

(m, 2H, CH<sub>2</sub>), 1.74 (m, 2H, CH<sub>2</sub>), 3.56 (s, 2H, CH<sub>2</sub>), 3.97 (t, 2H, *J*=5 Hz, CH<sub>2</sub>), 4.26 (t, 2H, *J*=6 Hz, CH<sub>2</sub>), 7.35 (d, 2H, *J*=8 Hz, aromatic H-3, 5), 8.01 (d, 2H, *J*=8 Hz, aromatic H-2, 6); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 13.4 (CH<sub>3</sub>), 13.6 (CH<sub>3</sub>), 18.9 (CH<sub>2</sub>), 19.1 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>), 40.5 (CH<sub>2</sub>), 41.2 (CH<sub>2</sub>), 64.6 (CH<sub>2</sub>), 64.7 (CH<sub>2</sub>), 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<sup>+</sup>, 9), 237 (19), 219 (29), 191 (21), 181 (36), 180 (19), 163 (7), 136 (61), 58 (100), 43 (70), 32 (70); IR (ν<sub>CO</sub>) 1721 and 1738 cm<sup>-1</sup>.

**Methyl 2-carbomethoxyphenylacetate.** colorless oil; <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ 3.60 (s, 3H, CH<sub>3</sub>), 3.80 (s, 3H, CH<sub>3</sub>), 3.90 (s, 2H, CH<sub>2</sub>), 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<sub>CO</sub>) 1740 cm<sup>-1</sup>.

**Ethyl 2-carboethoxyphenylacetate.** colorless oil; <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ 1.27 (t, 3H, *J*=7 Hz, CH<sub>3</sub>), 1.39 (t, 3H, *J*=7 Hz, CH<sub>3</sub>), 3.98 (s, 2H, CH<sub>2</sub>), 4.16 (q, 2H, *J*=7 Hz, CH<sub>2</sub>), 4.35 (q, 2H, *J*=7 Hz, CH<sub>2</sub>), 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<sub>CO</sub>) 1717 and 1738 cm<sup>-1</sup>.

**"Propyl 2-carbo-"propoxyphenylacetate.** colorless oil; <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ 0.90 (t, 3H, *J*=7 Hz, CH<sub>3</sub>), 1.20 (t, 3H, *J*=7 Hz, CH<sub>3</sub>), 1.60 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>), 3.95 (s, 2H, CH<sub>2</sub>), 3.90 (t, 2H, *J*=6 Hz, CH<sub>2</sub>), 4.17 (t, 2H, *J*=6 Hz, CH<sub>2</sub>), 7.30 (m, 3H, aromatic H-3, 4, 5), 7.90 (m, 1H, aromatic H-6).

**"Butyl 2-carbo-"butoxyphenylacetate.** colorless oil; <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ 0.98 (m, 6H, (CH<sub>3</sub>)<sub>2</sub>), 1.55 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 3.93 (s, 2H, CH<sub>2</sub>), 4.10 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>), 7.30 (m, 3H, aromatic H-3, 4, 5), 7.90 (m, 1H, aromatic H-6).

**Methyl 3-carbomethoxyphenylacetate.** colorless oil; <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ 3.60 (s, 2H, CH<sub>2</sub>), 3.63 (s, 3H, CH<sub>3</sub>), 3.85 (s, 3H, CH<sub>3</sub>), 7.44 (m, 2H, aromatic H-4, 5), 7.91 (m, 2H,

aromatic H-2, 6); Mass (m/e) 209 (4), 208 (M<sup>+</sup>, 34), 178 (4), 177 (47), 164 (6), 151 (9), 149 (100), 119 (17), 105 (15), 91 (21), 90 (21), 80 (28); IR (ν<sub>CO</sub>) 1724 cm<sup>-1</sup>.

**Ethyl 3-carboethoxyphenylacetate.** colorless oil; <sup>1</sup>H-NMR (CCl<sub>4</sub>) δ 1.23 (t, 3H, *J*=7 Hz, CH<sub>3</sub>), 1.37 (t, 3H, *J*=7 Hz, CH<sub>3</sub>), 3.57 (s, 2H, CH<sub>2</sub>), 4.12 (q, 2H, *J*=7 Hz, CH<sub>2</sub>), 4.37 (q, 2H, *J*=7 Hz, CH<sub>2</sub>), 7.47 (m, 2H, aromatic H-4, 5), 7.90 (m, 2H, aromatic H-2, 6); Mass (m/e) 237 (2), 236 (M<sup>+</sup>, 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<sub>CO</sub>) 1721 cm<sup>-1</sup>.

