Journal of Organometallic Chemistry, 67 (1974) 243—255

THE MECHANISM OF NUCLEOPHILIC SUBSTITUTION AT SILICON. ACTION OF ORGANOMETALLIC REAGENTS ON CHIRAL BIFUNCTIONAL SILANES

R.J.P. CORRIU and G.F. LANNEAU
Laboratoire des Organométalliques, associé au C.N.R.S. N° 82, Université des Sciences et Techniques, 34060 Montpellier (France)

(Received July 19th, 1973)

Summary

The study of nucleophilic substitution of monofunctional organosilanes has been extended to bifunctional derivatives. The reactions are both selective and stereoselective. Our results can be interpreted in terms of leaving group polarisability and the softness/hardness of the attacking nucleophile.

The presence of two electronegative substituents only slightly modifies the stereochemistry. A pseudorotation mechanism could not explain the retention observed in certain cases. We envisage two possible modes of attack, either with axial or equatorial entry, leading respectively to inversion or retention at the silicon atom.

Introduction

In 1958 Sommer proposed the "leaving group rule" [1,2] to explain the stereochemistry of nucleophilic substitution at silicon.

A group X, which has a conjugate acid HX of pK_a less than 6, is considered a good leaving group. This is displaced with inversion by the S_N2—*Si* mechanism.

A group X, with a conjugate acid HX of pK_a greater than 10, is a poor leaving group. It is displaced with retention by the S_Ni—*Si* mechanism.

S_N2—*Si*

S_Ni —*Si*

The S_N2—*Si* mechanism implies backside attack by the nucleophile with formation of a trigonal bipyramidal intermediate (TBP).

The authors explain the retention mechanism by postulating frontal attack of the nucleophile, forming trigonal bipyramidal or tetragonal pyramidal intermediates of similar energies [3]. They then propose, by analogy with results obtained in the hydrolysis of alkyl phosphates [4], an axial departure corresponding to an axial entry [5] with pseudorotation of the trigonal intermediate (TBP). However, whatever the geometry of the pentacoordinate intermediate, it is the electrophilic assistance of Si—X bond rupture which is considered to be the essential driving force of the reaction.

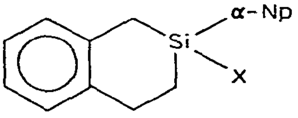
More recent studies [6,7], in particular the coupling reactions between organometallic reagents and organosilanes [8], have placed in doubt the generality of electrophilic assistance as the driving force of the $S_N i$—Si process.

Study of factors affecting the stereochemistry

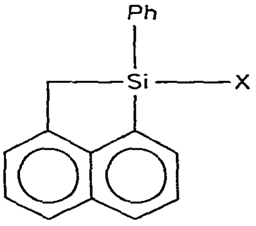
Many factors seem to alter the stereochemistry of substitution, some are of a structural nature, others are due to electronic influences.

(1) Structure of silane

The study of the cyclic compounds (A) has shown the influence of the environment of the silicon atom. Our results for coupling reactions with organometallic compounds have shown the higher reactivity of this system in comparison with acyclic derivatives, and a general tendency of the stereochemistry towards retention of configuration [9]. This influence is even more clearly illustrated with the strained ring compound studied by Sommer [6]. The chlorosilane (B) is substituted with retention of configuration by the nucleophiles OH^- and H^-, whereas for acyclic derivatives inversion is observed.



(A)



(B)

We find a phenomenon already observed in organophosphorus chemistry, namely that the strain within small rings affects the reactivity of the heteroatom [4,10].

(2) Electronic factors

The extensive study of organometallic coupling reactions with different acyclic functional silanes has shown [11 - 13] that two principal factors count in the stereochemistry of the substitution process for the same silane: the polarisability of the leaving group and the “soft” or “hard” nature of the attacking nucleophile.

(A). Polarisability of the leaving group. It may be considered that the stereochemistry in general is related to the polarisability of the leaving group

TABLE 1

Ph-α-NpRSiX + R'M → Ph-α-NpRSiR' + MX[a]

Reactant	Cl	SCH_3	F	OCH_3	H
AlkylLi	Inv	Ret	Ret	Ret	Ret
$PhCH_2Li$	Inv	Inv	Inv	Inv	Ret
Ph_2CHLi	Inv		Inv	Inv	Inv

[a] For R = Me, see refs. 11 and 14. R = Et, i-Pr, Vi See ref. 12.

which may be in one of two categories [14]: polarisable substituents (Cl, SCH_3) reacting preferentially with inversion (Inv.), and, non-polarisable substituents (H, OCH_3) normally reacting with retention (Ret.) (see Table 1).

