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Convenient Synthesis of β-Silyl Ketones from β-Stannyl Enol Silyl Ethers via a [1,4] Anionic Rearrangement of Silicon

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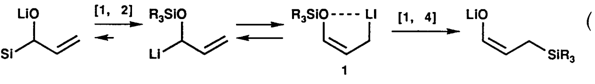
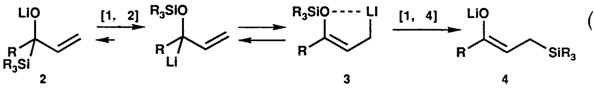
Synopsis. The transmetalation (Sn to Li) and [1,4] anionic rearrangement of β-stannyl enol silyl ethers have been achieved, providing a convenient method for synthesis of β-silyl ketones.

The [1,4] anionic rearrangement of silicon from oxygen to carbon, which corresponds to the vinylogous reverse Brook rearrangement,1) has been first observed by Still in the system of 1-siloxyallyl anions **1** (Eq. 1).2) Shortly after, Kuwajima and Reich have observed independently3) an analogous [1,4] rearrangement of silicon from 1-alkyl-1-siloxyallyl anions **3** as a side reaction in their work on the generation and the use of **3** as a β-acylcarbanion equivalent (Eq. 2).4) The method for **3** shown in Eq 2 involves the 1,2-addition of alkyllithiums to acylsilanes or the treatment of 1-(trimethylsilyl)allylic alcohols with *n*-BuLi to give **2** and the subsequent Brook rearrangement. We envisioned that one could obtain **3** directly by carrying out Li–Sn exchange reaction between β-stannyl enol silyl ethers **5**5) and *n*-BuLi. In this paper we report a convenient method for β-silyl ketones6) from **5** via a [1,4] anionic rearrangement of silicon.

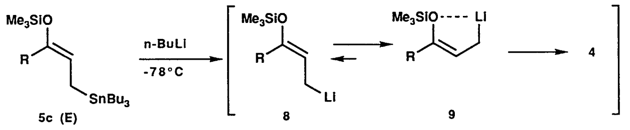


(1)



(2)

We have found that enol silyl ethers **5** undergo rapid Li–Sn exchange at −78 °C to afford **3**. In accorod with previous observation,3a) by warming up to 0 °C, a [1,4] anionic rearrangement of silicon took place to give quantitatively β-silyl ketone enolates **4**. Since rearrangements have been stereochemically ambiguous as to the possibility of rearrangement from *E*-form species,7) we attempted the reaction starting with an *E*/*Z* mixture of enol silyl ether **5c** (*E*/*Z*=47/53). Thus, treatment of **5c** with *n*-BuLi (1 equiv) at −78 °C for 30 min gave a mixture of **6** and **7** ("rearrangement") in 97% total yield (**6**/**7**=86/14) after quenching with Et_3SiCl (Scheme 1). Interestingly, both **6** and **7** are in stereochemically pure *Z*-form. After warming up to 0 °C, **7** was only obtained in 96% yield. This means that: (a) transmetalation (Sn to Li) readily occurs at −78 °C, irrespective of the stereochemistry of **5c**, (b) *E*-form of β-lithio species **8** readily isomerizes to *Z*-form **9** after transmetalation at −78 °C (Eq. 3), (c) a [1,4] rearrangement of silicon from O to C proceeds via *Z*-form **9** stereospecifically.



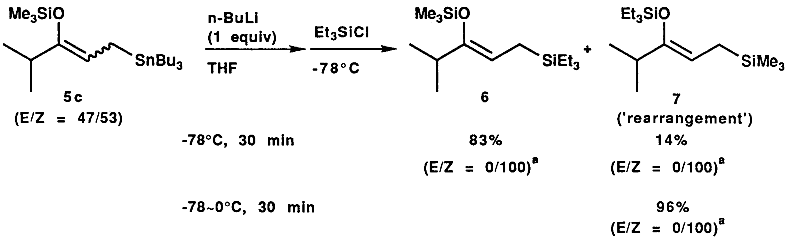
(3)

The enolates thus obtained from the rearrangements can be trapped by electrophiles to give a variety of α-substituted β-silyl ketones. As shown in Table 1, in general the reaction is clean, affording high yields of β-silyl ketones.

