MASS-SPECTROMETRIC INVESTIGATION OF THE STEREOISOMERS OF 1-(3-PHENYL-2-PROPYNYL)-2-METHYLDECAHYDROQUINOLIN-4-ONE(OL)

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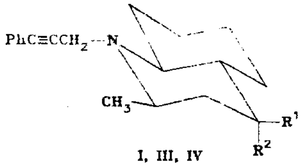
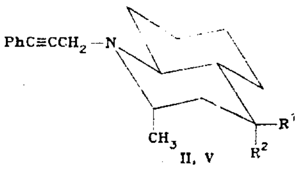
The fragmentation of the stereoisomers of 1-(3-phenyl-2-propynyl)-2-methyldecahydroquinolin-4-one(ol) under electron impact was investigated. The elemental composition of the characteristic ions was determined from the high-resolution mass spectra.

Mass-spectrometric investigations of decahydroquinoline and its derivatives were undertaken a long time ago. Thus, the main dissociation paths of decahydroquinoline and its deutero derivatives [1], the stereoisomers of 2-methyl- and 1,2-dimethyldecahydroquinoline [2], their secondary [3, 4] and tertiary alcohols [5, 6], and 1-benzoyl-2-methyldecahydroquinoline [7] under electron impact have been investigated. The effect of the geometry of the molecule on the principal fragmentation processes was studied in [2-7]. The positions of the substituents at the $C(_4)$ and $C(_4)$ atoms in the trans isomers of 2-methyl-4-alkyldecahydro-4-quinolols were determined in a series of mass-spectrometric investigations into the intensity ratios of the characteristic ions [8-11].

We have investigated the mass spectra of the stereoisomers:



I, III, IV



II, V

I, II $R^1=R^2=O$ (T_{mp} 104 and 66° respectively); III $R^1=OH$, $R^2=C\equiv CH$ (T_{mp} 126°); IV $R^1=C\equiv CH$, $R^2=OH$ (T_{mp} 115°); V $R^1=OH$, $R^2=C\equiv CH$ (T_{mp} 139°)

All the investigated compound had trans-coupling of the rings and differed in the positions of the substituents at the $C(_2)$ and $C(_4)$ atoms (axial, equatorial).

Fragmentation of the amine type was mainly observed in all the previously investigated [2-6] N–H and N-alkyl derivatives of decahydroquinoline. The introduction of a benzoyl substituent at the nitrogen atom led to substantial changes in the main directions of fragmentation [7] and greatly reduced the stability of the molecular ion (M^+); the strongest peak in the mass spectra corresponded to the $C_6H_5CO^+$ ion, while the contributions from the $[M - CH_3]^+$ and $[M - C_3H_7]^+$ ions were greatly reduced [7]. For this reason it seemed of interest to study the effect of an aromatic substituent introduced at the nitrogen atom, but with a more distant phenyl group, on the fragmentation of decahydroquinoline derivatives and also the effect of the molecular geometry on the fragmentation.

The mass spectra of compounds (I-V) are given in Table 1 as percentages of the total ion current. The small number of signals (4-5) in the mass spectra giving more than 50% of the total ion current indicates that the fragmentation processes are highly selective. The probable formation paths and structures of the characteristic ions in the mass spectra of compounds (I-V) are shown in the scheme. The high-resolution mass spectra of compound (I) were determined in order to establish the composition of the main fragment ions (Table 2).

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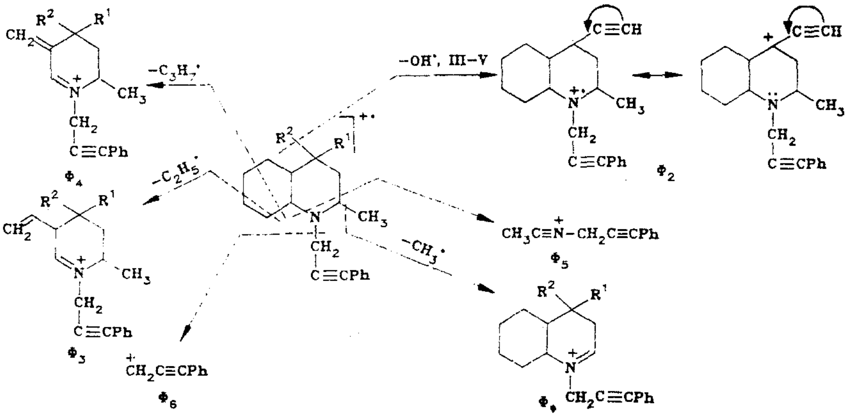
TABLE 1. The Peak Intensities of the Characteristic Ions in the Mass Spectra of Compounds (I-V) (% Σ_{27})

