mixture is distilled to dryness, the residue is dissolved in water, the solution is made alkaline with potassium carbonate to pH 8-9, and steam-distilled. The distillate, containing the crystalline product, is extracted by ether. The solvent is distilled to yield 0.45 g (87%) of 2-anilinopyridine, mp 106-107°C; according to the data in [5], mp 106-108°C.

Acid Hydrolysis of Compound VII. A 1 g portion (28 mmoles) of compound VII is dissolved in 5 ml of concentrated hydrochloric acid, and the solution is boiled for 34 h. The reaction mixture is evaporated to dryness, and the residue is dissolved in water, alkaline with potassium carbonate to pH 8-9, and extracted by ether. The ether is distilled off and the residue is treated with benzene. After distillation of benzene, 2-p-anisidinopyridine (IX) is obtained in a yield of 0.40 g (73%), mp 85-87°C (from petroleum ether), according to the data in [6], mp 85°C.

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SYNTHESIS OF SUBSTITUTED 2-PYRIDONES AND 4-AZA-3-FLUORIDONES

N. S. Prostakov, Saha Shibu Rani, N. M. Mikhailova,
V. K. Shevtsov, and N. D. Sergeeva

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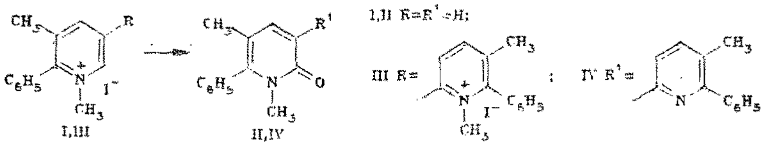
Substituted N-methyl-2-pyridones and N-methyl-4-aza-3-fluoridones, a previously unknown group of heterocyclic compounds, were obtained by oxidation of 3-methyl-2-phenylpyridine, 3-methyl-2-phenyl-5-(3'-methyl-2'-phenylpyridin-6'-yl)pyridine iodomethylates, as well as of 4-aza-fluorenes substituted at the 9-position.

For the synthesis of 4-aza-3-fluoridones we used 4-azafluorene, which is obtained by catalytic dehydrocyclization of 3-methyl-2-phenyl-pyridine [1]. It was found that in the synthesis of this pyridine base by phenylation of β-picoline [2], 3-methyl-2-phenyl-5-(3'-methyl-2'-phenyl-3',4'-dehydropiperidin-6'-yl)pyridine is formed in relatively appreciable amounts; the compound readily converts into a similarly substituted β,α-dipyridyl [3].

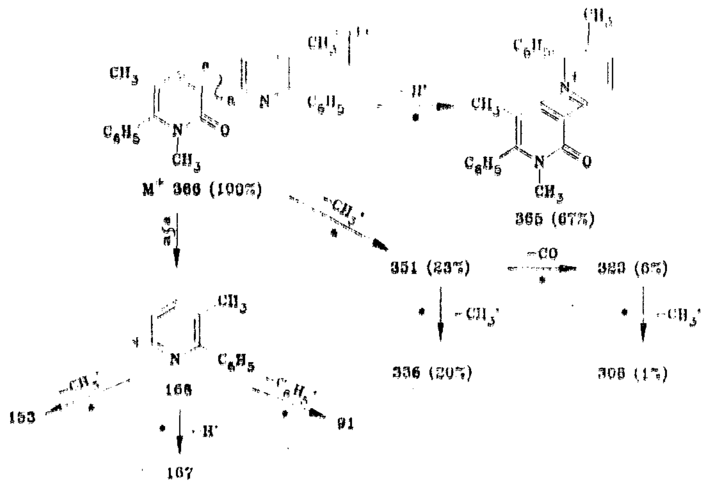
Having at our disposal practical methods for the preparation of these two pyridine bases, as well as of 4-azafluorene, we turned our attention to the synthesis of new substitutd 2-pyridones and previously unknown 4-aza-3-fluoridones. They are formed by oxidation under alkaline conditions of iodomethylates of the corresponding bases.



For the oxidation of 3-methyl-2-phenylpyridine iodomethylate (I), we used potassium hexacyanoferrate (Fe^{3+}). Irrespective of the time of reaction, 1,5-dimethyl-6-phenyl-2-pyridone (II) is formed in a yield of ~20%; a considerable amount of the starting salt is recovered unchanged.

Patrice Lumumba Peoples' Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 939-942, July, 1986. Original article submitted March 12, 1985.

