# Fragmention Behaviour of ω-Functionalized Allenes and their Isomeric Acetylenes under Electron Impact. Study on the Isomerization of Molecular Ions and Structural Assignment of Heteroatom Migration related to a McLafferty-type Rearrangement by CAD-MIKE Spectrometry†

**Siméon Arseniyadis and Jacques Goré**
*Laboratoire de Chimie Organique I, E.R.A. n°. 611, Université Claude Bernard, E.S.C.I.L., 69622 Villeurbanne Cedex, France*
**Pierre Guenot**
*Centre Régional de Mesures Physiques, Université de Rennes I, 35042 Rennes Cedex, France*
**Robert Carrié***
*Groupe de Physicochimie Structurale, E.R.A. n°. 389, Université de Rennes I, 35042 Rennes Cedex, France*

CAD-MIKE Spectra of ions (**1**)—(**6**) are discussed. The main fragmentation pathway, loss of an ethylenic fragment leading to $C_4H_5X^{+\cdot}$ ion, has been confirmed to proceed *via* a McLafferty-type rearrangement by comparison of the CAD-MIKE spectra of this ion to those of model structures. It is further shown, by means of kinetic-energy-release measurements (*T* values), that the investigated isomeric species do not interconvert after electron impact to an appreciable extent.

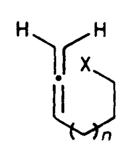
We previously reported a heteroatom transfer, suggested to proceed through a McLafferty-type rearrangement of allenic[1] and acetylenic[2] linkages, leading in almost all cases investigated to the base peak of the 70 eV conventional electron-impact spectra. The importance of this unusual process has prompted us to carry out a more systematic study of ω-substituted allenes and isomeric acetylenes using ion-structure identification by means of their CAD-MIKE spectra and clarifying if interconversion or isomerization to a common molecular ion of unknown structure occurs after ionization.

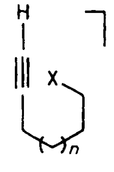
The use of collision activation as a tool for establishing ion structure, initiated by McLafferty and his co-workers,[3] has found wide application in the chemistry of isolated organic cations.[4] In a preliminary report of this work[5] we described the use of CAD-MIKE spectrometry in elucidating the fragmentation behaviour of some isomeric allenes and acetylenes. We now report a detailed investigation of this subject.

Our strategy is first to assign the structure of fragment ions resulting from chlorine, hydroxy, and hydrogen transfer, then to combine the information found in the intensity distributions in the CAD-MIKE spectra with the kinetic energy released (*T* values) in the common decomposition leading to McLafferty-type rearrangement in order to establish whether or not the isomeric species investigated interconvert, or isomerize, prior to the formation of $C_4H_5X^{+\cdot}$ ions. The behaviour of ions (**1**)—(**6**), derived from compounds (**1′**)—(**6′**), are studied.

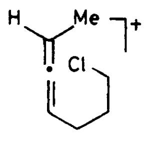
## Results and Discussion

*Structure Identification of* $C_4H_5X^{+\cdot}$ *Ions* (**7**).—The structure of ions $C_4H_5{}^{35}Cl^{+\cdot}$ (*m*/*z* 88), generated from (**1a**)—(**4a**), have been characterized by matching their CAD-MIKE spectra with those of the molecular ion of (**7a′**) and (**9a**) generated from (**11**) and (**9a′**) taken as possible models (Schemes 1 and 2). CAD-MIKE Spectra (relative abundances and peak widths of all fragment ions) of *m*/*z* 88 ions formed by chlorine transfer of all ω-functionalized allenes or acetylenes and the molecular ion of chloroprene (**7a**) are superimposable (Figure 1, Table 1). In Tables 1—4 the peaks observed on the

