1,2-Dimethylfuro[2,3-f]indole-3,6-dicarboxylic Acid (VI). A mixture of 0.5 g (1.5 mmole) of V and 16 ml of a 23.5% solution of potassium hydroxide in 95% ethanol was refluxed at 80° for 40 min, after which it was cooled to room temperature (20°), and the resulting precipitate was removed by filtration. The precipitate was dissolved in the minimum amount of water, and the solution was treated with activated charcoal and filtered. The filtrate was acidified with respect to Congo red (pH ≈ 3) with 2 N hydrochloric acid solution, and the precipitated VI was removed by filtration, washed on the filter with water, and dried in a vacuum desiccator over phosphorus pentoxide. The yield of VI was 0.34 g (1.2 mmole). The yellowish crystals were only slightly soluble in water, alcohol, acetone, and benzene and moderately soluble in DMF and DMSO. The product showed up as an individual substance in UV light when it was chromatographed on Silufol with a benzene–methanol system (9:1).

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SYNTHESIS OF ISOMERIC PYRROLOQUINOLINES FROM 5- AND 6-AMINOINDOLES

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UDC 547.836.3.07

In the case of 2,3-dimethyl-, 2-methyl-, and 2,3,6-trimethyl-5-aminoindoles, as well as 2,3-dimethyl- and 1,2,3-trimethyl-6-aminoindoles, it was shown that the enamino ketones formed in the reaction of 5- or 6-aminoindoles with 1,3-diketones undergo cyclization under the influence of acidic agents to substituted pyrroloquinolines with linear or angular ring fusion. The formation of the latter is limited by steric factors. Thus, the pronounced ortho effect of a substituent attached to the C_4 atom (in the pyrrole ring) or 5-indolylaminovinyl ketones substantially hinders cyclization in the 4 position of the indole and promotes primary or exclusive formation of the linear isomer. Similarly, in the case of enamino ketones obtained from 6-aminoindoles, the substituent attached to the pyrrole nitrogen atom sterically hinders electrophilic attack at C_7, i.e., formation of the angular isomer.

The condensation of aromatic amines with 1,3-diketones is well known as the Combes–Beyer synthesis of 2,4-disubstituted quinolines [1, 2]. The direction of cyclization depends on the presence of a second substituent in the benzene ring and is subject to the general principles of orientation during electrophilic attack [3]. The situation is more complex in the case of condensed systems. Thus, a mixture (21:1) of the linear and angular benzoquinolines is obtained in the condensation of 2-naphthylamine with acetylacetone under the influence of sulfuric acid [4]. However, it has been reported that the reaction gives only the angular isomer when zinc chloride is used as the cyclizing agent and that exclusively the linear benzoquinoline is obtained in hydrogen fluoride [4, 5]. 5-Aminocarbazole is converted to linear pyridocarbazoles in 15-20% yields when it is heated with 1,3-diketones in the presence of polyphosphoric acid (PPA) [6]. Thus, up until now the data on the

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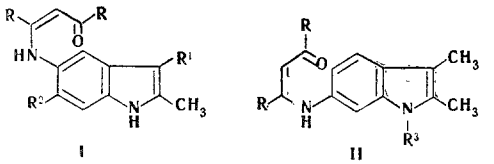
mechanism of ring formation in the Combes–Beyer reaction for condensed structures have been fragmentary and even contradictory.

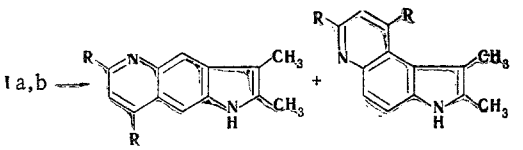
In connection with the search for convenient methods for the synthesis of pyrroloquinolines and isomeric carbolines, we investigated the behavior of 5- and 6-aminoindoles in the Combes–Beyer reaction. Careful heating of these amines with acetylacetone or dibenzoylmethane leads to the corresponding indolylaminovinyl ketones I and II [7].



