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Unimolecular Dissociations of the [2-Hexanone]$^{+\bullet}$ Metastable Ion

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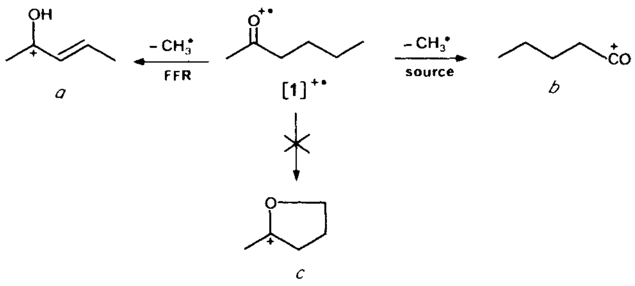
The metastable molecular ion of 2-hexanone loses a methyl radical mainly (~80%) from positions C(4) and C(6), in equal proportions, as indicated by ^{13}C labelling. The necessary skeletal rearrangement of the butyl chain is interpreted in terms of a 1,2-[enol–olefin]$^{+\bullet}$ shift. The results and the mechanisms concerning the minor eliminations of C_2H_4, $C_2H_5^\bullet$, $C_3H_5^\bullet$ and C_3H_6 neutrals are also discussed.

INTRODUCTION

The dominant metastable fragmentation of the [2-hexanone]$^{+\bullet}$ ([**1**]$^{+\bullet}$) radical cation is the loss of one methyl group.[1-5] In the mass-analysed ion kinetic energy (MIKE) spectrum of [**1**]$^{+\bullet}$, the [**1** − $CH_3^\bullet$]$^+$ ions represent more than 90% of the total fragment ion current; the remaining ion abundances are shared between the elimination of C_2H_4, $C_2H_5^\bullet$, $C_3H_5^\bullet$ and C_3H_6 neutrals. In marked contrast, the major signals in the 70 eV mass spectrum of **1** correspond to ions m/z 43 and 58, the peak, at m/z 85, [**1** − $CH_3^\bullet$]$^+$, amounting to only 3% of the total ion current.

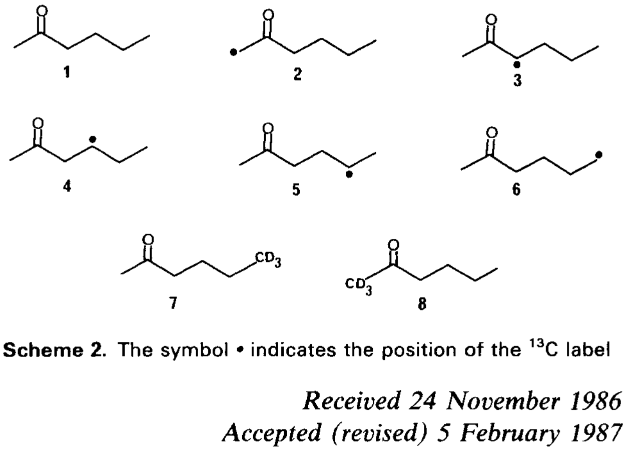
Partial deuterium labelling has been used to improve the understanding of such conflicting behaviour.[1,2,4] In 1969, Yeo and Williams[1] and McLafferty *et al.*[2] pointed out that ionized 1,1,1,3,3-d_5-2-hexanone loses principally $CD_3^\bullet$ in the source of the mass spectrometer and that exclusive elimination of unlabelled $CH_3^\bullet$ occurs in the field-free region (FFR). To illustrate the extent of the phenomenon, it may be recalled that under the impact of 70 eV ionizing electrons the peak height ratio $[M-CD_3^\bullet]^+/[M-CH_3^\bullet]^+$ is equal to 3.0, while its value is less than 0.02 for the metastable dissociations.[1,2] A similar observation was made more recently using 1,1,1-d_3-2-hexanone.[4] It was thus concluded that the source process was principally the loss of the C(1) methyl group (α-cleavage process) while the metastable dissociation involves essentially the elimination of a $CH_3^\bullet$ from the butyl chain, possibly from the C(6) position.[1,2]

The structure of the [**1** − $CH_3^\bullet$]$^+$ product ions has been assigned using collisionally activated decomposition (CAD) spectra.[4,6] It has been established that the protonated 3-penten-2-one hydroxy carbenium ion (a) is produced from the metastable ion [**1**]$^{+\bullet}$ and that the acylium ion (b) is indeed produced by α-cleavage of [**1**]$^{+\bullet}$ in the source of the mass spectrometer (Scheme 1). The formation of the oxonium ion (c), suggested earlier,[1,2] may be excluded on the basis of the CAD spectra.



Scheme 1

In spite of these experimental indications, no clear origin of the atoms involved during the metastable reaction $[\mathbf{1}]^{+\bullet} \rightarrow (a) + CH_3^\bullet$ is actually established. In this context, the present work provides some new experimental results. For this purpose, the variously ^{13}C and D labelled compounds **2**–**8** (Scheme 2) have been prepared, and the mass spectral characteristics of the corresponding metastable molecular ions have been studied.



