was added 1.65 mL of methanol, and the resulting mixture was saturated with potassium carbonate. The mixture was stirred for 1 h, and the organic phase was separated and stirred overnight with an excess of potassium carbonate. The reaction mixture was diluted with ether, filtered, dried over potassium carbonate, and concentrated under reduced pressure to give 5.2 g (89%) of a clear oil, whose structure was assigned as *N*-benzyl-*N*-(methoxymethyl)-*N*-[phenyl(trimethylsilyl)methyl]amine (**37**) on the basis of its spectral properties: IR (neat) 3060, 1710, 1650, 1600, 1450, 1070, 760, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 0.10 (s, 9 H), 3.15 (s, 3 H), 3.65 (s, 1 H), 3.71 (d, 1 H, J = 13.2 Hz), 3.78 (d, 1 H, J = 13.2 Hz), 4.00 (d, 1 H, J = 9.3 Hz), 4.15 (d, 1 H, J = 9.3 Hz), and 7.1–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 0.17, 54.5, 56.9, 66.6, 85.8, 126.8, 127.3, 128.5, 129.8, 130.2, and 132.3; MS, m/e 313 (M^+), 267, 196, 178, and 91. Anal. Calcd for $C_{19}H_{27}NOSi$: C, 72.79; H, 8.68; N, 4.47. Found: C, 72.83; H, 8.70; N, 4.45.

Cycloaddition of 37 with 1,1-Bis(*p*-tolylsulfonyl)ethylene in the Presence of Lithium Fluoride. A solution containing 500 mg of **37**, 540 mg of 1,1-bis(*p*-tolylsulfonyl)ethylene,[30] and 80 mg of lithium fluoride in 6 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting oil was subjected to silica gel chromatography with a 35% ethyl acetate–hexane mixture as the eluent. The oil that was obtained was recrystallized from methylene chloride–petroleum ether to give 0.13 g (15%) of a white solid, mp 187–188 °C, whose structure was assigned as *N*-benzyl-2-phenyl-3,3-bis(*p*-tolylsulfonyl)pyrrolidine (**34**) on the basis of its spectral properties: IR (KBr) 3050, 1600, 1495, 1330, 1150, 1020, 880, 770, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.87 (ddd, 1 J, J = 5.8, 8.8 and 11.2 Hz), 2.58 (dd, 1 H, J = 5.8 and 14.6 Hz), 3.03 (dd, 1 H, J = 7.5 and 8.8 Hz), 3.05 (d, 1 H, J = 13.4 Hz), 3.17 (ddd, 1 H, J = 7.5, 11.2, and 14.6 Hz), 3.82 (d, 1 H, J = 13.4 Hz), 4.43 (s, 1 H), and 7.1–8.0 (m, 18 H); MS, m/e 545 (M^+), 415, 401, 167, 149, and 91; UV (95% ethanol) 232 nm (ϵ 10400). Anal. Calcd for $C_{31}H_{31}NO_4S_2$: C, 68.23; H, 5.73; N, 2.57. Found: C, 67.94; H, 5.77; N, 2.53. This same material was formed from the reaction of silyl methoxy amine **33** with lithium fluoride in the presence of 1,1-bis(*p*-tolylsulfonyl)ethylene.

