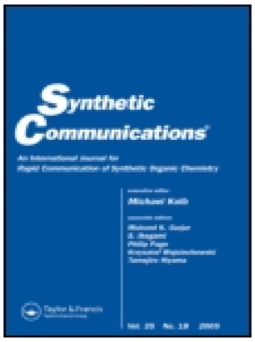

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SYNTHESIS AND HYDROLYTIC STABILITY OF *TERT*-BUTOXYDIMETHYLSILYL ENOL ETHERS

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ABSTRACT

tert-Butoxydimethylsilyl enol ethers derived from aldehydes and ketones were synthesized in good yields with high regio- and stereoselectivities, under thermodynamically and kinetically controlled conditions. The hydrolytic stability of *tert*-butoxydimethylsilyl enol ether of cyclohexanone was studied under acidic and basic conditions and compared to that of trimethylsilyl, *tert*-butyldimethylsilyl and (2,4,6-tri-*tert*-butylphenoxy)dimethylsilyl enol ethers.

Silyl enol ethers have shown to be useful enolate equivalents for the synthesis of enones,[1] α-hydroxy ketones,[2] 1,4-diketones,[3] and other functionalized carbonyl compounds,[4] which in turn are versatile intermediates for the syntheses of some natural products. Several methods for the preparation of silyl enol ethers have been reported.[5,6] House described the preparation of

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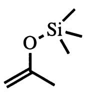
trimethylsilyl enol ethers (**1**) from aldehydes and ketones with trimethylsilyl chloride.[7] However, the utility of these enol ethers is limited by their susceptibility to hydrolysis. This problem was overcome by the use of the *tert*-butyldimethylsilyl derivatives (**2**).[8] *tert*-Butyldimethylsilyl chloride, however, is considerably more expensive than trimethylsilyl chloride.[9,10] In an effort to find a silylating agent which could provide hydrolytic stability similar to that of the *tert*-butyldimethylsilyl moiety at a more reasonable cost, Rathke prepared the solid (2,4,6-tri-*tert*-butylphenoxy) dimethylsilyl chloride (TPS, **3**) from 2,4,6-tri-*tert*-butylphenol.[11] Here, we explore the possibility of using an alkoxy dimethylsilyl chloride instead of the phenoxy analog **3**. Therefore, *tert*-butoxydimethylsilyl chloride (TBOSCI, **4**), was chosen in our study. TBOSCI is a colorless liquid that can be prepared readily and more inexpensively than **3** from dichlorodimethylsilane and *tert*-butanol in the presence of urea.[12]



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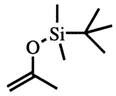

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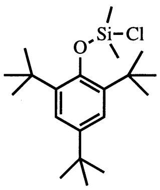

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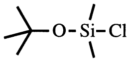
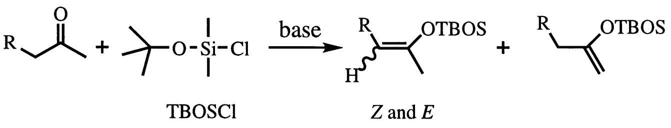


4

RESULTS AND DISCUSSION

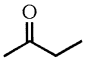
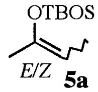
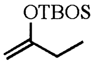
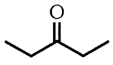
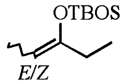
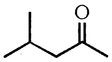
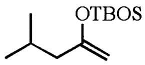
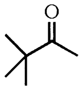
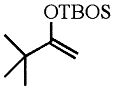
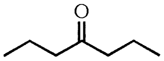
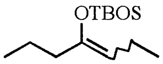
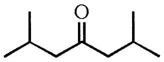
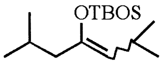
Several *tert*-butoxydimethylsilyl enol ethers were prepared for the first time in good to excellent yields (50–98%) from the reaction of *tert*-butoxydimethylsilyl chloride with a number of ketones and aldehydes (eq. 1, Table 1) by two distinctive methods based on thermodynamic and kinetic control.



Equation 1.

