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Polycyclic Compounds. Part V: Reaction of Aminoanthraquinones with α,β-Unsaturated Carbonyl Compounds; Synthesis of Disperse Dyes for Polyester*

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SUMMARY

*The reaction of 1-aminoanthraquinone (**1**) and 1,5-diaminoanthraquinone (**2**) with α,β-unsaturated ketones in the presence of anhydrous aluminium chloride led to the facile formation of new substituted dihydroanthrapyridinequinones **3** in a one-stage synthesis. 2-Aminoanthraquinone failed to react under identical conditions. The investigations were extended to the reaction of **1** and **2** with acrylonitrile, methyl acrylate, methyl methacrylate and diethyl ethoxymethylenemalonate to yield the substituted aminoanthraquinones **4**. The new compounds were evaluated as disperse dyes on polyester.*

1 INTRODUCTION

Reactions of aminoanthraquinones with α,β-unsaturated esters or nitriles have been previously reported.[1–4] Thus, several *N*-(anthraquinonyl)-β-aminopropionic acids and *N*-(anthraquinonyl)-β-aminopropionitriles have been synthesised by reacting aminoanthraquinones with methyl acrylate and acrylonitrile respectively in the presence of sulphuric acid in a sealed tube at 100–115°C for 36 h. These compounds are of interest as disperse dyes having improved fastness properties.[1] Disperse dyes with excellent fastness properties have been synthesised by reacting 1-amino-4-substituted anthraquinones with methyl acrylate or acrylic acid in the presence of sulphuric acid.[2–4] In this communication, investigations of the reaction of

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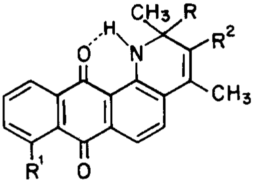
1-amino- and 1,5-diaminoanthraquinones with α,β-unsaturated ketones in the presence of anhydrous aluminium chloride as an acid catalyst are presented. The reactions led to the facile formation of new substituted dihydroanthrapyridinequinones (**3**) in a one-stage operation.

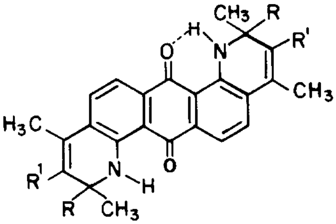
2 RESULTS AND DISCUSSION

1-Aminoanthraquinone (**1**) and 1,5-diaminoanthraquinone (**2**) were reacted with acetone and methyl ethyl ketone (MEK) in the presence of an excess of anhydrous aluminium chloride as catalyst. Excess of the ketone was used as solvent and the reactions were carried out at reflux temperatures. The ketones, by a process of self-condensation in the presence of anhydrous aluminium chloride, were converted into the corresponding α,β-unsaturated ketones, which then reacted with the aminoanthraquinones to yield the new substituted dihydroanthrapyridinequinones (**3a**–**3f**). Whilst the reactions of the ketones with 1-aminoanthraquinone gave good yields of the products **3a** and **3b**, the reactions with 1,5-diaminoanthraquinone were sluggish and the products **3c**, **3e** and **3f** were obtained in lower yields. The reaction of 1,5-diaminoanthraquinone with MEK yielded **3f** as the sole product. The formation of product **3d**, analogous to **3c**, was not observed. Under identical conditions, 2-aminoanthraquinone failed to react. Pyridinoanthraquinones have been previously synthesised by first preparing 'anthraquinonyl aminoacrylates' and the subsequently cyclising them in diphenyl ether at 200°C.[5-7]



3a–3d

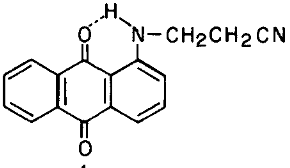
3a: $R = CH_3$, $R^1 = H$, $R^2 = H$
3b: $R = C_2H_5$, $R^1 = H$, $R^2 = CH_3$
3c: $R = CH_3$, $R^1 = NH_2$, $R^2 = H$
3d: $R = C_2H_5$, $R^1 = NH_2$, $R^2 = CH_3$



