(m, 2H, CH₂), 1.74 (m, 2H, CH₂), 3.56 (s, 2H, CH₂), 3.97 (t, 2H, $J=5$ Hz, CH₂), 4.26 (t, 2H, $J=6$ Hz, CH₂), 7.35 (d, 2H, $J=8$ Hz, aromatic H-3, 5), 8.01 (d, 2H, $J=8$ Hz, aromatic H-2, 6); ^{13}C-NMR (CDCl₃) δ 13.4 (CH₃), 13.6 (CH₃), 18.9 (CH₂), 19.1 (CH₂), 30.4 (CH₂), 30.6 (CH₂), 40.5 (CH₂), 41.2 (CH₂), 64.6 (CH₂) 64.7 (CH₂), 129.1 (aromatic C-3, 5), 129.2 (aromatic C-1), 129.6 (aromatic C-2, 6), 139.1 (aromatic C-4, 166.2 (COO), 170.7 (COO); Mass (m/e) 292 (M⁺, 9), 237 (19), 219 (29), 191 (21), 181 (36), 180 (19), 163 (7), 136 (61), 58 (100), 43 (70), 32 (70); IR (ν_{CO}) 1721 and 1738 cm⁻¹.

Methyl 2-carbomethoxyphenylacetate. colorless oil; ¹H-NMR (CCl₄) δ 3.60 (s, 3H, CH₃), 3.80 (s, 3H, CH₃), 3.90 (s, 2H, CH₂), 7.50 (m, 4H, aromatic H); Mass (m/e) 177 (28), 176 (85), 175 (14), 149 (81), 148 (100), 133 (94), 119 (36), 105 (15), 91 (82), 90 (34), 89 (30); IR (ν_{CO}) 1740 cm⁻¹.

Ethyl 2-carboethoxyphenylacetate. colorless oil; ¹H-NMR (CCl₄) δ 1.27 (t, 3H, $J=7$ Hz, CH₃), 1.39 (t, 3H, $J=7$ Hz, CH₃), 3.98 (s, 2H, CH₂), 4.16 (q, 2H, $J=7$ Hz, CH₂), 4.35 (q, 2H, $J=7$ Hz, CH₂), 7.23-8.20 (m, 4H, aromatic H); Mass (m/e) 191 (31), 190 (51), 163 (16), 162 (40), 135 (100), 134 (60), 118 (20), 90 (2), 89 (2); IR (ν_{CO}) 1717 and 1738 cm⁻¹.

ⁿPropyl 2-carbo-ⁿpropoxyphenylacetate. colorless oil; ¹H-NMR (CCl₄) δ 0.90 (t, 3H, $J=7$ Hz, CH₃), 1.20 (t, 3H, $J=7$ Hz, CH₃), 1.60 (m, 4H, (CH₂)₂), 3.95 (s, 2H, CH₂), 3.90 (t, 2H, $J=6$ Hz, CH₂), 4.17 (t, 2H, $J=6$ Hz, CH₂), 7.30 (m, 3H, aromatic H-3, 4, 5), 7.90 (m, 1H, aromatic H-6).

ⁿButyl 2-carbo-ⁿbutoxyphenylacetate. colorless oil; ¹H-NMR (CCl₄) δ 0.98 (m, 6H, (CH₃)₂), 1.55 (m, 8H, (CH₂)₄), 3.93 (s, 2H, CH₂), 4.10 (m, 4H, (CH₂)₂), 7.30 (m, 3H, aromatic H-3, 4, 5), 7.90 (m, 1H, aromatic H-6).

Methyl 3-carbomethoxyphenylacetate. colorless oil; ¹H-NMR (CCl₄) δ 3.60 (s, 2H, CH₂), 3.63 (s, 3H, CH₃), 3.85 (s, 3H, CH₃), 7.44 (m, 2H, aromatic H-4, 5), 7.91 (m, 2H,

aromatic H-2, 6); Mass (m/e) 209 (4), 208 (M⁺, 34), 178 (4), 177 (47), 164 (6), 151 (9), 149 (100), 119 (17), 105 (15), 91 (21), 90 (21), 80 (28); IR (ν_{CO}) 1724 cm⁻.

Ethyl 3-carboethoxyphenylacetate. colorless oil; ¹H-NMR (CCl₄) δ 1.23 (t, 3H, $J=7$ Hz, CH₃), 1.37 (t, 3H, $J=7$ Hz, CH₃), 3.57 (s, 2H, CH₂), 4.12 (q, 2H, $J=7$ Hz, CH₂), 4.37 (q, 2H, $J=7$ Hz, CH₂), 7.47 (m, 2H, aromatic H-4, 5), 7.90 (m, 2H, aromatic H-2, 6); Mass (m/e) 237 (2), 236 (M⁺, 17), 218 (11), 192 (5), 191 (36), 164 (26), 165 (100), 136 (23), 135 (36), 119 (47), 91 (30), 89 (30), 32 (74); IR (ν_{CO}) 1721 cm⁻¹.

