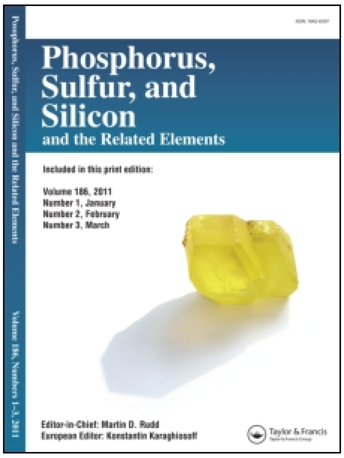

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REACTIVITIES OF PHOSPHORUS DITHIOACIDS AND S-TRIMETHYLSILYL DITHIOPHOSPHATES IN REACTIONS WITH p-QUINONES

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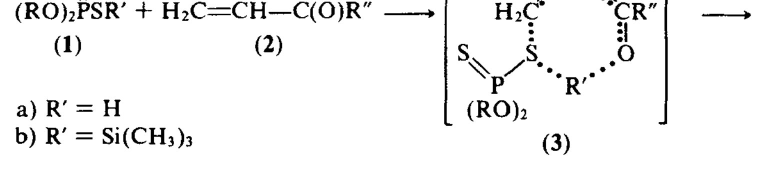
Reactions between phosphorus dithioacids and S-trimethylsilyl dithiophosphates and p-quinones yield S-2-hydroxy(trimethylsiloxy)aryl dithiophosphates which are further capable of isomerizing to the respective O-2-mercaptoaryl thiophosphates. On the basis of investigations of the kinetics of dithiophosphate addition to p-benzoquinone in various solvents and kinetic isotopic effect, some conclusions have been reached concerning the mechanism of the reaction. Investigation of the S → O isomerization of S-aryldithiophosphates suggest that the reaction involves formation of intermediates with hydrothiophosphorane structure. In the case of S-2,4-*bis*(trimethylsiloxy)phenyl dithiophosphates, the migration of the thiophosphoryl group has been found to be reversible. Isomerization of this kind has also been found to occur in products of addition of dithiophosphates to p-naphthoquinone and N-benzenesulfonyl-p-benzoquinoneimine.

INTRODUCTION

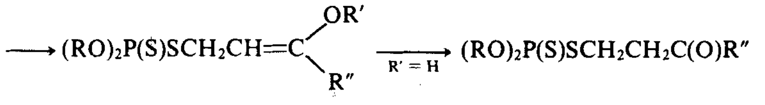
The high reactivity of dithioacids of phosphorus (**1a**) in reactions with α, β-unsaturated carbonyl compounds allows different functionally substituted S-alkyldithiophosphates, many of which are highly effective pesticides, to be obtained easily and with high yields.[1] Recently, we have shown that S-trimethylsilyl dithiophosphates (**1b**) are also able to combine with unsaturated aldehydes and ketones to produce dithiophosphorylated enolsilanes (**4**).[2] The predominant Z-configuration of the 1,4-addition products indicates that the reaction is a coordinated one and suggests participation in the activated complex (**3**) of the S-*cis* conformation of an unsaturated partner. Investigations of the kinetics of phosphorus dithioacid reactions with unsaturated carbonyl- and cyano-containing systems (**2**) have shown that, in this case as well, the process occurs via the six-centered cyclic transition state (**3**) in the rate-controlling stage.[3] Further stabilization of the intermediate (**4**) takes place owing to proton migration to the α-carbon atom, which yields a product of dithiophosphoric acid addition at the carbon–carbon double bond (**5**).



