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STEREOCHEMICAL PROOF OF THE EXISTENCE OF NUCLEOPHILIC ACTIVATION AT A SILICON ATOM IN NUCLEOPHILIC SUBSTITUTION REACTIONS. SUBSTITUTION OF THE Si—Cl-BOND WITH RETENTION OF CONFIGURATION

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Summary

Hydrolysis (or alcoholysis) of chlorosilanes shows nucleophilic assistance by hexamethylphosphorotriamide, dimethylsulfoxide or dimethylformamide; the reaction is entropy controlled and takes place with retention of configuration at silicon instead of the inversion always previously observed with acyclic chlorosilanes. A mechanism involving a nucleophilic attack of water (or alcohol) on pentacoordinate silicon is proposed.

The kinetics of hydrolysis and alcoholysis of Si—F and Si—Cl bonds have been studied extensively, [1—4]. Activation of the reaction by an additional nucleophile has been observed, but the action of the latter was not clearly established.

Two explanations were proposed. The first, suggested by Modena [5] and Gibson [2], involves an increase in the nucleophilicity of the alcohol by hydrogen bonding with the added nucleophile (Scheme 1-I). The second (Scheme 1-II)

SCHEME 1

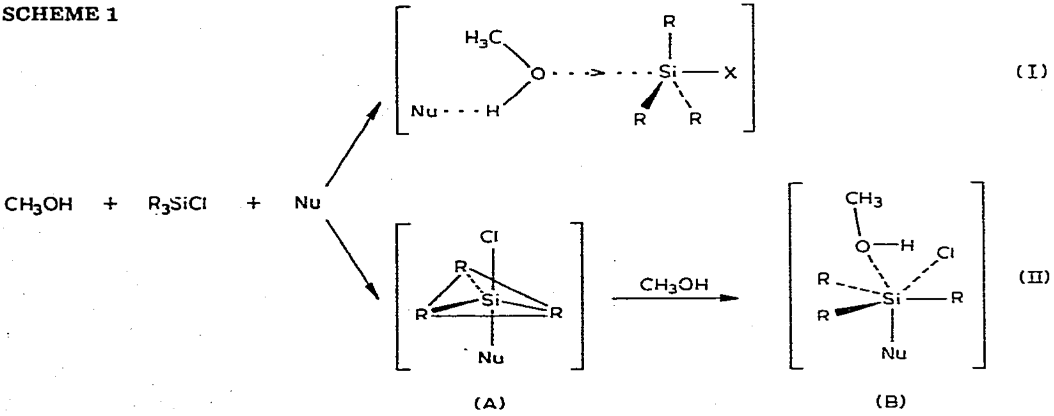


TABLE 1

COMPARISON BETWEEN RACEMISATION AND HYDROLYSIS OF CHLOROSILANES

	Rate law	k_3 (s^{-1} mol^{-2} l^2)	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})
Racemisation of:		(25°C)		
i-PrPh-1-NpSiCl (HMPT/CCl_4)	$v = k_3[R_3SiCl]\ [Nu]^2$	2.3×10^{-2}	3.15	55 (15)
EtPh-1-NpSiCl (HMPT/CCl_4)	id.	1.2	0.39	57 (15)
EtPh-1-NpSiCl (DMF/CCl_4)	id.	0.46×10^{-2}	0	70 (15)
Hydrolysis of:		(20°C)		
Ph_3SiCl (HMPT/anisole)	$v = k_3[R_3SiCl]\ [Nu]\ [H_2O]$	1200	−3.4	56
MePh-1-NpSiCl (DMSO/anisole)	id.	180	1.4	43
MePh-1-NpSiCl (DMF/anisole)	id.	40	2.6	40
Ph-1-NpOMentSiCl (HMPT/anisole)	id.	220	−2.9	46

involves coordination of the added nucleophile at silicon to give a pentacoordinate intermediate [1,6,10]. Scheme 1 illustrates these two hypotheses.

Comparison shows that hydrolysis and racemisation of chlorosilanes activated by nucleophilic agents such as hexamethylphosphorotriamide (HMPT), dimethylsulfoxide (DMSO) or dimethylformamide (DMF) are very similar processes; the similarity of the rate laws and the activation parameters is evident from Table 1. Both reactions are activated by a nucleophile and controlled by the activation entropy. We have previously shown that racemisation implies an extension of coordination at silicon [15,18] (cf. Scheme 2), and since the kinetics indicate the similarity of the two processes, we think that the nucleophilic effect is a result of coordination at silicon (cf. Scheme 1-A).

