SYNTHESIS OF NEW 1,10,11,20-TETRAHYDRODIBENZO[c,j]DIPYRAZOLO[3,4-f:3',4'-m]-1,2,5,8,9,12-HEXAAZACYCLOTETRADECENE DERIVATIVES

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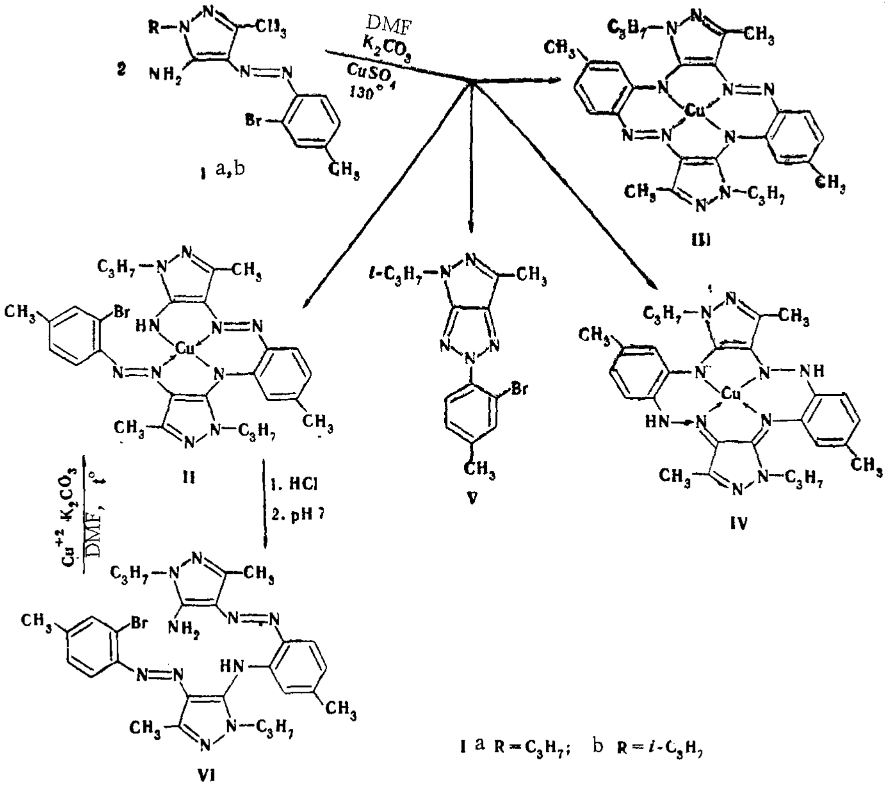
UDC 541.572.54:543.422.25:547.778.4.07

1,10,11,20-Tetrahydrodibenzo[c,j]dipyrazolo[3,4-f:3',4'-m]-1,2,5,8,9,12-hexaazacylotetradecene derivatives were obtained by the reaction of copper sulfate with 5-amino-4-(2-bromo-4-methylphenylazo)-3-methyl-1-R-pyrazoles in dimethylformamide in the presence of potassium carbonate; 2-(2-bromo-4-methylphenyl)-4-methyl-6-isopropyl-2,6-dihydropyrazolo[2,3-d]-1,2,3-triazole was isolated as a side product. 5-amino-4'-bromo-3,3'-dimethyl-1-R',4,5-'azobispyrazoles do not undergo template synthesis under the given conditions. All of the compounds obtained were characterized by the results of elementary analysis and data from the IR, UV, and mass spectra. The copper complexes were investigated by EPR spectroscopy, while the remaining complexes were investigated by NMR spectroscopy.

