

## NUCLEOPHILIC SUBSTITUTIONS AT SILICON

### EVIDENCE FOR ION-PAIR DISSOCIATION AS CONTROLLING FACTOR OF THE STEREOCHEMISTRY AND A SIMPLE MECHANISTIC PROPOSAL.

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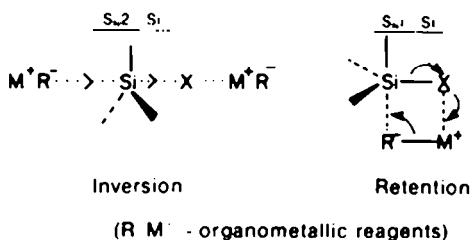
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**Abstract**—Stereochemical and kinetic data are reported for reactions between organolithiums or  $\text{LiAlH}_4$  and some chiral organosilanes. They rule out a mechanism involving complexation control, such as the  $\text{S}_{\text{N}}2\text{-Si}$  process proposed by Sommer *et al.* Electrophilic assistance to the cleavage of a Si-X bond does not control the stereochemistry, but acts as an additional factor which can facilitate the inversion by increasing the ability of the leaving group to depart. The results reveal the dominant influence of ion-pair dissociation, and thus of the electronic character of the nucleophile: the consequences of the use of either hard reagents with a localized negative charge, such as alkylolithiums, or softer reagents with a more delocalized negative charge, support this dependence. A simple mechanistic interpretation of the data is proposed, based on a description of nucleophilic substitutions at silicon as a frontier orbital process.

#### INTRODUCTION

The stereochemistry of nucleophilic substitutions at asymmetric silicon has been studied for a number of different chiral organosilanes  $\text{R}_1\text{R}_2\text{R}_3\text{Si-X}$ . The reactions are stereoselective, occurring with either retention or inversion. The stereochemical outcome appears to depend at first on the nature of the leaving group<sup>1,2</sup> and a parallel between its lability ( $\equiv\text{Si-Br} > \equiv\text{Si-Cl} > \equiv\text{Si-SR} \approx \equiv\text{Si-F} > \equiv\text{Si-OMe} > \equiv\text{Si-H}$ ) and the observed stereochemistry has been proposed.<sup>3,4</sup> However, for a given leaving group, dramatic changes of stereochemistry have been observed on changing the nature of the attacking nucleophile; hard reagents with a localized negative charge on an  $\text{sp}^3$  carbon atom favor retention of configuration, whereas resonance-stabilized carbon nucleophiles lead preferentially to inversion.<sup>1,5,6,7</sup>

Sommer *et al.* initially attempted to rationalize all the experimental observations with a  $\text{S}_{\text{N}}2\text{-Si}$  mechanism for inversion of configuration and with an  $\text{S}_{\text{N}}1\text{-Si}$  process for retention<sup>1</sup> (Scheme 1):



Scheme 1.

In the  $\text{S}_{\text{N}}1\text{-Si}$  process, electrophilic assistance by the  $\text{M}^+$  cation to the cleavage of the  $\equiv\text{Si-X}$  bond is the controlling factor for the stereochemistry: with tight ion-pairs, the Si-X and R-M<sup>+</sup> bond-breakings are mutually helpful in promoting formation of Si-R and MX bonds. However, for coupling reactions between optically active organosilanes and Grignard reagents, it has been shown that the results are not consistent with such

a process. The study involved the examination of the effect of the solvation of the Grignard reagents on the stereochemistry<sup>8</sup> and on the substitution rate<sup>3</sup> and it was found that an increase in the solvating power of the solvent promotes retention of configuration and accelerates the reaction. This is consistent with our hypothesis that the electronic character of the nucleophile controls the stereochemistry<sup>9</sup>: solvation of the magnesium atom increases the "hardness" of the nucleophile by increasing the negative charge on the anionic carbon, and thus favors retention of configuration.

We now report new stereochemical and kinetic data for reactions between some chiral organosilanes and alkylolithiums or lithium aluminium hydride in which the lithium cation is solvated to varying extents. These reagents differ from organomagnesium compounds in possessing an ionic character. The organolithiums are known to lead only to 1,2-addition with  $\alpha$ -enones and thus to behave as hard reagents.<sup>10</sup> In contrast, Seyden-Penne *et al.*, noted that  $\text{LiAlH}_4$  attacks only at carbon-4 of  $\alpha$ -enones when the lithium cation is trapped by a specific cryptand,<sup>11</sup> which clearly demonstrates the soft electronic character of the  $\text{AlH}_4^-$  anion.