(B). Nature of the nucleophile. In the case of coupling with organometallics, retention of configuration is observed with hard nucleophiles which have a concentrated charge (for example [15] saturated organolithium reagents). However, inversion is predominant in the case of soft reactants, having a delocalised charge [16] (e.g. allylorganomagnesium reagents). This is illustrated by a brief description of the results (cf. Table 2). Our explanation is similar to that of Anh and colleagues which concerns the addition modes of organometallics to α, β-ethylenic carbonyl compounds [17]. The present authors think that the orientation of addition to the 1,2 or 1,4 position is a function of hardness (softness) of the attacking nucleophile. The greater the *p* character of the anion R^- (ie. the softer it becomes) the higher the preference for R to add in position 4.

In the present case, the observed stereochemistry may be compared with the *s* or *p* character of the organometallic; this is illustrated by the case of benzyl- and benzhydryl-lithium. Benzhydryllithium is considered to be a softer reactant than benzyllithium [18] and the results show a greater tendency for Ph_2CHLi to give inversion. For example, this reagent is the only organolithium compound capable of substituting the Si—H bond with inversion [14].

A second aspect concerns the nature of the metal. Grignard reagents are softer than the corresponding organolithium compounds and in general they favour inversion of configuration in cases where lithium derivatives give retention. We have also reported that alkoxygermanes are substituted by Ph_3GeLi, a soft reagent, with inversion, the same stereochemistry as with $PhCH_2Li$ [19].

We can also cite the behaviour [9] of Grignard and organolithium reagents with respect to the cyclic silane (A) (cf. Table 2), and that of allylic or-

TABLE 2[a]

Reactant	Cl	F	OMe
EtLi	Ret	Ret	Ret
$CH_2{=}CH{-}CH_2Li$	Inv	Ret	Ret
$Ph{-}CH_2Li$	Inv	Ret	Ret
EtMgBr	Inv	Ret	Ret
$CH_2{=}CH{-}CH_2MgBr$	Inv	Inv	Inv
$Ph{-}CH_2MgCl$	Inv	Inv	Inv

[a] See ref. 9.

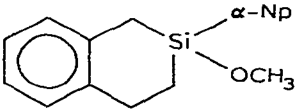
TABLE 3[a]

	$CH_2{=}CH{-}CH_2Li$	$CH_2{=}CH{-}CH_2MgBr$
Ph-α-NpHSiOMen	Ret	Inv
Ph-α-Np(MeO)SiOMen	Ret	Ret

[a] See ref. 20.

ganometallic compounds (M = Li, Mg) with bifunctional organosilane [20], (cf. Table 3). Solvent effects agree with this classification [21]. The increasing solvation of the organometallic polarises the carbon—metal bond; this, according to our classification, increases the hardness of the nucleophile (or decreases its softness), and accounts for the tendency towards retention. Table 4 summarises some of the results.

TABLE 4

Silane	Reactant	Solvent	Stereochemistry	Ref.
Ph-α-NpViSiF	$CH_3{-}CH_2{-}CH_2MgBr$	Et_2O	Inv	12
	$CH_3{-}CH_2{-}CH_2MgBr$	DME	Ret	
	$CH_3{-}CH{=}CH{-}CH_2MgBr$ (+ $MgBr_2$)	Et_2O	Inv	
	$CH_3{-}CH{=}CH{-}CH_2MgBr$	THF	Ret	9
Ph-α-NpHSiOMen	$CH_2{=}CH{-}CH_2MgBr$	Et_2O	Inv	20
	$CH_2{=}CH{-}CH_2MgBr$	THF	Ret	

It is worth noting that whatever the degree of silane substitution, mono- or bi-functional, the factors influencing the stereochemistry (character of the nucleophilic carbanion, and nature of the metal and solvation) are the same in the two series.

Under these conditions, it was interesting to study the behaviour of dialkoxysilanes. These compounds have two functional substituents of similar polarisability, the selectivity must thus be directly related to the nature of the nucleophile.

Study of alkoxysilanes

The results that we have presented in previous publications on Ph-α-Np-(—)-MenOSiOMe [22] show that its reactions are stereoselective and may be summarised as follows: the hard saturated or vinylic organolithium and Grignard reagents substitute only the less bulky methoxy group with retention of configuration [23], the soft reactants, essentially α-unsaturated Grignard reagents, substitute the bulkier menthoxy group with inversion of configuration.

As before, we have observed a variation of stereochemistry according to the solvent [20]. In THF the high solvation of the metal causes polarisation of the R—M bond, this increases the hardness of the nucleophile (decreasing its softness) and retention of configuration is favoured (cf. Scheme 1).

