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Optical Resolutions and Configurations of Benzylmethylphenylsilylmethylamine and Its Derivatives

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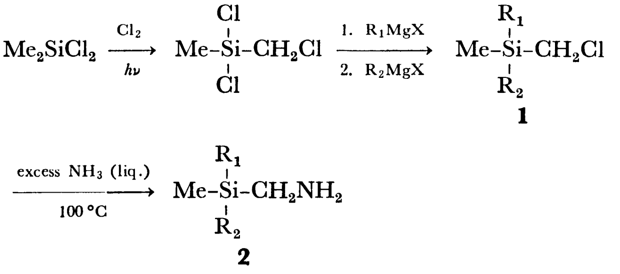
New optically active α-amino organosilanes, such as benzylmethylphenylsilylmethylamine, benzylmethyltolylsilylmethylamines, and anisylbenzylmethylsilylmethylamines, were obtained by the fractional crystallization of the salts of the amines and (+)-tartaric acid. Benzylmethylphenylsilylmethylamine was converted into benzylmethyl-1-naphthylphenylsilane, of which the configuration had been known. From these observations, it was found that benzylmethylphenylsilylmethylamine, benzylmethylphenylsilane, and benzylmethoxymethylphenylsilane had *S*(+), *S*(−), and *S*(+) configurations respectively.

The progress of the stereochemistry of organosilicon compounds owes much to the studies of L. H. Sommer and his co-workers of the reaction mechanism of the asymmetric silicon center using the optically active methyl-1-naphthylphenylsilyl systems.[1] However, only a few successful methods for obtaining optically active organosilanes in a high optical purity have been reported.[2] The difficulty of the resolution of organosilanes can be ascribed in part to the nature of their poor crystallizability. On the other hand, in the course of our studies of the synthesis of silacyclopentane derivatives, it was found that *trans*-3,3,5-trimethyl-3-silacyclopentylamine formed crystalline salts with (+)-tartaric acid.[3] In this paper, we wish to describe the resolution[4] of such α-amino silanes as benzylphenylmethylsilylmethylamine (**2a**), benzylmethyl-(*p*-, *m*-, *o*-)-tolysilylmethylamine(**2b**, **2c**, **2d**), (*p*-, *o*-)-anisylbenzylmethylsilylmethylamine(**2e**, **2f**), and benzylbutylmethylsilylmethylamine(**2g**) by using (+)-tartaric acid as a resolving reagent, and to describe the chemical interconversion of **2a** into benzyl-1-naphthylphenylmethylsilane.

Results and Discussion

Optical Resolution. The α-chlorosilanes (**1a**—**1g**) were synthesized by the step-by-step treatment of dichloromethylsilylmethyl chloride with the corresponding Grignard reagents. Then the chlorides were treated with excess ammonia in a stainless steel autoclave for 1.5 h at 100 °C.[4,6] The α-amino silanes (**2a**—**2g**) were obtained in 50—60% yields (Scheme 1 and Table 1).



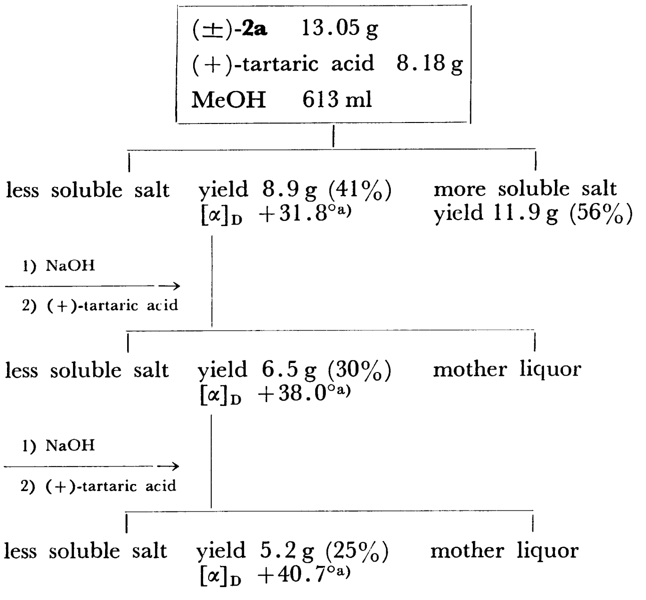
$$\mathrm{Me_2SiCl_2} \xrightarrow[h\nu]{\mathrm{Cl_2}} \mathrm{Me\text{-}\underset{Cl}{\overset{Cl}{Si}}\text{-}CH_2Cl} \xrightarrow[\text{2. } \mathrm{R_2MgX}]{\text{1. } \mathrm{R_1MgX}} \mathrm{Me\text{-}\underset{R_2}{\overset{R_1}{Si}}\text{-}CH_2Cl}\ \mathbf{1} \xrightarrow[100\,^\circ\mathrm{C}]{\text{excess } \mathrm{NH_3}\text{ (liq.)}} \mathrm{Me\text{-}\underset{R_2}{\overset{R_1}{Si}}\text{-}CH_2NH_2}\ \mathbf{2}$$

a R_1=Ph, R_2=$PhCH_2$-. **b** R_1=*p*-tolyl, R_2=$PhCH_2$-. **c** R_1=*m*-tolyl, R_2=$PhCH_2$-. **d** R_1=*o*-tolyl, R_2=$PhCH_2$-. **e** R_2=*p*-anisyl-, R_2=$PhCH_2$-. **f** R_1=*o*-anisyl, R_2=$PhCH_2$-. **g** R_1=Ph, R_2=*n*-Bu.

Scheme 1.

