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γ-Regioselective Reaction of Metaloxysilyl-substituted Allyllithium Derived from Allyldiphenylsilanol

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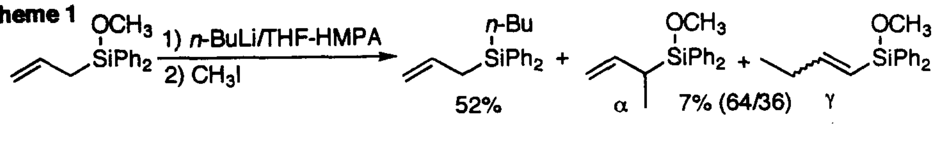
Abstract: Treatment of allyldiphenylsilanol (**1**) with two equivalents of butyllithium in the presence of HMPA at –45°C afforded silylallyllithium **2a** bearing an oxide anion on the silicon atom. The reaction of **2a** with various electrophiles gave γ-products selectively in good yields. Higher regio- and stereoselectivities were achieved in the reaction of silyl-substituted allyllithium derived from potassium allylsilanolate with butyllithium. © 1997 Elsevier Science Ltd.

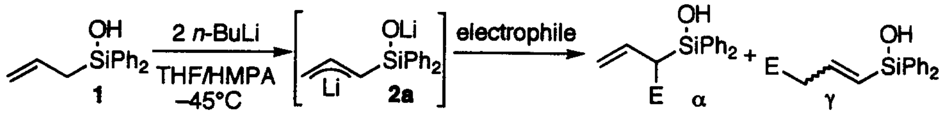
Silicon-substituted carbanions have been widely used for construction of various kinds of organic molecules.[1] Oxidative cleavage of a C–Si bond to alcohol (C–OH) is one of the most versatile transformations of the products derived from the reaction of silicon-substituted carbanions with electrophiles.[2] In general, a heteroatom on the silicon greatly facilitates the oxidative cleavage of a C–Si bond. Metallation of organosilanes bearing a heteroatom on the silicon atom with butyllithium is, however, often complicated by nucleophilic substitution reaction at the silicon. In fact, treatment of allylmethoxydiphenylsilane with butyllithium followed by quenching with iodomethane gave methylation products (α-product and γ-product) in only 7% combined yield along with allylbutyldiphenysilane (52%) which was generated by the substitution at the silicon (Scheme 1).[3] We wish to report here that dilithiated organosilicon compound **2a**, prepared from allyldiphenylsilanol[4] (**1**) and 2 equivalents of butyllithium, gave γ-products selectively upon treatment with various electrophiles.

Scheme 1



An addition of 2 equivalents of butyllithium to a solution of allyldiphenylsilanol (**1**, 1.0 mmol) in THF (5 ml) at –45°C in the presence of HMPA (2.4 mmol) provided an orange solution of silyl-substituted allyllithium[5,6] **2a**. After being stirred for 30 min, an addition of benzaldehyde afforded 1,1,5-triphenyl-1-sila-2-penten-1,5-diol selectively in 66% yield. No trace of a butylated product was observed. The results of the reaction of **2a** with various electrophiles are summarized in Table 1.[7] Higher or the same degree of γ-selectivity was observed in all cases compared to the reaction of triphenylsilylallyllithium with each electrophile. It is notable that a large difference in selectivities was observed in the reaction with ethylene oxide. A pure γ-product was obtained in the reaction of **2a**. In contrast, an α-product was predominantly provided in the case of triphenylsilylallyllithium.[6e]

Table 1. Reaction of silyl-substituted allyllithium **2a** with various electrophiles

