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# Molecular Rearrangements Accompanied by the Migration of Phosphoryl Groups between Two nucleophilic Centres

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The review surveys instances of the reversible and irreversible migration of phosphoryl groups $\left(\geq P{=}O,\ \geq P{=}S,\ \geq P{=}N{-}\right)$ between two heteroatoms (N, O, S, and Se); this type of rearrangement is characterised by retention of the coordination number of the phosphorus atom. The rearrangements of phosphorylated aminoalcohols, mercaptoalcohols, oximes, and the products of the addition of partially esterified acids of tetracoordinate phosphorus to cyano-compounds, carbodiimides, and keten imines, proceeding via a stage involving the formation of unstable phosphoranes are considered. Much attention is devoted to tautomeric processes in which the phosphoryl, thiophosphoryl, and iminophosphoryl groups are the migrating moieties.
The bibliography includes 109 references.

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## I. INTRODUCTION

There has been a considerable development in recent years of the study of rearrangements accompanied by the migration of phosphoryl and other groups with a tetracoordinate phosphorus atom, whose driving force is the deficiency of electron density at the phosphorus atom. In an isomerisation process, the deficiency of electron density at the phosphorus atom in the final or intermediate product diminishes.

The study of rearrangements of this type makes it possible to discover the causes and factors promoting the stabilisation or rupture of bonds in the P–S–C, P–N–C, P–O–C, etc. groups present in derivatives of tetracoordinate phosphorus acids and throws light on the characteristics of the mechanism of nucleophilic substitution at the tetrahedral phosphorus atom. The phosphorylation and phosphoryl group transfer reactions are responsible for many vitally important biochemical processes.

The aim of the present review was to examine and (wherever possible) to treat systematically studies devoted to rearrangements involving the migration of phosphoryl groups between two nucleophilic centres in which the coordination number of the phosphorus atom remains ultimately unaltered. Attention is devoted also to the preparative aspect, since the migration of phosphoryl groups is observed in the synthesis of many organophosphorus compounds and also in the preparation of biologically active phosphoric acid derivatives.

In view of the wide variety and novelty of the rearrangements considered, their mechanisms have been inadequately investigated and the schemes put forward are tentative and open to discussion. The most characteristic migrations of phosphoryl and thiophosphoryl groups are of the 1,3- and 1,4-types, which can occur via both intramolecular and intermolecular mechanisms depending on the nature of the nucleophilic centre and the migrating moiety. Sometimes the 1,3-migration is accompanied by the elimination of the phosphorus-containing group.

The 1,2-migrations of phosphoryl groups between two heteroatoms occur in tetracoordinate phosphorus derivatives (I) with P–P bonds and are always accompanied by a decrease of the coordination number of one of the phosphorus atoms; such reactions have been largely surveyed in earlier publications[1,2]:

$$RR^1P(X)-PRR^1(Y) \rightleftarrows RR^1P(X)-X-PRR^1(Y)\ ;$$
(I)

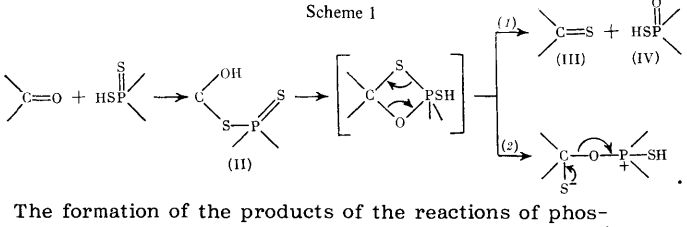
X, Y=O, S; R, R¹=Alk, AlkO, Ar, ArO, $Alk_2N$ .

The isomerisation of symmetrical pyrophosphorothioates to asymmetric compounds[3] and of *S*-phosphorylthiocyanates to *N*-phosphorylisothiocyanates [4] has also been described in detail in the literature and is not therefore discussed here.

## II. THE 1,3-S → O MIGRATIONS

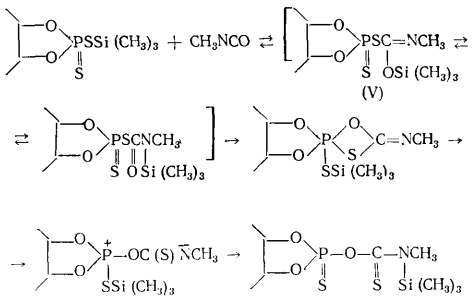
There are few examples of such migrations. The transformation of unstable *gem*-monothioketals (1-hydroxylalkyl phosphorodithioates) (II) into thiocarbonyl compounds (III) and tetracoordinate phosphorus thioacids can be regarded formally as the 1,3-O → S migration of the thiophosphoryl groups[5] (Scheme 1). A one-stage mechanism (pathway *1*) and not a two-stage mechanism (pathway *2*) is then postulated with formation of a transition state analogous to that in the Wittig reaction[6]:

Scheme 1




The formation of the products of the reactions of phosphorodithioic acid with aromatic aldehydes and ketones[6], carbostyril[7], carboxylic acid esters and amides[8,9], isocyanates[10,11], and triphenylphosphine oxide[11] and of *O,O*-dialkyl S-trimethylsilyl phosphorodithioates with benzaldehyde and acetophenone[12] has been described in terms of this or an analogous scheme. There are no data confirming the mechanism of these reactions which are referred to as the "*O,S*-exchange reactions".

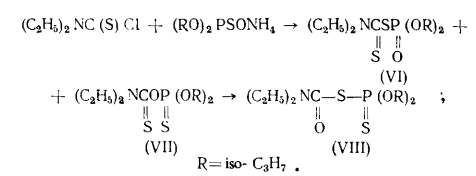
A rearrangement of compounds (V) in which the 1,3-S → O shift is not accompanied by the elimination of the phosphorus-containing fragment, and it is therefore possible to assume that it proceeds via a number of stages, has been reported recently[13]:



(V)

A thiophosphoryl group with acyclic substituents migrates in this situation to the nitrogen and not the oxygen atom[13].

When *N*,*N*-diethylthiocarbamoyl chloride reacts with ammonium di-isopropyl phosphorothioate in acetone, a mixture of *N*-acylation and *O*-acylation products [compounds (VI) and (VII)] is formed in proportions of 4 : 1; the *O*-acylation products (VII) predominate in dimethylformamide (in proportions of 3 : 1):[14]

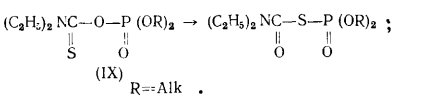


(VI) (VII) (VIII)

R = iso-$C_3H_7$ .

On heating and vacuum distillation, the mixed anhydride (VII) rearranges to the carbamate (VIII).[14]

An analogous rearrangement of compounds (IX) with migration of the phosphoryl group takes place much more readily than in the synthetic process:



(IX)

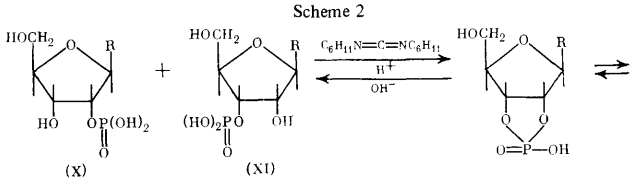
R = Alk .

It has been shown that these rearrangements are irreversible both at room temperature and on heating.

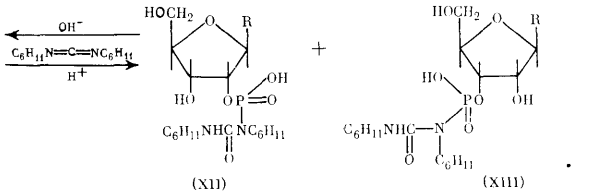
## III. REARRANGEMENTS OF IMIDOYL DERIVATIVES OF PHOSPHORIC AND PHOSPHOROTHIOIC ACIDS

The first reports of the 1,3-O → N migration of phosphoryl groups in imidoyl phosphates were associated with the development of the carbodiimide phosphorylation method, which has found extensive applications in the synthesis of biologically important phosphate esters[15,16]. *N*-Phosphorylated ureas (XII) and (XIII) were identified among the products of the reaction of phosphoric acid monoesters (X) and (XI) with dicyclohexylcarbodiimide (Scheme 2):[17]

Scheme 2

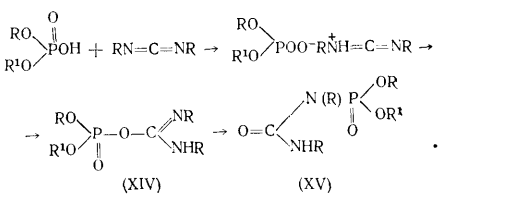


(X) (XI)



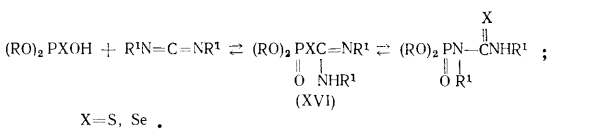
(XII) (XIII)

Subsequently the formation of *N*-phosphorylated ureas in the carbodiimide phosphorylation method was frequently confirmed[18-22]. In all cases the initial formation of the intermediates (XIV), which rearrange to the ureas (XV), was postulated. The "imidoyls" (XIV) have been recently isolated[23]:



(XIV) (XV)

The rearrangements of analogous S- or Se-phosphorylated isothio- or isoselenoureas have been reported in a study of the reactions of dialkyl phosphorothioates, phosphoroselenoates, and phosphorodithioates with carbodiimides[24]. Dialkyl phosphorothioates and phosphoroselenoates add to the C=NH group via the sulphur or selenium atom respectively:



(XVI)

X = S, Se .

The addition products (XVI) can be detected by $^{31}P$ NMR.[25] Their rearrangement is reversible[24]; under the usual conditions, the equilibrium is almost wholly displaced to the right. In the reactions of dicyclohexylcarbodiimide with sterically hindered dialkyl phosphorodithioates the intermediate has been isolated in the form of a salt (XVII) with $HBF_4$,[23] while in the reactions with the corresponding dialkyl phosphates this cannot be done. According to X-ray diffraction data, the distance between the nitrogen and phosphorus atoms in the molecule of compound (XVII) is 3.49 Å. For the oxygen analogue with the same bond angle, the distance between the nitrogen and phosphorus atoms has been estimated as 2.34 Å, which is equal to the sum of the van der Waals radii of the nitrogen and phosphorus atoms; according to the authors[23], this is the cause of the faster rearrangement of *O*-phosphorylisoureas.

