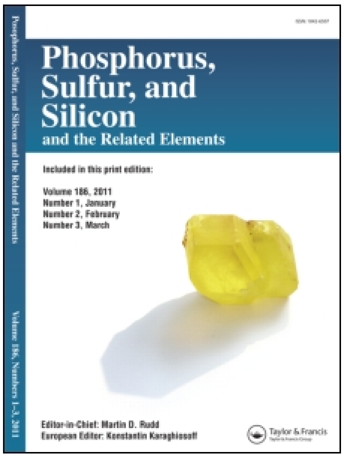

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ALKOXYPHOSPHONIUM SALT INTERMEDIATES IN THE THIONO–THIOLO REARRANGEMENT OF PHOSPHYLTHIONATES IN PROTIC ACID MEDIA

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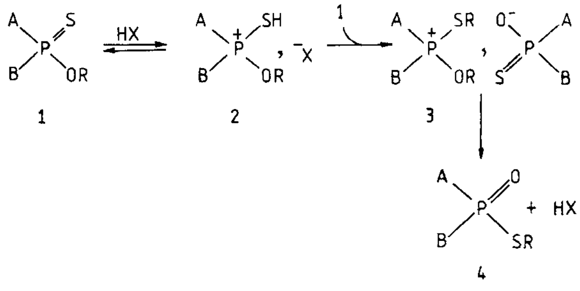
The thiono–thiolo rearrangement reaction of phosphylthionates **1** catalyzed by protic acids proceeds with the formation of two types of intermediate alkoxyphosphonium salts **2** and **3**. The first of these is formed by the protonation of the substrate **1** at the sulfur atom. Formation of **2** is evident from the changes in chemical shifts in ^{31}P NMR spectroscopy of phosphylthionates upon their interaction with trifluoroacetic acid and also from the appearance of electrical conductivity in the solutions of substrates in TFA. The extent of protonation is consistent with the expected substituent effect on the basicity of thiophosphoryl sulfur. The second type of alkoxyphosphonium salt is formed by the alkylation of neutral esters with **2**. The formation of **3** is observed in both ^{1}H and ^{31}P NMR spectra. **3** were identified by their spectroscopic comparison with alkoyxphosphonium salts produced by alkylation of **1** with strong alkylation agents. The relative reactivity of a model alkoxyphosphonium salt towards a neutral ester and a phosphylthioate anion was investigated. In the absence of acid the rate of alkylation of the anion exceeds that of the alkylation of a neutral ester by three orders of magnitude. The protonation of phosphylthioate anion under acidic conditions results in a dramatic decrease in the rate of alkylation thereby leading to accumulation of **3** in the acidic reaction media.

INTRODUCTION

In our previous work on the mechanism of the thiono–thiolo rearrangement of primary alkyl phosphylthionates **1** in carboxylic acids we have postulated the formation of transient alkoxyphosphonium salts **2** and **3** (Scheme 1).[1]

According to our proposal[1,2] in the first step of the rearrangement process protonation of the thiophosphoryl sulfur occurs with the formation of the phosphonium salt **2**. The electrophilic solvation of the substrate enhances reactivity of **2** as compared to the neutral molecule. Phosphonium salt **2** is thus able to alkylate the next molecule of the substrate **1** with the formation of the alkoxyalkylthiophosphonium salt **3**. The direct transfer of the alkyl group from the phosphonium cation to the phosphylthioate anion within **3** brings about the formation of two molecules of S-alkyl product **4**.

The participation of alkoxyphosphonium salt intermediates in the thiono–thiolo rearrangement has been a subject of dispute. The existence of this type of intermediates was postulated by Teichmann and Hilgetag in thermally induced[3] and Lewis acid catalyzed[4] reactions while other workers proposed different mechanisms involving free radicals for primary alkyl esters[5] and carbonium ion-pair[6,7] or sigmatropic rearrangement mechanism[8] for allyl esters without intervention of alkoxyphosphonium salts. The existence of phosphonium salt



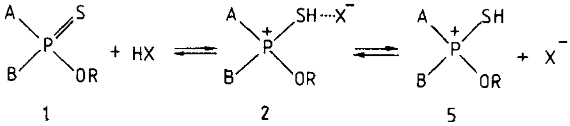
Scheme 1

intermediate was unequivocally proved only in the case of the rearrangement of 0,0,0-trimethyl phosphorothioate in the presence of $SbCl_5$.[4]

In Arbuzov reactions induced by alkyl halides, thought to proceed by the similar type of mechanism, the intermediacy of alkoxyphosphonium salts has been proved by spectroscopic data.[9,10]

In this report we present evidences for the formation of the alkoxyphosphonium salts **2** and **3** as intermediates in the investigated reaction.

