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SYNTHESES BASED ON DIMETHYLPYRAZOLES.

8.* REACTION OF 3,4- AND 4,5-DIAMINOPYRAZOLES WITH 4-NITRONAPHTHALIC ANHYDRIDE

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Mono- and diacylation products were obtained in the reaction of 3,4-diamino-1,5-dimethylpyrazole with 4-nitronaphthalic anhydride in acetic acid; the monoacylation products do not undergo cyclization even in polyphosphoric acid (PPA). The reaction of 4,5-diamino-1-methylpyrazole under similar conditions gives 2-(5-amino1-1-methyl-4-pyrazolyl)-7-nitrobenzo[d,e]isoquinoline-1,3-(1H,3H)dione, during heating of which in polyphosphoric acid ethyl ester only mono- and diethylation at the amino group occurs.

We have previously synthesized 4-amino-5-carbamoyl-1-methylpyrazole and have shown that it reacts with naphthalic anhydride in the same way as anthranilic acid amide to give 1-methyl-1H-pyrazolo[3,4-5',6']pyrimidino[1,2-a]benzo[d,e]isoquinoline-5,13-(5H, 13H) dione [1]. 4-Amino-N-pyrazolylnaphthalimides have intense luminescence, and the photostabilities of daytime fluorescent pigments obtained from them exceed the photostabilities of pigments that contain 4-amino-N-phenylnaphthalimide [2]. Naphthoylene-benzimidazoles, which are effective luminophores, are formed in the reaction of o-phenylenediamine with substituted naphthalic anhydrides [3]. These are the reasons that we became interested in a study of the possibility of the synthesis of pyrazole analogs of naphthoylenebenzimidazole from 3,4-diamino-1,5-dimethylpyrazole (I) and 4,5-diamino-1-methylpyrazole (II).

The reduction of 1,5-dimethyl-3,4-dinitropyrazole (III) [4] and 5-amino-1-methyl-4-nitropyrazole (IV) [5] with hydrazine hydrate on Raney nickel was used to synthesize, respectively, o-diamino-pyrazoles I and II, which are resistance to the action of air oxygen and were isolated in the form of hydrochlorides. Immediately prior to the reaction aqueous

*See [1] for communication 7.

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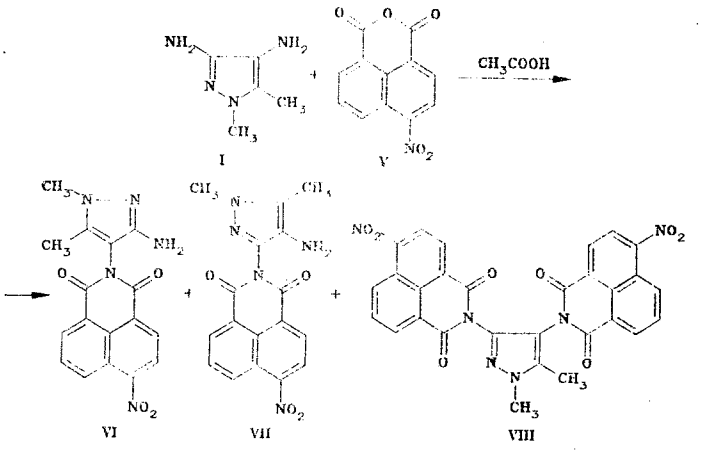
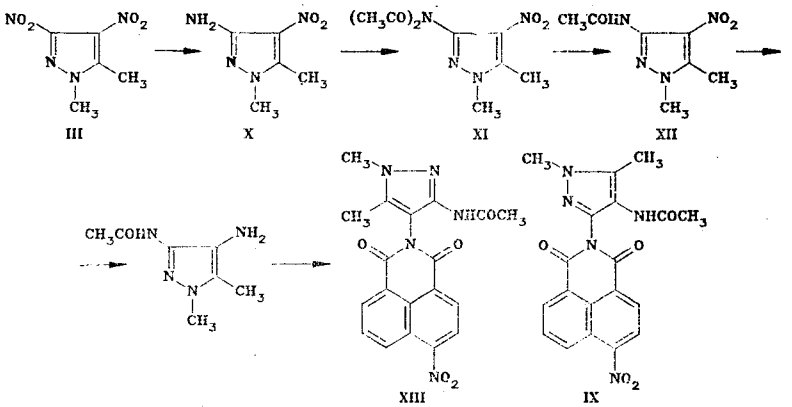
solutions of the salts were treated with sodium carbonate until they had pH 7-8, and free diamino-pyrazoles I and II were obtained.



