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Cyclization of 3-Ethoxycarbonylmethyl-, 3-Cyanomethyl-, and 3-Acetylmethyl-1-amino-2-methylbenzimidazolium Salts Effected by Acetic Anhydride in the Presence of a Base

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Abstract—3-Ethoxycarbonylmethyl- and 3-cyanomethyl-1-amino-2-methylbenzimidazolium chlorides cyclized at treatment with acetic anhydride in the presence of potassium carbonate to afford a mixture of derivatives of pyrazolo[1,5-*a*]benzimidazole and 4-aminopyrrolo[1,2-*a*]benzimidazole. Therewith in the first case prevails the process of pyrazole ring fusion, and in the latter pyrrole ring is fused. 3-Aroyl(thenoyl)methyl-1-amino-2-methylbenzimidazolium bromides under the same conditions are converted into 1-aroyl(thenoyl)-2-methyl- and 2-4-acetamido-3-acetylpyrrolo[1,2-*a*]benzimidazoles.

3-Alkoxycarbonylmethyl- and 3-cyanomethyl-1-alkyl-2-methylbenzimidazolium salts were reported [1] to cyclize under treatment with carboxylic acids anhydrides in the presence of bases furnishing functionally-substituted 2,4-dialkylpyrrolo[1,2-*a*]benzimidazoles. The pyrrole ring closure occurred here involving an activated methyl group in substituents in the position *3* of benzimidazole ring. The cations of 1-amino-3-alkyl-2-methylbenzimidazolium transformed under these conditions involving N-amino- and 2-methyl groups into 2,4-dialkyl-pyrazolo[1,5-*a*]-benzimidazoles [2].

In the present study we investigated the features of reaction of acetic anhydride and potassium carbonate with 3-ethoxycarbonylmethyl- **I**, 3-cyanomethyl- **II**, and 3-acylmethyl-1-amino-2-methylbenzimidazolium **IIIa–c** salts which presumably might undergo cyclization both into derivatives of 4-aminopyrrolo[1,2-*a*]benzimidazole and pyrazolo[1,5-*a*]benzimidazole.

Initial chlorides **I** and **II** were obtained by fusion of 1-amino-2-methylbenzimidazole with the corresponding monochloroacetic acid derivatives. The synthesys of ketones **III** is described in [3].

It was established that at boiling of ether **I** with acetic anhydride and potassium carbonate formed a mixture of 3-acetyl-2-methyl-4-ethoxycarbonylmethylpyrazolo[1,5-*a*]benzimidazole **IV** and 3-acetyl-4-di-acetylamino-1-ethoxycarbonylpyrrolo[1,2-*a*]benzimidazole **V** in a ratio ~ 4:1 (according to ^{1}H NMR spectrum).

† Deceased.

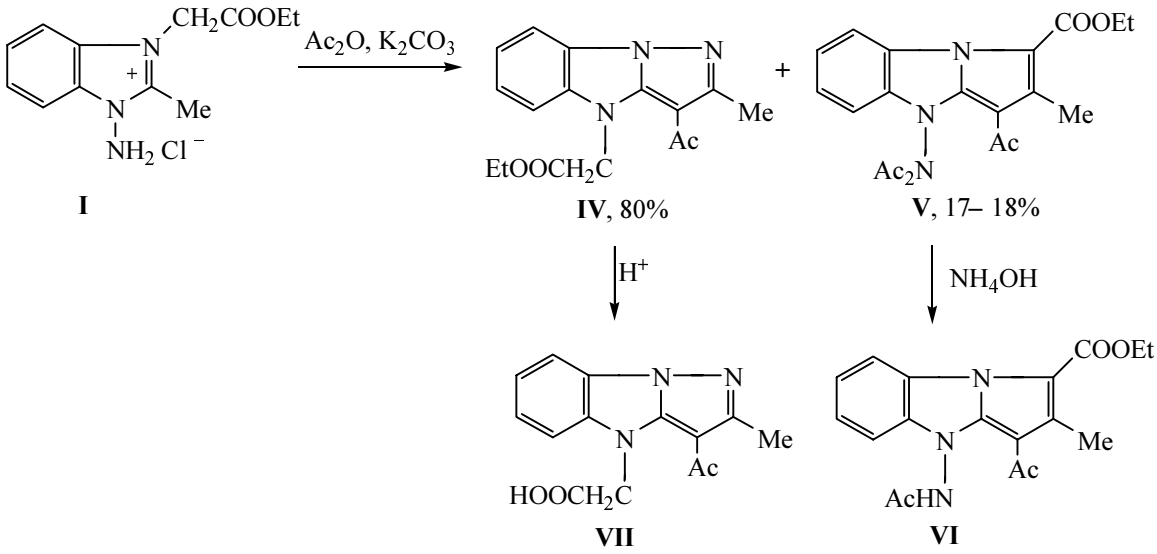
The double recrystallization of the mixture from ethanol afforded in the pure state pyrazolobenzimidazole **IV** whose structure is confirmed by the presence in the ^{1}H NMR spectrum of the signal from the protons of methylene group at δ 5.7 ppm. In the IR spectrum of compound **IV** appear two strong bands at 1630 and 1733 cm^{-1} assigned to the absorption of acetyl and ester carbonyls respectively. At short boiling in concn. HCl ether **IV** readily yielded acid **VII**.

