

## Mass Spectra of $\alpha$ -Allenic Alcohols and Some Isomeric Acetylenic Analogues\*

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The mass spectra of eleven  $\alpha$ -allenic alcohols have been recorded. Deuterium labelling in some of the compounds studied made possible a structural interpretation of the principal fragments. The main fragmentation route consists of  $\alpha$ -cleavage with loss of the allenyl group. A comparison has also been made between some isomeric tertiary allenic,  $\alpha$ -acetylenic (propargylic), and  $\beta$ -acetylenic alcohols in order to investigate the possibility of using mass spectrometry to differentiate between isomeric allenenes and acetylenes. In spite of the similarities of the spectra of the allenic and the  $\beta$ -acetylenic compounds it can be concluded that mass spectrometry is useful for such purposes.

Only scant attention has been paid to the mass spectra of allenenes.<sup>1-4</sup> As part of an investigation currently in progress on the chemistry of allenenes<sup>5</sup> it was necessary to use GLC and MS as major tools of identification. In the present paper we summarize our experience on the mass spectral behaviour of eleven  $\alpha$ -allenic alcohols, I–XI.

Allene-acetylene isomerization is a well known problem encountered in most work with these types of compounds. Few attempts<sup>6</sup> have been made to use mass spectrometry to differentiate between isomeric allenenes and acetylenes. Thus we found it of importance to include also this approach in the present investigation. We have compared two allenic tertiary alcohols (VII and XI) with their isomeric acetylenic compounds XII, XIII and XIV, XV respectively. Deuterium labelling in some of these compounds (cf. Table I and Fig. 1) made possible structural

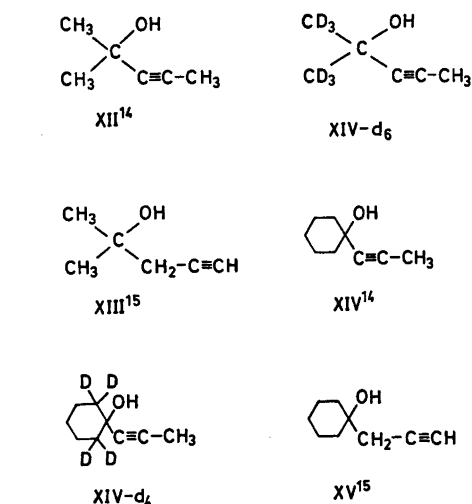


Fig. 1. Tertiary acetylenic alcohols and some deuterated analogues.

assignments to the principal fragments. The fragmentation discussed is supported by appropriate shift(s) in the deuterated analogues. The mass spectra of compound I–XV are given in Table 2.

*$\alpha$ -Allenic alcohols.* In general, the molecular peaks of the allenic alcohols studied are small (0.01–0.7 %, cf. Table 2). As expected, only the primary alcohols I and II exhibit a prominent  $M^+ - H_2O$  peak while the secondary derivatives have smaller peaks of this kind (5–10 %). The molecular ions of the tertiary alcohols show no tendency to lose water on electron impact. However, this type of fission

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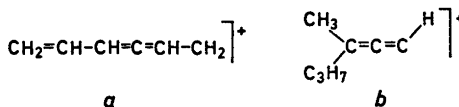


Table 2. Continued.

