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Intermediate Ion–Neutral Complexes Formed During the Gas-phase Protonolysis of *p*-(*tert*-Butyl)-substituted *a*,*ω*-Diphenylalkanes†‡

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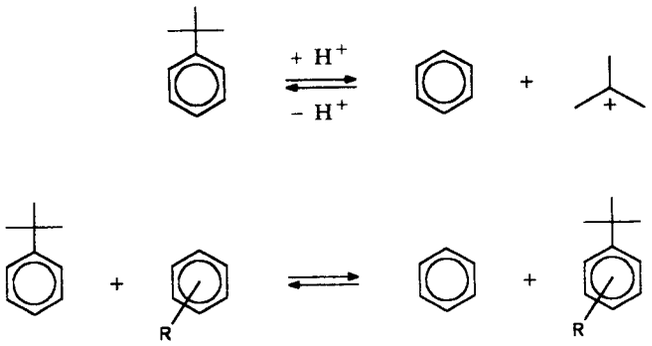
Loss of isobutane is the exclusive fragmentation channel of long-lived protonated *tert*-butyl-substituted *α*,*ω*-diphenylalkanes with chain lengths $n = 2$–12. Methane chemical ionization/mass-analysed ion kinetic energy spectrometry of the $[M + H]^+$ ions and several deuterium-labelled *tert*-butyl-substituted 1,2-, 1,3- and 1,10-diphenylalkanes revealed that the reaction involves with equal probability and maximum regioselectivity a hydride ion from both the adjacent and the remote benzylic methylene groups, irrespective of the length of the aliphatic chain. The isotope effect of the hydride abstraction step was found to be same in all cases, $k[C_4H_{10}]/k[C_4H_9D] = 1.6 \pm 0.1$. A sterically restricted system, protonated 1-benzyl-4-(*tert*-butylbenzyl)benzene, shows the same behaviour. This implies, as a general phenomenon, the formation of intermediate ion–neutral complexes $[C_4H_9^+ \ Ar(CH_2)_nAr]$ along with (or instead of) the corresponding *π* complexes $[C_4H_9^+ \cdots Ar(CH_2)_nAr]$ prior to isobutane elimination (Ar represents a phenyl or substituted-phenyl group).

INTRODUCTION

Dealkylative C—C bond fission of alkylaromatic compounds occurs in the liquid phase in strong Brønsted acid solution or by Lewis acid catalysis.[2] De-*tert*-butylation of *tert*-butylbenzenes is particularly easily achieved in superacidic media,[3] and trans-*tert*-butylation between aromatic compounds is induced by Lewis acid catalysts (Scheme 1).[4]

Beyond any doubt, *σ* complexes are crucial intermediates in these electrophilic aromatic substitution reactions. The structure, relative stabilities and reactivities of such covalently bound complexes, in particular of those of alkylbenzenes, have been studied in great detail in liquid media by NMR spectrometry;[3b,5] gaseous *σ* complexes have been investigated by various mass spectrometric techniques,[6–9] gas-phase radiolysis[10,11] and computational approaches.[6a,12,13] Important key data from all these studies are the facts that *σ* complexes readily interconvert by unimolecular ('intraannular') proton shifts[14] and that the *ipso*-protonated form is generally the least stable among all tautomers.[6,13,15] Further, *σ* complexes of diphenylalkanes and related alkylbenzenes undergo fast interannular proton transfer reactions.[6a,16]



Scheme 1

In contrast to these truly covalent species, the role and properties of *π* complexes in the course of electrophilic aromatic substitution are much less clear. *π* Complexes have been invoked as intermediates during the attack of the electrophile on the arene, during the isomerization of interconverting *σ* complexes and during the expulsion of the electrofuge. Since the early liquid-phase work on this problem,[17] no experimental evidence has been reported confirming the existence and nature of *π* complexes in solution. Recent computational studies[12] corroborate the existence of stable, non-covalent adducts of an electrophile and an arene in the gas phase, but the bonding nature of these complexes may be more adequately described as 'electrostatic' ion–molecule complexes.

The formation of ion–neutral complexes during the fragmentation of gaseous ions has attracted wide interest in recent years.[18–21] Most interesting are those cases where the formation of such intermediates opens up new and unexpected fragmentation channels for the reactive ions, rather than representing a mere mechanistic modification of the fragmentation process. In the

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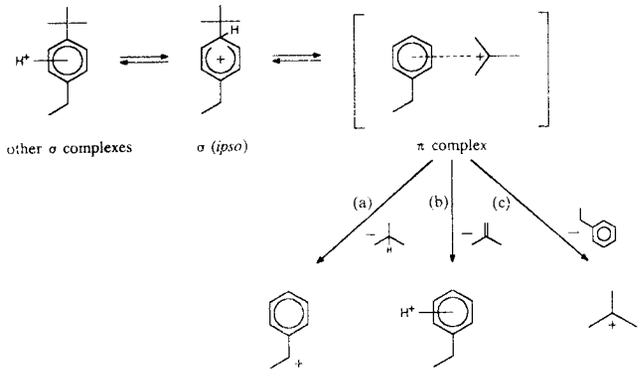


Scheme 2. Fragmentation paths of higher alkylbenzenium ions.

field of gaseous protonated alkylbenzenes (alkylbenzenium ions),[6a] representing the prototype species for intermediates in electrophilic aromatic substitution chemistry, the formation of ion–molecule complexes has been envoked several times since the very first idea[22] that such species may be formed during mass spectrometric fragmentation processes. Thus, the formation of 'disolvated protons' has been suggested;[23] more recently, convincing evidence for the possible intermediacy of π complexes was published.[9,24,25] However, no clear proof has been presented for the existence of truly non-covalently bound ion–molecule complex intermediates in the regime of gaseous alkylbenzene ions.[1]

In this paper, we present full experimental evidence for the formation of ion–neutral complexes during the fragmentation of 'large' alkylbenzenium ions. We suggest that the fragmentation of protonated *tert*-butylbenzenes bearing at least one additional phenyl group (Ar) forms, in addition to or instead of the classical π complexes, electrostatically bound ion–molecule complexes $[C_4H_9^+ \ Ar(CH_2)_nAr]$ prior to fragmentation.

Our study was based originally on the observation of Audier *et al.*[25] that protonated 1-(*tert*-butyl)-4-ethylbenzene and related benzenium ions dissociate preferentially by elimination of isobutane (path a, Scheme 2) rather than by loss of isobutene (path b) or ethylbenzene (path c). This finding showed convincingly that (at least[1]) a π complex should be involved after the cleavage of the σ(*ipso*) complex. Also, Kebarle and coworkers[26] and Cacace and Ciranni[27] studied the intermolecular *trans-tert*-butylation of arenes in the gas phase. The former group formulated a transient species which, in terms of geometry, is reminiscent of the pentacoordinate transition state of an S_N2 reaction (see below). In view of our extended studies of the fast inter- and intraannular proton transfer reactions in protonated diphenyl- and oligophenylalkanes,[6a,16,28] we started a systematic investigation of the proton-induced fragmentation of *tert*-butyl-substituted diphenylalkanes and related aromatic alkylbenzenium ions.[1] In particular, we aimed to learn more of the details of the mobility of alkyl cations in such extended ionic systems bearing at least two isolated, i.e. non-conjugated, aromatic rings. As will be shown, this system provides compelling experimental evidence for the high mobility of *tert*-butyl ions trapped, within a unimolecularly formed ion–molecule complex, at the backbone of a large alkylbenzene neutral counterpart.