I II

I a $R=R^1=CH_3$, $R^2=H$; b $R=C_6H_5$, $R^1=CH_3$, $R^2=H$; c $R=CH_3$, $R^1=R^2=H$; d $R=C_6H_5$, $R^1=R^2=H$; e $R=R^1=R^2=CH_3$; f $R=C_6H_5$, $R^1=R^2=CH_3$; II a $R=CH_3$, $R^3=H$; b $R=C_6H_5$, $R^3=H$; c $R=R^3=CH_3$; d $R=C_6H_5$, $R^3=CH_3$

The formation of four types of pyrroloquinolines (III-VI) that differ with respect to their ring fusion was possible in the cyclization of the latter. It was found that emanino ketone Ia reacts with trifluoroacetic acid at room temperature to give only linear pyrrolo-

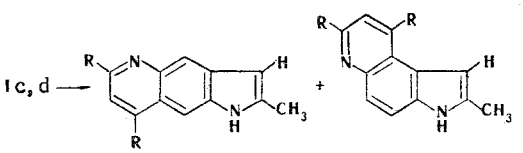


IIIa,b IVb

III a $R=CH_3$; III, IV b $R=C_6H_5$

quinoline IIIa in 80% yield, i.e., cyclization takes place only in the 6 position, as demonstrated by a comparative study of the PMR spectra (see below).

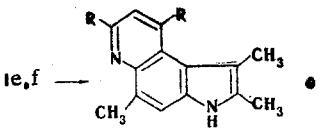
The angular pyrroloquinoline was not isolated. Replacement of trifluoroacetic acid by sulfuric acid, PPA, or zinc chloride does not change the direction of cyclization. Compound Ib also forms linear pyrroloquinoline IIIb, but we were also able to isolate angular pyrroloquinoline IVb in low yield when the reaction was carried out in Dowtherm at 250°C. We were able to isolate only angular pyrroloquinoline IVc from the markedly resinified reaction mixture in the cyclization of enamino ketone Ic, which does not have a substituent in the β position of the indole ring.



IIId IVc,d

III, IV d $R=C_6H_5$; IV c $R=CH_3$

In contrast to the two singlets in the PMR spectrum of the isomeric linear structure (IIIa, for example), the two ortho-coupling 5-H and 4-H protons in the PMR spectrum of IVc appear in the form of two doublets (7.64 and 7.46 ppm; J = 9 Hz). The low yield (40%) in the reaction makes it possible to assume that, in addition to the angular isomer, the linear pyrroloquinoline is also formed here and, due to the very nucleophilic β position in the pyrrole ring, reacts with the starting enamino ketone, as evidence by the formation of a colored polymer. Condensations of this type with aldehydes or ketones are extremely characteristic for indoles and 2-alkylindoles [8]. The β-pyrrole position in angular isomer IVc is hindered by the methyl group, and this restricts side condensations. Thus, the formation of the pyridine ring from 5-aminoindoles depends substantially on steric factors. Cyclization proceeds primarily with attack on the 4 position, but a substituent in the β position of the pyrrole ring (Ib) substantially hinders the formation of angular isomer IVb. Nevertheless, the latter is formed at elevated temperatures but with a certain amount of disruption of the coplanarity of the substituents. Thus, the signal of the phenyl photons in the PMR spectrum of IVb shows up as a multiplet (in contrast to IIIb), and this constitutues evidence for restricted rotation of the benzene ring. Correspondingly, the signal of the protons of the CH_3 group is shifted by 1 ppm (as compared with IIIb) to strong field.



