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THE CHEMISTRY OF THE PHOSPHORUS-PHOSPHORUS BOND

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CONTENTS

I. Introduction.....	617
II. The Nature of the Phosphorus-Phosphorus Linkage.....	617
III. Preparation of Diphosphines.....	619
IV. Reactions of Diphosphines.....	621
A. Disproportionation Reactions.....	621
B. Cleavage of the P-P Bond.....	621
C. Phosponium Salt Formation.....	622
D. Donor and Acceptor Properties of Diphosphines.....	622
V. Diphosphorus Tetrahalides.....	624
A. Preparation of Diphosphorus Tetrahalides.....	624
B. Reactions of Diphosphorus Tetrahalides.....	624
C. Dihalodiphosphines.....	625
VI. Stereochemistry of Diphosphorus Compounds.....	625
VII. Diphosphine Disulfides and Related Compounds.....	625
A. Preparation of Diphosphine Disulfides.....	625
B. Reactions of Diphosphine Disulfides.....	627
C. Stereochemistry of Diphosphine Disulfides.....	627
D. Diphosphine Monosulfides and Diphosphine Dioxides.....	627
VIII. Triphosphines.....	628
IX. Cyclopolyphosphines.....	628
A. Preparation of Cyclopolyphosphines.....	628
B. Reactions of Cyclopolyphosphines.....	629
C. Structural Aspects of Cyclopolyphosphines.....	630
X. References.....	631

I. INTRODUCTION

Whereas silicon and sulfur, which are situated to the left and right of phosphorus in the periodic table, form numerous chain and cyclic structures, it is only recently that an interest in compounds involving phosphorus-phosphorus bonds has developed. A sufficient amount of information has now accumulated to merit a review of the synthetic approaches, characteristic reactions, and stereochemistry of the various compounds involving the P-P linkage. The subject has been briefly summarized by Huheey (76), and monographs by Maier (124), Paddock (136), and Sasse (157) contain sections that deal with certain aspects of polyphosphine chemistry. The perfluoroalkyl derivatives have been discussed by Banks and Haszeldine (5).

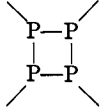
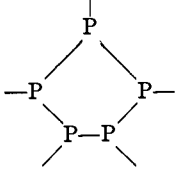
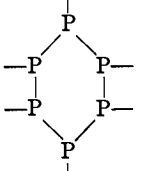
The principal structures involving phosphorus to phosphorus bonds are shown in Table I. The name "diphosphine" rather than "biphosphine" for P_2H_4 and its derivatives conforms to the latest I.U.P.A.C. report on inorganic nomenclature. When the sub-

stituents on a single P-P bond are halogens, it is customary to name the compound as a binary nonmetal halide rather than a diphosphine derivative. The names of the two oxyacids also conform to the I.U.-P.A.C. rules. The phosphorus(III) ring compounds are designated as cyclopolyphosphines (117) by extension from diphosphine. This review is concerned with all the structures in Table I except elemental phosphorus, the phosphorus oxyacids, and the phosphorus sulfides. The phosphorus sulfides have been reviewed recently (36), and the literature on the other two subjects is extensive enough to merit separate consideration.

II. THE NATURE OF THE PHOSPHORUS-PHOSPHORUS LINKAGE

Why study the phosphorus-phosphorus bond? Part of the answer lies in the importance of determining its relationship to other compounds with M-M bonds. Furthermore, group V elements in the trivalent state

TABLE I
 STRUCTURES INVOLVING P-P BONDS

Structure	
$>P-P<$	Diphosphine or diphosphorus tetrahalide
$\begin{array}{c} \\ >P-P-P< \end{array}$	Triphosphine
$\begin{array}{c} S \\ \uparrow \\ >P-P< \end{array}$	Diphosphine monosulfide
$\begin{array}{c} S \quad S \\ \uparrow \quad \uparrow \\ >P-P< \end{array}$	Diphosphine disulfide
$\begin{array}{c} O \quad O \\ \uparrow \quad \uparrow \\ HO-P-P-OH \\ \quad \\ HO \quad OH \end{array}$	Hypophosphoric acid
$\begin{array}{c} O \quad O \\ \uparrow \quad \uparrow \\ HO-P-P-OH \\ \quad \\ HO \quad H \end{array}$	Diphosphorous acid
P_2	Elemental phosphorus
P_4S_3, P_4S_5, P_4S_7	Phosphorus sulfides
	Cyclotetraphosphines
	Cyclopentaphosphines
	Cyclohexaphosphines

have lone pairs available, and there is much to be learned concerning the extent to which these electrons are involved in the bonding between the M atoms. The ultimate objective is that an understanding of these bonding principles will facilitate the preparation of many new straight-chain and cyclic polyphosphines.

The P-P bond displays a number of peculiarities. Not the least of these is the existence of 60° angles in the P_4 tetrahedron of white phosphorus and in the basal plane of P_4S_3 . Arnold (4) has suggested that the valence state of phosphorus in P_4 is $(3p)(3d)^2$, but as pointed out by Moffitt (129) the promotion of two electrons without a compensating increase in valence is not very plausible on energetic grounds. It is more likely that the phosphorus orbitals used in P_4 and the three-membered phosphorus ring of P_4S_3 are predominantly $3p$ in type and that the bonds are "bent" in the sense that the lines of maximum charge density do not coincide with the direction of attachment of the phosphorus atoms.

Another interesting feature of the P-P bond is the essential constancy of its length (Table II). With the possible exception of P_4S_7 the P-P bond length appears to be insensitive to the electronic characteristics of the substituents or to changes in oxidation state. It is important to realize, however, that invariance of bond length does not preclude a variation in the extent of π -bonding.

 TABLE II
 P-P BOND LENGTHS

Molecule	Bond length, Å.	Ref.
P_2I_4	2.21 ± 0.06	110
$(C_2H_5)_2P(S)P(S)(C_2H_5)_2$	2.22 ± 0.01	44
$(CH_3)(C_6H_5)P(S)P(S)(C_6H_5)(CH_3)$	2.21	185
$(CF_3P)_4$	2.213 ± 0.005	137
$(CF_3P)_5$	2.223	166, 167
$(PO_2)_6^{6-}$	2.20 (av.)	184
P_4S_3	2.235 ± 0.005	111
P_4Se_3	2.25	97
P_4S_5	2.21 ± 0.025	75
P_4S_7	2.35 ± 0.01	179, 180
$P_4S_2I_2$	2.20 ± 0.04	187
P_4	2.21 ± 0.02	126
Black phosphorus	2.18	77

Like other second row elements, phosphorus prefers catenation to multiple bonding, due to increased inner shell repulsions and less effective π -bonding between $3p$ -orbitals. Extensive multiple bonding seems confined to P_2 , the dissociation energy of which corresponds to about 1.3 π -bonds per σ -bond (177). The P-P single bond is comparable in strength to the Si-Si bond, but weaker than the S-S bond. Elemental phosphorus (P_4) has a P-P bond energy in the range 44-48 kcal. (35, 40, 165). Various estimates (40, 129, 141, 142, 165) of the steric strain in the P_4 molecule have been used to derive an unstrained P-P single bond energy between 47.2 and 54.5 kcal. Slightly lower values are reported for diphosphine (58, 154) and a somewhat higher value (156) for P_2Cl_4 . Although the P-P bond energy is relatively small the ease of decomposition of P_2H_4 and P_2Cl_4 cannot be attributed to this alone, since some organo-substituted diphosphines are stable up to almost 300° . Such factors as reaction mechanism, steric effects, and inductive effects must also be considered.

Another question of importance concerns the extent to which lone pairs participate in the bonding between the phosphorus atoms. For simplicity we will just consider one P-P bond, although the argument also applies to more complicated ring and chain polyphosphines. In a diphosphine the two phosphorus atoms are joined by a σ -bond and a lone pair of electrons remains on each atom [I(a)]. Evidence for the con-



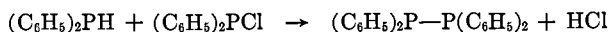
tribution of structures I(b), I(c), and I(d), which involve p_π - d_π bonding, comes from the intense ultraviolet spectra of diphosphines compared with the corresponding monophosphines. For example, $(\text{CF}_3)_4\text{P}_2$ shows (18) an intense band (ϵ 7800) at 2160 Å. Replacement of the CF_3 by CH_3 groups moves the maximum to higher wave lengths (55), corresponding to a closer spacing of the energy levels. There is a simultaneous diminution of intensity of the band, indicating that there is less delocalization of the lone pairs in $(\text{CH}_3)_4\text{P}_2$ than in $(\text{CF}_3)_4\text{P}_2$. It is also noteworthy that the unsymmetrical diphosphine $(\text{CH}_3)_2\text{P}-\text{P}(\text{CF}_3)_2$ has its absorption maximum much closer to that of $(\text{CH}_3)_4\text{P}_2$ than to that of $(\text{CF}_3)_4\text{P}_2$ (55).

There is some theoretical interest in the relative signs and magnitudes of n.m.r. coupling constants between directly bonded nuclei. Since the P^{31} nucleus has a spin of $1/2$ and a natural abundance of 100%, phosphorus is the most suitable of the group V elements for this type of study. Only a few values of J_{PP} are presently available. Like other coupling constants J_{PP} varies with valence state. Thus, J_{PP} is 108.2 c.p.s. for P_2H_4 (114), between 220 and 243 c.p.s. for tetraalkyldiphosphine monosulfides (60, 123), and 480 c.p.s. for the diphosphite anion (30). The value of 18.7 c.p.s. reported for tetramethyldiphosphine disulfide is so small that the accepted structure has been questioned (60). Three of the four existing J_{PP} values appear to be negative (60, 114). This is unexpected, but there is no fundamental reason why coupling between directly bonded nuclei should be positive.

III. PREPARATION OF DIPHOSPHINES

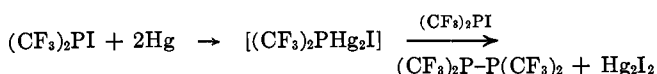
Diphosphine, the simplest compound involving a P-P bond, has been known for many years. Several methods of preparation are recorded in the literature, including the reaction of white phosphorus with strong bases and the neutral hydrolysis of various metallic phosphides, of which calcium phosphide appears to be the most suitable (45).

