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Electron Impact Induced Fragmentation of β-Allenic and γ-Acetylenic Alcohols

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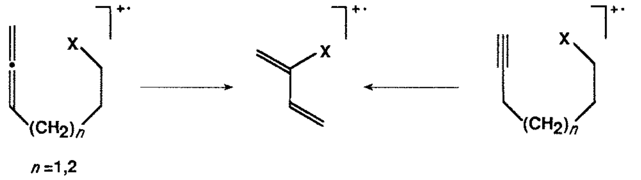
The main fragmentation pathway of ionized hydroxyallenes (1) consists of a methyl loss. Extensive deuterium-labelling experiments indicate that the terminal allenic carbon is implied in this fragmentation. Collisional activation spectra indicate a propenyl-acylium structure (*a*) for these $[M - CH_3]^+$ ions which can originate from a 1,4-hydroxyl migration followed by hydrogen rearrangements. Isomeric hydroxyacetylenes (2) behave similarly, also giving rise, by methyl loss, to acylium ions *a*. It is proposed that $2^{+\cdot}$ is irreversibly isomerized into $1^{+\cdot}$ by a 1,3-hydrogen transfer 'catalysed' by the hydroxy group. The proposed internal proton-bound complex justifies also the easier loss of water from $2^{+\cdot}$. Ethyl loss is also a prominent fragmentation for the hydroxyallene and hydroxyacetylene homologues.

INTRODUCTION

We have already reported in previous studies that γ- and δ-functionalized allenes and isomeric δ- and ε-functionalized acetylenes show closely similar mass spectra, the main fragmentation pathway proceeding by a McLafferty-type heteroatom migration[1] (Scheme 1).



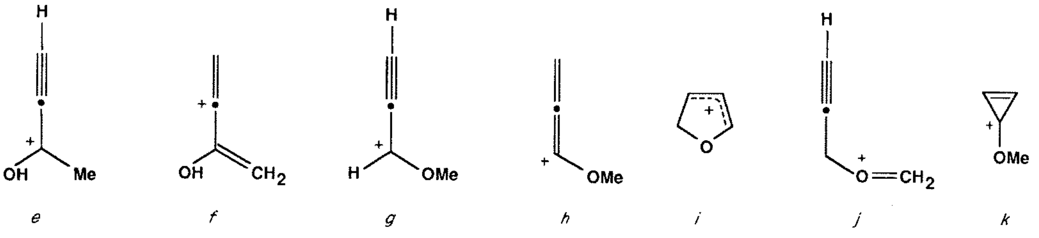
Scheme 1

As part of our investigations on the fragmentational behaviour of these ionized ω-functionalized allenes and acetylenes, we have also been interested in the present study in the fragmentation pattern of β-allenic and γ-acetylenic alcohols.

It was established that a number of non-interconverting isomeric $[C_4H_5O]^+$ ions exist in the gas phase. Of these, the four $C_3H_5-\overset{+}{C}=O$ acylium isomers $CH_3CH=CH-\overset{+}{C}=O$ (*a*), $CH_2=C(CH_3)-\overset{+}{C}=O$ (*b*), $CH_2=CHCH_2-\overset{+}{C}=O$ (*c*) and $\overline{CH_2CH_2C}H-\overset{+}{C}=O$ (*d*) were shown to be stable for $>10^{-5}$ s from their collisional activation (CA) spectra, from the shape of the metastable peaks and the associated kinetic energy release (KER) values from the loss of CO.[2] Simple cleavage reactions of radical cations derived from α-acetylenic alcohols[3] or α-acetylenic (allenic) ethers[4] also yield isomeric stable $[C_4H_5O]^+$ ions described in Scheme 2.

Convincing CA and MI evidence has also been provided to demonstrate the gas-phase stability of methoxy cyclopropenium ions (*k*).[5]

The $[C_4H_5O]^+$ ions are usually key fragment ions in the spectra of various classes of oxygen-containing compounds and the assessment of the ion structure is necessary to establish the reaction mechanisms. This is exemplified in the case of ionized hydroxyallene (**1**), described in a preliminary communication,[6] which loses



