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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, Me_2CuLi, Et_3Al, and Et_2Zn resulted in complicated reactions, organocerium reagents 4 ($M=CeCl_2$) added selectively to the carbonyl carbon of 3 to generate enolate anions A, which were treated with aqueous NH_4Cl 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 acid[3] or fluoride ion.[4] Other attractive synthetic utilities of **1** exist in stereospecific alkene formation[5] 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** ($M=CeCl_2$) 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** ($R^1=Me$) 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 bissilylketene **6** ($R^1_3=$ *tert*-$BuMe_2$) in 96% yield.[18] Attempts to use MeMgBr, Me_2CuLi, Et_3Al, or Et_2Zn 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** ($M=CeCl_2$)[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*-$BuCeCl_2$, prepared from anhydrous $CeCl_3$ and *n*-BuLi by the usual method. The mixture was stirred for 1.5 h at −78 °C, then the

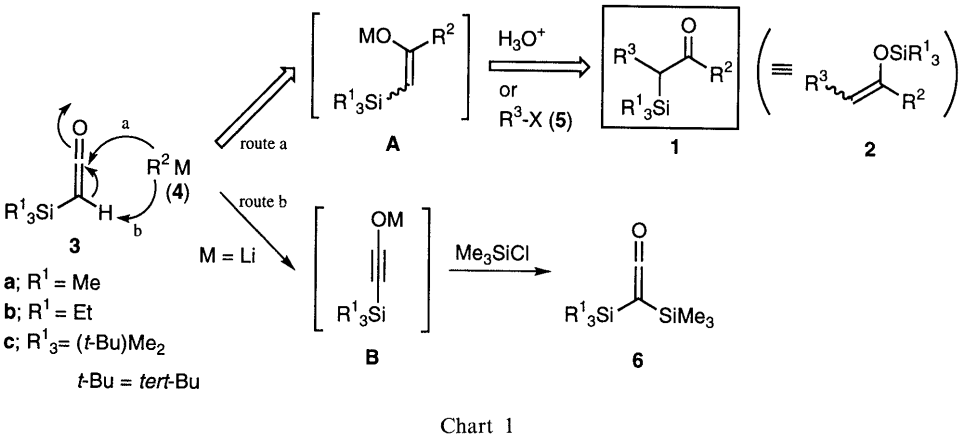

Chart 1

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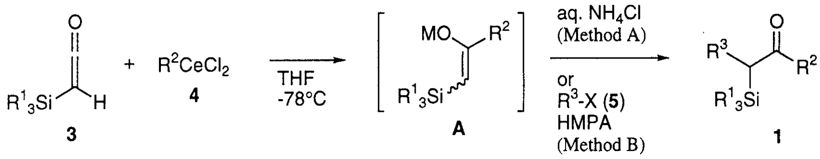
Table 1. Preparation of α-Silylketones **1**



Entry	Silylketene 3	Cerium reagent 4 $R^2=$	Quenching method[a] (R^3-X5 for method B)	α-Silylketone 1				
					$R^1_3=$	$R^2=$	$R^3=$	% 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**	*n*-Bu	A	**1c**	Et_3	*n*-Bu	H	$93^{c)}$
4	**3b**	Ph	A	**1d**	Et_3	Ph	H	$99^{b)}$
5	**3c**	Me	A	**1e**	(*tert*-Bu)Me_2	Me	H	$82^{b)}$
6	**3c**	Et	A	**1f**	(*tert*-Bu)Me_2	Et	H	$68^{d)}$
7	**3c**	*n*-Pr	A	**1g**	(*tert*-Bu)Me_2	*n*-Pr	H	$72^{d)}$
8	**3c**	*n*-Bu	A	**1h**	(*tert*-Bu)Me_2	*n*-Bu	H	$91^{b)}$
9	**3c**	*sec*-Bu	A	**1i**	(*tert*-Bu)Me_2	*sec*-Bu	H	$40^{d)}$
10	**3c**	*n*-Bu	B (MeI)	**1j**	(*tert*-Bu)Me_2	*n*-Bu	Me	$76^{d,e)}$ ($48^{d,f)}$)
11	**3c**	*n*-Bu	B (EtI)	**1k**	(*tert*-Bu)Me_2	*n*-Bu	Et	$53^{d,e)}$
12	**3c**	*n*-Bu	B (EtBr)	**1k**	(*tert*-Bu)Me_2	*n*-Bu	Et	$10^{d,e)}$
13	**3c**	*n*-Bu	B (*n*-PrI)	**1l**	(*tert*-Bu)Me_2	*n*-Bu	*n*-Pr	$31^{d)}$
14	**3c**	*n*-Bu	B ($CH_2=CHCH_2I$)	**1m**	(*tert*-Bu)Me_2	*n*-Bu	$CH_2CH=CH_2$	$70^{d,e)}$
15	**3c**	*n*-Bu	B ($CH_2=CHCH_2Br$)	**1m**	(*tert*-Bu)Me_2	*n*-Bu	$CH_2CH=CH_2$	$47^{d,e)}$
16	**3c**	*n*-Bu	B ($PhCH_2Br$)	**1n**	(*tert*-Bu)Me_2	*n*-Bu	$PhCH_2$	$57^{d)}$
17	**3c**	*n*-Bu	B (EtO_2CCH_2Br)	**1o**	(*tert*-Bu)Me_2	*n*-Bu	CH_2CO_2Et	$41^{d,e)}$
18	**3c**	Ph	A	**1p**	(*tert*-Bu)Me_2	Ph	H	$98^{b)}$
19	**3c**	Ph	B (MeI)	**1q**	(*tert*-Bu)Me_2	Ph	Me	$48^{d,e)}$

