−23.5° (alcohol, c 0.5). Found: C, 39.1; H, 5.1%. $C_{10}H_{14}BrN \cdot HBr$. Calculated: C, 38.9; H, 4.9]. Rotatory power in alcohol (c 0.045), [M]° (λ, nm): 510 (300), 547 (290), 615 (285), 649 (275), 479 (268), 958 (265), 822 (262), 1199 (258), 1026 (255), 1335 (250), 2550 (230).

(−)-1-Methyl-1,2,3,4-tetrahydroisoquinoline (I). A mixture of 0.04 mole of compound IV, 0.09 mole of $AlCl_3$, and 150 ml of decaline distilled from over sodium is heated for three hours at 145-150°C. After the end of the heating, the reaction mixture is decomposed with ice and conc. HCl, the decaline layer is separated, the aqueous layer is extracted with benzene or ether (5 × 50 ml), then made alkaline with NaOH and extracted with ether (5 × 50 ml). The ether extract is dried with NaOH, the ether distilled off, and the residue redistilled. Yield 2.9 g (54%), T_{bp} 90°C (2 mm), $[\alpha]_D^{20}$ −76.1° (alcohol, c 0.1). Rotatory power in isooctane (c 0.1), [M]° (λ, nm): −375 (300), −91 (274), −524 (270), −205 (268), −1140 (249), 0 (230), 410 (225). CD in isooctane (c 0.5), [θ]° (λ, nm): 774 (273), 463 (270), 873 (266); (c 0.05): −1170 (30), 615 (218).

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MASS SPECTROSCOPIC STUDY OF 9-AMINO- AND 9-ALKYL(DIALKYL, SPIRO)-1- AND 4-AZAFLUORENES

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UDC 543.51:547.678.3'83

Elimination of a substituent from the 9-position appears to be the main pathway for decomposition of 9-amino-4-azafluorenes. An amine type fragmentation pattern has been observed as well. Decomposition of 9-spiro-4-azafluorenes occurs via cleavage of the radical bound to the three-membered ring. 9-Alkyl-(dialkyl)-1- and 4-azafluorenes also readily lose a substituent in position 9. The observed pathways and principles allow one to determine the nature of the substituent in the 9-position and also to differentiate 1-azafluorenes from 4-azafluorenes.

We have previously developed methods for the synthesis of, and have studied the properties and chemical reactions of, 9-amino- and 9-alkyl(dialkyl, spiro)-1- and 4-azafluorenes [1-4]. The presence of functional substituents in these molecules makes them not only of synthetic importance, but also of practical utility. In analogy with fluorene derivatives

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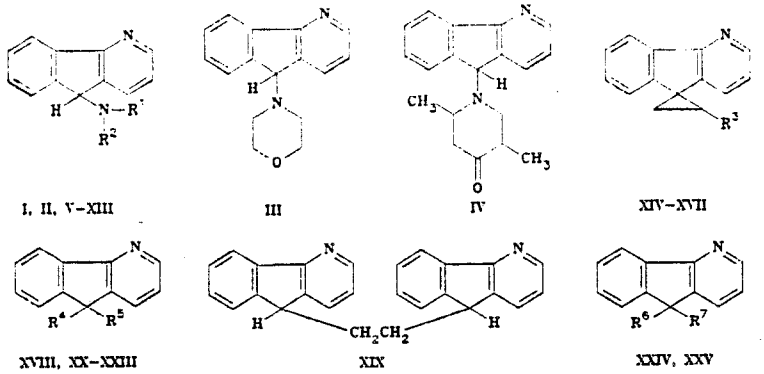
[5], this group of azafluorenes exhibits a range of diverse physiological activity; 9-morpholino-4-azafluorene (III), for instance, has been shown to be significantly more active [6] that the known pharmacological drug amidopyrine, with strong antioxidant properties.

In the present paper we have examined the dissociative ionization of this group of substances, I-XXV, and have determined the effect of the amine nitrogen atom and the substituents bonded to it on the decomposition pathways of compounds I-XIII. The dependence of the fragmentation pathway of 1- and 4-azafluorene derivatives XIV-XXV on the position of the nitrogen atom in the ring and on the nature of substituents found in position 9 has also been clarified. The observed principles have enabled us to establish the structural and analytical utility of mass spectrometry for this series of azafluorene derivatives.

