Analogies between Nucleophilic Substitutions at Silicon and Phosphorus: Kinetic and Stereochemical Studies of Five- and Six-membered Ring Oxasilacycloalkanes

By Robert J. P. Corriu,* Christian Guérin, and (in part) G. Guiraud

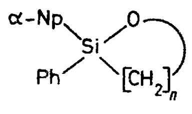
(*Laboratoire des Organométalliques, Equipe de Recherche associée au C.N.R.S. No.* 554, *Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon,* 34060 *Montpellier-Cédex, France*)

Summary A kinetic study of hydrolysis and methanolysis of the five-membered ring oxasilacyclopentane (I) shows a very large rate acceleration relative to the six-membered ring and open-chain analogues (II) and (III), the reactions occurring with inversion of configuration; this further analogy between nucleophilic substitutions at silicon and phosphorus suggests a similar mechanism for both processes.

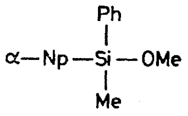
Cyclic five-membered phosphates and phosphonates undergo hydrolysis 10^6—10^8 times faster than their acyclic analogues;[1,2] the same phenomenon is observed with certain five-membered ring sulphates and sultones.[3] Thus, just as methyl ethylene phosphate is hydrolysed about 10^6 times faster than trimethyl phosphate, so catechol sulphate is hydrolysed 2×10^8 times faster than diphenyl sulphate.

In the case of phosphorus derivatives, Westheimer[1] has made a convincing case that the rate acceleration is due to a relief of strain in the five-membered ring that occurs on going from the starting ester to a trigonal-bipyramidal intermediate in which the ring spans an apical and equatorial position.

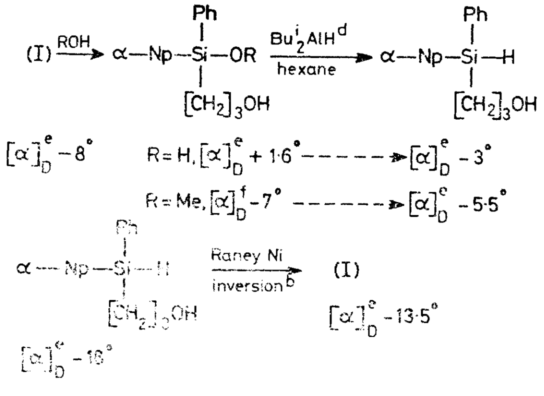
Because of some mechanistic analogies between nucleophilic substitutions at silicon and at phosphorus,[4] we have compared the rates of hydrolysis and methanolysis of the cyclic silicon compounds (I) and (II) with those reported for the acyclic compound (III).[5] These reactions occur with inversion of configuration at silicon. (Si–X bonds are always displaced by Bu^i_2AlH in hexane with retention;[7]



(I), $n = 3$[a,b]
(II), $n = 4$[a]



(III)[c]



α-Np = α-naphthyl

[a] R. Corriu, A. Kpoton, J. Barrau, and J. Satgé, *J. Organometallic Chem.*, 1976, **114**, 21; R. Corriu and J. Moreau, *ibid.*, p. 135. [b] Ref. 6. [c] L. H. Sommer, 'Stereochemistry, Mechanism and Silicon,' McGraw-Hill, New York, 1965. [d] Ref. 7. [e] In benzene. [f] In diethyl ether.

Ni-catalysed cyclisation occurs with inversion.[6,8] Thus both methanolysis and hydrolysis occur with inversion).

The kinetics of hydrolysis and methanolysis of racemic (I) and (II) were followed by n.m.r. spectroscopy under neutral conditions; the nucleophile was always present in large stoicheiometric excess. The results are summarized in the Table.

TABLE. Kinetics of hydrolysis and methanolysis of (I), (II), and (III) at 25 °C

Run	Substrate[a]	Nucleophile	$t_{1/2}$/s
1	(I)	H_2O	60
2	(II)	H_2O	3×10^5
3	(I)	MeOH	30
4	(II)	MeOH	5×10^5
5	(III)	MeOH	$9{\cdot}4 \times 10^5$

[a] Runs 1—4, [substrate] = 0·06 M; run 5, [substrate] = 0·04 M (ref. 5).

The five-membered ring compound (I) always reacts much faster than its six-membered ring analogue, *i.e.*, 10^3—10^4 times faster [$t_{1/2}$(II)/$t_{1/2}$(I) = 5×10^3 for hydrolysis and $1{\cdot}6 \times 10^4$ for methanolysis]. The rate of methoxy exchange between the open-chain compound (III) and methanol is of the same order of magnitude as that of the methanolysis of (II) [t(III)/t(II) = 2]; the reaction also proceeds predominantly with inversion of configuration.

The larger rate accelerations observed with cyclic five-membered phosphates or phosphonates are believed to be due to the existence of significant strain in the cyclic substrates, which is relieved on going to a trigonal-bipyramidal intermediate.[1,2] It was also proposed that stereoelectronic effects between the lone pairs of electrons of the oxygen atom in an equatorial position and the leaving group were responsible for a significant proportion of the observed kinetic acceleration.[9]

This assumption is not sufficient for explaining the rate acceleration observed with the cyclic five-membered ring phosphonate or with the oxasilacyclopentane (I). It explains only the acceleration shown by the five-membered phosphate relative to its phosphonate analogue[1,2] in which the equatorial oxygen is replaced by a carbon atom. Thus we think that much of the kinetic acceleration in the hydrolysis and methanolysis of the oxasilacyclopentane is a result of entropy changes.[1,2]

The observed stereochemical course of the reaction (inversion of configuration) shows that the bipyramidal intermediate has a symmetrical planar geometry with both oxygen leaving and entering groups in apical positions. We suggest that the fact that the lowest energy corresponds to the five-membered ring intermediate is due to the planarity of the ring; this optimizes the electronic interactions between the lone pairs of electrons on the oxygen leaving and entering groups. In contrast, the non-planar six-membered ring and open-chain geometries cannot show a similar effect.

Finally, it is noteworthy to find here a new analogy between nucleophilic substitutions at silicon and phosphorus; as we suggested previously,[4] many results could be explained in terms of similar mechanisms for silicon and phosphorus compounds.

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