Ion	*m/z*	I	II	*m/z*	III	IV	V
M^+	281	9,5	11,3	307	7,2	7,4	5,7
$[M-H]^+$	280	0,8	0,8	306	1,0	1,0	1,2
Φ_1	266	7,5	8,5	292	10,1	11,2	17,5
Φ_2	264	0,8	0,9	290	2,7	3,8	2,2
	253	1,0	0,7				
Φ_3	252	2,4	2,3				
Φ_4	238	12,3	11,8	264	10,6	9,4	8,5
				225	1,6	1,1	1,1
Φ_5	156	1,2	1,3	156	0,6	0,7	0,8
Φ_6	115	27,0	26,2	115	20,2	20,3	21,5
	89	1,0	0,9	89	1,0	1,1	0,9
	81	1,3	1,2	81	1,2	1,1	1,1
	56	1,0	1,0	56	1,0	1,1	1,1
	41	1,9	1,8	41	2,0	2,2	1,9

TABLE 2. Data from the High-Resolution Mass Spectrum of Compound (I)

Ions	Position	Mass of ion	
		found	calculated
Φ_1	$C_{18}H_{20}NO$	266,2362	266,2396
Φ_3	$C_{17}H_{18}NO$	252,2140	252,2195
Φ_4	$C_{16}H_{16}NO$	238,1991	238,1994
Φ_6	C_9H_7	115,0965	115,0916



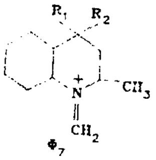
The M^+ signal in the spectra of the investigated compounds is fairly strong and makes a much larger contribution to the total ionic current than the signal in the spectrum from N-benzoyl-2-methyldecahydroquinolines [7]. The M^+ peak is stronger in the mass spectra of the ketones than in the spectra of the alcohols.

The Φ_1 ion is formed by the loss of a methyl radical from M^+ as a result of α-dissociation and is typical of the derivatives of 2-methyldecahydroquinoline [2-6]. The peak intensity of this ion is higher in the mass spectra of the alcohols than in the mass spectra of the ketones and shows a clear dependence on the orientation of the methyl group; it is highest in the axial position. The marked increase in the peak intensity of the $[M - CH_3]^+$ ion in the transition from compounds (III, IV) to compound (V) is evidently due to the possibility of diaxial 1,3-interaction between the hydroxy and methyl groups in compound (V) [12].

The Φ_4 ions are formed during α-dissociation with loss of part of the hydrocarbon ring and are typical of decahydroquinolines [1-6]. The high-resolution mass spectra (Table 2) confirm this composition of the ion. The intensity of this peak is high, which demonstrates the great probability of formation and the stability of the Φ_4 ion. The peak of the Φ_4 ion is stronger in the ketones than in the alcohols and also with the methyl group in the equatorial position.

The strongest peak in the mass spectra of (I-V) correspond to the Φ_6 ion, which contains an aromatic ring and is formed during cleavage of the exocyclic C—N bond. Such a fragmentation process is uncharacteristic of decahydroquinoline, piperidine, and their derivatives but has been observed in the N-benzoyl derivatives of decahydroquinoline [7]. The contribution from the Φ_6 ion to the total ion current is larger in the ketones and in the stereoisomers with the methyl substituent in the axial position. The differences in the intensities of the peaks of the $\Phi_4(\Phi_6)$ ions in the transition from the mass spectra of the ketones to the spectra of the alcohols are evidently due to the fact that the fragmentation process is more selective in the ketones, whereas the ions in the region of small masses, formed during secondary dissociation processes, make a large contribution in the mass spectra of the alcohols; this must reduce the contribution from the $\Phi_4(\Phi_6)$ ions to the total ion current in the mass spectra of the alcohols.

A strong peak for the Φ_7 ion, formed by cleavage of the β-C—C bond in the alkyl substituent, is observed in the mass spectra of the N-alkyl-substituted decahydroquinaldines [4]:



Φ_7

The peak of the analogous ion is absent in the mass spectra of compound (I-V). At the same time the peak for the Φ_6 ion is strong. We will try to explain the reason for this effect. The intensity of the ion peaks in the mass spectrum depends on their stability, the energy favorability of the processes leading to their formation, and the probability of localization of the charge on the given fragment. Our data and published data show that the Φ_6 and Φ_7 ions have comparable stability and the probability of charge localization. Consequently, the differences in the intensities of these ions must be sought in the energy characteristics of the dissociation processes. We have to explain why the C—N bond is broken preferentially and the exocyclic C—C bond is not broken. We will use published data on the dissociation energies of the bond [13]. As model compounds we will take ethylamine and ethylacetylene. The dissociation energies of the bonds in these compounds are as follows:

$$\mathrm{CH_3{-}CH_2{-}NH_2} \begin{array}{l} \nearrow \mathrm{CH_3^{\cdot} + {}^{\cdot}CH_2NH_2} \quad (\Delta H = 341{,}8\ \mathrm{kJ/mole}) \\ \searrow \mathrm{CH_3{-}CH_2^{\cdot} + {}^{\cdot}NH_2} \quad (\Delta H = 337{,}6\ \mathrm{kJ/mole}) \end{array}$$

$$\mathrm{CH_3{-}CH_2{-}C{\equiv}CH} \begin{array}{l} \nearrow \mathrm{CH_3^{\cdot} + {}^{\cdot}CH_2{-}C{\equiv}CH} \quad (\Delta H = 311{,}7\ \mathrm{kJ/mole}) \\ \searrow \mathrm{CH_3{-}CH_2^{\cdot} + {}^{\cdot}C{\equiv}CH} \quad (\Delta H = 452{,}7\ \mathrm{kJ/mole}). \end{array}$$

In other words, whereas no appreciable difference in the dissociation energies of the C—N and C—C bonds is observed in the amine molecule, in the ethylacetylene molecule there is an energy preference for cleavage of the C—C bond in the ethyl radical (~140 kJ/mole). This makes it possible to understand why the process leading to the formation of the Φ_6 ion is preferred of the two possible dissociation processes near the nitrogen atom.

The Φ_2 ion, formed by the loss of the hydroxyl group, has high intensity in the mass spectra of the alcohols.

In the mass spectra of the ketones there is a peak of low intensity with m/z 252, to which the Φ_3 ion evidently coresponds. The high-resolution mass spectra confirm the elemental compositions of this ion.

EXPERIMENTAL

The mass spectra were obtained on an MX1320 mass spectrometer at 70 eV, and the high-resolution spectra were recorded with a resolving power of 6000.

The synthesis and the structures of the investigated compounds were described in [14, 15].

LITERATURE CITED

1. C. K. Oldfield and D. B. MacLean, Org. Mass. Spectrom., 4, 147 (1970).
2. A. E. Lyuts, O. V. Agashkin, V. I. Artyukhin, G. S. Litvinenko, and D. V. Sokolov, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., No. 2, 48 (1968).

3. A. E. Lyuts, O. V. Agashkin, V. I. Artyukhin, G. S. Litvinenko, and D. V. Sokolov, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., No. 1, 39 (1969).
4. N. Matamarov, O. V. Agashkin, A. E. Lyuts, K. I. Khludneva, D. V. Sokolov, and G. S. Litvinenko, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., No. 1, 53 (1971).
5. N. Matamarov, A. E. Lyuts, K. D. Praliev, and D. V. Sokolov, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., No. 5, 74 (1974).
6. N. S. Vul'fson, V. G. Zaikin, A. A. Bakaev, A. A. Akhrem, and L. I. Ukhova, Khim. Geterotsikl. Soedin., No. 7, 962 (1975).
7. A. E. Lyuts, O. V. Agashkin, V. I. Artyukhin, D. V. Sokolov, K. I. Khludneva, and G. S. Litvinenko, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., No. 1, 74 (1970).
8. V. G. Zaikin, N. S. Vul'fson, (Wulfson), V. J. Zaretskii, A. A. Bakaev, A. A. Akhrem, L. I. Ukhova, and N. F. Uskova, Org. Mass Spectrom., 2, 1257 (1969).
9. N. S. Vul'fson (Wulfson), A. A. Bakaev, V. G. Zaikin, A. A. Akhrem, L. I. Ukhova, A. P. Marochkin, and G. V. Bludova, Org. Mass Spectrom., 6, 533 (1972).
10. N. S. Vul'fson, A. E. Bakaev, V. G. Zaikin, A. A. Akhrem, L. I. Ukhova, and N. F. Marchenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 209 (1972).
11. V. G. Zaikin, A. A. Bakaev, N. S. Vul'fson, A. A. Akhrem, L. I. Ukhova, and A. I. Sergeeva, Khim. Geterotsikl. Soedin., No. 6, 809 (1976).
12. K. Bruns and W. Sanderman, Tetrahedron, 24, 1357 (1968).
13. L. V. Gurvich, G. V. Karachevtsev, V. N. Kondrat'ev, Yu. A. Lebedev, V. A. Medvedev, K. K. Potapov, and Yu. S. Khodeev, Dissociation Energies of Chemical Bonds. Ionization Potentials and Electron Affinity [in Russian], Nauka, Moscow (1974), p. 63.
14. S. A. Tarakov, K. D. Praliev, D. V. Sokolov, V. I. Kurilenko, and Zh. N. Khlienko, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., No. 3, 70 (1985).
15. L. P. Krasnomolova, S. G. Klepikova, O. V. Agashkin, K. D. Praliev, M. Z. Esenalieva, and S. A. Tarakov, Zh. Fiz. Khim., 58, 2597 (1984).