We failed to isolate 4-diacetylaminopyrrolo[1,2-*a*]-benzimidazole **V** from the reaction mixture by chromatography due to very close values of R_f of compounds **IV** and **V**. Therefore by treatment with concn. NH_4OH compound **V** (R_f 0.6) was converted into monoacetylamino derivative **VI** (R_f 0.3). In the IR spectrum of compound **VI** alongside the three absorption band of carbonyl groups at 1630, 1685, and 1710 cm^{-1} appears a band ν_{NH} at 3250 cm^{-1}. The proton signal of the NH group in the ^{1}H NMR spectrum is observed at 9.4 ppm (Scheme 1).

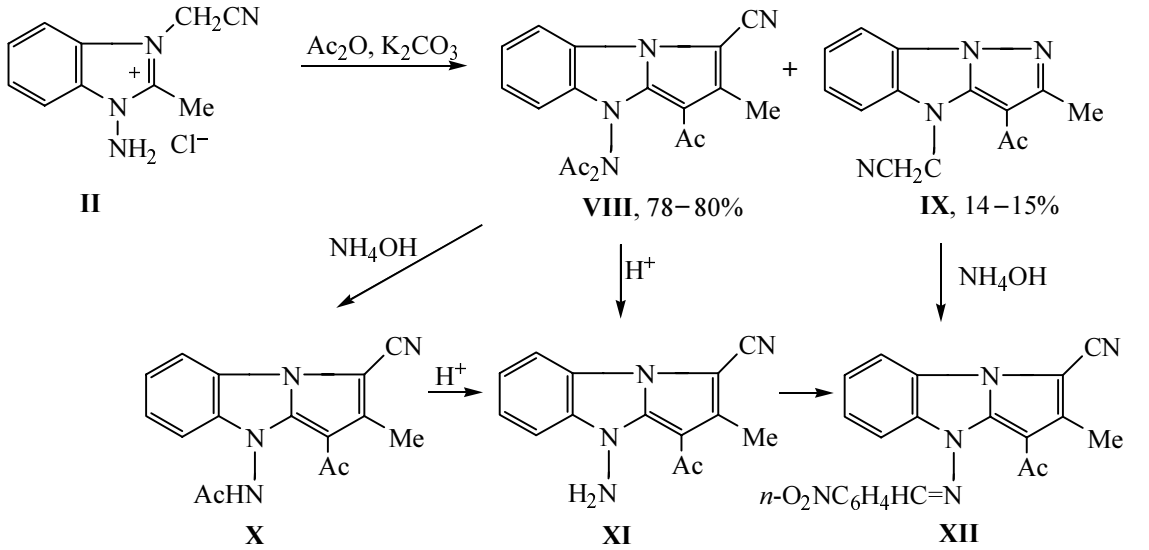
The cyclization of 1-amino-2-methyl-3-cyano-methylbenzimidazolium chloride **II** under the same conditions also afforded a mixture of the corresponding compounds from the pyrrolo- and pyrazolobenzimidazole series. However here the main reaction product was 1-cyano-pyrrolobenzimidazole **VIII**, and the yield of 4-cyano-methylpyrazolo[1,5-*a*]benzimidazole **IX** did not exceed 14–15% (Scheme 2).

Diacetylamino derivative **VIII** partially loses one of its N-acetyl groups even in the process of chromato-

Scheme 1.



Scheme 2.



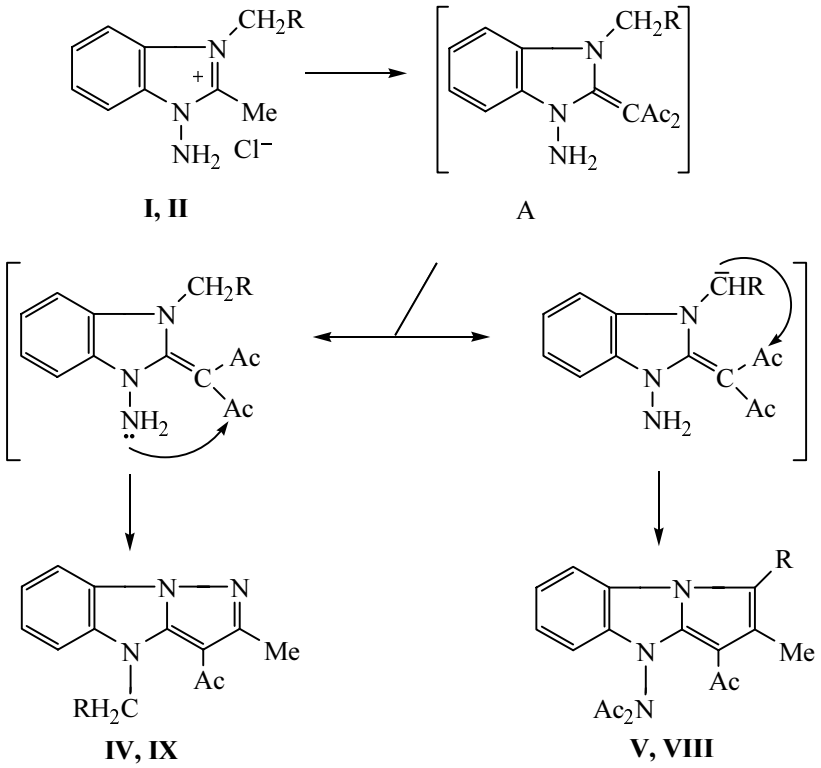
graphic separation on alumina giving compound **X**. The latter was obtained in a quantitative yield at treating diacetylamine **VIII** with the concn NH_4OH. Therewith in the IR spectrum of compound **X** were retained two absorption band of C=O groups at 1632 and 1650 cm^{-1} present in the spectrum of the initial compound **VIII** and the band in the 1736 cm^{-1} region disappeared.