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Deoxygenation of β-Aryl-α,β-Epoxy Silanes to Vinylsilanes by Magnesium-Magnesium Halide

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The reactions of β-aryl-α,β-epoxy silanes with magnesium bromide or magnesium iodide in the presence of excess magnesium in ether at room temperature afforded vinylsilanes in 18-100% yields. E-Vinylsilanes were predominant over Z-isomers (>80%) regardless of the stereochemistry of α,β-epoxy silanes.

Introduction

The deoxygenation of epoxides to olefins has been studied and numerous reagents have been developed.[1] The deoxygenation of α,β-epoxy silanes was largely ignored in spite of its synthetic interest.[2] This reaction could provide a good route to vinylsilanes which have received increasing attention as a highly versatile synthon in organic synthesis.[3] Y.

Ito and coworkers have reported that copprer-catalyzed Grignard reagent caused deoxygenation of α,β-epoxy silanes having one or two alkoxy groups on silicon.[4] However, the reaction with α,β-epoxy trimethylsilanes gave a normal ring-opening product. No deoxygenation was observed. Recently, we found that lithium was more effective than copper-catalyzed Grignard reagent for the deoxygenation of α,β-epoxy silanes; α,β-epoxy trimethylsilanes, which are more readily

Deoxygenation of α,β-Epoxy Silanes by Mg-MgX₂

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Table 1. Yields and Ratio of Z/E Isomers of 3

	3	Yield*	Ratio of
Compound	Ar	(%)	Z/E isomer**
a***	C_6H_5	90	77/23
b	p-ClC₆H₄	70	82/18
c	m-ClC₆H₄	60	97/3
d	o-ClC₆H₄	67	97/3
e	p-BrC₆H₄	70	77/23
f	o-BrC₆H₄	70	96/4
g	p-CH₃C₆H₄	65	96/4
h	p-OCH₃C₆H₄	68	95/5

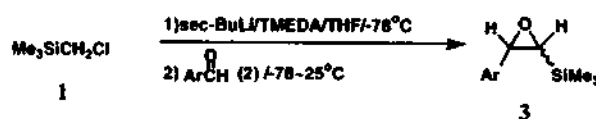*Isolated yields. **Determined by ¹H-NMR and GC (See Table 2) analysis. ***See ref. 6.

available than alkoxysilyl ones underwent the deoxygenation to give vinyisilanes stereoselectively.[5] The yields of vinylsilanes were good for aliphatic α,β-epoxy silanes, but, very low for aromatic ones with lithium.

We now report that β-aryl-α,β-epoxy silanes can undergo a deoxygenation reaction with magnesium-magnesium halide to afford vinylsilanes in improved yields.

Results and Discussions

Synthesis of α,β-Epoxy Silanes. α,β-Epoxy trimethylsilanes (3) were prepared by Magnus method.[6] When a THF solution of chloromethyltrimethylsilane (1) was treated with sec-BuLi (1.2 M in cyclohexane) at −78℃ in the presence of N,N,N′,N′-tetramethylethylenediamine (TMEDA) (1.05 eguiv), and then with an aromatic aldehyde 2 between −78℃ and 25℃ a mixture of Z and E isomers of α,β-epoxy silane 3 was obtained in good yields (Table 1).
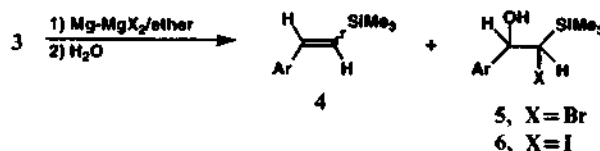
The Z and E isomers of 3-(4′-chlorophenyl)-2-trimethylsil-

yloxirane (3b) were isolated by preparative tlc (silica gel, *n*-hexane : ether=8 : 1); the ratio of Z/E isomers was 82 : 18. Both showed M+2 ion at m/e 228 and molecular ion at m/e 226 in the mass spectra. Other α,β-epoxy silanes could only be separated to their Z and E isomers by capillary GC, however, the structures were all assigned by spectroscopic correlation with Z and E-3b (Table 2).

¹H-NMR data of 3 revealed the following characteristics: (1) the coupling constants between the oxirane ring protons were larger for the Z than for the E isomer (eg., 3b: 5.4 vs. 3.0 Hz); (2) The silicon methyls absorbed at slightly higher field for the Z than for the E isomer (eg., 3b: δ −0.16 vs. 0.13). Z isomers were prdouced predominantly over E isomers in every case.

Reactions of α,β-Epoxy Silanes with Magnesium-Magnesium Halide. When the reaction of α,β-epoxy silane 3b with Mg-MgBr₂ suspension prepared from magnesium (3.3 mmol) and dibromoethane (2.0 mmol) in ether (3 ml) was performed at −10℃, bromohydrin 5 was produced as a single product in 77% yield (Table 3, entry 1). However, when the reaction was carried out at room temperature for 16 h, vinylsilane 4b (25%) was obtained along with bromhydrin 5 (53%) (entry 2). Similar results were obtained in homogeneous MgBr₂ etherate prepared by using a large amount of ether (entry 3).

