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POLYMETHYL-SUBSTITUTED 2-AZAFLUORENES AND SYNTHESIS OF AZAFLUORANTHENE DERIVATIVES FROM THEM

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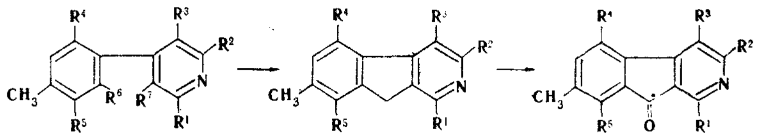
It was established that polymethyl-substituted 2-azafluorenes obtained by catalytic dehydrocyclization of pyridine- and benzene-ring-substituted γ-arylpyridines have different structures depending on the position of the methyl groups in the starting compound and which methyl group participates in the cyclization reaction. The 1,4,7-trimethyl-2-azafluorene synthesized by this method was used for the preparation of new condensed heterocyclic systems of the 3-azafluoranthene and cyclohexano-8-azafluoranthene type.

2-Azafluorenes were obtained by the method described in [1] by dehydrocyclization of γ-arylpyridines containing a methyl group in the β position of the pyridine ring. In the case of β-methyl-γ-phenylpyridine this reaction proceeds unambiguously to give 2-azafluorene. We have demonstrated in the present research that dehydrocyclization of the analogous pyridine bases with one or several methyl groups in the benzene ring may proceed with the participation of different methyl groups.

We studied the compounds formed by dehydrocyclization of the following pyridine bases on a K-16 catalyst at 560-580°C: 2,5-dimethyl-4-(3,4-dimethylphenyl)- (I), 2,5-dimethyl-4-(2,4,5-trimethylphenyl)- (II), and 2,5-dimethyl-4-(2,4,6-trimethylphenyl)pyridine (III), as well as 2,5-dimethyl-4-(2,4-dimethylphenyl)pyridine (IV), the dehydrocyclization of which was described in [2]. The polymethyl-substituted 2-azafluorenes were isolated in up to 20% yields.



I-IV V-VIII IX-XII

I $R^1=R^3=R^4=R^6=H$, $R^2=R^5=R^7=CH_3$; II $R^1=R^3=R^6=H$, $R^2=R^4=R^5=R^7=CH_3$; III $R^1=R^3=R^5=H$, $R^2=R^4=R^6=R^7=CH_3$; IV $R^2=R^4=R^5=R^7=H$, $R^1=R^3=R^6=CH_3$; V, IX $R^1=R^3=R^4=H$, $R^2=R^5=CH_3$; VI, X $R^1=R^3=H$, $R^2=R^4=R^5=CH_3$; VII, XI $R^1=R^3=R^5=H$, $R^2=R^4=CH_3$; VIII, XII $R^2=R^4=R^5=H$, $R^1=R^3=CH_3$

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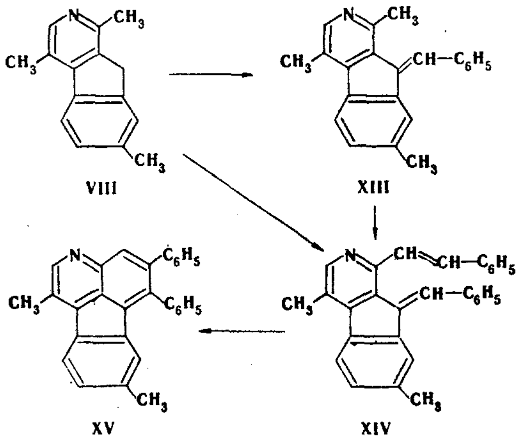
TABLE 1. Characteristics of V-VII

