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CHEMICAL AND STEREOCHEMICAL BEHAVIOUR OF BIFUNCTIONAL ENANTIOMERIC SILICON COMPOUNDS

I. STUDY OF α-NAPHTHYLFERROCENYL-FLUOROSILANE AND -CHLOROFLUOROSILANE

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Summary

The synthesis of the first bifunctional enantiomeric silicon compounds is described. A high selectivity between the two functional groups is observed in substitution reactions with organolithium compounds and Grignard reagents, the more polarizable group being specifically replaced. The stereochemistry of the reactions has been determined by chemical correlations. The stability of the pentacoordinated intermediate (discussed in terms of apicophilicity of the various groups) does not suffice to explain the results. Inversion of the configuration comes from an axial attack of the reactant and retention of configuration is explained by an equatorial attack.

Introduction

Phosphorus and silicon chemistries present many similarities but the stereochemistry of nucleophilic substitution reactions is explained in a very different way for the two elements.

The stereochemistry of nucleophilic substitution at a ≡Si—X bond essentially depends on two factors: the lability of the ≡Si—X bond and the electronic nature of the nucleophile [1]. We have shown that "hard" reagents with localized charge attack in the equatorial position with retention of the configuration [2]. Such a reaction is a charge controlled process [3]. "Soft" reagents with delocalized charge attack in apical position giving inversion of the configuration [2]. This reaction is an orbital controlled process [4].

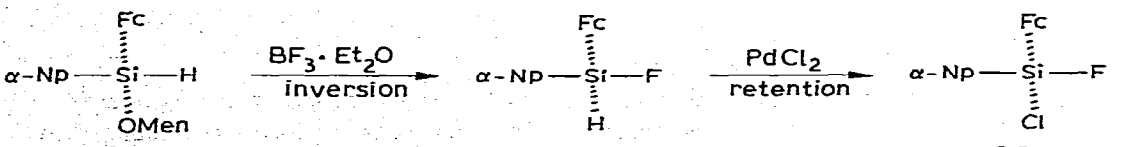
For phosphorus, the stereochemical results are explained differently [5]. An apical attack of the reactant is postulated, with formation of the most stable pentacoordinated intermediate. The departure of the leaving group always takes

place from an apical position. Furthermore, the pentacoordinated intermediates can undergo isomerisation by pseudo rotation. However, most of the stereochemical studies on phosphorus [6] have been made on polyfunctional chiral systems, whereas in the case of silicon, the compounds were monofunctional [1,7]. The comparison of the stereochemical results in the two series is more meaningful when the the environment of the two atoms is similar, and so it seemed desirable to examine bi- or poly-functional chiral organosilanes. We recently described the syntheses of bifunctional chiral organosilanes in which the silicon atom is the only asymetric center [8] and below we describe the preparation of some of those enantiomeric compounds and a study their chemical and stereochemical behaviour towards organometallic compounds (RMgX and RLi).

Results

Scheme 1 shows the preparation of two bifunctional enantiomeric silicon compounds: α-naphthylferrocenylfluorosilane (II) and α-naphthylferrocenylfluorochlorosilane (III).

SCHEME 1



(I) $[\alpha]_D$ + 27° (II) $[\alpha]_D$ −77° (III) $[\alpha]_D$ +8.4°

(α-Np: α-naphthyl, Fc: ferrocenyl, OMen: Menthoxy)

The action of $BF_3 \cdot Et_2O$ on α-naphthylferrocenylmenthoxysilane (I) (of which the absolute configuration known) [9], gives α-naphthylferrocenylfluorosilane (II). This compound reacts with $PdCl_2$ to give α-naphthylferrocenylfluorochlorosilane (III). In this paper we describe the reactions of organometallic compounds on II and III.

Grignard reagents and organolithium compounds always react with II with selective replacement of the fluorine atom, to give a quantitative yield of the corresponding silane (cf. Table 1).

The presence of a ferrocenyl group does not change the stereochemistry of the reactions, for we have shown that mono- and bi-functional ferrocenyl compounds behave like analogous compounds having no ferrocenyl group [10].

From the results in Table 1 three observations can be made: (i) Organolithium compounds always react with retention of the configuration. (ii) With Grignard reagents, mixed stereochemistry is found, (iii) When Grignard reagent is used in solvents with increasing basicity (Et_2O, THF, DME) the stereochemistry changes from inversion to retention.

The stereochemistries of all the reactions were determined by chemical correlations. As an example, the stereochemistry of the action of EtLi, EtMgBr, and CH_2=$CHCH_2MgBr$ will be considered (see Scheme 2). The other cases are described in the Experimental.

