Oxidation of Hydroquinones with Oxygen in the Presence of Bis(1,3-propanediaminato)copper(II) Chloride

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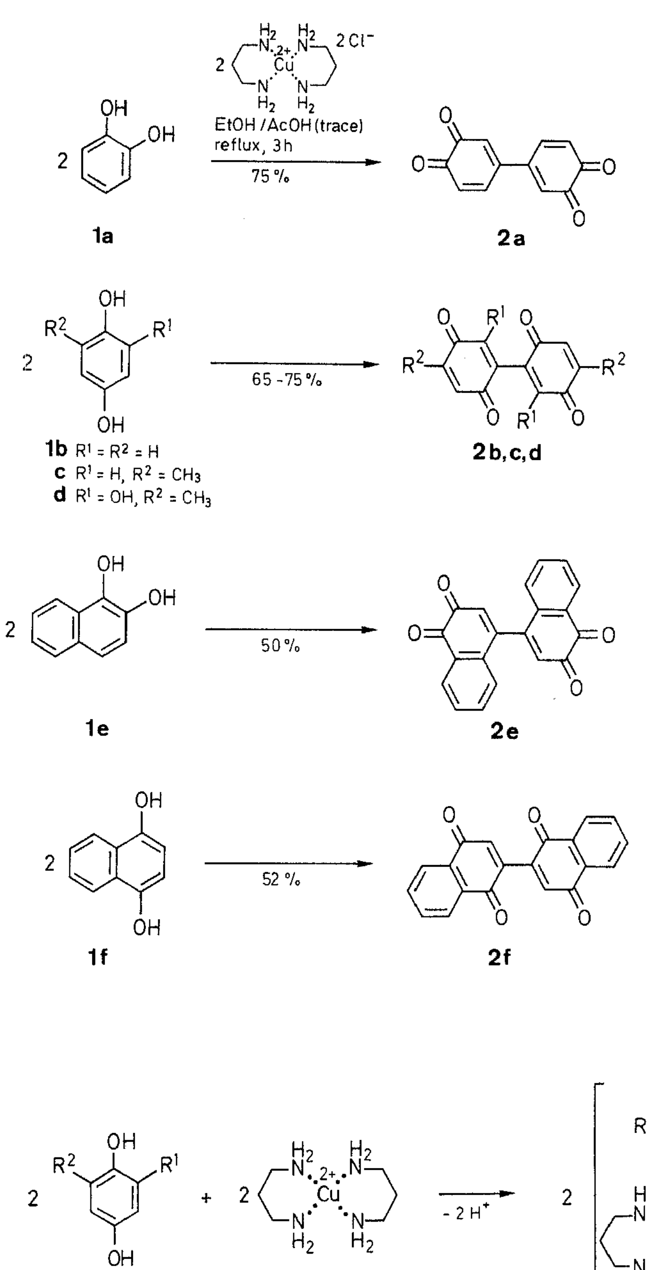
Treatment of hydroquinones such as 1,2-dihydroxybenzene, 1,4-dihydroxybenzene and its 2-methyl derivative, 1,2,4-trihydroxy-6-methylbenzene, 1,2- and 1,4-dihydroxynaphthalene with oxygen in ethanol in the presence of bis(1,3-propanediaminato)copper(II) chloride and a few drops of acetic acid effects oxidative *C—C* coupling plus oxidation of the hydroquinone to the quinone system to afford the corresponding biquinones in yields exceeding 75%.

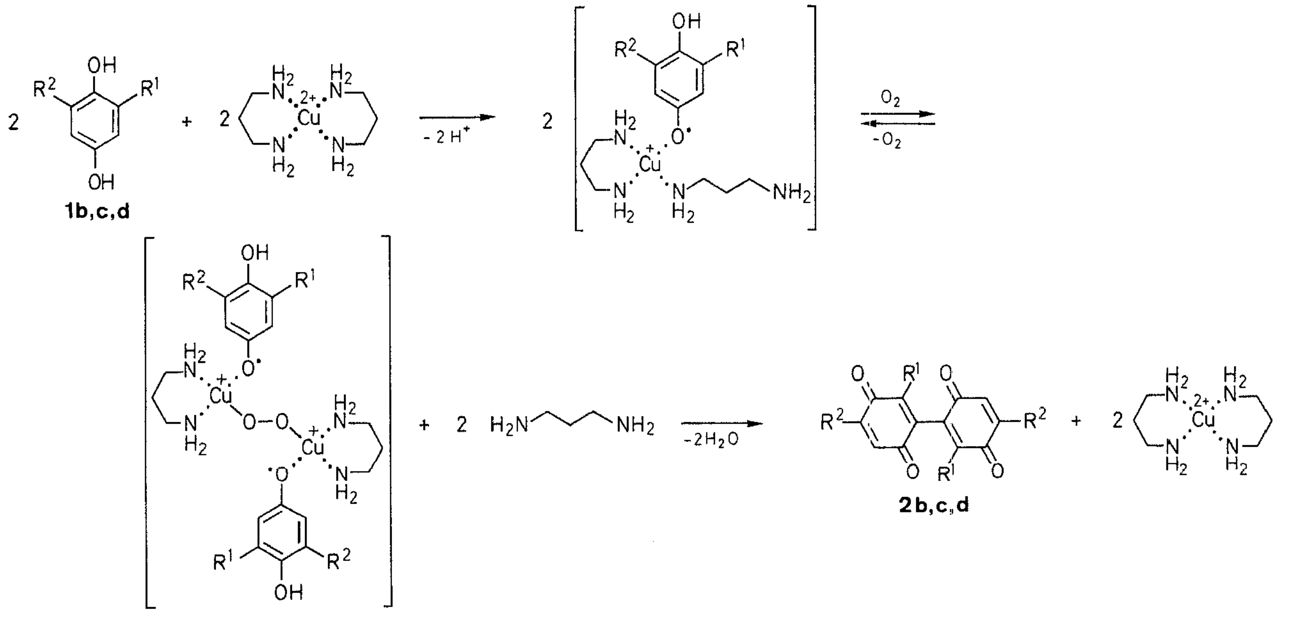
Diamine-copper complexes are known to catalyze the oxidative coupling of substituted phenols by means of air or oxygen.[1,2] However, a systematic investigation of the influence of the chain length of the 1,ω-diamines in the complex on the yield of the "dimeric" products of oxidative *C—C* coupling seems to have hitherto not been published.

