Journal of Organometallic Chemistry, 152 (1978) 21—24

MECHANISM OF NUCLEOPHILIC SUBSTITUTION AT SILICON: EVIDENCE AGAINST COMPLEXATION CONTROL (S_Ni—*Si*) FOR COUPLING REACTIONS BETWEEN ORGANOSILANES AND ORGANOLITHIUMS TAKING PLACE WITH RETENTION

R.J.P. CORRIU *, J.M. FERNANDEZ and C. GUERIN

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)

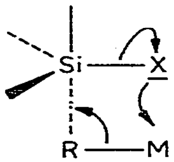
(Received December 5th, 1977)

Summary

New stereochemical and kinetic results are reported for reactions between organolithium reagents and some fluoro- and methoxy-silanes. They reveal the dominant influence of ion-pair dissociation, and thus of the electronic character of the nucleophile, and, allow elimination of a mechanism involving complexation control (S_Ni—*Si*).

Inversion or retention of configuration at silicon is the commonly observed stereochemical outcome. The main question is the nature of the dominant factor which controls the stereochemistry. For instance electrophilic assistance by the M^+ cation to the cleavage of the Si—X bond could be the controlling factor for the stereochemistry of nucleophilic substitutions by organometallic reagents (RM) taking place with retention, and this would be consistent with an S_Ni—*Si* process [1] (Scheme 1).

SCHEME 1. S_Ni—*Si* process: retention of configuration.

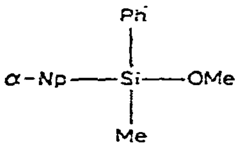


It has been shown for couplings between optically active organosilanes and Grignard reagents that the data are not in agreement with such a process. This involved studying the effect of the solvation of the Grignard reagents on the stereochemistry [2] and on the substitution rate [3]; an increase in the solvating power of the solvent promotes retention of configuration and accelerates the reaction. These observations are consistent with our hypothesis that the electronic character of the nucleophile controls the stereochemistry [4]: the solvation of the magnesium atom increases the "hardness" of the nucleophile by increasing the negative charge on the anionic carbon, and thus favours retention of configuration.

We report here new stereochemical and kinetic results for reactions between organolithium reagents and some fluoro- or methoxy-silanes in which the lithium cation is solvated to varying extents. In contrast to the covalent Grignard reagents, the organolithiums have ionic character [5], and it thus is of interest to test the following two hypotheses: (1) The lithium cation can afford electrophilic assistance to the cleavage of Si—OR and Si—F bonds (Scheme 1). (2) The controlling force of the stereochemistry is the electronic character of the nucleophile [4].

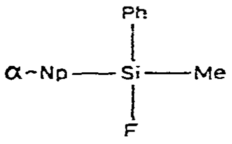
The stereochemical studies were carried out with two organolithium reagents each of which has a well-localised negative charge on an sp^3 carbon atom (n-BuLi and EtLi). In order to avoid lithium salt in the medium, these reagents are prepared from lithium and the corresponding dialkylmercury [6]. The results are given in Table 1.

TABLE 1



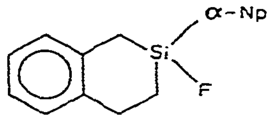
$[\alpha]_D$ −16.5°

(I)



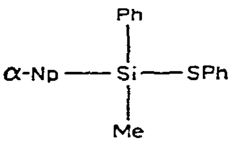
$[\alpha]_D$ +47°

(II)



$[\alpha]_D$ −34°

(III)



$[\alpha]_D$ +27°

(IV)

Run no.	Reagents	I	II	III	IV
1	EtLi/K_{Li}+/Et_2O ^{a}	98% RN ^{d}	95% RN	100% RN	
2	EtLi/TMDA/Et_2O ^{b}	96% RN	91% RN	99% RN	
3	EtLi/Et_2O	90% RN	90% RN	96% RN	
4	EtLi/LiBr/Et_2O ^{c}	90% RN	88% RN	96% RN	
5	EtLi/$LiClO_4$/Et_2O	85% RN	57% IN	75% RN	
6	EtLi/benzene	76% RN	70% RN		
7	n-BuLi/K_{Li}+/Et_2O	100% RN	98% RN		86% RN
8	n-BuLi/TMDA/Et_2O	90% RN	82% RN		-
9	n-BuLi/Et_2O	85% RN	80% RN		65% RN
10	n-BuLi/$LiClO_4$/Et_2O	83% RN	55% RN		
11	n-BuLi/heptane	68% RN			

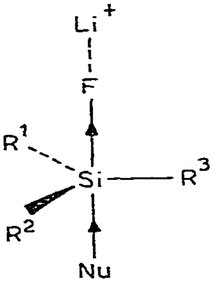
[a] K_{Li}+ = kryptofix 211, specific for Li^+ cation. [b] TMDA = tetramethylethylenediamine. [c] EtLi/LiBr/Et_2O is prepared by coupling reaction between EtBr and lithium: a small amount of LiBr salt is present in the medium. [d] Predominant stereochemistry: The $[\alpha]_D$ of optically pure R_3SiEt and R_3Si-n-Bu are known [1]. A predominant stereochemistry of 90% inversion indicates a reaction path that is 90% invertive and 10% retentive, giving a product which is 80% optically pure.

