535. *The Preparation of Some* 2,3:6,7-*Dibenzobiphenylenes.*

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The photodimer of 1,4-naphthaquinone has been converted into 1,4,5,8-tetrahydroxy-2,3:6,7-dibenzobiphenylene, and the tetramethyl ether and tetra-acetate of this compound have been prepared. Evidence is presented concerning the structure of the enolic form of the photodimer of 2,3-dimethyl-1,4-benzoquinone.

The formation of cyclobutanes by photodimerisation of 1,4-quinones is now well established,[1-3] but in most cases the photodimers carry angular groups which prevent aromatisation to biphenylenes. The 1,4-naphthaquinone photodimer (I), which lacks such groups, was prepared by Schönberg *et al.*,[4] who reported that it was insoluble in aqueous sodium hydroxide. Although the fused cyclobutane system would be expected to help to stabilise

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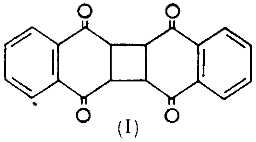
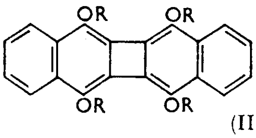
[1] Mustafa, *Chem. Rev.*, 1952, **51**, 1.
[2] Zavarin, *J. Org. Chem.*, 1958, **23**, 47.
[3] Cookson, Cox, and Hudec, *J.*, 1961, 4499.
[4] Schönberg, Mustafa, Barakat, Latif, Moubasher, and Mustafa, *J.*, 1948, 2126.

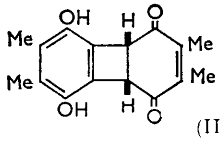
the keto-form, this property is surprising since the Diels–Alder adducts formed from 1,4-naphthaquinone and buta-1,3-dienes are readily enolised,[5] and it was therefore of interest to examine further the properties of the photodimer (I).

Treatment of the dimer (I), prepared by illumination of 1,4-naphthaquinone in benzene or ethyl acetate, with sodium hydroxide in aqueous dioxan gave an orange solution from which the tetrahydroxydibenzobiphenylene (II; R = H) was obtained by acidification. The tetramethyl ether (II; R = Me) was prepared by reaction of the alkaline solution with dimethyl sulphate, and the tetra-acetate (II; R = Ac) by acetylation of either the phenol (II; R = H) or the dimer (I) with acetic anhydride and sodium acetate. These compounds, like 2,3:6,7-dibenzobiphenylene itself,[6] give solutions which have a strong bluish fluorescence, and the assignment of dibenzobiphenylene structures to them is confirmed by their infrared and ultraviolet absorption spectra. The latter are particularly characteristic, and closely resemble that [6,7] of the parent hydrocarbon.


(I)



(II)



(III)

Exposure of 2,3-dimethyl-1,4-benzoquinone to daylight afforded a yellow dimer (III) which readily formed a diacetate, but not a tetra-acetate. The properties of these compounds are essentially identical with those recently reported by Cookson *et al.*,[3] and evidence supporting structure (III) has now been obtained from the proton nuclear magnetic resonance spectrum, which has three sharp peaks in the ratio 1 : 3 : 3 with $\tau = 5{\cdot}45$, 7·84, and 7·94, respectively. The band at 5·45 is lower than that observed for protons in related cyclobutane systems (*e.g.*, 2,3-dimethyl-1,4-benzoquinone photodimer,[3] 6·10; tetramethyl cyclobutane-*cis*-*trans*-*cis*-1,2,3,4-tetracarboxylate, 6·23; thymoquinone photodimer,[2] 6·70), but the absence of absorption in the olefinic proton region (3·25 and 3·29, respectively, in 2,3-dimethyl-1,4-benzoquinone and thymoquinone photodimer) indicates that the enedione system must carry two methyl groups, and to these is assigned the band at 7·94, since the methyl groups in 2,3-dimethyl-1,4-benzoquinone absorb at 7·95. The aromatic methyl groups are responsible for the peak at 7·84, in agreement with the value 7·87 observed for 2,3-dimethylquinol.

The resistance of the enedione (III) to enolisation is surprising in view of the ease with which the photodimer of 1,4-naphthaquinone can be converted into enolic derivatives.

EXPERIMENTAL

Solvents were freshly distilled, and were removed from solutions on the water-bath, where necessary under reduced pressure (water-pump). Sublimation temperatures are those of the heating-bath. Infrared spectra, in Nujol, were measured in a Perkin–Elmer model 21 double-beam spectrometer (absorption is strong unless stated otherwise), and ultraviolet spectra, in purified [8] dioxan, in a Perkin–Elmer model 4000 recording spectrophotometer. Nuclear magnetic resonance spectra, in deuterochloroform unless stated otherwise, were determined at 60 Mc./sec. with an Associated Electrical Industries model RS2 spectrometer, tetramethylsilane being used as internal standard. M. p.s are corrected.