Table 2. Spectral Data of α,β-Epoxy Silanes

α,β-Epoxy Silane	¹H-NMR (CDCl₃) δ, J (Hz)	¹³C-NMR (CDCl₃) δ	MS m/e (relative intensity, %)
(Z)-3b	−0.16 (s, 9H, SiMe₃), 2.15 (d, 1H, J=5.4, SiCH), 4.20 (d, 1H, J=5.4, ArCH), 7.29 (s, 4H)	−2.20, 53.36, 56.52, 127.51, 128.20, 133.14, 136.58	228 (M+2, 8), 226 (M⁺, 23), 211 (M⁺-CH₃, 6), 195 (M⁺-CH₃-O, 17), 152 (M⁺-Me₃Si-1, 9), 115 (M⁺-C₆H₄Cl, 7), 95 (12), 93 (34), 89 (33), 73 (100)
(E)-3b	0.13 (s, 9H, SiMe₃), 2.27 (d, 1H, J=3.0, SiCH), 3.65 (d, 1H, J=3.0, ArCH), 7.1-7.4 (m, 4H)	−3.66, 55.37, 58.01, 126. 64, 128.62, 133.49, 137.92	228 (28), 226 (M⁺, 77), 211 (9), 195 (19), 152 (9), 115 (9), 95 (9), 93 (34), 89 (37), 73 (100)
(Z)-3c	0.15 (s, 9H, SiMe₃), 2.52 (d, 1H, J=5.4, SiCH), 4.21 (d, 1H, J=5.4, ArCH), 7.2-7.4 (m, 4H)	−2.23, 53.59, 56.46, 124. 31, 126.28, 127.57, 129.34, 134.07, 140.16	228 (16), 226 (M⁺, 46), 211 (11), 195 (21), 115 (18), 95 (17), 93 (47), 89 (38), 73 (100)
(E)-3c	0.15 (s, 9H, SiMe₃), 2.29 (d, 1H, J=3.0, SiCH), 3.65 (d, 1H, J=3.0, ArCH), 7.2-7.4 (m, 4H)	*	228 (32), 226 (M⁺, 88), 211 (17), 195 (16), 115 (8), 95 (15), 93 (41), 89 (29), 73 (100)
(Z)-3d	−0.17 (s, 9H, SiMe₃), 2.65 (d, 1H, J=5.4, SiCH), 4.26 (d, 1H, J=5.4, ArCH), 7.2-7.4 (m, 4H)	−2.41, 53.50, 56.03, 126.38, 127.73, 128.65, 133.00, 136.19	228 (3), 226 (M⁺, 9), 211 (12), 195 (22), 152 (9), 118 (M⁺-Me₃Si-Cl, 17), 95 (39), 93 (100), 89 (53), 73 (95).
(E)-3d	0.17 (s, 9H, SiMe₃), 2.14 (d, 1H, J=3.0, SiCH), 4.02 (d, 1H, J=3.0, ArCH), 7.2-7.4 (m, 4H)	*	228 (37), 226 (M⁺, 100), 211 (3), 195 (2), 152 (4), 118 (4), 95 (29), 93 (79), 73 (54)
(Z)-3e	−0.16 (s, 9H, SiMe₃), 2.51 (d, 1H,	−2.21, 53.42, 56.49.	272 (61), 270 (M⁺, 59), 198 (12), 196 (11),