Scheme 1



I, II, V–XIII III IV XIV–XVII

XVIII, XX–XXIII XIX XXIV, XXV

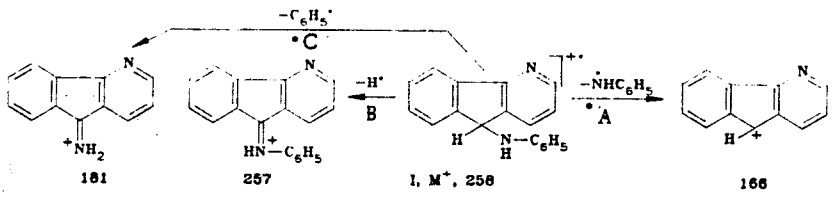
I R^1=H, R^2=C_6H_5; II R^1=D, R^2=C_6H_5; V—XI R^1=CH_3; V R^2=CH_2CH_2Cl; VI R^2=CH_2CH_2OH; VII R^2=CH_2CH_2OD; VIII R^2=$CH_2CH_2OCOC_2H_5$; IX R^2=$CH_2CH_2OCOC_6H_5$; X R^2=$CH_2CH_2OCONHC_6H_5$; XI R^2=$CH_2CH_2OCONHC_6H_4$-*n*; XII R^1=R^2=CH_2CH_2OH; XIII R^1=R^2=$CH_2CH_2OCOC_2H_5$; XIV R^3=CN; XV R^3=COOH; XVI R^3=COOD; XVII R^3=$COOC_2H_5$; XVIII R^4=H, R^5=CN; XX R^4=H, R^5=CH_2CH_2OH; XXI R^4=H, R^5=$CH_2CH_2CH_2CH_2OH$; XXII R^4=H, R^5=$(CH_2)_4OCONHC_6H_5$; XXIII R^4=R^5=CH_2CH_2CN; XXIV R^6=R^7=CH_2CH_2CN; XXV R^6=R^7=CH_2CH_2COOH

The most stable molecular ions (W_M values) in the mass spectra of compounds I-XIII (Table 1) are observed for compounds I-III and V-VII, which contain a phenyl radical, morpholine ring, and β-chloro- or β-hydroxyethyl substituents of the amine nitrogen atom in position 9.

The main fragmentation pathway for compounds I-XIII involves cleavage of the $C_{(9)}$—N bond with ensuing localization of positive charge on the azafluorene ring, which leads to the ion at 166*, with maximum peak intensity (Scheme 2, path A). An unexpected feature of the decomposition of 9-amino-4-azafluorenes is the absence of intense ion peaks due to $[M-H]^+$ (Scheme 2, path B) in their mass spectra; these ions would have been expected with high probability, due to the fact that the hydrogen atom of $C_{(9)}$ is located in the β-position to an amine nitrogen atom [7], and to pyridine [8] and benzene [9] rings, simultaneously.

The mass spectral character of 4-azafluorene derivatives I-XIII in the region of high and medium m/e values is determined primarily by cleavage of the bonds between substituents and the exocyclic nitrogen atom, which makes it possible to deduce important structural information (from their mass spectra). Thus, the presence of an NHC_6H_5 radical in the 9-position in compound I leads to the appearance of a $[M - C_6H_5]^+$ fragment (181). Its 1 amu shift to higher m/e in the mass spectrum of the deuteroanalog II, as well as the elemental composition of the $C_{12}H_9N_2$ ion, as determined from its high-resolution mass spectrum (found, 181.0758; calc 181.0752), confirm its formation pathway (Scheme 2, path C). Analogous

Scheme 2



181 257 I, M^+, 256 166

*The numbers given to characterize ions, both in the text and in the schemes, correspond to m/e values.