TABLE 1

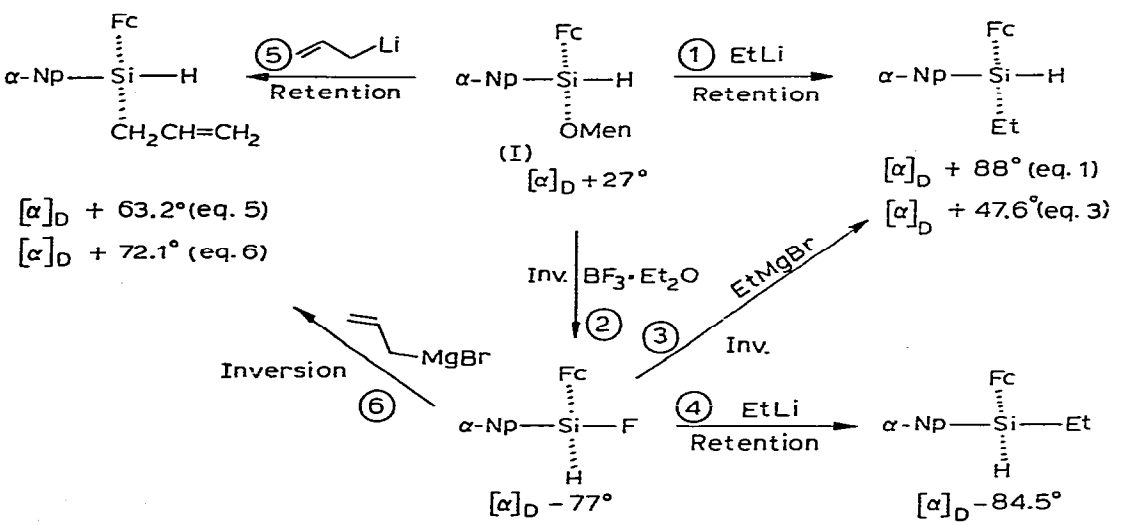
α-NpFcSi*(H)F $\xrightarrow[\text{or RLi}]{\text{RMgX}}$ α-NpFcRSi*H

Reagent	Solvent [a]	$[\alpha]_D$ exp.	$[\alpha]_D$ max [b]	Stereochemistry [c]	Stereoselectivity (%) [d]
MeLi	Et_2O	−47.8°	80°	RET	80
EtLi	Et_2O	−84.5°	88°	RET	98
PhLi	Et_2O	−15.9°	16.6°	RET	98
 Li	Et_2O	−8.9°	72.1°	RET	56
PhC≡CLi	Et_2O	+84.7°	103°	RET	91
MeMgI	Et_2O	+80°	80°	INV	100
MeMgI	THF	+31.6°	80°	INV	69
MeMgBr	THF	+31°	80°	INV	69
MeMgI	DME	−26.7°	80°	RET	67
MeMgBr	DME	−24.7°	80°	RET	65
EtMgBr	Et_2O	+47.6°	88°	INV	77
 MgBr	Et_2O	+72.1°	72.1°	INV	100
PhMgBr	Et_2O	−15.5°	16.6°	RET.	97
PhC≡CMgBr	Et_2O	+65°	103°	RET	82

[a] THF, tetrahydrofuran, DME, dimethoxyethane. [b] $[\alpha]_D$ is measured in benzene. [c] RET, retention of the configuration; INV, inversion. [d] Stereoselectivities are calculated from the best rotation obtained for the silane. % SS = ($[\alpha]_D$ max + $[\alpha]$ exp)/2$[\alpha]_D$ max.

The absolute configuration of I is known [9], and reactions 1 and 5 take

SCHEME 2



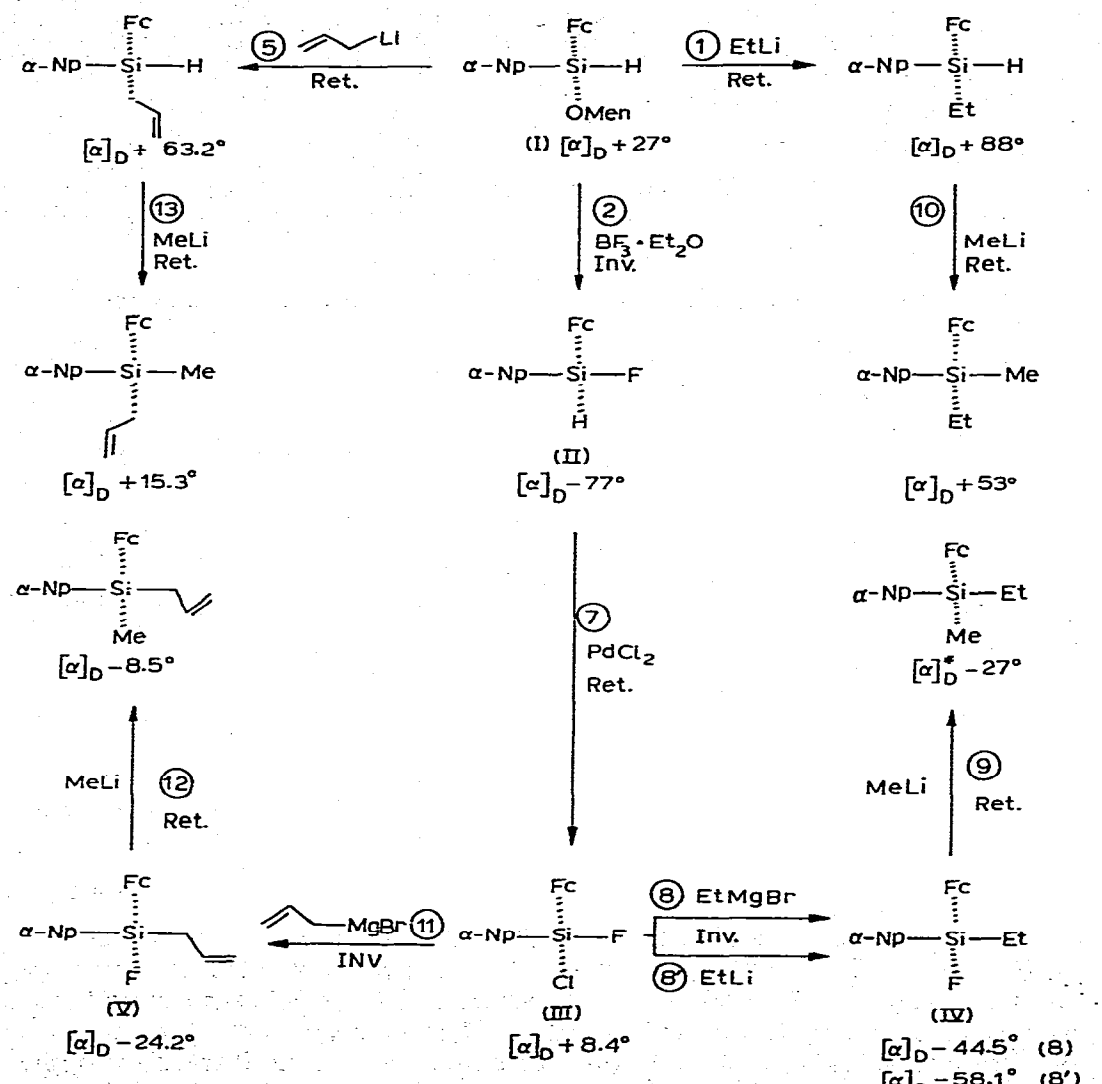
place with retention of the configuration [11]. The experimental results show that the reaction 3 and 4 have opposite stereochemistries, and it is known that with monofunctional fluorosilanes the Grignard reagent reacts with inversion and the organolithium compound with retention of configuration [1]. The stereochemistries of eq. 1, 3 and 4 imply the stereochemistry of eq. 2 and show that, this involves inversion. (This result is similar to those obtained in formation of fluorides on from monofunctional alkoxysilanes [12].) Similarly, the stereo-