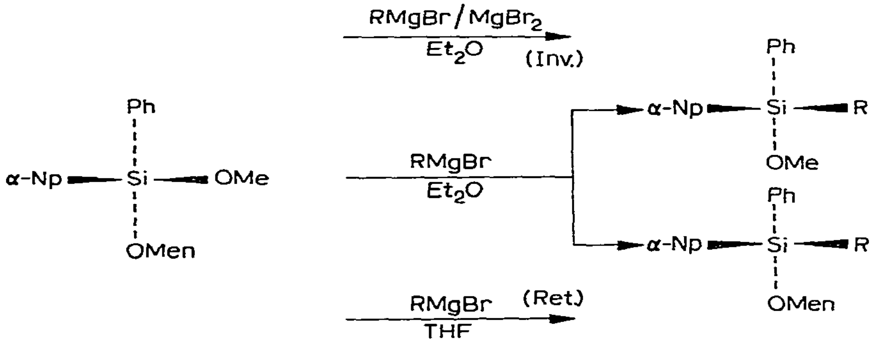
On the other hand, the presence of $MgBr_2$ lowers the basicity of the medium, this agrees with the observed results: displacement of the stereochemistry towards inversion and an increase in reaction rates.

TABLE 5

Ph-α-Np(R′O)SiOMen + RLi → Ph-α-NpRSiOR′ + Ph-α-NpRSiOMen

RLi	R	Ph-α-NpRSiOR′ (%)	Ph-α-NpRSiOMen (%)
MeLi	Me	27	73
EtLi	Me	15	85
	Et	22	78
n-BuLi	Me	13	87
	Et	79	21
MePhLi	Me	11	89

SCHEME 1



The experimental importance of this work was the observation of the relationship between high selectivity and stereochemistry for the substitution of the alkoxy OR groups by organomagnesium reagents. The hard nature of saturated organolithium compounds is more marked than in corresponding Grignard reagents, thus it was interesting to study the loss of selectivity which would result from a higher reactivity. Our results are reported in Table 5. We observe a large fall in selectivity by comparison with Grignard reagents. Steric factors seem to play an important role in the percentage of cleavage of the two functional groups.

The stereochemistry of substitution of the two labile groups has been demonstrated in two cases. The concurrent cleavage of the two groups occurs with retention of configuration and the stereoselectivity is always greater than 90%.

MeLi + Ph-α-Np(MeO)SiOMen → Ph-α-NpMeSiOMen + Ph-α-NpMeSiOMe

	68%	32%
	(97) Ret.	(97) Ret.*

EtLi + Ph-α-Np(EtO)SiOMen → Ph-α-NpEtSiOMen + Ph-α-NpEtSiOEt

	78%	22%
	(92) Ret.	(92) Ret.*

---

* Calculated stereochemistry

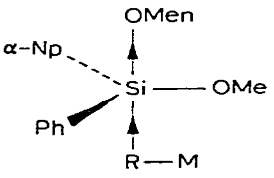
This type of reaction is thus very different to that of a crotyl [20] Grignard. For the latter, the lack of selectivity corresponded to two concurrent reactions of opposite stereochemistries with a different group (OR). In the present case, the cleavage stereochemistry is retention of configuration for both groups.

Mechanism

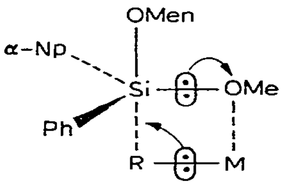
The results previously obtained have allowed us to reinvestigate the applicability of the $S_N i$–Si process to the case of coupling with organometallic compounds. The stereochemistry observed with bifunctional silanes is not in accord with generally accepted mechanisms.

(A). $S_N i$–Si process

If we consider the two possible mechanisms $S_N 2$–Si and $S_N i$–Si corresponding to the substitution of the two alkoxy groups with opposing stereochemistry [1] we must write the same intermediate to account for our results: menthoxy substitution with inversion and methoxy substitution with retention. We should thus find a lack of selectivity in all our reactions. However in general they are highly selective. Moreover, the solvent effects are contrary to a mechanism which invokes electrophilic assistance by the metal as the reaction driving force for retention.



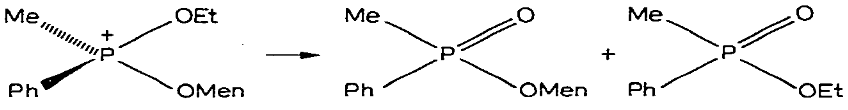
Inv.



Ret.

(B). Process involving pseudorotation

The presence of two electronegative substituents allows consideration of a mechanism by pseudorotation [24 - 27]. We can suppose that the difference in stability of the intermediates is sufficient to promote such a process due to the presence of alkoxy group in an axial position, and the other in an equatorial position. Such a mechanism has already been envisaged for phosphorus compounds similar to a dialkoxysilane [4]. Also, Mislow and colleagues have postulated that all loss of specificity in the hydrolysis of dialkoxyphosphonium salts must come from a pseudorotation of the intermediate phosphorane [28].