Table 1. Fragmentation of the metastable $[M + H]^+$ ions of (4-*tert*-butyl)diphenylmethanes 1 and 8 and α-(4-*tert*-butylphenyl)-ω-phenylalkanes 2–7 (MIKE spectra)

Ion	Loss of C_4H_{10} (%)	Formation of $C_4H_9^+$ (%)	Loss of C_4H_8 (%)	Formation[a] of $RC_7H_6^+$ (%)
$[1 + H]^+$	89	6	—	5[b]
$[2 + H]^+$	>99	<1	—	—
$[3 + H]^+$				
$[4 + H]^+$				
$[5 + H]^+$				
$[6 + H]^+$				
$[7 + H]^+$				
$[8 + H]^+$	49	—	29	14[c], 6[b], 2[d]

[a] Products of C(aryl)—C(alkyl) protonolysis.
[b] R = *t*-C_4H_9.
[c] R = C_7H_7.
[d] R = *t*-$C_4H_9C_7H_6$.

RESULTS AND DISCUSSION

Isobutane loss from metastable ions

Seven unbranched α-(4-*tert*-butylphenyl)-ω-phenylalkanes (**1**–**7**, with n = 1–4, 6, 10 and 12 methylene groups), a congener containing a third arene as a spacer group, 1-benzyl-(4-*tert*-butyl)diphenylmethane (**8**), and several deuterium-labelled analogues of selected members of this series were synthesized (see Experimental) and the mass-analysed ion kinetic energy (MIKE) spectra of their $[M + H]^+$ ions generated in the chemical ionization (CI) (methane) source were measured. With the exception of the two diphenylmethane derivatives, **1** and **8**, elimination of isobutane is the exclusive fragmentation reaction of the metastable $[M + H]^+$ ions (Table 1). As an example, the MIKE spectrum of ions $[2 + H]^+$ is shown in Fig. 1. With **1** and **8**, this process is still the dominating fragmentation route, but the common heterolytic cleavage reactions of the other C(aryl)—C(alkyl) bonds increasingly compete with

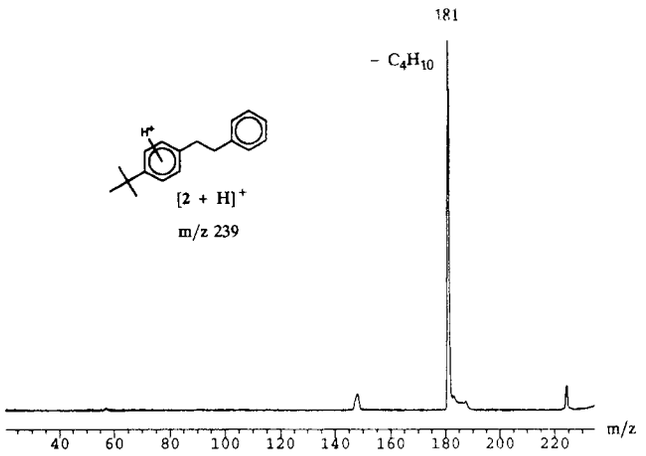
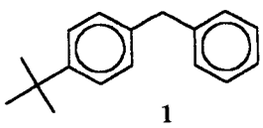


Figure 1. CI(CH_4)/MIKE spectra of protonated 1-(4-*tert*-butylphenyl)-2-phenylethane (**2**). All minor peaks are due to fragmentation of the isobaric radical ions $[^{13}C]$-$\mathbf{2}^{+\cdot}$.

increasing size of the araliphatic backbone. Simple heterolysis of the C(4)—$C(CH_3)_3$ bond (path c) represents a minor fragmentation channel for **1** (6%) and is absent for **8**. In contrast, loss of isobutene (path b) gains importance, representing ~30% of the fragmentation of metastable $[\mathbf{8} + H]^+$ ions. In addition, both ions $[\mathbf{1} + H]^+$ and $[\mathbf{8} + H]^+$ undergo heterolytic cleavages of the benzylic bonds with relative rates which reflect the relative stability of the corresponding σ(*ipso*) complexes.



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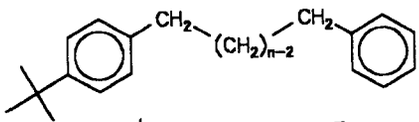
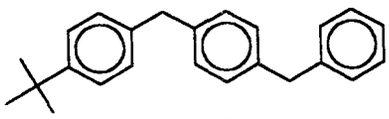


	2	3	4	5	6	7
n	2	3	4	6	10	12



8

The competition of the benzylic fragmentation of the diphenylmethane-type ions $[\mathbf{1} + H]^+$ and $[\mathbf{8} + H]^+$ is certainly due to the favourable thermochemistry of this 'simple-cleavage' process. The corresponding fragmentation of the C(aryl)—C(alkyl) bonds in ions $[\mathbf{2} + H]^+$ to $[\mathbf{7} + H]^+$ is at least kinetically disfavoured because it would require some rearrangement or cyclization steps.[6a,16] Moreover, the fact that loss of isobutene is observed exclusively in the case of **8** may suggest that the proton affinities of the araliphatic backbone increases with increasing number of arene rings rather than with size.[29]

So far, the results demonstrate that loss of isobutane (path a) from protonated *tert*-butyl-substituted diphenylalkanes and related systems is a general and clearly favoured fragmentation channel. This is in agreement with thermochemical estimations which place the heat of reaction of this process by at least 20 kJ mol^{-1} below that of the formation of free $C_4H_9^+$ ions (path c).[25,29]

Regioselectivity of hydride abstraction

The $[M + H]^+$ ions of the two chain-labelled isotopomers [1,1-D_2]- and [2,2-D_2]-1-(4-*tert*- butylphenyl) -2- phenylethane (**2a** and **2b**), respectively, show identical MIKE spectra (Fig. 2). In both cases, [D_0]isobutane and [D_1]isobutane are eliminated in the ratio of 1.59 (±0.05). In the case of the ring-D_5-labelled isotopomer **2c** (not shown in Fig. 2), the label is completely retained in the ionic fragment. This clearly shows that the *tert*-butyl group combines at random with one of the four benzylic hydrogen atoms. The primary kinetic isotope effect, $k_H/k_D = 1.59$ (±0.05), discriminating against the incorporation of deuterium into the neutral isobutane, follows directly from these observations. Interestingly, the same value has been observed for the isobutane loss from the simple, monoannular *tert*-butyl-substituted alkylbenzenium ions.[25]

