a column filled with aluminum oxide (by elution with chloroform) and crystallized from acetone to give 0.3 g (50%) of yellow crystals of XIII with mp 214-216°C. PMR spectrum (80 MHz, DMSO): 7.70 (d, $J_{1,2}$ = 4.5 Hz, 1H, 1-H), 8.22 (d, $J_{5,6}$ = 7.5 Hz, 1H, 5-H), 8.31 (d, $J_{6,8}$ = 2.5 Hz, 1H, 8-H), 8.61 (d, $J_{6,5}$ = 7.5, $J_{6,8}$ = 2.5 Hz, 1H, 6-H), 8.90 (m, 1H, 2-H), and 9.36 ppm (broad s, 1H, 4-H). Mass spectrum, m/z (%): M^+ 226(100), 180(28), 168(14), 153(16), 152(45), 149(21), 125(42), 98(30), 97(20). IR spectrum: 1730 (CO), 1535, 1342 cm^{-1} (NO_2). Found: C 63.5; H 3.5; N 12.4%; M^+ 226. $C_{12}H_6N_2O_3$. Calculated: C 63.7; H 3.5; N 12.4%; M 226.

3-Azafluorenone N-Oxide (XIV). The oxidation of 3-azafluorenone (II) with hydrogen peroxide in acetic acid was carried out as described in [8]. Workup of the reaction mixture gave orange crystals of XIV (56%) with mp 246-247°C (from ethanol). Found: C 73.1; H 3.6; N 7.1%; M^+ 197. $C_{12}H_7NO_2$. Calculated: C 73.3; H 3.4; N 6.8%; M 197.

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QUATERNARY 1-AMINOBENZIMIDAZOLIUM SALTS IN REACTIONS WITH β-DICARBONYL COMPOUNDS. FORMATION OF PYRIDAZINO[1,6-a]BENZIMIDAZOLIUM CATIONS AND 1-ARYLPYRAZOLES

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Pyridazino[1,6-a]benzimidazolium cations and 1-(o-methylaminoaryl)-4-acetylpyrazoles are formed simultaneously in approximately equal amounts in the reaction of excess acetylacetone with quaternary 1-aminobenzimidazolium salts in aqueous potassium carbonate solution. Mesoionic pyridazinobenzimidazoles and the corresponding 4-ethoxycarbonylpyrazoles were obtained with acetoacetic ester under similar conditions.

Data on the reaction of the cations of N-amino derivatives of nitrogen heterocycles with β-dicarbonyl compounds are limited to N-amino-substituted pyridines and sym-triazoles [1-2]. It has been recently shown that 1-aminobenzimidazoles react with β-diketones to give pyridazino[1,6-a]benzimidazoles [3]. In the present research we set out to study the peculiarities of this reaction for quaternary 1-aminobenzimidazolium salts and, in particular, to ascertain the possibility of the synthesis of pyrazolo[1,5-a]benzimidazoles via this scheme, as in the N-aminopyridine series [1].

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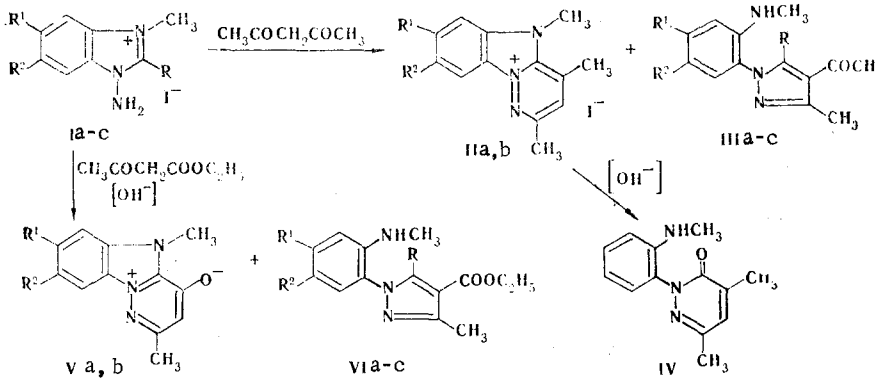
We have previously synthesized 3-acetyl-2,4-dimethylpyrazolo[1,5-a]benzimidazole [4], and its formation in the reaction of 1-amino-3-methylbenzimidazolium iodide (Ia) with acetylacetone therefore could have been easily established. However, the reaction of salt Ia with excess acetylacetone in aqueous potassium carbonate solution at 70-80°C leads to other products, viz., pyridazino[1,6-a]benzimidazolium iodide IIa and 1-(o-methylaminophenyl)-3-methyl-4-acetylpyrazole (IIIa) in approximately equal amounts.



