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NUCLEOPHILIC SUBSTITUTION AT SILICON: INFLUENCE OF THE ATTACKING ALLYLLITHIUM AND ARYLOXIDE ANION ON THE STEREOCHEMISTRY AND A SIMPLE MECHANISTIC PROPOSAL

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Summary

The stereochemistry of reaction of some optically active organosilanes $R_3Si^*—X$ with a representative series of *p*-substituted aryloxides and allyllithium emphasizes the relative influence of the attacking anion.

For a given leaving group, the stereochemistry essentially depends upon the electronic character of *p*-substituents and of the iron-pair dissociation of the aryloxides. This dependence is also supported by the stereochemical behavior of allyllithium.

A simple mechanistic interpretation of the data is proposed, based on a description of nucleophilic substitutions at silicon as a frontier-orbitals process.

I. Introduction

In previous papers [1,2] we reported stereochemical and kinetic data for reactions between alkyl organolithiums or $LiAlH_4$ and some chiral organosilanes. They reveal in both cases the dominant influence of the electronic character of the nucleophile on the mechanism. Either hard reagents with a localized negative charge, such as alkyllithiums, or the softer $LiAlH_4$ support this dependance.

In the present work, we extend this study to delocalized π-electron nucleophiles, such as allyllithium, and *p*-substituted phenoxides. Since our main objective is to focus attention on the relation between the electronic character of the nucleophile and the corresponding stereochemical outcome. The follow-

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* In honor of Professor Henry Gilman for his pioneering and outstanding research which was fundamental to the development of organometallic chemistry.

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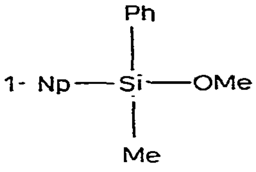
ing two main reasons suggest an investigation of the behaviour of these reagents:

1) The electron distribution in phenoxide reagents is well known to be directed by the + or — *M* effect of the substituent X attached in the *para* position (). Therefore clear changes of stereochemistry can be expected according to the nature of X.

2) The solvation of the M^+ counter-cation can afford further information concerning the influence of the electrophilic assistance on the mechanism of the nucleophilic substitutions at silicon.

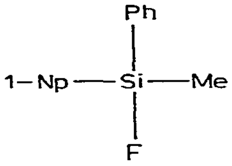
TABLE 1

STEREOCHEMICAL BEHAVIOUR OF ALLYLLITHIUM



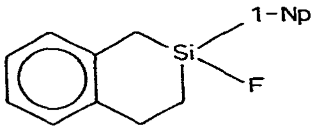
$[\alpha]_D = -16.5°$ [3]

(I)



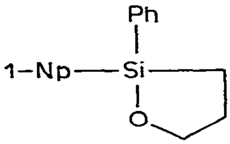
$[\alpha]_D = +47°$ [3]

(II)



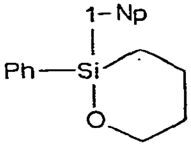
$[\alpha]_D = -34°$ [4]

(III)



$[\alpha]_D = -16°$ [5]

(IV)



$[\alpha]_D = -8°$ [6]

(V)

Runs	Substrate	Predominant stereochemistry with	
		allyl-Li/ether [b]	allyl-Li/K_{Li^+} [a]/ether
1	I	85% RN [c]	75% RN
2	II	71% IN	90% IN
3	III	87% RN [10]	75% RN
4	IV	$[\alpha]_D = -5°$ IN [5]	$[\alpha]_D = -10°$ IN
5	V	$[\alpha]_D = -1.3°$ RN [6]	$[\alpha]_D = -1°$ RN

[a] K_{Li^+} is Kryptofix 211, Merck (tetraoxa-4,7,13,18-diaza-1,10-bicyclo-8,5,5-eicosane), specific for Li^+ cation [7]. [b] Allyllithium was prepared according to the Seyferth method [8]. [c] Sommer et al. reported previously predominant inversion of configuration (55% IN) [9]. In our hands, the same reaction leads several times to predominant retention (85% RN).

