

# A Mass Spectral Study of Some C<sub>10</sub>H<sub>16</sub> Monoterpenes\*

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## Résumé

On présente les résultats d'une étude de spectroscopie de masse approfondie effectuée sur des monoterpènes C<sub>10</sub>H<sub>16</sub>. Les spectres de masse 70 eV, les caractéristiques des ions métastables ainsi que les spectres de dissociation induite par collision (CID) ne montrent aucune migration importante des liaisons doubles dans les ions moléculaires. Les isomères peuvent donc être reconnus dans leurs spectres de masse et même, de façon plus subtile, dans les spectres de masse d'ions métastables des ions moléculaires. Cependant, dans le cas des ions moléculaires dont la durée de vie est longue, les données permettent de conclure à l'isomérisation d'un certain nombre d'isomères bicycliques sous forme de structure caractéristique d'un isomère monocyclique précis. C'est ainsi que les ions moléculaires des paires 2-carène et  $\alpha$ -terpinène, 3-carène et  $\gamma$ -terpinène ainsi que  $\alpha$ -pinène et  $\alpha$ -phellandrène possèdent des caractéristiques d'ions métastables ainsi que des spectres de masse CID très semblables même si leurs spectres de masse 70 eV sont très différents. Les spectres de masse de stripping de charge des ions fragmentés C<sub>7</sub>H<sub>9</sub> montrent que leur structure n'est pas celle du toluène protoné. Les résultats sont indicateurs d'une contribution importante provenant d'une structure cycloheptatriène protonée même si une ou plusieurs autres structures pourraient être impliquées.

## Abstract

A detailed mass spectral study of ten C<sub>10</sub>H<sub>16</sub> monoterpenes has been carried out. The 70 eV mass spectra, the metastable ion characteristics, and the collision-induced dissociation (CID) mass spectra indicate that

double bond migration does not occur to a significant extent in the molecular ions. Thus the isomers can be distinguished from their mass spectra and, to a lesser extent, from the metastable ion mass spectra of the molecular ions. However, for long-lived molecular ions there is substantial evidence that a number of bicyclic isomers isomerize to a structure common to a specific monocyclic isomer. Thus the molecular ions of the pairs 2-carene and  $\alpha$ -terpinene, 3-carene and  $\gamma$ -terpinene, and  $\alpha$ -pinene and  $\alpha$ -phellandrene show very similar metastable ion characteristics and CID mass spectra, although the 70 eV mass spectra are substantially different. Charge stripping mass spectra of the C<sub>7</sub>H<sub>9</sub><sup>+</sup> fragment ions show that they do not have a protonated toluene structure. The results indicate a significant contribution of a protonated cycloheptatriene structure although another structure or other structures also may be involved.

## Introduction

The terpenes are important natural products (1,2); consequently, their electron ionization mass spectra were studied extensively (3-8) in the early days of the application of mass spectrometry to the identification and structure elucidation of organic compounds. However, most of the studies of the monoterpenes were carried out prior to the development of more sophisticated mass spectral techniques such as metastable ion scanning, kinetic energy release measurements and collisional activation techniques which have proven to be particularly powerful in probing gaseous ion structures and, thus, providing information on possible isomerization reactions of the ions produced in the initial electron ionization process (9).

The present work reports a detailed mass spectral examination of ten C<sub>10</sub>H<sub>16</sub> monoterpenes whose structures are indicated in Figure 1. As can be seen, a considerable number of these compounds, limonene/isolimonene,  $\alpha$ -phellandrene/ $\alpha$ -terpinene/ $\gamma$ -terpinene, 2-carene/3-carene and  $\alpha$ -pinene/ $\beta$ -pinene are isomers

