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ADDITION REACTIONS OF PARTIALLY-ESTERIFIED PHOSPHORUS ACIDS. REARRANGEMENTS OF α-HYDROXYALKYL PHOSPHORUS ESTERS AND THEIR α-MERCAPTO AND α-AMINO-ANALOGUES

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Abstract - In 1947 at the session of the Chemistry Division of the USSR Academy of Sciences one of us reported on the results of studying the reactions of chloroallyl compounds with salts of dialkylphosphorous acids. Along with substitution products, these reactions also yielded the products of dialkylphosphorous acids addition to multiple bonds of unsaturated phosphonic esters (Refs. 1). Based on these observations a new, generally applicable method was later developed to synthetize phosphorus acids derivatives with a phosphorus-carbon bond. The method consists in adding partial esters of phosphorous, phosphonous and phosphinous acids and their thioanalogues to compounds containing double, triple, allene and diene multiple bond systems, as well as multiple carbon-element and element-element bonds (Refs. 2). The products of addition to carbon-carbon multiple bonds-various derivatives of phosphonic acids esters and their analogues - are stable compounds which do not undergo any changes at moderate heating. On the contrary, the products of addition to carbon-element multiple bonds - oxy-, mercapto-, and aminoderivatives of tetracoordinated phosphorus acids, as well as the products of addition of phosphorothioic and phosphorodithioic acids partial esters to compounds having carbon-nitrogen multiple bonds - undergo a number of characteristic transformations, which manifest themselves in the capability of having their P-C and P-S bonds broken and of undergoing various rearrangements. All these questions are treated in the present paper.

1. Reactions of partial esters of phosphorus (III) acids with carbonyl compounds and the ways to stabilize α - oxyderivatives of the acids of tetracoordinated phosphorus atom.

We first observed the phosphonate- phosphate rearrangement of α-oxyalkyldiphosphonates when studying the reactions of partial esters of phosphorus (III) acids with vinyl acetate under the conditions of alkaline catalysis (Refs. 3 & 5). It was found that acetylation, and not the addition of partial esters to multiple bonds, is taking place in these reactions.

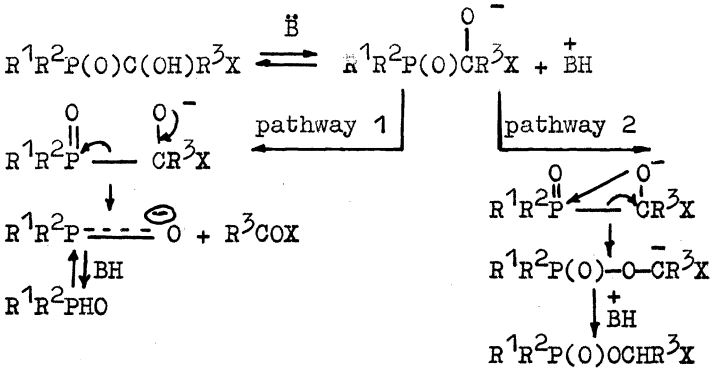
$$CH_3COOCH = CH_2 + (RO)_2PHO \longrightarrow CH_3CHO + CH_3COP(O)(OR)_2$$

1. $$CH_3CHO + (RO)_2PHO \longrightarrow CH_3CH(OH)P(O)(OR)_2 \xrightarrow[CH_3COOCH=CH_2]{} CH_3CH(OCOCH_3)P(O)(OR)_2$$

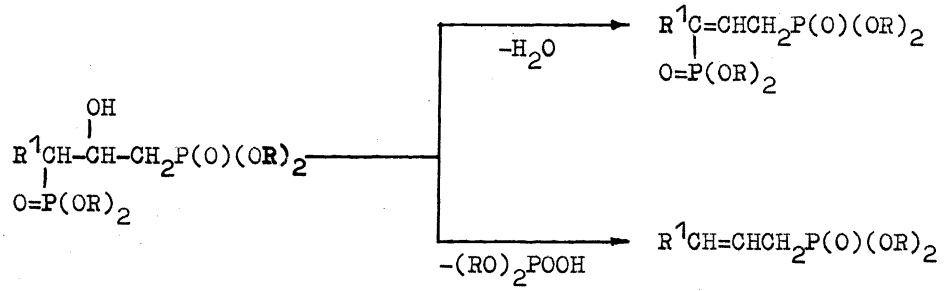
2. $$CH_3COP(O)(OR)_2 + (RO)_2PHO \longrightarrow CH_3C\underset{OH}{[}P(O)(OR)_2]_2 \quad (1)$$

$$\xrightarrow{RO^-} \underset{O=P(OR)_2}{CH_3\overset{|}{C}H-OP(O)(OR)_2} \quad (2)$$

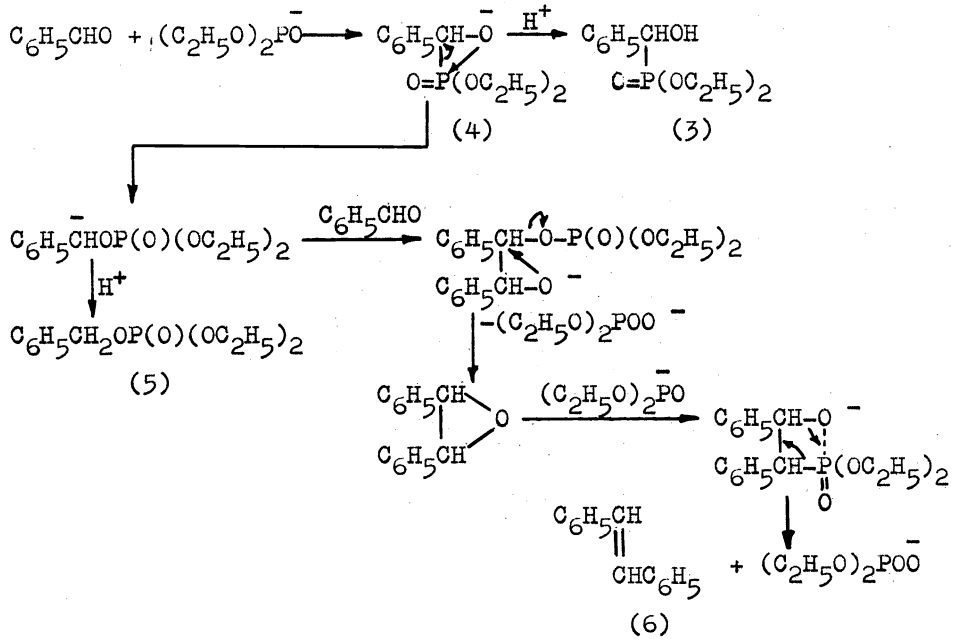
The formed methyldi (dialkylphosphonyl) carbinol (1) is isomerized in the reaction conditions into phosphate (2). Proceeding from the previously available data (Refs. 6 & 7), we later showed that the formation of a new P-O-C bond is a characteristic and sufficiently common reaction taking place on heatig, and also in the conditions of basic catalysis, for a number of α-oxyderivatives of tetracoordinated phosphorus acids containing at the carbinyl carbon atom an aceto (Refs. 7-12), benzoyl (Refs. 10 & 13 & 14), carbalcoxyl (Refs. 9 & 10 & 11), trifluoromethyl (Refs. 22), nitrile (Refs. 6 & 23 & 24), phosphoryl (Refs. 9-11 & 15 & 24-27), phenyl (Refs. 18 & 19 & 28 & 29) or substituted phenyl (Refs. 26 & 27 & 30 & 31) groups, i.e., groups in which -I and -M effects are expressed rather clearly. We reported on this at the International Colloquium on the Chemistry of Organophosphorus Compounds (Paris, 1969) (Refs. 32). In our subsequent investigations of phosphonate-phosphate rearrangement much attention was given to determining the limits within which it is taking place. Addition to dialkylphosphites and their analogues to the simplest aldehydes and ketones is a reversible reaction. In a number of cases the rearrangement and the decomposition into starting compounds go parallel (Refs. 31); the direction of reaction can be affected by the quantity of the base present (Refs. 33). The processes taking place are described as follows (Refs. 34).



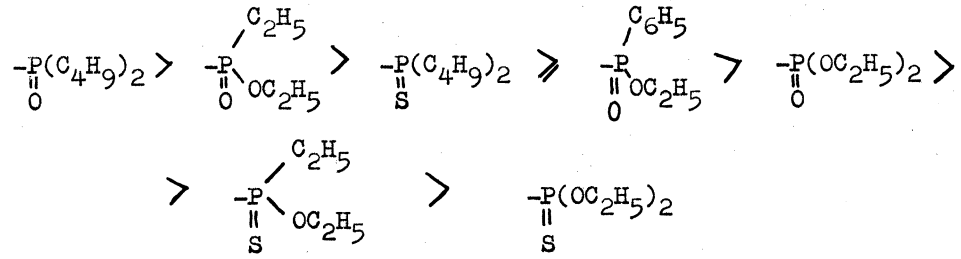
The direction of stabilization along pathway 1 or 2 primarily depends on the nature of X. If X is a strong electron-accepting substituent, rearrangement is taking place (pathway 2). If X is an electron-donating group, we usually have dissociation (pathway 1) into initial products. Thermal effect on the esters of α-oxyalkylphosphonic acids containing at the carbinyl carbon atom weak electronoaccepting groups, such as phenyl (Refs. 35), allyl (Refs. 36), and propargyl (Refs. 37) groups, does not result in the formation of a new P-O-C bond. The displacement of electron-accepting groups (C=O, CN, COOR) from α to β position with respect to the OH groups also deprives α-phosphorylated alcohols of the capability to undergo phosphonate-phosphate rearrangement. According to our data (Refs. 38 & 39) as well as those published in literature (Refs. 40), β-phosphorylated alcohols usually undergo PO olefination or dehydration, or both of them simultaneously (Refs. 41 & 42).



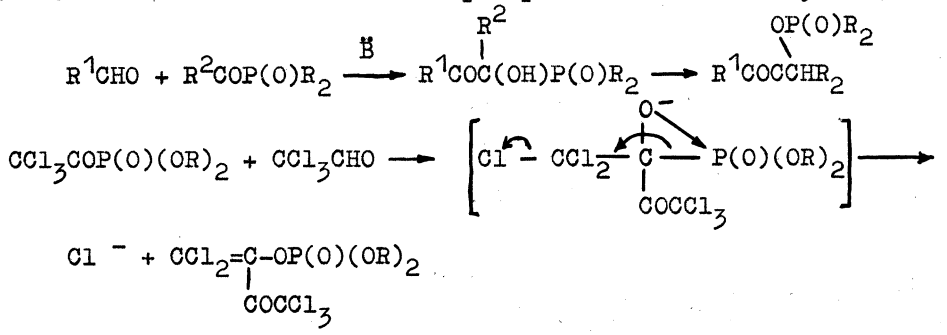
Further studies of these reactions revealed, however, that the limits within which the rearrangement proceeds can be extended on to the carbonyl compounds with weak electron-accepting substituents as well by conducting the reactions not with the dialkylphosphorous acids themselves, but with their sodium or potassium salts. The reaction of equimolar quantities of sodium diethylphosphite and benzaldehyde at 20-50° yielded: α-oxybenzylphosphonate (3), trans-stilbene (6.43%), diethylbenzylphosphate (5.8-10%) and diethylphosphoric acid (Refs. 43).



