Homogeneous Catalytic Activation of Grignard Reagents by Nickel Complexes. A New Stereospecific Method for Reduction of Alkoxy-, Chloro-, and Fluoro-silanes

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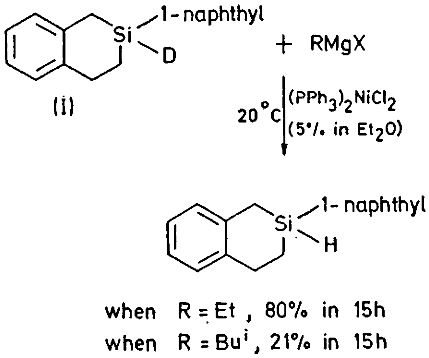
Summary A highly stereospecific preparative route to $R^1R^2R^3Si^*H$ is described involving the reaction between $R^1R^2R^3Si^*X$ ($X = OMe$, F, or Cl) and Grignard reagents possessing β-hydrogens (Et, Pr^n, Pr^i, Bu^n, Bu^i) activated by a nickel catalyst.

PREVIOUSLY, we have shown that whereas unsaturated Grignard reagents activated by nickel complexes substitute hydrosilanes, saturated Grignard reagents do not.[1] In the case of carbon compounds, the hydrogenolysis of allylic alcohols by Pr^nMgBr activated by $(PPh_3)_2NiCl_2$ has been demonstrated.[3]

An exchange reaction with the deuteriosilane (I) showed the reductive properties of saturated Grignard reagents in the presence of $(PPh_3)_2NiCl_2$. This reaction takes place with absolute retention of configuration at silicon. The order of reactivity of the Grignard reagents is: EtMgBr > $Pr^nMgBr \sim Bu^nMgBr > Pr^iMgBr > Bu^iMgBr$. The ratio of silicon hydride to deuteride was quantitatively determined by i.r. spectroscopy.



Application of these reactions to organosilanes of the type $R^1R^2R^3Si^*X$ (X = OMe, F, or Cl) provides a novel method for their stereospecific reduction [*e.g.* reaction (1)]. It is

$$Et(1\text{-naphthyl})PhSi^*X + RMgX \rightarrow Et(1\text{-naphthyl})PhSi^* \qquad (1)$$

interesting that $LiAlH_4$, but not $NaBH_4$, reduces methylphenyl-1-naphthylmethoxysilane giving the silicon hydride.[4] The reaction of various saturated Grignard reagents with (+)-ethylphenyl-1-naphthylmethoxysilane in the presence of $(PPh_3)_2NiCl_2$ gives (+)-ethylphenyl-1-naphthylsilane (see Table), predominantly with retention of configuration based on the relative configurations previously determined.[5]

The order of reactivity of the Grignard reagents is the same as that for the D/H exchange reaction. The reaction was followed by g.l.c.

The reduction of fluoro- and chloro-silanes was studied under the same conditions. The reduction of fluorosilane takes place with 90% retention of configuration at silicon, and that of chlorosilane with inversion of configuration (100% stereospecificity).

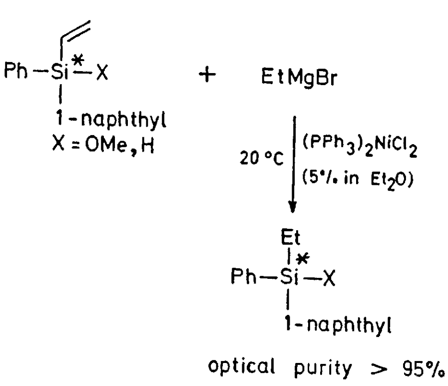
It should be noted that the system 'RMgX–nickel' induces different stereochemistry than does $LiAlH_4$. It has been shown[6] that the latter reduces methoxy-, fluoro-, and chloro-silanes with, respectively, retention, inversion, and inversion of configuration. However the 'RMgX-nickel' system reduces these same functional groups with, respectively, retention, retention, and inversion.

Table[a]

RMgBr R =	% of $R^1R^2R^3SiH$ after 72 h	Retention of configuration (%)
Et	90	100
Pr^n	62	98
Pr^i	24	94
Bu^n	85	99
Bu^i	6	97
Bu^t	0	—

[a] All the reactions were carried out under standard conditions: nitrogen atmosphere; temp. 20 °C; methoxysilane, 2 mM; Grignard reagent 20 mM; catalyst 0·1 mM. After the methoxysilane had reacted completely, the reduction product was isolated and purified by chromatography on a column of neutral alumina (yield > 80%).

N.B. For Pr^iMgBr and Bu^iMgBr the reactions are very slow. However, 50% of $R^1R^2R^3SiH$ is isolated after 8 days in refluxing Et_2O.



This new method of reduction can also be applied to vinylsilanes [equation (2)]. The reduction of the Si–X function is much slower than that of the Si–Vinyl. It is therefore possible to isolate R^1R^2EtSiX quantitatively.

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