SYNTHESIS OF DIQUINOLINOANTHRACENE AND PYRIDONOANTHRAQUINOLINES

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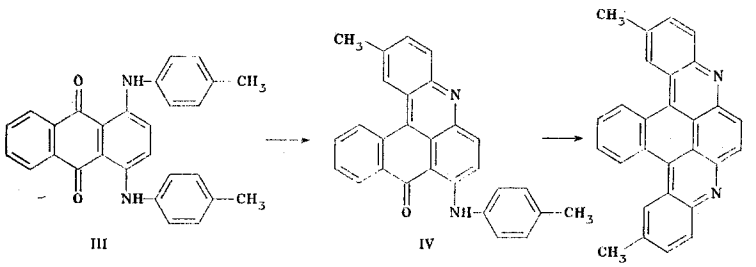
UDC 547.836.3'837.6:542.953.2

New heterocyclic polycondensed systems — diquinolinoanthracene and pyridinoanthraquinoline — were synthesized by the action of polyphosphoric acid on 1,4-di(p-toluidino)anthraquinone and 6-arylaminoanthrapyridones. Dipyridonoanthraquinoline with an amino group in the pyridone ring was produced from N-[6-(p-toluidino)anthrapyridonyl-1]-pyridinium chloride by cyclization and cleavage of the pyridinium group.

Derivatives of a series of heterocyclic anthrone systems, for example, pyridinoanthrone (anthrapyridone) [1-3] and quinolinoanthrone (ceramidonine) [4] possess fluorescent properties of practical value. In connection with this it seemed interesting to synthesize anthracene systems with the two indicated peri-annelated heterocycles — diquinolinoanthracene (dibenzo[b, j]naphtho[1,2,3,4-ℓmn][4, 7]phenanthroline) (I) and pyridonoanthraquinoline (8H-benzo[b]naphtho[1,2,3,4-ℓmn][4, 7]phenanthrolin-9-one) (II). The literature contains information on attempts to produce system I. It is known that heating of 1-arylaminoanthraquinones in 70-80% sulfuric acid at a temperature on the order of 120°C leads to derivatives of ceramidonine [5]. According to the data of the patent [6], 1,4-di(p-toluidino)anthraquinone (III) is converted under analogous conditions to 2,11-dimethyldiquinolinoanthracene (I). However, the authors of [7], reproducing the experiment of [6], showed that the reaction stops at the stage of monocyclization with the formation of 8-(p-toluidino)-2-methylceramidonine (IV). There is no information on system II at all.

We suggested that the synthesis of diquinolinoanthracenes can be accomplished using polyphosphoric acid as the condensing agent. Actually, in a medium of the latter at 170-180°C, compound III, originally forming a red compound IV, is converted upon further heating (for up to 24 h) to an orange compound I, which was isolated with a yield of 80%. Its structure is confirmed by the absence of the band of the CO group in the IR spectrum.



Under analogous conditions the cyclization of 6-arylaminoanthrapyridones (Va-c) proceeds far more rapidly (3-6 h) and leads to the formation of pyridonoanthraquinolines IIa-c with high yields. In contrast to the production of system I, the reaction can also be conducted in sulfuric acid at the temperature 170°C, but it proceeds more slowly and less smoothly than in polyphosphoric acid. The heating of 6-(2-carboxyphenylamino)-N-methyl-anthrapyridone (Vd) leads in both cases to decarboxylation and subsequent formation of compound IIa, produced from 6-phenylamino-N-methylanthrapyridone (Va). There is no doubt of the structure of compounds IIa-c, since the very fact of cyclization is indicated by the change in the bluish-red color of the initial compounds to yellow, while the alternative probability of cyclization at positions 3 and 2' with the formation of carbazole derivatives is excluded by the data of

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 962-964, July, 1984. Original article submitted December 14, 1983.

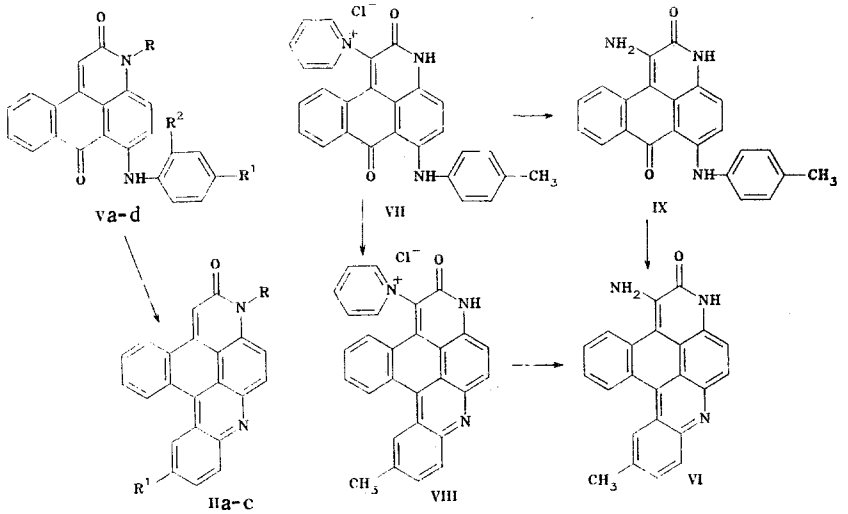
 0009-3122/84/2007-0784$08.50

TABLE 1. Derivatives of 8H-Benzo[b]naphthol[1,2,3,4-lmn][4, 7]phenanthrolin-9-one