I—III, V, VI a R=R¹=R²=H; b R=H, R¹=R²=CH₃; c R=CH₃, R¹=R²=H

The structures of IIa and IIIa were confirmed by the analytical and spectral data and also by certain chemical transformations. Thus the IR spectrum of the cation of IIa doesnot contain characteristic absorption bands. Three singlets of methyl groups at 2.33, 2.58, and 4.03 ppm, a lone signal of the 3-H proton of the pyridazine ring at 7.23 ppm, a multiplet of three benzimidazole protons at 7.43 ppm, and a multiplet with an intensity of one proton unit at 7.98 ppm, which was assigned to the 9-H proton of the heterosystem, were observed in its PMR spectrum.

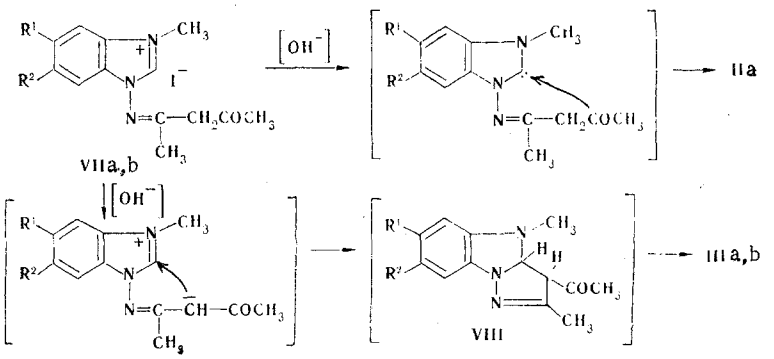
To identify the second reaction product it was necessary to establish whether it is formed as a result of the alkaline hydrolysis of salt IIa or is produced along with the latter through an independent reaction. We found that salt IIa is converted to 3,5-dimethyl-1-(o-methylaminophenyl)-3-oxopyridazine (IV), which differs from IIIa with respect to its physicochemical characteristics, by prolonged refluxing in aqueous potassium carbonate solution or by refluxing in alcoholic alkali for a few minutes. Bands of carbonyl absorption (1665 cm^{-1}) and of an amine bond (3400 cm^{-1}) show up distinctly in the IR spectrum of pyrazole IIIa. The PMR spectrum contains, in addition to three signals of methyl groups at 2.35, 2.48, and 2.75 ppm, a broad signal of the proton of the NH group (5.13 ppm), which vanishes after deuteration, signals of four phenyl ring protons (6.65-7.1 ppm), and a lone signal of the 5-H proton of the pyrazole ring (7.98 ppm). The presence of an acetyl group in the molecule was proved by the formation of a 2,4-dinitrophenylhydrazone and a chalcone analog in the reaction of IIIa with p-nitrobenzaldehyde.

1-Amino-2,3-dimethylbenzimidazolium iodide (Ic) is converted to 3,5-dimethylpyrazole IIIc in 67% yield upon reaction with acetylacetone in aqueous potassium carbonate solution.

Salt Ia reacts with acetoacetic ester under these conditions to give dipolar pyridazinobenzimidazole Va and 4-ethoxycarbonylpyrazole VIa. Compound Va is extremely resistant to alkaline and acidic hydrolysis. In analogy with other mesoionic heterocycles [2], the intense band at 1630 cm^{-1} in the IR spectrum of Va was assigned to vibrations of the C=O bond. Two signals of methyl groups at 2.25 and 4.05 ppm and a lone proton of a pyrazole ring at 6.78 ppm are recorded in the PMR spectrum of Va.

The only reaction products in the reaction of salts Ia, b with acetylacetone in dimethylformamide (DMF) in the presence of potassium carbonate are pyridazinobenzimidazoles IIa, b. In the acetonitrile—triethylamine system salt Ia does not react with either acetylacetone or acetoacetic ester.

