

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

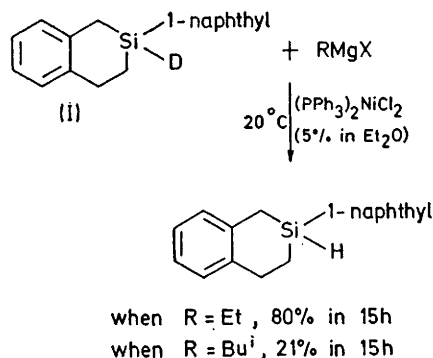
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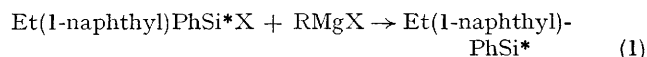
**Summary** A highly stereospecific preparative route to  $R^1R^2R^3Si^*H$  is described involving the reaction between  $R^1R^2R^3Si^*X$  ( $X = OMe, F, \text{ or } Cl$ ) and Grignard reagents possessing  $\beta$ -hydrogens ( $Et, Pr^n, Pr^l, Bu^n, Bu^l$ ) activated by a nickel catalyst.

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

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



interesting that  $LiAlH_4$ , but not  $NaBH_4$ , reduces methylphenyl-1-naphthylmethoxysilane giving the silicon hydride.<sup>4</sup> 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.<sup>5</sup>

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

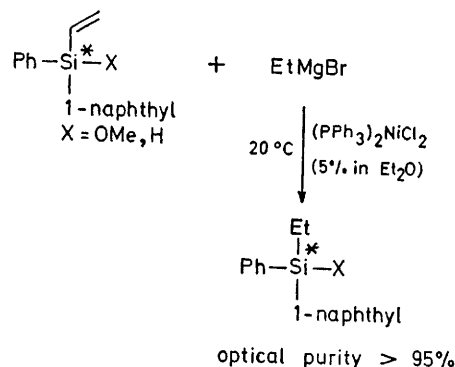
Table<sup>a</sup>

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	—

<sup>a</sup> 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  $Et_2O$ .

been shown<sup>6</sup> 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.



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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<sup>6</sup> L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 3271.