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STRUCTURE AND FORMATION OF $C_4H_7O^+$ IONS RESULTING FROM ELECTRON IMPACT INDUCED DECOMPOSITION OF CYCLIC PRECURSORS[1]

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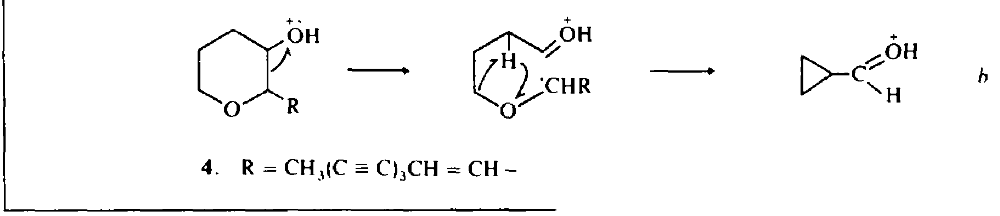
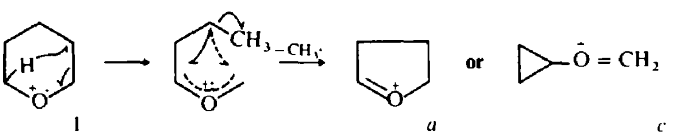
Abstract—Possible structures and modes of formation of $C_4H_7O^+$ ions formed by electron impact induced decomposition of tetrahydrofuran and tetrahydropyran derivatives are discussed in view of labelling results and MIKE, CA and T data. Limitations of these techniques are pointed out.

Tetrahydropyran (**1**) and several of its derivatives yield ions of the composition $C_4H_7O^+$ (m/z 71). Various suggestions have been offered for their structure and mode of formation some of which have been substantiated by deuterium labelling experiments. The main results are:



4. $R = CH_3(C\equiv C)_3CH=CH-$

1. Tetrahydropyran[2] (**1**) loses a β-CH_2 group together with an α-H (>50%; the origin of the remainder could not be clarified due to the low abundance of $[M-CH_3]^+$ despite of labelling of all positions). For m/z 71 structures **a** and **c** have been discussed.



1 a c

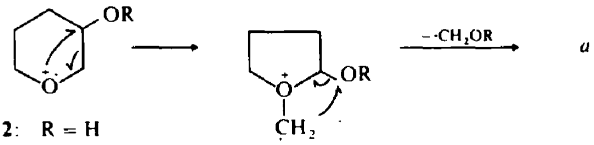
2. 3-Hydroxy (**2**) and 3-acetoxy tetrahydropyran[3] (**3**) lose the OH and OAc group, resp., together with the neighbouring α-CH_2 (labelling at positions 2,3,4,OD and replacement of OH by SH). Formation of **a** has been discussed.

3. For ichthyothereol[4] (**4**) formation of **b** has been postulated, but no labelling data are available. In the case of the O-acetate which also forms $C_4H_7O^+$ additional loss of ketene has to be assumed.

4. 3-Hydroxy-3-methyl tetrahydropyran[3] (**5**) yields $C_4H_7O^+$ with 96% rel. int. In contrast to **2** the hydroxyl-H is retained in the ion.

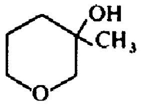
5. 3-Keto tetrahydropyran[3] (**6**) and its 2-n-nonyl derivative[4] lose CO together with H˙ and R˙, resp., from C-2 (2,2,4,4-d_4 derivative of **6**).

6. For 2,3-diacetoxy tetrahydropyran[5] (*cis*-**7**, and *trans*-**8**) formation of **a** has been formulated by rather unlikely mechanisms (loss of α-CHOAc and β-OAc). 2-Alcoxy-3-hydroxy tetrahydropyrans[6] (e.g. **9**) lose ˙OR and the hydroxyl-H while C-3–H remains in the ion (D-labelling). Again, formation of **a** has been postulated by loss of ˙OR, the α-CH_2 group and the



2: R = H
3: R = Ac

ether oxygen in a rather complex sequence of rearrangement steps.



