ture of diastereomeric amines Va,b, 2.26 g (16 mmole) of benzoyl chloride, and 1.62 g (16 mmole) of triethylamine in 30 ml of benzene was refluxed for 10 h, after which it was extracted with 17% hydrochloric acid. The hydrochloric acid solution was made alkaline with potassium carbonate and extracted with chloroform. The chloroform was removed by distillation, and the residue was recrystallized from ethyl acetate to give 1.85 g (36%) of a mixture of diastereomeric Xa,b with mp 150-151°C. Found: C 74.6; H 7.8; N 8.4%. $C_{21}H_{24}N_2O$. Calculated: C 74.5; H 7.7; N 8.7%.

3-(β-Benzamido-β-phenylethyl)quinuclidines (XIa,b). The reaction with 2 g (8.7 mmole) of the mixture of amines VIa,b, 1.22 g (8.7 mmole) of benzoyl chloride, and 0.88 g (8.7 mmole) of triethylamine in 20 ml of benzene was carried out as described in the preceding experiment. The residue obtained after evaporation of the chloroform extract was dissolved in 10 ml of acetone, and the acetone solution was acidified with an alcohol solution of hydrogen chloride and diluted with ether until it became turbid. The liberated oil was triturated with ether to give 2.3 g (68%) of a mixture of the diastereomeric hydrochlorides of XIa,b with mp 45-47°C (dec.). Found: C 68.2; H 7.3; Cl 9.2%. $C_{22}H_{26}N_2O \cdot HCl \cdot H_2O$. Calculated: C 68.0; H 7.5; Cl 9.1%.

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REACTION OF 1-AMINOBENZIMIDAZOLES WITH β-DIKETONES. SYNTHESIS OF PYRIDAZINO[1,6-a]BENZIMIDAZOLES

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The action of acetyl- and benzoylacetone on 1-aminobenzimidazoles in the presence of catalytic amounts of zinc chloride was used to synthesize 1-ylidene derivatives, which at higher temperatures undergo thermal cyclization to 2,4-disubstituted pyridazino[1,6-a]benzimidazoles.

In contrast to α-amino derivatives of nitrogen heterocycles, the reaction of which with β-dicarbonyl compounds is quite widely known [1], the analogous reactions for N-amines of the azole series have remained almost undescribed [2, 3]. In the present research we investigated the behavior of 1-aminobenzimidazoles with respect to 1,3-diketones.

Considering the fact that 1-aminobenzimidazoles condense with ketones only upon prolonged heating (150-160°C) in the presence of catalytic amounts of zinc chloride [4], the β-diketones were subjected to reaction under similar conditions. We found that, depending on the structure of the starting amines, this reaction has its own peculiarities. Thus 1-amino- (Ia) and 1-amino-2-methylbenzimidazole (Ib) react with acetylacetone to give ketimines IIa,b. Under the same conditions 1-amino-5,6-dimethylbenzimidazole (Ic) undergoes cyclization to py-

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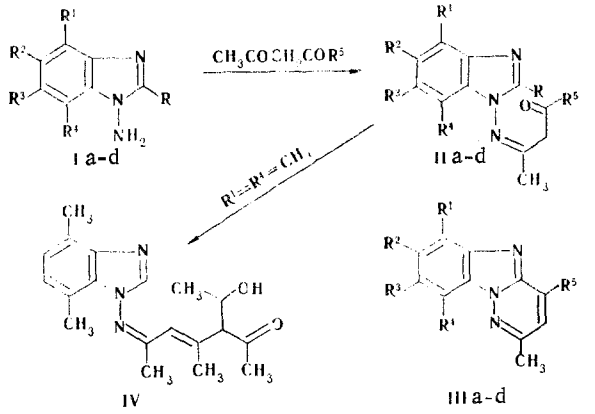
ridazinobenzimidazole IIIb in high yield. 1-Amino-4,7-dimethylbenzimidazole (Id) gives IV, which judging from the analytical and spectral data, is the product of crotonic condensation of the initially formed ketimine of the II type with a second molecule of the diketone. The PMR spectrum of IV contains five types of methyl groups, a methylidyne proton at 4.3 ppm, four aromatic protons, and a broad signal of an OH group at 11.75 ppm, which vanishes after deuteration.



