2,3-(Ethylenedisulfonyl)-1,3-butadiene, a Versatile Diels-Alder Diene and Dienophile

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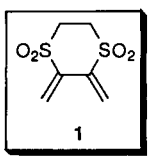
2,3-(Ethylenedisulfonyl)-1,3-butadiene (**1**) may be readily prepared from its stable 3-sulfolene precursor **10**. Compound **1** undergoes Diels-Alder reactions with a number of dienophiles ranging from electron-deficient to electron-rich alkenes as well as an aldimine. It also reacts as both the diene and the dienophile in some [4 + 2] cycloadditions.

Recently, several studies on the synthesis and properties of sulfonylated 1,3-dienes have been reported[1]. One of the characteristic properties of these dienes is their dual behavior in [4 + 2] cycloadditions. On the one hand, they can undergo cycloaddition reactions with a variety of olefins ranging from electron-deficient to electron-rich dienophiles[2]. On the other hand, sulfonylated 1,3-dienes, being electron-poor olefins, react as dienophiles with some reactive diene compounds[3]. These diverse reactivities, coupled with the versatility of the sulfonyl group in functionality transformation[4], make sulfonylated 1,3-dienes very useful intermediates in organic synthesis.

With one more group attached, disulfonylated 1,3-dienes should display even more diversified reactivity and synthetic versatility. 2,3-Bis(phenylsulfonyl)-1,3-butadiene reacts with various primary amines as a Michael acceptor in the synthesis of 3-pyrrolines[5]. It also reacts as a bisdienophile in the cycloaddition reaction with cyclopentadiene[6]. In addition, 2,3-bis(arylsulfonyl)-substituted dienes react with several imines to give novel rearranged cycloadducts[2d,7], and with oximes to give intramolecular dipolar cycloadducts[8]. However, the use of 2,3-disulfonylated 1,3-dienes or other 2,3-dihetero-substituted 1,3-dienes as four-electron components in Diels-Alder cycloaddition reactions has been so far unsuccessful[9].

By linking the two sulfonyl groups with a carbon chain as in 2,3-(ethylenedisulfonyl)-1,3-butadiene (**1**) the diene would be fixed in a *cisoid* conformation, and Diels-Alder reactions should be facilitated. In this paper we report on the details of this strategy[10] and the study of compound **1** in hetero and crossed Diels-Alder reactions.



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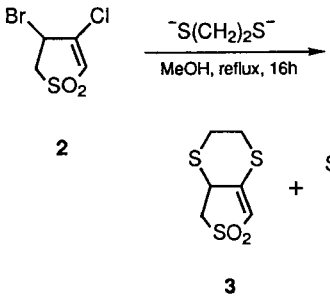
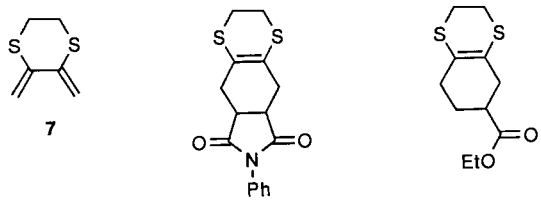
Results and Discussion

Substitution of the known 4-bromo-3-chloro-2-sulfolene (**2**)[11] with the sodium salt of 1,2-ethanedithiol gave a 4.4:1 mixture of 3,4-(ethylenedithio)-2-sulfolene (**3**) and 3,4-(ethylenedithio)-3-sulfolene (**4**) in 84% yield[12] along with compound **5** and some unidentified impurities in small quantities (eq. 1). Although sulfolenes **3** and **4** could be easily separated from other impurities by column chromatography, the separation of these two isomers could only be achieved by careful HPLC (*n*-hexane/EtOAc 3:2).



2 **3** **4** **5** (eq 1)

A mixture of **3** and **4** was then thermolyzed at 130°C in the presence of a basic catalyst, pyridine, in the hope that **3** might be isomerized to **4** and subsequently lose SO_2 to give the diene **7**. Although compound **3** was indeed isomerized to **4** in the presence of pyridine, the isomerization was incomplete even after 10 h, so that thermolysis always produced mixtures of **3** and **7**. However, by replacing pyridine by triethylamine[11b] as the basic catalyst, the thermolysis gave compound **7** as the main product with no trace of **3**. Although compound **7** was stable long enough to record its ^{1}H-NMR spectrum, an analytically pure sample could not be obtained. Attempts to prepare **7** under milder conditions, e.g. by treatment of a mixture of **3** and **4** with $LiAlH_4$, were unsuccessful[13]. Despite the difficulties encountered in preparing **7** in a synthetically useful form, we found that **4** reacted successfully with *N*-phenylmaleimide and ethyl ac-

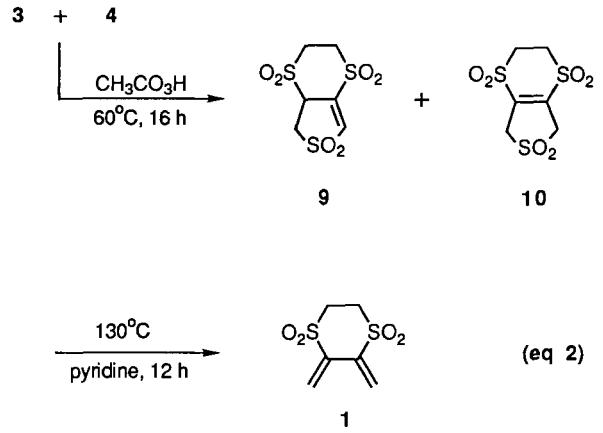


7 **8a** **8b**

  0009–2940/92/0202–0499 $ 3.50+.25/0

rylate under thermal conditions to give the cycloadducts **8a** and **8b**, respectively[12]. However, no further studies along this line were carried out for lack of easy access to pure **4** or **7**.

