Homo-cheleotropic Addition of Sulphur Dioxide to Norbornadiene

Ottorino De Lucchi and Vittorio Lucchini*

Centro Meccanismi di Reazioni Organiche del CNR, Universitá di Padova, Via Marzolo 1, 35100 Padova, Italy

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 conjugated¹ or cumulated² double bonds have been reported and we have recently proposed³ 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 dienophiles,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 sp³ 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



temperature over a long period of time. At 70 °C extensive polymerization and some thermal decomposition to benzene and ethylene are observed¹⁰ 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 SO₂ 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 cheleotropic homo-addition of SO₂ 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 tetracyanoethylene (TCNE) may be compared with those with SO₂. 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 back⁶ 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 SO₂ (which has b₁ symmetry)¹³ and the highest orbital in the diene with proper symmetry. It has been shown that the highest b₂ 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 b₂ 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-cheleotropic 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, CDCl₃) δ 1.93 (2nd order m, ${}^{3}J_{1.2}$ 2.25; ⁴J_{1.3} and ⁴J_{2.5} 0.2; ${}^{3}J_{1.5}$ and ${}^{3}J_{2.3}$ 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; ${}^{3}J_{1.8}$ and ${}^{3}J_{2.8}$ 4.45 Hz, 1- and 2-H), 3.94 (2nd order m, ${}^{4}J_{3.7}$ 2.55; ${}^{3}J_{3.6}$ and ${}^{3}J_{5.6}$ 2.95; ${}^{4}J_{3.7}$ and ${}^{4}J_{5.7}$ 0.8; ⁴J_{3.7}, and ⁴J_{5.7} 0.0; ${}^{4}J_{3.8}$ and ${}^{4}J_{5.8}$ 0.25 Hz, 3- and 5-H), 2.79 (tt quart., ${}^{3}J_{6.7}$ and ${}^{3}J_{6.7}$ (1.45; ${}^{4}J_{6.8}$ 1.3 Hz, 6-H), 1.70 (apparent tt, ²J_{7.7}, non-determinable; ${}^{3}J_{7.8}$ and ${}^{3}J_{7.8}$ 1.4 Hz, 7- and 7'-H), and 2.19 (br. t quart., 8-H).