Functionalized α-Trimethylsilyl Allenones

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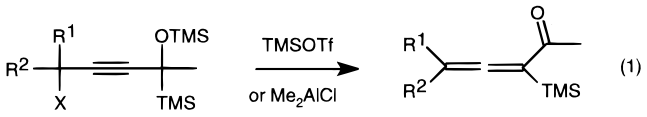
Functionalized allenes have proven to be useful intermediates in organic synthesis,[1] and the utility of both allenylsilanes[2] and allenyl ketones[3] have recently been demonstrated. Pursuant to our interest in the approach to α-trimethylsilyl allenones shown in eq 1,[4] we have explored possible extensions within the substitution pattern of R^1 and R^2 with a view toward introducing additional functionality to these species. Table 1 summarizes our results.

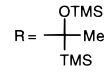
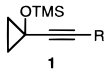
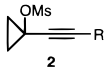
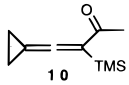
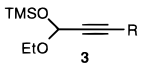
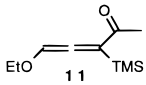
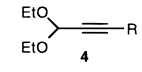
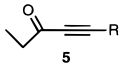
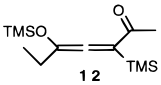
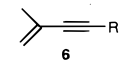
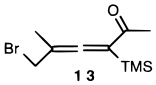
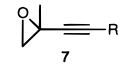
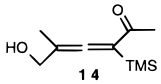
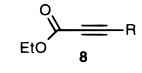
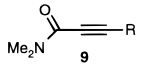


(1)

The use of this methodology to prepare cycloalkylidene allenones had not yet been explored, and the cyclopropylidene case was chosen as the most stringent example due to its inherent strain. This facet was reflected in the reactivity of its acetylenic precursors. Thus, **1** afforded only tarry materials when treated with trimethylsilyl trifluoromethanesulfonate (TMSOTf) under conditions that had quickly afforded good yields of allenone when $R^1 = R^2 =$ Me.[4a] The methanesulfonate **2**, while exhibiting unusual stability compared to a previous instance,[4a] did, however, give the allenone **10** in excellent yield upon treatment with Me_2AlCl.

Acetylenic precursors containing groups that would lead to additionally functionalized α-trimethylsilyl allenones were then explored. Both the acetals **3** and **4** smoothly afforded the same allenyl ether **11**, while trimethylsilylation of ketone **5** gave the allenyl ether **12**. This last result indicated that leaving groups per se are not necessary at the propargylic terminus, and rearrangement can be initiated by generating electrophilic character at this site by other means. It was therefore anticipated that attack at the π-bond of **6** by electrophilic agents would provide the impetus for rearrangement to occur, and simple bromination was chosen as an example. In the event, addition of Br_2 led to complex mixtures, but the use of *N*-bromosuccinimide in *N*-methyl-2-pyrrolidinone proved effective for the formation of **13**. The epoxide **7** was next targeted for examination, but attempts to derive it from **6** by *m*-chloroperbenzoic acid oxidation led to multicomponent mixtures, possibly due to the acidic nature of the reagent. The use of dimethyldioxirane was then found to be superior for this purpose. Subsequent treatment of the epoxide with TMSOTf led directly to the alcohol **14**, presumably the result of an in situ desilylation. All attempts to convert the ester **8** (TMSOTf, MeOTf, Et_3OBF_4, $TiCl_4$) or the amide **9** (TMSOTf, MeOTf) to the respective allenones were unsuccessful. Nevertheless, the preceding results show that a number of multifunctional allenones, compounds that should exhibit a rich subsequent chemistry, are readily accessible by this methodology.

Table 1. Preparation of α-Trimethylsilyl Allenones

Acetylene	Reagent	Allene	Yield (%)
			
 **1**	TMSOTf	—	—
 **2**	Me_2AlCl	 **10**	93
 **3**	TMSOTf	 **11**	90
 **4**	TMSOTf	**11**	67
 **5**	TMSOTf	 **12**	69
 **6**	NBS	 **13**	65
 **7**	TMSOTf	 **14**	67
 **8**	a	—	—
 **9**	a	—	—

[a] See text.