It was thus of interest to study the stereochemistry of hydrolysis and alcoholysis of optically active chlorosilanes [7] in reactions activated by a nucleophile, such as HMPT.

If the hydrolysis mechanism (Scheme 1-II) is correct, namely: formation of a pentacoordinated silicon in the first step followed by attack of a molecule of water (or alcohol) with displacement of chloride ion, one could expect retention of configuration at silicon. Since all hydrolyses or alcoholyses of acyclic halogenosilanes involve inversion [1,7,8], the most probable pentacoordinated silicon intermediate (A) would be a trigonal bipyramid with chlorine and the nucleophile in apical positions. Thus we could expect displacement of chloride ion by frontal attack of water (or alcohol), with retention of configuration (B).

Results

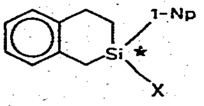
The variation of the optical rotation with time for hydrolysis and alcoholysis of optically active chlorosilanes was studied for reactions in anisole at 20° C in the presence of HMPT. Table 2 gives the values of the initial optical rotations of the compounds used. All the compounds of one series have the same configuration.

The variations of the optical rotation with time are much changed when

(continued on p. 39)

TABLE 2

SPECIFIC ROTATIONS OF $R_3Si^{*}X$ COMPOUNDS

$R_3Si^{*}X$	[α] at 365 nm			
	X = Cl	X = OH	X = OMe	X = O-t-Bu
MePh-1-NpSi*X	−15° [a] −4.3° [b]	−280° [a]	−148° [a]	−44° [f]
EtPh-1-NpSi*X	−57° [a] −56° [b]	+62° [c]	+84° [c]	
VinylPh-1-NpSi*X	−13° [c] −18.3° [b]	−66° [c]	−84° [c]	
	−48° [d] −21° [e] −92° [b]	−47° [e]	−152° [d]	

[a] [1]. [b] In anisole. [c] [17]. [d] In cyclohexane. [e] In dioxane [16]. [f] In carbon tetrachloride.

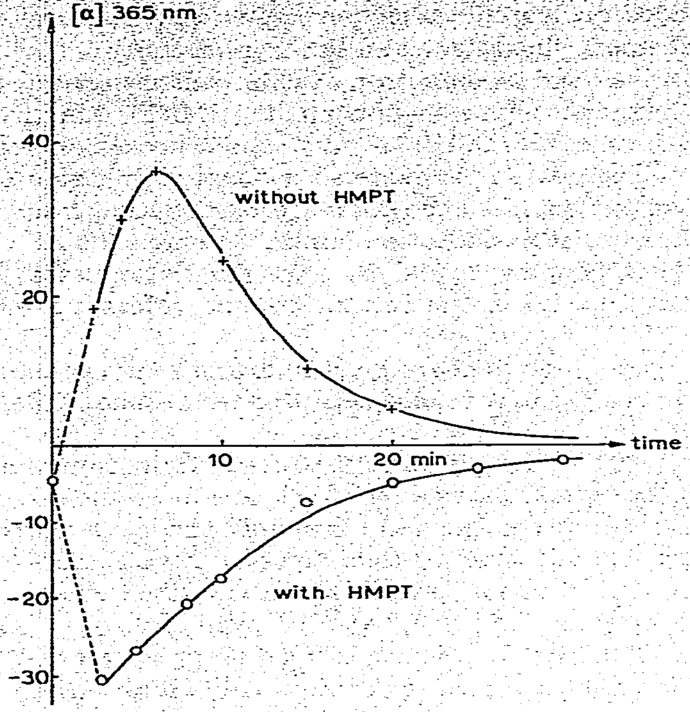


Fig. 1. Hydrolysis of (+)1-NpPhMeSiCl.

