MASS SPECTRA OF BENZYLPYRIDINES

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The mass spectra of dimethylbenzyl- and dimethyldibenzylpyridines at different ionizing electron energies were investigated. The anomalously low intensities of the molecular ion peaks of 3,4-dibenzylpyridines, as compared with the 2,5-isomers, and the greater probability of the formation of primary $(M-2)^+$ ions in the mass spectra are explained by the synchronous loss of a neutral H_2 particle and the formation of cyclic fragment ions from the weakly excited molecular ions.

The primary process of dissociative ionization under the influence of electron impact of the simplest benzylpyridines and isomeric p-tolylpyridines [1] consists in the loss of a proton of the benzyl (methyl) group with subsequent rearrangement of the resulting fragment ion to a pyridyltropylium ion, which then undergoes subsequent disintegration with the loss of HCN. Dissociative ionization at the C–C bond that connects the two aromatic rings was not a primary process.

In the present paper, we have studied the mass spectral behavior of 4-methyl-2-benzyl- (I), 2,5-dimethyl-4-benzyl- (II), 2,5-dimethyl-4,6-dibenzyl- (III), 2,5-dimethyl-3,4-dibenzyl- (IV), 2,5-dimethyl-4-(p-tolylmethyl)- (V), and 2,5-dimethyl-3-benzyl-4-(p-tolylmethyl)pyridine (VI). The synthesis of these compounds was described in [2].

The mass spectra were recorded with an MKh-1303 spectrometer with a modified recording system at 250°C. The accelerating voltage was 2 kV, the emission current was 1.5 mA, and the ionizing electron energies were 50, 30, 20, and 15 eV. The mass spectra obtained at an ionizing electron energy of 50 eV are presented in Table 1.

TABLE 1. Mass Spectra of Methylbenzylpyridines*

I: 39 (9,5), 50 (5,1), 63 (7,2), 65 (11,1), 77 (10,6), 83,5 (6,4), 89 (5,3), 91 (19,2), 105 (9,3), 115 (9,3), 139 (5,6), 141 (6,8), 166 (6,6), 167 (32,3), 168 (100,0), 169 (7,4), 170 (8,8), 183 (14,3); $W_M=3{,}0$; $S_{1/2}$ 4.

II: 39 (42,3), 40 (21,0), 41 (21,9), 42 (19,0), 43 (13,4), 50 (7,1), 51 (23,7), 52 (11,5), 53 (12,7), 63 (14,7), 64 (6,2), 65 (36,5), 76 (8,4), 77 (40,8), 78 (18,6), 79 (11,0), 89 (12,0), 90 (7,1), 91 (84,7), 92 (9,1), 101 (6,0), 102 (6,6), 104 (6,8), 106 (13,6), 115 (33,9), 118 (21,5), 119 (100,0), 120 (64,4), 128 (20,3), 129 (8,7), 139 (9,1), 141 (19,0), 151 (5,4), 152 (19,6), 153 (17,6), 165 (8,9), 166 (6,9), 167 (27,7), 168 (7,2), 180 (19,8), 181 (36,5), 182 (44,1), 183 (9,6), 194 (8,3), 195 (11,0), 196 (47,5), 197 (100,0), 198 (16,5); $W_M=6{,}5$; $S_{1/2}$ 15.

III: 65 (9,9), 77 (7,4), 91 (23,4), 128 (7,5), 152 (7,5), 153 (5,8), 165 (5,5), 180 (8,6), 181 (8,7), 194 (13,1), 195 (14,6), 196 (10,7), 208 (16,2), 209 (5,4), 270 (5,6), 272 (25,7), 273 (6,4), 284 (18,6), 285 (7,7), 286 (94,5), 287 (100,0), 288 (33,0); $W_M=11{,}8$; $S_{1/2}$ 16.

IV: 39 (5,6), 41 (7,4), 43 (8,8), 51 (7,9), 65 (6,1), 77 (12,5), 78 (5,8), 79 (5,6), 91 (7,2), 127 (6,4), 128 (5,8), 151 (6,0), 152 (16,0), 153 (5,2), 165 (24,1), 166 (7,9), 167 (5,8), 178 (19,3), 179 (19,8), 180 (5,3), 191 (5,0), 192 (13,7), 193 (5,8), 194 (68,2), 195 (11,9), 206 (15,4), 207 (48,0), 208 (19,3), 215 (7,9), 226 (7,7), 227 (5,9), 228 (14,2), 229 (8,5), 239 (6,4), 241 (5,4), 254 (6,0), 268 (8,6), 269 (6,0), 270 (35,6), 271 (9,1), 284 (18,2). 285 (100,0), 286 (30,9), 297 (7,4); $W_M=0{,}4$; $S_{1/2}$ 24.

