284. The Mass Spectra of Organic Compounds

6th Communication[1])

The Ring Opening Reaction of Isomeric Cyclanones $C_8H_{14}O^+$ in Metastable and Collisional-Activation Spectra

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Summary

The molecular ions from three isomeric cyclanones isomerize to the ethyl-2-cyclohexanone ion prior to C_2H_4 elimination. With D- and ^{18}O-labelled compounds it is shown by Mass Analyzed Ion Kinetic Energy Spectroscopy (MIKES.) that both isomerization and C_2H_4 loss are specific processes. By high resolution collisional activation spectra it is shown that the resultant fragment ion $[C_6H_{10}O]^+$ (*m/z* = 98) differs in structure from the cyclohexanone molecular ion.

1. Introduction. - The 70 eV electron-impact mass spectra of cyclic ketones with 7 to 15 ring members are difficult to unravel, but they become much simpler by lowering the ionizing electron energy. As an example: for 2-ethylcyclohexanone (**1a**), 2-methylcycloheptanone (**2a**) and cyclooctanone (**3a**) only the fragment at *m/z* 98 persists at low eV among the peaks *m/z* 97 and 83, corresponding to elimination of ethyl and propyl radical respectively, and *m/z* 98 and 84 (loss of ethylene and propylene). Following an earlier suggestion [1] [2] we would like to make use of the unimolecular (MIKE.) and the collisional activation (CA.) metastable decay spectra in order to show that the two ions of *m/z* 98 and 84 are generated in two consecutives steps: a ring contraction reaction of the molecular ion followed by an elimination of ethylene or propene. This interpretation has been confirmed by *MacLeod et al.* [3a, b] in an ion cyclotron resonance (ICR.) investigation for the ion *m/z* 98 formed from **1a** and **3a**. He was able to prove the six-membered structure of this fragment ion, independent of its precursor. On the other hand, the study of CA. spectra of *m/z* 98 ions by one of us [4] seems to contradict his conclusion. In this work we make use of metastable spectra recorded under condition of high mass resolution of the parent ion [5] and D- and ^{18}O-labelling in order to demonstrate the specificity of the isomerization of the molecular ion of various cyclanones of formula $C_8H_{14}O$.

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[1]) 5th Communication, see [2].

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2. Experimental part. - MIKE. and CA. spectra have been measured with a VG/ZAB-2F mass spectrometer of reversed geometry connected on line with a PDP-11 computer. The mass resolution of the magnetic sector was set to 2000 in order to separate C,H- from C,H,O-containing fragments before subjecting the ions for a kinetic-energy analysis. The energy of the ionizing electrons was 70 eV. The energy resolution at 8000 V accelerating voltage was about 3000. The values given in the tables are the computer-averaged values of at least 5 scans. The following compounds were used: 2-ethylcyclohexanone (**1a**), 2-methylcycloheptanone (**2a**), cyclooctanone (**3a**), 2-[2,2,2-$^2H_3$]ethylcyclohexanone (**1b**), 2-[$^2H_3$]methylcycloheptanone (**2b**), [2,2,8,8-$^2H_4$]cyclooctanone (**3b**), 2-ethyl-[^{18}O]cyclohexanone (**1c**), 2-methyl-[^{18}O]cycloheptanone (**2c**) and [^{18}O]cyclooctanone (**3c**).

3. Results and Discussion. - 3.1. *Decomposition of the molecular ion.* The molecular ions of the three isomers **1a**, **2a** and **3a** exhibit the same metastable spectra for the unimolecular fragmentation, *i.e.* *m/z* 111, 108, 98, 97, 84 and 83 with very similar relative intensities *(Table 1).* The results with the ^{18}O-labelled precursors **1c**, **2c** and **3c** show that the base peak *m/z* 98 in the spectra of **1a**, **2a** and **3a** is formed by elimination of C_2H_4 only. With deuteriation, this peak is shifted to *m/z* 99 for **1b** and **2b** and to *m/z* 100 for **3b**. Thus the spectra are slightly more complex than the low-eV-source spectra [1]. The results demonstrate that the H-lost to the neutral ethylene originates at least from two locations: *e.g.* the *α*-position to the carbonyl group and from the methyl group of the chain, if present. We propose a reaction sequence for fragmentation which is shown in *Scheme 1* for **3b** and *2* for **2b**.