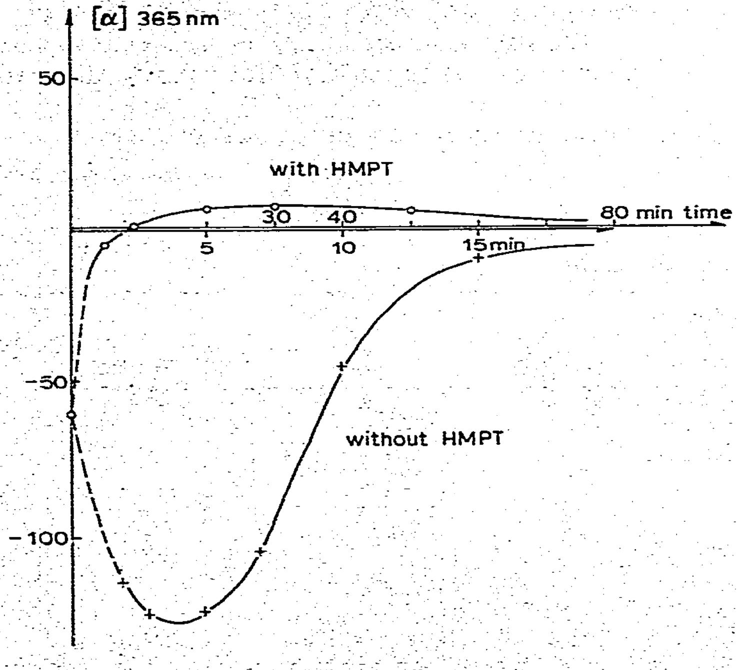


Fig. 2. Hydrolysis of (—)1-NpPhEtSiCl.

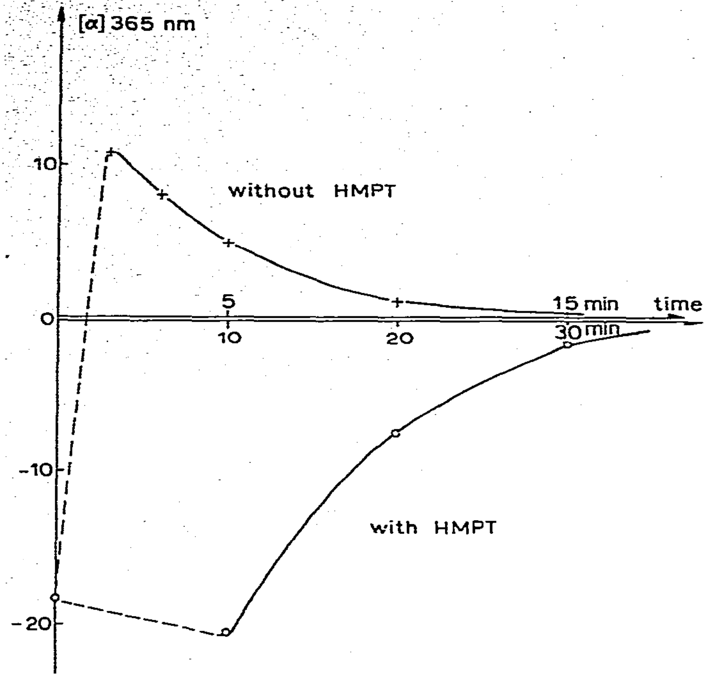


Fig. 3. Hydrolysis of (+)1-NpPhvinylSiCl.

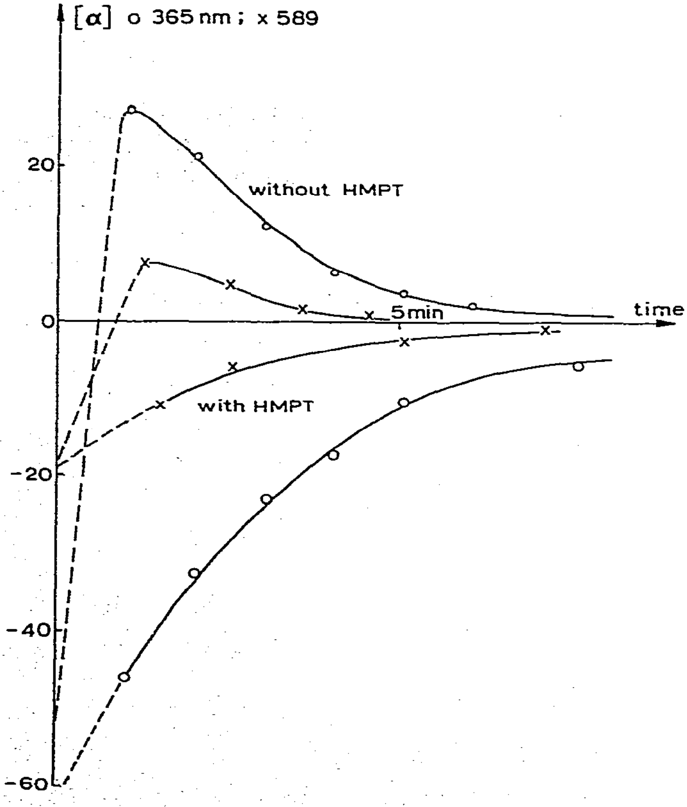
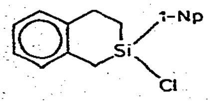