chemistries of eq. 2 and 5 imply for eq. 6 inversion of configuration. (This result also agrees with previous observations; whatever the nature of the fractional group X, α,β unsaturated Grignard reagents always react with acyclic fluorosilanes with inversion [1d, f].)

Organolithium compounds and Grignard reagents react with III with selective replacement of the chlorine atom, to give the corresponding fluorosilane. The stereochemistry is always inversion (cf. Table 2).

As in the previous case, the stereochemistry of reactions was determined by chemical correlations, and the results for the reactions with REtLi, EtMgBr and $CH_2=CHCH_2MgBr$ are shown in Scheme 3.

SCHEME 3



* Eq. 9 was carried out with fluorosilane having $[\alpha]_D$ − 44.5°

TABLE 2

α-NpFcSi*(F)Cl $\xrightarrow[\text{or RLi}]{\text{RMgX}}$ α-NpFcRSi*F

Reactant	Solvent	$[\alpha]_D$ exp. [a]	Stereochemistry [b]	Stereoselectivity [c]
EtLi	Et_2O	−58.1°	INV	83 (a)
PhLi	Et_2O	−4.7°	INV	68 (c)
≈—Li	Et_2O	−27.5°	INV	77 (b)
EtMgBr	Et_2O	−44.5°	INV	75 (a)
PhMgBr	Et_2O	−5.5°	INV	71 (a)
≈—MgBr	Et_2O	−24.2°	INV	74 (b)

[a] $[\alpha]_D$ is measured in benzene. [b] INV, inversion of the configuration. [c] a, stereoselectivity is calculated from α-naphthylferrocenylethylmethylsilane $[\alpha]_D$ max + 53°; b, stereoselectivity calculated from α-naphthylferrocenylallylmethylsilane $[\alpha]_D$ max + 17.5°; c, stereoselectivity calculated from α-naphthylferrocenylphenylfluorosilane $[\alpha]_D$ max + 13.2°. % SS = $([\alpha]_D$ max + $[\alpha]_D$ exp)/2 $[\alpha]_D$ max.

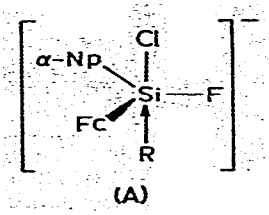
The stereochemistry of eq. 1, 2 and 5 are been determined previously, and eq. 9, 10, 12 and 13 are known to involve retention of configuration. (Monofunctional silanes or fluorosilanes having similar structures react with this stereochemistry [1a, b, c, e].) The absolute configuration of I (which is known) and the stereochemistry of the various reactions imply the absolute configurations of products II, IV and V, from these reactions. Therefore, there are two possibilities for the stereochemistry of the reactions 7, 8, 8′ and 11, viz.: (a) 7 retention; 8, 8′ inversion; 11 inversion; (b) 7 inversion; 8, 8′ retention; 11 retention.

Hypothesis a seems the best for three reasons: (i) a monofunctional acyclic chlorosilane is always substituted with inversion of the configuration whatever the nature of the nucleophilic reagent is [1,12]. (ii) Conversion from a Si—H to a Si—Cl bond always involves retention of configuration [12]. (iii) α,β Unsaturated Grignard reagents always replace a Si—X bond with inversion of configuration [1d, f].

