MASS SPECTROMETRIC STUDY OF THE STEREOISOMERS OF 2-FURYL- AND 2-PHENYLDECAHYDRO-4-QUINOLINONE AND THEIR TERTIARY ALCOHOLS

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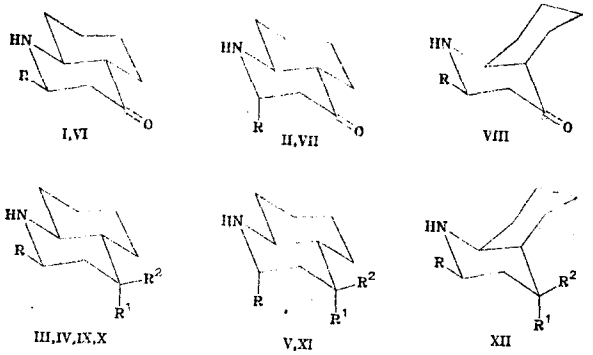
A study was carried out on the major pathways for the decomposition of stereoisomers of 2-furyl- and 2-phenyldecahydro-4-quinolinone and their tertiary alcohol derivatives upon electron impact. The elemental composition of the characteristic ions was determined by high-resolution mass spectrometry. The introduction of a heavy substituent at $C_{(2)}$ leads to marked changes in the directions of the major fragmentation pathways of decahydroquinoline. The dependence of the probability for the formation of characteristic ions on the molecular geometry in the stereoisomer series was demonstrated.

Mass spectrometry has found common use in the study of decahydroquinoline and its derivatives. The major fragmentation pathways upon electron impact have been determined for decahydroquinoline [1], the stereoisomers of 2-methyl- and 1,2-dimethyldecahydroquinoline [2, 3], 2-methyl- and 1,2-dimethyldecahydroquinolols [4], their benzoic esters [5], 1-alkyl-2-methyldecahydro-4-quinolol [6], stereoisomers of tertiary alcohols [7, 8], 2-methyl-4-chlorodecahydroquinoline [6], and decahydro-4-quinolol N-oxides [10]. The effect of molecular geometry on decomposition has also been examined [2-9, 11]. The configuration at $C_{(2)}$ and $C_{(4)}$ in the trans stereoisomers of 2-methyl- and 1-alkyl-2-methyl-4-alkyldecahydro-4-quinolols was determined using the ratio of the mass spectral intensities for the characteristic ions [12-15].

We have studied the mass spectra of the following stereoisomers of 2-furyl- and 2-phenyldecahydro-4-quinolinones and the tertiary alcohol derivatives I-XII:



I-V R = α-Fu, VI-XII R = Ph; III, IX R^1 = C≡CH, R^2 = OH, IV, V, X-XII R^1 = OH, R^2 = C≡CH

We attempted to investigate the effect of the replacement of the methyl group at $C_{(2)}$ by a furyl or phenyl group and of alteration in the molecular structure on the efficiences of different fragmentation pathways.

The mass spectra of I-XII were studied for the first time. Tables 1 and 2 give the peak intensities of the major ions in the total ion current scale, while Table 3 gives the elemental composition of several characteristic ions determined by high-resolution mass spectrometry. The major fragmentation pathways of the molecular ions of these compounds are depicted in the

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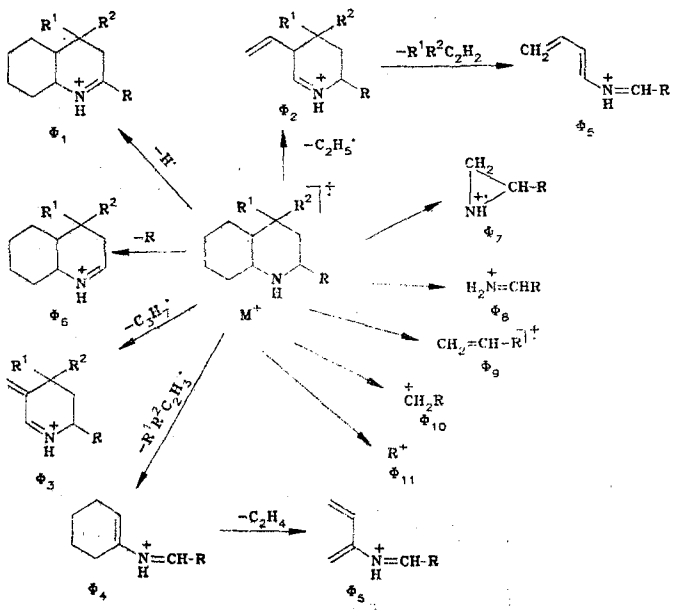
TABLE 1. Mass Spectra of I-V (peak intensities in % of Σ_{39})