The first organo-substituted diphosphine was synthesized over 70 years ago by the reaction of diphenylphosphine with diphenylphosphinous chloride (43).

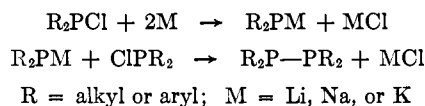


More recently this method has been extended to the synthesis of tetraalkyldiphosphines (23) and the unsymmetrical diphosphines $(\text{CH}_3)_2\text{P}-\text{P}(\text{CF}_3)_2$ (55) and $\text{CH}_3(\text{H})\text{P}-\text{P}(\text{CF}_3)_2$ (25).

A well-known way of coupling carbon atoms is by the Wurtz-Fittig synthesis. The first application of this approach to phosphorus chemistry was the coupling of $(\text{CF}_3)_2\text{PI}$ with mercury (18). The reaction seems to

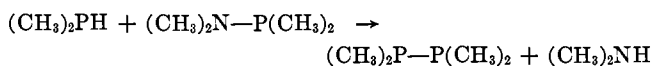


proceed *via* an intermediate phosphorus-mercury compound (26). The activity of the halogen toward mercury increases in the order $\text{Cl} < \text{Br} < \text{I}$. Thus, $(\text{CF}_3)_2\text{PI}$ reacts at room temperature, $(\text{CF}_3)_2\text{PBr}$ requires 100° (24), and $(\text{CF}_3)_2\text{PCl}$ does not attack mercury. The less reactive but more accessible phosphinous chlorides can be coupled by using active metals such as lithium (70), sodium (88, 131, 132, 135, 178), potassium (131, 132), and magnesium (61, 131). In one interesting case (49) the chlorine atoms were abstracted with tri-*n*-butylphosphine. Alkali metal coupling probably proceeds *via* the metal organophosphide (88, 132) since diphosphines have been produced



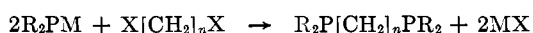
from the second step of the reaction (178). It is a good practice to avoid an excess of alkali metal in these coupling reactions since it is possible to cleave the newly formed P-P bond, particularly when the substituents are electron-attracting. Difficulties due to disproportionation are minimized by lowering the reaction temperature and by using more reactive alloys (163).

One of the most interesting diphosphine syntheses depends on Burg's recognition that the P-P bond can form two π -bonds [I(d)] whereas the P-N bond can only form one (23). This, together with the higher bond energy of the N-H bond compared to the P-H bond, is the reason why dimethylphosphine or dimethylphosphonium chloride will displace dimethylamine from dimethylphosphinous dimethylamide.



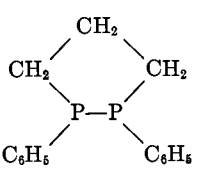
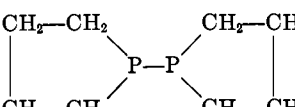
Certain Grignard reagents react "anomalously" with PSCl_3 to produce diphosphine disulfides rather than the expected tertiary phosphine sulfides (*vide infra*). When a diphosphine disulfide is readily available in this manner, desulfurization represents a very convenient diphosphine synthesis. Among the reducing agents that will effect this desulfurization are zinc (106, 118, 134), iron (132), copper (132), lead (132), cadmium (132), sodium (93), triethyl phosphite (139), and tertiary phosphines (123, 139), of which tri-*n*-butylphosphine seems to be the most efficient.

The reaction of a metal organophosphide with an organic dihalide has been used in the synthesis of some interesting ditertiary phosphines (90). However, when



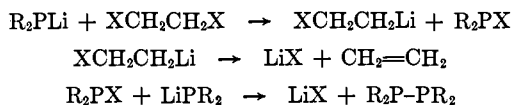
$n = 2$, $\text{X} = \text{Cl}$ or Br , $\text{M} = \text{Li}$, and $\text{R} = \text{C}_2\text{H}_5$ or C_6H_{11} in the above equation, it is not possible to isolate the expected ditertiary phosphine (84). Instead lithium-halogen interconversion takes place, resulting in

TABLE III
 PREPARATION AND PROPERTIES OF DIPHOSPHINES

Substituents	Method ^a	B.p. (mm.), °C.	M.p., °C.	Ref.
Symmetrical Diphosphines, R ₂ P-PR ₂				
H	5	66.7 (est.)	-99	45
D	5			45
CH ₃	1, 3	138	-2.25 to -2.15	23, 93, 123, 132, 134, 139
CF ₃	2	84		18
C ₂ H ₅	2, 3, 4, 5	221-222		61, 70, 79, 85, 88, 90, 93, 123, 132
<i>n</i> -C ₃ H ₇	3	144-145 (16)		93, 106, 132
<i>n</i> -C ₄ H ₉	3	180-181 (14)		88, 93, 132
C ₆ H ₅	1, 2, 3, 4, 5	258-260 (1)	120.5	49, 73, 85, 90, 92, 105, 132
C ₆ H ₁₁	4		173	79, 85, 88, 90
<i>p</i> -CH ₂ C ₆ H ₄	3			132
(CH ₃) ₂ N	2	50 (0.01)	48	135
(C ₆ H ₅) ₃ Sn	5		95-110	160
Unsymmetrical Diphosphines, R ₁ R ₂ P-PR ₁ R ₂				
R ₁ = H, R ₂ = CF ₃	5	69.5 (est.)		116, 117
R ₁ = H, R ₂ = C ₆ H ₅	4		151-152	80
R ₁ = CH ₃ , R ₂ = C ₂ H ₅	3	188-190		118, 123
R ₁ = CH ₃ , R ₂ = C ₄ H ₉	3	51-52 (0.01)		124
R ₁ = CH ₃ , R ₂ = C ₆ H ₅	3, 5	128-130 (0.5)		123, 148
R ₁ = C ₂ H ₅ , R ₂ = N(C ₂ H ₅) ₂	2	142-145 (12)		163
R ₁ = C ₆ H ₅ , R ₂ = C ₆ H ₅ CO	5		117-117.5	148
R ₁ = C ₆ H ₅ , R ₂ = N(CH ₃) ₂	2	150 (0.5)		178
R ₁ = C ₆ H ₅ , R ₂ = N(C ₂ H ₅) ₂	2	236-238 (15)		163
R ₁ = C ₆ H ₁₁ , R ₂ = N(C ₂ H ₅) ₂	2	234-235 (15)		163
Unsymmetrical Diphosphines, R ₁ R ₁ P-PR ₂ R ₂				
R ₁ = CH ₃ , R ₂ = CF ₃	1	120 (est.)	-79.2 to -79.1	55
R ₁ = C ₆ H ₅ , R ₂ = N(CH ₃) ₂	5	137-140 (0.001)		178
Miscellaneous Diphosphines				
(CF ₃) ₂ P-P(H)CH ₃	1	91.6 (est.)		25
(CH ₃) ₃ P ⁺ -PCF ₃ ⁻	5			28
(<i>n</i> -C ₄ H ₉) ₃ P ⁺ -PCF ₃ ⁻	5			28
	4	184-190 (4)		81
	3	50 (0.05)		159

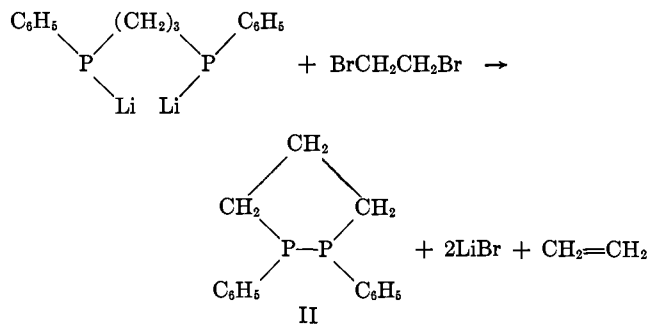
^a Methods: 1, R₂PH + R₂PX; 2, coupling of R₂PX with active metal; 3, desulfurization of diphosphine disulfide; 4, from metal organophosphide; 5, mentioned in text.

ethylene evolution and the production of a diphosphine.



This type of reaction is a valuable source of diphosphines since metal organophosphides are relatively easy to prepare (70). Issleib and co-workers have extended the scope of the reaction to include other halides such as CH₂Cl₂ (84), halocarboxylic esters (90), and COCl₂ (85). Other metal organophosphides can also be used, *e.g.*, (C₆H₅)₂PNa (84) and C₆H₅PHK (80).

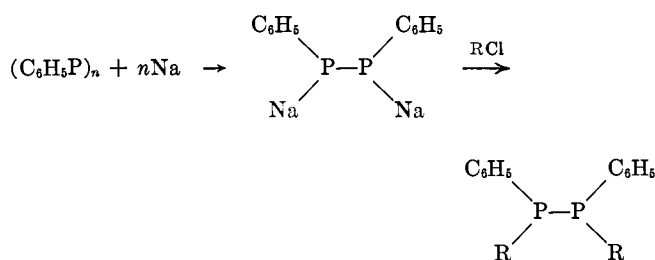
Metal-halogen exchange has also made available some diphosphines that would be inaccessible by other routes, such as 1,2-diphenyldiphosphine (80) and the novel heterocyclic diphosphine II (81). Metal-halo-



gen interconversions are quite well known in organolithium chemistry (95). The ease of interconversion is proportional to the degree of positive polarization of the halogen. Relatively "positive" iodine or bromine atoms exchange readily with lithium, the less "posi-

tive" chlorine less rapidly, and the negative fluorine does not exchange at all. In general the same observations are made with phosphorus. For instance, metal-chlorine exchange proceeds more readily with electron-releasing substituents on the lithium organophosphide (79). Also, the exchange reaction is sensitive to change of solvent, *e.g.*, $(C_2H_5)_2PLi$ undergoes lithium-chlorine exchange with CH_2Cl_2 in diethyl ether or dioxane (84), but not in tetrahydrofuran (70). Possibly the solvent alters the degree of ionization of $(C_2H_5)_2PLi$ and thereby influences the course of the reaction.

