

Synthesis of 2-Chloro-4-[*p*-Nitrophenyl Thiourea]-6-[3'-Arylazo-4'-Hydroxy-1'-Naphthyl]-*s*-Triazine Derivatives and Their Application on Cotton and Wool Fibres

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Attempts have been made to prepare cyanuric chloride derivatives by condensation of naphthol with cyanuric chloride and then with *p*-nitrophenylthiourea and then diazotised and coupled with various diazo components. These compounds were evaluated for their dyeing properties on cotton and wool. The structure of these compounds have been confirmed by elemental analysis, IR and NMR spectral studies.

INTRODUCTION

The discovery and development of reactive dyes for cellulose is of great significance in chemistry and technology of synthetic dyes.¹ The idea is that the establishment of a covalent bond between dye and substrate would result in improved wash fastness.² ICI is the pioneer in first placing in the market these reactive dyes under the name of *procions*. Reactive dyes as a group have made it of bright shades in dyeing and in printing.³ Reactive azo dyes have wider commercial applicability for wool,⁴ cellulose⁵ and leather⁶ etc.

In the present paper we report the synthesis of dyes based on 1-naphthol, cyanuric chloride and various diazo components as a chromophoric system.

EXPERIMENTAL

All the melting points were determined by open capillary method and are not corrected. IR-spectra were recorded in KBr pellets on FTIR-8101 spectrophotometer. PMR spectra (DMSO) were run on Varion 360L spectrophotometer using TMS as an internal standard. The purity of the compound in addition to elemental analysis was checked by TLC.

Preparation of 2,4-dichloro-6-(4'-hydroxy-1'-naphthyl)-s-triazine

In 250 mL flat-bottom flask fitted with an air condenser and guard tube, a mixture of 1-naphthol (14.4 g, 0.1 mole) and cyanuric chloride (18.4 g, 0.1 mole)

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were dissolved in sodium-dried benzene at 5–10°C temperature and stirred; anhydrous AlCl_3 (13.4 g) was added as a catalyst during 2 h at 5–10°C temperature. The temperature was raised to 25–30°C and kept for 12 h. The mixture was filtered and washed with benzene; the product was decomposed in conc. HCl and ice-cold water, and recrystallized from toluene. Yield 83%, m.p. 228°C.

Formation of 2-chloro-4-(*p*-nitrophenylthioureido)-6-(4'-hydroxy-1'-naphthyl)-*s*-triazine (A)

p-nitrophenylthiourea (19.7 g, 0.1 mole) dissolved in acetone was added to the suspension of 2,4-dichloro-6-(4'-hydroxy-1'-naphthyl)-*s*-triazine (29.20 g, 0.1 mole) in acetone (200 mL). The mixture was refluxed at 90°C for 3 h maintaining the pH 7 by addition of sodium carbonate solution (10% w/v). The mixture was allowed to cool to room temperature and poured on crushed ice. The product separated was filtered and dried. It was used as reactive coupling component for the synthesis of monoazo and diazo dyes.

Synthesis of Monoazo Reactive Dyes from 2-Chloro-4-*p*-Nitrophenylthioureido-6-(4'-Hydroxy-1'-Naphthyl)-*s*-Triazine

Diazotization of H-acid and coupling with 2-chloro-4-nitrophenylthioureido-6-(4'-hydroxy-1'-naphthyl)-s-triazine

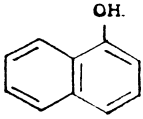
H-acid (3.19 g, 0.01 mole) was suspended in water (36 mL). Hydrochloric acid (1.08 g; 0.03 mole) was added dropwise to the well stirred suspension. The solution was cooled to 0–5°C in an ice bath. A solution of sodium nitrite (0.7 g, 0.01 mole) previously cooled to 0°C was added. The reaction mass was stirred until getting positive test for nitrous acid on starch iodide paper. Excess of nitrous acid was destroyed by adding required amount of sulphamic acid. The resulting diazo solution was used for subsequent coupling reaction.

2-chloro-4-*p*-nitrophenylthioureido-6-(4'-hydroxy-1'-naphthyl)-*s*-triazine (4.53 g; 0.01 mole) was dissolved in acetone. The solution was cooled below 5°C in an ice bath. To this well stirred solution, the above mentioned diazo solution was added maintaining the pH 8 by addition of sodium carbonate solution (10% w/v). The stirring was continued for 3 h keeping the temperature at 0–5°C. After completion of the reaction, sodium chloride solution (10% w/v) was added to the reaction mixture with mechanical stirring, until the solid material was precipitated. It was filtered and washed with small amount of sodium chloride solution (5% w/v). The reactive dye was dissolved in DMF and filtered. To the filtrate acetone was added to precipitate a violet dye. The precipitated dye was filtered and washed with acetone and chloroform and dried. Yield 73%, m.p. 268°C.

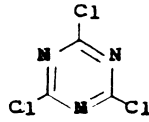
RESULTS AND DISCUSSION

The yield, melting point and elemental analysis of reactive dyes are reported in Table 1.

