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# Large hydrocarbon ion/molecule complexes formed during the unimolecular fragmentation of protonated *tert*-butyl-substituted tri- and tetrabenzylmethane

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In memoriam Pierre Longevialle.

**Abstract**

The reactivity of two large gaseous ion/neutral complexes generated by protonolysis of *tert*-butyl-substituted tribenzylmethane (**1**) and *tert*-butyl-substituted tetrabenzylmethane (**3**) has been studied on the metastable ion time scale. These complexes, [*t*-$C_4H_9^+$($C_6H_5CH_2$)$_3$CH] and [*t*-$C_4H_9^+$($C_6H_5CH_2$)$_4$C], undergo competitive intra-complex proton transfer from the ionic component and hydride transfer to the ionic component, generating isobutene and isobutane, respectively. The hydride transfer process involves all of the benzylic methylene groups with the same probabilities, i.e., without any regioselectivity, demonstrating the formation of truly non-covalent adducts in which the ionic constituent moves relatively freely with respect to the neutral partner. The kinetic isotope effect found ubiquitously for simpler *tert*-butylbenzenium ions, $k_H/k_D = 1.6$, operates in these large all-hydrocarbon complexes as well. The facile protonolytic release of the *t*-$C_4H_9^+$ ion into the complexes does not suppress the fast and apparently complete exchange between the 15 and, respectively, 20 protons at the aromatic rings of ions $[\mathbf{1} + H]^+$ and $[\mathbf{3} + H]^+$. In both cases, loss of isobutane from the ion/molecule complexes is followed by fast elimination of one or even two molecules of benzene. Similarly, loss of isobutene from $[\mathbf{3} + H]^+$ is followed by a fast two-fold benzene elimination. This is evident from the unusual observation that two or even three neutral hydrocarbon molecules are expelled within the same field-free region of the sector-field mass spectrometer. (Int J Mass Spectrom 217 (2002) 131–151)


*Keywords:* Ion/molecule complexes; Metastable ions; Hydride transfer; Proton transfer; H/D exchange; Cyclization reactions; *tert*-Butylbenzenes

## 1. Introduction

### 1.1. Prologue

The lively discussion on the formation of ion/neutral complexes in the course of the unimolecular fragmentation of gaseous organic ions has been clearly resolved. Pierre Longevialle was one of the most convincing (although always remarkably modest) protagonists in the debate on the existence of gaseous ion/molecule complexes. Back in the 1980s, he would answer doubtful and even challenging comments on his important discoveries by asking, with some disappointment: "So you don't believe it?" More than two decades later, the existence of ion/neutral complexes formed by a primary fragmentation step and

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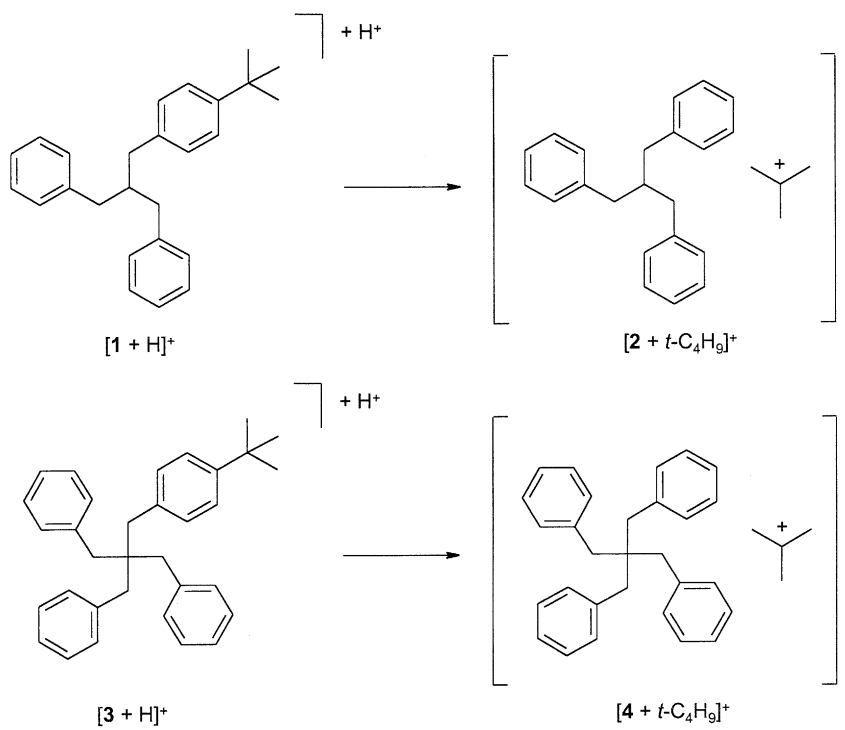
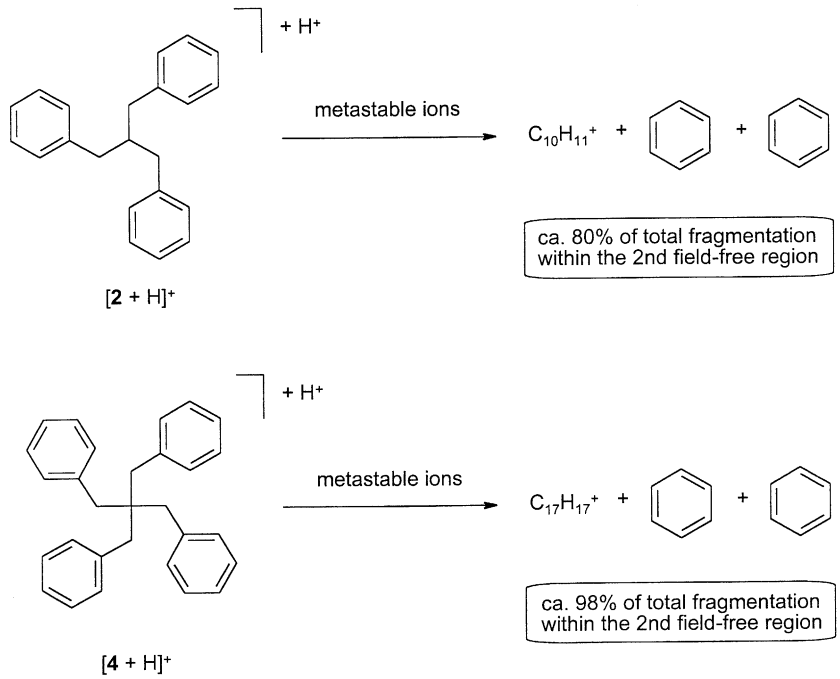
the (most relevant) possibility of subsequent chemical reaction between the partners within that complex—producing unexpected fragment ions and thus unexpected (and possibly "irritating") peaks in the mass spectrum—has been completely accepted. What has been left in this domain of organic mass spectrometry is to explore, on the one hand, the structural and thermodynamic features of a compound and the experimental conditions which enable the occurrence of ion/molecule-mediated fragmentation pathways and, on the other, to design the formation of ion/molecule complexes to perform directed fundamental studies on their intrinsic reactivity. Thanks to Pierre, inter alia, we have been encouraged to keep this fascinating aspect of fundamental gas-phase ion chemistry in mind.

### *1.2. Large all-hydrocarbon ion/molecule complexes*

The observation of hydrogen transfer reactions occurring between functional groups which are mutually inaccessible for steric reasons in convalently bound molecular or fragment ions generated from large organic molecules such as steroids, in particular [1–6], was a major key to the discovery of ion/neutral complexes [2–10]. Since, through ion/dipole interactions, the presence of polar functional groups in the precursor ion is considered a favorable factor for the intermediacy of ion/neutral complexes during unimolecular fragmentation, many steroid-type ions represent good candidates for complex formation. Remarkably, for a long time, there have been only a few convincing examples for the occurrence of *reactive* ion/neutral complexes during the fragmentation of hydrocarbon-derived ions, that is, complexes which contain a neutral component of low dipole moment but potentially large polarizability. These examples were restricted to the fragmentation of alkane radical cations [10–13]. Ion/molecule complexes derived from aromatic hydrocarbons were discovered through intramolecular proton exchange [14–17], but




Scheme 1. Unimolecular formation of the complexes of *tert*-butyl cations and tribenzylmethane **2** and tetrabenzylmethane **4**.




Scheme 2. Predominant consecutive loss of two molecules of benzene from protonated tri- and tetrabenzylmethane.

an intriguing hint to the formation of "large" hydrocarbon ion/molecule complexes was obtained by ourselves based on the observation of a fast consecutive loss of two benzene molecules from protonated oligophenylisoalkanes (cf. Scheme 2) [18,19]. Only in 1990, Audier et al. disclosed compelling evidence for the intermediacy of all-hydrocarbon ion/molecule complexes based on a necessarily intra-complex hydride transfer [20]. For this reason, we then started a series of studies on large arylaliphatic hydrocarbon ions which, akin to their lower, mononuclear congeners [20,21], undergo a highly characteristic hydride transfer reaction indicative of ion/molecule complexes as intermediates during unimolecular fragmentation [22–25]. Thus, α,ω-diphenylalkanes of varying chain lengths bearing a *tert*-butyl group at one of the aromatic rings were found to undergo loss of isobutane, $C_4H_{10}$, after protonation in the CI($CH_4$) plasma. Protonolytic release of the *t*-$C_4H_9^+$ ion generates a complex of the cation and the de-*tert*-butylated α,ω-diphenylalkane, which fragments only after "intra-complex" hydride transfer from either of the benzylic (α or ω) methylene groups of the aliphatic chain to the *t*-$C_4H_9^+$ ion. Additional substituents on the aromatic rings were found to markedly affect the regioselectivity of the hydride transfer, and the preferred coordination of the *reacting* carbocation between the two aromatic rings was suggested [25].

In this paper, we present the extension of this approach to even larger ion/molecule complexes (Scheme 1). By analogy to our studies on the fast proton transfer in protonated tri- and tetraphenylisoalkanes [26], we have investigated the fragmentation of long-lived protonated *tert*-butyl-substituted tribenzylmethane $[\mathbf{1} + H]^+$ and tetrabenzylmethane $[\mathbf{3} + H]^+$ by means of deuterium labeling and MIKE spectrometry. It will be demonstrated here that, in fact, these large oligonuclear alkylbenzenium ions react via the all-hydrocarbon ion/molecule complexes $[\mathbf{2} + t\text{-}C_4H_9^+]$ and $[\mathbf{4} + t\text{-}C_4H_9^+]$, respectively, containing tribenzylmethane (**2**) and tetrabenzylmethane

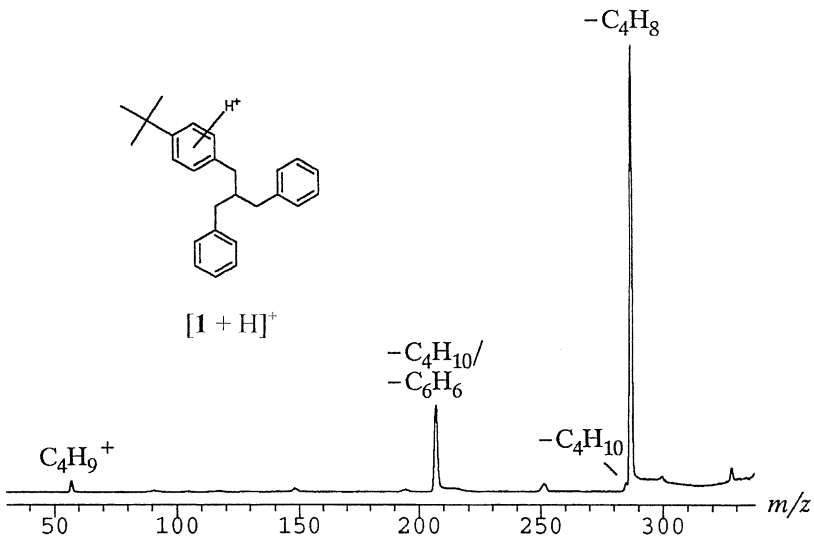



Fig. 1. CI($CH_4$)/MIKE spectrum of protonated *tert*-butyl-substituted tribenzylmethane 1 (*m/z* 343). The small unassigned signals indicate fragmentations of isobaric $M^{\bullet+}$ ions containing naturally occurring $^{13}C$.