VII- <i>d</i> <sub>6</sub>	104(0.2), 89(2), 88(3), 87(3), 86(3), 73(13), 66(3), 65(100), 64(4), 59(7), 58(4), 46(60), 45(65), 44(12), 43(16), 42(6), 41(8), 40(8), 39(11).	XIV	138(3), 123(13), 110(8), 109(11), 105(3), 96(9), 95(100), 91(5), 83(5), 82(38), 81(16), 79(5), 77(5), 73(5), 69(5), 68(5), 67(22), 65(6), 63(4), 55(31), 54(8), 53(12), 52(4), 51(8), 50(3), 45(22), 44(3), 43(16), 42(8), 41(31), 40(9), 39(56).
VIII	166(0.3), 151(2), 133(5), 105(3), 100(5), 99(70), 91(5), 83(4), 81(16), 79(7), 77(5), 73(4), 67(6), 65(5), 59(5), 55(11), 53(15), 51(7), 45(30), 44(5), 43(100), 42(3), 41(40), 40(5), 39(30).	XIV- <i>d</i> <sub>4</sub>	142(2), 127(3), 124(3), 113(3), 112(3), 110(4), 102(3), 99(4), 97(8), 96(73), 95(5), 94(3), 85(17), 84(17), 83(20), 82(7), 81(4), 80(4), 79(3), 73(3), 72(7), 70(5), 69(12), 68(8), 67(33), 66(7), 65(4), 58(5), 57(13), 56(67), 55(15), 54(11), 53(8), 52(8), 51(5), 46(3), 45(13), 44(33), 43(40), 42(37), 41(50), 40(100), 39(90).
IX	154(0.5), 87(100), 81(5), 69(11), 68(24), 67(11), 59(13), 57(24), 55(21), 53(10), 51(6), 45(40), 44(6), 43(33), 42(5), 41(45), 39(24).	XV	138(0.1), 100(6), 99(100), 95(3), 89(3), 87(3), 82(4), 81(64), 79(6), 73(9), 69(4), 67(3), 59(4), 57(14), 55(43), 54(5), 53(10), 51(3), 45(31), 44(5), 43(28), 42(9), 41(36), 40(9), 39(39).
IX- <i>d</i> <sub>1</sub>	155(0.2), 88(5), 87(27), 73(3), 70(3), 69(33), 68(9), 67(3), 59(4), 58(3), 57(23), 56(12), 55(9), 54(5), 53(4), 52(3), 51(3), 46(3), 45(100), 44(8), 43(27), 42(15), 41(27), 40(9), 39(13).		
X	152(1), 137(2), 124(3), 123(4), 114(7), 113(100), 109(13), 97(4), 95(62), 93(4), 91(7), 84(5), 83(6), 82(7), 81(5), 79(7), 77(9), 73(5), 69(19), 68(7), 67(32), 65(5), 64(4), 57(11), 56(4), 55(38), 54(9), 53(14), 51(7), 45(19), 43(24), 42(7), 41(57), 39(49).		
XI	138(1), 123(3), 109(4), 100(6), 99(100), 96(8), 95(23), 91(4), 82(6), 81(63), 79(7), 77(7), 73(6), 69(4), 67(13), 65(5), 64(4), 63(3), 59(3), 57(14), 55(40), 54(10), 53(17), 51(8), 45(30), 43(37), 42(14), 41(53), 40(11), 39(73).		
XI- <i>d</i> <sub>1</sub>	139(1), 124(2), 110(4), 100(6), 99(100), 97(10), 96(31), 95(3), 92(4), 89(5), 87(5), 83(6), 82(7), 81(64), 80(6), 79(7), 78(6), 77(3), 73(17), 71(4), 70(4), 69(4), 68(15), 67(5), 66(4), 65(6), 59(8), 58(5), 57(17), 56(6), 55(43), 54(9), 53(13), 52(5), 51(6), 45(64), 44(11), 43(45), 42(21), 41(51), 40(38).		
XI- <i>d</i> <sub>4</sub>	142(1), 127(1), 104(5), 103(85), 97(8), 96(18), 95(3), 94(4), 93(3), 86(4), 85(60), 84(25), 83(9), 82(8), 81(7), 80(6), 79(5), 78(5), 71(5), 70(8), 69(10), 68(20), 67(8), 66(9), 65(6), 64(4), 60(5), 59(14), 58(16), 57(40), 56(60), 55(30), 54(20), 53(15), 52(15), 51(13), 50(4), 47(4), 46(19), 45(45), 44(60), 43(75), 42(60), 41(65), 40(75), 39(100).		
XII	98(0.2), 84(3), 83(100), 82(4), 67(3), 53(5), 43(66), 41(5), 40(4), 39(9).		
XII- <i>d</i> <sub>6</sub>	104(0.1) 86(100), 64(9), 46(43), 45(3), 44(4), 42(6), 41(7), 40(33), 39(33).		
XIII	98(0.03), 83(2), 60(3), 59(100), 55(4), 53(5), 51(4), 45(41), 44(43), 43(73), 42(27), 41(86), 40(19), 39(68).		

occurs as a secondary process in the fragmentation of compounds V, VI, and VIII.

Two primary alcohols (I and II) were examined, their mode of fragmentation being quite similar. Compound II is the methyl analogue of I which facilitates the interpretation of the spectra because of the possibility to exploit the shift technique. The spectra are complex and many peaks correspond to fragments formed after loss of alkyl moieties, *e.g.*  $m/e$  97 ( $M^+ - 15$ ), 84 ( $M^+ - 28$ ), 83 ( $M^+ - 29$ ), and 69 ( $M^+ - 43$ ) in the spectra of I. This type of cleavage is sometimes combined with consecutive or preceding losses of water. Two common routes of importance are noticed: (i). The molecular ions lose  $H_2O$  and the species formed then expel a methyl radical as shown by a metastable peak. This decomposition pathway leads to the base peak at  $m/e$  79 (*a*) in the spectrum of compound I while the analogous peak  $m/e$  93 in the spectrum of II amounts to 40 %.