Table 1. Amination of **1**

	1 g(mol)	NH_3(liq.) g(mol)	**2** Bp(°C/Torr)	Yield g(%)
a	26.8(0.10)	70(4.1)	160—163/4	16.5(66.5)
b	30.6(0.12)	74(4.3)	163—165/3	16.2(57.0)
c	70.0(0.26)	240(14.1)	155—158/2	34.6(52.7)
d	15.1(0.06)	36(2.2)	161—164/3	7.5(53.4)
e	37.5(0.13)	75(4.3)	170—174/2	20.6(58.8)
f	16.8(0.058)	36(2.2)	143—146/1	8.0(50.7)
g	54.7(0.24)	240(14.1)	143—145/18	24.3(48.9)



a) c=4 in DMF

Fig. 1. Fractional crystallization of **2a**.

The optical resolutions of the amine **2** were carried out by using (+)-tartaric acid as the resolving reagent (Table 2). Since the less soluble salts obtained by the method of fractional crystallization appeared to be unstable in methanol solution above 40 °C, further recrystallization of the salts was not undertaken. Instead, the partially resolved amines, which had been liberated from the less soluble salts by treating them with a caustic alkali solution, were treated with an equimolar amount of (+)-tartaric acid in methanol. Some typical results of the resolution of **2a** are shown in the flowing chart (Fig. 1). The optical resolutions

TABLE 2. RESOLUTION OF **2** USING (+)-TARTARIC ACID AS THE RESOLVING REAGENT

	(±)-**2** (g)	A a) (g)	MeOH (ml)	Less soluble salt		Optically active amine	
				Yield g(%)	$[\alpha]_D$(°)	Yield g(%)	$[\alpha]_D$(°)
2a	13.05	8.18	613	8.7(41)	+31.8 b)	4.6(35)	+9.5 e)
2b	10.12	6.02	602	6.3(39)	−25.5 c)	3.4(34)	−10.6 f)
2c	10.85	6.38	510	7.2(42)	+32.1 b)	3.8(35)	+9.9 g)
2d	4.00	2.19	220	2.8(45)	+20.7 b)	1.6(40)	+6.6 e)
2e	7.31	4.05	181	2.6(23)	−29.3 c)	1.3(18)	−9.6 e)
2f	9.44	5.22	260	4.3(30)	+37.8 c)	2.4(25)	+15.8 e)
2g	20.54	15.21	380 h)	17.1(56)	+20.6 d)	—	—

a) (+)-Tartaric acid. b) c=4 in DMF. c) c=1 in DMF. d) c=2 in MeOH. e) c=4 in Et_2O. f) c=3 in Et_2O. g) c=5 in Et_2O, h) c=4 in H_2O.

TABLE 3. THE SPECIFIC ROTATIONS OF THE SALTS AND AMINES

	Salt			Amine	
	$[\alpha]_D$(°) a)	(c)	Mp(°C)	$[\alpha]_D$(°) b)	(c)
2a	+40.7	4	175	+12.7	2
2b	−40.0	1	165	−16.6	3
2c	+34.5	4	164	+10.7	5
2d	+25.5	4	163	+8.1	4
2e	−44.2	1	167	−14.5	4
2f	+45.2	4	170	+19.4	4
2g	+21.1	2 c)	147	−0.54 d)	—

a) DMF. b) Et_2O. c) MeOH. d) Neat.

TABLE 4. THE DEPENDENCE OF THE SPECIFIC ROTATIONS OF THE SALTS ON THE CONCENTRATION IN DMF

	$[\alpha]_D$(°)		
	c=1	c=2	c=4
2a	+30.8	+38.0	+40.7
2b	−40.0	−41.5	—
2c	+23.0	+28.0	+34.5
2d	+10.6	+14.5	+25.5

were carried out in this manner until the specific rotations of the salts became constant (Table 3).

In the course of these experiments, it was noticed that the specific rotation of the salts changed remarkably in their dependence on the concentration of the salts in DMF (Table 4).

The partial discrepancy of the data in Table 3 with that of our preliminary communication4) may result from the variability in the specific rotation of the salts. The optical purities of the **2a**—**2f** obtained from the first step of fractional crystallization (Table 2) were 75, 64, 93, 82, 66, and 81% respecitvely, based on the corresponding specific rotations in Table 3. These results indicate that the optically active organosilanes obtained from the first step of resolution are quite sufficient to be used for stereochemical studies.

*Chemical Conversion of **2a**.* Recently, an interesting intramolecular rearrangement reaction which converts α-aminosilanes, such as *N*-benzyl- and *N*-cyclohexyltrimethylsilylmethylamine, into aminosilanes appeared in the literature.7) We considered that this reaction could be used to convert the optically active amine **2a** ($R'_3SiCH_2NH_2$) into siliconfunctional aminosilane. In this section, we wish to describe our attempt at the chemical interconversion of **2a** into benzylmethyl-1-naphthylphenylsilane (**9**), the absolute configuration of which is known.5)

$$(+)R'_3\overset{*}{Si}CH_2NH_2 \xrightarrow{PhCH_2Cl/Et_3N} (+)R'_3\overset{*}{Si}CH_2NHCH_2Ph$$

2a **3**

$[\alpha]_D$ +12.5°(c=2, Et_2O) $[\alpha]_D$ +10.0°(c=2, MeOH)

$$\xrightarrow[\text{(ret.)}]{n\text{-BuLi/THF}} (-)R'_3\overset{*}{Si}N(CH_2Ph)Me \xrightarrow[\text{(inv.)}]{0.2\,M\ HCl,\ 0\,°C}$$

