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Interconversion of gaseous bicyclo[3.2.1]oct-2-en-4-yl cations and protonated 7-alkylcycloheptatrienes: [5 + 2] cycloreversion in competition with fragmentation by way of alkylbenzenium ions

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Abstract

Several bicyclo[3.2.1]oct-2-en-3-yl cations, as isomers of protonated 7-methyl- and 7-ethylcycloheptatriene and of the protonated C_8H_{10} and C_9H_{12} alkylbenzenes, respectively, have been studied by deuterium labeling and mass-analyzed ion kinetic energy (MIKE) and collision-induced dissociation/MIKE spectrometry. Labeling reveals that the bicyclic framework undergoes fast and apparently complete hydrogen equilibration prior to fragmentation, involving a series of skeletal and hydrogen rearrangements (1,2-C and 1,2-H shifts). Fragmentation of the bicyclic ions $C_8H_{11}^+$ and $C_9H_{13}^+$ is manyfold: It occurs in part by way of the isomeric alkylbenzenium ions, e.g. $CH_3CH_2C_6H_6^+$ and $CH_3C_6H_5CH_3^+$, and $C_2H_5C_6H_5CH_3^+$ and $CH_3CH_2CH_2C_6H_6^+$, respectively, with the corresponding 7-alkyldihydrotropylium ions as intermediates. Another fraction of the bicyclic ions does not fragment by way of alkylbenzenium ions but apparently by [5 + 2] cycloreversion of bicyclo[3.2.1]octenyl framework itself. This process is indicated by ethene expulsion associated with an unusually large kinetic energy release ($T^* \approx 300$ meV). The characteristic high-KER ethene loss was also found for protonated 7-ethylcycloheptatriene but not for protonated 7-methylcycloheptatriene, suggesting a delicate balance of the activation energies and confirming, in turn, that bicyclo[3.2.1]oct-2-en-yl cations are intermediates during the fragmentation of higher alkyldihydrotropylium ions. (Int J Mass Spectrom 210/211 (2001) 531–544) © 2001 Elsevier Science B.V.

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1. Introduction

The gas-phase ion chemistry of alkylbenzenium ions has been the subject of numerous studies since Field's early work more than 30 years ago [1]. In particular, isomerization and fragmentation of higher protonated alkylbenzenes, diaryl- and oligo(arylalkyl) benzenium ions is well understood [2–4]. However, benzenium ions and lower protonated alkylbenzenes such as toluenium and xylenium ions have mainly been studied by computational approaches [5] and with respect to their bimolecular gas-phase ion chemistry [6,7]. Relatively few detailed experimental stud-

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Dedicated to Nico M. M. Nibbering in recognition of his many contributions to the field of gas-phase ion chemistry.

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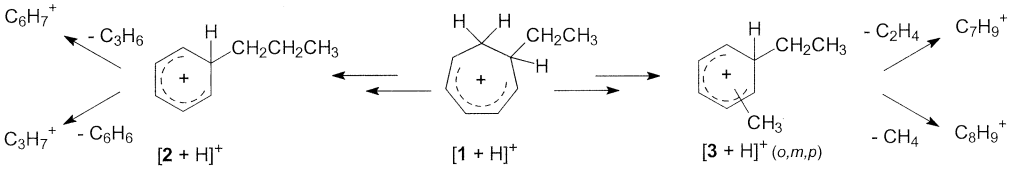


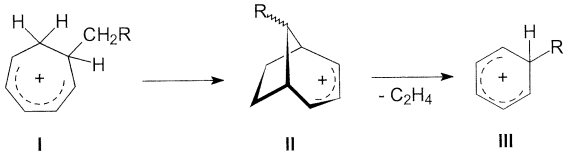
Scheme 1. Ring contraction of protonated ethylcycloheptatriene to protonated alkylbenzenes.

ies have been published on the unimolecular reactivity of lower alkylbenzenium ions and of the parent benzenium ion, $C_6H_7^+$, itself [8–12]. Williams and Hvistendahl suggested a ring expansion process of toluenium ions to protonated 1,3,5-cycloheptatriene (dihydrotropylium ions) as the energy-determining step of the loss of dihydrogen giving the tropylium ion [9]. Evidence for partial ring expansion reactions of protonated toluene based on the detailed examination of the methane loss from these ions was published from our laboratory [10a]. Further support for the intermediacy of seven-membered ring isomers during the fragmentation of lower alkylbenzenium ions was based on the finding that metastable xylenium ions eliminate ethene along with dihydrogen and methane [10b–d]. As a counterpart to the ring-expanded isomers, ring-contracted isomers of benzenium ions have also been studied. Thus, both theoretical and experimental evidence has been published for the formation of stable fulvenium-type ions on the $C_6H_7^+$ ions' hypersurface [13]. In a recent experimental study, we have demonstrated the remarkable thermochemical stability of methyl-substituted fulvenium ions, $C_7H_9^+$ and $C_8H_{11}^+$ [14].

Although being somewhat out of the focus of attention, many of these results underline the relevance of protonated nonaromatic cycloolefins for the gas-phase ion chemistry of the isomeric alkylbenzenium ions. It is also noteworthy that only few efforts have been made to understand the gas-phase chemistry of protonated conjugates of cyclic polyenes, whereas the radical ions and the anions of dienes and polyenes in general have been studied in great detail [15]. Therefore, we have recently investigated the unimolecular reactivity of long-lived protonated 7-alkyl-1,3,5-cycloheptrienes [16]. In fact, protonated 7-methylcycloheptatriene undergoes ring contraction to the isomeric alkylbenzenium ions, i.e. to xylenium ions and ethylbenzenium ions, with preference of latter isomer [10b,16], from which ethene is expelled eventually. Likewise, higher 7-alkyldihydrotropylium ions such as protonated 7-ethylcycloheptatriene $[\mathbf{1} + H]^+$ isomerize by ring contraction to the corresponding chain-elongated *n*-alkylbenzenium ions, e.g. $[\mathbf{2} + H]^+$, and alkyltoluenium ions, e.g. $[\mathbf{3} + H]^+$, prior to fragmentation (Scheme 1) [16].

