Composite C- and H-scrambling and fragmentation of long-lived protonated 6-methylfulvene and 6,6-dimethylfulvene—alternative entry to the gas-phase chemistry of gaseous toluenium ($C_7H_9^+$) and xylenium ($C_8H_{11}^+$) ions

Michael Mormann [1,2], Björn Decker [1], Dietmar Kuck [*]

Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany

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In memoriam Sharon Lias.

Abstract

The fragmentation of metastable 6-methylfulvenium and 6,6-dimethylfulvenium ions, generated by gas-phase protonation of the neutral hydrocarbons in the CI(CH4) plasma, has been investigated by means of mass-analyzed kinetic energy (MIKE) spectrometry. The $C_7H_9^+$ ions formed from 6-methylfulvene lose H_2 and CH_4, and the $C_8H_{11}^+$ ions formed from 6,6-dimethylfulvene lose H_2, CH_4 and C_2H_4 in relative amounts and with kinetic energy release characteristics that are reminiscent of the fragmentation behavior of toluenium and xylenium ions, respectively. The isomerization reactions preceding the fragmentation of long-lived protonated 6,6-dimethylfulvene, $C_8H_{11}^+$, have been studied in detail by [13]C- and [2]H-labelling of this cycloolefin and analysis of the isotope distributions observed in the MIKE spectra of the [M + H − methane]+ and [M + H − ethene]+ ions, in particular. Composite scrambling was found to occur prior to both of these fragmentation reactions, that is, metastable $C_8H_{11}^+$ ions form two populations that react through different isomerization channels prior to loss of the same neutral fragment. The loss of CH_4 is largely (95%) C-specific but only CH_3-specific for ca. 50% of the ions, whereas the other 50% fraction of the ions suffer complete H scrambling. The loss of C_2H_4 is much less specific: it takes place from a 70–80% fraction of $C_8H_{11}^+$ ions in which one of the two methyl groups is retained intact, whereas the other is involved in a fast C- and H-scrambling of the remaining C_7H_8 backbone, and also from a 20–30% fraction in which all of the eight C- and the eleven H atoms undergo complete scrambling. The composite scrambling behavior observed through expulsion of ethene is almost identical to that found previously upon protonation of *para*-xylene by CI(CH4). Therefore, it is suggested that the $C_8H_{11}^+$ ions generated by protonation of 6,6-dimethylfulvene readily isomerize to 1,1-dimethylbenzenium and the related xylenium ions. The minor (20–30%) fraction of the latter ions undergoes a further, reversible ring expansion to methyldihydrotropylium ions before re-contracting the seven-membered ring to yield ethylbenzenium ions; the major (70–80%) fraction does so irreversibly before re-contraction to ethylbenzenium ions, from which ethene is expelled eventually.

1. Introduction

It has been known for more than two decades that protonated fulvene, $[\mathbf{1}+H]^+$, is only moderately less stable than the stabilomer among the gaseous $C_6H_7^+$ ions, viz. benzenium ion, $[\mathbf{2}+H]^+$ [1]. Whereas the gas-phase ion chemistry and thermochemical data of the latter ions are known particularly well [2,3], knowledge about fulvenium ions, $[\mathbf{1}+H]^+$, has remained relatively scarce. Both isomers were found to co-exist in mixtures of $C_6H_7^+$ ions generated by bimolecular [1,4–6]

* Corresponding author at: Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany. Tel.: +49 521 106 2060; fax: +49 521 106 6417.
  E-mail address: dietmar.kuck@uni-bielefeld.de (D. Kuck).
[1] Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany. Tel.: +49 521 106 2060; fax: +49 521 106 6417.
[2] Present address: Institute for Medical Physics and Biophysics, University of Münster, Robert-Koch-Str. 31, D-48149 Münster, Germany.
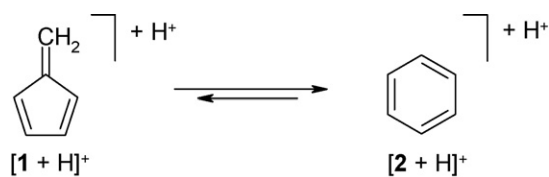
Scheme 1.

Chart 1.

and unimolecular reactions [1,7] of suitable precursors. Recent theoretical work has confirmed the order of thermodynamic stabilities of the $C_6H_7^+$ ions and suggested that the parent fulvenium ion, $[1 + H]^+$, may undergo ring expansion to benzenium ions, $[2 + H]^+$, below the energy limit required for dissociation (Scheme 1) [8].

Based on these findings, alkylfulvenium ions have been considered reactive intermediates during the isomerization of dimethylbenzenium ions prior to fragmentation [9]. In all cases other than that of the parent $C_6H_7^+$ ions, however, protonated alkylbenzenes, and toluenium and other methylbenzenium ions in particular, may also undergo reversible ring *expansion* prior to fragmentation. This has been envoked from the early work on chemical ionization of alkylbenzenes [10] and on the kinetic energy release accompanying the elimination of H_2 from various carbenium ions, including toluenium ions [11,12], and further substantiated in the course of our work on the "composite scrambling" behavior of protonated *para*-xylene on the metastable ions' timescale [3,13,14]. In addition, protonation of 1,3,5-cycloheptatriene and its 7-alkyl derivatives has been shown to induce ring contraction to toluenium and the corresponding higher alkylbenzenium ions prior to fragmentation [15] and recent gas-phase titration experiments revealed that even non-decomposing protonated cycloheptatriene and 6-methylfulvene isomerize to toluenium ions in considerable amounts [16]. In this context, the gas-phase basicities and proton affinities of these C_7H_8 and related C_8H_{10} cycloolefins have been determined [17–19]. In extended theoretical work on alkylbenzenium ions concerning the technically important methanol-to-hydrocarbon (MTH) reaction [20], various isomerization channels of lower alkylbenzenium ions have been compared [9,21]. One important result of this extended computational work is that the ring expansion/re-contraction and the ring contraction/re-expansion pathways of methylbenzenium ions are energetically comparable but that the former sequence is the more favorable one [9]. The composite scrambling [14] behavior and some other crucial details of the isomerization and fragmentation reactions occurring in gaseous $C_7H_9^+$ ions were recently confirmed by two IRMPD studies [22,23] and an ab-initio study on the dynamics of the addition of CH_3^+ to benzene ([24] and (Motell et al., private communication)[3]. Thus, at present, a variety of experimental and computational studies on the gas-phase ion chemistry of $C_7H_9^+$ and $C_8H_{11}^+$ ions is known. Ironically, the apparently simple methylbenzenium ions (and their cycloolefinic isomers)
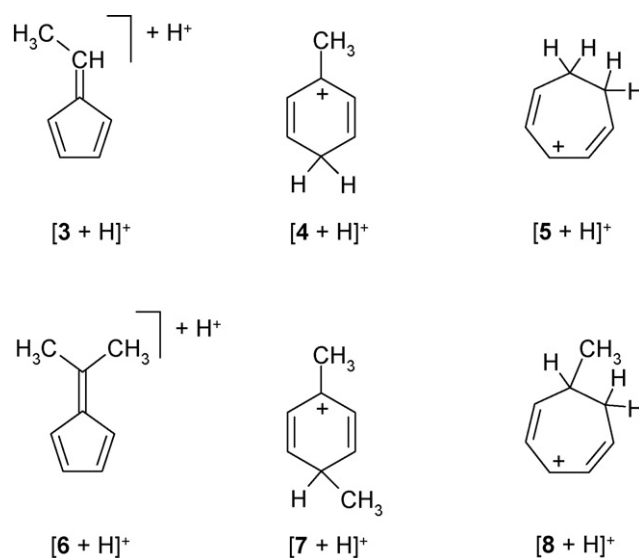
have revealed particularly complicated isomerization chemistry, which certainly pertains to the higher analogues as well [25] (Chart 1.).