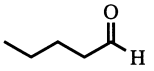
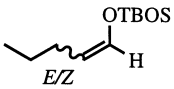
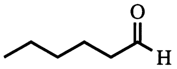
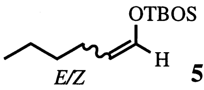
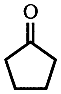
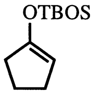
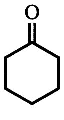
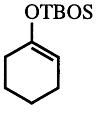
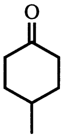
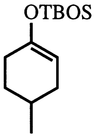
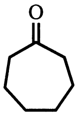
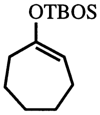
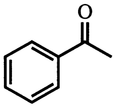
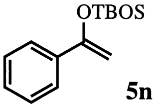
In the thermodynamically controlled method A (Table 1), a mixture of a ketone, triethylamine, sodium iodide and the silylating agent **4** in acetonitrile, was stirred at room temperature for 40–120 min, depending on the substrate. Yields of TBOS enol ethers ranged from 70 to 98%. For aldehydes, the reaction mixtures were refluxed (method B, Table 1). Since aldehyde enolates are more reactive than ketone enolates toward aldol condesation,[7] heat is required to enhance the retroaldol reaction of aldehydes.

Table 1. Formation of *tert*-Butoxydimethylsilyl Enol Ethers

substrate	product(s)	method[a]	reaction time (min)	%yield[b] (*E/Z*)
	 *E/Z* **5a**  **5b**	A	70	**5a**: 70 (3/68) **5b**: 28
		C	30	**5a**: 13 (16/4) **5b**: 53
		D	30	**5a**: 13 (18/1) **5b**: 53
	 *E/Z* **5c**	A	85	82 (7/93)
		C	30	90 (70/30)
		D	30	90 (86/14)
	 **5d**	A	120	91
		C	72	80
	 **5e**	A	40	79
		C	30	83
	 *E/Z* **5f**	A	70	85 (8/92)
		C	72	79 (67/33)
		D	72	79 (73/27)
	 *E/Z* **5g**	A	70	70 (24/76)
		C	15	70 (70/30)

(*continued*)

Table 1. Continued

substrate	product(s)	method[a]	reaction time (min)	%yield[b] (*E/Z*)
	 **5h**	B	75	80 (23/77)
		C	15	50 (96/4)
	 **5i**	B	105	76 (18/82)
		C	15	50 (96/4)
	 **5j**	A	90	95
		C	30	95
	 **5k**	A	70	85
		C	72	79
	 **5l**	A	60	82
		C	22	82
	 **5m**	A	60	76
		C	40	75
	 **5n**	A	70	85
		C	16	97

[a] In method A, the carbonyl compound was stirred at room temperature with a mixture of Et_3N, TBOSCl and NaI in CH_3CN. In method B, the reaction mixture of method A was refluxed. In method C, the enolate formed by the reaction of the cabonyl compound with LDA in THF, was quenched withTBOSCl. In method D, LiTMP was used instead of LDA. [b] GC yield.

The kinetically controlled methods C and D (Table 1), involve initial formation of the enolate ions via reaction of the carbonyl compound either with a solution of lithium diisopropylamide (LDA, generated from diisopropylamine and *n*-butyllithium, method C) or lithium

2,2,6,6-tetramethylpiperidide (LiTMP, prepared from 2,2,6,6-tetramethylpiperidine and *n*-butyllithium, method D) in tetrahydrofuran (THF), under nitrogen. Subsequent quenching of the produced enolate ions with *tert*-butoxydimethylsilyl chloride produced the *tert*-butoxydimethylsilyl enol ethers. The products were obtained within 15–72 min with yields in the range of 50–97% (Table 1).

