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Asymmetric Synthesis of Organosilicon Compounds Using a C_2 Chiral Auxiliary

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Optically active silanes were synthesized by a novel asymmetric synthesis which involved the diastereoselective ring-opening reaction of 1,3-dioxa-2-silacycloheptanes bearing a C_2 chiral auxiliary with Grignard reagents, followed by a lithium aluminum hydride ($LiAlH_4$) reduction. (*R*)-Ethylmethylphenylsilane and (*R*)-methylphenylpropylsilane were derived in 93%ee and 98%ee, respectively. The preparation of the other optical silanes is also described. The maximum rotations of some of them have been determined by ^1H NMR and/or capillary GC methods. A mechanism for a diastereoselective ring-opening reaction is proposed based on the stereochemical results.

Many strategies have been developed for asymmetric synthesis in the field of carbon chemistry. However, in the field of silicon chemistry, comparatively little effort has been devoted to exploring the asymmetric synthesis of silane. Nevertheless, there is a great possibility for the industrial and pharmaceutical use of optically active silanes. To our knowledge, the reported asymmetric syntheses of silanes so far are as follows. Richter[1] obtained some optically active alkoxysilanes by the alkylation of the dimenthoxysilane with ethyllithium reagent. Kumada,[2] Ojima,[3] Corriu[4] and their co-workers have explored the catalytic asymmetric hydrosilylative reduction of ketones or aldehydes by the chiral rhodium phosphine complexes, and successively obtained some optically active silanes; these investigation have been summerized in a book.[5] Further, these reactions did not give a high enantiomer excess. Recently, however, this strategy has been developed by Takaya using such C_2 catalysts as 2,2′-bis(diphenylphosphino)-1,1′-binaphtyl rhodium and 2,2′-bis(dicyclohexylphosphino)-1,1′-binaphtyl rhodium to give methyl(1-naphthyl)phenylsilane.[6]

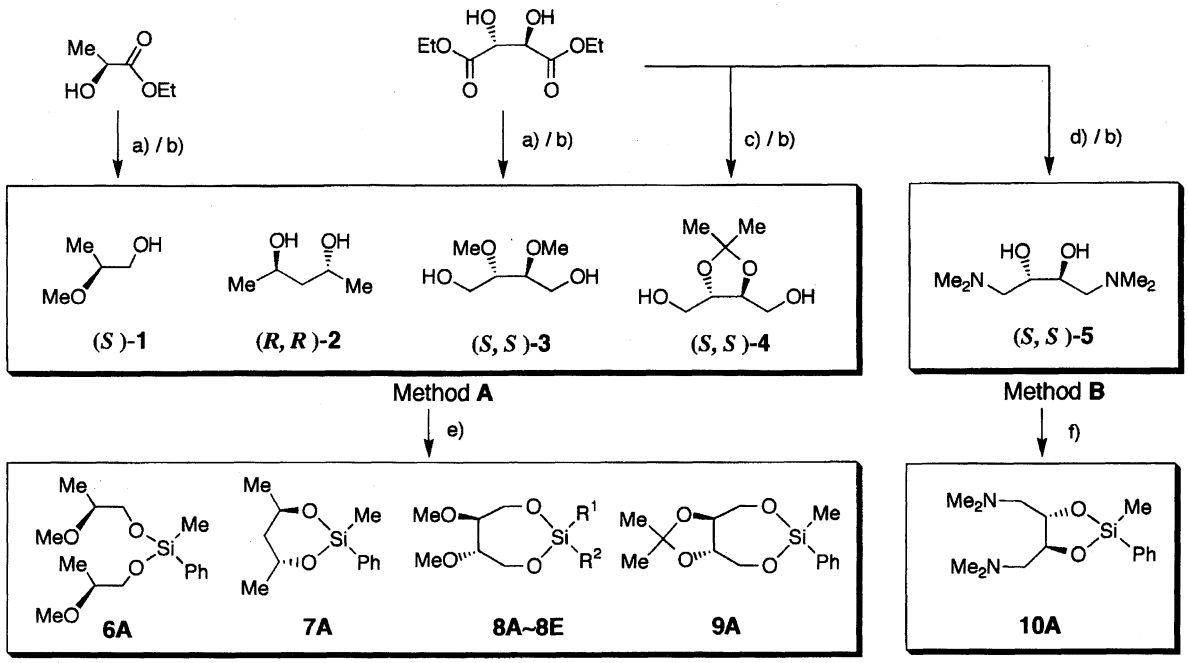
In the field of carbon chemistry, also prominent among many asymmetric methods, has been the use of C_2 symmetry compounds as a chiral auxiliary.[7] Since the pioneering work concerning the addition of Grignard reagents combined with such a C_2 symmetric chiral ether as (*R*)-2,3-dimethoxybutane to phenyl isocyanate was reported by Cohen and Wright,[8] the C_2 symmetry compound has attracted our special attention. Recently, a new methodology for asymmetric synthesis using a C_2 chiral synthon has been developed by Noyori, Yamamoto, and their co-workers.[9] That is, the Lewis acid-catalyzed cleavage reactions of homochiral acetals or ketals derived from the condensation of such C_2 chiral glycols as (2*R*,4*R*)-2,4-pentanediol and aldehydes or unsymmetrical ketones with various nucleophiles have been reported to proceed in a highly diastereoselective manner, ultimately providing a route for preparing some chiral secondary or tertiary alcohols in high optical yields.

Here, we tried to explore an effective asymmetric synthesis of silane by an improved chiral synthon method that employs such ketal analog as 1,3-dioxa-2-silacycloalkanes containing a C_2 chiral auxiliary in the ring structure and having an appropriate substituent (e.g. MeO-, Me_2N-) that can coordinate with a metal ion. This is because these chiral 1,3-dioxa-2-silacycloalkanes should form a stronger stereospecific coordination of organo-magnesium or -lithium reagent to one of the oxygens in the ring and the appropriate substituent on it, followed by a nucleophilic attack to the cleaved silicon–oxygen bond diastereoselectively.

In this regard, we first synthesized several C_2 symmetry glycols from (2*R*,3*R*)-tartaric acid, being very briefly available, and then condensed them with prochiral dichloro- or dihydroxy-substituted silanes to obtain various chiral 1,3-dioxa-2-silacycloalkanes (**8A—8E**, **9A**, and **10A** (Scheme 1)). In accordance with this expectation, their diastereoselective alkylation (or arylation) with organometals followed by $LiAlH_4$ reduction afforded a high enantiomer excess. Although the structures of these obtained optically active silanes were very simple, most of their maximum rotations have not been reported. We thus estimated the enantiomer excess of silanes by measuring the ratio of the diastereomers formed during the first stage of the reaction.

Results and Discussion

Preparation of Acyclic Bis(2-methoxypropoxy)methylphenylsilane (6A) and Chiral 1,3-Dioxa-2-silacycloalkanes 7A, 8A—8E, 9A, 10A. Optically active glycols having C_2 symmetry (*S*,*S*)-**3**, (*S*,*S*)-**4**, (*S*,*S*)-**5** were derived from the obtainable (2*R*,3*R*)-tartaric acid via the known procedure,[10] and (*S*)-2-methoxy-1-propanol (**1**) was similarly derived from ethyl (*S*)-lactate by the same procedure



Scheme 1. Reagents and conditions: a) Me_2SO_4, NaH in Et_2O at −10—0 °C; b) $LiAlH_4$ in Et_2O at reflux; c) $Me_2C(OMe)_2$, *p*-Toluenesulfonic Acid in PhH at reflux; d) $NHMe_2$ in Et_2O at −78——20 °C; e) $Cl_2SiR^1R^2$, Pyridine in PhH at reflux; f) $H_2SiR^1R^2$, Pd/C in PhH at 50 °C.

for (*S*,*S*)-**3**. Using them and (2*R*,4*R*)-2,4-pentanediol (**2**), acyclic silyl ether **6A** and cyclic optically active silyl ethers, i.e. 1,3-dioxa-2-silacycloalkanes **7A**, **8A**—**8E**, **9A**, and **10A**, were prepared by one of two established methods, A and B, as shown in Scheme 1. The optical purity of (2*R*,3*R*)-tartaric acid and ethyl (*S*)-lactate were 100 and 97%ee, respectively. During the course of the transformation of these compounds to corresponding alcohols, we did not touch the asymmetric points. Thus, the optical purity of silyl ethers were the same as at the beginning of the compounds.

