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REDUCTION OF QUATERNARY SALTS OF 3-AZAFLUORENE AND 3-AZAFLUORENONE AND THEIR CONVERSION TO INDENOINDOLIZINES

N. S. Prostakov, A. T. Soldatenkov, P. K. Radzhan, A. Samal'oa, V. F. Zakharov, and V. P. Zvolinskii

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The tetrahydro and hexahydro derivatives with respect to the nitrogen-containing ring were obtained by reduction of 3-azafluorene and 3-azafluorenone methiodides, respectively, with sodium borohydride. Indenoindolizines with linear and angular structures were synthesized from the N-phenacyl quaternary salts of 3-azafluorenones via 1,3-dipolar cycloaddition and by the Chichibabin method. 7-Nitro-3-azafluorenone and 3-azafluorenone N-oxide were obtained.

Until recently, virtually no information regarding the properties and chemical transformations of 3-azafluorene was available. In connection with the development of a relatively simple method for its preparation [1] it seemed possible to begin a study of this previously difficult-to-obtain heterocycle.

In pharmacological tests of the partially hydrogenated 1-azafluorene derivatives obtained in our laboratory we established that they have psychotropic properties [1]. It seemed of interest to synthesize similar compounds on the basis of 3-azafluorene (I) and 3-azafluorenone (II).

For this, we obtained N-methyl-3-azafluorenium iodide (III) and N-methyl-9-oxo-3-azafluorenium iodide (IV) from I and II. Quaternary salt V, which was obtained from ketone II and ω-bromoacetophenone, was used in the synthesis of indenoindolizines.

The reduction of salts III and IV was carried out by using a large excess of sodium borohydride; their transformations proceed ambiguously in this case. 2-Methyl-1,2,3,4-tetrahydroindeno[1,2-c]pyridine (VI) was obtained in 87% yield in the reduction of salt III, while 5-hydroxy-2-methylindano[1,2-c]piperidine (VII) was obtained in 20% yield from salt IV. Intense (75 and 100%, respectively) molecular-ion peaks are present in the mass spectra of VI and VII. The PMR spectrum of tetrahydro derivative VI does not contain the signal of a vinyl proton, on the basis of which it may be concluded that the double bond is located in the $C_{(4a)}$-$C_{(9b)}$ position in the nitrogen-containing ring. The fact that the mass spectrum of VII does not contain a peak corresponding to the tetrahydro derivative (m/z 201) also may serve as a confirmation of its structure. The signal of a methyl group (2.18 ppm) and a doublet at 4.97 ppm (1H) with a spin-spin coupling constant (SSCC) of 6.5 Hz, which can be assigned to the proton attached to the $C_{(5)}$ atom, are observed in its PMR spectrum.

Free bases VI and VII are unstable compounds. They are transformed rapidly in air. They were therefore converted to the hydrochlorides for identification and further study.

To obtain new condensed heterocycles of the indenoindolizine type we subjected N-phenacyl-9-oxo-3-azafluorenium bromide (V) to 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate. As expected, we obtained products of condensation in both the α and α' positions of the pyridine ring, viz., 6-oxo-3-benzoyl-1,3-dicarbomethoxyindeno[2,1-g]indolizine (VIII) and 5-oxo-1-benzoyl-2,3-dicarbomethoxyindeno[2,1-f]indolizine (IX), the isolation of which was accomplished by means of chromatography [3].

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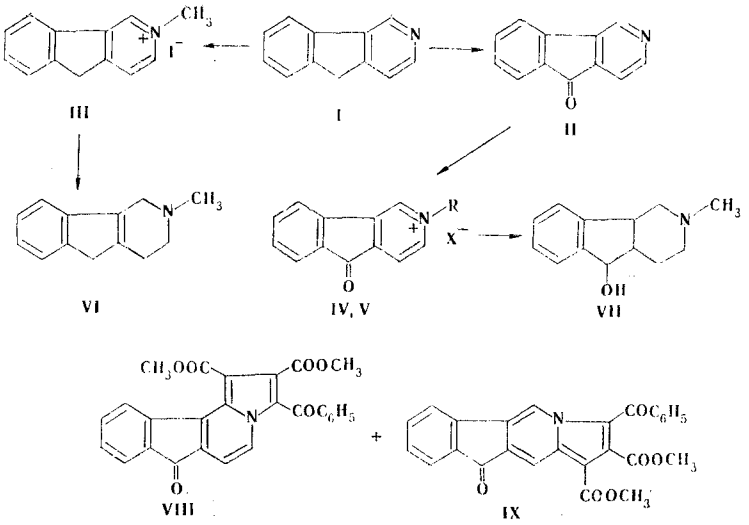
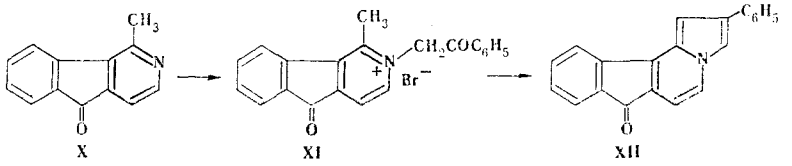


