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Gaseous [t-$C_4H_9^+$ α,ω-diphenylalkane] complexes: methyl substituent effects on the intracomplex proton transfer and regioselective hydride abstraction

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Abstract

The loss of isobutane and isobutene from a series of long-lived protonated 1-(4-*tert*-butylphenyl)-3-phenylpropanes bearing two or three methyl substituents on the aromatic rings have been studied by mass-analyzed ion kinetic energy spectrometry and deuterium labelling. Both processes occur via intermediate ion/neutral complexes consisting of the *tert*-butyl cation and the corresponding di- or trimethyl-substituted 1,3-diphenyl-propanes, and the competition between these intracomplex proton and hydride transfer processes is governed by the (overall) gas-phase basicity of the 1,3-diphenylpropane, on the one hand, and by the localized activation of the benzylic C–H bonds acting as hydride donors, on the other. In addition to the benzylic α- and ω-methylene groups, *ortho*-sited methyl substituents are also involved in the hydride transfer, in contrast to those at the *meta* and *para* positions, and their fractional contributions to the overall isobutane loss strongly depends on the electronic influence of the other methyl group(s) at the same ring. Regioselectivities of the intracomplex hydride abstraction by t-$C_4H_9^+$ from the α and γ or α, γ and *ortho* positions of the 1,3-diphenylpropanes have been evaluated assuming the kinetic isotope effect k_H/k_D that is found to operate ubiquitously in these complexes. While acting as hydride donors on their own, *ortho*-methyl groups attenuate the hydride donor ability of the adjacent benzylic methylene group by steric hindrance, in particular in the case of twofold (2,6-dimethyl) substitution. Comparison with the fragmentation behavior of the 2-methyl- and 2,6-dimethyl-substituted mononuclear 4-(*tert*-butyl)ethylbenzenium ions corroborate the kinetic isotope effect and, in particular, the activating effect of the second ("spectator") ring on the hydride abstraction within the [t-$C_4H_9^+$ α,ω-diphenylalkane] complexes. (Int J Mass Spectrom 199 (2000) 155–187) © 2000 Elsevier Science B.V.

Keywords: Hydride abstraction; Proton transfer; Alkylbenzenes; Benzenium ions; Ion/neutral complexes; Substituent effects

1. Introduction

Protonated alkylbenzenes bearing a *tert*-butyl group and a sufficiently activated benzylic C–H bond are known to undergo facile elimination of isobutane [1,2]. This reaction channel represents an alternative to the two common fragmentation routes of alkylbenzenium ions, viz. elimination of the corresponding alkene and/or release of the related alkyl cation (Scheme 1) [3,4,5,6,7,8]. The unimolecular elimination of isobutane from simple *tert*-butyl-substituted alkylbenzenium ions or the bimolecular formation from the corresponding alkylbenzenes and the *tert*-

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Dedicated to Professor Henri Édouard Audier on the occasion of his 60th birthday.

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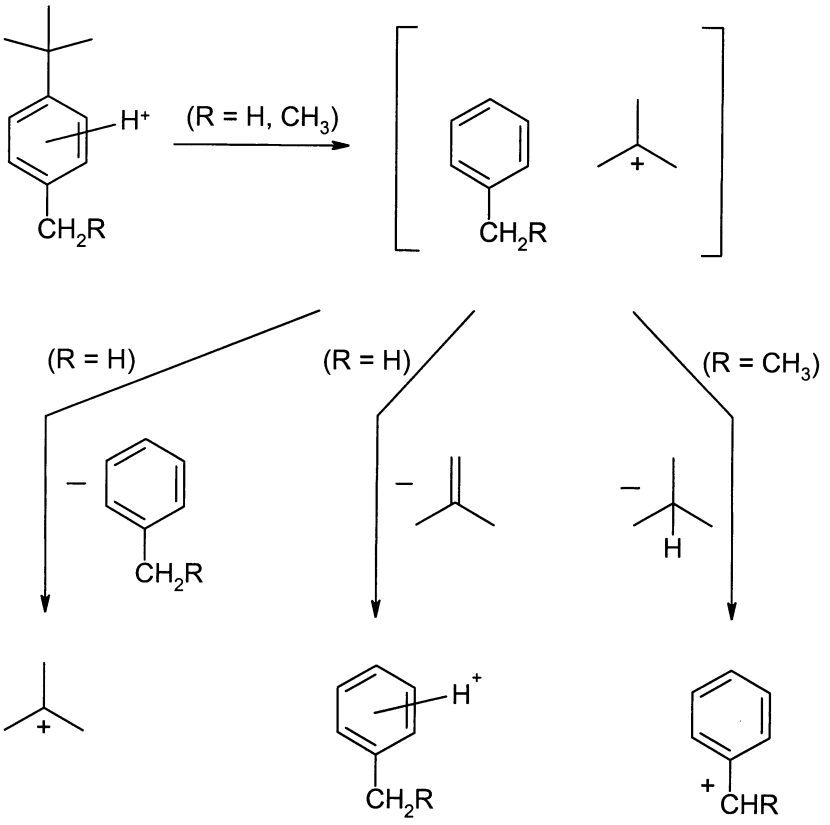
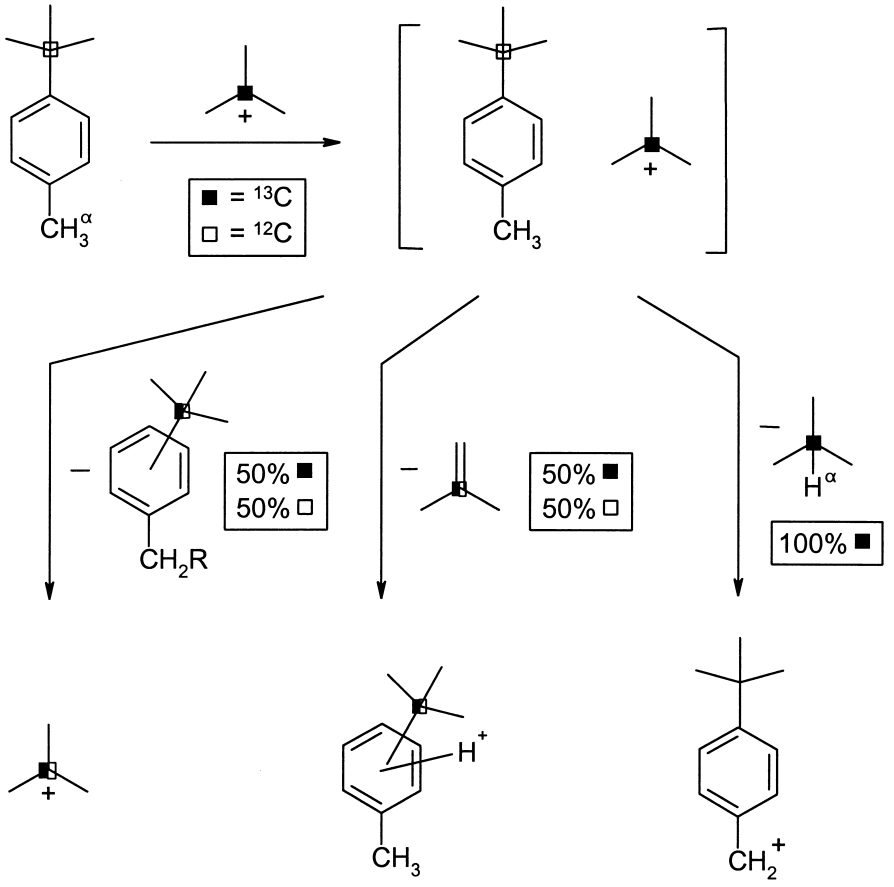


Scheme 1.

butyl cation was first reported by Audier and his associates in 1991 [1], who postulated the intermediacy of an ion/molecule complex consisting of the *tert*-butyl cation and the neutral alkylbenzene formed upon dealkylation. Audier also demonstrated that the hydride donating benzylic C–H bond requires some electronic activation by an alkyl (e.g. methyl) group in either the α or the *para* position of the toluene nucleus. For example, both protonated 4-(*tert*-butyl) ethylbenzene and the complex generated from *t*-$C_4H_9^+$ and *para*-xylene or other *para*-alkyltoluenes expel isobutane [1,9], whereas protonated 4-(*tert*-butyl)toluene and the complex generated from *t*-$C_4H_9^+$ and toluene do not [1]. In the same line, the "isomeric" ion/molecule complexes containing *ortho*- or *meta*-xylene undergo isobutane loss to a much lesser extent [9a]. Regioselective hydride abstraction in gaseous ion/molecule complexes has been observed in various other cases including oxygenated reactants [10,11,12].

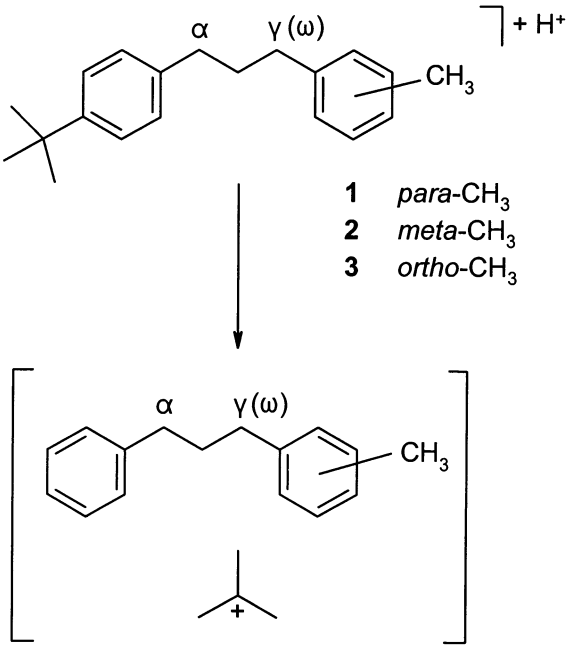
Among the series of related cases that demonstrate the ubiquity of the isobutane elimination route in simple (*tert*-butyl)alkylbenzenium ions, Audier et al. also found an intriguing case where all three of the fragmentation channels compete, but obviously involve different, noninterconverting, ion/molecule complexes [9a]. In the ion/molecule reaction of *t*-$C_4H_9^+$ ions with 4-*tert*-butyltoluene the incoming ion specifically abstracts an α-hydride from the neutral reactant, whereas it becomes equivalent with the covalently bonded *tert*-butyl group prior to the release of both isobutene and *t*-$C_4H_9^+$ ions (Scheme 2). This is remarkable in view of the particularly low thermodynamic stability of the σ complexes formed upon protonation of *tert*-butylbenzenes as compared to isomeric alkylbenzenium ions [9b,13] and the consid-



Scheme 2.

erable stability of the corresponding ion/molecule complexes [t-$C_4H_9^+$ (alkyl)benzene] [9,14].

In a systematic series of investigations, we adapted Audier's findings [1] and studied the reactions of various *tert*-butyl-substituted α,ω-diphenylalkanes and related alkylbenzenes under gas-phase protonolysis [2,15,16]. It became evident that the heterolytic cleavage of the C^{arene}–$C(CH_3)_3$ bond gives rise to noncovalently bonded complexes [t-$C_4H_9^+$ diphenylalkane] in which the *tert*-butyl cation is coordinated to the entire diphenylalkane molecule and is free to abstract a hydride from each sufficiently reactive (benzylic) C–H donor bond of this neutral constituent, irrespective of the initial position (α or ω] of the *tert*-butyl group and of the length of the aliphatic chain [16a]. Moreover, electronic activation of the C^{ω}–H (i.e. the C^{γ}–H) bonds by a single *para*- or *meta*-methyl group at the remote ring leads to a pronounced preference for elimination of isobutane containing a hydride from the $\omega(\gamma)$ position, viz. $[C_4H_9H^{\gamma}]/[C_4H_9H^{\alpha}] = 3.3{:}1$ for the *para* isomer $[\mathbf{1} + H]^+$ and $[C_4H_9H^{\gamma}]/[C_4H_9H^{\alpha}] = 1.7{:}1$ for the *meta* isomer $[\mathbf{2} + H]^+$ (Scheme 3) [16b]. In contrast, an *ortho*-sited methyl group in $[\mathbf{3} + H]^+$, in spite of its electronically activating influence, gave no preference for hydride abstraction from the remote position, hence suggesting that steric hindrance operates against hydride abstraction in this case. However, it was found that the *ortho*-methyl group in $[\mathbf{3} + H]^+$, in contrast to *meta*- or *para*-methyl, acts as an additional, albeit weak, hydride donor toward the complexed *tert*-butyl cation [16b]. Finally, the pres-



From ref. [16b]	$\frac{[C_4H_{10}]}{[C_4H_8]}$	$\frac{[C_4H_9H^{\gamma}]}{[C_4H_9H^{\alpha}]}$
1	100 : 0	3.3 : 1
2	35 : 65	1.7 : 1
3	87 : 13	1.0 : 1

Scheme 3. Competing fragmentation paths and regioselectivity of hydride abstraction in metastable ions $[\mathbf{1} + H]^+$, $[\mathbf{2} + H]^+$ and $[\mathbf{3} + H]^+$.

ence of methyl groups in ions $[\mathbf{2} + H]^+$ and $[\mathbf{3} + H]^+$ not only affected the hydride donor ability of the remote benzyl group but also the overall proton affinity of the diphenylpropane molecule; as a consequence, hydride abstraction by the *tert*-butyl cation from the diphenylalkane was found to compete with

the (counterdirectional) proton transfer from the *tert*-butyl cation to the diphenylalkane.