The regio- and stereoselectivity of the *tert*-butoxydimethylsilyl enol ethers are influenced by the different methods used in their formation (thermodynamic *vs*. kinetic). As expected, kinetic control favors the formation of the *E* enolate, resulting from α-proton abstraction from the less sterically hindered side (Table 1). The use of the more hindered base LiTMP (method D) increases the ratio of *E*/*Z* enolates even further (Table 1, **5a**, **5c**, and **5f**).[13,14]

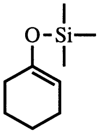
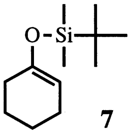
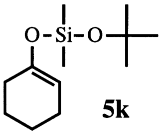
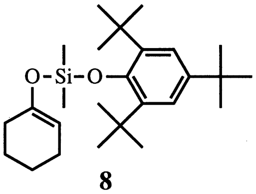
The rate of hydrolysis of TBOS enol ether derived from cyclohexanone (**5k**, Table 2) was investigated under acidic and basic conditions. Our experimental data were compared with the literature rates of hydrolysis of TMS enol ether **6**, TBS enol ether **7**, and TPS enol ether **8** derived from cyclohexanone under the same reaction conditions (Table 2).[7] It is clear that TBOS enol ether **5k** is by far more resistant to acid hydrolysis than the TMS derivative **6**, and **5k** is even slightly more resistant to acid hydrolysis than the TBS derivative **7**. Also, it may be noted that **5k** is almost as resistant to acid hydrolysis as the TPS enol ether **8**. All three enol ethers **5k**, **7**, and **8** are stable to base treatment.

In conclusion, the facile, inexpensive synthesis and easy handling of *tert*-butoxydimethylsilyl chloride may rank it as the reagent of choice for the synthesis of silyl enol ethers compared to (2,4,6-tri-*tert*-butylphenoxy)-dimethylsilyl and *tert*-butyldimethylsilyl chloride which are more expensive. The latter reagent is also more difficult to prepare. In addition, the hydrolytic stability of the resulting TBOS enol ethers is superior to TMS and comparable to TBS and TPS enol ethers.

EXPERIMENTAL

IR spectra were recorded on a Pye-Unican SP-300 spectrometer. ^{1}H NMR spectra were obtained in $CDCl_3$ with a Bruker WP 80 EY spectrometer. Mass spectra were recorded on a sector field double focusing unit VG 7070E GC-MS spectrometer at an accelerating voltage of 6k volts. Vapor phase chromatographic analysis and preparative work were carried out on Varian Aerographs 1400 and 3400 with thermal conductivity detectors. Elemental analysis was performed by M-H-W Laboratories, Phoenix AZ.

Table 2. Hydrolysis of Silyl Enol Ethers[a]

substrate	hydrolysis conditions[b]	reaction time, h	% ketone[c]
 **6**	A	6	100
	B	0.25	100
	C	1	<5
 **7**	A	6	0
	B	0.25	80
	B	1	100
	C	1	0
 **5k**	A	6	0
	B	0.25	70
	B	1	90
	B	2	100
	C	1	0
 **8**	A	6	0
	B	0.2	10
	B	1	70
	B	2	100
	C	1	0

[a]Hydrolysis of compounds **6**, **7**, and **8** are from literature.[7] [b]A, HOAc/THF/H_2O, 1:10:1; B, THF/1 M HCl. 20 : 1; C, THF/1 M NaOH, 20:1. [c]Determined by GC with decane as internal standard.

All starting materials and reagents were from Aldrich. Tetrahydrofuran was distilled from lithium aluminum hydride, and triethylamine was distilled from calcium hydride prior to use.

Preparation of *tert*-Butoxychlorodimethylsilane (4)

Following the procedure of Krovelets et al.,[12] urea (70 g, 1.2 mol) and dichlorodimethylsilane (120 ml, 1 mol) were stirred vigorously for 15 min at room temperature, under nitrogen, followed by the dropwise addition of *tert*-butanol (94 ml, 1 mol). The reaction mixture was stirred for an additional 1.5 h at room temperature followed by filtration (moisture should be excluded during the filtration since urea hydrochloride is very hygroscopic). The filtrate was subjected to fractional distillation to give **4** as a colorless liquid. Yield: 86%; bp 100°C/760 mm Hg (lit.[12] bp 107–108°C/747 mm Hg); ^{1}H NMR δ 0.43 (6H, s), 1.32 (9H, s).