IV R=CH_3, X=I; V R=$C_6H_5COCH_2$, X=Br

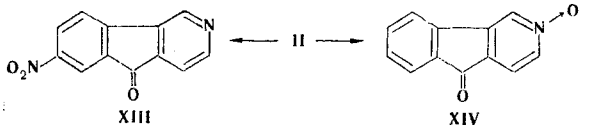
We used 4-methyl-3-azafluorenone (X) to synthesize an indenoindolizine with an angular structure. The N-phenacyl-9-oxo-4-methyl-3-azafluorenium bromide (XI) obtained from it was converted to 6-oxo-2-phenylindeno[2,1-g]indolizine (XII) by the Chichibabin method.



To obtain other derivatives of 3-azafluorenone (II) we carried out its nitration, as well as ozidation in the pyridine ring. The following estimates of the reactivities of the positions in the phenylene fragment in electrophilic substitution reactions were obtained on the basis of calculations of the boundary electron densities by the Pariser–Parr–Pople (PPP) method: $C_{(5)}$ 0.180, $C_{(6)}$ 0.037, $C_{(7)}$ 0.313, and $C_{(8)}$ 0.061.

7-Nitro-3-azafluorenone (XIII) was obtained in 50% yield by nitration of ketone II with potassium nitrate in sulfuric acid. Data from its PMR spectrum (see the experimental section) confirm that the nitro group is attached to the $C_{(7)}$ atom, which is in agreement with the estimates of the reactivities presented above.

A similar orientation is realized in the nitration of fluorenone and the isomeric (with respect to the position of the nitrogen atom) azafluorenones [4, 5].



The standard method was used to obtain 3-azafluorenone N-oxide (XIV), which was isolated in the form of high-melting colored crystals.

EXPERIMENTAL

The PMR spectra of the compounds were measured with BS-497 (100 MHz), WP-80 (80 MHz), and Hitachi–Perkin–Elmer R-22 (90 MHz) spectrometers with tetramethylsilane as the internal standard. The IR spectra of KBr pellets of the compounds were obtained with a UR-20 spectrometer. The mass spectra were obtained with an MKh-1303 spectrometer at an ionizing voltage of 70 eV.

3-Azafluorene Methiodide (III), 3-Azafluorenone Methiodide (IV), and 3-Azafluorenone Bromophenacylate (V). These compounds were obtained as described in [6]. Salt III was obtained in 91% yield in the form of colorless crystals with mp 188-189°C (from acetone). Found: N 4.4%. $C_{12}H_9N \cdot CH_3I$. Calculated: N 4.5%. Salt IV was obtained in 91% yield in the form of red crystals with mp 219-220°C (from acetone). Found: N 4.0%. $C_{12}H_7NO \cdot CH_3I$. Calculated:

N 4.3%. Salt V was obtained in 79% yield in the form of yellow-green crystals with mp 189-191°C (from acetone). Found: N 3.4%. $C_{20}H_{14}BrNO_2$. Calculated: N 3.7%.

2-Methyl-1,2,3,4-tetrahydroindeno[1,2-c]pyridine (VI). A 1.2-g (32 mmole) sample of sodium borohydride was added at 40°C to a suspension of 0.5 g (1.5 mmole) of salt III in 25 ml of methanol, and the mixture was refluxed with stirring for 1.5 h. It was then poured into 100 ml of water, and the aqueous mixture was extracted with ether. The extract was purified with a column filled with aluminum oxide to give 0.25 g (87%) of an oily substance that rapidly darkened. Found: M^+ 185. $C_{13}H_{15}N$. Calculated: M 185. The hydrochloride of base VI had mp 235-236°C (from ethanol). Found: C 70.2; H 7.3; N 6.0%. $C_{13}H_{15}N \cdot HCl$. Calculated: C 70.4; H 7.2; N 6.3%.

