Reactions of Five-Membered Cyclic Triaminophosphines with Hexafluoroacetone, Trifluoroacetophenone, and Fluorenone. Attack by Phosphorus on Carbonyl Oxygen and Isolation of Crystalline 2,2,2-Triamino-1,3,2-dioxaphospholanes

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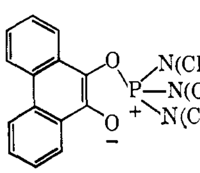
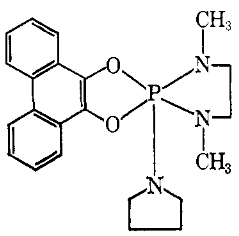
Abstract: The phosphorus of five-membered cyclic tris(dialkylamino)phosphines attacked the carbonyl oxygen of hexafluoroacetone and of trifluoroacetophenone. At low temperatures (<0°), the 1:1 adducts with P–O–C bonds added to more ketone and gave 2:1 adducts with pentavalent phosphorus. At 20° the 1:1 adducts underwent extensive deoxygenation. At elevated temperatures (>100°) the 1:1 adducts underwent deoxygenations and defluorinations; the latter produced difluoro(trisdialkylamino)phosphoranes, $(R_2N)_3PF_2$. The 2:1 adducts were stable below 140°. A 2:1 adduct has been obtained from fluorenone and the cyclic triaminophosphines. Only deoxygenation could be observed from fluorenone and acyclic triaminophosphines; the products in this case were the phosphoroamidate and dibiphenyleneethylene.

Previous papers from this laboratory showed that the phosphorus of tris(dialkylamino)phosphines added to the carbonyl oxygen of *o*-quinones,[2] α-diketones,[3,4] vicinal triketones,[2] and α-keto esters.[2,4] The products of these reactions were 1:1 adducts whose structures depended on the structures of the triaminophosphines. The adducts derived from tris(dimethylamino)phosphine were triaminooxyphosphonium dipolar ions, for example, I. The P^{31} nmr shifts of these adducts were strongly negative relative to H_3PO_4. The adducts derived from five-membered cyclic tris(dialkylamino)phosphines, on the other hand, were 2,2-dihydro-2,2,2-triamino-1,3,2-dioxaphospholenes, for example, II. These had strongly positive P^{31} nmr shifts.



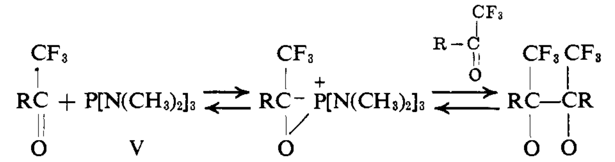
I, $\delta P^{31} = -38.6$ ppm *vs.* H_3PO_4



II, $\delta P^{31} = +35.1$ ppm

The difference in the structures of these adducts appears to be related to the considerable intramolecular overcrowding which is present in the trigonal bipyramidal configuration of pentacovalent phosphorus, as revealed by the X-ray analysis of related compounds.[5] This crowding decreases the stability of the phosphorane structure relative to that of the open dipolar structure.

The phosphorus of tris(dimethylamino)phosphine, V, also attacked the carbonyl oxygen of hexafluoroacetone, III, and of trifluoroacetophenone,[6,7] IV. There was indirect evidence for the formation of 1:1 adducts, VI and VII, and of 2:1 adducts, VIII and IX. However, the formation of these intermediates could not be demonstrated. The main product of these reactions was difluorotris(dimethylamino)phosphorane, X, which was accompanied by smaller amounts of hexamethylphosphoroamidate, XI, and of at least four other products.[6] Mechanisms for the formation of the observed products from the intermediates, VI and VII, were proposed.

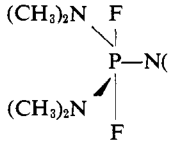


III, R = CF_3
IV, R = C_6H_5

V

VI, R = CF_3
VII, R = C_6H_5

VIII, R = CF_3
IX, R = C_6H_5



$[(CH_3)_2N]_3PO$

X, $\delta P^{31} = +65.7$ ppm, $J_{PF} = 700$ cps

XI, $\delta P^{31} = -23.2$ ppm

This paper describes the reactions of hexafluoroacetone and trifluoroacetophenone with five-membered cyclic aminophosphines. We also studied the reactions of fluorenone with the cyclic and acyclic tris(dialkylamino)phosphines.

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[1] This investigation was supported by National Science Foundation Grant CP-6690-Y and by Public Health Service Grant No. CA-04769-08 from the National Cancer Institute.

[2] (a) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Am. Chem. Soc.*, **87**, 4973 (1965); (b) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *ibid.*, **89**, 6276 (1967).

[3] (a) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, 3053 (1966); (b) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron*, in press.

[4] Burgada also suggested the attack of trisdialkylaminophosphines on carbonyl oxygen of α-diketones and of α-keto esters. He formulated the adducts incorrectly. *Cf.* (a) R. Burgada, *Bull. Soc. Chim. France*, 347 (1967); (b) R. Burgada, *Compt. Rend.*, **258**, 4789 (1964).

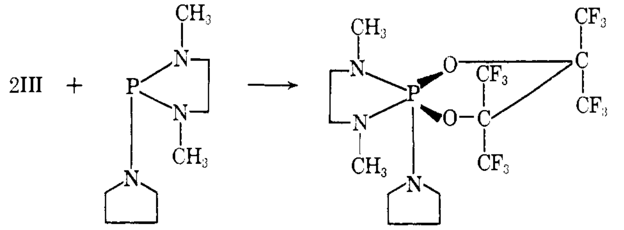
[5] (a) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965); (b) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967); (c) R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).

