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Preparation and Chemistry of Some Phosphoranes Containing Phosphorus–Sulfur Bonds

Byron C. Burros, Norman J. De'Ath, Donald B. Denney,* Dorothy Z. Denney, and Irving J. Kipnis

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903.

Received April 24, 1978

Abstract: The dithiete, **2**, has been allowed to react with a variety of trivalent phosphorus compounds. In some cases phosphoranes are formed which contain a five-membered ring with two sulfurs bonded to phosphorus. In others unstable phosphoranes may have been formed which then decomposed to a variety of products. Variable temperature NMR studies of the phosphoranes have been conducted. In most cases it was not possible to determine whether the materials are rapidly interconverting trigonal bipyramids or whether they are static or rapidly interconverting square or rectangular pyramids.

Thus far, very few pentacoordinate phosphorus compounds, phosphoranes,[1] have been prepared in which one or more sulfur atoms are bonded to phosphorus. Peake and Schmutzler[2] prepared a number of alkyl and arylthio substituted fluorophosphoranes and studied their variable temperature ^{19}F NMR spectra. They found at low temperatures that the alkylthio and arylthio groups prefer an equatorial position in the trigonal bipyramidal structure (TP) and that there is inhibition to rotation about the P–S bond.

More recently, Trippett and co-workers[3] prepared a series

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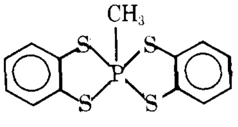
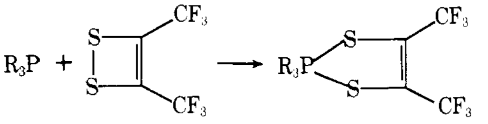
of spirophosphoranes containing sulfur bonded to phosphorus. They studied lone-pair orientations and strain effects in these systems.

The compound **1** has been prepared and its structure has been determined by X-ray analysis.[4] The structure is intermediate between a TP and a square or rectangular pyramid SP (RP). This interesting finding and others have been reviewed.[5]



1

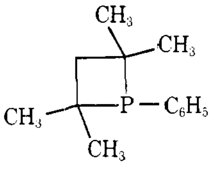
Studies in this laboratory have demonstrated that trivalent phosphorus compounds often react with substances with weak σ bonds to give pentacoordinate phosphorus compounds.[1] One such reactant is the dithiete, **2**. Earlier reports have appeared on some of these reactions.[6] The present work extends these studies and provides full details of some of the previously reported data.[6a]



2

Results and Discussion

Reaction of 2 with Phosphines. The phosphetane **3** reacts readily with **2** to give the phosphorane **4**. Compound **4** has been obtained as a yellow, crystalline solid of considerable stability. Its ^{31}P NMR spectrum has one absorption at δ −17.5 ppm relative to external 85% phosphoric acid.[7] The ^{1}H NMR spectrum of **4** is distinguished by having two absorptions for hydrogens of methyl groups at δ 1.30 ($J_{\mathrm{PCCH}} = 21$ Hz) and 1.80 ($J_{\mathrm{PCCH}} = 21$ Hz). The ^{19}F NMR spectrum shows that all of the fluorines of the trifluoromethyl groups are equivalent. The absorption is found as a doublet at δ +53.9 ($J_{\mathrm{PSCCF}} = 0.2$ Hz). The presence of coupling indicates that the equivalence of the fluorines is not due to ionization or reversible formation of **2** and **3**. Variable temperature ^{1}H NMR studies of **4** from −50 to 147 °C led to no significant changes in the spectra. At the elevated temperatures, decomposition to the phosphetane sulfide occurred. The data do not establish any single structure for **4**. If it is **4**, then ligand reorganization must be occurring between two equivalent TP structures. Similarly, a static SP (RP), **4a**, can accommodate the NMR findings. Recent work of Trippett has shown that compounds analogous to **4**, in which the five-membered ring has been replaced by one containing four trifluoromethyl groups and two oxygens bonded to phosphorus, exist in the solid state as SPs.[8]