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Registry No. 1, 93102-05-7; 3, 97998-53-3; 4, 87813-05-6; 5, 87813-06-7; 6, 101767-83-3; 7, 105518-91-0; 8, 105518-92-1; 9, 105518-93-2; 10, 104143-95-5; 11, 105518-94-3; 12, 105518-95-4; 13, 105537-40-4; 14, 105518-96-5; 15, 105518-97-6; 16, 105518-98-7; 17, 105518-99-8; 18, 105519-00-4; 19, 1483-42-7; 20, 13657-16-4; 23, 105537-41-5; 25, 105519-01-5; 26, 87813-07-8; 27, 105519-02-6; 28, 105519-03-7; 29, 105519-04-8; 30, 105537-42-6; 31, 105519-05-9; 33, 105519-06-0; 34, 105519-07-1; 35, 105519-08-2; 36, 105519-09-3; 37, 105519-10-6; 38, 105519-11-7; 39, 105519-12-8; $TMSCH_2NHCH_2Ph$, 53215-95-5; CsF, 13400-13-0; LiF, 7989-24-4; $ZnCl_2$, 7646-85-7; $PhCH_2OCOCN$, 5532-86-5; $HC{\equiv}CCO_2CH_3$, 922-67-8; *N*-benzyl-*trans*-3,4-dicyanopyrrolidine, 87813-02-3; 2,6-dioxo-1-phenyl-4-benzyl-1,4-diazobicyclo[3.3.0]octane, 93102-03-5; *o*-vinylbenzyl chloride, 22570-84-9; benzaldehyde, 100-52-7; fumaronitrile, 764-42-1; *N*-phenylmaleimide, 941-69-5; dimethyl fumarmate, 624-49-7; dimethyl maleate, 624-48-6; phenyl vinyl sulfine, 5535-48-8; *N*-benzyl-*N*-[(trimethylsilyl)methyl)]-*N*-[(β-(phenylsulfonyl)ethyl)]amine, 105519-13-9; 1,1-bis(*p*-tolylsulfonyl)ethylene, 39837-38-2; benzophenone, 119-61-9; acetone, 67-64-1; thiobenzophenone, 1450-31-3; ethoxymethacrolein, 62055-46-3; 5-hexenal, 764-59-0; [(trimethylsilyl)methyl]amine, 18166-02-4; *N*-(*o*-vinylbenzyl)-*N*-[(trimethylsilyl)methyl]amine, 105519-14-0; *N*-benzylaziridine, 1074-42-6; *N*-benzylmethylamine, 103-67-3; *N*-benzylethanolamine, 104-63-2; 3-hexanone trimethylsilyl enol ether, 105519-15-1; thioacetamide, 62-55-5; *N*-benzyl-*N*-[(α-trimethylsilyl)ethyl)]amine, 97998-46-4; (trimethylsilyl)dibenzylamine, 70601-93-3.

Convenient Syntheses of Precursors of Silylated 1,3-Dienes

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Several 2- or 3-silylated 3-sulfolenes have been prepared from 3-sulfolenes by the direct deprotonation/substitution sequence. These sulfolenes serve as the stable precursors for the silylated 1,3-dienes and can be used directly in Diels–Alder reactions without isolation of the diene intermediates.

The Diels–Alder reaction of a silylated 1,3-diene with a dienophile results in the formation of either a cyclic vinylsilane or a cyclic allylsilane.[1] Both vinylsilanes and allylsilanes are useful functionalities and find broad applications in organic synthesis.[2] For this reason, the preparation of silylated 1,3-dienes[1,3] and the regio- and stereoselectivity of their cycloaddition reactions[1] have received much attention from organic chemists. Literature methods for the preparation of 2-silylated 1,3-dienes normally involve the use of 1,4-difunctionalized 2-butynes,[3a-c] the catalyzed cross-coupling of silylated alkenes,[3d,e] and the LAH reduction of silylated allenic alcohols,[3f] while those for 1-silylated 1,3-dienes involve the condensation reactions of silylated carbanions with carbonyl compounds,[1a,d,3g] the Wittig reaction of silylated acrolein,[1c] and the hydroalumination of silylated 1,3-diynes.[3g] These procedures either are multistep or require starting materials that are not readily accessible. In addition, the silylated dienes are often difficult to purify because of their tendency to decompose upon distillation and because they readily polymerize upon long-term storage. Herein we report a very convenient method for the preparation of the stable precursors for the silylated 1,3-dienes, the silylated 3-sulfolenes, via the direct de-