5-Oxo-2-methylindano[1,2-c]piperidine (VII). This compound was similarly obtained from salt IV in 20% yield. Found: M^+ 203. $C_{13}H_{17}NO$. Calculated: M 203. The hydrochloride of base VII had mp 190-192°C (dec., from ethanol). Found: C 65.1; H 7.3; N 5.5%. $C_{13}H_{17}NO \cdot HCl$. Calculated: C 65.3; H 7.1; N 5.8%.

6-Oxo-3-benzoyl-1,2-dicarbomethoxyindeno[2,1-g]indolizine (VIII) and 5-Oxo-1-benzoyl-2,3-dicarbomethoxyindeno[2,1-f]indolizine (IX). A 0.45-g (3.8 mmole) sample of dimethyl acetylenedicarboxylate and 0.5 g (4.9 mmole) of triethylamine were added successively to a suspension of 0.5 g (1.3 mmole) of salt V in 25 ml of chloroform, and the mixture was stirred to 40°C for 3 h. The precipitate was washed with water, dried, and chromatographed (on activity II aluminum oxide by elution with ether). Initially eluted was 0.12 g (21%) of VIII in the form of bright-red crystals with mp 195-197°C (from ether–chloroform). PMR spectrum ($CDCl_3$): 3.21 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 7.72 and 9.2 ppm (d, J = 6.5 Hz, 5-H and 4-H, respectively). IR spectrum: 1744, 1734, and 1714 cm^{-1} (CO). Mass spectrum, m/z (%): M^+ 439 (100), 438(20), 425(12), 393(27), 321(23). Found: C 71.1; H 3.8; N 3.1%. $C_{26}H_{17}NO_6$. Calculated: C 71.1; H 3.9; N 3.2%.

Subsequent elution gave 0.15 g (26%) of yellow crystals of IX with mp 213-214°C (from ether–chloroform). PMR spectrum ($CDCl_3$): 3.27 (s, 3H, CH_3); 3.87 (s, 3H, CH_3); 7.21-7.64 (m, 10H, aromatic protons); 8.60 and 9.52 ppm (s, $J_{4,10} \approx 1$ Hz, 1H, 4-H and 10-H, respectively). IR spectrum: 1746, 1734, and 1715 cm^{-1} (CO). Mass spectrum, m/z (%): M^+ 439(100), 438(26), 425(81), 424(27), 406(29), 393(7), 380(28), 372(33), 336(73), 321(68), 304(77), 293(68), 292(63). Found: C 70.9; H 3.9; N 3.4%. $C_{26}H_{17}NO_6$. Calculated: C 71.1; H 3.9; N 3.2%.

4-Methyl-3-azafluorenone (X) and Its Bromophenacylate (XI). A catalysate containing, according to the results of gas-liquid chromatography (GLC), 17% 4-methyl-1-azafluorene and 13% 4-methyl-3-azafluorene was obtained by catalytic dehydrocyclization of 2,4-dimethyl-3-phenylpyridine. The 4-methyl-1-azafluorene was isolated in 9% yield by crystallization of the azafluorene fraction [7]. 4-Methyl-3-azafluorene was characterized by the PMR spectrum of a mixture with methyl-substituted 1-azafluorene (CCl_4), δ: 2.73 (s, 3H, 4-CH_3), 3.61 (s, 2H, CH_2), 6.77 (d, J = 5.0 Hz, 2H, 1-H and 3-H), 7.00-7.70 (m, 8H, aromatic protons of both azafluorenes), and 8.15 ppm (d, J = 5.0 Hz, 2H, 2-H).

A stream of air was passed through a solution of 1 g of the azafluorene fraction [0.43 g (2.4 mmole) of 4-methyl-3-azafluorene] in 25 ml of hexane for 36 h, and the resulting precipitate was crystallized from hexane to give 0.38 g (81%) of yellow crystals of ketone X with mp 132-133°C. PMR spectrum (CCl_4): 2.72 (s, 3H, 4-CH_3), 7.04-7.60 (m, 5H, aromatic protons), 7.20 (d, J = 4.5 Hz, 1H, 1-H), and 8.35 ppm (d, J = 4.5 Hz, 1H, 2-H). Found: C 79.9; H 4.8; N 7.2%; M^+ 195. $C_{13}H_9NO$. Calculated: C 80.0; H 4.6; N 7.2%; M 195.

