  Bull. Chem. Soc. Jpn., 62, 1193—1197 (1989)

Sequential Reactions of Michael Addition and Peterson Condensation of 1-Silylvinyl Ketones with Grignard Reagents: Study of Stereoselectivity

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(Received October 26, 1988)

1-Silylvinyl ketones undergo smooth Michael addition with Grignard reagents generating magnesium enolates which are then trapped with benzaldehyde to give *E*- and *Z*-isomers of enones after Peterson condensation. (*E*)-Olefins become major products under a thermodynamic control when the condensation with benzaldehyde is carried out at room temperature in diethyl ether, while *Z*-isomers are more favored as kinetically controlled products at −78 °C in THF. Reaction mechanism is briefly discussed.

Nucleophilic addition of organocopper reagents to α,β-unsaturated carbonyl compounds and subsequent trapping of the intermediate enolates with a variety of electrophiles are now synthetically useful.[1] Applications of this sequence to α,β-unsaturated ketones followed by enolate-trapping with aldehydes lead to β-hydroxy ketones.

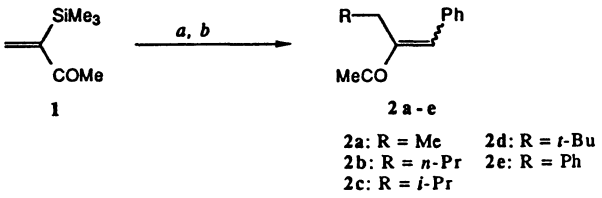
Michael addition of organometallics to 3-silyl-3-buten-2-ones[2,3] would offer a convenient and direct route to silyl-substituted metal enolates with a variety of counter cations. Hopefully the intermediate enolates may be utilized, in the same flask, to the Peterson condensation with carbonyl compounds leading to highly substituted enones.

In a previous communication,[4] we have reported the Michael addition-Peterson condensation sequence of methyl 2-(trimethylsilyl)acrylate with organomagnesium and -lithium compounds. As an extension of this program we have investigated the Michael addition-Peterson condensation sequence of 1-silylvinyl ketones with Grignard reagents. The details are presented here.

Results and Discussion

The Michael addition and Peterson condensation sequence of 3-trimethylsilyl-3-buten-2-one (**1**) was simply carried out by the initial treatment of **1** with a Grignard reagent followed by the reaction with benzaldehyde after completion of the Michael addition. No copper catalyst was needed in the Michael addition. For example, methylmagnesium iodide was added to a solution of **1** in diethyl ether at −15 °C, benzaldehyde was introduced after 1 h, and the reaction was continued at the same temperature for additional 1 h. The mixture was quenched with aqueous ammonium chloride to give a 6.7:1 mixture (by GLC) of *E*- and *Z*-isomers of 3-ethyl-4-phenyl-3-buten-2-one (**2a**) in 45% yield based on **1** (Scheme 1 and Entry 1 in Table 1). Both isomers could be separated from each other by column chromatography on silica gel.

Formation of (*E*)-olefins was again preferred in the



Scheme 1.

reactions of **1** with propyl-, isopropyl-, and phenylmagnesium bromides under the equal conditions, **2b** (*E*:*Z*=5.2 : 1, Entry 3), **2c** (5 : 1, Entry 6), and **2e** (6.5 : 1, Entry 21) being produced. However, *Z*-isomer was predominantly produced (*E* : Z=1 : 4.7, Entry 20) in the reaction of **1** with *t*-butylmagnesium chloride, which was carried out in tetrahydrofuran (THF).[5] This unusual selectivity will be discussed below.

Stereostructures of (*E*)-**2** and (*Z*)-**2** were based on the chemical shifts of the olefin proton and the acetyl methyl protons. One typical example is shown as follows in the case of **2b**. (*E*)-**2b**: δ=2.44 (MeCO) and 7.46 (4-H). (*Z*)-**2b**: 2.05 (MeCO) and 6.64 (4-H).

The reaction of **1** with isopropylmagnesium bromide and benzaldehyde was performed under a variety of conditions to know factors by which the *E*/*Z* selectivity is influenced. The *E*/*Z* ratios were determined by gas-liquid chromatography (GLC) using (*E*)-4-phenyl-3-buten-2-one as an internal reference.