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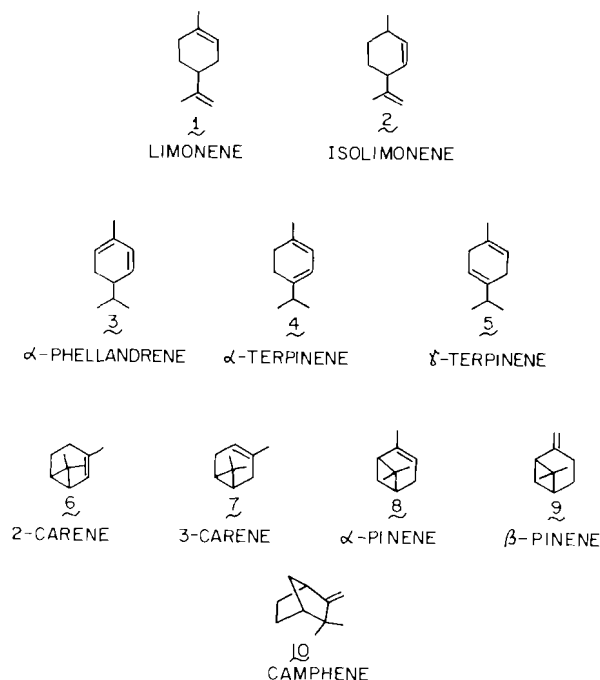


Figure 1. Structure of ten C<sub>10</sub>H<sub>16</sub> monoterpenes.

which differ only in the location of the double bond(s). Since there are many examples in simpler hydrocarbons of facile double bond migration (10), particular attention has been paid to the question of double bond migration in the molecular ions of these compounds. Although the results indicate that double bond migration does not occur to a significant extent, the results do show isomerization between a number of specific bicyclic and monocyclic isomers for long-lived molecular ions.

## Experimental

All experimental work was carried out using a VG Analytical ZAB-2FQ mass spectrometer, which has been described in detail previously (11). The features of the instrument essential to the present work are that it is a reversed-geometry (magnetic sector preceding the electric sector) double-focussing mass spectrometer with a collision cell located at the focal point in the field-free region between the magnetic and electric sectors.

Electron ionization mass spectra were obtained using 70 eV electrons and a source temperature of 200°C and were recorded using the double-focussing mass spectrometer. The combined EI/CI source was used in the electron impact mode. Unimolecular metastable fragmentation reactions of the ions of interest were recorded for reactions occurring in the drift region between the magnetic and electric sectors by the MIKES technique

(12). In this technique the ion of interest is mass-selected by the magnetic sector at 8 keV kinetic energy and the products of unimolecular fragmentation in the drift region were identified according to their kinetic energy by scanning the electric sector. The kinetic energy releases associated with selected unimolecular fragmentation reactions were determined, under conditions of good energy resolution, from the peak widths at half height after correction for the inherent energy spread of the ion beam according to the relation (13)

$$W_{\text{corr}} = (W_{\text{met}}^2 - W_{\text{mb}}^2)^{1/2} \quad [1]$$

where  $W_{\text{met}}$  is the measured width of the daughter ion beam and  $W_{\text{mb}}$  is the width of the parent ion main beam, all measured at half height.

Collision-induced dissociation reactions of mass-selected ions were similarly obtained by the MIKES technique by introducing He into the collision cell to a pressure sufficient to attenuate the main beam by approximately 20%. In these studies the collision cell was floated at -1000 V to separate, on the energy scale, fragmentation reactions occurring outside the cell (mostly unimolecular) from those occurring inside the cell (collision-induced). The data presented in the following correspond to processes occurring only within the cell.

Charge stripping mass spectra of the  $m/z$  93 ions were obtained by the MIKES technique using, separately, O<sub>2</sub>, N<sub>2</sub> and He as collision gases at pressures sufficient to give approximately 40% attenuation of the mass-selected ion beam. In these studies the electric sector voltage was scanned over a narrow range near  $E/2$  where  $E$  is the voltage necessary to transmit the respective singly-charged ion.

The monoterpenes were obtained from the Fluka Chemical Corporation and were used as received. They were introduced into the source from a heated metal inlet system maintained at 160°C. No evidence for thermal decomposition, as reported by Ryhage and von Sydow (3) using GC/MS, was observed.

## Results and Discussion

Partial 70 eV EI mass spectra of the ten C<sub>10</sub>H<sub>16</sub> isomers are presented in Table I. The spectra are in good agreement with those reported for some of the isomers by Thomas and Willhalm (4), Hill *et al.* (6) and Ryhage and von Sydow (3), particularly if one takes into account that the latter workers used 20 eV electron ionization. Our spectra for limonene (1) and 3-carene (7) are in good agreement with those reported by von Bunau *et al.* (7), but our spectrum for 2-carene (6) differs substantially from the spectrum they report; the reasons for this dif-

Table I. 70 eV Mass Spectra of Monoterpenes.