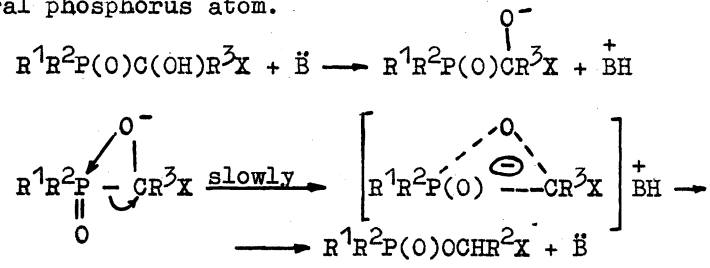
Anion (4) formed from the sodium derivative undergoes phosphonate-phosphate rearrangement yielding diethylbenzylphosphate (5), and stilbene oxide, formed by the interaction with the second benzaldehyde molecule, reacting with sodium diethylphosphite produces stilbene (6) and diethylphosphoric acid. The course of each stage has been either described in literature or modelled by us. Stabilization pathway of α-oxyderivatives of tetracoordinated phosphorus acids also depends on the structure of the phosphoryl group. With the help of differential thermal analysis and the refractometric method a series was obtained which characterizes the decrease in the capacity of α-oxyalkylphosphonic and posphonothioic esters to undergo isomerization (Refs. 24 & 44).



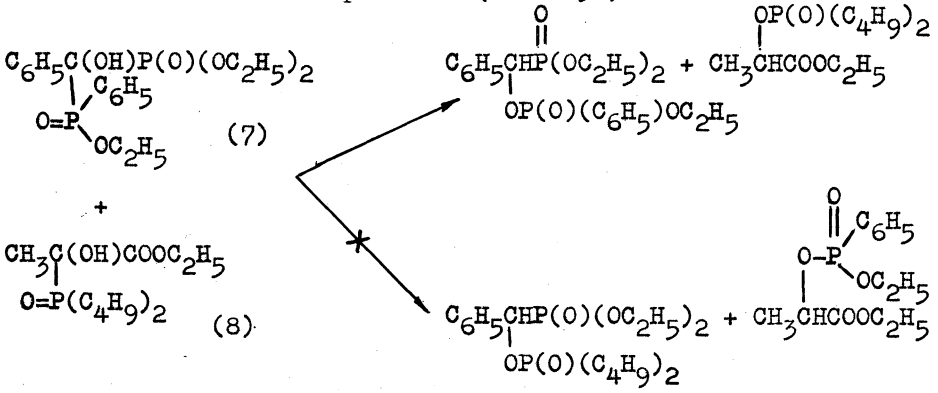
Phosphonate-phosphate rearrangement is a widespread phenomenon in the chemistry of organophosphorus compounds. We observed it in the reactions of various acidic (Refs. 44) and neutral (Refs. 45) esters of P(III) acids with carbonyl compounds, the salts of partial esters of phosphorous acid and its analogues with carboxylic chlorides and carboxylic anhydrides (Refs. 46 & 47), vinyl esters of carboxylic acids (Refs. 3). It accompanies the benzoin condensation of α-ketophosphonates with aldehydes (Refs. 48-50).



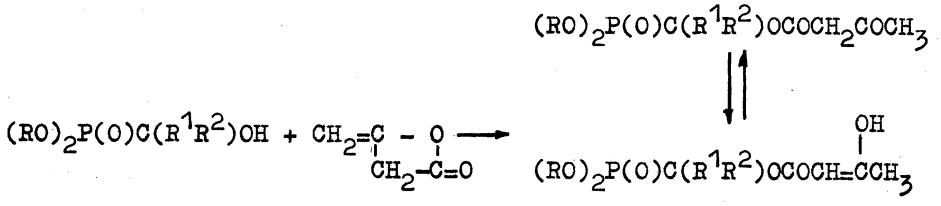
These reactions confirm the previously made assumption (Refs. 44) that the isomerization products - phosphates - are formed as a result of the rearrangement of α-oxyphosphonates and their analogues, and not by dialkylphosphite anion directly attacking the carbonyl group oxygen atom. The mechanism of phosphonate-phosphate rearrangement is widely discussed in literature. According to our data (Refs. 44), as well as the data of Janzen and Smyrl (Refs. 22), this rearrangement is tricentral and proceeds following the mechanism of intramolecular nucleophilic substitution at the tetrahedral phosphorus atom.



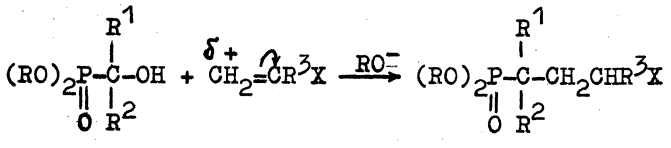
The first order of reaction was found for the isomerization in the absence of a catalyst (Refs. 44 & 51) and the pseudofirst order - for the isomerization in the presence of bases (Refs. 22 & 51). The intramolecular rearrangement mecahanism is confirmed by the absence in the reaction mixture of the products of "mixed isomerization" of phosphorylated alcohols (7) and (8) isomerized at the same temperature (Refs. 51).



α-Oxyphosphonate have an increased acidity and constitute a very reactive type of compounds. Some of their reactions were studied by us. They can proceed without the breaking of OH bond, and in that case they are not accompanied by phosphonate-phosphate rearrangement. Carboxylic esters are easily formed from α-oxyphosphonates under the action of carboxylic halogenides and anhydrides (Refs. 35 & 52-54) or diketene (Refs.55).

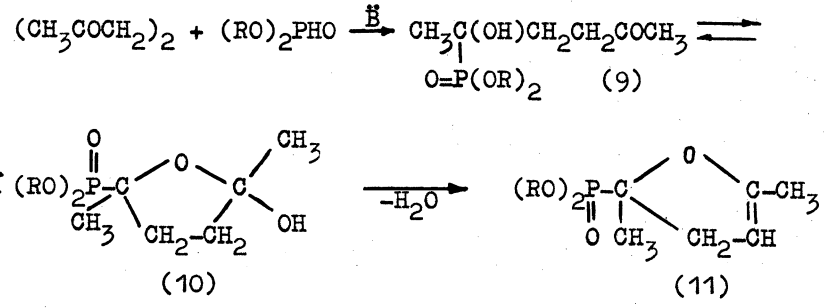


α-Oxyphosphonates are added to C=C bonds of unsaturated electrophilic compounds. The addition does not proceed in accordance with Markovnikov's rule (Refs. 56).



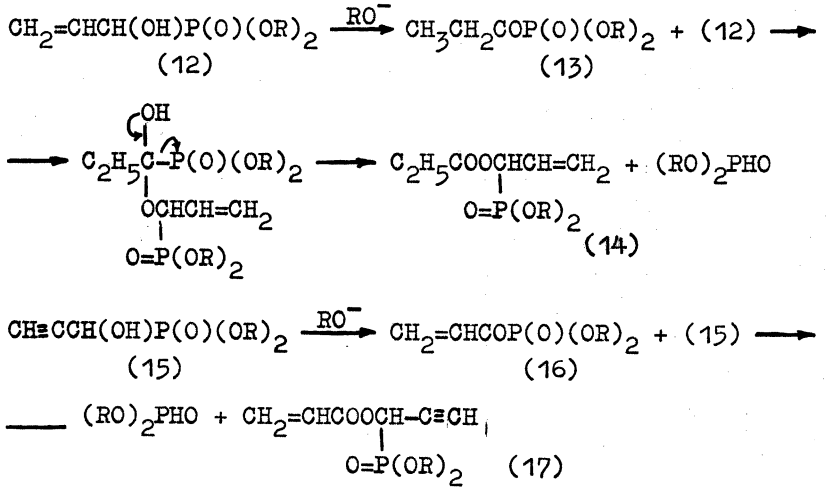
Ring-chain tautomerism was found to exist for 2-dialkylphosphonyl-2-oxyhexane-5-ones (9) formed in reactions of dialkylphosphites with acetonylacetone (Refs. 57). Furan oxyderivatives (10) dehydrate, and phosphorylated

dehydrofurans (11) are formed

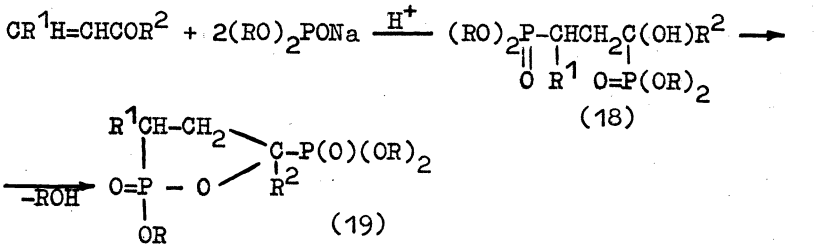


(10) (11)

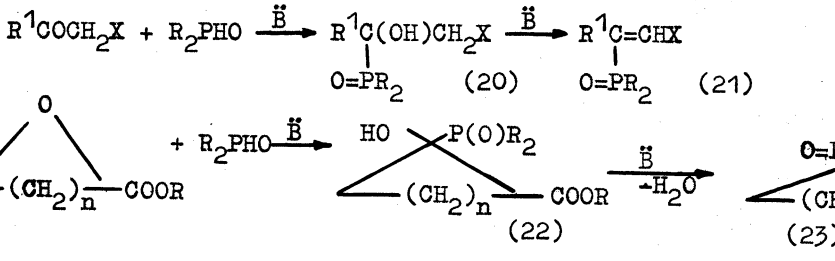
α-Oxyallyl- (12) and α-oxypropargyl- (15) phosphonates, when heated in the presence of a catalytic quantity of sodium alkoxide, are correspondingly transformed into the esters of α-propionyloxyphosphonic (14) and α-acryloxypropargylphosphonic (17) acids (Refs. 36 & 37).



Formation of reaction products (14) and (17) includes the prototropic isomerization of α-oxyallyl- and propargylphosphonates followed by the breaking of P-C bond in the addition products subsequently formed. It is of interest that the esters of 1-oxy-3-dialkylphosphonylalcanophosphonic acid (18) are not rearranged at heating, but split off the alcohol yielding 1, 2-dioxaphospholans (19) (Refs. 58).