IVe,f

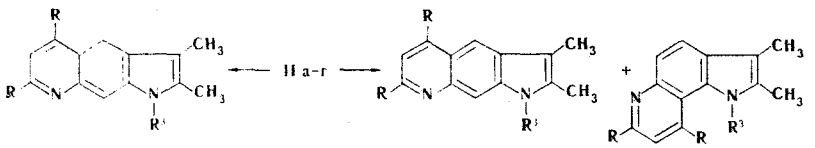
IVe R = CH_3; f R = C_6H_5

Cyclization of enamine Id in trifluoroacetic acid leads not only to the angular isomer (IVd) but also to the linear isomer (IIId) in a ratio of 10:1 (in an overall yield of 50%). In this case the linear isomer apparently undergoes side reactions to a lesser extent, since the activity of the benzoyl group in Id is lower than that of the acetyl group (in Ic). The PMR spectrum of angular isomer IVd differs from the spectrum of IIId in that the signal of the β-pyrrole proton is shifted by 0.9 ppm to strong field under the influence of the adjacent phenyl group. In dimethyl sulfoxide (DMSO), in addition to the 3-H signal for IIId and the 1-H signal for IVd (6.20 and 5.19 ppm), a singlet at 8.14 and 8.09 ppm for IIIb, d or at 7.73 and 7.74 ppm for IVb, d, which corresponds to the β-pyridine proton, stands out from the multiplet (7.3-7.7 ppm).

To synthesize model structures with an authentic angular structure, we carried out the cyclization of enamino ketones Ie, f, obtained from 2,3,6-trimethyl-5-aminoindole.

The reaction for these substances requires more severe conditions (refluxing in trifluoroacetic acid for 4-5 h). The character of the PMR spectra and the UV absorption of pyrroloquinolines IVe, f is in agreement with angular structures IVb, c.

Similar results were obtained with 6-aminoindoles: 6-indolylaminovinyl ketone IIa is converted by the action of trifluoroacetic acid to a mixture of two isomeric pyrroloquinolines, linear Va and angular VIa, which were isolated in a ratio of 4:1.



Vc,d Va,b VIa,b

V, VI a R = CH_3, R^1 = H; b R = C_6H_5, R^1 = H; V c R = R^1 = CH_3; d R = C_6H_5, R^1 = CH_3

The aromatic portion of the PMR spectrum of Va contains 6-H, 9-H, and 4-H singlets (6.90, 7.68, and 7.85 ppm). A shift of the signal of the β-pyridine proton to weaker field (7.08 ppm) is observed in the case of angular isomer IVa, and ortho coupling of the protons in the 5 and 4 positions appears in the form of two doublets (7.67 and 7.46 ppm; J = 8 Hz). The primary formation of a linear pyrroloquinoline in this case also is evidently associated with partial overlapping of the N-H proton of indole with the methyl group in the 2 position. Complete blocking of the 7 position occurs when the N-H proton is replaced by a methyl group, i.e., IIc forms only linear pyrroloquinoline Vc. In trifluoroacetic acid, enamino ketone IIb also gives two isomeric pyrroloquinolines, which were isolated (in a ratio of 2:1) by chromatography. The phenyl group in the γ position of the pyridine ring in pyrroloquinoline VIb evidently deviates from the plane of the system, since the protons of the phenyl group appear in the PMR spectrum in the form of a multiplet. The same protons in linear isomer Vb give a singlet.

Thus, the PMR spectra of the linear isomers, i.e., compounds of the III and V type, differ from those of the angular isomers (IV and VI) in that the signals of the protons of the benzene ring in the angular isomers appear in the spectra in the form of two doublets of an AB system. However, this criterion for the evaluation of the linearity and angularity is applicable only for pyrroloquinolines with methyl substituents. In the case of compounds with phenyl groups, in which these signals are difficult to uncover, the difference between the linear and angular isomers is manifested in the nonequivalence of the protons of the γ-pyridine phenyl group and also in the difference in the shifts of the β protons of the pyrrole ring and the β-pyridine proton. In contrast to the angular isomers, the appearance of an additional long-wave maximum is characteristic in the electronic spectra of pyrroloquinolines with linear ring fusion; this is in agreement with the literature data [6].

