A Re-investigation of the Structure of a Putative Dibenzo[*a*,*e*]cyclo-octenetrione

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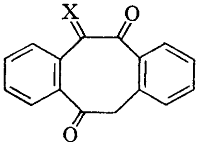
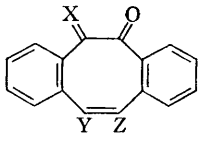
CONSIDERABLE interest attaches to the synthesis of cyclo-octatetraenoquinones because of their potential aromaticity.[1,2] Many years ago Wawzonek[3] reported the preparation of an orange compound, m.p. 254—256°, which he considered was probably dibenzo[*a*,*e*]cyclo-octene-5,6,11-trione (I) and which has subsequently become enshrined in the chemical literature as such.[1,4] A compound of structure (I) would be converted by enolization into the dibenzocyclo-octatetraenoquinone derivative (II). Our re-investigation of Wawzonek's compound has, however, led to the revision of the structure he provisionally assigned to it.

This compound was prepared by Wawzonek from dibenzo[*a*,*e*]cyclo-octene-5,12-dione (III) by its conversion into the enol acetate (IV), bromination of this in acetic acid to give a compound, $C_{18}H_{13}O_3Br$, assigned structure (V); further treatment of this compound with bromine in chloroform to give a product which was not obtained in a pure state, and reaction of this in refluxing aqueous-ethanolic ammonia followed by sublimation.

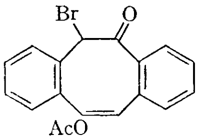


(I) X=O
(II) X=H_2

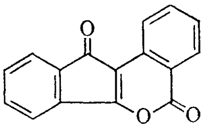


(II) X=O, Y=OH, Z=H
(IV) X=H_2, Y=OAc, Z=H
(V) X=H_2, Y=OAc, Z=Br
(VIII) X=O, Y=Z=H

In the present work, the dione (III) was prepared by an improved method involving treatment of 5,11-dibromo-5,6,11,12-tetrahydrodibenzo[*a,e*]-cyclo-octene[5] with dimethyl sulphoxide and collidine.[6] This was converted into the enol acetate (IV), plates, m.p. 137—138° (lit.[3] m.p. 138—139°), $\lambda_{max}(CCl_4)$ 5·66, 5·96, 8·34, 8·41 (sh) μ, δ $(CDCl_3)$ 2·17 (s, 3H), 4·0—5·0 (m, 2H),† 6·82 (s, 1H), 7·0—7·6 (m, 7H), 8·1—8·3 (m, 1H) p.p.m. Bromination of this compound in acetic acid yielded prisms, $C_{18}H_{13}O_3Br$, m.p. 229—229·5° (lit.[3] m.p. 219—223°), to which the revised structure (VI) is assigned on the basis of spectroscopic data [λ_{max} (CCl_4) 5·64, 5·90, 8·36, 8·50 μ, δ $(CDCl_3)$ 2·23 (s, 3H), 7·00 (s, 2H),‡ 7·2—7·6 (m, 6H), 7·7—8·0 (m, 1H), 8·3—8·5 (m, 1H) p.p.m.] and its reduction by zinc and acetic acid to (IV). Bromination of (VI) in chloroform gave microprisms, $C_{16}H_{10}O_2Br_4$, m.p. 205—206·5° dec., λ_{max}(Nujol) 2·95 (w), 8·24, 9·87, 10·11 μ, δ $(CDCl_3)$ 4·71 [s, 1H(OH)], 5·66 (s, 1H), 7·2—7·7 (m, 6H), 7·7—8·2 (m, 2H) p.p.m., which apparently correspond to the impure further bromination product, m.p. 173—178°, previously isolated.[3]



(VI)



(VII)

Treatment of the tetrabromo-compound with ethanolic aqueous ammonia followed by sublimation of the crude product, gave orange needles, m.p. 254·5—255°, corresponding to the compound previously assigned structure (I). Infrared spectroscopy and thin-layer chromatography demonstrated that this compound was not present in the crude product from the reaction of the tetrabromo-compound with ammonia, but was formed only after sublimation. Mass spectrometry showed that the orange compound has the formula $C_{16}H_8O_3$ (molecular ion: *m/e* 248), rather than the formula $C_{16}H_{10}O_3$ originally assigned. Its spectra, λ_{max} (CCl_4) 5·69, 5·80 (m), 5·84, 6·13 (m) μ, δ $(CDCl_3)$ 7·3—7·9 (m, 6H), 8·2—8·5 (m, 2H) p.p.m., and origin suggested that it was the indone derivative (VII). This structural assignment was confirmed by direct comparison (t.l.c., infrared spectra, and mixed m.p., 255—256°) with an authentic sample of (VII), m.p. 255·5—256·5° (lit. 257°), prepared by the method of Pailer, Wörther, and Meller.[7]

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† At 0° these protons gave rise to an AB system, $J = 12{\cdot}5$ c./sec.

‡ Spectra taken in trifluoroacetic acid or dimethyl sulphoxide, or at 100 Mc./sec., showed this two-proton signal to be due to superimposed one-proton singlets.

[1] D. McIntyre, G. R. Proctor, and L. Rees, *J. Chem. Soc.* (*C*), 1966, 985.
[2] For a more jaundiced view of such endeavours, see: M. J. S. Dewar, *Tetrahedron*, 1966, **Suppl. 8**, 75.
[3] S. Wawzonek, *J. Amer. Chem. Soc.*, 1940, **62**, 745.
[4] L. E. Craig, *Chem. Rev.*, 1951, **49**, 103
[5] A. C. Cope and S. W. Fenton, *J. Ame.r. Chem. Soc.*, 1951, **73**, 1668.
[6] *Cf.*, D. N. Jones and M. A. Saeed, *J. Chem. Soc.*, 1963, 4657.
[7] M. Pailer, H. Wörther, and A. Meller, *Monatsh.*, 1961, **92**, 1037; It may be noted that the synthesis of the cyclooctatetraenenoquinone (VIII) has recently been reported: V. I. Bendall and J. F. Neumer, Abstracts of Papers Presented at the 153rd Meeting, American Chemical Society, Miami Beach, Florida, April, 1967, 088.