The Chloride-induced Racemization and Fast ^{36}Cl-Exchange Reaction of an Optically Active Chlorosilane

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RECENT mechanistic studies indicate that most reactions in organosilicon chemistry are stereospecific,[1] proceeding with retention or inversion of configuration depending on the nature of the attacking and leaving groups, and the solvent. The chief exception is found in some reactions of chlorosilanes in which both solvent-induced racemization and racemization by various salts in chloroform were believed to take place by an ionization mechanism.[2] Since this appears to be the only well documented evidence for this mechanism in organosilicon chemistry, and because there appears to be no good reason why chlorosilanes should be unique in this respect, we have re-examined the problem and used a different solvent.

We have measured the rate of fast exchange (by a flow-quench technique[3]) and the rate of racemization for the reaction of lithium [^{36}Cl]-chloride with (−)-1-naphthylphenylmethylchlorosilane in a mixed solvent, dioxan–acetone 5 : 1 v/v, chosen to provide sufficiently slow racemization rates while remaining an adequate solvent for the salt. No solvent-induced racemization of the chlorosilane was observed during several days.

The Table shows the first-order rate constants for exchange and inversion at a fixed concentration of lithium chloride of 1·07 × 10^{-3}M. The reaction is clearly first-order in chlorosilane, and, within experimental error, the rates of exchange and inversion are the same.

Racemization and exchange of 1-*naphthylphenylmethylchlorosilane in acetone–dioxan at* 23·5°

	[LiCl] = 1·07 × 10^{-3}M [SiCl] (10^2M)	$10^5 k_1$ (sec.$^{-1}$)
Exchange	1·87	5·5 ± 0·5
	0·76	5·2 ± 0·5
	1·04	5·2 ± 0·5
	4·03	4·6 ± 0·4
		Mean 5·1 ± 0·4
Racemization	10·3	4·6 ± 0·03
	4·03	4·9
	7·55	5·2
	20·4	5·0
	5·32	4·5
		Mean 4·9 ± 0·3

Additional evidence for the inversion mechanism is obtained from the order of the reaction in salt. Over a four-fold concentration change of salt, the order for the exchange is 0·49 ± 0·02, and for the racemization is 0·48 ± 0·02. The order of one half is that predicted for attack by free chloride ion if ion pairs are kinetically inert, as long as most of the salt exists in the ion-pair form. This is a reasonable assumption for this solvent, which has a low dielectric constant.

Finally, we find no racemization of the chlorosilane by 2 × 10^{-3}M-lithium perchlorate over 8 hr. (the half-life for the chloride-induced racemization is about 2 hr.). This confirms that it is nucleophilic attack by the anion which causes racemization. On the other hand 2 × 10^{-3}M-tetrabutylammonium chloride causes complete racemization within 30 sec., as expected for the (presumed) more highly ionized nature of the salt in acetone–dioxan.

Thus, all the evidence points to a bimolecular mechanism for the chloride-exchange reaction both in this low-dielectric solvent and in the more polar solvents, acetone[3] and nitromethane.[4] With our techniques we were unable to study the chloride-exchange reaction in chloroform (and also in 1 : 2 dichloroethane) because of decomposition of the solvent and/or chloride exchange.

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[1] L. H. Sommer, 'Sterochemistry, Mechanism, and Silicon', McGraw-Hill, 1965.

[2] Ref. 1, chap. 5.

[3] M. W. Grant and R. H. Prince, *J. Chem. Soc.*, to be published.

[4] A. D. Allen and G. Modena, *J. Chem. Soc.*, 1957, 3671; G. Tagliavini and R. H. Prince, unpublished results.