February 1994 Chem. Pharm. Bull. 42(2) 233—236 (1994)

Chemistry of Silylketenes: Simple Preparation of Silylallenes by the Reaction of Silylketenes with Phosphorus Ylides

Yasuyuki KITA,* Yasunori TSUZUKI, Shinji KITAGAKI, and Shuji AKAI

Faculty of Pharmaceutical Sciences, Osaka University, 1–6 Yamada-oka, Suita, Osaka 565, Japan.

Received July 1, 1993; accepted September 18, 1993

Reaction of silylketenes 1a, b with stabilized ylides 2a—e readily gave silylallenes 3a—f in high yields. However, similar reaction of 1a with the less stable ylides 2f, g resulted in low yields of the allenes 3g, h. Use of silylketenes 5a, c with an additional trimethylsilyl group overcame this problem to give silylallenes 3c, g—k directly in considerable to good yields. In this reaction, the additional trimethylsilyl group apparently worked as a masking group.

Keywords silylketene; Wittig reaction; phosphorus ylide; silylallene; deprotonation; bissilylketene

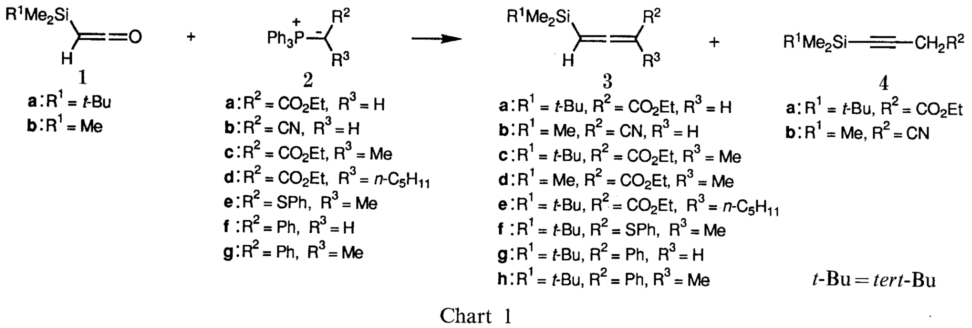
In connection with our study on the reaction of silylketenes **1** with nucleophiles leading to silylated reactive compounds,[1] we have been interested in the Wittig-type reaction[2] of **1** and phosphorus ylides **2**. It is expected that addition of **2** to the carbonyl group of **1** will give the corresponding betaine, from which spontaneous elimination of phosphine oxide occurs to provide silylallene **3**.[3—7] Although two papers have already been presented on this topic, examples are limited to the reaction of (trimethylsilyl)ketene and a few stabilized phosphorus ylides **2** ($R^2 = CO_2Me$, CO_2Et, CN; $R^3 = H$) and the products were obtained as mixtures of the silylallenes **3** and their isomers, silylacetylenes **4**.[8] Even in the reactions of the parent ketene or substituted ketenes with phosphorus ylides, successful preparation of allenes has been limited to a few exceptional cases.[9] We have investigated the reaction of silylketenes **1a, b**, **5a—c** with several types of phosphorus ylides **2a—i** and found that i) several stabilized ylides **2a—e** readily reacted with **1a, b** to give **3a—f** in high yields, while reaction of the less stable ones **2f, g** gave low yields of **3g, h** and ii) in the latter case, use of bissilylated ketenes **5a, c** instead of **1a, b** overcame this problem to give the mono-silylated allenes **3c, g—k** in considerable to good yields.