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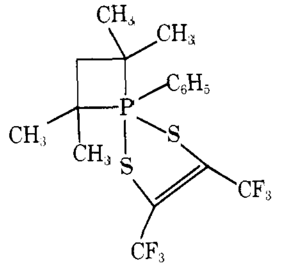

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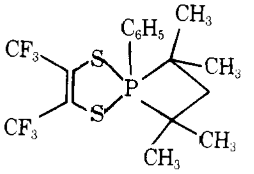
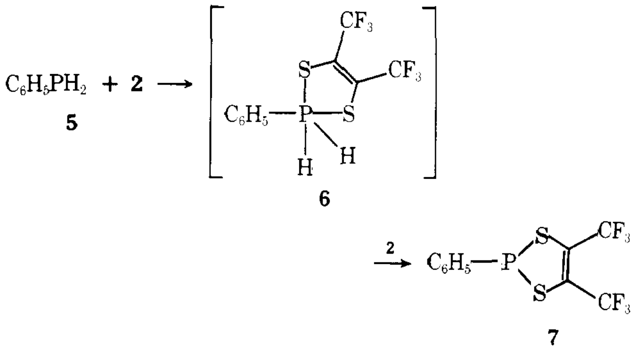
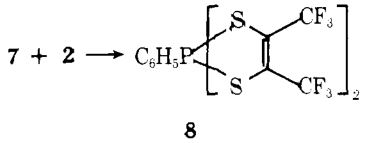


4a

When **2** was allowed to react with phenylphosphine (**5**), the interesting cyclic phosphine **7** was produced. The reaction probably proceeds with initial production of **6** which reacts with more **2** to give **7** and uncharacterized products. The overall stoichiometry was shown to be 1 mol of **5** to 2 mol of **2**. There was no evidence for the production of hydrogen gas.

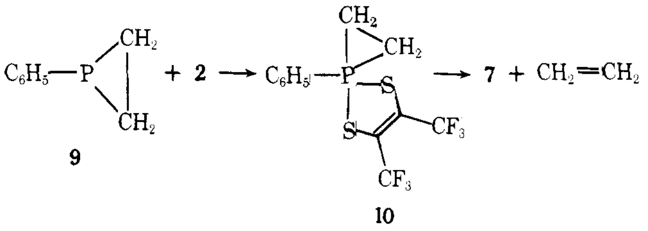


Compound **7** reacts rapidly with **2** at −78 °C to give phosphorane **8**. Compound **8** absorbs at δ −11.5 in its ^{31}P NMR spectrum. The ^{19}F NMR spectrum of **8** shows that all of the fluorines of the trifluoromethyl groups are equivalent and that they are coupled to phosphorus ($J_{\mathrm{PSCCF}} = 2.25$ Hz). These data do not distinguish between TP structures or SP (RP) structures. Variable temperature ^{19}F NMR studies from −100 to 30 °C showed no significant changes in the spectra.



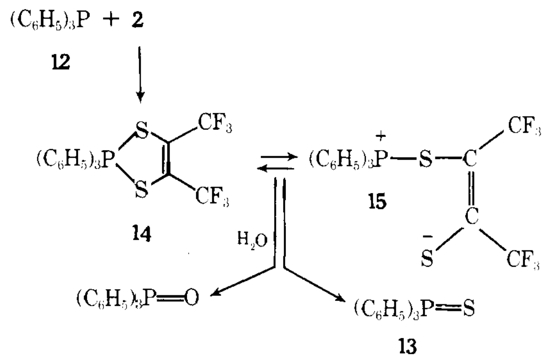
Although compound **8** has been obtained as yellow crystals at −70 °C, attempts to work with the crystals resulted in their conversion into a gum, and finally on attempted sublimation an oil resulted. The mass spectrum of **8** had no molecular ion. An intense peak was found for the sulfide of **7** which is an expected decomposition product of **8**.

