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SYNTHESIS AND STUDY OF THE REACTIONS OF 2,5- AND 1,2,5-SUBSTITUTED 6-AMINOINDOLES

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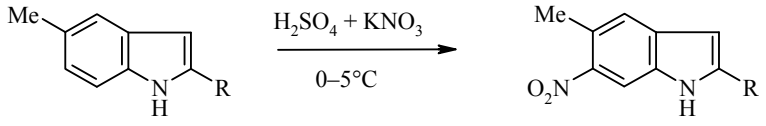
It has been shown that nitration with a KNO_3 + H_2SO_4 mixture of 2,5-dimethyl- and 5-methyl-2-phenylindoles proceeds strictly selectively with the formation of 6-nitro derivatives, by reduction of which the corresponding aminoindoles were synthesized. It was established that the condensation of the aminoindoles obtained with β-diketones leads initially to enamino ketones, which in the presence of various acidic reagents are not subject to cyclization, i.e. may not be used for the synthesis of the corresponding pyrroloquinolines.

Keywords: acetylacetone, dibenzoylmethane, 2,5-dimethyl- and 5-methyl-2-phenylindoles, 2,5-dimethyl-, 1,2,5-trimethyl-, 5-methyl-2-phenyl, 1,5-dimethyl-2-phenyl-6-nitro- and 6-aminoindoles.

Interest in aminoindoles is linked with their use as precursors of tricyclic nitrogen heterocycles, which are potential physiologically active compounds of the pyrroloquinoline series [1, 2].

One of the methods of obtaining nitroindoles with the nitro group in the benzene ring is direct nitration under electrophilic substitution reaction conditions. The direction of the nitration reaction, depending on the conditions of carrying it out, has been studied for a large series of indoles with various substituents both in the pyrrole and in the benzene portions of the molecule [2, 3]. However, 2,5-dimethyl- (**1**) and 5-methyl-2-phenylindole (**2**) were absent from this number of compounds. We therefore investigated the nitration of these indoles with a KNO_3 + H_2SO_4 mixture.

For 2,5-dimethylindole **1** an alternative introduction of the nitro group might be expected into positions 3, 4, 6, 7 with the formation of four possible isomeric nitroindoles. However we discovered that the reaction occurs strictly selectively and leads in high yield only to 2,5-dimethyl-6-nitroindole (**3**) (Table 1).



1, **2** **3**, **4**

1, **3** R = Me; **2**, **4** R = Ph

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This is shown by the ^{1}H NMR spectrum (Table 2) of compound **3**, in which the singlet signals of the benzene ring protons (H-4, 7) and the H-3 proton of the pyrrole fragment are displayed.

The possibility of forming a nitro derivative at the 2-phenyl group is also not excluded on nitrating indole **2**. However in the case of 5-methyl-2-phenylindole (**2**) the sole reaction product was 5-methyl-6-nitro-2-phenylindole (**4**). The ^{1}H NMR spectrum of compound **4** differed from the spectrum of compound **3** by the absence of a singlet for the protons of the 2-CH_3 group and the presence of two triplets and a doublet for the protons of the phenyl group in position 2.

The character of substitution in the pyrrole ring of indoles does not therefore show a significant effect on the course of the nitration reaction in strongly acidic medium, and the direction of electrophilic attack is determined by the substitution in the benzene ring, which confirms the regularity detected previously [2, 3].