It has been known for some time that in nonaqueous strongly acidic media phosphorothioate bases with sulfur in non-bridged position exist in the form protonated at sulfur such as **2** and/or **5**[11] (Scheme 2).



Scheme 2

The formation of species **2** or **5** was manifested by the characteristic changes of chemical shifts in ^{31}P and ^{1}NMR,[11,12] observation of the geminal coupling constant $^{2}J_{PSH}$ in ^{1}H NMR,[11] the dipole moment of the interaction between the base and the acid,[13,16] and also by the electrical conductivity of the solutions.[13,15] On the other hand interaction of weak acids like alcohols,[16] phenols[17] and weak carboxylic acids[13,18] with thiophosphoryl donors leads to the formation of the hydrogen bonded complexes[16] within the entire range of basicity of phosphorothioyl compounds. In solutions of trialkyl phosphine oxides and chlorinated carboxylic acids in nonpolar solvents such as CCl_4 the acid-base equilibria involve free bases **1**, hydrogen bonded complexes **6** as well as proton transfer complexes **2** and dissociated ions **5**.[13,16] Based on the dipole moment measurements it was believed that no appreciable proton transfer occurs unless enthalpy of interaction exceeds 38 KJ/mole.[13]

RESULTS

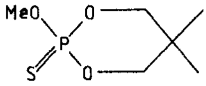
The interaction of trifluoroacetic acid with phosphorothioyl esters

In our previous papers we have found that trifluoroacetic acid alone or its mixtures with methylene chloride are the most convenient media to perform the thiono–thiolo rearrangement reactions of a wide variety of phosphylthionate esters.[2] We therefore, have chosen the same solvents for the study of acid-base interactions.

^{31}P and ^{1}H NMR spectroscopy was used to study the protonation process. Thiophosphoryl esters of expected high basicity were used as bases: O-propyl dimethylphosphinothioate **7**, O-methyl diphenylphosphinothioate **8**, and methylphenylpropylphoshine sulfide **9**. NMR spectra were recorded using CH_2Cl_2 and SO_2-CF_3COOH solvent systems. It appeared that even at the lowest temperature technically achievable (−173°K), we failed to observe the formation of a distinct protonated species **2**. The only spectral changes seen in the low-temperature ^{31}P NMR spectra upon addition of TFA to the solutions of compounds **7**–**9** was a small shift of the resonances towards the low field region. The data collected in the Table I illustrate the influence of the substituents at phosphorus in phosphylthionates **1** on the magnitude of chemical shift difference obtained upon transfer from 0.2 M CH_2Cl_2 solution into CF_3COOH at room temperature.[21] Because the chemical shift measured under the conditions of fast proton exchange is a weighted mean of the chemical shifts of all species involved in acid-base equilibrium (Scheme 2) the small differences for phosphorothionates (Table I, entries 6–8) may originate either from the small differences in $\delta_{^{31}P}$ of free bases and their conjugate acids and/or low concentration of the protonated species. The former seems not to be the case since $\Delta\delta$ for trialkyl phosphorothionates approximates 20 ppm.[11] Consequently, the small values of $\Delta\delta$ may arise from a low concentration of the proton transfer complexes **2** or free phosphonium ions in

TABLE I

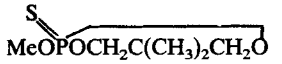
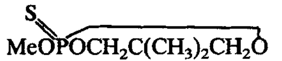
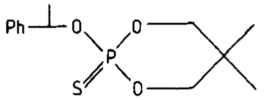
The influence of the substituents at phosphorus on the magnitude of ^{31}P NMR chemical shift change for **1** upon transfer from 0.2 M solution in CH_2Cl_2 to TFA at 298°K

Exp. no.	Thiophosphoryl base	$\delta_{^{31}P}$ $[CH_2Cl_2]^a$ [ppm]	$\delta_{^{31}P}$ $[TFA]^a$ [ppm]	$\Delta\delta$ $[ppm]^b$
1	$Me_2P(S)OPr^n$	91.5	101	9.5
2	$MePrPhP{=}S$	38.5	44.7	6.2
3	$Ph_2P(S))Me$	83.1	86.3	3.2
4	$Ph_3P{=}S$	42.5	43.0	0.5
5	$Ph_2P(Se)OMe$	87.5^c	88.5^d	1.0
6	$(MeO)_3P{=}S^e$	72.3	70.8	−1.5
7	$MeO(PHO)(1\text{-}NaphO)P{=}S$	59.5	59.7	0.2
8		63.3	63.3	0.0

