13. A. Albert and E. Serjeant, Ionization Constants of Acids and Bases, Wiley (1962).
14. N. N. Suvorov, Zh. F. Sergeeva, A. P. Gryaznov, V. P. Shabunova, L. G. Tret'yakova, T. K. Efimova, T. A. Volodina, I. A. Morozova, R. N. Akhvelediani, A. M. Vasil'ev, and T. K. Trubitsyna, Tr. Mosk. Khim.-Technol. Inst., No. 94, 27 (1977).
15. H. Rydon and S. Sidappa, J. Chem. Soc., 82, 2462 (1951).
16. J. A. Joule and G. F. Smith, Heterocyclic Chemistry, Van Nos Reinhold (1972).

2,4-DIPHENYL-3-AZAFLUORENE

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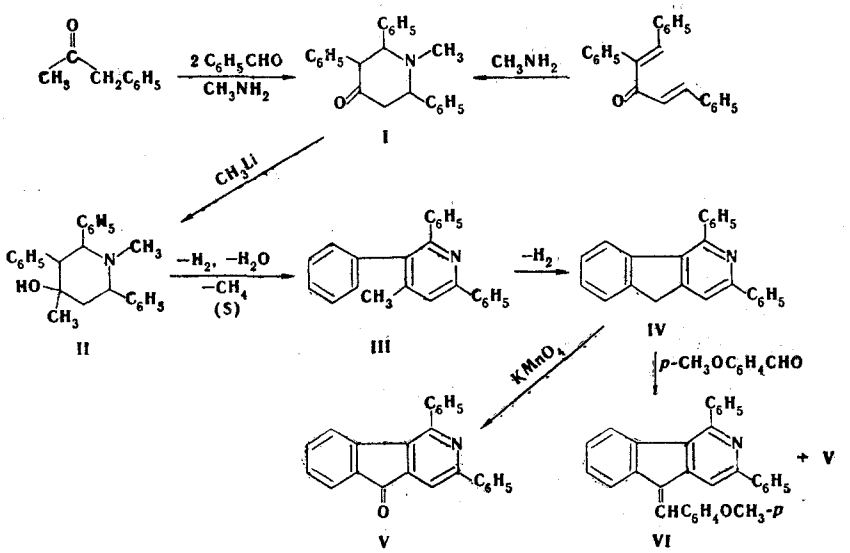
UDC 547.836

Among azafluorenes isomeric with respect to the position of the nitrogen atom, 3-azafluorenes are less well known than the others. Information about them is limited to reports on the synthesis of 3-azafluorenone by the pyrolysis of 3-o-carboxyphenylisonicotinic acid, obtained by oxidation of benzo[h]isoquinoline [1, 2], and on its synthesis from 3-phenylisonicotinoyl chloride [3]. The reduction of 3-azafluorenone to 3-azafluorene, which was only isolated in the form of the picrate [2, 3], and also the formation of a mixture of 1- and 3-azafluorenes by pyrolysis of phenyl-3-pyridyldiazomethane [2] have been described.

In order to obtain one of the first representatives of this heterocyclic system we used a scheme of three-stage synthesis, by which 3-methyl-2-azafluorene had previously been obtained in our laboratory from 1,2,5-trimethyl-4-piperidone [4]. As starting compound we used 1-methyl-2,3,6-triphenyl-4-piperidone (I), obtained by condensation of methyl benzyl ketone with benzaldehyde and methylation and also by reaction of 1,2,5-triphenyl-1,4-pentadien-3-one with methylamine.

From the piperidone (I) and methyllithium we obtained 1,4-dimethyl-2,3,6-triphenyl-4-piperidol (II). This tertiary γ-piperidol is formed as a single geometric isomer out of the eight possible isomers, and it evidently corresponds to the conformation with the equatorial orientation of the methyl group at C_4 and the phenyl radicals. When heated (200°C) with sulfur (by the method described in [5]), the piperidol (II) gave a high yield of 4-methyl-2,3,6-triphenylpyridine (III) as a result of simultaneously occurring dehydration, dehydrogenation,



P. Lumumba University of the Friendship of Peoples, Moscow 117302. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1098-1100, August, 1979. Original article submitted September 26, 1978.

0009-3122/79/1508-0899$07.50

and demethylation reactions. Dehydrocyclization of this pyridine base, which was realized a catalyst of grade K-16 by the method in [4], occurs by elimination of hydrogen atoms from the methyl group at the γ position of the pyridine ring and from the ortho position of the phenyl radical at C_3. The structure of the 2,4-diphenyl-3-azafluorene (IV) isolated as a result was demonstrated by analytical and spectral data and also by chemical transformations, i.e., by oxidation to 2,4-diphenyl-3-azafluorenone (V) and by the production of 2,4-diphenyl-9-(p-methoxybenzylidene)-3-azafluorene (VI) from it by condensation with anisaldehyde. In the last case azafluorenone (V) is also formed in a considerable amount. The method of catalytic dehydrocyclization of the corresponding methyl- and aryl-substituted pyridine bases is evidently general for the synthesis of all azafluorenes isomeric with respect to the position of the nitrogen atom.