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %	Picrate			
		C	H	N		C	H	N		mp, °C	N found %	empirical formula	N calc., %
V	128—129,5	86,0	7,5	6,9	$C_{15}H_{15}N$	86,1	7,2	6,7	20,0	193—195	12,5	$C_{21}H_{18}N_4O_7$	12,8
VI	155—157	85,9	7,7	6,3	$C_{16}H_{17}N$	86,1	7,6	6,3	17,8	214—216	12,2	$C_{22}H_{20}N_4O_7$	12,1
VII	113—114	85.9	7,4	6,4	$C_{15}H_{15}N$	86,1	7,2	6,7	23,4	231—233	12,8	$C_{21}H_{18}N_4O_7$	12,8
VIII	100—101,5	85.9	7,4	6,4	$C_{15}H_{15}N$	86,1	7,2	6,7	15,4	207—209	13,1	$C_{21}H_{18}N_4O_7$	12,8
IX	146—147	80.5	5,6	6,3	$C_{15}H_{13}NO$	80,7	5,8	6,3	46.7	229—230	12.1	$C_{21}H_{16}N_4O_8$	12,4
X	149—151	80,8	6,2	5,7	$C_{16}H_{15}NO$	81,1	6,3	5,9	55,0	219—221	12.2	$C_{22}H_{18}N_4O_8$	12,0
XI	195—197	80,7	6.1	6,3	$C_{15}H_{13}NO$	80,7	5,8	6,3	57,0	265—267	12,0	$C_{21}H_{16}N_4O_8$	12,4
XII	112—114	80.9	5,9	6.3	$C_{15}H_{13}NO$	80,7	5,8	6,3	59.5	222—224	12,1	$C_{21}H_{16}N_4O_8$	12,4

The formation of two azafluorenes — 3,6,7-trimethyl-2-azafluorene and 3,7,8-trimethyl-2-azafluorene (V) — is possible in the dehydrocyclization of base I. Azafluorene structure V was assigned to the isolated compound on the basis of the fact that its PMR spectrum (Table 2) contains signals of two ortho protons, which indicates that the methyl groups are attached to the C_7 and C_8 atoms. 3,5,7-Tetramethyl-2-azafluorene (VI) is formed by dehydrocyclization of γ-arylpyridine II. The dehydrocyclization of 2,5-dimethyl-4-mesitylpyridine (III) proceeds with splitting out of one of the adjacent methyl groups (R^6 or R^7), as a result of which 3,5,7-trimethyl-2-azafluorene (VII) is formed.

On the basis of the PMR spectral data (Table 2) it was concluded that the azafluorene formed in the dehydrocyclization of pyridine base IV has a 1,4,7-trimethyl-2-azafluorene structure (VIII) rather than the 3,5,7-trimethyl-2-azafluorene structure indicated in [2]. In this case dehydrocyclization evidently takes place through the o-methyl group of the aryl ring and the hydrogen atom in the β position of the pyridine ring.

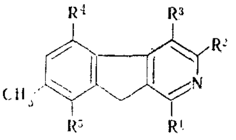


Azafluorenones IX-XII were obtained by oxidation of azafluorenes V-VIII.

1,4,7-Trimethyl-9-benzylidene-2-azafluorene (XIII) was obtained in 40% yield by condensation of 1,4,7-trimethyl-2-azafluorene (VIII) with benzaldehyde in the presence of potassium ethoxide. Prolonged heating (at 170-180°) of XIII with benzaldehyde gave 4,7-dimethyl-1-styryl-9-benzylidene-2-azafluorene (XIV), which is also obtained directly from azafluorene VIII by prolonged refluxing with benzaldehyde.

A crystalline yellow substance with mp 182-184°, the individuality of which was confirmed by thin-layer chromatography (TLC), was isolated in ~40% yields in both syntheses of XIV. On the basis of the spectral and analytical data it can be assumed that this compound is 1,8-dimethyl-5,6-diphenyl-3-azafluoranthene (XV). Two singlets at δ 2.13 (3H) and 2.62 ppm (3H) due to two methyl groups, a singlet at δ 8.57 ppm (1H) related to the α proton of the pyridine ring, and a singlet at δ 7.83 ppm due to 4-H are observed in its PMR spectrum. The absence of signals at δ 3-5 ppm indicates substitution of the azafluorene system at the C_9 atom. The integral intensity of the protons in the aromatic region at 6.53-8.57 ppm (15H) also corresponds to the XV structure. The UV spectra of XV and fluoranthene are close. The mass spectrum of XV contains an intense molecular ion peak with m/e 383 (the principal peak) and a large number of peaks of doubly charged ions, the formation of which is characteristic for polynuclear N-heteroaromatic compounds. The polynuclear heterocyclic system of substi-

