Nucleophilic–Electrophilic Interactions between Pairs of Trivalent Phosphorus Compounds. Tertiary Phosphines and Halophosphines

Fausto Ramirez[1] and E. A. Tsolis

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790.
Received April 22, 1970

Abstract: Trimethylphosphine reacts with chlorodiphenylphosphine to give a crystalline 1:1 adduct which we have formulated as an ion pair in which the cation has a P—P bond joining tetracoordinated and tricoordinated phosphorus. The same type of adduct is obtained with dimethylphenylphosphine. The 1:1 adducts revert to the original components upon heating under vacuum. The 1:1 adducts are in equilibrium with the original components in CH_2Cl_2 solution. The structure of the adducts was deduced from ^{31}P nmr spectra of their solution, in the presence and in the absence of an excess of the trivalent phosphorus precursors. The ^1H nmr spectrum of the $[(CH_3)_3PP(C_6H_5)_2]^+Cl^-$ adduct in $CDCl_3$ at $-21°$ shows the coupling of the CH_3 protons with the two different phosphorus atoms. Methyldiphenylphosphine does not react with chlorodiphenylphosphine. The products of the reactions of the tertiary phosphines with dichlorophenylphosphine and with phosphorus trichloride are more complex. The tertiary phosphines react with difluorophenylphosphine to give the corresponding difluorophosphorane, R_3PF_2, and pentaphenylcyclopentaphosphine $(C_6H_5P)_5$.

The reactions of secondary phosphines with monochlorophosphines[2]

$$R_2PH + PClR_2 \longrightarrow R_2PPR_2 + HCl$$

and the reactions of primary phosphines with dichlorophosphines[2]

$$RPH_2 + PCl_2R \longrightarrow (RP)_n + 2HCl$$

have been known for over 80 years.[3,4] The nature of the products suggests that some sort of interaction can occur between two tricoordinated phosphorus atoms. This matter has been recently discussed in terms of the donor and the acceptor properties of trivalent phosphorus compounds.[5,6]

Inorganic chemists have been concerned with the ability of phosphorus trichloride to combine with Lewis bases,[7] $R_3N \cdot PCl_3$, and with Lewis acids,[8,9] $Cl_3P \cdot BCl_3$. These interactions seem to play a role in the ability of the phosphorus trihalides to undergo "reorganizations" or exchange of their halogen atoms.[10]

More recently, a solid but relatively unstable 2:1 adduct has been obtained from 2 mol of trimethylphosphine and 1 mol of phosphorus trichloride[7] $[(CH_3)_3P_{1.96} \cdot PCl_3]$. Evidently, these phenomena can affect the outcome of the rather complex reactions of Grignard reagents, RMgX, with phosphorus trichloride since the intermediates are haloalkylphosphines and tertiary phosphines.[11,12] The so-called Friedel–Craft reactions of aromatic compounds, with PCl_3 in the presence and in the absence of $AlCl_3$, owe their complexity to the biphilicity of PCl_3 and the halophosphines.[11]

Seidel[12] mentioned the formation of "pentaalkylbiphosphonium salts, from the reactions of tertiary phosphines with diorganohalophosphines."

$$R_3P + R_2'PX \longrightarrow [R_3PPR_2']X$$

Spangenberg and Sisler[13] reported the following observations. (1) The reaction of tri-*n*-propylphosphine with chlorodiphenylphosphine gives tri-*n*-propyldichlorophosphorane[14,15] $(n\text{-}C_3H_7)_3PCl_2$, and tetraphenyldiphosphine, $(C_6H_5)_2PP(C_6H_5)_2$. (2) The reaction of triethylphosphine with chlorodimethylphosphine gives a 1:1 adduct, $[(C_2H_5)_3PP(CH_3)_2]Cl$. (3) The reaction of triethylphosphine with dichlorophenylphosphine at $-20°$ gives a 1:1 adduct, $[(C_2H_5)_3PP(C_6H_5)Cl]Cl$, which is transformed into triethyldichlorophosphorane, $(C_2H_5)_3PCl_2$,[14] and tetraphenylcyclotetraphosphine[16–18]

(1) This work was supported by Public Health Service Grant No. CA-04769-10 from the National Cancer Institute and by the National Science Foundation Grant GP-6690; to whom correspondence should be addressed.

(2) $PClR_2$, phosphinous chloride; PCl_2R, phosphonous dichloride.

(3) C. Dörken, *Chem. Ber.*, 21, 1505 (1888).

(4) (a) H. Köhler and A. Michaelis, *ibid.*, **10**, 807 (1877); (b) W. Kuchen and H. Buchald, *ibid.*, **91**, 2296 (1958); (c) M. L. Nielsen, J. V., Pustinger, Jr., and J. Strobel, *J. Chem. Eng. Data*, **9**, 167 (1964); (d) A. H. Cowley and R. P. Pinnell in "Topics in Phosphorus Chemistry," Vol. 4, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1967, p 1; (e) J. J. Daly, *J. Chem. Soc.*, 428 (1966).

(5) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967, pp 15–19, 25, 237–241.

(6) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, pp 32–36, 113, 215.

(7) (a) R. R. Holmes, *J. Phys. Chem.*, **64**, 1295 (1960); (b) R. R. Holmes and R. P. Wagner, *Inorg. Chem.*, 2, 384 (1963); (c) R. R. Holmes and E. F. Bertaut, *J. Amer. Chem. Soc.*, **80**, 2980 (1958).

