Diels-Alder Reactions of 1,1-Bis[benzenesulfonyl]ethene*

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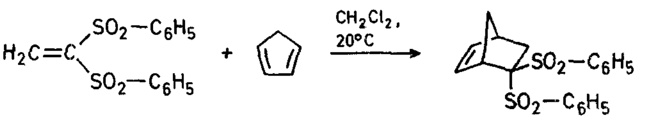
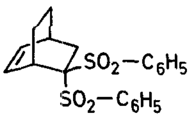
Diels-Alder reactions of vinyl sulfones have attracted considerable attention in recent years[1]. However, no reports are available concerning the Diels-Alder reaction of 1,1-bis[benzenesulfonyl]ethene (**1**)[2], a geminal disulfone. In continuation of our investigations in the chemistry of geminal disulfones[3], we have studied the Diels-Alder reaction of **1** with some representative dienes.

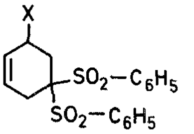
The reaction between cyclopentadiene (**2a**) and **1** proceeds smoothly at room temperature in dichloromethane solution to give the corresponding [4 + 2]-cycloadduct, 5,5-bis[benzenesulfonyl]-2-norbornene (**3a**) in 80% yield as a colourless crystalline solid. The structure of **3a** and thus the presence of a Diels-Alder addition is clearly established from the spectral data of the product (Table).



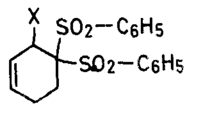
1 **2a** **3a**



3b



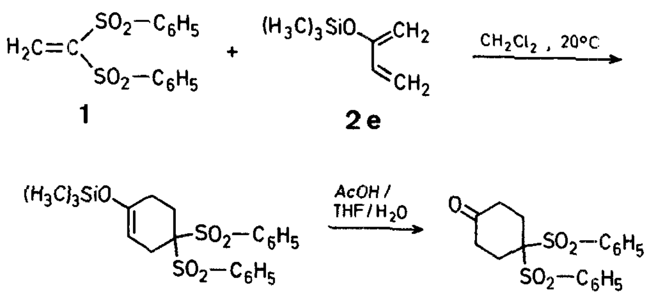
3c X = H



3d X = O–CO–CH₃

Similarly **1** reacts with 1,3-cyclohexadiene (**2b**), 1,3-butadiene (**2c**, generated *in situ* from 3-sulfolene) and 1-acetoxy-1,3-butadiene (**2d**) to give the corresponding adducts **3b–d** in reasonable yields. Due to the lower reactivity of these dienes in comparison to cyclopentadiene, the reactions require elevated temperatures (100–110 °C, benzene, sealed tube). The spectral data of compounds **3b–d** are in accordance with the assigned structures (Table).

The activated diene 2-trimethylsiloxy-1,3-butadiene (**2e**) reacts with **1** at room temperature to give the cycloadduct **3e** in good yield. The trimethylsilylenol ether **3e** is immediately



3e **4**

Table. Cycloadducts **3a–d** prepared.

Product	Yield[a] [%]	m.p. [°C]	Molecular formula[b]	I.R. (KBr)[c] ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$/TMS)[d] δ [ppm]	M.S. m/e (M$^+$)
3a	80	157–158°	$C_{19}H_{18}O_4S_2$ (374.4)	1150, 1320, 1450, 3100	1.16–1.4 (m, 2H); 2.2 (d, J = 2 Hz, 1H); 2.6–2.8 (dd, 1H); 2.92 (br. s, 1H); 3.32 (br. s, 1H); 5.95–6.2 (m, 1H); 7.4–7.84 (m, 10H$_{arom}$)	374
3b	42	148–150°	$C_{20}H_{20}O_4S_2$ (388.5)	1140, 1300, 1440, 2950	1.04–2.12 (m, 4H); 2.02–2.80 (m, 3H); 3.36–3.4 (d, J = 8 Hz, 1H); 5.44–5.56 (t, J = 7 Hz, 1H); 5.76–5.88 (t, J = 7 Hz, 1H); 7.44–8.12 (m, 10H$_{arom}$)	388
3c	75	156°	$C_{18}H_{18}O_4S_2$ (362.5)	1150, 1340, 1460, 2920	2.36 (m, 4H); 2.84 (m, 2H); 5.64–5.72 (m, 2H); 7.6–8.2 (m, 10H$_{arom}$)	362
3d	57	145–147°	$C_{20}H_{20}O_6S_2$ (420.5)	1160, 1340, 1760	1.92 (s, 3H); 2.04–2.2 (m, 2H); 2.52–2.84 (m, 2H); 5.4–5.48 (d, J = 10 Hz, 1H); 5.8–5.88 (d, J = 10 Hz, 1H); 7.16 (br. s, 1H); 7.52–8.32 (m, 10H$_{arom}$)	420

