Translated from *Uspekhi Khimii*, 53, 1675-1708 (1984) U.D.C. 547.241

The Reactivity of Organosilicon Derivatives of Phosphorus in Addition Reactions

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The results of studies of the reactivity of organosilicon derivatives of tricoordinate and tetracoordinate phosphorus containing the P-X-Si (X = O, N, or S) groups in reactions involving addition to various unsaturated systems are examined and surveyed. Attention has been concentrated on the elucidation of the specific influence of the trialkylsilyl group on the character of the reaction of phosphorus-silicon compounds.
The bibliography includes 137 references.

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I. INTRODUCTION

During the last one and a half decades, organosilicon derivatives of phosphorus have been vigorously investigated in many world laboratories. The interest in these compounds is caused primarily by the possibility of synthesising on their basis a wide range of new organoelemental structures, many of which have important practical applications. The combination of phosphorus and silicon atoms in a single molecular system has its specific manifestation in the character of the chemical behaviour of phosphorus–silicon reagents, which differs from that of the corresponding organophosphorus or organosilicon analogues. The determination of the interrelation between the structure and chemical reactivity of such two-element compounds and the elucidation of the specific role of the phosphorus- and silicon-containing fragments in the molecule are of undoubted theoretical interest for organoelemental chemistry.

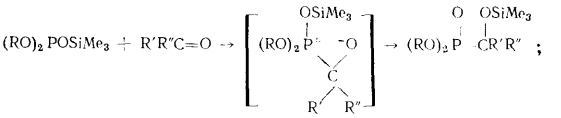
In the literature there are almost no reviews devoted to the reactivity of phosphorus–silicon compounds. Data concerning the synthesis of organosilicon derivatives of phosphorus and certain reactions of silyl phosphites, which may be used for the synthesis of phosphorus compounds, are summarised in the monograph of Voronkov and co-workers[1] and in publications of Japanese investigators.[2]

The present review deals with the reactivity of organosilicon derivatives of tervalent and quinquevalent phosphorus containing the P–X–Si group (X = O, N, or S) in addition reactions. Wherever possible, the reactivities of silylated phosphorus systems and phosphorus compounds of analogous structures without organosilicon groups have been compared in order to discover the factors which control the processes under discussion.

II. ORGANOSILICON DERIVATIVES OF TERVALENT PHOSPHORUS

1. Reactions with Aldehydes and Ketones

The silyl esters of tervalent phosphorus acids readily add to the carbonyl groups of aldehydes and ketones with formation of α-trialkylsiloxyalkylphosphonates:[3–10]

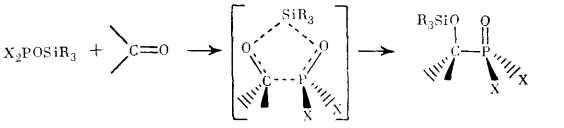


(I)

R′=Alk, Ar; R″=H, Alk, Ar .

It has been suggested[6,9–11] that the reaction begins with nucleophilic attack by the phosphorus atom on the carbonyl carbon atom with formation of an intermediate dipolar ion (I). This mechanism is supported by the fact that the more nucleophilic trimethylsilyl dibutylphosphinite adds to acetaldehyde more readily than trimethylsilyl diethyl phosphite and the interaction of the same phosphinite with trifluoroacetone proceeds much faster than with acetone.[9]

At the same time, in contrast to trialkyl phosphites,[12] for phosphorus–silicon reagents one cannot rule out the possibility of a concerted 1,2-addition mechanism,[10] because the trialkylsilyl group can migrate as a result of frontal substitution at the silicon atom with retention of its configuration:[13,14]



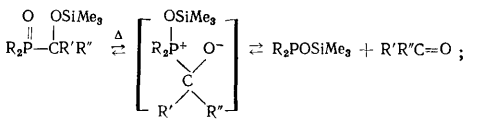
The results of a "cross-experiment" with participation of equimolar amounts of diethyl trimethylsilyl phosphite, t-butyldimethylsilyl dimethyl phosphite, and two equivalents of benzaldehyde confirm the intramolecular character of the migration of the silicon atom:[10]

$$(EtO)_2POSiMe_3 + (MeO)_2POSiMe_2Bu\text{-}t + 2PhCHO \rightarrow$$
$$\rightarrow PhCH(OSiMe_3)P(O)(OEt)_2 + PhCH(OSiMe_2Bu\text{-}t)P(O)(OMe)_2 .$$

With increasing steric hindrance at the silicon atom, the rate of addition diminishes under these conditions. The insertion of trialkyl phosphites in the carbonyl group takes place as a result of intermolecular alkyl transfer.[12]

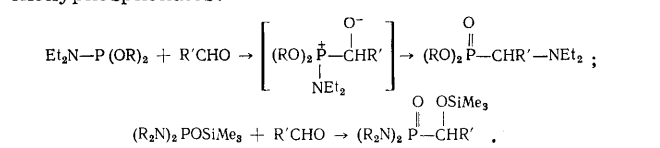
The adducts obtained by the interaction of silyl phosphites with aromatic aldehydes and ketones are thermally unstable and decompose on heating into the initial compounds.[15] The decomposition of α-trimethylsiloxyphosphonates via a pathway which is the reverse of the

Arbuzov reaction is accelerated with increasing nucleophilicity of the phosphoryl oxygen and with enhancement of the polarisation of the Si–O bond as a result of the electron-accepting influence of the substituents at the α-carbon atom:

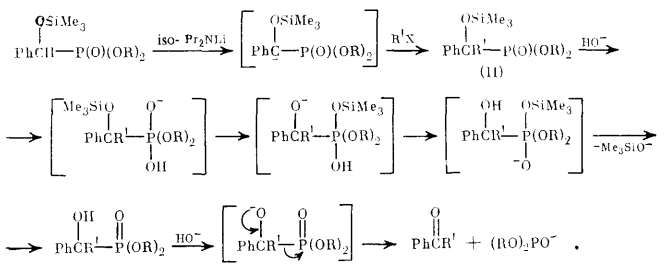


R=Bu, MeO, EtO; R′=H, Me; R″=Ph, COOEt, P(O)(OMe)$_2$.

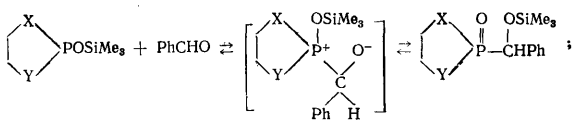
In contrast to dialkyl phosphoramidites, which react with aldehydes to form α-aminophosphonates,[16] trimethylsilyl *N,N,N′,N′*-tetra-alkylphosphorodiamidites give α-trimethylsiloxyphosphonates:[11,17,18]



The adducts of silyl phosphites with aldehydes have been recently used widely in the synthesis of asymmetric ketones.[19–21] The ready dissociation of the P–C bond in compound (II), obtained by alkylating the comparatively acidic α-hydrogen atom in α-trimethylsiloxybenzylphosphonate, is promoted by the sigmatropic migrations of the Me_3Si group in the course of the nucleophilic attack by the hydroxide anion on the phosphorus atom:



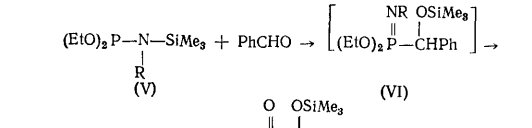
The P–N bond is cleaved and 1,4,2-oxazaphosphorinanes are formed on interaction of 2-alkoxy(alkyl)-1,3,2-oxazaphospholans with carbonyl compounds.[22] In contrast to this, the cyclic fragments are retained in the reactions of 2-siloxy-derivatives of 1,3,2-diheterophospholans with benzaldehyde. The reaction is reversible and on heating α-trimethylsiloxyphosphonate decomposes into the starting materials:[23]



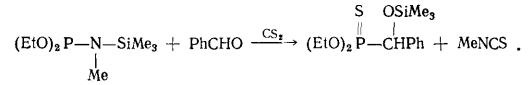
(a, X=Y=O; (b) X=NMe, Y=O; (c) X=NPh, Y=O; (d) X=Y=NBu .

Two versions of the relative orientations of the benzaldehyde and oxazaphospholan molecules in the intermediates (III, b and c) determine the formation of diastereoisomeric cyclic α-trimethylsiloxybenzylphosphonates (IV).

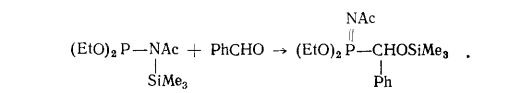
The interaction of phosphorous acid *N*-trimethylsilylamides (V) with benzaldehyde proceeds differently.[24,25] The phosphonimidate (VI), formed as a result of the nucleophilic addition of the phosphoramidite to the carbonyl group, reacts vigorously with a second benzaldehyde molecule, which leads to α-trimethylsiloxybenzylphosphonate and benzylideneamine:



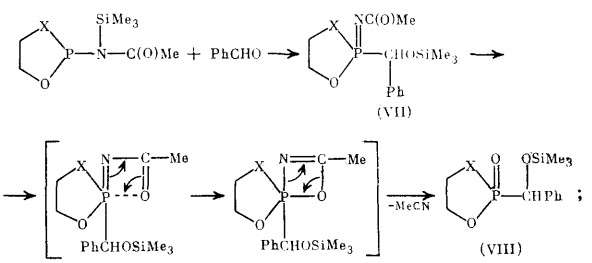
In the presence of carbon disulphide the intermediate phosphonimidate (VI) is converted into a phosphonothioate:[24]



The introduction of the electron-accepting acetyl group at the nitrogen atom of *N*-silylphosphoramidite stops the reaction at the stage of the formation of the phosphonimidate:[23]



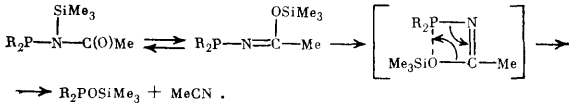
In the case of 2-(*N*-trimethylsilylacetamido)-1,3,2-diheterophospholans the reaction with benzaldehyde leads to the formation of the cyclic α-trimethylsiloxybenzylphosphonate:[23]



X=O, NMe .

The process involves the initial formation of *N*-acetylphosphonimidates (VII), which are converted into the phosphonates (VIII) by nucleophilic attack by the carbonyl oxygen at phosphorus. The ease of the intramolecular rearrangement depends significantly on the nature of the substituents at the phosphorus atom. In the series of 1,3,2-diheterophospholans the replacement of oxygen in the ring by the more electron-donating nitrogen reduces the electrophilicity of the phosphimide phosphorus and thereby stabilises the phosphonimidate structure (VII) (X = NMe). The interaction of 3-methyl-2-(*N*-trimethylsilylacetamido)-1,3,2-oxazaphospholan with benzaldehyde leads to the phosphonimidate (VII), which is stable under the usual conditions and is converted on heating to 65 °C into the phosphonate (VIII). In the series of dioxaphospholan derivatives (X = O) the phosphonimidate cannot be detected even at a low temperature.[23] A similar rearrangement of diethyl α-trimethylsiloxybenzylacetylphosphonimidate has been achieved only at 135 °C.

Acetyl and trimethylsilyl substitution at the nitrogen atom reduces significantly the thermal stability of the phosphoramidite. The migration of the Me_3Si group in *N*-acetyl-*N*-trimethylsilylphosphoramidite to the carbonyl oxygen promotes intramolecular nucleophilic substitution at the phosphorus atom and the formation of silyl phosphites and acetonitrile:[26,27]



The decomposition of *N*-silylated acetamido-derivatives of tervalent phosphorus depends on the nature of the substituents R at the electrophilic centre and, according to the results of the differential thermal analysis, is retarded with increase of their electron-donating capacity[27] (Table 1).