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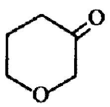

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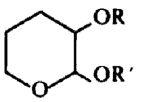
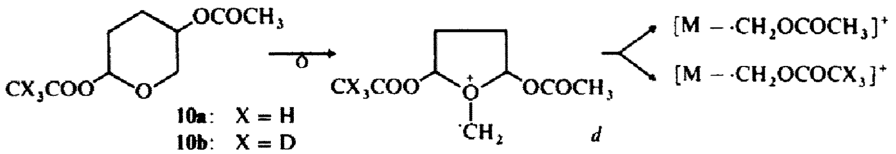


7, **8**: R = R' = OAc
9: R = H, R' = C_4H_9

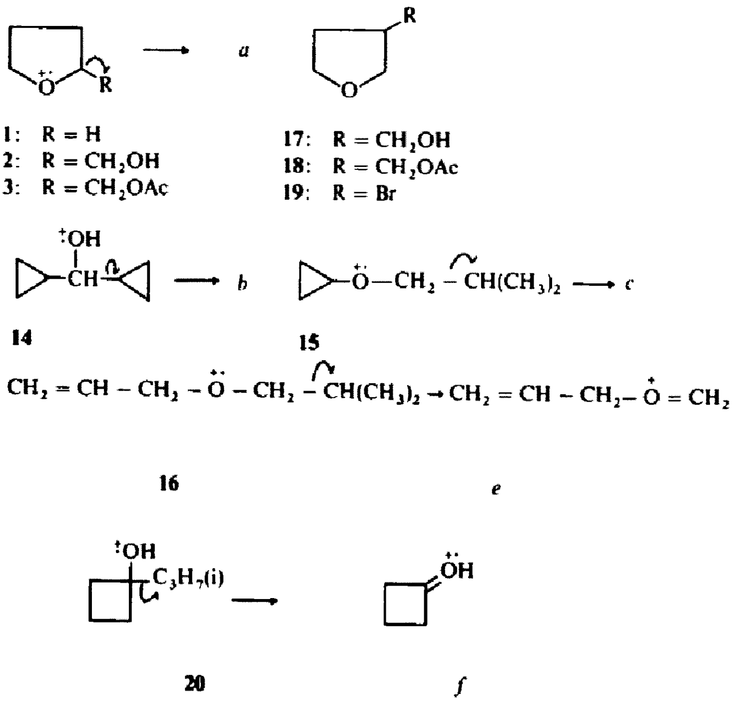
7. For 3,6-diacetoxy tetrahydropyran[3] (**10a**) it has been shown that loss of $\cdot CH_2OAc$ (*cf* **3** → **a**) occurs via a symmetrical intermediate (**d**) since **10b** loses CH_2OCOCH_3 as well as CH_2OCOCD_3.



10a: X = H
10b: X = D

8. For more complex tetrahydropyran derivatives and analogous systems with other hetero atoms see Refs 3 and 7.

For the comparison of ion structures several methods are known today.[8] Ions of *known* structure, however, have to be available from other sources. For even electron species which by electron impact can be obtained as fragment ions only it is assumed that the arrangement of atoms in the fragment ion is the same as in the unionized molecule provided the former arises, e.g. from α-cleavage induced by a hetero-atom. This hypothesis seems to be justified. As compounds which can produce **a** by α-cleavage have been selected tetrahydrofuran (**11**), tetrahydrofurfuryl alcohol (**12**) and its acetate (**13**); as precursors for **b** dicyclopropyl carbinol (**14**) and for **c** isobutyl cyclopropyl ether (**15**). In addition, allyl isobutyl ether (**16**) (which should yield **e** by α-cleavage), 3-hydroxymethyl (**17**) 3-acetoxymethyl (**18**) and 3-bromo tetrahydrofuran (**19**) as well as 1-isopropyl cyclobutanol (**20**) (should yield **f**) were investigated in order to test whether rapid isomerisation of the $C_4H_7O^+$ ions is to be expected.



