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Three-membered Organophosphorus Heterocycles

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The methods of synthesis, structural characteristics, and properties of compounds with three-membered rings and containing at least one phosphorus atom and one carbon atom, including bicyclic and tricyclic compounds, are examined. The bibliography includes 76 references.

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I. INTRODUCTION

Three-membered rings occupy a special position in theoretical and applied organic chemistry as a consequence of characteristic features of orbital hybridisation, the high angular strain, and the consequent ease of ring opening or expansion. The introduction of a heteroatom into a three-membered ring lowers the molecular symmetry and results in the non-equivalence of the angles and bonds, expressed to the greatest extent in the case of a ring containing a phosphorus atom.

It is noteworthy that compounds with three-membered phosphorus-containing heterocycles (phosphirans) have been studied comparatively little, since they have been obtained only very recently. In the monograph of Kirby and Warren[1], the English edition of which was published in 1967, it is still stated that "stable three-membered rings containing phosphorus are unknown except for the elemental phosphorus P_4. However, they can arise as intermediates or in transiton states...".[2,3] The intermediate formation of unstable compounds with a three-membered phosphorus-containing ring was invoked to account for the mechanism of formation of reaction products and has also been postulated in a number of other studies[4-10], while the synthesis of relatively stable phosphirans and element-substituted phosphirans as well as the study of their properties have been described as a rule only during the last decade.

Baudler's review[11], devoted to compounds with three-membered rings consisting solely of phosphorus atoms, or of two phosphorus atoms and a single carbon, silicon, germanium, arsenic, boron, or sulphur atom, or of two arsenic atoms and a single phosphorus atom, i.e. in most cases referring to inorganic rings, was published in 1980. The present review deals solely with three-membered phosphorus-containing rings with at least one carbon atom, so that the data presented constitute an organic supplement to Baudler's review[11].

Data on the synthesis and NMR spectra of phosphirans containing only phosphorus and carbon atoms are also considered in Quin's monograph[12] devoted to P-C heterocycles.

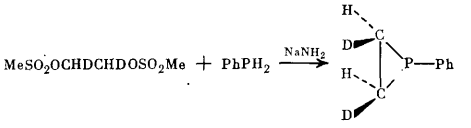
II. SYNTHESIS

1. Rings with Tetracoordinate Phosphorus

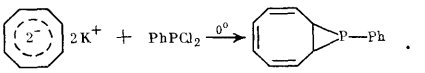
The simplest compound, the unsubstituted phosphiran, was the first to be synthesised among compounds containing a three-membered heterocycle with a phosphorus atom and a P-C bond. In their study of the reaction of α,ω-dihalogenoalkanes with alkali metal phosphides in liquid ammonia, which was undertaken with the aim of synthesising α,ω-diphosphinoalkanes, Wagner and co-workers[13,14] unexpectedly observed that, when 1,2-dichloroethane is used, the product is phosphiran or 1-methylphosphiran. According to Wagner et al.[14], this course of the reaction can be explained by the fact that the hydrogen linked to the phosphorus atom in the intermediate formed on substitution of the first chlorine atom in dichloroethane readily exchanges for the metal on treatment with sodium phosphide or methylphosphide, which then leads to cyclic products:

$$ClCH_2CH_2Cl \xrightarrow[-Cl^-]{RPH^-} ClCH_2CH_2PHR \xrightarrow[-RPH_2]{RPH^-} \rightarrow ClCH_2CH_2\bar{P}R \xrightarrow[-Cl^-]{} \underset{\diagdown P \diagup}{CH_2—CH_2} \; ;$$
$$\quad\quad\quad

The cyclisation of 1,2-disubstituted ethanes can take place not only as a result of the elimination of the halogen from the carbon atom, the methanesulphonyloxy-substituent also being capable of functioning as the leaving group. For example, in the presence of sodium amide, phenylphosphine interacts with 1,2-dideutero-1,2-bis(methanesulphonyloxy)ethane to form *cis*-2,3-dideutero-1-phenylphosphiran[18]:

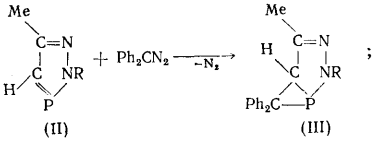


When readily eliminated halogen atoms are present at the phosphorus atom, the phosphorus compound can be involved in the synthesis of phosphirans as an electrophile. Thus 9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene (I) has been obtained by the condensation of the dipotassium salt of cyclo-octatetraene with dichlorophenylphosphine under mild conditions[19,20]:



(I)

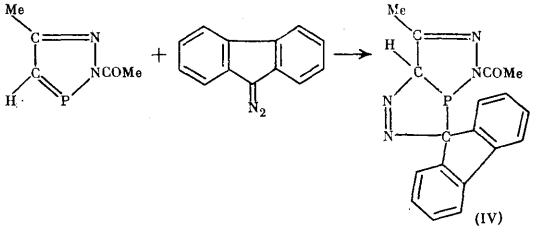
Arbuzov and co-workers recently described a method for the formation of the phosphiran ring with a tervalent phosphorus atom, which consists in the addition of diphenyldiazomethane to the P=C bond in compounds with dicoordinate phosphorus[21,22]. In this case the phosphorus atom is shared by two rings. The products are crystalline substances (III) with high melting points and some of the highest thermal stabilities among compounds with a phosphiran ring. Their structure has been confirmed by infrared spectroscopy and ^{1}H and ^{31}P NMR, by determining their molecular weights, and by a series of reactions:



(II) (III)

R=Ph, MeCO .

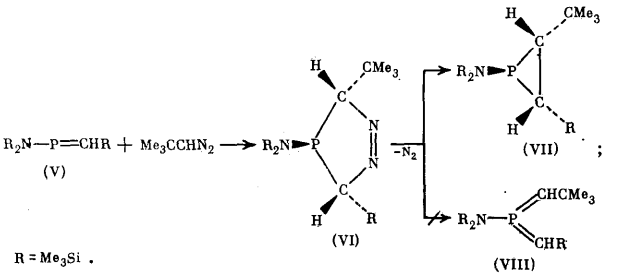
Despite the conditions being varied, products containing the phosphiran ring are not formed in the analogous interaction of the diazaphosphole (II, R=MeCO) with 9-diazofluorene. However, when the reaction is carried out in pentane or hexane, the adduct (IV) is produced in almost quantitative yield, its formation suggesting that diazoalkanes add to the P=C bond in diazaphospholes (II) via the 1,3-cycloaddition mechanism and not via a carbene[23]:



(IV)

The interaction of 2,2-dimethyldiazopropane with a noncyclic derivative of dicoordinate phosphorus (V) also leads to a stable 1,3-cycloaddition product, namely 3-trimethylsilyl-4-[bis(trimethylsilyl)amino]-5-t-butyl-1,2,4λ^3-diazaphospholine (VI). However, on heating *in vacuo* at temperatures between 80° and 120 °C, the diazaphospholine (VI) splits off nitrogen and gives rise to the corresponding phosphiran (VIII), whose configuration has been postulated on the basis of spectroscopic data.

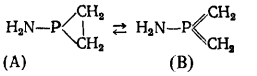
The possibility of the formation of aminodimethylenephosphine (VIII) has also been postulated in the decomposition of the diazaphospholine (VI).



(V) (VI) (VII) (VIII)

R = Me_3Si .

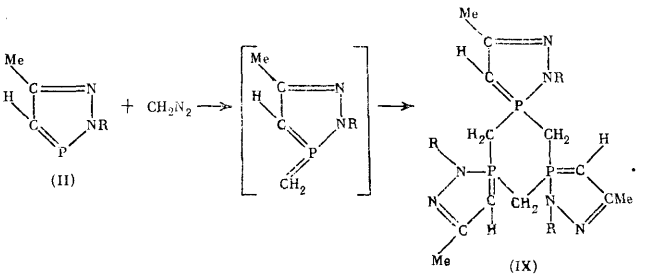
However, calculation of the energy surface for the valence isomerisation of the model structure



(A) (B)

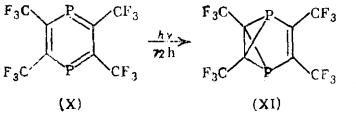
by the MINDO/3 method showed that the cyclic form (A) is more favourable by 22 kcal $mole^{-1}$ than the dimethylenephosphine form (B) and that the A⇌B transition has a comparatively high energy barrier[24].