4

$[\alpha]_D$ −15.5° (c=2, Et_2O)

$$(-)R'_3\overset{*}{Si}OH \xrightarrow[\text{(ret.)}]{LiAlH_4/n\text{-}Bu_2O} (-)R'_3\overset{*}{Si}H$$

5 **6**

$[\alpha]_D$ −13.2°(c=2, Et_2O) $[\alpha]_D$ −17.8°(c=2, Et_2O)

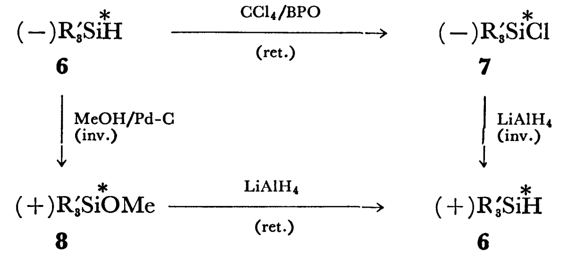
$R'_3Si- = (PhCH_2)MePhSi-$

Scheme 2.

(+) - *N* - Benzylbenzylmethylphenylsilylmethylamine (**3**) was obtained by treating the (+)-**2a** with an equimolar amount of benzyl chloride in triethylamine. After the mixture of (+)-**3** and butyllithium in THF had been stirred 10 h at room temperature, (−)-*N*-benzyl-*N*-methylbenzylmethylphenylsilylamine (**4**) was obtained in a good yield. Although the steric course of this reaction has not yet been established, it may be assumed that this reaction proceeds with a retention of the configuration by considering to be an intramolecular rearrangement.7) Then (−)-**4** was treated with 0.2 M (1 M=1 mol dm^{-3}) HCl at 0 °C to give (−)-benzylmethylphenylsilanol (**5**). It was observed that considerable racemization took place when the reaction was carried out at a temperature above 0 °C. The reduction of (−)-**5** with $LiAlH_4$ in dibutyl ether gave (−)-benzylmethylphenylsilane (**6**). The stereochemistry of these two reactions has been clarified by using methyl-1-naphthylphenylsilyl systems; *i.e.*, the former proceeds with inversion,8) while the latter proceed with a retention of configuration9) (Scheme 2).

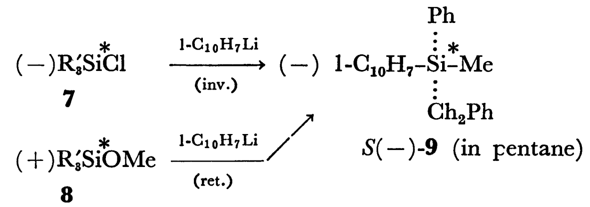
Although optically active silane (**6**) had already been obtained by the partial reduction of (±)-benzylmethoxymethylphenylsilane (**8**) with asymmetric reduction reagents, *i.e.*, $LiAlH_4$–alkaloid systems, the specific rotation of **6** reported in the litrature is −7.8°,[10] which corresponds to the optical purity of 40% (e.e.) based on our sample $[\alpha]_D$ −17.8° (c=2, Et_2O).

Some reactions of (−)-**6** were carried out in order to establish its configuration (Scheme 3). The chlorination of (−)-**6** in CCl_4 in the presence of a small amount of benzoyl peroxide[11] gave (−)-benzyl(chloro)methylphenylsilane (**7**). On the other hand, the methanolysis of (−)-**6** in the presence of Pd–C in pentane[12] at 0 °C afforded (+)-**8**. The reduction of (−)-**7** and (+)-**8** by $LiAlH_4$ in ether gave (+)-**6**. These results are in accordance with those of similar reactions of the methyl-1-naphthylphenylsilyl systems reported in the literature.[11,12]



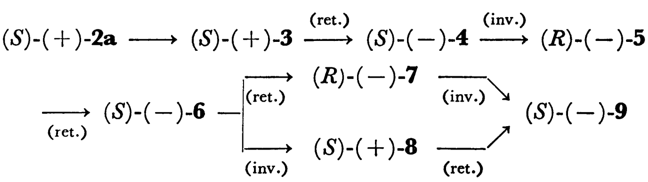
Scheme 3.

Further, the reactions of (−)-**7** and (+)-**8** with 1-naphthyllithium in ether were carried out; both reactions gave the same product, *i.e.*, (S)-(−)-benzylmethyl-1-naphthylphenylsilane (**9**)[5] (Scheme 4).



Scheme 4.

From these observations, it has become apparent that **7** and **8** have the R(−) and S(+) configurations respectively. Consequently, the configurations of the benzylmethylphenylsilyl systems treated in this paper are assigned as follows Scheme 5:

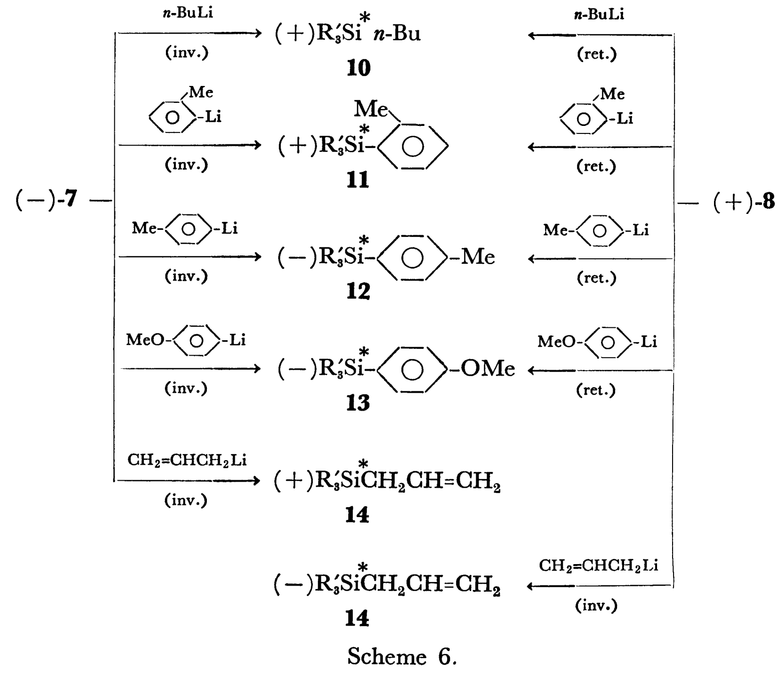


Scheme 5.

