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ELECTROPHILIC SUBSTITUTION OF 1-METHYLINDENO-1H-[2,1-b]PYRIDINE

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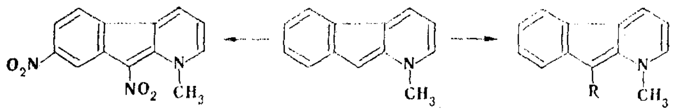
It is shown that electrophilic substitution of 1-methylindeno-1H-[2,1-b]pyridine takes place at the C_9 atom in the case of acylation (acetylation, benzoylation, and formylation), bromination, and nitration. Data from the ^{13}C NMR spectrum of this pseudoazulene confirm sp^2 hybridization of the C_9 atom.

1-Methylindeno-1H-[2,1-b]pyridine (I), which is formed by treatment of 1-azafluorene methiodide with 40% potassium carbonate solution [1], is classified as an aromatic system. In order to study its structure we used ^{13}C NMR spectroscopy. The spectra were obtained under conditions with and without proton decoupling; in this way we were able to assign the signals from five carbon atoms [the chemical shifts and ^{13}C and H spin-spin coupling constants (SSCC) are presented in Table 1].

It is apparent from Table 1 that the signal of the C_9 atom is localized at stronger field; however the $^1J_{C,H}$ value of 166 Hz constitutes evidence for its sp^2 hybridization [2], just as does the $^3J_{9\text{-}C,\ 8\text{-}H}$ value of 4 Hz. Thus the aromatic character of the five-membered ring of this pseudoazulene is confirmed. With respect to the chemical shift of 85.4 ppm for the C_9 atom (according to the established correlation of the chemical shifts of the ^{13}C nuclei with the π density in aromatic systems [3]), this ring fits into the category of aromatic anions. Quantum-chemical calculations of the pseudoazulene system [4] also show increased π-electron density on the C_9 atom, from which it follows that it would be the center of electrophilic substitution.

In order to obtain substituted 1-methylindeno-1H-[2,1-b]pyridines and to experimentally confirm the direction of its electrophilic substitution pseudoazulene I was subjected to acylation, formylation, bromination, and nitration.



VI I II-V

II $R=COCH_3$; III $R=COC_6H_5$; IV $R=CHO$; V $R=Br$

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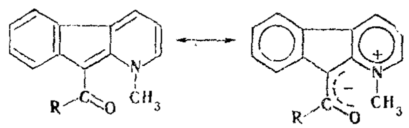
TABLE 1. Parameters of the ^{13}C NMR Spectrum of 1-Methylindeno-1H-[2,1-b]pyridine (I)

Carbon atoms	δ, ppm	$J_{^{13}C,H}$, Hz
1-CH_3	41,9	$^1J_{C,H}=138$; $^4J_{CH_3,\,9\text{-}H}=4$
C_2	133,3	$^1J_{C,H}=176$; $^3J_{2\text{-}C,\,CH_3}=3$; $^3J_{2\text{-}C,\,4\text{-}H}=10$
C_3	102,5	$^1J_{C,H}=164$; $^2J_{3\text{-}C,\,2\text{-}H}=4$; $^2J_{3\text{-}C,\,4\text{-}H}=1{,}5$
C_9	85,4	$^1J_{C,H}=166$; $^3J_{9\text{-}C,\,8\text{-}H}=4$
C_{10}	142,6	

1-Methyl-9-acetylindeno-1H-[2,1-b]pyridine (II) was obtained in quantitative yield by acetylation of pseudoazulene I with acetic anhydride in acetic acid. Its benzoyl analog III is formed by treatment of I with benzoyl chloride under the conditions of the Schotten–Baumann reaction. 1-Methyl-9-formylindeno-1H-[2,1-b]pyridine (IV) was obtained by Vilsmeier formylation of pseudoazulene I, and 1-methyl-9-bromoindeno-1H-[2,1-b]pyridine (V) was isolated by bromination of I in carbon tetrachloride.

Substituted indenopyridines II-V were isolated in the form of deeply colored crystalline substances. Absorption at 440-690 nm, which is characteristic for pseudoazulenes, is observed in their UV spectra.

Weak absorption bands (~1730 cm^{-1}) are observed in the IR spectra of acyl derivatives II-IV in the usual absorption region of the carbonyl group. However, in addition to absorption bands of aromatic rings (1600, 1580, and 1500 cm^{-1}), an intense absorption band at 1544-1552 cm^{-1}, which can evidently be ascribed to the vibrations of the carbonyl group of the resonance zwitter-ion structure, is present in the 1500-1600 cm^{-1} region for all three acyl derivatives.



