Synthesis of derivatives of the new heterocyclic system pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indole*

*S. Yu. Ryabova, L. M. Alekseeva, N. S. Masterova, and V. G. Granik**

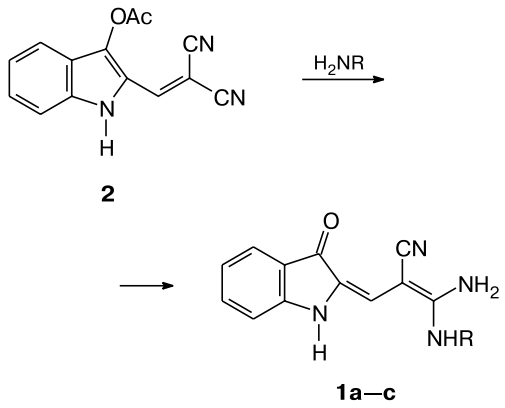
State Scientific Center for Antibiotics,
3a ul. Nagatinskaya, 117003 Moscow, Russian Federation.
Fax: +7 (495) 225 6104. E-mail: vggranik@mail.ru

Derivatives of the new heterocyclic system 1,11-dihydro-4*H*-pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indol-4-one were synthesized by the reactions of 2-(2-cyanoprop-2-enylidene)indolin-3-ones, bearing the primary and secondary amino groups in position 3 of the side chain, with DMF diethyl acetal. A scheme of formation of the synthesized compounds was proposed and confirmed.

Key words: 2-(3,3-diamino-2-cyanoprop-2-enylidene)indolin-3-ones, DMF diethyl acetal, condensation, ring closure, pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indol-4-ones.

We have previously[1] studied the reactions of 2-(2-cyanoprop-2-enylidene)indolin-3-ones, bearing the primary and tertiary amino groups in position 3 of the side chain, with amide acetals. It turned out that the reactions did not cease at the step of intermediate amidine formation: they underwent ring closure with elimination of secondary amine and formation of 3-alkylaminomethyleneamino-2-cyano-9-oxopyrrolo[1,2-*a*]indoles and simultaneously with elimination of substituted formamidine and formation of the corresponding 3-alkylaminopyrrolo[1,2-*a*]indoles. It seemed interesting to continue the study of these reactions using as an example the reaction of dienediamines, bearing the primary and secondary amino groups in position 3 of the side chain, with dimethylformamide diethyl acetal. As the starting compounds we chose dienediamines bearing the methylamino (**1a**), benzylamino (**1b**) and anisidino (**1c**) groups. Compounds **1b,c** have been synthesized earlier,[2] and compound **1a** was synthesized similarly[2] by reflux of 3-acetoxy-2-(2,2-dicyanovinyl)indole (**2**) with methylamine in benzene or isopropyl alcohol (Scheme 1).

Scheme 1



R = Me (**a**), CH_2Ph (**b**), C_6H_4OMe-4 (**c**)

Reagents and conditions: RNH_2, benzene or propan-2-ol, reflux, 1 h.

For the reactions of dienediamines **1a—c** with twofold DMF diethyl diacetal excess, we assumed that they would proceed *via* the pathway described earlier[1] (Scheme 2).

In this scheme, the major reaction products should be amidine **4** and the corresponding pyrroloindoles **5a—c**.

However, it turned out that in these reactions amidine **4** is formed only as a by-product. In the case of the reactions of the acetal with dienediamines **1b,c**, the formation of compound **4** was observed only chromatographically, whereas in the case of **1a** amidine **4** was isolated from the mother liquors by column chromatography in 4.5% yield. In the reaction of dienediamine **1c** with acetal, 3-(4-methoxyphenyl)amino-2-cyano-9-oxo-9*H*-pyrrolo[1,2-*a*]indole (**5c**) was isolated similarly in ~5% yield, and its structure was confirmed by the mass and ^{1}H NMR spectral data. The mass spectrum (EI) of this compound exhibits the molecular ion peak corresponding to the molecular mass of pyrroloindole **5c**, and its ^{1}H NMR spectrum contains signals from the aromatic protons at 7.15—7.63 ppm as multiplets and a singlet signal from H(1) at 7.31 ppm along with the signals from the protons of the *para*-anisidine substituent. The chemical shifts of the signals from analogous protons for com-