The *E*/*Z* ratio was found to be dependent upon the reaction temperature as shown in Entries 5—8. Since (*E*)-**2c** was relatively more favored at a higher temperature (Entry 8, *E* : *Z*=5.4 : 1), (*E*)-**2c** must be a thermodynamically controlled product, and hence (*Z*)-**2c** is a kinetically controlled one. This indicates that either the Michael addition step or the Peterson condensation step is reversible.

Figure 1 shows a possible reaction course for the formation of both isomers of olefin **2c**. The Michael addition between **1** and isopropylmagnesium bromide forms (*E*)- **C** and/or (*Z*)-enolate(s) **D**. As the carbonyl

Table 1. The Michael-Peterson Sequence of 3-Trimethylsilyl-3-buten-2-one (**1**)

Entry	RMgX[a]	Solvent	Additive	Michael addition		Peterson condensation		Product	Yield/%[b]	$E:Z$[c]
				Temp/°C	Time/h	Temp/°C	Time/h			
1	MeMgI	Et_2O		−15	1	−15	1	**2a**	45	6.7:1
2	MeMgI	Et_2O		rt	1	rt	1	**2a**	59	*E* only
3	*n*-PrMgBr	Et_2O		−15	1	−15	1	**2b**	61	5.8:1
4	*n*-PrMgBr	Et_2O		rt	1	rt	1	**2b**	67	5.7:1
5	*i*-PrMgBr	Et_2O		−78	1	−78	1	**2c**	59	1.6:1[d]
6	*i*-PrMgBr	Et_2O		−15	1	−15	1	**2c**	48	5:1[d]
7	*i*-PrMgBr	Et_2O		0	1	0	1	**2c**	55	5.1:1[d]
8	*i*-PrMgBr	Et_2O		rt	2	rt	1	**2c**	45	5.4:1[d]
9	*i*-PrMgBr	Et_2O		−78 °C 1 h then rt 1 h		rt	1	**2c**	73	6.8:1[d]
10	*i*-PrMgBr	Et_2O		rt 1 h then −78 °C 1 h		−78	1	**2c**	57	2.2:1[d]
11	*i*-PrMgBr	Et_2O		rt	1	−78[e]	1	**2c**	77	6.8:1[d]
12	*i*-PrMgBr	THF		−78	1.5	−78	1	**2c**	64	1:1.9[d]
13	*i*-PrMgBr	THF		−15	1	−15	1	**2c**	60	1:2.6[d]
14	*i*-PrMgBr	Et_2O	THF[f]	−15	1	−15	1	**2c**	59	1:2[d]
15	*i*-PrMgBr	Et_2O	HMPA[g,h]	−15	1	−15	1	**2c**	51	1.1:1[d]
16	*i*-PrMgBr	Et_2O	HMPA[g,i]	−15	1	−15	1	**2c**	52	1.1:1[d]
17	*i*-PrMgBr	Et_2O	$SnCl_4$[g,h]	−78	1	−78	1	**2c**	51	1.6:1[d]
18	*i*-PrMgBr	Et_2O	$SnCl_4$[g,j]	−78	1	−78	1	**2c**	53	1.8:1[d]
19	*t*-BuMgCl	THF		−78	1	−78	1	**2d**	47	1:5.8
20	*t*-BuMgCl	THF		−15	1	−15	1	**2d**	40	1:4.7
21	PhMgBr	Et_2O		−15	1	−15	1	**2e**	63	6.5:1

a) 1.2 Equivalnt of a Grignard reagent was employed. b) Yield of isolated products based on **1**. c) Ratio of isolated isomers. d) Detemined by GLC. e) Cooled to −78 °C immediately after benzaldehyde was added. f) THF: Et_2O=1:3 v/v. g) Additive was added 0.5 h after the Michael addition was started. h) A catalytic amount. i) HMPA: Et_2O=1:2 v/v. j) 1 Equivalent was used.