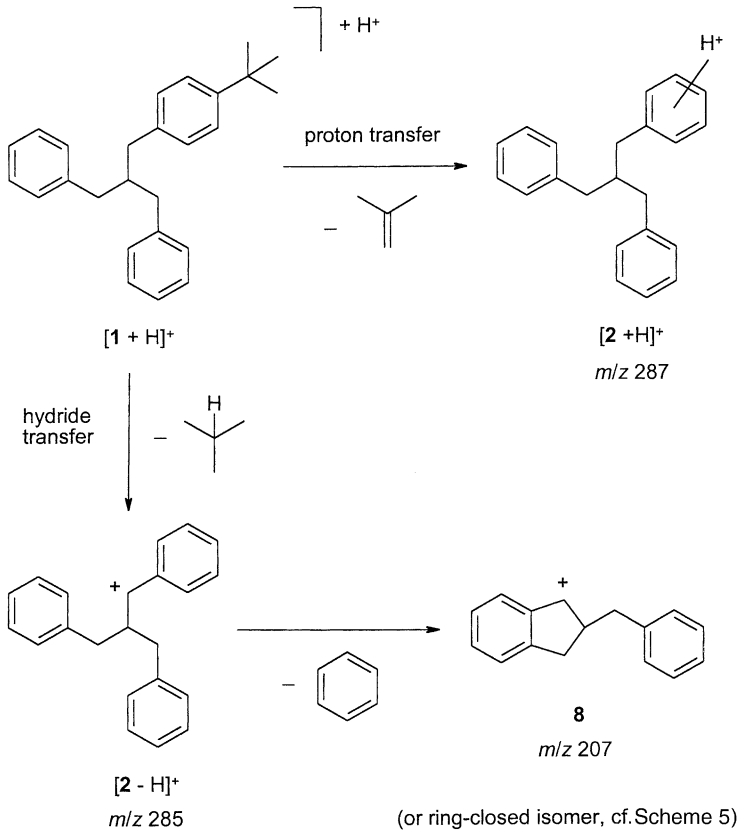
(**4**) as the neutral components. This study also provides evidence for the remarkable two-fold or even three-fold loss of neutral fragments from long-lived metastable ions within the same field-free region of a sector-field mass spectrometer, a phenomenon which has been treated in detail recently for the respective protonated parent hydrocarbons, $[\mathbf{2} + H]^+$ and $[\mathbf{4} + H]^+$ [19]. As mentioned above, the elimination of two molecules of benzene from a reactive ion *within the same field-free region* had intrigued us during the past decades with respect to the possible intermediacy of ion/molecule complexes [18,19].

## 2. Results and discussion

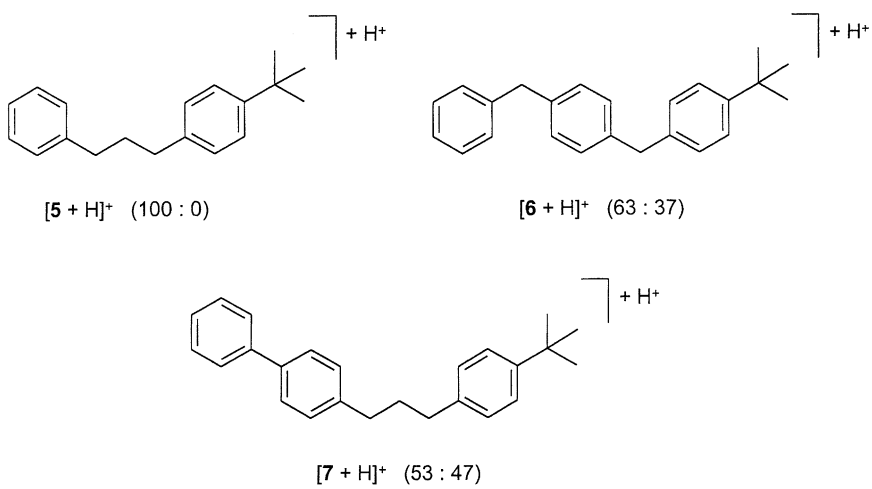
### *2.1. The gaseous complex of t-$C_4H_9^+$ and tribenzylmethane (2)*

The MIKE spectrum of protonated *tert*-butyl-substituted tribenzylmethane $[\mathbf{1} + H]^+$ is reproduced in Fig. 1. The most intense signal corresponds to the fragment ion at *m/z* 287, which is formed by loss of isobutene. This is in sharp contrast to the spectrum of the lower congener, *tert*-butyl-substituted 1,3-diphenylpropane $[\mathbf{5} + H]^+$, and its homologues which undergo *isobutane* loss exclusively [22] (Scheme 4). Related metastable precursor ions, e.g., protonated 1,4-dibenzylbenzene $[\mathbf{6} + H]^+$ and 1-biphenylyl-3-phenylpropane $[\mathbf{7} + H]^+$ containing, as do ions $[\mathbf{1} + H]^+$, three aromatic rings, eliminate isobutane and isobutene in comparable amounts [23].[1] Clearly, the dominance of isobutene loss from metastable $[\mathbf{1} + H]^+$ ions has to be attributed to a significant increase of the proton affinity of the tribenzylmethane framework as compared to that of **5**, a "dibenzylmethane." The effects of the second (neutral) ring on the thermodynamic stabilization of protonated α,ω-diphenylalkanes [27] and also on their reactivity [28] have been well documented. Since *both* of the protonated conjugates, $[\mathbf{1} + H]^+$ and $[\mathbf{2} + H]^+$, should be more strongly stabilized by the presence of two aromatic "spectator" rings as compared to the diphenylalkane congeners, the isobutene loss should be similarly favorable in both $[\mathbf{1} + H]^+$

[1] Note that the major part of isobutane loss from metastable ions $[\mathbf{1} + H]^+$ is evident through the fast consecutive loss of benzene (*m/z* 207, Fig. 1).




Scheme 3. Major proton-induced fragmentation paths of *tert*-butyl-substituted tribenzylmethane **1**.

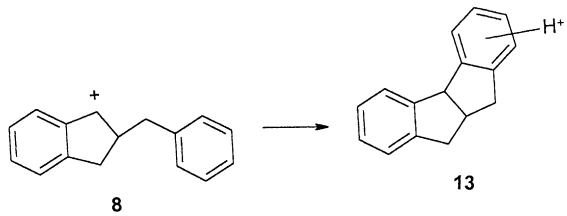



Scheme 4. Isobutane vs. isobutene loss from metastable $[M + H]^+$ ions of hydrocarbons **5**–**7**.

and $[\mathbf{5}+\mathrm{H}]^+$. In contrast, the hydride transfer reaction producing isobutane does not generate $[M+\mathrm{H}]^+$ ions but benzylic, $[M-\mathrm{H}]^+$-type, ions such as $[\mathbf{2}-\mathrm{H}]^+$ (Scheme 3), which should not be subject to significant intramolecular stabilization by the pendant benzylic groups. As a consequence, the isobutane loss from ions $[\mathbf{1}+\mathrm{H}]^+$ should require somewhat more energy than in the case of ions $[\mathbf{5}+\mathrm{H}]^+$, whereas the endothermicity of the isobutene loss should remain essentially unchanged.

As expected for a normal MIKE spectrum, the product ions generated by isobutene loss, ions $[\mathbf{2}+\mathrm{H}]^+$, do not undergo secondary fragmentation within the same field-free region. In contrast to isobutene loss, elimination of isobutane produces very minor amounts (ca. 1.5%) of *m/z* 285 ions, similar to those of $t\text{-}C_4H_9{}^+$ ions (*m/z* 57) released as such from the complex. Most interesting, however, is the formation of ions $C_{16}H_{15}{}^+$ at *m/z* 207, being 136 atomic mass units lighter than the precursor ions $[\mathbf{1}+\mathrm{H}]^+$. Their formation cannot be explained by elimination of a single neutral fragment but only by consecutive loss of two neutral molecules, viz. isobutane and benzene. There are good arguments to assume that the hydride transfer reaction precedes the elimination of benzene (see below), as shown in Scheme 3. The $[\mathbf{1}+\mathrm{H}-C_4H_{10}]^+$ ions correspond to $[M-\mathrm{H}]^+$ ions of α,ω-diphenylalkanes, which are known to expel benzene after cyclization [29]. In the case of ions $[\mathbf{1}+\mathrm{H}]^+$, isobutane loss generates $[M-\mathrm{H}]^+$ ions of tribenzylmethane, $[\mathbf{2}-\mathrm{H}]^+$, in which the probability of cyclization and subsequent elimination of benzene is enhanced by the presence of two benzyl groups. The structure of ions $[\mathbf{1}+\mathrm{H}-C_4H_{10}-C_6H_6]^+$ should be either that of 1-phenyl-2-benzylindane-1-yl cations (**8**, Scheme 3) or that of the corresponding ring-closed isomer, a protonated diindane (Scheme 5) [30].[2]

To study the reactivity of ions $[\mathbf{1}+\mathrm{H}]^+$ and the derived ion/molecule complex, $[\mathbf{2}+t\text{-}C_4H_9]^+$, in more detail, six deuterium-labeled isotopomers of the neutral precursor, **1a**–**1f**, were synthesized and the fragmentation of the metastable $[M+\mathrm{H}]^+$ ions was studied by MIKE spectrometry. As expected from the results of the previous studies [22–25], the dominating loss of isobutene did not show any evidence for a preceding proton exchange between the fragments and/or between the rings. However, the combined losses of isobutane and benzene allowed us to determine the regioselectivity of the hydride abstraction and detect the fast interannular proton exchange. In spite of the heavy overlapping of the MIKE signals (Fig. 2), the relative abundances of the isotopomeric $[M+\mathrm{H}-\text{isobutane}-\text{benzene}]^+$ ions provided unequivocal information.




Scheme 5. Putative cyclization of ions **8**.