Ions	m/z	I	II	m/z	III	IV	V
M^+	219	13,1	12,9	245	7,5	9,0	6,0
Φ_1	218	1,2	1,3	244	1,7	1,8	1,5
$[M-OH]^+$	202	1,0	1,2	228	2,2	3,7	2,9
$[M-H_2O]^+$				227	0,6	3,3	2,4
Φ_2	190	1,4	1,7	216	1,0	1,0	0,9
Φ_3	176	10,8	10,0	202	2,2	2,4	3,1
Φ_4	176			176	2,3	1,2	1,1
Φ_5	148	1,7	1,7				
Φ_7	109	3,7	3,3	109	1,2	1,1	1,3
Φ_8	96	13,8	10,4	96	21,5	20,1	17,3
Φ_9	94	6,2	7,9	94	2,4	2,3	3,0
Φ_{10}	81	2,3	2,1	81	2,8	2,6	2,9
Φ_{11}	67	1,6	1,5	67	1,4	1,3	1,5
	65	1,6	1,8	65	1,2	1,2	1,3
	55	1,9	2,2	55	1,0	0,7	0,9
	54	1,1	1,1	54	0,7	0,6	0,8
	53	1,2	1,3	53	1,5	1,4	1,8
	41	2,8	2,8	41	2,0	1,9	2,2
	39	2,3	2,4	39	1,4	1,5	1,7

scheme. Since the decomposition of the furyl and phenyl derivatives of decahydroquinoline is similar, it was represented in a single scheme and the substituent at $C_{(2)}$ was given as R.

The molecular ion peak (M^+) is one of the strongest in the mass spectra of I-XII. The fraction for M^+ in the total ion current is an index of its stability. This fraction is higher for ketones relative to the corresponding alcohols, for the trans ketone isomers VI and VII relative to the cis isomers (VIII), and for ketones with an equatorial substituent at $C_{(2)}$ relative to an axial substituent. The stability of the molecular ion in the case of the alcohols is higher for the cis isomer relative to the trans isomer and for the trans isomers with an equatorial substituent at $C_{(2)}$ relative to the epimer with an axial hydroxy group. The low stability of M^+ in the case of alcohols V and XI may be related to a through-space interaction of the axial substituents at $C_{(2)}$ and $C_{(4)}$.



The strong ion peak $[M - 43]^+$ in the mass spectra of the ketones is a composite peak and is attributed to two ion types, namely, Φ_3 and Φ_4 (see Table 3). Ion Φ_3 is characteristic for the decomposition of previously studied derivatives of decahydroquinoline [1-9] and is formed upon the fragmentation of the hydrocarbon ring. Ion Φ_4 is formed upon bond breakage in the piperidine ring. Such fragmentation is not characteristic for decahydroquinolines not substituted at $C_{(4)}$ [2] whose mass spectra do not display a peak for the analogous ion $[M - C_2H_5]^+$. Ion Φ_4 in the mass spectra of the alcohols makes a smaller contribution relative to ion Φ_3, while the total contribution of ions Φ_3 and Φ_4 to the total ion current for the alcohols is

TABLE 2. Mass Spectra of VI-XII (peak intensities in % of Σ_{39})

Ions	m/z	VI	VII	VIII	m/z	IX	X	XI	XII
M^+	229	12,4	12,2	11,0	255	6,4	8,4	7,0	9,7
Φ_1	228	1,2	1,5	1,2	254	2,0	2,1	1,7	1,3
$[M-OH]^+$	212	1,2	1,6	1,4	238	2,5	3,5	3,2	3,7
$[M-H_2O]^+$					237	0,8	1,8	1,5	0,8
Φ_2	200	1,7	2,3	2,4					
Φ_3	186	12,1	12,6	13,1	212	3,7	4,1	5,6	9,9
Φ_4	186				186	2,4	1,5	1,4	0,8
Φ_5	158	1,9	1,9	2,9					
Φ_6	152	1,4	1,9	1,2	178	1,4	1,5	1,8	1,0
Φ_7	119	1,3	0,9	1,0	119	0,9	0,7	0,7	0,6
Φ_8	106	11,8	8,8	8,0	106	20,0	18,7	15,2	11,9
Φ_9	104	3,7	4,0	4,6	104	1,9	2,2	2,1	2,1
Φ_{10}	91	2,5	1,9	1,8	91	3,0	2,9	3,0	2,6
	81	2,1	2,0	1,7					
	79	2,1	1,5	1,7	79	1,8	2,1	1,7	1,7
Φ_{11}	77	2,0	1,7	2,1	77	1,6	1,7	1,6	1,7
	67	1,3	1,1	1,0	67	1,2	1,2	1,2	0,8
	55	1,3	1,3	1,3					
	54	1,1	0,9	0,9					
					53	1,2	1,3	1,5	1,4
	41	2,0	1,8	1,9	41	1,6	1,8	1,6	1,4
	39	1,0	0,9	1,2	39	0,8	1,0	0,8	0,9