The boiling of acetamides **VIII** and **X** in concn HCl for 20–25 min resulted in pyrrolobenzimidazole **XI** unsubstituted at the N-amino group. Interestingly, the 3-actyl group wasnot affected although as a rule 1- and 3—acylpyrrolobenzimidazoles were easily hydrolysable in acid media [1, 4]. In contrast to 4-amino-pyrrolo-benzimidazoles with unoccupied positions *1* and *3* [3], amine **XI** cleanly formed Schiff bases of **XII** type at heating with aromatic aldehydes in acetic acid.

In the IR spectra of 1-cyanopyrrolobenzimidazoles **VIII**, **X–XII** a strong absorption band of the cyano group is observed in the region 2200 cm^{-1}, whereas in the spectra of initial salt **II** and 4-cyanomethylpyrazolobenzimidazole **IX** where this group is not conjugated with the heterocycle this band does not appear.

We believe that the considerably different ratio of derivatives of pyrrolo[1,2-*a*]- and pyrazolo[1,5-*a*]benzimidazoles arising at cyclization of chlorides **I** and **II** originates from unlike CH-acidity of 3-methylene groups in these salts. In keeping with the generally accepted

Scheme 3.



R = COOEt (**I, IV, V**), CN (**II, VIII, IX**).

views both pyrazolo[1,5-*a*]benzimidazoles and pyrrolo-[1,2-*a*]benzimidazoles should form under these conditions through the same intermediate compound, acetyl-substituted methylene anhydrobase A (Scheme 3) [5].

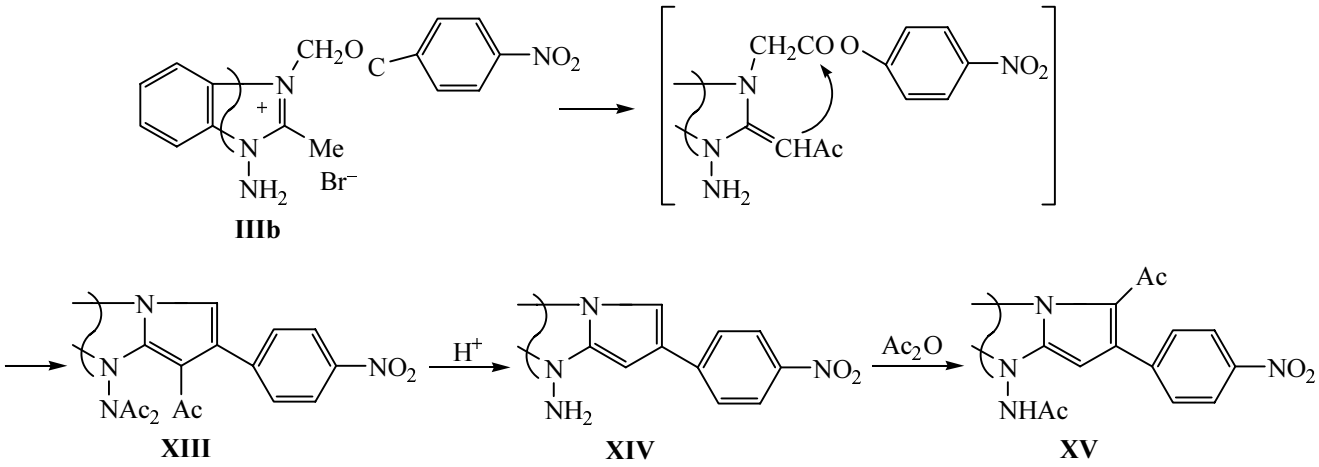
It is clear that the cyclization of diacetylmethine A occurs rather involving the arising in the reaction mixture more nucleophilic carbanion than the neutral N-amino group (as shown in [6], formation of an N-anion under these conditions is hardly possible). The values of σ constants of groups COOEt (0.398) and CN (0.678) [7] show that the C-anion would be easier generated from the cyanomethyl salt **II** resulting in the prevailing formation of pyrrolobenzimidazole **VIII**. Inasmuch as the CH-acidity of the 3-methylene group in ester **I** is lower, dominates the cyclization process involving the N-amino group of pyrazolobenzimidazole **IV**.

