327. *Conversion of the Photodimer of 2,3-Dimethylbenzoquinone into Derivatives of Biphenylene.*

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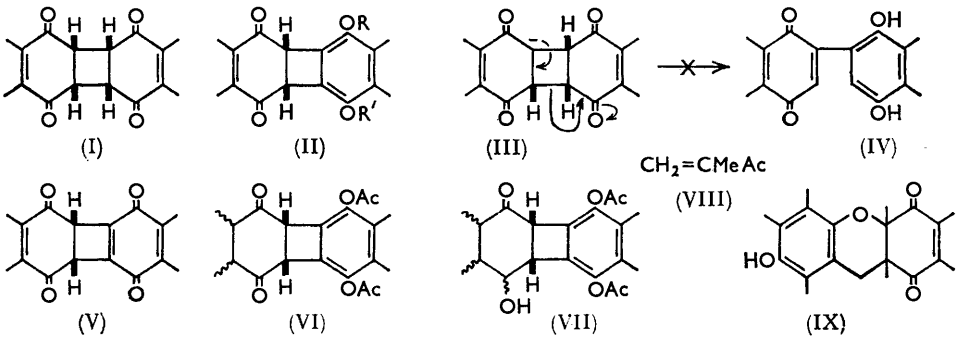
The photodimer of 2,3-dimethylbenzoquinone (I) enolises to a quinol (II) that can be dehydrogenated to a quinone (V), but a second double bond could not be introduced into the central cyclobutane ring.

Probable structures were recently suggested for a series of photodimers of dimethylbenzoquinones, but the structures were rigorously proved only for the dimers of the 2,3-dimethyl-compound.[1] The *cis*-dimer (I) was of the type we had sought for the synthesis of derivatives of biphenylene or cyclobutadiene, for each carbon atom carries, adjacent to a carbonyl group, a hydrogen atom which might be removed by enolisation or dehydrogenation.

In the presence of alkali the dimer (I) formed the di-enol (II; R = R′ = H); this gave a diacetate[1] (II; R = R′ = Ac) which could be made more conveniently directly from the dimer with acetic anhydride and pyridine at room temperature. Although the quinol (II; R = R′ = H) very rapidly decolorised a solution of Fremy's salt,[2] no crystalline product could be isolated. Shaking of an alkaline solution of the quinol (II; R = R′ = H) in air at room temperature[3] produced no reaction, while at higher temperatures the material was again destroyed without formation of an identifiable product. However,



heterogeneous reaction with silver oxide or active manganese dioxide yielded yellow crystals, the spectra of which ($\lambda_{max.}$ 253 and 360 mμ, ε 16,400 and 240; $\nu_{max.}$ 1672 and 1602 cm.$^{-1}$) were consistent with their being the quinone (V). Before attempts were made to convert these compounds (II) into more highly unsaturated derivatives, confirmation of their structures was desirable: in particular the alternative (IV) had to be excluded, as it would have explained most of the spectroscopic properties and might have arisen by a reversed Michael reaction rather than a second enolisation of the anion (III). Such isomers should be most easily distinguished chemically by their different behaviour on reduction.

The spectra of the compound formed on reduction of either the diacetate (II; R = R′ = Ac) or the quinone (V) with zinc dust and acetic acid in acetic anhydride showed absorption from unconjugated carbonyl groups ($\lambda_{max.}$ 292 mμ, ε 320; $\nu_{max.}$ 1720 cm.$^{-1}$) as well as from a quinol diacetate group ($\lambda_{max.}$ 270 mμ, ε 580; $\nu_{max.}$ 1768 cm.$^{-1}$). The presence of the former bands is consistent only with the cyclohexanedione structure (VI): a quinone of structure (IV) would, of course, have given the aromatic tetra-acetoxytetramethylbiphenyl.

[1] Cookson, Cox, and Hudec, *J.*, 1961, 4499.
[2] Teuber and Rau, *Chem. Ber.*, 1953, **86**, 1036, and refs. therein.
[3] Dauben, Boswell, and Templeton, *J. Org. Chem.*, 1960, **25**, 1853; Hill, Ph.D. Thesis, Southampton, 1961, and unpublished observations.

