Chemistry of Heterocyclic Compounds, Vol. 34, No. 5, 1998

2,3,7-TRIMETHYL-5- AND 2,3,7-TRIMETHYL-6-AMINOINDOLES IN THE SYNTHESIS OF PYRROLOQUINOLINES

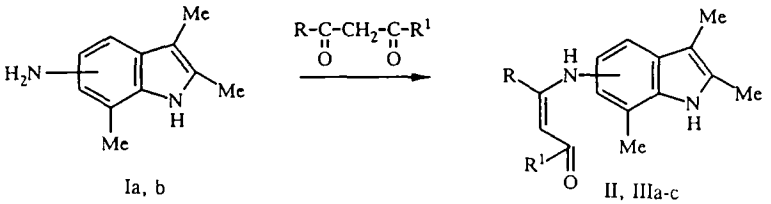
S. A. Yamashkin, N. Ya. Kucherenko, and M. A. Yurovskaya

The possible utilization of 2,3,7-trimethyl-5- and 2,3,7-trimethyl-6-aminoindoles for different approaches to the synthesis of pyrroloquinolines was investigated. It was established that enamines, obtained from 2,3,7-trimethyl-6-aminoindole, undergo ready cyclization to substituted pyrrolo[3,2-g]quinolines, which is a convenient preparative method for their synthesis. It was shown that the peri-effect of the methyl group prevails over the ortho-effect of the methyl substituent at the position 7 with the ring binding of the pyridine nucleus to the benzene ring in the process of the cyclization of the corresponding 5-enaminoindoles.

In the continuation of investigation into benzaminoindoles [1], we studied the possible utilization of 2,3,7-trimethyl-5- and 2,3,7-trimethyl-6-aminoindoles in different processes for the formation of the pyrroloquinoline system. If indole with the amino group at the position 6 can be the initial compound for the synthesis of pyrroloquinolines with known linear ring coupling then, in the case of the 5-amino analog with two free ortho positions, especially in conditions of the Coomb reaction, there arises the problem associated with the regio-orientation of the closure of the pyridine ring to form either the linear or angular isomer. On the one hand, it is known that the methyl group in the benzene ring of anilines usually blocks cyclization in the ortho position in relation to it [2]. On the other hand, we showed previously [3] that the formation of pyrroloquinolines, with one or the other ring coupling, from 5-aminoindoles depends significantly on the character of the substituent at the position 3 of the pyrrole ring. Therefore, it should be expected that the methyl group at the position 3 should inhibit the formation of angular pyrroloquinolines from 2,3,7-trimethyl-5-aminoindoles, and the formation of the linear compounds should be inhibited by the methyl group at position 7. Therefore, the object of our investigation was to test these assumptions and develop methods for the synthesis of new substituted pyrroloquinolines.

The initial aminoindoles were obtained by the reduction of the corresponding nitroindoles, synthesized by the direct nitration of the benzene ring of 2,3,7-trimethylindole. The nitration leads to the formation of the ~1:1 mixture of the 5- and 6-nitro compounds. Preparative separation of this mixture in a thick layer of Al_2O_3 only renders it possible to obtain the more chromatographically mobile 5-nitroindole in the pure form. The 2,3,7-trimethyl-6-nitroindole can only be isolated as the mixture with the 5-nitro isomer. Therefore, after the chromatographic separation of the 6-nitro isomer, additional purification by recrystallization from chloroform is necessary before the reduction.

The reaction of 2,3,7-trimethyl-5- and 2,3,7-trimethyl-6-aminoindoles, (Ia) and (Ib) respectively, with dicarbonyl compounds leads to the formation of the corresponding enamines (II), (III):



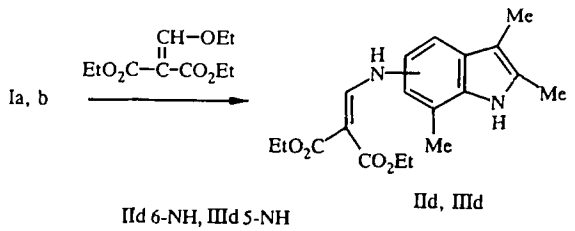
Ia, b II, IIIa-c

Ia 6-NH_2, b 5-NH_2; II (6-NH), III (5-NH); a R = R^1 = Me, b R = R^1 = Ph, c R = Me, R^1 = OEt

M. E. Evsev'ev Mordovo State Pedagogical Institute, Saransk 430007, Russia. M. V. Lomonosov Moscow State University, Moscow 119899, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 673-680, May, 1998. Original article submitted October 29, 1997.