A similar dimethylenephosphino-derivative, analogous to compound (VIII), is apparently formed as an intermediate in the reaction of 1,2,3-diazaphospholes with diazomethane, since the products are not phosphirans but three-dimensional compounds (IX):



(II) (IX)

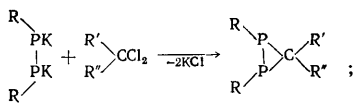
When 2,3,5,6-tetrakis(trifluoromethyl)1,4-diphosphabenzene (X) is illuminated for a long time, the product is a tricyclic compound containing two phosphiran rings with tervalent phosphorus—2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphatricyclo[3.1.0.$0^{4,6}$]hex-2-ene (XI). This compound is the first representative of the analogues of benzvalene with heteroatoms in the ring[25-27]:



(X) (XI)

Three-membered rings with two phosphorus atoms, namely diphosphirans (XII), were obtained for the first time by the reaction of the dipotassium salts of symmetrical dialkyl(aryl)-diphosphines with geminal dichloroalkanes in pentane or toluene at −30 °C.[11,28,29]. Their formation reaction can be regarded as an unusual version of the Wagner synthesis of

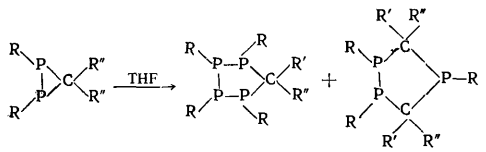
phosphirans, since in this case too the halogen at the saturated carbon atom undergoes nucleophilic substitution by the phosphide anion:



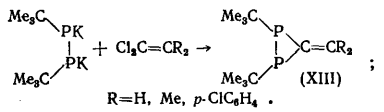
(XII)

R = t-Bu, R′, R″=H, Me; R=Ph, R′, R″=Me .

It is of interest that, when this reaction is carried out in tetrahydrofuran (THF), five-membered and not three-membered phosphorus-containing heterocycles are produced[29], which has been explained by a rapid rearrangement of the diphosphirans in the more polar solvent[11]:



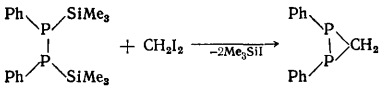
Diphosphirans (XIII) having an exocyclic C=C bond have been obtained by the reaction of 1,2-di-t-butyl-1,2-dipotassio-diphosphine with 1,1-dichloro-olefines as well as geminal dichloroalkanes[11]:



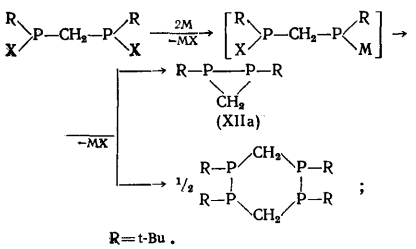
(XIII)

R=H, Me, *p*-ClC$_6$H$_4$.

The reaction of 1,2-bis(trimethylsilyl)-1,2-diphenyldiphopshine with di-iodomethane in THF at −30°C apparently also leads to 1,2-diphenyldiphosphiran[28], since a signal in the appropriate region appears in the ^{31}P NMR spectrum:



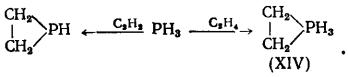
1,2-Di-t-butyldiphosphiran (XIIa) has also been obtained by the intramolecular 1,3-cyclisation of the corresponding *P,P*-dihalogenodiphosphinomethane by treatment with a liquid potassium–sodium alloy at temperatures between 0° and 10 °C (yet another version of the Wagner reaction). Diphosphiran is then obtained in the form of a mixture with a dimer—1,2,-4,5-tetra-t-butyl-1,2,4,5-tetraphosphacyclohexane—and constitutes 80% of the mixture. The diphosphiran could not be detected in the analogous reaction of *P,P*-dihalogenodiphosphinomethane with isopropyl groups at the phosphorus atoms—the corresponding tetraphosphacyclohexane is formed immediately[30]:



(XIIa)

R=t-Bu .

Thus the most general methods of synthesis of phosphirans with tervalent phosphorus are different versions of the interactions of alkali metal phosphides with compounds containing two readily removed groups (a halogen or the methanesulphonyloxy-group) in the 1,2- or 1,1-positions and also the addition of diazoalkanes to compounds of dicoordinate phosphorus, which has also been used to synthesise phosphirans with tetracoordinate phosphorus and with a nitrogen atom in the phosphiran ring (see below). Other syntheses known at present have been described only in relation to individual examples. The theoretical possibility of yet another method of synthesis of unsubstituted phosphirans as well as the synthesis of a phosphiran with a pentacoordinate phosphorus atom [structure (XIV)] as a result of the addition of phosphine to acetylene and ethylene respectively has been predicted on the basis of the analysis of Woodward–Hoffman correlation diagrams:

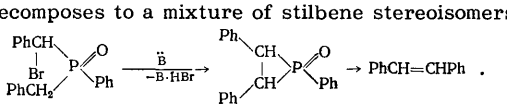


(XIV)

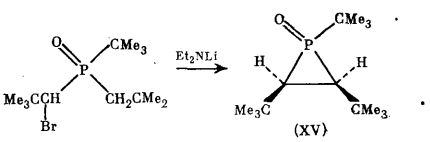
The authors believe that the first reaction can occur in the ground state, while the second takes place on photochemical oxidation of the molecules and also under the conditions of acid and base catalysis. Substitution of the hydrogen atoms in the phosphine by more electronegative groups should impair the energetics of the formation of the phosphiran ring[31]. However, hitherto this synthesis has not been realised.

2. Rings with Tetracoordinate Phosphorus

Only one method of synthesis of phosphiran oxides has been described so far. It involves the 1,3-cyclisation under the influence of a base of acyclic oxides containing a halogen atom in the α-position in one of the substituents at the phosphorus atom and a mobile hydrogen atom in the α-position in the other substituent. Thus 1,3-elimination of hydrogen halide from α-bromobenzylphenylbenzylphosphine oxide results in the formation of 1,2,3-triphenylphosphiran oxide, which decomposes to a mixture of stilbene stereoisomers[32]:

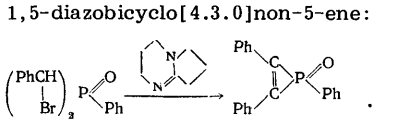


A stable phosphiran oxide (XV) with the *cis*-configuration and containing three t-butyl groups has been obtained recently as a result of an analogous cyclisation[33,34]. The configuration of the product has been proposed on the basis of ^{1}H and ^{13}C NMR data:



(XV)

It has been reported[32,35] that 1,2,3-triphenylphosphiran oxide (XVI) has been obtained as a result of the analogous cyclisation of bis(α-bromobenzyl)phenylphosphine oxide on treatment with 1,5-diazobicyclo[4.3.0]non-5-ene:



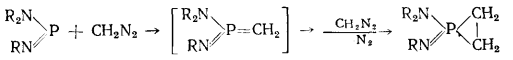
(XVI)

However, the formation of this phosphiran oxide has been refuted[36] on the basis of the physical and spectroscopic characteristics of the product obtained on repeating the above reaction, although one should note that the infrared and mass spectra of the compounds synthesised by the two groups of investigators are different.

Nevertheless the possibility, in principle, of the existence of compounds with a phosphiren ring forming an aromatic system as a consequence of delocalisation of the $p\pi$ electrons of the double bonds via p_π–d_π conjugation, has been considered in a study[37] whose authors concluded that fairly stable phosphirenium salts and phosphiren oxides (analogues of cyclopropenone) exist:



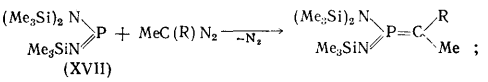
Like the analogous compounds with the C = P–N group (see above), compounds of dicoordinate phosphorus with the N = P–N group are capable of reacting with diazoalkanes although via a somewhat different mechanism. For example, the addition of diazomethane to bis(trimethylsilyl)aminotrimethylsilyliminophosphine (XVII) leads to 1-bis(trimethylsilyl)amino-1-trimethylsilyliminophosphiran (XVII)—a representative of phosphirans with an exocyclic phosphazo-group[38]:



(XVII) (XVIII) ;

R = Me_3Si .

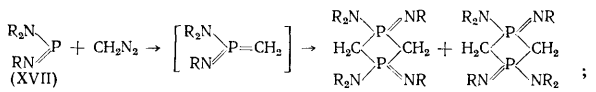
The intermediate formation of an ylide with a tricoordinate phosphorus atom is confirmed by the fact that the reaction of the aminoiminophosphine (XVII) with other diazoalkanes stops at the ylide stage. The ylides are stable for steric reasons, as suggested by Niecke and Wildredt[39]:



(XVII)

R = Me, Et, iso-Pr, t-Bu .