Scheme 2. The symbol • indicates the position of the ^{13}C label

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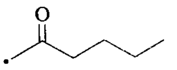
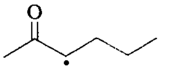
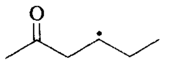
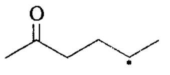
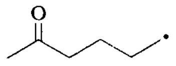
Table 1. Metastable decompositions of ^{13}C labelled 2-hexanone[a]

Precursor		Neutral:	$^{12}CH_3^{\bullet}$	$^{13}CH_3^{\bullet}$	$^{12}C_2H_4$	$^{12}C^{13}CH_4$ $^{12}C_2H_5^{\bullet}$	$^{12}C^{13}CH_5^{\bullet}$	$^{12}C_3H_5^{\bullet}$	$^{12}C_2{}^{13}CH_5^{\bullet}$ $^{12}C_3H_6$	$^{12}C_2{}^{13}CH_6$
		m/z:	86	85	73	72	71	60	59	58
	C(1) **2**		100	2.5	8.7	1.3	0.0	1.0	3.7	0.3
	C(3) **3**		100	9.8	2.6	5.7	0.4	0.5	2.5	1.9
	C(4) **4**		100	58	6.3	7.5	1.3	0.4	3.3	7.2
	C(5) **5**		100	10.4	5.5	3.0	0.7	0.06	1.4	4.2
	C(6) **6**		100	56	6.0	7.2	1.2	0.5	3.2	5.4

[a] All these peaks are Gaussian in shape and no $^{13}C/^{12}C$ isotope effect is observed on the corresponding $T_{0.5}$ values.

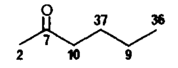
RESULTS

The metastable decompositions of ionized molecules **2**-**8** are presented in Tables 1 and 2 for ^{13}C and CD_3 derivatives, respectively.

The $CH_3^{\bullet}$ loss

Assuming no $^{13}C/^{12}C$ isotope effect, the ratio of the different positions which participate in the $CH_3^{\bullet}$ elimination may be directly deduced from the data in Table 1. For each position C(*n*), the probability of C(*n*)$H_3^{\bullet}$ loss may be equated to the ratio of peak heights $[M-{}^{13}CH_3^{\bullet}]/[M-{}^{12}CH_3^{\bullet}]+[M-{}^{13}CH_3^{\bullet}]$, thus leading to the percentages given in Scheme 3. An error of ±0.5% is expected in these values owing to the experimental uncertainties on peak height measurement and reproducibility.

It is clear from Scheme 3 that the methyl group eliminated from the metastable $[2\text{-hexanone}]^{+\bullet}$ cation contains principally either C(4) or C(6). The second origin of the expelled methyl group involves positions C(3) and C(5). Considering only the butyl chain contribution for $CH_3^{\bullet}$ loss (it accounts for more than 90% of the $CH_3^{\bullet}$ elimination form the metastable molecular cation), one may consider that C(4) and C(6) each participate in the total $CH_3^{\bullet}$ loss by ~40%, while positions C(3) and C(5) each participate by 10%. Consequently, a perfect equivalency of the C(3)/C(5) positions and of the C(4)/C(6) positions is observed.



Scheme 3

The two other points of interest are

(i) that C(1)$H_3^{\bullet}$ elimination is negligible (2%)

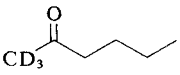
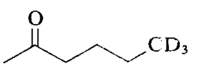
(ii) that a small fraction of the total $CH_3^{\bullet}$ elimination seems to involve the carbonyl carbon C(2) (7%).

Deuterium labelling (Table 2) demonstrates the occurrence of a hydrogen/deuterium exchange before methyl elimination. The distribution of $CH_3^{\bullet}/CH_2D^{\bullet}/CHD_2^{\bullet}/CD_3^{\bullet}$ losses is 100:45:31:28 in the case of 6,6,6-d_3-2-hexanone. This may be compared with the statistical distribution 78:100:25:1, calculated assuming a complete H_9D_3 equilibration. A similar result has been obtained for 1,1,1-d_3-2-hexanone.[4]

The C_2H_4 and $C_2H_5^{\bullet}$ losses

Clearly, C(1) is never found in the eliminated $C_2H_5^{\bullet}$ radical as indicated by the lack of significant peak at

Table 2. MIKE spectra of 1,1,1-d_3-2-hexanone and 6,6,6-d_3-2-hexanone

Precursor		Neutral lost: $CH_3^{\bullet}$	$CH_2D^{\bullet}$	$CHD_2^{\bullet}$	$CD_3^{\bullet}$	C_2H_4	$C_2H_5^{\bullet}$ C_2H_3D	$C_2H_4D^{\bullet}$ $C_2H_2D_2$	$C_2H_3D_2^{\bullet}$ C_2HD_3	$C_2H_2D_3^{\bullet}$	$C_3H_5^{\bullet}$	C_3H_6 $C_3H_4D^{\bullet}$	C_3H_5D $C_3H_3D_2^{\bullet}$	$C_3H_3D_2$ $C_3H_2D_3^{\bullet}$	$C_3H_3D_3$
		m/z: 88	87	86	85	75	74	73	72	71	62	61	60	59	58
	**8**[a]	100	35	4.8	1.6	6.1	7.8	1.7	0.1	—	0.4	3.3	3.9	2.1	0.3
	**7**	100	45	31	28	6.1	6.7	5.4	1.6	0.5	0.2	1.2	3.7	3.8	1.3

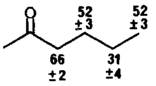
[a] Presented in Ref. 4.

