and 10 ml of carbon tetrachloride were used for the reaction. The reaction and the isolation of the products were carried out as in the preceding experiment to give 0.14 g (10%) of dichloride VI as colorless crystals with mp 139-140°C (from heptane) and R_f 0.6. Found: Cl 28.1; N 5.3%; M⁺235. C₁₂H₇Cl₂N. Calculated: Cl 29.4; N 6.0%; M 235. Spiro compound IVa [0.45 g (28%)] was also obtained and had mp 123-124°C (from heptane) and R_f 0.52. PMR spectrum: 8.06 (m, 5-H), 7.4-7.6 (the signals of the phenyl substituent covered up the signals of the 6-H, 7-H, and 8-H protons), and 4.97 ppm (1H, s, 3'-H). The protons of the pyridine ring, which give an ABC spectrum, were calculated by means of the ITRCAL method and had the following values: 6.77 (1-H), 6.81 (2-H), and 8.48 ppm (3-H); $J_{1,2} = 7.8$, $J_{1,3} = 1.2$, and $J_{2,3} = 5.7$ Hz. Found: C 84.4; H 4.8; N 5.2%; M⁺ 271. $C_{1,9}H_{1,3}NO$. Calculated: C 84.2; H 4.9; N 5.2%; M 271. Chromatography ultimately yielded 0.44 g (27.7%) of spiro compound IVb in the form of colorless crystals with mp 163.5-165°C (from heptane) and Rf 0.4. PMR spectrum: 4.95 (1H, s, 3'-H). The protons of the pyridine ring, which give an ABC spectrum, were calculated by means of the ITRCAL method and had the following values: 7.63 (1-H), 7.18 (2-H), and 8.60 ppm (3-H); $J_{1,2} = 7.5$, $J_{1,3} = 1.5$, $J_{2,3} = 5.0$ Hz. The protons of the phenylene ring, which give an ABCD spectrum, were calculated by means of the ITRCAL method and had the following values: 7.98 (5-H), 7.36 (6-H), 7.01 (7-H), and 6.53 ppm (8-H); $J_{5_{6}6} = 7.6$, $J_{5,7} = 1.3, J_{5,8} = 0.7, J_{6,7} = 7.5, J_{6,8} = 1.1, and J_{7,8} = 7.5$ Hz. Found: C 84.3; H 5.1; N 5.2%; M⁺ 271. C₁₉H₁₃NO. Calculated: C 84.2; H 4.9; N 5.2%; M 271. Dimer VIII [0.01 g (0.52%)] was also isolated. Found: M⁺ 330. C₂₄H₁₄N₂. Calculated: M 330.

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N-OXIDES OF 2- AND 4-AZAFLUORENONES AND NITRO DERIVATIVES

OF 2- and 4-AZAFLUORENES

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It was demonstrated by PMR spectroscopy that mixtures of N-oxides of 6- and 7nitro derivatives are formed in the nitration of the N-oxides of 3-methyl-2- and 4-azafluorenes. The products were deoxygenated to give nitro derivatives of 2and 4-azafluorenes. The N-oxides of nitro-substituted azafluorenes were converted to salts of the aci forms by the action of alkali.

Information regarding the N-oxides of azafluorenes is limited to two communications [1, 2]. We obtained N-oxides I and II from the recently accessible 3-methyl-2-aza- and 4-azafluorenes, which are obtained by catalytic dehydrocyclization of, respectively, 2,5-dimethyl-4-phenyl- and 3-methyl-2-phenylpyridines [1, 3]. The N-oxides of 3-methyl-2-aza- (III) and 4-azafluorenone (IV) were obtained in rather high yields in the oxidation of N-oxides I and II with potassium permanganate in the presence of ammonium nitrate.