(8) D. S. Payne in "Topics in Phosphorus Chemistry," Vol. 4, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1967, pp 96, 107, 116.

(9) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience, New York, N. Y., 1958, pp 231–233.

(10) E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Amer. Chem. Soc.*, **81**, 6363 (1959).

(11) K. D. Berlin, T. H. Austin, M. Petersen, and M. Nagabhushanam in "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1964, p 20.

(12) W. Seidel, *Z. Anorg. Allgem. Chem.*, **330**, 141 (1964).

(13) S. F. Spangenberg and H. H. Sisler, *Inorg. Chem.*, **8**, 1006 (1969).

(14) There is no evidence proving that this material has pentacoordinated phosphorus in the trialkyldichlorophosphorane series (see ref 15).

(15) (a) F. Ramirez, A. J. Bigler, and C. P. Smith, *Tetrahedron*, **24**, 5041 (1968); (b) F. Ramirez, A. J. Bigler, and C. P. Smith, *J. Amer. Chem. Soc.*, **90**, 3507 (1968).

(16) In a later reference[17] (*cf.* 11) Summers and Sisler modified the tetramer structure to the pentamer $(C_6H_5P)_5$ on the basis of other evidence (*cf.* ref 4e).

(17) J. C. Summers and H. H. Sisler, *Inorg. Chem.*, **9**, 862 (1970).

(18) As described in the present paper (*vide infra*) the analogous reaction between $(CH_3)_3P$ and $PCl_2(C_6H_5)$ did not give $(C_6H_5P)_5$ or

Table I. ^{31}P Nmr Signals[a] of Tertiary Phosphines, of a Monochlorophosphine, and of the Crystalline 1:1 Adducts Formed by Reaction of the Tertiary Phosphines with the Monochlorophosphine

$$R_3P + PClR_2' \rightleftharpoons [R_3PPR_2']^+Cl^-$$

Experimental conditions[b]	$(CH_3)_3P$ + $PCl(C_6H_5)_2$		$(C_6H_5)(CH_3)_2P$ + $PCl(C_6H_5)_2$	
	$\partial^{31}P$ no. 1[c]	$\partial^{31}P$ no. 2[c]	$\partial^{31}P$ no. 1[c]	$\partial^{31}P$ no. 2[c]
Tertiary phosphine alone; 2.5 M CH_2Cl_2	+62.0		+46.0	
Chlorodiphenylphosphine alone; 2.5 M CH_2Cl_2		−81.8		−81.8
1:1 adduct alone; 2.5 M CH_2Cl_2	−17.4	+24.7	−3.8	+2.3
1:1 adduct alone; 1.5 M CH_2Cl_2	−15.9	+23.5	−2.5	−1.1
1:1 adduct + 1 mol equiv of chlorodiphenylphosphine; 2.5 M CH_2Cl_2[d]	−18.0	−40.0[e]	−11.0	−33.7[e]
1:1 adduct + 1 mol equiv of tertiary phosphine; 2.5 M CH_2Cl_2	+11.6[e]	+24.8	+16.6	+13.5

[a] In parts per million *vs.* H_3PO_4 as zero, measured at 40.5 Mcps, at 25° in CH_2Cl_2 solutions. [b] Chlorodiphenylphosphine was added to 1 mol equiv of the tertiary phosphine. The crystalline adduct was dissolved in CH_2Cl_2 and the ^{31}P nmr spectrum was determined under the specified conditions. [c] Solutions of the 1:1 adducts had two ^{31}P nmr signals. Signal no. 1 is ascribed to the tetracoordinated phosphonium nucleus of the adduct, "mixed" with the signal of the tertiary phosphine in equilibrium with the adduct. Signal no. 2 is ascribed to the tricoordinated phosphino nucleus of the adduct, "mixed" with the signal of chlorodiphenylphosphine in equilibrium with the adduct. [d] Solutions of the 1:1 adducts containing 1 additional mol equiv of either the chlorophosphine or the tertiary phosphine also had two ^{31}P nmr signals. [e] Very broad signal.

when heated to room temperature. (4) The reaction of triethylphosphine with dichloromethylphosphine gives a 1:1 adduct, $[(C_2H_5)_3PP(CH_3)Cl]Cl$, which is also transformed into triethyldichlorophosphorane[14] and the corresponding tetraethylcyclotetraphosphine[16,17] upon heating.

