APPLICATION OF MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL INVESTIGATIONS

IV.* PECULIARITIES OF THE MASS SPECTRA OF β-OXOQUINUCLIDINES AND THEIR ANALOGS

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The mechanism of the process $M^{+\cdot} \to (M-CO)^{+\cdot}$ during fragmentation, under the influence of electron impact, of some bicyclic amines with a nodal nitrogen atom and containing an oxo group in various positions of the bridged system is discussed. Data on the ionization potentials and low-voltage mass spectra and from high-resolution mass spectrometry are used.

It has been shown [2, 3] that the relative intensities of the $M^{+\cdot}$ molecular ion peak and the peak of the $(M-CO)^{+\cdot}$ fragment in the mass spectra of various substituted β-oxoquinuclidines at 10-70 eV are independent of a change in the ionizing-electron energy. It follows from Fig. 1 that the $M^{+\cdot}$ and $(M-CO)^{+\cdot}$ peaks and their $M^{+\cdot}/(M-CO)^{+\cdot}$ ratio have practically equal values in the spectra of β-oxoquinuclidine (I) at 70 and 12 eV. Regularities of this sort are absent in the mass-spectrometric disintegration of both monocyclic [4, 5] and bicyclic [6] compounds containing a CO group.

In order to explain this unusual regularity we determined the ionization potential of the β-oxoquinuclidine molecule and the energy characteristics of the formation of the fragment ions. These measurements may give an unambiguous answer to the nature of the elementary act of ionization of the investigated compounds, inasmuch as removal of an electron from the unshared electron pairs of both the nitrogen atom and the oxygen atom is possible during the formation of $M^{+\cdot}$. In addition, the results obtained make it possible to estimate the activation energies of the processes under consideration. The ionization and appearance potentials were determined with a photoionization mass spectrometer.

The ionization potentials (IP) and appearance potentials (AP), the excess energy (AP − IP) necessary for the formation of the ions, and the relative intensities (I) of the peaks formed at ionizing-photon energies of 12.08 eV are presented in Table 1.

The ionization potential of the β-oxoquinuclidine molecule (IP = 7.95 eV) is typical for saturated amines. It is known that the ionization potentials of diethylamine and triethylamine, which are 8.0 and 7.58 eV, respectively, correspond to detachment of an electron from the unshared electron pair of the nitrogen atom [7]. However, the ionization potentials of various oxo-containing compounds usually are on the order of 9.1 eV and higher [8, 9]. From
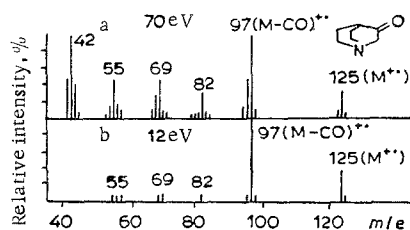

Fig. 1. Mass spectrum of β-oxo-quinuclidine at 70 (a) and 12 eV (b).

*See [1] for communication III.

TABLE 1. Mass Spectrum of I and Its Energy Characteristics

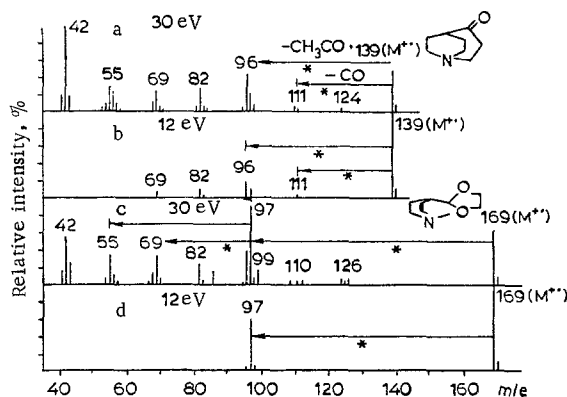| Ion mass, m/e	Rel. intensity, I, %	Ionization (IP) and appearance (AP) potentials, eV	Activation energy (AP−IP), eV
125	40	7,95÷0,03	
97	100	8,40÷0,05	0,45
82	17	10,8 ÷0,05	2,85
69	26	10,87÷0,05	2,92
56	7		
55	31		
42	5	11,5< AP <12	
41	2		

