INTERMEDIATE PRODUCTS AND DYES BASED ON 1-METHYLNAPHTH[2, 3-d]IMIDAZOLE-4, 9-DIONE

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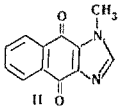
Nitration of 1-methylnaphth[2, 3-d]imidazole-4, 9-dione affords about 30% of β-nitro isomers. It is shown that it is possible to synthesize various dyes based on 1-methylnaphth[2, 3-d]imidazole-4, 9-dione. The dyes obtained resemble the corresponding anthraquinones in their color and spectral properties.

Naphth[2, 3-d]imidazole-4, 9-dione (I) is a heterocyclic analog of anthraquinone, and resembles it closely in chemical properties [1, 2]. It was, therefore, of interest to obtain intermediates and dyes derived from I and to compare them with the analogous anthraquinones. In view of the poor solubility of I, and of its derivatives with hydrogen in the 1-position, we have examined the reactivity of 1-methylnaphth[2, 3-d]imidazole-4, 9-dione (II). The nitration of II was examined first. It has been generally considered that nitration of anthraquinone gives the α-nitro derivative only [3]. Nitration of II, therefore, would be expected to give a mixture of the two α-(5 and 8) nitro derivatives.

In fact, this reaction afforded a mixture (III) from which there were isolated by fractional crystallization three nitro derivatives, differing in mp's and UV spectra, but having similar IR spectra (Table 1).



Catalytic reduction of this mixture to the corresponding amines (IV), followed by thin layer chromatography on alumina (benzene-ethyl acetate) gave four compounds. Three of these were shown to be chromatographically identical with the reduction products of the individual nitro compounds.

In order to determine the positions of the amino-groups, use was made of the ability of α-aminoanthraquinones, as distinct from the β-isomers, to form colored complexes with boroacetic ester [4]. Of the three isomeric amines, two (a and b) give colored complexes, which is taken to indicate that the amino groups in these compounds are located in one of the α-(5 or 8) positions. The third isomeric amine (c) forms no such complex, indicating that the amino group occurs in the β-(6 or 7) position. The electronic spectra of alcoholic solutions of the α-isomers resemble each other very closely, but differ substantially from those of the β-isomer (Table 1). The fourth isomeric amine (d), which was isolated in very small amounts by chromatography of the amine mixture, had an electronic spectrum similar to that of the β-isomer, thus confirming the β-position of the amino group.

Table 1. Properties of the Isomeric Nitro Compounds

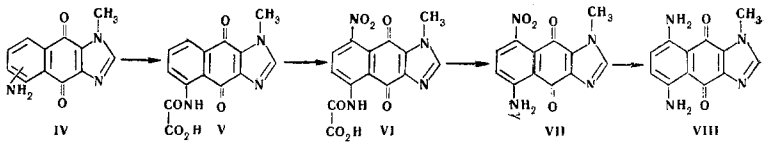
Isomeric nitro-1-methylnaphth[2,3-d]imidazole4,9-diones	Mp, °C	UV Spectra, in ethanol, λ_{max}, nm (lg ε)	IR Spectra			Molecular formula	N, %	
			C=O, cm⁻¹	NO_2, cm⁻¹ Asymm	NO_2, cm⁻¹ Symm		Found	Calculated
a	297	250(4.39), 332(3.42)	1670	1534	1342	$C_{12}H_7N_3O_4$	16.11; 16.32	16.32
b	291—292	250(4.58), 330(3.58)	1671	1540	1348		16.21; 16.27	16.30
c	306	228(4.43), 266(4.57), 334(3.67)	1663	1532	1342		16.22; 16.52	

Since the amine mixture could not be separated cleanly by column chromatography, we resorted to determination of the composition of the mixture from the electronic spectra, by a known method [5]. This showed that the proportion of α- to β-isomers was about 2 : 1. It should be noted, however, that it was necessary to make several

assumptions in carrying out the calculations, thus reducing the precision of the method and making it impossible to determine the content of the individual isomers.

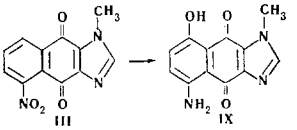
We have also established that in the nitration of naphth[2, 3-d]-imidazole-4, 9-dione some β- (6) isomer is also formed, in contradiction of the findings of Wilbur and Day [6], who first investigated this reaction. For this purpose, naphth[2, 3-d]imidazole-4, 9-dione was nitrated with nitrating mixture, and the nitro compounds were methylated with dimethyl sulfate, and then reduced catalytically. The monoamine mixture, to judge from its electronic spectrum and chromatographic behavior, resembled closely in composition that obtained by the nitration of II, The presence of a methyl group in the 1-position, therefore, is not the reason for the formation of β-nitro isomers. Attention is drawn to the fact that one of the α-isomers (**a**) is obtained in approximately twice the amount of the other. The free base of II must, therefore, be involved in the reaction, rather than the salt, in which the heterocyclic ring would have a much more symmetrical structure.