TABLE 1. Physicochemical Characteristics of Compounds **3-18**

Compound	Empirical formula	Found, % / Calculated, %		R_f*	mp, °C*[2]	Yield, %
		C	H			
3	$C_{10}H_{10}N_2O_2$	63.14 / 63.15	5.31 / 5.30	0.38	127-128	82
4	$C_{15}H_{12}N_2O_2$	71.41 / 71.42	4.80 / 4.79	0.37	209-210	93
5	$C_{11}H_{12}N_2O_2$	64.44 / 64.69	6.11 / 5.92	0.38	102-103	98
6	$C_{16}H_{14}N_2O_2$	72.00 / 72.16	5.42 / 5.30	0.43	162-164	97
7	$C_{11}H_{14}N_2$	75.48 / 75.82	8.41 / 8.10	0.41	120-123	83
8	$C_{16}H_{16}N_2$	81.13 / 81.32	6.97 / 6.82	0.59	151-153	86
9	$C_{10}H_{12}N_2$	74.95 / 74.97	7.56 / 7.55	0.34	122-123	95
10	$C_{15}H_{14}N_2$	80.95 / 81.05	6.27 / 6.35	0.5	215-216	89
11	$C_{16}H_{20}N_2O$	74.80 / 74.97	7.98 / 7.86	0.53	131-132	50
12	$C_{21}H_{22}N_2O$	79.01 / 79.21	7.08 / 6.96	0.53	122-124	30
13	$C_{26}H_{24}N_2O$	82.06 / 82.07	6.37 / 6.36	0.68	146-147	18
14	$C_{31}H_{26}N_2O$	83.90 / 84.13	6.13 / 5.92	0.47	173-174	22
15	$C_{15}H_{18}N_2O$	74.20 / 74.35	7.65 / 7.49	0.44	142-143	58
16	$C_{20}H_{20}N_2O$	78.67 / 78.92	6.82 / 6.62	0.54	191-192	84
17	$C_{25}H_{22}N_2O$	81.60 / 81.94	6.26 / 6.05	0.41	170-171	34
18	$C_{30}H_{24}N_2O$	83.74 / 84.08	5.91 / 5.65	0.68	220-221	37

*Systems: benzene (compounds **3, 4, 14, 17**), benzene–hexane, 3:1 (compounds **5, 6**), benzene–ethyl acetate, 1:4 (compounds **7, 10**), 1:1 (compounds **8, 9**), 3:1 (compounds **11, 15, 16**), and 10:1 (compounds **12, 13, 18**).

*[2]Solvent for crystallization: benzene–hexane (compound **3**), chloroform–petroleum ether (compound **4**), heptane (compounds **5, 6**), methanol (compounds **7-10**), and benzene–petroleum ether (compounds **11-18**).

