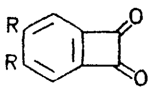
Synthesis of 4,5-Dihydroxybenzocyclobutene-1,2-dione (a Benzologue of Squaric Acid) and a General Synthesis of Benzocyclobutene-1,2-diones

By John F. W. McOmie* and David H. Perry

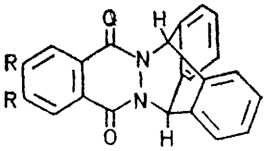
(*The School of Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary 4,5-Dihydroxybenzocyclobutene-1,2-dione has been prepared by demethylation of its dimethyl ether which was made by vapour-phase pyrolysis of the anthracene adduct of 6,7-dimethoxyphthalazine-1,4-dione; other benzocyclobutene-1,2-diones have been made in 71—98% yield by this pyrolysis method.

BENZOCYCLOBUTENE-1,2-DIONE (**1**; R = H) has been prepared from 1,2-dibromobenzocyclobutene *via* the 1,2-dinitrate[1] and *via* the 1,1,2,2-tetrabromide.[1] It has also been made by the vapour-phase pyrolysis of indanetrione,[2] of the Diels–Alder adducts of phthalazine-1,4-dione with cyclopentadiene[3] and with indene,[3] and also by similar pyrolysis of *SS*-dimethyl- (and -diphenyl)-*N*-phthalimidosulphoximide.[4] Our attempts to use these routes for the synthesis of 4,5-dimethoxybenzocyclobutenedione were unsuccessful except for the pyrolysis of the cyclopentadiene adduct of 6,7-dimethoxyphthalazine-1,4-dione which gave the desired compound (**1**; R = OMe) in 12% yield. However, when the anthracene adduct (**2**; R = OMe) was pyrolysed by passing its vapour through a silica tube (35 × 1 cm) at 450° and 0·01 mmHg it gave a 98% yield of the dione (**1**; R = OMe) as almost colourless needles, m.p. 222—223°. Demethylation of the latter with 48% hydrobromic acid gave the pale yellow dihydroxy-compound (**1**; R = OH) (44%), m.p. 243—245° (decomp.), which is a benzologue of squaric acid. It gives with alcoholic FeCl$_3$ a deep green colour, typical of catechols.



(1)



(2)

Compound (**1**; R = OH) is a relatively strong acid (pK_1 4·48, pK_2 8·05) although, rather surprisingly, it is weaker than the dibenzologue of squaric acid, namely 6,7-dihydroxybiphenylene-2,3-quinone (pK_1 4·21, pK_2 6·70).[5] Compound (**1**; R = OH) is stable to alkali: it can be recovered unchanged after 24 h at pH 10, whereas benzocyclobutenedione itself is cleaved readily at room temperature by 5% aqueous methanolic sodium hydroxide to give the sodium salt of phthalaldehydic aicd in 94% yield.[1]

We have found that the pyrolysis of anthracene adducts of type (**2**) of appropriately substituted phthalazine-1,4-diones gives 75—98% yields of benzocyclobutene-1,2-dione itself and of the following derivatives: 4-chloro, 4-methoxy, 3,6-dichloro, 4,5-dichloro, 4,5-dibromo, and 4,5-dimethyl. Similarly naphtho[*b*]cyclobutene-1,2-dione can be made in 71% yield.

Many substituted phthalic anhydrides are readily available and since they are easily converted into the corresponding 2,3-dihydrophthalazine-1,4-diones (cyclic hydrazides), and thence into adducts of type (**2**) by oxidation with lead tetra-acetate in the presence of anthracene, the above method constitutes a convenient synthesis of benzocyclobutenediones. Hitherto, only two substituted benzocyclobutenediones have been prepared, namely 3,8-diphenyl naphtho[*b*]cyclobutene-1,2-dione[6] and 3,4,5,6-tetrachlorobenzocyclobutenedione.[7]

We thank Dr. D. D. Perrin (John Curtin School of Medical Research, Australian National University, Canberra) for the spectrometric determination of the pK values.

(*Received*, 1*st February* 1973; *Com.* 136.)

---

[1] M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, 1963, **85**, 2076.

[2] R. F. C. Brown and R. K. Solly, *Austral. J. Chem.*, 1966, **19**, 1045.

[3] D. L. Forster, T. L. Gilchrist, C. W. Rees, and E. Stanton, *Chem. Comm.*, 1971, 695.

[4] D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, *J.C.S. Chem. Comm.*, 1972, 1317.

[5] J. F. W. McOmie and D. E. West, *J. Chem. Soc.* (*C*), 1969, 2579.

[6] M. P. Cava and B. Hwang, *Tetrahedron Letters*, 1965, 2297.

[7] A. Roedig, G. Bonse, R. Helm, and R. Kohlhaupt, *Chem. Ber.*, 1971, **104**, 3378.