Stable Sulfur Ylides. XI.[1] Facile Preparation of Silyloxydienes from Stable Sulfur Ylides

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Disilyloxydienes (2a—c) were easily obtained by treatment of stable sulfur ylides (1a—c) with chlorotrimethylsilane in the presence of triethylamine. Cycloaddition reaction of these dienes with some dienophiles was carried out.

Keywords stable sulfur ylide; chlorotrimethylsilane; enol silylation; silyloxydiene; dienophile; Diels–Alder reaction

In a previous paper,[1] we reported that dimethylsulfonium diacetylmethylide (**1a**) was easily converted to 2-acetoxy-3-methylthio-2-penten-4-one and 2,4-diacetoxy-3-methylthio-1,3-pentadiene by treatment with acetyl chloride, and the latter compound did not behave as a diene in the Diels–Alder reaction.

Recently, a number of papers have been published on the preparations of dienes possessing trimethylsilyloxy and/or methoxy groups as electron-donating groups. These dienes have been widely applied in syntheses of carbocyclic and heterocyclic compounds.[2]

In this paper we describe an easy and convenient preparation of bis(trimethylsilyloxy)dienes (**2a—c**) by the treatment of ylides (**1a—c**) with chlorotrimethylsilane (TMSCl) and reaction of the dienes with some dienophiles to give the corresponding cycloadducts.

Treatment of the ylide (**1a**) with TMSCl (3 eq) and triethylamine (3 eq) in chloroform at room temperature gave 2,4-bis(trimethylsilyloxy)-3-methylthio-1,3-pentadiene (**2a**) in 95% yield. The structure of **2a** was confirmed by elemental analysis, the mass spectrum (MS), and the proton nuclear magnetic resonance (^{1}H-NMR) spectrum. The ^{1}H-NMR spectrum of **2a** showed characteristic peaks at δ 4.25 and 4.48 due to terminal methylene protons and δ 2.02 and 2.13 due to methylthio and C-methyl protons, and was concluded to be a mixture of geometrical isomers (Table I). Similarly, **1b** and **1c** were converted to 2,4-bis(trimethylsilyloxy)-3-phenylthio-1,3-pentadiene (**2b**, a mixture of *E*/*Z* isomers) and 2,4-bis-(trimethylsilyloxy)-3-(4-chlorobutylthio)-1,3-pentadiene (**2c**, a mixture of *E*/*Z* isomers), respectively. However, in the case of dimethylsulfonium acetylcarbomethoxymethylide (**3a**) with TMSCl in the presence of triethylamine, no reaction proceeded and **3a** was recovered. Therefore, **3a** was treated with TMSCl, triethylamine, and sodium iodide in acetonitrile,[3] and methyl 2-methyltio-3-trimethylsilyloxy-2-butenoate (**4a**) was obtained in 65% yield. The ylide **3b** was also converted to methyl 2-phenylthio-3-trimethylsilyloxy-2-butenoate (**4b**) in 71% yield (crude) in the same manner as described above. However **4b** could not be purified because of its lability.

Several investigators[4] have reported the usefulness of 1,3-bis(trimethylsilyloxy)-1-methoxy-1,3-butadiene, derived from methyl acetoacetate, as the dianion equivalent of methyl acetoacetate. Therefore, we attempted to prepare the disilyloxydiene (**5**) from **4a**. The treatment of **4a** with lithium diisopropylamide (LDA), followed by TMSCl gave an oily product (**5**), which showed the signals of terminal methylene at δ 4.40 and 4.50 in the