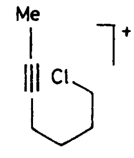




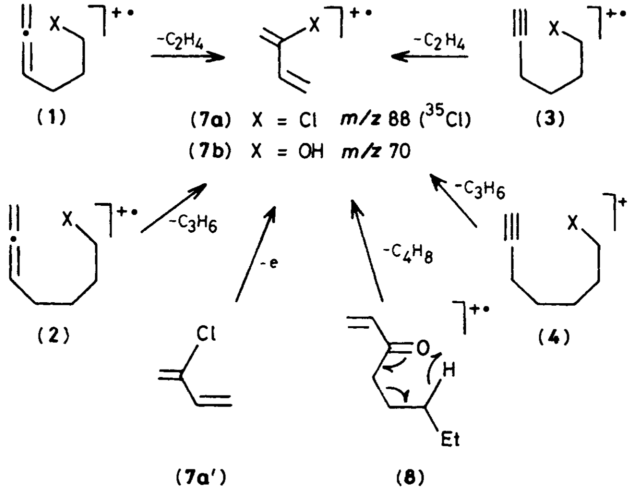
(**1**) *n* = 1 **a**; X = Cl (**3**) *n* = 1
(**2**) *n* = 2 **b**; X = OH (**4**) *n* = 2
**c**; X = Ph



(**5**)



(**6**)



**Scheme 1.**

---

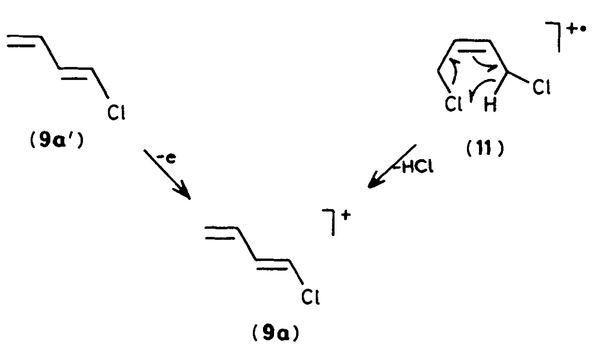
† Part of this work was carried out during the postdoctoral visit of S. Arseniyadis to the University of Rennes.

MIKE spectra (unimolecular decomposition) are indicated in parentheses in the CAD-MIKE spectra.

The CAD-MIKE spectra of 1-chlorobuta-1,3-diene molecular ion (**9a**) and that of the $m/z$ 88 ion generated from (**11**) are both quite different from the CAD-MIKE spectrum of (**7a**). This provides useful information concerning the site specificity of chlorine migration.

From these observations it follows that the structure of the $C_4H_5Cl^{+\bullet}$ radical cations formed by a hetero-McLafferty-type rearrangement is that of the molecular ion (**7a**).

Having reached conclusions about the identity of $C_4H_5{}^{35}Cl^{+\bullet}$ ions, we investigated the analogous, and possible hydroxy group, migration for the corresponding alcohols (**1b**)—(**3b**), leading to the $C_4H_5OH^{+\bullet}$ ions (**7b**), $m/z$ 70. Pentyl vinyl ketone (**8**′), 2-chlorobut-3-en-1-ol (**12**′), and (*Z*)-but-2-ene-1,4-diol (**13**′) were used as reference compounds for structure characterization (Scheme 3). Identical CAD-MIKE spectra for $C_4H_5OH^{+\bullet}$ ions formed by (**1b**)—(**3b**) and (**8**) were observed. Spectra were markedly different from those of $C_4H_5OH^{+\bullet}$ ions produced from (**12**) and (**13**). Evidence for the enol structure[6] of the ion (**7b**) has been inferred from CAD-MIKE investigations on (**14**), the molecular ion of the methyl vinyl ketone, which exhibits a completely different MIKE and CAD-MIKE spectra (Table 2, Figure 2).



**Scheme 2.**

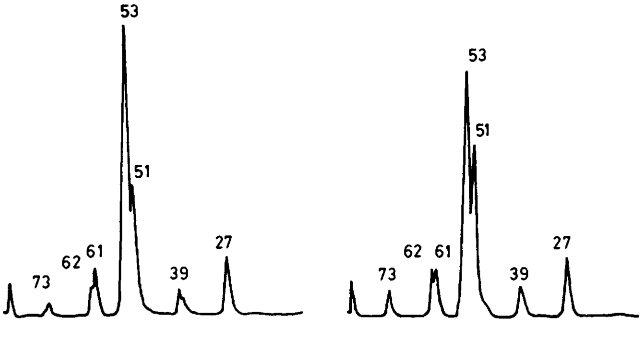
**Table 1.** CAD-MIKE Mass spectra of $C_4H_5{}^{35}Cl^{+\bullet}$ ions ($m/z$ 88)

