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MASS SPECTROMETRY OF STEREOISOMERIC 3-HYDROXY-4-PIPERIDONES

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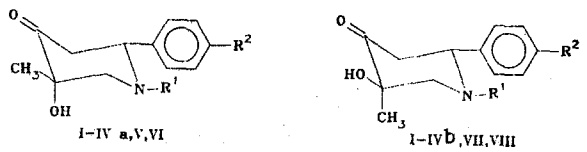
The existence of several sites of charge localization upon the mass spectrometric decomposition of stereoisomeric 3-hydroxy-4-piperidones leads to a large number of fragmentation products both with retention and destruction of the piperidine ring. Analysis of the mass spectra of the compounds studied showed that the appearance of $[M - CO]^+$ ion peaks for isomers with an axial hydroxyl group may serve as a method for determining the configuration of the carbinol site of such cyclic structures.

A mass spectrometric study was carried out on the major characteristic pathways for the decomposition of the molecular ions (M^+) of stereoisomeric 3-hydroxy-4-piperidones in order to establish correlations between the structure of these compounds and their mass spectra and possible analytical applications. The mass spectra of the compounds studied are published for the first time although Ermakov [1, 3, 4] and Bartanyan [2] have already discussed the fragmentation of alkyl derivatives of 4-piperidone and 4-piperidol.

3-Hydroxy-4-piperidones (I)-(VIII) contain a tertiary nitrogen atom, carbonyl, hydroxyl and phenyl groups, which may serve as positive charge localization sites in M^+. Thus, these mass spectra were interpreted assuming predominant charge localization on one of these sites. The concept of charge localization on individual molecular sites is used in mass spectrometry to explain pathways for the decomposition of organic compounds, including piperidine compounds [1-6]. The decomposition of piperidones Ia, IIb, IIIa, IIIb and IVa was studied using high-resolution mass spectrometry. The fragmentation sequence for several of these derivatives was studied using metastable ions by the DADI method.



Ia, b, V R^1=H, IIa, b, IIIa, b, VII, VIII R^1=CH_3, IVa, b, VI R^1=CH_2Ph; Ia, b, IIa, b, IVa, b R^2=H, IIIa, b, V, VI R^2=F, VII R^2=CH_3, VIII R^2=Cl

These compounds are characterized by an M^+ peak with intensity $\geqslant$10% of the maximal peak (Table 1). Analysis of the mass spectra showed that two competing pathways obtain upon charge localization in M^+ on the piperidine ring nitrogen atom (scheme 1) involving both opening and retention of the piperidine ring. One of the major decomposition processes of previously studied derivatives of piperidine [1-4, 7] and 3,4-dihydroxypiperidines [6] containing a substituent in the α-position relative to the nitrogen atom is loss of this substituent. How-

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TABLE 1. Mass Spectra of I-VIII at 70 eV Electron Energy (most intense peaks)

Compound	m/z value (relative peak intensity as % of the strongest peak)
I a	205 (38), 188 (8), 187 (19), 177 (20), 162 (9), 134 (10), 133 (21), 120 (14), 119 (62), 118 (100), 106 (49), 105 (67), 104 (80), 103 (19), 91 (42)
I b	205 (39), 188 (19), 187 (35), 162 (14), 134 (14), 133 (31), 120 (15), 119 (81), 118 (100), 106 (44), 105 (65), 104 (79), 103 (20), 91 (48)
II a	219 (24), 202 (52), 201 (27), 191 (13), 176 (10), 134 (19), 133 (68), 132 (100), 120 (8), 118 (27), 105 (68), 104 (32), 103 (26), 91 (36)
II b	219 (23), 202 (42), 201 (21), 176 (8), 134 (16), 133 (63), 132 (100), 120 (7), 118 (21), 105 (65), 104 (23), 103 (20), 91 (37)
III a	237 (33), 220 (38), 219 (23), 209 (13), 194 (16), 152 (24), 151 (70), 150 (100), 138 (15), 136 (42), 123 (62), 122 (75), 121 (41), 109 (80) 101 (33)
III b	237 (53), 220 (54), 219 (24), 194 (10), 152 (25), 151 (87), 150 (100), 138 (9), 136 (25), 123 (54), 122 (32), 121 (19), 109 (60), 101 (17)
IV a	295 (11), 278 (59), 277 (22), 209 (28), 208 (37), 204 (75), 134 (12), 120 (75), 118 (78), 105 (62), 104 (33), 92 (33), 91 (100)
IV b	295 (11), 278 (31), 277 (12), 209 (14), 208 (19), 204 (55), 133 (14), 120 (36), 118 (77), 105 (34), 104 (17), 92 (17), 91 (100)
V	223 (45), 206 (12), 205 (19), 195 (14), 180 (24), 152 (17), 151 (29), 149 (32), 137 (52), 136 (94), 124 (45), 123 (46), 122 (100), 121 (29), 109 (84)
VI	313 (13), 296 (42), 295 (18), 227 (23), 226 (17), 222 (69), 152 (17), 151 (35), 123 (39), 122 (31), 121 (19), 120 (90), 109 (77), 91 (100)
VII	233 (41), 216 (56), 215 (17), 190 (23), 148 (37), 147 (75), 146 (66), 132 (42), 119 (69), 118 (55), 117 (40), 105 (100), 91 (41)
VIII	255 (30), 253 (83), 238 (39), 237 (30), 236 (91), 235 (39), 210 (22), 170 (17), 169 (48), 168 (91), 167 (96), 166 (100), 154 (24), 152 (30), 139 (78), 125 (91), 91 (57)