Intriguingly, the loss of ethene from ions $[\mathbf{1} + H]^+$ is even more complex. In addition to ring contraction to alkylbenzenium ions shown in Scheme 1, additional reactions compete, involving relatively complex rearrangement processes. The observation [16] of unusually high amounts of kinetic energy release in the mass-analyzed ion kinetic energy (MIKE) spectra of ions $[\mathbf{1} + H]^+$ and the loss of ethene originating from constituents of the seven-membered ring, rather than from the side chain, indicates "nonalkylbenzenium"-type behaviour. Whereas alkene and benzene elimination from alkylbenzenium ions are characterized by relatively narrow Gaussian peak shapes in the MIKE spectra and heterolytic cleavage of the C^{ipso}–C^{α} bond(s), as shown by deuterium labeling experiments, the major fraction of ions $[\mathbf{1} + H]^+$ expels ethene from the interior of the seven-membered ring and with considerable peak broadening, i.e., accompanied with unusually large release of kinetic energy.

In this article we present experimental evidence for the origin of this observation. It will be demonstrated that, in fact, higher protonated alkylcycloheptatrienes **I**, with the ethyl congener $[\mathbf{1} + H]^+$ being the first and most clear-cut case, expel ethene not only by ring contraction to the corresponding alkylbenzenium ions



Scheme 2. Ethene loss from higher protonated alkylcycloheptatrienes by [5 + 2] cycloreversion of bicyclo[3.2.1]oct-2-en-4-yl cations as intermediates.

[16] but also by a "cycloolefinic route," that is, by way of bicyclic isomers **II**, on the way to the products **III** (Scheme 2). These insights are based on the synthesis of a number of bi- and tricyclic neutral precursors of ions **II** (R = H) including some methyl derivatives and several deuterium-labeled analogues, and the measurements of the spontaneous fragmentation of the long-lived species in comparison to that of the isomeric metastable alkyldihydrotropylium ions **I**.

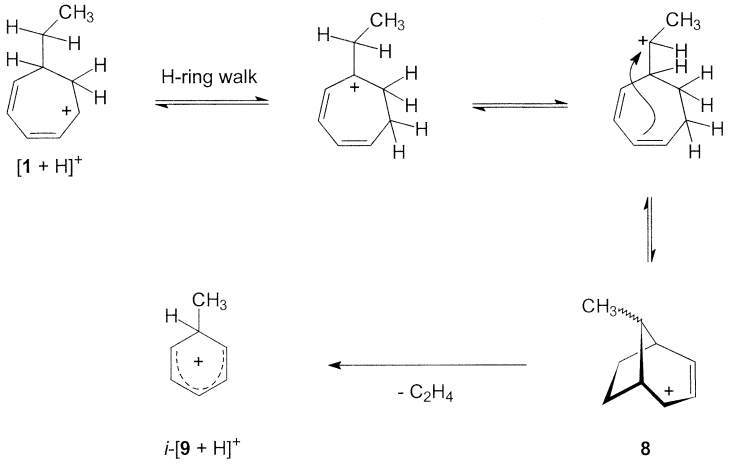
2. Experimental

2.1. Mass spectrometric measurements

All measurements were carried out using a double focusing sector-field instrument (AutoSpec, Fisons, Manchester/UK) with a three-sector EBE geometry. Samples were introduced into the electron ionization (EI) source by way of a heated septum inlet. The acceleration voltage, electron energy, emission current and source temperature were set to 8 kV, 70 eV, 200 μA, and 160 $\pm$ 10 °C, respectively. Collision induced dissociation/MIKE (CID/MIKE) measurements were performed by introducing helium into the collision cell within the third field-free region of the mass spectrometer such that the signal of the main beam was attenuated to ~50% of the original value. All relative abundances were calculated from the peak areas. Kinetic energy release (KER) distributions were determined by using the method developed by Szilágyi and Vékey [17]. The KER values given in this article denote the most probable (T^*) and the average ($\langle T \rangle$) values of the kinetic energy released during the respective fragmentation reaction.

2.2. Syntheses of compounds

4-Bromobicyclo[3.2.1]oct-2-ene **4** was synthesized by bromination of bicyclo[3.2.1]oct-2-ene using *N*-bromosuccimide (NBS), as described by Jefford and Yen [18]. 3-Bromotricyclo[3.2.1.$0^{2,4}$]octane **5** and its derivatives **5a**–**7a** were obtained by addition of monobromocarbenoids, generated from dibromomethane and sodium bis(trimethylsilyl)amide in *n*-pentane, to norbornene, norbornadiene and the corresponding methyl derivatives, as recently described by Dehmlow and Lustinetz [19]. In this way, cyclopropanation of norbornene gave 3-bromotricyclo[3.2.1.$0^{2,4}$]octane **5** and several of its diastereomers. [6,7-D_2]-3-Bromotricyclo-[3.2.1.$0^{2,4}$]octane **5a** was synthesized by single monobromocarbenoid addition to norbornadiene yielding the corresponding monoadduct; subsequent saturation of the remaining double bond with deuterium was achieved with perfect regioselectivity using Wilkinson's catalyst (as confirmed by ^{1}H NMR spectroscopy, see the following), in accordance with previous work [20]. 7-Methylnorbornadiene and 7-[D_3]methylnorbornadiene were synthesized by addition of methylmagnesium iodide or [D_3]methylmagnesium iodide, respectively, to 7-tert-butoxynorbornadiene in benzene [21,22]. Cyclopropanation of the product led to 3-bromo-8-methyltricyclo [3.2.1.$0^{2,4}$]oct-6-ene and 3-bromo-8-[D_3]methyltricyclo-[3.2.1.$0^{2,4}$]oct-6-ene, respectively, which were hydrogenated or deuterogenated as mentioned above to yield compounds **6**, **6a**, and **6b**, respectively. 5-Methylnorbornene and 5-[D_3]methylnorbornene were prepared by Diels-Alder reactions of cyclopentadiene and acrylic acid [23], followed by reduction of the products to the corresponding alcohols with lithium aluminium hydride or lithium aluminium deuteride, respectively, in diethyl ether. The alcohols were converted to the corresponding 5-methylnorbornenes by treatment with *p*-toluenesulfonyl chloride in pyridine, giving the *p*-toluolsulfonates which, in turn, were reduced with either $LiAlH_4$ or $LiAlD_4$ in diethyl ether [24]. Finally, monobromocarbenoid addition to the 5-methylnorbornenes furnished 3-bromo-6-methyltricyclo[3.2.1.$0^{2,4}$]octane **7** and 3-bromo-6-[D_3] methyltricyclo[3.2.1.$0^{2,4}$]octane **7a**.



Scheme 3. H shifts and cyclization of ethyldihydrotropylium ions prior to ethene expulsion.