Within this complex scenario, the isomerization paths preceding the proton-induced unimolecular fragmentation of simple methylfulvenes has not been studied so far [3,26]. Therefore, as a part of our extensive investigations on the gas-phase chemistry of protonated cycloolefins and methylarenes, we report here on the fragmentation of long-lived metastable $C_7H_9^+$ and $C_8H_{11}^+$ ions generated from 6-methylfulvene (**3**) and 6,6-dimethylfulvene (**6**), respectively, as determined by mass-analysed kinetic energy (MIKE) spectrometry. In particular, some [^{13}C]- and [^{2}H]-labelled 6,6-dimethylfulvenes, **6a**–**6d**, were synthesized and the fragmentation of the corresponding 6,6-dimethylfulvenium ions was compared to that of the correspondingly labelled xylenium ions [13a,14].

2. Experimental

2.1. Syntheses – general

[^{1}H] NMR spectra were recorded with a Bruker DRX 500 (500 MHz) instrument. EI mass spectra (70 eV) were measured by use of an Autospec instrument (see below). All compounds used were purified by standard procedures, solvents were dried immediately prior to use in most cases. All reactions were carried out under an atmosphere of dried argon. [2-^{13}C]acetone and [1,3-^{13}C$_2$]acetone were obtained from Deutero GmbH, Kastellaun, Germany (^{13}C contents ≥97%). Perdeuterocyclopentadiene was obtained by sucessive H/D exchange in a freshly prepared sodium deuteroxide solution as described previously [27].

2.2. Compounds

6-methylfulvene (**3**) was synthesized as described previously [17,28]. The synthesis of 6,6-dimethylfulvene **6** was performed by condensation of acetone and cyclopentadiene using sodium

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[3] A SIFT study of the CH_3^+/C_6H_6 system was performed: E. Motell, M.S. Robinson, R. Gareyev, V.M. Bierbaum, C.H. DePuy, unpublished work (private communication, 2000).

ethanolate as a base as described by Thiele [29]. The [13]C- and deuterium-labeled isotopomers **6a–6d** were prepared by the method published by Zhao et al. [30]. Condensation of cyclopentadiene with [2-^{13}C]acetone, [1,3-[13]C_2]acetone, and hexadeuteroacetone, using *n*-butyllithium as a base, furnished compounds **6a**, **6b** and **6d**, respectively. The d_4-labeled isotopomer **6c** was obtained by use of the same method using perdeuterocyclopentadiene (see above) and acetone. The label contents of compounds **6a** and **6b** was found to be unchanged (NMR); the label contents of compound **6c** was 92% and that of compound **6d** was 91% (by ^{1}H NMR).

2.3. Mass spectrometric measurements

All measurements were performed by use of a double focusing sector-field instrument (AutoSpec, Fisons, Manchester, UK) with a three-sector EBE geometry. Samples were introduced into the ion source via a heated septum inlet. Methane (Linde, Wiesbaden, Germany, stated purity >99.9%) was used as the reactant gas for the CI measurements at a nominal pressure of ca. $4–7 \times 10^{-5}$ mbar. The acceleration voltage, electron energy, emission current and source temperature were set to 8 kV, 70 eV, 200 μA and $140 \pm 10\,°C$, respectively. The MIKE spectra obtained represent the average of 100 scans per measurement and the data given in the tables represent the average of 2–10 measurements. All relative abundances were calculated from peak areas. The data were corrected for the contributions by EI-induced fragmentation of naturally occurring isobaric $[^{13}C_1]M^{\bullet +}$ ions after measurement of the MIKE spectra of the corresponding $[^{13}C_0]M^{\bullet +}$ ions. The determination of the peak areas was performed by numerical integration. Kinetic energy release (KER) distributions were determined by use of the method developed by Szilágyi and Vékey [31]. In the case of the isotope-labelled ions, peak areas were evaluated by fitting with appropriate Gaussian functions followed by numerical integration. The KER values given in this paper denote the most probable (T^*) and the average ($<T>$) values of the kinetic released during the respective fragmentation reaction.

3. Results and discussion

3.1. Protonated 6-methylfulvene

Before focusing on the labelling experiments obtained for the higher analogues, ions $[6 + H]^+$, we will first present and discuss the fragmentation of long-lived 6-methylfulvenium ions, $[3 + H]^+$, and its similarity to that of the toluenium ions, $[4 + H]^+$, and protonated cycloheptatriene (1,2-dihydrotropylium ions), $[5 + H]^+$. The MIKE spectrum of the $C_7H_9^+$ ions (*m/z* 93) generated from 6-methylfulvene **6** under CI(methane) is reproduced in Fig. 1. It is dominated by the strongly broadened signal corresponding to the expulsion of dihydrogen, giving $C_7H_7^+$ ions (*m/z* 91), but it also exhibits a minor, Gaussian-type signal for the loss of methane, leading to $C_6H_5^+$ (*m/z* 77). The relative fragment ion abundances and the kinetic energy release associated with the
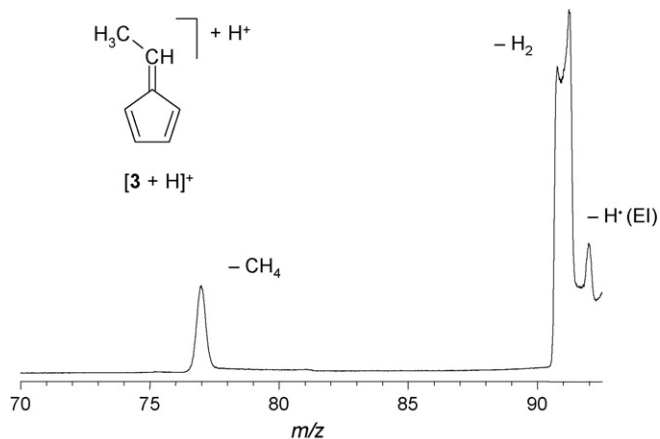

Fig. 1. CI(CH_4)/MIKE spectrum of ions $[3 + H]^+$ ($C_7H_9^+$, *m/z* 93).

elimination of H_2 from ions $[3 + H]^+$ and its isomers $[4 + H]^+$ and $[5 + H]^+$ are collected in Table 1. Whereas the branching ratios $[C_7H_7^+]$: $[C_6H_5^+]$ are almost the same for the $C_7H_9^+$ ions formed from the cycloolefins **3** and **5**, the ratio obtained for the protonated arene **4** is somewhat higher. It was shown that protonation of the cycloolefins **3** and **5** produces mixtures of stable $C_7H_9^+$ ions containing both the protonated arene, $[4 + H]^+$, and varying amounts of the isomers $[3 + H]^+$ and $[5 + H]^+$, whereas protonation of **4** gives rise to ions $[4 + H]^+$ exclusively. It appears reasonable to trace the slightly enhanced loss of CH_4 observed with the former ions to the slightly higher excitation energies imparted to the protonated cycloolefins and, thus, to the toluenium ions, $[4 + H]^+$, formed by isomerization (see below). In fact, the activation barrier toward the loss of CH_4 from toluenium ions, $[4 + H]^+$, was recently calculated to exceed that of the H_2 expulsion by 41 kJ mol^{-1} [23].

