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Synthetic Equivalents to Substituted Acetylenes in Cycloaddition Reactions. Dienophilic Reactivity of 2-Methyl-, 2-Phenyl- and 2,3-Trimethylene-1,4-Benzodithiins-1,4-Tetroxides

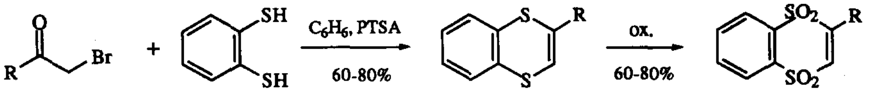
Andrea Giacometti, Ottorino De Lucchi,* Francisco Dilillo
Dipartimento di Chimica, Università di Venezia, Dorsoduro 2137, I-30123 Venezia, Italy
Sergio Cossu
Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy
Karl Peters, Eva-Maria Peters, and Hans G. von Schnering[1]
Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70506 Stuttgart, Germany

Abstract: Dienophiles 2-methyl-1,4-benzodithiin-1,4-tetroxide (**3a**), 2-phenyl-1,4-benzodithiin-1,4-tetroxide (**3b**) and 2,3-trimethylene-1,4-benzodithiin-1,4-tetroxide (**3c**) have been prepared with different methods starting from benzene-1,2-dithiol (**1**). Their reactivity was tested towards cyclopentadiene, sulfolene, furan and 1,3-cyclohexadiene. The Diels-Alder adducts to cyclopentadiene were converted into the corresponding unsaturated hydrocarbons, mimicking the Diels-Alder reaction of substituted acetylenes. The X-ray structure determinations of **4b**, a secondary product in the preparation of 2-phenyl-1,4-benzodithiin-1,4-tetroxide and of the adduct of the phenyl substituted derivative with cyclopentadiene **8b** are reported.

Sulfonyl dienophiles have been shown to be useful reagents in organic synthesis because of their reactivity and versatility in subsequent transformations of the adducts.[2] A main feature of these reagents that has been largely exploited is their ability to function as equivalents of acetylene in cycloaddition reactions.[3] Except for a very few cases,[4] however, this equivalence is limited to the parent acetylene because of the unreactivity of substituted dienophiles. For example, a single methyl group in the otherwise very reactive bis(arylsufonyl)ethylenes[5] (*i.e.* $ArSO_2CCH_3{=}CHSO_2Ar$) is sufficient to deprive completely its reactivity.[6] Similarly, other substituted bis(arylsulfonyl)ethylenes have been shown to be unreactive as dienophiles,[7] preventing the utilization of these molecules for the preparation of more complex targets. In order to solve this synthetic problem, we have investigated the reactivity of an alkyl, an aryl and a cyclic derivative of 1,4-benzodithiin tetroxide towards a few representative dienes. The parent derivative (R = H in structure **3**) has been reported to be more reactive than the bis(arylsulfonyl)ethylenes.[8]

RESULTS AND DISCUSSION

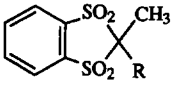
The preparation of the methyl and phenyl compounds **3a** and **3b** was accomplished in the more convenient way *via* the sequence of reactions illustrated in eq 1. The cyclization step was adjusted over similar procedures.[9]



(1)

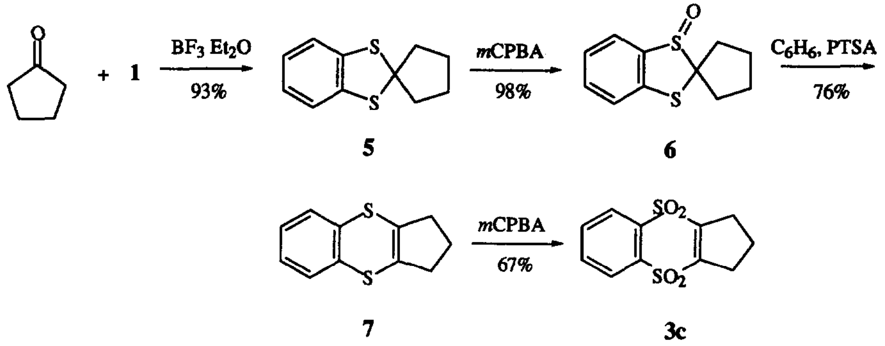
R = CH_3 R = C_6H_5 **1** **2a** (R = CH_3) **2b** (R = C_6H_5) **3a** (R = CH_3) **3b** (R = C_6H_5)

Benzene-1,2-dithiol (**1**) is readily available by a number of routes, some of which can be accomplished on a large scale.[10] In order to simplify the preparation of **3a** and **3b**, it is possible to oxidise the crude cyclized products **2**. In the final chromatographic separation of **3a** or **3b**, the side products **4a** or **4b** were also obtained in *ca.* 10-15%. These products probably arise from dithiol mediated debromination followed by standard thioketalisation. The identity of **4b** was confirmed by X-ray analysis (Figure 1).



4a ($R = CH_3$)
4b ($R = C_6H_5$)

The cyclic derivative **3c** was obtained by a different route engaging Pummerer dehydration of the sulfoxide **6**[11] as the key step (eq 2). Because of the several related examples reported in the literature,[12] the sequence of reactions of eq 2 represents a general method for the preparation of a large number of cyclic, mono- or disubstituted 1,4-dithiins tetroxides.



