Reaction of Silylketenes with Carbanions: Simple Preparation of α -Silylketones Using Organocerium Reagents

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Preparation of α -silylketones 1 by the reaction of three kinds of silylketenes 3a—c with various organometallic reagents 4 was studied. Although the use of *n*-BuLi, MeMgBr, Me₂CuLi, Et₃Al, and Et₂Zn resulted in complicated reactions, organocerium reagents 4 (M = CeCl₂) added selectively to the carbonyl carbon of 3 to generate enolate anions A, which were treated with aqueous NH₄Cl or alkyl halides 5 to give 1. Seventeen α -silylketones 1a—q were prepared in 31—99% yields from three components, 3, alkyl- or arylcerium reagents 4, and proton or alkyl halides 5. This method was applied to a regiocontrolled preparation of two isomeric α -silylketones 1r, s.

Key words silylketene; α -silylketone; organocerium reagent; silyl enol ether

α -Silylketones 1 rearrange stereoselectively to either (*E*)- or (*Z*)-silyl enol ethers 2 depending on the choice of the reaction conditions.¹⁾ In addition to the wide range of useful reactions of 2,²⁾ compounds 1 react with carbon and heteroatom electrophiles with the assistance of Lewis acid³⁾ or fluoride ion.⁴⁾ Other attractive synthetic utilities of 1 exist in stereospecific alkene formation⁵⁾ and silicon-directed diastereoselective reactions.⁶⁾ Therefore, effective preparation of 1 is of increasing interest. Although a variety of synthetic methods for 1 have been reported, most of them need several steps *via* individual intermediates.^{7–11)}

In the course of our studies to establish a convenient preparation of silylated reactive compounds using silylketenes 3,¹²⁾ we planned a one-pot preparation of the α -silylketones 1 from 3.^{13,14)} Thus, addition of carbanions 4 to the carbonyl carbon of 3 would generate silylated enolate anions A (route a), and then quenching with proton or alkyl halides 5 would afford α -silylketones 1. However, the reaction of 3 with *n*-BuLi had been reported by Rathke *et al.* to cause proton abstraction (route b) exclusively generating the ynolate anion B (Chart 1).¹⁵⁾ Other than this report, no studies on the reaction of 3 with carbanions 4 have ever been presented.^{16,17)} Therefore, we focused on how to achieve the route a reaction. Very recently, we briefly communicated that the use of organocerium reagents 4 (M = CeCl₂) cleanly solved this issue, leading

to a one-pot synthesis of 1.^{12b)} Here we present full details of these studies.

Results and Discussion

As mentioned above, Rathke *et al.* reported that the reaction of (trimethylsilyl)ketene 3a with *n*-BuLi resulted in a complicated reaction without formation of any carbonyl compounds, due to preferential abstraction of the proton by *n*-BuLi. This was deduced because the same reaction run at -100°C followed by quenching with trimethylsilyl chloride gave the bis(trimethylsilyl)ketene 6 (R¹ = Me) in 85% yield.¹⁵⁾ Though the use of bulkier (*tert*-butyldimethylsilyl)ketene 3c instead of 3a was expected to suppress the proton abstraction and to cause addition to the carbonyl group, our examination of the reaction of 3c and *n*-BuLi at -100°C and quenching with trimethylsilyl chloride gave only the bis(silyl)ketene 6 (R₃¹ = *tert*-BuMe₂) in 96% yield.¹⁸⁾ Attempts to use MeMgBr, Me₂CuLi, Et₃Al, or Et₂Zn for the reaction with 3c produced complex mixtures with little or none of the desired α -silylketones 1. On the other hand, the organocerium reagent 4 (M = CeCl₂)¹⁹⁾ selectively added to the carbonyl group of 3c to afford 1 in high yield. For example, a tetrahydrofuran (THF) solution of 3c was slowly added over 10 min to a THF solution of *n*-BuCeCl₂, prepared from anhydrous CeCl₃ and *n*-BuLi by the usual method. The mixture was stirred for 1.5 h at -78°C , then the

Chart 1

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Table 1. Preparation of α -Silylketones **1**

