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# A New Synthesis of 3-Hydroxy-2,5-dialkyl-1,4-benzoquinone from 3-Halo-3,6-dialkyl-1,2-cyclohexanedione Using Iodine–Copper(II) Acetate

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The reaction of 3-iodo-3,6-dialkyl-1,2-cyclohexanedione (**2**) with iodine–copper(II) acetate in acetic acid–water (5:1) at 80 °C gave the respective 3-hydroxy-2,5-dialkyl-1,4-benzoquinone in 38—80% yields. On the other hand, the reaction of **2** with copper(II) acetate in acetic acid–water (10:1) under refluxing afforded the respective 3,3′-dihydroxy-2,2′,5,5′-tetraalkyl-4,4′-diphenoquinone (**5**) in 41—85% yields. In the case of 3-bromo-3,6-dialkyl derivative (**3**) with copper(II) acetate, the diphenoquinone derivatives and 3-hydroxy-2,5-dialkyl-1,4-benzoquinone were obtained.

3-Hydroxy-2,5-dialkyl-1,4-benzoquinones are important as intermediates,[1–4] and hydroxy-1,4-benzoquinone derivatives are known as natural products.[5–9] Much work has been reported on the syntheses of 3-hydroxy-2,5-dialkyl-1,4-benzoquinone.[1,2,10,11] However, all of these methods give only a low yield and involve several steps in preparing the starting materials. Diphenoquinone derivatives and 3,3′-dihydroxy-4,4′-diphenoquinones, both those having and not having alkyl groups, are often used as dyes, possessors of biological activity, electron acceptors, and synthetic intermediates.[12] 3,3′-Dihydroxy derivatives are prepared by one of the following methods: the reaction of 2-hydroxy-5-methoxybenzaldehyde with hydrogen peroxide–sodium hydroxide;[13] the reaction of 3-hydroxy-2,5-dimethyl-1,4-benzoquinone with boron trifluoride etherate;[3] or the Ullmann Reaction of 4-iodoveratrole.[14] Though these methods involve several steps to prepare the starting materials, they have been little afforded 3,3′-dihydroxy-2,2′,5,5′-tetraalkyl-4,4′-diphenoquinone. There has been no information concerning a direct synthesis from the cyclic 1,2-diketone derivative. In connection with our studies, we have found that iodine–copper(II) acetate in acetic acid is a useful reagent for the syntheses of some iodo compounds.[16] In a previous paper[17] we reported on a new synthesis of 3-hydroxy-2,5-dialkyl-1,4-benzoquinones using iodine–copper(II) acetate.

In the present paper we would like to report that the reaction of 3-bromo- and 3-iodo-3,6-dialkyl-1,2-cyclohexanedione with iodine–copper(II) acetate or copper(II) acetate in acetic acid–water gave the corresponding 3-hydroxy-2,5-dialkyl-1,4-benzoquinone or 3,3′-dihydroxy-2,2′,5,5′-tetraalkyldiphenoquinone, respectively.

The reaction of **2c**—**2e** with iodine (0.5 mol equiv)–copper(II) acetate (1.0 mol equiv) in acetic acid–water (5:1) at 80 °C for 5 h gave the 3-hydroxy-2,5-dialkyl-1,4-benzoquinone (47% for **4c**; 67% for **4d** and **4′d**; and 38% for **4e**). These 1,4-benzoquinones showed IR absorption at 3288—3296 (OH), 1656—1668 (C=O), 1634—1640 (C=O), and 1614—1616 cm$^{-1}$ (C=C) in their IR spectra. The IR and UV spectra indicated that they had *p*-quinonoid structures with a hydroxyl group in the molecule. The $^1$H NMR spectra of these hydroxy-1,4-benzoquinones (**4c**—**4e**) showed a doublet at $\delta$ 6.42 ($J$=0.70 Hz) for **4c**, a triplet at $\delta$ 6.49 ($J$=1.71 Hz) for **4d**, and a triplet at $\delta$ 6.46 ($J$=1.0 Hz) for **4e** assignable to the C$_6$-H. Compound **4′d** showed a doublet at $\delta$ 2.07 ($J$=1.71 Hz) and a triplet at $\delta$ 6.49 ($J$=1.71 Hz) in the $^1$H NMR spectrum. Therefore, **4c**, **4d**, and **4e** were presumed to be 3-hydroxy-2,5-dialkyl-1,4-benzoquinone and **4′d** was presumed to be 5-hydroxy derivative. These were also supported by the $^{13}$C NMR spectral data.