$m/z$	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
137	2.7	5.7	2.9	5.7	4.0	6.5	2.6	1.1	1.1	2.4
136	24.4	52.0	23.0	53.0	35.4	56.0	21.8	8.0	9.0	21.8
121	19.4	48.6	2.0	100.0	31.2	90.0	22.6	14.0	11.8	24.5
108	4.4	14.0		4.4		4.0				8.0
107	16.0	60.4	2.0	12.2	6.0	12.2	7.6	6.0	4.4	30.0
106	2.1	2.0		4.3	2.0	4.8	2.0	2.0		
105	4.3	11.8	2.2	19.8	8.2	27.4	10.2	8.0	2.3	
95	7.6	9.2		3.0		2.6	2.4		2.0	1.8
94	21.2	20.9	8.0	9.8	8.0	11.0	11.8	9.6	13.6	19.8
93	55.8	82.4	100.0	96.0	100.0	100.0	100.0	100.0	100.0	100.0
92	16.1	9.8	26.4	15.6	20.1	13.6	22.2	32.0	9.0	12.2
91	15.0	32.7	34.4	43.4	34.0	40.0	30.0	25.0	18.0	27.0
82	1.8	2.3								3.6
81	11.7	15.0		6.0	2.6	5.6	5.6	3.8	2.2	10.4
80	11.7	14.2	1.8	7.2	7.0	8.0	20.3	9.9	9.6	17.4
79	23.6	100.0	7.6	27.5	20.0	38.0	26.0	19.8	20.2	40.3
78	2.3	7.6	4.1	7.4	5.6	6.4	4.2	3.2	2.3	5.7
77	12.4	33.6	30.4	34.4	30.0	37.7	27.6	23.2	18.0	23.8
69	6.4	3.0		2.1		2.0			37.4	7.6
68	100.0	37.1		4.0		2.3	2.4	4.0	2.0	15.6
67	42.0	31.6		6.1	2.2	8.2	8.0	6.4	8.3	26.0
66	2.3	4.4		1.8						5.6
65	5.6	11.8	3.7	11.8	7.0	9.2	4.8	4.0	4.2	7.6
55	6.1	25.4		9.6	3.2	10.2	6.0	5.2	4.4	11.5
53	20.7	23.2	3.0	10.4	6.0	12.1	9.1	7.9	8.0	14.0
51	5.4	20.2	4.0	11.0	6.2	8.1	4.3	4.7	4.0	6.4
43	2.1	13.0	3.8	24.4	25.0	23.6	19.7	14.0	8.3	10.6
41	22.6	38.4	7.9	26.8	16.2	30.0	40.4	16.0	44.3	34.4
40	4.6	8.0		3.5	2.1	4.0	2.3	2.1	2.0	5.7
39	22.6	39.9	9.1	23.0	14.7	30.4	19.7	15.6	17.8	25.3

ference are not clear. It is particularly interesting to note that the terpenes which differ only by the relative position of double bonds show distinctly different mass spectra, indicating that there is little double bond migration in the molecular ions prior to fragmentation. This is particularly noticeable for the isomeric pair limonene (**1**) and isolimonene (**2**). The isomer trio  $\alpha$ -phellandrene (**3**)  $\alpha$ -terpinene (**4**)/ $\gamma$ -terpinene (**5**) also show substantial differences as do the isomer pairs 2-carene (**6**)/ $\beta$ -carene (**7**) and  $\alpha$ -pinene (**8**)/ $\beta$ -pinene (**9**), although in these latter two cases it might not be possible to identify a particular isomer without having the spectra of the other isomers recorded under the same conditions.

The unimolecular metastable ion fragmentation reactions of the molecular ions of the terpenes as observed in the second field-free region of the mass spectrometer are recorded in Table II. A number of these metastable ion fragmentation reactions have been observed by pre-

vious workers (3,6,7) as diffuse peaks in the normal mass spectra but relative intensities have not been reported and some metastable peaks were missed because of overlap with normal peaks in the mass spectra. For example, the fragmentation reaction  $136 \rightarrow 94^+$  gives  $m^* = 94^2/136 = 64.97$  and is obscured by the normal mass spectral peak at  $m/z$  65. Harris *et al.* (14) have reported the unimolecular fragmentation reactions of the molecular ion of limonene obtained using a B.E linked scan in a double-focussing instrument of normal geometry. The relative intensities they have reported are not in agreement with our measurements; in addition they report a number of fragment ions (*e.g.*,  $m/z$  122 and 95) which we do not observe.

