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

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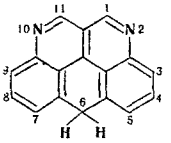
Derivatives of a new heterocyclic system – 6H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine – were obtained by condensation of 1,8-diaminoanthraquinone with malonic ester, acetoacetic ester, and benzoylacetic ester.

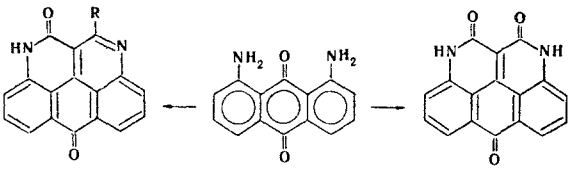
Of the anthracene derivatives condensed with two pyridine rings in the peri positions, only the 1,9-4,10- and 1,9-5,10 isomers (I and II) [1] were known up until now. The 1,9-9,8 isomer – 6H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine (III) – has not been described in the literature.



III

The synthesis of 1,6,11-tricarbonyl derivative (IV) seemed of particular interest. Owing to the peri orientation of the carbonyl groups, the properties of anthranaphthyridone IV may differ fundamentally from the properties of the corresponding 2,6- and 2,8-dicarbonyl derivatives of I and II, which have isolated pyridine rings.

2H,10H-Anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (IV) was obtained by condensation of 1,8-diaminoanthraquinone with diethyl malonate in the presence of potassium acetate.



V, VI IV

V $R = CH_3$; VI $R = C_6H_5$

It is known that 1-aminoanthraquinone reacts with esters of β-ketocarboxylic acids in the presence of alkali metal acetates to give 1-acylanthrapyridones [2] and in the presence of acidic agents to give 1-carbalkoxyanthrapyridines [3]. 1-Aminoanthraquinones that contain such substituents as halogens or sulfo groups in the 8 position cannot be converted to the corresponding 1-acylanthrapyridines because of steric hindrance [4]. However, when the 8 position is occupied by a group that is capable of cyclization, one might expect the formation of two condensed rings simultaneously. In fact, methyl- and phenyl-substituted anthrapyridinepyridones (V and VI), respectively, are formed from 1,8-diaminoanthraquinone and ethyl acetoacetate and ethyl benzoylacetate under the conditions used to obtain IV.

Treatment of anthranaphthyridone IV with phosphorus oxychloride in the presence of dimethylformamide (DMF) gives, in high yield, 1,11-dichloroanthranaphthyridine (VII), the structure of which was proved

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TABLE 1. Anthranaphthyridines IV-VIII

Compound	Crystallization solvent	Empirical formula	Found, %			Calc., %			UV spectra, λ_{max}, nm nm (log ε)	Yield, %
			C	H	N	C	H	N		
IV	—	$C_{17}H_8N_2O_3$	70,7	2,9	9,7	70,8	2,8	9,7	240 (4,55) 340 (4,08) 420 (3,87) (в H_2SO_4)	91
V	p-Xylene	$C_{18}H_{10}N_2O_2$	75,2	3,9	9,5	75,5	3,5	9,8	242 (4,60) 295 (4,67) 405 (3,96) (in CH_3COOH)	86
VI	CH_3COOH	$C_{23}H_{12}N_2O_3$	79,5	3,4	7,9	79,4	3,5	8,0	245 (4,51) 290 (4,37) 402 (3,94) (в H_2SO_4)	92
VII	p-Xylene	$C_{17}H_6Cl_2N_2O$*	62,8	1,7	8,8	62,8	1,9	8,6	245 (4,58) 290 (4,42) 330 (3,88) 340 (3,84) 360 (3,80) 380 (3,77) 410 (3,85) (in dioxane)	99
VIII	Nitrobenzene	$C_{19}H_{12}N_2O_3$	72,4	3,8	8,9	72,1	3,8	8,9	240 (4,37) 340 (3,92) 430 (3,85) (в H_2SO_4)	47

*Found %: Cl 21.2. Calculated %: Cl 21.8.

by mass spectrometry. The starting IV is formed when VII is treated with an aqueous dioxane solution of alkali. Attempts to obtain a monochloro derivative from IV have not yet been successful.

It was of interest to investigate the possibility of the cyclization of N-alkyl-substituted 1,8-diaminoanthraquinone to give a tricarbonyl derivative incapable of keto–enol tautomerism.

Under the conditions used to obtain IV, we synthesized 2,10-dimethyl-2H,10H-anthra[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (VIII) in 47% yield.

EXPERIMENTAL

2H,10H-[1,9,8-c,d,e,f]-2,7-naphthyridine-1,6,11-trione (IV). A mixture of 1.2 g (0.005 mole) of 1,8-diaminoanthraquinone, 1.5 g of potassium acetate, and 30 g (0.185 mole) of malonic ester was stirred at 180° for 15-20 min until a thick yellow suspension had formed. It was diluted with alcohol, and the precipitate was removed by filtration and washed with alcohol and water to give 1.2 g (91%) of product. For purification, the product was dissolved in 30 ml of concentrated H_2SO_4, and the solution was gradually diluted with water until the H_2SO_4 concentration was 70%. After 20 h, the precipitate was removed by filtration and washed successively with 25-ml portions of 70%, 55%, and 30% H_2SO_4 to give yellow prisms. The product was almost insoluble in most organic solvents but could be recrystallized from large volumes of nitrobenzene or N-methylpyrrolidone. The analytical and spectral data are presented in Table 1.

Under similar conditions, compounds V and VI were obtained from 1,8-diaminoanthraquinone and acetoacetic and benzoylacetic esters, while VIII was obtained from 1,8-bismethylaminoanthraquinone and malonic ester.

1,11-Dichloroanthra[1,9,8-c,d,e,f]-2,7-naphthyridin-6-one (VII). A mixture of 2.0 g (0.008 mole) of anthranaphthyridone IV, 127.5 g (0.83 mole) of phosphorus oxychloride, and 10 ml of DMF was refluxed for 30 min, after which it was cooled and poured over ice. Workup gave 2.2 g (99%) of dichloro derivative VII. For purification, the product was recrystallized from p-xylene to give a material with mp 310° (dec.).

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