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OMS Letters

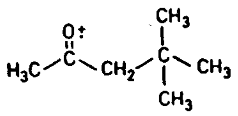
Dear Sir,

SKELETAL REARRANGEMENT OF THE MOLECULAR IONS OF KETONES $C_7H_{14}O$ VIA ION/MOLECULE COMPLEXES

The isomerization of the molecular ions of simple ketones[1], acids[2] and esters[3] has been studied intensively. Most of these radical ions studied show extensive hydrogen rearrangements via 3-, 5-, and 6-membered transition states[4]. However, the molecular ions of isobutyric acid and its methyl ester[5] as well as of some aliphatic ketones[6] exhibit an interesting skeletal rearrangement by a 1,2-shift of the C(OH)OH-, C(OH)OR- and C(OH)R- group, respectively. These skeletal rearrangements are of special interest firstly because of the insight gained by these reactions into the reactivity of gaseous organic ions and secondly because of their relevance to the analytical applications of metastable ion techniques.

In this connection we have observed the loss of structural identity of certain ketone ions in the CID spectra obviously due to a profound skeletal rearrangement, which cannot be explained by the mechanism elucidated for the isomerization of isobutyric acid and related compounds[5]. Here we report on these rearrangements of ketone ions $C_7H_{14}O^{+\cdot}$ which occur by a back-reaction in intermediate ion/molecule complexes. The structures of the molecular ions of compounds **1**-**8** were investigated by their CID spectra obtained with a VG ZAB-2F mass spectrometer[7] (Table 1).

Structures of isomeric $C_7H_{14}O^{+\cdot}$ ions 1 - 8



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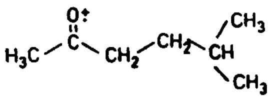

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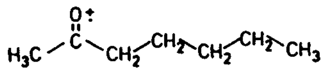

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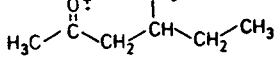

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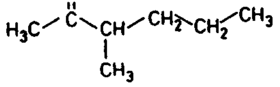

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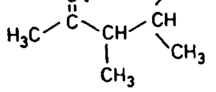

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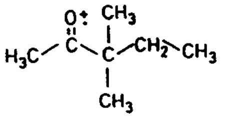

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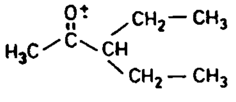

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TABLE 1. CID-SPECTRA OF THE MOLECULAR IONS 1 - 8 [a]

m/z	1	2	3	4	5	6	7	8
99	(2.4)	(1.9)	(12.1)	(7.7)	(45.8)	(106.0)	(14.2)	(7.5)
96	-	(0.5)	(2.9)	(1.3)	(2.4)	(4.1)	(0.9)	-
86	(12.4)	(6.6)	(2.3)	(4.2)	(1.9)	(2.8)	(118.8)	(274.0)
85	(50.8)	(56.3)	(49.9)	(110.7)	(2.9)	(1.8)	-	(44.9)
83	-	-	-	-	1.0	3.7	0.9	-
81	-	-	0.4	-	1.4	2.3	0.9	-
73	-	-	-	-	(1.9)	(1.8)	-	-
72	(4.3)	(6.1)	(26.0)	(16.1)	(171.8)	(125.3)	(5.7)	(6.0)
71	22.8	41.3	40.9	27.7	14.3	11.1	36.5	18.3
70	2.8	4.2	-	2.6	4.8	6.5	43.1	6.9
69	1.0	0.9	2.1	2.9	1.9	1.8	0.9	3.3
67	0.8	1.4	0.8	2.9	1.0	0.9	0.9	4.2
65	-	-	-	-	-	-	-	0.9
59	(26.4)	(20.7)	(11.6)	(17.1)	(1.9)	(1.4)	-	(0.6)
58	37.0	25.8	15.2	18.7	2.4	1.8	-	3.3
57	8.5	5.6	1.7	3.2	4.3	2.8	3.8	2.4
56	3.7	2.8	1.2	2.6	1.9	1.8	3.8	-
55	2.4	2.3	3.7	3.9	5.2	5.1	5.7	6.6
53	1.2	1.4	1.2	1.9	3.3	3.7	0.9	2.4
45	0.3	0.2	0.6	0.9	1.3	1.5	0.2	1.2
43	11.9	10.0	15.5	18.3	33.6	36.3	29.0	33.2
41	3.9	3.6	5.6	6.3	8.6	9.4	6.7	8.7
39	2.4	1.6	3.7	3.9	7.1	7.0	3.4	5.4
31	0.4	0.3	0.8	0.6	1.0	0.7	0.2	0.6
29	1.6	1.1	2.6	2.8	3.6	3.5	2.7	3.9
27	1.6	1.1	3.4	2.8	7.0	5.5	2.5	4.5
15	0.3	0.5	0.6	0.6	1.1	1.0	0.9	1.2

a) In % total fragment ions. Values in parenthesis correspond to ions also formed by unimolecular reactions.