Reactions accompanied by the breaking of C-O bond are less numerous. E.g., α-oxyphosphonates (20), (22) and their analogues containing an active methylene group are capable, along with dissociation into initial components, of dehydration to substituted vinyl phosphonates (21), (23) (Refs. 35 & 48 & 52-54 & 59).



R^1 = Alk, Ar, $CH_2P(O)(OR)_2$, $CH_3COCHCOOC_2H_5$;

X = COOR, $P(O)(OR)_2$, $CH(CN)C_6H_5$, $CH{=}C(CH_3)_2$, $CH_2CH{=}CH_2$, CN;

n = 2, 3

Oxyesters(20) and (22) with an active methylene group can be obtained by adding the partial esters of P(III) acids to easily enolysed carbonyl compounds (Refs. 35 & 53 & 54 & 59). Dehydration is facilitated by an increase in the lability of hydrogen atoms in the methylene group. The yield of unsaturated phosphonates, types (21) and (23), is increased by the pyrolysis of α-acetoxyalkylphosphonates. These reactions served as the basis for the development of a convenient method of synthetizing unsaturated organophosphorus compounds.

2. Thiophosphonate-thiophosphate rearrangement in the reactions of partial esters of P (III) acids and their salts with thiocarbonyl compounds

We have ascertained that phosphonate-phosphate rearrangement is of more general nature: under appropriate conditions phosphoryl groupings are capable of 1,2 migration from the carbon atom not only to the nucleophilic oxygen atom but also to that of sulfur. We designated this kind of isomerization as thiophosphonate-thiophosphate rearrangement. It was first observed in the reactions of partial esters of P(III) acids and their salts with thiobenzophenone (Refs. 60 & 61). Diethylthiophosphorous acid reacts with thiobenzophenone in the presence of catalytic quantities of sodium ethylate or diethyl amine at 20-100°C. Reactions of monoethyl esters of ethyl- and phenylthiophosphonous acids proceed in the presence of sodium ethylate or diethyl amine at 20°, and in the absence of catalysts - at 100° within 4-6 hours. Dibutylphosphinous and -thiophosphinous acids react in the absence of catalysts at room temeperature. In all cases, instead of the expected α-sulfhydryl derivatives of tetracoordinated phosphorus acids (24), isomeric to them S-benzhydrylthio- or dithiophosphates were isolated (25) (Refs.60 & 61).

$$(C_6H_5)_2C{=}S + R^1R^2PHX \xrightarrow{\ddot{B}} (C_6H_5)_2\underset{\displaystyle X{=}PR^1R^2}{\overset{\displaystyle \downarrow \ddot{B}}{C}}\text{-SH} \qquad (24)$$

$$(C_6H_5)_2CN_2 + HSSPR^1R^2 \longrightarrow (C_6H_5)_2CH\text{-}SP(X)R^1R^2 \qquad (25)$$

Observing the course of the reaction with the helpot IR spectrometry we could detect the formation of intermediate compounds, type (24), with a P-C bond. Thiophosphonate-thiophosphate rearrangement seems to follow the mechanism suggested for the isomerization of α-oxyphosphonates. With the help of NMR (31 P) spectroscopy the rearrangement was shown to be irreversible under the conditions of this reaction. Reactions of thiobenzophenones with sodium dialkylphosphites and sodium ethylphosphonites also yield O,O-dialkyl-benzhydrylphosphorothioates and ethylphosphonothioates. In the continuation of these investigations we studied the possibility of the rearrangement of phosphonoxanthogenic acid derivatives where the phosphorus atom is also considerably deficient in electron density. The interaction of sodium diethylphosphite with carbon sulfide at 70-100° in benzene or tetrahydrofuran medium followed by alkylation with methyl iodide resulted in the formation of O, O-diethyl-S-acetyl-phosphorothioate (27) (Refs. 62).

$$(C_2H_5O)_2PONa + CS_2 \longrightarrow \underset{(26)}{(C_2H_5O)_2P(O)CSSNa} \longrightarrow$$

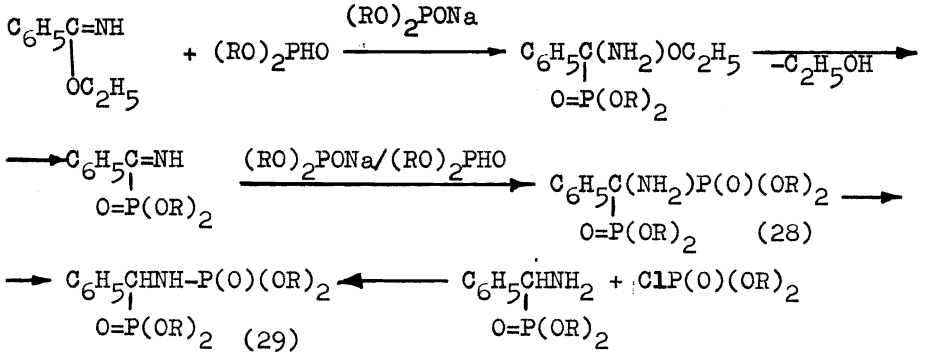
$$\left[(C_2H_5O)_2P(O)\text{-}\underset{\displaystyle S}{\overset{\displaystyle \diagdown}{C}}{=}S\right]^{\ominus}\ \overset{\oplus}{Na}\ \xrightarrow{CH_3I} (C_2H_5O)_2P(O)S\underset{\displaystyle S}{\overset{\displaystyle \downarrow}{C}}CH_3 \qquad (27)$$

$$\xrightarrow[C_2H_5ONa]{C_2H_5OH} (C_2H_5O)_2P(O)SC_2H_5 + CH_3COSH$$

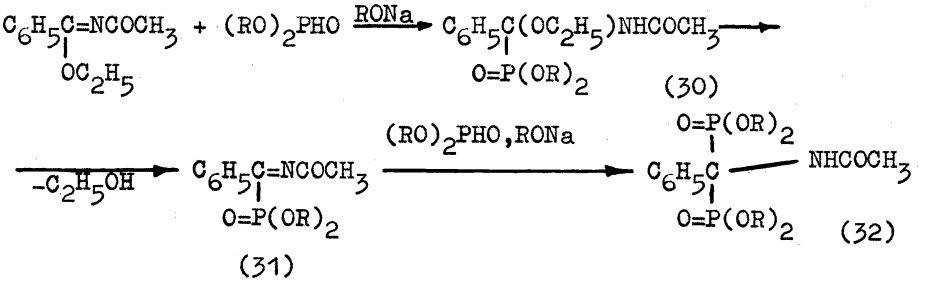
At the first stage of the reaction, phosphonoxanthogenic acid derivative (26) is formed. With heating it undergoes rearrangement with C → S migration of the phosphoryl group and being alkylated yields reaction product (27). A study of the rearrangements accompanied by 1,2 migration of the phosphoryl or the thiophosphoryl groups from carbon to heteroatom confirms the assumption that the motive force of these processes is deficiency of electron density on the phosphorus atom. Migration is observed in those cases when the formation of final reaction products or intermediate stages with a smaller deficiency of electron density on the phosphorus atom is possible.

3. Aminophosphonate-amidophosphate rearrangement in the reaction of partial esters of P(III) acids and their salts with azomethines

The addition of partial esters of phosphorous acid and its homologues to C=N bond of Schiff bases was first accomplished by one of us in 1952 (Refs. 63). At present these reactions are widely studied, which is facilitated by our establishing in 1972 (Refs. 64) the existence of aminophosphonate-amidophosphate rearrangement for aminophosphonates derivatives. In 1959 Kreutzkamp and Cordes (Refs. 65) assigned the structure of bis (dialkylphosphonyl) alkyl amines (28) to the products of multistage reaction of dialkylphosphites with benziminoethyl ester.

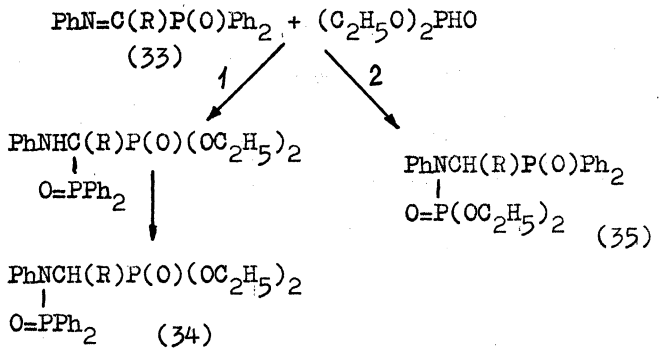


They also arrived at similar results when studying the reactions with diethyl-N-phenylbenziminophosphonate. Having reproduced these data we isolated compounds whose constants correspond to those given for them in literature (Refs. 65). However, the presence of a secondary NH amide group bands in the IR spectra, of a ≥CH proton in the PMR spectra, and of two signals from phosphorus nuclei of phosphonate (δ_P - 18 ÷ -21 p.p.m.) and amidophosphate (δ_P -5 ÷ -7 p.p.m.) environment in the NMR (31 P) spectra made it possible to arrive at the conclusion that the final reaction products have amidophosphate (29) structure (Refs. 66). Formation of amidophosphates (29) is a result of the rearrangement of the derivatives of α-aminoalkylphosphonic acid (28) (Refs. 66). The structure of amidophosphates, type (29), was also confirmed by special synthesis. We found that a similar rearrangement takes place with the interaction of dialkylphosphites, in the presence of sodium dialkylphosphite, with iminoformates (Refs. 67). In reactions of dialkylphosphites with N-acetylbenziminoethyl ester (Refs. 66) we succeded in accomplishing a stage-by-stage course of these reactions and in isolating the intermediate compounds (30-32).