In addition, when the conditions of the reaction between the phosphine (XVII) and diazomethane are modified somewhat, a mixture of isomeric diphosphetans, which are cyclic dimers of the intermediate phosphazoylide, is formed[40]:

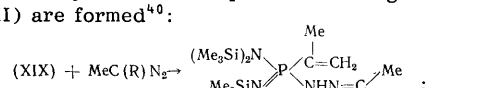


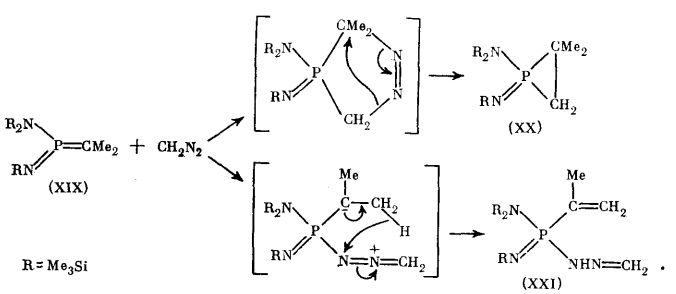
(XVII)

R = Me_3Si .

When diazomethane adds to the iminomethylenephosphine (XIX), the product is, as in the formation reaction of compound (XVIII), a compound (XX) with a phosphiran ring together with an acyclic compound (XXI) (in proportions of 7 : 3).[40]

The addition of α-alkyldiazoethanes to the iminoethylenephosphine (XIX) takes place, as in the case of compound (XVII), without cyclisation and products analogous to compound (XXI) are formed[40]:



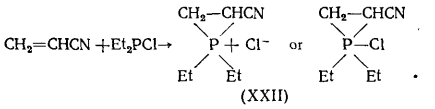


(XIX) (XX) (XXI)

R = Me_3Si .

3. Rings with Pentacoordinate Phosphorus

When chlorodiethylphosphine was made to add to acrylonitrile, a crystalline very hygroscopic substance was obtained. On the basis of infrared and ^1H NMR spectra as well as the study of its hydrolysis products, it was assumed to have the structure of 2-cyano-1,1-diethylphosphiranium or a derivative of pentacoordinate phosphorus—1-chloro-2-cyano-1,1-diethylphosphiran (XXII)[41]:



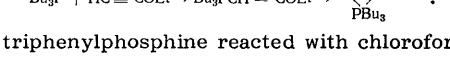
(XXII)

The formation of this compound is the only example of the 1,2-addition of a chlorophosphine to an activated olefinic bond. However, one should note that the interaction of chlorodiethylphosphine with acrylic and methacrylic acids and their chlorides also results in the formation of hygroscopic crystalline adducts. Whether these compounds are products of the 1,2-addition of the phosphine to the C = O bond is unknown, since their structure has not been investigated[42].

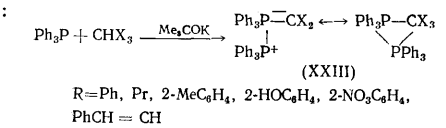
Even in the presence of antimony pentachloride, chlorodiphenylphosphine does not react with acrylonitrile[41].

The intermediate formation of compounds with pentacoordinate phosphorus containing a phosphiran ring is postulated in the reactions of 1-phenylphosphiran with 3,3,4-trimethyldioxetan and 3,4-bis(trifluoromethyl)dithietan[18,43] (see Section IV).

The products of the reactions of triorganylphosphines with ethoxyacetylene may contain a phosphiren ring with pentacoordinate phosphorus[7]:

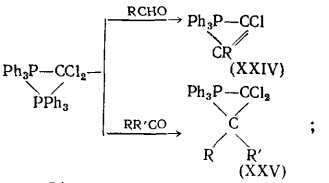


When triphenylphosphine reacted with chloroform or bromoform and potassium t-butoxide in proportions of 2 : 1 : 1, high-melting products (XXIII), having the structure of diphosphirans or betaines (XXIII), were obtained. The reaction of the chloro-compound (XXIII, X = Cl) with a series of aldehydes is accompanied by the elimination of a hydrogen chloride molecule and leads to products to which the structure of phosphirens (XXIV) was attributed. In the reactions involving benzophenone and 2-methoxybenzaldehyde, compounds (XXV) with a saturated phosphiran ring are obtained. Their structure has been postulated on the grounds that their infrared spectra contain absorption bands at frequencies characteristic of the three-membered phosphorus-containing ring[44–46]:



(XXIII)

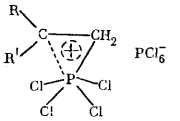
R = Ph, Pr, 2-MeC_6H_4, 2-HOC_6H_4, 2-$NO_2C_6H_4$, PhCH = CH



(XXIV) (XXV)

R, R′ = Ph; R = H, R′ = 2-$MeOC_6H_4$.

The structure of a three-centre epiphosphiran cation[47] of the type

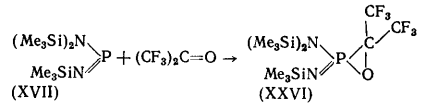


has been attributed to the transition state in the reactions of alkenes with phosphorus pentachloride.

4. Element-substituted Phosphirans

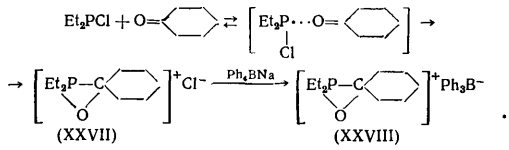
Element-substituted phosphirans, whose three-membered ring contains, apart from phosphorus and carbon atoms, also oxygen, sulphur, or nitrogen atoms, are very few. The possibility of the intermediate formation of unstable compounds with an oxaphosphiran ring has been postulated in considering the mechanisms of reactions important in the chemistry of organophosphorus compounds such as that of trialkyl phosphites with α-diketones[8] or α-halogenoketones[9].

The first stable oxaphosphiran derivative (XXVI) was obtained only recently[48] as a result of the addition of hexafluoroacetone to the aminoiminophosphine (XVII). As in the reaction with diazomethane, only the phosphorus atom of (XVII) is involved in the reaction with hexafluoroacetone:



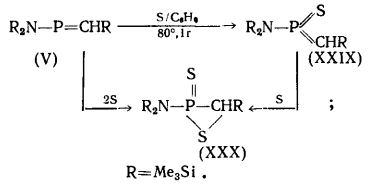
(XVII) (XXVI)

A crystalline compound, which is unstable in air and has the structure of a substituted oxaphosphiranium salt (XXVII), was isolated from the mixture of the products of the reaction of chlorodiethylphosphine with cyclohexanone. The more stable oxaphosphiranium salt (XXVIII) was obtained in the exchange of the anion of the chloride (XXVII) [49]:



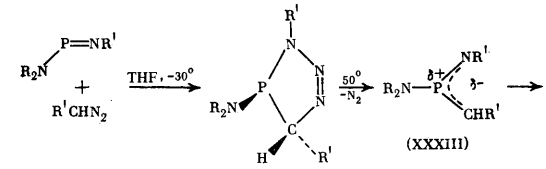
(XXVII) (XXVIII)

When an equivalent amount of sulphur adds to the aminomethylenephosphine (V), the corresponding sulphide (XXIX) is obtained together with a small amount of the thiaphosphiran (XXX), characterised by hydrogen, phosphorus, carbon, and silicon NMR data; the preferential formation of the sulphide (XXIX) shows that the thiaphosphiran ring is closed as the result of the addition of sulphur to the P=C bond of the sulphide and not the initial phosphine (V). The phosphine (V) reacts with two equivalents of sulphur to give a quantitative yield of the thiaphosphiran (XXX), which is the first representative of this heterocyclic system[50]:

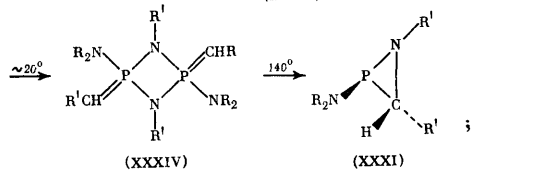


R=Me_3Si.

The interaction of t-butyliminodi-isopropylaminophosphine with 2,2-dimethyldiazopropane leads ultimately to 1,3-di-t-butyl-2-di-isopropylaminoazaphosphiridine (XXXI). The formation of compound (XXXI) completes the chain of transformations of the intermediates having structures (XXXII), (XXXIII), and (XXXIV), which were isolated in a pure state and characterised by ^1H, ^{13}C, and ^{31}P NMR data[51]:



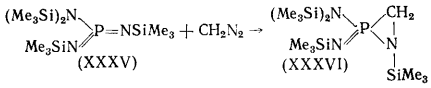
(XXXII) (XXXIII)



(XXXIV) (XXXI)

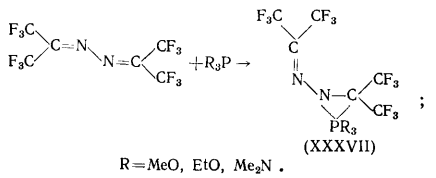
R = Me_2CH; R' = Me_3C.

