TRANSFORMATIONS OF N-ACETYL(AROYL)-1-AZAFLUORENIUM CHLORIDES TO GIVE 9-α-HYDROXYETHYLIDENE(ARYLIDENE)-1-AZAFLUORENES

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N-Acetyl(benzoyl)-1-azafluorenium chlorides were converted to 9-acetyl(benzoyl)-1-azafluorenes, which exist in the enol form, when they were treated with triethylamine in benzene in the presence of boron trifluoride etherate. The first step in the rearrangement is the conversion of the starting chlorides to N-acyl-substituted pseudoazulenes with subsequent N → C_9 migration of the acyl group.

When N-phenyl(N-methyl)-1-azafluorenium halides are treated with aqueous solutions of bases, they are converted to pseudoazulenes, viz., 1-phenacyl(1-methyl)-1H-indeno[2,1-b]pyridines, which are stable, crystalline, dark-violet substances [1, 2].

In order to study the transformations under the influence of bases of 1-azafluorenium quaternary salts with an acetyl (aroyl) substituent attached to the nitrogen atom we obtained, on the basis of 1-azafluorene (I) and 7-nitro-1-azafluorene (II), N-acetyl- (III), N-benzoyl- (IV), and N-(p-nitrobenzoyl)-1-azafluorenium (V) chlorides, as well as N-benzoyl-7-nitro-1-azafluorenium chloride (VI). Upon treatment of aqueous solutions of these products with bases, they underwent quantitative conversion to azafluorenes I and II.

Different transformations take place with quaternary salts III, IV, and VI when suspensions of them in absolute benzene are treated with triethylamine. In this case the reaction mass immediately takes on a deep dark-violet coloration, which indicates the conversion of these salts to N-acyl-substituted anhydro bases, which, as a result of an N → C_9 acyl rearrangement, are converted, respectively, to 9-α-ethylidene- (VII) and -benzylidene-1-azafluorene (VIII) and 7-nitro-9-α-hydroxybenzylidene-1-azafluorene (X).

The data from the PMR spectra of the crystalline product isolated in the case of treatment of salt III with triethylamine without the use of boron trifluoride etherate constitute evidence for stepwise conversion of the resulting pseudoazulene to $C_{(9)}$-substituted azafluorene VII: Their ratios were, respectively, ∿1:2 in the case of recording of the PMR spectrum of the mixture of substances immediately after isolation and ∿1:8 in the case of re-recording of the spectrum of the sample after 24 h. The ratio of the anhydro base and azafluorene VIII in the mixture obtained by treatment of salt IV was ∿3:2 (and ∿1:10 after 24 h), whereas in the case of salt VI the ratio of the analogous isomers was ∿1:1 (and ∿1:5 after 24 h). The ratio of the isomeric acyl-substituted derivatives in their mixtures was determined by comparison of the intensities of the signals of the 3-H protons (triplet at 6.3-6.5 ppm, J = 6.5 Hz) of the anhydro bases and the 4-H protons (doublet of doublets at 8.6-8.7 ppm, J = 7 and 1 Hz) of azafluorenes VII, VIII, and X.

The complete conversion of the anhydro bases obtained from chlorides III, IV, and VI to VII, VIII, and X upon treatment with triethylamine takes place in the presence of catalytic amounts of boron trifluoride etherate. The degree of conversion of the anhydro base to the $C_{(9)}$-substituted azafluorene evidently depends on the structure of the acyl substituent. One might assume that the relative stability of the pseudoazulene would increase under the influence of an electron-acceptor group in the phenylene ring. A nitro group in the ring of the N-aroyl grouping has an opposite effect. Quaternary salt V is converted completely to 9-α-hydroxy(p-nitrobenzylidene)-1-azafluorene (IX) when it is treated with triethylamine without subsequent addition of boron trifluoride etherate; the formation of the corresponding anhydro base was not established experimentally in this case.