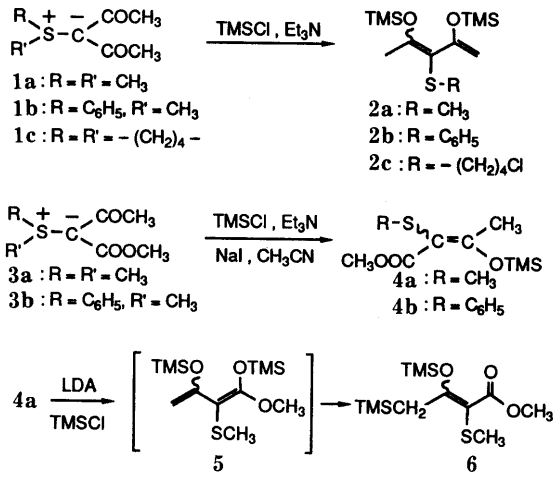

Chart 1

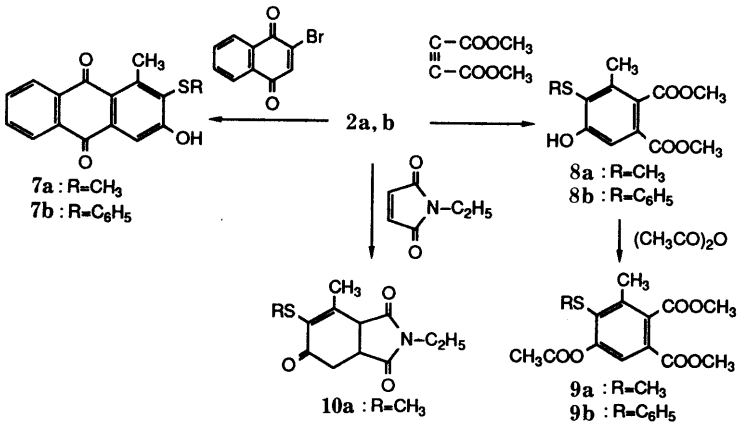

Chart 2

^{1}H-NMR spectrum. The oily product (**5**) was distilled under reduced pressure in an attempt at purification, but we obtained methyl 2-methylthio-3-trimethylsilyloxy-4-trimethylsilyl-2-butenoate (**6**). The conversion of **5** to **6** was observed simply on standing at room temperature for a few hours.

We examined the Diels–Alder reaction of the dienes obtained here with typical dienophiles such as 2-bromo-1,4-naphthoquinone, dimethyl acetylenedicarboxylate, and *N*-ethylmaleimide (Chart 2). In all cases, the corresponding cycloadducts were obtained in moderate yields. Therefore, the dienes (**2a** and **2b**) are expected to be useful as Diels–Alder dienes.

Experimental

Melting points were taken on a Yanaco micro melting point apparatus, and are uncorrected. Infrared (IR) spectra were recorded with a JASCO IR-810 or IRA-2 spectrophotometer, and the ultraviolet (UV) spectra with a Hitachi 323 spectrophotometer. ^{1}H-NMR spectra were recorded with a Hitachi R-600, a JEOL JNM FX-90Q, or a JEOL JNM GX-400 spectrometer. Chemical shifts are given in the δ (ppm) scale with tetramethylsilane as an internal standard. Mass spectra (MS) were taken with a JEOL JMS-DX 303 spectrometer and a JEOL JMA-DA 5000 data processor.

2,4-Bis(trimethylsilyloxy)-3-methylthio-1,3-pentadiene (2a) TMSCl (3.26 g, 30 mmol) was added dropwise to a solution of **1a** (1.60 g, 10 mmol) and triethylamine (3.03 g, 30 mmol) in dry $CHCl_3$. The mixture was stirred at room temperature for 12 h under N_2, then concentrated. Ether (30 ml) was added to the residue, and the resulting precipitate was filtered off. The filtrate was concentrated to give a brown oil. Distillation of the oil gave **2a** (2.75 g, 95%) as a colorless oil (Table I).

2,4-Bis(trimethylsilyloxy)-3-phenylthio-1,3-pentadiene (2b) The same procedure as described above was applied to **1b** (8.84 g, 40 mmol), triethylamine (16.20 g, 160 mmol), and TMSCl (17.36 g, 160 mmol) to give **2b** (13.00 g, 98%) as a colorless oil (Table I).