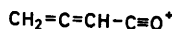
(ii). A major mode of fission of I and II corresponds to  $M^+ - \text{CH}_2\text{OH}$  and gives rise to the base peak  $m/e$  95 (*b*) in the spectrum of II. This indicates that the positive charge of the

molecular ion can reside on the allenic function and trigger the ejection of the hydroxymethyl group. However, the secondary and tertiary alcohols exhibit this fragmentation to a less extent.

The decomposition of the secondary alcohols III and IV occurs mainly through cleavage  $\alpha$  to the hydroxyl group. The base peak  $m/e$  69 in the spectrum of III corresponds to loss of the butyl group, while the molecular ion splits off the allenyl group less easily. In the present investigation compound IV is the only alcohol containing an aromatic group. As expected, this group governs the decomposition, *e.g.* the  $\alpha$ -fission occurs exclusively with loss of the allenyl group to form  $m/e$  107 (base peak). The presence of the aromatic group is also reflected in the intensity of the molecular ion (9 %).

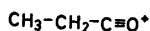
The tertiary alcohols V, VI, and VII all have a terminal allenyl group. In principle, three different types of groups, methyl, vinyl, and allenyl can be lost in an  $\alpha$ -cleavage of compound V. However, the loss of the latter group dominates and the  $M^+ - 39$  peak is the base peak in the spectrum. The  $\alpha$ -cleavage of compound VI occurs to an equal extent with loss of the propyl ( $m/e$  83) and the allenyl group ( $m/e$  87).

A peak at  $m/e$  67, which is shifted to  $m/e$  68 in the deuteriated analogue V- $d_1$ , is represented by species *c*. This fragment is also formed in the decomposition of compounds VI, X, and XI which likewise have a terminal allenyl group.



*c*

The spectrum of compound V exhibits an abundant peak at  $m/e$  43 (93 %) corresponding to an acetyl moiety. This species is associated with the methyl group located on the  $\alpha$ -carbon to the hydroxyl group. A prominent acetyl fragment is also found in the breakdown pattern of compounds VI, VII, and VIII. The corresponding peak sometimes constitutes the base peak, *e.g.* in the spectrum of VI. A comparable ion having structure *d* is formed in the fragmentation of compound IX.

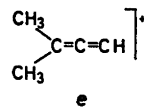


*d*

The spectrum of compound VII shows a small peak at  $M^+ - \text{CH}_3$  ( $m/e$  83). In the spectrum of the hexadeuteriated analogue VII- $d_6$ , which has an isotopic purity of at least 99 %, this peak is split into four peaks corresponding to  $M^+ - \text{CH}_3$ ,  $M^+ - \text{CDH}_2$ ,  $M^+ - \text{CD}_2\text{H}$ ,  $M^+ - \text{CD}_3$  of almost equal intensity. The reason for this behaviour may be an incomplete hydrogen scrambling, since the calculated values for a random loss of the above methyl groups from the molecular ion of VII- $d_6$  are 1:9:15:5, respectively.

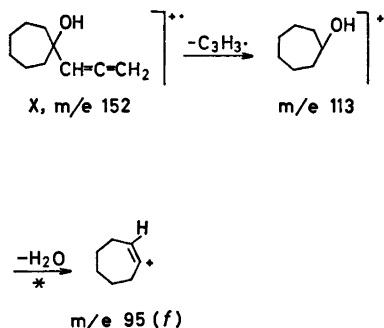
Compounds VIII and IX do not have a terminal allenyl group. The main fragmentation pathway of these compounds is  $\alpha$ -cleavage with loss of the allenic group. This behaviour is analogous to that of the other tertiary alcohols studied. Thus the  $M^+ - 67$  peak corresponding to the loss of the allenic group is the base peak in the spectrum of compound IX. The formed moiety then expels  $\text{H}_2\text{O}$ , *e.g.* to rise to  $m/e$  81 in the spectrum of VIII.

