cis-Bromination of a Non-conjugated Cyclic Alkene. Unprecedented Electrophilic Stereoselection by Means of a Remote SO_2 Group

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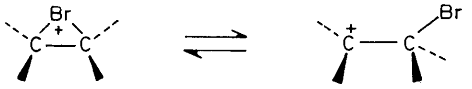
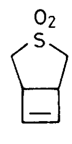
Contrary to expectation, addition of molecular bromine to 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (**1**) yields substantial amounts of the *cis*-1,2-dibromide (confirmed by *X*-ray diffraction), suggesting that the remote SO_2 group exerts an extraordinary directive influence by means of a long-range Coulomb interaction that stabilises an open carbocation intermediate at the expense of the usually favoured bridged bromonium ion.

Formation of *cis*-1,2-dibromides by bromination of alkenes under ionic conditions is rare.[1] In the few cases reported, *syn*-addition is made kinetically attractive by the presence of conjugating groups on the double bond that stabilise open carbocations *vis-à-vis* a cyclic bromonium ion, equation (1). When such features are absent, the overwhelming preference is for *trans*-bromination. One notable exception is the reported[2] formation of a *cis*-1,2-dibromide (albeit as a 30 : 70 mixture with its *trans*-isomer) from Dewar benzene, but the compound was too unstable to be isolated and characterisation rested on chemical evidence. We now report another example, this time fully authenticated by a crystal structure determination, in which *syn*-addition to an isolated double bond is unexpectedly brought about by a favourable long-range Coulomb interaction between a remote SO_2 group and the open carbocation.

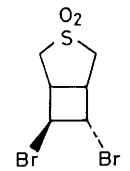
The compound in question is the bicyclic sulphone (**1**) formed by oxidative decarboxylation of the photoadduct of 2,5-dihydrothiophene 1,1-dioxide with maleic anhydride.[3] In contradistinction to the general behaviour of other non-conjugated alkenes, electrophilic addition of bromine to (**1**) in methylene chloride proceeded sluggishly and gave a 1 : 1 mixture (by n.m.r.) of isomeric dibromides which could be separated readily by 'flash' chromatography. That the mixture represented a kinetically controlled product distribution was established by the stability of the isomeric dibromides to the conditions of reaction. The structural assignment of one of the isomers, isolated as colourless rhombs (m.p. 160—163 °C), to the *trans*-dibromide (**2**)† followed convincingly from its ^{13}C n.m.r. spectrum which exhibited six signals at δ 54.17, 52.03, 49.32, 48.28, 42.28, and 39.45. The ^{13}C n.m.r. spectrum of the second isomer, also obtained in a pure state as stable colourless needles (m.p. 168–168.5 °C), was entirely compatible with the symmetry of the *cis*-dibromide structure (**3**) in that only three signals appeared, at δ($CDCl_3$) 53.39, 48.54, and 43.30. Because bromine addition to non-conjugated alkenes normally takes place with *trans*-stereochemistry, the structure of (**3**), shown in Figure 1 with relevant bond parameters, was validated by an *X*-ray diffraction study.‡



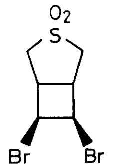
(1)



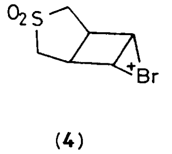
(**1**)



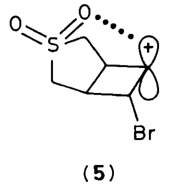
(**2**)



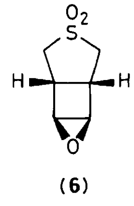
(**3**)



(**4**)



(**5**)



(**6**)

Formation of the *cis*-dibromide (**3**) at the expense of an equal amount of the expected *trans*-product (**2**) requires the intermediacy of the open carbocation (**5**) and subsequent *syn*-attack by Br^- at a rate that is competitive with *anti*-collapse of the bromonium ion (**4**). From an inspection of Dreiding models, there is no question that the SO_2 group can provide sufficient steric bias to divert the incoming Br^- away from the *anti*-face and hence cause the *syn*-attachment of two

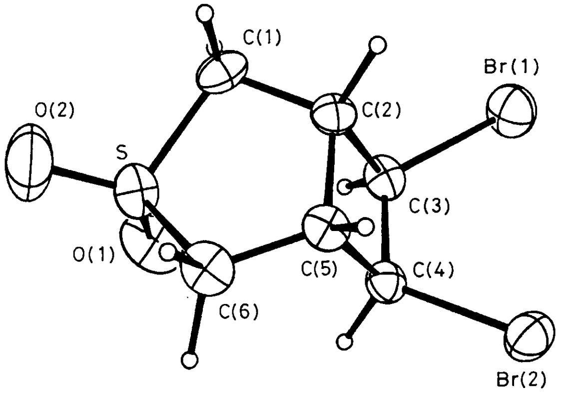


Figure 1. Molecular structure of (**3**). Selected bond lengths (Å) are: S–O(1) 1.436(5), S–O(2) 1.435(5), S–C(1) 1.791(8), S–C(6) 1.793(7), C(1)–C(2) 1.527(9), C(2)–C(3) 1.520(9), C(2)–C(5) 1.574(9), C(3)–C(4) 1.527(9), C(3)–Br(1) 1.947(6), C(4)–C(5) 1.544(9), C(4)–Br(2) 1.962(6), C(5)–C(6) 1.520(9).