Entry	Silylketene 3	Cerium reagent 4 R ² =	Quenching method ^{a)} (R ³ -X5 for method B)	α -Silylketone 1				
				R ¹ =	R ² =	R ³ =	% Yield	
1	3a	Ph	A	1a	Me ₃	Ph	H	79 ^{b)}
2	3b	Me	A	1b	Et ₃	Me	H	77 ^{c)}
3	3b	<i>n</i> -Bu	A	1c	Et ₃	<i>n</i> -Bu	H	93 ^{c)}
4	3b	Ph	A	1d	Et ₃	Ph	H	99 ^{b)}
5	3c	Me	A	1e	(<i>tert</i> -Bu)Me ₂	Me	H	82 ^{b)}
6	3c	Et	A	1f	(<i>tert</i> -Bu)Me ₂	Et	H	68 ^{d)}
7	3c	<i>n</i> -Pr	A	1g	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Pr	H	72 ^{d)}
8	3c	<i>n</i> -Bu	A	1h	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	H	91 ^{b)}
9	3c	<i>sec</i> -Bu	A	1i	(<i>tert</i> -Bu)Me ₂	<i>sec</i> -Bu	H	40 ^{d)}
10	3c	<i>n</i> -Bu	B (MeI)	1j	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	Me	76 ^{d,e)} (48 ^{d,f)})
11	3c	<i>n</i> -Bu	B (EtI)	1k	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	Et	53 ^{d,e)}
12	3c	<i>n</i> -Bu	B (EtBr)	1k	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	Et	10 ^{d,e)}
13	3c	<i>n</i> -Bu	B (<i>n</i> -PrI)	1l	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	<i>n</i> -Pr	31 ^{d)}
14	3c	<i>n</i> -Bu	B (CH ₂ =CHCH ₂ I)	1m	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	CH ₂ CH=CH ₂	70 ^{d,e)}
15	3c	<i>n</i> -Bu	B (CH ₂ =CHCH ₂ Br)	1m	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	CH ₂ CH=CH ₂	47 ^{d,e)}
16	3c	<i>n</i> -Bu	B (PhCH ₂ Br)	1n	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	PhCH ₂	57 ^{d)}
17	3c	<i>n</i> -Bu	B (EtO ₂ CCH ₂ Br)	1o	(<i>tert</i> -Bu)Me ₂	<i>n</i> -Bu	CH ₂ CO ₂ Et	41 ^{d,e)}
18	3c	Ph	A	1p	(<i>tert</i> -Bu)Me ₂	Ph	H	98 ^{b)}
19	3c	Ph	B (MeI)	1q	(<i>tert</i> -Bu)Me ₂	Ph	Me	48 ^{d,e)}

^{a)} Quenching with saturated aqueous NH₄Cl (method A) or R³-X **5** (method B). ^{b)} Pure **1** ($\geq 95\%$ determined by 250 MHz ¹H-NMR analysis) was obtained without purification. ^{c)} Yields determined by 250 MHz ¹H-NMR analysis of crude **1**. The only contaminant was THF used for the reaction. Isolated yields (by distillation) were as follows: **1b**, 58%; **1c**, 60%. ^{d)} Yields of pure **1** isolated by SiO₂-flash column chromatography. ^{e)} Formation of the corresponding protonated products **1h**, **p**, was observed by ¹H-NMR analyses of the crude products. Their ratios were as follows: **1h**:**1j**=1:15 (entry 10), **1h**:**1k**=1:2 (entry 11), **1h**:**1k**=8:1 (entry 12), **1h**:**1m**=1:8 (entry 14), **1h**:**1m**=1:2.5 (entry 15), **1h**:**1o**=1:1.1 (entry 17), **1p**:**1q**=1:3.2 (entry 19). ^{f)} Result from the reaction without HMPA.