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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.<sup>1</sup> The deoxygenation of α,β-epoxy silanes was largely ignored in spite of its synthetic interest.<sup>2</sup> This reaction could provide a good route to vinylsilanes which have received increasing attention as a highly versatile synthon in organic synthesis.<sup>3</sup> Y.

Ito and coworkers have reported that copper-catalyzed Grignard reagent caused deoxygenation of α,β-epoxy silanes having one or two alkoxy groups on silicon.<sup>4</sup> 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

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

Compound	Ar	Yield* (%)	Ratio of Z/E isomer**
a***	C <sub>6</sub> H <sub>5</sub>	90	77/23
b	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	70	82/18
c	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	60	97/3
d	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	67	97/3
e	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	70	77/23
f	<i>o</i> -BrC <sub>6</sub> H <sub>4</sub>	70	96/4
g	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	65	96/4
h	<i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	68	95/5

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

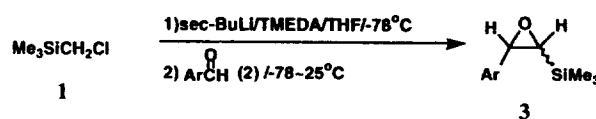
available than alkoxy silyl ones underwent the deoxygenation to give vinylsilanes stereoselectively.<sup>5</sup> The yields of vinylsilanes were good for aliphatic  $\alpha,\beta$ -epoxy silanes, but, very low for aromatic ones with lithium.

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

## Results and Discussions

**Synthesis of  $\alpha,\beta$ -Epoxy Silanes.**  $\alpha,\beta$ -Epoxy trimethylsilanes (**3**) were prepared by Magnus method.<sup>6</sup> When a THF solution of chloromethyltrimethylsilane (**1**) was treated with *sec*-BuLi (1.2 M in cyclohexane) at  $-78^\circ\text{C}$  in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (1.05 equiv), and then with an aromatic aldehyde **2** between  $-78^\circ\text{C}$  and  $25^\circ\text{C}$  a mixture of Z and E isomers of  $\alpha,\beta$ -epoxy silane **3** was obtained in good yields (Table 1).

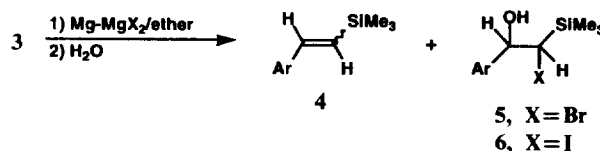
The Z and E isomers of 3-(4'-chlorophenyl)-2-trimethylsil-



loxirane (**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  $\alpha,\beta$ -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).

<sup>1</sup>H-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**:  $\delta$  -0.16 vs. 0.13). Z isomers were produced predominantly over E isomers in every case.

**Reactions of  $\alpha,\beta$ -Epoxy Silanes with Magnesium-Magnesium Halide.** When the reaction of  $\alpha,\beta$ -epoxy silane **3b** with Mg-MgBr<sub>2</sub> suspension prepared from magnesium (3.3 mmol) and dibromoethane (2.0 mmol) in ether (3 ml) was performed at  $-10^\circ\text{C}$ , 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 bromohydrin **5** (53%) (entry 2). Similar results were obtained in homogeneous MgBr<sub>2</sub> etherate prepared by using a large amount of ether (entry 3).