TABLE 1. Indolylaminovinyl Ketones Ic-f and IIc, d

	Compound	R_f[a]	mp, °C	Found, %		Empirical formula	Calc., %		UV spectrum		Yield, %
				C	H		C	H	λ_{max}, nm	lg ε	
Ic	4-(2-Methyl-5-indolylamino)pent-3-en-2-one	0,35	115—115,5	73,7	7,6	$C_{14}H_{16}N_2O$	73,8	7,4	216, 317	4,39, 4,35	82
Id	1,3-Diphenyl-3-(2-methyl-5-indolylamino)prop-2-en-1-one	0,76	223—224	82,2	5,9	$C_{24}H_{20}N_2O$	81,9	5,7	225, 280, 385	4,57, 4,29, 4,44	71
Ie	4-(2,3,6-Trimethyl-5-indolylamino)-pent-3-en-2-one	0,37	170—171	75,1	7,7	$C_{16}H_{20}N_2O$	75,1	7,9	229, 315	4,28, 4,27	79
If	1,3-Diphenyl-3-(2,3,6-trimethyl-5-indolylamino)-prop-2-en-1-one	0,75	178—179	82,1	6,6	$C_{26}H_{24}N_2O$	82,2	6,4	232, 293, 382	4,62, 4,27, 4,41	70
IIc	4-(1,2,3-Trimethyl-6-indolylamino)-pent-3-en-2-one	0,50	85	74,7	8,1	$C_{16}H_{20}N_2O$	75,1	7,9	226, 314	4,51, 4,40	69
IId	1,3-Diphenyl-3-(1,2,3-trimethyl-6-indolylamino)-prop-2-en-1-one	0,87	142—143	82,2	6,7	$C_{26}H_{24}N_2O$	82,2	6,4	248, 291, 345, 401	4,55, 4,26, 4,22, 4,40	64

Thus, the Combes—Beyer synthesis on the basis of 5- and 6-aminoindoles makes it possible to obtain four types of pyrroloquinolines (with different ring fusions) with alkyl or aryl groups in the pyrrole or pyridine portion of the molecule. The orientation of ring formation is in conformity with the known facts of electrophilic substitution in the benzene ring of indoles. It is known that indoles with an electron-donor substituent [for example, 5-hydroxy(methoxy)indoles] are nitrated in the 6 position with initial protonation of the pyrrole ring [9]. Aminomethylation of the same models in weakly acidic or neutral media [10] takes place in the 4 position. In our case the side chain rather than the pyrrole portion of enamino ketones of the I and II type is protonated (as evidenced by a distinct singlet of the protons of the 3-CH_3 group in the spectrum of Id in trifluoroacetic acid), and electrophilic attack of the carbonyl group is directed primarily to the carbon atom in the 4 position to give compounds of the IV type. However, the pronounced ortho effect of the substituent attached to the 3-C atom (in the pyrrole ring) substantially hinders this sort of cyclization and promotes the principal or exclusive formation of isomer III due to closing of the ring in the 6 position.

A similar regularity, i.e,, predominant cyclization with the participation of the 7-C atom (compare with aminomethylation in the 7 position of 6-hydroxyindoles [10] and nitration in the 5 position of the same models) and the strong effect of steric factors in the case of a substituted pyrrole nitrogen atom, which leads to the formation of only linear isomer V due to cyclization at the 5-C atom, is observed for 6-aminoindole derivatives (IIa-d).

We did not observe any effect of the nature of the acidic agent on the direction of ring formation.

EXPERIMENTAL

The PMR spectra of solutions of the compounds of DMSO—acetone (2:1) (with hexamethyldisiloxane as the internal standard) and in trifluoroacetic acid (with tetramethylsilane as the internal standard) were recorded with a Varian S-100 XL spectrometer. The mass spectra were obtained with an MKh-1303 mass spectrometer with direct introduction of the samples into the ion source at 100-250° at an ionization energy of 50 eV and an emission current of 1.5 mA. The electronic spectra of ethanol solutions of the compounds were recorded with a Cary-15 spectrophotometer. We have already reported [7] the method for the preparation of and the physical constants of 2,3-dimethyl-5- and 2,3-dimethyl-6-aminoindoles and the corresponding indolylaminovinyl ketones. The physicochemical constants of the previously undescribed indolylaminovinyl ketones are presented in Table 1.