Experimental Section

General Methods. THF and diethyl ether were distilled from benzophenone ketyl immediately before use. All reactions were carried out under anhydrous conditions and positive Ar pressure. Activated MnO_2 was prepared by a literature procedure.[5] NBS was dried over P_2O_5. Unless otherwise indicated, workup prior to distillation or chromatography consisted of pouring the reaction mixture into saturated $NaHCO_3$, extracting with pentane, drying the organic phase by passage through anhydrous

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$MgSO_4$, and concentration by rotary evaporation. ^1H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were obtained in $CDCl_3$ unless otherwise indicated. Distillation data refer to Kugelrohr oven temperatures.

1-[1-[(Trimethylsilyl)oxy]cyclopropyl]-3-trimethylsilyl-3-[(trimethylsilyl)oxy]-1-butyne (1). This was prepared by the silylation of the corresponding alcohol, **1-[3-(trimethylsilyl)-3-[(trimethylsilyl)oxy]-1-butynyl]cyclopropanol**, which was made by a modification of the method of Salaün.[6]

Cyclopropanone ethyl hemiacetal[7] (0.58 g, 5.6 mmol) in 10 mL of THF at 0 °C was treated with 2.8 mL of EtMgBr (2 M in Et_2O, 5.6 mmol), allowed to warm to 25 °C, and stirred for 2 h. A second flask containing 3-(trimethylsilyl)-3-[(trimethylsilyl)-oxy]-1-butyne (1.21 g, 5.6 mmol) and 10 mL of THF at 0 °C was treated with 3.0 mL of EtMgBr (2 M in Et_2O, 6.0 mmol) and then stirred for 2 h at 25 °C. Both solutions were then recooled to 0 °C, and the hemiacetal solution was cannulated into the other flask. After 45 h at 25 °C, workup and distillation (50 °C, 0.05 mmHg) gave a colorless liquid that NMR analysis indicated contained some starting acetylene. Evacuation for 45 min under high vacuum removed this impurity and afforded 0.94 g (62%) of the title alcohol. ^1H NMR: δ 0.05 (s, 9H), 0.16 (s, 9H), 0.95 (m, 2H), 1.08 (m, 2H), 1.39 (s, 3H), 2.22 (br s, 1H). ^{13}C NMR: δ −4.2, 2.5, 17.6, 26.2, 46.3, 62.4, 87.1, 84.3. IR: 3400 (br), 2200 (vw) 1250, 1070 cm^{-1}. Anal. Calcd for $C_{13}H_{26}O_2Si_2$: C, 57.72; H, 9.69. Found: C, 57.66; H, 9.70. A mixture of this alcohol (0.87 g, 3.2 mmol), 4 mL CH_2Cl_2, and 0.47 mL (0.45 g, 3.2 mmol) of TMS-imidizole was stirred for 4.5 h. Workup and distillation (90 °C, 0.05 mmHg) gave 0.88 g (80%) of **1**. ^1H NMR: δ 0.04 (s, 9H), 0.15 (s, 9H), 0.21 (s, 9H), 0.92 (m, 2H), 0.99 (m, 2H), 1.40 (s, 3H). ^{13}C NMR: δ −4.1, 1.3, 2.5, 17.7, 18.0, 26.1, 46.8, 62.4, 85.8, 90.1. Anal. Calcd for $C_{16}H_{34}O_2Si_3$: C, 56.07; H, 10.00. Found: C, 55.90; H, 10.11.