Results and Discussion

We first examined the reaction of **1a, b** with stabilized phosphorus ylides **2a, b**. A methylene chloride solution of **1a** was added to a methylene chloride solution of **2a** at 0 °C (method A). The reaction was completed instantly, and only silylacetylene **4a** was obtained in a quantitative yield (entry 1 in Table I). Among various reaction conditions tried, including reaction temperature, addition rate, and so on, reverse addition at low temperature provided **3a** selectively. Thus, a methylene chloride solution of **2a** was gradually added to a methylene chloride solution of **1a** (1.2 eq to **2a**) over 1 h at −40 °C (method B) to give **3a**, which was confirmed by direct IR and ^{1}H-NMR (chloroform-*d* was used as a solvent instead of methylene chloride) analyses of the reaction mixture. However, when the reaction mixture was warmed to room temperature, **3a** gradually isomerized into **4a**, and even quick concentration of the mixture in an ice-bath completely converted **3a** into **4a**. The reaction of **1b** and **2b** showed a similar result. The very facile isomerization of **3a, b** into **4a, b** is presumably caused by a trace of remaining **2a, b** or the eliminated triphenylphosphine oxide, and this was suppressed by using a 9 : 1 mixture of hexane–methylene chloride as the solvent and/or addition of hexane to the reaction mixture followed by filtration of **2a, b** and triphenylphosphine oxide before concentration of the reaction mixture. Thus, **3a, b** were obtained in 89% and 98% yields with less than 10% contamination with **4a, b** (entries 2 and 3).

On the other hand, reaction of the stabilized ylides **2c, d** having an alkyl substituent as R^3 readily gave the pure silylallenes **3c—e** in high yields (entries 4—6). The ylide **2e** with a phenylthio group also gave the (phenylthio)silylallene **3f** in 64% yield (entry 7) (Chart 1).

Next, we studied the reaction of the less stable ylides **2f, g** having a phenyl substituent. Reaction of **2f, g** with **1a** proceeded at 0 °C within 1 h. However, the expected silylallenes **3g, h** were obtained in only 15—21% yields accompanied with complex mixtures. These results are probably owing to the nature of the nucleophiles. That is, addition of soft nucleophiles **2a—e** to the softer



1
a: R^1 = *t*-Bu
b: R^1 = Me

2
a: $R^2 = CO_2Et$, R^3 = H
b: R^2 = CN, R^3 = H
c: $R^2 = CO_2Et$, R^3 = Me
d: $R^2 = CO_2Et$, R^3 = n-C_5H_{11}
e: R^2 = SPh, R^3 = Me
f: R^2 = Ph, R^3 = H
g: R^2 = Ph, R^3 = Me

3
a: R^1 = *t*-Bu, $R^2 = CO_2Et$, R^3 = H
b: R^1 = Me, R^2 = CN, R^3 = H
c: R^1 = *t*-Bu, $R^2 = CO_2Et$, R^3 = Me
d: R^1 = Me, $R^2 = CO_2Et$, R^3 = Me
e: R^1 = *t*-Bu, $R^2 = CO_2Et$, R^3 = n-C_5H_{11}
f: R^1 = *t*-Bu, R^2 = SPh, R^3 = Me
g: R^1 = *t*-Bu, R^2 = Ph, R^3 = H
h: R^1 = *t*-Bu, R^2 = Ph, R^3 = Me