The MIKE spectrum of the [2-D]-labeled ions $[\mathbf{1}a+\mathrm{H}]^+$ indicates complete retention of the label in the product ions. Thus, the overall sequence comprises exclusively the losses of unlabeled isobutane and unlabeled benzene. In agreement with previous results [22,23], the homobenzylic position, although bearing a tertiary C–H bond here, does not act as a hydride donor. The spectra of the two isotopomeric ions $[\mathbf{1}b+\mathrm{H}]^+$ and $[\mathbf{1}c+\mathrm{H}]^+$, which contain the deuterium label at one and, respectively, both of those benzylic positions that are remote (i.e., at γ and γ′) from the originally *tert*-butyl-substituted (i.e., α) phenyl ring, clearly show that all of the benzylic groups act as hydride (and deuteride) donors. Based on the previous results [22–25], there is no doubt that the deuteride is incorporated into the isobutane and not into the benzene fragment. Careful evaluation of the signals reveals the abundance ratios [*m/z* 209]: $[m/z\,208] = [C_4H_{10}+C_6H_6]/[C_4H_9D+C_6H_6] = 3.2$ for the combined losses of isobutanes and benzene from ions $[\mathbf{1}b+\mathrm{H}]^+$ and [*m/z* 211]: $[m/z\,210] = [C_4H_{10}+C_6H_6]/[C_4H_9D+C_6H_6] = 0.77$ for

[2] Diindanes of type **13** are known to form easily from 2-benzylindane-1-yl ions in solution.

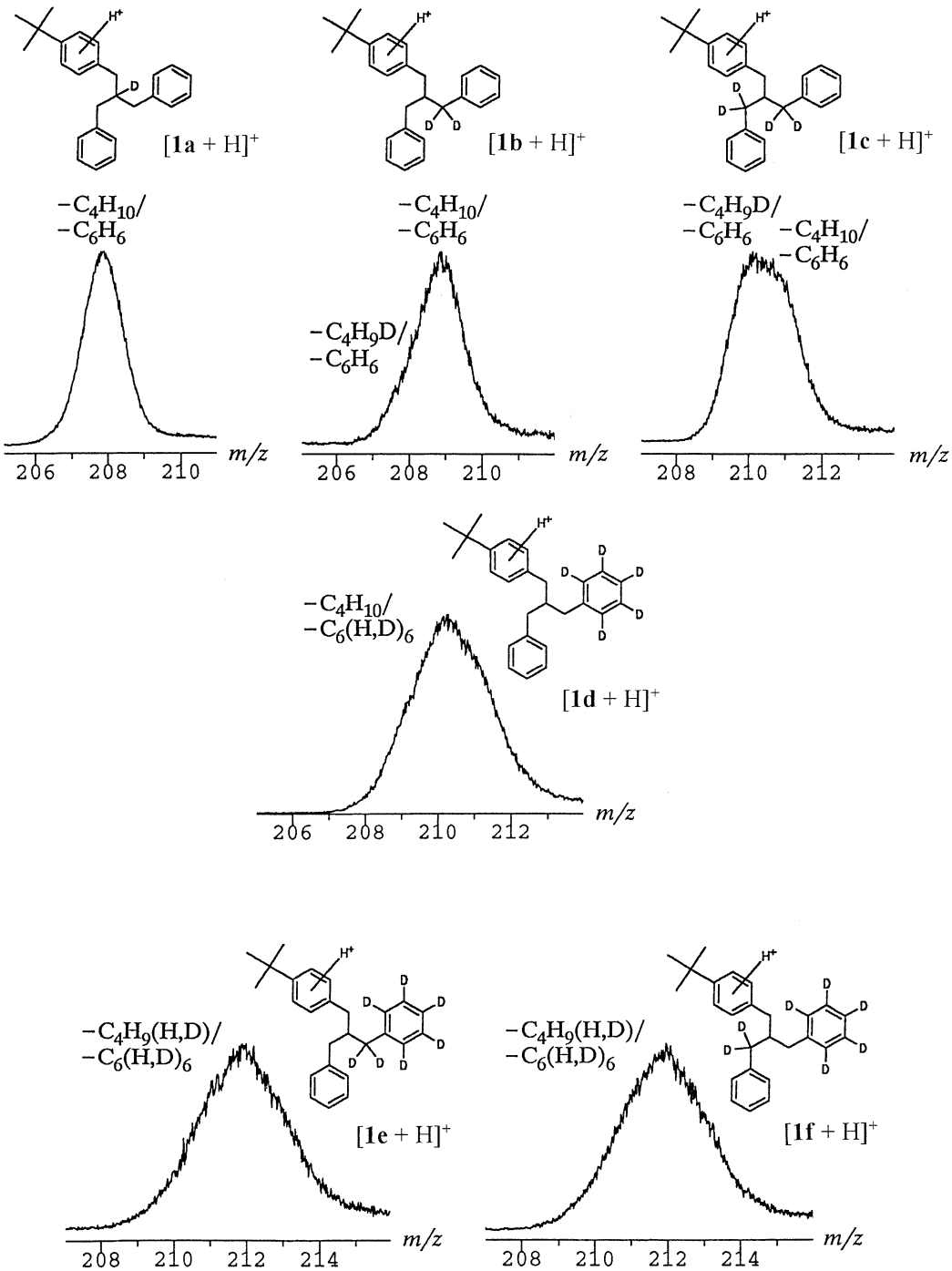



Fig. 2. Partial CI($CH_4$)/MIKE spectra showing the combined losses of isobutane and benzene isotopomers from protonated analogues [**1a** + H]$^+$ − [**1f** + H]$^+$.

the combined losses of isobutanes and benzene from ions $[\mathbf{1}c + H]^+$. To account for the numbers of H and D atoms present in the three benzylic groups of the two isotopomeric ions, the experimental ratios are normalized to $(0.5[C_4H_{10} + C_6H_6])/[C_4H_9D + C_6H_6] = 1.6$ for ions $[\mathbf{1}b + H]^+$ and to $[C_4H_{10} + C_6H_6]/(0.5[C_4H_9D + C_6H_6]) = 1.54$. These two values are the same within the limits of experimental error (estimated to be $\leq \pm 0.15$) and identical to the kinetic isotope effect, $k_H/k_D = 1.6$, the value found to be ubiquitous for the loss of isobutane from sterically unhindered *tert*-butyl-substituted alkylbenzenium ions [20,22–25]. Thus, the regioselectivity of the hydride abstraction from the three benzylic methylene groups at the α, γ and γ′ positions in the unlabeled ions $[\mathbf{1}+H]^+$ is unity, 1 : 1 : 1, within the limits of experimental error. As a mechanistic consequence, protonolysis releasing the *t*-$C_4H_9^+$ ion produces an ion/molecule complex in which the two constituents move so freely relative to each other that the three benzylic hydride donor sites become equivalent. This result is in full agreement with expectations based on the behavior of the dinuclear congeners such as $[\mathbf{5} + H]^+$ and $[\mathbf{6} + H]^+$ [22,23].

Protonated α,ω-diphenylalkanes are known to undergo a fast interannular proton transfer leading to complete equilibration of the "aromatic" protons prior to loss of benzene on the microseconds' timescale [14b,15,26,31]. In the case of the *tert*-butyl-substituted derivatives, e.g., $[\mathbf{5} + H]^+$, there is no such suitable probe reaction since neither the isobutane nor the isobutene neutral fragments contain ring hydrogen atoms. Therefore, it has been uncertain to date whether fast interannular proton exchange takes place prior to the release of the *t*-$C_4H_9^+$ ion into the complex. It may be noted that the presence of the proton-labile *tert*-butyl substituent could conceivably attenuate or even suppress the otherwise high intramolecular mobility of the "aromatic" protons between the aromatic rings. Interestingly, the triaryl congeners such as $[\mathbf{1} + H]^+$ offer an answer to this problem since benzene elimination follows the isobutane loss as an obviously very rapid reaction of low energy demand.

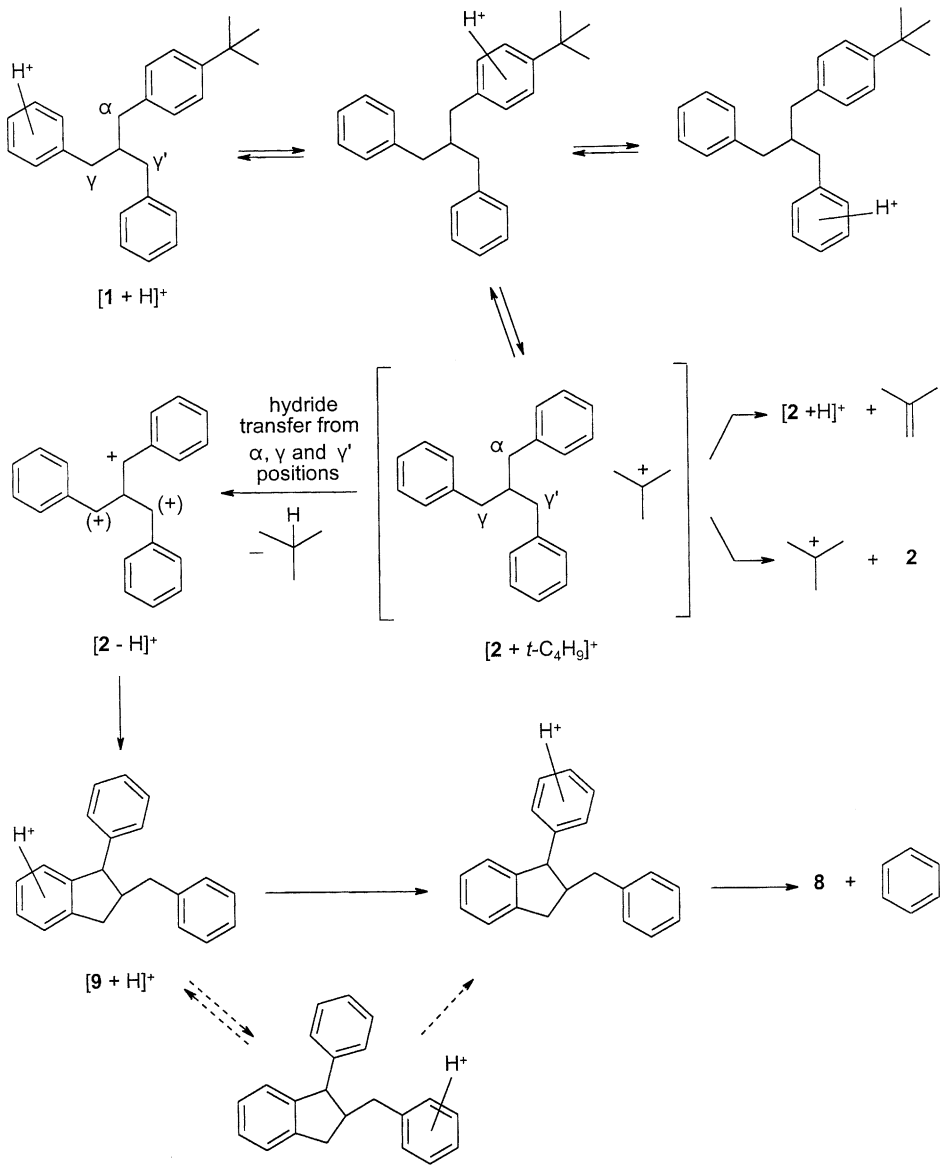
As shown in Fig. 2, the MIKE spectrum of the [*phenyl*-$D_5$] isotopomer $[\mathbf{1}d + H]^+$ exhibits a broad signal containing all possible individual contributions for the combined losses of $C_4H_{10}$ and $C_6H_{6-x}D_x$ ($0 \leq x \leq 5$). The B/E linked scan spectrum confirms this qualitatively [23b]. Simulation of the signal shape assuming complete scrambling of the total of 15 H and D atoms at the rings predicts an almost symmetrical distribution centered at *m*/*z* 210 for the combined losses of $C_4H_{10}$ and $C_6H_4D_2$ (42.0% Σ).[3] Thus, the experimental peak shape indicates fast proton exchange between the three rings leading to complete or nearly complete equilibration of the 15 ring hydrogens in ions $[\mathbf{1} + H]^+$ prior to isobutane loss.

