extract was dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the residue was chromatographed with a column filled with silica gel [elution with chloroform–carbon tetrachloride (1:2)]. The yields are indicated in Table 1.

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UNUSUAL FISCHER REACTION IN THE 1-AMINOBENZIMIDAZOLE SERIES. SYNTHESIS OF PYRIDO[1,2-a]BENZIMIDAZOLE DERIVATIVES

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UDC 547.785.5'83:542.953.4

The reaction of N-aminobenzimidazoles with ketones under the conditions of the Fischer reaction, as a result of which derivatives of 1,3-disubstituted pyrido-[1,2-a]benzimidazoles are unexpectedly formed, was investigated. The structure of the latter was established on the basis of data from IR, PMR, and mass spectroscopy, as well as by an independent method based on 2-cyanomethylbenzimidazole and β-diketones.

The formal similarity between N,N-disubstituted hydrazines and N-amino derivatives of nitrogen heterocycles compelled us to study the Fischer reaction in the 1-aminobenzimidazole series.

It is known that 1-aminobenzimidazoles (I) readily react with aldehydes to give Schiff bases [1]. At the same time, the corresponding ketimines II cannot be obtained under the ordinary conditions for the synthesis of hydrazones. The latter were isolated only after heating solutions of the starting components in the presence of catalytic amounts of anhydrous zinc chloride with the simultaneous removal of water by distillation and excess ketone. The resulting compounds are quite labile and are readily hydrolyzed not only by dilute mineral acids but also during chromatography on aluminum oxide.

Ammonia is evolved in conformity with the classical scheme of the reaction when ketimines II are heated under the conditions of the Fischer reaction (at 200-250°C with an equivalent amount of $ZnCl_2$). However, judging from the results of elementary analysis, two molecules of the ketone are included in the composition of the resulting III (in 20% yield). The yields of the reaction products increase substantially in the reaction of 1-aminobenzimidazole with excess ketone. We subsequently established that α,β-unsaturated ketones, viz., mesityl oxide and dypnone, react with 1-aminobenzimidazoles similarly but under milder conditons.

Since the formation of indoles via the Fischer route is an electrophilic reaction [2],

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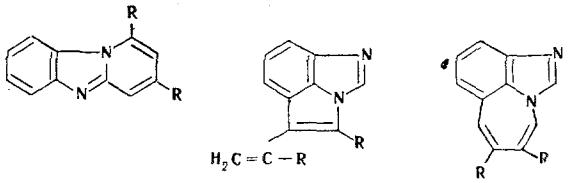
we assumed that the pyrrole ring is attached at the 7 position of the benzimidazole ring, where, as is well known, the partial negative charge is concentrated [3], to five IV. However, an analysis of the PMR spectrum of the compound obtained (R = CH_3), in which signals of methylene protons were absent at 4-6 ppm, made it possible to conclude that the original assumption was erroneous.

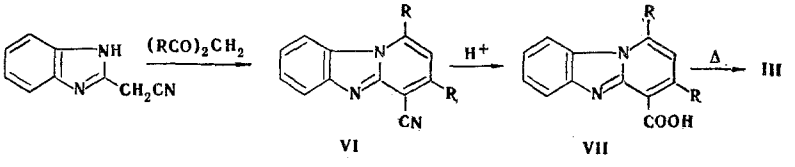
In addition to two singlets of identical intensity of the protons of methyl groups at 2.3 and 2.83 ppm, the spectrum contains a singlet of one proton at 6.3 ppm and two multiplets at 7.25 (3H) and 7.88 ppm (2H). Taking these data into account, it may be assumed that another possible reaction pathway is the formation of a seven-membered ring, which leads to compounds of the V type. Considering the fact that a weak-field shift of the