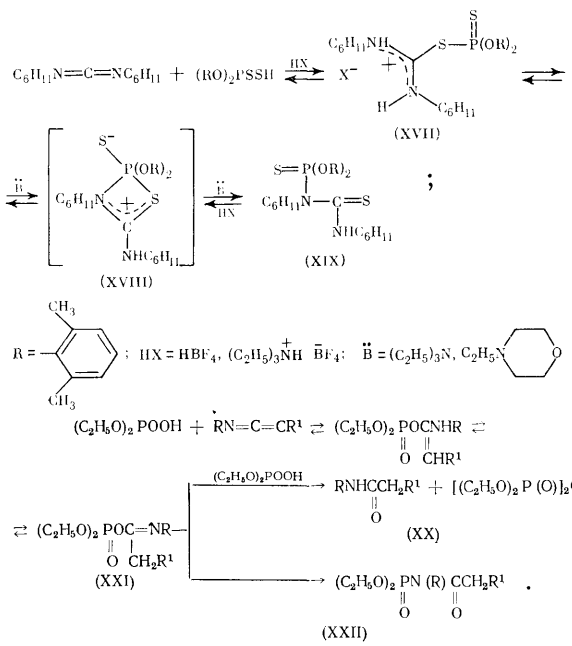
The rearrangement of *S*-thiophosphorylisothioureas (XVII) and the reverse rearrangement are controlled by the acidity of the medium[26]. Bases and acids promote the S → N and N → S migrations respectively. The rearrangement of compounds (XVII) and (XIX) proceeds via the intermediate (XVIII); the transformation (XIX) → (XVII) proceeds via the protonation of the nitrogen in the P–N bond (Scheme 3). The acid-catalysed transformations of compounds (XVII) and (XIX) into the initial compounds show that the reaction system is in overall equilibrium.

A kinetic study of the rearrangement of compounds containing the C–S–P fragment to *N*-phosphorylthioureas showed[26] that the reaction is of first order and takes place without the formation of other kinetically significant intermediates.

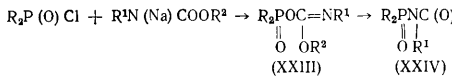
The study of the stereochemistry of the transformation of S(Se)-phosphorylisothio(seleno)ureas into *N*-phosphorylthio-(seleno)ureas [27] demonstrated the complete retention of the configuration at the phosphorus atom. The data obtained support an intramolecular isomerisation mechanism.

The products of the reactions of diethylphosphoric acid with keten imines[28] are, together with tetraethyl pyrophosphate and the amide (XX), the *N*-phosphorylated amides (XXII), formed as a result of the rearrangement of the *O*-phosphorylated derivatives (XXI).

Scheme 3



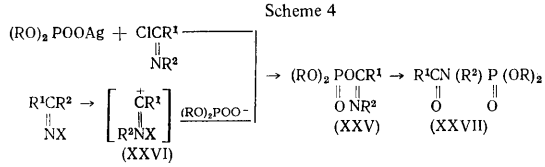
The kinetically controlled products of the phosphorylation of the sodium derivatives of alkyl carbamates are the imidoyl phosphates (XXIII), which were detected in the reaction mixture by infrared spectroscopy[29]:



Compounds (XXIII) readily isomerise to the *N*-phosphorylated carbamates (XXIV).

The high phosphorylating capacity of imidoyl phosphates stimulated investigators to develop convenient methods for their synthesis. The imidoyl phosphates (XXV) have been synthesised (in accordance with Scheme 4) by the reaction of iminochlorides with the silver salts of dialkylphosphoric acids and by a method involving the Beckmann rearrangement[30]. They have not been isolated in a pure form.

Scheme 4

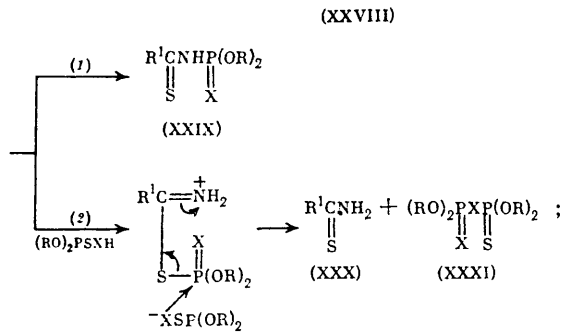


Their formation has been demonstrated by hydrolytic and aminolytic reactions. It has been noted that, when the substituent $R^2$ in compounds (XXV) is a methyl group, then isomerisation to compounds (XXVII) takes place readily, whereas in the case where $R^2$ is a secondary alkyl or phenyl group, there is no appreciable migration of the dibenzylphosphoryl group[31]. According to the data of Zieman et al.[32], the products of the reactions of the alkali metal or ammonium salts of dialkylphosphoric acids with iminochlorides are *N*-phosphorylated amides. The high stability of the imidoyl phosphates (XXV), formed as a result of the thermal Beckmann rearrangement from *O*-phosphorylated derivatives of acetophenone oxime is, therefore, incomprehensible[30].

The O → N migration of the phosphoryl groups in imidoyl phosphates is due to the considerable energy gain on formation of the amide structure, the energy of formation difference $E_{amide} - E_{imidoyl}$ being capable of reaching 20 to 25 kcal mol$^{-1}$ and for this reason the rearrangements are usually irreversible. However, the transformation of *N*-phosphorylamides into *O*-phosphorylisoamides has been observed in the gas phase by mass spectrometry[33]. The analogous 1,3-S → N migrations of phosphoryl groups are reversible. The isomerisation of *N*-phosphorylthioamides has been observed mass-spectrometrically[34]. Such reversibility can also be illustrated in relation to the rearrangement of the products of the addition of partially esterified tetracoordinate thio-acids to cyano-compounds.

The reactions of tetracoordinate phosphorus thioacids with cyano-compounds have attracted the attention of investigators as a method of synthesis of thioamides[35]. In recent years they have been investigated from the standpoint of the rearrangements of imidoyl phosphorothioates. The products of the interaction of tetracoordinate phosphorus dialkylthio- and dialkyldithio-acids with nitriles[36-39], iminoesters[40,41], thiocyanates[42,43], phenyl cyanate[44], and cyanamides[45] isomerise. It has been shown in relation to a large number of examples that, in the first stage of these reactions, the phosphorus thio- and dithio-acids add to the cyano-group with formation of the imidoyl derivatives (XXVIII) (Scheme 5). Phosphoromonothioic acids attack the cyano-group via the sulphur atom[38,44]. However, these compounds are extremely unstable and isomerise even during the reaction to the corresponding *N*-phosphorylated thioamides, thio- and dithio-carbamates, and thioureas (XXIX) (pathway *1*). Compound (XXVIII) can be detected in certain cases by $^{31}$P NMR.[37]

Scheme 5

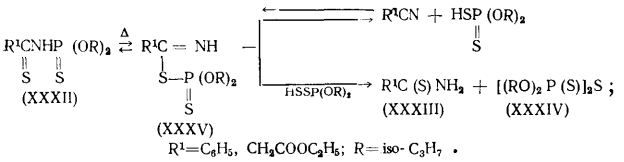


$R^1$=Alk, Ar, $Alk_2N$, AlkS, ArS, ArO, $CCl_3$, $CHCl_2$, $CH_2COOC_2H_5$; R=Alk .

The imidoyl phosphorothioates (XXVIII) also exhibit an exceptionally high phosphorylating capacity and are cleaved at the P–S bond already in the course of the reaction under the influence of the initial thio-acid (pathway *2*), which leads

to the formation of thioamides, thio- and dithio-carbamates, thioureas (XXX), and pyrophosphates (XXXI).

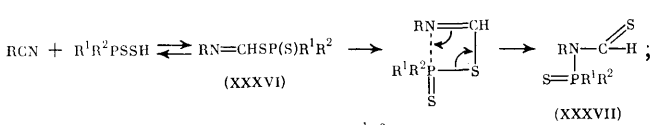
All these reactions are complex and a large number of a wide variety of products are formed. However, under certain conditions, the isomerised products can be isolated in high yields[36,43,46]:



On heating, there is a possibility also of the reverse N → S migration of the thiophosphoryl groups. Thus, when *N*-phosphorylated thiobenzamide or ethoxycarbonylthioacetamide (XXXII), obtained from phosphorous dithioacids and nitriles, were heated, the thioamides of the corresponding carboxylic acids (XXXIII) and pyrophosphorotrithioate were isolated[36]. Compounds (XXXII) are then converted into the imidoyl phosphates (XXXV) with a P–S–C linkage, which are in equilibrium with the initial dithioacids and nitriles, which is confirmed by the isolation of nitriles from the reaction mixture. The dithioacid formed as a result of the dissociation of compound (XXXV) cleaves the P–S bond in the imidoyl phosphorodithioate, as described above. This pathway is characteristic of all the reactions of tetracoordinate phosphorus thio- and dithioacids with cyano-compounds.

The products (XXXVI) of the α-addition of phosphorus dithioacids to 2,6-dimethyl- or 2,6-diethyl-phenylisonitrile (XXXVI) [47] isomerise to *N*-thiophosphorylthioformamides (XXXVII). The main products of the reactions of cyclohexyl-, phenyl-, 4-tolyl-, or 2,5-xylyl-isonitriles with phosphorus dithioacids (Scheme 6) are the formimidoyl phosphorodithioates (XXXVI).[48] In some cases they were isolated in a pure form.

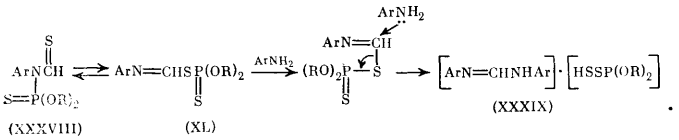
Scheme 6



Even at room temperature, compounds (XXXVI) gradually isomerise to the thioformamides (XXXVII). It has been found[47] that the rearrangement is a first-order reaction. On replacement of the ethoxy-substituents at the phosphorus atom by methoxy-substituents, the rate of rearrangement increases. The reaction is sharply retarded on passing from phosphorodithioates to phosphonodithioates; derivatives of diphenylphosphinodithioic acid are altogether incapable of the rearrangement[47,48]. The tendency towards isomerisation increases with increase of the nucleophilicity of the nitrogen[48,49]. These data suggested[49] that the rearrangement proceeds via an intramolecular four-centre mechanism involving nucleophilic substitution at the tetrahedral phosphorus atom. However, the intramolecular character of this rearrangement cannot be regarded as rigorously demonstrated.