The identity and purity of all compounds were checked by ^{1}H NMR and ^{13}C NMR spectrometry (Bruker DRX 500, 500 and 126 MHz, respectively), and EI mass spectrometry (Fisons Autospec, for instrument parameters, see above). The neutral precursors were obtained and used as mixtures of two or several diastereomers, in accordance to the literature [19], but without relevance to the mass spectrometric investigation presented here. The isotopic purity of the deuterium-labeled 3-bromotricyclo[3.2.1.$0^{2,4}$] octanes was determined by EI mass spectrometry and correction for naturally occurring ^{13}C. Due to the low relative abundance of the molecular ions, the isotopic pattern of the $[M - Br]^+$ peaks was used in each case. Deuterium contents and distributions were found to be as follows: **5a** (98.0%; 97.2% d_2, 1.9% d_1, 0.9% d_0); **6a** (98.3%; 97.4% d_2, 1.7% d_1, 0.9% d_0); **6b** (97.1%; 95.2 d_3, 2.1% d_2, 1.6% d_1, 1.1% d_0); **7a** (97.0%; 94.7 d_3, 2.8% d_2, 1.7% d_1, 0.9% d_0).

3. Results and discussion

3.1. Formation of bicyclic ions from higher alkyldihydrotropylium ions

As pointed out before, ethene elimination from protonated 7-ethylcycloheptatriene $[\mathbf{1} + H]^+$ is dominated by loss of C_2H_4 from the interior positions of the seven-membered ring [16]. A mechanistic route that accounts for this unexpected observation comprises the formation of [3.2.1]bicyclic allyl cations of type **II**, thus generating two additional sp^3-hybridized carbon centers which allow for an energetically favourable formal cycloreversion process (Scheme 2). Under CI(CH_4) conditions, fast proton ring walk should occur within the seven-membered ring of dihydrotropylium ions **I** [25]. In contrast to the methyl homologue $[\mathbf{12} + H]^+$, ethyldihydrotropylium ions $[\mathbf{1} + H]^+$ were found to undergo significant hydrogen exchange between the side-chain methylene (α-CH_2) group and the ring [16]. Therefore, 1,2-H shifts from the α-CH_2 group to the carbenium centre at the C-7 carbon should be similarly facile as 1,2-H shifts within the ring and lead to deconjugated secondary carbenium ions (Scheme 3). The so-formed carbenium centre at the α-carbon should undergo a facile electrophilic attack across the ring, generating the 8-methylbicyclo[3.2.1]oct-2-en-4-yl cations **8**. Whereas cyclizations involving this kind of "transannular" bond formation [26] are common in the gas-phase ion chemistry of radical cations of highly unsaturated species [15], e.g. of 4-vinylcyclohexene [27], only few examples for the corresponding isomerization have been reported for closed-shell systems [28]. In the final step of the fragmentation, the bicyclic carbenium ions **8** can expel ethene by a formal [5 + 2]

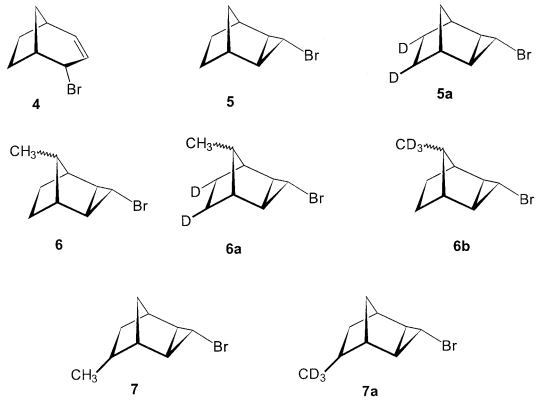


Chart 1. Precursor compounds for the generation of the bicyclic ions.

cycloreversion reaction, possibly as a orbital-symmetry-allowed, suprafacial concerted process involving six electrons [29], eventually producing *ipso*-protonated toluenium ions *i*-[**9** + H]$^+$.

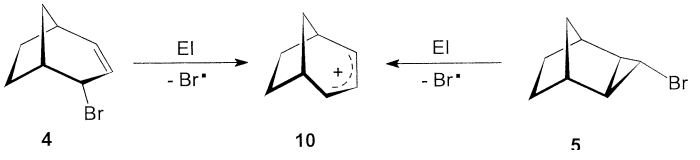
To examine the reactivity of the bicyclic carbenium ions independently, suitable precursors such as 4-bromobicyclo[3.2.1]oct-2-ene **4** and 3-bromotricyclo[3.2.1.0^{2,4}]octane **5** and the methyl derivatives of the latter, **6** and **7**, as well as several deuterium-labeled isotopomers were synthesized and their fragmentation studied by MIKE spectrometry (Chart 1). In this way, we probed not only some bicyclic isomers such as ions **8** of protonated 7-ethylcycloheptatriene [**1** + H]$^+$ but also the parent bicyclo[3.2.1]oct-2-en-4-yl ions **10** as an isomer of 7-methylcycloheptatriene [**12** + H]$^+$.

3.2. Bicyclo[3.2.1]oct-2-en-4-yl cations

Loss of bromine from the radical cations **4**$^{\cdot+}$ and **5**$^{\cdot+}$ generated upon electron ionization leads to the bicyclo[3.2.1]oct-2-en-4-yl cations **10** (Scheme 4). Whereas formation of ions **10** from **4**$^{\cdot+}$ is straightforward, cleavage of the C–Br bond of **5**$^{\cdot+}$ should give rise to the formation of annelated cyclopropyl cations, which yield the bicyclic allyl cations **10** by [2 + 1]-cycloreversion, a facile isomerization process known to occur generally with cyclopropyl cations [30].

To confirm that the $C_8H_{11}^+$ ions (**10**, *m/z* 107) generated from ions **4**$^{\cdot+}$ and **5**$^{\cdot+}$ have identical structures, collision-induced dissociation (CID/MIKE) spectra of the fragment ions [**4** − Br]$^+$ and [**5** − Br]$^+$ were measured. As expected, the CID spectra are indistinguishable from each other [Fig. 1(a) and (b)]. However, they are clearly distinct from the CID spectra of protonated methylcycloheptatriene [**12** + H]$^+$ [Fig. 1(c)] and ethylbenzene [**14** + H]$^+$ [Fig. 1(d)] [31]. Thus, the bicyclo[3.2.1]oct-2-en-4-yl cations **10** represent stable species on the energy hypersurface of the $C_8H_{11}^+$ ions and a significant energy barrier separates them from the isomers [**12** + H]$^+$ and [**14** + H]$^+$. The latter two isomers appear to interconvert relatively easily since their CID spectra are mutually more similar than in comparison to those of the bicyclic ions **10**. In fact, the facile ring contraction of methyldihydrotropylium ions [**12** + H]$^+$ to ethylbenzenium ions [**14** + H]$^+$ has been deduced from the fragmentation of the metastable ions [10b,16].