[6] F. Ramirez, C. P. Smith, and S. Meyerson, *Tetrahedron Letters*, 3651 (1966).

[7] The work described in ref 6 showed that a previous communication by Mark [V. Mark, *Tetrahedron Letters*, 3139 (1964)] on the course of the reaction of trisdimethylaminophosphine with trifluoroacetophenone was in error. See also: A. W. Johnson, "Ylide Chemistry," Academic Press Inc., New York, N. Y., 1966, p 78.

Results

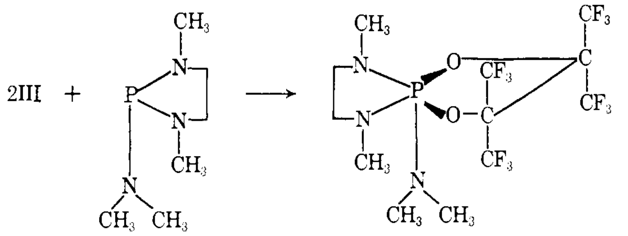
Reactions of Perfluoroketones with Five-Membered Cyclic Tris(dialkylamino)phosphines. Hexafluoroacetone, III, reacted with 2-N-pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, XII, in hexane at −70°. The product was a crystalline 2:1 adduct formulated as the spirotriaminodioxaphosphorane, XIII.



XII, $\delta P^{31} = -104.8$ ppm XIII, $\delta P^{31} = +30.9$ ppm

The phosphorane structure XIII was based mainly on the positive value of the P^{31} nmr shift. Related compounds such as II had very similar P^{31} nmr shifts.[2,3] The H^1 nmr and the infrared spectra were in agreement with structure XIII.

The reaction of hexafluoroacetone, III, with 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane, XIV, in hexane at −70° gave also a crystalline triaminodioxyphosphorane, XV. This reaction was investigated also in benzene and methylene chloride solutions at −70° without significant differences.

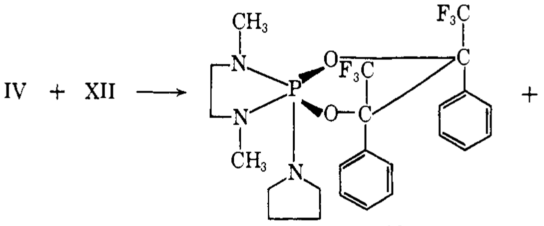


XIV, $\delta P^{31} = -114.2$ ppm XV, $\delta P^{31} = +28.3$ ppm

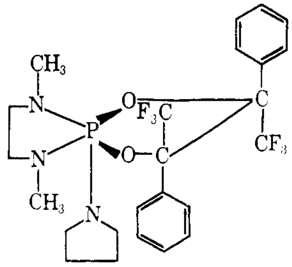
Trifluoroacetophenone reacted with the pyrrolidino phospholane XII in hexane at −70°. The two possible diastereomers of the triaminodioxyphosphoranes, XVIa and XVIb, were produced in a 1:3 proportion. The assignment of configuration to these isomers is uncertain; however, the minor isomer with the phosphorus signal at lower magnetic field probably has the *cis*-CF_3,CF_3 configuration, and the major isomer with the signal at higher magnetic field probably has the *trans*-CF_3,CF_3 configuration, as shown.[8]

An exothermic reaction was observed when 2 moles of trifluoroacetophenone, IV, was added to 1 mole of the aminophosphine XII in benzene at 20°. Under these conditions, the amount of 2:1 adduct, XVI, decreased significantly, and a new product, the cyclic phosphoroamidate XVII appeared.

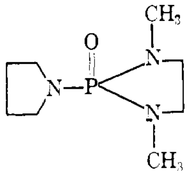
When the aminophosphine XII was added to 2 mole equiv of trifluoroacetophenone, IV, at 20° in the absence of solvent, a nearly explosive reaction was observed. The temperature of the mixture reached 153°. Under these conditions, no 2:1 adduct, XVI, was obtained; two products were produced in a 1.4:1 proportion. The major product was the phosphoroamidate XVII, and the minor product was the difluorotris(dialkylamino)phosphorane XVIII. This structure was based[6] on the appearance of a triplet in the P^{31} nmr spectrum,[9] which should be compared with the triplet of difluorotris(dimethylamino)phosphorane[6] X.



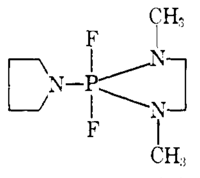
XVIa, $\delta P^{31} = +38.5$ ppm



XVIb, $\delta P^{31} = +40.5$ ppm

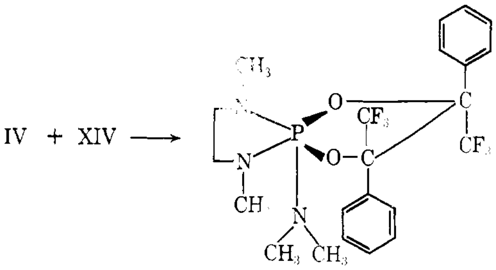


XVII, $\delta P^{31} = -23.1$ ppm



XVIII, $\delta P^{31} = +50.6$ ppm
$J_{PF} = 796$ cps (triplet)

The behavior of trifluoroacetophenone, IV, toward 2-dimethylamino-1,3-dimethyl-13,2-diazophospholane, XIV, gave similar results. The reaction in hexane at −70° gave a pure diastereomer of the spirotriaminodioxyphosphorane XIX in 71% yield. This isomer probably has the *trans*-CF_3,CF_3 configuration, but this point was not established conclusively.



