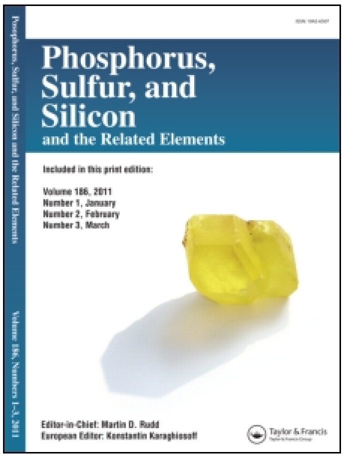

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R. M. Kamalov[a]; G. S. Stepanov[a]; N. I. Hailova[a]; M. A. Pudovik[a]; R. A. Cherkasov[a]; A. N. Pudovik[a]
[a] Arbuzov Institute of Organic and Physical Chemistry, USSR Academy of Sciences, Kazan, USSR

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THIOCYANIC ACID DERIVATIVES IN ORGANOPHOSPHORUS SYNTHESES

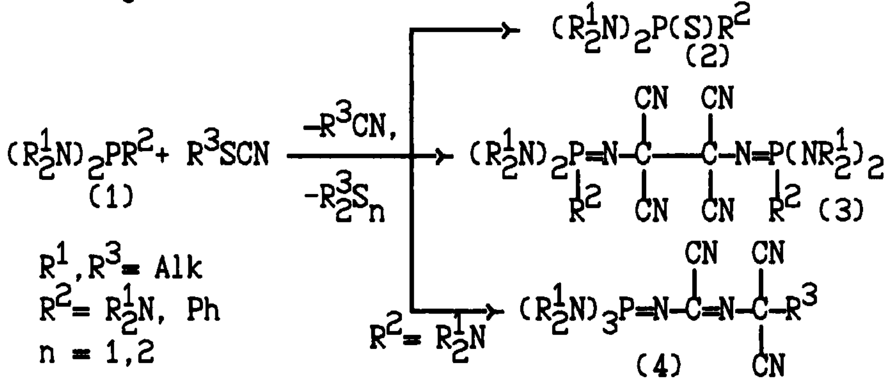
R.M.Kamalov, G.S.Stepanov, N.I.Hailova, M.A.Pudovik, R.A.Cherkasov, A.N.Pudovik
Arbuzov Institute of Organic and Physical Chemistry, USSR Academy of Sciences, Kazan, USSR.

Abstract The application of thiocyanates and isothiocyanates as convenient and available synthones in the syntheses of a wide variety of nitrogen- and sulfur-containing organophosphorus compounds with linear, cyclic, bipolar structures has been investigated. Thiocyanates react with organophosphorus reagents depending on the reactivity of the latter via cyano- or thiocyanato-groups substitutions, or addition to C≡N bond. The examples of reactions, including homolytic routes, have been found and studied. Isothiocyanates can add organophosphorus reagents both to C=N and C=S bonds.

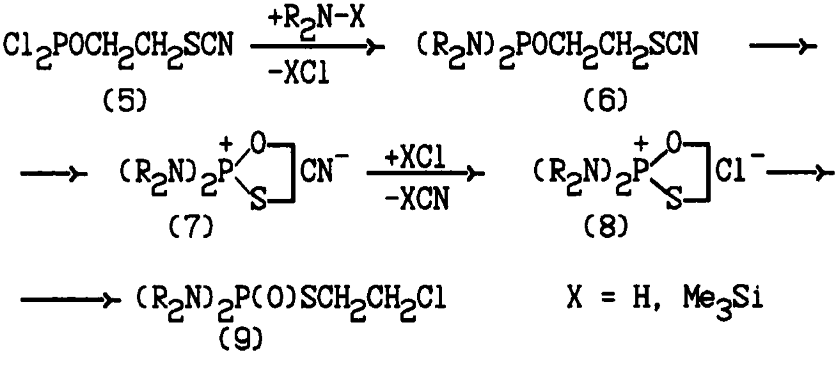
It is known[1], that P(III)-acid esters react with alkylthiocyanates according to the Arbuzov reaction scheme, producing trialkylthiolphosphates and nitriles. We have found, that when alkylthiocyanates are allowed to react with trimethylsilyldialkylphosphites or tetraalkylpyrophosphites desilylation or dephosphorylation of intermediate quazi-phosphonium salts respectively rather than dealkylation occur. Such reactions can be used as an effective method for synthesizing trimethylsilylcyanide and dialkylcyanophosphites with good yields.

It has been established that amidoesters of phosphorous acid react with alkylthiocyanates giving rise to amidothiolphosphates and nitriles. Successive interaction of hexaalkyltriamidophosphites with alcohols and then with alkylthiocyanates can be used as a technique for transformation of the hydroxy-group into the cyano-group.

