Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 228 (2003) 321–339

www.elsevier.com/locate/ijms

Proton-induced intra-complex hydride transfer involving bicyclo[2.2.2]octane units as a rigid spacer and as a carbocation precursor

Carsten Matthias, Björn Bredenkötter, Dietmar Kuck*

Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25 Postfach 100131, D-33615 Bielefeld, Germany

Received 8 January 2003; accepted 17 March 2003

Dedicated to Professor Helmut Schwarz on the occasion of his 60th birthday.

Abstract

An α,ω-diphenylalkane bearing a *tert*-butyl group at one of the aromatic rings and a rigid and, ostensibly, inert alicyclic spacer unit (bicyclo[2.2.2]octa-1,4-diyl) within the aliphatic chain has been synthesized and subjected to protonolysis under CI(CH_4) conditions. The metastable $[M + H]^+$ ions of this hydrocarbon, 1-benzyl-4-(4-*t*-butylbenzyl)bicyclo[2.2.2]octane, undergo predominantly loss of isobutane via intermediate ion/neutral complexes. By contrast to expectation and to the straightforward interpretation of the results, and at variance to the fragmentation behavior of many related *tert*-butyl-substituted α,ω-diphenylalkanes lacking such a spacer, the intra-complex hydride transfer reaction leading to the isobutane loss involves the bicyclo[2.2.2]octane unit as the hydride donor. This has been revealed by careful deuterium labeling of not only one of the benzylic methylene groups but both of them. Notwithstanding these unexpected findings, it is also demonstrated that the bicyclo[2.2.2]octane unit can be used to generate ion/neutral complexes that contain the bicyclo[2.2.2]oct-1-yl cation solvated to an α,ω-diphenylalkane. In this case, well-behaved intra-complex hydride transfer has been observed between the bicyclic carbocation and alkylbenzene.

Keywords: Ion/molecule complexes; Metastable ions; Protonolysis; Hydride transfer; Proton transfer; *tert*-Butylbenzenes; Bicyclo[2.2.2]octanes; Skeletal rearrangement

1. Introduction

The proton-induced cleavage (protonolysis) of C–C single bonds represents a major elementary step during the fragmentation of even-electron organic ions in the gas phase. Carbenium ions and carbonium ions, formed either directly by protonation of hydrocarbons under chemical ionization (CI) conditions [1,2], or by loss of a radical or molecule from a precursor odd- or even-electron cation, can undergo a large variety of fragmentation reactions. Some of them are initiated by classical bonding of a proton to an unsaturated C–C bond, as it is the case with *ipso*-tautomers of benzenium ions, that subsequently expel an alkyl substituent as a neutral alkene or as an alkyl cation [3–5]. Formation of ion/neutral complexes after C–C bond

---

* Corresponding author. Tel.: +49-521-106-2060; fax: +49-521-106-6417.
E-mail address: dietmar.kuck@uni-bielefeld.de (D. Kuck).

1387-3806/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00201-X

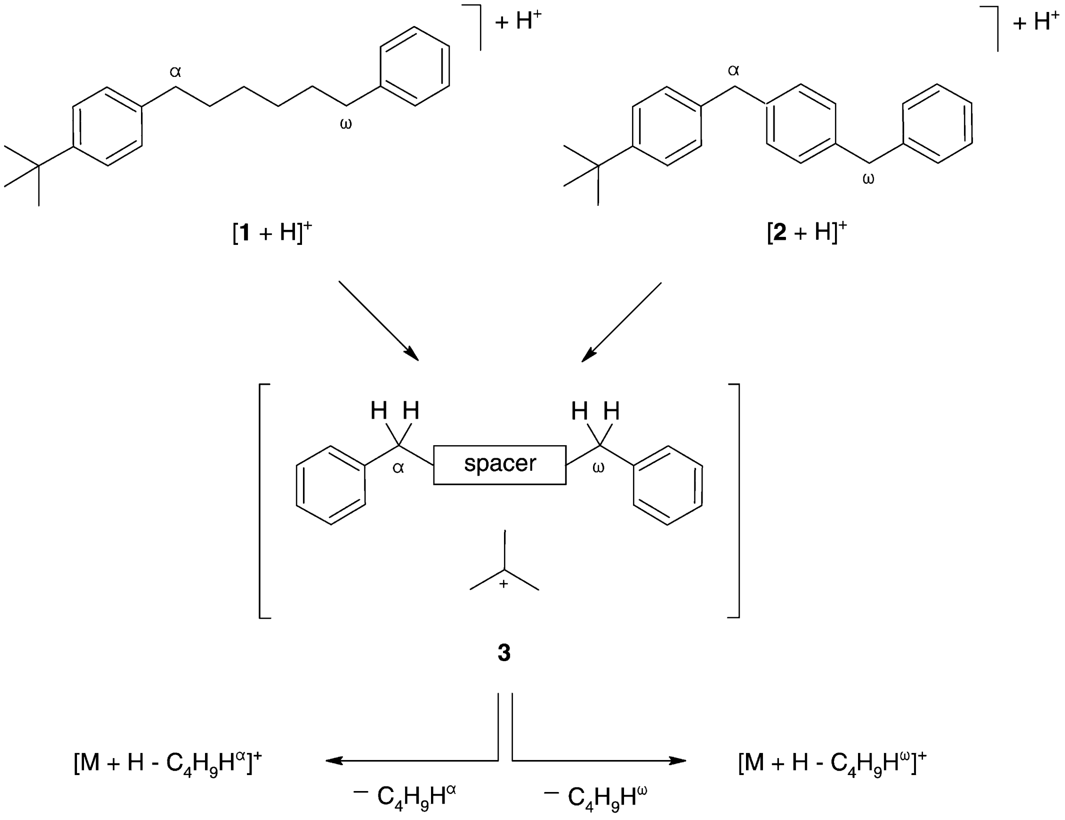
cleavage can give rise to intra-complex hydride transfer and elimination of a neutral alkane [6–8]. In other proton-induced C–C bond dissociations, non-classical carbocations ("carbonium ions") are involved, such as during the loss of methane from protonated toluene and xylenes [9,10].

However, the proton affinity of C–C single bonds is notoriously low and protonation of several bonds may compete efficiently, thus giving rise to a variety of fragmentation processes under sufficiently harsh CI conditions [11,12]. A pertinent example for this behavior is the fragmentation of *n*-butylbenzene and *n*-pentylbenzene in the CI(CH_4) ion source [13]. Besides the loss of the entire C_5 side chain as pentyl cation, heterolytic cleavage of the formally remote C–C bonds occurs as well. Extensive labeling experiments of this parent alkylbenzenium ion [13] revealed the interplay of complicated isomerization processes prior to fragmentation, thus contributing to the general view that highly excited protonated alkylbenzenes suffer not only cleavage triggered by the aromatic ring (viz., of the C^{ipso}–C^{α} and C^{α}–C^{β} bonds) but also cleavage of the remote C–C bonds of the aliphatic chain.

Notwithstanding, less excited protonated alkylbenzenes, representing prototypical species of the covalently bonded intermediates of electrophilic substitution of arenes (σ-complexes) [5,14,15], mostly react through well controllable isomerization and fragmentation channels. Therefore, numerous studies on metastable alkylbenzenium ions have been published during the past two decades. These studies revealed that congeners bearing more than one benzene ring undergo not only fast intra-ring (intraannular) but also fast ring-to-ring (interannular) proton exchange prior to fragmentation [5,16]. Similarly, fast migration of *tert*-butyl cations between the arene units has been found to occur during the microseconds' lifetime of protonated *tert*-butyl-substituted α,ω-diphenylalkanes, e.g., $[\mathbf{1} + H]^+$ (Scheme 1), and branched congeners bearing three or even four phenyl groups [7,17–20]. Systematic investigations of the reactivity of these ions have revealed that ion/neutral complexes of the type [t-$C_4H_9^+$ arene] represent the crucial intermediates en route to the loss of isobutane and isobutene.

One interesting piece of evidence in favor of the intermediacy of electrostatically bonded complexes [t-$C_4H_9^+$ arene] was obtained from the fragmentation of metastable ions $[\mathbf{2} + H]^+$, in which both of the two methylene groups act as hydride donors in the rate-determining step of the isobutane loss [17]. This finding clearly demonstrates that the *tert*-butyl cation can be transferred in a sliding motion from one arene unit to the adjacent one, meaning in the same time that neither an S_N2-type (pentacoordinate) transition state nor a sandwich-type solvation of the two arene rings are necessary conditions to allow the migration to occur. However, extended studies on the intra-complex hydride abstraction with derivatives bearing methyl substituents at various positions of the arene rings indicate that solvation of the t-$C_4H_9^+$ ion between two arene units is preferred. Furthermore, very recent theoretical studies on the complex [t-$C_4H_9^+$benzene] [21] and experimental investigations on the reactivity of the complex [s-$C_4H_9^+$benzene] generated by radiolysis of optically pure (*R*)-*sec*-butylbenzene [22] suggest that such π-complexes composed of stable alkyl cations and arenes can adopt structures that are less symmetrical than assumed earlier [6a,23] and should be classified as η_1-complexes.

In this context, we wish to report on a quite special effort made in this laboratory to study the mobility of the t-$C_4H_9^+$ ion solvated to a specifically designed α,ω-diphenylalkane, in which the two arene rings are separated by a rigid and voluminous spacer that would prevent the mutual approach of the aromatic π-electron systems and hence, the sliding transfer of the t-$C_4H_9^+$ ion from one arene to the other. A model hydrocarbon that was expected to fulfill all criteria required to clarify the character of the intermediate ion/molecule complex of this type is 1-benzyl-4-(4-*t*-butylbenzyl)bicyclo[2.2.2]octane (**4**). Because of the bicyclic framework of the bicyclo-[2.2.2]octa-1,4-diyl spacer, the aromatic rings are kept strictly apart from each other, such that the t-$C_4H_9^+$ ion is prevented from electrostatic and/or cation/π-electron interaction [24] with both of the



Scheme 1. Two examples for the regioselective loss of isobutane from *tert*-butyl-substituted alkylbenzenes occurring via ion/neutral complexes.

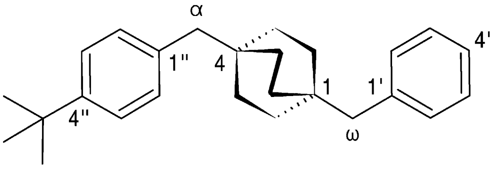
arene rings at the same time. Therefore, deuterium labeling of the remote (ω-)methylene group with respect to the *tert*-butyl-substituted (α-)phenyl group could reveal the ability of the $t\text{-}C_4H_9^+$ ion to migrate, within the ion/neutral complex **5**, around a purely saturated, alicyclic core.