However, our results on the configuration of **6** and **8** are not in accordance with those of the previously reported assignments.[10,13] The configuration of **8** was previously determined based on the inversion reaction of **8** with the Grignard reagent of 1-bromonaphthalene in ether. Unfortunately, we could not succeed in following the reaction of **8** with 1-naphthylmagnesium bromide in ether. Therefore, some reactions of (−)-**7** and (+)-**8** with such organolithium reagents as butyllithium, (p-, o-)-tolyllithium, p-anisyllithium, and allyllithium were carried out in order to investigate the steric course of these reactions (Scheme 6).

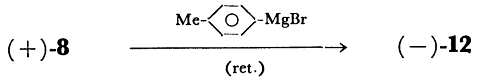
From these observations, it is clear that the reactions of the alkyl- and the aryllithium with (+)-**8** proceed with a retention of the configuration, whereas that of allyllithium with (+)-**8** proceeds with an inversion of the configuration, if the reactions of the organolithium reagents with (−)-**7** are assumed to proceed with an inversion of the configuration. These results are in fair agreement with those for methyl-1-naphthylphenylsilyl systems.[14]

On the other hand, when the reaction of p-tolylmagnesium bromide with (+)-**8** was carried out, (−)-**12** was obtained as the product. Although it has been described in the literature[13] that the reactions



Scheme 6.

of such aryl Grignard reagents as mesityl-, and 1-naphthylmagnesium bromide with a methoxysilane proceed with an inversion of the configuration, our results indicate that the Grignard reaction with (+)-**8** proceeds with a retention of the configuration (Scheme 7). Many detailed studies of the Grignard reactions with (+)-**8** are in progress.

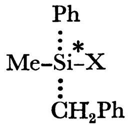


$[\alpha]_D$ +3.5°(c=2, pentane) $[\alpha]_D$ −3.7°(c=6, CH_2Cl_2)

Scheme 7.

The enantiomers, the configurations of which have been assigned on the basis of the evidence presented in this paper, are listed in Table 5.

Table 5. $R_3'SiX$ enantiomers with the (S)-(−)-$R_3'\overset{*}{Si}H$ configuration



$$\begin{array}{c} Ph \\ \vdots \\ Me\text{-}\overset{*}{Si}\text{-}X \\ \vdots \\ CH_2Ph \end{array}$$

X	Sign of rotation	Solvent
H	S(−)	Et_2O
OH	R(−)	Et_2O
$N(CH_2Ph)Me$	R(+)	Et_2O
CH_2NH_2	R(−)	Et_2O
CH_2NHCH_2Ph	R(−)	MeOH
Cl	R(−)	CCl_4
OMe	R(−)	pentane
n-Bu	R(−)	CH_2Cl_2
p-Tolyl	R(+)	CH_2Cl_2
o-Tolyl	R(−)	CH_2Cl_2
p-Anisyl	R(+)	CH_2Cl_2
CH_2=$CHCH_2$	R(−)	CH_2Cl_2
1-$C_{10}H_7$	R(+)	pentane

Experimental

The melting points and boiling points are uncorrected. The IR spectra were determined with a JASCO IR-A2 spectrometer. The NMR spectra were determined at 60 MHz with a Varian A-60D spectrometer in CCl_4, using TMS as the internal standard. The optical rotations were measured with a JASCO DIP-181 polarimeter. All the reactions of the chlorosilanes and the methoxysilane with Grignard and organolithium reagents were carried out under a dry nitrogen atmosphere. The column chromatography was carried out using silica gel (200 mesh).

*Benzylmethylphenylsilylmethyl Chloride (**1a**).* In a three-necked flask, equipped with a magnetic stirrer and a reflux condenser, dichloromethylsilylmethyl chloride (114.5 g, 0.7 mol) and dry ether (150 ml) were placed. To the flask was added the Grignard reagent prepared from bromobenzene (121.2 g, 0.77 mol) and Mg (20 g, 0.82 mol) in ether (150 ml). The mixture was refluxed for 3 h with stirring. After the subsequent addition of THF (70 ml) to the mixture, the Grignard reagent prepared from benzyl chloride (96.6 g, 0.77 mol) and Mg (20 g, 0.82 mol) in ether (150 ml) was added, and the mixture was refluxed a further 5 h with stirring. Then the mixture was hydrolyzed with dil HCl. The organic layer was washed with water and dried ($CaCl_2$). Subsequent evaporation and distillation gave **1a** in 90% (164.6 g) yield. Bp 153—157 °C/3 Torr. NMR δ 0.30 (s, 3, Si-CH_3), 2.43 (s, 2, CH_2-Ph), 2.88 (s, 2, CH_2-Cl), 7.3—7.7 (m, 10, Ph).

The compounds (**1b**—**1g**) were obtained in manners similar to that described above. The yields and boiling points are as follows (yield (%), Bp (°C/Torr)): **1b** 74, 171—172/1, **1c** 78, 160—163/1, **1d** 64, 158—162/2, **1e** 78, 165—169/3, **1f** 77, 150—156/3, **1g** 87, 132/25.