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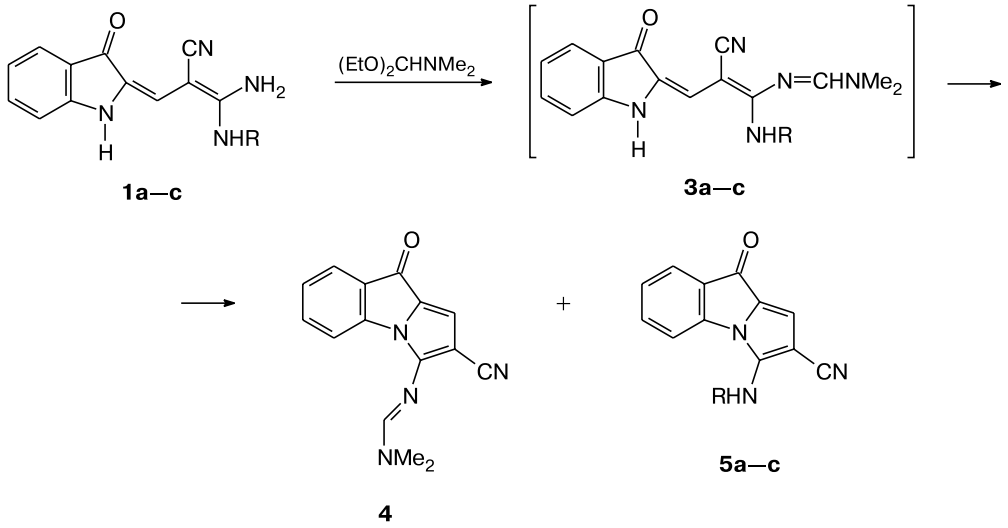
Scheme 2

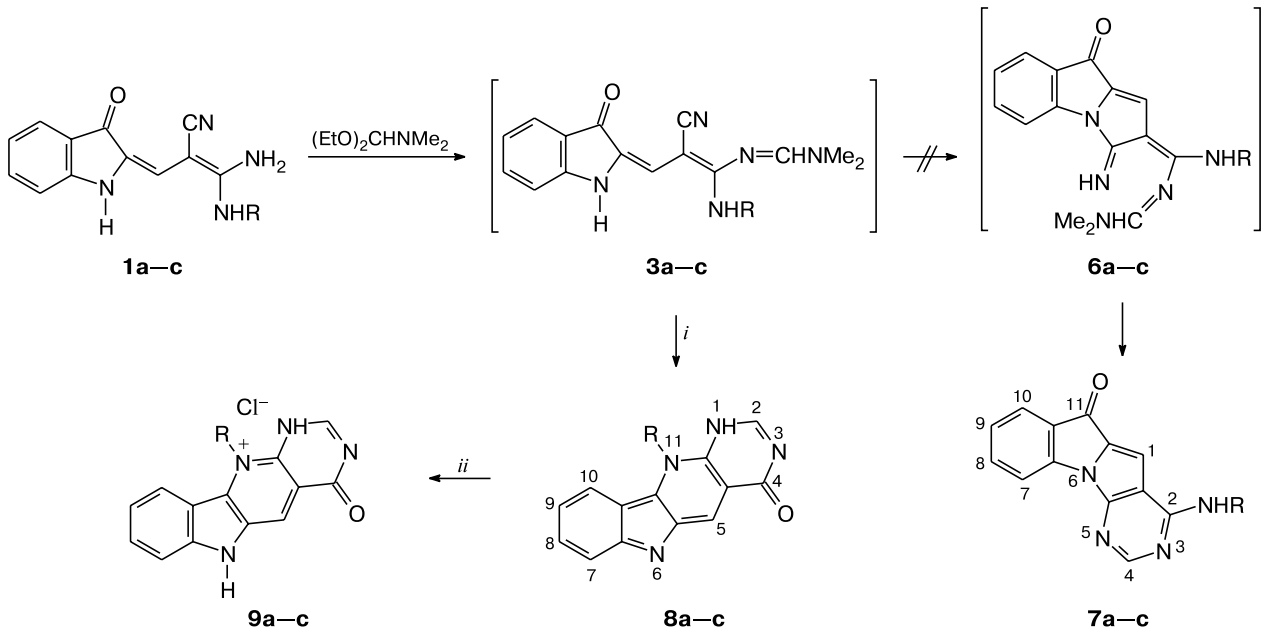


R = Me (**a**), CH_2Ph (**b**), C_6H_4—OMe-4 (**c**)

pound **5c** coincided with those[1] for 3-morpholino- and 3-piperidinopyrroloindoles.