The diacetate (II; R = R′ = Ac) took up four atoms of hydrogen over platinum, giving a product that retained the quinol diacetate group ($\lambda_{max.}$ 267 mμ, ε 540; $\nu_{max.}$ 1762 cm.$^{-1}$) and contained an unconjugated carbonyl (289 mμ, ε 140; 1700 cm.$^{-1}$) and a hydroxyl group (3530 cm.$^{-1}$). In agreement with formula (VII) this tetrahydro-derivative was smoothly oxidised by chromic oxide in pyridine to a compound with the spectral characteristics of (VI). Although the ultraviolet spectrum of this new diketone was very like that of the diketone made by reduction of (II; R = R′ = Ac) with zinc, its m. p. was 20° higher and the infrared spectra of the two samples, while very similar, showed significant differences. Attempts to establish the stereoisomeric relationship of the two diketones by interconverting them by treatment with acid or base resulted either in the recovery of unchanged material or in the production of resins. Too little material remained to allow thorough attempts to turn both isomers back into the enedione (II; R = R′ = Ac) with selenium dioxide.

The proton magnetic resonance spectra of the dimer (I), the quinol, and its diacetate (II; R = R′ = H and Ac), which are very simple because of the symmetry of the molecules and the lack of coupling between different types of protons, further prove the structures (Table 1). The spectrum of the dimer (I) consists of only two sharp lines and is quite

TABLE 1.

Proton magnetic resonance spectra in deuterochloroform: τ values (relative intensities in parentheses).

	Type of proton				
Compound	Enedione methyl	Aromatic methyl	Acetyl	Cyclobutane	Hydroxyl
(I)	8·12 (3)	—	—	6·10 (1)	—
(II; R = R′ = H) ...	7·98 (3)	7·97 (3)	—	5·52 (1)	5·43 (1)
(II; R = R′ = Ac) ...	8·08 (3)	7·65 (3)	7·93 (3)	5·57 (1)	—

unambiguous. The resonance from the methyl protons occurs at almost the same field as Jackman [4] quotes (τ 8·125) for the analogous protons in the ketone (VIII), while that from the cyclobutane protons falls near the value (τ 6·15) for those in tetramethyl cyclobutane-*trans-cis-trans*-tetracarboxylate.[5] The values for the two sorts of methyl group in the quinol (II; R = R′ = H) are too close to be separately assigned with any confidence, but, of the two peaks corresponding to two protons, the resonance at lower field can be attributed to the hydroxyl because of its relative broadness and its appearance in the region expected for a weakly hydrogen-bonded phenolic hydroxyl group. The protons of

TABLE 2.

$n \longrightarrow \pi^*$ Absorption of ketones in ethanol: wavelengths in mμ (ε in parentheses).

(I)		374 (150)
(II); R = R′ = H)		403 (620)
(II; R = H, R′ = Ac)	322 (490)	368 (480)
(II; R = R′ = Ac)		368 (210)
(V)		360 (240)
(VIa)	292 [a] (320)	
(VIb)	297 (250)	
(VII)	289 [a] (140)	

[a] Shoulder.

the aromatic methyl groups in the diacetate (II; R = R′ = Ac) may be unshielded by the ester carbonyl groups. The relatively large shift of the cyclobutane protons in the aromatic compounds (II) no doubt results from the current induced in the benzene ring.

The long-wavelength ultraviolet bands of these ketones (Table 2) show an interesting trend. Compared with the bis-enedione (I) the $n \longrightarrow \pi^*$ transition of lowest energy in

[4] Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, London, 1959, p. 58.
[5] Griffin, Vellturo, and Furukawa, *J. Amer. Chem. Soc.*, 1961, **83**, 2725.

the compounds (V) and (II) is progressively intensified in the quinone (negligible intensification after allowing for quinone absorption; *e.g.*, duroquinone, $\lambda_{max.}$ 340 mμ, ε 240), the diacetate (three times), the monoacetate (six times), and the quinol (eight times as intense).† The increased intensity is derived from the mixing of the oxygen *n*-electrons with the aromatic π-electrons, which allows the $n \longrightarrow \pi^*$ transition to borrow intensity from the charge-transfer transition that must occur at shorter wavelengths and provides the electric transition moment that would otherwise be lacking. Progressive removal of the acetyl groups lowers the ionisation potential of the aromatic system and thus reduces the gap in energy between the charge-transfer and $n \longrightarrow \pi^*$ transitions, with consequent intensification of the latter.[6] Examples of the phenomenon [7] are known also where the oxygen atom is part of a simple ketone,[8,9] an α-diketone,[6,10] a conjugated ketone,[6] or a *p*-benzoquinone.[6] Evidently the ionisation potential of the quinone group in (V) is too high to be effective.