1,4-*Naphthaquinone Photodimer* (I).—A solution of 1,4-naphthaquinone (1 g.) in dry benzene (22 c.c.) contained in a 150 × 16 mm. Pyrex tube was degassed, sealed under a vacuum, and suspended vertically in a 25-mm. diameter Pyrex tube through which cold water was

[5] Diels and Alder, *Ber.*, 1929, **62**, 2337.
[6] Curtis and Viswanath, *J.*, 1959, 1670.
[7] Ward and Pearson, *J.*, 1959, 1676.
[8] Vogel, " A Text-Book of Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p 175.

circulated. The solution was then illuminated for 24 hr. with a medium-pressure mercury-vapour lamp, the apparatus being surrounded by a polished aluminium reflector. The precipitate was collected, washed with cold benzene, and twice crystallised from glacial acetic acid, to give the dimer (65 mg., 6·5%) as hexagonal plates, m. p. 273—274° after becoming brown at 267° [lit.,[4] 244—248° (decomp.)] (Found: C, 75·9; H, 3·9. Calc. for $C_{20}H_{12}O_4$: C, 76·0; H, 3·8%), $\nu_{\text{max.}}$ 1711sh, 1700, 1609, 1579w, sh, 1284, 1226m, sh, 1222m, 1168m, 1807m, 1081m, 1028m, 992w, 959, 951, 862w, 779, 706, 678 cm.$^{-1}$, $\lambda_{\text{max.}}$ 230, 299, 308 mμ (log ε 4·82, 3·52, 3·52), $\lambda_{\text{min.}}$ 280, 303 mμ (log ε 3·25, 3·49), λ_{sh} 250 mμ (log ε 4·39). Identical (m. p., mixed m. p., and infrared spectrum) material was obtained in 1·5% yield when the solvent was ethyl acetate. The dimer, introduced into the ionisation chamber at 290°, gave a mass spectrum identical with that of 1,4-naphthaquinone. It dissolved in hot aqueous sodium hydroxide, giving an orange solution which became blue, then green, and finally brown when exposed to air.

1,4,5,8-*Tetrahydroxy*-2,3:6,7-*dibenzobiphenylene* (II; R = H).—A mixture of the foregoing dimer (20 mg.), dioxan (4 c.c.), and water (6 c.c.) was refluxed for 5 min. in a rapid stream of oxygen-free nitrogen, and then treated, all at once, with freshly boiled aqueous 10% sodium hydroxide (5 c.c.). The resulting orange-red solution, which had a green fluorescence, was refluxed for 2 min., cooled to 50°, and acidified with 15% hydrochloric acid (10 c.c.). After the mixture had cooled to room temperature the precipitate was collected, washed with water, and boiled for a short time with ethanol (10 c.c.). The mixture was filtered, and the filtrate was quickly concentrated to 1·5 c.c. The *tetrahydroxy-compound* (9·5 mg., 48%) separated as yellowish-green irregular blades, m. p. 260—265° after becoming orange-brown at 185° and blackening at 245° (Found: C, 75·3; H, 3·6. $C_{20}H_{12}O_4$ requires C, 76·0; H, 3·8%), $\nu_{\text{max.}}$ 3436, 3246, 3163 (all broad), 1661m, 1596m, 1520w, 1430m, 1366, 1298, 1266m, 1244, 1199, 1187, 1144m, 1093m, 1060w, 1029w, 976w, 947w, 919, 791m, 756, 720w cm.$^{-1}$, $\lambda_{\text{max.}}$ 218, 257, 293, 306, 346, 376·5, 399, 424 mμ (log ε 4·36, 4·33, 4·85, 5·14, 4·15, 3·41, 3·72, 3·90), $\lambda_{\text{min.}}$ 239, 264, 297, 339, 369, 388, 412·5 mμ (log ε 3·92, 3·94, 4·83, 4·06, 3·25, 3·11, 3·08), λ_{sh} 227·5, 251, 280, 333 mμ (log ε 4·25, 4·14, 4·43, 4·10). Solutions in organic media were yellow with a blue fluorescence; in hydroxylic solvents the fluorescence slowly decayed, and a brown resin was formed.