The kinetic energy release characteristics observed for the three isomeric ions are also very similar. The most probable values (T^*) and the mean values ($<T>$) are almost identical for all of the three cases (Table 1). The large discrete amount of kinetic energy released during the elimination of H_2 is a ubiquitous feature of $C_7H_9^+$ and higher methylbenzenium ions. Therefore, and because of the results of our gas-phase titration experimes reported recently [16], it can be assumed that a major fraction of the protonated 6-methylfulvene, $[3 + H]^+$, undergoes a skeletal rearrangement to toluenium ions, $[4 + H]^+$,
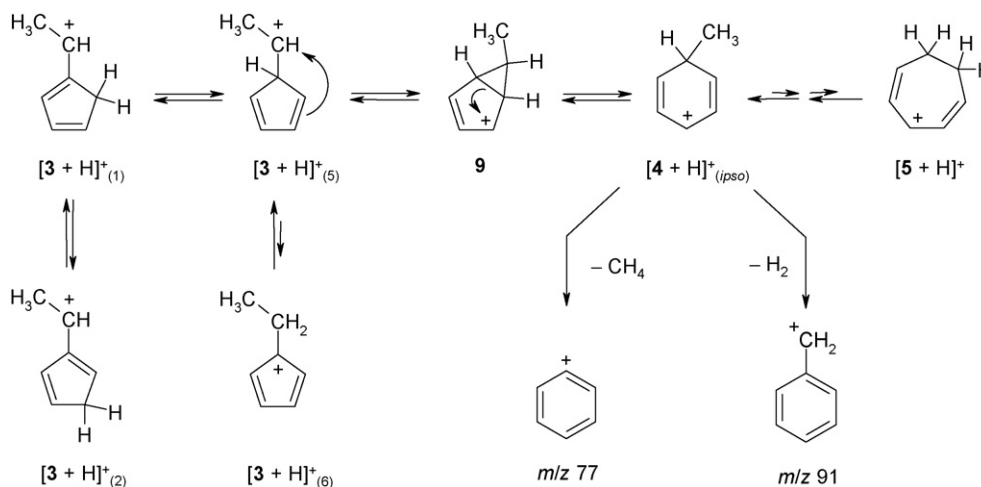
Table 1
Fragmentation of metastable $C_7H_9^+$ ions and kinetic energy release

Ion/Loss[a] T_{kin}[b]	H_2 T^* ($<T>$) (meV)	CH_4 T^* ($<T>$) (meV)
$[3 + H]^+$	82.6 1030 (1080)	17.4 22.0 (53.4)
$[4 + H]^+$	88.1 1090 (1140)[c]	11.9 24.5 (57.1)
$[5 + H]^+$	84.1 1050 (1150)[c]	15.9 22.3 (51.6)

[a] Data given in %Σ of peak area (±0.5% Σ).
[b] Most probable (T^*) and mean ($<T>$) values (±2% rel.).
[c] Ref. [15].

Scheme 2. Isomerization and fragmentation of ions $[3+H]^+$.

prior to fragmentation not only by CH_4 but also by H_2 loss. The ring expansion mechanism involving the 1- and 5-protonated forms of $[3+H]^+$ tautomers and the bicyclic isomer **9** represents an analogy to that suggested by Bouchoux et al. [8] for the parent fulvenium ions, $[1+H]^+$ (Scheme 2). The sequence starts by an 1,5-H shift converting the most stable 1-tautomer, $[3+H]^+_{(1)}$, into the less stable 5-protonated form $[3+H]^+_{(5)}$, which is prone to undergo transannular cyclization giving ions **9**. In the case of the parent ions, this cyclization step was calculated to be the most energetically demanding step ($E_a = 179\,kJ\,mol^{-1}$ for ions $[3+H]^+$) [8]. The 6-methylbicyclo[3.1.0]hex-3-en-2-yl cation, **9**, should occupy a local energy minimum. Electrocyclic opening of the cyclopropane ring ($E_a = 89\,kJ\,mol^{-1}$ for $[3+H]^+$ [8]) gives then rise to the *ipso*-protonated toluenium ions, $[4+H]^+_{(ipso)}$, and its tautomers. Loss of CH_4 from the latter tautomers is considered characteristic for toluenium ions and thus reflects the preceding skeletal isomerization. In accordance with this, it has been confirmed recently [23] that the expulsion of H_2 gives rise to benzyl rather than tropylium ions (m/z 91) and thus takes place via the *ipso*-form of the toluenium ions, $[4+H]^+_{(ipso)}$, as suggested previously (cf. also refs. [3,12] and (see footnote 3).

3.2. Protonated 6,6-dimethylfulvene

The higher analogues of ions $[3+H]^+$, protonated 6,6-dimethylfulvene, $[6+H]^+$, were studied also by MIKE spectrometry. In this case, the investigation of four ^{13}C- or ^{2}H-labelled isotopomers, $[6a+H]^+$ to $[6d+H]^+$, turned out to be particularly valuable and confirmed the close relationship of dimethylfulvenium and dimethylbenzenium ions (Chart 2).

The MIKE spectrum of the unlabelled 6,6-dimethylfulvenium ions, $[6+H]^+$, is reproduced in Fig. 2. The relative abundances and the kinetic energy release data are collected in Table 2. In analogy to the isomeric $C_8H_{11}^+$ ions, $[7+H]^+$ and $[8+H]^+$, three fragmentation reactions compete with each other, viz. the elimination of dihydrogen, methane and ethene. The relative rates are similar to those observed in the other cases. Again, the H_2 loss is associated by the release of a large and

Chart 2.
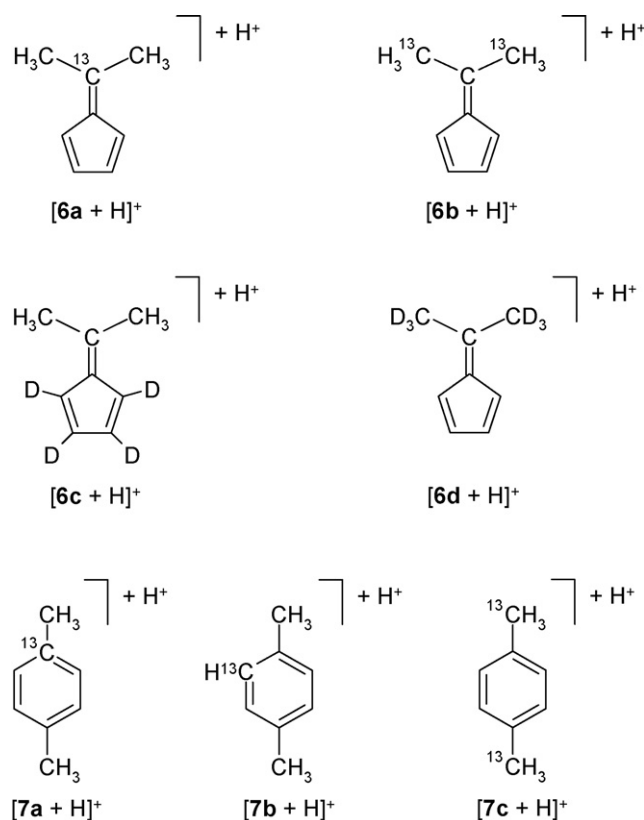
discrete amount of kinetic energy. The most probable value is $T^* = 1110\,meV$ and the mean value is $<T> = 1200\,meV$.[4]

Loss of dihydrogen from the ^{2}H-labelled isotopomers $[6c+H]^+$ and $[6d+H]^+$ provides a qualitative impression of the rearrangements occurring in gaseous protonated 6,6-dimethylfulvene (Fig. 3). The ring-labelled ions $[6c+H]^+$ expel H_2 and HD in a ratio close to unity, whereas D_2 loss occurs in

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[4] The T_{kin} values for the H_2 loss from ions $[7+H]^+$ and $[8+H]^+$ published in ref. [15] were re-evaluated; the corrected data are given in Table 2.
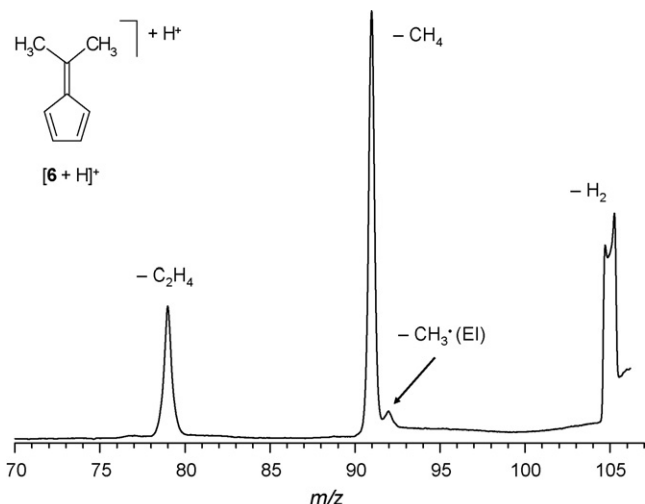
Fig. 2. CI(CH$_4$)/MIKE spectrum of ions [**6** + H]$^+$ (C$_8$H$_{11}$$^+$, *m/z* 107).