The high extinction of the two ketones (VI) suggests that if the cyclohexane ring has a boat conformation it must be mainly the one in which the oxygen atoms are directed towards the aromatic ring.

Attempts to introduce more carbon–carbon double bonds into the molecule by enolisation or dehydrogenation of (II) or (V) produced either no reaction or unidentifiable gums. The diacetate (II; R = R′ = Ac), for example, was recovered from hot acetic anhydride containing sodium acetate or sulphuric acid, so the additional strain that would be introduced must make enolisation very slow. The diketone (II; R = R′ = H) is probably more stable than the fully aromatic tetrahydroxytetramethylbiphenylene tautomer.

When the bis-enedione (I) was treated with alkali the quinol (II; R = R′ = H) was accompanied by a dimer (*i.e.*, a tetramer of 2,3-dimethylbenzoquinone). For comparison of spectra we made some of the dimer [11] (IX) formed by duroquinone with alkali: several derivatives are described in the Experimental section.

Experimental

Ultraviolet spectra of ethanol solutions were recorded on a Unicam SP. 700 (on loan from the Royal Society) and infrared spectra of Nujol mulls on a Unicam SP. 100 spectrometer. Only O–H and double-bond stretching frequencies are quoted. Proton magnetic resonance spectra at 60 Mc./s. were kindly measured by Mr. M. Fitches on an A.E.I. RS 2 spectrometer, using solutions in deuterochloroform with tetramethylsilane as internal reference.

Reaction of the Dimer (I) *with Alkali.*—A few drops of 2N-sodium hydroxide were added to a solution of the dimer (0·72 g.) in ethanol (40 ml.). After 1 hr. the dark brown solution was acidified with a few drops of dilute sulphuric acid, and it turned deep yellow. The solution was diluted with water and extracted with ether. The solid from the extract was chromatographed on silica gel. Benzene eluted a white solid that crystallised from ether as feathery needles (4 mg.) with $\nu_{max.}$ 3485, 1715, and 1635w cm.$^{-1}$.

Benzene with 5% of ethyl acetate eluted the quinol (II; R = R′ = H), which crystallised from methanol as orange-red needles (190 mg.), m. p. 225—226°, identical with the sample already described [1] [Found: *M* (Rast), 285. Calc. for $C_{16}H_{16}O_4$: *M*, 272].

With 20% of ethyl acetate the *tetramer* was obtained; it separated from ethanol as yellow crystals (40 mg.), m. p. 277° (decomp. and formation of a white sublimate) [Found: C, 70·8 H, 5·9%; *M* (Rast), 586. $C_{32}H_{32}O_8$ requires C, 70·6; H, 5·9%; *M*, 544], shoulder 247 (ε 26,500), $\lambda_{max.}$ 387 mμ (ε 1050); $\nu_{max.}$ 3450, 1675, and 1620 cm.$^{-1}$. Treatment of the tetramer (47 mg.) with acetic anhydride (1 ml.) and pyridine (4 ml.) at room temperature for 10 hr.

† Allowing ε 75 for each enedione group in the standard compound (I).

[6] Birnbaum, Cookson, and Lewin, *J.*, 1961, 1224.
[7] Labhart and Wagnière, *Helv. Chim. Acta*, 1959, **42**, 2219; Mason, *Quart. Rev.*, 1961, **15**, 287.
[8] Cookson and Wariyar, *J.*, 1956, 2302, and refs. therein.
[9] Cookson and Hudec, *J.*, 1962, 429; the first sentence in the footnote ¶ on p. 434 should read: "This is not to deny that electrostatic fields from the incomplete screening of atomic nuclei may not also play a part."
[10] Cookson and Lewin, *Chem. and Ind.*, 1956, 984.
[11] Smith, Tess, and Ullyot, *J. Amer. Chem. Soc.*, 1944, **66**, 1320.

gave the *penta-acetate* as white crystals (23 mg.), m. p. 305° (from ether) (Found: C, 66·9; H, 5·95. $C_{42}H_{42}O_{13}$ requires C, 66·8; H, 5·6%), $\lambda_{max.}$ 257 (ε 21,300) and 361 mμ (ε 630), $\nu_{max.}$ 1785, 1700 (shoulder), 1675, and 1628 cm.$^{-1}$.