The spectral study of the major products obtained in the reactions of dienediamines **1a—c** with acetal showed that, in this case, the ring closure of intermediate amidines **3a—c** involves the cyano group, because the IR spectra of these compounds contain no characteristic absorption bands at 2220 cm^{-1}. Since all compounds synthesized by us earlier from substituted 2-(3,3-diamino-2-cyanoprop-2-enylidene)indolin-3-ones[1,2] were formed due to intramolecular ring closures involving the indole nitrogen atom and had the pyrroloindole structure, we assumed that the pyrrole ring closure with the formation of compounds **6a—c** (Scheme 3) should be the first step in this case as well. It was reasonable to suppose that the second step of ring closure would follow: pyrimidine ring closure

Scheme 3



Reagents and conditions: *i*. $(EtO)_2CHNMe_2$, DMF; *ii*. MeOH, HCl/EtOAc

Table 1. ^{1}H NMR spectra for compounds **8a—c**, **9a—d**

Compound	Chemical shifts (δ)						
	H(2) (s, 1 H)	H(5) (s, 1 H)	H(7) (m, 1 H)	H(8), H(9)	H(10) (m, 1 H)	R(11)	N^+H (br.s, 1 H)
8a	8.97	8.46	7.43 (m, 1 H), 7.80 (m, 2 H)		8.56	4.76 (s, 3 H, Me)	
8b	9.09	8.41	7.77	7.68 (m, 1 H)	8.09	6.60 (br.s, 2 H, CH_2); 7.11, 7.27 (both m, 2 H each and 4 H, H(8) or H(9), Ph)	
8c	9.10	8.20	7.74	7.05, 7.63 (both m, 1 H each)	6.32	3.95 (s, 3 H, OMe); 7.31, 7.59 (A_2B_2, 4 H, C_6H_4)	13.50
9a	9.19	8.72	7.53 (m, 1 H), 7.91 (m, 2 H)		8.66	4.92 (s, 3 H, Me)	
9b	9.34	8.69	7.90	7.38, 7.83 (both m, 1 H each)	8.20	6.74 (br.s, 2 H,CH_2); 7.20—7.32 (m, 5 H, Ph)	13.62
9c	9.37	8.53	7.89	7.20, 7.78 (both m, 1 H each)	6.37	3.96 (s, 3 H, OMe); 7.38, 7.65 (A_2B_2, 4 H, C_6H_4)	13.46
9d	9.45	8.56	7.92	7.16, 7.85 (both m, 1 H each)	6.39	8.11, 8.73 (A_2B_2, 4 H, C_6H_4)	13.75

with dimethylamine elimination and the formation of pyrimidopyrroloindole derivatives **7a—c**. The mass spectral data did not contradict the pyrimidopyrroloindole structure. However, in the ^{1}H NMR spectra of the synthesized compounds, the chemical shift values of the protons of the benzene fragments of the molecules depended substantially on the substituent R, which could hardly be consistent with the structure proposed for compounds **7**. For instance, for the compound with R = Me, these signals ranged from 7.43 to 8.56 ppm, whereas for the compound with R = C_6H_4OMe they were in a range of 6.32—7.74 ppm. At the same time, in structures **7** the chemical shifts of the downfield singlet signals from H(1) arranged in the close vicinity of the NHR(2) substituent changed slightly: 8.97—9.10 ppm.

The contradictions observed between structure **7** and the ^{1}H NMR spectral data forced us to assume that the reactions afforded compounds with the alternative pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indole structure **8**. To confirm the structures of compounds **8a—c**, we synthesized the corresponding chlorides **9a—c** and recorded the NOEDIFF spectra of compounds **8b** and **9a,b**. Saturation of the signal from the methyl group (4.92 ppm) in the spectrum of chloride **9a** showed the resonance of the multiplet* signal (8.66 ppm) belonging, most likely, to the proton in position 10 and no resonance of the singlet signal from H(2) (9.19 ppm) was observed, which confirmed that the methyl groups are spatially close to the benzene part of the molecule (the increase in the intensity of the signal from H(10) due to NOE was 14%). In the spectra of compounds **8b** and **9b**, saturation of the signals from the methylenic protons at 6.60 and 6.74 ppm showed the resonance of the same order of magnitude for the multiplets at 8.09 and 8.20, respectively.

The structure proposed for compounds **8** explains some specific features of the ^{1}H NMR spectra of the synthesized compounds (Table 1). The upfield position of the signal from H(10) in the spectrum of compound **8c** (6.32 ppm) is related, most likely, to the shielding effect of the benzene ring of the substituent in position 11, which is shifted from the plane of the molecule due to steric hindrance. This upfield position of the aromatic proton (H(4) of indole) was observed in the spectra of tricyclic compounds of the δ-carboline,[3,4] [1,4]diazepino[3,2-*b*]indole, and pyrimido[5,4-*b*]indole[5] series in which position 1 of the tricycle is occupied by an aryl substituent. The downfield position of the H(10) signal in the spectrum of compound **8a** (8.56 ppm) and the downfield position of the methyl (4.76 ppm (**8a**), 4.92 ppm (**9a**)) and methylene (6.60 ppm (**8b**), 6.74 ppm (**9b**)) groups are related, most likely, to the strong electron-withdrawing effect of such a fragment of the tetracyclic molecule as the fused pyrimidine cycle. Note that the ^{1}H NMR spectra contained no signals from the NH protons, probably, because of fast exchange.