reaction was quenched with saturated aqueous NH₄Cl solution to give **1h** in 91% yield (method A) (entry 8). Similarly, α -trimethylsilyl **1a**, α -triethylsilyl **1b—d**, and α -*tert*-butyldimethylsilylketones **1e—h** and **1p** were easily obtained from the corresponding silylketenes **3a—c** and several *n*-alkyl- and arylcerium reagents **4** in moderate to quantitative yields, as summarized in Table 1 (entries 1—8, and 18). The reaction of *sec*-BuCeCl₂ with **3c** gave the silylketone **1i** in 40% yield (entry 9), while similar reaction of *tert*-BuCeCl₂ resulted in a complex mixture. Use of the cerium reagents generated from organolithium compounds is preferable for the present reactions, because the cerium reagents generated from EtMgBr or PhMgBr gave **1f** and **1p** in low yields (*ca.* 20—30%).

We then tried to treat the enolate intermediates **A**, generated in this reaction, with alkyl halides **5**. When MeI was added to a solution of the cerium enolate **A** (M=CeCl₂) at -78°C and the reaction mixture was gradually warmed to 40°C , the methylated product **1j** was obtained in 48% yield, along with *ca.* 30% yield of the protonated product **1h**. However, addition of hexamethylphosphoramide (HMPA) (one-third volume of THF) before quenching with MeI effectively accelerated the alkylation to give **1j** in 76% yield and the yield of **1h** was reduced to less than 5% (method B) (entry 10). By this method, the second alkylation using other **5** proceeded in moderate to good yields (entries 11—17, and 19); the use of reactive alkyl halides is essential to obtain good yields of the products **1** (entries 11, 12, 14, 15).

The advantage of the present method is as follows. Although silyl enol ethers are usually prepared from the corresponding ketones through base-induced enolization and subsequent *O*-silylation, regioselective enolization of asymmetric ketones having two similar alkyl groups, such as hexan-3-one **7** or its homologous congeners, is difficult. In fact, treatment of **7** by the usual method (lithium diisopropylamide (LDA) in THF at -78°C and then *tert*-butyldimethylsilyl chloride with HMPA at -78°C to room temperature) gave a mixture (64:36) of the two regioisomers **2r** and **2s** (Chart 2). On the other hand, the present method readily achieved a regiocontrolled synthesis of the two isomeric α -silylketones **1r** and **1s**. Thus, the reaction of **3c** with *n*-PrCeCl₂ and subsequent quenching with MeI gave a 67% yield of **1r**, and that with EtCeCl₂ and EtI gave the regioisomer **1s** in 54% yield. Because selective conversion of α -silylketones **1** to (*E*)- and (*Z*)-*O*-silyl enol ethers **2** has been developed,¹⁾ our method would provide an alternative and promising preparation of *O*-silyl enol ethers **2**.

Thus, we have developed a convenient synthetic method for various types of α -silylketones featuring the operational convenience of silylketenes, the use of readily available organocerium reagents and alkyl halides, and a simple procedure.

Experimental

All boiling points are uncorrected. IR absorption spectra were recorded on JASCO HPIR-102 and Shimadzu FTIR-8100 spectrometers. ¹H-

Chart 2

NMR spectra were recorded on JEOL JNM-FX90 and Hitachi R-250HT spectrometers with CHCl_3 as an internal standard. Mass spectra (MS) and high-resolution mass spectra (HR-MS) were recorded at 70 or 20 eV with a direct inlet system on a JEOL JMS-HX100 spectrometer. E. Merck Silica gel 60 (230–400 mesh ASTM) was used for flash column chromatography. Anhydrous THF was obtained by distillation from sodium benzophenone ketyl. Silylketenes **3a**,^{14b} **3b**^{12a} and **3c**^{12a} were prepared according to the reported methods. Anhydrous CeCl_3 was prepared from commercially available $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ by means of the reported procedure.¹⁹