TABLE 2. Pyrroloquinolines III-VI

No.	Compound	Starting enamine	Preparative method	Reaction time, h	Purification method	R_f[a]	mp, °C	Found C, %	Found H, %	Found M[b]	Empirical formula	Calc. C, %	Calc. H, %	Calc. M	UV spectrum λ_{max}, nm	UV spectrum lg ε	Yield, %
IIIa	2,3,6,8-Tetramethylpyrrolo[2,3-g]-quinoline	Ia	A	1	a, b		290—292	80,4	7,3	224	$C_{15}H_{16}N_2$	80,4	7,2	224	225, 266 340, 375	4,49, 4,81, 4,03, 3,64	80
IIIb	2,3-Dimethyl-6,8-diphenylpyrrolo-[2,3-g]quinoline	Ib	A	2	b	0,63	210—212	86,2	5,5	348	$C_{25}H_{20}N_2$	86,3	5,8	348	246, 295 358, 400c	4,61, 4,77, 4,02, 3,56	78
IIId	2-Methyl-6,8-diphenylpyrrolo-[2,3-g]quinoline	Id	A	3	c	0,54	196—198	86,3	5,4	334	$C_{24}H_{18}N_2$	86,3	5,4	334	243, 290 355, 390c	4,58, 4,82, 4,14, 3,77	9
IVb	1,2-Dimethyl-7,9-diphenylpyrrolo-[3,2-f]quinoline	Ib	B	0,5	c	0,44	259—262	86,2	6,0	348	$C_{25}H_{20}N_2$	86,3	5,8	348	250, 305 360	4,53, 4,65, 3,91	8
IVc	2,7,9-Trimethylpyrrolo[3,2-f]-quinoline	Ic	A	2	a, b		282—283	80,2	6,7	210	$C_{14}H_{14}N_2$	80,1	6,7	210	222, 260 334	4,49, 4,44, 3,98	40
IVd	2-Methyl-7,9-diphenylpyrrolo-[3,2-f]quinoline	Id	A	3	c	0,51	225—226	86,0	5,4	334	$C_{24}H_{15}N_2$	86,3	5,4	334	342, 294 346	4,49, 4,72, 4,00	40
IVe	1,2,5,7,9-Pentamethylpyrrolo-[3,2-f]quinoline	Ie	A	4	b		200—201	80,9	7,6	238	$C_{16}H_{18}N_2$	80,7	7,6	238	232, 274 345	4,56, 4,36, 3,85	88
IVf	1,2,5-Trimethyl-7,9-diphenyl-pyrrolo[3,2-f]quinoline	If	A	5	b	0,93	235—236	85,9	6,4	362	$C_{26}H_{22}N_2$	86,3	6,1	362	263, 310 346c	4,38, 4,59, 3,82	85
Va	2,3,5,7-Tetramethylpyrrolo[3,2-g]-quinoline	IIa	A	1	b	0,21	258—260	80,3	6,8	224	$C_{15}H_{16}N_2$	80,4	7,2	224	224, 265 340, 372	4,51, 4,88 4,05, 3,64	65
Vb	2,3-Dimethyl-5,7-diphenylpyrrolo-[3,2-g]-quinoline	IIb	A	2	c	0,41	210—212	86,0	5,8	348	$C_{25}H_{20}N_2$	86,3	5,8	348	241, 288 355, 405	4,64, 4,83 4,21, 3,88	48
Vc	1,2,3,5,7-Pentamethylpyrrolo-[3,2-g]quinoline	IIc	A	1	b	0,23	184—186	80,5	7,4	238	$C_{16}H_{18}N_2$	80,7	7,6	238	226, 268 341, 378	4,38, 4,78 3,90, 3,52	73
Vd	1,2,3-Trimethyl-5,7-diphenyl-pyrrolo[3,2-g]quinoline	IId	A	2	b	0,70	206—208	85,9	6,2	362	$C_{26}H_{22}N_2$	86,3	6,1	362	243, 292 354, 410	4,51, 4,81 4,04, 3,65	63
VIa	2,3,7,9-Tetramethylpyrrolo-[2,3-f]quinoline	IIa	A	1	c	0,25	220—222	80,2	6,9	224	$C_{15}H_{16}N_2$	80,4	7,2	224	225, 275 324	4,49, 4,71, 3,55	22
VIb	2,3-Dimethyl-7,9-diphenylpyrrolo-[2,3-f]quinoline	IIb	A	2	c	0,96	177—179	86,0	6,0	348	$C_{25}H_{20}N_2$	86,3	5,8	348	266, 296, 370	4,52, 4,75, 4,02	24

[a]Silufol, benzene—ethyl acetate—methanol (10:10:1) (for Va, c and VIa); Silufol, benzene—ethyl acetate (4:1) (for all of the remaining compounds). [b]By mass spectrometry. [c]Shoulder.