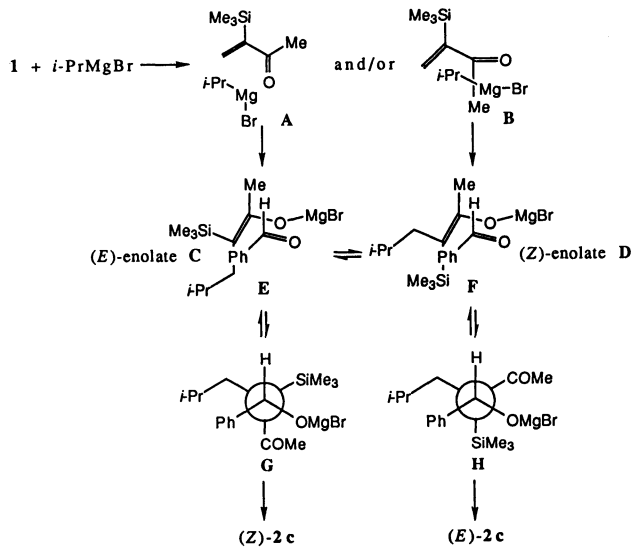


Fig. 1. Stereochemical course of the Michael-Peterson sequence between enone **1** and isopropylmagnesium bromide.

addition of magnesium enolates should be chelation-controlled,[6] the chair transition state **E** involving (*E*)-enolate **C** forms adduct alkoxide **G**; similarly its diastereomeric alkoxide **H** is formed from **F**. Cis-elimination is the far major path in the alkoxide-mediated Peterson condensation.[7] Therefore, (*Z*)-**2c** and (*E*)-**2c** are produced from **G** and **H**, respectively.

A high isomer ratio ($E:Z$=6.8:1, Entry 9) was obtained when the Michael adduct formed at −78 °C was warmed at room temperature for 1 h and the reaction with benzaldehyde was followed at the same temperature, while the stereoselectivity was poor ($E:Z$=2.2:1, Entry 10) when the adduct formed at room temperature was cooled to −78 °C and reacted with benzaldehyde.

It is concluded, on the ground of these results, that the stereostructures of product **2c** do not reflect those of magnesium enolate intermediates **C** and **D**,[8] and that the step of carbonyl addition is reversible. Thus, the thermodynamically controlled olefin, (*E*)-**2c**, was produced as a major product from the mixture of adduct alkoxides **G** and **H** which were equilibrating via **E** and **F**. The thermodynamic preference of (*E*)-**2c** might be due to the higher stabilization of (*Z*)-enolate **D** than **C** by an attractive interaction between the silyl and the alkoxide moieties.

Unlike in diethyl ether, (*Z*)-**2c** was produced as a major isomer in the reaction of **1** with isopropylmagnesium bromide and benzaldehyde in THF where the $E:Z$ ratio was not very much affected by the reaction temperature (Entries 12 and 13). A similar result was observed when THF (25 vol%) was added as an additive in the reaction performed in diethyl ether (Entry 14).

The aforementioned reaction of **1** with *t*-butylmagnesium chloride and benzaldehyde (Entry 20) in THF became a little more selective in favor of (*Z*)-**2c** when carried out at −78 °C ($E:Z$=1:5.8, Entry 19).

Thus the reaction in THF is kinetically controlled. As shown in Fig. 1, the Grignard reagent adds to enone **1** leading to (*E*)-enolate **C** as a kinetic adduct which

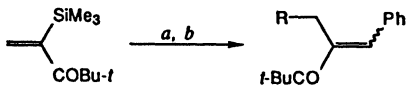
Table 2. The Michael-Peterson Sequence of 4,4-Dimethyl-2-trimethylsilyl-1-penten-3-one (**3**)

Entry	RMgX	Solvent	Michael addition		Peterson condensation		Product	Yield/%[a]	$E:Z$[b]
			Temp/°C	Time/h	Temp/°C	Time/h			
1	MeMgI	Et_2O	−78	1	−78 °C 1 h then	0 °C 30 min	Recovered **3**		
2	MeMgI	Et_2O	rt	1	rt	1	**4a**	80	1 : 1
3	*i*-PrMgBr	Et_2O	rt	1	rt	1	**4b**	84	1 : 1.5
4	*t*-BuMgCl	THF	−15	1	−15 °C 1 h then	0 °C 30 min	Recovered **3**		
5	*t*-BuMgCl	THF	rt	1	rt	1	**4c**	85	1 : 3.7

a) Yield of isolated products based on **3**. b) Determined by GLC.

gradually isomerizes into (*Z*)-enolate **D**. This isomerization presumably took place also in the reactions carried out in diethyl ether. As soon as the chelation-controlled addition of **C** to benzaldehyde forms the adduct alkoxide **G**, the elimination of silanol takes place quickly to give (*Z*)-**2c**. The elimination reaction is accelerated in THF because THF has a greater solvation ability than diethyl ether and therefore the oxygen-magnesium bond is much more polarized in this solvent.