New 1,10,11,20-tetrahydrodibenzo[c,j]dipyrazole[3,4-f:3',4'-m]-1,2,5,8,9,12-hexaazacyclotetradecene derivatives were obtained. They were synthesized via the scheme



When we subjected azo compound Ia to reaction with both anhydrous copper(II) sulfate and its crystal hydrate, in addition to macrocyclic complex III, we isolated II — a metal chelate of copper(II) with quadridentate bisazo ligand VI, obtained as a result of single nucleophilic substitution — and IV. The IR spectrum of III does not contain characteristic bands in the region of vibrations of NH bonds. Narrow absorption bands of an NH group are

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All-Union Scientific-Research Institute of Chemical Reagents and Ultrapure Chemical Reagents, Moscow 107258. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1530-1535, November, 1980. Original article submitted December 12, 1979.

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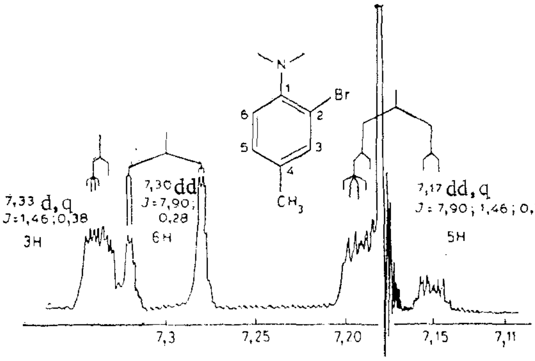

Fig. 1. PMR spectrum of 2-(2-bromo-4-methylphenyl)-4-methyl-6-isopropyl-2,6-dihydropyrazolo[4,5-d]-1,2,3-triazole in $CDCl_3$.

observed in the IR spectra of II and IV at 3360 cm^{-1} (in CCl_4). Compound VI was isolated from quadridentate bisazo chelate II by treatment with hydrochloric acid and subsequent neutralization to pH 7. Its IR spectrum contain characteristic absorption bands of an NH group at 3323 cm^{-1} and a doublet of NH_2 ν_{sym} (3375 cm^{-1}) and ν_{asym} (3475 cm^{-1}) bands (in $CHCl_3$). It was established from the PMR spectrum that the bisazo ligand consists of two isomers, viz., VIa and VIb, in a ratio of 70:30 (from the integrals of the peaks).

As in [1, 2], in which the cis-trans isomerization of azoaryls was studied, we recorded the PMR spectra of VI in d_6-DMSO at 30, 80, 120, and 150°C and in $CDCl_3$ at 30°C. However, the isomer ratio always remained constant, and one may consequently assume that cis-trans (syn-anti) isomerism involving the azo groups of chelating agent VI is not observed in this case.

We were unable to separate isomers VIa,b by chromatography. Chelate II was obtained when they were heated under the conditions of template synthesis in the presence of Cu^{2+}.

The mass spectra of II-IV contain molecular-ion peaks with m/e 651-653-655, which correspond to nonmacrocyclic copper chelate II, the existence of an isomeric structure with a remotely separated NH group and a bromine atom can be assumed for II, since the splitting out of a molecule of HBr that is typical for nonmacrocyclic metal chelates [3, 4] is not observed in its fragmentation: one observes peaks with m/e 571-573, corresponding to macrocyclic chelate III, and with m/e 573-575, corresponding to the dihydro derivative of macrocyclic chelate III (M + 2). The ratio of the intensities of the isotope peaks of the molecular ions of metal chelates II-IV indicates the presence of a copper atom.

The EPR spectrum* of III in $CHCl_3$ at room temperature has the following parameters; $g_{iso} = 2.078 \pm 0.005$, $A_{iso}{}^{Cu} = 84 \pm 5$ Oe, and $A_{iso}{}^{N} = 13.8 \pm 0.5$ Oe. The number of hyperfine coupling (HFC) lines from the nitrogen nuclei attests to coupling of the unpaired electron of copper with three or four equivalent nitrogen atoms (the number cannot be determined more precisely because of superimposition of the HFC lines from the adjacent HFC lines for copper).