Not surprisingly, the two [$D_7$]-isotopomers $[\mathbf{1}e + H]^+$ and $[\mathbf{1}f + H]^+$ confirm the conclusions drawn so far. The MIKE signals registered of these ions are identical and contain heavily overlapping contributions for the combined losses of $(C_4H_{10} + C_6H_{6-x}D_x)$ and $(C_4H_9D + C_6H_{6-x}D_x)$ ($0 \leq x \leq 5$), hence stretching over one additional mass unit. Simulation accounting for the kinetic discrimination of the latter sequence by a factor of $k_D/k_H = 1 : 1.6$, similar to the fragmentation of ions $[\mathbf{1}b + H]^+$, agrees well with the measured spectra.

### 2.2. The order of consecutive isobutane and benzene losses from the metastable ions

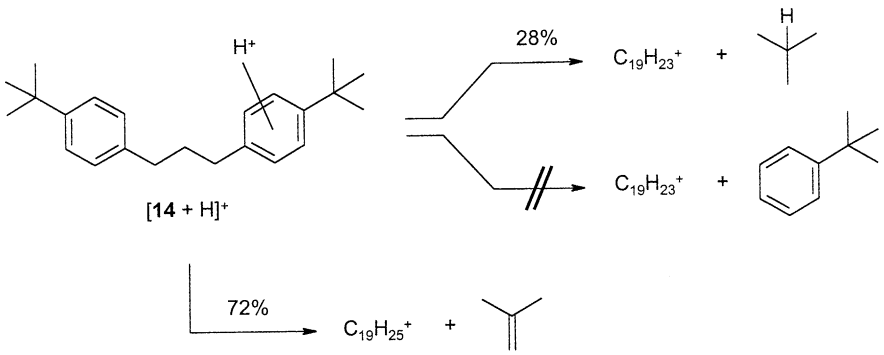
These experiments clearly corroborate the fast interannular proton exchange prior to fragmentation of ions $[\mathbf{1} + H]^+$. According to the mechanism shown in Scheme 6, isobutane loss precedes that of benzene. The reason to exclude the reverse order, viz. loss of benzene followed by loss of isobutane, lies in the fact that heterolysis of an unbranched protonated alkylbenzene at the $C^{ipso}$–$C^{\alpha}$ bond requires considerably more energy than heterolysis of a *tert*-alkylbenzenium ion [32,33]. In the case of ions $[\mathbf{1}+H^+]$, the release of the

[3] The relative abundances of benzene isotopomers after complete equilibration of 10 H and 5 D were calculated to be $[C_6H_6]/[C_6H_5D]/[C_6H_4D_2]/[C_6H_3D_3]/[C_6H_2D_4]/[C_6HD_5] = 4.2 : 25.2 : 42.0 : 24.0 : 4.5 : 0.2$.




Scheme 6. Isomerization reactions preceding and succeeding the formation of ion/molecule complex $[2 + t\text{-}C_4H_9{}^+]$.

$t$-$C_4H_9{}^+$ ion into the complex $[\mathbf{2} + t\text{-}C_4H_9^+]$ should be particularly favorable owing to the efficient solvation of the cation by the large tridentate alkylbenzene **2** [21a]. Notably, the strongest argument in favor of the sequence given in Scheme 6 is provided by the experiment itself (Fig. 1): Elimination of *tert*-butylbenzene (or combined losses involving this process) does not occur; thus, this process cannot compete with the observed sequential loss of isobutane and benzene. If ions **8** were formed by loss of benzene as the first step followed by loss of isobutane, elimination of *tert*-butylbenzene should also be observed




Scheme 7. Fragmentation of metastable ions $[\mathbf{14}+\mathrm{H}]^+$.

because the heterolysis of the $C^{ipso}$–$C^{\alpha}$ bond should require the same or even somewhat less energy than the heterolyses of the $C^{ipso}$–$C^{\gamma}$ and $C^{ipso}$– bonds [34].[4]

The interannular proton exchange could occur not only in the precursor ions $[\mathbf{1}+\mathrm{H}]^+$ but also after cyclization of ions $[\mathbf{2}-\mathrm{H}]^+$ to the intermediates $[\mathbf{9}+\mathrm{H}]^+$ being, once again, protonated arenes. However, it has been demonstrated that elimination of benzene from protonated diphenylmethane [35] and, even more so, from protonated 1-phenylindane [29] are particularly facile processes, which strongly attenuate or even suppress the interannular proton exchange. Therefore, ions $[\mathbf{9}+\mathrm{H}]^+$ should nearly instantly expel benzene from the protonated 1-phenyl group and hence intercept the otherwise fast interannular proton exchange in these protonated diaryl(cyclo)alkanes. The complete mechanism leading of the consecutive isobutane and benzene losses from ions $[\mathbf{1}+\mathrm{H}]^+$ is shown in Scheme 6.

### *2.3. The gaseous complex of t-$C_4H_9^+$ and tetrabenzylmethane (4)*

As compared to ions $[\mathbf{1}+\mathrm{H}]^+$, and as a further step beyond the simple mono- and dinuclear alkylbenzenium ions, protonated 4-*t*-butyl-substituted tetrabenzylmethane $[\mathbf{3}+\mathrm{H}]^+$ contains a further aromatic ring at a flexible alkyl group. Therefore, it is expected that the particular reactivity of the lower congener should be even more pronounced in this case. The MIKE spectrum of ions $[\mathbf{3}+\mathrm{H}]^+$ is reproduced in Fig. 3 and the fragmentation pathways are summarized in Scheme 8.

Loss of isobutene from ions $[\mathbf{3}+\mathrm{H}]^+$ is even more pronounced than in the case of ions $[\mathbf{1}+\mathrm{H}]^+$. Probably, proton transfer from the *t*-$C_4H_9^+$ ion to the neutral partner, tetrabenzylmethane **4**, within the complex is most favorable because of the increased proton affinity of this large alkylbenzene as compared to tribenzylmethane **2**. Here again, it can be reasonably assumed that the close proximity of the three neutral benzyl groups to the protonated aromatic ring efficiently stabilize both the $[\mathbf{3}+\mathrm{H}]^+$ and the $[\mathbf{3}+\mathrm{H}-\mathrm{C_4H_8}]^+$ ions (which are identical to $[\mathbf{4}+\mathrm{H}]^+$) but does not increase the stability of the $[\mathbf{3}+\mathrm{H}-\mathrm{C_4H_{10}}]^+$ ions, thus giving rise to a discrimination of the hydride transfer process. Interestingly, the isobutene loss from ions $[\mathbf{3}+\mathrm{H}]^+$ is followed by two fast consecutive elimination reactions, viz. loss of two molecules of benzene. This is evident from the small signal at *m*/*z* 221 (2% $\Sigma$) in the MIKE spectrum and exactly parallels the consecutive two-fold benzene loss of protonated tetrabenzylmethane $[\mathbf{4}+\mathrm{H}]^+$ [19,26]. Similar to the latter ions, single loss of benzene is not observed for $[\mathbf{3}+\mathrm{H}]^+$. Thus, the peculiar two-fold elimination of

[4] In agreement with this argument, metastable protonated 4,4′-bis-(*tert*-butyl)-substituted 1,3-diphenylpropane $[\mathbf{14}+\mathrm{H}]^+$ does not undergo loss of *tert*-butylbenzene but only elimination of isobutane and isobutene (Scheme 7) [23b].

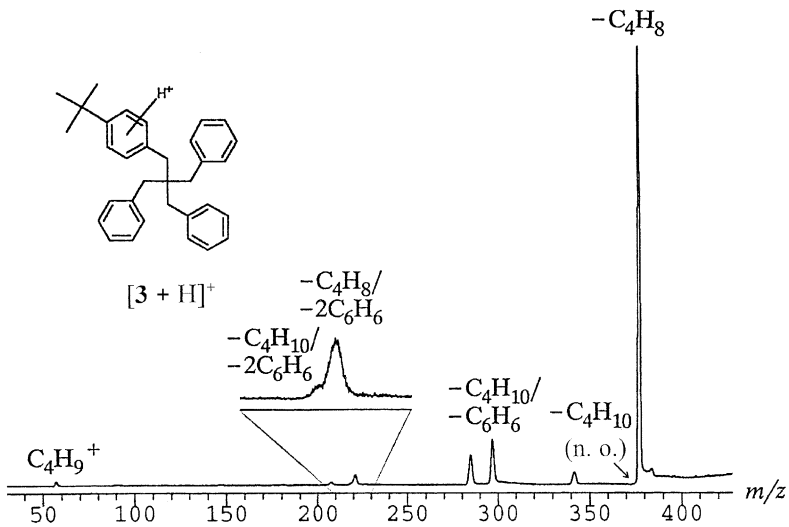


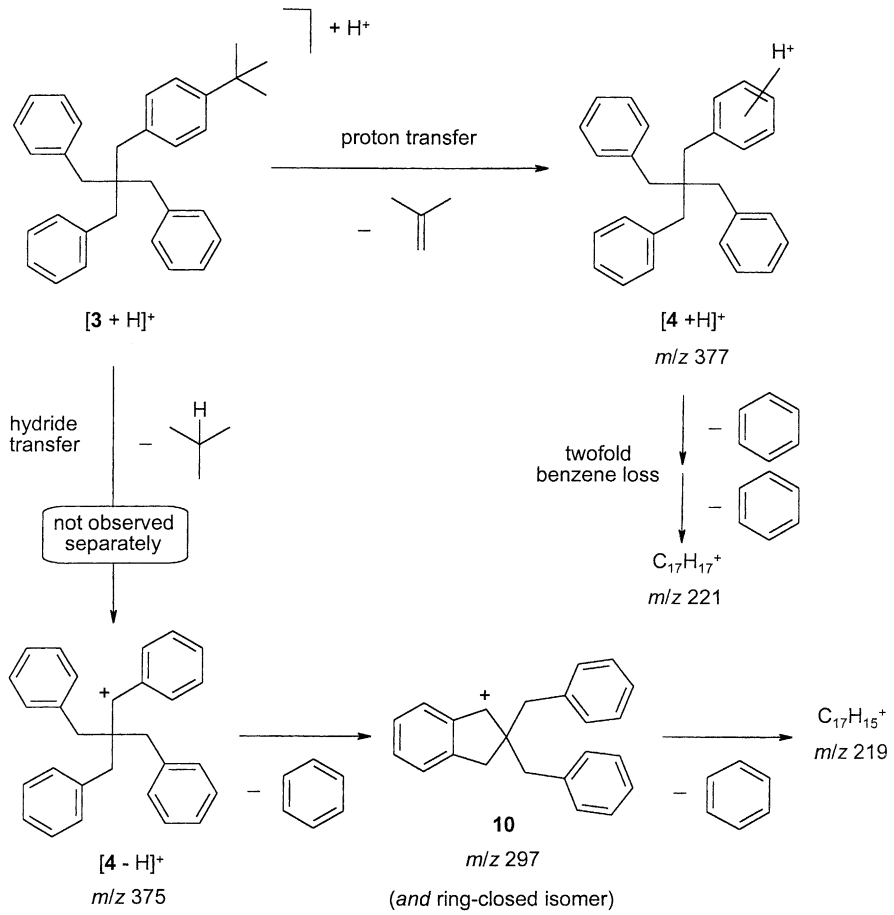

Fig. 3. CI($CH_4$)/MIKE spectrum of protonated *tert*-butyl-substituted tetrabenzylmethane **3** (*m/z* 433). The signal for isobutane loss is not observed (n.o.). The unassigned signals indicate fragmentations of isobaric $M^{\bullet+}$ ions containing naturally occurring $^{13}C$.

