Direct 1,5-Cycloaddition of Sulphur Dioxide to Cyclo-octatetraene. 9-Thiabarbaralane 9,9-Dioxide

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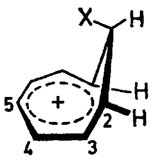
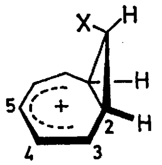
Summary Reaction of cyclo-octatetraene with antimony pentafluoride in liquid sulphur dioxide leads directly to 9-thiatricyclo[3,3,1,$0^{2,8}$]nona-3,6-diene 9,9-dioxide by unprecedented 1,5 cycloaddition; 9-thiabicyclo[4,2,1]nona-2,4,7-triene 9,9-dioxide is formed concomitantly and is the thermodynamically more stable $C_8H_8O_2S$ isomer.

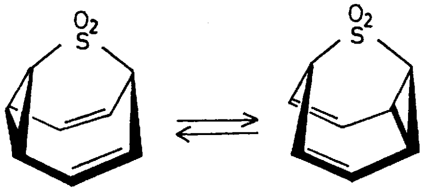
Electrophilic additions to cyclo-octatetraene, now recognized to involve initial formation of *endo*-8-substituted homotropylium ions (**1**), proceed to completion by capture of gegenion at C-2 (biparticulate capture)[1] or C-4 (during uniparticulate[2] additions).[3] Alternative reaction pathways for charge neutralisation in (**1**) have not been observed, so that it has been assumed that (**1**) is invariably both more stable and more reactive than its classical bicyclic counterpart (**2**). We now describe a re-examination of the SbF$_5$-promoted reaction of cyclo-octatetraene with liquid sulphur dioxide[3d] and report the formation of 9-thiabarbaralane 9,9-dioxide (**3**) in addition to (**4**). This one-step synthesis of the previously unknown (**3**), the most direct route to a 9-heterobarbaralane yet,[4] may involve intramolecular collapse in (**2**; X = SO$_2$ . . . SbF$_5^-$) by bonding of S^{IV} to C-5.†



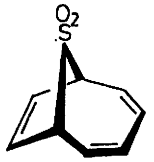
(**1**)



(**2**)



(**3**)



(**4**)

Addition of freshly distilled cyclo-octatetraene to SbF$_5$ (1 equiv.) in liquid SO$_2$ at −70° for 2·5 h, followed by removal of solvent *in vacuo* below −40°, addition of cold (−30°) CH$_2$Cl$_2$, and hydrolysis by pouring into rapidly stirred hydrogen carbonate solution affords a mixture of sulphones (**3**) and (**4**) (60—85%). Chromatography on silica gel gives pure (**3**), m.p. 166—166·5°, in yields up to 12% [ν_{max} (CHCl$_3$) 1306, 1286, and 1121 cm^{-1}; δ (40°; CDCl$_3$) 5·96 (2H), 4·48 (4H), and 3·33 (2H); three pseudotriplets]. As the signal shapes and multiplicities are anallogous to those for related compounds,[4,5] this sulphone is also in a state of rapid flux. Its vapour-phase pyrolysis at 240° (contact time 1—2 s) results in exclusive conversion into cyclo-octatetraene.

Low-temperature ^{1}H n.m.r. studies show that both (**3**) and (**4**) at −50° in SO$_2$ containing SbF$_5$ (2·5 equiv.) can be converted into [**1**; X = S(O . . . SbF$_5$)OSbF$_5^-$]. When such solutions were neutralized as above but without careful control of conditions, the bicyclic sulphone (**4**) was readily isolated but only trace amounts of (**3**) were found. The formation of (**4**) is thermodynamically favoured and the ease with which (**3**) is isomerized to (**4**) under these conditions may explain the earlier inability of Gasteiger and Huisgen[3d] to isolate (**3**).

We thank the National Science Foundation for financial support.

(*Received*, 3*rd December* 1974; *Com.* 1464.)

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† Direct closure of (**1**) with concomitant cyclopropyl C–C and C–S bond formation cannot be dismissed; the prevailing electron densities at C-2, C-4, and C-5 in monohomotropylium cations appear to be quite similar.[6]

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