This study will first demonstrate the apparent feasibility of this strategy and that the experimental results have led us to a tempting conclusion. However, it also shows that accordance with anticipated outcome can still be questionable. The final conclusion, therefore, will be a demonstration of the quandry as to whether a seemingly reasonable conclusion should be published or whether the result of a one-too-many experiment should, or should not, be awaited. In any case, however, this work sheds further light on the protonolysis of the C–C single bonds of alkylbenzenium ions and of the highly branched bicyclo[2.2.2]octane framework, in particular. As a special extension, the proton-induced fragmentation of a related, bicyclo[2.2.2]oct-1-yl-substituted, α,ω-diphenylalkane is presented, in which a bicyclo[2.2.2]octyl cation reacts as a Lewis acid within an ion/neutral complex.

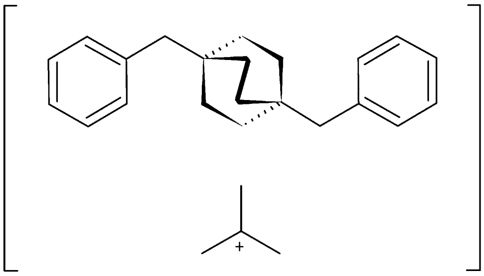
2. Experimental

2.1. Mass spectrometric measurements

All measurements were carried out on a double-focusing instrument, AutoSpec (Fisons, Manchester,



4



5

UK) with a three-sector, EBE geometry. The compounds were introduced into the CI source via the heatable inlet rod. Throughout, methane was used as the reactant gas with the (nominal) pressure being 4×10^{-5} to 1×10^{-4} mbar. The electron energy was set at 70 eV, the trap current at 200 μA, the accelerating voltage at 8000 V, and the source temperature at 160–200 °C. Fragmentation of the metastable ions in the third field-free region was registered by selecting the precursor ion by the magnetic field and scanning the field of the second electrostatic analyzer. The MIKE spectra are representative examples for several independent measurements and averaged from at least 10 consecutive scans.

2.2. Synthesis—general

^{1}H NMR spectra (300 MHz) were measured on a Bruker AM 300 instrument ($CDCl_3$/TMS). Mass spectra: VG Autospec; electron ionization (EI, 70 eV). Deuterium contents were evaluated from the EI mass spectrometric data after correction for naturally occurring ^{13}C. IR spectra: Perkin-Elmer model 841; solids were measured in KBr pellets and liquid as films. Melting points (uncorrected): electrothermal melting point apparatus. Combustional analyses: Leco CHNS-932. All distillations were performed using a Büchi GKR 50 kugelrohr apparatus. TLC: silica (Kieselgel 60) on aluminum foil with fluorescence indicator F_{254}, thickness 0.2 mm (Merck).

A relatively brief description of the extended synthetic work, on which the mass spectrometric measurements have been based, is given in Appendix A.

3. Results and discussion

3.1. Fragmentation of unstable and metastable ions $[\mathbf{4} + H]^+$

The $CI(CH_4)$ mass spectrum of **4** (Fig. 1) reveals a close similarity with the CI spectrum of *tert*-butyl-substituted 1,6-diphenylhexane (**1**) and its homologues [7,17]. The peak at *m*/*z* 57 indicates the facile protonolysis of the $C^{4''}$–$C^{\alpha''}$ bond of the twofold substituted arene ring, releasing the t-$C_4H_9^+$ ion within the CI ion source. Also, the peaks of the molecular radical cations $\mathbf{4}^{\bullet+}$ (*m*/*z* 346) and the quasi-molecular ions $[\mathbf{4} - H]^+$ (*m*/*z* 345) are clearly visible. Charge transfer and hydride abstraction within the $CI(CH_4)$ plasma are common features with α,ω-diphenylalkanes [5a,11]. Ions $[\mathbf{4} + H]^+$ (*m*/*z* 347) occur with extremely low relative abundance only, most of the peak intensity at that mass-to-charge ratio being attributed to the naturally occurring isotopomers $[^{13}C]\mathbf{4}^{\bullet+}$.

Not only is the release of the t-$C_4H_9^+$ ions similarly dominant as in the $CI(CH_4)$ mass spectra of comparable congeners, e.g., $[\mathbf{1} + H]^+$ [17], but the other fragment ions observed also correspond to the usual protonolysis known for this type of alkylbenzenes. The peak at *m*/*z* 291 indicates the loss of isobutene from ions $[\mathbf{4} + H]^+$, which can be assumed to yield protonated 1,4-dibenzylbicyclo[2.2.2]octane. Interestingly, ions $[\mathbf{4} + H - C_4H_8]^+$ are observed with low relative abundance only, but its secondary fragmentation, viz., loss of benzene giving ions *m*/*z* 213, is predominant.

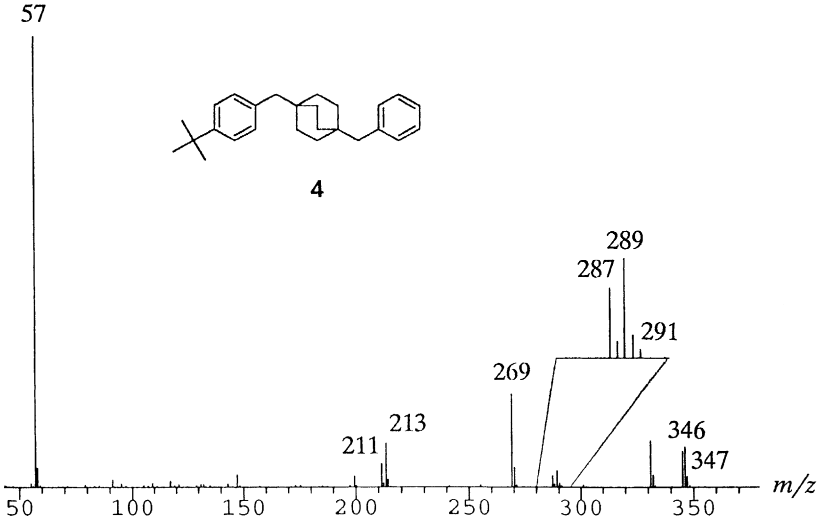
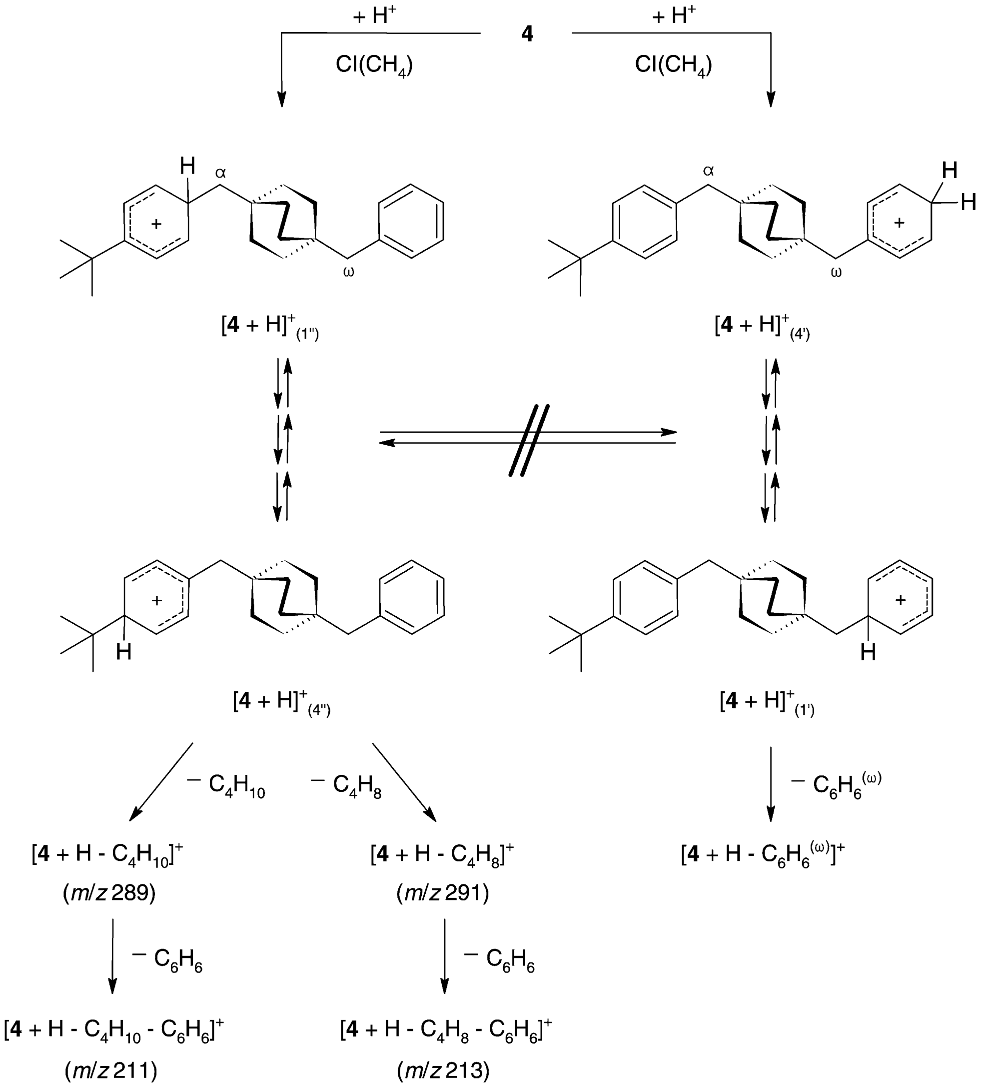


Fig. 1. CI(CH_4) mass spectrum of 1-benzyl-4-(4-*t*-butylbenzyl)bicyclo[2.2.2]octane (**4**).

Loss of isobutane from the quasi-molecular ions leads to ions $[\mathbf{4}+\mathrm{H}-\mathrm{C_4H_{10}}]^+$ (*m/z* 289) and subsequent loss of benzene gives ions with *m/z* 211. Notably, the quasi-molecular ions $[\mathbf{4}-\mathrm{H}]^+$ eliminate also isobutane, giving ions with *m/z* 287, and loss of isobutene from $[\mathbf{4}-\mathrm{H}]^+$ may contribute to the peak *m/z* 289 in the CI mass spectrum. This observation points to the possible occurrence of skeletal rearrangements of the quasi-molecular ions in the CI source.

