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6H-ANTHRA[1,9,8-c,d,e,f]-2,7-NAPHTHYRIDINE DERIVATIVES

II.* NITRATION OF ANTHRANAPHTHYRIDINE-1,6,11-TRIONES

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5,7-Dinitro derivatives are formed in the nitration of 2H,10H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione and its N,N'-dimethyl derivatives. 5,7-Dichloro- and 5,7-dibromoanthranaphthyridine-1,6,11-triones were obtained by reaction of 1,8-diamino-4,5-dihaloanthraquinones with diethyl malonate. Disubstituted anthranaphthyridine triones react with amines to give the corresponding 5,7-diaryl(alkyl)aminoanthranaphthyridine 1,6,11-triones.

We have previously synthesized 2H,10H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (Ia) and its N,N'-dimethyl derivative (Ib) [1]. In a study of the nitration of these compounds it was observed that a difficult-to-separate mixture of the starting compound and the mono- and dinitro derivatives is formed when one equivalent of nitric acid in sulfuric acid is used. When two equivalents of nitric acid are used, dinitro derivatives (IIa, IIb) are formed smoothly. It might have been expected that, like anthraquinone [2] and anthrapyridone [3], nitration leads to substitution of the free α positions of the anthrone ring. To verify the structure of dinitro derivative IIa, it was converted by exchange reaction with p-toluidine to the di-p-tolylamino derivative (IIIa), which in turn was obtained by arylamination of 5,7-dichloroanthranaphthyridinetrione (IVa).

Compound IVa was obtained by condensation of 1,8-diamino-4,5-dichloroanthraquinone (Va) with diethyl malonate in the presence of potassium acetate. Compound Va was synthesized by nitration of 1,8-dichloroanthraquinone and subsequent reduction.

*See [1] for communication I.
†Deceased.

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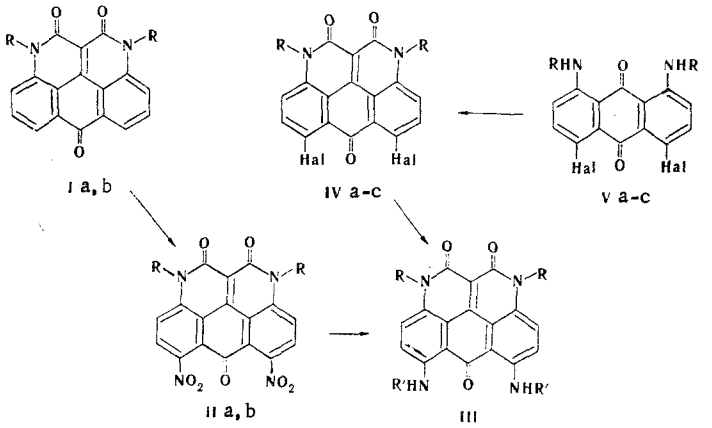

I, II a R=H; b R=CH_3; III a R=H, R′=p-$CH_3C_6H_5$; b R=CH_3, R′=p-$CH_3C_6H_5$; c R=H, R′=C_6H_5; d R=H, R′=CH_3; IV, V a R=H, Hal=Cl; b R=H, Hal=Br; c R=CH_3, Hal=Br.

The previously undescribed 1,8-diamino-4,5-dibromoanthraquinone (Vb), which, like Va, reacts with diethyl malonate to give 5,7-dibromoanthranaphthyridinetrione (IVb), was obtained by bromination of the di-(p-toluenesulfonamide) derivative of 1,8-diaminoanthraquinone and subsequent hydrolysis. Arylamination of IVb with p-toluidine gives IIIa; this verifies the position of the bromine atoms in Vb. Like IIa, dinitro derivative IIb exchanges nitro groups on reaction with p-toluidine to give a ditolylamino derivative (IIIb). The electronic spectra of IIIa and IIIb are close but are not identical; this compelled us to verify the structure of IIIb by alternative synthesis from 5,7-dibromoanthranaphthyridinetrione (IVc). The difference in the spectra of IIIa and IIIb can be explained by the possibility of the existence of a chelate ring for IIIa with respect to the 1 and 11 positions with the participation of a hydrogen bond.

