

Coupling of 2,7-Dihydroxynaphthalene by Mercuric Oxide

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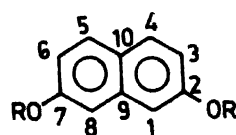
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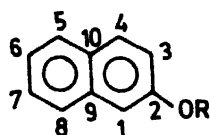
Oxidative phenol coupling on 2,7-dihydroxynaphthalene by HgO leads to 1,6,7,12-perylenetetrol in 60% yield.

Mercuric oxide (HgO) acts as an oxidising agent¹ in many cases like Ag₂O, CuCl₂, air/NaOH, O₃, Br₂/H₂O etc. This prompted us to explore its possibility to bring about oxidative phenol coupling² reaction. However, the possibility of mercuration can not be ruled out and as a consequence an organomercury compound may result as reported in our previous work³ with 2-naphthol which on reflux with alkaline HgCl₂ in ethanol produced 1,1'-bis(2-hydroxynaphthyl)mercury. Oxidative coupling of phenols utilising Hg^{II} salt is still an unexplored field and only one report⁴, to our knowledge, appeared in the literature.

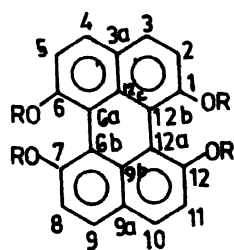
In our study we have chosen 2,7-dihydroxynaphthalene (1a) as our model where coupling is possible in two positions to give rise to two different products.



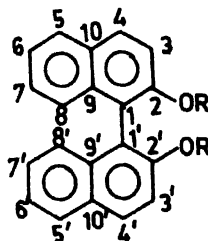
1a: R=H
b: R=Ac



3a: R=H
b: R=Ac



2a: R=H
b: R=Ac



4a: R=H
b: R=Ac

Results and Discussion

2,7-Dihydroxynaphthalene when refluxed for 12 h with HgCl₂ in alkaline ethanol (which instantaneously produced yellow mercuric oxide) afforded a single isolable product (yield ~60%). The product was identified as 1,6,7,12-perylenetetrol (2a) from spectral evidences. The point of attachment was determined from a detailed comparison of the ¹H and ¹³C nmr spectra of its tetraacetylated derivative (2b) with those of 2,7-diacetoxynaphthalene (1b), 2-naphthyl acetate (3b) and 2,2'-diacetoxynaphthalene (4b). These three compounds were obtained by acetylating 2,7-dihydroxynaphthalene (1a), 2-naphthol (3a) and 2,2'-dihydroxy-1,1'-binaphthyl (4a)⁵ respectively. In the mass spectra of 2b the molecular ion peak appeared at *m/z* 484 (25.6%). This was followed by the successive losses of four 42 mass units (corresponding to ketene) giving peaks at *m/z* 442 (21.8), 400 (25.8), 358 (48.1) and 316 (100.0). Among others, peaks at *m/z* 315 (99.0), 297 (12.9), 287 (15.9), 286 (16.9), 258 (14.6), 229 (11.8) and 43 (45.5) are worth mentioning.

The position of coupling has been ascertained from the ¹H nmr spectra of 2b when compared with those of 1b, 3b and 4b (Table 1). The ¹H nmr spectra (CDCl₃) of 2b showed peaks at δ 7.38 (d, *J* 8.8 Hz, H-2, H-5, H-8, H-11), 7.82 (d, *J* 8.8 Hz, H-3, H-4, H-9, H-10), 2.28 (s, OCOCH₃). The downfield shift of H-2, H-5, H-8 and H-11 may be due to their presence in deshielding zone created by the adjacent acetyl carbonyl group. Further support regarding the structure has been obtained from a comparison of the ¹³C nmr spectra showing peaks at δ (CDCl₃) 21.27 (OCOCH₃), 118.30 (C-6a, C-6b, C-12a, C-12b), 122.41 (C-2, C-5, C-8, C-11), 127.81 (C-3, C-4, C-9, C-10), 128.20 (C-9b, C-3b), 132.89 (C-3a, C-9a), 146.74 (C-1, C-6, C-7, C-12), 169.32 (OCOCH₃) with those of 1b, 3b and 4b (Table 2).