The MIKE spectra of the bicyclic carbenium ions **10** generated from **4**$^{\cdot+}$ and **5**$^{\cdot+}$ and those of the isomeric methyldihydrotropylium ions [**12** + H]$^+$, *p*-xylenium ions [**13** + H]$^+$ and ethylbenzenium ions [**14** + H]$^+$ are collected in Table 1. In the MIKE spectra of ions **10**, ethene loss represents the main fragmentation pathway, whereas the eliminations of hydrogen and methane are largely suppressed. This finding is similar to the observations made for ions [**12** + H]$^+$ and [**14** + H]$^+$ obtained under CI(CH$_4$)



Scheme 4. Generation of the parent bicyclo[3.2.1]oct-2-en-4-yl cations **10** by electron ionization.

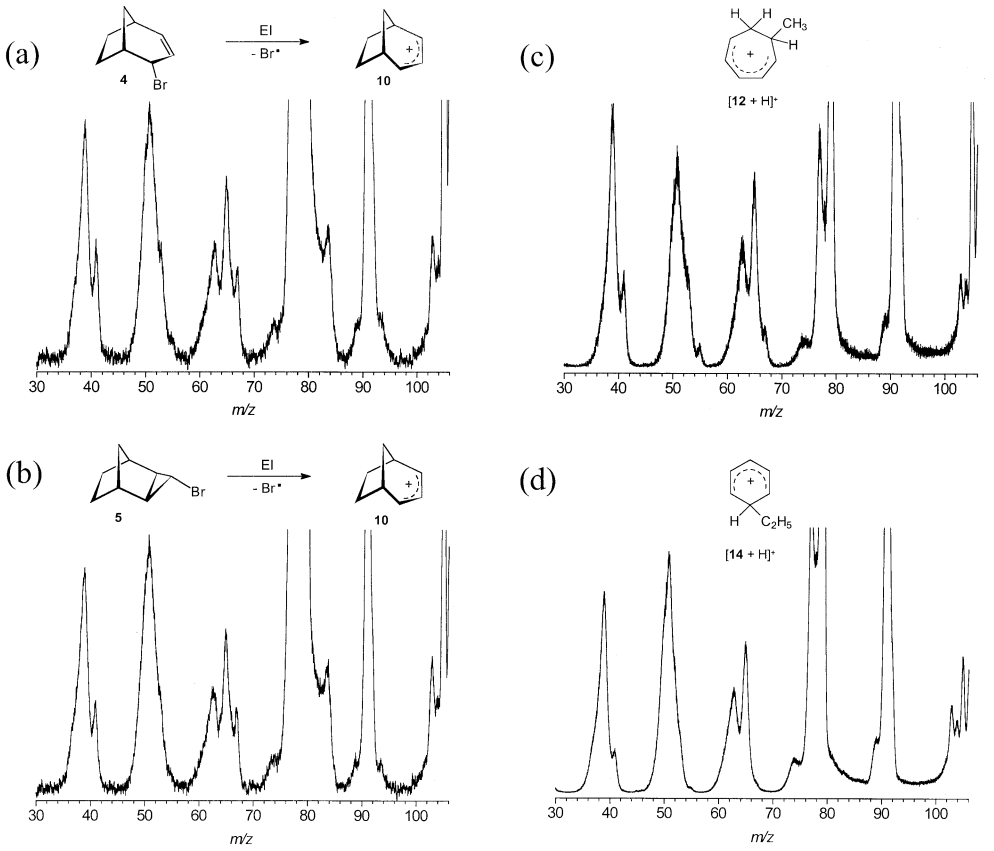


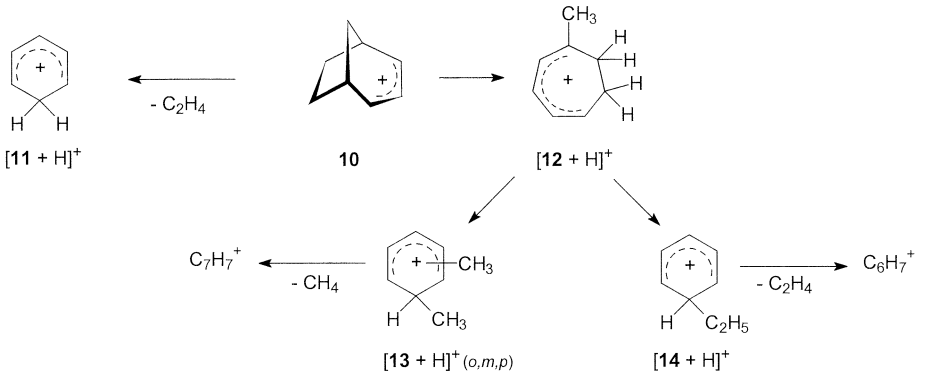
Fig. 1. CID/MIKE spectra of isomeric $C_8H_{11}^+$ ions: (a and b) Bicyclic ions **10**, (c) protonated methylcycloheptatriene [**12** + H]$^+$, and (d) protonated ethylbenzene [**14** + H]$^+$.

and, in particular, under the milder CI(*i*-C_4H_{10}) conditions [10b,16]. Most importantly, however, peak shape analysis reveals that ethene loss from ions **10** is associated with a composite peak, indicating again two competing processes associated with two individual kinetic energy release characteristics (cf. Table 1). In contrast, ethene elimination from ions [**12** + H]$^+$, [**13** + H]$^+$, and [**14** + H]$^+$ exhibits near-Gaussian

Table 1
Fragmentation of metastable $C_8H_{11}^+$ ions formed from various precursors[a]

Precursor	**4**	**5**	7-CH_3–*c*C_7H_7 (**12**)	*p*-CH_3–*c*C_6H_5–CH_3 (**13**)	C_2H_5–*c*C_6H_5 (**14**)
Ion generated	**10**[b]	**10**[b]	[**12** + H]$^+$ [c]	[**13** + H]$^+$ [c]	[**14** + H]$^+$ [c]
Loss of					
H_2	2.6	5.2	24.7	31.6	1.3
CH_4	4.1	7.7	9.1	59.4	2.7
C_2H_4 (T_1^* [meV])	93.3[d] (21.5)	87.1[d] (14.6)	66.2 (16.5)	9.0 (12.3)	96.0 (13.9)
(T_2^* [meV])	(264)	(283)			

[a] Relative abundances given as %Σ (from peak areas).
[b] Generated under EI conditions.
[c] Generated under CI(CH_4) conditions, see [16].
[d] Composite peaks (see text).