Table 2
Fragmentation of metastable C$_8$H$_{11}$$^+$ ions and kinetic energy release

Ion/Loss[a] T_{kin}[b]	H$_2$ T^* (<T>) (meV)	CH$_4$ T^* (<T>) (meV)	C$_2$H$_4$ T^* (<T>) (meV)
[**6** + H]$^+$	35.1	46.3	18.6
	1110 (1200)	16.3 (49.8)	17.9 (53.9)
[**7** + H]$^+$	31.6	59.4	9.0
	1180 (1240)[c]	32.6 (92.4)	12.3 (49.9)
[**8** + H]$^+$	24.7	9.1	66.2
	1020 (1030)[c]	18.0 (46.2)	16.5 (51.4)

[a] Data given in %Σ of peak area (±0.5% Σ).
[b] Most probable (T^*) and mean (<T>) values (±2% rel.).
[c] See ref. [34].

ca. 3% only. By contrast, the methyl-labelled ions [**6d** + H]$^+$ expel predominantly HD and minor amounts of H$_2$ and D$_2$. The results clearly indicate that the dehydrogenation process involves mainly one hydrogen atom from the protonated five-membered ring and one from the methyl groups of ions [**6** + H]$^+$, if we assume fast equilibration of the five ring hydrogens and a kinetic isotope effect operating in favor of H$_2$ versus HD loss. A similar behavior was found in the case of the isomeric *para*-xylenium ions bearing one CD$_3$ group [13a] and also for the dihydrogen loss from toluenium ions, [**4** + H]$^+$, [12,23]. In fact, fast isomerization of ions [**6c** + H]$^+$ by ring expansion to xylenium ions [C$_6$HD$_4$(CH$_3$)$_2$]$^+$, followed by predominant 1,2-

elimination of H$_2$ and HD from the respective *ipso*-tautomers is in agreement with observation. In the case of ions [**6d** + H]$^+$, ring expansion gives rise to xylenium ions [C$_6$H$_5$(CD$_3$)$_2$]$^+$, and 1,2-HD elimination from the respective *ipso*-tautomers should be the only fragmentation channel. However, as shown earlier [13a], the C$_8$H$_{11}$$^+$ ions generated from *para*-xylene undergo another, partially reversible, ring expansion leading to dihydrotropylium ions, [**8** + H]$^+$, and the observation of D$_2$ loss from ions [**6c** + H]$^+$ and H$_2$ and D$_2$ loss from ions [**6d** + H]$^+$ points to such more complex isomerization. However, with the data given here, partial H/D exchange within the initial 6,6-dimethylfulvenium ions cannot be excluded, and some insights obtained from the methane loss from ions [**6c** + H]$^+$ and [**6d** + H]$^+$ corroborate this possibility (see below).
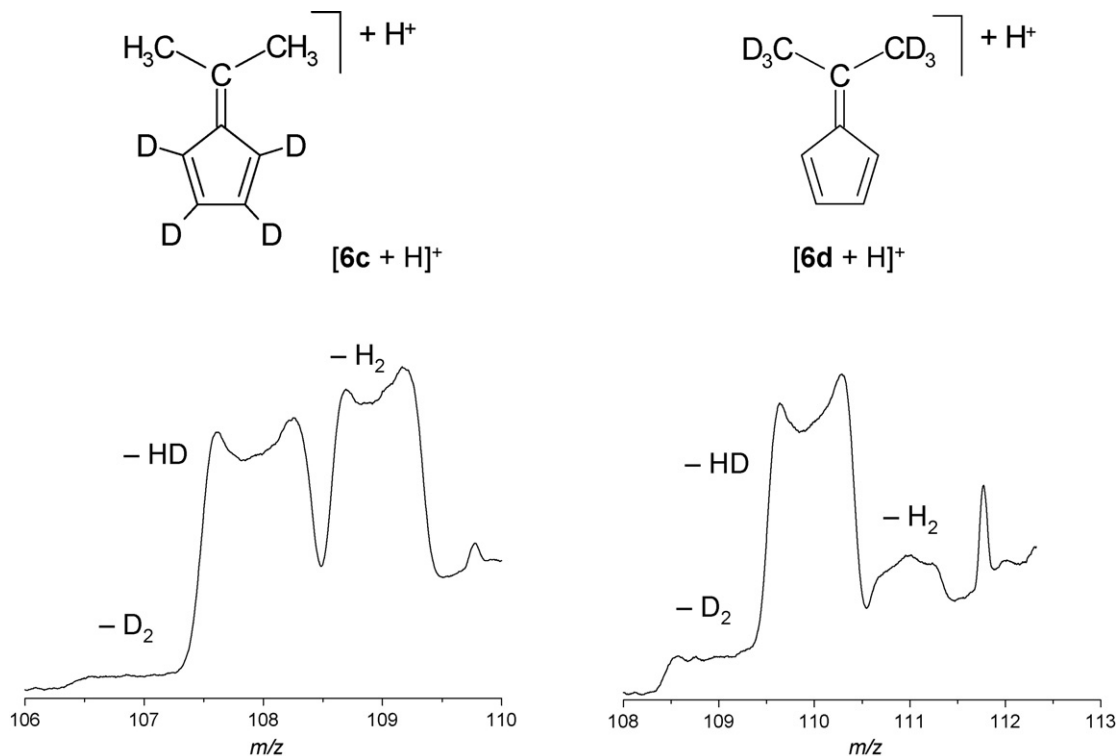

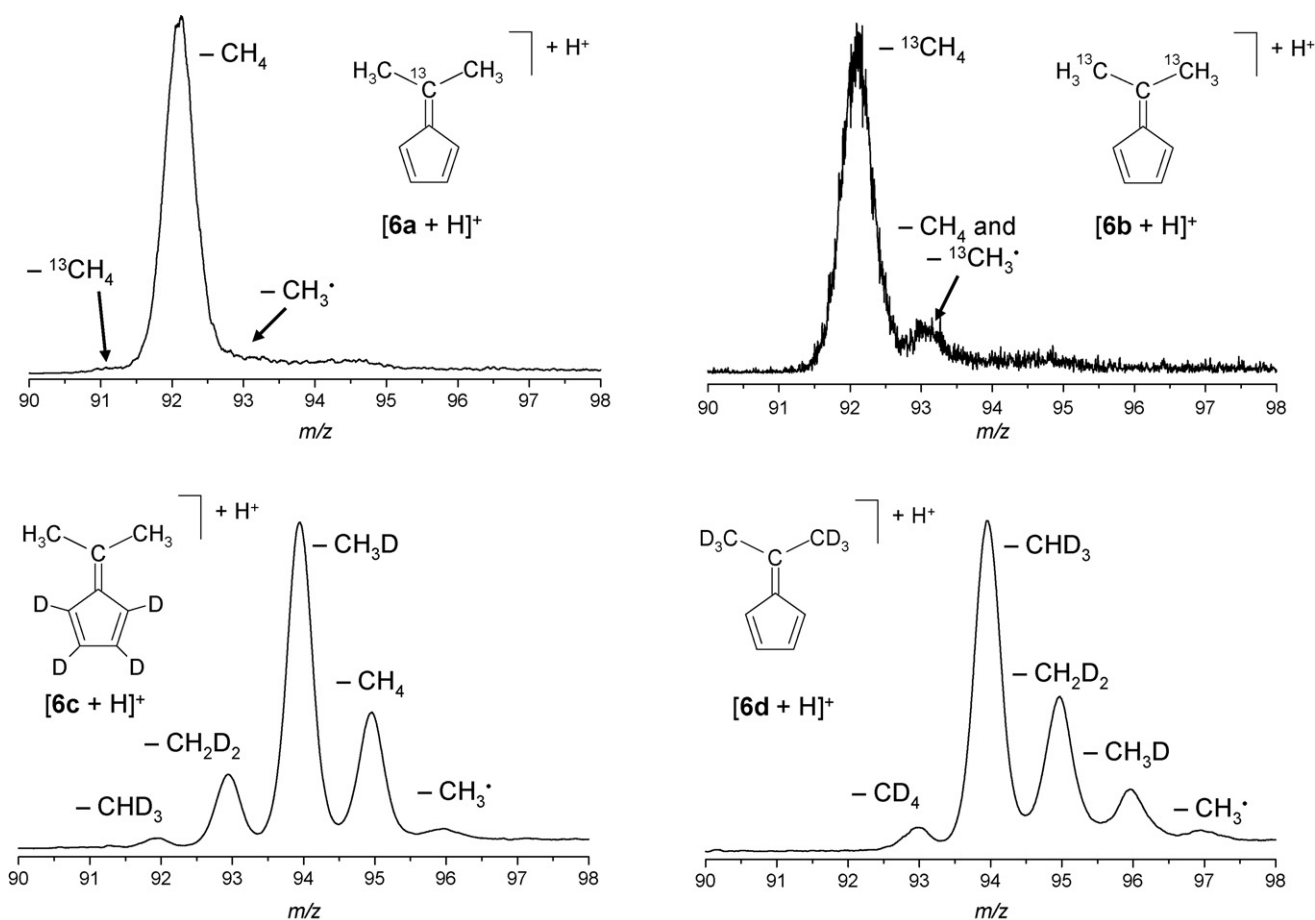Fig. 3. Loss of dihydrogen from protonated 6,6-dimethylfulvenes **6c** and **6d** (MIKE spectra).