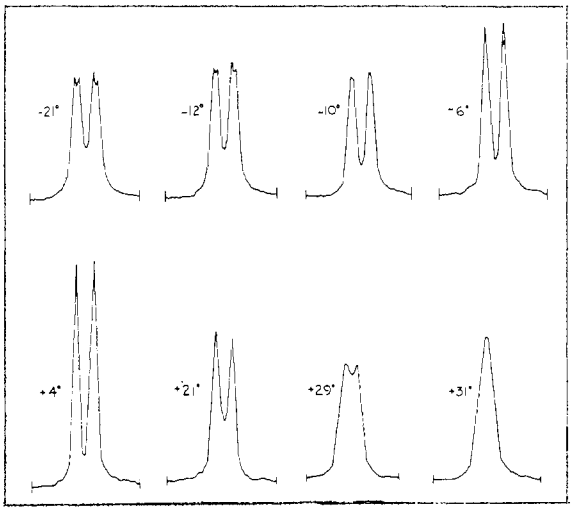


Figure 1. Variable-temperature ^1H nmr spectrum of the $(CH_3)_3P \cdot PCl(C_6H_5)_2$ adduct, in 1.2 M $CDCl_3$ solution, at 60 Mcps. All spectra are at the same amplitude. At −21°, the signal was a doublet of doublets, J = 13.4 cps, J = 3.0 cps, τ 7.70 ppm *vs.* TMS = 10. The separation between the lines was 13.4 cps at +4° and 8.0 cps at +29°. Pure $(CH_3)_3P$ in $CDCl_3$, at room temperature, gave one doublet, J = 1.9 cps at τ 9.00 ppm.

The purpose of the present investigation was to study the reactions of a given series of tertiary phosphines of decreasing basicity and nucleophilicity:[5,6] $(CH_3)_3P$, $(CH_3)_2PC_6H_5$, $(CH_3)P(C_6H_5)_2$, with a series of halophosphines of increasing electrophilicity: $ClP(C_6H_5)_2$, $Cl_2PC_6H_5$, Cl_3P. Our objective was to characterize the first intermediate which is produced in these reactions by means of ^{31}P nmr and variable-temperature ^1H nmr, and to ascertain the effect of temperature on this type of intermediate. The known[19] difluorophenylphosphine was included in the investigation in order to ascertain the effect of halogen electronegativity on the behavior of the electrophile toward the nucleophile.

Results

Reactions of Tertiary Phosphines with Chlorodiphenylphosphine. Trimethylphosphine (**1**) and the monochlorophosphine **2** react at 20° in the absence of solvent or in benzene solution. The product is a colorless, crystalline, 1:1 adduct, **3**, which is insoluble in benzene but soluble in methylene chloride. The adduct undergoes no significant changes at 20° in the solid state or in solutions, if moisture is excluded. The adduct reverts to its precursors, the phosphine **1** and the chlorophosphine **2**, at 100° under vacuum.

The variable-temperature ^1H nmr spectrum of adduct **3** in $CDCl_3$ is reproduced in Figure 1. At −21° the signal is a doublet of doublets. At about −10° the signal begins to look like one doublet which coalesces to a broad band at +31°. The low-temperature spectrum shows that the protons of the methyl groups are engaged in spin–spin splitting with the two types of phosphorus nuclei. The ratio of the aliphatic protons to the aromatic protons (not shown in Figure 1) confirms the 1:1 stoichiometry in the formation of adduct **3**.

Elucidation of the structure of the 1:1 adduct **3** in the solid state awaits an X-ray crystallographic analysis. However, the nature of the solutions of the adduct in aprotic solvents can be discussed in the light of the ^1H nmr spectra shown in Figure 1 and of the ^{31}P nmr spectra summarized in Table I. These data are consistent with the existence in the solutions of a relatively rapid equilibrium between the two trivalent phosphorus compounds, **1** and **2**, on the one hand, and the adduct **3**, on the other hand. This equilibrium is shifted in favor of the adduct at 20° in 1–3 M methylene chloride solutions. The adduct is formulated as an ion pair in which the cation has a P–P covalent bond joining tetracoordinated and tricoordinated phosphorus.

$$\underset{\mathbf{1}}{(CH_3)_3P} + \underset{\mathbf{2}}{ClP(C_6H_5)_2} \rightleftharpoons \underset{\mathbf{3}}{[(CH_3)_3\overset{+}{P}P(C_6H_5)_2]Cl^-}$$

$(CH_3)_3PCl_2$. We have no explanation for the discrepancy between our results and those described in ref 13.

(19) (a) R. Schmutzler, *Chem. Ber.*, **98**, 552 (1965); (b) F. Seel, K. Rudolph, and R. Budenz, *Z. Anorg. Allgem. Chem.*, **341**, 196 (1965).

Table I shows that the ^{31}P nmr spectrum of adduct **3** in solution has two signals. The signal at lower magnetic field (signal no.1) should represent the average of the value of the tetracoordinated phosphonium nucleus[20,21] and the value of the small amount of trimethylphosphine that is present in equilibrium with the adduct. The average is therefore weighed in favor of the adduct. Note that dilution causes only a slight shift to higher magnetic field (slight shift of the equilibrium to the left, hence a little more of the positive phosphine). The addition of 1 mol equiv of chlorophosphine **2** to the solution of the adduct **3** causes only a slight shift of signal no. 1 to lower magnetic field (slight shift of the equilibrium to the right, hence less of the positive phosphine). However, the addition of 1 mol equiv of trimethylphosphine (**1**) to the solution of the adduct **3** produces a dramatic shift of signal no. 1 to high magnetic field. This is to be expected since signal no. 1 is now the average of about equal amounts of the phosphonium nucleus, which has a negative shift, and of the phosphine nucleus, which has a relatively large positive shift.