m/z 71 in the MIKE spectrum of $[\mathbf{2}]^{+\cdot}$ (Table 1). Similarly, the position C(1) seems not to be implied in the C_2H_4 elimination if one considers the close values of the peak height ratio $(m/z\ 72)/(m/z\ 71) = 85:15$ in the case of 2-hexanone and $(m/z\ 73)/(m/z\ 72) = 87:13$ in the case of ^{13}C(1)-2-hexanone (**2**). We may therefore evaluate the distribution of metastable losses of $^{12}C_2H_4$, $^{12}C^{13}CH_4$, $^{12}C_2H_5^{\cdot}$ and $^{12}C^{13}CH_5^{\cdot}$ for the four remaining molecules M = **3**-**6** assuming a constant ratio

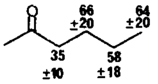
$$([M-{}^{12}C_2H_4]^{+\cdot}+[M-{}^{12}C^{13}CH_4]^{+\cdot})/([M-{}^{12}C_2H_5^{\cdot}]^{+}+[M-{}^{12}C^{13}CH_5^{\cdot}]^{+}) = 87:13$$

The resulting values are presented in Table 3; these estimations lead to the participation of each position of the butyl chain in the ethylene and ethyl losses presented below.

The C_2H_4 molecule eliminated from metastable ion $[\mathbf{1}]^{+\cdot}$ contains C(3), C(4), C(5) and C(6) in the relative proportions indicated in Scheme 4. These results constitute new evidence for the identical behaviour of positions C(4) and C(6). However, the preference for C(3) elimination should be emphasized. Considering the weakness of the $C_2H_5^{\cdot}$ elimination, the uncertainty on the participation of each position is increased (Scheme 5). Consequently, it may reasonably be said that the $C_2H_5^{\cdot}$ elimination involves, in nearly equal proportions, all positions of the butyl chain, with perhaps a preferred retention of C(3) in the fragment ion. In addition, the results presented in Table 2, especially the very low intensity of the m/z 71 signal due to $[M-C_2H_2D_3^{\cdot}]^+$, indicate that the three H atoms in either position C(1) or C(6) are never simultaneously eliminated.



Scheme 4



Scheme 5

The $C_3H_5^{\cdot}$ and C_3H_6 losses

The metastable molecular ion of 2-hexanone ($[\mathbf{1}]^{+\cdot}$) eliminates $C_3H_5^{\cdot}$ and C_3H_6 in the ratio 18:82. This value is identical (*within the limit of experimental error*) to the ratio of peak heights $(m/z\ 60)/(m/z\ 59 + m/z\ 58) = 20:80$ observed in the case of $[\mathbf{2}]^{+\cdot}$. It may therefore be assumed that a negligible loss of $^{12}C_2{}^{13}CH_5^{\cdot}$ occurs from this latter metastable ion. In this instance, the distribution of the ^{13}C label in the eliminated $C_3H_5^{\cdot}$ and C_3H_6 neutrals from $[\mathbf{3}]^{+\cdot}$-$[\mathbf{6}]^{+\cdot}$ may be evaluated (Table 4).

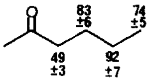
Table 3. Distribution of the ^{13}C label in the C_2H_4 and $C_2H_5^{\cdot}$ eliminations from metastable ions $[\mathbf{2}]^{+\cdot}$-$[\mathbf{6}]^{+\cdot}$

	Neutral lost			
Compound	$^{12}C_2H_4$	$^{12}C^{13}CH_4$	$^{12}C_2H_5^{\cdot}$	$^{12}C^{13}CH_5^{\cdot}$
2	87	0	13	0
3	30	57	8	5
4	42	45	4	9
5	60	27	5	8
6	42	45	5	8

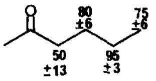
Table 4. Distribution of the ^{13}C label during the $C_3H_5^{\cdot}$ and C_3H_6 eliminations from metastable ions $[\mathbf{2}]^{+\cdot}$-$[\mathbf{6}]^{+\cdot}$

	Neutral lost			
Compound	$^{12}C_3H_5^{\cdot}$	$^{12}C_2{}^{13}CH_5^{\cdot}$	$^{12}C_3H_6$	$^{12}C_2{}^{13}CH_6$
2	20	0	74	6
3	10	10	41	39
4	4	16	14	66
5	1	19	6	74
6	5	15	21	59

As depicted in Scheme 6, the C_3H_6 elimination nearly always involves the carbons C(4), C(5) and C(6). The position C(3) is also partially involved, probably to the detriment of C(4) and C(6). The minor loss of the $C_3H_5^{\cdot}$ radical follows a very similar selectivity (Scheme 7). The neutral always contains C(5) and essentially C(4) and C(6), the position C(3) being involved only half the time.