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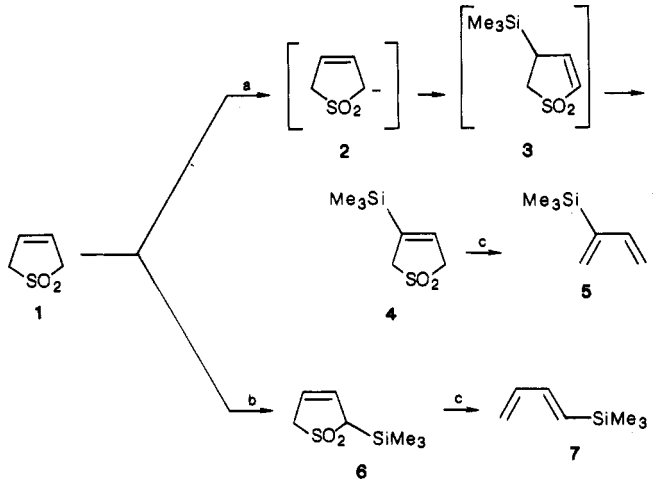
0022-3263/87/1952-0244$01.50/0

Scheme I[a]



[a] (a) i, *n*-BuLi (1 equiv), −105 °C; ii, Me_3SiCl (0.67 equiv). (b) i, *n*-BuLi (1 equiv)/NaI (1 equiv), −105 °C; ii, Me_3SiCl (1 equiv). (c) Thermolysis, 240 °C.

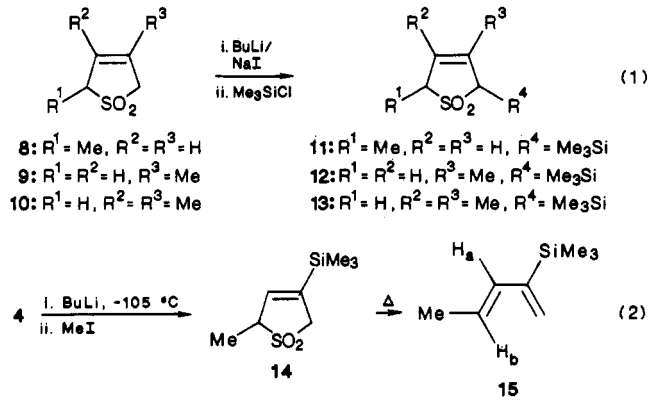
protonation/substitution reaction sequence that we developed recently.[4]

Treatment of 3-sulfolene (**1**) with *n*-BuLi (1 equiv) at −105 °C produced a brown solution of the sulfolene anion **2**. Addition of trimethylsilyl chloride (Me_3SiCl, 0.67 equiv) at once via syringe followed by workup and chromatography gave pure 3-(trimethylsilyl)-3-sulfolene (**4**) in 25% yield. The reaction must be run at −105 °C; otherwise the ring-opening reaction and decomposition of the sulfolene anion would take place.[4c] Increasing the ratio of Me_3SiCl to 3-sulfolene in the reaction did not increase the yield of **4** but caused disilylation to take place. The yield of this convenient one-step preparation is slightly higher than the overall yield of the multistep preparation sequence starting with 1,4-dichloro-2-butyne.[1b] Compound **4** was thermolyzed by GC (injection temp 240 °C) to produce the 2-silylated butadiene **5** of which the structure was identical with an authentic sample prepared by a literature procedure.[1b] Compound **4** is believed to come from the double-bond isomerization of **3**, which is the product of the γ-silylation of the anion **2**. (See Scheme I).