TABLE 2. UV and ^{1}H NMR Spectra of Compounds **3-18**

Com-pound	UV spectrum, λ_{max}, nm (log ε)	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
3	208 (4.60), 259 (4.13), 360 (4.11)	2.44 (3H, s, 2-CH_3); 2.58 (3H, s, 5-CH_3); 6.24 (1H, s, H-3); 7.40 (1H, s, H-4); 8.06 (1H, s, H-7); 11.52 (1H, s, H-1)
4	212 (4.34), 246 (4.13), 280 (sh) (4.03), 380 (4.03)	2.61 (3H, s, 5-CH_3); 7.01 (1H, s, H-3); 7.42 (1H, t, *J* = 7.5, H-*p* 2-Ph); 7.53 (2H, t, *J* = 7.5, H-*m* 2-Ph); 7.56 (1H, s, H-4); 7.92 (2H, d, *J* = 7.5, H-*o* 2-Ph); 8.15 (1H, s, H-7); 12.12 (1H, s, H-1)
5	214 (4.42), 261 (3.92), 340 (3.92)	2.45 (3H, s, 2-CH_3); 2.58 (3H, s, 5-CH_3); 3.73 (3H, s, 1-CH_3); 6.31 (1H, s, H-3); 7.41 (1H, s, H-4); 8.22 (1H, s, H-7)
6	210 (4.45), 250 (4.15), 274 (sh) (4.02), 360 (4.02)	2.63 (3H, s, 5-CH_3); 3.83 (3H, s, 1-CH_3); 6.66 (1H, s, H-3); 7.51 (1H, t, *J* = 7.5, H-*p* 2-Ph); 7.54 (2H, t, *J* = 7.5, H-*m* 2-Ph); 7.56 (1H, s, H-4); 7.64 (2H, d, *J* = 7.5, H-*o* 2-Ph); 8.34 (1H, s, H-7)
7	210 (4.50), 228 (4.52), 281 (3.89), 304 (3.96)	2.10 (3H, s, 2-CH_3); 2.29 (3H, s, 5-CH_3); 3.31 (3H, s, 1-CH_3); 4.42 (2H, s, 6-NH_2); 5.89 (1H, s, H-3); 6.53 (1H, s, H-4); 6.96 (1H, s, H-7)
8	210 (4.49), 248 (4.21), 343 (4.09)	2.15 (3H, s, 5-CH_3); 3.58 (3H, s, 1-CH_3); 4.65 (2H, s, 6-NH_2); 6.30 (1H, s, H-3); 6.64 (1H, s, H-4); 7.13 (1H, s, H-7); 7.34 (1H, t, *J* = 7.5, H-*p* 2-Ph); 7.45 (2H, t, *J* = 7.5, H-*m* 2-Ph); 7.51 (2H, d, *J* = 7.5, H-*o* 2-Ph)
9	207 (4.55), 225 (4.52), 267 (3.87), 304 (3.96)	2.08 (3H, s, 5-CH_3); 2.26 (3H, s, 2-CH_3); 4.34 (2H, s, 6-NH_2); 5.79 (1H, s, H-3); 6.53 (1H, s, H-4); 6.92 (1H, s, H-7); 10.15 (1H, s, H-1)
10	207 (4.70), 225 (4.52), 337 (4.59)	2.12 (3H, s, 5-CH_3); 4.61 (2H, s, 6-NH_2); 6.62 (1H, s, H-3); 6.65 (1H, s, H-4); 7.08 (1H, s, H-7); 7.19 (1H, t, *J* = 7.5, H-*p* 2-Ph); 7.37 (2H, t, *J* = 7.5, H-*m* 2-Ph); 7.73 (2H, d, *J* = 7.5, H-*o* 2-Ph); 10.79 (1H, s, H-1)
11	202 (4.42), 223 (4.47), 310 (4.35)	1.85 (3H, s, =C–CH_3); 1.99 (3H, s, O=C–CH_3); 2.20 (3H, s, 2-CH_3); 2.37 (3H, s, 5-CH_3); 3.62 (3H, s, 1-CH_3); 5.22 (1H, s, =CH); 6.13 (1H, s, H-3); 7.23 (1H, s, H-4); 7.29 (1H, s, H-7); 12.33 (1H, s, 6-NH)
