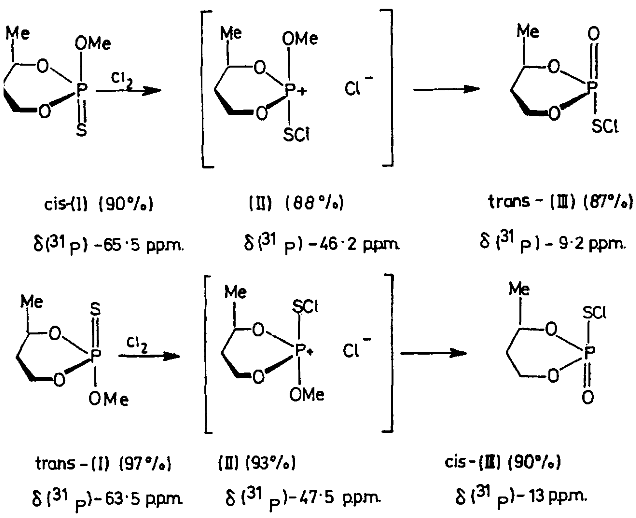
Five-co-ordinate and Phosphonium Intermediates in Reactions of Phosphorus Thionesters, >P(S)OR, with Elemental Chlorine and Sulphuryl Chloride

By Aleksandra Skowrońska,* Jerzy Mikolajczak, and Jan Michalski*

(*Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, 90-362 Łodź, Boczna 5, Poland*)

Summary The results of stereochemical and product studies on the chlorination of phosphorus thionesters are rationalized in terms of phosphonium and five-co-ordinate intermediates which in the case of thionophosphonates and cyclic five-membered thionophosphates undergo nucleophilic ligand exchange.

In our studies of thiophosphorus compounds, the chlorination of esters containing the thionester >P(S)OR, by elemental chlorine or sulphuryl chloride is of especial interest.[1] The reaction depends markedly on the structure of the group >P(S)OR. Acyclic phosphorothionates and six-membered cyclic thionates are chlorinated with release of alkyl chlorides exclusively and formation of oxophosphoranesulphenyl chlorides, >P(O)SCl. In contrast, acyclic phosphonothionates and cyclic five-membered thionates release alkyl chlorides and elemental sulphur. We report a study of these reactions and propose a general mechanistic scheme.



cis-(I) (90%) δ(^{31}P) -65·5 ppm.

(II) (88%) δ(^{31}P) -46·2 ppm.

trans-(III) (87%) δ(^{31}P) - 9·2 ppm.

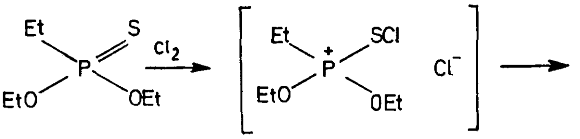
trans-(I) (97%) δ(^{31}P)-63·5 ppm.

(II) (93%) δ(^{31}P)-47·5 ppm.

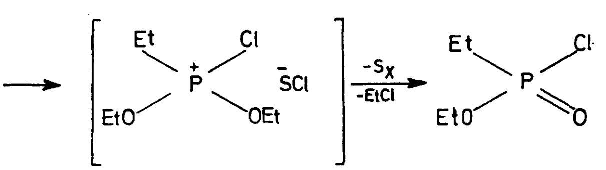
cis-(III) (90%) δ(^{31}P)-13 ppm.

Reaction of the diastereoisomeric 2-methoxy-4-methyl-1,3,2-dioxaphosphorinan-2-thiones, *cis*- and *trans*- (I),† with chlorine (sulphuryl chloride) in CH_2Cl_2 at −70 °C affords the phosphonium intermediates (II). These undergo dealkylation at −30 °C to form the sulphenyl chlorides *trans*- and *cis*-(III). The reaction takes place with full retention of configuration at phosphorus.[2] Similar phosphonium intermediates $(EtO)_3P^+SCl\ Cl^-$ (IV) δ (^{31}P)‡ −43 p.p.m., and $(Bu^nO)_3P^+\ SCl\ Cl^-$ (V) δ (^{31}P) −45 p.p.m., were observed in the chlorination of tri-*O*-ethyl and tri-*O*-n-butyl phosphorothioates.

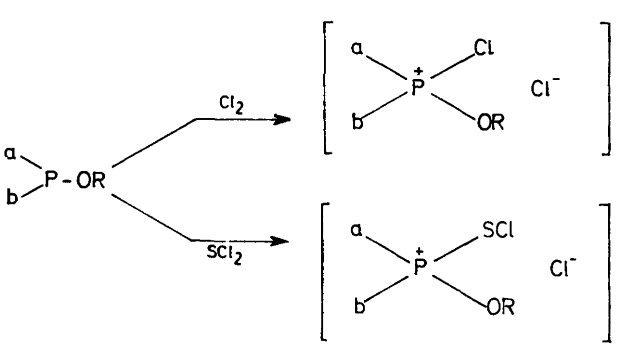
The di-*O*-ethyl ethylphosphonothioate (VI) at −90 °C in ethyl chloride solution forms the phosphonium intermediate (VII) which at −50 °C reacts further by ligand exchange at phosphorus to give the phosphonium intermediate (VIII). The process of nucleophilic displacement in the phosphonium salt (VII) leading to (VIII) is in accord with the higher electrophilicity of the phosphorus centre in (VII) compared with that in (II) or (V) and is most likely to proceed with inversion of configuration at phosphorus.