Diphosphines have also been produced by breakdown of more complex structures that involve several P-P bonds. Mention has already been made of the preparation of P_2H_4 by OH^- cleavage of the P_4 molecule. Recently it has been reported (160) that a triphenyltin-substituted diphosphine can be isolated from the sealed tube reaction of tetraphenyltin with elemental phosphorus. Under carefully controlled conditions it is possible to isolate 1,2-disodio-1,2-diphenyldiphosphide from the reaction of sodium with the cyclopolyphosphine $(C_6H_5P)_n$ (148).



The disodium salt is a valuable intermediate for the production of unsymmetrical diphosphines, $R = \text{alkyl}$ or aryl. Burg has used the CF_3 -substituted cyclopolyphosphines as a source of several unusual compounds. The diphosphine $(CF_3PH)_2$ is one of the products (117) of plain water hydrolysis of $(CF_3P)_4$ or $(CF_3P)_5$, while reaction of these compounds with tertiary phosphines results in (28) interesting polar isomers of diphosphines, $R_3P^+-P-CF_3$, which consist of phosphonium and phosphide ions in the same molecule. Although the reversibility of the reaction precluded their isolation the zwitterion formulation is consistent with the stoichiometry of the reaction and F^{19} n.m.r. spectra. These unusual compounds employ the PCF_3 unit in the same role as $=O$, $=NH$, and $=CH_2$.

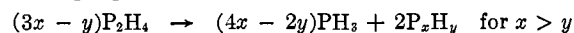
Among the miscellaneous methods that have been used to produce diphosphines are the LiH reduction of $(C_6H_5)_2PCl$ (73), the simultaneous desulfurization and coupling of $(C_2H_5)_2P(S)Cl$ with copper bronze (132), and the reaction of $(C_6H_5)_2PNa$ with benzophenone (92).

The preparation and properties of diphosphines are summarized in Table III.

IV. REACTIONS OF DIPHOSPHINES

A. DISPROPORTIONATION REACTIONS

The thermal stability of diphosphine itself is so low that disproportionation according to the equation



takes place rapidly above 0° (45). The constitution of the amorphous yellow hydrides of general formula P_xH_y has been the subject of several papers (45, 59, 150-152, 158, 169-171). Earlier interpretations (59, 150-152) that these are "absorbates" of phosphine on yellow phosphorus is probably an oversimplification. They are more likely high polymers, made up of $-PH_2$ terminal units, $=PH$ middle units, and $\equiv P$ branching units. Equilibrium between these units and PH_3 would account for their nonstoichiometric composition.

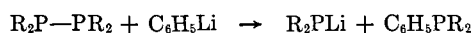
Substitution of just two of the hydrogen atoms of P_2H_4 by CF_3 groups is enough to raise the thermal stability to around 200° (117). Complete substitution by alkyl, perfluoroalkyl, or aryl groups raises the thermal stability above 200° . Slow disproportionation takes place in the $300-350^\circ$ range (23, 105, 117) to give in each case a tertiary phosphine, R_3P , plus a polymeric material such as $(P_3C_2H_4)_x$, a cyclopolyphosphine, or red phosphorus.

The unsymmetrical diphosphines of type R'_2P-PR_2 are noticeably less thermally stable than their symmetrical analogs (55). In these cases decomposition is probably facilitated by the formation of intermolecular P-P bonds between the relatively basic and acidic phosphorus atoms. A similar argument may account for the low thermal stability of $[N(CH_3)_2]_4P_2$ (135).

B. CLEAVAGE OF THE P-P BOND

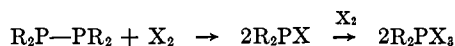
Homolytic cleavage of the P-P bond is a useful source of reactive monophosphorus compounds. For instance, a series of alkali metal organophosphides has been produced by alkali metal cleavage of diphosphines (70, 93, 103, 107, 130-132, 174). The ease of cleavage varies with the substituents and decreases in the order $C_6H_5 > CH_3 > C_2H_5 > n-C_3H_7 > n-C_4H_9$; hence, the best combination of solvent and metal depends on the particular P-P compound. As expected, replacement of alkyl by aryl groups weakens the P-P bond because of the electron-withdrawing effect of the aryl groups and the stabilization of the anion R_2P^- by delocalization of negative charge onto the benzene rings.

Recently it has been shown (82) that certain organometallic reagents will also cause cleavage of diphosphines.



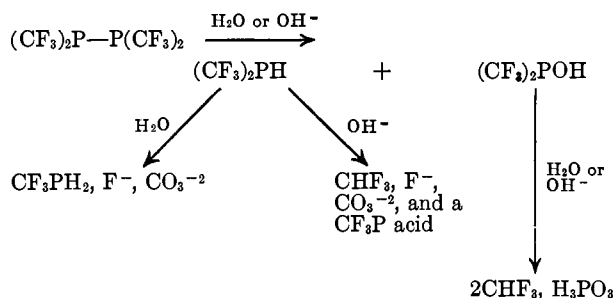
The relative ease of cleavage closely resembles that for the alkali metals and the reactivity of the organometallic follows the sequence $LiC_6H_5 > LiC_2H_5 > Mg(C_2H_5)_2 > Al(C_2H_5)_3 \gg Pb(C_2H_5)_4$.

Equimolar amounts of the halogens, usually in indifferent solvents at room temperature, cause essentially quantitative P-P bond cleavage of both symmetrical (73, 88, 105) and unsymmetrical (123, 163) diphosphines. If the halogen is in excess, this is followed by conversion of the phosphinous halide to the corresponding phosphorane (24, 135, 178).



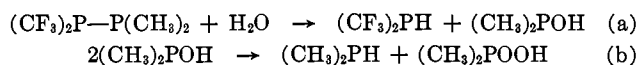
Simultaneous cleavage of the P-C bonds is also possible when these bonds are weakened by electron withdrawal; *e.g.*, all the CF₃ groups of (CF₃)₄P₂ can be removed as CF₃Br as low as 90° (24).

In general, substituted diphosphines do not react with water at room temperature. Hydrolytic cleavage of the P-P bond is possible, however, under more forcing conditions. The CF₃-substituted diphosphines have received the most attention because the evolved fluoroform can give vital clues both to the reaction mechanism and to the structure of the diphosphine. With (CF₃)₄P₂, for example, it was found that alkaline hydrolysis yields 3 moles of CHF₃ while plain water or dilute HCl hydrolysis at 100° yields only 2 moles (19).



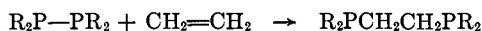
It has been shown (19) by separate experiments that under basic conditions the initially formed cleavage products (CF₃)₂PH and (CF₃)₂POH can yield 1 and 2 moles of CHF₃, respectively, while with plain water or dilute acid hydrolysis the phosphine (CF₃)₂PH decomposes without fluoroform evolution.

Similar information has been obtained from the hydrolysis of unsymmetrical diphosphines. In agreement with its proposed structure (CF₃PH)₂ yields half its CF₃ groups on basic hydrolysis (117), and (CH₃)₂P-P(CF₃)₂ hydrolyzes according to the sequence (55)



Step a may involve a rapid exchange between (CF₃)₂-POH and (CH₃)₂PH (56).

One of the most elegant concepts in polyphosphine chemistry in Burg's "pseudo-halogen" concept whereby the R₂P- moiety of a diphosphine is likened to a halogen atom. Thus, (CF₃)₄P₂ or (CH₃)₄P₂ will add across ethylenic or acetylenic multiple bonds in much the same way as a halogen molecule (23).

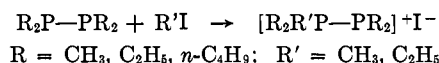


A similar approach has been used to obtain small yields of *o*-phenylenebis(diethylphosphine) by adding (C₂H₅)₄P₂ across the triple bond of benzyne (31).

One final cleavage reaction that might be mentioned is reduction. It is interesting that, whereas diphosphine disulfides are cleaved (and desulfurized) by LiAlH₄, the corresponding diphosphines are not (91). One reason may be that a complex forms between the diphosphine disulfide and LiAlH₄ which facilitates P-P bond rupture. Cleavage of the P-P bond of a diphosphine can be achieved, however, by hydrogenation in the presence of a Raney nickel (19) or active copper catalyst.

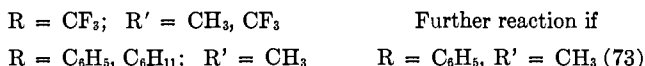
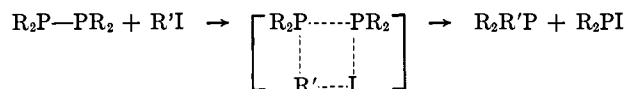
C. PHOSPHONIUM SALT FORMATION

One of the characteristic reactions of a tertiary phosphine is phosphonium salt formation. Even though two trivalent phosphorus atoms are available on a diphosphine it is only possible to quaternize one of them.



Apparently the positive charge on the adjacent phosphorus atom diminishes the basicity of the second site (88) since bisphosphonium salt formation only becomes possible when the interaction between the phosphorus atoms is reduced by methylene group insertion (70).

Cleavage rather than quaternization takes place when the P-P bond is weakened by electron-withdrawing substituents (38, 73, 92) or when the alkyl groups are replaced by bulkier C₆H₁₁ groups (88). Unsymmetrical diphosphines of type (C₂H₅)₂N(R)P-P(R)-N(C₂H₅) are also cleaved by alkyl iodides (162).



In contrast the tetraalkyl diphosphines require a temperature of 200° to effect such a decomposition (134). The cleavage reaction probably involves an intermediate complex rather than a free-radical mechanism since the reaction proceeds in the dark (38). Märkl (125) has prepared an interesting series of cyclic monophosphonium salts by using dihalides in place of CH₃I in the cleavage reaction.

Diphosphines which have sites of differing basicity, such as (CF₃)₂P-P(CH₃)₂ and [(CH₃)₂N]₄P₂, undergo disproportionation with CH₃I, possibly involving an unstable monophosphonium salt as the first step (55, 135).