It is interesting to note that we observed the smoothest exchange of substituents by an arylamino group in the presence of hydrogen chloride, which was added to the reaction mixture in the form of the corresponding amine hydrochloride. These transformations usually are carried out in the presence of copper compounds and an agent that ties up the acid. The nitro groups in II are readily exchanged with aliphatic amines in dimethylformamide (DMF) in the absence of catalysts.

EXPERIMENTAL

The absorption spectra of the compounds were recorded with a VSU-2P spectrophotometer. Chromatography was carried out on chromatographic paper moistened with a 5% alcohol solution of α-bromonaphthalene in acetic acid saturated with α-bromonaphthalene.

5,7-Dinitro-2H,10H-anthra[1,9,8-c,d,e,f]-2,7-anphthyridine-1,6,11-trione (IIa). A 0.5-g (1.7 mmole) sample of Ia was dissolved in 5 ml of concentrated H_2SO_4, and 0.5 ml (12.5 mmole) of fuming HNO_3 was added to it at 20°. After 30 min, a yellow suspension formed. The mixture was diluted with water and filtered, and the solid material was washed with water to give 0.5 g (86%) of yellow plates (from HCOOH) with mp > 340°. See Table 1 for the analytical and spectral data.

Under similar conditions, dinitro derivative IIb, with mp > 356°, was obtained from Ib in 80% yield.

5,7-Di(p-tolylamino)-2H,10H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (IIIa). A mixture of 0.2 g (0.53 mmole) of IIa, 0.2 g (1.4 mmole) of p-toluidine hydrochloride, and 4 g (38 mmole) of p-toluidine was stirred at 140° for 9 h, after which it was diluted with alcohol, and the resulting precipitate was separated and washed with alcohol and water to give 0.25 g (96%) of violet plates [from dimethylformamide (DMF)]. Under the same conditions, IIIa, with mp > 450°, was obtained in 95 and 96% yields, respectively, from IVa and IVb. The IR spectra of the compounds obtained from the various 5,7-disubstituted compounds were identical.

5,7-Dianilino-2H,10H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (IIIc). A mixture of 0.8 g (2.1 mmole) of IIa, 10 ml of aniline, and 0.4 g (3 mmole) of aniline hydrochloride was heated at 150° for 8 h. Dilution with alcohol gave 0.91 g (91.6%) of IIIc with mp > 450° (from DMF).

5,7-Di-(p-tolylamino)-2,7-dimethyl-2H,10H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (IIIb). A) This compound was obtained in 70% yield by the method used to prepare IIIa.

B) A mixture of 0.2 g (4.2 mmole) of IVb, 0.2 g (1.4 mmole) of p-toluidine hydrochloride, and 1 g of p-toluidine was stirred at 180° for 6 h, after which the alcohol was removed to give 0.19 g (90.5%) of a product with mp > 460° (from DMF). The IR spectra of the compounds obtained by methods A and B were identical.

TABLE 1. Anthranaphythyridine-1,6,11-triones (II-IV)

