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

N. V. Latypov, V. A. Silevich,
P. A. Ivanov, and M. S. Pevzner

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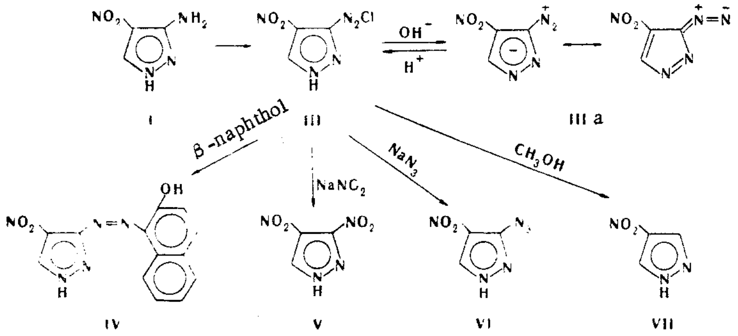
3(5)-Diazonia-4-nitropyrazole hydrochloride, which readily undergoes nucleophilic substitution, is formed by diazotization of 3(5)-amino-4-nitropyrazole. Depending on the conditions, in the diazotization of 3,5-diamino-4-nitropyrazole one or both amino groups undergo reaction. Moreover, a nitro group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



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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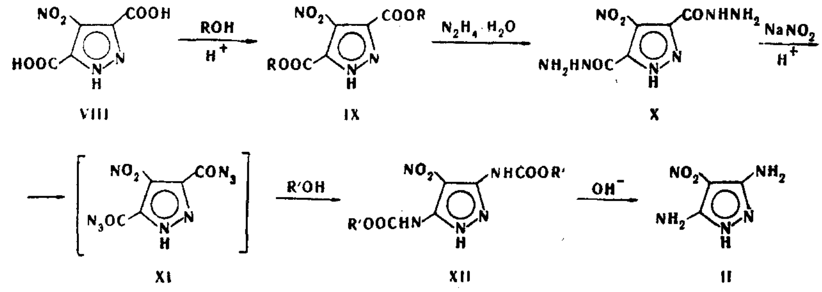
observations are in good agreement with the data in [2] and confirm the presence in aqueous solutions of III of an acid-base equilibrium with the formation of zwitterion structure IIIa.

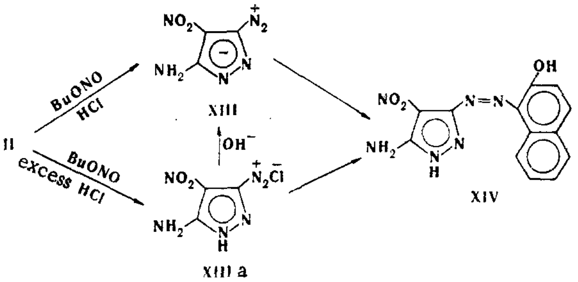
The activity of the diazo group in III is very high. Thus, III reacts with β-naphthol to give product IV and with sodium nitrite or azide to give 3,4-dinitro- (V) and 3-azido-4-nitropyrazoles (VI), respectively. A refluxing solution in methanol rapidly reduces III to 4-nitropyrazole (VII).

A more complex picture is observed in the diazotization of 3,5-diamino-4-nitropyrazole (II), which we obtained via the following scheme:



A substance having, according to its spectral characteristics, zwitterion structure XIII (IR spectrum: ν_{N_2} 2150 cm^{-1}; UV spectrum: λ_{max} 320 nm) was obtained by diazotization of II with butyl nitrite in methanol in the presence of an equivalent amount of hydrogen chloride. When the reaction was carried out in the presence of excess hydrogen chloride, a compound having the absorption band of a diazonium group at 2240 cm^{-1} in its IR spectrum was isolated. The absorption maximum in its UV spectrum is shifted to 305 nm; this constitutes evidence in favor of structure XIIIa. When sodium bicarbonate is added to an aqueous solution of XIIIa, the absorption maximum in the UV spectrum is shifted from 305 to 320 nm; this indicates the XIIIa → XIII transition.

