REACTION OF DIALKYLPYRIDINES WITH STYRENE AND MASS-SPECTROMETRIC BEHAVIOR OF THE REACTION PRODUCTS

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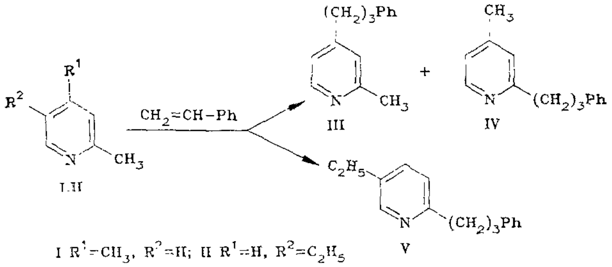
The reaction of 2,4-dimethylpyridine with styrene gives 2-(3'-phenyl-propyl)-4-methyl- and 2-methyl-4-(3'-phenylpropyl)pyridine, but in the case of 2-methyl-5-ethylpyridine, the reaction gives only 2-(3'-phenylpropyl)-5-ethylpyridine. The mass spectra of the compounds obtained have been studied.

Styrene is added to 2-, 3-, and 4-methylpyridine with the formation of the corresponding 2-, 3-, and 4-phenylpropylpyridines [1]. It seemed to be of interest to study the direction of the reactions of styrene with dialkylated pyridines. For this purpose we carried out the reactions of 2,4-dimethylpyridine (I) and 2-methyl-5-ethylpyridine (II) with styrene in the presence of metallic sodium at 150-160°C. In this case, it was found that two products (III and IV) form from 2,4-dimethylpyridine (I).



In this case of 2,4-dimethylpyridine (I), the methyl group in position 4 was found to be more reactive, since compound III forms in this reaction with a greater yield (22%) than compound IV (10%). At the same time, the reaction of 2-methyl-5-ethylpyridine with styrene gives a single product V with a 60% yield. In this case, the ethyl group is not affected, and the reaction takes place only at the methyl group.

The structures of compounds III-V were confirmed by the data from the IR, PMR, and mass spectra. The IR spectra of isomeric methylpyridines III and IV are identical. In the PMR spectra of compounds III and IV the protons of the methylene and methyl groups form a group of lines at 1.46-2.74 ppm. The aromatic protons produce a multiplet at 6.34-6.95 ppm, and the signals at 8.12-8.28 ppm may be assigned to the CH═N— proton. The PMR spectrum of compound V shows a triplet for the ethyl group at 0.96 ppm with a spin-spin coupling constant $J_{CH_3CH_2}$ = 7.2 Hz. The methylene protons form a multiplet at 1.62-2.68 ppm. The signals at 6.42-6.98 ppm are assigned to the aromatic protons, and the broadened signal at 8.22 ppm is assigned to the —CH═N— proton. The ratio between 2- and 4-methylpyridines III and IV was determined with the aid of GLC.

TABLE 1. Intensity of Characteristic Peaks in the Mass Spectra of Compounds III-V (%Σ_{40})

Compound	W_m	F_1	F_2	F_3	F_4	F_5
III	3,35	3,5	5,9	4,1	31,7	7,5
IV	4,9	2,8	5,7	3,1	29,4	6,8
V	0,8	13,3	2,0	—	2,3	28,8

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TABLE 2. Mass Spectra of Compounds III-V*

Compound	Values of m/z (relative intensity, %)
III	211 (8), 196 (12), 134 (13), 120 (19), 107 (100), 106 (11), 92 (13), 91 (24), 79 (8), 77 (11), 65 (12)
IV	211 (15), 134 (11), 120 (20), 107 (100), 106 (10), 92 (10), 91 (22), 79 (7), 77 (8), 65 (8), 43 (13)
V	225 (2), 134 (7), 121 (8), 120 (46), 107 (9), 106 (40), 92 (21), 91 (100), 79 (8), 77 (10), 65 (10)

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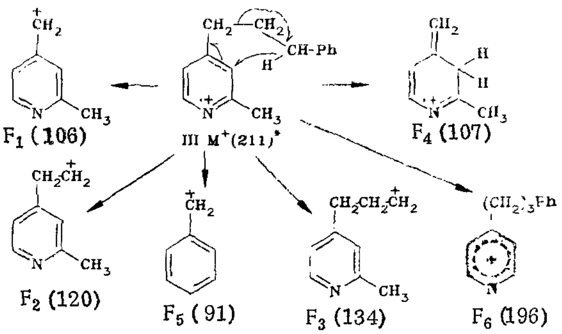
*The peak of the molecular ion and the 10 most intense peaks are given.

The mass-spectrometirc investigation established that the stability (W_M) of the molecular ions (M^+) of compounds III-V ranges from 0.8 to 4.9% (see Table 1). The mass spectra of isomeric methylpyridines III and IV do not differ significantly (see Table 2).

The main paths for the fragmentation of the molecular ions of methylpyridines III and IV are associated with the splitting of the α, β, γ C—C bonds (relative to the pyridine nucleus) and the formation of the F_1, F_2 and F_3 ions. The characteristic features of the fragmentation of M^+ in the case of compounds III and IV include the elimination of a neutral styrene molecule as a result of a McLafferty rearrangement and the formation of the F_4 fragment ion. Cleavage of the β bond results in the formation of the F_5 benzyl cation along with the F_2 ion (Scheme 1).

