IDENTIFICATION OF DERIVATIVES OF 2H-CHROMENES AND THEIR ACYCLIC TAUTOMERIC FORMS IN THE GAS PHASE BY MASS SPECTROMETRY

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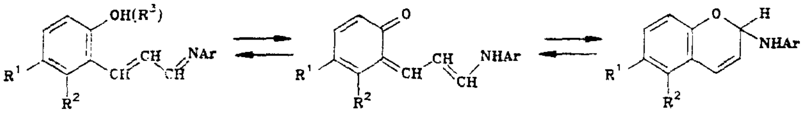
It was established that mass spectrometry makes it possible to identify in the gas phase molecular ions with both the 2H-chromene structure and their acyclic tautomers from the characteristic $(M - OH)^+$ and $(M - ArNH)^+$ fragment ions, respectively. The fragmentation scheme was confirmed by methods involving dissociation of ions activated by collision and deuterium labeling. Measurement of the ionization energies of the investigated compounds makes it possible to exclude the possibility of the existence in the gas phase of a tautomeric form with an o-quinoid structure.

The identification and investigation of ring-chain tautomers play an important role in the development of the fundamental concepts of organic chemistry. In a number of cases the tautomeric transformations that occur through the electronically excited states of one of the tautomers lie at the foundation of photochromic systems that are widely used in the technology of recording information and self-regulating devices. Derivatives of 2H-chromenes occupy an important position among compounds of this type [1, 2].

Vinylogs of imines of hydroxybenz- and hydroxynaphthaldehydes were recently synthesized, and their ring-chain tautomeric transformations in solutions were investigated. It was established that the ratios of the tautomeric forms of these systems depend on the polarity of the solvent and the substituent in the N-aryl ring. In the crystalline state and in nonpolar solvents the compounds exist in the form of the cyclic 2H-chromene structure. The tautomeric equilibrium is shifted to favor the open tautomer with a quinoid structure when the polarity of the solvent increases or when electron-donor substituents are introduced into the N-aryl ring [3, 4]. It is known that spectral methods (PMR, UV, and IR spectroscopy) are used most effectively to obtain information regarding the percentages in solutions of the individual tautomeric forms [5]. It has been shown in recent years that the individual tautomeric forms of organic compounds can be identified extremely successfully in the gas phase by mass spectroscopy and that one can even establish their quantitative relationship [6-8].

In this connection it seemed of interest to conduct an analysis of vinylogs (I-X) of imines of hydroxybenz- and hydroxynaphthaldehydes by mass spectrometry, to ascertain which of the tautomeric forms are realized in the gas phase, and, if possible, to establish the quantitative relationship betweeen these structures.

In principle, the investigated compounds can exist in the form of three tautomeric structures A, B, and C (let us note that the A form is observed in solutions only in the case of I).



A I-X B C

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TABLE 1. Mass Spectra of I-X*