Method A involves a coupling reaction of the glycols or the alcohol and prochiral dichlorosilanes in the presence of pyridine as a base in a large amount of benzene solution. The results are summarized in Table 1. **7A**, having a six-membered ring skeleton, was obtained from (*R*,*R*)-**2** and dichloromethylphenylsilane in 50% yield. Seven-membered **8A**—**8E**, and (*S*,*S*)-**9A** were obtained from (*S*,*S*)-**3** or (*S*,*S*)-**4** and the corresponding dichlorosilanes. Furthermore, in order to make a comparison with cyclic silyl ether **8A**, acyclic silyl ether **6A**, having almost the same constituents as **8A**, was also prepared from (*S*)-**1** and diclorometylphenylsilane in a high yield of 85%. However, method A is inapplicable to a reaction with glycols having a basic functional group like an amino group.

Method B eliminates this problem. The coupling reaction of glycol (*S*,*S*)-**5** and methylphenylsilane catalyzed by Pd/C in benzene solution allowed the preparation of **10A** having two dimethylamino groups on its five-membered cyclic skeleton in 74% yield. All of these 1,3-dioxa-2-silacycloalkanes were purified by distillation under reduced pressure. These products gave satisfactory ^1H, ^{13}C NMR and MS spectra. **6A** and **10A** not only had a tendency to readily dimerize and polymerize to give an equilibrium mixture upon standing at room temperature, but were also very sensitive to moisture, and decomposed to the corresponding siloxane and glycol as do acyclic dialkoxysilanes.[11] Thus, **6A** and **10A** were freshly distilled prior to use in the next experiment. However, 1,3-dioxa-2-silacycloheptanes were found to be very stable to moisture, even after washing with water to remove pyridinium chloride as a by-product from the reaction mixture. Furthermore, they didn't dimerize. They can thus be stored for a long time at room temperature in the usual sample tube.

Table 1. Yield and Specific Optical Rotation of Silyl Ethers **6A**—**10A**

Silyl ether	R^1	R^2	Yield/%[a]	$[\alpha]_D$/deg[b]	Bp/°C (Pa)
6A	Me	Ph	85	—	114 (1.1×10^2)
7A	Me	Ph	50	+20.3 (*c* 9.78)	78 (1.1×10^2)
8A	Me	Ph	84	+46.1 (*c* 11.63)	116 (1.1×10^2)
8B	Me	1-Np	57	+38.2 (*c* 9.35)	154 (4.7×10)
8C	Ph	1-Np	53	+85.5 (*c* 11.14)	191 (4.0×10)
8D	Et	Ph	56	+48.3 (*c* 12.05)	125 (1.1×10^2)
8E	Me	Allyl	62	+61.8 (*c* 11.45)	77 (1.2×10^2)
9A	Me	Ph	41	+15.9 (*c* 8.17)	105 (6.7×10)
10A	Me	Ph	74	−10.1 (*c* 10.11)	128 (2.7×10)

a) Isolated yield based on glycol or alcohol. b) The solvent was PhH.

Asymmetric Synthesis of Silanes. The results of an asymmetric synthesis of methyl(1-naphthyl)phenylsilane (**11**) (Sommer's compound),[12a] which is one of the best known optically active silane, are summarized in Table 2. Since the optical purities of the starting silyl ethers were almost complete, the enantiomer excess % of each silane ob-

Table 2. Asymmetric Synthesis of Methyl(1-naphthyl)phenylsilane (**11**)

Entry	Silyl ether	R^3M[a]	**11**			
			Yield/%[b]	$[\alpha]_D$/deg[e]	ee %[f]	Abs. config.
1	**7A**	1-NpMgBr	30	+2.48 (*c* 3.86)	7.3[g]	***R***
2	**8A**	1-NpMgBr	40	−8.78 (*c* 4.99)	25.6	***S***
3	**8A**	1-NpLi	10	−0.95 (*c* 5.03)	2.8	***S***
4	**8B**	PhMgBr	65	+26.0 (*c* 5.41)	75.8	***R***
5	**8C**	MeMgBr	66	+8.91 (*c* 8.39)	26.0	***R***
6	**9A**	1-NpMgBr	—[c]	—	—	—
7	**9A**	1-NpLi	30[d]	+8.30 (*c* 4.48)	24.2	***R***
8	**10A**	1-NpMgBr	30	−11.4 (*c* 10.68)	33.2	***S***

a) The reaction was carried out in Et_2O by using equimolar amount of silyl ether and 1.5 to 2.5 molar amounts of R^3M at 0 °C. b) Isolated yield. c) Trace. d) GC yield. e) The solvent was cyclohexane. f) Based on (***R***)-**11**, $[\alpha]_D$ +34.3° (*c* 10.9 cyclohexane).[12a] g) Calculated as **7A** being 99% pure.

tained reflects the optical yield of each reaction. Among the reactions of 1-NpMgBr (1-Np : 1-naphthyl) under the same conditions, the reaction of **10A** (Entry 8) gave a better enantiomer excess (33.2%ee) than did the others (Entries 1, 2, 6). The bicyclic sily ether **9A** was found to be so stable that it didn't react with 1-NpMgBr, but sluggishly reacted with 1-NpLi (Entries 6, 7).

The highest one (75.8%ee) was obtained from the reaction of **8B** with PhMgBr (Entry 4). However, the enantiomer excesses of the reactions using analogus **8A** and **8C** were moderate. The reaction of **8A** with 1-NpLi gave a nearly racemic product of (−)-**11** (2.8%ee). These results suggest that two aryl reagents reacted by different mechanisms and the interaction of Grignard reagents with **8A** should be stronger than that of lithium reagents.

The results of the asymmetric synthesis of ethylmethylphenylsilane (**12**) are summarized in Table 3. To obtain the scope of the asymmetric reaction, we tried various kinds of reactions. The highest value of the specific rotation of −6.97° was obtained from the reaction of **8A** with EtMgBr at −70 °C, which is larger than the reported one (2.53°).[12b] The specific rotation of **12** decreased along with a rise in the reaction temperature. Such an influence of the reaction temperature on the optical yield was recognized in other reactions, e.g. Entries 1, 2, 5, 6, 8, 9, 12, 13. Under the same reaction conditions, the specific optical rotations of (−)-**12** obtained from the reaction of **8A** with EtMgBr was higher than that with EtLi, though the yields of the reaction using EtLi were superior to the reaction using EtMgBr. The optical rotation of **12** fell dramatically to one eighth when the reaction was carried out in such a basic solvent as THF (Entry 7). These results suggest that the Grignard reagent forms a com-

Table 3. Asymmetric Synthesis of Ethylmethylphenylsilane (**12**)

Entry	**6—10**	R^3M[a]	**12**			
			Yield/%[b]	$[\alpha]_D$/deg[d]	ee %[e]	Abs. config.
1	**6A**	EtMgBr	40	−0.14 (*c* 6.73)	1.9[f]	***R***
2	**6A**	EtMgBr (−70 °C)	33	−1.09 (*c* 7.21)	15[f]	***R***
3	**6A**	EtLi (−70 °C)	76	+3.02 (*c* 5.76)	42[f]	***S***
4	**7A**	EtMgBr	80	−1.34 (*c* 8.65)	18[g]	***R***
5	**8A**	EtMgBr	75	−6.01 (*c* 6.05)	80	***R***
6	**8A**	EtMgBr (−70 °C)	70	−6.97 (*c* 5.65)	93	***R***
7	**8A**	EtMgBr (THF)	65	+0.75 (*c* 6.62)	10	***S***
8	**8A**	EtLi	85	−0.52 (*c* 5.69)	6.9	***R***
9	**8A**	EtLi (−70 °C)	70	−2.62 (*c* 7.70)	35	***R***
10	**8A**	Et_2Zn (0—30 °C)	—[c]	—	—	—
11	**8A**	Et_3Al (0—30 °C)	—[c]	—	—	—
12	**8D**	MeMgBr	77	+3.92 (*c* 7.13)	52	***S***
13	**8D**	MeMgBr (−45 °C)	85	+4.13 (*c* 7.60)	55	***S***
14	**8D**	MeMgI	50	+2.74 (*c* 11.80)	37	***S***
15	**9A**	EtMgBr	29	+1.86 (*c* 7.95)	25	***S***
16	**9A**	EtLi	35	+2.51 (*c* 10.05)	33	***S***
17	**10A**	EtMgBr	78	−0.25 (*c* 9.24)	3.3	***R***
18	**10A**	EtLi	64	+2.17 (*c* 8.18)	29	***S***

a) The reaction was carried out in Et_2O by using equimolar amount of silyl ether and 1.5 to 2.5 molar amounts of R^3M and unless otherwise noted, carried out at 0 °C. b) Isolated yield. c) Not reacted. d) The solvent was CCl_4. e) Based on (***S***)-**12**, $[\alpha]_D$ +7.5° (CCl_4), estimated in this report. f) Calculated as **6A** being 97% pure. g) Calculated as **7A** being 99% pure.