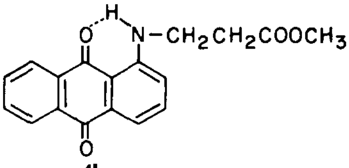
3e–3f

3e: $R = CH_3$, $R^1 = H$
3f: $R = C_2H_5$, $R^1 = CH_3$

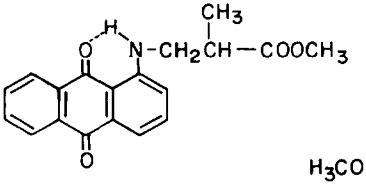
The investigations were extended to the reaction of **1** and **2** with other α,β-unsaturated compounds such as acrylonitrile, methyl acrylate, methyl methacrylate and diethyl ethoxymethylenemalonate, to yield the substituted aminoanthraquinones **4a**–**4e**. Similar reactions had been previously effected



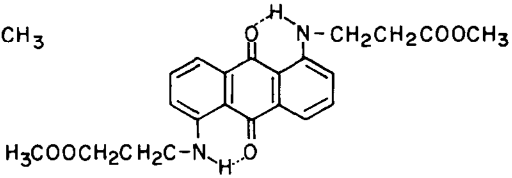
4a



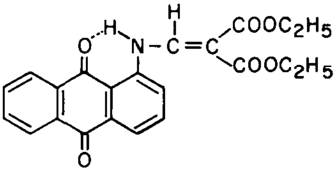
4b



4c



4d



4e

under sealed-tube conditions in the presence of sulphuric/acetic acid at about 110°C[1–3] using reaction times of 36–72 h. The reaction conditions reported in this present work involve reflux for only about 8 h. Further, the products **4a**–**4e** were obtained in better yields (45–60%). A discrepancy in the melting points of the products (**4a**, **4b** and **4d**) was observed compared with those reported earlier.[1,2] The compounds **4** synthesised in the present work were purified by column chromatography and their structures confirmed by visible, IR and ^{1}H-NMR spectral analyses. In general, the condensations were carried out by refluxing equimolar quantities of **1** or **2** and α,β-unsaturated compounds in ethylene dichloride in the presence of two molar equivalents of anhydrous aluminium chloride. However, the reaction of **1** with diethyl ethoxymethylenemalonate could be accomplished at 30°C to yield **4e** in quantitative yield. Earlier workers had carried out the reaction in refluxing xylene for 4 h to obtain **4e** in 92% yield.[5]

The structures of the dyes **3a**–**3e** and **4a**–**4e** were assigned on the basis of their visible, IR and ^{1}H-NMR spectral data (Table 1). The microanalytical data for C, H and N (Table 2) were in accordance with the assigned structures. These dyes were applied to polyester and the shades produced, pick-up and fastness properties are recorded in Table 3.

The reactions were found to be dependent on the quantity of anhydrous aluminium chloride used. In the presence of an equimolar quantity of the