Compound	m/z (relative intensity, %)
I	*257 (2,3)*; *240 (1,4)*; *138 (2,0)*; 131 (100,0); *127 (1,5)*; 111 (8,6); 103 (3,7); 91 (5,8); 77 (11,0); 75 (10,2); 51 (8,8)
II	*271 (15,0)*; *270 (13,5)*; *256 (12,0)*; *240 (38,0)*; *140 (12,5)*; 131 (100,0); *127 (15,0)*; *111 (20,0)*; 103 (10,0); 91 (15,0); 77 (20,0)
III	*301 (3,0)*; *284 (4,0)*; 220 (3,0); *209 (100,0)*; 199 (1,5); *165 (2,0)*; 130 (13,0); 118 (3,0); 111 (7,0); 104 (22,0); 89 (5,0)
IV	*381 (3,6)*; *209 (100,0)*; 196 (2,0); 191 (7,0); *182 (6,0)*; *171 (5,0)*; 166 (7,0); *155 (15,0)*; 130 (59,0); 102 (41,0); 89 (23,5)
V	*315 (10,0)*; *298 (30,0)*; *224 (6,0)*; *209 (28,0)*; 130 (6,0); 118 (7,0); 106 (6,0); 102 (4,0); 91 (100,0); 65 (11,0); 51 (5,0)
VI	*344 (11,0)*; *327 (1,0)*; *209 (19,5)*; 147 (7,0); 135 (100,0); 121 (15,0); 108 (8,0); 102 (12,0); 93 (12,0); 77 (16,0); 55 (11,0)
VII	345 (4,6); 286 (39,1); 181 (100,0); 168 (3,0); 152 (10,9); 134 (12,8); 115 (4,0); 107 (7,7); 92 (9,4); 77 (17,3); 63 (5,0)
VIII	*351 (2,0)*; *334 (1,1)*; *224 (2,7)*; 197 (2,0); 181 (100,0); *171 (41,0)*; 152 (11,0); 143 (1,7); 139 (2,0); 92 (23,0); 63 (5,0)
IX	303 (6,0); 286 (2,6); 260 (2,0); 197 (2,0); 181 (100,0); 152 (15,0); 149 (8,5); 134 (10,0); 123 (20,0); 108 (26,0); 77 (5,0)
X	287 (2,3); 270 (19,8); 181 (18,7); 168 (4,6); 152 (6,7); 141 (7,4); 115 (7,0); 91 (100,0); 77 (4,0); 65 (19,8)

*The molecular-ion peaks and the 10 most intense peaks are presented. The $(M + 1)^+$ ions are not presented. The ions that contain the lightest isotope of the halogen atom are given in italics.

Considering the general concepts regarding the mass-spectral behavior of compounds of this type [9] and the data in [10, 11], one might have expected the formation of the $(M - ArN{=}CH)^+$ ion and, possibly, the $(M - OH)^+$ ion when structure A is present in the gas phase.

The mass-spectrometric behavior of compounds with structures B and C should not differ substantially. Although the presence of the $(^+CH{=}CHNHAr)$ ion in the spectrum may unambiguously confirm the existence in the gas phase of structure B, ions of this type usually have a high appearance energy, and the probability of their formation is low. The appearance of intense peaks of $(M - H)^+$ and $(M - ArNH)^+$ ions might have been expected for both form B and for the cyclic form of 2H-chromenes.

An analysis of the mass spectra of the investigated compounds (Table 1) showed that the peak of a molecular ion, the stability of which ranges from 0.9 to 5.5, is present in the spectra of all of the compounds. It must be noted that the substituent in the benzene ring has virtually no effect on the stability of the molecular ions; however, W_M increases when an electron-donor substituent is introduced into the N-aryl ring or when an aryl substituent is replaced by a benzyl substituent (Table 2). This makes it possible to assume that the charge in the molecular ion is localized primarily on the azomethine fragment. It is apparent from the data in Table 2 that the most intense peak in the mass spectra of almost all of the compounds is the F_6 ion, which evidently has a cyclic structure, while the intensities of the peaks of the F_1-F_4 ions, the formation of which can be conceived of only from the A form, vary over a wide range, and the peaks of the F_8 ions, which determine the B form, are either absent or have low intensities.

