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INFLUENCE OF ANGLE STRAIN ON THE STEREOCHEMISTRY OF THE NUCLEOPHILIC DISPLACEMENTS AT SILICON: STEREOCHEMICAL BEHAVIOUR OF OPTICALLY ACTIVE SYSTEMS CONTAINING BOTH AN INTRACYCLIC SILICON ATOM AND AN INTRACYCLIC LEAVING GROUP.

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Summary

A detailed study of the stereochemistry of nucleophilic displacements at silicon by organometallics is reported for optically active systems containing both an intracyclic silicon atom and an intracyclic leaving group (1-naphtyl-2 phenyl-2 sila-2 oxa-1 cyclopentane and -hexane derivatives). The stereochemistry is always controlled by the electronic character of the nucleophile, but the strained geometry of a five-membered ring directs the stereochemistry towards inversion in borderline cases (allyllithium, $LiAlH_4$/4 CuI, *p*-$CH_3OC_6H_4CH_2Li$). Analysis of the results and those reported previously for exocyclic leaving groups permits evaluation of the influence of angle strain on the stereochemistry at silicon. The gradual displacement of the stereochemistry as the angle strain at silicon is varied is explained in terms of a change of hybridization of the σ^*(Si—X) orbital [1].

1. Introduction

Nucleophilic substitution at silicon has been extensively studied with acyclic chiral organosilanes [2]. The results show that the stereochemistry is mainly controlled by the following two factors:

(i) The tendency of the leaving group to be replaced by a nucleophile [3]; an increase the leaving group ability leads to a change of the stereochemistry towards inversion, as indicated below:

the leaving group ability to be replaced: Cl, Br > SR, F > OR >> H

predominant stereochemistry: IN → RN

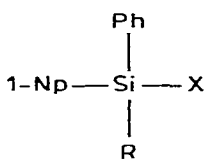
(ii) The electronic character of the nucleophile. For a given leaving group, the stereochemistry is extremely sensitive to the nature of the reagent. Nucleophiles

in which the negative charge is highly delocalized, lead mainly to inversion, whereas charge-delocalized reagents favour retention [2,4].

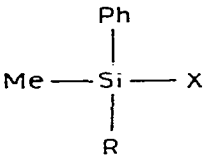
Concerning the influence of the structure of the organosilane, the stereochemical patterns reported for optically active 1-naphthyl phenyl methyl silanes [2] can generally be extended to other acyclic R_3Si^*—X systems (Scheme 1):

SCHEME 1

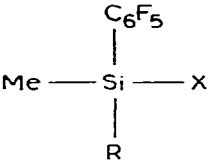
R_3Si^*—X :



R = Et, i-Pr, Vi [5,6]



R = t-Bu [7]
i-Pr [7]
Et [7]
Ph_3Si [8]
Ph_3Ge [9]



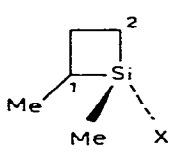
R = 1-Np [10]
Ph [10]

In the above optically acitve derivatives, the substituents attached to silicon cover a substantial range of steric and polar effects. The following features can be identified:

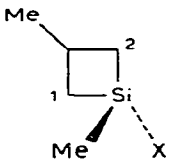
(i) Variation of the R groups over a range of moderate to large steric requirements leaves the stereochemistry unchanged.

(ii) Polar effects do not modify the stereochemistry. Comparison of 1-NpPhMeSi—X and 1-NpC_6F_5MeSi—X systems is revealing in this respect; although the pentafluorophenyl group is a powerful electron-withdrawing group relative to phenyl [11], these two systems show significant differences in stereochemistry. A similar observation can be made for 1-NpPhEtSi—X and 1-NpPhViSi—X derivatives.

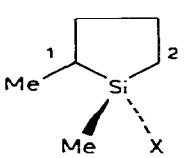
On the other hand, structures in which silicon is part of a ring, particularly a strained ring, show stereochemical behavior which is strongly influenced by the geometry of the substrate. For instance, important changes of stereochemistry compared with those for acyclic silanes were reported for the following compounds:



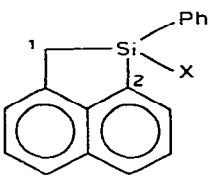
(I [12,13])



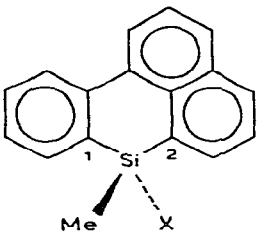
(II [12])

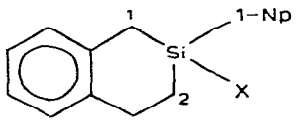


(V [16])



(III [14])





(VI [17])

The most significant data are summarized in Table 1, and have three main implications:

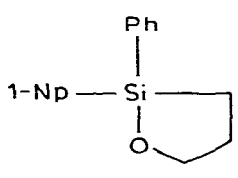
(i) Increased angle strain at silicon always leads to a change of the stereochemistry towards retention. This trend is most marked in the case of the most strained systems I, II and III. Both silacyclobutanes I and II react with retention, whatever the nature of the nucleophile. Even coupling reactions between I (Si—Cl) and $LiAlH_4$ or Grignard reagents (R = *p*-$MeOC_6H_4$ or *p*-MeC_6H_4) occur with complete retention of configuration, whereas the same reactions in the case of 1-NpPhMeSi—Cl occur with complete inversion. In compound III (C_2—Si—C_1 angle = 93.4°), the Si—Cl bond is also cleaved by $LiAlH_4$ with retention of configuration.