Compound	Empirical formula	Found, %			Calculated, %			UV spectra,* λ_{max}, nm (log ε)
		C	H	N	C	H	N	
IIa	$C_{17}H_6N_4O_7$	53,7	2,1	14,9	54,0	1,6	14,8	255 (4,35), 334 (4,25), 415 (4,35)
IIb	$C_{19}H_{10}N_4O_7$	56,8	2,4	13,8	56,3	2,5	13,8	260 (4,30), 390 (4,10), 430 (4,00)
IIIa	$C_{31}H_{22}N_4O_3$	74,1	5,0	11,2	74,7	4,5	11,2	304 (4,40), 455 (3,80), 540 (4,25), 572 (4,30)
IIIb	$C_{33}H_{24}N_4O_3$	75,8	5,0	9,8	75,6	4,6	9,2	300 (4,46), 530 (3,80), 592 (4,62)
IIIc	$C_{29}H_{18}N_4O_3$	73,4	4,1	11,9	74,0	4,1	11,9	299 (4,35), 449 (4,75), 560 (4,25)
IIId	$C_{19}H_{14}N_4O_3$	65,5	3,9	16,0	65,9	4,1	16,2	288 (4,35), 420 (3,28), 450 (3,55), 525 (4,29), 560 (4,30)
IVa	$C_{17}H_6Cl_2N_2O_3$†	57,1	1,5	7,6	57,2	1,7	7,8	256 (4,55), 338 (4,26), 425 (3,84)
IVb	$C_{17}H_6Br_2N_2O_3$†	46,0	1,3	6,1	46,0	1,4	6,2	245 (4,45), 280 (4,30), 335 (4,15), 360 (3,30), 410 (4,20)
IVc	$C_{19}H_{10}Br_2N_2O_3$†	48,0	2,0	5,8	48,1	2,1	5,9	244 (4,25), 290 (4,10), 400 (3,81)

*The spectra of IIa, b and IVa-c were obtained from solutions in H_2SO_4, and the spectra of IIIa-d were obtained from solutions in DMF.

†The compositions of IVa-c were also confirmed by determination of the halogen content.

5,7-Bis(methylamino)-2H,10H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (IIId). A 1.0-g (2.7 mmole) sample of IIa was dissolved in 50 ml of DMF, and the solution was stirred at 20° for 2 h with periodic saturation with methylamine. The resulting precipitate was removed by filtration and washed with ether to give 0.64 g (76%) of violet needles with mp 376° (from DMF).

5,7-Dibromo-2H,10H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (IVb). A mixture of 9 g (23 mmole) of Vb, 9 g of potassium acetate, and 50 ml of diethyl malonate was stirred at 180° for 30 min until a yellow suspension formed. The solid material was separated and washed with alcohol and water to give 10 g (98%) of a product with mp > 450° (from HCOOH).

Anthranaphthyridines IVa and IVc (Table 1) were obtained in 89 and 72% yields, respectively, from 1,8-diamino-4,5-dichloroanthraquinone (Va) and 1,8-bis(methylamino)-4,5-dibromoanthraquinone (Vc) under similar conditions.

1,8-Diamino-4,5-dibromoanthraquinone (Vb). A 10-g (0.072 mole) sample of potassium carbonate was added in the course of 2 h at 180° (during which foaming was observed) to a mixture of 10 g (36 mmole) of 1,8-dichloroanthraquinone, 20 g (145 mmole) of p-toluenesulfonamide, and 0.5 g (2.8 mmole) of anhydrous copper acetate in 150 ml of nitrobenzene, after which 100 ml of the nitrobenzene was removed by distillation, and the residue was diluted with cyclohexane. The residue was removed by filtration and washed with cyclohexane, alcohol, and water to give 14 g of the disulfonamide derivative, which was brominated in 150 ml of water with 10 g (62 mmole) of bromine by refluxing until the starting material vanished (monitored by chromatography after hydrolysis of a sample in H_2SO_4). The precipitate was removed by filtration and washed with alcohol and water to give 18.5 g of product. Hydrolysis in 50 ml of concentrated H_2SO_4 on a water bath for 1 h gave 12.6 g (94.5%) of red needles of Vb with mp 256-257° (from toluene). Found: Br 40.1%. $C_{14}H_8Br_2N_2O_2$. Calculated: Br 40.4%.

