2-(2,2-Dipropoxyacetyl)-5-methylthiophene (III). PMR spectrum (CCl_4): 0.88 (6H, t, J = 7.0 Hz, CH_3CH_2); 1.58 (4H, m, J = 6.6 Hz, CH_3CH_2); 2.40 (3H, s, CH_3); 3.42 and 3.52 (4H, t and t, J = 6.0 Hz, OCH_2); 4.80 (1H, s, OCHO); 6.68 (1H, d, $J_{3,4}$ = 3.5 Hz, 4-H); 7.47 ppm (1H, d, $J_{4,3}$ = 3.5 Hz, 3-H).

2-(2,2-Dipropoxyacetyl)-5-methylfuran (IV). PMR spectrum (CCl_4): 0.88 (6H, t, J = 7.0 Hz, CH_3CH_2); 1.56 (4H, m, J = 7 Hz, CH_3CH_2); 2.30 (3H, s, CH_3); 3.48 and 3.54 (4H, t and t, J 6 Hz, OCH_2); 4.90 (1H, s, OCHO); 6.08 (1H, d, $J_{3,4}$ = 3.3 Hz, 4-H); 7.24 ppm (1H, d. d., $J_{4,3}$ = 3.3 Hz, 3-H).

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MASS-SPECTROMETRIC BEHAVIOR OF N-SUBSTITUTED 2-METHYL-3-ACETYL PYRROLES

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UDC 547.741:543.51

In the dissociation of N-substituted derivatives of 2-methyl-3-acetylpyrroles by the action of electron impact, the methyl group splits off from the acetyl substituent, and then the exocyclic N—C bond is ruptured due to the preferential localization of the charge on the $C_{(2)}$—$C_{(3)}$ bond in the pyrrole ring.

It is known that under electron impact, 1-alkylpyrroles preferentially eliminate the alkyl group in the form of an olefin or that, as the result of splitting of the C—C β-bond in the aliphatic radical, stable 1-methylenepyrrolyl cations are formed [1, 2]. However, in the case of acylhetarenes, especially 2-acetylpyrrole, stable acylium ions are formed [3, 4]. It was therefore of interest to study the character of the dissociative ionization processes of pyrrole derivatives simultaneously containing an alkyl (aryl) substituent at the nitrogen atom and an acetyl group at the β-position of the heterocyclic ring. We obtained compounds I-IX by the reaction of 2-methyl-5-ethoxy-3-acetyl-4,5-dihydrofuran with primary amines. Thei mass spectra are given in Table 1.

Table 1 shows that the stability of the molecular ions (M^+) is of an order of magnitude of 10-14%, and decreases uniformly with increase in the length of the aliphatic radical, but in the case of N-aryl derivatives practically does not change in the presence of electron-dono

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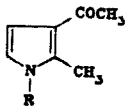
0009-3122/87/2306-0641$12.50

TABLE 1. Mass Spectra of N-Substituted 2-Methyl-3-acetylpyrroles*



I–IX

Compound	R	m /z values (relative intensity, %)
I	H	123 (49), 108 (100), 80 (15), 59 (13), 53 (28), 52 (21), 43 (17), 42 (45), 40 (12), 39 (16)
II	CH_3	137 (40), 122 (100), 94 (5), 87 (7), 59 (7), 53 (14), 44 (12), 42 (24), 41 (29), 40 (10)
III	C_3H_7	165 (43), 150 (100), 123 (7), 122 (8), 108 (43), 94 (8), 80 (6), 53 (10), 42 (41), 40 (17)
IV	C_4H_9	179 (53), 164 (100), 150 (8), 137 (16), 123 (10), 122 (29), 108 (57), 94 (35), 53 (14), 42 (59)
V	C_6H_{11}	205 (6), 190 (6), 123 (9), 108 (19), 99 (4), 82 (3), 69 (4), 56 (36), 42 (24), 39 (100)
VI	C_6H_5	199 (36), 184 (100), 156 (5), 154 (6), 128 (6), 115 (4), 77 (24), 53 (10), 51 (19), 42 (19)
VII	p-$CH_3C_6H_4$	213 (36), 198 (100), 170 (4), 154 (8), 128 (6), 91 (14), 65 (13), 53 (8), 51 (7), 42 (20)
VIII	p-$CH_3OC_6H_4$	229 (44), 214 (100), 199 (10), 108 (3), 92 (6), 77 (15), 64 (8), 63 (9), 43 (16), 42 (34)
IX	$C_6H_5CH_2$	213 (25), 198 (32), 170 (3), 122 (3), 91 (100), 65 (16), 51 (4), 44 (9), 42 (14), 40 (4)

