SHORT PAPER

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Polycyclic aromatics from veratrole and ninhydrin and acenaphthenequinone†

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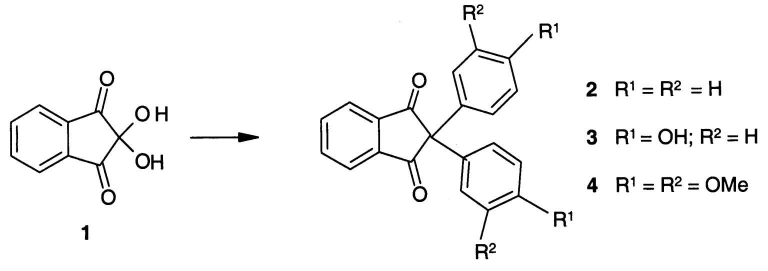
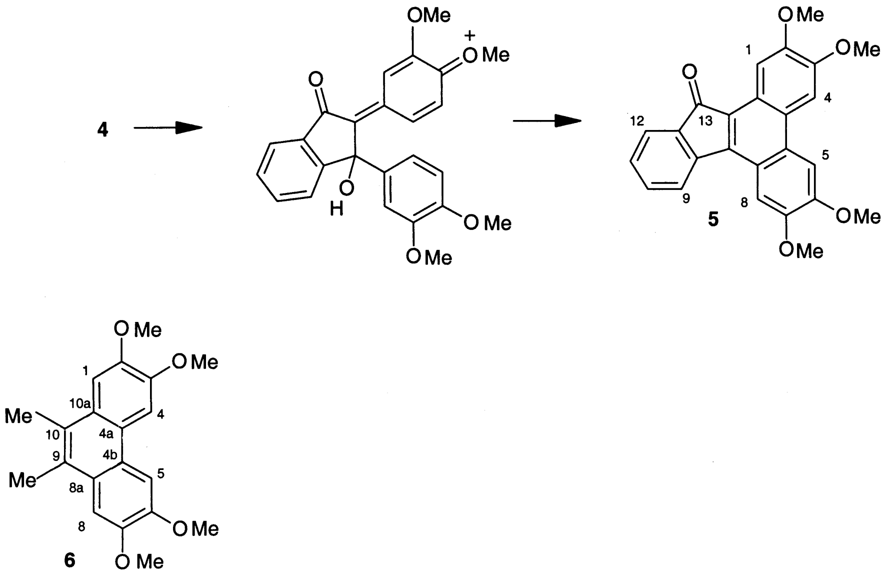
Treatment of 2,2-di(3,4-dimethoxyphenyl)indane-1,3-dione with concentrated sulfuric acid gives 2,3,6,7-tetramethoxydibenzo[*a,c*]fluoren-13-one while under the same conditions 2,2-di(3,4-dimethoxyphenyl)acenaphthenone produces 2,3,6,7-tetramethoxydibenzo[*j,l*]fluoranthene.

Keywords: ninhydrin, acenaphthenequinone, tetramethoxydibenzofluorenone, tetramethoxydibenzofluoranthene.

Ninhydrin **1** is known[1] to react with benzene in concentrated sulfuric acid (Scheme 1) to give the 2,2-diphenylindanedione **2**. We have found that phenol reacts with ninhydrin under somewhat milder conditions, in aqueous 75% v/v sulfuric acid, to produce a high yield of the analogous dihydroxy compound **3**. Veratrole behaves in a similar fashion to give **4** which on treatment with *concentrated* (98%) sulfuric acid at room temperature undergoes a rearrangement of the *retro*-pinacol type followed by cyclisation and the loss of water (Scheme 2) to yield the dibenzofluorenone **5** (8.4%). The structure of the latter follows from its ^{1}H and ^{13}C NMR spectra and their comparison with those of the known tetramethoxyphenanthrene **6.** The proximity of the C-13 carbonyl group is responsible for the downfield shift (to δ8.58) of the proton at C-1 while the four adjacent protons of the indenone system give rise to the expected[2] pattern of two doublets and two doublets-of-doublets, the signals being slightly broadened as a result of further small couplings. The direct reaction of veratrole and ninhydrin in concentrated sulfuric acid results in the formation of a complex mixture containing only a trace of **5** and does not provide an attractive alternative to the two-stage preparation.



