tube, and the test tube was heated for ~5 min in a burner flame until the evolution of white vapors ceased. The tube was then cooled, and the reaction mixture was extracted with acetone. The extract was applied to silica gel, and linear isomer I and angular isomer IV were separated with a column filled with 100/250 μ silica gel (elution with benzene). Workup gave 0.12 g (8%) of indole I with mp 206°C (mp > 200°C [2]) and 0.11 g (7%) of indole IV with mp 86°C (mp 86°C [3]). The PMR spectra of I and IV were in agreement with symmetrical structures. PMR spectrum of I (in d_6-acetone): 9.7 (NH), 7.20 (1H, dd, 2-H, J_{13} = 2.4 Hz, $J_{23} \approx J_{12} \approx$ 2.7 Hz), 6.36 (1H, dd, 3-H), and 7.46 ppm (1H, s, 4-H). PMR spectrum of IV (in d_6-acetone): 6.64 (1H, dd, 1-H, J_{13} = 2.2 Hz, J_{12} = 2.9 Hz), 7.21 (1H, dd, 2-H, J_{23} = 2.5 Hz), 10.0 (NH), and 7.20 ppm (1H, s, 4-H). These data are in agreement with the data obtained in [3].

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SYNTHESIS OF 3-OXOISOTHIAZOLO[5,4-b]PYRIDINES

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3-Oxoisothiazolo[5,4-b]pyridines were synthesized for the first time by the reaction of 3-cyanopyridine-2-thiones or bis(3-cyanopyridyl) disulfides with concentrated sulfuric acid. It is demonstrated that 3-carbamoylpyridine-2-thiones are formed as intermediates. The 3-oxoisothiazolopyridines were converted to 3-bromoisothiazolopyridines and pyridine-2-thiones. The bromination of pyridine-2-thione was studied.

3-Cyanopyridine-2-thiones react with bromine [1], chloranil [2], and sulfamide [3] with the formation of an isothiazole ring to give, respectively, 3-bromo- and 3-aminoisothiazolo-[5,4-b]pyridines.

We have shown that 3-cyanopyridine-2-thiones (I) in concentrated sulfuric acid form the previously undescribed 3-oxo derivatives of isothiazolo[5,4-b]pyridines (III). In contrast to the previously described cyclocondensation of I with bromine, which leads to the formation of 3-bromoisothiazoles [1], treatment of pyridinethiones I with concentrated sulfuric acid leads initially to hydrolysis of the nitrole group to an amide group, after which the resulting 3-carbamoyl-4,6-diphenylpyridine-2-thiones (II) undergo oxidative cyclization to III. The formation of amides II as intermediates is confirmed by the formation of an isothiazole ring when a model compound, viz., 3-carbamoyl-4,6-diphenylpyridine-2-thione (IIa), which was synthesized from 2-bromo-3-carbamoyl-4,6-diphenylpyridine (VI) with thiourea, is treated with concentrated sulfuric acid.

The difference between oxoisothiazolo[5,4-b]pyridine III and the corresponding acylic amide II was proved by spectroscopy.

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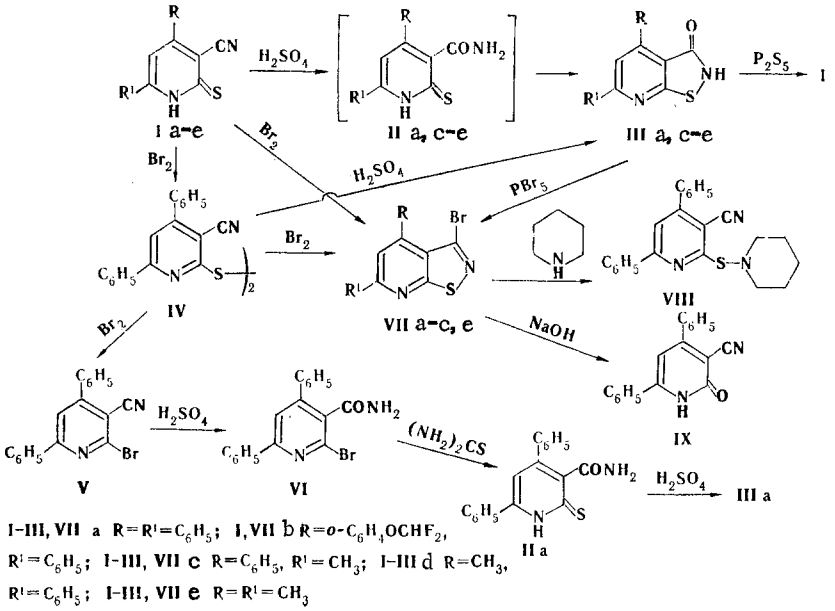
In the IR spectra the band of the carbonyl group for cyclic amide IIIa is 16 cm^{-1} higher as compared with the corresponding acyclic amide IIa. In contrast to acyclic amide IIa, for which there are characteristic vibrations of NH_2 and NH groups at 3205-3322 cm^{-1}, only vibrations of NH groups are observed for the spectra of solutions of oxoisothiazolopyridines III at 3158-3170 cm^{-1}.



