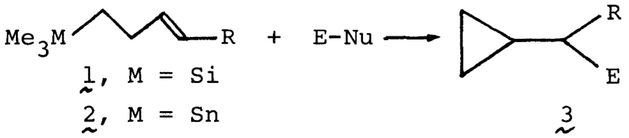
CHEMISTRY LETTERS, pp. 1763-1766, 1983.

REGIOSELECTIVE SYNTHESIS OF 3-ALKENYLSILANES AND 3-ALKENYLSTANNANES BY SILICON- AND TIN-DIRECTED ELIMINATION FROM γ-SILYL AND γ-STANNYL SUBSTITUTED SULFOXIDES AND SULFILIMINES(1)

Akira HOSOMI,* Masahiro INABA, and Hideki SAKURAI*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

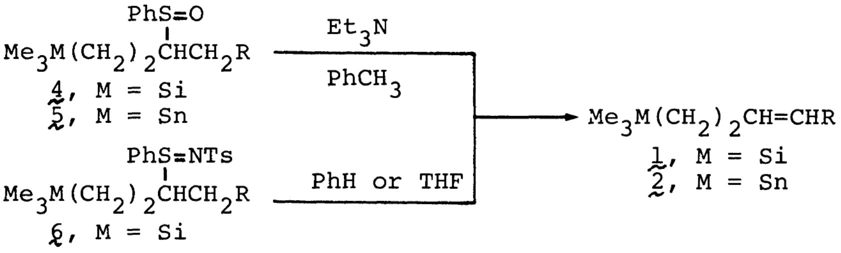
3-Alkenylsilanes and 3-alkenylstannanes are conveniently prepared by the silicon- and tin-directed regioselective elimination of sulfenic acid and sulfenamide from γ-silyl and γ-stannyl substituted sulfoxides and sulfilimines.

It has been known that 3-alkenylsilanes (**1**) and 3-alkenylstannanes (**2**) are interesting and important class of synthetic reagents for preparing cyclopropane derivatives[2] and we also have found recently that cyclopropanation accompanied by carbon-carbon bond formation occurred in the reaction of **1** with some carbon electrophiles (Eq. 1).[3] In this report we describe a novel and convenient synthesis of **1** and **2**, requisite precursors of the reaction, by the regioselective elimination reaction of γ-silyl and γ-stannyl substituted sulfoxides (**4** and **5**, respectively) and sulfilimines (**6**), which can be prepared from (3-trimethylsilylpropyl)phenylsulfide (**8a**) and (3-trimethylstannylpropyl)phenylsulfide (**9a**), respectively (Eq. 2).



1, M = Si
2, M = Sn
3

(1)



$Me_3M(CH_2)_2CH(S(=O)Ph)CH_2R$ **4**, M = Si; **5**, M = Sn

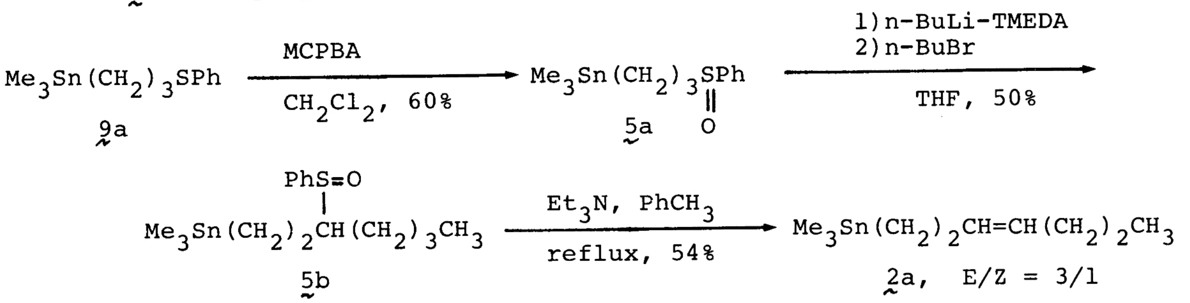
$Me_3M(CH_2)_2CH(S(=NTs)Ph)CH_2R$ **6**, M = Si

$\longrightarrow Me_3M(CH_2)_2CH{=}CHR$ **1**, M = Si; **2**, M = Sn

(2)