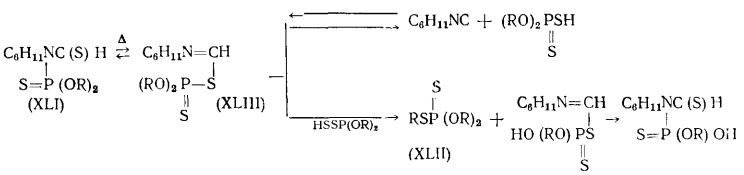
It is believed[47] that this isomerisation is irreversible. According to other investigations[48,49], heating of *N*-dialkylthiophosphorylthioformamides (XXXVIII) with aromatic amines leads to the formation of the phosphorodithioate salts of *N,N'*-diarylformamidines (XXXIX) (Scheme 7) with considerable yields (70–80%).

Scheme 7

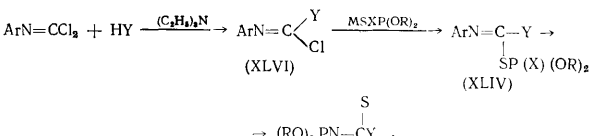


The formation of compound (XXXIX) can be explained only by postulating the reverse 1,3-N → S migration of the thiophosphoryl group, resulting in the formation of imidoyl phosphorodithioates (XL), which give rise to the salts (XXXIX) as a result of the attack by the amine on the imino-carbon atom. The direct interaction of compounds (XXXVIII) with amines results in the formation of other products[48,49].

*O,O,S*-Trialkyl phosphorodithioates (XLII) and cyclohexylisonitrile are obtained in high yields of pyrolysis *in vacuo* of *N*-dialkyl-*N*-cyclohexylthiophosphorylthioformamides (XLI), obtained by the reaction of phosphorus dithioacids with cyclohexylisonitrile[48]:

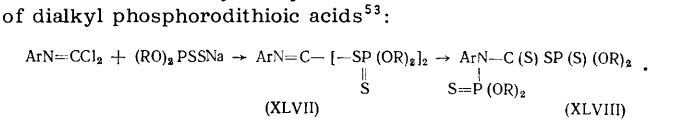


Evidently compounds (XLI) isomerise on heating to compounds (XLIII), which are in equilibrium with the initial isonitrile and the dithioacid. The dithioacid dealkylates[50] the ester group at the phosphorus atom, which results in the formation of the phosphorodithioates (XLII). According to Malz et al.[51], the stepwise substitution of the chlorine atoms in aryl isocyanide dichlorides initially by an alkoxy-, alkylthio-, or amino-group and then by the phosphorothioate or phosphorodithioate group results in the formation of stable compounds with the imidoyl structure of the type of (XLIV). It was later established[52] that in all cases the final products of these reactions are the products of the rearrangement of the imidoyl phosphates (XLIV), namely *N*-thiophosphorylated thio- and dithio-carbamates or the thioureas (XLV). It is noteworthy that, when salts of dialkylphosphoromonothioic acids are introduced into the reaction with the iminochlorides (XLVI), derivatives with the P=O group are formed:



X=O, S; M=H, Na, K, $NH_4$; R=$C_3H_7$, iso-$C_3H_7$; Y=$OCH_3$, iso-$SC_3H_7$, $N(C_2H_5)_2$.

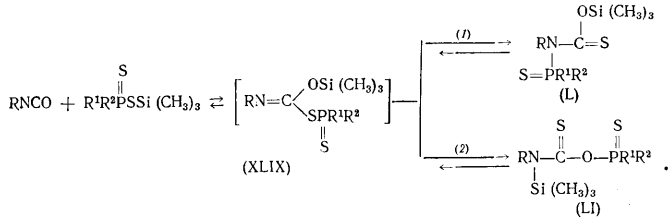
The structure of *S,S*-bis(dialkylthiophosphoryl) isodithiocarbamates (XLVII) has been attributed to the products of the interaction of aryl isocyanide dichlorides with the salts of dialkyl phosphorodithioic acids[53]:



However, detailed studies have shown[54] that in this case compounds (XLVII) rearrange to *N*,*S*-bis(dialkylthiophosphoryl) dithiocarbamates (XLVIII). It is noteworthy that the isomerisation of compounds (XLIV) and (XLVII) takes place irreversibly even at 160 °C.

An interesting situation arises when two groups capable of migration are present in imidoyl phosphorothioates. When silyl phosphorodithioates react with isocyanates[13] (Scheme 8), the imidoyl phosphorodithioates (XLIX) are formed in the first stage. In the case of the acylic dialkoxy-derivatives ($R^1 = R^2 = OAlk$), the 1,3-S → N migration with formation of compound (L) is observed. The introduction of the phenyl or trichloroacyl substituent at the nitrogen atom hinders the S → N migration of the thiophosphoryl group, apparently owing to the reduction of the nucleophilicity of the nitrogen atom:

Scheme 8

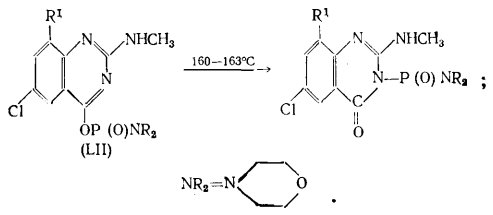


If the phosphorus atom is incorporated in a five-membered ring ($R^1R^2 =$ ), then compounds (XLIX) rearrange via the 1,3-S → O migration of the thiophosphoryl group to the *N*-silyl derivative (LI).

There are several reports in the literature of the 1,3-S → N or O → N migrations of the phosphoryl and thiophosphoryl groups in the series of heterocyclic compounds. The phosphorylation of the ambident anions of heterocyclic amides[55] by phosphorochloridates takes place both at the oxygen atom and at the nitrogen atom. *O*-Phosphorylation is the kinetically controlled reaction stage.

The stability of compounds of type (LII) (Scheme 9) compared with the acyclic imidoyl phosphates (XXV) and (XXI) is due to the presence of a conjugated system of multiple bonds:

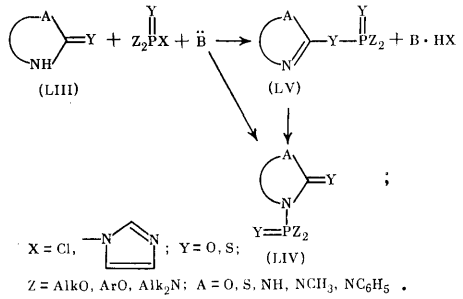
Scheme 9



The thermodynamically more favourable *N*-phosphorylated products are formed via the rearrangement of the *O*-derivatives, which has been demonstrated for compound (LII).

The phosphorylation of a series of heterocycles (LIII) containing urea, carbamate, thiourea, and dithiocarbamate fragments has been investigated (Scheme 10):[56]

Scheme 10

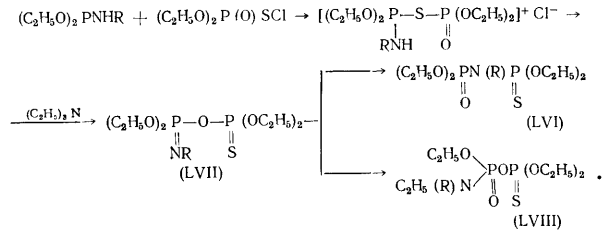


It was found that the phosphorylation is controlled by structural factors both in the substrate and in the reagent. In most cases *N*-phosphorylation products (LIV) are formed as a result of the isomerisation of the *O*- or *S*-phosphorylated intermediates (LV). In one instance the *S*-phosphorylation product (LV, A = Y = S, Z = $OC_6H_5$), which can be regarded as a model of "O-phosphobiotin", was isolated. However, this product does not rearrange. In the case of the oxygen analogues, evidence has been obtained for the existence of kinetically controlled *O*-phosphoryl derivatives on the basis of their ability to function as phorphoryl group transferring agents. The greater stability of the *S*-phosphorylation products compared with that of their oxygen analogues can be explained by the reduced electrophilicity of the phosphorus atom and the greater length of the P–S–C linkage compared with the P–O–C linkage, which hinders the intramolecular migration in the rigid cyclic molecule. Compounds with an open-chain structure, for example, phosphorylated isothioureas, readily isomerise[26,27] (see above).

Thus, in the 1,3-migration of phosphoryl and thiophosphoryl groups, there is a favourable situation in the N=C–O triad for an intramolecular reaction mechanism, while the question of the character of the migration in the N=C–S triad remains controversial; apparently these migrations proceed both intramolecularly and intermolecularly, depending on the structure, the experimental conditions, and the presence of catalysts.

Rearrangements accompanied by the 1,3-O → N migration of phosphoryl groups have been observed also in the iminophosphorus triad. After the reaction of phosphoramidites with phosphorylsulphene chloride[57,58], the phosphoramidite (LVI), formed via Scheme 11 as a result of the rearrangement of the phosphorimidate (LVII), was detected among the reaction products:

Scheme 11



Depending on the nature of the substituent at the nitrogen atom, compounds of type (LVII) are stabilised in two ways[58,59]. If R is an alkyl or phenyl group, the phosphorus-containing

substituent migrates with formation of compound (LVI). If R is an electron-accepting group, then the nucleophilicity of the nitrogen atom is reduced, which entails the migration of the ethyl substituent of the ethoxy-group with formation of compound (LVIII).

It has been found recently[60] that S → N migration takes place in the mixed anhydrides of phosphinimidic and phosphorodithioic acids (LIX):

$$(RO)_2P(S)-S-P(C_6H_5)_2 \rightarrow C_6H_5N(S)-P(OR)_2 ;$$
(LIX)

R=Alk .

The rearrangement proceeds irreversibly at room temperature.

## IV. PHOSPHORYLOTROPIC TAUTOMERISM

The tautomeric processes in which the phosphoryl, iminophosphoryl, or thiophosphoryl groups are the migrating moieties (phosphorylotropism) were first observed for imidoyl derivatives of phosphorothioic acid[61].

