Tetrahedron Letters,Vol.30,No.33,pp 4413-4416,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

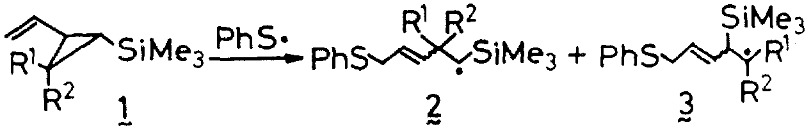
STABILIZING EFFECT OF TRIALKYLSILYL GROUP ON CARBON RADICAL: RADICAL INDUCED RING OPENING OF 1-TRIALKYLSILYL-2-VINYLCYCLOPROPANES

Katsukiyo Miura, Koichiro Oshima*, and Kiitiro Utimoto*
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan

Abstract: 1-Trialkylsilyl-2-vinylcyclopropane or 3-methyl-1-trialkylsilyl-2-vinylcyclopropane provided the corresponding homoallylic silane exclusively upon treatment with *PhSH*, *Ph_3SnH*, or *$C_6F_{13}I$*. On the other hand, 3-phenyl-1-trimethylsilyl-2-vinylcyclopropane or 3-acetyl-1-trimethylsilyl-2-vinylcyclopropane gave allylic silane selectively.

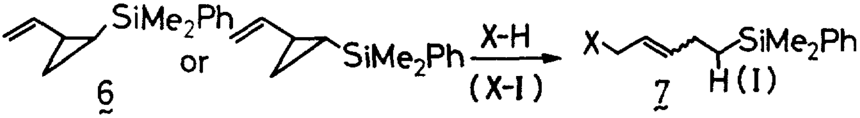
Trimethylsilyl substituents behave in a dichotomous manner, showing the properties of both electron donor and acceptor groups. α-Trimethylsilyl carbanions are stabilized by $(\sigma^*\text{-}p)\pi$ overlap between the antibonding σ^* level of the C-Si bond with the adjacent filled p-orbital of the carbanion, whereas reactions which involve carbonium ion formation or development β to silicon are positively encouraged. Organosilicon chemistry based on these ionic effects has been extensively studied.[1] In contrast, there has been little investigation of the stabilizing effect of the trimethylsilyl group on carbon radicals.[2] By using 3-substituted 1-trimethylsilyl-2-vinylcyclopropanes as models of free radical substituent effects we found that α-trimethylsilyl stabilization was substantial.

A priori, it is predictable that two isomers, homoallylic silane (**4**, $PhSCH_2CH{=}CHCR^1(R^2)CH_2SiMe_3$) and allylic silane (**5**, $PhSCH_2CH{=}CHCH(SiMe_3)$-CHR^1R^2) will be generated under cyclopropane ring cleavage in the reaction of vinylcyclopropane (**1**)[3] with PhSH, and the ratio of the two products will reflect the stabilizing effect of the Me_3Si group on the intermediary carbon radicals (α to silicon (**2**) and β to silicon (**3**)).



Treatment of cis-1-dimethylphenylsilyl-2-vinylcyclopropane (cis-**6**, 0.20 g, 1.0 mmol) with PhSH (0.12 g, 1.1 mmol) at 60°C in benzene (2.0 ml) provided homoallylic silane (**7**, 0.27 g, E/Z = 14/1) in 88% yield. Other reagents such as Ph_3SnH, $n\text{-}Bu_3SnH$, and $C_6F_{13}I$ also afforded the corresponding homoallylic silanes in the triethylborane-induced radical reaction,[4,5] and no trace of allylic silane was observed in the reaction mixture. The results are summarized in Table 1. The cis, trans stereochemistry of the cyclopropane did not affect the selectivity of the C-C bond fission. Cis isomer (cis-**6**) as well as trans isomer (trans-**6**) provided the same homoallylic silane **7** as a single regioisomer, although the E, Z ratios of the products **7** derived from cis-**6** were slightly different from those generated from trans-**6**. For instance, cis-**6** provided a mixture of (E)- and (Z)-1-phenylthio-5-dimethylphenylsilyl-2-pentene in 14/1 ratio upon treatment with benzenethiol, whereas trans-**6** gave a mixture of (E)/(Z) = 5/1.

Table 1. Radical-induced ring opening of 1-dimethylphenylsilyl-2-vinylcyclopropane