[a] ±0.1 ppm; [b] $\Delta\delta = \delta_{^{31}P}[TFA] - \delta_{^{31}P}[CH_2Cl_2]$; ±0.2 ppm;
[c] $^{1}J_{P-Se} = 803 \pm 4$ Hz; [d] $^{1}J_{P-Se} = 723 \pm 4$ Hz;
[e] $\delta_{^{31}P}$ of the conjugated acid is 50.2 ppm[11]

TABLE II

Conductivity of thiophosphoryl compounds in trifluoroacetic acid solutions at 303°K

Exp. no	Compound[a]	G_0^{30b} [μS]	Λ^{30c} [$cm^2\,\Omega^{-1}\,eq^{-1}$]
1	MePrPhP=S	802	10.1
2	$Ph_2(OMe)P{=}S$	83	1.05
3	 $MeO\overset{S}{P}OCH_2C(CH_3)_2CH_2O$	45.5	0.537
4	 $MeO\overset{S}{P}OCH_2C(CH_3)_2CH_2O$	109.6	0.138
5	MeO(PhO)(1-NaphO)P=S	5.4	$6{\cdot}8 * 10^{-2}$
6		~1	$\sim 2.5 * 10^{-3}$ [d]

[a] Concentration of phosphorothioyl compound was 10^{-2} M unless otherwise stated; [b] conductivity of the solution extrapolated to zero time (see Experimental Section); [c] $\Lambda^{30} = 1/c * p * G_0^{30}$ where: c—concentration of the base [M], p—cell constant [cm^{-1}], Λ^{30}—equivalent conductivity, [d] concentration 0.1 M, CH_2Cl_2: hexafluoroisopropanol (10% v/v) solution.

the equilibrium mixture or from the total absence of protonated forms. Clearly, the fraction of protonated species is much higher in case of more basic phosphylthionates containing carbon-phosphorus bond.

The difficulties associated with a low sensitivity of detection of proton transfer by such methods like dipole moment measurements or ^{31}P NMR are circumvented by the measurements of electric conductivity.[26] Despite the fact, that only free ions contribute to the measured electric conductivity, it can be assumed that the total concentration of protonated species is much higher than measured by this method, due to substantial aggregation of ionic species in weakly polar solvents such as methylene chloride or TFA. This technique is especially useful for the detection of proton transfer, when it proceeds to a very minor extent. The electric conductivities of the solutions of several representative thiophosphoryl compounds in trifluroracetic acid are tabulated in Table II.

In accordance with the results of ^{31}P NMR the highest conductivity in the group of investigated compounds was found for the solution of phosphine sulfide **9** and the lowest one for the solution of O-methyl-O-1-naphthyl-O-phenylphosphorothioate (**10**). Lowering the base concentration increases the equivalent conductivity (Λ^{30}). This can be attributed to enhanced ion-pairing in more concentrated solutions. The results collected in Tables I and II can be interpreted in terms of substituent effect on the basicity of phosphylthionates and on equilibrium constants for the formation of different protonated species (Scheme 2).

On the basis of the previously reported IR spectra of the mixture of **8** and TFA in CCl_4 (lowering of the stretching frequency for the P=S bond in **8** by 8 cm^{-1} in the presence of TFA)[1] and the $\Delta\nu_{P=S} - \Delta H$ correlation reported by Borovikov *et al.*[13b] we could calculate the approximate enthalpy of the interaction between

TFA and **8** as 30 KJ/mole. This value suggests the absence of proton transfer in [**8** + TFA] acid-base pair. On the contrary, the results of conductivity measurements are in favour of the occurrence of the proton transfer. Our conductivity data suggest that even in the case of weak base–weak acid pairs such as phosphorothioate esters and trifluoroacetic acid, proton transfer still occurs although to a lower extent than in the case of more basic phosphine sulfides.