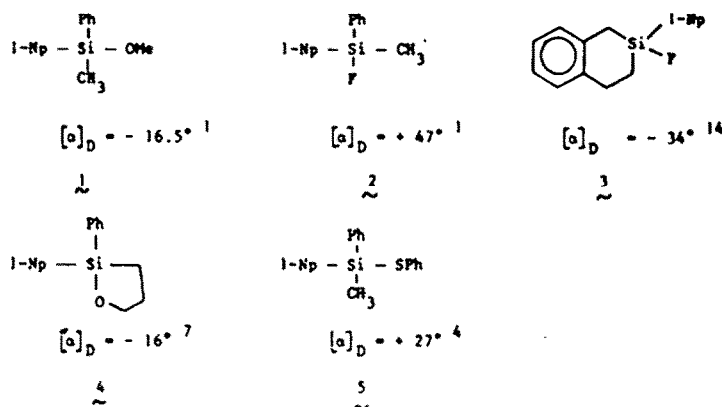
These considerations and the very close parallel between the stereochemistry of the substitution reactions at silicon and the regioselectivity of attack on  $\alpha$ -enones<sup>12</sup> prompted us to study more in detail the stereochemical behaviour of  $\text{LiAlH}_4$  and organolithiums, and especially the influence of the ion-pair dissociation on the mechanism.

#### RESULTS

##### (1) Coupling reactions with alkylolithiums

The stereochemical studies were carried out with two organolithium reagents, each of which has a well-localized negative charge on an  $\text{sp}^3$  carbon atom ( $n\text{-BuLi}$  and  $\text{EtLi}$ ). In order to avoid the presence of lithium salt, these reagents were prepared from lithium and the corresponding dialkylmercury.<sup>13</sup> The results are given in Table 1.

Table 1.



Runs N°	Reagents	Solvent	Predominant stereochemistry (a)				
			1	2	3	4	5
1	EtLi/KLi <sup>+</sup> (b)	ether	98 % RN	95 % RN	100 % RN	-	-
2	EtLi/TMDA (c)	"	96 % RN	91 % RN	99 % RN	-	-
3	EtLi	"	90 % RN	90 % RN	96 % RN	$[\alpha]_D = +3.2^\circ$ RN	-
4	EtLi/LiBr (d)	"	90 % RN	88 % RN	96 % RN	$[\alpha]_D = +3.1^\circ$ RN	-
5	EtLi/LiClO <sub>4</sub>	"	85 % RN	57 % IN	75 % RN	$[\alpha]_D = +3^\circ$ RN	-
6	EtLi	benzene	76 % RN	70 % RN	-	$[\alpha]_D = +0.7^\circ$ RN	-
7	EtLi	heptane	-	-	-	$[\alpha]_D = +0.7^\circ$ RN	-
<hr/>							
8	n-BuLi/KLi <sup>+</sup>	ether	100 % RN	98 % RN	-	-	86 % RN
9	n-BuLi/TMDA	ether	90 % RN	82 % RN	-	$[\alpha]_D = -16.1^\circ$ RN	-
10	n-BuLi	"	85 % RN	80 % RN	-	$[\alpha]_D = -14.1^\circ$ RN	65 % RN
11	n-BuLi/LiClO <sub>4</sub>	"	83 % RN	55 % RN	-	$[\alpha]_D = -13^\circ$ RN	-
12	n-BuLi	heptane	68 % RN	60 % RN	-	$[\alpha]_D = -12.5^\circ$ RN	-

<sup>(a)</sup>The absolute configuration and maximum  $[\alpha]_D$  of all R<sub>3</sub>Si-R' are known, except for 4 and 5.

<sup>(b)</sup>KLi<sup>+</sup> = Kryptofix 211, specific for Li<sup>+</sup> cation.<sup>15</sup>

<sup>(c)</sup>TMDA = Tetramethylethylenediamine

<sup>(d)</sup>The EtLi/LiBr was prepared from EtBr and lithium: a small amount of LiBr is present in the medium.