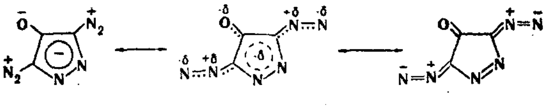
Compounds XIII and XIIIa react with β-naphthol to give the identical diazo coupling product XIV.



An attempt to replace the diazo group in XIII and XIIIa by a nitro or azido group was unsuccessful even when the Sandmeier catalyst was used. Compound XIIIa was isolated in all cases.

A reaction product, in the IR spectrum of which absorption bands of a nitro group are absent but in which bands corresponding to the stretching vibrations of a carbonyl group (ν 1665 cm^{-1}) and a diazo group, constructed in the manner of an "external" salt (ν 2185 cm^{-1}), are present, was isolated in the diazotization of II with excess nitrite in acidic medium.

The absence of signals of protons in the PMR spectrum and the experimentally determined molecular weight* make it possible to assume that XV, which has a 3,5-bisdiazo-4-pyrazolone structure, is formed in this case:



A product involving diazo coupling at both diazo groups (XVI) was isolated and identified in the reaction of XV with β-naphthol; this confirms structure XV as that of a bisdiazo derivative.

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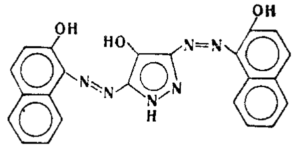
*The product exploded when it was heated above its melting point (113°), and we therefore were unable to determine its elementary composition.

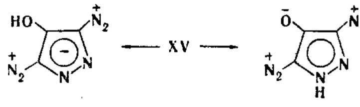


XVI

Compound XV was also obtained from XIII by the action of excess sodium nitrite on a solution of the latter in an acidic medium.

Thus, diazotization of II with excess sodium nitrite in acidic media proceeds at both amino groups. The resulting electron-acceptor diazonium groups increase the sensitivity of the nitro group to the action of nucleophilic agents to such an extent that it is replaced by a hydroxyl group even by the action of water.

One absorption maximum at ~250 nm is observed in the UV spectra of aqueous alkaline and acidic solutions of XV (up to 50% sulfuric acid). When the sulfuric acid concentration is increased to 90%, this maximum is shifted to ~230 nm, which evidently corresponds to the formation of monocation XVa or XVb.



xva xv b

EXPERIMENTAL

3-Diazonia-4-nitropyrazole Hydrochloride (III). A stream of hydrogen chloride was bubbled through a suspension of 2 g (15.6 mmole) of I [4] in 50 ml of methanol for 20-25 min, and 3 ml of butyl nitrite was added dropwise to the resulting solution at 0°, after which the mixture was cooled at 2-4° for 1 h. It was then poured into 200 ml of ether, and the resulting precipitate was removed by filtration, washed with ether, and air dried to give 2.7 g (98%) of a product with mp 104-105°. Found: Э 180*. $C_3H_2N_5O_2Cl$. Calculated: Э 175.5. IR spectrum, cm^{-1}: 2310 (diazo group); 1540, 1360 (nitro group).

Diazo Coupling of III with β-Naphthol. A hot solution of 2.5 g (16.7 mmole) of β-naphthol in 50 ml of 4% KOH was added with stirring to a solution of 2 g (11.3 mmole) of III in 50 ml of 15% H_2SO_4, and the resulting precipitate was removed by filtration, washed with water and ethanol (three 50-ml portions), and air dried to give 2.8 g (90%) of a product with mp 308-310°. Found: C 55.1; H 3.0; N 24.7%. Calculated: C 55.1; H 3.2; N 24.7%.