Fig. 4. Loss of methane from protonated 6,6-dimethylfulvenes **6a–6d** (MIKE spectra).

The two ^{13}C-labelled isotopomers exhibit a surprisingly specific fragmentation behavior prior to loss of methane (Fig. 4). Metastable ions [**6a** + H]$^+$, bearing the label at the exocyclic position C-6, eliminate almost exclusively unlabelled methane, whereas ions [**6b** + H]$^+$, bearing two [^{13}C]methyl groups, undergo almost exclusively the loss of the labelled methane (Table 3). These findings are in perfect agreement with the fragmentation reported for the correspondingly labelled xylenium

Table 3
Loss of methane from ^{13}C-labelled dimethylfulvenium ions [**6a** + H]$^+$ and [**6b** + H]$^+$ (MIKE spectra)

Ion or model/loss of[a]	^{13}CH$_4$	CH$_4$
[**6a** + H]$^+$ (experimental)	1.4	98.6
C^{methyl}-specific loss	0.0	100.0
Statistical loss (^{13}C$_1$/^{12}C$_7$)	12.5	87.5
Partial scrambling[b]	28.6[c]	71.4[c]
[**6b** + H]$^+$ (experimental)	97.5	2.5
C^{methyl}-specific loss	100.0	0.0
Statistical loss (^{13}C$_2$/^{12}C$_6$)	25.0	75.0
Partial scrambling[b]	57.1[c]	42.9[c]

[a] Data given in %Σ (±0.2% Σ).
[b] Disregarding isotope effects; see text.
[c] Corresponding to fractions of 4/14 vs. 10/14 of [**6a** + H]$^+$ and 6/14 and 8/14 of [**6b** + H]$^+$.

ions generated by protonation of [α,α′-^{13}C]$_2$-xylene, [**7c** + H]$^+$, and of two singly ring-labelled isotopomers, protonated [1-^{13}C]-xylene, [**7a** + H]$^+$, and [2-^{13}C]-xylene, [**7b** + H]$^+$ [13a]. Thus, similar to the arenium-type isomers, skeletal rearrangement channels giving rise to carbon scrambling plays only a minor role in the C$_8$H$_{11}^+$ ions generated from 6,6-dimethylfulvene.

We may assume a "composite scrambling" prior to the loss of methane from ions [**6** + H]$^+$, in analogy to that postulated to occur in metastable xylenium ions [13a,14], in particular. This model implies the C-specific loss of methane from the major fraction of ions, involving one of the original C^{methyl} atoms exclusively. A reasonable mechanism for this path involves isomerization of ions [**6** + H]$^+$ to xylenium ions, [**7** + H]$^+$. On the other hand, methane loss may occur from a minor fraction of completely C-scrambled C$_8$H$_{11}^+$ ions; however, this fraction cannot surmount ca. 10% of the total metastable ions' population undergoing methane loss. This limit follows from an estimation based on the data given in Table 3, which indicates that the metastable ^{13}C$_1$^{12}C$_7$H$_{11}^+$ ions generated from **6a** may contain up to (8 × 1.4%) = 11.2% of C-randomized ions and that the ^{13}C$_2$^{12}C$_6$H$_{11}^+$ ions generated from **6b** may contain up to (4/3 × 2.5%) = 3.3% of ions of this sort. Although the experimental error may be rather high due to the low relative abundances of ^{12}CH$_4$ and ^{13}CH$_4$ lost from ions [**6a** + H]$^+$ and [**6b** + H]$^+$, respectively, this discrepancy between the two

Scheme 3. Composite scrambling preceding methane loss.

values appears too high. Another, possibly more realistic, scenario includes limited C-scrambling involving only one of the methyl groups instead of both. In that case, the minor fraction of xylenium ions, $[7 + H]^+$, formed from ions $[6 + H]^+$ is assumed to undergo only one single ring expansion/recontraction cycle via dihydrotropylium ions, $[8 + H]^+$. Based on the data of Table 3, the corresponding model calculations indicate that the metastable $^{13}C_1{}^{12}C_7H_{11}{}^+$ ions generated from **6a** contain up to $(14/4 \times 1.4\%) = 4.9\%$ of partially C-randomized ions and that the $^{13}C_2{}^{12}C_6H_{11}{}^+$ ions generated from **6b** contain up to $(14/6 \times 2.5\%) = 5.8\%$ of ions of this kind. These two values are consistent within the limits of experimental error. Overall, the ^{13}C-labelling indicates that a major fraction (ca. 95%) of protonated 6,6-dimethylfulvene, $[6 + H]^+$, undergoes ring expansion to xylenium ions, $[7 + H]^+$ prior to C-specific loss of methane, and that a minor fraction (ca. 5%) suffers a subsequent, albeit slow and reversible ring expansion to dihydrotropylium ions, $[8 + H]^+$, prior to this fragmentation (Scheme 3).

Loss of methane from the ^2H-labelled dimethylfulvenium ions, $[6c + H]^+$ and $[6d + H]^+$, is obviously preceded by much more extended H/D scrambling than expected from the C-scrambling discussed above (Fig. 4). However, the pattern of the relative $C(H,D)_4$ abundances is again far from being statistical (Table 4). Interestingly, both patterns exhibit a relatively high contribution of specific loss of the original methyl groups as CH_3D and CHD_3, respectively. In analogy to the composite scrambling model developed for toluenium [12] and xylenium ions [13a,14], the experimental pattern can be simulated by assuming a fraction of $C_8(H,D)_{11}{}^+$ ions that expel methane containing one intact original methyl group (i.e., H^{methyl}-specific

Table 4

Loss of methane from ^2H-labelled dimethylfulvenium ions $[6c + H]^+$ and $[6d + H]^+$ (MIKE spectra)

| Ion or model/Loss of[a]	CD_4	CHD_3	CH_2D_2	CH_3D	CH_4
$[6c + H]^+$ (experimental)	**0.0**	**2.1**	**15.6**	**64.2**	**18.1**
H^{methyl}-specific loss[b]	0.0	0.0	0.0	80.0	20.0
Statistical loss ($^2H_4/{}^1H_7$)	0.3	8.5	38.2	42.4	10.6
Composite model[c]	*0.2*	*4.3*	*19.1*	*61.2*	*15.3*
$[6d + H]^+$ (experimental)	**6.2**	**66.8**	**19.3**	**5.7**	**0.0**
H^{methyl}-specific loss[b]	0.0	100.0	0.0	0.0	0.0
Statistical loss ($^2H_6/{}^1H_5$)	4.5	30.3	45.5	18.2	1.5
Composite model[c]	*2.3*	*65.2*	*22.8*	*8.9*	*0.8*

[a] Data given in $\%\Sigma$ ($\pm 0.2\% \Sigma$).
[b] Assuming fast equilibrium of the ring hydrogens, disregarding isotope effects.
[c] Calculated for composite scrambling (50% H^{methyl}-specific, 50% statistical), see text.

loss of methane) and another fraction that undergoes complete equilibration of the H/D atoms prior to this fragmentation.