4
a: R^1 = *t*-Bu, $R^2 = CO_2Et$
b: R^1 = Me, R^2 = CN

t-Bu = *tert*-Bu

Chart 1

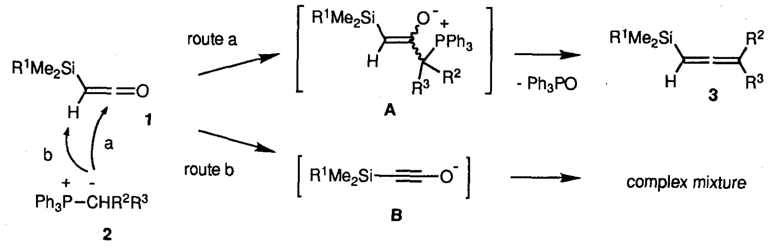


Chart 2

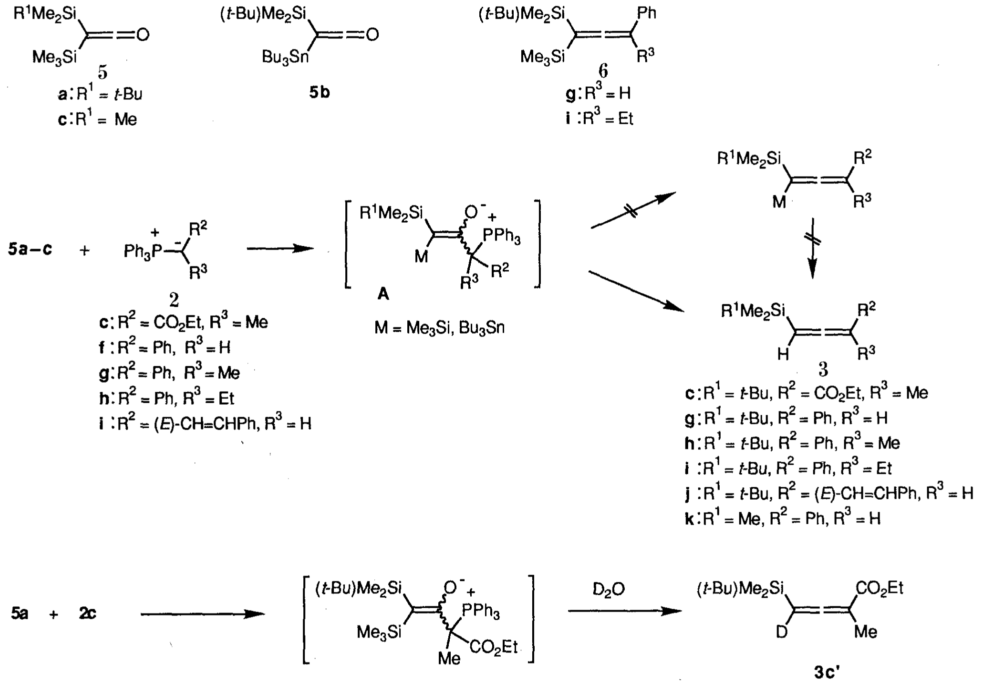


Chart 3

TABLE I. Preparation of Silylallenes **3** from Silylketenes **1** or **5** and Phosphorus Ylides **2**

Entry	Silylketene	Wittig reagent	Conditions[a]	Silylallene, % yield	
1	**1a**	**2a**	A, CH_2Cl_2, 0°C, 10 min	**3a**	— [**4a**, 99% (≤1:99)[b]]
2	**1a**	**2a**	B, hexane–CH_2Cl_2 (9:1), −40 °C, 1 h	**3a**	89[c] (91::9)[b] (≥99:1)[d]
3	**1b**	**2b**	B, CH_2Cl_2, −40 °C, 1 h	**3b**	98[c] (92:8)[b] (≥99:1)[d]
4	**1a**	**2c**	B, CH_2Cl_2, −40 → −20 °C, 2 h	**3c**	98
5	**1b**	**2c**	B, CH_2Cl_2, −40 °C, 1 h	**3d**	95
6	**1a**	**2d**	B, CH_2Cl_2, −40 → −20 °C, 4 h	**3e**	96
7	**1a**	**2e**	THF, r.t., 2 h	**3f**	64
8	**5a**	**2f**	C_6H_6, r.t., 1 d	**3g**	72 [15][e]
9	**5b**	**2f**	C_6H_6, r.t., 1 d	**3g**	51
10	**5a**	**2g**	C_6H_6, reflux, 7 h	**3h**	58 [21][e]
11	**5a**	**2h**	C_6H_6, reflux, 12 h	**3i**	62
12	**5a**	**2i**	Et_2O, r.t., 1.5 d	**3j**	47
13	**5a**	**2c**	CH_2Cl_2, r.t., 1 d	**3c**	91
14	**5c**	**2f**	Et_2O, r.t., 1 d	**3k**	55

a) A: Addition of a solution of **1** to a solution of **2**. B: Dropwise addition of a solution of **2** to a solution of **1** over 1 h. *b)* Ratio of **3** to **4** determined by IR and 200 MHz ^{1}H-NMR analyses of the product. *c)* Total yield of **3** and **4**. *d)* Ratio of **3** to **4** determined by IR and 200 MHz ^{1}H-NMR analyses of the reaction mixture after being stirred at −40 °C for 1 h. *e)* Yield of **3** by the reaction of **1a** and the corresponding **2** in Et_2O at room temperature for 1 h.

carbonyl carbon of **1** leads to **3** *via* the betaine **A** (route a in Chart 2), while the less soft **2f, g** abstract the harder proton of **1** to generate the ynolate anion **B**, resulting in formation of a complex mixture (route b).[10]