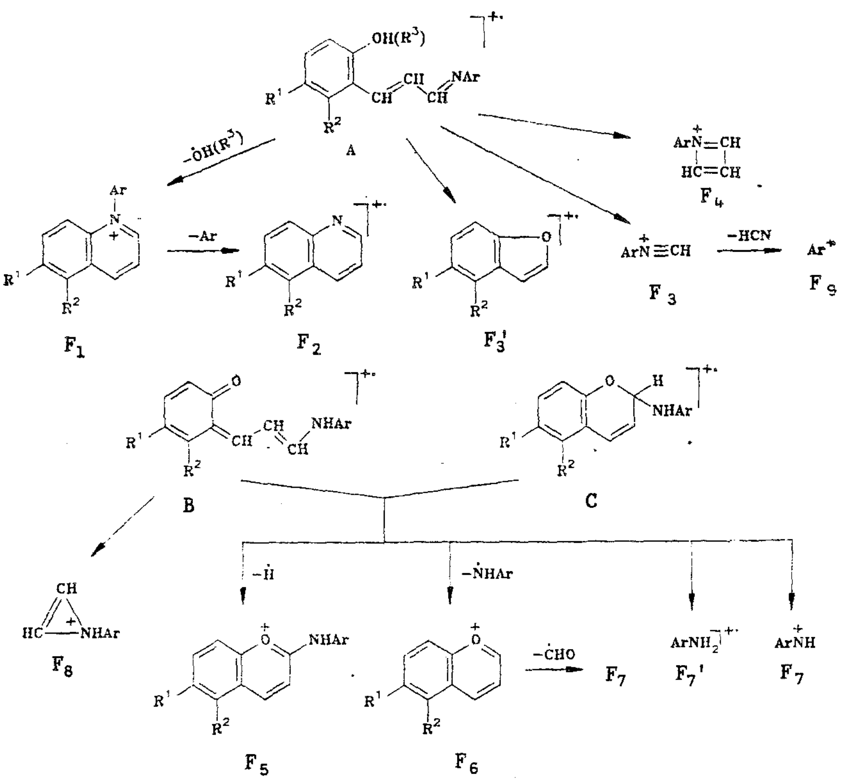
An analysis of the mass spectra of deuterium-labeled I, VIII, and X shows that the deuterium atom is actually not retained in either the F_1 ion or in the F_6 ion, while the mass numbers of the F_5, F_7, and F_8 ions increase by one unit. The F_1 ion is also present in the mass spectra of acetoxy derivative VII and methoxy derivative II; this also confirms the proposed fragmentation scheme [9, 10]. (Following page, below Table 2.)

For additional confirmation of the one-step character of the formation of the F_1, F_3, F_3', F_5, and F_6 fragments from the molecular ion we recorded the spectra of the products of dissociation of these ions of the activated-by-collision (the DAC spectra) VII, IX, and X with an instrument with double focusing and under the condition of scanning of the magnetic and electrostatic analyzer B/E-const, which makes it possible to observe the daughter ions formed in the first fieldless space (IFS) [12, 13]. The data obtained demonstrate that the F_1, F_5, and F_6 ions have a cyclic structure, and, consequently, the molecular ions of VII, IX, and X may have either cyclic form C or hydroxy form A.

TABLE 2. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of 2H-Chromene Derivatives I-X (%Σ_{39}) and Percent of Tautomeric Form A in the Gas Phase

Compound	Ar	W_M	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}	A, %
I	4-ClC_6H_4	0,9	0,7	0,4	1,1	0,5	0,7	34,7	0,6	—	3,3	1,2	6
II	4-ClC_6H_4	3,1	12,9	1,3	—	—	3,4	15,8	—	—	4,4	—	—
III	C_6H_5	1,6	2,5	2,1	5,5	3,0	0,8	51,2	0,8	0,8	—	—	20
IV	4-BrC_6H_4	0,9	0,3	—	1,8	—	—	24,0	1,2	0,5	3,8	—	8
V	$CH_2C_6H_5$	5,5	19,0	—	2,0	0,8	2,6	16,1	1,7	—	26,0	—	54
VI	4-$(CH_3)_2NC_6H_4$	4,4	0,7	—	1,3	—	0,9	8,6	19,2	—	2,3	—	17
VII	4-$CH_3OC_6H_4$	1,2	9,1	—	3,0	—	—	23,2	0,2	—	—	—	—
VIII	4-BrC_6H_4	1,1	0,7	0,4	—	—	0,6	29,3	24,5	0,8	0,8	3,0	12
IX	4-$CH_3OC_6H_4$	2,2	0,8	—	3,2	—	0,6	32,1	6,4	0,8	1,0	4,8	10
X	$CH_2C_6H_5$	0,9	6,2	0,2	0,5	0,1	5,9	5,9	0,6	—	31,4	2,1	46

*I, II R^1 = H, III-VI R^1 = Br, VII-X R^1 = $-(CH)_4$; I-VI R^2 = H; II R^3 = OCH_3, VII R^3 = $COOCH_3$.