TABLE 3. PMR Spectra of Pyrroloquinolines III-VI

Compound	δ, ppm
	In CF_3COOH
IIIa	7,95 (s, 4-H), 7,81 (s, 9-H), 7,30 (s, 7-H), 2,74 (s, 6H, 6- and 8-CH_3), 2,36 (s, 3H, 2-CH_3), 2,19 (s, 3H, 3-CH_3)
IIIb	8,23 (s, 4-H), 8,05 (s, 7-H), 7,84 (s, 9-H), 7,60 (s, 10H, 6- and 8-C_6H_5), 2,52 (s, 3H, 2-CH_3), 2,28 (s, 3H, 3-CH_3)
IVb	7,50—8,10 (m, 13H, 4-, 5-, 8-H, 7- and 9-C_6H_5), 2,62 (s, 3H, 2-CH_3), 1,20 (s, 3H, 1-CH_3)
IVf	7,40—8,40 (m, 12H, 4-, 8-H, 7- and 9-C_6H_5), 2,90 (s, 3H, 5-CH_3), 2,65 (s, 3H, 2-CH_3), 1,02 (s, 3H, 1-CH_3)
Vb	8,30 (s, 9-H), 8,16 (s, 4-H), 7,88 (s, 6-H), 7,72 (s, 10H, 5- and 7-C_6H_5), 2,44 (s, 3H, 2-CH_3), 2,28 (s, 3H, 3-CH_3)
Vd	8,38 (s, 9-H), 8,12 (s, 4-H), 7,90 (s, 6-H), 7,71 (s, 10H, 5- and 7-C_6H_5), 3,94 (s, 3H, 1-CH_3), 2,60 (s, 3H, 2-CH_3), 2,26 (s, 3H, 3-CH_3)
VIb	7,20—8,40 (m, 13H, 4-, 5-, 8-H, 7- and 9-C_6H_5), 2,34 (s, 3H, 2-CH_3), 2,25 (s, 3H, 3-CH_3)
	In DMSO + acetone
IVc	7,64 (d, 5-H; J=9 Hz), 7,46 (d, 4-H; J=9 Hz), 7,11 (s, 8-H), 6,70 (s, 1-H)
IVe	7,46 (s, 4-H), 7,04 (s, 8-H)
Va	7,85 (s, 9-H), 7,69 (s, 4-H), 6,90 (s, 6-H)
Vc	7,87 (s, 9-H), 7,69 (s, 4-H), 6,93 (s, 6-H)
VIa	7,67 (d, 5-H; J=8 Hz), 7,46 (d, 4-H; J=8 Hz), 7,06 (s, 8-H)

2-Methyl-5-nitroindole. A solution of 1.1 g (10 mmole) of potassium nitrate in 25 ml of 94% sulfuric acid was added with cooling and stirring to a solution of 1.5 g (10 mmole) of 2-methylindole in 25 ml of 94% sulfuric acid at such a rate that the temperature of the mixture did not rise above 15°. Five minutes after mixing, the reaction mass was poured over ice, and 200 ml of chloroform was added to the aqueous mixture. After all of the nitroindole had dissolved, the chloroform layer was separated, washed twice with 10-12% ammonium hydroxide and two to three times with water, and dried. The chloroform was removed by distillation, and the nitroindole was recrystallized from benzene to give 1.7 g (93%) of a product with mp 171-172° (mp 171.5-172.5° [11]).

2,3,6-Trimethyl-5-nitroindole. This compound was similarly obtained from 2,3,6-trimethylindole, but the nitration was carried out in 89% sulfuric acid. The nitroindole was purified with a column filled with Silica gel (L 100/160 μ) in chloroform. Workup gave a product with mp 162-163° in 79% yield. Found: M 204 (by mass spectrometry). Calculated: M 204. PMR spectrum (DMSO): 11.00 (s, NH), 8.00 (s, 4-H), 7.10 ppm (s, 7-H). UV spectrum: λ_{max} 217, 273, and 335 nm (log ε 4.40, 4.23, and 3.80).