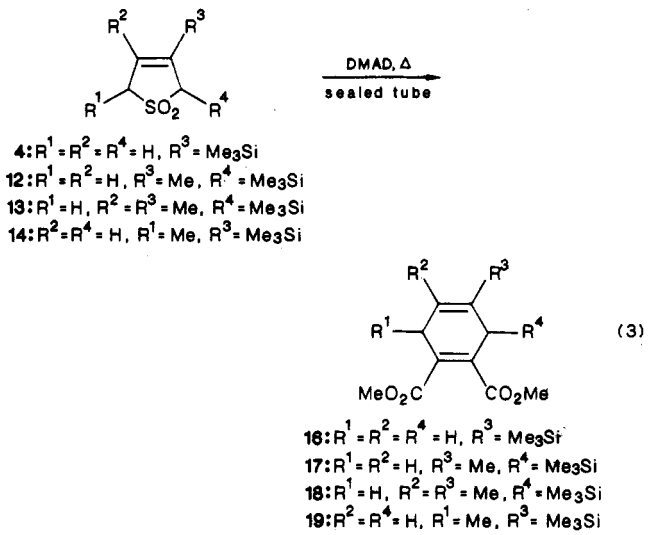
It is interesting that a slight change in the reaction conditions for silylation gave a completely different result. If NaI (1 equiv) was added during the generation of **2** and 1 equiv of Me_3SiCl was used in the substitution step, the reaction proceeded completely via α-silylation and gave 2-(trimethylsilyl)-3-sulfolene (**6**) in 43% yield. Compound **6** was thermolyzed similarly by GC to give the silylated butadiene **7** of which the NMR spectral data were identical with those reported earlier.[1a] The reason why the presence of NaI changes the site of silylation is not yet clear. However, it is noted that the reactions of the 3-sulfolene anions with alkyl iodides almost always give the 2-alkylated products.[4] (See Scheme I).

Under reaction conditions similar to those for the preparation of **6**, silylations of **8**, **9**, and **10** gave the α-silylation 3-sulfolenes **11**, **12**, and **13**, respectively (eq 1).

It was expected that silylated 3-sulfolenes could be further deprotonated and alkylated without difficulty, and this was indeed so. For example, treatment of **4** with *n*-BuLi at −105 °C followed by alkylation with MeI regioselectively produced 2-methyl-4-(trimethylsilyl)-3-sulfolene (**14**) in 90% yield (eq 2). The regiochemistry of the methylated product **14** was determined by extruding the SO_2 from the molecule and then analyzing the ^1H NMR spectrum of the corresponding diene **15**, where the coupling constant between H_a and H_b was 16 Hz, confirming the trans configuration of the double bond.



The silylated 3-sulfolenes prepared as described above are thermal and air stable and can be easily purified by HPLC without any appreciable decomposition. Although the corresponding silylated dienes can presumably be obtained from the sulfolenes by thermolysis, these silylated sulfolenes may be used directly in Diels–Alder reactions without isolating the diene intermediates. For example, the reactions of **4**, **12**, **13**, and **14** with dimethyl acetylenedicarboxylate (DMAD) in a sealed tube at 160 °C readily gave the cycloadducts **16**–**19**, respectively (eq 3).



Because of the advantages of their stability, ease of purification, and ease of use in reactions, the silylated sulfolenes serve as ideal precursors for the corresponding silylated dienes. Therefore, the one-step deprotonation/substitution reaction of 3-sulfolenes described in this paper provides a very convenient route for laboratory preparation of silylated 1,3-dienes.

Experimental Section

^1H NMR spectra were determined on a Varian EM-390 NMR spectrometer or a JEOL FX-100 NMR spectrometer for solutions in $CDCl_3$ unless otherwise indicated. IR spectra were determined on a Perkin-Elmer 297 IR spectrophotometer. Mass spectra were recorded on a JEOL JMS D-100 mass spectrometer. Elemental analyses were performed at the microanalysis laboratory of National Taiwan University. All reactions were carried out under an atmosphere of dry nitrogen. All solvents were freshly distilled before use.

