Reactions of Quadricyclane with Sulphur Dioxide: Formation of a Stable β-Sultine and Catalysed Isomerization to Norbornadiene

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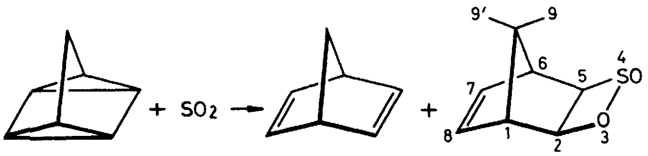
Sulphur dioxide, as solvent or in chloroform, catalyses the isomerization of quadricyclane (**1**) to norbornadiene and cycloadds to (**1**) to afford *exo*-3-oxa-4-thiatricyclo[4.2.1.$0^{2,5}$]non-7-ene 4-oxide (**3**); in the presence of a deficiency of sulphur dioxide, (**3**) is remarkably stable in solution, but decomposes rapidly as pure product.

Quadricyclane has long been recognized as being unique in cycloaddition reactions[1–3] because of its ability to cycloadd in a $[_{\sigma}2 + _{\sigma}2 + _{\pi}2]$ way.[4] In connection with our studies on the reactivity of a number of different substrates towards sulphur dioxide,[5] we have investigated quadricyclane and now report our preliminary results.

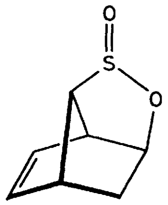
The ^{1}H n.m.r. spectrum of a solution of quadricylane (**1**) in liquid sulphur dioxide, immediately recorded at −60 °C, does not show any signal attributable to the reagent. Instead, the peaks of the valence tautomer norbornadiene (**2**) are easily recognized, together with a set of eight multiplets with unit integrated ratio. The same pattern, but for negligible chemical shift differences, is observed when quadricyclane is treated with an excess of sulphur dioxide in $CDCl_3$ at −30 °C. At room temperature however, rapid decomposition follows. With a deficiency of sulphur dioxide, on the other hand, the above described resonances, together with the signals of quadricyclane and norbornadiene, remain unaltered at room temperature for at least one week. The integrated ratio of the norbornadiene signals to the eight multiplets is 1 : 1.2 and is roughly independent of the experimental conditions.

Rapid rotoevaporation of the reaction mixture (*ca.* 0 °C, 15 Torr) affords an oily material which consists almost exclusively of the new substance, with residual impurities due to quadricyclane, as shown by n.m.r. spectroscopy. Prolonged rotoevaporation brings about decomposition with formation of an uncharacterizable solid polymer.

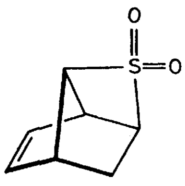
The spectral data of the new product are consistent with the β-sultinic structure of *exo*-3-oxa-4-thiatricyclo[4.2.1.$0^{2,5}$]non-7-ene 4-oxide (**3**). ^{1}H N.m.r. ($CDCl_3$ at room temp.): δ 6.23 (br.dd, $^{3}J_{7,8}$ 5.7, $^{3}J_{1,8}$ 2.9, $^{4}J_{8,9}$ *ca.* 0.5 Hz, 8-H), 5.95 (br.dd, $^{3}J_{6,7}$ 3.1, $^{4}J_{7,9}$ *ca.* 0.5 Hz, 7-H), 4.66 (dt, $^{3}J_{2,5}$ 4.7, $^{3}J_{1,2}$ 1.4, $^{4}J_{2,9'}$ 1.4 Hz, 2-H), 3.44 (dt, $^{3}J_{5,6}$ 1.5, $^{4}J_{5,9'}$ 1.4 Hz, 5-H), 3.32 (d quart., $^{3}J_{1,9}$ and $^{3}J_{1,9'}$ 1.4 Hz, 1-H), 3.16 (d quart., $^{3}J_{6,9}$ and $^{3}J_{6,9'}$ 1.5 Hz, 6-H), 2.79 (br. dt, $^{2}J_{9,9'}$ 10.0 Hz, 9-H), and 1.66 (d quint. 9′-H). ^{13}C N.m.r. ($CDCl_3$ at room temp.): δ 138.3 (d, *J* 172.1 Hz, C-8), 133.3 (d, *J* 171.7 Hz, 7-C), 77.5 (d, *J* 169.8 Hz, 2-C), 60.3 (d, *J* 162.1 Hz, 5-C), 46.3 (d, *J* 163.0 Hz,