11: R = H
12: R = CH_2OH
13: R = CH_2OAc

17: R = CH_2OH
18: R = CH_2OAc
19: R = Br

14 **15**

16 *e*

20 *f*

RESULTS

Decomposing ions

(a) *Spectra of metastables.* Upon electron impact ions are formed with differing internal energies and hence differing life times t. Short lived species ($t < 10^{-6}$ sec) fragment in the ion source. Owing to the large number of competing processes in the source a comparison of fragment ions of different origin is possible only under exceptional circumstances. Ions with $t \sim 10^{-6}$–10^{-5} sec which decompose in the fieldfree regions of a mass spectrometer possess lower internal energy and a narrower energy range ("metastable ions"). They allow to investigate decomposition modes of mass selected ions without interference by ions with a different mass. Owing to the lower internal energy low activation energy processes (i.e. especially rearrangement reactions) will be observed preferentially. For the same reason only those isomerisation reactions will prevail for which the isomerisation threshold will be low.

Ions with identical structure and identical internal energy should exhibit identical fragmentation reactions and thus yield identical fragments with identical relative abundances. However, it is possible that fragment ions with identical structure do possess different amounts of internal energy when derived from different precursor ions. The relative abundances of their decomposition products may then vary. Regarding the size of this effect for metastable ions differing opinions can be found in literature. Variation of the intensity ratio of two daughter ions arising from precursors of identical structure from <2 to >5 (esp. for ions of very low energy) have been discussed. The following examples can be considered as characteristic for the two extremes: For $[C_3H_7O{-}H_2O]^+/[C_3H_7O{-}C_2H_4]^+$ the values 2,6 ($C_2H_5O^+ = CH_2$), 1,8 ($C_2H_5{-}CH{=}OH^+$) and 0,5 ($(CH_3)_2C{=}OH^+$) are relevant for *different* ion structures.[9] On the other hand for decomposing $C_2H_6N^+$ ions the ratio $[C_2H_6N{-}H]^+/[C_2H_6N{-}C_2H_2]^+$ varies[10] for *identical* structures from 0.07 to 2,5 for $CH_3{-}CH{=}NH_2^+$ and from 0,07 to 3,6 for $CH_3{-}NH^+{=}CH_2$.

Corollary. In case the metastable spectra of two ions with the same elemental composition are identical within the range of reproducibility identical structures may be assumed with some confidence. Obvious differences (as the absence of a signal in one of the spectra) show conclusively non-identity. If, however, the metastable spectra differ from each other in the relative abundance of their peaks only any interpretation should be done with due caution.

The metastable spectra of the compounds investigated (Table 1) have been obtained by the MIKE technique with a modified[13] CH-4 and a ZAB-2F instrument. Since the CH-4 data are characterized by a higher abundance of $[C_4H_7O{-}H]^+$ obtained by

Table 1. MIKE Spectra of the ions m/z 71 and T values for the transition m/z 71 → m/z 43

Cpd.	T (meV) ZAB	MIKE-Spectra									
		ZAB					CH-4				
		m/z					m/z				
		39	41	43	53	70	39	41	43	53	70
11	87			100+		75			100		166
12	97			100		2			100		4
13	98			100		1			100		5
3	100			100		<1			100		4
7	98			100		<1			100		51
17	118			100	7	3					
18	116			100	6	4			100	8	13
2	102			100	6	3			100	8	13
14	105			100	8	1			100	11	9
8	97 (83%)			100	16	<1					
	10 (17%)										
20	117 (86%)			100	111	7					
	5 (14%)										
15	88	<1	42	100			3	50	100		20
16	109		3	100							
19	94	1	3	100			3	17	100		3

+ loss of CO (11-d_8 shows also loss of 28 u) simple bond cleavage as compared with $[C_4H_7O{-}28\,u]^+$ formed by a rearrangement process obviously ions with higher internal energy are compared with this instrument. The spectra suggest a subdivision of the decomposing ions *m/z* 71 into three groups: With group I (**3**, **7**, **11**, **12**, **13**) only $[C_4H_7O{-}28\,u]^+$ and $[C_4H_7O{-}H]^+$ is observed, with group II (**2**, **8**, **14**, **17**, **18**, **20**) in addition $[C_4H_7O{-}18\,u]^+$, while in group III (**15**, **16**, **19**) additional ions $[C_4H_7O{-}30\,u]^+$ and $[C_4H_7O{-}32\,u]^+$ are formed.