Discussion

The results show the high selectivity of substitution reactions of the compounds II and III. Two competing reactions corresponding to the departure of F and Cl could reasonably have been expected in the case of α-NpFcSiFCl III, Since we have shown that the rate constant ratio k(F)/k(Cl) is close to unity (0.32 to 1.7) when a fluorosilane and a chlorosilane, of similar structures react with the same organometallic compound [13]. However, when the two functions are bonded to the same silicon atom, the selectivity is completely changed, since only the chlorine atom is replaced. The selectivity is also very high for α-NpFcSiHF (II), only the fluorine atom being replaced. In the case of III, the replacement of the chlorine atom always occurs with inversion of configuration. Apical attack of the reactant, followed by the apical departure of the chlorine atom, explains the stereochemistry (intermediate A).

In the case of (α-NpFcSiHF) (II) the selective substitution of the fluorine atom involves either inversion or retention according to the nature of the nucleo-

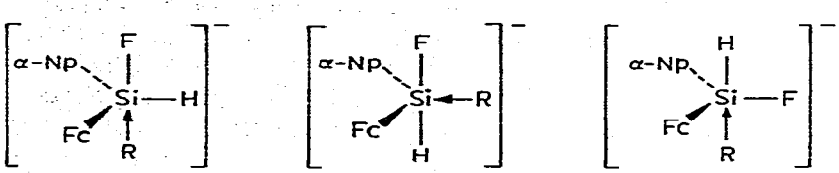


(A)

phile. Organolithium compounds always react with retention of configuration, while Grignard reagents react either with retention or inversion. In these reactions we find again the features which we have pointed out previously, viz.: (i) α,β unsaturated Grignard reagents (≈— MgBr) react with inversion of configuration [1d, f]; (ii) basic solvents favour retention of configuration (MeMgX, Et_2O, THF, DME) [1d, f, 14]; (iii) some Grignard reagents (MeMgI, EtMgBr) react with inversion of the configuration while corresponding organolithium compounds (MeLi, EtLi) substitute with retention of the configuration [1].

α-NpFcSiHF (II) shows an interesting feature, in that compared with monofunctional acyclic fluorosilanes there is a general shift of the stereochemistry towards retention of configuration. The significant cases are those involving CH_2=$CHCH_2Li$, PhMgBr and PhC≡CMgBr, which react with II with retention of configuration, whereas with acyclic fluorosilanes they give inversion [1].

The observed changes in stereochemistry on variation of the nucleophile cannot be explained by differences in the stabilities of the pentacoordinated intermediates. Since the substituted group is fluorine, only the intermediate B can explain the inversion of configuration if we assume that fluorine is the most electronegative group even in a negatively charged pentacoordinated silicon.



(B) (C) (D)

In order to explain the retention of configuration we must postulate the formation of another intermediate C or D.

It is obvious that the dominant factor on the stereochemistry cannot be the difference in the stabilities of the intermediates arising from the nature of R, since the differences in the apicophilicity between —CH_2CH=CH_2 and —$CH_2CH_2CH_3$ are certainly very low. The differences in the stereochemistry observed between RMgX (inversion) and RLi (retention) cannot be explained in this way. We think that the results are better explained by our previous hypothesis [2], namely that reactants with localized charge attack in an equatorial position (C) and being about retention of configuration, whereas reactants with delocalized charge attack in an apical position and cause inversion (B).

The difference in the behaviour of the compound II compared with monofunctional fluorosilanes certainly comes from a change in the case with which this group is substituted. The same feature is apparent with compound III. We think that the introduction of a second function on the silicon atom changes the

case with which the leaving group is replaced, and especially important is the tendency of the Si—X bond to undergo stretching during the reaction with a nucleophile.

Experimental

General technique

The reactions are carried out in a dry nitrogen stream. A measured amount of organometallic compound is added to a measured amount of organosilane, usually in the same solvent. When reaction is complete, the mixture is hydrolyzed with acid. After extraction with ether, the organic layer is dried. After removal of the solvent, the residue is purified by preparative thin-layer chromatography (Kieselgel PF 254 Merck, eluant benzene/pentane 1 : 9).

Titration of organometallic compounds is by Jolibois's method [15].

Preparation of α-naphthylferrocenylfluorosilane (α-NpFcSiHF) $[\alpha]_D$ —77°(benzene)

1.650 g (3.32×10^{-3} mol) of α-naphthylferrocenylmenthoxysilane (α-NpFcSi(H)OMen) $[\alpha]_D$ +27° (benzene) [10a] are dissolved in 3 ml of benzene and 3.5 ml of hexane, and cooled at 0°C. Then 0.5 ml of $BF_3 \cdot Et_2O$ (distilled before use) is added. When the mixture reaches room temperature, it is stirred for 30 min. Crystals appear. They are filtered and recrystallized from a mixture of benzene and pentane. After crystallization 778 mg of α-naphtylferrocenylfluorosilane, $[\alpha]_D$ —77° (*c* 30, benzene), m.p. 127—128°C, are obtained. Analysis: Found: C, 66.76; H, 4.77; F, 5.15. $C_{20}H_{17}FFeSi$, calcd.: C, 66.66; H, 4.72; F, 5.27%. NMR (C_6D_6) δ (ppm): 3.95 (5H, Si—Fc), 4.10, 4.40 (4H, Si—Fc), 6.05 (1H, Si—H, doublet), >7 (aromatic protons).