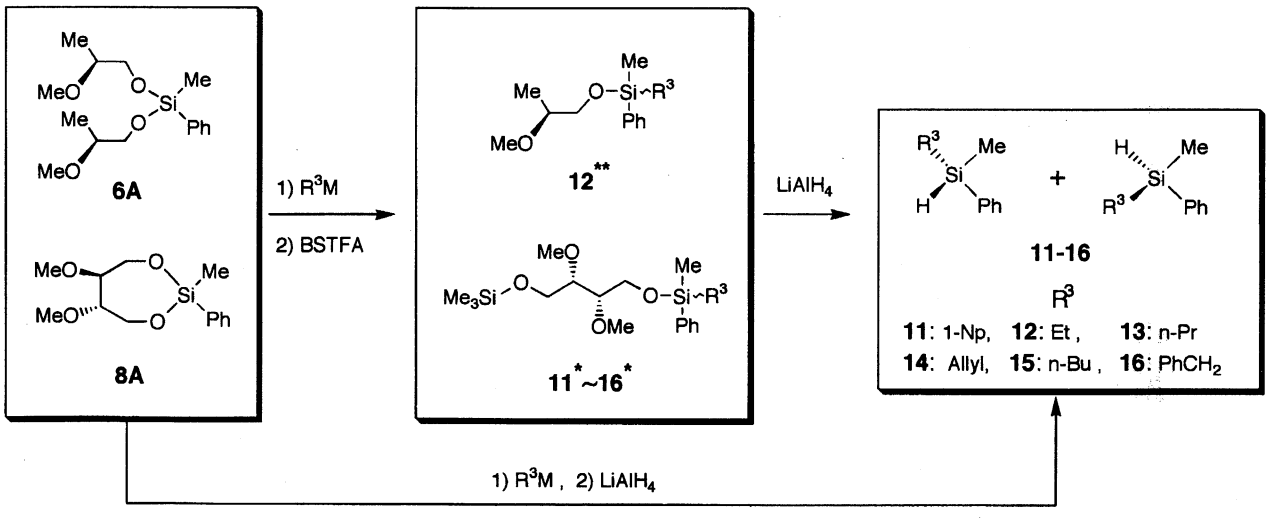
plex with **8** in ether solution, but does not in THF. However, the effect of halogen of the Grignard reagents for these reactions was very small (Entries 12, 14). This result was also observed in the later experiments (Entries 2, 3 in Table 4). The reaction of **8A** with other organometalic reagents, such as Et_2Zn or Et_3Al, did not proceed even at elevated temperature (30 °C). To extend this asymmetric synthesis to obtain various chiral silanes **13**—**17**, the reactions of **8A**—**8E**, **9A** and **10A** with corresponding organometallic reagents were conducted, as given in Table 4. The reaction of **8A** with Grignard reagents gave silane **14** and **15** in higher optical rotation than did that of **9A** and **10A**, respectively (Entries 2, 5, 6, 7). In spite of the fact that these obtained chiral silanes have a relatively simple structure, most of their maximum specific rotations have unfortunately not been reported, except for **17**; thus, the optical yield of these reactions could not be calculated.

Estimation of the Specific Rotation of Optically Pure Chiral Silanes 11—16. As described above, the optical rotation of **12** obtained in this experiment was extremely higher than that of those already reported. Furthermore, most of the maximum specific rotations of silanes **11**—**16** have not yet been reported, although they have a relatively simple structure. We thus tried to estimate these values by measuring the diastereomer ratios of the ring-opening products, **11***—**16*** or **12****, those that were precursors of chiral silanes **11**—**16** (Scheme 2). These diastereomer ratios reflect the enantiomer excess of silanes **11**—**16**, since the reduction of silyl ether, like **11***—**16*** or **12****, with $LiAlH_4$ proceeds with almost complete retention of their configuration.[12c] These results are summarized in Table 5. The maximum rotation of chiral silane **11** was estimated to be 32.9°, which is in close agreement with the already reported data of +34.3°.[12a] The maximum rotations of chiral silane **12**, obtained from some different conditions, ranged from +7.2 to −7.96°, and the average of these absolute values was 7.5°. Thus, the optical yields of **12**—**16** in these asymmetric reactions were calculated from these estimated maximum rotations, and are listed in Tables 3 and 4. These results show some excellent optical yields of these asymmetric reactions. That is, the optical

Table 4. Asymmetric Synthesis of $R^1R^2R^3$-Silanes **13**—**17**

	8—10				Silane 13—17			
Entry		R^1	R^2	R^3M[a]		Yield/%[b]	$[\alpha]_D$/deg[d]	ee %[g]
1	**8A**	Me	Ph	*n*-PrMgBr	**13**	50	−7.55 (*c* 7.33)	98.0
2	**8A**	Me	Ph	AllylMgCl	**14**	40	−11.77 (*c* 7.54)[e]	40.7
3	**8A**	Me	Ph	AllylMgBr	**14**	50	−12.85 (*c* 9.05)[e]	44.5
4	**8E**	Me	Allyl	PhMgBr	**14**	86	−0.45 (*c* 3.98)[e]	1.6
5	**10A**	Me	Ph	AllylMgCl	**14**	34[c]	−3.43 (*c* 4.78)[e]	11.9
6	**8A**	Me	Ph	*n*-BuMgBr	**15**	40	−6.02 (*c* 8.30)	72.2
7	**9A**	Me	Ph	*n*-BuMgBr	**15**	50[c]	+2.18 (*c* 5.95)	26.6
8	**8A**	Me	Ph	$PhCH_2MgCl$	**16**	70[c]	+9.55 (*c* 6.97)	45.9
9	**8C**	Ph	1-Np	EtMgBr	**17**	12	−1.86 (*c* 3.17)[f]	7.6[h]

a) The reaction was carried out in Et_2O by using equimolar amount of silyl ether and 1.5 to 2.5 molar amounts of R^3M at 0 to 10 °C. b) Unless otherwise noted, isolated yield. c) GC yield. d) Unless otherwise noted, the solvent was CCl_4. e) The solvent was pentane. f) The solvent was cyclohexane. g) Based on max $[\alpha]_D$ estimated in this report, except for **17**. h) Based on (***R***)-**17**, $[\alpha]_D$ +24.6° (CCl_4)[13] absolute configulation was ***S***.



Scheme 2.