II. Results

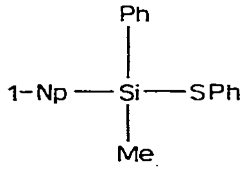
1) Coupling reactions with allyllithium

Table 1 summarizes the results for substitution at silicon. The predominant stereochemistry is obtained as indicated below. (i) The $[\alpha]_D$ of optically pure R_3Si allyl corresponding respectively to I, II and III are known [3,10]; a predominant stereochemistry of 90% inversion indicates a reaction path involving 90% inversion and 10% retention, thereby giving a product that is 80% optically pure. (ii) Chiral organosilanes IV and V are liquid and we do not know the corresponding maximum $[\alpha]_D$. Therefore the proportion of retention or inversion cannot be given. Predominant stereochemistry was determined by chemical correlations [5,6].

In a previous paper [1], we noted that complexation reagents or polar solvents which favour dissociation of ion-pairs, always change the stereochemistry to retention in the case of alkyllithiums. The opposite effect is observed with the resonance-stabilized allyllithium; the complexation of the lithium cation favours inversion. It is consistent with an increase of the soft character of the allyl anion when Li^+ is trapped.

2) Coupling reactions with phenoxide reagents

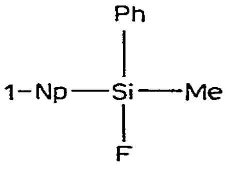
We investigated these reactions for the following organosilanes:



$$\text{1-Np}-\overset{\text{Ph}}{\underset{\text{Me}}{\text{Si}}}-\text{SPh}$$

$[\alpha]_D = +27°$ [11]

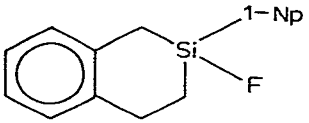
(VI)



$$\text{1-Np}-\overset{\text{Ph}}{\underset{\text{F}}{\text{Si}}}-\text{Me}$$

$[\alpha]_D = +47°$

(II)



$[\alpha]_D = -34°$

(III)

The stereochemical data are summarized in Table 2.

The predominant stereochemistries were determined as indicated in Scheme 1. The stereochemistry of eq. 1 has been determined previously [11]. The metal-catalyzed reaction of phenols (eq. 2) with Si—H bonds occurs with inversion [13]. Phenolysis of Si—Cl bonds is known to involve inversion of configuration [14] (eq. 3): this assignment is based on the accepted assumption that R_3Si^*—Cl reacts always with inversion of configuration [3,6]. Cleavage of Si—X bonds by dibal in hexane (dibal = diisobutylaluminium hydride) occurs always with retention [15] (eq. 4). Moreover (+)1-NpPhMeSiH and (+)1-NpPhMeSiSPh have opposite configurations; (+)1-NpPhMeSiH and (+)1-NpPhMeSiF have the same configurations.

The above data have the following implications:

1) The stereochemical outcome depends strongly upon the nature of the *para*-substituent Y. The most significant data are observed in the case of the (+)1-NpPhMeSi-SPh. The electron-acceptor nitro group favors a delocalization

TABLE 2

STEREOCHEMICAL BEHAVIOUR OF PHENOXIDE REAGENTS

Run	Nucleophile (solvent)	Predominant stereochemistry			
		VI (SS %) [a]	II (SS %) [a]	III (SS %) [b]	VII [c]
1	p-$MeOC_6H_4ONa$ (benzene)	$RN[\alpha]_D = +4°$ (72)			
2	p-$MeOC_6H_4ONa$ (THF)	$RN[\alpha]_D = +6°$ (83)	$RN[\alpha]_D = -4.5°$ (75)	$RN[\alpha]_D = -24°$ (90)	$RN[\alpha]_D = +8.5°$
3	p-$MeOC_6H_4O[N(n\text{-}Bu)_4]$ (THF)	$RN[\alpha]_D = +8°$ (94)			
4	p-$MeOC_6H_4ONa/K_{Na^+}$ [d] (THF)	$RN[\alpha]_D = +9°$ (100)	$RN[\alpha]_D = -6°$ (83)		
5	C_6H_5ONa (benzene)	$IN[\alpha]_D = +2°$ (62)			
6	C_6H_5ONa (THF)	$IN[\alpha]_D = +2°$ (62)	$RN[\alpha]_D = +3°$ (66)	$RN[\alpha]_D = -45°$ (90)	$IN[\alpha]_D = -2.6°$
7	$C_6H_5O[N(n\text{-}Bu)_4]$ (THF)	$IN[\alpha]_D = +1.5°$ (60)			
8	C_6H_5ONa/K_{Na^+} [d] (THF)	$IN[\alpha]_D = +5°$ (76)	$IN[\alpha]_D = -2.5°$ (65)		
9	p-$NO_2C_6H_4ONa$ (benzene)	$IN[\alpha]_D = +2.5°$ (65)			
10	p-$NO_2C_6H_4ONa$ (THF)	$IN[\alpha]_D = +3°$ (69)	$RN[\alpha]_D = +0.5°$ (53)		
11	p-$NO_2C_6H_4O[N(N\text{-}Bu)_4]$ (THF)	$IN[\alpha]_D = +5°$ (82)	$IN[\alpha]_D = -4°$ (75)		
12	p-$NO_2C_6H_4ONa/K_{Na^+}$ [d] (THF)	$IN[\alpha]_D = +8°$ (100)			

