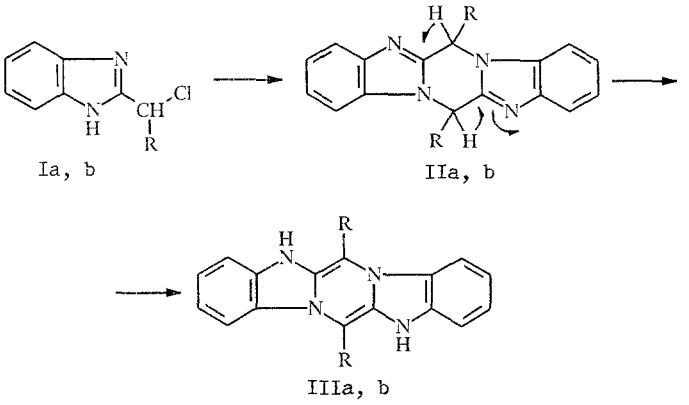
CONVERSIONS OF 2-α-CHLOROALKYLBENZIMIDAZOLES

I. I. Popov

Upon interaction with caustic in a DMSO medium, 2-chloromethylbenzimidazoles are subjected to cyclodimerization, forming 5H,12H-pyrazino[1,2-a:4,5-a']bis-benzimidazoles; in the presence of nucleophiles (ammonia, amines, anions of β-diketones), under the indicated conditions, the products are the corresponding substituted amines or derivatives of pyrrolo[1,2-a]benzimidazole.

Treatment of 2-α-chloromethylbenzimidazole (Ia) with sodium ethylate gives the dihydropyrazine derivative IIa, but treatment of 2-α-chloroethylbenzimidazole (Ib) with a sodium carbonate solution gives a low-molecular-weight polymer [1, 2].

It has been established that the dehydrochlorination of compounds Ia,b in a two-phase aqueous system (saturated sodium or potassium carbonate solution, DMSO, triethylbenzylammonium chloride) at 20°C affords derivatives of 5H,12H-pyrazino[1, 2-a:4,5-a']bis-benzimidazole IIIa,b.



I-IIIa R=H, b R=Me

In the PMR spectrum of the product from dehydrochlorination of compound Ia, there are no signals of methylene protons; this is evidence in favor of the aromatic structure of the tautomer IIIa. In the PMR spectrum of compound IIIb there are singlets of methyl-group protons but no signals of methine or methylene protons that are characteristic for the tautomer IIb or for the polymer. The formation, in our case, of 6,13-dimethyl-5H,12H-pyrazino[1,2-a:4,5-a']bis-benzimidazole (IIIb) instead of 2-vinylbenzimidazole, in contrast to the dehydrobromination of 2-β-bromoethylbenzimidazole [3], is unusual in the series of hetaryl-substituted chloroalkanes.

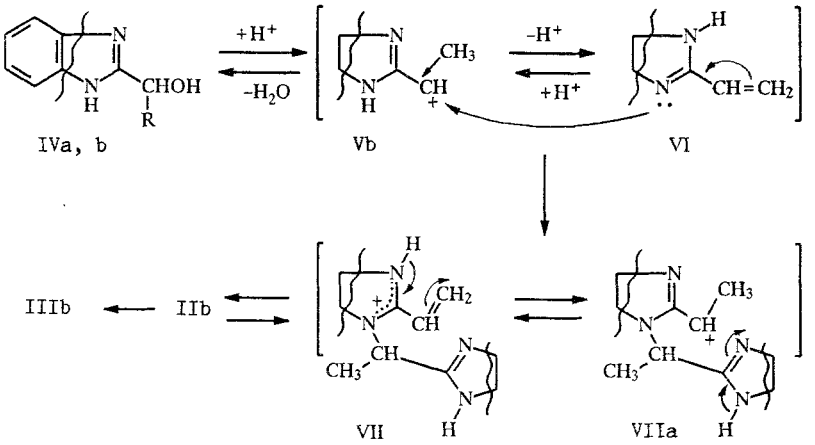
It is curious that compound IIIb is formed instead of the 2-vinylbenzimidazole (VI) upon dehydration of 2-α-hydroxyethylbenzimidazole (IVb) in polyphosphoric or sulfuric acid. Only in the initial stage of dehydration of the carbinol IVb in PPA do we find traces of compound VI, and even these disappear in the concluding stage of the reaction. In a control experiment, it was established that 2-vinylbenzimidazole [4] is subjected to cyclodimerization by PPA, forming the pyrazine derivative IIIb.

Since 2-hydroxymethylbenzimidazole (IVa) is not subjected to cyclodimerization under analogous conditions, we have no grounds for believing that the pyrazine derivative IIIb is formed solely as the result of cyclodimerization of the carbocation Vb. Apparently, the 2-vinylbenzimidazole (VI) that is initially formed as a result of hydration is subject, under the conditions

Rostov State University, Rostov-on-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 664-672, May, 1993. Original article submitted January 6, 1991.

