PYRROLOQUINOLINES.

II*. SYNTHESIS OF 1H-PYRROLO[2,3-f]- AND 3H-PYRROLO[3,2-f]-QUINOLINES

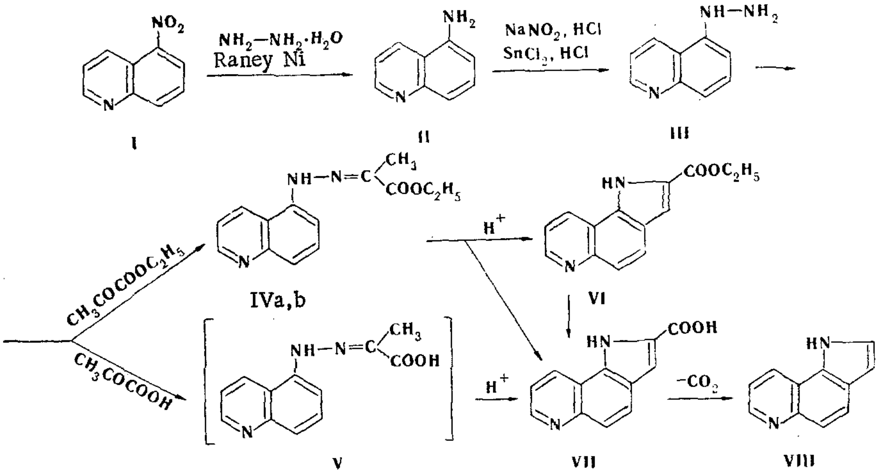
A. P. Gryaznov, R. N. Akhvlediani,
T. A. Volodina, A. M. Vasil'ev,
T. A. Babushkina, and N. N. Suvorov

UDC 547.757.07:541.69

A method was developed for the preparation of 1H-pyrrolo[2,3-f]- and 3H-pyrrolo-[2,3-f]quinolines. Their IR and PMR spectra are described. The syn–anti isomerism of 5- and 6-quinolylhydrazones of ethyl pyruvate was studied.

Continuing out study of pyrroloquinolines, we synthesized 1H-pyrrolo[2,3-f]- and 3H-pyrrolo[2,3-f]quinolines. These compounds have already been obtained for the proof of the structure of one of the strychnine alkaloids [2-4]. However, this synthesis has a number of disadvantages in a preparative respect and cannot be used for their preparation in any significant amount.

We synthesized 1H-pyrrolo[2,3-f]quinoline (VIII) via the following scheme:



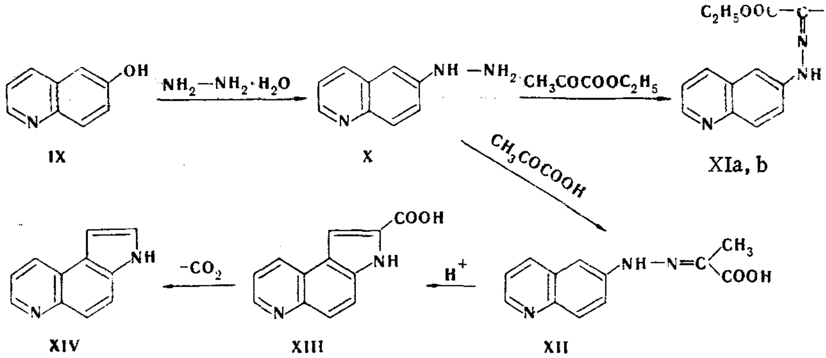
The reduction of 5-nitroquinoline (I) with iron in acetic acid (the yield is not indicated) [5], stannous chloride (80-82.4% yield) [6], and hydrazine sulfate in liquid ammonia under pressure (80% yield) [7] has been described. Reduction with stannous chloride proved to be inconvenient because of difficulties in the isolation of the reduction product. We reduced I with hydrazine hydrate in the presence of Raney nickel; this made it possible to simplify the isolation of 5-aminoquinoline II and raise its yield to 92%. 5-Quinolylhydrazine (III) was obtained by a modified method [2]. To isolate hydrazine III we used ethyl acetate and carried out the condensation of III with ethyl pyruvate directly in the resulting solution. This method enabled us to obtain IVa-b in greater than 90% yields. We used a mixture of acetic and sulfuric acids (3:1) as the cyclizing agent and isolated ethyl 1H-pryyolo[2,3-f]-quinoline-2-carboxylate (VI) and acid VII in a ratio of 1:2. The formation of acid VII is evidently associated with hydrolysis of ester VI (hydrolysis of ester VI with alcoholic alkali gives acid VII). The overall yield of acid VII was 73-78%. We obtained 1H-pyrrolo-[2,3-f]quinoline (VIII) in 90-95% yield by heating acid VII to 260-290°.