III IV V

signal of the proton attached to the meso-carbon atom occurs in the PMR spectrum in the benzimidazole series on passing from the base to the cations [4], we measured the spectrum of this compound in trifluoroacetic acid. In fact, the spectrum of the cation at weakest field contains a broad doublet (8.0 ppm) with an intensity of one proton unit, and this, it would seem, made it possible to prefer structure V. However, this pattern is not observed in the PMR spectrum of the compound obtained from 1-amino-5,6-dimethylbenzimidazole and acetone or mesityl oxide. In the spectrum of the base the signal of the protons of two methyl groups in the benzene ring appears at 2.3 ppm (superimposed) on the signal of one of the methyl groups of the ketone), the protons of the second methyl group are observed at 2.75 ppm, and four singlets of aromatic protons are observed at 6.23, 7.18, 7.55, and 7.62 ppm. On passing to the cation, the signal of the protons of the CH_3 group is disconnected from the broad singlet of nine protons (2.1 ppm) and moved to weak field (2.2 ppm), and the protons of yet another methyl group appear at 2.78 ppm; three singlets are present in the aromatic proton region at 6.73, 7.15, and 7.75 ppm with a relative intensity of 1:2:1.

We were unable to obtain a rigorous confirmation of the V structure by means of data from IR, mass, and PMR spectroscopy. We therefore advanced the paradoxical (at first glance) assumption that the new ring is attached to the μ-carbon atom of benzimidazole, which bears a significant positive charge [3], to give pyrido[1,2-a]benzimidazole III. The inertness of 2-substituted 1-aminobenzimidazoles to the reagents indicated above consitituted indirect evidence in favor of structure III. To ascertain the structures of the compounds obtained we accomplished the alternative synthesis of compounds of the III type. The pyrido[1,2-a]-benzimidazoles obtained by an independent method from 2-cyanomethylbenzimidazole and β-diketones by the method in [5] proved to be identical with respect to all of the physicochemical constants to III.

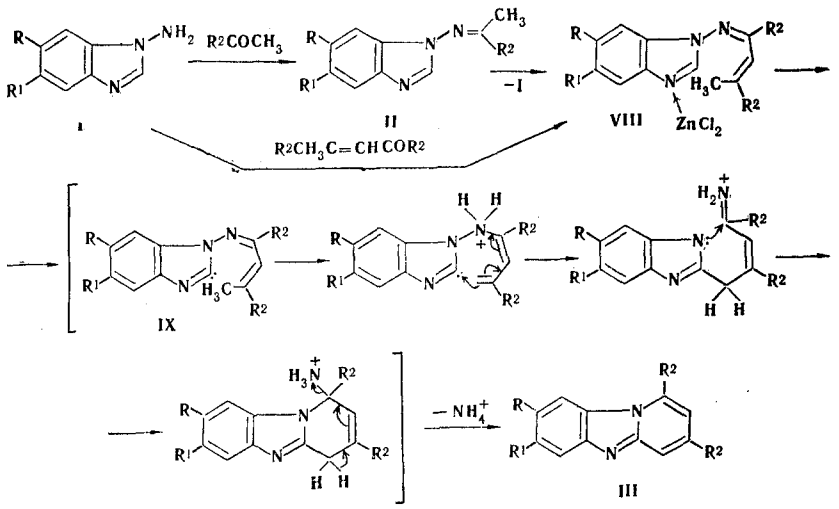


VI VII

III a R = CH_3, b R = C_6H_5

Thus the unusual Fischer reaction in the 1-aminobenzimidazole series consists not only in the formation of a pyridine ring but also in the fact that the formation of this ring takes place in the π-deficient position of the benzimidazole molecule.

This reaction pathway can be explained by coordination of the zinc chloride molecule at the pyridine nitrogen atom of the benzimidazole fragment of ketimine VIII. In the case of coordination of this type the positive charge on the meso carbon atom is increased considerably, and this leads to an increase in the lability of the proton bonded to this carbon atom. Under the influence of a base, which is a role that can be played by the starting N-aminobenzimidazole or the ketimine molecule, "ylid" IX is formed. Intramolecular cyclization to pyrido[1,2-a]benzimidazole III via the following scheme is realized in the ylid:



III a R=R¹=H, R²=CH₃; b R=R¹=R²=CH₃; c R=R¹=H, R²=C₆H₅; d R=R¹=CH₃, R²=C₆H₅; e R=R¹=H, R²=*p*-ClC₆H₄; f R=R¹=H, R²=*p*-BrC₆H₄; g R=R¹=CH₃, R²=*p*-BrC₆H₄; h R=R¹=H, R²=3,4-(Cl)₂C₆H₃; i R=R¹=CH₃, R²=3,4-(Cl)₂C₆H₃

The formation of a ketimine with structure VIII can be explained, first, by the reaction of 1-aminobenzimidazole with α,β-unsaturated ketones, which can be formed under the reaction conditions, and, second, by condensation of two ketimines II formed in the first step, and, finally, by condensation of ketimine II with excess ketone.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform were measured with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-467 spectrometer with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with a JMS-01-SG2 spectrometer by direct introduction of the samples at an ion-source temperature of 175°C, an accelerating voltage of 8 kV, an ionizing voltage of 75 eV, and a cathode emission current of 300 μA.

1-(α-Methylbenzylideneamino)benzimidazole (IIa). A mixture of 1.33 g (10 mmole) of 1-aminobenzimidazole (Ia), 1.3 g (11 mmole) of acetophenone, and catalytic amounts of $ZnCl_2$ was heated with stirring at 160-170°C for 1 h. It was then cooled and dissolved in 20 ml of benzene and purified by chromatography with a column filled with Al_2O_3 (benzene) to give 1.9 g (81%) of colorless needles with mp 93-94°C (from benzene-petroleum ether). Found: C 76.6; H 5.9; N 18.2%. $C_{15}H_{13}N_3$. Calculated: C 76.6; H 5.6; N 17.9%.

1,3-Dimethylpyrido[1,2-a]benzimidazole (IIIa). A) A 0.6-g (2.5 mmole) sample of 1,3-dimethyl-4-carboxypyrido[1,2-a]benzimidazole [4] was heated at 260-265.C for 5 min, during which vigorous CO_2 evolution was observed. The residue was dissolved in 10 ml of chloroform and purified by chromatography on Al_2O_3 (elution with chloroform) to give 0.49 g (a quantitative yield) of light-yellow needles with mp 114-115°C (from isooctane). IR spectrum: 1660 cm^{-1} (C=N). Found: C 79.4; H 6.4; N 14.1%. $C_{13}H_{12}N_2$. Calculated: C 79.6; H 6.1; N 14.3%.

B) A mixture of 3.99 g (30 mmole) of amine Ia and 4.08 G (30 mmole) of anhydrous $ZnCl_2$ in 15 ml of acetone was refluxed for 2 h, during which the solid material initially dissolved, after which a new precipitate began to form in a few minutes. The acetone was removed by distillation, and the residue was heated at 240-250°C for 6.5 min, after which another 2.72 g (20 mmole) of $ZnCl_2$ was added, and heating was continued for 2.5 h. The mixture was then cooled and dissolved in 20 ml of alcohol, 10 ml of 57% $HClO_4$ was added, and the precipitated perchlorate was removed by filtration and washed with ethyl acetate and hexane. The perchlorate was dissolved by heating in 100 ml of water, and the base was liberated with 10% NaOH to give 0.6 g (10%) of yellowish needles with mp 115°C (from hexane). PMR spectrum ($CDCl_3$): 2.3 (3H, s, 3-CH_3), 2.83 (3H, s 1-CH_3), 6.3 (1H, s, 2-H), 7.25 (3H, m, aromatic protons), and 7.88 ppm (2H, m, aromatic protons); (CF_3COOH): 2.25 (3H, s, 3-CH_3), 2.8 (3H, s, 1-CH_3), 6.83 (1H, s, 2-H), 7.3 (4H, m, aromatic protons), and 8.0 ppm (1H, m).

C) A mixture of equimolar amounts of 1-aminobenzimidazole and zinc chloride in excess mesityl oxide was heated at 200°C for 2 h, after which it was cooled and dissolved in hot alcohol, and the precipitated complex was removed by filtration. The precipitate was treated

with excess 22% NH_4OH and extracted with chloroform. Workup gave pale yellow needles, with mp 114-115°C (from isooctane), in 30% yield. No melting-point depressions were observed for mixtures of samples from experiments A, B, and C.