**Table 2.** Spectral Data of  $\alpha,\beta$ -Epoxy Silanes

$\alpha,\beta$ -Epoxy Silane	<sup>1</sup> H-NMR (CDCl <sub>3</sub> ) $\delta$ , J (Hz)	<sup>13</sup> C-NMR (CDCl <sub>3</sub> ) $\delta$	MS m/e (relative intensity, %)
(Z)- <b>3b</b>	-0.16 (s, 9H, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 23), 211 (M <sup>+</sup> -CH <sub>3</sub> , 6), 195 (M <sup>+</sup> -CH <sub>3</sub> -O, 17), 152 (M <sup>+</sup> -Me <sub>3</sub> Si-1, 9), 115 (M <sup>+</sup> -C <sub>6</sub> H <sub>4</sub> Cl, 7), 95 (12), 93 (34), 89 (33), 73 (100)
(E)- <b>3b</b>	0.13 (s, 9H, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 77), 211 (9), 195 (19), 152 (9), 115 (9), 95 (9), 93 (34), 89 (37), 73 (100)
(Z)- <b>3c</b>	0.15 (s, 9H, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 46), 211 (11), 195 (21), 115 (18), 95 (17), 93 (47), 89 (38), 73 (100)
(E)- <b>3c</b>	0.15 (s, 9H, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 88), 211 (17), 195 (16), 115 (8), 95 (15), 93 (41), 89 (29), 73 (100)
(Z)- <b>3d</b>	-0.17 (s, 9H, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 9), 211 (12), 195 (22), 152 (9), 118 (M <sup>+</sup> -Me <sub>3</sub> Si-Cl, 17), 95 (39), 93 (100), 89 (53), 73 (95).
(E)- <b>3d</b>	0.17 (s, 9H, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 100), 211 (3), 195 (2), 152 (4), 118 (4), 95 (29), 93 (79), 73 (54)
(Z)- <b>3e</b>	-0.16 (s, 9H, SiMe <sub>3</sub> ), 2.51 (d, 1H,	-2.21, 53.42, 56.49,	272 (61), 270 (M <sup>+</sup> , 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, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 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, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 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, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 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, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 74), 191 (M <sup>+</sup> -CH <sub>3</sub> , 32), 176 (M <sup>+</sup> -2CH <sub>3</sub> , 22), 175 (100), 133 (M <sup>+</sup> -Me <sub>3</sub> Si, 7), 132 (24), 115 (16), 105 (18), 91 (16), 77 (21), 73 (86)
(E)-3g	0.13 (s, 9H, SiMe <sub>3</sub> ), 2.34 (s, 4H), 3.66 (d, 1H, $J=3.67$ , SiCH), 7.13-7.23 (m, 4H)	*	206 (M <sup>+</sup> , 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, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 100), 207 (M <sup>+</sup> -CH <sub>3</sub> , 20), 192 (44), 191 (M <sup>+</sup> -CH <sub>3</sub> O, 22), 149 (M <sup>+</sup> -Me <sub>3</sub> Si, 10), 148 (16), 121 (27), 91 (18), 89 (16), 73 (62)
(E)-3h	0.12 (s, 9H, SiMe <sub>3</sub> ), 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 <sup>+</sup> , 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-MgBr<sub>2</sub>\*

Entry	Mg (eq)	BrCH <sub>2</sub> CH <sub>2</sub> Br (eq)	Ether (ml)	Time (h)	Product (Yield,** %)	
					Vinylsilane ( <b>4b</b> )	Bromohydrin ( <b>5b</b> )
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°C). \*\*Isolated yield.

When the reaction was carried out with more than three equivalents of MgBr<sub>2</sub> 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 MgBr<sub>2</sub> improved the yield of **4b** (entry 5). However, when less than three equivalents of MgBr<sub>2</sub> 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-MgBr<sub>2</sub> etherate was effective for the deoxygenation of  $\alpha,\beta$ -epoxy silane **3b** to vinylsilane **4b**, we examined this for other  $\alpha,\beta$ -epoxy silanes to confirm its generality. The reactions of **3a**, **3b** and **3d** with Mg-MgBr<sub>2</sub>

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-MgBr<sub>2</sub> 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  $\alpha,\beta$ -epoxy silanes. The yields of the vinylsilanes **4b**, **4f** and **4h** were greatly improved than those in the reactions with Mg-MgBr<sub>2</sub> (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-MgX<sub>2</sub> 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 <sup>1</sup>H-NMR spectra, the silicon methyls appeared at slightly lower field for the E than for the Z isomer (eg., **4b**:  $\delta$  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**:  $\delta$  6.39 and 6.75) in E isomers, while one of them (ArCH) overlapped with the aromatic proton signals in Z isomer. The <sup>1</sup>H-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  $\alpha,\beta$ -epoxy silanes **3** with Mg-MgX<sub>2</sub> afforded E isomer of vinylsilanes **4** in greater than 80%. The stereoselectivity observed in this reaction is very similar to the results by Ito<sup>4</sup>, Barluenger<sup>7</sup> and us<sup>5</sup>.

**Table 4.** Reaction of **3** with Mg-MgX<sub>2</sub>\*

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

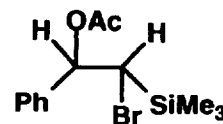
\*Reaction was carried out at room temperature except entry 1 (at  $-10^{\circ}\text{C}$ ). \*\*Isolated yield.