benzene from ions $[\mathbf{4} + H]^+$ occurring in the same field-free region and as the sole fragmentation path (cf. Scheme 2), is clearly reflected in the fragmentation of ions $[\mathbf{3} + H]^+$ as well. In total, this results in a most remarkable sequence of three consecutive elimination reactions taking place within the same field-free region of a sector-field mass spectrometer.[5]

As a single step, elimination of isobutane is not observed from ions $[\mathbf{3} + H]^+$. The corresponding signal is completely absent in the MIKE spectrum (Fig. 3) but the consecutive losses of isobutane and benzene within the same field-free region are manifested by a relatively small peak at *m/z* 297 (10% $\Sigma$). Thus, it appears that the presence of three benzyl groups in ions $[\mathbf{3} + H]^+$ instead of only two in the case of ions $[\mathbf{1} + H]^+$ further accelerates the subsequent loss of benzene. This appears to be reasonable since cyclization should become kinetically even more favorable. In fact, the MIKE spectrum of ions $[\mathbf{3}+H]^+$ exhibits a minute signal at *m/z* 219 (0.4% $\Sigma$) indicating another sequence of three consecutive elimination steps within the same field-free region, viz. the loss of isobutane and *two* molecules of benzene.

The origin of the hydride abstracted by the *t*-$C_4H_9^+$ ion within the ion/molecule complex formed from ions $[\mathbf{3} + H]^+$ was investigated by means of five deuterium-labeled isotopomers (Fig. 4). The MIKE spectrum of the $[D_2]$-labeled isotopomers $[\mathbf{3}a + H]^+$ and $[\mathbf{3}b + H]^+$ bearing the label in one of the originally remote ($\gamma$–$\gamma''$) or in the originally adjacent ($\alpha$) methylene groups, respectively, exhibit exactly the same peak shapes for the combined losses of isotopomeric isobutanes and benzene. Although the contribution of the combined $C_4H_9D$ and $C_6H_6$ losses is hardly detectable, the identity of the two signals again confirms that all the four methylene groups become equivalent in the complex [*t*-$C_4H_9^+$ **4**]. In the case of the $[D_4]$-labeled isotopomer $[\mathbf{3}c + H]^+$, the combined $C_4H_9D$ and $C_6H_6$ losses give rise to a significant contribution at *m/z* 300, and deconvolution yields [*m/z* 301]: $[m/z\,300] = [C_4H_{10} + C_6H_6]/[C_4H_9D + C_6H_6] = 1.6 \pm 0.2$. The spectrum of the $[D_6]$-labeled analogue $[\mathbf{3}d + H]^+$ exhibits predominant deuteride transfer, with [*m/z* 303]:

[5] The consecutive loss of *t*-$C_4H_8C_6H_5$ and $C_6H_6$ can be excluded since, here again, both single and two-fold loss of $C_6H_6$ from ions $[\mathbf{3} + H]^+$ are not observed.




Scheme 8. Proton-induced fragmentation paths of *tert*-butyl-substituted tetrabenzylmethane **3**.

$[m/z\,301] = [C_4H_{10} + C_6H_6]/[C_4H_9D + C_6H_6] = 0.53 \pm 0.07$. Both cases reflect, either directly or after normalization of the ratio of methylene H and D atoms present, the "usual" kinetic isotope effect of the hydride transfer, $k_H/k_D = 1.6 \pm 0.2$. These data confirm the equivalence of all of the four hydride donor sites in the neutral component of the complex [**4** + *t*-$C_4H_9^+$], by analogy to the complex [**2** + *t*-$C_4H_9^+$] discussed above, and represent another example for the uniform size of the kinetic isotope effect observed for the loss of isobutane from all kinds of *tert*-butylbenzenium ions. Finally, the MIKE spectrum of the [$D_8$]-labeled isotopomer [**3e** + H]$^+$ displays the exclusive combined loss of $C_4H_9D$ and $C_6H_6$ at *m/z* 304. This result is in line with the mechanistic conclusions and shows that the presence of deuterium atoms at all of the donor positions does not suppress the isobutane loss channel.[6]

Although [*ring*-D]-labeled isotopomers of ions [**3**+H]$^+$ were not studied in the present work, it can be assumed that, by analogy to the lower congener [**1**+H]$^+$, the fast interannular proton exchange precedes also the formation of the complex [*t*-$C_4H_9^+$ **4**]. Thus, we have to rackon with several independent symmetriza-

[6] It is noted that, as compared to the isobutene loss, the consecutive isobutane and benzene losses are increasingly discriminated with increasing deuterium label in the methylene positions.

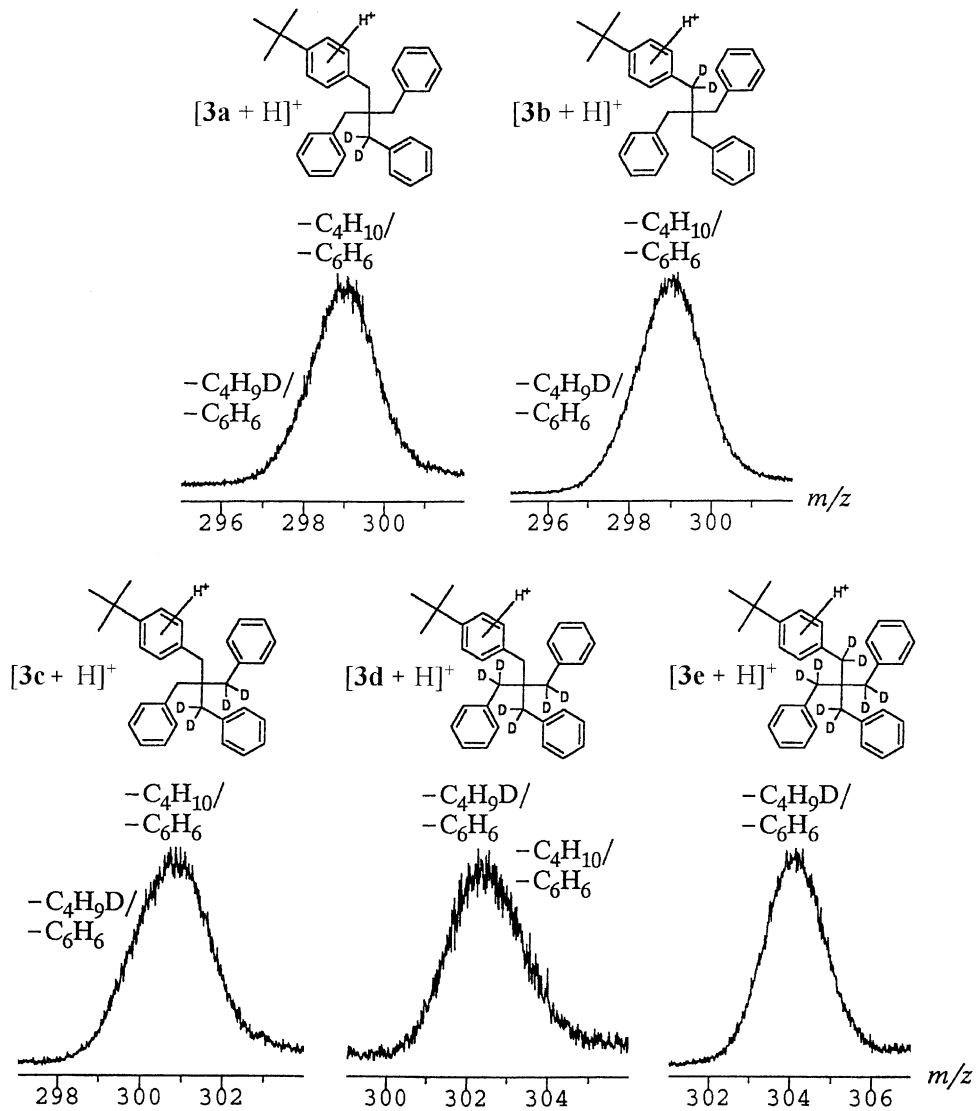
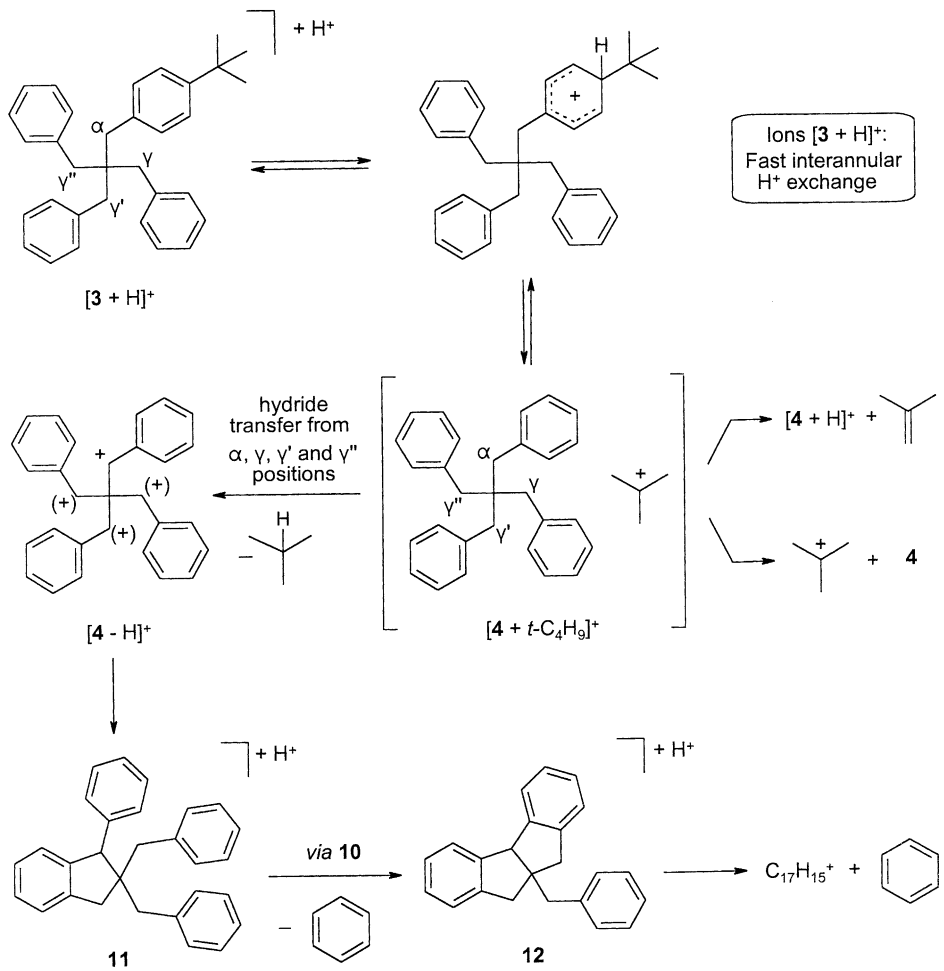