 0009-3122/98/3405-0594$20.00

The same aminoindoles form the corresponding aminomethylenemalonates with ethoxymethylenemalonic ester:

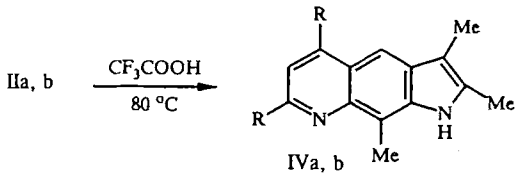


IId 6-NH, IIId 5-NH

IId, IIId

The spectral and other characteristics of the compounds (II) and (III) are presented in Table 1. The compounds (IIc) and (IIIc) were utilized for further conversions without isolation.

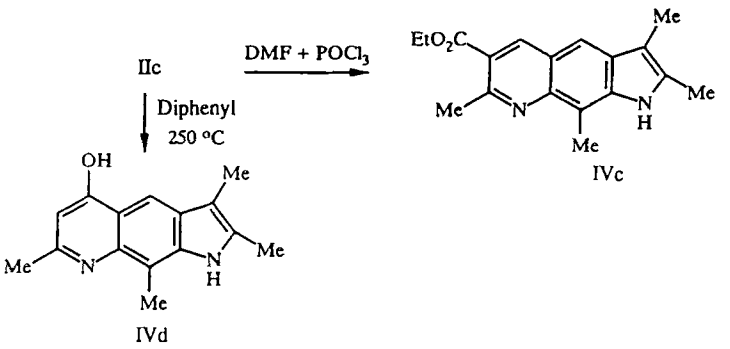
It should be expected that the cyclization of the enamines (II) should lead to the corresponding pyrroloquinolines with linear ring coupling. In fact, the enamines (IIa,b) in trifluoroacetic acid give the alkyl- and phenyl-substituted pyrrolo[3,2-g]quinolines (IVa,b).



IVa, b

IV a R = Me, b R = Ph

Under conditions of the Vilsmeier reaction, the enaminocrotonate (IIc) is converted to the pyrroloquinoline (IVc), and, on boiling in diphenyl, it forms the pyrroloquinoline (IVd).

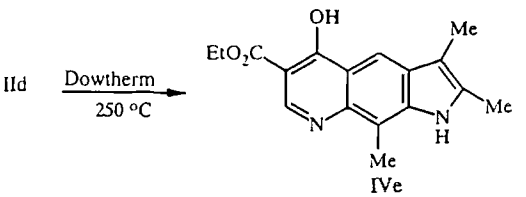


IVc

IVd

Under conditions of high-temperature cyclization (boiling Dowtherm), the enamine (IId) also forms the corresponding pyrroloquinoline (IVe).

The high yields of the pyrrolo[3,2-g]quinolines in reactions, described above, of the cyclization of enamines, obtained from 2,3,7-trimethyl-6-aminoindole, render this a preparative method.



IVe

As was already noted, there are two free ortho positions in the enamines (III) for ring closure; this may lead to the formation of a mixture of linear and angular pyrroloquinolines under conditions of the cyclization reactions.

TABLE 1. Characteristics of the Enamines (II) and (III)