12	208 (4.52), 229 (4.52), 318 (4.59)	1.92 (3H, s, =C–CH_3); 2.01 (3H, s, O=C–CH_3); 2.26 (3H, s, 5-CH_3); 3.72 (3H, s, 1-CH_3); 5.25 (1H, s, =CH); 6.50 (1H, s, H-3); 7.37 (1H, s, H-4); 7.43 (1H, t, *J* = 7.5, H-*p* 2-Ph); 7.45 (1H, s, H-7); 7.51 (2H, t, *J* = 7.5, H-*m* 2-Ph); 7.59 (2H, d, *J* = 7.5, H-*o* 2-Ph); 12.41 (1H, s, 6-NH)
13	208 (4.42), 289 (3.97), 393 (4.14)	2.29 (3H, s, 2-CH_3); 2.40 (3H, s, 5-CH_3); 3.26 (3H, s, 1-CH_3); 6.04 (1H, s, =CH); 6.18 (1H, s, H-3); 6.57 (1H, s, H-4); 7.23 (1H, s, H-7); 7.30-7.60 (8H, m, H-*p*, -*m*, -*o* =C–Ph; H-*m*, -*p* O=C–Ph); 8.01 (2H, d, *J* = 7.5, H-*o* O=C–Ph); 13.00 (1H, s, 6-NH)
14	206 (4.58), 239 (4.39), 317 (4.24), 400 (4.28)	2.49 (3H, s, 5-CH_3); 3.35 (3H, s, 1-CH_3); 6.26 (1H, s, =CH); 6.42 (1H, s, H-3); 6.68 (1H, s, H-4); 7.30-7.80 (14H, m, H-7; H-*p*, -*m*, -*o* 2-Ph; H-*p*, -*m*, -*o* =C–Ph; H-*p*, -*m* O=C–Ph); 8.03 (2H, d, *J* = 7.5, H-*o* O=C–Ph); 13.02 (1H, s, 6-NH)
15	200 (4.52), 222 (4.40), 315 (4.24)	1.82 (3H, s, =C–CH_3); 1.99 (3H, s, O=C–CH_3); 2.20 (3H, s, 2-CH_3); 2.36 (3H, s, 5-CH_3); 5.21 (1H, s, =CH); 6.04 (1H, s, H-3); 7.05 (1H, s, H-4); 7.26 (1H, s, H-7); 10.83 (1H, s, H-1); 12.29 (1H, s, 6-NH)
16	203 (4.62), 230 (4.39), 330 (4.57)	1.89 (3H, s, =C–CH_3); 2.01 (3H, s, O=C–CH_3); 2.24 (3H, s, 5-CH_3); 5.25 (1H, s, =CH); 6.84 (1H, s, H-3); 7.18 (1H, s, H-4); 7.31 (1H, t, *J* = 7.5, H-*p* 2-Ph); 7.37 (1H, s, H-7); 7.45 (2H, t, *J* = 7.5, H-*m* 2-Ph); 7.84 (2H, d, *J* = 7.5, H-*o* 2-Ph); 11.51 (1H, s, H-1); 12.40 (1H, s, 6-NH)
17	203 (4.74), 291 (4.14), 391 (4.31)	2.25 (3H, s, 2-CH_3); 2.43 (3H, s, 5-CH_3); 5.96 (1H, s, =CH); 6.15 (1H, s, H-3); 6.50 (1H, s, H-4); 7.23 (1H, s, H-7); 7.30-7.56 (8H, m, H-*p*, -*m*, -*o* =C–Ph; H-*m*,-*p* O=C–Ph); 8.01 (2H, d, *J* = 7.5, H-*o* O=C–Ph); 10.60 (1H, s, H-1); 12.96 (1H, s, 6-NH)
18	204 (4.72), 240 (4.54), 325 (4.50), 395 (4.34)	2.49 (3H, s, 5-CH_3); 6.21 (1H, s, =CH); 6.60 (1H, s, H-3); 6.79 (1H, s, H-4); 7.20-7.76 (14H, m, H-7; H-*p*, -*m*, -*o* 2-Ph; H-*p*, -*m*, -*o* =C–Ph; H-*m*, -*p* O=C–Ph); 8.04 (2H, d, *J* = 7.5, H-*o* O=C–Ph); 11.23 (1H, s, H-1); 13.00 (1H, s, 6-NH)