D. DONOR AND ACCEPTOR PROPERTIES OF DIPHOSPHINES

By reason of their lone pairs diphosphine and substituted diphosphines will form complexes with several Lewis acids. The reactivity toward the various accep-

tors seems to depend on the basicity of the phosphorus atoms. Thus, $(CF_3)_4P_2$ is inert toward B_2H_6 or BF_3 up to 300° (19, 55), whereas $(CH_3)_4P_2$ readily forms diadducts with the BH_3 group (22, 23, 134) and $Al(C_2H_5)_3$ (164), and a monoadduct with difunctional B_2Cl_4 (50). When the diphosphine substituents are mildly electron withdrawing, it is only possible to isolate monoadducts, such as $(C_6H_5)_4P_2 \cdot BF_3$ (105) and $(C_6H_5)_4P_2 \cdot Al(C_2H_5)_3$ (82). Apparently steric effects are also important since $(CH_3)_4P_2$ only forms an unstable monoadduct with $(CH_3)_3B$ (23).

Diphosphine itself is sufficiently basic to form diadducts with BF_3 and the BH_3 group (17). It is noteworthy that $P_2H_4 \cdot 2BH_3$ is more stable than either P_2H_4 or the BF_3 adduct. This is probably due to interaction of the B-H bonding electrons with the phosphorus 3d-orbitals, leading to greater electron density in the P-P bond. Evidently this type of supplemental π -bonding from the B-H bonds is less important than steric hindrance and the electron-withdrawing effect of the first P→B dative linkage in the complex $(CH_3)_4P_2 \cdot 2BH_3$ since Burg (23) has noted that the second BH_3 group is more weakly attached than the first.

Tetrakis(dimethylamino)diphosphine is an interesting case because either the N or the P atoms could coordinate. Since it appears to be the P atoms that coordinate in the adduct $[(CH_3)_2N]_4P_2 \cdot 2BH_3$ (135), one can argue for increased basicity of the phosphorus atoms through p_π - d_π bonding.

Unsymmetrical diphosphines of type R_2P-PR_2' have a behavior intermediate between their symmetrical analogs. Thus, $(C_6H_5)_2P-P[N(CH_3)_2]_2$ forms a diborane adduct (178) and $(CH_3)_2P-P(CF_3)_2$ forms a monoborane adduct (55). In fact the $(CF_3)_2P$ -group of the latter diphosphine is acidic enough to form a complex with the donor $(CH_3)_3N$ (55).

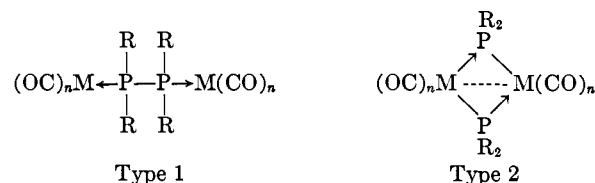
Protic acids cause P-P bond cleavage. Again the reactivity of the diphosphine appears to depend on base action by at least one of the phosphorus atoms; hence, $(CF_3)_4P_2$ is inert toward HCl up to 300° (19, 55), and other diphosphines are cleaved to a secondary phosphine and a phosphinous halide. The only evidence for some kind of adduct is the isolation of $[(CH_3)_2N]_4P_2 \cdot 2HCl$ at low temperature (135), and even here quaternization of the nitrogen atoms cannot be excluded. At higher temperatures the dialkylamino-diphosphines undergo disproportionation and simultaneous P-P and P-N cleavage (135, 162, 178).

In recent years there has been considerable interest in the reactions of various transition metal compounds with phosphine ligands. The first indication that a diphosphine could behave as a ligand was Burg and Mahler's observation (27) that $(CF_3)_4P_2$ reacts with nickel carbonyl to form a complex of stoichiometric composition $(CF_3)_4P_2 \cdot 2Ni(CO)_3$. Hayter and others have now developed the field to the point where it is

TABLE IV
PHOSPHORUS-BRIDGED COMPLEXES FROM MONOMERIC METAL CARBONYLS

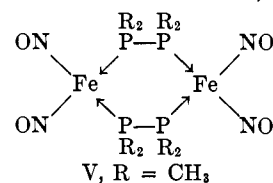
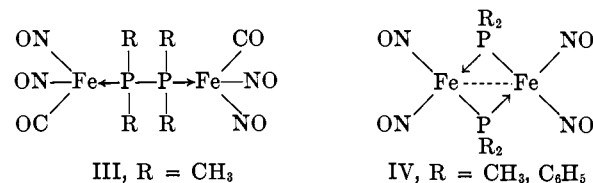
	M	n	R	Ref.
Type 1	Ni	3	CF_3	27
	Ni	3	CH_3	64
	Ni	3	C_6H_5	64, 161
	Fe	4	CH_3	32, 64
	Fe	4	C_6H_5	161
	Cr	5	CH_3	33, 64
	Mo	5	CH_3	32, 33, 64
	Mo	5	C_2H_5	32
	W	5	CH_3	32, 33, 64
	W	5	C_2H_5	32
Type 2	Ni	2	C_6H_5	64
	Fe	3	CH_3	32, 64
	Fe	3	C_2H_5	32
	Cr	4	CH_3	32, 33, 64
	Cr	4	C_2H_5	32
	Mo	4	CH_3	33, 64
	Mo	4	C_2H_5	32
	Mo	4	C_6H_5	32
	W	4	CH_3	33, 64
	W	4	C_2H_5	32
W	4	C_6H_5	32	

possible to distinguish two general types of reaction product with monomeric metal carbonyls (Table IV). Depending on the reaction conditions the diphosphine can either remain intact and behave as a bidentate ligand (type 1), or P-P bond cleavage can take place to yield phosphido-bridged carbonyls (type 2).



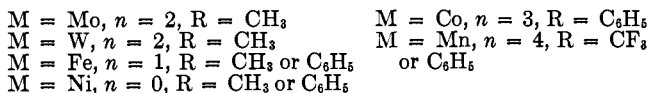
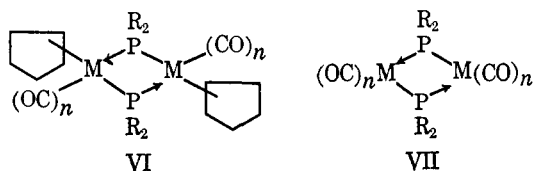
The phosphido-bridged carbonyls are formulated with metal-metal bonds to account for their diamagnetic behavior and more intense colors. In general the M_2P_2 ring of the type 2 complexes is expected to be planar. However, when $M=Fe$ the indications are (32, 64) that, as in the analogous sulfur-bridged compounds (39), the ring is folded, with a bent metal-metal bond occupying the vacant octahedral positions between the iron atoms.

Diphosphine (III) and phosphido-bridged (IV)



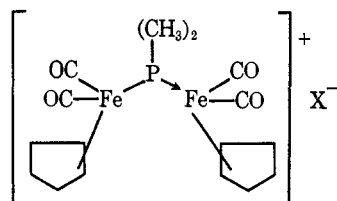
carbonyls can also be obtained from $\text{Fe}(\text{CO})_2(\text{NO})_2$ (66). In this case it is also possible to isolate a double diphosphine-bridged complex (V).

The dimeric cyclopentadienyl metal carbonyls of Fe (63), Ni, Mo, and W (62), and the dimeric metal carbonyls $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$ (57, 65) only react by P-P bond cleavage to give the diamagnetic phosphido-bridged complexes VI and VII. One reason for

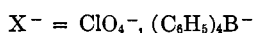


this may be that the P-P bond is reduced by the electron-rich metal-metal bond of the dimeric metal carbonyl compounds.

Under certain circumstances it is possible to isolate compounds other than those described above. Examples are the single-bridged ionic complex VIII (67)

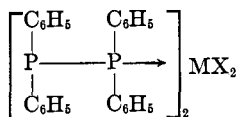


VIII

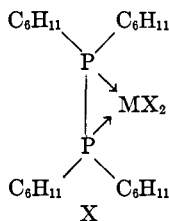
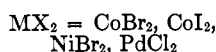


and the trinuclear cobalt complex $\text{Co}_3[\text{P}(\text{CH}_3)_2]_2(\text{CO})_7$ (65). There are only a few cases where definite compounds cannot be obtained.

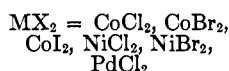
There is an interesting difference in behavior between $(\text{C}_6\text{H}_5)_4\text{P}_2$ and $(\text{C}_6\text{H}_{11})_4\text{P}_2$ in their reactions with transition metal halides. Whereas $(\text{C}_6\text{H}_5)_4\text{P}_2$ behaves as a monodentate ligand to give 2:1 complexes (IX) (86, 92), $(\text{C}_6\text{H}_{11})_4\text{P}_2$ gives 1:1 complexes (87, 88) for which the structure X has been suggested on the basis of dipole moment and magnetic measurements. Possibly



IX



X



the increased basicity of $(\text{C}_6\text{H}_{11})_4\text{P}_2$ enables it to function as a bidentate ligand, although the unusual

character of the three-membered chelate ring should be pointed out. The unsymmetrical diphosphine $(\text{C}_6\text{H}_5\text{PH})_2$ appears to behave as a monodentate ligand, since a 2:1 NiBr_2 complex has been isolated (80).

V. DIPHOSPHORUS TETRAHALIDES

A. PREPARATION OF DIPHOSPHORUS TETRAHALIDES

Only two of the four possible diphosphorus tetrahalides are known. The preparation of P_2I_4 dates back to 1813 when Gay-Lussac (52) obtained the compound in an impure state by direct fusion of the elements. Many other preparations have been described since then (127), the most convenient being the reaction of stoichiometric amounts of iodine with white phosphorus in CS_2 (6, 53). Recently syntheses involving the reduction of PI_3 (53, 112) and the reaction of iodine with red phosphorus (112) have been described.

Chemical methods of preparation of P_2Cl_4 have met with little success (51). Milligram quantities of this compound have been obtained by microwave (94) or mercury discharge (48) reduction of PCl_3 vapor and by zinc-aluminum arc reduction of liquid PCl_3 (172), but the most productive methods are the conduction of an electrical discharge above a solution or suspension of elemental phosphorus in PCl_3 (155) and the reduction of PCl_3 with hydrogen in a gaseous discharge (20, 155). It might be added that the experimental conditions for the last reaction are very important since it is possible to completely reduce the PCl_3 to elemental phosphorus.