3,4-Dinitropyrazole (V). A solution of 2.5 g (0.02 mole) of I in 10 ml of 20% H_2SO_4 was added to 80 ml of a 10% aqueous solution of $NaNO_2$, and the temperature was maintained at 50° for 3 h. The solution was then cooled and extracted with ether (10 times with 30-ml portions), and the ether solution was dried with $MgSO_4$. The ether was evaporated, and the residue was crystallized from benzene to give 0.6 g (36%) of a product with mp 77-78°. Found: C 22.8; H 1.2; N 35.4%. $C_3H_2N_4O_4$. Calculated: C 22.8; H 1.3; N 35.5%. IR spectrum, cm^{-1}: 1560 and 1540 (nitro groups).

3-Azido-4-nitropyrazole (VI). A solution of 5.6 g (81 mmole) of $NaNO_2$ in 20 ml of water was added dropwise with vigorous stirring at 0-5° to a solution of 10 g (78 mmole) of I in 160 ml of 10% H2SO_4, after which a solution of 6 g (92.5 mmole) of sodium azide in 40 ml of water was added, and the mixture was heated at 50-55° for 2.5 h. It was then cooled, and the resulting precipitate was removed by filtration and air dried to give 9.5 g (71%) of a product with mp 84° (from water). Found: C 23.2; H 1.3; N 54.6%; $C_3H_2N_6O_2$. Calculated: C 23.4; H 1.3; N 54.5%. IR spectrum, cm^{-1}: 2120 (azide group); 1550 and 1370 (nitro group).

Reduction of III with Methanol. A 1-g (5.7 mmole) sample of III was dissolved in 30 ml of methanol, and the solution was heated at 50° for 15 min. The methanol was evaporated, and the residue was crystallized from ethanol to give 0.6 g (94%) of a product with mp 159-160° (mp 158-160° [5]).

Dimethyl 4-Nitropyrazole-3,5-dicarboxylate (IX). A 50-g sample of the monopotassium salt of VIII [6] was added to a solution of 40 ml of 100% H_2SO_4 in 600 ml of methanol, and the mixture was refluxed for 5 h. The resulting solution was cooled to room temperature, and the precipitated potassium bisulfate was removed by filtration. The excess sulfuric acid was neutralized with a solution of 25 g of NaOH in 150 ml of methanol, and the precipitated sodium bisulfate was removed by filtration. The methanol was evaporated, and the residue was washed with cold water (three 100-ml portions) to give 38-40 g (80-84%) of a product with mp 122-124° (from

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*By potentiometry.

water). Found: C 36.8; H 3.1; N 17.9%; M 226. $C_7H_7N_3O_6$. Calculated: C 36.6; H 3.1; N 18.3%; M 229. IR spectrum, cm^{-1}: 1740 (ester groups); 1540 and 1350 (nitro group). The product had pK_a 5.62 (by potentiometry of an aqueous solution).

4-Nitropyrazole-3,5-dicarboxylic Acid Dihydrazide (X). A 50-ml sample [51.5 g (1.03 mole)] of hydrazine hydrate was added with stirring to a solution of 50 g (0.218 mole) of IX in 300 ml of methanol, and the mixture was heated at 52-55° for 1.5-2 h. It was then cooled to room temperature, and the resulting precipitate was removed by filtration and washed with methanol (two 40-ml portions) to give 46-49 g (85-90%) of a product with mp 178° (from 50% aqueous ethanol). Found: C 23.1; H 4.1; N 47.9%. $C_5H_{11}N_9O_4$. Calculated: C 23.0; H 4.2; N 48.3%. IR spectrum, cm^{-1}: 3340 and 3160 ($NHNH_2$); 1680 (carbonyl groups); 1550 and 1350 (nitro group).