Alkoxyphosphonium salts formed in the course of the rearrangement process

Monitoring the progress of the rearrangement reaction of O-methyl diphenylphosphinothioate (**8**) in TFA medium by means of ^{31}P and ^{1}H NMR allowed us to detect the formation of an intermediate in this process (Figure 1). ^{31}P NMR spectrum of the reaction mixture [**8** + TFA] recorded after 1.5 h at 296°K showed two signals at 86.3 ppm and at 62.8 ppm in addition to peaks corresponding to substrate (85.6 ppm) and product (60.7 ppm). After a longer reaction time the first three signals disappeared and only one signal for the product S-methyl diphenylphosphinothiolate (**12**) could be observed. The structure of the observed intermediate was proved by the separate synthesis of methoxymethylthiodiphenylphosphonium tetrafluoroborate (**11**, Scheme 3)[20] and comparing its spectral parameters with those characteristic of the intermediate.

The second peak of the intermediate was identified as diphenylphosphinothioic acid. The formation of alkoxyphosphonium salts of type **3** (Scheme 1) at higher concentration level was also observed in the rearrangement reactions of O-3,3-d_2-allyl dimethylphosphinothioate (**14**), and O-benzyl dimethylphosphinothioate (**15**) in TFA. In cases of rearrangement reactions of 2-alkoxy-2-thiono-5,5-dimethyl-

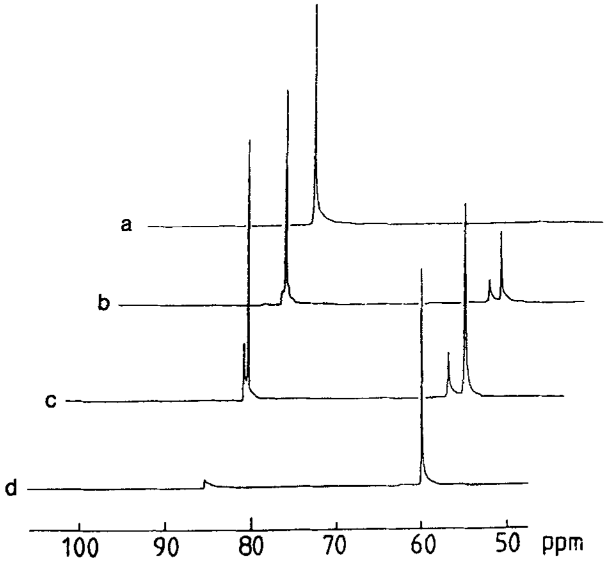
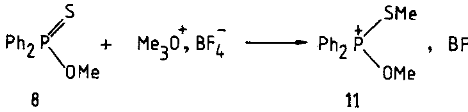
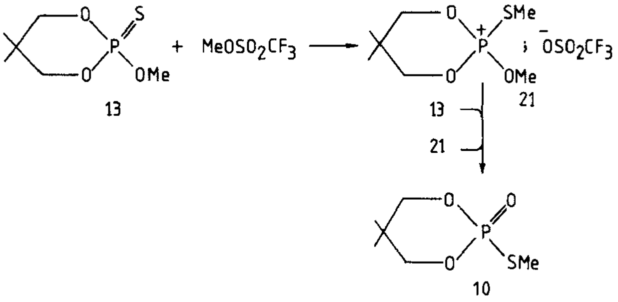


FIGURE 1 The formation of phosphonium intermediate as seen by ^{31}P NMR spectra: of the solution of **8** (1.0 M) in TFA at 296°K immediately after dissolving **8** in TFA (a), after 1.5 h (b), after 14 h (c), after 100 h (d).



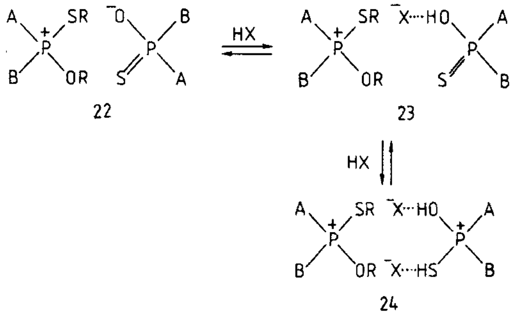
Scheme 3

1,3,2-dioxaphosphorinanes such as 2-methoxy- (**13**), 2-n-propoxy- (**16**), 2-allyloxy (**17**), 2-(2-buten-1-yloxy)- (**18**) and 2-(3-buten-2-yloxy) (**19**) formation of similar intermediates was observed at a trace level. In the latter cases very low concentrations of these intermediates have humpered more detailed spectral investigations except for determining their ^{31}P NMR chemical shifts. The structure of these compounds was determined in a different manner. The 2-methoxy derivative (**13**) was treated with 10 molar % of methyl trifluoromethanesulfonate in methylene chloride solution at 223°K and the reaction was monitored by means of ^{31}P NMR. Formation of the compound giving rise to the resonance at 51.5 ppm was seen initially, and after warming the sample to 273°K thiono–thiolo rearrangement proceeded yielding the S-methyl derivative **20** (Scheme 4).