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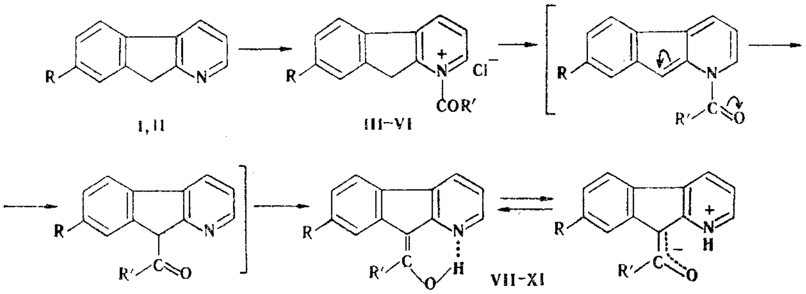
7-Nitro-9-α-hydroxyethylidene-1-azafluorene (XI) was obtained by the same method from azafluorene II, although it was modified somewhat (all of the reagents were introduced into the reaction simultaneously).



I, III—V, VII—IX R=H; II, VI, X, XI R=NO_2; III, VII, XI R′=CH_3; IV, VI, VIII R′=C_6H_5; V, IX R′=p-$NO_2C_6H_4$

The observed rearrangement evidently proceeds through a step involving the formation of a four-ring cyclic complex; this is promoted by the orientation of the nitrogen atom and the nucleophilic reaction center [$C_{(9)}$]. Aromatization of the nitrogen-containing ring and the formation of a cyclopentadiene fragment should facilitate the rearrangement.

One might have assumed that the formation of $C_{(9)}$-acyl derivatives does not take place by intramolecular rearrangement but rather as a result of intermolecular acylation. To verify this assumption we subjected fluorene to the reaction of quaternary salt III with triethylamine; we found that fluorene is not acetylated in this case. It is recovered unchanged in quantitative yield, which also confirms the mechanism of the rearrangement under consideration.

Acyl derivatives VII-XI exist in the enol form, the stabilization of which is due to the formation of an intramolecular hydrogen bond or a zwitterion. The physical properties of these substances, viz., their relatively high melting points (above 200°C), the intense color of the crystals, and the slight solubility in aprotic solvents, as well as in acetone, are evidently determined by the existence of a dipolar structure.

The enol structure of VII-X is confirmed by data from the IR spectra. The bands at 1620-1637 cm^{-1} are related to the absorption of the exocyclic double bond of the cyclopentadiene fragment, whereas the intense absorption bands at 3400-3500 and 3100-3200 cm^{-1} are related to free and associated hydroxy groups. A signal of a proton of the hydroxy group of the enol form (δ 6.95 ppm) is observed in the PMR spectrum of VII, and long-range spin–spin coupling of the protons of the hydroxyethylidene fragment (1 Hz) is realized.

A strong-field shift (6.7-6.9 ppm) of the 8-H signal is noted in the PMR spectra of VIII-X; this constitutes evidence for a cis orientation of the aryl group attached to the double bond relative to the phenylene fragment. In the case of VII-X the 4-H signal is located at weaker field than the 2-H signal, and this confirms the possibility of the formation of an intramolecular hydrogen bond.

Maximally intense molecular-ion peaks, which constitute evidence for the stability of their molecules, are characteristic for the mass spectra of these compounds.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in DMSO were recorded with Tesla 467-BS (100 MHz) and Brucker-WP 80 (80 MHz) with DSS as the internal standard. The mass spectra were recorded with an MKh-1303 spectrometer at 70 V. The IR spectra of KBr pellets were obtained with a UR-20 spectrometer.

N-Acetyl(benzoyl, p-nitrobenzoyl)-1-azafluorenium Chlorides (III-V) and N-Benzoyl-7-nitro-1-azafluorenium Chloride (VI). Benzene solutions of azafluorene I (II) (5 mmole in 25 ml of solvent) and the acyl chloride (23 mmole in 25 ml of solvent) were mixed at 20°C, and the mixture was maintained at 20°C for 16 h and at 80°C for 1 h. The resulting precipitate was washed with benzene and crystallized from acetone. The characteristics of III-VI are presented in Table 1.