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	R_f (system)	UV spectrum		PMR spectrum, δ, ppm	Yield, %
		C	H	N			λ_{max}	log ε		
1	2	3	4	5	6	7	8	9	10	11
(IIa), 4-(2,3,7-trimethylindolyl-6-amino)pent-3-en-2-one	$C_{16}H_{20}N_2O$	75,23 / 75,00	7,81 / 7,81	10,79 / 10,96	159...160	0,11 (A)	227 313	4,46 4,29	1,63 (3H, s, β-CH_3); 1,92 (3H, c, α-CH_3); 2,05 (3H, s, 3-CH_3); 2,17 (3H, s 2-CH_3); 2,25 (3H, s:, 7-CH_3); 4,98 (1H, s, H_{vin}); 6,57 (1H, d, J = 9 Hz, 5-H); 7,03 (1H, д, J = 9 Hz, 4-H); 9,12 (1H, s, 1-H); 12,17 (1H, s, NH_{imin})	72
(IIb), 1,3-diphenyl-3-(2,3,7-trimethylindolyl-6-amino)prop-2-en-1-one	$C_{26}H_{24}N_2O$	82,10	6,40	7,10 / 7,36	211...212	0,48 (A)	205 227 345	4,41 4,38 4,07	2,10 (3H, s. 3-CH_3); 2,35 (3H, s:, 2-CH_3); 2,46 (3H, s, 7-CH_3); 6,11 (1H, s, H_{vin}); 6,38 (1H, d, J = 7 Hz:, 5-H); 6,94 (1H, д, J = 7 Hz, 4-H); 7,65 (10H, m, $2C_6H_5$); 10,50 (1H, s, 1-H); 12,94 (1H, s:, NH_{imin})	38
(IId), diethyl N-(2,3,7-trimethylindolyl-6-amino)methylenemalonate	$C_{19}H_{24}N_2O_4$	66,09 / 66,26	7,05 / 7,02	8,14 / 8,13	210...211	0,20 (A)	227 277 357	4,30 4,06 4,27	1,30 (6H, m, $2OCH_2\underline{CH_3}$); 2,15 (3H, s:, 3-CH_3); 2,35 (3H, s, 2-CH_3); 2,40 (3H, s, 7-CH_3); 4,20 (4H, m, $O\underline{CH_2}CH_3$); 6,97 (1H, d, J_{45} = 9 Hz, 4-H); 7,28 (1H, d:, J_{54} = 7 Hz, 5-H); 8,39 (1H, d, J = 16 Hz, H_{vin}); 10,57 (1H, s, 1-H); 10,96 (1H, d, J = 16 Hz, NH_{imin})	66

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11
(IIIa), 4-(2,3,7-trimethylindolyl-5-amino)-3-pent-2-one	$C_{16}H_{20}N_2O$	75,17 75,00	7,79 7,81	11,05 10,94	161...162	0,17 (A)	206 233 319	4,32 4,36 4,29	1,93 (3H, s, β-CH_3; 2,00 (3H, s, α-CH_3); 2,12 (3H, s, 3-H_3); 2,35 (3H, s, 2-CH_3); 2,46 (3H, s, 7-CH_3); 5,14 (1H, s, H_{vin}); 6,60 (1H, s, 6-H); 6,95 (1H, s, 4-H); 10,50 (1H, s, 1-H); 12,33 (1H, s, NH_{imin})	46
(IIIb), 1,3-diphenyl-3-(2,3,7-trimethylindolyl-5-amino)prop-2-en-1-one	$C_{26}H_{24}N_2O$	82,10	6,31	7,01 7,36	116...117	0,56 (A)	213 290 (shoulder) 397	4,67 4,02 4,08	1,94 (3H, s, 3-CH_3); 2,26 (6H, s, 2- and 7-CH_3); 6,06 (1H, s, H_{vin}); 6,40 (1H, s, 6-H); 6,63 (1H, s, 4-H); 8,65 (10H, m, $2C_6H_5$); 10,40 (1H, s, 1-H); 13,00 (1H, s, NH_{imin})	39
(IIId), diethyl N-(2,3,7-trimethyl-indolyl-5-amino)-methylenemalonate	$C_{19}H_{24}N_2O_4$	66,26	7,02	7,73 8,14	169...170	0,25 (A)	205 229 292 341	4,24 4,19 4,16 4,20	1,30 (6H, m, $2OCH_2\underline{CH_3}$); 2,18 (3H, s, 3-CH_3); 2,34 (3H, s, 2-CH_3); 2,53 (3H, s, 7-CH_3); 4,20 (4H, m, $O\underline{CH_2}CH_3$); 6,80 (1H, s, 6-H); 7,11 (1H, s, 4-H); 8,43 (1H, d, J = 16 Hz, H_{vin}); 10,50 (1H, s, 1-H); 10,77 (1H, d, J = 16 Hz, NH_{imin})	66

TABLE 2. Characteristics of the Pyrroloquinolines (IV)-(VI)