In the interpretation of the experimental results it seemed possible to assume that the two competitive reactions proceed through the same intermediate, viz., a ketimine of the VII type, and are due to the presence in its molecule to two centers with comparable CH acidities, viz., the μ-carbon atom of the benzimidazole ring and the CH_2 group of the ylidene residue.



Pyridazino derivatives II and V are formed by deprotonation of the μ-carbon atom as a result of electrophilic attack on the resulting ylid by the carbonyl group of the ylidene residue. If a proton is accepted from the methylene group, a pyrazole ring is formed by addition of the generated carbanion to the electron-deficient $C_{(2)}$ atom of the heterosystem. Intermediate dihydropyrazolobenzimidazoles VIII are stabilized through openings of the imidazole ring at the 1,2 bond. Tamura and co-workers [5] have also observed a similar transformation in the cycloaddition of acetylenedicarbonyl compounds to salts I.

To substantiate the proposed scheme we synthesized ketimines VIIa, b by heating salts Ia, b in excess acetylacetone at 140-160°C; we were unable to accomplish a similar transformation with acetoacetate ester.

In fact, we found that in aqueous potassium carbonate solution VIIa, b undergo hydrolysis at the azomethine bond to give salts Ia, b and are converted to pyrazoles IIIa, b in 49% yield. A mixture of the cation of IIa and pyrazole IIIa is formed when VIIa is refluxed in acetonitrile in the presence of triethylamine.

An unexpected result is obtained when ketimines VIIa, b are heated in a solution of potassium carbonate in DMF. Whereas only pyridazinobenzimidazoles II are formed from salts Ia, b under these conditions, the corresponding ketimines are converted smoothly and exclusively to pyrazoles IIIa, b. These results forced us to assume that the scheme that stipulates the initial formation of ketimines of the VII type is not universal. The meso carbon atom of the products of salts I evidently may also undergo deprotonation with subsequent reaction of the resulting ylid with the diketone and cyclization to a pyridazinobenzimidazolium cation.

EXPERIMENTAL

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

1-Amino-3-methylbenzimidazolium Iodide (Ia). A solution of 1.33 g (0.01 mole) of 1-aminobenzimidazole and 2.1 g (0.015 mole) of methyl iodide in 5 ml of alcohol was refluxed for 3 h, after which it was cooled, and the precipitate was separated and washed with alcohol to give 2.5 g (91%) of colorless needles with mp 205-207°C (dec., from water). IR spectrum (mineral oil): 1620 (C=N); 3070, 3235 cm^{-1} (NH_2). Found: C 35.0; H 3.7; I 45.9; N 15.2%. $C_8H_{10}IN_3$. Calculated: C 34.9; H 3.6; I 46.2; N 15.3%.

1-Amino-3,5,6-trimethylbenzimidazolium Iodide (Ib). A suspension of 7.5 g (0.047 mole) of 1-amino-5,6-dimethylbenzimidazole and 3 ml of methyl iodide in 50 ml of alcohol was refluxed for 3 h, during which the solid material dissolved completely. The solution was cooled, and the resulting precipitate was removed by filtration and washed with alcohol and acetone to give 9.2 g of product. The mother liquor was evaporated to dryness, and the residue was triturated with acetone. The precipitate was separated and washed with acetone to give an additional 2.8 g of salt Ib for a total yield of 12.0 g (86%). The colorless crystals had mp 194-195°C (dec., from alcohol). Found: C 39.8; H 4.5; I 42.0; N 13.8%. $C_{10}H_{14}IN_3$. Calculated: C 39.6; H 4.6; I 41.9; N 13.9%.