In summary, this paper reports transmetalation/rearrangement of β-stannyl enol silyl ethers, which offer a convenient way for the synthesis of β-silyl ketones.

Experimental

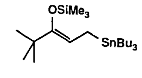
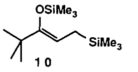
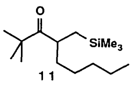
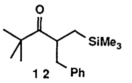
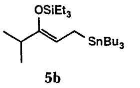
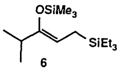
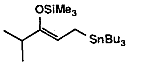
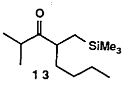
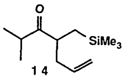
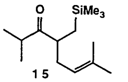
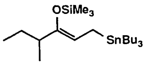
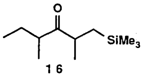
Instruments. For column chromatography, silica gel 60 (230—400 mesh ASTM, E. Merck) was used. GLC analysis was carried out with a Shimadzu GC-12A apparatus using Hicap-CBP10-M25-025 (OV-1 type) column. ^{1}H NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) or a JEOL JNM-GSX-400 (400 MHz) spectrometer in $CDCl_3$. ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-270 (68 MHz) spectrometer in $CDCl_3$. IR spectra were obtained from a Perkin–Elmer 1610 FTIR spectrometer. Mass spectra and high-resolution mass spectra were recorded on a JEOL JMS-DX303 HF spectrometer using electronical ionization



a) Determined by GC analysis of the crude mixture.

Scheme 1.

Table 1. Synthesis of β-Silyl Ketones by a 1,4-Anionic Rearrangement of Silicon[a)]

Entry	β-Stannyl enol silyl ether	Electrophile (equiv) temp, time	Product	Yield/%[b)]
1	 5a	Me_3SiCl (1.2 equiv) −78 °C, 15 min	 10	92[c)]
2	5a	n-$C_5H_{11}I$ (2 equiv) −78—20 °C, 1 h	 11	96
3	5a	$PhCH_2Br$ (2 equiv) −78—20 °C, 30 min	 12	91
4	 5b	Me_3SiCl (1.2 equiv) −78 °C, 15 min	 6	93
5	 5c	n-C_4H_9I (2 equiv) −78—20 °C, 1 h	 13	81
6	5c	$CH_2{=}CHCH_2Br$ (2 equiv) −78—20 °C, 1 h	 14	88
7	5c	$(CH_3)_2C{=}CHCH_2Br$ (2 equiv) −78—20 °C, 1 h	 15	90[d)]
8	 5d	MeI (2 equiv) −78—20 °C, 3 min	 16	99 (67/33)[e)]

a) The procedure was described in the experimental section. b) Isolated yield. c) Li/Sn exchange of **5a** proceeded to completion at −78 °C in 30 min. d) S_N2 adduct was only obtained. e) Ratio of diastereoisomers were determined by ^1H NMR spectrum at 400 MHz. The relative configuration of the diastereomers has not yet been assigned.

(EI) mass spectrometry. Elemental analyses were performed by the Analytical Center, Faculty of Engineering, Osaka University.