(VI) δ (^{31}P) -101 ppm. (VII) δ (^{31}P) -71·5 ppm

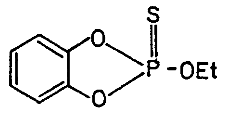


(VIII) δ (^{31}P) -59 ppm. (IX) δ (^{31}P) -45 ppm.

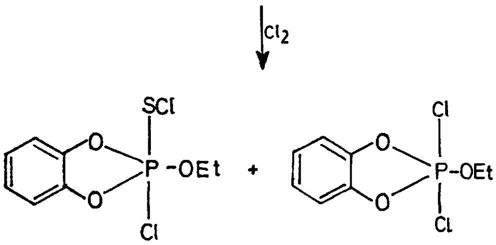


Indeed, the optically active *O*-ethyl *O*-methyl ethylphosphonothioate, $[\alpha]^{20}_{578}$ −1·72° (neat), was converted into *O*-ethyl ethylphosphonochloridate, $[\alpha]_{578}$ −13·5° (neat), with inversion of configuration, as shown by reactions of known stereochemistry.[3] The structure of the phosphonium intermediates (II), (IV), (V), (VII), and (VIII) was confirmed by their formation in the Arbuzov reaction between the corresponding tricovalent phosphorus esters and elemental chlorine or sulphur dichloride. Ligand exchange of this type in reactions involving phosphonium intermediates has often been postulated;[4] in this case the intermediates were directly observed by ^{31}P-n.m.r. spectroscopy.

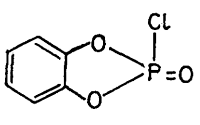
Although it is known that the five-membered ring has a stabilizing effect on phosphoranes,[5] it is nevertheless remarkable that the five-co-ordinate intermediates (XI) and (XII) are formed from the cyclic five-membered thionate (X) in its reaction with an equimolar quantity of chlorine in ethyl chloride solution at −90 °C. Both (XI) and (XII) have high-field chemical shifts characteristic of five-co-ordinate phosphorus compounds and have been prepared independently from the corresponding cyclic phosphite by



(X) δ (^{31}P) -80·5 ppm.



(XI) δ (^{31}P) +25 ppm. (XII) δ (^{31}P) +35 ppm.



(XIII) δ (^{31}P) -19·5 ppm.

---

† *cis* and *trans* refer to the relative stereochemistry of the singly bonded substituents.

‡ All ^{31}P chemical shifts are relative to 85% H_3PO_4 as external standard.

the Arbuzov reaction.[6] The intermediate (XI) is slowly

$$(XI) + Cl_2 \longrightarrow (XII) + SCl_2 \qquad (1)$$

$$(XI) + SCl_2 \longrightarrow (XII) + S_2Cl_2 \qquad (2)$$

transformed into (XII) by reactions (1) and (2). A related observation was made by Denney *et al.*[7] When the temperature is raised the phosphorochloridate (XIII) is the only product.

(*Received, 5th September* 1975; *Com.* 1005.)

[1] J. Michalski and A. Skowrońska, *Chem. and Ind.*, 1958, 1199; J. Michalski, B. Pliszka-Krawiecka, and A. Skowrońska, *Roczniki Chem.*, 1963, **37**, 1479.

[2] A. Skowrońska, J. Mikołajczak, and J. Michalski, *Bull. Acad. Polon. Sci., Sér. Sci. chim.*, 1973, **21**, 451.

[3] J. Michalski and M. Mikołajczyk, *Tetrahedron*, 1966, **22**, 3055; H. S. Aaron, A. T. Uyeda, H. F. Frack, and J. I. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 620.

[4] D. B. Denny and R. R. DiLeone, *J. Amer. Chem. Soc.*, 1962, **84**, 4737; I. M. Downie, J. B. Lee, and M. F. S. Matough, *Chem. Comm.*, 1968, 1350; B. Castro and C. Selve, *Bull. Soc. chim. France*, 1971, 2296.

[5] F. Ramirez, *Synthesis*, 1974, 90, and references cited therein.

[6] A. Skowrońska, J. Mikołajczak, and J. Michalski, *J.C.S. Chem. Comm.*, 1975, 791.

[7] L. L. Chang and D. B. Denney, *J.C.S. Chem. Comm.*, 1974, 84.