2,4,5-Trimethylpyridazino[1,6-a]benzimidazolium Iodide (IIa) and 1-(o-Methylaminophenyl)-3-methyl-4-acetylpyrazole (IIIa). A mixture of 2.75 g (0.01 mole) of salt Ia, 4.0 g (0.03 mole) of potassium carbonate, and 2.5 ml (0.025 mole) of acetylacetone in 20 ml of water

was heated at 80°C for 3 h, after which it was cooled, and the precipitate was removed by filtration and washed with water and a small amount of chloroform to give 0.55 g (16%) of yellow-green crystals of pyridazinobenzimidazolium iodide IIa with mp 275-276°C (from alcohol). PMR spectrum (CF_3COOH): 2.33 (3H, s, 4-CH_3), 2.58 (3H, s, 2-CH_3), 4.03 (3H, s, N-CH_3), 7.23 (1H, s, 3-H), 7.43 (3H, m, 6- and 8-H), and 7.98 ppm (1H, m, 9-H). Found: C 46.1; H 4.1; I 37.1; N 12.5%. $C_{13}H_{14}IN_3$. Calculated: C 46.0; H 4.1; I 37.5: N 12.4%.

The mother liquor was extracted with chloroform, and the chloroform solution was evaporated to the minimal volume and chromatographed with a column filled with Al_2O_3 by elution with chloroform. Workup of the first fraction gave 0.3 g (13%) of colorless needles of pyrazole IIIa with mp 112°C (from hexane). PMR spectrum ($CDCl_3$): 2.35 (3H, s, 3-CH_3), 2.48 (3H, s, $COCH_3$), 2.75 (3H, s, $NHCH_3$), 5.13 (1H, m, NH), 6.65 (2H, m, o-H, C_6H_4), 7.1 (2H, m, n-H, C_6H_4), and 7.98 ppm (1H, s, 5-H). Found: C 68.0; H 6.5; N 18.0%. $C_{13}H_{15}N_3O$. Calculated: C 68.1; H 6.5; N 18.3%. The dinitrophenylhydrazone was obtained in the form of red crystals with mp 243-244°C (from DMF). Found: N 24.3%. $C_{19}H_{19}N_7O_4$. Calculated: N 24.0%.

1-(o-Methylaminophenyl)-3-methyl-4-(p-nitrocinnamoyl)pyrazole. This compound was obtained by brief heating of acetylpyrazole IIIa with p-nitrobenzaldehyde in alcohol in the presence of a catalytic amount of 40% alkali. The golden-orange crystals had mp 225-226°C (from butanol). Found: C 66.0; H 4.9; N 15.3%. $C_{20}H_{18}N_4O_3$. Calculated: C 66.3; H 5.0; N 15.5%.

2,4,5,7,8-Pentamethylpyridazino[1,6-a]benzimidazolium Iodide (IIb) and 1-(2-Methylamino-4,5-dimethylphenyl)-3-methyl-4-acetylpyrazole (IIIb). A solution of 1.5 g (5 mmole) of salt Ib, 2.0 g (15 mmole) of potassium carbonate, and 1.2 ml (12 mmole) of acetylacetone in 8 ml of water was heated with stirring at 70-80°C for 2 h, after which it was cooled, and the resulting precipitate was removed by filtration and washed with water and chloroform to give 0.2 g (11%) of pale-green needles of salt IIb with mp > 300°C (from alcohol). PMR spectrum (CF_3COOH): 2.11 (6H, s, 7-CH_3 and 8-CH_3), 2.32 (3H, s, 4-CH_3), 2.58 (3H, s, 3-CH_3), 4.0 (3H, s, 5-CH_3), 7.2 (2H, m, 3-H and 6-H), and 7.75 ppm (1H, s, 9-H). Found: C 49.1; H 5.1; I 34.5; N 11.3%. $C_{15}H_{18}IN_3$. Calculated: C 49.0; H 4.9; I 34.6; N 11.4%.

The mother liquor was worked up as in the preceding experiment to give 0.4 g (27%) of colorless prisms of pyrazole IIIb with mp 111-112°C (from aqueous alcohol). Found: C 69.9; H 7.2; N 16.1%. $C_{15}H_{19}N_3O$. Calculated: C 70.0; H 7.4; N 16.3%.