These stereochemical results have two main implications:

(1) They provide good evidence for a mechanism controlled by the electronic character of the nucleophile. Complexing agents for the Li^+ cation, such as TMDA, or better K_{Li^+}, which generate free anions [9], promote retention. Moreover non polar solvents such as benzene or n-heptane in which alkyllithiums are more aggregated increase the proportion of inversion instead of retention, as predicted by Scheme 1.

(2) They provide informations about the effect of an external electrophilic assistance on the stereochemistry. Added $LiClO_4$ or LiBr has a very small effect in the reactions of the Si—OMe bond, and we conclude that the Si—OR bond is insensitive to electrophilic assistance by the Li^+ cation. With the Si—F bond we get either a change from retention to inversion [run 5, fluorosilane (II)] or a decrease of the stereoselectivity of retention (run 10, fluorosilane (III)). Ashby et al. [7] have shown that $LiClO_4$ does not complex with an organolithium reagent and therefore its only effect is to provide external assistance to the cleavage of the ≡Si—F bond, thus increasing the proportion of inversion (Scheme 2).

SCHEME 2



We have also examined the kinetic effect of the addition of a lithium cryptand. In this case the cation is trapped, and so we are dealing with the reaction of a naked anion and a free silane. There are two possibilities:

(a) The mechanism is under complexation control [10] (Scheme 1): the cryptand must then cause a rate decrease, because the electrophilic assistance has been removed.

TABLE 2

$R_3SiX^a \xrightarrow{\text{n-BuLi}^b} R_3Si\text{-n-Bu}$ (R_3Si = α-NpPhMeSi)

Runs no.	Substrat	Solvent	T (°C)	Cryptand	$t_{1/2}$ (sec)
1	R_3SiOMe	Ether	−73°C		$t_1 = 1100$
2	R_3SiOMe	Ether	−73°C	TMDA	$t_2 = 500$
3	R_3SiOMe	Heptane	0°C		$t_3 = 30500$
4	R_3SiOMe	Heptane	0°C	K_{Li^+}	$t_4 = 35$
5	R_3SiF	Ether	−73°C		$t_5 = 1150$
6	R_3SiF	Ether	−73°C	TMDA	$t_6 = 200$
7	R_3SiF	Heptane	0°C		$t_7 = 54000$
8	R_3SiF	Heptane	0°C	K_{Li^+}	$t_8 = 5$

[a] R_3SiOMe/n-BuLi = 4 with [R_3SiOMe] = 10 mmol l^{-1}; R_3SiF/nBuLi = 4 with [R_3SiF] = 5 mmol l^{-1}.

[b] The n-BuLi/K_{Li^+} complex is insoluble in ether; we cannot report kinetic data in this case.

(b) The mechanism is controlled by the electronic character of the nucleophile: the cryptand must then cause a rate acceleration because of the increase of the nucleophilicity of the anion. The kinetic data are summarized in Table 2.

The data show that there is a rate increase when a more dissociating solvent such as ether is used instead of heptane (runs 1—3 or runs 5—7). The influence of ion-pair dissociation on the kinetic is apparent in runs in the presence of cryptands: thus when the Li^+ cation is trapped, and so the electrophilic assistance removed, we get a 10^3- ($t_3/t_4 \simeq 10^3$) or 10^4-fold ($t_7/t_8 \simeq 10^4$) rate acceleration.

For reactions with retention at silicon, both the stereochemical and kinetic data allow elimination of a mechanism involving complexation control, of the type shown in Scheme 1 [1]. On the contrary, they are consistent with a mechanism controlled by the electronic character of the nucleophile. For instance complexation reagents and polar solvents which favor the dissociation of ion-pairs increase the negative charge on the $C(sp^3)$ atom of the nucleophile (and thus its hardness): the stereochemistry is always displaced towards retention with rate acceleration. We can also point out that the $\equiv$Si—OMe bond is very insensitive to electrophilic assistance by Li^+ cation.

References

1 (a) L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965; (b) L.H. Sommer, Intrascience Chem., Rept., 7 (1973) 1.
2 R. Corriu, J. Massé and G. Royo, J. Chem. Soc. Chem. Commun., (1971) 252.
3 R. Corriu and B. Henner, J. Organometal. Chem., 102 (1975) 407.
4 (a) R. Corriu and J. Massé, J. Organometal. Chem., 35 (1972) 51; (b) R. Corriu and G. Lanneau, Bull. Soc. Chim. Fr., (1973) 303; (c) R. Corriu, C. Guerin and J. Massé, J. Chem. Res. Magn., (1977) 1877.
5 (a) G.E. Coates, M.L.H. Green, P. Powell and K. Wade, Principles of organometallic compounds, Methuen and Co, Ltd., London, 1971; (b) A. Streitwieser, J.E. Williams, S. Alexandratos and J.M. McKelvey, J. Amer. Chem. Soc., 98 (1976) 4778.
6 L.G. Makarova and A.N. Nesmeyanov, Methods of Elemento-organic chemistry, North-Holland Publishing Company, Amsterdam, Vol. 4, 1967, p. 386.
7 E.C. Ashby, J.J. Lin and J.J. Watkins, Tetrahedron Lett., (1977) 1709.
8 R. Corriu and G. Lanneau, Bull. Soc. Chim. Fr., (1973) 3102.
9 (a) J.M. Lehn, J. Simon and W. Wagner, Angew. Chem., 85 (1973) 621; (b) H. Normant, T. Cuvigny and P. Savignac, Synthesis, (1975) 805.
10 J.M. Lefour and A. Coupy, results to be published.