In the present communication we present the results of experiments on the nitration of N-oxides of azafluorenes and the transformations to nitro derivatives under the influence of bases. In the first case it was necessary to solve the problem of the orientation in the electrophilic substitution of these heterocyclic systems. Since the position of the nitro group and the isomeric composition of the nitration products were determined from the PMR spectra, for comparison we investigated the PMR spectra of the starting N-oxides and the prod-

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Com- pound	Solvent		δ, ppm									I Ho			
		1-H	2-H	3-н	4-H	5-H	6-H	7-н	8-H	9-H	3-CH3	j, 112			
I	CD₃OD	8,9		-	7,88	7,86	7,47	7,45	7,6	4,19	2,55	(56) 8,19, (57) 0,71, (58) 0,49, (67) 6,98, (68) 1,33, (78) 7,49			
II	CD₃OD	7,62	7,31	8,10		8,55	7,41	7,43	7,53	4,0		$\begin{array}{cccccccccccccccccccccccccccccccccccc$			
III	CD₃OD	8,24	 	-	7,59	7,61	7,52	7,35	7,56		2,58				
IV	CDCl ₃	7,45	7,32	8,11	—	8,44	7,54	7,39	7,66		 I 	(12) 7,33, (13) 0,86, (23) 6,60, (56) 7,62, (57) 1,0, (58) 0,58, (67) 7,22, (68) 0,94, (78) 7,46			
v	d ₆ -DMSO	8,48	÷	8,0	8,40	8,66	8,0	8,40	7, 7 8	4,10	2,47	(57) 2,2, (87) 8,5			
VI	d ₆ -DMSO	7,68 ^a	7,48	8,38	—	9,38		8,40	7,94	4,20		$\begin{array}{cccccccc} (12) & 8,0, & (13) & 0,7, \\ (23) & 6,4, & (57) & 2,4, \\ (78) & 8,0 \end{array}$			
		7,66 ^b	7,50	8,40		8,84	8,36		8,54	4,22		$\begin{array}{cccccccc} (12) & 8,0, & (13) & 0,8, \\ (23) & 6,4, & (56) & 8,4, \\ (58) & 0,5, & (68) & 2,0 \end{array}$			
VII	d ₆ -DMSO	8,66		-	7,82	8,18	8,24	—	8,40	4,12	2,6	(56) 8,15, (58) 1,0, (68) 2,2			
VIII	CDCl₃	7,88	7,29		8,63	8,15	8,30	—	8,38	4,3		(12) 7,45, (13) 1,48, (23) 4,72, (56) 8,47, (58) 0,38, (68) 2,70			

TABLE 1. PMR Spectra of the Synthesized Compounds

^aThe 6-nitro derivative. ^DThe 7-nitro derivative. The isomer ratios were estimated from the integral intensities of the 5-H proton in the 6-nitro derivative and the protons of the CH_2 group in the case of V and from the integral intensities of the 5-H and 8-H protons in the case of VI.

ucts of deoxygenation of the nitro-substituted N-oxides (Table 1).



I, III, V $X^1=N \rightarrow O$, $X^2=CH$, $R=CH_3$; II, IV, VI $X^1=CH$, $X^2=N \rightarrow O$, R=H; VII $X^1=N$, $X^2=CH$, $R=CH_3$; VIII $X^1=CH$, $X^2=N$, R=H

The nitration of N-oxide I was carried out with a nitrating mixture at a reduced temperature. According to the PMR spectral data, the isolated high-melting yellow crystals are mixtures of 6- and 7-nitro-3-methyl-2-azafluorenes (V) in a ratio of \sim 2:3 (see Table 1). We were unable to isolate the individual isomers.

The nitration of N-oxide II was carried out similarly. A mixture of N-oxides of 6- and 7-nitro-4-azafluorenes (VI) in a ratio of 8:11 was also obtained in this case.

A mixture of 6- and 7-nitro-3-methyl-2-azafluorenes (VII) was obtained as a result of the successive treatment of the mixture of isomers of the nitro derivatives V with phosphorus tribromide and sodium hydroxide. According to the PMR spectral data, the mixture contained \sim 95% of the 7-nitro isomer. 7-Nitro-4-azafluorene (VIII) was obtained by a similar method from VI.