Scheme 6



Scheme 7

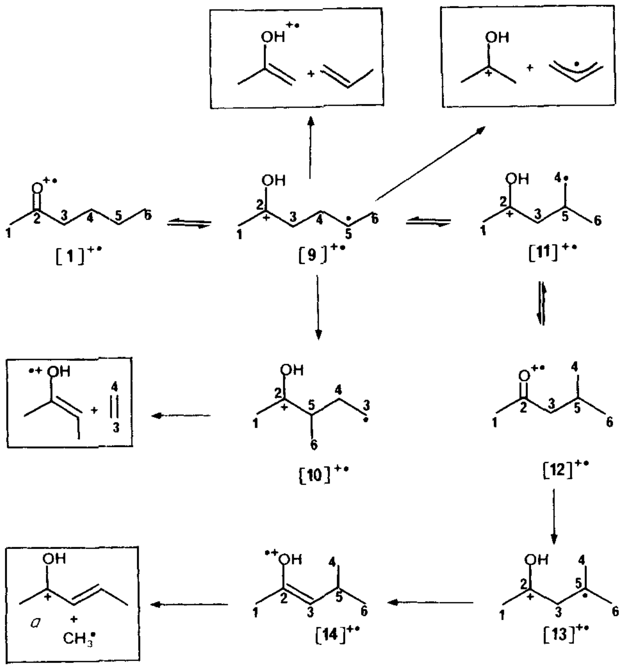
DISCUSSION

The present findings, together with the existing knowledge of the chemistry of $[C_nH_{2n}O]^{+\cdot}$ radical cations,[7] allow us to suggest an isomerization-dissociation sequence explaining the formation of protonated 3-penten-2-one (a) by methyl loss from $[\mathbf{1}]^{+\cdot}$. Simultaneously, the formation of the least abundant fragment ions arising from metastable dissociations, i.e. $[\mathbf{1}-C_2H_4]^{+\cdot}$, $[\mathbf{1}-C_2H_5^{\cdot}]^+$, $[\mathbf{1}-C_3H_5^{\cdot}]^+$ and $[\mathbf{1}-C_3H_6]^{+\cdot}$, is also discussed. The thermochemical arguments sustaining the proposed mechanisms is presented in the final part of this discussion.

Mechanistic aspect

The isomerization steps explaining most of the ^{13}C labelling data are shown in Scheme 8. Starting from the molecular ion $[\mathbf{1}]^{+\cdot}$, the first step is the transfer of one hydrogen from C(5) on to the carbonyl oxygen, leading to the central intermediate $[\mathbf{9}]^{+\cdot}$. This latter distonic[7,8] radical cation may give rise to several kinds of reactions.

The most obvious is the direct C(3)—C(4) bond cleavage giving the products $[CH_3C(OH)CH_2]^{+\cdot} + CH_2{=}CHCH_3$ (the McLafferty rearrangement). Following Scheme 8, this fragmentation leads to elimination



Scheme 8

of C(4)C(5)C(6)H$_6$, as observed for more than 80% of the C$_3$H$_6$ loss occurring from $[\mathbf{1}]^{+\bullet}$ in the 2nd FFR of the VG-ZAB-2F mass spectrometer (Scheme 6).

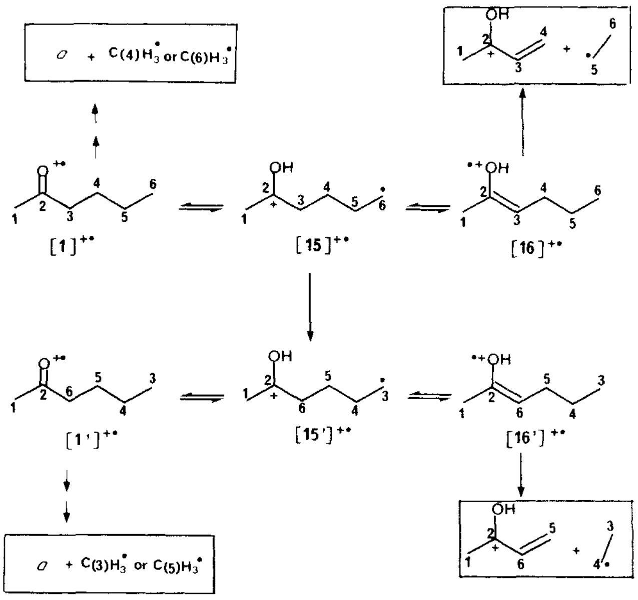
The second possible evolution of cation $[\mathbf{9}]^{+\bullet}$ is a 1,3-CH$_3$COH migration giving the branched distonic cation radical $[\mathbf{10}]^{+\bullet}$, which may further decompose by eliminating one ethylene molecule containing the C(3) and C(4) atoms. This process affords explanation of the favoured presence of C(3) in the eliminated ethylene molecule as demonstrated by ^{13}C labelling (66%, Scheme 4). The equivalency between atoms C(4) and C(6) will be understood after complete examination of Scheme 8.

The two other dissociation channels leading to $[\mathbf{1}-\mathrm{CH}_3^\bullet]^+$ and $[\mathbf{1}-\mathrm{C}_3\mathrm{H}_5^\bullet]^+$ ions are likely to originate from $[\mathbf{9}]^{+\bullet}$ by rupture of the C(3)—C(C4) bond accompanied by a rearrangement. For example, the C$_3$H$_5^\bullet$ loss can result from a hydrogen transfer from C(6) to C(3) during the C(3)-C(4) elongation. Similarly, a 1,2-shift of the enol moiety with respect to the remaining part of cation $[\mathbf{9}]^{+\bullet}$ can replace the C(3)—C(4) bond by a C(3)—C(5) linkage as depicted by the step $[\mathbf{9}]^{+\bullet} \rightarrow [\mathbf{11}]^{+\bullet}$ in Scheme 8. Note that these two processes may be seen as ion-molecule reactions occurring between the products of the McLafferty rearrangement in a transient species $[\mathrm{CH_3C(OH)CH_2\cdots CH_2CHCH_3}]^{+\bullet}$. The former reaction consists of a hydrogen exchange between the two components of the transient, while the latter process gives rise to a new covalent association. Whatever its visualization, the above-described mechanism for C$_3$H$_5^\bullet$ loss predicts elimination of C(4)C(5)C(6)H$_5^\bullet$ in a proportion identical to C(4)C(5)C(6)H$_6$ elimination. This point is experimentally confirmed by the ^{13}C data (compare Schemes 6 and 7).