Synthesis of α-naphtylferrocenylfluorochlorosilane α-NpFcSiFCl $[\alpha]_D$ +8.4° (benzene)

200 mg (5.55×10^{-4} mol) of α-naphthylferrocenylfluorosilane (α-NpFcSiHF) $[\alpha]_D$ —77° (benzene) are dissolved in 3 ml of benzene, and 97 mg (5.55×10^{-4} mol) of palladium chloride, are added. The progress of the reaction is followed by thin-layer chromatography (Kieselgel G nach stahl type 60 Merck, eluant pentane/benzene 9 : 1).

When the reaction is over the mixture is filtered. An oily residue is quantitatively isolated and identified as α-naphthylferrocenylfluorochlorosilane $[\alpha]_D$ + 8.4° (*c* 54, benzene).

The product undergoes slow racemization in benzene. Analysis: Found: C, 60.02; H, 3.95; Cl, 8.92. $C_{10}H_{16}ClFFeSi$ calcd.: C, 60.83, H, 4.05; Cl, 8.99%. NMR (C_6D_6) δ (ppm): 4.05 (5H, Si—Fc), 4.10, 4.45 (4H, Si—Fc), disappearing of the doublet centered at 6.05, >7 (aromatic protons).

Synthesis of α-naphthylferrocenylmethylsilane

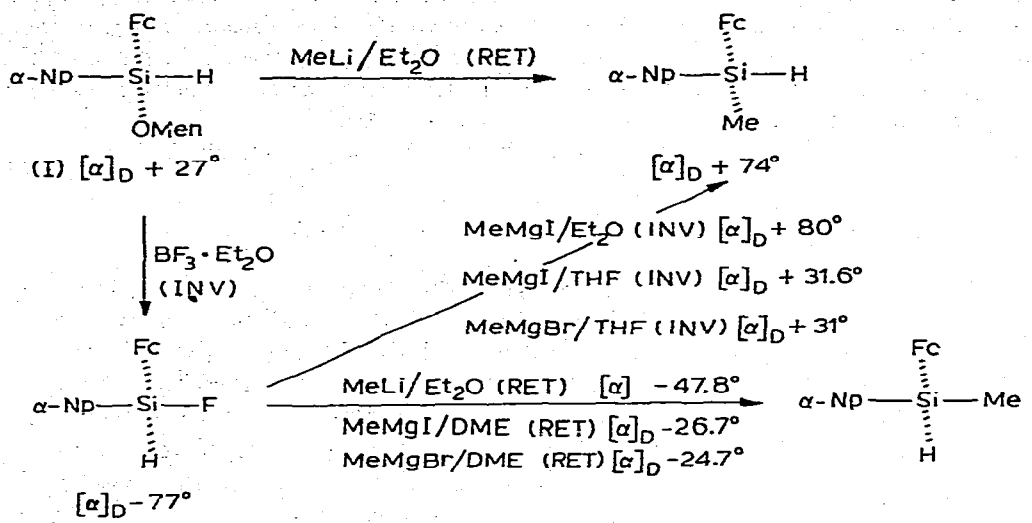
(a) From α-naphthylferrocenylmenthoxysilane $[\alpha]_D$ + 27° (benzene). This product has already been described [10b] $[\alpha]_D$ +74° (*c* 35, benzene). (b) From α-naphthylferrocenylfluorosilane $[\alpha]_D$ — 77° (benzene) by the action of MeLi/

Et_2O, MeMgI/Et_2O, MeMgI/THF, McMgBr/THF, MeMgI/DME, MeMgBr/DME.

The technique is the same for all those reactions (see General Technique). The yields of α-naphthylferrocenylmethylsilane are quantitative. The silane obtained is identified by comparison with authentic sample of α-naphthylferrocenylmethylsilane.

The rotatory powers are shown in Table 1.

SCHEME 4



(c) The stereochemistries can be deduced by examination of Scheme 4 since the absolute configuration of each product is known.

Synthesis of α-naphthylferrocenylethylsilane

(a) From α-naphthylferrocenylmenthoxysilane $[\alpha]_D$ +27° (benzene). This product has already been described [10b] $[\alpha]_D$ + 88° (benzene).

(b) From α-naphthylferrocenylfluorosilane $[\alpha]_D$ — 77° (benzene) by the action of EtLi/Et_2O or EtMgBr/Et_2O (see General Technique). The yields of α-naphthylferrocenylethylsilane are quantitative in both cases, and the characteristics are identical with those of an authentic sample. The rotatory powers are given in Table 1.

(c) The stereochemistries of the reactions are indicated in Scheme 2.

