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A Simple Procedure for Preparing Annulated p-Benzoquinones. Improved Synthesis of 1,4-Dihydro-1,4-methanonaphthalene-5,8-dione

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Abstract. A simple and efficient two-step, one-pot synthesis of substituted 1,4dihydro-1,4-methanonaphthalene-5,8-diones is reported. This synthesis, which utilizes readily available starting materials and inexpensive reagents, can be used to prepare **1a-1c** in 70-90% overall yield. This procedure was extended successfully to prepare a more highly complex annulated *p*-benzoquinone i.e., **8**.

1,4-Dihydro-1,4-methanonaphthalene-5,8-dione (1) has been used extensively as an electron-poor Diels-Alder dienophile in [4 + 2] cycloaddition reactions with a variety of cyclic and polycyclic dienes. Recently, 1a has been employed as a starting material for the synthesis of (i) homo- and secologs of a variety of [n]prismanes (e. g., n = 5-7)¹ and (ii) strained, functionalized quadricyclanes² and also as a substrate for the study of π -facial selectivities in Diels-Alder cycloadditions.³

As part of a research program that is directed toward the synthesis of unusal polycarbocyclic "cage" compounds,⁴ it was necessary for us to prepare relatively large quantities of **1a**. The most commonly used method for this purpose, shown in Scheme 1, was described in 1958 by Meinwald and Wiley.⁵ In our hands, application of this procedure afforded **1a** in *ca*. 40% overall yield. More recently, Pandey and coworkers⁶ reported that tricyclic dienedone **2** can be oxidized to **1a** in 85% yield by using SmI₂ (2 equivalents; see Scheme 1).

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We now report a short and efficient two-step, one-pot method for producing 1a and some halogenated derivatives of 1a (Scheme 2). This simple procedure affords annulated *p*-benzoquinones 1a-1c in excellent overall yield. In an effort to further simplify our approach, we attempted to promote direct oxidation of 2a to 1a by using commercially available 10% Ce(NH₄)₂(NO₃)₆ impregnated on either silica gel or alumina (Aldrich). However, these attempts were not successful.

Scheme 1



25 °C 25 °C ó HO 0.5 h overnight 2a (X = Y = H) $4\mathbf{a} (\mathbf{X} = \mathbf{Y} = \mathbf{H})$ la (X = Y = H)2b (X = Y = Cl4b (X = Y = Cl1b (X = Y = Cl $2c (X \approx H)$ 4c (X = H,lc (X = H, $Y,Y = -CH_2CH_2-)$ $Y,Y \approx -CH_2CH_2$ -) $Y,Y = -CH_2CH_2$ -) $2d (X = Cl, Y = OCH_3)$ 4d (X = Cl, Y = OCH_3)

Like enediones 2a-2c, compound 2d can be aromatized over silica gel to afford the corresponding annulated hydroquinone, 4d (Scheme 3). However, unlike 4a-4c, subsequent CAN promoted oxidation of 4d *failed* to afford the corresponding annulated *p*-benzoquinone. Instead, cleavage of the norbornadiene ring occurred with concomitant aromatization, thereby affording a substituted 1,4-naphthoquinone⁷ (i. e., **5**, Scheme 3).

p-BENZOQUINONES

The foregoing approach has been further extended to permit the synthesis of a more highly complex, polycarbocyclic-annulated p-benzoquinone, i.e., 8 (Scheme 4). In particular, it was of interest to determine whether oxidation of 7 might pro-



duce the corresponding annulated quinone, **8**, or if instead oxidation might proceed with concomitant cleavage of the norbornene ring, as was the case for the corresponding oxidation of **4d** (see Scheme 3). In our hands, CAN promoted oxidation of **7** proceeded uneventfully to afford **8** (Scheme 4).

Scheme 4



Experimental Section

Melting points are uncorrected. Elemental microanalyses were performed by personnel at M-H-W Laboratories, Phoenix, AZ.

General Procedure. To a solution of the substrate (2a-2c, 1.0 mmol) in CH₂Cl₂ (10 mL) was added silica gel (60-200 mesh, 10 g), and the resulting mixture was stirred at ambient temperature for 0.5 h to promote adsorption of the substrate onto the silica gel surface.⁸ The resulting suspension was placed onto a silica gel column (50 g, dimensions 50 cm x 2 cm) and then was allowed to stand on the column at ambient temperature ovenight. The next morning, the column was

flushed by using 25% EtOAc-hexane (50 mL) as eluent. The eluate was concentrated *in vacuo*, and the residue was washed with CH₂Cl₂ (10 mL), thereby affording an essentially quantitative yield of **4a-4c**. Compounds **4a-4c** were characterized via analysis of their IR, ¹H NMR, and ¹³C NMR spectra and then were used as obtained in the next synthetic step without further purification.