	$J=5.5$, SiCH), 4.17 (d, 1H, $J=5.5$, ArCH), 7.13-7.23, 7.43-7.46 (m, 4 H)	121.18, 127.81, 131.08, 137.06	176 (68), 161 (83), 139 (8), 137 (7), 118 (18), 90 (20), 89 (46), 73 (100)
(E)-3e	0.13 (s, 9H, SiMe₃), 2.26 (d, 1H, $J=3.0$, SiCH), 3.64 (d, 1H, $J=3.0$, ArCH), 7.13-7.23, 7.43-7.46 (m, 4 H)	−3.70, 55.33, 57.94, 121.47, 126.92, 131.49, 138.44	272 (86), 270 (M⁺, 81), 198 (10), 196 (10), 176 (69), 161 (79), 139 (7), 137 (7), 118 (22), 90 (20), 89 (45), 73 (100)
(Z)-3f	−0.16 (s, 9H, SiMe₃), 2.65 (d, 1H, $J=5.1$, SiCH), 4.20 (d, 1H, $J=5.1$, ArCH), 7.1-7.6 (m, 4H)	−2.18, 53.64, 58.15, 122.51, 126.95, 128.17, 129.04, 131.81, 137.74	272 (17), 270 (M⁺, 16), 255 (3), 198 (8), 176 (75), 161 (46), 139 (57), 137 (54), 118 (18), 90 (30), 89 (55), 73 (100)
(E)-3f	0.17 (s, 9H, SiMe₃), 2.13 (d, 1H, $J=3.2$, SiCH), 3.97 (d, 1H, $J=3.2$, ArCH), 7.1-7.6 (m, 4H)	*	272 (21), 270 (M⁺, 20), 255 (3), 198 (9), 176 (90), 161 (58), 139 (69), 137 (75), 118 (10), 90 (25), 89 (42), 73 (100)
(Z)-3g	−0.16 (s, 9H, SiMe₃), 2.34 (s, 3H) 2.49 (d, 1H, $J=5.4$, SiCH), 4.21 (d, 1H, $J=5.4$, ArCH), 7.14-7.23 (m, 4H)	−2.20, 21.18, 53.40, 56.99, 125.99, 128.63, 134.93, 136.98	206 (M⁺, 74), 191 (M⁺-CH₃, 32), 176 (M⁺-2CH₃, 22) 175 (100), 133 (M⁺-Me₃Si, 7), 132 (24), 115 (16), 105 (18), 91 (16), 77 (21), 73 (86)
(E)-3g	0.13 (s, 9H, SiMe₃), 2.34 (s, 4H) 3.66 (d, 1H, $J=3.67$, SiCH), 7.13-7.23 (m, 4H)	*	206 (M⁺, 100), 191 (26), 176 (26), 175 (59), 133 (4), 132 (8), 115 (7), 105 (10), 91 (3), 77 (12), 73 (35)
(Z)-3h	−0.16 (s, 9H, SiMe₃), 2.47 (d, 1H, $J=5.5$, SiCH), 3.79 (s, 3H), 4.19 (d, 1H, $J=5.5$, ArCH), 6.81-6.83, 7.22-7.26 (m, 4H)	−2.23, 53.40, 55.14, 56.69, 113.36, 127.17, 128.54, 130.04	222 (M⁺, 100), 207 (M⁺-CH₃, 20), 192 (44), 191 (M⁺-CH₃O, 22), 149 (M⁺-Me₃Si, 10), 148 (16), 121 (27), 91 (18), 89 (16), 73 (62)
(E)-3h	0.12 (s, 9H, SiMe₃), 2.32 (d, 1H, $J=3.1$, SiCH), 3.64 (d, 1H, $J=3.1$, ArCH), 3.71 (s, 3H), 6.81-6.83, 7.22-7.26 (m, 4H)	*	222 (M⁺, 100), 207 (15), 192 (29), 191 (15), 149 (10), 148 (9), 121 (20), 91 (9), 89 (12), 73 (28)

*The relative amount of the E isomer was too small to characterize the spectrum

Table 3. Reaction of **3b** with Mg-MgBr₂*

Entry	Mg (eq)	BrCH₂CH₂Br (eq)	Ether (ml)	Time (h)	Product (Yield,** %)	
					Vinylsilane (4b)	Bromohydrin (5b)
1	3.3	2.0	3	5	−	77
2	3.3	2.0	3	16	25	53
3	3.3	2.0	22	14	14	68
4	5.5	3.4	6	15	74	−
5	37.2	22.6	20	17	94	−
6	11.2	2.3	9	12	59	−
7	7.6	15.6	9	14	−	53

*Reaction was carried out at room temperature except entry 1 (at −10℃). **Isolated yield.

When the reaction was carried out with more than three equivalents of MgBr₂ in the presence of more than two equivalents of excess magnesium, only vinylsilane **4b** was obtained in 74% yield (entry 4). Large excess of Mg and MgBr₂ improved the yield of **4b** (entry 5). However, when less than three equivalents of MgBr₂ was used the yield became lower (entry 6). Vinylsilane **4b** was not formed in the absence of excess magnesium (entry 7).

Since we found that Mg-MgBr₂ etherate was effective for the deoxygenation of α,β-epoxy silane **3b** to vinylsilane **4b**, we examined this for other α,β-epoxy silanes to confirm its generality. The reactions of **3a, 3b** and **3d** with Mg-MgBr₂

etherate at room temperature afforded vinylsilanes **4a, 4b** and **4d** as single products in good yields, respectively (Table 4, entries 2, 3 and 6). From the reactions of **3e** and **3f** with Mg-MgBr₂ the vinylsilanes **4e** and **4f** were also obtained respectively, however, the yields were very low (Table 4, entries 7 and 9).

Magnesium-magnesium iodide etherate was also effective for the deoxygenation of α,β-epoxy silanes. The yields of the vinylsilanes **4b, 4f** and **4h** were greatly improved than those in the reactions with Mg-MgBr₂ (Table 4, entries 3, 10 and 13). However, there was no considerable improvement in the cases of **3e** and **3g** (Table 4, entries 8 and 12).

The reactions of **3** with Mg-MgX₂ afforded a mixture of E and Z isomers of vinylsilanes **4**. Z and E isomers of **4** could only be separated by capillary GC with the retention time of E isomer being longer than that of Z isomer in each case. In the ¹H-NMR spectra, the silicon methyls appeared at slightly lower field for the E than for the Z isomer (eg., **4b**: δ 0.10 vs. 0.00), and the coupling constants between the vinylic protons were larger for the E than for the Z isomer (eg., **4b**: 19.4 vs. 15.1 Hz). The vinylic protons appeared as a pair of doublets (eg., **4b**: δ 6.39 and 6.75) in E isomers, while one of them (ArC$\underline{H}$) overlapped with the aromatic proton signals in Z isomer. The ¹H-NMR spectral data and ratio of Z and E isomers of **4** were summarized in Table 5. It is interesting to note that the deoxygenation of α,β-epoxy silanes **3** with Mg-MgX₂ afforded E isomer of vinylsilanes **4** in greater than 80%. The stereoselectivity observed in this reaction is very similar to the results by Ito[4], Barluenger[7] and us[5].