Scheme 1



Scheme 2

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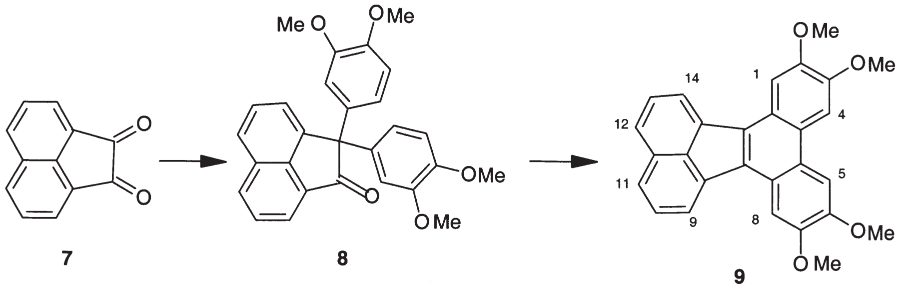
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 3

Acenaphthenequinone **7** resembles ninhydrin **1** in having carbonyl groups in a five-membered ring and reacts with veratrole in aqueous 75% v/v sulfuric acid in a similar manner[3] to give the acenaphthenone **8** (Scheme 3). Again, concentrated sulfuric acid causes the latter to undergo rearrangement and cyclisation resulting in the formation of the dibenzofluoranthene **9** (ll.3%). In this case the symmetry of the molecule results in a somewhat simpler NMR spectrum in which the "naphthalene" ring protons give rise to two doublets and one doublet-of-doublets as observed with acenaphthylene itself,[4] all the signals again being slightly broadened.

Although the polycyclic products are obtained in only moderate yield their preparation is simple and their precursors are readily accessible. Moreover, they contain functional groups which are available for further elaboration.

Experimental

General: IR spectra were measured for KBr discs and UV absorptions for chloroform solutions unless otherwise stated; "infl" denotes an inflection. ^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions, unless otherwise stated, at 250 and 63 MHz respectively using residual $CHCl_3$ in the solvent as internal standard. Mass spectra were obtained using EI at 70eV and ES+ at 34V. PLC was performed on silica gel (Merck, GF_{254}) and melting points were determined in open capillaries.

2,2-Di(4-hydroxyphenyl)indane-1,3-dione **3**: A mixture of phenol (5.28 g, 56.1 mmol), ninhydrin (5 g, 28.0 mmol) and aqueous 75% v/v sulfuric acid (50 ml) was stirred at room temperature for 4h and poured into water. Extraction with chloroform gave a solid which after PLC (chloroform) crystallised from chloroform to give the *indanedione* **3** (8.26 g, 25.0 mmol, 89%) as yellow needles, m.p. 197–198.5°C (Found: M^+, 330.0900. $C_{21}H_{14}O_4$ requires: *M*, 330.0892); *m/z* 330 (100%, M^+), 273 (23, M–CHO–CO), and 181 (8, 273–C_6H_4O); λ_{max}/nm 228 (log ε 4.74), 247infl (4.04) and 275infl (3.76); ν_{max}/cm^{-1} 3340 (phenolic OH), 1721 and 1690 (indanedione C = O), 1610 and 1586 (aromatic C = C), 822 (2 adjacent ArH), and 77l (4 adjacent ArH); δ_H [$(CD_3)_2CO$] 6.75, 6.79, 7.04 and 7.08 (8H, AA′XX′ m, 4-hydroxyphenyl ArH), and 7.99–8.10 (4H, m, ArH).

2,2-Di(3,4-dimethoxyphenyl)indane-1,3-dione **4**: A similar reaction between ninhydrin (5 g, 28.0 mmol), veratrole (8.63 g, 62.5 mmol) and aqueous 75% v/v sulfuric acid (50 ml) gave a solid which after PLC ($CHCl_3$) crystallised from chloroform to give the *indanedione* **4** (11.39 g, 27.2 mmol, 97%) as yellow needles m.p. 139–140°C (lit.,[5] 144°C for a sample with no supporting analytical data); (Found: M^+, 418.1412, $C_{25}H_{22}O_6$ requires *M*, 418,1413); *m/z* 418 (100%, M^+) and 403 (5, M-Me); λ_{max}/nm (MeOH) 230 (log ε 4.67), 252infl (4.12), and 281 (3.81); ν_{max}/cm^{-1} 2812 (methoxy C-H), 1737 and 1701 (indanedione C = O), 1586 (aryl C = C), 841 (2 adjacent ArH), 786 and 760 (4 adjacent ArH); δ_H 3.79, 3.86 (each 6H, s, ArOMe), 6.76–6.85 (6H, m, dimethoxyphenyl ArH) and 7.85–7.93 and 8.02–8.10 (4H, AA′XX′ m, indanedione ArH).

