# Analogies Between the Dynamic Stereochemistry at Silicon and Phosphorus. Kinetic Study of Solvent-induced Epimerisation of Menthyl Chloro(phenyl)phosphonate

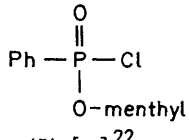
By R. J. P. CORRIU,* G. F. LANNEAU, and D. LECLERCQ

(*Laboratoire des Organométalliques, Equipe de Recherche Associée au C.N.R.S. No 554, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cédex, France*)

*Summary* A kinetic study of the solvent-induced epimerisation of menthyl chloro(phenyl)phosphonate shows an overall third-order process, first-order in chlorophosphonate and second-order in nucleophilic agent; activation parameters are consistent with a mechanism involving extension of co-ordination at phosphorus which is similar to that for silicon compounds.

THE stereochemistry of nucleophilic substitution at silicon and phosphorus compounds is generally interpreted in terms of completely different pathways.[1] In phosphorus chemistry, the usually accepted view is that apical attack by the nucleophile on the position opposite the most apicophilic group is generally preferred. The retention pathway is interpreted in terms of formation of a trigonal bipyramidal intermediate followed by pseudorotation prior to apical departure of the leaving group. For silicon compounds, the driving forces governing the stereochemical outcome of retention or inversion are: (i) the lability of the leaving group, and (ii) the electronic character of the nucleophile. With 'soft' nucleophiles predominant inversion at silicon is generally observed, whereas with 'hard' nucleophiles nucleophilic substitutions proceed with retention of configuration. However, many reported results[2] could be explained in terms of similar mechanisms for silicon and phosphorus compounds.

In order to extend the analogies between the phosphorus and silicon series, we have studied the racemization of halogenophosphonates by nucleophilic reagents such as dimethylformamide (DMF) or dimethylacetamide (DMA). Such a racemization process is very characteristic of the stereochemistry of group 4B elements.[3,4] Moreover epimerisation or optical instability of compounds having a P–Cl bond have been reported.[5] We have studied the kinetics of the epimerisation of menthyl chloro(phenyl)-



(I) $[\alpha]_D^{22}$ −80·4° (*c* 11·6 g/l in $CCl_4$)

phosphonate (**1**) in $CCl_4$, catalysed by the nucleophilic agents DMF and DMA. Compound (I) was obtained by chlorination of menthyl phenylphosphinate[6] with *N*-chlorosuccinimide in $CCl_4$.

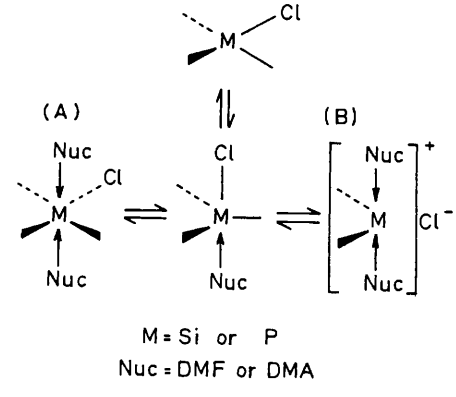
Kinetic experiments were studied by both polarimetry and $^{31}P$ Fourier transform n.m.r. spectroscopy, well separated singlets being observed for the two diastereoisomers [$\delta$ ($^{31}P$) − 26 and −25·6 p.p.m. with respect to external reference $H_3PO_4$ in $D_2O$].

The rate-law [equation (1)] is an overall third-order process, first-order in chlorophosphonate and second-order in nucleophilic agent, and is similar to that observed in the case of chloro-silanes, -germanes, and -stannanes.[3,4] Experimental data are in the Table.

$$v_{rac} = k_{rac}\,[R^1(R^2O)P(O)Cl][Nuc]^2 \qquad (1)$$

Apart from epimerisation, DMF and DMA promoted some phosphorylation, as in $Me_2SO$.[7] In order to test the extent of this competitive reaction, the amount of pyrophosphonate formed along with the epimerisation process was determined by $^{31}P$ n.m.r. spectroscopy.

At half-reaction, < 10% of pyrophosphonate was detectable [$\delta$($^{31}P$) *ca.* −7·4 p.p.m.]. Kinetic rate constants determined by the n.m.r. technique and polarimetry had comparable values. The large negative activation entropy suggests nucleophilic solvent participation, involving extension of the co-ordination number at phosphorus.