Concerning the methyl loss, the 1,2-[enol-olefin]$^{+\bullet}$ shift, $[\mathbf{9}]^{+\bullet} \rightarrow [\mathbf{11}]^{+\bullet}$, is the first mechanistic key affording explanation of the major and equal elimination of atoms C(4) and C(6). The dissociation step is suggested (Scheme 8) to occur from ionized enol $[\mathbf{14}]^{+\bullet}$, which decomposes competitively by loss of either C(4)H$_3$ or C(6)H$_3$ to give cation *a*. Rather than a direct 1,3-H migration $[\mathbf{11}]^{+\bullet} \rightarrow [\mathbf{14}]^{+\bullet}$, the lowest-energy route connecting these two structures is probably formed by the three successive hydrogen transfers $[\mathbf{11}]^{+\bullet} \rightarrow [\mathbf{12}]^{+\bullet} \rightarrow [\mathbf{13}]^{+\bullet} \rightarrow [\mathbf{14}]^{+\bullet}$. The formal exchange between positions C(4) and C(6) is consequently simply explained by the formation of the radical cation $[\mathbf{14}]^{+\bullet}$ in the case of the methyl loss. For the other fragmentations, it is necessary to assume that some isomerization steps occur in the backward direction. The reversibility of the reaction sequence $[\mathbf{9}]^{+\bullet} \rightleftharpoons [\mathbf{12}]^{+\bullet}$ would, at least, give equivalent C(3)C(4)H$_4$/C(3)C(6)H$_4$ eliminations, a prediction which is confirmed by the experimental observations (Scheme 4).

In order to complete the description of the metastable dissociations of $[\mathbf{1}]^{+\bullet}$, three points must be examined: (i) the minor CH$_3^\bullet$ loss involving, in equal proportions, positions C(3) and C(5); (ii) the presence of ~30% of C(5) in the eliminated ethylene; and (iii) the mechanism of C$_2$H$_5^\bullet$ elimination.

An explanation is suggested in Scheme 9. The transfer of one H atom from position C(6) to the oxygen atom gives the distonic ion $[\mathbf{15}]^{+\bullet}$, which may support either 1,4-hydrogen migration, giving the ionized enol $[\mathbf{16}]^{+\bullet}$, or 1,4-CH$_3$COH transfer, giving the radical cation $[\mathbf{15'}]^{+\bullet}$. The C$_2H_5^\bullet$ elimination is obviously explained by the allylic rupture of the C—C bond from $[\mathbf{16}]^{+\bullet}$ or $[\mathbf{16'}]^{+\bullet}$ leading to the $[\mathbf{1}-\mathrm{C}_2\mathrm{H}_5^\bullet]^+$ cation of the protonated 3-buten-2-one structure.[9] Note that the reversibility of the $[\mathbf{1}]^{+\bullet} \rightleftharpoons [\mathbf{12}]^{+\bullet}$ sequence (Scheme 8) explains the equivalent C(5)C(6)H$_5^\bullet$ eliminations, i.e. ~60% of the C$_2$H$_5^\bullet$ loss (Scheme 5).



Scheme 9

The formation of $[\mathbf{1'}]^{+\bullet}$ in conjunction with the mechanism of methyl loss depicted in Scheme 8 explains the losses of similar amounts of C(3)H$_3$ and C(5)H$_3$. However, isomerization $[\mathbf{1}]^{+\bullet} \rightarrow [\mathbf{1'}]^{+\bullet}$ appears to be only partial (~20%), as attested by the ^{13}C labelling results concerning $CH_3^{\cdot}$ eliminations (Scheme 3). Similarly, the formation of the radical cation $[\mathbf{1'}]^{+\cdot}$ allows the prediction of some $C(5)C(6)H_4$ and $C(3)C(6)H_4$ eliminations in accordance with the experimental results (Scheme 4).

Thermochemical aspect

The thermochemistry associated with Schemes 8 and 9 may be partly established on experimental grounds.

Photoionization spectroscopy has been used to determine accurately the 298 K appearance energies (AE) of $[\mathbf{1}]^{+\cdot}$, $[\mathbf{1}-CH_3^{\cdot}]^+$, $[\mathbf{1}-C_2H_5^{\cdot}]^+$ and $[\mathbf{1}-C_3H_6]^{+\cdot}$.[10] The AE values are, respectively, equal to 9.37, 9.66, 10.03 and 10.00 eV. In the case of $[\mathbf{1}-C_3H_6]^{+\cdot}$, the AE has also been measured using energy-resolved electron impact;[11] the value obtained (10.04 eV) is in good agreement with the above photoionization result and is compatible with the formation of the enol ion of acetone plus a molecule of propene. These experimental data, combined with $\Delta H_f^{\circ}(\mathbf{1}) = -280$ kJ mol^{-1},[12] lead to the 298 K threshold heats of formation of 619, 653, 690 and 686 kJ mol^{-1} for $[\mathbf{1}]^{+\cdot}$ and the products associated with losses of $CH_3^{\cdot}$, $C_2H_5^{\cdot}$ and C_3H_6, respectively, with an accuracy certainly better than 4 kJ mol^{-1}.