In the preparation of the macrocyclic chelate compound of copper(II) from azo compound Ib with $CuSo_4 \cdot 5H_2O$ in dimethylformamide (DMF) in the presence of K_2CO_3 we were able to isolate in pure form only V, which was identified from the PMR spectrum and by mass spectrometry as 2-(2-bromo-4-methyl-1-phenyl)-4-methyl-6-isopropyl-2,6-dihydropyrazolo[4,5-d]-1,2,3-triazole.

The PMR spectrum (Fig. 1, 0.2 M in $CDCl_3$) contains signals of an isopropyl group at 1.59 (d, J = 6.0 Hz, $2CH_3$) and 4.59 ppm (p, CH) and two singlets of methyl grups at 2.41 (CH_3 attached to a benzene ring) and 2.55 ppm (CH_3 attached to a pyrazole ring). A complex multiplet is observed in the aromatic signal region: at 7.17 ppm (dd, q, $J_{5H-6H}{}^{o} = 7.9$, $J_{5H-3H}{}^{m} = 1.46$, and $J_{5H-CH_3} = 0.7$ Hz for 5-H), at 7.30 ppm (dd, $J_{6H-5H}{}^{o} = 7.9$, $J_{6H-3H}{}^{p} = 0.27$

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*The authors thank Doctor of Physical-Mathematical Sciences V. A. Shvets (Institute of General Chemistry, Academy of Sciences of the USSR, Moscow) for recording the EPR spectra (with an EPR-3 radiospectrometer at a klystron operating frequency of ~9.4 GHz).

TABLE 1. Physicochemical Constants of II-VI, VIIIb, and IX

Compound	mp, °C	Found, % C	Found, % H	Found, % Br	Found, % N	Empirical formula	Calc., % C	Calc., % H	Calc., % Br	Calc., % N	M	M*	Yield, %
II	181—182	51,4	5,0	12,4 9,9-Cu	21,5	$C_{28}H_{33}N_{10}BrCu$	51,5	5,1	12,2 9,7-Cu	21,5	653,09	651	22
III	162—164	58,7	5,5	11,2-Cu	24,7	$C_{28}H_{32}N_{10}Cu$	58,8	5,6	11,1-Cu	24,5	572,18	571	15
IV	166—168	58,6	5,8	11,0-Cu	24,4	$C_{28}H_{34}N_{10}Cu$	58,6	6,0	11,1-Cu	24,4	574,20	573	18
V	74—76	50,3	4,7	24,0	20,9	$C_{14}H_{16}N_5Br$	50,3	4,8	23,9	21,0	334,22	333	20
VI	137—139	56,7	6,0	13,7	23,7	$C_{28}H_{35}N_{10}Br$	56,9	6,0	13,5	23,7	591,56	590	80
VIIIb	109—110	38,4	5,6	36,5	19,4	$C_7H_{12}N_3Br$	38,5	5,6	36,6	19,3	218,10	217	90
IXa	233 dec.	46,7	3,9	22,1	27,1	$C_{14}H_{14}N_7Br$	46,7	3,9	22,2	27,2	360,22	359	11,7
IXb	60—62	50,9	5,0	19,9	24,7	$C_{17}H_{20}N_7Br$	50,8	5,0	19,9	24,4	402,30	401	18
IXc	144—145	55,0	4,2	18,2	22,6	$C_{20}H_{18}N_7Br$	55,1	4,2	18,3	22,5	436,32	435	30

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*The molecular weights (M) were obtained by mass spectrometry; the lightest isotope is presented.

Hz for 6-H), and at 7.33 ppm (d, q, $J_{3H-5Hm} = 1.46$ $J_{3H-CH_3} = 0.38$ Hz for phenyl ring 3-H). The J_{5H-CH_3} constant (0.7 Hz) is overstated as compared with the long-range spin–spin coupling (cis- and trans-HC–C=CH –0.5...–3.0 Hz), i.e., it may be assumed that the double bonds in the benzene ring are localized between the C_2 and C_3, C_5 and C_6, and C_6 and C_1 atoms.