XIX, $\delta P^{31} = +34.9$ ppm

When the reaction was carried out in benzene at 20°, the products were the adduct, XIX, and the corresponding phosphoroamidate XX, in a 1.3:1 proportion.

The vigorous reaction of trifluoroacetophenone with the aminophosphine XIV produced the adduct XIX and the phosphoroamidate XX plus the difluoro(trisdialkylamino)phosphorane XXI in the approximate proportion of 1.1:1.0:3.4.

Thermal Decompositions of the Triaminodioxaphosphoranes, XIII, XV, XVI, and XIX, Derived from the Perfluoro Ketones. The spirotriaminophosphoranes exhibited a remarkable thermal stability. They were not

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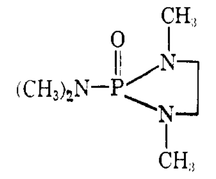
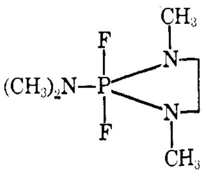
(8) (a) F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967); (b) F. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Org. Chem.* **31**, 4105 (1966); (c) F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966); (d) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

(9) For extensive discussions of fluorophosphoranes, see: (a) R. Schmutzler, *Inorg. Chem.*, **3**, 421 (1964); (b) R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964); (c) *ibid.*, **4**, 496 (1965).



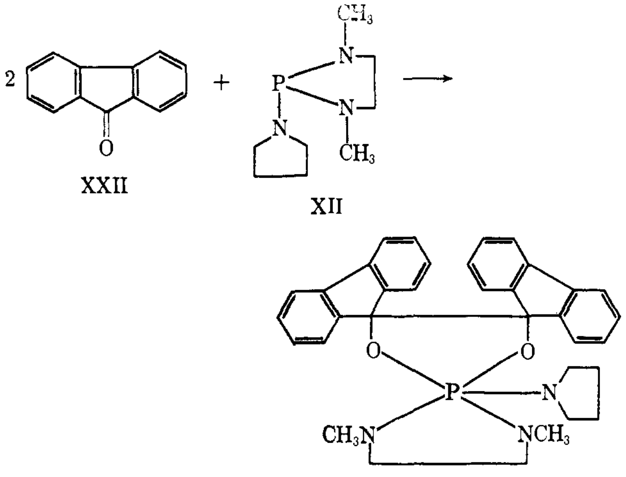
XX, $\delta P^{31} = -26.4$ ppm



XXI, $\delta P^{31} = +46.8$ ppm
$J_{PF} = 800$ cps (triplet)

appreciably changed at temperatures below 140°; however, they underwent extensive decompositions in the temperature range of 150–160°. These decompositions were accompanied by transfer of fluorine to phosphorus, as shown by the P^{31} nmr spectra; however, no pure compounds could be isolated from these pyrolyses.

Reaction of Fluorenone with Tris(dialkylamino)phosphines. Fluorenone, XXII, reacted with the cyclic tris(dialkylamino)phosphine XII in methylene chloride at 0°. The product was a crystalline 2:1 adduct, XXIII, formed in quantitative yield. The analytical and spectral data supported the triaminodioxyphosphorane structure, XXIII.



XXII

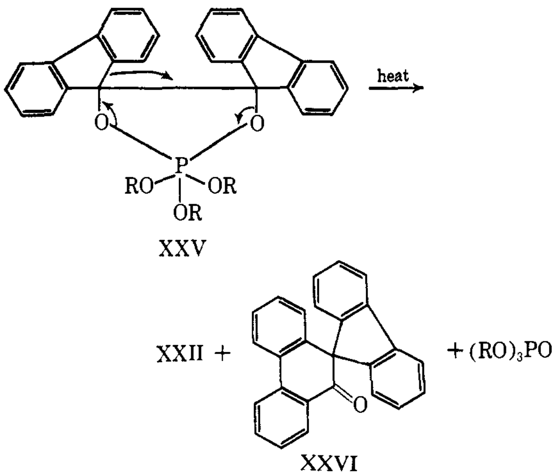
XII

XXIII, $\delta P^{31} = +40.3$ ppm

When a diglyme solution of the 2:1 adduct, XXIII, was immersed in a bath at 150°, rapid decomposition occurred with formation of a dark red solution. This solution contained fluorenone, XXII, the cyclic phosphoroamidate XVII, and a third material which was not characterized at this time. Further work on the pyrolytic decomposition of this and of other oxyphosphoranes and aminooxyphosphoranes will be described elsewhere.

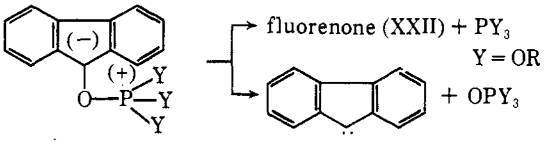
The pyrolyses of the triaminooxyphosphorane XXIII did not produce 9-diphenylenephenanthrone, XXVI, which was the main product of the pyrolyses of the pentaoxyphosphoranes XXV made from fluorenone and trialkyl phosphites.[10,11]

These observations suggested that both 2:1 adducts, XXIII and XXV, underwent thermal dissociations[11] to 1 mole of fluorenone, XXII, and 1 mole of the 1:1 adducts, XXVII and XXVIII, respectively. The fates of the 1:1 adducts were different. The *phosphite* adduct, XXVIII, gave a second mole of fluorenone, XXII, and the trialkyl phosphite by dissociation, while the *aninophosphine* adduct, XXVII, lost a molecule of the cyclic amidate XVII and produced a carbenoid intermediate,[12] XXIX. The latter could undergo several transformations at the relatively high temperature at which it was generated.