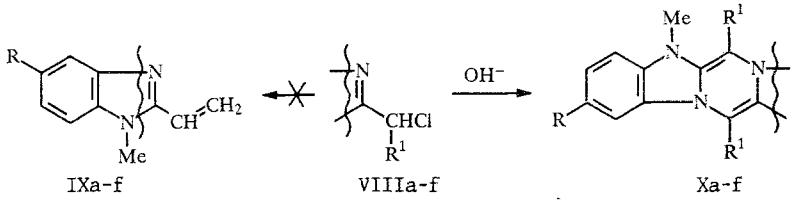
0009-3122/93/2905-0567$12.50

of the reaction, to attack by the carbocation Vb to form the mesomeric cation VII, intramolecular cyclization of which leads to the derivative IIb, which is converted to the tautomer IIIb.



This conversion is probably due to the influence of the +I effect of the methyl group, favoring stabilization of the cation Vb. The carbinol IVa is inert under analogous conditions: Apparently, formation of the less stable carbocation Va in this case is hindered, since the reaction of 2-aminomethylbenzimidazole with nitrous acid in a solution of orthophosphoric acid, which obviously proceeds through the corresponding diazonium salt and the carbocation Va, ultimately leads to the pyrazine derivative IIIa. At the same time, it is known that dihydropyrazine derivatives are formed as a by-product in the hydroxymethylation of 2,4(5)-dialkylimidazoles [5].

Cyclocondensation under the influence of caustic to form pyrazine derivatives is characteristic for 2-benzimidazolyl-α-chloroalkanes. For example, upon dehydrochlorination of the 1-methyl-2-α-chloroethylbenzimidazoles VIIId-f in a two-phase aqueous system (40-50% NaOH, DMSO, TEBAC [triethylbenzylammonium chloride]), instead of 1-methyl-2-vinyl-benzimidazoles IXd-f [4] we obtained 5,6,12,13-tetramethyl derivatives of pyrazino[1,2-a:4,5-a']bis-benzimidazoles Xd-f.



VIII—X a R=R^1=H, b R=Me, R^1=H, c R=OMe, R^1=H, d R=H, R^1=Me, e R=R^1=Me, f R=OMe, R^1=Me, VIIIg R=NO$_2$, R^1=H; VIIIh R=NO$_2$, R^1=Me

Under analogous conditions, the 1-methyl-2-chloromethylbenzimidazoles VIIIa-c, under the influence of caustic, form 5,12-dimethyl derivatives of pyrazine Xa-c. 5-Nitro-1-methyl-2-benzimidazolylchloroalkanes VIIIg,h break down when exposed to caustic under conditions of interfacial catalysis.

Compounds Xa-f form stable crystal hydrates; this was confirmed by determinations of water of crystallization by the Fischer method. In the mass spectrum of compound Xa, the signals m/e 389 (0.06) $[M + 1]^+$ and m/e 387 (0.04) $[M - 1]^+$ are low in intensity. The most intense signals are those of the ions of 1,2-dimethylbenzimidazole m/e 146, its methylated form m/e 161, its protonated form m/e 147, and its deprotonated form m/e 145, as well as the fragment ion m/e 131, which should be assigned to the mesomeric cation XI.

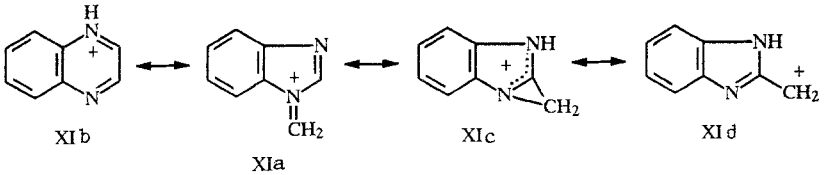


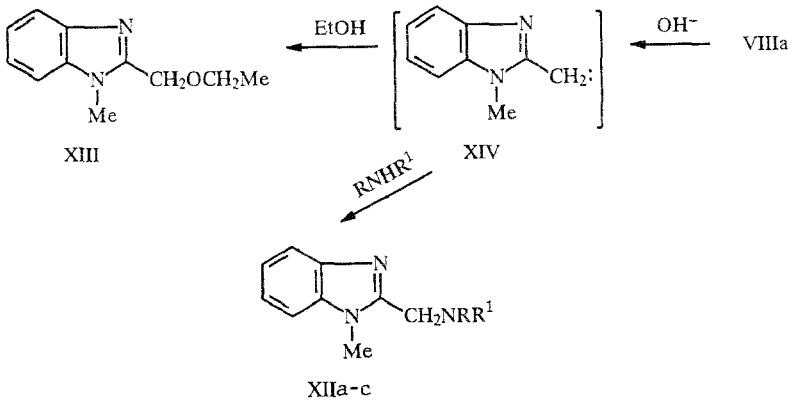
TABLE 1. Characteristics of Compounds Xa-f, XIIa,c, and XIXa-c