Scheme 4

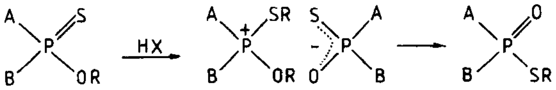
The signal at 51.5 ppm can be attributed to the alkoxyphosphonium salt **21**. Attempts at isolation of this compound in a pure state have failed. However, in the spectra of reaction mixtures of phosphorothionate **13** in TFA the low intensity signals at 51.5 ppm and at 32.0 ppm also appear at intermediate conversions. It can be assumed that they correspond to phosphonium cation and protonated phosphorothioate anion respectively, such as the ones in salt **24** (Scheme 5). The



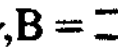
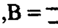
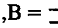
Scheme 5

TABLE III

^{31}P and ^{1}H NMR data for the intermediate alkoxyalkylthiophosphonium salts, their precursor phosphylthionates and the products of the thiono–thiolo rearrangement[a,b]



^{1}H NMR $A = B = PH$, $R = -Me$ (**8**)		
δ_{OMe} 3.50 (d) $^{3}J_{POMe} = 14.0$	δ_{OMe} 3.84 (d) δ_{SMe} 2.22 (d) $^{3}J_{POMe} = 14.0$ $^{3}J_{PSMe} = 14.9$	δ_{SMe} 2.11 (d) $^{3}J_{PSMe} = 13.8$
$A = B = CH_3$, $R = CH_2—CH = CD_2$ (**14**)[c]		
δ_{OCH} 4.39 (dd) $^{3}J_{POCH} = 10.9$ $^{3}J_{HC=CH} = 5.5$	δ_{OCH} 4.50 $^{3}J_{POCH} = 11.5$ $^{3}J_{OHCCH} = 6.9$ δ_{SCH} 3.61 (dd) $^{3}J_{PSCH} = 14.5$ $^{3}J_{SCHCH} = 7.1$	δ_{SCH} 3.52 (dd) $^{3}J_{PSCH} = 12.7$ $^{3}J_{SCHCH} = 6.7$
$A = B = -Me$, $R = CH_2Ph$ (**15**)		
δ_{OCH} 4.90 (d) $^{3}J_{POCH} = 12.9$	δ_{OCH} 4.94 (d) $^{3}J_{POCH} = 9.3$ δ_{SCH} 4.01 (d) $^{3}J_{PSCH} = 12.0$	

^{31}P NMR		$\delta_{^{31}P}$ (α)[d]	$\delta_{^{31}P}$ (β)[e]
A = B = Ph,	R = Me (**8**)	86.3	62.8
A,B =  ,	$R = CH_3$ (**13**)	51.5	32.0
A,B =  ,	$R = C_3H_7$ (**15**)	49.5	33.6
A,B =  ,	$R = C_3H_5$ (**16**)	47.5	27.1

[a] Phosphylthioate anion exists in the form of heteroconjugate with one or two molecules of TFA, [b] All reactions were performed at 296°K unless otherwise stated, [c] At 328°K, [d] α—corresponds to ^{31}P nuclei in phosphonium cation, [e] β—corresponds to ^{31}P nuclei in phosphylthioate anion.

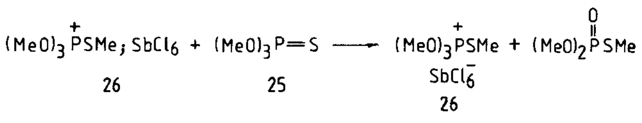
upfield chemical shift of phosphorothioate anion as compared to normal range of chemical shifts of phosphorothioate diesters is in agreement with the postulated structure of heteroconjugated trimer containing two molecules of trifluoroacetic acid (Scheme 5). The association of tetralkylammonium salts of O,O-dialkyl phosphorothioic acids with carboxylic acids resulting in a similar effect on their chemical shifts was described earlier.[2]

Spectral data of several alkoxyphosphonium intermediates are collected in Table III.

