

REACTION OF CYCLOHEPTATRIENES WITH SULPHUR DIOXIDE:  
FORMATION OF BENZENEALKANESULPHINIC ACIDS

Ottorino De Lucchi, Fabiola Filipuzzi, and Vittorio Lucchini\*

Centro Meccanismi di Reazioni Organiche del CNR, Università di Padova,  
Via Marzolo 1, 35131 Padova, Italy

Cycloheptatriene, 7-methylcycloheptatriene, and 7-phenylcycloheptatriene in liquid  $\text{SO}_2$  convert in about 3 d at  $18^\circ\text{C}$  to benzenemethanesulphinic acid, 1-benzeneethanesulphinic acid, and dibenzenemethanesulphinic acid respectively; benzonorcaradiene gives in 2 h the  $\alpha$ - and  $\beta$ -naphthalenemethanesulphinic acids.

The reactivity of sulphur dioxide is continuously attracting interest because of the variety of reaction modes in which it can interact with substrates.<sup>1</sup> For example with the series of cyclic polyenes the reactivity is remarkably different: with cyclopentadiene, 1,3-cyclohexadiene, and 1,5-cyclooctadiene copolymeric materials are formed;<sup>2</sup> 1,4-cyclohexadiene undergoes in  $\text{SO}_2$  oxidative aromatization to benzene;<sup>3</sup> with 1,3-cycloheptatriene<sup>3</sup> and 1,3,5-cyclooctatriene<sup>5</sup>  $\text{SO}_2$  reacts in the [4+2] chelotropic addition mode; 1,3-cyclooctadiene<sup>2</sup> (in the absence of a polymerization starter) and cyclooctatetraene (in the absence of  $\text{SbF}_5$ )<sup>6</sup> are inert. The reactivity with cycloheptatriene and its derivatives, on which we wish to report here, is also peculiar and different from those observed with the other cyclic polyenes.

Cycloheptatriene (1a) in sulphur dioxide as solvent is quantitatively converted in about 3 d at  $18^\circ\text{C}$  to benzenemethanesulphinic acid (2a):

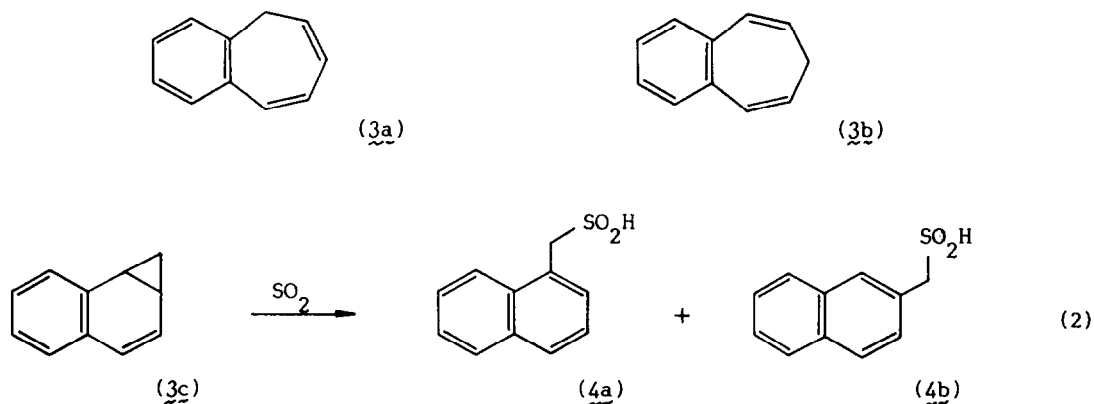


a R = H; b R = Me; c R = Ph

This product is unambiguously recognized from the NMR pattern [ $\delta$ : 7.28 (s, ArH), 4.00 (s, CH<sub>2</sub>), while SO<sub>2</sub>H shifts from 4.3 to 8.3 during the course of the reaction] and from the analysis of decomposition products.<sup>7</sup>

