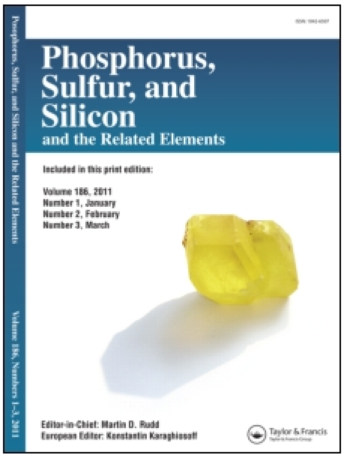

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THE MECHANISM OF THIONYL CHLORIDE REACTION WITH DIALKYL ALKYLPHOSPHONOTHIONATE USING ^{31}P NMR

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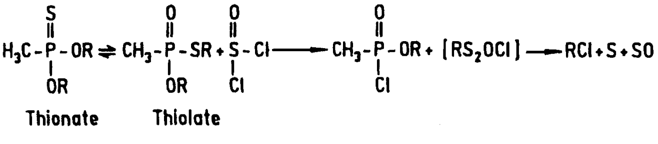
Based on ^{31}P NMR studies of thionyl chloride reaction with dialkyl alkylphosphonothionates, a method for preparation of alkylphosphonic dichloride has been investigated. A mechanism via intermediacy of ester chloride is suggested.

Keywords: Alkylphosphonothioic acids; dialkyl alkylphosphonothionates; diphenyl methylphosphonate; diphenyl methylphosphonothionate; ester chlorides; thionyl chloride

INTRODUCTION

Previously studied reaction[1] of thionyl chloride with dialkyl methylphosphonothionate describes product as ester chloride and free sulfur. An explanation is given by thiono-thiolo isomerisation of the substrate and the thiolo form reacting quickly as follows (Eq. 1).



$$\mathrm{H_3C-\underset{OR}{\overset{\overset{S}{\|}}{P}}-OR \rightleftharpoons CH_3-\underset{OR}{\overset{\overset{O}{\|}}{P}}-SR + \underset{Cl}{\overset{\overset{O}{\|}}{S}}-Cl \longrightarrow CH_3-\underset{Cl}{\overset{\overset{O}{\|}}{P}}-OR + [RS_2OCl] \longrightarrow RCl + S + SO} \qquad (1)$$

$\mathrm{R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7}$
$\mathrm{iso\text{-}C_3H_7,\ n\text{-}C_4H_9}$

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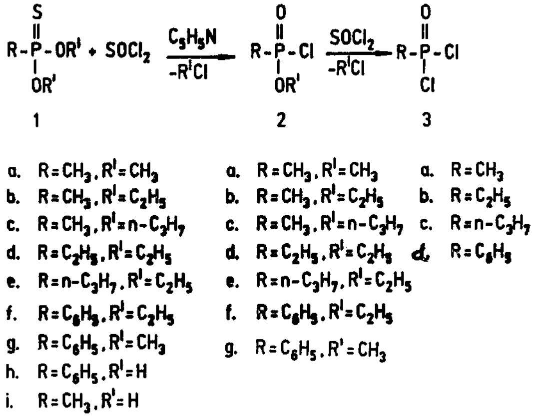
Herein, we describe the conversion of thionates into dichlorides via ester chlorides. ^{31}P NMR chemical shift (δ) values have been utilized for identification of thionate and thiolate esters. A mechanism of pyridine catalysed transformation of ester chloride into phosphonic dichloride has been proposed.

RESULTS AND DISCUSSION

Esters **1a–g** were prepared by adopting Hoffmann's method.[2] IR and ^{31}P NMR spectra were used for distinguishing thiono-thiolo equilibrium of esters. Infrared spectrum, in particular of **1a–f** did not show the frequency characteristic to P=O bond ($\sim$1270 cm^{-1}),[3] but gave the frequency for P=S bond in 750 cm^{-1} region,[4] ^{31}P NMR spectrum of these compounds showed signals around δ 86.8–101.9 where peaks of thionates[5] are known to occur. However, the absence of signals in δ 46.2–57.2 region known for thiolates[5,6] demonstrated that esters **1a–f** do not show thiono-thiolo equilibrium. On the contrary, compound **1g** showed two signals at δ 89.8 and 46.4 for thiono and thiolo isomers respectively. Probably it is due to labile methyl group (OCH_3) and the phenyl group linked directly to the phosphorus atom.