A comparison of the DAC spectra of VII and IX showed that the F_1 and F_6 ions formed in the fragmentation of the molecular ions of these compounds have identical fragmentation character and, consequently, the same cyclic structure.

In order to make a comparative study of the structures of the molecular ions of VII and IX we determined the ionization energies (IE) of their molecules in the gas phase. The values found were identical within the limits of the experimental error (IE of VII = 7.53 ± 0.05 eV, IE of IX = 7.47 ± 0.05 eV), which makes it possible to assert that IX in the gas phase cannot exist in tautomeric form C. One can arrive at the same conclusion by comparing the obtained IE of IX with the IE of β-naphthol (7.78 eV) and naphthoquinone (9.56 eV) [14]. Since the electronic structures of the acyclic hydroxy form and the 2H-chromene form are similar, it might be assumed that the low ionization energy that we found does not contradict the chromene structure, at which we arrived also on the basis of an analysis of the mass spectra. It might be assumed that the remaining compounds, which exist in quinoid form B in polar solvents, in the gas phase also exist primarily in acyclic form A and cyclic form C.

For the quantitative evaluation of the A and C forms we used the intensities of the peaks of the F_1-F_4 ions for the hydroxy form and of the F_5, F_6, and F_{10} ions for chromene form C. In conformity with this the percentage of the A form was determined from the expression

$$[A] = (\Sigma F_1 - F_4) \cdot 100 / (\Sigma F_1 - F_6 + F_{10}).$$

We assumed that the positive charge in the molecular ions of the acyclic hydroxy forms is localized primarily on the azomethine fragment. In this case the deficit of electron density on the azomethine group should increase when electron-donor substituents are introduced into the arylamino part of the molecule, thereby decreasing the basicity of the nitrogen atom and, correspondingly, increasing the electrophilicity of the adjacent methylidyne carbon atom. This in turn should lead to an increase in the ease of formation of the cyclic 2H-chromene structure of the molecular ion. Electron-acceptor substituents in the benzene ring should decrease the nucleophilicity of the hydroxy group and may promote retention of tautomeric form A. It follows from the data in Table 2 that the percentage of the hydroxy form is small in the case of I and IV and large in the case of II, V, VI, and X. Let us note that cyclic chromene ion F_5 is also observed in the mass spectra of methoxy and acetoxy derivatives of II and VII. The appearance of the F_5 ion is evidently associated with primary electrophilic attack by the azomethine carbon atom on the nucleophilic oxygen atom of the methoxy (acetoxy) group, as a result of which the cyclic form of the 1-methyl(acetyl)-2H-chromenium molecular ion is formed with the subsequent elimination of a methyl (acetyl) group. Thus, from our point of view, the results obtained indicate rather convincingly that attempts to compare the quantitative amounts of the corresponding tautomeric forms in solution and in the gas phase under mass-spectrometric conditions are not always correct, since we are dealing with neutral molecules in solution, whereas in the gas phase the molecular ions have a positive charge that is localized on one of the fragments of the molecule, which leads to marked redistribution of the electron density.

EXPERIMENTAL

The electron-impact mass spectra were recorded with a Varian MAT-212 spectrometer with direct introduction of the substances into the ionization chamber; the ionizing voltage was 70 eV, and the temperature of the ionization chamber was 100-150°C.