---

*See [1] for communication I.

D. I. Mendeleev Moscow Chemical-Engineering Institute, Moscow 125047. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 369-376, March, 1977. Original article submitted January 1, 1976; revision submitted June 15, 1976.

The synthesis of 3H-pyrrolo[3,2-f]quinoline is distinguished by the fact that we obtained 6-quinolylhydrazine (X) by heating 6-hydroxyquinoline (IX) with hydrazine hydrate. The condensation and cyclization were carried out under similar conditions. In this case we obtained only 3H-pyrrolo[3,2-f] quinoline-2-carboxylic acid (XII) in 25% yield. We isolated 3H-pyrro-[3,2-f]quinoline (XIV) in 92-96% yield after decarboxylation of acid XIII.



A study of the conditions for cyclization of 6-quinolylhydrazone (XIa-b) showed that the hydrazone of acid XII is formed when XIa-b are heated in a mixture of acetic and sulfuric acids to 90°, i.e., the conversion of the ester to the acid occurs before the cyclization step. Proceeding from this, we carried out the cyclization of the hydrazone of acid XII under conditions similar to those in the cyclization of XIa-b and obtained acid XIII in the same yield. It might have been assumed that the high yield of VII is associated with the stabilities of the hydrazones of esters IVa-b and consequently with the ease of cyclization. To confirm this it was necessary to carry out the cyclization of the 5-quinolyhydrazone of pyruvic acid (V). We synthesized the hydrazone of acid V in quantitative yield by direct condensation of hydrazine III with pyruvic acid. The isolation of the acid hydrazone in pure form was difficult. The use of acetic acid as the solvent in the condensation of 5-quinolylhydrazine III with pyruvic acid enabled us to carry out the cyclization of hydrazone V without its isolation. In this case the yield of the acid remained the same as in the case of cyclization of hydrazones IVa-b. Consequently, the yield of acid XIII does not depend on whether the hydrazone of acid XII or the hydrazone of ester XIa-b cyclizes.

The structures of IVa-b, VI-VIII, XIa-b, and XIV were confirmed by IR, UV, PMR, and mass-spectroscopic data.

The UV spectra of VIII and XIV are in agreement with the data in [4]. The IR spectra of VI and XIV contain a band characteristic for the NG group of indoles. The chemical shifts (δ) and spin—spin coupling constants (J) are presented in Tables 1 and 2. The assignment of all of the signals of the proton was made by comparison of the PMR data of benzindoles [8] and pyrroloquinolines [1]. Thus in XIV condensation of the pyridine ring with the indole ring occurs in the 4,5 positions of the latter, although fusion at the 5, 6 positions (and at the 6, 7 positions in VIII) is also theoretically possible. This is evident from the following facts. 1) The $J_{3,4}$ constant of 0.7 Hz in the spectrum of XIV corresponds to the $J_{3,7}$ constant of 0.6 Hz characteristic for [4,5]benzindoles [8]. 2) In a comparison of the spectra of [4,5]-and [6,7]benzindoles, Babushkina and co-workers noted that the $\Delta\delta_{7,6} = \delta_7 - \delta_6$ difference in the chemical shifts of the H_7 and H_6 protons is less than the $\Delta\delta_{4,5} = \delta_4 - \delta_5$ difference. We noted a similar pattern in a comparison of the chemical shifts of the H_4 and H_5 protons ($\Delta\delta_{4,5}$) and XIV and VIII, the $\Delta\delta_{4,5}$ differences of which are 26 and 40 Hz, respectively. 3) A $J_{1,4}$ constant of 0.5 Hz, which is characteristic for [6,7]benzindoles and 1H-pyrrolo[3,2-h]quinolines, was obtained for VIII. We note that the chemical shifts of the pyrrole H_3 proton in the spectra of [4,5]- and [6,7]benzindoles in DMSO differ by 0.45 ppm. This difference is retained for XIV and VIII and amounts to 0.49 ppm. The shift of the signal of the NH proton to weak field (∿0.76 ppm) on passing from VIII to VI-VII is apparently due to an intramolecular hydrogen bonds with the C=O group. The position of the nitrogen atom in the pyridine ring was determined from the characteristic trans spin—spin coupling constant for quinolines ($J_{5,6}$ = 0.5 Hz for XIV, and $J_{5,6}$ = 0.6 Hz for VIII), and the sequence of the chemical shifts of the protons in the pyridine ring $\delta_\alpha > \delta_\gamma > \delta_\beta$ (relative to the nitrogen atom) observed in the case of quinolines [9] and pyrroloquinolines [1]. This sequence is disrupted for VI-VII. In the case of VIII, δ_{H_6} = 8.72 ppm and differs by less