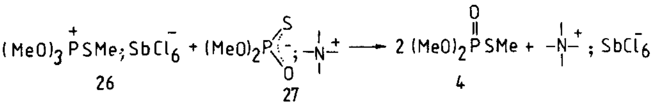
In several other cases like in the rearrangement of 0,0,0-trimethyl phosphorothioate (**25**) and O-methyl-O-1-naphthyl-O-phenylphosphorothioate (**10**) the reaction proceeds without formation of the phosphonium intermediate of type **3** in detectable quantities.

Reactivity of Phosphonium Salts Towards Phosphorothionates and Phosphorothioate Anions

In order to explain why reactive alkoxyphosphonium intermediates are formed in fair amounts during the rearrangement process in protic acid media but they are not observed in the absence of acid, the reactivity of O,O,O-trimethoxymethylthiophosphonium hexachloroantimonate (**26**) towards O,O,O-trimethyl phosphorothioate (**25**) and methyltriethylammonium O,O,dimethyl phosphorothioate (**27**) under the influence of trifluoroacetic acid was investigated (Schemes 6 and 7).



Scheme 6



Scheme 7

The rate of the first process was measured by ^{1}H NMR using cyclohexane as an internal standard and that of the second one by means of electric conductivity. Both reactions were carried out in CH_2Cl_2 solutions at 298°K. It was found that the alkylation of **25** with **26** follows pseudo-first order kinetics (**26** is not used up in this reaction) with the rate constant $k_2 = (1.83 + 0.22) \times 10^{-2}\,l\,mole^{-1}\,s^{-1}$. The

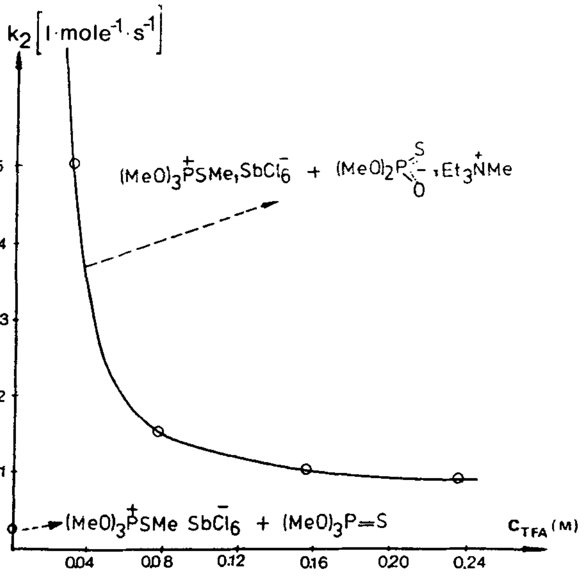


FIGURE 2 The dependence of the rate constant of the alkylation of **27** with phosphonium salt **26** on the concentration of trifluoroacetic acid in methylene chloride.

reaction is also first order with respect to phosphonium salt **26**. The alkylation of the salt **27** is first order with respect to both substrates with the rate constant $k_2 = 62 \pm 30\,l\,mol^{-1}\,s^{-1}$. In the real reaction mixture (e.g. **25** + TFA) the rate of alkylation of phosphorothioate by alkoxyphosphonium cation depends on the acid-base equilibrium similar to the one delineated in the Scheme 5. In the model system the dependence of the rate of alkylation upon trifluoroacetic acid concentration is shown in Figure 2. The rate constant of the alkylation of **27** with **26** declines rapidly as the concentration of TFA in the reaction system approaches that of phosphorothioate anion (0.01 M). After the initial descending phase further reduction of the rate constant brought about by increase in TFA concentration is much slower.

DISCUSSION

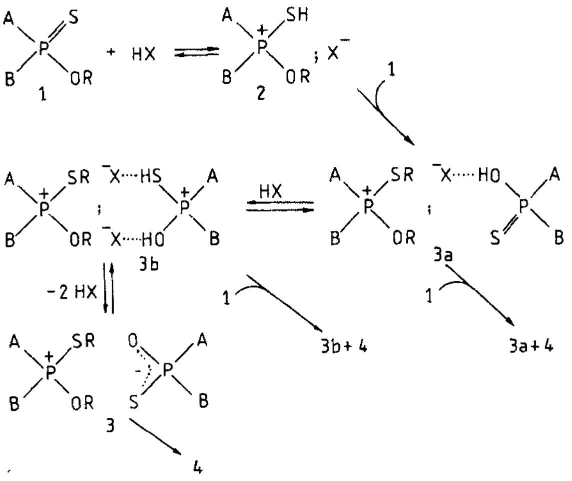
In our former papers we have postulated that alkoxyphosphonium salts **2** and **3** play the key role in the thiono–thiolo rearrangement process of phosphylthioates reacting via both S_N2 and S_N1 mechanisms. This suggestion was made intuitively rather than based on experimental evidence. In this paper we present direct proof for the participation of reactive phosphonium species in the investigated reaction.