The problem whether the precursors of compounds **IV, V, VIII** and **IX** are mono- or diacetylmethines of A type is open to discussion. However our experiments with ketones **III** has unambiguously demonstrated as we discuss below that the presence of the C-acetyl substituents in the final reaction products **XIII, XIVa, XIVc** originates just from acetylation of the methylene anhydrobases and not of tricyclic systems.

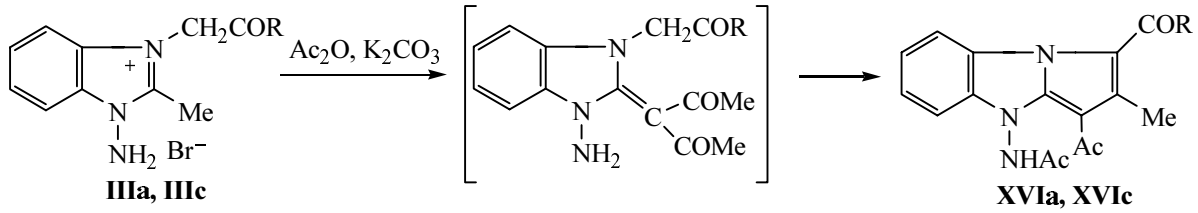
1-Amino-3-acylmethyl-2-methylbenzimidazolium bromides **IIIa–IIIc** like cyanomethyl salt **II** in reaction with acetic anhydride and potassium carbonate more favored conversion into pyrrolo[1,2-*a*]benzimidazoles. We failed to detect in this case formation of pyrazolo[1,5-*a*]-benzimidazole derivatives. The cyclization of 3-phenacyl- and 3-thenoylmethyl derivatives **IIIa, IIIc** afforded several products but here it was due to the possibility to build up the pyrrole ring both involving the activated methylene group and ketone carbonyl of the 3-acylmethyl moiety in the initial salt. 1-Amino-2-methyl-3-(4-nitrophenacyl)benzimidazolium bromide **IIIb** is an exception for it selectively reacts involving the keto group to afford light-yellow 3-acetyl-4-diacetylamino-2-(4-nitrophenyl)pyrrolobenzimidazole **XIII** (yield 75%) that easily loses one of its N-acetyl groups similarly to compound **VIII**.

The structure of compound **XIII** as 2-(4-nitrophenyl) derivative was proved by formation at its acid hydrolysis of orange 4-amino-2-(4-nitrophenyl)pyrrolobenzimidazole **XIV**. It should be noted that the attempt to obtain this pyrrolobenzimidazole from salt **IIIb** under Chichibabin reaction conditions failed [3]. In the ^{1}H NMR spectrum of compound **XIV** the signals of protons H^3 and H^1 appear

Scheme 4.



Scheme 5.



III, XVI, R = Ph (**a**), 2-thienyl (**c**).

as doublets (J 1.46 Hz) due to coupling with each other, and they are observed at δ 6.01 and 8.0 ppm respectively (cf. [4, 8]). On the contrary, in the spectrum of acetyl derivative **XIII** the signal of H^3 proton is lacking, and the peak of the H^1 proton turns out as a singlet thus indicating that the C-acetyl group is attached to position *3* of the heterosystem. A direct acetylation of 4-aminopyrrolobenzimidazole **XIV** gives 1-acetyl isomer **XV** in a good yield. Therefore it may be assumed that the formation of a 3-acetyl substituents in compound **XIII** is due to the reaction proceeding through B intermediate.

As already mentioned, from 1-amino-2-methyl-3-phenacylbenzimidazolium bromide **IIIa** by treating with acetic anhydride and potassium carbonate a mixture of two compounds was obtained to one of which was assigned the structure of 1-benzoyl-2-methylpyrrolobenzimidazole **XVIa** (yield 22%). Actually, only the presence of a C-benzoyl substituent can be responsible both for the bright yellow color of compound **XVIa** and for the isolation of benzoic acid from its hydrolysis products. The IR and ^{1}H NMR spectra are also completely consistent with structure **XVIa**.

We failed to isolate in the individual state the main product of salt **IIIa** cyclization because of its lability and high solubility in the majority of organic solvents. However it proved that a colorless low-melting precipitate obtained after separation of compound **XVIa** on boiling for a short time in the hydrochloric acid converted into a known 4-amino-2-phenylpyrrolo[1,2-*a*]benzimidazole [3]. 1-Acetyl-4-diacetylamino-2-phenylpyrrolo[1,2-*a*]-benzimidazole **XVII** obtained by acetylation of the latter was not similar to the cyclization product of ketone **IIIa** and thus presumably the unidentified compound was an analog of 3-acetylpyrrolobenzimidazole **XIII**.

In contrast to ketones **IIIa** and **IIIb** the cyclization of 1-amino-2-methyl-3-(2-thenoylmethyl)benzimidazolium bromide **IIIc** occurred predominantly with participation of the methylene and not the carbonyl group of the thenoylmethyl fragment affording yellow 3-acetyl-2-methyl-1-(2-thenoyl)pyrrolobenzimidazole **XVIc** in 57–60% yield.