1,2,3-Trimethyl-6-nitroindole. This compound was obtained by methylation of 2,3-dimethyl-6-nitroindole by the method in [12], but dimethyl sulfate was used as the methylating agent. Workup gave a product with mp 135-136° in 95% yield, Found: C 64.4; H 6.2%. $C_{11}H_{12}N_2O_2$. Calculated: C64.8; H 5.9%. UV spectrum: λ_{max} 218, 254, 276, 337, and 399 nm (log ε 4.32, 3.90, 3.85, 3.86, and 3.87).

2-Methyl-5-aminoindole. This compound, with mp 156° (mp 156-156.5° [11]), was obtained in 81% yield from 2-methyl-5-nitroindole by the method in [7].

2,3,6-Trimethyl-5-aminoindole. This compound, with mp 221-223°, was similarly obtained in 90% yield from 2,3,6-trimethyl-5-nitroindole. Found: M 174 (by mass spectrometry). Calculated: M 174. UV spectrum: λ_{max} 248, 280 (shoulder), and 372 nm (log ε 4.39, 3.91, and 3.55).

4-(1,2,3-Trimethyl-6-indolylamino)pent-3-en-2-one (IIc) and 1,3-Diphenyl-3-(1,2,3-trimethyl-6-indolylamino)prop-2-en-1-one (IId). A catalytic amount of Raney nickel was added to a solution of 0.51 g (2.5 mmole) of 1,2,3-trimethyl-6-nitroindole in 50 ml of methanol, and 4 ml (75 mmole) of hydrozine hydrate was then added with stirring. The mixture was heated and stirred for 30-60 min, after which the hot solution was filtered to remove the catalyst, and the methanol and excess hydrazine hydrate were removed from the filtrate by distillation. Acetylacetone or dibenzoylmethane was added to the dry residue, and the mixture was treated as described in [7].

General Method for the Preparation of III-VI. A) A 2-mmole sample of indolylaminovinyl ketone was dissolved in 5 ml of trifluoroacetic acid, and the solution was refluxed for 1-5 h, after which it was cooled and poured into a dilute (10%) aqueous solution of ammonia (alkaline medium). The resulting precipitate was removed by filtration, washed with water, and air dried.

B) A 2-mmole sample of indolylaminovinyl ketone was dissolved in 5 ml of Dowtherm, and the solution was refluxed for 30 min, after which it was cooled and diluted with hexane, and the precipitate was removed by filtration and washed with hexane.

The products were purified and separated (in the case of the formation of isomers) by the following methods: a) sublimation; b) recrystallization from alcohol and c) preparative separation on a loose layer of Al_2O_3 (Brockmann activity II). The preparative conditions, the purification method, and the physical constants of the products are presented in Table 2, and the PMR spectra are presented in Table 3. Incorrect numbering of the atoms of pyrroloquinolines was presented in [13].

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RESEARCH ON PYRROLO[3,2-f]INDOLIZINES.

V.* SYNTHESIS AND PROPERTIES OF 4-(ω-ALKOXYCARBONYLALKYL)- AND 4-PHENYL-6H-PYRROLOINDOLIZINES

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3-(α-Oxo-ω-alkoxycarbonylalkyl)- and 3-benzoyl-substituted pyrroles undergo condensation with α-unsubstituted pyrroles to give 6H-pyrrolo[3,2-f]indolizines that contain higher acid residues or a phenyl group in the 4 position of the heteroring.

We have previously observed the intramolecular condensation of 3-acetyldipyrrolemethanes to 6H-pyrrolo[3,2-f]indolizines [2]. In the present research we extended this reaction to other alkyl-substituted pyrroles during a study of the reaction of 3-(α-oxo-ω-alkoxycarbonylalkyl)- and 3-benzoyl-substituted pyrroles (II) with alkylpyrroles (III). The starting 1-

*See [1] for communication IV.

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