Methylation of the obtained nitroindoles **3, 4** with dimethyl sulfate in alkaline medium leads in good yield to 1,2,5-trimethyl- and 1,5-dimethyl-6-nitro-2-phenylindole (**5, 6**). The signal of the NH group proton was absent from their ^{1}H NMR spectra and the signal of the 1-CH_3 group protons was present.

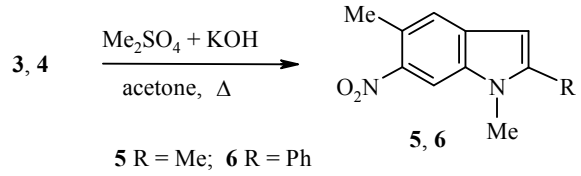
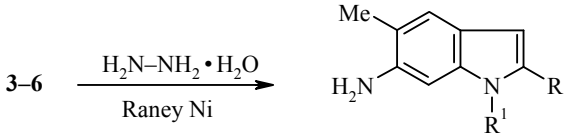


TABLE 3. Mass Spectra of Compounds **3-18**

Com-pound	*m/z* (I_{rel}, %)
3	190 $[M]^+$ (42), 173 (62), 160 (15), 145 (41), 144 (31), 143 (57), 142 (27), 132 (13), 130 (17), 128 (18), 118 (55), 117 (39), 116 (18), 115 (48), 104 (11), 103 (17), 102 (15), 91 (21), 90 (11), 89 (25), 78 (14), 77 (52), 76 (24), 75 (25), 74 (16), 65 (29), 64 (17), 63 (60), 62 (25), 59 (19), 53 (12), 52 (45), 51 (73), 50 (42), 46 (19), 42 (44), 41 (21), 40 (17), 39 (100), 38 (23)
4	253 (32), 252 $[M]^+$ (96), 236 (20), 235 (96), 222 (31), 207 (35), 206 (66), 205 (24), 204 (39), 203 (10), 194 (11), 193 (13), 191 (14), 190 (13), 180 (37) 178 (29), 177 (13), 176 (17), 165 (17), 153 (11), 152 (28), 151 (18), 139 (18), 128 (26), 127 (17), 126 (150), 115 (14), 104 (18), 103 (26), 102 (46), 101 (20), 90 (16), 89 (24), 88 (18), 87 (15), 78 (17), 77 (100), 76 (46), 75 (34), 74 (20), 65 (12), 64 (10), 63 (41), 62 (17), 52 (36), 51 (78), 50 (34), 39 (46)
5	205 (24), 204 $[M]^+$ (100), 187 (92), 159 (48), 158 (51), 157 (24), 156 (15), 143 (28), 142 (32), 132 (27), 131 (13), 130 (25), 129 (22), 128 (19), 127 (16), 115 (50), 89 (20), 77 (16), 76 (30), 66 (12), 65 (27), 64 (22), 63 (31), 59 (12), 58 (10), 57 (17), 56 (20), 52 (20), 51 (30), 45 (12), 43 (25), 42 (21).
6	267 (16), 266 $[M]^+$ (95), 250 (18), 249 (100), 236 (18), 221 (31), 220 (49), 219 (23), 218 (22), 217 (12), 205 (23), 204 (41), 194 (24), 178 (20), 165 (15), 152 (15), 151 (11), 115 (24), 109 (26), 103 (12), 102 (36), 101 (11), 97 (13), 96 (19), 91 (20), 90 (12), 89 (25), 88 (32), 87 (13), 77 (45), 76 (35), 75 (26), 74 (18), 63 (35), 62 (15), 52 (19), 51 (54), 50 (28), 42 (17), 40 (16), 39 (40)
7	175 (12), 174 $[M]^+$ (100), 173 (87), 159 (27), 158 (15), 87 (26), 86 (16), 79 (15)
8	237 (19), 236 $[M]^+$ (100), 235 (29), 221 (19), 118 (39), 117 (18), 116 (12), 110 (21), 109 (24), 103 (11), 89 (10), 77 (18), 51 (18), 39 (17)
9	161 (10), 160 $[M]^+$ (100), 159 (90), 145 (9), 80 (10), 79 (10), 42 (15), 41 (16), 39 (20)
10	223 (14), 222 $[M]^+$ (100), 221 (31), 111 (18), 77 (47), 76 (12), 52 (19), 51 (37), 50 (16), 41 (18), 39 (42)
11	257 (11), 256 $[M]^+$ (64), 241 (21), 239 (13), 226 (12), 225 (10), 213 (35), 199 (62), 198 (63), 197 (30), 184 (23), 183 (12), 174 (10), 173 (19), 172 (30), 158 (27), 157 (16), 156 (10), 148 (11), 142 (12), 128 (19), 120 (20), 115 (21), 99 (33), 98 (21), 91 (23), 89 (11), 84 (31), 78 (13), 77 (20), 65 (14), 63 (17), 52 (11), 51 (20), 43 (100), 42 (29), 41 (17), 40 (15), 39 (46)
12	319 (14), 318 $[M]^+$ (61), 303 (15), 301 (13), 275 (33), 261 (48), 260 (42), 259 (20), 246 (12), 235 (14), 234 (23), 220 (20), 204 (14), 159 (17), 152 (23), 151 (27), 130 (24), 129 (14), 128 (11), 115 (15), 108 (11), 102 (14), 91 (13), 89 (12), 84 (31), 77 (25), 76 (12), 63 (13), 51 (20), 43 (100), 42 (22), 41 (13), 40 (12), 39 (32)
13	380 $[M]^+$ (19), 363 (11), 275 (44), 261 (36), 260 (44), 259 (15), 173 (21), 172 (13), 158 (20), 157 (13), 142 (11), 130 (13), 115 (16), 105 (70), 102 (10), 91 (11), 77 (100), 51 (33), 39 (14)
14	442 $[M]^+$ (7), 425 (3), 337 (9), 323 (7), 322 (9), 220 (11), 105 (71), 102 (13), 78 (13), 77 (100), 51 (30)
15	242 $[M]^+$ (23), 227 (12), 225 (6), 199 (16), 185 (27), 184 (27), 183 (14), 158 (11), 84 (11), 63 (10), 51 (11), 43 (100), 39 (37)
16	304 $[M]^+$ (65), 289 (28), 287 (15), 261 (32), 247 (43), 246 (35), 245 (19), 220 (13), 84 (6), 78 (26), 77 (19), 51 (18), 43 (100), 39 (32)
17	366 $[M]^+$ (6), 349 (4), 261 (25), 247 (15), 246 (22), 159 (10), 105 (83), 102 (12), 78 (22), 77 (100), 76 (22), 51 (45), 39 (15)
18	428 $[M]^+$ (2), 411 (1), 323 (8), 309 (6), 308 (8), 221 (10), 105 (89), 77 (100), 51 (51), 50 (16), 44 (10), 39 (15)

