The Steric Course of the Formation of Benzocyclobutene by Thermal Desulphonylation of 1,3-Dihydrobenzo[c]thiophen 2,2-Dioxide

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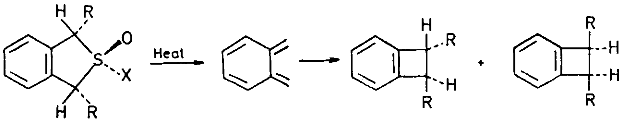
Summary Thermolysis of *cis*-[1,3-$^2H_2$]-dihydrobenzo[*c*]-thiophen 2,2-dioxide (**1b**) gives *trans*-[1,2-$^2H_2$]-benzocyclobutene (**3b**); in conjunction with the Woodward–Hoffmann rules and the stereochemistry of closely related reactions, this provides strong evidence for a mechanism involving disrotatory formation of *o*-quinodimethane (**2**) with extrusion of sulphur dioxide, followed by conrotatory closure of (**2**) to benzocyclobutene.

o-Quinodimethane (**2**) has been suggested[1] to be the intermediate in the thermolytic formation of benzocyclobutene (**3a**) from 1,3-dihydrobenzo[*c*]thiophen 2,2-dioxide (**1a**). Trapping experiments are consistent with the suggestion, but since analogous trapping products may be obtained starting from (**3a**),[2] the data are equally well explained in terms of a side equilibrium of (**2**) and (**3a**) subsequent to formation of the latter, *i.e.* (**1a**) → (**3a**) ⇌ (**2**). We now report stereochemical evidence for the original sequence (**1a**) → (**2**) → (**3a**) (Scheme).

Treatment of (**1c**) with NaOD–D_2O gave the *cis*-dideuteriated sulphoxide (**1d**) with a high level of isotopic and stereochemical purity;† oxidation of (**1d**) with H_2O_2 gave (**1b**).



(1) a; R=H, X=O
b; R=D, X=O
c; R=H, X=:
d; R=D X=:

(2)

(3) a; R = H
b; R = D

(4)

Scheme

The passage of (**1b**) through a quartz tube at 500 °C and *ca.* 1 μm Hg pressure gave [1,2-$^2H_2$]-benzocyclobutene (*ca.* 95%); at 400 °C the benzocyclobutene yield was much

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† A typical sample was estimated by mass spectrometry to contain 81% of the [$^2H_2$]-compound and about 13% of the [$^2H_3$]-compound; the n.m.r. spectrum indicated the remaining benzylic protons to be all in the same configuration relative to the oxygen.

reduced (6%) with most of the (**1b**) being recovered. The stereochemistry of the two deuterium atoms was found by examination of the deuterium-decoupled ^{13}C-satellite of the benzylic proton signal, which appeared as two superimposed doublets, *J* 2·5 and 5·5 Hz with relative areas about 3 or 4:1, due to the *trans*- and *cis*-isomers respectively.[3] For comparison a mixture of the *cis*- and *trans*-isomers, assumed from its mode of preparation‡ to be approximately equimolar, was found to show the same pair of doublets but with equal intensities; the n.m.r. spectra of the "3:1" and "equimolar" mixtures were otherwise indistinguishable. Comparison of the i.r. spectra of the "3:1" and "equimolar" mixtures allowed the assignment of characteristic bands to each isomer: *cis*, 645 and 895; *trans*, 825, 850, and 905 cm^{-1}. The composition of the "3:1" mixture independently estimated from the intensities of these bands (assuming conformance with Beer's Law) was in agreement with the n.m.r. value. Flash thermolysis[4] of (**1b**) at 500° and 10—14 μm Hg gave a 90% yield of a mixture of apparently identical composition to that obtained in the quartz-tube reaction indicating that significant surface effects are probably absent.

A sample from the quartz-tube thermolysis was further passed through the tube once at 500 °C and then twice at 600 °C. The *trans*:*cis* ratios from these runs were 65:35, 50:50, and 50:50 respectively (i.r.). These results prompted examination of the stereochemistry of the product obtained under mild conditions. Thermolysis at 430—440° gave a product consisting almost entirely of the *trans*-isomer with only a small amount of (**4b**) (<4%) detectable by i.r. [these conditions gave about 20% conversion to benzocyclobutene and complete recovery of unreacted (**1b**)].

The formation of a *trans*-dideuteriated product from a *cis*-dideuteriated starting material requires a mechanism involving stereoelectronically controlled reactions as in the Scheme with the first step a disrotatory extrusion of sulphur dioxide analogous to that found with derivatives of 2,4-dihydrothiophen 1,1-dioxide,[5] followed by a conrotatory ring closure of the *o*-quinodimethane,[6] both as expected from the Woodward–Hoffmann rules.[7]

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‡ Phthalaldehyde was reduced with $NaBD_4$ to phthalyl-[α,α'-$^{2}H_2$] alcohol; this was converted by known routes into the 1,2-dihydrobenzo[*c*]thiophen 2,2-dioxide which was then thermolysed as above.

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