Synthesis of 4-aminopyrido[3,2-*b*]indole derivatives

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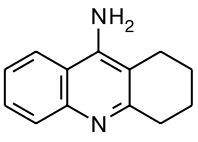
3-Arylamino-2-formylindoles were converted into oximes and then acetylated to give the corresponding *O*-acetyl derivatives. Chloroacetylation of the latter was accompanied by elimination of acetic acid, yielding 3-(*N*-aryl-*N*-chloroacetyl)amino-2-cyanoindoles. When heated in pyridine, these nitriles underwent cyclization into novel δ-carboline derivatives: 4-amino-1-aryl-2-oxo-1,2-dihydropyrido[3,2-*b*]indol-3-yl)pyridinium chlorides. The structures of the compounds obtained were proved by IR and ^{1}H NMR spectroscopy and mass spectrometry.

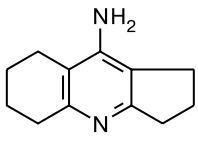
Key words: 3-arylaminoindoles, oximes, 3-(*N*-aryl-*N*-chloroacetyl)amino-2-formylindoles, cyanoindoles, δ-carbolines.

There are four classes of pyridoindoles (carbolines), δ-carbolines (pyrido[3,2-*b*]indoles) being less studied than isomeric α-, β-, and γ-carbolines. Nevertheless, some δ-carboline derivatives have been found to exhibit antitumor, antimuscarinic, antibacterial, and antiviral activities.[1—3] In the last decade, we developed new original methods for the synthesis of 1-aryl-δ-carbolines from 3-arylaminoindole derivatives.[4,5] The progress in the chemistry of 3-arylaminoindoles should give rise to new δ-carboline derivatives that are of synthetic, physicochemical, and biological interest.

A route to δ-carbolines we developed involves replacement of the Cl atom in the side chain of 3-(*N*-aryl-*N*-chloroacetyl)amino-2-formylindoles by a pyridinium fragment or a nitro group. In reaction intermediates containing strong electron-withdrawing substituents (pyridinium fragment and nitro group), the acidity of the adjacent CH_2 group is increased so considerably as to promote cyclization through this group and the 2-CHO substituent.[6,7] The present work was devoted to the synthesis of 3-(*N*-aryl-*N*-chloroacetyl)amino-2-cyanoindoles and their cyclization with pyridine through the 2-cyano group into new, earlier inaccessible 4-amino-δ-carbolines. These compounds could be of interest for the study of psychotropic activity because they contain the 4-aminopyridine fragment, which is found in such anticholinesterase drugs as Tacrine and Amiridin.[8]



Tacrine



Amiridin

Nitriles are most commonly synthesized by dehydration of appropriate oximes. Earlier,[6,9] we have found that 3-(*N*-aryl-*N*-chloroacetyl)amino-2-formylindoles react with hydroxylamine to give intermediate oximes, which are transformed *in situ* into substituted diazepino[6,5-*b*]indole 4-oxides. A literature method for the synthesis of nitriles directly from aldehydes involves hydroxylamine-*O*-sulfonic acid. This method has been successfully employed for some (both aliphatic and aromatic) aldehydes.[10] However, treatment of 3-[*N*-(chloroacetyl)-*N*-(4-nitrophenyl)amino]-2-formylindole (**1a**) with a double excess of hydroxylamine-*O*-sulfonic acid in methanol at 20 °C did not afford the expected nitrile **2a**. Instead, 3-[*N*-(chloroacetyl)-*N*-(4-nitrophenyl)amino]-2-formylindole dimethyl acetal (**3**) was obtained in 45% yield (Scheme 1).

Nor did a reaction of 2-formyl-3-[*N*-(4-nitrophenyl)amino]indole (**4a**) with hydroxylamine-*O*-sulfonic acid yield the corresponding nitrile **5**. The reaction product was 3-[*N*-(4-nitrophenyl)amino]indole-2-carbaldehyde oxime (**6a**) (Scheme 2).

For this reason, we tried to obtain 2-cyanoindoles of the type **2a,b** by transformation of 3-[(*N*-aryl)amino]indole-2-carbaldehyde oximes **6a,b** into nitriles **5a,b** followed by chloroacetylation.

Oximes **6a,b** were obtained in good yields by reactions of 2-dimethyliminiomethyl-3-[*N*-(4-nitrophenyl)amino]indole chloride (**7**) (an intermediate in the Vilsmeier synthesis of 2-formyl-3-[*N*-(4-nitrophenyl)amino]indole) and 3-arylamino-2-formylindoles **4a,b** with hydroxylamine (Scheme 3). The minor product (5.5%) in the synthesis of oxime **6a** from aldehyde **4a** was earlier obtained[4] 10-acetyl-2-nitroindolo[3,2-*b*]quinoline (**8**) (see Scheme 3, pathway *a*).