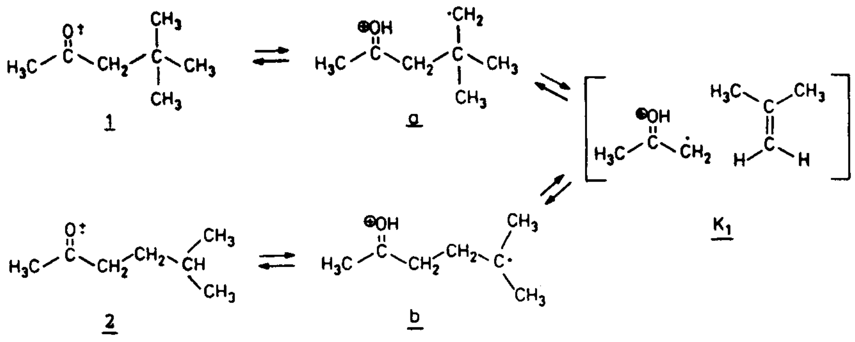
For a more reliable quantitative comparison of these CID spectra the similarity index (SI)[8] has been calculated taking into account all ions with the exception of those formed also by unimolecular fragmentations. The SI values are given in Table 2. A value of SI < 70 is taken as an indication of identical structures of the ions compared. Different structures of these ions are clearly indicated by large values of SI > 150. However, there is an intermediate range of SI = 70-150 characterizing CID spectra which are not very different and very likely arise from mixtures with different compositions of the same ions (Table 2).

TABLE 2. SIMILARITY INDICES OF IONS 1 - 8

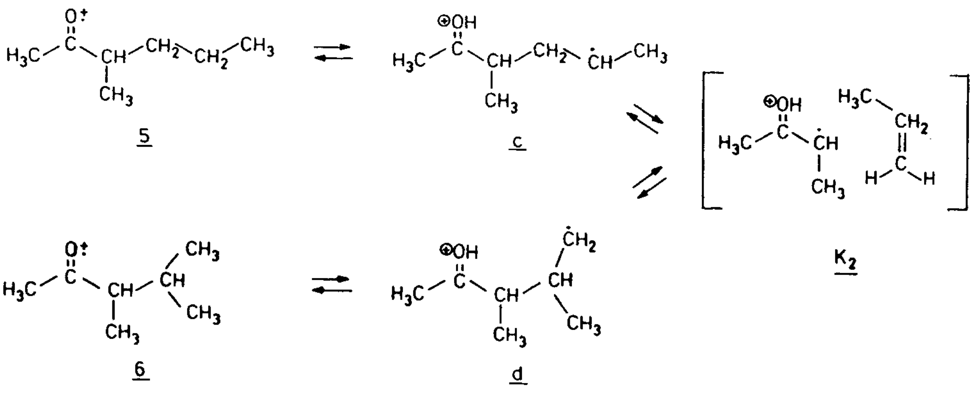
	2	3	4	5	6	7	8
1	45	128	146	349	506	2185	353
2		111	203	343	436	1370	313
3			129	174	304	819	181
4				230	385	1484	248
5					63	257	196
6						235	306
7							379

The SI values show that obviously ions **7** and **8** do not interconvert with any of the isomeric ions. However, the CID spectra of the ions **1** and **2** as well as those of **5** and **6** are identical indicating an equilibrium between these metastable molecular ions at long lifetimes before decomposition. Furthermore, the CID spectra of the ions **1**, **2** and **3** and of **1**, **3** and **4**, respectively, are very similar and probably arise from mixtures of partly isomerized ions.

The complete isomerization of the pairs of ions **1**/**2** and **5**/**6** cannot be explained by the mechanism suggested by Schwarz et al.[5]. However, an easy explanation of these isomerizations is given by assuming a mechanism involving ion/molecule complexes formed from the products of the McLafferty reaction. The ions **1** and **2** fragment to identical products consisting of an acetone enol radical cation and an isobutene molecule via the distonic ions **a** and **b** by this reaction. A mutual interconversion of the stable ions **a** and **b** is possible by an "intracomplexar" addition of the enol radical cation to the isobutene molecule:



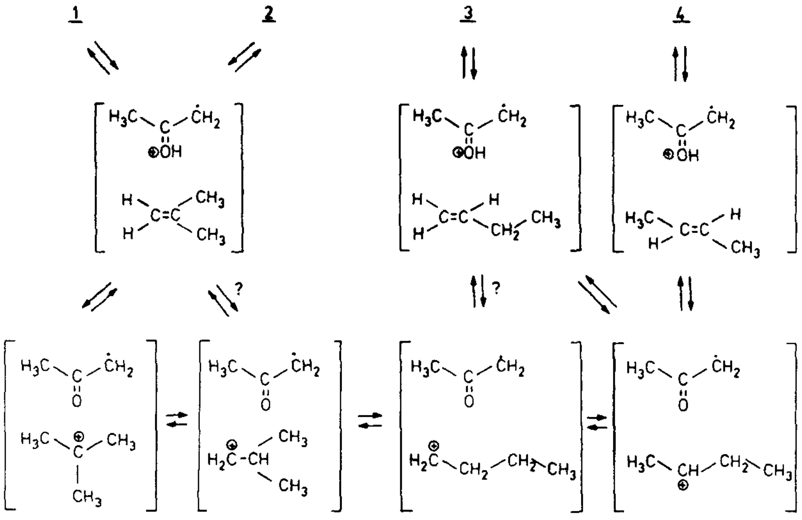
Similarly the ions **5** and **6** both produce a 2-butanone enol radical cation and a propene molecule by the McLafferty reaction via the distonic ions c and **d**, respectively, which again equilibrate by an intracomplexar addition reaction of the radical cation to the olefin:



Thus, our results show that the molecular ions of **1**/**2** and **5**/**6**, respectively, are in fact mixtures of the distonic ions **a**/**b** and c/**d** interconverting via ion/molecule complexes.

In contrast the ions **7** and **8** fragment to an ethene molecule and to unique enol radical cations within this series of ketone ions and, hence, are not expected to isomerize to any of the other ketone ions or distonic ions by the intracomplexar ion/molecule reaction suggested here.

It is of interest to note that the ions **1**, **2**, **3** and **4** decompose into the identical enol radical cation of acetone but to isomeric butene molecules by the McLafferty reaction. We suggest that the similarity of the CID spectra of the ketone ions **1** - **4** indicates an isomerization of at least some of the neutral olefin molecules by an intracomplexar reaction. A possible mechanism would be the transfer of a proton from the enol radical cation onto the butene to form a new ion/neutral complex consisting of a butyl cation and an acetonyl radical:



Calculation of the stabilization energy[9] of these complexes assuming a distance of 300 pm between ion and neutral reveals that the proton transfer reactions are energetically feasible. In fact the formation of this type of complexes could give rise to the well known "McLafferty + 1" fragmentation products[10].

It is known that the isomeric butyl cations isomerize when formed in the gas phase or in superacidic solutions[11]. A similar isomerization within the $C_4H_9^+/C_3H_5O$ complexes and back reaction to the distonic ions would interconvert the ions **1** - **4**, respectively. We are preparing a more detailed study of this interesting isomerization reaction within ion/neutral complexes from ketone ions by using labelled compounds.

Yours sincerely

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References

1. D.J. McAdoo and C.E. Hudson, Org.Mass Spectrom. **18**, 460 (1983).
2. D.J. McAdoo, D.N. Witiak, F.W. McLafferty and J.D. Dill, J.Am.Chem.Soc. **100**, 6639 (1978).
3. H. Schwarz and C. Wesdemiotis, Org.Mass.Spectrom. **14**, 25 (1979).
4. L.L. Griffin, K. Holden, Ch.E. Hudson and D.J. McAdoo Org.Mass Spectrom. **21**, 175 (1986).
5. H. Schwarz,in Adv.Mass Spectrom., ed. by J.F.J. Todd, Proc. of the 10th ISMC (1985), Part A, 13, John Wiley & Sons Ltd., Chichester, 1986.
6. C.E. Hudson and D.J. McAdoo, Org.Mass Spectrom. **20**, 402 (1985).
7. Temperature of inlet system and ion source, 200°C; electron energy, 70 eV; electron acceleration, 6kV; ion source pressure, 10^{-6} Torr; CID-spectra were obtained by admitting helium to the second drift region collision cell to reduce the parent ion signal to ca. 1/3 of the original intensity.
8. J.O. Lay, M.L. Zwinselman and N.M.M. Nibbering, Org.Mass Spectrom. **18**, 16 (1983).
9. J.J. Grabowski, C.H. DePuy and V.M. Bierbaum, J.Am.Chem.Soc. **105**, 2569 (1983).
10. P.G.I. Kingston, J.T. Bursey and M.M. Bursey ,Chem.Rev. **74**, 215 (1974).
11. P. Vogel, "Carbocation Chemistry", Elsevier, Amsterdam 1985.