In this article, we demonstrate the effect of two or several methyl substituents in protonated 1-(4-*tert*-butylphenyl)-3-phenylpropanes **4**–**11**: (i) on the competition between the intracomplex hydride abstraction and intracomplex proton transfer, (ii) on the regioselectivity of the intracomplex hydride transfer, and (iii) on the decisive role of the second ("spectator") ring in ion/molecule complexes. In this context, the hydride abstraction in the $[M + H]^+$ ions of some simple 2-methyl- and 2,6-dimethyl-substituted 4-(*tert*-butyl)ethylbenzenes (**13** and **14**) and of the related *ortho*,*ortho*-dimethyl-substituted 1-(4-*tert*-butylphenyl)-3-phenylpropanes (**8** and **9**) will also be examined. As will be shown, there is a severe steric hindrance toward hydride abstraction in the 2,6-dimethyl-substituted ions which, however, is attenuated by the presence of the spectator ring. The complete set of 36 compounds examined, most having been synthesized for the first time, is collected in Chart 1.

2. Experimental

2.1. Measurements

All measurements were carried out on a doubly focussing instrument, AutoSpec (Fisons, Manchester/UK) with three-sector EBE geometry. The compounds were introduced into the Cl source via the septum of the direct inlet system or by using the heatable inlet rod. Throughout, methane was used as the reactant gas at 4×10^{-5}–1×10^{-4} mbar (nominal); the electron energy was set at 70 eV, trap current 0.2 mA, accelerating voltage 8000 V, and source temperature 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. Spectral data represent averages of at least ten consecutive scans and the measurements were repeated on different days without significant change.

2.2. Synthesis—General

^{1}H nuclear magnetic resonance (NMR) spectra (300 MHz) were measured on a Bruker AM 300 instrument ($CDCl_3$/tetramethylsilane). Mass spectra: VG Autospec; electron impact ionization (70 eV). Accurate mass measurements: VG Autospec; peak matching method with perfluorokerosiu (PFK) as a reference. Deuterium contents were evaluated from the electron ionization (EI) mass spectrometric data after ^{13}C correction. Infrared (IR) spectra: Perkin Elmer model 841; solids were measured in KBr pellets, liquids, and oils as films. Melting points (uncorrected): Electrothermal melting point apparatus. Combustional analyses: Leco CHNS-932. All distillations were performed using a Büchi GKR 50 kugelrohr apparatus. Thin layer chromatography (TLC): silica (Kieselgel 60) on aluminum foil with fluorescence indicator F_{254}, thickness 0.2 mm (Merck).

2.3. Synthesis of the substituted 1,3-diphenylpropanes

The synthetic work on which the mass spectrometric measurements were based followed the general lines described in previous articles of this series [2,16]. Since most of the target hydrocarbons as well as the synthetic intermediates have been unknown, experimental details and characteristic data of the new compounds are collected in the Appendix. Briefly, the 1,3-diarylpropanes were synthesized by aldol condensation of the suitably substituted benzaldehydes and acetophenones. Typically, both of these compounds (15–40 mmol each) were dissolved in 20–30 mL of methanol and aqueous potassium hydroxide (20%) was added. The mixtures were stirred at ~25 °C for 12 h and the 1,3-diarylprop-1-ene-3-ones (chalcones) were isolated by standard procedures (filtration of solid crude products or acidification with AcOH and Et_2O followed by extraction in the case of nonprecipitating crude products). Purification of the chalcones was effected by recrystallization or kugelrohr distillation, respectively. Where appropriate, deuterium labelling of aromatic rings and methyl groups was

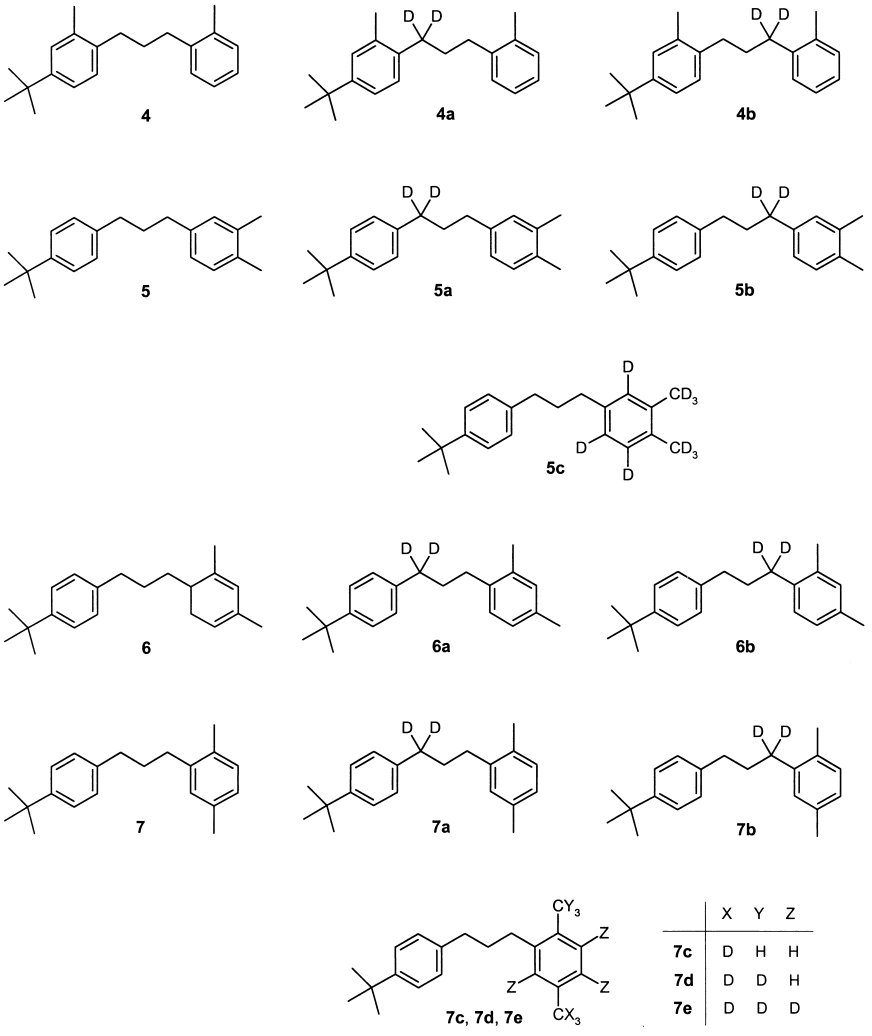


Chart 1 (part A)

effected before condensation, using the corresponding labelled acetophenones and following established procedures.

Conversion of the chalcones into the corresponding 1,3-diarylpropane-3-ones (dihydrochalcones) was achieved by catalytic hydrogenation of the chalcones (10 mmol) in ethyl acetate (~30 mL) at ~20 °C and 1 bar in the presence of Adam's catalyst, formed from $PtO_2 \cdot xH_2O$ (30 mg) during the beginning of each hydrogenation. After standard workup, the dihydrochalcones were purified by recrystallization from ethanol or, where appropriate, by kugelrohr distillation.

Reduction of the dihydrochalcones to the corresponding 1,3-diarylpropanes was performed either: (i) by catalytic hydrogenolysis under medium pressure, or (ii) by chloroalane reduction. The general protocols are given below.

(i) *Catalytic hydrogenolysis*: To a solution of the *tert*-butylated 1,3-diphenylpropane-1-one (1.0 mmol), or the corresponding 1,3-diphenylprop-2-ene-1-one (1.0 mmol), in glacial acetic acid (5 mL) was added

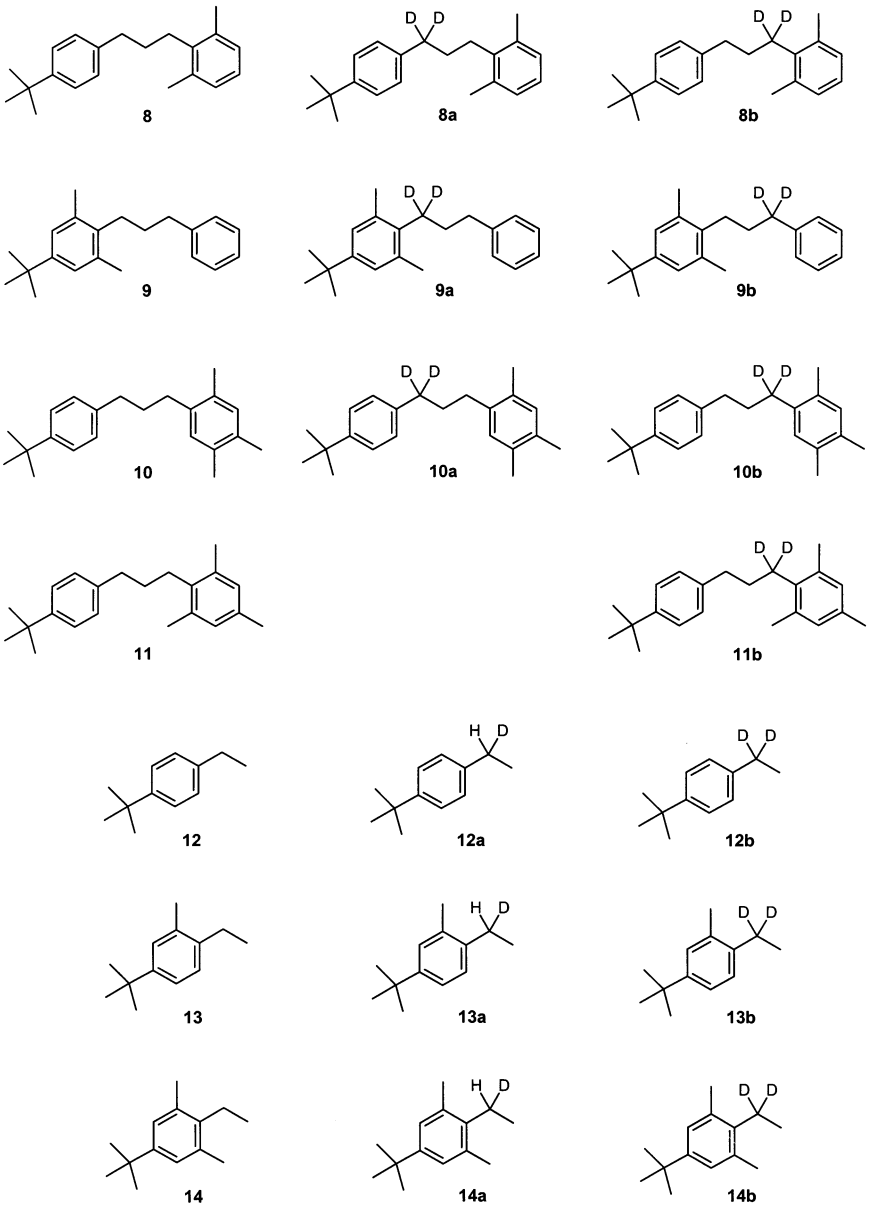


Chart 1 (part B)

palladium on charcoal (10%, Merck) (40 mg) and the mixture was shaken in a Parr apparatus for 4 h at ~20–25 °C under hydrogen (5 bar). The catalyst was removed by filtration, the filtrate was diluted with water (5 mL) and extracted three times with 10 mL portions of *n*-hexane. The combined organic layers were dried over sodium sulfate and concentrated to dryness. The residue was purified by kugelrohr distillation to give the desired hydrocarbon as a colorless, in most cases oily, liquid in yields of 50–80%.