| Precursor molecule | Ion structure | Neutral fragment lost | $m/z$ and intensities of daughter ions 73 | 62 | 61 | 53 | 51 | 39 | 27 |
|---|---|---|---|---|---|---|---|---|---|
| (**1a**′) | (**7a**) | $C_2H_4$ | 11 | 22 | 39 | (204) | 100 | 20 | 41 |
| (**2a**′) | (**7a**) | $C_3H_6$ | 11 | 22 | 36 | (213) | 100 | 20 | 44 |
| (**3a**′) | (**7a**) | $C_2H_4$ | 12 | 25 | 39 | (218) | 100 | 21 | 44 |
| (**4a**′) | (**7a**) | $C_3H_6$ | 13 | 25 | 42 | (205) | 100 | 20 | 43 |
| (**7a**′) | (**7a**) | | 12 | 21 | 37 | (223) | 100 | 20 | 40 |
| (**9a**′) | (**9a**) | | 16 | 28 | 28 | (144) | 100 | 19 | 35 |
| (**11**′) | (**9a**) | HCl | 18 | 31 | 30 | (146) | 100 | 18 | 30 |

Finally it should be mentioned that there is agreement between the CAD-MIKE spectra of the $m/z$ 54 ions, resulting on the one hand from γ-hydrogen migration in (**1**)—(**4**) ions (example, Scheme 4) and on the other hand from the molecular ion of buta-1,3-diene.

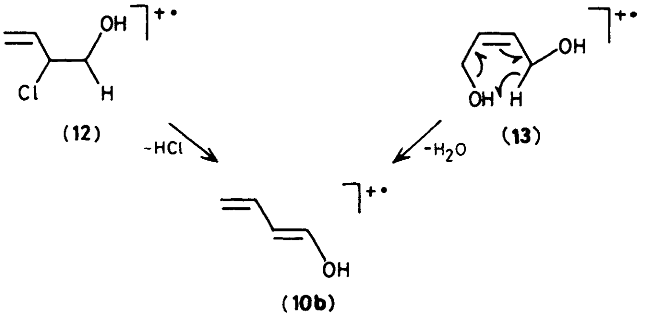
Hydrogen transfer to the allene linkage followed by β-cleavage was first observed by Polyakova and her co-workers[7] on the basis of conventional mass spectra. This McLafferty-type rearrangement was investigated by Djerassi's group[8] by using isotopic labelling and metastable peak analysis. Nevertheless, the structure characterization of the resulting $m/z$ 54 ions by CAD-MIKE spectrometry has not previously been reported.

The above results provide unequivocal structure information concerning the unusual McLafferty-type rearrangement we previously reported for γ-functionalized allenes. The product ions, resulting from collisionally activated decompositions of $C_4H_5X^{+\bullet}$ ions (X = Cl or OH), allowed the assignment of a common structure for all ions (**7a** and **b**). Moreover, reliable



(7a) from (1a′) or (7a′)    (9a) from (9a′)

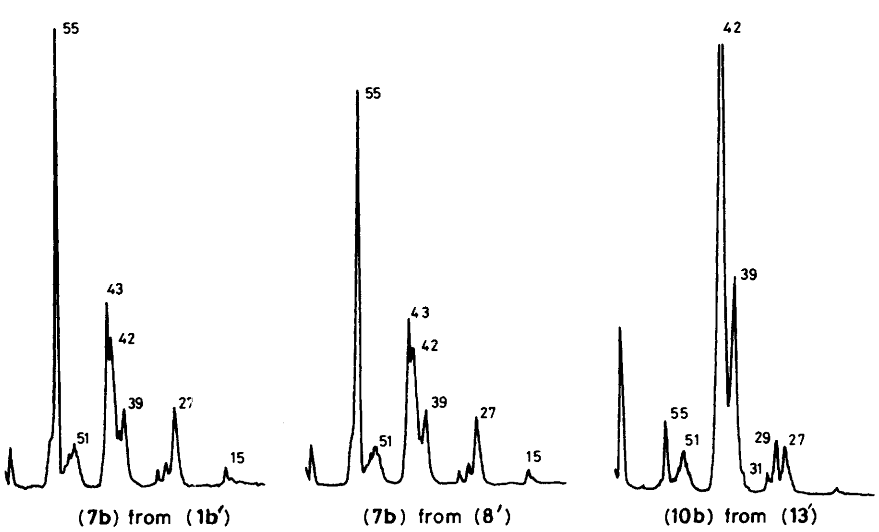
**Figure 1.** CAD-MIKE Spectra of $C_4H_5Cl^{+\bullet}$ ions ($m/z$ 88) for compounds (**1a**′), (**7a**′), and (**9a**′)