When **2** was allowed to react with phenylphosphirane (**9**), compound **7** and 1 mol of ethylene were produced. This interesting reaction is thought to proceed through the intermediacy of the phosphorane **10**, which loses ethylene to give **7**.[6b,9]



Triphenylphosphine (**12**) reacts with **2** to give a reaction mixture which shows two absorptions in its ^{31}P NMR spectrum at δ +40 and +42.5. The latter absorption is due to triphenylphosphine sulfide (**13**). The absorption at δ +40 is probably due to the zwitterion **15**, which may be in equilibrium with the phosphorane **14**. The magnitude of the downfield shift, δ +40, indicates that very little **14** can be present.[10] The compound which has the absorption at δ +40 disappears with the production of triphenylphosphine sulfide. In fact the absorption at δ +40 is not always observed, and in this situation only triphenylphosphine sulfide is found.

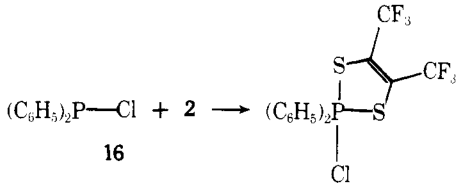
Addition of water to a reaction mixture containing the



material which absorbs at δ +40 led to its disappearance and to the production of triphenylphosphine oxide. This result is in agreement with the suggestion that **15** is present in the reaction mixture.

Phenyldi-*tert*-butylphosphine reacted with **2** to give phenyldi-*tert*-butylphosphine sulfide as the only phosphorus-containing product.

Reactions of 2 with Phosphorus Halides. Diphenylphosphinous chloride (**16**), reacted with **2** to give the phosphorane

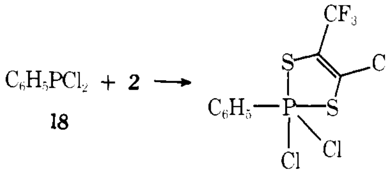


17

17. The ^{31}P NMR absorption for this material was found at δ −28. The compound **17** is relatively stable in methylene chloride. It decomposes fairly rapidly in acetonitrile. The ^{1}H NMR spectrum of **17** shows typical absorptions for aromatic protons. The ^{19}F NMR spectrum at room temperature has one broad absorption at δ +55. This absorption is ca. 113 Hz wide at the base and 30 Hz wide at half-height. The spectrum shows that there is some process that is rendering the fluorines of the trifluoromethyl groups equivalent. The finding of a broad line indicates that at room temperature the ^{19}F signal is near coalescence. This conclusion is amply supported by the ^{19}F NMR spectrum obtained at −50 °C. This spectrum has one absorption at δ +52.8 which is found as a doublet of quartets (J_{FCCCCF} = 10 and J_{FCCSP} = 8.6 Hz). Another absorption is found as a quartet at δ +56.4 (J_{FCCCCF} = 10 Hz). These data show that at −50 °C the process which renders the fluorines of the trifluoromethyl groups equivalent at room temperature is now slow on the ^{19}F NMR time scale. The activation energy, $\Delta G^{\ddagger}$, for this process was calculated to be ca. 13 kcal/mol.[11] Generally the process which renders groups equivalent in phosphoranes is thought to involve intramolecular permutational isomerization.[1] It has been recognized that ionization can often also account for the data, as can bimolecular association–dissociation interactions. These latter processes have been called "irregular".[12] In the case of **17**, it is not possible to distinguish between intramolecular isomerization or an irregular process as a means of accounting for the room temperature ^{19}F NMR data.

The −50 °C ^{19}F NMR data are very adequately satisfied by a TP structure in which the two phenyl groups occupy equatorial positions, the ring spans equatorial–apical positions, and the chlorine occupies the remaining apical position. Such a structure is in complete accord with the various rules that have been developed to account for TP phosphorane structures.[1] Unfortunately, there are four SP (RP) structures which can also account for the −50 °C ^{19}F NMR spectrum, and there is no way to eliminate them as possibilities with the available data.

Phenylphosphonous dichloride (**18**), reacted with **2** to give a material whose ^{31}P NMR spectrum showed one absorption at δ −18. The upfield shift is consistent with the production of the phosphorane **19**. The ^{19}F NMR spectrum of **19** showed one

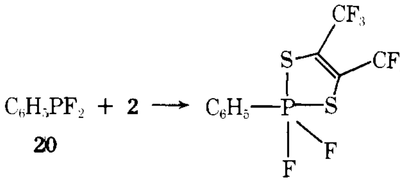


19

absorption at δ +54 at room temperature. At −80°C there was essentially no change in the ^{19}F NMR spectrum from that observed at room temperature. On distillation, **19**, partially decomposed with the production of some **18**.