Synthesis of α-naphthylferrocenylphenylsilane

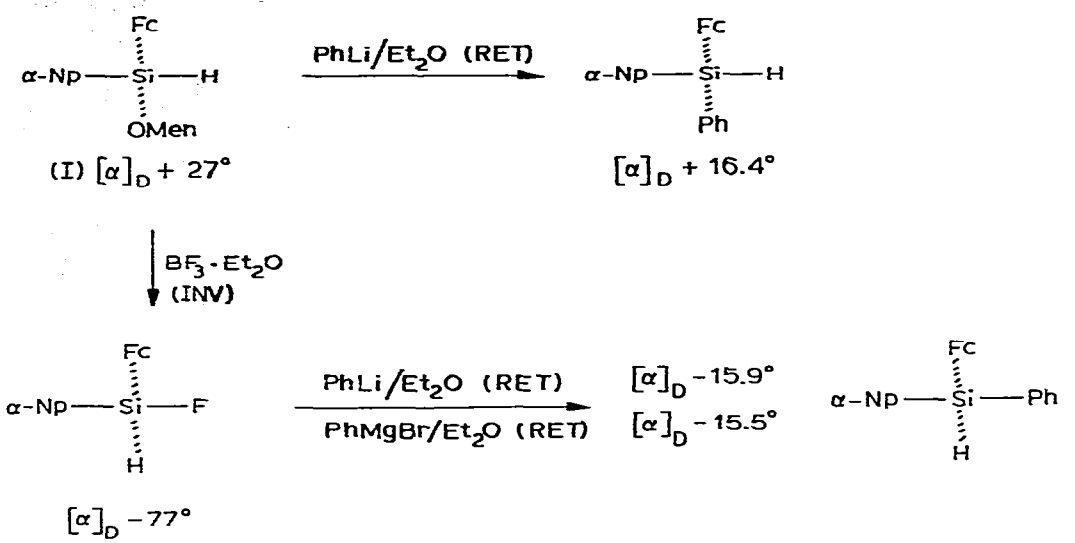
(a) From α-naphthylferrocenylmenthoxysilane $[\alpha]_D$ + 27° (benzene). This product has already been described [10b] $[\alpha]_D$ + 16.4° (benzene).

(b) From α-naphthylferrocenylfluorosilane $[\alpha]_D$ — 77° (benzene) by action of PhLi/Et_2O or PhMgBr/Et_2O (see General Technique).

The yields in α-naphthylferrocenylphenylsilane are quantitative in both cases. The characteristics of α-naphthylferrocenylphenylsilane obtained are identical with those of an authentic sample. The rotatory powers are given in the Table 1.

(c) The stereochemistry of the reactions is shown in Scheme 5. The stereo-

SCHEME 5



chemistries can deduced from the examination of Scheme 5 since the absolute configuration of each product is known [10a].

Synthesis of α-naphthylferrocenylallylsilane

(a) From α-naphthylferrocenylmenthoxysilane $[\alpha]_D$ + 27° (benzene). 233 mg (4.6×10^{-4} mol) of α-naphtylferrocenylmenthoxysilane (α-NpFcSi(H)OMen) $[\alpha]_D$ + 27° (benzene) are dissolved in 5 ml of anhydrous ether to which 1.3 ml of allyllithium (0.36 *M*), prepared from tetraallyltin, is added. After 30 min, 136 mg of an oily residue are isolated (see General Technique) and identified as α-naphthylferrocenylallylsilane $[\alpha]_D$ + 63.2° (*c* 50, benzene). Analysis: Found: C, 72.35; H, 5.78; Si, 7.36. $C_{23}H_{21}FeSi$ calcd.: C, 72.24; H, 5.75; Si, 7.32%. NMR (C_6D_6) δ (ppm): 2.25 (2H, Si—CH_2—), 3.95 (5H, Si—Fc) 4.05—4.30 (4H, SiFc), 4.75—5.20 (2H, Si—CH_2—CH=$\underline{CH_2}$), 5.50 (1H, Si—H, triplet), 5.70—6.25 (1H, Si—CH_2—$\underline{CH}$=CH_2).

(b) From α-naphthylferrocenylfluorosilane $[\alpha]_D$ −77°/PhH and allyllithium/Et_2O or allylMgBr/Et_2O (see General Technique). The yield of α-naphthylferrocenylallylsilane is quantitative in both cases. The characteristics of α-naphthylferrocenylallylsilane obtained are identical to those of an authentic sample. The rotatory powers are given in Table 1.

(c) For the stereochemistry of the reactions see Scheme 1.