Compound	Empirical formula	mp, °C*	PMR spectrum, δ, ppm			Yield, %
			Ar–H	N–CH_3	other signals	
Xa	$C_{18}H_{16}N_4 \cdot H_2O$	188	7,3 (10H, m)	3,7 (6H, s)		91
Xb	$C_{20}H_{20}N_4 \cdot 2H_2O$	138...140	7,1 (8H, m)	3,7 (6H, m)	2,2 (6H, s, Ar—CH_3)	88
Xc	$C_{20}H_{20}N_4O_2 \cdot H_2O$	180...181	7,0 (8H, m)	3,6 (6H, s)	3,5 (6H, s, Ar—OCH_3)	86
Xd	$C_{20}H_{20}N_4 \cdot H_2O$	98	7,3 (8H, m)	3,7 (6H, s)	1,4 (6H, s, $C_{6,13}$—CH_3)	76
Xe	$C_{22}H_{24}N_4 \cdot H_2O$	152	7,05 (6H, m)	4,0 (6H, s)	2,45 (6H, s, $C_{7,9}$—CH_3); 1,7 (6H, s., $C_{6,13}$—CH_3)	78
Xf	$C_{22}H_{24}N_4O_2 \cdot 1,5H_2O$	90...92	7,0 (6H, m)	3,7 (6H, s)	3,6 (6H, s, Ar—OCH_3); 1,4 (6H, s, $C_{6,13}$—CH_3)	79
XIIa**	$C_{11}H_{15}N_3$	70	7,0 (4H, m)	3,5 (3H, s)	3,3 (3H, s, CH_2); 2,1 (6H,s, NMe_2)	91
XIIc	$C_{18}H_{19}N_5$	113...114	7,35 (8H, m)	3,65 (6H, s)	5,1 (4H,s, CH_2)	51
XIXa	$C_{13}H_{12}N_2O \cdot H_2O$	192...193	7,25 (4H, m)		3,4 (1H, d, H-C_1); 2,1 (3H,s, CH_3); 1,9 (3H,s, $COCH_3$)	80
XIXb	$C_{18}H_{14}N_2O$	230	7,5...7,1 (10H, m)		3,3 (3H, s, CH_3)	55
XIXc	$C_{19}H_{16}N_2O$	110	7,5...7,1 (10H, m	3,7 (3H, s)	3,3 (3H, s, CH_3)	50

*Solvent for crystallization: Xa dioxane; Xb-f, XIIc, and XIXc aqueous alcohol; XIIa CCl_4; XIXa alcohol; XIXb DMF.

**PMR spectra were taken in CCl_4.

By the action of caustic on compound VIIIa under conditions of interfacial catalysis in a DMF or alcohol medium, instead of the pyrazine derivative Xa, the respective products are the amine XIIa [6] or the ether XIII. In the latter case, it appeared more probable that the carbinol IVa is formed as a result of hydrolysis of the chloroalkane in an aqueous-alcoholic caustic medium.



XIIa R=R^1=Me, b R=R^1=H; c R=H, R^1=1-Methyl-2-benzimidazolylmethyl

It was also estabished that compound VIIIa does not react with concentrated aqueous ammonia when held at room temperature for an extended period. However, when a small quantity of 40% NaOH is added to this reaction mixture under the same conditions, the reaction is completed in four days, with the formation of the amine XIIb [7] and traces of bis(1-methyl-2-benzimidazolylmethyl)amine (XIIc). Obviously, this conversion of compound VIIIa with ammonia in the presence of caustic suggests the intermediate formation of the carbene XIV.

TABLE 2. Mass Spectra of Compounds Xa and XIXa-c*

Compound	m/z (and I_{rel}, %)
Xa	307 (27), 161 (35), 147 (12), 146 (100), 145 (23), 131 (31)
XIXa	212 (7), 187 (100), 169 (10), 159 (6), 149 (51), 145 (29), 144 (9), 143 (9), 132 (5), 131 (8), 118 (5)
XIXb	265 (9), 264 (9), 235 (5), 160 (14), 159 (100), 145 (6), 105 (11), 77 (24)
XIXc	250 (7), 222 (3), 221 (3), 146 (11), 145 (100), 131 (3), 118 (2), 105 (9)

