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LETTERS

# Sequential Carbon-Carbon Bond Formation Reaction Using 1-Silyl-2-propenyllithium

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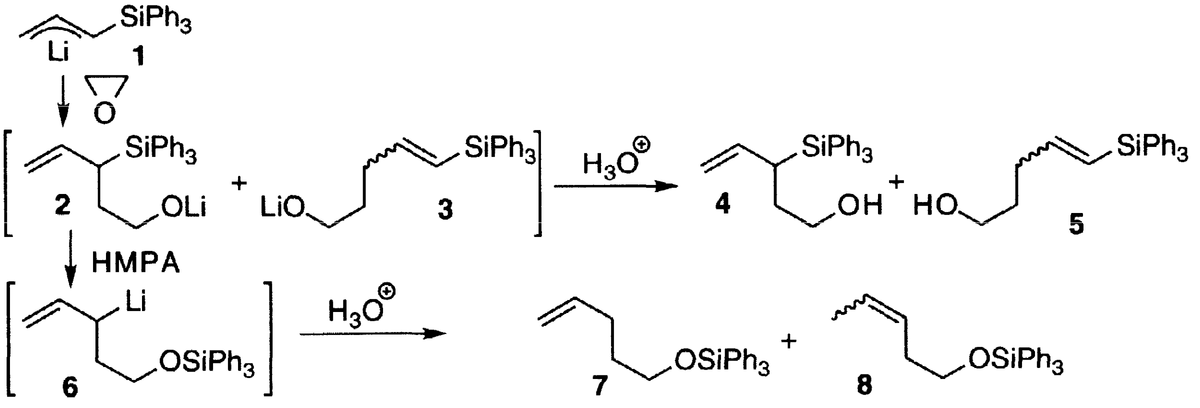
***Abstract:*** The reaction of 1-triphenylsilyl-2-propenyllithium with ethylene oxide afforded an adduct, a lithium salt of 3-triphenylsilyl-4-penten-1-ol, which regenerated an allyllithium species, 3-lithio-5-triphenylsiloxy-1-pentene via anionic rearrangement of a silyl group from carbon to oxide in the presence of HMPA. This allylic lithium compound could be trapped in one-pot by various electrophiles to provide the corresponding adducts as regioisomeric mixtures. A successive addition of epoxides, aldehydes, and HMPA to 1,3-bis(triphenylsilyl)-2-propenyllithium gave 1,4-diol monosilylethers in one-pot with high regioselectivity.

The tandem carbon-carbon bond formation reaction triggered by anionic rearrangement of a silyl group from carbon to oxide has increasingly attracted the attention of many chemists and has become a new methodology for the construction of complex organic molecules.[1,2] Herein we wish to report an HMPA-induced anionic 1,4-rearrangement of a silyl group[3] from carbon to oxide in the reaction of 1-triphenylsilyl-2-propenyllithium (**1**) and 1,3-bis(triphenylsilyl)-2-propenyllithium with epoxide.

The reaction of silylpropenyllithium[4] **1** with ethylene oxide has been reported to afford 3-silyl-4-pentenol **4** predominantly.[5] We found, however, that a mixture of triphenylsilyl ether of 4-penten-1-ol **7** and 3-penten-1-ol **8** was obtained in good combined yield in the presence of HMPA (Scheme 1). Obviously, the formation of these products was attributed to anionic rearrangement of a silyl group in the alkoxide **2** to regenerate allylic lithium compound **6**.

**Scheme 1**



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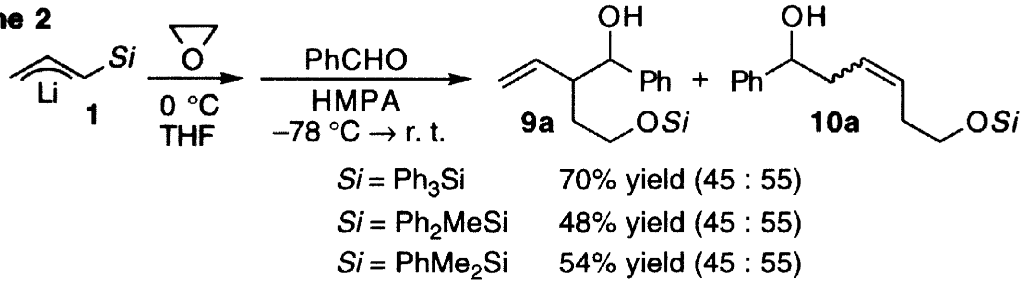
The allylic lithium species **6** could be trapped by benzaldehyde. An addition of butyllithium to a THF solution of allyltriphenylsilane at 0 °C provided 1-triphenylsilyl-2-propenyllithium (**1**) after stirring for 1 h. A sequential addition of ethylene oxide, benzaldehyde, and HMPA to the resulting solution of **1** gave a regioisomeric mixture of monosilyl ethers of 1,4-diol **9a** and 1,6-diol **10a** in 70% combined yield.[6] The yield heavily depended upon the nature of the substituent on the silicon atom (Scheme 2). The use of a triphenylsilyl group gave the best result.