$(RO)_2P(S)SR' + H_2C{=}CH{-}C(O)R'' \longrightarrow [\,(3)\,]^{\neq} \longrightarrow$

(**1**) (**2**) (**3**)

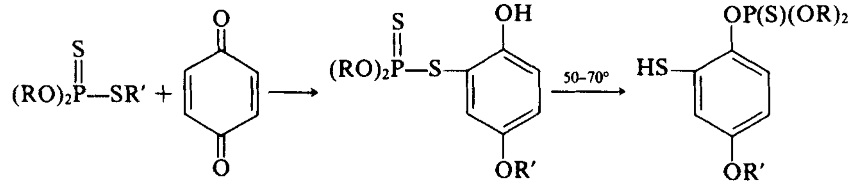
a) $R' = H$
b) $R' = Si(CH_3)_3$



$$\longrightarrow (RO)_2P(S)SCH_2CH{=}C(OR')R'' \xrightarrow[R'=H]{} (RO)_2P(S)SCH_2CH_2C(O)R''$$

(4) (5)

Silyl dithiophosphates, like dithioacids, readily combine with p-quinones (**6**), which have a fixed S-*trans*-position of the C=C and C=O bonds, to produce the corresponding S-aryl dithiophosphates (**7**).[4] On heating, the latter can isomerize to 0,0-dialkyl-0-2-mercapto-4-hydroxy(trimethylsiloxy)phenyl thiophosphates (**8**):



(1) (6) (7) (8)

The tendency for the dithiophosphate-thiophosphate rearrangement depends on the nature of the substituents at the phosphorus atom, the nature of the p-quinone, and the presence of a basic catalyst.

All the above data have prompted us to investigate in detail the mechanism of reactions of phosphorus dithioacids and silyl dithiophosphates with p-benzoquinone. The considerable difference between the rates of addition and isomerization reactions has permitted us to study the two processes independently by varying the experimental conditions.

RESULTS AND DISCUSSION

Kinetics and Mechanism of Dithiophosphate Addition to p-Benzoquinone

Spectrophotometric investigations of the addition of phosphorus dithioacids and silyl dithiophosphates to p-benzoquinone has shown that the reaction rate follows

TABLE I

Effect of substituents in dithiophosphates $RR^1P(S)SH$ and $RR^1P(S)S—Si(CH_3)_3$ on the rate of their reactions with p-benzoquinone (T = 20°C, solvent—heptane).

			$k \cdot 10^2$ L/(mol·s)	
No	R	R^1	$RR^1P(S)SH$	$RR^1P(S)S—Si(CH_3)_3$
1	CH_3O	CH_3O	12.37	0.36
2	C_2H_5O	C_2H_5O	8.39	0.37
3	i-C_3H_7O	i-C_3H_7O	6.99	—
4	C_3H_7O	C_3H_7O	5.31	0.99
5	CH_3	CH_3O	8.41	—
6	CH_3	C_2H_5O	5.83	1.37
7	C_2H_5	i-C_3H_7O	2.04	—
8	C_6H_5	C_6H_5	18.6	5.07
9	C_2H_5	C_2H_5	9.4	—
10	i-C_3H_7	i-C_3H_7	2.19	0.77

TABLE II

Effect of solvent on the rate constants of reactions between $(C_2H_5O)_2P(S)SH$ (k_a), $(C_2H_5O)_2P(S)S{-}Si(CH_3)_3$ (k_b) and p-benzoquinone (T = 20°C).

No	Solvent	$k_a \cdot 10^2$ L/(mol·s)	$k_b \cdot 10^2$ L/(mol·s)
1	Benzene	4.46	0.55
2	Chloroform	5.75	—
3	Toluene	7.25	0.32
4	Tetrachloromethane	8.04	0.23
5	n-Heptane	8.39	0.38
6	1,2-Dichloroethane	9.54	0.44
7	Diethyl Ether	146	80.1
8	1,4-Dioxane	197	49.0
9	Acetonitrile	340	297
10	Acetone	525	764

second-order kinetics, e.g., first-order in each reactant. It follows from Table I that silyl dithiophosphates are less active in heptane than the respective acids and the reaction susceptibility to the substituent at the phosphorus atom is small. And whereas one can observe a tendency for higher reaction rates with higher acidity in certain phosphorus dithio-compounds (phosphates, phosphonates, phosphinates), on the whole this tendency is undetectable. This may be due to the important role not only of the acid but also the nucleophilic properties exhibited by dithiophosphates in addition processes.