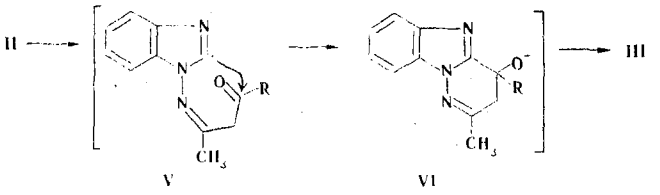
I a $R=R^1=R^2=R^3=R^4=H$, $R^5=CH_3$; b $R^1=R^2=R^3=R^4=H$, $R=R^5=CH_3$; c $R=R^1=R^4=H$, $R^2=R^3=R^5=CH_3$; d $R=R^2=R^3=H$, $R^1=R^4=R^5=CH_3$; II a $R=R^1=R^2=R^3=R^4=H$, $R^5=CH_3$; b $R^1=R^2=R^3=R^4=H$, $R=R^5=CH_3$; c $R=R^1=R^2=R^3=R^4=H$, $R^5=C_6H_5$; d $R=R^1=R^4=H$, $R^2=R^3=CH_3$, $R^5=C_6H_5$; III a $R^1=R^2=R^3=R^4=H$, $R^5=CH_3$; b $R^1=R^4=H$, $R^2=R^3=R^5=CH_3$; c $R^1=R^2=R^3=R^4=H$, $R^5=C_6H_5$; d $R^1=R^4=H$, $R^2=R^3=CH_3$, $R^5=C_6H_5$

In addition to ketimines IIc,d, N-aminobenzimidazole Ia and its 5,6-dimethyl derivative Ic form pyridazinobenzimidazoles IIIc,d with benzoylacetone. Although a mixture of isomeric ketimines (at the acetyl and benzoyl carbonyl groups) could be formed in this case, we obtained only one compound, the individuality of which was proved by the PMR spectrum. On the basis of the inertness of 1-aminobenzimidazole with respect to dibenzoylmethane structure IIc was assigned to the reaction product.

A complex mixture of transformation products, which we were unable to separate, is formed in the reaction of amines I with acetoacetic ester.

Ketimines II are low-melting readily hydrolyzed compounds. According to the data from the PMR spectra under neutral conditions, they exist primarily in the keto form, as evidenced by the signals of two methylene protons at 4.45-4.53 ppm; the presence of intense bands of carbonyl absorption at 1680-1700 cm^{-1} in their IR spectra is also in agreement with this. In an acidic medium (CF_3COOH) the equilibrium is shifted completely to favor the enol form, as indicated by the disappearance of the signal of methylene protons and the appearance of an additional proton in the aromatic region.

Heating ketimines IIa,c,d in the presence of zinc chloride at 200-220°C for 2 h leads to intramolecular cyclization to pyridazinobenzimidazoles IIIa,c,d. The characteristic signal at 8.5-9.0 ppm of the proton attached to the meso carbon atom of the benzimidazolium cation [5] is not observed in the PMR spectrum of IIIa (in CF_3COOH). The multiplet with an intensity of one proton unit at δ 7.95 ppm was assigned to the 9-H proton, the shift of which to weakest field can be explained by the peri-anisotropic effect of the unshared pair of electrons of the adjacent pyridine nitrogen atom (compare with other angular heterocycles [6]). In the simple PMR spectrum of the pyridazinobenzimidazolium cation of IIIb obtained from acetyl acetone and 5,6-dimethyl derivative IC the signal of the 9-H proton appears in the form of a singlet at 7.73 ppm. These data, as well as the inertness of 2-methyl-substituted ketimine IIb with respect to cyclization to a pyridazinobenzimidazole, constitute evidence that the formation of a new ring does not take place in the 7 position, as one might have expected in conformity with the electron density distribution in the benzimidazole molecule, but rather at the $C_{(2)}$ atom, where, as is well known, significant positive charge is concentrated [7]. This reaction pathway is probably due to the same reasons as in the case of the formation of pyrido[1,2-a]benzimidazoles from N-amines I and ketones under the conditions of the Fischer reaction [4], viz., initial coordination of zinc chloride with the pyridine nitrogen atom, which increases the CH acidity of the C–H bond at the meso carbon atom, which in turn favors the formation of an ylid of the V type.