TABLE 2. Data from the PMR Spectra of Azafluorenes V-VIII

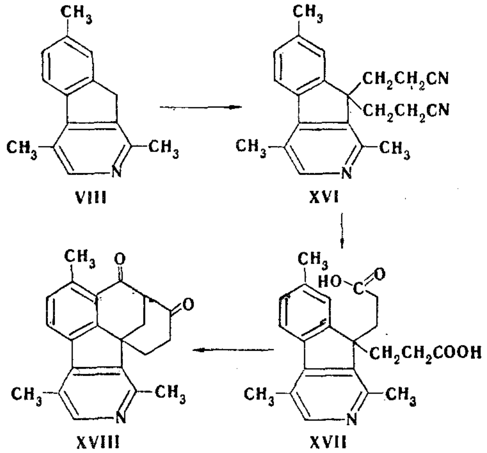


Compound	Chemical shifts, δ, ppm, J, Hz							
	H-1	H-3	H-4	H-5	H-6	H-8	CH_3 group	CH_2 group
V $R^2=R^5=CH_3$ $R^1=R^3=R^4=H$	8,4 1H; s		7,24 1H; s	7,36 1H; d; 8	7,01 1H; d; 8		2,50; 3H; s 2,16; 3H; s 2,26; 3H; s	3,51; 2H; s
VI $R^2=R^4=R^5=CH_3$ $R^1=R^3=H$	8,36 1H; s		7,21 1H; s		6,72 1H; s	—	2,53; 3H; s 2,43; 3H; s 2,21; 3H; s 2,06; 3H; s	3,36; 2H; s
VII $R^2=R^4=CH_3$ $R^1=R^3=R^5=H$	8,36 1H; s		7,20 1H; s	—	6,90 1H; s	6,70 1H; s	2,50; 3H; s 2,40; 3H; s 2,25; 3H; s	3,41; 2H; s
VIII $R^1=R^3=CH_3$ $R^2=R^4=R^5=H$	—	8,16 1H; s		7,73 1H; d; 8,0	7,13 1H; d 8,0	7,31 1H; s	2,50; 6H; s 2,36; 3H; s	3,65; 2H; s

*Broadening of the signals is observed.

tuted 3-azafluoranthene is evidently formed as a result of cyclization of the intermediates — products of condensation of azafluorene VIII with benzaldehyde.

Azafluorene VIII was also used in the synthesis of the condensed system of partially hydrogenated 8-azafluoranthene with cyclohexane.



1,4,7-Trimethyl-9,9-bis(β-cyanoethyl)-2-azafluorene (XVI), which is formed in the condensation of azafluorene VIII with acrylonitrile in the presence of the ethoxytrimethylphenylammonium ion (the Rodionov catalyst), is hydrolyzed to dibasic acid XVII, which undergoes intramolecular cyclodehydration under the influence of polyphosphoric acid (PPA) at 150°; yellow crystals of 3,7,10-trimethyl-4,13-dioxo-8-aza-4,5,6,6a-tetrahydro-5,6a-propanofluoranthene (XVIII), with mp 144-146°, were isolated in 11% yield. The UV and IR spectra of this compound are similar to the spectra of the first representative of compounds of this type obtained in our laboratory [3].

EXPERIMENTAL

The IR spectra of the compounds were measured with a UR-20 spectrometer. The UV spectra of ethanol solutions of the compounds were recorded with an EPS-3 (Hitachi) spectrophotometer. The PMR spectra of $CDCl_3$ solutions of the compounds were obtained with Varian HA-100D and T-60 spectrometers with hexamethyldisiloxane as the internal standard. The molecular weights were determined with an MKh-1303 mass spectrometer.

3,7,8-Trimethyl-2-azafluorene (V) and 3,7,8-Trimethyl-2-azafluorenone (IX). A solution of 30.8 g (0.146 mole) of pyridine base I in 60 ml of benzene was passed at a constant rate in the course of 3.5 h over 100 ml of K-16 catalyst. The temperature in the catalyst zone was 560-580°. A total of 8 liters of gas was collected at 24° and 756 mm. Fractionation of the catalyzate yielded 20.8 g of starting I [bp 135-138° (1 mm)] and 5.9 g of azafluorene V. Azafluorenes VI - VIII were similarly obtained.

A 1-g (6 mmole) sample of potassium permanganate was added gradually at 20° to a solution of 0.5 g (2.4 mmole) of azafluorene in 50 ml of acetone, and the mixture was stirred for 5 h. The precipitated manganese dioxide was removed by filtration and washed with acetone. The acetone was removed by filtration, and the residue (0.52 g) was crystallized from ligroin to give 0.25 g of azafluorenone IX. Azafluorenones X-XII were similarly obtained.

The characteristics ov V-XII are presented in Table 1.

IR spectra of the azafluorenones: IX 1715 (C=O), X 1715 (C=O), XI 1716 (C=O), and XII 1710 cm^{-1} (C=O).

