Small Ring-annelated Non-benzenoid Aromatic Compounds: 1,2-Dihydrocyclobuta[*e*]tropolone

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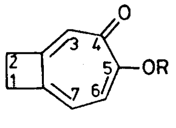
Summary 1,2-Dihydrocyclobuta[*e*]tropolone, formed by ring-enlargement of benzocyclobutene-4,5-quinone with diazomethane, exists in tautomeric equilibrium almost exclusively as one tautomer; the methyl ethers formed on methylation correspond to a 1 : 1 mixture of the two tropolone tautomers.

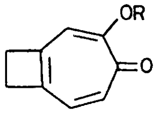
Benzocyclobutene[1] and benzocyclopropene[2,3] have been synthesised in order to study how small ring annelation will affect the aromaticity of the benzene ring. However, non-benzenoid aromatic compounds fused with a small ring seem to be more suitable for such a study.[4] We now report the synthesis and some properties of 1,2-dihydrocyclobuta-[*e*]tropolone (**1**).

The quinone (**2**)[5] was treated with an excess of diazomethane in the presence of boron trifluoride–diethyl ether to give (**3**), m.p. 85—86 °C, and the boron difluoride chelate (**4**), m.p. 152—154 °C, of (**1**). In the absence of boron trifluoride this ring-enlargement reaction gave no isolable crystalline product. The chelate (**4**) was hydrolysed in acidic aqueous ethanol to give (**1**), m.p. 113—114 °C, in moderate yield, which showed spectral properties characteristic of tropolone: ν (KBr), 1604 and 1513 cm^{-1}, δ ($CDCl_3$) 3·10 (s, CH_2CH_2), 7·00 (br. d, $J_{6,7}$ 9·8 Hz, 7-H), 7·17 (t, $J_{2,3}$ 0·7 Hz, 3-H), 7·29 (d, $J_{6,7}$ 9·8 Hz, 6-H), and 8·9 (br. s, OH). Compound (**1**) could not be extracted from chloroform solution with $NaHCO_3$ in contrast to tropolone but it was extracted with aqueous sodium carbonate; it gave a deep-red coloration in the chloroform layer with aqueous ferric chloride. Compound (**1**) was methylated with diazomethane to give an unseparable 1 : 1 mixture of the methyl ethers (**5a**) and (**5b**) (7 days, 75%). N.m.r. analysis of the mixture showed $J_{6,7}$ 10·0 Hz for (**5a**) and $J_{6,7}$ 11·8 Hz for (**5b**).

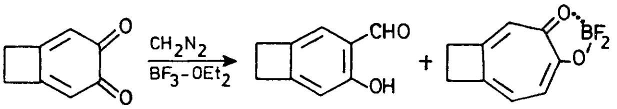
The n.m.r. signals of the seven-membered ring protons of (**1**) are simpler than those of tropolone,[6] and the $J_{6,7}$ value of 9·8 Hz for (**1**) is not only smaller than the corresponding $J_{3,4}$ value of 10·9 Hz in tropolone, in which tautomerism is possible, but is also smaller than the $J_{3,4}$ value of 10·1 Hz in tropolone methyl ether in which tautomerism is not possible. If (**1**) exists in fast reversible equilibrium between the tautomers (**1a**) and (**1b**), $J_{6,7}$ for (**1**) should be an average (10·9 Hz) of the corresponding values for (**5a**) and (**5b**).[6] The fact that $J_{6,7}$ for (**1**) is similar to the value for (**5a**) suggests that (**1**) is largely present as the single tautomer (**1a**). This is consistent with the lower acidity of (**1**) compared with tropolone. Compound (**1**), like tropolone, formed the corresponding dihydroxytropylium ion on dissolution in trifluoroacetic acid, the n.m.r. spectra of which showed a shift to low field (Δδ 0·95—1·06 p.p.m.) for the seven-membered ring protons which is similar to that (Δδ ca. 1·0 p.p.m.) observed on protonation of tropolone; the $J_{6,7}$ value of 10·2 Hz for the dihydroxytropylium ion formed from (**1**) is almost identical with an average of the values for $J_{2,3}$ (11·5 Hz) and $J_{3,4}$ (9·1 Hz) for the hydroxytropylium ion.[6]



(1a) R = H
(5a) R = Me



(1b) R = H
(5b) R = Me



(2) (3) (4)

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