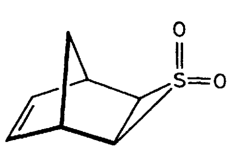
(**1**) (**2**) (**3**)



(**4**)



(**5**)



(**6**)

1-C), 42.6 (t, J 137.3 Hz, 9-C), and 41.4 p.p.m. (d, J 157.0 Hz, 6-C). I.r. (CCl_4): ν (cm^{-1}) 3075, 2990, 2880, 1325, 1185, 1165, and 1150.

Besides the β-sultine (**3**), two other isomeric addition products, the γ-sultine (**4**) and the sulphone (**5**), may give non-symmetric n.m.r. resonance patterns. Of particular significance for the assignment of the spectrum to the β-sultine (**3**) is the coupling constant (4.7 Hz) between the protons resonating at δ 4.66 and 3.44, which is typical for *endo–endo* vicinal coupling in norbornenes. The multiplets show further splittings (1.4 Hz) due to couplings with the resonances at δ 3.32 (or 3.16) and 1.66 (as shown by double-irradiation experiments); constants of this magnitude are predictable for the coupling with the vicinal bridgehead proton in norbornenes and for the long range coupling (W) with the *anti*-methylenic proton.† No skeletal fragment of compounds (**4**) and (**5**) can account for such a resonance pattern.

The i.r. spectrum shows a swallow-tailed band appearing at 1165 and 1150 cm^{-1}, which may be attributed to the SO stretching. The absorption frequency agrees with that reported for another stable β-sultine.[6]

Unfortunately, the relative instability of the β-sultine (**3**) in the pure state did not allow elemental analysis and physical data to be obtained.

The formation of the β-sultine (**3**) and the isomerization to norbornadiene (**2**) may be rationalized by considering different approaches of sulphur dioxide to quadricyclane (**1**). For the formation of a β-sultine the usual $[{}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s]$ addition mechanism of a π-dienophile to quadricyclane can be proposed, in which sulphur dioxide uses its S–O π-bond. The isomerization to norbornadiene can be explained by a linear $[{}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\omega}2_s]$ cheleotropic addition of sulphur dioxide and formation of the unstable oxide (**6**). This intermediate can subsequently dissociate to norbornadiene by a non-linear $[{}_{\pi}2_s + {}_{\omega}2_a]$ mechanism.[7]‡ As we could not detect the intermediate (**6**), even when the reaction was carried out in chloroform at −60 °C and monitored at the same temperature by n.m.r. spectroscopy, the proposed mechanism is so far only speculative.

The reactions here reported are, to the best of our knowledge, the first examples of sulphur dioxide reaction with strained σ bonds.[8] The remarkable stability of the polycyclic β-sultine (**3**) should also be noted. Other β-sultines are less stable[9] and have been isolated at room temperature only as fully substituted compounds.[6,10]

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† The noticeable deshielding of the 9-H methylenic proton in comparison with the geminal 9′-proton (1.13 p.p.m.) is to be attributed, rather than to the diamagnetic anisotropy of the double bond (which effect is never greater than 0.3 p.p.m.: A. P. Marchand and J. E. Rose, *J. Am. Chem. Soc.*, 1968, **90**, 3724, and papers cited therein), to the proximity of 9-H to the sulphinylic oxygen (*cf.* bridgehead proton chemical shifts in *endo*- and *exo*-4-thiatetracyclo$[3.3.0.0^{2,8}.0^{3,6}]$octane 4-oxide: D. J. H. Smith, J. D. Finlay, and C. R. Hall, *J. Org. Chem.*, 1979, **44**, 4757). Therefore (**3**) should be in the *exo*-oxide configuration.

‡ The non-reversible extrusion of sulphur dioxide from episulphones is well documented: W. L. Mock, *J. Am. Chem. Soc.*, 1975, **97**, 3666 and 3673.