$SbCl_6^-$

(S)p-1

(S)p-2 40%

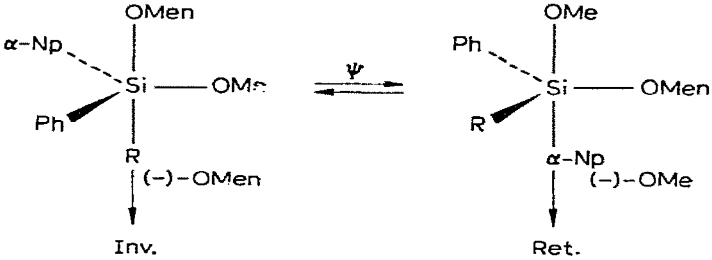
(R)p-2 20%

(S)p-3 38%

(R)p-3 2%

To explain the product distribution they suggest two possibilities of attack. In the first case, an attack at the opposite side to the group (OMen) corresponds either to a direct departure giving $(S)_P$—3 (inversion), or an axial departure of the group (OEt) (after pseudorotation) to give $(S)_P$—2 (retention). The second hypothesis is attack at the opposite side of the group (OEt), with a direct departure leading to $(R)_P$—2 (inversion), or pseudorotation and an axial departure of the menthoxy group to give $(R)_P$—3 (retention).

These two reaction schemes may be applied to the case of Ph-α-Np-(—)-MenO-SiOMe.



For example we can imagine an axial entry of the nucleophile opposite to the group (OMen), with formation of the intermediate (TBP), then axial elimination of the leaving group. Under these conditions, the departure of (OMen) gives inversion; on the other hand the departure of (OMe) after pseudorotation leads to retention. Such a pseudorotation can, a priori, be envisaged as being due to the fact that the incoming group R attached to silicon is less electronegative than the equatorial (OMe) group [29].

This scheme does not account for the experimental facts, since the reactions are both selective and stereoselective. Because two intermediates need to be postulated for an axial attack we should observe a variety of products, as in the case of phosphorus. Moreover, this mechanism does not account for the change in stereochemistry as a function of the soft or hard character of the organometallic compound.

We have seen that an allyl Grignard substitutes the group (OMen) uniquely with inversion, whilst a n-propyl Grignard replaces the methoxy group with retention [22]. The driving force for the pseudorotation is the electronegativity of the groups attached to silicon. Thus one cannot explain the reason for one group (n-Pr) causing pseudorotation and not the other (allyl). From the instant that the carbanion is attached to silicon, the bond (Si—C) has been formed, thus if there is the possibility of pseudorotation, one should observe it in every case. Finally, the mechanism does not account for substitution of the two groups (OR) with pure retention in the case of organolithium reagents.

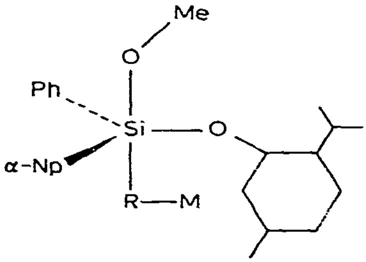
*It thus appears that the reaction stereoselectivity and selectivity are in*compatible with a mechanism involving pseudorotation. In addition, these results are identical with those for monofunctional compounds, showing that pseudorotation does not take part in the retentive mechanism. The presence of *a single electronegative group in these cases eliminates the possible driving force* for pseudorotation, but this emphasises the importance of electronic effects. Indeed, it is these effects which govern the stereochemistry of substitution both for monofunctional and bifunctional silanes.

Proposed mechanisms

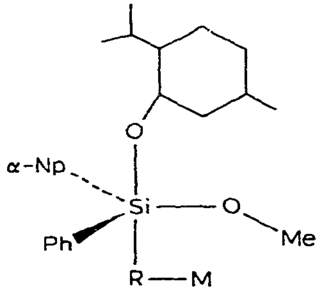
A nucleophile may approach a tetrahedral molecule either on a face or on an edge [26,27]. It is obvious that both Coulombic and steric effects play an important part in the possible approach pathways [30], and equally the energy of the intermediate formed must influence the mode of attack.

(1). Substitution with inversion by axial attack. We presume an axial attack of the reactant in the case of the inversion mechanism. The nucleophile arrives at the opposite face to the electronegative leaving group, forming a trigonal bipyramidal intermediate. We find here the hypothesis of the S_N2—Si mechanism proposed by Sommer [1].

One can explain the observed selectivity by considering the steric factors. The two TBP intermediates may be represented as (I) and (II).