**Scheme 3.**

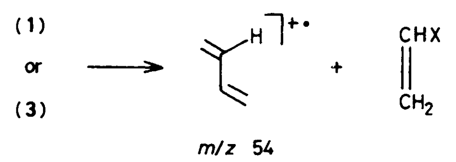
**Table 2.** CAD-MIKE Spectra of $C_4H_5OH^{+\bullet}$ ions ($m/z$ 70)

| Precursor molecule | Ion structure | Neutral fragment lost | $m/z$ and intensities of daughter ions 55 | 53 | 51 | 43 | 42 | 41 | 40 | 39 | 31 | 29 | 27 | 15 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (**1b**′) | (**7b**) | $C_2H_4$ | (245) | 18 | 22 | 100 | (83) | | 27 | 46 | 7 | 13 | 40 | 9 | 3 |
| (**2b**′) | (**7b**) | $C_3H_6$ | (303) | 20 | 28 | 100 | (138) | | 28 | 59 | 9 | 19 | 34 | 9 | 3 |
| (**3b**′) | (**7b**) | $C_2H_4$ | (258) | 21 | 21 | 100 | (86) | | 27 | 47 | 8 | 15 | 39 | 8 | 3 |
| (**8**′) | (**7b**) | $C_4H_8$ | (230) | 15 | 19 | 100 | (79) | | 25 | 43 | 8 | 10 | 41 | 10 | 4 |
| (**12**′) | (**10b**) | HCl | 16 | | 7 | | (189) | 89 | | 100 | 4 | 24 | 17 | 2 | |
| (**13**′) | (**10b**) | $H_2O$ | 25 | | 18 | | (265) | | | 100 | 8 | 26 | 22 | 4 | |
| $CH_2{=}CHOMe$<br>(**14**′) | (**14**) | | (410) | | | 100 | (86) | 17 | 5 | 10 | | | 28 | 6 | |

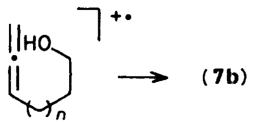


(7b) from (1b′) (7b) from (8′) (10b) from (13′)

**Figure 2.** CAD-MIKE Spectra of $C_4H_5OH^{+\cdot}$ ions (*m/z* 70) for compounds (**1b′**), (**8′**), and (**13′**)

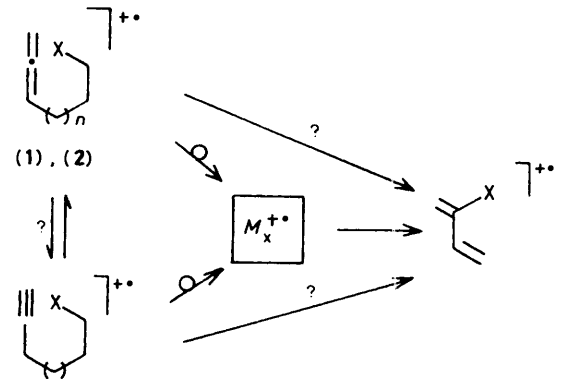


**Scheme 4.**



(**15**) *n* = 4

**Scheme 5.**



(1), (2)

(3), (4)