Thus far it has not been possible to prepare either P_2F_4 or P_2Br_4 . Attempts to convert P_2Cl_4 into its fluorine or bromine analogs by halogen exchange reactions lead only to P-P bond fission and the production of PX_3 (20, 48). Only ill-defined materials can be obtained from the discharge reduction of PBr_3 (20).

B. REACTIONS OF DIPHOSPHORUS TETRAHALIDES

Diphosphorus tetrahalides are potentially useful reagents for the synthesis of new diphosphorus compounds by replacement of their active halogens by other groups. However, attempts to use them in this fashion are nearly always frustrated by disproportionation of the type



Thus, alcohols (128), phenol (128), Grignard reagents (128), amines (128), and metal halides (8) lead to varying amounts of a tricovalent monophosphorus compound and polymeric solids resembling the lower phosphorus hydrides.

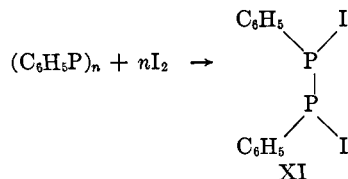
Cleavage of the P-P bond also results from attempted quaternization of P_2I_4 with $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (73) and certain Lewis acids (15). The complexes $\text{P}_2\text{I}_4 \cdot 2\text{BBr}_3$ (175), $(\text{P}_2\text{Cl}_4)_2\text{Ni}(\text{CO})_2$ (113), $\text{P}_2\text{Cl}_4[\text{Ni}(\text{CO})_3]_2$ (113), and the

unstable thioiodides P_2I_4S and $P_2I_4S_2$ (11, 37) appear to be the only cases where the phosphorus lone pairs are donated without P-P bond scission. It is interesting to note that reaction of P_2I_4 with oxygen produces polymeric $(P_3I_2O_6)_n$ rather than the expected oxyiodides (9).

Hydrolysis of P_2I_4 at 0° yields a large number of products (99, 100) which include H_3PO_4 , H_3PO_3 , H_3PO_2 , PH_3 , and HI . Upon oxidation of the hydrolytate it is possible to isolate $H_4P_2O_6$, suggesting that the new diphosphorus acid $P_2(OH)_4$ is an intermediate (7). Thiohydrolysis of P_2I_4 yields red phosphorus and a mixture of the phosphorus sulfides (176).

C. DIHALODIPHOSPHINES

Recently the first member (XI) of a new class of compounds intermediate in structure between diphosphorus tetrahalides and diphosphines has been reported (71, 72). It can be prepared by treating $(C_6H_5P)_n$ with the



appropriate quantity of iodine (72) or by reaction of $C_6H_5PCl_2$ with LiI in diethyl ether (47). Ether appears to catalyze the conversion of $C_6H_5PI_2$ to XI in much the same way as it catalyzes the conversion of PI_3 to P_2I_4 (46). The diiododiphosphine (XI) has also been produced by the reaction of alkyl iodides or $C_6H_5PI_2$ with $(C_6H_5P)_n$ (71, 72).

VI. STEREOCHEMISTRY OF DIPHOSPHORUS COMPOUNDS

It is possible to write six rotational isomers for a diphosphorus compound P_2X_4 (Figure 1), where X represents H, D, a halogen, or a carbon atom of an alkyl, perfluoroalkyl, or aryl substituent. It is reasonable to exclude the eclipsed form (a) on the basis of steric repulsion between the X groups, even when X is hydrogen. To a lesser extent the same comment applies to the semi-eclipsed forms (b) and (c); therefore, the expected configuration is either *trans* (d) or one of the spectroscopically indistinguishable *gauche* forms (e) and (f). For small rotational barriers it would be possible to have an equilibrium mixture of the staggered forms (d), (e), and (f), and for very small barriers essentially free rotation could lead to over-all C_{2v} symmetry.

Thus far investigations have been concerned mainly with P_2H_4 . Vibrational spectroscopic investigations of solid (133), liquid (13), and gaseous (133) P_2H_4 tend to favor the *gauche* conformations (e) and (f), although this could not be proved, partly because of complications from the peaks of decomposition products (12, 14).

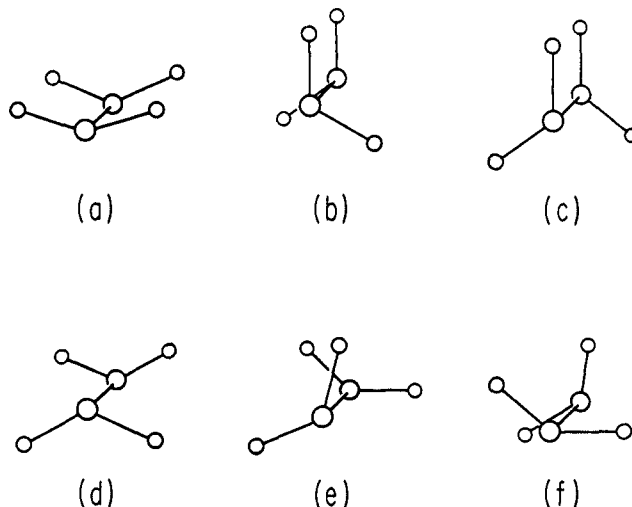


Figure 1.—Possible conformations of diphosphorus compounds

In a careful study of the H^1 and P^{31} n.m.r. spectra of P_2H_4 Lynden-Bell (114) found that all the hydrogens of P_2H_4 are equivalent and that the spectra could be satisfactorily analyzed as an A_2X_4 system. Although the preferred interpretation of the equivalence of the hydrogens was that there is rapid interconversion between the various forms, it is important to realize that the data are also consistent with either the *cis* (a) or *trans* (d) fixed forms.

It has been shown by X-ray crystallography that P_2I_4 exists in the *trans* conformation (d) in the solid state (110). However, dipole moment measurements indicate (10) that this molecule has a staggered conformation in solution, so possibly the *trans* arrangement is forced upon P_2I_4 by the efficiency of packing the relatively large iodine atoms into a lattice.

Additional isomerism can arise in organo-substituted diphosphines from restricted rotation about the P-C bonds. The observation that $(C_2H_5)_4P_2$ has three Raman-active P-C stretching modes, while the more sterically hindered $(n-C_4H_9)_4P_2$ has only one has been taken to support this view (168).

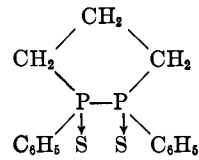
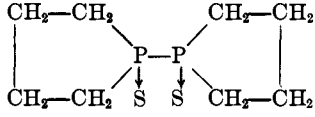
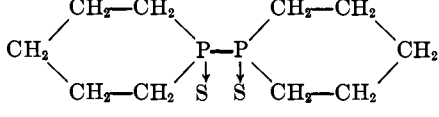
The H^1 n.m.r. spectrum of $(CH_3)_4P_2$ is a triplet (33, 60) and is thus an example of a "deceptively simple" spectrum (1). Since the ratio of the heights of the central to outer lines is 1.3:1 instead of the usual 2:1, it is evident that all the CH_3 groups are not magnetically equivalent, but it is impossible to be definitive about its configuration at present.

VII. DIPHOSPHINE DISULFIDES AND RELATED COMPOUNDS

A. PREPARATION OF DIPHOSPHINE DISULFIDES

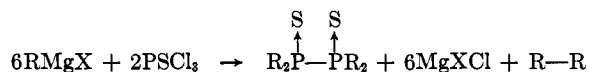
Although the reaction between $PSCl_3$ and alkyl Grignard reagents was studied as early as 1916 (173), it was not correctly interpreted until 1949, when Kabachnik and Shepeleva (96) found that the reaction of CH_3MgI with $PSCl_3$ gives tetramethyldiphosphine

TABLE V
 PREPARATION AND PROPERTIES OF DIPHOSPHINE DISULFIDES

Substituents	Method ^a	M. p., °C.	Ref.
Symmetrical Diphosphine Disulfides, R ₂ P(S)P(S)R ₂			
CH ₃	1	228-229	34, 119, 132, 143
C ₂ H ₅	1, 2	77-78	34, 88, 91, 106, 108, 132, 143
<i>n</i> -C ₃ H ₇	1	145	34, 106, 108, 132
<i>n</i> -C ₄ H ₉	1, 2	74-75	34, 88, 91, 106, 132, 143
<i>i</i> -C ₄ H ₉	1	92-93	34
C ₆ H ₁₁	1	43.5	108
C ₆ H ₁₁	2, 3	205 dec.	88, 90, 132
CH ₂ =CH-CH ₂	1	58-59	132
C ₆ H ₅	2, 3	168-169	90, 92, 105, 132
<i>p</i> -CH ₃ C ₆ H ₄	3	183-184	132
C ₆ H ₅ CH ₂	1	145-150	91
(CH ₃) ₂ N	2	227	135
Unsymmetrical Diphosphine Disulfides, R ₁ P(S)P(S)R ₁ R ₂			
R ₁ = CH ₃ , R ₂ = C ₂ H ₅	1	159-160 (A); 103-104 (B)	119
R ₁ = CH ₃ , R ₂ = <i>n</i> -C ₃ H ₇	1	155-156 (A); 92-94 (B)	119
R ₁ = CH ₃ , R ₂ = <i>n</i> -C ₄ H ₉	1	126-128 (A); 47-50 (B)	119
R ₁ = CH ₃ , R ₂ = C ₆ H ₅	1	206-208 (A); 145-146 (B)	119
R ₁ = CH ₃ , R ₂ = C ₆ H ₅ CH ₂	1	188-189 (A); 120-123 (B)	119
R ₁ = C ₂ H ₅ , R ₂ = C ₆ H ₅	1	156-157 (A); 85-87 (B)	143
R ₁ = C ₆ H ₅ , R ₂ = N(C ₂ H ₅) ₂	2	128 (A); 123 (B)	163
R ₁ = C ₆ H ₁₁ , R ₂ = N(C ₂ H ₅) ₂	2	191 (A); 158-160 (B)	163
Miscellaneous Diphosphine Disulfides			
	2	178-180	81
	1	185	159
	1	185-225	159

^a Methods: 1, anomalous Grignard reaction; 2, sulfurization of R₄P₂; 3, R₂P(S)H + R₂P(S)Cl.

disulfide rather than the expected (CH₃)₃P(S). Since then a substantial number of diphosphine disulfides have been prepared by what has been deemed the "anomalous" Grignard reaction (Table V). The course of this novel reaction is usually expressed by the equation

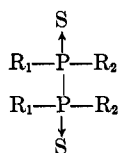


This equation is undoubtedly an oversimplification, however, particularly with respect to formation of the hydrocarbon, R-R. Although the appropriate hydrocarbons have been isolated in some instances, it has been shown (144) that the gaseous products formed during the preparation of (C₂H₅)₄P₂S₂ are ethane and ethylene and not butane as expected from the equation.

