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CLEAVAGE OF SILICON-VINYL CARBON BOND BY ^{n}Bu$_4$NF

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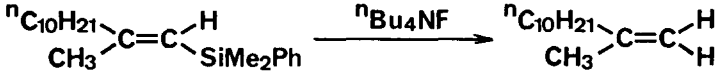
Abstract: Dimethylphenylsilyl- and diphenylmethylsilyl-vinyl carbon bonds are cleaved with ^{n}*Bu*$_4$*NF. Desilylation of 1-phenylthio-1-trimethylsilyl-1-alkenes in the presence of aldehyde moiety gives carbanion adducts.*

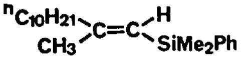
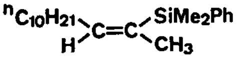
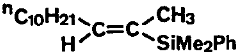
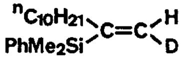
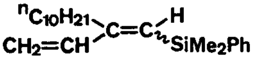
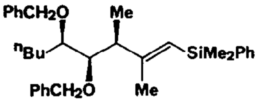
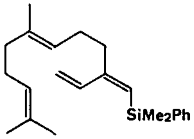
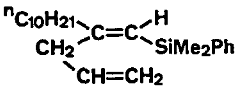
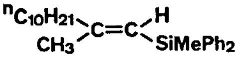
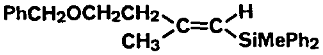
The affinity of fluoride ion for silicon has been well recognized and widely used for the cleavage of silicon-carbon bond.[1] Chan has reported that the cleavage of trimethylsilyl-vinyl carbon bonds is, however, difficult or impossible under ordinary conditions.[2] In connection with our new synthesis of vinylsilanes,[3] we have reexamined the cleavage of vinylsilanes. Surprisingly, ^{n}Bu$_4$NF has proved to be effective for the cleavage of PhMe$_2$Si- and Ph$_2$MeSi-vinyl carbon bonds. Not only special vinylsilanes[2,4] having the hydroxyl group at β-carbon but also prosaic ones were cleaved efficiently. The presence of one or two phenyl group on silicon atom plays a critical role, as similar vinyltrimethylsilanes are recovered completely unchanged under the same reaction conditions.[5] The results are summarized in Table 1.

A tetrahydrofuran solution of ^{n}Bu$_4$NF[6] (1.0 *M*, 2.5 ml, 2.5 mmol) was added to a solution of 1-dimethylphenylsilyl-2-methyl-1-dodecene (0.16 g, 0.5 mmol) in HMPA (4.0 ml) under an argon atmosphere and the whole was stirred for 0.5 h at 80°C. The resulting mixture was diluted with ethyl acetate (25 ml) and washed with water (10 ml x4). Purification by preparative thin layer chromatography on silica gel gave 2-methyl-1-dodecene (70 mg) in 77% yield. The reaction proceeded in DMSO and THF, although prolonged heating of the reaction mixture was needed in the case of THF.



High stereospecificity of the reactions is shown in the transformation of (*Z*) and (*E*)-2-dimethylphenylsilyl-2-tridecene into (*E*) and (*Z*)-tridecene, respectively (Entry 4 and 5). Substitution of silyl group by hydrogen proceeds with retention of configuration.

Table 1. Cleavage of Silicon-Vinyl Carbon Bond by $^{n}Bu_4NF$[a]

Entry	Starting Material	Reaction Conditions			Yield of Product (%)[b]
		Solvent	Temp (°C)	Time (h)	
1		HMPA	80	0.5	77
2		DMSO	80	1.0	70
3		THF	80	10	66 (28)[c]
4		DMSO	80	0.5	77[d]
5		DMSO	80	0.5	60[d]
6		DMSO	80	0.5	80[e]
7		HMPA	25	0.5	82
8		THF	80	2.0	82
9		DMSO	100	2.0	95[f]
10		DMSO	80	2.0	84[g]
11		HMPA	25	1.0	88[h]
12		DMSO	80	2.0	quant[h]
13		THF	80	2.0	89[h]
14		HMPA	80	0.5	70
15		THF	80	1.0	80