TABLE 1. Chemical Shifts of the Protons in Pyrroloquinolines

Compound	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8
VI[a]	12,89	—	7,28	7,92	7,54	9,12	7,52	8,79
VII[b]	12,79	—	7,21	8,04	7,64	9,13	7,50	8,77
VIII	12,13	7,45	6,59	7,91	7,51	8,72	7,48	8,72
XIV	11,56	7,43	7,08	7,76	7,50	8,58	7,42	8,70

[a] δ_{OCH_2} 4.33, $\delta_{OCH_2CH_3}$ 1.32 ppm. [b] δ_{OH} 4.78 ppm.

TABLE 2. Spin–Spin Coupling Constants of the Protons in Pyrroloquinolines (Hz)

Compound	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{1,4}$	$J_{4,5}$	$J_{5,5}$	$J_{3,4}$	$J_{6,7}$	$J_{7,8}$	$J_{6,8}$
VI	—	0,5	—	—	8,8	0,7	—	8,0	4,3	1,7
VII	—	—	—	—	8,6	—	—	8,1	4,3	1,6
VIII	2,6	2,0	3,0	0,5	8,8	0,6	—	—	—	—
XIV	2,8	2,0	3,0	—	8,8	0,8	0,7	8,0	4,2	1,2

TABLE 3. 5- and 6-Quinolylhydrazones of Ethyl Pyruvate

Compound	mp, °C (crystallization solvent)	Found, %*			IR spectra, cm^{-1}				UV spectra	
					C=O		NH			
		C	H	N	ν	Δν	ν	Δν	λ_{max}, nm (lg ε)	$\Delta\lambda_{max}$, nm
IVa	108—109 Acetone—water	65,3	5,8	16,3	1683	26	3240, 3280	110	204 (4,43), 255 (4,43), 383 (4,11)	20
IVb	117—118 (heptane)	65,3	5,8	16,4	1709		3390		204 (4,43), 252 (4,41), 363 (4,03)	
XIa	87—88 (heptane)	65,5	5,8	16,4	1685	22	3235, 3270	100	205 (4,38), 252 (4,31), 368 (4,27)	43
XIb	118—120 (benzene)	65,3	5,9	16,4	1707		3370		207 (4,40), 250 (4,27), 325 (4,32)	

*For IVa,b and XIa,b $C_{14}H_{15}N_3O_2$. Calculated: C 65.4; H 5.8; N 16.3%.

than 2 Hz from δ_{H_8}, whereas the sequence changes in the order $\delta_\gamma > \delta_\alpha > \delta_\beta$ for VI-VII. This is due to the shift of the signal of the H_6 proton to weak field due to the different degree of polarization of the NH bond in these compounds because of intramolecular hydrogen bonding. On comparing [1] the chemical shifts of the H_{11} proton in [6,7]benzindole and in 2-carboxymethyl[6,7]benzindole, one can note a similar change: $\delta_{H_{11}}{}^{2\text{-}COOCH_3\text{-}6,7} - \delta_{H_{11}}{}^{6,7} = 8.77 - 8.33 = 0.44$ ppm. The difference in the chemical shift of the analogous H_6 proton for VIII and VI is almost the same ($\delta_{H_6}{}^{VI} - \delta_{H_6}{}^{VIII} = 0.40$ ppm).

