} = 9.7 cps (6 H, –NCH_3–), and a broad signal at τ 8.44 (4 H, CCH_2CH_2C) [δP^{31} = +35.1 ppm (CH_2Cl_2)].

The infrared spectrum in methylene chloride had bands at (μ): 6.05 (m), 6.90 (m), 7.25 (s), 9.40 (ms), 9.50 (ms), and 10.43 (ms).

Reaction of 2-(N-Dimethylamino)-1,3-dimethyl-1,3,2-diazaphospholane, X, with Phenanthrenequinone. A solution of 5.6 g (0.027 mole) of phenanthrenequinone in 50 ml of methylene chloride cooled to −70° was treated at once with a solution of 4.33 g (0.027 mole) of phospholane X in 30 ml of methylene chloride. The solution was warmed to room temperature and the solvent was evaporated after 45 min at 20° (20 mm). The residue crystallized on standing at −20°. Recrystallization from methylene chloride–pentane afforded 8.5 g (85%) of the crystalline adduct XV, mp 121–123°.

Anal. Calcd for $C_{20}H_{24}N_3O_2P$: C, 65.0; H, 6.5; N, 11.4; P, 8.4. Found: C, 64.8; H, 6.3; N, 11.7; P, 8.4.

The H^1 nmr spectrum in $CDCl_3$ had the following signals: a multiplet at τ 2.0 (8 H, aromatic), a multiplet at τ 7.15 (4 H, NCH_2–), a doublet at τ 7.28 with J_{HP} = 9.7 cps (6 H, $N(CH_3)_2$), and a doublet at τ 7.35 with J_{HP} = 10.5 cps (6 H, $(NCH_3$–) [δP^{31} = +29.8 ppm (CH_2Cl_2)].

The infrared spectrum in CCl_4 had bands at (μ): 6.07 (m), 6.90 (m), 7.28 (m), 9.45 (ms), 9.51 (ms), 9.7 (m), 10.08 (m), and 10.45 (ms).

Reaction of 2-Methoxy-1,3-dimethyl-1,3,2-diazaphospholane, XI, with Phenanthrenequinone. A solution of phenanthrenequinone, 5.6 g (0.028 mole), in methylene chloride at −70° was treated with a solution of 4.1 g (0.028 mole) of phospholane XI in 30 ml of methylene chloride. The reaction mixture was allowed to warm to room temperature and evaporated. The residue was crystallized at 0°. Recrystallization from pentane–methylene chloride afforded 8.9 g (92%) of adduct XVI, mp 89–91°.

Anal. Calcd for $C_{15}H_{21}N_2O_3P$: C, 64.0; H, 5.9; N, 7.8; P, 8.8. Found: C, 63.9; H, 5.9; N, 7.72; P, 9.1.

The H^1 nmr had the following signals: multiplet at τ 2.0 (8 H, aromatic), a doublet at τ 6.62 with J_{HP} = 14.5 cps (3 H, CH_3OP), a broad absorption at τ 7.1 (4 H, NCH_2CH_2N), and a doublet at τ 7.22 with J_{HP} = 9.5 cps (6 H, NCH_3) [δP^{31} = +33.5 ppm (CH_2Cl_2)].

Reaction of Tris(dimethylamino)phosphine with Diphenylpropanetrione. The aminophosphine XII (1.63 g) was added over a 5-min period to a solution of diphenylpropanetrione (2.38 g, 1 mole equiv) in methylene chloride (5 ml) at 5° with stirring under N_2. The mixture was kept 15 min at 20° and the solution was evaporated first at 20 mm and then at 1 mm. The residue was triturated with 5 ml of cold benzene and the insoluble adduct XVII was filtered. The crude adduct (3.6 g, 90%), mp 117–121°, was dissolved in 20 ml of warm benzene and the solution was kept several hours at 20° to obtain crystallization. The analytical sample of XVII was obtained as orange prisms, mp 119–120°.

Anal. Calcd for $C_{21}H_{25}O_3N_3P$: C, 62.8; H, 7.0; N, 10.5; P, 7.7. Found: C, 62.9; H, 7.2; N, 10.3; P, 7.7.

The P^{31} nmr spectrum of a fresh methylene chloride solution gave a signal at −35.9 ppm. The infrared spectrum of this fresh solution had bands at (μ): 6.30 (w), 6.45 (w), *6.76* (*s*), 7.20 (m), 7.65 (w), 8.40 (m), 8.80 (w), 9.65 (m), 9.95 (s), and 11.20 (m). The H^1 nmr of this fresh solution had ten aromatic protons at τ 2.5 and an 18 H^1 doublet at τ 7.08, J_{HP} = 10.0 cps.