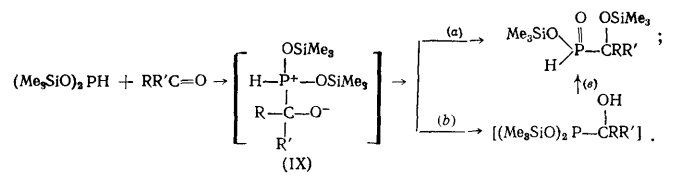
Table 1. The effect of substituents at the phosphorus atom on the rate of decomposition of the compounds $R_2P-N-SiMe_3$.[27]

	AC	
R_2	T_i, °C	T_m, °C
$-OCH_2CH_2O-$	35	88
$-OCH_2CH_2CH_2O-$	52	128
$-OCH_2CH_2N(Ph)-$	65	108
$-OCH_2CH_2N(Me)-$	70	130
$(EtO)_2$	95	135
Et_2*		

Notation: T_i is the temperature of the onset of the effect and T_m is the temperature of the maximum effects.

*Stable up to 200 °C.

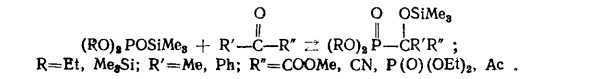
The addition of bis(trimethylsilyl) hypophosphite to aldehydes and ketones leads to bis(trimethylsilyl) alkylphosphonites with the retention of the P–H bond.[28,29] The dipolar ion (IX) formed initially can be stabilised by the migration of the Me_3Si group, which leads to the final reaction product [pathway (*a*)]; there is also a possibility of the intramolecular proton transfer [pathway (*b*)] and subsequent rearrangement of the intermediate bis(trimethylsilyl) α-hydroxyalkylphosphonite via pathway *c*:[29]



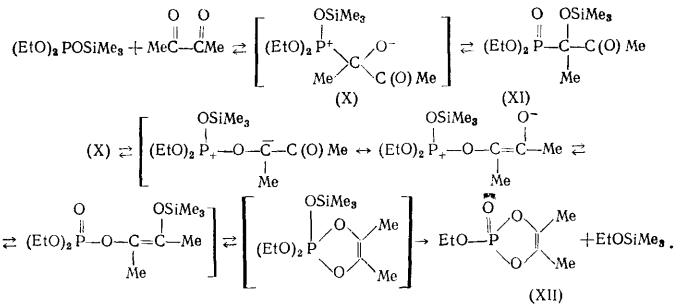
2. The Interaction with Carbonyl Compounds Containing Electron-Accepting Substituents

The introduction of electron-accepting substituents at the carbonyl group not only increases the reactivity of the carbonyl compounds in reactions with organosilicon derivatives of tervalent phosphorus but also in many cases influences significantly the mode of their interaction.

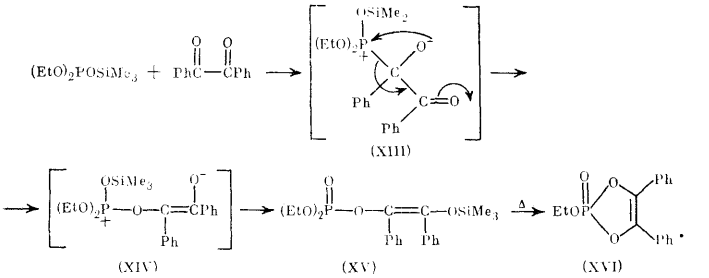
Silyl phosphites add vigorously to the esters and nitrile of pyruvic acids,[30] acetyl phosphonates,[31] benzoyl phosphonates,[32] and diacetyl[33–35] with formation of the corresponding α-trimethylsiloxyphosphonates:



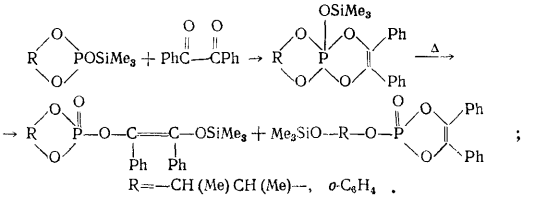
These reactions are as a rule reversible. However, after prolonged heating of the adducts, other processes can also occur. Thus, dioxaphospholen (XII) and ethoxysilane (XXXV) are formed from diethyl trimethylsilyl phosphite and diacetyl as a result of silotropic transformations and the phosphonate–phosphate rearrangement:[35]



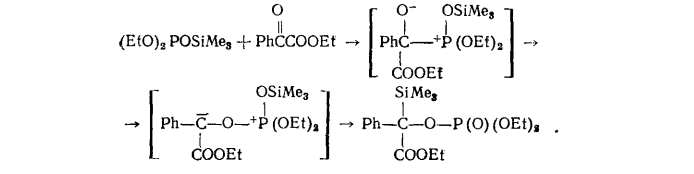
The dipolar intermediate can be stabilised by the intramolecular transfer of the trimethylsilyl or phosphoryl group. The ratio of the rates of these competing processes depends on the structure of the carbonyl reagent. For the diacetate, the α-siloxyphosphonate (XI) is the kinetically controlled product. In the reactions of silyl phosphites with benzil the phosphonate–phosphate rearrangement (XIII) → (XIV) is faster than the migration of the silyl group and the only product of the interaction is 2-trimethylsiloxy-1,2-diphenylvinyl phosphate (XV), which is converted into the dioxaphospholen (XVI) on heating:[34,36]



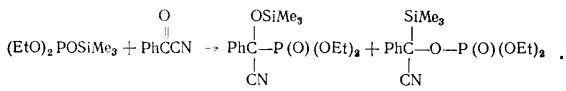
The formation of spiro-phosphorane structures, which is characteristic of the interaction of 1,3,2-diheterophospholans with dicarbonyl compounds,[37,38] is also observed in the reaction of 2-trimethylsiloxy-1,3,2-dioxaphospholans with benzil.[39] Silylated spiro-phosphoranes are formed at a low temperature (between −40 °C and −50 °C) and on heating are fully transformed into the corresponding cyclic phosphates:



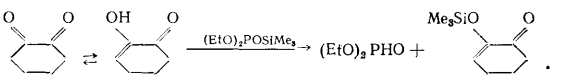
A product with a phosphate structure has also been isolated in the reaction of silyl phosphites with benzoylformic acid ester:[30]



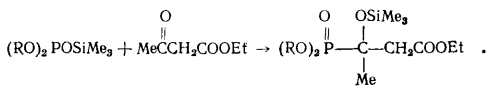
Both pathways leading to stabilisation, namely the migration of the Me_3Si group and the phosphonate–phosphate rearrangement, are realised in the reaction with the nitrile of benzoylformic acid:[30]



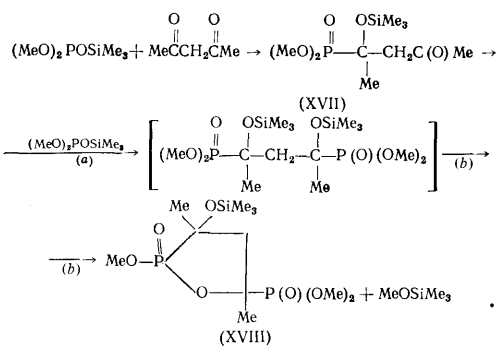
The attempt to obtain the products of the addition of diethyl trimethylsilyl phosphite to cyclohexane-1,2-dione was unsuccessful. The reaction results in the quantitative formation of diethylphosphorous acid and 2-trimethylsiloxycyclohexenone, i.e. the diketone reacts in the enolic form:[40]



The involvement of the enolic form also in the reaction of silyl phosphites with acetoacetic ester might have been expected, but in this case the product of addition to the C=O group is formed exclusively:[5,41]

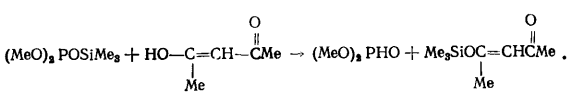


The reaction of acetylacetone resulted in the isolation of 5-dialkylphosphoryl-1,2-oxaphospholan (XVIII) together with α-siloxyphosphonate (XVII):[41]

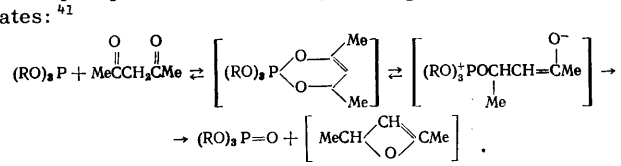


The preferential formation of only one diastereoisomer of 1,2-oxaphospholan (XVIII) has been explained[41] by the stereospecificity of the attack by silyl phosphite on the carbonyl group of the 1:1 adduct [stage (*a*)] and also by the stereospecificity of the cyclisation reaction (*b*), because there are three bulky groups at the interacting atoms in the transition state: two dialkylphosphoryl groups and one trimethylsilyl group.

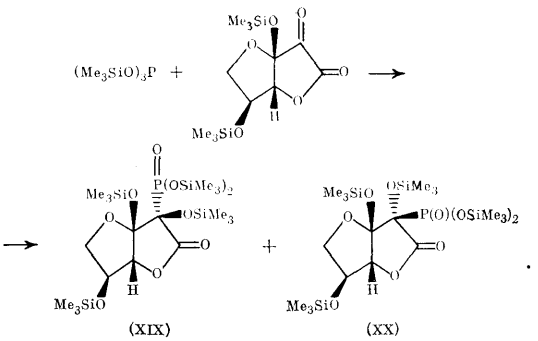
Another reaction pathway, namely the silylation of the enol of acetylacetone, has also been noted:



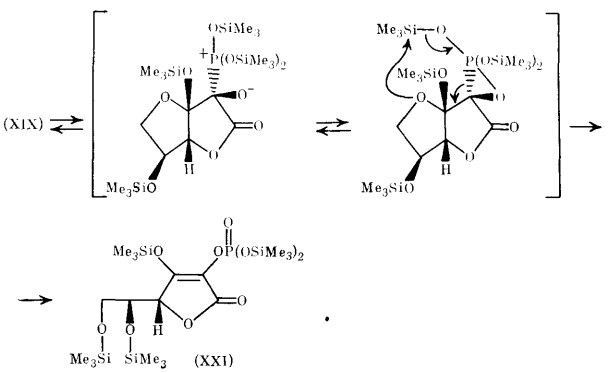
In contrast to silyl phosphites, trialkyl phosphites react with acetylacetone and acetoacetic ester via the intermediate phosphorane structures, forming trialkyl phosphates:[41]



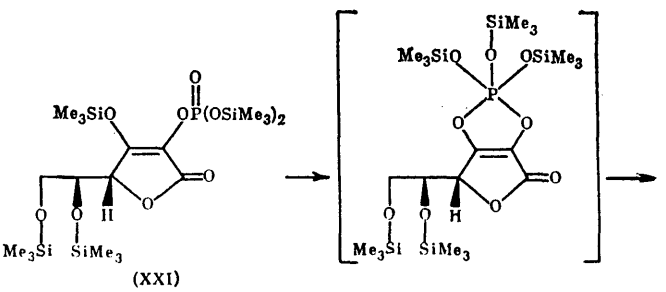
The conformational characteristics of bicyclic α-ketolactones are responsible for the possibility of the formation of the diastereoisomeric phosphorates (XIX) and (XX) as a result of the nucleophilic attack by silyl phosphite on the carbonyl carbon atom from different sides of the plane of the lactone ring:[42]

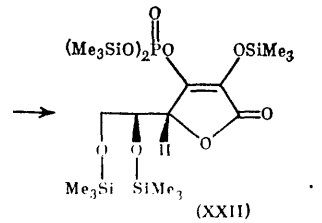


The adducts (XIX) and (XX) isomerise to the 2-*O*-phosphate (XXI) on heating. The diastereoisomer (XIX), which is a product of the attack by silyl phosphite on the carbonyl group from the rear of the plane of the ring, then undergoes a thermal rearrangement at a higher rate than the isomer (XX), which is caused by favourable conditions for the formation of a six-membered cyclic transition state:



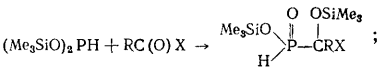
The transformation of the phosphonate (XX) into the 2-*O*-phosphate (XXI) evidently includes the decomposition of compound (XX) into the initial compounds and subsequent formation of the diastereoisomer (XIX), whose pyrolysis leads to the phosphate (XXI). The 2-*O*-phosphate (XXI) also isomerises to the 3-*O*-phosphate (XXII) via the intramolecular migration of the phosphoryl group during the thermal rearrangement:





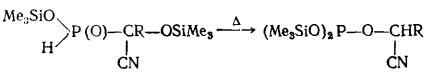
(XXII)

Bis(trimethylsilyl) hypophosphites add to the carbonyl group in ketophosphonates, ketonitriles, and acetoacetic ester with retention of the P–H bond: [29]

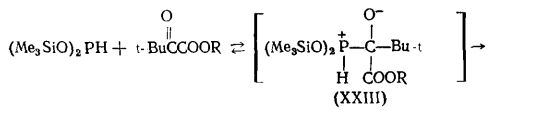


R=Me, t-Bu; X=P(O)(OEt)$_2$, CN, CH_2COOMe .