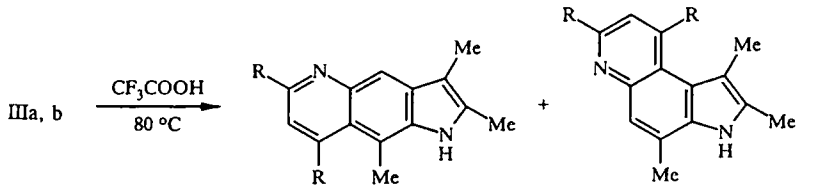
Compound	Empirical formula	Found, % / Calculated, %			mp, °C	R_f (system)	UV spectrum		PMR spectrum, δ, ppm	Yield, %
		C	H	N			λ_{max}	log ε		
(IVa), 2,3,5,7,9-pentamethylpyrrolo[3,2-g]quinoline	$C_{16}H_{18}N_2$	80,33 / 80,67	7,59 / 7,56	11,69 / 11,76	245...246	0,35 (C)	204 225 266 340	4,16 4,41 4,64 3,91	2,25 (3H, s 3-CH_3); 2,43 (3H, s, 2-CH_3); 2,60 (3H, s, 9-CH_3); 2,67 (3H, s, 5-CH_3); 2,83 (3H, s, 7-CH_3); 7,03 (1H, s, 6-H); 7,77 (1H, s, 4-H); 10,50 (1H, s, 1-H)	55
(IVb), 2,3,9-trimethyl-5,7-diphenylpyrrolo[3,2-g]quinoline	$C_{26}H_{22}N_2$	86,19	6,07	7,29 / 7,73	185...186	0,57 (C)	204 220 (shoulder) 243 292 344 (shoulder)	4,48 4,30 4,28 4,52 3,60	2,12 (3H, s, 3-CH_3); 2,24 (3H, s, 2-CH_3); 2,90 (3H, s, 9-CH_3); 7,65 (12H, m, $2C_6H_5$ and 4-, 6-H); 9,98 (1H, s, 1-H)	50
(IVc), 2,3,7,9-tetramethyl-6-ethoxycarbonylpyrrolo[3,2-g]quinoline	$C_{18}H_{20}N_2O_2$	72,83 / 72,98	6,85 / 6,80	9,17 / 9,45	221...222	0,55 (B)	217 256 294 370	4,28 4,18 4,71 3,84	1,40 (3H, s, $OCH_2\underline{CH_3}$); 2,27 (3H, s, 3-CH_3); 2,52 (3H, s, 2-CH_3); 2,96 (6H, s, 7- and 9-CH_3); 4,39 (4H, m, $O\underline{CH_2}CH_3$); 7,90 (1H, s, 4-H); 8,86 (1H, s, 5-H); 10,78 (1H, s, 1-H)	43
(IVd), 2,3,7,9-tetramethyl-5-hydroxypyrrolo[3,2-g]quinoline	$C_{15}H_{16}N_2O$	74,90 / 74,97	6,90 / 6,71	11,67	> 300	0,83 (C)	206 234 265 328	3,97 4,07 4,25 3,38	2,20 (3H, s, 3-CH_3); 2,30 (3H, s, 2-CH_3); 2,34 (3H, s, 9-CH_3); 2,65 (3H, s, 7-CH_3); 5,79 (1H, s, 6-H); 8,00 (1H, s, 4-H); 9,98 (1H, s, 8-H); 10,54 (1H, s, 1-H)	52

TABLE 2 (continued)