Addition of hexamethylphosphoric triamide (HMPA) or tin(IV) chloride, either with a catalytic or a comparable amount, lowered the $E:Z$ ratio (Entries 15 to 18). These additives presumably broke down the chelation in the transition state of carbonyl addition.



3 **4a-c**

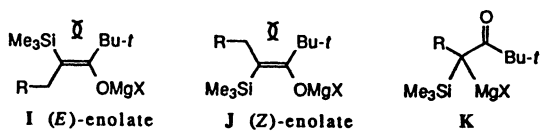
4a: R = Me
4b: R = *i*-Pr
4c: R = *t*-Bu

a: RMgX in diethyl ether at rt
b: PhCHO at rt

Scheme 2.

The vinylsilane with a bulky acyl substituent, 4,4-dimethyl-2-trimethylsilyl-1-penten-3-one (**3**), was employed to the Michael-Peterson sequence. No Michael addition of **3** proceeded with methylmagnesium iodide at −78 °C, and *t*-butylmagnesium chloride as a bulky Grignard reagent could not react even at −15 °C. The starting enone **3** was recovered in both cases (Entries 1 and 4 in Table 2). Therefore, all the sequences were carried out at room temperature.

Both reactions of **3** with methylmagnesium iodide (Entry 2) and isopropylmagnesium bromide (Entry 3) in diethyl ether gave almost 1 : 1 mixtures of the *E*- and *Z*-isomers of olefins **4**. The $E:Z$ selectivity was poor also in the reaction of **3** with *t*-butylmagnesium chloride in THF (Entry 5, $E:Z$=1 : 3.7).



Two sterically congested magnesium enolates, **I** and **J**, which are expected to form in the Michael additions of **3** with Grignard reagents, seem too unstable to be involved as reacting intermediates. Even if they exist, their thermodynamic stability can not be sufficiently high so as to fully contribute to such an equilibrium as Fig. 1 shows. Therefore the adduct anions formed in the Michael additions of **3** should have reacted with benzaldehyde in a way different from the case of **1**. Probably they were involved in the carbonyl condensations, at least partly, in the form of β-oxo Grignard reagents **K**. This would be the major reason why the $E:Z$ selectivity was so decreased both in the reactions in diethyl ether and THF.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-40 (90 MHz), a JEOL FX-100 (100 MHz), or a JEOL GSX-270 instrument (270 MHz), and ^{13}C NMR on a JEOL FX-100 (25.05 MHz) or a JEOL GSX-270 spectrometer (67.94 MHz). Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra as well as high-resolution mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. Elemental analyses were performed on a Hitachi 026 CHN analyzer. For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with an ionization flame detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×50000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Material. 3-Trimethylsilyl-3-buten-2-one (**1**) was prepared according to the reported method using 1-(trimethylsilyl)vinylmagnesium bromide.[2]

General Procedure for the Michael Addition and Peterson Condensation Sequence of 1-Silylvinyl Ketone 1. As a typical procedure, the reaction of **1** with methylmagnesium iodide and benzaldehyde is described. To a solution of freshly

prepared methylmagnesium iodide (1.2 mmol) in diethyl ether (3 ml) was added **1** (0.142 g, 1 mmol in diethyl ether (1 ml)) at −15 °C under dry nitrogen. After stirring for 1 h at this temperature, benzaldehyde (0.127 g, 1.2 mmol in diethyl ether (1 ml)) was added. The mixture was stirred at −15 °C for 1 h and then at 0 °C for 0.5 h. Saturated aqueous ammonium chloride was added and the organic products were collected in diethyl ether (30 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel by using hexane-ethyl acetate (30 : 1 v/v) to give (*Z*)-**2a** (0.01 g, 6%) and then (*E*)-**2a** (0.067 g, 39%).

In all other cases, the *E*- and *Z*-isomers were separated by silica-gel chromatography with hexane-ethyl acetate (30:1 v/v). The results are summarized in Table 1.