The reaction rate is markedly increased in basic solvents (Table II). In the correlation equations accounting for the effects of polarity, polarizability and specific properties of the solvent (Eq. 1)[5] on reaction rate of 0,0-diethyl dithiophosphoric acid (Eq. 2) and its S-trimethylsilyl ester (Eq. 3) with p-benzoquinone, it is only the contribution of nucleophilic solvation of solvent that is statistically meaningful (B):

$$\log k = \log k_0 + yY + pP + bB + eE \tag{1}$$

$Y = (\epsilon - 1)/(2\epsilon + 1)$; $P = (n^2 - 1)/(n^2 + 1)$; where B is nucleophilicity, and E is the electrophilicity of the solvents

$$\log k = (-2.076 \pm 0.508) + (0.0063 \pm 0.0014)\, B \tag{2}$$

$n = 10$, $R = 0.918$, $s_0 = 0.389$.

$$\log k = (-1.496 \pm 0.173) + (0.0076 \pm 0.0013)\, B \tag{3}$$

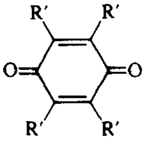
$n = 9$, $R = 0.935$, $s_0 = 0.393$.

In pronouncedly nucleophilic solvents, the reactivity of silyl dithiophosphates becomes comparable with that of phosphorus dithioacids.

To discover the reasons for such behavior, we have undertaken an investigation of the deuterium kinetic isotope effects (KIE) of dithiophosphorus acids and p-benzoquinone in different solvents (Table III). In all cases, the dithioacids exhibited a reverse KIE, indicating a much stronger attachment of the hydrogen atom in the transition stage of proton transport from the phosphoric reactant (**1a**) to p-benzo-

TABLE III

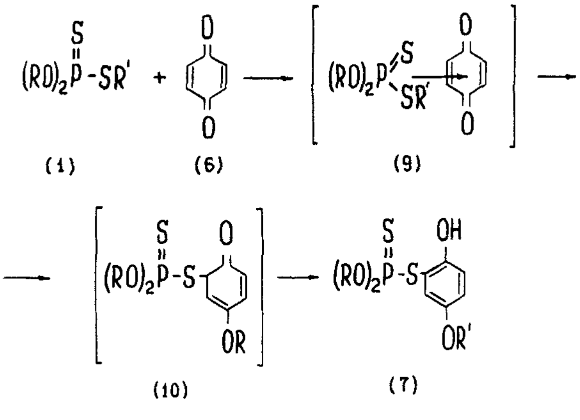
Effect of solvent on the kinetic isotope effect of reactions between $(C_2H_5O)_2P(S)SR$ and



(T = 20°C).

Solvent	R	R'	$k\cdot10^2$ L/(mol·s)	$\frac{k_H}{k_D}$	R = $Si(CH_3)_3$	$k\cdot10^2$ L/(mol·s)	$\frac{k_H}{k_D}$
					R'		
n-Heptane	H	H	8.39	0.46	H	0.376	1
	D	H	18.23		D	0.377	
	H	D	8.39	1			
	D	D	19.27	0.43			
Benzene	H	H	4.46	0.42	H	0.55	1
	D	H	10.54		D	0.55	
	H	D	4.46	1			
	D	D	10.21	0.44			
1,4-Dioxane	H	H	197	0.46	H	49	1.5
	D	H	425		D	32.6	
	H	D	97	2.03			
Acetonitrile	H	H	340	0.53	H	297	2.13
	D	H	642		D	139	
	H	D	95	3.58			

quinone (**6**) which may be due to similarity of the structures of the activated complex and the intermediate (**10**)[6] (Scheme 1):



a) R' = H (D)
b) R' = $Si(CH_3)_3$

SCHEME 1

For deuterated p-benzoquinone, the KIE of reaction with dithiophosphates (**1a, b**) in heptane and benzene was found to be equal to unity; that is, the ring-proton migration begins following the limiting stage of reaction. In basic solvents (dioxane, acetonitrile), where the k_H/k_D ratio is much above unity, it is the conversion of the intermediate (**10**) to the product (**7**) which is the controlling stage (Figure 1). A similar KIE behavior of p-benzoquinone is observed in its reaction with 0,0-diethyl-S-trimethylsilyl dithiophosphate (Table III).