1,8-Diamino-4,5-dichloroanthraquinone (Va). A 17-g (62.3 mmole) sample of 1,8-dichloroanthraquinone was dissolved in 100 ml of concentrated H_2SO_4, and a solution of 15.1 g (240 mmole) of fuming HNO_3 in 19.4 g of concentrated H_2SO_4 was added. The mixture was stirred at 80° for 1.5 h, after which it was cooled. The resulting precipitate was removed by filtration and washed successively with 50-ml portions of 94, 70, and 50% H_2SO_4 and water to give 16.2 g of 1,8-dinitro-4,5-dichloroanthraquinone. An 8-g sample of the dinitro derivative was reduced with 20 g of $SnCl_2$ in 60 ml of water and 150 ml of CH_3COOH at 105° for 2 h. The mixture was diluted with 200 ml of 17% HCl, and the precipitate was separated and extracted with acetone to give, after evaporation, 6 g (89%) of red crystals of Va with mp 234-236° (from toluene). Found: N 8.9%. $C_{17}H_8Cl_2N_2O_2$. Calculated: N 9.1%.

1,8-Bis(methylamino)-4,5-dibromoanthraquinone (Vc). A 1.4-g (5.5 mmole) sample of 1,8-bis(methylamino)anthraquinone was dissolved in 20 ml of CH_3COOH, and 0.91 g (11 mmole) of sodium acetate and 0.57 ml (11 mmole) of bromine were added. The mixture was heated at 75° for 5 h, after which the precipitate was removed by filtration and washed with 90% CH_3COOH to give 1.32 g (55%) of a product with mp 232-234° (from toluene) [4].

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DIAZOTIZATION OF AMINONITROPYRAZOLES

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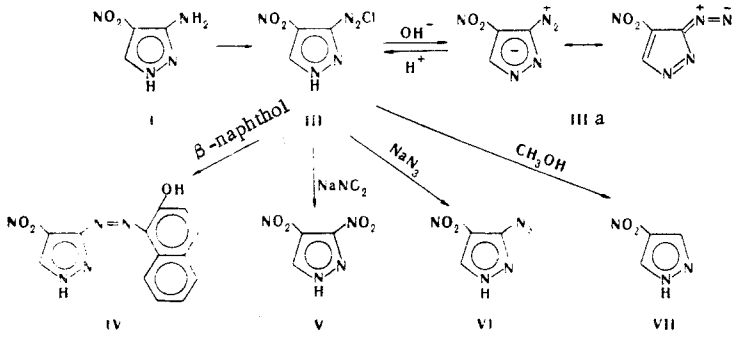
3(5)-Diazonia-4-nitropyrazole hydrochloride, which readily undergoes nucleophilic substitution, is formed by diazotization of 3(5)-amino-4-nitropyrazole. Depending on the conditions, in the diazotization of 3,5-diamino-4-nitropyrazole one or both amino groups undergo reaction. Moreover, a nitro group is simultaneously replaced by a hydroxyl group, and the final product is 3,5-bisdiazo-4-pyrazolone.

The data on the diazotization of aminopyrazoles [1-3] deal with unsubstituted aminopyrazoles and aminopyrazoles with electron-donor substituents in the ring. It might be expected that the introduction of electron-acceptor groups would lead, on the one hand, to an increase in the activity of the diazo group and, on the other, to an increase in the acidity of the imino group and the formation of zwitterion forms of the diazo compounds. With this in mind, we investigated the diazotization of 3(5)-amino-4-nitropyrazole (I) and 3,5-diamino-4-nitropyrazole (II).

3-Diazonia-4-nitropyrazole hydrochloride (III) was obtained in good yield by the action of butyl nitrite on a solution of pyrazole I in methanol in an acidic medium.



I III IIIa IV V VI VII

Its IR spectrum contains the strong absorption band at 2310 cm^{-1} characteristic of ordinary diazonium salts with an "external" anion. An increase in the pH of an aqueous solution of III is accompanied by a shift of this band to 2230 cm^{-1}. The absorption maximum in the IV spectrum is shifted from 325 to 310 nm. These

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