TABLE 1. Mass Spectra of 9-Amino- and 9-Alkyl(dialkyl, spiro)-1- and 4-Azafluorenes I-XXV*

Compound	m/e values (relative peak intensity as % of maximum)
I	258 (M^+, 27), 257 (8), 256 (4), 255 (2), 181 (7), 180 (2), 179 (4), 167 (6), 166 (100), 165 (4). W_M=6,3
II**	259 (M^+, 30), 258 (9), 257 (5), 256 (8), 182 (9), 181 (3), 180 (4), 167 (5), 166 (100), 165 (5). W_M=7,0
III	252 (M^+, 37), 251 (3), 224 (7), 195 (8), 194 (14), 193 (17), 167 (23), 166 (100), 95 (23), 86 (24). W_M=3,9
IV	292 (M^+, 8), 277 (14), 207 (7), 179 (5), 167 (6), 166 (100), 165 (10), 139 (10), 126 (5), 125 (10). W_M=1,2
V	258 (M^+, 5)***, 209 (24), 195 (1), 181 (2), 166 (100), 165 (2), 141 (4), 140 (7), 139 (9), 127 (7). W_M=3,0
VI	240 (M^+, 12), 239 (4), 209 (36), 194 (3), 193 (4), 167 (20), 166 (100), 165 (4), 140 (11), 139 (9). W_M=4,5
VII**	241 (M^+, 14), 240 (5), 209 (34), 194 (4), 167 (21), 166 (100), 165 (3), 164 (2), 140 (10), 139 (9). W_M=5,0
VIII	296 (M^+, 2), 222 (6), 209 (23), 195 (4), 166 (100), 165 (2), 141 (2), 140 (6), 139 (4), 100 (2). W_M=1,4
IX	222 (17), 209 (24), 208 (1), 207 (3), 195 (4), 167 (4), 166 (100), 140 (5), 139 (4), 105 (8), peak M^+ is absent
X	359 (M^+, 1), 240 (2), 222 (14), 209 (23), 195 (3), 167 (4), 166 (100), 140 (7), 119 (17), 78 (20). W_M=3,0
XI	373 (M^+, 2), 240 (2), 222 (30), 209 (23), 195 (1), 167 (5), 166 (100), 140 (7), 133 (14), 92 (5). W_M=0,05
XII	270 (M^+, 1), 239 (31), 225 (1), 193 (2), 167 (3), 166 (100), 140 (6), 139 (5), 138 (1), 131 (17). W_M=0,5
XIII	308 (1), 295 (5), 281 (0,5), 239 (3), 181 (3), 166 (100), 165 (1), 141 (1), 140 (3), 139 (2), peak M^+ is absent
XIV	218 (M^+, 100), 217 (25), 216 (11), 215 (2), 192 (15), 191 (13), 190 (6), 167 (8), 166 (10), 165 (9). W_M=14,9
XV	237 (M^+, 77), 219 (36), 192 (100), 191 (44), 190 (13), 167 (15), 166 (13), 165 (10), 97 (36), 95 (28). W_M=8,2
XVI***	238 (M^+, 80), 220 (16), 219 (14), 193 (30), 192 (100), 191 (35), 190 (14), 167 (28), 166 (12), 165 (8). W_M=9,0
XVII	265 (M^+, 31), 236 (13), 220 (18), 219 (22), 208 (18), 192 (100), 191 (26), 190 (18), 167 (10), 166 (22). W_M=3,4
XVIII	192 (M^+, 15), 191 (8), 166 (100), 165 (8), 164 (11), 140 (11), 139 (11), 138 (6), 97 (8), 95 (7). W_M=5,0
XIX	360 (M^+, 22), 194 (6), 193 (5), 192 (7), 191 (4), 181 (47), 180 (100), 166 (39), 153 (13), 140 (11). W_M=4,6
XX	211 (M^+, 22), 193 (100), 192 (20), 181 (18), 180 (36), 167 (16), 166 (57), 152 (17), 140 (15), 130 (15). W_M=7,8
XXI	239 (M^+, 34), 221 (31), 220 (16), 194 (21), 193 (29), 192 (21), 180 (64), 179 (89), 167 (54), 166 (100). W_M=4,5
XXII	358 (M^+, 22), 239 (48), 221 (54), 220 (26), 193 (9), 192 (30), 191 (28), 180 (100), 179 (85), 167 (52), 166 (67). W_M=3,6
XXIII	273 (M^+, 30), 233 (2), 219 (100), 193 (6), 192 (21), 191 (7), 179 (55), 178 (21), 177 (11), 166 (11). W_M=2,9
XXIV	273 (M^+, 26), 233 (6), 221 (13), 220 (40), 219 (30), 193 (13), 192 (38), 191 (15), 181 (36), 180 (100). W_M=3,2
XXV	311 (M^+, 14), 294 (3), 253 (5), 252 (10), 239 (44), 221 (13), 220 (14), 193 (33), 192 (58), 180 (100). W_M=1,9

*The 10 most intense peaks are given.
†Mass spectra of deuteroanalogs, corrected to 100% concentration of D.
‡Calculated based on the ^{35}Cl isotope.