Solutions of N-oxides V and VI in alcohol are light yellow. The color changes instantaneously to intense blue when a solution of sodium hydroxide is added to them. A similar phenomenon is observed when the quaternary salts of azafluorenes are treated with bases, in which case they are converted to NH-indenopyridines (pseudoazulenes). In the case of the in-

Com-	mn ℃		IR spectrum,	UV spectrum,	R.	Reac- tion	Found, %			Empirical	Calc., %			Yield,
pound	mp, c	MI+	cm-1	λ_{\max} , nm (log ϵ)	~~;	h	с	н	N	formula	с	Н	N	%
п	158—159	183	1245 (N→O)		0,14 ^a		78,5	4,8	7,4	C12H9NO	78,6	4,9	7,7	70
III	198—199	211	1705 (CO), 1290, 1240 (N→O)	220 (4,31), 272 (4,72), 324 (4,02), 338 (3,85), 4,28 (2,76)	0,68 ^b	3	73,8	4,4	6,4	C ₁₃ H ₉ NO ₂	73,9	4,3	6,6	70
IV	248—250	197	1730 (CO), 1285, 1240 (N→O)	230 (4,40), 256 (4,32), 276 (4,41), 430 (2,66)	0,53 ^C	3	73,0	3,3	7,2	$C_{12}H_7NO_2$	73,0	3,6	7,1	77
v	220 (dec.)	242	1525, 1340 (NO ₂), 1260, 1245 (NO)	204 (4,24), 230 (4,10), 300 (4,06), 341 (4,18)		1	64,1	4,2	11,2	C ₁₃ H ₁₀ N ₂ O ₃	64,5	4,1	11,6	83
VI	193— 194	228	1534, 1344 (NO₂), 1274, 1209 (N→O)	216 (4,14), 255 (4,25), 275 (4,14), 310 (4,0), 322 (4,02)	0,51C	1	63,0	3,8	12,0	$C_{12}H_8N_2O_3$	63,2	3,5	12,3	37
VII	200 (dec.)	226	1510, 1330 (NO ₂)	204 (4,38), 244 (4,00), 300 (4,00)	0,65 ^d	3	68,8	4,6	12,0	$C_{13}H_{10}N_2O_2$	69,0	4,4	12,4	74,7
VIII	200-202	212	1530, 1340 (NO ₂)	203 (4,32), 322 (4,35)	_	1,5	-	-	13,0	$C_{12}H_8N_2O_2$	-		13,2	93
IX	400 (dec.)	-	1644 (N=O), 840, 710 (NO)	206 (4,3), 286 (4,3), 326 (4,2), 480 (3,4), 644 (3,3)	-		-	-	9,2	C ₁₃ H ₉ N₂NaO₃ · •C₂H₅OH			9,1	92
X	400 (dec.)	-	1620 (N=O), 734 (N-O)	$ \begin{vmatrix} 210 & (4,24), & 244 \\ (4,32), & 295 & (4,18), \\ 440 & (3,74), & 575 \\ (3,20) \end{vmatrix} $			-		8,2	C ₁₂ H ₇ N ₂ N ₂ O ₃ · · 2C ₂ H₅OH	-		8,2	94

TABLE 2. Characteristics of the Synthesized Compounds

^aIn chloroform. ^DIn ethyl acetate-methanol (5:1). ^CIn acetone-chloroform (1:1). ^dIn ethyl acetate-hexane (1:1).

dicated nitro N-oxides these changes are associated with their conversion to the aci form via migration of a hydrogen atom of the methylene group and with rearrangement of the azafluorene system to a system with conjugated double bonds.

Salts IX in the form of dark-blue crystals, which, according to the IR spectral data $(3100-3400 \text{ cm}^{-1})$, contain a molecule of alcohol, were isolated from the intensely blue solution obtained by treatment of V with sodium ethoxide after removal of the alcohol.