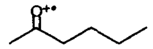
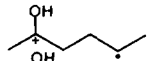
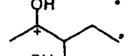
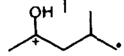
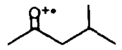
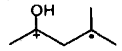
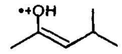
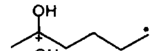
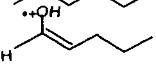
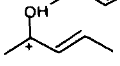
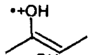
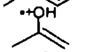
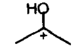
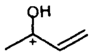
One must emphasize that CAD[4,6] and labelling[1,2,4] experiments demonstrate clearly that the source-produced $[\mathbf{1}-CH_3^{\cdot}]^+$ ions are of acylium structure (*b*). Owing to experimental conditions used by Murad and Inghram,[10] the determined AE($[\mathbf{1}-CH_3^{\cdot}]^+$) value is certainly associated with the formation of ion (*b*). Consequently, the corresponding threshold energy (653 kJ mol^{-1}) may be considered as an upper limit for the energy barriers associated with $CH_3^{\cdot}$ loss in the metastable time-frame. Some indications in favour of the fulfilment of this condition are now presented.

First of all, the intermediate structures $[\mathbf{9}]^{+\cdot}$–$[\mathbf{14}]^{+\cdot}$ and the final state of the fragmentation $a+CH_3^{\cdot}$ are indeed below the 653 kJ mol^{-1} limit. The $\Delta H_f^{\circ}(a)$ value has been estimated to be 490 kJ mol^{-1} after measurement of the gas-phase basicity of 3-penten-2-one.[13] This leads to a final state $(a)+CH_3^{\cdot}$ situated at 636 kJ mol^{-1} in the 298 K standard enthalpy of formation scale, i.e. 17 kJ mol^{-1} below the $(b)+CH_3^{\cdot}$ threshold. The 298 K heat of formation of distonic, ketonic and enolic radical cations $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{9}]^{+\cdot}$–$[\mathbf{16}]^{+\cdot}$ are less than 653 kJ mol^{-1}, as indicated in Table 5. (See Appendix for the details of ΔH_f° estimation.)

The second necessity is that the transition state energy of each isomerization reaction separating $[\mathbf{1}]^{+\cdot}$ from $[\mathbf{14}]^{+\cdot}$ must be situated below 653 kJ mol^{-1}. The low-energy requirement of the rearrangement steps involving 1,5-hydrogen migrations such as $[\mathbf{1}]^{+\cdot} \rightleftharpoons [\mathbf{9}]^{+\cdot}$ and $[\mathbf{11}]^{+\cdot} \rightleftharpoons [\mathbf{12}]^{+\cdot}$ is increasingly documented. Both experimental[7] and theoretical[14,15] results indicate that hydrogen transfer from C(5) toward the oxygen of the carbonyl group occurs without, or with a small (<17 kJ mol^{-1}), critical energy. There is thus little doubt that reactions $[\mathbf{1}]^{+\cdot} \rightleftharpoons [\mathbf{9}]^{+\cdot}$ and $[\mathbf{11}]^{+\cdot} \rightleftharpoons [\mathbf{12}]^{+\cdot}$ are allowed to occur at energies less than 653 kJ mol^{-1}.

A larger energy barrier is certainly associated with the 1,4-hydrogen migration $[\mathbf{12}]^+ \rightarrow [\mathbf{13}]^{+\cdot}$. One should note, however, that the tertiary character of the radical site in $[\mathbf{13}]^{+\cdot}$ acts in reducing the corresponding transition state energy. Similarly the 1,2-H shift toward a radical site, $[\mathbf{13}]^{+\cdot} \rightarrow [\mathbf{14}]^{+\cdot}$, needs a large amount of energy but is counterbalanced by the important stability gain afforded by the formation of ionized enol $[\mathbf{14}]^{+\cdot}$. There are now numerous examples of such 1,2-H migrations in the literature devoted to the chemistry of $[C_nH_{2n}O]^{+\cdot}$ radical cations.[7]

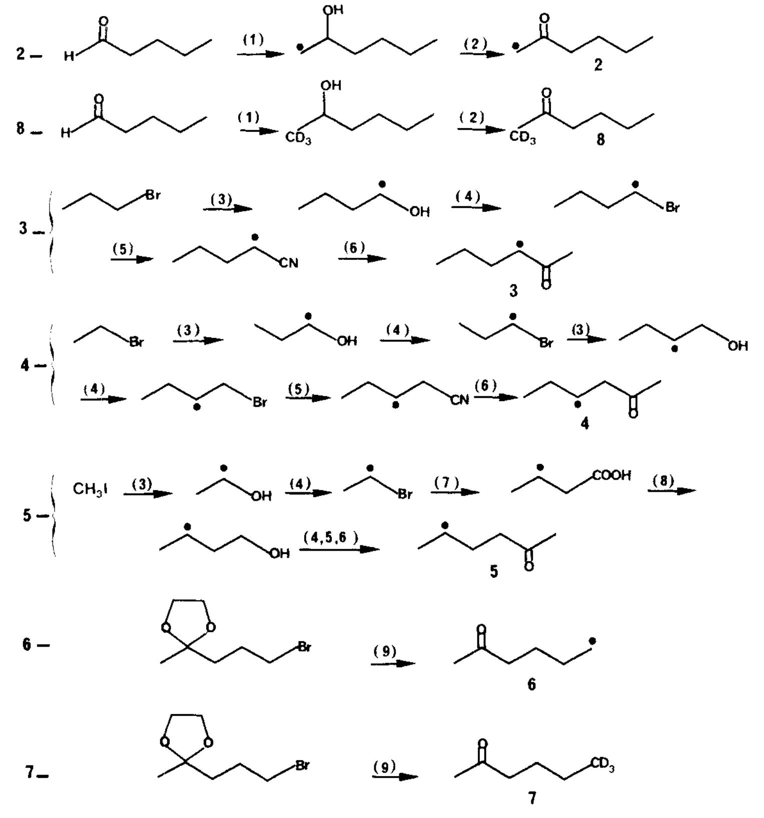
Table 5. Experimental and estimated heat (kJ mol^{-1}) of formation values for the $[C_6H_{12}O]^{+\cdot}$ system