Owing to low nucleophilicity of trifluoroacetic acid and its strong solvating properties towards anionic nucleophiles, longer half-life time for these reactive intermediates resulting in their accumulation in higher concentrations was expected for reactions performed in this medium. In TFA the acid-base equilibrium shown in Scheme 5 is expected to be shifted towards the protonated form of phosphylthioate anion, thus severely restricting its nucleophilicity. For this reason phosphonium intermediates can accumulate to higher levels during the rearrangement reactions of phosphylthionates in protic acid media.

The formation of the complexes between trifluroracetic acid and phosphylthionates is documented by changes in the ^{31}P NMR spectra summarized in Table I as well as by the appearance of significant electric conductivity of the solutions of **1** in TFA. Although the magnitude of the conductivity cannot be directly related to the concentrations of protonated forms in the complex acid—base equilibrium it is sensible to use it as a means of detection of proton transfer. In solvents with low dielectric constants such as TFA, the conductivity measured arises only from a fraction of the protonated species due to extensive ion-pairing in such solvents. The actual structure of protonated species remains unclear at this point, however based on the significant reduction in $^1J_{P\text{-}Se}$ as a result of interaction of O-methyl diphenylphosphinoselenoate with TFA (Table I, footnotes c, d) we propose that the protonation occurs at the atom doubly-bonded to phosphorus (whether sulfur or selenium).

The formation of alkoxyphosphonium salt intermediates **3** is demonstrated by both ^{1}H and ^{31}P NMR. As expected proton resonances in ^{1}H NMR spectra are shifted downfield and the vicinal coupling constants to phosphorus are increased as an effect of increased electronegativity of phosphorus in these compounds.

In the reaction medium alkoxyphosphonium salts can react in two ways: they can alkylate phosphorothioate anion or neutral phosphorothionate esters. In the



Scheme 8

model system in the absence of protic acid their reactivity towards negatively charged phosphorothioate anions exceeds their reactivity towards neutral esters by three orders of magnitude. Our result is consistent with the very high reactivity found for alkoxyphosphonium salts isolated as intermediates of the Arbuzov reaction towards nucleophiles such as iodide or water.[9] If these intermediates take part in the thiono–thiolo rearrangement reaction under nonacidic conditions (i.e. thermally induced) the level of their concentration must be very low since the dissociation of C—O bond in phosphorothioate esters is likely to be rate limiting. The acidic medium strongly depresses the rate of anion alkylation and at the same time the alkylation of the neutral ester is not expected to be strongly affected by the presence of protic acid. The result is that in acid medium the overall rate of consumption of alkoxyphosphonium intermediate becomes lower leading to accumulation of these intermediates during the rearrangement reaction.

The most feasible mechanism of protic acid catalyzed thiono–thiolo rearrangement is outlined in the Scheme 8. The attack of the unprotonated substrate **1** at one of the protonated species of **1** such as **2** affords the alkoxyalkylthiophosphonium salt **3a** in which phosphylthioate anion is stabilized by interaction with a molecule of acid HX. In acidic media such as TFA the attack of the unprotonated substrate at intermediates **3a** or **3b** is the predominant reaction especially if the phosphylthioate anion has inherent high basicity (e.g. phosphinothioate series). As a result of this attack phosphylthiolate **4** is formed, **3b** is reproduced and propagation reaction **3b** + **1** → **3b** + **4** is repeated. This kinetic chain continues to operate until the transfer of the alkyl group within the salt **3** or **3a** occurs. The probability of chain termination increases with the reduction in the acidity of the medium and of basicity of phosphorothioate anion (shift towards intermediate **3**). In summary it can be concluded that the formation of alkoxyphosphonium intermediates at higher levels during the thiono–thiolo rearrangement of phosphylthionates is facilitated by a high acidity of the medium and by an enhanced basicity of the corresponding phosphylthioate anion.

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EXPERIMENTAL

^{1}H NMR spectra were recorded at 60 MHz with a Perkin–Elmer R12B spectrometer. ^{31}P NMR spectra were obtained on a Jeol FX-60 spectrometer operating at 24.3 MHz with external H_3PO_4 as the reference. Positive chemical shifts are assigned for compounds absorbing downfield from the standard. Purity of the compounds was also checked by tlc (Merck silica gel plates).