(2)

The cycloaddition experiments were performed on cyclopentadiene, 1,3-butadiene (generated by SO_2 extrusion from 3-sulfolene), furan and 1,3-cyclohexadiene. The three dienophiles reacted with cyclopentadiene with decreasing order of reactivity changing from **3a** to **3c** and furnished the respective Diels-Alder adducts **8a,b,d**. For example, while **3a** reacted smoothly in *ca.* 30 min, **3b** reacted overnight and **3c** required several days at room temperature. The stereochemistry of the adducts was always *endo*, as expected on the basis of the Alder rule. The assignment was based on the coupling constants and decoupling experiments in the ^1H NMR spectrum and confirmed with the X-ray structure determination of adduct **8b** (Figure 2).

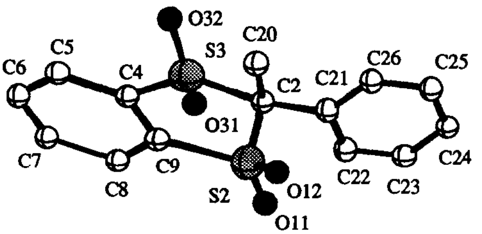


Figure 1 - Perspective drawing of compound **4b** (only non-hydrogen atoms shown) with the numbering scheme used.

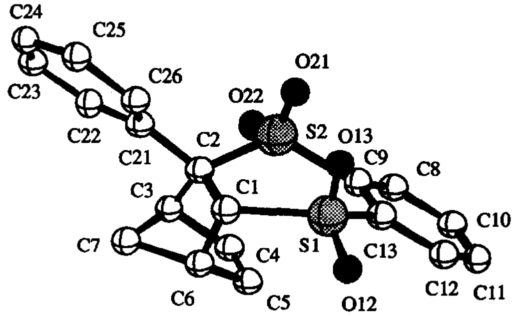
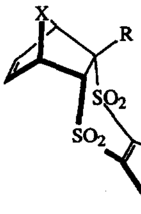
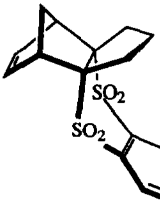


Figure 2 - Perspective drawing of compound **8b** (only non-hydrogen atoms shown) with the numbering scheme used.

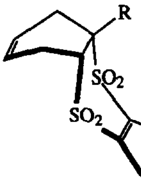
The same order of reactivity observed with cyclopentadiene was experienced with 1,3-butadiene (generated by SO_2 extrusion from 3-sulfolene). Only **3a** and **3b** proved reactive in a reasonable time at 60-80 °C neat while **3c** gave **9c** after several days. Finally, **3a** exhibited reactivity towards furan giving **8c** cleanly and in high yield and 1,3-cyclohexadiene affording cycloadduct **10**. The latter reaction needed activation and was carried out in ether containing 5M lithium perchlorate. It should be noted that lithium perchlorate in ether is amongst the very few systems effective in the catalysis of sulfonyl dienophiles.[13]



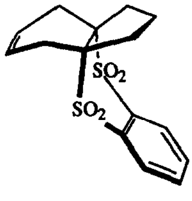
8a (R = CH_3; X = CH_2)
8b (R = C_6H_5; X = CH_2)
8c (R = CH_3; X = O)



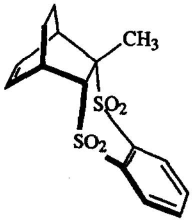
8d



9a (R = CH_3)
9b (R = C_6H_5)

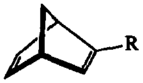


9c

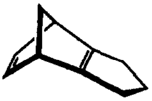


10

The utilization of the dienophiles **3a-c** as synthetic equivalents of substituted acetylenes in cycloaddition reactions was demonstrated with the sodium amalgam reduction of **8a,b,d** to the respective norbornadienes **11a,b,d**.



11a (R = CH_3)
11b (R = C_6H_5)



11d

So far, substituted norbornadienes of type **11a,b** could only be prepared *via* manipulation of certain Diels-Alder adducts[14] and disubstituted norbornadienes of type **11d** were virtually unknown. To the best of our knowledge, the dienophiles **3a-c** described here are the only ones able to function as true equivalents of substituted acetylenes in cycloaddition reactions.

EXPERIMENTAL

Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker AC 200 and on a Varian VXR 300 spectrometers operating at 200 and 300 MHz respectively, using tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded with a Varian VXR 300 operating at 75.4 MHz. IR spectra were performed on a Perkin Elmer 983 spectrophotometer. Microanalytical determinations were performed on a Perkin Elmer 2400 analyzer. Known compounds used in this research were either purchased from standard chemical suppliers or prepared according to literature procedures and purified to match the reported spectral and physical data.

2-Methyl-1,4-benzodithiin (2a) and 2-Phenyl-1,4-benzodithiin (2b). General Procedure

A solution of benzene-1,2-dithiol (5.55 g, 39 mmol), bromo ketone (39 mmol) and *p*-toluensulfonic acid hydrate (8.8 mg) in benzene (25 mL) was heated under reflux with a Dean-Stark receiver for 3 hours. After cooling to room temperature the reaction mixture was washed with sodium hydroxide 2*N* (3 x 50 mL) and with water (3 x 50 mL), then dried over sodium sulfate and concentrated under reduced pressure. Analytically pure samples were obtained by flash-chromatography on silica gel (230-400 mesh) eluting with *n*-hexane.