**Scheme 6.**

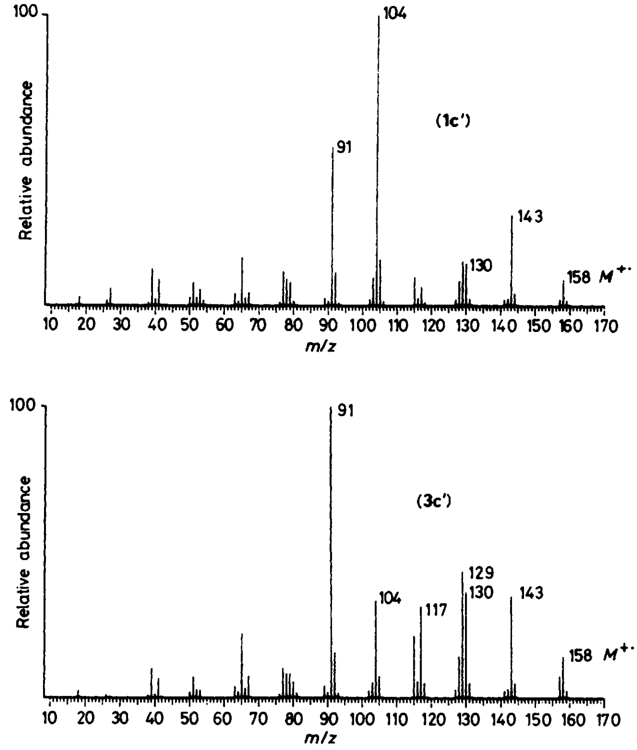


**Figure 3.** Conventional mass spectra (e.i.) of compounds (**1c′**) and (**3c′**)

information on the structure of the above ions could be obtained by comparison with appropriate literature data.

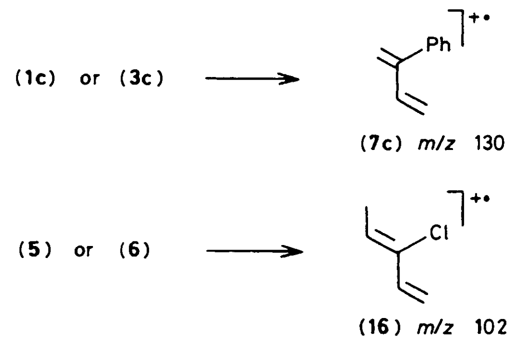
The question of whether the mechanism of the six-centre McLafferty rearrangement is stepwise or concerted has long been a matter of debate. McLafferty *et al.*[9] reported evidence supporting a stepwise mechanism, and our results are in agreement with this proposal. Thus, if a six-membered transition state is possible for (**1a** and **b**), it is more difficult to draw something analogous for ions (**2**)—(**4**) and also for the molecular ion (**15**) (Scheme 5) leading to (**7b**).

*Isomerization of Allenic and Acetylenic Molecular Ions.*—An important question remains to be discussed with regard to the possible interconversion[8,10] or isomerization[11] of molecular ions prior to decomposition. The question is whether or not the ions (**1**)—(**4**) retain their original structures upon ionization. Do they isomerize prior to fragmentation? If yes, do they interconvert, or isomerize, towards a common molecular ion of unknown structure $M_X^{+\cdot}$ (Scheme 6)?

**Table 3.** MIKE and CAD-MIKE spectra and kinetic energy released ($T$ values) for compounds (**1c′**) and (**3c′**)

| Precursor molecule | Selected ion | Neutral fragment lost | | 143 | 129* | 117 | 115 | 104 | 102 | 91 | 89 | 81 | 80 | 77 | 67 | 63 | 51 | 39 | 27 | $T$ Value (meV) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *m/z* and intensities of daughter ions | | | | | | | | | | | | | | | | |
| (**1c′**) | *m/z* 158* | | MIKE | 100 | 12 | 0.5 | | | | | | | | | | | | | | |
| | | | CAD | (3 250) | (630) | (75) | 100 | 25 | | 25 | | | | | | | | | | |
| | *m/z* 130 | $C_2H_4$ | MIKE | | | | 100 | | | | | | | | | | | | | 210 |
| | | | CAD | | | | (1 350) | | 100 | | 52 | | | 90 | | 62 | 62 | 31 | 7 | |
| (**3c′**) | *m/z* 158* | | MIKE | 100 | 73 | 3, 5 | | 1 | | | | 1.5 | | | 1 | | | | | |
| | | | CAD | (1 226) | (1 060) | (124) | 100 | (34) | | 68 | | (27) | 27 | 20 | (27) | 20 | 11 | 5 | | |
| | *m/z* 130 | $C_2H_4$ | MIKE | | | | 100 | | | | | | | | | | | | | 140 |
| | | | CAD | | | | (1 520) | | 100 | | 56 | | | 93 | | 63 | 56 | 33 | 11 | |

* Overlap with *m/z* 130. ** $M^{+\cdot}$.