In contrast to the P=N bond of the aminoiminophosphine (XVII) containing dicoordinate phosphorus, the analogous bond in the aminodi-iminophosphine (XXXV), containing tricoordinate phosphorus, is capable of the 1,2-addition reaction with diazomethane resulting in the formation of the azaphosphiridine (XXXVI), which is stable in the absence of moisture almost indefinitely[38]:



(XXXV) (XXXVI)

The addition of phosphorous acid derivatives to hexafluoroacetone azine takes place at only one C=N bond with formation of thermally stable azaphosphiridines (XXXVII) with a pentacoordinate phosphorus atom. Their structure has been postulated on the basis of infrared spectroscopic, ^{19}F and ^{13}C NMR and mass-spectrometric data[52]:



(XXXVII)

R=MeO, EtO, Me_2N.

III. STRUCTURE AND PHYSICAL PROPERTIES

The structure of compounds with a three-membered ring containing phosphorus has been of evident interest to chemists and the determination of the structural parameters of such compounds was therefore begun almost immediately after the synthesis of phosphiran and its first homologues.

The microwave spectra of phosphiran, [^{13}C]phosphiran, *cis*- and *trans*-2-deuterophosphirans, and 1-deuterophosphiran were investigated, which made it possible to determine the bond lengths and angles in the phosphiran molecule, the result being presented in the Table. The dipole moment of phosphiran is 1.12 D.

The structure of crystalline 4-methyl-2,6,6-triphenyl-1-phospha-2,3-diazabicyclo[3.1.0]hex-3-ene (III, R=Ph), containing the phosphiran ring combined with the 1,2,3-diazaphospholan ring, was determined by X-ray diffraction[54]. It was found that the phosphorus atom has a distorted pyramidal configuration in this compound and that the plane of the three-membered ring makes an angle of 108.4° with the almost flat five-membered ring. The P–C bond lengths and the angle at the phosphorus atom in the phosphiran ring proved to be somewhat greater than the values in the Table.

Comparison with dimethylphosphine, which is an acyclic analogue of phosphiran and has $r(P-C) = 1.853$ Å, $r(P-H) = 1.445$ Å, $\alpha(CPC) = 99°12'$, and $\alpha(HPC) = 96°30'$,[55] shows that ring closure decreases the valence angles at the phosphorus atom and leads to a corresponding increase in the length of its endocyclic bonds. This effect is responsible for the increase of the *p* character in the bonds involving the phosphorus atom and of the *s* character of its unshared electron pair. Indeed, an independent estimate of the amount of *s* character of the hybrid atomic orbital of phosphorus in the P–H bond from the spin–spin coupling constant $^1J_{HP}$ yielded 5.3% for phosphiran, which is lower than the corresponding value for Me_2PH (6.5%).[17]

The bond lengths (*r*, Å) and angles (α, deg) in cyclopropane and its heteroanalogues XC_2H_4.[53]

Bond or angle	X					
	CH_2	NH	O	SiH_2	PH	S
r(C—C)	1.510	1.480	1.472	1.520	1.502	1.492
r(C—H)	1.088	1.082	1.082	1.081	1.093	1.078
r(C—X)	1.510	1.488	1.436	1.826	1.867	1.819
r(X—H)	1.088	1.000	—	1.480	1.428	—
α(CXC)	60.0	60.0	61.4	49.2	47.4	48.5
α(HCH)	115.1	116.7	116.6	120.0	114.4	116.0
α(C—CH_2)	150	159.4	159.5	143.9	149.5	151.7
α(HXC_2)	117.6	112.0	—	120.0	95.7	—
α(XCC)	60.0	60.2	59.2	65.4	66.3	65.8

In conformity with this, it has been noted[33] that the formation of a phosphiran ring with a phosphoryl group is accompanied by a decrease of the spin–spin coupling in the endocyclic P–C bonds and an upfield shift of the signal in the ^{31}P NMR spectrum. The stretching vibration frequency of the P=O bond increases under these conditions.

An interesting feature of the molecular structure of phosphiran is the fact that the *cis*-hydrogen atom of the methylene group is more remote from the phosphorus atom by 0.035 Å than the *trans*-hydrogen atom, while the angle between the CH bond and the plane of the ring is greater by 2.2° in the case of the *cis*-atom[17]. In order to elucidate the cause of this phenomenon, a microwave spectroscopic study was made of *cis*- and *trans*-2-methylphosphirans[56]. In this case too the substituent at the carbon atom in the *cis*-isomer is somewhat more remote from the phosphorus atom than in the *trans*-isomer, but the barriers to internal rotation in these isomers differ insignificantly, which is difficult to reconcile with the possible interaction through space between the proton at the phosphorus atom and the substituents at the carbon atoms of the phosphiran ring. The difference between the free energies of the isomeric 2-methylphosphirans, which is a measure of the stability of the isomeric forms, is also small ($\Delta F_{200K} = 0.13$ kcal mol^{-1}; *F* is lower for the *trans*-isomer). This also indicates the absence of an appreciable interaction through space. On the other hand, analysis of the change in the density matrix obtained by the extended Hückel method with adjustment for self-consistency with respect to charges[57] shows that all the atoms of the phosphiran molecule, including the methylene protons, are involved in the inversion of the phosphorus pyramid. This demonstrates the occurrence of an explicit interaction of the methylene protons with the proton at the phosphorus atom. Estimation of the barrier to inversion from the change in the orbital population yielded 39.9 kcal mol^{-1}, which is much larger than the analogous change for aziridine and agrees well with the usually observed high barriers in acyclic phosphorus compounds.

The calculation of the barriers to pyramidal inversion by the specially parametrised semiempirical CNDO/2 method without taking into account the *d* orbitals yielded a still higher value of phosphiran: 80.4 kcal mol^{-1}. The inclusion of the inverted centre in a small ring increases the barrier to inversion because of the corresponding increase in *s* character of the unshared electron pair of the heteroatom. In particular, it has been shown that the barrier increases in the series of phosphorus compounds investigated: trimethylphosphine < 1-methylphospholan < 1-methylphosphetan < phosphiran[58].

The phosphiran molecule provides an excellent possibility for the observation of the stretching vibrations of the C–P–C linkages in a small strained ring and the influence of this ring on the vibration frequency of the P–H bond. A study of the infrared spectra of phosphiran, 1-deuterophosphiran, and 2,2,3,3-tetradeuterophosphiran in the gas phase and of the Raman spectrum of phosphiran in the liquid phase has been reported[16]. The observed bands were identified on the basis of the frequency shifts in the deuterated derivatives, the data for the polarisation of the Raman lines, the contours of the infrared bands for the gas phase, and the characteristic group frequencies. Two bands were assigned to symmetrical vibrations of the P–C bonds in the ring: at 598.1 and 656.7 cm^{-1}. They have undergone a bathochromic shift relative to the analogous stretching vibrations in dimethylphosphine (664 and 710 cm^{-1}).

The 2291.4 cm^{-1} band in the spectrum of gaseous phosphiran was assigned to the stretching vibrations of the P–H bond; bearing in mind that the analogous band in the spectrum of dimethylphosphine is observed in the region of 2290 cm^{-1}, it was concluded[16] that the three-membered ring has an insignificant influence on the frequency of these vibrations. On the other hand, the deformation vibrations of the P–H bond in the gas phase (769 and 680.4 cm^{-1}) are observed at lower frequencies than those known for the analogous acyclic phosphorus compounds. For example, the corresponding band in the dimethylphosphine spectrum is in the region of 1146 cm^{-1}.[59]

In contrast to aziridine, where the frequency of the out-of-plane deformation vibrations of the N–H bond is higher than the frequency of the corresponding in-plane vibrations, in phosphiran the above relation is reversed from the analogous vibrations of the P–H bond[60]. This is undoubtedly caused by the smaller valence angles at the heteroatom in phosphiran (Table 1), as a result of which the steric hindrance to the displacement of the heteroatom proton from the symmetry plane is much smaller than the hindrance to the deformations within this plane.