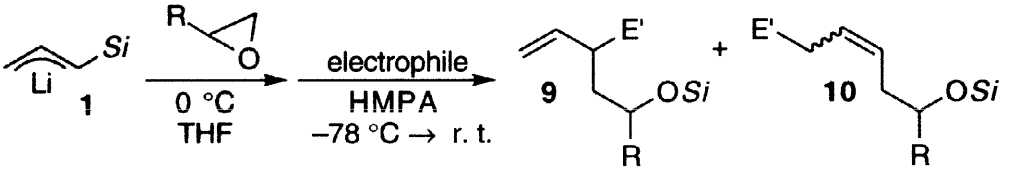
**Scheme 2**



$Si$ = $Ph_3Si$ 70% yield (45 : 55)
$Si$ = $Ph_2MeSi$ 48% yield (45 : 55)
$Si$ = $PhMe_2Si$ 54% yield (45 : 55)

Tandem carbon-carbon bond formation reaction of **1** with epoxides and various electrophiles is summarized in Table 1. In this reaction, silylpropenyllithium **1** behaved as a synthetic equivalent of dianion, 1,1- or 1,3-dilithio-2-propene. The yields of **9** and **10** were not very high because of the formation of a γ-addition product, 5-silyl-4-penten-1-ol derivative **5**, as a by-product. The use of 2-methyloxirane or 2-methoxymethyloxirane instead of oxirane provided the corresponding adducts (Entries 5 and 6 in Table 1). Unfortunately, styrene oxide or 1,2-epoxyoctane could not be used since these epoxides would react with **1** predominantly at the γ-position. Rearrangement of the silyl group did not occur in the γ-adducts **3**.

Table 1. Tandem carbon-carbon bond formation reaction of **1**.

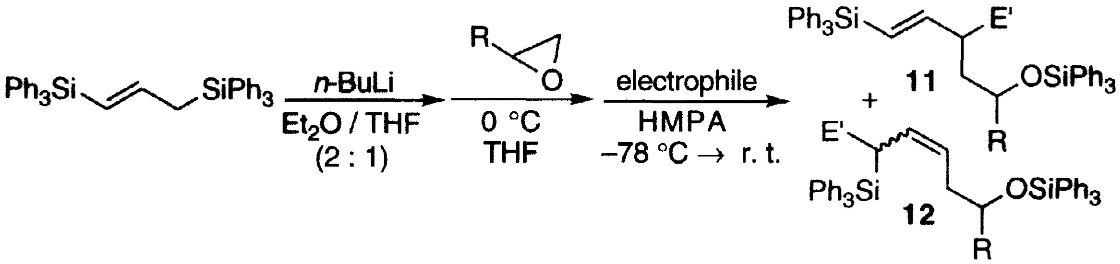


| Entry | R | Electrophile | E' | Yield(%) | **9** : **10** |
|---|---|---|---|---|---|
| 1 | H | PhCHO | PhCH(OH) | 70 | 45 : 55 |
| 2 | H | $c$-$C_6H_{11}CHO$ | $c$-$C_6H_{11}(OH)$ | 36 | 45 : 55 |
| 3 | H | $CH_3I$ | $CH_3$ | 41 | 31 : 69 |
| 4 | H | $CH_2=CHCH_2Br$ | $CH_2=CHCH_2$ | 56 | 55 : 45 |
| 5 | $CH_3$ | PhCHO | PhCH(OH) | 56 | 42 : 58 |
| 6 | $CH_3OCH_2$ | PhCHO | PhCH(OH) | 57 | 42 : 58 |

allyltriphenylsilane (1.0 mmol), *n*-BuLi (1.3 mmol), epoxide (1.3 mmol), electrophile (4.0 mmol), and HMPA (4.0 mmol) were employed.

Regioselectivities of the reaction described above were generally low. It then occurred to us that the use of 1,3-bis(triphenylsilyl)-1-propene as a starting material would give silyl-substituted allyllithium via the migration of silicon which might react with electrophiles with high regioselectivity.[4] Indeed, this proved to be the case and 1-lithio-1,3-bis(triphenylsilyl)-1-propene with epoxides followed by a sequential addition of benzaldehyde and HMPA in a mixed solvent (THF : ether = 1 : 2) gave 1,4-diol derivatives. The representative results are shown in Table 2. The use of a mixed solvent was essential for the successful reactions. In THF. even in the absence of HMPA, the rearrangement of silicon to oxide took place easily to provide 3-lithio-1-triphenylsilyl-5-triphenylsiloxy-1-pentene which reacted with another molecule of the epoxide to afford the complex reaction mixture.

