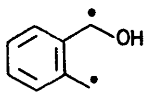
Cycloaddition Reactions of a Hydroxy-*o*-quinone Dimethide

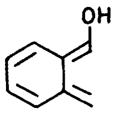
By B. J. Arnold and P. G. Sammes*
(*Chemistry Department, Imperial College, London* SW7 2AY)

Summary The (*E*)-dienol, hydroxy-*o*-quinone dimethide (**2**), formed preferentially by heating benzocyclobutenol, readily undergoes $({}_4\pi_s + {}_2\pi_s)$ cycloadditions and has been used as an entry into tetracyclic systems of the naphthacene series.

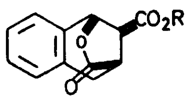
The stereospecific reaction between the photoenol from *o*-methylbenzaldehyde and maleic anhydride was recently described.[1] We now report an analogous thermal reaction. In the absence of dienophiles, the photolysis of aromatic ketones bearing *ortho*-alkyl groups often produces benzocyclobutenols.[2] Thus direct photolysis of *o*-methylbenzaldehyde in dilute solutions produces small amounts of benzocyclobutenol.[3] The benzocyclobutenol can arise either by collapse of the diradical (**1**), formed from *o*-methylbenzaldehyde by intramolecular hydrogen abstraction, or by electrocyclic rearrangement of the ground-state dienol (**2**).[4] Heating the benzocyclobutenols reconverts them into the starting carbonyl compounds[2] and this must proceed *via* a dienol, *e.g.* (**2**). Thus, in the absence of a dienophile, benzocyclobutenol reverts to *o*-methylbenzaldehyde by heating at 110° for 5 h. This conversion was not due to a base-catalysed process[5] (*e.g.*, at the walls of the reaction vessel) since, in the presence of maleic anhydride, very little *o*-methylbenzaldehyde was formed and the adduct (**3**) (84%) was isolated, identified as its methyl ester (**4**), m.p.



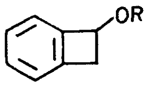
(1)



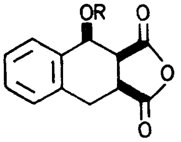
(2)



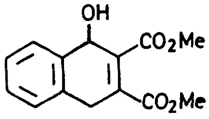
(3) R = H
(4) R = Me



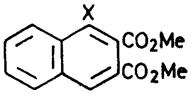
(6) R = Me
(7) R = Ac



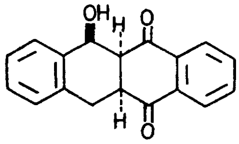
(5) R = H
(8) R = Me
(9) R = Ac



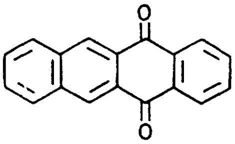
(10)



(11) X = H
(12) X = OH



(13)



(14)

90—91°. The ester (**4**) was identical to that produced by methylation of the lactone (**3**) also formed by heating the hydroxy-anhydride (**5**), itself obtained by irradiation of *o*-methylbenzaldehyde in the presence of maleic anhydride.[1] This result implies that benzocyclobutenol opens preferentially to the (*E*)-dienol (**2**) *via* a conrotatory process.[4]

The formation of (*E*)-dienol intermediates during photoenolisation has considerable precedent,[1,6] even though internal hydrogen abstraction must occur from a *cis*-configuration. It has been suggested that the initial intermediates [*e.g.*, (**1**)] can collapse to a vibrationally hot cyclobutenol, which can then open in a conrotatory mode to give the (*E*)-dienol.[7] The above result supports such a mechanism.

The methyl ether (**6**) and acetate (**7**) also reacted with maleic anhydride to give the corresponding anhydrides (**8**),† m.p. 134—135°, and (**9**), m.p. 128—131°, respectively, both shown to have the all-*cis* configuration by ^{1}H n.m.r. spectroscopy.

Thus reactive dienols, which were formerly obtained by photoenolisation, are now available thermally. Such intermediates are of wide synthetic utility.[8] For example, benzocyclobutenol and dimethyl acetylenedicarboxylate gave the unstable adduct (**10**), m.p. 114—115°, which could either be dehydrated to the substituted naphthalene (**11**),[9] m.p. 47° (80%), or oxidized by manganese dioxide to the naphthol (**12**), m.p. 145° (decomp.).‡ The reaction between benzocyclobutenol and 1,4-naphthoquinone in benzene under reflux gave the tetracyclic naphthacene derivative (**13**) directly and stereospecifically. This hydroxy-dione (yield 75%), m.p. 285°, could be dehydrated and then oxidized with manganese dioxide to give the known naphthacene-5,12-dione (**14**).[10] The comparable photoaddition, between naphthoquinone and *o*-methylbenzaldehyde gave complex mixtures.

We thank the S.R.C. for a research studentship (to B.J.A.).

(*Received, October 29th,* 1971; *Com.* 1883.)

---

† All new compounds gave satisfactory microanalytical and spectral data.

‡ We thank Dr. Susan Mellows for performing this reaction.

[1] S. M. Mellows and P. G. Sammes, *Chem. Comm.*, 1971, 21.

[2] T. Matsuura and Y. Kitaura, *Tetrahedron Letters*, 1967, 3309; H. G. Heine, *Annalen*, 1970, **732**, 165; Y. Kitaura and T. Matsuura, *Tetrahedron*, 1971, **27**, 1597.

[3] M. P. Cava and K. Muth, *J. Amer. Chem. Soc.*, 1960, **82**, 652; H. H. Wasserman and J. Solodar, *ibid.*, 1965, **87**, 4002.

[4] R. B. Woodward and R. Hoffman, *J. Amer. Chem. Soc.*, 1965, **87**, 395.

[5] *cf.* Ref. 3; L. Horner, P. V. Subramaniam, and K. Eiben, *Annalen*, 1968, **714**, 91.

[6] F. Nerdel and W. Brodowski, *Chem. Ber.*, 1968, **101**, 1398; E. F. Ullman and K. R. Huffman, *Tetrahedron Letters*, 1965, 1863; K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5417; W. A. Henderson, jun., and E. F. Ullman, *ibid.*, p. 5424.

[7] M. J. Bishop and N. K. Hamer, *J. Chem. Soc.* (*C*), 1970, 1193.

[8] *cf.* E. Block and R. Stevenson, *Chem. Comm.*, 1971, 711; W. Oppolzer, *J. Amer. Chem. Soc.*, 1971, **93**, 3834; W. Oppolzer and K. Keller, *ibid.*, p. 3836.

[9] E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1936, 1739.

[10] L. F. Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 2336.