The spectral data of solutions of adduct XVII in methylene chloride taken after 24 hr at 20° showed signs of decomposition.

When a 2 *M* solution of the aminophosphine XII in methylene chloride was added to a 2 *M* solution of the triketone in the same solvent at 0° over a 10-min period, a clear yellow solution was obtained. The P^{31} nmr of this solution after 30 min at 20° showed the presence of two nuclei in the proportions 4:1. The major product was the adduct XVII, δP^{31} = −35.9 ppm. The minor product had a signal at −9.2 ppm. The origin of the latter signal was not investigated further.

Crystals of adduct XVII separated from the benzene solution which was obtained by the addition of an 1.5 *M* solution of the aminophosphine XII to a 1.5 *M* solution of the triketone in this solvent at 5°. The crystals appeared within 30 min.

Reaction of 2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, IX, with Diphenylpropanetrione. A solution containing 4.38 g

(0.017 mole) of 1,3-diphenylpropanetrione in methylene chloride, cooled to −70°, was treated with a solution of 3.49 g (0.017 mole) of phospholane IX in 30 ml of methylene chloride. The reaction mixture was allowed to warm to 20°, kept there for 5 hr, and evaporated. It was not possible to find a suitable solvent or temperature to crystallize or distil the residue which was a yellow-orange gum, XVIII.

The H^1 nmr in $CDCl_3$ had the following signals: two multiplets at τ 2.10 and 2.70 (5 H each, aromatic), a complex absorption at τ 6.9 (8 H, four NCH_2– groups), a doublet at τ 7.41 with J_{HP} = 10.0 cps (6 H, –NCH_3–), and a broad signal at τ 8.28 (4 H, CCH_2-CH_2C) [δP^{31} = +37.5 ppm (CH_2Cl_2)].

Reaction of 2-(N-Dimethyl)-1,3-dimethyl-1,3,2-diazaphospholane, X, with Diphenylpropanetrione. A solution containing 3.1 g (0.013 mole) of 1,3-diphenylpropanetrione in 10 ml of methylene chloride at −70° was treated with a solution of 2.1 g (0.013 mole) of phospholane X in 6 ml of methylene chloride over a period of 3 hr. The residue was a thick yellow oil, which resisted all attempts at crystallization and which decomposed on distillation.

The H^1 nmr spectrum in $CDCl_3$ had the following signals: a multiplet at τ 2.10 (5 H, aromatic), a multiplet at τ 2.71 (5 H, aromatic), a multiplet (an apparent doublet) at τ 7.06 (4 H, NCH_2–), a doublet at τ 7.31 with J_{HP} = 11.0 cps [6 H, –$N(CH_3)_2$], and a doublet at τ 7.45 with J_{HP} = 10.0 cps (6 H, –NCH_3–).

Reaction of Tris(dimethylamino)phosphine with Diethyl Oxomalonate in the Absence of Solvent. Diethyl oxomalonate (5.44 g, 31.3 mmoles) was added dropwise over a 30-min period to the aminophosphine XII (5.61 g, 34.4 mmoles) at 0° under N_2 with stirring. An exothermic reaction was observed, resulting in the formation of colorless crystals. The mixture was kept several days at 20°, and was then treated with a small amount of cold hexane and filtered. These crystals (2.0 g, 20%) had mp 93–97°. A fresh solution of these crystals in $CDCl_3$ gave a P^{31} nmr signal at −38.8 ppm. This solution gave the following H^1 nmr signals: a 4 H^1 quartet at τ 5.85, J_{HH} = 7.0 cps, a 6 H^1 triplet at τ 8.73, J_{HH} = 7 cps, and an 18 H^1 doublet at τ 7.18, J_{HP} = 9.6 cps.

The crude crystalline adduct XX was dissolved in 5 ml of benzene, and the solution was mixed with 5 ml of hexane and was kept 2 days at 20°. The resulting colorless crystals had mp 111–113°. The analytical sample was dried at 20° (1 mm).

Anal. Calcd for $C_{13}H_{28}O_5N_3P$: C, 46.3; H, 8.3; N, 12.5; P, 9.2; mol wt, 337. Found: C, 46.3; H, 8.3; N, 12.3; P, 9.2; mol wt, 400 (thermoelectric method in benzene).