General Procedure for the Preparation of α -Silylketones (1a–i, 1p) (Method A) Under a nitrogen atmosphere, dry THF (6 ml) was added to anhydrous CeCl_3 (490 mg, 2.0 mmol) and the resulting suspension was stirred overnight at room temperature, then cooled to -78°C . $n\text{-BuLi}$ (1.6 M hexane solution, 1.25 ml, 2.0 mmol) was added and the mixture was stirred for 1.5 h. A solution of **3** (1.33 mmol) in dry THF (1 ml) was added gradually over 10 min, and the reaction mixture was stirred at -78°C for 1.5 h. The reaction was quenched with saturated aqueous NH_4Cl , and the mixture was vigorously stirred for 10 min and then filtered through Celite. The filtrate was extracted with Et_2O three times, and the combined organic layer was washed with brine, dried with MgSO_4 , and concentrated *in vacuo* to give **1**. The yields of the products are shown in Table 1. The purity ($\geq 95\%$) of **1a**, **d**, **e**, **h** and **p** thus obtained was determined by 250 MHz $^1\text{H-NMR}$ analysis. Yields of relatively volatile products (**1b**, **1c**) were determined by 250 MHz $^1\text{H-NMR}$ analysis of crude products, which were contaminated only by THF. Distillation of these products gave analytically pure samples in 58% (for **1b**) and 60% (for **1c**) yields. Other products (**1f**, **g**, **i**) were purified by flash column chromatography (pentane– Et_2O).

2-(Trimethylsilyl)-1-phenylethan-1-one (**1a**): A colorless oil; bp $65\text{--}70^\circ\text{C}$ (0.18 mmHg) (bath temp.) [lit.,^{1a} $78\text{--}79^\circ\text{C}$ (1 mmHg)]; IR (CHCl_3): 1655, 1595 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.08 (9H, s, SiMe_3), 2.76 (2H, s, SiCH_2CO), 7.34–7.62 (3H, m, arom. H), 7.88–7.99 (2H, m, arom. H). MS m/z : 192 (M^+), 177 ($\text{M}^+ - \text{Me}$).

1-(Triethylsilyl)propan-2-one (**1b**): A colorless oil; bp $85\text{--}90^\circ\text{C}$ (10 mmHg) (bath temp.) [lit.,^{1a} $89\text{--}90^\circ\text{C}$ (10 mmHg)]; IR (CHCl_3): 1680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.56–0.66 (6H, m, $\text{SiCH}_2 \times 3$), 0.87–1.00 (9H, m, $\text{CH}_3 \times 3$), 2.10 (3H, s, COCH_3), 2.23 (2H, s, SiCH_2CO). MS m/z : 172 (M^+), 143 ($\text{M}^+ - \text{Et}$).

1-(Triethylsilyl)hexan-2-one (**1c**): A colorless oil; bp $125\text{--}130^\circ\text{C}$ (25 mmHg) (bath temp.); IR (CHCl_3): 1680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.55–0.71 (6H, m, $\text{SiCH}_2 \times 3$), 0.85–1.02 (12H, m, $\text{CH}_3 \times 4$), 1.31 (2H, sextet, $J = 7.5\text{ Hz}$, CH_2), 1.53 (2H, quintet, $J = 7.5\text{ Hz}$, CH_2), 2.19 (2H, s, SiCH_2CO), 2.35 (2H, t, $J = 7.5\text{ Hz}$, COCH_2). MS m/z : 185 ($\text{M}^+ - \text{Et}$). Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$: C, 67.22; H, 12.22. Found: C, 67.17; H, 12.33.

2-(Triethylsilyl)-1-phenylethan-1-one (**1d**): A colorless oil; bp $125\text{--}130^\circ\text{C}$ (4 mmHg) (bath temp.) [lit.,^{1a} $106\text{--}107^\circ\text{C}$ (1.5 mmHg)]; IR (CHCl_3): 1660, 1600 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.57 (6H, q, $J = 8.5\text{ Hz}$, $\text{SiCH}_2 \times 3$), 0.92 (9H, t, $J = 8.5\text{ Hz}$, $\text{CH}_3 \times 3$), 2.70 (2H, s, SiCH_2CO), 7.33–7.62 (3H, m, arom. H), 7.88–7.92 (2H, m, arom. H). MS m/z : 205 ($\text{M}^+ - \text{Et}$).