The starting sulfoxides **4** were prepared by alkylation[4] of **8a**,[5] followed by oxidation with m-chloroperbenzoic acid (MCPBA) or by direct alkylation of (3-trimethylsilylpropyl)phenylsulfoxide (**4a**).[7] Pyrolysis of **4** proceeds very smoothly in the presence of triethylamine in toluene at reflux to give (3-alkenyl)trimethylsilane (**1**) regioselectively[8,9] in considerably good yield. The results are summarized in Table 1.[10]

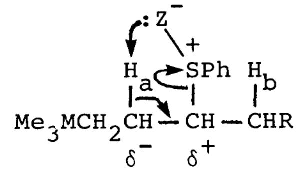
Various 3-alkenylsilanes (1) can be obtained in high yield. The pyrolysis of 4 at the temperature of refluxing toluene may be too vigorous as a condition in some cases. However this drawback can be overcome by using sulfilimines (6),[11a,b] instead of 4, which undergo syn elimination more mildly.[11c,d] The desired 6 was obtained by alkylation of α-lithiated 8a with alkyl bromides followed by the reaction with chloramine-T in acetic acid-methanol. The results are listed in Table 2. Yields of 1 from 6 were better than those from 4. Similarly, 3-alkenylstannane (2a) was prepared in the following sequences. (Eq. 3)



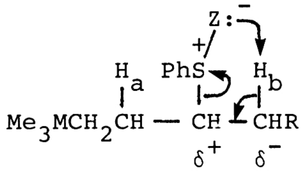
$$\underset{\mathbf{9a}}{\mathrm{Me_3Sn(CH_2)_3SPh}} \xrightarrow[\mathrm{CH_2Cl_2},\ 60\%]{\mathrm{MCPBA}} \underset{\mathbf{5a}}{\mathrm{Me_3Sn(CH_2)_3\underset{\overset{\|}{O}}{S}Ph}} \xrightarrow[\mathrm{THF},\ 50\%]{\text{1) n-BuLi-TMEDA} \atop \text{2) n-BuBr}}$$

$$\underset{\mathbf{5b}}{\mathrm{Me_3Sn(CH_2)_2\overset{\overset{PhS=O}{|}}{C}H(CH_2)_3CH_3}} \xrightarrow[\text{reflux, }54\%]{\mathrm{Et_3N,\ PhCH_3}} \underset{\mathbf{2a},\ E/Z\ =\ 3/1}{\mathrm{Me_3Sn(CH_2)_2CH=CH(CH_2)_2CH_3}} \quad (3)$$

It is known that sulfoxides and N-(p-tosyl)sulfilimines bearing a β-proton undergo facile thermal decomposition, affording sulfenic acid and sulfenamide in addition to the corresponding olefins, via a five-membered transition state of Ei elimination.[11c,d] The regioselectivity in the present elimination of 4 and 5, and 6 to 3-alkenylsilanes (1) and 3-alkenylstannanes (2), respectively, can be explained reasonably by the consideration of the charge separation, partially generated on carbon atoms in the transition state (A or B). Thus, the transition state A, in which a carbanion develops in some extent at the β-position of the metal (M), is less favorable than B due to σ-π conjugation.[12]



(A)



(B)

Z = O or NTs

Typical procedure is as follows. According to a similar procedure employed in the literature, the sulfide 8a (1 mmol) was metalated with t-butyllithium in pentane (1.0 mmol) in the presence of HMPA (1.7 ml) in THF (5 ml) at -78→-20 °C for 4-5 h. After work-up as usual, the alkylated sulfide 8 was purified by TLC. 8 (1.0 mmol) in ethanol (1.5 ml) was added to a solution of chloramine-T (1.1 mmol) in methanol-acetic acid (18:1, 4.8 ml) and the resulting mixture was stirred at 50 °C for 3-5 h,[10,11] and then aq 1 M NaOH (20 ml) was added to the mixture. The organic layer was extracted with chloroform and the combined extracts were dried and concentrated. The residue was purified by TLC to give the corresponding sulfilimine 6 . 6 was dissolved in benzene and the mixture was stirred at reflux for 3-5 h. After passing through a short column (silica gel, hexane), the solvent was evaporated and the residue was stirred in methanol (3 ml) in the presence of trifluoromethanesulfonic acid at 70 °C for 2 h. The reaction mixture was neutralized with pyridine and conducted to TLC purification to give 1.