In contrast to pyridine-2-thione derivatives Ia [4] and IIa, for which the long-wave maximum is shifted bathochromically to 405-418 nm, the long-wave maximum that characterizes the $n \rightarrow \pi^*$ transition of the pyridine ring is observed at 244-302 nm in the UV spectra of 3-oxoisothiazolopyridines III, 3-bromoisothiazolopyridines VII, and 3-carbamoylpyridine VI.

Intense molecular-ion peaks that constitute evidence for the high stability of the conjugated heterocyclic system with respect to electron impact are noted in the mass spectra of oxoisothiazolopyridines IIIa, c-e. As in the case of benzisothiazol-3-ones [5], the fragmentation of 3-oxoisothiazolopyridines III begins with destruction of the five-membered ring, and ions that are characteristic for benzisothiazol-3-ones, viz., $(M-CHO^{\bullet})^+$, $(M-COS)^{+\bullet}$, and $(M-CHO^{\bullet}-S)^+$, are observed in the spectra of III. In contrast to benzisothiazol-3-ones, the $(M-16)^+$ ion, the composition of which for IIIa was established by high resolution and corresponds to the loss of an oxygen atom from the molecular ion, is characteristic for the mass spectra of III. The mass spectra with an indication of the characteristic ions are presented in Table 1.

In addition to the spectral data, the structure of 3-oxoisothiazolopyridines III is confirmed by conversion of the latter upon reaction with phosphorus pentabromide to 3-bromoisothiazolo[5,4-b]pyridines VII, which were also obtained by direct bromination of nitriles I at high temperatures [1].

For the preparation of 3-thioisothiazolo[5,4-b]pyridines, 3-oxoisothiazolopyridine IIIa was treated with phosphorus pentasulfide. However, in this case the oxygen atom was not replaced by a sulfur atom, but the ring of IIIa underwent cleavage to give starting 3-cyanopyridine-2-thione Ia.

3-Oxoisothiazolopyridines III are also formed from pyridyl disulfides IV by treatment with concentrated sulfuric acid. In contrast to the previously described methods [4, 6], we obtained disulfide IV by the action of an equivalent amount of bromine on pyridinethione Ia. Whereas bis(3-nitropyridyl) disulfides react with halogens to give halosulfenylpyridines [7], 3-cyano derivative IV reacts with excess bromine at high temperatures to give 3-bromoisothiazolo[5,4-b]pyridine (VII) and with a large excess of bromine at room temperature to give 2-bromo-3-cyanopyridine (V).

The isothiazole ring of 3-bromoisothiazolopyridines VII is cleaved in basic media. Thus VIIa reacts with piperidine to give 2-piperidylmercaptopyridine (VIII) and with an aqueous solution of sodium hydroxide at high temperatures to give pyridone IX [8].