TABLE 2. Relative Intensities of Several Characteristic Fragments in the Mass Spectra of 3-Hydroxy-4-piperidones in % Relative to the Total Ion Current

Compound	M^+	Φ_1	Φ_6	Φ_7	Φ'_8	Φ''_8	Φ'_9	Φ''_{10}	Φ_{11}	Φ'_{11}
Ia	4,8	1,0	2,5	1,1	7,8	12,6	2,6	10,0	8,4	10,0
Ib	4,4	2,2	—	1,6	9,2	11,5	3,6	9,1	7,5	9,1
IIa	2,6	5,7	1,4	1,1	7,4	10,9	7,4	2,9	7,3	3,5
IIb	2,7	4,9	—	0,9	7,3	11,7	7,3	2,4	7,6	2,7
IIIa	2,7	3,1	1,0	1,3	5,7	8,2	5,7	3,4	5,1	6,1
IIIb	5,7	5,8	—	1,1	9,4	10,8	9,4	2,7	5,8	3,4
IVa	1,1	6,1	0,4	0,5	2,9	3,9	0,7	0,6	6,5	3,4
IVb	1,3	4,1	—	0,5	1,9	2,5	1,9	0,7	4,5	2,3
V	3,3	0,9	1,0	1,7	3,8	6,8	2,1	7,2	3,3	7,2
VI	1,3	4,1	0,4	0,5	2,2	1,7	3,3	0,4	3,8	3,0
VII	3,8	5,2	—	2,1	7,0	6,1	7,0	3,9	6,4	5,1

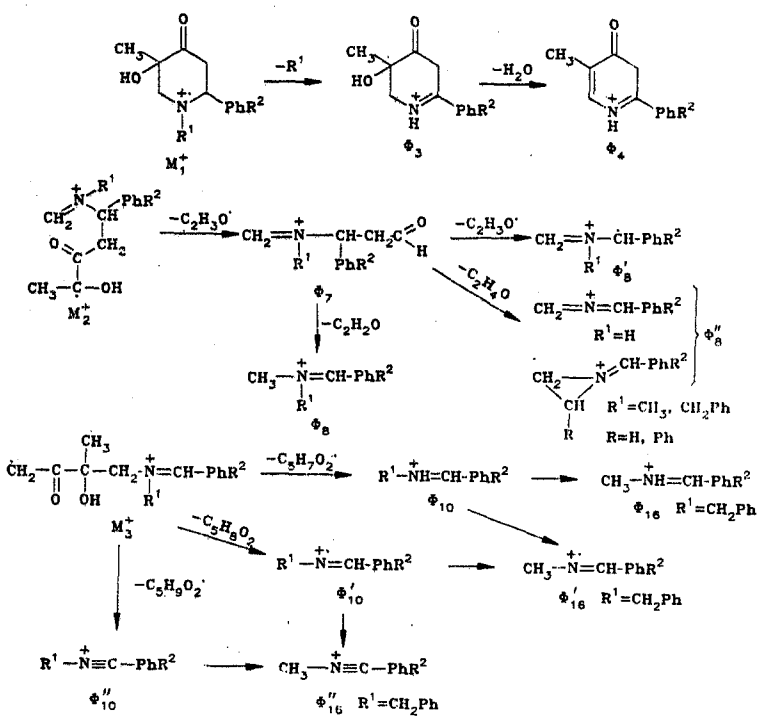
ever, the Φ_5 fragments formed in piperidones I-VIII as a result of this decomposition have low or zero intensity. This behavior may be attributed to the significant contribution of other decomposition pathways proceeding with ring opening and fragmentation of M^+ species, the charge in which is localized on other sites. The loss of the substituent at the ring nitrogen atom is clearly evident only for IV and VI which have an N-benzyl group. The mass spectra of these compounds have strong ion peaks at 204 and 222* ($[M - CH_2Ph]^+$, Φ_3) as well as Φ_4 fragment peaks formed due to the loss of a water molecule from Φ_3 ions.

