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Organic Phosphorus Compounds with a P-P Bond

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Data on the methods of synthesis and reactivities of organic diphosphines with a direct P-P bond between four-coordinated phosphorus atoms as well as compounds with a P-P bond between a three-coordinated phosphorus atom and a phosphorus atom with a higher degree of coordination are surveyed and described systematically. Problems of the steric structures and the results of structural analysis, spectroscopic studies, and studies by other methods are considered.
The bibliography includes 269 references.

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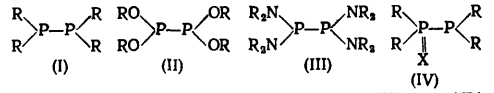
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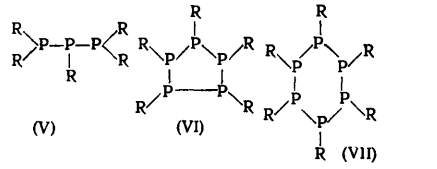
I. INTRODUCTION

Studies on organic compounds with P-P bonds have continued since 1877 when Kohler and Michaelis[1] obtained for the first time the so-called phosphobenzene[1]:

$$n\,PhPCl_2 + n\,PhPH_2 \rightarrow 2\,(PhP)_n + 2n\,HCl.$$

Numerous classes of organophosphorus compounds (OPC) with P-P bonds are now known; these compounds can be fairly formally classified as follows: (a) in terms of the valence state of the phosphorus atoms linked to one another; (b) in terms of the number of phosphorus atoms in the chain; (c) in terms of the number of phosphorus atoms in the ring. For example, it is possible to distinguish the following types of organic compounds with P-P bonds: tetra-alkyl(aryl)-diphosphines† (I), tetra-alkoxy(aryloxy)-diphosphines (II), tetra-aminodiphosphines (III), tetra-alkyl-(aryl)diphosphine monoxides (monosulphides, monoimides), tetra-alkyl(aryl)diphosphines (IV), penta-alkyl(aryl)triphosphines (V), polyalkyl(aryl)cyclopolyphosphines (VI) and (VII), etc.





A review published in 1965 is devoted to organic diphosphines[2]. Since then the number of data on this subject has significantly increased and in the present review we shall therefore consider only compounds with a P-P bond between two phosphorus atoms at least one of which is three-coordinated; mainly studies published after the above review[3] or not included in it are analysed.

† The term "diphosphanes" has also been suggested for organic diphosphines on the basis of the analogy between these compounds and organic disilanes, distannanes, etc.[2]: however, it does not reflect the valence state of the phosphorus atoms.

II. THE STRUCTURES OF ORGANIC DI- AND POLY-PHOSPHINES

The length of the P-P bond in organic di- and polyphosphines is ~ 2.22 Å,[4] is fairly constant, and does not deviate significantly from the value (2.24 Å) predicted by Pauling[5], which suggests either the absence of a higher degree of binding than in a simple σ bond or the presence of a constant additional binding. The latter is unlikely, since the length of the P-P bond is almost independent of the substituent, its electronegativity, or whether the molecular structure is cyclic or non-cyclic and even of the valence state of the phosphorus atom (Table 1). Thus the lengths of the P-P bond in tetramethyldiphosphine, diphosphine, and tetrakis(trifluoromethyl)diphosphine are 2.192, 2.216, and 2.160 Å respectively, while in the presence of the most electronegative substituent (fluorine) the longest P-P bond is formed (2.281 Å) (Table 1). The length of the P-P bond in diphosphine is not a simple function of the electronegativity of the groups and no evidence for the existence of $p\pi - d\pi$ conjugation can be obtained from the lengths of these bonds. However, even in difluorodiphosphine, where the greatest delocalisation should be expected, neither the bond length nor the conformation of the molecules (see below) permit the conclusion that $p\pi - d\pi$ conjugation obtains[7]. The Nyholm-Gillespie theory and semiempirical calculations predict satisfactorily the bond lengths and angles in organic phosphines[8-10] but have no predictive power as regards organic diphosphines[12,13]. On the other hand, *ab initio* calculations yield P-P bond lengths in good agreement with experiment[12,13].

Table 1. The P-P bond lengths.

Compound	P-P bond length, Å	Refs.	Compound	P-P bond length, Å	Refs.
H_2P-PH_2	2.218±0,004	6	$Me_2P-PMe_2\cdot 2Fe(CO)_4$	2,231±0.007	19
D_2P-PDH	2.219±0,0004	15	$Ph_2P-PPh_2\cdot 2Ni(CO)_3$	2,277±0,004	20
D_2P-PF_2	2.218±0,038	6	$Et_2P(S)-P(S)Et_2$	2.220±0,01	21
I_2P-PI_2	2.21±0.06	16	$(PhP)_5$	2,217±0,006	22,23
F_2P-PF_2	2.281±0.03	14,11	$(PhP)_6$	2,233±0,005	24,25
Me_2P-PMe_2	2,192±0.18	17	$(PCF_3)_4$	2.213±0,005	26
$(F_3C)_2P-P(CF_3)_2$	2,182±0.016	6	$(PCF_3)_5$	2,223±0,007	27
$Me_2P-PMe_2\cdot 2BH_3$	2,204±0.005	18			

The C–H and C–P bond lengths and the C–P–C and C–H–P dihedral angles in Me_4P_2 are close to the value in Me_nPH_{4-n} (n = 1–3).[3]

The P–P bond dissociation energies in diphosphine, measured mass-spectrometrically, are 61[28] and 74[29] kcal mole^{-1} for P_2H_4, 62 kcal mole^{-1} [30] for P_2Cl_4, 71 kcal mole^{-1} [28] for P_2I_4, and 86 kcal mole^{-1} [32] for Et_4P_2, but these data are subject to large systematic errors[28]. According to data obtained by other methods, the P–P bond energy varies from 44 to 58 kcal mole^{-1} (Table 2), which is significantly less than the energies of the P–N (67–77 kcal mole^{-1}) and P–C (65–71 kcal mole^{-1}) bonds[5,38,39], but is higher than the energy of the N–N bond (in N_2F_4, for example, the latter is 20.4 ± 1.3 kcal mole^{-1} [32]).

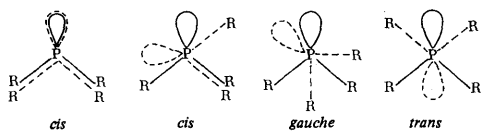
Table 2. The P–P bond energies.

Compound	P–P bond energy, kcal mole^{-1}	Method of determination	Refs.
$H_2P—PH_2$	46.8	Thermochemical	34
P_4	51,3	Calculation	35
P_4	51.3	Thermochemical	5
P_4	44	Spectroscopic	36
$Ph_2P—PPh_2$	50	Thermochemical	37

Experimental evidence for a planar configuration of the phosphorus atoms, which might indicate the occurrence of $p\pi - d\pi$ binding, has not been obtained for phosphines having the general formula $R_2P–PR_2$ either in the gas or in the solid phase. *Ab initio* calculations by the SCF LCAO-MO method for all the possible rotational isomers of the P_2H_4 molecule also indicate the absence of $p\pi - d\pi$ binding[40]. According to photoelectron spectroscopic data for di- and poly-phosphines (VIII)–(XI), the degree of $p\pi - d\pi$ binding is very insignificant[41]:

$(CF_3P)_4$ (VIII), $(CF_3P)_5$ (IX), $(CF_3)_2P—PMe_2$ (X), $CF_3P—C(=CF_2)—CF_3$ / $CF_3P—C(=CF_2)—CF_3$ (XI).

The substituents and the lone electron pair of the X atom in molecules having the general formula X_2Y_4*, where X = N, P, or As, have a pyramidal arrangement; in this case there is a possibility of three types of symmetry—C_2 (*cis*- and *gauche*), C_{2v} (*cis*), and C_{2h} (*trans*).[42]



Symmetry	C_{2v}	C_2	C_2	C_{2h}
Dihedral angle	0°	46°55′	93°50′	180°

The relative number of conformations, determined by their stabilities, depends in the general case on the interaction of the two lone electron pairs, on the steric repulsion between the substituents, on the electrostatic interaction, and other factors. Table 3 presents data for the conformational compositions of a series of inorganic and organic diphosphines. Evidently the *gauche*- or *trans*-conformation is the most stable. The proportion of the *trans*-conformer can be related in certain cases to the electronegativity of the substituents at the phosphorus atom: thus the contents of the *trans*-conformers of Me_4P_2 and Cl_4P_2 are respectively 40 and 95%[42–45]. This effect may be attributed wholly to the difference between the electronegativities of the Me group and the Cl atom (2.0 and 3.0 respectively), since the effective volumes of the substituents and the P–P bond lengths in these compounds are identical. This conclusion has also been confirmed by a comparison of the conformational compositions of $(CF_3)_4P_2$ and F_4P_2 (the electronegativities of the CF_3 group and the fluorine atom are 3.2 and 4 respectively); the content of the *gauche*-form of $(CF_3)_4P_2$ is much higher[46]. In this case steric hindrance is also apparently unimportant, since the P–P bond in $(CF_3)_4P_2$ is much shorter (2.16 Å) than in F_4P_2 (2.28 Å). If $(CF_3)_4P_2$ and Me_4P_2 are compared from this point of view, the latter should have the *gauche*-conformation and the former should exist as the *trans*-conformer. However, the shorter P–P bond in the perfluoro-compound prevents this and the contents of the *gauche*-conformers of $(CF_3)_4P_2$ and Me_4P_2 are 30 and 60% respectively.

Table 3. The P–P bond lengths in inorganic and organic diphosphines.