1-Amino-5,6-dimethylbenzimidazole (Ib). A neutralized (with $NaHCO_3$) solution of 30.0 g (240 mmole) of hydroxylamine-O-sulfonic acid in 70 ml of water was added in the course of 3-5 min to a heated (to 85°C) solution of 10.2 g (80 mmole) of 5,6-dimethylbenzimidazole and 51.2 g (365 mmole) of 85% KOH in 500 ml of water. After 5 min, the precipitated amine was removed by filtration of the hot mixture and washed with water to give 9.0 g (70%) of colorless prisms with mp 229°C (from butanol). The filtrate was cooled and worked up to give 2.2 g of starting benzimidazole. Found: C 67.1; H 6.9; N 26.4%. $C_9H_{11}N_3$. Calculated: C 67.1; H 6.8; N 26.1%.

1,3,7,8-Tetramethylpyrido[1,2-a]benzimidazole (IIIb). A) A mixture of 3.22 g (20 mmole) of amine Ib and 2.72 g (20 mmole) of anhydrous $ZnCl_2$ in 7 ml of acetone was refluxed for 2.5 h, after which the acetone was removed by distillation, and the residue was heated at 250°C for 6 h. The mixture was cooled and dissolved in 20 ml of alcohol, 10 ml of 57% $HClO_4$ was added, and the precipitated perchlorate was removed by filtration and washed with acetone. Treatment of the perchlorate with 10% NaOH gave 0.6 g (13%) of the base as slightly yellowish needles with mp 180-181°C (from heptane). IR spectrum: 1670 cm^{-1} (C=N). PMR spectrum ($CDCl_3$): 2.32 (9H, s, 3-, 7-, and 8-CH_3), 2.75 (3H, s, 1-CH_3), 6.23 (1H, s, 2-H), 7.18 (1H, s, 4-H), 7.55 (1H, s, 9-H), and 7.62 ppm (1H, s, 6-H); (CF_3COOH): 2.1 (6H, s, 7- and 8-CH_3), 2.2 (3H, s, 3-CH_3), 2.78 (3H, s, 1-CH_3), 6.73 (1H, s, 2-H), 7.17 (2H, s, 6- and 9-H), and 7.75 ppm (1H, s, 4-H). Found: C 79.9; H 7.5; N 12.3%. $C_{15}H_{16}N_2$. Calculated: C 80.3; H 7.1; N 12.5%.

B) A mixture of 1.61 g (10 mmole) of amine Ib and 1.36 g (10 mmole) of anhydrous $ZnCl_2$ in 3 ml of mesityl oxide was heated at 150°C for 45 min, during which the amine and zinc chloride initially dissolved, and a new precipitate formed after 20 min. The temperature was raised to 180-190°C, and the mixture was stirred for 2 h. It was then cooled, and the residue was dissolved in 15 ml of alcohol. The solution was treated with 5 ml of 57% $HClO_4$, and the precipitated perchlorate was removed by filtration and washed with alcohol. The perchlorate was treated with 20 ml of 22% NH_4OH and extracted with chloroform. Workup gave 0.55 g (25%) of light yellow needles with mp 180-181°C (from octane). No melting-point depression was observed for a mixture of this product with a sample obtained in experiment A.

1,3-Diphenyl-4-cyanopyrido[1,2-a]benzimidazole (VIb). A 2.8-g (18 mmole)sample of 2-cyanomethylbenzimidazole and 4.0 g (18 mmole) of dibenzoylmethane were added to a solution of 0.84 g (22 mmole) of sodium ethoxide in 20 ml of alcohol, and the mixture was refluxed for 5 h on a water bath, and the resulting precipitate was removed by filtration in the hot state and washed with hot alcohol to give 1.5 g (24%) of lemon-yellow prisms with mp 226-227°C (from DMF). IR spectrum: 2238 cm^{-1} (C≡N). Found: C 83.5; H 4.6; N 12.3%. $C_{24}H_{15}N_3$. Calculated: C 83.5; H 4.3; N 12.2%.