α-cleavage has been observed in the decomposition of all of the 9-aminosubstituted 4-azafluorenes, with the exception of compounds III and IV, which contain a cyclic amine nitrogen atom.

The presence of a morpholine ring in the 9-position in derivative III leads to the appearance of $[M - C_2H_4]^+$ (224), $[M - CH_2OCH_2CH_2]^+$ (194), $[M - CH_2OCH{=}CH_2]^+$ (195), and $[M - CH_2OCH_2CH_3]^+$ (193) fragments, which are due to cleavage of the morpholine ring.

The presence of a 2,5-dimethylpiperidine ring in the 9-position of azafluorene IV does not lead to cleavage of the $C_{(3')}$–$C_{(4')}$ and $C_{(6')}$–N bonds, or of the bonds symmetrical with these, as is characteristic of piperidines [10], but instead leads to the formation of an $[M - CH_3]^+$ ion (277), due to elimination of the methyl group located ortho to the nitrogen atom. For 9-amino-4-azafluorenes V-XIII, which contain acyclic substituents attached to the amine nitrogen atom, the characteristic cleavage pattern of saturated amines is observed [11], namely, cleavage of the β-C–C bond relative to the exocyclic nitrogen atom. The presence of

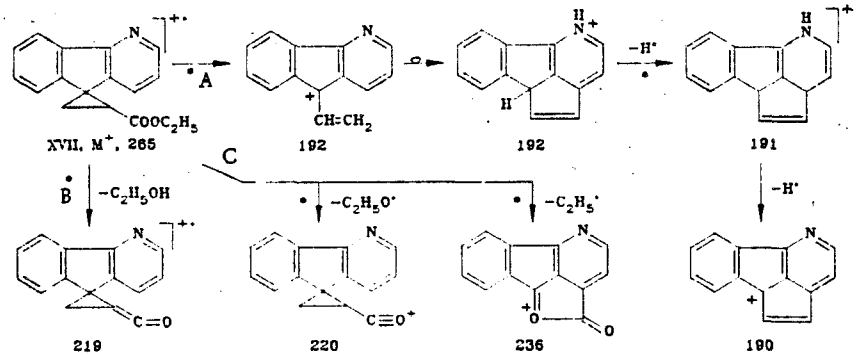
an ester functional group in compounds VIII, IX, and XIII is associated with the appearance of $[M - RCOOH]^+$ ions (R = C_2H_5; C_6H_5), while the presence of an arylcarbamoylhydroxyethyl functional group in compounds X and XI leads, in addition to the above, to the appearance of $[M - ArN{=}C{=}O]^+$, $ArN{=}C{=}O^+$ and ArH^+ fragments.

The presence of two β-hydroxyethyl radicals attached to the amine nitrogen atom in 4-azafluorene XII leads, at a secondary stage of decomposition (after β-cleavage), to elimination of a molecule of C_2H_5OH and the formation of an $[M - CH_2OH, - C_2H_5OH]^+$ ion (193).

The mass spectra of compounds XIV-XXV (Table 1) contain molecular ion peaks of both average and high intensity. Their stability (W_M) in the series of azafluorenes XIV-XVII, which contain a cyclopropane ring in the 9-position, is maximum for compound XIV, containing a nitrile group in this ring, and at a minimum for compound XVII, in which the ring contains an ester functional group.

The main pathway for decomposition of azafluorenes XIV-XVII involves loss of the substituents from the 1-position of the cyclopropane ring (Scheme 3, path A), which is accompanied, apparently, by cleavage of the cyclopropane ring in the 192 ion and subsequent cyclization of the ethenyl radical to the 4-azafluorene ring. The occurrence of this decomposition process is confirmed by the successive loss of two hydrogen atoms from the 192 fragment, as evidenced by the appearance of intense peaks due to doubly charged ions at 86 (12%), 85.5 (16%), and 85 (18%); this is indicative of the polycyclic structure of ions 192, 191, and 190 and of the high degree of conjugation.