1-($t\text{-BuMe}_2\text{Si}$)propan-2-one (**1e**): A colorless oil; bp $100\text{--}105^\circ\text{C}$ (150 mmHg) (bath temp.) [lit.,^{10b} $40\text{--}42^\circ\text{C}$ (100 mmHg)];

IR (CHCl_3): 1680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.05 (6H, s, SiMe_2), 0.87 (9H, s, $t\text{-Bu}$), 2.08 (3H, s, COCH_3), 2.20 (2H, s, SiCH_2CO). MS m/z : 157 ($\text{M}^+ - \text{Me}$), 115 ($\text{M}^+ - t\text{-Bu}$).

1-($t\text{-BuMe}_2\text{Si}$)butan-2-one (**1f**): A colorless oil; bp $75\text{--}80^\circ\text{C}$ (17 mmHg) (bath temp.); IR (CHCl_3): 1680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.05 (6H, s, SiMe_2), 0.90 (9H, s, $t\text{-Bu}$), 1.03 (3H, t, $J = 7.5\text{ Hz}$, CH_3), 2.19 (2H, s, SiCH_2CO), 2.38 (2H, q, $J = 7.5\text{ Hz}$, COCH_2). MS m/z : 171 ($\text{M}^+ - \text{Me}$), 129 ($\text{M}^+ - t\text{-Bu}$). Anal. Calcd for $\text{C}_{10}\text{H}_{22}\text{OSi}$: C, 64.45; H, 11.90. Found: C, 64.21; H, 11.94.

1-($t\text{-BuMe}_2\text{Si}$)pentan-2-one (**1g**): A colorless oil; bp $85\text{--}90^\circ\text{C}$ (12 mmHg) (bath temp.); IR (CHCl_3): 1680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.06 (6H, s, SiMe_2), 0.90 (9H, s, $t\text{-Bu}$), 0.91 (3H, t, $J = 7.5\text{ Hz}$, CH_3), 1.58 (2H, sextet, $J = 7.5\text{ Hz}$, CH_2), 2.18 (2H, s, SiCH_2CO), 2.33 (2H, t, $J = 7.5\text{ Hz}$, COCH_2). HR-MS Calcd for $\text{C}_7\text{H}_{15}\text{OSi}$ ($\text{M}^+ - t\text{-Bu}$): 143.0889. Found: 143.0886.

1-($t\text{-BuMe}_2\text{Si}$)hexan-2-one (**1h**): A colorless oil; bp $120\text{--}130^\circ\text{C}$ (48 mmHg) (bath temp.); IR (CHCl_3): 1680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.04 (6H, s, SiMe_2), 0.89 (9H, s, $t\text{-Bu}$), 0.90 (3H, t, $J = 7.5\text{ Hz}$, CH_3), 1.30 (2H, sextet, $J = 7.5\text{ Hz}$, CH_2), 1.53 (2H, quintet, $J = 7.5\text{ Hz}$, CH_2), 2.18 (2H, s, SiCH_2CO), 2.35 (2H, t, $J = 7.5\text{ Hz}$, COCH_2). HR-MS Calcd for $\text{C}_8\text{H}_{17}\text{OSi}$ ($\text{M}^+ - t\text{-Bu}$): 157.1046. Found: 157.1040. Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$: C, 67.22; H, 12.22. Found: C, 66.66; H, 12.24.

1-($t\text{-BuMe}_2\text{Si}$)3-methylpentan-2-one (**1i**): A colorless oil; bp $106\text{--}112^\circ\text{C}$ (52 mmHg); IR (CHCl_3): 1680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.06 (6H, s, SiMe_2), 0.89 (3H, t, $J = 7.0\text{ Hz}$, CH_3), 0.90 (9H, s, $t\text{-Bu}$), 1.04 (3H, d, $J = 7.0\text{ Hz}$, CH_3), 1.26–1.43 (1H, m, CH), 1.57–1.74 (1H, m, CH), 2.19 (1H, d, $J = 11.0\text{ Hz}$, SiCHCO), 2.22 (1H, d, $J = 11.0\text{ Hz}$, SiCHCO), 2.39 (1H, sextet, $J = 7.0\text{ Hz}$, COCH). MS m/z : 214 (M^+), 157 ($\text{M}^+ - t\text{-Bu}$). Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$: C, 67.22; H, 12.22. Found: C, 66.72; H, 12.11.