The P signal at higher magnetic field (signal no. 2) in the spectrum of the solution of the pure adduct **3** corresponds to the average of the value of the tricoordinated phosphine nucleus[20,22,23] in the adduct and the value of the small amount of chlorophosphine **2** which is present in equilibrium with the adduct. This average is again weighed in favor of the adduct. Dilution causes only a slight shift of signal no. 2 to lower field (*i.e.*, there is a little more of the negative chlorophosphine). The addition of 1 mol equiv of chlorophosphine **2** to the solution of the adduct leads to a large shift of signal no. 2 to lower field. Now, signal no. 2 is the average of about equal amounts of the phosphine nucleus in the adduct (which has a positive shift) and the chlorophosphine **2** (which has a large negative shift). The addition of 1 mol equiv of the tertiary phosphine **1** to the solution of adduct **3** results in a very small change, as would be expected from the interpretation given above.

It should be emphasized that the two phosphorus signals, no. 1 and no. 2, in the spectrum of adduct **3** show no detectable P,P spin–spin splitting[23] at room temperature, and that the addition of more chlorophosphine **2** or of more trimethylphosphine **1** does not increase the number of signals, but simply changes the value of one of the signals very strongly.

Dimethylphenylphosphine (**4**) reacts with chlorodiphenylphosphine (**2**) at 20° to give the 1:1 adduct **5**, which is analogous to the adduct made from trimethylphosphine. The ^{31}P nmr data are summarized in Table I. The ^{1}H nmr spectrum of a $CDCl_3$ solution of adduct **5** at 20° has a doublet at τ 7.52 ppm, J_{HCP} = 12.2 cps. The signal for the parent phosphine **4** is at τ 8.75 ppm, J_{HCP} = 2.7 cps.

$$\underset{\mathbf{4}}{(C_6H_5)(CH_3)_2P} + \underset{\mathbf{2}}{PCl(C_6H_5)_2} \rightleftharpoons \underset{\mathbf{5}}{[(C_6H_5)(CH_3)_2\overset{+}{P}P(C_6H_5)_2]Cl^-}$$

The adduct **5** reverts to its original components, the phosphine **4** and the chlorophosphine **2**, at 90° under vacuum. There is no evidence for the transfer of the chlorine atom from **2** to **4** during the thermal decomposition of adduct **5**.

Methyldiphenylphosphine (**6**) does not react with the chlorophosphine **2** under the conditions which resulted in the conversion of the more basic phosphines, **1** and **4**, into the corresponding 1:1 adducts **3** and **5**.

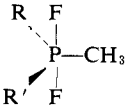
$$\underset{\mathbf{6}}{(C_6H_5)_2(CH_3)P} + \underset{\mathbf{2}}{PCl(C_6H_5)_2} \not\rightarrow \text{no reaction}$$

Reaction of Tertiary Phosphines with Dichlorophenylphosphine (7) and with Phosphorus Trichloride. Trimethylphosphine (**1**) reacts with dichlorophenylphosphine (**7**) at 20° to give a white solid which soon becomes brown-orange. This solid is not appreciably soluble in benzene or in methylene chloride. We have not elucidated the structure of this solid, but we feel reasonably certain that, under the conditions given, it does not contain trimethyldichlorophosphorane, $(CH_3)_3PCl_2$, nor pentaphenylcyclopentaphosphine, $(C_6H_5P)_5$.[18]

Dimethylphenylphosphine (**4**), but not methyldiphenylphosphine (**6**), reacts with the dichlorophosphine **7** at 20°. The three tertiary phosphines, **1**, **4**, **6**, react with phosphorus trichloride at 20°. In all these cases, the reactions produce white solids which soon become brown-orange. None of the solids have appreciable solubility in benzene or in methylene chloride, and all are very sensitive to moisture. Apparently, these solids are formed in reactions which have complex stoichiometry.[7]

Reaction of Tertiary Phosphines with Difluorophenylphosphine. Difluorophenylphosphine[19] (**8**) oxidizes the tertiary phosphines to the corresponding difluorotrialkylphosphorane **9** and difluoroalkylarylphosphoranes **10** and **11**. The second product of these reactions is pentaphenylcyclopentaphosphine (**12**). The difluorophosphoranes[24–26] and the cyclophosphine[4,27] are well-known compounds.

$$\underset{\mathbf{1},\ R = R' = CH_3;\ \mathbf{4},\ R = CH_3;\ R' = C_6H_5;\ \mathbf{6},\ R = R' = C_6H_5}{RR'(CH_3)P} + \underset{\mathbf{8}}{PF_2(C_6H_5)} \longrightarrow \underset{\mathbf{12},\ \partial^{31}P = +4.5\text{ ppm}}{(C_6H_5P)_5} +$$



	$\partial^{31}P$, ppm	J_{PF}, cps
9, R = R′ = CH_3	+13.9	553 (triplet)
10, R = CH_3; R′ = C_6H_5	+27.9	589 (triplet)
11, R = R′ = C_6H_5	+41.1	638 (triplet)

(20) J. H. Letcher and J. R. Van Wazer in "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1967.

(21) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

(22) (a) E. Fluck and K. Issleib, *Chem. Ber.*, **98**, 2674 (1965); (b) E. Fluck and H. Binder, *Z. Anorg. Allg. Chem.*, **354**, 113 (1967).

(23) For $(C_6H_5)_2PP(C_6H_{11})_2$, J_{pp} = 224 cps; see ref 22.