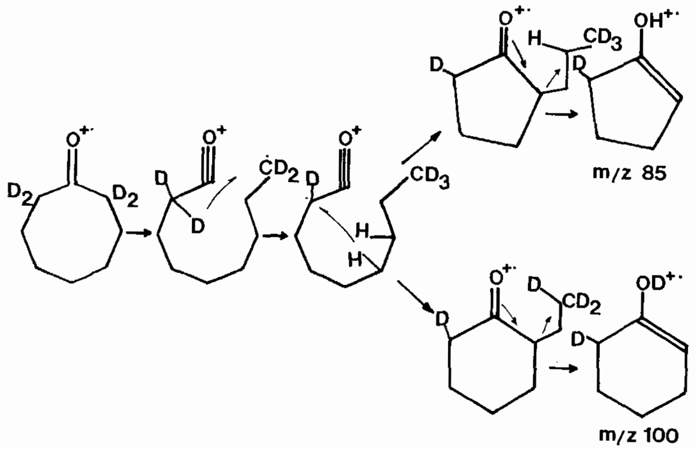
In the first step the ring is opened in the *α*-position to the carbonyl group; in this process both the charge and the radical site are separated. It is not unlikely

Table 1. *MIKE. Spectra of the molecular ions $C_8X_{14}O^{+\cdot}$* (X = H,D). The values are given in % of the total ion current (TIC.). Only ions with intensities above 0.1% TIC. are shown. The mass of the precursor ion is given in brackets.

m/z	2-Ethylcyclohexanone			2-Methylcycloheptanone			Cyclooctanone		
	1a (126)[a]	**1b** (129)	**1c** (128)	**2a** (126)	**2b** (129)	**2c** (128)	**3a** (126)	**3b** (130)	**3c** (128)
83	0.68			0.21			1.4	1.3	
84	1.4			2.0	1.0	1.4	9.9		
85			0.75		0.5	0.32		4.0	1.2
86		5.0[b]	1.4		0.19	2.3		0.92	10.3
87					0.40			2.3	
88								1.2	
97	25	16		9.1	7.1	0.1	9.6		
98	63	0.2		73	0.64		76	2.0	
99		63	24		67	9.3		3.4	8.5
100		2.3	65		1.8	75		71	76
101		2.2			4.4			9.3	
102								0.11	
108	1.3		1.2	9.4		7.3	2.4		2.4
110					0.23				
111	7.7	6.6		5.8	14.8		2.8	0.56	
112					0.13			2.4	
113			7.5			5.4		0.79	1.7
114					1.7			0.53	
115								0.65	

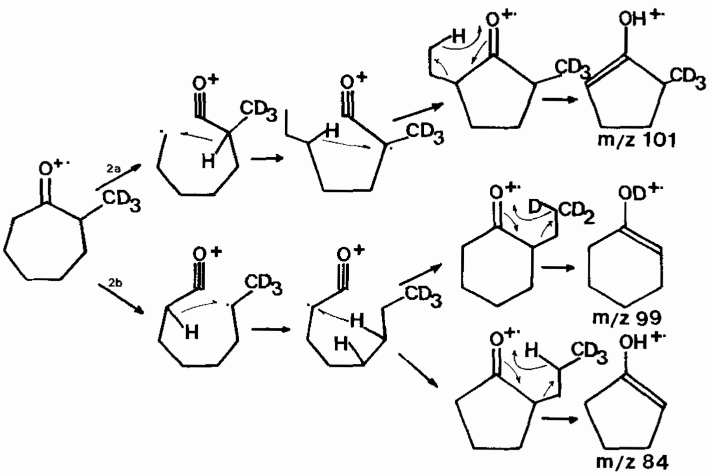
[a] *m/z* of the molecular ion. [b] This very high value is possibly due to an isotope effect.

