

## Light-induced and Related Reactions of Quinones. Part XI.<sup>1</sup> 4,4'-Diphenoquinones

By J. Malcolm Bruce \* and Arshad-ul-haq Chaudhry, Department of Chemistry, The University, Manchester M13 9PL

Irradiation of 4,4'-diphenoquinone [bi(cyclohexa-2,5-dienylidene)-4,4'-dione] with visible light in acetaldehyde gives 4,4'-dihydroxybiphenyl, 4-acetoxy-4'-hydroxybiphenyl, and 3-acetyl-4,4'-dihydroxybiphenyl. Analogous products result from irradiation in benzaldehyde. These results are compared with those previously reported for 1,4-benzoquinone.

3,3',5,5'-Tetramethyl-4,4'-diphenoquinone gives predominantly the hydroquinone when it is irradiated in acetaldehyde, but the 3,3',5,5'-tetra-*t*-butyl homologue was unchanged.

LIGHT-INDUCED and free radical reactions of 4,4'-diphenoquinone [bi(cyclohexa-2,5-dienylidene)-4,4'-dione] have been little studied. U.v. irradiation<sup>2</sup> of its aqueous solution causes reduction to 4,4'-dihydroxybiphenyl, and it has been used<sup>3</sup> as an inhibitor of free radical addition polymerisation, although its mode of action has not been established. 3,3',5,5'-Tetramethyl-4,4'-diphenoquinone has been examined<sup>4</sup> as a retarder for the autoxidation of benzaldehyde, and it yields<sup>5</sup> 4,4'-dibenzoyloxy-3,3',5,5'-tetramethylbiphenyl, probably by addition of benzoyl radicals, when heated with a mixture of benzaldehyde and benzoyl peroxide.

The products from light-induced reactions between 1,4-benzoquinones and aldehydes result from scavenging of acyl radicals by ground-state quinone; acetyl radicals are scavenged predominantly at the nucleus of 1,4-benzoquinone,<sup>6</sup> but at an oxygen atom of 1,4-benzoquinones with appreciably higher oxidation potentials.<sup>7,8</sup> 4,4'-Diphenoquinone has a significantly higher potential<sup>9</sup> (954 mV) than 1,4-benzoquinone (697 mV), and hence it was of interest to compare its photochemistry in the presence of aldehydes with that of 1,4-benzoquinone.

**Preparation of Quinones.**—4,4'-Diphenoquinone was prepared by oxidation of 4,4'-dihydroxybiphenyl with lead tetra-acetate using a slight modification<sup>10</sup> of the procedure described by König *et al.*;<sup>11</sup> other methods failed. The 3,3',5,5'-tetramethyl and -tetra-*t*-butyl homologues were obtained by oxidative coupling<sup>12</sup> of the corresponding 2,6-disubstituted phenols.

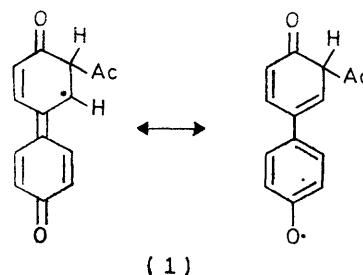
**Results of Irradiations.**—Irradiation of 4,4'-diphenoquinone in acetaldehyde with visible light gave a mixture from which 4,4'-dihydroxybiphenyl (14%), 4-acetoxy-4'-hydroxybiphenyl (7%), and 3-acetyl-4,4'-dihydroxybiphenyl (28%) were isolated. Irradiation in benzaldehyde gave analogous products, in yields of, respectively, 9, 14, and 21%. No identified product was obtained from irradiation in cinnamaldehyde (*cf.* ref. 7).

Irradiation of 3,3',5,5'-tetramethyl-4,4'-diphenoquinone in acetaldehyde gave an 80% yield of the correspond-

ing 4,4'-dihydroxybiphenyl, together with some biacetyl. 3,3',5,5'-Tetra-*t*-butyldiphenoquinone did not react under these conditions.

### DISCUSSION

4,4'-Diphenoquinone behaves as expected with acetaldehyde, giving a higher ratio of ester to ketone than does 1,4-benzoquinone, despite the statistically greater availability of nuclear sites for scavenging of acetyl radicals, and the fact that the unpaired electron in the radical resulting from such scavenging can be delocalised to a greater extent [as (1)]. The pattern with benzaldehyde is similar, and the proportion of ester is higher.