Our previous studies on the oxidation of substituted 1,4-dihydroxybenzenes as well as 1,2- and 1,4-dihydroxynaphthalenes in the presence of diamine copper complexes have shown that the reaction products are the corresponding bi-benzoquinones and bi-naphthoquinones, respectively. Results of kinetic measurements and of mechanistic studies on the activity of the copper(II) complexes[3,4] are already known.

We submitted the five hydroquinones **1a–f** to the reaction with oxygen in boiling ethanol containing an equimolecular amount of bis(1,3-propanediaminato)copper(II) chloride and a trace of acetic acid. Work-up after a reaction time of 3 h afforded the biquinones **2a–f** in yields of 50–75%. When oxygen was passed through the solution of hydroquinones **1** in the absence of the diamine-copper complex, formation of biquinones **2** was not observed; instead, the corresponding benzoquinones and naphthoquinones were obtained in low yield (7–10%).



From ESR-spectrometric studies,[5] we concluded that the reaction proceeds via copper-complexed aroxyl radicals as intermediates (formed by one-electron transfer from the aroxide anion to Cu^{++}), probably as outlined in the following scheme for the oxidative coupling of 1,4-dihydroxybenzenes **1b, c, d**.



All compounds prepared were compared (mp, IR and ^{1}H-NMR spectra) with authentic compounds prepared by known methods and their molecular weights determined kryoscopically. IR spectra were obtained using a Perkin-Elmer 521 spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian XL 200 MHz spectrometer and ESR spectra on a Varian E-4 apparatus.

The dihydroxybenzenes and -naphthalenes were purchased from Fluka and were "puris" grade; they were sublimated in high vacuum before use. The $CuCl_2 \cdot 2H_2O$ used was purchased from Merck & Co. and was of "pro analysi" grade. Anhydrous $CuCl_2$ was prepared by heating the dihydrate at 100°C for 20 h. 1,3-Propanediamine was purchased from Fluka and was of "puris" grade; it was dried with KOH and distilled in the absence of moisture.

Bis(1,3-propanediaminato)copper(II) Chloride:[8]

A solution of anhydrous $CuCl_2$ (1.34 g, 0.01 mol) and dry 1,3-propanediamine (1.5 g, 0.02 mol) in anhydrous EtOH (25 mL) is heated at reflux temperature for 15 min. Anhydrous Et_2O is then added until a blue precipitate forms; this is isolated by filtration under N_2 and dried over P_2O_5 at 100°C; yield: 2.75 g (97%).

		C	H	N	Cl	Cu
$C_6H_{20}N_4 \cdot CuCl_2$	calc.	25.48	7.08	19.82	25.13	22.49
(282.5)	found	25.32	7.02	19.75	25.10	22.36

IR (KBr): ν = 3120 sh, 3100 (NH_2); 945 (CH_2); 248 (N–Cu–N) cm^{-1}.

UV/Vis (EtOH): λ_{max} = 560 nm.

^{1}H-NMR (D_2O/TMS_{ext}): δ = 1.4, 2.8 (2 s, 20 H, $2(CH_2)_3 + 4NH_2$).

3,3′,6,6′-Tetraoxobi(1,4-cyclohexadien-1-yl) [2b; 2,2′-Bi(1,4-benzoquinone]; Typical Procedure:

Hydroquinone (**1b**; 1.10 g, 0.01 mol) and bis(1,3-propanediaminato)copper(II) chloride (2.38 g, 0.01 mol) are dissolved in anhydrous EtOH (50 mL) and AcOH (a few drops) is added. The mixture is heated at reflux temperature while a stream of O_2 is passed through it for 3 h. The solution becomes chestnut-colored and a black precipitate is formed. The precipitate is filtered off, dried, and stirred with acetone/EtOH (1:1; 50 mL) to remove resinous material and byproducts of unknown constitution (possibly humic compounds[9]). The precipitate is dissolved in hot nitrobenzene (30 mL). This solution is decolorized with charcoal, filtered while hot, and allowed to cool. The chestnutcolored product **2b** which crystallized is isolated by suction and dried at 180 °C for 3 h; yield: 1.60 g (75%); mp 230 °C (Lit.[10] mp 228 °C).