Another remarkable detail in the CI(CH_4) mass spectrum of **4** is the relatively intense peak at *m/z* 269, indicating the elimination of benzene from the protonated molecules. This fragmentation is unique amongst the *tert*-butyl-substituted α,ω-diphenylalkanes. It is known that protonolysis of the C^{ipso}–C^{α} bonds of alkylbenzenium ions is much easier for tertiary (i.e., doubly α-branched) congeners than for secondary (α-branched) and, in particular, primary (α-unbranched) ones [3,5a,25]. In protonated α,ω-diphenylalkanes, the fast and energetically highly favorable [26] interannular proton equilibration connects the reactivity of all tautomers; thus, protonolysis of the C^{arene}-(t-C_4H_9) bond in *tert*-butyl-substituted congeners such as $[\mathbf{1}+\mathrm{H}]^+$ occurs independently of the original protonation site. By contrast, the presence of the spacer in ions $[\mathbf{4}+\mathrm{H}]^+$ separates the reactivity of the α- and the ω-benzylic groups [27] (Scheme 2). The fast intraannular proton ring walk at the *tert*-butyl-substituted (α-)phenyl group of ions $[\mathbf{4}+\mathrm{H}]^+$ leads to the release of t-$C_4H_9^+$ via tautomer $[\mathbf{4}+\mathrm{H}]^+_{(4'')}$ and the loss of C_4H_{10} and C_4H_8, presumably via ion/molecule complex **5** or related species of type **3** (see below). Similarly, protonation at the unsubstituted phenyl group leads to the release of C_6H_6 from tautomer $[\mathbf{4}+\mathrm{H}]^+_{(1')}$. In the light of the previous results discussed above it appears very unlikely that a fraction of ions $[\mathbf{4}+\mathrm{H}]^+$ reacts by direct loss of *tert*-butylbenzene from tautomers $[\mathbf{4}+\mathrm{H}]^+_{(1'')}$.

Metastable ions decompose preferably through the low-energy fragmentation channels. Accordingly, the MIKE spectrum of ions $[\mathbf{4}+\mathrm{H}]^+$ (*m/z* 347) (Fig. 2) displays only a vanishingly small signal (<1%) for the release of t-$C_4H_9^+$ ions. However, elimination of benzene still occurs, albeit to a much smaller extent as compared to the loss of isobutane. The abundance ratio of ions $[\mathbf{4}+\mathrm{H}-\mathrm{C_6H_6}]^+$ (*m/z* 269) and $[\mathbf{4}+\mathrm{H}-\mathrm{C_4H_{10}}]^+$ (*m/z* 289) is only 2.1:100, whereas it is >1 in the normal CI spectrum. The direct loss of benzene from metastable alkylbenzenium ions bearing a *tert*-butyl group has never been observed with simpler congeners. As expected, it appears that protonation of **4** at the ω-phenyl group produces metastable



Scheme 2. Separate protonation of **4** and independent fragmentation of the tautomers $[\mathbf{4}+\mathrm{H}]^+$ bearing the extra proton at the disubstituted (α-) and at the monosubstituted (ω-)arene ring.

tautomers $[\mathbf{4}+\mathrm{H}]^+$ in which the proton mobility is in fact limited to that very benzene ring by the presence of the bicyclo[2.2.2]octa-1,4-diyl spacer.

Notably, the corresponding loss of *tert*-butylbenzene (or isobutene and benzene, see below) from metastable ions $[\mathbf{4}+\mathrm{H}]^+$ does not occur, in contrast to the normal CI mass spectrum. Thus, protonation at the *tert*-butyl-substituted phenyl group of **4** induces exclusively the cleavage of the $C^{4''}$–$C(CH_3)_3$ bond (Scheme 2), in line with the general experience. In fact, hydride abstraction by the t-$C_4H_9^+$ ion within an ion/neutral complex, leading to elimination of isobutane, is the by far dominating fragmentation channel, in line with the behavior of congeners containing a flexible linker between the two arene units. However, in addition to hydride transfer to the t-$C_4H_9^+$ ion, proton transfer from this ion to the neutral partner in the complex also occurs to low extent, leading to

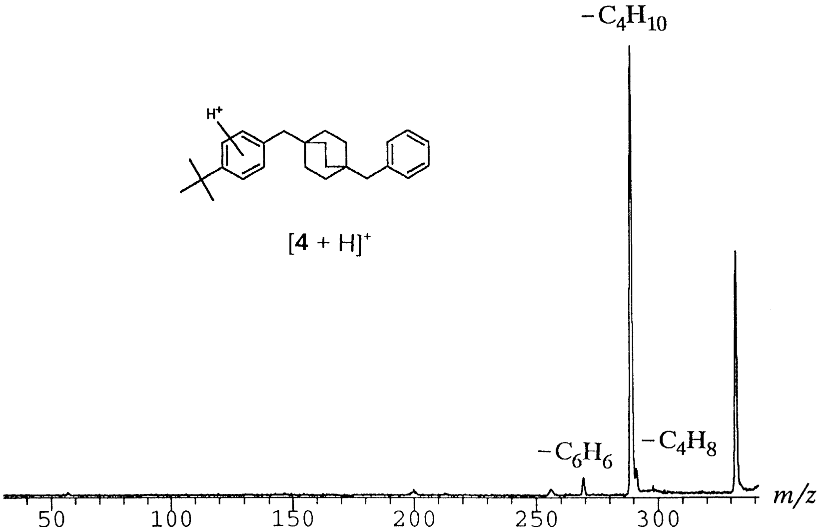


Fig. 2. MIKE spectrum of protonated 1-benzyl-4-(4-*t*-butylbenzyl)bicyclo[2.2.2]-octane [**4** + H]$^+$ (*m*/*z* 347). The signal at *m*/*z* 332 is completely due to the loss of $^{12}CH_3^{\bullet}$ from the naturally occurring isobaric radical cations [$^{13}C_1$]$\mathbf{4}^{\bullet+}$.

loss of isobutene (*m*/*z* 291, 3%). This process has never been observed in the fragmentation of simple protonated α-(*tert*-butylphenyl)-ω-phenylalkanes [7,17] but only takes place when their basicity is increased by electron-releasing substituents [18–20]. We can assume that the gas-phase basicity (GB) of the de-*tert*-butylated hydrocarbon, 1,4-dibenzylbicyclo[2.2.2]octane, is lower than the known GBs of 1,3-diphenylpropane and its higher homologues, in which internal solvation of the protonated arene ring by the second, neutral aryl group gives rise to markedly increased GB values, as compared to the lower homologues, which lack this stabilization [28–30]. Specifically, *trans*-1,4-dibenzylcyclohexane, bearing a comparably less rigid spacer between the benzyl groups, is by ca. $8\,\text{kJ}\,\text{mol}^{-1}$ less basic than flexible congeners bearing the same, or a similar, number of C–C bonds between the rings, viz., 1,6-diphenylhexane [28,30]. Likewise, *trans*-(4-phenylcyclohexyl)methyl ether has been found to be significantly less basic than the *cis*-isomer [31]. For these reasons, the proton transfer leading to loss of isobutene from metastable ions [**4** + H]$^+$ appears not to be due to an increase of the GB of the neutral constituent, 1,4-dibenzylbicyclo[2.2.2]octane, in the ion/neutral complex **5**, but rather to a decreased reactivity of this neutral hydrocarbon toward the competing hydride transfer process leading to the loss of isobutane. It is reasonable to assume significant steric hindrance during the hydride transfer step, thus, a kinetic discrimination of this process. Clearly, the neopentyl-type benzylic methylene groups as potential hydride donor sites are strongly shielded against the attack of the bulky *tert*-butyl cation. In fact, in the view of these arguments, it is rather surprising that the loss of isobutane is by far the most viable elimination channel of metastable ions [**4** + H]$^+$, accounting for 94% of their overall fragmentation (Fig. 2). Thus, the validity of the well-behaved formation of an ion/neutral complex **5** appears questionable and remains to be proven.

3.2. Deuterium labeling experiments

To investigate the course of the hydride transfer and, in particular, whether both of the benzylic methylene groups contribute to the loss of isobutane, the [α,α-D_2]- and [ω,ω-D_2]-labeled 1-benzyl-4-(4-*t*-butylbenzyl)bicyclo[2.2.2]octanes (**4a** and **4b**) were synthesized and studied by CI(CH_4)/MIKE

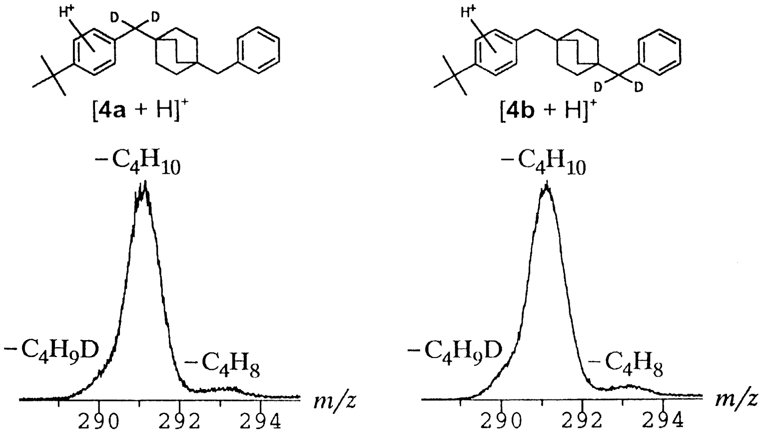
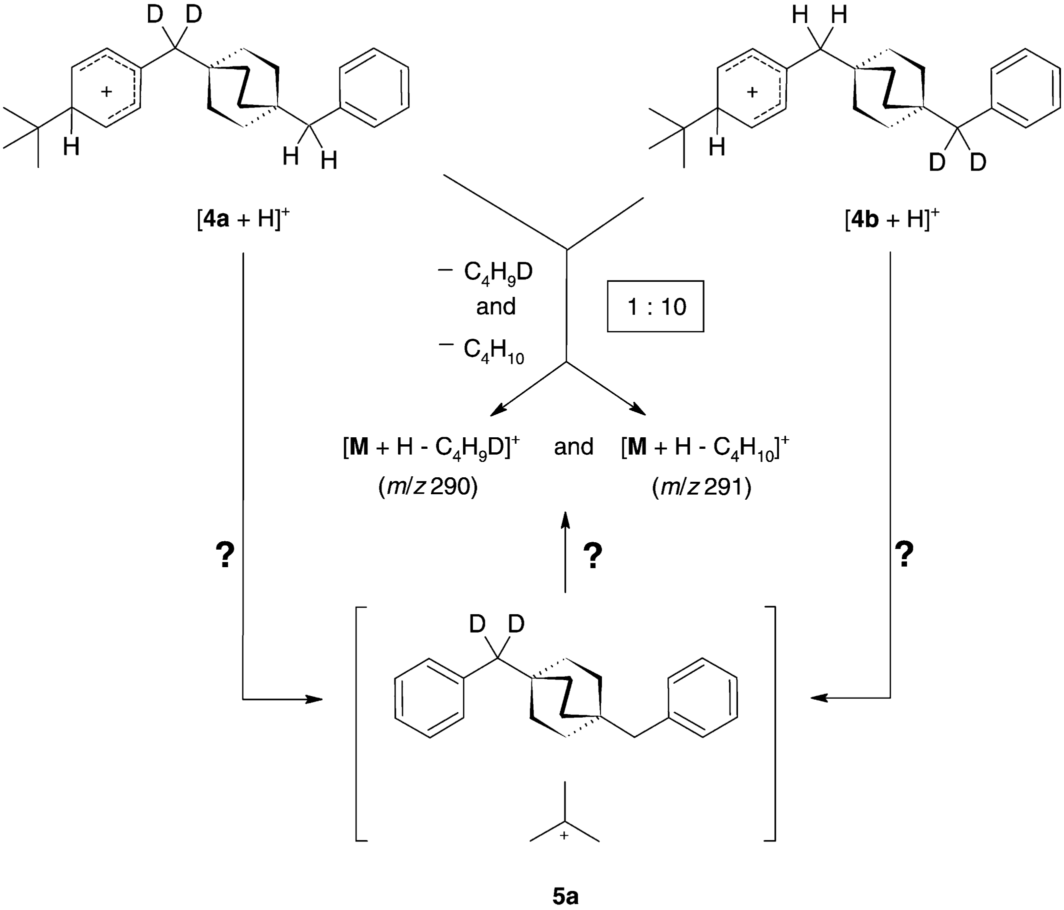