Preparation of β-Stannyl Enol Silyl Ethers 5. To a solution of lithium diisopropylamide (6 mmol) (for **5a**) or lithium hexamethyldisilylazine (6 mmol) (for **5b—d**) in THF (10 mL) at −78 °C was added β-trialkylstannyl ketone (5 mmol).[5b)] The reaction mixture was stirred at −78 °C for 2 h and quenched by addition of Me_3SiCl (6 mmol) (for **5a, c, d**) or Et_3SiCl (6 mmol) (for **5b**). Cold water and Et_2O were added and the aqueous layer was extracted with Et_2O. The combined organic extracts were washed (water), dried ($MgSO_4$), and concentrated. Flash chromatography (SiO_2, pentane eluent) of the residual oil gave β-stannyl enol silyl ether **5** (>90% yield). The preparation of the *E/Z* mixture of **5c** attained by the reaction of β-trialkylstannyl ketone with LDA (15 min)/Me_3SiCl in THF at −78 °C to give the three regio- and stereoisomers. These isomers were separated by flash column chromatography (SiO_2, pentane eluent). Under these conditions the *E/Z* mixture of **5c** eluted first from the column.

Reaction of β-Stannyl Enol Silyl Ether 5c with *n*-BuLi. *n*-BuLi (1.55 M in hexane, 0.286 mL, 0.444 mmol) was added to a solution of β-stannyl enol silyl ether **5c** (*E/Z*=47/53, 205 mg, 0.444 mmol) in THF (2 mL) at −78 °C. After 30 min, Et_3SiCl (80 mg, 0.532 mmol) was added to the solution at −78 °C. Cold water and Et_2O were added and the aqueous layer was extracted with Et_2O. The combined organic extracts were washed (water), dried ($MgSO_4$), and concentrated. Flash chromatography (SiO_2, pentane eluent) of the residual oil gave a mixture (123 mg, 97%) of **6** and **7** (**6**/**7**=86/14). The spectral data of β-silyl enol silyl ether **6** and **7** are as follows.

(*Z*)-3-(Trimethylsiloxy)-1-(triethylsilyl)-4-methyl-2-pentene (6). IR (NaCl) 1664 cm^{-1} (νC=C); ^1H NMR (270 MHz, $CDCl_3$) δ=0.19 (s, 9H, $SiMe_3$), 0.51 (q, J=7.8 Hz, 6H, $Si(C\underline{H}_2CH_3)_3$), 0.93 (t, J=7.8 Hz, 9H, $Si(CH_2C\underline{H}_3)_3$), 1.01 (d, J=6.8 Hz, 6H, $(C\underline{H}_3)_2CH$), 1.35 (d, J=7.8 Hz, 2 H, $C\underline{H}_2SiEt_3$), 2.08—2.20 (m, 1H, $(CH_3)_2C\underline{H}$), 4.43 (t, J=7.8 Hz, 1H, vinyl); ^{13}C NMR ($CDCl_3$) δ=0.84, 3.39, 7.43, 9.96, 20.93, 34.47, 100.31, 154.42; Found: C, 62.55; H, 12.03%. Calcd for $C_{15}H_{34}OSi_2$: C, 62.84; H, 11.97%.

(*Z*)-3-(Triethylsiloxy)-1-(trimethylsilyl)-4-methyl-2-pentene (7). IR (NaCl) 1664 cm^{-1} (νC=C; ^1H NMR (270 MHz, $CDCl_3$) δ=−0.02 (s, 9H, $SiMe_3$), 0.67 (q, J=7.8 Hz, 6H, $Si(C\underline{H}_2CH_3)_3$), 0.99 (t, J=7.8 Hz, 9H, $Si(CH_2C\underline{H}_3)_3$), 1.02 (d, J=6.8 Hz, 6H, $(C\underline{H}_3)_2CH$), 1.34 (d, J=8.3 Hz, 2H, $C\underline{H}_2SiMe_3$), 2.07—2.17 (m, 1H, $(CH_3)_2C\underline{H}$), 4.83 (t, J=8.3 Hz, 1H, vinyl); ^{13}C NMR ($CDCl_3$) δ=−1.75, 5.76, 6.89, 14.82, 21.27, 34.56, 99.53, 154.95; MS m/z (%) 286 (M^+, 31), 213 (100), 115 (96), 73 (58). Found: m/z 286.2151. Calcd for $C_{15}H_{34}OSi_2$ 286.2148.