The IR spectra of compounds **8a—d** recorded in KBr pellets in the 3414—3457 cm^{-1} region exhibited the broadened absorption bands, which could be assigned to both the NH and OH groups (note that many compounds under study are crystalline hydrates (Table 2)). At the same time, the absorption region of the carbonyl groups contained only low-frequency absorption bands at ~1630 cm^{-1}. Therefore, it seemed reasonable to discuss the problems of tautomerism, which is characteristic of pyrimidinones.[6] Probable tautomeric equilibria for fused pyrimidonones **8** are shown in Scheme 4.

It has been shown[7] that quinasolinones with *para*-quinoid arrangement of the double bonds in the

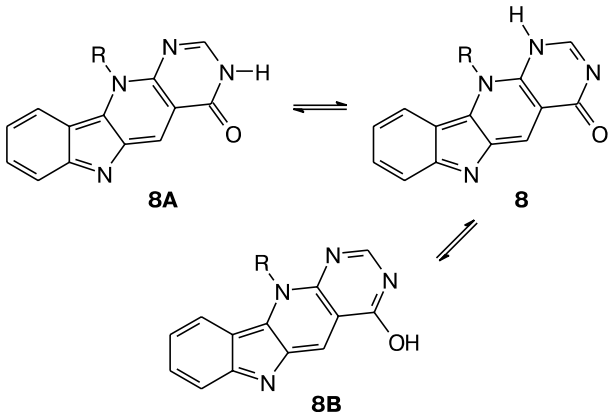
* The doublet (J_o = 8.4 Hz), whose each component is additionally split, is observed.

Table 2. Yields, melting points, elemental analysis data, and mass and IR spectral parameters for the synthesized compounds

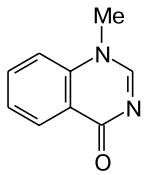
Compound	Yield (%)	M.p./°C (solvent)	M	Found / Calculated (%)				Molecular formula	MS, m/z (I_{rel} (%))	IR*, ν_{max}/cm^{-1}
				C	H	N	H_2O			
1a	58 (***A***) 57 (***B***)	221—223 (MeOH)	240	64.10 63.80	5.40 5.09	22.44 22.81	—	$C_{13}H_{12}N_4O\cdot$ $0.25\ H_2O$	241 $[M + H]^+$, 263 $[M + Na]^+$, 279 $[M + K]^+$, 481 $[2\ M + H]^+$, 503 $[2\ M + Na]^+$, 519 $[2\ M + K]^+$	1668 (CO), 1635 (C=C), 2190 (CN), 3440, 3285 (NH)
8a	53	~300 (DMF)	250	63.76 63.75	4.16 4.40	21.32 21.24	5.07 5.12	$C_{14}H_{10}N_4O\cdot$ $0.75\ H_2O$	251 $[M + H]^+$, 288 $[M + H]^+$, 523 $[2\ M + Na]^+$, 789 $[3\ M + K]^+$, 1001 $[4\ M + H]^+$, 1039 $[4\ M + K]^+$	1630 (CO), 3457, 3419 (sh) (NH)
8b	42	292—293 (DMF)	326	73.13 73.61	4.36 4.32	17.03 17.17	—	$C_{20}H_{14}N_4O$	327 $[M + H]^+$, 364 $[M + K]^+$, 652 $[2\ M + H]^+$, 674 $[2\ M + Na]^+$	1630 (CO), 3457, 3424 (NH)
8c	24	~350 (DMF)	342	68.42 68.37	4.20 4.30	15.90 15.95	—	$C_{20}H_{14}N_4O_2$ $\cdot 0.5\ H_2O$	342 $[M]^+$ (100), 327 $[M - Me]^+$ (12.07), 313 $[M - Me - HCO]^+$ (5.17);	1635 (CO), 3356 (NH)
8d	67	>360 (DMF)	357	63.69 63.86	3.76 3.10	19.16 19.60	—	$C_{19}H_{11}N_5O_3$	358 $[M + H]^+$, 380 $[M + Na]^+$, 396 $[M + K]^+$, 715 $[2\ M + H]^+$;	1635 (CO), 3414(br) (NH)
9a	71	255—257 (MeOH)	274	56.01 56.01	4.17 4.53	18.53 18.66	—	$C_{14}H_{11}ClN_4O\cdot$ $0.75\ H_2O$	—	1703 ($C=N^+$), 1627 (CO), 3512, 3420 (NH)
9b	63	232—236 (MeOH)	362	64.33 64.60	4.30 4.33	14.84 15.07	—	$C_{20}H_{15}ClN_4O\cdot$ $0.5\ H_2O$	—	—
9c	75	290—292 (MeOH)	378	60.55 60.53	3.99 4.31	13.94 14.11	4.47 4.54	$C_{20}H_{15}ClN_4O_2\cdot$ H_2O	—	1689 ($C=N^+$), 1630 (CO), 3653, 3425 (NH)
9d	57	>360 (MeOH)	405	55.14 55.42	3.81 3.43	17.07 17.01	5.57 5.41	$C_{19}H_{12}ClN_5O_3\cdot$ $1.25\ H_2O$	—	—