2a: 94 % yield. Oil. ^{1}H-NMR (200 MHz, $CDCl_3$), δ, ppm: 2.15 (3 H, d, *J* = 1.4 Hz), 6.12 (1 H, q, *J* = 1.4 Hz), 7.10-7.40 (4 H, m, Ar). *Elem. anal.*, found % (calcd for $C_9H_8S_2$): C, 59.67 (59.96); H, 4.40 (4.47).

2b: 70 % yield. Oil. ^{1}H-NMR (200 MHz, $CDCl_3$), δ, ppm: 6.67 (1 H, s), 7.00-8.00 (9 H, series of m, Ar). *Elem. anal.*, found % (calcd for $C_{14}H_9S_2$): C, 69.70 (69.67); H, 3.60 (3.76).

2,3-Trimethylene-1,4-benzodithiin (7)

A mixture of benzene-1,2-dithiol (5 g, 35 mmol), cyclopentanone (3.1 mL, 35 mmol) and boron trifluoride etherate (1.5 mL) was cooled with an ice bath and stirred for 2 hr. The reaction mixture was extracted with diethyl ether (100 mL), washed with sodium hydroxide 10% (3 x 50 mL) and water (3 x 50 mL), dried over anhydrous sodium sulfate and concentrated to afford **5** as a colorless oil: 6.75 g, (95% yield); ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 1.76-1.88 (4 H, m), 2.24-2.34 (4 H, m), 6.96-7.04 (2 H, m, Ar), 7.14-7.20 (2 H, m, Ar). A solution of **5** (6.75 g, 32.4 mmol) in dichloromethane (50 mL) was cooled with an ice bath, and a solution of m-CPBA (*ca.* 80% active; 6.99 g, 32.4 mmol) in dichloromethane (200 mL) was added during *ca.* 1 hr with efficient stirring. The reaction mixture was washed with sodium metabisulfite and then poured into a solution of sodium carbonate 10% (150 mL); the aqueous layer was extracted with dichloromethane (2 x 150 mL). The organic phases were collected and dried over anhydrous sodium sulfate and rotoevaporated to give **6** as a faint yellow oil: 7.73 g, (98% yield). ^{1}H-NMR (200 MHz, $CDCl_3$), δ, ppm: 1.62-2.10 (7 H, series of m), 2.58-2.70 (1 H, m), 7.08-7.16, 7.22-7.32, 7.67-7.72 (4 H, series of m, Ar). A solution of the intermediate **6** (1.0 g, 4.46 mmol) and *p*-toluensulfonic acid hydrate (106 mg, 0.56 mmol) in benzene (20 mL) was heated at reflux temperature with a Dean-Stark receiver for *ca.* 6 days. The reaction mixture was cooled to room temperature, washed with a saturated solution of sodium bicarbonate (5x100 mL), dried over anhydrous sodium sulfate and concentrated. The crude mixture was purified by flash-chromatography eluting with a gradient of *n*-hexane-dichloromethane to give a solid: 0.70 g, 76% yield. mp 68-70 °C (EtOH). ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 2.14 (2 H, quintet, *J* = 6.7 Hz), 2.42 (4 H, t, *J* = 6.7 Hz), 7.07-7.14, 7.15-7.22 (4 H, m, AA'BB' system, Ar). *Elem. anal.*, found % (calcd for $C_{11}H_{10}S_2$): C, 64.27 (64.04); H, 4.70 (4.89).

2-Methyl-1,4-benzodithiin Tetroxide (3a), 2-Phenyl-1,4-benzodithiin Tetroxide (3b), and 2,3-Trimethylene-1,4-benzodithiin Tetroxide (3c). General Procedure

A solution of either **2a**, **2b** or **7** (35 mmol) in dichloromethane (100 mL) was vigorously stirred in a ice bath, while a solution of mCPBA (*ca.* 80% active; 33.3 g, 193 mmol) in dichloromethane (200 mL) was added slowly during *ca.* 2 hr. The reaction mixture was heated at reflux temperature for 24 hr, then cooled to room temperature, washed with $Na_2S_2O_5$ (3 x 40 mL of a 10% aqueous solution), with sodium carbonate (5 x 100 mL of a 10% aqueous solution), dried over anhydrous sodium sulfate, and concentrated under reduced pressure.

3a: 83% yield. Purified by flash-chromatography eluting with a gradient of dichloromethane/*n*-hexane. mp 134-6 °C (EtOH). ^{1}H-NMR (200 MHz, $CDCl_3$), δ, ppm: 2.41 (3 H, d, *J* = 1.8 Hz), 6.99 (1 H, q, *J* = 1.8 Hz), 7.82-7.86, 8.07-8.18 (4 H, m, Ar). ^{13}C-NMR ($CDCl_3$), δ, ppm: 15.94, 124.96, 125.45, 133.66, 135.53, 137.45, 138.76, 150.16. IR (KBr disk): 3089, 3018, 1320, 1273, 1167, 1152, 1133, 849, 775, 746, 717, 706 cm^{-1}. *Elem. anal.*, found % (calcd for $C_9H_8O_4S_2$): C, 44.60 (44.25); H, 3.27 (3.30).

3b: 80% yield. Purified as described for **3a**. mp 161-163 °C (EtOH). ^{1}H-NMR (200 MHz, $CDCl_3$), δ, ppm: 7.14 (1 H, s), 7.48-7.70, 7.82-7.94, 8.13-8.26 (9 H, series of m, Ar). ^{13}C-NMR ($CDCl_3$), δ, ppm: 125.04, 125.74, 127.86, 128.83, 129.17, 131.87, 133.66, 133.90, 130.04, 138.62, 152.11. IR (KBr disk) 3083, 3017, 1436, 1323, 1259, 1154, 1130, 838, 811, 778, 703, 633 cm^{-1}. *Elem. anal.*, found % (calcd for $C_{14}H_{10}O_4S_2$): C, 54.70 (54.89); H, 3.20 (3.29).