Diethyl 4-Nitropyrazole-3,5-dicarbamate (XII). A) Nitrosation of X. Ether (120 ml) was added to a solution of 25 g (0.109 mole) of X in 100 ml of 20% HCl, the mixture was cooled to 0°, and a saturated aqueous solution of 30 g (0.435 mole) of $NaNO_2$ was added dropwise at this temperature. At the end of the addition, the organic layer was separated, and the aqueous layer was extracted additionally with ether (two 50-ml portions). The combined ether extracts were dried at 0-5° with $MgSO_4$ for 2 h.

B) Rearrangement of XI to XII. Absolute ethanol (300 ml) was added to a dry ether solution of diazide XI obtained as described above, and the mixture was refluxed for 2 h. It was then cooled to room temperature, and the resulting precipitate was removed by filtration and washed with 50 ml of ethanol to give 16 g (60%) of a product with mp 226° (from 50% aqueous DMF). Found: C 37.7; H 4.5; N 24.4%. $C_9H_{13}N_5O_6$. Calculated: C 37.6; H 4.6; N 24.4%. IR spectrum, cm^{-1}: 3320 and 2900 (NH); 1730 and 1710 (carbonyl groups); 1580 and 1360 (nitro group).

3,5-Diamino-4-nitropyrazole (II). A 15-g (52.5 mmole) sample of XII was added with vigorous stirring to a solution of 200 g of KOH in 135 ml of water, and the mixture was heated on a boiling-water bath for 2 h. The hot mixture was then diluted with 165 ml of water, and the mixture was heated for another 30 min. The resulting hot solution was neutralized with 20% HCl to pH 5-7, and the mixture was evaporated to dryness. The dry residue was extracted repeatedly with hot methanol. Evaporation of the methanol gave II containing potassium chloride. Compound II was purified by recrystallization from water to give 6.4-6.9 g (85-92%) of a product with mp 259-261° (bright-orange needles from water). Found: C 25.1; H 3.4; N 48.6%. $C_3H_5N_5O_2$. Calculated: C 25.2; H 3.5; N 48.8%. IR spectrum, cm^{-1}: 3530; 3480; 3200, 3120, and 2980 (NH_2); 1580 and 1350 (nitro group).

3-Diazo-4-nitro-5-aminopyrazole (XIII). A stream of HCl (750 ml) was bubbled with stirring through a cooled (to 0-2°) suspension of 2 g (13.6 mmole) of II in 80 ml of methanol, after which 4 ml of butyl nitrite was added, and the mixture was maintained at 2-4° for 1 h. It was then diluted with 300 ml of ether, and the resulting precipitate was removed by filtration to give 2.1 g (80%) of a product with mp 124-125°. IR spectrum, cm^{-1}: 2150 (diazo group); 1550 and 1340 (nitro group). UV spectrum in water: λ_{max} 320 nm (log ε 4.11).

3-Diazonia-4-nitro-5-aminopyrazole Hydrochloride (XIIIa). Hydrogen chloride (5 liters) was bubbled through a cooled (to 0-2°) suspension of 7 g (47.6 mmole) of II in 200 ml of methanol, after which 10-12 ml of butyl nitrite was added, and the mixture was maintained at 3-5° for 1 h. It was then diluted with 800 ml of ether, and the resulting precipitate was removed by filtration to give 8 g (85%) of a product with mp 136°. Found: M 196. $C_3H_3N_6O_2Cl$. Calculated: M 190.5. IR spectrum, cm^{-1}: 2240 (diazonium group); 1550 and 1340 (nitro group). UV spectrum: in 0.1 N_2SO_4; λ_{max} 305 nm (log ε 4.02), in 5% $NaHCO_3$; λ_{max} 320 nm (log ε 4.11).

Diazo Coupling of XIIIa with β-Naphthol. A solution of 2.6 g (18.0 mmole) of β-naphthol in 50 ml of 5% KOH was added with stirring to a solution of 2 g (10.5 mmole) of XIIIa in 100 ml of 10% H_2SO_4, and the resulting precipitate was removed by filtration, washed with ethanol (three 50-ml portions), and air dried to give 2.2-2.4 g (70-77%) of a product with mp 336-340°. Found: C 52.1; H 3.5; N 27.9%. $C_{13}H_{10}N_6O_3$. Calculated: C 52.3; H 3.4; N 28.2%.