The diacetate (II; R = R′ = Ac) is best made directly from the dimer (I): chromatography of the product of acetylation of the dimer (1·15 g.) with acetic anhydride in pyridine (1 : 4) at room temperature for 36 hr. gave the diacetate (1·05 g.), m. p. 169°, identical with a sample made [1] from the quinol (II; R = R′ = H), accompanied by the quinol (10 mg.) and unchanged dimer (10 mg.).

1α,8α-3-*Acetoxy*-6-*hydroxy*-4,5,10,11-*tetramethyltricyclo*[6,4,0,$0^{2,7}$]*dodeca*-2,4,6,10-*tetraene*-9,12-*dione* (II; R = H, R′ = Ac).—On addition of aqueous 4N-sodium hydroxide (5 drops) to a stirred solution of the diacetate (II; R = R′ = Ac) (140 mg.) in ethanol (25 ml.) the colour changed from pale yellow to deep red. After 15 min. the solution was diluted with water and acidified with dilute sulphuric acid. Chromatography on silica gel of the product from an ether extract gave, with benzene containing 5% of ethyl acetate, a gum which yielded yellow-green crystals (60 mg.) of the *monoacetate*, m. p. 161° (from light petroleum, b. p. 40—60°) (Found: C, 69·05; H, 5·6. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·8%); $\lambda_{max.}$ 253 (ε 13,600), 322 (ε 490), and 368 mμ (ε 480); $\nu_{max.}$ 3435, 3330, 1755, 1670, and 1618 cm.$^{-1}$. Acetylation of the monoacetate with acetic anhydride in pyridine regenerated the diacetate.

1α,8α-4,5,10,11-*Tetramethyltricyclo*[6,4,0,$0^{2,7}$]*dodeca*-2(7),4,10-*triene*-3,6,9,12-*tetraone* (V)—A mixture of powdered silver oxide and anhydrous sodium sulphate was added to the quinol (II; R = R′ = H) (135 mg.) in dry benzene (30 ml.). After 1·5 hr. with occasional shaking the solution was filtered and evaporated. Glistening yellow plates (100 mg.) of the *quinone* (V) crystallised from ethanol. They had m. p. 185—188° (decomp.) (Found: C, 70·8; H, 5·2. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%), $\lambda_{max.}$ 253 (ε 16,400) with a shoulder at 360 mμ (ε 240), $\nu_{max.}$ 1672 and 1602 cm.$^{-1}$. No quinone could be obtained when the mixture was set aside overnight. The quinone was also destroyed by chromatography on silica gel.

Oxidation of the quinol (100 mg.) with active manganese dioxide (100 mg.) in benzene for 2·5 hr. yielded the quinone (65 mg.).

1α,8α-3,6-*Diacetoxy*-4,5,10ξ,11ξ-*tetramethyltricyclo*[6,4,0,$0^{2,7}$]*dodeca*-2,4,6-*triene*-9,12-*dione* (VIa).—Zinc dust was added to a solution of the diacetate (II; R = R′ = Ac) (256 mg.) in acetic acid (5 ml.) and acetic anhydride (5 ml.), and the mixture was heated on a steam bath for 7 hr. The product was chromatographed on silica gel (benzene with 5% of ethyl acetate) to give a gum that crystallised from ethanol as needles (110 mg.) of the *dihydro-diacetate* (VIa), m. p. 160—162° (Found: C, 67·0; H, 6·1. $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·2%), $\lambda_{max.}$ 270 (ε 580) and a shoulder at 292 mμ (ε 320), $\nu_{max.}$ 1768 and 1720 with a shoulder at 1775 cm.$^{-1}$.

The same compound was formed by treating the diacetate (II; R = R′ = Ac) or the quinone (V) with zinc dust in acetic anhydride and a few drops of pyridine.