a) Quenching with saturated aqueous NH_4Cl (method A) or R^3-X **5** (method B). *b*) Pure **1** (≥95% determined by 250 MHz ^{1}H-NMR analysis) was obtained without purification. *c*) Yields determined by 250 MHz ^{1}H-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 SiO_2-flash column chromatography. *e*) Formation of the corresponding protonated products **1h**, **p**, was observed by ^{1}H-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 NH_4Cl 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*-$BuCeCl_2$ with **3c** gave the silylketone **1i** in 40% yield (entry 9), while similar reaction of *tert*-$BuCeCl_2$ 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$=CeCl_2$) 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*-$PrCeCl_2$ and subsequent quenching with MeI gave a 67% yield of **1r**, and that with $EtCeCl_2$ 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. ^{1}H-

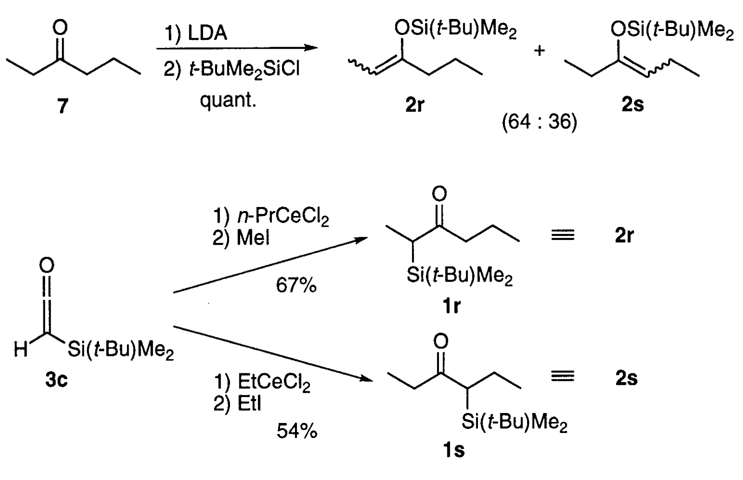


Chart 2

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 $CeCl_3 \cdot 7H_2O$ 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*-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 (≥95%) of **1a**, **d**, **e**, **h** and **p** thus obtained was determined by 250 MHz ^{1}H-NMR analysis. Yields of relatively volatile products (**1b**, **1c**) were determined by 250 MHz ^{1}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—70 °C (0.18 mmHg) (bath temp.) [lit.,[1a)] 78—79 °C (1 mmHg)]; IR ($CHCl_3$): 1655, 1595 cm^{-1}; ^{1}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 ($M^+ - Me$).

1-(Triethylsilyl)propan-2-one (**1b**): A colorless oil; bp 85—90 °C (10 mmHg) (bath temp.) [lit.,[1a)] 89—90 °C (10 mmHg)]; IR ($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.56—0.66 (6H, m, $SiCH_2 \times 3$), 0.87—1.00 (9H, m, $CH_3 \times 3$), 2.10 (3H, s, $COCH_3$), 2.23 (2H, s, $SiCH_2CO$). MS *m/z*: 172 (M^+), 143 ($M^+ - Et$).

