

The Diels–Alder Reaction of *o*-Benzoquinones

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THE dienophilic properties of *p*-benzoquinones are well known.¹ However *o*-benzoquinones often react as conjugated dienes rather than dienophiles. Thus 3,4-dimethyl-*o*-benzoquinone reacts² with cyclopentadiene to yield the adduct (I). In view of this result the reported formation³ of the adducts (II; R=H, Me, or Ph) from cyclopentadiene and the corresponding 4-substituted *o*-benzoquinones is unexpected. The adduct (II; R=Ph), which might enolise or aromatise spontaneously, was assigned the shown structure on spectroscopic evidence and its conversion by the action of pyridine and acetic anhydride into the naphthalene derivative (III). An alternative explanation of this reaction sequence, which is also consistent with the reported spectroscopic evidence, is that the reaction between cyclopentadiene and 4-phenyl-*o*-benzoquinone (at room temperature) gave an adduct of structure (IV) which then (at 100°) in the presence of pyridine and acetic anhydride

rearranged, as indicated, to yield the acetate (III) via the ene-dione (II, R=Ph). Such a rearrangement would be reversible (*vide infra*), but the equilibrium would be displaced in favour of the dione (II; R=Ph) due to the latter's aromatisation. This rearrangement is completely analogous to the reported⁴ interconversion (at 140°) of *syn*-8-hydroxydicyclopentadiene (V) and α -1-hydroxydicyclopentadiene (VI).

The adducts assigned the structures (VII) and (VIII) have been isolated⁵ from the reaction of cyclopentadiene and tetrabromo-*o*-benzoquinone. It is stated that compound (VII) "m.p. 140° resolidifies and remelts at 187° (decomp.) undepressed in admixture with (VIII)". This represents an example of the type of rearrangement postulated above. In view of this discussion the tentative structure (II; R=NHAc) assigned⁵ to adduct from 4-acetamido-*o*-benzoquinone and cyclopentadiene must be reconsidered.

¹ M. F. Ansell, B. W. Nash, and D. W. Wilson, *J. Chem. Soc.*, 1963, 3012.

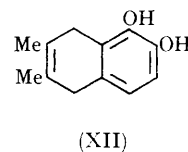
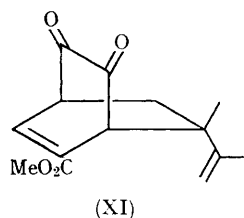
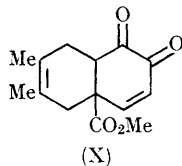
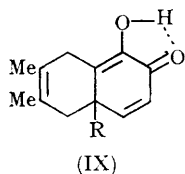
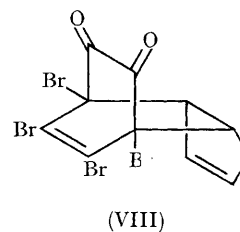
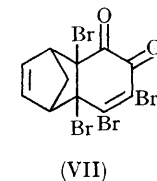
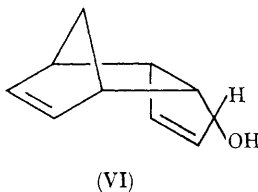
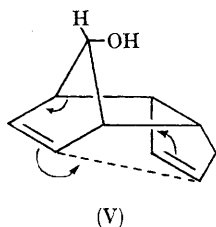
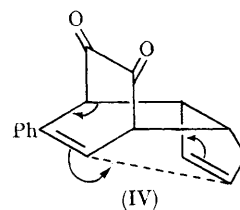
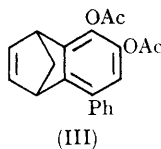
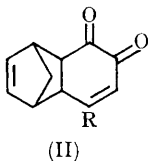
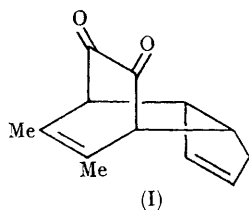
² L. Horner and D. W. Baston, *Chem. Ber.*, 1965, 98, 1252.

³ F. J. Evans, H. S. Wilgus, and J. W. Gates, *J. Org. Chem.*, 1965, 30, 1655.

⁴ R. B. Woodward and T. J. Katz, *Tetrahedron*, 1959, 5, 70.

⁵ J. A. Barltrop and J. A. D. Jeffreys, *J. Chem. Soc.*, 1954, 154.

We now report the ready formation of an adduct m.p. 127—128° in 75% yield from 2,3-dimethylbutadiene and 3-methoxycarbonyl-*o*-benzoquinone. The reaction was effected by the action of freshly prepared silver oxide on a solution of the diene and 4-methoxycarbonylcatechol in ether. The adduct, which analysed correctly, was shown to have the hydrogen-bonded structure (IX; R = CO₂Me), rather than the diketone structure (X;) from its



n.m.r. spectrum (CDCl₃): τ 8.33 (6,7-Me₂), 7.83—6.78 (5,8-H₄), 6.34 (4a-CO₂Me), 3.37 (1-OH), 3.06, 3.54 (3,4-H₂, quartet $J_{H-H} = 10$ c./sec.). The assignment of the peak at τ 3.37 was confirmed by its disappearance on deuteration. The infrared spectrum (CCl₄) of the adduct (IX; R = CO₂Me) exhibited a sharp hydroxyl absorption at 3430 cm.⁻¹ which was shifted on deuteration to 3520 cm.⁻¹ These spectral data are not consistent with an alternative structure of type (XI), which would result if the *o*-quinone had acted as a 1,3-diene. Confirmation of the vinylogous β -keto-ester structure (IX; R = CO₂Me) of the adduct was obtained by its easy conversion (85%) into 5,8-dihydro-1,2-dihydroxy-6,7-dimethylnaphthalene (XII) m.p. 114—115°, by the action (95°/5 min.) of 10% sodium hydroxide solution. The n.m.r. spectrum (deuteroacetone) τ 8.28 (6,7-Me₂), 6.83 (5,8-H₄),

3.56, 3.28 (3,4-H₂ quartet $J_{H-H} = 8$ c./sec.), 2.55 (broad) [1,2-(OH)₂] (lost on deuteration) of the latter compound is consistent with the assigned structure, which is also supported by the similarity of its ultraviolet spectrum with that of catechol.

It is of interest to note that this constitutes the indirect preparation of the aromatised form of the Diels-Alder adduct from *o*-benzoquinone and 2,3-dimethylbutadiene.

In order to obtain another example of the enhancement of the dienophilic properties of *o*-benzoquinones by electron-withdrawing substituents, the oxidation of 4-cyanocatechol in the presence of 2,3-dimethylbutadiene was attempted. The reaction was unsuccessful with silver oxide as the oxidant, but was achieved by the use of nickel "peroxide" (Ni₂O₃· x H₂O)⁶ as the oxidant. The adduct was shown to have the structure (IX; R = CN) from its n.m.r. spectrum [τ 8.22 (6,7-Me₂), 7.20—6.66 (5,8-H₄), 3.46, 3.00 (3,4-H₂ quartet $J_{H-H} = 9$ c./sec.), 3.30 (1-OH) (lost on deuteration)].

Nickel peroxide has not previously been used for the oxidation of *o*- or *p*-dihydric phenols to the corresponding quinones.

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⁶ K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, 1962, 27, 597.