1-Methyl-7,9-dinitroindeno-1H-[2,1-b]pyridine (VI) is formed in 7% yields as a result of the nitration of pseudoazulene I with acetyl nitrate at –5°C. An intense (78%) molecular-ion peak is observed in its mass spectrum. Intense absorption bands of nitro groups (1522 and 1340 cm^{-1}) are present in the IR spectrum. The positions of the nitro groups were established from the PMR spectrum, in which we were able to assign the signals of all of the aromatic protons by means of analysis with a computer. The SSCC obtained ($J_{5,6}$ = 8.5 Hz and $J_{6,8}$ = 2Hz) confirm the position of the second nitro group attached to the C_7 atom. The low yield of dinitro derivative VI is explained by rapid oxidation and polymerization of pseudoazulene I, which is unstable under the nitration conditions. Dinitro derivative VI is also colored, and the absorption maximum in its UV spectrum at 410 nm corresponds to its pseudoazulene structure.

EXPERIMENTAL

The PMR spectra were recorded with BS-497 (100 MHz) and Brucker WP-80 (80 MHz) spectrometers with tetramethylsilane as the internal standard. The ^{13}C NMR spectrum was obtained with a Brucker WP-80 spectrometer under pulse conditions without proton decoupling and with noise decoupling; the pulse duration was 7 μsec with a 2-5 min lag between the pulses. Indenopyridine I was studied in the form of a saturated solution in C_6D_6 with tetramethylsilane as the internal standard. The mass spectra were obtained with an MKh-1303 spectrometer, the IR spectra of KBr pellets were recorded with a UR-20 spectrometer, and the UV spectra of solutions in alcohol were obtained with a UV-vis spectrophotometer.

1-Methyl-9-acetylindeno-1H-[2,1-b]pyridine (II). A solution of 1 g (5.5 mmole) of indenopyridine I in 18 ml (0.18 mole) of acetic anhydride and 10.6 ml of acetic acid was refluxed for 5 h, after which it was poured into 50 ml of water, and the aqueous solution was made alkaline to pH 9. The precipitate was separated and washed with water to give 1.2 g (98%) of II as black crystals with mp 150-152°C (from acetone). IR spectrum: 1729 (m) and 1544 cm^{-1}(s). UV spectrum, λ_{max}: 460, 580, and 690 nm. Mass spectrum, m/z (%): 223 (51), M^+; 208 (65), $[M-CH_3]^+$; 205 (38), $[M-H_2O]^+$; 181 (100); 166 (50). Found: C 80.3; H 6.6; N 6.5%. $C_{15}H_{13}NO$. Calculated: C 80.7; H 6.3; N 6.3%; M 223.

1-Methyl-9-benzoylindeno-1H-[2,1-b]pyridine (III). A 2-ml sample of benzoyl chloride was added dropwise with vigorous stirring to a suspension of 0.9 g (5 mmole) of indenopyridine I in 10% sodium hydroxide solution, and the mixture was heated at 50°C for 1 h. It was then cooled, and the precipitate was separated and washed with water to give 0.9 g of crystals, which were purified with a column (25 by 4 cm) filled with aluminum oxide by elution with ether—alcohol (30:1) to give 0.8 g (56%) of dark-brown crystals of III with mp 140-142°C (from acetone). PMR spectrum (80 MHz, d_6-DMSO, 60°C): 4.02 (s, CH_3), 7.01 (3-H), 8.10 ($J_{2,3}$ = 6.5 Hz, $J_{2,4} \cong$ 0.8 Hz, 2-H), 8.52 ppm ($J_{4,3}$ = 7.5 Hz, 4-H) — pyridine ring protons, and AMX system. IR spectrum: 1730 (w) and 1546 cm^{-1} (s). UV spectrum, λ_{max} (log ε): 385 (4.0) and 480 nm (sh, 3.72). Mass spectrum, m/z (%): 285 (55), M^+, 270 (13), $[M-CH^3]^+$; 208 (100), $[M-C_6H_5]^+$, 180 (47), $[M-COC_6H_5]^+$. Found: C 84.1, H 5.4, N 4.9%. $C_{20}H_{15}NO$. Calculated: C 84.2, H 5.3, N 5.3%; M 285.