Scheme 2

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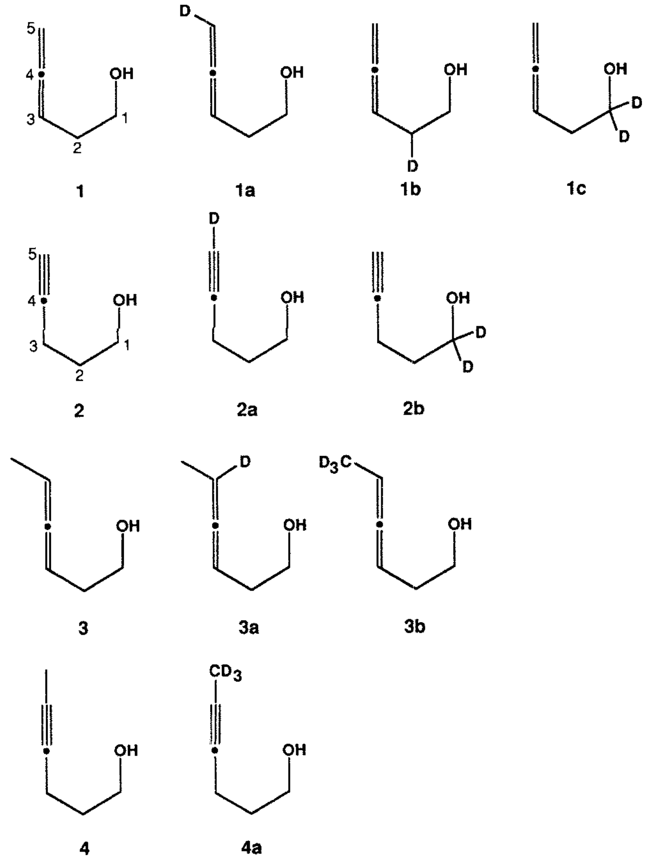


Scheme 3

a methyl group to give the propenylacylium ion (*a*) through a complex sequence involving hydroxyl and hydrogen migrations.

$$[CH_2{=}C{=}CH{-}CH_2CH_2OH]^{+\cdot} \underset{1^{+\cdot}}{} \rightarrow$$

$$\underset{a}{CH_3CH{=}CH{-}\overset{+}{C}{=}O} + CH_3^{\cdot}$$

This paper presents the complete experimental results relative to this peculiar fragmentation of $1^{+\cdot}$ using a combination of deuterium-labelling experiments, CA, MI and KER measurements. The results for the isomeric hydroxyacetylene (**2**) and the higher homologues, hydroxyallene (**3**) and hydroacetylene (**4**), are also discussed. All the compounds studied are listed in Scheme 3.

RESULTS AND DISCUSSION

The 17 eV mass spectra of compounds **1** and **2**, together with the deuterated analogues, are given in Table 1, whilst Fig. 1 shows the mass-analysed ion kinetic energy (MIKE) spectra of the molecular ions.

The mass spectrum of **1** is characterized by a prominent peak at *m*/*z* 69 due to a methyl loss from the molecular ions yielding $[C_4H_5O]^+$ fragment ions. This process is the least energetically demanding fragmentation as it is the dominant reaction observed for the

Table 1. Mass spectra (17 eV) of compounds 1 and 2, and their labelled analogues

m/*z*	1	1a	1b	1c	2	2a	2b
86		1		7 (M)		2	21 (M)
85		5 (M)	12 (M)	36	5	16 (M)	31
84	6[a] (M)	29	24	11	27 (M)	39	21
83	26	3	5	2	36	10	21
72				6			
71			8	100 (M − 15)		2	42 (M − 15)
70	8	12	100 (M − 15)	92 (M − 16)		8 (M − 15)	39 (M − 16)
69	100 (M − 15)	100 (M − 16)	29 (M − 16)	11 (M − 17)	77 (M − 15)	65 (M − 16)	21 (M − 17)
68		2	2	27 (M − 18)		5	100 (M − 18)
67		10 (M − 18)	11 (M − 18)	10	9	100 (M − 18)	
66	13 (M − 18)	3		6 (M − 20)	100 (M − 18)	18	14 (M − 20)
58		2		31		2	34
57		10	25	23		24	21
56	23	16	11	16	50	32	24
55	10	5	7	6	25	12	
54	4	2		15	14	3	
53	2			17			
46			7				
45			7	3	5	3	
44	2	4		11	21	15	14
43	6	5	7	16	14	6	15
42	9	4	7	18	14	15	14
41	6	1		6	14	5	
40		2		3			

[a] Percentage intensities relative to the base peak.

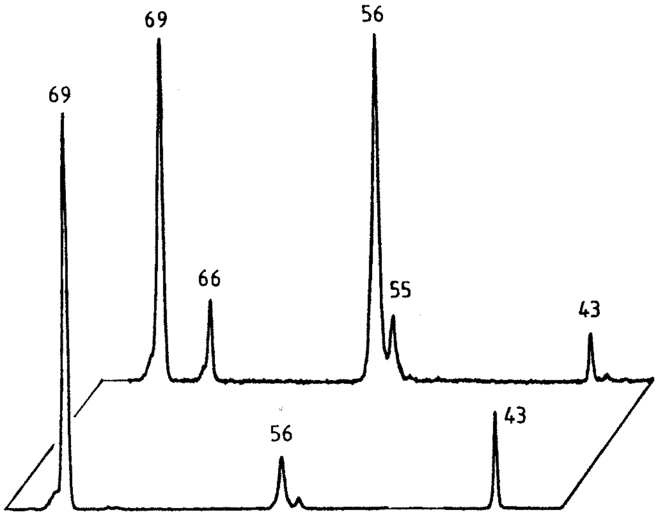


Figure 1. MIKE spectra of the molecular ions (m/z 84) of $CH_2{=}C{=}CHCH_2CH_2OH$ (**1**) (bottom), and $CH{\equiv}C{-}CH_2CH_2CH_2OH$ (**2**) (top).

metastable molecular ions (Fig. 1). Within the ion source, a competing loss of water (m/z 66) is also observed, although it is of minor importance (Table 1).