Group I. The constant ratio of $[m/z\,71 \rightarrow 70]^+/[m/z\,71 \rightarrow 43]^+$ for **3**, **12** and **13** (C-4) suggests identical structures. The high intensity of *m/z* 70 in the case of **11** most likely results from the transition $[^{12}C_3{}^{13}CH_8O]^+ \rightarrow [^{12}C_3{}^{3}CH_7O]^+$ in the 1st field-free region (*m/z* 71,01 reduction of the kinetic energy to 98,59% for $m/z\,71 \rightarrow 70$ and to 98,63% for $m/z\,73 \rightarrow 72$), since $[m/z\,71 \rightarrow 70]/[m/z\,71 \rightarrow 43]$ amounts to 18/100 in the 1st field-free region (ZAB) and would be expected to be smaller in the 2nd field-free region (loss of H requires a relatively large amount of energy and in the 2nd field-free region ions with lower internal energy prevail). The large dependance upon the instrument and the small dependance of the intensity ratio upon the precursor **3**, **12** and **13** suggest a pronounced energy dependance of the competing processes (as to be expected for a direct bond cleavage *vs.* a rearrangement process), but formation of the ions *m/z* 71 from **3**, **12** and **13** with a similar energy distribution.

Group II. The intensity ratio $[m/z\,71 \rightarrow 53]/[m/z\,71 \rightarrow 43]$ is only slightly influenced by the instrument. It allows to postulate identical structures for *m/z* 71 stemming from **2**, **14**, **17**, **18**. The loss of H˙ which requires more energy (*v. supra*) shows a more pronounced influence of the instrument.

Group III. The ions *m/z* 71 derived from **16** and **19** apparently have the same structure.

From the MIKE-spectra an unambiguous classification is not possible for the ions *m/z* 71 from **7**, **8**, **11**, **15** and **20**.

There is an additional technique which allows to compare ions of different genesis which decompose in the 2nd field-free region, *viz* a comparison of this portion of internal energy which is set free as kinetic energy (T) during the fragmentation and which can be determined from the width of the metastable signal.[11] In contrast to the MIKE-spectra T values could be shown to be independent from experimental parameters for ions of identical structure[12] (there are rare exceptions to this rule[12,13] which have not been explained adequately in the literature†). The T-values for the transition $m/z\,71 \rightarrow 43$ may be found in Table 1. They are means of 6 independent measurements. While the latter may differ from 10 to 16 meV the means are reproducible for ±2 meV.

The T-values suggest identical structures for at least those *m/z* 71 ions which lose 28u and for which the kinetic energy set free amounts to about 100 meV. They also suggest decomposition to *m/z* 43 ions of identical structure. Whether this statement can be extended to the "stray values" of **11** and **15** on the one, and **16**–**18** and **20** on the other side, cannot be said with certainty. It is, however, very likely for **17** and **18** if one takes the MIKE-data (*vide supra*) into account.

The compounds **8** and **20** yield composed signals the broad part of which corresponds to those of the other compounds investigated. The smaller one stems obviously from an isomeric ion structure. Possibly it is due to a loss of C_2H_4 which would be expected at least for 4-membered rings (**f**).

Non-decomposing ions

Ions with a life time > 10^{-5} sec can be induced to decompose by collision with an auxilliary gas in the 2nd field-free region. By this procedure a part of their kinetic energy is transformed into internal energy (CA method).[14] Collision induced fragmentation follows the same rules as observed with electron impact ionisation in the source. Hence, for the interpretation of CA-spectra the same structure-fragment correlations can be used[15] as have been deduced for EI spectra. Owing to the higher internal energy as compared with metastables direct bond cleavages are observed to a larger extent. Obviously, a comparison of spectra is also possible.