Salt XI (50%) was obtained in the same way as V in the form of greenish crystals with mp 195-197°C (from acetone). Found: N 3.5%. $C_{21}H_{16}BrNO_2$. Calculated: N 3.4%.

6-Oxo-2-phenylindeno[2,1-g]indolizine (XII). A solution of 0.18 g (0.45 mmole) of salt XI in 15 ml of water and 10 ml of 40% potassium carbonate solution was refluxed for 2 h, and the resulting precipitate was chromatographed (on aluminum oxide by elution with chloroform) to give 0.07 g (53%) of dark-brown crystals of XII with mp 235-236°C (from hexane). Found: C 85.4; H 4.4; N 4.7%; M^+ 295. $C_{21}H_{13}NO$. Calculated: C 85.0; H 4.2; N 4.6%; M 295.

7-Nitro-3-azafluorenone (XIII). A 0.3-g (3 mmole) sample of potassium nitrate was added with stirring and cooling (to 0°C) to a solution of 0.5 g (2.9 mmole) of 3-azafluorenone (II) in 3 ml of sulfuric acid, and the mixture was maintained at 20°C for 30 min and heated at 60°C for 1 h (with monitoring of the reaction by TLC). It was then poured over 50 g of ice, and the aqueous mixture was made alkaline. The resulting precipitate (0.5 g) was purified with

a column filled with aluminum oxide (by elution with chloroform) and crystallized from acetone to give 0.3 g (50%) of yellow crystals of XIII with mp 214-216°C. PMR spectrum (80 MHz, DMSO): 7.70 (d, $J_{1,2}$ = 4.5 Hz, 1H, 1-H), 8.22 (d, $J_{5,6}$ = 7.5 Hz, 1H, 5-H), 8.31 (d, $J_{6,8}$ = 2.5 Hz, 1H, 8-H), 8.61 (d, $J_{6,5}$ = 7.5, $J_{6,8}$ = 2.5 Hz, 1H, 6-H), 8.90 (m, 1H, 2-H), and 9.36 ppm (broad s, 1H, 4-H). Mass spectrum, m/z (%): M^+ 226(100), 180(28), 168(14), 153(16), 152(45), 149(21), 125(42), 98(30), 97(20). IR spectrum: 1730 (CO), 1535, 1342 cm^{-1} (NO_2). Found: C 63.5; H 3.5; N 12.4%; M^+ 226. $C_{12}H_6N_2O_3$. Calculated: C 63.7; H 3.5; N 12.4%; M 226.

3-Azafluorenone N-Oxide (XIV). The oxidation of 3-azafluorenone (II) with hydrogen peroxide in acetic acid was carried out as described in [8]. Workup of the reaction mixture gave orange crystals of XIV (56%) with mp 246-247°C (from ethanol). Found: C 73.1; H 3.6; N 7.1%; M^+ 197. $C_{12}H_7NO_2$. Calculated: C 73.3; H 3.4; N 6.8%; M 197.

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QUATERNARY 1-AMINOBENZIMIDAZOLIUM SALTS IN REACTIONS WITH β-DICARBONYL COMPOUNDS. FORMATION OF PYRIDAZINO[1,6-a]BENZIMIDAZOLIUM CATIONS AND 1-ARYLPYRAZOLES

V. V. Kuz'menko, T. A. Kuz'menko, and A. M. Simonov

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Pyridazino[1,6-a]benzimidazolium cations and 1-(o-methylaminoaryl)-4-acetylpyrazoles are formed simultaneously in approximately equal amounts in the reaction of excess acetylacetone with quaternary 1-aminobenzimidazolium salts in aqueous potassium carbonate solution. Mesoionic pyridazinobenzimidazoles and the corresponding 4-ethoxycarbonylpyrazoles were obtained with acetoacetic ester under similar conditions.

Data on the reaction of the cations of N-amino derivatives of nitrogen heterocycles with β-dicarbonyl compounds are limited to N-amino-substituted pyridines and sym-triazoles [1-2]. It has been recently shown that 1-aminobenzimidazoles react with β-diketones to give pyridazino[1,6-a]benzimidazoles [3]. In the present research we set out to study the peculiarities of this reaction for quaternary 1-aminobenzimidazolium salts and, in particular, to ascertain the possibility of the synthesis of pyrazolo[1,5-a]benzimidazoles via this scheme, as in the N-aminopyridine series [1].

Scientific-Research Institute of Physical and Organic Chemistry at Rostov State University, Rostov-on-Don 344006.

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