Table 1. Synthesis of 3-alkenylsilanes (1) via alkylated sulfoxides (4)

Entry	RX	Reaction time/h[a]	Sulfoxide (4) (% yield)[b]		3-Alkenylsilane (1)[c] (% yield,[b] E/Z[d])
1	n-$C_8H_{17}Br$	7	$Me_3Si(CH_2)_2CH$-n-C_8H_{17} (4b) PhS=O	(55)	$Me_3Si(CH_2)_2CH=CH$-n-C_7H_{15} (74, 1.3/1)
2	n-$C_8H_{17}Br$	5	4b	(60)[e]	
3	n-$C_8H_{17}I$	23	4b	(61)	
4	n-C_4H_9Br	7	$Me_3Si(CH_2)_2CH$-n-C_4H_9 (4c) PhS=O	(84)	$Me_3Si(CH_2)_2CH=CH$-n-C_3H_7 (50, 1/1)
5	n-C_4H_9Br	5	4c	(51)[e]	
5	Me_2CHCH_2Br	12[f]	$Me_3Si(CH_2)_2CHCH_2CHMe_2$ PhS=O	(50)	$Me_3Si(CH_2)_2CH=CHCHMe_2$ (22, 2/1)
6	$CH_2=CMeCH_2Cl$	9	$Me_3Si(CH_2)_2CHCH_2CMe=CH_2$ PhS=O	(44)	$Me_3Si(CH_2)_2CH=CHCMe=CH_2$ (34, 5/1)
7	$PhCH_2Cl$	8	$Me_3Si(CH_2)_2CHCH_2Ph$ PhS=O	(57)	$Me_3Si(CH_2)_2CH=CHPh$ (78, 1/0)
8	p-$CH_3\phi CH_2Cl$	14	$Me_3Si(CH_2)_2CHCH_2\phi CH_3$-p PhS=O	(64)	$Me_3Si(CH_2)_2CH=CH\phi CH_3$-p (62, 1/0)

a) Metalation of the sulfoxide 4a was conducted with n-BuLi-TMEDA in THF[7] at -70-0 °C for 1 h. Then alkyl halide was added at -78 °C and the reaction mixture was stirred for a given time at 0 °C. b) Yield after isolation by TLC. c) Pyrolysis was conducted in toluene in the presence of Et_3N at reflux for 4-6 h. After that, the mixture was stirred in MeOH including CF_3SO_3H as a catalyst at 70 °C for 2 h. d) Determined by NMR. e) Metalation[4] of the sulfide 8a with t-BuLi-HMPA was conducted in THF at -78 °C for 2 h. After alkyl halide was added, the mixture was stirred at -20 °C and worked up as usual. The alkylated sulfide 8 was isolated by TLC and oxidized with MCPBA in CH_2Cl_2. Overall yield is shown. f) s-BuLi-TMEDA was used as a metalating reagent.

Table 2. Synthesis of 3-alkenylsilanes (1)
via N-(p-toluenesulfonyl)sulfilimines (6)

Entry	Sulfide (8)[a] (% yield)[d]	Sulfilimine (6)[b] (% yield)[d]	3-Alkenylsilane (1)[c] (% yield,[d] E/Z[e])
1	$Me_3Si(CH_2)_2CH$-n-C_8H_{17} (8b) PhS (78)	$Me_3Si(CH_2)_2CH$-n-C_8H_{17} (6a) PhS=NTs (67)	$Me_3Si(CH_2)_2CH=CH$-n-C_7H_{15} (1a) (87, 1.5/1)
2	8b	6a	1a (78)[f]
3	8b	6a	1a (59)[g]
4	$Me_3Si(CH_2)_2CH$-n-C_4H_9 PhS (78)	$Me_3Si(CH_2)_2CH$-n-C_4H_9 PhS=NTs (81)	$Me_3Si(CH_2)_2CH=CH$-n-C_3H_7 (82, 1.5/1)
5	$Me_3Si(CH_2)_2CHCH_2CHMe_2$ PhS (85)	$Me_3Si(CH_2)_2CHCH_2CHCMe_2$ PhS=NTs (78)	$Me_3Si(CH_2)_2CH=CHCMe_2$ (62, 2.2/1)

a) Metalated with t-BuLi-HMPA at -78 °C and alkylated at -20 °C. b) See Ref. 11. c) Pyrolyzed in PhH at reflux for 3-5 h. d) Yield after isolation by TLC. e) Determined by NMR. f) Pyrolyzed in DMSO at 120 °C for 3 h. g) Pyrolyzed in THF at reflux for 14 h. 6 (25%) was recovered.