Phosphorus trichloride did not appear to react with **2** over a period of months.

Phenylphosphonous difluoride (**20**) reacted with **2** to give

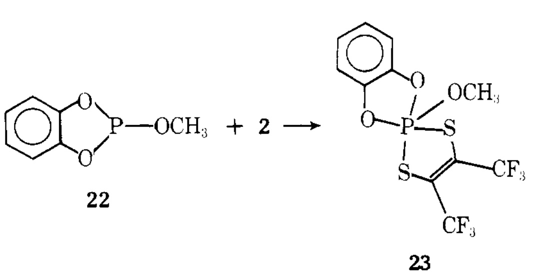


21

a phosphorane whose ^{31}P NMR spectrum was found as a triplet centered at δ +15 (J_{PF} = 980 Hz). The ^{19}F NMR spectrum showed two absorptions. One doublet centered at δ −11 (J_{PF} = 990 Hz) is assigned to the fluorines bonded to phosphorus, and the other, a singlet, at δ +53.5 is due to equivalent fluorines of two trifluoromethyl groups. These data strongly support the structural assignment. They further show that there is no P-F ionization. The P-F coupling constant is intermediate between those found for apical and equatorial fluorines. Perhaps the most satisfying method for explaining the NMR data is to consider that **18** is a TP and that the ring sulfurs exchange apical-equatorial positions as do the fluorines. This is by no means the only way for accounting for the data. The ^{19}F NMR spectrum at −80 °C was essentially unchanged from that found at room temperature.

Reactions of 2 with Phosphites. Some reactions of **2** with bicyclic phosphites have already been reported.[6c]

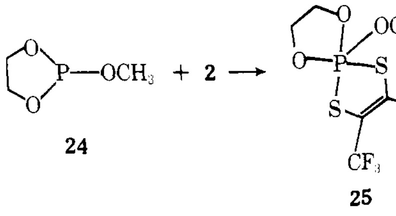
Methyl 1,2-diphenylenephosphite (**22**) reacted readily with



23

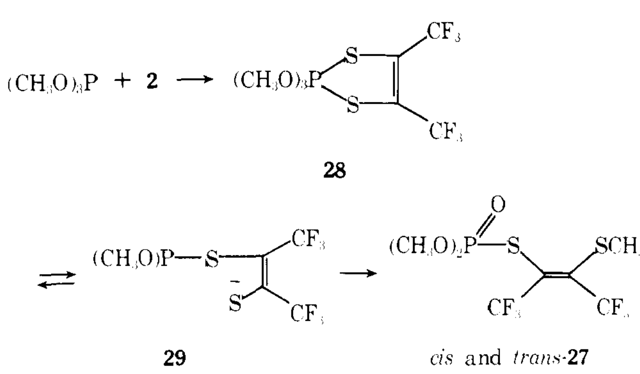
2 to give a liquid phosphorane, **23**, which could be distilled under reduced pressure at 100 °C without decomposition. The ^{1}H, ^{19}F, and ^{31}P NMR spectra of **23** are all in agreement with the assigned structure. The ^{19}F spectrum at room temperature shows that all of the fluorines of the trifluoromethyl groups are equivalent and furthermore that they are coupled to phosphorus (J_{PSCCF} = 3.2 Hz). The fact that coupling is observed demonstrates that the equivalency must be due to inherent symmetry in **23** or to intramolecular isomerization.

Methyl ethylenephosphite (**24**) also reacted with **2** to give a phosphorane, **25**, which is also quite stable. The ^{1}H, ^{19}F, and ^{31}P NMR spectra all support the contention that **25** is a



phosphorane. It is of interest to note that the hydrogens of the ring absorb as a complex multiplet and that there is no change on heating to 130 °C. It is required that either one of the rings become diequatorial before the hydrogens of the ring can become equivalent.