Compound	Conformational composition	Method of determination	Refs.
$H_2P—PH_2$	*gauche* (in solution)	RS*	6,15,47
$H_2P—PH_2$	*trans* (in solution)	RS	48
$H_2P—PH_2$	*gauche* (gas)	RS	49
$H_2P—PH_2$	*trans* (solid)	i.r. and RS	50
$H_2P—PH_2$	*gauche* > *cis* > *trans*	SCF and EHM** methods	10
$H_2P—PH_2$	*gauche* (10% *trans*)	PES***	51
$H_2P—PH_2$	*gauche* > *trans* > *cis*	*ab initio* calculation	52
$H_2P—PH_2$	*gauche*	*ab initio* calculation	13,40
$Me_2P—PMe_2$	*gauche* (60%) *trans* 40%) (liquid, gas)	i.r. and RS	43,44
$Me_2P—PMe_2$	*trans, gauche*	PES	54
$Me_2P—PMe_2$	*gauche*	PES	53
$Et_2P—PEt_2$	*trans* (solid)	i.r. and RS	43
$Et_2P—PEt_2$	*trans*	^{1}H NMR	55
Me(Et)P—P(Et)Me	*gauche* (liquid)	^{13}C NMR; ^{1}H NMR	56
Me(iso-Pr)P–P(iso-Pr)Me	*gauche* (liquid)	^{13}C NMR; ^{1}H NMR	56
Me(t-Bu)P–P-(t-Bu)Me	*gauche* (liquid)	^{1}H NMR; ^{31}P NMR	57
Me_2P-P(t-Bu)$_2$	*gauche* (liquid)	^{13}C NMR; ^{1}H NMR	56
(iso-Pr)$_2$P-P(Pr-iso)$_2$	*gauche* (liquid)	^{13}C NMR; ^{1}H NMR	56
(t-Bu)$_2$P–P(But)$_2$	*gauche* (5% *trans*) (liquid)	^{13}C NMR; ^{1}H NMR	58,59
$Cl_2P—PCl_2$	*trans* (95%) (liquid, solid)	i.r. and RS	45
$Cl_2P—PCl_2$	*trans* (95%)	CNDO and *ab initio* calculation	15
$Cl_2P—PCl_2$	*trans* (liquid)	Calculation by Kreevoy and Mason's method (Ref.60)	61
	trans (<10% *gauche*) (gas)	gas electron diffraction	62
	trans > *gauche* > *cis*	*ab initio* calculation	13
	gauche > *cis* > *trans*	SCF method	10
	trans (liquid)	i.r. and RS	63,64
	trans (90%), *gauche* (10%)	PES	65
	trans (in solution, solid)	RS	16,66
	gauche (in solution)	i.r.	67,68
	trans (in solution)	Calculation by Kreevoy and Mason's method(Ref.60)	61

*Raman spectroscopy (Ed. of Translation).
**Extended Hückel method (Ed. of Translation).
***Photoelectron spectroscopy.

Nevertheless, mainly the *gauche*-conformation obtains for the majority of organic diphosphines, which confirms the rule of the greatest stability of the conformer with the *gauche*-disposition of the lone pairs (the *gauche*-effect)[69,70]. In the solid phase the diphosphines investigated exist in the *trans*-conformation, which may be a consequence of their packing in the crystal[69].

The conformational behaviour of diphosphines differs somewhat from that of their nitrogen analogues—hydrazine and its derivatives: the *gauche*-conformation obtains exclusively for hydrazine and tetramethylhydrazine in the gas, liquid, and solid states[71-75] and a 50% content of the *trans*-conformer has been found only for tetrafluorohydrazine in the gas and liquid states[76-78].

Photoelectron spectroscopy (PES) has been resorted to recently in order to determine the conformational compositions of organic diphosphines. On the basis of PES data, the diphosphines Me_4P_2 and $(CF_3)_4P_2$ are regarded as mixtures of *gauche*- and *trans*-conformers[54]; however, Ames and Turner[53] treat PES data for Me_4P_2 as confirmation of the existence of the latter exclusively as the *gauche*-conformer.

The barriers to rotation about the P–P bond (calculated data) are presented in Table 4; there are no experimental literature data. According to calculations by the *ab initio* SCF LCAO-MO method, the barrier to rotation in diphosphine is 3.3 kcal mole^{-1},[79] while in hydrazine the corresponding value is 11.5 kcal mole^{-1} according to the same method of calculation and experimental data. This difference between the barriers is logically consistent with the greater P–P bond length compared with N–N and also with the greater diffuseness of the orbitals of the phosphorus atoms compared with those of the nitrogen atom[80].

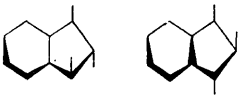
Table 4. The barriers to rotation about the P–P bond (kcal mole^{-1}).[13,15,63,64].

Compound	Method of calculation			
	EHM	SCF LCAO-MO	CNDO/2	*ab initio*
H_2P-PH_2	1.8 (*cis*)	9.2 (*cis*)	1.3 (*cis*)	4.1 (*cis*); 0.6 (*trans*)
H_2P-PH_2	4.9 (*trans*)	—	6.9 (*trans*)	2.3 (*cis*); 0.5 (*trans*)
F_2P-PF_2	4.6 (*cis*)	0.3 (*cis*); 3.9 (*trans*)	24.8 (*cis*)	4.9 (*trans*)
F_2P-PF_2	6.7 (*trans*)	4.9 (*cis*); 4.3 (*trans*)	31.6 (*trans*)	
H_2P-PF_2	—	12.0 (cis)	—	—
H_2P-PF_2	—	6.8 (*trans*)	—	—

If there are two different substituents at the same phosphorus atom in the organic diphosphine $R^1(R^2)P-P(R^1)(R^2)$, then the topology of this system is analogous to that of the system with two asymmetric carbon atoms: the lone electron pair plays the role of the fourth substituent. Indeed asymmetric organic diphosphines have the *meso*- and *d*, *l*-forms, whose interconversion (22–24 kcal mole^{-1}) involves rotation about the P–P bond and inversion of the phosphorus pyramid[81,82]. The main contribution to the transition energy comes from the energy of the inversion process, which is lower in diphosphines than in trialkylphosphines. Bulky and electron-donating substituents lower the inversion barrier, the influence of electronic factors predominating as a rule. The proportions of the racemate and the *meso*-form in solution are approximately the same for sterically non-hindered substituents (R^1 = Me, R^2 = Et). When R^1 = Me and R^2 = t-Bu, the *meso*-form is absent and (XII) exists as the racemate. Indeed in the two possible rotational *gauche*-isomers the bulky R^2 groups in the *meso*-form are brought closer together and their *gauche*-steric interaction is unfavourable. According to ^1H and ^{31}P NMR data, at 130–150°C equilibrium is attained rapidly (in terms of the NMR time scale) between the two diastereoisomers[83-85].

A large number of structures have been proposed for cyclic polyphosphines. Thus all structures, ranging from dimeric to polymeric, have been discussed for phosphobenzene. It has now been established that in the crystalline state phosphobenzene exists as the pentamer or hexamer (or their mixture)[22,25,86-88]. As a rule, standard methods of synthesis lead to a mixture with the preferential formation of the pentamer, but, if the reaction between dichlorophenylphosphine and phenylphosphine is carried out in tetrahydrofuran (THF), mainly the hexamer is obtained. On crystallisation from acetonitrile, it is possible to isolate the pure pentamer, whose molecule has the structure of a flat ring where the phenyl groups are located in the plane of the ring and the deviations from the D_{5d} symmetry are extremely insignificant[22]. The hexamer is polymorphic and exists in four modifications—monoclinic, orthorhombic, triclinic, and trigonal. The triclinic modification has the chair conformation with the equatorial disposition of the benzene rings[24,88]. The behaviour of phosphobenzene in solution is unusual: according to molecular weight determinations, both the pentamer and hexamer decompose to the tetramer and even the trimer; on the other hand, crystallisation from solution again leads solely to the pentamer and hexamer. In order to explain this, it is assumed that the P–P bonds readily dissociate in solution[23,89]—possibly with the intermediate formation of the phosphorus analogue of carbene, namely RP:[89]. In the solid phase rapid interconversion does not occur: thus, after two and a half years, the phosphobenzene hexamer was converted into the pentamer to the extent of only 50%.[90] Despite the large radius of the phosphorus atom, the size of the ring depends greatly on the nature of the substituent. Thus ethyl- and butyl-phosphorus consist as a rule of equal amounts of the tetramer and pentamer, but do not form hexamers[91-93]; propyl- and cyclohexyl-phosphorus are tetrameric in solution and in the solid state with the *trans*-position of the lone electron pairs[94,95]. Only the pentameric form [pentakis(pentafluorophenyl)pentaphospholane] has been found for pentafluorophenylphosphine[96].

Structural analysis of carbocyclic compounds with P–P bonds has undoubtedly revealed interesting characteristics of these substances. Hitherto the number of known compounds of this kind is comparatively small. Thus the configuration of the *trans*, *trans*-isomer has been established for 1,2,3-triphenyl-1,2,3-triphosphaindan in the crystalline state[25]:

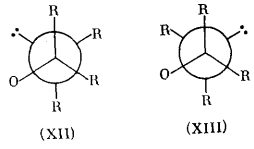


trans, trans *cis, trans*

According to NMR data[25], phosphaindan exists as the *cis*, *trans*-isomer in solution, in good agreement with its reactivity as a ligand in the reaction with iron carbonyls[97]. 1,2,3,4-Tetraphenyl-1,2,3,4-tetraphospholane[98] exists in the stable half-chair conformation, where all the phenyl groups are axial (C_2 symmetry).

The existence of two rotational isomers, (XII) and (XIII), may be expected for organic diphosphine monoxides, but these cannot be identified on the basis of ^{31}P NMR data

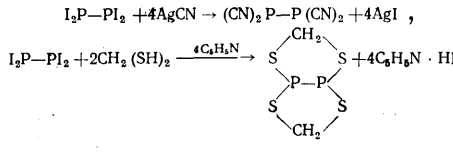
(the spectra of tetra-alkyldiphosphine monoxides do not change between −90° and +30°C)[99]:



(XII) (XIII)

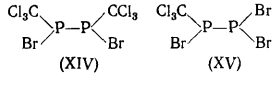
III. METHODS OF SYNTHESIS

At least two fundamentally different approaches to the synthesis of OPC with P–P bonds are possible: the first consists in the use of starting compounds already containing a P–P bond and in the second the P–P bond is formed during synthesis. In the first case it would appear convenient to employ the readily available tetra-iododiphosphine[100], but numerous attempts to use it (in reactions with alcohols, amines, alkyl halides, and organometallic compounds) have led as a rule to products with a single phosphorus atom in the molecule[101–104]. As an exception, one may mention the following reactions, which take place with extremely low yields[100,101]:



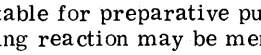
In a study of the alkylation of phosphorus di-iodide Kirsanov and coworkers[105–109] developed a convenient method for the synthesis of symmetrical diaryldi-iododiphosphines.