1,3;Diphenyl-4-carboxypyrido[1,2-a]benzimidazole (VIIb). A solution of 1.0 g (2.9 mmole) of VIb in 10 ml of an acidic solution prepared from 4.5 ml of concentrated H_2SO_4, 7.5 ml of acetic acid, and 7.5 ml of water was heated in a sealed ampul at 160°C for 20 h, after which it was cooled and made alkaline to pH 4-5 with 22% NH_4OH. The precipitate was removed by filtration and washed with water to give 0.84 g (80%) of light yellow prisms with mp 234-235°C (from aqueous DMF). IR spectrum (mineral oil): 1712 cm^{-1} (COOH). Found: C 79.0; H 4.6; N 7.9%. $C_{24}H_{16}N_2O_2$. Calculated: C 79.1; H 4.4; N 7.7%.

1,3-Diphenylpyrido[1,2-a]benzimidazole (IIIc). A) A 0.6-g (2.7 mmole) sample of acid VIIb was heated at 265°C for 5 min, after which it was cooled, dissolved in 10 ml of chloroform, and purified by chromatography with a column filled with Al_2O_3 (elution with chloroform) to give 0.53 g (quantitative) of light green needles with mp 168-169°C (from octane). IR spectrum: 1650 cm^{-1} (C=N). Found C 86.0; H 5.6; N 8.5%. $C_{23}H_{16}N_2$. Calculated: C 85.9; H 5.4; N 8.7%.

B) A mixture of 4.0 g (30 mmole) of amine Ia, 9.0 g (75 mmole) of acetophenone, and 14.0 g (100 mmole) of anhydrous $ZnCl_2$ was heated with stirring at 250°C for 2 h, after which it was cooled, finely triturated, and treated by heating with excess 40% NaOH solution. The mixture was extracted with benzene (four 100-ml portions), the solvent was removed by distillation, and the residue was treated with 20 ml of 57% perchloric acid. The precipitated perchlorate was removed by filtration and washed with acetone. The perchlorate was decomposed

with excess 22% NH_4OH, and the mixture was allowed to stand overnight. Workup gave 6.0 g (62%) of light yellow prisms with mp 168°C (from aqueous alcohol). PMR spectrum (CF_3COOH): 6.4 (1H, d, J = 9 Hz), 7.4 (14H, m, aromatic protons), and 7.7 ppm (1H, s, 4-H). Mass spectrum m/z, relative intensity, %): 322 (2.6), 321 (24.6), 320 (100), 319 (28.6), 318 (14.8), 316 (9,5), 242 (3.4), 160 (10.8), 159 (5.4), 158 (4.2), 152 (2.3), 146 (2.0), 140 (2.1), 115 (2.8), 102 (2.0), 89 (2.0), 89 (2.0), and 77 (4.9).

C) A mixture of 1.3 g (5.5 mmole) of ketimine II and 5.0 g (37 mmole) of anhydrous $ZnCl_2$ was heated at 240°C for 2 h, after which it was cooled and treated with excess 40% KOH solution. The mixture was worked up as in the preceding method to give 0.35 g (20%) of light yellow prisms with mp 168°C (from aqueous alcohol).

D) A mixture of 1.33 g (10 mmole) of amine Ia, 2.22 g (10 mmole) of dypnone, and 1.3 g (10 mmole) of anhydrous $ZnCl_2$ was heated at 200°C for 3 h, after which it was cooled and dissolved in 20 ml of hot alcohol. The solution was cooled, and the precipitated complex was removed by filtration. Treatment with excess 30% NaOH solution liberated the base, which was extracted with chloroform to give 1.6 g (80%) of a product with mp 170°C (from octane). The product was identical to the samples from experiments A-C with respect to all of its physicochemical constants.