**Scheme 7.**

In order to discuss this question, information on the translational-energy-release measurements for metastable transition in conjunction with the CAD-MIKE spectra was needed. Our interest focused on the metastable transition of molecular ions in the second field-free region, leading *via* a hetero-McLafferty-type rearrangement to the $C_4H_5X^{+\cdot}$ ions, which constitutes an important fragmentation process of all the allenes and acetylenes studied, in the conventional mass spectra.

However, the kinetic-energy-release measurements generally require a significant molecular ion, to get the peak width with a good accuracy; unfortunately, isomeric couples (**1a′**), (**1b′**) to (**4a′**), (**4b′**) did not permit either CAD experiments or kinetic-energy-release measurements with our equipment.

To overcome this drawback, we synthesized several γ- and δ-functionalized allenes and acetylenes. Couples (**1c′**), (**3c′**) and (**5**), (**6**) provided reasonably intense molecular ions, making our approach possible.

The conventional mass spectra of (**1c′**) and (**3c′**) are given in Figure 3. The MIKE and CAD-MIKE spectra (Table 3) which remained unchanged upon lowering the energy of the ionizing electrons are very different. The *m/z* 130 ions (**7c**), resulting from phenyl-group migration towards the allenic (acetylenic) linkage (Scheme 7), exhibit identical CAD-MIKE spectra.

Kinetic-energy measurements ($T^{50}$) had to be carried out by high-voltage-scan technique on the *m/z* 130 ions, because of the partial overlap of MIKE peaks at *m/z* 129 and 130. These $T$ values, associated with the ethylene lost in the high-voltage-scan spectra [210 and 140 meV for (**1c**) and (**3c**) respectively], are consistent with the non-interconversion of the molecular ions leading to McLafferty-type rearrangement prior to fragmentation.

The conventional mass spectra of the selected pair (**5′**) and (**6′**) are given in Figure 4. Both species give rise, after chlorine migration, to the *m/z* 102 ions (**16′**) (Scheme 7) whose CAD-MIKE spectra appeared to be identical. The MIKE and CAD-MIKE spectra of the *m/z* 130 ions of (**5**) and (**6**) which do not change upon lowering the energy of the ionizing electrons from 70 to 17 eV are shown in Table 4. One can observe significant differences in the *m/z* 41—102 region, the chlorine loss providing the base peak at *m/z* 95 for both isomers.