The metastable ion spectra of Table II show distinct spectra for double bond isomers, indicating that double bond migration has not occurred even for the long-lived molecular ions fragmenting in the second field-free

Table II. Metastable Ion Fragmentation of  $m/z$  136 Molecular Ions.

Compound	Fragment Ion $m/z$ and Neutral Loss							
	121 -CH <sub>3</sub>	108 -C <sub>2</sub> H <sub>4</sub>	107 -C <sub>2</sub> H <sub>5</sub>	106 -C <sub>2</sub> H <sub>6</sub>	94 -C <sub>3</sub> H <sub>6</sub>	93 -C <sub>3</sub> H <sub>7</sub>	92 -C <sub>3</sub> H <sub>8</sub>	80 -C <sub>4</sub> H <sub>8</sub>
<u>1</u>	36.0	2.0	30.4	2.4	100.0	6.0	18.2	3.9
<u>2</u>	75.2	33.2	100.0	2.0	56.0	38.0	18.2	4.4
<u>3</u>	32.0	10.6	31.0	2.0	20.6	23.8	100.0	3.8
<u>4</u>	100.0	8.2	31.2	1.4	7.8	22.0	11.8	3.8
<u>5</u>	100.0	8.6	52.0	3.8	26.8	34.0	62.0	36.0
<u>6</u>	100.0	12.2	26.4	2.0	6.0	27.8	15.4	6.8
<u>7</u>	100.0	8.0	38.4	2.0	28.0	45.9	57.8	37.9
<u>8</u>	32.0	2.2	10.5		12.8	12.4	100.0	7.7
<u>9</u>	100.0	11.2	47.8	2.0	8.8	31.2	47.4	84.8
<u>10</u>	100.0	4.0	28.2	4.0	33.6	9.3	25.2	6.7

Table III. Kinetic Energy Release for Fragmentation Reaction  $C_{10}H_{16}^{+\bullet} \rightarrow C_9H_{13}^+ + CH_3\cdot$ 

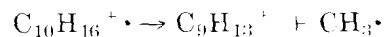
Compound	$T_{1/2}$ (meV)
<u>1</u>	20.0 ± 1.6 <sup>a</sup>
<u>2</u>	50.5 ± 3.2
<u>3</u>	38.3 ± 5.0
<u>4</u>	63.8 ± 4.9
<u>5</u>	55.1 ± 6.2
<u>6</u>	54.5 ± 3.3
<u>7</u>	57.8 ± 4.8
<u>8</u>	46.5 ± 3.4
<u>9</u>	51.1 ± 2.3
<u>10</u>	17.6 ± 1.4

<sup>a</sup> standard deviation of triplicate determinations

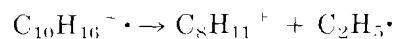
region. However, there are a number of cases where monocyclic and bicyclic isomers give similar metastable ion spectra. Thus, the spectrum obtained for  $\alpha$ -pinene (8) is similar to that observed for  $\alpha$ -phellandrene (3), that for 2-carene (6) is similar to that for  $\alpha$ -terpinene

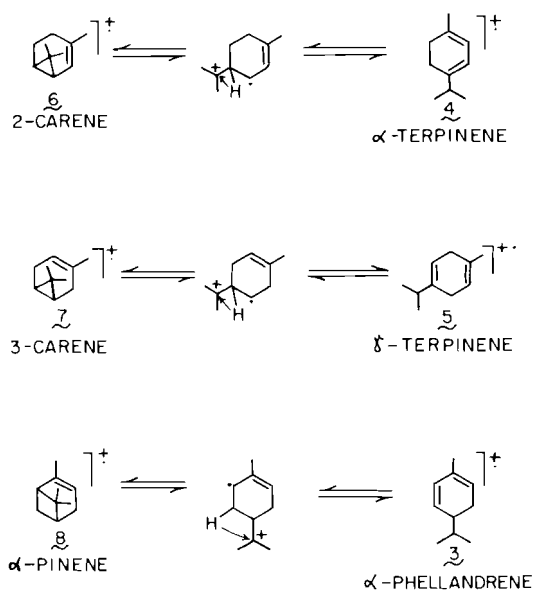
(4) and that for 3-carene (7) is similar to that for  $\gamma$ -terpinene (5). This suggests that for each of these pairs the long-lived molecular ions may be isomerizing to a common structure or mixture of structures prior to fragmentation on the metastable ion time scale. We suggest the possibility that the bicyclic isomers may be isomerizing to the respective monocyclic isomers as outlined in Scheme 1. Clearly, the mass spectral data of Table I show that these isomerization reactions are not occurring to a significant extent for the molecular ions fragmenting in the ion source.