We established that naphthoyleneimidazole derivatives are not formed in the reaction of 4-nitronaphthalic anhydride (V) with an equimolar amount of 3,4-diaminopyrazole I in refluxing acetic acid; instead, products of acylation of the diaminopyrazole, viz., 2-(3-amino-1,5-dimethyl-4-pyrazolyl)-7-nitrobenzo[d,e]isoquinoline-1,3-(1H, 3H)dione (VI), its isomer VII, and 3,4-bis[7-nitrobenzo[d, e]isoquinoline-1,3-(1H, 3H)dion-2-yl]-1,5-dimethylpyrazole (VIII), are obtained.

Dinaphthaloylaminopyrazole VIII was isolated by twofold dilution of the reaction mixture with water. Further dilution of the filtrate gave a precipitate containing a mixture of isomers VI and VII in a ratio of 2:1 (according to the PMR spectral data), recrystallization of which from water gave individual VI.

In order to exclude, insofar as possible, the formation of VIII, we carried out the reaction of anhydride V with excess diamine I by adding anhydride V to a refluxing solution of I in acetic acid. However, the reaction in this case is evidently complicated by acetylation of the starting diaminopyrazole, and, as a result, the principal product is 2-(4-acetamido-1,5-dimethyl-3-pyrazolyl)-7-nitrobenzo[d,e]isoquinoline-1,3-(1H, 3H)dione (IX), which precipitates when the reaction mixture is allowed to stand for a long time. The data from the PMR and mass spectra of the isolated compound provide evidence for the development of an acetylation product but do not make it possible to assign it to one of the two isomers that can be formed under the given conditions. We therefore synthesized 2-(3-acetamido-1,5-dimethyl-4-pyrazolyl)-7-nitrobenzo[d,e]isoquinoline-1,3-(1H,3H)dione (XIII) from dinitropyrazole III via the scheme

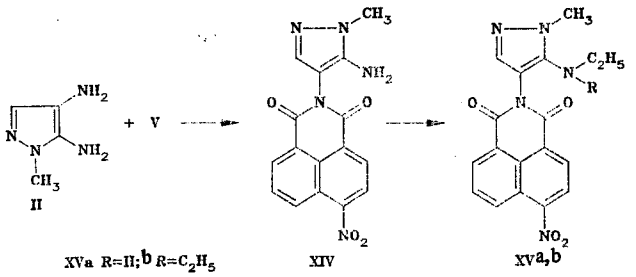


According to data from thin-layer chromatography (TLC) and the PMR spectrum, XIII differs from the compound obtained in the reaction of diaminopyrazole I and anhydride V; this is confirmed by the structure of isomer IX. A shift to strong field of the signals of the protons of the acetamido group relative to the analogous signals in the spectrum of isomer XIII (Table 1) is characteristic in the PMR spectrum of IX; this is associated with the greater nucleophilicity of the 4 position in the pyrazole ring as compared with the 3

position [6]. This is also responsible for the formation of only one of the two possible isomers, viz., dione IX.

We attempted to carry out the cyclization of isomers VI and VII to the corresponding naphthoyleneimidazole derivatives in polyphosphoric acid (PPA), but, as a result, the starting compounds were isolated unchanged.

The reaction of 4,5-diaminopyrazole II with anhydride V in acetic acid leads only to 2-(5-amino-1-methyl-4-pyrazolyl)-7-nitrobenzo[d,e]isoquinoline-1,3-(1H, 3H)dione (XIV). The absence in this case of a diacylation product of the VII type is evidently associated with steric hindrance to acylation of the amino group in the 5 position of the pyrazole ring. In order to cyclize dione XIV we heated it in polyphosphoric acid ethyl ester; we obtained two compounds (XVa, b), which were separated thanks to their different solubilities and were identified as products of mono- and diethylation at the amino group.



The results presented above provide evidence that the geometries of the VI, VII, and XIV molecules are evidently unfavorable for obtaining pyrazole analogs of naphthoylenebenzimidazole. In the synthesized 2-(amino-1-methylpyrazolyl)benzo[d,e]-isoquinoline-1,3-(1H,3H)diones the distance between the amino group and the carbonyl group is increased as compared with 2-(2-aminophenyl)benzo[d,e]isoquinoline-1,3-(1H,3H)diode, from which a naphthoylenebenzimidazole is readily formed; the increase in the distance is evidently a consequence of the difference in the bond angles in the benzene and pyrazole rings [7].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in d_6-DMSO were measured with a Tesla BS-497 spectrometer (100 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with an MKh-1309 spectrometer at an ionizing voltage of 70 eV and an ionization-chamber temperature of 150°C. Thin-layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} plates in a benzene–petroleum ether–ethanol system (5:2:1).

The characteristics of VI-IX and XII-XV are presented in Table 1.