To resolve this problem, the use of silylketenes **5a**—**c** masked by an additional trimethylsilyl or tributylstannyl group was quite effective. For instance, reaction of the bissilylated ketene **5a** with **2f** at room temperature for 1 d caused allene formation, and more interestingly, simultaneous removal of the trimethylsilyl group took place to provide the desired mono-silyl allene **3g** in 72% yield (entry 8). No other allenic products, such as the bissilylallene **6g**, were obtained. Similar successful one-step preparation of **3g** was achieved by use of the stannylated ketene **5b**, but the yield was slightly lower (51%) (entry 9). In these reactions, the trimethylsilyl and tributylstannyl groups of **5** apparently worked as masking groups of the proton of **1**, causing the nucleophile **2** to add to the carbonyl group of **5**, and then were removed spontaneously. Using **5a**, silylallenes **3h**—**j** were prepared from less stable ylides **2g**—**i** in moderate yields (entries 10—12). The stabilized ylide **2c** also reacted with **5a** to give **3c** in 91% yield (entry 13). Reaction of bis(trimethylsilyl)ketene **5c** with **2f** gave (trimethylsilyl)allene **3k** in 55% yield, in which one of two silyl groups worked as the masking group (entry 14) (Chart 3).

The cleavage mechanism of the masking trimethylsilyl group is quite interesting. Our preliminary study has revealed some facts: i) direct analysis of the reaction mixture of **5a** and **2c** in methylene chloride by IR spectroscopy disclosed that **3c** was already formed in the course of the reaction, and no absorption peaks of other allenic products were observed, ii) the bissilylallene **6i**, prepared from **3i** by lithiation and silylation, was not desilylated to **3i** under similar reaction conditions to those used for preparation of **3** [triphenylphosphine oxide with or without LiBr (formed during the preparation of **2**) in benzene in the range of room temperature to reflux for 2 d], iii) the bissilylketene **5a** was not converted into **1a** under the same conditions, and iv) reaction of **5a** with **2c** in methylene chloride in the presence of a few drops of deuterium oxide gave the silylallene **3c′** (95% deuteration at the allenic proton) in 92% yield (Chart 3). Therefore, the reaction plausibly proceeded to give the adduct **A** (M$=$SiMe$_3$) followed by very fast protodesilylation and subsequent elimination of triphenylphosphine oxide.

Further elucidation of the mechanism and application of these silylketenes **1** and **5** to organic syntheses are in progress.

Experimental

All boiling points are uncorrected. IR absorption spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H-NMR spectra were recorded on a Varian VXR-200 and a JEOL JNM-EX270 spectrometer with SiMe$_4$ or CHCl$_3$ as internal standards. High-resolution mass spectra (HRMS) were recorded at 70 or 20 eV with a direct inlet system on a JEOL JMS-D300 spectrometer. E. Merck Silica gel 60 (0.063—0.200 nm, 70—230 mesh ASTM) and E. Merck pre-coated TLC plates, Silica gel 60 F$_{254}$, were used for column chromatography and for preparative TLC, respectively. Silylketenes **1a**,[1a] **1b**,[8] and **5c**[10] and phosphorus ylides **2**[2] were prepared according to the reported methods. The silylketenes **5a, b** were prepared as follows.

(*tert*-Butyldimethylsilyl)(trimethylsilyl)ketene (5a) Under a nitrogen atmosphere, a solution of *n*-BuLi (1.6 M, 9.4 ml, 15 mmol) in dry THF (120 ml) was cooled to −100 °C. A solution of **1a** (2.3 g, 15 mmol) in dry THF (50 ml) was added over 30 min. The reaction mixture was stirred at the same temperature for 30 min, and Me$_3$SiCl (2.0 ml, 16 mmol) was added. The whole was stirred at the same temperature for 1 h and then at −78 °C for 3 h, and pentane (200 ml) and saturated aqueous NaHCO$_3$ (200 ml) were added. The organic layer was separated and the aqueous layer was extracted with pentane (200 ml). The combined organic layer was dried with Na$_2$SO$_4$ and concentrated under reduced pressure to give **5a** (3.3 g, 96%) as a colorless oil. Distillation under reduced pressure gave analytically pure **5a**: bp 75—76 °C (7.5 mmHg); IR (CHCl$_3$): 2078 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ: 0.14 (6H, s, SiMe$_2$), 0.21 (9H, s, SiMe$_3$), 0.93 (9H, s, Si^{t}Bu). *Anal.* Calcd for C$_{11}$H$_{24}$OSi$_2$: C, 57.82; H, 10.59. Found: C, 57.85; H, 10.36.