Direct oxidation of a mixture of **3** and **4** with peracetic acid at 60°C gave the corresponding disulfones **9** and **10** in 74% yield (eq. 2). Although **9** and **10** could again not be separated, even by HPLC, separation was unnecessary for synthetic purposes, since the thermolysis of the mixture at 130°C in the presence of pyridine furnished compound **1** in 80% yield[11b]. Presumably **9** isomerized rapidly to **10** under the reaction conditions. Diene **1** is a stable compound which may be stored at room temperature for over a month without appreciable decomposition.

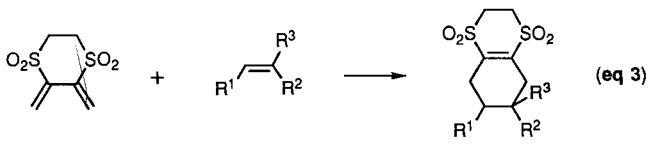


(eq 2)

Disulfone **1** is a very reactive diene. Thermal reactions with a number of alkenes in benzene or dichloromethane resulted in [4 + 2] cycloadditions (Table 1). It is important to note that **1**, although electron-deficient, readily reacted with both electron-rich (e.g. entries 1, 2, 3, 6 of Table 1) and electron-poor (e.g. entries 7, 8, 9 of Table 1) dienophiles. It is especially interesting that **1** reacted with trimethylvinylsilane (entry 4) in excellent yield. Vinylsilanes are regarded as moderate dienophiles, and only limited work has been done on their cycloaddition reactions[14]. The reaction of a poor dienophile, e.g. cyclohexene, with **1** (entry 5) gave cycloadduct **12e** in low yield. This result signals the high enophilicity of **1** in Diels-Alder reactions. However, the reaction with the notoriously poor dienophile 3-methyl-2-cyclohexene-1-one[15] did not afford any cycloadduct. For the cycloadduct of **1** with norbornene (entry 10), the NMR spectral and chromatographic data indicated it to be a single stereoisomer. Although the *exo*-site addition is expected to be preferred, the stereochemistry was not unambiguously determined.

All cycloadducts **12a–k** contain a vinylendisulfone functionality. It was naively anticipated that **12a–k** might react as dienophiles so that their Diels-Alder reactions with a reactive diene would produce cycloadducts possessing a propellane ring system[16]. However, treatment of **12i** with cyclopentadiene or 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (Danishefsky's diene) in DMSO at temperatures up to 120°C for several days resulted in recovery of starting material. The steric hindrance of the vicinal sulfonyl substituents of **12i** may be responsible for its low reactivity.

Table 1. Diels-Alder reactions of compound **1** with dienophiles



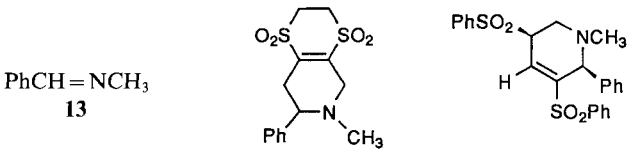
(eq 3)

entry	dienophile (equiv)	R^1	R^2	R^3	condition (solvent)	product (HPLC isolated yield, %)
1	**11a** (235)	H	OEt	H	60°C, 45 h (CH_2Cl_2)	**12a** (45)
2	**11b** (10)	$-(CH_2)_4-$		-N O	r. t., 2 h (CH_2Cl_2)	**12b** (80)
3	**11c** (15)	H	SPh	H	160°C, 48 h (C_6H_6)	**12c** (85)
4	**11d** (13)	H	TMS	H	140°C, 69 h (C_6H_6)	**12d** (97)
5	**11e** (xs.)	$-(CH_2)_4-$		H	150°C, 46 h (C_6H_6)	**12e** (16)
6	**11f** (xs.)	H	$OCOCH_3$	H	160°C, 48 h (C_6H_6)	**12f** (66)
7	**11g** (210)	H	$COOCH_3$	H	60°C, 45 h (CH_2Cl_2)	**12g** (84)
8	**11h** (215)	H	$COCH_3$	H	60°C, 45 h (CH_2Cl_2)	**12h** (77)
9	**11l** (5)	-CONPhCO-		H	130°C, 116 h (C_6H_6)	**12l** (49)
10	**11j** (30)	R^1 R^2=		H	60°C, 87 h (CH_2Cl_2)	**12j** (85)[a]
11	**11k** (xs.)	H	Ph	H	70°C, 180 h (CH_2Cl_2)	**12k** (26)

[a] The spectral and chromatographic data indicate that this compound exists as only one stereoisomer. However, the stereochemistry was not determined.

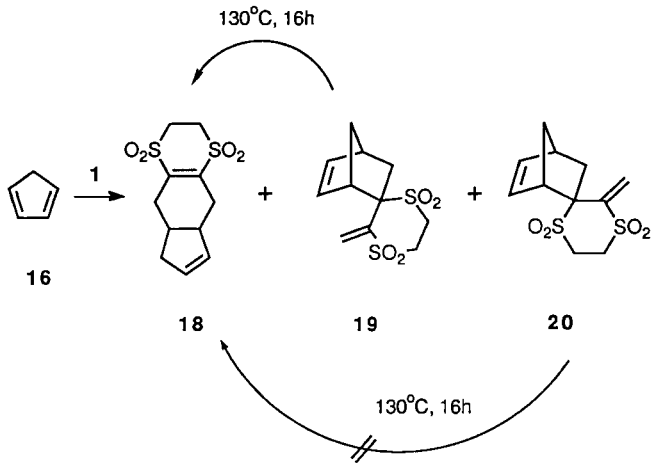
When diene **1** was heated with *N*-benzylidenemethylamine (**13**) at 110°C, a hetero Diels-Alder reaction took place to give **14** in 84% yield. In contrast, the rearranged Diels-Alder cycloadduct **15** was obtained when 2,3-bis(phenylsulfonyl)-1,3-butadiene was treated with **13**[7]. Presumably, the rigid linking of the two sulfonyl groups with an ethanediyl bridge in **1** prevents rearrangements from taking place so that normal [4 + 2] cycloadducts could be obtained. Attempted hetero Diels-Alder reactions of **1** with other heterodienophiles such as *N,N*-dimethylthioformamide, acetaldehyde, diethyl oxomalonate, and methyl azodicarboxylate have so far been unsuccessful.