Fig. 3. Partial MIKE spectra of protonated 1-benzyl-4-(4-*t*-butyl-[α,α-D_2]benzyl)bicyclo[2.2.2]octane [**4**a + H]$^+$ and 1-[α,α-D_2]benzyl-4-(4-*t*-butyl]benzyl)bicyclo[2.2.2]octane [**4**b + H]$^+$ (both *m*/*z* 349).

spectrometry. The partial MIKE spectra of the corresponding protonated conjugates, ions [**4**a + H]$^+$ and [**4**b + H]$^+$, are reproduced in Fig. 3. In analogy to all other protonated *tert*-butyl-substituted α,ω-diphenylalkanes bearing one benzylic CH_2 and CD_2 group each, elimination of [D_0]- and [D_1]isobutane occurs with both isotopomers in the same ratio, $\{[\mathbf{4}a + H - C_4H_{10}]^+\}/\{[\mathbf{4}a + H - C_4H_9D]^+\} = \{[\mathbf{4}b + H - C_4H_{10}]^+\}/\{[\mathbf{4}b + H - C_4H_9D]^+\} = 10.0 \pm 0.5$. Here again, the identity of the MIKE spectra of the [α,α-D_2]- and [ω,ω-D_2]-labeled isotopomers indicates a symmetrization of the fragmentation process, leading to the equivalence of the two benzylic methylene groups. However, at variance to all other [α,α-D_2]- and [ω,ω-D_2]-labeled *tert*-butyl-substituted α,ω-diphenylalkanes, whose metastable [M + H]$^+$ ions exhibit, throughout, a kinetic isotope effect $k_H/k_D = 1.6$ on the isobutane loss, transfer of H^- to the t-$C_4H_9{}^+$ ions released from ions [**4**a + H]$^+$ and [**4**b + H]$^+$ is much faster transfer than that of D^-. The ratio $[C_4H_{10}]/[C_4H_9D] = 10.0 \pm 0.5$ points either to an unusually large kinetic isotope effect or to the participation of other C–H bonds as hydride donors. A strong increase of the kinetic isotope effect could be attributed to the steric hindrance of the attack of the t-$C_4H_9{}^+$ ion at the neopentyl methylene groups. The transition state for the hydride transfer could be forced into a non-linear geometry, at variance from the simpler cases. The non-availability of the second (neutral) aromatic unit as a spectator ring, that is, the lack of internal solvation, cannot be a reason for the increase of the (apparent) isotope effect, because simple, monocyclic analogues, such as protonated *tert*-butyltoluenes, also exhibit low kinetic isotope effects ($k_H/k_D = 1.5$–1.6) [6,19].

As a summary at this point, it was tempting to us to deduce from the results so far obtained the unperturbated formation of an ion/molecule complex **5** as an intermediate on the way to loss of isobutane (Scheme 3). This would have proven the ability of the t-$C_4H_9{}^+$ ion to migrate freely around the bicyclo[2.2.2]octane spacer within the complex. However, our doubts about the unusual size of the $[C_4H_{10}]/[C_4H_9D]$ ratio and its interpretation as an exceptionally high kinetic isotope effect led us to synthesize another isotopomer of **4**, bearing the deuterium label in both of the benzylic methylene groups, viz., 1-[α,α-D_2]benzyl-4-(*tert*-butyl-[α,α-D_2]benzyl)bicyclo[2.2.2]octane (**4c**). In the case of a well-behaved hydride transfer, as originally assumed for the complexes **5** and **5a** (Scheme 3), ions [**4**c+H]$^+$ should lose C_4H_9D exclusively. However, in contrast to our expectations, the CI(CH_4)/MIKE spectrum of **4c** (Fig. 4) exhibits an abundance ratio of $[C_4H_{10}]/[C_4H_9D] = 3.2 \pm 0.3$, being only a factor of 3 lower than that found for the [D_2]-isotopomers (Scheme 4).



Scheme 3. Loss of isobutane from isotopomers [4a + H]$^+$ and [4b + H]$^+$ labeled in one of the benzylic positions, and putative mechanism involving the ion/neutral complex **5a**.

Obviously, the isobutane fragment expelled from ions [**4** + H]$^+$ is formed to a large extent by abstraction of non-benzylic hydride.

It appears extremely unlikely that any of the hydride incorporated into the isobutane fragment originates from the aromatic rings. As a consequence, the bicyclo[2.2.2]octane spacer has to be assumed to be a major hydride donor, in contrast to expectation. Also, we exclude a reversible course of the hydride transfer, by which the ionic component in complex **5** would rearrange by 1,2-H shift and/or Wagner–Meerwein rearrangements (1,2-shifts) to an isomeric carbocation which would re-abstract the tertiary hydride from the isobutane constituent of the complex. On the other hand, complex rearrangements of the [**4** + H − C_4H_{10}]$^+$ ion should occur rather easily as indicated by their secondary fragmentation. In particular, the MIKE spectrum of these ions exhibits exclusive loss of benzene, a reaction which is necessarily preceded by 1,2-C shift and proton transfer to the aromatic ring [32].

To account for the unexpected finding, we suggest two different explanations (Scheme 5). Protonation of **4** in the ion CI source may give rise to skeletal rearrangement of the bicyclo[2.2.2]octane spacer, generating a mixture of isomeric metastable ions. For example, protonation of a C–C bond of the neopentane unit could generate cyclohexyl cations **6** which,

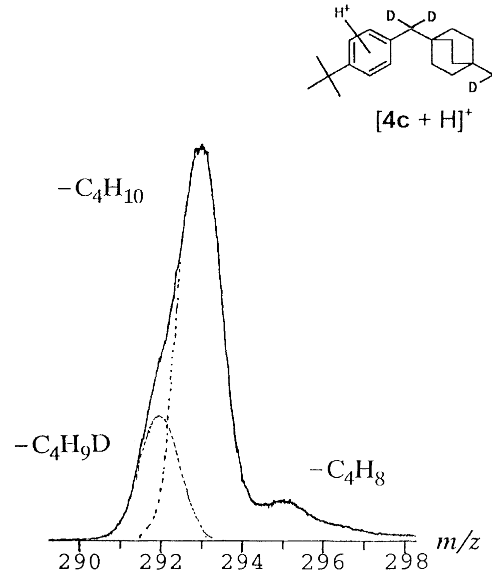
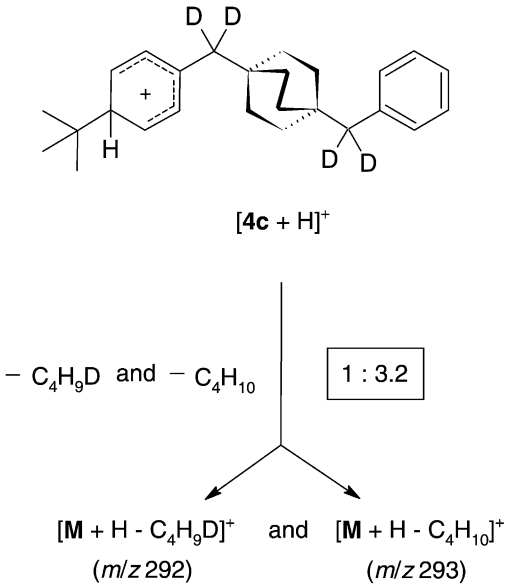


Fig. 4. Partial MIKE spectrum of protonated 1-[α,α-D_2]benzyl-4-(4-*t*-butyl-[α,α-D_2]benzyl)bicyclo[2.2.2]octane [**4**c + H]$^+$ (*m*/*z* 351).



Scheme 4. Loss of isobutane from isotopomer [**4**c + H]$^+$ labeled in both of the benzylic positions.