A convenient method for the synthesis of compounds used in the study of phosphorylotropism may be provided by the reactions of isothiocyanates with sodium dialkyl phosphites involving the phosphonate–phosphorothioate rearrangement[49] of thiocarbamoylphosphonic acid derivatives in which the P–C bond is influenced by the neighbouring electron-accepting group. The characteristic features of this rearrangement have been investigated recently. It was found that the isomerisation of thiocarbamoylphosphonates requires the presence of electron-accepting substituents at the nitrogen atom[62] and the use of an equimolar or a nearly equimolar amount of a strong base in order to convert the thiocarbamoyl phosphonate into the ionised form active in the rearrangement.

The reactions of sodium di-isopropyl phosphite with methyl and allyl isothiocyanates in boiling benzene for 10–12 h lead to unisomerised products with a P–C bond[62]; the interaction of dialkyl phosphites and their analogues with isothiocyanates in the presence of catalytic amounts of bases under mild conditions has the same result[63–65].

The interaction of the sodium or potassium salts of dialkyl phosphites with phenyl isothiocyanate at 80–145 °C is accompanied by the phosphonate–phosphorothioate rearrangement of the phenylthiocarbamoylphosphonates (LX) to dialkyl *S*-phenyliminomethyl phosphorothioates and phosphorodithioates (LXI).[66] The products (LXI) are also formed on heating the pure phenylthiocarbamoylphosphonates (LX) in an equimolar amount of sodium dialkyl phosphite[66]:

$$C_6H_5NCS + HP(X)R_2 \rightarrow \underset{(LX)}{C_6H_5NHC(S)P(X)R_2} \xrightarrow{NaXPR_2} \rightarrow \underset{(LXI)}{C_6H_5N{=}CH{-}S{-}P(X)R_2} \rightleftarrows \underset{X=PR_2}{C_6H_5NCH{=}S} \quad (LXII) ;$$

X=O, S .

Compounds (LXI) are capable of phosphorylotropic tautomerism[62]. At room temperature the equilibrium is 90–95% displaced towards the thioformamide (LXII). However, like the compounds described by Zinin and co-workers[48,67], compounds (LXI) undergo further reactions on heating. The interaction of sodium di-isopropyl phosphite with phenyl isothiocyanate (Scheme 12), followed by treatment of the reaction mixture with methyl iodide, yielded a tautomeric mixture, from which compound (LXIII) and (LXIV) can be isolated[62]:

Scheme 12

$$C_6H_5NCS + (RO)_2PO^- \rightarrow \underset{(LXV)}{C_6H_5N{=}C(S^-)P(O)(OR)_2} \xrightarrow{CH_3I} \underset{(LXIII)}{C_6H_5N{=}C(CH_3)SP(O)(OR)_2} \rightleftarrows \underset{(LXIV)}{C_6H_5N(CH_3)C(S){=}P(O)(OR)_2} ;$$

R = iso-$C_3H_7$

It has been suggested[66,68] that the rearrangement of thiocarbamoylphosphonates proceeds via a three-centre $S_N2(P)$-mechanism. In the anion (LXV) there are two nucleophilic centres capable of attacking the electrophilic phosphorus atom. The nucleophilic reactivity of sulphur is apparently greater than that of nitrogen. This has also been demonstrated in relation to the reaction of *O,O*-di-isopropylthiophosphoryl isothiocyanate with sodium diethyl phosphite (Scheme 13):

Scheme 13

$$(RO)_2P(S)NCS + (C_2H_5O)_2PO^- \rightarrow \underset{}{(RO)_2N{=}C(S^-)P(OC_2H_5)_2} \xrightarrow[\Delta]{CH_3I} \underset{(LXVI)}{(RO)_2PN{=}C(CH_3)SP(OC_2H_5)_2} ;$$

R = iso-$C_3H_7$ .

The 1,2-C → S migration product (LXVI) is then formed; compounds whose formation mechanism involves the 1,2-C → N migration of the diethylphosphoryl group were not detected. Separate experiments demonstrated that the presence of electron-accepting substituents at the imino-nitrogen atom in compounds of type (LXVI) prevents phosphorylotropic transformations. On the other hand, such transformations are characteristic of *N*-aryl-substituted compounds (LXVII), which can be obtained by the reaction of iminochlorides with salts of tetracoordinate phosphorus monothio- and dithioacids[61]:

$$RC(Cl){=}NC_6H_4Y + NaXSPR^1R^2 \rightarrow \underset{(LXVII)}{RC(S{-}P(X)R^1R^2){=}NC_6H_4Y} \rightleftarrows \underset{(LXVIII)}{RC(S)C_6H_4Y{-}N{=}P(X)R^1R^2} ;$$

X=O, S; Y=H, *p*-Br, *p*-$CH_3$, *p*-$CH_3O$, *p*-$NO_2$;
R=$C_6H_5$; $R^1$=$R^2$=AlkO .

The salts of tetracoordinate phosphorus monothio-acids always react via the sulphur atom of the thiophosphoryl group.

The occurrence of the phosphorylotropism of compounds of type (LXIII) and (LXVII) has been demonstrated by a combined infrared, $^1H$ NMR, and $^{31}P$ NMR spectroscopic study. Two signals in the ranges 58–64 and 78–85 p.p.m. (for the phosphorodithioate derivatives) or −3–−5 and 15–18 p.p.m. (for the phosphoromonothioate derivatives), referring to the thioamide (LXVIII) and imidothiolic (LXVII) forms respectively, are observed in the $^{31}P$ spectra at room temperature. On heating, the intensity of the indicator signal of the imidothiolic form (LXVII) increases, while that of the thioamide form (LXVIII) falls. When the initial temperature is restored, the system returns to the original state.

In certain cases the tautomers can be isolated in a pure form under the usual conditions. Thus the thioamide isomer is usually crystallised from solutions in pentane.

With increase of temperature, an increase of the content of the thermodynamically less favourable imidothiolic form (*a*) is observed in all cases (Table 1). Table 1 shows that the conversion of the isomer (A) into the isomer (B) is exothermic. The quantity $\Delta H$ does not change in the temperature range 19–120 °C.

Table 1. The influence of temperature on the thermodynamic characteristics of the tautomeric equilibrium (condensed phase) [54]*

$C_6H_5C{=}NC_6H_4Y\text{-}p \rightleftarrows C_6H_5C(S)\text{—}NC_6H_4Y\text{-}p$
$S\text{—}P(X)(OR)_2$ (A); $S\text{—}P(X)(OR)_2$ (B)

| R | X | Y | $-\Delta H$, kcal mol$^{-1}$ | 292 K: *a*, % | 292 K: $-T\Delta S$, kcal mol$^{-1}$ | 373 K: *a*, % | 373 K: $-T\Delta S$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $CH_3$ | S | H | 1.3 | 42 | 1.1 | 52 | 1.4 |
| $C_2H_5$ | S | H | 2.6 | 45 | 2.3 | 66 | 3.1 |
| $C_3H_7$ | S | H | 3.4 | 44 | 3.2 | 76 | 4.4 |
| iso-$C_3H_7$ | S | H | 3.4 | 51 | 3.4 | 83 | 4.5 |
| $C_4H_9$ | S | H | 5.0 | 48 | 4.7 | 82 | 6.3 |
| iso-$C_3H_7$ | S | $CH_3$ | 2.9 | 47 | 2.6 | 64 | 3.5 |
| iso-$C_3H_7$ | S | Br | 2.2 | 73 | 2.6 | 83 | 3.5 |
| iso-$C_3H_7$ | O | Br | 4.0 | 11 | 1.3 | 25 | 1.7 |
| $C_2H_5$ | O | H | 2.7 | 5 | 1.0 | 12 | 1.3 |

*Here and henceforth *a* represents the content of the isomer (A).

The free energies $\Delta G$ do not exceed 2 kcal mol$^{-1}$,[54] which falls within the range of tautomeric processes on the thermodynamic scale[69]. The quantities $\Delta H$ and $T\Delta S$ are comparable, from which it follows that the state of equilibrium is influenced not only by the difference between the heats of formation but also by the difference between the entropies. At room temperature the enthalpy factor predominates somewhat over the entropy factor, but, with increase of temperature, the entropy factor begins to play a major role and becomes dominant for imidoyl phosphorodithioates at 100 °C.

The observed relation reflects the influence of two opposed thermodynamic factors. As a consequence of the large barrier to the "amide rotation",[70] the transition to the thioamide entails the loss of degrees of freedom by the molecule and an increase of the absolute value of the entropy, which destabilises the thioamide. On the other hand, the large energy gain on formation of the P–N and C=S bonds stabilises the thioamide form.

Compounds with the P=O group are influenced by temperature to a lesser extent than their thio-analogues (Table 1). The enthalpy factor for these compounds predominates somewhat even at 100 °C; comparison of the $\Delta G$ shows that the replacement of the P=S group by P=O leads to an increase of the difference between the thermodynamic stabilities of the tautomers.

The composition of the tautomeric mixtures depends on the state of aggregation. In the crystalline state the imidothiolic isomer (A) is not usually detected by infrared spectroscopy. In the liquid phase at the same temperature the content of the isomer (A) is considerable.

The composition of the tautomeric mixture in solutions differs strongly from its composition in the liquid or crystalline state. Since the two forms belong to different classes of organic compounds, the influence of the nature of the solvent is significant. Transition to solutions affects the thermodynamic characteristics of the phosphorylotropic tautomerism in different ways and can entail a shift of equilibrium in the opposite direction. The equilibrium position in both the condensed phase and in solutions is influenced by the enthalpy and entropy factors.

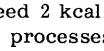
The results of the study of the dependence of $K_{TS}$ on the nature of the solvent (Table 2) were treated by the method described in Palm's book[71]. The regression equation is

$$\lg K_{TS} = 0.196 + (0.915 \pm 0,114)\,Y + (0,657 \pm 0.207)\,P + \\ + (0,124 \pm 0.017)\cdot 10^{-2}\,B \quad (r = 0.986),$$

where $P$ is the polarisability, $Y$ the polarity, and $B$ the nucleophilicity of the solvent. The contribution of the electrophilicity of the solvent is insignificant. Thus the position of the tautomeric equilibrium is greatly influenced not only by electrostatic interactions but also by specific interactions.