The molecular weights of VIII and XIV, determined by mass spectrometry, correspond to the calculated values. The mass spectra of these compounds contain an intense molecular ion peak $[M^+]$ at 168.

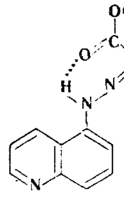
It is known that the hydrazones of α-keto acids exist in the isomeric syn and anti forms. The presence of an intramolecular hydrogen bond in the syn form and the evidently associated high solubility in many organic solvents make it possible to use simple methods to separate mixtures of the isomeric hydrazones [10-12]. We established by TLC that both hydrazones IVa-b and XIa-b are mixtures of two substances. We were able to separate both pairs of isomers by means of column chromatography on silica gel. We assigned syn configurations IVa and XIa to the low-melting substances with mp 108-109 and 87-88°, which are readily soluble in many organic solvents, and anti configurations IVb and XIb to the substances with mp 117-118 and 118-120°; this was also confirmed spectroscopically.

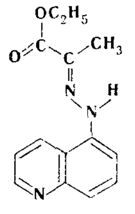
TABLE 4. Chemical Shifts of the Protons in 5- and 6-Quinolylhydrazones (δ, ppm)

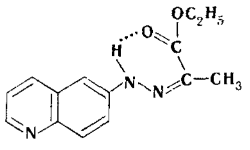
Compound	H_1	CH_3	OCH_2	OCH_2CH_3	H_2	H_3	H_4	H_5	H_6	H_7	H_8
IVa	12,68	2,10	4,25	1,27	8,85	7,51	8,15	—	7,56	7,56	7,56
IVb	9,68	2,18	4,16	1,24	8,83	7,43	8,79	—	7,53	7,53	7,53
XIa	12,00	2,08	4,21	1,24	8,63	7,35	8,14	7,55	—	7,63	7,93
XIb	10,07	2,08	4,19	1,24	8,62	7,35	8,14	7,55	—	7,73	7,95
XV	8,65	1,98	—	1,94	8,76	7,32	8,61	—	—	7,44	—
XVI	8,64	1,99	2,28	1,07	8,77	7,36	8,60	—	—	7,46	—

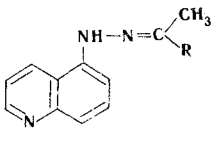
TABLE 5. Spin—Spin Coupling Constants of the Protons in 5- and 6-Quinolylhydrazones (Hz)

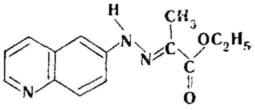
Compound	$J_{OCH_2CH_3}$	$J_{2,4}$	$J_{2,3}$	$J_{3,4}$	$J_{4,8}$	$J_{5,8}$	$J_{5,7}$	$J_{7,8}$
IVa	7,0	1,6	4,0	8,2	0,6	—	—	—
IVb	6,8	1,6	3,4	8,6	—	—	—	—
XIa	6,8	1,6	4,0	8,6	0,6	0,5	2,4	8,8
XIb	6,8	1,6	4,2	8,4	0,6	0,5	2,4	8,8
XV	—	1,6	4,0	8,3	0,5	—	—	—
XVI	—	1,6	4,0	8,4	0,5	—	—	—


IVa


IVb


XIa


XV, XVI


XIb

XV $R = CH_3$; XVI $R = C_2H_5$

A difference in the characteristic frequencies of the C=O and NH bonds is observed in the IR spectra* (see Table 3) of two pairs of hydrazones. The absorption bands of the carbonyl group of anti isomers IVb and XIb are found at 1707-1709 cm^{-1}, whereas a shift of these bands to the long-wave region of the spectrum at 1683-1685 cm^{-1} (Δν 22-26 cm^{-1}) is observed in the spectra of syn isomers IVa and XIa. An even more pronounced difference occurs in the region of absorption of the NH bond: 3370-3390 cm^{-1} in the case of the anti isomer, and 3270-3280 cm^{-1} in the case of the syn isomer (Δν 100-110 cm^{-1}).