In a similar way to the anthraquinone compounds [7], the mixture of amines was subjected successively to acylation, nitration, removal of the acyl group, and catalytic reduction of the nitro group to give 5, 8-diamino-1-methylnaphth[2, 3-d]imidazole-4, 9-dione (VIII).



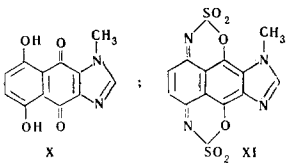
The β-amino isomers are lost from the amine mixture during the acylation and nitration stages.

We attempted to obtain VIII by a simpler method, namely by reductive rearrangement of III with sulfur in oleum [8], but this led to the formation of the amino-hydroxy derivative IX:



This was obtained as a mixture of two isomers, but owing to the low yield and the difficulty of purification, it was not feasible to use this reaction to obtain VIII.

Compound VIII was very reminiscent of 1,4-diaminoanthraquinone in its chemical properties. Thus, heating with stannous chloride in HCl, followed by oxidation of the leuco derivative, gave 5,8-dihydroxy-1-methylnaphth-[2,3-d] imidazole-4,9-dione (X), which resembles quinizarin in its color and properties.



In a similar way to 1, 4-diaminoanthraquinone, VIII reacts with high-strength oleum to give the cyclic sulfimide XI, the UV spectrum of which is similar to that of the corresponding anthraquinone compound (see figure). On heating in sulfuric acid, XI is hydrolyzed to VIII.

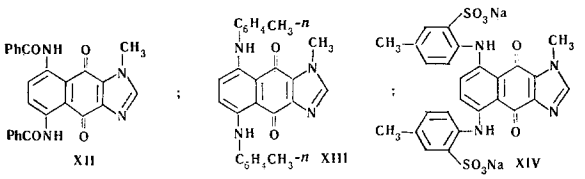
Reaction of VIII with benzoyl chloride gives 5, 8-dibenzamido-1-methylnaphth[2, 3-d]imidazole-4, 9-dione (XII), which is a heteroanalog of the vat dye Indanthrene Red 5GK. As in the case of 1, 4-diaminoanthraquinone, VIII readily exchanges the amino groups for p-toluidine residues in the presence of stannous chloride. Further sulfonation gave the hetero analog of Anthraquinone Acid Green (XIV).

Table 2. Results of Dyeing Acetate Silk and Caprone

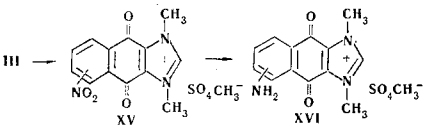
Dyestuff	Acetate silk							Caprone						
	Concentration of dyestuff, % of weight of cloth	Color	Stability of dyeing, in points					Concentration of dyestuff, % of weight of cloth	Color	Stability of dyeing, in points				
			Water	Soap, 40°	Perspiration	Light	Weather			Water	Soap, 40°	Perspiration	Light	Weather
XVII*	3	Violet, intense	4/2/4	4/3/4	4/3/4	5	4	3	Violet, muddy, intense	4/2—1/0	4/2/3	4/1/3	4—5	4
VIII	3	Bright reddish-violet, intense	4—3/1—2/2	4—3/2/3	4—3/2/3	5—4	2	3	Bright violet, intense, pure	4/2/2	4/3/3	4/2/2	5—4	3
XVIII**	3	Yellow, muddy, not intense	4/3/5	4/4/5	5	3	3		Yellow, not intense dull	4/3/4	4/3/4	4/3/4	4	3—2
IV	3	Bright orange, intense	4—3/2/3	4—3/2/3	4/2—3/3	5	2	3	Orange, less intense than on acetate	3—4/2/2	4—3/2/2	3—4/3/3	5	3
XIII	3	None							Green, dull, not intense	4/4/4	4/4/5	4/4/5	6—5	4—5

*XVII, 1,4-diaminoanthraquinone.

