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Preliminary communication

Reduction of silicon halides and alkoxides with diisobutylaluminum hydride. Stereochemistry-rate law correlations for the S_Ni–*Si* and S_N2–*Si* mechanisms

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SUMMARY

Stereochemistry-rate law correlations are given for the reduction of R_3Si^*X compounds with i-Bu_2AlH in ether and n-hexane.

A recent report by Pereyre, Pijselman and Valade[1] on kinetic support for the S_Ni–*Si* mechanism in the reaction of silicon hydrides with tin alkoxides, has prompted us to report on some work done in this laboratory giving kinetic support for both the

$$R_3SiH + R'_3SnOR'' \rightarrow R_3SiOR'' + R'_3SnH$$

S_Ni–*Si* mechanism and the S_N2–*Si* mechanism*.

The reduction of α-naphthylphenylmethylsilyl derivatives, R_3Si^*X, by i-Bu_2AlH in n-hexane or diethyl ether, proceeds in a homogeneous manner and at a slow enough rate to allow the reaction to be easily followed by polarimetry.

$$R_3Si^*X + \text{i-}Bu_2AlH \rightarrow R_3Si^*H + \text{i-}Bu_2AlX$$

The i-Bu_2AlH reductions of $R_3Si^*OCH(CH_3)_2$ in ether and R_3Si^*F in n-hexane, which both proceed with retention of configuration at silicon[3], were chosen as probable examples of an S_Ni–*Si* mechanism.

The i-Bu_2AlH reductions of R_3Si^*F in ether and R_3Si^*Cl in ether, which both proceed with inversion of configuration[3], were chosen as probable examples of an S_N2–*Si* mechanism. Standard pseudo first order techniques were used to study the reactions.

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* For detailed treatment of these two mechanisms see ref. 2.

The reduction of $R_3Si^*OCH(CH_3)_2$ in ether was found to be first order in silane and first order in i-Bu_2AlH. This is in agreement with the following equations:

$$R_3Si^*OR + \text{i-}Bu_2AlH \xrightarrow{k} R_3Si^*H + \text{i-}Bu_2AlOR$$

$$\frac{-d[R_3Si^*OR]}{dt} = k\,[R_3Si^*OR]\,[\text{i-}Bu_2AlH]$$

The reducing agent is actually the mono-etherate, i-$Bu_2(H)Al{:}OEt_2$ [4].

The reduction of R_3Si^*F in n-hexane was found to be first order in silane and one-half order in $(\text{i-}Bu_2AlH)_3$. This is in agreement with the following equations:

$$(\text{i-}Bu_2AlH)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{i-}Bu_2AlH)_2 + \text{i-}Bu_2AlH$$

$$R_3Si^*F + \text{i-}Bu_2AlH \xrightarrow{k_2} R_3Si^*H + \text{i-}Bu_2AlF$$

$$\frac{-d[R_3Si^*F]}{dt} = k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [R_3Si^*F]\,[(\text{i-}Bu_2AlH)_3]^{1/2}$$

Such a rate equation** comes about because i-Bu_2AlH is trimeric in n-hexane[4]. Thus, the above two retention reactions each contain one molecule of reducing agent in the transition state.

Turning now to the inversion reactions we found that the reduction of R_3Si^*F in ether is autocatalytic. The uncatalyzed reaction was found to be first order in silane and third order in i-Bu_2AlH, while the catalyzed reaction was found to be second order in i-Bu_2AlH. The order in i-Bu_2AlF varied between 0.3–0.8. This data is consistent with the following rate equation:

$$\frac{-d[R_3Si^*F]}{dt} = k_A\,[R_3Si^*F]\,[\text{i-}Bu_2AlH]^3 + k_B\,[R_3Si^*F]\,[\text{i-}Bu_2AlH]^2\,[\text{i-}Bu_2AlF]^{0.3-}$$

Where k_A is the uncatalyzed and k_B the catalyzed rate constant.

The invertive reduction of R_3Si^*Cl in ether was found to be first order in silane and between second and third order in i-Bu_2AlH. This corresponds to the following rate equation:

$$\frac{-d[R_3Si^*Cl]}{dt} = k[R_3Si^*Cl]\,[\text{i-}Bu_2AlH]^2 + k[R_3Si^*Cl]\,[\text{i-}Bu_2AlH]^3$$

Thus, for the first time we have demonstrated that a definite correlation exists between the stereochemical pathway of reactions at asymmetric silicon and the number of

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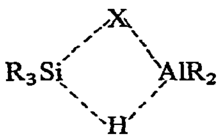
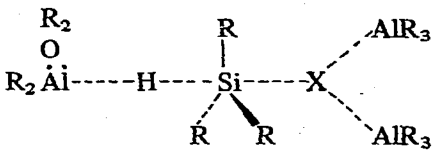
** To derive the third equation, we assume that, to a first approximation, $[(\text{i-}Bu_2AlH)_2] = [\text{i-}Bu_2AlH]$, and that the steady state approximation holds.

molecules of the nucleophile involved in the transition state. A reaction proceeding via an $S_N i$–*Si* mechanism would be expected to have only one molecule of the nucleophile in a



$S_N i$–*Si*



S_N2–*Si*

four-center transition state, while an S_N2–*Si* mechanism would be expected to have two or more molecules of nucleophile in the transition state. More detailed discussion will appear in a later full article which will also deal with alternative mechanistic rationalizations of the above rate data and our objections to them. For now, it seemed to us important to put on record the first stereochemistry-rate law correlations for silicon reaction centers.

ACKNOWLEDGMENT

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