Scheme 1

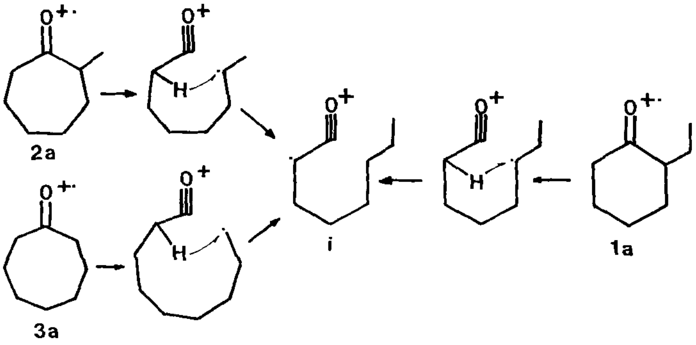


to assume that it is this process which has the highest activation energy. Sequential H(D)-transfers lead to an intermediate which has an ideal structure for reclosing either to a five- or a six-membered ring as will be proposed for cyclohexanone [6]. A *McLafferty*-type elimination of alkenes yields the stable radical cations of cyclohexen-1-ol, 5-methylcyclopenten-1-ol and cyclopenten-1-ol, respectively. The results with the deuteriated compounds show the high specificity of these reactions. From the deuterium distribution for ethylene loss from **2b** (*m/z* 99 significantly more abundant than *m/z* 101) it can be concluded that the activation energy for the process $\mathbf{2b}^{+} \rightarrow m/z\ 99 + C_2H_2D_2$ must be lower than that for the alternative reaction channel $\mathbf{2b}^{+} \rightarrow m/z\ 101 + C_2H_4$. It is likely that this result is a direct consequence of the fact that α-cleavage for the higher substituted C-atoms (process 2b, *Scheme 2*) is energetically more favoured. 2-Ethylcyclohexanone

Scheme 2



Scheme 3



loses methyl exclusively from its terminal position. This is not found to be the case for the isomeric **2a**; the spectrum of **2b** demonstrates that only one third of the total methyl radical yield to be eliminated consists of $CH_3^{\cdot}$. Due to the fact that we observe a considerable H-scrambling for the same reaction in ions of cyclooctanone, whereas a 'clean' process is found for the elimination of ethylene, we assume that both methyl and ethylene are eliminated from structurally and/or electronically different molecular ions.

A similar observation can be made for the elimination of an ethyl group. Whereas the elimination of the intact chain is still the main process for **1b**, in **2b** some scrambling of the D-atoms is found to occur that becomes more pronounced in the fragmentation of **3b**. Because of the interference peaks due to C_2H_4-elimination as main reaction, a quantitative assessment of the reaction is not possible.

From the similarity of the MIKE. spectra of the different $C_8H_{14}O^+$-isomers a common intermediate **i** could be assumed as shown in *Scheme 3*.

To account for the scrambling data in the MIKE. spectra it could be argued that this common species will decompose *via* different consecutive reaction sequences. However the CA. spectra of the various molecular ions shown in *Table 2* preclude such an hypothesis. We would like to stress the following observations: *i*) the methyl loss is not particularly favoured even in the case where it would be considered to consist of a simple fragmentation reaction as in **2a**; moreover the scrambling for **3b** is comparable in both the MIKE. and the CA. spectra. This is also observed for elimination of ethyl radical, although in the CA. spectrum its importance decreases; *ii*) in spite of the decrease in its intensity, the elimination of ethylene remains the main reaction and retains its character of being a clean process occuring without any H/D-scrambling.

Therefore we have to assume a set of several isomeric structures for the molecular ion that are not in equilibrium with each other.

3.2. *Decomposition of the* $(M-C_2H_4)^+$*-ion.* In order to avoid any ambiguity concerning the elemental composition of the radical cation *m/z* 98, we labelled the ketones with ^{18}O. The MIKE. spectra of this ion from different precursors are compared in *Table 3* with the spectrum of cyclohexanone. Three conclusions can be drawn immediately: *i*) under our experimental conditions the ion *m/z* 98 consists

Table 2. *CA. Spectra of the molecular ions* $C_8X_{14}O^+$ (X = H, D). The values are given in % TIC. Only ions with *m/z* > 54 and *I* > 0.2% TIC. are shown.