3,4-Diamino-1,5-dimethylpyrazole (I). This compound was obtained by reduction of dinitropyrazole III with hydrazine hydrate on Raney nickel [4]; the product was isolated in the form of the dihydrochloride, with mp 240°C (dec., ethanol) [mp 240°C (dec.) [4]], in 82% yield.

4,5-Diamino-1-methylpyrazole (II). This compound was similarly obtained from aminonitropyrazole IV [5]; the product was isolated in the form of the dihydrochloride, with mp 256-257°C (dec., isopropyl alcohol), in 79% yield. Found: C 30.8; H 5.3; H 30.6%. $C_4H_{10}Cl_2N_4$. Calculated: C 30.4; H 5.4; N 30.3%.

Reaction of 3,4-Diamino-1,5-dimethylpyrazole (I) with 4-Nitronaphthalic Anhydride (V). A) A solution of 0.5 g (2.5 mmole) of diaminopyrazole I dihydrochloride in 3 ml of water neutralized to pH 7-8 with sodium carbonate was added to a refluxing solution of 0.61 g (2.5 mmole) of anhydride V in 10 ml of acetic acid, and the mixture was refluxed for 2 h until anhydride V vanished (monitoring by TLC). It was then cooled to 20°C and diluted to twice its original volume with water. The resulting precipitate was removed by filtration, washed with water, and dried to give 0.32 g of VIII. The filtrate was diluted to twice its original volume with water to give 0.19 g of a precipitate containing a mixture of isomers VI and VII in a ratio of 2:1, according to the PMR spectral data. Recrystallization from water gave 0.08 g of chromatographically pure VI.

B) A 10-ml sample of acetic acid was added to a solution of 0.5 g (2.5 mmole) of diaminopyrazole I dihydrochloride in 3 ml of water, prepared as indicated above, and 0.61 g

TABLE 1. 2-Pyrazolyl-7-nitrobenzo[d,e]isoquinoline-1,3,-(1H, 3H)diones VI-IX and XII-XV

Compound	mp,[a] °C	R_f[b]	PMR spectrum,[c] δ, ppm (in d6-DMSO)					Found, %			Empirical formula	Calculated, %			M+	Yield, %
			1-CH_3	5-CH_3	$COCH_3$	NH or NH_2	3-H	C	H	N		C	H	N		
VI[d]	243—245	0,30	3,67	2,03		4,46		58,5	3,9	15,8	$C_{17}H_{13}N_5O_4$	58,1	3,7	16,0	351	9
VII		0,34	3,49	1,90												
VIII	235—236	0,54	3,83	2,15				60,7	2,9	14,3	$C_{29}H_{16}N_6O_8$	60,4	2,8	14,6	576	22
IX	299—300 (dec.)	0,25	3,73	2,17	1,73	9,00		57,9	3,6	17,5	$C_{19}H_{15}N_5O_5$	58,0	3,8	17,8	393	51
XIII	288—290 (dec.)	0,42	3,45	2,06	2,06	10,73		58,3	3,9	17,7	$C_{19}H_{15}N_5O_5$	58,0	3,8	17,8		87
XIV	236—237	0,10	3,65			5,35	7,53	56,7	3,4	20,3	$C_{16}H_{11}N_5O_4$	57,0	3,3	20,8	337	95
XVa	223—225	0,20	3,58			4,99	7,14	59,6	4,3	18,9	$C_{18}H_{15}N_5O_4$	59,2	4,1	19,2	365	44
XVb	190—192	0,80	3,67				7,33	61,1	4,9	17,5	$C_{20}H_{19}N_5O_4$	61,0	4,8	17,8	393	33

[a]The compounds were crystallized: VI from water, VIII, IX, and XIV from acetic acid—water (1:1), XIII from isopropyl alcohol, and XVa,b from isopropyl alcohol—water (1:1).
[b]In an ethyl acetate—benzene—petroleum ether system (10:1:1) for XIV and XVa,b.
[c]Multiplets of one and two ethyl groups, respectively, are present in the PMR spectra.
[d]Compound VII was obtained only in a mixture with VI.

(2.5 mmole) of anhydride V was added in portions in the course of 1 h to the refluxing solution. The mixture was then refluxed for another 30 min until the anhydride vanished on the chromatogram, after which it was allowed to stand overnight. The resulting precipitate was removed by filtration, washed with ether, and dried to give 0.5 g of IX. Twofold dilution of the filtrate with water gave 0.12 g of a precipitate containing (according to TLC and PMR spectral data) a mixture of VI, VII, and IX in a ratio of 2:1:1.

3-Amino-1,5-dimethyl-4-nitropyrazole (X). This compound, with mp 209-210°C (ethanol) (mp 209-210°C [8]), was obtained in 82% yield from dinitropyrazole III by the method in [8].