General Procedures for the Synthesis of β-Silyl Ketones (10—16). The preparation of β-silyl ketone **13** is described as a typical example. *n*-BuLi (1.55 M in hexane, 0.654 mL, 1.0 mmol) was added to a solution of β-stannyl enol silyl ether **5c** (461 mg, 1.0 mmol) in THF (3 mL) at −78 °C. The reaction mixture was allowed to warm to 0 °C and stirred for 30 min. After having been cooled to −78 C, *n*-butyl iodide

(368 mg, 2.0 mmol) and HMPA (0.5 mL) was added. The mixture was allowed to warm to 20 °C and stirred for 1 h. Water and $\mathrm{Et_2O}$ were added and the aqueous layer was extracted with $\mathrm{Et_2O}$. The combined organic extracts were washed (water), dried ($\mathrm{MgSO_4}$), and concentrated. Flash chromatography ($\mathrm{SiO_2}$, pentane eluent) of the residual oil gave β-silyl ketone **13** (185 mg, 81%). The spectral data of β-silyl ketones **10—16** are as follows.

(*Z*)-3-(Trimethylsiloxy)-1-(trimethylsilyl)-4,4-dimethyl-2-pentene (10). IR (NaCl) 1656 $\mathrm{cm^{-1}}$ (νC=C); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta=-0.02$ (s, 9H, $\mathrm{CH_2Si(C\underline{H}_3)_3}$), 0.22 (s, 9H, $\mathrm{OSiMe_3}$), 1.03 (s, 9H, $\mathrm{(CH_3)_3C}$), 1.29 (d, J=8.2 Hz, 2H, $\mathrm{C\underline{H}_2SiMe_3}$), 4.51 (t, J=8.2 Hz, 1H, vinyl); ^{13}C NMR $\mathrm{CDCl_3}$) $\delta=-1.79$, 1.19, 15.68, 28.73, 36.31, 98.81, 157.02; MS m/z (%) 258 ($\mathrm{M^+}$, 38), 185 (100), 169 (10), 73 (88). Found: C, 60.36; H, 11.71%. Calcd for $\mathrm{C_{13}H_{30}OSi_2}$: C, 60.37; H, 11.71%.

2,2-Dimethyl-4-(trimethylsilylmethyl)-3-nonanone (11). IR (NaCl) 1703 $\mathrm{cm^{-1}}$ (νC=O); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta=0.00$ (s, 9H, $\mathrm{SiMe_3}$), 0.58 (dd, J_vic=9.4 Hz, J_gem=14.9 Hz, 1H, $\mathrm{C\underline{H}_2\ SiMe_3}$), 0.69 (dd, J_vic=3.9 Hz, J_gem=14.9 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$), 1.10 (s, 9H, $\mathrm{(CH_3)_3C}$), 1.19—1.34 (m, 7H), 1.57—1.71 (m, 1H), 2.87—2.97 (m, 1H, CH); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=-0.63$, 13.96, 21.11, 22.46, 26.76, 27.79, 32.04, 34.04, 41.09, 44.21, 219.18; MS m/z (%) 256 ($\mathrm{M^+}$, 1), 241 (3), 199 (2), 171 (18), 73 (100), 57 (4). Found: C, 70.40; H, 12.79%. Calcd for $\mathrm{C_{15}H_{32}OSi}$: C, 70.22; H, 12.60%.

