

A convenient synthesis of 8-hydroxy-1-tetralones from naphthalene-1,8-diol

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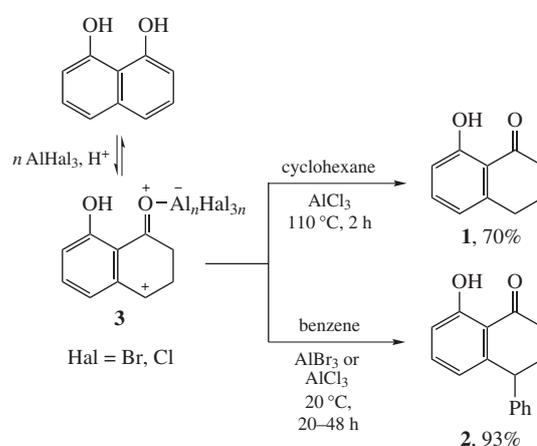
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Naphthalene-1,8-diol on superelectrophilic activation with aluminium halides smoothly reacts with cyclohexane and benzene to afford 8-hydroxy-1-tetralone and 8-hydroxy-4-phenyl-1-tetralone, respectively.

8-Hydroxy-1-tetralone **1** and its derivatives are useful intermediates in organic synthesis, which, however, are difficult to obtain in practice.¹ Here, we demonstrate that compound **1** as well as 8-hydroxy-4-phenyl-1-tetralone **2** can be prepared remarkably easily in a single-stage procedure using commercially available naphthalene-1,8-diol. The method herein developed is based on superelectrophilic² activation. A similar approach was applied earlier (with diverse efficiency) towards 1- and 2-naphthols and some isomeric naphthalenediols to involve them in reactions with aromatic compounds and alkanes.³

As appeared, naphthalene-1,8-diol undergoes selective ionic hydrogenation with cyclohexane in the presence of a 5-fold molar excess of AlCl₃ at elevated temperature to afford product **1** (Scheme 1).[†] In addition, the same diol smoothly reacts with benzene at room temperature in the presence of either AlCl₃ or AlBr₃ to give compound **2** in a nearly quantitative yield.

The mechanism of these reactions probably involves super-electrophilic species **3** as the key intermediates formed by C,C-



Scheme 1

[†] 8-Hydroxy-1-tetralone **1**. A mixture of naphthalene-1,8-diol (0.2 g, 1.25 mmol), AlCl₃ (0.84 g, 6.3 mmol) and cyclohexane (5 ml) was stirred in a 15 ml Ace pressure tube at 110 °C (oil bath temperature) for 2 h. The mixture was cooled and carefully treated with several grams of ice. The resulting mixture was extracted with diethyl ether. The organic phase was washed with water, then dried over anhydrous MgSO₄ and concentrated *in vacuo* to obtain a mixture of **1** and isomeric dicycloalkanes C₆H₁₁–C₆H₁₁ (the typical oxidation product in such reactions)^{3(c),(d),(h)} in a 1:1 molar ratio (GC-MS and ¹H NMR data). The mixture was separated by flash column chromatography with benzene–acetone (5:1) to give **1**^(a) (oil, 0.142 g, 70%). ¹H NMR (500 MHz, CDCl₃) δ: 2.05–2.12 (m, 2H), 2.66 (t, 2H, *J* 6.5 Hz), 2.91 (t, 2H, *J* 6.1 Hz), 6.68 (d, 1H, *J* 7.4 Hz), 6.77 (d, 1H, *J* 8.4 Hz), 7.33 (dd, 1H, *J* 8.4 and 7.4 Hz), 12.39 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ: 23.1, 29.9, 39.1, 115.7, 117.2, 118.9, 136.3, 145.6, 163.1, 205.1.

8-Hydroxy-4-phenyl-1-tetralone **2** (typical procedure). A mixture of naphthalene-1,8-diol (0.2 g, 1.25 mmol), AlCl₃ (0.84 g, 6.3 mmol) and benzene (5 ml) was stirred at 20 °C for 48 h. The mixture was carefully treated with ice and extracted with diethyl ether. The organic phase was washed with water, dried over anhydrous MgSO₄ and concentrated *in vacuo* to obtain compound **2** (pale-yellow solid, 0.278 g, 93%), mp 80–83 °C (EtOH). ¹H NMR (500 MHz, CDCl₃) δ: 2.25–2.34 (m, 1H), 2.38–2.47 (m, 1H), 2.62–2.78 (m, 2H), 4.25 (dd, 1H, *J* 6.5 and 3.3 Hz), 6.44 (d, 1H, *J* 7.4 Hz), 6.86 (d, 1H, *J* 8.4 Hz), 7.14 (d, 2H, *J* 7.3 Hz), 7.27 (dd, 1H, *J* 8.4 and 7.4 Hz), 7.33 (t, 3H, *J* 7.3 Hz), 12.52 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ: 31.3, 36.8, 45.4, 116.3, 117.4, 120.0, 127.0, 128.6, 128.8, 136.6, 143.4, 147.4, 163.1, 205.1. HRMS, *m/z*: 238.0989 (calc. for C₁₆H₁₄O₂, *m/z*: 238.0988).

diprotonation (see Scheme 1). A number of analogous dications have indeed been generated as long-lived species by dissolving 1-naphthol derivatives in liquid superacids,⁴ whereas DFT calculations have proved their enhanced electrophilicity.⁵

Note that a 5-fold molar excess of aluminum halides is not essential and a decrease in the loading is possible. This, however, slows down the reactions and the use of less than a 2-fold molar excess of aluminium halides suppresses them eventually. A catalytic amount of protic superacid (HHal–Al_nHal_{3n} or H₂O–Al_nHal_{3n}), which is required for generation of **3**, is normally present in the reaction media due to the presence of traces of water in the starting materials.² Clearly, the excess of aluminum halide provides an acid strength sufficient to form dicationic intermediates.³

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.01.031.

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