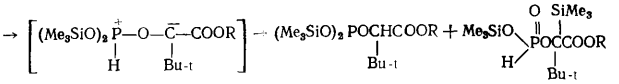
The products formed in this process are thermally unstable and decompose into a series of compounds on heating. α-Cyanoalkyl bis(trimethylsilyl) phosphites are formed from trimethylsilyl α-cyano-α-trimethylsiloxyalkylphosphonites: [29]



Increasing steric hindrance of the carbonyl carbon atom in trimethylpyruvic acid esters, combined with the electron-accepting influence of the alkoxycarbonyl group, promotes the rearrangement of the intermediate dipolar ion (XXIII) with a P–C bond to the ion (XXIV) with a P–O–C bond. The intermediate is then stabilised via the migration of a proton or Me_3Si group to the carbanionic centre: [29]

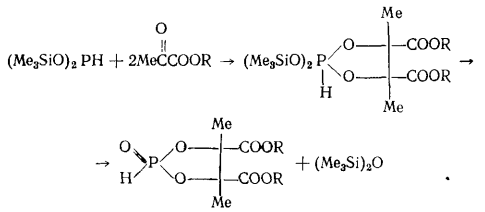


(XXIII)



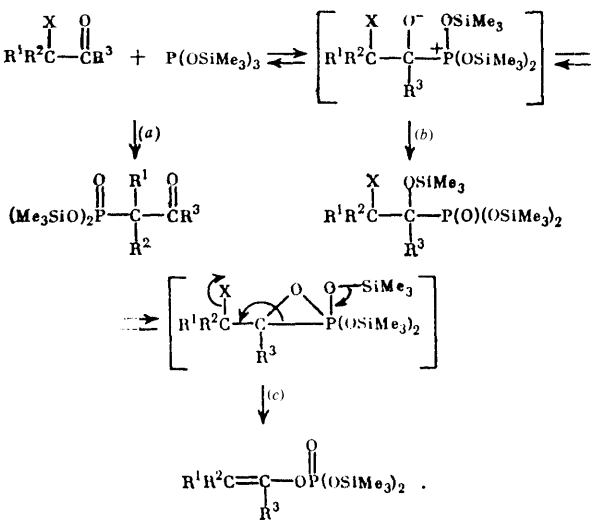
(XXIV)

The interaction of silyl hypophosphite with pyruvic acid esters leads to 4,5-dialkoxycarbonyl-2-hydro-4,5-dimethyl-2,2-bis(trimethylsiloxy)-1,3,2-dioxaphospholans with a pentacoordinate phosphorus atom, which are slowly converted into 4,5-dialkoxycarbonyl-2-hydro-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholans: [29]



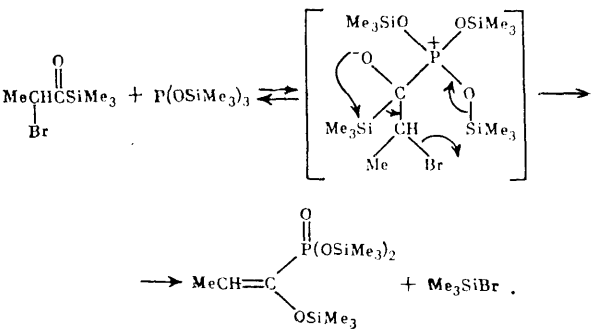
3. Interaction with Halogen-Containing Carbonyl Compounds

The reactions of trialkyl phosphites with α-halogeno-substituted carbonyl compounds result in the formation of either the enol phosphate esters (the Perkow reaction) or of 2-oxophosphonates (the Arbuzov reaction). [12] The ratio of the products depends on the structure of the carbonyl compound and the experimental conditions. A different pathway is characteristic of organosilicon derivatives of tervalent phosphorus in their reactions with α-halogeno-substituted aldehydes and ketones, namely addition to the C=O group with formation of α-trimethylsiloxyalkylphosphonates [pathway (*b*)]. [43,44] At the same time the products of the Arbuzov reaction [pathway (*a*)] and the Perkow reaction [pathway (*c*)] have been isolated in the reactions involving phenacyl halides, α-halogenoacetates, and esters of α-halogenopyruvic acid: [36,43,44]



A general reaction mechanism has been proposed, [43] including the initial formation of a dipolar intermediate and a subsequent rapid intramolecular transfer of the Me_3Si group to the *O*-anionic centre. Electron-accepting substituents (Ph, COOR) at the C=O group promote the phosphonate–phosphate rearrangement and the formation of the products of the Perkow reaction. The electron-donating alkoxy-group in α-halogenoacetates suppresses the addition of silyl phosphites to the carbonyl group—only the direct substitution of the halogen with the formation of alkoxycarbonylalkylphosphonates (the Arbuzov reaction) takes place.

An interesting result has been obtained in the reaction of α-bromoethyl trimethylsilyl ketone with tris(trimethylsilyl) phosphite. [44] The rapid 1,2-migration of the trimethylsilyl group to the negatively charged oxygen atom of the dipolar intermediate (XXV) overtakes the 1,4-silylotropic transition and the phosphonate–phosphate rearrangement. The subsequent β-elimination of the bromide ion leads to a mixture of the *Z*- and *E*-phosphonates (XXVI):



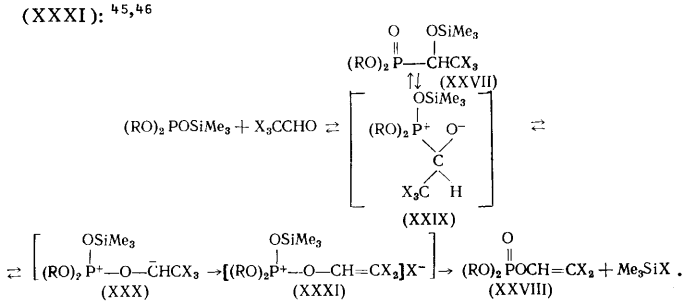
Z-, *E*-(XXVI)

A characteristic feature of the chemical behaviour of silyl phosphites in reactions with various carbonyl compounds, including α-halogeno-derivatives, is their capacity to add readily to the C=O group. As shown above, this constitutes a significant difference between silyl phosphites and trialkyl phosphites. One of the causes of such reactivity of silyl phosphites in carbonyl addition reactions is the possibility of formation of a five-membered cyclic transition state in the stage involving the transfer of the trimethylsilyl group to the *O*-anionic centre of the dipolar intermediate with formation of α-trimethylsiloxyalkylphosphonates. At the same time, according to Sekine et al.,[44] the electron-donating properties of the Me_3SiO substituent, which are more pronounced than those of the RO groups, may play an important role in this reaction pathway. The electron-donating effect promotes the stabilisation of the phosphonium centre of the intermediate and hinders the phosphonate–phosphate rearrangement. The successive introduction of trimethylsilyl groups into the phosphite molecule alters the reaction pathway: carbonyl addition becomes dominant even in the case of ethyl bis(trimethylsilyl) phosphite.[44] The tendency towards the addition to the carbonyl group of chloroacetone is more marked than in the reaction with bromoacetone (Table 2).

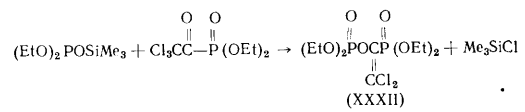
Table 2. The relative ease of various pathways in the interaction of phosphorus(III) derivatives with halogenoacetones (Ad = addition to the carbonyl group, A = Arbuzov reaction, P = Perkow reaction[44]).

$XCH_2C(O)Me$	$(EtO)_3P$	$(EtO)_2POSiMe_3$	$EtOP(OSiMe_3)_2$	$P(OSiMe_3)_3$
X=Cl	A< P	Ad	Ad	Ad
X=Br	A∼P	A< P	Ad	Ad

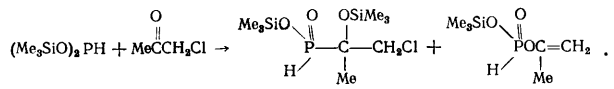
In those cases where there is a possibility of the formation of α-siloxyphosphonates and vinyl phosphates, the addition to the carbonyl group is the kinetically controlled process and the Perkow reaction takes place under the conditions of thermodynamic control. Thus the interaction of silyl phosphites with trihalogenoacetaldehyde leads initially to the formation of the phosphonates (XXVII), which decompose on prolonged heating into vinyl phosphates and a halogenosilane via a pathway involving the formation of the zwitter-ionic intermediates (XXIX) to (XXXI):[45,46]



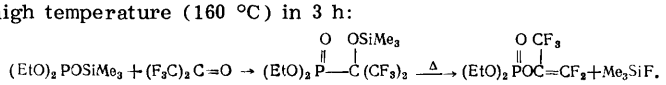
The reaction of diethyl trimethylsilyl phosphite with trichloroacetylphosphonate takes place via an analogous mechanism and leads to the unsaturated phosphoryloxyphosphonate (XXXII):[47]



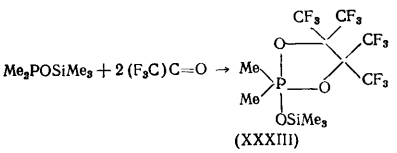
Bis(trimethylsilyl) hypophosphite reacts with chloroacetone to form α-siloxyphosphonate and vinyl phosphate:[29,48]



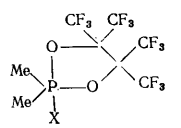
Various reaction pathways have been noted also for the reactions of diethyl trimethylsilyl phosphite and trimethylsilyl dimethylphosphinite with hexafluoroacetone. In the former case the authors[15] detected the formation of the intermediate diethyl hexafluoro-α-trimethylsiloxypropylphosphonate, which is converted into vinyl phosphate at a high temperature (160 °C) in 3 h:



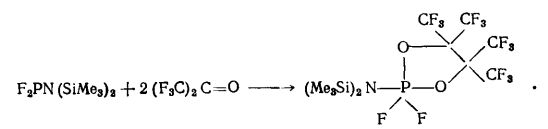
Trimethylsilyl dimethylphosphinite reacts with two moles of hexafluoroacetone even at −78 °C with the quantitative formation of the thermally highly stable λ^5-1,3,2-dioxaphospholan (XXXIII):[49]



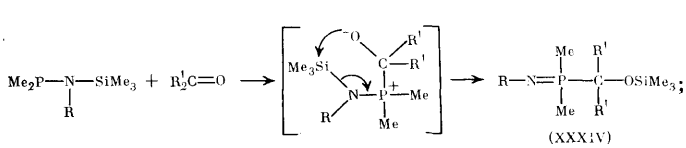
The presence of the mobile Me_3SiO group in compound (XXXIII) makes it possible to synthesise readily a number of derivatives of pentacoordinate phosphorus:



Bis(trimethylsilyl)aminodifluorophosphine reacts similarly with hexafluoroacetone:[50]



However, on passing to *N*-alkyl-*N*-silylaminodialkylphosphines, the process develops differently. Nucleophilic attack by the phosphorus atom of the aminophosphine on the carbonyl carbon atom is accompanied by the 1,4-transfer of the Me_3Si group from nitrogen to oxygen and leads to the adduct (XXXIV) having the imino-structure:[51]

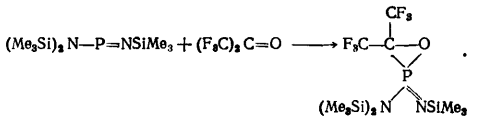


R = MeSi, t-Bu; R' = CF_3, Me .