(24) (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963); (b) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965); (c) R. Schmutzler, *Inorg. Chem.*, 7, 1327 (1968); (d) R. Schmutzler, "Halogen Chemistry," Vol. 2, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, p 31; (e) G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 1903 (1967); (f) W. C. Firth, S. Frank, M. Garber, and V. P. Wystrach, *ibid.*, **4**, 765 (1965); (g) R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, **3**, 753 (1964).

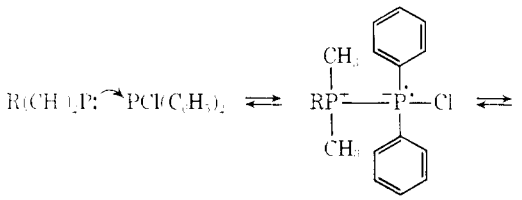
(25) Analogous difluorophosphoranes were made from tertiary phosphines and sulfur tetrafluoride; for example ($\partial^{31}P$ and J_{PF} values are given, respectively, in parentheses): $(C_6H_5)_3PF_2$ (+58.1 ppm, 659 cps); $(C_6H_5)_2(C_2H_5)PF_2$ (+44.1 ppm, 646 cps); $(C_6H_5)(C_2H_5)_2PF_2$ (+29.1 ppm, 687 cps); $(n\text{-}C_4H_9)_3PF_2$ (+16.0 ppm, 584 cps, see ref 26).

(26) (a) F. Ramirez and C. P. Smith, unpublished; (b) F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, **33**, 3787 (1968). The value J_{PF} = 65.9 cps for $(C_6H_5)_3PF_2$ in this reference is a typographical error; it should be 659 cps.

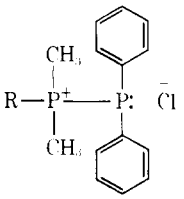
(27) The reported value for the P shift of $(C_6H_5P)_5$ is +4.6 ppm; see ref 4c.

Discussion

The tertiary phosphines are highly polarizable nucleophiles, hence soft bases in Pearson's nomenclature.[6,28,29] The chlorophosphines are electrophiles of relatively high electron density, *i.e.*, soft acids. The adducts **3** and **5** can, therefore, be regarded as products of the interaction between soft bases and acids. This interaction can be represented by formula **13** which may represent a true intermediate or may correspond to the transition state in the displacement of chloride ion from the chlorophosphine by the tertiary phosphine. Note

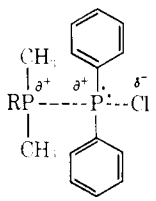


13



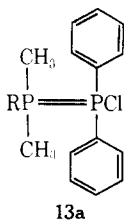
3, R = CH_3
5, R = C_6H_5

that a direct displacement of chloride ion implies the appearance of partial positive charge on the phosphorus of the nucleophile and of the electrophile depending on the relative extent of bond making and bond breaking in the transition state[30] **14**. This would justify the requirements of high polarizability of the nucleophile and of relatively high electron density of the electrophile, *i.e.*, of "soft" base–acid character of the reagents.[5,6,28–30]

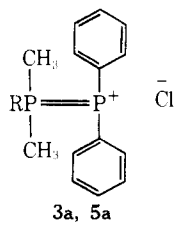


14

Formulas **13a** and **3a**, **5a** suggest the possibility of resonance stabilization in the intermediate **13** and in the adducts **3** and **5**, respectively.



13a



3a, 5a

The dissociation of the adducts **3** and **5** into the original trivalent phosphorus components is simply a nucleophilic attack by chloride ion on trivalent phosphorus, which is made electrophilic by the phosphonium ligand in **3** and **5**; the leaving group is now the tertiary phosphine.

Another mechanism for the formation of adducts **3** and **5** involves a nucleophilic attack by the tertiary phosphine on the chlorine[30] of the chlorophosphine to give the ion pair **15**. These could combine to form **16** which ionizes to the adducts **3** and **5**.

$$R(CH_3)_2P + ClP(C_6H_5)_2 \longrightarrow \underset{\mathbf{15}}{[R(CH_3)_2\bar{P}Cl + \bar{P}(C_6H_5)_2]} \longrightarrow$$

$$\underset{\mathbf{16}}{[R(CH_3)_2(Cl)PP(C_6H_5)_2]} \longrightarrow \mathbf{3, 5}$$

Nucleophilic attacks by trivalent phosphorus on certain halogenated compounds are known.[30] However, as pointed out by Miller,[30] the tendency for these attacks on halogen depends, among other things, on the acidity of the conjugate acid, HPR_2, of the leaving group, $\bar{P}R_2$. The secondary phosphine, $HP(C_6H_5)_2$, is a very weak acid and this factor alone would render the chlorophosphine unsuitable as a substrate on which to perform nucleophilic attacks by phosphorus on halogen.

