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Stereoselective Syntheses of Carbon Homologated Vinylsilanes and Desilylated Olefins from α,β-Epoxy Silanes Using Organolithium and Organolanthanoid Reagents

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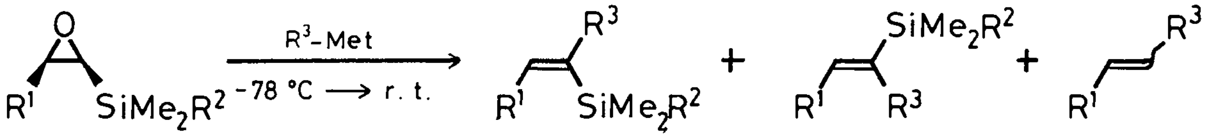
Synchronous insertion of alkyl group and deoxygenation reaction were achieved from α,β-epoxy silanes by the treatment with organolithium or organolanthanoid reagents in a regio- and stereoselective manner, *i.e.*, the reaction of (*Z*)-α,β-epoxy silanes gave the corresponding alkylated (*Z*)-vinylsilanes, and (*E*)-α,β-epoxy silanes were transformed into desilylated alkylated (*E*)-olefins.

Among a lot of organosilicon compounds, α,β-epoxy silane is one of the most valuable compounds because of its availability and facile transformation into various type of compounds.[1] Organometallic reagents containing Li, Mg, and Cu metals have been known to react with α,β-epoxy silanes resulting in deprotonation,[2] isomerization,[3] deoxygenation,[4] and ring-opening reaction.[5] Peterson reaction of β-hydroxy silanes, obtained by ring-opening reaction, with a base or acid is well-known to give alkylated silicon-free olefins.[5a,6] Relating to the preparation of alkylated silicon-containing olefins, treatment of 1,2-dideuteriotriphenylsilylethylene oxide with excess amounts of alkyllithium has only been reported to give substituted vinylsilane directly, but no stereoselectivity was observed.[7] Concerned with the reaction of epoxides, we reported direct preparation of substituted olefins from epoxides using organocerium reagents.[8] In this paper, we describe regio- and stereoselective one-step synthesis of alkylated vinylsilanes and silicon-free olefins by the reaction of α,β-epoxy silanes with organolithium and organolanthanoid reagents.

First, (*Z*)-4-phenyl-1-trimethylsilyl-1,2-epoxybutane (*Z*-**1A**) was treated with 5 molar equivalents of *n*-BuLi in THF, and (*Z*)-1-phenyl-4-trimethylsilyl-3-octene (*Z*-**2a**) was obtained regio- and stereoselectively (47%, *Z* : *E* = 87:13), accompanied with desilylated olefin **3a** (28%) (Entry 1). Vinylsilane **2** could be separated from



Z-1 **Z-2** **E-2** **3**

1A : R^1=$PhCH_2CH_2$ R^2=Me
1B : R^1=$PhCH_2CH_2$ R^2=Ph
1C : R^1=*n*-Bu R^2=Me

Table 1. Reaction of (*Z*)-α,β-epoxy silanes *Z*-1 with organometallics[a)]

Entry	R^1	R^2 (1)	R^3-Met	Solvent		Yield of 2/%	(*Z* : *E*)	Yield of 3/%
1	$Ph(CH_2)_2$	Me (**1A**)	*n*-BuLi	THF	a	47	(87 : 13)	28
2				DME	a	29	(99 : 1)	35
3				Et_2O	a	81	(97 : 3)	4
4	$Ph(CH_2)_2$	Ph (**1B**)	*n*-BuLi	Et_2O	b	76	(100 : 0)	2[b)]
5[c)]	$Ph(CH_2)_2$	Me (**1A**)	*n*-$BuCeCl_2$	THF	a	0		0
6				DME	a	4	(97 : 3)	5
7				Et_2O	a	62	(97 : 3)	8
8				*n*-Bu_2O	a	67	(97 : 3)	4
9			*n*-$BuLaCl_2$	Et_2O	a	75	(96 : 4)	7
10			*n*-$BuSmCl_2$	Et_2O	a	77	(95 : 5)	9
11			*n*-Bu_4CeLi	Et_2O	a	32	(98 : 2)	8
12	$Ph(CH_2)_2$	Me (**1A**)	*n*-$C_5H_{11}Li$	Et_2O	c	77	(95 : 5)	9
13			*n*-$C_5H_{11}LaCl_2$	Et_2O	c	88	(96 : 4)	6
14	$Ph(CH_2)_2$	Me (**1A**)	*t*-BuLi	Et_2O	d	75	(90 : 10)	7
15			*t*-$BuLaCl_2$	Et_2O	d	69	(94 : 6)	8
16	*n*-Bu	Me (**1C**)	*n*-BuLi	Et_2O	e	72	(99 : 1)	7
17			*n*-$BuCeCl_2$	Et_2O	e	78	(98 : 2)	8
18	$Ph(CH_2)_2$	Me (**1A**)	PhLi	Et_2O	f	0		78[d)]
19			$PhCeCl_2$	Et_2O	f	0		94[d)]