Phosphorus dichloride $(PCl_2)_2$ has been hardly used in syntheses, since it is difficult to obtain[110]. There have been few examples of the use of elemental phosphorus, which already contains P–P bonds. Thus ultraviolet irradiation of a solution of elemental phosphorus in bromotrichloromethane gives satisfactory yields of (XIV) and (XV)[110]:

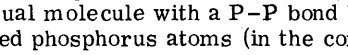


(XIV) (XV)

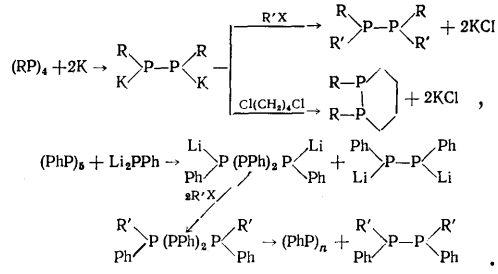
The reactions, which take place in the gas phase, are undoubtedly unsuitable for preparative purposes, but the following interesting reaction may be mentioned[111]:



The use of elemental phosphorus made it possible to obtain a very unusual molecule with a P–P bond between two two-coordinated phosphorus atoms (in the complex)[112]:

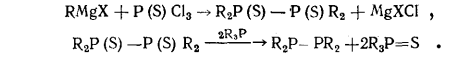


Red phosphorus reacts smoothly with sodium in liquid ammonia to form diphosphides, which can then be alkylated by alkyl halides to form tetra-alkyldiphosphines[113,114]. The necessity to carry out experiments in liquid ammonia and the comparatively low yields (not exceeding 25%), due to the cleavage of Alk_4P_2 to sodium phosphide, limit the applicability of this reaction. On the other hand, the ability of the P–P bonds to dissociate under the influence of alkali metals and a number of other nucleophiles has been used to synthesise di- and poly-phosphines from cyclopolyphosphines, which are frequently more readily available than other compounds with P–P bonds[115–121]:



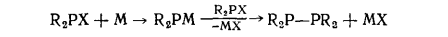
This method makes it possible to obtain a wide range of symmetrical and asymmetric organic diphosphines, as well as new compounds with a P–P bond in the ring, in 70–90% yields.

A very convenient preparative method for the synthesis of organic compounds with P–P bonds from inorganic phosphorus compounds was proposed by Kabachnik and coworkers and was subsequently developed by other investigators[122–125]:

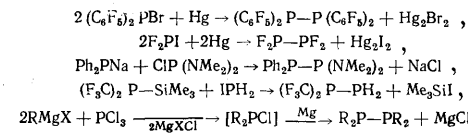


Tetra-alkyldiphosphine disulphides are formed in yields greater than 60% and are reduced by metals as well as trialkylphosphines and trialkyl phosphites to tetraalkyldiphosphines[81,82,126].

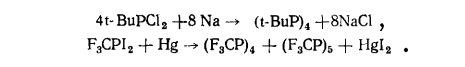
Numerous examples of the synthesis of organic diphosphines from halogenophosphines on treatment with various metals or metal phosphides via the general mechanism



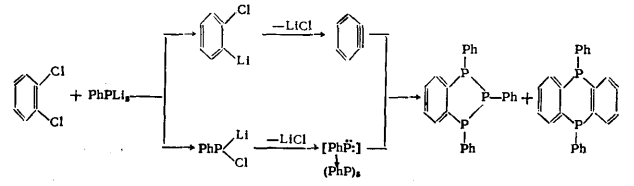
have been described in Cowley's review[3]; here we shall confine ourselves to new examples of this widely used method[63,127–129,131–135]:



The condensation principle proved to be convenient also for the synthesis of cyclopolyphosphines using alkyldichlorophosphines in the reaction[91,134]:



Presumably in these and analogous instances the reaction proceeds via the phosphinidene RP̈:—the phosphorus analogue of carbene, which has two lone electron pairs and vacant 3*d* and 4*d* orbitals in the singlet configuration. The formation of phosphinidene is possible also in the following case[117]:

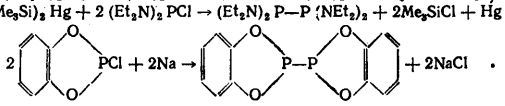


The generation of phosphinidene can apparently also be postulated in reactions of the following kind [134-137]:

$$PhPCl_2 \xrightarrow{LiAlH_4} (PhP)_5 ,$$
$$5MePCl_2 + 5Bu_3P \rightarrow (MeP)_5 + 5Bu_3PCl_2 ,$$
$$F_2CP(H)I + AgCN \rightarrow (F_2CP)_4 + AgI + HCN ,$$
$$R_3P + F_2PPh \rightleftarrows [R_3\overset{+}{P}-\overset{\cdot}{P}(Ph)F_2] \rightarrow [R_3\overset{+}{P}-\ddot{P}(F)Ph]F^- \rightleftarrows R_3P(F)-\ddot{P}Ph \rightarrow$$
$$\rightarrow R_3PF_2 + [Ph\ddot{P}:] \rightarrow (PhP)_5 .$$

The esters and amides of hypodiphosphorous acid have been obtained from phosphorochloridites using sodium and potassium as well as mercury derivatives [138-141]:

$$(Me_3Si)_2Hg + 2(RO)_2PCl \rightarrow (RO)_2P-P(OR)_2 + 2Me_3SiCl + Hg ,$$
$$(Me_3Si)_2Hg + 2(Et_2N)_2PCl \rightarrow (Et_2N)_2P-P(NEt_2)_2 + 2Me_3SiCl + Hg ,$$



$$+ 2NaCl .$$

As will be shown below, the reactivity of organic diphosphines depends significantly on the substituents at the phosphorus atom. For this reason, the synthesis of tetra-alkoxydiphosphines, which may be assumed to undergo all the numerous reactions known in the chemistry of trialkyl phosphites, is therefore of special interest. A new approach to the synthesis of tetra-alkoxydiphosphines is based on the employment of dialkoxyphosphines—the full esters of hypophosphorous acid [142,145]. It has been shown that soft bases (dialkoxyphosphines) react with soft acids (dialkyl phosphorochloridites) to form tetra-alkoxydiphosphines [144,145]:

$$(RO)_2PH + (R'O)_2PCl \xrightarrow[90\%]{Et_3N} (RO)_2P-P(OR')_2 + Et_3N \cdot HCl .$$

Symmetrical $(RO)_4P_2$ may be obtained (in yields up to 50%) without isolating $(RO)_2PH$:[146]

$$2(RO)_2PCl + R_3SnH \xrightarrow{Et_3N} [(RO)_2PH + (RO)_2PCl] \xrightarrow{Et_3N} (RO)_2P-P(OR)_2 + Et_3N \cdot HCl .$$

The synthesis (via the mechanism described above) of dialkoxydialkyldiphosphines—compounds with two centres of different basicity ("phosphite" and "phosphine")—is also of undoubted interest [14]:

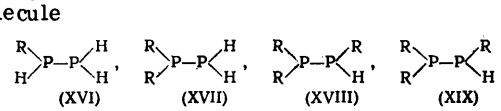
$$(RO)_2PH + R'_2PCl \xrightarrow{R''_3N} (RO)_2P-PR'_2 + R''_3N \cdot HCl ,$$
$$R_2PH + (R'O)_2PCl \xrightarrow{R''_3N} R_2P-P(OR')_2 + R''_3N \cdot HCl .$$

For the given type of interaction, the choice of the pair of reactants is not immaterial: the first reaction gives a yield of 70%, while that of the second is only 45%: dialkylphosphines (particularly when they are sterically hindered) react much more slowly than dialkoxyphosphines. The synthesis of trialkoxyalkyldiphosphines has been described [146]:

$$(RO)_2PH + \begin{matrix} R' \\ RO \end{matrix}\!\!>\!P-Cl \xrightarrow{R''_3N} \begin{matrix} RO \\ RO \end{matrix}\!\!>\!P-P\!<\!\begin{matrix} OR \\ R' \end{matrix} + R''_3N \cdot HCl .$$

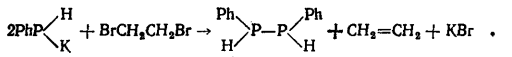
It is noteworthy that asymmetric diphosphines are as a rule difficult to obtain (the yields do not exceed 40%) owing to their disproportionation to symmetrical compounds.

The organic diphosphines (**XVII**)-(**XX**) with PH bonds in the molecule

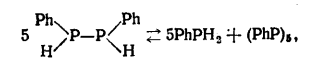


(XVI) (XVII) (XVIII) (XIX)

are known only in a few instances. Among di-s-diphosphines [compounds (**XIX**)], 1,2-bis(trifluoromethyl)diphosphine has been described [129]; it was obtained, among other products, by the cautious hydrolysis of $(CF_3P)_4$. A seemingly general method of synthesis of diphosphines of type (**XIX**) was proposed in 1971:[132]



However, the equilibrium



in which a diphosphine of type (**XIX**) exists as a distereoisomeric mixture of the *meso*- and *dl*-forms, occurs in the temperature range between 30° and 200°C. The energy of the transition between these forms is 22-24 kcal mole^{-1}, i.e. is of the same order of magnitude as the energy of the given transition for R_4P_2.[82] It has been suggested that the intermediates $Ph\ddot{P}$: occurs in this equilibrium, particularly since the process [147]

$$5(F_3CP)_4 + 20MePH_2 \rightarrow 20F_3CPH_2 + 4(MeP)_5$$

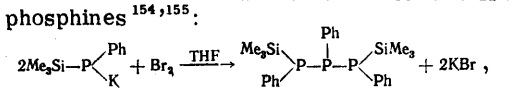
takes place.

Above 225°C, the di-s-diphosphine $(CH_3PH)_2$ is converted into a mixture of $(CF_3P)_n$ and CF_3PH_2, but in contrast to the previous process, the reaction is irreversible[9]. A diphosphine of type (**XVIII**) is formed from a mixture of difluorodiphosphine or EtP_2 and an excess of PH_3 at -78°C.[148]

P-P bonds are known to be readily cleaved by amines, but the reaction may be displaced in the opposite direction in the case of the low-boiling dimethylamine [23,149]:

$$(F_3C)_2N-P(CF_3)_2 + Me_2PH \rightarrow Me_2NH + (F_3C)_2P-PMe_2 ,$$
$$MeP(NMe_2)_2 + 2Ph_2PH \rightarrow MeP(PPh_2)_2 + 2Me_2NH ,$$
$$3PhP(NMe_2)_2 + 3PhPH_2 \rightarrow (PhP)_6 + 6Me_2NH .$$

Certain non-trivial methods of organic synthesis of diphosphines must also be mentioned. These include the electrochemical method for synthesising Ph_4P_2,[150] the condensation of Ph_2PCl with formation of a P-P bond on treatment with calcium carbide [151,152], and the reduction of di-t-butylmercury by secondary phosphines [153]. Di- and tri-phosphines with P-Si bonds have been obtained from silylated phosphines [154,155]:



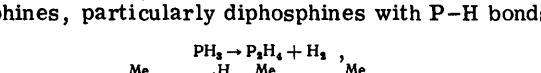
$$2(Me_3Si)_2PLi + BrCH_2CH_2Br \rightarrow (Me_3Si)_2P-P(SiMe_3)_2 + 2LiBr + CH_2=CH_2 .$$

A similar process occurs when lithium and potassium phosphides are acted upon by bis-(α-chlorobenzylidene)-hydrazine [156]:



A new method for the synthesis of thermodynamically unstable organic compounds—in a silent electric discharge at low pressures—has been proposed recently [15]. In the series of OPC this method was used for the first time to synthesise tetrachlorodiphosphine [31] and in recent years also for the synthesis of a number of unstable diphosphines, particularly diphosphines with P-H bonds[158]:

$$PH_3 \rightarrow P_2H_4 + H_2 ,$$



$$F_2CPH_2 \rightarrow F_2CP(H)-P(H)CF_3 + PH_3 + (F_3C)_2PH + (F_3C)_3P .$$

For methyldiphosphine, equilibrium with the cyclic form is established even at room temperature [159]:

$$MeP(H)PH_2 \rightleftarrows MePH_2 + \frac{1}{n}(MeP)_n .$$

Diphosphines with P–H bonds can also undergo further disproportionation in a silent discharge [158]:

$$F_3C(H)P{-}P(H)CF_3 \rightarrow F_3CPH_2 + (F_3C)_3P + (F_3C)_4P_2 .$$

P–P bonds are formed in the thermolysis or photolysis of metal complexes with tertiary or secondary phosphines [160,161]:

$$Fe(CO)_4 \cdot HPR_2 \xrightarrow{h\nu} Fe_2(CO)_8(PR_2)_2 ,$$
$$W(CO)_5 \cdot HPR_2 \xrightarrow{\Delta} W_2(CO)_8(PR_2)_2 + W_2 + (CO)_7(PR_2)_2 + R_2PH .$$

The presence of a P–P bond in the complexes formed was established by X-ray diffraction. Many of the above complexes cannot be synthesised directly from organic diphosphines (bidentate ligands) and metal carbonyls, since dissociation of P–P bonds is frequently observed in these reactions [161–170].

Compounds with a bond between two phosphorus atoms of different valence may be synthesised by the oxidation of organic diphosphines, i.e. using compounds with P–P bonds already present. These reactions are discussed below and can be used on a preparative scale when the corresponding organic diphosphines are available.

A set of reactions, which may be described in terms of the formal general mechanism

$$R_2P\overset{Y}{\underset{X}{\diagup\!\!\diagdown}} + ZPR'_2 \rightarrow R_2P{-}\underset{Y}{\overset{\|}{P}}R'_2 + XZ$$

and which give satisfactory yields in certain specific cases, have been suggested for the synthesis of diphosphine monoxides (monosulphides):

$$R_2P(O)H + R'_2PCl \xrightarrow[-HCl]{Et_3N} R_2P(O){-}PR'_2 \quad \text{(Ref.170)},$$
$$R_2P(O)H + R'_2P{-}NMe_2 \xrightarrow{-Me_2NH} R_2P(O){-}PR'_2 \quad \text{(Ref.99)},$$
$$R_2PONa + R'_2PCl \xrightarrow{-NaCl} R_2P(O){-}PR_2 \quad \text{(Refs. 172,173)}.$$

The interaction with dialkylphosphinous acids is complicated by the exchange reaction [174]:

$$R_2P(O)H + R'_2PCl \rightleftarrows R_2PCl + R'_2P(O)H,$$

which may be suppressed by an excess of a tertiary amine. The attack by dialkylchlorophosphine on the two basic centres of the ambident anion $R_2P{-}S^-$ proceeds in the same way as on the $R_2P{-}O^-$ anion—mainly on the phosphorus atom [174]:

$$R_2PSNa + R_2PCl \xrightarrow{-NaCl} \underset{95\%}{R_2P(S){-}PR_2} + \underset{5\%}{R_2P{-}S{-}PR_2} .$$

In the presence of primary substituents, monosulphides are formed exclusively; they are stable and do not rearrange to thioanhydrides. In the presence of tertiary substituents it is impossible to detect the corresponding monosulphide: only thioanhydrides of phosphinous acids are always isolated, which may be a consequence of thermodynamic control, i.e. a result of the rapid rearrangement of the monosulphide to the thioanhydride. In the presence of secondary substituents, a tautomeric mixture of the corresponding monosulphides and thioanhydrides is formed. Problems associated with the rearrangement in this series will be discussed in greater detail below.

Dialkoxydialkyldiphosphine monoxides are formed in virtually quantitative yields as a result of the exothermic reaction [175]

$$R_2PONa + ClP(OR)_2 \rightarrow R_2P(O){-}P(OR)_2 .$$

It makes it possible to obtain 2,2-dialkoxy-1,1-dialkyl-1-oxodiphosphines; the second isomer of the monoxide—2,2-dialkoxy-1,1-dialkyl-2-oxodiphosphine—is formed from dialkylchlorophosphines and dialkyl phosphites:

$$(RO)_2P(O)H + R'_2PCl \xrightarrow{Et_3N} R'_2P{-}(O)P(OR)_2 ,$$

and also from tetra-alkylpyrophosphites [175]:

$$(R'O)_2P{-}O{-}P(OR')_2 + R_2PCl \xrightarrow{R'_3N} R_2P{-}(O)P(OR')_2 + (R'O)_2PCl :$$

The monosulphides are also readily obtainable [176]:

$$R_2P(S)H + (RO)_2PCl \xrightarrow{R_3N} R_2P(S){-}P(OR)_2 .$$

It is noteworthy, that dialkylphosphinous acids give rise only to mixed anhydrides of phosphonous and phosphorous acids in this reaction. 2,2-Dialkoxy-1,1-dialkyl-2-thionodiphosphines can be synthesised from the 1-sulphides [176]:

$$R_2P(S){-}P(OR)_2 \xrightarrow{\Delta} R_2P{-}P(S)(OR)_2 .$$

Tetra-alkoxydiphosphine monoxides are stable for several hours, while tetra-alkoxydiphosphine monosulphides are entirely stable and can be formed via a similar mechanism [177,178]:

$$(RO)_2PXNa + (R'O)_2PCl \rightarrow (RO)_2P(X){-}P(OR')_2 + NaCl ,$$

where X = S or O.

The interaction of diphenylphosphine oxide with the mixed anhydride of acetic and diphenylphosphinous acids may be regarded as a variant of the above reactions [177]:

$$Ph_2P(O)H \xrightarrow{(MeCO)_2O} Ph_2PO(O)CMe \xrightarrow[-MeCOOH]{Ph_2P(O)H} Ph_2P(O){-}PPh_2 .$$

Using this scheme, it is possible to obtain compounds with three P–P bonds in the molecule in 63% yields [178]:

$$PCl_3 + 3(RO)_2P\overset{O}{\underset{H}{\diagup\!\!\diagdown}} \xrightarrow[-3HCl]{C_5H_5N} \left[(RO)_2\overset{O}{\overset{\|}{P}}\right]_3P .$$

The biphilic properties of compounds with a three-coordinated phosphorus atom suggest yet another method for the formation of a P–P bond between phosphorus atoms with different coordination [numbers?]. Indeed highly nucleophilic soft bases (trialkylphosphines, dialkylphosphines, or aminophosphines) react with electrophilic soft acids (dialkylchlorophosphines) to form crystalline adducts in which a P–P bond is formed according to NMR spectroscopic data [138,179–182]:

$$Me_3P + ClPR_2 \rightarrow [Me_3P{-}PR_2]^+Cl^- ,$$
$$R_2PH + R_2PCl \rightarrow [R_2P{-}P(H)R_2]^+Cl^- ,$$
$$R_3P{=}NPR'_2 + R''_2PCl \rightarrow [R_3P{=}N{-}P(R'_2){-}PR''_2]^+Cl^- .$$

The reaction is appreciably reversible in solution in methylene chloride and does not occur for weakly nucleophilic tertiary phosphines, for example, $MePh_2P$. However, the latter reacts with the more electrophilic chloride PCl_3 to form the corresponding adduct at 20°C. The adducts are usually stable up to room temperature. When two moles of dialkylchlorophosphines are used, the tertiary phosphine behaves as a "condensing" agent and tetraalkyldiphosphines are formed in satisfactory yields [138,179,183].

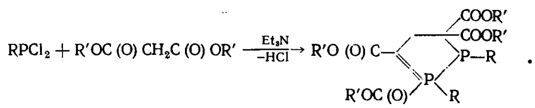
If esters of phosphonous, phosphinous, and phosphorous acids are used instead of tertiary phosphines, the Arbuzov rearrangement may occur in the system via intermediates of the type described above, which apparently have the structure of quasi-phosphonium compounds with P–P bonds [184–186]:

$$Ph_2POR + Ph_2PCl \rightarrow Ph_2P{-}P(O)Ph_2 + RCl ,$$
$$MeP(OMe)_2 + Ph_2PCl \rightarrow [Ph_2P{-}P(OMe)_2Me]^+Cl^- \rightarrow Ph_2P(O)(OMe)Me + MeCl ,$$
$$(RO)_3P + Ph_2PCl \rightarrow [(RO)_3P{-}P(Cl)Ph_2] \rightarrow (RO)_2P(O){-}PPh_2 + RCl ,$$
$$(RO)_3P + PhPCl_2 \rightarrow PhP(Cl){-}P(O)(OR)_2 + RCl .$$

The addition of a second equivalent of chlorophosphine leads to the dissociation of the P–P bond in the resulting monoxide; thus diphosphines may be obtained in satisfactory yields for a 1 : 2 reactant ratio[184]:

$$MeP(OMe)_2 + Ph_2PCl \rightarrow MeP(O)(OMe){-}PPh_2 \xrightarrow{Ph_2PCl} Ph_2P{-}PPh_2 + Me(MeO)P(O)Cl\ .$$

Ylids of a new type with a P–P bond between three- and four-coordinated phosphorus atoms have been obtained from malonic ester and a wide variety of alkyl(aryl)dichlorophosphines[187]:



Similar phosphoranes but with a linear structure are formed from malonic esters and Et_2PCl:[188]

$$CH_2(COOR)_2 + Et_2PCl \xrightarrow[-Et_3N\cdot HCl]{Et_3N} Et_2PCH(COOR)_2 \xrightarrow[Et_3N]{Et_2PCl} \rightarrow Et_2P{=}C(COOR)_2(PEt_2) + Et_3N\cdot HCl$$

The methods of synthesis of OPC with P–P bonds are closely interrelated with certain reactions of organic diphosphines, which lead to new OPC, also with P–P bonds. Part of the synthetic data will therefore be found in the next section of this review.

IV. THE REACTIVITIES OF COMPOUNDS WITH P–P BONDS

The idea of the biphilic nature of OPC with a three-coordinated phosphorus atom is widely used in phosphorus chemistry. It can be extended to organic diphosphines, which exhibit a high reactivity in relation to both nucleophiles and electrophiles; the P–P bond is then most "vulnerable". Numerous reactions involving the dissociation of P–P bonds are known and many of these may be said to involve the heterolytic dissociation of P–P bonds, although even indirect confirmation of the reaction mechanism is by no means always presented.