Deoxygenation of α,β-*Epoxy Silanes by Mg-MgX₂*

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Table 4. Reaction of 3 with Mg-MgX₂*

Entry	α,β-Epoxy Silane	Mg (equiv)	MgX₂ (equiv)	Time (h)	Product (Yield,** %)	
					Vinylsilane	Halohydrin
1	3a	0.0	MgBr₂(2.3)	0.7	—	5a(97)
2	3a	1.1	MgBr₂(2.2)	21	4a(82)	--
3	3b	2.1	MgI₂(2.3)	12	4b(89)	--
4	3c	2.1	MgBr₂(2.1)	18	4c(63)	--
5	3d	2.1	MgBr₂(3.4)	18	4d(22)	5c(59)
6	3d	4.6	MgBr₂(7.1)	17	4d(100)	—
7	3e	2.2	MgBr₂(3.4)	43	4e(18)	—
8	3e	10.7	MgI₂(2.7)	16	4e(13)	—
9	3f	2.1	MgBr₂(3.4)	22	4f(22)	5f(64)
10	3f	8.3	MgI₂(9.5)	13	4f(62)	--
11	3g	6.4	MgI₂(4.3)	14	4g(15)	6g(43)
12	3g	7.7	MgI₂(8.8)	50	4g(29)	--
13	3h	6.8	MgI₂(7.8)	18	4h(80)	--

*Reaction was carried out at room temperature except entry 1 (at −10℃). **Isolated yield.

Table 5. ¹H-NMR Data and the Ratio of E/Z Isomers of Vinylsilanes

| Vinylsilane	E/Z ratio	¹H-NMR (CDCl₃), δ, J (Hz)	
		E-Isomer	Z-Isomer
4a	84/16	0.10 (s, 9H, SiMe₃), 6.43 (d, 1H, J=19.4, SiCH), 6.82 (d, 1H, J=19.4, ArCH), 7.2-7.4 (m, 5H)	0.00 (s, 9H, SiMe₃), 5.78 (d, 1H, J=15.4, SiCH), 7.2-7.4 (m, 6H)
4b	89/11	0.10 (s, 9H, SiMe₃), 6.39 (d, 1H, J=19.4, SiCH), 6.75 (d, 1H, J=19.4, ArCH), 7.1-7.4 (m, 4H)	0.00 (s, 9H, SiMe₃), 5.81 (d, 1H, J=15.1, SiCH), 7.1-7.4 (m, 5H)
4c	81/19	0.10 (s, 9H, SiMe₃), 6.43 (d, 1H, J=19.4, SiCH), 6.74 (d, 1H, J=19.4, ArCH), 7.1-7.4 (m, 5H)	−0.06 (s, 9H, SiMe₃), 5.83 (d, 1H, J=15.4, SiCH), 7.1-7.4 (m, 5H)
4d	82/18	0.21 (s, 9H, SiMe₃), 6.51 (d, 1H, J=18.9, SiCH), 7.1-7.7 (m, 5H)	0.03 (s, 9H, SiMe₃), 6.00 (d, 1H, J=12.7, SiCH), 7.1-7.7 (m, 5H)
4e	93/7	0.16 (s, 9H, SiMe₃), 6.48 (d, 1H, J=19.4, SiCH), 6.87 (d, 1H, J=19.4, ArCH), 7.2-7.5 (m, 4H)	0.05 (s, 9H, SiMe₃), 5.8 (d, 1H, J=14.5, SiCH), 7.2-7.5 (m, 5H)
4f	93/7	0.19 (s, 9H, SiMe₃), 6.48 (d, 1H, J=18.9, SiCH), 6.88 (d, 1H, J=18.9, ArCH), 7.2-7.5 (m, 4H)	0.05 (s, 9H, SiMe₃), 5.84 (d, 1H, J=14.6, SiCH), 7.2-7.5 (m, 5H)
4g	92/8	0.15 (s, 9H, SiMe₃), 2.34 (s, 3H), 6.41 (d, 1H, J=19.5, SiCH),	0.07 (s, 9H, SiMe₃), 2.34 (s, 3H) 5.77 (d, 1H, J=15.3, SiCH),
4h	98/2	6.84 (d, 1H, J=19.5, ArCH), 7.11-7.35 (m, 4H) 0.07 (s, 9H, SiMe₃), 3.72 (s, 3H) 6.23 (d, 1H, J=18.9, SiCH), 6.70-6.79, 7.28-7.31 (m, 5H)	7.11-7.35 (m, 5H)

In every case, the halohydrins were the α-halo-β-hydroxysilanes. The structure bromohydrin **5a** was readily confirmed by the downfield shift of the β-protons (C$\underline{H}$OH) in the ¹H-NMR spectrum of its acetate derivtive **7**. The methine protons of **5a** appeared as a pair of doublet (J=6.0 Hz) at δ 3.65 (HCBr) and 4.84 (C$\underline{H}$OH), while the latter one was shifted to downfield (δ 5.95) in **7**. The halohydrins **5b, 5c, 5f** and **6g** were identified by comparision of the chemical shifts of the methine protons in ¹H-NMR spectum with those of **5a**.