Preparation of *tert*-Butoxydimethylsilyl Enol Ethers (5a–n)

Method A. Into a 10 ml round bottom flask, sodium iodide (3 mmol, 0.45 g), acetonitrile (3 ml), triethylamine (0.63 ml, 4.5 mmol), and *tert*-butoxychlorodimethylsilane (0.6 ml, 3.3 mmol) were added followed by the addition of ketone or aldehyde (3 mmol). The mixture was stirred at room temperature, under nitrogen for 40–120 min, depending on the substrate (Table 1). The reaction mixture was then diluted with 6 ml of petroleum ether (40–60°C) and washed with cold saturated aqueous $NaHCO_3$ (2×3 ml). The organic layer was dried over anhydrous Na_2SO_4, concentrated *in vacuo* followed by the addition of an appropriate standard (n-$C_{11}H_{24}$ to n-$C_{16}H_{34}$, 3 mmol), and GC analysis (10% SE-30, $1/8'' \times 5'$ or $1/8'' \times 20'$ column).

Method B. Same as method A except that after the addition of aldehyde the reaction mixture was refluxed for the indicated time (Table 1).

Method C. A 10 ml flask equipped with a magnetic stirring bar, septum, gas inlet valve, and mercury bubbler was flame-dried under nitrogen. *n*-Butyllithium as a 1.6 M solution in hexane (1.3 ml, 2 mmol) was added and the flask was immersed in an ice bath. Diisopropylamine (0.28 ml, 2 mmol) was added dropwise with stirring. After the evolution of butane had ceased, hexane was removed under vacuum, which was broken with nitrogen. LDA obtained as a white solid, was dissolved in 2 ml anhydrous THF, and 2 mmol of the carbonyl compound was added dropwise with stirring at 0°C over 2 min. The reaction mixture was stirred for 10 min at 0°C, then quenched with *tert*-butoxychlorodimethylsilane (0.36 ml, 2 mmol), and stirred for 5 min at 0°C. An appropriate standard (n-$C_{11}H_{24}$ to n-$C_{16}H_{34}$, 2 mmol) was added. The reaction mixture was stirred at room temperature for the indicated time (Table 1), followed by GC analysis (10% SE-30, $1/8'' \times 5'$ column). For product isolation, petroleum ether (2 ml) was added to the reaction mixture and washed with cold saturated aqueous $NaHCO_3$ (2 ml). The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo*, followed by fractional vacuum distillation.

Method D. Same as method C except that 2,3,6,6-tetramethyl piperidine was used instead of diisopropylamine.

***tert*-Butoxydimethylsilyl enol ethers from 2-butanone (5a and 5b)** Colorless liquid consisting of **5a** (*E* and *Z* isomers) and **5b**; bp 35°C (9 mm Hg); d 0.851 g/ml; MS, *m*/*e* 187(M^+-15), 145, 129, 115, 86, 75, 57, 45. Anal. Calcd for $C_{10}H_{22}SiO_2$: C, 59.35; H, 10.96. Found: C, 59.28; H, 10.79. The regioisomers **5a** and **5b** were separated by preparative GC. However, the *E* and *Z* isomers of **5a** were inseparable by this technique.

5a ($E+Z$): IR 1670 cm^{-1} (C=C); ^{1}H NMR δ 0.17 (6H, s), 1.29 (9H, s), 1.50 (3H, d, $J=6.9$ Hz), 1.80 (3H, s), 4.74 (q, $J=7.2$ Hz, *E*), 4.43 (q, $J=6.4$ Hz, *Z*).

5b: IR 1620 cm^{-1} (C=C); ^{1}H NMR δ 0.18 (6H, s), 1.02 (3H, t, $J=7.2$), 1.29 (9H, s), 1.96 (2H, q, $J=7.3$ Hz), 4.05 (1H, s), 4.16 (1H, s).

