

Solvent Effects on the Stereochemistry of Coupling Reactions of Grignard Reagents with Organosilanes

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Summary Stereochemical studies of coupling reactions of Grignard reagents at a silicon atom have shown new solvent and salt effects.

STEREOCHEMICAL studies of coupling reactions of organometallic compounds at silicon atom showed that the reactions are always highly stereospecific.^{1,2} It has also been reported that, in several cases, the stereochemistry depends on the nature of the solvent and dissolved salts.³⁻⁵

The results reported here indicate new solvent and salt

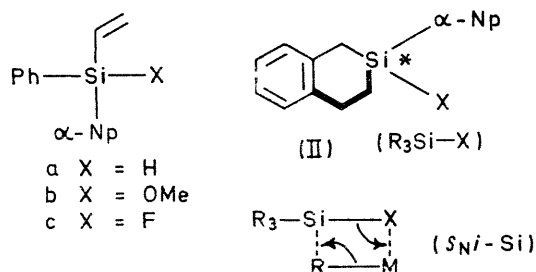
effects. They were obtained by studying coupling reactions of Grignard reagents with some derivatives of two optically active organosilanes, α -naphthylphenylvinylsilane (Ia) and 1,2,3,4-tetrahydro-2- α -naphthyl-2-silanaphthalene (IIa).

The fluorosilane (Ic) reacts with saturated Grignard reagents, in diethyl ether, with predominant inversion of the configuration (Table).† On the other hand, in glycol dimethyl ether (GDME) retention of the configuration predominates.

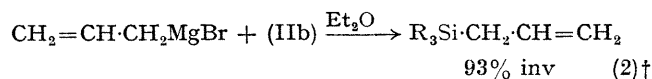
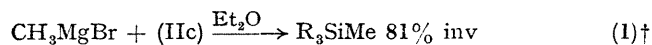
TABLE

(Ic)	MeMgBr	EtMgBr	Pr ⁿ MgBr	Bu ⁿ MgBr	AllylMgBr
$[\alpha]_D$ (Et ₂ O)	+0.8° inv.	-5° inv.	-3° inv.	-3.4° inv.	-7° inv.
$[\alpha]_D$ (GDME)	+0.2° ^a inv.	+3° ret.	+3.5° ret.	+4.3° ret.	-6.1° inv.

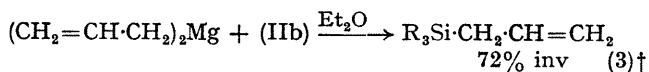
^a Though the stereochemistry is not inverted in this case, we note an important decrease of inversion.



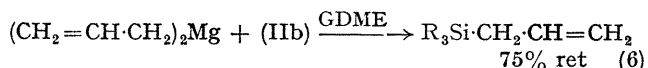
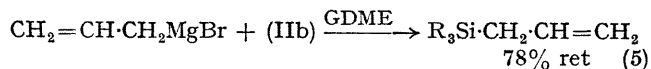
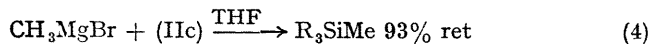
The reactions of methylmagnesium bromide with the fluorosilane (IIc) and of allylmagnesium bromide or diallylmagnesium with the methoxysilane (IIb) in diethyl ether take place with inversion of the configuration.



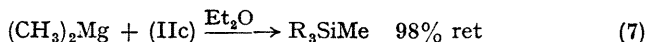
† The stereochemistry of these reactions has been already demonstrated: R. Corriu and G. Royo, Réunion Annuelle "Section Chimie Organique" de la Société Chimique de France, September, 1969.



These reactions follow the opposite stereochemical path-way if they are carried out in more basic solvents:



Dimethylmagnesium in diethyl ether also leads to retention of the configuration:



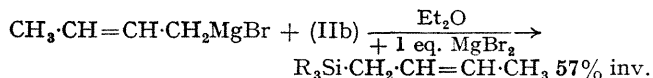
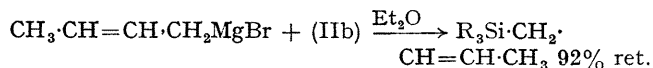
In these reactions there are two effects to be considered. First, a strongly-solvating solvent directs the stereochemistry towards the retention of the configuration and accelerates the reaction; secondly the presence of MgBr_2 promotes the inversion of configuration, since we can consider that MeMgBr is equivalent to Me_2Mg^6 and MgBr_2 .



It is this salt (MgBr_2) which, by electrophilic assistance on the leaving group would promote the inversion of the configuration. In fact, when MgBr_2 is highly solvated (THF) it becomes inefficient in electrophilic catalysis, and the

predominant stereochemistry is the retention of the configuration.

The electrophilic assistance with dissolved salts has been shown unambiguously in another case, the coupling reaction of the methoxysilane (IIb) with crotylmagnesium bromide.



The reaction in diethyl ether takes place with retention of the configuration. On the other hand, on adding to the Grignard reagent 1 equiv. of magnesium bromide, inversion of the configuration predominates.

These results are interesting in two respects: first, they show that the very nucleophilic solvents⁷ (GDME) which solvate the magnesium atom efficiently promote the retention of the configuration while accelerating the reaction. An analogous effect was observed when tetramethylethylenediamine⁸ was added to organolithium reagents.^{2c} Secondly, they indicate that Lewis-acid-type salts (MgBr_2) can make the inversion of the configuration easier. Thus, it seems that the retention of configuration at silicon does not necessarily arise through the $\text{S}_{\text{N}}\text{i}$ -Si mechanism¹ involving electrophilic catalysis by the metal of the organometallic reagent. This catalysis is certainly not always the driving force for such a mechanism.

(Received, November 23rd, 1970; Com. 2028.)

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² R. Corriu and J. Masse, (a) *Chem. Comm.*, 1968, 1373; (b) *Tetrahedron Letters*, 1968, 5197; (c) *Bull. Soc. chim. France*, 1969, 3491; (d) *Tetrahedron*, 1970, **26**, 5123; (e) unpublished results.

³ L. H. Sommer and H. Fujimoto, *J. Amer. Chem. Soc.*, 1968, **90**, 982; 1969, **91**, 7040.

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⁵ A. Jean and M. Lequan, *Tetrahedron Letters*, 1970, 1517.

⁶ E. C. Ashby, G. Parris, and F. Walker, *Chem. Comm.*, 1969, 1464.

⁷ C. Agami, *Bull. Soc. chim. France*, 1967, 4031.

⁸ G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, 1964, **29**, 2928.