The origin of the atoms lost as a methyl group have been deduced by deuterium-labelling experiments. Indeed, if one deuterium is introduced on C(5) (compound **1a**), one observes a quasi specific loss of $^{\cdot}CH_2D$ which indicates that this C(5) carbon is lost in the fragmentation. Compounds **1b** and **1c** indicate moreover that one hydrogen is transferred from *both* C(1) and C(2) *to an almost equal extent.* Hydroxy group deuteration by direct exchange with D_2O in the inlet system shows that this position is not involved in the methyl loss, the peak at m/z 69 for **1** being quantitatively shifted to m/z 70. These observations thus support the assumption that (i) the decomposition pathway for this elimination from the molecular ion consists of several steps, and (ii) C(1) and C(2) become identical in one of the intermediates.

The CA spectrum of the $[C_4H_5O]^+$ ions of the allene **1** is compared in Table 2 to the spectra of the acylium ions *a*–*d* which are supposed to be formed by dissociative ionization of the carbonylated molecules **5**–**13**. Other stable $[C_4H_5O]^+$ ions, such as ether-type ions, are not taken into account as the observed consecutive fragmentation consists of a decarbonylation reaction. *n* – Butylcyclopropyl ketone (**13**) is also included, as the ions resulting from an initial McLafferty rearrangement $[\overline{CH_2CH_2CH}C(OH)CH_2]^{+\cdot}$ may constitute the potential intermediate responsible for the identity of C(1) and C(2) in the fragmentation of $\mathbf{1}^{+\cdot}$.

In agreement with the previous work of Hommes and Terlouw,[2] we also observe that the isomeric $C_3H_5\overset{+}{C}{=}O$ ions can be easily differentiated owing to their different CA spectra (Table 2, Fig. 2). These spectra have all peaks in common, but their relative intensities are characteristically different: ions *a* and *b* which present a base peak at m/z 53 (loss of CH_4) are differentiated by the absence of a peak at m/z 42 for ion *b*. For the allylacylium ion *c* the region of the peaks m/z 29–25 is comparatively more intense, and finally the cyclopropylacylium ion *d* presents a strong peak at m/z 55 (loss of CH_2) which is of very low intensity for the isomers. Note also that the spectra of the $[C_4H_5O]^+$ ions generated from **12** and **13** are not completely identical suggesting that part of the ions have undergone ring opening into the allylacylium ion *c*.

In the case of the propenylacylium ion *a*, a significant and reproducible effect of ion formation has been clearly observed. The ratio between m/z 54 (loss of $CH_3^{\cdot}$) and m/z 53 (loss of CH_4) appears to be dependent upon the nature of the leaving group of the ionized precursors **5**–**9**. This ratio may thus reflect some internal energy differences[7,8] causing to some extent isomerization before collisional activation. One attempt to increase the internal energy of the ions before fragmentation by using two consecutive collision processes[9] in two separate field-free regions of the triple sector mass spectrometer (E/*(air)/B/*(helium)/E) failed however. Collisional activation of the beam entering the 2nd FFR

Table 2. Parts of the CA spectra of $[C_4H_5O]^+$ ions (m/z 69) with helium as the collision gas

Precursors		Collision-induced fragmentations[a]																	
		55	54	53	52	51	50	49	48	29	28	27	26	25	24	15	14	13	12	Structures
$CH_2{=}C{=}CHCH_2CH_2OH$	**1**	3	61	100	24	25	53	26	4	15	26	50	93	25	4	29	5	5	1	*a*
$CH{\equiv}CCH_2CH_2CH_2OH$	**2**	3	54	100	24	34	57	28	4	23	18	50	77	20	4	24	4	4	1	*a*
$CH_3CH{=}C{=}CHCH_2CH_2OH$	**3**	3	54	100	37	39	54	21	3	19	23	61	67	17	3	21	4	3	1	
$CD_3CH{=}C{=}CHCH_2CH_2OH$	**3b**	4	54	100	38	37	54	25	4	16	35	54	84	26	4	29	8	6	2	
$CH_3C{\equiv}CCH_2CH_2CH_2OH$	**4**	3	56	100	27	41	47	16	3	15	20	63	52	13	2	16	4	3	1	
$CD_3C{\equiv}CCH_2CH_2CH_2OH$	**4a**	6	67	100	42	45	53	26	7	19	36	51	75	21	4	31	8	7	3	
$CH_3CH{=}CHCOC1$	**5**	3	84	100	25	24	49	24	4	12	25	53	93	22	3	22	4	5	2	*a*
$CH_3CH{=}CHCOCH_3$	**6**	5	82	100	26	25	52	26	5	13	29	55	92	28	3	28	5	6	1	*a*
$CH_3CH{=}CHCO_2CH_3$	**7**	3	77	100	26	25	53	26	5	13	26	56	92	26	3	28	6	5	1	*a*
$CH_3CH{=}CHCO_2H$ (*Z*)	**8**	5	65	100	25	30	51	23	5	15	24	53	95	21	5	23	7	6	1	*a*
$CH_3CH{=}CHCO_2H$ (*E*)	**9**	5	60	100	26	26	48	24	5	14	26	56	91	27	5	25	5	4	2	*a*
$CH_2{=}C(CH_3)CO_2CH_3$	**10**	3	73	100	27	18	36	17	4	7	10	33	56	18	3	13	4	<1	<1	*b*
$CH_2{=}CHCH_2CO_2C_2H_5$	**11**	–	9	34	27	30	49	21	–	11	17	100	76	16	–	20	10	4	–	*c*
$\overline{CH_2CH_2CH}COCH_3$	**12**	68	9	42	22	18	36	17	3	14	35	100	66	21	4	18	8	7	1	*d*
$\overline{CH_2CH_2CH}OC_4H_9$[b]	**13**	46	16	41	19	20	39	18	3	13	37	100	76	21	5	20	8	7	2	*d*

