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ARYLATION, ALKYLATION, REDUCTION, AND PYROLYSIS OF 1H-1-METHYLINDENO[2,1-b]PYRIDINE

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Nucleophilic substitution (phenylation with phenyl lithium) of 1H-1-methylindeno[2,1-b]pyridine occurred at the $C_{(2)}$ and $C_{(4)}$ positions, and electrophilic substitution (methylation and benzylation with halogen derivatives) at $C_{(9)}$. Reduction of the starting anhydrobases gave 1-methyl-1,2,3,9a-tetrahydro-1-azafluorene, and pyrolysis gave 1-azafluorene and 1-azafluorenone.

In a continuation of our work on NH-indenopyridines [1, 2], we have studied the pyrolysis, reduction, and substitution reactions of some anhydrobases such as 1H-1-methylindeno 2, 1-b pyridine (I).

According to quantum mechanical calculations [3], nucleophilic substitution of the indenopyridine I should occur at positions $C_{(4)}$ and $C_{(2)}$. Arylation of compound I with phenyl lithium gave 1H-1-methyl-2-phenyl- and 4-phenylindeno[2,1-b]pyridine (II and III) in approximately equal amounts. A small amount of a crystalline substance, which, from mass-spectral data was assigned the structure 1H-1-methyl-2,4-diphenylindeno[2,1-b]pyridine was also obtained. In the PMR spectra of the anhydrobase II, the 4-H proton signal is further downfield and has a greater coupling constant (8.14 ppm, $J_{3,4}$ = 7.1 Hz) compared with the 2-H proton of its isomer III (7.71 ppm, $J_{2,4}$ = 6.7 Hz); this is characteristic for anhydrobases of this type [2]. The long-wave absorption maximum in the UV spectrum of compound II undergoes a bathochromic shift (608 nm) compared with that of compound III (590 nm).

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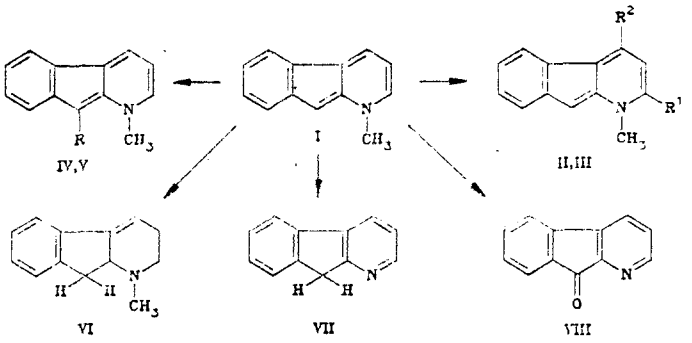

II $R^1=C_6H_5$, $R^2=H$; III $R^1=H$, $R^2=C_6H_5$; IV $R=CH_3$; V $R=C_6H_5CH_2$

Electrophilic substitution — treatment of indenopyridine I with methyl iodide or benzyl chloride, gave, respectively, the hydroiodide of compound IV and the hydrochloride of compound V, which were then converted to 1H-1,9-dimethylindeno[2,1-b]pyridine (IV) and 1H-1-methyl-9-benzylindeno[2,1-b]pyridine (V). The hydrochloride of the anhydrobase V was isolated as high-melting, intensely-colored crystals. The structure of this salt was confirmed by PMR, where in addition to singlets from the methylene and methyl group (at 3.8 and 4.6 ppm), signals from the dihydropyridine ring protons are seen (ABC system). The free anhydrobases IV and V are deep-violet crystalline substances.

Thus, nucleophilic arylation of indenopyridine anhydrobases took place at positions $C_{(2)}$ and $C_{(4)}$ of the π-deficient nitrogen-containing ring, and alkylation with alkyl halides resulted in electrophilic substitution at position $C_{(9)}$ of the π-excessive five-membered ring.

Reduction of compound I with sodium borohydride gave 1-methyl-1,2,3,9a-tetrahydro-1-azafluorene (VI). Earlier, we obtained this compound by reduction of 1-azafluorene iodomethylate with sodium borohydride [4].

Pyrolysis of the anhydrobase I at 650° gave 1-azafluorene VII in up to 50% yield, while pyrolysis in air at 300° gave 1-azafluorenone VIII in ~18% yield.

EXPERIMENTAL

PMR spectra (internal standard — TMS) were recorded on a BS-497 spectrometer (100 Hz). Mass spectra were obtained on an MX-1303 instrument at 70 eV with direct introduction to source. UV spectra were taken on a Hitachi spectrophotometer (in ethanol).

1H-1-Methyl-2-phenyl-, 4-phenylindeno[2,1-b]pyridines (II, III). To a solution of phenyllithium, prepared from 0.13 g (0.19 mmole) of lithium and 1.3 g (8.3 mmole) of bromobenzene in 75 ml of ether, was slowly added a solution of 1 g (5.5 mmole) of indenopyridine I in 75 ml of ether. The mixture was stirred for 1 h, then poured into 150 ml of water. The ether layer was dried over magnesium sulfate. The residue (1.5 g), after removal of the ether, was chromatographed on aluminum oxide (H 24 cm, d 1.1 cm, eluant — a 1:1 mixture of ether and hexane). The first fraction contained 0.15 g (11%) of compound III, as deep-violet crystals, mp 94-95° (from ether and hexane), R_f 0.62. PMR spectrum (acetone-D_6): 7.71 (d, $J_{2,3}$ = 6.7 Hz, 2-H); 6.35 (d, $J_{3,2}$ = 6.7 Hz, 3-H); 6.65 (t, J = 7.5 Hz, 5-H); 6.19 (s, 9-H); 7.58-6.98 (m, arom. protons); 4.01 ppm (s, 1-CH_3). UV spectrum, λ_{max} (log ε): 300 (4.3), 335 sh. (3.90), 480 sh. (3.14), 590 nm (3.50). Mass-spectrum, m/z, %: 257 (100), 256 (5), 242 (19), 183 (29), 105 (36), 77 (29). Found, %: C 88.4, H 5.1, N 5.7. $C_{19}H_{15}N$. Calculated, %: C 88.7, H 5.8, N. 5.5; M 257.