3c: 38% yield. mp 182-4°C (dichloromethane-*n*-hexane). ^{1}H-NMR (200 MHz, $CDCl_3$), δ, ppm: 2.24 (2 H, quintet, *J* = 7.8 Hz), 3.23 (4 H, t, *J* = 7.8 Hz), 7.80-7.90, 8.07-8.17 (4 H, AA'BB' system, Ar). ^{13}C-NMR ($CDCl_3$), δ, ppm: 20.64, 32.02, 124.78, 133.65, 138.476, 145.58. IR (KBr disk) 2961, 1436, 1382, 1322, 1154, 1119, 804, 706, 613 cm^{-1}. *Elem. anal.*, found % (calcd for $C_{11}H_{10}O_4S_2$): C, 48.70 (48.88); H, 3.71 (3.73).

4a: 12% yield. mp 140-1 °C (dichloromethane-*n*-hexane). ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 1.79 (6 H, s), 7.87-7.94, 7.98-8.05 (4 H, AA'BB' system, Ar). ^{13}C-NMR ($CDCl_3$), δ, ppm: 17.04, 73.69, 123.19, 135.19, 135.56. IR (KBr disk) 3079, 2995, 1450, 1442, 1325, 1188, 1176, 1158, 1103, 764, 724, 688, 647 cm^{-1}. *Elem. anal.*, found % (calcd for $C_9H_{10}O_4S_2$): C, 43.76 (43.89); H, 4.09 (4.09).

4b: 15% yield. mp 181-2 °C (dichloromethane-*n*-hexane). ^{1}H-NMR (300 MHz, $CDCl_3$), d, ppm: 2.18 (3 H, s), 7.48-7.55, 7.82-7.96, 8.04-8.12 (9 H, series of m, Ar). ^{13}C-NMR ($CDCl_3$), δ, ppm: 20.96, 79.59, 123.41, 125.40, 128.75, 130.10, 130.48, 135.00, 136.33. IR (KBr disk) 3077, 2991, 1494, 1440, 1337, 1326, 1177, 1157, 835, 783, 773, 708, 693, 655 cm^{-1}. *Elem. anal.*, found % (calcd for $C_{14}H_{12}O_4S_2$): C, 50.48 (50.53); H, 3.80 (3.92).

Cycloaddition of 3a-c to Cyclopentadiene

A solution of the dienophiles **3a**, **3b** or **3c** (0.4 mmol) in dichloromethane (2 mL) and a few drops of cyclopentadiene was introduced into a screw-capped Pyrex test tube, purged with argon, sealed and stirred at room temperature. The reaction was monitored by TLC (eluant: dichloromethane/*n*-hexane 9:1) up to completion. The precipited crystals were filtered by suction, washed with *n*-pentane, and recrystallized from the indicated solvent. For the preparation of **8c** the reaction mixture was heated at 70 °C for 48 hr.

8a: 95% yield. mp 300-1 °C (CH_2Cl_2-Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 1.69 (1 H, dt, *J* = 9.9, 2.1 Hz), 1.75 (1 H, d, *J* = 9.9 Hz), 2.05 (3 H, s), 3.25 (1 H, bs), 3.49 (1 H, bs), 3.89 (1 H, d, *J* = 3.0), 5.47 (1 H, dd, *J* = 5.5, 3.0 Hz), 5.90 (1 H, dd, *J* = 5.5, 3.0 Hz), 7.71-7.82 (2 H, m, Ar), 7.93-8.05 (2 H, m, Ar). ^{13}C-NMR (1/1 solution of DMSO d_6-$CDCl_3$), δ, ppm: 20.11, 45.84, 46.75, 52.72, 71.68, 72.75, 123.35, 124.33, 125.73, 132.15, 132.90, 133.22, 135.59, 138.76. IR (KBr disk): 2982, 2915, 1337, 1311, 1302, 1148, 1114, 886, 818, 772, 709, 622 cm^{-1}. *Elem. anal.*, found % (calcd for $C_{14}H_{14}O_4S_2$): C, 54.35. (54.18); H, 4.70. (4.55).

8b: 95% yield. mp 265-7 °C (EtOH). ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 1.44 (1 H, d, part of AB system, *J* = 9.3 Hz), 1.65 (1 H, dt, part of AB system, *J* = 9.3, 1.8 Hz), 3.56 (1 H, bs), 4.22 (1 H, bs), 4.71 (1 H, d, *J* = 3.6 Hz), 5.67 (1 H, dd, *J* = 5.4, 3.0 Hz), 5.93 (1 H, dd, *J* = 5.4, 3.0 Hz),7.40-7.64, 7.70-7.86, 7.95-

8.04, 8.10-8.20 (9 H, series of m, Ar).^{13}C-NMR ($CDCl_3$), δ, ppm: 47.57, 48.48, 52.98, 74.60, 81.14, 125.52, 125.85, 127.47, 128.84, 129.25, 129.34, 129.72, 132.64, 133.47, 133.58, 133.73, 133.82, 134.22, 136.02, 136.33, 137.55. IR (KBr disk): 3063, 3018, 2953, 1435, 1323, 1310, 1274, 1154, 1145, 1124, 1109, 804, 765, 739, 717 cm^{-1}. *Elem. anal.*, found % (calcd for $C_{19}H_{16}O_4S_2$): C, 61.40 (61.27); H, 4.37 (4.33).