[a] Yields after recrystallisation from benzene.

[b] Satisfactory microanalysis obtained: *C ±0.48, H ±0.32; except* **3a**, *H –0.60.*

[c] Recorded on a Perkin Elmer 297 spectrometer.

[d] Recorded at 100 MHz using JEOL MH-100 and FX-100 spectrometers.

hydrolysed by aqueous acid to 4,4-bis[benzenesulfonyl]cyclohexanone **(4)**. The structure of **4** is based upon the well known regioselectivity of the Diels-Alder reaction and spectral data. In particular the ^{1}H-N.M.R. and ^{13}C-N.M.R. spectra demonstrate a high degree of symmetry present in product **4**.

Experiments are in progress to study the synthetic utility of adducts **3a–d** and **4**.

5,5-Bis[benzensulfonyl]-2-norbornene (3a):
To a stirred solution of 1,1-bis[benzenesulfonyl]ethene (**1**; 0.616 g, 2 mmol) in dichloromethane (2 ml) cyclopentadiene (**2a**; 0.264 g, 4 mmol) is added and the mixture stirred for 24 h at room temperature. The solvent is removed and the crude product crystallized from benzene to give **3a**; yield: 0.60 g (80 %). The spectral data are given in the Table.

4,4-Bis[benzenesulfonyl]cyclohexene (3c); Typical Procedure:
A solution of 1,1-bis[benzenesulfonyl]ethene (**1**; 0.154 g, 0.5 mmol) and 3-sulfolene (0.09 g, 0.75 mmol) in dry benzene (2 ml) is heated to 100–110 °C in a sealed tube for 3.5 h. The mixture is cooled to room temperature and the solvent removed. The crude material is chromatographed over silica gel. Elution with hexane/ethyl acetate (90/10) gives **4**; yield: 0.14 g (75 %). The spectral data are given in the Table. The same procedure is applied for the preparation of products **3b**, **d** except that the dienes **2b**, **d** are used instead of sulfolene.

4,4-Bis[benzenesulfonyl]-cyclohexanone (4):
2-Trimethylsilyloxy-1,3-butadiene (**2e**; 0.284 g, 2 mmol) and **1** (0.154 g, 0.5 mmol) are reacted in the same way as described for the preparation of compound **3a** giving the cycloadduct **3e**; yield: 100 %.

The crude product **3e** (0.217 g, 0.5 mmol) is hydrolyzed in acetic acid/THF/water (1/50/50; 10.0 ml); yield: 0.15 g (79 % based on **1**); m.p. 218–220 °C.

$C_{18}H_{18}S_2O_5$	calc.	C 57.13	H 4.79
(378.4)	found	56.57	5.20

M.S.: m/e = 378 (M^+).

I.R. (KBr): ν = 1725, 1320, 1140 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 2.72 (s, 8 H), 7.2–8.1 ppm (m, 10 H_{arom}).

^{13}C-N.M.R. ($CDCl_3$/TMS): δ = 25.1 (C-3/5), 36.4 (C-2/6), 128.8, 131.4, 134.9, 135.6 (C_{arom}), 207.9 ppm (C=O).

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