Fig. 4. Hydrolysis of (−)



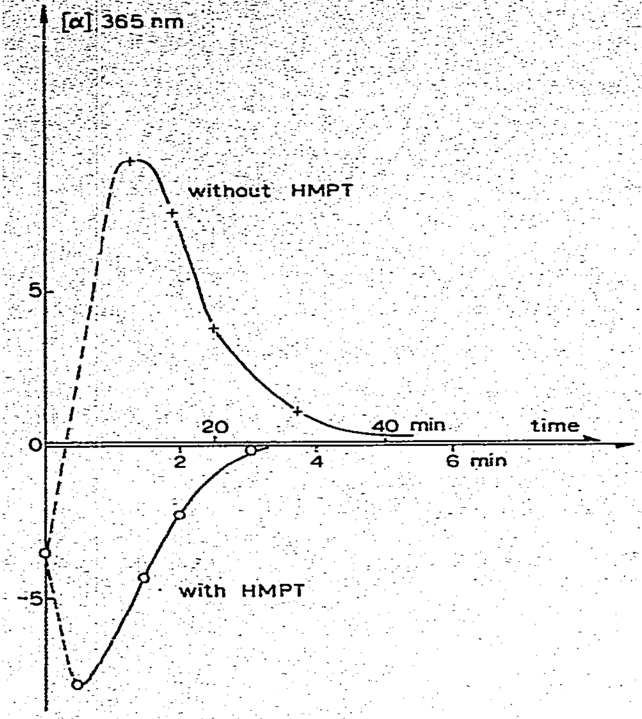


Fig. 5. Methanolysis of (+)1-NpPhMeSiCl.

nucleophile is present. Figs. 1—4 refer to the hydrolysis of the optically active halogenosilanes and Fig. 5—8 to the alcoholysis. It is clear that HMPT completely changes stereochemistry of the hydrolysis. Without the nucleophilic catalyst

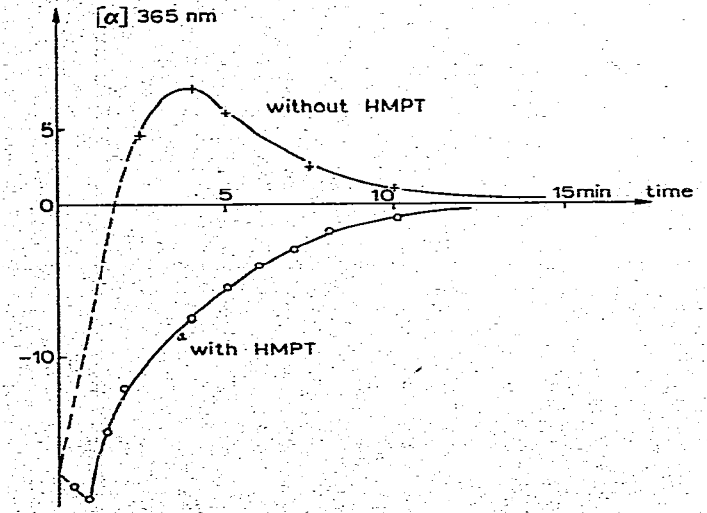


Fig. 6. Methanolysis of (+)1-NpPhvinylSiCl.