Fig. 4. Partial CI($CH_4$)/MIKE spectra showing the combined losses of isobutane and benzene isotopomers from protonated analogues $[\mathbf{3a}+\mathrm{H}]^+$–$[\mathbf{3e}+\mathrm{H}]^+$.

tion processes taking place during the fragmentation of ions $[\mathbf{3}+\mathrm{H}]^+$: (i) complete scrambling of the 20 "aromatic" protons in the covalently bound protonated precursor; (ii) at-random proton transfer in the complex from the *t*-$C_4H_9^+$ ion to the highly symmetrical tetrabenzylmethane partner which, on itself, is known to undergo rapid ring-to-ring proton transfer [26]; and (iii) similar at-random $H^-$ abstraction by the *t*-$C_4H_9^+$ ion from the four benzylic hydride donor sites of **4**. Thus, in the subsequent benzene elimination steps, all of the four aromatic rings participate with the same probability. Most of these unusual features of the fragmentation of ions $[\mathbf{3}+\mathrm{H}]^+$ are summarized in Scheme 9.




Scheme 9. Isomerization reactions preceding and succeeding the formation of ion/molecule complex [**4** + $t$-$C_4H_9^+$].

## 3. Conclusions

This work demonstrates two related examples of a study on the reactivity of all-hydrocarbon ion/molecule complexes which were generated "by design" from relatively large alkylaromatic hydrocarbon precursors, viz. the *tert*-butyl-substituted oligophenylisoalkanes **1** and **3**, upon unimolecular protonolysis in the plasma of a CI($CH_4$) source. It has been shown that, in agreement with previous results on smaller analogues, the *tert*-butyl cations move so freely within the complexes [$t$-$C_4H_9^+$ **2**] and [$t$-$C_4H_9^+$ **4**], that the hydride donor groups of the neutral constituents, tribenzylmethane (**2**) and tetrabenzylmethane (**4**), become completely equivalent. The overall fragmentation of these "large" complexes reflect the relatively dense packing of the aromatic rings in the oligophenylisoalkane-type ions, giving rise to unusually fast consecutive fragmentation, involving fast interannular proton transfer, electrophilic cyclization and benzene elimination steps. It is hoped that similar investigations may continue to contribute to our understanding on the elemental steps occurring in large organic ion/neutral complexes in the gas-phase.

## 4. Experimental

### 4.1. Measurements

All measurements were carried out on a double-focusing instrument, Autospec (Fisons, Manchester/UK) with a three-sector, EBE geometry. The compounds were introduced into the CI source via the heatable inlet rod. Methane was used as the reactant gas with the nominal pressure of $4 \times 10^{-5}$ to $1 \times 10^{-4}$ 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. Deconvolution of the peaks was performed graphically and the error limits denote an estimation of uncertainty associated with this procedure.

### 4.2. 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. Combustion 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).

### 4.3. Synthesis of compounds

The various tri- and tetrabenzylmethanes were synthesized from either 3-(4-*t*-butylphenyl)-1-phenylpropane-1-one (**16**) and its deuterium-labeled analogues (**18**, **19**) or from 4-*t*-butylacetophenone (Aldrich) by single, double, or triple benzylation and subsequent chloroalane reduction of the corresponding substituted dihydrochalcones [36].[7] The dihydrochalcones **16** and **18** were prepared by conventional condensation and hydrogenation methodology. Full experimental details on the syntheses are given below.

#### 4.3.1. 3-(4-t-Butylphenyl)-1-phenylprop-2-ene-1-one (5)

A mixture of 4-*t*-butylbenzaldehyde (8.1 g, 50 mmol) and acetophenone (6.0 g, 50 mmol), both freshly distilled, methanol (35 mL) and aqueous KOH (20%, 25 mL) was stirred at 25 °C for 48 h. An orange oil formed, which was separated, washed neutral with $H_2SO_4$ (2N) and diluted with diethyl ether. The residual methanolic solution was extracted with diethyl ether. Work-up of the combined organic solutions gave an oily residue which was purified by kugelrohr distillation yielding **15** (10.2 g, 77%) as an orange oil, bp 150 °C/0.04 mbar. $^1$H NMR ($CDCl_3$, 60 MHz): $\delta$ 7.9–8.1 (m, 2H), 7.2–7.6 (m, 9H), 1.30 (s, 9H); mass spectrum (EI): *m/z* 264 (30, $M^{\bullet+}$), 249 (66), 207 (94), 177 (100), 149 (75), 105 (36), 91 (43), 77 (51).

#### 4.3.2. 3-(4-t-Butylphenyl)-1-phenylpropane-1-one (16)

This compound was prepared by catalytic hydrogenation of **15** (10.2 g, 39 mmol), dissolved in ethyl acetate (100 mL), in the presence of Adams' catalyst (from 155 mg of $PtO_2$). Work-up and recrystallization from EtOH gave **16** as colorless crystals (6.16 g, 60%), mp 72 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.97 (m, 2H), 7.19–7.58 (m, 7H), 3.31 (t, $^3J$ = 7.8 Hz, 2H), 3.04 (t, $^3J$ = 7.7 Hz, 2H), 1.30 (s, 9H); mass spectrum (EI): *m/z* 266 (33, $M^{\bullet+}$), 251 (100), 147 (11), 131 (38), 117 (12), 105 (70), 91 (16), 77 (38), 57 (25); IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 3028, 2961, 1681, 1447, 1361, 1204, 975, 819, 742, 690. $C_{19}H_{22}O$ (266.39), calcd. C 85.67, H 8.32, found: C 85.88, H 8.29.

[7] For related work on the improved synthesis of the parent hydrocarbons **3** and **4**, see [26].

*4.3.3. 3-(4-t-Butylphenyl)-1-([$D_5$]phenyl)prop-2-ene-1-one (**17**)*

This compound was prepared by analogy to **15** using [$D_5$]acetophenone (10 mmol), yield 46%. $^1$H NMR ($CDCl_3$, 60 MHz): $\delta$ 7.2–7.9 (m, 6H), 1.30 (s, 9H).

*4.3.4. 3-(4-t-Butylphenyl)-1-([$D_5$]phenyl)-propane-1-one (**18**)*

This compound was prepared by catalytic hydrogenation of **17** (4.6 mmol) by analogy to **15**, yield 64%, mp 72 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.27 (AA′BB′, $^3J$ = 8.4 Hz, 4H), 3.30 (t, $^3J$ = 7.8 Hz, 2H), 3.04 (t, $^3J$=7.7 Hz, 2H), 1.31 (s, 9H); mass spectrum (EI): *m*/*z* 271 (32, $M^{\bullet+}$), 256 (100), 147 (13), 131 (48), 117 (16), 110 (66), 91 (16), 57 (21).

*4.3.5. 3-(4-t-Butylphenyl)-1-phenyl-2,2-[$D_2$]-propane-1-one (**19**)*

A mixture of **16** (1.10 g, 4.4 mmol), deuterium oxide (4 mL), triethylamine (0.4 mL) and dioxane (18 mL) was stirred overnight at 95 °C. Removal of the volatile components in vacuo and subsequent two-fold repetition of the procedure, and final recrystallization of the solid residue from EtOH gave **19** (0.70 g, 63%) as colorless needles, mp 72 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.96 (m, 2H), 7.18–7.59 (m, 7H), 3.03 (s, 2H), 1.29 (s, 9H); mass spectrum (EI): *m*/*z* 268 (33, $M^{\bullet+}$), 253 (100), 147 (14), 131 (37), 117 (12), 105 (71), 91 (12), 77 (38), 57 (20); 97 at.% D (94% $d_2$, 6% $d_1$).

*4.3.5.1. Benzylation of 3-(4-t-butylphenyl)-1-phenylpropane-1-one (**16**) and its deuterated analogues*

*4.3.5.1.1. Monobenzylation (general procedure A).* A solution of the dihydrochalcone (10.0 mmol) and the benzyl bromide (10.0 mmol) in anhydrous benzene (20 mL) was heated to reflux and a suspension of sodium *tert*-amylate (1.11 g, 10.0 mmol) in anhydrous benzene (25 mL) was added dropwise to the heated solution. If TLC (eluent $CH_2Cl_2$) showed the starting ketone to be still prevalent in the mixture after 4 h, further *tert*-amylate (0.56 g, 5.0 mmol) was added and heating was continued for another 2–4 h. The mixture was allowed to cool and worked up by washing it thrice with hydrochloric acid (10%) and four times with water. The aqueous layers were extracted with benzene and the combined organic solutions dried over sodium sulfate. Careful removal of the solvent gave a residue which was recrystallized twice from ethanol. TLC showed $R_f$($CH_2Cl_2$) 0.93 for compound **16**.

*4.3.5.1.2. Dibenzylation (general procedure B).* These syntheses were carried out by reacting the dihydrochalcone (10.0 mmol) with 20.0 mmol of the corresponding benzyl bromide in 20 mL of benzene, and by adding 2.22 g (20.0 mmol) of sodium *tert*-amylate base. If necessary (TLC control), further base (1.11 g, 10.0 mmol) was added at due time. The reactions were completed after 24–48 h, and work-up and recrystallization were done as described above. TLC of the product ketones showed $R_f$($CH_2Cl_2$) 0.94.

*4.3.6. 2-Benzyl-3-(4-t-butylphenyl)-1-phenylpropane-1-one (**20**)*

Procedure A (scale 4.0 mmol) starting from **16** (1.06 g) and benzyl bromide (740 mg) gave **20** (720 mg, 50%) as colorless needles, mp 80 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.73 (m, 2H), 7.05–7.48 (m, 12H), 4.02 (m, 1H), 2.75–2.85 and 3.06–3.11 (two m, 4H), 1.25 (s, 9H); mass spectrum (EI): *m*/*z* 356 (2, $M^{\bullet+}$), 265 (100), 209 (61), 117 (16), 105 (38), 91 (24), 77 (26), 57 (13); IR (KBr): $\bar{\nu}$ ($cm^{-1}$) 3026, 2972, 1679, 1445, 1240, 956, 753, 697. $C_{26}H_{28}O$ (356.51), calcd. C 87.60, H 7.92, found: C 87.19, H 7.97.