Table 5. Estimated Maximum Rotation of Silane **11**—**16**

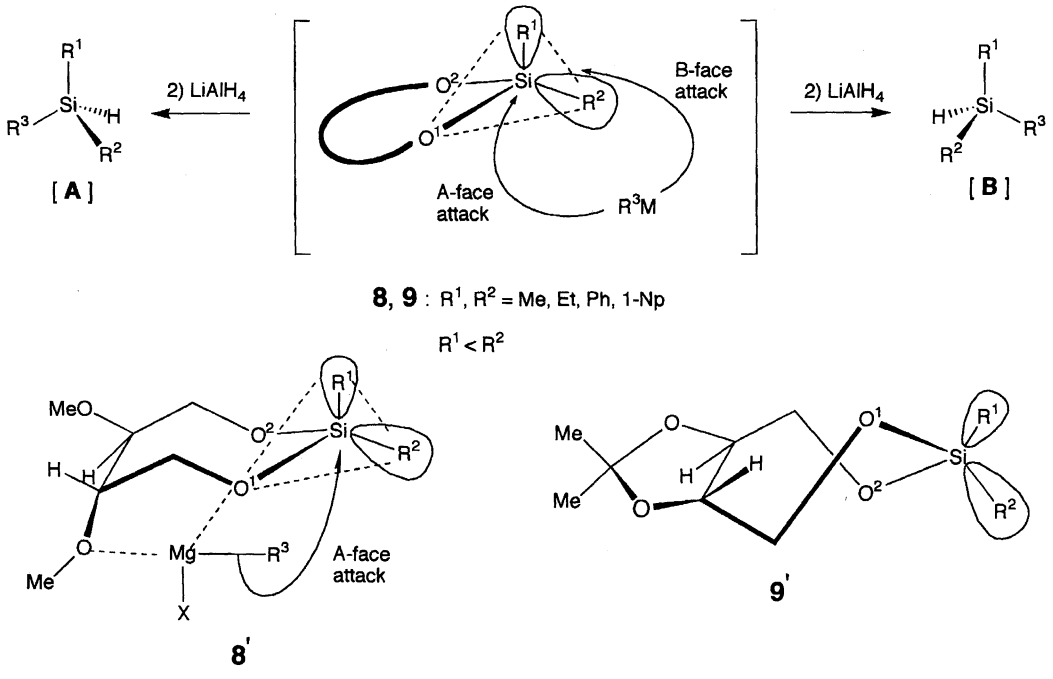
Silyl ether	R^3M[a]	Diastereomer[c]			Silane **11**—**16**				
			NMR (de %)	GC (de %)		Observed $[\alpha]_D$/deg[d]	Calculated $[\alpha]_D$/deg NMR	GC	Average
8A	1-NpMgBr	**11***	27.2	26.2	**11**	−8.78 (*c* 4.99)[e]	−32.3	−33.5	32.9[h]
6A	EtMgBr[b]	**12****	15.0	—	**12**	−1.09 (*c* 7.21)	−7.5[g]	—	
6A	EtLi[b]	**12****	39.6	—	**12**	+3.02 (*c* 5.76)	+7.9[g]	—	
8A	EtMgBr	**12***	72.5	81.3	**12**	−5.77 (*c* 10.14)	−7.96	−7.10	7.5[i]
8A	EtLi[b]	**12***	34.6	—	**12**	−2.62 (*c* 7.70)	−7.57	—	
8A	EtMgBr (THF)	**12***	10.4	—	**12**	+0.75 (*c* 6.62)	+7.2	—	
8A	*n*-PrMgBr	**13***	98.0	—	**13**	−7.55 (*c* 7.33)	−7.70	—	7.22
8A	*n*-PrMgBr	**13***	—	81.1	**13**	−5.47 (*c* 10.57)	—	−6.74	
8A	AllylMgBr	**14***	44.6	—	**14**	−12.85 (*c* 9.05)[f]	−28.8	—	28.8
8A	*n*-BuMgBr	**15***	72.2	—	**15**	−6.02 (*c* 8.30)	−8.34	—	8.34
8A	$PhCH_2MgCl$	**16***	27.5	—	**16**	+3.91 (*c* 5.70)	+14.2	—	14.2

a) The reaction was carried out at 0 to 10 °C, unless otherwise noted. b) The reaction was carried out at −70 °C. c) The diastereomer excess was determined by ^{1}H NMR or GC analysis. d) Unless otherwise noted, the solvent was CCl_4. e) The solvent was cyclohexane. f) The solvent was pentane. g) Calculated as **6A** being 97% pure. h) Reported (***R***)-**11**, $[\alpha]_D$ +34.3° (*c* 10.9, cyclohexane).[12a] i) Reported (***S***)-**12**, $[\alpha]_D$ +2.53° (*c* 10.1, CCl_4).[12b]

yield of the reaction of **8A** with EtMgBr to give **12** was calculated to be 93%ee, and that of **8A** with *n*-PrMgBr to give **13** was 98%ee (Entry 6 in Table 3, Entry 1 in Table 4).

Stereochemistry. In general, seven-membered ring compounds have two conformational families that can not interconvert each other due to a substantial barrier. One family consists of a chair, a twist-chair, and all of the intermediate forms between these. The other one is the similar conformational mixture of a boat and a twist-boat. The twist forms have been pointed out as having energy minima.[14] The substituents of silicon in cycloheptane, such as **8A**—**8E**, should affect the conformational equilibrium, and cause the twist forms to be more stable. The CPK model of **9A**, which have the [5.3.0]bicyclic structure, suggests that the 1, 3-dioxa-2-silacycloheptane ring is fused in the most stable twist-chair conformation. It therefore does not react with Grignard reagents, as mentioned before. The intermediate of this reaction should be another conformational isomer, such as a chair.

Considering the absolute configuration of silanes obtained from this asymmetric synthesis, the results of the stereochemistry can be summarized as follows. The bulkiness of the substituents at the silicon in cyclic silyl ether **8** and **9** should be Me < Et < Ph < 1-Np. Assuming $R^1 < R^2$, the absolute configuration of chiral silanes **11**, **12**, and **17** (Entry 9 in Table 4) obtained from **8** can be summarized as type **A**,



Scheme 3.

while, on the other hand, those from **9** can be summarized as **B** in Scheme 3.[14] The absolute configuration of the products in such an asymmetric reaction as ring opening of the cyclic compound having a C_2 chiral auxiliary depends on the face selectivity of reagent to the cyclic substrate, regardless of its stereospecificity (inversion or retention). In this regard, **A**-face and **B**-face correspond to the triangle $\triangle R^1R^2O^1$ and $\triangle R^1R^2O^2$, respectively, in Scheme 3. Since the smaller R^1 preferentially occupies an axial position in the chair form of **8**, it is obvious that the organometallic reagents attack for **8** takes place from the **A**-face rather than the **B**-face, considering that $LiAlH_4$ reduction of the Si–O bonds proceeds with a retention of the configuration.[12] The preference in **A**-face selectivity of the nucleophile in these reactions of **8** can lead to a simple interpretation, if one imagines the quasi-five-membered ring intermediate **8′** derived from the chair form of **8** and Grignard reagents, as illustrated in the Scheme 3.

In 1,2-asymmetric addition reactions of aldehydes and ketones in which one of the neighboring groups of the chiral center could strongly coordinate with organometallic reagents, Cram interpreted the complex results in terms of a competition of the cyclic model versus the dipolar and open-chain models.[15] An analogous explanation could be adapted to our results. The chiral intermediate **8′** in conformational equilibrium of the reaction intermediates should be predominant when the difference of the bulkiness of R^1 and R^2 is large and when the reaction temperature is low, as described above. The significant decrease of the stereoselectivity in THF solvent could also be explained by this competition reaction, since the more basic THF should prevent the formation of **8′** with Grignard reagents. The reason why the reactions of **9A** with Grignard reagents gave products having opposite configurations to those of products from **8** with low optical yields should be due to the difficulty to form such a quasi-ring type intermediate as **8′** because of having the twist chair structure, as shown **9′** in Scheme 3.

Experimental

IR spectra were recorded on a Shimadzu FT-IR-4200 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a FT-NMR JEOL GXS 270 spectrometer in $CDCl_3$. The mass spectra were taken on a JEOL JMS-DX 302 ultrahigh-resolution instrument and a Shimadzu QP-1000 spectrometer. GC analyses were performed on a Shimadzu 14A spectrometer with a CBP1-M25-025 capillary column. Specific Rotations were measured with a Horiba SEPA-200 polarimeter. Solvents were distilled prior to use. Molecular sieves (80 mesh) were dried in an oven at 110 °C for 4 h. Highly optically pure (2*R*,4*R*)-2,4-pentanediol (**2**) (> 99%ee) was purchased from Aldrich Chemical. According to a literature procedure,[11] chiral glycols (2*S*,3*S*)-2,3-dimethoxy-1,4-butanediol (**3**), (4*S*,5*S*)-4,5-bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (**4**), (2*S*,3*S*)-1,4-bis(dimethylamino)-2,3-butanediol (**5**) were prepared from (2*R*,3*R*)-tartaric acid ($[\alpha]_D$ 12.40° (*c* 20.53, H_2O), 100%ee). (*S*)-2-Methoxy-1-propanol (**1**) was prepared from ethyl (*S*)-lactate (> 97%ee) by the same procedures as that of (*S*,*S*)-**3**. All Grignard reagents were prepared in diethyl ether, except for 1-NpMgBr, which was prepared in a mixture of THF/Et_2O/benzene (1/2/3).