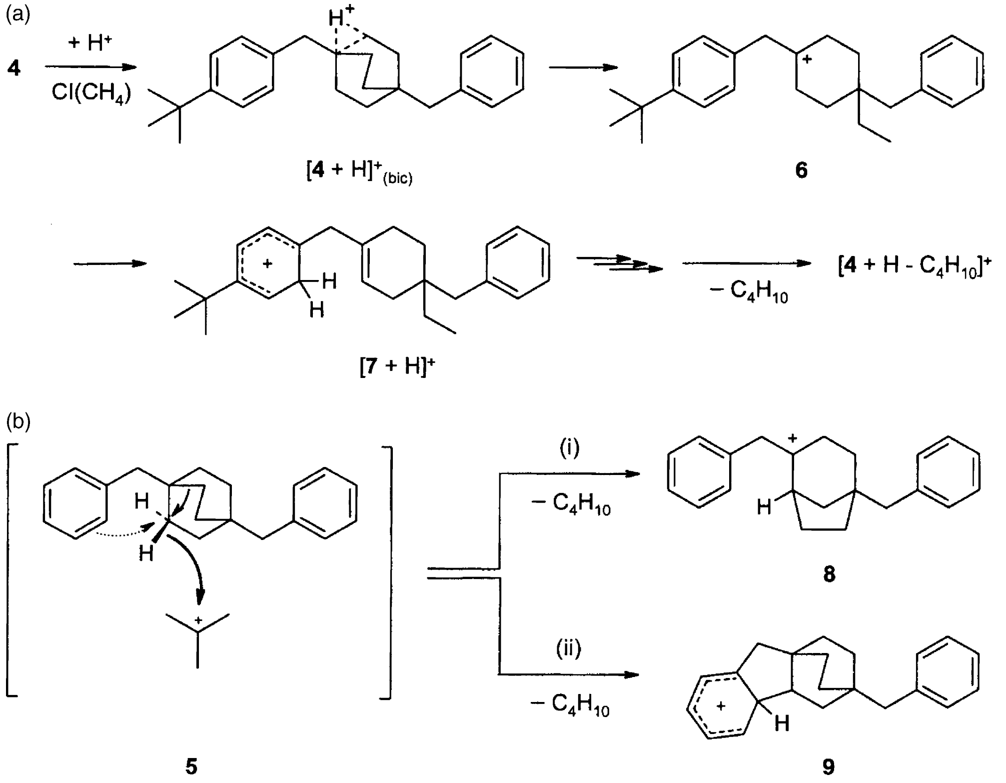
by proton transfer would generate arenium ions **7**, from which the *t*-$C_4H_9^+$ ion would be released into an ion/neutral complex and abstract a hydride (Scheme 5a). Subsequent skeletal rearrangements of ions **6** and **7** are also very likely [33].

Another mechanistic possibility consists in the direct hydride abstraction from the bicyclo[2.2.2]octane unit, involving anchimeric assistance [34] to enable hydride transfer from a secondary C–H bond (Scheme 5b) [35]. 1,2-C shift within the spacer would generate a bicyclo[3.2.1]octyl ion **8**, and probably an array of related, bicyclic isomers [36,37]. Alternatively, neighboring group participation of the adjacent benzyl group could give rise to cyclization. In fact, the framework of **4** forces the benzyl groups into close proximity to the methylene groups of the spacer. Thus, hydride transfer from the methylene group of the bicyclo[2.2.2]octane unit could be facilitated by electrophilic attack on the π-electron density of the aromatic ring [38], generating indane derivatives as their protonated conjugates, e.g., **9**.

Thus, the bicyclo[2.2.2]octane unit has turned out here to be reactive itself rather than to be an inert alicyclic spacer. This is in sharp contrast to the oligomethylene linkers used in our previous studies [7,17–20]. It is possible that the intact ions [**4** + H]$^+$, protonated at either of the aromatic rings, and isomers generated by skeletal rearrangement are formed within the CI(CH_4) ion source. In this case, a mixture of [M + H]$^+$ ions, together with related ion/molecule complexes, determine the fragmentation in the second field-free region. Less exothermic protonation conditions could help to suppress the undesired cleavage of the saturated framework of ions [**4** + H]$^+$, however, further studies into these problems are beyond the scope of this research. In addition, a study focused on the hydride transfer reactivity of bicyclo[2.2.2]octanes is warranted.

3.3. The bicyclo[2.2.2]octane unit as a precursor for bicyclo[2.2.2]octyl cations

The bicyclo[2.2.2]octyl framework can also be used as a source of the cationic component of the ion/



Scheme 5. Mechanistic suggestions for the origin of the hydride transfer from the bicyclo[2.2.2]octane spacer of **4**. (a) Proton-induced fragmentation of the bicyclic skeleton; (b) intra-complex hydride abstraction involving: (i) anchimeric assistance (full arrow); and (ii) cyclization (dashed arrow).

molecule complexes of the general type **3**, in which the *tert*-butyl cation is replaced by a bicyclo[2.2.2]oct-1-yl cation. As a part of our investigations into this field, we synthesized the bicyclo[2.2.2]oct-1-yl-substituted 1,3-diphenylpropane **10** and its [1,1-D_2]-labeled analogue **10a**. The CI(CH_4)/MIKE spectrum of the unlabeled hydrocarbon (Fig. 5) indicates the predominant loss of C_8H_{14}, presumably bicyclo[2.2.2]octane, giving $C_{15}H_{15}^+$ ions (*m/z* 195). Also, a small but marked signal for the formation of free $C_8H_{13}^+$ ions (*m/z* 109) is observed, and elimination of C_7H_{12} (*m/z* 209) occurs to a similar extent. Thus, it appears that the major reaction consists in the release of the bicyclo[2.2.2]oct-1-yl cation into a complex with neutral 1,3-diphenylpropane, which subsequently collapses by hydride abstraction and expulsion of a C_8H_{14} neutral fragment of the expected bicyclic constitution. In fact, the bicyclo[2.2.2]oct-1-yl cation represents a *tert*-butyl cation being fixed in a nonplanar geometry by the mutual connection of the three alkyl groups in the back of the carbocationic center.

Confirmation for the intermediacy of ion/molecule complex **11** is provided from the fragmentation of the metastable ions [**10**a + H]$^+$ (Fig. 6). In strict parallel to the fragmentation behavior of all *tert*-butyl-substituted protonated α,ω-diphenylalkanes and their branched congeners—except for ion [**4**+H]$^+$ and its isotopomers discussed in the present work—the competition of the intra-complex hydride and deuteride results in the usual abundance ratio of $[C_8H_{14}]/[C_8H_{13}D] = [C_4H_{10}]/[C_4H_9D] = 1.6 \pm 0.2$. Therefore, on the one hand, it is very likely that the bicyclo[2.2.2]oct-1-yl cation remains intact during its lifetime within complex **11** and can undergo hydride

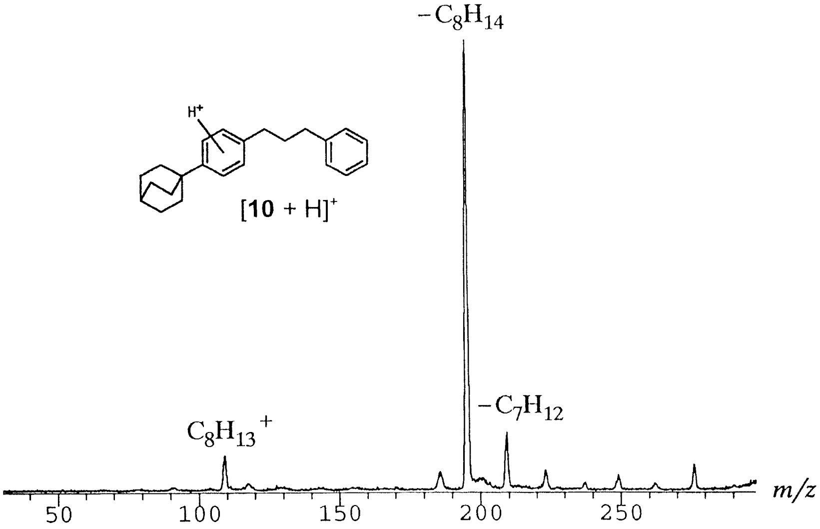


Fig. 5. MIKE spectrum of protonated 1-[4-(bicyclo[2.2.2]oct-1-yl)phenyl]-3-phenylpropane [**10** + H]$^+$ (*m/z* 305).

or deuteride abstraction from both of the (α- and the ω-)benzylic positions (Scheme 6).

On the other hand, however, the increased relative abundance of free $C_8H_{13}{}^+$ ions from metastable ions [**10** + H]$^+$ as compared to that of t-$C_4H_9{}^+$ ions in the "normal" cases (e.g., ions [**1** + H]$^+$ and even ions [**4** + H]$^+$) points to the rearrangement of the $C_8H_{13}{}^+$ ions, which give rise to isomers that are more stable than the bicyclo[2.2.2]oct-1-yl cation.[1] Accordingly, the observed elimination of C_7H_{12} from ions [**10** + H]$^+$ indicates isomerization of the bicyclo[2.2.2]octyl framework prior to the hydride transfer step. Rearrangement may take place either by protonation of the bicyclic framework, in analogy to the proton-induced cleavage of the alicyclic skeleton of ions [**4** + H]$^+$ suggested in Scheme 5, or within the bicyclo[2.2.2]oct-1-yl cation solvated in the complex **11**. Again, it is beyond the scope of this investigation to unravel the details of this—obviously complicated—isomerization. However, the fragmentation of long-lived bicyclo[2.2.2]octyl-substituted ions [**10** + H]$^+$ confirms the view that this bicyclic hydrocarbon framework tends to undergo skeletal rearrangements upon protonation in the CI(CH_4) plasma or later during the ions' lifetime. In the same time, further investigations appear to be promising to study the reactivity of more complex, bicyclic or highly

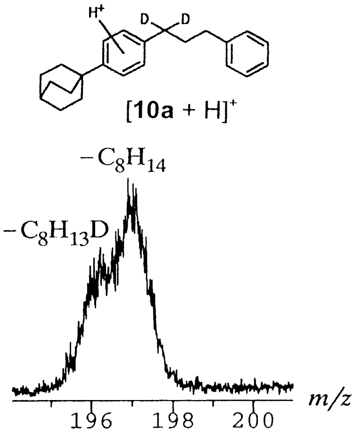
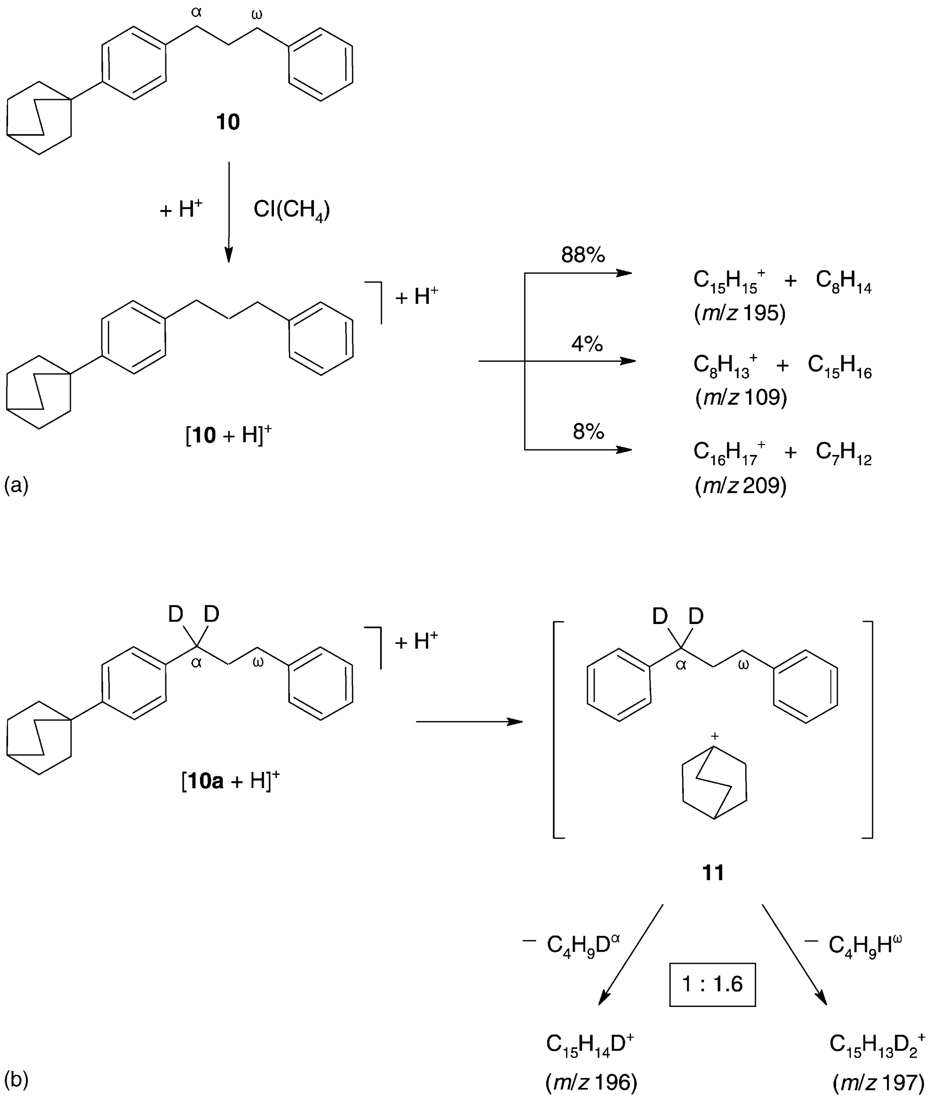