The progress of reactions of **1a–f** with thionyl chloride (3 mol excess) and catalytic amount (6–10 mol %) of pyridine (Scheme 1)



SCHEME 1

were monitored by recording of ^{31}P NMR spectrum of aliquots drawn at 15 min time intervals. We observed that ^{31}P NMR spectra obtained for aliquots drawn after 15–30 min showed peaks at δ 86.8–101.9 due to thionates, which disappear with concomitant appearance of signals at δ 29.9–47.1. On the basis of both reported shift values and spiking experiments, these peaks were identified as ester chlorides (R—PO(OR)Cl)[5] **2a–d**. Further refluxing of reaction mixtures followed with recording of spectrum revealed that new peaks appear and grow slowly in the range of δ 34.7–54.4 at the expense of peaks corresponding to that of ester chloride. Chemical shift values in this region are known for phosphonic dichlorides[5–8] **3a–d**. The spectrum of aliquots drawn at the end of 4–5 h of refluxing showed complete disappearance of signals related to ester chlorides. The reactions were terminated, cooled, and excess thionyl chloride removed by distillation. The residual liquids so obtained, on distillation gave colourless pungent smelling liquids and a little amount of pyridine hydrochloride [^{1}H NMR (CD_3OD) δ 8.1 (d, 2H), 8.7 (t, 1H) δ 8.9 (d, 2H)] adhering on to the condenser walls. However, a careful examination of ^{1}H NMR spectra of the residues showed no peaks corresponding to N-alkyl pyridine hydrochlorides (by reaction with pyridine and liberated alkyl chloride). Apart from these observations, we noticed that ^{1}H NMR spectrum of recovered thionyl chloride gave three signals as 7.2 (dd, 2H), 7.6 (t, 1H), 8.5 (d, 2H) characteristics of free pyridine. These measurements demonstrated the presence of free pyridine as well as pyridine hydrochloride in the reaction mixture.

We were interested to know whether pyridine hydrochloride acts as catalyst, three separate sets of reactions each consisting the substrate **1a** were carried out using three different catalyst such as pyridine hydrochloride (freshly prepared by passing dry HCl in benzene solution of pyridine) and inorganic salts[9] ($CaCl_2$ and KF) according to Scheme 1. After work up of all the three reaction mixtures and isolation of **3a**, therefrom in equivalent amounts established the catalytic power of salts.

The liquids were unequivocally identified as alkylphosphonic dichlorides **3a–d** (Table I) by comparison of IR, ^{1}H, and ^{31}P NMR and mass spectra with those of authentic samples prepared from the standard methods.[10–13] It may be pointed out that though the uncatalyzed reactions gave ester chlorides at same rate, but its further conversion into dichlorides was at very slow rate, and required more than 24 h of refluxing to give **3a–d** and that too in very poor yields (5–10%).

Furthermore, we found that the replacement of an usual substrate in Scheme 1 typically by diphenyl methylphosphonothionate[5,14] gave diphenyl methylphosphonate[5,15] (by oxidation of P=S to P=O) instead of the chlorinated product. From this experiment it became evident that alkyl chloride elimination is an important step of the reaction. Moreover, these facts have lead to envisage the following two mechanisms for the formation of **2**.

TABLE I Alkylphosphonic Dichlorides and Ester Chlorides from Reaction of Thionates with Thionyl Chloride and Catalytic Amounts of Pyridine

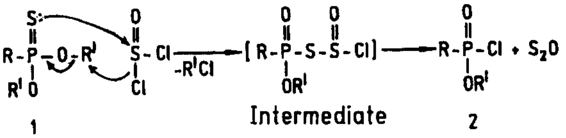
Entry	Thionate	^{31}P NMR δ (ppm)^{b}	Ester chloride	^{31}P NMR δ (ppm)^{b}	Phosphonic dichloride	B.P. (°C)^{c} mm/Hg	Yield (%)	^{31}P NMR δ (ppm)^{b}
1	1a	100.1 (99.7)	2a	42.9 (43)	3a	155–163 (161)	71	44.1 (43.5–44.8)
2	1b	93.9 (94.3)	2b	39.5 (39.5)	3a	155–163	65	44.1
3	1c	91.4	2c	40.1 (40.1)	3a	155–163	62	44.1
4	1d	101.9	2d	47.1 (44.6)	3b	80–82/9 (53–60/4)	59	54.4 (52–54.8)
5	1e	100.1	2e	45.5	3c	90–92/12 (62–64/9)	55	54.6
6	1f	86.8	2f	30.0	3d	106–108/4 (104/4)	50	34.7 (35.5)
7	1g	89.6	2g	29.9	3d	106–108/4	65	34.7
8	1h^{a}	—	—	—	3d	106–108/4	70	34.7
9	1i^{a}	—	—	—	3a	155–163	75	44.1

[a] Alkaline hydrolysis of corresponding thiophosphonyl dichlorides followed by acidification and extraction with ether and then from evaporation of ether layer acids 1h and 1i were obtained.

[b] ^{31}P NMR δ values given in parenthesis for thionates, ester chlorides and dichlorides are literature values.[5]

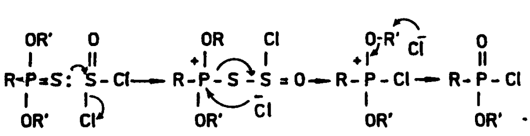
[c] Boiling points given in parenthesis are reported values.[10,13]

1. An elimination of alkyl chloride followed by a nucleophilic attack of sulfur (of P=S) at electrophilic sulfur of S=O bond. The resulting chlorothiosulfite type intermediate decomposes quickly into **2** (Eq. 2).