The P–P bond in organic diphosphines and cyclopolyphosphines is readily cleaved by nucleophiles such as alkali metals[115,189,190], the ease of dissociation depending both on the substituents at the phosphorus atoms and on the alkali metal (K > Na > Li). Tetraphenyldiphosphine is more reactive in relation to sodium than tetra-alkyldiphosphines, which may be accounted for by the greater stability of the Ph_2P^- anion formed compared with R_2P^-. Typical nucleophiles (organolithium compounds) also dissociate P–P bonds[118,191]:

$$R_2P{-}PR_2 + PhLi \rightarrow R_2PLi + R_2PPh\ .$$

The reactivity of organic diphosphines in this interaction (for example, in relation to PhLi) is consistent with the ideas concerning the mechanism of bimolecular nucleophilic substitution at a phosphorus atom. Thus the reactivity decreases in the sequence Ph > Me > Et > n-Pr > n-Bu. The reaction results in the formation of new anion R_2P^-, the stability of which (and hence the ease of its elimination) decreases with increase of the $-I$ effect of the substituents. Steric factors also play a significant role in this reaction: it does not occur at all for R = iso-Pr, t-Bu, or cyclo-C_6H_{11}.

Cyclopolyphosphines are also cleaved by organolithium compounds[118,192,193]. The reaction consists of many stages, a product resulting from the dissociation of one P–P bond being formed initially:

$$(EtP)_n + PhLi \rightarrow (Et)(Li)P{-}(EtP)_{n-2}{-}P(Et)(Li)\ .$$

The product then reacts rapidly with phenyl-lithium to form secondary cleavage products: $EtP(Li)(PEt)_2P(Li)Et$ and Et_4P_2. The final products are lithium di- and monoalkylphosphides and ethyldiphenylphosphine.

A detailed study of the interaction of Ph_4P_2 with phenyllithium[192,193] made it possible to establish the following electrophilicity series in relation to phenyl-lithium: $Li(PPh)_{n-1}PPh_2 (n \geq 3) > (PhP)_n (n = 3-5) > Li(PPh)_4Li > Ph_2P{-}PPh_2$, $Li(PPh)_3Li > (Ph)(Li)P{-}PPh_2 > Li(PPh)_2Li$.

The cleavage of P–P bonds in cyclopolyphosphines is used to synthesise linear polyphosphines (as was considered in the previous section). In addition, the availability and high reactivity of cyclopolyphosphines made it possible to develop on their basis a general method for the synthesis of chiral tertiary phosphines and also compounds with P–Ge, P–Si, and P–Sn bonds[194]:

$$(RP)_n + n\,LiR' \rightarrow n\left[LiP{<}^{R}_{R'}\right] \xrightarrow{R''X} RR'P{-}R'' + LiX\ ,$$

$$(RP)_n + n\,LiR' + Me_3XCl \rightarrow RR'P{-}XMe_3\ ;$$

X = Si, Ge, or Sn.

The interaction of organic diphosphines with alkali metal phosphides, the nucleophilic properties of which are weaker than those of organolithium compounds, takes place more slowly[193]:

$$Ph_2P{-}PPh_2 + LiPR_2 \rightarrow Ph_2P{-}PR_2 + LiPPh_2\ ,$$
$$Ph_2P{-}PR_2 + LiPR_2 \rightarrow R_2P{-}PR_2 + LiPPh_2\ ,$$

and may be stopped at the first stage. In the second stage attack by the R_2P^- anion is directed to the most nucleophilic centre in the molecule, which is probably associated with the ease of formation of the Ph_2P^- anion.

Cyclic polyphosphines are cleaved only by the more reactive Li_2PPh; the yield of the reactions with monolithium phosphides does not exceed 2–3%.[189–193]

Depending on the nature of the substituents at the phosphorus atom, the reactivity of organic diphosphines in relation to nucleophiles may be altered sharply: electron-accepting substituents promote the cleavage of the P–P bond. Thus water does not react at all with tetra-alkyldiphosphines[3], but reacts rigorously with tetra-alkoxydiphosphines[130]:

$$(RO)_2P{-}P(OR)_2 + H_2O \rightarrow (RO)_2PH + (RO)_2P(O)H\ .$$

In the cold it causes quantitative dissociation of the P–P bond in diphosphines with electron-accepting substituents[3,63,179]:

$$F_2P{-}PF_2 + H_2O \rightarrow F_2PH + F_2P{-}O{-}PF_2\ ,$$
$$Me_2P{-}P(CF_3)_2 + H_2O \rightarrow Me_2P(O)H + (CF_3)_2PH\ .$$

The reaction is accelerated sharply in the presence of an inorganic acid: the formation of $(CF_3)_2PH$ and $Me_2P(O)H$, and not $(CF_3)_2P(O)H$ and Me_2PH, as a result of the reaction may be accounted for by the initial protonation of the Me_2P group by traces of acid, the presence of which could not be as a rule avoided owing to the method used to synthesise dimethyldi(trifluoromethyl)diphosphine, and subsequent nucleophilic attack by water molecules on the phosphonium centre.

Owing to the high reactivity of the P–Cl and P–I bonds, tetraiodo- and tetrachloro-diphosphines form further hydrolysis products with dissociation of the P–P bond [195–197].

There are comparatively few data on the alcoholysis of organic diphosphines. 1,2-Dibromo-1,2-bis(trichloromethyl)diphosphine reacts with ethanol even at low temperatures to form diethyl trichloromethylphosphonite [129]. Tetra-alkoxydiphosphines undergo quantitative exothermic cleavage by ethanol [130].

Like tetra-alkyldiphosphines, cyclopolyphosphines are resistant to neutral hydrolysis but are readily cleaved by aqueous alkali: the P–C and P–P bonds in $(CF_3P)_4$ and $(CF_3P)_5$ dissociate with formation of CF_3H, H_2, and CF_3PH_2. The process is appreciably accelerated in diglyme and at low temperatures the interaction with water and alcohol leads to di-, tri-, and tetra-phosphines with linear structures [198]:

$$(F_3CP)_5 + H_2O \rightarrow H(CF_3)P{-}P(CF_3)H + F_3C(H)P{-}P(CF_3)P(H)CF_3 + H(F_3C)P(PCF_3)_2{-}P(H)CF_3$$

$$(F_3CP)_4 + MeOH \rightarrow F_3C(H)P{-}P(CF_3)OMe + F_3C(H)P{-}P(H)CF_3 + (F_3C)_2POMe + H(F_3C)P{-}\underset{\displaystyle CF_3}{\underset{|}{P}}{-}P(CF_3)H \ .$$

The mechanism of the homolytic cleavage of the P–P bond has been discussed [199]. Isolated instances where alcoholysis goes to completion without the dissociation of the P–P bond have been reported [140].

Ammonia is relatively unreactive in relation to $(CF_3)_4P_2$: only 48% of the latter reacts after 28 days at 20° C. Chloramine proved to be somewhat more reactive in this process [200]:

$$R_2P{-}PR_2 + NH_2Cl \rightarrow R_2PCl + R_2PNH_2 \ .$$

Secondary amines do not dissociate the P–P bond in di-iododiphosphines at 20° C, since under these conditions the reactivities of the P–P and P–I bonds apparently become comparable [131]. However, the P–P bond dissociates even on boiling in ether [201]:

$$PhP(I){-}P(I)Ph + 3HN(CH_2)_5 \rightarrow (PhP)_n + PhP[N(CH_2)_5]_2 + 2(CH_2)_5NH_2I \ .$$

Nucleophilic attack on asymmetric alkoxydialkyldiphosphines is directed to the most electrophilic phosphite centre in the molecule [202]:

$$(iso\text{-}Pr)_2P{-}P(OBu)_2 + PhNHEt \rightarrow (iso\text{-}Pr)_2NH + (BuO)_2PN(Et)Ph \ .$$

Since the less basic diphenylamine reacts much more slowly and piperidine does not react at all, the hypothesis of an optimum ratio of the nucleophilicity of the amine and its capacity for electrophilic cooperation (i.e. its acidity), whereupon the process proceeds at the maximum rate, appears to be very well-founded. The equilibrium in the reactions of tetra-alkyldiphosphines, whose electrophilic properties are fairly weak, with amines is known to be displaced in the opposite direction [3]:

$$EtPNMe_2 + R_2PH \rightarrow Et_2P{-}PR_2 + Me_2NH \ .$$

The interaction with stronger nucleophiles (secondary phosphines) takes place non-selectively, simultaneously at the phosphite and phosphine centres [202]:

$$(iso\text{-}Pr)_2P{-}P(OBu)_2 + Ph_2PH \rightarrow (iso\text{-}Pr)_2P{-}PPh_2 + (BuO)_2PH + Ph_2P{-}P(OBu)_2 + (iso\text{-}Pr)_2PH$$

$$Ph_2P{-}P(OBu)_2 \xrightarrow{Ph_2PH} Ph_2P{-}PPh_2 + (BuO)_2PH \ .$$

Organic diphosphines (at least those with one highly electrophilic centre) react with tertiary phosphines to form complexes—for example, the complex $(CF_3)_2P{-}PMe_2$.

Me_3P. Secondary phosphines and arsines dissociate the P–P bond only in $(CF_3)_4P_2$: [149]

$$(CF_3)_2P{-}P(CF_3)_2 + Me_2XH \rightarrow (CF_3)_2P{-}XMe_2 + (CF_3)_2PH \ ; \quad X = P \text{ or As.}$$

As described above, the P–P bond in the cyclic analogue $(CF_3)_4P_4$ is broken quantitatively under the influence of primary phosphines even at room temperature [147,203].

Organic diphosphine monoxides are much more resistant to nucleophiles than the diphosphines themselves. Thus tetra-isopropyldiphosphine monoxide requires a week for its hydrolysis by water at 20° C; the reaction with alcohol is just as slow [174]:

$$(iso\text{-}Pr)_2P(O){-}P(Pr\text{-}iso)_2 + H_2O \rightarrow 2\,(iso\text{-}Pr)_2P(O)H \ ;$$

$$(iso\text{-}Pr)_2P(O){-}P(Pr\text{-}iso)_2 + EtOH \rightarrow (iso\text{-}Pr)_2P(O)H + (iso\text{-}Pr)_2POEt \ .$$

The monoxides do not react with diethylamine even on heating.