TABLE 1. Mass Spectra of IIa, III, and VIIa

Compound	m/z values (relative intensities, %)*
IIa	306 (33) $M^{+\cdot}$, 305 (46), 289 (100), 288 (70), 287 (35), 273 (6), 272 (8), 271 (6), 263 (14), 262 (10), 261 (26), 260 (21), 257 (8), 256 (11), 255 (16), 245 (6), 244 (6), 230 (11), 229 (8), 228 (14), 227 (14), 203 (10), 202 (22), 201 (6), 77 (13), 43 (6), 41 (5)
IIIa	304 (91)† $M^{+\cdot}$, 303 (100), 288 (36), 287 (33), 272 (11), 271 (6), 256 (48), 255 (79), 244 (8), 228 (18), 227 (21), 203 (6), 202 (14), 201 (11), 200 (7), 152 (14), 83 (5), 81 (5), 71 (5), 69 (9), 57 (9), 55 (10), 43 (10), 41 (11)
IIIc	242 (96) $M^{+\cdot}$, 241 (100), 226 (5), 225 (5), 167 (5), 166 (6), 140 (6), 139 (5), 127 (7), 71 (7), 57 (10), 55 (7), 43 (7)
IIId	242 (100) $M^{+\cdot}$, 241 (8), 226 (27), 225 (6), 213 (5), 194 (8), 193 (7), 182 (13), 181 (12), 168 (11), 167 (10), 166 (8), 141 (7), 140 (7), 139 (6), 129 (12), 128 (7), 127 (7), 73 (24), 71 (14), 69 (17), 60 (26), 57 (51), 55 (46),
IIIe	43 (42), 41 (41)
	180 (100) $M^{+\cdot}$, 164 (6), 151 (8), 120 (6), 119 (13), 106 (13), 105 (8), 104 (8), 81 (10), 79 (9), 77 (11), 57 (10), 55 (12), 43 (8), 41 (14)
VIIa	366 (100) $M^{+\cdot}$, 365 (18), 334 (10), 287 (64), 255 (15), 254 (9), 253 (14), 228 (13), 227 (19), 184 (7), 183 (7), 160 (11), 140 (21), 69 (15), 60 (18), 57 (29), 55 (31), 43 (9), 41 (33)

*The peaks with intensities less than 5% are not presented; the ions corresponding to the ^{79}Br and ^{32}S isotopes are presented.
†The compositions of the ions with m/z 304, 288, and 255 were determined at a resolution of ~60,000 and were found to be $C_{18}H_{12}N_2OS$, $C_{18}H_{12}N_2S$, and $C_{18}H_{11}N_2$, respectively.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in ethanol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of the compounds in dimethyl sulfoxide (DMSO) were recorded with a Perkin–Elmer R-12A spectrometer (60 MHz) with tetramethylsilane as the internal standard. The mass spectra were recorded with an MS-50 AEI spectrometer at an ionizing voltage of 70 eV and an ion-source temperature of 150°C with direct introduction of the substances into the source. The course of the reaction and the individuality of the substances were monitored by thin-layer chromatography (TLC) in a chloroform–acetone–hexane system (2:1:1) on Silufol UV-254 plates.

4,6-Diphenyl-3-oxoisothiazolo[5,4-b]pyridine (IIIa). A) A mixture of 1.44 g (5 mmole) of 3-cyano-4,6-diphenylpyridine-2-thione (Ia) and 5 ml of concentrated H_2SO_4 was heated in a water bath for 5 h, after which it was cooled and poured into water. The precipitate was removed by filtration to give 1.33 g (84%) of oxoisothiazolopyridine IIIa with mp 256-258°C (from nitromethane).

B) A mixture of 0.58 g (1 mmole) of 2,2'-bis(3-cyano-4,6-diphenylpyridyl) disulfide (IV) and 2 ml of concentrated H_2SO_4 was heated in a water bath for 3 h, after which it was cooled and poured into water. The precipitate was removed by filtration to give 0.38 g (63%) of IIIa with mp 256-258°C (from nitromethane).

C) A mixture of 0.3 g (1 mmole) of 3-carbamoyl-4,6-diphenylpyridine-2-thione (IIa) and 2 ml of concentrated H_2SO_4 was heated in a water bath for 1 h, after which it was cooled and poured into water. The precipitate was separated to give 0.16 g (55%) of IIIa with mp 256-258°C (from nitromethane).

Compounds IIIc-e were obtained in the same way as IIIa by method A. Data on the 3-oxoisothiazolopyridines are presented in Tables 1 and 2.

Reaction of 4,6-Diphenyl-3-oxoisothiazolo[5,4-b]pyridine with Phosphorus Pentasulfide. A mixture of 1.5 g (5 mmole) of IIIa and 0.5 g (2 mmole) of phosphorus pentasulfide was suspended in 100 ml of dry toluene, and the suspension was refluxed for 3 h. The hot solution was filtered and cooled, and 0.6 g (42%) of 3-cyano-4,6-diphenylpyridine-2-thione (Ia), with mp 226-228°C, crystallized out. The product did not depress the melting point of a genuine sample [4].