* The IR spectra of compounds **1a**, **9a**, and **9c** were obtained in Nujol, and those for compounds **8a—d** were recorded in KBr pellets.

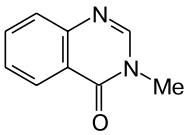
Scheme 4



pyrimidinone cycle are characterized by the low-frequency shift of the absorption bands of the carbonyl groups in the IR spectra.



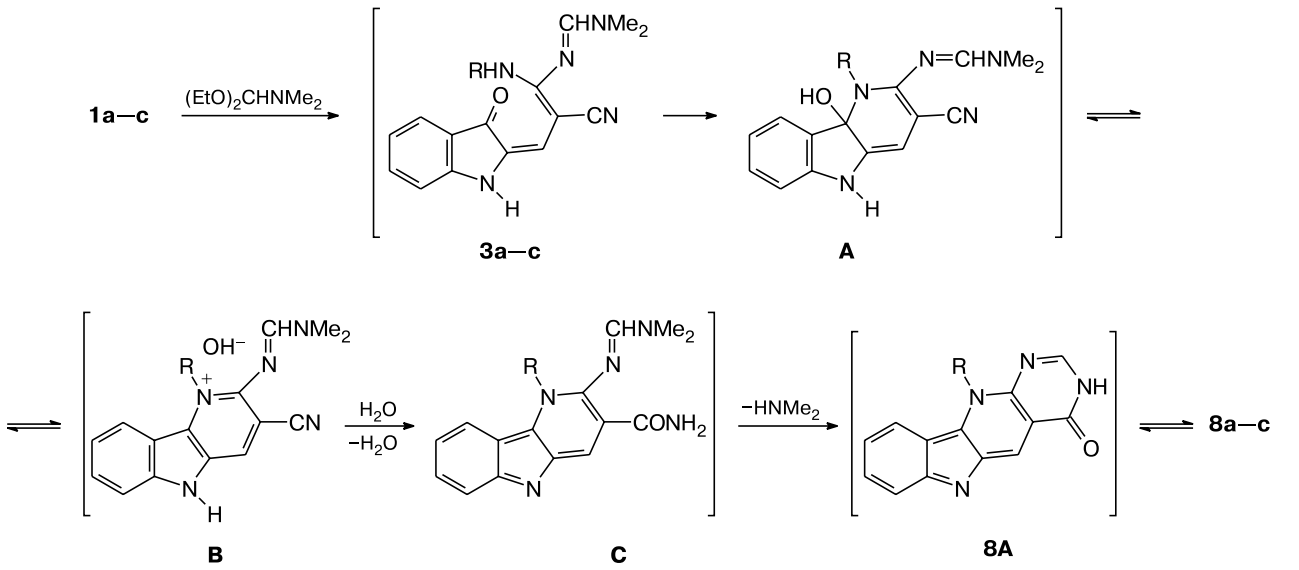
ν = 1638 cm^{-1} (CO)



ν = 1676 cm^{-1} (CO)

Therefore, it seems reasonable to assume that compounds **8** synthesized in this work (and correspondingly, **9**) exist in the tautomeric quinoid form. More detailed in-

Scheme 5



vestigation of tautomerism of compounds **8** is beyond the scope of the present study.

Thus, the reactions of dienediamines **1a—c** with DMF diethyl acetal afforded derivatives of the new heterocyclic system: 1,11-dihydro-4*H*-pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indol-4-ones (**8a—c**). A probable scheme for the formation of these compounds was proposed (Scheme 5).

The first step of the process is the addition of the acetal to the primary amino group to form intermediate amidines **3a—c**. Then the secondary amino group adds to the third position of the indole to form δ-carboline of structure **A***, which dissociates reversibly to cation **B**. Then the cyano group was hydrolyzed by water evolved during the reaction with the formation of the carboxamide group (**C**), and further dimethylamine eliminated to form 1,11-dihydro-4*H*-pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indol-4-ones **8a—c**.