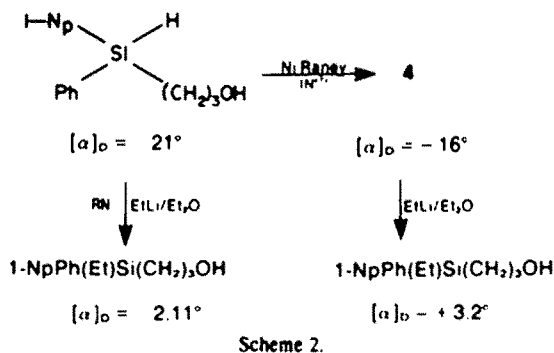
The stereochemistries were established as indicated below:

(i) The  $[\alpha]_D$  of optically pure R<sub>3</sub>Si-Et and R<sub>3</sub>Si-n-Bu, corresponding respectively to 1, 2, 3 and 5 are known<sup>1,6</sup>; a stereochemistry of 90% inversion indicates a reaction path that is 90% invertive and 10% retentive, giving a product which is 80% optically pure.

(ii) The chiral substrate 4 is liquid and we do not know the corresponding maximum  $[\alpha]_D$ , so no RN or IN proportion can be given. The predominant stereochemistry was determined by chemical correlations as reported previously with n-BuLi<sup>7</sup> and as indicated in Scheme 2 for EtLi.

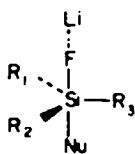
These stereochemical data and those reported below for reactions with LiAlH<sub>4</sub>, show that the stereochemistry is extremely sensitive to the nature of the solvent and salts in the medium. Two main features require discussion.

(i) Our data provide good evidence for a mechanism controlled by the electronic character of the nucleophile. Complexing agents for Li<sup>+</sup> cation such as TMDA or, better, KLi<sup>+</sup>, which generate free anions,<sup>15</sup> promote retention of configuration (runs 1, 2, 8, 9). Moreover non-



polar solvents such as benzene or n-heptane, in which alkyllithiums are more aggregated (runs 6, 7, 12), increase the proportion of inversion, instead of retention as predicted by an S<sub>N</sub>i-Si mechanism.<sup>1</sup> Complexation reagents and polar solvents which favor dissociation of ion-pairs increase the negative charge on the C(sp<sup>3</sup>) atom of the nucleophile and thus its hardness, so that the stereochemistry is displaced toward retention.

(ii) The results provide information about the effect of external electrophilic assistance on the stereochemistry. Added  $\text{LiClO}_4$  has a very small effect in the reactions of the Si-OMe bond (runs 5, 11), and we conclude that the Si-OR bond is insensitive to electrophilic assistance by the  $\text{Li}^+$  cation. With the Si-F bond, there is either a change from retention to inversion (run 5, fluorosilane 2) or a decrease of the stereoselectivity of retention (run 5, fluorosilane 3). Ashby *et al.*<sup>16</sup> have shown that  $\text{LiClO}_4$  does not complex with an organolithium reagent and therefore its only effect is to provide an external assistance to the cleavage of the Si-F bond. It converts the fluorine to a better leaving group by coordinates with  $\text{Li}^+$  (Scheme 3): such an increase of the ability of the leaving group to leave implies a shift of the stereochemistry towards inversion.<sup>1,4</sup>



Scheme 3.

In contrast,  $\text{LiBr}$  does not direct the stereochemistry toward inversion, as observed for  $\text{LiClO}_4$ .  $\text{LiBr}$  is known to form mixed aggregates with  $\text{MeLi}$ .<sup>17</sup> No external assistance to the cleavage of the Si-F bonds occurs. The reaction shows a stereoselectivity which is near the same as that obtained with  $\text{EtLi}$  alone (runs 3, 4).

When a lithium cryptand is present the cation is trapped, and so we are dealing with the reaction of a naked anion and a free silane. There are two possibilities:

(i) The mechanism is under complexation control<sup>18</sup> (Scheme 1,  $\text{S}_{\text{N}}\text{i-Si}$  mechanism), and so the cryptand will

cause a rate decrease, because the electrophilic assistance has been removed.

(ii) The mechanism is controlled by the electronic character of the nucleophile, and so the cryptand will cause a rate acceleration because of the increase of the nucleophilicity of the anion.

The kinetic data are summarized in Table 2.