If one neglects those processes of lowest activation energy which occur also as metastable transitions the remaining CA spectra should be independent from the internal energy of the precursor ion. The relative intensities of these residual CA spectra should within the limits of reproducibility (stated to be better than ±10 rel. %[16]) be identical for ions of identical structure even if they are derived from different precursors. Larger differences suggest non-identical structures, dependance on the electron energy a mixture of non-interconverting structures. Nevertheless, statements to the contrary can also be found in the literature. Thus,[17] for $C_4H_5O^+$ ions formed by the loss of X˙ from $CH_3CH{=}CHCOX$ which all should have identical structures the intensity ratio for $[m/z\,68]/[m/z\,41]$ varies between 118:100 and 31:100. Similarly, a dependance of the CA spectra of $C_7H_5O^+$ ions of identical structure on the precursor and hence on the internal energy has been reported.[18] If this energy dependance can be verified the reliability of the comparison of CA spectra will be reduced to that of metastable spectra- and the same limitations will be valid (*vide supra*).

The CA spectra of the *m/z* 71 ions investigated can be found in Tables 2–4. The spectra obtained with ZAB (100 eV) and CH-4 (70 eV) agree well with each other. One finds the same classification as obtained from the MIKE spectra. Compounds **7** and **11** may be added to group II and **15** to group III.

Group I. The 10 eV spectra are identical; at 100 eV the rel. int. of *m/z* 42 is somewhat enhanced for **3** and **11**–**13**.

Group II. Due to their low intensity no 10 eV spectra could be obtained for **2** and **17**. Obvious differences in

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†The internal energy of the decomposing activated complex comprises the activation energy of the back reaction ($\varepsilon_{a'}$) which is determined by the structure of the decomposing ion only, and by that part of internal energy of the decomposing ion which exceeds the activation energy for the decomposition reaction ($\varepsilon^{\ddagger}$). Especially for ions which decompose by direct bond cleavage the size of T is determined by $\varepsilon^{\ddagger}$ since following the Hammond principle $\varepsilon_{a'}$ should be small. In such cases a dependance of T on the internal energy of the decomposing ion and hence on the "history" of the latter cannot be excluded.

Table 2. 100 eV CA spectra (ZAB)$^+$

Cpd.	14	15	26	27	29	31	37	39	41	42	43	50	51	53	55	68	69	70
11	1.2	2.6	5.6	17.6	14.4	1.2	5.1	33.2	25.3	21.6	80.9	0.8	0.6	0.9	0.4	2.6	4.9	15.0
12	1.3	2.7	5.8	17.8	14.5	1.2	5.0	33.1	24.4	20.6	76.2	0.9	0.7	1.0	0.5	3.1	5.1	16.1
13	1.1	2.9	5.5	19.6	15.9	1.2	4.1	31.1	25.9	19.3	92.1	1.0	0.7	1.0	0.4	3.3	4.6	16.5
3	1.2	2.3	6.6	17.5	14.2	1.5	5.8	33.1	26.3	21.3	87.0	1.3	1.0	1.1	1.0	2.2	6.3	9.4
7	1.4	2.8	6.9	21.4	15.6	1.6	6.8	32.2	26.2	16.4	88.0	1.4	1.0	1.7	0.9	1.7	4.7	9.8
17	1.4	2.7	6.3	19.6	14.2	5.5	5.7	31.3	28.5	16.4	84.3	4.3	4.1	17.3	6.9	2.6	19.9	13.3
18	0.8	2.6	6.4	19.3	13.9	5.7	5.8	32.6	28.5	16.0	77.0	4.1	3.8	14.5	5.0	2.9	20.2	11.6
2	1.6	3.4	8.3	20.9	14.4	3.2	7.6	30.6	24.9	16.6	90.6	3.3	2.6	6.0	3.9	1.1	8.4	10.9
14	1.4	2.8	8.4	23.9	15.1	5.5	8.6	32.1	25.7	9.9	94.6	4.2	3.4	7.5	3.4	0.8	12.7	3.1
8	1.8	2.7	10.5	19.6	14.7	1.6	7.0	31.2	22.0	16.2	67.2	1.7	1.2	4.9	1.5	1.8	4.5	15.2
20			6.2	15.8	10.4	6.6	9.0	34.6	32.2	23.6	93.0	13.4	11.5	47.2	22.6	2.8	28.5	25.1
15			7.0	13.1	13.0	3.7	12.1	63.2	312.6		52.3						6.8	3.2
16	1.7	3.4	6.6	10.8	12.4	2.9	11.3	67.4	345.7		58.7						4.9	
19	1.7	3.2	7.8	15.0	14.8	2.6	13.4	59.0	209.2		66.4						5.4	1.5