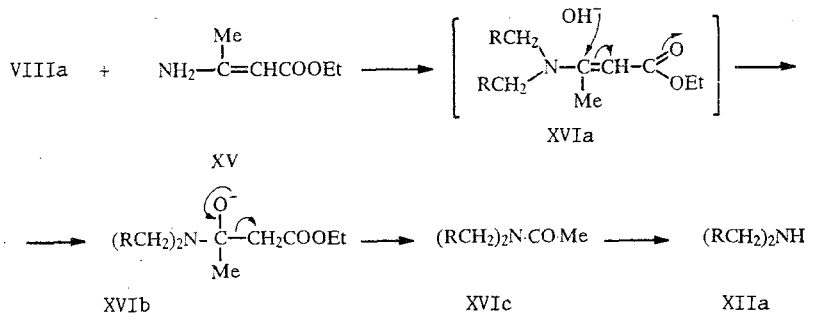
*Ion peaks with intensity >5% of the maximum are listed.

The amine XIIb was also obtained with a good yield upon addition of formalin to a suspension of compound VIIIa in 40% NaOH; in this case, the exothermic reaction is completed in a matter of a few minutes.

In the PMR spectra of compounds XIIa and XIII, along with the signals of the N-methyl groups (3H, s, 3.3 and 3.5 ppm) and methylene groups (2H, s, 3.5 and 4.5 ppm) of the benzimidazole fragment, signals are observed from the dimethylamino group (6H, s, 2.1 ppm) and the ethyl group (2H, m, 3.3 ppm; and 3H, t, 1.05 ppm).

Thus, analysis of these conversions of compound VIIIa with nucleophilic reagents shows that when it interacts with caustic, the first step is apparently generation of the carbene XIV, which is then rapidly captured by the nucleophile (for example, dimethylamine formed by hydrolysis of DMF, or the ethylate anion). If there is no strong nucleophile in the reaction medium, the carbene XIV undergoes cyclodimerization, forming the pyrazine derivative Xa. The fact that compound VIIIa, at 20°C, reacts with aqueous ammonia only when caustic is present can be regarded as unambiguous evidence in favor of the hypothesis of intermediate formation of the carbene XIV and its participation in these conversions.

Compound VIIIa under conditions of interfacial catalysis, even when the temperature is raised to 60-70°C, does not react with weak nucleophiles such as anthranilic acid or its methyl or ethyl esters. In this case, the reaction process is concluded with the formation of the product of a competing reaction — the pyrazine derivative Xa. Along with this, interaction of compound VIIIa with β-aminoethyl crotonate (XV) under these conditions gives an unexpected product: bis(1-methyl-2-benzimidazolylmethyl)amine (XIIc). The intermediate product in this reaction is apparently the amino ester XVIa, which undergoes cleavage in an alkaline medium.



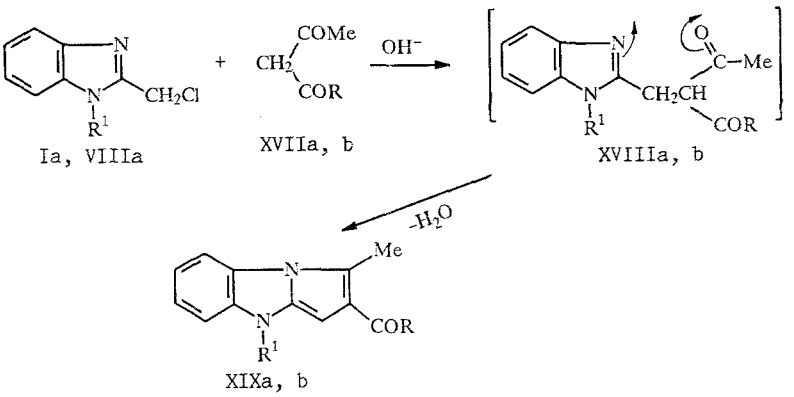
The formation of the intermediate reaction products XVIa-c is confirmed by the observation of absorption bands in the IR spectrum of the unpurified amine XIIc corresponding to ester groups (1770 cm^{-1}) and amide groups (1670 cm^{-1}). Compound XIIc was obtained by countersynthesis from ammonia and compound VIIIa, under the above-indicated conditions of interfacial catalysis.

Analogous to compound VIIIa, the amino ester XV reacts with benzyl chloride, forming dibenzylamine.