(ii) Even a small angular strain suffices to cause such a stereochemical change. 1-Naphthyl-2-sila-9 tetrahydro-1,2,3,4-naphthalene, VI (C_1—Si—C_2 ≃ 105°), shows significant deviations compared to 1-Naphthylphenylmethylsilane (R_3Si—X) (bond angle ≃109°). Compound VI (with X = Cl) reacts with alkyllithiums with complete retention compared with inversion for R_3Si—Cl. Allyl- or benzyl-lithium and alkyl Grignard reagents also replace the Si—F bond VI (X = F) with retention compared with inversion for R_3Si—F.

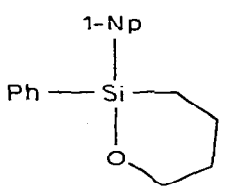
(iii) It is noteworthy that the cyclic strain does not change the factors which mainly govern the stereochemistry at silicon, i.e., the nature of the leaving group and the electronic character of the nucleophile. In both cases, the stereochemistry changes from inversion to retention on going from ≡Si—Cl to ≡Si—H. Moreover, charge-delocalized nucleophiles favor inversion, whereas highly charge-localized reagents lead to inversion. The cyclic strain only acts as an additional factor favouring displacement of the stereochemistry towards retention.

The above discussion on the influence of ring strain on the stereochemistry at silicon includes only stereochemical data obtained from substitution of exocyclic leaving groups. We describe below studies of optically active systems containing both an intracyclic silicon and an intracyclic leaving group (Scheme 2).

SCHEME 2



(VII, $[\alpha]_D = -16°$)



(VIII, $[\alpha]_D = -8°$)

TABLE 1

STEREOCHEMISTRY OF NUCLEOPHILIC DISPLACEMENTS AT SILICON

Substrate	Angle (C_1—Si—C_2) (°)	$LiAlH_4$	RLi (R = alkyl)	RLi (R = aryl)	RLi (R = benzyl or allyl)	RMgX (R = alkyl)	RMgX (R = aryl)	RMgX (R = allyl or benzyl)	Ref.
I (Si—Cl)	<90 [18]	RN					RN		12, 13
I (Si—F)	<90	RN	RN			RN			12, 13
I (Si—OR)	<90	RN	RN			RN			12, 13
II (Si—F)	<90		RN			RN			12
II (Si—OR)	<90	RN	RN			RN			12
II (Si—NMe_2)	<90					RN			12
III (Si—Cl)	93.4	RN							14
IV (Si—Cl)	≃90[a]	RN							15
IV (Si—F)	≃90	RN							15
V (Si—Cl)	92—96 [19]	IN		IN			IN		
V (Si—F)	92—96	Rac							16
V (Si—H)	92—96								
VI (Si—Cl)	≃105 [20]	IN	RN	RN	IN	IN	RN	IN	21, 22
VI (Si—F)	≃105	Rac	RN	RN	RN	RN	RN	IN	21, 22
VI (Si—OMe)	≃105	RN	RN	RN	RN	RN	RN	RN	21, 22
VI (Si—H)	≃105	—	RN	RN	RN	—	—	—	21, 22
R_3Si—Cl[b]	≃109 [23]	IN	IN	IN	IN	IN	IN	IN	24
R_3Si—F	≃109	IN	RN	—	IN	IN	IN	IN	24
R_3Si—OMe	≃109	RN	RN	RN	RN				24
R_3Si—H	≃109	—	RN	RN					24