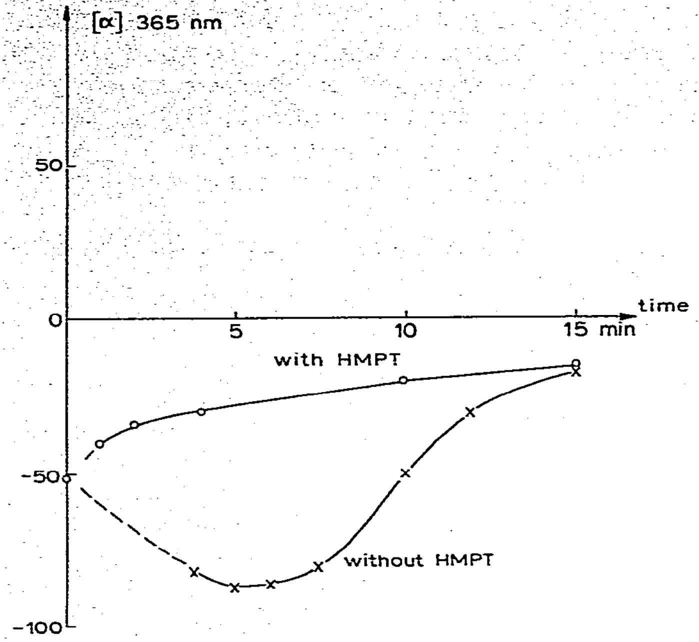


Fig. 7. Methanolysis of (—)1-NpPhEtSiCl.

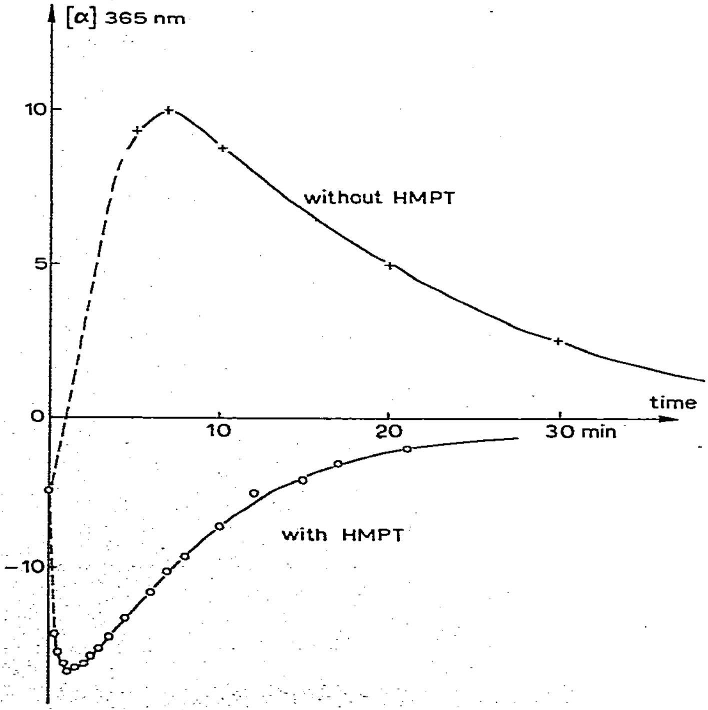


Fig. 8. Tertiobutanolysis of (+)1-NpPhMeSiCl.

inversion precedes racemisation [7], but in the presence of HMPT there is retention of configuration before the subsequent racemisation. (The compounds 1-NpMePhSiCl and 1-NpMePhSiOH with the same configuration are known to have rotations of the same sign at 365 nm.) It was shown previously that the observed variation of the rotation paralleled the substitution reaction [7], and the present results show that in presence of HMPT the reaction takes place with retention of configuration.

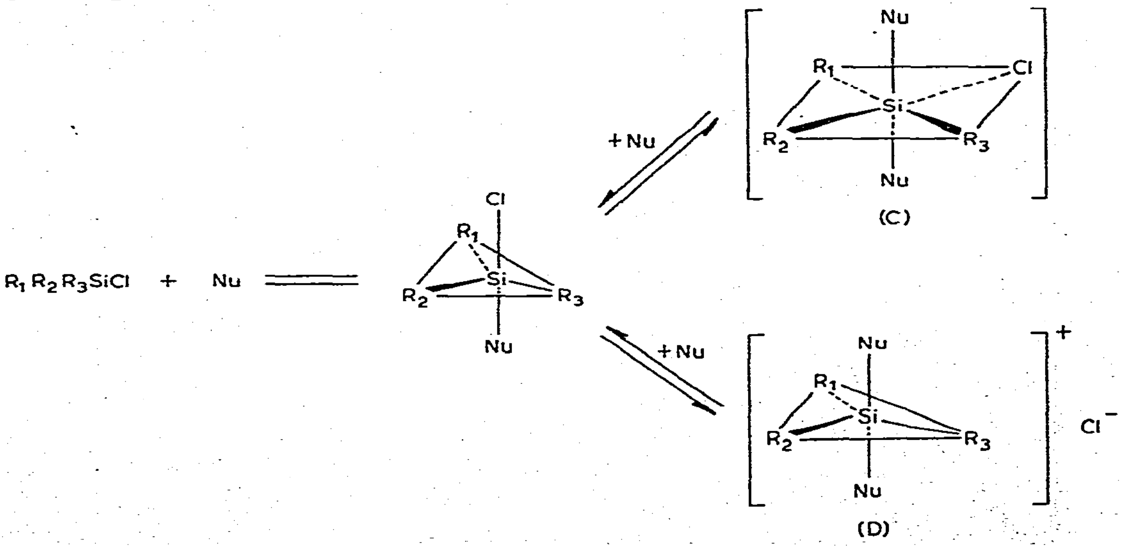
All these reactions take place with racemisation, which is due to the reaction between HCl and the silanol (or alkoxysilane) [7].