2,4-Bis(trimethylsilyloxy)-3-(4-chlorobutylthio)1,3-pentadiene (2c) The same procedure as described above was applied to **1c** (9.30 g, 50 mmol), triethylamine (15.20 g, 150 mmol), and TMSCl (16.30 g, 150 mmol) to give **2c** (13.70 g, 75%) as an yellowish oil (Table I).

Methyl 2-Methylthio-3-trimethylsilyloxy-2-butenoate (4a) TMSCl (10.85 g, 100 mmol) was added dropwise to a suspension of **3a** (8.80 g, 50 mmol), NaI (3.75 g, 25 mmol), and triethylamine (10.10 g, 100 mmol) in dry CH_3CN (50 ml) and the mixture was refluxed for 3 h under N_2. After evaporation of the solvent, ether (100 ml) was added to the residue. The resulting mixture was filtered. The filtrate was concentrated to give a brown oil. Distillation of the oil gave **4a** (7.80 g, 65%) as an yellowish oil (Table I).

Methyl 2-Phenylthio-3-trimethylsilyloxy-2-butenoate (4b) The same procedure as described above was applied to **3b** (1.19 g, 5 mmol), NaI (0.38 g, 2.5 mmol), triethylamine (1.10 g, 10 mmol), and TMSCl (1.08 g, 10 mmol) to give **4b** (1.13 g, 71%) as a crude brown oil (Table I). Distillation of the crude oil gave a colorless oil which was an approximately 3:2 mixture of **4b** and methyl 2-(phenylthio) acetoacetate as judged from the ^{1}H-NMR spectrum.

Reaction of 4a with TMSCl in the Presence of LDA A 1.5 M solution of *n*-butyllithium in hexane (6 ml, 6.0 mmol) was added to a solution of diisopropylamine (0.84 ml, 6.0 mmol) in dry tetrahydrofuran (THF) (10 ml) under N_2, followed by addition of dry tetramethylethylenediamine (TMEDA) (0.7 ml) at 0°C. The mixture was cooled to −78 °C, and **4a** (1.20 g, 5 mmol) in THF (5 ml) was added. The yellow-colored solution was quenched with TMSCl (0.97 g, 9.0 mmol). The mixture was allowed to warm to 0 °C and the solvent was removed under reduced pressure. The residue was triturated with dry hexane with cooling. The resulting precipitate was filtered off. The filtrate was concentrated to give a brown oil (crude **5**). ^{1}H-NMR ($CDCl_3$) δ: 0.1—0.28 (18H, each s, 2 × $SiMe_3$), 2.11 and 2.15 (3H, each s, SMe), 3.66 and 3.70 (3H, each s, OMe), 4.40 and 4.50 (2H, each s, $=CH_2$), an approximately 2:1 mixture of *E*/*Z* (or *Z*/*E*) isomers. IR spectrum shows no C=O stretching absorption band. This crude oil (0.5 g) was distilled under reduced pressure to give 0.30 g of a colorless oil (**6**), bp 80—85 °C/0.3 mmHg. IR (neat) cm^{-1}: 1705 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 0.07—0.29 (18H, m, 2 × $SiMe_3$), 2.14 and 2.17 (3H, each s, SMe), 2.25 and 2.28 (2H, each s, CH_2-Si), 3.76 and 3.78 (3H, each s, COOMe), an approximately 2:1 mixture of *E*/*Z* (or *Z*/*E*) isomers. High-resolution MS calcd for $C_{12}H_{26}O_3SSi_2$ (M^+) *m*/*z*: 306.1141. Found: 306.1139.

3-Hydroxy-1-methyl-3-(methylthio)anthraquinone (7a) A solution of **2a** (1.0 g, 3.4 mmol) and 2-bromo-1,4-naphthoquinone (0.4 g, 1.7 mmol) in dry benzene (5 ml) was stirred at room temperature for 10 h under N_2. The reaction mixture was concentrated and the residue was heated for 1.5 h at 130 °C, then treated with water (2 ml). The resulting mixture was extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4 and concentrated to give an yellow solid. Recrystallization of the solid from EtOH gave **7a** (0.2 g, 42%).