Synthesis of α-naphthylferrocenyl(phenylethynyl)silane

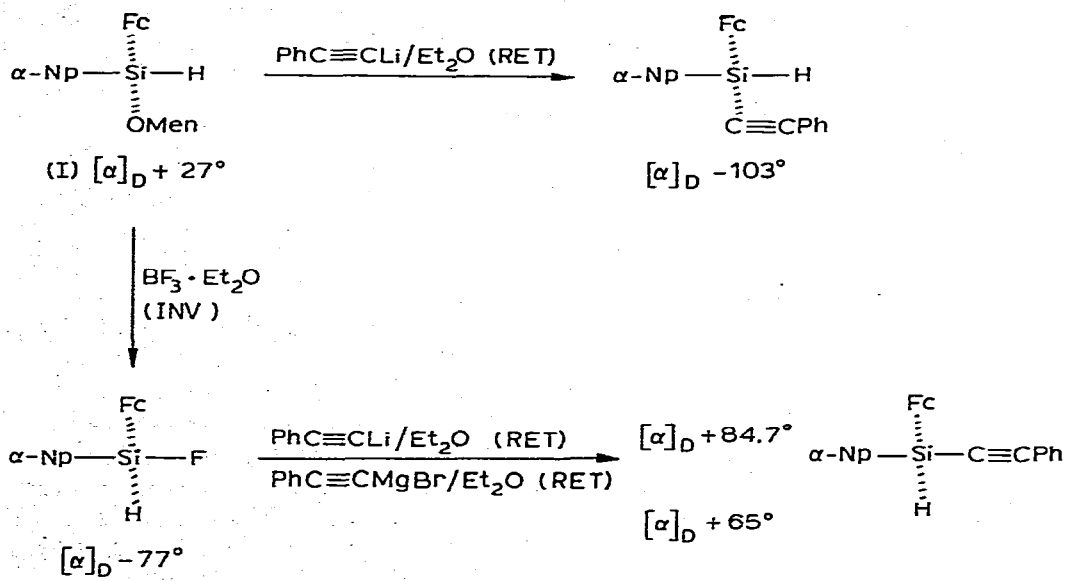
(a) From α-naphthylferrocenylmenthoxysilane $[\alpha]_D$ + 27° (benzene). 300 mg (5.04×10^{-4} mol) of α-naphthylferrocenylmenthoxysilane (α-NpFcSi(H)OMen) $[\alpha]_D$ + 27° (benzene) are dissolved in 5 ml of anhydrous ether to which 4 ml of PhC≡CLi (0.75 *M*), prepared by exchange with n-BuLi, are added. After 4 h, 256 mg of an oily residue are isolated (see General Technique) and identified as being α-naphthylferrocenyl(phenylethynyl)silane $[\alpha]_D$ −103° (*c* 36, benzene). Analysis: Found: C, 75.82; H, 5.04; Si. 6.50. $C_{28}H_{22}FeSi$ calcd.: C, 76.01; H,

4.97; Si, 6.33%. IR (benzene): ν(C≡C) 2160, ν(SiH) 2150 cm^{-1}. NMR (C_6D_6) δ (ppm): 3.95—4.5 (9H, ferrocenyl), 6 (1H, Si—H), 6.80—8.7 (12H, aromatic protons).

(b) From α-naphthylferrocenylfluorosilane $[\alpha]_D$ —77°/PhH by the action of PhC≡CLi/Et_2O or PhC≡CMgBr/Et_2O (see General Technique). The lithium compound and the Grignard reagent are used in 5 fold excess. They are prepared by exchange either with n-BuLi or with n-BuMgBr. The yields in α-naphthtlferrocenyl(phenylethynyl)silane are quantitative in both cases, and the characteristics identical with those of an authentic sample. The rotatory powers are given in the first part (Table 1).

(c) Stereochemistry of the reactions (see Scheme 6). The stereochemistries

SCHEME 6



are deduced from the examination of Scheme 6 by analogy with reactions whose stereochemistry is known.

Synthesis of α-naphthylferrocenylethylfluorosilane

(a) From α-naphthylferrocenylfluorochlorosilane by the action of EtLi/Et_2O or EtMgBr/Et_2O. α-Naphthylferrocenylfluorochlorosilane is prepared from α-naphthylferrocenylfluorosilane $[\alpha]_D$ —77° (benzene) immediately before use as previously described. (It is not isolated in order to avoid racemization.) To the filtered mixture the stoichiometric amount of EtLi or EtMgBr is added. After 30 min an oily residue is isolated (see General Technique) and identified as being α-naphthylferrocenylethylfluorosilane. The yield in both cases was quantitative. The rotatory powers are given in Table 2. Analysis: Found: C, 68.21; H, 5.65; F, 4.69. $C_{22}H_{21}FFeSi$ calcd.: C, 68.04; H, 5.41; F, 4.89%. NMR (C_6D_6) δ (ppm): 1.15 (5H, Si—Et, multiplet), 4.0 (5H, Si—Fc), 4.15 (4H, Si—Fc), >7 (aromatic protons).

(b) For the stereochemistry of the reactions see Scheme 3.

Synthesis of α-naphthylferrocenylallylfluorosilane

(a) From α-naphthylferrocenylfluorochlorosilane by the action of CH_2=$CHCH_2Li/Et_2O$ or CH_2=$CHCH_2MgBr/Et_2O$. As the previous case, α-naphthylferrocenylfluorochlorosilane is prepared just before use and not isolated. A stoichiometric amount of allyllithium or allylmagnesium bromide is added to the filtered mixture. After 30 min, an oily residue is isolated (see General Technique) and identified as α-naphthylferrocenylallylfluorosilane (in quantitative yield). The rotatory powers are given in Table 2. Analysis: Found: C, 68.91; H, 5.32; F, 4.55. $C_{23}H_{21}FFeSi$ calcd.: C, 69.00; H, 5.25; F, 4.75%. NMR (C_6D_6) δ (ppm): 2.25 (2H, Si—$\underline{CH_2}$—CH=CH_2), 3.90—4.30 (9H, Si—Fc), 4.70—5.20 (2H, Si—CH_2—CH=$\underline{CH_2}$), 5.50—6.20 (1H, Si—CH_2—$\underline{CH}$=CH_2), >7 (aromatic protons).

(b) For the stereochemistry of the reaction see Scheme 3.

Synthesis of α-naphthylferrocenylphenylfluorosilane

(a) From α-Naphthylferrocenylfluorochlorosilane by the action of $PhLi/Et_2O$ or $PhMgBr/Et_2O$.