These results support the previous conclusion<sup>8</sup> that the oxidation potential of the quinone exerts a controlling influence on the course of the reaction, although the failure of 3,3',5,5'-tetramethyldiphenoquinone to scavenge acetyl radicals, despite the fact that its oxidation potential<sup>9</sup> (845 mV) is higher than that of 1,4-benzoquinone, suggests the importance of steric factors. The observation<sup>5</sup> that the tetramethyldiphenoquinone will scavenge benzoyl radicals at 80° may in part reflect the lower ionisation potential of the benzoyl radical compared with that of the acetyl radical (*cf.* ref. 8). The formation of biacetyl during the irradiation of 3,3',5,5'-tetramethyl-4,4'-diphenoquinone in acetaldehyde indicates that acetyl radicals were formed.

The failure of the tetra-*t*-butyldiphenoquinone to react is unexpected, since the *t*-butyl-1,4-benzoquinones afford products of reorganisation of the side-chain,

<sup>7</sup> J. M. Bruce, D. Creed, and J. N. Ellis, *J. Chem. Soc. (C)*, 1967, 1486.

<sup>8</sup> J. M. Bruce and K. Dawes, *J. Chem. Soc. (C)*, 1970, 645.

<sup>9</sup> H. Musso, K. Figge, and D. J. Becker, *Chem. Ber.*, 1961, 94, 1107.

<sup>10</sup> *Cf.* B. R. Brown and A. R. Todd, *J. Chem. Soc.*, 1954, 1280.

<sup>11</sup> K.-H. König, W. Schulze, and G. Möller, *Chem. Ber.*, 1960, 93, 554.

<sup>12</sup> V. Balogh, M. Fétizon, and M. Golfier, *J. Org. Chem.*, 1971, 36, 1339, and references therein.

<sup>1</sup> Part X, J. M. Bruce, A.-u.-h. Chaudhry, and K. Dawes, preceding paper.

<sup>2</sup> H. I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, 1966, 88, 3273.

<sup>3</sup> E. F. Samarin and A. A. Berlin, *Tr. po. Khim. i Khim. Tekhnol.*, 1963, 300 (*Chem. Abs.*, 1964, 61, 9582c).

<sup>4</sup> J. R. Dunn and W. A. Waters, *J. Chem. Soc.*, 1953, 2993; J. R. Dunn, W. A. Waters, and C. Wickham-Jones, *ibid.*, 1952, 2427.

<sup>5</sup> R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 1952, 2432.

<sup>6</sup> J. M. Bruce and E. Cutts, *J. Chem. Soc. (C)*, 1966, 449.

although it may be significant that 2,6-di-*t*-butyl-1,4-benzoquinone reacts particularly slowly in acetaldehyde.<sup>13</sup>

*Structures of Products.*—The structures of the products from irradiations in acetaldehyde were confirmed by comparison with authentic materials, and those from reactions in benzaldehyde by their spectra.

3-Acetyl-4,4'-dihydroxybiphenyl was obtained in good yield by Fries rearrangement of 4-acetoxy-4'-hydroxybiphenyl with aluminium chloride in the absence of solvent,<sup>14</sup> and in lower yield by similar rearrangement of 4,4'-diacetoxybiphenyl with aluminium chloride in 1,1,2,2-tetrachloroethane;<sup>15</sup> some 3,3'-diacetyl-4,4'-dihydroxybiphenyl was also formed under the latter conditions, but this compound was obtained almost exclusively when the solvent was omitted.<sup>14</sup>

#### EXPERIMENTAL

Aldehydes were freshly distilled. Irradiations were carried out as described previously.<sup>16</sup> Solvents were removed under reduced pressure. Sublimation and bulb-to-bulb distillation temperatures are those of the heating bath. I.r. spectra were measured for Nujol mulls. <sup>1</sup>H N.m.r. spectral bands (100 MHz) are singlets unless otherwise indicated (*J* in Hz); resonances assigned to OH groups were removed by addition of D<sub>2</sub>O. Molecular weights were determined mass spectrometrically.

*4,4'-Diphenoquinone.*—A solution of freshly sublimed 4,4'-dihydroxybiphenyl (500 mg) in warm purified dioxan (20 ml) was added dropwise to a vigorously stirred slurry of freshly crystallised lead tetra-acetate (3 g) in freshly distilled glacial acetic acid (35 ml) at room temperature. Stirring was continued for 5 min, and the yellow precipitate was filtered off and crystallised from dry benzene (200 ml) to give the quinone as scarlet-red needles (290 mg); concentration of the mother liquor afforded the golden form of the quinone (60 mg). Both forms decomposed at 176° (lit.,<sup>17</sup> 166°), and had  $\nu_{\max}$  735w, 785m, 858s, 969s, 988w, 1108w, 1168w, 1173w, 1258m, 1279w, 1549w, 1591s, 1606m, and 1634s cm<sup>-1</sup>,  $\lambda_{\max}$  (CHCl<sub>3</sub>) 253, 263, and 396 nm (log  $\epsilon$  3.4, 3.4, and 4.84),  $\tau$  (ca. 1% in CDCl<sub>3</sub>) 2.09 (d, *J* 10, H-2, H-2', H-6, and H-6'), and 3.37 (d, *J* 10, H-3, H-3', H-5, and H-5').