(*tert*-Butyldimethylsilyl)(tributylstannyl)ketene (5b) Similarly to the preparation of **5a**, the ketene **5b** (0.46 g, 95%) was obtained from **1a** (0.156 g, 1.0 mmol), *n*-BuLi (0.63 ml, 1.0 mmol) and Bu$_3$SnCl (0.36 g, 1.1 mmol) as a colorless oil; IR (CHCl$_3$): 2056 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ: 0.07 (6H, s, SiMe$_2$), 0.91 (9H, t, $J=7.5$ Hz, CH$_3$ × 3), 0.93 (9H, s, Si^{t}Bu), 1.01—1.06 (6H, m, CH$_2$ × 3), 1.22—1.41 (6H, m, CH$_2$ × 3), 1.42—1.61 (6H, m, CH$_2$ × 3).

Ethyl 4-(*tert*-Butyldimethylsilyl)-2,3-butadienoate (3a). A Typical Procedure for the Preparation of Silylallenes 3a, b from Silylketenes 1a, b and Stabilized Phosphorus Ylides 2a, b (Entries 2 and 3 in Table I) Under a nitrogen atmosphere, a solution of **2a** (0.35 g, 1.0 mmol) in a mixture of dry hexane (12 ml) and dry CH$_2$Cl$_2$ (1.3 ml) was added dropwise to a solution of **1a** (0.19 g, 1.2 mmol) in the same mixed solvent (13 ml) over 1 h at −40 °C. The mixture was stirred for 1 h at the same temperature, hexane (30 ml) was added, and the precipitates were filtered off. The filtrate was concentrated under reduced pressure below room temperature to about 20% of its initial volume. Hexane (30 ml) was added again, and similar filtration and concentration were repeated two more times. Finally, complete concentration gave a 91 : 9 mixture (0.20 g, 89% yield) of the silylallene **3a** and the silylacetylene **4a** as a colorless oil; bp 64—65 °C (0.25 mmHg); *Anal.* Calcd for C$_{12}$H$_{22}$O$_2$Si: C, 63.66; H, 9.80. Found: C, 63.18; H, 9.63. HRMS Calcd for C$_{11}$H$_{19}$O$_2$Si (M$^+-$Me): 211.1155. Found: 211.1162. Spectral data for **3a** are as follows; IR (CHCl$_3$): 1933, 1703 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ: 0.10 (6H, s, SiMe$_2$), 0.91 (9H, s, Si^{t}Bu), 1.24 (3H, t, $J=8$ Hz, CH$_3$), 4.05—4.24 (2H, m, CH$_2$), 5.26 (1H, d, $J=6.5$ Hz, CH$=$), 5.38 (1H, d, $J=6.5$ Hz, CH$=$).

4-(Trimethylsilyl)-2,3-butadienonitrile (3b) Similarly to the above procedure, except for the solvent (CH$_2$Cl$_2$ was used instead of a mixture of hexane and CH$_2$Cl$_2$), a 92:8 mixture of the silylallene **3b** and the silylacetylene **4b** was obtained as a colorless oil; bp 47—49 °C (1.5 mmHg); HRMS Calcd for C$_7$H$_{11}$NSi (M$^+$): 137.0659. Found: 137.0653. Spectral data for **3b** are as follows: IR (CHCl$_3$): 2224, 1935 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ: 0.20 (9H, s, SiMe$_3$), 4.86 (1H, d, $J=6.5$ Hz, CH$=$), 5.54 (1H, d, $J=6.5$ Hz, CH$=$).

A General Procedure for the Preparation of Silylallenes 3c—e from Silylketenes 1a, b and Stabilized Phosphorus Ylides 2c, d (Entries 4—6) Similarly to the preparation of **3a**, a solution of **2** (1.05 mmol) in dry CH$_2$Cl$_2$ (13 ml) was added to a solution of **1** (1.0 mmol) in dry CH$_2$Cl$_2$ (13 ml) at −40 °C. The reaction mixture was stirred under the reaction conditions shown in Table I. The reaction mixture was concentrated under reduced pressure to give a residue, and hexane (30 ml) was added. The precipitates were filtered off, and the filtrate was concentrated under reduced pressure to give **3**. The yield of the product is shown in Table I, and its purity ($\geq$98%) was determined by ^{1}H-NMR analysis.