It will be seen that there is a rate increase when a more dissociating solvent such as ether is used instead of heptane (runs 1-4 and 6-9). The influence of the ion-pair dissociation on the kinetics is also apparent in runs with cryptand, in which there is a  $10^3 - (t_4/t_5 = 10^3)$  or  $10^4$ -fold ( $t_7/t_{10} = 10^4$ ) rate acceleration. The absence of any rate variation for Si-OR compounds and the small acceleration with  $\text{R}_3\text{SiF}$  (run 8) confirm the conclusion from the stereochemical observations, that external electrophilic assistance by the  $\text{Li}^+$  cation cannot be the controlling factor.

## (2) Reduction with $\text{LiAlH}_4$

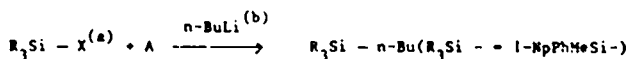
The stereochemical results are given in Table 3.

The results in Table 3 enable us to conclude that the ionic interaction between  $\text{Li}^+$  and  $\text{AlH}_4^-$  is the controlling factor for the stereochemistry, since:

(i) Complexation of  $\text{Li}^+$  by a cryptand, giving free anions  $\text{AlH}_4^-$ , promotes inversion of configuration, and an increase of the ionic radius of the cation (run 4) has a similar effect. This behavior is opposite to that of hard alkylolithiums for which is observed an increase of retention when  $\text{Li}^+$  was trapped. It is consistent with a soft electronic character for the naked  $\text{AlH}_4^-$  anion (which gives predominant inversion for displacement of Si-F or Si-OR bonds and 1,4-addition to  $\alpha$ -enones<sup>12</sup>).

(ii) In all cases (runs 1) added  $\text{LiBr}$  salt promotes retention of configuration. The most significant changes

Table 2.



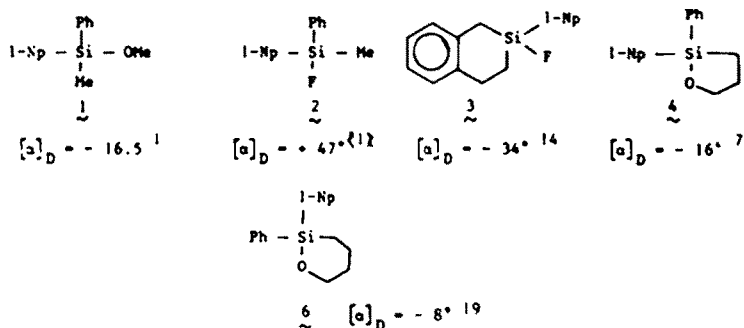
A = cryptand, TMDA or  $\text{LiClO}_4$

Runs N°	Substrate	Solvent	t°C	A	t 1/2 (seconds)
1	$\text{R}_3\text{Si}-\text{OMe}$	ether	-78°C	-	$t_1 = 1100$
2	$\text{R}_3\text{Si}-\text{OMe}$	"	-78°C	TMDA	$t_2 = 500$
3	$\text{R}_3\text{Si}-\text{OMe}$	"	-78°C	$\text{LiClO}_4$	$t_3 = 450$
4	$\text{R}_3\text{Si}-\text{OMe}$	heptane	0°C	-	$t_4 = 30500$
5	$\text{R}_3\text{Si}-\text{OMe}$	"	0°C	$\text{KLi}^+$	$t_5 = 35$
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6	$\text{R}_3\text{Si}-\text{F}$	ether	-78°C	-	$t_6 = 1150$
7	$\text{R}_3\text{Si}-\text{F}$	"	-78°C	TMDA	$t_7 = 200$
8	$\text{R}_3\text{Si}-\text{F}$	"	-78°C	$\text{LiClO}_4$	$t_8 = 1800$
9	$\text{R}_3\text{Si}-\text{F}$	heptane	0°C	-	$t_9 = 54000$
10	$\text{R}_3\text{Si}-\text{F}$	"	0°C	$\text{KLi}^+$	$t_{10} = 5$

<sup>(a)</sup> $[\text{n-BuLi}]/[\text{R}_3\text{SiOMe}] = 4$  with  $[\text{R}_3\text{SiOMe}] = 10$  mmoles/l  $[\text{n-BuLi}]/[\text{R}_3\text{SiF}] = 4$  with  $[\text{R}_3\text{SiF}] = 5$  mmoles/l

<sup>(b)</sup>The  $\text{n-BuLi}/\text{KLi}^+$  complex is insoluble in ether, so we could not obtain kinetic data.