[a] SS, %. Our purpose is to report comparative variations in the stereochemistry of substitution with the electronic character of the aryloxide anions. Since we do not know the maximum $[\alpha]_D$ of the compounds 1-NpPhMeSiOC$_6$H$_4$(p-Y) with Y = MeO, H or NO$_2$, the variation of stereoselectivities is evaluated as follows:

Reactions carried out with p-methoxyphenoxides: the experimental higher $[\alpha]_D$ is found for reaction 4. This value is assigned as the $[\alpha]_{max}$ in the equation,

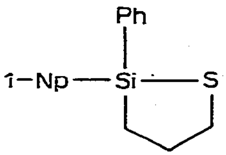
$$SS = \frac{[\alpha]_D \text{ exp.} + [\alpha]_D \text{ max.}}{2\,[\alpha]_D \text{ max.}} \times 100\%$$

Reactions carried out with phenoxides and p-nitrophenoxides. The same approximation is made with:

$[\alpha]_D$ max = $-8.7°$ for 1-NpPhMeSi-OC$_6$H$_5$

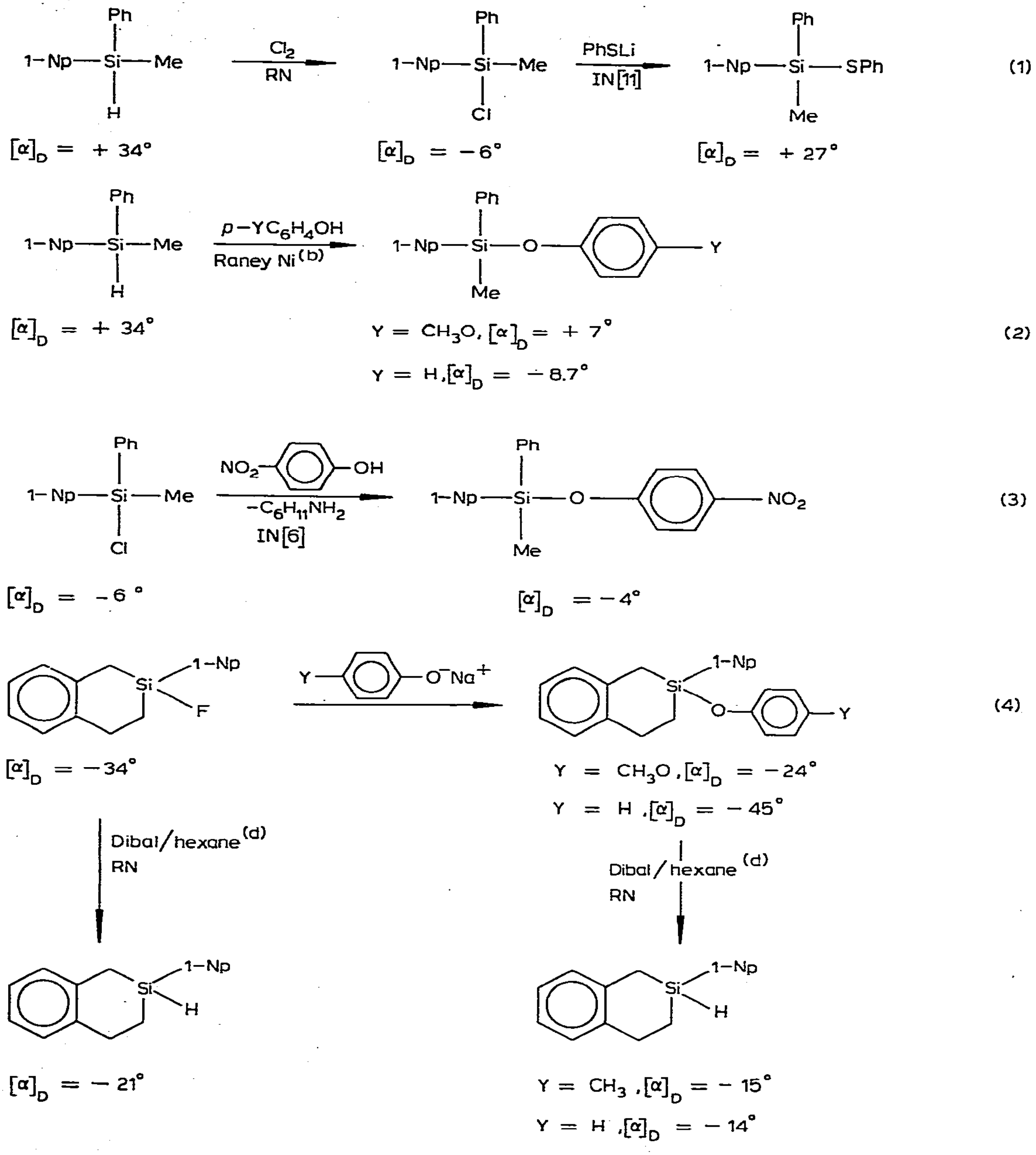
$[\alpha]_D$ max = $+8°$ for 1-NpPhMeSiOC$_6$H$_4$NO$_2$