Hydrogenation of the Diacetate (II; R = R′ = Ac).—A solution of the diacetate (497 mg.) in ethyl acetate (100 ml.) was shaken under hydrogen with Adams catalyst for 2 hr. Chromatography of the product on silica gel gave, with 20% of ethyl acetate in benzene, the *dihydro-alcohol* (VII) as long feathery needles (435 mg.), m. p. 184° (Found: C, 66·8; H, 6·7. $C_{20}H_{24}O_6$ requires C, 66·65; H, 6·7%), $\lambda_{max.}$ 267 (ε 540) with shoulders at 273 (ε 490) and 289 mμ (ε 140), $\nu_{max.}$ 3500, 1762, and 1700 cm.$^{-1}$. It was unchanged after 6 hr. in acetic anhydride and pyridine.

A solution of the dihydro-alcohol (105 mg.) in pyridine (1 ml.) was added to a slurry of chromic oxide (100 mg.) in pyridine (1 ml.), and left for 12 hr. The product was chromatographed on silica gel. 5% of ethyl acetate in benzene eluted the *diketone* (VIb), which separated from ether as crystals (60 mg.), m. p. 180—183° (Found: C, 66·9; H, 6·2. $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·2%), $\lambda_{max.}$ 269 (ε 530) and 297 mμ (ε 250), $\nu_{max.}$ 1780, 1767, and 1720 cm.$^{-1}$. With 40% of ethyl acetate unchanged alcohol (20 mg.) was eluted.

Derivatives of Duroquinone Dimer (IX).—The dimer, orange cubes, m. p. 215—216°, from benzene [Found: C, 72·9; H, 7·4%; *M* (f. p. depression of benzene), 302. Calc. for $C_{20}H_{24}O_4$: C, 73·1; H, 7·4%; *M*, 328], had $\lambda_{max.}$ 257 (ε 13,000) and 294 mμ (ε 3700), and $\nu_{max.}$ 3500, 1680, and 1610 cm.$^{-1}$. The acetate separated from light petroleum (b. p. 40—60°) as pale yellow crystals, m. p. 140—141° (Found: C, 71·4; H, 7·25. Calc. for $C_{22}H_{26}O_5$: C, 71·3; H, 7·1%), with $\lambda_{max.}$ 257 (ε 15,800) and 288 mμ (ε 2400), and $\nu_{max.}$ 1755, 1695 (shoulder), 1670, and 1618 cm.$^{-1}$ [cf. durohydroquinone diacetate: $\lambda_{max.}$ 265 mμ (ε 250) and $\nu_{max.}$ 1760 cm.$^{-1}$].

The *monoxime* (oxime group probably next to the ether oxygen atom), prepared by heating the dimer on a steam bath for 5 days with excess of hydroxylamine hydrochloride in pyridine,

was purified by chromatography; it crystallised from benzene as yellow crystals, m. p. 217—219° (Found: C, 69·8; H, 7·2; N, 4·2. $C_{20}H_{25}NO_4$ requires C, 69·95; H, 7·3; N, 4·1%), with a shoulder at 222 (ε 12,500) and $\lambda_{max.}$ 279 mμ (ε 9900), and $\nu_{max.}$ 3620, 3380, 1653, and 1610 cm.$^{-1}$.

After 2 days the colour of a solution of the monoxime (99 mg.) and sodium borohydride (150 mg.) in ethanol had completely faded. Chromatography of the product on silica gel gave (with 20% of ethyl acetate in benzene) the *oxime-alcohol*, which formed crystals (61 mg.) from benzene (Found: C, 69·8; H, 8·1; N, 4·2. $C_{20}H_{27}NO_4$ requires C, 69·5; H, 7·9; N, 4·1%). It had m. p. 221—223°, shoulders at 226 (19,000), 237 (15,500) and $\lambda_{max.}$ 289 mμ (ε 2600), and $\nu_{max.}$ 3425, 3320, 3150, and 1625w cm.$^{-1}$.

Similar reduction of the dimer acetate gave the *dihydroxy-acetate*, crystallised from light petroleum (b. p. 40—60°), m. p. *ca.* 100° (not sharp: possibly a mixture of stereoisomers) (Found: C, 70·5; H, 8·05. $C_{22}H_{30}O_5$ requires C, 70·6; H, 8·1%). It had $\lambda_{max.}$ 288 mμ (ε 1500), and $\nu_{max.}$ 3500 (broad) and 1755 cm.$^{-1}$. Treatment with acetic anhydride in pyridine gave a *triacetate*, m. p. *ca.* 205° [from light petroleum (b. p. 100—120°)] (Found: C, 68·1; H, 7·8. $C_{26}H_{34}O_7$ requires C, 68·1; H, 7·5%).

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