1,3-Diphenyl-7,8-dimethylpyrido[1,2-a]benzimidazole (IIId). A mixture of 1.61 g (10 mmole) of amine Ib, 1.8 g (15 mmole) of acetophenone, and 7.0 g of anhydrous zinc chloride was heated at 250°C for 1.5 h, after which it was cooled and treated with excess 40% NaOH solution. The reaction product was extracted with chloroform, and the extract was worked up as in the preceding experiment to give 1.2 g (34%) of light yellow needles with mp 195°C (from alcohol). IR spectrum: 1655 cm^{-1} (C=N). PMR spectrum (D_6-DMSO): 2.08 (3H, s, 8-CH_3), 2.35 (3H, s, 7-CH_3), 6.19 (1H, s, 2-H), and 7.23 ppm (13H, m, aromatic protons). Mass spectrum (m/z, relative intensity, %): 349 (31.0), 348 (100.0), 347 (22.5), 346 (3.1), 345 (5.1), 334 (9.0), 333 (38.0), 332 (7.5), 321 (2.3), 320 (2.7), 203 (2.4), 202 (2.8), 174 (3.0), 173 (3.8), 166 (13.0), 160 (2.0), 144 (2.3), 103 (2.1), 101.5 (2.0), 91 (2.0), 77 (3.3). Found: C 86.3; H 6.1; N 7.7%. $C_{25}H_{20}N_2$. Calculated: C 86.2; H 5.7; N 8.0%.

1,3-Bis(p-chlorophenyl)pyrodo[1,2-a]benzimidazole (IIIe). This compound was similarly obtained from 2.66 g (20 mmole) of amine Ia, 7.73 g (50 mmole) of p-chloroacetophenone, and 9.35 g (70 mmole) of $ZnCl_2$ by heating at 250°C for 1.5 h. Workup gave 3.4 g (44%) of bright-yellow prisms with mp 234°C (from benzene). IR spectrum: 1640 cm^{-1} (C=N). Found: C 71.2; H 3.2; Cl 18.1%. $C_{23}H_{14}Cl_2N_2$. Calculated: C 71.0; H 3.6; Cl 18.2%.

1,3-Bis(p-bromophenyl)pyrido[1,2-a]benzimidazole (IIIf). This compound was obtained as in the preceding experiment from 2.66 g (20 mmole) of amine Ia, 9.95 g (50 mmole) of p-bromoacetophenone, and 9.35 g (70 mmole) of $ZnCl_2$. Workup gave bright-yellow needles with mp 261°C (from benzene) in 51% yield. Found: C 57.5; H 3.2; Br 33.2%. $C_{23}H_{14}Br_2N_2$. Calculated: C 57.8; H 3.0; Cl 33.4%.

1,3-Bix(p-bromophenyl)-7,8-dimethylpyrido[1,2-a]benzimidazole (IIIg). This compound was similarly obtained in 60% yield from amine Ib and p-bromoacetophenone. Workup gave yellow prisms with mp 271-272°C (from DMSO). IR spectrum: 1640 cm^{-1} (C-N). PMR spectrum (CF_3COOH): 1.78 (3H, s, 8-CH_3), 2.0 (3H, s, 7-CH_3), 6.12 (1H, s, 2-H), 7.25 (10H, m, aromatic protons), and 7.6 ppm (1H, s, 4-H). Found: C 59.3; H 3.4; Br 31.7%. $C_{25}H_{16}Br_2N_2$. Calculated C 59.3; H 3.6; Br 31.6%.

1,3-Bis(3,4-dichlorophenyl)pyrido[1,2-a]benzimidazole (IIIh). This compound was similarly obtained in 48% yield from 1-aminobenzimidazole and 3,4-dichloroacetone. Workup gave bright yellow prisms with mp 233-234°C (from butanol). Found: C 60.5; H 3.0; Cl 31.1%. $C_{23}H_{12}Cl_4N_2$. Calculated: C 60.3; H 2.6; Cl 30.9%.