The hypothetical carbene XIV does not react with unsaturated compounds such as styrene and phenylacetylene, rather being subjected to cyclodimerization to form the pyrazine Xa, apparently because of the greater accessibility of the free pair

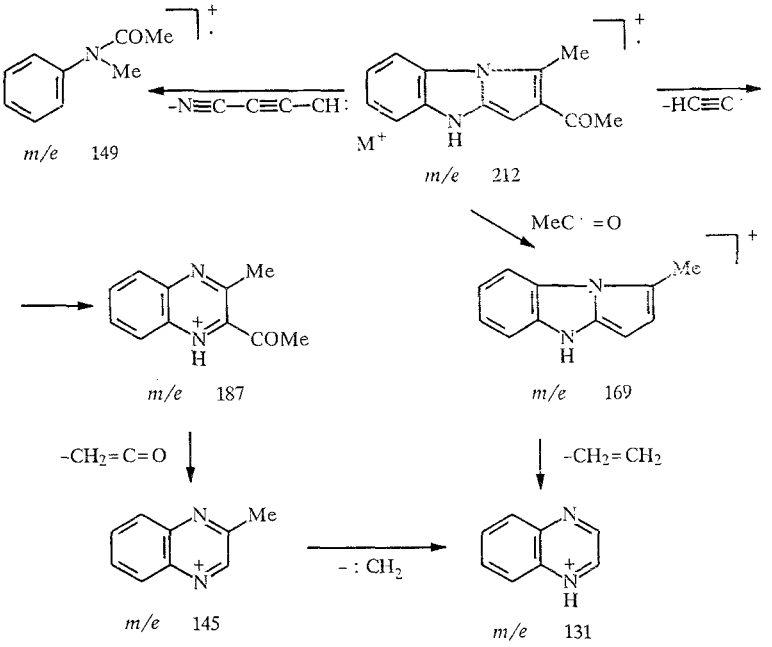
of electrons of the N atom of the nonbonding MO of the benzimidazole ring for the carbene XIV in comparison with the π-electrons of the HUMO of unsaturated compounds (compare [8]).

At the same time, the electron pair of the nonbonding MO of anions of C–H acids can be captured by the carbene XIV. Thus, compound VIIIa reacts with benzoylacetone (XVIIb), and compound Ia reacts with the β-diketones XVIIa,b under conditions of interfacial catalysis, apparently forming at first the monosubstituted derivatives of β-diketones XVIIIa-c, intramolecular cyclization of which leads to derivatives of 3-methylpyrrolo[1,2-a]benzimidazole XIXa-c.



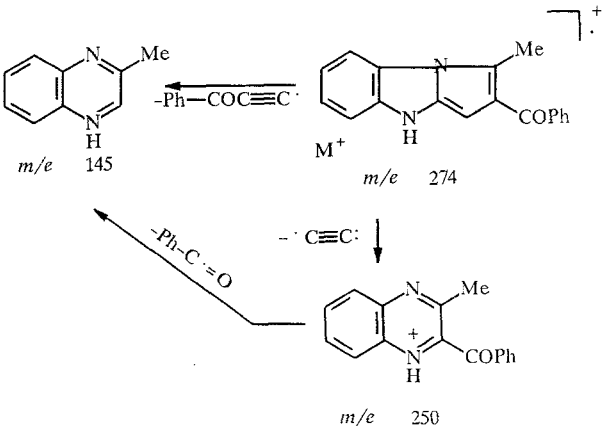
XVIIa R=Me, b R=Ph; XVIII—XIXa R^1=H, R=Me; b R^1=H, R=Ph, c R^1=Me, R=Ph

In the IR spectrum of compound XIXa there is an absorption band of the acetyl group (1712 cm^{-1}), and in the PMR spectrum there are signals at 2.1 ppm (3H, s, CH_3) and 1.9 ppm (3H, s, $COCH_3$). In the mass spectrum of this compound there is a rather intense peak of the molecular ion M^+ 212. The signal that is observed from the fragment ion m/e 63 (3) suggests that the formation of the ion m/e 149 is due to the loss of nitriloethynylcarbene. Loss of acetyl fragments obviously leads to the ion m/e 169; and loss of acetylene, ketene, and carbene fragments leads to the formation of fragment ions of quinoxaline derivatives, m/e 187, 145, and 131, respectively.