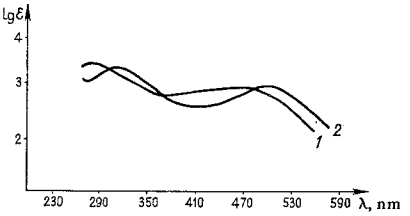
**XVIII, 1-methyl-2-morpholinonaphth[2,3-d]imidazole-4,9-dione, prepared previously [2].



The presence of the imidazole ring in II makes it possible to obtain cationic dyes derived from it. We have synthesized such a dye, with an amino group in the benzene ring (XVI).



It appears that XVI is rather unstable in alkaline solution. Nevertheless, this does not prevent its use for dyeing synthetic fibers.



Absorption spectra in benzene solution: 1) XI; 2) anthraquinone sulfimide.

The heterocyclic analogs of the anthraquinone dyes have been compared with the latter in respect to dyeing conditions and color properties. The methods of dyeing and of determining the quality of the resulting shades were standard ones. The results of dyeing acetate silk and caprone (a synthetic fiber) are shown in Table 2. The table shows that dyes derived from II have high light stability, but, in comparison with the anthraquinone dyes, the stability to weathering was insufficiently high, probably as a result of the high water solubility of the hetero analogs. The colors were very similar to those of the anthraquinone analogs.

On polyester fiber, dystuffs VIII, XVIII, and IV did not give very intense colors (Table 2). Nevertheless, the dyes displayed high stability to sublimation. This property is of real interest, since the present range of dyes for polyester fibers has only a few members which meet the requirements for stability to sublimation. The light stability is high (5–6 points).

In addition to the dispersed dyes, other types were investigated. The acid dye XIV was comparable to Anthraquinone Acid Green (Table 3). The hetero analogs gave stronger colors, but after chroming this difference almost disappeared. The stability of the hetero analogs to light and various other treatments was high, but unlike the anthraquinones, they were only partially taken up from the dye bath.

Table 3. Comparative Dyeing Results for XIV and Anthraquinone Acid Green

Dyestuff	Without chroming					With chroming				
	Soap, 40°	Perspiration	Scouring	Rubbing	Light	Soap, 40°	Perspiration	Scouring	Rubbing	Light
Anthraquinone Acid Green	5—4/4/5	4/3—3/4	4/2—3/4	4	7	4/4/4	4/3/4	4/3/4	3—4	7
Hetero analog of Anthraquinone Acid Green (XIV)	4/4/4	4/3—2/4	4/4/3—2/4	3—4	6	4/4/5	4/3/4—5	4/3/4—5	3—4	6

The vat dyestuff XI was comparable with Indanthrene Red 5GK. The shades obtained were deeper than in the case of the anthraquinone, but the substantivity was lower. It should be mentioned that the heteroanalog was reduced with hydrosulfite, and oxidized by air, more readily than Indanthrene Red 5GK, and the light stability was greater.

The cationic dyestuff did not dye pure polyacrylonitrile, apparently as a result of its low basicity. However, modified nitrone was dyed in good shades from an acid bath, the color being stable on boiling in sodium carbonate solution.

Thus, the properties of dyes based on 1-methylnaphth[2, 3-d]-imidazole-4, 9-dione resemble those of the anthraquinones, but the presence of the heterocycle in many cases influences the reactivity of these compounds.

EXPERIMENTAL

Nitro-1-methylnaphth[2, 3-d]imidazole-4, 9-dione (III). Twenty grams of II were heated with a mixture of 100 ml of conc H_2SO_4 and 5 ml of HNO_3 (d 1.51) for 3 hr on a boiling water bath. The cooled reaction mixture was poured onto 2 kg of ice, and the precipitate filtered off and washed with a 5% solution of sodium bicarbonate, then with water. Yield 19 g (79%), mp 216-230°C, of a yellod solid, soluble in acetic acid and dioxan, sparingly soluble in alcohol, and insoluble in water and benzene. Found, M 243 (by the reverse ebullioscopic method); calculated, M 257. The isomers were separated by fractional crystallization from aqueous dioxan, their properties being given in Table 1.

Amino-1-methylnaphth[2, 3-d]imidazole-4, 9-dione (IV). 3.7 g of III was reduced with hydrogen in 50 ml of ethanol over 1.5 g of Raney nickel at 40–50° C. The carbonyl group was not reduced under these conditions. After the theoretical amount of hydrogen had been taken up, the reaction mixture was poured into a solution of 2.5 g of sodium hydrosulfite and 3 g of sodium hydroxide in 250 ml of water, and filtered quickly. Air was bubbled through the filtrate for 1 hr, and the precipitate which separated was filtered off and washed with water, giving 3 g (92%) of IV as a red solid, mp 273° C (decomp., from alcohol). It was readily soluble in dimethylformade and strong acids, moderately so in dioxan and alcohol, and sparingly soluble in water and benzene. Found, %: N 18.54. Calculated for $C_{12}H_9N_3O_2$, %: N. 18.5. The isomeric nitro compounds were reduced similarly, to the corresponding amines. They were purified by chromatography on alumina in dimethylformamide followed by recrystallization from alcohol.