If the adduct were the ion pair[31,32] **15**, it should react with more chlorodiphenylphosphine to form tetraphenylbiphosphine and chlorotrimethylphosphonium chloride. The biphosphine is known to have $\delta^{31}P = +15.2$ ppm[22] and is a stable, easily characterized solid. We found no evidence for its formation.

$$\underset{\mathbf{15}}{(CH_3)_3\overset{+}{P}Cl\,\bar{P}(C_6H_5)_2} + PCl(C_6H_5)_2 \longrightarrow$$

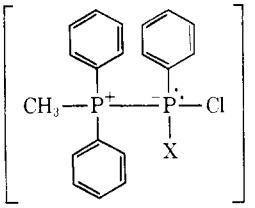
$$(CH_3)_3\overset{+}{P}Cl\bar{Cl} + (C_6H_5)_2PP(C_6H_5)_2$$
not observed

We have no information on the structure of the methylene chloride insoluble adducts made from tertiary phosphines and dichlorophosphines[13] or PCl_3.[7] By analogy, they could be formed as

$$R_3P + PCl_2X \rightleftharpoons \underset{\mathbf{17}}{[R_3\overset{+}{P}PClX]Cl} \xrightarrow{R_3P} \underset{\mathbf{18}}{[R_3\overset{+}{P}PX\overset{+}{P}R_3]2\bar{Cl}}$$

where X = C_6H_5 or Cl.

The lack of reactivity of methyldiphenylphosphine with both chlorodiphenyl- and dichlorophenylphosphines is significant and could reflect a steric repulsion in the transition state leading to the adduct, or a decrease in nucleophilicity of the phosphine.[33]



19, not formed; X = C_6H_5 or Cl

(28) (a) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963); (b) R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).

(29) (a) H. G. Schuster-Walden and F. Basolo, *ibd.*, **88**, 1657 (1966); (b) E. M. Thorsteinson and F. Basolo, *ibid.*, **88**, 3929 (1966).

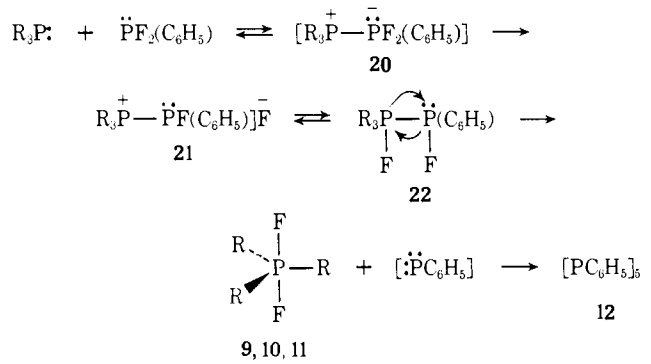
(30) B. Miller in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1965, p 133.

(31) The P shift of lithium diphenylphosphide, $[LiP(C_6H_5)_2 \cdot 1\text{-dioxane}]$ has been given as +23.0 ppm; the sodium analog had +24.4 ppm; see ref 32. Since one of the signals for adduct **3** was +24.7 (Table I) the presence of $P^-(C_6H_5)_2$ has to be excluded. Note also that adduct **5** did not give a signal at that magnetic field (Table I); hence no $P^-(C_6H_5)_2$ was present.

(32) (a) E. Fluck and K. Issleib, *Z. Naturforsch.*, **206**, 1123 (1965); (b) *Z. Anorg. Allg. Chem.*, **339**, 274 (1965).

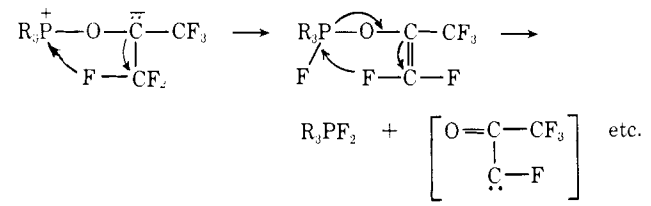
(33) R. D. Temple and J. E. Leffler, *Tetrahedron Lett.*, 1893 (1968).

The mechanism of the reaction of tertiary phosphines with difluorophenylphosphine can be formulated also as a nucleophilic attack by phosphorus on electrophilic phosphorus. The main difference is that fluorine has a greater tendency than chlorine to form compounds with pentacoordinated phosphorus,[21,24] **22**. From **22**, the observed products, the difluorophosphoranes, **9–11**, and the cyclophosphine, **12**, can be reasonably derived. Since fluoride ion is a poor leaving group, the conversion of **20** into **22** may proceed directly rather than through the ion pair, **21**.



The arguments presented in connection with the reactions of trivalent phosphorus compounds with "positive halogens"[30] would suggest that a direct nucleophilic attack on halogen by tertiary phosphines is less likely in the fluorophosphines than in the chlorophosphines. However, further work is required to settle this aspect of the mechanism of formation of difluorophosphoranes from the difluorophosphine.

We have discussed the formation of difluorophosphoranes,[34,35] $(RO)_3PF_2$, $(R_2N)_3PF_2$, and R_3PF_2, from the reactions of phosphites, triaminophosphines, and tertiary phosphines with hexafluoroacetone,[36] CF_3COCF_3, and with trifluoroacetophenone, $CF_3COC_6H_5$. The proposed mechanisms[34,35] involve the attack by the nucleophile on the oxygen atom of the activated carbonyl group, *i.e.*, the "softer" acid rather than on the fluorine of the fluoro ketones, or on the carbon of the carbonyl.



One of the simplest routes to difluorophosphoranes is the reaction of trivalent phosphorus compounds with sulfur tetrafluoride,[24–26] SF_4. These reactions can be written as nucleophilic attacks on sulfur (A), etc., or on fluorine (B), etc. This question has not been settled.

The conversion of triphenylphosphine into difluorotriphenylphosphorane by perfluoro-*N*-fluoropiperidine has been interpreted[37] as an attack by phosphorus on the fluorine of the F—N< bond. If this is indeed the mechanism, the point of attack may be related to the special features of the "electrophile", *i.e.*, to the 11 fluorine atoms in it.