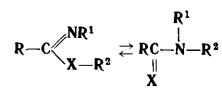
Table 2. The influence of the nature of the solvent on the position of the equilibrium ($c$ = 0.1 M, 292 K) [54]

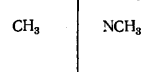
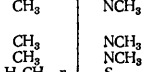
$C_6H_5C{=}NC_6H_4OCH_3\text{-}p \rightleftarrows C_6H_5C(S)\text{—}NC_6H_4OCH_3\text{-}p$
$S\text{—}P(S)(OC_3H_7\text{-iso})_2$ (A); $S\text{—}P(S)(OC_3H_7\text{-iso})_2$ (B)

| Solvent | *a*, % | $K_{TS}$ | $-\Delta G$, kcal mol$^{-1}$ |
|---|---|---|---|
| —* | 19 | 4.26 | 0.81 |
| $CCl_4$ | 36 | 1.78 | 0.33 |
| $CS_2$ | 33 | 2.03 | 0.41 |
| $C_6H_5CH_3$ | 33 | 2.03 | 0.41 |
| $C_6H_6$ | 31 | 2.23 | 0.46 |
| $CHCl_3$ | 31 | 2.23 | 0.46 |
|  | 29 | 2.45 | 0.52 |
| $CH_2Cl_2$ | 27 | 2.70 | 0.58 |
| $C_6H_5NO_2$ | 26 | 2.85 | 0.61 |
| $C_6H_5Br$ | 26 | 2.85 | 0.61 |
| $C_6H_5I$ | 25 | 3.00 | 0.64 |
| $C_6H_5Cl$ | 24 | 3.17 | 0.67 |
| $C_6H_4(CH_3)_2\text{-}p$ | 31 | 2.23 | 0.46 |
| $C_6H_5CN$ | 23 | 3.35 | 0.70 |
| $BrCF_2\text{—}CF_2Br$ | 22 | 3.55 | 0.73 |
| $CH_3CN$ | 18 | 4.56 | 0.84 |
| $C_6H_5C(O)CH_3$ | 16 | 5.25 | 0.96 |
| $(CH_3)_2C{=}O$ | 14 | 6.14 | 1.05 |

*Condensed phase.

Table 3. The activation paramters for the tautomeric transformation [54,73]

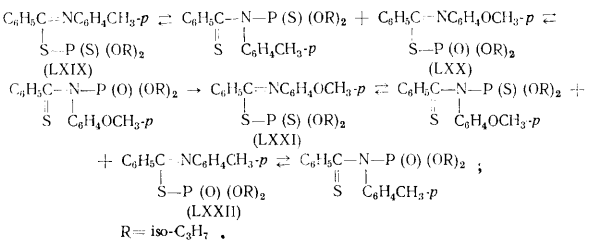


| Compound | R | $R^1$ | X | $R^2$ | $\Delta G^{\neq}$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|
| (LXXIII) | $C_6H_5$ | $CH_3$ | $NCH_3$ | $O{=}P(OC_2H_5)_2$ | 24.9 (447 K) |
| (LXXIV) * | $C_6H_5$ | $CH_3$ | $NCH_3$ | $C_6H_5N{=}P(OC_2H_5)_2$ | 23.6 (447 K) |
| (LXXV) ** | $C_6H_5$ | $CH_3$ | $NCH_3$ | $O{=}P(OCH_2CF_2CHF_2)_2$ | 18.8 (350 K) |
| (LXXVI) | $C_6H_5$ | $CH_3$ | $NCH_3$ |  | ⩽8 (173 K) |
| (LXXVII) | $CF_3$ | $CH_3$ | $NCH_3$ |  | 21.7 (447 K) |
| (LXXVIII) | $C_6H_5$ | $CH_3$ | $NCH_3$ | $P(O)F_2$ | ⩽8 |
| (LXXIX) | $CHCl_2$ | $CH_3$ | $NCH_3$ | $O{=}P(OC_2H_5)_2$ | >25 |
| (LXXX) | $C_6H_5$ | $C_6H_4CH_3\text{-}p$ | S | $P(S)(OC_3H_7\text{-iso})_2$ | 21.2 (398 K) |
| (LXXXI) *** | $C_6H_5$ | $C_6H_4OCH_3\text{-}p$ | S | $P(S)(OC_3H_7\text{-iso})_2$ | 20.0 (388 K) |

*$\Delta H^{\neq}$ = 18.1 kcal mol$^{-1}$, $\Delta S^{\neq}$ = −12.4 e.u.
**$\Delta H^{\neq}$ = 9.4 kcal mol$^{-1}$, $\Delta S^{\neq}$ = −27 e.u.
***$\Delta H^{\neq}$ = 17.1 kcal mol$^{-1}$, $\Delta S^{\neq}$ = −8.1 e.u.

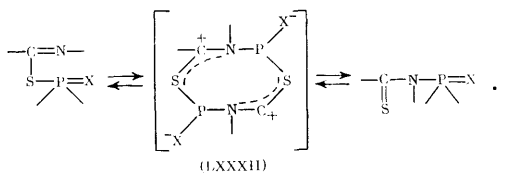
The barrier to the *E*, *Z*-topomerisation of the imidoyl form is evidently low (~10 kcal mol$^{-1}$) and the individual tautomers are not detected by $^1$H NMR in the temperature range 30 to 100 °C. The barriers to the "amide" rotation about the P–N bond in N-di-isopropylphosphorylthioacetanilide and *N*-di-isopropylphosphorylthiopropionanilide are 14.8 and 14.6 kcal mol$^{-1}$ respectively[70]. The phosphorylotropism in the thioamide triad is the slowest dynamic process ($\Delta G$ = 20–21 kcal mol$^{-1}$) (Table 3).

It has been noted that the rate of equilibration for *N*-thiophosphorylthioamides depends on the concentration of the solution, which indicates the intermolecular character of the tautomerism. This is confirmed by the identity of the $^1$H NMR spectra of compounds (LXIX) and (LXX) and the artificial mixture of the tautomers (LXIX)–(LXXII) prepared taking into account the intermolecular exchange:



EPR and $^{31}$P NMR studies using the method of chemically induced nuclear polarisation have made it possible to exclude the radical mechanism of phosphorylotropism. It has been suggested[54] that the phosphoryl exchange involving the imidoyl derivatives of tetracoordinate phosphorus proceeds via the cyclic dimeric form (LXXXII) and constitutes a kind of transacylation reaction involving the transfer of the reaction centre (Scheme 14):

Scheme 14



(LXXXII)

The dependence of the tendency towards tautomerism on structural factors is consistent with the proposed mechanism. The introduction at the carbon atom of the C=N double bond in imidoyl phosphorothioates and imidoyl phosphorodithioates of substituents which promote the delocalisation of the positive charge on the carbon atom of the intermediate (LXXXII) facilitates the tautomeric transformations. This is manifested by the fact that the replacement of the phenyl group by the methyl group or by a hydrogen atom leads to the absence of tautomerism. In this case imidoyl phosphorodithioates (LXVII) readily isomerise at room temperature to the corresponding thioamides (LXVIII),[48,54] but the reverse transformation is observed only on heating. When the phenyl group is replaced by the t-butyl group, the imidoyl isomer is the only one present and is incapable of rearrangement.

The environment of the phosphorus atom influences radically the position of the tautomeric equilibrium (Table 4). With increase of the length of the alkoxy-group, the equilibrium is displaced somewhat towards the imidoyl isomer, while on replacement of the P=S by the P=O group, there is a sharp shift in the direction of the thioamide isomer. The replacement of one alkoxy-group at the phosphorus atom by an alkyl or phenyl substituent in compounds with both P=O and P=S groups results in the attainment of equilibrium only at 180–200 °C. It has been demonstrated by differential thermal analysis that the process proceeds via a single stage, which is not inconsistent with the proposed mechanism. When both alkoxy-groups are replaced by phenyl groups, the rearrangement of imidoyl phosphinodithioates does not take place either at room or elevated temperatures. The products of the postulated isomerisation (*N*-phosphinothioylthioamides), obtained by other methods[72], are incapable of the reverse rearrangement with the 1,3-N → S migration of the diphenylphosphinothioyl group. An increase of the barrier to the interconversion in this instance is evidently associated with the decrease of the electrophilicity of the phosphorus atom and steric hindrance. In particular, the ligand exchange in the intermediate (LXXXII) is hindered by the weaker apicophilic properties of the alkyl and phenyl groups compared with the alkoxy-groups[74].

Table 4. The influence of the nature of the substituent at the phosphorus atom on the tautomeric transformation (292 K) [54]



| R$^1$ | R$^2$ | X | Y | *a*, % | |
|---|---|---|---|---|---|
| | | | | 0.3 M solution in $CCl_4$ | Condensed phase |
| $CH_3O$ | $CH_3O$ | S | H | — | 42 |
| $C_2H_5O$ | $C_2H_5O$ | S | H | 45 | 45 |
| $C_3H_7O$ | $C_3H_7O$ | S | H | 47 | 44 |
| iso-$C_3H_7O$ | iso-$C_3H_7O$ | S | H | 57 | 51 |
| $C_4H_9O$ | $C_4H_9O$ | S | H | 58 | 48 |
| iso-$C_3H_7O$ | iso-$C_3H_7O$ | O | H | — | 5 |
| iso-$C_3H_7O$ | iso-$C_3H_7O$ | S | $NO_2$ | 100 | 100 |
| iso-$C_3H_7O$ | iso-$C_3H_7O$ | O | $NO_2$ | — | 40 |
| iso-$C_3H_7O$ | $C_2H_5$ | S | H | 100 | 100 |
| iso-$C_3H_7O$ | $C_2H_5$ | S | $CH_3$ | 100 | 100 |
| $C_6H_5$ | $C_2H_5$ | S | H | 100 | 100 |
| $C_6H_5$ | $C_6H_5$ | O | H | 100 | 100 |

Table 5. The influence of the substituents at the nitrogen atom on the position of the tautomeric equilibrium (condensed phase, 292 K) [54]

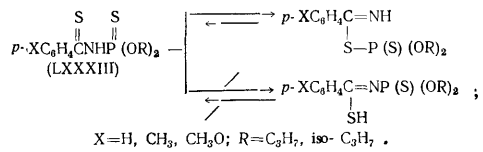


| R | X | *a*, % | R | X | *a*, % |
|---|---|---|---|---|---|
| $C_2H_5$ | $C_6H_4OCH_3$-*p* | 19 | $C_2H_5$ | $C_6H_4Br$-*p* | 65 |
| $C_2H_5$ | $C_6H_4OCH_3$-*o* | 20 | iso-$C_3H_7$ | $C_6H_4NO_2$-*p* | 100 |
| $C_2H_5$ | $C_6H_4CH_3$-*p* | 35 | iso-$C_3H_7$ | $CH_3$ | 0 |
| $C_2H_5$ | $C_6H_5$ | 45 | iso-$C_3H_7$ | H | 0 |

The introduction of electron-accepting substituents into the benzene ring at the nitrogen atom shifts the equilibrium towards the imidoyl isomer (Table 5). Electron-donating substituents displace the equilibrium in the opposite direction. When the aryl group is replaced by a methyl group or a hydrogen atom, the thioamide isomer is the only one present. For compound (LXXXIII), equilibrium, strongly displaced in the direction of the thioamide isomer, is

observed at elevated temperatures[75]. Thus substituents capable of delocalising the positive charge on the nitrogen atom of the intermediate (LXXXII) promote the tautomeric transformations.