TABLE 1
Visible, IR and ^{1}H-NMR Spectral Data

Dye	*Visible*		*IR* (cm^{-1})	^{1}*H-NMR* δ *(ppm)*
	λ_{max} *(nm)*	*(ε)*		
3a	550	(7 653)	3210(NH) 1650(C=O)	1·50 (s, 6H, 2C-($\mathrm{C\underline{H}_3}$)), 2·05 (s, 3H, 4C-$\mathrm{C\underline{H}_3}$), 5·63 (s, 1H, 3C-$\underline{\mathrm{H}}$), 7·22 (d, 1H, 5C-$\underline{\mathrm{H}}$, $J = 8$ Hz), 7·55 (d, 1H, 6C-$\underline{\mathrm{H}}$, $J = 8$ Hz), 8·2–8·43 (m, 2H, 8C, 11C-$\underline{\mathrm{H}}$), 7·6–7·88 (m, 2H, 9C-, 10C-$\underline{\mathrm{H}}$), 10·3 (bs, 1H, -$\mathrm{N\underline{H}}$)
3b	535	(6 196)	3280(NH) 1640(C=O)	0·92 (t, 3H, 2C-$\mathrm{CH_2C\underline{H}_3}$), 1·5 (s, 3H, 2C-$\mathrm{C\underline{H}_3}$), 1·63 (q, 2H, 2C-$\mathrm{C\underline{H}_2CH_3}$), 1·87 (s, 3H, 3C-$\mathrm{C\underline{H}_3}$), 2·0 (s, 3H, 4C-$\mathrm{C\underline{H}_3}$), 7·19 (d, 1H, 5C-$\underline{\mathrm{H}}$, $J = 9$ Hz), 7·55 (d, 1H, 6C-$\mathrm{C\underline{H}}$, $J = 9$ Hz), 7·43–7·68 (m, 2H, 8C, 11C-$\underline{\mathrm{H}}$), 8·0–8·23 (m, 2H, 9C, 10C-H), 10·0 (bs, 1H, -$\mathrm{N\underline{H}}$)
3c	580	(5 026)	3290($\mathrm{NH_2}$) 1620(C=O)	1·53 (s, 6H, 2C-($\mathrm{C\underline{H}_3}$)$_2$), 1·9 (s, 3H, 4C-$\mathrm{C\underline{H}_3}$), 5·1 (s, 1H, 2C-$\underline{\mathrm{H}}$), 6·32 (d, 1H, 5C-$\underline{\mathrm{H}}$, $J = 9$ Hz), 6·8–7·0 (m, 4H, 6C-, 9C-, 10C-, 11C-$\underline{\mathrm{H}}$), 9·43 (bs, 1H, -$\mathrm{N\underline{H}}$)
3e	560	(17 000)	3260(NH) 1610(C=O)	1·31 (s, 12H, 2C, 9C-($\mathrm{C\underline{H}_3}$)$_2$), 1·85 (s, 6H, 4C, 11C-$\mathrm{C\underline{H}_3}$), 5·05 (s, 2H, 3C-, 10C-$\underline{\mathrm{H}}$), 6·6 (d, 2H, 5C, 12C-$\underline{\mathrm{H}}$, $J = 8$ Hz), 6·82 (d, 2H, 6C-, 13C-$\underline{\mathrm{H}}$, $J = 8$ Hz), 9·2 (bs, 2H, 1C-, 8C-$\mathrm{N\underline{H}}$)