We confirmed the mechanism of formation of compounds **8a—c** *via* Scheme 5. The reaction of earlier[8] synthesized 2-amino-3-carbamoyl-1-(4-nitrophenyl)-1*H*-pyrido[3,2-*b*]indole (**10**) with DMF acetal gave the 11-(4-nitrophenyl) derivative of pyrimidopyridoindol-4-one **8d** and further its hydrochloride **9d** (Scheme 6).

The physicochemical characteristics of compounds **9d** and **9c** (R = C_6H_4OMe) are analogous (see Table 1).

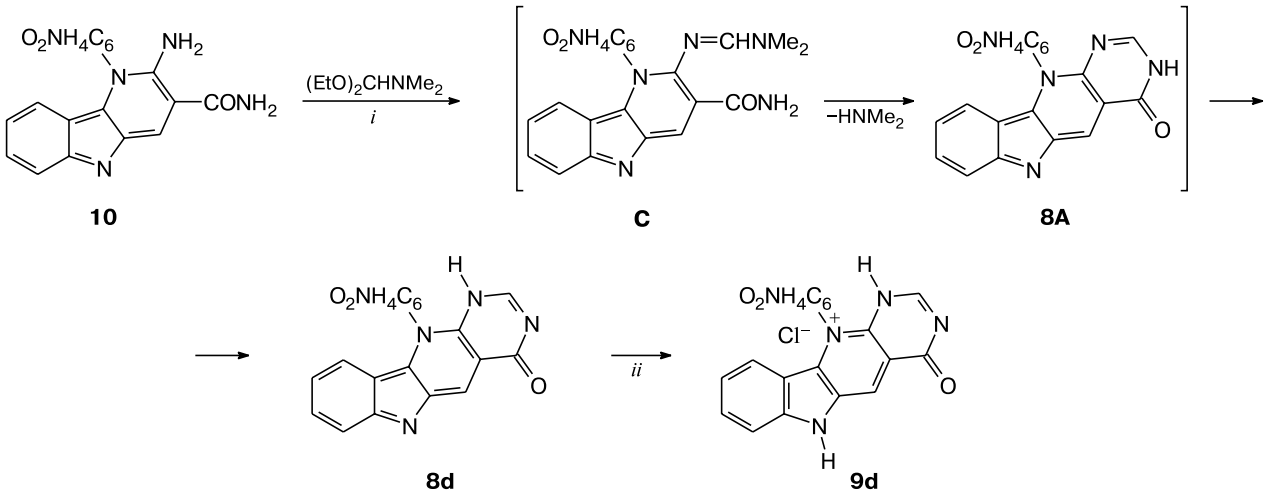
Thus, it was found that in the reactions of dienediamines, bearing the secondary amino group in position 3 of the side chain, with dimethylformamide diethyl acetal, unlike the reactions of dienediamines containing the tertiary amino group in position 3 of the side chain,[1] ring closure of intermediate amidines occurs to an insignificant extent *via* the formation of compounds with pyrroloindole structure (**4**, **5**) (Scheme 2) and the second route occurs mainly (Scheme 5) to form δ-carbolines (**A**, **B**, **C**) followed by the elimination of dimethylamine. The reaction of 2-amino-3-carbamoyl-δ-carboline with DMF acetal afforded one more representative of the pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indol-4-one series, which confirmed the above proposed scheme for the transformation of dienediamines **1a—c**.

Finally, it seems necessary to discuss the question why of two alternative routes (pathway *via* Scheme 2, *viz.*, synthesis of amidines **4** or pyrroloindoles **5**, and pathway *via* Scheme 5: synthesis of pyrimido[5′,4′:,5,6]pyrido[3,2-*b*]indoles **8a—c**) the second pathway predominates in the reaction of compounds **1a—c** with dimethylformamide acetal. To answer this question, let us consider the assumed transition states (TS) of both ring closure processes. The first of them is PS 1 (for the first pathway (*a*) proposed in the previous article of this series),[1] and the second transition state is TS 2 (for the second pathway (*b*)). They are shown in Scheme 7.

The pathway through TS 1 results in a system in which the five-membered rings contain the carbon and nitrogen atoms with the sp^3-configuration, providing substantial destabilization due to non-bonded interactions.[9,10] The second transition state (TS 2) is close, in essence, to the aromatic system and, correspondingly, possesses a low energy. As a result, the process is predominantly directed *via* route *b* toward the formation of δ-carbolines and their subsequent annulation with the pyrimidine cycle. Compounds **4** and **5** (route *a*) are formed only in low yields.