1,4,7-Trimethyl-9-benzylidene-2-azafluorene (XIII), 4,7-Dimethyl-1-styryl-9-benzylidene-2-azafluorene (XIV), and 1,8-Dimethyl-5,6-diphenyl-3-azafluoranthene (XV). A) A total of 25 ml of a 10% solution of potassium ethoxide was added to a solution of 3 g (14.3 mmole) of azafluorene VIII and 3 g (27 mmole) of benzaldehyde in 85 ml of ethanol, and the mixture was refluxed for 6 h. Water (200 ml) was added, and the alcohol was removed by distillation, and the benzaldehyde was removed by steam distillation. The residue from the ether extract (4.3 g) was purified with a chromatographic column (activity II Al_2O_3, elution with ether) to give 1.8 g (42%) of yellow crystals of XIII with mp 121-123° (from ligroin) and R_f = 0.82 (with the same system). IR spectrum: 1638 cm^{-1} (C=C). Found: C 88.7; H 6.1; N 4.5%. $C_{22}H_{19}N$. Calculated: C 88.9; H 6.4; N 4.7%. The picrate had mp 254-255° (from alcohol). Found: N 10.3%. $C_{22}H_{19}N \cdot C_6H_3N_3O_7$. Calculated: N 10.6%.

B) A mixture of 4 g (19.1 mmole) of azafluorene VIII and 8 g (75 mmole) of benzaldehyde was heated at 170-180° for 20 h, after which the excess benzaldehyde was removed by steam distillation, 20 ml of water was added to the residue, and the reaction products were extracted with ether. The residue (6.2 g) from the extract was separated with a chromatographic column (h = 70 cm, d = 1.7 cm, activity II Al_2O_3, ether) to give, initially, 2.4 g (40%) of light-yellow crystals of XIV with mp 147-149° (from ligroin) and R_f 0.76 [activity II Al_2O_3, ethyl acetate–hexane (1:3)]. PMR spectrum, δ: 2.33 and 2.53 (3H, 3H, s, 4-CH_3, 7-CH_3) and 6.87 (1H, s, 8-H). Found: C 90.1; H 6.2; N 3.3.6%; 385. $C_{29}H_{23}N$. Calculated: C 90.4; H 6.0; N 3.6%; M 385. The picrate has mp 250-252° (from alcohol). Found: N 9.1%. $C_{29}H_{23}N \cdot C_6H_3N_3O_7$. Calculated: N 9.0%.

Subsequent elution gave 2.5 g (41%) of yellow crystals of XV with mp 182-184° (from ligroin) and R_f 0.53 (with the same system). The UV spectrum of XV is similar to the UV spectrum of fluoranthene [4]. Mass spectrum, m/e: 383 (M^+), 368 (M-CH_3), 353 (M-CH_3, -CH_3). Found: C 90.5; H 5.5; N 4.0%. $C_{29}H_{21}N$. Calculated: C 90.7; H 5.5; N 3.7%. The picrate has mp 214-215° (from alcohol). Found: N 9.1%. $C_{29}H_{21}N \cdot C_6H_3N_3O_7$. Calculated: N 9.1%. A total of 0.72 g of starting azafluorene VIII was isolated at the end of the chromatographic separation.

C) A mixture of 0.9 g (3 mmole) of XIII and 2 g (19 mmole) of benzaldehyde was heated at 170-180° for 20 h. Similar workup of the mixture, separation of the reaction products, and crystallization from ligroin gave 0.12 g (10%) of XIV with mp 147-149°.

1,4,7-Trimethyl-9,9-bis(β-cyanoethyl)-2-azafluorene (XVI). A 1-ml sample of a freshly prepared Rodionov catalyst and 10 g (0.2 mole) of acrylonitrile were added to a solution of 6 g (29 mmole) of azafluorene VIII in 100 ml of benzene, and the mixture was stirred at 50° for 2 h, after which 50 ml of water was added. The benzene solution was washed with water and evaporated, and the residue (8.24 g) was crystallized from alcohol to give 6 g (66%) of XVI with mp 162.5-164°. IR spectrum: 2232 cm^{-1} (C≡N). Found: C 79.8; H 6.9; N 13.2%. $C_{21}H_{21}N_3$. Calculated: C 80.0; H 6.7; N 13.3%. The picrate had mp 241-243° (from alcohol). Found: N 15.8%. $C_{21}H_{21}N_3 \cdot C_6H_3N_3O_7$. Calculated: N 15.4%.