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

Vinylsilane	E/Z ratio	<sup>1</sup> H-NMR (CDCl <sub>3</sub> ), $\delta$ , J (Hz)	
		E-Isomer	Z-Isomer
<b>4a</b>	84/16	0.10 (s, 9H, SiMe <sub>3</sub> ), 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, SiMe <sub>3</sub> ), 5.78 (d, 1H, $J=15.4$ , SiCH), 7.2-7.4 (m, 6H)
<b>4b</b>	89/11	0.10 (s, 9H, SiMe <sub>3</sub> ), 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, SiMe <sub>3</sub> ), 5.81 (d, 1H, $J=15.1$ , SiCH), 7.1-7.4 (m, 5H)
<b>4c</b>	81/19	0.10 (s, 9H, SiMe <sub>3</sub> ), 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, SiMe <sub>3</sub> ), 5.83 (d, 1H, $J=15.4$ , SiCH), 7.1-7.4 (m, 5 H)
<b>4d</b>	82/18	0.21 (s, 9H, SiMe <sub>3</sub> ), 6.51 (d, 1H, $J=18.9$ , SiCH), 7.1-7.7 (m, 5H)	0.03 (s, 9H, SiMe <sub>3</sub> ), 6.00 (d, 1H, $J=12.7$ , SiCH), 7.1-7.7 (m, 5H)
<b>4e</b>	93/7	0.16 (s, 9H, SiMe <sub>3</sub> ), 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, SiMe <sub>3</sub> ), 5.8 (d, 1H, $J=14.5$ , SiCH), 7.2-7.5 (m, 5 H)
<b>4f</b>	93/7	0.19 (s, 9H, SiMe <sub>3</sub> ), 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, SiMe <sub>3</sub> ), 5.84 (d, 1H, $J=14.6$ , SiCH), 7.2-7.5 (m, 5 H)
<b>4g</b>	92/8	0.15 (s, 9H, SiMe <sub>3</sub> ), 2.34 (s, 3H), 6.41 (d, 1H, $J=19.5$ , SiCH),	0.07 (s, 9H, SiMe <sub>3</sub> ), 2.34 (s, 3H) 5.77 (d, 1H, $J=15.3$ , SiCH),

6.84 (d, 1H,  $J=19.5$ ,  
ArCH), 7.11-7.35 (m,  
4H)  
**4h** 98/2 0.07 (s, 9H, SiMe<sub>3</sub>),  
3.72 (s, 3H) 6.23 (d,  
1H,  $J=18.9$ , SiCH),  
6.70-6.79, 7.28-7.31  
(m, 5H)

In every case, the halohydrins were the  $\alpha$ -halo- $\beta$ -hydroxy-silanes. The structure bromohydrin **5a** was readily confirmed by the downfield shift of the  $\beta$ -protons (CH<sub>2</sub>OH) in the <sup>1</sup>H-NMR spectrum of its acetate derivative **7**. The methine protons of **5a** appeared as a pair of doublet ( $J=6.0$  Hz) at  $\delta$  3.65 (HCB<sub>2</sub>) and 4.84 (CH<sub>2</sub>OH), while the latter one was shifted to downfield ( $\delta$  5.95) in **7**. The halohydrins **5b**, **5c**, **5f** and **6g** were identified by comparison of the chemical shifts of the methine protons in <sup>1</sup>H-NMR spectrum with those of **5a**.

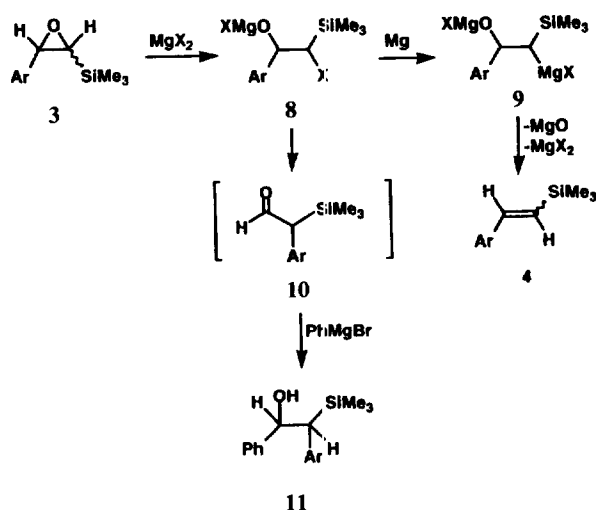


7

The exclusive  $\alpha$ -regioselective ring-opening of aliphatic  $\alpha,\beta$ -epoxy silanes in reactions with magnesium halide<sup>8</sup> and various nucleophiles<sup>9</sup> is well established. Such an exclusive  $\alpha$ -opening was also observed even in the aromatic  $\alpha,\beta$ -epoxy silanes **3** where  $\beta$ -cleavage would result in a developing benzyl cation  $\beta$  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 MgBr<sub>2</sub> (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  $\alpha$  ring-opening of  $\alpha,\beta$ -epoxy silane affords the magnesium salt of halohydrin **8**, which react with excess magnesium to produce Grignard reagent **9**. The spontaneous  $\beta$ -elimination of this unstable Grignard reagent leads to the expected vinylsilanes **4**.<sup>10</sup>