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† All new compounds were characterised by combustion analysis as well as by ^1H and ^{13}C n.m.r., i.r., and mass spectrometry

‡ *Crystal data:* (**3**), $C_6H_8Br_2O_2S$, M = 304.01, monoclinic, space group $P2_1/c$ (No. 14), a = 10.430(3), b = 6.650(2), c = 12.723(8) Å, β = 91.20(4)°, U = 882(1) $Å^3$, Z = 4, D_c = 2.29 g cm^{-3}, $F(000)$ = 584, $\mu(Mo\text{-}K_\alpha)$ = 92.8 cm^{-1}, R = 0.042, R_w = 0.047 for 1366 reflections [293 K, $1.0 \leqslant 2\theta \leqslant 56°$, $I \geqslant 3.0\sigma(I)$, Enraf-Nonius CAD-4 diffractometer, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 73 Å]. A weighting scheme of the form $w^{-1} = \sigma^2(F) + (0.22 \times F)^2 + 1.8$ {where $\sigma(F) = [F^2 + 2F \times \sigma(F)]^{-\frac{1}{2}} - F$} gave a satisfactory analysis of variance and a goodness-of-fit of 1.05.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

large bromine atoms.§ We have also discounted intramolecular participation by the SO_2 group as the source of the *cis*-stereoselection. The *X*-ray structure of the alkene (**1**) shows a least distance of 3.23 Å between the *exo*-oxygen atom of the SO_2 group and the double bond,¶ making any bonding to the reaction centre in (**4**) unlikely, particularly as the SO_2 group is a very poor nucleophile. Furthermore, even if bonding could occur, it should lead to overall *syn*-addition, whereas there is an equal preference for *anti*-addition. In our view, the relaxation in the usual demand for bridging by bromine in (**4**) is brought about by the unprecedented stabilising effect of a long-range Coulomb interaction between the highly polar SO_2 group and the carbocation centre as depicted in (**5**).

As a corollary to these findings we have observed the same type of proximity effect in the ring-opening of the *anti*-epoxide (**6**) with aqueous HBr (60%) in glacial acetic acid. This is borne out by the loss of the *trans*-stereospecificity usually associated with epoxides in which the effect of conjugation is absent.[5] Thus, on the basis of nuclear Overhauser enhancement studies, we found that the bromohydrins from (**6**) contained 37% of the *cis*-isomer, the formation of which demands the intermediacy of an open carbocation. In this connection it is of some significance that the reaction of the alkene (**1**) with *N*-bromoacetamide in aqueous acetone gives only a single bromohydrin which is derived by exclusive *anti*-attack on the bridged intermediate (**4**). This apparently paradoxical behaviour may be explained by hydration of the polar SO_2 group, resulting in a loss of its directive influence. This interpretation is supported by the observation that bromination of (**1**) in aqueous 1,2-dimethoxyethane proceeds normally to give, as the only product, the *trans*-1,2-dibromide (**2**).

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References

1 For a comprehensive account of the stereochemistry of electrophilic addition by bromine to double bonds, see P. B. D. De La Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, 1982.

2 E. E. van Tamelen and D. Carty, *J. Am. Chem. Soc.*, 1971, **93**, 6102; see also, R. Caple, F. M. Hsu, and C. S. Islenda, *J. Org. Chem.*, 1968, **33**, 4111, for a report of the occurrence of formal *cis*-addition to *anti*-7-bromobenzonorbornadiene (*anti*-9-bromo-1,4-dihydro-1,4-methanonaphthalene), but the result is complicated by the possibility of skeletal rearrangements.

3 R. A. Aitken, J. I. G. Cadogan, I. Gosney, B. J. Hamill, and L. M. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 1982, 1164.

4 S. M. Roberts and Z. Grudzinski, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1767.

5 For a specialised review devoted to the stereospecificity in opening of an epoxide ring, see A. A. Akhrem, A. M. Moiseenkov, and V. N. Dobrynin, *Russ. Chem. Rev.*, 1968, **37**, 448.

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§ Even in the comparatively hindered system, 7,7-dimethylbicyclo[3.2.0]hept-2-en-6-one, bromination occurs exclusively with *trans*-stereochemistry.[4]

¶ Full crystallographic data for (**1**) will be published elsewhere.