The crossed Diels-Alder reactions (CDA) of some acyclic 2-sulfonylated 1,3-butadienes and 2-(phenylsulfonyl)-1,3-cyclohexadiene with reactive dienes have been systematically

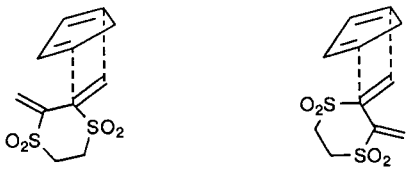


studied[3]. Since a disulfonylated diene is quite different from a monosulfonylated diene both sterically and electronically, we were interested in comparing their behavior in CDA reactions. When **1** was treated with cyclopentadiene (**16**) at 130°C, a mixture of **18**, **19**, and **20** in a ratio of 1:2.3:1.2 (77% yield) was obtained, whereas the same three isomers were obtained in a ratio of 1:9:2 (62%) when the reaction was performed at room temperature (Scheme 1). Product **18** is the cycloadduct from the reaction with **1** as the diene and **16** as the dienophile. Stereoisomers **19** and **20** are the cycloadducts of the reaction with the opposite orientation of **1** and **16**. Heating **19** at 130°C for 16 h resulted in the complete conversion to **18**, presumably by a Cope-rearrangement process which is known to occur at elevated temperature in similar compounds[17]. Heating **20** under the same conditions did not give any appreciable amount of **18**. Thus, the possibility of a retro Diels-Alder reaction mechanism is unlikely for the transformation of **19** to **18**. This result indicates that **18**, **19**, and **20** are the primary products of the room-temperature crossed cycloaddition reaction between **1** and **16**, whereas at 130°C compound **18** could be obtained partially from the direct cycloaddition reaction and partially from the Cope rearrangement of the cycloadduct **19**.

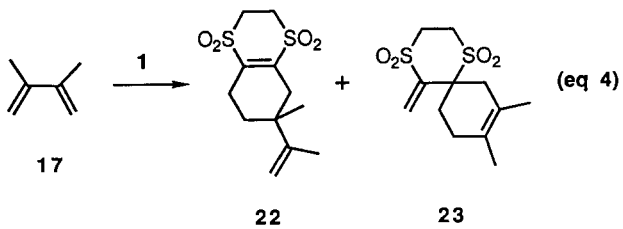
Scheme 1



Although no spectral analyses were performed, the assignment of the stereochemistry of **19** and **20** may be inferred from indirect evidence. In order for **19** to be converted into **18** by a sigmatropic Cope-rearrangement process, the terminal vinyl group must be on the *endo* face. It is noteworthy that the yield of compound **19** in the primary reaction is higher than that of **20**. This preferential formation of **19** agrees with the more favored transition state **21A** leading to the formation of **19** rather than **21B** resulting in the formation of **20**. Similar product ratios and thermal Cope rearrangement of the primary products were observed in the CDA reactions of **16** with 2-(phenylsulfonyl)-1,3-dienes[3a].



Treatment of 2,3-dimethyl-1,3-butadiene (**17**) with **1** at 100°C led to the formation of two types of cycloadducts **22** and **23** (eq. 4). The structures of **22** and **23** were assigned by means of their ^{1}H-NMR spectra. The ratio of **22**/**23** (1:8) indicates that the dienophilic character of **1** is more pronounced than its dienic character in the CDA reaction with **17**. A comparison of the product ratios from the CDA reactions of **1** with those from the CDA reaction of 2-(phenylsulfonyl)-1,3-diene[3a] indicates a higher tendency for **1** to react as a dienophile. This may be attributed to the electronic effect of the additional sulfonyl group.



In summary, 2,3-(ethylenedisulfonyl)-1,3-butadiene (**1**) undergoes Diels-Alder reactions with a variety of electron-rich or electron-deficient dienes. It also reacts with *N*-benzylidenemethylamine to give the hetero Diels-Alder cycloadduct without skeletal rearrangement. In addition, compound **1** can also react as a dienophile with reactive dienes in crossed Diels-Alder reactions.

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Experimental

All reagents were of reagent grade and purified prior to use. All solvents were freshly distilled before use. — ^{1}H and ^{13}C NMR: Bruker AW-80 (80 MHz), Bruker AC-200 (200/50.288 MHz) or Bruker MSL-200 (200/50.288 MHz), $CDCl_3$ solutions unless indicated otherwise. — IR: Perkin-Elmer 882. — MS: Hewlett-Packard 5995B or high-resolution MS: VG 70-250S. — Elemental analyses: Perkin-Elmer 240C. — Melting points: Yamato MP-21, uncorrected. — HPLC: Waters HPLC-Pump 501, Waters RI-Detector 410, column LiChrosorb Si 60 (7 μm, 1 × 25 cm) from Merck. — Analytical TLC plates: Merck.