It has been shown for compounds (LXXXIII) [75] that, when the capacities for the 1,3-migration of hydrogen and the phosphoryl group are identical, phosphorylotropic and not thione–thiol tautomerism obtains:



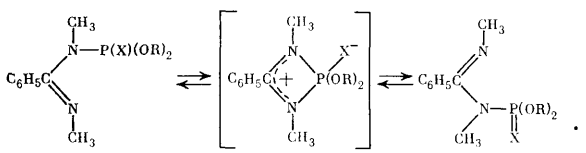

The study of the chemical behaviour of tautomeric *N*-phosphorylthioamides revealed their phosphorylating capacity and a high tendency to undergo reactions of the type of transacylation. When a mixture of the tautomers (LXXXV) and (LXXXVI) in benzene, where the contents of the imidoyl and amide forms are approximately the same, was treated with aromatic amines, the phosphorodithioate salts of arylamidines (LXXXVII) were isolated (Scheme 15). The tautomers (LXXXV) and (LXXXVI) hydrolyse to the thioamides (LXXXVIII), disproportionate with formation of the pyrophosphate (LXXXIX) and the sulphide (XC), and react with heavy metal ions to form complexes with the isoamide structure (XCI).[75,76] The products of the reaction of the tautomers (LXXXV) and (LXXXVI) with carboxylic acids are the amides (XCII) and the acyl phosphorothioates and phosphorodithioates (XCIII) (thioacetic acid reacts analogously).

The formation of the benzamides (XCII) and the phosphorothionates (XCIII) shows that the reactions with acids proceed via a mechanism involving transacylation as the first stage; this can be demonstrated by $^{31}P$ NMR and by isolating the product of the addition of di-isopropylphosphorodithioic acid to acrylonitrile when the reaction with acetic acid is carried out in the presence of the latter. These results suggest that the dissociative mechanism of the tautomeric transformation is unlikely. If the P=S bond were dissociated, one would expect the formation of thiobenzanilide and dialkyl phosphite, which, however, have not been isolated or detected by physicochemical methods.

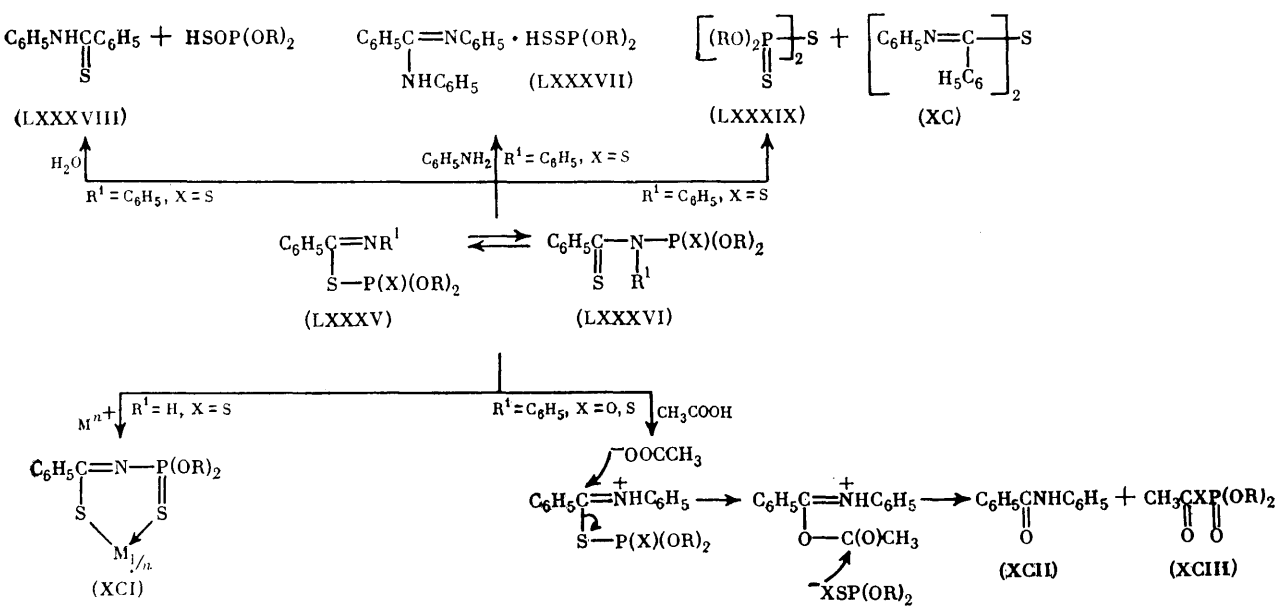
Thus not only the thioamide but also the imidoyl form possesses dual reactivity involving both electrophilic centres—the phosphorus atom and the carbon atom of the C=N bond.

After the discovery of phosphorylotropism in the thioamide triad, the stereochemical behaviour of the phosphorylated *N*,*N'*-dimethylbenzamidines was explained by the occurrence of tautomeric transformations (Scheme 16):[77]

Scheme 16

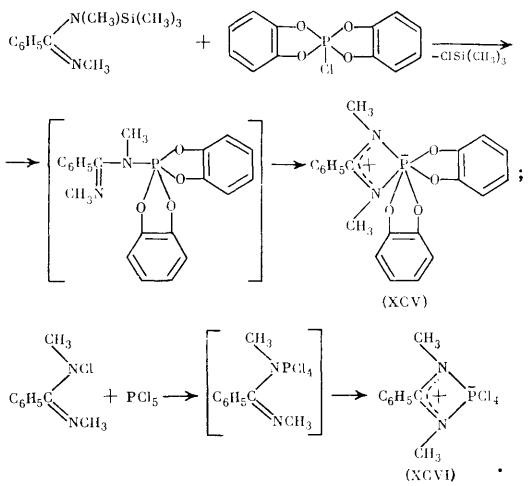



Scheme 15



The presence of the degenerate amidine triad, which makes it possible to enter automatically the region of tautomeric processes on the thermodynamic scale, and the existence of methods developed for the investigation of such tautomerism[69] made it possible to obtain important information about the mechanism of the phosphoryl exchange. The phosphoryl migrations in the amidine triad usually occur via an intramolecular mechanism, tentatively via a stage involving the formation of the cyclic intermediate (XCIV) with a trigonal-bipyramidal configuration of the phosphorus atom[73]. Treatment of amidine derivatives with spiro-chlorobis(phenylenedioxy)phosphorane or $PCl_5$ leads to the formation of the phosphorane derivatives (XCV) and (XCVI) via Scheme 17.[78]

Scheme 17

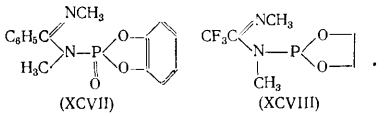


(XCV)

(XCVI)

Although this entails the formation of hexacoordinate and not pentacoordinate derivatives of phosphorus, presumably this type of mutual approach of reaction centres, necessary for intramolecular migrations, can be achieved also in phosphorane intermediates. However, the phosphorane intermediates cannot be detected by physicochemical methods.

It has been concluded[79] that there is no intermolecular exchange of phosphorus-containing groups when compounds (XCVII) and (XCVIII) are heated together. The intermolecular tautomeric process N ⇌ N′ with migration of phosphorus(III) was observed for the latter compound:

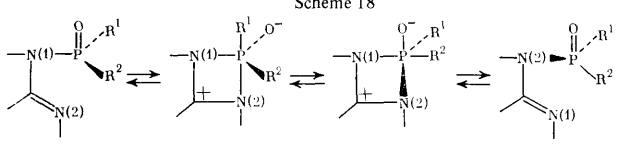


(XCVII) (XCVIII)

The intramolecular mechanism of the phosphoryl migration in amidines has been confirmed by the retention of the spin–spin coupling constants $J(PH)$ and $J(PC)$, whereas in the case of intermolecular migrations these constants would have been averaged out to zero[77].

The geometry of the amidine triad ensures the possibility of only the axial-equatorial disposition of the attacking and leaving nitrogen atoms in the phosphorane intermediate, so that, in conformity with the principle of microscopic reversibility, the latter should undergo ligand exchange via Scheme 18.[69]

Scheme 18

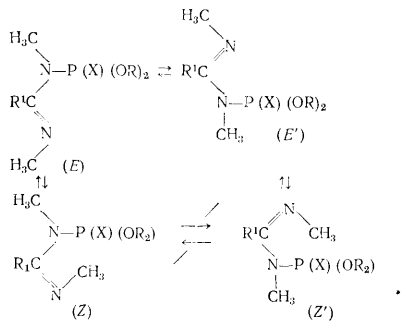


The negative activation entropies (Table 3) indirectly confirm the intramolecular multistage mechanism of the tautomeric transformation, requiring a considerable reorganisation of the molecule. A stereochemical study showed that the tautomeric transformations take place without inversion of the configuration of the phosphorus atom[79]. If the attack on, and elimination of, the nitrogen atom occurred synchronously, for example via an $S_N2$ mechanism, bypassing the permutation isomerisation stage, this would entail inversion of the configuration of the phosphorus atom. The considerable decrease of the free energy of activation for the tautomeric process (Table 3), involving the incorporation of the phosphorus atom in a dioxa- or benzodioxa-phospholan ring, stabilising the phosphorane intermediate, is consistent with the proposed mechanism[80].

Apart from phosphorylotropism, $E \rightleftharpoons Z$ topomerisation is observed for phosphorylated amidines. The activation energies for these processes can be similar [for example, for compounds (LXXIII), (LXXIV), and (LXXVII); Table 3].