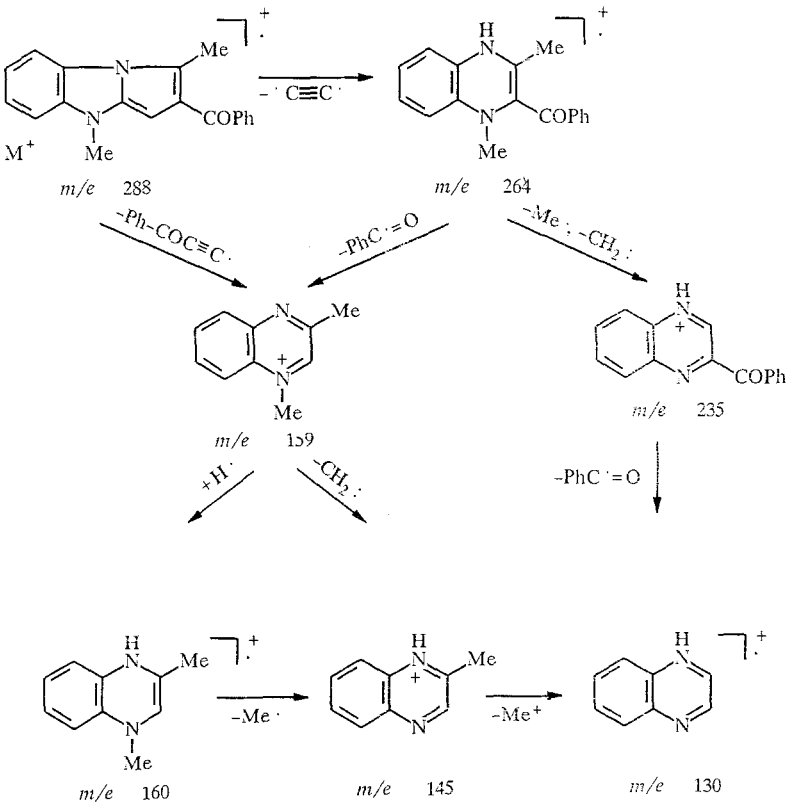


In the IR spectra of the benzoylacetone derivatives XIXb,c there are absorption bands corresponding to the benzoyl group (1675 and 1678 cm^{-1}, respectively); in the PMR spectrum there are signals at 3.3 ppm (3H, s, CH_3) and 3.7 ppm (3H, s, NCH_3).

Compounds XIXb,c, in comparison with the acetylacetone derivative XIXa, were found to be less stable under electron impact. The origin of the fragment ions m/e 250 and 145 in the mass spectrum of compound XIXb should apparently be attributed to loss of acetylene and benzoyl, or benzoylacetylene:



The molecular ion of compound XIXc apparently breaks down in a similar manner.



EXPERIMENTAL

The IR spectra were recorded in a UR-20 instrument, in white mineral oil; the PMR spectra were recorded in a Tesla BS-487 C instrument (80 MHz), in CF_3COOH or CCl_4 (internal standard HMDS). The mass spectra were obtained in an MAT-311A spectrometer with direct introduction of the sample into the ion source. The accelerating voltage was 3.0 kV, ionizing voltage 70 eV, cathode emission current 1.0 mA, ionization chamber temperature 150°C.

The chromatography was performed on Al_2O_3 (Stage III activity on the Brockman scale). The physicochemical characteristics and the parameters of the PMR spectra of the compounds that we obtained are listed in Table 1.

The results of elemental analyses for C, H, and N were in agreement with the experimental values.

5H,12H-Pyrazino[1,2-a:4,5-a']bis-benzimidazole (IIIa). A. To a mixture of 10 g (0.06 mole) of compound Ia in 10 ml of acetone and 10 ml of DMSO, 30 ml of a saturated solution of sodium or potassium carbonate (or 4 g of NaOH in 1 ml of water) and 0.3 g of triethylbenzylammonium chloride were added, and the mixture was stirred until the exothermic reaction had been completed, after which it was treated with excess dilute HCl until the precipitate was dissolved. The reaction mixture was then shaken with activated carbon and filtered; the filtrate was neutralized with ammonia, and the resulting precipitate was filtered off and crystallized from DMF or acetic acid: mp 296-298°C (300°C according to [1]). PMR spectrum: 7.55, m (10 H, arom). Yield of compound IIIa 7.5 g (96%).

B. To a solution of 2.2 g (0.015 mole) of 2-aminomethylbenzimidazole in 4 ml of 87% orthophosphoric acid, at 0°C with stirring, 0.7 g of sodium nitrite in 2 ml of water was added over the course of 10 min. The thickened reaction mixture was allowed to stand overnight and then diluted with 5 ml of water, neutralized with 10% KOH, and heated on a water bath at 80°C until the intense evolution of gas had ended. After cooling, the precipitated compound IIIa was filtered off. Yield 1.0 g (90%).

6,13-Dimethyl-5H,12H-pyrazino[1,2-a:4,5-a']bis-benzimidazole (IIIb, $C_{18}H_{16}N_4$). A. This compound was obtained in the same manner as IIIa (variant A); mp 155°C. PMR spectrum: 7.6 (8H, m, arom), 2.85 (3H, s, CH_3), 2.8 (3H, s, CH_3). Yield 93%.

B. A mixture of 1.62 g (0.01 mole) of 2-α-hydroxyethylbenzimidazole and 10 g of polyphosphoric acid was heated slowly to 160°C, where it was held for 40 min. Gas evolution began at 140°C. In a sample taken at this time, we found traces of 2-vinylbenzimidazole (TLC on aluminum oxide in chloroform). After cooling, the reaction mixture was diluted with water and neutralized with dilute KOH; the resulting precipitate was filtered off and purified by reprecipitation from a hydrochloric acid solution. Yield of compound IIIb 0.65 g (45%).