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	R_f (system)	UV spectrum		PMR spectrum, δ, ppm	Yield, %
		C	H	N			λ_{max}	log ε		
(IVe), 2,3,9-trimethyl-5-hydroxy-6-ethoxycarbonylpyrrolo[3,2-g]quinoline	$C_{17}H_{18}N_2O_3$	68,13 68,44	6,34 6,08	9,35 9,39	> 300	0,37 (C)	227 253 (shoulder) 273 299 363	4,06 4,06 4,28 4,15 4,59	1,30 (3H, t, $OCH_2\underline{CH_3}$); 2,33 (3H, s, 3-CH_3); 2,37 (3H, s, 2-CH_3); 2,60 (3H, s, 9-CH_3); 4,22 (2H, q, $O\underline{CH_2}CH_3$); 8,12 (1H, s, 4-H); 8,40 (1H, s, 7-H); 10,76 (1H, s, 1-H); 11,28 (1H, s, OH)	43
(Va), 2,3,6,8,9-pentamethylpyrrolo[2,3-g]-quinoline	$C_{16}H_{18}N_2$	80,70 80,67	7,60 7,56	11,76	> 300	0,05 (D)	231 272 357	4,30 4,43 3,84	2,27 (3H, s, 3-CH_3); 2,50 (3H, s, 2-CH_3); 2,83 (3H, s, 6-CH_3); 3,08 (3H, s, 9-CH_3); 3,13 (3H, s, 8-CH_3); 7,36 (1H, s, 7-H); 8,14 (1H, s, 4-H); 11,33 (1H, s, 1-H)	30
(VIa)* 1,2,4,7,9-pentamethylpyrrolo[3,2-f]-quinoline	$C_{16}H_{18}N_2$	80,67	7,56	11,76	> 300	0,30 (D)	230 267 340	4,12 4,04 3,55	2,49 (3H, s, 2-CH_3); 2,74 (3H, s, 1-CH_3); 2,67 (3H, s, 4-CH_3); 2,78 (3H, s 7-CH_3); 2,86 (3H, s, 9-CH_3); 7,41 (1H, s, 8-H); 7,50 (1H, s, 5-H); 11,89 (1H, s, 1-H)	8
(VIc), 1,2,4,7-tetramethyl-8-ethoxycarbonylpyrrolo-[3,2-f]quinoline	$C_{18}H_{20}N_2O_2$	72,98	6,80	8,94 9,45	212...213	0,11 (B)	242 291 360	4,48 4,11 3,79	1,40 (3H, m, $OCH_2\underline{CH_3}$); 2,45 (3H, s, 1-CH_3); 2,60 (3H, s, 2-CH_3); 2,84 (3H, s, 4-CH_3); 4,40 (2H, m, $O\underline{CH_2}CH_3$); 7,38 (1H, s, 5-H); 9,13 (1H, s, 9-H); 11,26 (1H, s, 3-H)	59
(VId), 1,2,4,7-tetramethyl-9-hydroxypyrrolo[3,2-f]-quinoline	$C_{15}H_{16}N_2O$	75,04 74,97	6,62 6,71	11,73 11,66	208...210	0,68 (C)	220 246 255 291 345	4,30 4,21 4,21 3,97 3,86	2,30 (3H, s, 1-CH_3); 2,39 (3H, s, 2-CH_3); 2,49 (3H, s, 7-CH_3); 2,60 (3H, s, 4-CH_3); 5,77 (1H, s, 8-H); 6,88 (1H, s, 5-H); 10,75 (1H, s, 3-H); 10,89 (1H, s, 6-H)	69

*M^+: Found 238; calculated 238 (by mass spectrometry).

We established that, under conditions of acid cyclization (boiling in trifluoroacetic acid) of the enamine (IIIa), both the angular pyrroloquinoline (VIa) and the linear pyrroloquinoline (Va) are detected in the ratio of 4:1 in the reaction mixture.

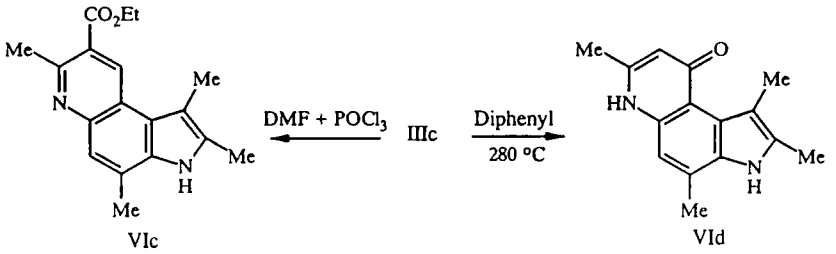


V, VI a R = Me, b R = Ph

The isomers obtained differ from each other in the chemical shifts of the protons of the γ-H of the pyridine portion, the β-methyl group, and the NH group of the pyrrole ring in the PMR spectra, the character of which agrees with the spectra previously described for analogous structures [4]. The UV spectra of the pyrroloquinolines (Va) and (VIa) show differences in the ratio of intensities of absorption bands in the short-wave spectral region, characteristic of pyrroloquinolines with such ring coupling [4]. Under conditions of acid cyclization, the enaminoketone (IIIb) also gives a mixture of the linear and angular pyrroloquinolines in approximately the same proportion as for the enamine (IIIa) according to the integral intensity of signals of characteristic protons in the PMR spectra. However, the isomers were not isolated in the free form due to difficulties in separation.