To a solution of 4a-4c (1.0 mmol) in CH₃CN (10 mL) was added a solution of Ce(NH₄)₂(NO₃)₆ (2.5 mmol, excess) in water (10 mL) at ambient temperature, and the resulting mixture was stirred at ambient temperature for *ca*. 0.5 h. The progress of the reaction was monitored via thin layer chromatographic (tlc) analysis. The reaction mixture was extracted with Et₂O (3 x 50 mL). The combined organic extracts were washed sequen-tially with water (2 x 50 mL) and brine (2 x 50 mL). The organic layer was dried (Na₂SO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatographic or silica gel by eluting with 15% EtOAc-hexane. Workup of the chromatographic eluate afforded pure **1a-1c**, in each case.

1,4-Dihydro-1,4-methanonaphthalene-5,8-dione (1a). Application of the general procedure described above for the reaction of **2a** with silica gel afforded pure **4a** (900 mg, 90%) as a colorless microcrystalline solid: mp 143-144 °C (lit⁵ mp 144-145 °C); IR (KBr) 3100 (s), 1624 (m), 1603 (w), 1492 (s), 1451 (s), 1443 (m), 1350 (w), 1299 (s), 1218 (s), 1154 (m), 1114 (w), 995 (m), 953 (m), 805 (s), 732 (s), 606 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 2.06-2.08 (m, 2 H), 4.08 (s, 2 H), 6.28 (s, 2 H), 6.68-6.69 (m, 2H); ¹³C NMR (CDCl₃) δ 47.2 (d), 69.7 (t), 114.6 (d), 137.9 (s), 143.0 (d), 144.6 (s).

Cerium(IV) promoted oxidation of **4a**, when performed by using the procedure described above, produced pure **1a** (600 mg, 70%) as a bright yellow microcrystalline solid: mp 65-66 °C (lit.⁵ mp 66-67 °C); IR (KBr) 1649 (s), 1591 (m), 1560 (w), 1290 (m), 835 (m), 727 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 2.27-2.31 (m, 2 H), 4.07-4.10 (m, 2 H), 6.54 (s, 2 H), 6.84-6.86 (m, 2 H); ¹³C NMR (CDCl₃) δ 48.8 (d), 74.2 (t), 136.1 (d), 142.9 (d), 161.0 (s), 184.3 (s).

1,4-Dihydro-1,2,3,4,9,9-hexachloro-1,4-methanonaphthalene-5,8-di-one (1b). Application of the general procedure described above for the reaction of **2b** with silica gel afforded pure **4b** (800 mg, 80%) as a colorless microcrystalline solid: mp 185-186 °C (lit.⁹ mp 187-188 °C); IR (KBr) 3420 (vs), 2958 (w), 1602 (s), 1489 (vs), 1342 (m), 1261 (m), 1162 (m), 914 (s), 787 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 5.84 (s, 2 H), 6.72 (s, 2 H); ¹³C NMR (CDCl₃) δ 82.2 (s), 111.5 (s), 120.2 (d), 123.0 (s), 138.1 (s), 146.9 (s).

Cerium(IV) promoted oxidation of **4b**, when performed by using the procedure described above, produced pure **1b** (450 mg, 76%) as a bright orange microcrystalline solid: mp 116-117 °C (lit.⁹ mp 119 °C; lit.¹⁰ mp 117-118 °C); IR (KBr) 1665 (vs), 1574 (m), 1298 (s), 1104 (m), 956 (m), 845 (s), 843 cm⁻¹ (m);

¹H NMR (CDCl₃) δ 6.74 (s, 2 H); ¹³C NMR (CDCl₃) δ 82.2 (s), 116.2 (s), 136.7 (s), 138.4 (s), 147.0 (d), 180.6 (s).

1,4-Dihydro-11-(Spirocyclopropyl)-1,4-methanonaphthalene-5,8-di-one (1c). Application of the general procedure described above for the reaction of **2c** with silica gel afforded pure **4c** (700 mg, 70%) as a colorless microcrystalline solid: mp 217-218 °C; IR (KBr) 3310 (vs), 2995 (w), 1603 (w), 1485 (vs), 1359 (w), 991 (m), 798 (m), 782 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 0.41-0.56 (m, 4 H), 3.50 (s, 2 H), 6.22 (s, 2 H), 6.80 (s, 2 H), 8.35 (s, 2 H); ¹³C NMR (CDCl₃) δ 8.9 (t), 9.6 (t), 51.9 (d), 64.5 (s), 113.7 (d), 137.0 (s), 142.3 (d), 144.3 (s). Anal. Calcd for C₁₃H₁₂O₂: C, 77.98; H, 6.04. Found: C, 77.79; H, 6.14.