less than for the ketones. A clear dependences of the contribution of ion Φ_3 to the total ion current on molecular geometry is found in the mass spectra of the alcohols: cis > trans, $R_{ax} > R_{eq}$, $OH_{ax} > OH_{eq}$. The contribution of ion Φ_4 also depends on the molecular geometry and is greater for the trans isomers and for axial orientation of the hydroxyl group.

Ion Φ_8 corresponds to the major peak in the mass spectra of alcohols III-V and IX-XII and is one of the strongest peaks in the mass spectra of ketones I, II, and VI-VIII. These ions are formed as a result of breakage of the $C_{(2)}$—$C_{(3)}$ and $C_{(9)}$—N bonds with rearrangement of the hydrogen atom to the nitrogen atom and include the substituent R. The probability of the formation of analogous ions with m/z 58 in the mass spectra of 1,2-dimethyldecahydroquinolines [2] and their tertiary alcohols [7] is low, while the maximum peak in the mass spectrum of 1-methyl-2,6-diphenylpiperidine corresponds to the ion m/z 120 formed upon analogous decompositions [16]. The high intensity of the peak of this ion in the mass spectra of the 2-furyl and 2-phenyl derivatives relative to their methyl derivatives may be understood assuming that these ions have two possible sites for charge localization, while the nitrogen atom is the only charge localization site in the ion with m/z 58 for derivatives of 1,2-dimethyldecahydroquinoline [2, 7]. The intensity of the Φ_8 ion peak depends on the molecular geometry. The probability of the formation of this ion is higher for trans isomers relative to cis isomers; the axial orientation of the furyl or phenyl group facilitates the formation of this ion. The peak for this ion in the case of the trans alcohol isomers is higher for equatorial orientation of the hydroxyl group.

Ions Φ_9, whose appearance probability is much higher in the ketones (I, II, VI-VIII), do not contain a nitrogen atom and are formed upon breakage of the $C_{(2)}$—N and $C_{(3)}$—$C_{(4)}$ bonds. The intensity of the peak of this ion is higher in the case of the cis isomers (compare the spectra data for VIII relative to VI and VII) and, in the case of the trans isomers, is higher for axial orientation of the substituent at $C_{(2)}$ (compare the data for II vs. I and for VII vs. VI), i.e., the intensity of the Φ_9 ion peak for the ketones is inversely dependent on the molecular geometry relative to the Φ_8 ions. This may be understood considering that both these peaks contain the substituent R and are formed upon competitive decomposition with bond breakage at $C_{(2)}$.

Other ions which include the substituent R (Φ_{10} and Φ_{11}) make an independent contribution to the total ion current and there is no clear dependence for the intensities of these ion peaks on molecular geometry.

Decomposition with the loss of the methyl group at $C_{(2)}$ is characteristic for the fragmentation of 2-methyldecahydroquinoline and its derivatives [2-8]. The peaks of such ions (Φ_6) are seen in the mass spectra of phenyl derivatives VI-XII. The probability for the formation of these ions does not show a clear dependence on the molecular geometry in the stereoisomer series.