2-($t\text{-BuMe}_2\text{Si}$)-1-phenylethan-1-one (**1p**): A colorless oil; bp $90\text{--}95^\circ\text{C}$ (0.4 mmHg) (bath temp.); IR (CHCl_3): 1655, 1595 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 0.01 (6H, s, SiMe_2), 0.95 (9H, s, $t\text{-Bu}$), 2.73 (2H, s, SiCH_2CO), 7.31–7.65 (3H, m, arom. H), 7.80–7.95 (2H, m, arom. H). HR-MS Calcd for $\text{C}_{10}\text{H}_{13}\text{OSi}$ ($\text{M}^+ - t\text{-Bu}$): 177.0737. Found: 177.0744.

General Procedure for the Preparation of α -Silylketones (1j–o, 1q–s) (Method B) By the same procedure as described in method A, **3c** (154 mg, 1.0 mmol) was treated with the organocerium reagent, prepared from anhydrous CeCl_3 (370 mg, 1.5 mmol) and the organolithium reagent (1.5 mmol) in dry THF (4.5 ml). The reaction mixture was stirred at -78°C for 1.5 h, and to it were added dry HMPA (1.5 ml) and alkyl halide **5** (5 mmol). The whole mixture was gradually warmed to room temperature and stirred overnight and then at 40°C for 2 h–1 d. Work-up as described in method A gave a crude product, which was purified by flash column chromatography (pentane– Et_2O) to give pure **1** in the yields shown in Table 1 or Chart 2.

2-($t\text{-BuMe}_2\text{Si}$)heptan-3-one (**1j**): A colorless oil; bp $80\text{--}85^\circ\text{C}$ (20 mmHg) (bath temp.); IR (CHCl_3): 1670 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : -0.01 (3H, s, SiMe), 0.04 (3H, s, SiMe), 0.90 (3H, t, $J = 7.5\text{ Hz}$, CH_3), 0.93 (9H, s, $t\text{-Bu}$), 1.20 (3H, d, $J = 7.0\text{ Hz}$, CH_3), 1.24–1.39 (2H, m, CH_2), 1.42–1.62 (2H, m, CH_2), 2.31–2.39 (2H, m, COCH_2), 2.52 (1H, q, $J = 7.0\text{ Hz}$, SiCHCO). MS m/z : 171 ($\text{M}^+ - t\text{-Bu}$).

Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.43; H, 12.51.

3-(*tert*-Butyldimethylsilyl)octan-4-one (**1k**): A colorless oil; bp 105–110 °C (8 mmHg) (bath temp.); IR ($CHCl_3$): 1680 cm^{-1} ; 1H -NMR ($CDCl_3$) δ : –0.05 (3H, s, SiMe), 0.02 (3H, s, SiMe), 0.85 (3H, t, $J=7.5$ Hz, CH_3), 0.91 (3H, t, $J=7.0$ Hz, CH_3), 0.92 (9H, s, *tert*-Bu), 1.24–1.66 (5H, m, $CH_2 \times 2$, CH), 1.88–2.07 (1H, m, CH), 2.18–2.43 (3H, m, $COCH_2$, SiCHCO). MS m/z : 227 ($M^+ - Me$), 185 ($M^+ - tert$ -Bu). Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47. Found: C, 69.09; H, 12.48.

4-(*tert*-Butyldimethylsilyl)nonan-5-one (**1l**): A colorless oil; bp 105–110 °C (8 mmHg) (bath temp.); IR ($CHCl_3$): 1680 cm^{-1} ; 1H -NMR ($CDCl_3$) δ : –0.04 (3H, s, SiMe), 0.04 (3H, s, SiMe), 0.86 (3H, t, $J=7.0$ Hz, Me), 0.91 (3H, t, $J=7.0$ Hz, Me), 0.93 (9H, s, *tert*-Bu), 1.07–1.62 (7H, m, $CH_3 \times 2$, CH), 1.95–2.03 (1H, m, CH), 2.24–2.40 (2H, m, $COCH_2$), 2.51 (1H, dd, $J=4.5$, 1.0 Hz, SiCHCO). MS m/z : 256 (M^+), 199 ($M^+ - tert$ -Bu). Anal. Calcd for $C_{15}H_{32}OSi$: C, 70.24; H, 12.57. Found: C, 70.12; H, 12.45.