Fig. 2. Mass spectra of 4-oxo-1-azabicyclo-[3.2.2]nonane at 30 (a) and 12 eV (b) and of β-oxoquinuclidine ethyleneketal at 30 (c) and 12 eV (d).

a comparison of these data one can probably conclude that the ionization of the β-oxoquinuclidine molecule is realized via the unshared pair of the nitrogen atom.

It follows from the last column of Table 1 that the activation energy (ε) for the elimination of carbon monoxide from $M^{+\cdot}$ is 0.45 eV, disregarding the kinetic shift. Moreover, the values for all of the other processes are higher by a factor of six or more than the analogous parameter for the reaction $M^{+\cdot} \rightarrow (M-CO)^{+\cdot}$. The kinetic shift usually does not exceed 0.2 eV [10]. Consequently, the predominance of the peak of the $(M-CO)^{+\cdot}$ fragment in the spectra of the investigated compounds at 70 and 12 eV might have been explained by the extremely low activation energy (ε =0.25 eV) for the splitting out of a neutral CO molecule. However, this assumption does not explain the constancy of the $M^{+\cdot}/(M-CO)^{+\cdot}$ ratio as the ionizing voltage is varied from 12 to 70 eV.

On the basis of the literature data, this regularity can be explained by two factors: by a reaction with a low activation energy and a low frequency factor [11] and by fragmentation from the isolated electronic state [12-14].

As shown in [2, 3, 15, 19], the fragmentation of various functional substituted quinuclidines should be considered from the open form of the molecular ion that is formed during cleavage of one of the bridge bonds. On the basis of the low-voltage mass spectra and measurements of the ionization potential with the energy characteristics of the appearance of the fragment ions it should be assumed that opening of $M^{+\cdot}$ of β-oxoquinuclidine occurs in only one way, namely, at the bridge bond containing the oxo group to give ion A_1 (scheme 1). The open form of molecular ion A_1 is a typical amine fragment. Subsequent splitting out of a CO molecule from A_1 is accompanied by the skeletal rearrangement B→C and the formation of rearranged ion B [2, 3]. From the measurement of the energy characteristics of the disintegration of $M^{+\cdot}$ of β-oxo-quinuclidine and an analysis of the literature data it can apparently therefore be concluded that the investigated β-oxoquinuclidines are a class of compounds, in the disintegration of which the formation of an energetically favorable amine fragment (fragmentation from the isolated state) is successfully coupled with the subsequent rearrangement process $M^{+\cdot} \rightarrow (M-CO)^{+\cdot}$, which has a low frequency factor and an extremely small activation energy. Unfortunately, it is impossible to evaluate the contributions of these effects sep-
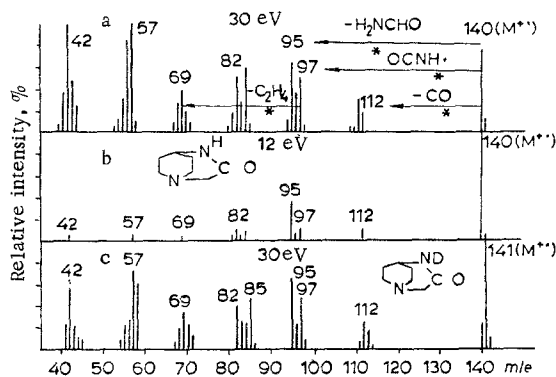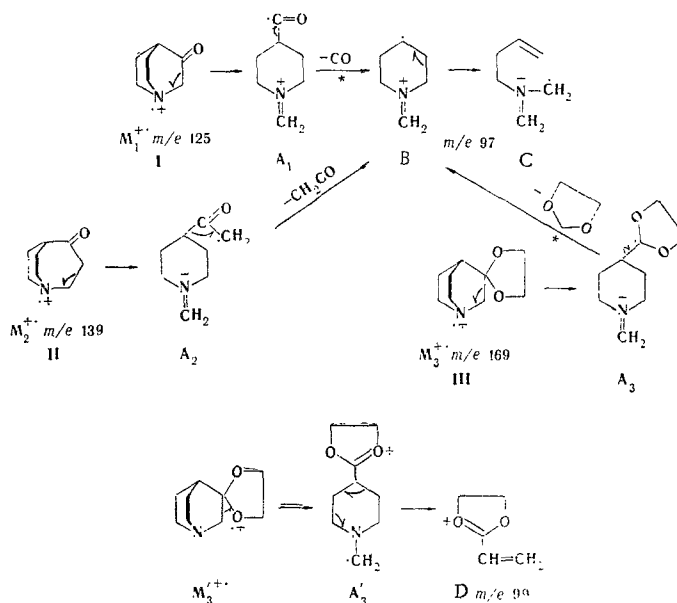
Fig. 3. Mass spectra of 3-oxo-1,4-diazobi-
cyclo[3.2.2]nonane at 30 (a) and 12 eV (b).