XXV

XXVI



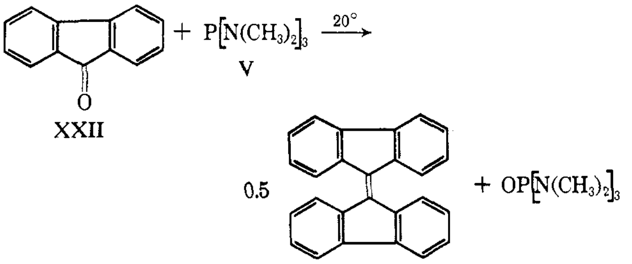
XXVII, Y = NR2
XXVIII, Y = OR

XXIX

XVII, Y = NR2

A second mechanistic path was open to the 2:1 phosphite adduct, XXV, but not to the aminophosphine adduct, XXIII, namely, the pinacolic rearrangement to diphenylenephenanthrone,[10] XXVI.

Tris(dimethylamino)phosphine, V, was less reactive than the cyclic analog, XII, toward fluorenone. The reaction had a 1:1 stoichiometry and gave dibiphenyleneethylene,[13] XXIV, and hexamethylphosphoroamidate, XI.



XXII

V

XXIV

XI

These results can be explained by the formation of a 1:1 adduct analogous to XXVII, which rapidly lost the amidate, XI and formed the carbenoid, XXIX. The latter can give the product XXIV in two ways: (1) by dimerization; (2) by reaction with more aminophosphine V followed by condensation of the resulting triaminoalkylidenephosphorane with fluorenone: $(R_2N)_3P{=}CR_2' + OCR_2' \rightarrow R_2'C{=}CR_2' + (R_2N)_3PO$. This mechanism is speculative since the formation of the carbene XXIX was not demonstrated. However, it is fairly certain that a 2:1 phosphorane analogous to XXIII was not an intermediate.

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[10] (a) F. Ramirez and C. P. Smith, *Chem. Commun.*, 662 (1967); (b) I. J. Borowitz and N. Anschel, *Tetrahedron Letters*, 1517 (1967); (c) I. J. Borowitz, M. Anschel, and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967); (d) A. C. Poshkus and J. E. Herweh, *ibid.*, **29**, 2567 (1964).

[11] Thermal dissociations of other oxyphosphoranes have been reported: F. Ramirez, A. V. Patwardhan, and C. P. Smith, *ibid.*, **31**, 3159 (1966).

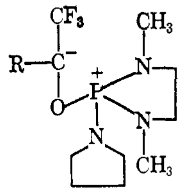
[12] (a) A. W. Johnson and R. B. LaCount, *J. Am. Chem. Soc.*, **83**, 1417 (1961); (b) A. W. Johnson and R. B. LaCount, *Chem. Ind.* (London), 1440 (1958).

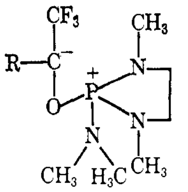
[13] J. C. Wood, R. M. Elofson, and D. M. Saunders, *Anal. Chem.*, **30**, 1339 (1958), and references therein.

The formation of biphthalyl from phthalic anhydride and trialkyl phosphites at elevated temperatures was explained by a similar mechanism.[14] The formation of XXIV from fluorenone and tributylphosphine was described recently in a preliminary note.[10b]

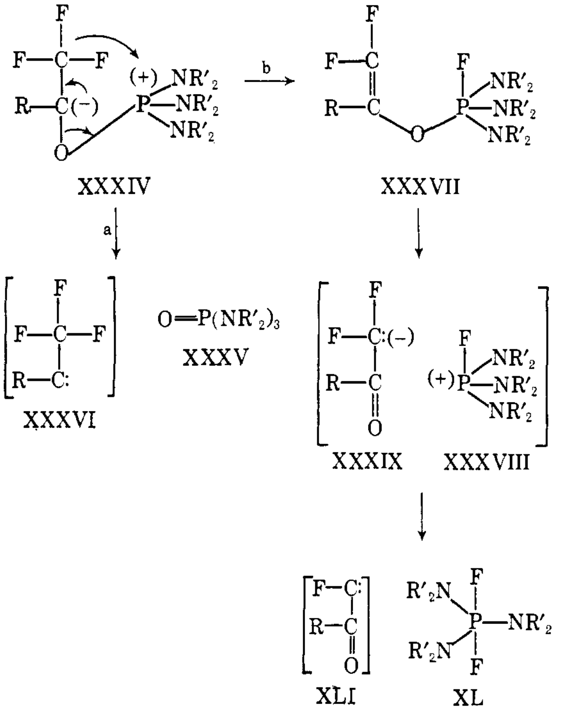
Discussion

This work showed that the phosphorus of tris(dialkylamino)phosphines is capable of adding to the carbonyl oxygen of perfluoroketones without causing defluorinations. The adducts formed in these reactions varied greatly in stability depending on the structure of the aminophosphines. The 1:1 adducts, VI and VII, and the 2:1 adducts, VIII and IX, made from tris(dimethylamino)phosphine and the perfluoro ketones were extremely unstable and underwent defluorinations and other decompositions even below 0°. The corresponding 1:1 adducts, XXX–XXXIII, and 2:1 adducts, XIII, XV, XVI, and XIX, made from the 5-cyclic aminophosphines were relatively stable.