Further evidence for significant integrity of the molecular ion structures comes from measurement of the kinetic energy releases associated with the metastable ion fragmentation reaction



As shown in Table III, these exhibit significant variation from isomer to isomer, although the  $T_{1/2}$  values for the bicyclic and monocyclic isomers discussed above tend to be similar; all peaks were Gaussian in shape. In contrast with this variation, the kinetic energy releases associated with the unimolecular fragmentation reaction:





were all in the range 20.4 to 27.5 meV, suggesting a common precursor structure in this fragmentation reaction. This is not particularly surprising since, clearly, substantial structural rearrangement of the molecular ions is necessary before elimination of an ethyl radical can occur; by contrast, a methyl radical, in principle, can be eliminated without significant structural rearrangement.

Table IV and V present the relative fragment ion intensities observed for metastable ion fragmentation of the  $m/z$  121 and  $m/z$  107 fragment ions formed in the EI mass spectra of the ten isomers. There is little variation in the relative fragment ion signals from isomer to isomer and it is likely that all  $m/z$  121 fragment ions have a common structure as do all  $m/z$  107 fragment ions. The results of Tables II and IV show that there are two routes to the  $m/z$  93 ( $C_7H_9^+$ ) fragment ion, which in many cases is the base peak in the mass spectrum; one of these pathways involves direct elimination of  $C_3H_7\cdot$  from the molecular ion while the second involves sequential elimination of  $CH_3\cdot$  and  $C_2H_5\cdot$ .

Further evidence concerning the integrity of the molecular ion structures comes from the 8 keV collision-induced dissociation (CID) mass spectra of the molecular ions reported in Table VI. The double bond isomers give distinct spectra, however, as in the metastable ion spectra, the pairs  $\alpha$ -phellandrene/ $\alpha$ -pinene,  $\alpha$ -terpinene/2-carene and  $\gamma$ -terpinene/3-carene give fairly similar spectra. This is consistent with formation of a common structure or mixture of structures for each of these pairs for the long-lived molecular ions subjected

Table IV. Metastable Ion Fragmentation of  $C_{10}H_{16}^+$  ( $m/z$  121) Ions.

Compound	Fragment Ion and Neutral Loss			
	119 $H_2$	105 $CH_4$	93 $C_2H_4$	79 $C_3H_6$
1	11	56	100	17
2	12	57	100	18
3	16	88	100	12
4	13	78	100	10
5	15	84	100	11
6	14	84	100	10
7	17	100	86	9
8	18	100	87	16
9	10	54	100	16
10	6	32	100	29

Table V. Metastable Ion Fragmentation of  $C_{10}H_{16}^+$  ( $m/z$  107) Ions.

Compound	Fragment ion and neutral loss		
	105 $H_2$	91 $CH_4$	79 $C_2H_4$
1	78	100	71
2	68	92	100
3	75	100	55
4	80	100	41
5	80	100	35
6	80	100	40
7	77	100	32
8	80	100	36
9	77	100	74
10	81	100	59

to collisional activation. It is interesting to note that the  $C_5H_8^+$  ( $m/z$  68) fragment ion is of only low intensity in the CID mass spectrum of limonene despite being the base peak in the EI mass spectrum; clearly, this fragment is formed only from ions of quite high internal energy. Schwarz *et al.* (15) have reported the CID mass spectra of a selection of  $C_{10}H_{16}^+$  isomers, however, they were unable to separate the unimolecular and collision-induced components of the spectra so their results cannot be compared with our results.