Fig. 6. Partial MIKE spectrum of protonated 1-[4-(bicyclo-[2.2.2]oct-1-yl)phenyl]-3-phenyl-[1,1-D_2]propane [**10**a + H]$^+$ (*m/z* 307).

---

[1] However, these isomers cannot be more acidic than bicyclo[2.2.2]oct-1-yl cations, which would be the case for, e.g. bicyclo[2.2.2]oct-2-yl cations: proton transfer to the neutral constituent of complex **11**, giving rise to loss of C_8H_{12}, e.g. bicyclo[2.2.2]oct-2-ene, is not observed. For papers on a related aspect concerning adamant-1-yl and adamant-2-yl cations, see Refs. [39–41].



Scheme 6. Fragmentation of metastable ions $[\mathbf{10} + \mathrm{H}]^+$ (a) and $[\mathbf{10}\mathrm{a} + \mathrm{H}]^+$ (b) generated by $\mathrm{CI(CH_4)}$.

branched, carbenium ions solvated in an ion/molecule complex with neutral partners.

4. Conclusions

This work allows us to draw three conclusions: (i) the bicyclo[2.2.2]octane grouping used as a rigid spacer unit in a protonated α,ω-diphenylalkane is not inert under $\mathrm{CI(CH_4)}$ conditions. Either it reacts by proton-induced skeletal rearrangement within the ion source or by hydride transfer to a *tert*-butyl cation generated by protonolysis of an built-in *tert*-butylbenzene unit. Thus, in contrast to its original purpose, the bicyclo[2.2.2]octa-1,4-diyl spacer cannot be used to study the mobility of the *tert*-butyl cation within ion/neutral complexes with alkylbenzenes and α,ω-diphenylalkanes, at least not under the

CI(CH_4) conditions used in the present study; (ii) the bicyclo[2.2.2]oct-1-yl substituent, representing a particular derivative of the *tert*-butyl group, can be used to generate ion/neutral complexes bearing the bicyclo[2.2.2]oct-1-yl cation. Specifically, gas-phase protonolysis of *para*-(bicyclo[2.2.2]oct-1-yl)-substituted alkylbenzenes under CI conditions provides a viable approach to study the reactivity of such complex carbocations within ion/neutral complexes; and (iii) as a special conclusion, this work has demonstrated, at least to us, that a straightforward explanation, based on the welcome convergence of the experimental results with previous findings and obvious arguments, can be strongly misleading.

Acknowledgements

We would like to thank Dr. Heinrich Sievers and Michael Asresahegn (Terrey) for valuable instrumental assistance. We are also grateful to the European Commission (HUCAMO Project No. CHRX-CT93 0291, “Fundamental Studies in Gas-phase Ion Chemistry and Mass Spectrometry”) and to the Fonds der Chemischen Industrie for financial support.

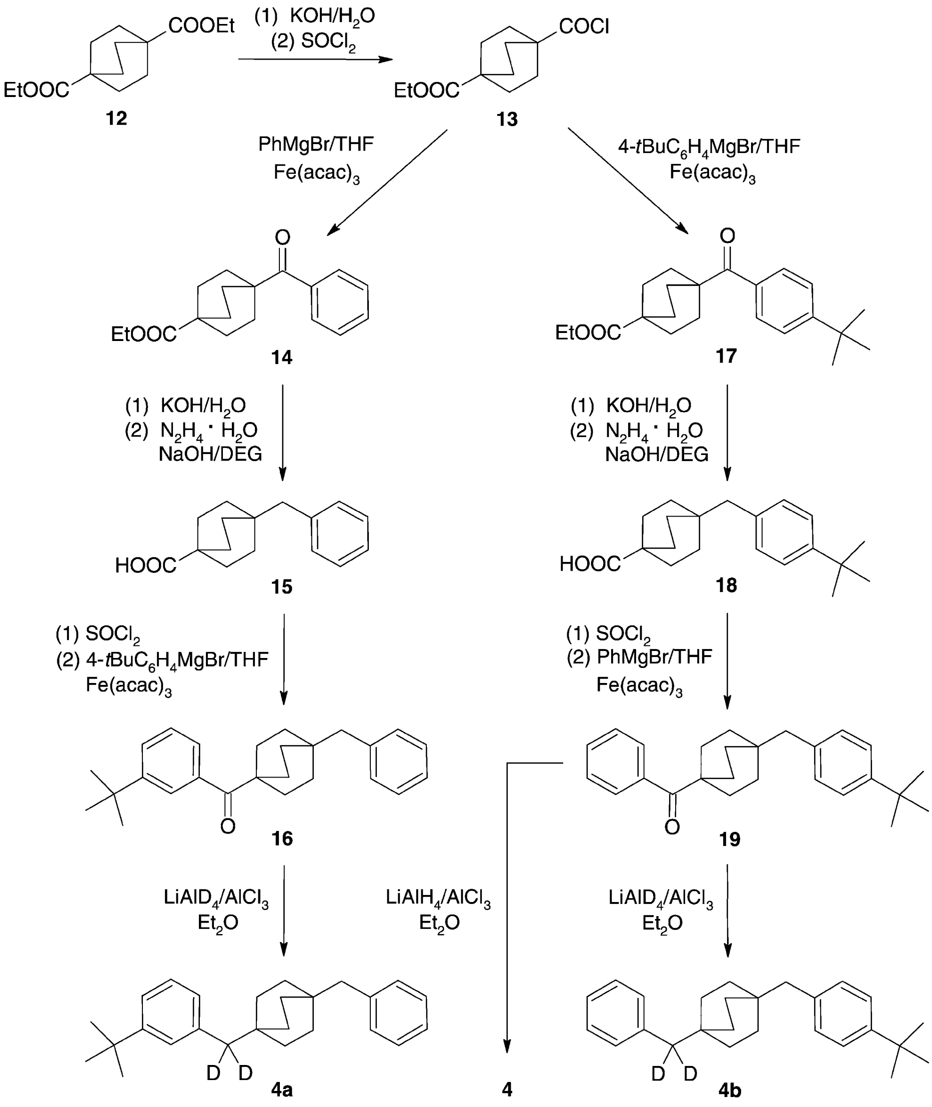
Appendix A

A.1. *tert-Butyl-substituted 1,4-dibenzylbicyclo[2.2.2]octanes (**4**, **4a** and **4b**)*

Because of the unsymmetrical structure of **4** and its labeled analogues **4a**–**4c**, the syntheses of these neutral precursors comprised multistep procedures, as sketched in Scheme 7. Details on the individual steps and intermediate products will be reported elsewhere [42]. However, a brief description is given here.

Diethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (**12**) was synthesized according to published procedures [43]. The corresponding diacid monoethyl ester was prepared [43] and converted to the monoester monochloride **13** by using thionyl chloride. Introduction of one appropriate aryl group proved successful only by applying the $Fe(acac)_3$-catalyzed C–C coupling [44] of **13** with the Grignard compounds prepared from bromobenzene and 4-bromo-1-*tert*-butylbenzene. In this manner, ethyl 1-benzoylbicyclo[2.2.2]octane-4-carboxylate (**14**, mp 62.5–64 °C, EtOH) and ethyl 1-(4-*t*-butylbenzoyl)bicyclo[2.2.2]octane-4-carboxylate (**17**, mp 52–53.5 °C, EtOH), respectively, were obtained in good yields. Saponification of the residual ester functionalities afforded the corresponding 4-substituted bicyclo[2.2.2]octane acids, which were converted to 1-benzylbicyclo[2.2.2]octane-4-carboxylic acid (**15**, mp 177 °C, *n*-hexane) and 1-(4-*t*-butylbenzyl)bicyclo[2.2.2]octane-4-carboxylic acid (**18**, mp 208–211 °C, *n*-hexane), respectively, by Wolff–Kishner reduction in diethylene glycol. Subsequent treatment of **15** and **18** with thionyl chloride, followed by $Fe(acac)_3$-catalyzed reactions of the respective acid chlorides with 4-*t*-butylphenylmagnesium bromide and phenylmagnesium bromide furnished the corresponding benzyl-benzoyl derivatives of bicyclo[2.2.2]octane, viz., 1-benzyl-4-(4-*t*-butylbenzoyl)bicyclo[2.2.2]octane (**16**, mp 87 °C, EtOH) and 1-benzoyl-4-(4-*t*-butylbenzyl)bicyclo[2.2.2]octane (**19**, mp 102–103 °C, EtOH). Finally, chloroalane reduction of **19** using $LiAlH_4/AlCl_3$ in diethyl ether yielded the unlabeled hydrocarbon, 1-benzyl-4-(4-*t*-butylbenzyl)bicyclo[2.2.2]octane (**4**) as a colorless solid, 83–86.5 °C (EtOH). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.29 (s, 9 H), 1.35 (s, 12 H), 2.33 (s, 2 H), 2.37 (s, 2 H), 6.94–6.97 (m, 2 H), 7.02–7.05 (m, 2 H), 7.16–7.26 (m, 5 H); mass spectrum (EI, 70 eV): *m/z* 346 (45, $M^{\bullet +}$), 331 (76), 199 (41), 147 (43), 143 (34), 132 (32), 117 (49), 105 (13), 95 (37), 91 (100), 57 (95); IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3031, 3005, 2931, 2859, 1601, 1512, 1494, 1453, 1442, 1410, 1361, 1259, 1115, 1076, 835, 818, 766, 700, 660. $C_{26}H_{34}$ calcd. 346.2661, found: 346.2658.