m/z	2-Ethylcyclohexanone			2-Methylcycloheptanone			Cyclooctanone		
	1a	**1b**	**1c**	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**
55	9.4	5.2	6.9	7.8	4.8	7.9	5.9	1.3	4.8
56				1.0	1.3	1.1	0.1	3.6	0.1
57	0.4	0.6	3.2	0.1	0.94	2.7	0.1	1.8	3.8
58		2.3		0.3	2.3		0.2	1.1	
59			0.4		0.9	0.2		0.4	0.2
60						0.4			0.2
61					0.3			0.1	
65	0.9		0.8	0.2	0.1		0.2		0.4
67	3.5	1.5	3.3	1.8	1.0	2.6	1.4	0.5	1.8
68	0.2	0.7		1.8	1.3	2.1	1.6	1.0	1.4
69	2.3	1.4	1.3	3.2	1.8	2.3	1.4	1.6	1.0
70	1.5	0.8	0.6	1.4	1.0	1.0	1.5	1.1	0.6
71		1.4	1.2		1.6	2.0	0.7	1.2	0.7
72		0.8	1.4		2.2	1.3		1.1	1.5
73		0.4			0.7	0.2		0.6	0.8
74								0.6	
77	1.8	0.7	1.7	0.6	0.4	0.7	0.4		0.8
78								0.9	
79	2.1	1.2	1.9	0.9	0.8	1.2	1.0	0.2	1.2
80							0.2	0.4	
81	1.4	1.1	0.9	0.9	0.7	0.8	0.6	0.4	0.5
82	1.6		1.3	2.6	0.2	2.6	2.2	0.7	1.7
83	3.7	1.7	0.5	2.2	1.2	0.4	3.1	0.7	0.6
84	0.9	1.8		2.6	3.0		7.5	2.4	
85		2.6	3.6		3.1	2.6		5.8	3.2
86		4.3	0.9		1.0	2.9		1.8	6.3
87		0.2			0.4			1.8	
88								0.8	
91	0.8		0.8	0.4	0.2	0.4	0.2		0.3
93	0.8	0.5	0.7	1.3	0.8	1.1	0.5		0.5
95	1.4	0.6	0.2	0.7	0.2	0.2	0.6	0.2	0.1
96					0.6			0.2	
97	12.8	13.2	1.6	6.6	4.6	0.7	11.3	0.3	0.8
98	29	1.7		4.2	0.9		46	2.9	
99		36	13		37	5.4		5.4	9.4
100		1.8	27		1.1	37		38	36
101		1.0			3.5			5.7	
108	0.6		0.5	3.4		2.4	1.5		1.0
111	7.3	8.0	6.2	4.4	5.7	0.1	3.9	0.4	0.1
112					0.7			1.8	
113								1.8	3.1
114						3.6		0.6	
115								0.5	

only of $C_6H_{10}O^+$; however we observed that on other instruments (*e.g. Atlas* CH5) a contribution from the isobaric $C_7H_{14}^+$-ion can be found. This rather astonishing observation may explain eventually the reported discrepancies between the different results mentioned in the *Introduction; ii*) the CA. spectra obtained for **1a**, **2a** and **3a** as precursors of *m/z* 98 are rather similar; the loss of CH_3 forms the base

Table 3. *MIKE. Spectra of* $C_6H_8X_2O^{+}$ (X = H,D) *originating from the ketones* **1**, **2** *and* **3**. The values are given in % TIC.

m/z	2-Ethylcyclohexanone			2-Methylcycloheptanone			Cyclooctanone			Cyclohexanone
	1a (98)[a]	**1b** (99)	**1c** (100)	**2a** (98)	**2b** (99)	**2c** (100)	**3a** (98)	**3b** (100)	**3c** (100)	(98)
43	0.9	0.5		0.9	0.6		1.0	0.3		1.4
44								0.2		
45			0.8			1.1			1.0	
55		0.3			0.3		0.3			0.5
56	0.5	0.3		1.8	0.7		1.2	0.2		1.8
57		0.4			3.7			0.4		
58			0.4			1.0			0.8	
69	0.8	0.3	0.2	2.0	0.6	0.4	1.6		0.5	4.5
70	2.8	0.8	1.1	6.6	1.5	3.3	4.2	0.6	1.7	5.0
71		2.6	0.3		3.4	0.7		1.6	0.8	
72			1.2			1.7		3.8	1.5	
80	1.6	0.5	1.4	3.4	0.6	3.4	3.8		3.8	67
81		1.6			1.7			1.7		
82		0.2			0.1			3.1		
83	58	0.4		54	0.5		53	0.3		15
84		53			48			6.4		
85			57			54		47	55	
97	36	0.4		30	0.6		34			4.9
98		38			34			0.2		
99			36			34		33	35	