In fact, assuming that just half of the populations of ions $[6 + H]^+$ undergo the specific loss of methane as $(CH_3)^{methyl}H^{ring}$ and the other half undergo full randomization of all hydrogen atoms, both of the experimentally obtained pattern of $C_8(H,D)_{11}{}^+$ ions generated from dimethylfulvenes **6c** and **6d** can be reproduced satisfactorily (Table 4, Scheme 3). Thus, the scrambling behavior of ions $[6 + H]^+$ resembled that of the xylenium ions, $[7 + H]^+$, but the fraction of ions that suffer complete hydrogen scrambling (50%) exceeds considerably that found for the latter isomers (12%) [13a]. It appears reasonable to attribute this finding to the somewhat higher excitation
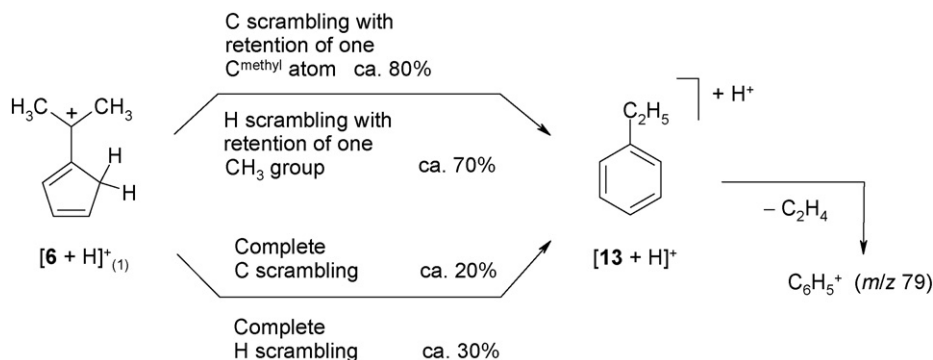
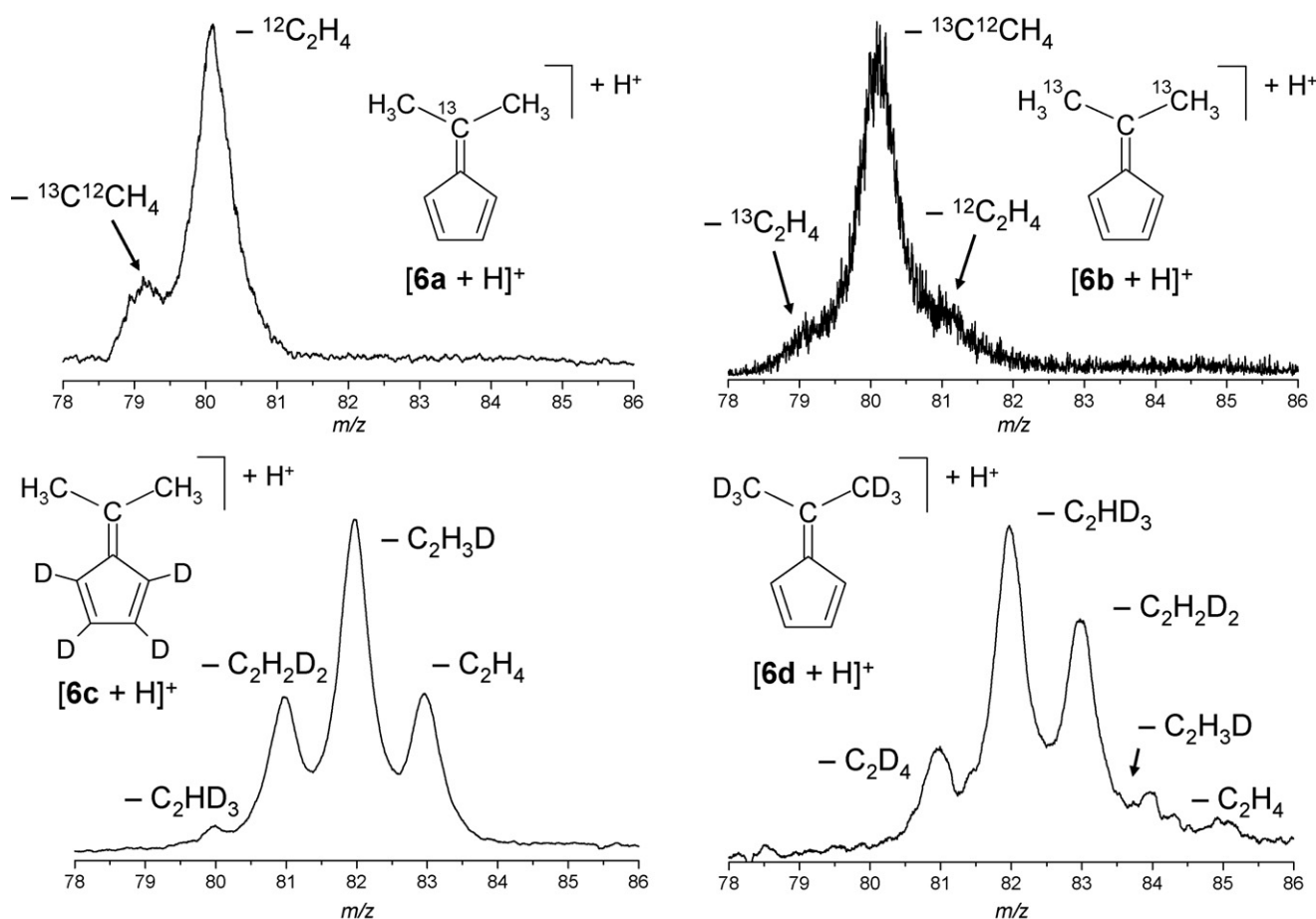Scheme 4. Composite scrambling preceding to ethene loss.

Fig. 5. Loss of ethene from protonated 6,6-dimethylfulvenes **6a–6d** (MIKE spectra).

of the fulvenium ions, which in turn is due to the considerably higher proton affinity of cycloolefin **6** as compared to the xylenes ($\Delta PA = 78$–$96\,kJ\,mol^{-1}$) [17]. This excitation may accelerate the proton exchange not only within the protonated five-membered ring of ions [**6c** + H]$^+$ ions [**6d** + H]$^+$ but also between the isopropylidene group and the ring. More than one single mechanistic pathways can be envisaged for this process (see below) (Scheme 5).