(ii) *Chloroalane reduction*: A suspension of lithium aluminum hydride (1.0 mmol) or lithium aluminum deuteride (1.0 mmol) in anhydrous diethyl ether (5.0 mL) was cooled to 0 °C and a solution of

anhydrous aluminum trichloride (3.0 mmol) in diethyl ether (5.0 mL) was added rapidly. While cooling was maintained, a solution of the *tert*-butylated 1,3-diphenylpropane-1-one (1.0 mmol) in diethyl ether (5.0 mL) was added dropwise. The mixture was heated until the conversion was completed (~2 h), as monitored by TLC (silica/CH_2Cl_2), then cooled to room temperature, hydrolysed with ice/water, and acidified with 10 N hydrochlorid acid. After extraction of the aqueous layer with diethyl ether, the combined organic layers were dried over sodium sulfate and concentrated to dryness. The residue was purified by kugelrohr distillation to give the desired products as colorless, mostly oily, liquids (yields 60–80%). In several cases, the corresponding propenes, i.e. the product(s) of elimination were formed as mostly minor contaminations; in a few cases, the corresponding α- and/or γ-chloro-substituted diphenylpropane derivatives were also observed. No efforts were made to remove these contaminations since they did not affect the mass-analyzed ion kinetic energy (MIKE) measurements.

The unlabelled and the α,α-dideuterated 4-(*tert*-butyl)ethylbenzenes **12**–**14** and **12b**–**14b** were prepared by standard methods from the corresponding acetophenones, similar to the procedures given above for the 1,3-diphenylpropanes. The α-D_1 isotopomers **12a**–**14a** were obtained via the related phenylethanols and/or styrenes, outlined as follows.

A suspension of lithium aluminum deuteride (500 mg, 11.9 mmol) in anhydrous diethyl ether (40 mL) was stirred under argon while a solution of the appropriate 4-*tert*-butylacetophenone (43.3 mmol) in anhydrous diethyl ether (30 mL) was added dropwise. The reaction was completed by heating (TLC control with silica/CH_2Cl_2). Hydrolysis with ice/water followed by treatment with some sulfuric acid (2 N) and standard workup gave a crude product, which was purified by recrystallization from ethanol or by kugelrohr distillation. In a test tube, the 1-(4-*tert*-butylphenyl)-[1-D_1]ethanols or 4-*tert*-butyl-[α-D_1]styrenes (6.0 mmol each) were dissolved in glacial acetic acid (10 mL) and 80 mg of palladium on charcoal (10%, Merck) was added. The tube was placed in a steel bomb and the mixture was magnetically stirred for 4 h at 20 °C under hydrogen (5 bar). Workup as described above for the 1,3-diphenylpropanes followed by kugelrohr distillation furnished the hydrocarbons as colorless liquids.

3. Results and discussion

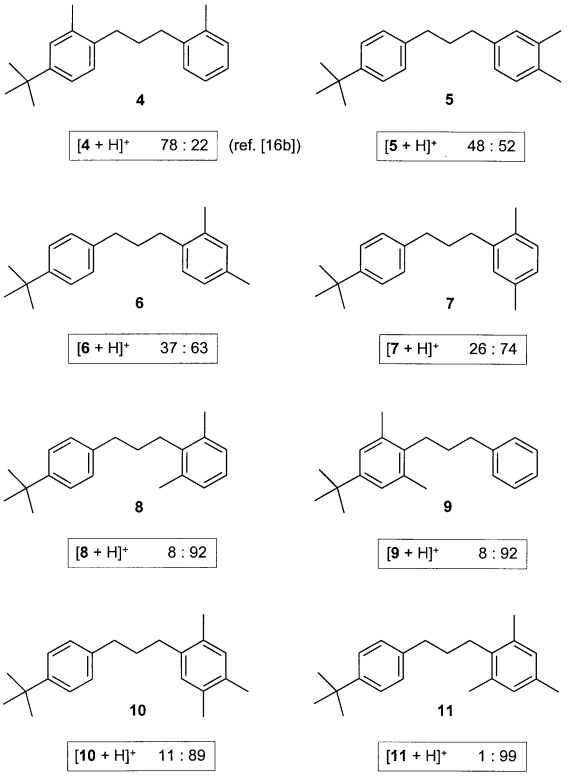
3.1. Competition between intracomplex hydride and proton transfer

As expected, introduction of two or several methyl groups increases the proton affinity of the diphenylpropane neutral partner in the ion/molecule complexes. Depending on the number and position of the substituents, loss of isobutene, in competition with that of isobutane, may almost completely suppress the latter process. This is evident from the ratios [C_4H_{10}]/[C_4H_8] measured for eight different protonated di- or trimethyl-substituted 1-(4-*tert*-butylphenyl)-3-phenylpropanes, [**4** + H]$^+$–[**11** + H]$^+$ (Table 1). In all cases, however, hydride abstraction and proton transfer represent the only fragmentation channels, besides very minor formation of *t*-$C_4H_9^+$ ions (*m/z* 57, <1% Σ), as found earlier [16b].

Protonated *ortho,ortho′*-dimethylated diphenylpropane [**4** + H]$^+$, bearing a methyl group at each of the aromatic rings, loses isobutene to a greater relative extent than its monomethyl-substituted analogue [**3** + H]$^+$ (cf. Scheme 3) [16b]. This suggests that the proton affinity of the entire 1,3-diarylpropane neutral, rather than the individual proton affinity of one of arene rings (be it the originally *tert*-butylated one or the more basic one), governs the course of the fragmentation. Irrespective of spectator-ring effects [17], which may facilitate hydride abstraction (see below), the enhanced basicity of α,ω-diphenylalkanes due to the presence of two cooperating aromatic rings is a well established phenomenon [18,19].

Ions [**5** + H]$^+$, [**6** + H]$^+$, and [**7** + H]$^+$ represent protonated *tert*-butylated 1,3-diphenylpropanes bearing two methyl groups at the same ring in either *para,meta*, *para,ortho*, or *ortho,meta* position. Hence all of these remote rings represent 1,2,4-trialkylbenzene nuclei. Nevertheless, the ratios [C_4H_{10}]:[C_4H_8]

Table 1
$[C_4H_{10}]/[C_4H_8]$ ratios for the losses of isobutane and isobutene from the metastable $[M + H]^+$ ions of *tert*-butyl-substituted 1,3-diphenylpropanes **4–11**

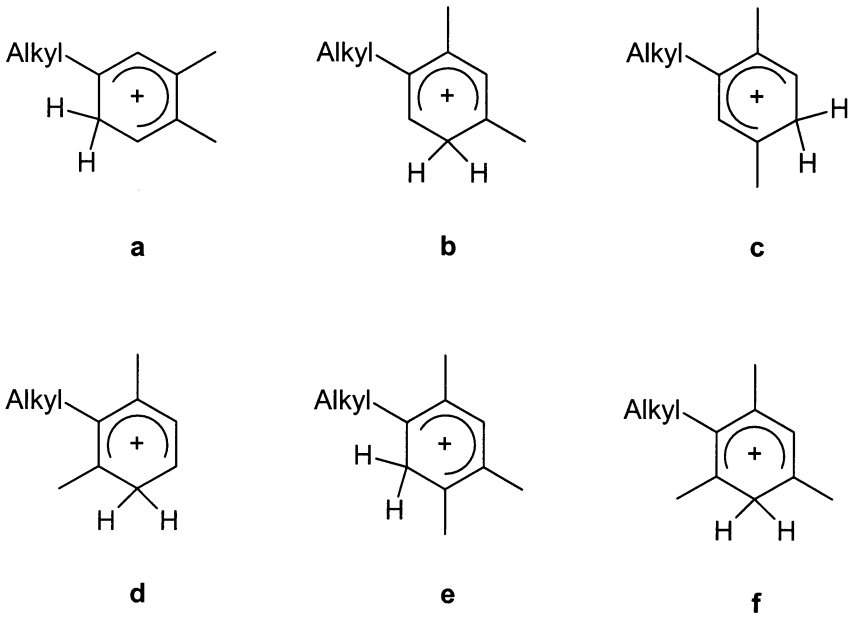


were found to be different, decreasing in the series *para,meta-* > *para,ortho-* > *ortho,meta*-dimethyl (Table 1). Among all dimethyl-substituted isomers, loss of isobutane is reduced most for protonated 1-(4-*tert*-butylphenyl)-3-(2,6-dimethylphenyl)propane $[\mathbf{8} + H]^+$, bearing *two* methyl groups in the *ortho* positions of the γ-phenyl ring. Interestingly, the ratio $[C_4H_{10}]/[C_4H_8]$ for $[\mathbf{8} + H]^+$ is identical to that of the isomer $[\mathbf{9} + H]^+$, which bears the two methyl groups at the *ortho* positions of the α-phenyl ring. This finding again demonstrates that the proton transfer from the *tert*-butyl cation occurs within an ion/molecule complex. One of the trimethyl-substituted analogues, protonated 1-(4-*tert*-butylphenyl)-3-(2,4,5-trimethylphenyl)propane $[\mathbf{10} + H]^+$, exhibits a similar extent of hydride abstraction (11%), whereas the mesitylene-type isomer $[\mathbf{11} + H]^+$ with the three methyl groups occupying the two *ortho* and the *para* positions of the remote phenyl nucleus, undergoes proton transfer almost exclusively.

Obviously, proton transfer within the complex gives a preferable rise to those σ complexes, i.e. alkylbenzenium ions, that are stabilized by electronic effects. According to the well established additivity of the inductive effects of alkyl groups in alkylbenzenium ions [3,20], the most stable σ complexes of the $[M + H - C_4H_8]^+$ fragments formed from $[\mathbf{5} + H]^+$, $[\mathbf{6} + H]^+$, $[\mathbf{7} + H]^+$, and $[\mathbf{8} + H]^+$ (ions **a–d**, Scheme 4) should be energetically very close since, in total, of the three alkyl substituents are sited one in *para*, one in *meta* and one in *ortho* positions of the remote ring. Thus, to a good approximation, the proton affinities of the neutral dimethyl-substituted 1,3-diphenylpropanes formed within the complexes should be very similar.

As a consequence, the finding that the ratios $[C_4H_{10}]/[C_4H_8]$ observed for the dimethyl-substituted precursor ions differ must be attributed to substituent effects on the hydride transfer reaction. Ions $[\mathbf{5} + H]^+$ expel isobutane to the greatest extent most probably because this is the only isomer in which kinetic attenuation of the hydride abstraction cannot take place because of the lack of methyl substituents at *ortho* positions relative to the aliphatic chain. Among the isomers that do contain such *ortho*-methyl groups, the *para,ortho*-dimethylated ions $[\mathbf{6} + H]^+$ exhibit the higher ratio $[C_4H_{10}]/[C_4H_8]$ as compared to ions $[\mathbf{7} + H]^+$ because the hydride abstraction is particularly strongly favored by the *para*-methyl substituent (cf. ions $[\mathbf{1} + H]^+$). With the protonated diphenylpropanes bearing two *ortho*-methyl groups at the same arene ring, viz. $[\mathbf{8} + H]^+$ and $[\mathbf{9} + H]^+$, hydride abstraction is strongly suppressed by steric hindrance (see below).

An independent factor that has to be taken into account concerns the role of *ortho*-methyl groups in 1,3-diphenylpropanes as hydride donors, as found earlier [16b] for the singly methylated ions $[\mathbf{3} + H]^+$. This effect will be analyzed in detail for ions $[\mathbf{7} + H]^+$, in which the *meta*-methyl group provides a particularly strongly activating effect on the C–H bonds of the *ortho*-methyl group because of their



Scheme 4. Most stable σ-complexes corresponding to ions $[M + H - C_4H_8]^+$.

mutual 1,4-orientation at the ring. Notwithstanding, the *ortho*-methyl substituents in the neutral counterparts of the complexes formed from ions $[\mathbf{6} + H]^+$, $[\mathbf{8} + H]^+$, and $[\mathbf{9} + H]^+$ may also act as hydride donors during the loss of isobutane. The origin for the overall dominance of the proton transfer channel observed for the dimethyl-substituted precursor ions will be discussed in the context of the regioselectivity of the hydride abstraction.

All arguments mentioned above are also relevant for the fragmentation behavior of the trimethyl-substituted isomers $[\mathbf{10} + H]^+$ and $[\mathbf{11} + H]^+$. Although the remote phenyl ring of ions $[\mathbf{10} + H]^+$ bears three methyl groups, the proton affinity of the neutral counterpart to the t-$C_4H_9^+$ ions in the complex should scarcely differ from that of the dimethylated diphenylpropanes [20,21]. The particular substituent pattern of 1,2,4,5-tetra-alkylbenzenes (Scheme 4) does not provide *para*-oriented alkyl substituents (relative to the protonation site) in otherwise energetically favorable σ complexes such as **e**. In contrast, in the case of the mesitylene-type isomer $[\mathbf{11} + H]^+$ both the high proton affinity of isodurene-type benzenium ions such as **f** (Scheme 4) and the steric hindrance give rise to almost complete suppression of hydride transfer, in favor of proton transfer, within the ion/molecule complex.