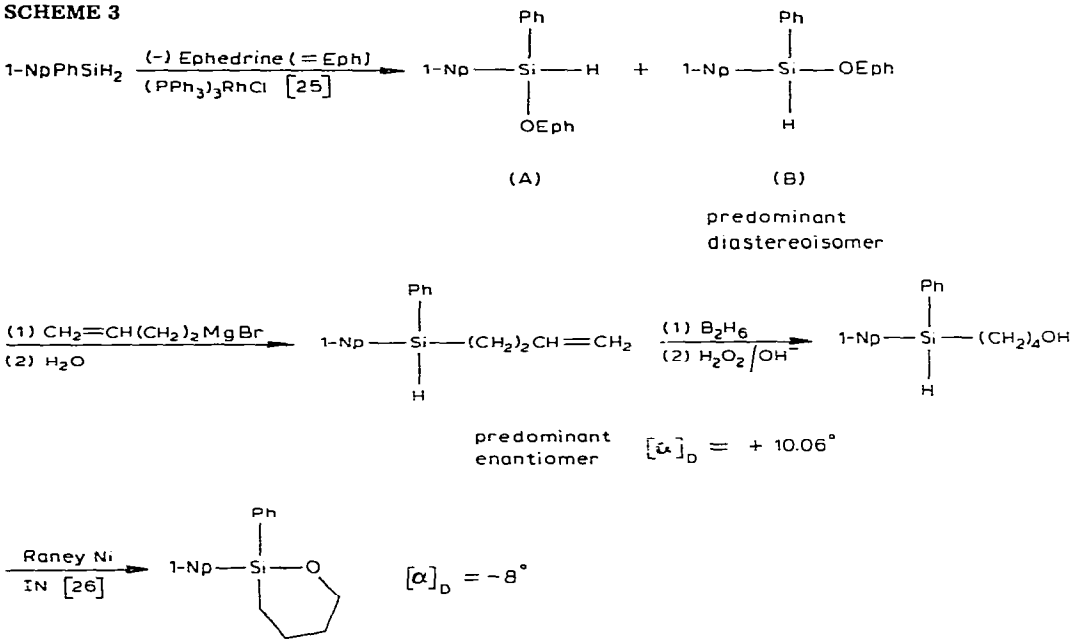
[a] No experimental value is reported in literature: the approximate value has been calculated by use of the following bond lengths [20], ≡Si—Ph = 1.87 Å, ≡Si—1-Np = 1.35 Å, C=C (Aryl) = 1.38 Å. [b] R_3Si—X = 1-NpPhMeSiX

II. Results

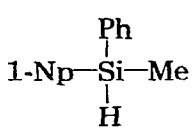
A. Synthesis of the optically active sila-oxa-cycloalcanes VII and VIII

The compound VII was described previously [4a, b]. A convenient route for synthesis of the six-membered ring derivative is shown in Scheme 3.

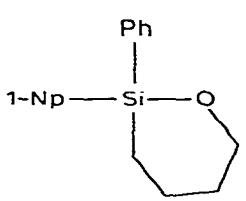
SCHEME 3



It has been shown previously that the coupling reaction between MeMgBr and the diastereoisomeric mixture A + B leads predominantly to (*R*) (+)—1-NpPhMeSi-H [25], the absolute configuration of which is known [2]:



Alkyl Grignard reagents are known always to cleave Si—O bonds with retention of configuration; so it is reasonable to assume the same absolute configuration for (*R*) (+) 1-NpPhMeSi—H and for the substitution product obtained with CH_2=$CH(CH_2)_2MgBr$ as indicated in Scheme 3. Thus the (—)-1-naphthyl-2-phenyl-2-sila-2-oxa-1-cyclohexane has the following absolute configuration.



$[\alpha]_D = -8°$

TABLE 2

STEREOCHEMICAL BEHAVIOR OF ENDOCYCLIC OR LEAVING GROUP

Runs	Nucleophile	Products	1-NpPhMeSi—OMe	Predominant chemistry	
				VII	VIII
1	EtLi	R_3Si—Et	95% RN [2,3]		
2	CH_3Li	R_3Si—CH_3	—	$[\alpha]_D = 8^\circ$ RN [3b]	$[\alpha]_D = -2.6^\circ$ RN
3	CH_3MgBr	R_3Si—CH_3	—	$[\alpha]_D = -8^\circ$ RN [3b]	$[\alpha]_D = -2^\circ$ RN
4	$LiAlH_4$q	R_4Si—H	90% RN [2,3]	$[\alpha]_D = +13^\circ$ RN [3b]	$[\alpha]_D = -7^\circ$ RN
5	$LiAlH_4$/4 CuI/THF	R_3Si—H	55% RN	$[\alpha]_D = -18^\circ$ IN [30]	$[\alpha]_D = -0.6^\circ$ RN
6	CH_2=$CHCH_2Li$	R_3SiCH_2—CH=CH_2	85% RN [b]	$[\alpha]_D = -5^\circ$ IN [3b]	$[\alpha]_D = -2.4^\circ$ RN
7	CH_2=$CHCH_2MgBr$	R_3Si-CH_2—CH=CH_2	—	$[\alpha]_D = -6.5^\circ$ IN [3b]	$[\alpha]_D = +3.3^\circ$ IN
8	p-$CH_3OC_6H_4CH_2Li$	R_3Si—$CH_2C_6H_4$—(p. OCH_3)	90% RN [2,3]	$[\alpha]_D = -4^\circ$ IN	$[\alpha]_D = -2^\circ$ RN
9	$C_6H_5CH_2Li$	R_2Si—CH_2Ph	79% IN [2,3]	$[\alpha]_D = -3^\circ$ IN [3b]	$[\alpha]_D = +4^\circ$ IN
10	$C_6H_5CH_2MgBr$	R_3Si—CH_2Ph	75% IN [2,3]	$[\alpha]_D = -3.7^\circ$ IN [3b]	$[\alpha]_D = +8^\circ$ IN

[a] VII + Nu → $R_1R_2NuSi(CH_2)_3OH$, (VIII) + Nu → $R_1R_2NuSi(CH_2)_4OH$
(=R_3Si—Nu) (=R_3Si—Nu)