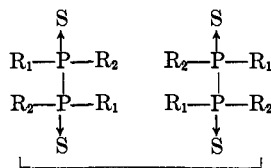
The yield of diphosphine disulfide depends on many factors (91, 132), such as temperature, rate of reaction, and the steric and electronic characteristics of the group on the Grignard reagent. Optimum yields appear to be obtained (132) with a 3.2:1 ratio of alkyl magnesium bromide to PSCl₃ in the 0-20° range. In-

creasing the length of the aliphatic chain favors the production of R₃P(S) at the expense of diphosphine disulfide (108), while aromatic Grignard reagents lead exclusively to R₃P(S) (132). The reaction also takes another course with branched-chain aliphatic (except isobutyl) (34), cycloaliphatic (91, 132), and vinyl (132) Grignard reagents, leading to R₃P(S) and/or other products. In certain cases, such as benzyl and amyl, the diphosphine disulfide has been isolated by one group (91, 108), but not others (34, 132). Apparently in these cases the isolation of a diphosphine disulfide is critically dependent upon reaction conditions.

Alkyl or aryl phosphonothioic dihalides, RP(S)X₂, can also react "anomalously" with Grignard reagents (118, 199) resulting in asymmetric diphosphine disulfides, R₁R₂P(S)P(S)R₁R₂, which have two asymmetric phosphorus atoms and are therefore stereochemically analogous to tartaric acid. Although four optical isomers are possible, Maier (118, 119) was only able to isolate the optically inactive *meso* (XII) and racemic (XIII) forms. It has been shown by X-ray crystallog-



XII



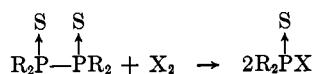
XIII

raphy (185) that the high melting form (A) of 1,2-dimethyl-1,2-diphenyldiphosphine disulfide is *meso* and the low melting form (B) is probably racemic. Presumably this is the case for the other asymmetric diphosphine disulfides. Finally it is interesting to contrast the "normal" behavior of aryl magnesium halides with PSCl_3 to their "anomalous" behavior with $\text{CH}_3\text{P}(\text{S})\text{Br}_2$ [but not $\text{CH}_3\text{P}(\text{Se})\text{Br}_2$] (119).

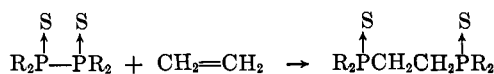
When diphosphine disulfides are not available from the "anomalous" Grignard reaction, they are usually prepared by sulfurization of a diphosphine or by the reaction of $\text{R}_2\text{P}(\text{S})\text{H}$ with $\text{R}_2\text{P}(\text{S})\text{Cl}$ (132). It has also been possible (132) to obtain a small yields of $(\text{C}_2\text{H}_5)_4\text{P}_2\text{S}_2$ by Wurtz-type coupling of $(\text{C}_2\text{H}_5)_2\text{P}(\text{S})\text{Cl}$.

B. REACTIONS OF DIPHOSPHINE DISULFIDES

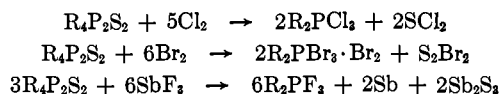
Under certain circumstances it is possible for the P-P and P→S bonds of a diphosphine disulfide to undergo reaction independently. Mention has already been made of the desulfurization of diphosphine disulfides without P-P bond cleavage. Examples of P-P bond cleavage without attack of the P→S bonds are halogenation with the theoretical quantities of Cl_2 (108, 120), Br_2 (106, 108, 118, 120), PCl_5 (108), SO_2Cl_2 (120), Hg_2Cl_2 (120), or SCl_2 (120)



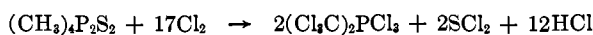
and the ethylene insertion reaction (139, 159).



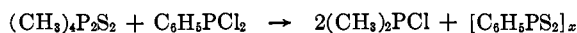
It is more usual, however, for the P-P and P→S bonds to react simultaneously. Thus, an excess of Cl_2 (108, 149) or Br_2 (108) causes halogenation of both the P-P and P→S bonds, as does fluorination with SbF_3 or AsF_3 (159).



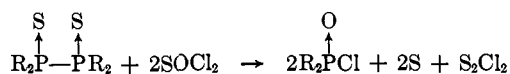
Under more vigorous chlorination conditions it is possible to chlorinate the P-C bonds (149), presumably according to the equation



Desulfurization plus chlorination of the P-P bond takes place when $(\text{CH}_3)_4\text{P}_2\text{S}_2$ is heated with $(\text{C}_6\text{H}_5)_2\text{PCl}$ (120) or $\text{C}_6\text{H}_5\text{PCl}_2$ (138)

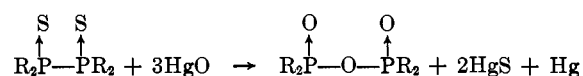


and an interesting sulfur-oxygen exchange plus P-P bond cleavage results from the reaction of SOCl_2 with tetraalkyl diphosphine disulfides (118, 121, 143).



It has been shown by n.m.r. (121) that P-P bond cleavage precedes sulfur-oxygen exchange.

Diphosphine disulfides can be oxidized to disubstituted phosphonic acids by a variety of oxidizing agents which includes HNO_3 (96), H_2O_2 (106, 118), organic peroxides (118), and HgO (106, 118, 120). In the case of HgO oxidation. The reaction probably involves the phosphonic anhydride as intermediate.



The extent to which a diphosphine disulfide is reduced depends on the particular reducing agent. Hydrogenation with Raney copper (130, 132) or reduction with LiAlH_4 (91, 118) lead directly to the secondary phosphine, certain metals (132) and tertiary phosphines (123) only remove the sulfur atoms, and reduction with metal hydrides (132) results in mixtures of diphosphines and secondary phosphines.

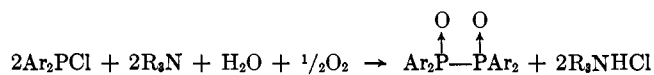
C. STEREOCHEMISTRY OF DIPHOSPHINE DISULFIDES

X-Ray crystallographic studies have shown that both $(\text{C}_2\text{H}_5)_4\text{P}_2\text{S}_2$ (44) and the *meso* form of $(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}_2\text{S}_2$ (185) exist in the *trans* conformation in the solid state. The same conformation has been suggested for $(\text{CH}_3)_4\text{P}_2\text{S}_2$ on the basis of its infrared and Raman spectra (54). Although certain of the latter's assignments have been questioned (34), the indications are that other diphosphine disulfides possess the same configuration. The observation that there are considerable differences between the spectra of solid and liquid samples (34) may be due to the existence of restricted rotation about the P-C bonds. In both $(\text{C}_2\text{H}_5)_4\text{P}_2\text{S}_2$ and $(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\text{P}_2\text{S}_2$ the bond angles around the phosphorus atoms depart only slightly from tetrahedral, and the fact that the P-C distances are sensibly the same for a phosphorus atom attached to a methyl, ethyl, or phenyl group indicates that there is little or no conjugation between the phenyl group and the P-P bond.

D. DIPHOSPHINE MONOSULFIDES AND DIPHOSPHINE DIOXIDES

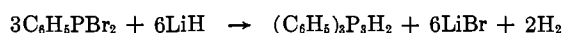
Closely related to the diphosphine disulfides are the diphosphine monosulfides, $\text{R}_2\text{P}(\text{S})\text{PR}_2$, and the diphosphine dioxides, $\text{R}_2\text{P}(\text{O})\text{P}(\text{O})\text{R}_2$. The diphosphine monosulfides can be prepared by removal of one sulfur atom from a diphosphine disulfide (123), heating a 1:1 mixture of $\text{R}_4\text{P}_2\text{S}_2$ and R_4P_2 (122), or by addition of the appropriate quantity of sulfur to a diphosphine (122).

The remaining lone pair makes diphosphine monosulfides sensitive to oxidation, and, as expected, the P-P bond can be cleaved by halogens (123). Diphosphine dioxides are generally prepared (88, 105, 135) by controlled oxidation of a diphosphine, but recently (146) some aryl derivatives have been prepared by exposure of air of an ethereal solution containing equimolar amounts of a diaryl phosphinous chloride and a tertiary amine in the presence of small quantities of water.

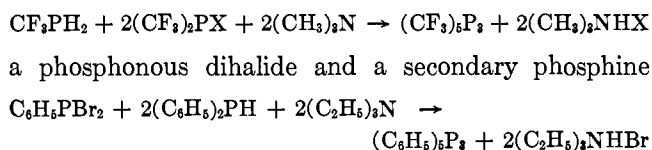


VIII. TRIPHOSPHINES

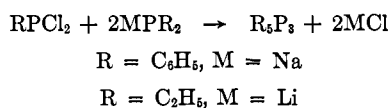
Although there is some mass spectrographic evidence (153) for P_3H_5 , this compound has never been isolated. Even partial replacement of hydrogens by less labile groups stabilizes the P_3 chain sufficiently to permit the preparation of trisubstituted triphosphines of general formula $\text{RHP}-\text{P}(\text{R})-\text{PHR}$. 1,2,3-Tris(trifluoromethyl)triphosphine, the first triphosphine to be isolated (117), is one of the products of hydrolysis of the cyclopentaphosphine, $(\text{CF}_3\text{P})_5$, and 1,2,3-triphenyltriphosphine can be prepared (186) by the reaction of $\text{C}_6\text{H}_5\text{PH}_2$ with $\text{C}_6\text{H}_5\text{PBr}_2$. The $\text{C}_6\text{H}_5\text{PH}_2$ is not added as such, but is produced *in situ* by reduction of part of the $\text{C}_6\text{H}_5\text{PBr}_2$ with LiH which also functions as the HBr acceptor.



