

A STUDY OF THE REACTION OF BICYCLO[5.1.0]OCTA-
2,5-DIENE WITH SULPHUR DIOXIDE

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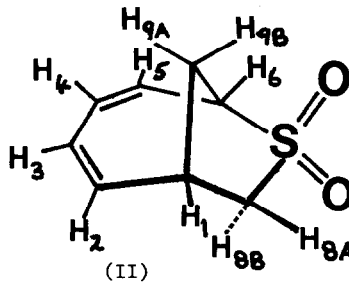
SUMMARY

□ Thermally-induced reaction between bicyclo[5.1.0]octa-2,5-diene (I) and sulphur dioxide under dry conditions in toluene- d_8 as solvent leads to the unexpected formation of the hitherto unknown diene sulphone 7-thiabicyclo[4.2.1]nona-2,4-diene 7,7-dioxide (II). □

Recently we have described¹ the direct bridging of bicyclo[5.1.0]octa-2,5-diene (I) by elemental sulphur or selenium to produce the corresponding 9-heterobicyclo[3.3.1]nona-2,6-dienes. We now report the novel course of thermal reaction between (I) and SO_2 . Reaction runs were

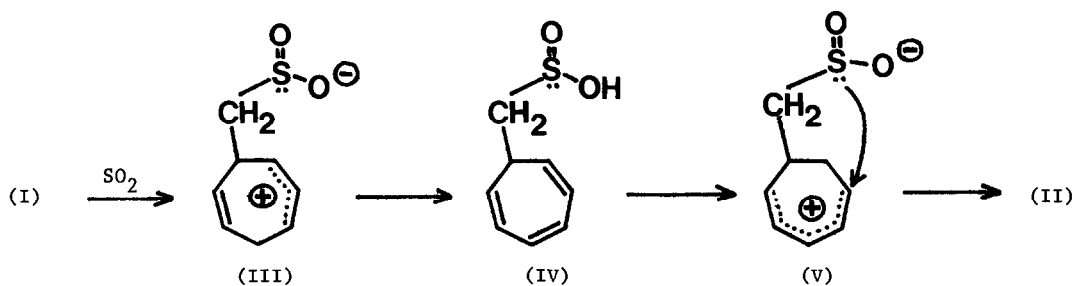


typically carried out in thick-walled n.m.r. tubes, employing toluene- d_8 as solvent so that reaction progress could be conveniently monitored. Heating pure hydrocarbon (I)¹ with excess dry² sulphur dioxide for 5 days at 150°C, led to the disappearance of starting material and production of a new sulphone (II). Compound (II) was purified chromatographically (Mallinckrodt silicic acid, 20% ethyl acetate/ n -pentane as eluent) and recrystallisation from benzene/ CS_2 gave a moderate yield of (II) as colourless crystals, m.p. 60.5–61.5°C: i.r. 1300, 1160, and 1110 cm^{-1} $\nu(SO_2)$; λ_{max}^{EtOH} 259 m μ ($\epsilon = 4900$); m/e 170.04026 ($C_8H_{10}O_2S$ requires 170.04015); ^{13}C n.m.r. (δ_c in CS_2/C_6D_6 , ca. 10:1 v./v.) 26.9 (t), 33.0 (d), 61.1 (d), 62.2 (t), 124.1 (d), 126.5 (d), 128.7 (d), and 137.8 (d). Definitive information was obtained from 360 MHz 1H n.m.r. spectra,³ δ : 2.91, H_1 ; 6.12, H_2 ; 5.82, H_3 ; 6.03, H_4 ; 5.74, H_5 ; 3.72, H_6 ; 3.07, H_{8A} ; 2.72, H_{8B} ; 1.81, H_{9A} ; 2.56, H_{9B} ; the geminal and vicinal coupling constants⁴ are: J_{8A8B} , -13.1; J_{9A9B} , -13.4; J_{12} , 8.1; J_{23} , 11.0; J_{34} , 7.4; J_{45} , 11.6; J_{56} , 7.6; J_{69A} , 1.0; J_{69B} , 5.7; J_{18A} , 9.7; J_{18B} , 3.0; J_{19A} , 1.0; J_{19B} , 6.4; the long range couplings also being in complete accord with assigned structure (II).



The mechanism of formation of (II) is of interest. A possible mechanism is shown in the Scheme.

SCHEME



After possible initial complex information⁵ between (I) and SO₂, direct cyclopropane ring opening⁶ gives (III) which proceeds, via (IV) and (V), to (II).

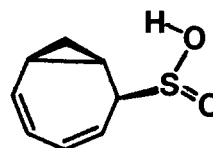
Acknowledgement.

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References and Notes

1. E. Cuthbertson, J.H. Gall, and D.D. MacNicol, Tetrahedron Letters, 1977, 3203.
2. V/v ratios of toluene-d₈: SO₂ of ca. 10:1 were employed. The SO₂ was dried (3A molecular sieves) and all solutions were carefully, degassed. In preliminary runs from which moisture was not rigorously excluded, product signals from the known sulphone 9-thiabicyclo[4.2.1]nona-2,7-diene 9,9-dioxide were observed, this compound being independently synthesised by the method of W.L. Mock and J.H. McCausland, J. Org. Chem., 1976, 41, 242, for ¹H n.m.r. comparison.
3. Measured in CS₂/C₆D₆ (ca. 10:1 v/v). The assignments given have been confirmed by extensive spin decoupling experiments.
4. Based on first order analysis: a detailed computer analysis is in hand.
5. Cf. M.M. Rogic and D. Masilamani, J. Amer. Chem. Soc., 1977, 99, 5219; and refs. therein.
6. Alternatively, prior attack of SO₂ at a double bond (cf. ref.5) may occur giving two carbonium species each capable of possible conversion to (VI): appropriate nucleophilic attack of the sulphur lone pair in a cyclopropane ring-protonated species may then give (II).

(VI)



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