1-(o-Methylaminophenyl)-3,5-dimethyl-6-oxopyridazine (IV). A suspension of 0.45 g (1.4 mmole) of pyridazinobenzimidazolium salt IIa and 0.3 g (5 mmole) of potassium hydroxide in 5 ml of alcohol was refluxed for 30 min, after which the solution was diluted to twice its original volume with water and extracted with chloroform. The chloroform solution was purified with a column filled with Al_2O_3 (elution with chloroform). Workup of the first fraction gave 0.2 g (62%) of pale-yellow crystals with mp 147-158°C (from benzene with octane). IR spectrum (in $CHCl_3$): 1605 (C=N), 1650 (C=O), and 3450 cm^{-1} (NH). PMR spectrum (d_6-DMSO): 2.05 (3H, s, 5-CH_3), 2.18 (3H, s, 3-CH_3), 3.38 (1H, m, NH), 6.5-6.7 (2H, m, o-H, C_6H_4), 6.9-7.2 (2H, m, m-H, C_6H_4), and 7.25 ppm (1H, s, 4-H). Found: C 68.1; H 6.6; N 18.5%. $C_{13}H_{15}N_3O$. Calculated: C 68.1; H 6.6; N 18.3%.

1-(o-Methylaminophenyl)-3,5-dimethyl-4-acetylpyrazole (IIIc). A mixture of 2.89 g (0.01 mole) of salt Ic [4], 4.0 g (0.03 mole) of potassium carbonate, and 2.5 ml (0.025 mole) of acetylacetone in 15 ml of water was heated at 70-80°C for 2 h, after which it was cooled, and the resulting oil began to crystallize. The crystals were removed by filtration and washed with water to give 1.9 g of product. The precipitate was dried and treated with 20 ml of chloroform, and the mixture was filtered to give 0.9 g of a colorless substance, which was recrystallized from alcohol to give a product with mp 204-205°C (no melting-point depression was observed for a mixture of this product with a sample of the starting salt). The chloroform solution was passed through a column filled with Al_2O_3 by elution with chloroform to give 1.0 g (65% with allowance for regeneration of the starting salt) of colorless needles of IIIc with mp 122-123°C (from heptane). IR spectrum (in $CHCl_3$): 1670 (C=O) and 3420 cm^{-1} (NH). PMR spectrum (CCl_4): 2.27 (6H, s, 3- and 5-CH_3), 2.32 (3H, s, $COCH_3$), 2.65 (3H, s, $NHCH_3$), 4.35 (1H, s, NH), and 6.47-7.37 ppm (4H, m, C_6H_4). Found: C 69.2; H 7.0; N 17.5%. $C_{14}H_{17}N_3O$. Calculated: C 69.1; H 7.0; N 17.3%.

2,5-Dimethylpyridazino [1,6-a]benzimidazolia-4-one (Va) and 1-(o-Aminomethylphenyl)-3-methyl-4-carbethoxypyrazole (VIa). A solution of 2.75 g (0.01 mole) of salt Ia, 4.0 g (0.03 mole) of potassium carbonate, and 3 ml of acetoacetic ester in 15 ml of water was heated with stirring at 80°C for 3 h, after which it was cooled, and the resulting precipi-

tate was removed by filtration and washed with acetone and ether to give 1.1 g (50%) of colorless needles of Va with mp 254-255°C (from water). IR spectrum (mineral oil): 1630 cm^{-1} (C=O). PMR spectrum (CF_3COOH): 2.25 (3H, s, 2-CH_3), 4.05 (3H, s, 5-CH_3), 6.78 (1H, s, 3-H), 7.43 (3H, m, 6- and 8-H), and 7.95 ppm 1H, m, 9-H). Found: C 67.6; H 5.2; N 20.5%. $C_{12}H_{11}N_3O$. Calculated: C 67.6; H 5.0; N 20.7%. The mother liquor was extracted with chloroform, and the combined organic layers were evaporated to the minimal volume and passed through a column filled with Al_2O_3 (elution with benzene). The oil (0.6 g) that remained after removal of the benzene by distillation was dissolved in acetone, and the solution was acidified to pH 2-3 with concentrated HCl. The precipitate was separated and washed with acetone to give give 0.4 g (13%) of colorless crystals of the hydrochloride of pyrazole VIa with mp 189-191°C (from alcohol with ethyl acetate). IR spectrum (mineral oil): 1700 (C=O), 2510 ($\overset{+}{N}H\equiv$), and 3085 cm^{-1} (NH). PMR spectrum (CF_3COOH): 1.0 (3H, t, CH_2—CH_3), 2.2 (3H, s, 3-CH_3), 2.8 (3H, s, $NHCH_3$), 4.05 (2H, q, CH_2—CH_3), 7.28 (4H, m, C_6H_4), and 8.35 ppm (1H, s, 5-H). Found: C 57.1; H 6.0; Cl 11.8; N 14.1%. $C_{14}H_{17}N_3O_2 \cdot HCl$. Calculated: C 56.9; H 6.1; Cl 12.0; N 14.2%.