[a] The m/z 42–38 region is not included because it is largely dominated by the strong unimolecular peak at m/z 41.
[b] $[C_4H_5O]^+$ ions produced by consecutive losses of C_3H_6 and $CH_3^{\cdot}$.

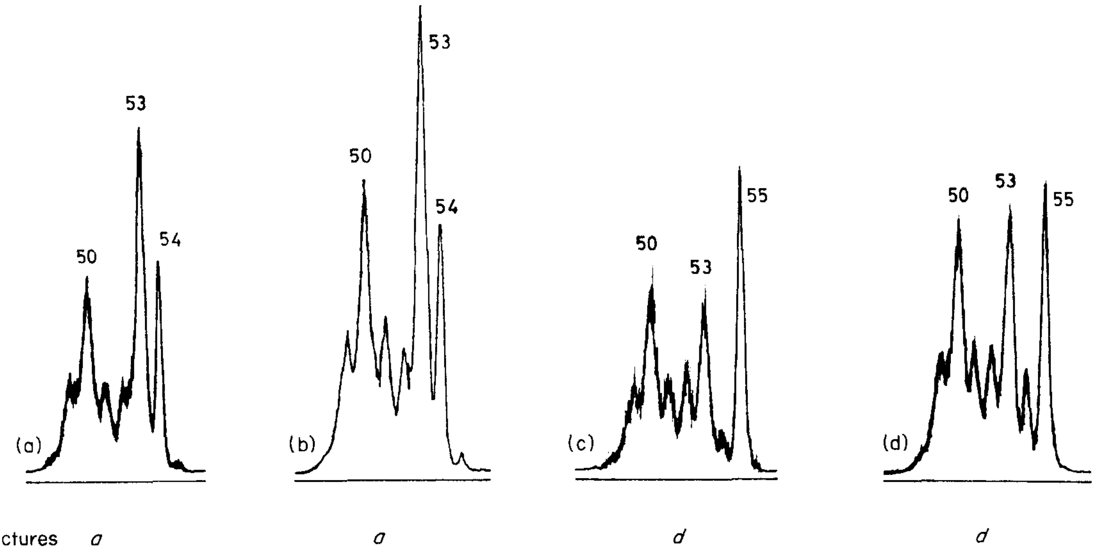
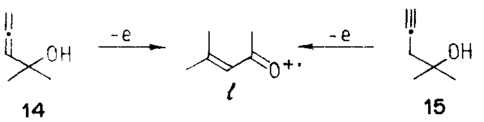


Figure 2. Part (m/z 55 to 49) of the CA spectra of $[C_4H_5O]^+$ ions (m/z 69) produced by dissociative ionization of (a) $CH_2{=}C{=}CHCH_2CH_2OH$ (**1**), (b) $CH{\equiv}C{-}CH_2CH_2CH_2OH$ (**2**), (c) $CH_2CH_2CHCOCH_3$ (**12**) and (d) $CH_2CH_2CHCOC_4H_9$ (**13**).

with air, selection of the *m*/*z* 69 ions with the magnet, and fragmentation by collision with helium in the 3rd FFR decreases the abundance of *m*/*z* 54 relative to *m*/*z* 53, but we observe that this effect is simply due to some diffusion of air from the 2nd FFR to the 3rd FFR. In fact, the replacement of helium by air or pure nitrogen reduces the relative intensity of the *m*/*z* 54 peak by approximately 20–30%. The nature of the target gas upon the efficiency of collisional activation of polyatomic ions has been discussed already,[10,11] but, to our knowledge, no such effect upon the relative intensities of peaks has been mentioned.

Acylium ion formation has already been described[12] for ionized α-hydroxyallene (**14**) and β-hydroxyacetylene (**15**) which were shown to be irreversibly rearranged to ionized α, β-unsaturated ketone *l* (Scheme 4). No interconversion prior to dissociation was noted for the molecular ions $\mathbf{14}^{+\cdot}$ and $\mathbf{15}^{+\cdot}$.