Upon heating 1.62 g (0.01 mole) of the carbinol IVb with 5 ml of concentrated sulfuric acid for 48 h at 100°C, 1.1 g (76%) of compound IIIb was obtained.

C. A mixture of 0.144 g (1 mmole) of 2-vinylbenzimidazole and 5 ml of polyphosphoric acid was heated for 6 h at 175°C. Under these conditions, compound VI forms a "knot" (aggregate) that is difficultly soluble in polyphosphoric acid. After completion of the reaction, the mixture was dissolved in 100 ml of water and neutralized with 10% NaOH, and the precipitate was filtered off. Yield of compound IIIb 0.12 g (83%).

5,12-Dimethylpyrazino[1,2-a:4,5-a']bis-benzimidazoles (Xa-f). To a solution of 3 g of NaOH in 3 ml of water, 0.03 mole of 1-methyl-2-α-hydroxyalkybenzimidazole VIIIa-f [4] was added, along with 3 ml of DMSO and 0.1 g of triethylbenzylammonium chloride; the reaction mixture was stirred 3 h until the reaction was completed (monitored by TLC on aluminum oxide in chloroform). The reaction mixture was then treated with 10% HCl, after which the precipitated hydrochloride of compound Xa was filtered off, suspended in water, and neutralized with ammonia; the crystals were then transferred to a filter. Compounds Xb-f remained in the hydrochloric acid solution; when this was neutralized, oily substances separated out; they were extracted with chloroform and chromatographed on aluminum oxide (eluent 2:1 ether–chloroform).

1-Methyl-2-dimethylaminomethylbenzimidazole (XIIa) and 1-Methyl-2-ethoxymethylbenzimidazole (XIII). These compounds were synthesized under conditions analogous to those described above for compounds Xa-f, except that the DMSO was replaced by DMF or ethanol. The reaction mixture was stirred for 3 h and left overnight, after which it was diluted with water. The oily reaction product was extracted with chloroform and chromatographed (in ether) in a column with aluminum oxide, after which the solvent was driven off. The amine XIIa crystallized gradually; mp of dihydrochloride 243-244°C (244°C according to [6]).

The ester XIII remained as a colorless, thick oil, mp of picrate ($C_{11}H_{14}N_2O \cdot C_6H_3N_3O_7$) 215°C. PMR spectrum in CCl_4: 7.05 (4H, m arom), 4.5 (2H, s, CH_2O), 3.5 (3H, s, NCH_3), 3.3 (2H, q, OCH_2), 1.05 ppm (3H, t, CH_3). Yield of ester XIII 78%.

Interaction of 1-Methyl-2-chloromethylbenzimidazole (VIIIa) with Formamide and Ammonia. A. To 3 ml of 40% NaOH, 1.8 g (0.01 mole) of compound VIIIa and 2 ml of formamide were added while cooling with water. The mixture was stirred for 3 h and allowed to stand overnight, after which it was diluted with water. The resulting precipitate was filtered off and reprecipitated from dilute HCl. Yield of 1-methyl-2-aminomethylbenzimidazole XIIb 1.15 g (71%).

B. The reaction was carried out in the same manner as described for **A**, using 3 ml of a saturated sodium carbonate solution, 1.5 g of NaOH, 2 ml of concentrated NH_4OH, 2 ml of formamide, and 2 ml of dioxane. Yield of amine XIIb 1.45 g (90%).

C. The reaction was carried out in the same manner as described for **A**, using 3 g of sodium carbonate, 3 ml of concentrated NH_4OH, and 2 ml of formamide; this mixture was stirred for 2 h. According to TLC on aluminum oxide in chloroform, no observable traces of the amine XIIb had been formed. Then 1.2 g of NaOH was added to the reaction mixture, which was stirred for 3 h, after which the residue of the amine XIIb was precipitated with water: mp 72°C (from water, 72.3-73.5°C according to [7]). PMR spectrum: 7.4 (4H, m, arom), 4.5 (2H, s, CH_2), 3.75 (3H, s, NCH_3). Yield 0.8 g (50%).

Bis(1-methyl-2-benzimidazolylmethyl)amine (XIIa). A. To a solution of 7.5 g of NaOH in 20 ml of water, 6.45 g (0.05 mole) of β-aminoethyl crotonate, 10 ml of DMSO, and 0.2 g of triethylbenzylammonium chloride were added; then 9 g (0.05 mole) of compound VIIIa was added in portions; the reaction mixture was stirred for 1.5 h and heated for 1 h at 70°C, after which it was neutralized with 5% HCl; the resulting precipitate was filtered off. Yield of amine XIIa 3.9 g.