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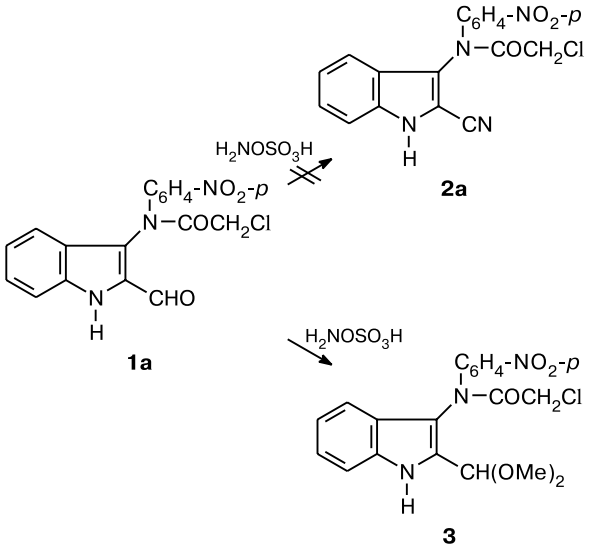
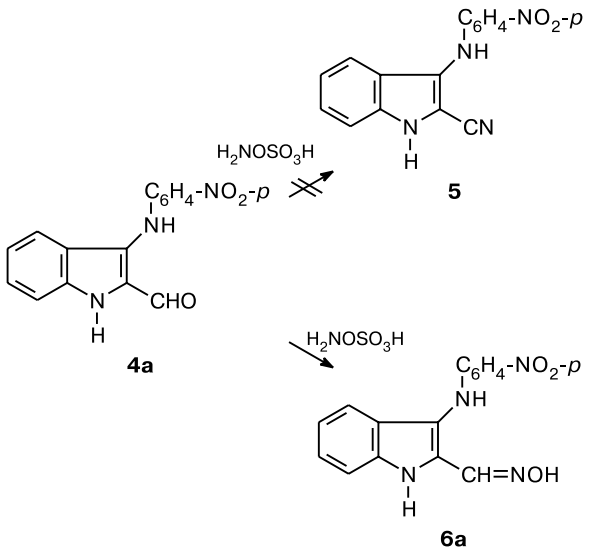
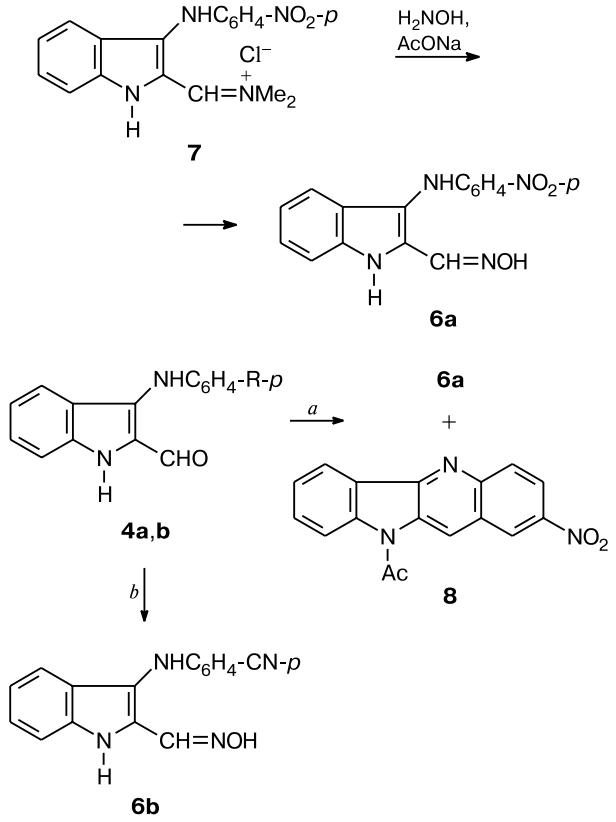
Scheme 1



Scheme 2



Scheme 3



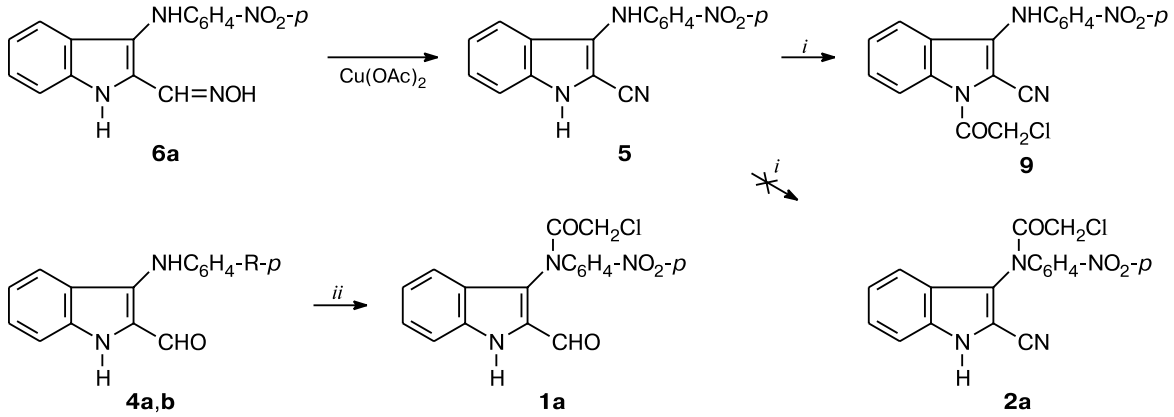
Reagents: (*a*) H_2NOH, AcONa, **4a**; (*b*) H_2NOH, AcONa, **4b**.