Starting materials. Trifluoroacetic acid was purified as described previously,[21] O-methyl diphenylphosphinothioate (**8**), methylphenyl-n-propylphosphine sulfide (**9**), O-methyl diphenylphosphinoselenoate (**8**), 2-alkoxy-5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinanes **13**, **16–21**, O-3,3-d_2-allyl dimethylphosphinothionate (**14**), O,O,O-trimethyl phosphorothionate (**25**), and methylthiotrimethoxyphosphonium hexachloroantimonate (**26**) were prepared by the methods described in the literature.[1,21–24] O-propyl- (**7**) and O-benzyldimethylphosphinothionate (**15**) was prepared from the corresponding alcohol and dimethylphosphinothiobromidate in the presence of triethylamine. **7**: yield 73%, bp. 45–47°C/0.01 mm Hg, $n_{20D} = 1.497$, δ_{31P} 91.5 ppm ($CHCl_3$), MS: $M^{+\cdot}$ (62%), m/z 111 (100%), m/z 93 (99%), m/z 94 (90%) **15**: bp. 81°C/0.001 mmHg, $n_{20D} = 1.566$, δ_{31P} 93.4 ppm ($CHCl_3$), MS: $M^{+\cdot}$ (44%), m/z 94 (61%), m/z 91 (100%).

O-methyl-O-1-naphthyl-O-phenyl phosphorothionate (**10**) was obtained analogously as described by Akintonwa,[25] and was purified by column chromatography, yield 74%, oil, δ_{31P} 59.5 ($CHCl_3$), ^{1}H NMR ($CDCl_3$): δ 3.67 (d, Me), $^3J_{POMe} = 14.1$ Hz, δ 6.89–8.15 (m, Ar), MS: $M^{+\cdot}$ (100%), m/z 187 (23%), m/z 115 (31%).

Methoxymethylthiodiphenylphosphonium tetrafluoroborate (**11**). Into the solution of trimethyloxonium tetrafluoroborate (1.1 g, 7.6 mmole, Alpha) in nitromethane (10 mL) and methylene chloride (10 mL) was added at −55°C the solution of **8** (1.5 g, 6 mmole) in methylene chloride. The mixture was left standing at −30°C for 5 h, the solvent was evaporated under reduced pressure and the residue was crystallized from CH_2Cl_2-diethyl ether under vacuum (due to the hygroscopic properties of the product). Yield of **11** 1.5 g (17%), mp. 121–128°C, δ_{31P} 86.3 ppm (CF_3COOH), ^{1}H NMR (CD_3CN): δ 2.29 (d, SMe), $^3J_{PSMe} = 14.6$ Hz, δ 4.0 (d, OMe), $^3J_{POMe} = 14.1$ Hz, δ 7.7 (m, Ph).

Alkylation of 2-methoxy-5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinane (**13**). The samle of **13** (0.5 g, 2.55 mmole) and freshly distilled methyl triflurormethanesulfonate (91 mg, 0.55 mmole) in CH_2Cl_2 (3 mL) was prepared under vacuum line conditions in the NMR tube and was frozen in liquid nitrogen. The tube was next placed in the NMR probe and was gradually warmed up while monitoring the reaction by ^{31}P NMR. After recording the spectra the reaction was quenched by adding water. Product **20** and the substrate **13** were separated by column chromatography on silica gel and were identified by mass spectrometry.

The measurement of electric conductivity of the solutons of phosphylthionates in TFA. Phosphylthionate was dissolved in TFA in the vacuum conductivity cell (cell constant $p = 0.136\,cm^{-1}$) using vacuum line technique. The cell was thermostated at 303°K and the measurement was carried out. Because, the electric conductivity of the solutions were a function of time (except for the solution of sulfide **7** where it was stable), the values of conductivity given in Table II were obtained by least square extrapolation to t_0 (the moment of mixing of **1** with TFA) using equation:

$$1/G = 1/G_0 + at$$

where: G_0 is the initial conductivity
G is conductivity at time t

Measurement of the rate constant of the alkylation reaction. The measurements were carried out at 298°K in methylene chloride solution at the concentration of **25** and **26** 0.525 M and 0.0491 M, respectively. The reaction was followed by means of ^1H NMR using cyclohexane as an internal standard. Samples were prepared in the NMR tubes and then sealed under vacuum. The reaction can be described by pseudo-first order kinetics up to 75% of conversion.

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