Preparation of Cyclic and Acyclic Silyl Ethers.

(5*S*,6*S*)-5,6-Dimethoxy-2-methyl-2-phenyl-1,3-dioxa-2-silacycloheptane (8A): Method A. A typical experimental procedure is described for the synthesis of **8A**. To a stirred dry benzene (1 dm^3) at 70—80 °C, a solution of (*S*,*S*)-**3** (30 g, 0.2 mol) and pyridine (0.4 mol) in benzene (150 ml) and a solution of dichloromethylphenylsilane (40 ml, 0.25 mol) in benzene (200 ml) were simultaneously added dropwise. After stirring for 3 h followed by standing for 3 h, the precipitate was filtered off. The filtrate was washed with sat. $NaHCO_3$ (30 ml×2) and water (30 ml), then dried over anhydrous $MgSO_4$. After evaporation of the solvent, distillation of the residue gave (*S*,*S*)-**8A** in 84% yield; bp 116 °C/1.1×10^2 Pa; IR (neat) 2830, 1430, 1260, 1095 cm^{-1}; ^{1}H NMR δ = 0.40 (s, 3H, SiMe), 3.30—3.40 (m, 2H, 2CH), 3.48 (s, 3H, MeO), 3.49 (s, 3H, MeO), 3.93—4.08 (m, 4H, $2CH_2$), 7.30—7.71 (m, 5H, Ph); ^{13}C NMR δ = −4.35, 56.81, 57.24, 58.74, 59.23, 80.13, 80.68, 127.79, 130.24, 133.90; MS *m/z* 253 (M − Me; 22), 191 (83), 51 (80), 121 (67), 105 (100). Found: *m/z* 253.0877. Calcd for $C_{12}H_{17}O_4Si$: M − Me, 253.0896. $[\alpha]_D$ +46.1° (*c* 11.63, PhH).

(5*S*,6*S*)-5,6-Dimethoxy-2-methyl-2-(1-naphthyl)-1,3-dioxa-2-silacycloheptane (8B): It was prepared from (*S*,*S*)-**3** and dichloromethyl(1-naphthyl)silane. Yield 57%; bp 154 °C/4.7×10 Pa; IR (neat) 2830, 1505, 1260, 1080, 780 cm^{-1}; ^{1}H NMR δ = 0.56 (s, 3H, SiMe), 3.34—3.49 (m, 2H, 2CH), 3.49 (s, 3H, MeO), 3.54 (s, 3H, MeO), 4.07—4.27 (m, 4H, $2CH_2$), 7.49—8.39 (m, 7H, Np); ^{13}C NMR δ = −2.22, 56.90, 57.41, 59.03, 59.63, 80.39, 80.85, 125.00, 125.49, 126.15, 128.22, 128.74, 130.76, 132.08, 133.24, 134.53, 136.60; MS *m/z* 318 (M; 8), 303 (100), 273 (36), 201 (37), 178 (80). Found: *m/z* 318.1290. Calcd for $C_{17}H_{22}O_4Si$: M, 318.1287. $[\alpha]_D$ +38.2° (*c* 9.35, PhH).

(5*S*,6*S*)-5,6-Dimethoxy-2-(1-naphthyl)-2-phenyl-1,3-dioxa-2-silacycloheptane (8C): It was prepared from (*S*,*S*)-**3** and dichloro(1-naphthyl)phenylsilane. Yield 53%; bp 191 °C/4.0×10 Pa; IR (neat) 2830, 1505, 1430, 1090, 780 cm^{-1}; ^{1}H NMR δ = 3.45—3.49 (m, 2H, 2CH), 3.51 (s, 3H, MeO), 3.57 (s, 3H, MeO), 4.12—4.29 (m, 4H, $2CH_2$), 7.32—8.35 (m, 12H, Ph, Np); ^{13}C NMR δ = 56.84, 56.98, 59.17, 59.34, 80.42, 80.54, 124.97, 125.52, 126.12, 127.82, 128.60, 128.80, 130.38, 131.10, 133.24, 133.44, 134.59, 135.77, 137.01; MS *m/z* 381 (M+1; 20), 303 (92), 273 (37), 254 (77), 179 (88), 107 (100). Found: *m/z* 380.1433. Calcd for $C_{22}H_{24}O_4Si$: M, 380.1444. $[\alpha]_D$ +85.5° (*c* 11.14, PhH).

(5*S*,6*S*)-2-Ethyl-5,6-dimethyoxy-2-phenyl-1,3-dioxa-2-silacycloheptane (8D): It was prepared from (*S*,*S*)-**3** and dichloro(ethyl)phenylsilane. Yield 56%; bp 125 °C/1.1×10^2 Pa; IR (neat) 2830, 1430, 1265, 1090 cm^{-1}; ^{1}H NMR δ = 0.87—1.07 (m, 5H, Et), 3.32—3.40 (m, 2H, 2CH), 3.49 (m, 6H, 2MeO), 3.49 (m, 6H, 2MeO), 3.96—4.15 (m, 4H, $2CH_2$), 7.36—7.68 (m, 5H, Ph); ^{13}C NMR δ = 4.57, 6.30, 56.84, 57.21, 59.11, 59.29, 80.34, 80.85, 127.79, 130.18, 134.16; MS *m/z* 253 (M − Et; 40), 223 (49), 137 (55), 167 (88), 107 (100). Found: *m/z* 253.0889. Calcd for $C_{12}H_{17}O_4Si$: M−Et, 253.0896. $[\alpha]_D$ +48.3° (*c* 12.05, PhH).

(5*S*,6*S*)-2-Allyl-5,6-dimethoxy-2-methyl-1,3-dioxa-2-silacycloheptane (8E): It was prepared from (*S*,*S*)-**3** and dichloroallylmethylsilane. Yield 62%; bp 77 °C/1.2×10^2 Pa; IR (neat) 2830, 1630, 1260, 1090 cm^{-1}; ^{1}H NMR δ = 0.13 (s, 3H, SiMe), 1.60 (d, 2H, *J* = 1.22 Hz, CH_2), 3.28—3.31 (m, 2H, 2CH), 3.44 (s, 3H, MeO), 3.47 (s, 3H, MeO), 3.93—3.95 (m, 4H, $2CH_2$), 4.84—5.02 (m, 2H, =CH_2), 5.60—5.94 (m, 1H, =CH); ^{13}C NMR δ = −5.00, 21.80, 57.09, 57.10, 59.39, 59.50, 81.09, 81.09, 115.06, 133.47; MS *m/z* 218 (M − Me + 1; 0.4), 192 (8), 160 (92), 117 (29), 105 (100). Found: *m/z* 217.0887. Calcd for $C_9H_{17}O_4Si$: M − Me, 217.0896. $[\alpha]_D$ +61.8° (*c* 11.45, PhH).

Bis(2-methoxypropoxy)methylphenylsilane (6A): It was pre-

pared from (*S*)-**1** and dichloro(methyl)phenylsilane in a similar manner as that of **8A**, except for the procedure of washing the reaction mixture with sat. $NaHCO_3$ and water to avoid the hydrolysis of **6A**. Yield 85%; bp 114 °C/1.1×10^2 Pa; IR (neat) 2830, 1430, 1265, 1095 cm^{-1}; ^{1}H NMR δ = 0.37 (s, 3H, SiMe), 1.11 (d, 3H, J = 1.47 Hz, MeCHMeO), 1.13 (d, 3H, J = 1.47 Hz, MeCHMeO), 3.32—3.44 (m, 2H, 2CH), 3.32 (s, 3H, MeO), 3.35 (s, 3H, MeO), 3.59—3.77 (m, 4H, 2CH_2), 7.31—7.64 (m, 5H, Ph); ^{13}C NMR δ = −1.00, 15.11, 56.35, 66.14, 77.28, 127.85, 130.01, 133.01, 133.35, 133.70; MS *m/z* 284 (M − Me + 1; 5), 222 (20), 210 (15), 152 (100), 121 (49), 105 (56). Found: *m/z* 298.1589. Calcd for $C_{15}H_{26}O_4Si$: M, 298.1600.