As usual α-naphthylferrocenylfluorochlorosilane is prepared just before use and not isolated. A quantitative amount of phenyllithium or phenylmagnesium bromide is added to the filtered mixture. After 30 min an oily residue isolated (see General Technique) and identified as α-naphthylferrocenylphenylfluorosilane (quantitative yield). The rotatory powers are given in the Table 2. Analysis: Found: C, 71.71; H, 4.99; F, 4.21. $C_{25}H_{22}FFeSi$ calcd.: C, 71.55; H, 4.81; F, 4.35%. NMR (C_6D_6) δ (ppm): 3.95—4.40 (9H, Si—Fc), >7 (aromatic protons)

(b) For the stereochemistry of the reactions see ref. [8a].

Reactions enabling correlations of configuration

Synthesis of α-naphthylferrocenylethylmethylsilane. (a) From α-naphthylferrocenylethylsilane $[\alpha]_D$ + 88° (benzene). 200 mg (5.4×10^{-4} mol) of αnaphthylferrocenylethylsilane $[\alpha]_D$ + 88° (benzene) are dissolved in 5 ml of anhydrous ether to which 4 ml of MeLi (0.95 *M*) are added. After 12 h. 175 mg of an oily residue are isoalted (see General Technique) and identified as α-naphthylferrocenylethylmethylsilane $[\alpha]_D$ + 53° (*c* 48, benzene). Analysis: Found: C, 71.75; H, 6.37; Fe, 14.65. $C_{23}H_{25}FeSi$ calcd.: C, 71.87; H, 6.25; Fe, 14.58%. NMR (C_6D_6) δ (ppm): 0.70 (3H, Si—Me), 1.15 (5H, Si—Et). 4.00 (5H, Si—Fc), 4.25 (4H, Si—Fc), >7 (aromatic protons). (b) From α-naphthylferrocenylethylfluorosilane $[\alpha]_D$ — 44.5° (benzene). 110 mg (2.83×10^{-4} mol) of α-naphthylferrocenylethylfluorosilane $[\alpha]_D$ — 44.5° (benzene) are dissolved in 5 ml of anhydrous ether to which 2 ml of MeLi (1 *M*) are added. After 12 h, 76 mg of an oil are isolated (see General Technique) and identified as α-naphthylferrocenylethylmethylsilane, $[\alpha]_D$ — 27° (*c* 30, benzene).

The physical characteristics are identical to those of an authentic sample.

Synthesis of α-naphthylferrocenylallylmethylsilane. (a) From α-naphthylferrocenylallylsilane $[\alpha]_D$ + 63.2° (benzene). 105 mg (2.74×10^{-4} mol) of α-naphthylferrocenylallylsilane $[\alpha]_D$ + 63.2° (benzene) are dissolved in 5 ml of anhydrous ether to which 1.2 ml of methyllithium (1.5 *M*) is added. After 12 h, 79 mg of an oily residue are isolated (see General Technique) and identified as α-naphthylferrocenylallylmethylsilane, $[\alpha]_D$ + 15.3° (*c* 66, benzene). Analysis: Found: C, 72.47; H, 6.04; Fe, 14.02. $C_{24}H_{25}FeSi$ calcd.: C, 72.72; H, 6.06; Fe,

14.14%. NMR (C_6D_6) δ (ppm): 0.80 (3H, Si—Me), 2.30 (2H, Si—$\underline{CH_2}$—CH=CH_2), 4.00 (5H, Si—Fc), 4.30 (4H, Si—Fc), 4.80—5.30 (2H, Si—CH_2—CH=$\underline{CH_2}$) 5.40—6.30 (1H, Si—CH_2—$\underline{CH}$=CH_2), >7 (aromatic protons). (b) From α-naphthylferrocenylallylfluorosilane $[\alpha]_D$ — 24.2° (benzene). 95 mg (2.3×10^{-4} mol) of α-naphthylferrocenylallylfluorosilane $[\alpha]_D$ — 24.2° (benzene) are dissolved in 5 ml of anhydrous ether to which 2 ml of MeLi (1.1 *M*) are added. After 12 h, 76 mg of an oil are isolated (see General Technique) and identified as α-naphthylferrocenylallylmethylsilane, $[\alpha]_D$ — 8.5° (*c* 76, benzene).

The physical characteristics are identical with those of an authentic sample.

Synthesis of α-naphthylferrocenylphenylmethoxysilane. This product is prepared from α-naphthylferrocenylphenylchlorosilane $[\alpha]_D$ — 35° (benzene). Treatment with methanol gives α-naphthylferrocenylphenylmethoxysilane $[\alpha]_D$ + 16° (benzene) (the experimental technique has been described [8a, 10a]).

Synthesis of α-naphthylferrocenylphenylfluorosilane. 78 mg (1.74×10^{-4} mol) of α-naphthylferrocenylphenylmethoxysilane $[\alpha]_D$ + 16° (benzene) are dissolved in 5 ml of anhydrous ether to which 0.5 ml of freshly distilled $BF_3 \cdot Et_2O$ is added. After 12 h, 53 mg of α-naphthylferrocenylphenylfluorosilane are isolated (neutral hydrolysis, extraction, according to the General Technique), $[\alpha]_D$ + 13.2° (*c* 34, benzene). The characteristics are identical with those of an authentic sample.

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