1,3-Bis(3,4-dichlorophenyl)-7,8-dimethylpyrido[1,2-a]benzimidazole (IIIi). This compound was similarly obtained in 67% yield from amine Ib and 3,4-dichloroacetophenone. Workup gave yellow prisms with mp 246-247°C (from DMSO). IR spectrum: 1640 cm^{-1} (C=N). Found: C 62.0; H 3.3; Cl 29.8%. $C_{25}H_{16}Cl_4N_2$. Calculated: C 61.8; H 3.3; Cl 29.3%.

1,3-Diphenylpyrido[1,2-a]benzimidazole Perchlorate. A 1-ml sample of 57% perchloric acid was added to a warm solution of 0.32 g (1 mmole) of IIIc in 5 ml of acetonitrile, and the precipitated perchlorate was removed by filtration, washed with acetonitrile, and dried to give colorless prisms with mp 250°C (from acetonitrile) in quantitative yield. Found: C 65.8; H 4.0; Cl 8.0%. $C_{23}H_{17}ClN_2O_4$. Calculated: C 65.6; H 4.1; Cl 8.4%.

5-Methyl-1,3-diphenylpyrido[1,2-a]benzimidazolium Perchlorate. A solution of 0.32 g (1 mmole) of IIIc and 0.5 ml of methyl iodide in 7 ml of alcohol was refluxed for 3 h, after which it was cooled, and the precipitated methiodide was removed by filtration and dissolved in the minimum amount of acetonitrile. The solution was treated with 1 ml of 57% $HClO_4$, and the precipitated perchlorate was removed by filtration and washed with acetonitrile to give 0.35 g (80%) of a product with mp 246-247°C.

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REACTION OF 3-INDOLYLPHENYLIODONIUM BETAINE WITH ELECTROPHILIC AGENTS

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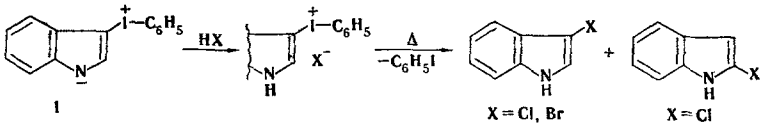
UDC 547.754'759

3-Indolylphenyliodonium chloride and bromide, respectively, were obtained by the action of hydrochloric and hydrobromic acids on 3-indolylphenyliodonium betaine. Pyrolysis of the chloride leads to a mixture of 2- and 3-chloroindoles, while pyrolysis of the bromide leads only to 3-bromoindole. 1-Benzyl-2-chloroindole is obtained in the reaction of the betaine with benzyl chloride. The betaine reacts with dimethyl sulfate to give an iodonium salt, the reaction of which with lithium chloride and ammonium chloride leads to 1-methyl-2-chloroindole.

Unstable 3-indolylphenyliodonium betaine (I) is formed by the action of phenyliodoso diacetate on indole in a solution of alcoholic alkali [1]. The dipolar betaine molecule is capable of reacting with both electrophilic and nucleophilic agents. In fact, protic acids with weakly nucleophilic anions react with the betaine to give indolyliodonium salts. This method has been used to obtain 3-indolylphenyliodonium tetrafluoroborate [1], tosylate [1, 2], and trifluoroacetate [2]. However, if the anion of the acid is sufficiently nucleophilic, further reaction between it and the iodonium salt is possible. In fact, haloindoles are formed by the action of hydrochloric and hydrobromic acids on 3-indolylphenyliodonium betaine. The intermediately



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formed iodonium salt can be isolated in this case. As we have already mentioned [3], bromide ion gives only 3-bromoindole, whereas a mixture of 2- and 3-chloroindoles is formed in the case of the chloride. The formation of 2-chloroindole is apparently associated with dissociation of the chloride of the iodonium salt and subsequent attack by the chloride ion on the α-carbon atom. Thus betaine I is initially protonated at the nitrogen atom, after which the phenyliodonium grouping undergoes nucleophilic substitution.

One might have expected that some other reagents would also be capable of acting similarly. In fact, 1-benzyl-2-chloroindole is formed when betaine I is heated with benzyl chlo-

*Deceased.

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