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Influence of the *p*-Dimethylamino Group on Oxidation in the 3-Hydroxy-2-phenylphenalene Series

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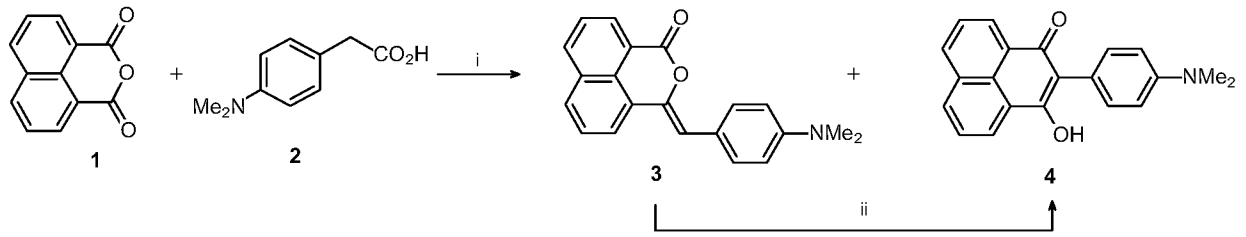
Oxidation of 2-(4-dimethylaminophenyl)-3-hydroxyphenalene-1-one with chromium trioxide or iodine leads to the solvolysis products of an intermediate carbonium ion.

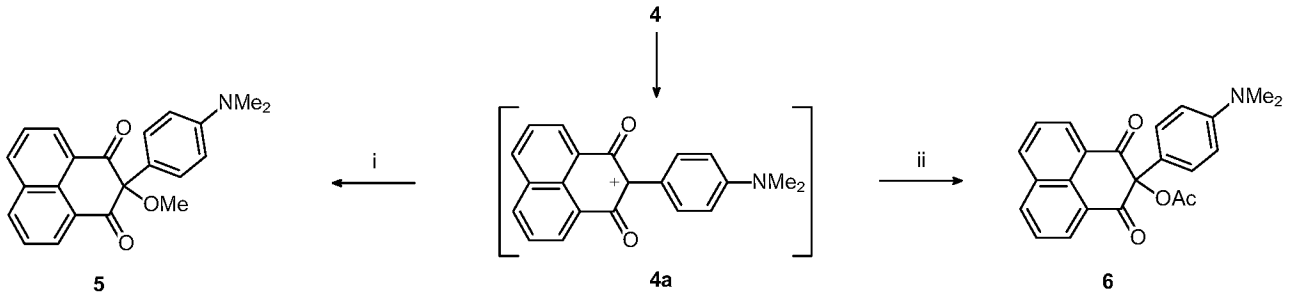
We have studied the oxidation of 2-(4-dimethylaminophenyl)-3-hydroxyphenalene-1-one under different conditions in order to obtain organic compounds which can dissociate into free radicals.[1] The starting keto-enol **4** was synthesized *via* condensation of naphthalic anhydride **1** with 4-dimethylaminophenylacetic acid in the presence of a catalytic amount of sodium acetate.[2] As a result, a mixture of two compounds, the naphthalide **3** (yield 21%) and the keto-enol **4** (30%), was obtained. Compound **4** was separated due to its solubility in aqueous alkali. Upon treatment with sodium methylate, the naphthalide **3** was rearranged into **4** in high yield (Scheme 1).

It is known that oxidation of 3-hydroxy-2-phenylphenalene-1-one leads to the formation of the symmetric 2,2′-dehydro dimer,[3] which normally forms in the 2-phenylindan-1,3-dione series, regardless of the oxidizer and the solvent. Treatment of **4** with iodine and sodium methylate in



Scheme 1 *Reagents and conditions*: i, cat. AcONa, 240 °C, 1 h; ii, MeONa, MeOH, 65 °C, 1 h, 86%.

methanol solution gave the 2-methoxy derivative **5**, while chromium trioxide in acetic acid gave the 2-acetoxy derivative **6**† (Scheme 2).



Scheme 2 *Reagents and conditions*: i, MeONa, I_2, MeOH, 25 °C, 64%; ii, CrO_3, AcOH, 50 °C, 1.5 h → 25 °C, 15 h, 70%.

Such an unusual result can be explained in terms of two-electron oxidation (or two successive one-electron oxidations) of the perinaphthenone **4** and formation of carbonium ion **4a** followed by trapping. The ease of two-electron loss from **4** can be explained by a reduction in the oxidation potential caused by the electron-donating dimethylamino group. In comparison with the indandione series, the perinaphthenones (*i.e.* **4**) also have a smaller potential for two-electron oxidation due to the presence of the additional benzene ring and the reduced mutual effects of the carbonyl groups.

† All compounds obtained were characterized by IR, ^{1}H and ^{13}C NMR spectroscopy and gave satisfactory elemental analyses.

5: m.p. 221–223 °C; IR (KBr) 1697 and 1670 (C=O), 1602, 1573 and 1517 cm^{-1} (C=C, Ar); ^{1}H NMR ($CDCl_3$) δ 2.82 (s, NMe_2), 3.57 (s, OMe), 6.46 (m, H-3′, $J_{2',3'} = 9.3$ Hz), 7.12 (m, H-2′, $J_{2',3'} = 9.3$ Hz), 7.70 (dd, H-5, $J_{4,5} = 7.3$, $J_{5,6} = 8.3$ Hz), 8.12 (dd, H-6, $J_{4,6} = 1.0$, $J_{5,6} = 8.3$ Hz), 8.44 (dd, H-4, $J_{4,5} = 7.3$, $J_{4,6} = 1.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 39.84 (q, NMe_2), 55.42 (q, OMe), 94.99 (s, C-2), 112.05 (d, Ar), 128.98 (d, C-2′), 129.56 (d, Ar) 130.31 (s, Ar), 132.68 (s, Ar), 134.00 (d, Ar), 150.73 (d, C-4′), 194.50 (s, C-l).

6: m.p. 177–179 °C (decomp.); IR (KBr) 1737 (C=O, Ac), 1705 and 1680 (C=O), 1607, 1579 and 1524 (C=C, Ar), 1240 cm^{-1} (O–Ac); ^{1}H NMR ($CDCl_3$), δ 2.30 (COMe), 2.84 (NMe_2), 6.52 (m, H-3′, $J_{2',3'} = 9.1$ Hz), 7.20 (m, H-2′, $J_{2',3'} = 9.1$ Hz), 7.72 (dd, H-5, $J_{4,5} = 7.2$, $J_{5,6} = 8.3$ Hz), 8.18 (dd, H-6, $J_{4,6} = 1.1$, $J_{5,6} = 8.3$ Hz), 8.49 (dd, H-4, $J_{4,5} = 7.2$, $J_{4,6} = 1.1$ Hz).

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