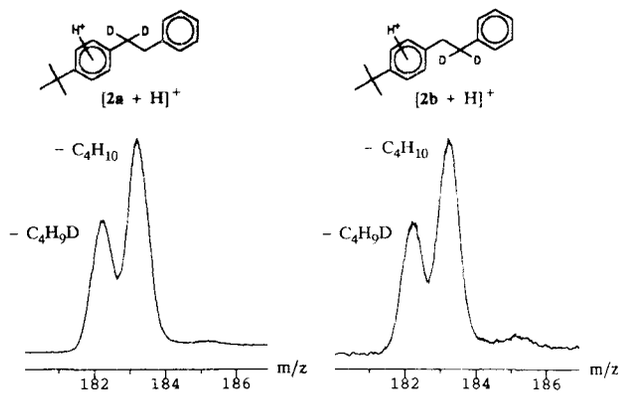
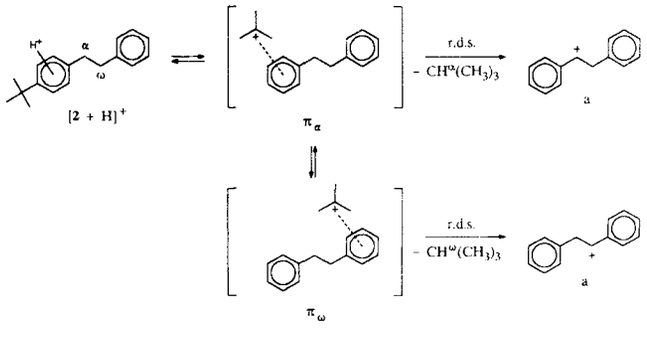


Figure 2. MIKE spectra of protonated 1-(4-*tert*-butylphenyl)-2-phenylethanes **2a** and **2b**. Note: the minor signals are due the loss of C_4H_8 from $[^{13}C_1]$-$M^{+\cdot}$ ions.

It is obvious that the reaction proceeds stepwise, that is, by formation of a *tert*-butyl cation which, in a pseudo-intramolecular process, abstracts a hydride or deuteride ion[30] from either the adjacent [C(α)] or the remote [C(β)] benzylic methylene groups. Clearly, the second step is the rate-limiting step of the overall process. Irrespective of the site of hydride abstraction, it leads irreversibly to identical fragments, viz. 1,2-diphenylethyl cation (*a*) and isobutane (Scheme 3). Since hydrogen equilibration within the aliphatic C_2 link of the diphenylethane moiety cannot occur prior to the hydride abstraction step, two degenerate π complexes (π_α and π_ω) have to be formed. It will be shown, however, that steric consideration requires, in addition, the intermediacy of a non-covalent ion–molecule complex $[C_4H_9^+ \ Ar(CH_2)_2Ar]$ along with the π complexes.

This argument is corroborated by the fragmentation of the isotopomers of the next-higher homologue, protonated [1,1-D_2]-, [2,2-D_2]-, [3,3-D_2]-1-(4-*tert*-butylphenyl)-3- phenylpropane (**3a–c**) and the [ring-D_5] isotopomer **3d** (Fig. 3).[1] Again, the expelled isobutane molecule incorporates exclusively one of the four benzylic hydrogens. Whereas ions $[\mathbf{3a} + H]^+$ and



Scheme 3

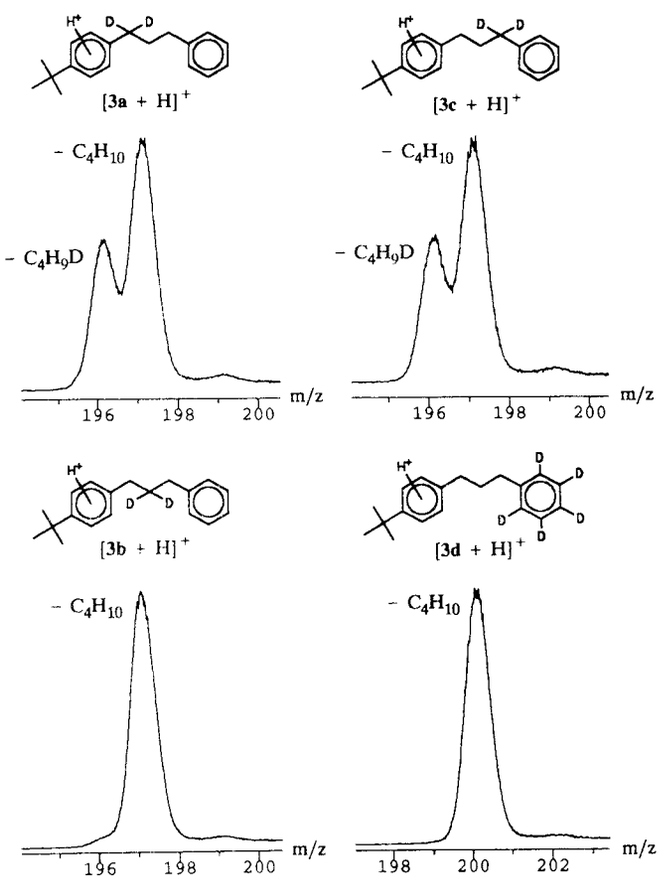


Figure 3. MIKE spectra of protonated 1-(4-*tert*-butylphenyl)-3-phenylpropanes **3a–d**. See note to Fig. 2.

[**3c** + H]$^+$ eliminate [D_0]isobutane and [D_1]isobutane in the same ratio, the isotopomers [**3b** + H]$^+$ and [**3d** + H]$^+$ undergo only loss of [D_0]isobutane. Hence, here again, no hydrogen exchange occurs within the aliphatic chain prior to the perfectly regioselective and random hydride abstraction from the benzylic positions. Moreover, the kinetic isotope effect observed, $k_H/k_D = 1.6 \pm 0.1$, is identical with that found for the lower homologue.

In fact, the highly selective and 'symmetrical' hydride abstraction from the benzylic positions is not limited to the lower homologues. Long-chain *tert*-butyl-substituted diphenylalkanes behave identically. Although close to the limit of the peak resolution, the CI/MIKE spectra of [1,1-D_2]- and [10,10-D_2]-1-(4-*tert*-butylphenyl)-10-phenyldecanes **6a** and **6b** (Fig. 4) unequivocally exhibit loss of [D_0]- and [D_1]isobutane in the same, and obviously general, ratio of 1.6 ($\pm$0.1). Even without cross-checking with complementarily labelled isotopomers, it seems certain that, here again, the homobenzylic and further non-activated C—H bonds do not serve as hydride donors for the elimination of isobutane. It is therefore concluded from these results that the mechanism and regioselectivity of isobutane loss from the [M + H]$^+$ ions of *tert*-butyl-substituted α,ω-diphenylalkanes are independent of the length of the aliphatic chain.