The decomposition of M^+ due to charge localization on the nitrogen atom proceeding with ring opening is most characteristic for the compounds studied. The peaks for the corresponding fragments are rather strong. The variety of the products of this fragmentation is

*Here and subsequently, the m/z value is used to characterize the ions.

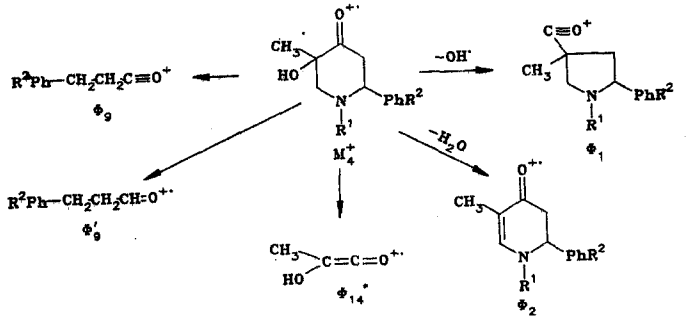
apparently related to the possibility of ring opening with breakage of either the $C_{(2)}-C_{(3)}$ or $C_{(5)}-C_{(6)}$ bonds with subsequent decomposition of the fragments formed, which may occur with hydrogen atom migration. Thus, the appearance of the peaks for series of rearrangement ions $\Phi_8 - \Phi_8''$ and $\Phi_{10} - \Phi_{10}''$ upon the decomposition of Φ_7 ions is related to hydrogen atom transfer to a charged fragment or neutral fragment. This is also true in the case of ions $\Phi_{16} - \Phi_{16}''$ for IV and VI, which contain a benzyl group as the R^1 substituent; a phenyl radical is eliminated from the benzyl group in ions $\Phi_{10} - \Phi_{10}''$. The formation of the Φ_7 fragment upon ring opening at the $C_{(2)}-C_{(3)}$ bond was indicated by the mass spectrum of deuterated analogs of piperidone IIIb containing one or two deuterium atoms at $C_{(5)}$. The peaks for ions 42 and 44 have elemental composition C_2H_4N and C_2H_6N, respectively and, thus, they are also formed upon the decomposition of M^+ with charge localization at the nitrogen atom.

SCHEME 1



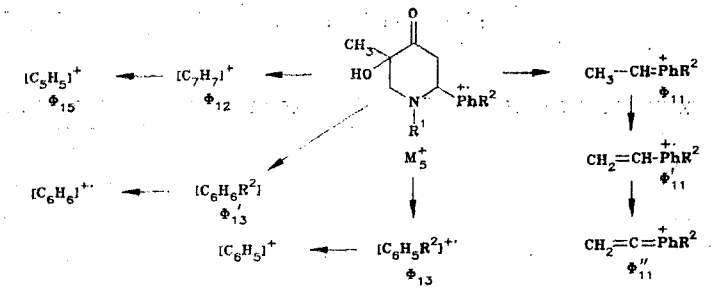
Peaks for the $[M - OH]^+$ and $[M - H_2O]^+$ ions are virtually absent in the mass spectra of previously studied piperidinediols [6] although such fragments are characteristic for cyclic alcohols. Thus, the presence of strong peaks for the Φ_1 and Φ_2 fragments (scheme 2) in the mass spectra of piperidones I-VIII may be related to the formation of M^+, in which the charge is located on the carbonyl group oxygen atom. The decomposition of such M^+ proceeding with ring opening apparently gives rearrangement ions Φ_9 and Φ'_9 (confirmed by the mass spectra of analogs of IIIb deuterated at $C_{(5)}$ as well as Φ_{14} (72), whose strong peak was found in the spectra of all the compounds studied. The peak for a fragment with such composition was found lacking in the mass spectra of previously studied piperidine derivatives.

SCHEME 2



The high resolution mass spectra of the compounds studied show that a series of ions is due to ions not containing heteroatoms. Ions $\Phi_{11} - \Phi''_{11}$, Φ_{13} and Φ'_{13} (scheme 3) are hydrocarbon species and contain a phenyl group. These fragments and Φ_{15} are apparently formed from M^+ ions, in which the charge is localized in the phenyl group. For compounds containing an N-benzyl group, ion Φ_{12} is formed from both aryl substituents since fragment Φ_{12} in the case of VI gives two peaks. This occurs because the aromatic ring at $C_{(6)}$ contains a fluorine atom. The mass spectra of III and VI-VIII which have F, Cl and CH_3 substituents in the para position of the phenyl ring were studied largely to confirm the peak assignments given.