The allenic group is not a preferred site for the charge localization in the ionizing process of the secondary and tertiary alcohols studied. There is an abundant peak at  $m/e$  39 in the spectra of the compounds having a terminal allenyl group (III, IV, V, VI, VII, X, and XI) but on the other hand, the analogous fragment *e* corresponding to  $m/e$  67 in the spectra of VIII and IX is of minor importance.

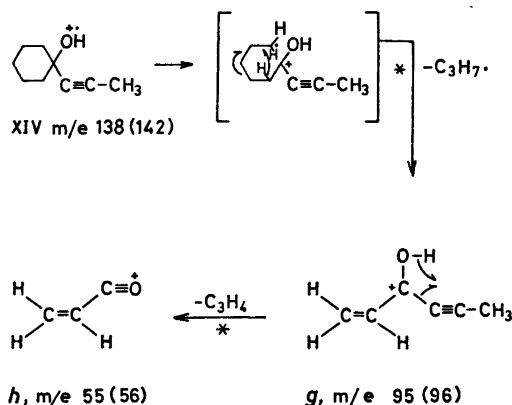


The breakdown pattern of compounds X and XI is dominated by peaks corresponding to ions derived from the cycloalkyl rings. The major mode of fragmentation is loss of the allenyl group and subsequent expulsion of  $\text{H}_2\text{O}$  from the formed ion to give a stable fragment, corresponding to  $m/e$  95 (*f*) and  $m/e$  81 in the fragmentation of X and XI, respectively (*cf.* Scheme 1).

Compounds XI and XIV are exposed to a dissociation route involving complex fissions of the ring as outlined in Scheme 2. It is substantiated by metastable ions, high resolution measurements, and by shifts in the spectra of the deuteriated analogues XI- $d_1$ , XI- $d_4$ , and



Scheme 1.



Scheme 2.

XIV- $d_4$ , respectively, *e.g.* species *g* and *h* are shifted only one mass unit.

**Acetylenic tertiary alcohols.** Compounds XII and XIV exhibit modes of fragmentation which differ from those of their allenic counterparts VII and XI and their  $\beta$ -acetylenic isomers XIII and XV. The important difference is that no  $M^+ - 39$  peak is present in the spectra, *i.e.* no fission occurs in the acetylenic chain. The acetylenic group behaves similarly to a vinyl group in this respect and analogous results have been noticed for acetylenic amines.<sup>7,8</sup> Instead, the major fragmentation route for XII implies loss of a methyl radical. The fragmentation of compound XIV occurs mainly in the cyclohexyl ring, *e.g.* the formation of  $M^+ - 29$  and  $M^+ - 43$ . Deuterium labelling reveals that the  $M^+ - 15$  ion is formed through loss of a methyl group from the acetylenic chain. The most

important route of fragmentation is outlined in Scheme 2 and involves a site-specific hydrogen transfer to the expelled radical.

The  $\beta$ -acetylenic alcohols XIII and XV afford essentially the same breakdown pattern as their allenic isomers VII and XI (*cf.* Table 2). However, there are differences in the relative intensities of various peaks, which make it possible to differentiate between the isomers. Compared to compound XI, the fragmentation mode of XV seems to involve to a less extent the cyclohexyl ring,  $m/e$  95 is only 3%. To obtain an accurate identification of these two types of compounds only based on mass spectral data, a comparison with reference compounds is needed.

In conclusion, the allenic alcohols studied mainly fragment through  $\alpha$ -cleavage. In this type of fission, the allenyl group can be anticipated to behave similarly to a vinyl or to a propargyl group. Judging from the similarity of the spectra of the  $\beta$ -acetylenic and allenic alcohols, the latter case seems to be relevant.  $\alpha$ -Cleavage with loss of the allenyl group is the main fragmentation route of the tertiary alcohols. However, in some compounds, *e.g.* III, an alkyl group of similar size is lost to an equal extent.

The study of the isomeric allenic,  $\alpha$ -acetylenic, and  $\beta$ -acetylenic tertiary alcohols shows that the  $\alpha$ -acetylenic derivatives behave quite differently due to the fact that fission does not occur preferentially next to an acetylenic bond.

In spite of the similarities of the spectra of the allenic and  $\beta$ -acetylenic compounds it can be concluded that mass spectrometry is a useful method for distinguishing between isomeric allenic and acetylenic alcohols.

## EXPERIMENTAL

Infrared and NMR spectra of all compounds are in full agreement with the proposed structures.

All reactions with  $LiAlH_4$  or Grignard reagents were performed under a nitrogen atmosphere.

Elemental analyses were performed in the laboratories of Dr. A. Bernhardt, Mülheim, West Germany.