*Irradiation of 4,4'-Diphenoquinone.*—(a) The quinone (500 mg) in acetaldehyde (50 ml) was irradiated for 2 days, the solvent was removed (no paraldehyde was present), and the residue was sublimed at 180° and 10<sup>-2</sup> mmHg to give a yellow solid (380 mg). A portion (100 mg) of this was subjected to p.l.c. on silica gel using 9 : 1 benzene-acetic acid as eluant. The first band afforded 4-acetoxy-4'-hydroxybiphenyl (12 mg), m.p. 186°, identical with material prepared as described below, the second, yellow band afforded 3-acetyl-4,4'-dihydroxybiphenyl (51 mg), m.p. 192°, identical with material prepared as described below, and the final band gave 4,4'-dihydroxybiphenyl (19 mg), m.p. 272°.

(b) The quinone (500 mg) was irradiated in benzaldehyde (50 ml) for 2 days, and the solvent was then removed. The residue was rinsed with cold pentane (5 × 10 ml), dissolved in benzene (40 ml), and the solution was washed with

aqueous sodium hydrogen carbonate, then with water, and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent and distillation (bulb-to-bulb) of the residue at 200° and 10<sup>-2</sup> mmHg gave a semi-solid (430 mg), a portion (100 mg) of which was subjected to p.l.c. as described under (a). The slowest-moving band afforded 4,4'-dihydroxybiphenyl (10 mg), m.p. 269—271°. The leading, yellow band was a mixture of 4-benzoyloxy-4'-hydroxybiphenyl ( $\nu_{\max}$  1729 cm<sup>-1</sup>) and 3-benzoyl-4,4'-dihydroxybiphenyl ( $\nu_{\max}$  1621 cm<sup>-1</sup>) which could not be conveniently separated. It was therefore hydrolysed by refluxing with aqueous 16% sodium hydroxide (2.5 ml) for 24 h: acidification of the solution with hydrochloric acid and p.l.c. of the precipitate as above gave, after sublimation of the yellow band at 110° and 10<sup>-2</sup> mmHg, 3-benzoyl-4,4'-dihydroxybiphenyl (44 mg), m.p. 130° (Found: C, 78.4; H, 4.3%; *M*<sup>+</sup>, 290. C<sub>19</sub>H<sub>14</sub>O<sub>3</sub> requires C, 78.6; H, 4.7%; *M*, 290),  $\nu_{\max}$  1518m, 1570m, 1582s, 1595m, 1608m, 1621s, and 3290m, br cm<sup>-1</sup>,  $\tau$  (2% in CDCl<sub>3</sub>) —1.66 (4-OH), 1.61 (4'-OH), 2.16—2.48 (m, H-2, H-6, and Ph), 2.68 (d, *J* 9, H-2' and H-6'), 2.94 (d, *J* 9, H-5), and 3.19 (d, *J* 9, H-3' and H-5'). The slow-running band afforded 4,4'-dihydroxybiphenyl (16 mg), m.p. 268—270°.

*Irradiation of 3,3',5,5'-Tetramethyl-4,4'-diphenoquinone.*—The quinone (500 mg) in acetaldehyde (50 ml) was irradiated for 21 days, the solvent was removed, and the residue was sublimed at 200° and 10<sup>-2</sup> mmHg. Chromatography of the sublimate on silica gel using benzene as eluant gave 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl (400 mg, 80%), m.p. 226° (lit.,<sup>18</sup> 227°), identical with material prepared by reduction of the quinone with zinc dust in acetic acid. G.l.c. examination of the distillate from the irradiation revealed the presence of biacetyl.

*Irradiation of 3,3',5,5'-Tetra-*t*-butyl-4,4'-diphenoquinone.*—The quinone (1 g) in acetaldehyde (50 ml) was irradiated with continuous stirring for 50 days. The quinone (84% after recrystallisation) was recovered, and no other product was obtained.