3.2. Regioselectivity of intracomplex hydride abstraction

As shown previously, the protonated *tert*-butyl-substituted 1,3-diphenylpropane $[\mathbf{4} + H]^+$ bearing an *ortho*-methyl substituent at each of the aromatic rings undergoes the intracomplex hydride abstraction from the α-CH_2 and the γ-CH_2 groups with equal probability. This follows from the identical MIKE spectra of the $[\alpha,\alpha\text{-}D_2]$- and the $[\gamma,\gamma\text{-}D_2]$-labelled isotopomers of this dimethylated congener. The data, viz. $[C_4H_{10}]/[C_4H_9D] = 1.9{:}1$ in both cases, were explained by assuming the kinetic isotope effect operating generally in this type of ion ($k_H/k_D \equiv i = 1.6$) [1,2,16] and a significant hydride donor reactivity of the two methyl groups.

The MIKE spectra of the other labelled dimethyl-substituted precursor ions as well as those of the trimethyl-substituted analogues exhibit characteristic differences, reflecting the regioselectivity of the hy-

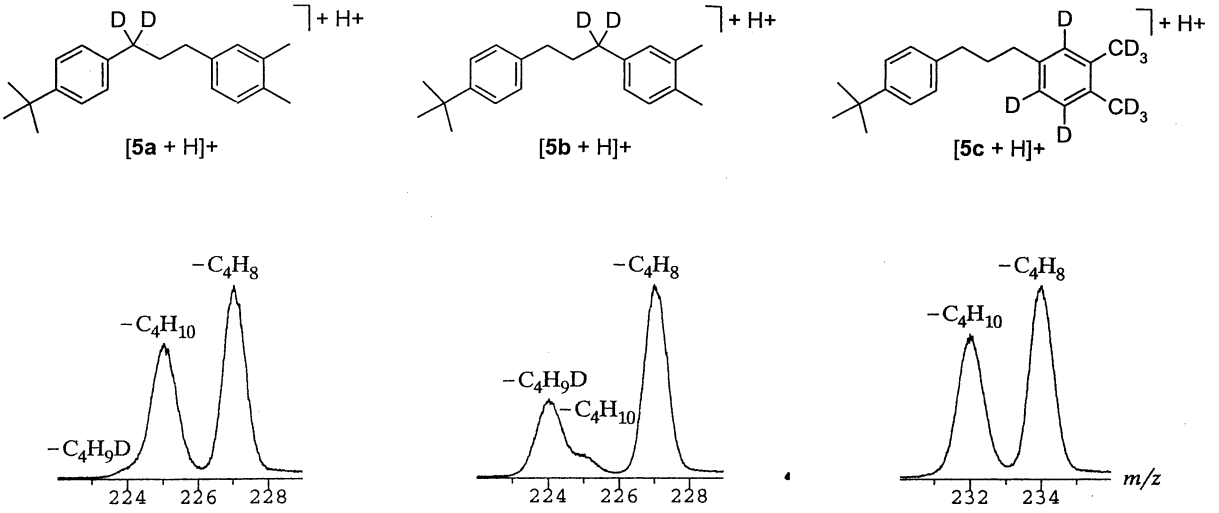
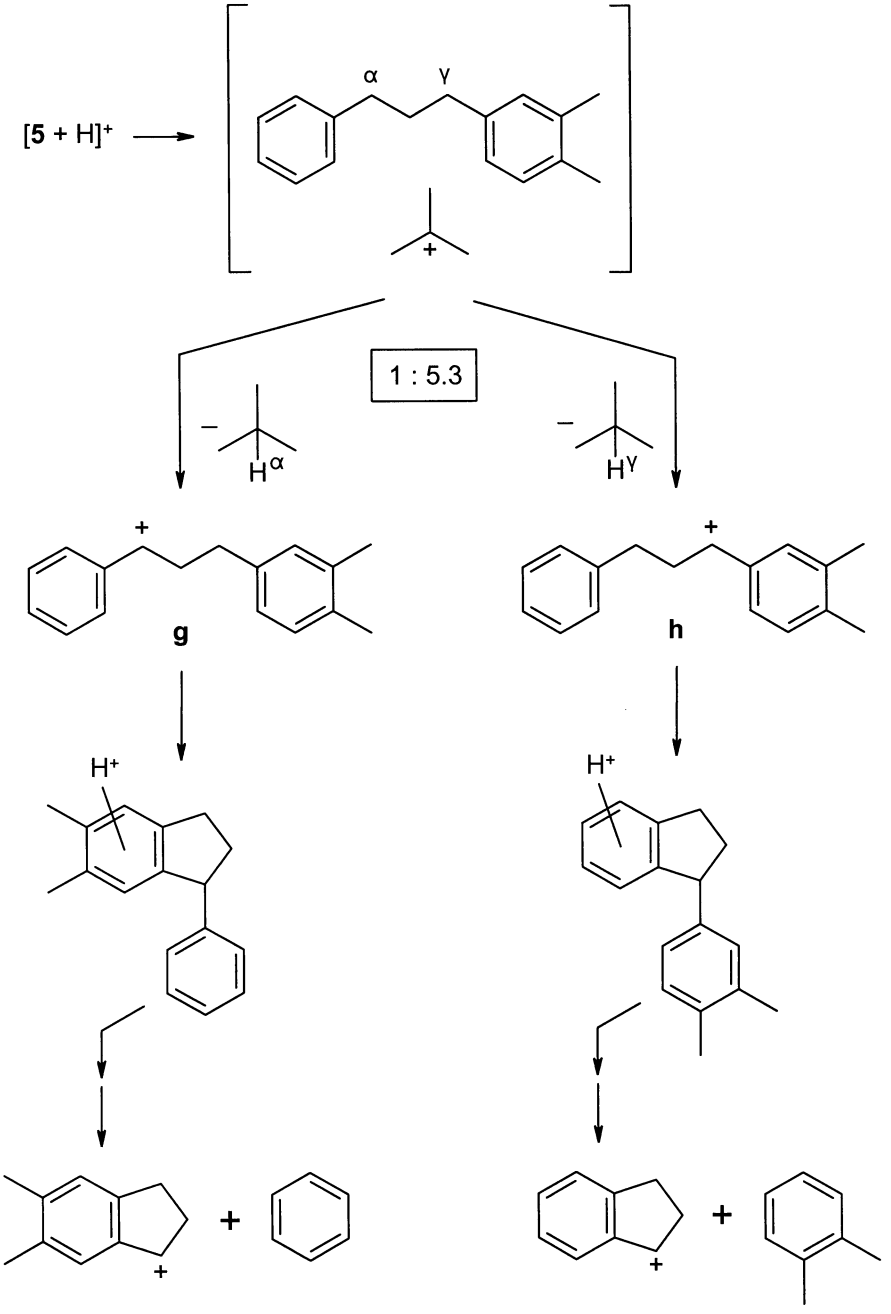


Fig. 1. MIKE spectra of labelled isotopomers of ions $[\mathbf{5} + H]^+$.

dride abstraction from the α-CH_2 and the γ-CH_2 donor groups. As a clearcut example, the MIKE spectra of three labelled protonated 1-(4-*tert*-butylphenyl)-3-(3,4-dimethylphenyl)propanes are reproduced in Fig. 1. The spectra of $[\mathbf{5a} + H]^+$ and $[\mathbf{5b} + H]^+$ clearly reveal that both the (originally adjacent) α-CH_2 and the (originally remote) γ-CH_2 groups contribute to the isobutane loss. This is in accordance with the fact that the metastable ions $[\mathbf{5} + H - C_4H_{10}]^+$ (**g** and **h**) formed in the Cl source eliminate both C_6H_6 and C_8H_{10} in the secondary fragmentation step, i.e. benzene and, most probably, *ortho*-xylene (Scheme 5). Sequential cyclization, interannular proton transfer, and arene elimination is an ubiquitous fragmentation path for the $[M - H]^+$ ions of diphenylalkanes [22]. Furthermore, the MIKE spectrum of the isotopomer $[\mathbf{5c} + H]^+$ bearing a perdeuterated γ-toluene nucleus clearly reveals that neither the *meta*- nor the *para*-methyl groups, nor any positions of that ring, contribute to the hydride transfer process in the complex formed from $[\mathbf{5} + H]^+$.

This confirms the results obtained for the labelled monomethyl-substituted congener $[\mathbf{1} + H]^+$, and demonstrates that *para*- and *meta*-sited methyl groups, even if electronically activated by other substituents on the same ring, are not involved in the intracomplex reactions [16b]. Also, the fragmentation behavior of $[\mathbf{5c} + H]^+$ again allows us to exclude any proton exchange processes between the components of the complex. Quantitative inspection of the ratios $[C_4H_{10}]/[C_4H_9D]$ for ions $[\mathbf{5a} + H]^+$ and $[\mathbf{5b} + H]^+$, viz. 8.4:1 and 1:3.3 (Table 2), respectively, clearly reveal the strong dominance of the γ-CH_2 group as the hydride donor. By reasonably assuming that the same kinetic isotope effect operates at both the α and γ donor sites, we obtain a regioselectivity $r_{\gamma/\alpha} \equiv [C_4H_9H^{\gamma}]/[C_4H_9H^{\alpha}] = 5.3$ and, again, $k_H/k_D = 1.6$. The regioselectivity of hydride abstraction in ions $[\mathbf{5} + H]^+$ reflects the combined effects of the methyl substitutents in the singly substituent ions $[\mathbf{1} + H]^+$ and $[\mathbf{2} + H]^+$, viz. $r_{\gamma/\alpha} = 3.3$ and 1.7, respectively.

In contrast to the case of ions $[\mathbf{5} + H]^+$, evaluation of the $[C_4H_{10}]/[C_4H_9D]$ ratios measured for the other methylated D_2-labelled protonated diphenylpropanes does not allow us to unravel strictly quantitative data on the regioselectivity. In these cases, we have not only to *assume* the kinetic isotope effect to be the same for all donor sites but also its size. This is because the *ortho*-methyl substituents act as additional hydride donor sites under the influence of the spectator ring. With this restriction, however, the fragmentation of the labelled isotopomers of ions $[\mathbf{6} + H]^+$–$[\mathbf{11} + H]^+$ reveals consistent semiquanti-



Scheme 5. Sequential losses of isobutane and arenes from ions $[\mathbf{5} + H]^+$. Only one of two possible cyclization routes involving ions **g** are shown.

tative information, which is useful to characterize the chemistry of gaseous hydrocarbon ion/molecule complexes. The $[C_4H_{10}]/[C_4H_9D]$ ratios measured for the D_2-labelled di- and trimethyl-substituted isotopomers are collected in Table 2.