Experimental Section

All reactions were carried out in an atmosphere of argon. All solvents were thoroughly dried. The reagents were carefully purified.

Reaction of Trimethylphosphine with Chlorodiphenylphosphine. (a) In the Absence of Solvent. The chlorophosphine was added to 1 mol equiv of trimethylphosphine at 25°, with stirring. The reaction was exothermic and yielded a colorless, crystalline adduct, **3**, within 10 min. The adduct, **3**, was soluble in CH_2Cl_2 and $CDCl_3$; the solutions did not change within 12 hr at 20°. The adduct was insoluble in hexane and in benzene.

(b) **In Benzene.** The chlorophosphine was added to 1 mol equiv of trimethylphosphine in benzene solution. The adduct, **3**, precipitated in quantitative yield within a few minutes and was collected by filtration.

The adducts made by procedures (a) and (b) were identical. The ^{31}P nmr spectra of solutions of adduct **3** in CH_2Cl_2 are summarized in Table I.

Thermal Dissociation of Adduct 3. The trimethylphosphine–chlorodiphenylphosphine 1:1 adduct, **3** (3.2 g), was placed in a bath preheated to 100°, under vacuum (0.2 mm). The adduct melted and partly distilled. The distillate was collected in a trap and was shown to be trimethylphosphine (70% of the theoretical yield). The residue was identified as chlorodiphenylphosphine (100% of the theoretical yield).

Reaction of Dimethylphenylphosphine with Chlorodiphenylphosphine. This reaction gave the corresponding crystalline adduct, **5**, in the absence of solvent using procedure a described above. The ^{31}P nmr spectra of solutions of adduct **5** in CH_2Cl_2 are summarized in Table I.

Thermal Dissociation of Adduct 5. The dimethylphenylphosphine–chlorodiphenylphosphine adduct (**5**) was placed in a bath preheated to 90°, under vacuum (0.02 mm). The distillate proved to be dimethylphenylphosphine (81% of the theory). The residue was chlorodiphenylphosphine (100% of the theory).

Attempted Reaction between Methyldiphenylphosphine and Chlorodiphenylphosphine. No changes were detected when equimolar amounts of the reagents were kept 24 hr at 20°. The mixture was dissolved in CH_2Cl_2; the ^{31}P nmr spectrum of the solution had one signal at +27.6 ppm due to $CH_3(C_6H_5)_2P$ and one signal at −81.8 ppm due to $PCl(C_6H_5)_2$.

Reactions of Tertiary Phosphines with Difluorophenylphosphine. Difluorophenylphosphine,[19] $\delta^{31}P = -207.0$ ppm, $J_{PF} = 1180$ cps (in $CDCl_3$), was prepared by the reaction of NaF with dichlorophenylphosphine as described; the literature[19] reported $\delta^{31}P = -208.3$ ppm, $J_{PF} = 1174$ cps.

Reaction with Trimethylphosphine. The tertiary phosphine was added to 1 mol equiv of the fluorophosphine at 20°. No reaction was noted within 15 min; the mixture was then dissolved in CH_2Cl_2 and the solution (3.5 *M*) was kept 5 days at 20°. The ^{31}P nmr spectrum had two signals: $\delta^{31}P = +4.5$ ppm due to $(C_6H_5P)_5$[4c] (**12**) (*vide infra*), and $\delta^{31}P = +13.9$ ppm, $J_{PF} = 553$ cps (triplet); reported for trimethyldifluorophosphorane[24a] (**9**), $J_{FP} = 545$ cps (from the ^{19}F nmr spectrum).

Reaction with Dimethylphenylphosphine. (a) An equimolar mixture of the tertiary phosphine and the fluorophosphine was kept

(34) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6276 (1967).

(35) (a) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Lett.*, 2151 (1966); (b) F. Ramirez, C. P. Smith, and S. Meyerson, *ibid.*, 3651 (1966); (c) F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6283 (1967).

(36) N. P. Gambaryan, E. M. Rokhlin, Yu. V. Zeifman, C. Ching-Yu, and I. L. Knunyants, *Angew. Chem., Int. Ed. Engl.*, **5**, 947 (1966).

(37) R. E. Banks, R. N. Haszeldine, and R. Hatton, *Tetrahedron Lett.*, 3993 (1967).

15 min at 85°. Distillation gave dimethylphenyldifluorophosphorane[25,26] (**10**) in 91% yield. This substance had bp 30° (0.02 mm). The ^{1}H nmr spectrum of a fresh solution in $CDCl_3$ at 25° had six protons at τ 8.20 ppm, J_{HP} = 17.7 cps, J_{HF} = 12.5 cps (doublet of triplets), and five aromatic protons. For $(C_6H_5)(CH_3)_2P$: τ 8.75 ppm, J_{HP} = 2.7 cps. See ^{31}P nmr data in the Results section.

The residue from the above distillation solidified and was characterized as $(C_6H_5P)_5$ (**12**), mp 150–155°, $\delta^{31}P$ = +4.3 ppm; the material was isolated in 85% yield.