SCHEME

Polar aprotic solvents are good ligands for elements with vacant *d* orbitals. Halogenosilanes are known to give stable complexes, *e.g.* $SiX_4,2Me_2SO$[8] or $R^1R^2SiF_2,n$DMF.[9] Analogously co-ordinated complexes of halogenophosphorus compounds with DMF[10] or, more generally, donor

TABLE. Rate constants and activation parameters for the epimerisation of (I) catalysed by nucleophilic agents in $CCl_4$.

| | $k$(25 °C)/ $mol^{-2}\,l^{-2}\,s^{-1}$ | $E_a$/kcal $mol^{-1}$ | $\Delta H^{\ddagger}$/kcal $mol^{-1}$ | $\Delta G^{\ddagger}$/kcal $mol^{-1}$ | $\Delta S^{\ddagger}$/cal $K^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|---|
| DMF | $4·5 \times 10^{-5}$ | 10·4 | 9·8 | 23·3 | −45 |
| DMA | $1·8 \times 10^{-5}$ | 6·5 | 5·9 | 23·8 | −60 |

ligands[11] have been isolated. Intermediates with penta- and hexa-co-ordinated phosphorus have been postulated in the nucleophilic catalysis of the phosphorylation of alcohols[12] or group transfer reactions.[13]

Similar kinetic data at a silicon centre have been rationalized[3] by a two-step process (Scheme) involving co-ordination of the nucleophilic solvent with the silicon atom, followed by a rate-determining attack of another solvent molecule giving either an hexaco-ordinated species (process A) or a pentaco-ordinated siliconium ion $(Si^{V})^{+}$ (process B).

A mechanism involving the possibility of pseudorotation of a pentaco-ordinated species was dismissed on the basis of reaction orders. A similar argument can be used in our case, and it is reasonable to propose such a two-step process for the epimerisation of the chlorophosphonate (I). The rate-law involves two molecules of nucleophilic agent in the rate-determining step. Although in the case of silicon compounds, process (B) is well documented, process (A) cannot be excluded. A choice between the two pathways at a phosphorus centre would therefore be highly speculative at present.

(*Received*, 29*th September* 1977; *Com.* 1017.)

[1] L. H. Sommer, 'Stereochemistry, Mechanism, and Silicon, McGraw Hill, New York, 1965; R. J. P. Corriu and G. F. Lanneau, *J. Organometallic Chem.*, 1974, **67**, 243 and references therein; R. Corriu, C. Guerin, and J. Masse, *J.C.S. Chem. Comm.*, 1975, 75; F. K. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70; K. Mislow, *ibid.*, 1970, **3**, 321; W. E. McEwen, in 'Topics in Phosphorus Chemistry,' eds. M. Grayson and E. J. Griffith, Interscience, New York, 1965; S. Trippett, *Pure Appl. Chem.*, 1974, **40**, 595.

[2] K. E. de Bruin and D. M. Johnson, *J.C.S. Chem. Comm.*, 1975, 753; I. Granoth, Y. Segall, and H. Leader, *ibid.*, 1976, **74**, M. Mikołajczyk and J. Krzywanski, *Tetrahedron Letters*, 1975, 607; J. M. Harrison, T. D. Inch, and G. J. Lewis, *J.C.S. Perkin I*, 1974, 1053.

[3] R. J. P. Corriu and M. Henner, *J. Organometallic Chem.*, 1974, **74**, 1; F. Carre, R. Corriu, and M. Leard, *ibid.*, 1970, **24**, 101.

[4] F. K. Cartledge, B. G. McKinnie, and J. M. Wolcott, *J. Organometallic Chem.*, 1976, **118**, 7; M. Gielen and H. Mokhtar-Jamai, *ibid.*, 1977, **129**, 325.

[5] H. S. Aaron, R. T. Uyeda, H. F. Frack, and J. I. Miller, *J. Amer. Chem. Soc.*, 1962, **84**, 617; W. S. Wadsworth, S. Larsen, and H. L. Horten, *J. Org. Chem.*, 1973, **38**, 256.

[6] W. B. Farnham, R. K. Murray, and K. Mislow, *J. Amer. Chem. Soc.*, 1970, **92**, 5809.

[7] M. A. Ruveda, E. N. Zerba, and E. M. De Moutier, *Tetrahedron*, 1972, **28**, 5011.

[8] M. Gielen and N. Sprecher, *J. Organometallic Chem.*, 1966, **1**, 455.

[9] V. A. Drozdov, A. P. Kreshkov, and A. D. Romanova, *J. Gen. Chem. U.S.S.R.*, 1970, **40**, 2574.

[10] F. Cramer and M. Winter, *Chem. Ber.*, 1961, **94**, 989.

[11] J. C. Summers and H. H. Sisler, *Inorg. Chem.*, 1970, **9**, 862.

[12] F. Ramirez and J. F. Marecek, *Tetrahedron Letters*, 1976, 3791.

[13] W. G. Voncken, A. M. C. F. Castelijns, S. A. J. De Leeuw, and H. M. Buck, *Tetrahedron Letters*, 1977, 729.