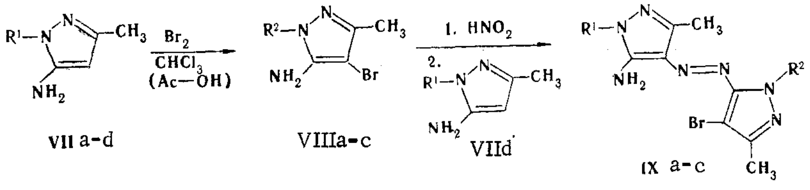
Molecular-ion peaks with m/e 333-335, which constitute 56.4% of the maximum peak, are present in the mass spectrum of V. It was established from the spectra recorded at an ionizing-electron energy of 12 eV that the compound is an individual substance. The presence of a bromine atom is identified from the ratio of the intensities of the isotope peaks in the molecular ions and from the ion peaks with m/e 254 (4.9) due to splitting out of a Br atom and m/e 169-171 (32.2) due to a bromotropylium cation.

The formation of triazoles in template self-condensation reactions was also observed in [6]; in addition, 2-(2-chloro-3-pyridyl)-4-methyl-6-phenyl-2,6-dihydropyrazolo[4,5-d]-1,2,3-triazole was isolated in 24.4% yield in the preparation of the macrocyclic chelate compound of copper. This side process in template self-condensation reactions occurs as a result of oxidative dehydrocyclization of the starting azo compounds.

We were unable to isolate a macrocyclic chelate compound in pure form from the template self-condensation of azo compound Ib.

5-Amino-3-methyl-1-R-pyrazoles VIIa-d were obtained by the methods in [7-10].

Compounds IXa-c were obtained by diazotization of the corresponding pyrazoles in hydrochloric acid and coupling at pH 1.0 with pyrazoles VIIa, c, d. The PMR spectra of azobispyrazoles IXa-c contain signals of two methyl groups and signals of protons of the



VII a $R^1=H$; b $R^1=C_3H_7$; c $R^1=i\text{-}C_3H_7$; d $R^1=C_6H_5$; VIII a $R^2=H$; b $R^2=i\text{-}C_3H_7$; c $R^2=C_6H_5$; IX a $R^1=C_6H_5$, $R^2=H$; b $R^1=C_6H_5$, $R^2=i\text{-}C_3H_7$; c $R^1=R^2=C_6H_5$

substituent attached to the pyrazole nitrogen atom; a signal of an NH_2 group is observed at 6.95-7.20 ppm (d_6-acetone). Bands of symmetrical and asymmetrical stretching vibrations of an NH_2 group at ∿ 3480 and 3375 cm^{-1} are observed in the IR spectra. In contrast to the pyrazolone azo analogs, which exist in the hydrazone form [11], IXa-c are o-amino azo compounds.

When the template condensation of IXa-c was carried out under standard conditions with anhydrous copper(II) sulfate, molecular ions of a macrocyclic complex were not detected in

TABLE 2. Electronic Spectra of II-VI and IX

Compound	Solvent	λ_{max}, nm (lg ε)		
II	$CHCl_3$	360 (4,46)	440 (4,40)	600 (3,18)
III	$CHCl_3$		470 (4,20)	580 (3,28)
IV	$CHCl_3$	380 (4,10)	468 (4,38)	585 (3,70)
V	$CHCl_3$			410 (4,00)
VI	$CHCl_3$		385 (4,33)	420 (4,24)
IXa	Methanol	241 (4,10)	375 (4,56)	410 (4,55)
IXb	Methanol		390 (4,57)	410 (4,57)
IXc	Methanol		390 (4,52)	420 (4,53)

the reaction mass by mass spectrometry. Template cyclization takes place with the highest yield (∿ 40%) in the case of the pyrazolazopyridine. The yield of product decreases when the reaction time is increased.

The effect of the anion was determined in [13]; the yields were in the 30% range when template synthesis was carried out in the presence of $CuSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$- and $Cu(CH_3COO)_2 \cdot H_2O$, whereas they were in the 13% range in the presence of Cu(0).