Apparently the reactivity of the keto group here is due to the conjugation with the π-rich thiophene ring. Taking into account the existing data on lack of further acetylation of 1-acylpyrrolobenzimidazoles even under very severe conditions [9] the presence of 3-acetyl substituents in compounds **XVIa, c** can be rationalized

only by assuming intermediate formation of diacetylated methylene anhydrobases of A type.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord 75IR from mulls in mineral oil. ^{1}H NMR spectra were registered on spectrometer Unity-300 (300 MHz). The reaction progress was monitored and the homogeneity of the compounds synthesized was checked by TLC on plates with Al_2O_3 of the III activity grade, eluent chloroform, development in iodine vapor in a humid chamber.

1-Amino-2-methyl-3-ethoxycarbonylmethylbenzimidazolium chloride (I). A mixture of 1.47 g (0.01 mol) of 1-amino-2-methylbenzimidazole [2] and 2.1 ml (0.02 mol) of ethyl monochloroacetate was fused for 5 min at 100°C. On cooling the melt was ground with 20 ml of acetone, and the precipitate was filtered off. Yield 2.60 g (97%), colorless crystals, mp 278–279°C (EtOH). IR spectrum, cm^{-1}: 1651 (C=N), 1736 (C=O), 3130, 3200 (NH_2). Found, %: C 53.25; H 6.07; Cl 13.32; N 15.71. $C_{12}H_{16}ClN_3O_2$. Calculated, %: C 53.44; H 5.98; Cl 13.14; N 15.58.

1-Amino-2-methyl-3-cyanomethylbenzimidazolium hydrate chloride (II). A mixture of 1.47 g (0.01 mol) of 1-amino-2-methylbenzimidazole and 1.3 ml (0.02 mol) of chloroacetonitrile was fused for 10 min at 110–115°C. On cooling the melt was ground with 20 ml of acetone, and the precipitate was separated and dried at 100°C. Yield 1.98 g (82%), colorless crystals that started to melt at 167–168°C, then again crystallized and melted for another time at 183–184°C (from EtOH). IR spectrum, cm^{-1}: 1640 (C=N), 3121, 3211 (NH_2), 3388, 3464 (H_2O). Found, %: C 50.10; H 5.41; Cl 14.58; N 23.12. $C_{10}H_{11}ClN_4 \cdot H_2O$. Calculated, %: C 49.90; H 5.44; Cl 14.73; N 23.28.

3-Acetyl-2-methyl-4-ethoxycarbonylmethylpyrazolo[1,5-*a*]benzimidazole (IV) and 4-acetamido-3-acetyl-2-methyl-1-ethoxycarbonylpyrrolo[1,2-*a*]benzimidazole (VI). A dispersion of 1.62 g (6 mmol) of chloride **I** and 0.83 g (6 mmol) of anhydrous potassium carbonate in 30 ml of acetic anhydride was heated at reflux for 3 h. On cooling 60 ml of water was added, and the precipitate separated after decomposition of excess acetic anhydride (1.76 g) was filtered off and washed with water. After two-fold recrystallization from ethanol 0.92 g of pyrazolo[1,5-*a*]benzimidazole **IV** was obtained.

The combined mother liquors containing compounds **IV** and **V** were evaporated to dryness, the residue was dissolved in 10 ml of chloroform, and the solution was shaken for 4 h at 20–25°C with 1 ml of concn. NH_4OH. Then the chloroform solution was separated, evaporated till the volume of 5 ml, and subjected to chromatography on a column (20×200 mm) packed with Al_2O_3, eluent chloroform As first fraction with R_f 0.6 was additionally obtained 0.24 g of pyrazolobenzimidazole **IV**. Yield 1.16 g (64%), mp 171–172°C (from EtOH). IR spectrum, cm^{-1}: 1630 (COMe), 1733 (COOEt). ^{1}H NMR spectrum, δ, ppm: 1.20 t (3H, $CH_2\underline{CH_3}$, *J* 7.2 Hz), 2.43 s (3H, CH_3), 2.63 s (3H, $COCH_3$), 4.18 q (2H, $\underline{CH_2}CH_3$, *J* 7.2 Hz), 5.57 s (2H, CH_2), 7.28 m (3H, H$^{5-7}$), 7.79 m (1H, H^8). Found, %: C 64.27; H 5.85; N 14.18. $C_{16}H_{17}N_3O_3$. Calculated, %: C 64.20; H 5.72; N 14.04.

From the second fraction with R_f 0.3 pyrrolo[1,2-*a*]-benzimidazole **VI** was isolated in amount of 0.26 g (yield 13%), mp 186–187°C (from EtOH). IR spectrum, ν, cm^{-1}: 1630 (COMe), 1685 (NHCOMe), 1710 (COOEt), 3250 (NH). ^{1}H NMR spectrum, δ, ppm: 1.46 t (3H, $CH_2\underline{CH_3}$, *J* 7.1 Hz), 2.21 s (3H, $NHCOCH_3$), 2.48 s (3H, CH_3), 2.69 s (3H, C-$COCH_3$), 4.46 q (2H, $\underline{CH_2}CH_3$, *J* 7.1 Hz), 7.21–7.35 m (3H, H$^{5-7}$), 8.56 d (1H, H^8, *J* 8.06 Hz), 9.40 s (1H, NH). Found, %: C 63.44; H 5.47; N 12.42. $C_{18}H_{19}N_3O_4$. Calculated, %: C 63.33; H 5.61; N 12.31.