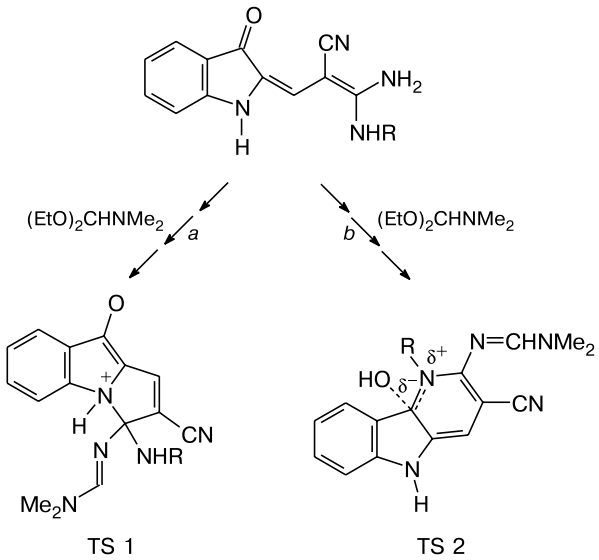
* It should be noted that 2-(3,3-diamino-2-cyanoprop-2-enylidene)indolin-3-ones bearing the primary and tertiary amino groups in position 3 of the side chain cannot form intermediate compounds of the type **A**.

Scheme 6



Reagents and conditions: *i*. $(EtO)_2CHNMe_2$, DMF, reflux, 1 h, *ii*. MeOH, HCl/EtOAc

Scheme 7



Experimental

The IR spectra of compounds **1c** and **9a,c** were recorded on an FSM-1201 instrument in Nujol, and those for compounds **8a—d** were obtained on a Perkin—Elmer 457 instrument in KBr pellets. The mass spectra (EI) of compounds **5c** and **8c** were measured on a Finnigan SSQ-710 mass spectrometer with direct sample injection into the ion source. The mass spectra of compounds **8a,b,d** were recorded on a Waters ZQ-2000 mass spectrometer (electrospray, sample injection missing the chromatographic column). ^{1}H NMR spectra were obtained on a Bruker AC-300 spectrometer in DMSO-d_6 using standard procedures of the Company. The reaction course and individual character of the substances were monitored on Silicagel 60 F_{254} plates (Merck) in chloroform—methanol (10 : 1) and ethyl acetate—isopropyl alcohol—ammonia (5 : 3 : 1) systems. The ^{1}H NMR spectra of compounds **8a—c** and **9a—d** are given in Table 1. The yields, elemental analysis data, physicochemical characteristics, and mass and IR spectral data for the synthesized compounds are presented in Table 2.

2-(3-Amino-2-cyano-3-methylaminoprop-2-enylidene)indolin-3-one (1a). Method ***A*** (see Ref. 2). A 33% solution of methylamine (1.5 mL, 16 mmol) in anhydrous ethanol was added to a suspension of dicyanovinylindole **2** (1 g, 4 mmol) in benzene (30 mL). The substance was dissolved, and a new precipitate was simultaneously formed. The suspension was refluxed with stirring for 1 h and cooled. The precipitate was filtered off, washed with propan-2-ol and ether, and dried. Methylamine salt with 3-hydroxy-2,2-dicyanovinylindole (0.8 g) was obtained. The salt was dissolved in propan-2-ol (20 mL), and the solution was refluxed with stirring for 1 h and cooled. The precipitate was filtered off, washed with propan-2-ol and ether, and dried. Dienediamine **1a** was obtained in a yield of 0.66 g. ^{1}H NMR (DMSO-d_6), δ: 2.81 (d, 3 H, CH_3, $^3J_{NH,Me}$ = 5.6 Hz); 6.76, 7.17, 7.20, 7.46 (all m, 1 H each, H(4)—H(7)); 6.87 (s, 1 H, CH); 7.45 (br.s, 2 H, NH_2); 7.64 (q, 1 H, N<u>H</u>CH_3); 8.20 (s, 1 H, N(1)H).

Method ***B***. A 33% solution of methylamine (1.5 mL, 16 mmol) in anhydrous ethanol was added to a suspension of dicyanovinylindole **2** (1 g, 4 mmol) in propan-2-ol (30 mL). The mixture was refluxed with stirring for 1 h and cooled. The precipitate was filtered off, washed with propan-2-ol and ether, and dried. Dienediamine **1a** was obtained in a yield of 0.61 g. The mother liquor was evaporated to dryness, and the residue was triturated with methanol. An additional amount (0.04 g) of compound **1a** was obtained.

The melting temperature of a sample of the substance mixed with the sample synthesized according to method ***A*** showed no depression.