The work was supported by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research, No. 57118002). We also thank Toshiba Silicone Co., Ltd., for chlorosilanes.

References

1) Chemistry of Organosilicon Compounds. 184.

2) Sn: D. J. Peterson, M. D. Robbins, and J. R. Hansen, J. Organomet. Chem., 73, 237 (1974); D. J. Peterson and M. D. Robbins, Tetrahedron Lett., 1972, 2135; Y. Ueno, M. Ohta, and M. Okawara, ibid., 23, 2577 (1982); D. D. Davis, R. L. Chambers, and H. T. Johnson, J. Organomet. Chem., 25 , C13 (1970); H. G. Kuivila and N. M. Scarpa, J. Am. Chem. Soc., 92, 6990 (1970). Si: L. H. Sommer, R. E. Van Strien, and F. C. Whitmore, ibid., 71, 3056 (1949); V. A. Ponomarenko, B. A. Sokolov, Kh. M. Minachev, and A. D. Petrov, Dokl. Akad. Nauk SSSR, 106, 76 (1956); V. M. Vdovin., N. S. Nametkin, V. I. Zav'yalov, and K. S. Pushchevaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1965, 1453.

3) H. Sakurai, T. Imai, and A. Hosomi, Tetrahedron Lett., 1977, 4045; T. Imai, Doctoral Theses, Tohoku University, 1977.

4) T. M. Dolak and T. A. Bryson, Tetrahedron Lett., 1977, 1961.

5) The compound 8a was readily prepared by the anti-Markovnikov addition of thiophenol to allyltrimethylsilane6) (76% yield) or by the condensation of (3-bromopropyl)trimethylsilane with potassium thiophenoxide (73% yield). 8a was converted quantitatively to the sulfoxide 4a by the oxidation with MCPBA.

6) H. Sakurai, A. Hosomi, and M. Kumada, J. Org. Chem., 34, 1764 (1969).

7) B. M. Trost and A. J. Bridges, J. Org. Chem., 40, 2014 (1975); B. M. Trost, Chem. Rev., 78, 363 (1978) and references cited therein.

8) A small amount of allylic silanes (less than a few per cent) that contaminates in the pyrolysate can be readily removed by the treatment with a catalytic amount of trifluoromethanesulfonic acid or iodine in methanol at 70 °C for 2 h. See G. A. Olah, A. Husain, B. G. B. Gupta, G. F. Salem, and S. C. Narang, J. Org. Chem., 46, 5212, (1981); T. Morita, Y. Okamoto, and H. Sakurai, Synthesis, 1981, 745; A. Hosomi and H. Sakurai, Chem. Lett., 1981, 85.

9) It has been recently reported that β-silyl substituted sulfoxides undergo the fast syn elimination to give regioselectively vinylsilanes. See I. Fleming and D. A. Perry, Tetrahedron Lett., 22, 5095 (1981); M. Ochiai, S. Tada, K. Sumi, and E. Fujita, J. Chem. Soc., Chem. Commun., 1981, 281.

10) All compounds obtained in this work gave satisfactory spectral data and correct elemental analysis.

11) a) B. H. Nicholet and I. D. Willard, Science, 53, 217 (1921); b) K. Tsujihara, N. Furukawa, and S. Oae, Tetrahedron, 27, 4921 (1971); c) S. Oae and N. Furukawa, ibid., 33, 2359 (1977); d) N. Furukawa and S. Oae, Ind. Eng. Chem., Prod. Res. Dev., 20, 260 (1981).

12) The β-carbocation of the metal atom is stabilized considerably by the interaction between a metal-carbon σ bond and adjacent vacant p-orbital, but the carbanion, to the contrary, is destabilized. See J. M. Jerkunica and T. G. Traylor, J. Am. Chem. Soc., 93, 6278 (1971); T. G. Traylor, H. J. Berwin, J. M. Jerkunica, and M. L. Hall, Pure Appl. Chem., 30, 599 (1972).

(Received September 10, 1983)