***tert*-Butoxydimethylsilyl enol ether from 3-pentanone (5c)**: Colorless liquid consisting of *E* and *Z* isomers; bp 30°C (3 mm Hg), d 0.845 g/ml; IR 1650 cm^{-1} (C=C). The *E* and *Z* isomers were separated by preparative GC. ^{1}H NMR δ *E*: 0.14 (6H, s), 1.0 (3H, t, $J=7.6$ Hz), 1.28 (9H, s), 1.52 (3H, d, $J=7.1$ Hz), 2.1 (2H, q, $J=7.6$ Hz), 4.70 (1H, q, $J=6.9$ Hz); *Z*: 0.17 (6H, s), 1.02 (3H, t, $J=7.6$ Hz), 1.29 (9H, s), 1.52 (3H, d, $J=7.1$ Hz), 2.10 (2H, q, $J=7.6$ Hz), 4.48 (1H, q, $J=7.1$ Hz); MS, *m*/*e* 201 (M$^+$-15), 159, 143, 75. Anal. Calcd for $C_{11}H_{24}SiO_2$: C, 61.06; H, 11.18. Found: C, 60.88; H, 11.40.

***tert*-Butoxydimethylsilyl enol ether from 4-methyl-2-pentanone (5d)**: Colorless liquid; bp 65°C (8 mm Hg); d 0.815 g/ml; IR 1615 cm^{-1} (C=C); ^{1}H NMR δ 0.17 (6H, s), 0.88 (7H, m), 1.29 (9H, s), 1.86 (2H, m), 4.01 (1H, s), 4.18 (1H, s); MS, *m*/*e* 230 (M$^+$), 216, 215, 207, 188, 173, 159, 157, 75, 57. Anal. Calcd for $C_{12}H_{26}SiO_2$: C, 62.55; H, 11.37. Found: C, 62.43; H, 11.33.

***tert*-Butoxydimethylsilyl enol ether from 3,3-dimethyl-2-butanone (5e)**: Colorless liquid; bp 42°C (3 mm Hg); d 0.826 g/ml; IR 1610 cm^{-1} (C=C); ^{1}H NMR δ 0.17 (6H, s), 1.04 (9H, s), 1.29 (9H, s), 4.09 (2H, s); MS, *m*/*e* 230 (M$^+$), 215, 173, 159, 157, 77, 75. Anal. Calcd for $C_{12}H_{26}SiO_2$: C, 62.55; H, 11.37. Found: C, 62.34; H, 11.12.

***tert*-Butoxydimethylsilyl enol ether from 4-pentanone (5f)**: Colorless liquid consisting of *E* and *Z* isomers (inseparable by preparative GC); bp 66°C (7 mm Hg); d 0.815 g/ml; IR 1660 cm^{-1} (C=C); ^{1}H NMR δ 0.16 (6H, s), 0.89 (6H, t, $J=6.3$ Hz), 1.29 (9H, s), 1.37–1.58 (2H, m), 2.00 (4H, q, $J=7.3$ Hz), 4.39 (1H, t, $J=7.5$ Hz, *Z*), 4.74 (1H, t, $J=7.6$ Hz, *E*); MS, *m*/*e* 229 (M$^+$-15), 188, 187, 173, 171, 145, 75, 57. Anal. Calcd for $C_{13}H_{28}SiO_2$: C, 63.86; H, 11.55. Found: C, 63.93; H, 11.61.

***tert*-Butoxydimethylsilyl enol ether from 2,6-dimethyl-4-heptanone (5g)**: Colorless liquid consisting of *E* and *Z* isomers (inseparable by preparative GC); bp 77°C (5 mm Hg); d 0.826 g/ml; IR 1650 cm^{-1} (C=C); ^{1}H NMR δ 0.15 (6H, s), 0.92 (13H, m), 1.28 (9H, s); 1.91 (2H, m), 2.28 (1H, m), 4.23 (1H, d, $J=9$, *Z*), 4.62 (1H, d, $J=9.7$ Hz, *E*); MS, *m*/*e* 256 (M$^+$-16), 214, 200, 198, 109, 75, 57. Anal. Calcd for $C_{15}H_{32}SiO_2$: C, 66.11; H, 11.84. Found: C, 66.13; H, 11.70.