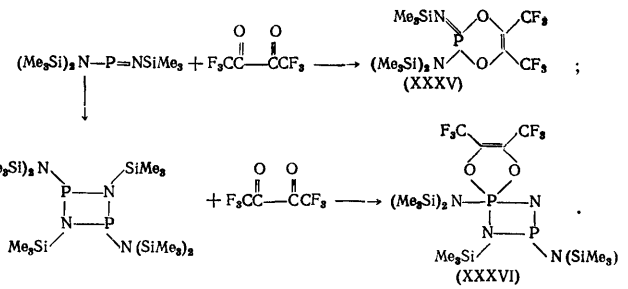
Thus the variation of the nucleophilic properties of the phosphorus(III) centre combined with the high lability of the Si–N bond in silylaminophosphines is reflected significantly in the character of the interaction with carbonyl

reagents, permitting the synthesis of various types of organophosphorus compounds with functional group substituents.

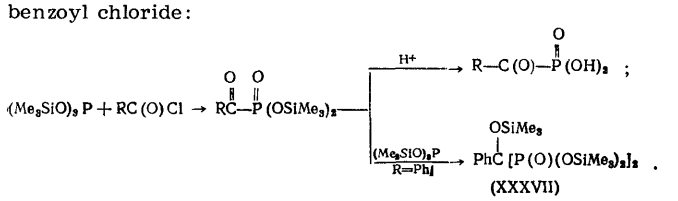
The reaction of the *N*-silylated amide of phosphenimidous acid with hexafluoroacetone is unusual. The [1 + 2]-cycloaddition yielded a new three-membered cyclic adduct, namely 2-[bis(trimethylsilyl)amino]-3,3-bis(trifluoromethyl)-2-trimethylsilylimino-1,2-λ^5-oxaphosphiran: [52]



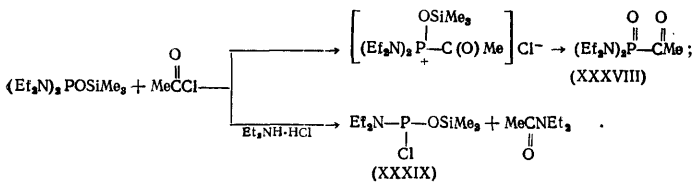
The reactions of the phosphenimidous amide and its dimer with hexafluorodiacetyl lead to the [1 + 4]-cycloaddition products (XXV) and (XXXVI) respectively: [52]



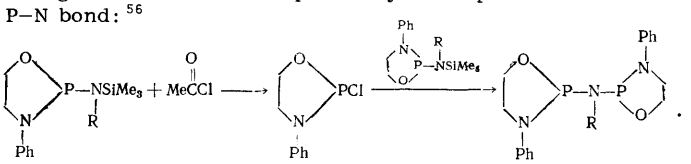
Like trialkyl phosphites, silyl phosphites give rise to the corresponding acylphosphonates on interaction with acyl halides. [53,54] The use of tris(trimethylsilyl) phosphite in this reaction makes it possible to synthesise readily the free acylphosphonic acids; the silylated α-hydroxybenzyldiphosphonate (XXXVII) can be obtained by reaction with benzoyl chloride:



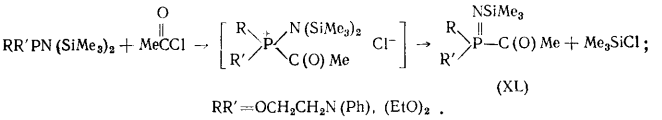
Trimethylsilyl *N,N,N',N'*-tetra-alkylphosphorodiamidites react with acetyl chloride to form the Arbuzov reaction products (XXXVIII) and the products (XXXIX) resulting from the substitution of the amino-group: [55]



The interaction of monosilylated 2-amino-1,3,2-oxazaphospholans with acetyl chloride proceeds with involvement of the nitrogen atom and is accompanied by the rupture of the P–N bond: [56]



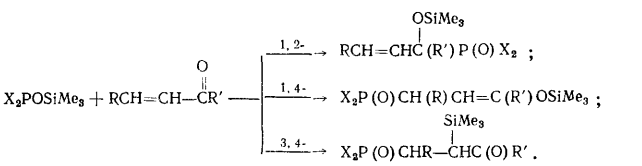
The introduction of a second Me_3Si group results in a change of the reaction centre—*N*-trimethylsilylacetylphosphonimidates (XL) are formed in the reaction: [56]



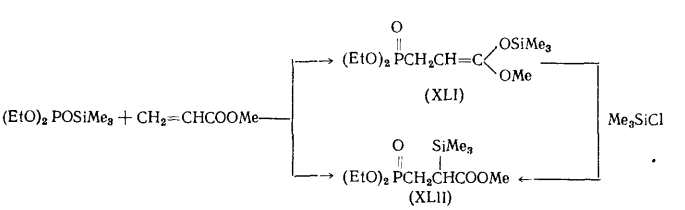
Thus the character of the interaction of the organosilicon derivatives of tervalent phosphorus with halogenocarbonyl compounds depends on the nature of the substituents in the reactant. In most cases the reactions apparently proceed via a nucleophilic mechanism; a dipolar ion with a P–C bond is formed initially and can be stabilised in different ways: (1) by the 1,4-transfer of the Me_3Si group to the oxygen ion with formation of α-siloxyphosphonates; (2) by the Perkow reaction with elimination of a halogenosilane; (3) by the addition of a second molecule of the carbonyl compound and the formation of 1,3,2-dioxaphospholans. Other reaction pathways are also possible, particularly those involving organosilicon reagents containing the P(III)–N–Si fragment.

4. Reactions with αβ-Unsaturated Carbonyl Compounds

The reactions involving addition to unsaturated carbonyl compounds occupy an important place in the chemistry of phosphorus–silicon compounds containing the P(III)–X–Si (X = O or N) group. The possibility of the involvement of the carbonyl and vinyl centres of the unsaturated reactant in these processes determines the simultaneous occurrence of three competing reactions: addition to the 1,2-, 3,4-, and 1,4-positions of the enone; their ratios are determined by the nature of the substituents in the initial compounds:

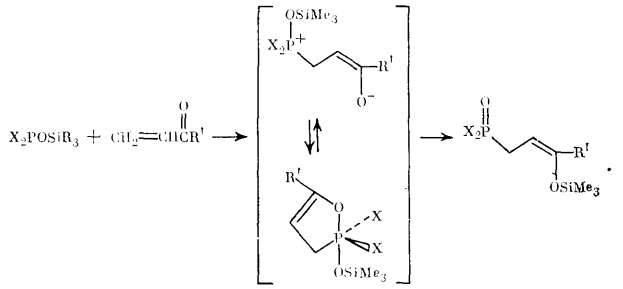


Dialkyl trimethylsilyl phosphites react vigorously with unsaturated aldehydes via the 1,2- and 1,4-addition pathways in the absence of catalysts, [5,10,11,18–20] while silyl phosphoramidites form exclusively the 1,2-adducts. [11] The interaction of trialkylsilyl phosphites and trialkylsilyl phosphoramidites with vinyl ketones takes place under more severe conditions and is accompanied by the preferential formation of 1,4-adducts. [10,11,19,57] The introduction of electron-donating alkoxy-substituents at the carbonyl centre (esters of αβ-unsaturated carboxylic acids) renders only the 1,4- and 3,4-addition reactions energetically favourable. [4,5,58] The phosphorylated derivatives of alkyltrimethylsilylketen acetals (XLI) rearrange to the *C*-silylated phosphonates (XLII) on treatment with halogenosilanes: [7]



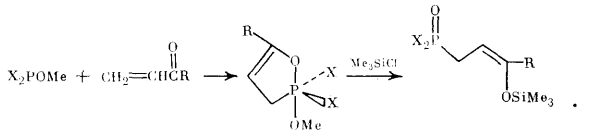
The study of the stereochemical characteristics of the reactions of silyl phosphites with unsaturated carbonyl compounds and the elucidation of the factors determining

the composition of the reaction products resulted in two pathways leading to the formation of 1,2- and 1,4-adducts being proposed.[19] The first is analogous to the mechanism of the addition of silyl phosphites to the carbonyl groups of unsaturated aldehydes and ketones examined above. The mechanism of the 1,4-addition is presented below:



(XLIIIa)

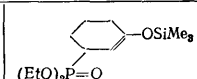
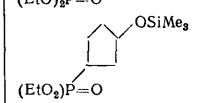
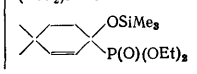
The preferential formation of the *Z*-adduct as well as the absence of the interaction of the silyl phosphite with an equimolar amount of cyclohexene (100 °C, 52 h) shows that the cisoid geometry of the enone promotes the 1,4-addition. It is believed that[19] the intermediate formation of the oxaphospholen (XLIIIa) in this reaction is probable, because the silylation of the methoxy-analogues (XLIIIb) also results in phosphorylated *Z*-silylenols:



(XLIIIb)

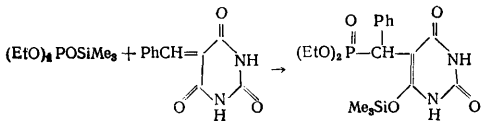
The independent occurrence of the 1,2- and 1,4-addition reactions is confirmed by the finding that the corresponding adducts are thermally stable and do not isomerise to one another (200 °C, 24 h).[19] The low sensitivity of the ratio of the 1,2- and 1,4-adducts to changes in the solvating properties of the medium indicates only a small charge separation in the transition states of the rate-determining stages of both addition reactions.

Table 3. Reactions of cyclic enones with $(EtO)_2POSiMe_3$.[60]

Initial enone	Main product	*T*, °C	τ, h	α
		80 180	75 12	8:1 16:1
		80 180	12 12	100:1 100:1
		80 180	200 18	1:3 1:19

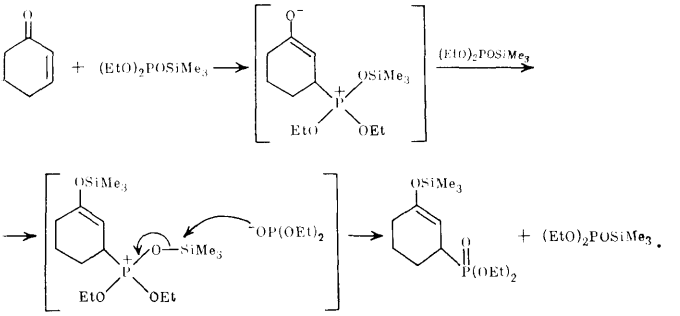
Notation: *T* is the reaction temperature, τ the reaction time, and α the ratio of the 1,4- and 1,2-adducts.