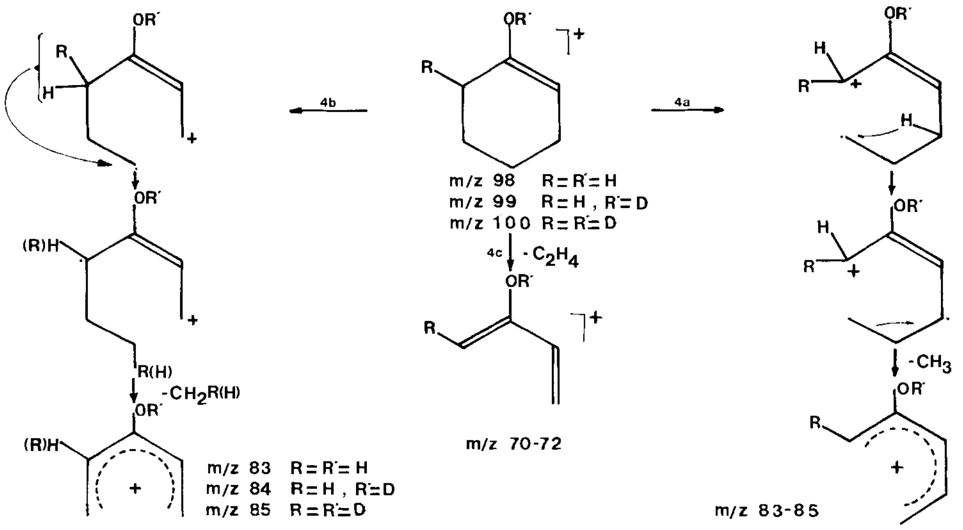
[a] *m/z* of the parent ion.

peak with little scrambling in case of deuteriation; *iii*) the base peak in the MIKE. spectrum of cyclohexanone is *m/z* 80, corresponding to the loss of H_2O. It is a minor peak in the compounds **1–3** and does not seem to be generated in a very specific process concerning the origin of the H-atoms.

We suggest that the small differences in the distribution of the fragment ions from the precursors **1–3** are due to small differences in internal energy of the parent ions [7]. *Hass et al.* proposed a reaction model for the loss of CH_3 for the homologous ion *m/z* 84 generated from ionized 2-ethylcyclopentanone [8]. It corresponds to the cleavage of the C,C-bond in a α-position to the hydroxyl group of the enol ion of cyclopentanone, followed by a loss of the resulting terminal methyl group of the resulting open chain. The results from the decomposition of paraffin(and olefin)molecular ions show that this reaction is neither important nor specific if the resulting ion is not specifically stabilized [9]. The results for the ions labelled with D (**1b**, **2b** and **3b**) show the following features: *i*) the ion *m/z* 97 is shifted to *m/z* 98, 98 and 99, respectively, by deuteriation without any loss of D; *ii*) the elimination of CH_3 is specific from **1b** and **2b**; also **3b** eliminates 90% of the methyl as CH_3 and 10% as $CH_2D\cdot$; *iii*) the ions *m/z* 69 and 70 are isobaric doublets. The ions containing oxygen do lose C_2H_4, retaining the D-atoms present in the precursor ion.

The MIKE. spectra of *m/z* 98 from **1a**, **2a** and **3a** show a composite peak at *m/z* 70 resulting from the loss of C_2H_4 or CO with different values of the kinetic energy release. The use of ^{18}O as a label allows to assign the broader, less intense

Scheme 4



component to the loss of CO. The measured kinetic energy release *T* for this process is around 185 meV for the precursors originating from the three isomers. The same value (183 ± 10 meV) is found for the loss of $C^{18}O$ from ^{18}O-labelled cyclohexanone and for the loss of CO from 3-methyl-[2,2,5,5-$^2H_4$]cyclopentanone (184 ± 10 meV). From this observation the following conclusion can be drawn: as the products of the reaction have the same structure (the CA. spectra of the $C_5H_{10}^+$ being identical), only the reverse activation energy of the reaction $C_6H_{10}O^+ \rightarrow C_5H_{10}^+ + CO$ is partitionned in the fragmentation.

The non-randomization of the D-atoms in spite of the lifetime of the metastable ion is particularly intriguing. We suggest the reaction sequence proposed in *Scheme 4*, where reaction 4a is the major path, reaction 4b contributing only to a minor extend. Reaction 4c gives rise to the expulsion of C_2H_4 in a formal *retro-Diels-Alder* elimination. The fact that the elimination of CH_3 is the main reaction from a structure as put forward in *Scheme 4* is corroborated by the MIKE. spectrum of cyclohexenol, where a similar observation can be made [10]. The proposed *Scheme* yields a structure of the ion *m/z* 83 that should be particularly stable. This is not the case in the reaction path suggested by *Hass et al.* [8].

The CA. spectra given in *Table 4* are similar to the MIKE. spectra except for a more pronounced fragmentation in the former. Similar conclusions can be drawn concerning the absence of an extensive scrambling. This allows us to state that also the ion *m/z* 98 having a lifetime of about 6–10 µs consists either of a unique structure of an enol or, less likely of a mixture of rapidly equilibrating isomeric forms [11]. Although we cannot exclude the latter possibility with certainty, we believe it to be less probable. This interpretation is consistent with the experimental results that little or no H/D-randomization is observed in case of deuteriation.