Scheme 3



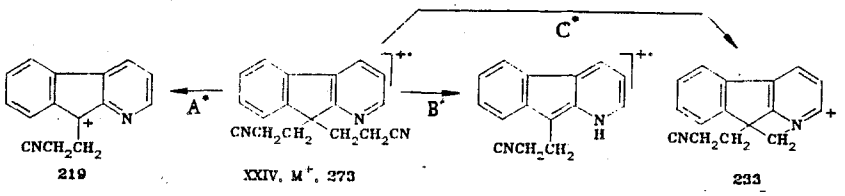
Dissociative ionization of the nitrile derivative XIV is characterized by the appearance of $[M - nH]^+$ fragments in its mass spectrum, where n = 1-3, while the distinguishing feature of the decomposition of compounds XV and XVII, containing carboxyl and ester groups, is the facile cleavage of molecules of H_2O and C_2H_5OH, respectively (Scheme 3, path B). Another characteristic feature of compound XVII is the elimination of C_2H_5O and C_2H_5 radicals, leading to the appearance of 220 and 236 fragments (Scheme 3, path C). Although the appearance of the first of these ions is typical of the decomposition of esters [12], the appearance of the second of these ions is unexpected and appears to be accompanied by expansion of the cyclopropane ring via incorporation of the oxygen atom of the ethoxy group, which results in the formation of a five-membered lactone ring. This is qualitatively confirmed by the subsequent loss of a molecule of CO from the $[M - C_2H_5]^+$ ion, giving the fragment 208.

It is interesting to note that the mass spectrum of deuteroanalog XVI exhibits partial displacement of the $[M - H_2O]^+$ and $[M - COOH]^+$ ions by 1 amu toward higher mass numbers. This observation indicates the presence of an exchange pathway between the carboxyl hydrogen atom in compound XV and the cyclopropane ring hydrogen atoms, since the azafluorene fragment at 167 does not exhibit displacement upon deuteration. We assume that this process takes place via the formation of the enediol form of compound XV.

Azafluorenes XVIII-XXV, which contain one or two substituents attached to the $C_{(9)}$ atom, undergo loss of both or one of these substituents, without transfer, or with accompanying transfer of a hydrogen atom to the azafluorene ring (Scheme 4, paths A and B). The probability of this first process is significantly higher than the second process in the series of 4-azafluorene derivatives XVIII-XXIII, although it decreases with the incorporation of active hydrogen atoms in the substituent and with an increase in the number of carbon atoms contained in the substituent. The inverse dependence is noted for 1-azafluorenes XXIV and

XXV: the second process gives rise to more intense ions than the first, which may be explained in terms of a more facile migration of a hydrogen atom from the substituent to the nitrogen atom of the 1-azafluorene ring. This makes it possible to distinguish unequivocally compounds in this series which are isomeric with respect to the position of the nitrogen atom in the ring.

Scheme 4



219 XXIV, M^+, 273 233

Each of the compounds XVIII-XXV displays its own characteristic dissociative ionization pattern, which is associated with the nature of the substituents at the $C_{(9)}$ atom. The presence of a nitrile group in compound XVIII gives rise to, in contrast with other compounds, a significantly intense $[M - H]^+$ ion peak; this peak is probably due to loss of a hydrogen atom from the 9-position of the azafluorene ring, which leads to conjugation of this ring with the CN radical. For the ethylene group in compound XIX, two characteristics are noted, namely, cleavage of the bond between the carbon atoms of this group, giving the peak with maximum intensity at 180, and also cleavage of the $C_{(9)}$–$C_{(1')}$ bond, giving rise to the 166 and 194 ions. Azafluorene derivatives XX and XXI, which contain 2-hydroxyethyl and 4-hydroxybutyl substituents, readily eliminate a molecule of H_2O. In the mass spectrum of the first of these compounds, the $[M - H_2O]^+$ fragment has maximum intensity, which is probably the result of ring closure between the $C_{(2')}$ atom of the ethylene radical and the $C_{(9)}$ carbon atom of the azafluorene ring to form a cyclopropane ring.