[b] SS (%) based on the specific rotation of optically pure R$_3$SiH ($[\alpha]_D = -21°$) [4]. [c] See ref. 12. VII =



, $[\alpha]_D = +51°$. [d] K_{Na^+} = Kryptofix 221, Merck (pentaoxa-4,7,13,21-diaza-1,10-bicyclo-8,8,5-tricosane).

SCHEME 1



of the negative charge and the *p*-nitrophenoxide (soft reagent) leads to inversion. On the contrary, the *p*-methoxyphenoxide, in which the negative charge is more localized on the oxygen atom, reacts always with retention. These data are consistent with a mechanistic process controlled by the electronic character of the nucleophile.

2) The influence of the ion-pair dissociation on the stereochemistry also provides good evidence for such a mechanism. A more dissociating solvent than

benzene (THF) or a complexing agent for the Na$^+$ cation (K_{Na^+}) favours retention with *p*-methoxyphenoxide (runs 2, 4): an increase of the ionic radius of the cation leads to a similar change (run 3). The ion-pair dissociation enhances retention. The *p*-methoxyphenoxide behaves as an harder reagent in which the methoxy group would prevent the delocalization of the negative charge. In contrast, similar ion-pair dissociation favors the delocalization of the negative charge in the case of *p*-nitrophenoxide anion, which behaves as a softer reagent and enhanced inversion is observed (run 12).

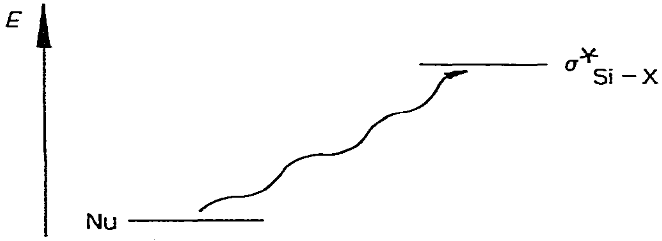
3) Finally these data show the dependence of the stereochemistry upon the nature of the leaving group and the geometry of the organosilane. For instance, a comparison of (+)-1-NpPhMeSiSPh and (+)1-NpPhMeSiF shows that the fluorine leaving group leads preferentially to retention (runs 2, 6 and 10). The cyclic strain in compound III (runs 2 and 6) leads also to an overall change of the stereochemistry towards retention. These two factors have been previously discussed in detail [6,11,16].