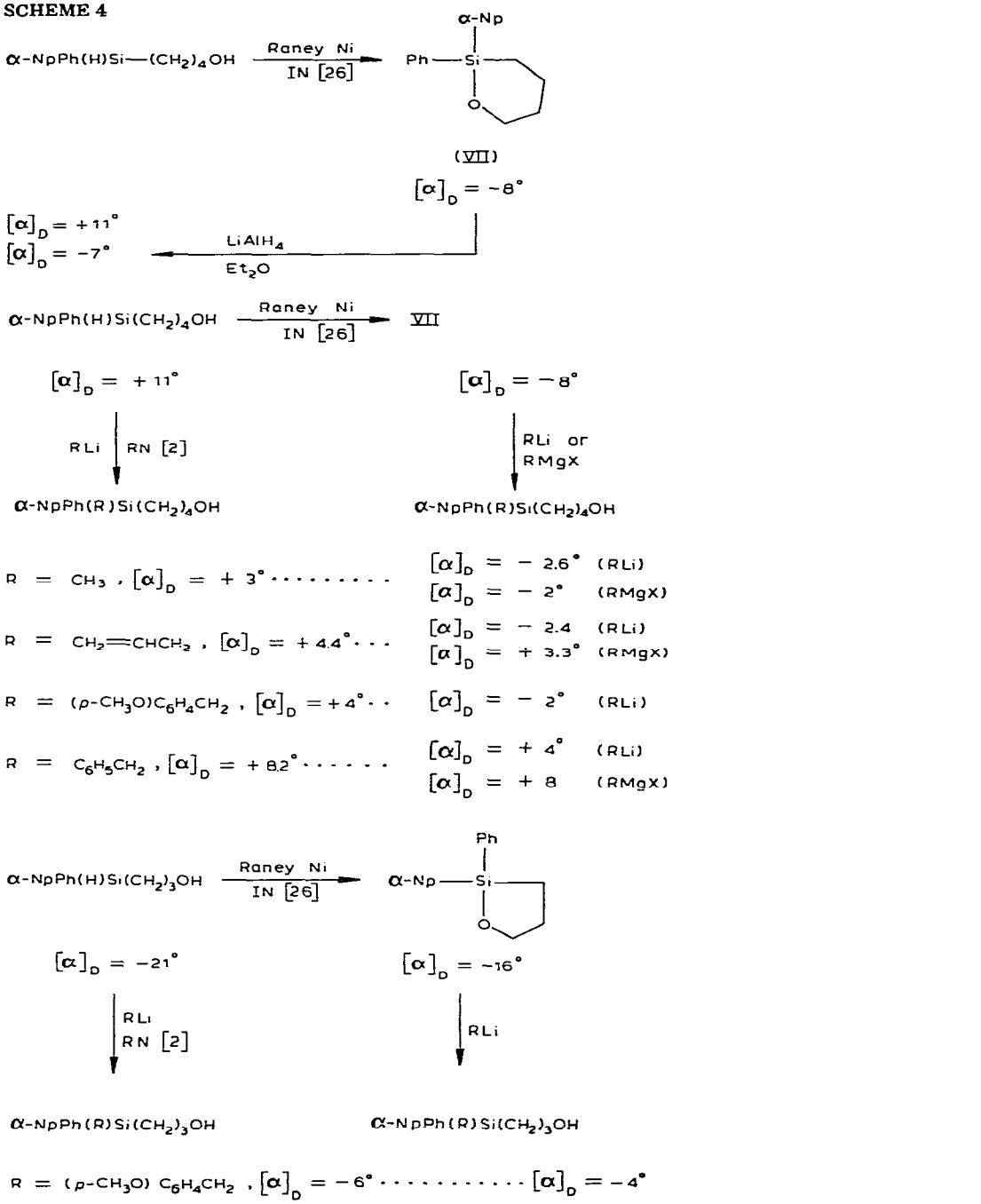
[b] Sommer et al. reported inversion of configuration [27]: in our hands this reaction always in several elements, gave predominant retention.

B. Stereochemical data

Stereochemical data are summarized in Table 2 along with some previously reported data for VII and the acyclic 1-NpPhMeSi—OMe.

The unknown stereochemistries were determined by chemical correlations (Scheme 4):

SCHEME 4



Several points in Table 2 are noteworthy:

(i) Again we see the dominant influence of the nucleophile: cyclic compounds VII and VIII show behaviour similar to that of their acyclic analog R_3Si—OMe. Charge-localized nucleophiles (alkyllithiums or alkyl Grignard reagents) and $LiAlH_4$ lead to the expected stereochemical outcomes in the case of alkoxy leaving groups, i.e., retention of configuration (Table 2, runs 1—4). Charge-delocalized nucleophiles react with inversion (Table 2, runs 7, 9, 10).