Ethyl 4-(*tert*-Butyldimethylsilyl)-2-methyl-2,3-butadienoate (3c) A colorless oil; bp 73—75 °C (0.4 mmHg); IR (CHCl$_3$): 1933, 1694 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ: 0.08 (6H, s, SiMe$_2$), 0.93 (9H, s, Si^{t}Bu), 1.25 (3H, t, $J=7.5$ Hz, CH$_3$), 1.81 (3H, d, $J=3.5$ Hz, CH$_3$), 4.05—4.28 (2H, m, CH$_2$), 5.27 (1H, q, $J=3.5$ Hz, CH$=$). HRMS Calcd for C$_{13}$H$_{24}$O$_2$Si (M$^+$): 240.1545. Found: 240.1561.

Ethyl 2-Methyl-4-(trimethylsilyl)-2,3-butadienoate (3d) A colorless oil; bp 48—49 °C (1.5 mmHg); IR (CHCl$_3$): 1933, 1694 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ: 0.14 (9H, s, SiMe$_3$), 1.24 (3H, t, $J=7$ Hz, CH$_3$), 1.81 (3H, d, $J=3.5$ Hz, CH$_3$), 4.02—4.30 (2H, m, CH$_2$), 5.29 (1H, q, $J=3.5$ Hz, CH$=$). HRMS Calcd for C$_{10}$H$_{18}$O$_2$Si (M$^+$): 198.1075. Found: 198.1105.

Ethyl 4-(*tert*-Butyldimethylsilyl)-2-pentyl-2,3-butadienoate (3e) A colorless oil; bp 94—95 °C (0.5 mmHg); IR (CHCl$_3$): 1929, 1694 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ: 0.09 (6H, s, SiMe$_2$), 0.88 (3H, t, $J=7$ Hz, CH$_3$), 0.93 (9H, s, Si^{t}Bu), 1.16—1.46 (6H, m, CH$_2$ × 3), 1.24 (3H, t, $J=7.5$ Hz, CH$_3$), 2.13—2.21 (2H, m, CH$_2$), 4.04—4.21 (2H, m, CH$_2$), 5.33 (1H, t, $J=3.5$ Hz, CH$=$). HRMS Calcd for C$_{17}$H$_{32}$O$_2$Si (M$^+$): 296.2169. Found: 296.2167.

3-(*tert*-Butyldimethylsilyl)-1-methyl-1,2-propadienyl Phenyl Sulfide (3f) (Entry 7) Under a nitrogen atmosphere, the ylide **2e** was prepared from (ethyl)triphenylphosphonium bromide (0.30 g, 0.80 mmol), *n*-BuLi (1.6 M, 0.50 ml, 0.80 mmol), and PhSCl (58 mg, 0.40 mmol) in dry tetrahydrofuran (THF) (3 ml) according to the reported method.[11] To the above solution was added a solution of **1a** (31 mg, 0.20 mmol) in THF (0.2 ml) and the whole was stirred at room temperature for 2 h. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (hexane as an eluent) to give **3f** (35 mg, 64%) as a colorless oil. IR ($CHCl_3$): 1929, 1582 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.07 (3H, s, SiMe), 0.08 (3H, s, SiMe), 0.90 (9H, s, Si^{t}Bu), 1.92 (3H, d, $J=3.5$ Hz, CH_3), 5.03 (1H, q, $J=3.5$ Hz, CH=), 7.17—7.51 (5H, m, arom. H). HRMS Calcd for $C_{16}H_{24}SSi$ (M^+): 276.1367. Found: 276.1367.