a) The reactions were performed with 4 or 5 molar equivalents of R^3-Met at -78 °C and gradually warmed to r.t., and the yields and ratios were determined by capillary GLC (FFAP) after the isolation of the mixture of 2 and 3 by TLC on silica gel. b) The product **3b** is the same as **3a**. c) 1-Chloro-4-phenyl-1-(trimethylsilyl)-2-butanol was obtained in 94% yield. d) Only (*E*)-isomer was obtained.

desilylated olefin **3** by careful purification using TLC on silica gel or distillation. Selective synthesis of (*Z*)-vinylsilane under various conditions was investigated (Table 1, Entries 1-11). Yields of the present reaction were much effected by solvent used (Entries 1-3), and (*Z*)-vinylsilane *Z*-**2a** was obtained in higher yield and selectively (81%, *Z* : *E* = 97:3) in Et_2O. The reaction of α,β-epoxy silane *Z*-**1B** possessing dimethylphenylsilyl group instead of trimethylsilyl group afforded (*Z*)-vinylsilane *Z*-**2b** with high selectivity (Entry 4). In the reaction of (*Z*)-epoxy silane *Z*-**1A** with *n*-$BuCeCl_2$, prepared *in situ* from *n*-BuLi and $CeCl_3$,[9)] alkylated (*Z*)-vinylsilane *Z*-**2a** was also selectively produced especially using Et_2O or *n*-Bu_2O as a solvent (Entries 7 and 8). Lanthanum and samarium were also as effective as cerium (Entries 9 and 10). The reaction with ate-cerium reagent *n*-Bu_4CeLi, however, afforded vinylsilane in low yield (Entry 11). As described in the preceding paper, in the direct transformation of styrene oxide into substituted styrene derivatives, *n*-Bu_4CeLi was more effective than *n*-$BuCeCl_2$ and the reaction with *n*-BuLi resulted in poor yield.[8)] These contrasts between styrene

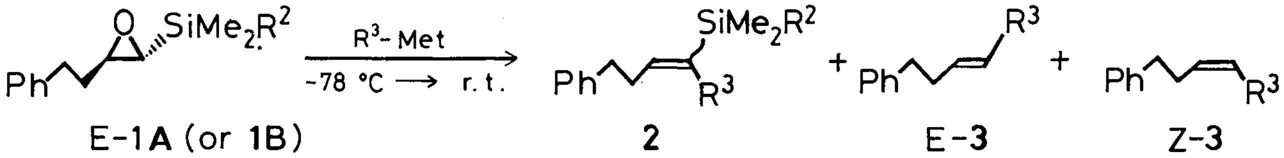


Table 2. Reaction of (*E*)-α,β-epoxy silane *E*-1A or 1B with organometallics[a]

Entry	R^2 (1)	R^3-Met	Solvent	Yield of 2/%		Yield of 3/%	(*E* : *Z*)[b]
1	Me (1A)	*n*-BuLi	Et$_2$O	a	13	66	(97 : 3)
2			DME	a	3	85	(98 : 2)
3			DME[c]	a	5	70	(97 : 3)
4	Ph (1B)	*n*-BuLi	DME[c]	b	5	75	(97 : 3)
5	Me (1A)	*n*-BuCeCl$_2$	DME	a	2	72	(98 : 2)
6		*n*-BuLaCl$_2$	DME	a	3	73	(99 : 1)
7		PhLi	DME	f	0	72	(100 : 0)
8		PhCeCl$_2$	DME	f	0	64	(100 : 0)

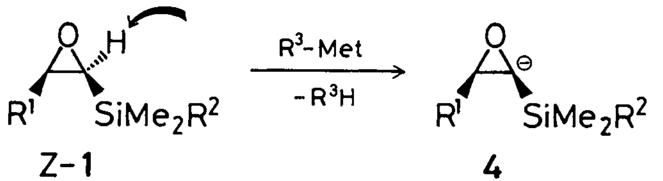
a) The reaction conditions were the same as written in Table 1. b) The ratios were determined by capillary GLC (PEG). c) Tetramethylethylenediamine was added.

oxide and (*Z*)-epoxy silane in the olefination reaction are noteworthy.