Nucleophilic Substitution Reaction of 4-Bromo-3-chloro-2-sulfolene (**2**): A mixture of **2**[11] (1.01 g, 4.36 mmol) and sodium 1,2-ethanedithiolate (generated from 1.2 equiv. of 1,2-ethanedithiol and 2 equiv. of NaOMe) in MeOH/EtOH (1:1) was heated under reflux for 16 h. The reaction was then quenched with saturated aqueous NH_4Cl. The aqueous solution was extracted several times with

$CHCl_3$. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude mixture was separated by careful HPLC (*n*-hexane/EtOAc 3:2) to give **3** in 68 and **4** in 16% yield along with **5** in 8% yield.

3,4-(Ethylenedithio)-2-sulfolene (**3**): White solid, m.p. 188–189.5°C. – IR (KBr): $\tilde{\nu}$ = 1271, 1115 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 2.84–3.08 (m, 3H), 3.16–3.38 (m, 2H), 3.58 (dd, 1H, J_1 = 13.6, J_2 = 7.8 Hz, 5-H), 4.30 (td, 1H, J_1 = 7.8, J_2 = 1.5 Hz, 4-H), 6.50 (d, 1H, J = 1.5 Hz, 2-H). – MS (70 eV): *m/z* (%) = 208 (98) [M^+], 144 (17) [$M^+ - SO_2$], 116 (100) [$M^+ - SCH_2CH_2S$], 71 (53).

$C_6H_8O_2S_3$ (208.3) Calcd. C 34.59 H 3.87
Found C 34.77 H 3.71

3,4-(Ethylenedithio)-3-sulfolene (**4**): White solid, m.p. 159.5–161°C. – IR (KBr): $\tilde{\nu}$ = 1318, 1134 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 3.29 (s, 4H, CH_2CH_2S), 3.79 (s, 4H, $CH_2SO_2CH_2$). – MS (70 eV): *m/z* (%) = 208 (27) [M^+], 144 (100) [$M^+ - SO_2$], 116 (33) [$M^+ - SCH_2CH_2S$], 70 (19), 58 (65).

$C_6H_8O_2S_3$ (208.3) Calcd. C 34.59 H 3.87
Found C 34.80 H 4.10

1,4,7-Trithiaspiro[4.4]non-8-ene 7,7-Dioxide (**5**): White solid, m.p. 118–120°C. – IR (KBr): $\tilde{\nu}$ = 1297, 1126 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 3.47 (s, 4H, CH_2CH_2S), 3.76 (s, 2H, CH_2SO_2), 6.43 (d, 1H, J = 6.48 Hz, $=CH-SO_2$), 6.60 (d, 1H, J = 6.48 Hz, $CH=CH$). – ^{13}C NMR (50.288 MHz, [D_6]acetone): δ = 42.07 (C-2, -3), 64.38 (C-5), 65.04 (C-6), 130.18 (CH=CH), 143.70 (CH=CH). – MS (70 eV): *m/z* (%) = 208 (100) [M^+], 180 (51), 144 (17) [$M^+ - SO_2$], 118 (37), 116 (69) [$M^+ - SCH_2CH_2S$], 60 (39), 58 (53), 45 (48).

$C_6H_8O_2S_3$ (208.3) Calcd. C 34.59 H 3.87
Found C 34.89 H 4.16

4,5-(Ethylenedithio)-1,2,3,6-tetrahydro-N-phenylphthalimide (**8a**): A suspension of **4** (19 mg, 0.089 mmol), *N*-phenylmaleimide (77 mg, 0.45 mmol), and a trace of hydroquinone (<5%) in completely degassed benzene (5 ml) was heated to 150°C in a sealed tube for 10 h. The solvent was removed under reduced pressure, and the obtained crude product was purified by HPLC (LiChrosorb column, *n*-hexane/EtOAc, 2:1) to give the pure product **8a** (22 mg, 78%). White solid, m.p. 147–148.5°C. – IR (KBr): $\tilde{\nu}$ = 1712 cm^{-1} (C=O), 1386, 1186. – ^1H NMR (200 MHz): δ = 2.50–2.68 (m, 4H, $CH_2C=CCH_2$), 3.08–3.18 (m, 4H, SCH_2CH_2S), 3.20–3.33 (m, 2H, O=CCHCHC=O), 7.21–7.53 (m, 5H, aromatic H). – MS (70 eV): *m/z* (%) = 317 (83) [M^+], 170 (39), 169 (100), 168 (55), 142 (92), 141 (58), 91 (42), 78 (60), 77 (65).

$C_{16}H_{15}NO_2S_2$ (317.4) Calcd. C 60.54 H 4.76 N 4.41
Found C 60.79 H 4.68 N 4.06

Ethyl 3,4-(Ethylenedithio)-3-cyclohexene-1-carboxylate (**8b**) was obtained in 90% yield from the sealed-tube reaction of **4** (57 mg, 0.27 mmol) with ethyl acrylate (82 mg, 0.82 mmol) in benzene (7 ml) at 140°C for 10 h. Yellow oil. – IR (neat): $\tilde{\nu}$ = 1736 cm^{-1} (C=O), 1616, 1463, 1374. – ^1H NMR (80 MHz): δ = 1.23 (t, 3H, J = 7.2 Hz, CH_3), 2.00–2.70 (m, 7H), 3.17 (s, 4H, SCH_2CH_2S), 4.12 (q, 2H, J = 7.2 Hz, OCH_2). – MS (70 eV): *m/z* (%) = 244 (100) [M^+], 171 (40) [$M^+ - CH_3CH_2OC=O$], 170 (95), 142 (25), 110 (42).

