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The Synthesis of Some 5-Arylazo-2,4,6-trichloropyrimidines and 4-Arylamino-5-arylazo-2,6-dichloropyrimidines and Their Application as Disperse Reactive Dyes for Polyamide Fibres

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SUMMARY

Diazotised arylamines were coupled with barbituric acid to give 5-arylazo-6-hydroxypyrimidine-2,4-diones which were then refluxed with phosphorus oxychloride to give 5-arylazo-2,4,6-trichloropyrimidine dyes. The condensation of some of these with arylamines at low temperature gave 4-arylamino-5-arylazo-2,6-dichloropyrimidine dyes. The dyes were applied to polyamide fibres as disperse reactive dyes and their fastness properties studied.

1 INTRODUCTION

Although polyamide fibres are generally dyed with disperse dyes or acid dyes, certain difficulties are faced using these dyes. Thus, disperse dyes applicable to polyester fibres generally give low fastness on polyamide fibres and acid dyes can result in uneven dyeings due to fibre irregularities.

Disperse reactive dyes[1–8] are applied to polyamide fibres initially as disperse dyes, followed by the reaction on the fibre in an alkaline bath.

The disperse reactive dyes can overcome the above difficulties with acid and disperse dyes and yield even dyeings with good fastness properties.[9] Arylazochloropyrimidines have been reported as disperse reactive dyes.[10,11] We report here the synthesis of some 5-arylazo-2,4,6-trichloropyrimidine and 4-arylamino-5-arylazo-2,6-dichloropyrimidine dyes, their application to polyamide as disperse reactive dyes and an evaluation of their fastness properties.

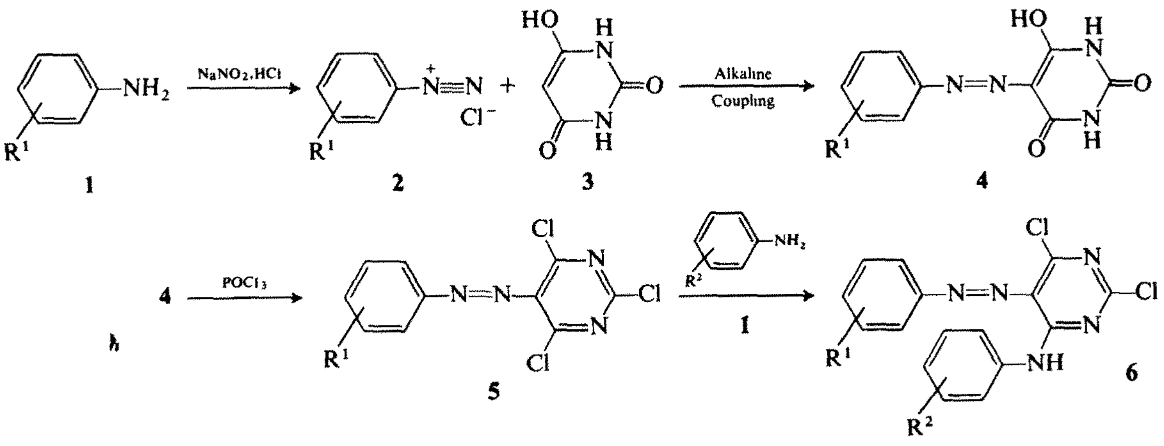
2 RESULTS AND DISCUSSION

Aromatic amines (**1a**–**1k**, Scheme 1) were diazotised and coupled to barbituric acid (**3**) in alkaline coupling conditions to give the corresponding 5-arylazo-6-hydroxypyrimidine-2,4-diones **4a**–**4k**. These dyes were refluxed with phosphorus oxychloride to give the corresponding 5-arylazo-2,4,6-trichloropyrimidine dyes **5a**–**5k**, which contain three labile chlorine atoms. The chlorine atom in the 4- or 6-position is the next labile, being deactivated by the adjacent nitrogen atom in the pyrimidine heterocycle and also by the electron-withdrawing 5-arylazo group. In most cases the reactivity was observed to be such that the chlorine atom was readily replaced by an aromatic amine at low temperature (10–15°C) without the use of an acid-binding agent such as sodium carbonate. The resulting dyes **5a**–**5k** were converted to the 4-arylamino-5-arylazo-2,6-dichloropyrimidine dyes **6a**–**6t** by condensation with representative aromatic amines (**1a**–**1e**, Scheme 1).