2,5,7,8-Tetramethylpyridazine[1,6-a]benzimidazolia-4-one (Vb) and 1-(2-Methylamino-4,5-dimethylphenyl)-3-methyl-4-carbethoxypyrazole (VIb). These compounds were obtained from salt Ib by a procedure similar to that used to obtain Va and VIa. Compound Vb was obtained in 44% yield in the form of colorless needles with mp 299-300°C (from aqueous alcohol). IR spectrum (mineral oil): 1600 cm^{-1} (C=O). PMR spectrum (CF_3COOH): 2.15 (6H, s, 7- and 8-CH_3), 2.28 (3H, s, 2-CH_3), 4.03 (3H, s, 5-CH_3), 6.75 (1H, s, 3-H), 7.23 (1H, s, 6-H), and 7.73 ppm (1H, s, 9-H). Found: C 70.0; H 6.1; N 17.3%. $C_{14}H_{15}N_3O$. Calculated: C 69.7; H 6.2; N 17.4%.

Pyrazole VIb was obtained in 14% yield. The hydrochloride was obtained by treatment of an acetone solution of VIb with concentrated HCl. The colorless needles had mp 204-205°C (from alcohol with ethyl acetate). Found: C 59.3; H 6.6; Cl 10.8; N 12.9%. $C_{16}H_{21}N_3O_2$. Calculated: C 59.4; H 6.8; Cl 11.0; N 13.0%.

1-(o-Methylaminophenyl)-3,5-dimethyl-4-carbethoxypyrazole (VIc). A solution of 2.89 g (0.01 mole) of salt Ic [4], 4.0 g (0.03 mole) of potassium carbonate, and 2.5 ml of acetoacetic ester in 8 ml of water was heated at 80°C for 2 h, after which it was cooled, and the precipitate was removed by filtration, washed with water, dried, and treated with 20 ml of chloroform to give 0.9 g of the starting salt. Extraction of the aqueous layer with chloroform gave 0.25 g of salt Ic. The chloroform filtrate was purified with a column filled with Al_2O_3 (elution with chloroform) to give 0.75 g (62%) of colorless needles of VIc with mp 111-112°C (from heptane). IR spectrum ($CHCl_3$): 1700 (C=O) and 3430 cm^{-1} (NH). PMR spectrum (CCl_4): 1.27 (3H, t, CH_2—CH_3), 2.25 (3H, s, 3-CH_3), 2.30 (3H, s, 5-CH_3), 4.17 (2H, q, CH_2—CH_3); 4.35 (1H, s, NH), and 6.47-7.37 ppm (4H, m, C_6H_4). Found: C 65.8; H 6.9; N 15.3%. $C_{15}H_{19}N_3O_2$. Calculated: C 65.9; H 7.0; N 15.4%.

Reaction of Salt Ia with Acetylacetone in a Solution of Potassium Carbonate in DMF. A mixture of 1.5 g (5 mmole) of salt Ia, 2.0 g (15 mmole) of potassium carbonate, and 1.2 ml of acetylacetone in 10 ml of DMF was heated with stirring at 80°C for 2 h. After 15-20 min, a yellowish precipitate formed. The reaction mixture was cooled, and the precipitate was removed by filtration and washed with water and acetone to give 0.7 g (38%) of pyridazinobenzimidazolium iodide IIa. The product was identical to a genuine sample of salt IIa. A complex mixture of substances that could not be separated was isolated by dilution of the DMF with water and subsequent extraction with chloroform. Chromatography of the mixture in a thin layer of Al_2O_3 (elution with chloroform) did not reveal the presence of a substance that was identical to pyrazole IIIa.