Finally, three isotopomers of the *tert*-butyl-substituted 1,4-dibenzylbenzene **8** were studied. In addition to the two complementarily labelled isotopomers **8a** and

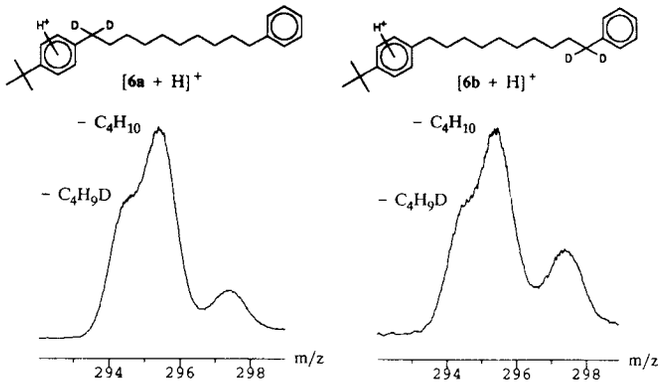


Figure 4. MIKE spectra of protonated 1-(4-*tert*-butylphenyl)-10-phenyldecanes **6a** and **6b**. See note to Fig. 2.

8b, a third (**8c**) bearing complete deuterium labelling at both of the benzylic positions was synthesized and subjected to CI/MIKE spectrometry (Fig. 5). Because of the competition of other fragmentation channels, in particular of isobutene loss (path c), in ions [**8** + H]$^+$, the rate-limiting role of the hydride abstraction may be probed. In fact, and in agreement with the results discussed above, isobutane loss is discriminated as compared with isobutene loss by ~40% in the MIKE spectrum of the tetradeuterated ions [**8c** + H]$^+$. For another time, the (partial) MIKE spectra of the two dideuterated isotopomers [**8a** + H]$^+$ and [**8b** + H]$^+$ are identical, and the ratio of [D_0]isobutane and [D_1]isobutane loss,

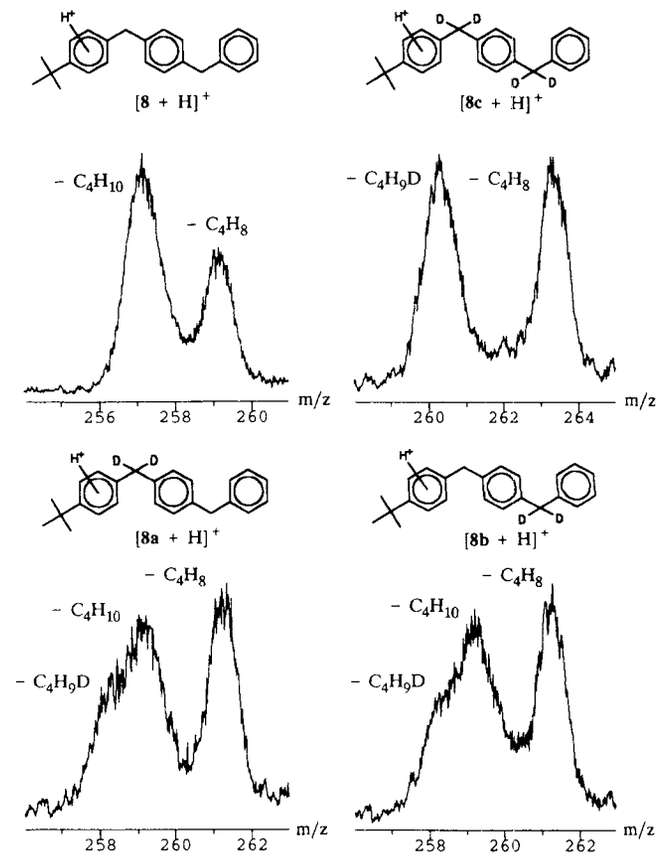


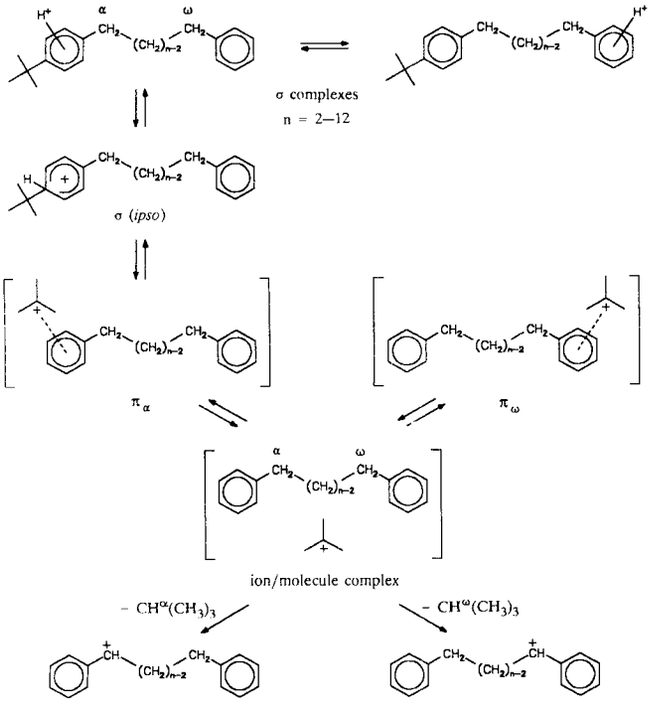
Figure 5. Partial MIKE spectra of protonated 1-benzyl-(4-*tert*-butylbenzyl)benzenes **8a–d**. In this case, the loss of C_4H_8 originates mainly from the [M + H]$^+$ ions (*cf.* path b, Scheme 2).

1.6 ± 0.15, is again very close to the value obtained for the α,ω-diphenylalkane-type homologues.

Formation of ion–neutral complexes $[C_4H_9^+ \ Ar(CH_2)_nAr]$

As demonstrated above, the loss of isobutane displays the same characteristics in all systems studied so far. Most importantly, the 'symmetrization' of the araliphatic backbone during the reaction appears to be ubiquitous, and, likewise, the constancy of the kinetic isotope effect associated with the hydrogen abstraction step indicates common mechanistic features. It is obvious that, at least in the metastable ions, the C—C bond heterolysis enables the *tert*-butyl group to move freely as a *tert*-butyl cation in the vicinity of all of the arene rings present in the araliphatic moiety and to pick up at random a hydride ion from the benzylic methylene groups. Thus, a primarily formed π_α complex appears to be in equilibrium with another, equivalent one (π_ω), in which the *tert*-butyl ion is coordinated to the other arene ring (Scheme 4). In the case of **8**, three such π complexes should coexist: a 'central' one, being slightly more stable than the other two, 'terminal', tautomers. Such an equilibrium of π complexes is in line with previous reports which suggested the intermediacy of π complexes during the fragmentation of protonated alkylbenzenes.[24,25] Interestingly, recent *ab initio* calculations place prototype π complexes such as [benzene···*t*-$C_4H_9^+$] at ~56 kJ mol^{-1} below the thermochemical fragmentation threshold.[12]

Beyond this, the results presented in this study indicate the formation of electrostatically bound ion–neutral complexes prior to fragmentation (Scheme 4). This follows from a closer inspection of the steric requirements for the *tert*-butyl cation transfer between the aromatic rings.