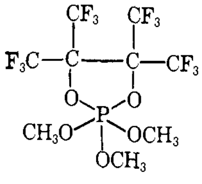

XXX, R = CH_3
XXXI, R = C_6H_5

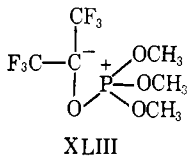

XXXII, R = CF_3
XXXIII, R = C_6H_5

The 1:1 cyclic aminophosphine adducts, XXX–XXXIII, were capable of defluorinations and of other decompositions above certain temperatures, as shown by the formation of the amidates XVII and XX and of the difluorotriaminophosphoranes XVIII and XXI. The following mechanisms explain these transformations: path a, the 1:1 adduct with a P–O–C bond, XXXIV, can lose amidate XXXV, and form a trifluoromethylcarbene, XXXVI; path b, the 1:1 adduct XXXIV can undergo a transfer of fluorine from carbon to phosphorus to give a fluorotriaminooxyphosphorane, XXXVII. The latter can form a series of ion pairs by P–O, P–F, and P–N bond fissions, respectively. One of these ion pairs consists of a fluorotriaminophosphonium cation, XXXVIII, and of an enolate anion, XXXIX. Transfer of fluoride in [XXXVIII–XXXIX] would produce the observed difluorotriaminophosphorane, XL, and the fluoroacylcarbene, XLI.



The behavior of perfluoro ketones toward cyclic aminophosphines and toward trialkyl phosphites[15] was strikingly similar. The reactions of the phosphites gave the stable phosphoranes, for example, XLII, formed *via* the 1:1 adducts, like XLIII.


XLII, $\delta P^{31} = +50.1$ ppm


XLIII

It has now been established conclusively that the phosphorus of tris(dialkylamino)phosphines and of trialkyl phosphites shows a tendency to add to the carbonyl oxygen and not to the carbonyl carbon of a wide variety of vicinal polycarbonyl compounds and of certain activated monocarbonyl compounds.[2,3,6,9,10,14–16] Moreover, the aminophosphines are considerably more reactive than the phosphite esters, and the nitrogen atoms of the former are not involved in the additions to the carbonyl oxygen. These observations can be accommodated in the schemes proposed by Pearson[17] and by Hudson[18,19] if one assumes that the phosphorus is a "softer base" than the nitrogen in the aminophosphines, that the phosphorus is a "softer base" in the aminophosphines than in the phosphite esters, and that the carbonyl function can be regarded as having a "soft-acid" site at its oxygen atom, $RC^{-}(R)O^{+}$.

Experimental Section

The analyses were performed by Schwarzkopf Microanalytical Laboratory, 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 shifts are given in parts per million from TMS as 10 (τ values); they were determined at 60 Mcps.

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[14] (a) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Org. Chem.*, **24**, 1838 (1959); (b) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Am. Chem. Soc.*, **83**, 173 (1961).

[15] (a) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Letters*, 2151 (1966); (b) N. P. Gambaryan Yu. A. Cheburkov, and I. L. Knunyants, *Bull. Acad. Sci. USSR*, **8**, 1433 (1964); (c) E. M. Rokhlin, Yu. V. Zeifman, Yu. A. Cheburkov, N. P. Gambaryan, and I. L. Knunyants, *Dokl. Akad. Nauk USSR*, **161**, 1356 (1965).

[16] For related discussions dealing with the mechanisms of the reactions of α-halo ketones with trialkyl phosphites see: (a) D. W. Wiley and H. E. Simmons, *J. Org. Chem.*, **29**, 1876 (1964); (b) B. Miller, *ibid.*, **30**, 1964 (1965); (c) B. Miller in "Topics in Phosphorus Chemistry," Vol. 3, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, p 133; (d) P. A. Chopard, V. M. Clark, H. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965); (e) A. J. Speziale and R. D. Partos, *J. Am. Chem. Soc.*, **87**, 5068 (1965); (f) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

[17] R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967).

[18] R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapters 4 and 5.

[19] E. H. Amonoc-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 4296 (1965).

Reaction of Hexafluoroacetone, III, with 2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, XII. An excess of hexafluoroacetone, III, was passed through a solution of 2-N-pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, XII (7.2 g), in hexane (35 ml) at −70°. The reaction flask was equipped with a condenser cooled by means of Dry Ice–solvent mixture. The reaction mixture was kept 1 hr at −70° and was then allowed to reach 20°, where it was kept an additional 5 hr. The solvent was removed first at 20 mm and then at 0.1 mm, leaving a crystalline residue (18.1 g, 91%), mp *ca.* 55–60°. This material was kept several hours at −20° under 40 ml of hexane and was then filtered. The insoluble material (8 g) had mp 70–71°. The P^{31} nmr shift in methylene chloride had one signal at +30.9 ppm. One crystallization from hexane (20 ml) gave the analytical sample of the adduct XIII, mp 74–75°. The original hexane extract gave additional adduct XIII (9 g) on standing at −20°

Anal. Calcd for $C_{14}H_{18}O_2N_3F_{12}P$: C, 32.4; H, 3.5; N, 8.1; F, 43.9; P, 6.0; mol wt, 519. Found: C, 32.7; H, 3.7; N, 8.4; F, 43.7; P, 6.0; mol wt, 509 (thermoelectric method in benzene); $\delta P^{31} = +30.9$ ppm (CH_2Cl_2).

The infrared spectrum in methylene chloride had bands at (μ): 6.9 (vw), 7.5 (vw), 7.80 (w), 8.1 (s), 8.3 (m), 8.6 (m), 8.8 (m), 9.25 (m), 9.50 (m), 9.80 (m), 10.4 (m), and 11.3 (m).

