Chemical and Stereochemical Behaviour of Enantiomeric Bifunctional Silicon Compounds

By Claire Brelière, Robert J. P. Corriu,* and Gérard Royo

(*Laboratoire de Chimie des Organométalliques, Equipe de Recherche associée au C.N.R.S. No* 554, *Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon,* 34060 *Montpellier-Cédex, France*)

Summary A new bifunctional organosilane, α-naphthylferrocenylfluoroethoxysilane, is described; organolithium reagents substitute the fluorine atom with inversion of configuration, whereas Grignard reagents substitute the ethoxy group with retention of configuration.

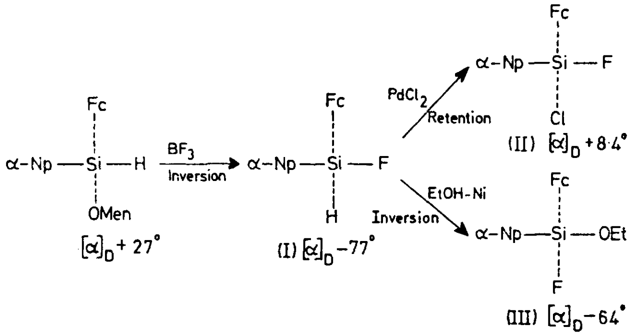
In a previous communication[1] we reported the synthesis and absolute configuration of two enantiomeric bifunctional organosilicon compounds: α-naphthylferrocenylfluorosilane (α-NpFcSiHF) and α-naphthylferrocenylfluorochlorosilane (α-NpFcSiClF). We now describe the preparation of a new bifunctional organosilane, α-naphthylferrocenylfluroethoxysilane. The similar reactivity of the ≡Si–F and ≡Si–OEt bonds makes the reactions with organolithium compounds and Grignard reagents particularly interesting.

The Scheme shows the preparation of the fluoroethoxy

TABLE

Reagent	Reaction	Product isolated	$[\alpha]_D$	Stereochemistry
MeLi	i	α-NpFcMeSiOEt	−9·8°	Retention
EtLi	i	α-NpFcEtSiOEt	−2·9°	Inversion
(Allyl)Li	i	α-NpFc(CH$_2$=CH–CH$_2$)SiOEt	−3·5°	Inversion
PhLi	i	α-NpFcPhSiOEt	+11·8°	Inversion
MeMgI	ii	α-NpFcMeSiF	−31°	Retention
EtMgBr	ii	α-NpFcEtSiF	−64°	Retention
(Allyl)MgBr	i	α-NpFc(CH$_2$=CH–CH$_2$)SiOEt	−1·9°	Inversion
PhMgBr	ii	α-NpFcPhSiF	−10·7°	Retention

derivative (III), and its stereochemical relationship to the compounds previously reported. Compounds (I) and (II) react with organometallic reagents with similar stereochemical results to those of monofunctional organosilanes,[2] but compound (III) displays certain anomalies which are illustrated by the results in the Table.



SCHEME. Np = naphthyl, Fc = ferrocenyl, OMen = menthoxy

$$\alpha\text{-NpFcSiROEt} \xleftarrow{\text{i}} \alpha\text{-NpFcSiFOEt} \xrightarrow{\text{ii}} \alpha\text{-NpFcSiFR}$$

The results show that substitution occurs with remarkable selectivity at one or other of the reactive groups. Grignard reagents with saturated or aromatic groups substitute the ethoxy function with retention of configuration, whereas the αβ-unsaturated reagent, allylmagnesium bromide, replaces the fluorine with inversion of configuration. On the other hand the dominant stereochemistry with the organolithium reagents is inversion of configuration with substitution of the fluorine atom.

These results are surprising in several respects. Other bifunctional organosilanes generally suffer replacement of the most labile function whatever the organometallic reagent.[2,3] In the present case substitution of either function is observed. It is known that ≡Si–F reacts more rapidly than ≡Si–OR in monofunctional organosilanes.[4] However only the ethoxy group in (III) is replaced in the reaction with Grignard reagents. We have previously shown that Grignard reagents direct the stereochemistry predominantly towards inversion of configuration, whereas organolithium reagents direct towards retention.[5] Compound (III) displays a reversal of this stereochemistry.

This unusual behaviour suggests that the stereochemical course of the reactions is strongly influenced by interactions existing between the two reactive functions bonded to the same silicon atom.

We thank Dr. J. C. Young for help with the preparation of the English version of the manuscript.

(*Received*, 26*th July* 1976; *Com.* 840.)

---

[1] R. J .P. Corriu, F. Larcher, and G. Royo, *J. Organometallic Chem.*, 1975, **C25**, 102.

[2] R. J. P. Corriu, F. Larcher, and G. Royo, unpublished work.

[3] R. J. P. Corriu, G. F. Lanneau, and M. Leard, *J. Organometallic Chem.*, 1974, **64**, 79; R. J. P. Corriu and G. Lanneau, *Bull. Soc. chim. France*, 1973, 3102.

[4] R. J. P. Corriu and B. J. L. Henner, *J. Organometallic Chem.*, 1975, **102**, 407.

[5] R. J. P. Corriu and G. Royo, *Bull. Soc. chim. France*, 1972, 1497; R. J. P. Corriu and J. Masse, *J. Organometallic Chem.*, 1972, **34**, 221; 1972, **35**, 51; R. J. P. Corriu and G. Royo, *ibid.*, 1972, **40**, 229.