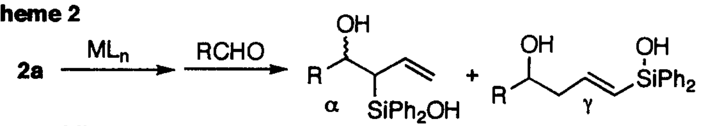


Electrophile	E	Yield	$\alpha : \gamma$ $(\alpha : \gamma)^a$	Z/E of γ
PhCHO	PhCH(OH)	66%	<1 : >99 (<1 : >99)	31/69
n-BuCHO	*n*-BuCH(OH)	45%	<1 : >99 (<1 : >99)	33/67
CH_3COCH_3	$(CH_3)_2C(OH)$	54%	2 : 98 —	49/51
CH_3I	CH_3	81%	36 : 64 (68 : 32)	26/74
EtI	Et	73%	26 : 74 —	15/85
Me_3SiCl	Me_3Si	74%^{b}	<1 : >99 —	25/75
D_2O	D	81%	63 : 37 (74 : 26)	22/78
ethylene oxide	CH_2CH_2OH	54%	<1 : >99 (81 : 19)	<1/>99

a) The ratio in parentheses is that of the reaction of triphenylsilylallyllithium with electrophiles.
b) Trimethylsilyl ether ($Me_3SiCH_2CH{=}CHSiPh_2(OSiMe_3)$) was obtained.

An addition of Me_3Al[9] to α-silylallyllithium **2a** gave allylic alanate, which afforded silyl-substituted β-hydroxysilane (α-product) selectively upon treatment with an aldehyde (Scheme 2). The use of $ClTi(O\text{-}i\text{-}Pr)_3$[10] in place of Me_3Al gave *anti* β-hydroxysilane selectively although the regioselectivity of the product was moderate.

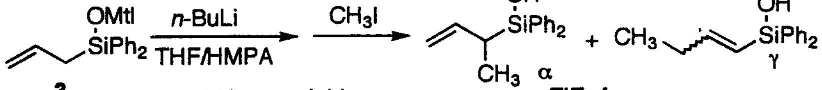
Scheme 2



ML_n	RCHO	yield	$\alpha : \gamma$	*syn*/*anti*
Me_3Al	PhCHO	42%	84 : 16	46/54
	n-$C_6H_{13}CHO$	67%	>99 : <1	58/42
$ClTi(O\text{-}i\text{-}Pr)_3$	PhCHO	51%	71 : 29	4/96
	n-$C_6H_{13}CHO$	36%	78 : 22	<1/>99

It turned out that a counter cation of silanolate anion **2** heavily affected the α- *v.s.* γ-regioselectivity in the reaction with iodomethane (Scheme 3). The stereoselectivities (*Z v.s. E*) of the γ-product were also changed by the counter cations. The use of potassium silanolate **3c** gave the highest γ- and *E*-selectivities. It is obvious that the selectivities depended upon the ionic character of the O–Mtl bond of silanolate **3**. The stronger the ionic character, the higher are the obtained regio- and stereoselectivities of the product.

Scheme 3

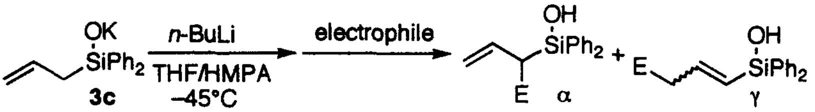


3

	Mtl	yield	$\alpha : \gamma$	Z/E of γ
3a	Li	81%	36 : 64	26/74
3b	Na	54%	30 : 70	6/94
3c	K	67%	10 : 90	3/97

High γ- and *E*-selectivity of the products were generally achieved in the reaction of potassium silanolate **3c** with various electrophiles other than iodomethane. The results are summarized in Table 2.