(4*R*,6*R*)-2,4,6-Trimethyl-2-phenyl-1,3-dioxa-2-silacyclohexane (7A): It was prepared from (*R*,*R*)-**2** and dichloro(methyl)phenylsilane, except for the procedure of washing the reaction mixture with sat. $NaHCO_3$ and water to avoid the hydrolysis of **7A**. Yield 50%; bp 78 °C/1.1×10^2 Pa; IR (neat) 2912, 1429, 1379, 1257, 1151, 980 cm^{-1}; ^{1}H NMR δ = 0.41 (s, 3H, SiMe), 1.28 (d, 3H, J = 6.59 Hz, Me), 1.36 (d, 3H, J = 6.34 Hz, Me), 1.69—1.85 (m, 2H, CH_2), 4.43—4.51 (m, 2H, 2CH), 7.34—7.66 (m, 5H, Ph); ^{13}C NMR δ = −0.46, 23.46, 23.58, 42.70, 66.46, 67.06, 127.79, 129.92, 133.44, 137.07; MS *m/z* 223 (M+1; 3), 208 (100), 164 (85), 145 (35), 138 (59). Found: *m/z* 222.1071. Calcd for $C_{12}H_{18}O_2Si$: M, 222.1076. [α]$_D$ +20.3° (*c* 9.78, PhH).

(1*S*,7*S*)-4,9,9-Trimethyl-4-phenyl-3,5,8,10-tetra-4-oxasilabicyclo[5.3.0]decane (9A): It was prepared from (*S*,*S*)-**4** and dichloromethylphenylsilane, except for the procedure of washing the reaction mixture with sat. $NaHCO_3$ and water to avoid the hydrolysis of **9A**. Yield 41%; bp 105 °C/6.7×10 Pa; IR (neat) 1430, 1380, 1370, 1260, 1080 cm^{-1}; ^{1}H NMR δ = 0.34 (s, 3H, SiMe), 1.33 (s, 3H, Me), 1.40 (s, 3H, Me), 3.60—4.05 (m, 4H, 2CH_2), 4.13—4.40 (m, 2H, 2CH), 7.28—7.63 (m, 5H, Ph); ^{13}C NMR δ = −2.24, 26.69, 27.03, 63.69, 64.24, 80.91, 81.23, 110.14, 128.17, 130.38, 133.67, 134.39; MS *m/z* 265 (M − Me; 12), 206 (23), 144 (100), 130 (70), 114 (75), 105 (43). Found: *m/z* 265.0900. Calcd for $C_{13}H_{17}O_4Si$: M − Me, 265.0896. [α]$_D$ +15.9° (*c* 8.17, PhH).

Preparation of (4*S*,5*S*)-Bis(dimethylaminomethyl)-2-methyl-2-phenyl-1,3-dioxa-2-silacyclohexane (10A): Method B. To a stirred solution of (*S*,*S*)-**5** (0.14 mol) and methylphenylsilane (0.17 mol) in dry benzene (300 ml) and slowly added a suspension of Pd/C (10%, 2.3 g) in benzene (50 ml) at 45 °C. After stirring for 15 h, an insoluble material was filtered off and the filtrate was evaporated in vacuo. Distillation of the residue gave (*S*,*S*)-**10A**; Yield 74%; bp 128 °C/2.7×10 Pa; IR (neat) 2825, 2770, 1430, 1250 cm^{-1}; ^{1}H NMR δ = 0.37 (s, 3H, SiMe), 1.94—2.87 (m, 16H, 2CH_2NMe_2), 3.45—4.02 (m, 2H, 2CH), 7.34—7.66 (m, 5H, Ph); ^{13}C NMR δ = 0.73, 45.84, 62.22, 68.73, 127.69, 127.74, 133.02, 133.64; MS *m/z* 250 (M − NMe_2; 3), 236 (100), 163 (15), 137 (16), 121 (17). Found: *m/z* 250.1267. Calcd for $C_{13}H_{20}O_2NSi$: M − NMe_2, 250.1263. [α]$_D$ −10.1° (*c* 10.1, PhH).

Asymmetric Synthesis of Silicon Compounds: A typical experimental procedure is described for the synthesis of ethylmethylphenylsilane (**12**). To a stirred solution of **8A** (10 mmol) in dry ether (90 ml) was added dropwise a solution of EtMgBr (12 mmol) in diethyl ether at 0 °C. After 30 min, $LiAlH_4$ (about 0.5 g) was added to the reaction solution, followed by stirring at room temperature for 1 h. After the resulting mixture was poured into 2—3% HCl containing crushed ice, the product was extracted several times with diethyl ether. The combined ethereal layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The distillation of the residue gave (+)-**12**, Yield 75%; bp 113 °C/1.1×10^4 Pa; IR (neat) 2870, 2120, 1430, 1250 cm^{-1}; ^{1}H NMR δ = 0.33 (d, 3H, J = 3.66 Hz, SiMe), 0.76—1.05 (m, 5H, Et), 4.31 (sext, 1H, J = 3.66 Hz, SiH), 7.32—7.56 (m, 5H, Ph); ^{13}C NMR δ = −6.16, 5.26, 7.91, 127.82, 129.18, 134.33, 136.49; MS *m/z* 150 (M; 17), 135 (3), 121 (100), 105 (18). The other similar reactions producing chiral silane **12** were carried out under the reaction conditions summarized in Table 3.

Methyl(1-naphthyl)phenylsilane (11): IR (neat) 2120, 1505, 1430, 1250, 780 cm^{-1}; ^{1}H NMR δ = 0.78 (d, 3H, J = 3.79 Hz, SiMe), 5.38 (q, 1H, J = 3.91 Hz, SiH), 7.34—8.10 (m, 12H, Ph, Np); ^{13}C NMR δ = −4.52, 125.17, 125.60, 126.04, 126.58, 127.94, 127.99, 128.86, 129.46, 130.44, 133.18, 134.85, 135.19, 135.34, 137.04; MS *m/z* 248 (M; 58), 233 (31), 170 (76), 155 (58), 120 (100), 105 (72).

Methylphenyl(*n*-propyl)silane (13): IR (neat) 2860, 2120, 1430, 1250 cm^{-1}; ^{1}H NMR δ = 0.33 (d, 3H, J = 3.79 Hz, SiMe), 0.72—1.04 (m, 5H, $CH_2CH_2CH_3$), 1.25—1.56 (m, 2H, $CH_2CH_2CH_3$), 4.34 (sext, 1H, J = 3.59 Hz, SiH), 7.28—7.58 (m, 5H, Ph); ^{13}C NMR δ = −5.64, 15.89, 17.82, 127.79, 129.12, 134.30, 136.75; MS *m/z* 164 (M; 9), 149 (3), 121 (100), 105 (18), 86 (58). Found: *m/z* 164.1013. Calcd for $C_{10}H_{16}Si$: M, 164.1021. [α]$_D$ +85.5° (*c* 11.14, PhH).

Allylmethylphenylsilane (14): IR (neat) 2120, 1630, 1430, 1250 cm^{-1}; ^{1}H NMR δ = 0.36 (d, 3H, J = 3.78 Hz, SiMe), 1.77—1.89 (m, 2H, $CH_2CH{=}CH_2$), 4.35 (sext, 1H, J = 3.56 Hz, SiH), 4.81—5.01 (m, 2H, $=CH_2$), 5.60—5.94 (m, 1H, CH=), 7.32—7.59 (m, 5H, Ph); ^{13}C NMR δ = −6.28, 21.04, 114.00, 127.85, 129.41, 134.16, 134.33, 135.63; MS *m/z* 162 (M; 13), 147 (6), 121 (100), 105 (25).