Reaction of Hexafluoroacetone, III, with 2-Dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane, XIV. An excess of hexafluoroacetone, III, was passed through a solution of 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane, XIV (1.2 g), in hexane (10 ml) at −70°. The reaction flask was equipped with a condenser cooled by a Dry Ice–solvent mixture. After 20 min at −70°, the reaction mixture was allowed to reach 20°. The clear yellow solution was kept 1 hr at 20°. Most of the solvent was removed at 20 mm, and the residue was analyzed by P^{31} nmr spectroscopy. There was only one P^{31} nucleus at +28.3 ppm. The solution was evaporated to dryness at 20 mm and then at 0.1 mm. The residue was extracted with 20 ml of warm hexane, and the hexane solution was evaporated to dryness. No change in the P^{31} nmr shift was noted; the crude material did not have absorptions corresponding to carbonyl functions in the infrared spectrum (in CH_2Cl_2). The residue was submitted to short-path distillation (0.1 mm) at a bath temperature of 90°. The fraction boiling at 58–60° (0.1 mm) was analyzed. This material became crystalline on prolonged standing in hexane solution at −20°. The colorless crystals of XV had mp 86–87° and exhibited the same elemental analysis and spectral characteristics of those of the liquid adduct. In subsequent preparations, crystallization of the crude adduct XV without prior distillation could be achieved in hexane at −20°. The adduct XV was obtained in 90° yield.

Anal. Calcd for $C_{12}H_{16}O_2N_3F_{12}P$: C, 29.2; H, 3.2; N, 8.5; P, 6.3. Found: C, 29.1; H, 3.2; N, 8.4; P, 6.2; $\delta P^{31} = +28.3$ ppm (CH_2Cl_2).

The infrared spectrum (in CH_2Cl_2) had the following bands (μ): 6.85 (w), 7.45 (w), 7.80 (m), 8.12 (s), 8.20 (s), 8.65 (m), 8.90 (ms), 9.50 (m), 10.05 (ms), 10.40 (ms), and 11.35 (m).

The H^1 nmr in $CDCl_3$ had a complex series of signals at τ 7.0, 7.1, and 7.3.

If the adduct is heated excessively during the distillation, it undergoes decomposition as shown by a very weak absorption in the infrared spectrum at 6.0 μ.

The reaction gave analogous results when carried out in methylene chloride or in benzene solutions at −70°.

Reaction of Trifluoroacetophenone, IV, with 2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, XII. a. In Hexane at −70°. The aminophosphine XII (3.7 g, 19.9 mmoles), was added dropwise over a 3-min period to a solution of trifluoroacetophenone, IV (6.7 g, 38.7 mmoles), in hexane (18 ml) kept at −70°. Reaction was observed even at this low temperature. The mixture was allowed to reach 20° and was then decanted from a very small amount of a brown gummy insoluble residue. The pale yellow hexane solution was evaporated to dryness first at 20 mm and then at 0.1 mm. The crystalline residue (9.6 g) had spectral characteristics similar to those of the pure adduct XVI. The crude adduct was dissolved in hexane (15 ml) and the solution was kept at −20°, giving colorless crystals (6 g) of adduct XVI, mp 105–107°. Recrystallization from hexane gave the analytical sample of one diastereomer, mp 106–107°, of adduct XVI assumed to have *trans*-CF_3,CF_3.

Anal. Calcd for $C_{24}H_{28}O_2N_3F_6P$: C, 53.8; H, 5.2; N, 7.8; F, 21.3; P, 5.8. Found: C, 54.3; H, 5.4; N, 8.1; F, 21.7; P, 5.9; $\delta P^{31} = +39.7$ ppm (CH_2Cl_2).

The infrared spectrum in CCl_4 had the following bands (μ): 6.85 (w), 6.93 (w), 7.35 (w), 8.00 (m),8 .42 (shoulder), 8.50 (s), (8.70) (s), 9.40 (m), 9.90 (m), 10.50 (m), and 10.65 (m).

The H^1 nmr in $CDCl_3$ had ten aromatic protons at τ 2.5 and 3.0, 14 H^1, which included a doublet at τ 7.25, $J_{HP} = 10.0$ cps (CH_3N), and a multiplet at τ 6.9 (α-methylene), and a 4 H^1 signal at τ 8.32 (β-methylene).

In another experiment, 2 mmoles of the aminophosphine XII was added to 4 mmoles of trifluoroacetophenone, IV, in 2 ml of hexane at −70°. The mixture was kept 1 hr at 20°, and the hexane was removed under vacuum. The residue was dissolved in CH_2Cl_2, and the pale yellow solution was analyzed by P^{31} nmr. Two nuclei were present in a proportion of 1:3. The minor isomer, XVIa, $\delta P^{31} = +38.5$ ppm, was assumed to have the *cis*-CF_3,CF_3 configuration, and the major isomer, XVIb, $\delta P^{31} = +40.5$ ppm, was assumed to have the *trans*-CF_3,CF_3 configuration.

b. In Benzene at 20°. A solution of trifluoroacetophenone (21.7 mmoles) in 5 ml of benzene at 20° was added dropwise to a stirred solution of the aminophosphine XII (10.8 mmoles) in 7 ml of benzene at 20°. An exothermic reaction was observed which raised the temperature to 60°. The solution was kept 0.5 hr at ambient temperature and then was concentrated to one-half of its original volume. The P^{31} nmr spectrum showed the presence of two nuclei in a 3:1 proportion. The major signal, $\delta P^{31} = +40.1$ ppm, was due to the 2:1 adduct, XVI, and the minor signal, $\delta P^{31} = -23.1$ ppm, was due to 2-N-pyrrolidino-2-oxo-1,3-dimethyl-1,3,2-diazaphospholane, XVII.

c. In the Absence of Solvent without Temperature Moderation. The aminophosphine XII (25.3 mmoles) was added to trifluoroacetophenone, IV (50.6 mmoles), at 20°. *Caution:* this reaction is quite vigorous. The mixture became dark brown and thick, and the internal temperature reached 153°. The mixture was dissolved in CH_2Cl_2 and found to contain two P^{31} nuclei in the proportion of 1.4:1. The major signal, $\delta P^{31} = -22.9$ ppm, was due to the phosphoroamidate XVII; the minor signal was a triplet at $\delta P^{31} = +50.6$ ppm, $J_{PF} = 796$ cps, which is attributed to a difluorotris(dialkylamino)phosphorane, XVIII.