Scheme 5. Competing fragmentation paths of ions **10** (H_2 loss not shown).

peak shapes in all cases and is accompanied by small kinetic energy releases [12,16].

Obviously, loss of ethene from bicyclo[3.2.1]oct-2-en-4-yl cations **10** is mechanistically distinct from that from methyldihydrotropylium ions $[\mathbf{12} + H]^+$ and ethylbenzenium ions $[\mathbf{14} + H]^+$ and proceeds by two different pathways. On the one hand, the narrow near-Gaussian component (T_1^* = 15–22 meV) resembles the signals found for the elimination of ethene from ions $[\mathbf{12} + H]^+$ and $[\mathbf{14} + H]^+$, suggesting that these isomers are involved in the fragmentation of ions **10**. Likewise, elimination of methane indicates the competing isomerization of ions **10** to the xylenium isomers $[\mathbf{13} + H]^+$. On the other hand, however, the broad component (T_2^* = 184–193 meV) is absent in the MIKE spectra of the metastable arenium ions $[\mathbf{12} + H]^+$ to $[\mathbf{14} + H]^+$. This indicates an independent pathway for the elimination of ethene from the bicyclic $C_8H_{11}^+$ ions **10** and a relatively large reverse activation energy towards the products [32]. The reverse energy barrier may be attributed to an energetically favourable, exoergic and concerted orbital-symmetry allowed cycloreversion process **10** → $[\mathbf{11} + H]^+$ (Scheme 5). In this way, a literally true "expulsion" of the C_2H_4 bridge from the bicyclo[3.2.1]oct-2-en-4-yl cations **10** may release a part of the angular strain energy during the formation of the planar benzenium ion $[\mathbf{11} + H]^+$ and the reorganization of the electronic system [33]. However, a stepwise elimination process and the formation $C_6H_7^+$ isomers other than benzenium ions, e.g. fulvenium ions [13,14], cannot be strictly excluded at this point.

To check whether the expulsion of ethene from the bicyclic species is a site-specific process involving exclusively the constituents of the original ethano bridge ($C^6H_2C^7H_2$), we have examined the fragmentation of metastable $C_8H_9D_2^+$ ions (*m/z* 109) formed upon bromine loss from the tricyclic precursor **5a**. Such a specific fragmentation would result in the specific elimination of $C_2H_2D_2$ associated with the large kinetic energy release, accompanied with minor contributions of $C_2(H,D)_4$ isotopomers associated with small peak broadening. The MIKE spectrum of the dideuterated bicyclic ions **10a** is shown in Fig. 2 and the relative abundances of the fragment ions are given in Table 2.

The observation is straightforward. In contrast to

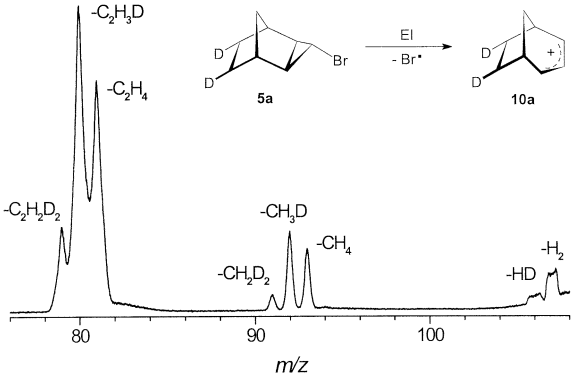


Fig. 2. MIKE spectrum of deuterium-labeled ions **10a**.

Table 2
Fragmentation of metastable deuterium labeled ions **10a**

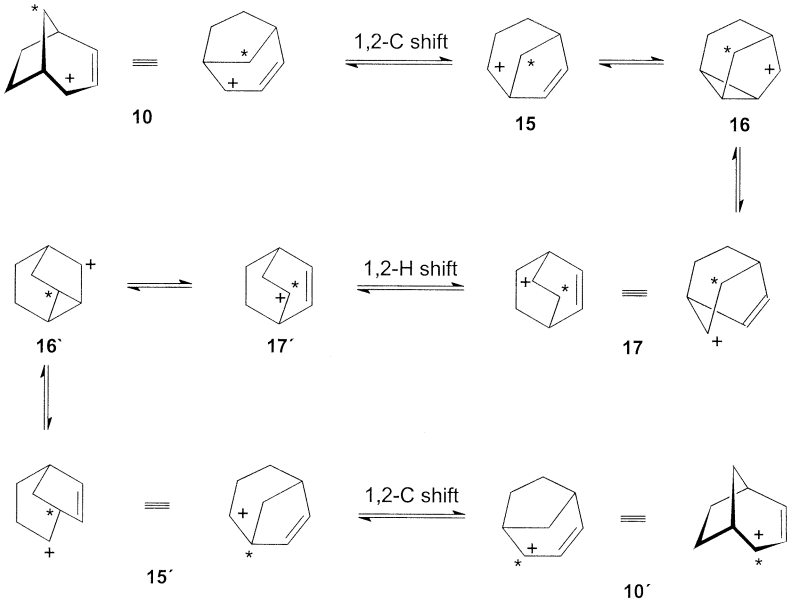
Loss of	Experimental[a]	Statistical[a,b]
H_2	70.3	65.5
HD	29.7	32.7
D_2	(<3.0)	1.8
CH_4	39.8	38.2
CH_3D	49.6	50.9
CH_2D_2	10.6	10.9
C_2H_4	39.8[c]	38.2
C_2H_3D	48.8[c]	50.9
$C_2H_2D_2$	11.4[c]	10.9

[a] Data given as %Σ for each group of isotopomers (from peak areas).
[b] Calculated for scrambling of all H and D atoms.
[c] Overlapping and composite peaks (see Fig. 2).

expectation, fast and complete H/D equilibration is observed involving all of the eleven hydrogen and deuterium atoms of ions **10a** and preceding all of the fragmentation reactions. In particular, composite peaks are found for the loss of the three ethene isotopomers in similar proportions as observed for the unlabeled ions **10**.