According to ^{1}H NMR data, oximes **6a,b** exist as a mixture of the *syn*- and *anti*-isomers (2 : 3). The spectra show doubled signals for the H(4), NH, OH, and CH protons. Oxime **6a** was converted into nitrile **5** in 72% yield by heating with copper(II) acetate in acetonitrile.[11] Other dehydration procedures (heating in a mixture of pyridine and acetic anhydride and heating in toluene or DMF with $MgSO_4$ in the presence of *p*-toluenesulfonic acid) failed. It should be noted that the yield of nitrile **5** (72%) was not reproduced on a larger scale: with increased amounts of the reagents, the yield diminished. Nevertheless, we obtained a sufficient amount of compound **5** for a study of its chloroacetylation under various conditions. On heating of nitrile **5** with chloroacetyl chloride in ethyl acetate, as well as in toluene in the presence of anhydrous Na_2CO_3 (*i.e.*, under similar conditions for the synthesis of 3-(*N*-aryl-*N*-chloroacetylamino)-2-formylindole **1a** (see Ref. 9), the reaction did not occur, the starting reagent being recovered. Chloroacetylation in DMF in the presence of triethylamine at room temperature gave 1-chloroacetyl derivative **9** rather than 3-(*N*-chloroacetyl) derivative (**2a**) (Scheme 4). The ^{1}H NMR spectrum of compound **9** shows no signals at δ 11—12 characteristic of the proton at the indole N atom but contains a singlet at δ 9.88 due to the proton at N(3). This fact motivated us to carry out chloroacetylation of 2-formylindole **4a** in DMF in the presence of triethylamine. In this case, earlier reported compound **1a** was obtained (see Ref. 9 and Scheme 4).

The first step in the chloroacetylation in the presence of a base is deprotonation of 2-formyl- (**4a,b**) and 2-cyano derivatives (**5**), which ultimately determines the regioselectivity of the reaction.

The deprotonation of compound **4** can proceed in two ways leading to anions **A** and **B** (Scheme 5). Anion **B** is stabilized by the existence of its two resonance structures, which makes it thermodynamically more favorable

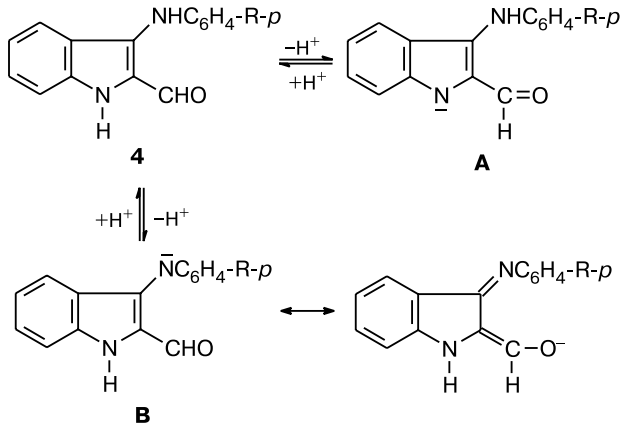
Scheme 4



Reagents and conditions: *i.* $ClCH_2COCl$, DMF, Et_3N; *ii.* $ClCH_2COCl$, DMF, Et_3N or toluene, Na_2CO_3.

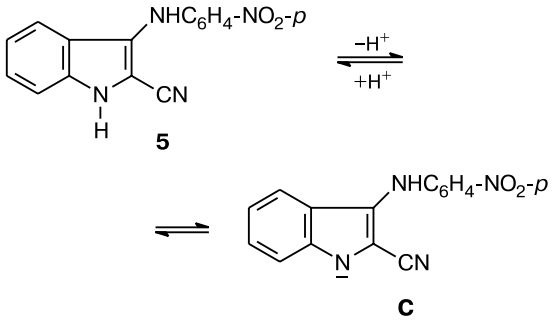
than anion **A**. For this reason, the chloroacetylation of 2-formylindole **4** at the exocyclic N atom to give compound **1** is dominant.

Scheme 5



A different pattern was observed in the deprotonation of 2-cyanoindole **5** (Scheme 6).