(2)

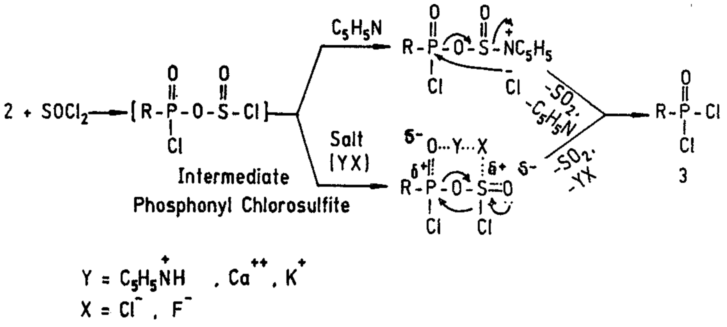
2. A nucleophilic attack of P=S sulfur at the electrophilic sulfur (of S=O) resulting into charged intermediate species which on subsequent elimination of alkyl chloride can produce **2** (Eq. 3).



(3)

Because the rate of formation of **2** has been found proportional to the concentration of thionyl chloride used, therefore Eq. 2 seems to be a plausible mechanism of the reaction.

From ^{31}P NMR analysis and catalysis experiments it is evident that smooth conversion of ester chlorides **2** into dichlorides **3** occurs under the influence of catalyst. It is believed that interaction between **2** and the second molecule of thionyl chloride resulted into chlorosulfite type intermediate: RPO(Cl) OS(O)Cl. A quick decomposition of the intermediate into **3** by free pyridine may be explained via pyridine complex (Scheme 2), as described by Cowdrey et al.[16] for the reaction of $SOCl_2$ with alcohols in the presence of pyridine. However, the catalysis noticed due to salts may be attributed to P=O bond polarization, as



SCHEME 2

predicted for phosphorylation of phenols using catalytic amounts of the metal halides.[17] Probably a six-membered transition state has been invoked involving P=O and S=O bonds of the intermediate with metal salts. A subsequent attack by chlorine (of S—Cl) at phosphorus atom followed by the cleavage of P—O bond seems to be resulted into dichlorides **3** as represented by Scheme 2.

EXPERIMENTAL

The boiling points are uncorrected. Infrared spectra were recorded on Nicolet FTIR spectrophotometer model Impact 410. ^{1}H and ^{31}P nuclear magnetic resonance were recorded on Bruker Avance DPX-400 spectrometer in $CDCl_3$ using Tetramethyl silane as internal standard for ^{1}H NMR and 85% phosphoric acid as external standard for ^{31}P NMR measurements. Mass spectra were obtained by Finnigan MAT, TSQ 7000, coupled with GC varian-3400, mass spectrometer. Methyl, ethyl, and n-propyl phosphonothioic dichlorides were synthesized following the standard procedure.[13] Phenylphosphonothioic dichloride procured from Aldrich Chemical Company was distilled before use. Diphenyl methylphosphonates[15] and diphenyl methylphosphonothionates[14] were prepared according to standard methods. Freshly distilled thionyl chloride and pyridine (collected over NaOH) were utilized in all our experiments.

Methylphosphonic dichlorides (3a): To dimethyl methylphosphonothionate 1b (42 gr. 0.3 mol) in a 250 ml two necked round flask fitted with a double walled condenser and $CaCl_2$ tube was added freshly distilled thionyl chloride (178.5 g, 1.5 mol) and pyridine (2g, 0.025 mol, 10 mmol %). The reaction mixture was refluxed with stirring for 4 h. Excess thionyl chloride was removed and the residual liquid distilled at 155–163°C gave colourless pungent liquid 32 g (71%), IR (neat) νmax 2994–2849, 1301, 1270, 890, 761, 545 cm^{-1} and; ^{1}H NMR δ 2.47(d) ppm; m/z (70 ev) 132 (M^+), 134, 136, 119, 97, 51.

Ethylphosphonic dichloride (3b): IR (neat) νmax 2985–2886, 1276, 1032, 991, 952, 750, 723, 567 cm^{-1}; ^{1}H NMR δ 1.28–1.42 (dt 3H), 2.52 (m, 2H) ppm; m/z (70 ev) 147 ($M^+ + 1$) 149, 120, 118.

n-Propylphosphonic dichloride (3c): IR (neat νmax 2984–2881, 1465, 1274, 1243, 683, 563 cm^{-1}, ^{1}H NMR δ 1.06 (t, 3H), 1.82 (m, 2H), 2.53 (m, 2H) ppm; m/z (70 ev), 161($M^+ + 1$), 163, 165, 134, 125.

Phenylphosphonic dichloride (3d): IR (neat) νmax 3003, 1440, 1274, 1108, 720, 687, 561, 541 cm^{-1}; ^{1}H NMR δ 7.5–8.2 (m) ppm; m/z (70 ev) 194 (M^+), 196, 161, 159, 77.

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