The *ortho* disposition of the substituents in the benzene ring of indoles **3-6** also confirms their behavior under electron impact. In the mass spectra of all the obtained nitroindoles (Table 3) the molecular ion peak was most intense as also were the fragment ions with *m/z* $[M-17]^+$ and $[M-46]^+$, which correspond to elimination of OH and NO_2 groups. Such fragmentation is characteristic of *o*-methylnitrobenzene [4].

Reduction of nitroindoles **3-6** with hydrazine hydrate in the presence of Raney nickel according to the known procedure of [5] leads in good yield to the corresponding aminoindoles **7-10.**



7–10

7 R = R^1 = Me; **8** R = Ph, R^1 = Me; **9** R = Me, R^1 = H; **10** R = Ph, R^1 = H

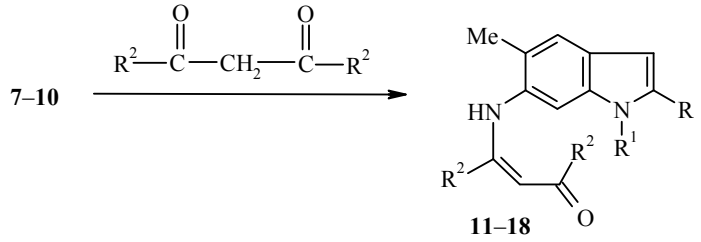
The ^{1}H NMR spectra of compounds **7-10** contain a two-proton singlet for the amino group in addition to all the proton signals in the spectra of the corresponding nitroindoles. The aminoindoles obtained, like all aromatic amines [4], are stable to the action of electron impact. In the mass spectra of amines **7-10** investigated by us the intensity of the molecular ion peak was maximal. Fragment ions with *m/z* $[M-1]^+$ and $[M-15]^+$ are probably caused by the presence of a methyl group in the molecule.