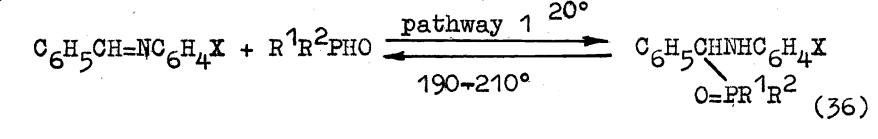


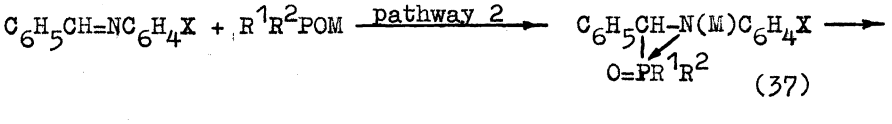
Somewhat later similar results were obtained by Gross with coworkers (Refs. 68). At first Gross assigned a structure with three phosphorus atoms at one carbon atom to the adducts of P(III) acids partial esters to N-[bis(phospho-

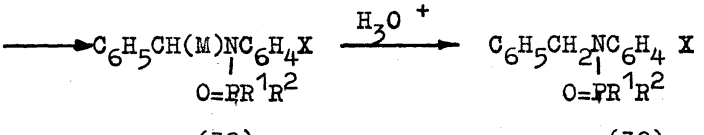
ryl) methylene] anilines (Refs. 69). Later (Refs. 70) he arrived at the conclusion on the reverse order of addition and established the structure of N-aryl-N-phosphorylamino(bisphosphoryl) methane. In 1974 Gross (Refs. 71) also considered it possible for amidophosphates to be formed as a result of the rearrangement of aminophosphonates. This point of view is supported by the following reasoning. When imines (33) interact with diethylphosphite the compounds being formed are amidophosphates (34), and not (35) (Refs. 68 & 71 & 72).



As shown by investigations, only those α-aminophosphonates which contain electron-accepting substituents at the amine carbon atom undergo rearrangement (Refs. 66 & 71-72). This suggests an analogy between aminophosphonate-amidophosphate rearrangement and isomerization of α - oxyalkylphosphonates. In the opinion of Gross (Refs. 72), intermediate α-aminophosphonates are capable of rearrangement if the amine carbon atom has two phosphoryl and one electronegative (CN, $COOC_2H_5$, C_6H_5) groups at it. When there are two phenyl groups at the carbon atom, no rearrangement is taking place (Refs.72) We showed that with the presence of one phosphoryl and one phenyl group at the amine carbon atom α-aminophosphonates are decomposed but their N (Na, K or Mg) - derivatives are capable of isomerization. When dialkylphosphites, phosphonites and phosphinites interact with benzal aniline and its N-substituted homologues (Refs. 73-76) in the presence of catalytic quantities of bases, α-aminoderivatives of tetracoordinated phosphorus acids (36) are being formed.

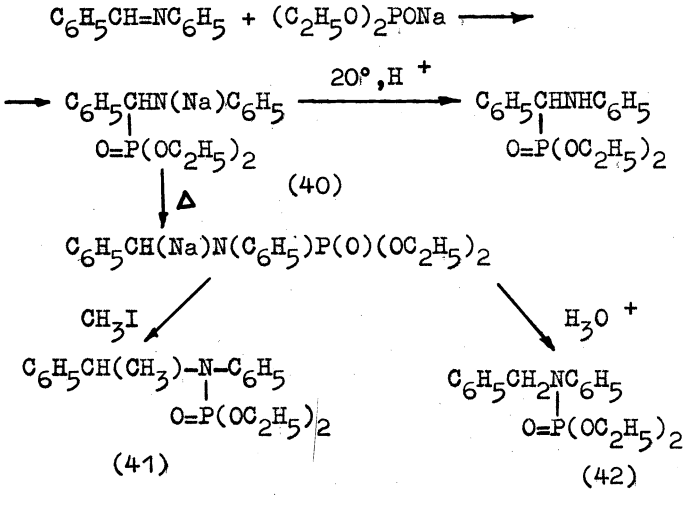




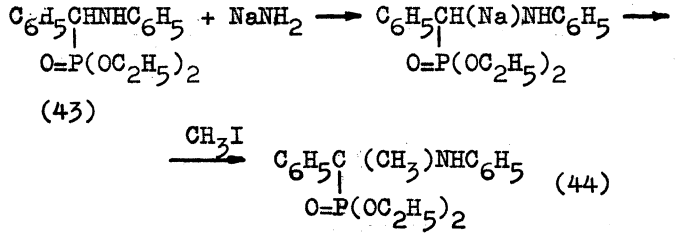


As distinct from α-oxyphosphonates, α-aminoalkylphosphonates are thermally more stable. The heating of aminophosphonates (36) in the absence of catalysts at 190÷210° results, however, not in isomerization but in decomposition into benzal anilines and partial esters (pathway 1) (Refs. 74). The interaction of sodium and potassium salts with benzal aniline and its N-substituted homologues at 70÷100° yielded amidophosphates (39) (pathway 2) (Refs. 73-75). With increasing temperature the course of reaction tends to shift towards 2. Under identical conditions the yield of amidophosphates (39) is proportionate to the quantity of the phosphite salt. In the reaction with an equimolar quantity of the phosphite salt the yield of (39) amounts to 80÷90%. A decrease in the quantity of the salt in the mixture with the partial ester decreases the yield of amidophosphates (39) and increases the yields of aminophosphonates (36). With a catalytic quantity of salt the main reaction products are aminophosphonates (36). These observa-

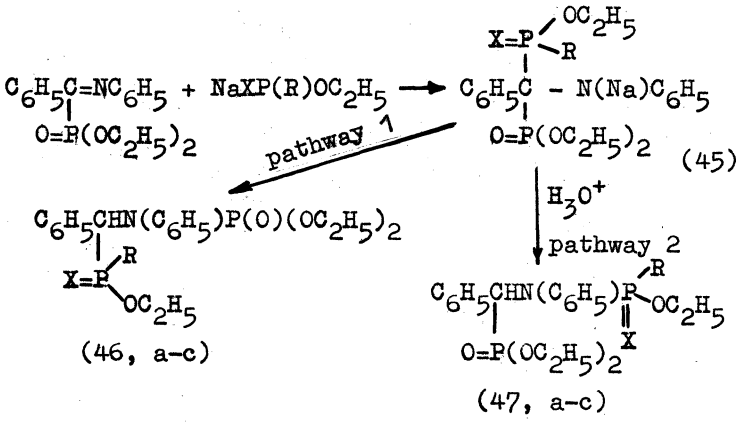
tions make it possible to draw the conclusion that it is not the aminophosphonates themselves that undergo rearrangement, but the anions formed from N-metallic derivatives (37) (Refs. 77). The charged anion on the nitrogen attacks the electrophilic phosphorus atom, which results in the breaking of the P-C and the formation of new PNC and CH bonds. It is of interest to note that the interaction of benzal aniline with diethylphosphite and its Li salt produces non isomerized products, type (36), while the interaction with Mg salt produces a mixture of aminophosphonates (36) and amidophosphates (39) (Refs. 75). This is, obviously, associated with a differing ionization capacity of the nitrogen-metal bond in (37); the higher it is the higher is the degree of rearrangement that takes place. We have recently (Refs. 77) isolated N-sodium derivative of aminophosphonate (40) using the reaction of sodium diethylphosphite with benzal aniline.



By heating derivative (40) with subsequent neutralization by acid the amidophosphate (42) was obtained, and under the action of methyl iodide - the C-methylated amidophosphate (41) (Refs. 77). From the above-mentioned it follows that N-metallic derivatives of aminophosphonates do actually undergo rearrangement, and that this is a common phenomenon for all the cases of aminophosphonate-amidophosphate rearrangement described up to now. Attempts at direct transformation into amidophosphates by heating dialkyl N-phenylbenzylphosphonates in the presence of $NaNH_2$, RONa and other alkaline catalysts end in failure (Refs. 77). This is caused by the differing lability of CH and NH protons in aminophosphonates, type (43).



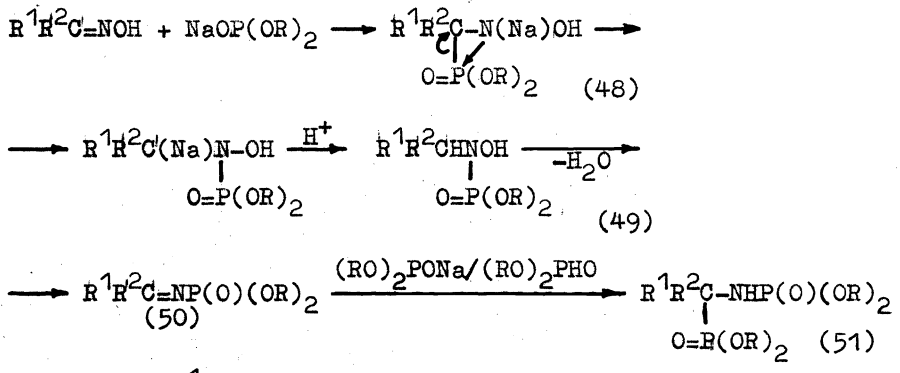
As a result of the interaction of an equimolar quantity of sodium amide with aminophosphonate (43) followed by the action of methyl iodide on the mixture, C-methylated aminophosphonate (44) (Refs. 77) was isolated. The results obtained indicate that under the action of bases a more labile CH proton is substituted, and a C-Na derivative (or its anion) is formed without any rearrangement. With the help of NMR (31 P) spectroscopy the rearrangement in the -50 ÷ 80°C temperature range was shown to be irreversible (Refs. 74). When phosphonates (45) include a diethylphosphonyl and a diethylthiophosphonyl or a diethylphosphonyl and an ethoxyethyl(phenyl) phosphinyl groups, isomerization proceeds in two directions (1 and 2) with both the diethylphosphonyl and the diethylthiophosphonyl or ethoxyethyl (phenyl) phosphinyl groups migrating to the nitrogen atom (Refs. 77).



(46, a-c) (47, a-c)

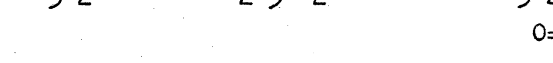
X=S, R=OC_2H_5 (a); X=O, R=C_6H_5 (b); X=O, R=C_2H_5 (c).