3-Ethyl-4-phenyl-3-buten-2-one (2a): (*E*)-**2a**: Colorless oil; IR (neat) 1662, 1490, 1380, 1345, 1228, 1115, 1020, 755, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.11 (3H, t, J=7.0 Hz, Et), 2.45 (3H, s, MeCO), 2.53 (2H, q, J=7.0 Hz, Et), 7.40 (5H, br s, Ph), and 7.47 (1H, s, 4-H); ^{13}C NMR ($CDCl_3$) δ=13.78, 19.63 (each Et), 26.09 (MeCO), 128.22, 128.58, 129.23, 135.81 (each Ph), 139.35 (4-C), 144.11 (3-C), and 200.08 (MeCO); MS m/z (rel intensity, %) 174 (M^+, base peak), 173 (62), 159 (56), 131 (72), 129 (19), 116 (23), 115 (28), 91 (55), 73 (50), and 43 (68). HRMS Found: m/z 174.1033. Calcd for $C_{12}H_{14}O$: M, 174.1044. (*Z*)-**2a**: Pale yellow liquid; IR (neat) 1655, 1430, 1380, 1340, 1220, 1115, 1020, 755, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.15 (3H, t, J=7.0 Hz, Et), 2.05 (3H, s, MeCO), 2.3—2.6 (2H, m, Et), 6.66 (1H, s, 4-H), and 7.1—7.5 (5H, m, Ph); MS m/z (rel intensity, %) 174 (M^+, base peak), 173 (66), 159 (74), 131 (93), 129 (25), 128 (18), 116 (31), 115 (49), 102 (24), 91 (85), 77 (36), 51 (25), and 43 (97). HRMS Found: m/z 174.1044. Calcd for $C_{12}H_{14}O$: M, 174.1044.

3-Butyl-4-phenyl-3-buten-2-one (2b): (*E*)-**2b**: Colorless liquid; IR (neat) 1660, 1375, 1350, 1240, 1215, 740, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (3H, t, *n*-Bu), 1.3—1.5 (4H, m, *n*-Bu), 2.44 (3H, s, MeCO), 2.50 (2H, t, J=7.0 Hz, *n*-Bu), 7.3—7.4 (5H, m, Ph), and 7.46 (1H, s, 4-H); ^{13}C NMR ($CDCl_3$) δ=13.85, 22.98, 26.16, 31.35 (each *n*-Bu), 31.35 (MeCO), 128.53, 129.24, 135.89, (each Ph), 139.38 (4-C), 143.12 (3-C), and 200.27 (MeCO); MS m/z (rel intensity, %) 202 (M^+, 31), 201 (15), 159 (22), 129 (30), 117 (47), 116 (17), 115 (49), 91 (36), 77 (16), and 43 (base peak). HRMS Found: m/z 202.1350. Calcd for $C_{14}H_{18}O$: M, 202.1357. (*Z*)-**2b**: Colorless oil; IR (neat) 1680, 1485, 1345, 1190, 1115, 750, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—1.1 (3H, m, *n*-Bu), 1.1—1.6 (4H, m, *n*-Bu), 2.04 (3H, s, MeCO), 2.2—2.5 (2H, m, *n*-Bu), 6.64 (1H, s, 4-H), and 7.1—7.6 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=13.88, 22.38, 30.40 (each *n*-Bu), 30.87 (MeCO), 35.20 (*n*-Bu), 127.83, 128.38, 128.46, 130.16 (each Ph), 136.52 (4-C), 145.01 (3-C), and 208.00 (MeCO); MS m/z (rel intensity,%) 202 (M^+, 4), 129 (20), 128 (15), 117 (47), 116 (16), 115 (60), 91 (35), 77 (16), and 43 (base peak). HRMS Found: m/z 202.1361. Calcd for $C_{14}H_{18}O$: M, 202.1357.

