

A Facile Synthesis of 4,5-Dialkoxy-*o*-benzoquinones by the Oxidation of Catechol with Iodates in Alcohol

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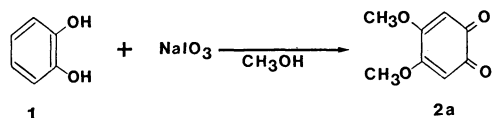
Synopsis. 4,5-Dimethoxy-*o*-benzoquinone has been prepared by the oxidation of catechol with sodium iodate in methanol. In higher alcohols, the same oxidation occurs in the presence of a crown ether to give the corresponding 4,5-dialkoxy-*o*-benzoquinones. In the latter cases using 18-crown-6, the potassium salt is more effective than the sodium salt.

o-Benzoquinone derivatives are conventionally prepared by the oxidation of the corresponding catechols. Wanzlick and Jahnke have reported the preparation of 4,5-dimethoxy- and 4,5-diethoxy-*o*-benzoquinones by the oxidation of catechol with lead(IV) oxide in methanol and ethanol, respectively, in the presence of alkoxide.¹⁾

In this note, a novel and simple method for the synthesis of 4,5-dialkoxy-*o*-benzoquinones from catechol will be reported using potassium and sodium iodates as oxidizing agents in alcohols from methyl to pentyl alcohol as solvents in the presence or absence of a crown ether. The products, except for dimethoxy and diethoxy derivatives, are unknown. 4-Substituted catechols have been oxidized with iodates to the corresponding quinones,^{2,3)} but to date there has been no report on the oxidation of unsubstituted catechol with the oxidants.

Results and Discussion

A mixture of catechol and two equivalents of sodium iodate in absolute methanol at 60 °C gradually darkened and became black after 20 h. Isolation by column chromatography gave 4,5-dimethoxy-*o*-benzoquinone (**2a**) in 58.3% yield. The structure of the quinone was elucidated from the spectral data and elemental analysis. The NMR spectrum of **2a** showed a singlet at $\tau=4.2$ (2H; olefinic protons at C-3 and C-6) and a singlet at $\tau=6.1$ (6H; methyl protons). The UV spectrum showed peaks at 413 nm ($\epsilon=560$) and 287 nm ($\epsilon=12500$). These data are consistent with those reported by Wanzlick and Jahnke.¹⁾



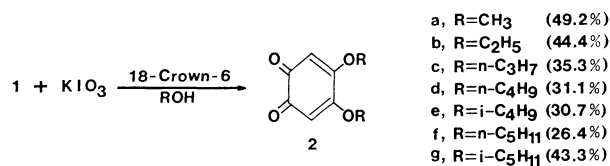
The use of potassium iodate as the oxidant decreased the yield of the quinone to 36.9%.

The oxidation of catechol with sodium or potassium iodate in ethanol gave 4,5-diethoxy-*o*-benzoquinone (**2b**) in very low yield (less than 2% in both cases). No reaction occurred in propyl and higher alcohols.

The observation that the yield of the quinone de-

creases with the length of the alcohol chain is ascribed to the decrease in the solubility of the iodates in alcohols. Crown ethers have been well-known to enhance the solubility of inorganic salts in organic solvents,^{4,5)} and consequently the effect of 18-crown-6 has been examined using potassium iodate as the oxidant. The addition of 18-crown-6 (2.33 mmol) to the mixture of catechol (10 mmol) and potassium iodate (20 mmol) in absolute methanol (100 ml) increased the yield of **2a** to 49.2%. The effect was more dramatic in ethanol. Under similar conditions, the addition of 1.25 and 2.73 mmol of the crown ether gave **2b** in 20.7 and 44.4% yields, respectively.

The same method was employed for the preparation of several 4,5-dialkoxy-*o*-benzoquinones in higher alcohols.



In primary alcohols, catechol reacted with iodate to give the corresponding dialkoxy-quinones. All of the quinones exhibited a singlet at $\tau=4.2$ in the NMR spectra and two peaks in the 413—416 and 289—291 nm region of the UV spectra.

In the alcohols which branched at the α -position of the hydroxyl group, *e.g.*, isopropyl and *t*-butyl alcohols, however, the reaction did not give the corresponding dialkoxy-*o*-benzoquinone derivative but a red amorphous solid. A similar product was obtained from the reaction in acetonitrile. In both cases, the IR spectrum of the product showed two absorption bands in the region of 1600—1700 cm⁻¹, possibly due to carbonyl groups. The solid however could not be purified because of the low solubility in organic solvents and a broad melting range.

There are few reports of the oxidation of substituted catechols by iodates to quinone derivatives in water and in water-alcohol mixtures during a short reaction period.^{2,3)} In such experiments here the products were complex substances which could not be separated.

Experimental

Melting points were determined with a Yamato Capillary Melting Point apparatus and are uncorrected. Proton magnetic resonance spectra were obtained on a JEOL Model JNM-C-HL spectrometer in deuterated chloroform. Electronic spectra were recorded on a Hitachi 124 spectrophotometer in ethanol. The alcohols were purified by distillation after drying over molecular sieves 4A. All other materials

were commercially available.