8d: quantitative yield of a 9:1 mixture of *endo-exo* isomers. ^{1}H-NMR (300 MHz, $CDCl_3$, only one major isomer), δ, ppm: 1.70 (1 H, dt, 1/2 of AB system, J = 10.2, 1.8 Hz), 1.76-1.88 (2 H, m), 1.91 (1 H, d, 1/2 of AB system, J = 10.2 Hz), 2.17-2.29 (1 H, m), 2.50-2.70 (1 H, m), 3.11 (2 H, dd, J = 15.0, 6.3 Hz), 3.31 (2 H, t, J = 1.5 Hz), 5.68 (2 H, t, J = 1.5 Hz), 7.70-7.78, 7.96-8.04 (4 H, AA'BB' system, Ar). ^{13}C-NMR ($CDCl_3$, only major isomer), δ, ppm: 29.80, 33.69, 46.05, 52.06, 85.44, 125.38, 133.50, 137.42, 139.61. Selected ^{1}H-NMR (300 MHz, $CDCl_3$) for minor isomer, δ, ppm: 3.63 (2 H, t, J = 1.5 Hz, bridgehead proton), 6.56 (2 H, t, J = 1.5 Hz, vinylic proton). IR (KBr disk): 3073, 2936, 1309, 1154, 1145, 1134, 1117, 878, 782, 737, 703, 687, 628 cm^{-1}. *Elem. anal.*, found % (calcd for $C_{16}H_{16}O_4S_2$ of a 9:1 mixture of *endo-exo* isomers): C, 56.96 (57.12); H, 4.56 (4.79).

Reaction of 3a-c with 3-Sulfolene

A mixture of the dienophile (0.4 mmol) and 3-sulfolene (0.8 mmol) was placed in a Pyrex test tube and heated at 60 °C monitoring by TLC (eluant: dichloromethane/*n*-hexane 9:1). The excess of 3-sulfolene was removed by heating at 80° C under reduced pressure. The crude mixture was purified by chromatography (eluant dichloromethane) on a short silica gel column and the solid collected was recrystallized from ethanol.

9a: 94% yield. mp 218-20 °C. ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 2.39 (1 H, 1/2 AB system, d, J = 18.0 Hz), 2.70 (2 H, m), 3.10 (1 H, 1/2 AB system, d, J = 18.0 Hz), 4.36 (1 H, d, J = 6.6 Hz), 5.72 (1 H, m), 5.84 (1 H, m), 7.79-8.08 (4 H, series of m, Ar). *Elem. anal.*, found % (calcd for $C_{18}H_{15}O_4S_2$): C, 52.45 (52.33); H, 4.90 (4.73).

9b: 90 % yield. mp 237-9 °C. ^{1}H-NMR (300 MHz, $CDCl_3$),δ, ppm: 2.30-2.44 (1 H, m), 2.90-3.08 (2 H, m), 3.30-3.42 (1 H, m), 5.15-5.21 (1 H, m, 5.55-5.65 (1 H, m), 5.70-5.86 (1 H, m), 7.44-7.52, 7.65-7.72, 7.78-7.92, 8.06-8.13 (9 H, series of m, Ar). *Elem. anal.*, found % (calcd for $C_{13}H_{14}O_4S_2$): C, 59.89 (60.15); H, 4.02 (4.21).

9c: 92 % yield. mp 168 °C (dec). ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 1.76-2.08 (4 H, m), 2.42 (2 H, dd, J = 15.9, 2.4 Hz, 1/2 of AB system), 2.50-2.62 (2 H, m), 2.78 (2 H, dd, J = 15.9, 2.4 Hz, 1/2 of AB system), 5.95 (2 H, t, J = 2.7 Hz), 7.79-7.86, 8.11-8.18 (4 H, series of m, Ar). *Elem. anal.*, found % (calcd for $C_{15}H_{16}O_4S_2$): C, 55.30 (55.54); H, 4.71 (4.97).

Cycloaddition of 3a to Furan. Preparation of 8c

A solution of **3a** (90 mg, 0.36 mmol), furan (0.4 mL; 5.5 mmol) and dichloromethane (2 mL) was stirred at room temperature in a screw-capped Pyrex tube. After one month the reaction was virtually completed and the crystals precipitated were collected by suction on a glass sintherized filter, washed with diethyl ether (10 mL) and dried to give only the *endo* isomer (95 % yield): mp 157-8 °C (EtOH). ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 2.08 (3 H, s, Me), 3.99 (1 H, d, J = 4.5 Hz), 4.91 (1 H, bs), 5.30 (1 H, bs), 5.89 (1 H, dd, J = 5.7, 1.5 Hz), 6.16 (1 H, dd, J = 5.7, 1.8 Hz), 7.76-7.86 (2 H, m, Ar), 7.92-7.97 (1 H, m, Ar), 7.95-8.05 (1 H, m, Ar). ^{13}C-NMR ($CDCl_3$), δ, ppm: 20.48, 53.42, 70.58, 72.33, 80.67, 86.01, 102.93, 125.39, 125.73, 133.94, 134.41, 134.50, 134.63, 136.77. IR (KBr disk): 3104, 3084, 2991, 2935, 1440, 1319, 1283, 1264, 1246, 1162, 1147, 1118, 1102, 1071, 1043, 1023, 888, 867, 825, 771, 741 cm^{-1}. *Elem. anal.*, found % (calcd for $C_{13}H_{12}O_5S_2$): C, 50.12 (49.99); H, 3.94 (3.87).