Organotin hydrides, in which the amount of ionic character of the Sn–H bond is greater than in the Si–H and Ge–H bonds, cleave the P–P bond in the most electrophilic organic diphosphines at 20° C: [204]

$$(F_3C)_2P{-}P(CF_3)_2 + Me_3SnH \xrightarrow{20^\circ} Me_3Sn{-}P(CF_3)_2 + HPMe_2 \ ,$$

$$(F_3CP)_4 + Me_3SnH \xrightarrow{20^\circ} Me_3Sn{-}P(CF_3)H + (Me_3Sn)_2PCF_3 + H_2PCF_3 \ ,$$

$$(F_3C)_2P{-}PH_2 + R_3SnH \rightarrow R_3Sn{-}P(CF_3)_2 + PH_3 \ .$$

Trimethylgermane reacts very slowly only at 150° C and the corresponding silicon hydrides do not react even at this temperature. Under the conditions of radical interaction, it is possible to achieve the reaction also with trimethylsilane:

$$(F_3C)_2P{-}P(CF_3)_2 + HSiMe_3 \xrightarrow{h\nu} Me_3Si{-}P(CF_3)_2 + HP(CF_3)_2 \ .$$

Protic acids HX in aqueous media readily cleave the P–P bond [205,206]. In the presence of electron-accepting substituents at the phosphorus atom the reactivity of the compounds in reactions with protic acids is greatly reduced. Thus Ph_4P_2 reacts with hydrochloric acid more vigorously than the asymmetric dimethyldi(trifluoromethyl)-diphosphine: anhydrous protic acids do not react with $(CF_3)_4P_2$ and the reaction with $(CF_3P)_n$ ($n = 4$ or 5) takes place only after prolonged heating (up to 100° C in the case of sulphuric acid). [207] Carboxylic acids cleave the P–P bond in Ph_4P_2 under very severe conditions (150°–200° C) and the process is complicated by many side reactions [208]. The ability of the P–P bond to be cleaved by acids has been used in the elimination of diphosphines from phosphines [209].

The reduction of aromatic diphosphines at carbon or mercury electrodes involves the dissociation of the P–P bond [210,211]. Their reduction by $LiAlH_4$ also takes place with dissociation of the P–P bond. [212]

Being typical nucleophiles, organic diphosphines form, like tertiary phosphines, stable complexes with Lewis acids [213,214]. Thus Ph_4P_2 forms a complex with a single molecule of trialkylaluminium. The more nucleophilic Me_4P_2 forms a complex with two triethylaluminium molecules [213]. Like tertiary phosphines, Et_4P_2 forms a stable 1 : 1 complex with CuBr. [215,216]

Like tertiary phosphines, organic di- and poly-phosphines are extremely sensitive to oxidation. On oxidation, there is a possibility of the formation of the following structures:

$$R_2P{-}PR_2 \longrightarrow \begin{cases} \longrightarrow R_2P{-}\underset{\displaystyle X}{\underset{\|}{P}}{-}PR_2,\ R_2P{-}X{-}PR_2 \\ \longrightarrow R_2P{-}\underset{\displaystyle X}{\underset{\|}{P}}{-}PR_2,\ R_2P{-}\underset{\displaystyle X}{\underset{\|}{P}}{-}X{-}PR_2 \\ \qquad\qquad\qquad\quad \underset{\displaystyle X}{\underset{\|}{P}} \\ \longrightarrow R_2P{-}X{-}\underset{\displaystyle X}{\underset{\|}{P}}{-}PR_2 \end{cases} ; \qquad X = O,\ S, \text{ or } NR.$$

It has been shown [151,152] that the result of the oxidation of Ph_4P_2 depends on the purity of the test specimen. In all other cases only the structure of the final product was deduced as a rule:

$$P_2F_4 + O_2 \rightarrow F_2P{-}O{-}PF_2\text{,(Ref.129)}$$

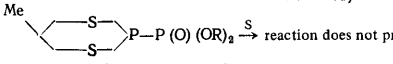
$$Alk_2P{-}PAlk_2 + S \rightarrow Alk_2P{-}P\,(S)\,Alk_2 \xrightarrow{S} \xrightarrow{(O_2)} \rightarrow Alk_2P\,(S){-}P\,(S)\,Alk_2\,[Alk_2P\,(O){-}P\,(O)\,Alk_2]_2\text{(Refs.134,136,190,217,218)}$$

$$(t\text{-Bu})_2P\text{-}P(Bu\text{-}t)_2 \xrightarrow{S} (t\text{-Bu})_2P\,(S){-}P\,(Bu\text{-}t)_2 \rightarrow \xrightarrow{S} (t\text{-Bu})_2\,P\,(S){-}S{-}P\,(S)\,(Bu\text{-}t)_2\text{,(Refs.134,202)}$$

$$R_2P\,(O)\,PR_2 \xrightarrow{O_2(S)} R_2P\,(O){-}P\,(O,\ S)\,R_2\text{,(Ref.98)}$$

$$(RO)_2\,P{-}P\,(OR)_2 \xrightarrow{O_2} (RO)_2\,P{-}O{-}P\,(OR)_2\text{,(Ref.220)}$$

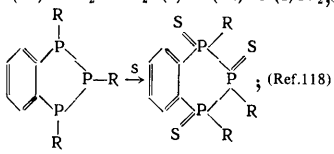
$$(RO)_2\,P{-}P\,(OR)_2 \xrightarrow{S} (RO)_2\,P\,(S){-}P\,(S)\,(OR)_2\text{,(Ref.221)}$$



reaction does not proceed (Ref.219),

$$I_2P{-}PI_2 \xrightarrow{Se} I_2P\,(Se){-}PI_2 \xrightarrow{Se} I_2P\,(Se){-}P\,(Se)\,I_2\text{,(Ref.118)}$$

$$Ph_2P{-}P\,(Me){-}PPh_2 \xrightarrow{S} Ph_2P\,(S){-}P\,(Me){-}P\,(S)\,Ph_2\text{,(Ref.202)}$$

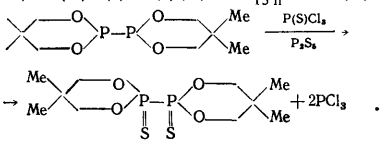


; (Ref.118)

R=Et, or Ph.

Apart from oxygen, a large number of oxidants have been used to oxidise organic diphosphines. In particular, it has been shown that diphosphine disulphides [202], $PSCl_3$, and P_2S_5 [140] may be oxidised:

$$Me\,(Et)\,P{-}P\,(Et)\,Me + Me\,(Et)\,P\,(S){-}P\,(S)\,(Et)\,Me \xrightarrow[15\ h]{190^\circ} 2Me\,(Et)\,P{-}P\,(S)\,(Et)\,Me\ ,$$



$+ 2PCl_3$.

The oxidation of tetra-alkoxydiphosphines by nitric oxide and pyridine *N*-oxide results in the formation of a mixture of products containing compounds with a single phosphorus atom and tetra-alkyl pyrophosphites. The use of dimethyl sulphoxide (DMSO) in the oxidation of tetra-alkoxydiphosphines is preparatively convenient [221]:

$$(RO)_2\,P{-}P\,(OR)_2 + Me_2S{=}O \begin{cases} \xrightarrow{1:1} (RO)_2\,P{-}O{-}P\,(OR)_2 + Me_2S \\ \xrightarrow{1:2} (RO)_2\,P\,(O){-}O{-}P\,(OR)_2 + 2Me_2S \\ \xrightarrow{1:3} (RO)_2\,P\,(O){-}O{-}P\,(O)\,(OR)_2 + 3Me_2S\ . \end{cases}$$

It is logical to treat this reaction as one involving electrophilic attack by one of the phosphorus atoms on the oxygen atom in the DMSO molecule with subsequent rearrangement of the intermediate tetra-alkoxydiphosphine monoxide. Such rearrangement has been postulated in the study of the alkylation of tetra-alkoxydiphosphines [221] and its occurrence has been demonstrated [173]. It has been shown that tetra-alkyl pyrophosphite is a secondary product of the reaction of dialkyl phosphorochloridites with dialkyl phosphite salts and that the monoxide formed initially is stable for several hours.

In the absence of a solvent, the interaction of tetra-alkoxydiphosphines with DMSO proceeds in a different manner [221]:

$$(RO)_2\,P{-}P\,(OR)_2 + 2Me_2S{=}O \rightarrow (RO)_2\,P\,(O)\,CH_2SMe + (RO)_2\,P\,(O)\,H + Me_2S\ .$$

It appears that a definite analogy may be drawn between data for the above interaction and the reaction of DMSO with acetic anhydride (the Pummerer reaction). [222]

The oxidation of tetra-alkyldiphosphines to the corresponding *P*-imines by trimethylsilyl azide proceeds in stages [207,223]:

$$R_2P{-}PR_2 \xrightarrow[-N_2]{Me_3SiN_3} R_2P\,(=NSiMe_3){-}PR_2 \xrightarrow[-N_2]{Me_3SiN_3} R_2P\,(=NSiMe_3){-}P\,(=NSiMe_3)\,R_2\ .$$

The existence of three isomeric structures of the monoxides of asymmetric organic diphosphines was already mentioned above:

$$R_2P{-}PR'_2 \qquad R_2P{-}PR'_2 \qquad R_2P{-}X{-}PR_2\ .$$
$$\quad\ \|\ \qquad\quad\ \|$$
$$\quad\ X \qquad\quad\ X$$

The problem of the conditions governing the formation and stability of these structures is of independent significance and its detailed elucidation made it possible to discover new rearrangements and the previously unknown phenomenon of non-prototropic tautomerism of OPC [224,225]. Thus it has been found that irreversible rearrangements take place in the following series of compounds [172]:

$$Ph_2P{-}PR_2 \rightarrow Ph_2P{-}P\,(O)\,R_2\ ;$$
$$\quad\ \|$$
$$\quad\ O$$

R = iso-Pr, cyclo-C_6H_{11}, or t-Bu.

The rate of rearrangement depends on the nature of the alkyl substituent and increases in the presence of a catalyst and on heating. For R = cyclo-C_6H_{11}, the rearrangement is completed in five weeks at room temperature and in 4 h at 80° C in the presence of $MgBr_2$. Tetra-alkyldiphosphine monoxides rearrange under more severe conditions [172]:

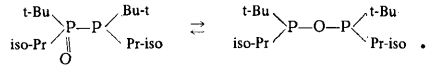
$$Bu_2P\,(O){-}P\,(Bu\text{-}t\,)_2 \xrightarrow[190\text{-}200^\circ,\ 3\text{-}4\ h]{MgBr_2} (t\text{-Bu})_2P(O){-}PBu_2\ .$$

These data show that the thermodynamic stability of the isomeric monoxides of asymmetric diphosphines is determined by the nature of the substituent.