Direct synthesis of various (*Z*)-vinylsilanes *Z*-2 from (*Z*)-α,β-epoxy silanes *Z*-1 was examined. As shown in Table 1 (Entries 12-17), (*Z*)-vinylsilanes were selectively obtained. It was noted that the reaction of (*Z*)-epoxy silane *Z*-1A with PhCeCl$_2$ and PhLi selectively afforded (*E*)-desilylated olefin *E*-3f in 94% and 78%, respectively,[10] and no production of vinylsilane was detected (Entries 18 and 19)(*vide infra*).

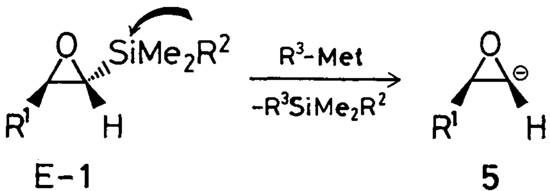
Further, the reaction of (*E*)-α,β-epoxy silanes with organolithium and lanthanoid reagents was examined and the results are listed in Table 2. When (*E*)-α,β-epoxy silane *E*-1A was treated with *n*-BuLi in Et$_2$O, desilylated (*E*)-olefin *E*-3a was predominantly obtained (Entry 1). Using DME as a solvent, yield of 3a was increased (Entry 2). The reaction of 1B with *n*-BuLi gave (*E*)-olefin *E*-3b (=3a) and 53% of butyldimethylphenylsilane was obtained (Entry 4). High stereoselection was also realized by the use of *n*-BuCeCl$_2$ and *n*-BuLaCl$_2$ (Entries 5 and 6). In the reaction of (*E*)-epoxy silane with phenyl metallics, (*E*)-olefin *E*-3f was only obtained (Entries 7 and 8).

The mechanism of the present reaction of α,β-epoxy silanes might be elucidated by carbenoid pathway as reported previously.[8,11,12] The difference between (*Z*)- and (*E*)-epoxy silanes would be caused from the first attack of organometallic reagent to α-hydrogen or silicon atom. In the case of (*Z*)-epoxy silane *Z*-1, the deprotonation of α-proton of silicon initially occurs (Scheme 1). On the other hand, (*E*)-α,β-epoxy silane is subjected to attack on the silicon atom rather than on an α-proton to silicon because of steric hindrance (Scheme 2),[2] and the fact that butyldimethylphenylsilane was isolated in the reaction of *E*-1b



Z-1 4

Scheme 1.



E-1 5

Scheme 2.

with *n*-BuLi, supports this reaction pathway.[13] In the reaction of (*Z*)-epoxy silane with phenyl metallics, the attack to silicon occurs predominantly, and the more stable (*E*)-olefin *E*-3f is produced through the isomerization before the deoxygenation to olefin.

Thus, stereoselective preparation of olefinic compounds accompanied with introduction of alkyl group from α,β-epoxy silane was directly accomplished by the reaction with organolithium and organolanthanoid reagents. The obtained (*Z*)-vinylsilanes can be selectively converted to (*E*)-olefins by the treatment with HI,[14] which means both isomers of α,β-epoxy silanes could be transformed into alkylated (*E*)-olefins. As previously reported, in the direct olefination reaction of ethylene oxide substituted by aliphatic group, regio- and stereoselectivity was not satisfactory.[8] In the present reaction of silicon-introduced epoxides at α-position, high regio- and stereoselectivity was realized.

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10) Stereochemistry of *E*-3f was assigned by the comparison of ^{1}H NMR spectrum with the data of lit.[15] Our result was different from that of lit.[6a] in which the reaction of (*Z*)-α,β-epoxy silane with PhLi was reported to give (*Z*)-olefin.
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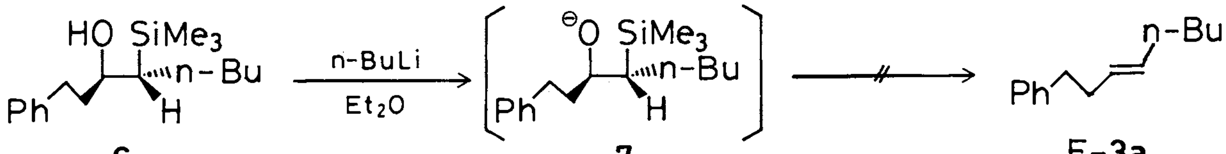
12) The pathway through ring-opening and *syn*-β-elimination might be unacceptable by the following observation: The treatment of β-hydroxy silane **6** with *n*-BuLi in Et_2O, resulting in the formation of an intermediate **7** which is the same as that from the ring-opening reaction of *E*-**1A** with *n*-BuLi, did not give the olefin *E*-**3a** and 88% of **6** was recovered.



6 **7** **E-3a**

13) One possible explanation for high stereoselection is as follows: α-Elimination from **4** or **5** and the following insertion of R^3-Met might be nearly concerted, *i.e.*, introduction of R^3 might occur in S_N2-like way.
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