The spectra of ions $[\mathbf{6} + H]^+$ bearing two methyl

Table 2
Loss of isobutane isotopomers from metastable $[M + H]^+$ ions of α,α- and γ,γ-D_2-labelled 1-(4-*tert*-butylphenyl)-3-phenylpropanes **5a**–**10a** and **5b**–**11b**

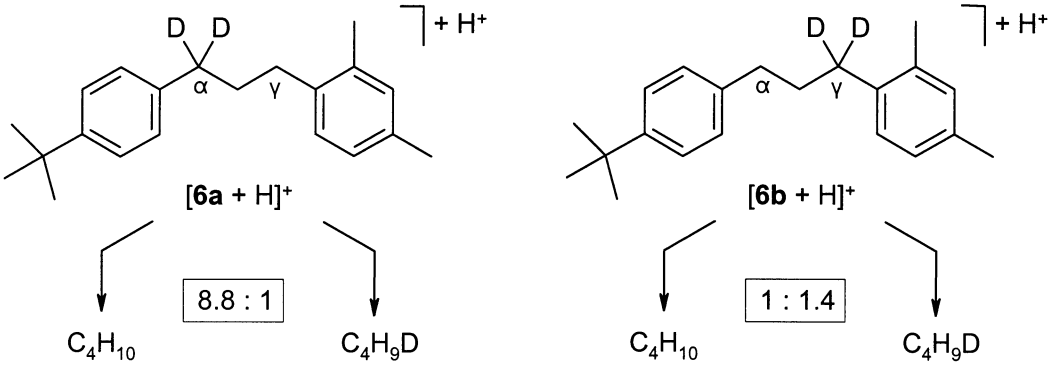
Substitution at the γ- or α-phenyl ring	Ion α,α-D_2	$[C_4H_{10}]/[C_4H_9D]$	Ion γ,γ-D_2	$[C_4H_9D]/[C_4H_{10}]$
γ-[3,4-$(CH_3)_2$]	[**5a** + H]$^+$	8.4:1	[**5b** + H]$^+$	3.3:1
γ-[2,4-$(CH_3)_2$]	[**6a** + H]$^+$	8.8:1	[**6b** + H]$^+$	1.4:1
γ-[2,5-$(CH_3)_2$]	[**7a** + H]$^+$	8.9:1	[**7b** + H]$^+$	1:3.6
γ-[2,6-$(CH_3)_2$]	[**8a** + H]$^+$	4.2:1	[**8b** + H]$^+$	~1:12
α-[2,6-$(CH_3)_2$]	[**9a** + H]$^+$	~12:1	[**9b** + H]$^+$	1:4.2
γ-[2,4,5-$(CH_3)_3$]	[**10a** + H]$^+$	≥20:1	[**10b** + H]$^+$	1:2.0
γ-[2,4,6-$(CH_3)_3$]			[**11b** + H]$^+$	<1:10

groups in the *para* and *ortho* positions of the remote arene ring also point to a high regioselectivity that operates in favor of the γ-CH_2 group. Whereas in ions [**3** + H]$^+$ the *ortho*-methyl group contributes ~6% to isobutane formation, we may expect a higher donor reactivity in the case of ions [**6** + H]$^+$ due to the inductive effect of the additional *para*-methyl group. In fact, assuming the usual kinetic isotope effect $k_H/k_D = 1.6$, the experimental data are consistent with an estimated regioselectivity of $r_{\gamma/\alpha} = 4.6$ for ions [**6** + H]$^+$ and a contribution of 15% of the overall hydride being transferred from the *ortho*-methyl group (Scheme 6). This follows from calculations based on Eqs. (1) and (2), which relate the measured abundance ratios $[C_4H_{10}]/[C_4H_9D]$ with the fractional contributions f_i of the hydride donor sites at the α, γ and *ortho*-methyl positions for all the ions under investigation. In the case of ions [**6** + H]$^+$, the fractional contributions are determined to be f_α:f_γ:f_o = 15:70:15; thus, the methyl group is involved to about the same extent in the loss of isobutane from the complex as is the α-CH_2 group [23].

$$\left(\frac{[C_4H_9D]}{[C_4H_{10}]}\right)_{\alpha,\alpha\text{-}D_2} = \frac{f_\alpha}{i(f_\gamma + f_o)} \quad (1)$$

$$\left(\frac{[C_4H_9D]}{[C_4H_{10}]}\right)_{\gamma,\gamma\text{-}D_2} = \frac{f_\gamma}{i(f_\alpha + f_o)} \quad (2)$$

An extended labelling study has been performed in the case of ions [**7** + H]$^+$ bearing two methyl substituents in *ortho* and *meta* positions of the remote arene ring and in mutual *para* orientation (i.e. at positions 2′ and 5′). The MIKE spectra of the α,α-D_2- and γ,γ-D_2-labelled isotopomers [**7a** + H]$^+$ and [**7b** + H]$^+$ show preponderance of the hydride transfer in *both* cases (Table 2, Fig. 2), in sharp contrast to the pair of isomers [**6a** + H]$^+$ and [**6b** + H]$^+$. The origin of this finding is attributed to a rather large fraction of hydride being abstracted from the *ortho*-



Scheme 6.

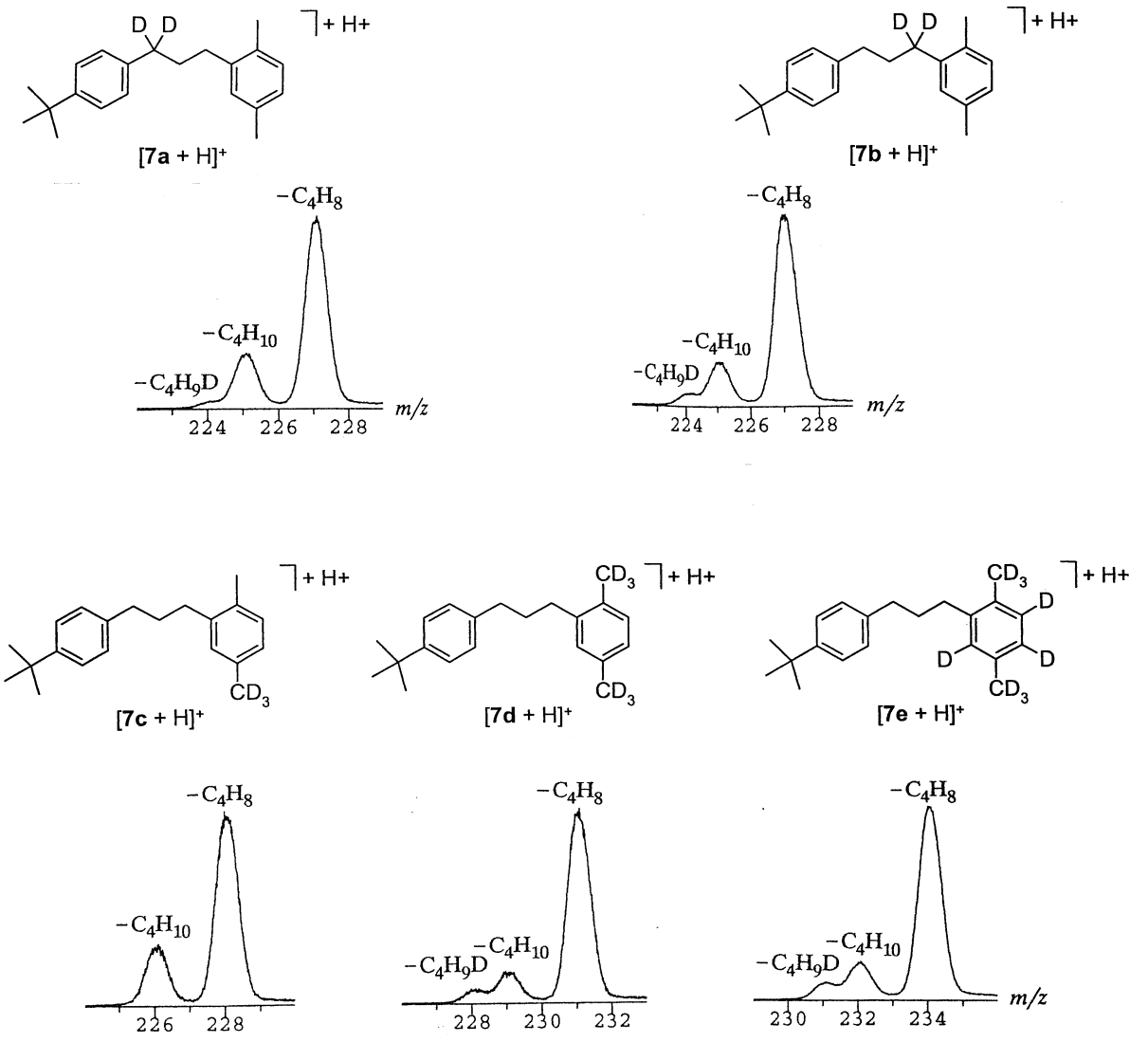


Fig. 2. MIKE spectra of labelled isotopomers of ions $[7 + H]^+$.

methyl group of both $[\mathbf{7a} + H]^+$ and $[\mathbf{7b} + H]^+$. In fact, the investigation of the three isotopomers $[\mathbf{7c} + H]^+$, $[\mathbf{7d} + H]^+$, and $[\mathbf{7e} + H]^+$ clearly shows that the *ortho*-CD_3 substituent is strongly involved in the isobutane loss, whereas the *meta*-methyl group and the ring hydrogens are not at all. This is in full accordance with the behavior of ions $[\mathbf{5c} + H]^+$ and the CD_3-labelled isotopomers of ions $[\mathbf{1} + H]^+$ studied previously. It may be noted here that some H/D exchange was found with ion/molecule complexes containing substituted neutral arenes [11]. Evaluation of the data, again assuming a kinetic isotope effect $k_H/k_D = 1.6$ for all of the hydride donor sites, suggests that a contribution of ~54% of the overall hydride transferred to the *tert*-butyl cation originates from the *ortho*-methyl group of ions $[7 + H]^+$. Correcting for the ratio of donor C–H bonds in a "statistical" manner leads to the striking insight that the

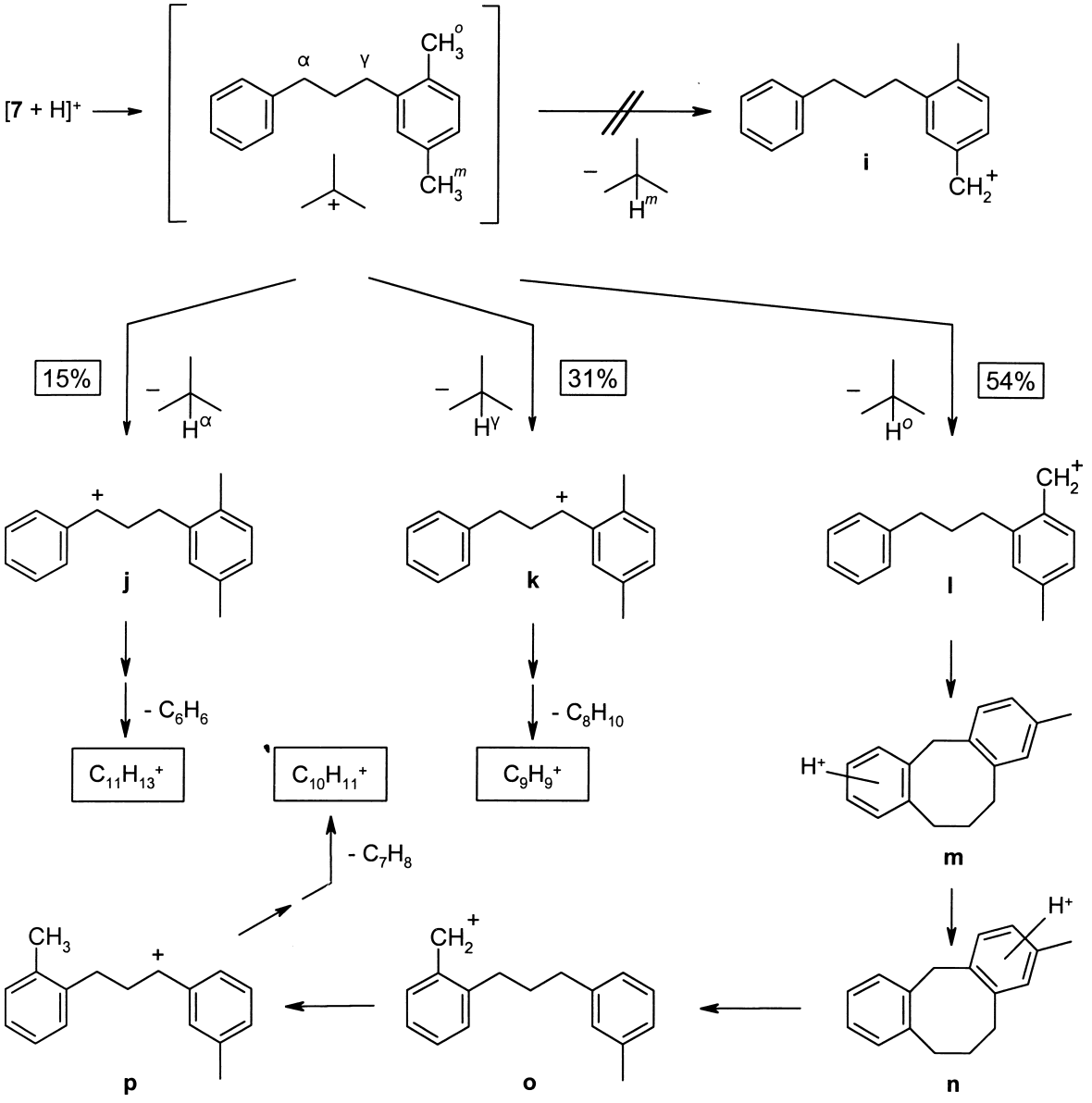
ortho-methyl group $[\mathbf{7} + H]^+$ is similarly efficient a hydride donor as are, on the average, the two methylene groups. The regioselectivity between the two methylene groups is $r_{\gamma/\alpha} = 2.0$, i.e. rather similar to that found for ions $[\mathbf{2} + H]^+$ bearing a single methyl group in a *meta* position ($r_{\gamma/\alpha} = 1.7$). Similar to the case of ions $[\mathbf{5} + H]^+$ discussed above, the combined influence of two methyl groups in ions $[\mathbf{7} + H]^+$ appears to reflect the individual substituent effects in the singly methylated ions, viz. $[\mathbf{2} + H]^+$ and $[\mathbf{3} + H]^+$. In terms of fractional contributions of hydride within the complex, ions $[\mathbf{7} + H]^+$ are characterized by the ratios f_α:f_γ:f_o = 15:31:54.