The reaction of diethyl trimethylsilyl phosphite with 5-benzylidenebarbituric acid apparently also proceeds by the 1,4-shift mechanism:[59]



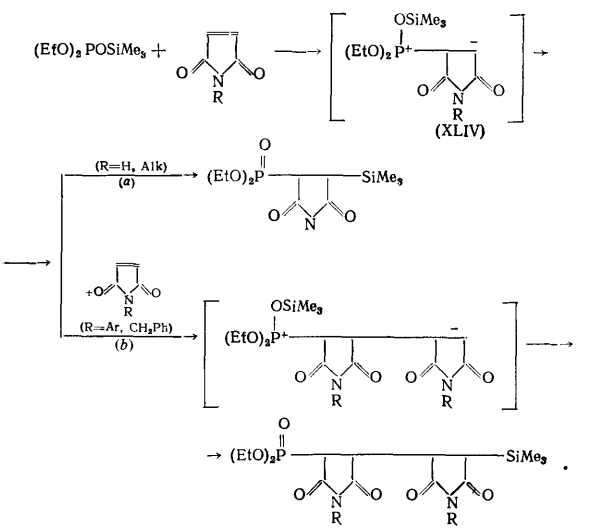
The rigid fixation of the *s-trans*-conformation of the unsaturated carbonyl compound alters the mechanism of the addition reaction. Cyclic enones form stable 1,4- and 1,2-adducts with diethyl trimethylsilyl phosphite only after prolonged heating of the reactants.[60] The ratio of the 1,4- and 1,2-adducts depends significantly on the experimental temperature and on the steric accessibility of the β-carbon atom of the unsaturated cyclic ketone (Table 3).

The mechanism of the formation of 1,4-adducts from cyclic enones presupposes the intermolecular transfer of the Me_3Si group with participation of a second silyl phosphite molecule:



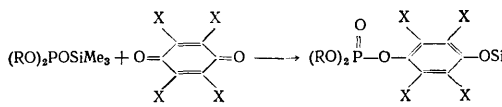
The appreciable acceleration of the reaction in the presence of an excess of silyl phosphite and the high sensitivity to changes in the dielectric properties of the medium (the reaction with $CHCl_3$ is much slower than that with MeCN), which confirms the formation of intermediate dipolar structures, are evidence in support of the mechanism proposed by the authors.[60]

The stabilisation of the intermediate (XLIV) in the reactions of silyl phosphites with maleimides, which also have the *s-trans*-configuration of the C=C and C=O bonds, can be achieved in different ways depending on the nature of the substituents R at the nitrogen atom:[61,62]



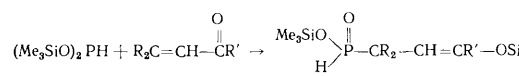
In order to elucidate the causes of the different types of chemical behaviour of *N*-substituted maleimides, measurements were made of the half-wave potentials of the polarographic reduction of these substances.[61] The values of $E_{\frac{1}{2}}$ for compounds with R = Ph, CH_2Ph, or *p*-ClC_6H_4, determined in dimethylformamide (DMF), proved to be greater than the corresponding values for the imides with R = H or Bu, which indicates more pronounced electrophilic properties of the *N*-aryl and *N*-benzyl structures. Maleimides containing electron-accepting substituents readily add to the carbanionic centre of the intermediate zwitter-ion (XLIV) [pathway (*b*)] and this reaction is faster than the 1,4-shift of the trimethylsilyl group [pathway (*a*)]. The stabilisation of the intermediate (XLIV) by electron-accepting groups in maleimide, which increases the lifetime of the intermediate compound and thereby favours the intermolecular addition of a second molecule of the unsaturated reactant [pathway (*b*)] plays an important role in the formation of adducts having the 1:2 composition. On the other hand, a decrease of the nucleophilicity of the carbanion in the 1:1 intermediate lowers the rate of the competing silylotropic process.

The interaction of silyl phosphites with *p*-quinones proceeds differently. The addition is at the 1,6-positions of the quinonoid system and leads to products having the phosphate structure:[34,63]

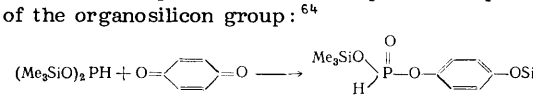


X=H, Cl .

Mainly 1,4-adducts are formed in the reactions of bis(trimethylsilyl) hypophosphite with unsaturated carbonyl compounds by migration of an Me_3Si group to carbonyl oxygen:[29]



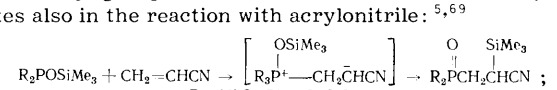
The addition to *p*-quinones also takes place with participation of the organosilicon group:[64]



The character of the interaction of silyl phosphites with nitro-olefins is in many respects similar to that of reactions involving 1,4-addition to unsaturated carbonyl compounds. The nucleophilic attack by the phosphorus atom on the β-carbon atom of the ethylenic bond results in the formation of the intermediate dipolar ion (XLV), which rapidly isomerises to the silyl ester of the phosphorylated nitronic acid (XLVI).[65,66] In the reaction of 3,3-trichloro-1-nitroprop-1-ene the dipolar intermediate can be stabilised not only by the transfer of the Me_3Si group but also by the prototropic transition (XLV) → (XLVII) with the subsequent elimination of chlorosilane from the unsaturated quasi-phosphonium intermediate (XLVIII).[67]
Trialkyl phosphites under the same conditions form esters of alkylenephosphonic acids and alkyl nitrites.[68]

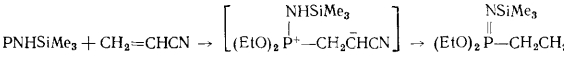
5. Reactions with Other Unsaturated Compounds

Organosilicon derivatives of tervalent phosphorus are capable of reacting with various unsaturated compounds containing the C=C, C=N, C=S, N=O, and S=O bonds and heterocumulene fragments. An example, namely the addition to maleimides, was examined above. The mechanism, involving the initial addition of silyl phosphites to the β-carbon atom of the activated double bond and the subsequent migration of the silyl group to the carbanionic centre, evidently operates also in the reaction with acrylonitrile:[5,69]

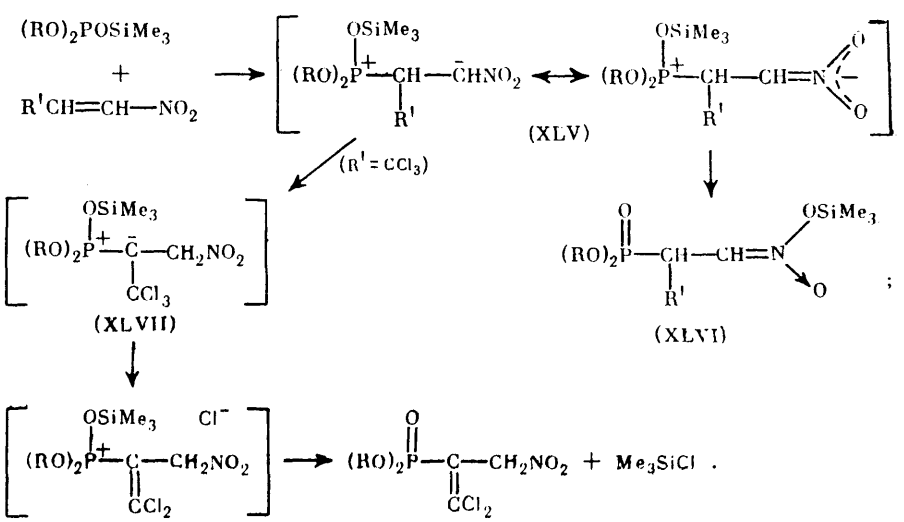


R=AlkO, Ph, Me_3SiO .

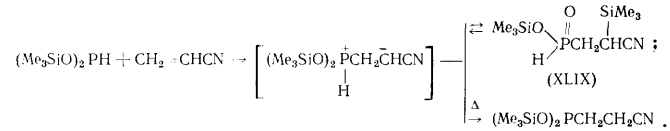
Diethyl *N*-trimethylsilylphosphoramidite also readily reacts with acrylonitrile. As a result of the prototropic transition, diethyl *N*-trimethylsilyl-β-cyanoethylphosphonimidate is formed under these conditions:[70]



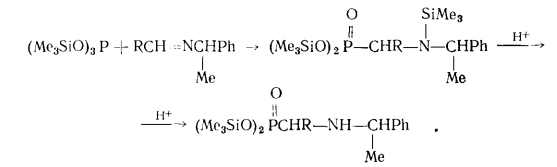
The interaction of bis(trimethylsilyl) hypophosphite with acrylonitrile and styrene leads to substituted bis(trimethylsilyl) ethylphosphonites.[71,72] It has been established by low-temperature ^{31}P NMR [72] that the reaction of the hypophosphite with acrylonitrile involves the initial formation, as a result of the migration of the Me_3Si group, of monosilyl phosphonite (XLIX), which isomerises at a higher



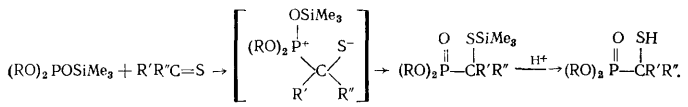
temperature to a thermodynamically controlled product—the disilyl phosphonite (L):



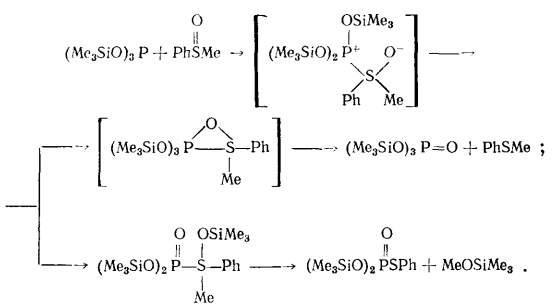
Tris(trimethylsilyl) phosphite is capable of adding to the C=N bond in aldimines: [73]



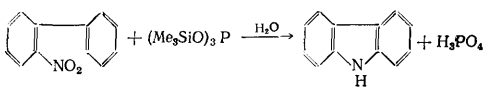
The reactions of silyl phosphites with cyclohexanethione and ethyl methyl thioketone lead readily to the dialkyl esters of α-trimethylsilylthioalkylphosphonic acid: [74]



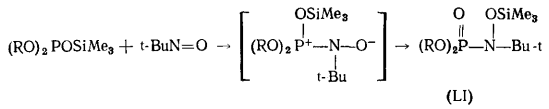
Tris(trimethyl silyl) phosphite exhibits a very high *deoxygenating activity in interaction with sulphoxides and* nitro-compounds. [75] In the reaction with methyl phenyl sulphoxide the main products are a sulphide and a silyl phosphate. However, the decomposition of the dipolar intermediate arising in the first stage takes place apparently also via the 1,4-migration of the organosilicon group and leads to *S*-phenyl phosphorothioate via a phosphorylated sulphurane:



The deoxygenation of nitro-compounds can lead to nitrogen-containing heterocycles: [75]

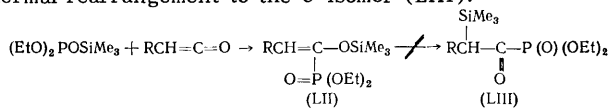


Nitroalkanes react with silyl phosphites like carbonyl compounds: the initial step in the interaction is nucleophilic attack by the phosphorus atom on the nitrogen atom of the nitroso-group; the subsequent 1,4-silylotropic shift leads to stable adducts having the phosphoramidate structure (LI): [76]

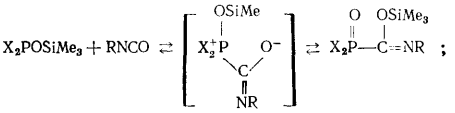


Trialkyl phosphites are oxidised by nitrosoalkanes to phosphates. [77]

A characteristic feature of the interaction of silyl phosphates with heterocumulenes is the possibility of the involvement in the reaction of one or several reaction centres of the unsaturated system. The addition of silyl phosphites to keten leads to the quantitative formation of the *O*-silyl derivative (LII), which does not undergo a thermal rearrangement to the *C*-isomer (LIII): [78,79]



An analogous addition to the carbonyl fragment of a heterocumulene has also been observed in the reactions of silyl phosphites or silyl phosphoramidites with isocyanates: [80,81]



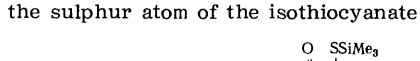
X=Et_2N, RO, Me_3SiO; R=Alk, Ar .