*Benzylmethylphenylsilylmethylamine (**2a**).* In a stainless steel autoclave (200 ml), **1a** (26.8 g, 0.10 mol) and liquid ammonia (70 g, 4.1 mol) were added under a nitrogen atmosphere. The autoclave was then maintained for 1.5 h at 100 °C. The excess ammonia was liberated from the autoclave, and the contents were washed out with aqueous alkali (52 g, NaOH/ 300 ml H_2O) and benzene. The organic layer was separated, washed with aqueous alkali several times, and dried (Na_2SO_4). Subsequent evaporation and distillation gave **2a** in a 66% (16.5 g) yield. Bp 160—163 °C/4 Torr. IR (neat) 3400, 3300 cm^{-1} (w, -NH_2), 1250 cm^{-1} (s, Si-CH_3). NMR δ 0.32 (s, 3, Si-CH_3), 1.20 (s, 2, NH_2), 2.33 (s, 4, Si-CH_2-Ph, Si-CH_2-N), 6.7—7.5 (m, 10, Ph). Found: N, 5.74%. Calcd for $C_{15}H_{19}NSi$: N, 5.80%.

The amines (**2b**—**2g**) were obtained in manners similar to that described above. The boiling points and yields of the amines are listed in Table 1. **2b** NMR δ 0.14 (s, 3, Si-CH_3), 1.30 (s, 2, NH_2), 2.15—2.30 (7, CH_3-Ph, Si-CH_2Ph, Si-CH_2-N), 6.7—7.4 (m, 9, Si-C_6H_4-, Si-Ph). Found: N, 5.34%. Calcd for $C_{16}H_{21}NSi$: N, 5.48%. **2c** NMR δ 0.20 (s, 3, Si-CH_3), 0.57 (s, 2, NH_2), 2.10—2.25 (7, CH_3-Ph, Si-CH_2-Ph, Si-CH_2-N), 6.4—7.0 (m, 9, Si-C_6H_4-, Ph). Found: N, 5.54%. Calcd for $C_{16}H_{21}NSi$: 5.48%. **2d** NMR δ 0.26 (s, 3, Si-CH_3), 0.77 (s, 2, NH_2), 2.30—2.40 (7, CH_3-Ph, Si-CH_2-Ph, Si-CH_2-N), 6.6—7.4 (m, 9, Si-C_6H_4-, Ph). Found: N, 5.38%. Calcd for $C_{16}H_{21}NSi$: N, 5.48%. **2e** NMR δ 0.27 (s, 3, Si-CH_3), 1.63 (s, 2, NH_2) 2.4 (4, Si-CH_2-C, Si-CH_2-N), 3.80 (s, 3, O-CH_3), 6.8—7.5 (m, 9, Si-C_6H_4-, Ph). Found: N, 5.22%. Calcd for $C_{16}H_{21}NOSi$: N, 5.16%. **2f** NMR δ 0.20 (s, 3, Si-CH_3), 1.68 (s, 2, NH_2), 2.4 (4, Si-CH_2-C, Si-CH_2-N), 3.78 (s, 3, O-CH_3), 6.6—7.5 (m, 9, Si-C_6H_4-, Ph). Found: N, 5.21%. Calcd for $C_{16}H_{21}NOSi$: N, 5.16%. **2g** NMR δ 0.29 (s, 3, Si-CH_3), 0.62—1.67 (m, 11, Si-Bu, NH_2), 2.39 (s, 2, Si-CH_2-N), 7.3—7.5 (m, 5, Ph).

*Optical Resolution of **2a**.* To the solution of (+)-tartaric acid (8.18 g, 0.054 mol) in methanol (600 ml) in a 1 litre Erlenmeyer flask was added a solution of (±)-**2a** (13.05 g, 0.054 mol) in methanol (13 ml). A white crystalline precipitate started to separate almost immediately. The flask was then allowed to stand overnight at room temperature. The crystalline precipitate was filtered off, washed with a small amount of cold methanol, and then dried *in vacuo*. To the salt we added a 10% aqueous solution of NaOH at 0 °C. The liberated amine was extracted three times with 30 ml portions of ether. The extract was then dried (Na_2SO_4). Evaporation and distillation gave (+)-**2a** in a 35% (4.6 g) yield. $[\alpha]_D$ +9.5° (c=4, Et_2O).

The resolution of **2b**—**2g** were carried out in manners similar to that described above; the yields and specific rotations are shown in Table 2.

*(+)-N-Benzylbenzylmethylphenylsilylmethylamine (**3**).* A solution of **2a** (17.5 g, 0.0726 mol) $[\alpha]_D$ +12.5° (c=2, Et_2O), benzyl chloride (9.2 g, 0.0727 mol), and triethylamine (22.0 g,

0.257 mol) was stirred for 5 h at 100 °C. A large amount of a white solid was precipitated at the end of the reaction. Into the reaction mixture, water (20 ml) and hexane (100 ml) were then added. The organic layer was separated, washed with a 10% NaOH solution until the white precipitate could not be observed, and then dried (Na_2SO_4). Evaporation and distillation gave (+)-**3**. Bp 155—160 °C/0.07 Torr. Yield, 20.1 g (83.6%). $[\alpha]_D$ +10.0° (*c*=2, MeOH). NMR δ 0.25 (s, 3, Si–CH_3), 1.05 (broad s, 1, NH), 2.30 (s, 2, Si–CH_2–N), 2.40 (s, 2, Si–CH_2–Ph), 3.75 (s, 2, N–CH_2–Ph), 7.0—7.5 (m, 15, Ph). Found: N, 4.32%. Calcd for $C_{22}H_{25}NSi$: N, 4.22%.