3-Acetyl-2-methyl-4-carboxymethylpyrazolo[1,5-*a*]benzimidazole (VII). A solution of 0.6 g (2 mmol) of ester **IV** in 10 ml of conc. HCl was boiled for 30 min. On cooling the separated precipitate was filtered off and washed with water. Yield 0.50 g(92%), mp 273– 274°C (from BuOH). IR spectrum, cm^{-1}: 1629 (COMe), 1727 (CO), 3340–3560 (OH). ^{1}H NMR spectrum, δ, ppm: 2.40 s (3H, CH_3), 2.58 s (3H, $COCH_3$), 5.58 s (2H, CH_2), 7.32 t (1H, H^7, *J* 7.54 Hz), 7.37 t (1H, H^6, *J* 7.39 Hz), 7.69 d (1H, H^5, *J* 7.40 Hz), 7.80 d (1H, H^8, *J* 7.54 Hz), 13.04 br.s (1H, OH). Found, %: C 61.82; H 4.91; N 15.32. $C_{14}H_{13}N_3O_3$. Calculated, %: C 61.99; H 4.83; N 15.49.

Reaction on chloride II with acetic anhydride. A dispersion of 1.22 g (5 mmol) of salt **II** and 0.69 g (5 mmol) of potassium carbonate was boiled in 15 ml of acetic anhydride for 3 h. On cooling the excess acetic anhydride was decomposed by adding 30 g of ice. The separated crystals were filtered off, washed with water, and dried in a vacuum desiccator over P_2O_5. From this precipitate (1.25 g) by means of two-fold recrystallization from butanol was separated **3-acetyl-4-diacetylamino-2-methyl-1-cyanopyrrolo[1,2-*a*]benzimidazole (VIII)**

in 0.63 g (38%) yield, mp 220–221°C (from BuOH). IR spectrum, cm^{-1}: 1632 (COMe), 1650 (NCOMe), 1736 (NCOMe), 2200 (CN). ^1H NMR spectrum, δ, ppm: 2.44 s (3H, CH_3), 2.46 s [6H, $N(COCH_3)_2$], 2.62 s (3H, C–$COCH_3$), 7.26 m (1H, H^8), 7.42 m (2H, $H^{6,7}$), 7.98 m (1H, H^5). Found, %: C 64.40; H 4.63; N 16.58. $C_{18}H_{16}N_4O_3$. Calculated, %: C 64.28; H 4.79; N 16.66.

The butanol mother liquors were treated as described above for isolation of compounds **IV** and **VI** to obtain 0.15 g of **3-acetyl-2-methyl-4-cyanomethylpyrazolo[1,5-*a*]benzimidazole (IX)** (yield 12%, R_f 0.6) and 0.28 g of **4-acetamido-3-acetyl-2-methyl-1-cyanopyrrolo[1,2-*a*]benzimidazole (X)** (yield 19%, R_f 0,3). Compound **IX** has mp 239–240°C (from BuOH). IR spectrum, cm^{-1}: 1627 (COMe). ^1H NMR spectrum, δ, ppm: 2.52 s (3H, CH_3), 2.70 s (3H, $COCH_3$), 6.19 s (2H, CH_2), 7.50 m (3H, H^{5-7}), 7.87 m (1H, H^8). Found, %: C 66.73; H 4.82; N 22.38. $C_{14}H_{12}N_4O$. Calculated, %: C 66.65; H 4.79; N 22.21.

For compound **X** mp 231–232°C (EtOH). IR spectrum, ν, cm^{-1}: 1633 (COMe), 1652 (NHCOMe), 2197 (CN), 3198 (NH). ^1H NMR spectrum, δ, ppm: 2.12 s (3H, CH_3), 2.32 s (3H, $COCH_3$), 2.40 s (3H, $NHCOCH_3$), 7.25 m (3H, H^{6-8}), 7.72 m (1H, H^5), 9.20 s (1H, NH). Found, %: C 65.48; H 4.65; N 19.17. $C_{16}H_{14}N_4O_2$. Calculated, %: C 65.30; H 4.79; N 19.04.

4-Amino-3-acetyl-2-methyl-1-cyanopyrrolo-[1,2-*a*]benzimidazole (XI). A solution of 0.34 g (1 mmol) of diacetylamino derivative **VIII** in 10 ml of concn. HCl was boiled for 20 min. On cooling the precipitate was filtered off and washed with water. Yield 0.22 g (88%), mp 213–214°C (from 1-BuOH). IR spectrum, ν, cm^{-1}: 1633 (COMe), 2202 (CN), 3221, 3312 (NH_2). ^1H NMR spectrum, δ, ppm: 2.52 s (3H, CH_3), 2.58 s (3H, $COCH_3$), 6.42 s (2H, NH_2), 7.34 t (1H, H^6, ^3J 8.13, ^4J 1.17 Hz), 7.47 t (1H, H^7, ^3J 7.47, ^4J 1.09 Hz), 7.62 d (1H, H^5, ^3J 8.13 Hz), 7.76 d (1H, H^8, ^3J 7.47 Hz). Found, %: C 66.72; H 4.85; N 22.12. $C_{14}H_{12}N_4O$. Calculated, %: C 66.65; H 4.79; N 22.21.