The nmr spectral data of the analytical sample and of the initial crystals were identical. The infrared spectrum of a fresh methylene chloride solution had the following bands (μ): *6.30 (strong and broad)*, 6.95 (w), 7.20 (w), 7.35 (w), 7.50 (w), 7.65 (m), 8.40 (w), 9.10 (s), 9.35 (vs), 9.95 (vs), and 10.50 (m). The spectra did not appreciably change within 24 hr.

Reaction of Tris(dimethylamino)phosphine XII with Diethyl Oxomalonate in Various Solvents. In these experiments, a solution of diethyl oxomalonate, 3.7 mmoles in 1.8 ml of a given solvent, was added to a solution of the aminophosphine XII, 5.6 mmoles, in 2.5 ml of the same solvent at 0°. The mixtures were kept 50 min at 0° and 30 min at 20°. The results were as follows.

1. In Hexane. The 1:1 adduct, XX, separated in the form of very pale yellow crystals.

2. In Benzene. A nearly colorless solution was observed; δP^{31} = −38.0 ppm after 1 hr, −38.3 ppm after 24 hr. The infrared spectrum did not change from 20 min to 24 hr; the spectrum exhibited the bands for the 1:1 adduct, and a weak band at 5.72 μ attributed to the 2:1 adduct, XXI (*vide infra*). The H^1 nmr had a doublet at τ 7.42, J_{HP} = 9.5 cps, attributed to the 1:1 adduct, XX, in addition to the doublet, at τ 7.53, J_{HP} = 9.0 cps, due to an excess of the aminophosphine XII.

3. In Methylene Chloride. The pale yellow solution had δP^{31} = −38.2 ppm after 1 hr, and −38.4 ppm after 24 hr. The infrared spectrum showed the presence of small amounts of the 2:1 adduct, XXI, and large amounts of the 1:1 adduct, XX. The H^1 nmr had a doublet at τ 7.17, J_{HP} = 9.7 cps, due to the 1:1 adduct, XX.

4. In Tetrahydrofuran. The pale yellow solution had δP^{31} = −38.8 ppm after 1 hr; the spectrum after 24 hr showed a considerable amount of hexamethylphosphoramidate, $[(CH_3)_2N]PO$, δP^{31} = −24 ppm.

In another experiment, tris(dimethylamino)phosphine (8.15 g, 50 mmoles) was added dropwise to diethyl oxomalonate (8.7 g, 50 mmoles) in 10 ml of tetrahydrofuran.[8] The addition was effected over a 25-min period, and *the temperature of the solution was kept at ca. 42°*. The P^{31} nmr spectrum of this solution showed the presence of five nuclei: δP^{31} = −121.9 (tris(dimethylamino)-phosphine), −38.8 (1:1 adduct, XX; these two nuclei were in a proportion of 2:1), −23.3, −22.1, and −20.2 ppm. The latter three nuclei were in the approximate proportion of 1.5:3:2. The combined intensities of these three signals was about twice that of the signal due to the 1:1 adduct. One of the signals was due to hexamethylphosphoroamidate and the other is attributed to the 2:1 adduct, XXI; the third is of unknown origin.

The infrared spectrum of the residue obtained after removal of the tetrahydrofuran showed a strong band at 5.70 μ attributed to the 2:1 adduct, XXI, and a weaker band at 6.30 μ due to the 1:1 adduct, XX (in CH_2Cl_2).

Reaction of 1 Mole of Tris(dimethylamino)phosphine, XII, with 2 Moles of Oxomalonate. The aminophosphine XII (6.7 mmoles in 5 ml of CH_2Cl_2), was added to diethyl oxomalonate (13.4 mmoles in 10 ml of CH_2Cl_2) at 20° over a 30-min period. The pale yellow solution obtained after 1 hr exhibited an infrared spectrum with a very strong band at 5.70 μ attributed to the 2:1 adduct, XXI, and a very weak band at 6.30 μ due to the 1:1 adduct, XX. The H^1 nmr spectrum had a doublet at τ 7.17, J_{HP} = 9.8 cps (1:1 adduct, XX), a doublet at τ 7.32, J_{HP} = 10.2 cps (possible 2:1 adduct, XXI), and a doublet at τ 7.36, J_{HP} = 9.3 cps (hexamethylphosphoroamidate). It was not possible to separate this mixture without affecting the structure of the components.