*4.3.7. 2-[$\alpha$,$\alpha$-$D_2$]Benzyl-3-(4-t-butylphenyl)-1-phenylpropane-1-one (**21**)*

Procedure A (scale 3.0 mmol) starting from **16** (800 mg) and [$\alpha$,$\alpha$-$D_2$]benzyl bromide (519 mg) gave **21** (490 mg, 44%) as colorless needles, mp 80.5 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.72 (m, 2H), 7.05–7.48 (m, 12H), 4.00 (t, $^3J$ = 7.0 Hz, 1H), 2.74–2.81 (m,

2H), 1.25 (s, 9H); mass spectrum (EI): *m/z* 358 (2, $M^{\bullet+}$), 265 (100), 211 (35), 117 (11), 105 (37), 93 (16), 77 (18), 57 (17).

#### *4.3.8. 2-Benzyl-3-(4-t-butylphenyl)-1-phenyl-2-[D]propane-1-one (**22**)*

Procedure A (scale 2.6 mmol) starting from **19** (700 mg) and benzyl bromide (480 mg) gave **22** (640 mg, 69%) as colorless needles, mp 79.5 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.72 (m, 2H), 7.05–7.48 (m, 12H), 2.75–2.83 and 3.07–3.15 (two m, 4H), 1.25 (s, 9H); a residual signal at $\delta$ 4.01 indicated D contents of ca. 65% only. Mass spectrum (EI): *m/z* 357 (3, $M^{\bullet+}$), 266 (100), 210 (59), 209 (39), 117 (20), 91 (32), 77 (33), 57 (26); 60 at.% D.

#### *4.3.9. 2-Benzyl-3-(4-t-butylphenyl)-1-([$D_5$]-phenyl)-propane-1-one (**23**)*

Procedure A (scale 1.7 mmol) starting from **18** (450 mg) and benzyl bromide (283 mg) gave **23** (230 mg, 36%) as colorless needles, mp 80 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.05–7.25 (m, 9H), 4.01 (m, 1H), 2.75–2.85 and 3.06–3.17 (two m, 4H), 1.25 (s, 9H); mass spectrum (EI): *m/z* 361 (1, $M^{\bullet+}$), 270 (100), 215 (20), 214 (66), 213 (14), 117 (28), 110 (54), 91 (38), 57 (29).

#### *4.3.10. 2-[ring-$D_5$]Benzyl-3-(4-t-butylphenyl)-1-phenylpropane-1-one (**24**) and 2,2-bis[ring-$D_5$]-benzyl-3-(4-t-butylphenyl)-1-phenylpropane-1-one (**25**)*

A solution of **16** (1.33 g, 5.0 mmol) and [*ring*-$D_5$]-benzyl bromide (1.75 g, 10.0 mmol) in anhydrous benzene (10 mL) was heated to reflux and a suspension of sodium *tert*-amylate (1.11 g, 10.0 mmol) in anhydrous benzene (30 mL) was added dropwise. The reaction was monitored by TLC ($CH_2Cl_2$) and additional portions of base (0.56 g, 5.0 mmol each) were added after 4, 8 and 24 h. After 80 h, the mixture was allowed to cool and washed thrice with hydrochloric acid (10%) and then thrice with water. The aqueous solutions were extracted with benzene and the combined organic layers dried over sodium sulfate. The solvent was removed in vacuo and the residue separated by column chromatography (silica gel, $CH_2Cl_2$).

The first-eluting fractions were recrystallized from ethanol, yielding **25** (240 mg, 10%) as a colorless solid; mp 138–139 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.32–7.38 (m, 1H), 7.22–7.26 (m, 4H),7.17 (m, 2H), 7.03 (m, 2H), 3.26 (s, 2H), 3.25 (s, 2H), 3.24 (s, 2H), 1.29 (s, 9H); mass spectrum (EI): *m/z* 456 (<1, $M^{\bullet+}$), 441 (1), 360 (55), 309 (29), 252 (54), 201 (30), 147 (93), 132 (22), 117 (20), 105 (100), 96 (77), 77 (37), 57 (79).

The second-eluting fractions were also recrystallized from ethanol, yielding **24** (360 mg, 20%) as a colorless solid; mp 75.5–78 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.70–7.73 (m, 2H), 7.07 and 7.22 (AA′BB′, $^3J$ = 8.3 Hz, 4H), 7.42–7.48 (m, 1H), 7.30–7.35 (m, 2H), 4.01 (*quin*, $^3J$ = 7.8 Hz, 1H), 3.06–3.17 (m, 2H), 2.74–2.85 (m, 2H), 1.25 (s, 9H); mass spectrum (EI): *m/z* 361 (<1, $M^{\bullet+}$), 346 (3), 265 (100), 250 (10), 214 (59), 147 (19), 132 (14), 131 (11), 117 (20), 105 (54), 96 (28), 91 (10), 77 (34), 57 (27).

#### *4.3.11. 2,2-Dibenzyl-3-(4-t-butylphenyl)-1-phenylpropane-1-one (**26**)*

Procedure B (scale 4.0 mmol) starting from **16** (1.06 g) and benzyl bromide (1.48 g) gave **26** (490 mg, 28%) as colorless needles, mp 136–137 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.02–7.38 (m, 19H), 3.25 (br s, 4H), 3.24 (s, 2H), 1.29 (s, 9H); mass spectrum (EI): *m/z* 446 (2, $M^{\bullet+}$), 355 (64), 299 (36), 252 (82), 207 (12), 196 (38), 147 (72), 105 (100), 91 (77), 77 (32), 57 (80); IR (KBr): $\bar{\nu}$ ($cm^{-1}$) 3058, 2963, 1673, 1451, 1421, 1263, 951, 755, 697. $C_{33}H_{34}O$ (446.64), calcd. C 88.75, H 7.67, found: C 88.89, H 7.52.

#### *4.3.12. 2,2-[α,α-$D_2$]Benzyl-3-(4-t-butylphenyl)-1-phenylpropane-1-one (**27**)*

Procedure B (scale 1.60 mmol) starting from **16** (420 mg) and [α,α-$D_2$]benzyl bromide (560 mg) gave **27** (370 mg, 51%) as colorless needles, mp 138–139 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.02–7.35 (m, 19H). 3.23 (s, 2H), 1.29 (s, 9H); mass spectrum (EI): *m/z* 450 (1, $M^{\bullet+}$), 357 (66), 303 (24),

254 (72), 211 (12), 149 (11), 147 (77), 105 (100), 93 (80), 77 (29), 57 (87).

#### *4.3.13. 2,2-Dibenzyl-1-(4-t-butylphenyl)-3-phenylpropane-1-one (**28**)*

A solution of 4-*t*-butylacetophenone (1.76 g, 10.0 mmol) and benzyl bromide (5.13 g, 30.0 mmol) in anhydrous benzene 820 mL) was heated to reflux and a suspension of sodium *tert*-amylate (3.32 g, 30.0 mmol) in anhydrous benzene (60 mL) was added dropwise. Heating was continued for a total of 36 h with TLC monitoring ($CH_2Cl_2$); after 6 h, further benzyl bromide (0.60 g, 3.5 mmol) and sodium *tert*-amylate (1.0 g, 9.0 mmol) were added and after 24 h, further base (1.0 g, 9.0 mmol). After 36 h, TLC control indicated that the product of three-fold benzylation had formed in addition to that of two-fold benzylation. The mixture was allowed to cool and washed thrice with hydrochloric acid (10%) and four times with water. The aqueous solutions were extracted with benzene and the combined organic layers were dried over sodium sulfate. The solvent was removed in vacuo to leave an orange oil which was purified by kugelrohr distillation (250 °C/0.05 mbar) and then by crystallization from ethanol yielding **28** (2.09 g, 47%) as colorless needles; mp 109–110.5 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.32 (m, 4H), 7.19–7.22 (m, 9H), 7.05–7.09 (m, 6H), 3.27 (s, 6H),1.30 (s, 9H); mass spectrum (EI): *m/z* 446 (<1, $M^{\bullet+}$), 431 (1), 389 (4), 355 (21), 299 (12), 265 (26), 252 (30), 161 (100), 146 (14), 131 (10), 118 (18), 104 (17), 91 (69), 57 (27); IR (KBr): $\bar{\nu}$ ($cm^{-1}$) 3028, 2969, 2911, 2870, 1663, 1603, 1494, 1446, 1273, 946, 845, 755, 748, 699. $C_{33}H_{34}O$ (446.64), calcd. C 88.74, H 7.67, found: C 88.70, H 7.67.

#### *4.3.14. 2,2-Bis-[α,α-$D_2$]benzyl-1-(4-t-butylphenyl)-3-phenyl-[3,3-$D_2$]propane-1-one (**29**)*

Similar to the procedure given above for **28**, 4-*t*-butylacetophenone (0.88 g, 5.0 mmol) and [α,α-$D_2$]-benzylbromide (3.03 g, 17.5 mmol) dissolved in anhydrous benzene (15 mL) were reacted with sodium *tert*-amylate (1.93 g, 17.5 mmol) dissolved in 40 mL of the same solvent. After 24 h, further base (1.00 g, 9.0 mmol) was added to the heated reaction mixture. The conversion was found to be almost complete after 48 h (TLC). Work-up and purification as described above yielded **29** (0.6 g, 17%) as a colorless solid, mp 109–111 °C (EtOH). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.32 (br s, 4H) 7.18–7.25 (m, 9H), 7.05–7.09 (m, 6H),1.30 (s, 9H); mass spectrum (EI): *m/z* (%) 452 (<1, $M^{\bullet+}$), 437 (1), 395 (3), 359 (21), 303 (10), 161 (100), 146 (9), 118 (14), 93 (46), 57 (15).

#### *4.3.15. 2-Benzyl-2-[ring-$D_5$]benzyl-3-(4-t-butylphenyl)-1-phenylpropane-1-one (**30**)*

This compound was prepared by reacting **24** (360 mg, 1.0 mmol) with benzyl bromide (200 mg, 1.2 mmol) and sodium *tert*-amylate (130 mg, 1.2 mmol) in anhydrous benzene (8 mL) by analogy to the procedures given above. Three-fold recrystallization from ethanol yielded 30 (260 mg, 58%) as a colorless solid; mp 139.5–140.5 °C. $^1$H NMR ($CDCl_3$, 250 MHz): $\delta$ 7.01–7.36 (m, 14H), 3.26 (s, 4H), 3.23 (s, 2H), 1.29 (s, 9H); mass spectrum (EI): *m/z* 451 (1, $M^{\bullet+}$), 436 (1), 360 (27), 355 (27), 304 (25), 252 (48), 201 (10), 196 (10), 147 (65), 132 (12), 117 (12), 105 (100), 96 (28), 91 (40), 77 (25), 57 (54).