Trimethyl phosphite (**26**) reacted with **2** to give ultimately a mixture of what is believed to be *cis*- and *trans*-phosphorothiolates, **27**. When the reaction was conducted in cyclohexane at 0 °C, there was formed initially a material (ca. 90%) which absorbed at δ +1 along with ca. 10% of trimethyl phosphorothionate. On standing the δ +1 absorption disappeared and it was replaced by one at δ +19. This absorption is attributed to a mixture of *cis*- and *trans*-**27**, whereas the absorption at δ +1 is attributed to either the phosphorane **28** or the zwitterion **29** or a mixture of the two. The mixture of isomers **27** had the correct analyses and showed the expected molecular ion in its mass spectrum. The ^{31}P NMR absorption is in the correct region for a mixed thiooxyphosphate. The ^{1}H NMR spectrum has two doublets at δ 3.98 (J_{POCH} = 13 Hz) and 3.86 (J_{POCH} = 13 Hz) in the ratio 3.3:1. There are also two singlets at δ 2.58 and 2.50 in the ratio 3.15:1. These data suggest the proposed structures as *cis*- and *trans*-**27**. Triethyl phosphite behaved similarly; however, the intermediate phosphorane was more stable as would be expected if the decomposition involves an S$_N$2 reaction on carbon, ethyl being less reactive than methyl.



The results of this study indicate that reactions of **2** with trivalent phosphorus compounds are extremely facile and stable phosphoranes often are products. The phosphoranes do not seem to be as stable as their oxygen-containing counterparts. For example, Ramirez and co-workers[13] have prepared a number of phosphoranes by condensation of trivalent phosphorus compounds with hexafluorobiacetyl. These materials contain a five-membered ring which is the same as those reported here except that oxygens replace the sulfur atoms. Where comparisons can be made, it is quite clear that the hexafluorobiacetyl derivatives are more stable than the dithiete derived phosphoranes.

Experimental Section

^{1}H NMR spectra were recorded with Varian A-60, T-60, and HA-100 NMR spectrometers. The ^{31}P and ^{19}F NMR spectra were recorded with a Varian HA-100 NMR spectrometer. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-7 mass spectrometer. The dithiete **2** was prepared according to the procedure reported in the literature.[14]

Reaction of the Phosphetane 3 with 2. A solution of 1.13 g (0.005 mol) of **2** in 3 mL of methylene chloride was added dropwise with stirring to a solution of 1.03 g (0.005 mol) of **3** in 2 mL of methylene chloride at −78 °C. When half of the solution of **2** had been added, the product began to precipitate; 2 mL of methylene chloride was added to solubilize the product. The last quarter of the solution of **2** was added at −20 °C. The product was recrystallized twice from methylene chloride by slowly cooling the reaction mixture to −20 °C. The mother liquor was removed with a pipette; the crystals were washed with 1-2 mL of methylene chloride at −78 °C. This procedure yielded 1.3 g (60%) of product. One recrystallization from carbon tetrachloride gave 0.54 g of yellow prisms, mp 109-112 °C (sealed tube).

Anal. Calcd for $C_{17}H_{19}F_6PS_2$: C, 47.30; H, 4.43. Found: C, 47.05; H, 4.52.

The mass spectrum gave a molecular ion *m/e* 432 (calcd, 432).

The ambient and reduced temperature NMR spectra of **4** were recorded on methylene chloride solutions. The elevated temperature spectra were obtained on an *o*-dichlorobenzene solution.

Reaction of Phenylphosphine (5) with 2. In a typical experiment, 4.52 g (0.02 mol) of **2** in 5 mL of methylene chloride was added dropwise with stirring to a solution of 2.2 g (0.02 mol) of **5** in 10 mL of methylene chloride at −78 °C. The reaction mixture was allowed to warm to room temperature and it was stirred for 2 h. The solvent was distilled and the residue was distilled in vacuo to give 3.09 g (46%) of **7**, bp 87-89 °C (1.5 mm).

Anal. Calcd for $C_{10}H_5F_6PS_2$: C, 35.90; H, 1.50. Found: C, 35.70; H, 1.79.

The mass spectrum gave a molecular ion *m/e* 334 (calcd, 334).