The same procedure as described above applied to **2b** (1.06 g, 3.0 mmol) and 2-bromo-1,4-naphthoquinone (0.71 g, 3.0 mmol) to give **7b** (0.63 g, 60%) as yellow needles (Table II).

Dimethyl 5-Hydroxy-3-methyl-4-(methylthio)phthalate (8a) A solution of **2a** (2.00 g, 6.9 mmol) and dimethyl acetylenedicarboxylate (0.50 g, 3.5 mmol) in dry toluene (15 ml) was refluxed for 17 h under N_2. After removal of the solvent, the residue was dissolved in 5% HCl–MeOH (10 ml), and stirred for 1 h at room temperature. After evaporation of the solvent, the residue was extracted with ether. The extract was washed with 5% $NaHCO_3$, dried over Na_2SO_4, and evaporated. The residue was chromatographed on a silica gel column using benzene as an eluent to give **8a** (0.56 g, 59%) as a colorless oil. IR (neat) cm^{-1}: 3380 (OH), 1730 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.18 (3H, s, SMe), 2.51 (3H, s, Me), 3.82

TABLE I. Analytical and ^{1}H-NMR Spectral Data for **2a—c**, **4a**, **b**

Compd. No.	bp (°C) (mmHg)	Formula	Analysis (%) Calcd (Found) C	H	^{1}H-NMR ($CDCl_3$) δ
2a	75— 78 (0.25)	$C_{12}H_{26}O_2SSi_2$	49.60 (49.28	9.02 8.74)	0.22 and 0.25 (each 9H, s, $SiMe_3$), 2.02 (3H, s, SMe), 2.13 (3H, s, C-Me), 4.25 and 4.48 (each 1H, s, $=CH_2$)
2b[a]	100 (0.25)	$C_{17}H_{28}O_2SSi_2$	57.90 (57.82	8.00 7.83)	0.08 and 0.11 (ratio 1:2, 9H, each s, $SiMe_3$), 0.17 and 0.26 (ratio 2:1, 9H, each s, $SiMe_3$), 2.16 (3H, s, C-Me), 4.34 (2H, s, $=CH_2$), 7.0—7.4 (5H, m, Ph)
2c	109—110 (0.5)	$C_{15}H_{31}ClO_2SSi_2$	49.08 (49.08	8.51 8.64)	0.52 (18H, s, 2 × $SiMe_3$), 2.08 (4H, m, CH_2CH_2), 2.34 (3H, s, C-Me), 2.92 (2H, m, SCH_2), 3.84 (2H, m, Cl-CH_2), 4.55 and 4.75 (2H, each s, $=CH_2$)
4a[a]	124—126 (8.0)	$C_9H_{18}O_3SSi$	46.07 (45.82	7.67 7.41)	0.18 and 0.24 (ratio 1:2, 9H, each s, $SiMe_3$), 2.10 and 2.11 (ratio 1:2, 3H, each s, SMe), 2.18 and 2.21 (ratio 2:1, 3H, each s, C-Me), 3.67 and 3.71 (ratio 2:1, 3H, each s, COOMe)
4b[a]	—	$C_{14}H_{20}O_3SSi$	—	—	0.20 and 0.30 (ratio 2:1, 9H, each s, $SiMe_3$), 2.23 and 2.42 (ratio 1:2, 3H, each s, C-Me), 3.62 and 3.64 (ratio 2:1, 3H, each s, COOMe), 7.0—7.4 (5H, m, Ph)

a) ^{1}H-NMR spectra indicated them to be an approximately 2:1 mixture of *E* and *Z* (or *Z* and *E*) isomers.