Table 2. Tandem carbon-carbon bond formation reaction of bissilylallyllithium.



| Entry | R | Electrophile | E' | Yield(%) | **11** : **12** |
|---|---|---|---|---|---|
| 1 | H | PhCHO | PhCH(OH) | 50 | >99 : <1 |
| 2 | H | $n$-$C_6H_{13}CHO$ | $n$-$C_6H_{13}(OH)$ | 39 | >99 : <1 |
| 3 | H | $c$-$C_6H_{11}CHO$ | $c$-$C_6H_{11}(OH)$ | 41 | >99 : <1 |
| 4 | H | $CH_3I$ | $CH_3$ | 50 | 81 : 19 |
| 5 | H | $CH_2=CHCH_2Br$ | $CH_2=CHCH_2$ | 51 | 24 : 76 |
| 6 | $CH_3$ | PhCHO | PhCH(OH) | 52 | >99 : <1 |
| 7 | $CH_3OCH_2$ | PhCHO | PhCH(OH) | 50 | >99 : <1 |
| 8 | Ph | PhCHO | PhCH(OH) | 52 | >99 : <1 |
| 9 | $n$-$C_4H_9$ | PhCHO | PhCH(OH) | 35 | >99 : <1 |

Experimental procedure is as follows. To a solution of 1,3-bis(triphenylsilyl)-1-propene (279 mg, 0.5 mmol) in a mixed solvent of ether (5.6 ml) and THF (2.8 ml) was added butyllithium in hexane (1.57 *M* hexane solution, 0.32 ml, 0.5 mmol) at 0 °C. After stirring for 2 h at that temperature, to the resulting solution ethylene oxide (0.5 mmol) in THF was added and stirred for 1 h. Then, after the mixture was cooled to −78 °C, benzaldehyde (2.0 mmol) and HMPA (2.0 mmol) was added and the whole reaction mixture was allowed to warm to ambient temperature with stirring for another 6 h. The mixture was poured into saturated aqueous ammonium chloride and extracted with ethyl acetate (20 ml × 3). The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The residual oil was diluted with THF (5 ml) and a solution of tetrabutylammonium fluoride (1.0 *M*, 1.0 ml, 1.0 mmol) was added at 0 °C and the mixture was stirred for 1 h. Extractive workup followed by silica gel column purification gave 1-phenyl-2-((*E*)-2-triphenylsilylethenyl)-1,4-butanediol (113 mg, 0.25 mmol, 59:41 isomeric mixture) in 50 % yield: Faster moving band; $R_f = 0.46$ (Hexane/AcOEt = 1/1); IR (nujol) 3360, 1612, 1430, 1111, 1044, 998, 773, 698 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.41–1.87 (bs, 2H), 1.48–1.73 (m, 2H), 2.74 (dddd, *J* = 3.3, 6.0, 8.7, 14.1 Hz, 1H), 3.58 (ddd, *J* = 6.3, 7.5, 10.8 Hz, 1H), 3.68 (ddd, *J* = 6.0, 6.0, 10.8 Hz, 1H), 4.61 (d, *J* = 6.0 Hz, 1H), 6.05 (dd, *J* = 8.7, 18.6 Hz, 1H), 6.29 (d, *J* = 18.6 Hz, 1H), 7.22–7.50 (m, 20H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 33.48, 52.32, 60.94, 76.45, 126.73, 127.65, 127.98, 128.35, 128.93, 129.65, 134.47, 142.31, 152.21. slower moving band; $R_f = 0.36$ (Hexane/AcOEt = 1/1); IR (nujol) 3360, 1612, 1440, 1110, 1019, 697 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.66 (dddd, *J* = 5.4, 5.4, 8.3, 13.7 Hz, 1H), 1.98 (dddd, *J* = 5.4, 5.4, 8.1, 13.7 Hz, 1H), 1.79–2.62 (bs, 2H), 2.78 (dddd, *J* = 5.4, 7.8, 8.3, 8.7 Hz, 1H), 3.63 (ddd, *J* = 5.4, 8.1, 10.8 Hz, 1H), 3.74 (ddd, *J* = 5.4, 5.4, 10.8 Hz, 1H), 4.53 (d, *J* = 7.8 Hz, 1H), 5.82 (dd, *J* = 8.7, 18.6 Hz, 1H), 6.06 (d, *J* = 18.6 Hz, 1H), 7.19–7.44 (m, 20H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 33.98, 52.21, 61.06, 77.21, 126.96, 127.72, 127.86, 128.43, 129.51, 134.49, 135.90, 142.84, 152.46.

## References and Notes

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6. Both **9a** and **10a** consist of two regioisomeric monosilyl ethers of 1,4- or 1,6-diol. The products were isolated as 1,4- or 1,6-diol after treatment with tetrabutylammonium fluoride in THF. The 1,4-diol was obtained as a mixture of two stereoisomers (isomeric ratio = 1/1).