Scheme 6



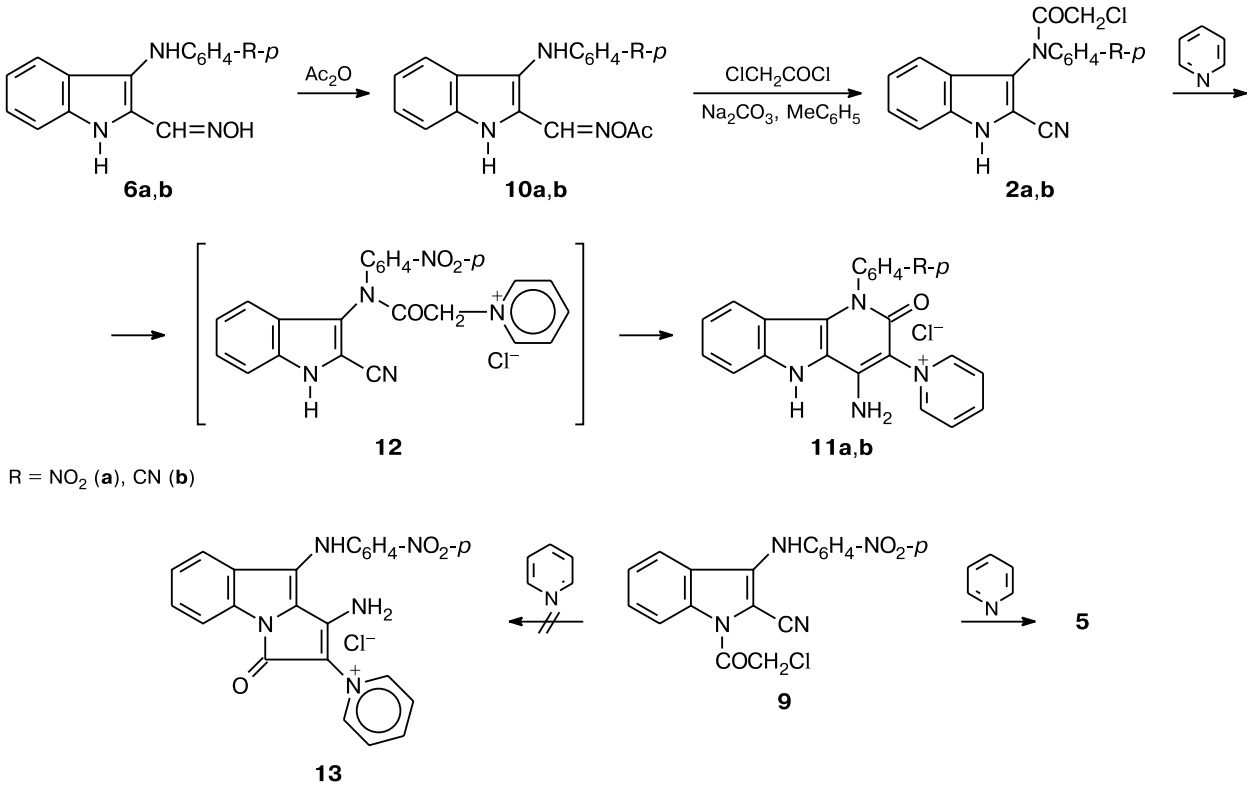
In this case, the stabilizing effect on the anionic center can be exerted mainly by the cyano group. The difference is that this group (in contrast to the formyl one) only slightly affects the conjugation with the reactive site (σ_R-constants for the CN and CHO groups are 0.08 and 0.24, respectively).[12] In contrast, the inductive electron-withdrawing effects of the CN and CHO groups are opposite (their σ_I-constants are 0.56 and 0.25, respectively);[12] in compound **5**, the cyano group stabilizes the *N-endo* anion mainly by the inductive mechanism. The above structure of anion **C** suggests its stability and explains why an acylating agent attacks the indole N atom.

The target 3-(*N*-chloroacetylamino)-2-cyanoindoles **2a,b** were obtained in 26 and 15% yields, respectively, by chloroacetylation of *O*-acetyloximes of 3-[(*N*-aryl)amino]-2-formylindoles **10a,b** under the same conditions as for aldehydes **4a,b** (see Ref. 9). The chloroacetylation was accompanied by elimination of acetic acid to form the nitrile function. *O*-Acetyloximes **10a,b** had been obtained in good yields by treatment of oximes **6a,b** with acetic anhydride (Scheme 7).

Refluxing of compounds **2a,b** in pyridine gave new pyridoindole derivatives **11a,b**. Apparently, first the active Cl atom in the side chain is replaced by the pyridinium fragment to form intermediate **12**, which undergoes *in situ* Thorpe—Ziegler intramolecular cyclization through the CN group and the activated methylene unit. At the same time, 1-chloroacetyl-2-cyanoindole **9** in pyridine underwent only deacylation even at room temperature to give 1-unsubstituted 2-cyanoindole **5**. Because of this, possible product **13** of the Thorpe—Ziegler cyclization was not obtained (see Scheme 7).