#### Studies of the $C_7H_9^+$ ( $m/z$ 93) Fragment Ion

The  $C_7H_9^+$  ion is a major fragment ion in the mass spectra of many  $C_{10}H_{16}$  monoterpenes. As detailed above, there are at least two pathways to this ion, direct elimination of  $C_3H_7\cdot$  and sequential elimination of  $CH_3\cdot$  and  $C_2H_5\cdot$ . Schwarz *et al.* (15) have reported a study of the unimolecular and collision-induced dissociation of the

Table VI. 8 keV CID Mass Spectra of  $C_{10}H_{16}^{+}$  Molecular Ions.

m/z	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
121	43	70	6	100	88	100	93	13	50	100
119	6	9	6	11	12	10	13	4	6	4
117	3	5	3	6	6	4	6	2	3	2
115	2	3		3	5	2	4		2	
107	37	100	4	16	19	15	26	5	16	28
105	10	21	6	19	20	14	20	6	10	8
103	4	6	2	4	6	4	4	2	3	3
95	16									12
94	57	18								17
93	100	48	100	36	100	32	100	100	100	46
92	36		43		34		37	56	20	19
91	52	32	27	22	32	20	28	25	27	16
83	6	6							2	2
81	9	5		2	2				2	4
80	11				6		16		12	6
79	15	19	5	7	9	6	12	5	10	10
77	13	12	8	8	12	6	10	8	9	6
68	3									

Table VII. Charge Stripping Mass Spectra of  $C_7H_8^{+}$  (m/z 93) Ions ( $O_2$  collision gas).

Compound	% of base peak ( $\pm$ standard deviation)			
	<u>93</u> <sup>+</sup>	<u>92</u> <sup>+</sup>	<u>91</u> <sup>+</sup>	<u>90</u> <sup>+</sup>
<u>1</u>	46.1 $\pm$ 1.9	15.3 $\pm$ 1.2	100.0	58.7 $\pm$ 3.8
<u>2</u>	27.8 $\pm$ 3.1	12.1 $\pm$ 1.2	100.0	54.2 $\pm$ 5.2
<u>3</u>	21.4 $\pm$ 0.2	11.0 $\pm$ 0.9	100.0	53.4 $\pm$ 4.2
<u>4</u>	23.0 $\pm$ 0.7	11.1 $\pm$ 0.8	100.0	52.7 $\pm$ 4.3
<u>5</u>	25.6 $\pm$ 0.8	12.5 $\pm$ 2.2	100.0	52.3 $\pm$ 4.4
<u>6</u>	20.2 $\pm$ 1.5	10.6 $\pm$ 1.3	100.0	53.7 $\pm$ 8.0
<u>7</u>	38.6 $\pm$ 1.2	13.5 $\pm$ 1.5	100.0	55.9 $\pm$ 5.1
<u>8</u>	29.9 $\pm$ 2.1	12.2 $\pm$ 0.7	100.0	57.7 $\pm$ 6.2
<u>9</u>	54.0 $\pm$ 2.4	13.1 $\pm$ 1.7	100.0	57.4 $\pm$ 6.1
<u>10</u>	45.7 $\pm$ 1.7	14.7 $\pm$ 1.5	100.0	57.9 $\pm$ 5.7
Toluene.H <sup>+</sup>	100.0	25.8 $\pm$ 1.2	77.1 $\pm$ 6.2	62.3 $\pm$ 5.3
Cyclo- heptatriene.H <sup>+</sup>	69.0 $\pm$ 5.4	16.1 $\pm$ 2.1	100.0	62.9 $\pm$ 7.1

Table VIII. Charge Stripping Mass Spectra of  $C_7H_9^+$  ( $m/z$  93) Ions (He collision gas).