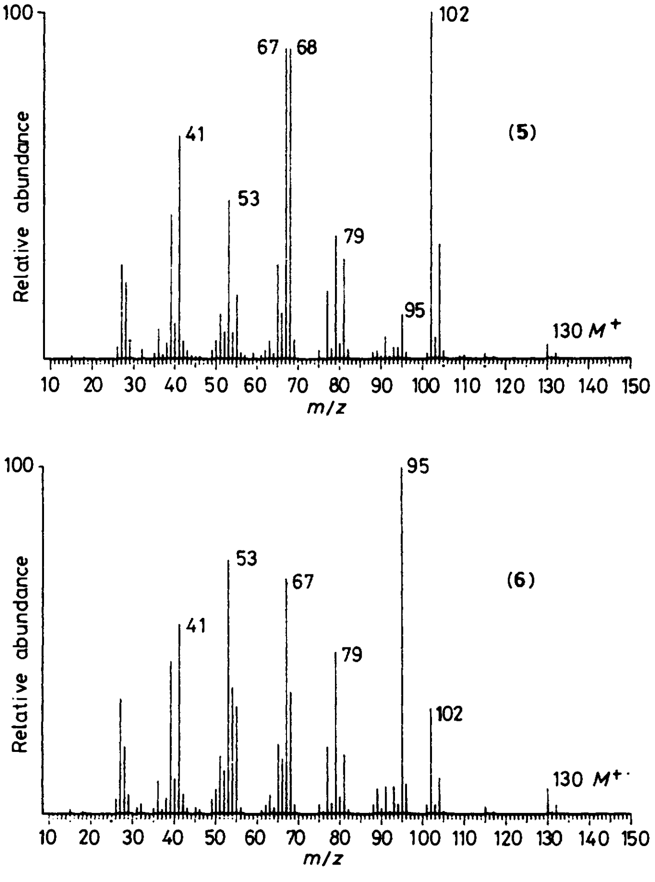


**Figure 4.** Conventional mass spectra (e.i.) of compounds (**5′**) and (**6′**)

In order to establish whether or not the isomeric species (**5**) and (**6**) interconvert, or undergo isomerization to a common structure, $T$ values were measured for the metastable transition (**5**) ⟶ (**16**) and (**6**) ⟶ (**16**) with the aid of MIKE and high-voltage-scan methods. The $T$ values obtained for the above metastable transitions were 24 and 70 meV respectively. Since the kinetic-energy release has been shown to be a valuable ion-structure test, $T$ values (MIKE and high-voltage-scan techniques) observed for the metastable transitions (**1c**), (**3c**) ⟶ (**7c**) and (**5**), (**6**) ⟶ (**16**) indicate that the precursors of

**Table 4.** MIKE and CAD-MIKE spectra, and kinetic energy released (*T* values) for compounds (**5′**) and (**6′**)

| Precursor molecule | Selected ion | Neutral fragment lost | | *m*/*z* and intensities of daughter ions | | | | | | | | | | | | | | | | *T* Value (meV) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 102 | 95 | 87 | 82 | 79 | 75 | 72 | 68 | 67 | 65 | 53 | 51 | 49 | 41 | 39 | 27 | |
| (**5′**) | *m*/*z* 130* | | MIKE | 25 | 100 | | 21 | | | | | | | | | | | | | |
| | | | CAD | (64) | (156) | | (113) | 27 | | | 100 | | | 20 | | | 19 | | | |
| | *m*/*z* 102 | $C_2H_4$ | MIKE | | | | | | | | | 100 | | | | | | | | 24 |
| | | | CAD | | | 10 | | | 19 | 15 | | (480) | 100 | 21 | 30 | 19 | 57 | 76 | 19 | |
| (**6′**) | *m*/*z* 130* | | MIKE | 46 | 100 | | | | | | 8 | | | | | | | | | |
| | | | CAD | (512) | (1 250) | | | 100 | | | (162) | | | 63 | | | 25 | | 13 | |
| | *m*/*z* 102 | $C_2H_4$ | MIKE | | | | | | | | | 100 | | | | | | | | 70 |
| | | | CAD | | | 10 | | | 18 | 15 | | (500) | 100 | 20 | 31 | 20 | 60 | 80 | 20 | |

* $M^{+\bullet}$.

(**7c**) and (**16**) are different and hence, neither interconversion nor isomerization to a common structure (Scheme 6) occurs to an appreciable extent.

## Conclusions

The behaviour of a selected set of molecular ions has been investigated and the results obtained so far allow the following generalizations.

Fragment ions (X = Cl, OH, H) generated from (**1a**)—(**4a**) and (**1b**)—(**4b**), by a McLafferty-type rearrangement, give identical CAD-MIKE spectra. The structure of this common fragment ion and the site specificity of the heteroatom migration toward the allenic and acetylenic linkages have been definitely assigned by comparison with the CAD-MIKE spectra of suitable precursors.

The clearly different MIKE and CAD-MIKE spectra of the molecular ions (**1c**), (**3c**), (**5**), and (**6**) combined with the information gathered from kinetic energy released (*T* values), preclude an isomerization to a common structure or interconversion upon ionization, to an appreciable extent.

## Experimental

The purity and the structure of the compounds synthesized was checked by g.l.c. and i.r. and n.m.r. spectra. Chromatography was performed on either Varian Aerograph 90 P or 1700 instruments, utilizing 20% Carbowax (3 m) on Chromosorb W, unless otherwise cited, with helium as carrier gas. Experimental details have been described previously for most reactions involved.[1,2] Compound (**8′**) was prepared according to the method of Corey using pyridinium dichromate (PDC) as oxidizing reagent.[12] Compounds (**7a′**) and (**9a′**) were obtained as described in ref. 13. They were separated by preparative g.l.c. (PEG, 3 m, 75 °C) and fully characterized by $^{13}C$ n.m.r. spectra. Compounds (**11**), (**13**), and (**14**) were commercially available. 2-Chlorobut-3-en-1-ol (**12**) was prepared from 3,4-epoxybut-1-ene[14] (HCl concentrated; $Et_2O$; 5 °C) and purified by preparative g.l.c. (XE 60, 3 m, 160 °C).