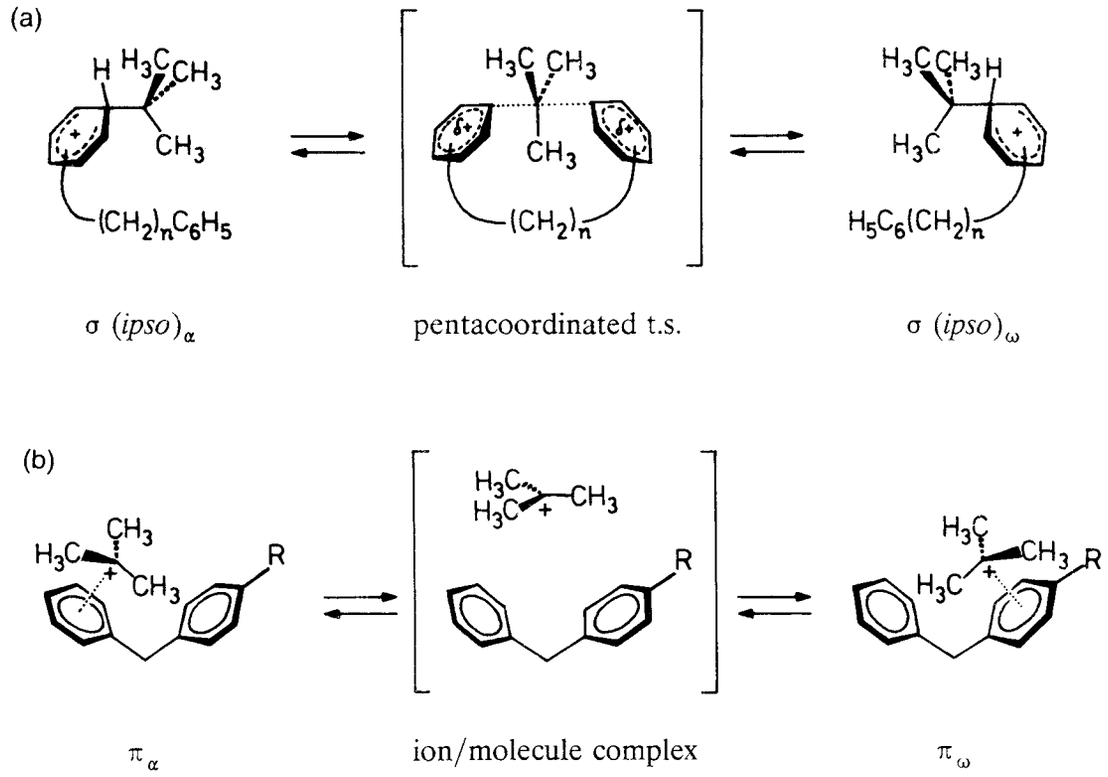


Scheme 4. Fragmentation of protonated α-(4-*tert*-butylphenyl)-ω-phenylalkanes via σ, π and ion–molecule complexes.

Two limiting cases are considered. (i) In the first [Scheme 5(a)], the *tert*-butyl cation is handed on from one arene ring to the other via a pentacoordinated transition state, corresponding to the anionic counterpart formed during a bimolecular nucleophilic (S_N2) substitution reaction. Such a situation has been assumed for the gas-phase *trans-tert*-butylation between *tert*-butylbenzenium ions and toluene.[26] Such an arrangement would require, however, an essentially linear orientation of the *C(ipso)*—$C(CH_3)_3$ bonds being broken and formed more or less simultaneously. Actually, a pentacoordinated transition state does not at all implicate the formation of any π complex intermediates since it is the corresponding σ complexes which would react via the pentacoordinated transition state. (ii) In the second case [Scheme 5(b)], the π complexes are mutually converted via a transient species in which the *tert*-butyl is associated with the neutral alkylbenzene molecule by electrostatic attractive forces. The non-covalent character of such ion–neutral complexes allows the two partners to move much more freely within the complex than in the first case, and steric restrictions implied by the limited flexibility of the alkylbenzene molecule would be negligible. Similar ion–neutral complexes containing mobile acetyl cations and extended aromatic molecules have been reported recently.[32]

The long-chain homologues, such as ions $[\mathbf{6} + H]^+$, do not allow one to differentiate between the two models. The 1,10-diphenylalkane molecule is sufficiently flexible to form, hypothetically, a well aligned pentacoordinated transition state. Yet another possibility is that the long aliphatic chain would also allow the formation a doubly π complexed, sandwich-type intermediate [Ar···$C_4H_9^+$···Ar], that is, of a truly disolvated cation in which the arene units are linked by the polymethylene chain. Much in contrast, however, the shorter homologues such as $[\mathbf{2} + H]^+$ and $[\mathbf{3} + H]^+$ should *not* be able to form a pentacoordinated transition state or a sandwich-type π complex for steric reasons. This is particularly obvious for the diphenylethane-derived ions $[\mathbf{2} + H]^+$, in which the parallel orientation of the two benzene rings is energetically not accessible. In the case of the diphenylmethane-derived ions $[\mathbf{1} + H]^+$ and $[\mathbf{8} + H]^+$, steric restrictions are even further increased [Scheme 5(b)].

Hence the formation of electrostatically bound ion–neutral complexes $[C_4H_9^+ \ Ar(CH_2)_nAr]$ is necessary to explain the degenerate regioselectivity of the hydride abstraction during isobutane loss. As shown by the common isotope effect for all systems studied so far, ion–neutral complex intermediates $[C_4H_9^+ \ Ar(CH_2)_nAr]$ may coexist with the π complexes, $[C_4H_9^+\cdots Ar(CH_2)_nAr]$, and interconvert with them prior to the irreversible hydride abstraction step. It is striking to note that the rate of thermal intermolecular *tert*-butylation of 1,2-diphenylethane and its higher homologues exceeds that of the *tert*-butylation of toluene by a factor of 2.9,[11] and more[33], respectively). Although this may be explained[11] by the extra stabilization by the neutral 'spectator ring' within the conventional σ complexes, it may also point to the role of electrostatic complexes which involve attractive interactions[12] of the *tert*-butyl cation with both of the arene units, a situation which is close to if not identical



Scheme 5. *tert*-Butyl cation transfer via (a) a pentacoordinated transition state and (b) an ion–molecule complex. The conformation shown in (a) would be accessible for $n \geqslant 3$. For (b), the cases of $n = 1$ are illustrated (with R = H or $CH_2C_6H_5$).

with the ion–neutral complex intermediates deduced from the unimolecular fragmentation studied here. Notwithstanding, the question as to the relative stability of such ion–molecule complexes as compared with π complexes remains open.

CONCLUSION

Gas-phase protonolysis of *tert*-butyl-substituted α,ω-diphenylalkanes and related alkylbenzenes gives rise to the formation of a *tert*-butyl cation bound to the diphenylalkane neutral species within ion–molecule complexes $[C_4H_9^+ \; Ar(CH_2)_nAr]$, which eventually decompose by elimination of isobutane. This follows (i) from the highly regioselective incorporation of a hydride from either of the two benzylic methylene groups of the diphenylalkane moiety into the isobutane fragment and (ii) from the ubiquity of this phenomenon even in sterically restricted systems which do not allow for a pentacoordinated (hypervalent) transition state for the *tert*-butyl cation transfer. The corresponding π complexes $[C_4H_9^+ \cdots Ar(CH_2)_nAr']$ (π_α) and $[C_4H_9^+ \cdots Ar'(CH_2)_nAr]$ (π_ω) may also be formed but are in fact not required to explain the 'α,ω regioselectivity' of the process. Further research is underway to determine the limits to the mobility of the *tert*-butyl cation within these complexes and more details about the possible coexistence of π complexes and electrostatic ion–molecule complexes.