TABLE 3. Elemental Composition of the Characteristic Ions of I, II, V, VI and IX by High-Resolution Mass Spectrometry

Compound	Ion mass	Elemental composition	Ratio
I	190	$C_{12}H_{16}NO : C_{11}H_{12}NO_2$	1 : 1
	176	$C_{11}H_{14}NO : C_{10}H_{10}NO_2$	2 : 1
	109	C_8H_7NO	
	96	C_5H_8NO	
	94	C_3H_6O	
II	190	$C_{12}H_{16}NO : C_{11}H_{12}—NO_2$	3 : 4
	176	$C_{11}H_{14}NO : C_{10}H_{10}NO_2$	3 : 2
	109	C_8H_7NO	
	96	$C_5H_6NO : C_6H_{10}N$	10 : 1
	94	C_6H_6O	
	81	$C_6H_9 : C_5H_5O$	1 : 1
	55	$C_4H_7 : C_3H_3O$	2 : 3
	41	$C_3H_5 : C_2H_3N$	5 : 1
V	216	$C_{14}H_{18}NO$	
	202	$C_{13}H_{16}NO : C_{12}H_{12}NO_2$	1 : 10
	109	$C_8H_7—NO$	
	96	C_5H_6NO	
	94	$C_6H_8N : C_6H_6O$	1 : 5
	81	$C_6H_9 : C_5H_7N : C_5H_5O$	2 : 1 : : 3
	67	$C_5H_7 : C_4H_3O$	4 : 1
	65	C_5H_5	
	53	$C_4H_5 : C_3HO$	1 : 1
	41	$C_3H_5 : C_2H_3N$	10 : 1
VI	200	$C_{13}H_{14}NO$	
	186	$C_{13}H_{16}N : C_{12}H_{12}NO$	2 : 1
	152	$C_9H_{14}NO$	
	106	C_7H_8N	
	104	$C_8H_8 : C_7H_6N$	4 : 1
	91	C_7H_7	
	81	$C_5H_9 : C_5H_5O$	5 : 1
	55	$C_4H_7 : C_3H_3O$	2 : 3
	54	$C_4H_6 : C_3H_4N$	2 : 1
	43	$C_3H_7 : C_2H_5N : C_2H_3O$	1 : 2 : : 10
IX	41	$C_3H_5 : C_3H_3N$	10 : 1
	238	$C_{17}H_{20}N$	
	212	$C_{14}H_{14}NO : C_{15}H_{18}N$	10 : 1
	186	$C_{13}H_{16}N$	
	178	$C_{11}H_{16}NO$	
	106	C_7H_8N	
	104	C_8H_8	
	91	C_7H_7	

Let us examine some other ions which give weak peaks. Ion Φ_1 is apparently formed upon loss of a hydrogen atom as a result of the breakage of the α-bond relative to the nitrogen atom.

The $[M - 29]^+$ peak in the mass spectra of phenyl derivatives VI-XII corresponds to one Φ_2 ion formed upon fragmentation of the hydrocarbon ring, while $[M - CHO]^+$ ions also contribute to this signal in the mass spectra of furyl derivatives I-V (see Table 3); these ions are formed upon the decomposition of the furan ring. Ion Φ_7 contains the nitrogen atom and is obtained upon breakage of the piperidine ring. The peak for this ion is strongest in the mass spectra of ketones I and II and is not diagnostic for stereoisomer determination.

The peak for the $[M - OH]^+$ ion is found in the spectra of all the compounds studied. This ion is characteristic for the mass spectra of alcohols but it is not clear why the peaks for this ion have comparable intensity in the spectra of the ketones and alcohols. This finding may be related to stabilization of the enol form of ketones I, II, and VI-VIII, at least in M^+. In the case of the alcohols, we find that the $[M - OH]^+$ ion peak is higher for the trans isomers with axial orientation of the hydroxyl group. The peak for the $[M - H_2O]^+$ ion in the mass spectra of the ketones is an order of magnitude less than for the alcohols.

Thus, we have established the characteristic pathways for the decomposition of 2-phenyl- and 2-furyldecahydro-4-quinolinones and their tertiary alcohol derivatives upon electron impact and studied the effect of ring fusion and the orientation of the substituents at $C_{(2)}$ and $C_{(4)}$ on the fragmentation of these compounds. The introduction of substituents at $C_{(2)}$ capable of participating in charge delocalization leads to the formation of ions due to specific fragmentation in addition to the fragmentation ions characteristic for 2-methyldecahydroquinoline and its derivatives.

EXPERIMENTAL

The syntheses of I-V were described in our previous work [17-19] and their structures were demonstrated in our earlier communications [20, 21]. The syntheses and structures of VI-XII were described in our earlier work [22, 23].

The mass spectra were obtained on an MKh-1320 mass spectrometer with direct sample inlet into the ion source. The ionization voltage was 70 V and the acceleration voltage was 2.5 kV. The temperature of the ionization chamber was 100°C. The high-resolution mass spectra were taken on the same spectrometer with $M/(\Delta M) = 10{,}000$.

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