1-[1-[(Methanesulfonyl)oxy]cyclopropyl)]-3-(trimethylsilyl)-3-[(trimethylsilyl)oxy]-1-butyne (2). A mixture of 1-[3-(trimethylsilyl)-3-[(trimethylsilyl)oxy]-1-butynyl]cyclopropanol (0.95 g, 3.5 mmol), 12 mL of CH_2Cl_2, and 0.50 mL (0.35 g, 3.6 mmol) of triethylamine was cooled to −78 °C, and treated with methanesulfonyl chloride (0.27 mL, 0.40 g, 3.5 mmol). After the mixture was stirred for 3 h at 25 °C, workup and chromatography on silica gel (3% EtOAc−hexane) gave 0.78 g (64%) of **2**. ^1H NMR: δ 0.06 (s, 9H), 0.16 (s, 9H), 1.2 (m, 2H), 1.43 (s, 3H), 1.6 (m, 2H), 3.17 (s, 3H). ^{13}C NMR: δ −4.3, 2.3, 16.8, 17.0, 25.8, 40.0, 54.5, 62.3, 85.0, 91.0. IR: 2215, 1366 cm^{-1}. Anal. Calcd for $C_{14}H_{28}O_4SSi_2$: C, 48.23; H, 8.09. Found: C, 48.28; H, 8.31.

1-Ethoxy-4-(trimethylsilyl)-1,4-bis[(trimethylsilyl)oxy]-2-pentyne (3). Butyllithium (2.5 M, 0.56 mL) was added to 0.30 g (1.4 mmol) of 3-(trimethylsilyl)-3-[(trimethylsilyl)oxy]-1-butyne in 8 mL of THF at −78 °C. After 0.5 h, ethyl formate (0.21 g, 2.8 mmol) was added, and the mixture was stirred for 1 h. TMS-imidazole (0.25 mL, 0.24 g, 1.7 mmol) was then added and the mixture allowed to warm to 0 °C (2.5 h). Following workup, distillation (90 °C, 0.05 mmHg) gave 0.32 g (63%) of **3**. ^1H NMR: δ 0.04 (s, 9H), 0.13 (s, 9H), 0.16 (s, 9H), 1.19 (t, 3H), 1.39 (s, 3H), 3.61 (m, 2H), 5.52 (s, 1H). ^{13}C NMR (C_6D_6): δ −4.4, 0.4, 2.3, 15.4, 26.0, 60.1, 62.4, 86.0, 87.4, 88.1. IR: 2170, 1251 cm^{-1}. Anal. Calcd for $C_{16}H_{36}O_3Si_3$: C, 53.28; H, 10.06. Found: C, 53.28; H, 10.10.

1,1-Diethoxy-4-(trimethylsilyl)-4-[(trimethylsilyl)oxy]-2-pentyne (4). Propiolaldehyde diethyl acetal (0.54 g, 4.2 mmol) in 15 mL of ether at −78 °C was treated with butyllithium (1.6 mL, 2.5 M, 4.0 mmol). After 15 min, acetyltrimethylsilane (0.46 g, 4.0 mmol) was added and, sequentially, 10 min later, TMS-imidazole (0.56 g, 4.0 mmol) and TMSOTf (0.44 g, 2.0 mmol). After 1 h at −78 °C, the mixture was slowly warmed over 45 min to 0 °C and poured into aqueous $NaHCO_3$. Distillation (95 °C, 0.1 mmHg) afforded 0.80 g (63%) of **4**. ^1H NMR: δ 0.04 (s, 9H), 0.13 (s, 9H), 1.19 (t, 6H), 1.40 (s, 3H), 3.58 (m, 2H), 3.67 (m, 2H), 5.29 (s, 1H). ^{13}C NMR (1:3 v/v C_6D_6−CCl_4): δ −4.1, 2.5, 15.5, 26.1, 60.6, 62.3, 83.8, 89.0, 91.8. IR: 1250, 1180 cm^{-1}. Anal. Calcd for $C_{15}H_{32}O_3Si_2$: C, 56.91; H, 10.19. Found: C, 56.76; H, 10.01.