The reaction of 3-iodo-1,2-diketone (**2a**, **2b**, **2c**, **2d**, and **2e**) with copper(II) acetate (1.5 mol equiv.) in acetic acid–water (10:1) under refluxing for 4 h yielded reddish crystals (**5a**, **5b**, **5c**, **5d**, and **5e**) in a 41—82% yield, and 3-hydroxy-1,4-benzoquinones (**4a**, **4b**, **4c**, and **4e**) in a 3—14% yield. These compounds showed absorption at 3440—3480 (OH), 1650—1654 (C=O), 1636—1642 (C=O), and 1594—1600 cm$^{-1}$ (C=C) in their IR spectra. The $^1$H NMR spectra of these compounds showed a singlet at $\delta$ 6.89—7.00 due to the CH of the *p*-quinonoid structure. The UV spectra showed absorption at 406 nm due to diphenoquinone.

On the basis of the IR, $^1$H NMR, UV, and HRMS spectral data for **5a**, **5b**, **5c**, **5d**, and **5e**, the structures of these diphenoquinones were determined to be 3,3′-dihydroxy-2,2′,5,5′-tetraalkyl-4,4′-diphenoquinone.

Table 1. Products and Isolated Yields (%) in the Reaction of 3-Iodo-1,2-cyclohexanedione (**2a**—**2e**) with Iodine–Copper(II) Acetate

$$\mathbf{2}\ \xrightarrow[\text{AcOH-H}_2\text{O}]{\text{I}_2\text{-Cu(OAc)}_2}\ \mathbf{4}$$

| Substrate | Products (%) |
|---|---|
| **2a** | **4a** (80) |
| **2b** | **4b** (50) **7b** (34) |
| **2c** | **4c** (47) |
| **2d** | **4d,4′d** (67)[a] |
| **2e** | **4e** (38) |

a) **4d**:**4′d**=60:40.

Table 2. Products and Isolated Yields (%) in the Reaction of 3-Iodo- (**2a**—**2e**) and 3-Bromo-1,2-cyclohexanedione (**3a**—**3e**) with Copper(II) Acetate

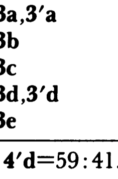
$$\mathbf{2} \text{ or } \mathbf{3} \xrightarrow[\text{AcOH-H}_2\text{O}]{\text{Cu(OAc)}_2} \mathbf{4}+\mathbf{5}$$

| Substrate | Products (%) | |
|---|---|---|
| **2a** | **4a** (3) | **5a** (43) |
| **2b** | **4b** (5) | **5b** (41) |
| **2c** | **4c** (12) | **5c** (82) |
| **2d** | **4d** (1) | **5d** (72) |
| **2e** | **4e** (14) | **5e** (44) |
| **3a,3′a** | **4a** (19) | **5a** (25) |
| **3b** | **4b** (22) | **5b** (21) |
| **3c** | **4c** (16) | **5c** (16) |
| **3d,3′d** | **4d,4′d** (8)[a] | **5d** (60) |
| **3e** | **4e** (15) | **5e** (41) |

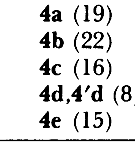
a) **4d**:**4′d**=59:41.

These were also supported by the $^{13}$C NMR spectral data. The oxidation of 3,3′,4,4′-tetrahydroxy-2,2′,5,5′-tetraalkylbiphenyl (**8a** and **8b**) produced as an intermediate with copper(II) acetate yielded the diphenoquinone derivative (**5a** and **5b**).