1,4,7-Trimethyl-9,9-bis(β-carboxyethyl)-2-azafluorene (XVII). A mixture of 4.5 g (0.014 mole) of XVI, 180 ml of 20% potassium hydroxide, and 50 ml of alcohol was refluxed for 18 h, after which the alcohol was removed by distillation, and the residual solution was filtered and acidified to pH 1 with 70% sulfuric acid. The resulting precipitate was washed with water until the turbidity of a barium chloride test solution vanished. Workup gave 3 g (60%) of XVII with mp 217-218° (from alcohol). IR spectrum: 2520 (bonded O-H) and 1732 cm^{-1} (C=O). Found: N 3.6%. $C_{21}H_{23}NO_4$. Calculated: 3.9%.

3,7,10-Trimethyl-4,13-dioxo-8-aza-4,5,6,6a-tetrahydro-5,6a-propanofluoranthene (XVIII). A mixture of 3 g (8.5 mmole) of dibasic acid XVII and 140 g of PPA was heated with stirring at 150-160° for 2.5 h, after which 300 ml of water was added, and the mixture was neutralized with sodium carbonate. The reaction products were extracted with chloroform, and the extract was worked up to give 0.3 g (11%) of light-yellow crystals of XVIII with mp 144-146° [from benzene-hexane (2:1.5)]. IR spectrum: 1683 and 1727 cm^{-1} (arylalkyl and dialkyl C=O, respectively). PMR spectrum, δ: 8.00 (1H, 1-H), 7.36 (1H, J = 8.0 Hz, 2-H), 8.3 (1H, s, 10-H), 3.7 (1H, m, 4a-H), 2.73 (3H, s, CH_3), and 2.63 (3H, s, CH_3). Found: C 78.1; H 7.7; N 4.2%; M 317. $C_{21}H_{19}NO_2$. Calculated: C 79.5; H 6.0; N 4.4%; M 317. The picrate had mp 178-180° (from alcohol). Found: N 10.0%. $C_{21}H_{19}NO_2 \cdot C_6H_3N_3O_7$. Calculated: N 10.2%.

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PREPARATION OF 3-ARYL-2-QUINOXALONES

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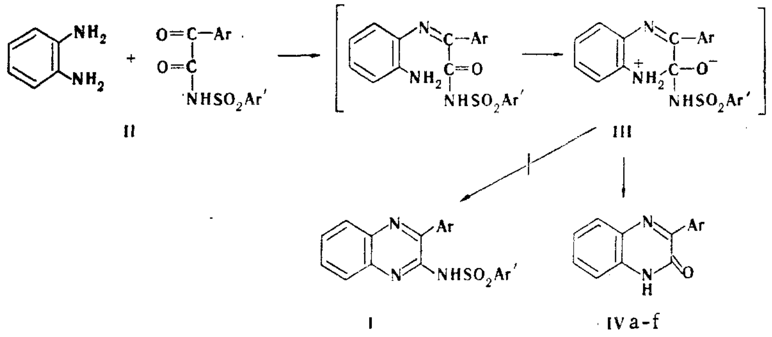
UDC 547.863.16

Arenesulfonamides are split out in the reaction of N-(arylsulfonyl)arylglyoxylamides with o-phenylenediamine to give 3-aryl-2-quinoxalones.

Quinoxaline derivatives that have bacteriostatic action are known [1]. We made an attempt to obtain arenesulfamido derivatives (I) of quinoxaline by condensation of o-phenylenediamine with N-(arylsulfonyl)arylglyoxylamides (II). Amides II were synthesized by arenesulfonamidation of arylglyoxals [2]. However, regradless of the nature of the arylsulfonyl group, 3-aryl-2-quinoxalones (IVa-f) rather than I are formed, and arenesulfonamides are split out.



$Ar' = C_6H_5$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $3\text{-}NO_2C_6H_4$, $4\text{-}CH_3C_6H_4$; Ar see Table 1

The first act in the reaction is probably formation of a C=N bond between the nitrogen atom of one amino group of o-phenylenediamine and the carbonyl carbon atom of the aroyl residue of II. Nucleophilic attack on the free amino group by the carbon atom of a second carbonyl group evidently leads to the formation of dipolar ion III. Its stabilization may occur via two pathways: either by splitting out of water to give an arenesulfonamidoquinoxaline

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