In contrast to the enamines (IIIa,b), compound (IIIc) affords the angularly coupled pyrroloquinolines (VIa,b) in conditions of the Vilsmeier reaction and on boiling in diphenyl.

The structure of the pyrroloquinolines was shown by comparative analysis of the PMR and UV spectral data of the compounds (VI) with spectra of similar structures described in the literature (see Table 2) [3, 4].



Therefore, the preferred formation of linear pyrroloquinolines under conditions of the acid cyclization of compounds (IIIa, b) indicates that, in the process of closure of the pyridine ring, the peri effect of the methyl group in the β-position of the pyrrole ring prevails over the ortho influence of the analogous substituent at the position 7, which basically also determines the direction of the reaction. The regio-orientation of cyclization of other enamines is contained in the general concept of the formation of angular and linear pyrroloquinolines from 2,3-dimethyl-5-aminoindoles, previously expressed [2].

EXPERIMENTAL

The PMR spectra were registered on the Bruker AC-200P instrument in DMSO-D_6 in relation to TMS. The UV spectra were measured on the Specord instrument in ethanol. Monitoring of the course of reactions and the purity of the compounds isolated was accomplished on plates of Silufol UV-254 in the 10:1 system of benzene–ethyl acetate (A), the 1:1 system of benzene–ethyl acetate (B), the 1:1 system of ethyl acetate–methanol (C), and the 10:10:1 system of benzene–ethyl acetate–methanol (D).

2,3,7-Trimethyl-6-nitro- and 2,3,7-Trimethyl-5-nitroindole. To the solution, cooled to 0°C, of 1.59 g (10 mmole) of freshly recrystallized 2,3,7-trimethylindole in 25 ml of 96% sulfuric acid is added, with cooling and stirring, the cooled solution of 1.01 g (10 mmole) of potassium nitrate in 25 ml of H_2SO_4 at the same concentration and with the rate such that

the temperature should not exceed 10°C. After 10-15 min, the reaction mass is poured onto ice. When the residue with large particles is formed, it is filtered off, washed repeatedly with water, and dried in air. In the case of the formation of a finely dispersed residue, it is extracted with ~200 ml of chloroform, and the extract is washed twice with the 10-12% solution of aqueous ammonia and two or three times with water; it is dried with Na_2SO_4, and the chloroform is distilled off.The mixture of two isomers (in the 1:1 ratio according to PMR spectral data) is separated preparatively on plates with a loose thick layer of Al_2O_3 (neutral, Grade 1 activity) in chloroform. The yield of the less polar 2,3,7-trimethyl-5-nitroindole is 15%; it has the mp 205-206°C (from chloroform). The PMR spectrum (CCl_4–DMSO-D_6) is as follows: 2.13 ppm (3H, s, 3-CH_3), 2.30 ppm (3H, s, 2-CH_3), 2.40 ppm (3H, s, 7-CH_3), 7.50 ppm (1H, d, J_{64} = 2 Hz, 6-H), 7.95 ppm (1H, d, J_{46} = 2 Hz, 4-H), and 10.75 ppm (1H, s, 1-H). The UV spectrum, given as the λ_{max} (log ε), is as follows: 215 nm (4.14), 267 nm (4.01), and 333 nm (3.73). Found, %: C 64.5 and H 5.7. $C_{11}H_{12}N_2O_2$. Calculated, %: C 64.7 and H 5.9.

The yield of the more polar 2,3,7-trimethyl-6-nitroindole with an admixture of the isomeric 5-nitroindole is 42%. The 6-nitroindole is separated from the isomeric indole by multiple crystallization from the mixture of chloroform–heptane; the mp is 198-199°C. The PMR spectrum (CCl_4–DMSO-D_6) is as follows: 2.00 ppm (3H, s, 3-CH_3), 2.20 ppm (3H, s, 2-CH_3), 2.55 ppm (3H, s, 7-CH_3), 6.97 ppm (1H, d, J_{45} = 9 Hz, 4-H), 7.50 ppm (1H, d, J_{54} = 9 Hz, 5-H), and 10.75 ppm (1H, s, 1-H). The UV spectrum, given as the λ_{max} (log ε), is as follows: 222 nm (4.18), 260 nm (3.74), and 313 nm (3.60). Found, %: C 64.4 and H 5.6. $C_{11}H_{12}N_2O_2$. Calculated, %: C 64.7 and H 5.9.