TABLE 1
Characterisation Data for 5-Arylazo-6-hydroxypyrimidine-2,4-dione Dyes (**4a**–**4k**)[a]

Dye	*Physical appearance*	*Yield (%)*	*M.p. (°C)*	*Molecular formula*	*Elemental analysis (%)*				
						C	*H*	*N*	*Cl*
4a	Yellow needles	82	>360	$C_{11}H_{10}N_4O_3$	Calculated	53·7	4·1	22·7	—
					Found	53·8	4·0	22·7	—
4b	Yellow needles	80	>360	$C_{11}H_{10}N_4O_4$	Calculated	50·4	3·8	21·4	—
					Found	50·2	3·6	21·5	—
4c	Yellow needles	85	>360	$C_{10}H_7N_4O_3Cl$	Calculated	45·0	2·6	21·0	13·3
					Found	44·9	2·4	20·9	13·2
4d	Yellow crystals	90	>360	$C_{10}H_8N_4O_3$	Calculated	51·7	3·5	24·1	—
					Found	51·5	3·7	24·0	—
4e	Deep yellow needles	86	>360	$C_{10}H_7N_5O_5$	Calculated	43·3	2·5	25·3	—
					Found	43·5	2·4	25·1	—
4f	Yellow needles	75	>360	$C_{11}H_{10}N_4O_3$	Calculated	53·7	4·1	22·7	—
					Found	53·8	4·1	22·9	—
4g	Yellow crystals	84	>360	$C_{11}H_{10}N_4O_4$	Calculated	50·4	3·8	21·4	—
					Found	50·3	3·9	21·3	—
4h	Yellow crystals	88	>360	$C_{10}H_7N_4O_3Cl$	Calculated	45·0	2·6	21·0	13·3
					Found	45·0	2·7	21·2	13·5
4i	Yellow needles	90	>360	$C_{11}H_{10}N_4O_3$	Calculated	53·7	4·1	22·7	—
					Found	53·5	4·0	22·6	—
4j	Yellow needles	95	>360	$C_{10}H_7N_4O_3Cl$	Calculated	45·0	2·6	21·0	13·3
					Found	45·1	2·8	20·8	13·1
4k	Deep yellow needles	85	>360	$C_{10}H_7N_5O_5$	Calculated	43·3	2·5	25·3	—
					Found	43·6	2·7	25·4	—

[a] Crystallised from water.



					R^1		R^1	R^2		R^1	R^2
1a	**2a**	**3a**	**4a**	**5a**	4-CH_3	**6a**	4-CH_3	4-CH_3	**6k**	4-Cl	4-CH_3
1b	**2b**	**3b**	**4b**	**5b**	4-OCH_3	**6b**	4-CH_3	4-OCH_3	**6l**	4-Cl	4-OCH_3
1c	**2c**	**3c**	**4c**	**5c**	4-Cl	**6c**	4-CH_3	4-Cl	**6m**	4-Cl	H
1d	**2d**	**3d**	**4d**	**5d**	H	**6d**	4-CH_3	4-NO_2	**6n**	4-Cl	4-NO_2
1e	**2e**	**3e**	**4e**	**5e**	4-NO_2	**6e**	4-CH_3	H	**6o**	2-CH_3	4-OCH_3
1f	**2f**	**3f**	**4f**	**5f**	2-CH_3	**6f**	2-OCH_3	4-CH_3	**6p**	2-CH_3	4-CH_3
1g	**2g**	**3g**	**4g**	**5g**	2-OCH_3	**6g**	2-OCH_3	4-OCH_3	**6q**	2-CH_3	4-NO_2
1h	**2h**	**3h**	**4h**	**5h**	2-Cl	**6h**	2-OCH_3	4-Cl	**6r**	2-CH_3	4-Cl
1i	**2i**	**3i**	**4i**	**5i**	3-CH_3	**6i**	2-OCH_3	4-NO_2	**6s**	2-CH_3	H
1j	**2j**	**3j**	**4j**	**5j**	3-Cl	**6j**	2-OCH_3	H	**6t**	4-OCH_3	4-Cl
1k	**2k**	**3k**	**4k**	**5k**	3-NO_2						

Scheme 1

Characterisation data for dyes **4a–4k**, **5a–5k** and **6a–6t** are shown in Tables 1, 2 and 3, respectively.

The IR spectra of dyes **4a–4k** indicated that azohydroxy and hydrazoketo tautomeric forms exist in these dyes. Thus, the IR spectra of dyes **5a–5k** showed the absence of hydroxy, keto and imidic —NH— functions, but the spectra of dyes **6a–6t** showed a peak between 3180 and 3200 cm^{-1} indicating the presence of an imidic —NH— of the arylamino group.