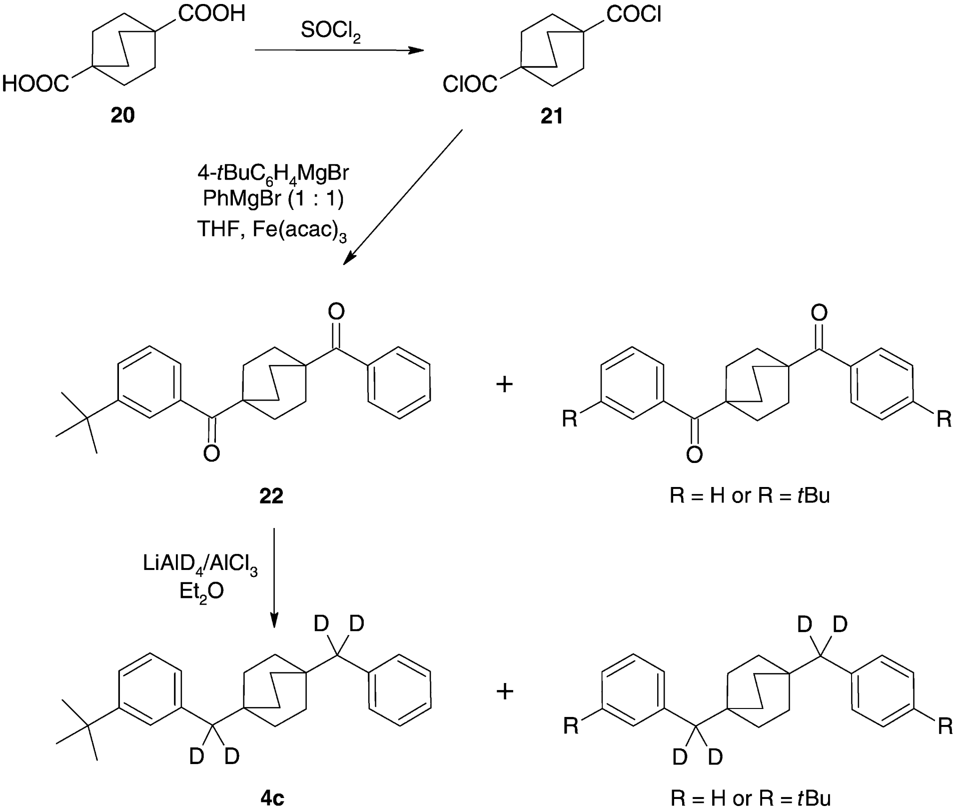
Reduction of ketone **16** with $LiAlD_4/AlCl_3$ in diethyl ether afforded 1-benzyl-4-(4-*t*-butyl-[α,α-D_2]benzyl)bicyclo[2.2.2]octane (**4a**) as a colorless solid, mp 85–87.5 °C (EtOH). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.29 (s, 9 H), 1.35 (s, 12 H), 2.37 (s, 2 H), 6.94–6.97 (m, 2 H), 7.01–7.04 (m, 2 H), 7.15–7.30 (m, 5 H); mass spectrum (EI, 70 eV): *m/z* 348 (60, $M^{\bullet +}$), 333



Scheme 7. Multistep synthesis routes to hydrocarbons **4**, **4a**, and **4b**.

(68), 201 (10), 199 (37), 149 (23), 143 (26), 134 (19), 119 (14), 117 (28), 95 (28), 91 (77), 57 (100). D content (mass spectrometry): 96% (94% d_2, 4% d_1, 3% d_0). A minor by-product bearing a chlorine instead of a deuterium atom (i.e., an α-CDCl group) was identified by mass spectrometry and ^{1}H NMR spectroscopy (δ 2.38 (s, ω-CH$_2$)).

Reduction of ketone **19** with $LiAlD_4/AlCl_3$ in diethyl ether furnished 1-(α,α-[D$_2$]benzyl)-4-(4-*t*-butylbenzyl)bicyclo[2.2.2]octane (**4b**, mp 78–80 °C, EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.29 (s, 9 H), 1.35 (s, 12 H), 2.33 (s, 2 H), 6.94–6.97 (m, 2 H), 7.02–7.05 (m, 2 H), 7.15–7.26 (m, 5 H); mass spectrum (EI, 70 eV): *m/z* 348 (49, $M^{\bullet+}$), 333 (83), 201 (32), 199 (15), 147 (48), 145 (24), 132 (39), 119 (20), 117 (35), 105 (9), 93 (77), 92 (30), 91 (30), 57 (100). D content (mass spectrometry): 95% (91% d_2, 8% d_1, 1% d_0). A minor by-product bearing a chlorine

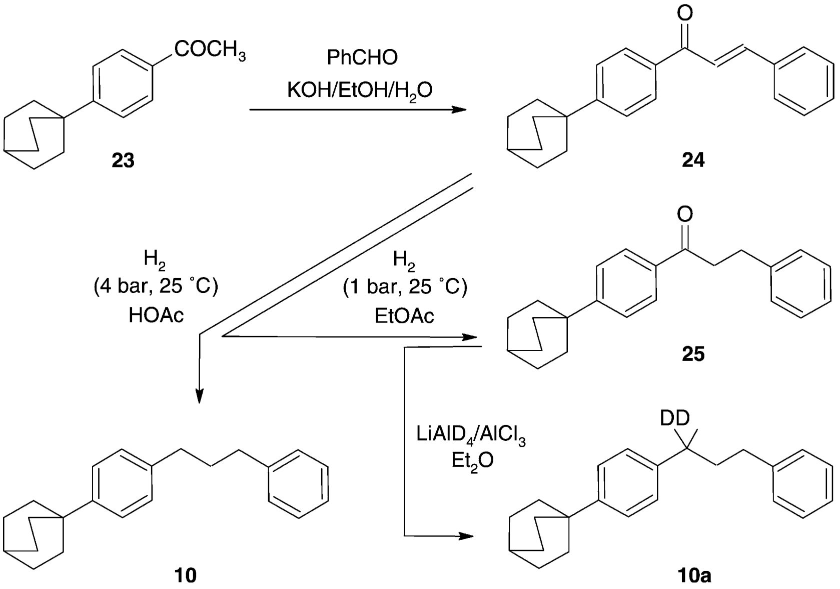


Scheme 8. Synthesis of isotopomers **4c** in a mixture with its analogues bearing no or two *para*-(*tert*-butyl) substituents.

instead of a deuterium atom (i.e., an α-CDCl group) was identified by mass spectrometry and ^{1}H NMR spectroscopy (δ 2.35 (s, ω-CH_2)).

A.2. *tert-Butyl-substituted 1,4-dibenzylbicyclo[2.2.2]octane (**4c**)*

Isotopomer **4c** labeled in both of the benzylic methylene groups was obtained by an independent approach (Scheme 8). Bicyclo[2.2.2]octane 1,4-dicarboxylic acid **20** [45] was converted into the diacid dichloride **21** [46], which was then reacted with a mixture of 4-*t*-butylphenylmagnesium bromide and phenylmagnesium bromide (prepared from a 1:1 mixture of the corresponding bromobenzenes) in the presence of Fe(acac)$_3$. This furnished an ca. 2:1:1 mixture of 1-benzoyl-4-(4-*t*-butyl-benzoyl)bicyclo[2.2.2]octane (**22**), 1,4-dibenzoylbicyclo[2.2.2]octane and 1,4-di(4-*t*-butylbenzoyl)bicyclo[2.2.2]octane, as documented by mass spectrometry and ^{1}H NMR. This mixture was then subjected to chloroalane reduction using LiAlD$_4$/AlCl$_3$ in diethyl ether, yielding a ca. 2:1:1 mixture of 1-[α,α-D_2]benzyl-4-(4-*t*-butyl-[α,α-D_2]benzyl)bicyclo[2.2.2]octane **4c**, 1,4-di-([α,α-D_2]benzyl) bicyclo[2.2.2]octane and 1,4-di(4-*t*-butyl-[α,α-D_2]benzyl)bicyclo[2.2.2]octane as a colorless solid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.29 (s, 9 H), 1.34 (s, 12 H), 6.956 (d, $^3J \approx 8.3$ Hz, 2 H), 7.027 (m, $^3J \approx 7.0$ Hz, 2 H), 7.115 (t, $^3J \approx 7.4$ Hz, 1 H), 7.205–7.242 (m, ca. 4 H); mass spectrum (EI, 70 eV): *m*/*z* 406 (9, M$^{\bullet+}$), 391 (14) 350 (25, **4c**$^{\bullet+}$), 335 (39), 294 (12, M$^{\bullet+}$), 279 (24), 57 (100). D content of **4c** (mass



Scheme 9. Synthesis routes to hydrocarbons **10** and **10a**.

spectrometry): 95% (89% d_4, 9% d_3, 2% d_2). Minor by-products bearing a chlorine instead of a deuterium atom were identified by mass spectrometry.

*A.3. Bicyclo[2.2.2]oct-1-yl-substituted 1,3-diphenylpropanes (**10** and **10a**)*

The bicyclo[2.2.2]oct-1-yl-substituted 1,3-diphenylpropanes (**10** and **10a**) were synthesized by starting from 4-(bicyclo[2.2.2]oct-1-yl)acetophenone (**23**) and benzaldehyde (Scheme 9). Base-catalyzed condensation gave the corresponding chalcone **24**, 1-[4-(bicyclo[2.2.2]oct-1-yl)phenyl]-3-phenylprop-2-en-1-one as a yellow solid, mp 141 °C (EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.69–1.75 (m, 7 H), 1.81–1.85 (m, 6 H), 7.39–7.43 (m, 3 H), 7.45 and 7.96 (AA′BB′, $^3J = 8.6$ Hz, 4 H), 7.54 and 7.81 (AB, $^3J = 15.7$ Hz, 2 H), 7.62–7.66 (m, 2 H); MS (EI, 70 eV): *m*/*z* 316 (100, $M^{\bullet +}$), 315 (76), 287 (287 (12), 259 (22), 233 (12), 207 (30), 131 (84), 115 (17), 109 (23), 103 (48), 87 (42), 77 (28)); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3028, 2941, 2863, 1655, 1608, 1596, 1448, 1336, 1210, 1012, 992, 980, 767. $C_{23}H_{24}O$ (316.45), calcd. C 87.30, H 7.64, found: C 87.25, H 7.65.