These results, considered all together, suggest that the addition of dithiophosphates to p-benzoquinone follows Scheme 1. The similarity of the mechanisms of interaction of phosphorus dithioacids (**1a**) and their S-trimethylsilyl esters (**1b**) with quinone (**6**) is corroborated by a correlation between the log k of the two processes in the solvents used (Eq. 4), (Table II);

$$\log k_a = (0.066 \pm 0.054) + (0.771 \pm 0.049) \log k_b \tag{4}$$

$R = 0.988$, $s_0 = 0.131$.

Subscripts "a" and "b" stand for addition of $(C_2H_5O)_2P(S)SH$ and $(C_2H_5O)_2P(S)S{-}Si(CH_3)_3$ to p-benzoquinone, respectively.

Considering the high electron-acceptor activity of p-benzoquinone[7] and the nucleophilicity of the sulfur atom of dithiophosphates,[8] one may conclude that the first to be formed is an n-π-complex (**9**) whose concentration and stability is apparently too low, since it was impossible to detect it spectrally. This circumstance, however, does not mean that a reversal of the initial reaction is impossible under certain experimental conditions. After that, the complex is endothermally converted to the intermediate (**10**), which process may be the rate-controlling one in weakly basic solvents. This is the reason for the lower activity of silyl dithiophosphates than acids (Table II). The fact that there is a complexing stage and a late rate-limiting transition state explains why the reaction rate is so little affected by the substituent at phosphorus atom and the dielectric constant of the solvent. In markedly nucleophilic solvents, it is the transport of the ring proton to the carbonyl group of the intermediate (**10** → **7**) which becomes rate-limiting, and the reactivity of silyl dithiophosphates becomes comparable with those of phosphorus acids (Figure 1).

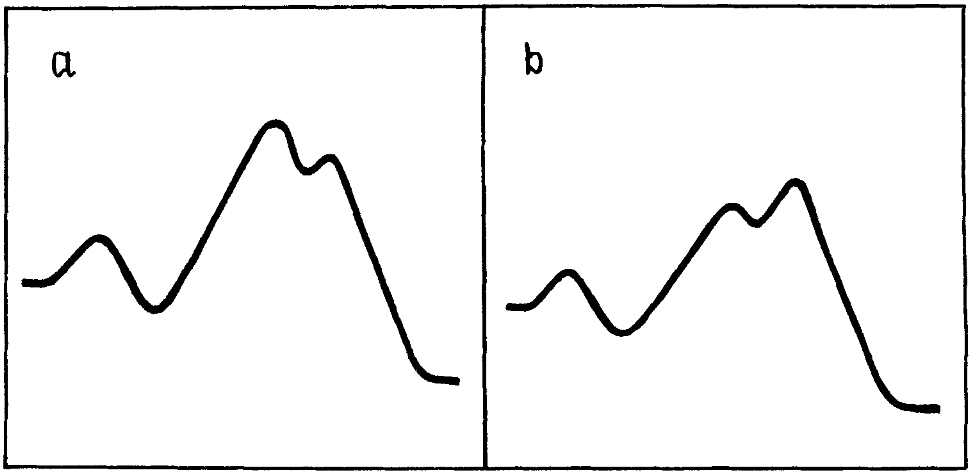
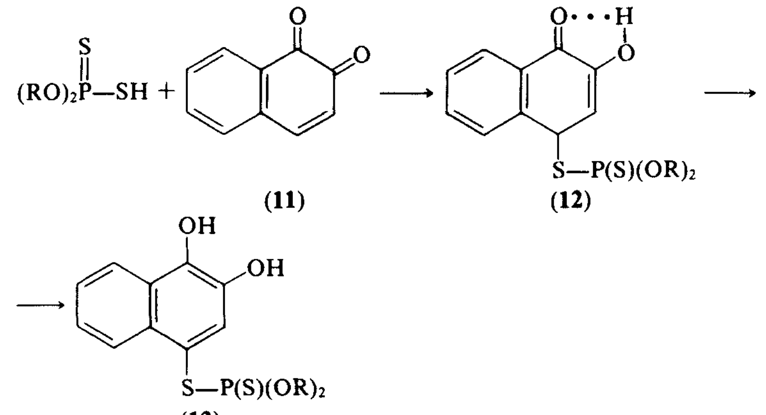


FIGURE 1 Energy profile of the addition of dithiophosphates (1) to p-benzoquinone: (a) in weakly basic solvents, (b) in basic solvents.