Thus, we discovered a route to previously inaccessible 4-aminopyrido[3,2-*b*]indoles, which can be of interest for the synthesis of functionalized aminopyrido[3,2-*b*]indoles and for pharmacological investigations.

Scheme 7



Experimental

The IR spectra (Nujol) were recorded on Perkin—Elmer 457 (compounds **6a**, **8**, **5**, **2a**, **9**, and **10a**) and FSM-1201 instruments (compounds **3**, **6b**, **2b**, **10b**, and **11a,b**). The mass spectra (EI) of compounds **6a**, **8**, **5**, **2a**, **9**, and **10a** were recorded on a Finnigan SSQ-710 mass spectrometer (direct inlet probe). The mass spectra of compounds **3**, **6b**, **2b**, **10b**, and **11a,b** were recorded on a Waters ZQ-2000 mass spectrometer (ESI, direct inlet probe). ^{1}H NMR spectra were recorded on Bruker AC-200 and Bruker AC-300 spectrometers in DMSO-d_6 according to Bruker standard procedures. The course of the reactions was monitored and the purity of the products was checked by TLC on Merck 60 F_{254} plates. The physicochemical characteristics of the compounds obtained are given in Tables 1 and 2.

3-[*N*-(Chloroacetyl)-*N*-(4-nitrophenyl)amino]-2-formylindole (1a). Triethylamine (1 mL, 6.5 mmol) was added at 20 °C to a stirred solution of 2-formylindole **4a** (0.6 g, 2.1 mmol) in DMF (8 mL). Then a solution of chloroacetyl chloride (0.56 mL, 6.5 mmol) in DMF (4 mL) was added dropwise. The reaction mixture was kept at 20 °C for 2.5 h and poured onto ice with water (~50 mL). The resinous precipitate that formed was filtered off, washed with water, and dissolved in chloroform. The solution was clarified with activated charcoal. The solvent was removed and the residue was recrystallized from benzene (8 mL) with activated charcoal and dried to a constant weight. The yield of compound **1a** was 0.25 g (30%). Its physicochemical characteristics were identical with those of the compound obtained earlier according to a known procedure.[9]

3-[*N*-(Chloroacetyl)-*N*-(4-nitrophenyl)amino]-2-cyanoindole (2a). Anhydrous Na_2CO_3 (0.21 g, 2 mmol) and chloroacetyl chloride (0.16 mL, 2 mmol) were added to a suspension of *O*-acetyloxime **10a** (0.34 g, 1 mmol) in toluene (35 mL). The reaction mixture was stirred at 80 °C for 3.5 h and left at 20 °C for 16 h. The inorganic precipitate was filtered off. The mother liquor was clarified by heating with activated charcoal, concentrated by three quarters of the initial volume, and cooled. The precipitate that formed was filtered off, washed with toluene, and dried to give compound **2a** (0.09 g). ^{1}H NMR (DMSO-d_6), δ: 4.21 (s, 2 H, $COCH_2Cl$); 7.14, 7.32, 7.43, 7.55 (all m, 1 H each, H(4)—H(7)); 7.54, 8.14 (both m, 2 H each, $C_6H_4NO_2$); 13.00 (br.s, 1 H, N(1)H).

3-[*N*-Chloroacetyl-*N*-(4-cyanophenyl)amino]-2-cyanoindole (2b) was obtained analogously from *O*-acetyloxime **10b** (0.9 g, 2.8 mmol), anhydrous Na_2CO_3 (0.32 g, 3.1 mmol), and chloroacetyl chloride (0.25 mL, 3.1 mmol) in toluene (75 mL). The yield of compound **2b** was 0.14 g. ^{1}H NMR (DMSO-d_6), δ: 4.31 (s, 2 H, $COCH_2Cl$); 7.25, 7.43, 7.54, 7.67 (all m, 1 H each, H(4)—H(7)); 7.60, 7.88 (both m, 2 H each, $C_6H_4NO_2$); 13.00 (br.s, 1 H, N(1)H).

3-[*N*-(Chloroacetyl)-*N*-(4-nitrophenyl)amino]-2-dimethoxymethylindole (3). A solution of hydroxylamine-*O*-sulfonic acid (0.22 g, 2 mmol) in methanol (2 mL) was added to a suspension (cooled with ice water) of aldehyde **1a** (0.36 g, 1 mmol) (see Ref. 8) in methanol (10 mL). After 7—10 min, the resulting solution with a promptly formed precipitate was stirred at 20 °C for 1 h. The precipitate was filtered off and washed with methanol. The yield of acetal **3** was 0.17 g. ^{1}H NMR (DMSO-d_6), δ:

Table 1. Physicochemical characteristics of the compounds obtained

Compound	Yield (%)	M.p./°C (solvent)	*M*	Molecular formula	Found / Calculated (%)		
					C	H	N
2a	26	206—208 (Pr^iOH)	354	$C_{17}H_{11}N_4O_3Cl$	57.35 57.56	3.22 3.13	15.55 15.79
2b	15	212—215 (Pr^iOH)	334	$C_{18}H_{11}N_4OCl$	64.56 64.58	3.55 3.31	16.62 16.74
3	45	218 (MeOH)	403	$C_{19}H_{18}N_3O_5Cl$	56.74 56.51	4.56 4.49	10.39 10.41
5	72	271 decomp. (EtOH)	278	$C_{15}H_{10}N_4O_2$	64.55 64.74	3.64 3.62	20.02 20.14
6a	95 (***A***) 93 (***B***) 87 (***C***)	248—250 decomp. (MeCN)	296	$C_{15}H_{12}N_4O_3$	60.81 60.81	4.10 4.08	18.96 18.91
6b	92	185 (50% EtOH)	276	$C_{16}H_{12}N_4O$	69.82 69.55	4.65 4.38	19.79 20.28
9	72	240 ($MeOH—Me_2O$)	354	$C_{17}H_{11}N_4O_3Cl$	57.27 57.56	2.99 3.13	15.82 15.79
10a	70	175 decomp. (MeCN)	338	$C_{17}H_{14}N_4O_4$	60.31 60.35	4.36 4.17	16.85 16.56
10b	77	155—158 (MeCN)	318	$C_{18}H_{14}N_4O_2$	67.69 67.91	4.42 4.43	17.47 17.60
11a	89	>360 (MeOH)	433	$C_{22}H_{16}N_5O_3Cl\cdot\cdot H_2O$	58.41 58.48	4.09 4.02	15.53 15.50
11b	81	>360 (MeOH)	413	$C_{23}H_{16}N_5OCl\cdot\cdot 0.5H_2O$	65.11 65.35	4.30 4.05	16.56 16.57

Table 2. MS data and IR spectra of the compounds obtained

Compound	MS, m/z (I_{rel} (%))	IR (ν_{max}/cm^{-1})
2a	354 $[M]^+$ (24), 278 $[M - COCH_2Cl]^+$ (100), 248 $[M - COCH_2Cl - NO]^+$ (37), 205 $[M - COCH_2Cl - HCN]^+$ (68)	3410, 3238 (NH), 2226 (CN), 1698 (CO)
2b	357 $[M + Na]^+$, 691 $[2\,M + Na]^+$, 1025 $[3\,M + Na]^+$	3254 (NH), 2227 (CN), 1689 (CO),
3	426 $[M + Na]^+$, 829 [2 M + Na]	3300 (NH), 1760 (CO)
5	278 $[M]^+$ (100), 248 $[M - NO]^+$ (85), 231 $[M - HNO_2]^+$ (58), 205 $[M - NO_2 - HCN]^+$ (42)	3691 (NH), 2226 (CN)
6a	296 $[M]^+$ (83), 278 $[M - H_2O]^+$ (100), 248 $[M - H_2O - NO]^+$ (17), 233 $[M - HNO_3]^+$ (80), 218 $[M - O - HCO - NO_2]^+$ (77), 218 $[M - H_2O - 2\,NO]^+$ (27)	3389, 3358 (NH, OH)
6b	575 $[2\,M + Na]^+$, 851 $[3\,M - Na]^+$	3329 (NH, OH), 2225 (CN)
9	354 $[M]^+$ (52), 278 $[M - COCH_2Cl]^+$ (100), 248 $[M - COCH_2Cl - NO]^+$ (77), 232 $[M - COCH_2Cl - NO_2]^+$ (70), 231 $[M - C_6H_4NO_2]^+$ (76], 205 $[M - COCH_2Cl - HCN]^+$ (57)	3367, 3352 (NH), 2204 (CN), 1716, 1697 (CO)
10a	296 $[M - AcOH]^+$ (100), 248 $[M - AcOH - NO]^+$ (31), 232 $[M - AcOH - NO_2]^+$ (54), 231 $[M - AcOH - HNO_2]^+$ (60), 205 $[M - AcOH - NO_2 - HCN]^+$ (50)	3309 (NH), 1745 (CO)
10b	341 $[M + Na]^+$, 659 $[2\,M + Na]^+$	3344, 3294 (NH), 2214 (CN), 1757 (CO)
11a	398 [M − Cl], 352 $[M - Cl - NO_2]$	3526, 3344, 3304, 3117, 3651 (NH, NH_2), 1629 (CO)
11b	378 [M − Cl], 755 [2 M − 2 Cl + H]	3554, 3340, 3304, 3117 (NH, NH_2), 2233 (CN), 1658, 1631 (CO)

3.19, 3.30 (both s, 3 H each, $(OMe)_2$); 4.22 (AB system, 2 H, $COCH_2Cl$); 5.70 (s, 1H, CH); 7.10, 7.22 (both m, 1 H each, H(4)—H(7)); 7.45 (m, 2 H, H(4)—H(7)); 7.57, 8.19 (both m, 2 H each, $C_6H_4NO_2$), 11.76 (br.s, 1 H, N(1)H).