Compound	R	R^1	R^2	mp, °C[a]	Found, %			Gross formula	Calculated, %			Yield, %
					C	H	N		C	H	N	
IIa	Me	H	H	287—288	82,4	4,3	8,5	$C_{23}H_{14}N_2O$	82,6	4,2	8,4	96
IIb	Me	Me	H	295—296,5	82,7	4,9	8,1	$C_{24}H_{16}N_2O$	82,5	4,6	8,0	99
IIc	4-BuC_6H_4	Bu	H	233—233,5	85,0	6,4	5,5	$C_{36}H_{32}N_2O$	85,0	6,3	5,5	85
VI	H	Me	NH_2	>350	79,1	4,6	12,3	$C_{23}H_{15}N_3O$	79,1	4,3	12,0	80[a]
VIII	H	Me	$ClO_4^-C_5H_5N^+$	>350	65,6	3,7	8,0	$C_{28}H_{18}ClN_3O_5$[b]	65,7	3,6	8,2	75

[a]Solvent for crystallization: for IIa — DMFA, for IIb — chloroform, for IIc — white spirit, for VI — nitrobenzene, and for VIII — water. [b]Found: Cl 6.6%. Calculated: Cl 6.9%.

elementary analysis, since the latter reaction does not involve dehydration, and also by the absence of the NH band in the IR spectrum. The indicated alternative must always be taken into account, since the formation of ceramidonines and phthaloylcarbazoles can occur under the same conditions.



a R=Me, $R^1=R^2=H$; b $R=R^1=Me$, $R^2=H$; c R=4-BuC_6H_4, $R^1=Bu$, $R^2=H$; d R=Me, $R^1=H$, $R^2=COOH$

Using cyclization in polyphosphoric acid, in conjunction with a previously developed method of synthesis of 1-aminoanthrapyridones [2], we also obtained the first functional derivatives of system II — 10-amino-2-methylpyridonoanthraquinoline (VI). The synthesis of compound VI was performed by two pathways, starting with 1-chloroacetylamino-4-(p-toluidino)anthraquinone, which was converted by heating in pyridine to N-[4-(p-toluidino)anthrapyridonyl-1]pyridinium chloride (VII). The latter can undergo cyclization to a 10-pyridinium derivative of pyridonoanthraquinoline (VIII), and then, by heating in aniline, the amine VI can be obtained, or, by changing the order of the steps, first 1-amino-6-(p-toluidino)anthrapyridone (IX) is obtained, and then it is cyclized. The second pathway is more convenient from the preparative standpoint.

Compounds I and IIa-c possess intense fluorescence, which, in particular, is responsible for the interest in the study and further synthesis of derivatives of systems I and II. It should be noted that, in contrast to anthrapyridones, the fluorescence intensity of which increases greatly when an amino group is introduced into the 1-position [3], the introduction of an amino group into the analogous position of pyridonoanthraquinolines (compound VI) appreciably quenches the fluorescence.

EXPERIMENTAL

Cyclization in Polyphosphoric Acid. General Procedure. Into 10 ml of polyphosphoric acid, 1 g of the starting material is introduced, and it is mixed until it disappears accord-

ing to thin-layer chromatography at 175-180°C, then the mixture is poured out onto water with ice, filtered off, washed with water, and dried.

2,11-Dimethyldibenzo[b, j]naphtho[1,2,3,4-lmn][4, 7]phenanthroline (I). Produced from 1,3-di(p-toluidino)anthraquinone (III) according to the general procedure, observing rather rapid formation of ceramidonine IV and gradual formation of compound I; the reaction was continued for 24 h until IV disappeared. After chromatography on silica gel (benzene) yield 79%, mp >350°C (from propanol). Found: C 87.6; H 4.6; N 7.3%. $C_{28}H_{18}N_2$. Calculated: C 87.9; H 4.8; N 7.3%.

Note. At 130°C only compound IV is formed; reaction time, 3 h.

Derivatives of 8H-Benzo[b]naphtho[1,2,3,4-lmn][4, 7]phenanthrolin-9-one (IIa-c). Produced from 6-arylaminoanthrapyridones (Va-d) according to the general procedure, reaction time 3-6 h; the yields and characteristics are cited in Table 1.

10-Amino-2-methyl-8H-benzo[b]naphtho[1,2,3,4-lmn][4, 7]phenanthrolin-9-one (VI). A. Produced analogously from 1-amino-6-(p-toluidino)-anthrapyridone (IV), which was synthesized from N-[6-(p-toluidinoanthrapyridonyl-1]pyridinium chloride (VII) according to the procedure of [2]; reaction time, 4 h (Table 1).

B. Produced according to the general procedure from the salt VII [2], reaction time 4 h; after pouring out into water, the solution formed was neutralized with soda to pH 6.5, and by the addition of $NaClO_4$, the perchlorate VIII was isolated (Table 1), introduced into 10 ml of aniline, heated to boiling, cooled, diluted with methanol, filtered off, washed with methanol, and compound VI was obtained with a yield of 64%; calculated on the basis of the salt VII.

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