*Ion peaks with an intensity > 5.0 relative to the maximum are presented.

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TABLE 1 (continued)

V: 39 (10,6), 40 (6,2), 41 (6,2), 42 (6,0), 43 (82,1), 65 (5,7), 77 (15,0), 78 (6,4), 79 (8,3), 105 (18,0), 115 (5,8), 118 (6,7), 119 (100,0), 120 (11,0), 128 (5,5), 152 (5,9), 153 (5,6), 180 (5,0), 181 (15,0), 194 (8,3), 195 (8,5), 196 (60,6), 197 (5,0), 210 (12,9), 211 (55,4), 212 (9,3); $W_M = 7,7$; $S_{1/2}$ 9.

VI: 39 (53,5), 40 (7,3), 41 (11,9), 42 (7,3), 43 (12,1), 51 (5,5), 65 (8,9), 77 (15,4), 78 (6,1), 79 (8,2), 91 (42,0), 101 (5,4), 105 (5,0), 119 (56,4), 120 (9,5), 127 (6,4), 128 (8,2), 141 (6,1), 152 (10,8), 153 (6,1), 165 (18,6), 166 (7,5), 178 (14,7), 179 (7,5), 180 (5,6), 181 (9,3), 191 (6,4), 192 (7,5), 193 (16,1), 194 (11,4), 195 (5,7), 196 (12,9), 206 (25,7), 207 (14,3), 208 (79,0), 209 (14,0), 210 (8,6), 211 (31,4), 212 (5,0), 220 (5,4), 221 (22,2), 228 (6,1), 239 (6,5), 241 (6,1), 242 (5,5), 243 (5,4), 268 (8,1), 269 (5,4), 284 (42,5), 285 (10,4), 298 (10,4), 299 (100,0), 300 (27,2), 301 (4,1); $W_M = 0,3$; $S_{1/2}$ 29.

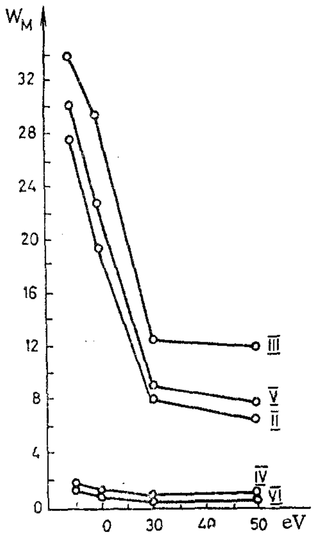


Fig. 1. Dependence of W_M on the ionizing electron energy.

It should be noted that I, II, and V, which contain one, two, and three methyl groups, are less stable than unsubstituted 2- and 4-benzylpyridines, and, as in the case of the latter, the 2 isomer (compound I) is less resistant to electron impact than the 4 isomer, which contains one more methyl group (II). The introduction of a methyl group into the benzyl grouping somewhat stabilizes the molecule (V); this was also noted previously in a comparison of the stabilities of phenyl- and p-tolylpyridines [1, 3].

The introduction of a second benzyl grouping into the 2,5-dimethyl-4-benzylpyridine molecule (II) has a different effect on the stability of the molecular ion – the presence of a second benzyl grouping in the 2 position (III) makes the molecule twice as stable, while a second benzyl group in the 3 position lowers the stability of the molecule by an order of magnitude (IV and VI).

As one should have expected, the stability of the molecular ions increases as the ionizing electron energy decreases from 50 to 15 eV (Fig. 1), but an appreciable change in the W_M value is observed only for II, III, and V: this effect is minimal in IV and VI (which have benzyl groups in the 3 position of the pyridine ring).

At the same time, a considerable portion of the total ion current in the case of IV and VI goes into the $(M-2)^+$ ions, which constitute 7.3-6.9% of the total ion current at 50 eV. It is remarkable that the intensity of these ions increases to 27% as the energy is lowered to 15 eV, while the intensity of the analogous peak for III changes only slightly and does not exceed 2% of the total ion current (Fig. 2).