Cycloaddition of 3a to 1,3-Cyclohexadiene. Preparation of 10

A mixture of **3a** (60 mg, 0.24 mmol), lithium perchlorate 5*M* (1.8 g, 16.8 mmol) in ethyl ether (3.6 mL) and a few drops of the diene was stirred at room temperature in a screw-capped Pyrex tube, monitoring by TLC (eluant: dichloromethane). After 15 days the crude mixture was diluted with dichloromethane (50 mL), washed with water (3 x 30 mL), dried over anhydrous sodium sulfate and rotoevaporated. The crude solid was flash-chromatographated on silica gel eluting with a gradient dichloromethane/*n*-hexane, and recrystallized from the same solvents: 78 mg of only the *endo* isomer as colorless crystals. 98% yield. mp 264-266 °C. ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 1.28 (1 H, tt, J = 12.4, 3.5 Hz), 1.42 (1 H, tt, J = 12.4, 3.5 Hz), 1.60-1.76 (2 H, m), 1.92 (3 H, s, Me), 3.21 (1 H, m), 3.30 (1 H, bs), 3.49 (1 H, s), 5.59 (1 H, m), 6.09 (1 H, m), 7.60-7.80, 7.95-8.05 (4 H, series of m, Ar). ^{13}C-NMR ($CDCl_3$), δ, ppm: 20.55, 24.72, 29.66, 33.05, 75.34, 125.62, 126.67, 129.95, 133.14, 134.01, 134.22. IR (KBr disk): 3085, 3016, 2967, 1435, 1323, 1311, 1280, 1148, 1132, 1093, 881, 851, 801, 770, 715, 699 cm^{-1}. *Elem. anal.*, found % (calcd for $C_{15}H_{16}O_4S_2$): C, 55.12 (55.54); H, 4.94 (4.97).

Reduction of 8a, 8b, and 8d with Sodium Amalgam in MeOH/NaH_2PO_4

A typical procedure is described below. A mixture of either **8a**, **8b**, or **8d** (0.68 mmol) and NaH_2PO_4 (0.5 g, 4.17 mmol) in dry methanol (25 mL) was purged with argon. Under very efficent stirring, 6% sodium amalgam (8.22 g, *ca.* 8:1 equivalent ratio sodium to substrate) was added in portions. The reaction mixture was stirred continuously at room temperature and monitored by TLC, eluting with *n*-hexane. After 24 h conversion was virtually complete. Water was added and the reaction mixture extracted with pentane (3 x 50 mL). The combined extracts were washed with brine, dried over sodium sulfate and cautiously concentrated. Compounds **11a** (95 % yield) and **11b** (90 % yield) were recognized by comparison with an authentic sample.[14]

11d: oil, 92% yield. ^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm: 1.78-1.95 (2 H, m), 2.00-2.40 (6 H, series of m), 3.30 (2 H, bs, bridgehead protons), 6.73 (2 H, t, J = 1.8 Hz, vinylic protons).

X-Ray Structure Determinations of 4b and 8b

Figures 1 and 2 represent the perspective drawings of **4b** and **8b** as obtained from the *X*-ray structure determinations. Crystal data and summary of the intensity data collected and structure refinement are reported in Table 1. Positional and thermal parameters are collected in Tables 2 and 3, interatomic distances and bond angles are reported in Tables 4 and 5. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the deposition number CSD-400698 for **4b** and CSD-400699 for **8b**, the names of the authors, and the journal citation. The atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

Table 1 - Crystal Data and Summary of Intensity Data Collection and Structure Refinement for **4b** and **8b**.

Empirical formula	$C_{14}H_{12}O_4S_2$	$C_{19}H_{16}O_4S_2$
Mol wt	276.38	372.46
Space group	$P2_1/a$	$P2_12_12_1$
Crystal system	monoclinic	orthorhombic
Cell constants:		
a [pm]	1611.5(5)	1307.3(5)
b [pm]	856.6(3)	1356.8(6)
c [pm]	1009.2(5)	939.7(3)
β	103.50(3)°	
Cell vol. [pm^3]	1369(1) x 10^6	1667(1) x 10^6
Z	4	4
$D_{calc.}$[g cm^{-3}]	1.341	1.484
Diffractometer	Siemens R3m/V	Siemens R3m/V
Radiation	Mo Kα	Mo Kα
Monochromator	graphite	graphite
Data collection mode	Wyckoff scan	Wyckoff scan
Crystal size [mm]	0.4 x 0.55 x 0.3	0.25 x 0.25 x .1.30
Theta range [deg]	1.75 - 27.5	1.75 - 30.0
Recip. latt. segment:		
h	0 - 20	0 - 18
k	0 - 11	0 - 19
l	-13 - 12	0 - 13
Reflections measured	3460	2780
Reflections observed [$F > 3\ s(F)$]	2951	2184
Unique refl.	3148	2756
Lin. abs. coeff. [mm^{-1}]	0.38	0.33
Abs. correction	ψ-scan	ψ-scan
R, R_w [w=1/$s^2(F)$]	0.042, 0.043	0.049, 0.044
Largest difference peak	0.43 eÅ^{-3}	0.36 eÅ^{-3}
Largest difference hole	0.30 eÅ^{-3}	0.31 eÅ^{-3}

Table 2 - Atomic Parameters (x 10^4) and Equivalent Isotropic Displacement Parameters (pm^2 x 10^{-1}) for Adduct **4b**.