In reactions between dithiophosphoric acids and 1,2-naphthoquinone (**11**), the aromatic ring proton migrates so slowly that it is possible to detect the formation of the intermediate (**12**). The IR spectrum of the reaction mixture shows new absorption bands for the carbonyl (1650 cm^{-1}) and hydroxyl (3430 cm^{-1}) groups bonded through an intramolecular H—bond, whereas the bands corresponding to the S—H group in the range 2550–2600 cm^{-1} disappear. Later on, the intermediate (**12**) is gradually transformed to the product (**13**). Here, the disappearance of the C=O band (1650 cm^{-1}) is concurrent with appearance of two new intensive OH bands in the 3560 and 3610 cm^{-1} regions that are weakly H—bonded:



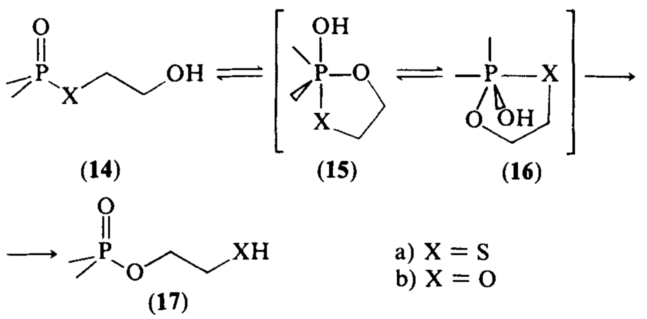
(**11**)

(**12**)

(**13**)

Isomerization of s-Aryldithiophosphates (**7**) *to Monothiophosphates* (**8**)

As noted above, the addition products of dithioacids of phosphorus and S-trimethylsilyl dithiophosphates to p-benzoquinone are capable of isomerizing more or less easily to 0-2-mercaptoaryl esters of phosphorus dithioacids (**8**). Isomerization of phosphorus acid esters containing a gamma-hydroxy substituent was investigated earlier for a number of compounds. For instance, S-2-hydroxyalkyl thiophosphates (**14**), which are products of reaction between thiophosphoric acids and oxetanes, quite readily isomerize to 0-2-mercaptoalkyl phosphates (**17**).[9] In solutions, hydroxyphenyl phosphinates are in a state of dynamic equilibrium maintained by the phosphinate group migration to the ortho-oxygen atom.[10] Most probably, all these rearrangements occur via hydroxyphosphoranes (**15**, **16**), and the isomerization is easy because of the relative stability of the intermediates of the trigonal-bipyramidal structure



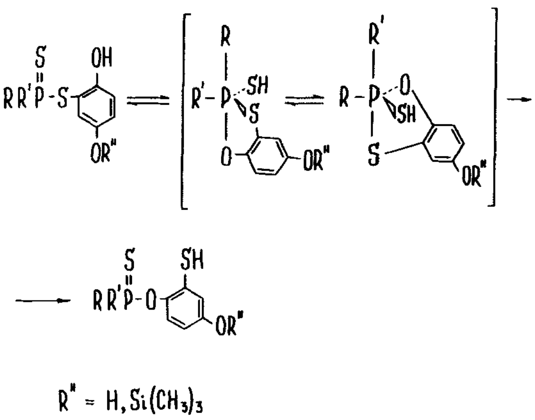
(**14**) (**15**) (**16**)

(**17**)

a) X = S
b) X = O

The formation of hydroxyphosphoranes in prototropic processes of this kind has been observed for 2-hydroxyphenyl-phenylene phosphate.[11] The stability of hydroxyphosphoranes is increased when the spirophosphorane structure is formed, especially when the phosphorus atom is part of a five-membered ring and the number and electron-acceptor activity of the substituents in cyclic fragments are increased.[12]