On heating, the reaction products decompose into the initial compounds. The thermal stability of the adducts with phenyl isocyanate is much higher than that of the adducts with the alkyl analogues by virtue of the conjugation of the C=N bond with the aromatic ring. [81]

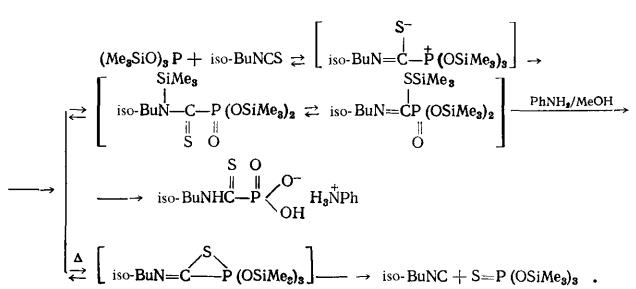
The interaction of phosphorus–silicon reagents with isothiocyanates does not proceed quite so unambiguously. Silyl phosphoramidites readily add to the C=N bond of phenyl isothiocyanate with formation of the amides of *N*-phenyl-*N*-trimethylsilylthiocarbamoylphosphonic acids: [80]



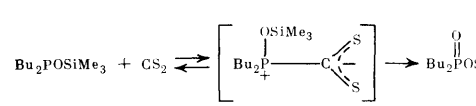
In the case of tris(trimethylsilyl) phosphite the Me_3Si group migrates to the sulphur atom of the isothiocyanate: [81]



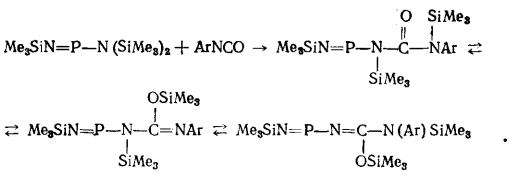
The mode of reaction of silyl phosphite with isobutyl isothiocyanate is determined by the experimental temperature. At room temperature a 1:1 adduct is formed and has been isolated in the form of the monoanilinium salt of *N*-isobutylthiocarbamoylphosphonic acid (LIV). Heating of the reaction mixture at 100 °C is accompanied by the desulphurisation of the isothiocyanate: [81]



The mechanism of the formation of phosphorothioates in this reaction is apparently analogous to the mechanism of the interaction of silyl phosphinites with carbon disulphide: [82]

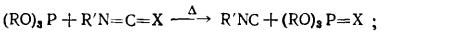


The addition of the *N*-silylated amide of *N*-(trimethylsilyl)phosphenimidous acid to aryl isocyanates leads to an equilibrium mixture of adducts;[83] the phosphorus atom remains dicoordinate under these conditions:

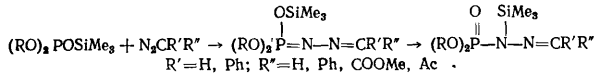


The complexity of the signals due to the Me_3Si group in the ^1H NMR spectrum and its dependence on temperature and the nature of the solvent demonstrate, according to the authors,[83] the occurrence of the amide–imide tautomerism and the 1,3-migration of the silyl group in the N=P–N triad.

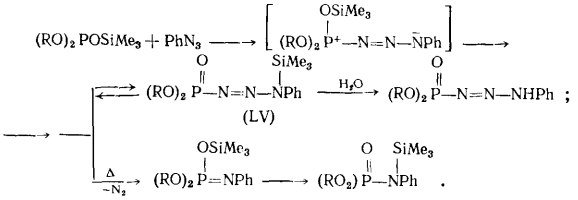
Trialkyl phosphites are known[84] to react with isocyanates and isothiocyanates under severe conditions (150–180 °C) with formation of isonitriles:



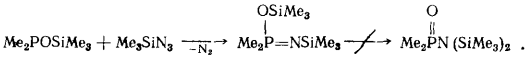
The first stage of the reaction of silyl phosphites with diaza-compounds involves the formation of phosphazenes, which isomerise to phosphorohydrazidates even at room temperature:[85,86]



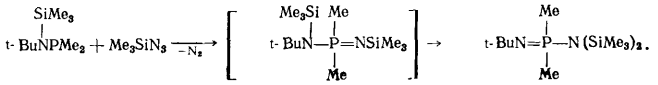
When silyl phosphite reacts with phenyl azide, the kinetically controlled product is 1-dialkylphosphoryl-3-phenyl-3-silyltriazene (LV), which is readily hydrolysed by atmospheric moisture. With increase of temperature, conditions are attained for the irreversible decomposition of the intermediate betaine with evolution of nitrogen and formation of *N*-silylphosphoramidate:[87]



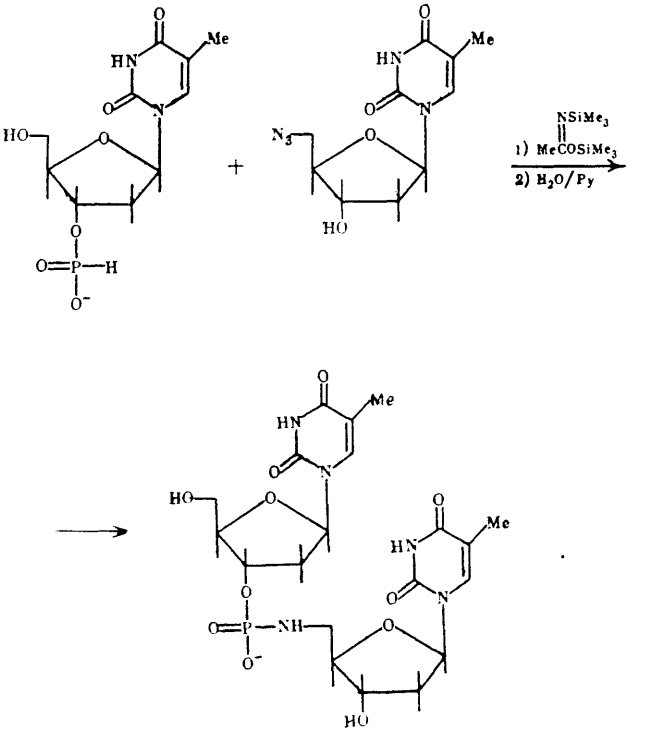
An increase of steric hindrance at the nitrogen atom in the phosphimine prevents the O → N migration of the Me_3Si group:[88,89]



The imination of *N*-t-butyl-*N*-trimethylsilylaminodimethylphosphine with trimethylsilyl azide results in the formation of a phosphimine with the sterically most favourable disposition of the bulky groups:[90]



The silyl phosphite–azide method of synthesis of phosphoramidates can be applied successfully to the synthesis of biologically important compounds:[88]



The data on the reactions involving the addition of organosilicon derivatives of tervalent phosphorus to various unsaturated compounds examined in this Section show that in the majority of the processes, as in the case of systems containing the P–X–C fragment, the initial step of the interaction is attack by the phosphorus(III) atom on the electrophilic centre of the other reactant. Consequently the replacement of the organic substituent in the phosphorus-containing reactant by the trialkylsilylgroup does not have a significant influence on the nucleophilic character of the phosphorus atom.

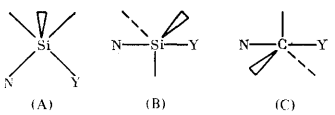
Extensive experimental and theoretical data showing that the overall electronic effect of the R_3Si group consists of the inductive and mesomeric interactions have accumulated in the literature.[91–98] The inductive effect is quantitatively expressed by the σ^* constants.[99] The electron-accepting influence of the R_3Si group [conjugation of the $(p-d)_\pi$, $(\sigma-4s)$, and $(\sigma-3d)_\sigma$ types] depends both on the nature of the heteroatom X in the fragment $\overset{\frown}{Si-X}-R$ and on the competing interaction $\overset{\frown}{X-R}$.[93,100] The replacement of the alkyl substituent at the oxygen or nitrogen atom by the trimethylsilyl group in isotypical compounds leads to a decrease of electron density at the heteroatom. The basicity of silyl ethers and silylamines is lower than that of their carbon analogues.[101–105]

The available literature data concerning comparative estimates of the nucleophilic properties of organosilicon derivatives of tervalent phosphorus are contradictory. Qualitative comparison of the reactivities of trialkyl and silyl phosphites shows, in the view of a number of investigators,[19,106,107] that the introduction of the Me_3SiO substituent at the phosphorus atom increases the nucleophilic reactivity of the phosphorus(III) system. On the other hand, the half-wave potentials $E_{1/2}$ (in volts) of the full esters of phosphorous acids, determined at a platinum electrode in acetonitrile[108,109] [1.60 for $(EtO)_3$; 1.66 for

$(MeO)_3P$; 1.74 for $(EtO)_2POSiMe_3$; 1.78 for $(MeO)_2$. $.POSiMe_3$; 1.96 for $(Me_3SiO)_3P$] indicate the electron-accepting influence of the organosilicon group.

Spectroscopic study of the hydrogen-bonded complexes of dialkyl and bis(trimethylsilyl) phosphites with phenol demonstrated approximately identical basicities of the oxygen atom in the P=O group in the two compounds.[110]

All these factors suggest that the unusual chemical behaviour of systems incorporating the P(III)–X–Si group is determined not only, and even not so much, by the change in electron density at the phosphorus atom as by the specific role of the trialkylsilyl group in stabilising the dipolar intermediates formed. Nucleophilic substitution at the silicon atom requires a low activation energy and can proceed via two transition states of types (A) and (B) having similar energies.[111–113] Depending on the structure of the intermediate compound and the experimental conditions, a particular version of the silylotropic transition obtains:



(A) (B) (C)

In the case of alkyl derivatives of tervalent phosphorus the only possible way in which the nucleophile can approach the sp^3-carbon atom leads to a trigonal bipyramidal structure of the transition state (C) with an axial disposition of the entering (N) and leaving (Y) groups. The distance between the nucleophilic centres should then be 3.5–4.5 Å.[113] All this increases sharply the energy barrier to the intramolecular transfer of the alkyl group and is responsible for the intermolecular reaction mechanism.

The driving force of the Ad† reactions of silyl phosphites with unsaturated compounds is in our view the thermodynamic ease of the formation of the phosphoryl group; for *N*-silylphosphoramidates, both the differences between the energies of the N–P(III) and N–P(IV) bonds and the greater strength of the Si–O bond compared with the Si–N bond play an important role in stabilising the adducts.

III. ORGANOSILICON DERIVATIVES OF TETRACOORDINATE PHOSPHORUS

The reactivity of organosilicon derivatives of tetracoordinate phosphorus has been studied to a much lesser extent than that of the corresponding phosphorus(III) compounds. It is known that the systems containing the P(IV)–X–Si (X = O, N, or S) group are capable of splitting off the trialkylsilyl group readily on treatment with proton-donating reagents,[1,114] acid halides,[115] and certain metal salts.[114] The reactions of silyl phosphates and their thio- and seleno-analogues with iodotrimethylsilane have been surveyed in a review.[116] There are no literature data concerning the addition of silyl phosphates or *N*-silylphosphoramidates to unsaturated compounds but the Ad processes involving *S*-trimethylsilyl phosphorodithioates have been studied in fair detail. The cause of this situation will be discussed below.

†Addition to carbonyl group—see Table 2 (Ed.of Translation).

We have analysed the reactivity of *S*-trimethylsilyl phosphorodithioates in addition reactions in comparison with phosphorodithioic acids, because *S*-organyl phosphorodithioates do not enter into Ad reactions. Such comparison of the chemical reactivities of phosphorodithioates containing the S–Si and S–H bonds makes it possible to elucidate clearly the specific features of the reactions of silicon-containing phosphorus systems.