Aminoindoles **7-10** were investigated further by reaction with β-dicarbonyl compounds with the aim of obtaining pyrroloquinolines.

Reactions with diketones were studied for a large series of aminoindoles in [1, 2]. It was established that in a majority of cases the first condensation proceeds with the formation of indolylenamino ketones. However in the presence of a free β-position in the pyrrole fragment it is possible that the formation of a product of interaction of the carbonyl component at position 3 of the indole is not excluded. In this connection it was interesting to study the behavior of the synthesized 6-aminoindoles **7-10** unsubstituted in the β-position of the pyrrole ring with acetylacetone and dibenzoylmethane.

We have established that aminoindoles **7-10** on boiling in acetylacetone and heating with dibenzoylmethane are converted into compounds **11-18**, i.e. reaction proceeds exclusively at the amino group.

The formation of condensation products of amines with dibenzoylmethane requires more rigorous conditions (~180°) and a longer time, which is explained by the lower reactivity of the benzoyl group. In the ^{1}H NMR spectra of enamino ketones **11-18** signals were observed for protons of =CH, H-3, and 6-NH groups. The values of the chemical shifts of the amine and vinylic protons indicates the *Z*-form of the obtained enamines [6].



11–18

11–14 R^1 = Me, **15–18** R^1 = H; **11**, **15** R = R^2 = Me; **12**, **16** R = Ph, R^2 = Me;
13, **17** R = Me, R^2 = Ph; **14**, **18** R = R^2 = Ph

Enamines **11-18** readily underwent decomposition under the action of electron impact (the intensity of the molecular ion peaks was 20-60%). On the basis of the presence of fragment ions $[M-OH]^+$, $[M-(COR^2)]^+$, $[M-(CH_2COR^2)]^+$, $[M-(R^2C{=}CH{-}COR^2)]^+$ it may be stated that for the investigated compounds in the gas phase there are enolic and imine forms besides the enaminoketone. The character of the behavior of enamines **11-18** is on the whole contained within the general scheme of dissociative ionization of similar structures studied previously [7].

It is known that enamines obtained from 6-amino-2,3,5-trimethylindole and β-diketones (acetylacetone and dibenzoylmethane) on boiling in trifluoroacetic acid are converted in good yield into the corresponding pyrroloquinolines with an angular junction of the rings, while their N-methyl-substituted analogs are not subject to cyclization [1].

While investigating the behavior of enamino ketones **11-18** in the cyclization reaction under the action of various acidic reagents ($ZnCl_2$, CF_3COOH, H_2SO_4), and also thermally by boiling in diphenyl, we did not establish the formation of pyrroloquinolines not only for the N–Me-substituted enamines **11-14**, but also for compounds **15-18**. Only the starting materials and their decomposition products were detected in the reaction mixture after carrying out the reaction.

Indolyl-6-aminovinyl ketones **11-18** may not be used to obtain the corresponding pyrroloquinolines. The reason for their inability to cyclize has been clarified and will be the subject of a separate investigation.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker DRX 500 SF instrument (500 MHz) in DMSO-d_6, internal standard was TMS. The mass spectra were obtained on a Finnigan MAT Incos-50 mass spectrometer with direct insertion of samples into the ion source at an ionization energy of 70 eV, emission current was 1.5 mA, and temperature 70-250°C. Electronic spectra were recorded on a Specord instrument in ethanol. Purification of reaction products was carried out by filtering boiling solutions of substances through a layer (2-3 cm) of Al_2O_3 (neutral, Brockmann activity grade I and II). A check on the progress of reactions and the purity of the compounds obtained was effected by TLC on Silufol UV-254 plates.

Nitroindoles **3-6** and aminoindoles **7-10** were obtained by the known procedures given in [5].

2,5-Dimethyl-6-nitroindole (3) was obtained from 2,5-dimethylindole **1** (1.20 g, 8.2 mmol) and was chromatographed in a mixture of benzene and hexane. Yield 1.30 g.