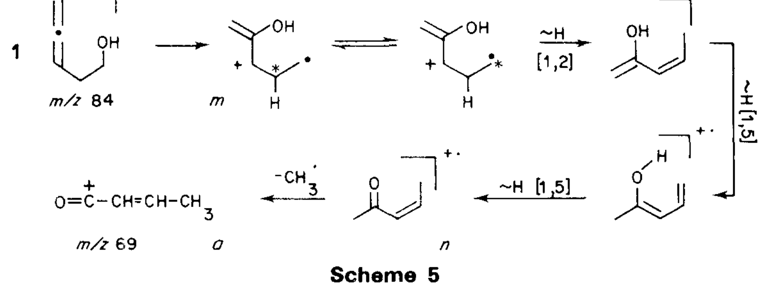


Scheme 4

All of the above discussion supports the assumption that the decomposition pathway for the methyl radical elimination from the $\mathbf{1}^{+\cdot}$ molecular ion consists of several steps (Scheme 5). After ionization, the hydroxyl group is transferred on to C(4) of the allenic linkage giving rise to a distonic ion *m* which can be subjected to a degenerate rearrangement by a fast 1,2-migration of the cationic centre to the radical centre.[13] Such a rearrangement, which has been studied theoretically[14] and experimentally,[15] justifies the equal participation of the hydrogens on C(1) and C(2). After one 1,2- and two 1,5-hydrogen shifts, the ionized 2-pentene-4-one (*n*) is formed which in turn gives rise to the propenylacylium ion (*a*). The kinetic energy release associated with the loss of $CH_3^{\cdot}$ is measured to be 40 meV for $\mathbf{1}^{+\cdot}$ and only 21 meV for $\mathbf{6}^{+\cdot}$ (Table 3). This can be understood if one of the steps (probably the 1,2-hydrogen shift) is the rate determining step of the reaction sequence.[16]

The mass spectrum of the acetylenic alcohol **2** is qualitatively similar to the spectrum of **1**. The main distinction is the importance of the *m*/*z* 66 peak resulting from a water loss (Table 1). The second peak which assumes greater importance upon lowering the electron voltage is due to the loss of a methyl radical at *m*/*z* 69. Labelled compound **2*a*** indicates that the methyl lost incorporates C(5), whereas compound **2b** shows that extensive hydrogen migrations occur in the molecular ions.

Collisional activation of the *m*/*z* 69 ions indicates that the propenylacylium ion (*a*) is also formed in the fragmentation of $\mathbf{2}^{+\cdot}$. Some minor differences are however



Scheme 5

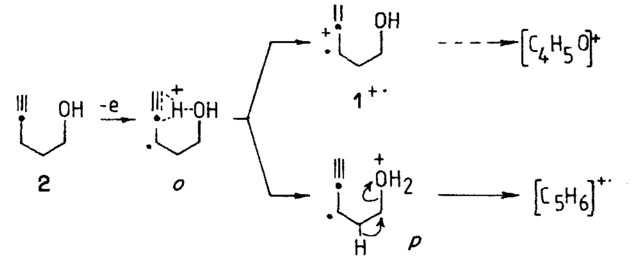
Table 3. Kinetic energy releases corresponding to the loss of $CH_3^{\cdot}$ from some molecular ions and to the loss of CO from $[C_4H_5O]^+$ ions

Precursors		Kinetic energy releases (meV) $T^{0.5}_{CH3}$	$T^{0.5}_{CO}$	$T^{0.22}_{CO}$
$CH_2{=}C{=}CHCH_2CH_2OH$	**1**	40	29	80
$CH{\equiv}CCH_2CH_2CH_2OH$	**2**	56	30	81
$CH_3CH{=}C{=}CHCH_2CH_2OH$	**3**	–	32	82
$CH_3C{\equiv}CCH_2CH_2CH_2OH$	**4**	–	31	76
$CH_3CH{=}CHCOCl$	**5**		48	105
$CH_3CH{=}CH_3COCH_3$	**6**	21	31	91
$CH_3CH{=}CHCO_2CH_3$	**7**	–	36	94
$CH_3CH{=}CHCO_2H$ (*Z*)	**8**	–	31	82
$CH_3CH{=}CHCO_2H$ (*E*)	**9**	–	36	95
$CH_2{=}C(CH_3)CO_2CH_3$	**10**	–	11	28
$CH_2{=}CHCH_2CO_2CH_3$	**11**	–	11	45
$\overline{CH_2CH_2C}HCOCH_3$	**12**	27	135	238
$\overline{CH_2CH_2C}HCOC_4H_9$[a]	**13**	41	169	257

[a] The $[C_5H_8O]^{+\cdot}$ ion was produced by a C_3H_6 loss (McLafferty rearrangement).

seen, mainly at *m*/*z* 51 and 26, pointing to the coexistence of a small percentage of isomeric ions. The kinetic energy release for the decarbonylation confirms the acylium structure *a* (Table 3).