6-Trimethylsilyl-6-[(trimethylsilyl)oxy]-4-heptyn-3-one (5). This was prepared by the oxidation of **6-trimethylsilyl-6-[(trimethylsilyl)oxy]-4-heptyn-3-ol.** Butylithium (2.5 M, 0.56 mL, 1.4 mmol) was added to a solution of 3-(trimethylsilyl)-3-[(trimethylsilyl)oxy]-1-butyne (0.30 g, 1.4 mmol) in 6 mL of THF at −78 °C. After 45 min, propionaldehyde (0.10 mL, 0.08 g, 1.4 mmol) was added and the mixture stirred at temperature for 1.5 h, followed by 0.5 h at 0 °C. The reaction was quenched with aqueous NH_4Cl (15% w/v). Distillation (80 °C, 0.2 mmHg) gave 0.28 g (71%) of the alcohol. ^1H NMR: δ 0.04 (s, 9H), 0.14 (s, 9H), 0.98 (t, 3H), 1.38 (s, 3H), 1.6 (s, 1H), 1.72 (m, 2H), 4.35 (t, 1H). Anal. Calcd for $C_{13}H_{28}O_2Si_2$: C, 57.29; H, 10.36. Found: C, 57.52; H, 10.46. This alcohol (0.46 g, 1.7 mmol), CCl_4 (10 mL), and activated MnO_2 (5 g, 60 mmol) were stirred vigorously for 13 h. After glass frit filtration, distillation (80 °C, 0.7 mmHg) gave 0.37 g (81%) of **5**. ^1H NMR: δ 0.08 (s, 9H), 0.17 (s, 9H), 1.12 (t, 3H), 1.46 (s, 3H), 2.55 (q, 2H). ^{13}C NMR (1:3 v/v C_6D_6−CCl_4): δ −4.2, 2.3, 8.2, 25.5, 38.5, 62.4, 88.3, 96.1, 185.4. IR: 2180, 1670 cm^{-1}. Anal. Calcd for $C_{13}H_{26}O_2Si_2$: C, 57.72; H, 9.69. Found: C, 57.95; H, 9.85.

2-Methyl-5-(trimethylsilyl)-5-[(trimethylsilyl)oxy]-3-hexyn-1-ene (6). *n*-BuLi (2.5 M, 22.0 mL, 55 mmol) was added to a solution of 3.6 g (55 mmol) of 3-methyl-3-buten-1-yne in 20 mL of ether at −78 °C, followed 25 min later by 7.0 g (60 mmol) of acetyltrimethylsilane. After 1 h, the mixture was allowed to warm and poured into NH_4Cl solution. Distillation (short path) gave 7.1 g (71%) of 5-methyl-2-(trimethylsilyl)-5-hexen-3-yn-2-ol, bp 80 °C (0.4 mmHg). ^1H NMR: δ 0.12 (s, 9H), 1.45 (s, 3H), 1.86 (s, 3H), 5.15 (s, 1H), 5.20 (s, 1H). ^{13}C NMR: δ −4.5, 23.6, 25.4, 61.2, 87.6, 92.3, 120.8, 126.8. IR: 3420 (br), 1251, 1048 cm^{-1}. The alcohol (6.0 g, 30 mmol), TMS-imidazole (4.6 g, 30 mmol), and CH_2Cl_2 (25 mL) were stirred for 10 h. Workup gave 6.1 g (72%) of **6**, bp 75 °C (0.1 mmHg). ^1H NMR: δ 0.04 (s, 9H), 0.14 (s, 9H), 1.39 (s, 3H), 1.86 (s, 3H), 5.14 (m, 2H). ^{13}C NMR: δ −4.5, 2.0, 23.4, 25.9, 62.5, 88.9, 93.0, 120.0, 127.1. IR: 2210, 1620 cm^{-1}. Anal. Calcd for $C_{13}H_{26}OSi_2$: C, 61.35; H, 10.29. Found: C, 61.34; H, 10.35.

1,2-Epoxy-2-methyl-5-(trimethylsilyl)-5-[(trimethylsilyl)-oxy]-3-hexyne (7). An acetone solution of dimethyldioxirane[8] (0.07 M, 35 mL, 2.4 mmol) was added at once to 0.30 g (1.2 mmol) of **6** and the mixture stirred 10 min. The solvent was removed and the residue distilled to give 0.23 g (72%) of **7**, bp 90 °C (1 mmHg). ^1H NMR: δ 0.03 (s, 9H), 0.13 (s, 9H), 1.36 (s, 3H), 1.52 (s, 3H), 2.73 (d, 1H, J = 6 Hz)), 2.93 (d, 1H, J = 6 Hz). ^{13}C NMR (C_6D_6): δ −4.4, 2.4, 23.2, 26.1, 47.1, 54.9, 62.6, 86.4, 87.9. IR: 1937, 1249 cm^{-1}. Anal. Calcd for $C_{13}H_{26}O_2Si_2$: C, 57.72; H, 9.69. Found: C, 57.65; H, 9.65.