We propose that isomerization of 2-hydroxyaryl dithiophosphates (**7**) also involves formation of hydrothiophosphoranes at an intermediate stage (**18a, b**) (Scheme II)



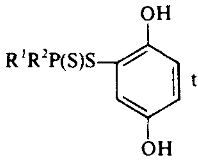
SCHEME 2

It was not possible to detect formation of the intermediates of the type (**18a, b**) either by spectral methods or fixing with diazomethane, as in the case of isomerization of 2-hydroxyaryl esters of diphenylthiophosphinic acid.[10] This is apparently the result of the primarily unstable nature of the hydrothiophosphorane structures.

The ^{31}P NMR spectroscopic investigation of the isomerization kinetics of S-2,5-dihydroxyphenyl esters of phosphorus dithioacids has revealed the monomolecular nature of the process. From the results (Table IV) it is seen that the effect of the substituent at the phosphorus atom in acyclic acid derivatives is made up of electronic and steric factors and is generally not strong. Addition of alkyl donors to the phosphorus atom (compounds **2**, **3**, Table IV) reduces the isomerization rate, apparently due to the reduction of effective positive charge on phosphorus. This hind-

TABLE IV

Effect of substituents and solvents on the rate of isomerization of dithiophosphates (**7**)



to thiophosphates (**8**). (C = 1 mol/L, T = 100°C).

No	R^1	R^2	$k \cdot 10^3$ sec^{-1} p-Xylene	$k \cdot 10^3$ sec^{-1} Nitrobenzene
1	CH_3O	CH_3O[a]	0.90	0.81
2	CH_3	C_2H_5O	0.48	0.38
3	C_2H_5	C_2H_5	0.35	—
4	i-C_3H_7O	i-C_3H_7O	—	0.12
5	—$OCH(CH_3)CH(CH_3)O$—		fast	

[a] $k \cdot 10^3$ sec^{-1}: CH_3COOH 1.0, C_6H_5Cl 1.2, $C_6H_5CH_3$ 0.8.

ers the ortho-hydroxy attack on the phosphorus atom. Furthermore, when intermediates have the trigonal-bipyramidal structure, the less apicophilic substituents have to take one of the apical positions in phosphoranes (**18a** or **18b**).

The marked reduction of the isomerization rate of 0,0-diisopropyl dithiophosphate is brought about by the steric effect of the isopropoxy-group which is in the apical position in structures (**18a, b**). Interaction with the three equatorial substituents reduces the apicophility of the groups having high steric requirements[13] and, therefore, increases the intermediates' (**18**) energy.

However, in the case of cyclodithiophosphate (Compound **5**, Table IV), isomerization is so fast that the corresponding 2,5-dihydroxyphenyl dithiophosphate (**7**) cannot be isolated even at room temperature. The low energy of the intermediate spirocyclic hydrothiophosphoranes is responsible for such acceleration. Spirocyclization promotes all sorts of prototropic processes involving formation of hydroxyphosphoranes.[11,12]

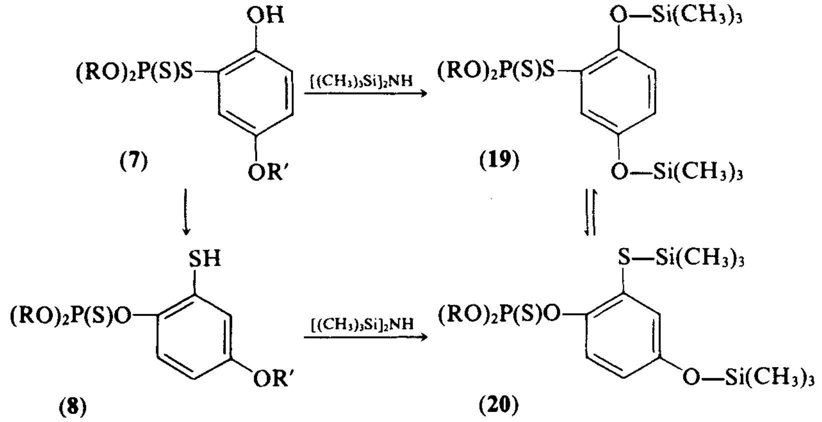
A similar effect of the substituents at the phosphorus atom on isomerization rate has been observed in 2-hydroxyethyl thiophosphates.[9,14]

The rather weak effect of solvent polarity and acidity on isomerization rate is a noteworthy fact. Insensitivity of the process to variation of the dielectric properties of the solvent is indicative of the fact that no appreciable charge separation occurs in the transition state of the rate-limiting stage which, in turn, is evidence in favor of the proposed rearrangement path (Scheme II).