***n*-Butylmethylphenylsilane (15):** IR (neat) 2860, 2120, 1430, 1250 cm^{-1}; ^{1}H NMR δ = 0.33 (d, 3H, J = 3.79 Hz, SiMe), 0.71—0.94 (m, 5H, $CH_2(CH_2)_2CH_3$), 1.22—1.41 (m, 4H, $CH_2(CH_2)_2CH_3$), 4.34 (sext, 1H, J = 3.78 Hz, SiH), 7.31—7.58 (m, 5H, Ph); ^{13}C NMR δ = −5.67, 13.07, 13.76, 26.17, 26.51, 127.79, 129.12, 134.30, 136.78; MS *m/z* 178 (M; 6), 163 (1), 121 (100), 105 (16), 100 (44).

Benzylmethylphenylsilane (16): IR (neat) 2120, 1490, 1430, 1250 cm^{-1}; ^{1}H NMR δ = 0.30 (d, 3H, J = 3.66 Hz, SiMe), 2.20—2.51 (m, 2H, CH_2), 4.44 (sext, 1H, J = 3.25 Hz, SiH), 6.94—7.54 (m, 10H, 2Ph); ^{13}C NMR δ = −6.19, 23.55, 124.37, 127.82, 128.28, 128.34, 129.43, 134.39, 135.54, 139.20; MS *m/z* 212 (M; 22), 197 (2), 134 (10), 121 (100), 105 (20).

Ethyl(1-naphthyl)phenylsilane (17): IR (neat) 2870, 2120, 1505, 1430, 780 cm^{-1}; ^{1}H NMR δ = 1.22—1.49 (m, 5H, Et), 5.38 (t, H, J = 3.66 Hz, SiH), 7.44—8.22 (m, 12H, Ph, Np); ^{13}C NMR δ = 4.46, 8.57, 125.17, 125.60, 126.01, 126.60, 127.99, 128.86, 129.46, 130.41, 133.29, 134.65, 135.14, 135.51, 137.32; MS *m/z* 262 (M; 42), 233 (100), 155 (43), 105 (40).

Estimation of the Specific Rotation of Optically Pure Chiral Silanes. Diastereomeric ring-opening products that were precursors of chiral silane **11**—**16** were submitted to silylation with trimethylsilyl *N*-(trimethylsilyl)trifluoroacetimidate (BSTFA). Some small parts of the trimethylsilyl (TMS) ethers **11***—**16*** or silyl ether **12**** (being the precursor of **12** derived from **6A** as shown in Scheme 2) were purified by preparative gas chromatography. Their diastereomer ratios were determined by the capillary GC method and/or ^{1}H NMR method (compared with the integral value of peaks for MeO groups or $SiMe_3$ groups of TMS ethers). The reduction of the other parts with $LiAlH_4$ afforded optically active hydrosilanes **11**—**16** with an almost complete retention of the configuration, as described in the report.[12c] A typical experimental procedure is described for preparing the TMS ether **12*** of the diastereomers being the precursor of chiral silane **12** (Scheme 2, Table 3). To a stirred

solution of **8A** (10 mmol) in dry ether (90 ml) was added dropwise an ether solution of EtMgBr at 0 °C. After 30 min, the reaction mixture (20 ml) was poured into sat. NH_4Cl (30 ml), and the product was extracted two times with diethyl ether (50 ml). The combined ethereal layer was washed with water, dried with anhydrous Na_2SO_4 immediately, and then with anhydrous molecular sieves. After the dried solution was condensed to 2—3 ml, the resulting mixture was allowed to react with **5** ml of the reagent BSTFA. The silylated diastereomers **12*** was then purified by preparative gas chromatography, and their diastereomeric ratio was determined by the ^{1}H NMR method; compared with the integral value of peaks for MeO groups and $SiMe_3$ group of **12***, average ratio = 72.5 : 27.5 and/or the capillary GC method; compared with the integral value of diastereomer peaks, ratio = 81.3 : 18.7 in Table 5.

5,6-Dimethoxy-2,2-dimethyl-9-(1-naphtyl)-9-phenyl-3,8-dioxa-2,9-disiladecane (11*): IR (neat) 2825, 1505, 1430, 1250, 1095, 780 cm^{-1}; ^{1}H NMR δ = 0.100, 0.105 (2s, 9H, diastereomeric $SiMe_3$), 0.80 (s, 3H, SiMe), 3.33, 3.35, 3.38, 3.40 (4s, 6H, two sets of diastereomeric MeO), 3.32—3.50 (m, 2H, 2CH), 3.61—3.94 (m, 4H, $2CH_2$), 7.32—8.19 (m, 12H, Ph, Np); ^{13}C NMR δ = −2.01, −0.54, 59.08, 59.14, 59.20, 60.90, 61.79, 61.96, 80.77, 80.91, 125.00, 125.49, 125.92, 127.91, 128.57, 128.77, 129.81, 130.73, 133.32, 133.70, 134.27, 135.14, 136.55, 136.95; MS *m/z* 454 (M − Me + 1; 2), 392 (11), 341 (9), 277 (4), 247 (42), 151 (25), 73 (100). Found: *m/z* 468.2151. Calcd for $C_{26}H_{36}O_4Si_2$: M, 468.2152.

5,6-Dimethoxy-2,2,9-trimethyl-9-phenyl-3,8-dioxa-2,9-disilaundecane (12*): IR (neat) 2825, 1430, 1250, 1095, cm^{-1}; ^{1}H NMR δ = 0.10 (s, 9H, $SiMe_3$), 0.36 (s, 3H, SiMe), 0.80—1.00 (m, 5H, SiEt), 3.35—3.46 (m, 2H, 2CH), 3.38, 3.38, 3.39, 3.40 (4s, 6H, two sets of diastereomeric MeO), 3.63—3.76 (m, 4H, $2CH_2$), 7.34—7.57 (m, 5H, Ph); ^{13}C NMR δ = −4.43, −0.54, 6.67, 6.82, 59.17, 60.98, 61.47, 61.59, 80.77, 80.83, 127.79, 129.52, 133.72, 136.83; MS *m/z* 356 (M − Me + 1; 0.2), 341 (2), 294 (2), 277 (6), 235 (17), 151 (29), 149 (24), 73 (100). Found: *m/z* 370.1990. Calcd for $C_{18}H_{34}O_4Si_2$: M, 370.1995.

Ethyl(2-methoxypropyl)methylphenylsilane (12):** IR (neat) 2830, 1430, 1255, 1085 cm^{-1}; ^{1}H NMR δ = 0.38 (s, 3H, SiMe), 0.80—1.04 (m, 5H, SiEt), 1.11 (d, 3H, J = 6.28 Hz, Me), 3.34, 3.36 (2s, 3H, diastereomeric MeO), 3.33—3.45 (m, 1H, CH), 3.47—3.66 (m, 2H, CH_2), 7.37—7.61 (m, 5H, Ph); ^{13}C NMR δ = −4.35, 6.67, 6.79, 16.29, 56.78, 66.54, 77.54, 127.76, 129.49, 133.72, 136.92; MS *m/z* 223 (M − Me; 0.7), 209 (9), 161 (9), 151 (100), 150 (29), 121 (62). Found: *m/z* 223.1148. Calcd for $C_{12}H_{19}O_2Si$: M − Me, 223.1154.

5,6-Dimethoxy-2,2,9-trimethyl-9-phenyl-3,8-dioxa-2,9-disiladodecane (13*): IR (neat) 2830, 1430, 1255, 1090 cm^{-1}; ^{1}H NMR δ = 0.10, 0.11 (2s, 9H, diastereomeric $SiMe_3$), 0.37 (s, 3H, SiMe), 0.81—0.88 (m, 2H, $SiCH_2$), 0.92—0.98 (m, 3H, $CH_2CH_2CH_3$), 1.39—1.42 (m, 2H, $CH_2CH_2CH_3$), 3.38, 3.39, 3.39, 3.42 (4s, 6H, two sets of diastereomeric MeO), 3.38—3.42 (m, 2H, 2CH), 3.66—3.73 (m, 4H, $2CH_2$), 7.34—7.59 (m, 5H, Ph); ^{13}C NMR δ = −3.86, −0.52, 16.64, 17.73, 18.14, 59.17, 60.93, 61.21, 61.39, 80.71, 80.77, 127.79, 129.49, 133.67, 137.12; MS *m/z* 369 (M − Me; 0.2), 341 (3), 307 (2), 277 (7), 249 (13), 163 (37), 151 (46), 73 (100). Found: *m/z* 341.1613. Calcd for $C_{16}H_{29}O_4Si_2$: M − Pr, 341.1604.