(−)-N-Benzyl-N-methylbenzylmethylphenylsilylmethylamine (4). To a solution of (+)-**3** (20.1 g, 0.0606 mol) $[\alpha]_D$ +10.0 (*c*=2, MeOH), in THF (150 ml) we added *n*-BuLi (5 ml of a 10% wt/v hexane solution, *ca.* 8 mmol) by means of a syringe under a nitrogen atmosphere. The color of the solution changed to red immediately. After the solution had been stirred for 10 h at room temperature, water (50 ml) was added to the red solution. The organic layer was separated, washed with water, and then dried (K_2CO_3). Subsequent evaporation and distillation gave (−)-**4**. Bp 150 °C/0.04 Torr. Yield, 15.5 g (77.1%). $[\alpha]_D$ −15.5° (*c*=2, Et_2O). NMR δ 0.32 (s, 3, Si–CH_3), 2.36 (s, 3, N–CH_3), 2.52 (d, 2, Si–CH_2–Ph), 3.86 (s, 2, N–CH_2–Ph), 6.8—7.7 (m, 15, Ph). Found: N, 4.38%. Calcd for $C_{22}H_{25}NSi$: N, 4.22%.

(−)-Benzylmethylphenylsilanol (5). A solution of (−)-**4** (15.8 g, 0.0477 mol) $[\alpha]_D$ −15.5° (*c*=2, Et_2O) in ether (150 ml) was treated with 0.2 M HCl (150 ml) in a separating funnel at 0 °C. The organic layer was washed with water and then dried (K_2CO_3). Evaporation of the solvent gave (−)-**5**. The silanol, (−)-**5**, was used in the next reaction without further purification. $[\alpha]_D$ −13.2° (*c*=2, Et_2O). IR (neat) 3250 cm^{-1} (OH). NMR δ 0.25 (s, 3, Si–CH_3), 2.30 (s, 2, Si–CH_2–Ph), 2.7—3.0 (1, OH), 6.8—7.5 (m, 10, Ph).

(−)-Benzylmethylphenylsilane (6). A solution of (−)-**5**, obtained from the experiment described above, in dibutyl ether was added to a suspension of $LiAlH_4$ (6.0 g, 0.158 mol) in ether (150 ml). The mixture was kept at 90 °C for 30 min and then the solvent was removed. Then the mixture was stirred for 3 h at 140—145 °C. After satu. aqueous Na_2SO_4 had been carefully added to the mixture with ice cooling, the organic layer was separated, washed with dil HCl with water, and then dried ($CaCl_2$). Subsequent evaporation and distillation gave (−)-**6**. Bp 150—154 °C/20 Torr. Yield, 8.0 g (79.2% based on (−)-**4**). $[\alpha]_D$ −17.8° (*c*=2, Et_2O). IR (neat) 2100 cm^{-1} (Si–H). NMR δ 0.29 (d, *J*=3.5 Hz, 3, Si–CH_3), 2.34 (d, 2, Si–CH_2–Ph), 4.43 (sixted, 1, Si–H), 6.8—7.5 (m, 10, Ph).

(−)-Benzyl(chloro)methylphenylsilane (7). A solution of (−)-**6** (1.0 g, 0.0047 mol) and BPO (84 mg, 0.3 mmol) in CCl_4 (5 ml) was sealed in a sample tube under nitrogen atmosphere. The tube was then maintained for 11 h at 80 °C. The subsequent evaporation of the solvent gave (−)-**7**, $[\alpha]_D$ −25.0° (*c*=1, CCl_4). From the IR spectrum of the product, it was observed that the product contained about 10% of unreacted (−)-**6**. The chlorosilane (−)-**7** was extremely moisture-sensitive, and racemization occurred immediately in the presence of a trace of moisture. The product was used without further purification.

(+)-Benzylmethoxymethylphenylsilane (8). To a mixture of (−)-**6** (2.0 g, 0.0094 mol) $[\alpha]_D$ −17.8° (*c*=2, Et_2O), 5% Pd–C (0.2 g) in pentane (20 ml) we added methanol (1.0 g, 0.031 mol) at 0 °C. The evolution of hydrogen occurred over a period of 3 h. After bubbling had stopped, the reaction mixture was filtered to remove the catalyst. Subsequent evaporation and distillation gave (+)-**8**. Bp 158—160 °C/20 Torr. Yield, 1.8 g (78.9%). $[\alpha]_D$ +4.4° (*c*=2, pentane), $[\alpha]_D$ +5.3° (*c*=2, Et_2O). NMR δ 0.24 (s, 3, Si–CH_3), 2.32 (s, 2, Si–CH_2–Ph), 3.60 (s, 3, O–CH_3), 6.8—7.6 (m, 10, Ph).

When the reaction was carried out at a temperature above 0 °C, it was observed that racemization took place.

Reduction of (−)-7 with $LiAlH_4$. To a suspension of $LiAlH_4$ (1 g, 0.026 mol) in ether (15 ml) was added (−)-**7**, $[\alpha]_D$ −18.9° (*c*=2, CCl_4). The mixture was refluxed for 2 h with stirring and then hydrolyzed with satur. Na_2SO_4. The organic layer was separated, washed with dil HCl, water, and then dried ($CaCl_2$). Subsequent evaporation and distillation gave (+)-**6**. Bp 150 °C/20 Torr. Yield, 0.45 g (45%). $[\alpha]_D$ +8.3° (*c*=2, Et_2O). The IR spectrum of the product was identical with that of (−)-**6**.