(b) An equimolar mixture of dimethylphenylphosphine and difluorophenylphosphine was kept 5 min at 20°. The mixture was dissolved in CH_2Cl_2 and the solution was analyzed by ^{31}P nmr spectrometry. It contained unreacted tertiary phosphine and fluorophosphine and relatively small amounts of the phosphorane, **10**, and $(C_6H_5P)_5$, **12**, but no other intermediates or by-products.

Reaction with Methyldiphenylphosphine. Equimolar amounts of the reagents were kept 15 min at 20°. No reaction was detected. Reaction was complete after 7 days at 20°. The products were methyldiphenyldifluorophosphorane[25,26] (**11**) and $(C_6H_5P)_5$ (**12**).

Conformationally Isomeric Carbonium Ions in Condensed Ring Systems[1]

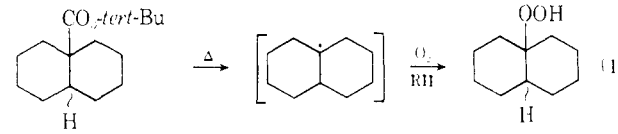
Raymond C. Fort, Jr.,[2] Rex E. Hornish,[3] and Gao A. Liang

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44240. *Received May 2, 1970*

Abstract: The *p*-nitrobenzoate esters of cis- and trans-bridgehead alcohols in the decalin, hydrindan, and perhydropentalene systems have been synthesized stereospecifically and solvolyzed in aqueous acetone. The observed rates do not correspond to those expected if both stereoisomers of a given system lead to the same carbonium ion, and the product composition is a function of the stereochemistry of the starting material. When solvolysis is interrupted before completion, recovered *p*-nitrobenzoate has not isomerized. It is, therefore, concluded that solvolysis proceeds by way of conformationally isomeric carbonium ions.

Although many studies have been made of bridgehead carbonium ion reactivity in bridged polycyclic systems,[4–6] bridgeheads in condensed ring systems have received scant notice. There are many qualitative observations of carbonium ion formation at such sites,[7–16] but information of a quantitative sort bearing upon the ease of formation of these bridgehead carbonium ions and their subsequent behavior is lacking. The greater flexibility of the condensed rings offers the possibility that they will be of "normal" reactivity;[6] interesting stereochemical problems are raised by the existence of the condensed rings in diastereomeric forms.

An example of this latter point may be found in the radical chemistry of the decalins. When the *tert*-butyl peresters of the decalin-9-carboxylic acids are decomposed thermally in the presence of high pressures of oxygen (eq 1),[17] the stereochemistry of the hydro-



(1)

peroxide product is found to be a function of the stereochemistry of the perester precursor. This observation implies the brief existence of two discrete 9-decalyl radicals. A similar result was obtained when the isomeric 9-decalyl carbinyl hypochlorites were decomposed.[18] In each case, it was suggested that the distinction between the two radicals is a conformational one: a cis-like radical relaxing to a trans-like one.

It seemed to us that a search for such behavior in a carbonium ion process might well prove interesting, and it is thus that we report in this paper our results on the solvolysis of bridgehead derivatives of bicyclo[4.4.0]decane (decalin), bicyclo[4.3.0]nonane (hydrindane), and bicyclo[3.3.0]octane (perhydropentalene). Our aims are to place these systems in the general scheme of bridgehead reactivity and to demonstrate that their reactions are best rationalized by postulating the intervention of conformationally isomeric carbonium ions.

Results

The synthesis of the compounds studied is outlined in Chart I and detailed in the Experimental Section. The necessary alkenes were obtained by literature methods,[14,16,19–21] and their conversion to alcohols

(1) Portions of this work have been reported previously: R. C. Fort, Jr., and R. E. Hornish, *Chem. Commun.*, 11 (1969); Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN 2.
(2) Author to whom inquiries should be addressed.
(3) University Fellow, 1969–1970; abstracted from the Ph.D. Dissertation of R. E. H., Kent State University, 1970.
(4) D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954).
(5) U. Schollkopf, *Angew. Chem.*, 72, 147 (1960).
(6) R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.*, 1, 283 (1966).
(7) G. R. Clemo and J. Ormston, *J. Chem. Soc.*, 1778 (1932).
(8) A. Zlatkis and E. A. Smith, *Can. J. Chem.*, **29**, 162 (1951).
(9) F. E. Condon, *J. Amer. Chem. Soc.*, **73**, 3938 (1951).
(10) W. G. Dauben, R. C. Tweit, and R. L. MacLean, *ibid.*, 77, 48 (1955).
(11) H. Köch and W. Haaf, *Angew. Chem.*, 70, 311 (1958).
(12) G. Baddeley and E. Wrench, *J. Chem. Soc.*, 1324 (1959).
(13) R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **81**, 6332 (1959).
(14) H. Christol and G. Solladié, *Bull. Soc. Chim. Fr.*, 1299 (1966).
(15) H. Christol and G. Solladié, *ibid.*, 3193 (1966).
(16) H. Christol and J.-M. Bessiere, *ibid.*, 2141, 2147 (1968).
(17) P. D. Bartlett, R. E. Pincock, J. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, **87**, 2590 (1965).
(18) F. D. Greene and B. R. Lowry, *J. Org. Chem.*, **32**, 875 (1967).
(19) W. P. Campbell and G. C. Harris, *J. Amer. Chem. Soc.*, **63**, 2721 (1941).
(20) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969).
(21) L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **91**, 3870 (1969).