1-Methyl-9-formylindeno-1H-[2,1-b]pyridine (IV). A 0.24-ml sample of phosphorus oxychloride was added slowly at 0°C to 0.83 ml (9 mmole) of freshly distilled dimethylformamide (DMFA), and the mixture was maintained at 20°C for 1 h. A solution of 0.36 g (2 mmole) of indenopyridine I in 2 ml of DMF was then added, and the reaction mixture was heated at 40°C for 3 h. Ice (6 g) was added to the cooled mixture, and the aqueous mixture was made alkaline to pH 8. The precipitate (0.3 g) was separated and dissolved in 3 ml of DMSO, the solution was treated with 3 ml of water and made alkaline to pH 10, and the precipitate was separated and dried to give 84 mg (20%) of dark-cherry-red crystals of IV with mp 110-111°C. PMR spectrum (100 MHz, d_6-DMSO, 70°C): 4.45 (s, CH_3) and 10.35 ppm (s, 1H, CH_o); pyridine ring protons, and AMX system: 7.17 (3-H), 8.28 (2-H), 8.67 ppm (4-H); $J_{2,3}$ = 6.5, $J_{2,4}$ = 1.1, and $J_{3,4}$ = 7.5 Hz; phenylene protons: 7.24 (6-H), 7.47 (7-H), 8.18 (5-H), and 8.60 ppm (8-H); $J_{8,7} \approx J_{5,6} \approx J_{6,7} \simeq$ 7.5, $J_{8,6} = J_{5,7}$ = 1.5, $J_{8,5}$ = 0.8 Hz. IR spectrum: 1552 cm^{-1} (s). UV spectrum, λ_{max}(log ε): 440 nm (3.3). Mass spectrum, m/z (%): 209 (100), M^+; 208 (56), $[M-H]^+$; 180 (48), $[M-HC)]^+$; 166 (35), 152 (43). Found: C 80.3; H 5.6; N 6.4%. $C_{14}H_{11}NO$. Calculated: C 80.4; H 5.3; N 6.7%; M 209.

1-Methyl-9-bromoindeno-1H-[2,1-b]pyridine (V). A 0.8-g (5 mmole) sample of bromine was added dropwise with stirring to a solution of 1 g (5.5 mmole) of indenopyridine I in 25 ml of carbon tetrachloride, and the resulting precipitate was separated, washed with ether, and dissolved in 5 ml of DMF. The precipitate that formed when the solution was made alkaline and diluted with water (20 ml) was separated, washed with water, and crystallized from aqueous DMF and dried to give 0.9 g (63%) of dark-brown crystals of V with mp 204-205°C. PMR spectrum (60 MHz, CF_3COOH): 6.37 (s, 1H, 9-H); 4.61 ppm (s, CH_3). Mass spectrum, m/z (%): 261 (1), M^+; 259 (1), M^+; 181 (41); 153 (18); 127 (23); 94 (82) $[CH_3Br]^+$; 96 (100) $[CH_3Br]^+$; 81 (27); 79 (23). UV spectrum, λ_{max}: 580 nm. Found: C 59.7; H 4.4; N 5.2%. $C_{13}H_{11}BrN$. Calculated: C 60.0; H 4.2; N 5.4%; M 261, 259.

1-Methyl-7,9-dinitroindeno-1H-[2,1-b]pyridine (VI). A 2.5-ml sample of nitric acid (sp.gr. 1.40) containing a catalytic amount of sulfuric acid was added gradually with stirring in the course of an hour at −5°C to a solution of 1 g (5.5 mmole) of indenopyridine I in 15 ml of acetic anhydride, and the mixture was maintained under these conditions for 7 h. It was then poured over ice, and the aqueous mixture was made alkaline to pH 10. The precipitate was separated and purified with a column (30 by 4 cm) filled with aluminum oxide by elution with ether—alcohol (1:1) to give 0.1 g (7%) of brown crystals of VI with mp 233-235°C (from alcohol). PMR spectrum (80 MHz, d_6-DMSO): 4.38 (s, CH_3), phenylene protons, an ABX system (calculated with a BNC-28 computer by means of the ITRCAL iteration program): 8.16 (5-H), 8.15 (6-H), and 8.98 ppm (8-H); $J_{5,6}$ = 8.5; $J_{6,8}$ = 2 Hz; pyridine ring protons, an AMX system: 8.42 (2-H), 7.47 (3-H), 8.95 ppm (4-H), $J_{2,3}$ = 6.2, $J_{3,4}$ = 7.5, $J_{2,4} \simeq$ 0.7 Hz. IR spectrum: 1522 and 1340 cm^{-1}. UV spectrum, λ_{max}(log ε): 410 nm (4.34). Mass spectrum, m/z (%): 271 (78), M^+, 256 (9), $[M-CH_3]^+$, 241 (90), $[M-NO]^+$, 226 (36), 195 (100). Found: C 57.8; H 3.6; N 15.1%. $C_{13}H_9N_3O_4$. Calculated: C 57.7; H 3.7; N 15.5%; M 271.

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