

Synthesis of Acid Dyes Based on 4-Hydroxy-1-Phenyl-2-Oxoquinoline System and Their Application

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4-Hydroxy-1-phenyl-2-oxoquinoline (HPOQ) used as coupling component was synthesised by the condensation of *o*-chlorobenzoic acid and aniline, followed by acetylation and ring closure. Some new azo dyes were prepared by coupling HPOQ with various diazo components. Dyeing properties of these dyes on silk, wool and nylon were assessed. The percentage exhaustion of dye-bath on silk, wool and nylon was 58–74%, 66–80% and 57–69% respectively. A study of the fastness of dyed patterns showed that dyes were good on silk and wool and fair for nylon.

INTRODUCTION

The utility of quinoline derivatives¹ for the production of some commercial dyes and pigments has been reported. The quinoline based dyes using quinoline as coupling component² and as diazo component³ have been reported. Hence, it was thought interesting to undertake synthesis and study of dyeing properties of the azo dyes based on HPOQ system.

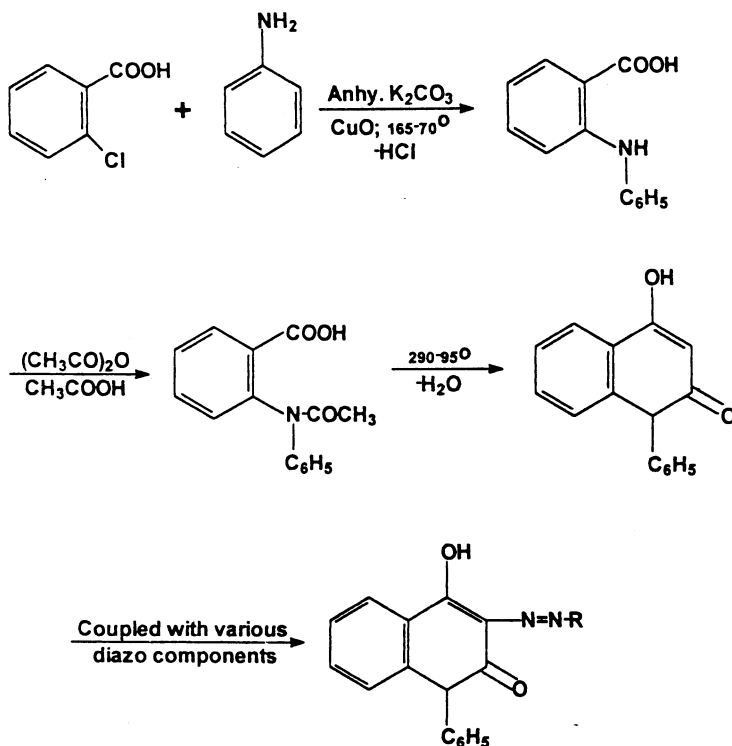
EXPERIMENTAL

N-Phenylanthranilic acid: It was prepared by Ullman's reaction⁴.

N-Phenyl-*N*-acetylanthranilic acid: A mixture of *N*-phenylanthranilic acid (21.3 g; 0.1 mol) glacial acetic acid (22 mL) and acetic anhydride (22 mL) was refluxed for 2 h. The reaction mixture was poured over ice and allowed to stand at room temperature for 24 h. The product was crystallised from ethanol, (68%), m.p. 288°C. [Found: N, 5.32%; C₁₅H₁₃O₃N required: N, 5.49%]; IR (KBr): 3560–3260 ν (—OH), 1620 ν (C=O), 1230 ν (C—O), 1330 ν (C—N) cm⁻¹.

4-Hydroxy-1-phenyl-2-oxoquinazoline (HPOQ): *N*-Phenyl-*N*-acetylanthranilic acid (12.75 g; 0.05 mol) was heated in an oil-bath at 290–295°C for ninety minutes. The brown residue was collected and crystallised from ethanol (78%), m.p. 310–312°. [Found: N, 5.73%; C₁₅H₁₁O₂N required: N, 5.91%]; IR (KBr): 3600–3200 ν (—OH), 1630 ν (C=O), 1220 ν (C—O), 1320 ν (C—N of Ph—N) cm⁻¹; NMR (DMSO-d₆): δ 2.45 (5H, N—C₆H₅), 7.32 (1H, —OH) quinoline ring.

Diazotisation of 1-amino-2-naphthol-4-sulphonic acid: 1-Amino-2-naphthol-4-sulphonic acid (2.39 g; 0.01 mol) was diazotised in the usual manner.



R = Various diazo components

Coupling of diazo solution with HPOQ: A clear solution of HPOQ (2.37 g; 0.01 mol) in NaOH (30 mL; 10%) and acetone (60 mL) was cooled below 5°C. To this well-stirred solution, diazo solution was added dropwise over a period of 15 min maintaining pH 7.5–8.0. The stirring was continued for 2 h at 0–5°C. The reaction mixture was then heated to 60°C and sodium chloride was added until the colouring material was precipitated. The mixture was stirred for 1 h and the resulting solid was dried and purified from DMF-acetone.