2-Benzyl-4,4-dimethyl-1-(trimethylsilyl)-3-pentanone (12). IR (NaCl) 1702 $\mathrm{cm^{-1}}$ (νC=O); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta=0.00$ (s, 9H, $\mathrm{SiMe_3}$), 0.59—0.81 (m, 2H, $\mathrm{C\underline{H}_2SiMe_3}$), 0.69 (s, 9H, $\mathrm{(CH_3)_3C}$), 2.53 (dd, J_vic=3.9 Hz, J_gem=12.9 Hz, 1H, $\mathrm{C\underline{H}_2Ph}$), 2.83 (dd, J_vic=10.7 Hz, J_gem=12.9 Hz, 1H, $\mathrm{C\underline{H}_2Ph}$), 3.07—3.17 (m, 1H, $\mathrm{C\underline{H}CH_2SiMe_3}$), 6.95—7.13 (m, 5H, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=-0.54$, 21.47, 25.93, 33.94, 44.05; 44.10, 126.04, 128.12, 129.16, 140.48, 218.04; MS m/z (%) 276 ($\mathrm{M^+}$, 1), 261 (4), 185 (5), 91 (7), 73 (100), 57 (6). Found: C, 73.55; H, 10.40%. Calcd for $\mathrm{C_{17}H_{28}OSi}$: C. 73.83; H. 10.22%.

2-Methyl-4-(trimethylsilylmethyl)-3-octanone (13). IR (NaCl) 1711 $\mathrm{cm^{-1}}$ (νC=O); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta=0.00$ (s, 9H, $\mathrm{SiMe_3}$), 0.56 (dd, J_vic=7.9 Hz, J_gem=14.6 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$), 0.83 (dd, J_vic=5.8 Hz, J_gem=14.6 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$), 0.87 (t, J=7.0 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.06 (d, J=3.5 Hz, 3H, $\mathrm{(C\underline{H}_3)_2CH}$), 1.08 (d, J=3.5 Hz, 3H, $\mathrm{(C\underline{H}_3)_2CH}$), 1.14—1.40 (m, 7H), 1.59—1.67 (m, 1H), 2.59—2.76 (m, 2H); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=-0.86$, 13.96, 18.55, 18.76, 22.81, 29.79, 33.35, 39.29, 46.09, 217.86; MS m/z (%) 228 ($\mathrm{M^+}$, 1), 213 (8), 185 (3), 171 (6), 157 (14), 73 (100). Found: m/z 228.1897. Calcd for $\mathrm{C_{13}H_{28}OSi}$ 228.1909.

2-Methyl-4-(trimethylsilylmethyl)-6-hepten-3-one (14). IR (NaCl) 1712 $\mathrm{cm^{-1}}$ (νC=O), 1641 $\mathrm{cm^{-1}}$ (νC=C); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta=0.00$ (s, 9H, $\mathrm{SiMe_3}$), 0.58 (dd, J_vic=7.5 Hz, J_gem=14.9 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$), 0.86 (dd, J_vic=6.3 Hz, J_gem=14.9 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$), 1.04 (d, J=7.0 Hz, 3H, $\mathrm{(C\underline{H}_3)_2CH}$), 1.07 (d, J=7.0 Hz, 3H, $\mathrm{(C\underline{H}_3)_2CH}$), 2.04—2.14 (m, 1H, $\mathrm{C\underline{H}_2CH{=}CH_2}$), 2.32—2.42 (m, 1H, $\mathrm{C\underline{H}_2CH{=}CH_2}$), 2.64—2.78 (m, 2H, $\mathrm{C\underline{H}C(O)C\underline{H}}$) 4.95—5.01 (m, 2H, $\mathrm{CH{=}C\underline{H}_2}$), 5.57—5.72 (m, 1H, $\mathrm{C\underline{H}{=}CH_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=-0.91$, 18.27, 18.40, 18.61, 38.14, 39.49, 45.91, 116.65, 135.93, 216.88; MS m/z (%) 212 ($\mathrm{M^+}$, 1), 197 (8), 171 (7), 141 (16), 73 (100). Found: C, 67.64; H, 11.62%. Calcd for $\mathrm{C_{12}H_{24}OSi}$: C, 67.83; H, 11.40%.

