5- (II), 7- (IV), and 8-Nitro-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthrone (V). A 17-ml sample of a nitrating mixture consisting of 6 ml of nitric acid (sp. gr. 1.5 g/cm^3) and 11 ml of sulfuric acid (sp. gr. 1.84 g/cm^3) was added at 20°C in the course of 50 min to a solution of 3 g (12.5 mmole) of 10,10-dimethyl-10-sila-2-azaanthrone in 25 ml of concentrated H_2SO_4. After 1 h, the reaction mixture was poured over ice, and the aqueous mixture was made alkaline with ammonia. The reaction products were extracted with chloroform, the extract was dried with magnesium sulfate, the chloroform was removed, and the residue (3 g) was chromatographed with a column (H = 34 cm, d = 3.5 cm) packed with silica gel. Elution with ethyl acetate–heptane (1:4) gave 0.7 g (20%) of II with mp 215-217°C (from ethyl acetate). Found, %: C 59.2, H 4.47, N 9.6. $C_{14}H_{12}N_2O_3Si$. Calculated, %: C 59.1, H 4.2, N 9.8.

After this, we used the same solvents to successively elute 0.2 g (6%) of IV [mp 230-232°C (from ethyl acetate); found, %: C 59.2, H 4.4, N 9.6. $C_{14}H_{12}N_2O_3Si$. Calculated, %: C 59.1, H 4.2, N 9.8]; 0.75 g of a mixture of IV and V, and 0.17 g (4.8%) of V [mp 208-210°C (from heptane–ethyl acetate); found, %: C 59.2, H 4.5, N 9.6. $C_{14}H_{12}N_2O_3Si$. Calculated, %: C 59.1, H 4.2, N 9.8].

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SYNTHESIS OF SPIRO COMPOUNDS WITH 3-METHYL-2-AZAFLUORENE, INDAN, PYRAZOLINE, AND CYCLOPROPANE FRAGMENTS ON THE BASIS OF 3-METHYL-9-PHENYLETHYNYL-2-AZAFLUOREN-9-OL

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3-Methyl-9-phenylethynyl-2-azafluoren-9-ol, 3-methyl-9-phenacylidene-2-azafluorene, and spiro compounds with 2-azafluorene, indan, pyrazoline, and cyclopropane fragments were obtained starting from 3-methyl-2-azafluorenone by successive transformations. Information regarding the spatial structures of the synthesized compounds was obtained.

Continuing our research on the synthesis and study of the transformations of azafluorene derivatives, we directed our attention to the preparation of 3-methyl-9-phenylethynyl-2-azafluoren-9-ol (II) from the now accessible 3-methyl-2-azafluorenone (I). We used the Iotsich complex in the reaction.

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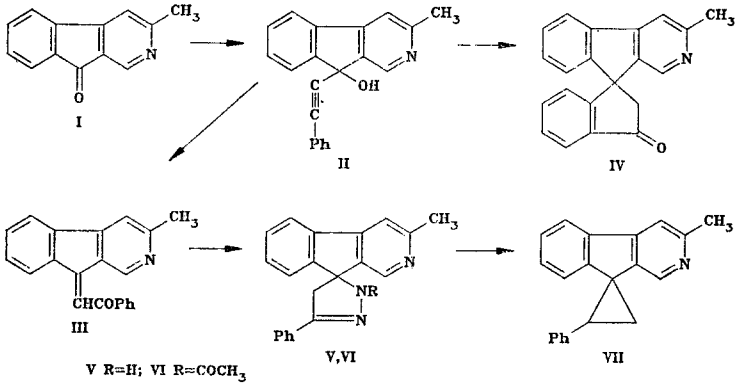
Like its analog 9-phenylethynyl-4-azafluoren-9-ol [1], acetylenic alcohol II is converted, under the influence of 70% sulfuric acid, to the methylidyne derivative, viz., 3-methyl-9-phenacylidene-2-azafluorene (III), which is produced in the form of a mixture of Z and E isomers, which we were unable to separate. The existence and quantitative ratio of the isomers was proved by PMR spectroscopy. Two signals at δ = 9.17 and 9.32 ppm (J = 1 Hz), which are related to the 1-H protons of the pyridine ring of the isomers of III, are present in the weak-field part of the PMR spectrum. In analogy with the corresponding 4-azafluorene derivatives [1], the signal at weaker field can be assigned to the Z isomer, for which the 1-H proton is deshielded due to the effect of the magnetically anisotropic benzoyl group. In conformity with the integral intensities of these signals, the ratio of the Z and E isomers is 1:3, whereas it is 2:1 in the case of the analogous 4-azafluorene derivative.