Preparation of 8 from Phenylphosphine (5) and 2. A solution of 2.26 g (0.01 mol) of **2** in 5 mL of methylene chloride was added dropwise with stirring to a cooled, −78 °C solution of **5** (0.55 g, 0.005 mol) in 5 mL of methylene chloride. After 1 h the ^{31}P NMR spectrum of the reaction mixture had two absorptions, one at δ +44, which was due to **7** (70%), and another at δ −11.5, **8** (30%). Another portion, 0.7 g, of **2** was added at −78 °C. The ^{31}P NMR spectrum of the reaction mixture showed 20% **7** and 80% **8**. The product **8** could be obtained as yellow crystals by cooling the reaction mixture to −70 °C. Attempts to isolate the material led to its decomposition.

Reaction of Triphenylphosphine (12) with 2. A solution of 0.216 g (0.001 mol) of **2** in 1 mL of methylene chloride was added dropwise to a solution of 0.262 g (0.001 mol) of triphenylphosphine in 2 mL of methylene chloride at −78 °C. The ^{31}P NMR spectrum of the reaction mixture had two absorptions at δ +42.5 and +40. Addition of authentic triphenylphosphine sulfide augmented the absorption at δ +42.5. On standing the absorption at δ +40 disappeared and the δ +42.5 peak increased in intensity. Addition of water to a reaction mixture containing the δ +40 absorbing material led to its disappearance and the production of a new absorption at δ +28 which is due to triphenylphosphine oxide.

Reaction of Diphenylphosphinous Chloride (16) with 2. In a typical experiment, 0.59 g (0.007 mol) of **2** in 1.0 mL of methylene chloride was added to 1.55 g (0.007 mol) of **16** in 5 mL of methylene chloride at −78 °C. The reaction mixture was allowed to warm to room temperature and the solution was concentrated with a stream of nitrogen. The ^{31}P NMR spectrum of the reaction mixture indicated that there was present ca. 15% of diphenylphosphinous chloride and 85% of the phosphorane. The various spectral measurements reported were obtained on this solution.

Reactions of Phenylphosphonous Difluoride (20) and Dichloride (18) with 2. These substances were allowed to react with equimolar amounts of **2** in methylene chloride at −78 °C. Attempts to isolate the products led to decomposition. The product **19** from **18** absorbs at δ −18.5 in the ^{31}P NMR and δ +54 in the ^{19}F NMR. The spectral data for **21** are reported in the text.

Reaction of 22 with 2. A solution of 1.7 g (0.0075 mol) of **2** in 2 mL of methylene chloride was added dropwise with stirring to a solution of 1.27 g (0.0075 mol) of **22** in 3 mL of methylene chloride at −78 °C. The solvent was removed and the residue was distilled, bp 100-102 °C (0.05 mm), to give 1.1 g (37%) of **23**. A satisfactory hydrogen analysis was obtained. The carbon was 0.7% high. The mass spectrum showed a molecular ion at *m/e* 396 (calcd 396). Compound **23** absorbs at δ +17.5 in its ^{31}P NMR spectrum. The ^{19}F NMR spectrum has a doublet centered at δ +54 (J_{PSCCF} = 3.2 Hz).

Reaction of 24 with 2. A solution of 2.26 g (0.001 mol) of **2** was added with stirring to a solution of 1.229 g (0.001 mol) of **24** in 3 mL of methylene chloride at −78 °C. The solvent was removed and the residue was distilled, bp 94–96 °C (0.3 mm), to give 1.1 g (32% yield) of **25**.

Anal. Calcd for $C_7H_7F_6O_3S_2$: C, 24.14; H, 2.01. Found: C, 24.15; H, 2.42.

The mass spectrum gave a molecular ion *m/e* 348 (calcd, 348).

The 100-MHz ^1H NMR spectrum of **25** in *o*-dichlorobenzene had a doublet centered at δ 3.51 (J_{POCH} = 17 Hz) which is assigned to the hydrogens of the methyl group. A complex multiplet was found between δ 3.73 and 4.37. The ^1H NMR spectrum did not change on heating to 130 °C.