Reduction of (+)-8 with $LiAlH_4$. A solution of (+)-**8** (2.0 g, 0.0083 mol) $[\alpha]_D$ +2.7° (*c*=2, Et_2O) in ether (20 ml) was added to a suspension of $LiAlH_4$ (1 g, 0.026 mol) in ether (15 ml). The mixture was then refluxed for 3 h, followed by hydrolysis with satur. Na_2SO_4. The organic layer was separated, washed, and then dried ($CaCl_2$). Subsequent evaporation and distillation gave (+)-**6**. Yield, 1.5 g (86%). $[\alpha]_D$ +7.6° (*c*=2, Et_2O). The IR spectrum of the product was identical with that of (−)-**6**.

Reaction of (−)-7 with 1-Naphthyllithium. To a solution of 1-bromonaphthalene (2 g, 0.0097 mol) in ether (100 ml) we added *n*-BuLi (4 ml of a 10% wt/v solution in hexane, *ca.* 0.0063 mol) by means of a syringe under a nitrogen atmosphere.[15] The mixture was then stirred for 30 min at room temperature. After a solution of (−)-**7** (1.0 g, 0.0047 mol) $[\alpha]_D$ −15.0° (*c*=1, CCl_4) in ether (5 ml) had been added to this mixture, it was stirred for 4 h at room temperature and then hydrolyzed. The organic layer was separated, washed with dil HCl, water, and then dried ($CaCl_2$). The subsequent evaporation of the solvent gave a pale yellow residue. Column chromatography of the residue was carried out (silica gel, hexane:benzene=4:1). The eluent was evaporated, and the viscous residue was distilled. Bp 182 °C/0.08 Torr. Yield, 0.8 g (54%). $[\alpha]_D$ −2.0° (*c*=3, pentane) (lit,[5] $[\alpha]_D$ −6.68° (*c*=2.8, pentane)). IR (neat) 1595, 1495, 1210, 985 cm^{-1}. NMR δ 0.57 (s, 3, Si–CH_3), 2.81 (s, 2, Si–CH_2–Ph), 6.7—8.1 (m, 18, Ph, 1-$C_{10}H_7$).

Reaction of (+)-8 with 1-Naphthyllithium. To a solution of 1-naphthyllithium prepared from 2 g (0.0097 mol) of 1-bromonaphthalene in ether (100 ml) and 4 ml of 10% wt/v *n*-BuLi in hexane as described above, we added (+)-**8** (1.0 g, 0.0041 mol) $[\alpha]_D$ +2.1° (*c*=2, pentane) in ether (5 ml). After the mixture had been stirred for 4 h at room temperature, it was hydrolyzed. The organic layer was separated, washed with dil HCl, water, and then dried ($CaCl_2$). The subsequent evaporation of the solvent gave an oily product. Chromatography (silica gel, hexane:benzene=4:1) and subsequent distillation gave (−)-**9**. Bp 191 °C/0.1 Torr. $[\alpha]_D$ −1.9° (*c*=2, pentane). The IR spectrum of the product was identical with that of (−)-**9**, obtained from the reaction of (−)-**7** with 1-naphthyllithium.

Reaction of (−)-7, and (+)-8 with n-BuLi. To a solution of (−)-**7**, $[\alpha]_D$ −19.0° (*c*=3, CCl_4), prepared from (−)-**6** (1 g, 0.0047 mol), $[\alpha]_D$ −13.5° (*c*=2, Et_2O) in ether (100 ml) we added 4 ml of a 10% wt/v solution of *n*-BuLi by means of a syringe at 0 °C. After having been stirred for 1 h at 0 °C, the mixture was hydrolyzed. The usual work-up of the mixture gave (+)-**10**. Bp 155—160 °C/14 Torr. Yield, 67.2%. $[\alpha]_D$ +5.0° (*c*=3, CH_2Cl_2). NMR

δ 0.20 (s, 3, Si–$\mathrm{CH_3}$), 0.5—1.5 (m, 9, Bu), 2.28 (s, 2, Si–$\mathrm{CH_2}$–Ph), 6.7—7.5 (m, 10, Ph). The reaction of (+)-**8** (1 g, 0.0041 mol) $[\alpha]_D$ +2.7° (c=2, $\mathrm{Et_2O}$) with n-BuLi was carried out in the same manner. The compound (+)-**10** was thus obtained in a 72% (0.8 g) yield. $[\alpha]_D$ +5.8° (c=3, $\mathrm{CH_2Cl_2}$). The IR and NMR spectra of the product were identical with those of (+)-**10**, obtained from the reaction of (−)-**7** with n-BuLi, as has been described above.

Reaction of (−)-7, and (+)-8 with o-*Tolyllithium.* To a solution of o-bromotoluene (1 g, 0.0058 mol) in ether (70 ml) we added 3 ml (*ca.* 0.0047 mol) of a 10% wt/v hexane solution of butyllithium by means of a syringe.16) After the mixture has been stirred for 30 min at room temperature, (−)-**7** (1 g, 0.0041 mol) $[\alpha]_D$ −10.6° (c=2, $\mathrm{CCl_4}$) in ether (5 ml) was added to the mixture at 0 °C. The usual work-up of the mixture gave (+)-**11** in a 75% (0.92 g) yield. Bp 155 °C/0.2 Torr. $[\alpha]_D$ +5.0° (c=4, $\mathrm{CH_2Cl_2}$). NMR δ 0.43 (s, 3, Si–$\mathrm{CH_3}$), 2.18 (s, 3, C–$\mathrm{CH_3}$), 2.64 (s, 2, Si–$\mathrm{CH_2}$–Ph), 6.7—7.5 (m, 10, Ph).