Ethyl 4-(Trimethylsilyl)-4-[(trimethylsilyl)oxy]-2-pentynoate (8). Butyllithium (2.5 M, 0.28 mL, 0.70 mmol) was added to a solution of 3-(trimethylsilyl)-3-[(trimethylsilyl)oxy]-1-butyne (0.15 g, 0.70 mmol) in THF (8 mL) at −78 °C. After 30 min, ethyl chloroformate (70 μL, 0.080 g, 0.73 mmol) was added, and the mixture was allowed to slowly warm to 25 °C (2 h). Aqueous NH_4Cl (15% w/v) was then added. Distillation (70 °C, 1.4 mmHg) gave 0.14 g (72%) of **8**. ^1H NMR: δ 0.08 (s, 9H), 0.16 (s, 9H), 1.30 (t, 3H), 1.45 (s, 3H), 4.21 (q, 2H). ^{13}C NMR: δ −4.6, 1.8, 14.0, 25.0, 61.5, 62.1, 80.3, 92.8, 153.8. IR: 2220, 1710 cm^{-1}. Anal. Calcd for $C_{13}H_{26}O_3Si_2$: C, 54.52; H, 9.11. Found: C, 54.49; H, 9.32.

***N,N*-Dimethyl-4-(trimethylsilyl)-4-[(trimethylsilyl)oxy]-2-pentynamide (9).** Following the procedure employed for **8**, but using dimethylcarbamyl chloride, an 81% yield of **9** was obtained as a yellow solid (mp 42−45 °C) after distillation (80 °C, 0.6 mmHg). ^1H NMR: δ 0.08 (s, 9H), 0.16 (s, 9H), 1.47 (s, 3H), 2.95 (s, 3H), 3.14 (s, 3H). ^{13}C NMR: δ −4.6, 1.9, 25.2, 33.9, 38.0, 62.2, 80.6, 96.3, 154.5. IR: 2210, 1635 cm^{-1}. Anal. Calcd for $C_{13}H_{27}NO_2Si_2$: C, 54.68; H, 9.83; N, 4.91. Found: C, 54.56; H, 9.53; N, 4.83.

5,5-Dimethylene-3-(trimethylsilyl)-3,4-pentadien-2-one (10). A mixture of 0.28 g (0.80 mmol) of **2** and 2 mL of CH_2Cl_2 at −78 °C was treated with 2.0 mL (2.0 mmol) of 1.0 M Me_2AlCl in hexane (lower molar ratios of catalyst to substrate led to incomplete conversion) and allowed to slowly warm to 25

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°C. After workup, distillation (85 °C, 0.08 mmHg) gave 0.14 g (93%) of **10**. ^{1}H NMR: δ 0.14 (s, 9H), 1.87 (m, 4H), 2.26 (s, 3H). ^{13}C NMR: δ −0.8, 11.9, 28.4, 71.9, 106.1, 201.5, 202.5. IR: 1995, 1645. Anal. Calcd for $C_{10}H_{16}OSi$: C, 66.60; H, 8.94. Found: 66.42; H, 9.16.