Amine **XI** was obtained in the same way from reagent **X.**

3-Acetyl-2-methyl-4-(4-nitrobenzylideneamino)-1-cyanopyrrolo[1,2-*a*]benzimidazole (XII). A solution of 0.25 g (1 mmol) of 4-aminopyrrolobenzimidazole **XI** and 0.15 g (1 mmol) of 4-nitro-benzaldehyde in 3 ml of acetic acid was boiled for 20 min. On cooling the separated yellow precipitate was filtered off and washed with water. Yield 0.31 g (79%), mp 203–204°C (from DMF). IR spectrum, cm^{-1}: 1635 (COMe). ^1H NMR spectrum, δ, ppm: 2.59 s (3H, CH_3), 2.68 s (3H, $COCH_3$), 7.41 t (1H, H^6, *J* 7.62 Hz), 7.48 t (1H, H^7, *J* 7.47 Hz), 7.83 d (1H, H^5, *J* 7.63 Hz), 7.85 s (1H, N=CH), 7.99 d (1H, H^8, *J* 7.47 Hz), 8.02 d (2H, $H^{2',6'}$, *J* 8.73 Hz), 8.33 d (2H, $H^{3',5'}$, *J* 8.72 Hz). Found, %: C 65.34; H 3.83; N 18.35. $C_{21}H_{15}N_5O_3$. Calculated, %: C 65.45; H 3.92; N 18.17.

3-Acetyl-4-diacetylamino-2-(4-nitrophenyl)pyrrolo[1,2-*a*]benzimidazole (XIII). A solution of 0.82 g (2 mmol) of salt **IIIb** and 0.28 g (2 mmol) of potassium carbonate in 10 ml of acetic anhydride was boiled for 25 min. On cooling the light-yellow precipitate was filtered off and washed with ether on the filter. Yield 0.63 g (75%), mp 233–234°C (from BuOH). IR spectrum, cm^{-1}: 1613 (COMe), 1653 (NCOMe), 1760 (NCOMe). ^1H NMR spectrum, δ, ppm: 1.94 s (3H, $COCH_3$), 2.52 s [6H, $N(COCH_3)_2$], 7.06 s (1H, H^1), 7.25 d (1H, H^8, *J* 7.04 Hz), 7.35 t (1H, H^7, *J* 7.04 Hz), 7.40 t (1H, H^6, *J* 7.33 Hz), 7.61 d (1H, H^5, *J* 7.33 Hz), 7.63 d (2H, $H^{2',6'}$, *J* 8.78 Hz), 8.30 d (2H, $H^{3',5'}$, *J* 8.79 Hz). Found, %: C 63.30; H 4.47; N 13.50. $C_{22}H_{18}N_4O_5$. Calculated, %: C 63.15; H 4.34; N 13.39.

4-Amino-2-(4-nitrophenyl)pyrrolo[1,2-*a*]-benzimidazole (XIV). A solution of 0.84 g (2 mmol) of compound **XIII** in 10 ml of conc. HCl was boiled for 15 min. On cooling the precipitate was filtered off, treated on the filter with 2 ml of concn. NH_4OH, and washed with water to obtain 0.32 g of orange solid. Alkalizing of the mother liquor provided additional 0.16 g of compound **XIV.** Yield 0.48 g (83%), mp 219–221°C (BuOH). IR spectrum, cm^{-1}: 3349, 3440 (NH_2). ^1H NMR spectrum, δ, ppm: 5.75 s (2H, NH_2), 6.01 d (1H, H^3, ^4J 1.76 Hz), 7.10 t (1H, H^7, *J* 7.03 Hz), 7.28 t (1H, H^6, *J* 7.54 Hz), 7.35 d (1H, H^8, *J* 7.03 Hz), 7.71 d (1H, H^5, *J* 7.51 Hz), 7.90 d (2H, $H^{2',6'}$, *J* 9.08 Hz), 8.01 d (1H, H^1, *J* 1.47 Hz), 8.20 d (2H, $H^{3',5'}$, *J* 9.08 Hz). Found, %: C 65.81; H 4.27; N 19.28. $C_{16}H_{12}N_4O_2$. Calculated, %: C 65.75; H 4.14; N 19.17.