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3-(Trimethylsilyl)-2,5-dihydrothiophene 1,1-Dioxide (4). To a mixture of 3-sulfolene (1, 300 mg, 2.54 mmol) and hexamethyl phosphoramide (HMPA, 1 mL) in THF (10 mL) at −105 °C was added *n*-BuLi (2.54 mmol) dropwise. After the addition was complete, the mixture turned brown and was stirred for an additional 10 min. Freshly distilled trimethylsilyl chloride (Me_3SiCl, 180 mg, 1.65 mmol) was added at once via syringe, and the reaction mixture turned reddish-brown. The resulting mixture was allowed to warm to room temperature gradually over 2.5 h, and an excess of EtOAc (10 mL) was added. The solvent was removed under reduced pressure. The crude product was eluted through a silica gel column (hexane/EtOAc, 2:1) to remove HMPA and then further purified by a flash column (silica gel, hexane/EtOAc, 3:1) to give the pure product 4 in 25% yield. The analytical sample was obtained by HPLC (LiChrosorb column, hexane/EtOAc, 3:1): IR (neat) 3040, 2960, 1590, 1400, 1310, 1250, 1230, 1130, 1030, 840 cm^{-1}; ^1H NMR δ 0.18 (br s, 9 H), 3.70 (br s, 4 H), 6.17 (br s, 1 H); MS, m/z 126 ($M^+ - 64$), 111, 85, 73 (100%).

Anal. Calcd for $C_7H_{14}O_2SSi$: C, 44.2; H, 7.4. Found: C, 44.1; H, 7.4.

Syntheses of 2-Silylated 3-Sulfolenes 6, 11, 12, and 13. To the mixture of a 3-sulfolene (1, 8, 9, or 10, 1.6 mmol), NaI (1.67 mmol), and HMPA (1.1 mL) in THF (6 mL) at −105 °C was added *n*-BuLi (1.6 mmol) dropwise. After the addition was complete, the reaction mixture was stirred for an additional 10 min whereupon Me_3SiCl (1.64 mmol) was added at once via syringe. The mixture was allowed to warm up to room temperature gradually over 2.5 h, and an excess of EtOAc (10 mL) was added. The solvent was removed under reduced pressure. The crude product was eluted through a silica gel column (hexane/EtOAc, 2:1) to remove HMPA and then further purified by a flash column (silica gel, hexane/EtOAc, 3:1). The analytical sample was obtained by HPLC (LiChrosorb column, hexane/EtOAc, 3:1).

2-(Trimethylsilyl)-3-sulfolene (6). This was obtained from the reaction of 3-sulfolene (1) in 43% yield: IR (neat) 3060, 2960, 1610, 1410, 1300, 1250, 1190, 1140, 1090, 980, 840 cm^{-1}; ^1H NMR δ 0.24 (br s, 9 H), 3.35 (br s, 1 H), 3.7 (br s, 2 H), 5.95 (br s, 2 H); MS, m/z 175 ($M^+ - 15$), 111, 83, 73 (100%), 59.

Anal. Calcd for $C_7H_{14}O_2SSi$: C, 44.2; H, 7.4. Found: C, 43.9; H, 7.6.

2-Methyl-5-(trimethylsilyl)-3-sulfolene (11). This was obtained from the reaction of 2-methyl-3-sulfolene (8) in 27% yield: IR (neat) 3070, 2970, 1610, 1450, 1300, 1250, 1120, 850, 750, 630 cm^{-1}; ^1H NMR δ 0.27 (br s, 9 H), 1.4 (d, 3 H, J = 7 Hz), 3.4 (br s, 1 H), 3.8 (q, 1 H, J = 7 Hz), 5.85 (br s, 2 H); MS, m/z 204 (M^+), 175, 156, 125, 114, 97, 86, 82, 75, 73 (100%), 67.

Anal. Calcd for $C_8H_{16}O_2SSi$: C, 47.0; H, 7.9. Found: C, 47.0; H, 7.9.