3f	585	(15 818)	3200(NH) 1610(C=O)	0·9 (t, 6H, 2C, 9C-$\mathrm{CH_2C\underline{H}_3}$), 1·47 (s, 6H, 2C, 9C-$\mathrm{C\underline{H}_3}$), 1·7 (q, 4H, 2C-, 9C-$\mathrm{C\underline{H}_2CH_3}$), 1·87 (s, 6H, 3C-, 10C-$\mathrm{C\underline{H}_3}$), 2·0 (s, 6H, 4C, 11C-$\mathrm{C\underline{H}_3}$), 7·03 (d, 2H, 5C-, 12C-$\underline{\mathrm{H}}$, $J = 9$ Hz), 7·45 (d, 2H, 6C-, 13C-$\underline{\mathrm{H}}$, $J = 8$ Hz), 10·03 (bs, 2H, 1C, 8C-$\mathrm{N\underline{H}}$)
4a	510	(5 419)	3270(NH), 2186(CN) 1650(C=O)	3·25 (t, 2H, C-$\mathrm{C\underline{H}_2}$), 4·1 (t, 2H, N-$\mathrm{C\underline{H}_2}$), 7·87–8·34 (m, 4H, 2C-, 3C-, 6C-, 7C-$\underline{\mathrm{H}}$), 8·28–8·53 (m, 3H, 4C-, 5C-, 8C-$\underline{\mathrm{H}}$)
4b	500	(6 017)	3350(NH) 1660(C=O)	2·7 (t, 2H, $\mathrm{C\underline{H}_2COOCH_3}$), 3·53 (t, 2H, N-$\mathrm{C\underline{H}_2}$), 3·72 (s, 3H, O-$\mathrm{C\underline{H}_3}$), 6·9 (m, 1H, 2C-$\underline{\mathrm{H}}$), 7·32–7·7 (m, 4H, 3C-, 4C-, 6C-, 7C-$\underline{\mathrm{H}}$), 7·97–8·2 (m, 2H, 5C-, 8C-$\underline{\mathrm{H}}$), 9·7 (bs, 1H, $\mathrm{N\underline{H}}$)
4c	510	(6 325)	3280(NH) 1725($\mathrm{COOCH_3}$) 1650(C=O)	1·33 (d, 3H, C-$\mathrm{C\underline{H}_3}$), 2·97 (m, 1H, $\mathrm{C\underline{H}}$), 3·53 (d, 2H, C-$\mathrm{CH_2}$), 7·03 (m, 1H, 2C-$\underline{\mathrm{H}}$), 7·53–7·97 (m, 4H, 3C-, 6C-, 7C-$\underline{\mathrm{H}}$), 8·2–8·53 (m, 2H, 5C-, 8C-$\underline{\mathrm{H}}$), 10·02 (bs, 1H, N-$\underline{\mathrm{H}}$)
4d	525	(10 142)	3410(1-NH), 3250(5-NH) 1720, 1730($\mathrm{COOCH_3}$) 1620, 1630(C=O)	3·27 (t, 4H, C-$\mathrm{C\underline{H}_2}$), 3·92 (t, 4H, N-$\mathrm{C\underline{H}_2}$), 3·95 (s, 6H, $\mathrm{OCH_3}$), 7·98–8·17 (m, 4H, 2C-, 3C-, 6C-, 7C-$\underline{\mathrm{H}}$), 8·4–8·6 (m, 2H, 4C-, 8C-$\underline{\mathrm{H}}$)
4e	445	(6 364)	3140(NH) 1700, 1670	1·35–1·5 (t, 3H, $\mathrm{CH_2C\underline{H}_3}$), 4·3–4·5 (q, 2H, $\mathrm{C\underline{H}_2CH_3}$), 7·7–8·4 (m, 7H, 2C-, 3C-, 4C-, 5C-, 6C-, 7C-, 8C-$\underline{\mathrm{H}}$), 8·57 (d, 1H, C-$\mathrm{C\underline{H}}$, $J = 13$ Hz), 13·53 (d, 1H, $\mathrm{N\underline{H}}$)