2,3,7-Trimethyl-5-aminoindole (Ib). To the solution of 1.02 g (5 mmole) of 2,3,7-trimethyl-5-nitroindole in 100 ml of abs. ethanol are added 8 ml of concentrated hydrazine hydrate and a catalytic amount of active Raney nickel. The reaction mass is stirred with heating for 1-1.5 h. At completion of the reaction, with chromatographic monitoring, the mixture, still hot, is filtered from the catalyst. The methanol is distilled off to a minimal volume, and 50 ml of water are added. The precipitated residue is filtered off, washed repeatedly with water, and dried. The yield is 0.64 g (73%). The mp is 169-170°C (from benzene). The PMR spectrum (CCl_4–DMSO-D_6) is as follows: 1.98 ppm (3H, s, 3-CH_3), 2.18 ppm (6H, s, 2-, 7-CH_3), 3.28 ppm (2H, s, NH_2), 6.03 ppm (1H, broad s, 6-H), 6.23 ppm (1H, broad s, 4-H), and 9.10 ppm (1H, s, 1-H). The UV spectrum, given as the λ_{max} (log ε), is as follows: 214 nm shoulder (4.19), 282 nm (4.33), and 303 nm (3.63). Found, %: C 75.4 and H 7.6. $C_{11}H_{14}N_2$. Calculated, %: C 75.9 and H 8.0.

2,3,7-Trimethyl-6-aminoindole (Ia). This compound is obtained analogously from 2,3,7-trimethyl-6-nitroindole; the yield is 65%, and the mp is 154-155°C (from benzene). The PMR spectrum (CCl_4–DMSO-D_6) is as follows: 1.98 ppm (3H, s, 3-CH_3), 2.13 ppm (3H, s, 7-CH_3), 2.17 ppm (3H, s, 2-CH_3), 3.12 ppm (2H, s, NH_2), 6.20 ppm (1H, d, J_{54} = 9 Hz, 5-H), 6.68 ppm (1H, d, J_{45} = 9 Hz, 4-H), and 8.78 ppm (1H, s, 1-H). The UV spectrum, given as the λ_{max} (log ε), is as follows: 208 nm shoulder (4.13), 275 nm (4.38), and 303 nm (3.37).

Enamines (II), (III) and Pyrroloquinolines (IV)-(VI). These compounds were obtained by methods described in the works [1, 3]. The conditions of formation of enamines of aminoindoles are as follows: (II), (IIIa) by the boiling with acetylacetone for 1-1.5 h; (II), (IIIb) by the heating with dibenzoylmethane at 170°C for 1.5-2 h; (II), (IIIc) by the boiling in benzene with acetoacetic ester and traces of acetic acid for 10-14 h; (II), (IIId) by the boiling with ethoxymethylenemalonic ester in alcohol for 2 h. The conditions of cyclization of the enamines are as follows: (II), (IIIa,b) by the boiling in trifluoroacetic acid for 1-2 h; (II), (IIIc) by boiling in diphenyl for 5-10 min (method A) or boiling in chloroform with the Vilsmeier reagent for 6 h (method B); (IId) by boiling in Dowtherm for 5-10 min. The compounds (II), (IIIa,c) are purified by passage of the heated solution in the mixture of benzene with heptane through a layer of Al_2O_3 and the subsequent recrystallization from heptane. Compounds (II), (III), (IVb) are purified preparatively in a thick layer of Al_2O_3 in chloroform. Compounds (II), (III), (IVd), (IVe), (VIc) are purified by recrystallization from aqueous ethanol with activated carbon. Compounds (V), (VIa) are purified preparatively in a thick layer of Al_2O_3 in the 10:1:1 system of benzene–ethyl acetate–methanol with the subsequent recrystallization from ethanol. The physicochemical characteristics of the compounds obtained are presented in Tables 1 and 2.

REFERENCES

1. S. A. Yamashkin and M. A. Yurovskaya, Khim. Geterotsikl. Soedin., No. 11, 1486 (1997).
2. S. A. Yamashkin, L. G. Yudin, and A. N. Kost, Khim. Geterotsikl. Soedin., No. 8, 1011 (1992).
3. A. N. Kost, S. A. Yamashkin, and L. G. Yudin, Khim. Geterotsikl. Soedin., No. 6, 770 (1977).
4. S. A. Yamashkin, Khim. Geterotsikl. Soedin., No. 11, 1520 (1992).