$$\begin{array}{l}(+)R_3SiCl + R'OH \rightleftharpoons (-)R_3SiOR' + HCl \\ \qquad\qquad\qquad\qquad\qquad\quad \upharpoonleft\downharpoonright \\ (\pm)R_3SiCl + R'OH \rightleftharpoons (\pm)R_3SiOR' + HCl\end{array}$$

Discussion

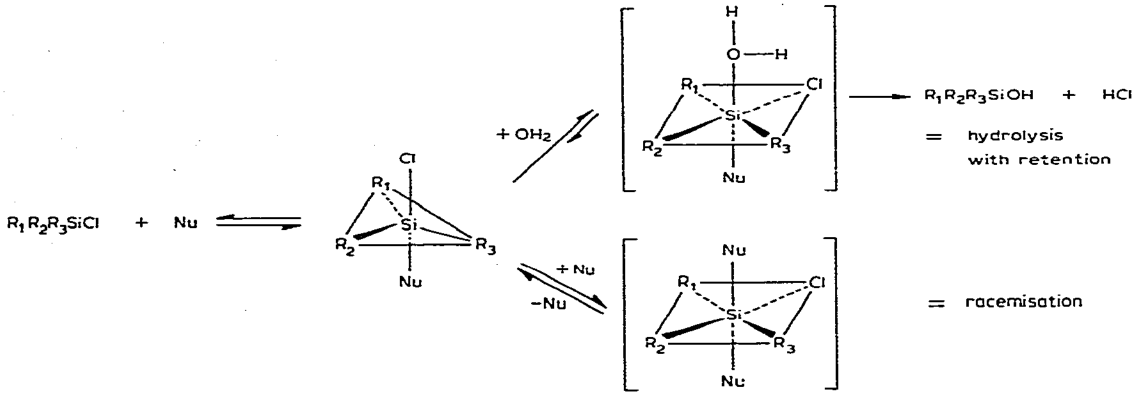
The kinetic study of the racemisation of chloro- and bromo-silanes shows that coordination of two molecules of nucleophile occurs at the silicon atom. There is always a very small activation enthalpy ($-3 < \Delta H^{\ddagger} < 3$ kcal mol^{-1}) and a highly negative activation entropy ($\Delta S^{\ddagger} \simeq -60$ cal mol^{-1} K^{-1}) [15]. This interpretation implies the reversible formation of a pentacoordinated silicon intermediate as a first stage. This is followed by the attack of a second molecule of nucleophile in the rate determining step; this step involves either a symmetrical octahedral intermediate (Scheme 2-C) or a pentacoordinated siliconium ion (Scheme 2-D), leading in either case to racemisation. It is difficult to choose between these possibilities: arguments [20,8] have been put in favour of both the hexacoordinate silicon (Scheme 2-C) and the pentacoordinate siliconium ion (Scheme 2-D) [19].