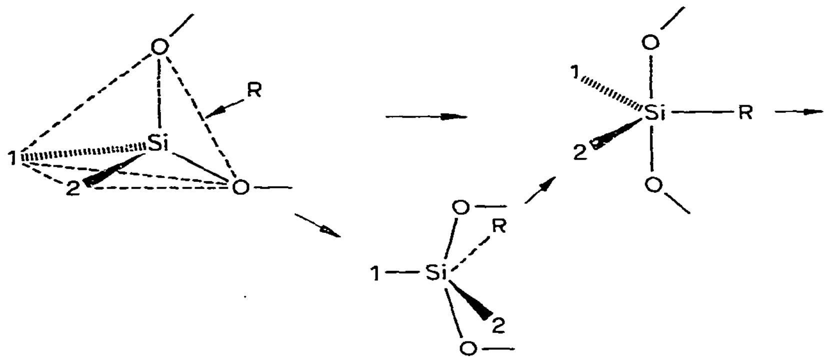
(I)



(II)

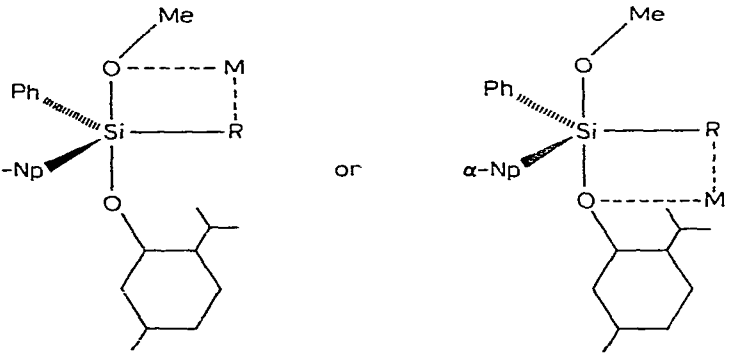
It is clear that steric hindrance must be more important in (I) than in (II). This is due to the presence in (I) of the bulky (OMen) group in an equatorial position and adjacent to the strongly solvated nucleophilic reactant. It is therefore logical that the nucleophilic approach leading to (II), is energetically favoured, giving an axial departure of the (OMen) group. We recall that in the case of hydrolysis of phosphonium salts [28] the observed results correspond to 78% of this mode of attack, in spite of the attacking nucleophile being an OH^- group which is less bulky than an organometallic compound.

(2.) Substitution with retention by equatorial attack. Since the S_Ni—Si mechanism, with axial attack and equatorial departure, does not account for the results we observed with organolithium or organomagnesium reagents we propose another reaction mechanism with equatorial attack of the nucleophile and axial departure of the leaving group, leading to retention at silicon. With this hypothesis, the intermediate with the two oxygen atoms in axial positions must have, as in the case of phosphorus [31], a much lower energy. One can reasonably suppose that the nucleophilic attack proceeds in such a way to lead directly to this structure [32]. One perceives that a frontal attack on the edge joining the two oxygen atoms represents this geometry, and the carbanion coordinates to silicon with equatorial entry.



Certain authors admit that an attack on the edge of a tetrahedron corresponds to the formation of a tetragonal pyramid. One can postulate a pathway by such a geometry. However the energy difference between a tetragonal pyramid and a trigonal bipyramid is in this case such that one can only consider this geometry for a transition state [33,34]. It is the TBP structure which must be envisaged as an intermediate and it is this species which reacts afterwards to lead to the products.

This scheme explains the selectivity observed in the action of Grignard reagents. The covalent magnesium is sufficiently solvated for the steric crowding to hinder electrophilic assistance, favouring the substitution of the smaller (OMe) group.



However, in the case of relatively polarised organolithium reagents the carbanion has a more concentrated charge, and the cation Li^+ has a much lower capacity for electrophilic assistance. The steric effects thus play a lesser role, which explains the lower selectivity of the reaction. It must be emphasised that the slow step of the reaction is the attack of the nucleophile; this is controled by electronic factors and not electrophilic assistance of the departure of the leaving group. This assistance only intervenes in the last rapid step, during the cleavage of the Si—X bond.

We will attempt to relate the idea of softness/hardness [35] to the geometry of the formal intermediate. We have seen that the mechanism giving retention implies that the attacking nucleophile should be sufficiently charged to repel the leaving group and place it in the axial position. We therefore have ionic interactions and the reaction can be considered as "charge-controlled" [36]. This explains why the harder a reactant, the greater the retention. However, in the inversion mechanism, the driving force of the reaction is the possible interaction of the carbanion with a vacant orbital of silicon. One has a reaction under "frontier orbital control", a mechanism characteristic of soft reactants [37]. It is then reasonable to suppose that it is the d_{z^2} orbital, of lowest energy, which hybridises to sp^3d for formation of the pentacooordinated intermediate.