EXPERIMENTAL

The MIKE spectra were recorded with an AutoSpec double-focusing instrument (Fisons VG, Manchester, UK) under the following conditions: acceleration voltage 8 kV, electron energy 70 eV, emission current 200 μA. The $[M + H]^+$ ions were generated by protonation in the CI methane plasma (methane from Matheson, stated purity >99.95%). Samples were introduced by using a heated solid probe inlet system. The ion-source temperature and pressure were 180 ± 10 °C and 6×10^{-4}–8×10^{-4} mbar (1 mbar = 100 Pa), respectively.

Melting points (uncorrected) were determined with an Electrothermal melting point apparatus. ^{1}H NMR spectra were measured with Varian EM 360 A (60 MHz) and Bruker AM 300 (300 MHz) instruments using $CDCl_3$–TMS as solvent. Analytical mass spectrometric measurements [electron impact (EI) ionization, 70 eV] were performed with Finnigan MAT CH5 and VG AutoSpec instruments. Combustion analyses were carried out with a Leco CHNS-932 instrument.

4-*tert*-Butyldiphenylmethane (**1**) was synthesized as described previously.[1]

The synthesis of the 1-(4-*tert*-butylphenyl-2-phenylethanes **2**–**2c** was achieved by Friedel–Crafts reaction of phenylacetyl chloride and *tert*-butylbenzene in carbon disulphide,[34] followed by reduction of the resulting 4-*tert*-butyldesoxybenzoin with a 3:1 mixture of $AlCl_3/LiAlH_4$ or $AlCl_3/LiAlD_4$ in diethyl ether.[35] [2,2-D_2]-1-(4-*tert*-Butylphenyl)-2-phenylethane-1-one was

prepared from the parent compound by threefold H/D exchange with D_2O/NEt_3 in dioxane solution.[36]

1-(4-*tert*-Butylphenyl)-2-phenylethan-1-one: m.p. 41–42 °C (from methanol; lit.[34] 43–44 °C); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.33 (s, 9 H), 4.26 (s, 2 H), 7.24–7.33 (m, 5 H), 7.45–7.98 (AA'BB', ^3J = 8.5 Hz, 4 H); MS (EI, 70 eV), *m/z* 252 (1, $M^{+\cdot}$), 161 (100), 91 (63). [2,2-D_2]-1-(4-*tert*-Butylphenyl)-2-phenylethan- 1-one: ^{1}H NMR (300 MHz), δ (ppm) 1.33 (s, 9 H), 7.24–7.33 (m, 5 H), 7.45–7.98 (AA'BB', ^3J = 8.6 Hz, 4 H); MS (EI, 70 eV), *m/z* 254 (1; $M^{+\cdot}$), 161 (100), 93 (27), 91 (11).

1-(4-*tert*-Butylphenyl)-2-phenylethane (**2**): m.p. 34.5–35.5 °C (from light petroleum; lit.[37] m.p., 34–35 °C); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.32 (s, 9 H), 2.91 (br s, 4 H), 7.15–7.34 (m, 9 H); MS (EI, 70 eV), *m/z* 238 (31; $M^{+\cdot}$), 223 (28), 147 (100), 91 (31). [1,1- D_2]-1-(4-*tert*-Butylphenyl)-2-phenylethane (**2a**): ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.32 (s, 9 H), 2.90 (s, 2 H), 7.14–7.35 (m, 9 H); MS (EI, 70 eV), *m/z* 240 (44, $M^{+\cdot}$), 225 (37), 149 (100), 91 (35); label contents (from MS) 98% (96% D_1, 4% D_1). [2,2-D_2]-1-(4-*tert*-Butylphenyl)-2-phenylethane (**2b**): ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.32 (s, 9 H), 2.88 (s, 2 H), 7.14–7.34 (m, 9 H); MS (EI, 70 eV), *m/z* 240 (30; $M^{+\cdot}$), 225 (26), 147 (100), 93 (34), 91 (30); label contents (from MS) 94% (90% D_2, 8% D_1, 2% D_0). The [ring-D_5] isotopomer **2c** was obtained by Wittig reaction of [ring-D_5]benzyltriphenylphosphonium bromide and 4-*tert*-butylbenzaldehyde followed by hydrogenation of the stilbene with Pd/C in ethyl acetate. 1-(4-*tert*-Butylphenyl)-2-[D_5]phenylethene: m.p. 89–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.33 (s, 9 H), 7.09 (s, 2 H), 7.37–7.48 (AA'BB', ^3J = 8.5 Hz, 4 H); MS (EI, 70 eV), *m/z* 241 (66; $M^{+\cdot}$), 226 (100). 1-(4-*tert*-Butylphenyl)-2- [D_5]phenylethane (**2c**): m.p. 37.5–39 °C (from ethanol); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.32 (s, 9 H), 2.91–2.92 (m, 4 H), 7.14–7.34 (AA'BB', ^3J = 8.3 Hz, 4 H); MS (EI, 70 eV), *m/z* 243 (22; $M^{+\cdot}$), 228 (27), 147 (100), 132 (28), 117 (30), 96 (42), 91 (18); label contents (from MS) 95% (88% D_5, 8% D_4, 4% D_3).

The 1-(4-*tert*-butylphenyl)-2-phenylpropanes **3**–**3d** were synthesized via the corresponding 4- and 4'-*tert*-butylchalcones and -dihydrochalcones. The latter were reduced with H_2/Pd/C in acetic acid or D_2/Pd/Cin [*O*-D]acetic acid, respectively, in a Parr hydrogenation apparatus at 5 bar and room temperature.[37] In order to improve the regioselectivity of the labelling in **3a**,[1] the corresponding dihydrochalcone was subjected to reduction with $AlCl_3/LiAlD_4$ in diethyl ether.[35] [2,2-D_2]-3-(4-*tert*-butylphenyl)-1-phenylpropan-1-one was prepared by H/D exchange in dioxane/D_2O/Net_3.[36]