It is interesting to note that further rearrangement of the magnesium salt of halohydrin to  $\alpha$ -trimethylsilyl aldehyde (**8**→**10**) was not observed in this reaction when the excess magnesium was present.<sup>11</sup> 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  $\alpha,\beta$ -epoxy silanes with Grignard reagents to give  $\beta$ -hydroxysilane (**11**) in the absence of excess magnesium.<sup>12</sup> We will report the results soon.

## Experimental

All reactions were carried out on the argon atmosphere. <sup>1</sup>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. <sup>13</sup>C-NMR spectra were obtained on a JEOL JSX270 (58 MHz) spectrometer with CDCl<sub>3</sub> 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°C (10°C/min). Chloromethyltrimethylsilane was purchased from Fluka, distilled before use and stored over molecular sieves 4A.

**Synthesis of  $\alpha,\beta$ -Epoxy Silanes.** sec-BuLi (1.2 M in cyclohexane, 12 mL, 16 mmol) was added dropwise to a THF (15 mL) solution of chloromethyltrimethylsilane **1** (1.84 g, 15 mmol) at –78°C 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°C, and then for 2 h at room temperature. The reaction mixture was poured into a saturated aqueous ammonium chloride solution (30 mL) and extracted with di-

chloromethane (20 mL×3). The dried (Na<sub>2</sub>SO<sub>4</sub>) solution was concentrated in vacuo, the residue was distilled with a kugelrohr under reduced pressure (70–80°C/ 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** (R<sub>f</sub> = 0.70) and Z-**3b** (R<sub>f</sub> = 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<sub>t</sub> = 6.22 min; E-**3b**, R<sub>t</sub> = 6.68 min). **3a** and **3c-j** were prepared similarly. The E and Z isomeric ratio of them was determined by <sup>1</sup>H-NMR and GC analysis. The yields, the ratio of Z and E isomers and spectral data of  $\alpha,\beta$ -epoxy silanes are listed in Table 1 and 2.

**General procedure for the reaction of  $\alpha,\beta$ -epoxy silane with magnesium-magnesium halide.** Deoxygenation reaction of **3b** to **4b** by Mg-MgBr<sub>2</sub> is representative. To a suspension of Mg-MgBr<sub>2</sub> prepared from Mg (120 mg, 4.9 mmol) and 1,2-dibromoethane (564 mg, 3.0 mmol) in ether (3 mL), **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 mL×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<sup>+</sup>, 25), 197 (34), 195 (M<sup>+</sup>-CH<sub>3</sub>, 100), 181 (21), 179 (55), 169 (22), 159 (15), 115 (15), 73 (Me<sub>3</sub>Si, 7%). Z-**4b**: GC 4.80 min (11%); MS 212 (M+2, 8), 210 (M<sup>+</sup>, 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 <sup>1</sup>H-NMR spectra were summarized in Table 5 and GC-MS and <sup>13</sup>C-NMR data were as follows.