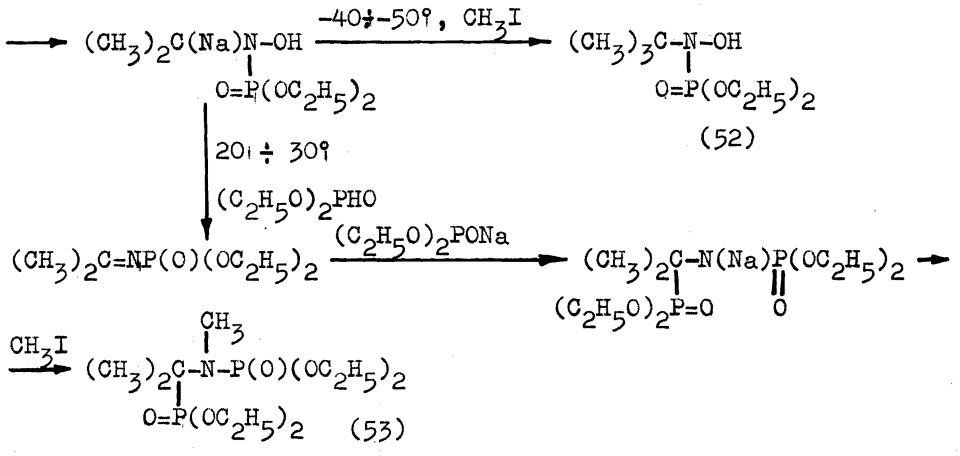
It is of interest to note that the isomerization of α-aminophosphonates containing diethylphosphonyl and dibutylphosphine oxide groups at the amine carbon atom proceeds with the predominant migration of dibutylphosphine oxide group (Refs. 71). The effect of substituents at the nitrogen atom on the tendency to aminophosphonate-amidophosphate rearrangement has been studied to a small extent. Bis (dialkylphosphoryl) alkyl amides or their metallic derivatives are incapable of rearrangement (Refs. 66), which is explained by a decrease in the nucleophilcity of nitrogen in them. Not long ago we found that α-phosphorylated hydroxyl amines and their sodium derivatives easily undergo aminophosphonate-amidophosphate rearrangement. The reaction of sodium dialkylphosphites, in the presence of an equimolar quantity of dialkylphosphorous acid, with keto - and aldoximes produce dialkyl- N(1-dialkylphosphonylalkyl) amidophosphates (51). In a similar way proceeds the interaction of carboxylic esters and oximes with sodium dialkylphosphites.



R = alkyl, R^1R = alkyl, cycloalkyl, aryl, hydrogen

At the first stage, sodium dialkylphosphites are added to the C=N bond of oximes with sodium derivatives (48) being formed. These undergo aminophosphonate-amidophosphate rearrangement, and compounds (49) are formed. Hydroxyamidophosphates (49) are capable of dehydrating to imines (50). N-Alkylideneamidophosphates (50) contain an electrophilic multiple bond, and a second dialkylphosphite molecule is easily added to them producing (51). Each stage of this reaction has been modelled. Substances (49) and (50) have also been found in the reaction products. To confirm the suggested scheme we carried out the reaction of acetone oxime with sodium diethylphosphite and diethylphosphorous acid followed by subjecting the mixture to the action of methyl iodide. At the temperature of -50÷- 40°C, the main product is O,O-diethyl-N-tertbutylhydroxyamidophosphate (52). At the temperature of 20÷ 30°, the main product is N-methylamidophosphate (53).

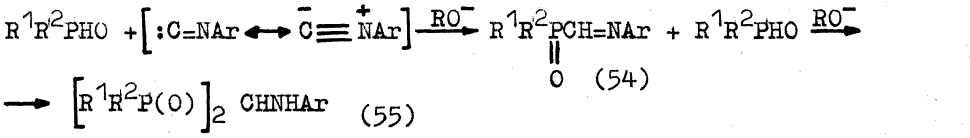




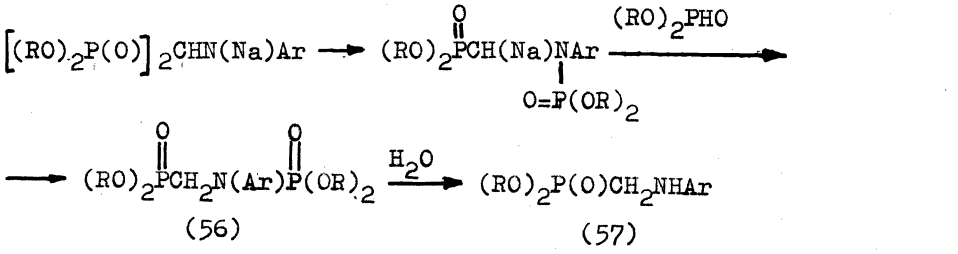
Rearrangement capability of the sodium derivatives of α-hydroxyaminophosphonates not containing any electron-accepting substituents can be explained by a considerable nucleophilicity of nitrogen in α-hydroxyaminophosphonates as compared with its nucleophilicity in aminophosphonates.

4. Aminophosphonate-amidophosphate rearrangement in the reactions of partial esters of P(III) acids and their salts with nitriles and isonitriles.

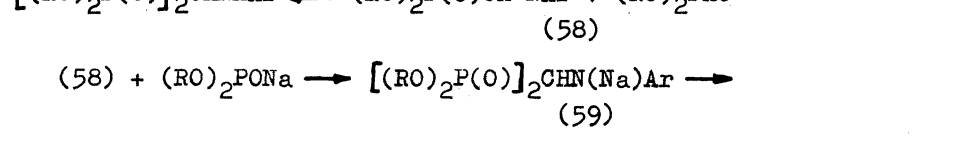
In the recent years we have studied intensively the reactions of organophosphorus compounds with isonitriles. Aryl isonitriles react with partial esters of P(III) acids in the presence of traces of bases and form N-arylaminotetraalkyldiphosphonyl (phosphinooxide) methanes and their analogues (55) (Refs. 67).



The suggested reaction scheme includes, at the first stage, the insertion of isonitrile into the P-H bond with the formation of iminophosphonates (54), to which a second molecule of the partial ester is added, forming (55). Interaction with sodium dialkylphosphites in the presence of dialkylphosphorous acid proceeds in a similar way and, at the final stage, is accompanied by aminophosphonate-amidophosphate rearrangement.



Special experiments showed that N-phenyltetraalkyldiphosphonylmethanes (55), when heated in the presence of equimolar quantities of $NaNH_2$ or sodium dialkylphosphite, rearrange to amidophosphates (56), identified as products (57) Since compounds (55) have been shown to dissociate into dialkylphosphite and imine (54), it can be assumed that, in this case too, N-sodium derivatives (59), formed as a result of the competing reaction of imine (58) with sodium dialkylphosphite, undergo rearrangement.



$$\longrightarrow (RO)_2P(O)CH(Na)N(Ar)P(O)(OR)_2 \xrightarrow{H_3O^+}$$

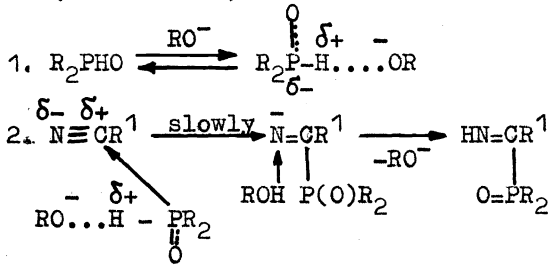
$$\longrightarrow (RO)_2P(O)CH_2NHAr + (RO)_2POOH$$

(57)

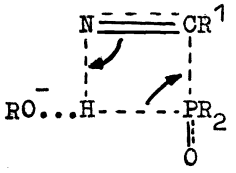
We began studying the reactions of partial esters of P(III) acids with nitriles in 1971 (Refs. 78& 79). Dialkyl (aryl) phosphinous acids interact with activated nitriles in the presence of sodium alcoholates, forming oxides of substituted dialkyl (aryl) iminophosphines (60) (Refs. 79-82).

$$R_2P(X)H + R^1CN \xrightarrow{RONa} R^1\underset{\underset{X=PR_2}{|}}{C}=NH \quad (60)$$

Only one nitrile group takes part in the reaction with malonic dinitrile, and the addition products are capable of imino-amine tautomerism (Refs.80). As a result of kinetic studies the following mechanism of these reactions was proposed (Refs. 81-82).



The reaction rate is determined by the nucleophilic sttack of phosphorus atom on the positively charged carbon atom of the nitrile group. This is followed by a rapid elimination of the proton and the formation of the final product. In an extreme case there seems to be a possibility of the formation of a four-center transition complex with cyclic electron transfer.



In the reactions of phosphinous acids with chloroacetonitrile, chlorine substitution is followed by the addition of a second molecule of phosphinous acid to the phosphine acetonitrile acid (61) that has been formed (Refs.79).

$$R_2PHO + ClCH_2CN \xrightarrow[-HCl]{} R_2P(O)CH_2CN \xrightarrow{R_2PHO}$$

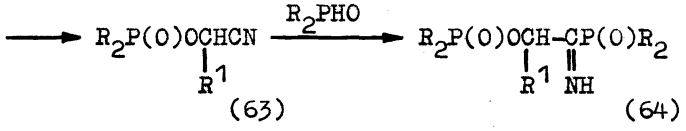
(61)

$$\longrightarrow R_2\underset{\underset{O}{\|}}{P}CH_2\underset{\underset{NH}{\|}}{C}P(O)R_2 \rightleftharpoons R_2\underset{\underset{O}{\|}}{P}CH=\underset{\underset{NH_2}{|}}{C}P(O)R_2$$

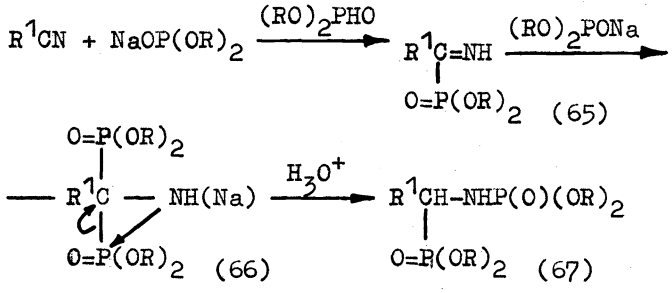
When dialkylphosphinous acid react with the nitriles of pyruvic and benzoylformic (Refs.83) acids, at first there is addition to the carbonyl group with the formation of α-oxyphosphine oxides (62) which undergo phosphonate-phosphate rearrangement to phosphinates (63). These are capable of attaching a second phosphinous acid molecule to the C≡N group with the formation of products (64).

$$R_2PHO + R^1COCN \longrightarrow R_2P(O)\underset{\underset{R^1}{|}}{C}(OH)CN \longrightarrow$$

(62)



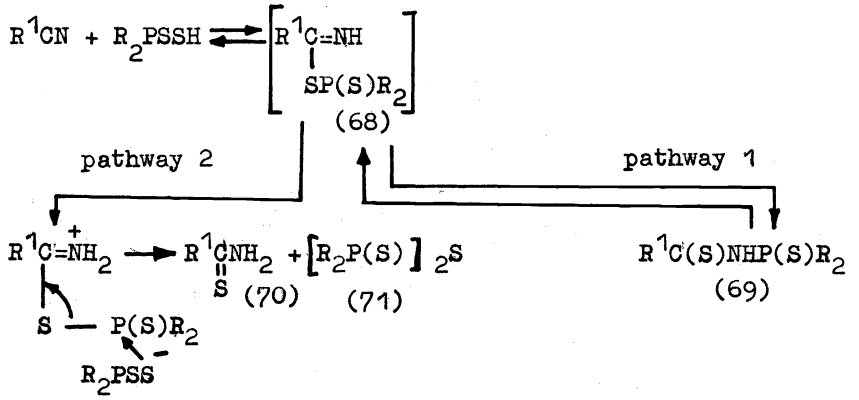
Dialkyphosphorous acids, in the presence of catalytic quantities of bases, do not react with nitriles. As shown by Orlovsky and Vovsi (Refs. 84), in the presence of HCl two dialkylphosphite molecules are added. We found that in the reactions of sodium dialkylphosphites with nitriles compounds with a P-N-C bond (67) are formed (Refs. 85).