Table 3.



Runs N°	Reagent (a)	Solvent	Predominant stereochemistry (c)				
			1	2	3	4	6
1	LiAlH <sub>4</sub> (LiBr) <sup>(b)</sup>	Et <sub>2</sub> O	98 % RN	62 % RN	95 % RN	$[\alpha]_D = +13^{\circ}$ RN	$[\alpha]_D = -7^{\circ}$ RN ( $[\alpha]_{365} = -36.5^{\circ}$ )
2	LiAlH <sub>4</sub> (a)	"	95 % RN <sup>(1)</sup>	95 % IN <sup>(1)</sup>	rac <sup>(2)</sup>	$[\alpha]_D = +13^{\circ}$ RN	$[\alpha]_D = -7^{\circ}$ RN <sup>(19)</sup> ( $[\alpha]_{365} = -35.5^{\circ}$ )
3	LiAlH <sub>4</sub> (SLi <sup>+</sup> )	"	75 % IN	-	65 % IN	$[\alpha]_D = -13^{\circ}$ IN	$[\alpha]_D = +2^{\circ}$ IN
4	R <sub>3</sub> N <sup>+</sup> AlH <sub>4</sub> <sup>(a)</sup>	benzene	65 % RN	-	58 % IN	$[\alpha]_D = +5^{\circ}$ RN	-

<sup>(a)</sup>Homogeneous LiAlH<sub>4</sub> ethereal solutions were prepared by refluxing LiAlH<sub>4</sub> in Et<sub>2</sub>O, followed by filtration under N<sub>2</sub>. The reductions were carried out with [LiAlH<sub>4</sub>]/[R<sub>3</sub>SiX] = 2 - R<sub>3</sub>N<sup>+</sup>AlH<sub>4</sub><sup>-</sup>; R<sub>3</sub>N<sup>+</sup> = (n.octyl), n-propyl-ammonium cation<sup>19</sup>

<sup>(b)</sup>[LiBr]/[LiAlH<sub>4</sub>] = 10; these reactions were carried out under homogeneous conditions.

<sup>(c)</sup>The absolute configuration and maximum  $[\alpha]_D$  of the optically pure 1, 2, 3 and R<sub>3</sub>Si-H compounds are known.<sup>1,14</sup> Since the chiral organosilanes 4 and 6 are liquids and we do not know the maximum  $[\alpha]_D$ , the predominant stereochemistry was determined by chemical correlations.<sup>7,19</sup>

are observed with the fluorosilanes 2 and 3. We showed earlier that the Li<sup>+</sup> cation provides some external assistance to the cleavage of a Si-F bond which increases the proportion of inversion, so we conclude that the main effect of LiBr is not the complexation of the organosilane. We think that Li<sup>+</sup> and AlH<sub>4</sub> are tightly associated in aggregates, which have a stereochemical effect contrary to that of the "naked" anions AlH<sub>4</sub><sup>-</sup>, in that they behave as "hard" reagents.

#### MECHANISM AND COMMENTS

The stereochemical and kinetic data show that the stereochemistry at silicon is extremely sensitive to the electronic character of the nucleophile. The contrasting behavior of the hard alkyl anions and of the soft AlH<sub>4</sub><sup>-</sup> anion illustrates this marked dependence. We have to note that the electronic character of the nucleophile is that indicated by the behavior of the relevant "naked" anion (in the presence of a cryptand specific for the counter-cation): hard reagents lead to retention in nucleophilic substitutions at silicon and attack at carbon-2 of  $\alpha$ -enones, whereas soft anions promote inversion of configuration at silicon and attack at carbon-4 of  $\alpha$ -enones.