3-(2-Methylpropyl)-4-phenyl-3-buten-2-one (2c): (*E*)-**2c**: Colorless oil; IR (neat) 1670, 1470, 1380, 1350, 1225, 1130, 750, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.82 (6H, d, J=6.6 Hz, *i*-Bu), 1.6—1.8 (1H, m, *i*-Bu), 2.45 (3H, s, MeCO), 2.48 (2H, d, J=7.3 Hz, *i*-Bu), 7.3—7.4 (4H, m, Ph), and 7.50 (1H, s, 4-H); ^{13}C NMR ($CDCl_3$) δ=22.59, 26.34 (each *i*-Bu), 28.06 (MeCO), 34.47 (*i*-Bu), 128.35, 128.52, 129.25, 136.06 (each Ph), 139.78 (4-C), 142.70 (3-C), and 200.80 (MeCO); MS m/z (rel intensity, %) 202 (M^+, 7), 128 (10), 116 (12), 115 (52), 91 (12), and 43 (base peak). HRMS Found: m/z 202.1350. Calcd for $C_{14}H_{18}O$: M, 202.1357. (*Z*)-**2c**: Colorless oil; IR (neat) 1685, 1460, 1365, 1350, 1200, 1120, 755, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.79 (6H, d, J=6.6 Hz, *i*-Bu), 1.6—1.7 (1H, m, *i*-Bu), 1.86 (3H, s, MeCO), 2.10 (2H, dd, J=7.3 and 1.1 Hz, *i*-Bu), 6.49 (1H, s, 4-H), and 7.0—7.2 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=22.62 (*i*-Bu), 27.30 (MeCO), 31.08, 45.39 (each *i*-Bu), 128.17, 128.67, 128.73 (each Ph), 132.01 (4-C), 136.75 (Ph), 144.27 (3-C), and 208.02 (MeCO); MS m/z (rel intensity, %) 202 (M^+, 24), 159 (17), 117 (21), 116 (19), 115 (35), 91 (16), and 43 (base peak). HRMS Found: m/z 202.1354. Calcd for $C_{14}H_{18}O$: M, 202.1357.

3-(2,2-Dimethylpropyl)-4-phenyl-3-buten-2-one (2d): (*E*)-**2d**: Colorless oil; IR (neat) 1675, 1470, 1360, 1235, 1200, 1160, 755, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.69 (9H, s, *t*-Bu), 2.45 (3H, s, MeCO), 2.66 (2H, s, *t*-BuCH_2), 7.2—7.5 (5H, m, Ph), and 7.50 (1H, s, 4-H); ^{13}C NMR ($CDCl_3$) δ=29.86 (*t*-Bu), 33.23 (MeCO), 36.76 (*t*-Bu), 49.08 (*t*-BuCH_2), 128.45, 128.48, 129.00, 136.76 (each Ph), 139.61 (4-C), 142.43 (3-C), and 201.51 (MeCO); MS m/z (rel intensity, %) 216 (M+, 10), 160 (34), 159 (24), 145 (29), 117 (21), 116 (30), 115 (36), 56 (59), and 42 (base peak). HRMS Found: m/z 216.1510. Calcd for $C_{15}H_{20}O$: M, 216.1513. (*Z*)-**2d**: Pale yellow oil; IR (neat) 1675, 1470, 1360, 1200, 1155, 760, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (9H, s, *t*-Bu), 2.00 (3H, s, MeCO), 2.39 (2H, s, *t*-BuCH_2), 6.74 (1H, br s, 4-H), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=29.60 (*t*-Bu), 30.60 (MeCO), 32.17 (*t*-Bu), 49.07 (*t*-BuCH_2), 127.99, 128.43, 128.47 (each Ph), 135.11 (4-C), 136.70 (Ph), 143.15 (3-C), and 207.19 (MeCO); MS m/z (rel intensity, %) 216 (M^+, 27), 201 (16), 160 (base peak), 159 (48), 145 (42), 117 (30), 116 (78), 115 (30), and 56 (87). HRMS Found: m/z 216.1512. Calcd for $C_{15}H_{20}O$: M, 216.1513.