5, 8-Diamino-1-methylnaphth[2, 3-d]imidazole-4, 9-dione (VII). Thirty grams of IV, obtained by catalytic reduction of the mixture of nitro isomers III in dimethylformamide, was heated with 180 g of oxalic acid for 5 hr at 135° C. The hot mixture was poured into 2 *l* of hot water, the precipitate filtered off, and the solid washed with water, giving 36 g (91%) of product. This was dissolved in 150 ml of conc H_2SO_4, and 5 ml of NNO_3 (d 1.51) added slowly at 0°. The reaction mixture was kept at 0° C for a further 5 hr, and overnight in the refrigerator. The mixture was then poured on to 1 kg of ice, the precipitate filtered off, and the solid washed well with water. The damp product was transferred to 1 *l* of 5% potassium carbonate, and the solution heated for 3 hr at 90° C. The solid was filtered off and washed with water to give 19 g (60%) of dark red solid, readily soluble in dimethylformamide and ethylene glycol, moderately in nitromethane, and sparingly soluble in alcohol and water. Mp 295° C (decomp., from nitromethane). Chromatography on alumina in ethyl acetate gave two adjacent spots. Found, %: C 52.81; H 2.93; N 20.77. Calculated for: $C_{12}H_8N_4O_4$, %: C 52.95; H 2.94; N 20.6%.

5, 8-Diamino-1-methylnaphth[2, 3-d]imidazole-4, 9-dione (VIII). Ten grams of VII in 200 ml of dimethylformamide was reduced with hydrogen over Raney nickel at 70° C. The carbonyl group was not reduced under these conditions. When the reduction was complete, the mixture was filtered hot from the nickel. The filtrate was evaporated in vacuo to a volume of 50 ml, and diluted with four times its volume of water. The precipitate which separated was filtered off, and the solid washed with water and dried to give 8.65 g (96.5%) of deep violet solid, mp 280–290° C (decomp., from nitromethane). The compound was soluble in dimethylformamide, nitromethane, and strong acids, but only sparingly in water and alcohol; and insoluble in benzene. Chromatography on alumina in ethyl acetate–dimethylformamide (1 : 1) gave a single spot. Found, %: C 59.27; H 4.40; N 23.02. Calculated for $C_{12}H_{10}N_4O_2$, %: C 59.5; H 4.15; N 23.1.

5-Amino-8-hydroxy-1-methylnaphth[2, 3-d]imidazole-4, 9-dione (IX). Five grams of III, 0.4 g of sulfur, and 1.25 g of boric acid were heated in 25 ml of 30% oleum for 3 hr at 50° C. The mixture was then poured onto 300 g of ice, and the precipitate was filtered off and washed with water to give 6 g of product. This was boiled in 1 π of water, and the mixture filtered hot. The precipitate which separated on cooling was filtered off and washed with water to give 2.3 g of material which was heated with 200 ml of nitromethane, and the insoluble portion filtered off. The filtrate was treated with aluminum hydroxide and evaporated to dryness to give 1.3 g (27.5%) of pale violet product, mp 211–214° C. It was readily soluble in nitromethane, moderately soluble in alcohol, and sparingly soluble in benzene. It dissolved in caustic alkali to give a violet solution, and in conc H_2SO_4 to give a yellow solution. Found, %: N 17.39. Calculated for $C_{12}H_9N_3O_3$, %: N 17.3.

5, 8-Dihydroxy-1-methylnaphth[2, 3-d]imidazole-4, 9-dione (X). Three grams of VIII and 7 g of stannous chloride

were heated for 2.5 hr in 40 ml of conc HCl. The mixture was cooled, and the solid was filtered off and washed with 5% HCl followed by ice water. The product was boiled for 30 min in 50 ml of 5% caustic soda, and the mixture was filtered. Compound X was precipitated from the filtrate by addition of conc HCl, filtered off, and washed with a small amount of water to give 2 g (66%) of yellow product, mp 284–286° C (decomp.). The compound was soluble in alcohol, toluene, and acetic acid, but sparingly soluble in water. Found, %: N 11.25%. Calculated for: $C_{12}H_8N_2O_4$, %: N 11.5.