2-Cyano-3-[*N*-(4-nitrophenyl)amino]indole (5). A mixture of oxime **6a** (0.3 g, 1 mmol) and cupric acetate (0.2 g, 1 mmol) was refluxed in acetonitrile (15 mL) for 1 h and then evaporated to dryness. After 5% H_2SO_4 (25 mL) was added, the mixture was stirred and the precipitate was filtered off, washed with water, and mixed with acetone (20 mL). The undissolved black precipitate was filtered off. The mother liquor in acetone was clarified with activated charcoal and concentrated to give 2-cyanoindole **5** (0.2 g). ^{1}H NMR (DMSO-d_6), δ: 6.82, 8.02 (both m, 2 H each, $C_6H_4NO_2$); 7.08 (1 H), 7.25 (3 H) (both m, H(4)—H(7)); 9.27 (br.s, 1 H, C(3)NH); 12.13 (br.s, 1 H, N(1)H).

2-Hydroxyiminomethyl-3-[*N*-(4-nitrophenyl)amino]indole (6a). Procedure *A*. Hydroxylamine-*O*-sulfonic acid (0.12 g, 1 mmol) in methanol (1 mL) was added to a suspension of aldehyde **4a** (0.14 g, 0.5 mmol) (see Ref. 4) in methanol (5 mL). The reaction mixture was stirred at 20 °C for 15 min, refluxed for 0.5 h, cooled, and concentrated. The residue was triturated with water and the resulting precipitate was filtered off, washed with water, and dried. The yield of oxime **6a** as a mixture of the *syn*- and *anti*-isomers (2 : 3) was 0.14 g (95%). ^{1}H NMR (DMSO-d_6), δ: 6.68, 8.03 (both m, 2 H each, $C_6H_4NO_2$); 7.01 (1 H), 7.20 (2 H), 7.42 (1 H), 7.63 (1 H) (all m, H(4)—H(7)); 7.45 and 8.06 (s, 1 H, CH); 8.99 and 9.07 (br.s, 1 H, C(3)NH); 11.38 and 11.98 (s, 1 H, OH); 11.42 and 11.43 (br.s, 1 H, N(1)H).

B*.** Hydroxylamine hydrochloride (0.2 g, 3 mmol) and melted sodium acetate (0.5 g, 6 mmol) were added to a suspension of immonium salt **7** (0.69 g, 2.0 mmol) (see Ref. 4) in isopropyl alcohol (20 mL). The reaction mixture was stirred under reflux for 0.5 h and cooled. The inorganic precipitate was filtered off, the filtrate was concentrated to dryness, and the residue was triturated with water. The resulting precipitate was filtered off, washed with water, and dried. The yield of oxime **6a** was 0.55 g. Its mixture with the oxime **6a** obtained according to procedure ***A did not depress the melting point.

C*.** Hydroxylamine hydrochloride (0.2 g, 3 mmol) and melted sodium acetate (0.25 g, 3 mmol) were added to a suspension of aldehyde **4a** (0.5 g, 1.8 mmol) in isopropyl alcohol (20 mL). The reaction mixture was stirred under reflux for 0.5 h and cooled. The precipitate was filtered off, washed with isopropyl alcohol and water, and dried to give **10-acetyl-2-nitroindolo[3,2-*b*]quinoline (8)** (0.03 g, 5.5%), m.p. 263.5—264 °C (*cf*. Ref. 4: m.p. 263.5—264 °C). Its spectroscopic characteristics agree with those reported earlier.[4] The mother liquor was evaporated to dryness and the residue was triturated with water. The resulting precipitate was filtered off, washed with water, and dried. The yield of oxime **6a** was 0.47 g. Its mixture with the oxime **6a** obtained according to procedure ***A did not depress the melting point.

3-[*N*-(4-Cyanophenyl)amino]-2-hydroxyiminomethylindole (6b). Hydroxylamine hydrochloride (0.46 g, 6.6 mmol) and melted sodium acetate (0.54 g, 6.6 mmol) were added to a suspension of aldehyde **4b** (1.04 g, 4 mmol) (see Ref. 8) in isopropyl alcohol (45 mL). The reaction mixture was refluxed with stirring for 0.5 h and cooled. The inorganic precipitate was filtered off. The mother liquor was clarified with activated charcoal and evaporated to dryness. The residue was triturated with water. The resulting precipitate was filtered off, washed with water, and dried. The yield of oxime **6b** as a mixture of the *syn*- and *anti*-isomers (2 : 3) was 1.01 g. A sample for analysis was recrystallized from 50% ethanol and purified on SiO_2 with chloroform as an eluent. ^{1}H NMR (DMSO-d_6), δ: 6.68, 7.47 (both m, 2 H each, $C_6H_4NO_2$); 6.99 (1 H), 7.20 (2 H), 7.40 (1 H), 7.62 (1 H) (all m, H(4)—H(7)); 7.43 and 8.05 (both s, 1 H each, CH); 8.43 and 8.52 (both br.s, 1 H each, C(3)NH); 11.24 and 11.83 (both s, 1 H each, OH); 11.24 (br.s, 1 H, N(1)H).