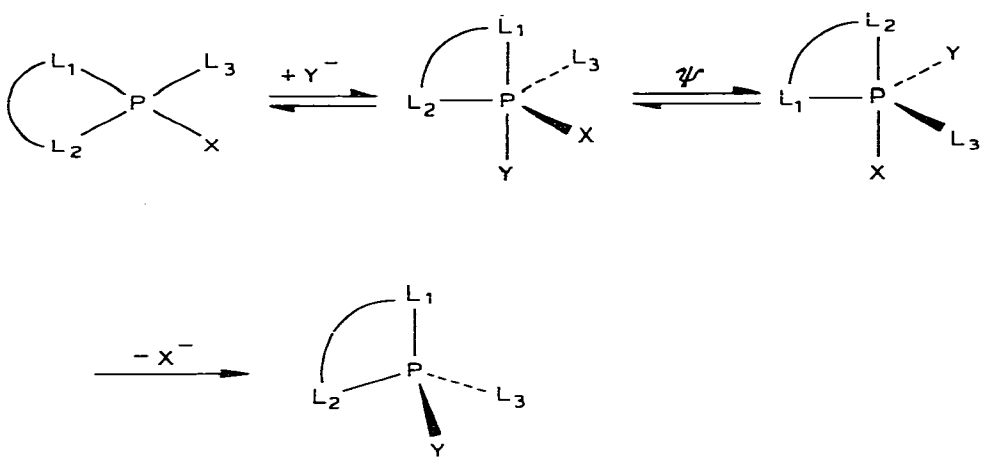
(ii) In borderline cases, some differences are apparent between analogous acyclic and cyclic organosilanes. Nucleophiles such as allyllithium, *p*-methoxybenzyllithium, or $LiAlH_4$-4 CuI lead to inversion in the case of the five-membered ring compound (Table 2, runs 5, 6, 8). On the other hand, the six-membered ring and the acyclic 1-NpPhMeSi—OMe both give retention.

(iii) A strained cyclic geometry shifts the stereochemistry towards inversion for intracyclic leaving groups. This is the opposite of the change towards retention for exocyclic leaving groups as the angle strain at silicon is increased.

III. Discussion

When the phosphorus atom of phospholane oxides and phosphonium ions is incorporated into a four- or five-membered ring, the reduction or displacement reactions proceed, as a rule, with retention of configuration, in contrast to the analogous reactions of acyclic systems where inversion is normal [28]. Ring strain is invoked as the main factor determining the stability of the intermediate. The reasoning is as follows. Four- or five-membered rings are unable to occupy the diequatorial position of a trigonal bipyramidal intermediate and must occupy the apical-equatorial position. Consequently, the nucleophile Y (Scheme 5) displaces the leaving group X with retention.

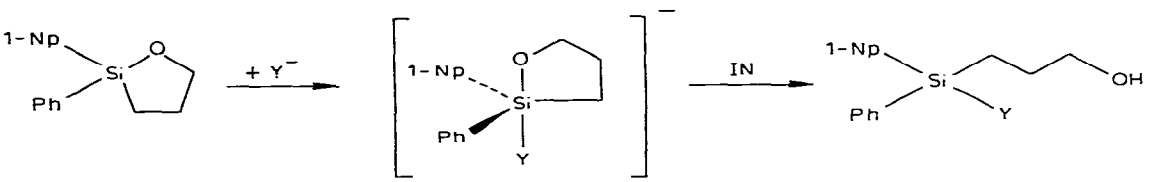
SCHEME 5



With organosilanes, we can also invoke such a factor to explain the stereochemical changes associated with angle strain. This would be in agreement with

the general shift towards retention for exocyclic leaving groups, with a change to inversion for intracyclic leaving groups. For instance, five-membered rings must occupy the preferred apical-equatorial position of a trigonal bipyramidal intermediate with the most electronegative group (oxygen atom) in the apical position (Scheme 6), so that inversion is favoured.

SCHEME 6



However, in the case of the nucleophilic displacements at silicon, all the large body of results obtained for variation of ring size, the nature of the leaving group and of the nucleophile permit a more refined analysis, and the following observations can be made.

(i) Except for the highly strained silacyclobutanes, ring strain does not overcome the dominant influence of the electronic character of the nucleophile (Tables 1 and 2) on the stereochemistry. For instance, the oxa-sila-cycloalkanes VII and VIII behave very similarly to the analogous acyclic 1-NpPhMeSi—OMe. Thus the stability of the intermediate does not govern the stereochemical path.

(ii) The results for exocyclic leaving groups show that there is a gradual change of the stereochemistry from inversion to retention when the angle strain at silicon is increased, as depicted in Scheme 7. The nature of the substituents attached to silicon must be taken into account; compared with alkyl groups, aryl groups change the nature (i.e. the hybridization) of the Si—X bond, and thus slightly influence the stereochemistry. This influence cannot be easily explained in

SCHEME 7

a) alkyl substituents around silicon:

RN ⟶	INV
<90°	92—96°
sila-cyclobutanes I and II	sila-cyclopentanes V

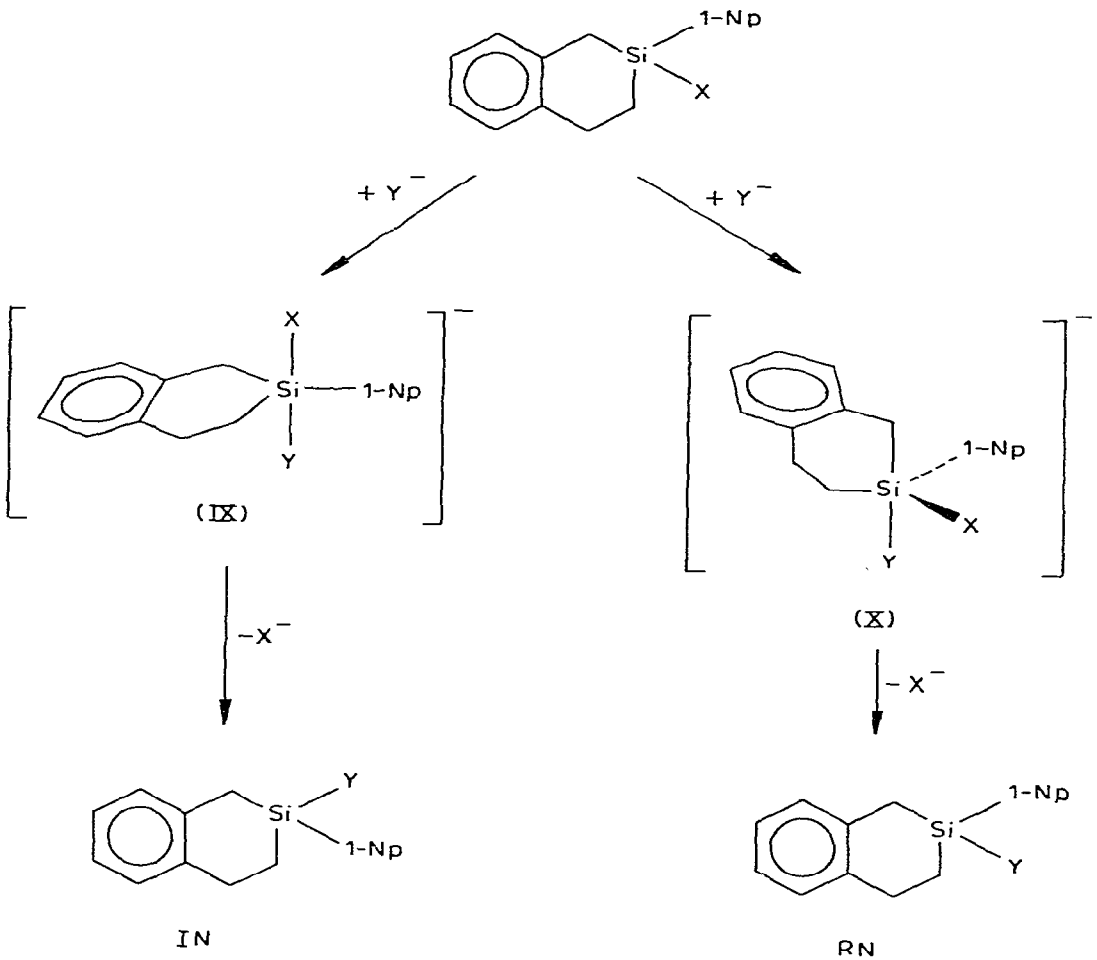
b) aryl substituents around silicon:

RN ⟶		INV
90—93,4°	105°	109°
III and IV	V	acyclic

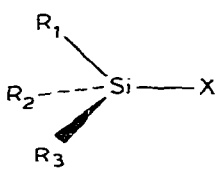
terms of geometric considerations. In particular the ring strain does not provide an explanation of why inversion is so disfavoured in the case of the six-membered ring. The size of the C_1—Si—C_2 angle, viz. 105°, suggests that intermediates such as IX and X have equal energies, and so inversion and retention would be expected together (Scheme 8).

Thus, we think that the better explanation is that proposed by Nguyên Trong Anh and C. Minot [1], which involves a change of the hybridization of

SCHEME 8



the Si—R bonds around the tetracoordinated silicon atom:



If the R_2SiR_3 angle becomes smaller than the tetrahedral value, the R_1SiX angle becomes larger than 109°28′. The four hybrid atomic orbitals of Si are no longer equivalent. The two used for making the SiR_2 and SiR_3 bonds have less *s* character than a sp^3 hybrid orbital, while the two remaining atomic orbitals acquire more *s* character. The authors show from orbital calculation that an increase in the *s* character implies an easier nucleophilic frontside attack at the σ^* Si—X, and, therefore, a greater proportion of retention. It follows that if the Si atom is included in a strained ring while X remains exocyclic, the percentage of the retention will increase. Similar reasoning shows that if Si and X

are both in the ring, inversion is favored. These conclusions agree well with the experimental data.

IV. Conclusion

The results show the influence of the structure of the organosilane on the stereochemistry of nucleophilic substitutions at silicon. There is a gradual displacement of the stereochemistry from inversion to retention upon increasing the angle strain at silicon, but this does not overcome the dominant influence of the leaving group ability of the group being replaced [3] and of the electronic character of the nucleophile [2,4]. The last two factors are the controlling factors while angle strain at silicon can only influence the predominant stereochemistry in borderline cases.