It is obvious that, in addition of the assistance by the spectator ring, that hydride abstraction from the *ortho*-methyl group of ions $[\mathbf{7} + H]^+$ is facilitated by the electronic effect of the second methyl group sited *para* relative to the donor methyl group, in agreement with Audier's findings that *para*-xylene readily undergoes hydride abstraction with *t*-$C_4H_9^+$, whereas *meta*-xylene does not [9]. The secondary fragmentation of ions $[\mathbf{7} + H]^+$, which will be discussed below, also reflects the sites which have suffered hydride abstraction, clearly including the *ortho*- but not the *meta*-methyl group (Scheme 7).

Similar to the primary fragments formed by isobutane loss from the 3,4-dimethyl isomers $[\mathbf{5} + H]^+$, metastable ions $[\mathbf{7} + H - C_4H_{10}]^+$ eliminate both C_6H_6 and C_8H_{10} (most probably benzene and *para*-xylene) but, in contrast to $[\mathbf{5} + H]^+$, they also expel C_7H_8 (i.e. toluene). As illustrated in Scheme 7, this process is initiated by an attack of the primary benzylic cation **l**, being formed in competition to the secondary ions **j** and **k**, at the unsubstituted phenyl ring of ions $[\mathbf{7} + H - C_4H_{10}]^+$. The cyclic intermediate(s) thus formed, e.g. **m**, represent condensed alkylbenzenium ions, which may undergo reciprocal opening of the eight-membered ring after interannular proton transfer (**m** → **n**) to form ions **o** [3,22,24]. Subsequent to another (intramolecular) hydride transfer step (**o** → **p**), cyclization to the corresponding protonated 1-arylindane (not shown, cf. Scheme 5) opens the way for elimination of toluene. This mechanism and the highly regioselective hydride transfer step are nicely confirmed by the respective secondary fragmentation of the deuterium labelled precursor $[\mathbf{7c} + H]^+$: In fact, ions $[\mathbf{7c} + H - C_4H_{10}]^+$ bearing an (originally *meta*-sited) CD_3 group eliminate exclusively D_3-labelled toluene.

The MIKE spectra of the four D_2-labelled *ortho*, *ortho*-dimethylated protonated 1,3-diphenylpropanes (Scheme 8) again reflect the pairwise identical behavior with respect to the initial site of the *tert*-butyl group in relation to that of the position of label and the methyl substituents, in accordance with the identical $[C_4H_{10}]/[C_4H_8]$ branching ratio found for the unlabelled ions $[\mathbf{8} + H]^+$ and $[\mathbf{9} + H]^+$ (see above). In all cases, hydride transfer is by far predominant. Thus, ions $[\mathbf{8a} + H]^+$ and $[\mathbf{9b} + H]^+$, bearing the label adjacent to the nonmethylated ring, exhibit the ratio $[C_4H_{10}]/[C_4H_9D] = 4.2$, whereas for ions $[\mathbf{8b} + H]^+$ and $[\mathbf{9a} + H]^+$, with the label and the methyl substituents adjacent to each other, give $[C_4H_{10}]/[C_4H_9D] \approx 12$. Again, the origin of the *tert*-butyl cation has no effect on the fragmentation behavior reflecting, once more, the intermediacy of an ion/molecule complex with freely moving constituents.

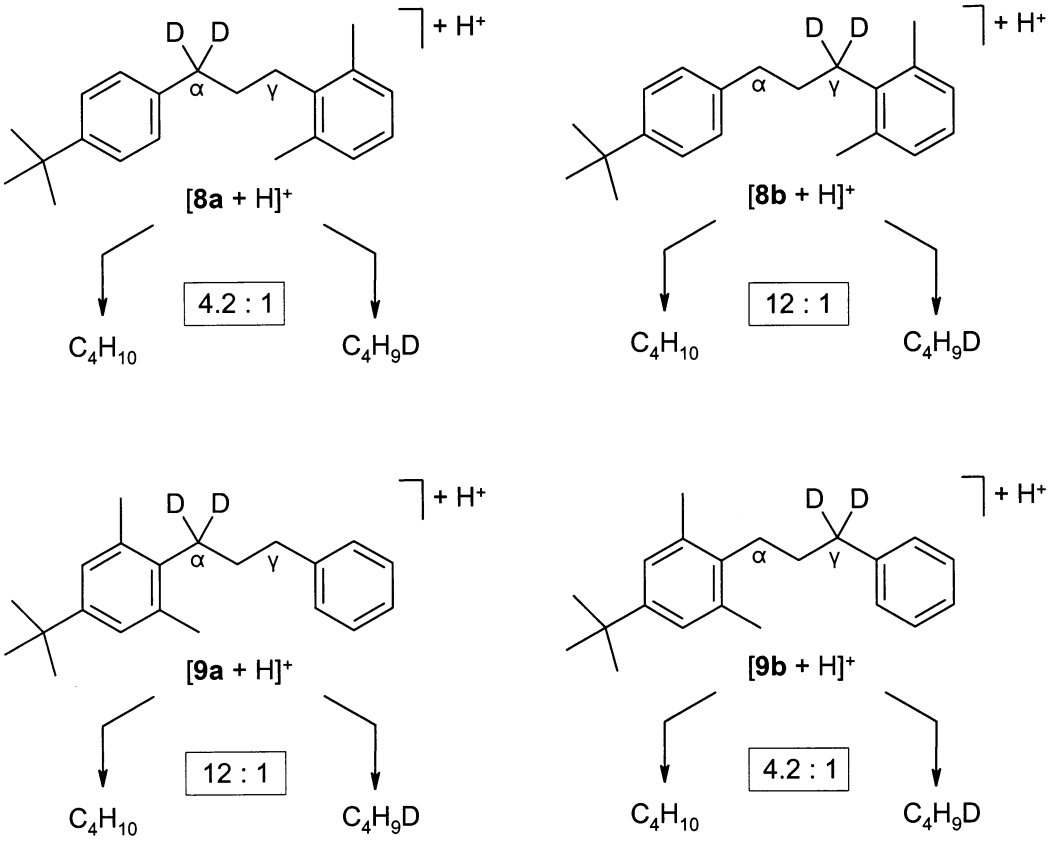
Due to the steric hindrance effected by two *ortho* substituents, we expected the complete suppression of the hydride (or deuteride) abstraction from the γ-methylene group. Obviously, some donor reactivity has pertained, as will be discussed in detail below, and the (apparent) γ/α regioselectivity of the hydride transfer is also not extremely shifted in favor of the unhindered α position. It is evident that the two *ortho*-methyl substituents act as efficient additional hydride donors, which may also contribute to the strong predominance of the competing proton transfer during the fragmentation of ions $[\mathbf{8} + H]^+$ and $[\mathbf{9} + H]^+$ (Table 2). Calculations according to Eqs. (1) and (2), again assuming $k_H/k_D = 1.6$ and correcting for the presence of two methyl donor groups, yield fractional contributions in the ratio f_α:f_γ:2$f_o \approx 28$:12:61, that is, each of the two *ortho*-methyl substituents exhibits nearly the same reactivity as the unhindered benzylic methylene group, and the reactivity of the sterically hindered benzylic methylene group is much attenuated ($r_{\gamma/\alpha} \approx 0.4$).



Scheme 7. Sequential losses of isobutane and arenes from ions [**7** + H]$^+$ (see text).

3.3. Spectator ring effects

The fact that, in the complex formed from ions [**8** + H]$^+$ and [**9** + H]$^+$, the *t*-$C_4H_9^+$ cation abstracts about 12% of the hydride from the strongly shielded benzylic methylene group is remarkable. It suggests a strong spectator ring effect. To study the effect of two *ortho*-methyl groups at the same arene nucleus with respect to intracomplex proton transfer and hydride donor reactivity, isotope effect, and the role of the spectator ring, we extended our investigation at this point to the corresponding simple alkylbenzenium ions, viz. the protonated 4-(*tert*-butyl)ethylbenzenes [**12** + H]$^+$, [**13** + H]$^+$, and [**14** + H]$^+$ (Fig. 3).



Scheme 8.

Again, loss of isobutane and/or isobutene are the only fragmentation paths of the metastable ions, in analogy to the fragmentation of the protonated 1,3-diphenylalkanes. The MIKE spectra of the unlabelled ions and of the α-D_1- and α,α-D_2-labelled isotopomers are reproduced in Fig. 3. As already shown by Audier et al. [1], protonated 4-(*tert*-butyl)ethylbenzene [**12** + H]$^+$, without an additional methyl substituent, loses isobutane exclusively. Similarly, ions [**13** + H]$^+$, bearing a single methyl group *ortho* to the ethyl side chain, eliminate very small amounts ($\sim$3%) of isobutene, along with isobutane, but ions [**14** + H]$^+$, bearing two methyl groups *ortho* to the side chain, expel isobutene almost exclusively ($>$99%). Thus, as compared to the "small" ion/molecule complex [*o*-$CH_3C_6H_4C_2H_5$ *t*-$C_4H_9^+$] formed from ions [**13** + H]$^+$, proton transfer in the "large" complex [*o*-$CH_3C_6H_4(CH_2)_3C_6H_5$ *t*-$C_4H_9^+$] formed from ions [**3** + H]$^+$ is much more pronounced. This is certainly because of the higher proton affinity of the larger alkylbenzene neutral in the complex. For the "small" complex formed from [**14** + H]$^+$, however, isobutene loss is clearly found to be more dominant than for the "large" one formed during the fragmentation of [**9** + H]$^+$ (and [**8** + H]$^+$) (cf. Table 1). Obviously, in the latter case(s), the hydride donor reactivity of the diphenylpropane neutral, and even of its hindered benzylic methylene group (see above), is preserved to a certain degree and can effectively compete with the proton transfer in spite of the enhanced proton affinity of the larger neutral.

The α-D_1-labelled isotopomers [**12a** + H]$^+$ and [**13a** + H]$^+$ both lose C_4H_{10} and C_4H_9D and directly reflect the kinetic isotope effect, viz. $k_H/k_D = 1.60 \pm$