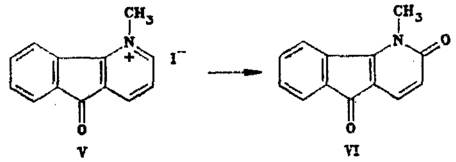
Scheme 1



Under similar conditions, from 3-methyl-2-phenyl-5-(3'-methyl-2'-phenyl-2'-pyridin-6-yl) pyridine diiodomethylate (III), 1,5-dimethyl-6-phenyl(3'-methyl-2'-phenylpyridin-6'-yl)-2-pyridone (IV) was obtained in a yield of 25%. In its mass spectrum, the peak of the molecular ion M^+ (366)* has the highest intensity. The formation of the highly intense peak of the $[M-H]^+$ ion (365.67%) is characteristic of the fragmentation of dipyridyls [4]. The presence of two methyl groups in the molecule is confirmed by the formation of characteristic fragments $[M-CH_3]^+$ (351.23%) and $[M-CH_3,-CH_3]^+$ (336.20%), while the relatively high intensity of the peaks of these ions indirectly indicates the ortho-position of the methyl and phenyl substituents. The presence of a keto group in the moelcule is manifested at the second stage of the fragmentation (Scheme 1).

The characteristic feature of the fragmentation of pyridone IV is splitting of the internuclear C—C bond between the rings. The charge is thus completely localized on the oxygenless fragment of the molecule (ion 168.8%), which further decomposes similarly to phenylpyridines [5].

For the synthesis of 4-aza-3-fluoridones we used quaternary salts of 4-azafluorenes substituted at the $C_{(9)}$ atom. The oxidation of 4-aza-florenone iodomethylate (V) was carried out by atmospheric oxygen in an aqueous potassium hydroxide solution. 9-Oxo-4-methyl-4-aza-3-fluoridone (VI) was formed in relatively low yield and, similarly as the above mentioned pyridones, was isolated in the form of colored crystals. Its structure was confirmed by PMR and IR spectra and elemental analysis.



In the mass spectrum (scheme 2) of azafluoridone VI, peak M^+ (211) has the mximum intensity. The presence of a peak of the $[M-H]^+$ ion with in appreciable intensity is possibly due to the elimination of a hydrogen atom as the result of cleavage of the β-bond in the methyl substituent [6]. The formation of intense ions 183 and 155 confirms the presence of two oxo groups. The splitting of the hydrogen cyanide molecule, characteristic for nitrogen-containing heterocyclic molecules, is observed at the secondary stages of the fragmentation of M^+. This fact, as well as the absence of a peak of the $[M-CH_3]^+$ ion, may serve as an indirect confirmation of the presence of the N-methylamide fragment in the molecule

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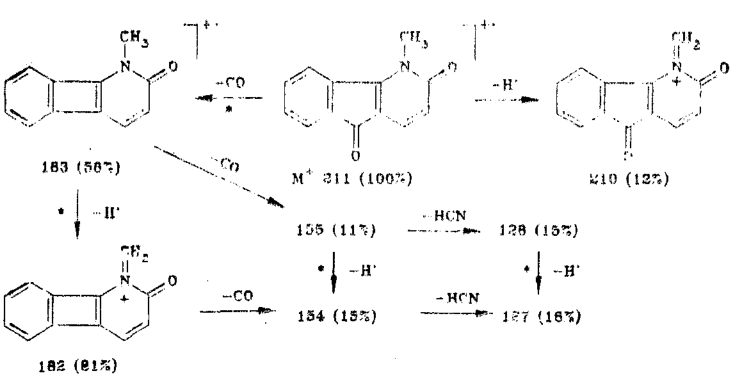
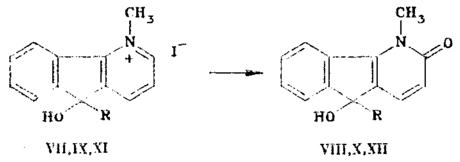
*In the text and in the schemes, the numbers characterizing the ion represent the m/z value.

Scheme 2



4-Aza-3-fluoridones containing a tertiary alcoholic group at the 9-position were obtained in a similar way. During the oxidation of 9-methyl-4-aza-fluoren-9-ol iodomethylate (VII), 9-hydroxy-4,9-dimethyl-4-aza-3-fluoridone (VIII) was obtained in a 21% yield.



VII, VIII R=CH_3; IX, X R=P-$CH_3OC_6O_4$; XI, XII R=P-$C_2H_5OC_6H_4$

In the case of the oxidation of quaternary salts of similar alcohols with aryl substituents at the 9-position, 4-aza-3-fluoridones are formed in yields of >40%. From salts IX and XI, 9-hydroxy-4-methyl-9-(p-methoxy-phenyl)-(X) and (p-ethoxyphenyl)-(XII) 4-aza-3-fluoridones were obtained. They are yellow high-melting crystalline substances.

EXPERIMENTAL

The mass spectra were obtained on MX-1303 mass spectrometer, fitted with a system for a direct introduction of the sample into the ion source, at a ionizing voltage of 70 eV and input temperature of 40°C. The IR spectra were recorded on a Specord UR-20 spectrophotometer. The PMR spectra were obtained on a BF-467 spectrometer (60 MHz, internal standard TMS). The chromatography was carried out on aluminum oxide, grade II of activity.