It should be specially stressed that in the case of 2-methyl-4-(3'-phenylpropyl)pyridine (II), the mass spectrum contains a fairly intense peak for the $[M - CH_3]^+$ ion (F_6), which corresponds to the elimination of the methyl group at position 2 from M^+, which is characteristic of 2-methylpyridine. It was found that the elimination of a methyl radical from position 2 is more advantageous than its elimination from position 3 or 4 [2].

Scheme 1



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*The values of m/z are given in parentheses.

Examination of the mass spectra of pyridines III and IV shows that their fragmentation under electron impact is analogous to the fragmentation of alkylpyridines [3].

The mass spectra of 2-(3'-phenylpropyl)-5-ethylpyridine (V) were also studied. From Table 1 it is seen that the replacement of the methyl group in position 4 in the molecule of methylpyridine III by an ethyl residue in position 5 sharply lowers the stability of the molecule with respect to electron impact, making the rearrangement with the elimination of a styrene molecule from M^+ less likely.

The main fragments in the mass spectrum of compound V form as a result of the cleavage of the α or β C—C bond with closure of the carbocationic center at the nitrogen atom, and the peak of the $[C_6H_5-CH_2]^+$ ion (91) has the maximum intensity in the spectrum (Table 2).

EXPERIMENTAL

The mass spectra were recorded on an MKh-1303 spectrometer with direct admission of the sample into the ion source and with an energy of the ionizing electrons equal to 50 eV. The PMR spectra were measured on an RYa-2310 spectrometer (60 MHz) with HMDS as an external reference. The IR spectra were obtained on a UR-20 instrument in thin layers and in KBr tablets. The GLC was performed on an LKhM-8MD instrument (3000 × 3 mm column) with 15% silicone DS-550 on Chromaton AWDMS (0.2-0.25 mesh) and helium as the carrier gas.

2-(3-Phenylpropyl)-4-methyl- and 2-Methyl-4-(3'-phenylpropyl)pyridine (III, IV). A 10.7-g portion (0.1 mole) of 2,4-dimethylpyridine and 0.8 g of metallic sodium are placed in a three-necked flask, heated to 160°C, and given a dropwise addition of 10.5 g (0.1 mole) of styrene. When the addition is completed, the reaction mass is heated for an additional 2 h at 150-160°C. Then it is cooled, given a slow addition of 10 ml of water with stirring, and left to stand. Afterwards the upper layer is separated, dried by boiling with granulated potassium hydroxide for 2 h, cooled, and filtered. Vacuum distillation gives 4.6 g (a 21.8% yield) of pyridine III [bp 195-200°C (5 mm Hg, 5.7 hPa), n_D^{20} 1.5560% and 2.1 g (10.0%) of isomer IV [bp 240-244°C (5 mm, 5.7 hPa), n_D^{20} 1.5700]. IR spectrum: 1608, 1570, 1498 (C═C) arom.); 3065, 3030, 3015 (CH arom.); 2000-1600 (form of absorption bands typical of monosubstituted benzene rings); 2920, 2865 (νCH_2); 2945, 2875 (νCH_3); 1455 and 1380 cm^{-1} (δ, CH^2, CH_3). PMR spectrum (CCl_4): 1.98 (3H, s, CH_3), 2.34 (6H, m, CH_2), 6.34-6.95 (7H, m, arom. protons), 8.22 ppm (1H, m, —HC═N—).

Found for isomer III: c, 85.2; H, 7.8; N, 7.0%. Found for isomer IV: C, 85.4; H, 8.1; N, 6.5%. Calculated for $C_{15}N_{17}N$: C, 85.3; H, 8.06; N, 6.63%.

2-(3'-Phenylpropyl)-5-ethylpyridine (V). A 24.3-g portion (0.2 mole) of pyridine II and 0.3 g of metallic sodium are placed in a three-necked flask, heated to 140°C, and then given an addition of 21 g (0.2 mole) of styrene with stirring. When the addition of the styrene is completed, the reaction mass is heated for an additional 1 h 30 min at 135-140°C, cooled, given a slow addition of 4 ml of water with stirring, and left to stand. Afterwards the upper layer is separated, dried with KOH for 2 h, cooled, and filtered. Vacuum distillation gives 27 g (a 60% yield of product V with bp 260-262°C (6 mm Hg, 8 hPa), n_D^{20} 1.5735. IR spectrum: 843, 790 (2,5-substituted pyridine ring); 700, 750, 455, 493, 565, and 600 (monosubstituted benzene ring); 2862, 2935 (CH_2); 2872, 2965 cm^{-1} (CH_3). PMR spectrum (CCl_4): 0.96 (3H, t, CH_3CH_2), 2.18 (6H, m, CH_2), 6.42-6.96 (7H, m, arom. protons), 8.25 ppm (1H, m, —CH═N—). Found: C, 86.0; H, 9.1; N, 6.82%. Calculated for $C_{16}H_{19}N$: C, 85.3; H, 8.5; N, 6.2%.

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