The reactions of alkylthiocyanates with amides of P(III) acids with no alkoxy-groups are of a specific charakter. The products formed in the interaction between alkylthiocyanates and aminophosphines (1) are the following: thiophosphonates or phosphates (2), 1,2-diphosphazotetracyanoethanes (3), N-dicyanoalkylmethylphosphazocyanoazomethines (4), nitriles, dialkylsulfides and disulfides. The reactions, leading to these products, are assumed to include homolytic stages.



Dichloro-(2-thiocyanatoethyl)phosphite (5) has been obtained by us by the interaction between 2-trimethylsiloxyethylthiocyanate and PCl_3. Treatment of this compound with dialkylamines or trimethylsilyldialkylamines produces diamido-(2-chloroethylthiol)phosphates (9).

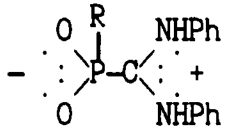


In the reactions with P(IV)-thioacids, showing a rather strong nucleophilicity, thiocyanates exibit the electrophilic triple bond properties. The first stage of the interactions between thiocyanates and dialkyl(di)thiophosphoric acids brings about unstable products of addition to the cyano-group. The latter either rearrange via the 1,3 S→ N migration of phosphoryl- or thiophosphoryl-groups into N-(thio)phosphorylated dithiocarbamates, or react with initial thioacids forming tetraalkyl(tri)thiopyrophosphates and dithiocarbamates. In appropriate conditions reactions can be used both as a convenient technique for obtaining dialkylthiophosphorylisothiocyanates and as an effective method of introducing the sulfhydrilic group into organic molecules, as well [2,3]. The protonation of nitrogen plays an important part in addition to C≡N bond reactions of thiophosphoric acids. The interaction between thiocyanates and salts of thio- or dithiophosphoric acids, when such protonation is impossible, gives rise to trialkyl(di)thiophosphates and salts of thiocyanic acid. In this case the thiocyanato-group behaves like a pseudohalogen.

The reactions of dithiophosphoric acids with chloroalkylthiocyanates involve the stage of rearrangement of the addition products to the C≡N bond into N-thiophosphorylated chloroalkyldithiocarbamates. The latter undergo cyclization to 2-(dialkoxythiophosphoryl)imino-1,3-dithietanes, dithiolanes and dithianes via HCl elimination. These can be partially split by the evolving HCl into chlorodialkylthiophosphates and 2-imino-1,3-dithietane, dithiolane and dithiane hydrochlorides.

The reactions of dithiophosphoric acids with thiocyanatoacetone originate with addition to C≡N bond, as well. Its products rearrange quickly into S-acetonyl-N-dialkoxythiophosphoryldithiocarbamates, which either disintegrate into dialkylmonothiophosphoric acids and 4-methyl-4-thiazolin-2-thione ("O,S-interchange process") (route 1), or when attached by initial dithioacids become isothiocyanatothiophosphates and O,O-dialkyl-S-(1-methyl-2-mercaptovinyl)dithiophosphates via a few stages (route 2) In these reactions small quantities of bis-(dialkylthiophosphoryl)disulfides, HSCN and acetone are formed, as well. (route 3). The products, similar to those formed by route 3, occur only in the reaction of thiocyanatoacetone with diphenyldithiophosphinic acid.

When treated with dithiophosphoric acids 10-(thiocyanatoacetyl)phenothiazine undergoes cyclization into 4-(10-phenothazinyl)-3-thiazolin-2-one. Besides, the formation of 2-dialkoxythiophosphoryl-4-thiazolin-2-one is observed. The rearrangement of addition products of the dithiophosphoric acids to the C≡N bond and the following cyclization via phenothiazine elimination is result. Amidiniophosphonates of type (10) with a bipolar structure are formed by subsequent treatment of phenylisothiocyanate with sodium dialkylphosphites, methyliodide and dithiophosphoric acids. The interactions between dithiophosphoric acids and the products of addition of dialkylphosphites or dialkylanilidophosphites to diphenylcarbodiimide result in similar products (10). The inner salt (10a) is shown to exist in E,E-form in a crystal state, but in CF_3COOH solution become a mixture of E,E- and E,Z-isomers.



(10) R = OMe(a), OEt(b), OPr(c), NHPh(d)

In contrast to alkyl- and arylisothiocyanates, dialkylphosphorylisothiocyanates add amides of the P(III) acids to C=S bond.

The N-(thio)phosphorylated thioureas, obtained from dialkyl(thio)phosphorylisothiocyanates and primary amines can be transformed into N-(thio)phosphorylated carbodiimides by the reaction with allylhalogenides in the presence of a base and the following thermal elimination of allylmercaptane. The carbodiimides can be produced from N-(thio)-phosphorylthioureas in the conditions of Appel reaction, as well. The alkylation of the latter by chloroacetic acid or their derivatives: chloroanhydrides,esters, amides gives rise to 2-(thio)phosphoriliminothiazolidin-4-one.

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