Cerium(IV) promoted oxidation of **4c** by using the procedure described above produced pure **1c** (460 mg, 78%) as a bright yellow microcrystalline solid: mp 95-96 °C ; IR (KBr) 3018 (vs), 2396 (w), 1650 (s), 1222 (vs), 939 (w), 745 (vs), 662 cm⁻¹ (vs); ¹H NMR (CDCl₃) δ 0.58-0.59 (m, 4 H), 3.53-3.54 (m, 2 H), 6.55 (s, 2 H), 6.86 (s, 2 H); ¹³C NMR (CDCl₃) δ 8.9 (t), 9.7 (t), 53.8 (d), 70.9 (s), 136.0 (d), 142.1 (d), 160.3 (s), 184.3 (s). Anal. Calcd for C₁₃H₁₀O₂: C, 78.87; H, 5.08. Found: C, 78.56; H, 5.20.

1,4-Dihydro-1,2,3,4-tetrachloro-9,9-dimethoxy-1,4-methanonaphthalene-5,8-dione (1d). Application of the general procedure described above for the reaction of 2d with silica gel afforded pure 4d (501 mg, 46%) as a colorless microcrystalline solid: mp 198-199 °C (lit.¹¹ mp 202-203 °C). The IR, ¹H NMR and ¹³C NMR spectra of this material are identical in all respects in with the corresponding spectra reported previously for authentic 4d.¹⁰

Cerium(IV) promoted oxidation of **4d**, when performed by using the procedure described above, produced pure **1d** (80 mg, 71%) as a yellow microcrystalline solid: mp 172-173 °C; IR (KBr) 1740 (s), 1670 (vs), 1437 (m), 1296 (s), 856 cm⁻¹ (w); ¹H NMR (CDCl₃) δ 4.02 (s, 3 H), 6.92 (AB, $J_{AB} = 10.3$ Hz, 1 H), 7.00 (AB, $J_{AB} = 10.3$ Hz, 1 H); ¹³C NMR (CDCl₃) δ 53.5 (q), 127.6 (s), 129.0 (s), 133.4 (s), 135.5 (s), 136.4 (d), 136.9 (s), 140.2 (d), 141.2 (s), 165.4 (s), 181.4 (s), 181.8 (s). Anal. Calcd for C₁₂H₅Cl₃O₄: C, 45.11; H, 1.58. Found: C, 45.23 ; H, 1.62.

Silica Gel Promoted Tautomerization of 6. Application of the general procedure described above for the reaction of 6^{12} (100 mg, 0.22 mmol) with silica gel afforded pure 7 (42 mg, 42%) as a colorless microcrystalline solid: mp 219-220 °C; IR (KBr) 3294 (vs), 2954 (w), 1606 (s), 1496 (s), 1194 (s), 995 (m), 792 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 2.67 (s, 2 H), 3.37 (br s, 6 H), 4.20 (m, 2 H), 5.91 (br s, 2 H), 6.19-6.23 (m, 2 H), 6.33 (s, 2 H); ¹³C NMR (CDCl₃) δ 33.3 (d), 51.9 (d), 52.3 (q), 53.0 (q), 77.7 (s), 114.2 (d), 115.2 (s), 128.1 (s), 131.5 (s), 132.9 (s), 144.5 (s). Anal. Calcd for C₁₉H₁₆Cl₄O₄: C, 50.70; H, 3.58. Found: C, 50.94; H, 3.84.

CAN Promoted Oxidation of 7. Cerium(IV) promoted oxidation of **7** (40 mg, 0.88 mmol), when performed by using the procedure described above, produced pure **8** (22 mg, 50%) as a yellow microcrystalline solid: mp 169-170 °C; IR (KBr) 2945 (w), 1655 (vs), 1580 (w), 1309 (s), 1178 (m), 848 (s), 800 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 2.74 (s, 2 H), 3.47 (s, 3 H), 3.51 (s, 3 H), 4.35 (br s, 2 H), 6.22-6.31(br s, 2 H), 6.66 (s, 2 H); ¹³C NMR (CDCl₃) δ 34.0 (d), 52.0 (d), 53.3 (q), 53.2 (q), 76.8 (s), 116.0 (s), 128.2 (s), 130.5 (d), 136.1 (d), 152.2 (s), 183.4 (s). Anal. Calcd for C₁₉H₁₄Cl₄O₄: C, 50.92; H, 3.15. Found: C, 51.12; H, 3.34.

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