***tert*-Butoxydimethylsilyl enol ether from pentanal (5h)**: Colorless liquid consisting of E and Z isomers; d 0.866 g/ml; IR 1660 cm^{-1} (C = C). The E and Z isomers were separated by preparative GC. ^{1}H NMR δ E: 0.15 (6H, s), 0.89 (3H, t, $J = 7$ Hz), 1.28 (9H, s), 1.3–1.6 (2H, m), 2.06 (2H, q, $J = 6.8$ Hz), 5.0 (1H, dt, $J_{trans} = 11.8$ Hz, $J = 7.5$ Hz), 6.23 (1H, d, $J_{trans} = 11.8$ Hz); Z: 0.15 (6H, s), 0.89 (3H, t, $J = 7$ Hz), 1.28 (9H, s), 1.3–1.6 (2H, m), 2.06 (2H, q, $J = 6.8$ Hz), 4.45 (1H, dt, $J_{cis} = 6.2$ Hz, $J = 7.5$ Hz), 6.2 (1H, d, $J_{cis} = 6.2$ Hz). Anal. Calcd for $C_{11}H_{24}SiO_2$: C, 61.06; H, 11.18. Found: C, 60.87; H, 10.99.

***tert*-Butoxydimethylsilyl enol ether from hexanal (5i)**: Colorless liquid consisting of E and Z isomers; d 0.875 g/ml; IR 1660 cm^{-1} (C = C). The E and Z isomers were separated by preparative GC. ^{1}H NMR δ E: 0.15 (6H, s), 0.88 (3H, t, $J = 6.5$ Hz), 1.28 (9H, s), 1.0–2.22 (6H, m), 5.0 (1H, dt, $J_{trans} = 11.8$ Hz, $J = 7.3$ Hz), 6.25 (1H, d, $J_{trans} = 11.8$ Hz); Z: 0.15 (6H, s), 0.88 (3H, t, $J = 6.5$ Hz), 1.28 (9H, s), 1–2.22 (6H, m), 4.46 (1H, dt, $J_{cis} = 6.2$ Hz, $J = 7.3$ Hz), 6.2 (1H, d, $J_{cis} = 6.2$ Hz). Anal. Calcd for $C_{12}H_{26}SiO_2$: C, 62.55; H, 11.37. Found: C, 62.35; 11.32.

***tert*-Butoxydimethylsilyl enol ether from cyclopentanone (5j)**: Colorless liquid; bp 65°C (5 mm Hg); d 0.890 g/ml; IR 1630 cm^{-1} (C = C); ^{1}H NMR δ 0.17 (6H, s), 1.28 (9H, s), 1.5–2.3 (4H, m), 2.23 (2H, q, $J = 5.9$ Hz), 4.70 (1H, br s); MS, *m/e* 214 (M^+), 199, 158, 157, 141, 133, 115, 75, 59, 57, 39. Anal. Calcd for $C_{11}H_{22}SiO_2$: C, 61.63; H, 10.34. Found: C, 61.71; H, 10.39.

***tert*-Butoxydimethylsilyl enol ether from cyclohexanone (5k)**: Colorless liquid; bp 54°C (1 mm Hg); d 0.876 g/ml; IR 1650 cm^{-1} (C = C); ^{1}H NMR δ 0.15 (6H, s), 1.28 (9H, s), 1.42–2.09 (8H, m), 4.89–4.97 (1H, m); MS, *m/e* 230 (M^+), 216, 215, 207, 188, 173, 159, 157, 75, 57. Anal. Calcd for $C_{12}H_{24}SiO_2$: C, 63.11; H, 10.60. Found: C, 63.16; H, 10.75.

***tert*-Butoxydimethylsilyl enol ether from 4-methylcyclohexanone (5l)**: Colorless liquid; bp 59°C (1.5 mm Hg); d 0.869 g/ml; IR 1660 cm^{-1} (C=C); ^{1}H NMR δ 0.14 (6H, s), 0.93 (3H, d, $J = 4.9$ Hz), 1.29 (9H, s), 1.37–2.50 (7H, m), 4.92 (1H, m); MS, *m/e* 242 (M^+), 227, 186, 185, 171, 169, 157, 144, 143, 129, 127, 75, 57. Anal. Calcd for $C_{13}H_{28}SiO_2$: C, 64.41; H, 10.81. Found: C, 64.33; H, 10.91.