Similarly, from 7-methylcycloheptatriene (1b) and 7-phenylcycloheptatriene (1c), 1-benzeneethanesulphonic acid (2b) [ $\delta$ : 7.29 (s, ArH), 3.87 (q CH), 1.59 (d, Me, <sup>3</sup>J 7.2 Hz), SO<sub>2</sub>H variable] and dibenzenemethanesulphonic acid (2c) [ $\delta$ : 7.35 (s, ArH), 5.04 (s, CH), SO<sub>2</sub>H variable] are exclusively obtained; no rearranged products, *i.e.* toluenemethanesulphonic acid or phenylbenzenemethanesulphonic acid were observed. 7-*i*-Propyl- and 7-*t*-butylcycloheptatrienes (1d) and (1e) are unreactive.

1,2- And 3,4-benzocycloheptatrienes (3a) and (3b) are again non reactive in liquid SO<sub>2</sub>; only the slow conversion (3 d at 18°C) of (3b) to the more stable (3a) isomer is observed, probably *via* SO<sub>2</sub> ene catalysis.<sup>8</sup>



On the other hand, when benzonorcaradiene (3c)<sup>9</sup> is dissolved in liquid SO<sub>2</sub>, its NMR pattern is converted in about 2 h to aromatic resonances at  $\delta$  7.5–8.2 and to two singlets at  $\delta$  4.55 and 4.23 in the 45:55 ratio. Resolution enhancement shows that these signals are a doublet and a triplet respectively, so that they can be attributed to the methylene resonances of  $\alpha$ - and  $\beta$ -naphthalenemethanesulphonic acids (4a) and (4b).

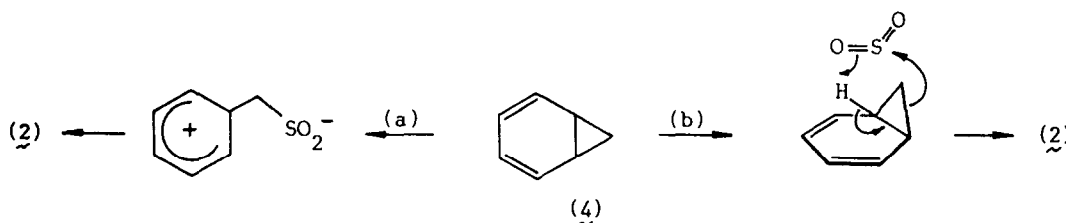
For the elucidation of the reaction mechanism the following experimental results are relevant: (i) from the reaction of (1a) in SO<sub>2</sub> saturated with D<sub>2</sub>O, non-deuterated (2a) is obtained in roughly the same time; (ii) the pseudo first-order constants for the conversion have been measured and are given in

Table. Rate constants for the reaction of cycloheptatrienes with SO<sub>2</sub>.

	R	k/sec <sup>-1</sup> x 10 <sup>5</sup> at 18°C
(1a)	H	.42
(1b)	Me	.41
(1c)	Ph	.88
(1d)	<u>i</u> -Pr	no reaction in 15 d
(1e)	<u>t</u> -Bu	
(3a)		
(3b)		
(3c)		

the table. In the case of cycloheptatrienes (1) the constants depend on steric factors, but are rather insensitive to the electronic properties of the substituents. These facts indicate that the SO<sub>2</sub> attack occurs at the 7-carbon atom and that every stage of the reaction is irreversible. Furthermore, the kinetic data suggest that also in the case of cycloheptatrienes (1) the reactive substrate may be norcaradiene (4) (electron-withdrawing substituents shift the equilibrium toward norcaradiene,<sup>10</sup> but hinder the electrophilic attack of SO<sub>2</sub>).