V VI

The inertness of 1-amino-4,7-dimethylbenzimidazole with respect to cyclization to the corresponding pyridazinobenzimidazole is associated, in our opinion, primarily with steric hindrance created by the methyl group in the 7 position, inasmuch as the electronic effect of two methyl groups in this case is comparable to that for the readily cyclized 5,6-dimethyl derivative. When there is a substituent in the 7 position, the C–N=N angle may evidently be distorted as compared with the optimal value of 109°, which leads to separation of the reaction centers (the C=O group and the μ-carbon atom) and creates additional hindrance to realization of a coplanar structure in transition state VI. We also observed the shielding effect of the methyl group in the 7 position in the N-amination of 4,7-dimethylbenzimidazole with hydroxylaminesulfonic acid (HASA), which, as compared with the 5,6-dimethyl derivative, proceeds quite sluggishly.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform were recorded with a UR-20 spectrometer. The PMR spectra were obtained with a Tesla BS-467 spectrometer with hexamethyldisiloxane as the internal standard.

1-Amino-4,7-dimethylbenzimidazole (Id). A neutralized (with $NaHCO_3$) solution of 20 g (0.16 mole) of HASA in 30 ml of water was added to a heated (to 70°C) solution of 5.0 g (0.034 mole) of 4,7-dimethylbenzimidazole and 40 g (0.57 mole) of 85% KOH in 300 ml of water and 30 ml of alcohol. After 15 min, a solution of 10 g (0.08 mole) of HASA in 15 ml of water was added, and the mixture was heated at 70°C for 1 h. It was then cooled and filtered to give 1.5 g of amine Id. An additional 2.0 g of the amine was extracted from the filtrate with chloroform. The yield of Id was 3.5 g (60%). The slightly brown crystals had mp 111-112°C (from benzene). IR spectrum: 1630 (C=N); 3387, 3310 cm^{-1} (NH_2). PMR spectrum (d_6-DMSO): 2.4 (3H, s, 4-CH_3), 2.65 (3H, s, 7-CH_3), 6.2 (2H, s, NH_2), 6.75 (2H, S, 5-H and 6-H), and 7.85 ppm (1H, s, 2-H). Found: C 63.3; H 7.0; N 24.7%. $C_9H_{11}N_3 \cdot 1/2H\ O$. Calculated: C 63.5; H 7.1; N 24.7%.

1-(Acetylisopropylidene)aminobenzimidazole (IIa). A mixture of 1.33 g (0.01 mole) of 1-aminobenzimidazole, 2.5 ml (0.025 mole) of acetylacetone, and catalytic amounts of anhydrous zinc chloride was stirred at 150-160°C for 2 h. It was then cooled and treated with 8 ml of 57% $HClO_4$ and 10 ml of water, and the precipitated perchlorate was removed by filtration and washed with water. Treatment with 22% NH_4OH gave 1.35 g (63%) of the desired product in the form of colorless needles with mp 101-102°C (from heptane). IR spectrum: 1625 (C=N); 1682 (C=O); 3380, 3480 cm^{-1} (H_2O). PMR spectrum (C_6F_6): 2.38 (6H, s, 1',4'-CH_3), 4.53 (2H, s, 2',2'-H), 6.73 (2H, m, 4-H and 5-H), 7.09 (2H, m, 6-H, 7-H), and 8.08 ppm (1H, s, 2-H); (in CF_3COOH): 2.2 (3H, s, 4'-CH_3), 2.25 (3H, s, 1'-CH_3), 7.28 (5H, m, 4–7-H and 2'-H), and 8.33 ppm (1H, s, 2-H). Found: C 67.1; H 6.3; N 19.5%. $C_{12}H_{13}N_3O$. Calculated: C 67.0; H 6.0; N 19.5%.