+) % Σ m/z 14, 15, 26, 27, 29, 31, 39, 42, 68 for 2, 3, 7, 8, 11–14, 17, 18; % Σ m/z 26, 27, 29, 31, 39, 68 for 15, 16, 19; % Σ m/z 26, 27, 29, 31, 39, 42, 68 for 20.

the rel. int. of *m/z* 69 can be observed for **18** when changing from 10 to 100 eV, and for **14** between the ZAB (10 *and* 100 eV) and the CH-4 (70 eV) measurements.

Group III. The spectra are identical and do not show any energy dependance.

Since within the groups I and II variations in the intensity of *specific* ions only are observed—and that to a much lesser degree than reported for the structure identical $C_7H_5O^+$ ions, *vide supra*—an interpretation invoking energy dependance in the formation of these ions seems to be more appropriate than to assume the presence of a mixture of ion structures. The 11 eV spectrum of **8** corresponds to the 10 eV spectra of group I. A completely different CA spectrum has been obtained from **20**.

Table 3. 10 eV CA spectra (ZAB)

Cpd.	14	15	26	27	29	31	37	39	41	42	43	50	51	53	55	68	69	70
11	1.6	3.3	7.8	19.8	16.5	1.3	7.3	32.0	22.2	15.9	54.7	1.3	0.8	0.8	0.6	1.9	3.6	18.0
12	1.6	3.3	7.6	19.7	16.8	1.2	8.1	32.6	21.7	15.5	60.1	1.0	0.7	0.8	0.4	1.6	3.2	15.9
13	1.4	3.2	7.3	19.0	17.8	1.5	6.8	32.7	21.6	15.9	74.5	1.0	0.7	1.0	0.4	1.3	3.2	14.0
3	2.1	3.2	7.4	21.2	15.6	2.1	8.6	32.7	25.6	13.8	70.5					1.8	4.8	9.7
7	1.8	3.1	7.5	20.7	15.7	1.9	7.9	32.2	24.0	15.2	71.6	1.5	1.2	1.5	1.0	1.9	5.1	11.8
18	1.6	3.0	7.7	20.8	15.9	5.1	8.1	31.4	24.8	12.6	75.9	3.7	2.9	10.3	3.8	1.8	11.0	10.5
14	2.1	3.0	8.5	22.1	14.9	5.8	9.1	31.3	24.0	10.8	80.8	4.4	4.1	7.7	3.8	1.5	12.8	4.0
8$^+$		4.2	8.5	19.9	16.2	2.5	+ +	30.6 57.1	20.4	15.7	54.5			+ +		2.5	5.3	20.6
19	1.7	4.0	7.6	15,9	16.0	3.4	11.9	57.1	220.7		82.0						3.0	1.9
16			7.2	11.8	12.7	3.5	12.0	64.9	377.1		59.8						7.2	

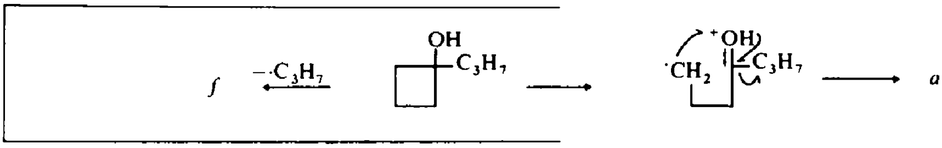
x) 11 eV, xx) cannot be recognized with certainty (background)

