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Preliminary communication

MECHANISM OF NUCLEOPHILIC SUBSTITUTION AT SILICON: KINETIC EVIDENCE ON THE SLOW FORMATION OF A FIVE COORDINATE SILICON INTERMEDIATE IN THE CASE OF INVERSION

GERARD CHAUVIERE, ROBERT J.P. CORRIU* and BERNARD J.L. HENNER
Laboratoire des Organométalliques associé au CNRS N°82, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 — Montpellier-Cédex (France)
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Summary

Kinetic studies of reactions of Grignard reagents with organosilicon derivatives (Si—Cl, Si—F) occurring with inversion of the configuration at silicon, show the rate-determining step to be the formation of a pentacoordinated silicon intermediate.

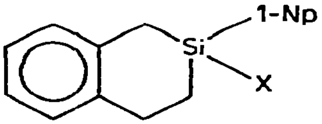
In a previous communication [1] we discussed the rate variations in nucleophilic substitution reactions of functionally-substituted silicon compounds (F, Cl, OMe, H). The results showed that for reactions occurring with configurational retention, the rates were all rather similar, and we explained this by the slow formation of a pentacoordinated silicon compound followed by rapid cleavage of the Si—X bond.

We report now kinetic studies of coupling reactions between Grignard reagents and fluoro- and chloro-silanes, which are known to take place with inversion at silicon [2]. The Grignard reagent is used in large exess in order to keep its concentration constant during the reaction. Runs were carried out at two different concentrations of the Si—X reagent, and followed by GLC.

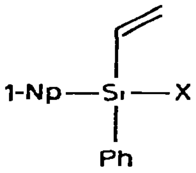
We studied the reaction of two types of substrates, I and II, with Grignard reagents. If the rupture of the Si—X bond occurs in the rate-controlling step we might expect the rate constant to be affected by the leaving group (i.e. Si—Cl or Si—F). The results obtained (see Table 1) show the ratios $k(F)/k(Cl)$ to be independent of both time and initial concentration. They also show that the rates $k(F)$ and $k(Cl)$ are rather similar. Thus it seems that the rate-controlling step of the reaction occurring with inversion at silicon, is the formation of a silicon(V) intermediate, as we proposed previously for the retention of configuration [1].

The similarity of the results in inversion and retention reactions also indicates that electrophilic assistance is not the driving force in the retention process.

TABLE 1



(Ia, X = F;
Ib, X = Cl)



(IIa, X = F;
IIb, X = Cl)

Solvent: Et_2O

Reactants	Organometallic compound	$k(F)/k(Cl)$
Ia, Ib	CH_3MgBr	1
	Allyl-MgBr	0.9
	Crotyl-MgBr	1
	$PhCH_2MgCl$	1.6
IIa, IIb	CH_3MgBr	0.3
	n-Propyl-MgBr	1.7
	Allyl-MgBr	0.5
	Crotyl-MgBr	0.5
	$PhCH_2MgCl$	0.7

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