Preparation of 4,5-Dimethoxy-o-benzoquinone (2a). Sodium iodate (4.0 g, 20 mmol) was suspended in a solution of catechol (1.1 g, 10 mmol) in dry methanol (100 ml) and the mixture vigorously stirred for 20 h at 60 °C. After filtration, the filtrate was condensed on a rotary evaporator under reduced pressure to a volume of *ca.* 30 ml and cooled to -15 °C. The precipitate formed was filtered and washed with diethyl ether (50 ml). The precipitate was separated by column chromatography using silica gel (*ca.* 11 g) and chloroform. Evaporation of the solvent from the first orange elute gave orange needles (0.98 g, 58.3%), which were recrystallized from methanol: mp 230–233 °C (lit, 225–227 °C).¹⁾ Found: C, 57.85; H, 4.74%. Calcd for C₈H₈O₄: C, 57.15; H, 4.80%.

Preparation of 4,5-Diethoxy-o-benzoquinone (2b). Potassium iodate (4.3 g, 20 mmol) was suspended in a solution of catechol (1.1 g, 10 mmol) and 18-crown-6 (0.72 g, 2.73 mmol) in absolute ethanol (100 ml) and the mixture vigorously stirred for 20 h at 65 °C. After filtration, the alcohol was evaporated under reduced pressure and the residue extracted twice with benzene (100 ml). The combined extracts were filtered and concentrated. The residual red-brown substance was further extracted with diethyl ether (150 ml). The residue was separated by column chromatography using silica gel and chloroform. Evaporation of the solvent from the first orange elute gave orange needles (0.87 g, 44.4%), which were recrystallized from ethanol: mp 172–174.5 °C (lit, 175 °C).¹⁾ NMR (CDCl₃) τ =8.5 (6H, t), 5.9 (4H, q) and 4.25 (2H, s); UV_{max} (C₂H₅OH) 289 (ϵ =13700) and 416 nm (ϵ =535). Found: C, 61.60; H, 5.75%. Calcd for C₁₀H₁₂O₄: C, 61.22; H, 6.17%.

Preparation of the 4,5-Dialkoxy-o-benzoquinones. The method described for the preparation of diethoxy derivative (2b) was employed except that the reaction was conducted in the corresponding alcohol at 90–95 °C. The physical properties are as follows;

4,5-Dipropoxy-o-benzoquinone (2c). Mp 153–154.5 °C from CCl₄. NMR (CDCl₃) τ =8.95 (6H, t), 8.1 (4H, m), 6.0 (4H, t), and 4.25 (2H, s); UV_{max} (C₂H₅OH) 290 (ϵ =

14000) and 415 nm (ϵ =532). Found: C, 65.20; H, 7.25%. Calcd for C₁₂H₁₆O₄: C, 64.29; H, 7.19%.

4,5-Dibutoxy-o-benzoquinone (2d). Mp 140.5–142 °C from CCl₄. NMR (CDCl₃) τ =9.0 (6H, t), 8.1 (8H, m), 6.0 (4H, t), and 4.3 (2H, s); UV_{max} (C₂H₅OH) 291 (ϵ =12800) and 414 nm (ϵ =487). Found: C, 67.18; H, 8.20%. Calcd for C₁₄H₂₀O₄: C, 66.65; H, 7.99%.

4,5-Diisobutoxy-o-benzoquinone (2e). Mp 157.5–159 °C from CCl₄. NMR (CDCl₃) τ =8.95 (12H, d), 7.95 (2H, m), 6.25 (4H, t), and 4.3 (2H, s); UV_{max} (C₂H₅OH) 290 (ϵ =13800) and 414 nm (ϵ =512). Found: C, 66.29; H, 7.89%. Calcd for C₁₄H₂₀O₄: C, 66.65; H, 7.99%.

4,5-Bis(pentyloxy)-o-benzoquinone (2f). Mp 130–131 °C from CCl₄-petroleum ether. NMR (CDCl₃) τ =9.0 (6H, t), 8.4 (12H, m), 6.0 (4H, t), and 4.3 (2H, s); UV_{max} (C₂H₅OH) 291 (ϵ =13400) and 413 nm (ϵ =496). Found: C, 68.36; H, 8.99%. Calcd for C₁₆H₂₄O₄: C, 68.55; H, 8.63%.

4,5-Bis(isopentyloxy)-o-benzoquinone (2g). Mp 119–120 °C from CCl₄-petroleum ether. NMR (CDCl₃) τ =9.0 (12H, d), 8.25 (6H, m), 5.95 (4H, t), and 4.3 (2H, s); UV_{max} (C₂H₅OH) 290 (ϵ =13800) and 414 nm (ϵ =512). Found: C, 68.61; H, 8.72%. Calcd for C₁₆H₂₄O₄: C, 68.55; H, 8.63%.

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