Table 4. 70 eV CA spectra (CH-4)

Cpd.	14	15	26	27	29	31	37	39	41	42	43	50	51	53	55	68	69	70
	m/z																	
11	1.1	1.9	7.6	15.9	13.3	1.0	5.4	33.2	23.3	23.5	84.5	1.1	0.8	1.0	0.8	2.5	5.6	23.3
12	1.0	2.0	7.3	17.3	14.2	1.1	5.5	33.8	23.9	21.1	102.4	1.2	0.9	1.1	0.7	2.2	5.3	17.4
13	0.9	1.6	6.8	15.2	13.1	1.0	5.3	34.5	25.1	23.9	102.3	1.2	0.9	1.3	0.9	3.0	7.1	19.8
3	0.9	1.6	6.8	16.5	13.5	1.2		32.9	25.3	23.9	122.5	1.3	1.0	1.6	1.5	2.7	7.1	12.5
7	1.6	2.4	11.5	18.9	14.3	1.6		29.0	19.4	17.8	45.6	2.1	1.6	3.9	2.1	2.7	7.6	23.2
18	1.0	1.7	7.8	16.3	12.9	4.9	6.4	35.1	28.1	17.2	91.0	5.0	4.8	15.4	6.6	3.1	23.4	20.4
2	1.3	2.2	8.4	17.2	12.4	2.1		32.4	25.3	21.9	97.8	3.0	2.7	6.9	4.7	2.1	12.2	23.9
14	1.3	2.0	9.8	17.7	13.2	3.6		33.4	25.0	15.3	109.5	4.5	4.1	7.4	4.8	3.6	20.2	13.2
15	2.5	2.6	11.3	14.4	14.4	2.4	11.5	57.6	135.7	8.5	49.2	1.6	1.7	2.7	6.9	0.7	7.3	5.9
19	1.4	2.4	7.0	14.6	15.0	2.9	7.5	60.4	185.6	16.6	142.2	1.1	1.0	1.5	1.2	1.0	8.9	6.9

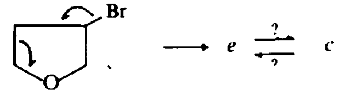
DISCUSSION

Group I can be correlated best with ion structure *a* which can be readily formed by α-cleavage from **11**–**13**. The somewhat low T value for **11** could be caused by the energy required for the loss of H which would result in a smaller amount of excess energy in **a**. (*cf* Footnote p. 784). The main fragments [**a**-CO, CHO, $CH_2O]^+$, $C_3H_3^+$, $C_2H_5^+$ and $C_2H_3^+$ as well as the low intensity of [**a**-$H_2O]^+$ can be explained readily. Regarding the labelling data for **3** and the mechanism of formation of **a** *vide supra*. With the same mechanism the genesis of **a** from **7** can be explained.



In Group II only **14** can yield $C_4H_7O^+$ (**b**) by α-cleavage. In addition to the loss of H_2O (*m/z* 53) to be expected for an ion with an OH group *m/z* 69 and 31 prevail. Pronounced loss of H_2 has been observed for $C_2H_5CH{=}OH^+$ ions which have the structural element CHOH in common with **b**. Finally, the formation of $CH_2{=}OH^+$ by elimination of C_3H_4 (cyclopropene?) is at least plausible. Only rather speculative mechanisms would lead from **17** and **18** (for which no labelling data are available) to **b**, as it is true for **2** for which the sequence **4** (R=H) → **b** is incompatible with the labelling results.

