Preparation and Application of Some New Disperse Anthraquinone Dyes

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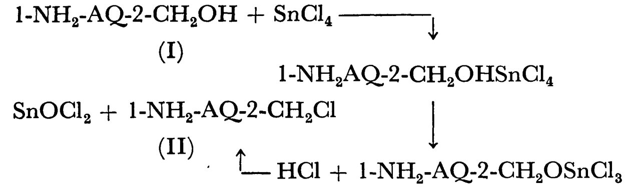
A series of anthraquinone derivatives free from water-solubilising groups were prepared. These compounds were found to be valuable for dyeing synthetic fibers with different shades of good fastness properties.

Anthraquinone dyes remain as the most important and pre-eminent class of all dyes because of their outstanding all-round fastness. On the other hand, disperse dyes are very useful and represent the main class of dyes for coloring synthetic textile materials.

In a previous note[1] we have reported that hydroxymethylanthraquinones could be used as alkylating agents for aromatic compounds using Friedel-Crafts catalysts. This paper gives the results of some experiments in regard to the reaction course and new examples are expressed.

(Hydroxymethyl)anthraquinones (I) react with aromatic hydrocarbons in the presence of aluminium chloride or tin tetrachloride to give the corresponding (arylmethyl)anthraquinones (III).[1] An equimolecular mixture of freshly fused tin tetrachloride and 1-amino-2-(hydroxymethyl)anthraquinone gave an addition product at 60 °C and heating of the addition product at 90—95 °C yielded the corresponding chloride (II). A determination of the hydrogen chloride evolved by heating of the addition product leads to the view that the reaction proceeds in the following steps.



$$\underset{(I)}{1\text{-}NH_2\text{-}AQ\text{-}2\text{-}CH_2OH} + SnCl_4 \rightarrow 1\text{-}NH_2AQ\text{-}2\text{-}CH_2OHSnCl_4 \rightarrow HCl + 1\text{-}NH_2\text{-}AQ\text{-}2\text{-}CH_2OSnCl_3 \rightarrow SnOCl_2 + \underset{(II)}{1\text{-}NH_2\text{-}AQ\text{-}2\text{-}CH_2Cl}$$

If aromatic hydrocarbon and more than equimolar amounts of tin tetrachloride are used, reaction with 1-amino-2-(chloromethyl)anthraquinone (II) yields III.

$$\underset{(II)}{1\text{-}NH_2\text{-}AQ\text{-}2\text{-}CH_2Cl} \xrightarrow[SnCl_4]{Ar\text{-}H} \underset{(III)}{1\text{-}NH_2AQ\text{-}2\text{-}CH_2Ar}$$

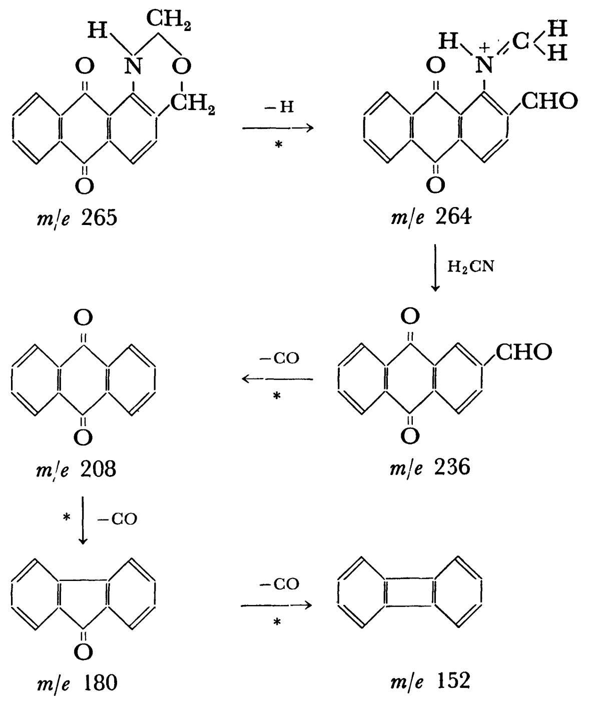
Heating of the addition product with aromatic hydrocarbon in the absence of the catalyst gave no III, indicating the necessity of two moles of tin tetrachloride to complete the reaction.