These facts compel us to assume the presence in IV and VI of definite steric conditions that favor the ready elimination of hydrogen from their molecules to form a relatively stable ion. The absence of intense $(M-H)^+$ ion peaks excludes the possibility of the successive loss of two hydrogen atoms.

Analysis of Briegleb–Stuart models shows that in the case of 2,5-dimethyl-3,4-dibenzylpyridine and 2,5-dimethyl-3-benzyl-4-(p-tolylmethyl)pyridine, the benzyl groups are very close to one another and have an extremely insignificant rotational mobility. This configuration probably promotes the formation of an ion with the loss of a hydrogen molecule, and one atom may break off from the benzyl group, while the other may break off from the phenyl ring.

The activation energy of this process is low, and the greater intensity of the $(M-H_2)^+$ ion peak for an electron energy of 15 eV once more confirms the decisive effect of steric factors on the direction of dissociation and also explains the anomalously low W_M values of the 3,4-isomers. The low activation energy of the $(M-H_2)^+$ process may lead to a large "consumption" of molecular ions that have an insignificant internal energy and thereby lower the intensity of the molecular ion peak.

The principal directions of disintegration of the investigated molecules differ from the relatively simple alkyl- and phenylpyridines [3, 4]. In the latter, the primary fragment ions, which are formed from

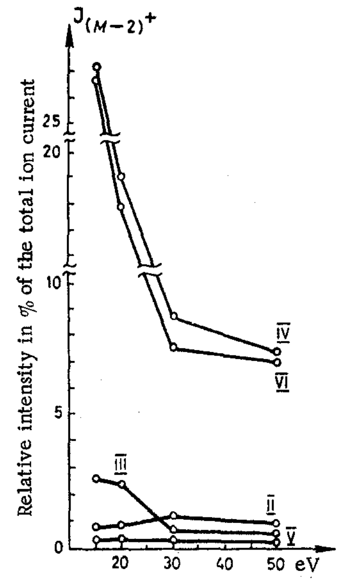
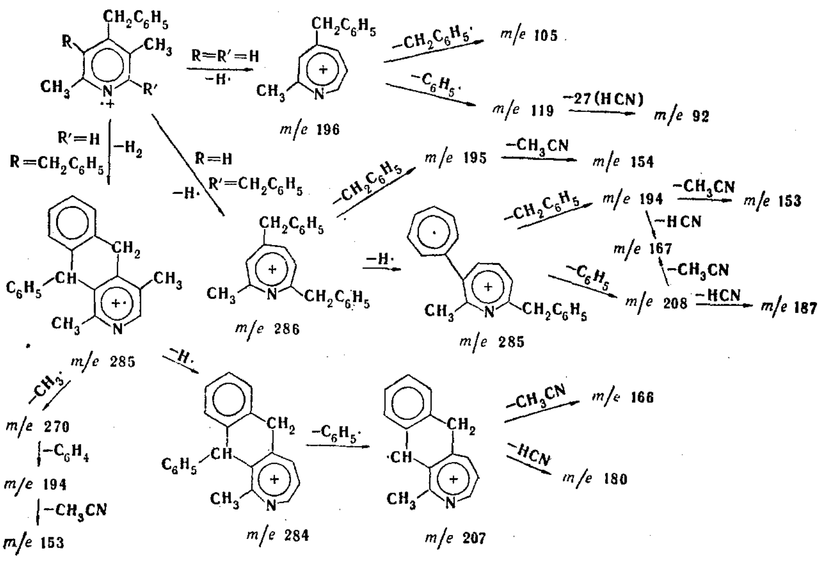


Fig. 2. Dependence of the intensity of the $(M-2)^+$ ion on the ionizing electron energy.



the molecular ion, disintegrated further with the elimination of HCN to form a series of intense hydrocarbon ions. However, the compounds investigated in the present study, after the loss of one or two hydrogen atoms in the second and third stages, eliminate substituents (CH_3, C_6H_5, $C_6H_5CH_2$, etc.) rather than HCN. This leads to the development of nitrogen-containing ions, the fraction of which accounts for about half the total ion current. However, the elimination of HCN generally occurs only from these secondary fragments.

It should be noted that in the cleavage of the pyridyl-benzyl C–C bond, the charge remains primarily on the benzyl residue, and the intensity of the ion with mass 91 is always considerably higher than that of the $(M-91)^+$ ion. We have previously noted a similar phenomenon during an analysis of the mass spectra of benzylpyrazoles [5].

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