	Structure		$\Delta H^{\circ}_{f,298}$	Origin[a]
$[\mathbf{1}]^{+\cdot}$			619	Exp.
$[\mathbf{9}]^{+\cdot}$			581	Est.
$[\mathbf{10}]^{+\cdot}$			594	Est.
$[\mathbf{11}]^{+\cdot}$			586	Est.
$[\mathbf{12}]^{+\cdot}$			607	Exp.
$[\mathbf{13}]^{+\cdot}$			565	Est.
$[\mathbf{14}]^{+\cdot}$			530	Est.
$[\mathbf{15}]^{+\cdot}$			594	Est.
$[\mathbf{16}]^{+\cdot}$			538	Est.
a		$+CH_3^{\cdot}$	636	Exp.
b		$+CH_3^{\cdot}$	653	Exp.
		$+C_2H_4$	632	Exp.
		$+CH_2CHCH_3$	682	Exp.
		$+CH_2\cdots CH\cdots CH_2$	661	Exp.
		$+C_2H_5^{\cdot}$	682	Exp.

[a] Exp. = experimentally derived and Est. = estimated; for both cases, see Appendix for the details of the methods and references used.

Finally, the approximately thermoneutral isomerization step $[\mathbf{9}]^{+\cdot} \rightarrow [\mathbf{11}]^{+\cdot}$ must possess a critical energy lower than 71 kJ mol^{-1} if the mechanism proposed in Scheme 8 is valid. This point may not be checked either by experiment or by precise theoretical calculations. However, comparable isomerization processes seem to be involved in other systems. For example, the skeletal rearrangement of the metastable [*n*-butyl ethyl ether]$^{+\cdot}$ $\rightleftharpoons$ [isobutyl ethyl ether]$^{+\cdot}$ molecular ion has been interpreted by a $1,2\text{-}[C_2H_5OHCH_2\cdots CH_2CHCH_3]^{+\cdot}$ migration.[16] More recently, the behaviour of metastable [3-methylbutanoic acid]$^{+\cdot}$ was described by a reaction analogous to $[\mathbf{9}]^{+\cdot} \rightarrow [\mathbf{11}]^{+\cdot}$.[17]

Besides the major $CH_3^{\cdot}$ loss from metastable ion $[\mathbf{1}]^{+\cdot}$, the low intensity of the signals associated with $C_2H_5^{\cdot}$, $C_3H_5^{\cdot}$ and C_3H_6 eliminations is well explained by the high heats of formation of the products: 682, 661 and 682 kJ mol^{-1}, respectively. In the case of the ethylene loss, the situation is different: the heat of formation of $[CH_3C(OH)CHCH_3]^{+\cdot}+C_2H_4$ (632 kJ mol^{-1}) is of the same order as that of $a+CH_3^{\cdot}$. Therefore a similar abundance of ions *m/z* 72 and 85 is expected from



Scheme 10

metastable ions $[\mathbf{1}]^{+\cdot}$ if the driving force of its decomposition is only the stability of the products. This is clearly observed for [3-pentan-2-one]$^{+\cdot}$, metastable molecular ions for which *m/z* 72 on the MIKE spectrum of **1** can be interpreted if one assume that the isomerization step $[\mathbf{9}]^{+\cdot} \rightarrow [\mathbf{10}]^{+\cdot}$ possesses a transition state energy slightly greater than that of the energy determining step of $[\mathbf{9}]^{+\cdot} \rightarrow a + \mathrm{CH}_3^{\cdot}$. In view of the similar intensity of peaks at *m/z* 72 and 58 in the MIKE spectrum of **1**, a transition state energy close to 686 kJ mol^{-1} is probably associated with $[\mathbf{9}]^{+\cdot} \rightarrow [\mathbf{10}]^{+\cdot}$.

CONCLUDING REMARKS

The central finding described in this study is that the metastable molecular cation $[\mathbf{1}]^{+\cdot}$ eliminates a methyl radical mainly (~80%) from positions C(4) and C(6), and this in equal proportions. The necessary skeletal rearrangement is interpreted in terms of a 1,2-[enol-olefin]$^{+\cdot}$ shift. The critical energy of such a process occurring from a distonic radical cation is suggested to be lower than 71 kJ mol^{-1}.

EXPERIMENTAL

All MIKE spectra were obtained using a VG Micromass ZAB-2F mass spectrometer at 8 kV accelerating voltage and energy resolving power of 2000. The source conditions were: temperature, 180 ± 20 °C; emission current, 100 μA; ionizing energy, 70 eV. All samples were introduced via the septum inlet system at a temperature of ~150 °C.