SCHEME 3



Interest was also found in the behavior of the peak for fragment Φ_6 formed upon the loss of a CO molecule from M^+ (Table 2). The intensity of this peak is significant (4-20%) only for the stereoisomers with axial orientation of the hydroxyl group. The Φ_6 fragment peak is virtually absent ($1 \ll 1\%$) for derivatives with an equatorial hydroxyl group. The lack of peaks for $[M - CO]^+$ ions for piperidones with an axial hydroxyl group is likely a consequence of the formation of a rather strong 3e-OH...OC intramolecular hydrogen bond ($\Delta\nu = 100$ cm^{-1}). This feature of the mass spectrometric behavior of steroisomeric 3-hydroxy-4-piperidones may be used as a method of establishing the orientation of the hydroxyl group in this class of compounds. We should note that identification of stereoisomeric 3-hydroxy-4-piperidones is possible only by PMR spectroscopy since the hydroxyl group stretching bands in the IR spectra of diluted solutions of both stereoisomers are virtually the same (OH...OC and OH...N) [8]. The appearance of peaks for $[M - CO]^+$ ions for 3a-hydroxy-4-piperidones may serve as a mass spectrometric method for determining the configuration of the carbonyl site of such cyclic structures.

EXPERIMENTAL

The mass spectra of I-VIII were taken on a Varian MAT-311 A mass spectrometer with direct sample inlet. The ionizing electron energy was 70 eV and the temperature of the ion source was 20-100°C. The precise ion masses were found relative to PFC at 10,000 resolution.

Samples of the compounds studied were obtained according to our previous procedures [9, 10].

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SYNTHESIS OF 5-ARYLPYRIMIDINE-2-CARBOXYLIC ACIDS AND THE LIQUID-CRYSTAL CHARACTERISTICS OF THEIR ARYL ESTERS

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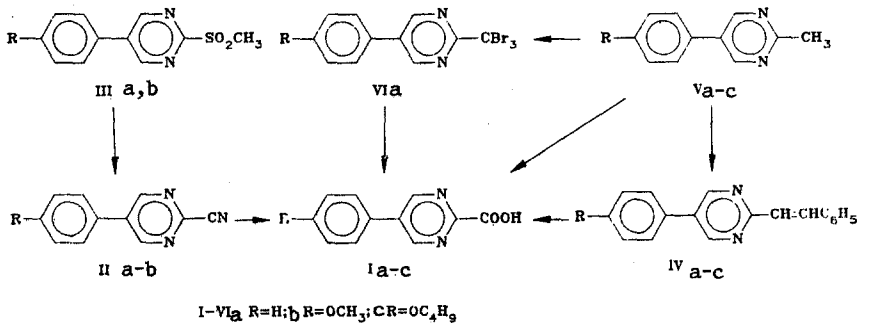
5-Arylpyrimidine-2-carboxylic acids were synthesized by the hydrolysis of 5-aryl-2-cyanopyrimidines and the oxidation of 5-aryl-2-styrylpyrimidines under the conditions of phase-transfer catalysis. The aryl esters of the acids were obtained, and their liquid-crystal characteristics were studied. The p-substituted aryl esters of 5-phenylpyrimidine-2-carboxylic acid do not exhibit mesomorphism, but the introduction of a butyloxy group at the p position of the phenyl residue leads to the appearance of nematic characteristics. Aryl 5-phenylpyrimidinylcarbonyloxybenzoates are nematic liquid crystals with a thermally stable meso phase and an existence range of 50-80°C.

The pyrimidine analogs of biphenyls have been widely studied [3, 4] in connection with advances in the study of cyanobiphenyls and the increased interest in liquid crystals with positive dielectric anisotropy [1, 2]. An important position among the various types of liquid-crystalline compounds is occupied by the esters, but with the large number of researches into liquid-crystalline aryl benzoates (e.g., [5-7]) the esters of heterocyclic acids have hardly been studied at all; there are only data on the nematic characteristics of the allyl esters of pyridine acids [8].

We have realized the synthesis of aryl pyrimidine-2-carboxylates, which are the analogs of mesomorphous compounds of the aromatic series [9-11], and we investigated their liquid-crystal characteristics. To obtain the acids I we used the traditional methods for synthesis of pyrimidine-2-carboxylic acids [12], i.e., hydrolysis of the cyanopyrimidines (II) obtained from the sulfones III and oxidation of styrylpyrimidines IV or methylpyrimidines V. Here special attention was paid to the possibility of producing the pure product, which is of primary significance during the synthesis of liquid-crystalline compounds.

SCHEME 1



I-VIa R=H; b R=OCH3; c R=OC4H9

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