2,2'-Bis(3-cyano-4,6-diphenylpyridyl) Disulfide (IV). A solution of 0.5 ml (10 mmole) of bromine in 20 ml of dry chloroform cooled to 5°C was added to 2.88 g (10 mmole) of 3-cyano-4,6-diphenylpyridine-2-thione (Ia), and the reaction mixture was maintained at 0°C for 20 h.

TABLE 2. Characteristics of the Synthesized IIa, III, and VII

Compound	mp,* °C	R_f	IR spectrum, ν, cm^{-1}		UV spectrum λ_{max}, nm (log ε)	PMR spectrum, δ, ppm	Found, %					Empirical formula	Calculated, %					Yield, %
			in Nujol	in dioxane			C	H	Br	N	S		C	H	Br	N	S	
IIa	216—218	0,14	1637,3188, 3282, 3360	1646 sh†1688, 3205, 3322 3500, 3567	248 (4,10), 273 (4,15), 308 sh(4,00), 405 (3,42)	13,69 (1H, s, NH); 7,8—7,4 (10H, m, $2C_6H_5$); 7,36 and 7,21 (2H, s, NH_2); 6,87 (1H, s, CH)	69,8	4,7	—	9,2	10,1	$C_{18}H_{14}N_2OS$	70,6	4,6	—	9,1	10,5	13
IIIa	256—258	0,54	1653	1682, 3160	257 sh(4,45), 275 (4,49), 344 (3,78)	8,2—7,4 (10H, m, $2C_6H_5$); 7,79 (1H, s, CH); 7,36 (1H, br s, NH)	71,2	4,1	—	9,3	10,8	$C_{18}H_{12}N_2OS$	71,0	4,0	—	9,2	10,5	84
IIIc	230—231	0,34	1660	1682, 3158	220 (4,19), 253 (4,28), 331 (3,60)	7,56—7,3 (7H, m, C_6H_5+ +CH+NH); 2,64 (3H, s, CH_3)	64,0	3,9	—	11,3	13,6	$C_{13}H_{10}N_2OS$	64,4	4,2	—	11,6	13,2	73
IIId	228—230	0,40	1645	1680, 3170	271 (4,51), 333 (3,82)	8,25—7,5 (5H, m, C_6H_5); 7,8 (1H, s, CH); 2,71 (3H, s, CH_3)	64,1	4,0	—	11,2	13,8	$C_{18}H_{10}N_2OS$	64,4	4,2		11,6	13,2	53
IIIe	197—198	0,26	1665	1680, 3168	228 (4,11), 247 (4,12), 318 (3,62)	6,89 (1H, s, CH); 2,63 (3H, s, CH_3); 2,51 (3H, s, CH_3)	52,9	4,4		15,2	17,9	$C_8H_8N_2OS$	53,1	4,5		15,5	17,8	68
VIIa	140—142	0,85	—	—	259 (4,45), 310 (4,35)	8,3—7,4 (10H, m, $2C_6H_5$); 7,94 (1H, s, CH)	59,0	3,2	22,4	7,4	8,9	$C_{18}H_{11}BrN_2S$	58,9	3,0	21,8	7,6	8,7	86
VIIb	114—115	0,82	—	—	258 (4,36), 311 (4,29)	8,2—7,2 (9H, m, C_6H_5+ +C_6H_4); 7,85 (1H, s, CH); 6,95 (1H, t, $OCHF_2$)	52,0	2,6	19,0	6,2	7,9	$C_{19}H_{11}BrF_2N_2OS$	52,7	2,6	18,4	6,5	7,4	72
VIIc	102—104	0,83	—	—	237 (4,49), 276 sh(3,87), 311 (3,93)	7,40 (5H, s, C_6H_5); 7,12 (1H, s, CH); 2,70 (3H, s, CH_3)	50,7	3,0	26,8	8,7	9,9	$C_{13}H_9BrN_2S$	51,2	3,0	26,2	9,2	10,5	72
VIIe	158—160 [1]	0,84	—	—	234 (4,45), 310 (3,90)	6,92 (1H, s, CH); 2,83 (3H, s, CH_3); 2,60 (3H, s, CH_3)	39,7	2,8	32,4	11,4	13,4	$C_8H_7BrN_2S$	39,5	2,9	32,9	11,5	13,2	55

*Compounds IIa, IIIc-e, and VIIa-c,e were recrystallized from ethanol, and IIIa was recrystallized from nitromethane.

