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NEGATIVE-ION MASS SPECTRUM OF SOME ANALOGS OF 11-DEOXYPROSTAGLANDINS E_1

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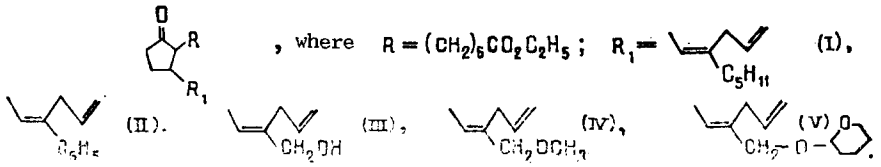
The results of a study of the mass spectra of the negative ions formed in the dissociative capture of electrons by the molecules of some analogs of 11-prostaglandins E_1 have shown that from the fragments of the compound under consideration it is possible to single out two "centers" of electron capture: R and the remaining fragment of the molecule. The presence of fragments characteristic for each group of processes and their simplicity and distinctness permit this method to be used successfully for determining the structures of compounds of the given class.

Particular attention is being devoted to the synthesis and study of the properties of the prostaglandins at the present time in view of the possibility of creating effective drugs from them. Positive-ion mass spectroscopy is one of the widely used methods for identifying these compounds [1]. However, the multiline mass spectra obtained on electron impact, the presence of a number of strong rearrangement peaks, and, as a rule, the low yield of the peak of the molecular ions make it difficult to use this method for the identification of the given class of compounds [2]. The necessity for seeking other methods of identification from this point of view is obvious. Furthermore, this class of compounds is a convenient object for revealing the mutual influence of functional groups on dissociative electron capture (DEC). With this aim, we have obtained the negative-ion (NI) mass spectra of the molecules of some analogs of the 11-deoxyprostaglandins E_1 with the common structural formula



The spectra were obtained on a MKh-1303 mass spectrometer re-equipped for recording NIs. The electron-energy scale was calibrated on the basis of the yield of $C_6H_5^-$ ions from the benzene molecule [3]. The NI mass spectra are given in Table 1. The relative intensities of the lines of the ions are shown as percentages of the maximum peak, and in parentheses are given the electron energies at the maxima of the resonance curves. As can be seen from Table 1, NIs are formed mainly in the region of electron energies of 8.5 eV. The effective-yield curves in the region of electron energies of 8.5 eV are relatively broad and do not exclude the possibility of the superposition of two resonance states of a molecular NI. A resonance in the 2.8 eV region of electron energies with the formation of $(M - H)^-$ is due to the presence of the R radical in the structure of the molecule and has been observed previously in a model compound – ethyl heptanoate [4]. The presence of an ester group in the structure of the molecule is shown more clearly in the second resonance region of electron capture. In this case, the mass spectra show the main types of breakdowns characteristic

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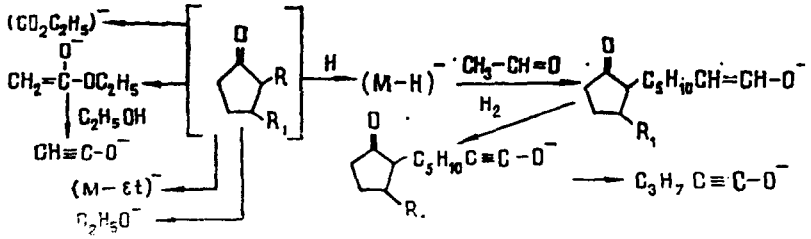
TABLE 1. Negative-Ion Mass Spectra of Some Analogs of 11-Deoxyprostaglandins E_1