Reaction of toluene with 1,4-dihydroxy-2-(hydroxymethyl)anthraquinone gave 1,4-dihydroxy-2-(4′-methylbenzyl)anthraquinone.[1] The mass spectrum of this product is different from that of 1,4-dihydroxy-2-(2′-methylbenzyl)anthraquinone which was prepared by a modified Marschalk's method.[2] The molecular ion in the former isomer is the base peak, while that in the latter one is 57.8% as relative abundance. Loss of water molecule from molecular ions is more intense in case of 1,4-dihydroxy-2-(2′-methylbenzyl)anthraquinone. This may be explained by the formation of the stable six-membered ring ion resulted from the loss of hydroxyl group in the 1-position and the hydrogen atom from the *ortho* methyl group. All these steps are indicated by metastable peaks and accurate mass measurements.

1-Amino-2-(4′-hydroxybenzyl)anthraquinone has been prepared using concentrated sulfuric acid as a catalyst.[2] Our trials to obtain this product according to the patent specification gave very low yield and also different side products. The side products were identified as 1-aminoanthraquinone, 1-aminoanthraquinone-2-carbaldehyde beside a red product

Table 1. Principal peaks in the mass spectrum of 1,2-dihydro-4*H*-anthra[1,2-*d*][1,3]oxazine-7,12-dione

m/e	28	75	75.5	76	76.5	
Rel. int.	20.7	5.3	2.3	14.8	2.4	
m/e	77	150	151	152	153	
Rel. int.	7.1	7.0	14.1	18.2	7.1	
m/e	165	180	181	207	208	
Rel. int.	7.2	12.2	4.9	4.5	14.8	
m/e	209	220	223	234	235	
Rel. int.	5.7	6.4	6.8	4.6	7.7	
m/e	236	237	264	265(M)	266	267
Rel. int.	40.9	12.3	100	83.0	16.2	3.8



Scheme A.

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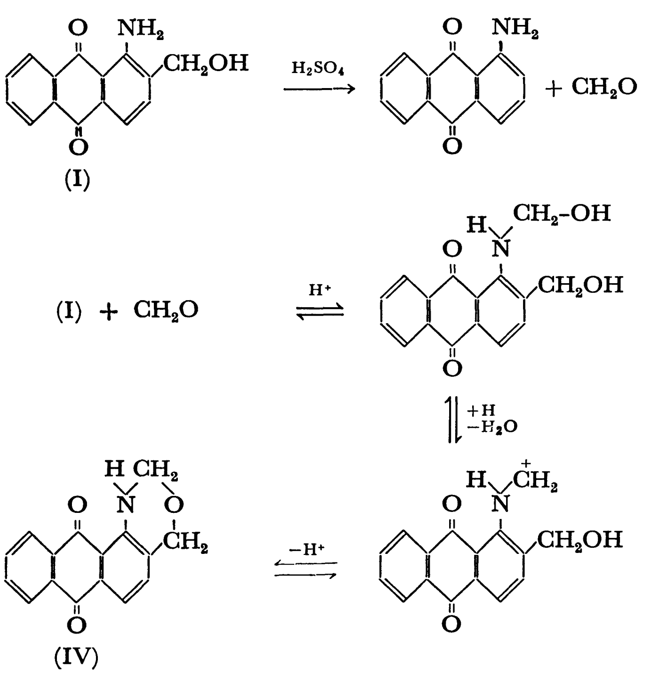
($C_{16}H_{11}NO_3$) which indicates the presence of a secondary amino group and a bathochromic schift of 20 nm in its ultraviolet spectrum as compared with the starting 1-amino-2-(hydroxymethyl)anthraquinone. Molecular weight of the red product was 265 by the mass spectrum.

Table 1 indicates the mass spectrum of this compound (*cf.* Scheme A). The molecular ion undergoes the loss of hydrogen atom to give the base peak which can lose H_2CN *via* an α, γ-proton schift to give anthraquinonecarbaldehyde cation radical. The latter loses carbon monoxide yielding the parent anthraquinone[3]. These steps were proved by accurate mass measurements and metastable peaks determinations. According to these facts, this compound was formulated as 1,2-dihydro-4*H*-anthra[1,2-*d*][1,3]oxazine-7,12-dione (IV).