These findings suggest that the scrambling process in metastable bicyclo[3.2.1]oct-2-en-4-yl cations **10** involves not only the hydrogen atoms but also the carbon skeleton, as a consequence of fast and reversible 1,2-C shifts (Wagner-Meerwein rearrangements) combined with 1,2-H shifts, as shown in Scheme 6. This fast skeletal isomerization parallels the rearrangement processes discussed for bicyclo[3.2.1]octane derivatives and bicyclo[3.2.1]octenes in the condensed phase [34,35] and does not require violations of Bredt's rule [36]. Also, formation of bridgehead carbenium ions [37] is circumvented, thus allowing for relatively low activation barriers and fast interconversion of the isomers involved, in accordance with observation.

Isomerization of ions **10** starts by a 1,2-C-shift giving the nonallylic bicyclo[3.2.1]oct-6-en-2-yl cations **15**, which react further to the tricyclic species **16** by homoallylic interaction [38]. Subsequent re-opening of the cyclopropane ring leads to bicyclo[2.2.2]oct-2-en-5-yl cations **17**, which undergo a facile degenerate 1,2-H shift (**17** ⇌ **17′**). In a reverse sequence, tricyclic ions **16′**, bicyclo[3.2.1]oct-6-en-2-yl cations **15′** and, finally, the initial bicyclo[3.2.1]oct-2-en-4-yl cations **10′** are regener-



Scheme 6. Degenerate isomerization of ions **10**. For clarity, the original methano bridge atom (C-8) is labeled with an asterisk.

Table 3
Fragmentation of metastable bicyclic $C_9H_{13}^+$ ions and labeled analogues[a,b]

Precursor	**6**	**7**	**6a**	**6b**	**7a**
Ion generated	**8**	**18**	**8a**	**8b**	**18a**
Loss of	[c]	[c]	[d]	[d]	[d]
CH_4	4.6	0.7	49.9	57.9	60.6
CH_3D	...	...	40.9	9.9	7.5
CH_2D_2	...	...	9.2	7.0	5.6
CHD_3	...	...	...	25.2	26.3
C_2H_4 (T_1^* [meV])	76.7 (17)	86.0 (16)	41.3[e]	83.2[e]	86.0[e]
(T_2^* [meV])	(310)	(285)	...	...	
C_2H_3D	...	...	46.5[e]	3.1[e]	2.9[e]
$C_2H_2D_2$	...	...	12.2[e]	9.5[e]	8.6[e]
C_2HD_3	...	...	...	4.2[e]	2.5[e]
C_3H_6 (T* [meV])	17.0 (18)[f]	13.0 (14)[f]	44.2	1.8	1.2
C_3H_5D	...	...	49.1	4.5	3.4
$C_3H_4D_2$	...	...	6.7	9.7	7.7
$C_3H_3D_3$	...	...	...	84.0	87.7
C_6H_6	1.7	0.3	14.8	100	100
C_6H_5D	...	...	49.6	0	0
$C_6H_4D_2$	...	...	35.6	0	0
$C_6H_3D_3$	...	...	...	0	0

[a] For CI(H_2O) data of the corresponding *n*-propylbenzenes, see [4].
[b] For CI(CH_4) data of the corresponding 7-ethylcycloheptatrienes, see [16].
[c] Data given as %Σ of total fragmentation (from peak areas).
[d] Data given as %Σ for each group of isotopomers (from peak areas).
[e] Composite and overlapping peaks.
[f] Near-Gaussian peak shapes; average kinetic energy release T: 63 meV (ions **8**), 37 meV (ions **18**).

ated, the latter ions bearing the original methylene carbon C-8 at position 2 (or 4) of the bicyclic framework. Several successive rearrangements of this type give rise to a complete scrambling of both hydrogens and carbon atoms of these cycloolefinic $C_8H_{11}^+$ ions.

3.3. Methyl-substituted bicyclo[3.2.1]oct-2-en-4-yl cations

To determine whether the particular features of ethene loss and the fast skeletal reorganization is a general behaviour of bicyclo[3.2.1]oct-2-en-4-yl cations, we have also studied the fragmentation of the methyl-substituted derivatives **8** and **18** and of three deuterium-labeled isotopomers **8a**, **8b**, and **18a**. The corresponding tricyclic compounds **6**–**7a** were used as the neutral precursors (Chart 1). As will be shown below, these $C_9H_{13}^+$ ions, being isomers of protonated ethylcycloheptatriene $[\mathbf{1} + H]^+$, lose ethene again through two competing fragmentation channels and skeletal rearrangement precedes the path associated with high kinetic energy release.

In the first step, loss of bromine from the molecular ions of 3-bromo-8-methyltricyclo[3.2.1.$0^{2,4}$]octane **6** and 3-bromo-6-methyltricyclo[3.2.1.$0^{2,4}$]octane **7** leads to the bicyclic ions **8** and **18** ($C_9H_{13}^+$, *m/z* 121), respectively. The MIKE spectra of these ions are similar (Table 3), corroborating the fast interconversion of the bicyclic structures prior to fragmentation. Elimination of ethene dominates in both cases and loss of benzene, propene and methane are also observed as minor processes. Peak-shape analysis of the $[\mathbf{8} - C_2H_4]^+$ and $[\mathbf{18} - C_2H_4]^+$ signals reveals composite peaks, whereas loss of propene from both ions is associated with narrow, near-Gaussian peak shapes.

The latter finding implies that elimination of C_3H_6 takes place by stepwise isomerization to *n*-propylbenzenium ions $[\mathbf{2} + H]^+$ rather than by [5 + 2] cycloreversion to give benzenium ions (Scheme 7). Ions $[\mathbf{2} + H]^+$ can be formed by cleavage of the bicyclic framework at either the methyl-substituted methano bridge ($>C^8HCH_3$) of ions **8** followed by ring contraction of the ethyldihydrotropylium ions $[\mathbf{1} + H]^+$ intermediates or at the methyl-substituted ethano bridge $[C^6H(CH_3)C^7H_2]$ of ions **18**. Isomerization of ions **8** and **18** to *n*-propylbenzenium ions $[\mathbf{2} + H]^+$ is also reflected by the minor loss of benzene, another typical fragmentation of these alkylbenzenium ions [4j,11a–c]. Intriguingly, loss of propene associated with large kinetic energy release, originally expected as a dominating path characterising the cycloreversion of ions **18**, does not occur.