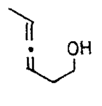
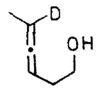
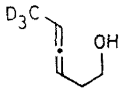
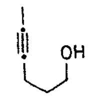
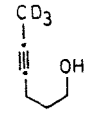
Common formation of ion *a* from **1** and **2** implies similar intermediate(s) in the reaction sequence, which may be the distonic ion *m*. A plausible mechanism which should also explain the intense loss of water involves a hydrogen migration from C(3) to C(5) *via* the intermediate *o* corresponding to a proton solvated by a triple bond and a hydroxyl group. This kind of proton-bound complex has already been described in the literature; e.g. the propyne–H$^+$–methanol complex[17] or the ethyne–H$^+$–water complex.[18] Completion of bond formation then gives rise to allene ions which then undergo the degenerate rearrangement after hydroxyl transfer as described in Scheme 5. The acetylene → allene isomerization can thus be viewed as the result of anchimeric assistance by the hydroxyl group on the proton transfer. Such a complex can also explain the easier dehydration reaction, as the intermediate oxonium ion can lose water with a concomitant hydrogen shift producing $[C_5H_6]^{+\cdot}$ ions (Scheme 6).



Scheme 6

Ethyl loss is also a prominent fragmentation of the homologue hydroxyallene (**3**) (Table 4). The second most intense peak occurs at *m*/*z* 83 and corresponds to a methyl loss. Similar behaviour is also noted for the metastable molecular ion $\mathbf{3}^{+\cdot}$ as evidenced by the MIKE spectrum of the molecular ion from the labelled allene **3b** (Fig. 3) which shows intense peaks at *m*/*z* 69 (loss of $C_2H_2D_3^{\cdot}$) and *m*/*z* 86 (loss of $CH_3^{\cdot}$). Although

Table 4. Partial mass spectra (17 eV) of compounds 3 and 4, and deuterated analogues 3a, 3b and 4a

m/*z*	 **3**	 **3a**	 **3b**	 **4**	 **4a**
101			16 (M)		5 (M)
100			16		26
99		6 (M)			
98	8[a] (M)	10		7 (M)	
97	8			21	
87					
86			52 (M – 15)		44 (M – 15)
85		6			5
84	6	68 (M – 15)			7
83	56 (M – 15)	8	32 (M – 18)	100 (M – 15)	94 (M – 18)
82			13		26
81		6	10	7	9
80	8	17		30	
79	8	17		50	4
73			13		13
72			13		22
71		8	8	8	9
70	13	19	19	36	7
69	100 (M – 29)	100 (M – 30)	100 (M – 32)	93 (M – 29)	100 (M – 32)
68		15			

[a] Percentage intensities relative to the base peaks: peaks less than 5% are not included.

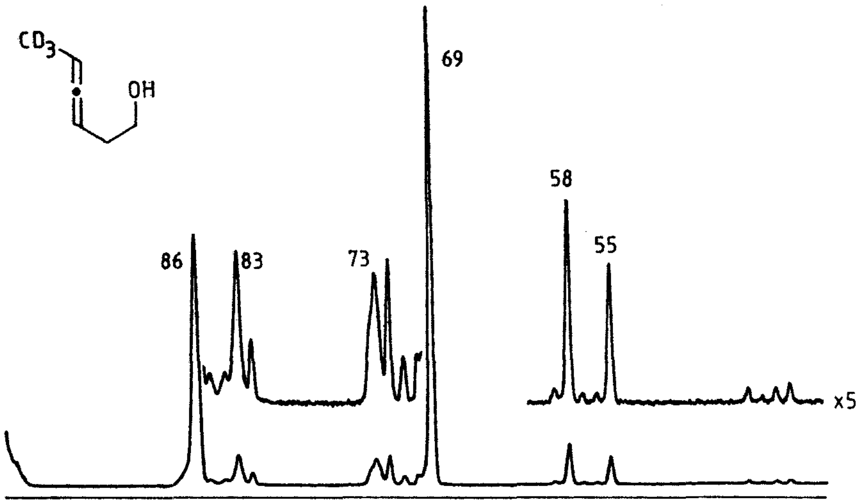
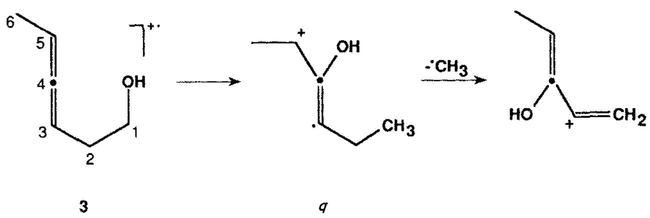


Figure 3. MIKE spectrum of the molecular ion (*m/z* 101) of $CD_3CH{=}C{=}CHCH_2CH_2OH$ (**3b**).