A bathochromic shift occurs in the UV spectra of the hydrazones for the syn isomers (see Table 3). These differences make it possible to assume the presence of an intramolecular hydrogen bond in the syn isomers.

The chemical shift (δ) and spin—spin coupling constants (J) for IVa-b, XIa-b, and XV-XVI are presented in Tables 4 and 5. For the syn form of IVa and XIa, the signal of the NH proton is observed at weaker field than in the spectra of anti forms IVb and XIb. As noted above, this difference (more than 2 ppm) in the chemical shifts is associated with the presence of an intramolecular NH...O=C hydrogen bond in the syn form of the hydrazones. The small change in the chemical shifts of the protons of both the methyl and ethyl groups in IVa and IVb is evidently associated with syn—anti isomerism. This difference is practically absent in the case of XIa and XIb.

---

*The IR spectra of the hydrazones were obtained from CCl_4 solutions at 0.005 M concentrations, which exclude the formation of intermolecular hydrogen bonds.

The chemical shifts of the protons of the pyridine ring of IVa-b and XIa-b were compared with the literature data for quinoline [9]. One's attention is directed to the marked change in the chemical shift of the H_4 proton on passing from IVa to IVb. An examination of spherical "Eugon" models makes it possible to propose that this change may be associated with the effect of the anisotropy of the C=N–N double bond. In the syn isomer it is possible for the H_4 proton to be located above the plane of the C=N bond. A spatial orientation of the H_4 proton and the plane of the C=N bond next to one another is much more likely for the anti isomer. To confirm the reason for the change in the chemical shift of the H_4 proton, we synthesized hydrazones XV and XVI, which do not contain a carbonyl group. It is apparent from the comparison of the chemical shifts of the H_2, H_3, and H_4 protons of IVb and XV that the $COOC_2H_5$ substituent has an effect on the changes in these chemical shifts:

$$\Delta\delta_{H_2}=0.07\text{ ppm}\ ;\ \Delta\delta_{H_3}=0.11\text{ ppm}\ ;\ \Delta\delta_{H_4}=0.19\text{ ppm}$$

Hence it follows that the change (0.64 ppm) in the chemical shift of the H_4 proton to high field on passing from IVb and IVa is due primarily to the anisotropy of the C=N bond, above the plane of which the H_4 proton may be located.

The protons of the substituted benzene ring of IVa-b constitute an ABC system with $\delta_{av} \sim$ 7.56 ppm, whereas those of IVa,b constitute an ABX system, the parameters of which are presented in Tables 2 and 3. The spin–spin coupling constants are characteristic for substituted quinolines.

EXPERIMENTAL

The IR spectra of solutions of the compounds were recorded with a UR-10 spectrometer. The UV spectra of ethanol solutions were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of d_6-DMSO solutions were recorded with a Varian HA-100D spectrometer (100 MHz) with hexamethyldisiloxane as the internal standard. The accuracy in the measurement of the chemical shifts was ±0.01 ppm, and the accuracy in the measurement of the spin–spin coupling constants was 0.1 Hz. The mass spectra were recorded with an MKh-1303 mass spectrometer with direct introduction of the samples into the ion source; the apparatus was equipped with a system for recording at an ionizing-electron energy of 50 eV, a cathode emission current of 1.5 mA, and an accelerating voltage of 2 kV.

5-Aminoquinoline (II). A 34.8-g (0.2 mole) sample of I was dissolved in 200 ml of isopropyl alcohol, 1 g of Raney nickel was added, and 68 ml (7 mole) of hydrazine hydrate was added in the course of 30 min. The mixture was then refluxed with stirring for 1 h, after which the catalyst was removed by filtration, and the solvent was removed by vacuum distillation. The residue was recrystallized from benzene–petroleum ether (1:1) to give 26.5 g (92%) of II with mp 110° (from ethanol) (mp 110° [2]).