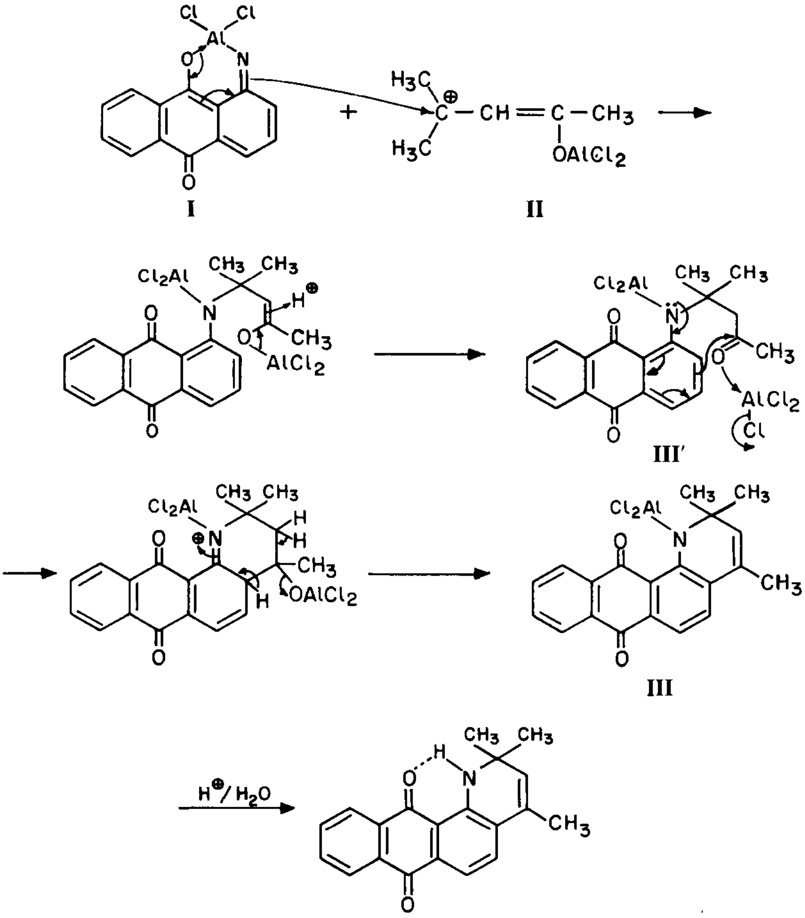
TABLE 2

Yield, Physical Properties and Elemental Analyses of Dyes **3** and **4**

Dye	*Colour*	*Yield (%)*	*Melting point (°C)*	*Molecular formula*	*Found (%)*			*Calc. (%)*		
					C	*H*	*N*	*C*	*H*	*N*
3a	Violet needles	52	173	$C_{20}H_{17}NO_2$	78·7	6·1	4·5	79·2	5·6	4·6
3b	Red plates	48	182	$C_{22}H_{21}NO_2$	79·9	6·5	4·5	79·8	6·3	4·2
3c	Red needles	13	264	$C_{20}H_{18}N_2O_2$	75·8	5·9	8·7	75·4	5·6	8·7
3e	Bluish-violet needles	13	220	$C_{26}H_{26}N_2O_2$	78·7	6·8	7·5	78·4	6·5	7·0
3f	Bluish-violet needles	15	271	$C_{30}H_{34}N_2O_2$	79·3	7·8	6·6	79·3	7·5	6·2
4a	Orange needles	54 (lit.[1,2] 52)	234 (lit.[1,2] 136)	$C_{17}H_{12}N_2O_2$	73·7	4·2	9·8	73·9	4·4	10·2
4b	Orange plates	56 (lit.[1,2] 52)	150 (lit.[1,2] 112–113)	$C_{18}H_{15}NO_4$	70·5	4·8	4·4	69·9	4·8	4·5
4c	Orange powder	50	149	$C_{19}H_{17}NO_4$	70·0	5·0	4·6	69·7	5·2	4·3
4d	Violet needles	42 (lit.[1] 40)	209 (lit.[1] 107)	$C_{22}H_{22}N_2O_6$	64·3	5·2	6·9	64·4	5·4	6·9
4e	Yellow needles	99 (lit.[5] 92)	169 (lit.[5] 169–170)	$C_{22}H_{19}NO_6$	66·9	4·4	3·8	67·2	4·8	3·6

TABLE 3
Dyeing Properties

Dye	*Shade (2%)*	*Reference depth*	*Lightfastness (Xeno test, 24 h exposure)*	*Sublimation fastness*					
				At 180°C for 1 min			*At 210°C for 1 min*		
				Loss in depth	*Change in tone*	*Staining on adjacent fibre*	*Loss in depth*	*Change in tone*	*Staining on adjacent fibre*
3a	Violet	1/1	2	4	4	2	3–4	4	1
3b	Violet	1/1	5	3–4	3–4	2–3	3–4	3–4	2
3c	Red-violet	1/3	1–2	2–3	3	2	2–3	3	1
3e	Violet	1/3	2	2–3	3	2–3	2	2	1–2
3f	Violet	1/3	1–2	3	3	3	3	3	2–3
4a	Yellow-orange	1/1	3	3	4	2	2–3	4	1–2
4b	Red	1/1	4	4	4	1–2	3–4	4	1
4c	Yellow-red	1/1	5	4	4	1–2	4	3–4	1–2
4d	Blue-red	1/1	3–4	3	3	2–3	2–3	2–3	1–2
4e	Orange	1/3	5	4–5	4–5	4–5	4	4	4



3a

Scheme 1

Lewis acid, the reaction gave insignificant yields of the anthrapyridinequinones (**3**). More than a two-fold excess of aluminium chloride was necessary to obtain reasonably good yields of **3**. The multiple role of aluminium chloride involved its complex formation with aminoanthraquinone to generate the intermediate **I**, catalysing the *in situ* generation of α,β-unsaturated carbonyl compounds such as mesityl oxide **II**, and the subsequent polarisation of **II**. Probable mechanistic pathways are shown in Scheme 1.