5,8-Di-(p-toluidino)-1-methylnaphth[2,3-d]imidazole-4,9-dione (XIII). A mixture of 5 g of VIII, 4 g of stannous chloride, 5 g of boric acid, and 50 g of p-toluidine was heated for 3 hr 30 min at 130° C. The reaction mixture was transferred into 1 π of hot 5% HCl, and the mixture was filtered hot. The precipitate was washed on the filter with warm water, giving 6 g (69%) of bluish-green product, mp 251–252°C (decomp., from aqueous DMF), insoluble in water, and soluble in H_2SO_4 to give a violet color. Found, %: C 73.72; H 5.22; N 13.22. Calculated for $C_{26}H_{22}N_4O_2$, %: C 73.9; H 5.2; N 13.25.

Hetero analog of Anthraquinone Acid Green (XIV). Two grams of XII was heated for 3 hr at 50° C in 10 ml of 10% oleum, and the mixture was kept for one day at room temperature. It was then poured on to 100 g of ice, 20 g of NaCl added, and the precipitate filtered off and crystallized from 100 ml of a 20% solution of sodium chloride. There was obtained 1.6 g (53.5%) of product, which on chromatography on alumina gave a single spot. The compound was soluble in water, and sparingly soluble in alcohol. Found, %: S 10.4. Calculated for $C_{26}H_{20}N_4O_8S_2Na_2$, %: S 10.2.

5,8-Dibenzamido-1-methylnaphth[2,3-d]imidazole-4,9-dione (XII). Two grams of VIII was dissolved in 30 ml of nitrobenzene, 2 ml of pyridine was added, and to the mixture was added 2 ml of benzoyl chloride at 150° C during 20 min. The mixture was kept at this temperature for a further 2 hr, cooled, and diluted with 200 ml of benzene. The precipitate was filtered off and washed with benzene to give 2 g (54%) of bright red product, mp 307–309° C (from dioxane). The compound was readily soluble in alcohol and benzene. Chromatography on alumina in ethyl acetate gave a single spot. Found, %: C 69.23; H 4.3; N 12.47%. Calculated for $C_{26}H_{18}N_4O_4$, %: C 69.4; H 4.0; N 12.44.

1-Methylnaphth[2,3-d]imidazole-4,9-dione disulfimide (XI). One gram of VIII was added slowly at 20° C to 10 ml of 65% oleum, and the mixture was kept for 1.5 hr at 55° C. The reaction mixture was then diluted to a volume of 20 ml with H_2SO_4 and poured on to 150 g of ice. The precipitate was filtered off, washed thoroughly with water, and dried. The solid was extracted with 500 ml of boiling toluene, and the toluene extract evaporated to dryness, giving 0.5 (33%) of bright orange product, soluble in benzene and acetic acid, and insoluble in water. The mp was indistinct. The compound XI dissolved in cold conc H_2SO_4 to give a yellow color, but on heating this solution the sulfimide hydrolyzed to give the starting diamine (VIII). Found, %: N 15.27; S 17.25. Calculated for $C_{12}H_6N_4O_6S_2$, %: N 15.28; S 17.15.

Nitro-1,3-dimethylnaphth[2,3-d]imidazole-4,9-dione methylsulfate (XV). Four grams of III was heated for 2 hr at 120° C with 30 ml of dimethyl sulfate, and the mixture kept overnight. The solid which separated was filtered off, and washed with alcohol and ether to give 3.45 g (58%) of yellow product, readily soluble in water and acetic acid, and insoluble in alcohol and benzene. Mp 278–279° C (decomp., from water). On heating XV with aqueous ammonia, a violet coloration was produced. Found, %: N 11.0. Calculated for $C_{14}H_{13}N_3O_8$, %: N 10.95.

Amino-1,3-dimethylnaphth[2,3-d]imidazole-4,9-dione methylsulfate (XVI). Two grams of XV was dissolved in 30 ml of conc HCl, and 5 g of zinc dust added slowly with cooling. The reaction mixture was diluted with twice its volume of water, and the precipitate filtered off and washed with water giving 1.4 g (76%) of brick-red product, mp 309° C (decomp. from water). The compound was soluble in water, sparingly soluble in dimethylformamide and acetic acid, and insoluble in alcohol and ether. On heating with aqueous ammonia or sodium carbonate, the color of the solution changed, apparently as a result of the opening of the imidazole ring. Found, %: N 11.8; S 9.00. Calculated for $C_{14}H_{15}N_3O_6S$, %: N 11.9; S 9.06.

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