1-(Acetylisopropylidene)amino-2-methylbenzimidazole (IIb). A mixture of 1.47 g (0.01 mole) of 1-amino-2-methylbenzimidazole and a few crystals of zinc chloride in 3 ml of acetylacetone was heated at 170-180°C for 3 h. The solid material dissolved completely after 1 h. The solution was cooled and treated with 20 ml of 10% NaOH, and the mixture was extracted with chloroform and purified by chromatography with a column filled with Al_2O_3 (elution with chloroform). Workup of the first fraction give 1.7 g (74%) of colorless crystals with mp 101-102°C (from benzene with hexane). IR spectrum: 1585 (C=N), 1635 (C=O), and 2800-3500 cm^{-1} (chelated OH). PMR spectrum (CCl_4): 1.53 (3H, s, 4'-CH_3), 1.88 (3H, s, 1'-CH_3), 2.35 (3H, s, 2-CH_3), 5.15 (1H, s, –CH=), 7.05 (3H, m, 4–6-H), 7.45 (1H, m, 7-H), and 12.05 ppm (1H, s, OH).

1-(1',3'-Dimethyl-4',4'-diacetylbutylen-2'-ylidene)amino-4,7-dimethylbenzimidazole (IV). A mixture of 0.5 g (3.1 mmole) of amine Id and catalytic amounts of zinc chloride in 2 ml of acetylacetone was heated at 160°C for 3 h, after which the product was isolated and purified as in the preparation of IIb. This procedure gave 0.6 g (60%) of colorless prisms with mp 130-131°C (from hexane). IR spectrum: 1570 (C=C), 1610 (C=N), and 1680 cm^{-1} (C=O). PMR spectrum (CCl_4): 1.4 (3H, s, 3'-CH_3), 1.75 (3H, s, 1'-CH_3), 2.1 (3H, s, 4-CH_3), 2.2 (6H, s,

4',4'-$COCH_3$), 2.33 (3H, s, 7-CH_3), 4.8 (1H, s, 2'-H), 7.1 (2H, s, 5- and 6-H), 7.75 (1H, s, 2-H), and 11.75 ppm (1H, m, OH). Found: 69.7; H 7.2; N 12.9%. $C_{19}H_{23}N_3O_2$. Calculated: C 70.2; H 7.1; N 12.9%.

2,4-Dimethylpyridazino[1,6-a]benzimidazole (IIIa). A mixture of 6.65 g (0.05 mole) of Ia, 5.5 g (0.055 mole) of acetylacetone, and 0.5 g of zinc chloride was heated with stirring at 150-160°C for 50 min, after which 13.6 g (0.01 mole) of $ZnCl_2$ was added, and the mixture was heated at 200-220°C for another 2.5 h. It was then cooled, and the melt was triturated and treated with hot 30-40% NaOH. The reaction product was extracted with chloroform (three 40-ml portions), and the solvent was removed by distillation. The residue was treated with 10 ml of 57% $HClO_4$ and 10 ml of water, and the precipitated perchlorate was separated and washed with water and ethyl acetate. Treatment of the perchlorate with 22% NH_4OH gave 5.1 g (52%) of colorless needles of pyridazinobenzimidazole IIIa with mp 149-150°C (from isooctane). IR spectrum: 1570 cm^{-1} (C=N). PMR spectrum (CF_3COOH): 2.4 (6H, s, 2-CH_3 and 4-CH_3), 7.3 (1H, s, 3-H), 7.45 (3H, m, 5-7-H), and 7.95 ppm (1H, m, 9-H).