A solution of 0.5 g (1.6 mmole) of salt IV was stirred in 25 ml of water and 10 ml of

TABLE 1. 1-Acetyl(aroyl)-1-azafluorenium Chlorides III-VI

Compound	mp, °C (dec.)	IR spectrum, cm^{-1}	PMR spectrum, ppm	N found, %	Empirical formula	N calc., %	Yield, %
III	195—196	1640 (C=O)	2,39 (CH_3); 4,39 (CH_2); 8,72 (dd, J=5,3 + 1,4 Hz, 2-H); 7,93 (t, 3-H); 8,86 (dd, J=7,9 + 1,4 Hz, 4-H)	6,0	$C_{14}H_{12}ClNO$	5,7	55
IV	198—200	1647 (C=O)	4,17 (CH_2); 8,72 (dd, J=6 + 1,8 Hz, 2-H); 8,85 (dd, J=8 + 1,7 Hz, 4-H)	4,7	$C_{19}H_{14}ClNO$	4,6	49
V	133—134	1740 (C=O), 1530 and 1353 (NO_2)	4,28 (CH_2); 8,12 (4H, d, J=3 Hz, 2′-, 3′-, 5′- + 6′-H); 8,57 (1H, dd, J=5 + 1,2 Hz, 2-H); 8,68 (1H, dd, J=7,5 + 1,5 Hz, 4-H)	7,9	$C_{19}H_{13}ClN_2O_3$	8,0	65
VI	>300	1733 (C=O), 1535 and 347 (NO_2)	—	7,6	$C_{19}H_{13}ClN_2O_3$	8,0	73

TABLE 2. 9-α-Hydroxyethylidene(arylidene)-1-azafluorenes VII-XI

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Color	Yield, %
		C	H	N		C	H	N		
VII	248—249 (dec.)	80,2	5,5	6,3	$C_{14}H_{11}NO$	80,4	5,2	6,7	Yellow	40
VIII	215—216	84,3	5,0	5,0	$C_{19}H_{13}NO$	84,1	4,8	5,2	Orange	53
IX	251—252	72,1	4,2	8,4	$C_{19}H_{12}N_2O_3$	72,2	3,8	8,9	Red-Orange	42
X	285—287	71,7	4,1	8,4	$C_{19}H_{12}N_2O_3$	72,2	3,8	8,9	Dark-brown	80
XI	>350	65,6	4,4	11,3	$C_{14}H_{10}N_2O_3$	66,1	3,9	11,0	Black	26

TABLE 3. Spectral Characteristics of VII-XI

Compound	M^+	IR spectrum, cm^{-1}	PMR spectrum, ppm
VII	209	1634 (C=C), 1710 (C=O) w, 3400 (OH) vs	2,81 (CH_3); 6,95 (OH); 7,48 (3-H); 8,50 (dd, J=6,7 + 0,7 Hz, 2-H); 8,64 (dd, J=7 + 0,7 Hz, 4-H)
VIII	271	1637 (C=C), 3200 + 3470 (OH)	6,9, 7,14 + 8,16 — ABCD spectrum of the 5-, 6-, 7- + 8-H; 7,3 (q, J=6,2 Hz, 3-H); 8,31 (dd, J=6 + 1,3 Hz, 2-H); 8,74 (dd, J=7,4 and 1,1 Hz, 4-H)
IX	316	1345 and 1547 (NO_2), 1635 (C=C), 3080—3200 and 3500 (OH)	6,72 (8-H); 7,1 (2H, 6- + 7-H); 7,23 (3-H); 8,17 (dd, J=6 + 1,2 Hz, 2-H); 8,04 (5-H); 8,66 (dd, J=7 and 1,2 Hz, 4-H); 7,72 and 8,23 (AA'BB' system)
X	—	1345 and 1530 (NO_2), 1640 (C=C), 3100—3200 and 3400—3500 (OH)	7,3 (3-H); 8,31 (dd, J=6 + 1,2 Hz); 8,89 (dd, J=7,5 + 1,2 Hz, 4-H)
XI	254	1345 + 1540 (NO_2), 1620 + 1640 (C=C), 1690 (C=O), 3100, 3200, 3400—3500 (OH)	—

a saturated solution of potassium carbonate. The resulting precipitate was washed with water, dried, and crystallized from hexane to give 0.26 g (96%) of 1-azafluorene (I) with mp 81-82°C [3]. Similar results were obtained when a 20% solution of potassium hydroxide and triethylamine were used in the reaction.