The following mechanisms are not proved, but consistent with the experimental data. Mechanism (a), the acidic attack of SO<sub>2</sub> to the cyclopropane ring of (4), was also proposed for the reaction of SO<sub>2</sub> with homocycloheptatriene.<sup>11</sup>



The ene mechanism (b) implies the SO<sub>2</sub> attack to the 1,7 or 6,7 bond in (4). With smaller [n.1.0] systems, the attack of other enophiles occurs on the zero-bridge bond,<sup>12</sup> which is in fact associated with the HOMO (as for example in bicyclobutane and bicyclo[2.1.0]pentane).<sup>13</sup> In norcaradiene (4), on the other hand, the HOMO is localized on the one-bridge bonds,<sup>14</sup> which can therefore be considered the more electrophilic ones in the cyclopropane ring.

Further experimental work is in progress for a more precise characterization of the reaction mechanism.

## REFERENCES AND NOTES

1. O. De Lucchi and V. Lucchini, J. Chem. Soc., Chem. Commun., 1982, 464; O. De Lucchi and V. Lucchini, Ibidem, 1982, 1105; G. Capozzi, V. Lucchini, F. Marcuzzi, and G. Melloni, Tetrahedron Lett. 1980, 21, 3289; A. Dondoni, P. Giorgianni, A. Battaglia, and G.D. Andretti, J. Chem. Soc., Chem. Commun., 1981, 350; and references cited on these papers.
2. T. Yamaguchi, K. Nagai, and T. Ono, Kobunshi Ronbunshu, 1974, 31, 361; Chem. Abs., 1974, 81, 121198b.
3. D. Masilimani and M.M. Rogic, Tetrahedron Lett., 1978, 3785.
4. T. Yamaguchi, K. Nagai, and O. Itabashi, Kobunshi Kagaku, 1973, 30, 464; Chem. Abs., 1974, 80, 71156t.
5. W.L. Mock, J. Amer. Chem. Soc., 1970, 92, 3807.
6. J. Gasteiger and R. Huisgen, J. Amer. Chem. Soc., 1972, 94, 6541; L.A. Paquette, U. Jacobsson, and M. Oku, J. Chem. Soc., Chem. Commun., 1975, 115.
7. The sulphinic acid (2a) disproportionates when isolation is attempted. Treatment with water gives benzyl benzenemethanethiosulphonate and bis-(methylphenyl)disulphone, identified by comparison of physical and NMR parameters [J.E. McCaskie, T.R. Nelsen, and D.C Dittmer, J. Org. Chem., 1973, 38, 3048; L.O. Farnig and J.L. Kice, J. Amer. Chem. Soc., 1981, 103, 1137]. A similar behaviour was observed with benzenesulphinic acid [Z. Yoshida, H. Miyoshi, and K. Kawamoto, Kogyo Kagaku Zasshi, 1969, 72, 1295; Chem. Abs., 1969, 71, 101463z].
8. D. Masilimani and M.M. Rogic, J. Amer. Chem. Soc., 1978, 100, 4634.
9. Prepared from (3a) by irradiation at 300 nm in cyclohexane [M. Pomerantz and G.W. Gruber, J. Amer. Chem. Soc., 1967, 89, 6798 and 6799].
10. G. Mayer, Angew. Chem., Int. Ed. Engl., 1967, 6, 402.
11. J. Dalling, J.H. Gall, and D.D. MacNicol, Tetrahedron Lett., 1979, 4789.
12. P.G. Gassman, Acc. Chem. Res., 1971, 4, 130; R.L. Amey and B.E. Smart, J. Org. Chem., 1981, 46, 4090.
13. W.L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals," Academic Press, New York and London, 1973, p. 203 and 228.
14. The interaction with the symmetric  $\pi^*$  orbital on the diene lowers the energy of the orbital localized on the zero-bridge bond, while the energy of the orbital on 1,7 and 6,7 bonds is increased through interaction with the antisymmetric  $\pi$  orbital, so that an energy reversal occurs: confirmed by ab-initio computational analysis at the STO-3G level.

(Received in UK 17 January 1984)