5-Arylazo-2,4,6-trichloropyrimidine dyes (**5a–5k**) and 4-arylamino-5-arylazo-2,6-dichloropyrimidine dyes (**6a–6t**) were applied to polyamide fibres as disperse reactive dyes and are yellow, orange and brown hues (see Table 4).

The pick-up of the 5-arylazo-2,4,6-trichloropyrimidine dyes **5a–5k** and of the 4-arylamino-5-arylazo-2,6-dichloropyrimidine dyes **6a–6t** varied from poor to excellent and the lightfastness of the dyeings was poor to fairly good.

TABLE 2

Characterisation Data for 5-Arylazo-2,4,6-trichloropyrimidine Dyes (**5a–5k**)[a]

Dye	*Physical appearance*	*Yield (%)*	*M.p. (°C)*	*Molecular formula*		*Elemental analysis (%)*			
						C	*H*	*N*	*Cl*
5a	Pale red needles	85	85	$C_{11}H_7N_4Cl_3$	Calculated	43·8	2·3	18·6	35·3
					Found	43·6	2·8	18·7	35·2
5b	Pale red needles	85	90–91	$C_{11}H_7N_4OCl_3$	Calculated	41·6	2·2	17·6	33·5
					Found	41·2	2·1	17·3	34·0
5c	Orange needles	83	71–72	$C_{10}H_4N_4Cl_4$	Calculated	37·3	1·2	17·4	44·1
					Found	37·5	1·2	17·6	43·8
5d	Yellow needles	82	89	$C_{10}H_5N_4Cl_3$	Calculated	41·8	1·8	19·5	37·0
					Found	41·5	1·9	19·3	36·8
5e	Brown needles	88	230	$C_{10}H_4N_5O_2Cl_3$	Calculated	36·1	1·2	21·1	32·0
					Found	35·8	1·4	20·9	31·7
5f	Orange needles	86	135	$C_{11}H_7N_4Cl_3$	Calculated	43·8	2·3	18·6	35·3
					Found	43·5	2·2	18·6	35·1
5g	Pale red needles	85	87–90	$C_{11}H_7N_4OCl_3$	Calculated	41·6	2·2	17·6	33·5
					Found	41·2	2·0	17·5	33·2
5h	Orange needles	89	80	$C_{10}H_4N_4Cl_4$	Calculated	37·3	1·2	17·4	44·1
					Found	37·1	1·2	17·3	44·3
5i	Orange needles	90	95–97	$C_{11}H_7N_4Cl_3$	Calculated	43·8	2·3	18·6	35·3
					Found	43·5	2·6	18·3	35·6
5j	Orange needles	86	120–122	$C_{10}H_4N_4Cl_4$	Calculated	37·3	1·2	17·4	44·1
					Found	37·0	1·3	17·2	44·8
5k	Brown needles	85	135	$C_{10}H_4N_5O_2Cl_3$	Calculated	36·1	1·2	21·1	32·0
					Found	35·7	1·1	20·7	32·7

[a] Crystallised from benzene.

TABLE 3

Characterisation Data for 4-Arylamino-5-arylazo-2,6-dichloropyrimidine Dyes (**6a–6k**)[a]