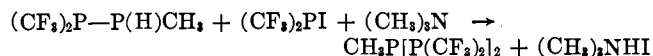
The general approach that has been used for the synthesis of fully substituted triphosphines is the reaction of a monofunctional with a difunctional reagent in a 2:1 ratio. These reagents can be a primary phosphine and a phosphinous halide (25, 29) (with tertiary amine as hydrogen halide acceptor)



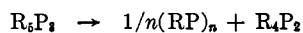
(186) or a phosphonous dihalide and an alkali metal organophosphide (186).



Triphosphines have also been obtained from diphosphines, in one case by disproportionation of $[(\text{CH}_3)_2\text{N}]_4\text{P}_2$ (135), and in the other by coupling of a monofunctional diphosphine with a phosphinous halide (25).



The salient property of a triphosphine is its tendency to disproportionate.



In the case of the CF_3 -substituted triphosphines this type of reaction is catalyzed by stopcock greases, mercury, and bases. This meant that special techniques had to be developed to avoid prolonged contact between the newly formed triphosphine and the HX acceptor (29).

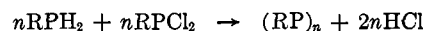
Triphosphines show ultraviolet absorption in the same region as diphosphines (25, 29) suggesting that there is some delocalization of lone pairs by interaction with adjacent phosphorus 3d-orbitals. Chemical evidence for this suggestion is the observation that only the terminal phosphorus atoms of pentaphenyltriphosphine are quaternized with HBr or CH_3I (186). This is contrary to expectation since the central phosphorus atom, which only bears one electron-withdrawing phenyl group, should be more basic than the terminal phosphorus atoms. Diminution of the basicity of the central phosphorus atom could be explained by delocalization of its lone pair onto the terminal phosphorus atoms, although it is important to realize that the central phosphorus atom is also the most sterically hindered.

The only open-chain tetraphosphine that appears to have been isolated is $\text{H}_2(\text{CF}_3\text{P})_4$ (181). Other attempts (186) to prepare open-chain polyphosphines involving more than three phosphorus atoms have been frustrated by disproportionation.

IX. CYCLOPOLYPHOSPHINES

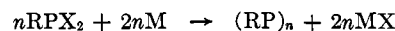
A. PREPARATION OF CYCLOPOLYPHOSPHINES

In general the methods which have been employed in the synthesis of diphosphines have been extended to cyclopolyposphines by replacement of monofunctional with difunctional reagents. One of the simplest cyclopolyposphine preparations involves the reaction of a primary phosphine with a phosphonous dichloride (Table VI).

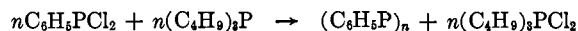


The primary phosphine can either be added as such or it can be generated *in situ* by reduction of the phosphonous dichloride with metal hydrides (69, 74, 140, 148) or sodium-ethanol (140).

Cyclization can also be effected by Wurtz-type coupling of phosphonous dihalides with mercury, magnesium, or alkali metals (21, 24, 69, 116, 117).



In one novel case the chlorine atoms were abstracted with tri-*n*-butylphosphine (49)



an approach which has also been applied to the coupling of $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{Cl}$. Equally interesting is the thermal polymerization of CH_3PF_2 (109).

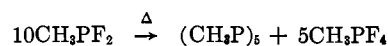
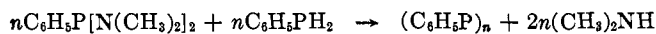


TABLE VI
 PREPARATION AND PROPERTIES OF CYCLOPOLYPHOSPHINES

Substituents	Method ^a	B.p. (mm.), °C.	M.p., °C.	Ref.
Cyclotetraphosphines, (RP) ₄				
CF ₃	2(a), 3	135 (est.)	66.3-66.4	24, 116, 117, 182
C ₂ H ₅	1, 2(b), 2(c)	124-129 (0.05)		69, 83
<i>n</i> -C ₃ H ₇	1	140-145 (0.03)		69
<i>i</i> -C ₃ H ₇	2(b)	110-14 (0.04)		69
CNCH ₂ CH ₂	1		87-89	69
<i>n</i> -C ₄ H ₉	1, 3	170 (0.02)		69, 147
<i>i</i> -C ₄ H ₉	1, 2(b), 2(c)	140 (0.1)		69
(C ₂ H ₅) ₂ CH	4		91-92	69
C ₆ H ₁₁	1, 4, 5		219-220	69, 78, 89
<i>n</i> -C ₈ H ₁₇	1, 2(b)	230 (0.1)		69
Cyclopentaphosphines, (RP) ₅				
CH ₃	2(b), 2(c), 5	110-112 (1)		69, 109
CF ₃	2(a)	190 (est.)	-33	24, 116, 117
C ₆ H ₅ (A)	1, 2(a), 2(b), 2(c), 5		150	21, 41, 49, 69, 74, 80, 98, 102, 104, 140, 145, 148, 186
Cyclohexaphosphines, (RP) ₆				
C ₆ H ₅ (B)	1		195-199	41, 69, 148, 183

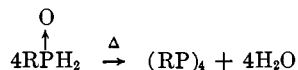
^a Methods: 1, reaction of RPH₂ with R₂PCl₂; 2, coupling of RPX₂ with (a) Hg, (b) Mg, or (c) alkali metal; 3, from elemental phosphorus; 4, dehydration of a primary phosphine oxide; 5, mentioned in text.

Other extensions of the preparative procedures used for diphosphines include the displacement of dimethylamine from a phosphonous dimethylamide (41)



and the isolation of cyclotetraphosphines from the reaction of elemental phosphorus with CF₃ radicals (182) and C₄H₉MgBr-C₄H₉Br mixtures (147).

New and fundamentally different routes to the cyclopolyposphine moiety are represented by the dehydration of a primary phosphine oxide (69)



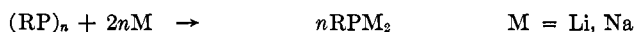
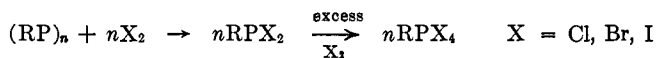
and the reaction of phenylphosphine with organo-mercury compounds (145).



Useful yields of cyclopolyposphines have also been obtained by heating simpler molecules such as (CF₃)₄P₂ and (CF₃)₂PH (117) and by reaction of metal organophosphides of the type RPHM with organic dihalides (78) and bromine (80).

B. REACTIONS OF CYCLOPOLYPHOSPHINES

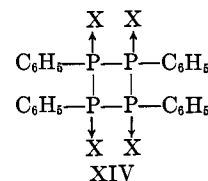
As expected, the reactions of the cyclopolyposphines closely resemble those of the corresponding diphosphines. All the P-P bonds of a cyclopolyposphine are cleavage by alkali metals (21, 104) and halogens (98, 102, 104, 148) to yield dialkali organophosphides, RPM₂, and phosphonous dihalides, respectively.



As usual, excess halogen causes conversion to the tetrahalophosphorane (83, 89, 117). Under carefully controlled conditions of halogenation and metalation it is possible to isolate XI (72) and the analogous 1,2-disodio-1,2-diphenyldiphosphide (104, 148).

Like the diphosphines the behavior of cyclopolyposphines towards alkyl halides or CF₃I depends on the electronic nature of the substituents. Thus with (C₂H₅P)₄ it is possible to isolate a monoquaternary salt, [(C₂H₅P)₄]CH₃⁺I⁻ (83), but the cyclopolyposphines bearing electron-withdrawing CF₃ or C₆H₅ groups undergo cleavage which is complete with CF₃I (16) or C₆H₅CH₂I (72), and partial (XI isolated) with CH₃I or C₂H₅I (72).

The reactivity of a cyclopolyposphine towards an acceptor depends on the basicity of the phosphorus atoms. The electron-withdrawing CF₃ group renders (CF₃P)₄ inert towards HCl, BF₃, B₂H₆, and H₂SO₄ within reasonable temperature limits (117), while the less electron-withdrawing phenyl group permits the isolation of tetraphenylcyclotetraphosphine tetrasulfide (104) and tetraselenide (XIV) (101) and an adduct of composition (C₆H₅P)₃·BF₃, the structure of which is unknown (104).



X = S or Se

Interestingly there are no oxygen analogs of XIV. Instead, controlled oxidation of the CF₃- and C₆H₅-substituted cyclopolyposphines yields polymeric

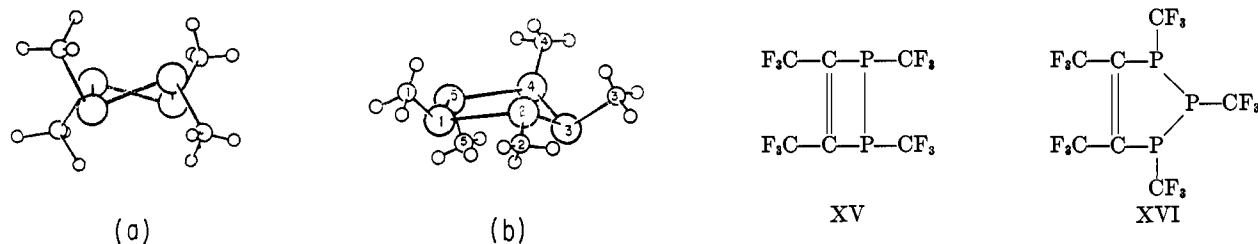


Figure 2.—Molecular conformations of (a) $(\text{CF}_3\text{P})_4$ and (b) $(\text{CF}_3\text{P})_5$ [Figure 2b reproduced, by permission, from *Acta Cryst.*, 14, 253 (1961)].

materials of general formula $[\text{RPO}_2]_x$, which are presumably mixtures of the corresponding phosphonic acid anhydrides (104, 117).