TABLE 1—¹H NMR SPECTRAL DATA FOR COMPOUNDS 1b, 3b AND 4b

Hydrogen	1b	3b	4b
H-1(-1')	7.53 (d, 1.7 Hz),	7.54 (d, <i>J</i> 3.0 Hz),	—
H-3(-3')	7.22 (dd, <i>J</i> ₁ 2.0 Hz; <i>J</i> ₂ 8.6 Hz)	7.24 (dd, <i>J</i> ₁ 3.0 Hz; <i>J</i> 8.0 Hz)	7.20 (d, <i>J</i> 8.4 Hz)
H-4(-4')	7.83 (d, <i>J</i> 8.6 Hz)	Embedded within the multiplet in range 7.72–7.92	7.95 (d, <i>J</i> 8.4 Hz)
H-5(-5')	7.83 (d, <i>J</i> 8.6 Hz)	7.72–7.92 (m)	8.02 (d, <i>J</i> 9.0 Hz)
H-6(-6')	7.22 (dd, <i>J</i> ₁ 2.0 Hz; <i>J</i> ₂ 8.6 Hz)	7.40–7.50 (m)	7.45 (d, <i>J</i> 9.0 Hz)
H-7(-7')	—	7.40–7.50 (m)	7.40–7.50 (m)
H-8(-8')	7.53 (d, 1.7 Hz)	7.72–7.92 (m)	7.22–7.33 (m)
O-COCH ₃	2.34, (s)	2.30 (s)	1.84 (s)

TABLE 2— ^{13}C NMR SPECTRAL DATA (δ) FOR **1b**, **3b** AND **4b**

Carbon	1b	3b	4b
C-1 (-1')	118.23 (d)	118.67 (d)	123.97 (s)
C-2 (-2')	148.94 (s)	148.48 (s)	147.31 (s)
C-3 (-3')	120.93 (d)	125.85 (d) ^a	126.73 (d) ^b
C-4 (-4')	129.15 (d)	127.74 (d)	128.59 (d)
C-5 (-5')	129.15 (d)	129.54 (d)	130.09 (d)
C-6 (-6')	120.93 (d)	126.65 (d) ^a	126.29 (d) ^b
C-7 (-7')	148.94 (s)	127.74 (d)	127.30 (d)
C-8 (-8')	118.23 (d)	121.26 (d)	122.43 (d)
C-9 (-9')	129.31 (s)	131.60 (s)	132.08 (s)
C-10 (-10')	134.15 (s)	133.93 (s)	133.90 (s)
Ar-O-COCH ₃	169.26 (s)	169.72 (s)	169.98 (s)
Ar-O-COCH ₃	21.03 (q)	21.26 (q)	21.27 (q)

^{a,b}Values are interchangeable.

Attempts to prepare the same compound from **1a** using common coupling procedures such as solid state FeCl_3 oxidation⁶ was unsuccessful. However, $\text{K}_3\text{Fe}(\text{CN})_6$ oxidation in aqueous alkaline solution⁷ could produce **1a** but in a much less efficient way. In this context it is worth to mention that in absence of HgO , **1a** could not give **2a** even on reflux for 10 h in alkaline ethanol.

Compounds having perylene skeleton with hydroxy substitution are important for having antitumor activities⁸ and thus this simple way described here may create a new entry to perylene system.

Experimental

M.ps. are uncorrected. Ir spectra were recorded on a Perkin-Elmer spectrophotometer, ^1H and ^{13}C nmr spectra on a Bruker AC-200 spectrometer, mass spectra on a Hewlett-Packard spectrometer, electronic spectra on a Shimadzu UV 160 spectrophotometer and fluorescence spectra on a Perkin-Elmer LS-50B instrument. Silica-gel 60–100 mesh for column chromatography and silica-gel plates with 0.2 mm thickness (E. Merck) for tlc analysis were used.

Coupling of 2,7-dihydroxynaphthalene ➔ An ethanolic solution of **1a** (1 g, ~6 mmol) was mixed with HgCl_2 (2 g; ~7 mmol) dissolved in ethanol (95%; 200 ml) and the

whole solution was made alkaline (pH ~9) when yellow precipitate of HgO appeared. It was then refluxed for 12 h. The reaction mixture was filtered and the solvent removed under reduced pressure followed by acidification and extraction successively with ether and ethyl acetate. The combined layers were dried over Na_2SO_4 , the solvent was evaporated and the residue was collected. The product was deep blue. Some part still remaining in water was collected by evaporating the solvent. Removal of the starting material from the residue was done by washing it thoroughly with 10 : 1 petrol-EtOAc mixture. Pure **2a**, m.p. >300°, showed ν_{max} (KBr) 3 423 (OH), 1 627, 1 550, 1 424, 1 245, 1 134, 836, 614, 449 cm^{-1} ; absorption at λ_{max} (H_2O : DMSO, 10 : 1) 637 nm (log ϵ = 2.65).

Acetylation of **2a** was done using $\text{Ac}_2\text{O}/\text{Py}$. Usual workup and column filter afforded the tetraacetylated derivative **2b**, m.p. >300°, R_F (tlc) 0.63 (on silica-gel, 1 : 2 petrol-EtOAc). It was a highly fluorescent compound having fluorescence band at λ_{em} (EtOH) 460 nm, λ_{ex} = 360 nm.

Following the usual procedure, **1a**, **3a** and **4a** were also acetylated to produce their acetylated derivatives **1b**, **3b** and **4b** respectively.

Acknowledgement

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