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in trichloromethane were obtained with SF-4 and Unicam-100A spectrometers. The PMR spectra were recorded with a Varian XL-100-12 spectrometer at 30°C (100 MHz) with tetramethylsilane as the internal standard. The mass spectra were obtained with an AEI MS-702 mass spectrometer with direct introduction ofthe samples into the ionization region, the ionizing-electron energy was 70 eV, and the temperature of the sample-vaporization system was 120-180°C. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates in an acetone—pentane system (1:5).

Compounds Ia,b were obtained by the method in [8].

Template Synthesis by Self Condensation of Azo Compound Ia in the Presence of Copper(II) Sulfate Pentahydrate. A mixture of 4.04 g (12 mmole) of Ia, 9.67 g (0.07 mole) of potassium carbonate, 1.5 g (6 mmole) of copper(II) sulfate pentahydrate, and 300 ml of DMF was heated at 130°C for 6 h (until starting azo compound Ia vanished according to TLC). The reaction mixture was cooled, 300 ml of water was added, and the precipitate was removed by filtration, washed successively with water, 300 ml of $DMF-H_2O$ (1:1), and water, and air dried. Three fractions were isolated by repeated column chromatography on silica gel 100/160 (elution with benzene), and the solvent was removed by evaporation.

Fraction 1. Workup gave 0.88 g of dark-brown (black) crystals of II, which was soluble in acetone, benzene, trichloromethane, DMF, DMSO, acetic acid, and methanol but insoluble in water and was identified as 5-{[(5-amino-3-methyl-1-propyl-4-pyrazolyl)azo]-4-methyl-2-phenylamino}-4-[(2-bromo-4-methylphenyl)azo]-3-methyl-1-propylpyrazolate(2-)-copper (II).

Fraction 2. This fraction yielded {1,4,5,9,11,14-hexahydro-1,11-dipropyl-3,8,13,18-tetramethyldibenzo[c,j]dipyrazolo[3,4-f:3',4'-m][1,2,5,8,9,12-hexaaza-5,9-2H-cyclotetradecenato(2-)-$N^{4(5)}$,N^{10},$N^{14(15)}$,N^{20}}copper (IV), which was soluble in hexane, tetrachloromethane, trichloromethane, DMF, and DMSO, but insoluble in water.

Fraction 3. This fraction yielded 0.25 g of {1,10,11,20-tetrahydro-1,11-dipropyl-3,8,13,18-tetramethyldibenzo[c,j]dipyrazolo[3,4-f:3',4'-m]-1,2,5,8,9,12-hexaazacyclotetradecenato(2-)-$N^{4(5)}$,N^{10},$N^{14(15)}$,N^{20}}copper (III) as a dark-brown crystalline substance that was quite soluble in hexane, tetrachloromethane, trichloromethane, acetone, DMF, and DMSO, but insoluble in water.

5-{[2-[(5-Amino-3-methyl-1-propyl-4-pyrazolyl)azo]-4-methylphenyl]amino}-4-[(2-bromo-4-methylphenyl)azo]-3-methyl-1-propylpyrazole (VI). A 0.65 g (1 mmole) sample of II was mixed in 20 ml of concentrated H_2SO_4 and 10 ml of acetic acid, after which the dark-cherry-red solution of complex II was cooled and neutralized with 40% sodium hydroxide solution to pH 3-5. The precipitate was removed by filtration, washed with water, dried, and purified with a column filled with neutral Al_2O_3 (activity II, elution with benzene) to give 0.47 g of light-brown crystalline VI, which was quite soluble in trichloromethane, acetone, DMF, and DMSO, but insoluble in water.