All the dyes D₂ to D₁₃ were prepared by the same procedure (Table-1).

Application

2% Shade on silk, wool and nylon

Materials and condition of the experiment are given in Table-2.

The dye-bath (40 mL; 0.1% w/v) with MLR 1 : 30 was adjusted to pH 3 by dilute acetic acid. The sample of fabric was introduced in a dye-bath at room temperature and the temperature was slowly raised to 100°C in 15 min. The fabric was worked up in dye-bath for 1 h. The dyeing was terminated by removing the fabric from dye-bath and stirring it into water (40 mL). The fabric was then removed, squeezed and rinsed with water (50 mL) and resqueezed.

TABLE-1
ANALYTICAL AND PHYSICAL DATA

| Dye No. | Diazo component (R) | Yield (%) | m.p. (°C) | Nitrogen % | |
|-----------------|--|-----------|-----------|------------|----------|
| | | | | Found | Required |
| D ₁ | 1-Amino-2-naphthol-4-sulphonic acid | 54 | > 300 | 8.10 | 8.25 |
| D ₂ | Sulphanilic acid | 67 | > 300 | 9.32 | 9.48 |
| D ₃ | Metanilic acid | 61 | > 300 | 9.24 | 9.48 |
| D ₄ | 3-Aminotoluene-4-sulphonic acid | 63 | > 300 | 9.02 | 9.19 |
| D ₅ | 4-Aminotoluene-3-sulphonic acid | 64 | > 300 | 8.96 | 9.19 |
| D ₆ | 5-Sulphoanthranilic acid | 71 | 190 (d) | 8.44 | 8.62 |
| D ₇ | 2 : 5-Dichloroaniline-4-sulphonic acid | 67 | > 300 | 8.04 | 8.20 |
| D ₈ | H-acid | 72 | > 300 | 6.70 | 6.87 |
| D ₉ | Chicago acid | 65 | 275 (d) | 6.65 | 6.87 |
| D ₁₀ | J-acid | 70 | > 300 | 8.08 | 8.25 |
| D ₁₁ | 2-Aminobenzoic acid | 64 | > 300 | 10.11 | 10.31 |
| D ₁₂ | 3-Aminobenzoic acid | 62 | 290 (d) | 10.09 | 10.31 |
| D ₁₃ | 4-Aminobenzoic acid | 59 | > 300 | 10.20 | 10.31 |

TABLE-2

| S. No. | Material/condition | |
|--------|---|--------|
| 1. | Fabric | 2 g |
| 2. | Dye solution under study (mL; 0.1% w/v) | 40 |
| 3. | pH | 3 |
| 4. | MLR | 1 : 30 |
| 5. | Dyeing time (min) | 60 |
| 6. | Dyeing temperature (°C) | 100 |
| 7. | Total volume of dye-bath (mL) | 60 |

Determination of R_f values: The dyes were separated on TLC using benzyl-alcohol-DMF-water (3 : 2 : 2) solvent system. The results are given in Table-3.

Determination of λ_{max} : Absorption maxima of the dyes were determined in water at 28°C using Bausch and Lomb Spectronic-20 spectrophotometer. The results are shown in Table-3.

Exhaustion study: The percentage exhaustion study of dyes was performed using the standard procedure. The results are given in Table-3.

TABLE-3

| Dye No. | Colour | λ_{\max} | R_f | % Exhaustion | | |
|-----------------|--------|------------------|-------|--------------|------|-------|
| | | | | Wool | Silk | Nylon |
| D ₁ | Brown | 318 | 0.83 | 74 | 62 | 56 |
| D ₂ | Yellow | 317 | 0.82 | 71 | 71 | 64 |
| D ₃ | Brown | 325 | 0.80 | 73 | 69 | 67 |
| D ₄ | Orange | 330 | 0.68 | 78 | 71 | 66 |
| D ₅ | Yellow | 320 | 0.69 | 74 | 72 | 64 |
| D ₆ | Brown | 328 | 0.78 | 85 | 73 | 71 |
| D ₇ | Orange | 320 | 0.83 | 80 | 67 | 72 |
| D ₈ | Brown | 335 | 0.81 | 67 | 54 | 53 |
| D ₉ | Brown | 322 | 0.77 | 71 | 62 | 66 |
| D ₁₀ | Brown | 318 | 0.82 | 83 | 73 | 68 |
| D ₁₁ | Brown | 325 | 0.73 | 74 | 68 | 64 |
| D ₁₂ | Brown | 330 | 0.70 | 73 | 70 | 59 |
| D ₁₃ | Yellow | 322 | 0.72 | 78 | 71 | 62 |

The IR spectra (KBr) of the dyes contained characteristic bands at 3560–3200 Br ν (—OH), 1650 ν (C=O), 1480 ν (N=N), 1220–1080 cm^{-1} ν (S=O).

NMR spectra of dye D₁ recorded in DMSO-d₆ solvent showed signals at δ 3.55 (3H, —NCH₃), 7.32 (1H, —OH) quinoline ring, 6.78 (1H, —OH) naphthol ring, 7.75 (H, —SO₃H).

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