7
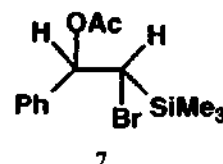
The exclusive α-regioselective ring-opening of aliphatic α, β-epoxy silanes in reactions with magnesium halide[8] and various nucleophiles[9] is well estabilished. Such an exclusive α-opening was also observed even in the aromatic α,β-epoxy silanes **3** where β-cleavage would result in a developing benzyl cation β to silicon.

The bromohydrin **5b** was treated with ethylmagnesium bromide in ether in order to prepare magnesium bromide salt of **5b**, and then this solution was added to the etheral solution of Mg (2.7 equiv) and MgBr₂ (4.0 equiv). The resulting mixture was stirred at room temperature for 21 h, vinylsilane **4b** was also formed in 51% yield. As shown in

entry 7 of Table 3, vinylsilane **4b** was not produced at all when the reaction was performed in the absence of excess magnesium. Based on these observations, we propose a reaction mechanism for the deoxygenation. The magnesium halide induced a ring-opening of α,β-epoxy silane affords the magnesium salft of halohydrin **8**, which react with excess magnesium to produce Grignard reagent **9**. The spontaneous β-elimination of this unstable Grignard reagent leads to the expected vinylsilanes **4**.[10]

$$3 \xrightarrow{MgX_2} 8 \xrightarrow{Mg} 9 \rightarrow 4$$
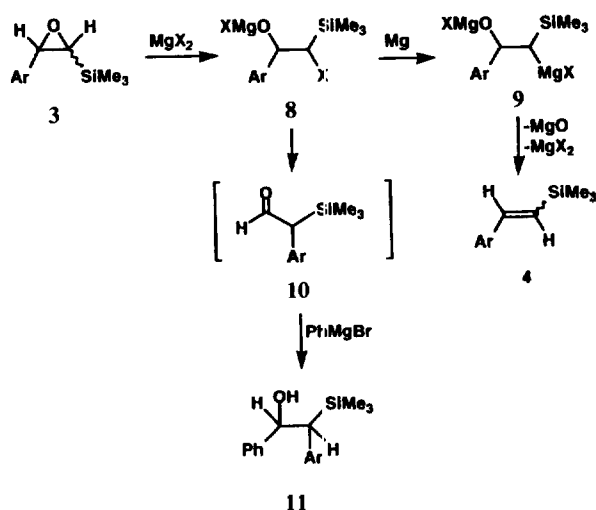
It is interesing to note that further rearrangement of the magnesium salt of halohydrin to α-trimethylsilyl aldehyde (**8→10**) was not observed in this reaction when the excess magnesium was present.[11] This indicates that the Grignard reagent (**8→9**) forms faster than the rearrangement product. However, we found that the rearrangement occurred in the reactions of α,β-epoxy silanes with Grignard reagents to give β-hydroxysilane (**11**) in the absence of excess magnesium.[12] We will report the results soon.

Experimental

All reactions were carried out on the argon atomosphere. ^{1}H-NMR spectra were recorded on a Varian EM-360A (60 MHz), a JEOL JSX270 (270 MHz) or a Bruker 300 MHz spectrometer using tetramethylsilane as an internal standard. ^{13}C-NMR spectra were obtained on a JEOL JSX270 (58 MHz) spectrometer with $CDCl_3$ as solvent and internal standard. GC-MS analyses were performed with a Hewlett-Packard 5971A spectrometer. An HP-1 column (0.2 mm ID, 15 m) was used at 100-280℃ (10℃/min). Chloromethyltrimethylsilane was purchased from Fluka, distilled before use and stored over molecular sieves 4A.

Synthesis of α,β-Epoxy Silanes. sec-BuLi (1.2 M in cyclohexane, 12 m*l*, 16 mmol) was added dropwise to a THF (15 m*l*) solution of chloromethyltrimethylsilane **1** (1.84 g, 15 mmol) at −78℃ under argon. After 5 min, TMEDA (1.86 g, 16 mmol) was added, and the resulting mixture was stirred for 1 h. *p*-Chlorobenzaldehyde **2b** (1.40 g, 10 mmol) was slowly added to the above solution. The solution was stirred for 40 min at −50℃, and then for 2 h at room temperature. The reaction mixture was poured into a saturated aqueous ammonium chloride solution (30 m*l*) and extracted with di-

chloromethane (20 m*l*×3). The dried (Na_2SO_4) solution was concentrated in vacuo, the residue was distilled with a kugelrohr under reduced pressure (70-80℃/ 0.1 mmHg) to give the Z and E mixtures of **3b** (1.58 g, 70%). The crude product was chromatographed (silica gel *n*-hexane : ether=8 : 1) to give E-**3b** (Rf=0.70) and Z-**3b** (Rf=0.65). The ratio of Z and E isomers of **3b** was determined to be 82 : 18 by preparative tlc and by GC (Z-**3b**, R_t=6.22 min; E-**3b**, R_t=6.68 min). **3a** and **3c-j** were prepared similarly. The E and Z isomeric ratio of them was determined by ^{1}H-NMR and GC analysis. The yields, the ratio of Z and E isomers and spectral data of α,β-epoxy silanes are listed in Table 1 and 2.