2-(2-Bromo-4-methylphenyl)-4-methyl-6-isopropyl-2-6-dihydropyrazolo[2,3-d]-1,2,3-triazole (V). A mixture of 4.036 g (0.012 mole) of Ib, 9.67 g (0.07 mole) of potassium carbonate, and 1.5 g (6 mmole) of copper(II) sulfate pentahydrate was heated with stirring in 50 ml of DMF at 130°C for 5 h [until starting azo compound Ib vanished according to TLC in an acetone–petroleum ether system (1:5)]. The reaction mixture was cooled and treated with 300 ml of water, and the aqueous mixture was acidified to pH 2.0 with 5% HCl solution. The resulting precipitate was removed by filtration, washed successively with water, 10% HCl solution, and water, and air dried. It was then purified by column chromatography with neutral Al_2O_3 (activity II, elution with tetrachloromethane). The first fraction was separated, the solvent was evaporated, and the residue was recrystallized from tetrachloromethane to give 0.85 g of V as a pale-brown finely crystalline substance that was quite soluble in trichloromethane, DMF, DMSO, acetone, and benzene.

5-Amino-4-bromo-3-methyl-1-R-pyrazoles (VIIIa,c). These compounds were obtained by the methods in [10, 13]. Compound VIIIa had mp 118-119°C (mp 118-119°C [13]); VIIIc had mp 103-104°C (mp 106.5°C [10]).

5-Amino-4-bromo-3-methyl-1-isopropylpyrazole (VIIIb). A 15.98-g (0.1 mole) sample of bromine was added dropwise with cooling and stirring to a suspension of 13.9 g (0.1 mole) of VIId in 25 ml of acetic acid, and the mixture was stirred at 20°C for 4 h. The acetic acid was removed by distillation, and the residue was made alkaline to pH 10 with 40% sodium hydroxide solution. The supernatant organic layer was separated and recrystallized from benzene to give 19.6 g of VIIIb as a white crystalline substance that was quite soluble in trichloromethane, hot water, and acetone. Thin-layer chromatography was carried out in an acetone–pentane system (5:1) with development with iodine. PMR spectrum (0.4 M in $CDCl_3$): 3.48 (2H, broad s, NH_2), 2.11 (3H, s, CH_3), 1.36 (3H, d, J = 6.5 Hz, CH_3—C), and 4.24 ppm (1H, m, CH).

5-Amino-4'-bromo-3,3'-(or 5')-dimethyl-4,5'(or 3')-azobis-1-phenyl-1'-H-pyrazole (IXa). A diazonium solution prepared from 4.40 g (0.025 mole) of VIIIa in 20 ml of acetic acid, 50 ml of water, 3.0 ml of concentrated HCl (0.03 mole), and 1.75 g (0.025 mole) of sodium nitrite in 10 ml of water (pH 2.0) was added to a solution of 4.33 g (0.025 mole) of VIId in 50 ml of water and 10 ml of acetic acid, and the resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from dichloroethane to give 1.5 g of IXa as a yellow finely crystalline powder that was quite soluble in DMF and DMSO and satisfactorily soluble in trichloromethane. Thin-layer chromatography was carried out in an acetone–pentane system (1:3). PMR spectrum (0.1 M in d_6-DMSO): 7.42-7.59 (5H, m, Ph), 12.97 (1H, broad s, NH), (0.05 M in d_6-acetone): 2.21 (3H, s, CH_3 ortho to a bromo group), 2.38 (3H, s, CH_3), 7.20 (2H, broad s, NH_2), and 7.35-7.65 ppm (5H, m, Ph).