The second fraction contained 0.14 g (10%) of compound II, as deep-violet crystals, mp 76-77°, R_f 0.29. PMR spectrum (acetone-D_6): 8.14 (d, $J_{4,3}$ = 7.1 Hz, 4-H); 7.74-6.70 (m, arom. protons); 6.42 (d, $J_{4,3}$ = 7.1 Hz, 3-H); 6.21 (s, 9-H); 3.54 ppm (s, 1-CH_3). UV spectrum, λ_{max} (log ε): 308 (4.54), 350 (4.0), 480-570 (3.1), 608 nm (3.23). Mass spectrum, m/z, %: 257 (40), 256 (16), 242 (2.5), 182 (26), 154 (52), 105 (100), 77 (73). Found, %: C88.4, H 6.0, N 5.4. $C_{19}H_{15}N$. Calculated, %: C 88.7, H 5.8, N 5.5; M 257.

Finally, the column was washed with ether to give 8 mg of deep violet crystals, mp 99-103°. Mass spectrum: M^+ 333. $C_{25}H_{19}N$. Calculated %: M 333.

1H-1,9-Dimethylindeno[2,1-b]pyridine (IV). A solution of 0.5 g (2.7 mmole) of the indenopyridine I and 1.5 ml (24 mmole) of CH_3I in 25 ml of acetone was refluxed for 3 h.

The precipitate (0.21 g) was separated, dissolved in water, and treated with a 20% potassium hydroxide solution to give 60 mg (11%) of the indenopyridine IV, as dark-violet crystals, mp 160-162°. UV spectrum, λ_{max} (log ε): 485 sh. (2.71), 585 nm (3.36). Mass spectrum, m/z, %: 195 (36), 194 (33), 182 (0), 181 (75), 180 (36), 179 (45), 166 (54), 142 (100), 139 (32), 127 (60). Found, %: N 7.4. $C_{14}H_{13}N$. Calculated, %: N 7.2; M 195.

1H-1-Methyl-9-benzylindeno[2,1-b]pyridine (V). A solution of 0.5 g (2.8 mmole) of compound I and 0.5 g (4 mmole) of benzyl chloride in 30 ml of benzene was allowed to stand for 7 days at room temperature. The material which precipitated was filtered, washed with benzene, and then with ether to yield 0.2 g (23%) of the hydrochloride of compound V, black crystals, mp 187-189°. PMR spectrum (DMSO-D_6): 3.8 (s, 2H, CH_2); 4.6 (s, 3H, CH_3); 6.63 (t, 1H, 3-H); 7.0-7.6 (m, arom. protons); 8.38 (d, $J_{2,3}$ = 6.6 Hz, 2-H); 8.69 (d, $J_{4,3}$ = 7.6 Hz, 4-H); 9.00 ppm (s, 1H, HCl). Found, %: N 4.6. $C_{20}H_{17}N \cdot HCl$. Calculated, %: N 4.6. Treatment of the hydrochloride with alkali gave compound V, as deep-violet crystals, mp 122-125°. Mass spectrum, m/z, %: 271(1), 256 (100), 254 (42), 182 (80), 181 (90), 91 (65), 77 (45). Found, %: N 5.4. $C_{20}H_{17}N$. Calculated, %: N 5.8; M 271.

1-Methyl-1,2,3,9a-tetrahydro-1-azafluorene (VI). To a solution of 1 g (5.5 mmole) of the indenopyridine I in 50 ml of methanol with vigorous mixing was slowly added 0.4 g (11 mmole) of sodium borohydride. The mixture was refluxed for 1 h and 30 ml of water added. The reaction product was extracted with benzene to give 0.44 g (43%) of compound VI, mp 50-51° [4].

Pyrolysis of 1H-1-Methylindeno[2,1-b]pyridine. A flow-through quartz reactor, filled with ground quartz, was heated to 650° and purged with nitrogen; through this was passed a solution of 0.5 g (2.8 mmole) of indenopyridine I. The condensate, after evaporation of the benzene gave 0.4 g of crystals, which were chromatographed on aluminum oxide (eluant 1:1 ether–hexane). First was eluted 0.1 g of diphenyl, followed by 0.25 g (50%) of 1-azafluorene VII, mp 84° [5].

In an analogous experiment at 300° in the presence of air, 1.3 g (7 mmole) of indenopyridine I gave 0.14 g (17.5%) of 1-azafluorenone VIII, mp 127-128° [5], 0.36 g of starting material (I) and 0.25 g of a mixture of compound I and 1-azafluorenone VIII in a ratio of 1:1, which were separated by chromatography.

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