4-(*tert*-Butyldimethylsilyl)non-1-en-5-one (**1m**): A colorless oil; bp 77–80 °C (10 mmHg); IR ($CHCl_3$): 1685, 1640 cm^{-1} ; 1H -NMR ($CDCl_3$) δ : –0.04 (3H, s, SiMe), 0.04 (3H, s, SiMe), 0.87 (3H, t, $J=7.0$ Hz, CH_3), 0.92 (9H, s, *tert*-Bu), 1.18–1.65 (4H, m, $CH_2 \times 2$), 2.08–2.42 (3H, m, $COCH_2$, SiCHCO), 2.53 (1H, dd, $J=12.0$, 2.0 Hz, $CHC=$), 2.63–2.76 (1H, m, $CHC=$), 4.88 (1H, brd, $J=10.0$ Hz, vinyl H), 4.95 (1H, dq, $J=17.0$, 1.0 Hz, vinyl H), 5.67 (1H, ddt, $J=17.0$, 10.0, 6.5 Hz, vinyl H); MS m/z : 254 (M^+), 197 ($M^+ - tert$ -Bu). Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88. Found: C, 70.45; H, 11.80.

2-(*tert*-Butyldimethylsilyl)-1-phenylheptan-3-one (**1n**): A colorless oil; bp 115–120 °C (0.1 mmHg) (bath temp.); IR ($CHCl_3$): 1680, 1600 cm^{-1} ; 1H -NMR ($CDCl_3$) δ : 0.00 (3H, s, SiMe), 0.13 (3H, s, SiMe), 0.73 (3H, t, $J=7.5$ Hz, CH_3), 0.99 (9H, s, *tert*-Bu), 0.96–1.35 (4H, m, $CH_2 \times 2$), 1.90–2.02 (1H, m, $COCH$), 2.16–2.28 (1H, m, $COCH$), 2.70–2.84 (2H, m, $PhCH_2$), 3.19–3.29 (1H, m, SiCHCO), 7.05–7.25 (5H, m, arom. H). HR-MS Calcd for $C_{19}H_{32}OSi$ (M^+): 304.2220. Found: 304.2220.

Ethyl 3-(*tert*-Butyldimethylsilyl)-4-oxooctanoate (**1o**): A colorless oil; bp 115–120 °C (4 mmHg) (bath temp.); IR ($CHCl_3$): 1725, 1690 cm^{-1} ; 1H -NMR ($CDCl_3$) δ : 0.00 (3H, s, SiMe), 0.06 (3H, s, SiMe), 0.90 (3H, t, $J=7.0$ Hz, CH_3), 0.93 (9H, s, *tert*-Bu), 1.23 (3H, t, $J=7.0$ Hz, CH_3), 1.21–1.69 (4H, m, $CH_2 \times 2$), 2.32–2.61 (3H, m, $COCH_2$, SiCHCO), 2.91 (1H, dd, $J=12.5$, 2.0 Hz, $CHCO_2$), 3.08 (1H, dd, $J=17$, 12.5 Hz, $CHCO_2$), 4.09 (2H, q, $J=7.0$ Hz, CO_2CH_2); MS m/z : 300 (M^+), 243 ($M^+ - tert$ -Bu). Anal. Calcd for $C_{16}H_{32}O_3Si$: C, 63.95; H, 10.73. Found: C, 63.83; H, 10.52.