3-Diacetamido-1,5-dimethyl-4-nitropyrazole (XI). Aminonitropyrazole X was acetylated with acetic anhydride by the method in [9] to give XI, with mp 119-120°C (isopropyl alcohol), in 86% yield. PMR spectrum ($CDCl_3$): 2.20 (6H, s, CH_3CO), 2.55 (3H, s, 5-CH_3), and 3.72 ppm (3H, s, 1-CH_3). Found: N 27.1%. $C_9H_{12}N_4O_2$. Calculated N 26.9%.

3-Acetamido-1,5-dimethyl-4-nitropyrazole (XII). Hydrolysis of XI was carried out by the method in [9] to give XII, with mp 179-180°C (isopropyl alcohol), in 80% yield. PMR spectrum ($CDCl_3$): 2.22 (3H, s, CH_3CO), 2.52 (3H, s, 5-CH_3), 3.68 (3H, s, 1-CH_3), and 9.00 ppm (1H, s, NH). Found: N 29.9%. $C_7H_{10}N_4O_2$. Calculated: N 29.8%.

2-(3-Acetamido-1,5-dimethyl-4-pyrazolyl)-7-nitrobenzo[d,e]-isoquinoline-1,3-(1H,3H)dione (XIII). A 0.05-g sample of Raney nickel and 0.5 ml of hydrazine hydrate were added at 60-65°C to a solution of 0.2 g (1 mmole) of XII in 5 ml of isopropyl alcohol, after which the mixture was allowed to stand until reduction was complete. The mixture was then cooled to 20°C, the catalyst was removed by filtration, and the filtrate was evaporated to dryness. The residue was dissolved in 5 ml of acetic acid, and the solution was heated to the boiling point and treated with 0.12 g (0.5 mmole) of anhydride V. The mixture was then refluxed for 1 h until the reaction was complete, after which it was diluted to twice its original volume with water, and the precipitate was removed by filtration, washed with water, and dried to give 0.17 g of XIII.

2-(5-Amino-1-methyl-4-pyrazolyl)-7-nitrobenzo[d,e]isoquinoline-1,3-(1H,3H)dione (XIV). A solution of 2.22 g (12 mmole) of diamine II dihydrochloride in 10 ml of water, neutralized to pH 7-8 with sodium carbonate, was added to a refluxing solution of .267 g (11 mmole) of anhydride V in 40 ml of acetic acid, after which the mixture was refluxed for 2 h until the anhydride vanished. It was then cooled, and the precipitate was removed by filtration, washed with ether, and dried to give 3.53 g of product.

2-(5-Ethylamino-1-methyl-4-pyrazolyl)-7-nitrobenzo[d,e]isoquinoline-1,3-(1H,3H)dione (XVa) and 2-(5-Diethylamino-1-methyl-4-pyrazolyl)-7-nitrobenzo[d,e]isoquinoline-1,3-(1H,3H)dione (XVb). A 1-g (3 mmole) sample of XIV was heated in 10 ml of polyphosphoric acid ethyl ester,

obtained by the method in [10], at 110-120°C for 4 h until it had dissolved completely. The solution was then cooled and poured into 50 ml of water, and the precipitate was removed by filtration, washed with water until the wash water was neutral, and dried to give 0.39 g of XVb. The filtrate was neutralized with sodium carbonate, and the resulting precipitate was removed by filtration, washed with water, and dried to give 0.48 g of XVa.

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RECYCLIZATION OF PYRIDINIUM SALTS WITH EXCHANGE AS A METHOD FOR THE PREPARATION OF N-SUBSTITUTED AROMATIC AMINES

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The conditions for the formation of N-substituted aromatic amines in the sulfite variant of recyclization of pyridinium salts, as well as the structural factors that affect the yields of the final substances, were investigated.

It has been previously shown that the rearrangements of quaternary pyridinium salts to N-alkylanilines are accompanied by various competitive processes, the chief of which are dealkylation of the quaternary pyridinium salt to give the starting pyridine base, hydrolysis of the open intermediate with the subsequent formation of phenol, and transamination in the step involving the open intermediate to give an aromatic amine with a radical attached to the nitrogen atom that differs from that in the starting pyridinium salt [1-3]. Until recently, all of these processes were considered to be side reactions and undesirable. However, an analysis of the accumulated experimental data made it possible to assume that the last reaction may have independent synthetic value as a fundamentally new method for the introduction of aromatic radicals into nitrogen bases. In this connection, it was necessary to ascertain the optimum reaction conditions and structural factors that affect the course of the transamination.

2-Picolinium (Ia) and 2-methyl-5-ethylpyridinium (Ib) propyliodides were used as the principal model structures for the investigation. We chose these compounds due to the fact

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