2,3,6,7-Tetramethoxydibenzo[a,c]fluoren-13-one **5**: A solution of the indanedione **4** (500 mg, 1.2 mmol) in concentrated sulfuric acid (98%, 50 ml) was kept at 20°C for 16 h and then poured into water. Extraction with chloroform gave a solid (450 mg) which was boiled with methanol (50 ml). The insoluble residue crystallised from chloroform–methanol and, after PLC using 2% methanol in chloroform, gave the *fluorenone* **5** (40 mg, 0.l mmol, 8.4%) as red microcrystals m.p. 290–293°C (Found: M^+, 400.1292. $C_{25}H_{20}O_5$ requires *M*, 400.1311); *m/z* 400 (100%, M^+), 200 (9, M^{2+}); λ_{max}/nm 276.0infl (log ε 4.49), 296.0infl (4.28), 314.7 (4.15), 328.9 (4.16) and 444.8 (3.69); ν_{max}/cm^{-1} 1686 (Ar_2C = O), 1618 and 1520 (ArC = C), 1482 and 1254 (ArOMe), 829.5 (isolated ArH) and 752 (4 adjacent ArH); δ_H 4.10 (9H, s, OMe), 4.12 (3H, s, OMe), 7.29 (1H, br. dd, *J* 8 and 8, 10-H), 7.46 (1H, br. dd, *J* 8 and 8, 11-H), 7.55 (1H, s, 8-H), 7.60 (1H, br. d, *J* 8, 9-H), 7.62 and 7.71 (each 1H, s, 4- and 5-H), 7.78 (1H, br, d, *J* 8, 12-H) and 8.58 (1H, s, 1-H); δ_C 55.8, 55.9, and 56.0 (OMe), 102.4, 103.3, 104.4, and 105.0 (C-1, -4, -5, and -8), 121.8, 122.3, 122.8, and 123.2 (C-9, -10, -11, and -12), 123.6, 125.5, 128.3, and 129.6 (C-4a, -4b, -8a, and -13b), 133.7 and 135.4 (C-8b and -8c), 141.3 and 144.2 (C-12a and -13a), 149.3, 149.5, 150.6, and 151.1 (C-2, -3, -6, and -7), and 195.7 (C-13). 9,10-Dimethyl-2,3,6,7-tetramethoxyphenanthrene[6] **6** had δ_H 2.64 (6H, s, ArMe), 4.05 and 4.11 (each 6H, s, OMe), 7.36 (2H, s, 1- and 8-H), and 7.78 (2H, s, 4- and 5-H); δ_C 16.0 (ArMe), 55.7 and 55.9 (OMe), 103.1 and 105.1 (C-1, -4, -5, and -8), 123.3 (C-9 and -10), 126.5 and 126.7 (C-4a, -4b, -8a, and -10a), and 148.0 and 148.4 (C-2, -3, -6, and -7).

2,3,6,7-Tetramethoxydibenzo[j,l]fluoranthene **9**: A similar reaction with 2,2-di(3,4-dimethoxyphenyl)acenaphthenone[3] (285 mg, 0.65 mmol) gave the *fluoranthene* 9 (31 mg, 0.07 mmol, 11.3%) as orange-yellow needles, m.p. 279–283°C [Found: M^+ (EI): 422.1518. $C_{28}H_{22}O_4$ requires: *M*, 422.1518]; *m/z* 422 (100%, M^+), 407 (13, M-Me), 379 (6, 407-CO), 364 (8, 379-Me), 348 (20, 379-OMe), and 211 (12, M^{2+}); [Found (ES): *m/z* 445 (100%, M+Na$^+$) and 867 (64, 2M+Na$^+$)]; λ_{max}/nm 251.9 (log ε 4.44), 296.4 (4.20), 305.6infl (4.05), 314 (4.01), 323.2infl (4.07), 328.8 (4.20), 337.7 (4.23), 344.0 (4.21), 414.0infl (3.73), 428.3 (3.78), 462.4infl (3.36), and 490.4infl (3.04); ν_{max}/cm^{-1} 1618 and 1522 (aromatic C = C), 1489 and 1254 (ArOMe), 83l (isolated ArH) and 766 (3 adjacent ArH); δ_H 4.06 and 4.11 (each 6H, s, OMe), 7.60 (2H, br. dd, *J* 8 and 8, 10- and 13-H), 7.70 (2H, s, 4- and 5-H), 7.77 (2H, br. d, *J* 8, 11- and 12-H), 7.99 (2H, s, 1- and 8-H), and 8.22 (2H, br. d, *J* 8, 9- and 14-H).

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