1-(4-*tert*-Butylphenyl)-3-phenylpropane (**3**) was obtained in near-quantitative yield as a colourless liquid, b.p. 148 °C/0.3 mbar (Kugelrohr); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.31 (s, 9 H), 1.96 (q, ^3J = 7.8 Hz, 2 H), 2.63 (t, ^3J = 7.8 Hz, 2 H), 2.66 (t, ^3J = 7.8 Hz, 2 H), 7.11–7.32 (m, 9 H); MS (EI, 70 eV), *m/z* 252 (33, $M^{+\cdot}$), 237 (100), 147 (9), 131 (18), 117 (26), 105 (22), 91 (78). [1,1-D_2]-1-(4-*tert*-Butylphenyl)-3-phenylpropane (**3a**) by deuterolysis:[1] ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.31 (s, 9 H), 1.92–1.94 (m, 2 H), 2.58–2.62 (m, 2 H), 7.11–7.32 (m, 9 H); partial MS (EI, 70 eV), *m/z* 253/254/255/256 (6.6/23.5/39.7/25.5; major $M^{+\cdot}$ isotopomers), 238 (17), 239 (63), 240 (100), 241 (71; major $[M - CH_3]^+$ isotopomers); label contents (from MS) 141% (see below). The product obtained alternatively by $AlCl_3/LiAlD_4$ reduction contained >91% of the $[D_2]$ isotopomer but ~30% of the corresponding $[D_1]$ olefin (MS) which, however, did not interfere in the MIKES measurements shown in Fig. 3. [2,2-D_2]-1-(4-*tert*-Butylphenyl)-3-phenylpropane (**3b**): ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.31 (s, 9 H), 2.61 (s, 2 H), 2.64 (s, 2 H), 7.11–7.34 (m, 9 H); MS (EI, 70 eV), *m/z* 254 (35; $M^{+\cdot}$), 239 (100), 147 (13), 133 (15), 117 (18), 92 (52), 91 (56), 57 (24); label contents (from MS) 92% (85% D_2). [3,3-D_2]-1-(4-*tert*-Butylphenyl)-3-phenylpropane (**3c**): ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.31 (s, 9 H), 1.94 (t, ^3J = 7.7 Hz, 2 H), 2.62 (t, ^3J = 7.8 Hz, 2 H), 7.11–7.32 (m, 9 H); MS (EI, 70 eV), *m/z* 254 (34; $M^{+\cdot}$), 239 (100), 147 (13), 131 (18), 117 (26), 93 (61), 57 (27); label contents (from MS) 97% (see below). 1-(4-*tert*-Butylphenyl)-3-[D_5]phenylpropane (**3d**): ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.31 (s, 9 H), 1.95 (q, ^3J = 7.8 Hz, 2 H), 2.62 (t, ^3J = 7.9 Hz, 2 H), 2.66 (t, ^3J = 7.8 Hz, 2 H), 7.11–7.31 (AA'BB', ^3J = 8.2 Hz, 4 H); MS (EI, 70 eV), *m/z* 257 (34; $M^{+\cdot}$), 242 (100), 147 (11), 131 (13), 96 (25), 57 (21); label contents (from MS) 97.5% (89% D_5).

As a general phenomenon, deuterolyses of 4-*tert*-butylphenones, $(4\text{-}t\text{-}C_4H_9C_6H_4CO)(CH_2)_nC_6H_5$, take place with relatively low regiospecificity compared with those of the unsubstituted phenones, $C_6H_5CO(CH_2)_n$-$C_6H_4(4\text{-}t\text{-}C_4H_9)$. In the extreme case of compound **3a**, repeated runs gave only low isotopic purity and site specificity (7% D_1, 27% D_2, 39% D_3, 23% D_4, 3% D_5; 141% D). By contrast, reduction to **3c** occurred relatively cleanly (16% D_1, 72% D_2, 9% D_3; 2% D_4; 96.6% D). The MIKES technique allows the $[M + H]^+$ isotopomer of interest to be selected, except for those isobaric ions containing natural ^{13}C. Thus for ions $[\mathbf{3a} + H]^+$, an increased experimental error ($\pm$5% Σ) has to be taken into account.

The 1-(4-*tert*-butylphenyl)-10-phenyldecanes **6**–**6b** were synthesized from diethyl sebacate (Aldrich), which was converted into the monoester monoacid chloride and subsequent Friedel–Crafts reaction with benzene to give 10-oxo-10-phenyldecanoic acid, as described.[39–41] The keto acid was reduced to 10-phenyldecanoic acid by hydrogenolysis under 4.5 bar of hydrogen in the presence of Pd/C (10%, Merck) in acetic acid.[38] Correspondingly, [10,10-D_2]-10-phenyldecanoic acid was obtained by using [*O*-D]acetic acid and D_2/Pd/C.[38b] Conversion into the acid chloride and Friedel–Crafts reaction with *tert*-butylbenzene in dichloromethane led to the 1-(4-*tert*-butylphenyl)-10- phenyldecan-1-ones, which were reduced by the chloroalanate method ($LiAlH_4/AlCl_3$ or $LiAlD_4/AlCl_3$) to give the *tert*-butyl-substituted 1,10-diphenyldecanes **6**–**6b**.[35b]

10-Phenyldecanoic acid: m.p. 42–44 °C (lit.[41] m.p. 40–42 °C); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.29 (br s, 10 H), 1.58–1.65 (m, 4 H), 2.34 (t, ^3J = 7.5 Hz, 2 H), 2.60 (t, ^3J = 7.7 Hz, 2 H), 7.16–7.30 (m, 5 H); MS (EI, 70 eV), *m/z* 248 (29; $M^{+\cdot}$), 230 (10), 92 (81), 91 (100). [10,10-D_2]-10-Phenyldecanoic acid: m.p. 41.5–43.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.29 (br s, 10 H), 1.59–1.65 (m, 4 H), 2.35 (t, ^3J = 7.5 Hz, 2 H), 7.15–7.31 (m, 5 H); label contents (from MS) 93% (88% D_2, 10% D_1, 2% D_0). 1-(4-*tert*-Butylphenyl)-10-phenyldecan-1-one: m.p. 43–45 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ

(ppm) 1.31–1.32 (m, 10 H), 1.34 (s, 9 H), 1.57–1.75 (m, 4 H), 2.60 (t, ^3J = 7.7 Hz, 2 H), 2.94 (t, ^3J = 7.4 Hz, 2 H), 7.17–7.30 (m, 5 H), 7.46–7.92 (AA'BB', ^3J = 8.6 Hz, 4 H); MS (EI, 70 eV), *m/z* 364 (14; $M^{+\cdot}$), 307 (17), 176 (97), 161 (100), 91 (70). [10,10-D_2]-1-(4-*tert*-Butylphenyl)-10-phenyldecan-1-one: MS (EI, 70 eV), *m/z* 366 (7; $M^{+\cdot}$), 309 (10), 176 (80), 161 (100), 93 (63), 91 (38).

1-(4-*tert*-Butylphenyl)-10-phenyldecane (**6**): b.p. 140 °C/0.01 mbar (Kugelrohr); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.25–1.36 (m, 12 H), 1.31 (s, 9 H), 1.58–1.64 (m, 4 H), 2.54–2.62 (m, 4 H), 7.10–7.31 (m, 9 H); MS (EI, 70 eV), *m/z* 350 (78; $M^{+\cdot}$), 335 (100), 147 (27), 131 (40), 117 (33), 91 (73), 57 (53). [1,1-D_2]-1-(4-*tert*-Butylphenyl)-10-phenyldecane (**6a**): ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.24–1.32 (m, 12 H), 1.31 (s, 9 H), 1.56–1.60 (m, 4 H), 2.59 (t, ^3J = 7.7 Hz, 2 H), 7.10–7.31 (m, 9 H); MS (EI, 70 eV), *m/z* 352 (55; $M^{+\cdot}$), 337 (98), 149 (23), 133 (44), 119 (29), 91 (100), 57 (52); label contents (from MS) 98% (96% D_2, 4% D_1). [10,10-D_2]-1-(4-*tert*-Butylphenyl)-10-phenyldecane (**6b**): ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.24–1.32 (m, 12 H), 1.31 (s, 9 H), 1.53–1.62 (m, 4 H), 2.52–2.58 (m, 2 H), 7.09–7.31 (m, 9 H); MS (EI, 70 eV), *m/z* 352 (34; $M^{+\cdot}$), 337 (69), 147 (26), 131 (41), 117 (33), 93 (43), 91 (34), 57 (100).