From the mixture of isomers of ketone III we obtained a mixture of oximes, the weak-field part of the PMR spectrum of which contains four signals at 11.6, 11.68, 11.80, and 11.97 ppm (with an intensity ratio of 3:3:1:1). These signals can be assigned to the protons of the hydroxy groups of the oximes of the syn and anti forms of the E and Z isomers of unsaturated ketone III. The 1-H signals of the syn and anti forms of the E isomer are located at 9.3 ppm. The remaining protons form overlapped multiplets at 6.8-8.5 ppm. A group of broad, intense, overlapped bands with chief maxima at 3500, 3460, 3380, 3230, and 2700 cm^{-1}, which are related to associated hydroxy groups, is observed in the IR spectrum of the mixture of oximes. The absorption band at 1620 cm^{-1}, which is shifted to the low-frequency side as a consequence of conjugation with the aromatic fragments of the molecule [2], corresponds to the stretching vibrations of the C=N bond.

When we treated alcohol II with sulfuric acid (monohydrate) at a higher temperature, we isolated[3'-oxospiro 2-azafluorene-9,1'-indan] (IV) from the reaction products in 25% yield. The formation of the spiro derivative is accompanied by characteristic changes in the PMR spectrum: a signal of a CH_2 group (a spectrum of the AB type: δ_A = 3.12 ppm, δ_B = 3.22 ppm, and J_{AB} = 18.0 Hz) appears, and the signals of the 8-H and 1-H protons are shifted to strong field as compared with 3-methyl-2-azafluorene [3]. As we have demonstrated for a similar example [1], the formation of spiro compound IV proceeds via intramolecular electrophilic cyclization of phenacylidene derivative III.



By condensation of α,β-unsaturated ketone III with hydrazine hydrate we obtained 3-methyl-3'-phenylspiro[2-azafluorene-9,5'-pyrazol-2'-ine] (V) in 68% yield and used it to prepare N-acetyl derivative VI. By heating cyclic hydrazone V with potassium hydroxide we converted it to 3-methyl-2-phenylspiro(2-azafluorene-9,1'-cyclopropane) (VII), which was obtained in the form of a mixture of two isomers that differ with respect to the orientation of the phenyl substituent in the cyclopropane ring relative to the nitrogen-containing ring of the azafluorene fragment. According to the PMR spectral data, the ratio of the Z and E isomers was 3:2.

EXPERIMENTAL

The PMR spectra of the compounds (II and III in d_6-DMSO, IV in d_6-DMSO + C_6D_6, and the remaining compounds in $CDCl_3$) were investigated with a Bruker WP-80 spectrometer (80 MHz) with tetramethylsilane (TMS) as the internal standard. The analysis of the multiplets was made within the first-order approximation. The IR spectra of KBr pellets of the compounds were measured with a UR-20 spectrometer. The mass spectra were obtained with an MKh-1303 mass spectrometer (70 eV) with direct introduction of the samples into the ion source.

3-Methyl-9-phenylethynyl-2-azafluoren-9-ol (II). The Iotsich complex was obtained from 1.6 g (66 mmole) of magnesium, 9.32 g (66 mmole) of methyl iodide, and 18 g (180 mmole) of phenylacetylene in 30 ml of absolute ether (activation by iodine). A solution of 1.5 g (7.7 mmole) of azafluorenone I in 40 ml of absolute benzene was then added gradually with heating, and the mixture was refluxed for 3 h. Water (50 ml) and 130 ml of a saturated solution of ammonium chloride solution were then added, and the resulting precipitate was removed by filtration and washed several times successively with water and ether until the yellow coloration vanished. This procedure gave 2.4 g (81%) of alcohol II with mp 163-165°C (from ethanol). PMR spectrum: 8.75 (1H, d, J = 1 Hz, 1-H), 7.70 (1H, broad s, 4-H), 7.4-7.6 (2H, m, 6-H and 7-H), 7.7-8.0 (2H, m, 5-H and 8-H), 7.38 (5H, narrow m, C_6H_5), 6.86 (1H, s, OH), and 2.56 ppm (3H, broad s, CH_3). IR spectrum: 3200 (OH) and 2230 cm^{-1} (C≡C). Found, %: C 84.8, H 4.9, N 4.5, M^+ 297. $C_{21}H_{15}NO$. Calculated, %: C 84.8, H 5.1, N 4.7, M 297.

3-Methyl-9-phenacylidene-2-azafluorene (III). A solution of 0.2 g (0.7 mmole) of II in 20 ml of 70% sulfuric acid was heated at 40°C for 10-15 min, after which it was cooled and neutralized with ammonia. The reaction products were extracted with ether, and the extract was dried with magnesium sulfate. The ether was removed by distillation to give 0.16 g of an oily brown residue. The residue was recrystallized from heptane to give 0.1 g (50%) of a mixture of isomers of III with mp 97-100°C. IR spectrum: 1663 cm^{-1} (C=O). Found, %: C 84.7, H 4.6, N 4.9, M^+ 297. $C_{21}H_{15}NO$. Calculated, %: C 84.8, H 5.1, N 4.7, M 297.