3-Benzyl-4-phenyl-3-buten-2-one (2e): (*E*)-**2e**: Colorless needles; mp 68—70 °C; IR (KBr) 1665, 1495, 1450, 1350, 1255, 1215, 970, 750, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.43 (3H, s, MeCO), 3.94 (2H, s, PhCH_2), 7.1—7.4 (10H, m, Ph), and 7.74 (1H, s, 4-H); ^{13}C NMR ($CDCl_3$) δ=26.29 (PhCH_2), 32.21 (MeCO), 126.04, 127.96, 128.55, 128.64, 128.94, 129.24, 135.36, 139.49 (each Ph), 139.87 (4-C), 141.22 (3-C), and 199.29 (MeCO); MS m/z (rel intensity, %) 236 (M^+, 35), 192 (25), 133 (20), 121 (69), 115 (62), 105 (43), 94 (27), 91 (49), 77 (28), 75 (24), 73 (40), 65 (35), and 43 (base peak). HRMS Found: m/z 236.1197. Calcd for $C_{17}H_{16}O$: M, 236.1200. (*Z*)-**2e**: Pale yellow oil; IR (neat) 1680, 1495, 1445, 1350, 1245, 1200, 830, 755, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.95 (3H, s, MeCO), 3.81 (2H, d, J=1.4 Hz, PhCH_2), 6.80 (1H, br s, 4-H), and 7.2—7.6 (10H, m, Ph); MS m/z (rel intensity, %) 236 (M^+, base peak), 235 (30), 221 (20), 193 (47), 192 (41), 178 (23), 115 (69), 91 (46), and 43 (36). HRMS Found: m/z 236.1196. Calcd for $C_{17}H_{16}O$: M, 236.1200.

4,4-Dimethyl-2-trimethylsilyl-1-penten-3-one (3): This compound was prepared by an application of the synthetic method of **1**.[2] From 1-bromo-1-(trimethylsilyl)ethene (5.0 g, 28 mmol), magnesium metal (0.83 g), and 2,2-dimethylpropanal (2.4 g, 28 mmol), enone **3** was obtained in 32% yield: Pale yellow liquid; bp 97—99 °C/4790 Pa (bulb-to-bulb); IR (neat) 2970, 1670, 1480, 1365, 1250, 1180, 1050, 1000, 940, 850, 760, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.15 (9H, s, Me_3Si), 1.19 (9H, s, *t*-Bu), 5.67, and 5.84 (each 1H, d, J=2.2 Hz, =CH_2); ^{13}C NMR ($CDCl_3$) δ=−1.02 (Me_3Si), 27.39, 44.06 (each *t*-Bu), 126.62 (=CH_2), 155.66 (2-C), and 215.57 (CO); MS m/z (rel intensity, %) 184 (M^+, 6), 127 (37), 73 (72), 57 (49), 45 (21), and 43 (base peak).

General Procedure for the Michael Addition and Peterson Condensation Sequence of 1-Silylvinyl Ketone 3. As a typical procedure, the reaction of **3** with methylmagnesium iodide and benzaldehyde is described. To a solution of freshly prepared methylmagnesium iodide (1.2 mmol) in diethyl ether (3 ml) was added **3** (0.168 g, 0.91 mmol in diethyl ether (1 ml)) at −15 °C under dry nitrogen. After stirring for 1 h at this temperature, benzaldehyde (0.127 g, 1.2 mmol in diethyl ether (1 ml)) was added. The mixture was stirred at −15 °C for 1 h. Saturated aqueous ammonium chloride was added and the organic products were collected in diethyl ether (30 ml × 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel by using hexane-ethyl acetate (50 : 1 v/v) to give an inseparable mixture of *E*- and *Z*-isomers of **4a** (0.158 g, 80%, *E* : *Z*=1 : 1 (GLC)).

All results obtained in other cases are listed in Table 2.

2-Ethyl-4,4-dimethyl-1-phenyl-1-penten-3-one (4a): Obtained as an inseparable 1 : 1 mixture of *E*- and *Z*-isomers (GLC). Colorless oil; IR (neat) 1680, 1475, 1460, 1390, 1360, 1170, 1080, 1065, 930, 750, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) *E*-isomer: δ=1.32 (9H, s, *t*-Bu), 1.17 (3H, t, *J*=7.7 Hz, Et), 2.54 (2H, dq, *J*=7.7 and 1.8 Hz, Et), 6.82 (1H, s, 1-H), and 7.2—7.4 (10H, m, Ph). *Z*-isomer: δ=0.99 (9H, s, *t*-Bu), 1.03 (3H, t, *J*=7.7 Hz, Et), 2.34 (2H, dq, *J*=7.7 and 1.8 Hz, Et), 6.35 (1H, s, 1-H), and 7.2—7.4 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=12.54, 13.43 (each Et), 22,52, 29,21 (each Et), 27.44, 28,29 (each *t*-Bu), 44.19, 44.25 (each *t*-Bu), 127.30, 127.57, 128.32, 128.38, 128.85, 129.72, 130.65, (each Ph), 136.04, 137.23, (each 1-C), 145.34, 144.39 (each 2-C), 212.65, and 218.50 (each CO); MS *m/z* (rel intensity, %) 216 (M^+, 9), 159 (base peak), 131 (90), 129 (26), 116 (37), 115 (58), 91 (87), 57 (37), and 41 (43). HRMS Found: *m/z* 216.1515. Calcd for $C_{15}H_{20}O$: M, 216.1513.