The inversion barrier in phosphiran, estimated from the calculated force field of the molecule, is 33 kcal mol^{-1}.[60]

The thermodynamic functions of phosphiran have been calculated in terms of the rigid rotator–harmonic oscillator approximation[60]. They differ appreciably from the values obtained in another study[61] in terms of the analogous approximation but on the basis of an assignment of the infrared bands of phosphiran and related molecules differing somewhat from that described above[62].

A ^{31}P NMR study[14] showed that the phosphiran spectrum consists of a doublet with the centre at −341 p.p.m. relative to 80% phosphoric acid. The chemical shift of phosphorus thus proved to be the highest upfield shift among the values reported for phosphines. The spin–spin coupling constant $^1J_{PH} = 155$ Hz is unusually small. Each component of the doublet is split in a complex manner by interaction with the

methylene proton. A qualitative description of the proton NMR spectrum is also given.

The ^{31}P NMR spectra of substituted phosphirans yield additional evidence for their configurational stability. The existence of the *cis*- and *trans*-isomers of 2-ethylphosphiran has been demonstrated[15] by the presence in the spectrum of two doublets with different chemical shifts and slightly different spin–spin coupling constants $^1J_{PH}$. The more pronounced upfield character of the ^{31}P chemical shifts and their greater sensitivity to structural changes in substituted phosphirans compared with the analogous secondary and tertiary phosphines have also been noted.

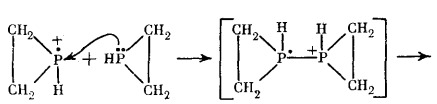
The chemical shifts in the ^{13}C NMR spectrum and the spin–spin coupling constants for 1-phenylphosphiran have been published[63]. The changes in these quantities with increase of the number of endocyclic C–C bonds and on ring opening are discussed in the same communication.

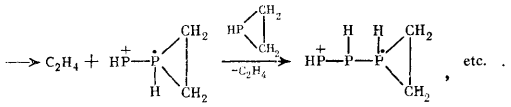
The results of mass-spectrometric studies of different types of phosphirans have been described: phosphirans with tricoordinate and tetracoordinate phosphorus, diphosphirans, element-substituted phosphirans, and others[15,29,64]. In all cases the spectra contain peaks due to molecular ions which are the most intense for monosubtituted phosphirans with tervalent phosphorus. The fragmentation of unsubstituted phosphiran and 1-deuterophosphiran is believed[15] to begin apparently with successive abstraction of the hydrogen atoms linked to the carbon atoms, while the P–H or P–D bonds remain unaffected. The introduction of methyl substituents into the molecule alters the preferred mode of fragmentation[15]. The mass spectra of all phosphirans with one phosphorus atom in the ring and of element-substituted phosphirans contain the peak of the fragment formed on rupture of both endocyclic phosphorus bonds. The fragmentation of 3,3-disubstituted 1,2-di-t-butyldiphosphirans takes place via the elimination of the t-butyl groups and their substitution by protons with subsequent formation of the $(M-C_4H_8)^+$ and $(M-2C_4H_8)^+$ ions[29].

The mass spectrum and the ion–molecule reactions of phosphiran and its mixtures with ammonia and deutero-, dideutero-, and trideutero-ammonia were also investigated by ionic cyclotron resonance spectrometry[64]. It was confirmed (see also Baudler and Saykowski[29]) that the most intense primary ions are the molecular ion M^+, the ions formed following the elimination of protons from the carbon atoms, $(M-2H)^+$ and $(M-3H)^+$, and also an ion with *m/e* 45 (PCH_2^+ or $HPCH^+$). There is no dominant secondary ion, as in the case of acyclic methylphosphines, and several ions in approximately equal proportions are formed. Another characteristic feature of phosphiran, found in the study of the influence of pressure (10^{-4}–10^{-6} mmHg) on the ionic ratios, proved to be a sharp decrease of the relative content of the molecular ions with increase of pressure (for methylphosphines, pressure has almost no influence on the content of the molecular ion).

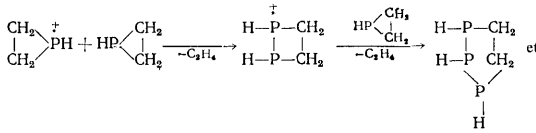
The ion–molecule reactions of phosphiran proceed mainly in three ways.

(a) The transfer of the P–H fragment from phosphiran to the molecular ion with evolution of ethylene and the formation of $R(PH)_n^+$ ions (where R = 1-phosphiranyl, $n = 1$–3), having an open phosphorus-containing chain or, which is more likely, having the structure of cyclic compounds with large rings formed as a result of the insertion of the P–H groups in the ring:

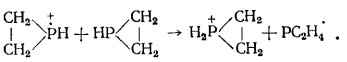




or

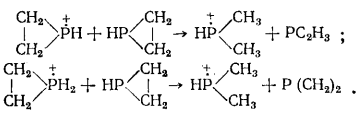


(b) The formation of protonated ions:

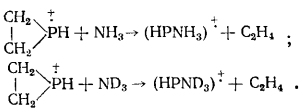


The determination of the rate constant for this reaction showed that phosphiran is protonated much more slowly than dimethylphosphine ($k = 0.54$ and 1.4×10^{-7} litre mole^{-1} s^{-1} respectively). The presence of the three-membered ring has a retarding influence on the rate of reaction (see Section IV).

(c) Ring decomposition:

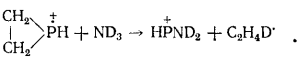


The reaction of ammonia and deuteroammonia with the molecular ion of phosphiran for an electron energy of 11 eV also entails the transfer of the P–H fragment and this process is not accompanied by deuterium exchange:



The reactions with NHD_2 and NH_2D take place analogously.

For an electron energy of approximately 15 eV and above, there is additiional abstraction of the proton or deuterium, for example:



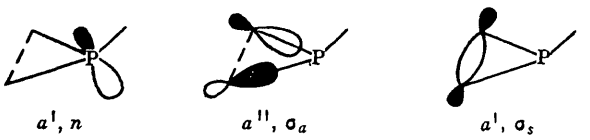
On the grounds that the molecular ion of phosphiran as well as the neutral molecule undergo PH transfer, it is concluded that the cyclic structure is retained in the molecular ion.

The interaction of phosphiran with the PH_3^+ radical-ion also proceeds as PH transfer with formation of the $P_2H_4^+$ radical-ion.

The relative stabilities of the cyclic onium ions $C_2H_4X^+$ have been investigated[65]. The study of the equilibrium $C_2H_4X^+ + HY \rightleftharpoons C_2H_4Y^+ + HX$ by the method of ionic cyclotron resonance made it possible to set up the series of increasing relative stabilities of ions for the following X: OH < Cl < Br < CH, $PH_2 < NH_2$.

The influence of angular strain in phosphiran on its electronic properties is of great interest to investigators. The study of the basicity and the ionisation potentials of phosphiran in relation to dimethylphosphine proved to be fruitful. The experimental photoelectron spectra of these compounds have been discussed[66] on the basis of *ab initio* quantum-chemical calculations. The removal of electrons from the highest occupied molecular orbitals with a′, a″, and a′ symmetries corresponds to the first three ionisation potentials of phosphiran and dimethylphosphiran. The orbital (*n*) with the highest energy is characterised by the dominant contribution of the unshared electron pair of the phosphorus atom

and the next two orbitals are characterised by the antisymmetric (σ_a) and symmetrical (σ_s) combinations of the *p* orbitals of the carbon atoms (Fig.1).



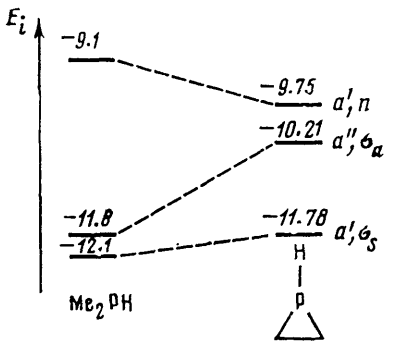


Figure 1. Correlation diagram for the orbital energies (in eV) of the three highest occupied molecular orbitals of dimethylphosphine and phosphiran[66].

The formation of the ring lowers the energy of the *n* molecular orbital by 15.4 kcal mol^{-1}. The stabilisation of this molecular orbital can be to a large extent accounted for by the enhanced *s* character of the unshared electron pair of the phosphorus atom in the three-membered ring. The repulsion of the electrons in the P–C σ-bonds increases with decrease of the C–P–C angle. The corresponding shift of electron density from P to C renders the phosphorus atom more positive, which also promotes the stabilisation of the *n* molecular orbital. The symmetrical combination of the πCH_2 orbitals of the two methylene groups is more strongly bonding than the symmetrical combination of the πCH_3 orbitals in dimethylphosphine. The hyperconjugation in phosphiran therefore destabilises the *n* molecular orbital to a lesser extent than in dimethylphosphine.