In the first step, the nucleophilic attack of **I** takes place at the electron-deficient centre in **II** to form the intermediate complex **III**. Cyclisation of **III** via dehydration would give rise to the product as an aluminium chloride complex. The complex on subsequent hydrolysis and acidification would yield **3**. The failure of β-aminoanthraquinone to react in a similar manner could be attributed to its inability to form a complex of the type **I**. On the other hand, the reactions involved during the formation of **4** did not go beyond the N-condensation stage. This could be explained on the basis of the inability of the ester carbonyl to form a complex with aluminium chloride similar to that in **III′**.

The visible spectra of the dyes **3a**–**3f** and **4a**–**4e** (Table 1) were recorded in dimethylformamide solutions. The polar effect of the alkyl substituents and the presence of an additional conjugated double bond in the dihydropyridine ring of **3a**–**3f** result in a considerable bathochromic shift in these dyes compared with the parent aminoanthraquinones. In comparison with the dyes **3**, the dyes **4** showed hypsochromic shifts of about 25–70 nm, due to their restricted conjugation. In general, the mono condensation dyes derived from 1-aminoanthraquinone were found to have extinction coefficients around 6000, whereas the bis condensation dyes derived from 1,5-diaminoanthraquinone showed an increase in ε values to 10 000–17 000.

The dyes **3** gave violet to bluish-violet shades of relatively poor light and sublimation fastness. The dyes **4** produced yellow to violet shades on polyester and, in general, showed moderate to good lightfastness depending on the N-substitution. Sublimation fastness was moderate to poor with the exception of the dye **4e** which showed good light and sublimation fastness. The dyeing properties are recorded in Table 3.

3 EXPERIMENTAL

Melting points are uncorrected. Visible spectra were recorded on a Beckman double-beam spectrophotometer model 216. Infrared spectra were recorded on Perkin–Elmer infrared spectrometer model 137B. ^{1}H-NMR spectra were recorded on a Varian 80A FT-NMR spectrometer using tetramethylsilane as internal standard.

3.1 General procedure for the synthesis of anthrapyridinequinones 3

The aminoanthraquinone (0·01 mol) was stirred in acetone or methyl ethyl ketone (50 ml) and anhydrous aluminium chloride (0·025 mol) was added. The reaction mixture became warm and turned bluish-violet. The solution was then refluxed for 12 h, excess ketone distilled off and the residue treated with cold dilute hydrochloric acid. The product was filtered, washed with water and dried. The products were purified by column chromatography on silica gel using benzene–petroleum ether (1:1) as eluent and by recrystallisation from benzene or benzene–petroleum ether mixtures. Spectral data are summarised in Table 1. Yield, physical properties and elemental analytical data are recorded in Table 2.

3.2 General procedure for the synthesis of dyes 4

Anhydrous aluminium chloride (0·02 mol) was added to a stirred mixture of the aminoanthraquinone (0·01 mol) and the appropriate α,β-unsaturated carboxylic ester (0·015 mol). The reaction mixture became warm and a clear blue solution was obtained. The solution was refluxed for 5 h (except in the case of **4e** when stirring at 30°C for 1 h was sufficient). At the end of the reaction, ethylene dichloride was removed by distillation. The residue was treated with cold dilute hydrochloric acid and the product filtered, washed with water and dried. Purification was effected by column chromatography on silica gel using benzene as eluent and by recrystallisation from benzene or benzene–petroleum ether mixtures. Spectral data, yields, physical properties and microanalytical data are recorded in Tables 1 and 2.

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