Table 2. Reaction of silyl-substituted allyllithium derived from potassium silanolate **3c**

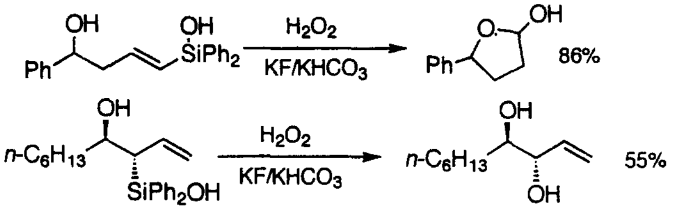


Electrophile	E	Yield	α : γ	*Z*/*E* of γ
PhCHO	PhCH(OH)	78%	<1 : >99	<1/>99
n-BuCHO	*n*-BuCH(OH)	57%	<1 : >99	<1/>99
CH_3COCH_3	$(CH_3)_2C(OH)$	40%	<1 : >99	<1/>99
CH_3I	CH_3	67%	10 : 90	3/97
EtI	Et	89%	2 : 98	2/98
Me_3SiCl	Me_3Si	70%[a]	<1 : >99	3/97
D_2O	D	78%	36 : 64	<1/>99
ethylene oxide	CH_2CH_2OH	38%	<1 : >99	<1/>99

a) Trimethylsilyl ether ($Me_3SiCH_2CH{=}CHSiPh_2(OSiMe_3)$) was obtained.

Since the adducts obtained above possess a hydroxyl moiety on the silicon atom, the oxidative cleavage of the C–Si bond proceeded smoothly without pretreatment with trifluoroacetic acid (Scheme 4). In the case of β-hydroxysilane, yield of the diol decreased slightly due to the partial 1,2-elimination giving the corresponding 1,3-alkadiene.

Scheme 4



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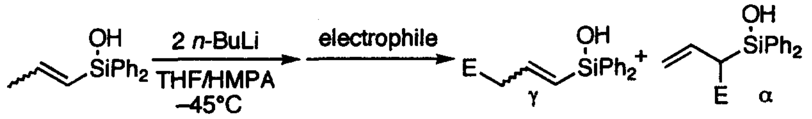
7 Treatment of 1-propenyl(diphenyl)silanol with 2 equivalents of butyllithium in the presence of HMPA also gave silyl-substituted allyllithium **2a** which afforded products in 48% yield (E = PhCH(OH), α:γ = <1:>99) and 56% yield (E = CH_3, α:γ = 31:69) upon treatment with benzaldehyde or iodomethane, respectively.[8]



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11 General procedure is as follows. To a suspension of potassium hydride (1.5 mmol) in THF (5 ml) was added a solution of allyldiphenylsilanol (240 mg, 1.0 mmol) in THF (5 ml) at 0 °C. After being stirred for 5 min, HMPA (430 mg, 2.4 mmol) and butyllithium (1.2 mmol, 0.75 ml, 1.6 *M* in hexane) was added dropwise at -45 °C and the mixture was stirred for 30 min. A solution of benzaldehyde (2.0 mmol) in THF (4 ml) was added and the whole mixture was stirred for an additional 45 min at the same temperature. The reaction mixture was poured into saturated aqueous ammonium chloride and extracted with ethyl acetate (20 ml×3). Concentration and purification by silica-gel chromatography gave (*E*)-1,1,5-triphenyl-1-sila-2-penten-1,5-diol (270 mg) in 78% yield: Mp. 115–116 °C IR (neat) 3340, 3036, 1616, 1427, 1313, 1117, 1074, 1002, 850, 788, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12 (s, 1H), 2.42 (s, 1H), 2.66 (dd, *J* = 6.3, 6.3 Hz, 1H), 4.78 (dd, *J* = 6.6, 6.6 Hz, 1H), 6.09 (d, *J* = 18.9 Hz, 1H), 6.30 (ddd, *J* = 6.6, 6.6, 18.6 Hz, 1H), 7.24–7.45 (m, 11H), 7.54–7.58 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 46.40, 73.26, 125.89, 127.64, 127.90, 128.49, 129.20, 129.97, 134.62, 134.68, 135.66, 135.71, 143.75, 148.32. Found: C, 75.97; H, 6.42%. Calcd for $C_{22}H_{22}O_2Si$: C, 76.26; H, 6.40.

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