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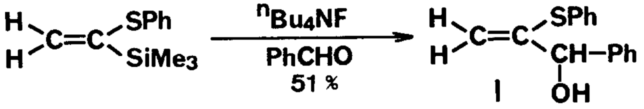
[a] One mmol of vinylsilanes and five mmol of $^{n}Bu_4NF$ were employed. [b] Yields represent isolated purified products. [c] Starting material was recovered in 28% yield. [d] Each product was not contaminated by the other stereoisomer. Purity of the product was >95% by glpc. [e] See ref. 7. [f] See ref. 8. [g] See ref. 9. [h] Migration of double bond accompanied with the desilylation. The product was 2-(1-propenyl)-1-dodecene.

It is worth noting that this new method is very effective for the formation of polyene which is sensitive to acidic conditions. For instance, treatment of 1-dimethylphenylsilyl-6,10-dimethyl-2-vinyl-1,5,9-undecatriene with ^{n}Bu$_4$NF in DMSO gave β-farnesene[9] in 84% yield, whereas the protodesilylation by means of HI[10] provided a complex mixture containing no desired tetraene (Entry 10).

All attempts to trap a supposed vinyl anion intermediate by the coexisting electrophiles such as PhCHO and MeI resulted in failure. Treatment of a mixture of 1-dimethylphenylsilyl-2-methyl-1-dodecene and PhCHO with ^{n}Bu$_4$NF in DMSO gave only desilylated product, 2-methyl-1-dodecene.

The introduction of anion-stabilizing groups on the carbon bearing silyl group facilitates the Si-C bond cleavage. Reaction of 1-phenylthio-1-trimethylsilylethene[11] with ^{n}Bu$_4$NF in the presence of PhCHO provided the adduct I in 51% yield along with the desilylated phenyl vinyl sulfide (20%). The cleavage of Si-C cond proceeded with high stereospecificity. (*E*)-1-Phenylthio-1-trimethylsilyl-1-octene and (*Z*)-isomer afforded (*E*)-1-phenylthio-1-octene and (*Z*)-isomer in 88% and 85% yields, respectively on treatment with ^{n}Bu$_4$NF in THF. The process was applied to the compounds containing formyl group to produce five- and six-membered ring products in good yields.[12,13]



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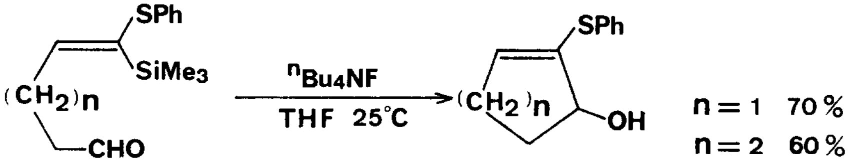

References and Notes

1. Silylacetylenes: C. S. Kraihanzel and J. E. Poist, *J. Organomet. Chem.*, 8, 239 (1967); A. B. Holmes, R. A. Raphael, and N. K. Wellard, *Tetrahedron Lett.*, 1976, 1539; E. Nakamura and I. Kuwajima, *Angew. Chem. Internat. Ed.*, 15, 498 (1976). Epoxysilanes: T. H. Chan, P. W. K. Lau, and M. P. Li, *Tetrahedron Lett.*, 1976, 2667; T. H. Chan, M. P. Li, W. Mychajlowskij, and D. N. Harpp, *ibid.*, 1974, 3511; H. Tomioka, T. Suzuki, K. Oshima, and H. Nozaki, *ibid.*, 23, 3387 (1982).
2. T. H. Chan and W. Mychajlowskij, *ibid.*, 1974, 3479.
3. Y. Okuda, M. Sato, K. Oshima, and H. Nozaki, *ibid.*, in press.