1-(Acetylisopropylidene)amino-3-methylbenzimidazolium Iodide (VIIa). A solution of 2.75 g (0.01 mole) of salt Ia in 10 ml of acetylacetone was heated at 140-160°C for 1 h, after which it was cooled, and the precipitate was removed by filtration and washed with acetone to give 1.8 g (50%) of pale-pink needles with mp 179-180°C (dec., from alcohol). IR spectrum (mineral oil): 1700 cm^{-1} (C=O). Found: C 43.9; H 4.5; I 35.4; N 12.0%. $C_{13}H_{16}IN_3O$. Calculated: C 43.7; H 4.5; I 35.6; N 11.8%.

1-(Acetylisopropylideneamino)-3,5,6-trimethylbenzimidazole (VIIb). This compound was obtained in 48% yield by a method similar to that used to prepare ketimine VIIa. The colorless needles had mp 189-190°C (dec., from alcohol). IR spectrum (mineral oil): 1705 cm^{-1} (C=O). Found: C 46.5; H 5.3; I 32.8; N 11.0%. $C_{15}H_{20}IN_3O$. Calculated: C 46.8 H 5.2; I 33.0; N 10.9%.

Action of Bases on Ketimines VII. A) Potassium Carbonate in Water. A solution of 0.3 g (0.8 mmole) of iodide VIIa and 0.1 g (0.7 mmole) of potassium carbonate in 2 ml of water was

heated at 80-90°C for 5 min, after which it was cooled, and the precipitate was removed by filtration and washed with acetone to give 0.1 g (47%) of colorless needles of salt Ia with mp 205-207°C (no melting-point depression was observed for a mixture with a genuine sample of iodide Ia). Evaporation of the acetone left 0.09 g (49%) of colorless needles of pyrazole IIIa with mp 111-112°C; the product was identical to IIIa.

B) Triethylamine in Acetonitrile. A solution of 0.7 g (2 mmole) of iodide VIIa and 0.35 ml (2.5 mmole) of triethylamine in 5 ml of acetonitrile was refluxed for 1 h, after which the mixture was evaporated to dryness, and the residue was washed with water and chloroform to give 0.05 g (14%) of yellow-green crystals that were identical to IIa. Chromatography of the chloroform solution with a column filled with Al_2O_3 (elution with chloroform) gave 0.3 g (66%) of pyrazole IIIa.

C) Potassium Carbonate in DMF. A mixture of 0.2 g (0.5 mmole) of ketimine VIIb and 0.1 g (0.7 mmole) of potassium carbonate in 2 ml of DMF was heated at 80-90°C for 5 min, after which it was cooled and diluted with 10 ml of water, and the precipitate was removed by filtration to give 0.11 g (86%) of colorless needles of IIIb with mp 111-112°C (no melting-point depression was observed for a mixture of this product with a genuine sample of pyrazole IIIb).

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ORGANIC LUMINOPHORES WITH ORANGE-RED AND RED LUMINESCENCE

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New organic luminophores that have orange-red and red luminescence and contain conjugated 1,3,5-triaryl-2-pyrazoline and 7H-imidazo[1,2-b]benz[de]isoquinoline-7-one groupings in the same molecule were synthesized. The introduction of a 2-naphthyl residue in the 1 position of the pyrazoline ring and annelation of 1,2-naphthylene or 4,5-naphthylene systems to the imidazole ring in place of the phenylene system lead to bathochromic and bathofluoric effects. The luminescence maxima of the synthesized compounds are found at 575 to 645 nm, and the quantum yields range from 0.7 to 0.9.

Primarily luminophores with blue luminescence are known in the 1,3,5-triaryl-2-pyrazoline series [1]. By combining 1,3,5-triaryl-2-pyrazoline and 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one groupings in the same molecule we have synthesized seldom encountered luminophores with orange-red luminescence, including 3(and 4)-(1,5-diphenyl-2-pyrazolin-3-yl)-7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one (Ia) with a luminescence maximum in toluene at 595 nm and a quantum yield of 0.9 [2]. Inasmuch as it is a strong electron acceptor, the 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one residue interacts with the unshared electrons of the $N_{(1)}$ atom, thereby giving rise to strong bathochromic and bathofluoric effects. Two isomers that differ from one another with respect to their melting points and IR spectra but have virtually identical electronic absorption spectra and luminescence spectra are formed in the synthesis of Ia. It is therefore unnecessary to isolate the individual isomers for various applications [3].

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