†Shoulders are indicated by the abbreviation "sh."

Ethanol (20 ml) was added, and the precipitate was separated, washed with cold ethanol, and recrystallized from chloroform to give 1.5 g (50%) of disulfide IVa with mp 243-244°C. The product did not depress the melting point of a genuine sample [4].

2-Bromo-3-cyano-4,6-diphenylpyridine (V). A solution of 3 ml (60 mmole) of bromine in 20 ml of dry chloroform was added to 1.15 g (2 mmole) of 2,2'-bis(3-cyano-4,6-diphenylpyridine) disulfide (IV), and the reaction mixture was maintained at 20°C for 2 h. The solvent was partially removed by evaporation, and 0.23 g (20%) of starting IV was removed by filtration. Ethanol (20 ml) was added to the filtrate, and the precipitate was removed by filtration to give 0.55 g (37%) of pyridine V with mp 164-166°C (from ethanol). IR spectrum: 2237 cm^{-1} (CN). UV spectrum, λ_{max} (log ε): 268 (4.46) and 320 nm (4.36). PMR spectrum: 7.5-8.3 (10H, m, C_6H_5) and 8.22 ppm (1H, s, CH). Found: C 64.2; H 3.2; Br 23.7; N 8,4%. $C_{18}H_{11}BrN_2$. Calculated: C 64.5; H 3.3; Br 23.8; N 8.4%.

2-Bromo-3-carbamoyl-4,6-diphenylpyridine (VI). A mixture of 1.68 g (5 mmole) of 2-bromo-3-cyano-4,6-diphenylpyridine (V) and 3 ml of concentrated H_2SO_4 was heated in a water bath for 3 h, after which it was cooled and poured into water. The precipitate was removed by filtration to give 1.45 g (82%) of VI with mp 212-214°C (from ethanol). IR spectrum: 1662 (CO); 3156, 3230, 3345 cm^{-1} (NH_2). UV spectrum, λ_{max} (log ε): 256 (4.49) and 302 sh nm (4.12). PMR spectrum: 7.3-8.1 (12H, m, $2C_6H_5 + NH_2$) and 7.76 ppm (1H, s, CH). Found: C 60.8; H 3.8; Br 21.8; N 8.0%. $C_{18}H_{13}BrN_2O$. Calculated: C 61.2; H 3.7; Br 22.6; N 7.9%.

2-Carbamoyl-4,6-diphenylpyridine-2-thione (IIa). A mixture of 3.54 g (10 mmole) of amide VI and 2.3 g (30 mmole) of thiourea was fused and maintained at 200°C for 10 min. It was then cooled and refluxed in ethanol for 5 min. The insoluble material was separated, and 50 ml of 2 N KOH was added to the filtrate. The precipitate was separated, and the filtrate was poured into acidified water. The precipitate was separated to give 0.4 g (13%) of IIa with mp 216-218°C (from ethanol). The rest of the data are presented in Tables 1 and 2.

3-Bromo-4,6-diphenylisothiazolo[5,4-b]pyridine (VIIa). A) A mixture of 0.7 g (2.3 mmole) of IIIa and 2.5 g (5.8 mmole) of phosphorus pentabromide was heated at 100°C for 2.5 h, after which it was cooled and diluted with ice water, and the precipitate was removed by filtration to give 0.6 g (68%) of bromide VIIa with mp 140-142°C (from ethanol).

B) A solution of 3 ml (60 mmole) of bromine in 20 ml of dry chloroform was added to 2.88 g (10 mmole) of thione Ia, and the mixture was refluxed in a water bath for 1 h. The solvent was evaporated, 20 ml of ethanol was added to the residue, and the precipitate was removed by filtration to give 3.15 g (86%) of VIIa with mp 140-142°C (from ethanol).

C) A solution of 0.36 ml (7·2 mmole) of bromine in 10 ml of dry chloroform was added to 0.35 g (0.6 mmole) of 2,2'-bis(3-cyano-4,6-diphenylpyridyl) disulfide IV, and the mixture was refluxed in a water bath for 1 h. The solvent was evaporated, 10 ml of ethanol was added, and the precipitate was removed by filtration to give 0.3 g (68%) of VIIa with mp 141-142°C (from ethanol).

Compounds VIIb, c, e were obtained in the same way as VIIa by method B. Data on 3-bromoisothiazolopyridines VIIa-c, e are presented in Tables 1 and 2.