TABLE II. Analytical and Physical Data for Cycloadducts

Compd. No.	mp (°C) Recryst. solvent	Formula	Analysis (%) Calcd (Found) C	H	S	IR (KBr) (cm^{-1})	^{1}H-NMR ($CDCl_3$[a]) δ
7a	211—213 (EtOH)	$C_{16}H_{12}O_3S$	67.59 (67.56	4.25 4.30	11.28 11.15)	3360 (OH) 1660 (CO)	2.29 (3H, s, SMe), 3.13 (3H, s, Me), 7.83—8.36 (6H, m, aromatic H and OH)
7b	227—228 (EtOH)	$C_{21}H_{14}O_3S$	72.81 (72.64	4.07 4.25	9.26 9.12)	3330 (OH) 1670 (CO)	2.89 (3H, s, Me), 6.9—7.4 (5H, m, Ph), 7.68 (1H, s, C4-H), 7.7—8.2 (4H, m, C5-8-H), 11.35 (1H, s, OH)
9a	70— 71 (Hexane)	$C_{14}H_{16}O_6S$	53.84 (53.77	5.16 5.17	10.27 10.34)	1760 (CO) 1725 (CO)	2.06 (3H, s, COMe), 2.33 (3H, s, SMe), 2.52 (3H, s, Me), 3.83 and 3.91 (6H, each s, 2×COOMe), 7.55 (1H, s, aromatic H)
9b	131—133 (AcOEt–hexane)	$C_{19}H_{18}O_6S$	60.95 (60.77	4.85 4.89	8.56 8.60)	1770 (CO) 1740 (CO) 1720 (CO)	2.16 (3H, s, COMe), 2.36 (3H, d, J=0.45, C-Me), 3.88 and 3.93 (6H, each s, 2×COOMe), 7.0—7.4 (5H, m, Ph), 7.66 (1H, d, J=0.45, aromatic H)
10a	88— 89 (Ether)	$C_{12}H_{15}NO_3S$	56.90 (56.72	5.97 5.97	12.66 12.44)	1775 (CO) 1710 (CO)	1.15 (3H, t, J=7.2, N-CH_2CH_3), 2.22 (3H, s, SMe), 2.49 (3H, s, Me), 2.71—3.82 (6H, m, N-CH_2, C4-H, C5-H, and C6-2H

a) The spectrum of **7b** was measured in dimethylsulfoxide-d_6 solution.

(3H, s, COOMe), 3.85 (3H, s, COOMe), 7.22 (1H, s, OH), 7.36 (1H, s, aromatic H). MS m/z: 270 (M^+).

8a was acetylated in the usual manner using acetic anhydride and pyridine to give the acetate (**9a**) as colorless needles (Table II).

The same procedure as described above was applied to **2b** and dimethyl acetylenedicarboxylate to give **8b** (65%) as a colorless oil. IR (neat) cm^{-1}: 3380 (OH), 1730 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.40 (3H, d, J=0.45 Hz, C-Me), 3.90 (6H, s, 2×COOMe), 7.05 (1H, s, OH), 7.0—7.4 (5H, m, Ph), 7.53 (1H, d, J=0.45 Hz, aromatic H). MS m/z: 332 (M^+).

Acetylation of **8b** gave **9b** as colorless prisms (Table II).

***N*-Ethyl-3-methyl-4-methylthio-5-oxo-3-cyclohexene-1,2-dicarboximide (10a)** A solution of **2a** (2.00 g, 6.9 mmol) and *N*-ethylmaleimide (0.44 g, 3.5 mmol) in dry toluene (15 ml) was refluxed for 55 h under N_2. After removal of the solvent, the residue was dissolved in 5% HCl–MeOH (10 ml), and stirred for 0.5 h at room temperature. After evaporation of the solvent, the residue was extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4, and evaporated. The residue was chromatographed on a silica gel column using benzene as an eluent to give **10a** (0.25 g, 28%) as colorless needles (Table II).

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