1-Chloroacetyl-2-cyano-3-[*N*-(4-nitrophenyl)amino]indole (9). Triethylamine (0.2 mL, 1.3 mmol) was added at 20 °C to a stirred solution of 2-cyanoindole **5** (0.12 g, 0.43 mmol) in DMF (1.5 mL). Then a solution of chloroacetyl chloride (0.11 mL, 1.3 mmol) in DMF (1 mL) was added dropwise. After 0.5 h, the mixture was poured onto ice with water (~10 mL). The precipitate that formed was filtered off and washed with water, methanol, and ether. The yield of compound **9** was 0.11 g. ^{1}H NMR (DMSO-d_6), δ: 5.20 (s, 2 H, $COCH_2Cl$); 7.13, 8.16 (both m, 2 H each, $C_6H_4NO_2$); 7.45, 7.67, 7.70, 8.22 (all m, 1 H each, H(4)—H(7)); 9.88 (br.s, 1 H, C(3)NH).

2-Acetoxyiminomethyl-3-[*N*-(4-nitrophenyl)amino]indole (10a). A mixture of oxime **6a** (0.2 g, 0.68 mmol) and acetic anhydride (1.5 mL) was kept at 20 °C for 16 h. The precipitate that formed was filtered off and washed with acetic anhydride and ether. The yield of *O*-acetyloxime **10a** was 0.16 g. ^{1}H NMR (DMSO-d_6), δ: 2.19 (s, 3 H, $OCOCH_3$); 6.76, 8.05 (both m, 2 H each, $C_6H_4NO_2$); 7.06 (1 H), 7.28 (2 H), 7.49 (1 H) (all m, H(4)—H(7)); 8.55 (s, 1 H, CH); 9.10 (br.s, 1 H, C(3)NH); 11.80 (br.s, 1 H, N(1)H).

2-Acetoxyiminomethyl-3-[*N*-(4-cyanophenyl)amino]indole (10b). A mixture of oxime **6b** (1.01 g, 3.6 mmol) and acetic anhydride (5 mL) was stirred at 20 °C for 2 h. The precipitate that formed was filtered off and washed with acetic anhydride and ether. The yield of *O*-acetyloxime **10b** was 0.9 g. ^{1}H NMR (DMSO-d_6), δ: 2.18 (s, 3 H, $OCOCH_3$); 6.74, 7.43 (both m, 2 H each, C_6H_4CN); 6.98 (1 H), 7.23 (2 H), 7.46 (1 H) (all m, H(4)—H(7); 8.49 (s, 1 H, CH); 8.59 (br.s, 1 H, C(3)NH); 11.63 (br.s, 1 H, N(1)H).

1-[4-Amino-1-(4-nitrophenyl)-2-oxo-1,2-dihydropyrido[3,2-*b*]indol-3-yl]pyridinium chloride (11a). A mixture of 3-[*N*-(chloroacetyl)-*N*-(4-nitrophenyl)amino]-2-cyanoindole (**2a**) (0.22 g, 0.62 mmol) and pyridine (2 mL) was heated with stirring to boiling. The resulting solution gave rise to a new yellow precipitate. The reaction mixture was refluxed for 0.5 h and cooled. The precipitate was filtered off and washed with pyridine and ether. The yield of compound **11a** was 0.24 g. ^{1}H NMR (DMSO-d_6), δ: 6.26, 6.87, 7.32, 7.55 (all m, 1 H each, H(9)—H(6)); 7.79, 8.48 (both m, 2 H each, $C_6H_4NO_2$); 7.85 (br.s, 2 H, C(4)NH_2); 8.31 (2 H), 8.76 (1 H), 9.11 (2 H) (all m, H(2′)—H(6′)); 12.79 (br.s, 1 H, N(5)H).

1-[4-Amino-1-(4-cyanophenyl)-2-oxo-1,2-dihydropyrido[3,2-*b*]indol-3-yl]pyridinium chloride (11b) was obtained analogously from 3-[*N*-chloroacetyl-*N*-(4-cyanophenyl)amino]-2-cyanoindole (**2b**) (0.14 g, 0.4 mmol) and pyridine (2 mL). The yield of compound **11b** was 0.14 g. ^{1}H NMR (DMSO-d_6), δ: 6.15, 6.89, 7.32, 7.56 (all m, 1 H each, H(9)—H(6)); 7.71, 8.13 (both m, 2 H each, C_6H_4CN); 7.77 (br.s, 2 H, C(4)NH_2); 8.32 (2 H), 8.76 (1 H), 9.11 (2 H) (all m, H(2′)—H(6′)); 12.52 (br.s, 1 H, N(5)H).

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