The stereochemical data are easily explained in terms of change of the hybridization of the Si—R bonds around the silicon atom with angle strain.

V. Experimental

Materials

The preparations of optically active (—) 1-NpPhMeSiOMe [26] and (—)-1-Np-2-phenyl-2-sila-2-oxa-1-cyclopentane (VII) [36] were described previously.

Preparation of (—) 1-Np-2 phenyl-2-sila-2-oxa-1-cyclohexane VIII:

The synthesis of VIII is shown in Scheme 3.

(a) 1-NpPhSi(H)$CH_2CH_2CH{=}CH_2$. To 9.25 mg of $(PPh_3)_3RhCl$ (10^{-5} mol) in 20 ml of anhydrous benzene at room temperature, were added 3.3 g (2×10^{-2} mol) of (—) ephedrine in 20 ml of benzene. 4.68 g of 1-NpPhSiH_2 were then added. When the hydrogen evolution had ceased, 30 ml of 2*M* $CH_2{=}CH$-$(CH_2)_2MgBr$ were quickly added. The reaction was allowed to proceed to completion at room temperature. The mixture was hydrolyzed with acid (10% HCl), extracted with ether and dried over Na_2SO_4. The solvent was pumped off and the oily residue chromatographed on silica gel (toluene/hexane: 1/9), to give 4.6 g of pure (+) 1-NpPhSi(H)$CH_2CH_2CH{=}CH_2$ (yield 80%; $[\alpha]_D = +10.6°$). Anal. Found: C, 81.18; H, 6.85. $SiC_{20}H_{20}$ Calcd., C, 83.33; H, 6.94%. NMR δ(ppm), 6.4—8 (12 H, m).

(b) 1-NpPhSi(H)$CH_2CH_2CH_2CH_2$-OH. This alcohol was prepared by the method described by H.C. Brown et al. [29].

To 576 mg of 1-NpPhSi(H)$CH_2CH_2CH{=}CH_2$ (20 mmol) and 200 mg of $NaBH_4$ in 10 ml of anhydrous THF, was added 1 g of BF_3· Et_2O in 10 ml of THF at 0°C and under N_2. The mixture was stirred for one hour at room temperature. The solution was treated with H_2O at 0°C, and then with 5 ml of H_2O_2 (110 v.) under basic conditions. The mixture was stirred for one hour before extraction with ether. The solvent was pumped off and the oily residue chromatographed on acid alumina ($CHCl_3$ as eluant). 430 mg of pure (+)-1-NpPhSi(H)$CH_2CH_2CH_2CH_2OH$ (yield 70%; $[\alpha]_D = +11°$, C. 10, benzene) were recovered; it was identified by comparison of the NMR and IR spectra with an authentic racemic sample prepared by another method [30].

(c) 1-Np-2-Ph-2-sila-2-oxa-1-cyclohexane, VIII. To 306 mg of the above alco-

hol ($[\alpha]_D$ = +11°) in 20 ml of anhydrous benzene were added 60 mg of Raney Ni. Reaction was allowed to proceed at room temperature under nitrogen until hydrogen evolution ceased. The solution was filtered and evaporated to give optically active compound VIII, which was purified by column chromatography. The pure optically active product VIII was isolated in 90% yield ($[\alpha]_D$ = −8°, C. 10, benzene) and identified by comparison of NMR and IR spectra with an authentic racemic sample prepared by another method [30].

Reactions

(a) Reactions of VIII with organolithium and Grignard reagents

General procedure. All reactions were carried out under nitrogen. An excess of the organometallic reagent (RLi/VIII ≃2 and RMgX/VIII ≃4) was usually added to the silane in anhydrous diethyl ether. The mixture was stirred until complete reaction (heating was necessary in the case of the Grignard reagents) and then hydrolyzed with acid (10% HCl). The silanes were purified by preparative TLC (silica gel PF 254) using chloroform as eluant, and identified by comparison of IR and NMR spectra with authentic racemic samples. The $[\alpha]_D$ values were measured with a Perkin-Elmer 151 polarimeter.

MeLi. Treatment of (—) 1-Np-2-Ph-2-sila-2-oxa-1-cyclohexane (0.5 mmol) with a MeLi solution (1.4 *M*, 0.8 cm^3) in ether for 12 h, gave 1-NpPhMeSi-$(CH_2)_4OH$. Chromatography over silica gel with $CHCl_3$ gave (—) 1-NpPhMeSi-$(CH_2)_4OH$, $[\alpha]_D$ = −2.6° (C.10, benzene); yield 85%.

MeMgBr. To a solution of (—) VIII (0.5 mmol) in ether as solvent was added 2 cm^3 of MeMgBr (1.1 *M*) in ether. The mixture was heated under reflux for 10 h. After the usual work-up, (—) 1-NpPhMeSi$(CH_2)_4OH$ was obtained ($[\alpha]_D$ = −2°, C.10, benzene; yield 80%).