At the first stage of the reaction dialkylphosphorous acid is added to the C≡N bond, and imines (65) are formed. These, reacting with sodium dialkylphosphite, yield N-sodium derivatives (66), which undergo rearrangement to compounds (67). It is impossible to separate the reactions into stages: in the conditions chosen all the stages proceed rather easily. In the isomerization of α-oxy-, α-amino-, and α-mercaptophosphonates we thus observe common regularities; the main difference lies in a differing capability of OH, NH and SH bonds of ionization.

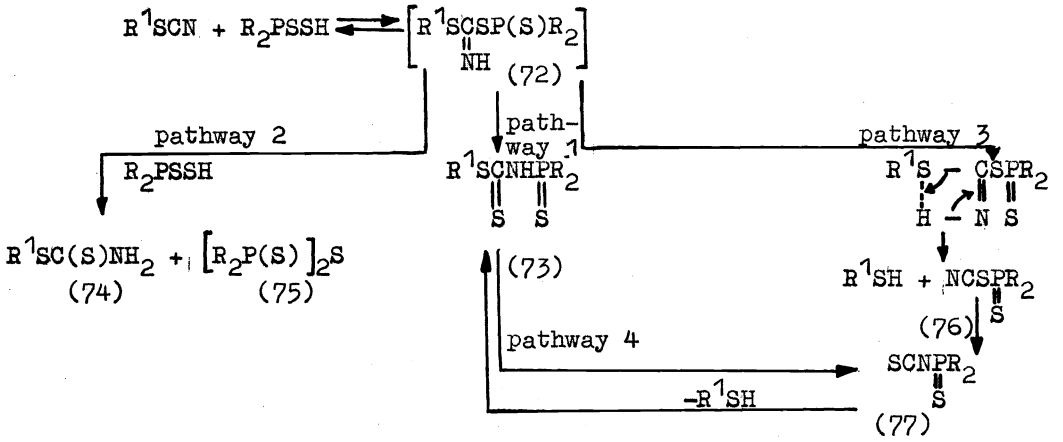
5. Rearrangements of the products of phosphoromono- and phosphorodithioic acids partial esters addition to compounds containing carbon-nitrogen multiple bonds.

Partial esters of phosphorothioic acids readily enter the reactions of addition to carbon-carbon multiple bonds. These reactions have at present been thoroughly studied (Refs. 2 & 86). The data on the reactions of phosphorothioic acids derivatives with compounds containing carbon-nitrogen bonds are not numerous. Addition products in this case are often capable of rearrangements. We have shown that rearrangements accompanied by 1.3 S → N migration of phosphoryl and thiophosphoryl groups take place in the reactions of dialkylphosphorothioic and phosphorodithioic acids with nitriles. Reactions of phosphorodithioic acids with nitriles attracted the attention of investigators as a method of obtaining thioamides (Ref. 87 & 88). Addition products, type (68) (Refs. 87), were assumed to be formed at the first stage. They were neither isolated nor fixed, however, because of the extreme ease with which they phosphorylate different substrates and stabilize into corresponding thioamides.

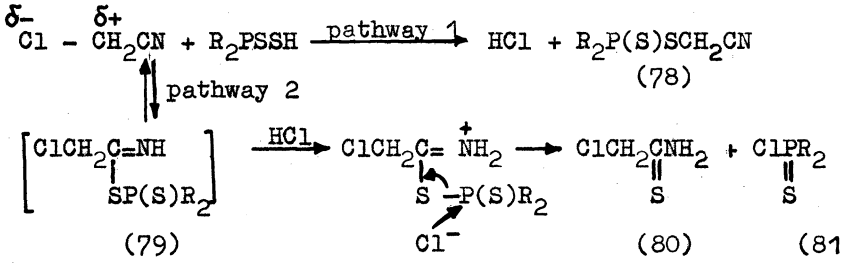


When carrying ont the reactions in mild conditions we could in many cases isolate thiophosphorylamides, type (69) (Refs. 89), isomeric to the expected

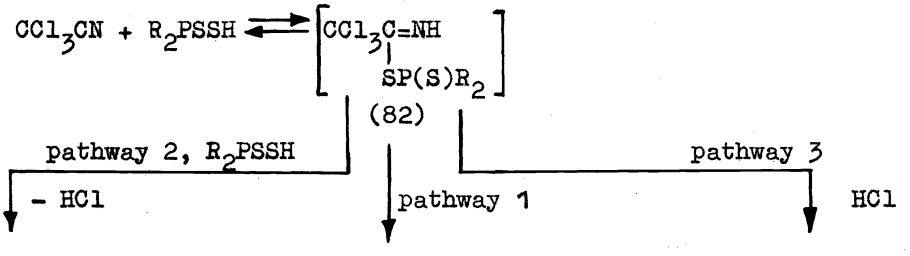
imidoyldithiophosphates (68) (Refs. 90 & 91) them. Using NMR (^{31}P) spectroscopy to follow the course of the reaction of diisopropylphosphorodithioic acid with trichloroacetonitrile we succeeded in recording the formation of a product of imidoyl structure (69) ($R^1=CCl_3$, $R=OC_3H_7$-iso). We believe that compounds (69) are formed as a result of (68) rearrangement (pathway 1). Imidoyldithiophosphates (68), in addition to rearrangement, are capable of splitting the P-S bond under the action of the initial dithioacid (pathway 2), which results in thioamides (70) and pyrophosphates (71). At elevated temperatures they often turn out to be the only reaction products (Refs. 89) It is of interest to note that the interaction of sodium or potassium salts of dithioacids with nitriles does not take place, which is indicative of the initial protonation of the CN group nitrogen atom. Imidoyldithiophosphates (72), formed as a result of phosphorodithioic acids being added to thiocyanates (Refs. 92).

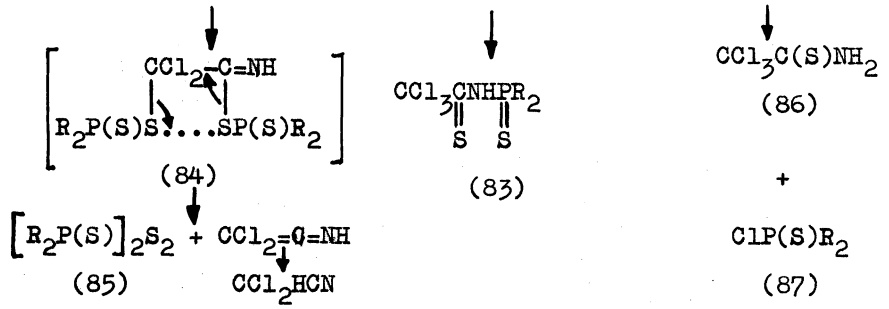


are more apt to rearrange to (73) than to have the C-S bond broken (pathway 3). Compounds (73), (74). (75), (77) were isolated and identified. Special experiments showed that compounds (73) even at room temperature split off thioles, and isothiocyanates are formed (pathway 4). Isothiocyanates (77) are the only products of the interaction between thiocyanates and dithioacids when the reaction occurs at an elevated temperature. It proved impossible to isolate or identify thiocyanates (76). This indicateds that pathway 3 can only be actualized to a small extent. The chlorine atom in monochloroacetonitrile, under the action of dithioacid, is substituted with a dithiophosphate group, and HCl and dithiophosphorylacetonitriles (78) are formed (pathway 1).

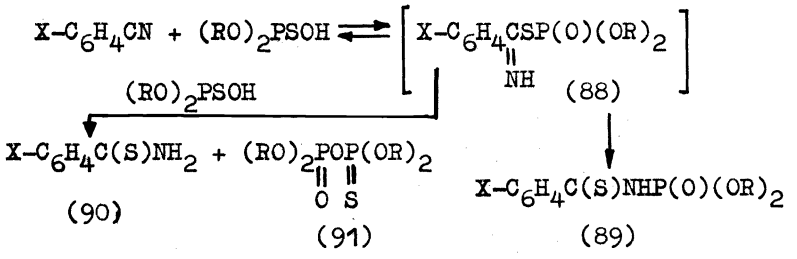


The simultaneously formed unstable products of imidoyl structure (79) are split by HCl, produced by pathway 1, to chlorothioacetamide (80) and chlorothiophosphates (81). Phosphorodithioic acids interact vigorously with trichloroacetonitrile. The presence of CCl_3 group activates the C≡N bond, as a result of which addition proceeds more easily than substitution.

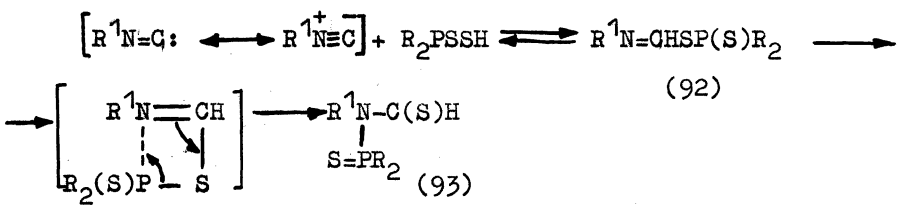




We isolated and identified the following reaction products: N-phosphorylated thioamides (83), bis (dithiophosphoryl) disulphides (85), trichlorothioacetamide (86), chlorothiophosphates (87). When following the course of the reaction with the help of NMR (31 P) spectroscopy we recorded the initial formation of intermediate (82). This compound is capable, besides rearrangement by pathway 1, of having its chlorine atom substituted with a dithiophosphate group (pathway 2) and the formation of the also unstable bis (dithiophosphoryl) imidoyl derivative (84), which is split to disulphide (85) and dichloroacetonitrile. A similar splitting of imidoyl derivative, type (84), we previously observed in the reactions of phosphorodithioic acids with α- ketonitriles and β -ketodithiophosphates (Refs. 93). Hydrogen chloride, produced by pathway 2, causes the formation of compounds (86) and (87). It is of interest to note that, of all the pathways of imidoylthiophosphates (84) stabilization, their rearrangement into (83) is the slowest process. For comparison we studied the reactions of O,O-dialkylmonothiophosphoric acids with benzonitriles. These reactions are also accompanied by the rearrangement of addition products (88)(Refs.94).