The existence of dialkylphosphinous acid anhydrides is limited by the very narrow range of suitable alkyl substituents, which is evidently associated with the steric and not electronic influence of the substituents [174,225]:

$$R_2P\,(O){-}PR_2 \xrightarrow[180^\circ]{MgBr_2} R_2P{-}O{-}PR_2\ ;$$
R = t-Bu.

Non-prototropic tautomerism has been observed in the following reaction [174] (we may note that the content of the anhydride increases appreciably with increase of temperature):



.

The accumulation of bulky substituents at the phosphorus atoms destabilises the monoxide to such an extent that its thermodynamic stability becomes comparable to that of the anhydride, since the stability of a compound with the P–O–P fragment should be less influenced by steric hindrance. Tetra-(t-butyl)diphosphine monoxide rearranges irreversibly to the anhydride of di-(t-butyl)phosphinous acid, as mentioned above.

Tetra-alkyldiphosphine monosulphides are entirely stable and usually do not rearrange on heating and under the influence of catalysts. An irreversible rearrangement occurs only for tetrahalogenodiphosphine monosulphides [117,226]:

$$F_2P\,(S){-}PF_2 \rightarrow F_2P{-}S{-}PF_2\ ,$$
$$I_2P\,(Se){-}PI_2 \rightarrow I_2P{-}Se{-}PI_2\ .$$

The rearrangement of tetra-alkyldiphosphine monosulphides [174] with secondary substituents is reversible:

$$(iso\text{-}Pr_2\,P\,(S){-}P\,(Pr\text{-}uso)_2 \rightleftarrows (iso\text{-}Pr)_2P{-}S{-}P\,(Pr\text{-}iso)_2.$$

An unusual pathway in the oxidation of organic diphosphines containing phosphorus atoms of different basicities has been discovered, namely the oxidation of the less basic phosphite centre in 2,2-dibutoxy-1,1-di-isopropyldiphosphine [227,228]:

$$(\text{iso-Pr})_2\text{P—P(OBu)}_2 + \text{HgO} \rightarrow (\text{iso-Pr})_2\text{P—P(O)(OBu)}_2 + \text{Hg},$$
$$(\text{t-Bu})_2\text{P—P(OBu)}_2 + \text{O=IPh} \rightarrow (\text{t-Bu})_2\text{P—P(O)(OBu)}_2\text{PhI}.$$

In the oxidation of iodosobenzene the monoxide is formed as a result of the kinetic control of the reaction. The oxidation with mercury(II) oxide involves the following rearrangement, the general characteristics of which have been established recently [173,175]:

$$\underset{\text{(XX)}}{R_2\text{P—P(OR)}_2(=O)} \rightarrow \underset{\text{(XXI)}}{R_2\text{P—O—P(OR)}_2} \rightarrow \underset{\text{(XXII)}}{R_2\text{P—P(OR)}_2(=O)}.$$

The monoxides (XXII) are thermodynamically the most stable in the series (XX)–(XXII) and represent the final products of the reactions in various systems containing the R_2P and $(R'O)_2P$ fragments and the oxygen atom in proportions of 1 : 1 : 1. The isomerisation of the monoxide (XX) to the mixed anhydride (XXI) may be induced both by phosphorus-containing electrophiles (above −20°C such catalytic isomerisation proceeds in the course of several minutes) and by nucleophiles, which are somewhat less effective. The rearrangement of the anhydride proceeds under more severe conditions [175]:

$$(\text{t-Bu})_2\text{POP(OBu)}_2 \xrightarrow[120°,\ 3\text{ h}]{\text{HgBr}_2} (\text{t-Bu})_2\text{P-P(O)(OBu)}_2.$$

As stated above, tetra-ethoxydiphosphine monoxide is stable only for several hours and readily rearranges to the pyrophosphite [176]. On the other hand, tetra-alkoxydiphosphine monosulphides are stable [176], in agreement with data for the oxidation of tetra-alkoxydiphosphine by sulphur [146]:

$$(\text{RO})_2\text{P—P(OR)}_2 \xrightarrow{S} (\text{RO})_2\text{P(S)—P(S)(OR)}_2.$$

The same series of rearrangements is also characteristic of aminodiphosphines [225,229]:

$$R_2\text{P(O)—P(NR}'_2)_2 \rightarrow R_2\text{P—O—P(NR}'_2)_2 \rightarrow R_2\text{P—P(O)(NR}'_2)_2.$$

The stability of the monoxide depends apparently on the extent to which the groups linked to the four-coordinated phosphorus atom can participate in the delocalisation of its partial positive charge, i.e. depends on the ratio of the inductive electron-accepting and mesomeric electron-donating properties of the substituents. This is why equilibria in the above reactions are displaced in the opposite directions:

$$(\text{Et}_2\text{N})_2\text{P—O—P(NEt}_2)_2 \rightleftarrows (\text{Et}_2\text{N})_2\text{P(O)—P(NEt}_2)_2,$$
$$\text{RO}\diagdown\text{P—O—P}\diagup\text{OR} \quad \diagdown\text{NR}_2 \quad \diagup\text{NR}_2 \rightleftarrows \text{RO}\diagdown\text{P(O)—P}\diagup\text{OR} \quad \diagdown\text{NR}_2 \quad \diagup\text{NR}_2.$$

The latter equilibrium is strongly displaced to the left, which can be accounted for by the ability of the alkoxy-groups, linked directly to the four-coordinated phosphorus atom, to participate effectively in the delocalisation of the charge on the phosphorus. This is also indicated by the irreversible rearrangement of $R_2P-O-P(OR)_2$ to $R_2P-P(O)(OR)_2$ and not $R_2P(O)P(OR)_2$. [173]

Related rearrangements have been observed also for *P*-imines [230]:

$$\underset{\text{NX}}{R_2\text{P—PR}_2} \rightarrow \underset{\text{X}}{R_2\text{P—N—PR}_2};$$
R = iso-Pr; X = *m*-YC_6H_4, where Y = H, OMe, Cl, Br, or CF_3.

This necessitates a re-examination of the problem of the structure of the products formed initially in the condensation of dialkylchlorophines with an amide salt [231,232]:

$$R_2\text{PCl} + R_2\text{PNXNa} \rightarrow \begin{cases} \rightarrow R_2\text{P—N(X)—PR}_2 + \text{NaCl} & \text{(XXIII)} \\ \rightarrow R_2\text{P—PR}_2(=NX) + \text{NaCl} & \text{(XXIV)} \end{cases}.$$

Dialkoxydialkyldiphosphine imines undergo a slow reaction, which is the opposite of the analogous rearrangement of the monoxides and monosulphides [230]:

$$\underset{\text{NX}}{R_2\text{P—P(OR)}_2} \rightarrow \underset{\text{NX}}{R_2\text{P—P(OR)}_2};$$
R = Et, X = NPh.

Cyclic polyphosphines are on the whole more resistant to oxidation than linear polyphosphines, although their reactivity also varies within wide limits. Thus $(CF_3P)_4$ and $(MeP)_4$ ignite in air [134–137], while 1,2,3-triphenyl-1,2,3-triphosphaindan is not oxidised by air in boiling toluene and alcohol [25]. Thus phenyl substituents increase sharply the resistance of the ring to oxidation and the result of the reaction of such compounds depends on the ring size [161–163]. For example, after being refluxed for 2 h in acetonitrile, $(PhP)_6$ does not react with sulphur and nickel tetracarbonyl, while the pentamer is cleaved by sulphur with formation of $(C_6H_5PS)_3$ and behaves as a ligand in relation to $Ni(CO)_4$.

Examination of the oxidation reactions shows that organic diphosphines are extremely reactive nucleophiles. Thus their interaction with both halogens and other halogenating reagents proceeds with dissociation of the P–P bond. It may be that a quasi-phosphonium compound is formed as an intermediate, decomposing subsequently with attack by the anion either on the phosphorus atom or on the carbon atom. In the presence of strongly electronegative substituents the carbon atom is attacked under these conditions, and the P–P bond may be actually retained [111]:

$$\text{Br}_2\text{C}(\text{Br})\text{P—P}(\text{Br})\text{CBr}_2 + \text{Br}_2 \rightarrow \left[\text{Br}_2\text{C}(\text{Br})\text{P—P}(\text{Br})(\text{Br})\text{CBr}_2\right]^+\text{Br}^- \rightarrow \text{Br}_2\text{C}(\text{Br})\text{P—P}(\text{Br})_2 + \text{CBr}_3\text{Br}.$$

Under more severe conditions, the P–P bond is cleaved even by carbon tetrachloride [234]:

$$R_2\text{P—PR}_2 + \text{CCl}_4 \underset{C_nH_{2n+2}}{\overset{\text{acetonitrile, } 120–140°,\ 5\text{ h}}{\rightleftarrows}} R_2\text{PCl} + R_2\text{PCCl}_3.$$

The rate of reaction depends to a considerable degree on the substituents at the phosphorus atom; for example, for R = cyclo-C_6H_{11}, heating in the course of 48 h is required and the reverse reaction takes place at 180°C in solution in a hydrocarbon. If the basicity of the diphosphine is enhanced, it is possible to isolate intermediate phosphonium salts of two types: $[Me_2P-P(Me_2)(CCl_2)]^+2Cl^-$ and $[Et_2P-P(Et_2)(CCl_3)]^+Cl^-$ and in the case of cyclopentaphosphines they may be entirely stable [234]:

$$(\text{EtP})_n\text{CCl}_4,\ n = 4,5 \rightarrow \begin{cases} \rightarrow [(\text{EtP})_4\text{CCl}_3]^+\text{Cl}^- \ 51\% \\ \rightarrow \text{EtP(Cl)CCl}_3 + \text{EtPCl}_2 \ 38\% \end{cases}$$
$$(\text{t-BuP})_4 \xrightarrow{\text{CCl}_4} \text{reaction does not occur.}$$

In two component primary or secondary amine–carbon tetrachloride systems the interaction is of the type of the Todd–Atherton reaction [235], the yield of the salt increasing

in parallel with the enhancement of the nucleophilic properties of the diphosphines and the basicity of the amines.