2,7-Dimethyl-4-(trimethylsilylmethyl)-6-octen-3-one (15). IR (NaCl) 1712 $\mathrm{cm^{-1}}$ (νC=O); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta=0.00$ (s, 9H, $\mathrm{SiMe_3}$), 0.58 (dd, J_vic=7.8 Hz, J_gem=14.6 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$), 0.83 (dd, J_vic=5.9 Hz, J_gem=14.6 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$), 1.02 (d, J=7.4 Hz, 3H, $\mathrm{(C\underline{H}_3)_2C{=}CH}$), 1.05 (d, J=7.4 Hz, 3H, $\mathrm{(C\underline{H}_3)_2C{=}CH}$), 1.60 (d, J=19.1 Hz, 3H, $\mathrm{(C\underline{H}_3)_2CH}$), 1.99—2.09 (m, 1H, $\mathrm{C\underline{H}_2CH{=}C}$), 2.22—2.33 (m, 1H, $\mathrm{C\underline{H}_2CH{=}C}$), 2.62—2.72 (m, 2H), 4.97 (like-t, J=7.3 Hz, 1H, CH=C); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=-0.88$, 17.77, 18.23, 18.60, 18.70, 25.69, 32.70, 39.71, 46.25, 121.90, 133.13, 217.63; MS m/z (%) 240 ($\mathrm{M^+}$, 0.1), 225 (2), 197 (7), 169 (7), 73 (100), 69 (17). Found: C, 69.81; H, 11.83%. Calcd for $\mathrm{C_{14}H_{28}OSi}$: C, 69.90; H, 11.75%.

2,4-Dimethyl-1-(trimethylsilyl)-3-hexanone (16). Obtained as a 67:33 mixture of diastereomers. IR (NaCl) 1711 $\mathrm{cm^{-1}}$ (νC=O); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) $\delta=0.01$ (s, 9 H, $\mathrm{SiMe_3}$ (minor isomer)), 0.02 (s, 9H, $\mathrm{SiMe_3}$ (major isomer)), 0.52 (dd, J=9.9 and 14.6 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$ (major)), 0.53 (dd, J=9.9 and 14.6 Hz, 1H, $\mathrm{C\underline{H}_2SiMe_3}$ (minor)), 0.83—0.93 (m, 1H, $\mathrm{C\underline{H}_2SiMe_3}$ (major and minor)), 0.85 (t, J=7.3 Hz, 3H, $\mathrm{C\underline{H}_3CH_2}$ (minor)), 0.86 (t, J=7.3 Hz, 3H, $\mathrm{C\underline{H}_3CH_2}$) (major)), 1.04 (d, J=6.9 Hz, 3H, $\mathrm{C\underline{H}_3CH}$ (major and minor)), 1.06 (d, J=6.9 Hz, 3H, $\mathrm{C\underline{H}_3CH}$ (minor)), 1.08 (d, J=6.9 Hz, 3H, $\mathrm{C\underline{H}_3CH}$ (major)), 1.27—1.37 (m, 1H, $\mathrm{CH_3C\underline{H}_2}$ (major and minor)), 1.60—1.71 (m, 1H, $\mathrm{CH_3C\underline{H}_2}$ (major and minor)), 2.54—2.70 (m, 2H, CHCOCH (major and minor)); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=-0.83$ (major and minor), 11.86 (minor), 11.92 (major), 16.59 (major), 16.60 (minor), 18.70 (major and minor), 19.96 (major), 20.23 (minor), 26.10 (major), 26.21 (minor), 41.07 (major), 41.15 (minor), 45.66 (major and minor), 218.17 (major and minor); MS m/z (%) 200 ($\mathrm{M^+}$, 1), 185 (7), 158 (5), 143 (12), 115 (16), 85 (2), 73 (100), 57 (7). Found: C, 66.12; H, 12.31%. Calcd for $\mathrm{C_{11}H_{24}OSi}$: C, 65.90; H, 12.09%.

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