General procedure for the reaction of α,β-epoxy silane with magnesium-magnesium halide. Deoxygenation reaction of **3b** to **4b** by Mg-MgBr$_2$ is representative. To a suspension of Mg-MgBr$_2$ prepared from Mg (120 mg, 4.9 mmol) and 1,2-dibromoethane (564 mg, 3.0 mmol) in ether (3 m*l*), **3b** (200 mg, 0.89 mmol) was added at room temperature. After 15 h, the solution was quenched with a saturated aqueous ammonium chloride solution and extracted with dichloromethane (20 m*l*×2). The combined extracts were concentrated and the residue was chromatographed on silica gel plate (*n*-pentane) to afford a mixture of E and Z isomers of vinylsilane **4b** (139 mg, 74%). The ratio of E and Z isomers was determined by GC analysis. E-**4b**: GC 5.84 min (89%); MS 212 (M+2, 10), 210 (M$^+$, 25), 197 (34), 195 (M$^+$-CH$_3$, 100), 181 (21), 179 (55), 169 (22), 159 (15), 115 (15), 73 (Me$_3$Si, 7%). Z-**4b**: GC 4.80 min (11%); MS 212 (M+2, 8), 210 (M$^+$, 19), 197 (37), 195 (100), 181 (21), 179 (56), 169 (23), 159 (14), 115 (14) 73 (10%).

Vinylsilanes **4a-4h** were prepared under the reaction conditions described in Table 4. The ^{1}H-NMR spectra were summarized in Table 5 and GC-MS and ^{13}C-NMR data were as follows.

E-**4c**: GC 5.78 min (81%); MS m/e 212 (7), 210 (M$^+$, 18), 197 (36), 195 (100), 181 (19), 179 (59), 169 (5), 160 (4), 159 (23), 115 (15), 73 (12%). Z-**4c**: GC 4.60 min (19%); MS m/e 212 (7), 210 (M$^+$, 18), 197 (36), 195 (100), 181 (22), 179 (59), 169 (15), 160 (3), 159 (23), 115 (15), 73 (12%).

E-**4d**: GC 5.36 min (82%); MS m/e 212 (M+2, 8), 210 (M$^+$, 21), 197 (37), 195 (100), 181 (7), 179 (15), 169 (13), 160 (M$^+$-CH$_3$-Cl, 15), 159 (96), 131 (33), 115 (26), 93 (40), 73 (16%). Z-**4d**: GC 4.39 min (18%); MS m/e 212 (3), 210 (M$^+$, 8), 197 (35), 195 (100), 181 (4), 179 (16), 169 (13), 160 (16), 159 (99), 131 (36), 115 (24), 93 (40), 73 (10%).

E-**4e**: GC 3.67 min (93%); MS m/e 177 (M$^+$-Br, 4), 176 (32), 162 (14), 161 (100), 150 (12), 147 (3), 146 (11), 145 (93), 135 (32), 73 (6%); ^{13}C-NMR δ −1.18, 126.33, 126.39, 128.50, 129.52, 138.36, 143.58. Z-**4e**: GC 2.91 min (7%); MS m/e 177 (M$^+$-Br, 4), 176 (22), 162 (13), 161 (100), 159 (10), 147 (3), 146 (11), 145 (70), 135 (37), 73 (10%).

E-**4f**: GC 3.66 min (93%); MS m/e 177 (M$^+$-Br, 5), 176 (35), 162 (M$^+$-Br-CH$_3$, 15), 162 (100), 159 (11), 147 (M$^+$-Br-2CH$_3$, 15), 146 (13), 145 (83), 73 (6%). Z-**4f**: GC 2.91 min (7%); MS m/e 177 (M$^+$-Br, 5), 176 (27), 162 (14), 162 (100), 159 (9), 147 (2), 146 (12), 145 (87), 135 (34), 73 (7%).

E-**4g**: GC 4.95 min (92%); MS m/e 190 (M$^+$, 37), 175 (M$^+$-CH$_3$, 100), 160 (M$^+$-2CH$_3$, 15), 159 (92), 149 (35), 115 (24), 73 (10%); ^{13}C-NMR δ −1.21, 21.20, 126.25, 128.13, 129.19, 135.69, 137.76, 143.46. Z-**4g**: GC 3.93 min (80%); MS m/e 190 (M$^+$, 34), 175 (100), 160 (15), 159 (76), 149 (33), 115

(19), 73 (7%).