$C_{11}H_{16}O_2S_2$ (244.4) Calcd. C 54.05 H 6.60
Found C 53.87 H 6.79

3,4-(Ethylenedisulfonyl)-2-sulfolene (**9**) *and 3,4-(Ethylenedisulfonyl)-3-sulfolene* (**10**): A solution of a 4.4:1 mixture of **3** and **4** (521 mg, 2.5 mmol) and 30% H_2O_2 (25 ml) in acetic acid (40 ml) was heated at 60°C for 16 h. The white precipitate which formed was washed with distilled water and saturated $NaHCO_3$ to afford 537 mg (74%) of a mixture of compound **9** and **10** as a white solid. A separation of the two components was unsuccessful. However, the peaks of the ^1H-NMR spectrum of the mixture are well resolved so that they can be assigned easily. The IR, MS and elemental analysis data were obtained from the mixture. – IR (KBr): $\tilde{\nu}$ = 1325, 1286, 1136 cm^{-1} (SO_2). – ^1H NMR of **9** (200 MHz, [D_6]DMSO): δ = 3.79–4.35 (m, 7H), 5.80–5.90 (m, 1H, $SO_2CH=C$). – ^1H NMR of **10** (200 MHz, [D_6]DMSO): δ = 4.50 (s, 4H, $SO_2CH_2CH_2SO_2$), 4.72 (s, 4H, $CH_2SO_2CH_2$). – MS (70 eV): *m/z* (%) = 208 (9) [$M^+ - SO_2$], 116 (21) [$M^+ - SO_2CH_2CH_2SO_2$], 52 (100).

$C_6H_8O_6S_3$ (272.3) Calcd. C 26.47 H 2.96
Found C 26.62 H 2.87

2,3-(Ethylenedisulfonyl)-1,3-butadiene (**1**): A solution of a mixture of **9** and **10** (263 mg, 0.963 mmol), a trace of hydroquinone, and pyridine (1 equiv.) in acetone (30 ml) was heated to 130°C in a sealed tube for 12 h. The solvent was removed under reduced pressure, and the resulting crude product was eluted through a silica gel column (eluent hexane/EtOAc, 1:1), to remove hydroquinone and then purified by HPLC (LiChrosorb column, *n*-hexane/EtOAc, 1:1) to afford 160 mg (80%) of **1** as a white solid; m.p. 195–195.5°C. – IR (KBr): $\tilde{\nu}$ = 3115 cm^{-1} (=C–H), 1295, 1104 (SO_2). – ^1H NMR (200 MHz): δ = 3.63 (s, 4H, $SO_2CH_2CH_2SO_2$), 6.19 (d, 2H, J = 1 Hz, $C=CH_2$), 6.53 (d, 2H, J = 1 Hz, $C=CH_2$). – MS (70 eV): *m/z* (%) = 208 (7) [M^+], 116 (48) [$M^+ - CH_2CH_2SO_2$], 52 (100) [$M^+ - SO_2CH_2CH_2SO_2$].

$C_6H_8O_4S_2$ (208.3) Calcd. C 34.60 H 3.87
Found C 34.51 H 3.84

General Procedure for the Diels-Alder Reactions of Compound **1**: A sealed tube containing a suitable amount of **1**, dienophile (**11**), and solvent as shown in Table 1 along with a catalytic amount of hydroquinone was heated for a certain period of time. After removal of the solvent, the residue was eluted through a silica gel column. The resulting solution was concentrated under reduced pressure and the residue purified by HPLC (LiChrosorb column, *n*-hexane/EtOAc) to give the pure product **12**. The HPLC-isolated yields of Diels-Alder reactions are summarized in Table 1. The room-temperature Diels-Alder reactions were carried out by stirring the reaction mixtures under nitrogen, which were subsequently worked up as described above.

4-Ethoxy-1,2-(ethylenedisulfonyl)-1-cyclohexene (**12a**): White solid, m.p. 110–111°C. – IR (KBr): $\tilde{\nu}$ = 1302, 1280, 1140, 1134 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 1.18 (t, 3H, J = 7 Hz, CH_3), 1.78–1.95 (m, 2H, 5-H), 2.50–2.86 (m, 4H, 3-, 6-H), 3.43–3.61 (m, 2H, OCH_2), 3.67–3.81 (m, 1H, 4-H), 3.85 (s, 4H, $SO_2CH_2CH_2SO_2$). – MS (70 eV): *m/z* (%) = 280 (5) [M^+], 236 (34), 124 (33) [$M^+ - SO_2CH_2CH_2SO_2$], 72 (100).

$C_{10}H_{16}O_5S_2$ Calcd. 280.0439 Found 280.0440 (MS)

2,3-(Ethylenedisulfonyl)-1,4,4a,5,6,7,8,8a-octahydro-4a-morpholinonaphthalene (**12b**): White solid, m.p. 184–184.5°C. – IR (KBr): $\tilde{\nu}$ = 1306, 1277, 1139, 1108 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 1.14–1.33 (m, 3H), 1.40–1.55 (m, 2H), 1.59–1.74 (m, 3H), 1.97–2.11 (m, 3H), 2.38–2.88 (m, 6H), 3.60 (t, 4H, J = 4.5 Hz, CH_2OCH_2), 3.73–3.88 (m, 4H, $SO_2CH_2CH_2SO_2$). – MS (70 eV): *m/z* (%) = 375 (2) [M^+], 219 (40) [$M^+ - SO_2CH_2CH_2SO_2$], 167 (100).

$C_{16}H_{25}NO_5S_2$ Calcd. 375.1176 Found 375.1143 (MS)

$C_{16}H_{25}NO_5S_2$ (375.5)
Calcd. C 51.16 H 6.71 N 3.73 S 17.09
Found C 50.97 H 6.69 N 3.74 S 16.79

1,2-(Ethylenedisulfonyl)-4-(phenylthio)-1-cyclohexene (**12c**): White solid, m.p. 196–198°C. – IR (KBr): $\tilde{\nu}$ = 1304, 1283, 1131,

1103 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 1.60–1.80 (m, 1H, 5-H), 2.03–2.18 (m, 1H, 5-H), 2.48–2.97 (m, 4H, $CH_2C{=}CCH_2$), 3.25–3.39 (m, 1H, CHSPh), 3.72–3.86 (m, 4H, $SO_2CH_2CH_2SO_2$), 7.19–7.42 (m, 5H, aromatic H). – MS (15 eV): *m/z* (%) = 344 (33) [M^+], 197 (31), 104 (34), 91 (100).

