

Benzoquinones and Related Compounds. Part 3.‡ Preparation of 1,4-Benzoquinones by Oxidation of Hydroquinones with Manganese Dioxide†

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Traditionally, silver oxide¹ has been the reagent of choice for the oxidation of hydroquinones to quinones; other oxidants² have been used occasionally. Manganese dioxide converts hydroquinone into 1,4-benzoquinone,^{3,4} and the activated⁵ material has been used for the preparation⁶ of 2-acetyl-5-methyl-6-nitro-1,4-benzoquinone. The formation of Diels–Alder adducts between 1,3-dienes and 3-acyl-1,2-benzoquinones generated *in situ* by oxidation of the corresponding catechols with manganese dioxide has also been described.

We now report that manganese dioxide is a convenient, and much cheaper, oxidant than silver oxide for the preparation of 1,4-benzoquinones from their hydroquinones, although it is less widely applicable.

The hydroquinones, in dry benzene, were oxidised by shaking with an excess of manganese dioxide. Activated^{5,8,9} material was inferior to commercial^{10,11} precipitated manganese dioxide in terms of quantity required, reaction time, and ease of work-up (filtration). Several different batches were used: all gave reproducible results (Table). Acetyl-, benzoyl-, and methoxycarbonyl-1,4-benzoquinones were suitable for use in preparative work^{2,12} without purification.

Although 5,8-dihydro-1,4-naphthoquinone was initially formed almost quantitatively (¹H n.m.r. monitoring using C₆D₆ as solvent), it was slowly converted into 1,4-naphthoquinone by disproportionation¹³ and oxidation. 4,5-Dimethylcatechol gave 4,5-dimethyl-1,2-benzoquinone, but attempts to prepare the parent quinone from catechol were unsuccessful.

Partial or irreproducible conversions were obtained with formyl-, 2,3-dicyano-, and 2,5-bismethoxycarbonylhydroquinone. 2,5-Diformylhydroquinone and quinizarin (1,4-dihydroxy-9,10-anthraquinone) were quantitatively recovered. Extensions of the oxidation period, use of more oxidant, or refluxing of the benzene solution did not give satisfactory results for these hydroquinones.

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Experimental

Benzene, dried azeotropically, was the solvent of choice. Commercial precipitated manganese dioxide was used in *ca.* 15 mol excess. Oxidation was complete after 15–30 min shaking at room temperature; progress of the reactions was monitored by removal of aliquots of solution, evaporation, and examination of ¹H n.m.r. spectra of the residues in CDCl₃ or C₆D₆. A typical procedure follows.

2-Methoxycarbonyl-5-methyl-1,4-benzoquinone. A mixture of methyl 2,5-dihydroxy-4-methylbenzoate (2.49 g), precipitated manganese dioxide^{10,11} (18 g), anhydrous sodium sulphate (6 g), and dry benzene (35 ml) was shaken mechanically at room temperature for 15 min. The suspension was filtered (Celite), and the filter cake was washed with dichloromethane (5 × 5 ml). Removal of the solvent from the combined filtrate and washings gave an oil which solidified: the orange-red quinone (2.23 g, 90%) had m.p. 36–38 °C, δ (CDCl₃) 2.08 (d, *J* 1.5 Hz, 5-Me), 3.90 (s, CO₂Me), 6.66 (q, *J* 1.5 Hz, 6-H), 7.08 (s, 3-H).

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Table Benzoquinones prepared by oxidation of hydroquinones with commercial precipitated manganese dioxide

| Benzoquinone | Yield (%) ^a | M.p.(°C) ^b | Lit. m.p.(°C) | Ref. |
|---|------------------------|-----------------------|---------------|------|
| 1,4-Benzoquinone | | | | |
| Unsubstituted | 58(c) | 114–116 | 116 | 14 |
| Methyl- | 56(c) | 68–68.5 | 69 | 15 |
| Cyano- | 75(c) | 115–118 | | |
| | 46(s) | 123–125 | 124–125 | 16 |
| Methoxycarbonyl- | 89(c) | 48–52 | | |
| | 79(s) | 51.5–52.2 | 53.5–54.5 | 17 |
| 2-Methoxycarbonyl-5-methyl- | 90(c) | 36–38 | 38.4–39.4 | 18 |
| Acetyl- | 74(c) | 58–61 | | |
| | 51(s) | 64–65.5 | 65.5–66.5 | 19 |
| 2-Acetyl-5,6-dimethyl- | 96(c) | (Oil) | (Oil) | 20 |
| Benzoyl- | 93(c) | 83–83.5 | 85–85.5 | 21 |
| 5,8-Dihydro-1,4-naphthoquinone ^c | 90(c) | 94–96 | 105.5–106.5 | 13 |
| 4,5-Dimethyl-1,2-benzoquinone | 96(c) | 97–101 | | |
| | 84(s) | 99–101 | 102 | 22 |

^aIn parentheses: c = crude, s = sublimed (0.005 mmHg). ^bStructures of quinones were confirmed by their spectra (n.m.r., i.r., mass), and by comparison with authentic materials. ^c δ (CDCl₃) 3.04 (br, s, 2 × CH₂), 5.79 (br, s, 6-H + 7-H), and 6.69 (s, 2-H + 3-H); δ (C₆D₆) 2.78 (br, s, 2 × CH₂), 5.40 (m, 6-H + 7-H), and 6.09 (s, 2-H + 3-H).