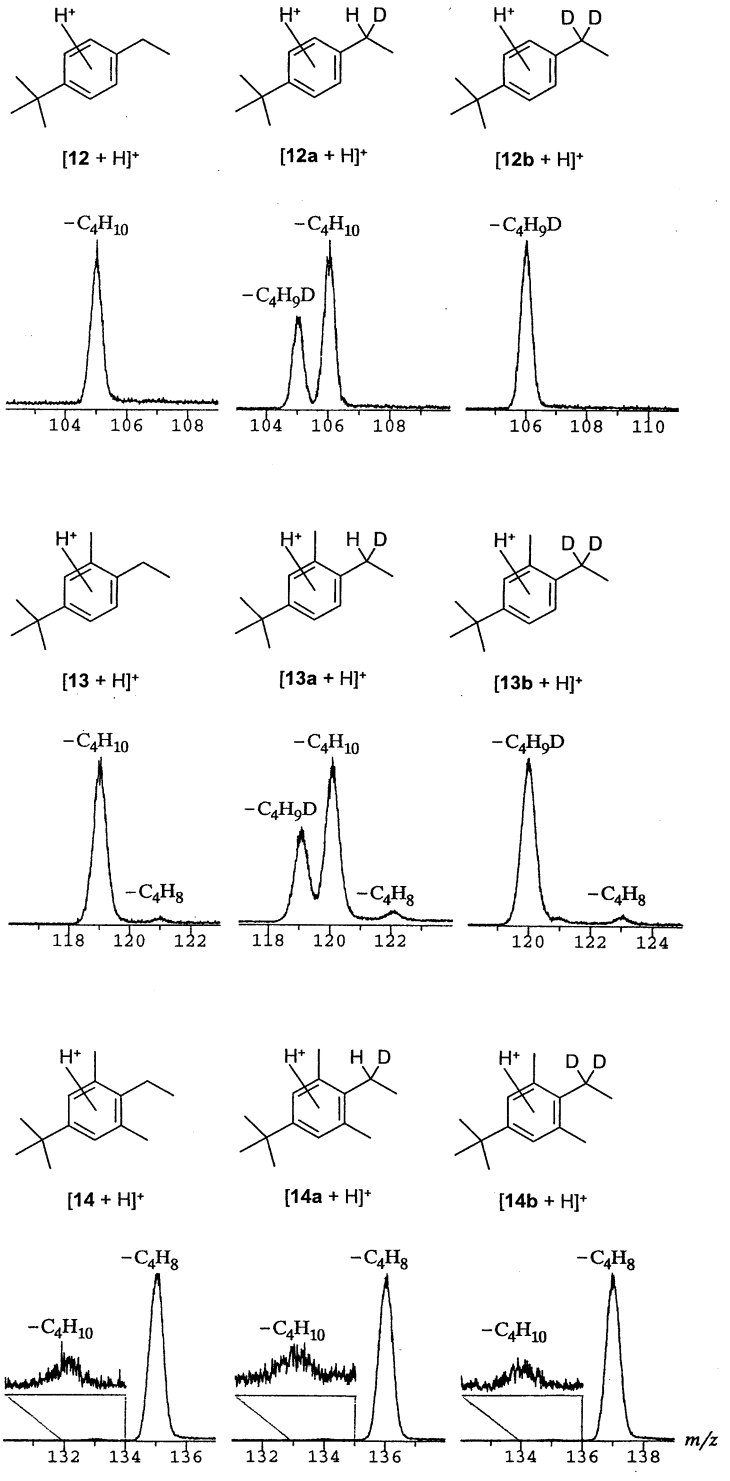


Fig. 3. MIKE spectra of ions [**12** + H]$^+$, [**13** + H]$^+$ and [**14** + H]$^+$ and of their α-D_1-α,α-D_2-labelled isotopomers.

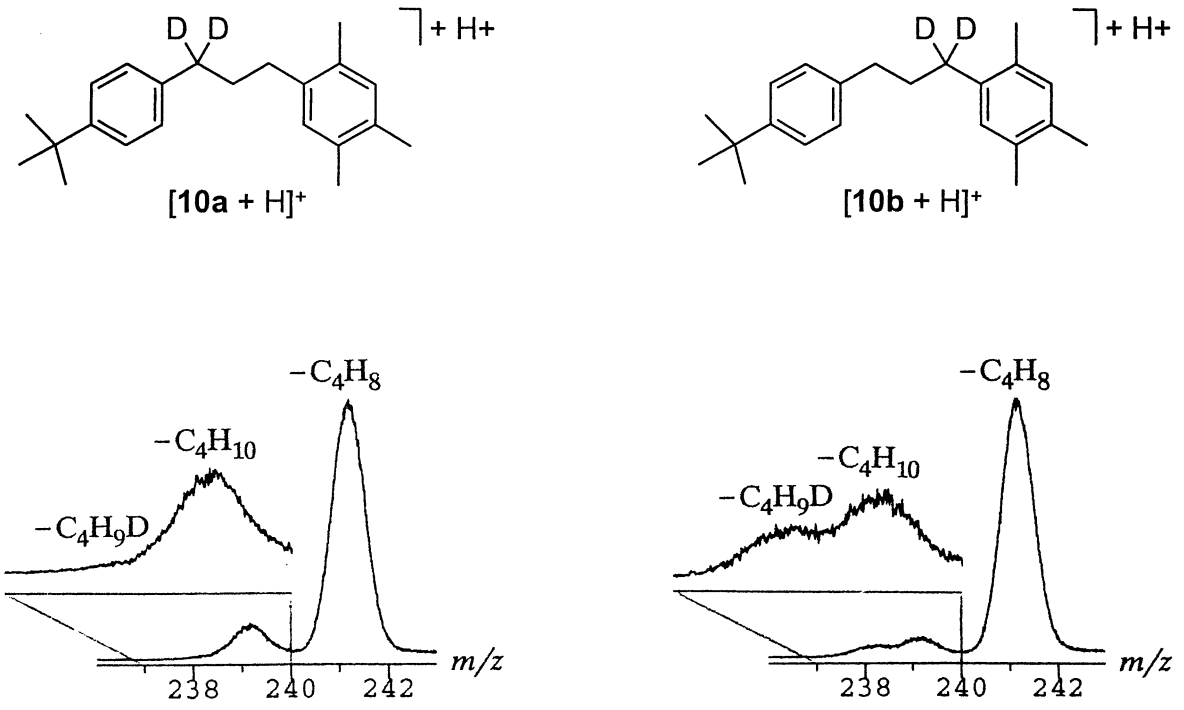
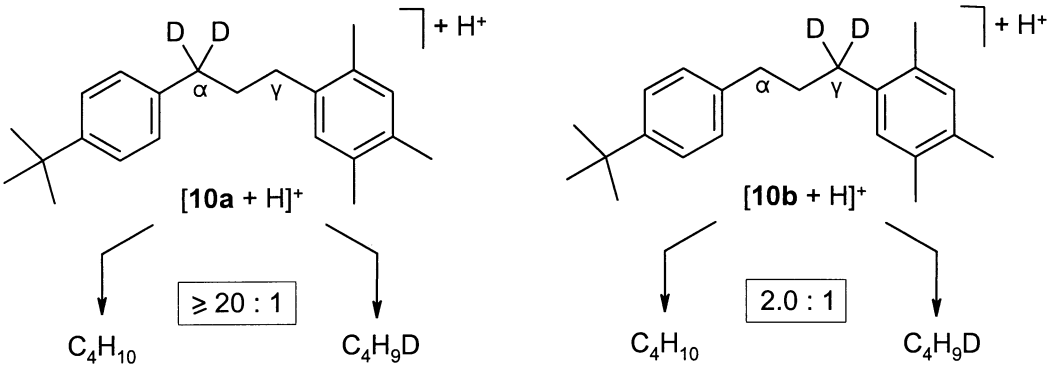


Fig. 4. MIKE spectra of labelled isotopomers of ions [**10** + H]$^+$.

0.05 in both cases, in agreement with the value reported previously for [**12a** + H]$^+$ [1]. Most importantly, the data for ions [**13a** + H]$^+$ clearly demonstrate that the presence of a single *ortho*-methyl substituent does not affect the isotope effect, a finding that strongly corroborates the results deduced from the data obtained for the *ortho*-methyl-substituted diphenylpropanes [**3** + H]$^+$ and [**7a** + H]$^+$, in particular. In sharp contrast to the binuclear analogues, however, the *ortho*-methyl group in ions [**13** + H]$^+$ does not exhibit hydride donor reactivity, as follows from the lack of C_4H_{10} loss ($\leq$1%) from ions [**13b** + H]$^+$ [25].

Finally, the *ortho*,*ortho*-dimethyl-substituted ethylbenzenes [**14a** + H]$^+$ and [**14b** + H]$^+$ eliminate exclusively unlabelled isobutane, besides the strongly predominant loss of isobutene, and in the same relative amounts as found for the unlabelled isotopomer. Therefore, the α-CH_2 group of the ethyl side chain does not contribute at all to the hydride transfer and the *tert*-butyl cation in the complex abstracts a hydride exclusively from the methyl groups [26]. The steric shielding and the lack of a spectator ring (see below) completely suppress the formation of secondary benzyl cations. At the same time, the formation of primary benzyl cations by hydride abstraction from the methyl groups cannot compete effectively with the proton transfer process, resulting in the loss of isobutene.

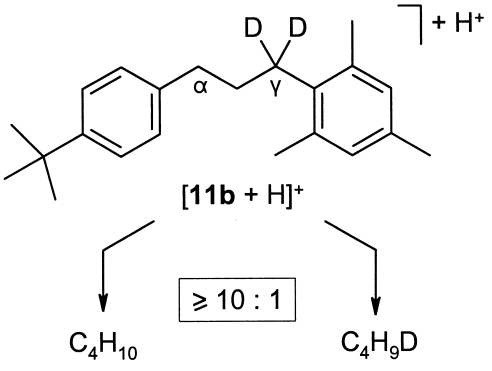
The results obtained from the investigation of the mononuclear alkylbenzenium ions strongly corroborate the findings on the binuclear ones, in particular on those concerning steric hindrance and the spectator ring effect. They clearly show that, in spite of the presence of a γ-phenylpropyl residue increasing the proton affinity as compared to the simple ethylbenzene-type ions, the relative rate of isobutane loss also increases significantly for the protonated 1,3-diphenylpropanes. Thus, in the complexes formed from ions [**8** + H]$^+$ and [**9** + H]$^+$, as well as from ions [**11** + H]$^+$ (see below), the interaction of the aromatic rings enables the hydride abstraction from all



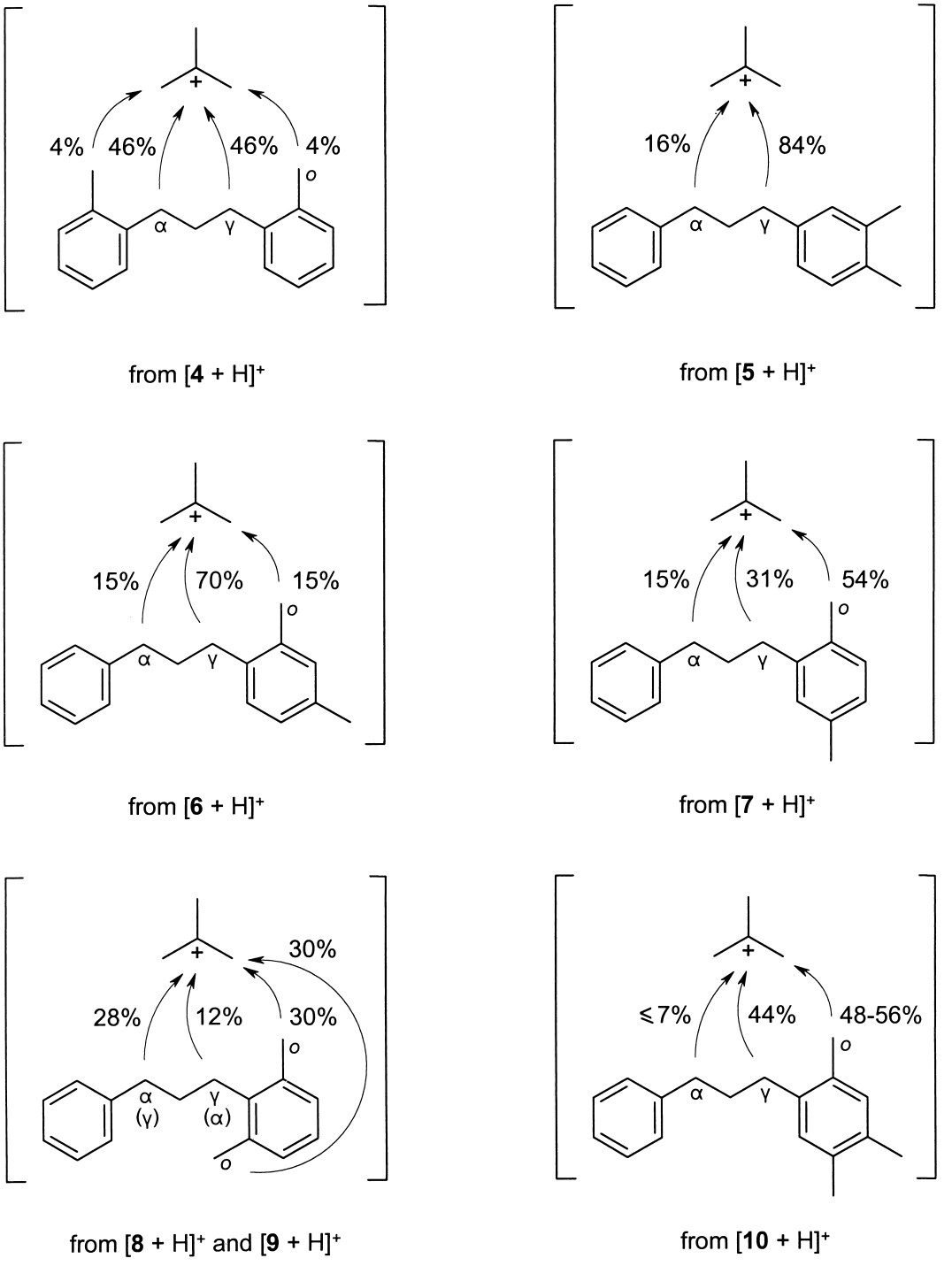
Scheme 9.

possible donor positions. The spectator ring activates, to a significant extent, the sterically hindered benzylic methylene groups as well as the *ortho*-methyl groups which, in contrast to *meta*- and *para*-sited ones, are spatially accessible. In this view, the investigation of the *ortho,ortho*-dimethyl-substituted protonated diphenylpropanes again demonstrates that the fragmentation of these large protonated alkylbenzenes involves weakly, noncovalently bonded ion/neutral complexes. The increased reactivity toward the intracomplex hydride transfer reaction, due to the spectator ring effect, represents another characteristic feature.