Reaction of Trifluoroacetophenone, IV, with 2-Dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane, XIV. a. In Hexane. The aminophosphine XIV (1.24 g, 7.7 mmoles) was added dropwise to a solution of trifluoroacetophenone, IV (2.70 g, 15.5 mmoles), in hexane (12 ml) at −70°. Reaction was noted at −70°; the mixture was kept 10 min at that temperature and was then allowed to reach 20°. The hexane solution was decanted from a small amount of a brown gummy material and was evaporated to dryness, yielding a solid adduct, XIX (2.8 g, 71%). This material was crystallized from hexane (10 ml) yielding adduct, mp 121–122°. One more crystallization from hexane did not change the melting point. This material is regarded as the isomer of the adduct XIX having *trans*-CF_3,CF_3.

Anal. Calcd for $C_{22}H_{26}O_2N_3F_6P$: C, 51.9; H, 5.1; P, 6.1. Found: C, 52.1; H, 5.2; P, 6.0; $\delta P^{31} = +34.9$ ppm (CH_2Cl_2).

The H^1 nmr in $CDCl_3$ had ten aromatic protons at τ 2.4 and 2.9, and 16 aliphatic protons. The latter included a doublet at τ 7.25, $J_{HP} = 9.5$ cps, and a doublet at τ 7.35, $J_{HP} = 11.5$ cps, attributed respectively to the two methyl groups attached to the ring nitrogens and to the two methyl groups of the dimethylamino residue. In addition, there was a multiplet at τ 6.9 due to the α-CH_2.

The infrared spectrum in CH_2Cl_2 had the following bands (μ): 6.9 (w), 6.92 (w), 7.45 (w), 7.80 (w), 8.50 (s), 8.70 (s), 9.10 (w), 9.3 (m), 9.5 (m), 10.1 (m), 10.4 (m), 10.6 (m), 11.5 (w), and 12.5 (w).

b. In Benzene at 20°. Trifluoroacetophenone, IV (5.9 mmoles), was added all at once to a solution of the aminophosphine XIV (2.9 mmoles) in 1 ml of benzene at 20°. The reaction was exothermic and raised the solution to its boiling point, The yellow-brown solution was analyzed by P^{31} nmr showing the presence of two nuclei in the proportion of 1.3:1. The major signal, $\delta P^{31} = -26.4$ ppm, was due to 2-dimethylamino-2-oxo-1,3-dimethyl-1,3,2-diazaphospholane, XX.

c. In the Absence of Solvent without Temperature Moderation. The aminophosphine XIV (6.2 mmoles) was added to trifluoroacetophenone, IV (12.5 mmoles), at 20°. *Caution:* this reaction is very vigorous. The P^{31} nmr spectrum of the dark brown solution was examined and was found to contain three nuclei in the proportion of 1.1:1.0:3.4. The first signal, $\delta P^{31} = +35.2$ ppm, was due to the 2:1 adduct, XIX. The second signal, $\delta P^{31} = -26.4$ ppm, was due to the phosphoroamidate XX. The third signal was a triplet, $\delta P^{31} = +47.3$ ppm, $J_{PF} = 798$ cps, attributed to the difluorotris(dialkylamino)phosphorane XXI.

Pyrolyses of the Triaminodioxyphosphoranes XIII, XV, XVI, and XIX. The phosphoranes XIII, XV, XVI, and XIX were stable up to 140°. Decomposition was quite rapid in the temperature range of 155–160°. No volatile perfluoro ketones were evolved during the pyrolyses. The residues were analyzed by P^{31} nmr with the following conclusions: (1) pyrolysis of the hexafluoroacetone–pyrrolidino phospholane adduct, XIII, at 155°; no phosphoroamidate, XVII, was produced. Two P^{31} nuclei were produced in a 1:1.6 ratio. The minor signal was a triplet, $\delta P^{31} = +16.6$, $J_{PF} = 954$ cps; the major signal was a quintuplet, $\delta P^{31} = +144.6$ ppm, $J_{PF} = 704$ cps. (2) With pyrolysis of hexafluoroacetone–dimethylaminophospholane, XV, at 160°, there were two nuclei in a 1:3 proportion. The minor signal was a triplet at $\delta P^{31} = +16.3$, $J_{PF} = 955$ cps. The major signal was a quintuplet at $\delta P^{31} = +144.4$ ppm, $J_{PF} = 713$ cps. (3) With pyrolysis of the trifluoroacetophenone–pyrrolidino phospholane adduct, XVI, at 155°, there were small amounts of amidate, XVII, at $\delta P^{31} = -23.8$ ppm. There was a triplet at $\delta P^{31} = +15.0$ ppm, $J_{PF} = 961$ cps. There was a very weak quintuplet, which was not calibrated. (4) With pyrolysis of the trifluoroacetophenone–dimethylaminophospholane adduct, XIX, at 158; three nuclei were present in a 2.5:1:3.0 proportion respectively at $\delta P^{31} = -27.5$ ppm (amidate XX), a triplet at $\delta P^{31} = +15.2$ ppm, and a quintuplet at $\delta P^{31} = +144.5$ ppm.