E-4h: GC 6.68 min (98%); MS m/e 206 (M⁺, 48) 191 (M⁺-CH₃, 100), 176 (15), 175 (56), 165 (50), 161 (8), 133 (M⁺-Me₃Si, 9), 73 (5%); ¹³C-NMR δ −1.17, 55.25, 113.86, 126.64, 127.56, 131.36, 142.99, 159.51. Z-4h: GC 5.56 min (2%); MS m/e 206 (M⁺, 47), 191 (100), 176 (18), 175 (50), 165 (51), 161 (7), 133 (7), 73 (5%).

Bromohydrin 5. To a suspension of magnesium (49 mg, 2.0 mmol) in ether (3 ml) was added 1,2-dibromoethane (376 mg, 2.0 mmol) at room temperature. The resulting mixture was cooled to −10℃ before the addition of **3a** (170 mg, 0.89 mmol) solution in ether (1 ml). After 40 min, the solution was quenched with aq NH₄Cl, and extracted with dichloromethane (20 ml×2). Purification by silica gel column chromatography, (n-hexane : ether=8 : 1) gave 235 mg (97%) of **5a**. ¹H-NMR δ 0.17 (s, 9H, SiMe₃), 2.56 (brs, 1H, OH) 3.65 (d, 1H, J=6.0 Hz, HCBr), 4.84 (d, 1H, J=6.0 Hz, HCOH) 7.2-7.4 (m, 5H).

The acetate **7** was prepared from the bromohydrin **5a** and acetic anhydride in pyridine (100℃, 3 h). ¹H-NMR (60 MHz) δ 0.10 (s, 9H), 2.13 (s, 3H), 3.60 (d, 1H, J=6.0 Hz, HCBr), 5.95 (d, 1H, J=6.0 Hz, HCOAc), 7.4 (s, 5H).

α,β-Epoxy silane **3b** (226 mg, 1.0 mmol) was treated with a suspension of Mg-MgBr₂ prepared from magnesium (80 mg, 3.3 mmol) and 1,2-dibromoethane (376 mg, 2.0 mmol) in ether (4 ml) at −10℃ for 5 h. Work-up as for **5a** gave 237 mg (77%) of **5b**. ¹H-NMR δ 0.05 (s, 9H, SiMe₃), 2.71 (brs, 1H, OH), 3.50 (d, 1H, J=4.9 Hz, HCBr), 4.85 (d, 1H, J=4.9 Hz, HCOH), 7.2-7.4 (m, 4H); ¹³C-NMR δ −2.09, 52.73, 74.10, 127.78, 128.63, 133.95, 140.11; MS m/e 220 (25), 218 (100), 216 (M⁺-Me₃SiOH, 80), 141 (ClC₆H₄CHOH, 93), 137 (M⁺-Me₃SiOH·Br, 60), 73 (Me₃Si, 44%).

To a suspension of Mg-MgBr₂ prepared from magnesium (120 mg, 4.9 mmol) and 1,2-bromoethane (564 mg, 3.0 mmol) in ether (5 ml), **3d** (200 mg, 0.89 mmol) was added at room temperature. After 18 h, work up described above and chromatography on silica gel plate (n-hexane : ether=8 : 1) gave vinylsilane **4d** (40 mg, 22%) and bromohydrin **5d** (160 mg, 59%). ¹H-NMR (60 MHz) δ 0.33 (s, 9H, SiMe₃), 2.7 (br, 1H, OH), 3.85 (d, 1H, J=4.0 Hz, HCBr), 5.3 (brs, 1H, HCOH), 7.1-7.6 (m, 4H).

To a suspension of Mg-MgBr₂ prepared from Mg (120 mg, 4.9 mmol) and 1,2-bromoethane (564 mg, 3.0 mmol) in ether (5 ml), **3f** (240 mg, 0.89 mmol) was added at room temperature. After 22 h, work up and purification by PLC (silica gel, n-hexane : ether=8 : 1) afforded vinylsilane **4f** (49 mg, 22%) and bromohydrin **5f** (201 mg, 64%). ¹H-NMR (60 MHz, CCl₄) δ 0.04 (s, 9H, SiMe₃), 2.20 (brs, 1H, OH), 3.55 (d, 1H, J=3.9 Hz, HCBr), 4.93 (brs, 1H, HCOH), 6.7-7.3 (m, 4H).

Iodohydrin 6g. To a suspension of Mg-MgI₂ prepared from Mg (240 mg, 9.9 mmol) and iodine (1.12 g, 4.0 mmol) in ehter (10 ml), **3g** (190 mg, 0.92 mmol) was added and stirred at room temperature for 14 h. After treatment described above **4g** (26.3 mg, 15%) and **6g** (133 mg, 43%) were

obtained. ¹H-NMR (60 MHz, CCl₄) δ 0.30 (s, 9H, SiMe₃), 2.25 (brs, 1H, OH), 2.47 (s, 3H), 3.60 (d, 1H, J=5.0 Hz, HCBr), 4.43 (d, 1H, J=5.0 Hz, HCOH), 7.1 (s, 4H).

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