CH_2=CHCH$_2$Li. Treatment of (—) VIII (0.5 mmol) with 2 mmol of CH_2=$CHCH_2Li$ prepared by Seyferth's method [31] in ether solvent for 24 h, gave 1-NpPh(CH_2=$CHCH_2$)Si$(CH_2)_4OH$. Chromatography over silica gel (eluant = $CHCl_3$) gave (—) 1-NpPh(CH_2=$CHCH_2$)Si$(CH_2)_4OH$, $[\alpha]_D$ = −2.4° (C.10, benzene), yield 75%.

CH_2=$CHCH_2MgBr$. Treatment of (—) VIII (0.5 mmol) with 2 mmol of CH_2=$CHCH_2MgBr$ in refluxing ether for 48 h gave (+) 1-NpPh(CH_2=$CHCH_2$)Si-$(CH_2)_4OH$, $[\alpha]_D$ = +3.3° (C.10, benzene), yield 65%.

p-$CH_3OC_6CH_2Li$. Treatment of (—) VIII (0.5 mmol) with 2 mmol of *p*-$CH_3OC_6H_4CH_2Li$ in ether at room temperature for 12 h gave (—) 1-NpPh-($CH_3OC_6H_4CH_2$)Si$(CH_2)_4OH$ $[\alpha]_D$ = −2° (C.10, benzene), yield 80%. Anal. found: C, 78.82; H, 6.78; Si, 6.61. Calc. C, 78.87; H, 7.04; Si, 6.57. IR (cm^{-1}): 3600, 3520—3400 (O—H) 1590. NMR: δ(ppm) 0.6—2.3 (7 H, m); 2.8 (2 H, s); 3.4 (2 H, m) 3.6 (3 H, s); 6.4—S (16 H, m).

$C_6H_5CH_2Li$. 2 mmol of $C_6H_5CH_2Li$ were added to 1 mmol of (—) VIII in ether and the mixture was refluxed for 5 h. After the usual work-up (+) 1-NpPh-($C_6H_5CH_2$)Si$(CH_2)_4OH$ was obtained in 80% yield ($[\alpha]_D$ = +4°, C.10, benzene).

$C_6H_5CH_2MgBr$. 4 mmol of $C_6H_5CH_2MgBr$ were added to 1 mmol of (—) VIII in ether: the mixture was heated under reflux for 48 h. After the usual work-up, (+) 1-NpPh($C_6H_5CH_2$)Si$(CH_2)_4OH$ was obtained in 50% yield ($[\alpha]_D$ = +8°, C.10, benzene).

(b) Reduction of VIII with $LiAlH_4$ and with $LiAlH_4$/4 CuI

Solutions of $LiAlH_4$ in ether were filtered before use and standardized by Felkin's method [32]. The $LiAlH_4$/4 CuI reagent was prepared as described by Ashby et al. [33]. The reactions were carried out under N_2. The reaction mixture was stirred until complete reaction and then hydrolyzed with cold, dilute hydrochloric acid (10%). The silanes were purified by preparative TLC (silica cel PF 254) using chloroform as eluant, and identified by comparison of the IR and NMR spectra with an authentic racemic sample [30].

$LiAlH_4$. To 1 ml of a $LiAlH_4$ solution in ether (1.38*M*), were added 0.5 mmol of VIII in anhydrous ether. The mixture was stirred under reflux for 2 h. After the usual work-up (—) 1-NpPhSi(H)$CH_2CH_2CH_2CH_2OH$ was obtained in quantitative yield ($[\alpha]_D$ = —7°, C.10, benzene).

$LiAlH_4$/4 CuI. The $LiAlH_4$/CuI/VIII ratio was 2/8/1. VIII in THF was added dropwise to the black $LiAlH_4$/4 CuI mixture at 0°C under N_2. The mixture was allowed to warm to room temperature to ensure complete reaction. (—) 1-NpPhSi(H)$(CH_2)_4OH$ was obtained in 40% yield ($[\alpha]_D$ = —0.6°, C.10, benzene).

Reactions enabling correlations of configuration. The compounds 1-NpPh(R)Si$(CH_2)_4OH$, R = CH_3, CH_2=$CHCH_2Li$, $PhCH_2$, *p*-$CH_3OC_6CH_2$ were obtained by coupling the appropriate organolithium with the (+) 1-NpPh(H)Si$(CH_2)_4OH$ ($[\alpha]_D$ = +11°, C.10, benzene).

To a standardized solution of the organolithium in ether, a solution of the optically active alcohol in ether (RLi/alcohol ratio = 4/1) was added dropwise. The reaction was allowed to proceed at room temperature. After standard work-up, the silanes were purified by TLC (silica gel PF 254, eluant: $CHCl_3$) and identified by comparison of IR and NMR spectra with authentic racemic samples [30].

R = CH_3	$[\alpha]_D$ = +3°, C.10, benzene
R = CH_2=$CHCH_2$	$[\alpha]_D$ = +4.4°, C.10, benzene
R = *p*-$CH_3OC_6H_4CH_2$	$[\alpha]_D$ = +4°, C.10, Benzene
R = $C_6H_5CH_2$	$[\alpha]_D$ = +8.2°, C.10, benzene

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