Compound	% of base peak ( $\pm$ standard deviation)			
	93 <sup>+2</sup>	92 <sup>+2</sup>	91 <sup>+2</sup>	90 <sup>+2</sup>
<u>1</u>	34.5 $\pm$ 1.0	21.9 $\pm$ 0.2	100.0	96.2 $\pm$ 1.0
<u>2</u>	19.8 $\pm$ 2.6	15.5 $\pm$ 1.0	100.0	85.5 $\pm$ 3.2
<u>3</u>	15.3 $\pm$ 0.4	13.9 $\pm$ 0.4	100.0	85.6 $\pm$ 0.9
<u>4</u>	17.2 $\pm$ 1.1	14.4 $\pm$ 1.1	100.0	82.6 $\pm$ 2.1
<u>5</u>	18.4 $\pm$ 0.6	14.7 $\pm$ 0.2	100.0	83.4 $\pm$ 2.1
<u>6</u>	13.9 $\pm$ 0.9	12.7 $\pm$ 0.4	100.0	80.7 $\pm$ 2.9
<u>7</u>	28.2 $\pm$ 1.6	18.1 $\pm$ 0.3	100.0	87.4 $\pm$ 2.1
<u>8</u>	23.2 $\pm$ 1.2	16.9 $\pm$ 0.1	100.0	87.8 $\pm$ 2.1
<u>9</u>	40.4 $\pm$ 2.1	19.4 $\pm$ 0.5	100.0	92.1 $\pm$ 1.5
<u>10</u>	34.8 $\pm$ 0.6	21.1 $\pm$ 0.8	100.0	92.9 $\pm$ 1.9
Toluene.H <sup>+</sup>	81.7 $\pm$ 6.7	39.4 $\pm$ 2.0	86.7 $\pm$ 2.0	100.0
Cyclo- heptatriene.H <sup>+</sup>	38.8 $\pm$ 1.7	19.6 $\pm$ 1.7	92.2 $\pm$ 3.4	100.0

$C_7H_9^+$  ions formed in the mass spectra of ten acyclic and cyclic monoterpenes. From metastable ion kinetic energy release measurements they concluded that different structures were involved in the  $H_2$ -elimination reaction and in the  $CH_1$ -elimination reaction. The CID spectra of the  $C_7H_9^+$  ions from the terpenes and a number of reference ions were identical preventing clear identification of the stable  $C_7H_9^+$  structure(s) involved.

In the present work we have compared the unimolecular, collision-induced dissociation and charge stripping reactions of the  $C_7H_9^+$  ions from the terpenes with the behaviour of two model  $C_7H_9^+$  ions- protonated toluene and protonated cycloheptatriene. In each case the protonated species was prepared by  $CH_1$  chemical ionization. We have observed that the unimolecular fragmentation of all  $C_7H_9^+$  ions, including the model ions, yields  $C_7H_8^+$ ,  $C_7H_7^+$  and  $C_6H_5^+$ , with the relative abundances showing little variation from species to species. Further, the CID mass spectra of all  $C_7H_9^+$  ions were identical within experimental error, including the ions derived by protonation of toluene and cyclohepta-

triene. However, substantial differences were observed in the charge stripping mass spectra. It is well-established (16) that charge stripping mass spectra frequently provide isomer distinction where CID mass spectra do not. This presumably arises from the fact that the charge stripping process involves the deposition of a large amount of energy (greater than 12 eV (17)) in the ion and thus samples ions of lower internal energy than are sampled in the CID process. These lower energy ions have less of a propensity to undergo isomerization prior to activation.

Table VII records the charge stripping mass spectra obtained using  $O_2$  as the collision gas. The protonated toluene and protonated cycloheptatriene ions are clearly distinguished from each other. The spectra of the ions derived from the monoterpenes are in reasonable agreement with each other and, clearly, are in much better agreement with the spectrum obtained for protonated cycloheptatriene than with the spectrum obtained for protonated toluene. However, there are still substantial differences in intensities for the  $C_7H_9^{+2}$  ion; it is not

clear whether these differences represent effects of internal energy differences on the charge stripping mass spectra or whether they indicate the presence of a second  $C_7H_9^+$  structure for the terpenes.

The charge stripping mass spectra obtained with  $N_2$  as collision gas showed only very small differences for the model ions and, thus, allowed no structure differentiation. Table VIII records the charge stripping mass spectra obtained with He as the collision gas. Again a clear distinction can be made between the two model ions, protonated toluene and protonated cycloheptatriene. The spectra obtained for the  $C_7H_9^+$  ions from the monoterpenes clearly are not in agreement with the spectrum obtained for protonated toluene. However, the agreement with the spectrum obtained for protonated cycloheptatriene is not as satisfactory as one would like. Whether this disagreement is due to internal energy effects or to the presence of more than one structure is not clear. We are inclined to have more faith in the latter interpretation. Thus, in agreement with Schwarz *et al.* (15) we are not able to definitively identify the  $C_7H_9^+$  structure(s) involved, although the present charge stripping experiments rule out a major contribution from a protonated toluene structure.

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