The lower-energy σ_a and σ_s orbitals are localised mainly at the carbon atoms. The shift of electron density from the P atom to C with decrease of the C–P–C angle, mentioned above, should destabilise both these orbitals. The mutual approach of carbon atoms enhances both the antibonding and the bonding interactions between them. As a result, the σ_a molecular orbital is most destabilised, while the energy level of the σ_s molecular orbital hardly changes.

The proton affinity of phosphiran is lower by 23.2 kcal mol^{-1} than that of dimethylphosphine[66]. The explanation is that, compared with the unstrained tetrahedral phosphorus atom in phosphonium salts, the angular strain in the protonated phosphiran is much greater than in its acyclic analogue. The enhanced *s* character of the unshared electron pair of the phosphorus atom in phosphiran and the shift of electron density in the P–C bonds from P to C also play an appreciable role.

Photoelectron spectroscopy combined with semiempirical quantum-chemical calculations has been used to investigate the electronic structures of three-membered heterocycles containing more than one phosphorus atom[67].

Investigators were naturally interested in the structural characteristics and physical properties of phosphiran relative to other known three-membered heterocycles which are derivatives of elements in Period II and III in Mendeleev's Table. This Table shows a steady decrease of the C–C bond length with increase of the atomic number of the element within the limits of each Period. This effect has been explained[68] by regarding the XC_2H_4 heterocycle as a donor–acceptor complex of ethylene C_2H_4 in the ground state and the fragment X in the valence state with the $(np_x)^2$ $(np_z)^0$ configuration of the endocyclic heteroatom ($n = 2$ or 3) (Fig.2).

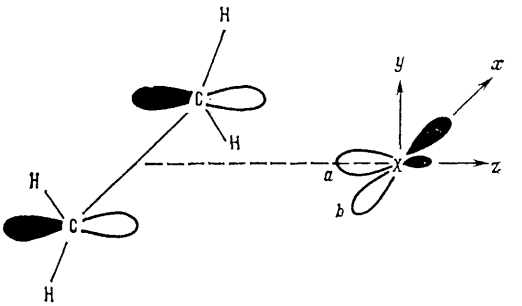


Figure 2. The heterocycle XC_2H_4 in the form of the $C_2H_4 + X$ donor–acceptor complex.

The C–C bond is weakened as a result of the transfer of electron density from the occupied *b* orbital of the fragment X (*yz* symmetry plane) to the vacant π* orbital of C_2H_4 and from the occupied π orbital of C_2H_4 to the vacant *a* orbital of X. The degree of such transfer is determined mainly by the energy levels of the *a* and *b* orbitals of X. Calculation of these levels by the *ab initio* SCF-MO method yielded a satisfactory explanation even for the non-uniformity of the shortening of the C–C bond within each Period.

Calculation of certain structural parameters of three-membered heterocycles, including phosphiran and the phosphiranium ion by the MNDO method without taking into account the *d* orbitals was used by Dewar and Ford[69] to set up the "π-complex character" series for these rings. The above authors expressed the view that, depending on the electronegativity and other properties of X, the compounds XC_2H_4 can constitute a continuous series, at one end of which there are the "classical" three-membered rings of the type of cyclopropane, while at the other there are π-complexes of the olefin–transition metal type. In the latter the intramolecular transfer of electron density from C_2H_4 to X greatly exceeds the reverse transfer. On the basis of the calculation of several criteria for the estimation of the "π-complex character" of the compounds XC_2H_4, series based on decreasing "π-complex character" of the heterocycles were established. Since compounds with X = PH and SiH_2 were found to be at the very end of this series, even beyond CH_2, phosphiran and siliran must be classified as the most typical "classical" three-membered rings in which electron transfer from X to C_2H_4 is the dominant feature.

It has been shown[53] that the C–C bond length in a three-membered heterocycle is determined mainly by the transfer of electron density from the *b* orbital of X to the π* orbital of ethylene. Increase of the electronegativity of X diminishes the effect of such transfer. As a result, the C–C bond is shortened and the angle β between the axis of this

bond and the normal to any of the CH_2 planes increases. The corresponding quantum-chemical calculations have shown that the overlap population of the C–C bond then increases and that of the X–C bond diminishes.

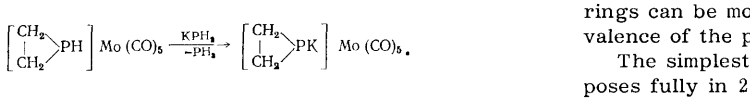
Several studies have been devoted to calculations on hypothetical molecules, which have not as yet been obtained, incorporating a three-membered phosphorus-containing ring, in particular cyclic spiro-compounds with a bridgehead phosphorus atom. A qualitative examination of the interaction of the *p* orbitals of the carbon atoms with the *d* orbitals of the phosphorus atom in symmetrical compounds with two mutually perpendicular rings[70] permits the conclusion that some of these systems are stable. Analogous systems have been considered quantitatively in a study[71] where the geometries and heats of formation of the individual spiro-compounds were calculated by the MINDO/3 method with minimisation of the total energy. The relative instability of these compounds is explained by the high energy level of the highest occupied molecular orbital and hence by their high reactivity towards electrophiles. Stabilisation can be achieved by the addition of electron-accepting groups to the central atom. The inclusion of the 3*d* orbitals of the phosphorus atom in the calculation greatly reduces the level of the highest occupied molecular orbital, thereby increasing the stability of the entire bicyclic system.

Thus the study of the structural characteristics and physical properties of compounds containing the phosphiran ring is being continued using all modern experimental and computational methods.

IV. CHEMICAL PROPERTIES

1. The Acidity of Phosphiran and Its Derivatives

Since direct measurements of the acidity of P-unsubstituted phosphirans have not been made, the conclusion that the mobility of the hydrogen atom linked to phosphorus is low can be reached only at a qualitative level on the basis of attempts to carry out exchange reactions. When phosphiran is treated with potassium in liquid ammonia or with ethyl-lithium in ether, hydrogen is not evolved. Nor does the exchange reaction occur with potassium phosphide in dimethyl ether. Such exchange does take place, however, in a complex of phosphiran with molybdenum carbonyl, i.e. pentacarbonylphosphiranmolybdenum(0), approximately 80% of the calculated amount of phosphine being evolved[72]:



^{1}H NMR data have shown that in methanol there is no rapid exchange of the hydrogen atom attached to phosphorus for the methanol protons[14]. Thus in this respect phosphiran does not differ from acyclic secondary phosphines[73].

2. The Basicity of Phosphiran and Its Derivatives

The few available literature data show that the phosphorus atom in the three-membered ring is much less basic than in acyclic phosphine and than the nitrogen atom in a similar ring. For example, the calculated potential energies of atomic interactions[57] have shown that the density of the free electron pair of the phosphorus atom in phosphiran is delocalised over the carbon atoms of the ring to a much greater extent than the electron density of nitrogen in aziridine. Only 62.3% of the free electron pair density is localised at the phosphorus atom, in contrast to the 76.3% at the nitrogen atom of aziridine.

This type of delocalisation is even more pronounced in 1-methylphosphiran, where only 57.1% of the free electron pair density remains at the phosphorus atom and Petersen and Brisotti[57] suggested that this compound should be the weakest base among the compounds which they examined (apart from those indicated, they also investigated 1-methyl- and 1-chloro-aziridines), provided that the basicity is correlated with the localisation of electron density at the heteroatom.

Comparison of the properties of the heteroatom in phosphiran and other three-membered rings containing elements in the Second and Third Periods (C, N, O, S, and Si) on the basis of quantum-chemical calculations by the CNDO method[53] showed that, with increase of the atomic number of the element, there is a systematic increase of the negative charge on the heteroatom in each Period and its decrease in each Group of the Periodic System. Thus the charge on the phosphorus atom of phosphiran is much less negative than on the nitrogen atom of aziridine (+0.109 and −0.167 respectively) and on the sulphur atom in thi-iran (−0.103), but is less positive than on the silicon atom in siliran (+0.316).