	R_1				
	I	II	III	IV	V
$(M-H)^-$	1,0 (2,8) 100 (8 0)	2,5 (2 6) 100 (8,2)	0,9 (2,8) 2,5 (7,6)	3,0 (2,7) 18,5 (7 6)	4,0 (2,6) 14,9 (7,7)
$(M-H-R'OH)^-$*			12 0 (8 0)	100 (8 0)	100 (8,4)
$(M-C_2H_5)^-$	20,0 (8,5)	30 0 (9,5)	8,0 (9,2)	27,0 (8.8)	19,0 (9,3)
$(M-CO_2C_2H_5)^-$	12,0 (8,3)	11 0 (8,2)		11,0 (7,8)	
$(M-HOC_2H_5-H)^-$	23,0 (8,3)	24 0 (8,5)	8,0 (8,1)	17,5 (8,0)	6,0 (8,3)
$(M-F)^-$	10,0 (8,3)	12,0 (8,9)	8,0 (7 7)	17,0 (7,7)	5,0 (7,8)
$RC\equiv C-O^-$	18,0 (8,3)	20,0 (8 4)			
R_1^-	0,5 (8,5)	22,0 (8,1)	100 (8,2)	10,0 (8,0)	5 0 (8,3)
$C_2H_5CO_2CH_2^-$	26,0 8 7)	39,0 (8,7)	15,0 (8,5)	9,0 (8,3)	27,0 (8,5)
$C_3H_7C\equiv C-O^-$	10,0 (8 5)	14,0 (8,7)	5,0 (8 5)		25,0 (8,4)
$C_2H_5CO_2^-$	10,0 (8,4)	13,0 (8 2)	5,0 (7,5)		
$C_2H_5O^-$	15,0 (8 2)	12 0 (8,1)	11,0 (8 5)	11,0 (8,2)	17,5 (8 5)
$HC\equiv C-O^-$	76 0 (9,2)	62,0 (9,2)	11 0 (8,5)	4 0 (9,0)	5,0 (9,0)
C_3H^-	30,0 (9,6)	13 0 (9,7)	2,0 (9,2)	3 0 (9 3)	
OR''^-		9,0 (8,9)	25,0 (6,7)	32,0 (8,3)	72 0 (8,5)
$C_6H_5^-$					

*R' = H(III), CH_3(IV),  (V).

of the molecular NI of the model compound, which can be represented by the following scheme*:



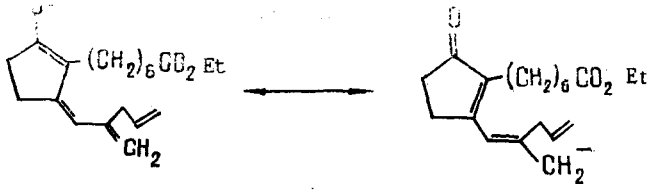
The processes forming NIs are connected with the capture of electrons in orbitals localized mainly in the fragments of the 3-R_1-cyclopentanones that are represented in the mass spectra by the peaks of the ions $(M-H)^-$†, $(M-R)^-$, R_1^-, OH^-, CH_3O^-, the tetrahydropyranyloxy anion, and ions with m/z 317 for compounds (III-V). The peak of the R_1^- ions in (III) is then the maximum, which is probably due to the stabilization of this ion by an intramolecular hydrogen bond.

Ions with m/z 317 are formed by the breakdown of the $(M-H)^-$ ions with the ejection of molecules of water, of methanol, and of tetrahydrofuranyl alcohol. The occurrence of such processes is confirmed by the presence of metastable peaks of ions with m/z 268 and 240 for compounds (IV) and (V), respectively. The motive force of this process is probably the stability both of the neutral fragments split out and that of the NI due to the formation of an unsaturated bond.‡

*The scheme of fragmentation is given by analogy with the fragmentation of the model compound – ethyl heptanoate [4].

†In the model compound, the intensity of the peak of the $(M-H)^-$ ions in the 8 eV region of electron energies is considerably lower than in the 2.8 eV resonance.

‡Such stabilization of the molecular NI has been observed previously [5].



It is characteristic that the occurrence of this process greatly decreases the ratio of the intensities of the peaks of the ions, which is connected both with the opening up of the five-membered ring (the R≡C—O⁻ ion for (I) and (II)) and with that of the maternal ions $(M - H)^-$.

Thus, with respect to the fragmentation of the compounds studied, it is possible provisonally to isolate two "electron-capture centers": the substituent with the ester group and the remainder of the molecule. The fact that, qualitatively, the fragmentation processes governed by the ester group do not appreciably change in comparison with the model compound shows the insignificant influence on the ester group on the structure of the remainder of the molecule. Conversely, a change in the structure of the radical R_1 appreciably changes the fragmentation of the 3-R_1-substituted cyclopentanones, which is not surprising, since in this case the carbonyl group and the substituent R_1 are separated spatially by a smaller number of carbon atoms.

EXPERIMENTAL

The mass spectra and the curves of the effective yields of NIs were obtained on a MKh-1303 instrument re-equipped for recording NIs [6]. The electron energy scale was calibrated in relation to the yield of $C_6H_5^-$ ions from benzene [3].

SUMMARY

The formation of negative ions on the resonance capture of electrons by the molecules of some analogs of the 11-deoxyprostaglandins E_1 has been studied. It has been shown that the fragmentation processes of the negative molecular ions of the compounds studied are determined mainly by the presence of spatially separated centers of localization of the added electron: the substituent with the ester group and the 3-R_1-substituted cyclopentanone in each case.

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