A General Procedure for the Preparation of Silylallenes 3c, g—k from Silylketenes 5a—c and Phosphorus Ylides 2c, f—i (Entries 8—14) Under a nitrogen atmosphere, a suspension of **2** in a dry solvent (1.5 ml) as shown in Table I was prepared from the corresponding phosphonium halide (0.38 mmol) and *n*-BuLi (0.38 mmol) according to the reported procedure,[2] and to this was added a solution of **5** (0.25 mmol) in the same solvent (1.5 ml) at 0 °C. The reaction mixture was stirred at the temperature for the period as shown in Table I. Hexane (5 ml) was added, and the precipitate was filtered off. Concentration of the filtrate under reduced pressure gave an oil, which was purified by silica gel column chromatography (hexane as an eluent) to give pure **3**. The yield of the product is shown in Table I.

1-(*tert*-Butyldimethylsilyl)-3-phenyl-1,2-propadiene (3g) A colorless oil; bp 64—65 °C (0.4 mmHg) (bath temp.); IR ($CHCl_3$): 1925, 1597 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.09 (3H, s, SiMe), 0.10 (3H, s, SiMe), 0.95 (9H, s, Si^{t}Bu), 5.40 (1H, d, $J=7$ Hz, CH=), 5.85 (1H, d, $J=7$ Hz, CH=), 7.12—7.29 (5H, m, arom. H). HRMS Calcd for $C_{15}H_{22}Si$ (M^+): 230.1491. Found: 230.1511.

1-(*tert*-Butyldimethylsilyl)-3-phenyl-1,2-butadiene (3h) A colorless oil; IR ($CHCl_3$): 1925, 1597 cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ: 0.07 (3H, s, SiMe), 0.09 (3H, s, SiMe), 0.94 (9H, s, Si^{t}Bu), 2.05 (3H, d, $J=3.5$ Hz, CH_3), 5.28 (1H, d, $J=3.5$ Hz, CH=), 7.12—7.36 (5H, m, arom. H). HRMS Calcd for $C_{16}H_{24}Si$ (M^+): 244.1644. Found: 244.1639.

1-(*tert*-Butyldimethylsilyl)-3-phenyl-1,2-pentadiene (3i) A colorless oil; IR ($CHCl_3$): 1923, 1597 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.08 (3H, s, SiMe), 0.09 (3H, s, SiMe), 0.96 (s, 9H, Si^{t}Bu), 1.15 (3H, t, $J=7$ Hz, CH_3), 2.41 (2H, qd, $J=7$, 4 Hz, CH_2), 5.40 (1H, d, $J=4$ Hz, CH=), 7.12—7.39 (5H, m, arom. H). HRMS Calcd for $C_{17}H_{26}Si$ (M^+): 258.1803. Found: 258.1813.

(*E*)-1-(*tert*-Butyldimethylsilyl)-5-phenyl-1,2,4-pentatriene (3j) A colorless oil; IR ($CHCl_3$): 1918, 1597 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.09 (3H, s, SiMe), 0.10 (3H, s, SiMe), 0.93 (s, 9H, Si^{t}Bu), 5.24 (1H, d, $J=6.5$ Hz, CH=), 5.72 (1H, dd, $J=10$, 6.5 Hz, CH=), 6.40 (1H, d, $J=16$ Hz, CH=), 6.57 (1H, dd, $J=16$, 10 Hz, CH=), 7.15—7.40 (5H, m, arom. H). HRMS Calcd for $C_{17}H_{24}Si$ (M^+): 256.1648. Found: 256.1651.

1-Phenyl-3-(trimethylsilyl)-1,2-propadiene (3k) A colorless oil; IR ($CHCl_3$): 1925, 1597 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.17 (9H, s, $SiMe_3$), 5.42 (1H, d, $J=7$ Hz, CH=), 5.86 (1H, d, $J=7$ Hz, CH=), 7.13—7.32 (5H, m, arom. H). HRMS Calcd for $C_{12}H_{16}Si$ (M^+): 188.1021. Found: 188.1021.

Ethyl 4-(*tert*-Butyldimethylsilyl)-4-deuterio-2-methyl-2,3-butadienoate (3c′) Similarly to the preparation of **3c**, this compound **3c′** (111 mg, 92%) was prepared from **1a** (125 mg, 0.55 mmol) and **2c** (181 mg, 0.05 mmol) in CH_2Cl_2 (5 ml) and D_2O (8 drops) as a colorless oil. The D-incorporation of **3c′** was estimated at 95% by 270 MHz ^{1}H-NMR analysis; IR ($CHCl_3$): 1927, 1694 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.08 (6H, s, $SiMe_2$), 0.92 (9H, s, Si^{t}Bu), 1.24 (3H, t, $J=7$ Hz, CH_3), 1.81 (3H, s, CH_3), 4.02—4.28 (2H, m, CH_2). HRMS Calcd for $C_{13}H_{23}DO_2Si$ (M^+): 241.1608. Found: 241.1608.