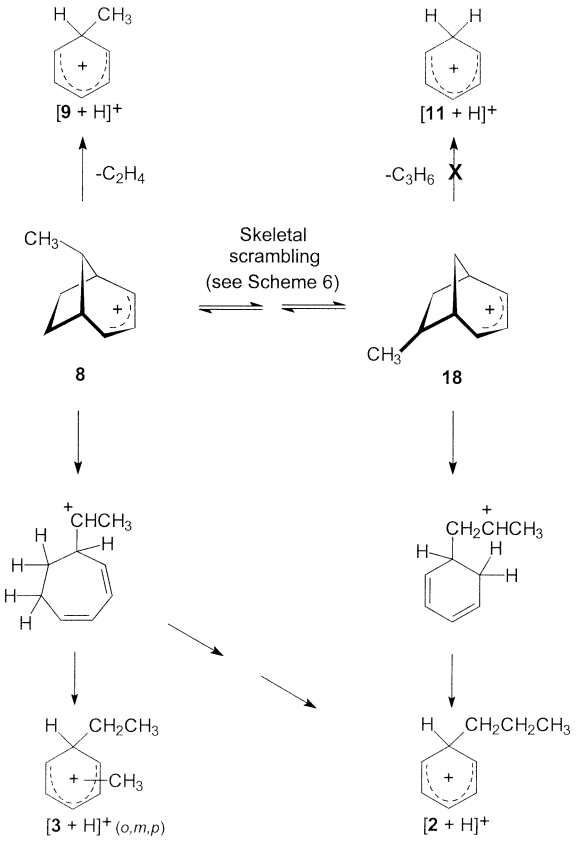
The finding that ethene loss proceeds again by way of two different pathways and that it dominates not only the fragmentation of ions **8** but also that of ions **18** points again to the facile interconversion of these isomers. Whereas the major fraction of the $C_9H_{13}^+$ ions expels ethene with large kinetic energy release (T_2^* = 285–310 meV), probably by way of cycloreversion of bicyclus **8**, a minor fraction undergoes also cleavage of the methyl-substituted methano bridge of **8** to give ethyltoluenium ions $[\mathbf{3} + H]^+$, from which ethene is lost with the low kinetic energy release (T_1^* = 16–17 meV), again typical for alkylbenzenium ions. Another typical feature for the formation of ions $[\mathbf{3} + H]^+$ is the methane loss observed.

The fragmentation of the deuterium-labeled ions confirms the competition between these various fragmentation reactions. The MIKE spectra of the $C_9(H, D)_{13}^+$ ions **8a**, **8b**, and **18a** are also collected in Table 3. The losses of benzene and propene are in line with isomerization to the corresponding *n*-propylbenzenium ions bearing the label mainly in the arenium ring (**8a**) or in the side chain (**8b** and **18a**). Most convincingly, no H/D exchange is observed prior to loss of benzene from the CD_3-labeled isotopomers **8b** and **18a**, in accordance with the fragmentation of the corresponding metastable ([β,β,β-D_3]ethyl)dihydrotropylium ions [16] and *n*-([γ,γ,γ-D_3]propyl)benzenium ions [4j]. The benzene and propene losses from the [D_3]-labeled ions **8b** and **18a** confirm that the methyl substituents largely remain intact, that is, the methyl hydrogens do not participate in the fast hydrogen exchange within the bicyclic skeleton.

The latter isomerization process is also evident from the loss of benzene from the D_2-labeled ions **8a**, in analogy to the complete H/D equilibration of ions **10a**. The relative abundances of benzene isotopomers, $[C_6H_6]:[C_6H_5D]:[C_6H_4D_2]$ = 14.8:49.6:35.6, are almost identical to the pattern calculated for complete hydrogen scrambling within the bicyclic framework, excluding the methyl group (13.3:53.3:33.4), prior to isomerization to *n*-propylbenzenium ions $[\mathbf{2} + H]^+$. This finding is in agreement with the reversible cyclization of ethyldihydrotropylium ions $[\mathbf{1} + H]^+$, for which significant mobility of the hydrogen atoms of the (exocyclic) α-CH_2 group was observed [16]. At variance from the CD_3-labeled ions **8b** and **18a**, which undergo predominantly loss of $C_3H_3D_3$ ($\geq$84.0%), the ring-D_2 isotopomers **8a** exhibit excessive H/D scrambling prior to propene elimination. Again, these data reflect the high hydrogen mobility within the bicyclic ions and the irreversible formation of *n*-propylbenzenium ions as the fragmenting species.

As mentioned previously, methane loss from the deuterium-labeled ions indicates isomerization to ethyltoluenium ions $[\mathbf{3} + H]^+$ prior to fragmentation. The CD_3-labeled isotopomers **8b** and **18a** eliminate predominantly CH_4 and CHD_3, indicating isomerization to $[\mathbf{3} + H]^+$ ions by way of dihydrotropylium isomers that eventually undergo ring contraction. In contrast, methane loss from the D_2-labeled isotopomer **8a** shows significant scrambling, in qualitative agreement with the mechanisms outlined in Scheme 7.

Ethene elimination from the metastable CD_3-substituted ions **8b** and **18a** is also identical and strikingly similar to that of the isomeric ([β,β,β-D_3]ethyl)dihydrotropylium ions $[\mathbf{1a} + H]^+$ [16] (Fig. 3). In all cases, the MIKE spectra exhibit predominant loss of the unlabeled C_2H_4 isotopomer associated with high kinetic energy release ($T_2^* \approx$ 300 meV), along with minor contributions of C_2H_4, $C_2H_2D_2$, and C_2HD_3 associated with low kinetic energy release (T_1^* = 14–26 meV) and near-Gaussian peak shapes.



Scheme 7. Interconversion and isomerization of the methyl-substituted ions **8** and **18** and selective [5 + 2] cycloreversion of ions **8**.

The latter low-KER contributions again reflect isomerization of ions **8** and **18** to ethyltoluenium ions $[\mathbf{3} + H]^+$ by way of methyldihydrotropylium ions $[\mathbf{1} + H]^+$. Quite reasonably, this process is more pronounced with ions $[\mathbf{1a} + H]^+$ than with ions $[\mathbf{8b} + H]^+$ and $[\mathbf{18a} + H]^+$, as can be seen from relatively higher fraction of the labeled ethenes from the former ions (Fig. 3). Further, the high-KER contributions in the MIKE spectra corroborate that the ethene expulsion from the bicyclic skeletons of ions **8** and **18** does not involve the constituents of the methyl groups. In contrast, and in accordance with the fast interconversion of the bicyclic framework of these ions, the MIKE spectrum of the D_2-labeled isotopomer **8a** exhibits composite peaks for the loss of all $C_2(H,D)_4$ isotopomers (Table 3). Again, this finding is in strict analogy to the $C_2(H,D)_4$ loss from ions **10a** (Table 2).