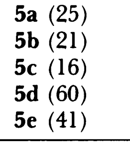
On the other hand, to investigate the properties of other halogen, the reaction of 3-bromo-1,2-diketone (**3a**, **3b**, **3c**, **3d**, and **3e**) with copper(II) acetate was carried out. These reactions gave the hydroxyquinone (8—22%) and diphenoquinone (16—60%). In the case of diosphenol (**1a**) with bromine–copper(II) acetate, the hydroxyquinone (**4a**) (21%) was obtained. It seemed that these results indicated our previously proposed reaction pathway: 3-iodo-3,6-dialkyl-1,2-diketone⟶3,6-dialkyl-1,2-benzenediol⟶4-iodo derivative⟶4-hydroxy-1,2-diketone⟶3-hydroxy-1,4-benzoquinone. It is assumed that copper(I) iodide can not recycle, but copper(II) bromide is given by the reaction of copper(I) bromide and hydrogen bromide produced with oxygen in the air. Therefore, in the case of 3-bromo-1,2-diketone, it seemed that a considerable sum of hydroxy-1,4-benzoquinone was yielded by the reaction pathway mentioned above. In the absence of halogen, the coupling reaction occurs preferentially, rather than the following pathway: halogenation⟶hydrolysis⟶oxidation.



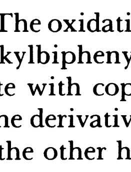
1a-1e



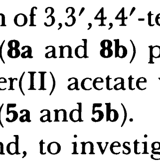
2a-2e (X=I)
3a-3e (X=Br)



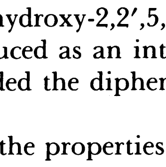
3'a,3'd



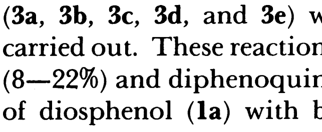
4a-4e



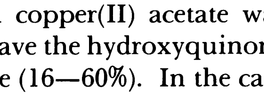
4'd



7b



8a,8b



5a-5e

a: $R_1$ =Me, $R_2$ =i-Pr
b: $R_1$ = $R_2$ =Me
c: $R_1$ =Me, $R_2$ =Cyclohexyl
d: $R_1$ =Me, $R_2$ =Et
e: $R_1$ = $R_2$ =Et

## Experimental

All the melting points are uncorrected. The IR apectra were measured using a Hitachi Model 270-30 grating infrared spectrometer. The NMR spectra were measured using JEOL FX 200 Model Spectrometer in deuteriochloroform with TMS as an internal standard. The high-resolution mass spectra were recorded at 75 eV on a JEOL JMS-O1SG-2 instrument with a direct inlet.

**3,6-Dialkyl-1,2-cyclohexanedione (1a—1e).** These compounds (**1a**—**1e**) were synthesized by the methods described in the literature.[18]

**3-Iodo-3,6-dialkyl-1,2-cyclohexanedione (2a—2e).** Diosphenol (**1a**) (0.50 g) in acetic acid-water (5:1) (48 ml) was treated with iodine (0.80 g) and copper(II) acetate (0.65 g) at room temperature for 8 h. The precipitated copper(I) iodide was removed by filtration, and the solvent was then removed under reduced pressure. The residue was poured into water and extracted with ether. The ethereal solution was washed successively with aqueous sodium hydrogencarbonate and with water, dried, and concentrated. Crystallization of the residue from ethanol gave needles of **2a** (0.80 g) (83%), mp 85—87 °C.[17]

**2b**: Yield 80%, mp 109—110 °C.[17]

**2c**: Yield 76%, mp 97—98 °C; IR (KBr): 3440, 1658, and 1624 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$=2.11 (s, 3H), 2.75 (m, 1H), and 6.10 (s, 1H); $^{13}$C NMR (CDCl$_3$): $\delta$=190.6, 138.8, 138.2, 46.0, 41.6, 38.8, 30.9, 30.0, 29.4, 26.2, 26.1, 26.0, and 25.4. Found: *m/z* 334.042. Calcd for $C_{13}H_{19}O_2I$: M, 334.043.

**2d**: Yield 67%; mp 81—83 °C; IR (KBr): 3440, 1670, and 1626 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$=0.96 (t, 3H), 1.94 (s, 3H), 2.04 (m, 2H), and 6.10 (s, 1H); $^{13}$C NMR (CDCl$_3$): $\delta$=189.4, 140.7, 130.0, 54.8, 37.1, 34.8, 30.8, 17.0, and 11.4. Found: *m/z* 279.995. Calcd for $C_9H_{13}O_2I$: M, 279.996.