SCHEME 2



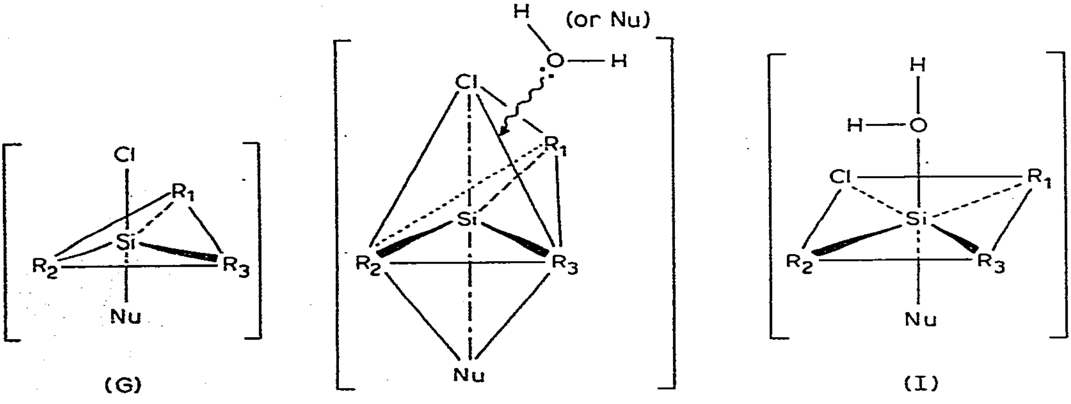
Hydrolysis and racemisation [4] activated by nucleophiles (HMPT, etc.) exhibit great similarities, and we suggest that in both processes the activation involves coordination of the additional nucleophile to silicon. The results obtained in this paper show that the presence of a nucleophile such as HMPT changes the stereochemistry of hydrolysis or alcoholysis to retention, instead of the inversion which is normally found in the absence of the nucleophilic catalyst [1,7,8,16]. (The lower optical activity observed in the presence of HMPT comes from the competiting racemisation caused by the nucleophilic agent [8].) These observations show that the nucleophilic activation involves the second process (B), involving pentacoordinate silicon. The following mechanism is therefore proposed:

SCHEME 3



This process implies nucleophilic assistance to nucleophilic substitution. The first step is the reversible coordination of the nucleophile to silicon, to give a pentacoordinated intermediate probably having the geometry of 4-G. (The Si—Cl bond is usually broken by nucleophiles with inversion of configuration and the geometry of (4-G) is the most stable-trigonal bipyramid, having the electronegative groups in apical positions.) The rate determining step is the nucleophilic attack of water (or alcohols) on the pentacoordinate silicon (cf. Scheme 4). It is not possible to decide whether the displacement of the chloride

SCHEME 4



(G)

(H)

(I)

ion is a concerted process with the transition state (4-H) or involves the hexacoordinated intermediate (4-I).

We can, however, predict the geometry of the attack. It is reasonable to assume that the second molecule attacks the pentacoordinated intermediate with the same geometry irrespective or whether it is HMPT or H_2O. This geometry must therefore explain both the racemisation when we are dealing with a second molecule of nucleophile and the retention of configuration when we are dealing with a molecule of H_2O. The attack on one of the upper faces is the only way of explaining these results. For instance the equatorial entry [6] could account for the retention, but not for the reacemisation.

Experimental

Starting materials

The preparations are described in the following references: methylphenyl-1-naphthylchlorosilane [21], (2-chloro-2-naphthyl)-2-sila-1,3,4-trihydro-3-naphthalene [13]; vinylphenyl-1-naphthylchlorosilane, ethylphenyl-1-naphthylchlorosilane [14].

Purification of solvents and reagents

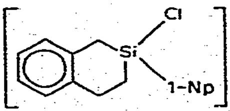
Anisole was distilled under reduced pressure from sodium under nitrogen. Dioxane was distilled from sodium. HMPT and the alcohols were purified as described in refs. [7] and [15].

Polarimetric measurements

The measurements were carried out with a Perkin—Elmer 141 polarimeter. The 1 ml polarimetric cell was thermostatted at 20° C. The chlorosilane was

TABLE 3

CONDITIONS OF THE POLARIMETRIC MEASUREMENTS

[Nucleophile] (mol l^{-1})	[MePh-1-NpSiCl] (mol l^{-1})	[HMPT] (mol l^{-1})
[H_2O] 0.071	0.069	0.011
[MeOH] 0.202	0.192	0.0056
[t-butanol] 0.27	0.146	0.0056
	[VinylPh-1-NpSiCl] (mol l^{-1})	
[H_2O] 0.069	0.068	0.0084
[MeOH] 0.247	0.089	0.0056
	 (mol l^{-1})	
[H_2O] 0.170	0.169	0.0084
	[EthylPh-1-NpSiCl] (mol l^{-1})	
[H_2O] 0.069	0.070	0.0084

dissolved in 10 ml of anisole to which 15 μl of water had been added; the resulting concentration of water is equivalent to that of the chlorosilane. After addition of HMPT, the mixture was transferred to the polarimeter cell and measurements were recorded at appropriate intervals. The conditions used are shown in Table 3.

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