#### *4.3.16. Reduction of the benzylated dihydrochalcones to the tert-butyl-substituted tribenzylmethanes and tetrabenzylmethanes (general procedure C)*

A suspension of lithium aluminum hydride (380 mg, 10.0 mmol) or lithium aluminum deuteride (420 mg, 10.0 mmol) in anhydrous diethyl ether (20 mL) was stirred at 0 °C while, under continuous cooling, solutions of aluminum chloride (4.00 g, 30.0 mmol) in 30 mL of the same solvent and, subsequently, of the benzylated or dibenzylated dihydrochalcone (10.0 mmol) in 20 mL of the same solvent were added dropwise. The cooling bath was removed and the mixture was heated until the starting ketone was completely consumed, as monitored by TLC ($CH_2Cl_2$). The total reaction time ranged up to 60 h. The mixture was then allowed to cool and hydrolyzed by addition

of ice/water and the liquid layers were separated without dissolution of the precipitate. The organic layer was dried over sodium sulfate and the solvent was distilled off to give liquid or solid residues, respectively. The *tert*-butyl-substituted tribenzylmethanes were purified by kugelrohr distillation as colorless oils, and the *tert*-butyl-substituted tetrabenzylmethanes were recrystallized from ethanol as colorless solids. Yields were generally in the range of 50–70%, if not noted otherwise.

#### *4.3.17. 2-Benzyl-1-(4-t-butylphenyl)-3-phenylpropane (**1**)*

Procedure C (scale 500 μmol) starting from **20** and $LiAlH_4/AlCl_3$ yielded **1** as a colorless oil, bp 180 °C/0.04 mbar. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.03–7.33 (m, 14H), 2.51–2.57 (m, 6H), 2.31 (m, 1H), 1.30 (s, 9H); mass spectrum (EI): *m/z* 342 (45, $M^{\bullet+}$), 327 (21), 194 (11), 147 (35), 132 (11), 117 (40), 92 (35), 91 (100), 57 (45); IR (film): $\bar{\nu}$ ($cm^{-1}$) 3029, 2966, 2870, 1494, 1453, 748, 699. $C_{26}H_{30}$ (342.53), calcd. C 91.17, H 8.83, found: C 91.22, H 8.73.

#### *4.3.18. [2-D]-2-Benzyl-1-(4-t-butylphenyl)-3-phenylpropane (**1a**)*

Procedure C (scale 1.00 mmol) starting from **22** and $LiAlH_4/AlCl_3$ yielded **1a** as a colorless oil, bp 176 °C/0.04 mbar. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.02–7.35 (m, 14H), 2.54 (s, 4H), 2.51 (s, 2H), 1.30 (s, 9H); a residual signal at $\delta$ 2.30 indicated D contents of ca. 60%. Mass spectrum (EI): *m/z* 343 (52, $M^{\bullet+}$), 328 (30), 194 (20), 147 (49), 132 (23), 118 (34), 117 (35), 92 (67), 91 (100), 57 (59); 58 at.% D.

#### *4.3.19. 2-Benzyl-1-(4-t-butylphenyl)-3-phenyl-[3,3-$D_2$]propane (**1b**)*

Procedure C (scale 400 μmol) starting from **21** and $LiAlH_4/AlCl_3$ yielded **1b** as a colorless oil, bp 180 °C/0.04 mbar. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.03–7.33 (m, 14H), 2.51–2.56 (m, 4H), 2.29 (quin, 1H), 1.30 (s, 9H); mass spectrum (EI): *m/z* 344 (50, $M^{\bullet+}$), 329 (26), 196 (9), 147 (48), 132 (16), 119 (32), 117 (21), 94 (16), 93 (100), 92 (38), 91 (80), 57 (88); 99 at.% D (99% $d_2$, 2% $d_1$).

#### *4.3.20. 2-[α,α-$D_2$]Benzyl-1-(4-t-butylphenyl)-3-phenyl-[3,3-$D_2$]propane (**1c**)*

Procedure C (scale 400 μmol) starting from **21** and $LiAlD_4/AlCl_3$ yielded **1c** as a colorless oil, bp 182 °C/0.05 mbar. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.03–7.33 (m, 14H), 2.52 (d, $^3J$ = 6.9 Hz, 2H), 2.27 (t, $^3J$ = 6.9 Hz, 1H), 1.30 (s, 9H); mass spectrum (EI): *m/z* 346 (27, $M^{\bullet+}$), 331 (15), 147 (26), 132 (10), 121 (11), 119 (12), 117 (10), 94 (16), 93 (100), 57 (55); 99 at.% D (97% $d_4$, 3% $d_3$).

#### *4.3.21. 2-Benzyl-1-(4-t-butylphenyl)-3-[$D_5$]phenylpropane (**1d**)*

Procedure C (scale 1.65 mmol) starting from **23** and $LiAlH_4/AlCl_3$ yielded **1d** as a colorless oil, bp 175 °C/0.01 mbar. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.24–7.33 (m, 2H), 7.11–7.20 (m, 3H), 7.04 and 7.27 (AA′BB′, $^3J$ = 8.3 Hz, 4H), 2.51–2.56 (m, 6H), 2.30 (*sep*, $^3J$ = 6.9 Hz, 1H), 1.30 (s, 9H); mass spectrum (EI): *m/z* 347 (54, $M^{\bullet+}$), 332 (42), 255 (7), 250 (8), 240 (6), 235 (9), 199 (16), 198 (12), 147 (74), 132 (27), 117 (53), 96 (93), 91 (100), 57 (90); 98 at.% D (95% $d_5$, 3% $d_4$, 2% $d_3$).

#### *4.3.22. 2-Benzyl-1-(4-t-butylphenyl)-3-[$D_5$]phenyl-[3,3-$D_2$]propane (**1e**)*

Procedure C (scale 300 μmol) starting from **23** and $LiAlD_4/AlCl_3$ yielded **1e** as a colorless oil, bp 180 °C/0.04 mbar. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.03–7.33 (m, 9H), 2.51–2.56 (m, 4H), 2.28 (*quin*, $^3J$ = 6.9 Hz, 1H), 1.30 (s, 9H); mass spectrum (EI): *m/z* 349 (45, $M^{\bullet+}$), 334 (25), 199 (23), 147 (52), 132 (24), 117 (42), 98 (72), 91 (100), 57 (89); 98 at.% D (87% $d_7$, 11% $d_6$, 2% $d_5$).

#### *4.3.23. 2-[α,α-$D_2$]Benzyl-1-(4-t-butylphenyl)-3-[$D_5$]phenylpropane (**1f**)*

Procedure C (scale 1.00 mmol) starting from **24** and $LiAlD_4/AlCl_3$ yielded **1f** as a colorless oil, bp 200 °C/0.1 mbar. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.03–7.33 (m, 9H), 2.51–2.57 (m, 4H), 2.27–2.32 (m, 1H), 1.30 (s, 9H); mass spectrum (EI): *m/z* 349 (89, $M^{\bullet+}$), 334 (58), 255 (8), 240 (8), 201 (8), 200 (11), 199 (8), 198 (9), 147 (76), 132 (25), 119 (34), 117

(35), 96 (92), 93 (100), 92 (41), 91 (14), 57 (93); 99 at.% D (93% $d_7$, 6% $d_6$, 1% $d_5$).

*4.3.24. 2,2-Dibenzyl-1-(4-t-butylphenyl)-3-phenylpropane (**3**)*

Procedure C (scale 500 μmol) starting from **26** and $LiAlH_4/AlCl_3$ yielded **3** as a colorless solid, mp 126 °C. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.16–7.29 (m, 19H), 2.74 (s, 6H), 2.71 (s, 2H), 1.32 (s, 9H); mass spectrum (EI): *m/z* 432 (2, $M^{\bullet+}$), 284 (9), 207 (24), 117 (10), 91 (100), 57 (62); IR (KBr): $\bar{\nu}$ ($cm^{-1}$) 3030, 2969, 2866, 1494, 1451, 1361, 1086, 1030, 741, 699. $C_{33}H_{36}$ (432.65), calcd. C 91.61, H 8.39, found: C 91.72, H 8.18.

*4.3.25. 2,2-Dibenzyl-1-(4-t-butylphenyl)-3-phenyl-[3,3-$D_2$]propane (**3a**)*

Procedure C (scale 400 μmol) starting from **26** and $LiAlD_4/AlCl_3$ yielded **3a** as a colorless solid, mp 127–128 °C. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.16–7.30 (m, 19H), 2.74 (s, 4H), 2.71 (s, 2H), 1.32 (s, 9H); mass spectrum (EI): *m/z* 434 (4, $M^{\bullet+}$), 286 (12), 209 (45), 147 (41), 132 (13), 117 (17), 93 (48), 91 (98), 57 (100).

*4.3.26. 2,2-Dibenzyl-1-(4-t-butylphenyl)-3-phenyl-[1,1-$D_2$]propane (**3b**)*

Procedure C (scale 3.40 mmol) starting from **28** and $LiAlD_4/AlCl_3$ yielded **3b** as a colorless solid, mp 125–126 °C. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.16–7.29 (m, 19H), 2.74 (s, 6H), 1.32 (s, 9H); mass spectrum (EI): *m/z* 434 (7, $M^{\bullet+}$), 284 (32), 209 (32), 207 (47), 193 (24), 181 (27), 149 (54), 134 (18), 119 (18), 117 (19), 91 (100), 57 (57); 98 at.% D (96% $d_2$, 3% $d_1$, 1% $d_0$).

*4.3.27. 2-[α,α-$D_2$]Benzyl-1-(4-t-butylphenyl)-3-phenyl-[3,3-$D_2$]propane (**3c**)*

Procedure C (scale 1.90 mmol) starting from **27** and $LiAlH_4/AlCl_3$ yielded **3c** (20%) as a colorless solid, mp 126–127 °C. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.16–7.29 (m, 19H), 2.74 (s, 2H), 2.71 (s, 2H), 1.32 (s, 9H); mass spectrum (EI): *m/z* 436 (3, $M^{\bullet+}$), 287 (21), 211 (61), 209 (25), 195 (14), 183 (15), 147 (67), 132 (23), 119 (20), 117 (28), 93 (100), 91 (59), 57 (81); 95 at.% D (80% $d_4$, 19% $d_3$, 1% $d_2$).

*4.3.28. 2,2-Bis-[α,α-$D_2$]benzyl-1-(4-t-butylphenyl)-3-phenyl-[1,1-$D_2$]propane (**3d**)*

Procedure C (scale 220 μmol) starting from **27** and $LiAlD_4/AlCl_3$ yielded **3d** as a colorless solid, mp 125–126 °C. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.16–7.29 (m, 19H), 2.70 (s, 2H), 1.32 (s, 9H); mass spectrum (EI): *m/z* 438 (12, $M^{\bullet+}$), 289 (23), 213 (43), 211 (28), 147 (43), 132 (15), 117 (16), 93 (100), 57 (53); 99 at.% D (93% $d_6$, 5% $d_5$, 2% $d_4$).

*4.3.29. 2,2-Bis-[α,α-$D_2$]benzyl-1-(4-t-butylphenyl)-3-phenyl-[1,1,3,3-$D_4$]propane (**3e**)*

Procedure C (scale 660 μmol) starting from **29** and $LiAlD_4/AlCl_3$ yielded **3e** as a colorless solid, mp 124–126 °C. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.16–7.29 (m, 19H), 1.32 (s, 9H); mass spectrum (EI): *m/z* 440 (10, $M^{\bullet+}$), 289 (19), 213 (50), 196 (12), 184 (18), 149 (39), 134 (16), 121 (16), 119 (16), 93 (100), 57 (54); 99 at.% D (93% $d_8$, 6% $d_7$, 1% $d_6$).

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