*4-Benzoyloxy-4'-hydroxybiphenyl.*—4,4'-Dihydroxybiphenyl (1.86 g) in dry ethanol (25 ml) was added to a stirred solution of sodium (0.25 g) in dry ethanol (10 ml), and the stirred mixture was then treated dropwise during 15 min with benzyl chloride (1 ml) in dry ethanol (5 ml), and refluxed for 1 h. The ethanol was removed, and the residue was stirred with aqueous 10% sodium hydroxide (50 ml); unchanged 4,4'-dihydroxybiphenyl dissolved. The insoluble material, containing the sodium salt of the monobenzyl ether, was filtered off, washed with aqueous 10% sodium hydroxide, and then just acidified with concentrated hydrochloric acid, and extracted with acetone. Removal of the solvent from the extract, sublimation of the residue at 220° and 10<sup>-2</sup> mmHg, and crystallisation of the sublimate from xylene gave the monobenzyl ether (1.9 g, 68%), m.p. 213° (Found: C, 82.1; H, 5.7%; *M*<sup>+</sup>, 276. C<sub>19</sub>H<sub>16</sub>O<sub>2</sub> requires C, 82.6; H, 5.8%; *M*, 276),  $\nu_{\max}$  1500s, 1595m, 1610m, and 3380m, br cm<sup>-1</sup>,  $\tau$  [2% in (CD<sub>3</sub>)<sub>2</sub>CO] 1.76 (OH), 2.45—2.75 (m, H-2, H-2', H-6, H-6', and Ph), 3.02 (d, *J* 8, H-3 and H-5), 3.18 (d, *J* 8, H-3' + H-5'), and 4.94 (CH<sub>2</sub>).

Sublimation of the acetone-insoluble fraction at 240° and 10<sup>-2</sup> mmHg gave 4,4'-dibenzoyloxybiphenyl (75 mg, 19%), m.p. 219° (lit.,<sup>19</sup> 219°).

<sup>13</sup> J. M. Bruce and A.-u.-h. Chaudhry, *J.C.S. Perkin I*, 1972, 372.

<sup>14</sup> Cf. G. C. Misra, L. M. Pande, G. C. Joshi, and A. K. Misra, *Austral. J. Chem.*, 1972, **25**, 1579.

<sup>15</sup> Cf. R. Pakkal, F. D. Thomas, and W. C. Fernelius, *J. Org. Chem.*, 1960, **25**, 282.

<sup>16</sup> J. M. Bruce and P. Knowles, *J. Chem. Soc. (C)*, 1966, 1627.

<sup>17</sup> R. Willstätter and L. Kalb, *Ber.*, 1905, **38**, 1232.

<sup>18</sup> S. C. Temin, *J. Org. Chem.*, 1961, **26**, 2518.

<sup>19</sup> J. Van Alphen, *Rec. Trav. chim.*, 1931, **50**, 415.

**4-Acetoxy-4'-benzyloxybiphenyl.**—A mixture of the foregoing monobenzyl ether (0.5 g) and anhydrous sodium acetate (0.1 g) in acetic anhydride (5 ml) was refluxed for 3 h, the solvent was removed, and the residue was triturated with water, and collected. Sublimation at 180° and 10<sup>-2</sup> mmHg followed by crystallisation of the sublimate from benzene gave the *acetate* (0.54 g, 90%), m.p. 155° (Found: C, 78.5; H, 5.6%; *M*<sup>+</sup>, 318.12629. C<sub>21</sub>H<sub>18</sub>O<sub>3</sub> requires C, 79.4; H, 5.7%; *M*, 318.12559),  $\nu_{\max}$  1496m, 1605m, and 1747s cm<sup>-1</sup>;  $\tau$  [saturated soln. in (CD<sub>3</sub>)<sub>2</sub>CO + (CD<sub>3</sub>)<sub>2</sub>SO] 2.30—3.01 (m, ArH<sub>13</sub>), 4.91 (CH<sub>2</sub>), and 7.78 (Me).

**4-Acetoxy-4'-hydroxybiphenyl.**—The foregoing benzyl ether (100 mg) in ethyl acetate (50 ml) was hydrogenolysed at room temperature and pressure over 5% palladium-charcoal (25 mg), the catalyst and solvent were removed, and the residue was sublimed at 160° and 10<sup>-2</sup> mmHg to give the *acetate* (64 mg, 89%), m.p. 186° (Found: C, 73.2; H, 5.3%; *M*<sup>+</sup>, 228. C<sub>14</sub>H<sub>12</sub>O<sub>3</sub> requires C, 73.7; H, 5.3%; *M*, 228),  $\nu_{\max}$  1500s, 1595m, 1610m, 1733vs, and 3460vs cm<sup>-1</sup>,  $\tau$  [2% in (CD<sub>3</sub>)<sub>2</sub>CO] 1.57 (OH), 2.44 (d, *J* 9, H-2 and H-6), 2.55 (d, *J* 9, H-2' and H-6'), 2.89 (d, *J* 9, H-3 and H-5), 3.11 (d, *J* 9, H-3' and H-5'), and 7.81 (Me).

