Thermal Decomposition of Phosphorothioates

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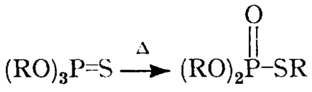
OOO-Trialkyl phosphorothioates undergo thermal isomerization to the *OOS*-trialkyl phosphorothioates followed by decomposition to yield the dialkyl sulphides. The intermediacy of the *OOS*-trialkyl phosphorothioates has been shown by spectral observation and independent synthesis.

THE *OOO*-trialkyl phosphorothioates (I) are reported to undergo thermal isomerization to the *OOS*-trialkyl phosphorothioates (II)[1-3] when heated at 100—140°; this reaction is of interest in the handling of the insecticide Systox,[4] as it leads to a significantly more toxic species.

We attempted to study the kinetics of the isomerization in the cases of the simple alkyl esters (Ia and b), following by proton n.m.r. the reaction occurring in a sealed tube. With heating at 130—190° the reaction in both cases appeared to proceed slowly and smoothly to about 30% completion; at this stage the signals for both the starting compound and the product decayed at sharply increasing rates concurrent with the appearance of a new signal in the spectrum and the observation of a semisolid material in the reaction tube. In view of this it was decided that other studies were needed before kinetic data would be of value.

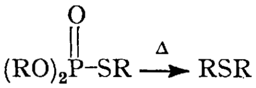


$$(RO)_3P{=}S \xrightarrow{\Delta} (RO)_2\overset{O}{\overset{\|}{P}}{-}SR$$

(I) (II)

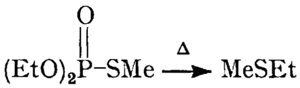
a; R = Me
b; R = Et
c; R = Bu^n

Prolonged heating of the *OOO*-trialkyl phosphorothioates (Ia—c) followed by distillation of the products gave the corresponding dialkyl sulphides (IIIa—c) (60—84%). The suspicion of the intermediacy of the *OOS*-trialkyl phosphorothioates, observed spectrally in the cases of the methyl and ethyl esters, was supported by the isolation of dibutyl sulphide (IIIc) from the thermal decomposition of *OOS*-trialkyl phosphorothioate (IIc) prepared by an independent route.[5] Further support was given by the isolation of the unsymmetrical product, ethyl methyl sulphide (V), from the thermal decomposition of *OO*-diethyl *S*-methyl phosphorothioate (IV).



$$(RO)_2\overset{O}{\overset{\|}{P}}{-}SR \xrightarrow{\Delta} RSR$$

(II) (III)

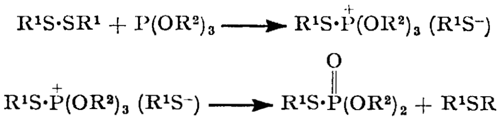


$$(EtO)_2\overset{O}{\overset{\|}{P}}{-}SMe \xrightarrow{\Delta} MeSEt$$

(IV) (V)

In all the decompositions there remained a substantial amount of involatile, dark, gummy material, only sparingly soluble in inorganic solvents, and presumably derived from the metaphosphate residue.

This decomposition is of interest in connection with the observations of mixed sulphide formation in the thermal reactions of trialkyl phosphites with disulphides.[6-8] The process shown (Scheme) was proposed as an explanation of the observed products. In the light of the present results, the formation of at least some of the sulphide by decomposition of the phosphorothioate cannot be ruled out.



$$R^1S{\cdot}SR^1 + P(OR^2)_3 \longrightarrow R^1S{\cdot}\overset{+}{P}(OR^2)_3\ (R^1S^-)$$

$$R^1S{\cdot}\overset{+}{P}(OR^2)_3\ (R^1S^-) \longrightarrow R^1S{\cdot}\overset{O}{\overset{\|}{P}}(OR^2)_2 + R^1SR^2$$

SCHEME

EXPERIMENTAL

OOO-Trialkyl phosphorothioates were prepared by the method of Arbuzov and Vinogradova,[9] from trialkyl phosphites and sulphur. The *OOS*-trialkyl phosphorothioates and the *OO*-diethyl *S*-methyl phosphorothioate were prepared by the method of Michalski and Wieczorkowski,[5] from trialkyl phosphites and alkyl thiocyanates.

The authenticity of the starting compounds was established by comparison of their physical properties with those reported, and by their i.r. and n.m.r. spectra (Perkin-Elmer 237B and Varian A-60A instruments, respectively). The proton n.m.r. (relative to tetramethylsilane) showed signals as follows: (Ia) δ 3·79 (d, J_{PH} 14 c./sec.); (Ib) δ 1·43 (3H, t, J 6 c./sec.) and 4·16 (2H, dq, J_{HH} 6 c./sec., J_{PH} 10 c./sec.); (Ic) δ 1·00 (3H, t, J 6 c./sec.), 1·53 (4H, m), and 4·05 (2H, dt, J_{HH} 5 c./sec., J_{PH} 10 c./sec.); (IIa) δ 3·79 (2H, d, J_{PH} 14 c./sec.) and 2·25 (1H, d, J_{PH} 15 c./sec.); (IIb) δ 1·47 (3H, t, J 6 c./sec.), 2·90 (1H, dq, J_{HH} 6 c./sec., J_{PH} 7 c./sec.), and 4·19 (2H, dq, J_{HH} 6 c./sec., J_{PH} 10 c./sec.); (IIc) δ 0·98 (9H, t, J 6 c./sec.), 1·50 (12H, m), 3·38 (2H, m),

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and 4·00 (4H, dt, J_{HH} 5 c./sec., J_{PH} 10 c./sec.); (IV) δ 1·32 (6H, t, J 6 c./sec.), 2·25 (3H, d, J_{PH} 15 c./sec.), and 4·09 (4H, dq, J_{HH} 6 c./sec., J_{PH} 9 c./sec.).

Starting compounds were vacuum distilled and their purity was checked by g.l.c. Products were identified by comparison of their b.p.s and i.r. and n.m.r. spectra with those of authentic materials.

General Procedure for the Decomposition of Phosphorothioates.—A flask equipped with a short Vigreaux column distilling head, charged with the phosphorothioate, was heated for 2 hr. under gentle reflux; the temperature was then increased to 250° and the sulphide product was distilled off.

OOO-*Trimethyl phosphorothioate* (Ia). From (Ia) (7·64 g., 0·049 mole) was obtained dimethyl sulphide (IIIa) (2·12 g., 0·034 mole, 70%). (Caution: if heating is performed too rapidly this reaction may be explosive.)

OOO-*Triethyl phosphorothioate* (Ib). From (Ib) (12·95 g., 0·065 mole) was obtained diethyl sulphide (IIIb) (4·94 g., 0·055 mole, 85%).

OOO-*Tributyl phosphorothioate* (Ic). From (Ic) (19·30 g., 0·068 mole) was obtained dibutyl sulphide (III c)(6·03 g., 0·041 mole, 61%).

OOS-*Tributyl phosphorothioate* (IIc). From (IIc) (19·00 g., 0·067 mole) was obtained dibutyl sulphide (IIIc) (4·50 g., 0·031 mole, 46%).

OO-*Diethyl* S-*methyl phosphorothioate* (IV). From (IV) (5·60 g., 0·030 mole) was obtained ethyl methyl sulphide (V) (1·04 g., 0·014 mole, 46%).

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