Cyclic phosphines will also react with metal carbonyls (3, 27) and NiBr_2 (83). Tetrakis(trifluoromethyl)cyclotetraphosphine reacts with $\text{Ni}(\text{CO})_4$ to give polymeric products of uncertain composition (27), while reaction of $(\text{C}_6\text{H}_5\text{P})_n$ with $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ gives compounds of composition $(\text{C}_6\text{H}_5\text{P})_4\text{Ni}(\text{CO})_3$, $(\text{C}_6\text{H}_5\text{P})_4[\text{Fe}(\text{CO})_4]_2$, $(\text{C}_6\text{H}_5\text{P})_5\text{Mo}(\text{CO})_5$, and $(\text{C}_6\text{H}_5\text{P})_5\text{W}(\text{CO})_5$, respectively (3). It is noteworthy that the Ni and Fe complexes involve a four-membered phosphorus ring while the Mo and W complexes involve a five-membered ring. In each case the polyphosphine ring appears to behave as a unidentate ligand. Reaction of $(\text{C}_2\text{H}_5\text{P})_4$ with NiBr_2 led to ill-defined products (83). The CF_3 -substituted cyclopolyphosphines react with tertiary phosphines and amines to form monomer complexes of type $\text{R}_3\text{E}^+\text{P}-\text{CF}_3$ (28). The reversibility of this reaction has offered a way of interconverting $(\text{CF}_3\text{P})_4$ and $(\text{CF}_3\text{P})_5$.

The cyclopolyphosphines range in thermal stability from $(\text{C}_6\text{H}_5\text{P})_5$, which decomposes on melting (104) to the alkyl cyclotetraphosphines which can be distilled without decomposition (83, 147). In general the thermal stabilities are comparable to the corresponding diphosphines.

Aqueous alkalis liberate exactly half the CF_3 groups of $(\text{CF}_3\text{P})_4$ as fluoroform (117). Presumably, the initially formed open-chain tetraphosphine, $\text{HP}(\text{CF}_3)\text{P}(\text{CF}_3)\text{P}(\text{CF}_3)\text{P}(\text{CF}_3)\text{OH}$ breaks down into CF_3PH_2 , $\text{CF}_3\text{PHO}(\text{OH})$, and the diphosphine, $\text{HOP}(\text{CF}_3)\text{P}(\text{CF}_3)\text{H}$, which in turn delivers CF_3PH_2 and a second molecule of $\text{CF}_3\text{PHO}(\text{OH})$. Of the two final products only $\text{CF}_3\text{HOP}(\text{OH})$ can produce fluoroform. Likewise, alkaline hydrolysis of $(\text{CF}_3\text{P})_5$ produces 2.5 moles of CHF_3 (117). Plain water hydrolysis is much slower and seems to involve a more random scission of the P_n chain. Among the products are the diphosphine, $(\text{CF}_3\text{PH})_2$, and the triphosphine, $\text{H}_2(\text{CF}_3\text{P})_3$.

Recently Mahler (115) has extended Burg's pseudohalogen concept to the preparation of new polyphosphine heterocycles (XV and XVI), by treating $(\text{CF}_3\text{P})_4$ and $(\text{CF}_3\text{P})_5$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$. It has been

suggested, on the basis of their ultraviolet spectra, that the orbitals of the polphosphine portion of the rings overlap with the carbon-carbon orbitals. Some saturated analogs of XV and XVI, containing two or four phosphorus atoms in five- and six-membered rings, have also been prepared (68).

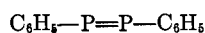
C. STRUCTURAL ASPECTS OF CYCLOPOLYPHOSPHINES

Certainly, one of the most challenging features of polyphosphine chemistry is the stereochemistry of the cyclic compounds. It has been shown by X-ray crystallography (137) that the four-membered phosphorus ring of $(\text{CF}_3\text{P})_4$ is twisted (Figure 2a), with an average PPP bond angle of 84.7° and a 34° ring torsion angle. The CF_3 groups, which alternate above and below the ring, are arranged such that a staggered conformation down each P-C bond is adopted and the molecule as a whole has D_{2d} symmetry. The nonplanarity of the ring is probably caused by relief of torsional strain. Cross-ring repulsion, which has been invoked in connection with the abnormally long bond of C_4 rings, is apparently of little importance in the P_4 ring. The Raman spectra of several tetraalkylcyclotetraphosphines have been interpreted (2) on the assumption that they have the same symmetry as $(\text{CF}_3\text{P})_4$. Of the six vibrations ($3N - 6$) expected for the P_4 ring, only the symmetric (A_1) and asymmetric (B_1) ring stretching modes could be assigned, due to considerable mixing of symmetry coordinates between the other four ring vibrations and the C-P-P deformation modes. Since neither of the ring stretching modes shifted appreciably with change of substituent, the presence of two strong Raman bands between 390 and 495 cm^{-1} can be considered diagnostic of a four-membered phosphorus ring.

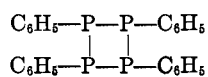
The P_5 ring of $(\text{CF}_3\text{P})_5$ is appreciably distorted from a planar configuration (166). In this molecule complete alteration of the substituents is impossible, so the CF_3 groups on phosphorus atoms numbered 3 and 4 (Figure 2b) lie on the same side of the ring, causing considerable steric hindrance in this area. Perhaps the most interesting aspect of the structure is that the CF_3 group on phosphorus atom 4 is bent towards the center of the ring, causing the $\text{P}_2 \cdots \text{F}_4$ distance across the ring to be approximately 0.2 Å shorter than the van der Waals distance. Furthermore, the P-P bond distances on either side of phosphorus atom 2 are significantly longer than the other three, and the isotropic temperature factor of fluorine atom 4 is smaller than the

average of the others. On the basis of this information it is tempting to conclude that there is some $P \cdots F$ interaction across the ring. However, as Donohue (42) noted in a paper comparing the ring compounds of phosphorus and arsenic, there is a remarkable similarity between the conformations of $(CF_3P)_5$ and $(CH_3As)_5$, and since such cross-ring interactions are not expected with the arsenic compound, the conformation may simply result from a balance of the various strains and torsions in the molecule.

Four different compositions corresponding to the empirical formula C_6H_5P appear to have been isolated. For convenience these can be called compound A, m.p. $\sim 150^\circ$; compound B, m.p. $\sim 190^\circ$; compound C, m.p. 252–256; and compound D, m.p. 260–285°. Compounds C and D are insoluble in organic solvents and are presumed polymeric (69). The question of the molecular weights of compounds A and B in solution is one of controversy. On the basis of several ebullioscopic, cryoscopic, and isopiestic methods the following identities have been suggested: A = B = XVII (183); A = XVII, B = XVIII (148); and A = XVIII (104, 140).

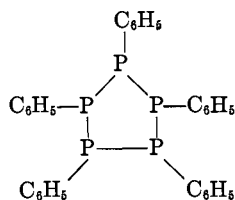


XVII

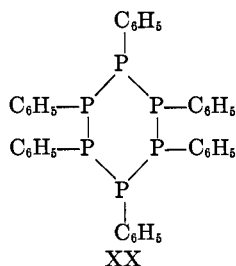


XVIII

Later it was found (69) that compounds A and B both exhibit a mass spectrographic peak corresponding to $(C_6H_5P)_4^+$ and that the solid phase Raman and solution infrared spectra of the two compounds are almost identical. Since it was only in the H^1 n.m.r. spectra that distinct differences between compounds A and B could be detected, it was concluded that they are both XVIII, differing from each other in conformation both in solution and in the solid state. However, it has now been shown (41) by X-ray crystallography that in the solid state compound A is XIX, while compound B is very probably XX. Furthermore, another crystalline form was isolated which involved one molecule of benzene per six C_6H_5P groups.

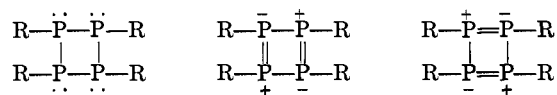


XIX



XX

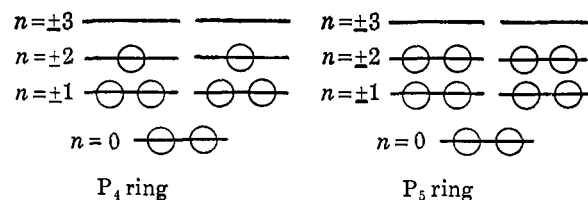
Another interesting aspect of cyclophosphines concerns the possibility of electron delocalization and possibly aromatic character, by contributions of the following types of resonance structure, which presumably involve the interaction of phosphorus lone pairs with neighboring phosphorus 3d-orbitals. This



idea is supported by the intense ultraviolet spectra of the cyclophosphines (69, 117) and the fact that alkyl cyclophosphines are nonbasic (69). Additional support comes from Burg and Mahler's free-electron molecular-orbital treatment of $(CF_3P)_4$ and $(CF_3P)_5$ (117), whereby the lone-pair electrons of each phosphorus atom are delocalized on to the periphery of a circle having the radius of the P_4 or P_5 ring. The energy levels for such a system are given by the expression

$$E_n = \frac{n^2 h^2}{8\pi^2 m R^2}$$

where n is a quantum number, m is the mass of the electron, and R is the radius of the circle taking the P-P bond distance as 2.2 Å.



Thus if an electron is excited from the $n = \pm 1$ to the $n = \pm 2$ level, as is the case with the tetramer, or from the $n = \pm 2$ to $n = \pm 3$ with the pentamer, bands are predicted at 2600 and 2300 Å., respectively, in reasonable agreement with one of the observed bands of the tetramer (2590 Å.) and the maximum of the pentamer (2400 Å.). To account for the observed diamagnetism, as well as the fact that more than one peak is observed, one presumes that the $n = \pm 2$ level is split by the nonplanarity of the P_4 ring.

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