Atom	x	y	z	U(eq)^a	Atom	x	y	z	U(eq)^a
S(1)	1606(1)	393(1)	7575(1)	48(1)	C(7)	342(2)	4445(3)	6751(3)	60(1)
O(11)	1450(1)	-454(2)	6327(2)	67(1)	C(8)	488(2)	2892(3)	7051(3)	54(1)
O(12)	1250(1)	-163(2)	8664(2)	73(1)	C(9)	1311(1)	2342(3)	7190(2)	43(1)
S(3)	2967(1)	2388(1)	7215(1)	41(1)	C(20)	2837(2)	1378(3)	9720(2)	56(1)
O(31)	3044(1)	1845(2)	5906(2)	56(1)	C(21)	3320(1)	-613(2)	8148(2)	41(1)
O(32)	3641(1)	3316(2)	8004(2)	60(1)	C(22)	3946(2)	-1077(3)	9270(3)	55(1)
C(2)	2754(1)	757(2)	8270(2)	38(1)	C(23)	4470(2)	-2322(3)	9176(3)	69(1)
C(4)	1967(1)	3307(3)	7036(2)	40(1)	C(24)	4381(2)	-3114(3)	7978(3)	71(1)
C(5)	1823(2)	4860(3)	6750(2)	48(1)	C(25)	3770(2)	-2664(3)	6850(3)	63(1)
C(6)	997(2)	5410(3)	6607(3)	57(1)	C(26)	3239(2)	-1416(3)	6920(3)	49(1)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 - Atomic Parameters (x 10^4) and Equivalent Isotropic Displacement Parameters (pm^2 x 10^{-1}) for Adduct **8b**.

Atom	x	y	z	U(eq)^a	Atom	x	y	z	U(eq)^a
S(1)	2733(1)	7786(1)	2309(1)	68(1)	C(8)	4828(3)	7755(3)	1983(3)	59(1)
S(2)	4891(1)	7062(1)	3589(1)	59(1)	C(9)	5741(3)	8041(4)	1343(5)	81(2)
O(11)	2508(3)	6754(2)	2194(4)	98(1)	C(10)	5707(5)	8612(4)	132(5)	92(2)
O(12)	1979(2)	8474(3)	1807(4)	97(1)	C(11)	4772(5)	8916(3)	-412(5)	94(2)
O(21)	4530(3)	6077(2)	3304(3)	84(1)	C(12)	3859(4)	8631(3)	224(4)	76(2)
O(22)	5900(2)	7191(3)	4159(3)	95(1)	C(13)	3886(3)	8055(3)	1428(4)	58(1)
C(1)	2980(2)	8040(3)	4132(4)	53(1)	C(21)	3835(3)	6894(3)	5984(4)	50(1)
C(2)	4009(2)	7661(3)	4818(3)	43(1)	C(22)	4513(3)	6826(3)	7120(4)	64(1)
C(3)	4446(3)	8671(3)	5412(4)	64(1)	C(23)	4345(4)	6153(3)	8217(5)	80(2)
C(4)	4653(3)	9382(3)	4203(4)	66(1)	C(24)	3520(3)	5534(3)	8157(5)	77(2)
C(5)	3772(3)	9683(3)	3683(5)	69(1)	C(25)	2865(3)	5566(3)	7029(5)	78(2)
C(6)	2948(3)	9156(3)	4518(5)	76(2)	C(26)	3026(3)	6233(3)	5941(5)	66(1)
C(7)	3443(4)	9107(3)	5979(5)	82(2)					

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4 - Interatomic Distances (pm) and Bond Angles (Deg) with Standard Deviations for Adduct **4b**.

S(1)-O(11)	142.8(2)	S(1)-O(12)	143.7(2)	C(5)-C(6)	139.0(4)	C(6)-C(7)	137.9(4)
S(1)-C(2)	184.6(2)	S(1)-C(9)	177.1(2)	C(7)-C(8)	138.6(4)	C(8)-C(9)	138.5(3)
S(3)-O(31)	143.5(2)	S(3)-O(32)	143.3(2)	C(21)-C(22)	138.9(3)	C(21)-C(26)	140.1(3)
S(3)-C(2)	184.8(2)	S(3)-C(4)	176.8(2)	C(22)-C(23)	128.6(4)	C(23)-C(24)	136.8(5)
C(2)-C(20)	153.5(3)	C(2)-C(21)	151.8(3)	C(24)-C(25)	137.6(4)	C(25)-C(26)	138.9(4)
C(4)-C(5)	138.3(3)	C(4)-C(9)	138.4(3)				
O(11)-S(1)-O(12)	118.9(1)	O(11)-S(1)-C(2)	112.2(1)	S(3)-C(4)-C(5)	124.3(2)	S(3)-C(4)-C(9)	114.7(2)
O(12)-S(1)-C(2)	108.1(1)	O(11)-S(1)-C(9)	108.2(1)	C(5)-C(4)-C(9)	121.0(2)	C(4)-C(5)-C(6)	117.7(2)
O(12)-S(1)-C(9)	110.6(1)	C(2)-S(1)-C(9)	96.6(1)	C(5)-C(6)-C(7)	121.3(2)	C(6)-C(7)-C(8)	121.0(2)
O(31)-S(3)-O(32)	118.5(1)	O(31)-S(3)-C(2)	110.4(1)	C(7)-C(8)-C(9)	117.7(2)	S(1)-C(9)-C(4)	115.3(2)
O(32)-S(3)-C(2)	109.1(1)	C(31)-S(3)-C(4)	109.0(1)	S(1)-C(9)-C(8)	123.4(2)	C(4)-C(9)-C(8)	121.3(2)
O(32)-S(3)-C(4)	111.0(1)	C(2)-S(3)-C(4)	96.6(1)	C(2)-C(21)-C(22)	119.7(2)	C(2)-C(21)-C(26)	121.8(2)
S(1)-C(2)-S(3)	102.5(1)	S(1)-C(2)-C(20)	106.2(2)	C(22)-C(21)-C(26)	118.5(2)	C(21)-C(22)-C(23)	120.5(2)
S(3)-C(2)-C(20)	107.1(1)	S(1)-C(2)-C(21)	113.8(1)	C(22)-C(23)-C(24)	120.7(2)	C(23)-C(24)-C(25)	119.8(3)
S(3)-C(2)-C(21)	110.7(2)	C(20)-C(2)-C(21)	115.5(2)	C(24)-C(25)-C(26)	120.5(3)	C(21)-C(26)-C(25)	120.0(2)