E-**4c**: GC 5.78 min (81%); MS m/e 212 (7), 210 (M<sup>+</sup>, 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<sup>+</sup>, 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<sup>+</sup>, 21), 197 (37), 195 (100), 181 (7), 179 (15), 169 (13), 160 (M<sup>+</sup>-CH<sub>3</sub>-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<sup>+</sup>, 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<sup>+</sup>-Br, 4), 176 (32), 162 (14), 161 (100), 150 (12), 147 (3), 146 (11), 145 (93), 135 (32), 73 (6%); <sup>13</sup>C-NMR  $\delta$  –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<sup>+</sup>-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<sup>+</sup>-Br, 5), 176 (35), 162 (M<sup>+</sup>-Br-CH<sub>3</sub>, 15), 162 (100), 159 (11), 147 (M<sup>+</sup>-Br-2CH<sub>3</sub>, 15), 146 (13), 145 (83), 73 (6%). Z-**4f**: GC 2.91 min (7%); MS m/e 177 (M<sup>+</sup>-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<sup>+</sup>, 37), 175 (M<sup>+</sup>-CH<sub>3</sub>, 100), 160 (M<sup>+</sup>-2CH<sub>3</sub>, 15), 159 (92), 149 (35), 115 (24), 73 (10%); <sup>13</sup>C-NMR  $\delta$  –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<sup>+</sup>, 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<sup>+</sup>, 48) 191 (M<sup>+</sup>-CH<sub>3</sub>, 100), 176 (15), 175 (56), 165 (50), 161 (8), 133 (M<sup>+</sup>-Me<sub>3</sub>Si, 9), 73 (5%); <sup>13</sup>C-NMR  $\delta$  -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<sup>+</sup>, 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°C before the addition of **3a** (170 mg, 0.89 mmol) solution in ether (1 ml). After 40 min, the solution was quenched with aq NH<sub>4</sub>Cl, and extracted with dichloromethane (20 ml  $\times$  2). Purification by silica gel column chromatography, (*n*-hexane : ether = 8 : 1) gave 235 mg (97%) of **5a**. <sup>1</sup>H-NMR  $\delta$  0.17 (s, 9H, SiMe<sub>3</sub>), 2.56 (brs, 1H, OH), 3.65 (d, 1H, *J* = 6.0 Hz, HCB<sub>r</sub>), 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°C, 3 h). <sup>1</sup>H-NMR (60 MHz)  $\delta$  0.10 (s, 9H), 2.13 (s, 3H), 3.60 (d, 1H, *J* = 6.0 Hz, HCB<sub>r</sub>), 5.95 (d, 1H, *J* = 6.0 Hz, HCOAc), 7.4 (s, 5H).

$\alpha,\beta$ -Epoxy silane **3b** (226 mg, 1.0 mmol) was treated with a suspension of Mg-MgBr<sub>2</sub> prepared from magnesium (80 mg, 3.3 mmol) and 1,2-dibromoethane (376 mg, 2.0 mmol) in ether (4 ml) at -10°C for 5 h. Work-up as for **5a** gave 237 mg (77%) of **5b**. <sup>1</sup>H-NMR  $\delta$  0.05 (s, 9H, SiMe<sub>3</sub>), 2.71 (brs, 1H, OH), 3.50 (d, 1H, *J* = 4.9 Hz, HCB<sub>r</sub>), 4.85 (d, 1H, *J* = 4.9 Hz, HCOH), 7.2-7.4 (m, 4H); <sup>13</sup>C-NMR  $\delta$  -2.09, 52.73, 74.10, 127.78, 128.63, 133.95, 140.11; MS m/e 220 (25), 218 (100), 216 (M<sup>+</sup>-Me<sub>3</sub>SiOH, 80), 141 (ClC<sub>6</sub>H<sub>4</sub>CHOH, 93), 137 (M<sup>+</sup>-Me<sub>3</sub>SiOH-Br, 60), 73 (Me<sub>3</sub>Si, 44%).

To a suspension of Mg-MgBr<sub>2</sub> 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%). <sup>1</sup>H-NMR (60 MHz)  $\delta$  0.33 (s, 9H, SiMe<sub>3</sub>), 2.7 (br, 1H, OH), 3.85 (d, 1H, *J* = 4.0 Hz, HCB<sub>r</sub>), 5.3 (brs, 1H, HCOH), 7.1-7.6 (m, 4H).

To a suspension of Mg-MgBr<sub>2</sub> 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%). <sup>1</sup>H-NMR (60 MHz, CCl<sub>4</sub>)  $\delta$  0.04 (s, 9H, SiMe<sub>3</sub>), 2.20 (brs, 1H, OH), 3.55 (d, 1H, *J* = 3.9 Hz, HCB<sub>r</sub>), 4.93 (brs, 1H, HCOH), 6.7-7.3 (m, 4H).

**Iodohydrin 6g.** To a suspension of Mg-MgI<sub>2</sub> prepared from Mg (240 mg, 9.9 mmol) and iodine (1.12 g, 4.0 mmol) in ether (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. <sup>1</sup>H-NMR (60 MHz, CCl<sub>4</sub>)  $\delta$  0.30 (s, 9H, SiMe<sub>3</sub>), 2.25 (brs, 1H, OH), 2.47 (s, 3H), 3.60 (d, 1H, *J* = 5.0 Hz, HCB<sub>r</sub>), 4.43 (d, 1H, *J* = 5.0 Hz, HCOH), 7.1 (s, 4H).

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