5-Methyl-6-nitro-2-phenylindole (4) was obtained from 5-methyl-2-phenylindole (**2**) (1.25 g, 6.0 mmol) and was chromatographed in a mixture of chloroform and petroleum ether. Yield 1.40 g.

1,2,5-Trimethyl-6-nitroindole (5) was obtained from compound **3** (1.19 g, 6.2 mmol) and was chromatographed in heptane. Yield 1.25 g.

1,5-Dimethyl-6-nitro-2-phenylindole (6) was obtained from compound **4** (1.00 g, 3.9 mmol) and was chromatographed in heptane. Yield 1.02 g.

6-Amino-1,2,5-trimethylindole (7) was obtained from compound **5** (1.00 g, 4.9 mmol). Yield 0.71 g.

6-Amino-1,5-dimethyl-2-phenylindole (8) was obtained from compound **6** (1.00 g, 3.7 mmol). Yield was 0.76 g.

6-Amino-2,5-dimethylindole (9) was obtained from compound **3** (1.10 g, 5.7 mmol). Yield 0.88 g.

6-Amino-5-methyl-2-phenylindole (10) was obtained from compound **4** (1.40 g, 5.5 mmol). Yield 1.10 g.

Preparation of Enamines (General Method). A. A mixture of aminoindole and a tenfold excess of acetylacetone was boiled for several hours. At the end of the reaction (check by TLC) the excess of acetylacetone was distilled in vacuum. The product was chromatographed in a mixture of benzene with petroleum ether.

B. Dibenzoylmethane (2 mmol) was added to the aminoindole (1 mmol) and the mixture maintained at 170-180°C. At the end of the reaction (check by TLC) the reaction product was isolated by TLC on aluminum oxide using chloroform as eluent.

(*Z*)-4-(1,2,5-Trimethyl-1H-indol-6-yl)aminopent-3-en-2-one (11) was obtained from compound **7** (0.30 g, 1.7 mmol) by procedure A (heated for 3 h). Yield 0.22 g.

(*Z*)-4-(1,5-Dimethyl-2-phenyl-1H-indol-6-yl)aminopent-3-en-2-one (12) was obtained from compound **8** (0.31 g, 1.4 mmol) by procedure A (heated for 3 h). Yield 0.12 g.

(*Z*)-1,3-Diphenyl-3-(1,2,5-trimethyl-1H-indol-6-yl)aminoprop-2-en-1-one (13) was obtained from compound **7** (0.30 g, 1.7 mmol) by procedure B (heated for 3 h). Yield 0.13 g.

(*Z*)-3-(1,5-Dimethyl-2-phenyl-1H-indol-6-yl)amino-1,3-diphenylprop-2-en-1-one (14) was obtained from compound **8** (0.30 g, 1.2 mmol) by procedure B (heated for 5 h). Yield 0.12 g.

(*Z*)-4-(2,5-Dimethyl-1H-indol-6-yl)aminopent-3-en-2-one (15) was obtained from compound **9** (0.33 g, 2.0 mmol) by procedure A (heated for 7 h). Yield 0.29 g.

(*Z*)-4-(5-Methyl-2-phenyl-1H-indol-6-yl)aminopent-3-en-2-one (16) was obtained from compound **10** (0.46 g, 2.0 mmol) by procedure A (heated for 2.5 h). Yield 0.53 g.

(*Z*)-3-(2,5-Dimethyl-1H-indol-6-yl)amino-1,3-diphenylprop-2-en-1-one (17) was obtained from compound **9** (0.32 g, 1.9 mmol) by procedure B (heated for 3 h). Yield 0.25 g.

(*Z*)-3-(5-Methyl-2-phenyl-1H-indol-6-yl)amino-1,3-diphenylprop-2-en-1-one (18) was obtained from compound **10** (0.30 g, 1.3 mmol) by procedure B (heated for 6 h). Yield 0.22 g.

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