2,4,7,8-Tetramethylpyridazino[1,6-a]benzimidazole (IIIb). A mixture of 1.6 g (0.01 mole) of amine Ic and catalytic amounts of $ZnCl_2$ in 2.5 ml of acetylacetone was stirred at 150-160°C for 1.5 h, after which it was cooled and treated with 7 ml of 57% $HClO_4$ and 20 ml of water. The precipitated perchlorate was removed by filtration and treated with excess 22% NH_4OH, and the base was dissolved in chloroform and purified with a column filled with Al_2O_3 (chloroform). The yield of IIIb was 1.4 g (90% based on the unchanged benzimidazole, 0.5 g of which was isolated from the perchloric acid filtrate by neutralization with ammonia). The colorless prisms had mp 212-213°C (from alcohol). IR spectrum: 1570 cm^{-1} (C=N). PMR spectrum (CF_3COOH): 2.1 (6H, s, 7- and 8-CH_3), 2.35 (6H, s, 2- and 4-CH_3), 7.2 (2H, s, 3- and 6-H), and 7.73 ppm (1H, s, 9-H).

1-(Benzoylisopropylidene)aminobenzimidazole (IIc) and 2-Methyl-4-phenylpyridazine[1,6-a]-benzimidazole (IIIc). A mixture of 1.33 g (0.01 mole) of amine Ia with 1.7 g (0.011 mole) of benzoylacetone and a few crystals of $ZnCl_2$ was heated at 150-160°C for 15 min and at 220°C for 5 min. It was then cooled and treated with 7 ml of 57% $HClO_4$, and the precipitated perchlorate IIIc was removed by filtration, washed with water and ethyl acetate, and crystallized from alcohol to give 0.6 g (19%) of perchlorate IIIc. Treatment with excess 22% NH_4OH gave yellow-green needles of base IIIc with mp 143-144°C (from alcohol). IR spectrum: 1570 cm^{-1} (C=N). PMR spectrum (CF_3COOH): 2.55 (3H, s, 2-CH_3), 7.33 (5H, m, C_6H_5), 7.5 (4H, m, 3-, 5-, 6-, 7-H), and 8.1 ppm (1H, m, 9-H). Found: C 78.7; H 5.1; N 16.1%. $C_{17}H_{13}N_3$. Calculated: C 78.8; H 5.0; N 16.2%.

Removal of the solvent from the alcohol filtrate gave 1.2 g (43%) of perchlorate IIc, the base of which was isolated by treatment with 22% NH_4OH. The colorless prisms had mp 117-118°C (from alcohol). IR spectrum: 1625 (C=N); 1645 (C=O); 3380, 3480 cm^{-1} (H_2O). PMR spectrum ($CDCl_3$): 2.55 (3H, s, 1'-CH), 4.45 (2H, s, 2'-H and 2-H), 6.8 (2H, m, 4-H and 5-H), 7.1 (2H, m, 6-H and 7-H), 7.5 (3H, m, m- and p-H, C_6H_5), 7.75 (2H, m, o-H, C_6H_5), and 7.85 ppm (1H, s, 2-H).

