Mechanism of Nucleophilic Substitution at Silicon: Kinetic Evidence on the Slow Formation of a Five-co-ordinate Silicon Intermediate

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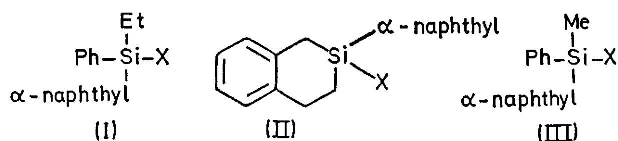
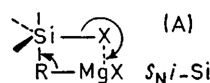
Summary Kinetic studies of the competitive reactions of an organometallic reagent with two silicon substrates differing only in their leaving group show that all the reactions studied occur with retention of the configuration at silicon, consistent with the occurrence of slow, rate-determining formation of a five-co-ordinate silicon intermediate.

WE have previously studied the stereochemistry of the coupling reactions of various organometallic reagents (RLi, RMgX, RNa) with the silicon compounds (I) and (II).[1] The results obtained, and, above all, the effects of solvents on the stereochemistry,[2] cannot all be explained by the S_Ni–Si mechanism initially proposed by Sommer *et al.*[3] to rationalise those cases in which retention of configuration of (III) occurs [structure (A)]. The driving force of this process is the stretching of the Si–X bond by electrophilic assistance.

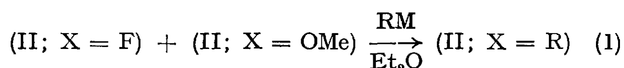
We have performed kinetic studies of the competitive reactions of an excess of an organometallic reagent with



X = OMe, F, Cl, and H



two silicon substrates differing only in their leaving groups [*e.g.* reaction (1)]. The reactions always take place with retention of configuration.



$$(II;\ X = F) + (II;\ X = OMe) \xrightarrow[Et_2O]{RM} (II;\ X = R) \quad (1)$$

The reactions were carried out using two or three different concentrations of the Si–X reagent and followed by g.l.c. The results obtained show the ratios k_F/k_{OMe} and k_{OMe}/k_H to be independent of both time and initial concentration. The data are given in the Tables 1 and 2.

TABLE 1. *Reactions with* (II; X = OMe and F)

RM	Solvent	k_F/k_{OMe}
EtMgBr	Et_2O	1·5—2·5
PhMgBr	,,	2—3
MeMgBr	THF	1—1·5
Allyl-Li	Et_2O	4—5

In the S_Ni–Si mechanism the breaking of the Si–X bond and the formation of the Si–R bond occur approximately simultaneously. We might therefore reasonably expect the rate constant to be affected both by the leaving group (*i.e.* F, OMe, or H) and by the reagent. We have studied the reaction of two different organosilicon substrates with two reagents (RLi, RMgX). The latter might be expected to stretch the Si–X bonds to very different extents, by electrophilic assistance.

TABLE 2. *Reactions with* (I)

X in (I) α	β	RM	Solvent	k_α/k_β
OMe	H	PhLi[a]	Et_2O	1·5—2
OMe	H	Bu^nLi	,,	5—6
OMe	H	,,	Hexane	40
H	D	PhLi[a]	Et_2O	1·3
H	D	Bu^nLi	,,	1
F	OMe	,,	,,	50
F	OMe	,,	Hexane	7

[a] PhLi is assumed to give the same stereochemistry as *p*-tolyl-Li.

The ratios k_F/k_{OMe} and k_{OMe}/k_H show that the reaction rates are of the same order of magnitude.† Further, we have not observed a significant isotope effect (see Tables). Thus it seems that the rate-controlling step of a reaction occurring with retention of configuration at silicon does not involve rupture of the Si–X bond. However, the similar reaction rates for different leaving groups, and the absence of a primary isotope effect are consistent with slow rate-determining formation of a five-co-ordinate silicon intermediate.

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† In two cases $k_\alpha/k_\beta > 10$. We are unable to explain these two values but they may be due to solvent effects and they do not conflict with the proposed mechanism.

[1] (a) R. J. P. Corriu and J. P. R. Masse, *J. Organometallic Chem.*, 1972, **34**, 221; (b) 1972, **35**, 51; (c) R. J. P. Corriu and G. Royo, *ibid.*, in the press.
[2] R. J. P. Corriu, J. P. R. Masse, and G. Royo, *Chem. Comm.*, 1971, 252.
[3] L. H. Sommer, 'Stereochemistry, Mechanism and Silicon,' McGraw-Hill, New York, 1965, p. 56.