

Disperse Dyes: Part XX—Synthesis of 4-Arylazo-1-naphthylaminoacrylates

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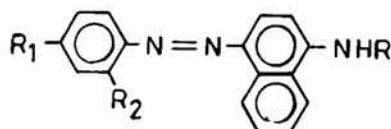
Several 4-arylazo-1-naphthylaminoacrylates have been synthesized by reacting 4-arylazo-1-naphthylamines with conjugated enol ethers like ethyl ethoxymethylenemalonate and ethyl ethoxymethylenecyanoacetate. The dyeing properties of these dyes together with those of the acyl and benzoyl derivatives of amino azo dyes have been studied. Incorporation of the acrylate chains in the dye structure has been found to improve the pick up of the dyes considerably. The light and sublimation fastness of the acrylate dyes varies from very good to excellent.

Since 4-arylazo-1-phenylaminoacrylate dyes have shown some improved fastness on polyester¹, it was considered of interest to extend the range of these dyes in naphthalene series and study their dyeing properties. In our initial studies, the monoazo dyes, synthesized using aniline and its derivatives as diazo components and 1-naphthylamine as the coupling component, were reacted with conjugated enol ethers like ethyl ethoxymethylenemalonate (EMME) to get the naphthylaminoacrylate dyes in 85-95% yield. Alternatively, the monoazo dyes were first reacted with ethyl orthoformate to get the formamidin compound², which on reacting with diethyl malonate or ethyl cyanoacetate in the presence of a base like piperidine gave identical naphthylaminoacrylate dyes in a little

lower yield (70-75%). The dyes derived from diazo components containing electron-withdrawing groups at the *o* and *p* positions of the amino group, such as NO₂, failed to give the desired aminoacrylates by either of the processes. This apparently was due to the considerably reduced basicity of the amino group of the azo dyes. Cyclization of the acrylates to the corresponding naphthopyridines in refluxing xylene or diphenyl ethers was also not successful.

For comparison, the dyeing properties of the parent aminoazo dyes and of their acyl and benzoyl derivatives were investigated together with those of the naphthylaminoacrylate dyes. The dyes gave golden-yellow to orange shades. The pick up of the dyes was much better than that of the acylated dyes. The light

Table 1—Yields, Melting Points and Visible Absorption Data of Dyes Synthesized



Dye No.	Substituents			Yield %	M.P. °C	Molecular formula	Visible absorption	
	R	R ₁	R ₂				λ _{max} nm	Log ε
D1	H	Cl	H	90	190(lit ² , 191)	C ₁₆ H ₁₂ N ₃ Cl	464	4.4876
D2	-CH=C	Cl	H	90(method I) 75 (method II)	135	C ₂₄ H ₂₂ N ₃ O ₄ Cl	426	4.5623
D3	-CH=C	Cl	H	88(method I) 72(method II)	220	C ₂₂ H ₁₇ N ₄ O ₂ Cl	426	4.5454
D4	-COCH ₃	Cl	H	95	250	C ₁₈ H ₁₄ N ₃ OCl	400	4.2538
D5	-COC ₆ H ₅	Cl	H	90	210	C ₂₃ H ₁₆ N ₃ OCl	400	4.3410
D6	-H	CH ₃	H	95	149 (Lit ³ , 149-50)	C ₁₇ H ₁₅ N ₃	438	4.4187

—Contd.

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Table 1—Yields, Melting Points and Visible Absorption Data of Dyes Synthesized—Contd.