$C_{12}H_6O_4$	calc.	C 50.70	H 4.22	O 45.07
(214.2)	found	50.68	4.19	45.02

IR (KBr): ν = 1660 (C=O); 1602, 1510 (C=C) cm^{-1}.

^{1}H-NMR (CDCl$_3$/TMS): δ = 6.72, 6.55 (2 s, 6H, each).

5,5′,6,6′-Tetraoxobi(1,3-cyclohexadien-2-yl) [2a; 4,4′-Bi(1,2-benzoquinone)]:
Prepared from pyrocatechol (**1a**; 1.10 g, 0.01 mol) and dried at 80 °C; yield: 1.60 g (75%); red crystals, mp 136 °C (dec) (mp not given in Lit.[10]).

$C_{12}H_6O_4$	calc.	C 50.70	H 4.22	O 45.07
(214.2)	found	50.65	4.20	45.15

IR (KBr): ν = 1660 (C=O); 1602, 1490 (C=C) cm^{-1}.

^{1}H-NMR (CDCl$_3$/TMS): δ = 6.72, 6.50 (2 s, 6 H each).

4,4′-Dimethyl-3,3′,6,6′-tetraoxobi(1,4-cyclohexadien-1-yl) (2c):
Prepared from methylhydroquinone (**1c**; 1.24 g, 0.01 mol) and dried at 100 °C; yield: 1.82 g (75%); dark yellow crystals, mp 162 °C (Lit.[11] mp 163 °C).

$C_{14}H_{10}O_4$	calc.	C 69.42	H 4.13	O 26.35
(242.2)	found	69.36	4.09	26.55

IR (KBr): ν = 1658, 1649 (C=O); 1585, 1480 (C=C) cm^{-1}.

^{1}H-NMR (DMSO-d_6/TMS): δ = 2.10 (s, 3 H, 2CH$_3$); 6.70, 6.58 (2 s, 4 H each).

2,2′-Dihydroxy-4,4′-dimethyl-3,3′,6,6′-tetraoxobi(1,4-cyclohexadien-1-yl) (2d; Phoenicin):
Prepared from 1,2,4-trihydroxy-6-methylbenzene (**1d**; 1.40 g, 0.01 mol) and dried at 120 °C; yield: 1.78 g (65%); chestnut-red crystals, mp 230 °C (dec) (Lit.[12] mp 230–231 °C, Lit.[13] dec 227–229 °C).

$C_{14}H_{10}O_6$	calc.	C 61.31	H 2.19	O 36.50
(274.2)	found	61.31	2.17	36.52

IR (KBr): ν = 3236 (OH); 1662, 1653 (sh) (C=O); 1647, 1611 (C=C) cm^{-1}.

^{1}H-NMR (DMSO-d_6/TMS): δ = 2.10 (s, 3 H, 2CH$_3$); 6.10 (s, 2 H each).

1,1′,2,2′-Tetraoxobi(1,2-dihydronaphthalen-4-yl) [2e;4,4′-Bi(1,2-naphthoquinone)]:
Prepard from 1,2-dihydroxynaphthalene (**1e**; 1.50 g, 0.01 mol) and dried at 160 °C; yield: 1.49 g (50%); yellow to orange-red crystals, mp 287 °C (Lit.[6] mp 289 °C).

$C_{20}H_{10}O_4$	calc.	C 81.08	H 4.70	O 14.22
(314.3)	found	80.99	4.68	14.33

IR (KBr): ν = 1685, 1610 (C=O); 1580, 1480 (C=C) cm^{-1}.

^{1}H-NMR (DMSO-d_6/TMS): δ = 6.95 (s, 2 H-2); 8.07 (s, 2 H-5, 2 H-8); 7.77 (s, 2 H-6, 2 H-7).

1,1′,4,4′-Tetraoxobi(1,4-dihydronaphthalen-2-yl)[2f;2,2′-Bi(1,4-naphthoquinone)]:
Prepared from 1,4-dihydroxynaphthalene (**1f**; 1.50 g, 0.01 mol) and dried at 150 °C; yield: 1.55 g (52%); yellow needles which become deep chestnut-colored above 270 °C and decompose at 273 °C with formation of foam [Lit.[6] mp 274–275 °C (dec)].

$C_{20}H_{10}O_4$	calc.	C 81.08	H 4.70	O 14.22
(314.3)	found	81.00	4.65	14.35

IR (KBr): ν = 1670, 1610 (C=O); 1589, 1480 (C=C) cm^{-1}.

^{1}H-NMR (DMSO-d_6/TMS): δ = 7.05 (s, 2 H-3); 8.07 (s, 2 H-5, 2 H-6); 7.77 (s, 2 H-6, 2 H-7).

Received: 31 March 1988; revised: 1 July 1988

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