The 4-(4-*tert*-butylbenzyl)-4′-benzylbenzenes **8**–**8c** were obtained as follows: 4-bromodiphenylmethane was prepared by reduction of 4-bromobenzophenone (Janssen) with $NaBH_4$ in trifluoroacetic acid.[42] [α,α-D_2]-4-bromodiphenylmethane was obtained by using $LiAlD_4/AlCl_3$ in dry diethyl ether as the reducing agent.[35a] The 4-bromodiphenylmethanes were reductively coupled to 4-*tert*-butylbenzaldehyde (obtained from 4-*tert*-butylbenzoic acid by sequential reduction with $LiAlH_4$ and reoxidation with MnO_2) using metallic lithium.[43] The corresponding 4-*tert*-butyl-4′-benzylbenzhydrols obtained in this way were in turn subjected to oxidation with MnO_2 to give the corresponding 4-*tert*-butyl-4′-benzylbenzophenones, which were reduced to the hydrocarbons **8**–**8c** with $LiAlH_4/AlCl_3$ or $LiAlD_4/AlCl_3$, respectively, in dry diethyl ether.[35a]

4-Bromodiphenylmethane: b.p. 110 °C/0.05 mbar (Kugelrohr); ^{1}H NMR (60 MHz, $CDCl_3$), δ (ppm) 3.9 (s, 2 H), 6.9–7.5 (m, 9 H); MS (EI, 70 eV), *m/z* 246/248 (32/34; $M^{+\cdot}$), 167 (100). [α,α-D_2]-4-Bromodiphenylmethane: b.p. 110 °C/0.05 mbar (Kugelrohr); ^{1}H NMR (60 MHz, $CDCl_3$), δ (ppm) 6.9–7.5 (m, 9 H); MS (EI, 70 eV), *m/z* 248/250 (55/49; $M^{+\cdot}$), 169 (100). 4-Benzyl-4′-*tert*-butylbenzhydrol: ^{1}H NMR (60 MHz, $CDCl_3$), δ (ppm) 1.3 (s, 9 H), 2.2 (br s, 1 H, OH), 4.0 (s, 2 H), 5.8 (s, 1 H, C*H*OH), 7.2–7.3 (m, 13 H); MS (EI, 70 eV), *m/z* 330 (57; $M^{+\cdot}$), 315 (23), 195 (100), 161 (65), 91 (50); combustion analysis (%), calculated C 87.23, H 7.93, found C 87.22, H 7.69. [α,α-D_2]-4-Benzyl-4′-*tert*-butylbenzhydrol: ^{1}H NMR (60 MHz, $CDCl_3$), δ (ppm) 1.3 (s, 9 H), 2.2 (br s, 1 H, OH), 5.7 (s, 1 H, C*H*OH), 7.2–7.3 (m, 13 H); MS (EI, 70 eV), *m/z* 332 (87, $M^{+\cdot}$), 317 (37), 197 (100), 161 (81), 93 (63), 91 (31). 4-Benzyl-4′-*tert*-butylbenzophenone: m.p. 72–74 °C; ^{1}H NMR (60 MHz, $CDCl_3$), δ (ppm) 1.3 (s, 9 H), 4.0 (s, 2 H), 7.2–7.8 (m, 13 H); MS (EI, 70 eV), *m/z* 328 (71; $M^{+\cdot}$), 313 (100), 195 (35), 165 (25), 91 (18); combustion analysis (%), calculated C 87.76, H 7.37, found C 87.13, H 7.32. [α,α-D_2]-4-Benzyl-4′-*tert*-butylbenzophenone: m.p. 72–73.5 °C; ^{1}H NMR (60 MHz, $CDCl_3$), δ (ppm) 1.3 (s, 9 H), 7.2–7.8 (m, 13 H); MS (EI, 70 eV), *m/z* 330 (51; $M^{+\cdot}$), 315 (100), 197 (35), 161 (26), 93 (25).

4-Benzyl-4′-*tert*-butyldiphenylmethane (**8**): m.p. 31.5–32.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.29 (s, 9 H), 3.91 (s, 2 H), 3.94 (s, 2 H), 7.09–7.30 (m, 13 H); MS (EI, 70 eV), *m/z* 314 (46; $M^{+\cdot}$), 299 (100), 165 (16), 91 (20); combustion analysis (%), calculated C 91.67, H 8.33, found C 91.69, H 8.03. [α,α-D_2]-4-Benzyl-4′-*tert*-butyldiphenylmethane (**8a**): m.p. 31.5–32.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.29 (s, 9 H), 3.94 (s, 2 H), 7.09–7.31 (m, 13 H); MS (EI, 70 eV), *m/z* 316 (47; $M^{+\cdot}$), 301 (100), 167 (15), 91 (13); label contents (from MS) 97% (94% D_2, 6% D_1). 4-([α,α-D_2]Benzyl)-4′-*tert*-butyldiphenylmethane (**8b**): m.p. 31.5–33 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.29 (s, 9 H), 3.91 (s, 2 H), 7.09–7.31 (m, 13 H); MS (EI, 70 eV), *m/z* 316 (54; $M^{+\cdot}$), 301 (100), 167 (20), 93 (30), 91 (20); label contents (from MS) 96% (93% D_2, 6% D_1, 1% D_0). [α,α-D_2]-4-([α,α-D_2]Benzyl)-4′-*tert*-butyldiphenylmethane (**8c**): m.p. 32–33 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) 1.29 (s, 9 H), 7.10–7.31 (m, 13 H); MS (EI, 70 eV), *m/z* 318 (57; $M^{+\cdot}$), 303 (100), 169 (23), 167 (20), 93 (31); label contents (from MS) 95% (80% D_4, 19% D_3, 1% D_2).

1-(4-*tert*-Butylphenyl)-4-phenylbutane (**4**), 1-(4-*tert*-butylphenyl)-6-phenylhexane (**5**), and 1-(4-*tert*-butylphenyl)-12-phenyldodecane (**7**) were prepared by Friedel–Crafts *tert*-butylation of the corresponding α,ω-diphenylalkanes[44] using *tert*-butyl chloride and $AlCl_3$ in cyclohexane. After standard work-up and Kugelrohr distillation, the product still contained considerable amounts of the corresponding twofold *tert*-butylated diphenylalkanes and some starting material. Nevertheless, the CI/MIKE spectra obtained from these mixtures gave unequivocal information on the fragmentation of the $[M + H]^+$ ions of interest.

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