Theoretical calculation of the $^1H$ NMR spectra for the four-position exchange of topomers ($Z \rightleftharpoons E \rightleftharpoons E' \rightleftharpoons Z'$; Scheme 19) and comparison of the theoretical and experimental spectra made it possible to exclude the possibility of phosphoryl migrations for the Z,Z-isomers:[79]

Scheme 19

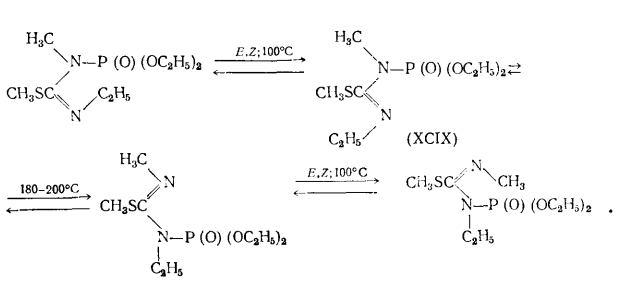


From the standpoint of the intramolecular mechanism, this can be explained by the unfavourable orientation of the unshared electron pair of the imino-nitrogen for a nucleophilic attack on the phosphorus atom.

The free energy of phosphoryl migrations (Table 3) is reduced somewhat when the $CHCl_2$ group at the carbon atom is replaced by a phenyl substituent, which promotes the delocalisation of the positive charge of the intermediate (XCIV). The introduction of electron-accepting substituents at the phosphorus atom greatly reduces the free energy of activation for the tautomeric transformation, which is caused by the increased electrophilicity of the phosphorus.

On passing from phosphorylated amidines to the corresponding derivatives of *S*-methylisothiourea (XCIX), the phosphoryl exchange is observed at a higher temperature (Scheme 20); $\Delta G^{\neq}$ increases to ~26 kcal mol$^{-1}$:[81]

Scheme 20



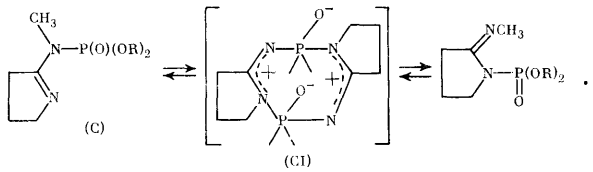
When even one alkyl group at the nitrogen atoms in *S*-alkyl-*N*-phosphorylisothioureas is replaced by hydrogen, the capacity for phosphorylotropism disappears[82]. Prototropic tautomerism occurs in this instance:

$$R^1R^2P(X)NHC(SR^3)=NH \rightleftarrows R^1R^2P(X)N=C(SR^3)NH_2 ,$$

X = O, S; $R^1$, $R^2$ = Alk, AlkO; $R^3$ = Alk, Ar .

The incorporation of one of the nitrogen atoms of the amidine triad in the ring alters the mechanism of the phosphoryl migration[83] (Scheme 21):

Scheme 21



The rate of migration and the half-life of *N*-phosphorylated 2-methylaminopyrrolines (C) depend on the concentration of the solution and the nature of the solvent. On passing to polar solvents, the process is accelerated, which indicates the intermolecular character of the tautomerism; it has been suggested that its mechanism involves the formation of the polar dimeric form (CI) as the intermediate state. The thermodynamic quantities of activation $\Delta G^{\neq} = 28$ kcal mol$^{-1}$ and $\Delta H^{\neq} \cong 21$ kcal mol$^{-1}$ for this type of tautomerism exceed somewhat the values for intramolecular migrations (cf. Table 3), but the activation entropy is the same (−22 e.u.). It is of interest to note that the ratio of the isomers in deuterochloroform and nitrobenzene is approximately the same[83].

The influence of the nature of the heteroatoms between which the phosphoryl or thiophosphoryl groups migrate can be traced in relation to the rearrangements and tautomeric transformations of phosphorylated thioamides and amidines. The 1,3-O → N and N ⇌ N′ shifts take place most readily. They are less susceptible to acid–base catalysis and an intramolecular mechanism involving a four-membered phosphorane intermediate is preferred for such processes with the exception of those cases where this is prevented by the orientation of the unshared electron pair of the imino-nitrogen. With increase of the difference between the electronegativities and apicophilicities of the atoms, the rearrangement cannot always be fitted within the framework of the intramolecular mechanism. The 1,3-S ⇌ N and 1,3-Se ⇌ N shifts can be catalysed by acids and bases. Furthermore, the S(Se)–C bonds are unusually labile in the thio(seleno)-phosphorylated isothioamides, isothioureas, and isothiocarbamates, which is manifested by the ease of the dissociation of the P–S(Se)–C fragment with elimination of the thio- or seleno-phosphoryl group.

## V. 1,4-MIGRATIONS AND LONGER-DISTANCE MIGRATIONS

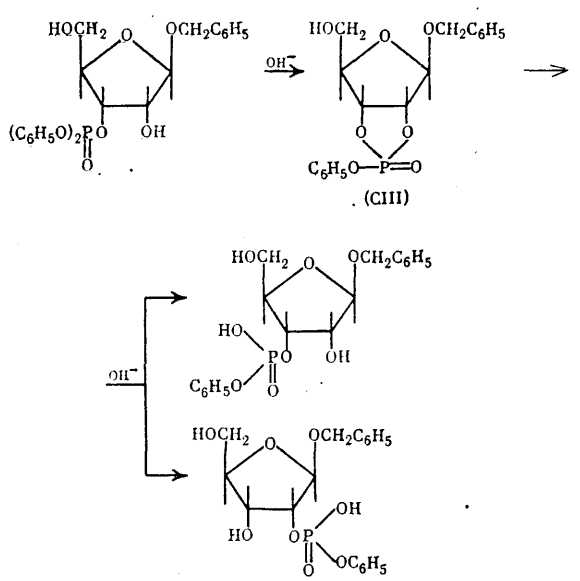
The 1,4-O ⇌ O′ shift of the phosphoryl group was first observed on refluxing an aqueous solution of 2-glycerophosphate (CII) in the presence of $H_2SO_4$.[84] This rearrangement is reversible[85]:

$$(HO)_2P(O)OCH(CH_2OH)CH_2OH \overset{H^+}{\rightleftarrows} (HO)_2P(O)OCH_2CH(OH)CH_2OH$$

(CII); 10% 90%

According to Khorana[15], the 1,4-O ⇌ O′ transfer of the phosphoryl group proceeds via the cyclic phosphate (CIII), as happens in the mild alkaline hydrolysis of sugar phosphates[86]. Under the influence of hydroxide ions, the phosphate ring can be cleaved on both sides (Scheme 22):

Scheme 22

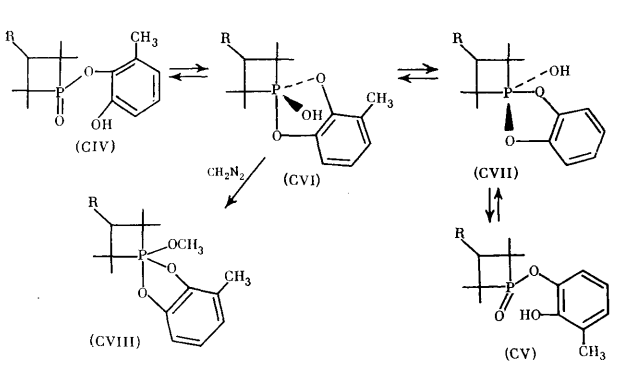


An analogous scheme has been proposed also for the reactions of sugar phosphates with carbodiimides[15,19]. In this case the 1,4-O → O′ shift is also accompanied by the 1,3-O → N shift of the phosphoryl group.

It has been shown recently[87] that the reversible isomerisation of *o*-hydroxyphenyl phosphinates (CIV) to compounds (CV) proceeds via intermediates (CVI) and (CVII) of the hydroxyphosphorane type via Scheme 23.

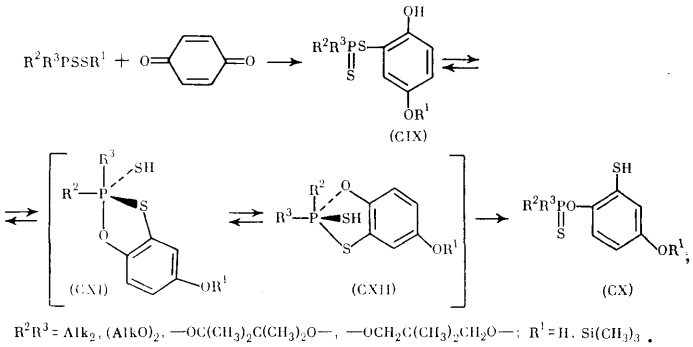
On treatment with diazomethane, the product of the methylation of the hydroxyphosphorane (CVIII) was isolated. The free energy of activation for the transition (CIV) ⇌ (CV) is 17.5 kcal mol$^{-1}$. When the phosphetan ring in compound (CIV), stabilising the spiro-phosphorane structure[88], is replaced by phenyl groups, the activation energy increases to 24.2 kcal mol$^{-1}$. The transition from phosphinates to their thio-analogues leads to an increase of the activation energy for the process by 4–5 kcal mol$^{-1}$. These results suggest that the isomerisation proceeds via a mechanism involving intramolecular nucleophilic substitution at the tetrahedral phosphorus atom:

Scheme 23



The isomerisation of *S*-(2-hydroxyphenyl) esters of phosphorus thioacids probably proceeds analogously via a stage involving the formation of mercaptophosphoranes. Products of type (CIX), formed in the reaction of dialkylphosphorodithioic acids and their silyl esters with *p*-benzoquinone, naphthoquinone, and *N*-benzenesulphonyl-*p*-benzoquinone, isomerise to phosphorothioates of type (CX).[89] This rearrangement proceeds only in one direction—towards the formation of the more acidic thiol (CX) (Scheme 24):

Scheme 24

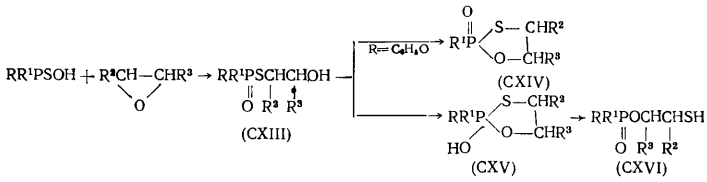


$R^2R^3$ = Alk$_2$, (AlkO)$_2$, —OC(CH$_3$)$_2$C(CH$_3$)$_2$O—, —OCH$_2$C(CH$_3$)$_2$CH$_2$O—; $R^1$ = H, Si(CH$_3$)$_3$.