$C_{14}H_{16}O_4S_3$ (344.4) Calcd. C 48.81 H 4.68
Found C 48.89 H 4.63

1,2-(Ethylenedisulfonyl)-4-(trimethylsilyl)-1-cyclohexene (**12d**): White solid, m.p. 160–162°C. – IR (KBr): ṽ = 1305, 1285, 1128, 1103 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 0.0 (s, 9H, Me_3Si), 0.70–0.90 (m, 1H, C*H*–$SiMe_3$), 1.25–1.45 (m, 1H), 1.90–2.05 (m, 1H), 2.20–2.50 (m, 2H, $=CCH_2$), 2.56–2.75 (m, 2H, $=CCH_2$), 3.61–3.95 (m, 4H, $SO_2CH_2CH_2SO_2$). – MS (40 eV): *m/z* (%) = 308 (14) [M^+], 293 (22) [$M^+ - CH_3$], 137 (21) [293 – $SO_2CH_2CH_2SO_2$], 122 (18), 73 (100).

$C_{11}H_{20}O_4S_2Si$ (308.5) Calcd. C 42.83 H 6.53
Found C 42.88 H 6.39

2,3-(Ethylenedisulfonyl)-1,4,4a,5,6,7,8,8a-octahydronaphthalene (**12e**): White solid, m.p. 192–194°C. – IR (KBr): ṽ = 1303, 1282, 1122, 1103 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 1.35–1.60 (m, 8H), 1.90–2.10 (m, 2H, methine), 2.50–2.59 (m, 4H, $CH_2C{=}CCH_2$), 3.84 (s, 4H, $SO_2CH_2CH_2SO_2$). – MS (20 eV): *m/z* (%) = 290 (13) [M^+], 209 (35), 198 (73) [$M^+ - CH_2CH_2SO_2$], 133 (100) [$M^+ - SO_2CH_2CH_2SO_2$], 91 (42), 82 (58).

$C_{12}H_{18}O_4S_2$ (290.4) Calcd. C 49.63 H 6.25
Found C 49.70 H 6.36

4-Acetoxy-1,2-(ethylenedisulfonyl)-1-cyclohexene (**12f**): White solid, m.p. 193.5–195°C. – IR (KBr): ṽ = 1722 cm^{-1} (C=O), 1303, 1131 (SO_2). – ^1H NMR (200 MHz): δ = 1.80–2.10 (m, 2H, 5-H), 2.06 (s, 3H, CH_3), 2.60–2.96 (m, 4H, $CH_2C{=}CCH_2$), 3.79–3.95 (m, 4H, $SO_2CH_2CH_2SO_2$), 5.15–5.28 (m, 1H, CHOC=O). – MS (20 eV): *m/z* (%) = 294 (10) [M^+], 235 (14) [$M^+ - OCOCH_3$], 138 (27) [$M^+ - SO_2CH_2CH_2SO_2$], 111 (77), 97 (100), 85 (68), 71 (85).

$C_{10}H_{14}O_6S_2$ (294.3) Calcd. C 40.81 H 4.79
Found C 40.92 H 4.53

Methyl 3,4-(Ethylenedisulfonyl)-3-cyclohexene-1-carboxylate (**12g**): White solid, m.p. 192–194°C. – IR (KBr): ṽ = 1727 cm^{-1} (C=O), 1300, 1141, 1112 (SO_2). – ^1H NMR (200 MHz): δ = 1.63–1.88 (m, 1H, 6-H), 2.06–2.22 (m, 1H, 6-H), 2.45–2.69 (m, 3H, 2-, 5-H), 2.72–2.92 (m, 2H, 1-, 2-H), 3.68 (s, 3H, CH_3), 3.78–3.90 (m, 4H, $SO_2CH_2CH_2SO_2$). – MS (70 eV): *m/z* (%) = 294 (21) [M^+], 262 (39) [$M^+ - CH_3OH$], 235 (21) [$M^+ - CH_3OCO$], 234 (100), 124 (51), 110 (56), 78 (59) [234 – $SO_2CH_2CH_2SO_2$], 77 (59), 68 (44).

$C_{10}H_{14}O_6S_2$ Calcd. 294.0232 Found 294.0238 (MS)

4-Acetyl-1,2-(ethylenedisulfonyl)-1-cyclohexene (**12h**): White solid, m.p. 169–171°C. – IR (KBr): ṽ = 1695 cm^{-1} (C=O), 1307, 1297, 1135, 1112 (SO_2). – ^1H NMR (200 MHz): δ = 1.63–1.82 (m, 1H, 5-H), 2.13–2.19 (m, 1H, 5-H), 2.25 (s, 3H, CH_3), 2.50–2.88 (m, 5H, 3-, 4-, 6-H), 3.76–4.03 (m, 4H, $SO_2CH_2CH_2SO_2$). – MS (70 eV): *m/z* (%) = 278 (5) [M^+], 235 (13) [$M^+ - CH_3C{=}O$], 122 (14) [$M^+ - SO_2CH_2CH_2SO_2$], 43 (100).