III. Mechanism and comments

Recently [17], Nguyên Trong Anh and C. Minot report a rationalization of the stereochemistries at silicon by an extension of Salem's treatment of the Walden inversion [18],

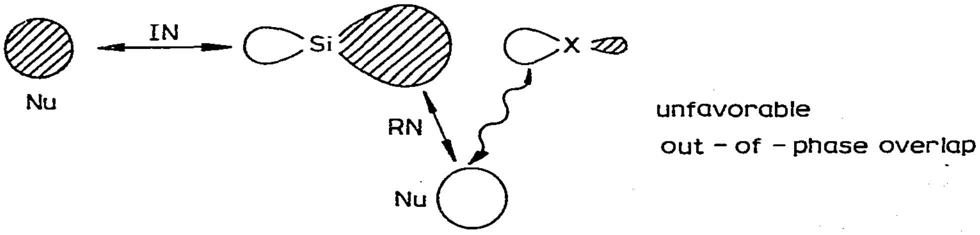
Frontier-orbitals approximation is assumed, i.e., the major interaction during the reaction occurs between the nucleophile's HOMO and the substrate's LUMO σ^*(Si—X) (Scheme 2).

SCHEME 2



The calculated structure of the latter is shown below, with the large lobes of the hydrid AO's pointing towards each other (Scheme 3).

SCHEME 3



Front-side attack, corresponding to an attack on the large lobe of silicon, leads to retention. When the unfavorable out-of-phase overlap between the nucleophile and the leaving group orbital predominates, nucleophilic attack occurs at the rear of the molecule opposite to X, leading to inversion.

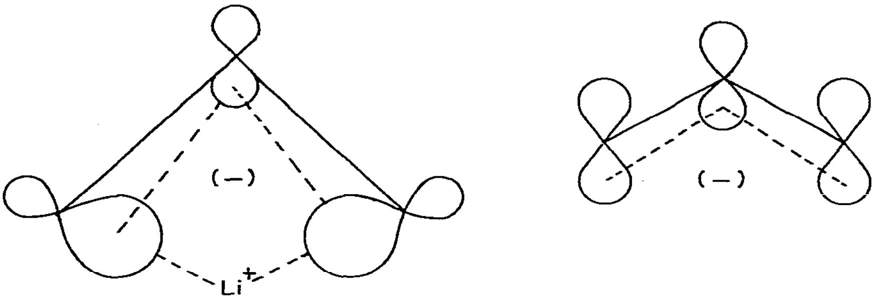
As we outlined in previous papers [1,19] for alkyllithiums and AlH_4^-, the dominant influence of the electronic character of the nucleophile on the stereochemistry can be analyzed as follows. A hard reagent is usually a small one [20] with contracted valence orbitals. Its long range out-of-phase unfavorable overlap with the leaving group is negligible and front-side attack leading to retention is therefore possible (Scheme 3). In contrast, a soft nucleophile has diffuse valence orbitals [20]. It has a sizable out-of-phase overlap with the leaving group and the stereochemistry is shifted towards inversion (Scheme 3).

Our purpose is now to generalize the above approach to allyllithium and phenoxides:

a) Allyllithium is a softer nucleophile compared to alkyllithiums. It leads to inversion in the case of II and IV instead of the retention of configuration observed for alkyllithiums [5,21]. When the Li^+ is complexed, the proportion of inversion is always increased (Table 1). We noted an opposite behavior in the case of alkyllithiums [1], i.e., a shift towards retention.

These experimental facts are easily rationalized using the approach of Nguyên Trong Anh and C. Minot. For instance, in the case of the alkyllithiums [1,19], we assumed that, when the Li^+ cation is trapped (naked anion), the negative charge is more concentrated on the reactive carbon center, i.e., we are faced with a "harder" nucleophile with smaller valence orbitals: therefore, retention is favored (Scheme 3). For allyllithium, Schleyer et al. have shown that the valence orbitals are centered towards Li^+ [22]: they have some sp^3 character. In contrast, for the naked allyl anion, the valence orbitals have a pure p character [23], and thus they are more diffuse. In the latter case, the unfavorable out-of-phase overlap with the leaving group is increased: the rear-side attack of the nucleophile is promoted and, therefore, more inversion is observed when Li^+ is trapped (Scheme 4).