Catalytic hydrogenation of **24** in glacial acetic acid with Pd/C under 4 bar of hydrogen afforded hydrocarbon **10**, 1-[4-(bicyclo[2.2.2]oct-1-yl)phenyl]-3-phenylpropane, as a colorless oil, bp 185 °C/0.01 mbar (kugelrohr). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.67–1.70 (m, 7 H), 1.76–1.78 (m, 6 H), 1.94 (t, $^3J = 7.8$ Hz, 2 H), 2.61 (t, $^3J = 7.7$ Hz, 2 H), 2.65 (t, $^3J = 7.7$ Hz, 2 H), 7.10 and 7.22 (AA′BB′, $^3J = 8.4$ Hz, 4 H), 7.15–7.30 (m, 5 H); mass spectrum (EI, 70 eV): *m*/*z* 304 (83, $M^{\bullet +}$), 275 (17), 248 (15), 199 (13), 185 (29), 144 (26), 143 (28), 129 (43), 117 (20), 115 (25), 105 (24), 91 (100), 79 (18), 77 (15), 57 (24), 41 (32); IR (film): $\bar{\nu}$ (cm^{-1}) 3029, 2941, 2863, 1514, 1495, 1453, 830, 748, 697. $C_{23}H_{28}$ calcd. 304.2191, found: 304.2188.

Catalytic hydrogenation of **24** in ethyl acetate with Pt (from $PtO_2 \cdot xH_2O$) under 1 bar of hydrogen afforded dihydrochalcone **25**, 1-[4-(bicyclo[2.2.2]oct-1-yl)phenyl]-3-phenylpropan-1-one, as a colorless solid, mp 87 °C (EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.69–1.72 (m, 7 H), 1.77–1.81 (m, 6 H), 3.05 (t, $^3J =$

7.7 Hz, 2 H), 3.28 (t, $^3J = 7.8$ Hz, 2 H), 7.18–7.33 (m, 5 H), 7.39 and 7.89 (AA′BB′, $^3J = 8.6$ Hz, 4 H); mass spectrum (EI, 70 eV): *m/z* 318 (9, $M^{\bullet +}$), 213 (100), 209 (54), 208 (21), 157 (10), 128 (9), 115 (11), 105 (9), 91 (23); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3434, 2940, 2861, 1685, 1603, 1452, 1404, 1246, 1232, 1209, 1187, 975, 826, 818, 745, 698. $C_{23}H_{26}O$ (318.46), calcd. C 86.75, H 8.23, found: C 86.54, H 8.30.

Chloroalane reduction of **25** with $LiAlD_4/AlCl_3$ in diethyl ether afforded the labeled isotopomer **10a**, 1-[4-(bicyclo[2.2.2]oct-1-yl)phenyl]-3-phenyl-[1,1-D_2]propane as a colorless oil, bp 180 °C/0.01 mbar (kugelrohr). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.67–1.70 (m, 7 H), 1.75–1.80 (m, 6 H), 1.93 (t, $^3J = 7.7$ Hz, 2 H), 2.65 (t, $^3J = 7.7$ Hz, 2 H), 7.10 and 7.22 (AA′BB′, $^3J = 8.4$ Hz, 4 H), 7.15–7.30 (m, 5 H); mass spectrum (EI, 70 eV): *m/z* 306 (100, $M^{\bullet +}$), 277 (22), 250 (16), 201 (15), 185 (42), 157 (15), 146 (28), 145 (33), 129 (46), 119 (15), 148 (16), 117 (13), 109 (20), 105 (18), 93 (30), 92 (26), 91 (48), 79 (16), 57 (11), 41 (16). D content (mass spectrometry): 86% (73% d_2, 26% d_1, 1% d_0).

References

[1] A.G. Harrison, Chemical Ionization Mass Spectrometry, 2nd ed., CRC Press, Boca Raton, 1992.
[2] W.J. Richter, H. Schwarz, Angew. Chem. 90 (1978) 449;
W.J. Richter, H. Schwarz, Angew. Chem. Int. Ed. Engl. 17 (1978) 424.
[3] J.A. Herman, A.G. Harrison, Org. Mass Spectrom. 16 (1981) 423.
[4] (a) D. Berthomieu, H.E. Audier, J.P. Denhez, C. Monteiro, P. Mourgues, Org. Mass Spectrom. 26 (1991) 271;
(b) D. Berthomieu, H.E. Audier, C. Monteiro, J.P. Denhez, Rapid Commun. Mass Spectrom. 5 (1991) 415
[5] For reviews on protonated alkylbenzenes and H/D scrambling, see: (a) D. Kuck, Mass Spectrom. Rev. 9 (1990) 583;
(b) D. Kuck, Int. J. Mass Spectrom. 213 (2002) 101.
[6] (a) D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié, H.E. Audier, J. Phys. Chem. 99 (1995) 712;
(b) H.E. Audier, C. Monteiro, P. Mourgues, D. Berthomieu, Org. Mass Spectrom. 25 (1990) 245.
[7] D. Kuck, C. Matthias, J. Am. Chem. Soc. 114 (1992) 1901.
[8] J.P. Denhez, H.E. Audier, D. Berthomieu, Rapid Commun. Mass Spectrom. 9 (1995) 1210.
[9] D. Kuck, J. Schneider, H.F. Grützmacher, J. Chem. Soc. Perkin Trans. II (1985) 689.
[10] M. Mormann, D. Kuck, Int. J. Mass Spectrom. 219 (2002) 497.
[11] M.S.B. Munson, F.H. Field, J. Am. Chem. Soc. 89 (1967) 1047.
[12] A.G. Harrison, P.H. Lin, H.W. Leung, Adv. Mass Spectrom. 7B (1978) 1394.
[13] C. Wesdemiotis, H. Schwarz, C.C. van de Sande, F. van Gaever, Z. Naturforsch. 34b (1979) 495.
[14] S. Fornarini, Mass Spectrom. Rev. 15 (1996) 365.
[15] S. Fornarini, M.E. Crestoni, Acc. Chem. Res. 31 (1998) 827.
[16] D. Kuck, W. Bäther, H.-F. Grützmacher, J. Am. Chem. Soc. 101 (1979) 7154.
[17] C. Matthias, D. Kuck, Org. Mass Spectrom. 28 (1993) 1073.
[18] C. Matthias, K. Weniger, D. Kuck, Eur. Mass Spectrom. 1 (1995) 445.
[19] C. Matthias, S. Anlauf, K. Weniger, D. Kuck, Int. J. Mass Spectrom. 199 (2000) 155.
[20] C. Matthias, D. Kuck, Int. J. Mass Spectrom. 217 (2002) 131.
[21] (a) D. Heidrich, Angew. Chem. 114 (2002) 3343;
(b) D. Heidrich, Angew. Chem. Int. Ed. Engl. 41 (2002) 3208.
[22] A. Filippi, G. Roselli, G. Renzi, F. Grandinetti, M. Speranza, Chem. Eur. J. 9 (2003) 2072.
[23] D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié, H.E. Audier, J. Am. Chem. Soc. 115 (1993) 2505.
[24] J.C. Ma, D.A. Dougherty, Chem. Rev. 97 (1997) 1303.
[25] J.P. Denhez, H.E. Audier, D. Berthomieu, Org. Mass Spectrom. 28 (1993) 704.
[26] F. Cacace, M.E. Crestoni, S. Fornarini, D. Kuck, J. Am. Chem. Soc. 115 (1993) 1024For the effect of *cis*- and *trans*-1,4-diyl spacers, see:.
[27] D. Kuck, D. Thölmann, H.F. Grützmacher, J. Chem. Soc. Perkin Trans. 2 (1990) 251.
[28] M.E. Crestoni, S. Fornarini, D. Kuck, J. Phys. Chem. 99 (1995) 3150.
[29] M. Meot-Ner (Mautner), P. Hamlet, E.P. Hunter, F.H. Field, J. Am. Chem. Soc. 100 (1978) 5466.
[30] E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413.
[31] A. Mandelbaum, Adv. Mass Spectrom. 13 (1994) 227.
[32] D. Kuck, manuscript in preparation.
[33] P. Vogel, Carbocation Chemistry, Elsevier, Amsterdam, 1985.
[34] (a) M.E. Crestoni, S. Fornarini, M. Lentini, M. Speranza, J. Chem. Soc. Chem. Commun. (1995) 121;
(b) M.E. Crestoni, S. Fornarini, M. Lentini, M. Speranza, J. Phys. Chem. 100 (1996) 8285.
[35] P. Ausloos, S.G. Lias, J. Am. Chem. Soc. 92 (1970) 5037.
[36] M. Mormann, D. Kuck, J. Mass Spectrom. 34 (1999) 384.
[37] M. Mormann, D. Kuck, Int. J. Mass Spectrom. 210/211 (2001) 531.
[38] D. Kuck, Int. J. Mass Spectrom. Ion Process. 117 (1992) 441.
[39] (a) C. Wesdemiotis, M. Schilling, H. Schwarz, Angew. Chem. 91 (1979) 1017;
(b) C. Wesdemiotis, M. Schilling, H. Schwarz, Angew. Chem. Int. Ed. Engl. 18 (1979) 950.
[40] (a) R. Houriet, H. Schwarz, Angew. Chem. 91 (1979) 1018;
(b) R. Houriet, H. Schwarz, Angew. Chem. Int. Ed. Engl. 18 (1979) 951.

[41] H. Schwarz, M.T. Reetz, W.F. Maier, C. Wesdemiotis, I. Chatziiosifides, M. Schilling, Angew. Chem. 91 (1979) 1019; H. Schwarz, M.T. Reetz, W.F. Maier, C. Wesdemiotis, I. Chatziiosifides, M. Schilling, Angew. Chem. Int. Ed. Engl. 18 (1979) 952.

[42] C. Matthias, D. Kuck, unpublished results; See C. Matthias, Doctoral thesis, Universität Bielefeld, 1996.

[43] J.D. Roberts, W.T. Moreland Jr., W. Frazer, J. Am. Chem. Soc. 75 (1953) 637.

[44] V. Fiandanese, G. Marchese, V. Martina, L. Ronzini, Tetrahedron Lett. 25 (1984) 4805.

[45] M.J.S. Dewar, R.S. Goldberg, J. Am. Chem. Soc. 92 (1970) 1582.

[46] J.C. Kauer, R.E. Benson, G.W. Parshall, J. Org. Chem. 30 (1965) 1431.