arately. This situation was previously noted in [16, 17], in which the possibility of fragmentation from the isolated electronic state for such compounds as aliphatic ketones, Schiff bases, and ketals was discussed.

Scheme 1

The mechanisms for the disintegration of ions B and C that were presented in [2] and were based on a study of metastable ions are confirmed by a study of the high-resolution mass spectrum of I. The precise masses of most of the fragments formed during the disintegration of quinuclidine I and the empirical formulas of the ions (in parentheses) found from them, which correspond precisely to the structures found in [2], are presented below: 97.0900 $(C_6H_{11}N)$; 96.0831 $(C_6H_{10}N)$; 82.0668 (C_5H_8N); 70.0873 (C_4H_8N); 69.0605 (C_4H_7N); 68.0535 (C_4H_6N); 57.0588 (C_3H_7N); 56.0495 (C_3H_6N); 55.0444 (C_3H_5N).

One's attention is drawn to the fact that all of the fragments in the spectrum of I that are of medium and high intensity contain nitrogen, and this once again indicates localization of the charge primarily on the nitrogen atom. The fragmentation of other compounds similar to it, which are considered below, served as a confirmation of the proposed mechanisms of the disintegration of β-oxoquinuclidines. The mass spectra of 4-oxo-1-azabicyclo [3.2.]nonone (II) and β-oxoquinuclidine ethyleneketal (III) are presented in Fig. 2. It follows from an examination of Fig. 2 (spectra a and b) that the peak of the $(M-CO)^+$· fragment in the spectrum of II is of extremely low intensity at 30 and 12 eV. A peculiarity of the disintegration of I-III is the presence in their spectra at mass numbers with m/e 97 and below of identical peaks of fragment, metastable, and doubly charged ions.*

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*The mass numbers of the metastable ions detected during the disintegration of I are presented in [2].
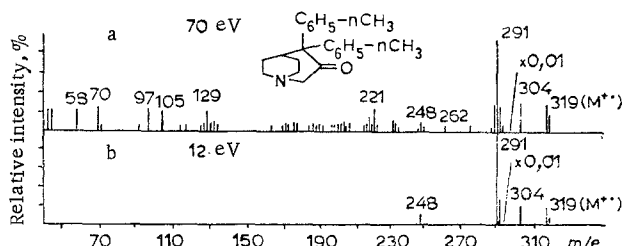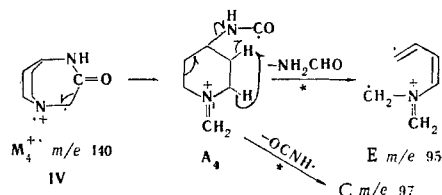
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Fig. 4. Mass spectrum of 4,4-di(p-tolyl)-3-oxo-1-
azabicyclo[3.2.2]nonane at 70 (a) and 12 eV (b).

