Homo-cheleotropic Addition of Sulphur Dioxide to Norbornadiene

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Sulphur dioxide adds in a cheleotropic way to norbornadiene giving 4-thiatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane 4,4-dioxide, while non-cycloaddition products are obtained with other homo-conjugated dienes.

Three-centred (cheleotropic) and four-centred addition modes of SO_2 to conjugated[1] or cumulated[2] double bonds have been reported and we have recently proposed[3] two such addition modes of SO_2 to the strained σ-system of quadricyclane. Since norbornadiene and some other homo-conjugated dienes are known to undergo homo-addition to a number of dieno-philes,[4-6] we have examined the reactivity toward SO_2 of cyclohexa-1,4-diene (1), hexamethylDewarbenzene (2), norbornadiene (3), and bicyclo[2.2.2]octa-2,5-diene (4), which differ in the number of bonds (from 0 to 3) connecting the sp^3 carbon atoms.

The reactions were carried out in liquid SO_2 at room or higher temperature and were followed by n.m.r. spectroscopy; *ca.* 0.5 ml of SO_2 was condensed in a n.m.r. tube containing the sample (*ca.* 0.5 mmol) and the tube was then sealed.

Cyclohexa-1,4-diene (1) underwent the previously reported oxidative aromatization to benzene,[7] the conversion being complete after *ca.* 30 days at room temperature. Compound (2) has been reported to be inert to SO_2,[8] but complete conversion into hexamethylbenzene was achieved in 3 days. This valence isomerization of (2) has been observed previously with Lewis acids,[9] and SO_2 may act as a Lewis acid catalyst in this case. Bicyclo-octadiene (4)† is inert to SO_2 at room

(1)   (2)   (3)   (4)

(5)
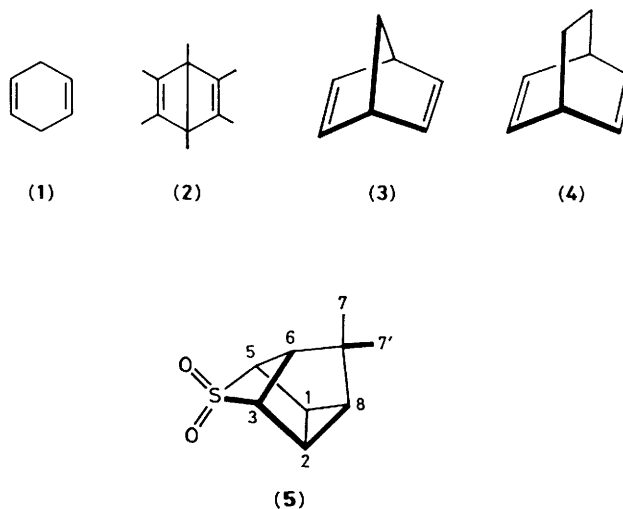
temperature over a long period of time. At 70 °C extensive polymerization and some thermal decomposition to benzene and ethylene are observed[10] in *ca.* 5 days.

Norbornadiene (3) seems to be the only homo-conjugated system so far that is capable of addition to SO_2; it is totally converted (in *ca.* 36 h at room temp.) into 4-thiatetracyclo-[3.3.0.0^{2,8}.0^{3,6}]octane 4,4-dioxide (5), which was identified by

† Prepared according to O. De Lucchi and G. Modena, *J. Chem. Soc., Chem. Commun.*, 1982, 914.

complete analysis of its n.m.r. spectrum‡ and by comparison with data reported in the literature.[11] Compound (5) can be obtained on a preparative scale by carrying out the reaction in a sealed thick-walled flask. The concentration of (3) in SO_2 is critical: with excessive concentration non-characterizable polymer material is also formed. The sulphone (5) can be recovered by evaporation of the solvent at 1 atm followed by sublimation at low pressure as white crystals, m.p. 136—137 °C (lit.[11] 135 °C); the yield is almost quantitative for low concentrations of (3) (<5%, v/v).

The sulphone (5) results from a cheletropic homo-addition of SO_2 to (3), which is an allowed $[_{\pi}2_s + _{\pi}2_s + _{\omega}2_s]$ process, and in principle one would expect the same type of addition also with (1), (2), and (4). The reactions of (1)—(4) with tetra-cyanoethylene (TCNE) may be compared with those with SO_2. The dienes (3)[4a] and (4)[6] give concerted homo-Diels–Alder additions, (3) being ca. 60 times more reactive than (4).[6] On the other hand, addition of TCNE to (2) is postulated to occur with an ionic mechanism.[12] Cyclohexa-1,4-diene (1) is again dehydrogenated to benzene.[5]

The lack of Diels–Alder reactivity of (1) and (2) and the lower reactivity of (4) in comparison with (3) have been traced back[6] to the distance between the double bonds, which increases in the order (3) < (4) << (2) and (1). Alternatively, a frontier orbital approach has been proposed.[5] From simple perturbation theory, the reactivity should decrease with increasing energy gap between the LUMO of SO_2 (which has b_1 symmetry)[13] and the highest orbital in the diene with proper symmetry. It has been shown that the highest b_2 orbital is the HOMO in (3) and (4), the orbital energy of (3) being greater than that of (4), but only the SHOMO in (1).[14] In (2) the distance between the double bonds should be more critical than the energy of the b_2 orbital, which is reported to be rather high.[15]

Thus consideration of the energy of the highest b_2 orbital and of the distance between the double bonds may explain why homo-cheletropic addition of SO_2 is observed with norbornadiene only; with the other dienes other modes of conversion take over.

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‡ ^{1}H N.m.r. (200 MHz, $CDCl_3$) δ 1.93 (2nd order m, $^3J_{1,2}$ 2.25; $^4J_{1,3}$ and $^4J_{2,5}$ 0.2; $^3J_{1,5}$ and $^3J_{2,3}$ 2.05; $^4J_{1,6}$ and $^4J_{2,6}$ 0.8; $^4J_{1,7}$, $^4J_{1,7'}$, $^4J_{2,7}$, and $^4J_{2,7'}$ 0.0; $^3J_{1,8}$ and $^3J_{2,8}$ 4.45 Hz, 1- and 2-H), 3.94 (2nd order m, $^4J_{3,5}$ 2.55; $^3J_{3,6}$ and $^3J_{5,6}$ 2.95; $^4J_{3,7}$ and $^4J_{5,7'}$ 0.8; $^4J_{3,7'}$ and $^4J_{5,7}$ 0.0; $^4J_{3,8}$ and $^4J_{5,8}$ 0.25 Hz, 3- and 5-H), 2.79 (tt quart., $^3J_{6,7}$ and $^3J_{6,7'}$ 1.45; $^4J_{6,8}$ 1.3 Hz, 6-H), 1.70 (apparent tt, $^2J_{7,7'}$ non-determinable; $^3J_{7,8}$ and $^3J_{7',8}$ 1.4 Hz, 7- and 7'-H), and 2.19 (br. t quart., 8-H).