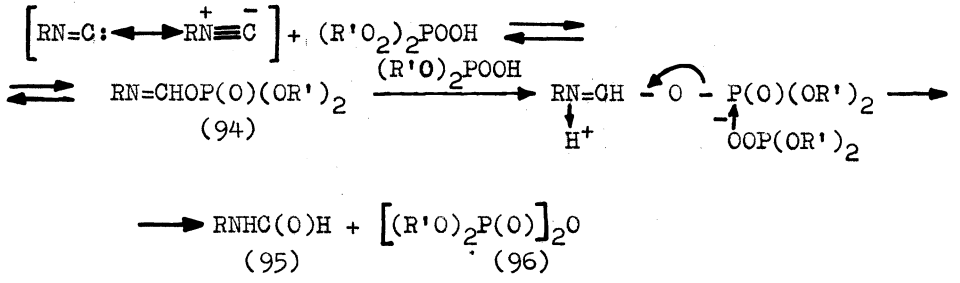


Thioamides (89) are soluble in alkalis, which makes it possible to isolate them from the reaction mixture. As in the case of phosphorodithioic acids, addition products (88) are split by the second molecule of thioacid to thioamides (90) and pyrophosphates (91). It can be noted that phosphorodialkylmonothioic acids react with nitriles to a smaller extent than dithiophosphates. The results obtained show that the addition of phosphoromonothioic acids to the CN group proceeds mainly on the sulfur atom, and the phosphorus in compounds (88) is mainly attacked by the oxygen atom of the POS triad. Of interest is the course of reactions of phosphorodithioic acids with isonitriles. The α -adducts of phosphorodithioic acids to 2.6(dimethyl) diethylphenylisonitriles, in the opinion of Chupp and Leschinsky (Refs. 95), are stabilized by the irreversible isomerization into N-thiophosphorylated thioformamides. We have found that the main products of the reactions with cyclohexyl-, phenyl-, 4-tolyl-, 2,5-xylylisonitriles with phosphorothioic acids are formimidoyldithiophosphates (92). In some cases they were isolated in pure state.

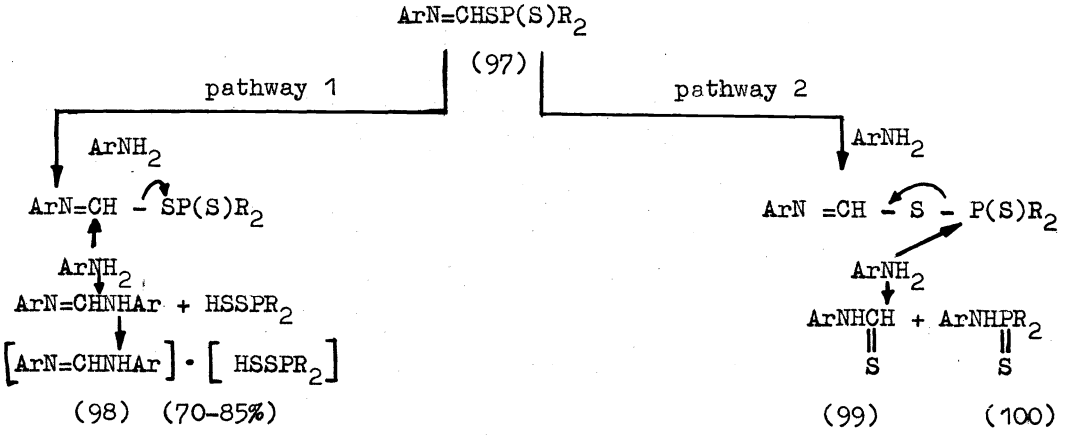


Even at room temperature, however, compounds (92) are gradually isomerized into thioformamides (93). The isomerization of imidoylphosphates and their thio-analogues can be visualized as an intramolecular four-center process resulting in the phosphorylation of the imine nitrogen. When tracking ont the course of isomerization with the help of NMR (31 P) spectroscopy we

found the tendency to rearrangement increasing with the replacement of aryl groups at the nitrogen atom by hydrogen or a cyclohexyl radical, i.e., with an increase in the nucleophilicity of nitrogen. The insertion of phenyl groups, instead of alkoxyl groups, to the phosphorus atom stabilizes imidoyldithiophosphates. Using the reactions of sodium or potassium salts of phosphoromonothioic and phosphorodithioic acids with iminochlorides as the examples, we showed that the tendency to 1,3 S → N migration of the P=O group is higher than that of the P=S group. As in the reactions with nitriles, the imidoyl derivatives of tetracoordinated phosphorus acids that are formed in the reactions with isonitriles are capable, besides rearrangement (intramolecular phosphorylation), of having their P-E-C (E=O, S) bonds split under the effect of various agents (intermolecular phosphorylation). In all cases, however, the tendency of imidoyl derivatives to undergo intermolecular phosphorylation remains greater than that for intramolecular phosphorylation. This is indicated by the variety of intramolecular phosphorylation reactions and the ease with which they proceed. Thus, imidoylphosphates (94), produced as a result of the formimidation of dialkylphosphoric acids by cyclohexyl- and 2,5-xylylisonitriles (Refs.96), split the P-O-C bond in the course of the reaction under the effect of the starting dialkylphosphoric acid molecule with formamides (95) and tetraalkylpyrophosphates (96) being formed. Because of the lower nucleophilicity of dialkylphosphoric acids their reactions with acetonitriles proceed slower than with dialkyldithiophosphates.

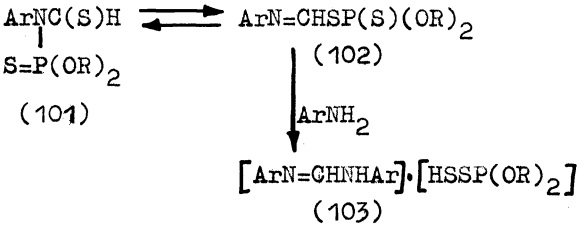


In these reactions it turns out to be impossible to separate imidoylphosphates (94) or compounds isomeric to them. This is caused by the fact that the splitting of P-O-C bond in (94) as a result of interaction with the acid molecule occurs more easily than the isomerization and by the slowness of the process whereby imidoylphosphates (94) are formed. These two factors in combination do not allow a sufficient amount of imidoylphosphates (94) to accumulate in the reaction mixture. Imidoyl derivatives of phosphorus acids are split not only by acids but also by bases. The main products of exothermic reactions

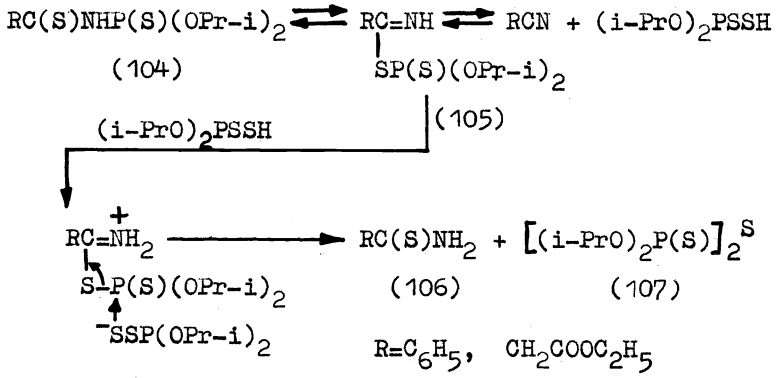


of imidoyldithiophosphates (97) with anilines are phosphorodithioic acid salts of N,N'-diarylformamidines (98) (70-85%), formed with the splitting of the C-S bond (pathway 1) as a result of aniline attacking the imine carbon atom. Simultaneously the P-S bond is also split (pathway 2) when aniline attacks the electrophilic phosphorus atom, which results in the formation of thioformamides (99) and anilidothiophosphates (100) (9-10%). The results obtained make understandable the dependence of the direction of reactions between phodphorodithioic acids and isonitriles on the way the latter have been obtained. When isonitriles generated from anilines, chloroform and alka-

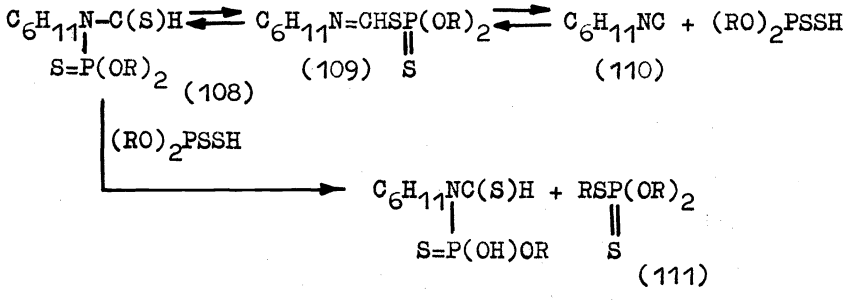
lis are used, imidoyldithiophosphates produced at the first stage do not have enough time to rearrange because they are rapidly split by aniline, and so phosphorodithioic acid salts of N,N'-diarylformamidines, type (98), are formed. The same compounds (98) are the products of the interaction of three components: dithioacid, isonitrile and aniline. The easy spliting of the C-S bond in imidoyldithiophosphates by anilines has been used by us to confirm the possibility of reverse isomerization of N-thiophosphorylated thioamides into compounds with imidoyldithiophosphate structure. It proved possible, by heating N-dialkylthiophosphorylthioformamides (101) with anilines, to isolate phosphorodithioic acid salts of N,N'-diarylformamidines (103) with high yields (70÷80%).



Formation of (103) can be explained by 1.3 N → S migration of the thiophosphoryl group, which represents infact by the isomerization of N-phosphorylated formamides (101) into imidoyldithiophosphates (102). The interaction between the nonisomerized products (101) and the anilines must result in other products. This is also confirmed by other experiments. By heating N(diisopropylthiophosphoryl) thioamides of benzoic and acetoacetic acids (104), obtained in the reactions of phosphorodithioic acids with nitriles, thioamides of benzoic and acetoacetic acids (106) and tetraisopropyltrithiopyrophosphates (107) were isolated (Refs. 91).

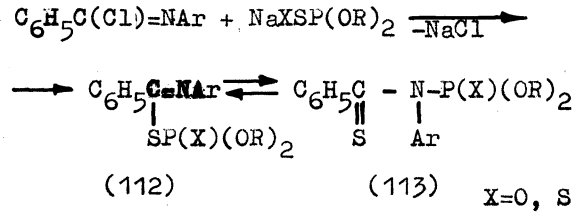


Their formation can be visualized as the transformation of compounds (104) into compounds with a P-S-C bond (105), which are in equilibrium with the initial dithioacid and nitriles. The appearance of free dithioacid in the reaction mixture causes the splitting of P-S bond in imidoyldithiophosphates (105), which finally results in products (106) and (107). The pyrolysis in vacuum of N-cyclohexyl-N-dialkylthiophosphorylthioformamides (108) obtained in reactions of phosphorodithioic acids with cyclohexylisonitrile resulted in the separation of O,O-S-trialkyldithiophosphates (111) and cyclohexylisonitrile (110) with high yields.