5-Quinolylhydrazine (III). A solution of 6.9 g (0.1 mole) of $NaNO_2$ in 20 ml of water was added in the course of 30 min to a suspension of 14.4 g (0.1 mole) of II in 180 ml of concentrated HCl and 30 ml of water cooled to –8° after which the mixture was stirred at –5° for 30 min. It was then added in small portions with vigorous stirring to a cooled (to –12°) solution of 60 g (0.22 mole) of $SnCl_2 \cdot 2H_2O$ in 60 ml of concentrated HCl. Stirring was continued for 30 min, and the precipitate was removed by filtration and transferred to 150 ml of water. The aqueous mixture was stirred vigorously and neutralized to pH 10 with 40% NaOH solution, and the precipitate was removed by filtration, squeezed thoroughly dry, and extracted by heating with several portions of ethyl acetate. The solvent was removed from the extract by vacuum distillation to give 15 g (78%) of III with mp 150-151° (from ethanol) (mp 150-151° [2]).

Ethyl Pyruvate 5-Quinolylhydrazone (IVa,b). A 15.9-g (0.1 mole) sample of III was dissolved with heating and stirring in 250 ml of ethyl acetate, after which 11.5 g (0.1 mole) of ethyl pyruvate was added slowly, and the mixture was heated at 60-70° for 30 min. Chromatography of the reaction mixture in a layer of Silufol [elution with chloroform–acetone (4:1)] gave two spots with R_f 0.57 (the anti form) and 0.84 (the syn form). The hydrazones were purified by passing a cooled solution through a column filled with silica gel with elution with chloroform–acetone (4:1). The eluent was removed by evaporation to give 24.2 g (94%) of a mixture of IVa,b. The isomers were separated by passing 3.5 g of the mixture through a column filled with silica gel with elution with chloroform–acetone (9:1). Removal of the eluent gave 0.5 g of the syn isomer (IVa) and 3 g of the anti isomer (IVb). The results of analysis and the IR and UV spectral data are presented in Table 3.

Ethyl 1H-Pyrrolo[2,3-f]quinolyl-2-carboxylate (VI). A 25.7-g (0.1 mole) sample of IVa, b was dissolved with heating and stirring in a mixture of 250 ml of glacial acetic acid and 75 ml of concentrated sulfuric acid, and the solution was stirred at 110° for 10 min. The cooled mixture was poured into 1.5 liters of water, and the mixture was neutralized to pH 8 with 40% NaOH solution. The precipitate was removed by filtration, washed with water, dried, and recrystallized from benzene to give 5.9 g (24.5%) of VI with mp 218-220° (from benzene). IR spectrum: 3460 (NH) and 1700 cm^{-1} (CO). Found: C 70.0; H 5.0; N 11.6%. $C_{14}H_{12}N_2O_2$. Calculated: C 70.0; H 5.0; N 11.7%.

1H-Pyrrolo[2,3-f]quinolyl-2-carboxylic Acid (VII). A) The filtrate from the preceding experiment was refluxed with charcoal, after which was filtered, and the filtrate was cooled and neutralized to pH 6 with 50% acetic acid solution. The resulting precipitate was removed by filtration, washed with water, and dried to give 13.2 g (57%) of VII with mp 256-258° (by reprecipitation) (mp ∿300° [2]). Found: C 62.3; H 4.3; N 12.5%. $C_{12}H_8N_2O_2 \cdot H_2O$. Calculated: C 62.6; H 4.3; N 12.2%.

B) A 4.8-g (0.02 mole) sample of ester VI was added to a solution of 6 g of potassium hydroxide in 60 ml of ethanol, and the mixture was refluxed for 2 h. The resulting solution was allowed to stand overnight, after which it was filtered, and the filtrate was acidified to pH 6 with 50% acetic acid solution. The resulting precipitate was removed by filtration, washed with water, and dried to give 4.4 g (95.5%) of VII. No melting-point depression was observed for a mixture of this product with a sample of VII obtained by method A.