Compounds **2**-**8** were synthesized by classical methods. The experimental conditions for the different steps summarized in Scheme 10 were as follows:

(1) 1-pentanal was added to the Grignard reagent of $^{13}CH_3I$;
(2) oxidation of crude labelled alcohols with pyridinium chlorochromate (PCC) in CH_2Cl_2;[18]
(3) ^{13}C labelled carbon dioxide (generated from barium carbonate $Ba^{13}CO_3$ and H_2SO_4) was added at −20 to −30 °C to a Grignard reagent of the appropriate alkyl halide in ether, and the resulting halomagnesium alkanoate was converted to the alcohol by addition of an ethanolic solution of $LiAlH_4$ and continuous hydrolysis;[19]
(4) alkyl alcohol was converted into alkyl bromide by means of HBr (49%) and concentrated H_2SO_4;
(5) reaction of the halide with NaCN in DMSO yielded the corresponding nitrile;[20]
(6) addition of CH_3MgI to the nitrile leads to 2-hexanone;
(7) alkylation of malonic acid by labelled bromoethane was done using $KrCO_3$ in the presence of crown ether[21] and followed by decarbonylation (Λ, KOH), thus yielding the intermediate $^{13}C(3)$-butanoic acid;
(8) reduction by $LiAlH_4$;
(9) ketones **6** and **7** were prepared by Grignard reactions using $^{13}CH_3I$ or CD_3I in THF[22] followed by acid hydrolysis of the ethylene acetal protective group.

All compounds were purified by preparative gas chromatography on a 3 m column packed with SE30 (30%) chromosorb W with a flow rate of ~40 cm^3 min^{-1} at 100 °C.

APPENDIX

The thermochemical data quoted in Table 5 have been derived using $\Delta H_f^\circ(\mathbf{1}) = -280$ kJ mol^{-1}[23] and $\Delta H_f^\circ(\mathbf{12}) = -289$ kJ mol^{-1}[24] and ionization energy values of 9.33 eV[10] and 9.30 eV,[24] respectively, for **1** and **12**. Distonic ions $[\mathbf{9}]^{+\bullet}$, $[\mathbf{10}]^{+\bullet}$, $[\mathbf{13}]^{+\bullet}$ and $[\mathbf{15}]^{+\bullet}$ may be formally constructed by hydrogen atom abstraction from the corresponding protonated ketone. On this basis, the heats of formation of these distonic ions, $\Delta H_f^\circ([\mathrm{DI}]^{+\bullet})$, were obtained using the relation

$$\Delta H_f^\circ([\mathrm{DI}]^{+\bullet}) = \Delta H_f^\circ(\mathrm{K}) - \mathrm{PA}(\mathrm{K}) + \mathrm{D}(\mathrm{CH}) + \mathrm{IE}(\mathrm{H}^\bullet)$$

where $\Delta H_f^\circ(\mathrm{K})$ is the heat of formation of the neutral ketone K (e.g. K = **1** for DI = **9**); PA(K) is the proton affinity of K; D(CH) is the bond energy of the broken C—H bond (e.g. C(5)H for DI = **9**); and finally IE(H$^\bullet$) is the ionization energy of the hydrogen atom. PA(**1**) is known to be 846 kJ mol^{-1}[25] and it has been assumed that PA(**12**) = PA(**1**) for the estimation of $\Delta H_f^\circ[\mathbf{11}]^{+\bullet}$ and $\Delta H_f^\circ[\mathbf{13}]^{+\bullet}$.

The bond dissociation energies of primary, secondary and tertiary CH bonds were taken equal to 410, 397 and 389 kJ mol^{-1}[26] and IE(H$^\bullet$) = 1312 kJ mol^{-1} was used.[27]

For ionized enols, ΔH_f° ($[\mathrm{CH_3C(OH)CHCH_2}]^{+\bullet}$) = 661 kJ mol^{-1} and ΔH_f° ($[\mathrm{CH_3C(OH)CHCH_3}]^{+\bullet}$) = 579 kJ mol^{-1} were established from AE measurements.[11] In the cases of $[\mathbf{14}]^{+\bullet}$ and $[\mathbf{16}]^{+\bullet}$, the ΔH_f° values were estimated using ΔH_f° ($[\mathrm{CH_3C(OH)CHCH_3}]^{+\bullet}$) and a correction term for the replacement of one methyl by an isopropyl group (−49 kJ mol^{-1} for $[\mathbf{14}]^{+\bullet}$[23]) and an *n*-propyl group (−41 kJ mol^{-1} for $[\mathbf{16}]^{+\bullet}$[23]).

The other heats of formation values are: $\Delta H_f^\circ(\mathrm{CH_3^\bullet})$ = 147 kJ mol^{-1},[28] $\Delta H_f^\circ(\mathrm{C_2H_5^\bullet})$ = 118 kJ mol^{-1},[29] $\Delta H_f^\circ(\mathrm{C_2H_4})$ = 52 kJ mol^{-1},[30] $\Delta H_f^\circ(\mathrm{CH_2CHCH_3})$ = 20 kJ mol^{-1},[30] ΔH_f° ($\mathrm{CH_2CHCH_2}$) = 170 kJ mol^{-1},[23] ΔH_f° ($[\mathrm{CH_3C(OH)CH_3}]^+$) = 490 kJ mol^{-1}[30] and ΔH_f° ($[\mathrm{CH_3C(OH)CHCH_2}]^+$) = 565 kJ mol^{-1}.[31]

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