**2e**: Yield 67%, mp 81—83 °C; IR (KBr): 3428, 1662, and 1630 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$=1.00 (t, 3H), 1.10 (t, 3H), 1.93 (m, 2H), 2.40—2.55 (m, 2H), and 6.12 (s, 1H); $^{13}$C NMR (CDCl$_3$): $\delta$=189.8, 140.1, 135.0, 55.0, 37.2, 34.8, 28.4, 24.0, 11.5, and 11.3. Found: *m/z* 294.012. Calcd for $C_{10}H_{15}O_2I$: M, 294.012.

**3-Bromo-3,6-dialkyl-1,2-cyclohexanedione (3a—3e).** Diosphenol (**1a**) (1.00 g) in acetic acid (50 ml) was treated with bromine (0.997 g) at room temperature for 5 min. After the usual work-up, the resulting oil, upon crystallization from ethanol, gave mixtures (60:40) of 3-bromo- (**3a**) and 6-bromo-3-methyl-6-isopropyl-1,2-cyclohexanedione (**3′a**) (1.440 g) (98%), mp 51—53 °C; IR (KBr): 3440, 1660, and 1634 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$=0.93 (d, 3H), 1.06 (d, 3H), 1.10 (d, 3H), 1.17 (d, 3H), 1.92 (s, 3H), 1.94 (d, 3H), 2.81 (m, 1H), 3.17 (m, 1H), 6.08 (s, 1H), and 6.14 (s, 1H); $^{13}$C NMR (CDCl$_3$): δ=188.9, 187.9, 141.7, 139.7, 139.4, 130.5, 39.4, 34.7, 29.9, 28.1, 28.0, 27.9, 21.8, 19.9, 19.4, 18.3, 18.1, and 17.1. Found: *m/z* 246.027. Calcd for $C_{11}H_{15}O_2Br$: M, 246.026.

**3b:** Yield 95%; mp 99—101 °C; IR (KBr): 3436, 1668, and 1632 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ=1.940 (s, 3H), 1.942 (s, 3H), and 6.05 (br s, 1H); $^{13}$C NMR (CDCl$_3$): δ=188.2, 140.8, 131.0, 61.1, 39.2, 28.6, 27.9, and 17.1; MS *m/z* 218 (M$^+$) and 220 (M+2).

**3c:** Yield 79%; mp 107—108 °C; IR (KBr): 3440, 1668, and 1630 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ=1.92 (s, 3H), 2.80 (m, 1H), and 6.04 (s, 1H); $^{13}$C NMR (CDCl$_3$): δ=188.9, 139.5, 134.8, 61.1, 39.4, 38.8, 29.9, 29.5, 27.9, 26.18, 26.12, 26.06, and 22.8. Found: *m/z* 286.051. Calcd for $C_{13}H_{19}O_2Br$: M, 286.057.

**3d, 3′d:** Yield 89% (**3d**:**3′d**=60:40); mp 67—70 °C, 75—77 °C; IR (KBr): 3444, 1668, 1641, and 1630 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ=1.02 (t, 3H), 1.10 (t, 3H), 1.94 (s, 3H), 1.95 (s, 3H), 6.04 (s, 1H), and 6.08 (s, 1H); $^{13}$C NMR (CDCl$_3$): δ=188.6, 188.0, 141.3, 140.1, 136.2, 130.8, 67.0, 61.2, 39.4, 35.1, 32.4, 28.3, 27.9, 26.1, 24.1, 17.1, 11.3, and 9.6. Found: *m/z* 232.006. Calcd for $C_9H_{13}O_2Br$: M, 232.010.

**3e:** Yield 99%; 86—89 °C; IR (KBr): 3436, 1668, and 1632 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ=1.02 (t, 3H), 1.10 (t, 3H), 1.98 (m, 2H), 2.45—2.57 (m, 2H), and 6.02 (s, 1H); $^{13}$C NMR (CDCl$_3$): δ=188.4, 140.7, 136.0, 67.1, 35.2, 32.4, 25.8, 24.1, 11.3, and 9.6. Found: *m/z* 246.024. Calcd for $C_{10}H_{13}O_2Br$: M, 246.026.