7,8-Dimethoxy-4,11,11-trimethyl-4-phenyl-5,10-dioxa-4,11-disila-1-dodecene (14*): IR (neat) 2830, 1630, 1430, 1250, 1090 cm^{-1}; ^{1}H NMR δ = 0.10, (s, 9H, $SiMe_3$), 0.39 (s, 3H, SiMe), 1.82—1.92 (m, 2H, $CH_2CH{=}CH_2$), 3.33—3.43 (m, 2H, 2CH), 3.37, 3.38, 3.39, 3.40 (4s, 6H, two sets of diastereomeric MeO), 3.61—3.80 (m, 4H, $2CH_2$), 4.84—4.98 (m, 2H, CH_2), 5.71—5.88 (m, 1H, CH), 7.30—7.58 (m, 5H, Ph); ^{13}C NMR δ = −4.23, −0.52, 23.12, 59.14, 59.23, 60.90, 61.82, 80.68, 80.83, 114.40, 127.82, 129.72, 133.38, 133.72, 136.26; MS *m/z* 341 (M − Allyl; 0.5), 277 (5), 247 (0.7), 161 (15), 151 (88), 73 (100). Found: *m/z* 341.1594. Calcd for $C_{16}H_{29}O_4Si_2$: M − Allyl, 341.1604.

5,6-Dimethoxy-2,2,9-trimethyl-9-phenyl-3,8-dioxa-2,9-disilatridecane (15*): IR (neat) 2835, 1430, 1255, 1050 cm^{-1}; ^{1}H NMR δ = 0.10, 0.11 (2s, 9H, diastereomeric $SiMe_3$), 0.37 (s, 3H, SiMe), 0.80—0.90 (m, 5H, $CH_2(CH_2)_2CH_3$), 1.29—1.36 (m, 4H, $CH_2(CH_2)_2CH_3$), 3.38, 3.38, 3.39, 3.39 (4s, 6H, 2MeO), 3.35—3.47 (m, 2H, 2CH), 3.63—3.75 (m, 4H, $2CH_2$), 7.32—7.52 (m, 5H, Ph); ^{13}C NMR δ = −3.91, −0.52, 13.73, 14.82, 25.22, 26.37, 59.17, 60.93, 61.39, 61.53, 80.71, 80.77, 127.79, 129.49, 133.70, 137.30; MS *m/z* 383 (M − Me; 0.2), 341 (3), 322 (1), 277 (7), 263 (10), 177 (8), 151 (53), 73 (100). Found: *m/z* 341.1595. Calcd for $C_{16}H_{29}O_4Si_2$: M − Bu, 341.1604.

5,6-Dimethoxy-2,9,9-trimethyl-1,2-diphenyl-3,8-dioxa-2,9-disilatridecane (16*): IR (neat) 2826, 1495, 1430, 1255, 1090 cm^{-1}; ^{1}H NMR δ = 0.108, 0.112 (2s, 9H, diastereomeric $SiMe_3$), 0.33 (s, 3H, SiMe), 2.31—2.48 (m, 2H, CH_2Ph), 3.34, 3.35, 3.35, 3.36 (4s, 6H, two sets of diastereomeric MeO), 3.44—3.47 (m, 2H, 2CH), 3.63—3.74 (m, 4H, $2CH_2$), 6.99—7.51 (m, 10H, 2Ph); ^{13}C NMR δ = −4.46, −4.37, −0.52, 25.56, 59.11, 59.17, 60.90, 61.73, 61.85, 80.71, 80.83, 124.31, 127.79, 128.14, 128.69, 129.75, 133.81, 136.14, 138.30; MS *m/z* 341 (M − Benzyl; 4), 297 (0.4), 277 (7), 211 (11), 151 (44), 73 (100). Found: *m/z* 341.1596. Calcd for $C_{16}H_{29}O_4Si_2$: M − Benzyl, 341.1604.

References

1) W. J. Richter, *J. Organomet. Chem.*, **169**, 9 (1979).

2) T. Hayashi, K. Yamamoto, and M. Kumada, *Tetrahedron Lett.*, **15**, 331 (1974).

3) I. Ojima, T. Kogure, and Y. Nagai, *Tetrahedron Lett.*, **15**, 1889 (1974).

4) a) R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, **64**, C51 (1974); b) R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, **120**, 337 (1976).

5) H. Brunner, H. Nishiyama, and K. Itoh, in "Catalytic Asymmetric Synthesis," ed by I. Ojima, VCH Publishers, Inc., (1993), pp. 319—320.

6) T. Ohta, M. Ito, A. Tsuneto, and H. Takaya, *J. Chem. Soc., Chem. Commun.*, **1994**, 2525.

7) a) H. B. Kagan, *Pure Appl. Chem.*, **43**, 401 (1975); b) R. Noyori, I. Tomino, and Y. Tanimoto, *J. Am. Chem. Soc.*, **101**, 3129 (1979); c) T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc.*, **102**, 5974 (1980); d) J. P. Mazaleyrat and D. J. Cram, *J. Am. Chem. Soc.*, **103**, 4585 (1981); e) J. Fujiwara, Y. Fukutani, M. Hasegawa, K. Maruoka, and H. Yamamoto, *J. Am. Chem. Soc.*, **106**, 5004 (1984); f) T. Hayashi, A. Yamamoto, M. Hojo, K. Kishi, Y. Ito, E. Nishioka, H. Miura, and K. Yanagi, *J. Organomet. Chem.*, **370**, 129 (1989).

8) H. L. Cohen and G. F. Wright, *J. Org. Chem.*, **18**, 432 (1953).

9) a) R. Noyori, I. Tomino, Y. Tanimoto, and M. Nishizawa, *J. Am. Chem. Soc.*, **106**, 6709 (1984); b) A. Mori, J. Fujiwara, K. Maruoka, and H. Yamamoto, *Tetrahedron Lett.*, **24**, 4581 (1983); c) A. Mori, K. Ishihara, I. Arai, and H. Yamamoto, *Tetrahedron*, **43**, 755 (1987).

10) D. Seebach, H. O. Kalinowski, B. Bastani, G. Crass, H. Daum, H. Dorr, N. P. DuPreez, V. Ehrig, W. Langer, C. Nussler, H. A. Oei, and M. Schmidt, *Helv. Chim. Acta*, **60**, 301 (1977).

11) a) H. Meyer, J. Klein, and A. Weiss, *J. Organomet. Chem.*,

177, 323 (1979); b) R. H. Cragg and R. D. Lane, *J. Organomet. Chem.*, **267**, 1 (1984); c) R. H. Cragg and R. D. Lane, *J. Organomet. Chem.*, **289**, 23 (1985); d) K. Kobayashi, T. Kato, and S. Masuda, *Chem. Lett.*, **1987**, 101.

12) a) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964); b) L. H. Sommer, K. W. Michael, and W. D. Korte, *J. Am. Chem. Soc.*, **89**, 868 (1967); c) L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Am. Chem. Soc.*, **86**, 3276 (1964).

13) R. J. P. Corriu and G. Royo, *J. Organomet. Chem.*, **14**, 291 (1968).

14) F. A. L. Anet, "Medium-Sized Oxygen Heterocycles," in "Conformational Analysis of Medium-Sized Heterocycles," ed by R. S. Glass, VCH Publishers (1988), pp. 35—95.

15) a) D. J. Cram and F. A. A. Elhafez, *J. Am. Chem. Soc.*, **74**, 5851 (1952); b) D. J. Cram and D. R. Wilson, *J. Am. Chem. Soc.*, **85**, 1245 (1963).