Base-catalysed Rearrangement of β-Hydroxyvinylsilanes to Allyl Silyl Ethers

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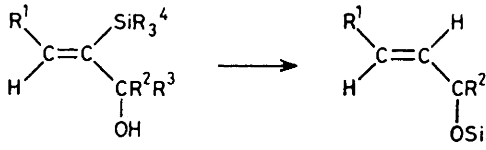
A 1,3-silyl group shift from carbon to oxygen occurs readily when β-hydroxyvinylsilanes are treated with catalytic amounts of sodium hydride in hexamethylphosphoric triamide, thus providing the first demonstration of the rearrangement of silicon from sp^2-carbon to oxygen.

Chan reported that β-hydroxyvinylsilanes (**1**) are stable under the conditions normally employed to effect elimination of silanol from β-hydroxyalkylsilanes. Indeed, treatment of the β-hydroxyvinylsilane (**1a**), prepared by the reaction of α-(triphenylsilyl)vinyl-lithium with benzaldehyde, with dilute sulphuric acid or sodium hydride resulted in recovery of (**1a**).[1] We were surprised, therefore, to find that a 1,3-silyl group shift from carbon to oxygen occurs readily when compounds (**1**) are treated with sodium hydride in hexamethylphosphoric triamide (HMPA).

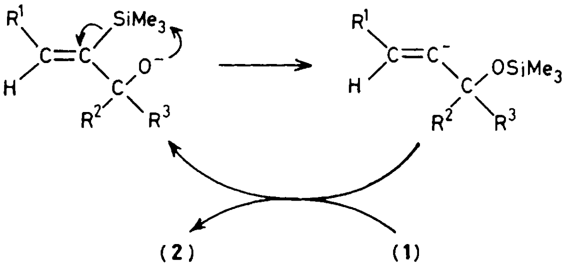
Treatment of (**1b**), obtained by the reaction of α-(trimethylsilyl)vinyl-lithium with octaldehyde, with a catalytic amount of NaH (10 mol %) in HMPA for 15 min at room temperature afforded the allyl trimethylsilyl ether (**2b**) in >95% yield (g.l.c.), together with a small amount of the allyl alcohol produced by hydrolysis of (**2b**). Similarly, the β-hydroxyvinylsilanes (**1c**—**g**), which were readily prepared by hydromagnesiation of 1-trimethylsilylhex-1-yne[2] followed by treatment with formaldehyde (84% yield based on the silylacetylene), acetaldehyde (85%), propionaldehyde (87%), acrolein (87%), and acetone (88%), respectively, were converted into the corresponding allyl trimethylsilyl ethers (**2c**–**g**), in essentially quantitative yields (Scheme 1). The stereochemistry of (**2c**—**g**) was determined by ^{1}H n.m.r. comparison of the hydrolysis products with authentic samples. When these reactions were carried out in tetrahydrofuran (THF), which was the solvent probably used by Chan, instead of HMPA, compounds (**1**) were recovered unchanged. However, the reaction does occur in THF if KH is used as base.



(**1**) (**2**)

	R^1	R^2	R^3	R^4
a	H	H	Ph	Ph
b	H	H	n-C_7H_{15}	Me
c	Bu^n	H	H	Me
d	Bu^n	H	Me	Me
e	Bu^n	H	Et	Me
f	Bu^n	H	CH=CH_2	Me
g	Bu^n	Me	Me	Me

Scheme 1



Scheme 2

Rearrangement reactions with migration of silicon have extensive precedents.[3] 1,3-Migration of silicon from carbon to oxygen has been observed with α-silyl sulphoxides[4] or selenoxides,[5] β-ketosilanes,[6] or 4,5-dihydro-3-(1-hydroxyethyl)-3-(trimethylsilyl)furan-2(3*H*)-one[7]. However, to the best of our knowledge, this is the first example of the rearrangement of silicon from sp^2-carbon to oxygen.

Although the precise reaction mechanism and a satisfactory explanation of the dramatic solvent effect on the present reaction must await further study, a plausible rationalization involves the intramolecular, concerted four-centre mechanism in Scheme 2, as is the case with a number of related 1,2- and 1,3-silicon migration reactions.[8]

Since the recently developed hydromagnesiation of silylacetylenes[2] makes the β-hydroxyvinylsilanes (**1**) readily available, the present reaction offers a convenient synthesis of various allyl silyl ethers (**2**), which recently have been shown to be useful precursors of silyl enol ethers.[9] However, it should be noted that the reaction must be carried out under anhydrous conditions and the products (**2**) should be isolated by non-aqueous work-up followed by bulb-to-bulb distillation, because allyl silyl ethers are readily hydrolysed by aqueous acid or base.

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References

1 T. H. Chan and W. Mychajlowskij, *Tetrahedron Lett.*, 1974, 171.
2 F. Sato, H. Ishikawa, and M. Sato, *Tetrahedron Lett.*, 1981, **22**, 85.
3 E. Colvin, 'Silicon in Organic Synthesis,' Butterworths, London, 1981, pp. 30—39.
4 A. G. Brook and D. G. Anderson, *Can. J. Chem.*, 1968, **46**, 2115; F. A. Carey and O. Hernandez, *J. Org. Chem.*, 1973, **38**, 2670; E. Vedejs and M. Mullins, *Tetrahedron Lett.*, 1975, 2017.
5 H. J. Reich and S. K. Shah, *J. Org. Chem.*, 1977, **42**, 1773; K. Sachdev and H. S. Sachedev, *Tetrahedron Lett.*, 1976, 4223.
6 A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Am. Chem. Soc.*, 1967, **89**, 5493.
7 K. Yamamoto, Y. Tomo, and S. Suzuki, *Tetrahedron Lett.*, 1980, **21**, 2861.
8 A. G. Brook, *Acc. Chem. Res.*, 1974, **7**, 77.
9 H. Suzuki, Y. Koyama, Y. Morooka, and T. Ikawa, *Tetrahedron Lett.*, 1979, 1415.