The sodium salts of the aci-nitro compounds (X) in the form of violet crystals with the same properties as salts IX were obtained by the same method from the mixture of N-oxides of 6- and 7-nitro-4-azafluorenes (VI). An important characteristic of the UV spectra of IX and X is the presence in the long-wave region of maxima at, respectively, 644 and 575 nm. These salts have the same color as azulenes; they are unstable and change relatively rapidly in air.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions in ethanol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra were obtained with Bruker WP-80 (I-V, and VIII) and Varian XL-200 (VI) spectrometers. The PMR spectra were analyzed by means of the ITRCAL program with a BNC-28X computer. The mass spectra were measured with an MKh-1303 mass spectrometer. Thin-layer chromatography (TLC) was carried out on activity II aluminum oxide. The characteristics of the compounds obtained are presented in Table 2.

<u>4-Azafluorene N-Oxide (II)</u>. A 4.2-ml (0.037 mole) sample of 30% hydrogen peroxide was added to a solution of 4 g (0.022 mole) of 4-azafluorene in 28 ml of acetic acid, and the reaction mixture was heated at 75°C for 5 h. The acetic acid was removed by distillation, 30 ml of water was added to the residue, and the mixture was made alkaline to pH 8-9 with so-

dium carbonate solution. The precipitate was crystallized from ethyl acetate. Compound II was obtained in the form of colorless crystals.

<u>3-Methyl-2- and 4-Azafluorenone N-Oxides (III, IV).</u> A 3.6-g (0.02 mole) sample of potassium permanganate was added in portions at 60°C in the course of 3 h to a suspension of 0.01 mole of N-oxide I (II) in a solution of 6.1 g (0.08 mole) of ammonium nitrate in 170 ml of water, after which the manganese dioxide was removed by filtration and refluxed in acetone (five 120-ml portions). The acetone solution was dried with magnesium sulfate, the acetone was removed by distillation, and III (IV) was crystallized from ethyl acetate. An additional amount of N-oxide III (IV) was isolated from the aqueous solution remaining after separation of the manganese dioxide by extraction with chloroform (two 250-ml portions). Compound III was obtained in the form of red crystals while IV was yellow.

<u>Nitration of 3-Methyl-2- and 4-Azafluorene N-Oxides.</u> A 2.4-ml sample of a nitrating mixture $[HNO_3-H_2SO_4\ (1:2)]$ was added with stirring at -10° C to 0.01 mole of N-oxide I (II) and 6.7 ml of sulfuric acid, and the mixture was maintained at 80°C for 1 h. It was then treated with a solution of sodium carbonate to pH 8. Nitro derivatives V were extracted with chloroform and crystallized from chloroform-acetone (1:1). Nitro derivatives VI were isolated by means of column chromatography (elution with acetone). Compounds V and VI were obtained in the form of yellow crystals.

Deoxygenation of N-Oxides V and VI. A mixture of 3.5 mmole of nitro derivatives V (VI) with 15.6 mmole of phosphorus tribromide was refluxed in 80 ml of chloroform, after which the mixture was cooled and treated with a solution of alkali up to pH 7-8. The deoxygenation products were extracted with ether or chloroform (VI). The extract was dried with magnesium sulfate, the chloroform was removed by distillation, and the residue was chromatographed with a column filled with aluminum oxide (elution with chloroform).

Aci-6- and Aci-7-nitro-3-methyl-2- and 4-Azafluorene N-Oxide Sodium Salts (IX, X). A solution of 0.02 g (0.3 mmole) of sodium ethoxide in 1.5 ml of ethanol was added at 50°C to a solution of 0.3 mmole of N-oxides V (VI) in 75 ml of ethanol, and the colored solution was maintained at 20°C for 25 h. The alcohol was removed by vacuum distillation, and the residue was washed with 1 ml of alcohol and ether and dried over phosphorus pentoxide.

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