In Group III, $C_4H_7O^+$ ions can be formed by α-cleavage from **15** (**c**) and from **16** (**e**) which—as can be deduced from a comparison of metastable and CA spectra–isomerize to a common structure for which *m/z* 41 (loss of CH_2O from $C_4H_7O^+$) dominates. Its much higher abundance in the CA spectra suggests a single bond cleavage. Expectedly, loss of H_2O is missing. Formation of **e** from **19** can be explained readily. While **7** seems to yield **a** exclusively, a second process takes place for **8** especially at higher energies, which is responsible for the composed metastable peak. This isomeric $C_4H_7O^+$ ion is characterized by pronounced loss of H_2O (esp. in the metastable, to a lesser degree in the CA spectrum which suggests a complex process). Whether the smaller T value can be correlated with *f* is a moot point. Also **20** yields to isomeric $C_4H_7O^+$ ions as evidenced by the composed metastable peak. Again, loss of H_2O is less pronounced in the CA spectrum. One may suggest at least that **20** and **10** yield mixtures of **a** and **f**.



The T values deserve a short comment. The range of variation *between* the groups is not larger than *within* the single groups. The neutral lost (CO) and most probably the daughter ion formed ($C_3H_7^+$) do have the same structure in all cases. Since—as shown by the metastable and the CA spectra—at least three different structures exist for decomposing as well as for non-decomposing ions—one has to conclude that independent from rearrangements which precede or accompany the loss of CO about the same amount of energy is set free in each case.

The $C_4H_7O^+$ problem shows that seemingly analogous fragmentation even of closely related compounds may camouflage a rather complex series of quite different processes if rearrangements come into the game. It also demonstrates that with increasing size of an ion the limitations of those methods become obvious which are available today for the structure elucidation of ions. Thus even the identity or non-identity of ion structures can be ascertained with less and less confidence.

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EXPERIMENTAL

All compounds investigated were purified by gas chromatography (Varian Aerograph 2700, column 20% carbowax, 8′) and characterized by their NMR spectra (for details see Ref. 19) **11**, **11**-d_8 and **12** are commercially available. **2**, **3**, **7**, **8**, **14** and **15** were prepared as described in literature (Refs. 3,20–22), **13** and **18** by acetylation (Ac_2O/pyridine) of the corresponding alcohols, **17** by LAH-reduction of tetrahydrofuran-3-carboxylic acid (from furan-3-carboxylic acid and 5% Pd/C–H_2 in glacial AcOH), **19** by treatment of 3-hydroxy-tetrahydrofuran with PBr_3, and **20** by reaction of cyclobutanone with isopropyl magnesium bromide in ether. **16** could be obtained by reacting K isobutylate (from 3,7 g isobutyl alcohol in 10 ml HMPTA and 2 g K by heating gently until the blue color disappeared) and 6.05 g allyl bromide (14 hr).

MIKE- and CA-measurements

(a) Modified Varian CH-4 instrument,[13] accelerating voltage 8 kV, electron energy 70 eV, source not heated. For the CA-measurements the He pressure in the 2nd field-free region was adjusted so that the intensity of *m/z* 71 decreased to 1/3 (b) ZAB-2F (VG Micromass) accelerating voltage 8 kV, electron energy 10 and 100 eV resp., source temperature 200°. Energy resolution about 3,000. He pressure: decrease of *m/z* 71 to 1/10.

T-measurements. ZAB-2F. Measurement of the peak width at 1/2 of the peak height; mean of 6 measurements for non-composed peaks. For the composed peak of **8** the peak obtained from **3** was adjusted to the lower part of the composed peak graphically by variation of its intensity. Substraction yielded the smaller part. The ratio of the areas and the peak widths yielded values between 15 and 19% and 8.8 and 12.6 meV for three measurements. **20** was treated analogously, but only one measurement was possible. For the calculation[11] of T equation (1) was used ($m_2 = 43$, $m_3 = 16$, $V = 8\,kV$; ΔE corrected for the energy distribution of the parent ion by $\Delta E' = \Delta E \cdot E_1/E_m$, E_m being the sector voltage of the peak centre and E_1 that of the registered daughter ion.

$$T = \frac{m_2 . e . V}{16 m_3}\left(\frac{\Delta E}{E_1}\right)^2 . \qquad (1)$$

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