4-Acetamido-1-acetyl-2-(4-nitrophenyl)pyrrolo-[1,2-*a*]benzimidazole (XV). A solution of 0.29 g (1 mmol) of 4-aminopyrrolobenzimidazole **XIV** in 3 ml of acetic anhydride was boiled for 1 h. On cooling the excess acetic anhydride was decomposed with 10 ml of water, the separated light-yellow precipitate was filtered off. Yield 0.30 g (79%), mp 275–276°C (from BuOH). IR spectrum, cm^{-1}: 1630 (COMe), 1710 (NHCOMe). ^1H NMR spectrum, δ, ppm: 1.45 s (3H, $COCH_3$), 2.13 s (3H, $NHCOCH_3$), 6.00 s (1H, H^3), 7.28 t (1H, H^7, *J* 8.40 Hz), 7.37 m (2H, $H^{6,8}$), 7.78 d (2H, $H^{2',6'}$,

J 8.49 Hz), 8.30 d (2H, $H^{3', 5'}$, *J* 8.45 Hz), 8.83 d (1H, H^5, *J* 8.20 Hz), 11.38 s (1H, NH). Found, %: C 63.92; H 4.38; N 14.75. $C_{20}H_{16}N_4O_4$. Calculated, %: C 63.83; H 4.28; N 14.89.

4- Acetamido-3-acetyl-1-benzoyl-2-methylpyrrolo[1,2-*a*]benzimidazole (XVIa). A dispersion of 1.38 g (4 mmol) of salt **IIIa** and 0.55 g (4 mmol) of potassium carbonate in 15 ml of acetic anhydride was boiled for 30 min. On cooling 40 ml of water was added, and after decomposition of excess acetic anhydride the reaction mixture was alkalized with concn. NH_4OH. The separated precipitate (1.23 g) was filtered off and washed with water. After crystallization from ethanol was isolated 0.35 g (yield 22%) of lemon-yellow crystals of mp 239–240°C. IR spectrum, cm^{-1}: 1602 (COPh), 1640 (COMe), 1723 (NHCOMe), 3272 (NH). ^1H NMR spectrum, δ, ppm: 2.05 s (3H, CH_3), 2.10 s (3H, $COCH_3$), 2.40 s (3H, $NHCOCH_3$), 7.20–8.13 m (9H, H arom), 11.38 s (1H, NH). Found, %: C 70.91; H 4.98; N 11.18. $C_{22}H_{19}N_3O_3$. Calculated, %: C 70.76; H 5.13; N 11.25.

Acid hydrolysis of compound (XVIa). A solution of 0.37 g (1mmol) of 1-benzoylpyrrolobenzimidazole **XVIa** in 5 ml of concn. HCl was boiled for 15 min. The separated precipitate of benzoic acid was filtered off on cooling and washed with cold water. Yield 0.09 g (74%), mp 121–122°C (from water).

At alkalizing the dark-green mother liquor with concn. NH_4OH separated an intractable resinous substance.

1-Acetyl-4-diacetylamino-2-phenylpyrrolo[1,2-*a*]-benzimidazole (XVII) was prepared similarly to compound **XV** by boiling 0.25 g (1 mmol) of 4-amino-2-phenylpyrrolo[1,2-*a*]benzimidazole [3] in 3 ml of acetic anhydride for 1 h. Yield 0.27 g (74%), mp 174–175°C (from EtOH). IR spectrum, cm^{-1}: 1620 (COMe), 1740 (NCOMe). ^1H NMR spectrum, δ, ppm: 2.03 s (3H, $COCH_3$), 2.49 s [6H, $N(COCH_3)_2$], 5.72 s (1H, H^3), 7.05 m (1H, H^8), 7.33 m (2H, $H^{6, 7}$), 7.42 m (5H, C_6H_5), 8.95 m (1H, H^5). Found, %: C 70.64; H 5.27; N 11.37. $C_{22}H_{19}N_3O_3$. Calculated, %: C 70.76; H 5.13; N 11.25.

4-Acetamido-3-acetyl-2-methyl-1-(2-thenoyl)-pyrrolo[1,2-*a*]benzimidazole (XVIc) was prepared by the same procedure as 1-benzoylpyrrolobenzimidazole **XVIa** from 0.7 g (2 mmol) of bromide **IIIc**, 0.28 g (2 mmol) of potassium carbonate, and 10 ml of acetic anhydride. After crystallization of the isolated precipitate from alcohol was obtained 0.44 g (yield 58%) of bright yellow crystals, mp 254–255°C (from BuOH). IR spectrum, cm^{-1}: 1600 (2-thenoyl), 1620 (COMe), 1721 (NHCOMe), 3270 (NH). ^1H NMR spectrum, δ, ppm: 2.14 s (3H, CH_3), 2.39 s (3H, $COCH_3$), 2.46 s (3H, $NHCOCH_3$), 7.29 m (2H, $H^{7,8}$), 7.40 t (1H, $H^{4'}$, *J* 8.20 Hz), 7.43 t (1H, H^6, *J* 8.20 Hz), 7.78–7.80 m (2H, $H^{5, 5'}$), 8.12 d (1H, $H^{3'}$, *J* 7.69 Hz), 11.47 s (1H, NH). Found, %: C 63.45; H 4.48; N 11.19; S 8.60. $C_{20}H_{17}N_3O_3S$. Calculated, %: C 63.31; H 4.52; N 11.07; S 8.45.

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