SCHEME 4



Supposed shape of the allyllithium's HOMO

Supposed shape of the naked allyl anion's HOMO

b) The behaviour of the phenoxide anions can be explained by similar arguments:

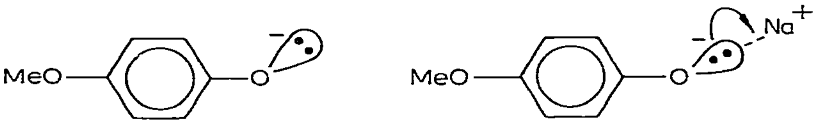
(i) In the case of the p-methoxyphenoxide anion, Taft et al. have shown that the oxygen atom has a high degree of sp^3 character [24]. We are faced with a nucleophile which is quite similar to hard alkyl anions from an electronic point of view, i.e., a nucleophile with contracted valence orbitals around oxygen. The unfavorable out-of-phase overlap with the leaving group is minimized (Scheme 3). A front-side attack, leading to retention, is therefore possible.

In contrast, the oxygen atom of the *p*-nitrophenoxide anions has a high degree of sp^2 character. The *p* character of the nucleophilic center, as we assumed in the case of the allyl anion, implies a delocalization of the negative charge over the aromatic system [24]. We are faced with diffuse valence orbitals around oxygen, and, thus, the sizable overlap with the leaving group prevails. A rear-side attack leading to inversion is so favored (Scheme 3).

(ii) Concerning the effect of the counter cation (Table 2), we propose similar explanations to those proposed in the case of alkyllithium [1] and allyllithium reagents. Sodium *p*-methoxyphenoxide has a behavior similar to that of alkyllithium reagents. It has a negative charge on oxygen which is in part transferred to the Na^+ cation. When the Na^+ cation is trapped (naked anion), the negative charge is concentrated on the oxygen reactive center (Scheme 5). In the latter case, as the valence orbitals are smaller, the out-of-phase overlap with the leaving group is diminished and, therefore, retention is favored (Scheme 3). This is in agreement with the experimental data. The retention increases when the ionic pair is separated (Table 2).

SCHEME 5

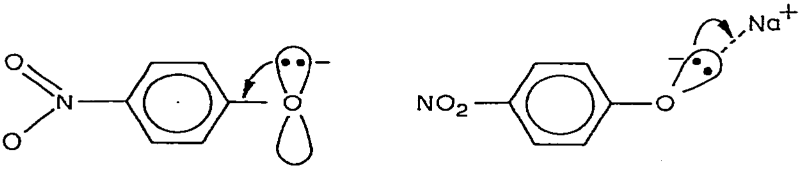
Supposed shapes of the HOMO of the *p*-methoxyphenoxide anion and of the sodium *p*-methoxyphenoxide



In contrast, the sodium *p*-nitrophenoxide is similar to the allyllithium case. The counter cation reduces the *p*-character of the oxygen and prevents the delocalization of the negative charge over the aromatic system. The valence orbitals are centered towards Na^+, while for the naked anion they are more disposable or, in other words, more diffuse (Scheme 6). Therefore, in the latter case, the unfavorable out-of-phase overlap with the leaving group is increased: the rear-side attack of the nucleophile is promoted and, therefore, inversion (Table 2).

SCHEME 6

Supposed shapes of the HOMO of the *p*-nitrophenoxide anion and of the sodium *p*-nitrophenoxide.



IV. Experimental procedure

Materials

The optically active organosilanes were prepared by published methods, viz. (—)1-NpPhSiOMe [13]; (+)1-NpPhMeSiF [14]; (+)1-NpPhMeSiSPh [11]; 1-Np-2-sila-2-fluoro-2-tetrahydro-1,2,3,4 naphthalene [4]; 1-Np-2-phenyl-2-sila-2-oxa-1-cyclopentane [5]; 1-Np-2-phenyl-2-sila-2-oxa-1-cyclohexane [6].