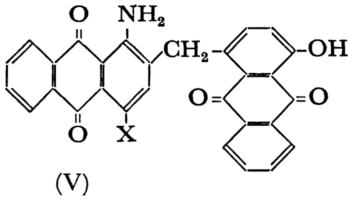
Compound IV was also prepared by the action of 70% sulfuric acid on 1-amino-2-(hydroxymethyl)anthraquinone.



Reaction of 1-amino-2-(hydroxymethyl)anthraquinone with formaldehyde in presence of dilute hydrochloric acid gave IV quantitatively.

The formation of the 1-aminoanthraquinone-2-carbaldehyde may be due to self oxidation of the starting (hydroxymethyl)anthraquinone derivatives in acidic medium.

The (arylmethyl)anthraquinone derivatives[1] have colors ranging from yellow, orange, red, magenta and blue. The work was extended for the preparation of green disperse dyes. This was done by alkylation of a yellow anthraquinone. An example for such preparation is 1,4-diamino-2-[(4'-hydroxyanthraquinon-1-yl)methyl] anthraquinone(Vb) which was prepared by heating 1,4-diamino-2-(hydroxymethyl)anthraquinone with 1-hydroxyanthaquinone in an inert solvent and in the presence of freshly fused tin tetrachloride.



(V)

a, X=H

b, X=NH_2

The visible spectra of such green dyes are characterized by the presence of two bands, one in the yellow and the other in the blue region of the spectra.

Experimental

Melting points are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 21 spectrophotometer, ultraviolet and visible spectra were measured on a Unicum 1800 spectrophotometer. Mass spectra were obtained using an AEI MS9 mass spectrometer operating at 70 eV. Samples were introduced through a heated inlet system at *ca.* 185 °C.

Preparation of 2-*(Chloromethyl) anthraquinones.* (Hydroxymethyl)anthraquinone (I) (0.5 mol) was added to freshly fused tin tetrachloride (0.5 mol) in dioxane, but only a trace of hydrogen chloride evolved. On heating, the solid product began to melt at 85—90 °C and hydrogen chloride was given off freely. About 0.5 mol of hydrogen chloride was collected at 95 °C for 2 hr. The reaction mixture was added to ice-cold water and the precipitates were washed throughly with water and dried. Some examples are summarized in Table 2.

Preparation of (Arylmethyl) anthraquinones. A mixture of (hydroxymethyl)anthraquinone (1 mol), 1-hydroxyanthraquinone (1 mol) and freshly fused tin tetrachloride (2 mol) was heated in dioxane under reflux for about one hour. The reaction mixture was poured into excess 4 M sodium hydroxide solution. The precipitated product was washed with excess water, dried and recrystallized from dimethylformamide.

Table 2. 2-(Chloromethyl) anthraquinones

Compound	Mp °C	Yield %		Analysis (%)				Solvent of crystallization	λ_{max}(nm) in C_6H_6	log ε
				C	H	N	Cl			
1-Amino-2-(chloromethyl)-anthraquinone	185	89	Calcd	66.31	3.71	5.16	13.10	Benzene	475	3.92
			Found	66.46	3.92	5.31	13.33			
1-Amino-2-(chloromethyl)-4-chloroanthraquinone	212	92	Calcd	58.85	2.97	4.57	23.15	Benzene	480	3.84
			Found	59.21	3.18	4.62	23.23			
1,4-Diamino-2-(chloromethyl)-anthraquinone	218	90	Calcd	62.83	3.83	9.77	12.37	Toluene	592	3.79
			Found	63.16	3.88	9.84	12.42			