3.3. *Conclusion.* The study of the metastable decay, either unimolecular (MIKE.) or collision induced (CA.) allows us to propose a six-membered enol

Table 4. *CA. Spectra of* $C_6H_8X_2O^+$ (X = H,D) *originating from the ketones* **1**, **2** *and* **3**. The values are given in % TIC.

m/z	2-Ethylcyclohexanone			2-Methylcycloheptanone			Cyclooctanone		
	1a (98)	**1b** (99)	**1c** (100)	**2a** (98)	**2b** (99)	**2c** (100)	**3a** (98)	**3b** (100)	**3c** (100)
39	8.3	6.2	8.0	7.4	6.8	7.4	7.4	3.4	8.8
40		0.6						2.3	
41	5.4	3.0	5.5	5.1	3.1	5.0	5.5	1.6	6.2
42	1.5	2.8		1.4	2.8		1.6	2.9	
43	3.2	3.1		3.5	2.9		3.4	3.2	
44		1.0			0.8	0.8		2.4	1.0
45			3.8			3.7		0.5	4.4
51	2.6	2.8	3.4	2.6	2.7	2.4	1.9	2.1	4.4
52		0.5			0.6	0.3		2.1	0.3
53	2.8	1.5	2.1	2.3	1.6	2.0	2.2	1.1	2.1
54		0.3	0.3		0.8	0.3			0.4
55	7.9	4.1	2.2	7.6	4.2	2.5	8.2	4.8	2.4
56	0.9	3.2		1.7	4.0		1.2	4.3	
57	0.5	0.3	6.8	0.4	1.4	6.8	0.6	1.7	8.1
58		0.6	0.9		0.6	1.8		0.4	1.1
59			0.7			0.7			0.8
63	0.6	0.7	1.0	0.8	0.4	0.2	0.5	0.3	0.4
65	0.9	0.6	1.0	1.0	0.5	0.6	1.0		0.8
66	0.4	0.6		0.3	0.5	0.1	0.4	0.7	
67	1.8	1.1	1.3	1.7	0.8	1.3	1.8	0.6	1.7
68	0.5	1.6		0.6	1.5		0.6	1.3	
69	2.8	0.8	0.9	3.4	0.9	1.0	3.6	1.6	1.0
70	11.0	3.1	0.8	11.5	3.1	0.9	13.7	2.0	0.8
71		13.1	1.9		12.0	2.1		3.5	2.3
72			11.5			10.8		12.2	12.8
77	2.4	2.8	2.3	2.5	2.5	2.2	2.8	0.5	2.9
78	0.2				0.3			1.6	
79	2.0	1.8	1.8	2.1	1.8	1.8	2.6	0.8	2.0
80	0.5	1.0	0.4	1.0	1.0	0.6	1.0	1.1	0.5
81	1.0	0.8		1.1	0.7		1.3	1.3	
82	0.4	0.9		0.6	0.9		0.5	0.8	
83	16.2	0.4	0.9	20.0	0.8	1.1	19.4	0.8	0.9
84		18.8	0.4		17.7	0.6		4.2	0.4
85			17.6			18.0		12.6	15.7
95	1.6	0.4		1.6	0.4		2.1		
96	1.3	2.1	0.3	1.2	1.9	0.4	1.6	0.7	0.4
97	15.1	1.6	1.8	13.4	1.5	1.9	12.1	1.7	1.7
98		14.3	1.4		14.5	1.4		1.6	1.2
99			14.0			14.1		14.3	11.8

structure for the fragment ion *m/z* 98 generated from different isomeric precursors. In the case of a ring with more than six ring atoms, the ring-contraction reaction could lead to a six- or a five-membered ring. The results allow us to conclude that the formation of an ionized cyclohexenol structure seems to be particularly favoured. To which extend the different forms of the proposed reaction sequence, in particular the generation of acyclic isomers, are of physical relevance, is open to question. If the initial ion is already a six-membered ring, it will lose a substituent in α-position if the side chain consists at least of two C-atoms. This is confirmed by results obtained from the investigation of 1-ethyl-2-hydrindanone and 1-methyl-2-decalone [12]. The high specificity of the elimination of H·, CH_3 and C_2H_4 is astonishing in view of the non-specificity of these losses in the case of the decay of hydrocarbon ions in the metastable time range.

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