The reaction involving sterically hindered amines proceeds with formation of a P–C bond [236]:

$$(RP)_4 + 2n\,CCl_4 + 4n\,R_2NH \rightarrow n\,[RP(NR_2)_3]^+Cl^- + 2n\,CHCl_3 + n\,[H_2NR_2]^+Cl^-$$
$$R_2P{-}P(O)R_2 + 2CCl_4 + 4HNR_2 \rightarrow [R_2P(NR_2)_2]^+Cl^- + R_2P(O){-}NR_2 + [R_2NH_2]^+Cl^- + 2CHCl_3 .$$

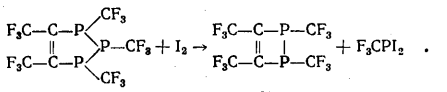
There are instances where the reactions with electrophiles are reversible; the interaction of R_4P_2 with CCl_4 described above is of this kind [202]. Equilibrium of this type may be wholly displaced towards the diphosphine if the halogenating agent is volatile [237]:

$$Cl_3Si{-}SiCl_3 + Me_2PCl \xrightarrow{-SiCl_4} Me_2P{-}SiCl_3 \xrightarrow{Me_2PCl} Me_2P{-}PMe_2 + SiCl_4 .$$

This reaction is also reversible when it involves the dissociation of the low-energy P–I bonds [238] and is analogous to the conversion of PI_3 into P_2I_4 in ethereal solution [239]:

$$2ArPI_2 \rightleftarrows ArP(I){-}P(I)Ar + I_2 .$$

In certain cases [structure (XI)] P–P bonds are not cleaved at all by iodine [117]:



(XI)

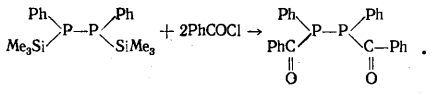
The synthetic possibilities of reactions involving the cleavage of P–P bonds are very extensive. Thus the use in this reaction of carboxylic acid chlorides made it possible to achieve for the first time the synthesis of α-ketophosphonites [240,241]; phosphorus acid chlorides have been used in the synthesis of certain asymmetric dialkoxydialkyldiphosphines [147]:

$$(RO)_2P{-}P(OR)_2 + R'{-}C(O)Cl \rightarrow (RO)_2PC(O)R' + (RO)_2PCl ,$$
$$(iso\text{-}Pr)_2P{-}P(OBu)_2 + (PhO)_2PCl \rightarrow (BuO)_2PCl + (iso\text{-}Pr)_2P{-}P(OPh)_2 .$$

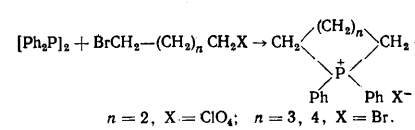
The latter reaction proceeds selectively at the phosphine centre of the dialkoxydialkyldiphosphine. The interaction of dialkoxydialkyldiphosphines with $PhPCl_2$ is unusual: as in the interaction of tetra-alkoxydiphosphines with PCl_3, the P–P bond undergoes oxidation-reduction cleavage and $PhPCl_2$ is reduced to $(PhP)_4$:

$$R_2P{-}P(OR)_2 + PhPCl_2 \rightarrow R_2PCl + (RO)_2PCl + (PhP)_4 .$$

The interaction of silylated organic diphosphines with carboxylic acid chlorides leads to α-ketophosphonites containing P–P bonds [242]:



Alkyl halides, which are typical electrophiles, react with organic di- and poly-phosphines to form 1 : 1 phosphonium salts, which are entirely stable in the case of cyclopolyphosphines. With enhancement of the electron-donating properties of the substituents at the phosphorus atom, the rate of alkylation increases [243]. The monophosphonium salts derived from tetra-alkyldiphosphines and linear organic triphosphines are as a rule unstable, particularly for compounds with bulky substituents or in the case of 2,2-dialkoxy-1,1-dialkyldiphosphines [134,202]. Pentafluorophenylphosphine does not react with methyl iodide [243]. Cyclic monophosphonium salts may be obtained by the reaction of the readily available Ph_4P_2 with α,ω-dihalogenoalkylenes [244]:



$n = 2$, $X = ClO_4$; $n = 3, 4$, $X = Br$.

The anomalous interaction of tetra-alkoxydiphosphines with methyl iodide [241] involves not only standard transformations via the mechanism of the Arbuzov rearrangement but also a rearrangement of the P(O)–P fragment to P–O–P:

$$(RO)_2P{-}P(OR)_2 + MeI \xrightarrow{-RI} [ROP(O)(Me){-}P(OR)_2] \rightarrow$$
$$\rightarrow [ROP(Me){-}O{-}P(OR)_2] \xrightarrow{MeI} Me_2P(O)OP(OR)_2 .$$

Inorganic and organic diphosphines add to C–C bonds, which made it possible to draw a formal analogy between the reactivities of diphosphines and halogens [3]. In certain cases the mechanism of this addition is apparently quite unambiguous. Thus, under the conditions of a radical reaction (irradiation with ultraviolet light), F_4P_2 adds smoothly to olefins [245–247] and the ease of addition varies in the sequence ethylene > propene > but-2-ene, in agreement with the usual treatment within the framework of "steric hindrance". In this case one may speak of radical addition, since in the absence of irradiation the reaction does not occur at all at room temperature but does take place at 200°C, where F_4P_2 dissociates with formation of the PF_2 radical [247,248]. The reaction with perfluoro-olefins, which readily combine with nucleophilic intermediates, takes place slowly and with very low yields. Its stereochemistry may be inferred from the addition to cyclohexene, whereupon only the *trans*-isomer is formed [248], the ratio of compounds with axial and equatorial orientations of the PF_2 group being 6 : 4.

Tetramethyldiphosphine reacts slowly at 100°C with butadiene in the presence of azobisisobutyronitrile to form exclusively the 1,4-addition product [249]:

$$Me_2P{-}PMe_2 + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Me_2P{-}CH_2{-}CH{=}CH{-}CH_2PMe_2 .$$

In the dark the reaction does not occur even at 100°C. [250] The addition of tetra-alkyldiphosphines to a triple bond is also apparently a radical process, since it proceeds only under ultraviolet irradiation or in the presence of initiators and leads to a mixture of the *cis*- and *trans*-isomers [251]:

$$PhC{\equiv}CH + R_2P{-}PR_2 \rightarrow R_2PC(Ph){=}CHPR_2 .$$

The tridentate ligand (XXV) is formed on ultraviolet irradiation at the wavelength at which F_4P_2 decomposes into F_2P radicals [252–254]:

$$F_2P{-}PF_2 + F_2PCH_2{-}CH{=}CH_2 \xrightarrow{h\nu} \underset{(XXV)}{F_2PCH_2{-}CH(PF_2){-}CH_2PF_2} .$$

Tetra-alkoxydiphosphines exhibit a high reactivity in reactions involving addition to multiple bonds activated in relation to nucleophilic attack [255]:

$$(RO)_2P{-}P(OR)_2 + CH_2{=}CH{-}R' \xrightarrow{20^\circ} (RO)_2PCH_2{-}CH(R')P(OR)_2 .$$

When the electrophilicity of the double bond is reduced (methyl methacrylate), the rate of reaction falls and the completion of the reaction requires heating to 60°C. Tetra-alkoxydiphosphines do not add to butadiene even at 150°C. [130]

The optimum conditions for the homolytic dissociation of the P–P bond are known to involve irradiation ($\lambda > 300$ nm) or heating above 180°C. [256,257] The addition of tetraphenyldiphosphine to the C=O bonds of aldehydes occurs in the temperature range between 180° and 200°C, apparently

via a free radical mechanism; the resulting ketophosphinites undergo a series of further transformations under the severe conditions employed [256].

It was mentioned above that the intermediate **RP**: (phosphinidene) is apparently a carbenoid species and cyclopolyphosphines can therefore be regarded as potential sources of phosphinidene, for example, for the synthesis of di-isopropenyl phenylphosphonites [258]:

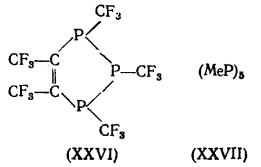
$$(PhP)_4 + 4Hg\,(CH_2COC_2H_5)_2 \rightarrow 4PhP\,[OC\,(Et)=CH_2]_2 + 4Hg$$

or for the insertion in a non-metal–non-metal bond. The first steps in this field were made in the study of the reactions of phosphinidenes with disulphides [258] and α-diketones [259]:

$$(PhP)_5 \xrightarrow{160^\circ} 5\,[PhP:] \xrightarrow{Et\text{-}S\text{-}SEt} PhP\,(SEt)_2\ .$$

The formation of the intermediate PhP: in the course of addition to substituted butadienes was demonstrated mass-spectrometrically. The insertion of phosphinidene in the P–N, As–As, Si–Si, and N–N bonds was investigated subsequently [260]. The reaction of *N*,*N*-(dimethyl)dimethylphosphinous amide with $(CF_3P)_4$ resulted in the formation of a mixture, the main component of which was a phosphinidene complex, which was subsequently converted into the product of the insertion of phosphinidene in the P–N bond. The insertion in the As–As bond in tetramethyldiarsine took place in the same way. The interactions with tetramethylhydrazine and hexamethyldisilane could not be observed.

Mass-spectrometric data on tetra-alkyldiphosphines have been interpreted to demonstrate complete binding in these compounds [261–263], which, as stated above, is fairly controversial. In connection with the problem of the p–d conjugation, an attempt was made to generate radical-anions from the heterocycles (VIII), (IX), (XXII), and (XXVII):



(XXVI) (XXVII)

by treatment with the NaK alloy or electrochemically at −125° C. [265] It was found that (XXVII) and (VIII) do not yield radicals at all. The spin densities of the radical-anions (XI) and (XXVI) are localised at the C=C bonds and not at the phosphorus atom. This shows that the d orbitals do not stabilise the lowest-lying molecular orbital of the phosphorus atom, so that, among the elements of the Second Period, ready reduction to radical-anions is characteristic only of silicon in cyclopolysilanes.

Infrared and Raman spectroscopy has been used widely, particularly for the conformational analysis of diphosphines; on the other hand, for the detection of the P–P bond in compounds of a wide variety of types, ^{31}P NMR, and to a much lesser extent ^1H NMR, is the most informative method. The theoretical predictions of the chemical shifts in ^{31}P NMR spectra are still unsatisfactory, but the experimental data accumulated in this field for a wide variety of types of compounds with P–P bonds are now so extensive that identification based on analogies is entirely satisfactory. The constants for the spin–spin coupling between directly linked phosphorus atoms ($^1J_{P-P}$) lie within very broad limits (up to 1000 Hz), depending on the nature of the substituent at the phosphorus atom [265,266]; for two three-coordinated phosphorus atoms, $^1J_{P-P}$ varies in the range 100–400 Hz. The sign of the constant $^1J_{P-P}$ for organic diphosphines is known reliably in isolated instances [55] and is negative, while that of the constant $^1J_{P-N}$ is positive [267].

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Thus the chemistry of organic di- and poly-phosphines has been developing vigorously in recent years both as regards theory (stereochemistry and conformational analysis of OPC, discovery and identification of non-prototropic tautomerism, etc.) and practical applications (tetra-alkyldiphosphines initiate the copolymerisation of chloral with isocyanates [268] and are effective phosphorylating agents in sugar chemistry [269]). There is no doubt that this comparatively inadequately investigated field of the chemistry of OPC will attract increasing attention in the coming years.

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