TABLE 3. FASTNESS PROPERTIES

Compound	WF[a)]	LF[b)]
1-Amino-2-benzylanthraquinone	4—5	6
1-Amino-2-(4′-methylbenzyl)anthraquinone	4—5	6—7
1-Amino-2-(4′-hydroxybenzyl)anthraquinone	4	6
1-Amino-2-[4′-(dimethylamino)benzyl]-anthraquinone	4—5	6—7
1-Amino-2-(2′-naphthylmethyl)anthraquinone	5	6—7
1-Amino-2-(1′-hydroxy-4′-naphthyl)-anthraquinone	3—4	5—6
1,4-Diamino-2-benzylanthraquinone	4	6
1,4-Diamino-2-(4′-methylbenzyl)-anthraquinone	4—5	6
1,4-Diamino-2-(4′-hydroxybenzyl)-anthraquinone	4	5—6
1,4-Diamino-2-[4′-(dimethylamino)benzyl]-anthraquinone	5	4—5
1,4-Diamino-2-(2′-naphthylmethyl)-anthraquinone	4	6
1,4-Diamino-2-(1′-hydroxy-4′-naphthyl)-anthraquinone	3—4	5—6
1,8-Diamino-2-benzylanthraquinone	4—5	6
1,8-Diamino-2-(4′-methylbenzyl)anthraquinone	4	6
1,8-Diamino-2-(4′-hydroxybenzyl)-anthraquinone	3—4	6
1-Amino-4-bromo-2-benzylanthraquinone	4	6—7
1-Amino-4-bromo-2-(4′-methylbenzyl)-anthraquinone	4—5	6
1-Amino-4-bromo-2-(4′-hydroxybenzyl)-anthraquinone	3—4	6—7
1-Amino-4-bromo-2-[4′-(dimethylamino)-benzyl]anthraquinone	4—5	6—7
1-Amino-4-bromo-2-(2′-naphthylmethyl)-anthraquinone	4—5	6
1-Hydroxy-2-benzylanthraquinone	3—4	6
1-Hydroxy-2-(4′-methylbenzyl)anthraquinone	4—5	5—6
1-Hydroxy-2-(4′-hydroxybenzyl)anthraquinone	3	6
1-Hydroxy-2-[4′-(dimethylamino)benzyl]-anthraquinone	4	6
1,4-Dihydroxy-2-benzylanthraquinone	3—4	5—6
1,4-Dihydroxv-2-(4′-methylbenzyl)-anthraquinone	3—4	6
1-Amino-2-[(4′-hydroxyanthraquinon-1-yl)-methyl]anthraquinone	3	5—6
1,4-Diamino-2-[(4′-hydroxyanthraquinon-1-yl)methyl]anthraquinone	3—4	5—6

a) Wash fastness. b) Light fastness.

Va; yield 81%; mp 210 °C; $\lambda_{\max}^{\mathrm{PhH}}$ 450 nm (log ε 3.61) Found: C, 76.13; H, 3.92; N, 3.17%. Calcd for $C_{29}H_{17}NO_5$: C, 75.81; H, 3.70; N, 3.05%.

Vb; yield 78%; mp 235 °C; $\lambda_{\max}^{\mathrm{PhH}}$ 412 nm (log ε 3.86) and 585 nm (log ε 3.25). Found: C, 73.28; H, 3.84; N, 6.12%. Calcd for $C_{29}H_{18}N_2O_5$: C, 73.41; H, 3.79; N, 5.90%

Preparation of other derivatives was reported previously.[1)]

*Preparation of 1,2-Dihydro-4*H*-anthra*[*1,2*-d][*1,3*]*oxazine-7, 12-dione(IV).* 1-Amino-2-(hydroxymethyl)anthraquinone (0.53 g), 30% aqueous formaldehyde solution (1 ml) and concentrated hydrochloric acid (0.5 ml) were dissolved at room temperature in dioxane (100 ml). The mixture was left for 30 min and then warmed at 45 °C for 15 min. The reaction mixture was poured into ice-cold water and the precipitated red product was washed with water and dried. It was crystallized from benzene into red fine needles, mp 162 °C, yield 0.52 g.

$\lambda_{\max}^{\mathrm{PhH}}$ 490 nm (log ε 3.72); IR 3252, 1592, 1660, and 1630 cm^{-1}. Found: C, 72.55; H, 4.16; N, 4.94%. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.15; N, 5.28%.

Application of Disperse Dyes to Synthetic Fibers. These disperse dyes were applied to polyamide fibres by immersing the textile materials in a dyebath containing the aqueous dispersion of these dyes and an anionic surface-active reagent. The dyeing process was done at the boil for 45 min. Table 3 indicates the fastness properties of such dyes on Nylon-66.[4)]

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