2-Piperidylmercapto-3-cyano-4,6-diphenylpyridine (VIII). A mixture of 1.1 g (3 mmole) of 3-bromo-4,6-diphenylisothiazolo[5,4-b]pyridine (VII) and 3 ml (30 mmole) piperidine in 10 ml of ethanol was refluxed in a water bath for 1 h, after which it was cooled, and the precipitate was removed by filtration and washed with water to give 0.53 g (48%) of piperidylmercaptopyridine VIII with mp 116-118°C (from ethanol). IR spectrum: 2222 cm^{-1} (CN). UV spectrum, λ_{max} (log ε): 266 (4.51) and 344 nm (4.04). PMR spectrum: 7.3-8.1 (10H, m, $2C_6H_5$), 7.62 (1H, s, CH), 3.62 [4H, m, $N(CH_2)_2$], and 1.55 ppm [6H, m, $(CH_2)_3$]. Found: C 73.6; H 5.6; N 11.3; S 8.0%. $C_{23}H_{21}N_3S$. Calculated: C 74.4; H 5.7; N 11.3; S 8.6%.

3-Cyano-4,6-diphenyl-2-pyridone (IX). A mixture of 0.73 g (2 mmole) of 3-bromo-4,6-diphenylisothiazolo[5,4-b]pyridine (VIIa) and 20 ml of 3 N NaOH solution was refluxed at 100°C for 2 h, after which it was cooled, and the precipitate was removed by filtration and chromatographed on silica gel [elution with chloroform–acetone–hexane (2:1:1)]. Evaporation of the fraction with R_f 0.4 gave 0.08 g (15%) of pyridone IX with mp 310-312°C. The product did not depress the melting point of a genuine sample [8].

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SYNTHESIS AND TRANSFORMATIONS OF 1-METHYL-4-AZAFLUORENE

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By means of catalytic dehydrocyclization of dimethyl-substituted 2-phenylpyridines in a pyridine ring to 1(2,3)methyl-4-azafluorenes with subsequent oxidation, synthesis of alkaloid onychine — 1-methyl-4-azafluorene — several of its isomers were achieved. Using 1-methyl-4-azafluorene, we obtained a C_9 furfurylidene product, substituted tetrahydroindine[1,2-b]pyridine and NH-indine[1,2-b]-pyridine. We obtained 7-nitro-1-methyl-4azafluorene by nitration of onychine and oxidation of nitro-substituted azafluorene; this indicates an identical orientation of 4-azafluoren(one) and fluoren(one) during nitration.

1-Methyl-4-azafluorenone — the alkaloid isolated from *Onychopetalum amazonicum* [1] — has been called onychine. Several reports have been devoted to the establishment of its structure and synthesis [2-4]. Continuing our research on azafluorenes, we addressed ourselves to the development of a new method for the synthesis of onychine and its analogs and to a study of some transformations of 1-methyl-4-azafluorene, the heterocyclic system of which is the foundation of this alkaloid.

As the starting compound in the synthesis of onychine we used 3,4-dimethyl-4-phenylpyridine (I), which was obtained by the Chichibabin method [5, 6] by condensation of crotonaldehyde with propiophenone and ammonia in the vapor phase on a cadmium calcium phosphate catalyst. 3,6-Dimethyl-2-phenylpyridine (II) is also formed in this condensation. The overall yield of isomeric pyridine bases I and II (in a ratio of 3.4:1) was ~50%. For the conversion of these pyridine bases to methyl-substituted 4-azafluorenes the mixture of them was subjected to catalytic dehydrocyclization, as described in [7]. 1-Methyl-4-azafluorene (III), 3-methyl-4-azafluorene (IV), and a very small amount of demethylation product, viz., 4-azafluorene, were isolated from the catalyzate by crystallization and chromatography. 2-Methyl-4-azafluorene (V) was similarly obtained from 3,5-dimethyl-2-phenylpyridine [6].

1-Methyl-4-azafluorenone (VI) (onychine) was obtained in high yield by the liquid-phase oxidation of III with oxygen in dimethyl sulfoxide (DMSO) in the presence of a catalytic amount of sodium hydroxide [8], while isomers of this alkaloid with respect to the position of the methyl group in the pyridine ring, viz., 3-methyl- (VII) and 2-methyl-4-azafluorenone (VIII), respectively, were obtained in the oxidation of azafluorenes IV and V.

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