The presence of a carbamoyl functional group in compound XXII gives rise to characteristic $[M - C_6H_5N{=}C{=}O]^+$ and $C_6H_5N{=}C{=}O^+$ ions at 239 and 119, respectively. Decomposition of compounds XXIII and XXIV, which contain β-cyanoethyl substituents, is characterized by elimination of a CH_2CN radical; in compound XXV, with a carboethoxy group in position 9, loss of an OH group is observed, which is typical of aromatic acids [13]. This latter observation may be rationalized in terms of cyclization of the carbon atom of the carboxy group at the pyridine nitrogen atom which is located in the 1-position relative to the azafluorene ring.

Dissociative ionization of 9-amino-4-azafluorenes and $C_{(9)}$-alkyl(dialkyl, spiro)-1- and 4-azafluorenes has thus been shown to occur via cleavage of the $C_{(9)}$–R bond and also by cleavage of bonds within the substituent groups, which makes it possible to determine the structures of the radical groups located in the 9-position relative to the azafluorene ring, to identify isomeric 1- and 4-azafluorenes, and also to differentiate 9-mono- and 9,9-disubstituted compounds in this series.

EXPERIMENTAL

Mass spectra of compounds I-XXV were obtained on an MX-1303 spectrometer, which was equipped with a system for direct introduction of the sample to the ion source at an ionizing energy of 70 eV and at temperatures of 60-150°C. The synthesis of these compounds has been described previously [1-4]. Compound purity and homogeneity was monitored by TLC, PMR, and mass spectrometry. Mass spectra of deuteroanalogs II, VII, and XVI were measured under conditions of deuterium exchange between vapors of precursor compounds I, VI, and XV and CH_3OD vapor directly in the ionization chamber of the spectrometer. The exact mass of the 181 ion in the mass spectrum of compound I was measured on a Varian MAT-311A spectrometer.

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SYNTHESIS OF AROMATIC PYRAZOLO[4,5-b]PYRIDINE DERIVATIVES

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Cyclocondensation of chalcones with 5-amino-3-methyl-1-phenylpyrazole leads to the formation of 2,4-diaryl-5-methyl-7-phenyl-3,4-dihydropyrazolo-[4,5-b]pyridines, which undergo aromatization upon treatment with N-bromosuccinimide.

Condensation of aminopyrazoles with β-dicarbonyl compounds represents a known method for the synthesis of pyrazolo[4,5-b]pyridines [1]. Partial hydrogenation reactions of these bicyclic derivatives have not been investigated however.

Our goal in the present paper was to study the condensation of 5-amino-3-methyl-1-phenylpyrazole (I) with chalcones (IIa-k) as a method for the synthesis of dihydropyrazolopyridine derivatives. We have found that reflux of equimolar amounts of compound I and IIa-k in DMF for 1 h leads to the formation of 2,4-diaryl-5-methyl-7-phenyl-3,4-dihydropyrazolo[4,5-b]-pyridines (IIIa-k, Table 1). If the reaction mixtures are subjected to further reflux, oxidation products IVa-e, g-k are formed; these may be separated from IIIa-e, g-k by chromatography. Compounds IVa-e, g-k (Table 2) can be obtained in excellent yield by treatment of the dihydro derivatives IIIa-e, g-k with N-bromosuccinimide. Compound IIIf is an exception. It does not undergo oxidation with N-bromosuccinimide, but can be converted to the pyrazolopyridine derivative IVf via the dibromide VIf.

Especially noteworthy is the reaction of benzylideneacetone VIII with amine (I); in contrast to the reactions of chalcones, the pyrazolopyridine IVℓ was formed directly, and the intermediate dihydroderivative IIIℓ could not be isolated even under an inert atmosphere.

Independent experiments revealed (see Scheme) that pyrazolo[4,5-b]pyridine derivatives IV could also be obtained in reactions of amine I with dibenzoylmethane V in acetic acid and with α,β-dibromides VIa, f and a chalcone α-epoxide VII; the reaction conditions were the same as those used in reactions with the chalcones themselves. The highest yields are obtained in reactions of the dibromides VIa, f; this represents a very convenient method for the direct synthesis of heterocycles IV.

The formation of dihydropyrazolo[4,5-b]pyridine derivatives (IIIa-k) and their oxidation products IVa-k were confirmed by elemental analysis and spectroscopic characterization.

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