**Reaction of 3-Iodo-3-methyl-6-isopropyl-1,2-cyclohexanedione (2a) with Iodine–Copper(II) Acetate in Acetic Acid–Water.** A mixture of **2a** (200 mg), iodine (160 mg), and copper(II) acetate monohydrate (140 mg) in acetic acid–water (5:1) (12 ml) was stirred at 80 °C for 5 h. The precipitated copper(I) iodide was removed by filtration, and the solvent was then removed under reduced pressure. The residue was poured into water and extracted with ether. The ethereal solution was washed successively with aqueous sodium hydrogencarbonate and with water, dried, and concentrated. Crystallization of the residue from ethanol gave needles of **4a** (150 mg) (80%), mp 167—168 °C (lit,[17] 167—168 °C). The IR and $^1$H and $^{13}$C NMR spectra[15] were identical with those of an authentic sample.

**4b:** Yield 50%; mp 138—140 °C (lit,[10] 141—142 °C). The IR and $^1$H NMR spectra were identical with those of an authentic sample.

**4c:** Yield 47%; mp 130—132 °C; IR (KBr): 3296, 1668, 1640, and 1614 cm$^{-1}$; UV (EtOH): 270 (ε 1.08×10$^4$) and 425 nm (ε 0.97×10$^3$); $^1$H NMR (CDCl$_3$): δ=1.92 (s, 3H), 2.65 (m, 1H), 6.16 (s, 1H), and 6.42 (d, *J*=0.70 Hz, 1H); $^{13}$C NMR (CDCl$_3$): δ=194.0, 178.7, 151.7, 141.8, 132.3, 117.1, and 7.8. Found: *m/z* 220.112. Calcd for $C_{13}H_{16}O_3$: M, 220.110.

**4d, 4′d:** Yield 67% (**4d**:**4′d**=60:40); mp 124—126 °C; IR (KBr): 3288, 1658, 1634, and 1616 cm$^{-1}$; UV (EtOH): 266 (ε 1.31×10$^4$) and 405 nm (ε 1.39×10$^3$); $^1$H NMR (CDCl$_3$): δ=1.07 (t, 3H), 1.15 (t, 3H), 1.94 (s, 3H), 2.07 (d, *J*=1.71 Hz, 3H), 2.40—2.54 (m, 4H), 6.49 (t, *J*=1.71 Hz, 1H), and 7.02 (br s, 2H); $^{13}$C NMR (CDCl$_3$): δ=184.4, 183.7, 151.4, 146.3, 133.6, 117.1, 21.4, 12.6, and 7.9 (for **4d**); δ=184.4, 183.7, 150.9, 141.0, 135.4, 122.6, 16.1, 14.8, and 11.6 (for **4′d**). Found: *m/z* 166.065. Calcd for $C_9H_{10}O_3$: M, 166.063.

**4e:** Yield 38%; mp 115—116 °C; IR (KBr): 3288, 1656, 1634, and 1614 cm$^{-1}$; UV (EtOH): 266 (ε 1.31×10$^4$) and 405 nm (ε 1.39×10$^3$); $^1$H NMR (CDCl$_3$): δ=1.00 (m, 6H), 2.48 (m, 4H), 6.46 (t, *J*=1.0 Hz, 1H), and 6.98 (s, 1H); $^{13}$C NMR (CDCl$_3$): δ=187.6, 183.9, 150.8, 146.1, 133.8, 122.5, 21.4, 16.1, 12.6, and 11.6. Found: *m/z* 180.080. Calcd for $C_{10}H_{12}O_3$: M, 180.079.

**Reaction of 3-Isopropyl-6-methyl-1,2-benzenediol (6) with Iodine–Copper(II) Acetate in Acetic Acid–Water (5:1).** A mixture of **6** (109 mg), iodine (173 mg), and copper(II) acetate monohydrate (130 mg) in acetic acid–water (5:1) (12 ml) was stirred at 80 °C for 1 h. After the usual work-up, the resulting oil, upon crystallization from ethanol, gave **4a** as needles (101 mg), mp 167—168 °C.

**Reaction of 4-Iodo-3,6-dimethyl-1,2-benzenediol (7d) with Iodine–Copper(II) Acetate in Acetic Acid–Water.** A mixture of **7** (3.0 mg), iodine (1.5 mg), and copper(II) acetate (2.2 mg) in acetic acid–water (5:1) (0.3 ml) was stirred at 80 °C for 4 h. After the usual work-up, the resulting oil, upon crystallization from ethanol, gave **4b** as needles (0.9 mg), mp 138—140 °C.