For reactions with alkyllithiums which take place with retention the results rule out a mechanism involving complexation control, of the type shown in Scheme 1.<sup>1</sup> Complexation reagents or polar solvents which favor the dissociation of ion-pairs increase the negative charge on

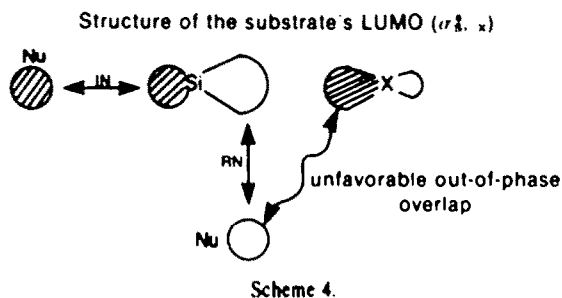
the sp<sup>3</sup> carbon atom of the nucleophile (and thus its hardness): the stereochemistry is always displaced toward retention (with rate acceleration) instead of the inversion predicted by Scheme 1.<sup>1</sup>

The influence of the ion-pair dissociation on the stereochemistry is also dominant in the case of the soft AlH<sub>4</sub><sup>-</sup> anion (1,4-addition to  $\alpha$ -enones and predominant inversion at silicon when Li<sup>+</sup> is trapped by a specific cryptand). When LiBr is added to LiAlH<sub>4</sub>, it favors the formation of aggregates, and the stereochemistry changes to retention.

Finally, behavior quite similar to that of the alkyllithiums has been previously reported with Grignard reagents<sup>8</sup> for which Lewis base solvents promote retention and increase the substitution rate.<sup>21</sup>

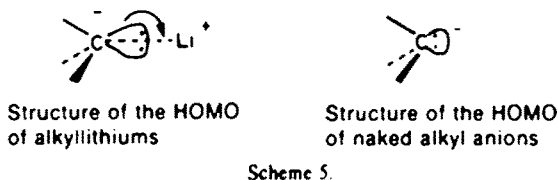
We assume, as proposed by Nguyễn Trọng Anh and Minot,<sup>22</sup> that nucleophilic substitutions at silicon can be described as orbital processes. In the reaction between a nucleophile Nu and an organosilane R<sub>3</sub>Si-X, the major interaction occurs between the HOMO of the nucleophile and the LUMO of the substrate  $\sigma^*$ Si-X. The above authors calculated the form of the  $\sigma^*$ Si-X<sup>22</sup> using an extension of Salem's orbital treatment of the Walden inversion<sup>23</sup> (Scheme 4).

Front-side attack, corresponding to an attack on the big lobe of silicon, leads to retention. When the unfavorable out-of-phase overlap between the nucleophile and the leaving group orbitals predominates, the nucleo-



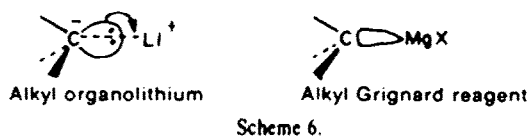
philic attack occurs at the rear of the molecule opposite to X, leading to inversion. Therefore, whether retention and inversion occurs, they can be regarded the result of a fine balance between the in-phase and out-of-phase orbital overlap between the nucleophile and the LUMO ( $\sigma_{Si-X}^*$ ) of the substrate.

Such an approach gives a good guide to the dominant influence of the electronic character of the nucleophile on the stereochemistry by taking account of the size of the valence orbitals around the nucleophilic center. Alkylolithiums have a negative charge on carbon which is in part transferred to the  $Li^+$  cation. When the  $Li^+$  is trapped (naked anion), the negative charge is concentrated on the reactive carbon center (Scheme 5).



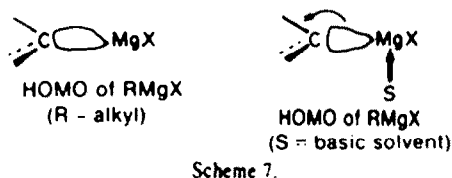
In the latter case, as the valence orbitals are smaller, the out-of-phase overlap with the leaving group is diminished and, therefore, the retention is favored. This is in agreement with the experimental data. The cryptand effect which results in increases of retention ratio and of the rate, can be explained by a higher energy level of the naked anion's HOMO. As a consequence, the frontier-orbital interaction is increased and, therefore, retention is kinetically favored.

The above description applies also to Grignard reagents, the behavior of which was reported previously:<sup>5-8</sup> compared to organolithiums, they promote the inversion of configuration. The carbon-magnesium bond is covalent. As a consequence, the electrons of the nucleophile are those of C-Mg bond which are localized in a MO pointing toward each other. It is more voluminous than the small valence orbitals around the nucleophilic carbon of an alkyl organolithium (Scheme 6).