Dye	*Physical appearance*	*Yield* (%)	*M.p.* (°*C*)	*Molecular formula*	*Elemental analysis* (%)		
						N	*Cl*
6a	Yellow crystals	96	200	$C_{18}H_{15}N_5Cl_2$	Calculated	18·8	19·1
					Found	18·8	18·7
6b	Orange crystals	97	206	$C_{18}H_{15}N_5OCl_2$	Calculated	18·0	18·3
					Found	17·3	18·1
6c	Yellow crystals	95	223	$C_{17}H_{12}N_5Cl_3$	Calculated	17·8	27·1
					Found	17·6	27·0
6d	Dark yellow crystals	96	210–211	$C_{17}H_{12}N_6O_2Cl_2$	Calculated	20·8	17·6
					Found	21·0	17·9
6e	Yellow crystals	98	213	$C_{17}H_{13}N_5Cl_2$	Calculated	19·6	19·8
					Found	20·0	20·2
6f	Yellow crystals	94	265	$C_{18}H_{15}N_5OCl_2$	Calculated	18·0	18·3
					Found	17·9	18·1
6g	Orange crystals	97	271–272	$C_{18}H_{15}N_5O_2Cl_2$	Calculated	17·3	17·6
					Found	17·1	18·0
6h	Dark yellow crystals	96	286	$C_{17}H_{12}N_5OCl_3$	Calculated	17·2	26·8
					Found	17·4	26·4
6i	Dark yellow crystals	97	275	$C_{17}H_{12}H_6O_3Cl_2$	Calculated	20·1	17·0
					Found	19·8	17·3
6j	Yellow crystals	94	230–231	$C_{17}H_{13}N_5OCl_2$	Calculated	18·7	19·0
					Found	19·0	18·8
6k	Yellow crystals	95	190–191	$C_{17}H_{12}N_5Cl_3$	Calculated	17·8	27·1
					Found	17·7	26·6
6l	Orange crystals	94	242	$C_{17}H_{12}N_5OCl_3$	Calculated	17·2	26·8
					Found	17·4	26·3
6m	Yellow crystals	95	181	$C_{16}H_{10}N_5Cl_3$	Calculated	18·5	28·1
					Found	18·1	28·3
6n	Dark yellow crystals	97	250	$C_{16}H_9N_6O_2Cl_3$	Calculated	19·8	25·2
					Found	19·3	25·4
6o	Orange crystals	95	228–230	$C_{18}H_{15}N_5OCl_2$	Calculated	18·0	18·3
					Found	18·4	18·1
6p	Yellow crystals	93	201	$C_{18}H_{15}N_5Cl_2$	Calculated	18·8	19·1
					Found	18·4	19·3
6q	Dark yellow crystals	95	218	$C_{17}H_{12}N_6O_2Cl_2$	Calculated	20·8	17·6
					Found	20·8	17·3
6r	Yellow crystals	98	246–250	$C_{17}H_{12}N_5Cl_3$	Calculated	17·8	27·1
					Found	17·6	26·9
6s	Yellow crystals	98	270	$C_{17}H_{13}N_5Cl_2$	Calculated	19·6	19·8
					Found	20·0	20·1
6t	Red crystals	96	211	$C_{17}H_{12}N_5OCl_3$	Calculated	17·2	26·8
					Found	17·5	27·0

[a] Crystallised from acetone.

TABLE 4
Hues, Pick-up and Lightfastness of Pyrimidine Reactive Disperse Dyes **5a**–**5k** and **6a**–**6t** on Polyamide (1% Shade)

Dye	*Hue*	*Pick-up*	*Light-fastness*	*Dye*	*Hue*	*Pick-up*	*Light-fastness*
5a	Golden yellow	4	4	**6f**	Golden yellow	1	2
5b	Bright golden yellow	4	4	**6g**	Orange	1	2
5c	Lemon yellow	2	2	**6h**	Lemon yellow	1	1
5d	Yellow	2	3	**6i**	Orange	1	2
5e	Yellow	1	2	**6j**	Bright orange	2	2
5f	Orange	4	4	**6k**	Golden yellow	1	2
5g	Orange	4	4	**6l**	Golden yellow	1	2
5h	Yellow	4	4	**6m**	Lemon yellow	2	2
5i	Pale yellow	1	1	**6n**	Golden yellow	4	4
5j	Bright orange	4	4	**6o**	Orange	2	3
5k	Orange	3	1	**6p**	Golden yellow	2	3
6a	Lemon yellow	1	2	**6q**	Orange	2	3
6b	Orange	2	2	**6r**	Yellow	4	3
6c	Lemon yellow	1	1	**6s**	Golden yellow	4	4
6d	Lemon yellow	2	1	**6t**	Bright orange	1	2
6e	Lemon yellow	2	1				

Dyes **5a**, **5b**, **5f**–**5h**, **5j**, **6n** and **6s** had excellent pick-up and fairly good lightfastness properties and may be considered as satisfactory new disperse reactive dyes.

3 EXPERIMENTAL

All melting points are uncorrected and are in °C. Infrared spectra were recorded on a Perkin–Elmer Model 397 spectrometer in nujol mull.

3.1 Preparation of starting materials

Barbituric acid (**3**), m.p. 248°, was prepared as previously described.[12]

3.2 5-(4-Methylphenyl)azo-6-hydroxypyrimidine-2,4-dione (4a)

A mixture of *p*-toluidine (2·14 g; 0·02 mol) and aqueous hydrochloric acid (4·8 ml of 1·6M; 0·05 mol) was heated on a waterbath to obtain a clear solution. The solution was cooled to 5°C and sodium nitrite (1·38 g; 0·02 mol) dissolved in water (20 ml) was slowly added with stirring over 15 min. The diazo solution thus formed was stirred for 30 min and excess nitrous acid was destroyed with urea (0·2 g). The resulting clear diazo solution was slowly run at 0–5°C into a fine suspension of barbituric acid (2·56 g; 0·02 mol) in water (300 ml) mixed with sodium carbonate (6·4 g; 0·06 mol) in water (150 ml). The pH of the mixture was maintained at 10 during coupling, which was complete in 30 min. The mixture was stirred at 0–10°C for a further 6 h and then neutralised with dilute hydrochloric acid (10%). The precipitated dye was filtered, washed with cold water and dried at 40–50°C. It was recrystallised from water in yellow crystals (82%), m.p. >300°.