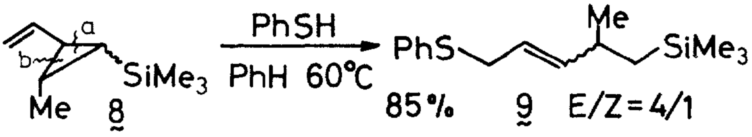


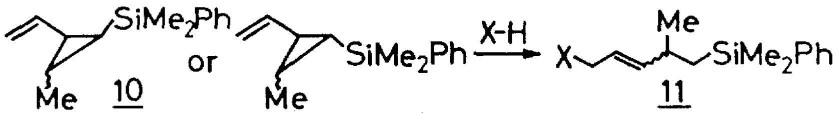
Substrate[b]	X-H (X-I)	Solvent	Initiator	Temp(°C)	Time(h)	Product 7 Y(%)	E/Z
cis-**6**	PhSH	benzene	——	60	3	88	14/1
trans-**6**	PhSH	benzene	——	60	5	88	5/1
cis-**6**	Ph_3SnH	benzene	Et_3B	25	1	96	7/2[c]
trans-**6**	Ph_3SnH	benzene	Et_3B	25	1	95	5/3
cis-**6**	$n\text{-}Bu_3SnH$	benzene	Et_3B	25	1	86	10/3
trans-**6**	$n\text{-}Bu_3SnH$	benzene	Et_3B	25	1	92	4/3
cis-**6**	$n\text{-}C_6F_{13}I$	hexane	Et_3B	25	3	91	50/1
trans-**6**	$n\text{-}C_6F_{13}I$	hexane	Et_3B	25	3	93	8/1

(Columns Solvent, Initiator, Temp(°C), Time(h) under "Reaction Conditions[a]".)

a) Silylcyclopropane (**6**, 1.0 mmol) and X-H (1.1 mmol) were employed in the absence or in the presence of Et_3B (0.2 mmol). b) See Ref. 6. c) See Ref. 7.

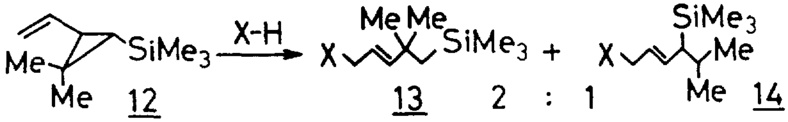
Methyl-substituted cyclopropane **8** or **10** gave homoallylic silane **9** or **11** exclusively upon treatment with PhSH or Ph_3SnH. Again, one (bond a) of two carbon-carbon bonds was broken selectively independent of the stereochemistry of the substrate. Thus, both cis isomer (cis-**10**) and trans isomer (trans-**10**) afforded the same homoallylic silane **11**.





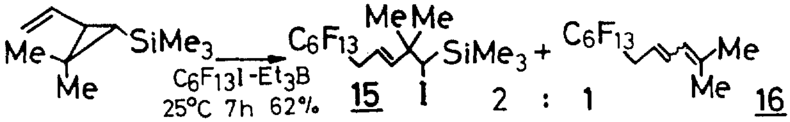
cis-**10**	PhSH	60°C	1 h	90%	E/Z = 18/1 (Ref. 8)
trans-**10**	PhSH	60°C	3 h	90%	E/Z = 8/1
cis-**10**	$Ph_3SnH-Et_3B$	25°C	0.5 h	79%	E/Z = 5/1
trans-**10**	$Ph_3SnH-Et_3B$	25°C	2 h	88%	E/Z = 7/2

Exposure of dimethyl-substituted trimethylsilylcyclopropane **12** to PhSH provided a mixture of homoallylic silane **13** and allylic silane **14** (**13**/**14** = 2/1) in 94% combined yield. In the case of $C_6F_{13}I$ as a reagent, 5-methyl-1-tridecafluorohexyl-2,4-hexadiene (**16**) was obtained instead of 5-iodo-5-methyl-1-tridecafluorohexyl-4-trimethylsilyl-2-hexene because (β-iodoalkyl)-trimethylsilane was extremely unstable with respect to β-elimination.

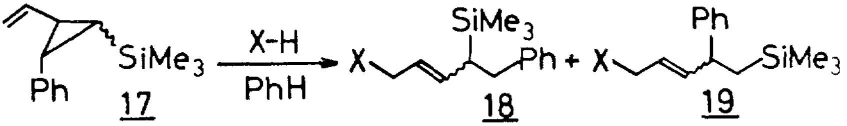


PhSH, 60°C 8 h 94%

$Ph_3SnH-Et_3B$ 25°C 2 h 93%

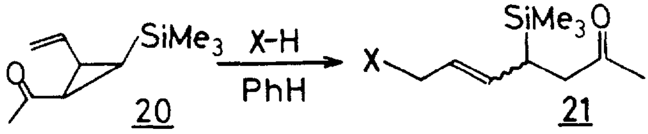


Two other vinylcyclopropanes (**17** and **20**) were prepared and treated with PhSH or $Ph_3SnH-Et_3B$. The results showed that the phenyl group or the acetyl group stabilized the radical on adjacent carbon more strongly than the trimethylsilyl group.[9]



PhSH 60°C 1.5 h, 88% **18**(E/Z):**19**(E/Z) = 20(15/1):1(5/2)

$Ph_3SnH-Et_3B$ 25°C 0.5 h, 74% **18**(E/Z):**19**(E/Z) = 16(15/1):1(2/1)



PhSH 60°C 3 h, 45% **21** (E only)

$Ph_3SnH-Et_3B$ 25°C 0.5 h, 65% **21** (E/Z = 12/1)