3-Methyl-2-(trimethylsilyl)-3-sulfolene (12). This was obtained from the reaction of 3-methyl-3-sulfolene (9) in 70% yield: IR 3060, 2950, 1640, 1440, 1410, 1380, 1300, 1250, 1140, 1110, 920, 850 cm^{-1}; ^1H NMR δ 0.31 (br s, 9 H), 1.85 (s, 3 H), 3.3 (br s, 1 H), 3.7 (s, 2 H), 5.6 (s, 1 H); MS, m/z 204 (M^+), 175, 125, 85, 73 (100%), 59.

Anal. Calcd for $C_8H_{16}O_2SSi$: C, 47.0; H, 7.9. Found: C, 47.2; H, 7.9.

3,4-Dimethyl-2-(trimethylsilyl)-3-sulfolene (13). This was obtained from the reaction of 3,4-dimethyl-3-sulfolene (10) in 81% yield: IR (neat) 2950, 1440, 1405, 1380, 1300, 1250, 1220, 1160, 1120, 1100, 920, 850 cm^{-1}; ^1H NMR δ 0.28 (br s, 9 H), 1.78 (s, 6 H), 3.3 (s, 1 H), 3.6 (s, 2 H); MS, m/z 218 (M^+), 201, 175, 139, 85, 79, 75, 73 (100%), 59, 53.

Anal. Calcd for $C_9H_{18}O_2SSi$: C, 49.5; H, 8.3. Found: C, 49.6; H, 8.3.

2-Methyl-4-(trimethylsilyl)-3-sulfolene (14). To a mixture of 4 (0.63 mmol) and HMPA (2.5 mmol) in THF (10 mL) cooled at −105 °C was added *n*-BuLi (0.63 mmol) dropwise. After the addition was complete, the reaction mixture was stirred for 10 min, and then MeI (1.2 mmol) was added at once via syringe. The mixture was allowed to warm up to room temperature over 2.5 h and concentrated to half of its volume before eluting through a silica gel column (hexane/EtOAc, 1:1) to remove HMPA and inorganic salts. The product was further purified by a flash column (silica gel, hexane/EtOAc, 3:1) to give 14 in 90% yield. The analytical sample was obtained by HPLC (LiChrosorb column, hexane/EtOAc, 3:1): IR (neat) 3040, 2960, 1590, 1320, 1120 cm^{-1}; ^1H NMR δ 0.13 (s, 9 H), 1.39 (d, 3 H, J = 7 Hz), 3.70 (br s, 2 H), 3.71 (q, 1 H, J = 7 Hz), 6.08 (br s, 1 H); MS, m/z 204 (M^+), 140, 125, 73 (100%).

Anal. Calcd for $C_7H_{14}O_2SSi$: C, 47.0; H, 7.9. Found: 46.6; H, 7.9.

Thermolyses of the Silylated 3-Sulfolenes 4, 6, and 14 to the Dienes 5, 7, and 15. A solution of the silylated 3-sulfolene in EtOAc (20%) was injected on a GC (injection temperature at 240 °C, oven temperature at 75 °C, and detector temperature at 280 °C) using an SE-30 column (3 m). The chromatogram showed the existence of only one product, which was collected with a dry-ice trap.

2-(Trimethylsilyl)-1,3-butadiene (5): IR (neat) 3090, 3070, 2960, 2900, 1620, 1250, 1050, 840 cm^{-1}; NMR δ 0.19 (s, 9 H), 5.05 (d, 1 H, J = 10 Hz), 5.16 (d, 1 H, J = 16 Hz), 5.36 (d, 1 H, J = 3 Hz), 5.66 (d, 1 H, J = 3 Hz), 6.4 (dd, 1 H, J = 10 Hz, 16 Hz); MS, m/z 126 (M^+), 111, 85, 73 (100%).