Diphenylphosphinodithioates rearrange only in the presence of an equimolar amount of triethylamine. The study of the kinetics of the isomerisation of *S*-2,5-dihydroxyphenyl esters of phosphorus dithioacids demonstrated the unimolecular nature of the process[90]. The replacement of the alkoxy-groups at the phosphorus atom in compounds (CIX) by alkyl groups reduces the rate of isomerisation, probably as a consequence of the decrease of the effective positive charge on the phosphorus atom, which hinders the attack on the *ortho*-hydroxy-group. In intermediates with the trigonal-bipyramidal structure (CXI) and (CXII), the alkyl substituents are forced to occupy apical positions. The interactions with three equatorial substituents reduce the apicophilicity of the groups having high steric requirements[91] and hence increases the energy of the intermediates. An appreciable acceleration of the isomerisation is observed for esters of cyclic ω-hydroxy- or ω-mercaptophosphates compared with their acyclic analogues, which may be associated with the cyclic spiro-hydroxyphosphoranes being favoured by energy factors to a greater extent[68]. The influence of the polarity and acidity of the solvents on the rate of rearrangements is very small, which indicates an insignificant charge separation in the transition state of the rate-determining stage.

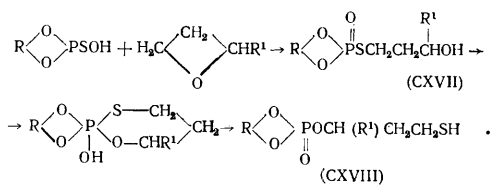
The replacement of a hydrogen atom in compound (CIX) by a trimethylsilyl group greatly stabilises the phosphorodithioate structure. In this case the S → O migration of the thiophosphoryl group can occur only in the presence of a basic catalyst or an excess of a sulphonating agent and the process becomes reversible. Its reversibility can be accounted for by the destabilisation of the phosphorodithioate structure due to the lower energy of the Si—S bond compared with the Si—O bond.

An analogous rearrangement of 2-hydroxyalkyl phosphorothioates was proposed as early as 1968 [92] and the isomerisation products were identified subsequently[93]:



The stability of *S*-(2-hydroxyalkyl) phosphorothioates (CXIII) is determined by the nature of the substituents at the phosphorus atom. Acyclic compounds are fairly stable at room temperature. The rate of their isomerisation increases[94] with decrease of the length of the alkoxy-groups $R = R^1$ in the sequence iso-$C_3H_7$ < $C_2H_5$ < $CH_3$. When the butoxy-group at the phosphorus atom is replaced by the t-butoxy-group, the capacity for rearrangement disappears[95]. In the presence of phenoxy-groups, isomerisation does not occur either, but there is an intramolecular substitution of the phenoxy-group with formation of compound (CXIV).[96] For a mixed environment of the phosphorus atom, the rate of isomerisation increases in the sequence[94] $R^2 = R^3 = H < R^2 = H$, $R^3 = CH_3 < R^2 = R^3 = CH_3$. A lower mobility of the thiophosphoryl group compared with the phosphoryl group has been observed[97,98]. 2-Hydroxyalkyl phosphorodithioates do not show a tendency towards isomerisation and the latter can be achieved only under more severe conditions[98]. The incorporation of the phosphorus atom in a five-membered ring accelerates the isomerisation to such an extent that 2-hydroxyalkyl phosphorothioates of the 1,3,2-dioxaphosphorinane series[99] can be detected only by $^{31}$P NMR. The characteristics of the rearrangement discovered agree with the mechanism involving intermediate formation of the hydroxyphosphoranes (CXV), which are converted into the phosphates (CXVI). The influence of the dioxyalkylene ring at the phosphorus atom on the rate of isomerisation can be explained by the lower energy of hydroxyphosphoranes of type (CXV), containing two five-membered rings, compared with the intermediates containing one five- or six-membered ring. In certain cases the phosphorane intermediates have been detected by $^{31}$P NMR.[99]

Conversely, the fact that the *S*-(3-hydroxyalkyl) phosphorothioates and phosphorodithioates, obtained by the addition of acyclic dialkylphosphorothioic and dialkyl phosphorodithioic acids to oxetans, do not isomerise can apparently be explained by the reduced stability of hydroxyphosphoranes with acyclic substituents at the phosphorus atom[100,101]. On the other hand, the products of the addition of five-membered cyclic phosphoromonothioic acids (CXVII) are readily converted into 3-mercaptoalkyl phosphates (CXVIII):[101]

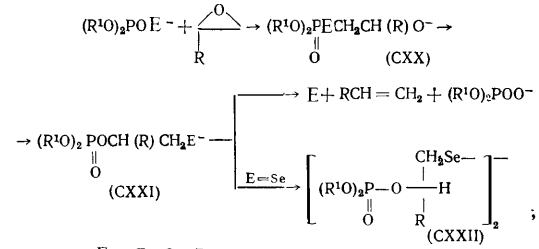


Derivatives of six- and seven-membered cyclic esters of phosphorus acids of type (CXVII) rearrange at 160–180 °C.[102]

The capacity of phosphoryl groups for 1,4-E → O (E = S, Se, or Te) migration is used to deoxygenate epoxides. The products of the interaction of salts of *O*,*O*-dialkylphosphoroselenoic[103] and *O*,*O*-dialkylphosphorotelluroic acids with olefin oxides are the olefins (CXIX), selenium (or tellurium),

and phosphates[104]. Their formation (Scheme 25) involves the rearrangement of the phosphoroselenoates or phosphorotelluroates (CXX):

Scheme 25

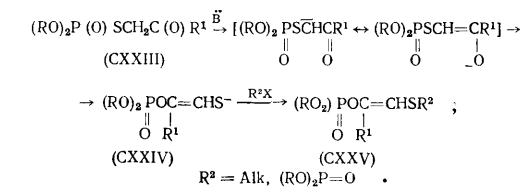


E = Te, Se; R = alkyl or monosaccharide residue.

In the case of salts of phosphonoselenoic acid, the rearrangement products (CXXI) are capable of undergoing also an oxidation-reduction reaction, in which they are converted into the diselenides (CXXII).

When *S*-(2-Oxoalkyl) phosphorothioates (CXXIII) are acted upon by bases, they rearrange to the enol phosphates (CXXIV), which have been isolated in the form of the derivatives (CXXV) [105] (Scheme 26).

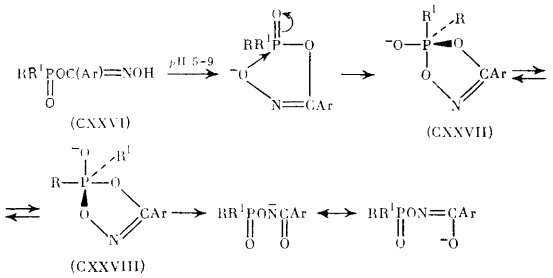
Scheme 26



$R^2$ = Alk, $(RO)_2P{=}O$.

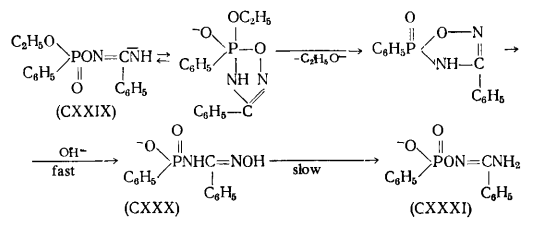
The mechanism of this rearrangement is probably analogous to that of the isomerisation of phosphorylated hydroxamic acids (CXXVI),[106] which proceeds in accordance with Scheme 27 via the intermediates (CXXVII) and (CXXVIII).

Scheme 27



The 1,4-O ⇌ N shift of the phosphono-group occurs in the alkaline hydrolysis of the imidoximes (CXXIX) [107] (Scheme 28):

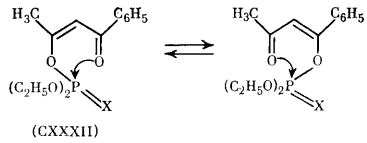
Scheme 28



The rearrangement of the intermediate (CXXX) to the phosphate (CXXXI) is kinetically a first-order reaction.

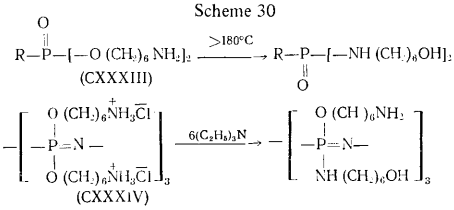
It has been suggested[108] that the reversible rearrangement of the *Z*-topomers of the enol phosphates (CXXXII) derived from 1,3-diketones proceeds via a mechanism involving intramolecular nucleophilic substitution at the tetrahedral phosphorus atom (Scheme 29):

Scheme 29



In contrast to the corresponding acyl derivatives[69], phosphoryl exchange (Scheme 29) is observed only above 150 °C. This is explained by the more stringent steric requirements which must be met by the trigonal-bipyramidal transition state, in which both oxygen atoms must be located in the axial positions. The formation of phosphorane intermediates containing larger than six-membered rings is apparently not a characteristic process.

Scheme 30



Thus the isomerisation of the phosphorylated aminoalcohols (CXXXIII) and (CXXXIV) [109] must be regarded as an intermolecular process.

* * *

The data presented in this review makes it possible to combine the wide variety of rearrangements involving the migration of electron-deficient phosphoryl groups on the basis of the mechanism involving nucleophilic substitution at a tetrahedral phosphorus atom, so that the characteristic features of the phosphoryl migrations can be described in most cases from the standpoint of the "hydroxyphosphorane concept", which constitutes the foundation of the modern interpretation of this mechanism.

The discovery and investigation of phosphorylotropic tautomerism, which will make it possible to examine the fine details of many biochemical processes in which the nature of the elementary reaction step is analogous, has been a great success. The study of the characteristic features and limits of the occurrence of phosphoryl migrations opens new pathways to the synthesis of various new organophosphorus compounds. The development of simple methods of synthesis of imidoyl derivatives of tetracoordinate phosphorus thio-acids and the study of their properties constitute a new field in thiophosphorylation methods.

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