Similar to the loss of methane, elimination of ethene from metastable dimethylfulvenium ions [**6** + H]$^+$ has been analysed on the basis of the ^{13}C- and ^{2}H-labelling (Fig. 5, Tables 5 and 6). As expected, ions [**6a** + H]$^+$ show no complete retention of the carbon atoms of the fulvene C_6 unit during this fragmentation and only a minor fraction of the ethene lost contains both of the C^{methyl} atoms, as revealed by the data obtained for the doubly labelled ions [**6b** + H]$^+$. Partial C scrambling, for which the retention of one of the C^{methyl} atoms and complete equilibration of the remaining seven carbons is assumed, could explain the $^{13}C^{12}CH_4$ distribution observed for ions [**6a** + H]$^+$; however, this scrambling model disagrees with the pattern of ions [**6b** + H]$^+$. Similarly, complete scrambling of all eight carbon atoms does not fit the experimental data. However, the experimental $^{13}C^{12}CH_4$ distributions of both ions [**6a** + H]$^+$ and [**6b** + H]$^+$ are in accordance with the pattern calculated for a "composite scrambling" model, which assumes that only an 80%

fraction of these ions undergo partial C scrambling, whereas a 20% fraction suffers randomization of all of the eight carbons (Scheme 4). Again, this behavior is reminiscent of the composite scrambling found for xylenium ions, [**7** + H]$^+$, prior to the loss of ethene. It is striking to note that, for the latter ions, the

Table 5
Loss of ethene from ^{13}C-labelled dimethylfulvenium ions [**6a** + H]$^+$ and [**6b** + H]$^+$ (MIKE spectra)

Ion/Loss of[a]	$^{13}C_2H_4$	$^{13}CCH_4$	C_2H_4
[**6a** + H]$^+$ (experimental)	–	**16.4**	**83.6**
C-specific loss[b]	–	100.0	0.0
Partial C scrambling[c]	–	14.3	85.7
Statistical loss ($^{13}C_1/^{12}C_7$)[d]	–	25.0	75.0
Composite model[c]	–	*16.4*	*83.6*
[**6b** + H]$^+$ (experimental)	**11.4**	**76.3**	**12.3**
C-specific loss[b]	0.0	100.0	0.0
Partial C scrambling[c]	14.3	85.7	0.0
Statistical loss ($^{13}C_2/^{12}C_6$)[d]	3.6	42.8	53.6
Composite model[e]	*12.2*	*77.1*	*10.7*

[a] Data given in %Σ ($\pm 0.2\%$ Σ).
[b] Excluding C scrambling of any kind (see text).
[c] Assuming specific loss of one C^{methyl} and statistical loss of the other (see text).
[d] Assuming complete scrambling of all 8 C atoms.
[e] Calculated for composite scrambling (80% partial C scrambling, 20% statistical loss), see text.

Table 6
Loss of ethene from ^{2}H-labelled dimethylfulvenium ions $[6c + H]^+$ and $[6d + H]^+$ (MIKE spectra)

Ion/Loss of[a]	C_2D_4	C_2HD_3	$C_2H_2D_2$	C_2H_3D	C_2H_4
$[6c + H]^+$ (experimental)	(<0.4)	2.3	24.2	50.0	23.5
H^{methyl}-specific loss[b]	0.0	0.0	18.4	56.2	25.4
Statistical loss (^{2}H$_4$/^{1}H$_7$)[c]	0.3	8.5	38.2	42.4	10.6
Composite model[d]	*0.1*	*2.6*	*24.3*	*52.0*	*21.0*
$[6d + H]^+$ (experimental)	13.9	44.4	32.8	7.1	1.8
H^{methyl}-specific loss[b]	23.7	51.8	24.5	0.0	0.0
Statistical loss (^{2}H$_6$/^{1}H$_5$)[c]	4.5	30.3	45.5	18.2	1.5
Composite model[d]	*17.9*	*45.3*	*30.9*	*5.5*	*0.4*

[a] Data given in %Σ ($\pm$0.2% Σ).

[b] Elimination of ethene from ethylbenzenium ions after retention of one methyl group during the isomerization of dimethylfulvenium ions via xylenium and dihydrotropylium ions.

[c] Assuming complete scrambling of all 11 H atoms.

[d] Calculated for composite scrambling (70% H^{methyl}-specific, 30% statistical), see text.

ratio of the fractions reacting partially C-specific and completely C-random was found to be very similar, viz. ca. 75:25 [13a].

Accordingly, the elimination of ethene from the ^{2}H-labelled ions $[6c + H]^+$ and $[6d + H]^+$ also reflects the occurrence of more than one scrambling process (Table 6). Again, neither the scrambling model implying the retention of one intact methyl group and complete scrambling of the remaining eight hydrogen atoms, nor the complete randomization of all of the eleven hydrogen atoms can explain the observed relative abundances of the $C_6(H,D)_7^+$ ions. However, the experimental patterns for $C_2(H,D)_4$ loss from both ions $[6c + H]^+$ and $[6d + H]^+$ is simulated satisfactorily by assuming that these ions form two populations in a ratio of 70:30, the major of which undergoes H/D scrambling within the monomethylfulvenium (C_7H_8) unit, retaining one methyl group unscrambled, and the minor of which suffers complete scrambling within the whole ion. Again, it is noteworthy that this composite H scrambling takes places with a similar fractional ratio (70:30) as the composite C scrambling prior to the loss of ethene. This strongly indicates that the H and C scrambling prior to this fragmentation may have the same mechanistic origins.

In fact, the isomerization processes occurring in gaseous protonated 6,6-dimethylfulvene, $[6 + H]^+$, prior to expulsion of both methane and ethene can be deduced in quite some detail from the composite scrambling behavior. Since there is a close similarity between the fragmentation and scrambling processes of ions $[6 + H]^+$ and the xylenium ions, $[7 + H]^+$, which have been analyzed previously by experiment [13a] and by computation [9], it is obvious that these isomeric cycloolefinic carbenium ions populate the same $C_8H_{11}^+$ hypersurface. As a consequence, the participation of methyldihydrotropylium ions, $[8 + H]^+$, is highly probable since the interconversion of the latter, seven-membered ring isomers with the arenium ions, $[7 + H]^+$, has been shown to occur easily. In particular, it has been demonstrated that protonated 7-methyl-1,3,5-cycloheptatriene, $[8 + H]^+$, and its higher 7-alkyldihydrotropylium ion homologues readily undergo ring contraction to ethylbenzenium ions, $[13 + H]^+$, and the respective higher alkylbenzenium ions [15].

Depending on the excitation energy imposed under the CI conditions used, ions $[8 + H]^+$ were found to isomerize to xylenium ions as well, but isomerization to ethylbenzenium ions is the energetically most favourable ring contraction pathway [15]. The major paths of the whole isomerization scenario preceding the fragmentation of the metastable ions formed upon gas-phase protonation of 6,6-dimethylfulvene (6) are depicted in Scheme 5.

First of all, this isomerization includes the most likely hydrogen shift processes within the initially formed 6,6-dimethylfulvenium ions, $[6 + H]^+$, probably by 1,2-H shifts within the five-membered ring (e.g., $[6 + H]^+_{(1)} \rightleftarrows [6 + H]^+_{(5)}$ and also $[10 + H]^+_{(2)} \rightleftarrows [10 + H]^+_{(5)}$) as well as by 1,4-H transfer between the methyl groups and the accessible ring positions at C-1 and C-4. Some of these shifts have been treated by computational methods for the parent ions, $[1 + H]^+$, [8] and their dimethyl derivatives, $[6 + H]^+$, [9]. These isomerization channels are likely to enable the fast scrambling involving all of the eleven hydrogen atoms in a ca. 50% fraction of ions $[6 + H]^+$ after the highly exothermic protonation of 6 in the CI(CH$_4$) plasma. Nevertheless, a transit from the fulvenium to the benzenium set of isomeric $C_8H_{11}^+$ ions via the bicyclic isomer 11 appears to be rather facile since the other 50% fraction of the ions retain an intact methyl group. Thus, the 1,1-dimethylbenzenium ions, 12, formed upon ring expansion, may or may not contain the original H and C atoms of the methyl groups present in the precursor cycloolefin, 6. A first 1,2-methyl shift in ions 12 gives rise to the isomeric xylenium ions, $[7 + H]^+$, which are known to undergo very facile proton ring walk [3,14] but also facile 1,2-methyl shifts [9,13a,32]. Similar to toluenium ions, $[4 + H]^+$, loss of dihydrogen and methane can occur via the *ipso*-tautomers of the three isomeric xylenium ions, $[7 + H]^+_{(ipso)}$. As the methane loss from the $C_8H_{11}^+$ ions is almost C-specific – only ca. 5% of the $C_8H_{11}^+$ ions form from 6 suffer complete C-scrambling, which is comparable to the 12% fraction deduced for metastable $C_8H_{11}^+$ ions form from 7 [13a] – the ring expansion step to the xylenium ions appears to be largely irreversible. Thus, the much higher extent of fully H-randomization in the $C_8H_{11}^+$ ions (50%) cannot be completely attributed to a re-contraction of the benzenium to the fulvenium isomers; rather, as mentioned above, it must have already been accomplished within the latter ions. Although ring contraction of a small fraction of xylenium-type $C_8H_{11}^+$ ions to dimethylfulvenium ions cannot be excluded, reversible ring expansion of the xylenium ions, once being formed, to methyldihydrotropylium ions, $[8 + H]^+$, appears more likely (see above) and could explain the observation of the 5% fraction of complete C-scrambling.