B. The amine XIIc was obtained under analogous conditions by the interaction of 9 g (0.05 mole) of compound VIIIa and 2.7 g (0.05 mole) of ammonium chloride. Yield 2.3 g (30%).

Dibenzylamine. To a solution of 3 g of NaOH in 5 ml of water, 2.6 g (0.02 mole) of β-aminoethyl crotonate, 0.1 g of triethylbenzylammonium chloride, 4 ml of DMSO, and 2.5 g (0.02 mole) of benzyl chloride were added; the reaction mixture was stirred for 1 h. The mixture was then diluted with 15 ml of water and extracted with ether, recovering a product with bp 185°C. Yield of dibenzylamine 1.6 g (43%).

2-Acetyl-3-methylpyrrolo[1,2-a]benzimidazole (XIXa). A. To 5 ml of a saturated sodium acetate solution, while stirring, 0.8 g of NaOH, 3 ml of acetylacetone, 3.3 g (0.02 mole) of compound Ia, and 3 ml of acetone were added. During this time, the reaction mixture was heated up to 60°C. The stirring was continued for 5 h, after which the mixture was allowed to settle, the aqueous layer was decanted, and the residue was transferred to a filter and washed with water. Yield of compound XIXa 4 g (87%).

B. To a saturated solution of 2.2 g of sodium carbonate in water, 3.3 g (0.02 mole) of compound Ia, 0.1 g of triethylbenzylammonium chloride, and 3 ml of dioxane were added while stirring; then, after 15 min, 3 ml of DMSO was added. The reaction mixture was stirred for 3 h and then allowed to settle for 2 h, after which it was acidified with dilute HCl to pH 3 and filtered; the mother solution was neutralized with ammonia, and the precipitate (which appeared to be more pure than that obtained by method A) was filtered off. This product was crystallized from aqueous dioxane or alcohol. IR spectrum: 1712 cm^{-1} (C=O). Yield 3.5 g (76%).

2-Benzoyl-3-methylpyrrolo[1,2-a]benzimidazole (XIXb). To a solution of 4 g of sodium carbonate in 10 ml of water, there were added 10 ml of acetone, 3 ml of DMSO, 0.1 g of triethylbenzylammonium chloride, and 3.2 g (0.02 mole) of benzoylacetone. The mixture was stirred for 0.5 h, after which 3.3 g (0.02 mole) of compound Ia was added, and the stirring was continued for 6 h, after which the reaction mixture was left overnight. Then, 3 ml of 40% NaOH was added while stirring; after 1 h, the precipitate was filtered off and washed with water and alcohol. IR spectrum: 1678 cm^{-1} (C=O), 3000-3200 cm^{-1} (NH, associated). Yield of compound XIXb 3.1 g.

2-Benzoyl-3,9-dimethylpyrrolo[1,2-a]benzimidazole (XIXc). To a solution of 4 g of potassium carbonate and 1.2 g of NaOH in 10 ml of water, 10 ml of acetone, and 3 ml of DMSO, while stirring, 0.1 g of triethylbenzylammonium chloride, 3.2 g (0.02 mole) of the diketone XVIIb, and 3.6 g (0.02 mole) of compound VIIIa were added. The reaction mixture was stirred for 6 h and then left overnight, after which it was acidified with 5% HCl and filtered. The filtrate was neutralized with ammonia, and the resulting precipitate was filtered off. IR spectrum: 1675 cm^{-1} (C=O). Yield of compound XIXc 2.9 g (50%).

REFERENCES

1. H. Scolnic, J. G. Muller, and A. R. Day, *J. Am. Chem. Soc.*, **65**, 1854 (1943).
2. G. B. Bachman and L. V. Heisey, *J. Am. Chem. Soc.*, **71**, 1985 (1949).
3. N. G. Kumar, *J. Polym. Sci. Lett. Ed.*, **11**, 461 (1973).
4. I. I. Popov, V. N. Narezhnaya, and A. A. Zubenko, *Khim. Geterotsikl. Soedin.*, No. 8, 1104 (1978).
5. M. Masui, K. Suda, M. Inone, K. Izukura, and M. Yamauchi, *Chem. Pharm. Bull.*, **22**, 2259 (1974).
6. H. Irving and O. Weber, *J. Chem. Soc.*, 2296 (1959).
7. V. M. Aryuzina and M. N. Shchukina, *Khim. Geterotsikl. Soedin.*, No. 3, 509 (1968).
8. A. E. Vasilevskii, V. M. Shostakovskii, and O. M. Nefedov, *Khim. Geterotsikl. Soedin.*, No. 6, 723 (1982).