1,5-Dimethyl-6-phenyl-2-pyridone (II). A solution of 10 g (32 mmoles) of potassium ferrocyanide (Fe^{+3}) and 4 g (80 mmoles) of sodium hydroxide in 50 ml of water is gradually added, with stirring and cooling, to a suspension of 5 g (16 mmoles) of quaternary salt I (mp 170-172°C) in 30 ml of water. The dark brown mixture is stirred for 4 h at 20°C, and then saturated with potassium carbonate. The reaction products are extracted by chloroform, and the extract is dried over magnesium sulfate. After the distillation of chloroform, 20 ml of acetone are added to the residue (3 g), and 2.7 g (54%) of the initial salt I are filtered. Acetone is distilled from the mother liquor. The residue is chromatographed using successively hexane—ether mixtures in ratios 3:1, 2:1, and 1:1. From the last eluate, 0.27 g (19.6%) of pyridone II is isolated, yellow crystals, mp 114-115°C (from heptane). IR spectrum: 1610 cm^{-1} (CO). Found: N 7.1%; M^+ 199. $C_{13}H_{18}NO$. Calculated: N 7.3%; M 199.

1,5-Dimethyl-6-phenyl-(3'-methyl-2'phenylpryidin-6'-yl)-2-pyridone (IV). In the reaction, 1.26 g (2 mmoles) of salt III, 7.9 g (26 mmoles) of potassium ferrocyanide, 1.5 g (20 mmoles) of potassium hydroxide, and 50 ml of water are used. The mixture is stirred for 24 h. The precipitate is filtered, washed with water, and dried to yield 0.52 g of the initial salt III. From the mother ligquor, the products are extracted by ether. After the distillation of ether, 0.11 g (25%) of pyridone IV is obtained, orange crystals, mp 178-179°C (from heptane). IR spectrum: 1642 cm^{-1} (CO). PMR spectrum ($CDCl_3$): 1.83 (3H, s, 5-CH_3); 2.40 (3H, s, 3-CH_3); 3.30 (3H, s, $NHCH_3$), 7.1-7.8 (11H, m, 5-H and 2·C_6H_5); 8.37 (1H, s, 4-H); 8.5 ppm (1H, d, J = 8.0 Hz, 4-H). Found: N 7.2%; M$^+$ 366. $C_{25}H_{22}N_2O$. Calculated: N 7.6%; M 366.

9-Oxo-4-methyl-4-aza-3-fluoridone (VI). A suspension of 0.5 g (1.5 mmoles) of quaternary salt V in 40 ml of a 15% aqueous solution of potassium hydroxide is stirred for 2 h at 20°C. From an ether extract of the reaction products, 0.05 g (15.6%) of the pyridone VI is isolated, light brown crystals, mp 195-196°C (from heptane). PMR spectrum ($CDCl_3$): 3.95 (3H, s, NCH_3), 6.45 (1H, d, J = 9.2 Hz, 2-H), 7.60 (1H, d, J = 9.1 Hz, 1-H), 7.4-7.7 ppm (4H, m 5,6,7,8-H). IR spectrum: 1710 and 1685 cm^{-1} (CO). Found: C 73.9; H 4.5; N 6.6%. $C_{13}H_9NO_2$. Calculated: C 73.9; H 4.3; N 6.6%.

9-Hydroxy-4,9-dimethyl-4-aza-3-fluoridone (VIII). A mixture of 1.3 g (3 mmoles) of salt VII (mp 227-228°C), 6.5 g (200 mmoles) of potassium ferrocyanide, 1.3 g (200 mmoles) of potassium hydroxide, and 110 ml of water is stirred for 8 h. The desired end product is isolated by extraction with ether. Yield 0.17 g (20.9%) of pyridone VIII, yellow crystals, mp 183-184°C (from heptane). PMR spectrum ($CDCl_3$): 1.41 (3H, s, 9-CH_3), 3.50 (3H, s, 4-CH_3), 3.83 (1H, br. s, OH), 6.15 (1H, d, J = 9.0 Hz, 2-H), 7.37 (1H, d, J = 9.0 Hz, 1-H), 7.3-7.9 (4H, m, 5,6,7,8-H). IR spectrum: 1665 (CO), 3318 cm^{-1} (OH). Found: N 5.9; M$^+$ 227. $C_{14}H_{13}NO_2$. Calculated: N 6.2%; M 227.

9-Hydroxy-4-methyl-9-(p-methoxyphenyl- and (p-ethoxyphenyl)-4-aza-3-fluoridones (X and XII) are obtained in a similar way from salts IX and XI, in a yield of 47 and 40%, respectively. Compound X. Yellow crystals, mp 214-215°C (from a heptane–acetone mixture, 10:1). IR spectrum: 1650 (CO), 3285 cm^{-1} (OH). Found: N 4.2%; M$^+$ 319. $C_{20}H_{17}NO_3$. Calculated: N 4.4%; M 319. Compound XII. Yellow crystals., mp 201-202°C (from heptane). IR spectrum: 1650 (CO), 3300 cm^{-1} (OH). Found: N 4.4%; M$^+$ 333. $C_{21}H_{19}NO_3$. Calculated: N 4.2%; M 333.

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