**Reaction of 3-Iodo-3-methyl-6-isopropyl-1,2-cyclohexanedione (2a) with Copper(II) Acetate in Acetic Acid–Water.** 3-Iodo-1,2-diketone (**2a**) (300 mg) in acetic acid–water (10:1) (25 ml) was treated with copper(II) acetate (305 mg) under refluxing for 4 h. The precipitated copper(I) iodide was removed by filtration, and the solvent was then removed under reduced pressure. The residue was poured into water and extracted with chloroform. After a similar work-up, the resulting oil (217 mg) was chromatographed on silica gel (25 g). Elution with benzene–chloroform (5:1) (120 ml) gave 3-hydroxythymo-1,4-quinone (**4a**) as needles (6 mg) from ethanol, mp 167—168 °C. The second fraction, eluted by the same solvent (320 ml) gave 3,3′-dihydroxy-2,2′-dimethyl-5,5′-diisopropyl-4,4′-diphenoquinone (**5a**) as needles (72 mg) from ethanol, mp 238—240 °C; IR (KBr): 3470, 1650, 1640, 1594, and 840 cm$^{-1}$; UV (CHCl$_3$): 245 (ε 1.09×10$^4$) and 406 nm (ε 4.57×10$^3$); $^1$H NMR (CDCl$_3$): δ=1.32 (t, 12H), 1.60 (br s, 2H), 2.08 (s, 3H), 2.36 (s, 3H), 3.46 (m, 2H), and 7.00 (s, 2H); $^{13}$C NMR (CDCl$_3$): δ=179.5, 149.4, 135.0, 126.0, 124.4, 121.2, 26.7 (24.6), 22.7 (20.2), and 14.7. Found: *m/z* 328.168. Calcd for $C_{20}H_{24}O_4$: M, 328.168.

**Reaction of 3-Iodo-3,6-dimethyl-1,2-cyclohexanedione (2b) with Copper(II) Acetate in Acetic Acid–Water.** By practically the same method as that in the case of **2a** above, **2b** (300 mg) was treated with copper(II) acetate. After the usual work-up, the resulting oil (185 mg) was chromatographed on silica gel (25 g). Elution with benzene–chloroform (5:1) (250 ml) gave 3-hydroxy-2,5-dimethyl-1,4-benzoquinone (**4b**),as needles (9 mg) from ethanol, mp 138—140 °C. The second fraction, eluted by the same solvent (160 ml) gave 4-iodo-3,6-dimethyl-1,2-benzenediol (**7**) as needles (14 mg) from ethanol, mp 88—90 °C.[17] The third fraction, eluted by the same solvent (200 ml), on crystallization from ethanol gave 3,3′-dihydroxy-2,2′,5,5′-tetramethyl-4,4′-diphenoquinone (**5b**) as reddish needles (64 mg), mp 238—239 °C; IR (KBr): 3450, 1654, 1642, 1606, and 836 cm$^{-1}$; UV (CHCl$_3$): 246 (ε 1.96×10$^4$) and 406 nm (ε 8.87×10$^3$); $^1$H NMR (CDCl$_3$): δ=1.59 (br s, 6H), 2.12 (s, 6H), 2.40 (s, 6H), and 6.96 (s, 2H); $^{13}$C NMR (CDCl$_3$): δ=181.8, 150.0, 139.5, 131.1, 126.4, 124.6, 14.7, and 7.7. Found: *m/z* 272.104. Calcd for $C_{16}H_{16}O_4$: M, 272.105.

**Reaction of 3-Iodo-6-cyclohexyl-3-methyl-1,2-cyclohexanedione (2c):** The 3-iodo-1,2-dione (**2c**) (275 mg) in acetic acid–water was treated with copper(II) acetate to give 23 mg of **4c** and 147 mg of **5c**.

**5c**: Reddish needles; mp 237—240 °C; IR (KBr): 3480, 1654, 1642, 1594, and 840 cm$^{-1}$; UV (CHCl$_3$): 244 ($\varepsilon$ 1.92×10$^4$) and 406 nm ($\varepsilon$ 8.16×10$^3$); $^1$H NMR (CDCl$_3$): $\delta$=1.61 (br s, 2H), 2.07 (s, 3H), 2.35 (s, 3H), 3.11 (m, 2H), and 6.98 (s, 2H); $^{13}$C NMR (CDCl$_3$): $\delta$=177.3, 148.0, 132.2, 124.5, 123.1, 120.5, and 7.8. Found: $m/z$ 408.230. Calcd for $C_{26}H_{32}O_4$: M, 408.230.