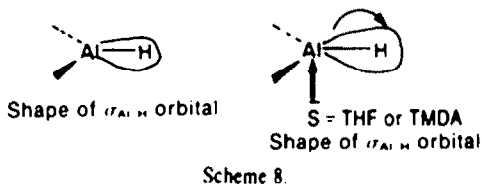
Thus the front-side attack is somewhat disfavored in the case of Grignard reagents: it explains their greater aptitude to give inversion compared to organolithiums. On the other hand, similar arguments allow us to discuss

the change of stereochemistry observed with Grignard reagents when increasing the solvent basicity.<sup>9</sup> The addition of a Lewis base solvent (THF, DME) implies a modification of the carbon-magnesium MO. The latter becomes more contracted on the carbon atom (Scheme 7).



In consequence, the nucleophile is smaller and the stereochemistry is shifted to retention.<sup>8</sup> Moreover, the contraction of the valence orbitals around the carbon atom implies a higher energy level for the HOMO of the  $RMgX$ , so the frontier-orbital interaction is increased: the observed increase of the substitution rate<sup>21</sup> is consistent with this.

In a previous paper,<sup>12</sup> we noted that in the case of the alanes  $AlH_2Y_{1-x}$  ( $Y = H, OR, SR$ ), the more the negative charge is displaced toward the hydrogen, the more favoured is the inversion. In hexane solutions valence orbitals around the hydrogen point toward the aluminium atom. In solvents, such as THF, able to coordinate the Al, the structure of the relevant HOMO of the nucleophile is modified by diffusion of electron density toward H (Scheme 8).

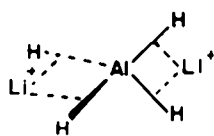


In the first case, the valence orbitals of nucleophile are compact. The unfavorable out-of-phase overlap with the leaving group is feeble, and whatever its nature, retention is observed. In contrast, in THF or TMDA, since the valence orbitals around hydrogen are more diffuse, the out-of-phase repulsion with the leaving group is dominant. Rear-side attack is favored and inversion is observed with fluoro-, chloro- and bromosilanes, i.e. with the best leaving groups.<sup>12, 24</sup>

In the case of the naked  $AlH_2^-$  anion, the negative charge is certainly localized in the hydrogen atoms. Therefore we can reasonably suppose diffuse valence orbitals around them.

This explains the general shift of the stereochemistry to inversion which is observed when naked  $AlH_2^-$  anions are used as reducing agents (Table 3). In contrast, when using  $LiAlH_4$  or  $LiAlH_4/LiBr$ , we observe an increase of the retention ratio.  $Li^+$  and  $AlH_2^-$  are tightly associated in aggregates. Our data and those of others<sup>25</sup> suggest aggregates in which the  $Li^+$  cations prevent the delocalization of the negative charge on the hydrogen. A possibility could be (Scheme 9).

Such assumptions are supported by the crystal structures of  $LiAl(Et)_4$ <sup>26</sup> and  $KAl(Me)_4$ .<sup>27</sup> The structure of the latter compound consists of isolated  $K^+$  and  $Al(Me)_4^-$  ions: the bonding between the central atom and ligands shows a highly polar character which causes a consider-



Scheme 9.

able weakening of the Al-C bond. We can find here a good model for the naked  $\text{AlH}_4^-$ 's structure: the negative charge is highly delocalized around the H atoms. On the other hand, the structure of  $\text{LiAl}(\text{Et})_4$  consists of linear chains of alternating lithium and aluminum: there is some evidence of weak covalent interaction involving lithium. Such an interaction would explain the behavior of  $\text{LiAlH}_4/\text{LiBr}$  aggregates in preventing the delocalization of the negative charge to hydrogen atoms.

#### EXPERIMENTAL

##### Materials

The optically active derivatives 1, 2, 3, 4, 5 and 6 were described previously [respectively Refs. 1, 14, 7, 4 and 19].