EXPERIMENTAL

The PMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz) in deuterochloroform with HMDS as internal standard. The ^{13}C $\{^1H\}$ NMR spectra were recorded at 309 and 328°K on an HX-90E instrument with proton decoupling. The field was stabilized against the deuterium signal of deuterochloroform (with TMS as internal standard). The number of scans was 6000-8000. The pulse width was 9-10 μsec. The IR spectra were recorded on a UR-20 spectrophotometer in tablets with potassium bromide. The UV spectra were recorded in ethanol on a Hitachi instrument. The mass spectra were recorded on an MX-1303 instrument with a system for direct injection of the sample into the ion source with an ionizing potential of 70 V at 50°C. Chromatography was realized on aluminum oxide of grade II activity.

1-Methyl-2,3-6-triphenyl-4-piperidone (I). A. A mixture of 96.2 g (0.72 mole) of methyl benzyl ketone [6], 160 g (1.5 mole) of benzaldehyde, and 52 g (1.68 mole) of methylamine in 100 ml of glacial acetic acid and 180 ml of ethanol was kept at room temperature for 15 h. The precipitate was filtered off, washed with 80 ml of ethanol, and dried. We obtained 80 g (34%) of the piperidone (I) in the form of colorless crystals; mp 162-163°C (from benzine). PMR spectrum: 1.76 (3H, s, NCH_3), 3.92-2.45 (5H, m, CH and CH_2), 7.4-6.61 ppm (15 H, m, aromatic protons). ^{13}C NMR spectrum: 204.9 (C=O), 77.4, 70.5, and 64.7 ($C_{(2)}$, $C_{(3)}$, $C_{(4)}$, 50.8 ($C_{(5)}$) 41.2 (NCH_3), 143.4-126.8 ppm (aromatic carbon atoms). UV spectrum, λ_{max} (log ε): 248-266 (2.8-2.9), 290 nm (2.4). IR spectrum: 1720 cm^{-1} (C=O). Found, %: C 84.2; H 6.5; N 4.1. Mol.wt. 341 (mass spectrometry). $C_{24}H_{23}NO$. Calculated, %: C 84.5; H 6.7; N 4.1. Mol. wt. 341. From the mother solution after 30 days we isolated 35 g (11%) of 1,2,5-triphenyl-1,4-pentadien-3-one; mp 118-121°C (from alcohol). IR spectrum: 1671 (C=O), 1617 cm^{-1} (C=C). Found, %: C 88.8; H 5.8. Mol.wt. 310 (mass spectrometry). $C_{23}H_{18}O$. Calculated, %: C 89.0; H 5.8. Mol.wt. 310.

B. Gaseous methylamine was passed into a solution of 35 g (0.11 mole) of 1,2,5-triphenyl-1,4-pentadien-3-one in 200 ml of ethanol, and the mixture was kept at room temperature for 48 h. The precipitate weighed 12 g (34%) and represented the piperidone (I); mp 162-163°C (from benzine).

1,4-Dimethyl-2,3,6-triphenyl-4-piperidol (II). To methyllithium, obtained from 12.9 g (0.09 mole) of methyl iodide and 1.25 g (0.18 g-atom) of lithium in 350 ml of absolute ether, while stirring, we added a solution of 20.5 g (0.06 mole) of the piperidone (I) in 250 ml of benzene. The ether was distilled, and the benzene solution was boiled for 3 h. We added 200 ml of a saturated solution of ammonium chloride. The benzene layer was removed and dried with magnesium sulfate. The residue (21.6 g) after distillation of the benzene was purified on a column of aluminum oxide with chloroform as eluent. We isolated 11.2 g (52%) of the piperidol (II); mp 126-127°C (from hexane). PMR spectrum: 0.91 (3H, s, C-CH_3), 1.73 (3H,s, NCH_3), 6.61 (1H, s, OH), 7.61-6.86 ppm (15H, m, aromatic protons). IR spectrum: 3530 cm^{-1} (OH). UV spectrum, λ_{max} (log ε): 248-266 (2.7-2.8), 290 nm (1.9 sh). Found, %: C 84.1; H 7.8; N 3.6. Mol.wt. 357 (mass spectrometry). $C_{25}H_{27}NO$. Calculated %: C 84.0; H 7.6; N 3.9. Mol.wt. 357.