Coupling reactions with allyllithium

The reactions were carried out under inert atmosphere. The allyllithium was prepared by Seyferth's method [8]. An excess of the organometallic reagent (organosilane: RM, 1 : 4) was added to a solution of the organosilane in anhydrous ether. The reaction mixture was stirred at room temperature until complete reaction. The reaction mixture was hydrolyzed with 2 *N* HCl, extracted with ether, and dried over anhydrous magnesium sulfate. Solvent was removed and the residue was chromatographed over SiO_2 (eluent, benzene : pentane, 10 : 90). The silanes were identified by comparison with IR and NMR spectra of authentic samples [4,5,6,11,14]. The $[\alpha]_D$ values were measured with a Perkin-Elmer 151 polarimeter (Table 1).

The allyllithium/K_{Li^+} reagent was prepared by slow addition of allyllithium in ether to an equimolecular amount of K_{Li^+} in the same solvent. The reactions were carried out as described in the case of the allyllithium.

Coupling reactions with phenoxides

Sodium *p*-substituted phenoxides were prepared from the corresponding phenols and sodium hydride dispersion in ether. Sodium salts were washed with ether, and dried in vacuo just prior to use. Tetrabutylammonium aryloxides were prepared by a published method [25].

The reactions were carried out under inert atmosphere. In a typical experiment, (+)1-NpPhMeSiSPh (0.005 mol) and sodium *p*-methoxyphenoxide (1.48 g; 0.010 mol) were dissolved in 20 ml of freshly distilled benzene or THF. The mixture was stirred at room temperature until complete reaction for 3 h. The solvent was removed under vacuo. The residue was extracted with pentane and chromatographed by TLC (SiO_2; eluent : $CHCl_3$). 1-NpPhMeSiOC_6H_4OMe was characterized by comparison with IR and NMR spectra of an authentic sample. The $[\alpha]_D$ value was measured with a Perkin-Elmer 151 polarimeter (Table 2).

The aryloxide-K_{Na^+} reagent was prepared by addition of the sodium aryloxide to an equivalent amount of K_{Na^+} in freshly distilled THF. The reactions were carried out as described in the case of the sodium aryloxides.

Preparation of (+)1-NpPhMeSiOC_6H_4OMe

To 0.124 g of (+)1-NpPhMeSiH (0.5 mmol; $[\alpha]_D = +34°$, $C = 10$, pentane) in freshly distilled benzene and 20 mg of Raney nickel, was added an equimolecular amount of 4-methoxyphenol in benzene. The mixture was stirred at room temperature until complete reaction. The solvent was removed under vacuo. 0.140 g of (+)1-NpPhMeSiOC_6H_4OMe, (80%; $[\alpha]_D = +7°$, $C = 10$, hexane) was recovered after purification by TLC (SiO_2; eluent: $CHCl_3$).

NMR (CCl_4) δ (ppm): 7.5 (12 H, m); 6.7 (4 H, s); 3.6 (3 H, s) 0.8 (3 H, s).

Anal. Found: C, 77.80; H, 5.98; Si, 7.58. Calcd. for $SiC_{24}H_{22}O_2$: C, 77.91; H, 6.09; Si, 7.90%.

Preparation of (—)1-NpPhMeSiOPh

The optically active (—)1-NpPhMeSiOPh was prepared by a published method [13]. ($[\alpha]_D = -8.7°$, C = 10, hexane).

Preparation of (—)1-NpPhMeSiOC$_6$H$_4$NO$_2$

To 0.070 g (0.5 mmol) of 4-nitrophenol and 0.050 g (0.5 mmol) of triethylamine in 10 ml of anhydrous ether, was added 0.5 mmol of (—) 1-NpPhMeSiCl ($[\alpha]_D = -6°$, $C = 10$, pentane) dissolved in 10 ml of anhydrous ether. The reaction mixture was stirred at room temperature for 2 h, and then filtered. After removal of the solvent, the residue was chromatographed over SiO_2 (eluent: benzene). 0.115 g of (—)1-NpPhMeSiOC$_6$H$_4$NO$_2$ (60%; $[\alpha]_D = -4°$, $C = 10$, hexane) was recovered.

NMR (CCl_4)(δ(ppm): 7.5 (12 H, m); 6.7 (4 H, s); 0.3 (3 H, s). Anal. Found: C, 71.85; H, 5.29; Si, 7.23. Calcd for $SiC_{23}H_{19}NO_3$: C, 71.67; H, 4.97; Si, 7.29%.

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