3,5-Bisdiazo-4-pyrazolone (XV). A suspension of 5 g (34.0 mmole) of II in 40 ml of 20% H_2SO_4 was added gradually with stirring at 0-3° to a solution of 20 g (0.280 mole) of $NaNO_2$ in 50 ml of water, after which the mixture was heated to 50-55° and maintained at this temperature for 30 min. The resulting solution was separated from the liberated impurities by filtration, and the filtrate was extracted with ethyl acetate. The solvent was evaporated from the filtrate, and the residue was crystallized from methanol to give 2.5 g (53%) of a product with mp 112-113°. Found: M 134. C_2N_6O. Calculated: M 136. IR spectrum, cm^{-1}: 2185 (diazo group); 1665 (carbonyl group). UV spectrum: in water and in up to 50% H_2SO_4 solutions: λ_{max} 250 nm (log ε 4.75); in 90% H_2SO_4: λ_{max} 230 nm (log ε 4.65).

Diazo Coupling of XV with β-Naphthol. A 4-ml sample of 96% H_2SO_4 was added dropwise at room temperature to a solution of 0.6 g (4.4 mmole) of XV in 50 ml of water, after which a solution of 1.3 g (9.1 mmole) of β-naphthol in 50 ml of 2% KOH was added. The resulting precipitate was removed by filtration and washed successively with water and ethanol to give 1.2 g (63%) of a product with mp 192-194°. Found: N 19.8%. $C_{23}H_{16}N_6O_3$. Calculated: N 19.9%.

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SYNTHESIS AND PROPERTIES OF AZOLES AND THEIR DERIVATIVES

XXX.* SYNTHESIS OF HETEROCYCLIC COMPOUNDS FROM 1,3-DICYANOADAMANTANE

G. A. Shvekhgeimer and L. K. Kuz'micheva

UDC 547.785.1.07

The corresponding mono- and bisheterocyclic derivatives of adamantane were obtained by reaction of the dinitrile or diimino ester of adamantane-1,3-dicarboxylic acid with ethylenediamine and related compounds.

The literature does not contain information regarding the synthesis of compounds simultaneously containing an adamantyl group and two azole residues. Feeling that compounds of this sort may be of interest as potential biologically active substances, we studied some methods for their synthesis.

Reactions of functional derivatives of adamantane-1,3-dicarboxylic acid with ethylenediamine, o-phenylenediamine, and o-aminophenol were used to construct the heterocyclic ring. Starting dinitrile I was obtained from adamantane-1,3-dicarboxamide (II) and was used for the synthesis of the diethyl diimino ester of adamantane-1,3-dicarboxylic acid (III). The structure of III was confirmed by conversion to the known adamantane-1,3-dicarboxamide [2].

The reaction of diimino ester III with ethylenediamine under the conditions usually employed for the preparation of imidazolines leads to an inseparable mixture of two compounds, the IR spectrum of which contain absorption bands at 1600 and 1670 cm^{-1}, which we assigned, respectively, to the stretching vibrations of the C=N bond in the imidazoline ring and the C=O bond in the amide grouping. Analysis of the mass spectrum showed that the reaction product contains two compounds with molecular weights of 272 and 247; these values are in agreement with empirical formulas $C_{16}H_{24}N_3$ and $C_{14}H_{21}N_3O$. We evidently obtained a mixture of 1,3-[bis(2-imidazolinyl)]adamantane (IV) and 3-(2-imidazolinyl)adamantane-1-carboxamide. Compound IV was synthesized by condensation of diimino ester III with fivefold excess of ethylenediamine at room temperature and also by refluxing dinitrile I with ethylenediamine in acidified cumene.

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*See [1] for communication XXIX.

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