To avoid lithium salt in the medium, the alkyl organolithium reagents were prepared from lithium and the corresponding dialkyl mercury<sup>13</sup>: the reaction was carried out at room temperature in ether and at 80° in heptane or benzene as solvent. The organolithium solutions were standardized by the Jolibois method.<sup>20</sup>  $\text{EtLi}/\text{LiBr}$  is prepared by coupling reaction between  $\text{EtBr}$  and lithium as usually described: a small amount of  $\text{LiBr}$  is present in the medium.  $\text{RLi}/\text{LiClO}_4$  was obtained by adding anhydrous  $\text{LiClO}_4$  to an ethereal solution of  $\text{RLi}$  (molecular ratio:  $\text{RLi}/\text{LiClO}_4 = 1/2.5$ ): the substitution reactions were carried out under homogeneous conditions.

Solutions of  $\text{LiAlH}_4$  in ether were prepared by refluxing  $\text{LiAlH}_4$  in ethyl ether, followed by filtration under  $\text{N}_2$  atmosphere.  $\text{R}_4\text{N}^+ \text{AlH}_4^- (\text{NR})_4^-$  (n-octyl), n-propylammonium cation) was prepared as described in literature.<sup>20</sup> The reducing reagent  $\text{LiAlH}_4/\text{LiBr}$  was obtained by adding anhydrous  $\text{LiBr}$  to an ethereal solution of  $\text{LiAlH}_4$  (molecular ratio:  $\text{LiAlH}_4/\text{LiBr} = 1/10$ ): the reduction reactions were carried out under homogeneous conditions. The  $\text{LiAlH}_4$  solutions were standardized by the Felkin method.<sup>20</sup>

$\text{KLi}^+$  is a cryptand specific of the  $\text{Li}^+$  cation: Kryptofix 211 = tetraoxa-4, 7, 13, 18-diaza-1, 10- bicyclo-8, 5, 5, eicosane, supplied by Merck, Darmstadt (R.F.A.).  $\text{RLi}/\text{KLi}^+$  reagents were prepared by slow addition of  $\text{RLi}$  in ether or heptane solution to an equimolecular amount of  $\text{KLi}^+$  in the same solvent.

##### Reactions

(a) *Reactions with organolithiums—general procedure.* All reactions were carried out under nitrogen atmosphere. To an excess of the organometallic reagent (molecular ratio:  $\text{RLi}/\text{organo-silane}$ , 4/1) in ether, benzene or heptane (Table 1), was added the organo-silane in the same solvent than  $\text{RLi}$ . The reaction mixture was stirred at room temperature until complete reaction and then hydrolyzed with acid (10%  $\text{HCl}$ ) at 0°. The silanes were purified by tlc (silica gel PF 254) using benzene/pentane, 10/90 or  $\text{CHCl}_3$  as eluants, and identified by comparison of IR and NMR spectra of authentic racemic samples.<sup>1, 7, 20</sup> The  $[\alpha]_D$  values were measured with a Perkin-Elmer 151 polarimeter.

##### Kinetics

The reactions were carried out under  $\text{N}_2$  atmosphere, either at -78° (dry ice-acetone) or at 0°.

##### glc apparatus

Girdel 75 FH 1 equipped with a capillary column (20 m × 0.5 mm) packed with OV 17 silicones. Column temperature: 190–230°, nitrogen flow rate: 4 ml/min.

##### glc measurements<sup>31</sup>

The sampling technique was by peak height measurement using an internal standard for the reference height. This

reference height was the same for anyone kinetic run, as determined by interpolation of the values from two different injections for each measurement. The method has the advantage of only considering the concentration to be a linear function of the peak height between the two measured values. For each reaction two standard points were used to plot relationship  $[C] = f(h)$  where C is the product concentration and h its peak height.

*Typical reaction:*  $n\text{-BuLi}/\text{Et}_2\text{O}$  (-78°)

$-\text{[R}_2\text{SiOMe]}/[\text{n-BuLi}] = 4$   $[\text{R}_2\text{SiOMe}] = 10 \text{ mmole l}^{-1}$ ; total volume: 50 ml.

Sampling: 2 ml in (20 ml 0.2 N  $\text{HCl}$  + 3 ml  $\text{Et}_2\text{O}$ ) + 1 ml  $\text{Ph}_2\text{Si}$  allyl (2g/l; standard); one extraction with 2 ml  $\text{Et}_2\text{O}$ . The ether phase was dried with  $\text{Na}_2\text{SO}_4$  and injected into the glc (Oven 230°; Inj. 280°). See Table 2 for data.

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