Reaction of Fluorenone, XXII, with 2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, XII. A solution of the aminophosphine XII (4.2 g) in 5 ml of CH_2Cl_2 was added over a 5-min period to a stirred solution of fluorenone, XXII (8.5 g, 2 mole equiv), in 5 ml of CH_2Cl_2 at 0°. The solution changed immediately from yellow to orange, and within 10 min crystallization took place. The mixture was kept 24 hr at 20°, and the solvent was evaporated (20 mm). The yellow solid was triturated with five 100-ml portions of ether. The colorless solid, XXIII (3.26 g), had mp 140–142°, and was analyzed without further purification. It can be recrystallized from benzene–pentane.

Anal. Calcd for $C_{34}H_{34}O_2N_3P$: C, 74.6; H, 6.2; N, 7.7; P, 5.7. Found: C, 74.7; H, 6.4; N, 7.9; P, 5.3; $\delta P^{31} = +40.3$ ppm (CH_2Cl_2).

The H^1 nmr in $CDCl_3$ had 16 aromatic protons at τ 2.5 and 3.1, and 18 aliphatic protons which included a doublet at τ 7.46, $J_{HP} = 9.7$ cps (CH_3N), a multiplet centered at τ 6.7 (α-CH_2), and a multiplet at τ 8.2 (β-CH_2).

The infrared spectrum in CH_2Cl_2 had bands at (μ): 6.25 (w), 6.35 (w), 6.95 (m), 7.50 (m), 8.30 (s), 8.65 (s), 9.05 (m), 9.30 (m), 9.6 (s), 9.95 (s), 10.5 (s), and 10.75 (s).

The ether solution was evaporated giving 9 g of additional material; the spectral characteristics of the latter were very similar to those of pure adduct XXIII; total yield: 90%.

Thermal Decomposition of the Fluorenone–2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane, XXIII. a. In Diglyme. A solution of the adduct (1.85 g, 3.4 mmoles) in 5 ml of diglyme was heated 30 min at 150°. The pale yellow solution became dark red. The P^{31} nmr spectrum contained only one signal for the amidate, XVII. The solution was passed through a column (12 × 1 in.) of neutral alumina. The column was eluted with C_6H_6 and the deep red fraction was collected. This solution was distilled first at 20° (20 mm) to remove benzene, then at 100° (0.1 mm) to remove the diglyme. The residue was sublimed at 150° (0.1 mm) to yield fluorenone (50% of the theoretical based on dissociation of the 2:1 adduct into the 1:1 adduct), identified by its infrared spectrum. No pure material could be obtained from the dark residue.

b. In Benzene. A benzene solution of the adduct XXIII was kept at reflux for 5 hr. The P^{31} nmr spectrum showed only traces of the amidate and unchanged adduct.

Reaction of Fluorenone, XXII, with Tris(dimethylamino)phosphine, V. The aminophosphine (2.66 g, 16.3 mmoles) was added to a solution of fluorenone (2.93 g, 16.3 mmoles) in 6.5 ml of methylene chloride (2.5 *M*) at 20°. The solution became deep red within 1–2 min. The infrared spectrum was examined at intervals. After 4 hr, the reaction was about 90% complete. The infrared band at 5.85 μ due to fluorenone had almost disappeared; the infrared band at 10.18 μ characteristic of hexamethylphosphoroamidate had appeared. The P^{31} nmr spectrum contained only a single peak at $\delta P^{31} = -23.9$ ppm due to the amidate. The solution was evaporated, and the residue was distilled at 0.1 mm and a bath temperature of 150° to recover the amidate (2.40 g, 82%). The solid residue was recrystallized from benzene to yield dibiphenyleneethylene, XXIV, in about 50% yield; it was identified by comparison of its infrared spectrum with an authentic sample. One recrystallization from ethanol gave deep red needles of XXIV, mp 183–185° (lit.[13] mp 187°).

A series of reactions of fluorenone with tris(dimethylamino)phosphine was carried out in methylene chloride solution at 20° with the reagents in 2:1, 1:1, and 1:2 proportions. The course of the reactions was followed by infrared and P^{31} nmr spectrometry. When 1 mole of the aminophosphine was added to 2 moles of the fluorenone, 1 mole of the latter remained unchanged at the end of the reaction. When 2 moles of the aminophosphine was added to 1 mole of fluorenone, the latter was completely consumed, but 1 mole of the aminophosphine remained unchanged at the end of the reaction. In the equimolar reaction, both reactants were consumed; the amidate was isolated in 85% yield and the dibiphenyleneethylene was *isolated* in 50% yield; the latter was formed in excess of this amount.

Boron–Pyrazole Chemistry. IV. Carbon- and Boron-Substituted Poly(1-pyrazolyl)borates

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Abstract: Syntheses of bidentate and tridentate alkali metal poly(1-pyrazolyl)borates containing substituents on carbon or boron and of transition metal compounds derived therefrom are described. Their properties are discussed.

In one of the preceding papers of this series,[1] we reported the syntheses and properties of salts, free acids, and coordination compounds derived from uninegative ligands of the general formula[2] $[H_nB(pz)_{4-n}]^-$ where *n* was 0, 1, and 2. The above structures where *n* is 2 and 1 are parent compounds, each representing a new class of coordinating ligands. The former is bidentate, resembling conventional chelating agents such as acetylacetonate ion; the latter is tridentate of C_{3v} symmetry and as such without precedent. Their optical, electronic, and nmr spectroscopic properties have been reported[3] as has the intriguing case of spin

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(1) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).

(2) "pz" stands for the 1-pyrazolyl residue.