***tert*-Butoxydimethylsilyl enol ether from cycloheptanone (5m)**: Colorless liquid; bp 45°C (1 mm Hg); d 0.906 g/ml; IR 1650 cm^{-1} (C = C); ^{1}H NMR δ 0.14 (6H, s), 1.28 (9H, s), 1.44–2.31 (10H, m), 5.09 (1H, t, $J = 6.6$ Hz); MS, *m/e* 241 (M^+-1), 226, 186, 185, 171, 169, 158, 157, 94, 75, 57. Anal Calcd for $C_{13}H_{28}SiO_2$: C, 64.41; H, 10.81. Found: C, 64.29; H, 10.98.

***tert*-Butoxydimethylsilyl enol ether from acetophenone (5n)**: Colorless liquid; bp 70°C (0.7 mm Hg); d 0.931 g/ml; IR 1610 cm^{-1} (C = C); ^{1}H NMR δ 0.27 (6H, s), 1.33 (9H, s), 4.61 (1H, d, $J = 1.5$ Hz), 4.93 (1H, d, $J = 1.4$ Hz), 7.25–7.28 (3H, m), 7.34–7.59 (2H, m); MS, *m/e* 235 (M^+-15), 193, 179, 135, 105, 103, 75, 45. Anal. Calcd for $C_{14}H_{22}SiO_2$: C, 67.15; H, 8.86. Found: C, 66.96; H, 8.86.

Hydrolysis. The hydrolysis of the silyl enol ether derived from cyclohexanone (**5k**) was investigated with the following solutions: A, HOAc/THF/H_2O. 1:10:1 (v/v); B, THF/1 M HCl, 20:1 (v/v); C, THF/1 M NaOH, 20:1 (v/v). For this purpose, silyl enol ether **5k** (1 mmol) was dissolved in 2.5 ml of solution A, B or C. After the indication time (Table 2), the internal standard, decane, was added, 10 ml of ether was used to extract the solution, and the solution was washed with H_2O (5 ml), dried with $MgSO_4$, and analyzed by GC.

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REFERENCES

1. (a) Ito, Y.; Hirao,T.; Saegusa, T. J. Org. Chem. **1978**, *43*, 1011; (b) Jung, M.E.; Pan, Y.; Rathke, M.W.; Sullivan, D.F.; Woodbury, R.P. J. Org. Chem. **1977**, *42*, 3961; (c) Murai, S.; Hatayama, Y.; Sonoda, N. Tetrahedron Lett. **1978**, 3455.
2. Hassner, A.; Reuss, R.H.; Pinnick, H.W. J. Org. Chem. **1975**, *40*, 3427.
3. Kobayashi, Y.; Taguchi, T.; Tokuno, E. Tetrahedron Lett. **1977**, 3741.
4. Rasmussen, J.K. Synthesis **1977**, *2*, 91.
5. Brownbridge, P. Synthesis **1983**, *1*, 85.
6. Yamamoto, Y.; Matui, C. Organometallics **1997**, *16*, 2204.
7. House, H.O.; Czuba, L.H.; Galiand, M.; Olmstead, H.P. J. Org. Chem. **1969**, *34*, 2324.
8. Stork, G.; Hudrlik, P.F. J. Am. Chem. Soc. **1968**, *90*, 4462.
9. Curent Aldrich prices: trimethyl silyl chloride ($26/mol, 99 + % purity); *tert*-butyldimethylsilyl chloride ($226/mol, 99% purity). The latter can be prepared from dimethylsilyl chloride and *tert*-butyllithium by the method of Corey for approximately half of the selling cost.[10]
10. Corey, E.J.; Venkateswarlu, A. J. Am. Chem. Soc. **1972**, *94*, 6190.
11. Manis, P.; Rathke, M.W. J. Org. Chem. **1981**, *46*, 5348.
12. Krolevets, A.A.; Antipova, V.V.; Popov, A.G.; Adamov, A.V. Zh. Obshch. Khim. **1988**, *58*, 2274.

13. Fataftah, Z.A.; Kopka, I.E.; Rathke, M.W. J. Am. Chem. Soc. **1980**, *102*, 3959.
14. Nakamura, E.E.; Hashimoto, K.; Kuwajima, I. Tetrahedron Lett. **1978**, 2079.

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