Dye No.	Substituents			Yield %	M.P. °C	Molecular formula	Visible absorption	
	R	R ₁	R ₂				λ_{\max} nm	Log ϵ
D7	-CH=C	COOEt COOEt	CH ₃ H	82(method I) 75(method II)	157	C ₂₅ H ₂₅ N ₃ O ₄	412	4.2083
D8	-CH=C	CN COOEt	CH ₃ H	85(method I) 70(method II)	210-12	C ₂₃ H ₂₀ N ₄ O ₂	410	4.2646
D9	-COCH ₃	CH ₃	H	95	238	C ₁₉ H ₁₇ N ₃ O	400	4.8083
D10	-COC ₆ H ₅	CH ₃	H	90	213	C ₂₄ H ₁₉ N ₃ O	400	3.9338
D11	-H	Cl	OCH ₃	89	152	C ₁₇ H ₁₄ N ₃ OCl	480	4.4662
D12	-CH=C	COOEt COOEt	Cl OCH ₃	95(method I) 72 (method II)	165	C ₂₅ H ₂₄ N ₃ O ₃ Cl	428	4.6251
D13	-CH=C	CN COOEt	Cl OCH ₃	85 (method I) 75(method II)	210	C ₂₃ H ₁₉ N ₄ O ₃ Cl	425	4.5462
D14	-COCH ₃	Cl	OCH ₃	98	245	C ₁₉ H ₁₆ N ₃ O ₂ Cl	410	4.3049
D15	-COC ₆ H ₅	Cl	OCH ₃	85	165	C ₂₄ H ₁₈ N ₃ O ₂ Cl	408	4.2520
D16	-H	OCH ₃	H	90	125 (Lit ³ , 125)	C ₁₇ H ₁₅ N ₃ O	—	—
D17	-CH=C	COOEt COOEt	OCH ₃ H	95(method I) 74(method II)	145	C ₂₅ H ₂₅ N ₃ O ₃	—	—
D18	-CH=C	CN COOEt	OCH ₃ H	80(method I) 75(method II)	240	C ₂₃ H ₂₀ N ₄ O ₃	—	—
D19	-COCH ₃	OCH ₃	H	95	216	C ₁₉ H ₁₇ N ₃ O ₂	—	—
D20	-COC ₆ H ₅	OCH ₃	H	90	150	C ₂₄ H ₁₉ N ₃ O ₂	—	—

All the dyes gave correct elemental analysis.

Table 2—Shades, Pick Up and Fastness of Dyes on Polyester

Dye No.	Colour of dyeing (1% shade)	Pick up	Xeno light fastness	Thermo test (30 sec, at 180°C)
D1	Yellowish orange	2	1	1-2
D2	Yellowish orange	+5	5-6	4-5
D3	Yellowish orange	+5	4-5	4-5
D4	Golden yellow	3	6	4
D5	Golden yellow	3	6	4-5
D6	Orange	4	1	1-2
D7	Golden yellow	+5	5-6	4-5
D8	Golden yellow	+4	4-5	4
D9	Golden yellow	3	6	4
D10	Golden yellow	3	6	4-5
D12	Orange	+5	5-6	4
D13	Orange	4	5	4-5
D14	Yellow	3	6	4
D15	Yellowish orange	3	4-5	4
D17	Yellowish orange	+5	5	4-5
D18	Reddish yellow	4	5	4-5
D19	Yellow	4	5	4
D20	Reddish yellow	+4	4	4-5

and sublimation fastness grades were satisfactory. The acrylate dyes, in general, showed better dyeing properties.

Experimental Procedure

Synthesis of 4-Arylazo-1-naphthylaminoacrylates

Method I—A solution of monoazo dye (0.01 mol)

and EMME (0.01 mol in 10 ml benzene) was refluxed for 4 hr. On cooling, the acrylate dye separated out and was isolated. More of the acrylate dye was obtained on concentrating and cooling the filtrate. The dye was crystallized from benzene; yield, 85-95%.

Method II—To a solution of monoazo dye (0.01 mol) in xylene (20 ml) ethyl orthoformate (0.012 ml) was added and the mixed solution was refluxed for 2 hr. The reaction solution was cooled to 60-70°C, and diethyl malonate (0.01 mol) and piperidine (0.01 mol) were added slowly in 15-20 min. The resultant solution was refluxed for 5 hr. After the reaction was over (tlc), the solvent was removed under vacuum. The residue was crystallized from benzene; yield, 70-75%.

Acetylation of aminoazo dyes was done with acetic anhydride and pyridine at room temperature for 12 hr. Benzoylation was carried out with excess of benzoyl chloride in refluxing benzene for 4 hr. All the dyes were dispersed and applied on polyester by the high temperature method. The details of the dyes and their dyeing properties are given in Tables 1 and 2.

References

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