Experimental

General techniques

The preparative method for the reactants has already been published [23]. The organometallic was added to the silane in diethyl ether at 0°C and the reaction mixture was hydrolysed by acid (10% HCl). The silanes obtained were purified by preparative TLC on Kieselgel—PF 254, using benzene/petroleum ether (5/95) as eluant. The percentages of the various products were determined by GLC using integration (retention time × peak height). Taking account of operating conditions and measurement techniques the reported values are given to an accuracy of ± 1%.

Determination of reaction stereochemistry

(A) Reaction of (S)-Ph-α-Np-(—)-MenOSiOMe with MeLi

(1) Action of methyllithium. Methyllithium (12 ml of 0.35 *M*, 0.0042 mol) was slowly added to an excess of (*S*)-phenyl-α-naphthylmethoxy-(—)-menthoxysilane (2.1g, 0.005 mol) ($[\alpha]_D$ — 58.4°) in anhydrous ether (60 ml), at — 15°C. The addition took 20 min, after which the mixture was allowed to warm to room temperature and the products were treated according to the described procedure. GLC (Girdel—1 Chromatograph; column OV 17) identified 4 products: Ph-α-NpSiMe$_2$ (19%); Ph-α-NpMeSiOMe (4%); Ph-α-NpMeSiOMen (48%); Ph-α-NpMeOSiOMen (29%).

(2) Reduction of alkoxysilanes. The preceding reaction mixture was treated by an excess of aluminium hydride [prepared in anhydrous ether (50 ml) from lithium aluminium hydride (0.24g, 0.006 mol) and aluminium chloride (0.26g, 0.002 mol). It was then heated under reflux for 1 h and the silanes obtained were purified by TLC. The products were identified as before by GLC (Girdel—2 chromatograph: Ph-α-NpSiH$_2$ (30%); Ph-α-NpMeSiH (51%); Ph-α-NpSiMe$_2$ (19%). Optical activity of the mixture: $\alpha = +0.164°$; $m = 0.06163$ g (5 ml pentane)$[\alpha]_D$ + 26.6° ± 0.5 [Ph-α-NpMeSiH (51% ± 1)].

Optical purity of the silane obtained, 77% ($[\alpha]_{D\,max.}$ + 34.4°, pentane) [38].

(3) Action of methyllithium (in excess). Under the same conditions as above, methyllithium (66 ml, 0.023 mol) was added to (*S*)-phenyl-α-naphthylmethoxy-(—)-menthoxysilane (8.4g, 0.02 mol) ($[\alpha]_D$ —58.4°, pentane) dis-

TABLE 6

THEORETICAL CALCULATION OF THE PURITY OF (+)-Ph-α-NpMeSiH

Stereochemistry	%Purity	% Purity (corrected for 97% Ret.)	$[\alpha]_D$
1st case retention	84 ± 2	79 ± 2	+27.1 ± 0.7°
2nd case racemisation	92 ± 2	86 ± 2	+29.6 ± 0.7°
3rd case inversion	100 ± 2	94 ± 2	+32.3 ± 0.7°

solved in anhydrous ether (50 ml). The addition was carried out over 30 min at −15°C, then the mixture was stirred at room temperature for 30 min. After the normal work-up, *l*-menthol (1.1g, 0.0071 mol) was eliminated by distillation and the residual silanes were identified by GLC (Girdel—1 chromatograph): Ph-α-NpSiMe$_2$ (34%); Ph-α-NpMeSiOMen (66%). After reduction with hydride by the technique above the following silanes were identified by GLC (Girdel—2 chromatograph): Ph-α-NpMeSiH (67%); Ph-α-NpSiMe$_2$ (33%). Optical activity of the mixture: α: 0.179°; m: 0.04486 g (5 ml pentane) $[\alpha]$ + 29.9° (Ph-α-NpMeSiH 67%). Optical purity of the silane obtained, 89%.

(4) Calculation of reaction stereospecificity. If one assumes that and alkoxysilane is reduced by AlH$_3$ with 98% retention [13], (*S*)-Ph-α-NpMeSiOMen is obtained with a calculated stereospecificity of 97% retention.

The stereospecificity for Ph-α-NpMeSi*OMe is calculated from the stereospecificity obtained for the menthoxysilane: Ph-α-NpMeSiOMe, 8 ± 1%; Ph-α-NpMeSiOMen, 92 ± 1%.

There are three stereochemical possibilities for the formation of Ph-α-NpMeSiOMe (Table 6).

Experimental value of the optical purity of (+)-Ph-α-NpMeSiH was $[\alpha]_D$ + 26.6°; corrected value (98% Ret. on reduction) $[\alpha]_D$ + 27.6°.

Whithin experimental error the experimental value coincides with that calculated for retention of configuration. We thus consider that the Ph-α-NpMeSiOMe is obtained with 97% retention.