References and Notes

1. E. W. Colvin, "Silicon in Organic Synthesis," Butterworths and Co., London (1981); W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin (1983); E. W. Colvin, "Silicon Reagents in Organic Synthesis," Academic Press, London (1988).
2. Addition of trichloromethyl radical to alkenylsilanes has been reported. H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, **34**, 1764 (1969).
3. Recently we reported the synthesis of vinylcyclopentanes from vinylcyclopropanes and alkenes promoted by benzenethiyl radical. K. Miura, K. Fugami, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **29**, 5135 (1988).
4. K. Miura, Y. Ichinose, K. Nozaki, K. Fugami, K. Oshima, and K. Utimoto, *Bull. Chem. Soc. Jpn.*, **62**, 143 (1989) and references cited therein.
5. Recent reviews for radical reactions: B. Giese,"Radicals in Organic Synthesis," ed by J. E. Baldwin, Pergamon Press Oxford (1986); D. P. Curran, *Synthesis*, **1988**, 417, 489.
6. Cis-**6** was prepared as follows. Simmons-Smith reaction (CH_2I_2, Et_2Zn) of (Z)-$PhMe_2SiCH=CHCH_2OH$ provided cyclopropane which was oxidized into 1-dimethylphenylsilyl-2-formylcyclopropane with DMSO-$(COCl)_2$ (Swern oxidation). Treatment of the aldehyde with $Ph_3P=CH_2$ gave cis-**6**. Trans-**6**, cis-**10**, and trans-**10** were prepared in similar fashion.
7. (E)-5-Dimethylphenylsilyl-1-triphenylstannyl-2-pentene: Bp 210°C (0.13 Torr, bath temp); IR (neat) 3060, 3044, 3010, 2950, 2902, 1654, 1480, 1428, 1248, 1113, 1074, 1022, 997, 959, 835, 772, 726, 697, 669 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.21 (s, 6H), 0.65-0.73 (m, 2H), 1.89-2.00 (m, 2H), 2.36 (d, *J* = 7.8 Hz, 2H), 5.42 (dt, *J* = 15.0, 6.3 Hz, 1H), 5.63 (dt, *J* = 15.0, 7.8 Hz, 1H), 7.33-7.73 (m, 20H); ^{13}C-NMR ($CDCl_3$) δ -3.04, 15.78, 15.87, 26.71, 125.3, 127.7, 128.4, 128.8, 128.9, 131.4, 133.5, 137.1, 138.7, 139.4. Found: C, 67.00; H, 6.18%. Calcd for $C_{31}H_{34}SiSn$: C, 67.28; H, 6.19%. (Z)-Isomer: Bp 205°C (0.13 Torr, bath temp); IR (neat) 3060, 3044, 3006, 2950, 2918, 1655, 1637, 1480, 1428, 1248, 1113, 1074, 1022, 997, 835, 818, 776, 725, 697, 656 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.56-0.65 (m, 2H), 1.83-1.96 (m, 2H), 2.33 (d, *J* = 8.9 Hz, 2H), 5.19 (dt, *J* = 10.5, 6.9 Hz, 1H), 5.62 (dt, *J* = 10.5, 8.9 Hz, 1H), 7.33-7.73 (m, 20H); ^{13}C-NMR ($CDCl_3$) δ-3.12, 12.20, 15.62, 21.25, 124.5, 127.7, 128.4, 128.7, 128.9, 130.1, 133.5, 137.0, 138.6, 139.3. Found: C, 67.34; H, 6.17%. Calcd for $C_{31}H_{34}SiSn$: C, 67.28; H, 6.19%.
8. (E)-4-methyl-1-phenylthio-5-dimethylphenylsilyl-2-pentene: Bp 121°C (1.0 Torr, bath temp); IR (neat) 3064, 3004, 2952, 2918, 2896, 2864, 1584, 1480, 1450, 1438, 1427, 1248, 1219, 1112, 1090, 1025, 967, 832, 792, 735, 698, 689 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.24 (s, 3H), 0.25 (s, 3H), 0.74 (dd, *J* = 14.6, 7.1 Hz, 1H), 0.83 (dd, *J* = 14.6, 7.1 Hz, 1H), 0.90 (d, *J* = 6.7 Hz, 3H), 2.15-2.36 (m, 1H), 3.43 (d, *J* = 5.6 Hz, 2H), 5.33 (dt, *J* = 15.0, 5.6 Hz, 1H), 5.42 (dd, *J* = 15.0, 6.0 Hz, 1H), 7.12-7.37 (m, 8H), 7.45-7.52 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ -2.13, -2.01, 24.12, 32.98, 36.42, 121.7, 126.0, 127.6, 128.6, 128.7, 129.9, 133.5, 136.2, 139.7, 142.3. Found: C, 73.44; H, 8.10%. Calcd for $C_{20}H_{26}SSi$: C, 73.56; H, 8.02%.
9. Financial support by the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Scientific Research #63470074) is acknowledged.

(Received in Japan 18 May 1989)