$C_{10}H_{14}O_5S_2$ Calcd. 278.0283 Found 278.0284 (MS)

4,5-(Ethylenedisulfonyl)-1,2,3,6-tetrahydro-N-phenylphthalimide (**12i**): White solid, m.p. 285–287°C. – IR (KBr): ṽ = 1713 cm^{-1} (C=O), 1315, 1144, 1125 (SO_2). – ^1H NMR (200 MHz, [D_6]-DMSO): δ = 2.74–3.04 (m, 4H, $CH_2C{=}CCH_2$), 3.53–3.62 (m, 2H, O=CCHCHC=O), 4.02–4.33 (m, 4H, $SO_2CH_2CH_2SO_2$), 7.13–7.57 (m, 5H, aromatic H). – MS (70 eV): *m/z* (%) = 381 (34) [M^+], 233 (46), 225 (86) [$M^+ - SO_2CH_2CH_2SO_2$], 119 (100), 91 (23), 78 (25), 77 (29).

$C_{16}H_{15}NO_6S_2$ (381.4) Calcd. C 50.38 H 3.96 N 3.67
Found C 50.18 H 3.98 N 3.53

6,7-(Ethylenedisulfonyl)-1,2,3,4,4a,5,8,8a-octahydro-1,4-methanonaphthalene (**12j**): White solid, m.p. 196–198°C. – IR (KBr): ṽ = 1299, 1126, 1106 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 1.10–1.32 (m, 4H, 2-, 3-H), 1.48–1.63 (m, 4H, 4a-, 8a-H, methano-H), 1.66–1.88 (m, 2H, 5-, 8-H), 2.12 (br. s, 2H, 1-, 4-H), 2.82–3.06 (m, 2H, 5-, 8-H), 3.83 (s, 4H, $SO_2CH_2CH_2SO_2$). – ^{13}C NMR (50.288 MHz): δ = 25.073, 29.095, 33.056, 42.715, 42.984, 48.268, 141.140 (CH=CH). – MS (70 eV): *m/z* (%) = 302 (22) [M^+], 210 (32) [$M^+ - CH_2CH_2SO_2$], 162 (59), 146 (66) [$M^+ - SO_2CH_2CH_2SO_2$], 145 (100), 131 (42), 118 (34), 117 (71), 91 (67), 79 (57), 77 (59).

$C_{13}H_{18}O_4S_2$ Calcd. 302.0647 Found 302.0632 (MS)

$C_{13}H_{18}O_4S_2$ (302.4) Calcd. C 51.62 H 6.00
Found C 51.59 H 6.08

1,2-(Ethylenedisulfonyl)-4-phenyl-1-cyclohexene (**12k**): White solid, m.p. 174–175°C. – IR (KBr): ṽ = 1601, 1493, 1449, 1418 cm^{-1} (aromatic), 1296, 1133, 1106 (SO_2). – ^1H NMR (200 MHz): δ = 1.76–2.00 (m, 1H, 5-H), 2.13–2.26 (m, 1H, 5-H), 2.53–3.06 (m, 5H, 3-, 4-, 6-H), 3.76–4.06 (m, 4H, $SO_2CH_2CH_2SO_2$), 7.16–7.42 (m, 5H, Ph). – MS (70 eV): *m/z* (%) = 312 (3) [M^+], 156 (3) [$M^+ - SO_2CH_2CH_2SO_2$], 104 (100).

$C_{14}H_{16}O_4S_2$ Calcd. 312.0491 Found 312.0486 (MS)

4,5-(Ethylenedisulfonyl)-1,2,3,6-tetrahydro-1-methyl-2-phenylpyridine (**14**) was obtained from the sealed-tube reaction of **1** (17 mg, 0.082 mmol) with *N*-benzylidenemethylamine (49 mg, 0.41 mmol) in CH_2Cl_2 (3 ml) at 110°C for 10 h in 85% yield; white solid, m.p. 161–162°C. – IR (KBr): ṽ = 1307, 1282, 1131, 1107 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 2.13 (s, 3H, CH_3), 2.81–2.86 (m, 2H, 3-H), 3.30–3.48 (m, 2H, 6-H), 3.78–4.00 (m, 5H, 2-H and $SO_2CH_2CH_2SO_2$), 7.24–7.40 (m, 5H, aromatic H). – MS (40 eV): *m/z* (%) = 327 (20) [M^+], 250 (18), 171 (100) [$M^+ - SO_2CH_2CH_2SO_2$], 118 (58).

$C_{14}H_{17}NO_4S_2$ (327.4) Calcd. C 51.36 H 5.23 N 4.28
Found C 51.47 H 5.12 N 4.13

Crossed Diels-Alder Reactions of **1** *with Cyclopentadiene:* A mixture of **1** (35 mg, 0.168 mmol) and cyclopentadiene (**16**) (30 equiv.) in CH_2Cl_2 (4 ml) was heated in a sealed tube at 130°C for 5 h. After removal of the solvent, the residue was eluted through a silica gel column. The resulting solution was concentrated under reduced pressure and the obtained residue purified by HPLC (LiChrosorb column, *n*-hexane/EtOAc, 1:1) to give **18**, **19**, and **20** in 17, 40, and 20% yield, respectively. The reaction at room temp. was carried out similarly by stirring a mixture of **1** and **16** in CH_2Cl_2 for 44 h. After work up as described above, **18**, **19**, and **20** in 5.2, 46, and 10% yield, respectively, were obtained.

5,6-(Ethylenedisulfonyl)-3a,4,7,7a-tetrahydroindene (**18**): White solid, m.p. 161–163°C. – IR (KBr): ṽ = 1305, 1285, 1135, 1108 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 2.00–2.09 (m, 1H, 3a-H), 2.30–2.83 (m, 6H, 3-, 4-, 7-H), 3.10–3.29 (m, 1H, 7a-H), 3.78 (s, 4H, $SO_2CH_2CH_2SO_2$), 5.42–5.47 (m, 1H, vinyl), 5.67–5.72 (m, 1H, vinyl). – MS (70 eV): *m/z* (%) = 274 (8) [M^+], 167 (32), 149 (100).