2-(*tert*-Butyldimethylsilyl)-1-phenylpropan-1-one (**1q**): A colorless oil; bp 110–120 °C (1.5 mmHg) (bath temp.); IR ($CHCl_3$): 1660 cm^{-1} ; 1H -NMR ($CDCl_3$) δ : –0.24 (3H, s, SiMe), 0.02 (3H, s, SiMe), 0.91 (9H, s, *tert*-Bu), 1.40 (3H, d, $J=8.5$ Hz, CH_3), 3.49 (1H, q, $J=8.5$ Hz, SiCHCO), 7.39–7.56 (3H, m, arom. H), 7.87–7.92 (2H, m, arom. H). MS m/z : 248 (M^+), 191 ($M^+ - tert$ -Bu). Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 72.51; H, 9.61.

2-(*tert*-Butyldimethylsilyl)hexan-3-one (**1r**): A colorless oil; bp 120–130 °C (45 mmHg) (bath temp.); IR ($CHCl_3$): 1670 cm^{-1} ; 1H -NMR ($CDCl_3$) δ : –0.01 (3H, s, SiMe), 0.05 (3H, s, SiMe), 0.91 (3H, t, $J=8.0$ Hz, CH_3), 0.93 (9H, s, *tert*-Bu), 1.20 (3H, d, $J=7.0$ Hz, CH_3), 1.46–1.69 (2H, m, CH_2), 2.27–2.37 (2H, m, $COCH_2$), 2.51 (1H, q, $J=7.0$ Hz, SiCHCO). HR-MS Calcd for $C_{12}H_{26}OSi$ (M^+): 214.1753. Found: 214.1759.

4-(*tert*-Butyldimethylsilyl)hexan-3-one (**1s**): A colorless oil; bp 95–100 °C (15 mmHg) (bath temp.); IR ($CHCl_3$): 1680 cm^{-1} ; 1H -NMR ($CDCl_3$) δ : –0.06 (3H, s, SiMe), 0.02 (3H, s, SiMe), 0.84 (3H, t, $J=7.5$ Hz, CH_3), 0.92 (9H, s, *tert*-Bu), 1.03 (3H, t, $J=7.0$ Hz, CH_3), 1.39–1.55 (1H, m, CH), 1.88–2.06 (1H, m, CH), 2.16–2.51 (3H, m, $COCH_2$, SiCHCO); MS m/z : 199 ($M^+ - Me$), 157 ($M^+ - tert$ -Bu). Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.25; H, 12.25.

Preparation of Silyl Enol Ethers (2r,s) from Hexan-3-one (7) Under a nitrogen atmosphere, a solution of **7** (200 mg, 2.0 mmol) in dry THF (0.5 ml) was added gradually over 10 min to a solution of LDA (2.1 mmol) in dry THF (4.8 ml) at –78 °C, and the reaction mixture was stirred for 1 h. Dry HMPA (1.2 ml) was added and the mixture was stirred for 30 min. A solution of *tert*-butyldimethylsilyl chloride (510 mg, 3.4 mmol) in dry THF (1 ml) was then added over 5 min, and the reaction mixture was stirred for 1 h at room temperature and concentrated *in vacuo*. The residue was diluted with pentane (50 ml), washed with ice water, dried

over Na_2SO_4 , and concentrated *in vacuo* to give an 18:46:9:27 mixture (430 mg, quant) of (*E*)- and (*Z*)-**2r** and (*E*)- and (*Z*)-**2s**. A colorless oil; 1H -NMR ($CDCl_3$; 500 MHz) data for the vinyl proton of four products δ : 4.40 (27/100 $\times$ 1H, t, $J=7.0$ Hz, (*Z*)-**2s**), 4.48 (46/100 $\times$ 1H, q, $J=6.5$ Hz, (*Z*)-**2r**), 4.57 (9/100 $\times$ 1H, t, $J=7.0$ Hz, (*E*)-**2s**), 4.62 (18/100 $\times$ 1H, q, $J=6.5$ Hz, (*E*)-**2r**).

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- 7) The reported methods are based on the reaction of carboxylic acid derivatives with α -silyl carbanions,^{1a,3b,5a,c,e,8} C-silylation of azaenolates^{6,9} or ester enolates^{1c} and successive conversion to ketones, migration from silicon-containing compounds prepared by other methods,¹⁰ oxidation of β -silyl alcohols,^{5a,d,10i} and Si–H insertion of diazo ketones.¹¹
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