The reaction of (+)-**8** (1.0 g, 0.0041 mol) $[\alpha]_D$ +2.7° (c=2, $\mathrm{Et_2O}$) with o-tolyllithium was carried out in a similar manner. The compound (+)-**11** was obtained in an 80% (0.99 g) yield. $[\alpha]_D$ +7.3° (c=2, $\mathrm{CH_2Cl_2}$). The IR and NMR spectra of the product were identical with those of the product obtained by the reaction of (−)-**7** with o-tolyllithium.

Reaction of (−)-7, and (+)-8 with p-*Tolyllithium.* To a solution of p-bromotoluene (1.0 g, 0.0058 mol) in ether (100 ml) we added 3 ml (*ca.* 0.0047 mol) of a 10% wt/v hexane solution of butyllithium.15) The mixture was stirred for 20 min at room temperature, and then (−)-**7** (1.0 g, 0.0041 mol) $[\alpha]_D$ −17.5° (c=1, $\mathrm{CCl_4}$) was added to the mixture at 0 °C. The usual work-up of the mixture gave (−)-**12** in a 58% (0.7 g) yield. Bp 160 °C/0.2 Torr. $[\alpha]_D$ −4.5° (c=2, $\mathrm{CH_2Cl_2}$). NMR δ 0.41 (s, 3, Si–$\mathrm{CH_3}$) 2.33 (s, 3, C–$\mathrm{CH_3}$), 2.55 (s, 2, Si–$\mathrm{CH_2}$–Ph), 6.7—7.5 (m, 10, Ph).

The reaction of (+)-**8** (1.0 g, 0.0041 mol) $[\alpha]_D$ +4.4° (c=2, pentane) with p-tolyllithium was carried out in a similar manner. The compound (−)-**12** was thus obtained in a 48% (0.6 g) yield. $[\alpha]_D$ −5.5° (c=2, $\mathrm{CH_2Cl_2}$).

Reaction of (−)-7, and (+)-8 with p-*Anisyllithium.* To a solution of p-anisyllithium prepared from p-bromoanisole (1.0 g, 0.0053 mol) in ether (100 ml) and 3 ml of 10% wt/v solution of butyllithium, we added (−)-**7** (1.0 g, 0.0041 mol) $[\alpha]_D$ −17.5° (c=1, $\mathrm{CCl_4}$). After the mixture had been stirred for 2 h at room temperature, the usual work-up of the mixture gave (−)-**13** in a 50% (0.65 g) yield. Bp 175—180 °C/0.2 Torr. $[\alpha]_D$ −7.7° (c=2.5, $\mathrm{CH_2Cl_2}$). NMR δ 0.40 (s, 3, Si–$\mathrm{CH_3}$), 2.55 (s, 2, Si–$\mathrm{CH_2}$–Ph), 3.75 (s, 3, O–$\mathrm{CH_3}$), 6.7—7.5 (m, 10, Ph).

The reaction of (+)-**8** (1.0 g, 0.0041 mol) $[\alpha]_D$ +3.5° (c=2, pentane) with p-anisyllithium was carried out in a similar manner. The compound (−)-**13** was obtained in a 54% (0.7 g) yield. $[\alpha]_D$ −7.8° (c=3, $\mathrm{CH_2Cl_2}$).

Reaction of (−)-7, and (+)-8 with Allyllithium. To a solution of allyllithium,18) prepared from allyltriphenyltin (3.2 g, 0.0082 mol) and PhLi (0.0080 mol) in ether (70 ml), we added (−)-**7** (1.0 g, 0.0041 mol) $[\alpha]_D$ −11.0° (c=2, $\mathrm{CCl_4}$) in ether (5 ml) with stirring at 0 °C. After the mixture had been stirred for 2 h at 0 °C, the precipitated tetraphenyltin was filtered off. The organic layer was washed with water and then dried ($\mathrm{CaCl_2}$). Subsequent evaporation and distillation gave (+)-**14** in a 68% (0.7 g) yield. Bp 132—135 °C/0.2 Torr. $[\alpha]_D$ +0.82° (c=3.6, $\mathrm{CH_2Cl_2}$). IR (neat) 1625 cm^{-1} (C=C). NMR δ 0.20 (s, 3, Si–$\mathrm{CH_3}$) 1.75 (d, J=7.5 Hz, 2, Si–$\mathrm{CH_2}$–C), 2.28 (s, 2, Si–$\mathrm{CH_2}$–Ph), 4.5—5.0 (m, 2, =$\mathrm{CH_2}$), 5.3—6.1 (m, 1, –CH=C), 6.7—7.5 (m, 10, Ph).

The reaction of (+)-**8** (1.0 g, 0.0041 mol) $[\alpha]_D$ +3.5° (c=2, pentane) with allyllithium was carried out in a similar manner. The compound (−)-**14** was thus obtained in a 59% (0.6 g) yield. $[\alpha]_D$ −1.0° (c=7, $\mathrm{CH_2Cl_2}$).

Reaction of (+)-8 with p-*Tolylmagnesium Bromide.* To a solution of p-tolylmagnesium bromide, prepared from p-bromotoluene (5.0 g, 0.029 mol) and Mg (0.85 g, 0.035 mol) in ether (50 ml), we added a solution of (+)-**8** (1.0 g, 0.0041 mol) $[\alpha]_D$ +3.5° (c=2, pentane) in ether (5 ml). The mixture was refluxed for 30 h with stirring. The usual work-up of the mixture gave (−)-**12** in a 45% (0.46 g) yield. $[\alpha]_D$ −3.7° (c=6, $\mathrm{CH_2Cl_2}$). The IR and NMR spectra of the product were identical with those of the product obtained by the reaction of (+)-**8** with p-tolyllithium.

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