5-Amino-4'-bromo-3,3'-dimethyl-4,5'-azobis-1-phenyl-1'-isopropyl-pyrazole (IXb). A diazonium solution prepared from 2.18 g (0.01 mole) of VIIIb in 40 ml of water, 2 ml of acetic acid, 2.1 ml of concentrated HCl (0.021 mole), and 0.7 g (0.01 mole) of sodium nitrite in 5 ml of water was added to a solution of 1.61 g (0.01 mole) of VIId in 5 ml of water and 25 ml of acetic acid, and the resulting precipitate (at pH 3-4) was removed by filtration washed with water, dried, recrystallized from acetone, washed with tetrachloromethane, and dried to give 0.72 g of IXb as a yellow finely crystalline powder that was quite soluble in DMF and DMSO. Thin-layer chromatography was carried out in an acetone–pentane (1:3) or acetone–petroleum ether (1:4) system. PMR spectrum (0.2 M in d_6-acetone): 1.43 (6H, d, J = 6.8 Hz, $2CH_3$), 2.16 (3H, s, CH_3 ortho to Br), 2.39 (3H, s, CH_3 ortho to $N{=}N$), 5.10 (1H, m, CH), 7.23-7.65 (5H, m, Ph), and 7.01 (2H, broad s, NH_2).

5-Amino-4'-bromo-3,3'-dimethyl-4,5'-azobis-1,1'-diphenylpyrazole (IXc). A diazonium solution prepared from 2.40 g (0.01 mole) of VIIIc in 20 ml (0.02 mole) of concentrated HCl, 4 ml of water, 5 ml of acetic acid, and 0.71 g (0.01 mole) of sodium nitrite in 5 ml of water was added with stirring to a solution of 2.161 g (0.01 mole) of VIId and 3.0 g of sodium acetate in 15 ml of water and 30 ml of acetic acid, and the mixture was then neutralized carefully with cooling with 10% sodium hydroxide solution to pH 3-5. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from a mixture of isopropyl alcohol with water (3:1) to give 1.3 g of IXc as a yellow crystalline substance. Thin-layer chromatography was carried out in an acetone–pentane (1:5) or acetone–petroleum ether (1:4) system. PMR spectrum (0.1 M in d_6-acetone): 2.25 (3H, s, CH_3 ortho to Br), 2.33 (3H, s, CH_3), 6.95 (2H, broad s, NH_2), 7.08-7.65 (10H, m, 2Ph), (0.1 M in $CDCl_3$): 2.35 (3H, s, CH_3 ortho to Br), 2.44 (3H, s, CH_3), 5.94 (2H, broad s, NH_2), and 7.30-7.59 (10H, m, 2Ph).

The physicochemical constants, results of elementary analysis, and yields of the compounds obtained are presented in Tables 1 and 2.

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SYNTHESIS OF ANALOGS OF 5(4)-AMINOIMIDAZOLE-4(5)-CARBOXAMIDE AND PURINES.

9.* PECULIARITIES OF THE REACTION OF 5(4)-AMINOIMIDAZOLE-4(5)-CARBOXHYDRAZIDE WITH NITROUS ACID AND OF 5-DIAZOIMIDAZOLE-4-CARBOXAZIDE WITH AMINES

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The reaction of 5(4)-aminoimidazole-4(5)-carboxhydrazide with nitrous acid was investigated. A mixture of four compounds, viz., 5-diazoimidazole-4-carboxazide, 5-diazoimidazole-4-carboxylic acid, 5(4)-aminoimidazole-4(5)-carboxazide, and 2-azahypoxanthine, is formed under all of the investigated conditions. 5(4)-Azidoimidazole-4(5)-carboxamide derivatives were obtained in the reaction of diazoimidazolecarboxazide with various amines in protic and aprotic solvents. 5-N-(Piperidyl)azoimidazole-4-carboxazide was isolated only in the reaction with piperidine in an aqueous medium.

5-Diazoimidazole derivatives are of great interest in the chemistry of heterocyclic diazo compounds. However, the available information on the diazotization of imidazole derivatives involves only compounds that have one substituent, viz., and amino group, that is reactive in this process [2-4].

In the present paper we examine the reaction of nitrous acid with 5(4)-aminoimidazole-4(5)-carboxhydrazide (I), which, as we have shown in [1], has approximately identically reactive groupings in the 4 and 5 positions of the imidazole ring.

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*See [1] for Communication 8.

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1536-1540, November, 1980. Original article submitted April 23, 1980.