C) A 15.9-g (0.1 mole) sample of hydrazine III was dissolved by heating in 250 ml of glacial acetic acid, and 7 ml (0.1 mole) of pyruvic acid was then added slowly with stirring. The mixture was stirred at 60-70° for another 30 min, after which 75 ml of concentrated H_2SO_4 was added cautiously. The mixture was heated to 110-115° and maintained at that temperature for 10-15 min. It was then cooled and poured into 300 ml of water, during which a precipitate formed. The precipitate was removed by filtration, washed with a small amount of acetic acid, and dissolved in 1 liter of water. The solution was neutralized to pH 6 with 40% NaOH, and the resulting precipitate was removed by filtration, washed with water, and dried to give 17.3 g (75%) of VII. No melting-point depression was observed for a mixture of this product with a sample of VII obtained by methods A and B.

1H-Pyrrolo[2,3-f]quinoline (VIII). A 4.6-g (0.02 mole) sample of acid VII was heated to 260-290° and held at that temperature for 10 min. It was then cooled and dissolved in ether, and the ether solution was passed through a column filled with Al_2O_3. Removal of the solvent from the eluate gave 3.2 g (95%) of pale-yellow crystals of VIII with mp 232-234° (from benzene) (mp 236-238° [4]). UV spectrum, λ_{max} (log ε): 215 (4.50), 268 (4.66), and 333 nm (3.55). Found: C 78.5; H 4.8; N 16.6%; M 168. $C_{11}H_8N_2$. Calculated: C 78.6; H 4.8; N 16.7%. A pink coloration formed when VIII was heated with Erlich's reagent.

6-Quinolylhydrazine (X). A 28.8-g (0.2 mole) sample of 6-hydroxyquinoline IX was heated with stirring in 108 ml (2 mole) of hydrazine hydrate, after which the mixture was heated at 115-118° for 24 h. It was then allowed to stand overnight, and the precipitate was removed by filtration, squeezed thoroughly, and dried to give 21.9 g (69%) of XI with mp 132° (from ethanol). Found: C 67.7; H 5.7; N 26.6%. $C_9H_9N_3$. Calculated: C 67.9; H 5.8; N 26.4%.

Ethyl Pyruvate 6-Quinolylhydrazone (XI). This compound was obtained by the method used to prepare IVa,b. The yield of XIa,b was 23.2 g (90%). Separation of 3.5 g of XIa,b gave 0.4 g of syn isomer XIa and 3.1 g of anti isomer XIb. The results of analysis and the IR and UV spectral data are presented in Table 3.

Pyruvic Acid 6-Quinolylhydrazone (XII). A 15.9-g (0.1 mole) sample of hydrazine X was dissolved by heating and stirring in 80 ml of benzene, and the solution was heated at 60-70° for 30 min. The resulting precipitate was removed by filtration, washed with benzene, and dried to give 22.8 g (99.7%) of XII with mp 171-173° (by reprecipitation). Found: C 62.4; H 4.7; N 18.3%. $C_{12}H_{11}N_3O_2$. Calculated: C 62.9; H 4.8; N 18.3%.

3H-Pyrrolo[3,2-f]quinolyl-2-carboxylic Acid (XIII). A) A 25.7-g (0.1 mole) of hydrazine XIa,b was dissolved by heating with stirring in a mixture of 250 ml of glacial acetic acid and 75 ml of concentrated H_2SO_4, after which the solution was heated at 110-115° for 10-15 min. It was then cooled and poured into 1.5 liters of water, and the aqueous mixture was neutralized to pH 8 with 40% NaOH solution. The solution was refluxed with charcoal for 1 h, after which it was filtered, and the filtrate was cooled, neutralized with 50% acetic acid solution, and allowed to stand overnight. The resulting precipitate was removed by filtration, washed with water, and dried to give 5.75 g (25%) of XIII with mp 318-319° (by reprecipitation) (mp >300° [3]). Found: C 62.2; H 4.3; N 12.4%. $C_{12}H_8N_2O_2 \cdot H_2O$. Calculated: C 62.6; H 4.3; N 12.2%.

B) A 22.9-g (0.1 mole) sample of hydrazine XII was dissolved by heating in 250 ml of glacial acetic acid, and 75 ml of concentrated H_2SO_4 was added cautiously with stirring. The mixture was heated to 110-115° and held at that temperature for 10-15 min. It was then worked up by the method in experiment A to give 5.75 g (25%) of XIII. No melting-point depression was observed for a mixture of this product with a sample of XIII obtained by method A.