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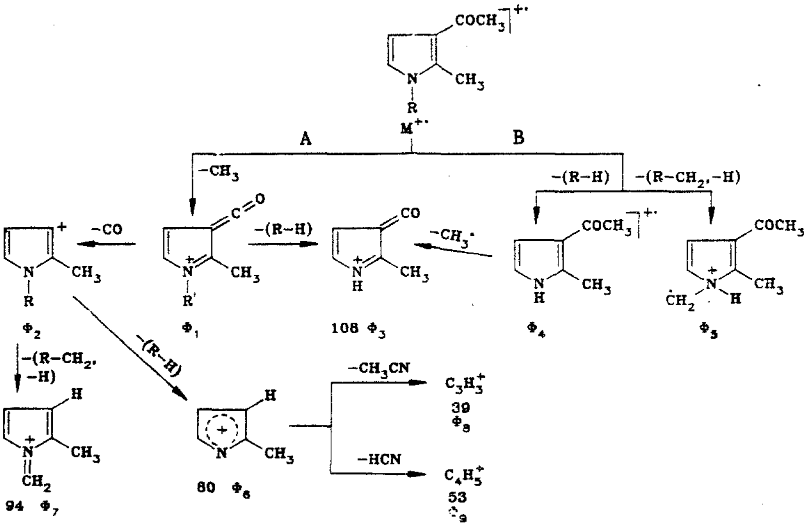
*The ten most intense peaks are listed.

substituents in the phenyl ring. Of the two most probable paths of the primary dissociation of M^+ in compounds I-IX, the most preferential is path A (scheme and Table 2), since the overall peak intensity of the Φ_1 and Φ_2 ions in most cases exceeds 25% of the total current, and only for compound V does it decrease to 2%. At the same time, the peak intensity of the Φ_4 ion, formed in the dissociation by path B (at R = C_3H_7, C_4H_9, C_6H_{11}), does not exceed 5%. The peak of the Φ_5 ion is observed only in the mass spectrum of the N-butyl substituted compound IV. These data allow us to assume that the positive charge in M^+ is preferentially localized on the $C_{(2)}$–$C_{(3)}$ bond in the pyrrole ring. In the case of compound III, the Φ_4 ion ($[M-42]^+$) could be formed also by the elimination of a ketene molecule from M^+. However, according to the high-resolution mass spectrum data, the composition of this ion includes both a nitrogen atom and an oxygen atom (found 123.0675, calculated, C_7H_9NO, 123.0684).



In the case of compound IX, the splitting proceeds at the exocyclic N–C bond with charge localization on the benzyl cation, having a lower energy of appearance, and therefore more than 40% of the ionic current is due to the ion with m/z 91. A similar dissociation of N-benzylpyrrole and benzylpyrazoles is described in [6-8].

TABLE 2. Intensities of Peaks of Characteristic Ions in the Mass Spectra of Compounds I-IX (% Σ_{39})

Compound	W_M	Φ_1	Φ_2	Φ_3	Φ_4	Φ_6	Φ_7	Φ_8	Φ_9	R^+
I	12,7	25,0	3,8	—	—	—	—	4,2	7,0	—
II	13,8	32,5	1,7	—	—	—	—	2,1	4,7	—
III	12,5	29,2	2,6	12,5	2,0	1,7	2,4	—	3,0	—
IV	10,6	20,0	1,9	11,4	1,8*	—	7,0	—	2,7	0,9
V	2,1	2,2	0,2	6,3	3,0	0,5	—	33,1	0,8	0,3
VI	12,7	35,7	1,8	—	—	—	—	1,1	3,6	8,6
VII	12,9	36,0	1,4	—	—	—	—	1,9	3,1	5,0
VIII	12,9	29,5	—	—	—	—	—	5,4	1,7	5,4
IX	10,9	13,9	1,3	—	—	—	—	—	—	43,5

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*In addition, there is a peak of the Φ_5 ion (3.2%).

A somewhat different behavior is shown in the mass spectrum of compound V, whose M^+ has a markedly lower stability, while intense peaks of hydrocarbyl ions appear (m/z 56, 55, 43, 42, 39), whose fraction of the overall ionic current is more than 35%. We should note that in this case the ion peaks formed during the fragmentation by path A have a higher intensity. The overall fraction of the ions listed in Table 2 for compounds I-IX is 50-60% of the total ionic current, which indicates a high selectivity of the dissociation of these compounds under electron impact.

Analysis of the mass spectra of the compounds that we studied enables us to identify both the presence of an acyl group (ions Φ_1 and Φ_2), and of substituents in the 1-position (ions Φ_4 and Φ_5).

EXPERIMENTAL

The mass spectra were measured on a Finnigan MAT-112S spectrometer with introduction via a Varian 3700 chromatograph (an OV-101 capillary column, 0.26 mm × 50 m) in an electron impact regime, at an ionization energy of 80 eV and temperature of the source of 220°C. The mass spectra were processed by means of a MAT-188 spectrosystem based on a Digital PDP 11/34 computer. In the high-resolution regime, the resolving power was 5000.

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