1-(Trimethylsilyl)-1,3-butadiene (7): The ^1H NMR spectrum was identical with that reported in the literature.[1a]

2-(Trimethylsilyl)-1,3-pentadiene (15): IR (neat) 3050, 2960, 1640, 1450, 1400, 1250, 960, 910, 830 cm^{-1}; NMR δ 0.15 (s, 9 H), 1.75 (d, 3 H, J = 5 Hz), 5.28 (d, 1 H, J = 4 Hz), 5.60 (d, 1 H, J = 4 Hz), 5.85 (dq, 1 H, J = 16 Hz, 5 Hz), 6.21 (d, 1 H, J = 16 Hz); MS, m/z 140 (M^+), 125, 73 (100%).

Cycloaddition Reactions of the Silylated 3-Sulfolenes 4 and 12–14 with DMAD To Give the Adducts 16–19. A mixture of silylated 3-sulfolene (1 mmol) and DMAD (1.1 mmol) dissolved in anhydrous benzene (5 mL) was heated in a sealed tube at 160 °C for 14 h. The cooled reaction mixture was concentrated and purified by a silica gel column (hexane/EtOAc, 2:1) to give the pure adduct. The analytical sample was obtained by HPLC (LiChrosorb column, hexane/EtOAc, 3:1).

1,2-Dicarbomethoxy-4-(trimethylsilyl)cyclohexa-1,4-diene (16). This was obtained from the reaction of 4 in 76% yield: IR (neat) 3000, 2950, 2870, 1730, 1665, 1625, 1430, 1370 cm^{-1}; NMR δ 0.06 (s, 9 H), 2.99 (s, 4 H), 3.77 (s, 6 H), 5.95 (s, 1 H); MS, m/z 268 (M^+), 253, 251, 163 (100%).

Anal. Calcd for $C_{13}H_{20}O_4Si$: C, 58.2; H, 7.5. Found: C, 57.8; H, 7.1.

1,2-Dicarbomethoxy-5-methyl-6-(trimethylsilyl)cyclohexa-1,4-diene (17). This was obtained from the reaction of 12 in 90% yield: IR (neat) 2950, 1730, 1630, 1440, 1260, 1080, 840, 740 cm^{-1}; NMR δ 0.07 (br s, 9 H), 1.73 (br s, 3 H), 2.7 (m, 1 H), 2.88 (br s, 2 H), 3.73 (s, 6 H), 5.23 (br s, 1 H); MS, m/z 282 (M^+), 251, 178 (100%), 176, 119, 91, 73.

Anal. Calcd for $C_{14}H_{22}O_4Si$: C, 59.5; H, 7.9. Found: C, 59.4; H, 7.9.

1,2-Dicarbomethoxy-4,5-dimethyl-6-(trimethylsilyl)-cyclohexa-1,4-diene (18). This was obtained from the reaction of 13 in 85% yield: IR (neat) 2960, 1730, 1660, 1440, 1280, 1160, 1080, 850 cm^{-1}; NMR δ 0.04 (s, 9 H), 1.53 (s, 6 H), 2.94 (s, 3 H), 3.78 (s, 6 H); MS, m/z 296 (M^+), 265, 192, 177, 133, 105, 73 (100%).

Anal. Calcd for $C_{15}H_{24}O_4Si$: C, 60.8; H, 8.2. Found: C, 60.8; H, 8.2.

1,2-Dicarbomethoxy-3-methyl-5-(trimethylsilyl)cyclohexa-1,4-diene (19). This was obtained from the reaction of 14 in 85% yield: IR (neat) 2950, 2870, 1735, 1670, 1630, 1440, 1260 cm^{-1}; NMR δ 0.06 (s, 9 H), 1.12 (d, 3 H, J = 7 Hz), 2.9–3.3 (m, 3 H), 3.75 (br s, 6 H), 5.86 (br s, 1 H); MS, m/z 282 (M^+), 267, 265, 235, 119 (100%).

Anal. Calcd for $C_{14}H_{22}O_4Si$: C, 59.5; H, 7.8. Found: C, 59.8; H, 7.9.

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