*General Considerations.*—All measurements were performed on a Varian MAT 311 double-focusing mass spectrometer with reversed Nier–Johnson geometry, equipped with a collision chamber in the second field-free region, at an electron-beam energy of 70 eV (emission current 300 μA) and an acceleration voltage of 3 kV. The source temperature was 90 °C. Samples were introduced *via* the heated inlet system at 60 °C.

Fragmentations in the first field-free region were recorded by the high-voltage-scan technique.[15] MIKE And CAD-MIKE spectra were obtained by scanning the electrostatic analyser (503—40 V). Helium was used as collision gas. The pressure in the collision chamber equipped with a differential pumping system was *ca.* $10^{-4}$ mmHg and the source pressure was then $2 \times 10^{-6}$ mmHg. Intensities of the collision-induced fragments were obtained from peak heights and normalized to the base peak. Elemental compositions for ions were determined at a resolving power of *ca.* 10,000.

## Acknowledgements

We are indebted to Professor A. Maquestiau and Dr. F. Flammang for discussions and technical assistance in building the collision chamber on our Varian MAT 311 instrument.

## References

1 S. Arseniyadis, J. Goré, and M. L. Roumestant, (*a*) *Org. Mass Spectrom.*, 1977, **12**, 262; (*b*) *Tetrahedron*, 1979, **35**, 353; (*c*) S. Arseniyadis, Thesis, University of Lyon, 1980.
2 S. Arseniyadis, J. Goré, and M. L. Roumestant, *Org. Mass Spectrom.*, 1978, **13**, 54.
3 (*a*) W. F. Haddon and F. W. McLafferty, *J. Am. Chem. Soc.*, 1968, **90**, 4745; (*b*) D. J. McAdoo, P. F. Benta III, and F. W. McLafferty, *ibid.*, 1972, **94**, 2027; (*c*) F. W. McLafferty, P. F. Benta III, R. Kornfeld, S. C. Tsai, and I. Howe, *ibid.*, 1973, **95**, 2120.
4 (*a*) K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, 1968, **1**, 227; (*b*) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and C. R. Lester, 'Metastable Ions,' Elsevier, New York, 1973; (*c*) R. G. Cooks, 'Collision Spectroscopy,' Plenum Press, New York, 1978.
5 S. Arseniyadis, P. Guenot, J. Goré, and R. Carrié, *Tetrahedron Lett.*, 1981, **22**, 2251.
6 (*a*) J. Diekman, J. K. Macleod, C. Djerassi, and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, 1969, **91**, 2069; (*b*) K. Levsen and H. Schwarz, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1231.
7 A. A. Polyakova, K. I. Zimins, A. A. Petrov, and R. A. Khmel'nitskii, *Zh. Obshch. Khim.*, 1960, **30**, 2977.
8 J. R. Wiersig, A. N. H. Teo, and C. Djerassi, *J. Am. Chem. Soc.*, 1977, **99**, 532.
9 J. S. Smith and F. W. McLafferty, *Org. Mass Spectrom.*, 1971, **5**, 483.
10 B. Ciommer and H. Schwarz, *Z. Naturforsch.*, 1979, **34b**, 1307.
11 (*a*) R. P. Morgan and P. J. Derrick, *Org. Mass Spectrom.*, 1975, **10**, 563; (*b*) K. Levsen, R. Weber, F. Borchers, H. Heimbach, and H. D. Beckey, *Anal. Chem.*, 1978, **50**, 1655; (*c*) P. N. T. Van Velzen and W. J. Van der Hart, *Org. Mass Spectrom.*, 1981, **16**, 237; (*d*) F. Borchers, K. Levsen, H. Schwarz, C. Wesdemiotis, and H. V. Winkler, *J. Am. Chem. Soc.*, 1977, **99**, 6359.
12 E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, 399.
13 H. Baader, K. Sennewald, and H. Reis, G. P. 1 272 916/1968.
14 R. G. Kadesch, *J. Am. Chem. Soc.*, 1946, **68**, 41.
15 K. Jennings, 'Some Newer Physical Methods in Structural Chemistry,' eds. R. Bonnand and J. G. Davies, London United Trade Press, 1967, p. 105.

*Received* 3rd *September* 1984; *Paper* 4/1517