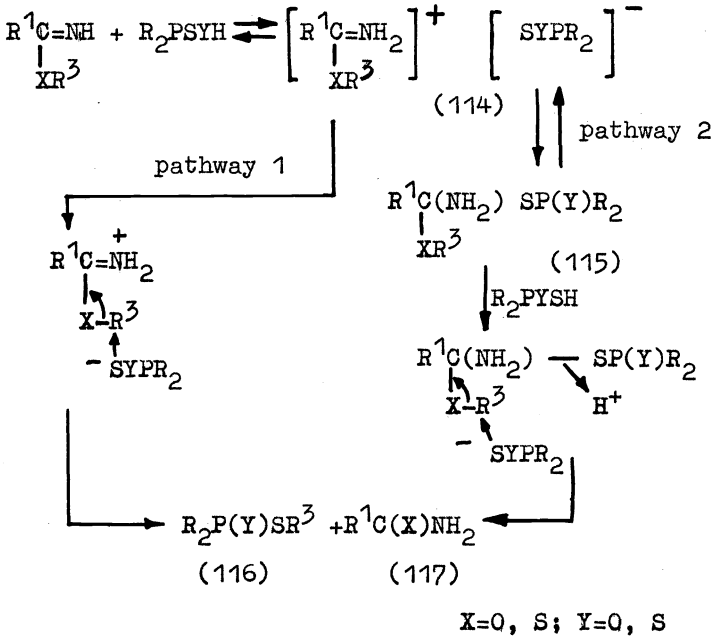


It is evident that with heating, as a result of N → S migration, (108) is isomerized into (109) in equilibrium with the initial isonitrile and dithio-

acid. Dithioacid dealkylates (Refs. 97) the ester radical at phosphorus, and dithiophosphates (111) are formed. As a result of the removal of isonitrile from the reaction sphere, dithioacid will react not with (109), as it was observed in the previous cases, but with amidophosphates (108) present in the reaction mixture. In the cases when the possibility of imidoylthiophosphates decomposing into initial components is excluded, imidoyl (112) - amide (113) tautomerism can be observed.

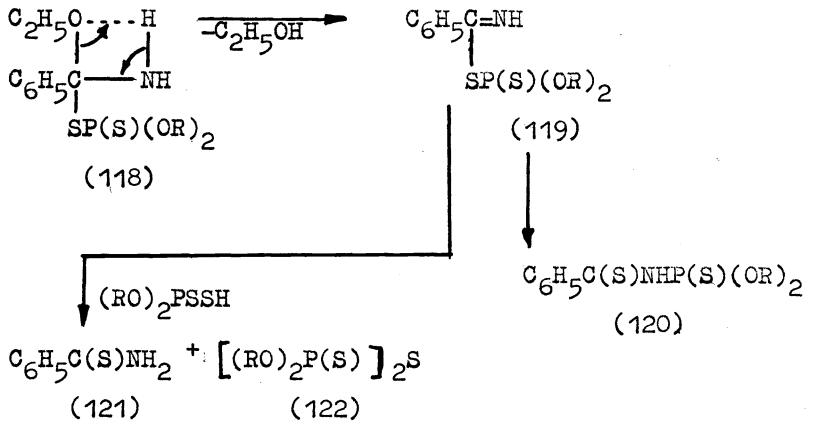


We have synthetized imidoylthiophosphates (112) from benziminochlorides and thiophosphates. In the condensed phase and in solutions they are in equilibrium with N-phosphorylated thioamides (113). In some cases it is possible to isolate the amide form (113) in crystalline state. With dissolution or heating, however, form (112) is observed to appear. A study of the IR, UV and NMR (31 P) spectra of these systems in different solvents and at different temperatures shows that they belong to tautomeric systems with the phosphoryl or thiophosphoryl groups acting as migrants. This new type of tautomerism has been designated by us as phosphorilotropism. Genetic relationship between nitriles and iminoesters has prompted us to study the behavior of the latter in reactions with the partial esters of phosphorothioic and phosphorodithioic acids (Refs. 98 & 99).



The reactions seem to include several stages. At the first stage, the nitrogen in C=N bond is protonated by the thioacid molecule, and (114) is formed. With X=Y=S, the reactions terminate at the stage when adducts, type (114), stable under normal conditions are formed. With X=O, Y=S, compounds (114) have been shown to form by monitoring the course of the reaction with the help of IR and NMR (31 P) spectroscopy (Refs. 99). The predominant direction of these reactions is the substitution of the alkyl group in the iminoester alkoxyl radical by the thiophosphate anion and the formation of neutral esters of phosphorothioic acid (116) and amides (117). This can take place either with direct dealkylation of the iminoester alkyl group by the thiophosphate anion (pathway 1) or through addition products (115). In this case, catalytic quantities of thioacid are sufficient for compounds (115) to be converted into (116) and (117). Formation of type (115) addition products is confirmed by the following experiments. When dipropyl - and diisopropylphosphorodithioic acids interact with benziminoethyl ester in

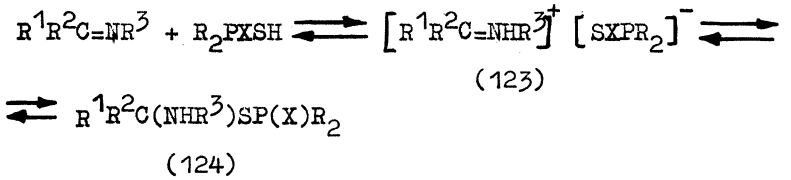
the ratio of 1:2, in addition to benzamide (70-75%) and S-ethyl-O, O-dialkyldithiophosphates (71-80%), we have isolated thiobenzamide (121) (3-7%) and N-phosphorylated thiobenzamides (120) (5%) (Refs. 98 & 99).



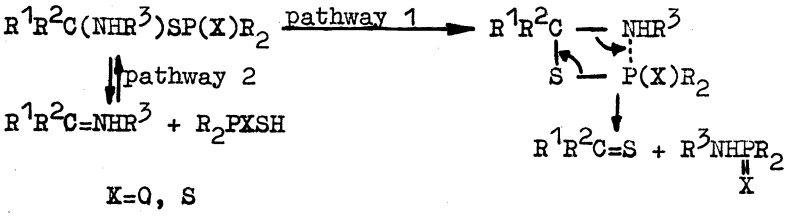
The formation of compounds (120) and (121) can only be visualized if we take into account the appearance of an intermediate (118) that splits off the alcohol molecule, which results in the formation of imidoyldithiophosphate (119). The latter is rearranged into (120) and splits the P-S bond under the action of the second dithioacid molecule to (121) and pyrophosphate (122). The rearrangement with 1.3 S → N migration of thiophosphoryl groups is thus also seen to take place in the reactions of phosphorothioic acids with iminoesters. The reactions of O,O-dialkylphosphorodithioic acids with iminoesters predominantly proceed on the sulfur. This is in agreement with the data on the predominant alkylation of POS triad via the sulfur atom (Refs.100). The results obtained indicate that iminoesters are alkylating agents not only for alkylphsphoric (Refs. 101 & 102), but also for dialkylthio and dithiophosphoric acids, which makes it possible to use them in phosphorylation processes (Refs.104). The completeness of reactions and the ease of their course will decrease in the series:

$$ABPSSH > ABPSOH > ABPOOH ,$$

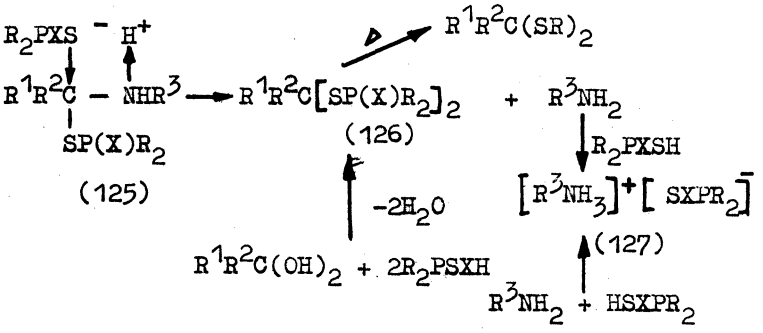
which corresponds to the decrease in the nucleophilicity of partial esters of phosphoric acids. In conclusion, we studied the possibility of the rearrangement of aminophosphates with 1.3 migration of phosphoryl or thiophosphoryl groups from the sulfur atom to the Sp^3 -hybridized nitrogen atom, similar to the "O,S exchange reaction" (Refs. 104). For this purpose we investigated the interaction of phosphorothioic acids with imines. It turned out that, reacting with nonactivated imines, dialkylmonothio- and dithiophosphoric (phosphinic) acids form adducts with a protonated C=N bond (123), which are, probably, converted into addition products (124), but, because of their aptitude to undergo various transformations, they cannot be isolated in pure state (Refs. 105).



For aniles, however, which contain electron-accepting substituents, e.g., N-acetyltrichloroacetaldimine and chloralaniline, addition products with a P-S-C bond, type (124), stable in normal conditions have been isolated. When both the adducts (123) and the addition products (124) are heated, there is no rearrangement by pathway 1; they are partially decomposed into initial components (pathway 2).



In this case, alkylidene-bisthiophosphates (126) and ammonium thiophosphates (127) were isolated from the reaction mixture or identified by physicochemical methods (Refs. 105 & 106).



We visualize their formation as resulting from the substitution of the amine group in aminothiophosphates (125) under the action of the second thioacid molecule that appears with the decomposition by pathway 2. The amine formed interacts with thioacids, producing ammonium thiophosphates (127). When compounds (123) and (124) are heated, dealkylation of ester radicals at phosphorus by the molecules of thioacids is also taking place (Refs. 105) Similar transformations occur when equimolar quantities of thioacid act upon pure aminothiophosphates (125). The results obtained show that it is easier for aminothiophosphates to decompose into initial components that to undergo isomerization. The interaction of phosphorus thioacids with compounds containing carbon-nitrogen multiple bonds is thus seen to proceed with unstable addition products being formed at first, which are then stabilized in different ways depending on their structure. When an imidoyl group is present, stabilization is accomplished by rearrangement with the migration of phosphoryl groups from the sulfur atom to nitrogen, as well as by intermolecular phosphrylation under the action of various reagents. Aminothiophosphates decompose into initial components, enter into the reactions of amine group substitution and dealkylation. All this makes it possible tc expand the possibilities of synthetizing various derivatives of thiophosphoric acids, as well as to insert a sulfur atom into various substrates with the help of partial esters of phosphorus thioic acids.

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