(B) Reaction of (S)-Ph-α-Np-(—)-MenOSiOEt with EtLi

(1) Action of ethyllithium. Ethyllithium (10 ml of 1*M*, 0.01 mole) was rapidly added to phenyl-α-naphthylethoxy-(—)-menthoxysilane (3.6 g, 0.006 mol) ($[\alpha]_D$ − 56.5°, pentane) in anhydrous ether (60 ml) at 0°C. The mixture was stirred for 2 h and after the usual work-up the silanes were identified by GLC (Intersmat IGC 12M chromatograph: column SE 30): Ph-α-NpEtSiOEt (10%); Ph-α-NpEtOSiOMen (55%); Ph-α-NpEtSiOMen (35%). A fraction of the reaction mixture was treated by preparative TLC and Ph-α-NpEtSiOMen (0.85 g) ($[\alpha]_D$ −68.7° [*c*, 6.8, pentane]) was isolated. This product was nearly optically pure.

(2) Reduction of Ph-α-NpEtSiOMen. The silane (0.45) ($[\alpha]_D$ −68.7°) was added to a mixture of LiAlH$_4$ (0.15 g) and AlCl$_3$ (0.17 g) in anhydrous ether (20 ml). The reaction was heated under reflux for 8h and after the normal work up (+)-Ph-α-NpEtSiH (0.18 g) ($[\alpha]_D$ + 18.9° [*c*, 9.0, pentane]) was isolated. Optical purity of the silane, 79% ($[\alpha]_{D\,max}$ + 24°) [39]:

TABLE 7

THEORETICAL CALCULATION OF THE PURITY OF (+)-Ph-α-NpEtSiH

Stereochemistry	%Purity	% Purity (corrected for 92% Ret)	$[\alpha]_D$
1st case retention	56 ± 4	47 ± 4	+11.3 ± 0.9°
2nd case racemisation	78 ± 4	66 ± 4	+15.7 ± 0.9°
3rd case inversion	100 ± 4	84 ± 4	+20.9 ± 0.9°

(3) Reduction of the reaction mixture. A fraction (0.65 g) of the preceeding reaction mixture was treated by an excess of aluminium hydride [$LiAlH_4$ (0.30 g) and $AlCl_3$ (0.35 g)] in anhydrous ether (30 ml). The reaction was heated under reflux for 12 h, after acid hydrolysis and normal work-up the silanes were purified by preparative TLC. The products were identified by GLC (Girdel—2 chromatograph; column OV 17) as Ph-α-$NpSiH_2$, 57%; Ph-α-NpEtSiH, 43%. Optical activity of the mixture: α, + 0.049°; *m*, 0.9370 g (10 ml pentane) $[\alpha]_D$ + 12.1°, Ph-α-NpEtSiH (43%). Optical purity of the silane obtained, 50% ($[\alpha]_{D\,max}$ + 24°) [39].

(4) Calculation of reaction stereospecificity. The stereospecificity of alkoxysilane reduction is known to be 98% retention [13]. One can thus calculate the stereospecificity of the action of ethyllithium using this value.

Ph-α-NpEtSiOMen is obtained with 92% retention. The stereospecificity of Ph-α-NpEtSiOEt is calculated as before from the stereospecificity obtained for the menthoxysilane: Ph-α-NpEtSiOEt, 22 ± 2%; Ph-α-NpEtSiOMen, 78 ± 2%. Just as with the preceding case, three stereochemistries are possible for the formation of Ph-α-NpEtSiOEt (Table 7).

Experimental value of the purity optical of (+)-Ph-α-NpEtSiH was $[\alpha]_D$ + 12.1°, corrected value (98% Ret. on reductions) $[\alpha]_D$ + 12.6°.

Within experimental error the experimental value coincides with that calculated for retention of configuration. We consider that Ph-α-NpEtSiOEt is obtained with the same stereospecificity as the corresponding menthoxysilane (i.e. 92% Ret.).

(5) Related reactions. (a) Attempted reaction of Ph-α-NpMeSiOMen with MeLi. Under the same conditions as the substitution of Ph-α-NpMeOSiOMen by MeLi, we added methyllithium (4.3 ml 0.35 *M*, 0.0015 mol) to phenyl-α-naphthylmethyl-(—)-menthoxysilane (0.6 g, 0.0015 mol) in anhydrous ether (60 ml) at — 15°C. After 2h the mixture was allowed to come to room temperature and was worked-up as before. By GLC the reactant silane Ph-α-NpMeSiOMen alone was identified. (*b*) Reaction of Ph-α-NpMeSiOMe with MeLi. With the conditions above we added methyllithium (4 ml, 0.0014 mol) to phenyl-α-naphthylmethylmethoxysilane in anhydrous ether (20 ml). After work-up the product obtained was phenyl-α-naphthyldimethylsilane.