The use of catalysts of basic nature that promote proton transport to the sulfur atom of the thiophosphoryl group and formation of the P—O—C bond in the intermediate (**18**) tangibly speeds up the process. Isomerization of S-2,5-dihydroxyphenyl diphenyl dithiophosphinate in the presence of equimolar quantities of triethylamine can occur at temperatures below 0°C; the rate constant of this reaction in acetone $K\ (170\ K) = 3.1 \times 10^{-2}\ sec^{-1}$.

Substitution of the trimethylsilyl group for the hydrogen atom of the ortho-hydroxy substituent by treating the adduct (**7**) with a stoichiometric amount of hexamethyldisilazane markedly stabilizes the dithiophosphate structure (**19**). The S → O migration of the thiophosphoryl group may occur only in the presence of a basic catalyst or excess of a silylating agent. The process is reversible in this case.

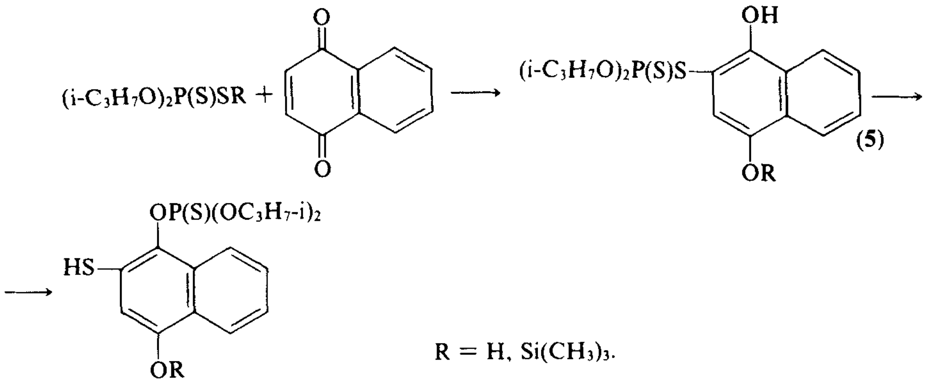
That the isomerization is an equilibrium process has been shown for the reaction of monothiophosphate (**8**) with hexamethylsilazane: the product (**20**) is partially converted to dithiophosphoric acid derivative (**19**) in the presence of a basic catalyst.



$R' = H, Si(CH_3)_3$.

Thus, the trimethylsilyl group which is strongly trapped by the oxygen of the ortho-substituent in S-aryl dithiophosphate (**19**) can migrate to the sulfur atom of the phosphorus fragment only in the presence of a base. In this process, the energy gain due to the dithiophosphate-thiophosphate rearrangement is accompanied by a certain destabilization of the system because the energy of the Si—S bond is smaller than that of Si—O.[15] All this renders the energies of the silicon-containing aryl dithio- and monothiophosphates almost equal and thus permits an equilibrium between them.

Reactions of 0,0-diisopropyl-S-trimethylsilyl dithiophosphate and dithiophosphoric acid with p-naphthoquinone also involve phosphorylotropic conversions (Eq. 5):