The mass spectra were recorded on an AEI MS-30 mass spectrometer, connected to a Pye 104 gas chromatograph. The ionizing energy was maintained at 70 eV, the accelerating voltage

at 4 kV and the temperature of the source at 200°. High resolution spectra were obtained on an Atlas MS 1 mass spectrometer in the laboratory of Dr. R. Ryhage.

*High resolution measurements of 1-(1-propynyl)cyclohexanol (XIV).*

Measured mass	Theoretical	Formula
55.0532	55.0547	C <sub>4</sub> H <sub>7</sub>
55.0170	55.0183	C <sub>3</sub> H <sub>5</sub> O (h)
67.0551	67.0547	C <sub>5</sub> H <sub>7</sub>
67.0184	67.0183	C <sub>4</sub> H <sub>5</sub> O
82.0418	82.0419	C <sub>5</sub> H <sub>6</sub> O
82.0775	82.0782	C <sub>6</sub> H <sub>10</sub>
95.0498	95.0450	C <sub>6</sub> H <sub>7</sub> O(g)
95.0858	95.0861	C <sub>7</sub> H <sub>11</sub>

*3-Methyl-6-(tetrahydro-2-pyranyloxy)-1-hexen-4-yn-3-ol (XVI)* was prepared as described for similar compounds<sup>18</sup> from 3-(tetrahydro-2-pyranyloxy)propyne (40.7 g; 0.29 mol) and methyl vinyl ketone (18.0 g; 0.26 mol). Yield 23%. B.p. 108°/0.15 mmHg. (Found: C 68.3; H 8.83. Calc. for C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>: C 68.5; H 8.63).

*1-Phenyl-4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ol (XVII)*. Prepared as above from 3-(tetrahydro-2-pyranyloxy)propyne (77.1 g; 0.55 mol) and benzaldehyde (53.0 g; 0.50 mol). Yield 95%. B.p. 130°/0.1 mmHg.

*2,4,7-Trimethyl-7-(tetrahydro-2-pyranyloxy)-2-octen-5-yn-4-ol (XVIII)*. Prepared as above from 3-methyl-3-(tetrahydro-2-pyranyloxy)butyne<sup>16</sup> (67.0 g; 0.40 mol) and mesityl oxide (36.2 g; 0.37 mol). Yield 69%. B.p. 100°/0.1 mmHg. (Found: C 72.4; H 9.61. Calc. for C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>: C 72.1; H 9.88).

*2-(Methyl-d<sub>3</sub>)-5-(tetrahydro-2-pyranyloxy)-3-pentyn-2-ol-1,1,1-d<sub>3</sub> (XIX)* was prepared as above using acetone-d<sub>6</sub>. B.p. 95°/0.15 mmHg. Yield 77%.

*[3-(Tetrahydro-2-pyranyloxy)-1-propynyl]cyclohexanol-2,2,6,6-d<sub>4</sub> (XX)* was prepared as above using cyclohexanone-2,2,6,6-d<sub>4</sub>. B.p. 128°/0.1 mmHg. Yield 40%.

*2-(Methyl-d<sub>3</sub>)-3-pentyn-2-ol-1,1,1-d<sub>3</sub> (XII-d<sub>4</sub>)* was synthesized as described for the undeuterated compound<sup>14</sup> using acetone-d<sub>6</sub>. B.p. 140°/760 mmHg. Yield 69%.

*1-(1-Propynyl)cyclohexanol-2,2,6,6-d<sub>4</sub> (XIV-d<sub>4</sub>)* was prepared as described for the undeuterated compound<sup>14</sup> using cyclohexanone-2,2,6,6-d<sub>4</sub>. B.p. 115°/20 mmHg. Yield 86%.

*α-Allenic alcohols IV, V, VII-d<sub>6</sub>, VIII and XI-d<sub>4</sub>*. Prepared according to Landor<sup>9</sup> from LiAlH<sub>4</sub> and the tetrahydropyranyl derivatives XVI–XX.

*Synthesis of the mono-deuterated allenic alcohols III-d<sub>1</sub>, V-d<sub>1</sub>, IX-d<sub>1</sub> and XI-d<sub>1</sub>*. From LiAlD<sub>4</sub> (0.315 g; 7.5 mmol) and the appropriate tetrahydropyranyl derivative (6.0 mmol) (*cf.*

the preparation of the undeuterated alcohols). Micro distillation was applied for the isolation. The yields were between 30 and 50%.

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