In this case, it can be assumed that fragment ions with m/e 97 and below should have identical structures in the fragmentation of I-III. We note that while the similarity in the spectra of I and II is not so obvious, the spectra of I and III are absolutely identical in the indicated range. The identical character of the disintegration of I-III and the extremely low intensity of the peak of the $(M-CO)^{+\cdot}$ fragment in the spectrum of II are due to the formation of the open form of the molecular ion for II and III in the form of structures A_2 and A_3, which are formed during α cleavage of the bond containing the functional group (scheme 1). In this case, elimination of CO from A_2 is impossible, and the known [2] disintegrative processes lead to identical fragments B and C for I-III. It is interesting to note two circumstances that follow from an examination of Fig. 2 (spectrum d). First, the ion peak with m/e 97 at 12 eV in the spectrum of quinuclidine III, in contrast to I, is not of maximum intensity. Inasmuch as the $A_1 \rightarrow B \rightarrow C$ and $A_3 \rightarrow B \rightarrow C$ processes are identical, this phenomenon apparently may attest to a considerable effect on the skeletal rearrangement of the stability of the neutral particles that are split out. Second, the mass of spectrum of III is an additional confirmation of charge localization in $M^{+\cdot}$ for I-III only on the nitrogen atom. In fact, in contrast to the fragmentation of a number of ethyleneketal derivatives [18], the peak of characteristic fragment D with m/e 99, for the formation of which all of the necessary conditions are present in the disintegration of ketal III $(M^{+\cdot} \rightarrow A'_3 \rightarrow m/e$ 99), is of relatively low intensity in the spectrum of III.

In view of the fact that the initial cleavage of the bridge bond in $M^{+\cdot}$ stabilizes the ion-radical center on the nitrogen atom, the driving force of the disintegration of the compounds under consideration is the presence of an unpaired electron on one of the carbon atoms in the open form of $M^{+\cdot}$.

Scheme 2

This assumption is illustrated graphically by an examination of the fragmentation of other compounds containing an oxo group in various positions of the bridge.

The mass spectrum of 3-oxo-1,4-diazobicyclo[3.2.2]nonane (IV) and its deutero analog (IVa) are presented in Fig. 3. The peculiarity of the disintegration of this compound is also explained by the structure of open molecular ion A_4 (scheme 2). The elimination of a CONH radical from A_4 with subsequent cleavage of a second bridge bond leads to known fragment C with m/e 97. Yet another possibility before the occurrence of the energetically favorable rearrangement process — formation from A_4 of an ion with conjugated bonds (E) with m/e 95 during elimination of a formamide molecule — is realized in the fragmentation of IV. The rearrangement character of the formation of fragments with m/e 97 and 95 is confirmed by the low; voltage mass spectrum, in which peaks of these ions are distinctly observed. The $A_4 \rightarrow E$ and $A_4 \rightarrow C$ mechanisms are confirmed by the spectrum of the deutero analog (IVa), in which the peaks of ions with m/e 97 and 95 have the same characteristics as those observed for IV. It follows from an examination of Fig. 3 that the $(M-CO)^{+\cdot}$ ion peak in the spectrum of 3-oxo-1,4-diazobicyclo[3.2.2]nonane at 70 and 12 eV has an approximately constant relative intensity. In this connection, it seems of interest to us to also study the mass spectra of other compounds similar to IV but substituted, for example, in the 4 position. The mass spectra of 4,4-di(p-tolyl)-3-oxo-1-azabicyclo[3.2.2]nonane (V) and 4,4-dimethyl-3-oxo-1-azabicyclo[3.2.2]-nonane (VI) are presented in Figs. 4 and 5. In contrast to II and IV, $(M-CO)^{+\cdot}$ fragments G (with m/e 291)
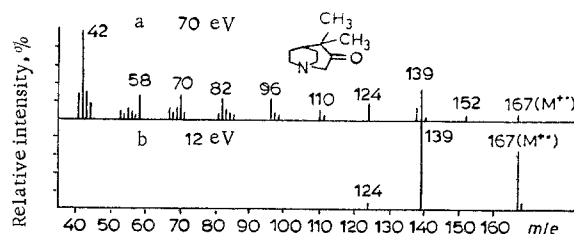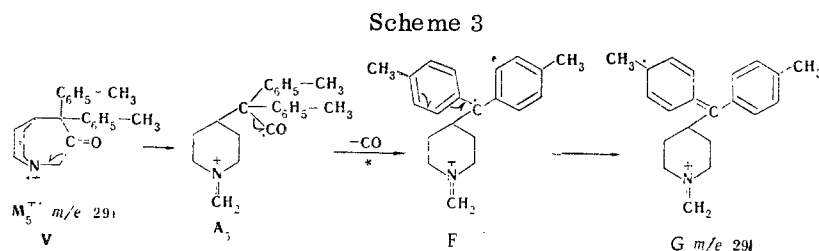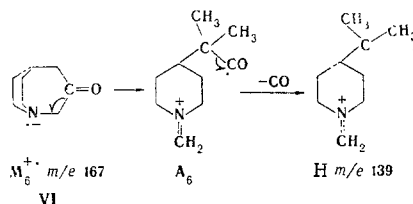
and H (with m/e 139) are primarily formed during the disintegration of V and VI at both 70 and 12 eV. The fundamental mechanisms of the disintegration of V and VI are presented in scheme 3. From an examination