1-(Triethylsilyl)hexan-2-one (**1c**): A colorless oil; bp 125—130 °C (25 mmHg) (bath temp.); IR ($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.55—0.71 (6H, m, $SiCH_2 \times 3$), 0.85—1.02 (12H, m, $CH_3 \times 4$), 1.31 (2H, sextet, $J = 7.5$ Hz, CH_2), 1.53 (2H, quintet, $J = 7.5$ Hz, CH_2), 2.19 (2H, s, $SiCH_2CO$), 2.35 (2H, t, $J = 7.5$ Hz, $COCH_2$). MS *m/z*: 185 ($M^+ - Et$). *Anal.* Calcd for $C_{12}H_{26}OSi$: 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—130 °C (4 mmHg) (bath temp.) [lit.,[1a)] 106—107 °C (1.5 mmHg)]; IR ($CHCl_3$): 1660, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.57 (6H, q, $J = 8.5$ Hz, $SiCH_2 \times 3$), 0.92 (9H, t, $J = 8.5$ Hz, $CH_3 \times 3$), 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 ($M^+ - Et$).

1-(*tert*-Butyldimethylsilyl)propan-2-one (**1e**): A colorless oil; bp 100—105 °C (150 mmHg) (bath temp.) [lit.,[10j)] 40—42 °C (100 mmHg)]; IR ($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.05 (6H, s, $SiMe_2$), 0.87 (9H, s, *tert*-Bu), 2.08 (3H, s, $COCH_3$), 2.20 (2H, s, $SiCH_2CO$). MS *m/z*: 157 ($M^+ - Me$), 115 ($M^+ -$ *tert*-Bu).

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

1-(*tert*-Butyldimethylsilyl)pentan-2-one (**1g**): A colorless oil; bp 85—90 °C (12 mmHg) (bath temp.); IR ($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.06 (6H, s, $SiMe_2$), 0.90 (9H, s, *tert*-Bu), 0.91 (3H, t, $J = 7.5$ Hz, CH_3), 1.58 (2H, sextet, $J = 7.5$ Hz, CH_2), 2.18 (2H, s, $SiCH_2CO$), 2.33 (2H, t, $J = 7.5$ Hz, $COCH_2$). HR-MS Calcd for $C_7H_{15}OSi$ ($M^+ -$ *tert*-Bu): 143.0889. Found: 143.0886.

1-(*tert*-Butyldimethylsilyl)hexan-2-one (**1h**): A colorless oil; bp 120—130 °C (48 mmHg) (bath temp.); IR ($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.04 (6H, s, $SiMe_2$), 0.89 (9H, s, *tert*-Bu), 0.90 (3H, t, $J = 7.5$ Hz, CH_3), 1.30 (2H, sextet, $J = 7.5$ Hz, CH_2), 1.53 (2H, quintet, $J = 7.5$ Hz, CH_2), 2.18 (2H, s, $SiCH_2CO$), 2.35 (2H, t, $J = 7.5$ Hz, $COCH_2$). HR-MS Calcd for $C_8H_{17}OSi$ ($M^+ -$ *tert*-Bu): 157.1046. Found: 157.1040. *Anal.* Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 66.66; H, 12.24.

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

2-(*tert*-Butyldimethylsilyl)-1-phenylethan-1-one (**1p**): A colorless oil; bp 90—95 °C (0.4 mmHg) (bath temp.); IR ($CHCl_3$): 1655, 1595 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.01 (6H, s, $SiMe_2$), 0.95 (9H, s, *tert*-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 $C_{10}H_{13}OSi$ ($M^+ -$ *tert*-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-(*tert*-Butyldimethylsilyl)heptan-3-one (**1j**): A colorless oil; bp 80—85 °C (20 mmHg) (bath temp.); IR ($CHCl_3$): 1670 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: −0.01 (3H, s, SiMe), 0.04 (3H, s, SiMe), 0.90 (3H, t, $J = 7.5$ Hz, CH_3), 0.93 (9H, s, *tert*-Bu), 1.20 (3H, d, $J = 7.0$ 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, $J = 7.0$ Hz, SiCHCO). MS *m/z*: 171 ($M^+ -$ *tert*-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}; ^{1}H-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}; ^{1}H-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}; ^{1}H-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, br d, $J=10.0$ 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}; ^{1}H-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}; ^{1}H-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}; ^{1}H-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}; ^{1}H-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}; ^{1}H-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; ^{1}H-NMR ($CDCl_3$; 500 MHz) data for the vinyl proton of four products δ: 4.40 (27/100 × 1H, t, $J=7.0$ Hz, (*Z*)-**2s**), 4.48 (46/100 × 1H, q, $J=6.5$ Hz, (*Z*)-**2r**), 4.57 (9/100 × 1H, t, $J=7.0$ Hz, (*E*)-**2s**), 4.62 (18/100 × 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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13) Silylketenes **3** are easy-to-handle, distillable liquid monomers, and can be stored for a long time without polymerization, in marked contrast to the parental ketene and alkylketenes.[14]

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