1-(Benzoylisopropylidene)amino-5,6-dimethylbenzimidazole (IId) and 2,7,8-Trimethyl-4-phenylpyridazino[1,6-a]benzimidazole (IIId). A mixture of 1.6 g (0.01 mole) of amine Ic and 1.62 g (0.01 mole) of benzoylacetone with a few crystals of $ZnCl_2$ was heated at 150-160°C for 1.5 h, after which it was cooled, treated with 20 ml of 10% NaOH, and extracted with chloroform. The mixture of substances was separated by chromatography with a column filled Al_2O_3 (elution with benzene). The fraction with R_f 0.55 was collected, and the solvent was removed by distillation to give 0.4 g (14%) of yellow-green prisms of pyridazinobenzimidazole IIId with mp 208-209°C (from butanol). IR spectrum: 1555 cm^{-1} (C=N). PMR spectrum (CF_3-COOH): 2.13 (6H, s, 7- and 8-CH_3), 2.45 (3H, s, 2-CH_3) 7.25 (5H, m, C_6H_5), 7.35 (2H, s, 3- and 6-H), and 7.8 ppm (1H, s, 9-H). Found: C 79.3; H 5.9; N 14.6%. $C_{19}H_{17}N_3$. Calculated: C 79.4; H 5.9; N 14.6%. The fraction with R_f 0.55 was also collected, and ketimine IId was eluted with chloroform and obtained in the form of an oil after removal of the solvent by distillation. Compound IId was converted to the perchlorate, which crystallized from alcohol in the form of cream-colored needles with mp 263-264°C (dec.). IR spectrum (mineral oil): 1605 (C=N); 1645 (C=O); 3132, 3180 cm^{-1}. PMR spectrum (CF_3COOH): 1.98 (6H, s, 7- and 8-CH_3), 2.33 (3H, s, 1'-CH_3), 7.0-7.6 (8H, m, aromatic protons), and 8.18 ppm (1H, s, 2-H). Found: C 56.6; H 5.0; N 10.2%. $C_{19}H_{19}N_3O \cdot HClO_4$. Calculated: C 56.4; H 4.9; N 10.4%.

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BENZIMIDAZOLE REARRANGEMENT OF DIHYDROBENZODIAZEPINES

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The rearrangements of 2,4-diphenyl-2,3-dihydro-1H-1,5-benzodiazepines under the influence of acids, temperature, and electron impact were studied. It is shown that the trend of the process is strictly specific for each case. The mechanism and the factors that regulate the trend of the benzimidazole rearrangement are discussed.

A peculiarity of dihydrobenzodiazepines is the ability to undergo conversion to benzimidazoles [1] both under the influence of acids and at elevated temperatures. Even the addition of catalytic amounts of acids to solutions of dihydrobenzodiazepines gives rise to this rearrangement, the general principle of which consists in retention of the substituent in the 2 position (Table 1). The reaction products are also substituted acetophenones, which were identified by chromatography and by means of 2,4-dinitrophenylhydrazine.

In the present research we studied the behavior of 2,4-diaryl-2,3-dihydro-1H-1,5-benzodiazepines I-XV in acidic media, upon heating, and under the influence of electron impact.

It is known [2, 3] that o-phenylenediamine reacts with aromatic aldehydes to give 2-arylbenzimidazoles (through the corresponding azomethines and benzimidazolines; the addition of hydride-ion acceptors promotes oxidation of the latter). One might have assumed that the rearrangement under discussion proceeds via an intermolecular mechanism that includes hydrolysis of the dihydrobenzodiazepines in acidic media to o-phenylenediamine and chalcones and subsequent reaction of the o-phenylenediamine with the aldehydes that are formed by the retroaldol process that is possible for chalcones [4]. However, this is repudiated experimentally. Thus if stoichiometric amounts of p-nitrobenzaldehyde and one to two drops of concentrated HCl are added successively to a methanol solution of II, the reaction products contain 2-phenylbenzimidazole (XVI) but do not contain even trace amounts of 2-(4-nitrophenyl)benzimidazole. Moreover, XVIII is formed in 60-80% yield in a blank experiment in which o-phenylenediamine is used in place of dihydrodiazepine II. p-Nitrobenzaldehyde is more active than benzaldehyde in reactions to form benzimidazoles [5], and the results therefore constitute evidence for the intramolecular character of the rearrangement.

It is known [6] that the optimum conditions for the synthesis of I-XV involve refluxing of alcohol solutions of o-phenylenediamine with chalcones with the addition of strong organic bases. However, if an acidic catalyst (for example, 10% HCl) is used in place of the base, exclusively benzimidazoles are obtained. However, spectral and chromatographic monitoring

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