Acknowledgement

The authors are grateful to Dr. D. Tune for helpful translation of the manuscript.

References

1 L.H. Sommer, Stereochemistry, Mechanisms and Silicon, McGraw Hill Book Company, New York, 1965.
2 L.H. Sommer and H. Fujimoto, J. Amer. Chem. Soc., 90 (1968) 982, and references therein.
3 L.H. Sommer, C.L. Frye and G.A. Parker, J. Amer. Chem. Soc., 86 (1964) 3276.
4 F.H. Westheimer, Accounts Chem. Res., 1 (1968) 70.
5 L.H. Sommer and H. Fujimoto, J. Amer. Chem. Soc., 91 (1969) 7040.
6 D.N. Roark and L.H. Sommer, J. Amer. Chem. Soc., 95 (1973) 969.
7 L.H. Sommer, J. Mc Lick and C.M. Golino, J. Amer. Chem. Soc., 94 (1972) 669.
8 R.J.P. Corriu and B.J.L. Henner, J. Chem. Soc., Chem. Commun (1973) 116.
9 R. Corriu and J. Massé, Chem. Commun., (1967) 1287; J. Organometal. Chem., 34 (1972) 221; 35 (1972) 51.
10 M.J. Gallagher and I.D. Jenkins, Top. Stereochem., 3 (1968) 70.
11 L.H. Sommer, W.D. Korte and P.G. Rodewald, J. Amer. Chem. Soc., 89 (1967) 862.
12 R. Corriu et G. Royo, Bull. Soc. Chim. France, 4 (1972) 1497.
13 R. Corriu et G. Royo, J. Organometal. Chem., 40 (1972) 229.
14 L.H. Sommer and W.D. Korte, J. Amer. Chem. Soc., 89 (1967) 5802.
15 T.L. Brown, Advan. Organometal. Chem., 3 (1965) 365.
16 J.E. Nordlander and J.D. Roberts, J. Amer. Chem. Soc., 81 (1959) 1769.
17 O. Eisenstein, J.M. Lefour, C. Minot, N.T. Anh et G. Soussan, C. R. Acad. Sci. Paris. Ser. C, 274 (1972) 1310.
18 R. Waack, M.A. Doran, E.B. Baker and G.A. Olah, J. Amer. Chem. Soc., 88 (1966) 1272.
19 F. Carré and R. Corriu, J. Organometal. Chem., 65 (1974) 343.
20 R. Corriu et G. Lanneau, Bull. Soc. Chim. France, in press.
21 R.J.P. Corriu, J.P. Massé and G. Royo, Chem. Commun., (1971) 252.
22 R. Corriu, G. Lanneau et G. Royo, J. Organometal. Chem., 35 (1972) 35.
23 R. Corriu, G. Lanneau et M. Leard, J. Organometal. Chem., 64 (1974) 79.
24 R.S. Berry, J. Chem. Phys., 32 (1960) 933.
25 R.F. Hudson, Angew. Chem., Int. Ed. Engl., 6 (1967) 749.
26 K. Mislow, Accounts. Chem. Res., 3 (1970) 321.
27 M. Gielen, C. Dehouck, H. Mokhtar-Jamai and J. Topart, Reviews on Silicon, Germanium, Tin and Lead Compounds, Vol 1, Freund Publishing House Ltd., Tel-Aviv, 1972, p. 9.
28 K.E. de Bruin and K. Mislow, J. Amer. Chem. Soc., 91 (1969) 7393.
29 R.J. Gillespie, J. Chem. Educ., 40 (1963) 295.
30 W. Hawes and S. Tripett, Chem. Commun., (1968) 577.
31 A. Rauk, L.C. Allen and K. Mislow, J. Amer. Chem. Soc., 94 (1972) 3035.
32 R.J.P. Gillespie and R.S. Nyholm, Quart. Rev. Chem. Soc., 11 (1957) 339.
33 R. Hoffmann, J.M. Howell and E.L. Muetterties, J. Amer. Chem. Soc., 94 (1972) 3047.
34 P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez and I. Ugi, Angew. Chem., Int. Ed. Engl., 10 (1971) 687.
35 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, J. Wiley and Sons, Inc., New York, 2nd edn., 1967; R.F. Hudson, Structure and Bonding, Vol. 1 (1966) 221.
36 G. Klopman, J. Amer. Chem. Soc., 90 (1968) 223.
37 For a review, see: J. Seyden-Penne, Bull. Soc. Chim. France, (1968) 3871; C. Duboc, ibid, 5 (1970) 1768.
38 L.H. Sommer, C.L. Frye, G.A. Parker and K.W. Michael, J. Amer. Chem. Soc., 86 (1964) 3271.
39 R. Corriu et G. Royo, Tetrahedron, 27 (1971) 4289.