The New Syntheses of 1-Amino-4-Hydroxy-anthraquinone

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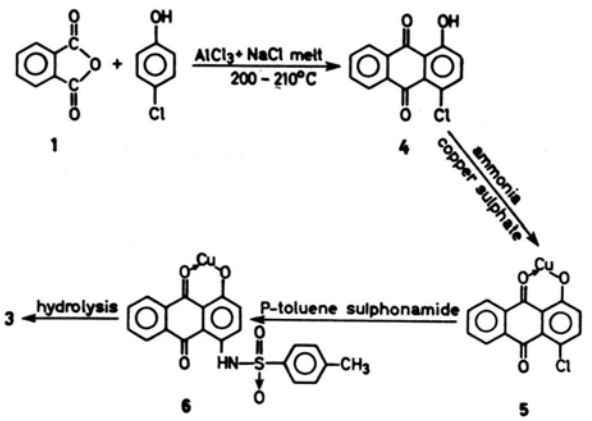
Friedel-Craft's acylation, anthraquinone

1-Amino-4-hydroxy-anthraquinone (**3**), commercially known as Celliton fast pink B, an important dye for all classes of fibers, has earlier been prepared from anthraquinone derivatives[1–4]. We wish to report its synthesis by condensing phthalic anhydride (**1**) with *p*-chlorophenol and *p*-aminophenol derivatives separately using Friedel-Craft's acylation and cyclisation reaction.

The compound **1** when condensed with *p*-chlorophenol in presence of aluminium chloride sodium chloride melt gave an intermediate 4-chloro-1-hydroxy-anthraquinone (**4**) which after protecting its hydroxy group and on treatment with *p*-toluene sulphonamide gave compound **3**; (80%).



The compound **3** was also obtained by direct condensation of compound **1** with aminophenols (**2a** – **2e**). The results are summarised in Table I. The lower yield in **2a** – **2c** is due to partial protection of amino group while in **2e** is due to steric hindrance.

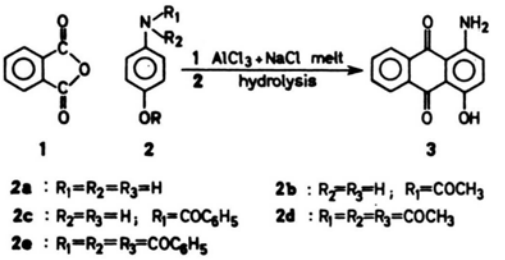


Table I. Condensation of **1** with aminophenols in presence of aluminiumchloride-sodium chloride melt.

S. No.	Compound	Reaction Temp. [°C]	Time [min]	Yield of **3** [%]
1.	4-Aminophenol (**2a**)	170 – 180	15	3
2.	*N*-Acetyl-4-aminophenol (**2b**)	180 – 200	30	10
3.	*N*-Benzoyl-4-aminophenol (**2c**)	190 – 200	30	15
4.	Triacetyl-4-aminophenol (**2d**)	200 – 210	45	45
5.	Tribenzoyl-4-aminophenol (**2e**)	200 – 210	45	20

Melting points are uncorrected. IR-Spectra were recorded using Perkin Elmer model 337 spectrophotometer. UV-Spectra were obtained using Hilger Uvispeck Spectrophotometer model H 700. The mass spectra were recorded with an AEI-MS 9 mass spectrometer operating with an ionisation energy of 70 eV.

1-Chloro-4-hydroxy-anthraquinone (**4**)

An intimate slurry of *p*-chlorophenol (5 g) phthalic anhydride (**1**) (5 g) was added in small portions to a clear melt of anhydrous aluminium chloride (50 g) sodium chloride (30 g) at 170 – 180 °C. The mixture was further stirred at 210 °C for 45 min. After cooling it was digested with 2 N hydrochloric acid and filtered. The residue after drying, was extracted with benzene which on crystallisation gave yellow neddles, (**4**) (5.5 g) m. p. 191 °C.

$C_{14}H_7O_3Cl$
Found: C 65.31 H 2.78 Cl 13.68,
Calcd.: C 64.99 H 2.70 Cl 13.73.
R_F = 0.42 (Silica gel-benzene).
IR: ν_{max} = 3480, 1670, 1640, 1250, 1180, 850 and 820 cm^{-1},
λ_{max} (methanol) = 265, 310 and 500 mμ.
Mass spectrum = M^{+} *m/e* 258, *m/e* 257, *m/e* 230, *m/e* 202, *m/e* 195, *m/e* 176, *m/e* 167, and *m/e* 139.

Copper complex of 4-chloro-1-hydroxy-anthraquinone (**5**)

1.3 g of **4** were dissolved in 7.5 ml of acetone and mixed with copper ammonia solution (prepared by adding 5 g of copper sulphate in 12 ml of 25% ammonia). The mixture after refluxing for two hours was distilled to remove acetone and kept at room

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temperature for twelve hours. The brown product separated was filtered, washed with water and dried, **5** (1.4 g).

4-p-Toluene-sulphonamide-1-hydroxy (copper complex)-anthraquinone (**6**)

Copper complex (**5**; 1.4 g), *p*-toluene sulphonamide (1.4g) fused sodium acetate (1.4g) and copper acetate (0.2 g) were placed in 100 ml flask containing 35 ml of *n*-pentanol. The mixture was stirred at 180 °C for twenty hours. The pentanol was removed by steam distillation. The product separated was filtered, washed with hot water and dried over calcium chloride (**6**) (1.9 g).

1-Amino-4-hydroxy-anthraquinone from **6**

The solution of **6** (1.3 g) in 50 ml of conc. sulphuric acid was stirred over steam bath for two hours. The mixture after cooling was poured into cold water and filtered. The residue was washed with water, dried over calcium chloride and was chromatographed over silica gel with benzene. The fast moving yellow band on crystallisation gave unreacted **4** (0.1 g). The pink band was then eluted which gave on crystallisation pink violet plates (**3**), 1.1 g, m. p. 215 °C.

$C_{14}H_9O_3N$

Found: C 70.42 H 3.69 N 5.78,

Calcd.: C 70.29 H 3.76 N 5.85.

$R_F = 0.32$ (silica gel benzene).

IR: $\nu_{max} = 3500, 3400, 1640, 1600, 1540, 1470, 1250, 1190$ and $840\ cm^{-1}$.

$\lambda_{max} = 255$ and $530\ m\mu$.

Mass spectra = $M^{+\cdot}$, *m/e* 239, *m/e* 212, *m/e* 211, *m/e* 183, *m/e* 182, *m/e* 107, *m/e* 100, and *m/e* 76.

1-Amino-4-hydroxy-anthraquinone from **2d**

An intimate slurry of **2d** (4 g) and phthalic anhydride (4.0 g) was gradually added with stirring to a clear melt of anhydrous aluminium chloride (40 g) and sodium chloride (10 g) at 170 – 180 °C. The mixture was further stirred at 200 – 210 °C for 35 min., cooled, digested with 2 N-hydrochloric acid. The precipitate was filtered, washed with water, dried and its benzene extract was chromatographed over silicagel. The pink band was separated which on crystallisation with same solvent gave pink plates (2.5 g) m. p. 215 °C and was found identical (in elemental analysis mixed m. p., IR, UV and mass spectral results) with compound prepared from **4**.

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