**4,4'-Diacetoxybiphenyl.**—A mixture of 4,4'-dihydroxybiphenyl (1.00 g), anhydrous sodium acetate (0.5 g), and acetic anhydride (10 ml) was refluxed for 2 h, the solvent was removed, and the residue was triturated with water, and then sublimed at 160° and 10<sup>-2</sup> mmHg to give the diacetate (1.15 g, 88%), m.p. 163.5° (lit.<sup>15</sup> 161—162.5). This procedure is more convenient than that described in ref. 14.

**3-Acetyl-4,4'-dihydroxybiphenyl.**—(a) An intimate mixture of 4-acetoxy-4'-hydroxybiphenyl (120 mg) and anhydrous aluminium chloride (300 mg) was slowly heated to 168—170°, and then maintained at this temperature for 6 h. The mixture was cooled, added to crushed ice (30 g), and the suspension was treated with concentrated hydrochloric acid (0.5 ml). The insoluble material was collected, sublimed at 180° and 10<sup>-2</sup> mmHg, and the sublimate was subjected to p.l.c. on silica gel using 9 : 1 benzene-acetic acid

as eluant: the yellow band afforded the *ketone* (68 mg, 57%), m.p. 193° (Found: C, 73.6; H, 5.5%; *M*<sup>+</sup>, 228. C<sub>14</sub>H<sub>12</sub>O<sub>3</sub> requires C, 73.7; H, 5.3%; *M*, 228),  $\nu_{\max}$  1588m, 1608m, 1628m, and 3280w,br cm<sup>-1</sup>,  $\tau$  [2% in (CD<sub>3</sub>)<sub>2</sub>CO] — 2.22 (4-OH), 1.64 (4'-OH), 1.94 (d, *J* 2, H-2), 2.21 (d, *J* 2, H-6), 2.27 (q, *J*<sub>1</sub> 9, *J*<sub>2</sub> 2), 2.52 (d, *J* 9, H-2' and H-6'), 3.02 (d, *J* 9, H-5), 3.10 (d, *J* 9, H-3' + H-5'), and 7.24 (Me); these assignments were confirmed by spin-decoupling.

(b) An intimate mixture of 4,4'-diacetoxybiphenyl (1 g) and anhydrous aluminium chloride (1.5 g) was stirred in dry 1,1,2,2-tetrachloroethane (25 ml) at 160° for 6 h, and the solution was cooled, and then treated with 10% hydrochloric acid (16 ml). The solvent was removed in steam, and the involatile solid residue was collected and sublimed at 180° and 10<sup>-2</sup> mmHg to give a yellow solid (0.83 g). A portion (100 mg) of this was subjected to p.l.c. on silica gel using 9 : 1 benzene-acetic acid as eluant. The first band afforded 3,3'-diacetyl-4,4'-dihydroxybiphenyl (12 mg), m.p. 219°, identical with material prepared as described below. The next band gave 3-acetyl-4,4'-dihydroxybiphenyl (35 mg), m.p. 192°, identical with material prepared as described under (a). 4,4'-Dihydroxybiphenyl (16 mg) was obtained from the slowest-moving band.

**3,3'-Diacetyl-4,4'-dihydroxybiphenyl.**—An intimate mixture of 4,4'-diacetoxybiphenyl (1.00 g) and anhydrous aluminium chloride (2.5 g) was slowly heated to 165°, and then maintained at this temperature for 3 h. The mixture was cooled, added to crushed ice (30 g), acidified with concentrated hydrochloric acid (1 ml), and the precipitate was collected, crystallised from ethanol, and sublimed at 195° and 10<sup>-2</sup> mmHg to give the yellow diketone (0.92 g, 92%), m.p. 220° (lit.<sup>15</sup> 215—216°),  $\nu_{\max}$  1591m, 1610m, and 1639s cm<sup>-1</sup>,  $\tau$  [4% in (CD<sub>3</sub>)<sub>2</sub>CO] — 2.22 [(OH)<sub>2</sub>], 1.84 (d, *J* 2, H-2 and H-2'), 2.17 (q, *J*<sub>1</sub> 9, *J*<sub>2</sub> 2, H-6 and H-6'), 3.00 (d, *J* 9, H-5 and H-5'), and 7.28 (Me<sub>2</sub>).

We thank the British Council for a Fees Award (to A.-u.-h. C.).

[3/1666 Received, 6th August, 1973]