References and Notes

1) *a*) Y. Kita, J. Sekihachi, Y. Hayashi, Y.-z. Da, M. Yamamoto, S. Akai, *J. Org. Chem.*, **55**, 1108 (1990); *b*) Y. Kita, S. Matsuda, S. Kitagaki, Y. Tsuzuki, S. Akai, *Synlett*, **1991**, 401; *c*) S. Akai, Y. Tsuzuki, S. Matsuda, S. Kitagaki, Y. Kita, *ibid.*, **1991**, 911; *d*) *Idem*, *J. Chem. Soc.*, *Perkin Trans. 1*, **1992**, 2813.

2) For reviews, see A. Maercker, *Org. React.*, **14**, 270 (1965); P. J. Murphy, J. Brennan, *Chem. Soc. Rev.*, **17**, 1 (1988); B. E. Maryanoff, A. B. Reitz, *Chem. Rev.*, **89**, 863 (1989).

3) Silylallenes are synthetically useful as propargyl anion equivalents,[4] in [3+2] and [3+3]annulation methods,[5] and in other applications.[6] Therefore, an effective method of preparation of silylallenes has become of interest.[7]

4) *a*) A. Jellay, M. Santelli, *Tetrahedron Lett.*, **21**, 4487 (1980); *b*) R. L. Danheiser, D. J. Carini, C. A. Kwasigroch, *J. Org. Chem.*, **51**, 3870 (1986); *c*) K. Nunn, P. Mosset, R. Grée, R. W. Saalfrank, *Angew. Chem. Int. Ed. Engl.*, **27**, 1188 (1988).

5) *a*) R. L. Danheiser, D. M. Fing, Y.-M. Tsai, *Org. Synth.*, **66**, 8 (1988) and references cited therein; *b*) R. L. Danheiser, E. J. Stoner, H. Koyama, D. S. Yamashita, C. A. Klade, *J. Am. Chem. Soc.*, **111**, 4407 (1989); *c*) S. R. Angle, D. O. Arnaiz, *Tetrahedron Lett.*, **32**, 2327 (1991).

6) *a*) Yu G. Gu, K. K. Wang, *Tetrahedron Lett.*, **32**, 3029 (1991); *b*) B. M. Trost, J. M. Tour, *J. Org. Chem.*, **54**, 484 (1989).

7) *a*) R. L. Danheiser, Y.-M. Tsai, D. M. Fink, *Org. Synth.*, **66**, 1 (1988) and references cited therein; *b*) T. Tabuchi, J. Inanaga, M. Yamaguchi, *Tetrahedron Lett.*, **27**, 5237 (1986); *c*) I. Fleming, K. Takaki, A. P. Thomas, *J. Chem. Soc.*, *Perkin Trans. 1*, **1987**, 2269.

8) *a*) R. A. Ruden, *J. Org. Chem.*, **39**, 3607 (1974); *b*) V. Yu. Orlov, S. A. Lebedev, S. V. Ponomarev, I. F. Lutsenko, *Zh. Obshch. Khim.*, **45**, 708 (1975).

9) W. S. Wadsworth, Jr., W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961); G. Wittig, A. Haag, *Chem. Ber.*, **96**, 1535 (1963); D. A. Phipps, G. A. Taylor, *Chem. Ind.*, (London), **1968**, 1279; G. Aksnes, P. Frøyen, *Acta Chem. Scand.*, **22**, 2347 (1968); Z. Hamlet, W. D. Barker, *Synthesis*, **1970**, 543.

10) Rathke and we[1b,d] have previously observed similar reactivities, see R. P. Woodbury, N. R. Long, M. W. Rathke, *J. Org. Chem.*, **43**, 376 (1978).

11) T. Mukaiyama, S. Fukuyama, T. Kumamoto, *Tetrahedron Lett.*, **1968**, 3787.