

LiAlH<sub>4</sub> ATTACK AT A SILICON CENTER : EVIDENCE FOR ION-PAIR DISSOCIATION AS CONTROLLING FACTOR OF THE STEREOCHEMISTRY

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The stereochemistry of the reduction of the  $\equiv\text{Si-X}$  bonds by LiAlH<sub>4</sub> depends on the nature of the leaving group : retention of configuration is the normal course for the reduction of  $\equiv\text{Si-OR}$  bonds, whereas  $\equiv\text{Si-F}$  and  $\equiv\text{Si-Cl}$  bonds are displaced with inversion in ethyl ether (1,2,3,4). It depends also on the nature of the solvent : a change from ethyl ether to tetrahydrofuran results in a change in stereochemistry of hydrogen-hydrogen and hydrogen-deuterium exchanges at silicon (5). This change is parallel to a large increase in the rate of exchange.

Recent stereochemical and kinetic data for reactions between hard organolithiums (nBuLi or EtLi) and some fluoro-or methoxy-silanes led us to the following conclusions (6) :

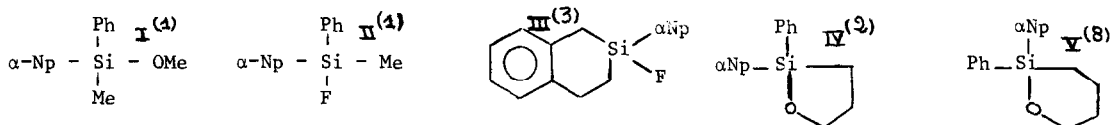
1) - the influence of the ion-pair dissociation on the stereochemistry and on the reaction rate is very important : complexation reagents which favor the dissociation of ion-pairs lead to a displacement of the stereochemistry towards retention and to a 10<sup>3</sup>-or 10<sup>4</sup>-fold rate acceleration.

2) - The  $\equiv\text{Si-OMe}$  bond is insensitive to the electrophilic assistance by Li<sup>+</sup> cation.

3) - The Li<sup>+</sup> cation provides some external assistance to the cleavage of the  $\equiv\text{Si-F}$  bonds, increasing at some extent the proportion of inversion.

Moreover Seyden-Penne et al. noted that LiAlH<sub>4</sub> leads to preferential attack at carbon-4 of  $\alpha$ -enones when the lithium cation is trapped by a specific cryptate(7), it shows clearly the soft electronic character of the AlH<sub>4</sub><sup>-</sup> anion. All these implications and the very close parallel between the stereochemistry of S<sub>N</sub>2 reactions at silicon and the regioselectivity of attack on  $\alpha$ -enones (8) suggest us to study more in details the stereochemical behaviour of LiAlH<sub>4</sub>. The data are given in the following table :

Runs N°	Reagent (a)	Solvent	Predominant stereochemistry (d)				
			I	II	III	IV	V
1	LiAlH <sub>4</sub> /LiBr <sup>(b)</sup>	Et <sub>2</sub> O	98% RN	62% RN	95% RN	[ $\alpha$ ] <sub>D</sub> = +13° RN	[ $\alpha$ ] <sub>D</sub> = -7° RN
2	LiAlH <sub>4</sub>	"	95% RN <sup>(1)</sup>	95% IN <sup>(1)</sup>	rac <sup>(2)</sup>	[ $\alpha$ ] <sub>D</sub> = +13° RN <sup>(2)</sup>	[ $\alpha$ ] <sub>365</sub> = -36,5° [ $\alpha$ ] <sub>D</sub> = -7° RN <sup>(9)</sup>
3	LiAlH <sub>4</sub> /KLi <sup>+(c)</sup>	"	75% IN	-	65% IN	[ $\alpha$ ] <sub>D</sub> = -13° IN	[ $\alpha$ ] <sub>365</sub> = -35,5° [ $\alpha$ ] <sub>D</sub> = +2° IN
4	R <sub>4</sub> N <sup>+</sup> AlH <sub>4</sub> <sup>-(a)</sup>	benzene	65% RN	-	58% IN	[ $\alpha$ ] <sub>D</sub> = +5° RN	



(a) -  $\text{LiAlH}_4$  solutions were prepared by refluxing  $\text{LiAlH}_4$  in ethyl ether, followed by filtration under  $\text{N}_2$  atmosphere. The reduction reactions were carried out with  $[\text{R}_3\text{SiX}]/[\text{LiAlH}_4] = 2$  -  $\text{R}_4\text{N}^+ \text{AlH}_4^-$  ( $\text{NR}_4^+ = (\text{tri-n.octyl})_3 \text{n.propyl ammonium cation}$ ) was prepared as described in literature (10). — (b) -  $[\text{LiBr}]/[\text{LiAlH}_4] = 10$ ; these reactions were carried out under homogeneous conditions. — (c) -  $\text{KLi}^+ = \text{Kryptofix 211}$ , specific for  $\text{Li}^+$  cation (11). — (d) - The  $[\alpha]_D$  of optically pure  $\text{R}_3\text{Si-H}$ , corresponding respectively to I, II and III are known (1,3); a predominant stereochemistry of 90 % inversion indicates a reaction path which is 90 % invertive and 10 % retentive. Chiral organosilanes IV and V are liquid and we do not know the corresponding  $[\alpha]_D$ : a RN or IN proportion cannot be given and the predominant stereochemistry was determined by chemical correlations (2,9).

The experimental data enable us to conclude that the ionic interaction between  $\text{Li}^+$  and  $\text{AlH}_4^-$  is the controlling factor of the stereochemistry :

1) - The complexation of  $\text{Li}^+$  by a cryptand giving free anions  $\text{AlH}_4^-$  (11), promotes inversion of configuration : an increase of the ionic radius of the cation ( $\text{NR}_4^+$  in runs 4) leads to a similar displacement. This behaviour is opposite to that of hard alkylolithiums for which we observed an increase of retention when  $\text{Li}^+$  was trapped. It is consistent with a soft electro-nic character for the naked  $\text{AlH}_4^-$  anion (predominant inversion for the displacement of  $\equiv\text{Si-F}$  or  $\equiv\text{Si-OR}$  bonds = 1.4 addition on  $\alpha$ -enones (8) ).

2) - Added  $\text{LiBr}$  salt promotes in all cases (runs 1) retention of configuration : the most significant stereochemical displacements are observed with the fluorosilanes II and III. We have previously stated that the  $\text{Li}^+$  cation provides some external assistance to the cleavage of the  $\equiv\text{Si-F}$  bond : it increases the ratio of inversion. We observe here the opposite effect : thus we can conclude that the main effect of  $\text{LiBr}$  is not the complexation of the organosilane. We think that it increases the degree of aggregation of the hydride molecules : the negative charge of the anion is more spread and the reducing agent  $\text{LiAlH}_4/\text{LiBr}$  behaves as a hard reagent.

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