C) A 15.9-g (0.1 mole) sample of hydrazine X was dissolved by heating in 250 ml of glacial acetic acid, and 7 ml (0.1 mole) of pyruvic acid was added slowly with stirring. The mixture was stirred at 60-70° for another 30 min, after which 75 ml of concentrated H_2SO_4 was added cautiously. It was then worked up by the method in experiment A to give 5.7 g (25%) of XIII. No melting-point depression was observed for a mixture of this product with a sample of XIII obtained by methods A and B.

3H-Pyrrolo[3,2-f]quinoline (XIV). This compound, with mp 163-164° (from benzene) mp 165° [3]), was obtained by the method used to prepare VIII. The yield was 3.2 g (95%). UV spectrum, λ_{max} (log ε): 216 (4.85), 263 (4.75), 333 nm (4.18). Found: C 78.5; H 4.8; N 16.6%; M^+ 168. $C_{11}H_8N_2$. Calculated: C 78.6; H 4.8; N 16.7%. A pink coloration was formed when XIV was heated with Erlich's reagent.

Acetone 5-Quinolylhydrazone (XV). This compound, with mp 138-139° (from ethanol) (mp 138-140° [2]), was obtained by the method in [2]. IR spectrum: 3390 cm^{-1} (NH) (chloroform). UV spectrum, λ_{max} (log ε): 210 (4.40), 257 (4.42), and 375 nm (3.62). Found: C 72.2; H 6.5; N 21.2%. $C_{12}H_{13}N_3$. Calculated: C 72.4; H 6.5; N 21.1%.

Methyl Ethyl Ketone 5-Quinolylhydrazone (XVI). A mixture of 1.59 g (0.01 mole) of hydrazine III, 0.72 g (0.01 mole) of methyl ethyl ketone, and 10 ml of benzene was heated for 15 min, after which the benzene was removed by distillation until crystallization commenced. The crystals were removed by filtration to give 1.23 g (75%) of XVI with mp 108-109° (from benzene). IR spectrum (in chloroform): 3390 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 210 (4.38), 257 (4.40), and 375 nm (3.60). Found: C 73.2; H 7.1; N 19.6%. $C_{13}H_{15}N_3$. Calculated: C 73.2; H 7.0; N 19.7%.

LITERATURE CITED

1. Zh. F. Sergeeva, R. N. Akhvlediani, V. P. Shabunova, V. I. Korolev, A, M. Vasil'ev, T. A. Babushkina, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 12, 1656 (1975).
2. S. F. Dufton, J. Chem. Soc., 61, 785 (1892).
3. H. Wieland and L. Horner, Ann., 536, 89 (1938).
4. L. Horner, Ann., 540, 73 (1939).
5. H. Kauffmann, Ber., 50, 1627 (1917).
6. I. A. Krasavin, B. V. Parusnikov, and V. M. Dziomko, Methods for the Synthesis of Chemical Reagents and Preparations [in Russian], Vol. 2, Moscow (1961), p. 89.
7. K. Takeda and M. Tokuyaomo, J. Pharm. Soc. Japan, 74, 1274 (1954).
8. T. A. Babushkina, A. M. Vasil'ev, L. B. Shagalov, V. N. Eraksina, T. A. Tkachenko, and N. N. Suvorov, Zh. Org. Khim., 11, 864 (1975).
9. J. W. Emsley, J. Feeney, and L. Sutcliffe, High-Resolution NMR Spectroscopy, Pergamon, Oxford (1965, 1966).
10. V. G. Avramenko, G. S. Mosina, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 9, 1212 (1970).
11. L. B. Shagalov, V. I. Eraksina, T. A. Tkachenko, V. I. Mamonov, and N. N. Suvorov, Zh. Org. Khim., 8, 2310 (1972).
12. N. N. Suvorov, E. I. Gordeev, and M. V. Vasin, Khim. Geterotsikl. Soedin., No. 11, 1496 (1974).