Table 5 - Interatomic Distances (pm) and Bond Angles (Deg) with Standard Deviations for Adduct **8b**.

S(1)-O(11)	143.5(3)	S(1)-O(12)	143.7(3)	S(1)-C(1)	177.7(4)	S(1)-C(13)	175.8(4)
S(2)-O(21)	144.1(3)	S(2)-O(22)	143.5(3)	S(2)-C(2)	182.3(3)	S(2)-C(8)	178.1(4)
C(1)-C(2)	157.8(5)	C(1)-C(6)	155.8(6)	C(2)-C(3)	158.6(5)	C(2)-C(21)	152.8(5)
C(3)-C(4)	151.5(5)	C(3)-C(7)	153.4(6)	C(4)-C(5)	131.6(6)	C(5)-C(6)	151.3(6)
C(6)-C(7)	151.9(6)	C(8)-C(9)	139.1(6)	C(8)-C(13)	139.7(5)	C(9)-C(10)	137.7(7)
C(10)-C(11)	138.8(8)	C(11)-C(12)	139.0(8)	C(12)-C(13)	137.6(6)	C(21)-C(22)	139.1(5)
C(21)-C(26)	138.7(5)	C(22)-C(23)	139.4(6)	C(23)-C(24)	136.9(7)	C(24)-C(25)	136.4(7)
C(25)-C(26)	138.1(6)						
O(11)-S(1)-O(12)	117.9(2)	O(11)-S(1)-C(1)	107.4(2)	O(12)-S(1)-C(1)	108.3(2)	O(11)-S(1)-C(13)	110.1(2)
O(12)-S(1)-C(13)	107.4(2)	C(1)-S(1)-C(13)	105.0(2)	O(21)-S(2)-O(22)	118.9(2)	O(21)-S(2)-C(2)	108.9(2)
O(22)-S(2)-C(2)	106.9(2)	O(21)-S(2)-C(8)	108.5(2)	O(22)-S(2)-C(8)	107.1(2)	C(2)-S(2)-C(8)	105.8(2)
S(1)-C(1)-C(2)	119.0(2)	S(1)-C(1)-C(6)	114.1(3)	C(2)-C(1)-C(6)	104.2(3)	S(2)-C(2)-C(1)	115.2(2)
S(2)-C(2)-C(3)	112.3(2)	C(1)-C(2)-C(3)	99.8(3)	S(2)-C(2)-C(21)	104.2(2)	C(1)-C(2)-C(21)	112.8(3)
C(3)-C(2)-C(21)	112.9(3)	C(2)-C(3)-C(4)	110.5(3)	C(2)-C(3)-C(7)	98.5(3)	C(4)-C(3)-C(7)	99.6(3)
C(3)-C(4)-C(5)	108.6(4)	C(4)-C(5)-C(6)	106.6(4)	C(1)-C(6)-C(5)	108.6(3)	C(1)-C(6)-C(7)	99.0(3)
C(5)-C(6)-C(7)	100.7(4)	C(3)-C(7)-C(6)	93.9(3)	S(2)-C(8)-C(9)	118.3(3)	S(2)-C(8)-C(13)	120.7(3)
C(9)-C(8)-C(13)	120.9(3)	C(8)-C(9)-C(10)	119.1(4)	C(9)-C(10)-C(11)	120.0(5)	C(10)-C(11)-C(12)	121.0(4)
C(11)-C(12)-C(13)	119.3(4)	S(1)-C(13)-C(8)	121.3(3)	S(1)-C(13)-C(12)	118.9(3)	C(8)-C(13)-C(12)	119.7(4)
C(2)-C(21)-C(22)	120.0(3)	C(2)-C(21)-C(26)	122.2(3)	C(22)-C(21)-C(26)	117.7(3)	C(21)-C(22)-C(23)	120.7(4)
C(22)-C(23)-C(24)	119.7(4)	C(23)-C(24)-C(25)	120.5(4)	C(24)-C(25)-C(26)	120.0(4)	C(21)-C(26)-C(25)	121.3(4)

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