C(5) and C(6) carbon atoms are ejected as ethyl radicals, it appears that the loss of methyl arises mainly by loss of an atom other than C(6), most likely C(1). Note however that the situation is less straightforward for ion-source reactions (Table 4). Collisional activation of the $[C_4H_5O]^+$ ions produced by dissociative ionization of **3** indicates, as expected, that they have mainly the propenylacylium structure *a* (Table 2). These ions are thus produced through a reaction sequence identical to the one depicted in Scheme 4. Some significant differences are however observed, particularly in the *m/z* 24–29 region, indicating the coexistence of isomeric, undefined $[C_4H_5O]^+$ isomers.

The high intensity of the C(1) methyl loss, as compared to the behaviour of the compounds **1** and **2**, can be understood if the C(6) methyl group favours the formation of a carbenium centre at position 5. We thus tentatively propose (Scheme 7) that $3^{+\bullet}$ is isomerized



Scheme 7

into a distonic ion intermediate, schematically represented by *q*, which loses $CH_3^{\bullet}$ to give the vinyl cation *r*. Support for this hypothesis can be found in the work of Terlouw *et al.*[3] who showed that vinyl ions like $CH_2{=}C(OH){-}\overset{+}{C}{=}CH_2$ are stable species for $> 10^{-5}$ s. Moreover, the CA spectrum of these $[C_5H_7O]^+$ ions (Table 5) presents a quite intense collision-induced water loss in agreement with the hydroxylated structure *r*.

The behaviour of the acetylenic isomer **4** parallels that of **3**; CA spectra indicate that a mixture of $[C_4H_5O]^+$ ions is also formed in this case and that vinyl ions $[C_5H_7O]^+$ result from the methyl loss. For comparison, the CA spectrum of the $[M - CH_3]^+$ ions of cyclohexene oxide, reported in the literature as having a cyclic structure *s*,[19] is also reported in Table 5.

CONCLUSION

The aim of the present investigation was to report mass spectral data of *β*-allenic and *γ*-acetylenic alcohols and to study the CA mass spectra of $[C_4H_5O]^+$ ions in an attempt to elucidate fragmentation mechanisms and the possibility of interconversion of molecular ions prior to dissociation. Using deuterium labelling, metastable ion characteristics and CA spectra, it is demonstrated that:

(i) methyl loss from $1^{+\bullet}$ and $2^{+\bullet}$ occurs after complete randomization of C(1) and C(2), and generates propenylacylium ions *a*;

(ii) $2^{+\bullet}$ is irreversibly isomerized into $1^{+\bullet}$ by a hydrogen transfer 'catalysed' by the hydroxyl group; and

(iii) the introduction of a supplementary methyl group on C(5) (compounds **3** and **4**) induces a new fragmentation pathway, a methyl loss probably involving C(1). This reaction, which is highly specific for

Table 5. CA spectra of $[C_5H_7O]^+$ ions (*m/z* 83) produced from compounds 3 and 4 and from cyclohexene oxide. Values in brackets refer to unimolecular fragmentations.

m/z	[68]	67	66	[65]	64	63	62	61	[55]	53	51	50	43	42	41	39	31	29	28	27	26	15	14
3	[19]	7	7	[41]	10	20	10	6	[544]	85	40	31	44	17	15	100	9	42	10	55	12	4	1
4	[6]	4	10	[36]	14	22	13	7	[304]	84	32	26	39	19	15	100	10	35	11	54	14	3	1
	[6]	–	–	[17]	–	5	4	–	[281]	100	47	36	22	5	9	95	4	61	18	79	18	<1	–

metastable molecular ions, results in the stabilization of new intermediates in the reaction sequence.