The decrease of the basicity of the heteroatom on passing from acyclic compounds to three-membered heterocycles is a general property, as shown by studies of the basicity of rings with N, O, S, and P heteroatoms and also of dimethyl-substituted acyclic compounds of these elements (Me_2NH, Me_2O, Me_2S, and Me_2PH) by ion cyclotron resonance[66]. The decrease of proton affinity is explained by the increase of the amount of s character of the orbtials of the free electron pair of the heteroatom and by the redistribution of electron density in the C–X bond as well as the increase of the angular strain on protonation, since this should entail a transition from a pyramidal to a tetrahedral angle. The influence of angular strain is the dominant factor in phosphiran, which has the smallest C–X–C angle. On passing from dimethylphosphine to phosphiran, a particularly sharp decrease of basicity is observed (the difference between proton affinities is in this instance 23.2 kcal mol^{-1}, while for the N, O, and S analogues it is only 3–5 kcal mol^{-1}).

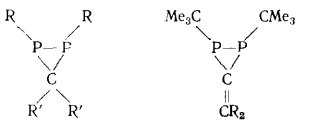
3. The Opening of the Three-membered Ring

(a) *Thermolysis of the phosphiran ring.* The high ring strain, which is a characteristic property of rings with three and four members, is also manifested in phosphirans, whose rings can be more or less readily opened depending on the valence of the phosphorus and the nature of the substituents.

The simplest phosphiran is thermally unstable and decomposes fully in 24 h even at room temperature on storage without a solvent, giving rise to ethylphosphine (15%), ethylene (6%), and an involatile viscous liquid. The decomposition in methanol at room temperature is slow[14].

The diphosphirans with tervalent phosphorus known at the present time showed a tendency towards dimerisation with formation of 1,2,4,5-tetraphosphacyclohexanes. The thermal stability of diphosphirans of this type depends on the bulk of the substituents and increases appreciably even on substitution of the hydrogen atoms at a ring carbon atom by methyl groups. Thus the conclusion that the heterocycle (XII, R = Ph, R′ = H) is formed also on interaction of 1,2-diphenyl-1,2-bis(trimethylsilyl)diphosphine with di-iodomethane at −30 °C was based solely on the appearance of a weak signal in the ^{31}P NMR spectrum of the reaction mixture with a chemical shift characteristic of the phosphorus atom in a three-membered ring, whereas compound (XII, R = Ph,

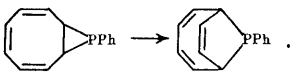
R′ = Me) can be obtained at −30 °C in a yield of approximately 10% and is stable in benzene at this temperature for several days[28]. The still more stable diphosphirans (XII, R = t-Bu) can be vacuum-distilled at approximately 30 °C without decomposition. However, whereas the diphosphiran (XIIa) dimerises at room temperature in a pure form in several hours (more slowly in solution and at −78 °C the dimerisation ceases [29,30]), compound (XII, R = t-Bu, R′ = Me) can be maintained at room temperature in an inert gas atmosphere for months and can be briefly heated to as much as 200 °C without visible decomposition; in air the last two compounds both rapidly oxidise without igniting[29]. On the other hand, the diphosphiran (XII, R = iso-Pr, R′ = H) cannot be obtained at all—the six-membered dimer is formed immediately[30]:



(XII) (XIII)

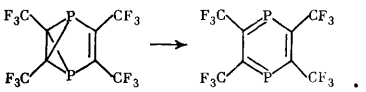
An analogous behaviour has been observed also for diphosphirans (XIII) with an exocyclic C = C bond. The methylenediphosphiran (XIII, R = H) begins to decompose in the reaction mixture already at −50 °C, so that it was possible to obtain it only with a purity of 70%, whereas its analogues with methyl or *p*-chlorophenyl groups are comparatively stable and have been isolated in a pure form by high-vacuum distillation or fractional cyrstallisation[11].

The bicyclic phosphiran with condensed rings 9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene can be stored in an inert atmosphere with cooling over a period of one year almost without changes, but, on raising the temperature the three-membered ring expands with formation of 9-phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene (XXXVIII), which has been isolated in a high yield[19,20]:



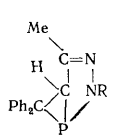
(I) (XXXVIII)

When the phosphorus analogue of benzvalene, which is stable at room temperature, is heated or illuminated with light from a low-pressure mercury lamp (λ = 2537 Å), it is reconverted into a 1,4-diphosphabenzene derivative (X) by a sigmatropic rearrangement (in hexafluorobenzene at −198 °C the half-life of the reaction is approximately 75 min[25,27]):



(XI) (X)

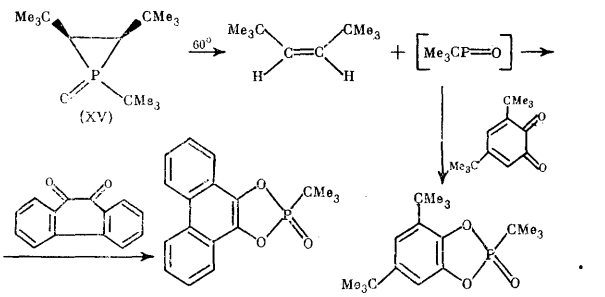
Despite the presence of tervalent phosphorus in the three-membered ring, derivatives of 1-phospha-2,3-diazabicyclo-[3.1.0]hex-3-ene exhibit an appreciable thermal stability, melting without decomposition at 135° and 145 °C [for R = Ph and MeCO respectively][21].



(III)
R=Ph, MeCO

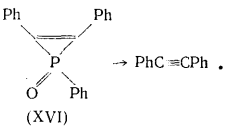
In the search for a quantitative approach to the problem of the comparative stabilities of the three-membered rings XC_2H_4 (X = CH_2, O, NH, PH, PH_3, or S), a group of Romanian investigators[31] calculated the enthalpies of decyclisation of the above compounds in several ways by an additive scheme using the tabulated bond energies and found that the ring with X = PH_3 has the highest positive enthalpy of decyclisation, i.e. derivatives of phosphiran with a pentavalent phosphorus atom, which had not yet been obtained at the time of the publication of the above study, should be resistant to thermal ring opening. Experimental data have shown that the stability of the ring depends on the structural features of each specific compound.

For example, *cis*-1,2,3-tri-t-butylphosphiran oxide (XV) is stable at room temperature but decomposes on heating in perdeuterobenzene at 60 °C, giving a quantitative yield of *cis*-2,2,5,5,-tetramethylhex-3-ene, i.e. the thermolysis is stereospecific. The second decomposition product, the unstable t-butylphosphinidene oxide with a dicoordinate phosphorus atom, cannot be detected when the thermolysis of the oxide (XV) is carried out in the presence of 1,2-bis-(trimethylsilyl)acetylene, 2,3-dimethylbutadiene, diacetyl, benzil, or *N*-(2,2-dimethylpropylidene)-t-butylamine, but 2-t-butylphenanthro[9,10-*d*]-1,3,2-dioxaphosphole oxide was obtained in 50% yield in the presence of 9,10-phenanthrenequinone, while 2,4,6-tri-t-butylbenzo-1,3,2-dioxaphosphole oxide is formed in a quantitative yield in the presence of 3,5-di-t-butyl-*o*-benzoquinone, which confirms the formation of a species with a dicoordinate phosphorus atom[32]:



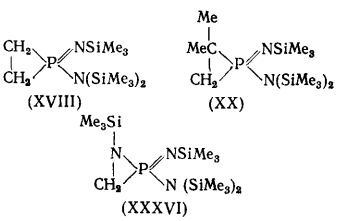
(XV)

1-Oxo-1,2,3-triphenylphosphiren (XVI) is cleaved analogously at 120 °C *in vacuo* (10^{-5}–10^{-6} mmHg), forming diphenylacetylene[35]:



(XVI)

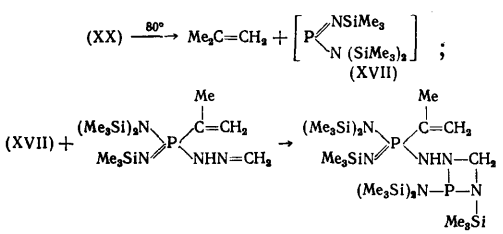
The positive influence of the steric shielding of the molecule on the thermal stability of the ring can be clearly traced in phosphirans with an exocyclic phosphazo-group and bulky substituents. Thus 1-[bis(trimethylsilyl)amino]-1-trimethylsilyliminophosphiran (XVIII), unsubstituted in the 2- and 3-positions, decomposes fairly rapidly at room temperature[38], while its analogue (XX) with two methyl groups in the 2-position[40] and the azaphosphiridine (XXXVI) with a bulky trimethylsilyl group at the ring nitrogen atom[38] are stable at room temperature:



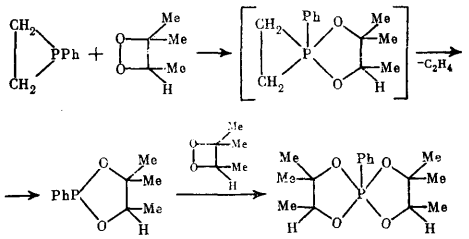
(XVIII) (XX)

(XXXVI)

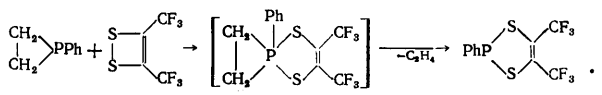
On heating to 80 °C, the phosphiran (XX) decomposes to 2-methylprop-1-ene, which has been characterised by infrared spectroscopic data, and the aminoiminophosphine (XVII), which undergoes further reactions as a result of the addition to the second product formed on synthesis of compound (XX):



In cyclic spirophosphoranes with a pentacoordinate phosphorus atom a three-membered phosphorus-containing ring has a low thermal stability. For example, in the reaction of 1-phenylphosphiran with 2,3,3-trimethyldioxetan, a cyclic spirophosphorane can be detected at −80 °C by ^{31}P NMR. At the above temperature the spectrum of the reaction mixture remains unchanged in the course of two weeks, but, on raising the temperature, ethylene is evolved and the signal assigned to the resonance of the phosphorus nucleus of the phosphorane with the three-membered phosphorus-containing ring disappears[43]:



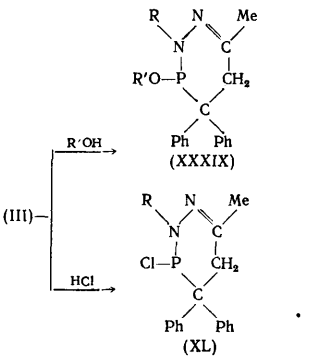
When 1-phenylphosphiran was treated with 3,4-bis(trifluoromethyl)dithieten at −78 °C, only ethylene and 2-phenyl-4,5-bis(trifluoromethyl)-1,3,2,-dithiaphospholen were obtained, i.e. the intermediate cyclic spirophosphorane decomposes even at this low temperature[18,74]:



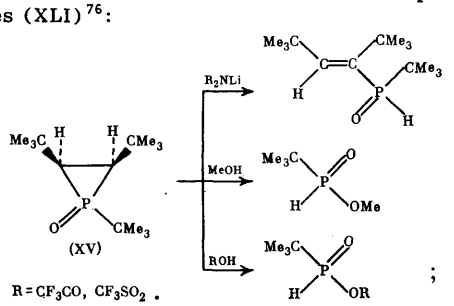
The decomposition proceeds via a concerted and not a two-stage mechanism, since the reaction involving *cis*-2,3-dideutero-1-phenylphosphiran yields, 1,2-dideuteroethylene containing mainly the *cis*-isomer (95 : 5).[18]

(b) *Ring opening on treatment with chemical reagents.* The phosphiran ring of the unsubstituted compound is rapidly decomposed by acidic and basic agents. Even at reduced temperatures, phosphiran is rapidly decomposed by hydrogen chloride, giving rise to 90% of ethylene, 20% of phosphine, 5% of ethylphosphine, and a yellow solid which is mainly a polymeric phosphine[14]. On interaction with sulphur dioxide at 0 °C, ethylene and a polymeric product are also formed[75]. The interaction of phosphiran with potassium in liquid ammonia gives rise, as a result of ring cleavage, to a mixture of the anions of a series of phosphines. Rupture of the phosphiran ring also occurs on treatment with methyl-lithium in ether[72].

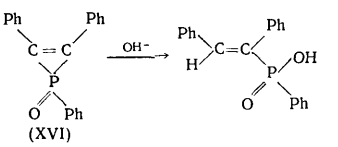
On heating with alcohols or on treatment with hydrogen chloride, the three-membered ring is also cleaved in derivatives of 1-phospha-2,3-diazabicyclo[3.1.0]hex-3-ene and the monocylic compounds (XXXIX) and (XL) are formed[22]. Under these conditions the P–C bond ruptured is that whose approach by the reagent apparently involves the smallest steric hindrance:



On the other hand, *cis*-1,2,3-tri-t-butylphosphiran oxide is very stable at room temperature in concentrated hydrochloric acid, trifluoroacetic acid, and trifluoromethanesulphonic acid and also in concentrated aqueous alkali, being decomposed only slowly by lithium diethylamide or piperidide with formation of t-butyl(1,2,-di-t-butylvinyl)phosphine oxide[34]. In boiling methanol the oxide (XV) is converted in 20 h into the monomethyl ester of t-butylphosphonous acid[33], while its thermolysis in trifluoroacetic or trifluoromethanesulphonic acid results in conversion into the corresponding anhydrides (XLI)[76]:



Hydrolysis of 1,2,3-triphenylphosphiren oxide by an aqueous solution of sodium hydroxide to phenyl(1,2-diphenylvinyl)phosphinic acid confirms the structure of this phosphiren derivative[35]:



2-Cyano-1,1-diethylphosphiranium chloride is converted on hydrolysis into a mixture of 2-cyanoethyl(diethyl)phosphine and diethylphosphinic acid, which is difficult to separate[41].

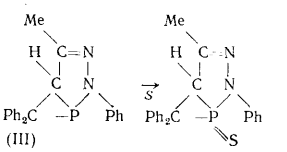
4. Reactions Occurring with Retention of the Phosphiran Ring

When phosphiran reacts with the *N*-methylpyridinium salt of pentacarbonylmolybdenum iodide, a molybdenum complex is formed in which phosphiran is one of the ligands, namely pentacarbonylphosphiranmolybdenum(0):



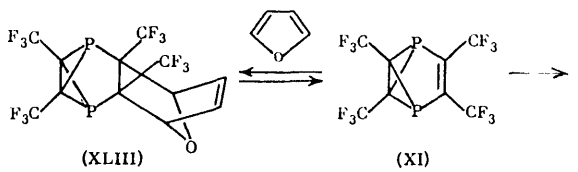
Phosphiran can displace also other ligands from molybdenum complexes: for example, pentacarbonylnorbornadienemolybdenum(0) and tricarbonylcyclohexatrienemolybdenum(0) give rise respectively to tetracarbonylbis(phosphiran)molybdenum(0) and tricarbonyltris(phosphiran)molybdenum(0). The complexes have been characterised by ^{1}H and ^{31}P NMR data[72]

The addition of sulphur to a derivative of 1-phospha-2,3-diazabicyclo[3.1.0]hex-3-ene also takes place with retention of the three-membered ring and has given rise to the first representative of a phosphiran with a P–S bond[22]:

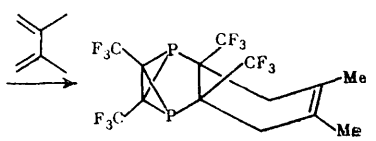


(III)

The phosphorus analogue of benzvalene (XI) is capable of entering into the Diels–Alder reaction as the dienophile, forming, for example, with 2,3-dimethylbutadiene, the adduct (XLII), to which the *exo*-configuration has been attributed by analogy with the adduct obtained from benzvalene. Reaction with furan results in the formation of an equilibrium mixture of the initial compound (XI) and the adduct (XLIII):



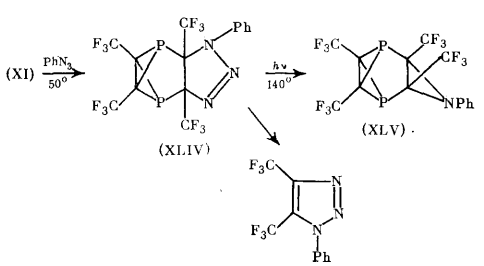
(XLIII) (XI)



(XLII)

When the adduct is dissolved in n-pentane, a solution is obtained whose ^{19}F NMR spectrum reveals the presence of compound (XI), equilibrium being established extremely rapidly at 70 °C.

Phenyl azide also adds to the double bond of the tricyclic compound (XI), giving the adduct (XLIV) with an additional triazoline ring, which evolves nitrogen on photolysis or heating at 140 °C and is converted into diphosphabenzvalenoaziridine (XLV); it has been shown by ^{19}F NMR that the initial compound (XI) is then obtained together with compound (XLV). Chromatography on silica gel entails the decomposition of this adduct (XLIV) with formation of 1-phenyl-4,5-bis(trifluoromethyl)triazole[27]:



---oOo---

The chemistry of heterocyclic phosphorus compounds is now passing through a period of vigorous development. The present review has dealt with the results of studies on three-membered organophosphorus heterocycles. It is of interest to examine the synthesis and properties of four-membered phosphorus-containing heterocycles.

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