1. Interaction with Carbonyl Compounds and Nitro-Compounds

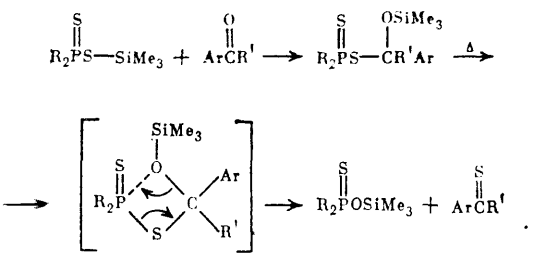
S-Trimethylsilyl esters of phosphorodithioic acids readily add to aliphatic aldehydes in the absence of a catalyst with formation of *S*-(α-trimethylsiloxy)-alkyl ethers:[117]

$$R_2P(S)S{-}SiMe_3 + R'CHO \rightarrow R_2P(S)S{-}CHR'{-}OSiMe_3;$$
R=AlkO, Alk, Ar; R' Alk .

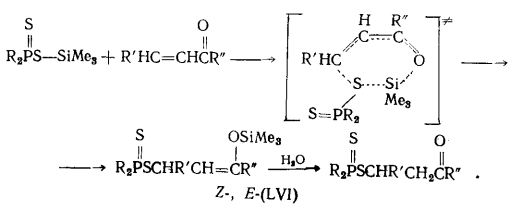
Under analogous conditions, phosphorodithioic acids form bis(dialkylphosphinodithioyl)alkanes:[118]

$$2R_2P(S)SH + R'CHO \rightarrow [R_2P(S)S]_2CHR'.$$

The adducts of silyl phosphorodithioates with aromatic aldehydes and ketones are unstable and decompose on heating via an O,S-exchange process,[117] noted previously for phosphorodithioic acids:[119]



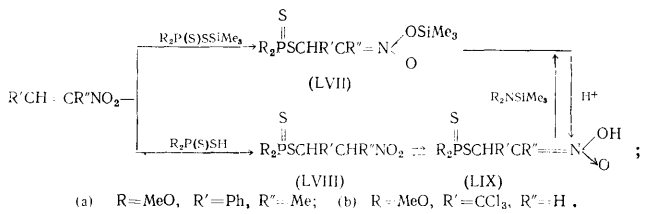
Unsaturated aldehydes and ketones combine vigorously with silyl phosphorodithioates with formation of a mixture of *Z*- and *E*-isomers of phosphorylated silylenols (LVI).[120] The hydrolysis of the adducts leads to 3-oxoalkyl phosphorodithioates obtained from the corresponding phosphorodithioic acids:



Z-, *E*-(LVI)

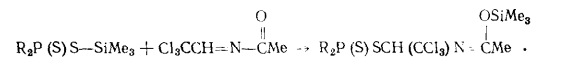
The appreciable, and in the case of acrolein preferential, formation of the *Z*-isomers can be due to the cyclic character of the transition state in the reaction. A similar structure of the activated complex has been proposed for the analogous reactions of phosphorodithioic acids.[121]

The interaction of silyl phosphorodithioates with nitroolefins leads to the formation of 1,4-adducts (LVII, a and b); the hydrolysis of the adduct (LVIIa) gives rise to a mixture of isomers—the nitro-compound (LVIIIa) and the *aci*-nitro-compound (LIXa):[117]



(a) R=MeO, R′=Ph, R″=Me; (b) R=MeO, R′=CCl_3, R″=H.

The silyl esters of phosphorodithioic acids do not add to acrylonitrile, alkyl acrylates, vinyl sulphones, alkyl vinyl ethers, and benzylideneaniline, while phosphorodithioic acids readily form 1,2-adducts with these compounds.[121,122] At the same time silyl phosphorodithioates react vigorously with *N*-acetyltrichloroaldimine:[117]



Thus silyl phosphorodithioates and phosphorodithioic acids show many features in common in their interaction with aromatic aldehydes and ketones but differ in their reactions with aliphatic aldehydes. Comparison of the ways in which the phosphorodithioates react with unsaturated carbonyl compounds and nitro-compounds suggests that the phosphorus-containing addend adds to the terminal positions of the unsaturated system. In the case of silyl phosphorodithioates the 1,4-adducts formed are thermodynamically stable. The addition of phosphorodithioic acids is in most cases accompanied by prototropic isomerisation.[121]

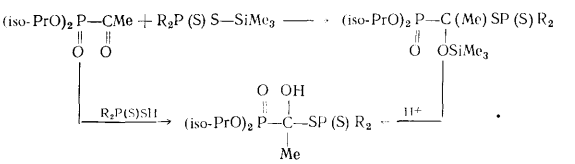
The fact that, in contrast to systems with a P(III)–X–Si group, silyl phosphorodithioates do not add to the C=C bond in unsaturated carbonyl reagents is apparently associated with the necessity for the 1,4-orientation of the silicon-containing phosphorodithioates in the course of the interaction. The driving force of such orientation is the high energy of the Si–O bond (89.3 kcal mol^{-1}) compared with the Si–C (69.3 kcal mol^{-1}) and Si–S (60.9 kcal mol^{-1}) bonds.[123] The coordination of the silicon and oxygen atoms in the transition state also promotes an increase of the nucleophilicity of the sulphur atom of the phosphorodithioate fragment. All these features significantly lower the activation energy for the Ad process.

The reactions of silyl phosphites begin with the nucleophilic attack by the phosphorus atom on the sp^2-carbon atom of the ethylenic bond of the unsaturated reactant.[107] The migration of the Me_3Si group to the basic centre of the intermediate takes place in the second stage of the reaction. The factor determining the reactivity of silyl phosphites is the thermodynamic ease of formation of the P=O bond.

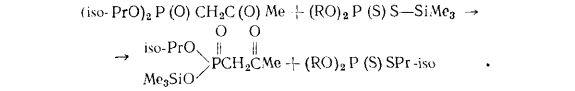
Hence it is clear why phosphorus–silicon reactants containing the P(IV)–O–Si group are incapable, in contrast to silyl phosphites, of adding to various unsaturated systems, including carbonyl systems. This applies to a large extent also to *N*-silylphosphoramidates, although in this instance the deliberate search for suitable reagents may lead to the occurrence of the Ad interaction.

2. Reactions with Organophosphorus Compounds Containing the C=O Group

The mode of reaction of silyl phosphorodithioates with phosphorus-containing carbonyl compounds depends significantly on the structure of the latter. Di-isopropyl acetylphosphonate combines with silyl phosphorodithioates via the carbonyl group, forming siloxy-derivatives. The hydrolysis of the adducts lead to phosphorylated carbinols, also obtained by specific synthesis—by the reaction of phosphorodithioic acid with α-ketophosphonates:[124]

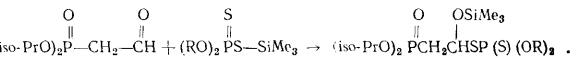


Under these conditions, *O*,*O*-di-isopropylphosphorylacetone undergoes dealkylation:

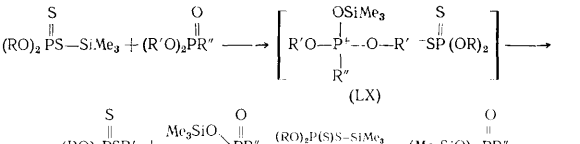


When an excess of silyl phosphorodithioate is used and when methoxy- or ethoxy-groups are introduced at the phosphorus atom of phosphorylacetone, complete silylation of the phosphonate is observed.[124]

It is noteworthy that *O*,*O*-di-isopropylphosphorylacetaldehyde, which is alkylated with greater difficulty and contains a more reactive carbonyl group, reacts with silyl phosphorodithioates to form adducts via the C=O group:[124]

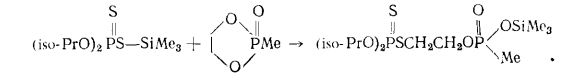


The dealkylation of phosphonates by silyl phosphorodithioates is a common feature:[124]

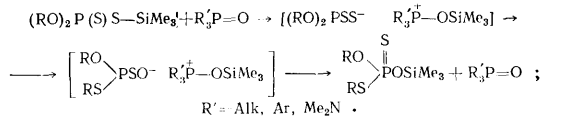


Initially the Me_3Si group of the phosphorodithioate migrates to the phosphoryl oxygen atom with formation of the intermediate quasi-phosphonium compound (LX). The phosphorodithioate anion attacks next the alkyl group of the phosphonium ion, forming the corresponding *S*-alkyl ester of the phosphorodithioic acid and alkyl trimethylsilyl phosphonate. In the case of dimethyl and diethyl phosphonates and in the presence of an excess of silyl phosphorodithioate the dealkylation reaction develops further.

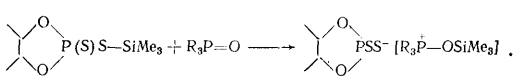
The use of cyclic phosphonates in this reaction makes it possible to synthesise readily compounds with two phosphorus atoms:[124]



The reaction of silyl phosphorodithioates with organophosphorus systems in which the dealkylation process is impossible (phosphines, phosphine oxides, and hexamethylphosphoramide) does not stop at the stage involving the formation of quasi-phosphonium structures: the isomerisation of the phosphorodithioate anion and subsequent silylation result in the formation of *O*-alkyl *O*-trimethylsilyl *S*-alkyl phosphorodithioates:[124]



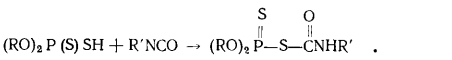
Stable quasi-phosphonium compounds have been isolated in the reaction of a cyclic *S*-silyl phosphorodithioate with phosphine oxides and hexamethylphosphoramide (HMP):



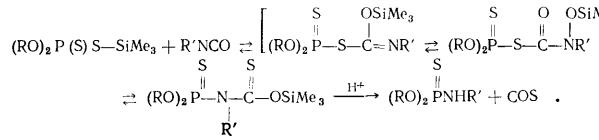
Phosphorodithioic acids react with phosphoryl compounds to form hydrogen-bonded complexes.[125]

3. Reactions with Heterocumulenes

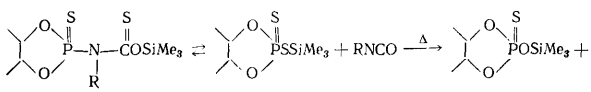
It is known that phosphorodithioic acids add vigorously to the C=N bond in isocyanates to form *N*-organylcarbamoyl phosphorodithioates:[122]



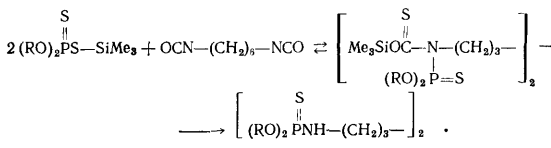
The reactions of silyl phosphorodithioates with various isocyanates have been widely investigated.[126] In the reactions with alkyl isocyanates the products of addition to the N=C=O group of the heterocumulene are formed initially and then rearrange to *N*-thiophosphorylated thiocarbamates via the intermolecular S → N migration of the thiophosphoryl group. The adducts are stable under the usual conditions, but on vacuum fractionation they decompose into the starting materials. This demonstrates the reversibility of the addition reaction and of the phosphorodithioate—phosphoramidothioate rearrangement. The hydrolysis of the reaction product leads to phosphoramidothioates and carbon oxide sulphide:[126]



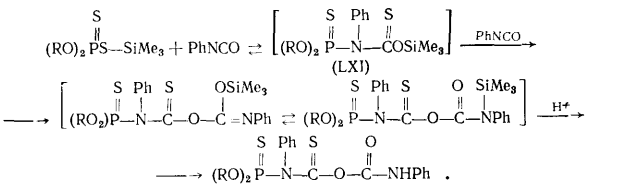
In the reactions involving cyclic silyl phosphorodithioates the products are *N*-thiophosphorylthiocarbamates, which are stable at room temperature, but on heating the O,S-exchange process takes place:



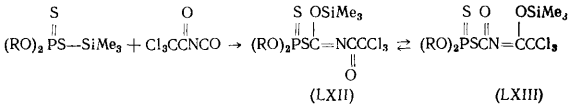
The reactions of the silyl esters of phosphorodithioic acids with hexamethylene di-isocyanate can proceed, depending on the reactant ratio, with participation of one or both isocyanate groups:[126]



The replacement of the alkyl group in the isocyanate by the phenyl group reduces the reactivity of the heterocumulene—the reaction proceeds at a higher temperature. Two phenyl isocyanate molecules are then involved in the process: the electronic effect of the aromatic ring promotes the nucleophilic addition of the intermediate (LXI) to a second molecule of the unsaturated reactant:[126]



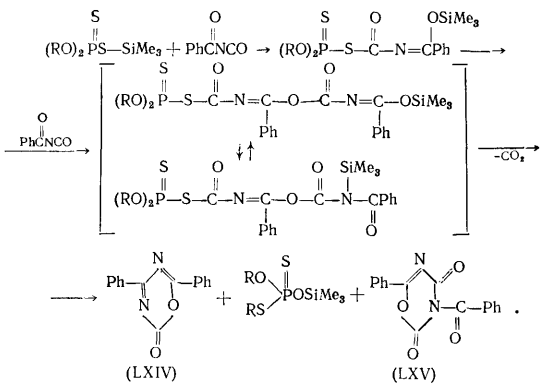
Trichloroacetyl isocyanate readily combines with silyl phosphorodithioates to form the (LXII) ⇌ (LXIII) equilibrium mixture, whose existence is associated with the reversible 1,5-migration of the trimethylsilyl group:



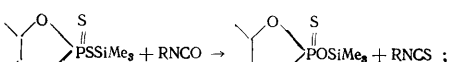
The reaction with phosphorodithioic acids leads to the product of addition to the C=N bond:[126]



In the interaction of silyl phosphorodithioates with benzoyl isocyanate the formation of adducts having the 1 : 2 composition is followed by the intramolecular substitution of the phosphorodithioate fragment under the influence of the siloxane or silazane groups. In the former case the cyclisation is accompanied by decarboxylation and leads to 6-oxo-2,4-diphenyl-1,3,5-oxadiazine (LXIV)—this is the main pathway. In the latter case the product is the benzoyl isocyanate dimer (LXV). The phosphorodithioate anion isomerises and is converted into the corresponding *S*-alkyl ester:[126]

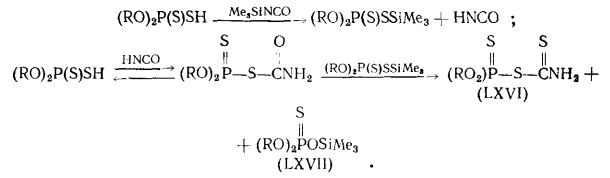


Cyclic silyl phosphorodithioates react with aryl and acyl isocyanates via the mechanism of the O,S-exchange process:[126]

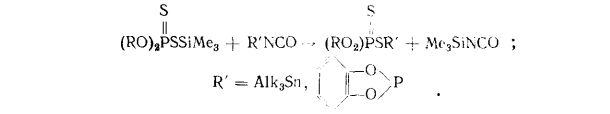


Silyl phosphorodithioates do not add to isocyanatosilanes; apparently the steric and electronic influences of the trimethylsilyl group in the heterocumulene prevent the stabilisation of the adduct via the S → N migration of the thiophosphoryl group.

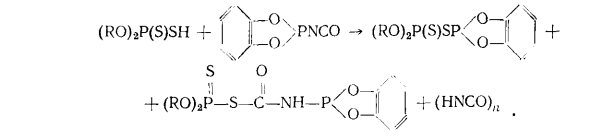
Phosphorodithioic acids readily rupture the Si–N bond in the trimethylsilyl isocyanate molecule and the subsequent reactions result in the formation of *S*-thiocarbamoyl phosphorodithioate (LXVI) and *O*-silyl phosphorothioate (LXVII):[127]



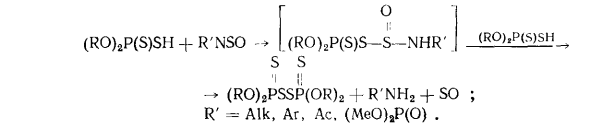
The interaction of silyl phosphorodithioates with other organoelemental isocyanates, namely isocyanatostannanes and phosphoroisocyanatidites, proceeds with cleavage of the element–nitrogen bond:[128]



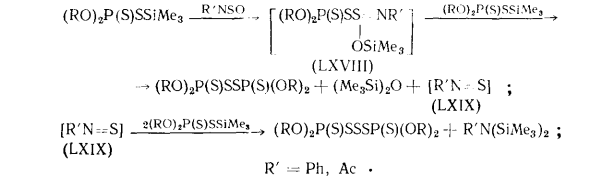
Both addition and substitution take place in the reactions of phosphorodithioic acids with *o*-phenylene phosphoroisocyanatidite:[128]



Significant differences in the chemical behaviour of silyl phosphorodithioates and phosphorodithioic acids have been observed also in their reactions with sulphinylamines. The reactions with phosphorodithioic acids result in the formation of bis(dialkylthiophosphoryl) disulphide, sulphur monoxide, and the corresponding amino-derivative:[129]



Silyl phosphorodithioates initially add to the S=O bond of the sulphinyl amine. The resulting intermediate (LXVIII) interacts with a second molecule of the phosphorodithioate to form bis(dialkylthiophosphoryl) disulphide, hexamethyldisiloxane, and an unstable intermediate (LXIX) having the thionitroso-structure, which reacts with two molecules of the silyl phosphorodithioate to form bis(thiophosphoryl) trisulphide and a disilylated amine:[130]

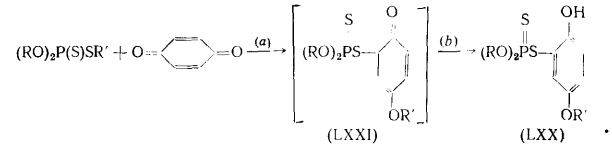


Thus the differences in the mode of reaction of silyl phosphorodithioates and phosphorodithioic acids with sulphinylamines are associated primarily with the different structures of the intermediates formed initially: phosphorodithioic acids form adducts involving the S=N bond, while silyl phosphorodithioates add to the S=O bond of the heterocumulene molecule.

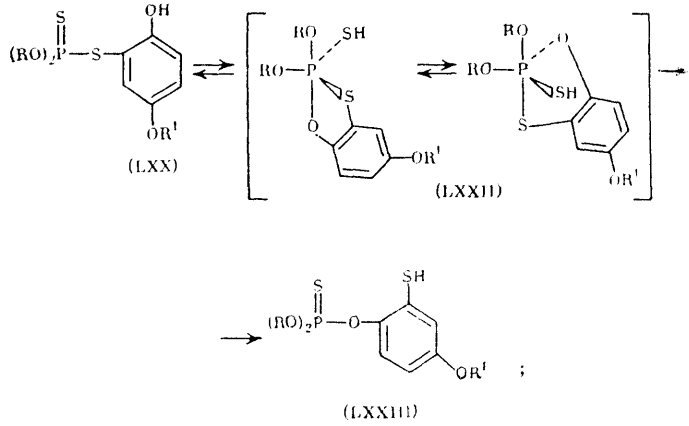
4. Reactions with *p*-Quinones

Like phosphorodithioic acids,[122] *S*-trimethylsilyl phosphorodithioates[131] are capable of adding readily to *p*-quinones, having a rigidly fixed *s*-transdisposition of the C=C and C=O bonds. The reactions with *p*-benzoquinone proceed vigorously in the absence of catalysts and are accompanied by the quantitative formation of *S*-aryl phosphorodithioates.

Kinetic study of these processes in various solvents using deuterated reactants showed[132] that both phosphorodithioic acids and their silyl esters initially react with *p*-benzoquinone to form 1,4-adducts (LXX). In non-polar weakly basic media the first stage of this reaction (*a*) determines the rate of the entire process ($k_H/k_D = 1$ for *p*-benzoquinone) and phosphorodithioic acids are therefore more reactive than silyl phosphorodithioates. With increase of the degree of nucleophilicity of the solvents, the proton transfer from the aromatic ring of the intermediate (LXXI) to the carbonyl group [stage (*b*); k_H/k_D is much greater than unity] becomes rate-limiting. The rates of reaction of phosphorodithioates (R′ = H or $SiMe_3$) are approximately the same under these conditions:



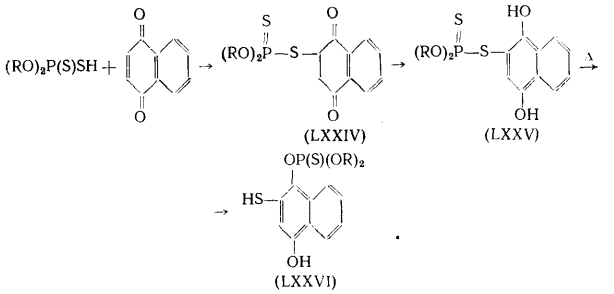
On vacuum distillation or heating, *S*-aryl phosphorodithioates (LXX) isomerise to the corresponding phosphoromonothioates.[131,132] The mechanism of their rearrangement includes the intermediate formation of mercaptophosphoranes (LXII):



R = H, Me_3Si .

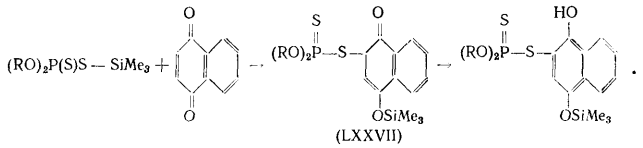
Kinetic study of the isomerisation,[132] occurring via a unimolecular mechanism, showed that the influence of the nature of the substituents at the phosphorus atom is determined by a set of electronic and steric factors and is described satisfactorily by the rules of the "hydroxyphosphorane concept".[133] The introduction of a phosphorus atom into the dioxaphospholan ring accelerates the isomerisation reaction so much that the phosphorodithioate adduct having the structure (LXX) cannot be isolated—the phosphoromonothioate (LXXIII) is formed immediately. This effect is associated with the low energy of the intermediate cyclic spiro-mercaptophosphoranes (LXXII) with R = $CH(CH_3)CH(CH_3)$. It is known[133–136] that spirocyclisation favours all prototropic processes involving the formation of hydroxyphosphoranes.

The interaction of phosphorodithioic acids and silyl phosphorodithioates with *p*-naphthoquinone proceeds via a mechanism formally analogous to that of the reaction with *p*-benzoquinone. However, detailed analysis of the changes in the infrared spectra of mixtures of solutions of *p*-naphthoquinone and a phosphorodithioic acid in CCl_4 as a function of time showed that the product of addition to the C=C bond of the quinone (LXXIV) is formed initially and is then gradually converted into the dithiophosphorylated dihydroxynaphthalene (LXXV).[137] Under severe conditions (100 °C), the phosphorodithioate isomerises to the phosphoromonothioate (LXXVI):[132]



(LXXIV) (LXXV) (LXXVI)

In the case of silyl phosphorodithioates the 1,4-adduct (LXXVII) is an intermediate, as in the reaction with *p*-benzoquinone:



(LXXVII)

Consequently the mechanism of the reactions of phosphorodithioic acids with *p*-quinones depends on the structure of the unsaturated reactant; silyl phosphorodithioates form initially 1,4-adducts in all cases.

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Summarising the discussion of the reactivity of organosilicon derivatives of phosphorus in addition reactions, one should note that the introduction of the trialkylsilyl group into the molecule of a phosphorus-containing system introduces significant, sometimes radical, changes into the character of Ad processes. The knowledge and purposeful employment of the specific features of the chemical behaviour of phosphorus–silicon reagents makes it possible to synthesise successfully new types of organoelemental compounds, which promotes the development and interpenetration of the chemistry of phosphorus and the chemistry of silicon.

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