The ^{31}P NMR spectrum had an absorption at δ +16.5 and the ^{19}F NMR spectrum had a doublet centered at δ +54.2 (J_{PSCCF} = 5.25 Hz).

Reaction of Trimethyl Phosphite with 2. A solution of 2.26 g (0.01 mol) of **2** in 2 mL of methylene chloride was added dropwise with stirring to a solution of 1.24 g (0.01 mol) of trimethyl phosphite in 2 mL of methylene chloride at −78 °C. The ^{31}P NMR spectrum of the reaction mixture at ambient temperature had the following absorptions: δ +73 (10%), +19 (90%), and +1 (trace). The first absorption is assigned to trimethyl phosphorothionate, the second to the mixture of products, *cis*- and *trans*-**27**, and the third to the phosphorane **28**. The solvent was removed and the residue was distilled, bp 92–93 °C (0.4 mm), to give 1.2 g (34%) of **27** whose structures are tentatively assigned on the following evidence.

Anal. Calcd for $C_7H_9F_6O_3PS_2$: C, 23.99; H, 2.59. Found: C, 24.22; H, 2.71.

The mass spectrum revealed a molecular ion *m/e* 350 (calcd, 350).

The 60-MHz ^1H NMR spectrum had a doublet at δ 3.88 (J_{POCH} = 13 Hz) and another at δ 3.86 (J_{POCH} = 13 Hz); there was also found a broad singlet, δ 2.58, with a shoulder, δ 2.50. Integration gave a ratio of 3:1 for the areas of the doublets to those of the singlets. The ratio of areas of the doublets was 3.3:1.0.

Acknowledgments. This research has been supported by the National Science Foundation and by the Public Health Service Research Grant CA-10737 from the National Cancer Institute. We also wish to thank the Mobil Chemical Co. for funds which aided in the purchase of NMR equipment.

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Role of Through Space 2p–3d Overlap in the Alkylation of Phosphines

William E. McEwen,* A. Blair Janes, Jerome W. Knapczyk, Vernon L. Kyllingstad, Wen-I Shiau, Stanley Shore, and Joanne H. Smith

Contribution from the Department of Chemistry, The University of Massachusetts, Amherst, Massachusetts 01003. *Received May 17, 1978*

Abstract: In order to gain additional insight into the scope of the through space 2p–3d overlap effect and into the structures of the transition states of the S_N2 reactions, we have prepared a wide variety of tertiary phosphines and have measured the rates of their reactions with benzyl chloride in benzene–methanol (3:2) solution. One of the most striking results is that diphenyl(2,6-dimethoxyphenyl)phosphine undergoes the quaternization reaction faster than any other phosphine we have used. In the attempted reaction of diphenyl(methoxymethyl)phosphine with benzyl chloride, the inductive, electron-withdrawing effect of the methoxy group bonded to a saturated carbon atom is so large that the rate of reaction with benzyl chloride in benzene–methanol at 31 °C is essentially zero. In spite of what must be large rate-depressing inductive effects in the reactions of diphenyl(2-methoxyethyl)phosphine and diphenyl(3-methoxypropyl)phosphine with benzyl chloride, these reactions are faster than those of diphenylethylphosphine and diphenyl-*n*-propylphosphine, respectively. Rationalizations for these and other results are presented.

Kinetics data for the S_N2 reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride, and of aryldiethylphosphines with ethyl iodide, have been presented in previous publications.[1,2] Three particularly important effects were observed. (1) The presence of an *o*-methoxy substituent on an aryl group of the phosphine causes a significant increase in the rate of the reaction. (2) The ratio of the rates of reaction of a given triarylphosphine with benzyl chloride and with *n*-butyl chloride is about 20, probably the smallest such ratio ever reported in S_N2 reactions of these alkyl chlorides. (3) Rate and activation parameter profiles for the reactions of the isomeric anisyldialkylphosphines and anisyldialkylamines, respectively, with alkyl halides are distinctly different. A rationalization of these effects has been presented, based partly on the concept of through-space overlap of a pair of 2p electrons of a 2-methoxyphenyl group with an empty 3d orbital (or hybrid orbital) of phosphorus in the transition state.[3]

0002-7863/78/1500-7304$01.00/0