Elimination of ethene from the $C_8H_{11}^+$ ions generated from protonated dimethylfulvene H, $[6 + H]^+$, requires more deep-seated skeletal rearrangements and the results of ^{13}C- and ^{2}H-labelling both indicate composite scrambling with similar fractions of ions behaving different. As shown in Scheme 5, this fragmentation involves ring expansion to dihydrotropylium ions, $[8 + H]^+$, and subsequent re-contraction of the seven-membered ring to form ethylbenzenium ions, $[13 + H]^+$. As shown above, this mechanism is assumed to be irreversible for a 70–80% fraction of the $C_8H_{11}^+$ ions generated from 6 (cf. 75% for $C_8H_{11}^+$ ions formed from 7 [13a]). In this fraction of ions, one of the
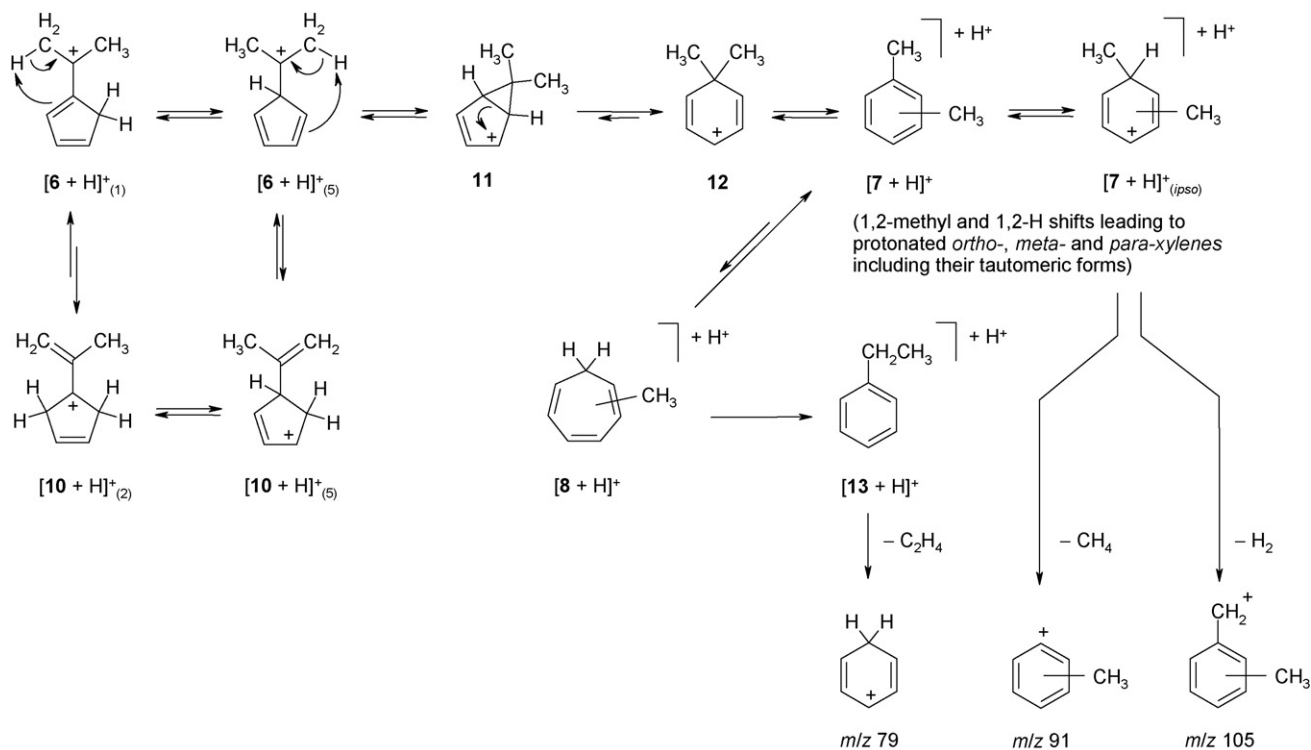
Scheme 5. Major isomerization pathways preceding the three fragmentation channels of 6,6-dimethylfulvenium ions $[6+H]^+$.

original methyl groups of ions $[6+H]^+$ survives as the (remote) CH_3 group of ions $[13+H]^+$. However, besides the fact that ethene loss is the energetically most favourable fragmentation path of ions $[13+H]^+$, the hydrogen rearrangement involved in this elimination is known to be non-specific, involving both α-H and β-H atoms [3,33,34]. Therefore, the calculation of the distribution of $C_2(H,D)_4$ isotopomers lost from ions $[6c+H]^+$ and $[6d+H]^+$ include the probabilities of participation of the α-H and β-H atoms elucidated for metastable ethylbenzenium ions by Audier et al. [34]. This overall isomerization takes place in 70–80% of ions $[6+H]^+$ and gives rise to partially C-scrambled ions $[13+H]^+$, whereas 20–30% of ions $[6+H]^+$ undergo similar isomerization but form $[13+H]^+$ ions which have suffered complete scrambling of all C and H atoms. As a result, loss of ethene from both fractions of ions is reflected in the composite scrambling pattern in the case of ^{13}C- or ^{2}H-labelled $C_8H_{11}^+$ ions.

4. Conclusions

The major insight obtained by this study is that methyl-substituted fulvenium ions $[3+H]^+$ and $[6+H]^+$, generated by protonation the 6-methyl- and 6,6-dimethylfulvene, exhibit almost the same isomerization and fragmentation behavior as do the corresponding methylbenzenium ions, i.e., protonated toluene, $[4+H]^+$, and the protonated xylenes, such as the *para*-xylenium ion, $[7+H]^+$. Elimination of dihydrogen and methane from the $C_7H_9^+$ ions, and of dihydrogen, methane and ethene from the $C_8H_{11}^+$ ions take place in similar branching ratios. Moreover, the rather complicated, "composite" C-

and H-scrambling processes observed with the four ^{13}C- or ^{2}H-labelled 6,6-dimethylfulvenium ions $[6a+H]^+$ to $[6d+H]^+$ was found to be very similar to that reported for the correspondingly labelled *para*-xylenium ions [13a,14]. Therefore, it is obvious that protonated 6,6-dimethylfulvene, $[6+H]^+$, not only undergoes ring expansion to the various isomeric xylenium ions (including the 1,1-dimethylbenzenium ion 12) but that, depending on the eventual fragmentation path, varying fractions of the xylenium ions react by a further, partially reversible, ring expansion to dihydrotropylium ions, $[8+H]^+$. The partial reversibility of this ring expansion/re-contraction process is reflected by the composite scrambling behavior of the $C_8H_{11}^+$ ions prior to methane loss. In the case of the ethene elimination from the 6,6-dimethylfulvenium ions, the composite scrambling is practically identical with that observed for xylenium ions, $[7+H]^+$. Thus, this fragmentation of ions $[6+H]^+$ involves several skeletal rearrangement steps and eventually occurs from the ethylbenzenium ion, $[13+H]^+$, as suggested earlier for the xylenium and methyldihydrotropylium ions [3,13–15].

Acknowledgements

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