Ethene loss from isotopomers **8a**, **8b**, and **18a** can be modeled by combining the two competing pathways (Table 4, Scheme 7). By fast and repetitive skeletal rearrangement and hydrogen shifts within the bicyclic framework, as shown in Scheme 6 for the case of ions **10**, the methyl groups lose positional identity without exchanging of their hydrogens with those of the bicyclic framework. Moreover, the ring contraction steps producing ethyltoluenium ions are assumed to be irreversible and elimination of the ethene isotopomers from the latter isomers is assumed to occur in analogy to the correspondingly labeled ethylbenzenium ions [12]. Combining the $C_2(H,D)_4$ contributions of this pathway with those of the cycloreversion of the bicyclic framework in the ratio of 1 : 4 leads to a pattern which is in good agreement with the experimental data (Table 4).

Summarizing at this point, the labeling of the experiments with ions **8** and **18** clearly reveal the skeletal rearrangement of the bicyclic framework and the similar reactivity of methylbicyclo[3.2.1]oct-2-en-4-yl ions and ethyldihydrotropylium ions. The results also indicate that the isomerization barrier between the methyl-substituted $C_9H_{13}^+$ ions **8**, **18**, and $[\mathbf{1} + H]^+$ is significantly smaller than that between the lower homologues $C_8H_{11}^+$, **10**, and $[\mathbf{12} + H]^+$, in agreement with the finding that the high-KER ethene loss is common for the former ions but unique for ions **10** among the latter ones.

4. Conclusion

It has been demonstrated in this article that gaseous bicyclo[3.2.1}oct-2-en-4-yl cations dissociate by isomerization to the corresponding alkyldihydrotropylium ions (protonated 7-alkylcycloheptatrienes) and alkylbenzenium ions (protonated alkylbenzenes). In competition to this alkylbenzenium-type fragmentation, bicyclo[3.2.1]oct-2-en-4-yl cations also undergo a characteristic loss of ethene associated with the release of relatively large amounts of kinetic energy ($T^* \approx 300 \pm 20$ meV), which is attributed to a

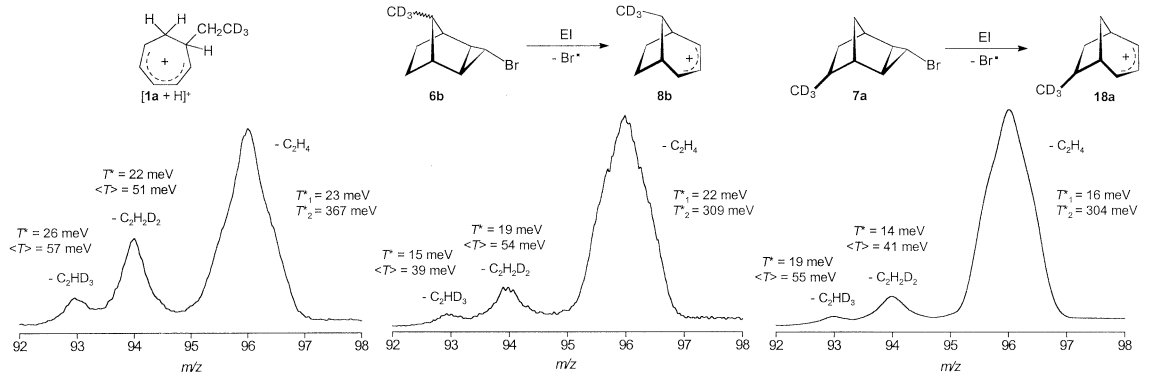


Fig. 3. Partial MIKE spectra showing the ethene loss from CD_3-substituted dihydrotropylium ions $[\mathbf{1a} + H]^+$ and the bicyclic isomers **8b** and **18a**.

specific [5 + 2] cycloreversion of the bicyclic skeleton. Fast skeletal rearrangements of the bicyclic framework coupled with 1,2-H shifts give rise to equilibration of the hydrogen (and probably carbon) atoms and this process precedes both the alkylbenzenium and the cycloreversion paths.

The results presented here suggest that alkyl-substituted bicyclo[3.2.1]oct-2-en-4-yl cations are easily accessible intermediates during the fragmentation of higher protonated alkylcycloheptatrienes, for which the particular high-KER loss of ethene was found originally [16]. They also provide a good basis for the mechanistic explanation of our previous finding that protonated alkylcycloheptatrienes eliminate ethene predominantly from the interior parts of the seven-membered ring. However, details of the energetics and dynamics of the [5 + 2] cycloreversion reaction remain obscure. What is the origin of the high energy release, and why is it that only ethene loss is accompanied with high energy release? Since the [5 + 2] cycloreversion postulated here represents a prototype case for a concerted, orbital-symmetry-

Table 4
Loss of ethene from metastable bicyclic $C_9(H,D)_{13}^+$ ions[a,b]

Loss of Ion generated	C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3
8a Experimental	41.3	46.5	12.2	...
Calculated				
(i) Randomization [8H/2D], then cycloreversion[c]	33.3	53.3	13.4	...
(ii) Randomization [8H/2D], via ethyltoluenium ions[d]	64.8	33.3	1.9	...
(iii) Combination of (i), 80 %, and (ii), 20%	39.6	49.3	11.1	...
8b Experimental	83.2	3.1	9.5	4.2
18a Experimental	86.0	2.9	8.6	2.5
Calculated				
(i) Ethene loss by cycloreversion[c]	100.0	...	...	...
(ii) Ethene loss via ethyltoluenium ions[d]	...	...	69.0	31.0
(iii) Combination of (i), 80%, and (ii), 20%	80.0	...	13.8	6.2

[a] Data given as %Σ (from peak areas).
[b] For CI(CH_4) data of the corresponding 7-ethylcycloheptatrienes, see [16].
[c] Calculated for total hydrogen randomization within the bicyclic skeleton, i.e. excluding the methyl group.
[d] Calculated for H/D randomization within the bicyclic skeleton followed by isomerization to ethyltoluenium ions by way of ethyldihydrotropylium ions (cf. Scheme 7). $C_2(H,D)_4$ loss from the ethyltoluenium ions thus formed was calculated based on the fragmentation of protonated $C_6H_5CD_2CH_3$ and $C_6H_5CH_2CD_3$ [12].

controlled process analogous to a retro-Diels-Alder reaction, detailed computational work should be invested to further clarify this intriguing fragmentation reaction. The fascinating field of gas-phase ion chemistry is broadening but it needs further in-depth understanding.

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