4. The reaction of (*Z*)-6-dimethylphenylsilyl-6-tridecen-5-ol with $^nBu_4NF$ in DMSO proceeded smoothly at 25°C (15 min) to give the corresponding allylic alcohol in 91% yield.
5. Vinyltriphenylsilane also could be cleaved but less effectively. Desilylation of 1-triphenylsilyl-2-methyl-1-dodecene with $^nBu_4NF$ in HMPA (80°C, 1 h) gave the desired product in <50% yield.
6. A THF solution purchased from Aldrich Chemical Co. and the reagent prepared according to the reported procedure (E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, 94, 6190 (1972)) were equally effective for the reaction.
7. (*Z*)-1-Deuterio-2-dimethylphenylsilyl-1-dodecene: NMR (CCl_4) δ0.36 (s, 6H), 0.87 (m, 3H), 1.06-1.47 (m, 16H), 1.89-2.21 (m, 2H), 5.56 (bs, 1H), 7.31-7.53 (m, 5H). Found: C, 78.98; H, 11.79%. Calcd for $C_{20}H_{33}DSi$: C, 79.13; H, 11.62%. (*E*)-1-Deuterio-1-dodecene: NMR (CCl_4) δ0.87 (m, 3H), 1.08-1.53 (m, 16H), 1.85-2.20 (m, 2H), 4.88 (bd, *J* = 17.0 Hz, 1H), 5.73 (m, 1H).
8. Starting vinylsilane: bp 162-166°C (bath temp, 0.06 Torr); IR (neat) 2960, 1615, 1252, 1110, 1064, 838, 725, 695 cm^{-1}; NMR (CCl_4) δ0.30 (s, 6H), 0.76-1.60 (m, 12H containing δ1.10 (d, *J* = 6.3 Hz, 3H)), 1.69 (s, 3H), 2.44 (m, 1H), 3.21-3.54 (m, 2H), 4.44 (d, *J* = 10.5 Hz, 1H), 4.47 (bs, 2H), 4.61 (d, *J* = 10.5 Hz, 1H), 5.44 (bs, 1H), 7.01-7.46 (m, 15H); Found: C, 79.18; H, 8.94%. Calcd for $C_{33}H_{44}O_2Si$: C, 79.14; H, 8.86%. Desilylated product: bp 132-138°C (bath temp, 0.06 Torr); IR (neat) 2950, 1646, 1456, 1378, 1210, 885 cm^{-1}; NMR (CCl_4) δ0.88 (m, 3H), 1.07 (d, *J* = 7.2 Hz, 3H), 1.16-1.63 (m, 6H), 1.71 (s, 3H), 2.18-2.56 (m, 1H), 3.26-3.53 (m, 2H), 4.33-4.83 (m, 6H), 7.19 (m, 10H); Found: C, 82.14; H, 9.47%. Calcd for $C_{25}H_{34}O_2$: C, 81.92; H, 9.35%.
9. Vinylsilane was easily prepared in one pot by CuI catalyzed silylmagnesation of 6,10-dimethyl-5,9-undecadien-1-yne followed by coupling with vinyl bromide in the presence of $NiCl_2(PPh_3)_2$. β-Farnesene: A. Yasuda, S. Tanaka, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 52, 1752 (1979).
10. K. Utimoto, M. Kitai, and H. Nozaki, *Tetrahedron Lett.*, 1975, 2825.
11. In this case, Me_3Si group was cleaved as easily as $PhMe_2Si$ and Ph_2MeSi groups.
12. 2-Phenylthio-2-cyclopenten-1-ol: IR (neat) 3330, 2940, 1580, 1480, 1440, 1040, 740, 680 cm^{-1}; NMR (CCl_4) δ1.2-2.6 (m, 5H), 4.52 (m, 1H), 5.77 (bs, 1H), 7.1-7.4 (m, 5H).
13. Financial support by the Nissan Kagaku Kogyo Ltd. and the Ministry of Education, Science, and Culture, Japanese Government (Grant-in-Aid for Special Project Research #57118006) is acknowledged.

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