Compound II was obtained by the Williamson synthesis by the reaction of methyl iodide with the sodium salt of I in ethanol. Deuteration was carried out by fourfold dissolving of the corresponding compound in CH_3OD with subsequent evaporation of the solvent in vacuo; this made it possible to achieve a high degree of deuteration (up to 95-98%). The recordings of the mass spectra of the deuterium-labeled compounds and methoxy derivative II, as well as control recordings of I and IV-VI, were realized with a Varian MAT-111 mass spectrometer at an ionization energy of 80 eV. The spectra of the same samples recorded with different instruments differed by no more than 10% (relative) with respect to the intensities of the peaks of the principal characteristic ions, while the percentages of hydroxy form A calculated from them differed by no more than 2% (absolute).

The ionization energies and appearance energies of the fragment ions were obtained by the photoionization method with an MS-1302 mass spectrometer. The ionization efficiency curves were recorded with simultaneous recording of the optical spectrum of a hydrogen lamp over the energy range 6-13 eV under conditions of stabilization with respect to the luminous flux.

The DAC spectra were recorded with a Varian MAT-212 spectrometer with direct introduction of the substances into the ionization source; the neutral gas was helium, and the coefficient of transmission of the beam of parent ions was 0.5-0.6.

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REACTIONS OF 7-AMINOCOUMARINS LEADING TO ALKYLIDENEBENZOPYRANS

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The reaction of 7-aminocoumarins with triethyloxonium tetrafluoroborate leads to benzopyrylium salts that react with sodium derivatives of compounds that contain an active methylene group to give substituted 2-methylene-2H-1-benzopyrans. The structures and physicochemical properties of the synthesized compounds are discussed.

The molecules of 7-aminocoumarins contain several reaction centers that are subject to electrophilic attack: the nitrogen atom, the $C_{(3)}$, $C_{(6)}$, and $C_{(8)}$ atoms of the benzopyran fragment, and the exocyclic oxygen atom of the pyrone ring. We have previously investigated [1] a number of reactions of coumarins I and II with electrophiles that lead to the synthesis of C-substituted derivatives. It was shown that soft Lewis acids ($ZnCl_2$, $HgCl_2$) are capable of coordinating with the carbonyl group of 7-aminocoumarins and of leading to regiospecific substitution reactions in the 3 position. In this connection we became interested in the possibility of the selective modification of the carbonyl group by means of electrophilic addition reactions.

Taking into account the potential tendency of 7-aminocoumarin dyes for marked charge separation within the molecule [2, 3], replacement of the carbonyl oxygen atom by the $=C\begin{smallmatrix}/X\\ \backslash Y\end{smallmatrix}$ fragment seemed of particular interest for the transition to other strongly polarized structures. As a result, the aim of the present research was to develop a method for the synthesis of 2-methylene-2H-1-benzopyrans on the basis of aminocoumarins I-III.

Benzopyrylium salts and 2,2-dialkoxybenzopyrans [4-6] could be potential sources of methylenebenzopyrans, and we therefore initially evaluated methods for the generation of benzopyrylium salts on the basis of coumarins I-III. We found that the reaction of I-III with electropyilic reagents such as triethyloxonium tetrafluoroborate, dimethyl sulfate, and phosphorus oxychloride in solution in methylene chloride, chloroform, or benzene leads to the formation of aminobenzopyrylium salts (for example, Ia and IIa) in 80-95% yields. (Formula, top, following page.)

The reactions with triethyloxonium tetrafluoroborate proceed most smoothly. The ready formation of salts Ia and IIa is evidently a privilege of precisely 7-aminocoumarins, in which the amino group acts as an additional factor in the stabilization of the benzopyrylium system.

The aminobenzopyrylium salts are bright-yellow substances that are relatively stable in solution in CH_2Cl_2 but decompose rapidly in air. For identification, as an example we isolated tetrafluoroborate salt Ia (mp 136°C) and, despite unsuccessful attempts to obtain satisfactory results of elementary analysis, determined its physicochemical parameters. Thus signals of

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