Scheme 3

of this scheme it should be assumed that the ease of elimination of a CO molecule from open molecular ions A_5 and A_6 is apparently due to the effective stabilization in the $(M-CO)^{+\cdot}$ ion of the radical center at C_4. In the first case, this is achieved through the effect of conjugation of the unpaired electron with the π electrons of the tolyl substituent, while in the second case it is achieved through inductive stabilization of the radical center by two electron-donor groups. Inasmuch as the process $M^{+\cdot} \rightarrow (M-CO)^{+\cdot}$ for V is not accompanied by simultaneous skeletal rearrangement, the practically constant $M^{+\cdot}/(M-CO)^{+\cdot}$ ratio in the spectrum of V at 70 and 12 eV can apparently be explained only by fragmentation from the isolated electronic state of the A_5 ion. It is obvious that the process $F \rightarrow G$ facilitates this to a great extent.

Thus it follows from an examination of the mass spectra of I-VI that the $(M-CO)^{+\cdot}$ ion is observed during the disintegration of all of the investigated bicyclic compounds with a nodal nitrogen atom and containing oxo groups in the β position. However, predominant elimination of a CO molecule is observed only if: a) the formation of the open form of $M^{+\cdot}$ occurs at the bridge bond that immediately contains the oxo group; b) stabilization of the radical center in the $(M-CO)^{+\cdot}$ ion is realized as a result of the energetically favorable skeletal rearrangement or due to other stabilizing factors. In this case, the process $M^{+\cdot} \rightarrow (M-CO)^{+\cdot}$ can be characterized by a low frequency factor and a low activation energy or by fragmentation from the isolated electronic state.

EXPERIMENTAL

The low-resolution mass spectra were investigated with an MKh 1303 spectrometer and an LKV-9000 chromatographic mass spectrometer with introduction of the substances directly into the ion source; the ionizing voltage was 10-70 eV, and the cathode emission current was 0.75 μA (MKh 1303) or 60 μA (LKV-9000). The inlet temperature of the substances was 20-50°C, and the ionization chamber temperature was 125° (MKh 1303) or 250° (LKV-9000). The ionization and appearance potentials were determined with an MKh 1311 photoionization mass spectrometer. The high-resolution mass spectrum was recorded with an IMS-01 SG-2 mass spectrometer with an automatic system for information processing.

The compounds were synthesized and purified by the method described for I [2], II [19], III [20], IV [21], V [22], and VI [22].

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