4,4-Dimethyl-2-(2-methylpropyl)-1-phenyl-1-penten-3-one (4b): Obtained as an inseparable 1 : 1.3 mixture of *E*- and *Z*-isomers (GLC). Colorless oil; IR (neat) 1685, 1480, 1465, 1370, 1095, 985, 755, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) *E*-isomer: δ=0.84 (6H, d, *J*=6.6 Hz, *i*-Bu), 1.33 (9H, s, *t*-Bu), 2.43 (2H, dd, *J*=7.3 and 1.1 Hz, *i*-Bu), 6.89 (1H, br s, 1-H), and 7.2—7.4 (10H, m, Ph). *Z*-isomer: δ=0.97 (6H, d, *J*=6.6 Hz, *i*-Bu), 1.00 (9H, s, *t*-Bu), 2.17 (2H, dd, *J*=7.3 and 1.1 Hz, *i*-Bu), 6.32 (1H, br s, 1-H), and 7.2—7.4 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) *E*-isomer: δ=22.61, 27.92 (each *i*-Bu), 28.55 (*t*-Bu), 37.68 (*i*-Bu), 44.15 (*t*-Bu), 143.11 (2-C), and 212.84 (CO). *Z*-isomer: δ=22.35, 26.80 (each *i*-Bu), 27.47, 44.28 (each *t*-Bu), 46.12 (*i*-Bu), 142.80 (2-C), and 217.65 (CO). Other signals are overlapped: δ=127.08, 127.32, 127.44, 128.30, 128.38, 128.91, 132.18, 136.22, 137.09; MS *m/z* (rel intensity, %) 244 (M^+, 3), 115 (32), 57 (98), 43 (38), and 41 (base peak). HRMS Found: *m/z* 244.1823. Calcd for $C_{17}H_{24}O$: M, 244.1826.

4,4-Dimethyl-2-(2,2-dimethylpropyl)-1-phenyl-1-penten-3-one (4c): Obtained as a 1 : 3.7 mixture of *E*- and *Z*-isomers (GLC) from which each isomer was roughly separated by column chromatography on silica gel with hexane-ethyl acetate (50 : 1 v/v). (*E*)-**4c**: Colorless oil; ^1H NMR ($CDCl_3$) δ=0.76, 1.38 (each 9H, s, *t*-Bu), 2.60 (2H, s, *t*-$BuCH_2$), 7.07 (1H, s, 1-H), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=29.45 (*t*-Bu), 29.69, 32.67, 40.03 (each *t*-$BuCH_2$), 44.06 (*t*-Bu), 127.35, 128.35, 128.81, (each Ph), 134.29 (1-C), 136.70 (Ph), 141.88 (2-C), and 212.69 (CO); MS *m/z* (rel intensity, %) 258 (M^+, 7), 201 (base peak), 145 (30), 115 (29), 57 (68), and 40 (40). HRMS Found: *m/z* 258.1968. Calcd for $C_{18}H_{26}O$: M, 258.1982. (*Z*)-**4c**: Colorless solid; mp 47—49 °C; IR (KBr) 1670, 1450, 1350, 1220, 1110, 980, 745, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.99, 1.00 (each 9H, s, *t*-Bu), 2.21 (2H, d, *J*=1.1 Hz, *t*-$BuCH_2$), 6.36 (1H, br s, 1-H), and 7.2—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=27.76 (*t*-Bu), 29.92, 32.89 (each *t*-$BuCH_2$), 44.22 (*t*-Bu), 49.66 (*t*-$BuCH_2$), 127.31, 128.17, 128.65 (each Ph), 129.93 (1-C), 136.84 (Ph), 141.67 (2-C), and 216.88 (CO); MS *m/z* (rel intensity, %) 258 (M^+, 6), 201 (base peak), 145 (24), 115 (25), 57 (60), and 40 (35). HRMS Found: *m/z* 258.1988. Calcd for $C_{18}H_{26}O$: M, 258.1982.

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