A New Aromatic System

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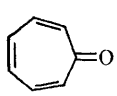
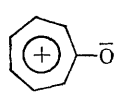
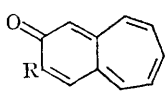
IT is well authenticated[1] that the charged structure (Ib) makes a significant contribution to the resonance hybrid of tropone (I). The synthesis of a ten-electron system (II; R = H) in which the average charge separation in (IIb) is increased to about 5·2 Å (compared with about 2·5 Å in tropone) has recently been reported:[2] the evidence available at present indicates that the parent molecule (II; R = H) is only stable in solution.



(Ia)



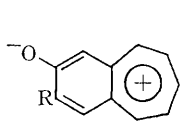
(Ib)



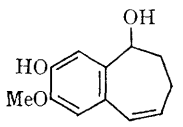
(IIa)

We therefore undertook the synthesis of (II; R = OMe) in an attempt to stabilise the system.

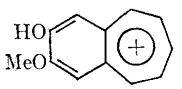
Accordingly 4′-hydroxy-5-methoxy-1,2-benzocyclohepta-1,6-dien-3-ol (III)* was heated for a few minutes with trityl fluoroborate in acetic acid to yield the tropylium salt (IV) as pale yellow crystals m.p. 160° (d).



(IIb)



(III)



(IV)

Treatment of the tropylium salt (IV) with mild bases[3] brought about an immediate deprotonation reaction resulting in a colour change from yellow to red. Rapid chromatography on neutral alumina followed by crystallisation from benzene–petroleum gave dark red hexagonal plates m.p. 142°. All the evidence available on this red material is compatible with structure (II; R = OMe). The infrared spectrum has no hydroxyl stretching absorption but shows two intense peaks at 1616 and 1575 cm.$^{-1}$. The visible and ultraviolet spectrum contains several strong and characteristic bands: *viz.*, λ_{max} 220, 267, 302, 347, 418, (infl) 434, and 494 mμ (log ϵ respectively 4·1, 4·4, 4·3, 4·2, 3·6, 3·6, and 3·6). Measurements on a benzene solution of (II; R = OMe) (vapour-pressure osmometer) showed that it was a monomer and this was confirmed by mass spectroscopy[4] which revealed a parent ion of *m/e* 186: the cracking pattern (which will be reported elsewhere) could also be accommodated by the proposed structure.

Finally the n.m.r. spectrum (in $CDCl_3$) showed a signal (area 3) at τ 6·0 (methoxyl) and a band (area 7) from τ 2·0 to 3·1 (ring protons): in so far as the latter signal indicates that the whole nucleus can sustain an induced ring current,[5] this new system is to be regarded as aromatic. The chemical reactivity of the system (II) and related products is currently being investigated.

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* Satisfactory analytical and spectral data were obtained for all new compounds.

[1] W. Baker and J. F. W. McOmie, *Progr. Org. Chem.*, 1955, **3**, 64.
[2] A. M. Khan, G. R. Proctor, and L. Rees, *J. Chem. Soc.* (*C*), 1966, 990.
[3] H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 4659.
[4] We cordially thank Mr. F. Preston (Glasgow University) for this measurement.
[5] J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 1961, 859.