5-Ethoxy-3-(trimethylsilyl)-3,4-pentadiene-2-one (11). Preparation from 3. A mixture of **3** (0.045 g, 0.12 mmol) and dry CH_2Cl_2 was treated at −78 °C with TMSOTf (2.5 μL) and then stirred for 10 min. Aqueous $NaHCO_3$ (1 M, 4 mL) was then added dropwise at −78 °C. The cooling bath was removed and the mixture allowed to warm to 25 °C. After workup, distillation (80 °C, 0.9 mmHg) gave 0.069 g (90%) of **11**. **Preparation from 4.** A solution of **4** (0.080 g, 0.24 mmol) in 5 mL of dry CH_2Cl_2 at −78 °C was treated with 2.5 μL of TMSOTf. Within 1 min, the reaction mixture was poured into $NaHCO_3$ solution (10 mL, 1 M). Workup as before gave 0.032 g (67%) of **11**. ^{1}H NMR: δ 0.13 (s, 9H), 1.29 (t, 3H), 2.27 (s, 3H), 3.57 (q, 2H), 6.95 (s, 1H). ^{13}C NMR (C_6D_6): δ −1.0, 15.0, 27.2, 65.4, 121.8 (2 coincident C), 199.3, 214.2. IR: 1930, 1670 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15. Found: C, 60.58; H, 9.40.

3-(Trimethylsilyl)-5-[(trimethylsilyl)oxy]-3,4-heptadien-2-one (12). Scrupulously dry conditions must be employed. A solution of **5** (0.11 g, 0.39 mmol) in CH_2Cl_2 (1 mL, Aldrich Chemical Co., 0.005% H_2O) was treated at −78 °C with 7 μL (0.04 mmol) of TMSOTf and stirred for 15 min. Triethylamine (54 μL, 0.39 mmol) was then added and the mixture held at temperature for 5 min. After slow warming to 25 °C (2h), aqueous $NaHCO_3$ (1 M) was added. Distillation (80 °C, 0.5 mmHg) gave 0.07 g (69%) of **12**. ^{1}H NMR: δ 0.13 (s, 9H), 0.16 (s, 9H), 0.98 (t, 3H), 2.22 (m, 2H), 2.22 (s, 3H). ^{13}C NMR: δ −1.1, 0.3, 10.7, 27.0, 27.4, 117.6, 128.8, 200.8, 216.2. IR: 1930, 1670 cm^{-1}. Anal. Calcd for $C_{13}H_{26}O_2Si_2$: C, 57.72; H, 9.69. Found: C, 57.97;H, 9.77.

6-Bromo-5-methyl-3-(trimethylsilyl)-3,4-hexadien-2-one (13). A solution of *N*-bromosuccinimide (0.22 g, 1.2 mmol) in *N*-methyl-2-pyrrolidinone (1 mL) was added dropwise by syringe to a mixture of **6** (0.30 g, 1.2 mmol) and *N*-methyl-2-prrolidinone (3 mL) at 0 °C. After 2 h at 0 °C, the $NaHCO_3$ solution was added, and the mixture was extracted with pentane, washed 3× with water, and dried. Distillation gave 0.20 g (65%) of **13**, bp 110 °C (2 mmHg). ^{1}H NMR: δ 0.14 (s, 9H), 1.91 (s, 3H), 2.25 (s, 3H), 4.06 (m, 2H). ^{13}C NMR: δ −1.1, 16.0, 28.7, 35.1, 95.0, 105.1, 200.4, 214.4. IR: 1936, 1665 cm^{-1}. Anal. Calcd for $C_{10}H_{17}BrOSi$: C, 45.97; H, 6.56. Found (best result): C, 46.97; H, 6.90.

6-Hydroxy-5-methyl-3-(trimethylsilyl)-3,4-hexadien-2-one (14). A solution of **7** (0.15 g, 0.55 mmol) in 5 mL of CH_2Cl_2 at −78 °C was treated with 5 μL of TMSOTf. After 1 min, the reaction was quenched with 1 M $NaHCO_3$. After workup, distillation (100 °C, 1 mmHg) gave 0.074 g (67%) of **14**. ^{1}H NMR: δ 0.12 (s, 9H), 1.45 (br s, 1H), 1.83 (s, 3H), 2.22 (s, 3H), 4.16 (d, 2H). ^{13}C NMR: δ −1.1, 14.4, 28.1, 63.7, 97.6, 105.7, 201.6, 213.3. IR: 3400 (br), 1940, 1655 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15. Found: C, 60.30; H, 9.19.

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