Calculated for $C_{11}H_{10}N_4O_3$: C, 53·7; H, 4·1; N, 22·7.
Found: C, 53·8; H, 4·0; N, 22·7%.

The other 5-arylazo-6-hydroxypyrimidine-2,4-diones **4b**–**4k** were prepared in the manner described above in 75–95% yield. They were yellow crystalline substances all melting above 300° and elemental analyses were in agreement with those calculated for their respective molecular formulae (Table 1).

3.3 5-(4-Methylphenyl)azo-2,4,6-trichloropyrimidine (5a)

A mixture of dye **4a** (2·46 g; 0·01 mol) and phosphorus oxychloride (40 ml; 0·432 mol) was gently refluxed. The colour of the mixture changed from yellow to green and after 1 h again became yellow. The mixture was refluxed until the reaction was complete (20 h) (monitored by TLC). Most of phosphorus oxychloride was distilled under vacuum and the remaining reaction mixture (about 10 ml) was poured into ice–water mixture (about 300 g) with vigorous stirring to give a red oil which on prolonged stirring (8 h) yielded an orange solid. The product was washed with cold water until the filtrate was neutral to Congo Red paper. It was dried at 40–50°C and recrystallised from benzene in pale red needles (85%), m.p. 85°.

Calculated for $C_{11}H_7N_4Cl_3$: C, 43·8; H, 2·3; N, 18·6; Cl, 35·3.
Found: C, 43·6; H, 2·8; N, 18·7; Cl, 35·2%.

The above procedure was followed for the preparation of the other 5-arylamino-6-arylazo-2,4,6-trichloropyrimidine dyes **5b**–**5k**, characterisation data for which are shown in Table 2.

3.4 4-(4-Methylphenyl)amino-5-(4-methylphenyl)azo-2,6-dichloropyrimidine (6a)

The dye **5a** (3·00 g; 0·01 mol) was dissolved in acetone (50 ml) and a solution of *p*-toluidine (**1a**) (1·07 g; 0·01 mol) in acetone (20 ml) was added slowly with stirring at 15°C. Stirring was continued at room temperature until the reaction was complete (1 h) (monitored by TLC) and during this time most of the product separated from solution. The dye was filtered and more dye was recovered from the filtrate by dilution with ice–water mixture (about 100 g). The dye was washed with dilute hydrochloric acid, then with cold water, dried at 40–50°C and recrystallised from acetone in yellow crystals (96%), m.p. 200°.

Calculated for $C_{18}H_{15}N_5Cl_2$: C, 58·1; H, 4·0; N, 18·8; Cl, 19·1.

Found: C, 57·8; H, 4·4; N, 18·8; Cl, 18·7%.

The above procedure was followed for the preparation of the other 4-arylamino-5-arylazo-2,6-dichloropyrimidines **6a–6t**, characterisation data for which are shown in Table 3.

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REFERENCES

1. H. Zollinger, *Rev. Text. Prog.*, **11**, 215 (1959).
2. E. Siegel, *Synthesis and Reaction Mechanisms in Colour Chemistry, Chimia* Supplement (1968), p. 100.
3. ICI, British Patent 833396 (1960); *Chem. Abstr.*, **55**, 3077 (1961).
4. ICI, British Patent 840903 (1960); *Chem. Abstr.*, **55**, 3989 (1961).
5. O. A. Stamm, *J. Soc. Dyers Colourists*, **80**, 416 (1964).
6. ICI, British Patent 836671 (1960); *Chem. Abstr.*, **54**, 23348 (1960).
7. ICI, British Patent 879263 (1961); *Chem. Abstr.*, **57**, 8698 (1963).
8. ICI, British Patent 868471 (1961); *Chem. Abstr.*, **56**, 1567 (1962).
9. D. F. Scott and T. Vickerstaff, *J. Soc. Dyers Colourists*. **76**, 104 (1960).
10. M. Capponi, *Amer. Dyestuff Reporter*, **50**, 505 (1961).
11. ICI, British Patent 822948 (1959); *Chem. Abstr.*, **54**, 8094 (1961).
12. J. B. Dickey and A. R. Gray, *Org. Synth. Coll. Volumes*, Vol. II, ed. A. H. Blatt, 60 (1943).