EXPERIMENTAL

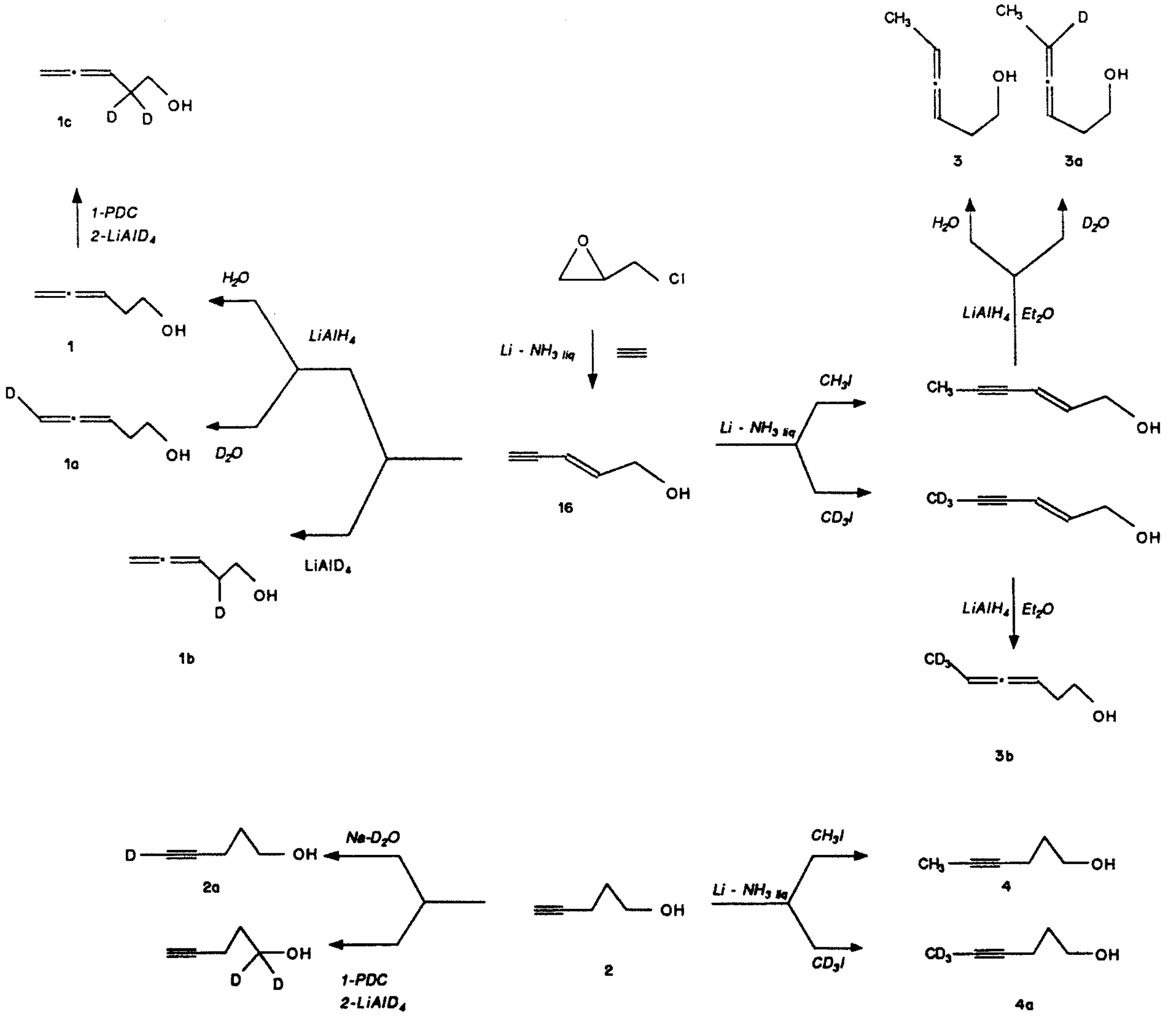
The conventional mass spectra were determined on a Varian MAT 311 double-focusing instrument with a source temperature of 120 °C, an ion accelerating potential of 3 kV, ionizing electrons of 70 eV and 300 μA (17 eV, 100 μA) and sample reservoir temperature of 70 °C.

The ion kinetic energy spectra have been recorded on a triple sector (E/B/E) instrument, modified AEI MS 902.[20] Typical conditions were 8 kV accelerating voltage, 100–500 μA trap current and 70 eV electron kinetic energy. For collisional activation, helium was introduced in the 3rd FFR in order to reduce the intensity of the main beam by ~30%.

All compounds investigated gave satisfactory IR, ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra. The synthesis of compounds **1**–**4** (all unlabelled compounds already known in the literature[21]) is outlined in Scheme 8 and described as follows.

Synthesis of the deuterium-labelled allenols (1a, b, c and 3*a*, *b*). Either the compound **1** or **1a** can be obtained by simple variation of the isolation procedure. The former was produced when the reaction mixture was poured into H_2O, whilst the deuterated isomer was easily obtained by quenching with D_2O. Thus, unsaturated alcohol **16** (0.01 mol) in Et_2O (10 cm^3) was added[22] dropwise to lithium aluminium hydride (0.01 mol) (LAD for **1b**) in Et_2O (50 cm^3). The addition was carried out at 0 °C over a period of 15 min. Stirring with cooling was continued for an additional 10 min. The mixture was then heated under reflux for 3 h. After dilution with Et_2O (100 cm^3) and addition of water (D_2O for **1a**) the mixture was filtered to remove solid suspension, dried over $MgSO_4$ and purified upon vpc (Carbowax 20M, 150 °C) to yield **1b** (85%) and **1a** (85%).

Oxidation of compound **1** afforded the corresponding carboxylic acid, using PDC in DMF at 25 °C.[23] LAD reduction of the latter led to **1c** in 80% yield. Alkylation of compound **16** with methyl iodide[22] (CD_3I for **3b**) then LAH reduction followed by hydrolysis (D_2O for **3a**) afforded the expected compounds in 80% yield. **3a** and **3b** were further purified by vpc before mass spectral analysis (Carbowax 20M, 150 °C).



Scheme 8

Synthesis of deuterium-labelled alkynols (2a, b and 4a). Alkynol **2a** was prepared in 90% yield by reacting terminal acetylene with Na–D_2O.[24] Compound **2b** was synthesized in the same manner as **1c**. Alkylation of pent-4-yn-1-ol with CD_3I afforded **4a** in 90% yield.

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