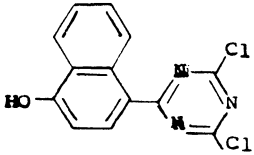
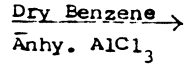
REACTION :



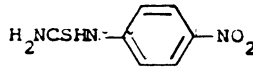
α -naphthol



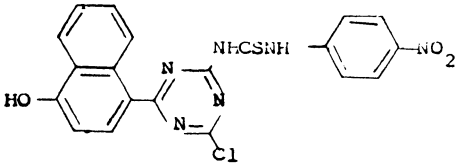
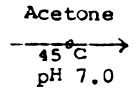
cyanuric chloride



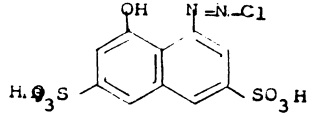
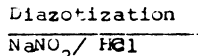
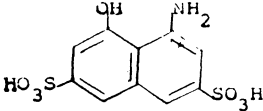
2,4-Dichloro-4'-(4-hydroxy-1'-naphthyl)-s-triazine



p-nitrophenylthiourea



2-Chloro-4-(p-nitrophenyl thiourea-6-(4'-hydroxy-1'-naphthyl)-s-triazine (A)



Coupling reaction
 with (A)
 0-5 C
 pH 8.0

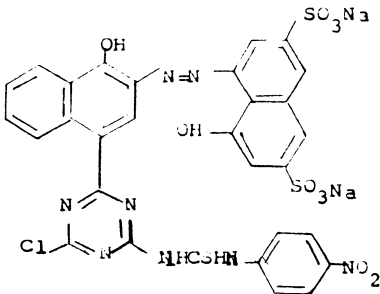


TABLE-I
YIELD, MELTING POINT AND ELEMENTAL ANALYSIS
OF REACTIVE DYES.

Dye No.	Diazo component R	Yield %	m.p. °C (d)	% Analysis Found (Calcd.)		
				C	H	N
D-1	H-Acid	73	268	43.51 (43.55)	2.01 (2.05)	13.51 (13.55)
D-2	J-Acid	76	304	49.64 (49.68)	2.44 (2.48)	15.40 (15.45)
D-3	Gamma-Acid	69	282	49.65 (49.68)	2.43 (2.48)	15.48 (15.45)
D-4	Tobias acid	76	237	50.85 (50.81)	2.58 (2.54)	15.76 (15.80)
D-5	Sulfo Tobias acid	80	265	44.38 (44.42)	2.13 (2.09)	13.81 (13.85)
D-6	Metanilic acid	67	246	47.34 (47.38)	2.47 (2.43)	16.96 (17.00)
D-7	5-sulphoanthranillic acid	76	287	46.16 (46.12)	2.23 (2.27)	15.99 (15.94)
D-8	1, 2, 4-Acid	72	310	49.67 (49.68)	2.43 (2.48)	15.41 (15.46)
D-9	Chicago acid	79	218	43.50 (43.55)	2.01 (2.05)	13.51 (13.55)
D-10	Sulphanilic acid	76	302	50.84 (50.81)	2.51 (2.54)	18.18 (18.22)
D-11	Peri acid	76	305	47.33 (47.38)	2.42 (2.43)	15.76 (15.80)

The dyes varied in hue from light to dark shade of violet-red colour depending on the nature of the diazo component used and their absorption maxima are reported in Table-2. The dyes were applied to cotton and wool. General dye bath exhaustion was assessed by spectrophotometric evaluation of the exhaust liquors. The dyes gave generally satisfactory dyeings on all fibres. Fastness to washing varied from moderate to good and the light fastness was better on wool fibre.

IR-spectroscopy: IR spectra of 2-chloro-4-(*p*-nitrophenylthiourea)-6-(3'-aryazo-4'-hydroxy-1'-naphthyl)-s-triazine derivatives were recorded. On careful observation of these spectra it is found that all the dyes showed a broad band at 1420–1430 cm^{-1} characteristic of N=N stretching; a band around 790–815 cm^{-1} characteristic of C_3N_3 stretching; a band around 725–745 cm^{-1} characteristic of C—Cl stretching; a band around 1170–1190 cm^{-1} characteristic of S=O stretching and a band around 1155–1165 cm^{-1} characteristic of NHCSNH stretching.

TABLE-2
 λ_{\max} R_f VALUE, % EXHAUSTION, SHADE AND WASH-FASTNESS
 OF REACTIVE DYES.

Dye No.	Colour of dyeing on fibre	R _f value	λ_{\max}	Exhaustion %	Fastness to	
					Light	Washing
D-1	Violet-Red	0.77	506	62.5	3	4
D-2	Orange-Red	0.90	532	59.5	4	4-5
D-3	Red-Violet	0.86	562	64.5	3-4	4
D-4	Red	0.77	538	60.0	3	4
D-5	Pink	0.71	546	55.5	4	5
D-6	Red	0.78	487	65.5	4	5
D-7	Red	0.80	518	57.0	3	3-4
D-8	Yellow	0.82	410	59.0	4	4
D-9	Yellow	0.76	498	53.4	4-5	5
D-10	Pink	0.72	520	63.5	4	4
D-11	Yellow	0.77	510	59.0	3	4

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