9-α-Hydroxyethylidene-1-azafluorene (VII). A) A 3-g (30 mmole) sample of triethylamine was added with stirring to a suspension of 3.4 g (14 mmole) of salt III in 50 ml of absolute benzene, and the mixture was maintained at 20°C for 17 h and at 80°C for 30 min. The triethylamine hydrochloride (1.8 g) was separated, and the filtrate was evaporated *in vacuo*. The residue was washed with benzene and dried in a vacuum desiccator to give 0.84 g (29%) of a mixture of 1-acetyl-1H-indeno[2,1-b]pyridine and VII in the form of dark-violet crystals with mp 87-89°C. UV spectrum, λ_{max} (log ε): 340 (2.9), 440 (2.2), and 500 nm (2.1). Found: C 81.6; H 6.3; N 7.0%; M^+ 209. $C_{14}H_{11}NO$. Calculated: C 80.4; H 5.2; N 6.7%; M 209.

A 0.2-ml sample of boron trifluoride etherate was added to a dark-violet solution of 0.5 g (2.4 mmole) of these crystals in 10 ml of benzene. The solution became light-yellow in color, and an oily substance which gradually crystallized, precipitated. The precipitated VII was separated, washed with benzene, and crystallized from acetone.

A similar procedure was used to obtain 9-α-hydroxybenzylidene-1-azafluorene (VIII), 9-α-hydroxy(p-nitrobenzylidene) (IX), and 7-nitro-9-α-hydroxybenzylidene-1-azafluorene (X). Compound IX was obtained without the use of boron trifluoride etherate.

B) A mixture of 2.3 g (14 mmole) of azafluorene I, 1.6 g (20 mmole) of acetyl chloride, and 2.9 g (30 mmole) of triethylamine in 50 ml of absolute benzene was refluxed for 17 h. The color of the reaction mixture changed from dark-green to dark-violet. The triethylamine hydrochloride was separated, and the benzene and excess triethylamine were removed by distillation, and several drops of boron trifluoride etherate were added to a solution of the residue in 25 ml of benzene. The almost colorless solution was evaporated to one third of its original volume, and the precipitated VII was purified with a column packed with aluminum oxide to give the product in 34% yield.

This method was also used to prepare VIII-XI; their characteristics are presented in Tables 2 and 3.

C) A 0.34-g (2 mmole) sample of fluorene and 0.4 g (4 mmole) of triethylamine were added to a suspension of 0.5 g (2 mmole) of salt III in 30 ml of benzene, and the mixture was stirred at 20°C for 6 h and refluxed with stirring for 6 h. The benzene and triethylamine were removed by distillation and the residue was shaken with 5 ml of benzene. The insoluble material (0.2 g) was starting salt III. The reaction products contained in the benzene solution were separated with a column packed with aluminum oxide [H 35 cm, d = 3 cm, elution with heptane–ether (1:1)]. The initial product isolated [0.28 g (85%)] was fluorene with mp 116°C, after which 0.09 g (40%) of 1-azafluorenone, with mp 127-128°C, was obtained.

LITERATURE CITED

1. N. S. Prostakov, A. T. Soldatenkov, V. O. Fedorov, and P. K. Radzhan, Khim. Geterotsikl. Soedin., No. 6, 850 (1980).
2. N. S. Prostakov, A. T. Soldatenkov, V. O. Fedorov, S. Mobio, and M. A. Galiullin, Khim. Geterotsikl. Soedin., No. 11, 1511 (1980).
3. N. S. Prostakov, A. T. Soldatenkov, and V. O. Fedorov, Khim. Geterotsikl. Soedin., No. 8, 1101 (1979).