Cycloaddition Reactions of a Hydroxy-o-quinone Dimethide

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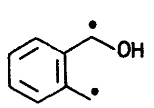
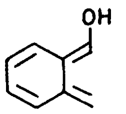
Summary The (*E*)-dienol, hydroxy-*o*-quinone dimethide (**2**), formed preferentially by heating benzocyclobutenol, readily undergoes $({}_{4}\pi_{s} + {}_{2}\pi_{s})$ cycloadditions and has been used as an entry into tetracyclic systems of the naphthacene series.

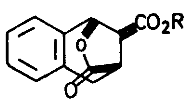
The stereospecific reaction between the photoenol from *o*-methylbenzaldehyde and maleic anhydride was recently described.[1] We now report an analogous thermal reaction. In the absence of dienophiles, the photolysis of aromatic ketones bearing *ortho*-alkyl groups often produces benzocyclobutenols.[2] 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.



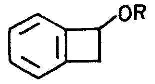
(1)



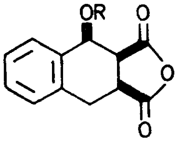
(2)



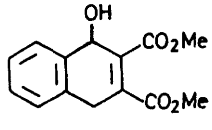
(3) R = H
(4) R = Me



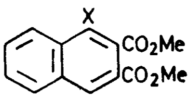
(6) R = Me
(7) R = Ac



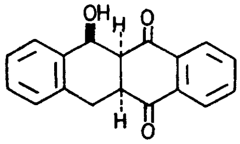
(5) R = H
(8) R = Me
(9) R = Ac



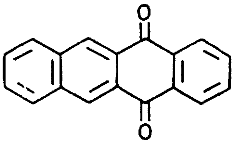
(10)



(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.

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† All new compounds gave satisfactory microanalytical and spectral data.

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

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