1,4,5,8-*Tetramethoxy*-2,3:6,7-*dibenzobiphenylene* (II; R = Me).—An alkaline solution of the dimer (20 mg.) was prepared as described in the foregoing experiment, cooled to 20°, and treated all at once with dimethyl sulphate (0·75 c.c.). The suspension was vigorously shaken for 10 min., further dimethyl sulphate (0·25 c.c.) was added, and shaking was continued for 20 min. more. The precipitate was collected, washed with water, and then dried, and extracted with boiling light petroleum (10 c.c., b. p. 60—80°). Crystallisation of the soluble material from light petroleum (b. p. 60—80°) and then from light petroleum (b. p. 100—120°) gave the *tetramethoxy-compound* (11 mg., 47%) as pale yellow rhombic tablets, m. p. 211° (Found: C, 77·8; H, 5·6. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%), $\nu_{\text{max.}}$ 1622, 1606m, sh, 1581m, 1512m, 1456, 1422w, 1402w, 1346, 1298w, 1286, 1215m, 1202m, 1181m, 1146w, 1100, 1082m, 1033m, 1017, 982w, 966, 920w, 872w, 791w, 771, 749m, 710w, 663m cm.$^{-1}$, $\lambda_{\text{max.}}$ 219, 259·5, 291·5, 303·5, 342·5, 389·5, 412 mμ (log ε 4·37, 4·16, 4·89, 5·16, 4·28, 3·12, 3·29), $\lambda_{\text{min.}}$ 243, 264·5, 294, 335·5, 380, 402 mμ (log ε 3·63, 4·08, 4·88, 4·15, 2·73, 2·62), λ_{sh} 279·5, 317·5, 330, 366 mμ (log ε 4·50, 4·48, 4·21, 3·21). The solid had a blue-green and the solutions a pinkish-blue fluorescence in ultraviolet light.

1,4,5,8-*Tetra-acetoxy*-2,3:6,7-*dibenzobiphenylene* (II; R = Ac).—A solution of 1,4-naphthaquinone photodimer (30 mg.) in boiling acetic anhydride (10 c.c.) was treated with anhydrous sodium acetate (100 mg.), then refluxed for 4 hr. and cooled, and the solid was collected, washed with cold acetic acid, and then with water, and dried. Sublimation at 280°/5 × 10^{-3} mm., and crystallisation of the sublimate from acetic anhydride afforded the *tetra-acetoxy-compound* (37 mg., 81%) as very pale yellow slender blades, m. p. 358—360° (decomp.) after becoming brown at 353° (Found: C, 69·3; H, 4·2. $C_{28}H_{20}O_8$ requires C, 69·4; H, 4·2%). Identical material was obtained when the catalyst was toluene-*p*-sulphonic acid. It had $\nu_{\text{max.}}$ 1770, 1725m, 1662m, 1585w, 1565w, 1514m, 1464m, 1379, 1344, 1307w, 1287, 1212, 1195sh, 1182, 1153m, sh, 1093, 1061m, 1039w, 1015, 955w, 945m, 899, 865w, 810w, 761, 740w, 733w, 720w, 700w cm.$^{-1}$, $\lambda_{\text{max.}}$ 220·5, 284·5, 296·5 333, 361, 380, 404·5 mμ (log ε 4·49. 4·93, 5·23, 4·37, 3·27, 3·52, 3·66), $\lambda_{\text{min.}}$ 244, 287·5, 323, 354·5, 372·5, 394 mμ (log ε 3·59, 4·90, 4·19, 3·16, 2·82, 2·61), and λ_{sh} 254, 264, 315, 384 mμ (log ε 3·86, 4·14, 4·40, 3·42). The solution in acetic anhydride had a blue fluorescence in ultraviolet light, pinkish-blue in daylight. Identical (mixed m. p., infrared spectrum) material was obtained in 95% yield from the enol (II; R = H).

2,3-*Dimethyl*-1,4-*benzoquinone Photodimer* (III).—The quinone [9] was exposed to daylight, and the benzene-soluble fraction of the product was sublimed at 180°/0·01 mm., to give the dimer as yellow rhombic plates [from benzene–light petroleum (b. p. 40—60°)], m. p. 229—229·5° (lit.,[3] 225—226°) (Found: C, 70·3; H, 6·1. Calc. for $C_{16}H_{16}O_4$: C, 70·6; H, 5·9%). The diacetate, pale greenish-yellow prisms by sublimation at 155°/6 × 10^{-3} mm., had m. p. 163·5—164° (lit.,[3] 165—166°). The infrared and ultraviolet spectra of these compounds were essentially identical with those reported by Cookson *et al.*[3]

2,3-*Dimethylquinol*.—Hydrogenation of 2,3-dimethyl-1,4-benzoquinone gave the quinol, needles (from toluene), m. p. 227·5° (lit.,[10] 221°), having (in MeOH) τ 3·48, 7·87 in the ratio 1 : 3.

Tetramethyl Cyclobutane-cis-trans-cis-1,2,3,4-*tetracarboxylate*.—Treatment of maleic anhydride photodimer with methanol and sulphuric acid yielded the tetraester, prisms (from methanol), m. p. 145·5—146° (lit.,[11,12] 144—145°, 145°) (Found: C, 50·5; H, 5·6. Calc. for $C_{12}H_{16}O_8$: C, 50·0; H, 5·6%), τ 6·23, 6·29 in the ratio 1 : 3.

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[9] Smith and Tess, *J. Amer. Chem. Soc.*, 1944, **66**, 1523.

[10] Nölting and Forel, *Ber.*, 1885, **18**, 2668.

[11] Griffin, Vellturo, and Furukawa, *J. Amer. Chem. Soc.*, 1961, **83**, 2725.

[12] Criegee and Höver, *Chem. Ber.*, 1960, **93**, 2521.