**Reaction of 3-Iodo-6-ethyl-3-methyl-1,2-cyclohexanedione (2d):** The 3-iodo-1,2-dione (**2d**) (85 mg) in acetic acid–water was treated with copper(II) acetate. After a similar work-up, the resultant oil was chromatographed on silica gel (25 g). Elution with benzene–chloroform (10:1) (150 ml) gave 3,3′-dihydroxy-5,5′-diethyl-2,2′-dimethyl-4,4′-diphenoquinone (**5d**) as reddish needles (33 mg), mp 184—187 °C; IR (KBr): 3440, 1652, 1625, 1600, and 840 cm$^{-1}$; UV (CHCl$_3$): 245 ($\varepsilon$ 2.18×10$^4$) and 406 nm ($\varepsilon$ 9.57×10$^3$); $^1$H NMR (CDCl$_3$): $\delta$=1.15 (t, 3H), 1.28 (t, 3H), 1.54 (s, 2H), 2.11 (s, 3H), 2.38 (s, 3H), 2.64 (q, 2H), 2.77 (q, 2H), and 6.95 (s, 2H); $^{13}$C NMR (CDCl$_3$): $\delta$=179.2, 149.1, 135.8, 130.2, 124.1, 121.1, 22.4, 14.7, and 7.8. Found: $m/z$ 300.135. Calcd for $C_{18}H_{20}O_4$: M, 300.136.

**Reaction of 3-Iodo-3,6-diethyl-1,2-cyclohexanedione (2e):** The 3-iodo-1,2-dione (**2e**) (483 mg) in acetic acid–water was treated with copper(II) acetate to give 44 mg of **4e** and 115 mg of **5e**.

**5e**: Reddish needles; mp 185—188 °C; IR (KBr): 3454, 1654, 1636, 1598, and 848 cm$^{-1}$; UV (CHCl$_3$): 245 ($\varepsilon$ 2.18×10$^4$) and 406 nm ($\varepsilon$ 9.46×10$^3$); $^1$H NMR (CDCl$_3$): $\delta$=1.15 (t, 6H), 1.31 (t, 6H), 1.71 (br s, 2H), 2.65 (q, 4H), 2.79 (q, 4H), and 6.89 (s, 2H); $^{13}$C NMR (CDCl$_3$): $\delta$=178.5, 148.6, 135.4, 129.9, 124.0, 120.6, 22.2, 15.9, 14.0, and 12.6. Found: $m/z$ 328.168. Calcd for $C_{20}H_{24}O_4$: M, 328.168.

**Reaction of 3,3′,4,4′-Tetrahydroxy-2,2′,5,5′-tetraalkylbiphenyl (8a,8b) with Copper(II) Acetate.** The tetrahydroxybiphenyl (**8a** and **8b**) (50 mg) in acetic acid–water was treated with copper(II) acetate. After the usual work-up, crystallization from ethanol afforded needles of **5a** (46 mg), mp 238—240 °C and **5b** (44 mg), mp 238—239 °C.

**Reaction of Diosphenol (1a) with Bromine and Copper(II) Acetate in Acetic Acid-Water.** The diosphenol (**1a**) (600 mg) in acetic acid–water (5:1) (60 ml) was treated with bromine (570 mg) and copper(II) acetate (712 mg) under refluxing for 5 h. After the usual work-up, the resulting oil (552 mg) was chromatographed on silica gel (25 g). Elution with benzene–ether (10:1) (220 ml) gave **4a** as needles (134 mg), mp 167—168 °C.

**Reaction of 3-Bromo-3,6-dialkyl-1,2-cyclohexanedione (3a—3e) with Copper(II) Acetate in Acetic Acid-Water. General Procedure.** A mixture of 3-bromo-1,2-diketone (**3a**—**3e**) (1.00×10$^{-3}$ mol), copper(II) acetate monohydrate (1.50×10$^{-3}$mol), and acetic acid–water (10:1) (16.5 ml) was stirred under refluxing for 4 h. After the usual work-up, the resulting oil was chromatographed on silica gel. Elution with benzene–chloroform (4:1) gave orange and reddish crystals from ethanol. These results are summarized in Table 2.

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