$C_{11}H_{14}O_4S_2$ (274.4) Calcd. C 48.16 H 5.14
Found C 48.14 H 5.13

endo-11-Methylene-7,10-dithia-1,4-methanospiro[5.5]undec-2-ene 7,7,10,10-Tetraoxide (**19**): White solid, m.p. 45–47°C. – IR (KBr): = 1306, 1280, 1127, 1102 cm^{-1} (SO_2). – ^1H NMR (200

MHz): δ = 1.49–1.59 (m, 1H, methano-H), 1.80–1.90 (m, 1H, 5-H), 2.34 (d, 1H, J = 10 Hz, methano-H), 2.47 (dd, 1H, J_1 = 14, J_2 = 4 Hz, 5-H), 3.04 (br. s, 1H, 4-H), 3.40–3.70 (m, 3H, SO_2CH_2), 3.77–3.80 (m, 1H, 1-H), 3.90–4.10 (m, 1H, SO_2CH_2), 5.93 (br. s, 1H, vinyl), 6.00–6.10 (m, 1H, 3-H), 6.20–6.30 (m, 1H, 2-H), 6.57 (d, 1H, J = 2 Hz, vinyl). – MS (70 eV): m/z (%) = 274 (68) [M^+], 210 (48) [$M^+ - SO_2$], 182 (96) [$M^+ - CH_2CH_2SO_2$], 117 (27) [$M^+ - SO_2CH_2CH_2SO_2$], 66 (100).

$C_{11}H_{14}O_4S_2$ (274.4) Calcd. C 48.16 H 5.14
Found C 48.23 H 5.41

exo-11-Methylene-7,10-dithia-1,4-methanospiro[5.5]undec-2-ene 7,7,10,10-Tetraoxide (**20**): White solid, m.p. 177–178.5°C. – IR (KBr): ν̃ = 1313, 1295, 1125, 1107 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 1.50–1.65 (m, 2H, methano-H), 2.00 (dd, 1H, J_1 = 2.3, J_2 = 13.3 Hz, 5-H), 2.70–2.90 (m, 1H, 5-H), 3.10 (br. s, 1H, 4-H), 3.20–3.85 (m, 5H, 1-H and $SO_2CH_2CH_2SO_2$), 6.18–6.25 (m, 1H, 3-H), 6.27 (d, 1H, J = 1.8 Hz, vinyl), 6.37–6.43 (m, 1H, 2-H), 6.76 (d, 1H, J = 1.8 Hz, vinyl). – MS (70 eV): m/z (%) = 274 (100) [M^+], 209 (18), 182 (38) [$M^+ - CH_2CH_2SO_2$], 133 (40).

$C_{11}H_{14}O_4S_2$ (274.4) Calcd. C 48.16 H 5.14
Found C 48.13 H 4.89

Cope Rearrangement of **19** *to* **18**: A solution of **19** (40.7 mg, 0.148 mmol) in CH_2Cl_2 (5 ml) was heated in a sealed tube at 135°C for 16 h. After removal of excess solvent and purification by HPLC (LiChrosorb column, *n*-hexane/EtOAC, 1:1), **18** was obtained in 86% yield.

1,2-(Ethylenedisulfonyl)-4-isopropenyl-4-methyl-1-cyclohexene (**22**) *and 8,9-Dimethyl-5-methylene-1,4-dithiaspiro[5.5]undec-8-ene 1,1,4,4-Tetraoxide* (**23**): A solution of **1** (34.2 mg, 0.164 mmol) and 2,3-dimethyl-1,3-butadiene (405 mg, 4.93 mmol) in CH_2Cl_2 (3.5 ml) was heated in a sealed tube at 100°C for 18 h. After removal of solvent and purification by HPLC (LiChrosorb column, *n*-hexane/EtOAc, 1:1), **22** and **23** were obtained in 6.3 and 53% yield, respectively.

22: Colorless oil. – IR (neat): ν̃ = 1638 cm^{-1} (C=C), 1314, 1290, 1144, 1108 (SO_2). – ^1H NMR (200 MHz): δ = 1.08 (s, 3H, CH_3), 1.68 (dd, 3H, J_1 = 0.6, J_2 = 1.4 Hz, CH_3), 2.23–2.60 (m, 4H), 2.77–2.80 (m, 1H), 2.82–2.90 (m, 1H), 3.70–3.90 (m, 4H, $SO_2CH_2CH_2SO_2$), 4.71 (br. s, 1H, vinyl), 4.83 (d, 1H, J = 1 Hz, vinyl). – MS (70 eV): m/z (%) = 290 (0.4) [M^+], 134 (18) [$M^+ - SO_2CH_2CH_2SO_2$], 133 (83), 132 (100), 91 (42), 82 (82), 67 (75).

$C_{12}H_{18}O_4S_2$ Calcd. 290.0646 Found 290.0646 (MS)

23: White solid, m.p. 123–124.5°C. – IR (KBr): ν̃ = 1325, 1307, 1128, 1104 cm^{-1} (SO_2). – ^1H NMR (200 MHz): δ = 1.58 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.97–2.40 (m, 4H, 11-, 10-H), 2.70–2.90 (m, 2H, 7-H), 3.26–3.50 (m, 2H, SO_2CH_2), 3.56–3.76 (m, 1H, SO_2CH), 3.87–4.13 (m, 1H, SO_2CH), 5.86 (d, 1H, J = 1.4 Hz, vinyl), 6.68 (d, 1H, J = 1.4 Hz, vinyl). – MS (70 eV): m/z (%) = 290 (50) [M^+], 134 (25) [$M^+ - SO_2CH_2CH_2SO_2$], 133 (84), 132 (100), 117 (40).

$C_{12}H_{18}O_4S_2$ (290.4) Calcd. C 49.63 H 6.25
Found C 49.61 H 6.42

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