11-Methyl-1,11-dihydro-4*H*-pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indol-4-one (8a). DMF diethyl acetal (0.21 mL, 1.4 mmol) was added to a solution of dienediamine **1a** (0.2 g,

0.83 mmol) in dimethylformamide (7 mL). The mixture was refluxed with stirring for 30 min. The hot precipitate was filtered off, washed with dimethylformamide and methanol, and dried. Compound **8a** was obtained in a yield of 0.11 g.

A methanolic mother liquor was evaporated, and the residue was subjected to column chromatography (SiO_2, chloroform as eluent) giving **3-dimethylaminomethyleneamino-2-cyano-9-oxo-9*H*-pyrrolo[1,2-*a*]indole (4)** (0.01 g, 4.5%), m.p. 244—245 °C (*cf.* Ref. 1: m.p. 244—245 °C).

11-Benzyl-1,11-dihydro-4*H*-pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indol-4-one (8b) was synthesized from benzylaminodieneamine **1b** (0.23 g, 0.73 mmol) and DMF acetal **8a** (0.22 mL, 1.46 mmol) similarly to compound **8a**. Compound **8b** was obtained in a yield of 0.05 g. After cooling of the mother liquor, an additional amount (0.05 g) of the same substance was obtained. The total yield of compound **8b** was 0.1 g.

11-(4-Methoxyphenyl)-1,11-dihydro-4*H*-pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indol-4-one (8c) was synthesized from 4-methoxyphenylaminodieneamine **1c** (0.5 g, 1.5 mmol) and DMF acetal (0.45 mL, 3 mmol) similarly to compound **8a**. Compound **8c** was obtained in a yield of 0.12 g. The mother liquor was evaporated, and the residue subjected to column chromatography (SiO_2, chloroform as eluent) gave **3-(4-methoxyphenyl)amino-2-cyano-9-oxo-9*H*-pyrrolo[1,2-*a*]-indole (5c)** (0.01 g, ~5%), m.p. 220—225 °C, molecular weight 315. MS (EI), m/z I_{rel} (%): 315 $[M]^+$ (100), 300 $[M - Me]^+$ (78), 272 $[M - CONH]^+$ (15). ^1H NMR (DMSO-d_6), δ: 3.74 (s, 3 H, OMe); 6.93, 7.15 (both m, 2 H each, C_6H_4), 7.32 (s, 1 H, H(1)); 7.29, 7.60 (both m, 1 H each, 3 H, H(6)—H(8)); 9.29 (br.s, 1 H, NH). We failed to obtain compound **5c** in the analytically pure form. н

11-(4-Nitrophenyl)-1,11-dihydro-4*H*-pyrimido[5′,4′:5,6]-pyrido[3,2-*b*]indol-4-one (8d). DMF acetal (0.14 mL, 0.1 mmol) was added to a solution of 2-amino-3-carbamoyl-1-(4-nitrophenyl)-1*H*-pyrido[3,2-*b*]indole[8] (**10**) (0.16 g, 0.46 mmol) in dimethylformamide (4 mL). The mixture was refluxed with stirring for 1 h. The hot precipitate was filtered off, washed with DMF and methanol, and dried. Compound **8d** was obtained in a yield of 0.11 g.

11-(Methyl)-1,6-dihydro-4-oxo-4*H*-pyrimido[5′,4′:5,6]-pyrido[3,2-*b*]indolium-11 chloride (9a). A saturated solution of HCl (0.4 mL) in ethyl acetate was added to a suspension of compound **8a** (0.11g) in methanol (20 mL), and the mixture was heated to boiling. The solution formed was filtered and cooled. The precipitate that formed was filtered off and washed with methanol and acetone. Chloride **9a** was obtained in a yield of 0.09 g.

11-(Benzyl)- and 11-(4-nitrophenyl)-1,6-dihydro-4-oxo-4*H*-pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indolium-11 chlorides (9b,d). A saturated solution of HCl (0.2 mL) in EtOAc was added to a suspension of compound **8b** or **8d** (0.3 mmol) in methanol (10 mL). The resulting solution was clarified with active carbon, filtered, and evaporated to dryness. The residue was triturated with acetone, and the precipitate was filtered off and washed with acetone. Chlorides **9b** and **9d** were obtained in yields of 0.07 g and 0.068 g, respectively.

11-(4-Methoxyphenyl)-1,6-dihydro-4-oxo-4*H*-pyrimido[5′,4′:5,6]pyrido[3,2-*b*]indolium-11 chloride (9c). A saturated solution of HCl (0.1 mL) in EtOAc was added to a suspension of compound **8c** (0.06 g, 0.18 mmol) in methanol (2 mL). A solution with immediate precipitation was formed. The precipitate was filtered off and washed with methanol and acetone. Chloride **9c** was obtained in a yield of 0.05 g.

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