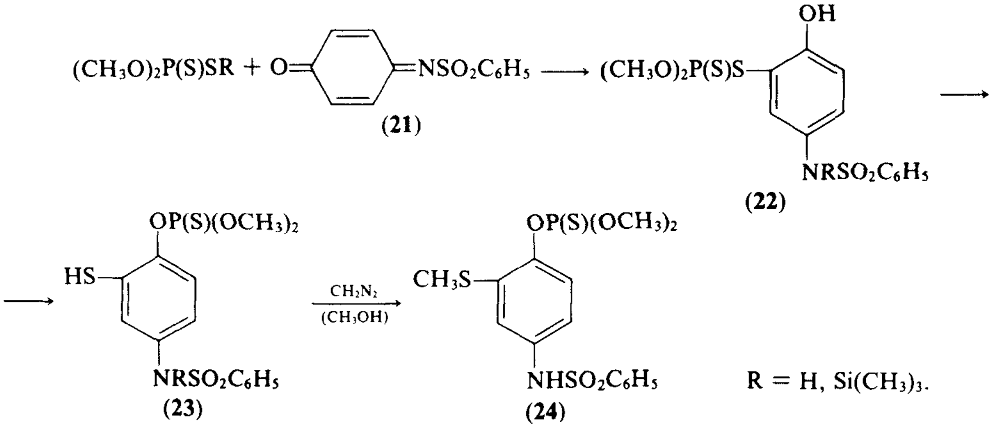


(5)

R = H, $Si(CH_3)_3$.

One would expect the products of the reaction of dithiophosphates (**1**) with p-quinoneimine to be the 1,4-adducts with participation by either the carbonyl or the imine. In the latter case, the reaction may involve isomerization of the dithiophosphoric compound to the corresponding thiophosphate.

0,0-Dimethyl dithiophosphoric acid as well as its S-trimethylsilyl ester rapidly combine with N-benzenesulfonyl-p-quinoneimine (**21**) yielding 0,0-dimethyl-S-(2-hydroxy-5-N-benzenesulfonylamino)phenyl dithiophosphates (**22**) which, on storage or heating, easily transform to the corresponding monothiophosphates (**23**); 0,0-dimethyl-0-(2-methylthio-4-N-benzenesulfonylamino)phenyl thiophosphate (**24**) has been isolated and identified by treatment with diazomethane.

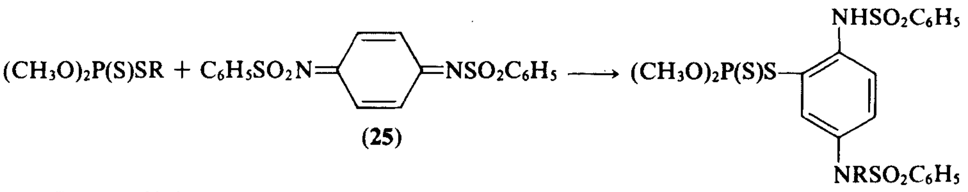


(**21**) (**22**) (**23**) (**24**)

R = H, $Si(CH_3)_3$.

Thus, unlike the reactions with p-benzoquinone, those of silyl dithiophosphates and phosphorus dithioacids with p-quinoneimine take place at the imino-bonds followed by the S → O migration of the thiophosphoryl group.

In the case of p-quinonediimines (**25**), the reaction terminates at the formation of adduct (**26**):



(**25**)

R = H, Si(CH$_3$)$_3$.

(**26**)

EXPERIMENTAL

S-Trimethylsilyl dithiophosphates (**1b**) were prepared as described elsewhere.[16] Deuterated 0,0-diethyl dithiophosphoric acid and p-benzoquinone were obtained using C_2H_5OD and D_2O. The constants of the adducts of dithiophosphates (**1**) and quinones as well as their isomerization products have been reported in an earlier work.[4] The IR spectra were taken with an UR-20 spectrometer.

Kinetic Experiments

The kinetics of addition of dithiophosphates (**1**) to p-benzoquinone was studied spectrophotometrically with a CΦ-26 instrument in thermostatted vessels. The solvents were purified by multiple distillation over dessicating agents. All the experiments were conducted in an inert atmosphere.

The isomerization rate was measured by ^{31}P NMR spectroscopy with a KGY-4 instrument at 10.2 MHz; the external reference was 85% orthophosphoric acid. The isomerization rate was measured according to the variation of intensity of the signals of the starting (**7**) and isomerized (**8**) aryl thiophosphates.

The kinetic results were statistically processed using a multidimensional regression analysis program on an ODRA-1304 computer.

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