4-Methyl-2,3,6-triphenylpyridine (III). A thoroughly ground mixture of 6.21 g (0.017 mole) of the piperidol (II) with 3.7 g (0.116 mole) of crystalline sulfur was kept at 200°C for 1 h and extracted with ether. The residue after distillation of the ether was chromatographed with a 4:1 mixture of petroleum ether and ether as eluent. A 4.1-g yield (73%) of the pyridine (III) was obtained in the form of transparent prismatic crystals; mp 115-115.5°C (from a mixture of petroleum ether and ether). PMR spectrum: 2.18 (3H, s, CH_3), 8.1-6.96 ppm (16H, m, aromatic protons). ^{13}C NMR spectrum: 21.0 (CH_3), 120.5-138.6 (carbon atoms of

phenyl groups), 139.4-157.2 ppm (carbon atoms of pyridine ring). UV spectrum, λ_{max} (log ε): 243 (4.4) and 286 nm (4.2). Found, %: C 89.6; H 5.9; N 4.6. Mol.wt. 321 (mass spectrometry). $C_{24}H_{19}N$. Calculated, %: 89.7; H 5.9; N 4.4. Mol.wt. 321.

2,4-Diphenyl-3-azafluorene (IV). A solution of 7 g (0.022 mole) of the pyridine (III) in 200 ml of benzene was passed for 8 h at a constant rate through a layer of catalyst of grade K-16 (20 ml) at 560°C. The residue (5 g) after distillation of the benzene from the catalysis product was chromatographed with a 4:1 mixture of heptane and ether as eluent. We isolated 1.7 g of the initial compound (III) and then 1.25 g [24% calculated on the reacted amounted of (III)] of the azafluorene (IV) in the form of light-yellow crystals; mp 139-140°C (from hexane). PMR spectrum: 2.1 (2H, s, CH_2), 3.5-4.06 ppm (14H, m, aromatic protons). UV spectrum, λ_{max} (log ε): 224 (4.5 sh), 242 (4.3 sh), and 304 nm (4.56). Found, %: C 89.9; H 5.4; N 4.2. Mol.wt. 319 (mass spectrometry). $C_{24}H_{17}N$. Calculated, %: C 90.3; H 5.3; N 4.4. Mol.wt. 319.

2,4-Diphenyl-3-azafluorenone (V). To a solution of 0.3 g (0.01 mole) of the azafluorene (IV) in 30 ml of acetone, while vigorously stirring, we added in portions 0.5 g (0.03 mole) of potassium permanganate. The mixture was kept at 20°C until completely colorless, and the manganese dioxide was filtered off. The acetone was distilled, and the residue was crystallized from acetone. We isolated 0.15 g (50%) of the azafluorenone (V) in the form of orange crystals; mp 197.5-198°C (from acetone). IR spectrum: 1719 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 220 (2.66); 258 (4.6); 360 (4.8); 453 nm (3.25). Found, %: C 86.3; H 4.8; N 4.0. Mol.wt. 333 (mass spectrometry). $C_{24}H_{15}NO$. Calculated %: C 86.5; H 5.5; N 4.2. Mol.wt. 333.

To a solution of 0.55 g (1.7 mmole) of the azafluorene (IV) in 70 ml of methanol we added 0.1 g (0.004 g-atom) of metallic sodium. The mixture was heated to boiling, and 0.27 g (2 mmole) of anisaldehyde was added. The mixture was then boiled for 3 min and kept at room temperature for 12 h. We isolated 0.39 g (53%) of the p-methoxybenzylidene derivative (VI) in the form of yellow crystals; mp 183-185°C (from hexane). PMR spectrum: 1.93 (3H, s, O – CH_3), 3.5-3.8 ppm (20H, m, aromatic and olefinic protons). UV spectrum, λ_{max} (log ε): 224 (4.9 sh); 256 (4.86); 286 (4.82); 320 (4.6 sh); 370 nm (4.4). IR spectrum: 1650 cm^{-1} (C=C). Found, %: C 87.6; H 5.6; N 3.5. Mol.wt. 437 (mass spectrometry). $C_{32}H_{23}NO$. Calculated, %: C 87.9; H 5.3; N 3.2. Mol.wt. 437.

LITERATURE CITED

1. J. N. Chatterjea and K. Prasad, J. Indian Chem. Soc., 37, 357 (1960).
2. C. Mayor and C. Wentrup, J. Am. Chem. Soc., 97, 7467 (1975).
3. J. N. Chatterjea and K. Prasad, Beriehte, 93, 1740 (1960).
4. N. S. Prostakov, K. D. Mat'yu, and V. A. Kurichev, Khim. Geterotsikl. Soedin., No. 5, 876 (1967).
5. V. Baliah and A. Ekambaram, J. Indian Chem. Soc., 32, 274 (1955).
6. O. Yu. Magidson and G. A. Garkusha, Zh. Obshch. Khim., 11, 339 (1941).