Mixture of Isomeric Oximes of III. This mixture was obtained in 74% yield and had mp 189-193°C (from ethyl acetate). Found, %: N 8.9. $C_{21}H_{16}N_2O$. Calculated, %: N 9.0.

3-Methyl-3'-oxospiro(2-azafluorene-9,1'-indan) (IV). A 1.5-g (5 mmole) sample of alcohol II was heated in 30 ml of sulfuric acid (monohydrate) at 80-90°C. The red reaction mixture initially turned brown. It was then cooled and neutralized with ammonia, the reaction products were extracted with ether, and the extract was dried with magnesium sulfate. The residue (0.79 g) from the ether extract was passed through a chromatographic column packed with aluminum oxide by successive elution with ether and ethanol to give 0.25 g (25%) of spiro compound IV in the form of colorless crystals with mp 218-219°C [from heptane–ethyl acetate (2:1)]. IR spectrum: 1720 cm^{-1} (C=O). Found, %: C 84.8, H 5.1, N 4.6, M^+ 297. $C_{21}H_{15}NO$. Calculated, %: C 84.8, H 5.1, N 4.7, M 297.

Oxime of Ketone IV. This compound was obtained inpyridine in 76% yield and had mp 259-259.5°C (from ethanol). PMR spectrum: 11.6 ppm (OH). IR spectrum: 3480, 3180, 3060, and 2700 cm^{-1} (associated OH). Foudn: N 8.8%; M^+ 312. $C_{21}H_{16}N_2O$. Calculated: N 9.0%; M 312.

3-Methyl-3'-phenylspiro(2-azafluorene-9,5'-pyrazol-2'ine) (V). A yellowish solution of 0.14 g (0.45 mmole) of the mixture of isomers of III and 67.5 mg (1.34 mmole) of hydrazine hydrate in 20 ml of ethanol was refluxed for 10 min, during which the mixture became colorless. It was then cooled, and the resulting precipitate was removed by filtration and washed with 10 ml of ether to give 0.1 g (68%) of spiro compound V with mp 217-218.5°C. PMR spectrum: 8.70 (1H, broad s, 1-H), 6.05 (1H, broad s, NH), 3.62 (2H, s, CH_2), and 2.62 ppm (3H, s, CH_3); the remaining protons formed an overlapped multiplet at 7.3-7.8 ppm (10H). IR spectrum: 3260 cm^{-1} (NH). Found: C 81.4; H 5.7; N 13.5%; M^+ 311. $C_{21}H_{17}N_3$. Calculated: C 81.0; H 5.5; N 13.5%; M 311.

3-Methyl-1'-acetyl-3'-phenylspiro(2-azafluorene-9,5'-pyrazol-2'-ine) (VI). A 0.4-g sample of V was heated in 10 ml of acetic anhydride at 90°C for 15 min, after which the mixture was cooled, and the gold-colored crystals of acetyl derivative V were crystallized from heptane–ethyl acetate (2:1) to give 0.42 g (93.3%) of VI with mp 172-174°C. PMR spectrum: 8.52 (1H, d, J = 0.8 Hz, 1-H), 2.62 (3H, s, 3-CH_3), 2.31 (3H, s, $COCH_3$); CH_2: spectrum of the AB type with δ_A = 3.72 ppm and δ_B = 3.84 ppm (J_{AB} = 18.2 Hz); the remaining protons were located at 7.2-7.8 ppm (10H, m). IR spectrum: 1680 cm^{-1} (NCO). Found, %: N 11.7, M^+ 353. $C_{23}H_{19}N_3O$. Calculated, %: N 11.8, M 353.

3-Methyl-2'-phenylspiro(2-azafluorene-9,1'-cyclopropane) (VII). A 0.2-g (0.6 mmole) sample of spiro compound V was heated with 1.5 g (14.8 mmole) of potassium hydroxide at 220 °C for 20 min, after which the mixture was cooled, treated with 25 ml of water, and extracted with ether. The extract was dried with magnesium sulfate, the ether was removed, and the residue was crystallized from heptane to give 39 mg (22%) of a mixture of two isomers of VII in the form of colorless crystals with mp 125-127°C. PMR spectrum: Z isomer: 7.9 (1H, broad s, 1-H) and 2.56 ppm (3H, s, 3-CH_3); E isomer: 6.16 (1H, d, J = 7.8 Hz, 8-H), 8.4 (1H, broad s, 1-H), and 2.68 ppm (3H, s, 3-CH_3). Found, %: N 4.7, M^+ 283. $C_{20}H_{17}N$. Calculated, %: N 4.9, M 283.

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