The trimethyl-substituted protonated 1,3-diphenylpropanes complete these insights. The MIKE spectra of the protonated α,α-D_2- and γ,γ-D_2-labelled 1-(4-*tert*-butylphenyl)-3-(2,4,5-trimethylphenyl)propanes [**10a** + H]$^+$ and [**10b** + H]$^+$ are reproduced in Fig. 4. Loss of C_4H_{10} and C_4H_9D occurs in both cases and, as expected from the results obtained so far, deuteride abstraction is clearly favored in the complex formed from the γ,γ-D_2-labelled ions [**10b** + H]$^+$, as compared to [**10a** + H]$^+$ (Scheme 9). The $[C_4H_{10}]/[C_4H_9D]$ ratios are similar to those observed for the 2,5-dimethylated congeners [**7a** + H]$^+$ and [**7b** + H]$^+$. The additional *para*-methyl substituent activates both the γ-CH_2 and *ortho*-CH_3 groups toward hydride abstraction. Calculations for the relative hydride donor reactivities provide some limiting values only because the $([C_4H_{10}]/[C_4H_9D])_\alpha$ ratio measured for ions [**10a** + H]$^+$ represents a lower limit. Thus, with $([C_4H_{10}]/[C_4H_9D])_\alpha = 20$ and $k_H/k_D = 1.6$, we obtain the fractional contributions $f_\alpha:f_\gamma:f_o = 7:44:48$ for ions [**10** + H]$^+$. However, the competition between the γ-CH_2 and the *ortho*-CH_3 group remains almost constant for $([C_4H_{10}]/[C_4H_9D])_\alpha > 20$ and the limiting ratio $f_\alpha:f_\gamma:f_o = 0:44:56$ would be reached if the loss of C_4H_9D from ions [**10a** + H]$^+$ were suppressed completely. It is also interesting to compare these data to the corresponding $f_\gamma:f_o$ values for the complexes formed from the 2,4,5-trimethyl-substituted ions [**10** + H]$^+$ with the 2,4- and 2,5-dimethylated ions [**6** + H]$^+$ and [**7** + H]$^+$. Thus, in ions [**6** + H]$^+$ ($f_\gamma:f_o = 70:15$), the *para*-methyl group strongly activates the γ-CH_2 but not the ortho methyl group and, accordingly, the *meta*-methyl group strongly activates the *ortho*-methyl but less than the γ-CH_2 group in ions [**7** + H]$^+$ ($f_\gamma:f_o$ =



Scheme 10.



Scheme 11. Regioselectivies of hydride abstraction within the complexes generated from selected precursor ions $[M + H]^+$ (for monomethyl analogues, see Scheme 3 and [16b]).

31:54). Ions $[\mathbf{10} + H]^+$ represent an intermediate case (f_γ:$f_o \approx 44$:50) since both the *para*- and *meta*-methyl substituents exert activating effects on the respective donor groups to which they themselves are *para* oriented.

Finally, our efforts to study the corresponding isotopomers of the mesitylene analogue $[\mathbf{11} + H]^+$ have to be mentioned. Synthesis of the respective α,α-D_2 precursor (compound **11a**, not displayed) failed, whereas that of the γ,γ-D_2 isotopomer (**11b**) was successful (see the Appendix). Isobutane loss from $[\mathbf{11} + H]^+$ is very minor (~1%, cf. Table 1), and besides the clearly measurable fraction of C_4H_{10} loss in the MIKE spectrum of ions $[\mathbf{11b} + H]^+$, that of C_4H_9D could not be detected. However, a lower limit $[C_4H_{10}]/[C_4H_9D] \geq 10$ was estimated (Scheme 10). Therefore, it remains uncertain whether the *para*-methyl group at the γ-arene ring further activates the hydride abstraction from the highly shielded benzylic methylene group as compared to ions $[\mathbf{8} + H]^+$ and $[\mathbf{9} + H]^+$.

4. Conclusions

The substituent effects of methyl groups on the fragmentation behavior of metastable ions $[\mathbf{5} + H]^+$–$[\mathbf{11} + H]^+$ clearly reflect the intermediacy of ion/neutral complexes [*t*-$C_4H_9^+$ 1,3-diarylpropane] complexes. The competition between the losses of isobutene and isobutane, i.e. proton transfer to the neutral constituent and hydride abstraction from it by the *tert*-butyl cation, strongly depends on the basicity of the whole diphenylalkane, rather than on the basicity of an individual ring, and on the local activation of hydride donating benzylic methylene and methyl groups. "Symmetrization" of the precursor ion during the generation of the complex, as shown by the identical behavior of the 2,6-dimethyl-substituted ions $[\mathbf{8} + H]^+$ and $[\mathbf{9} + H]^+$, also confirms that the *tert*-butyl cation can freely move within the complex. The hydride donor activity of the benzylic methylene groups, but also of the *ortho*-methyl groups are significantly affected by electronic and steric effects, and the regioselectivity of the intracomplex hydride abstraction can be determined by reasonably assuming the same kinetic isotope effect, $k_H/k_D = 1.6$, operating for all donor positions. The fractional contributions f_α:f_γ:f_o of the donor sites in the various complexes, including that generated from ions $[\mathbf{4} + H]^+$, are collected in Scheme 11.

Hydride abstraction from the benzylic methylene group of the more highly alkylated benzyl moiety is facilitated ($r_{\gamma/\alpha} > 1$) by the presence of a *meta*-methyl or, even more efficiently, a *para*-methyl substituent, or both. This is also true when an *ortho*-methyl substituent gives rise to partial shielding of the adjacent benzylic CH_2 donor group and acts as a hydride donor on its own. The hydride donor reactivity of the *ortho*-methyl substituents is increased in the same order by methyl groups oriented *meta* or/and *para* to that donor. Twofold shielding of the benzylic methylene group by 2,6-dimethyl substitution strongly discriminates that donor site in favor of both the unshielded benzylic and the two *ortho*-methyl groups; however, discrimination is far less efficient than in the complexes containing a mononuclear alkylbenzene only. This finding and the fact that *ortho*-methyl groups act as hydride donors, whereas *meta*- and *para*-methyl groups do not, clearly demonstrate the role of the spectator ring in gaseous ion/molecule complexes containing a neutral α,ω-diphenylalkane. Further examples describing the chemistry of ion/neutral complexes of the *tert*-butyl cation with even larger alkylbenzenes will be reported next in this series [15].

Appendix

A1. tert-Butylated 1,3-Diphenylpropenones (tert-Butylchalcones)

1-(4-*tert*-Butylphenyl)-3-(3,4-dimethylphenyl) prop-2-ene-1-one (15)

From 4-*tert*-butylacetophenone and 3,4-dimethylbenzaldehyde, yield 55%, pale yellow needles, m_p 121.5–123 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.37 (*s*, 9 H), 2.31 (*s*, 6 H), 7.17–7.20 (*m*, 1 H), 7.39–7.42 (*m*,

2 H), 7.50 and 7.78 (*AB*, ^3J 15.7 Hz, 2 H), 7.52 and 7.98 (*AA′BB′*, ^3J 8.7 Hz, 4 H); mass spectrum (EI): *m/z* (%) 292 (20, $M^{\cdot+}$), 291 (19), 277 (100), 235 (33), 131 (11), 117 (25), 91 (12); IR (KBr): $\bar{\nu}$ (cm^{-1}) 2970, 1655, 1593, 1238, 1224, 1189, 1109, 1033, 1013, 812. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.25 H 8.21.

3-(4-*tert*-Butylphenyl)-1-(3,4-dimethylphenyl) prop-2-ene-1-one (16)

From 3,4-dimethylacetophenone and 4-*tert*-butylbenzaldehyde; yield 68%, pale yellow solid, m_p 58–60 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.35 (*s*, 9 H), 2.35 (*s*, 6 H), 7.24–7.27 (*m*, 1 H), 7.44 and 7.60 (*AA′BB′*, ^3J 8.4 Hz, 4 H), 7.51 and 7.80 (*AB*, ^3J 15.7 Hz, 2 H), 7.76–7.82 (*m*, 2 H); mass spectrum (EI): *m/z* (%) 292 (45, $M^{\cdot+}$), 291 (29), 277 (79), 235 (100), 133 (22), 105 (18), 57 (11); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3034, 2965, 2870, 1655, 1608, 1592, 1413, 1324, 1136, 985, 816. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.05 H 8.05.

3-(4-*tert*-Butylphenyl)-1-(3,4-di[D_3]methyl[D_3] phenyl)prop-2-ene-1-one (16a)

From 3,4-di[D_3]methyl-[2,5,6-D_3]acetophenone and 4-*tert*-butylbenzaldehyde; yield 20% with recovery of ~60% of each of the starting materials, yellow crystals, m_p 99–100.5 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.35 (*s*, 9 H), 7.44 and 7.60 (*AA′BB′*, ^3J 8.4 Hz, 4 H), 7.50 and 7.79 (*AB*, ^3J 15.7 Hz, 2 H); mass spectrum (EI): *m/z* (%) 301 (47, $M^{\cdot+}$), 300 (39), 286 (66), 258 (21), 244 (100), 142 (33), 129 (28), 114 (31), 82 (20), 57 (16).

1-(4-*tert*-Butylphenyl)-3-(2,4-dimethylphenyl) prop-2-ene-1-one (17)

From 2,4-dimethylbenzaldehyde and 4-(*tert*-butyl) acetophenone; yield 46%, yellow crystals, m_p 95–96 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ 1.36 (*s*, 9 H), 2.35 (*s*, 3 H), 2.46 (*s*, 3 H), 7.05–7.08 (*m*, 2 H), 7.45 and 8.11 (*AB*, ^3J 15.6 Hz, 2 H), 7.52 and 7.99 (*AA′BB′*, ^3J 8.6 Hz, 4 H), 7.61–7.63 (*m*, 1 H); mass spectrum (EI): *m/z* (%) 292 (40, $M^{\cdot+}$), 291 (10), 277 (100), 235 (39), 161 (31), 147 (24), 131 (16), 117 (32), 91 (24), 57 (13); IR (KBr): $\bar{\nu}$ (cm^{-1}) 2969, 2871, 1649, 1605, 1582, 1340, 1222, 1010, 811, 704. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.32, H 8.51.

3-(4-*tert*-Butylphenyl)-1-(2,4-dimethylphenyl) prop-2-ene-1-one (18)

From 2,4-dimethylacetophenone and 4-*tert*-butylbenzaldehyde; yield 35%, yellow crystals, m_p 70 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.33 (*s*, 9 H), 2.38 (*s*, 3 H), 2.43 (*s*, 3 H), 7.07–7.10 (*m*, 2 H), 7.12 and 7.47 (*AB*, ^3J 16.0 Hz, 2 H), 7.41–7.44 (*m*, 1 H), 7.42 and 7.51 (*AA′BB′*, ^3J 8.5 Hz, 4 H); mass spectrum (EI): *m/z* (%) 292 (98, $M^{\cdot+}$), 291 (19), 277 (73), 235 (62), 147 (40), 145 (100), 133 (31), 105 (33), 91 (20), 77 (23), 57 (33); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3031, 2970, 2868, 1665, 1601, 1329, 1216, 1012, 991, 813. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.21, H 8.28.

1-(4-*tert*-Butylphenyl)-3-(2,5-dimethylphenyl) prop-2-ene-1-one (19)

From 2,5-dimethylbenzaldehyde and 4-*tert*-butylacetophenone; yield 75%, pale yellow crystals, m_p 77 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.37 (*s*, 9 H), 2.37 (*s*, 3 H), 2.44 (*s*, 3 H), 7.12–7.13 (*m*, 2 H), 7.47 and 8.10 (*AB*, ^3J 15.6 Hz, 2 H), 7.51–7.54 (*m*, 1 H), 7.53 and 8.00 (*AA′BB′*, ^3J 8.6 Hz, 4 H); mass spectrum (EI): *m/z* (%) 292 (33, $M^{\cdot+}$), 291 (6), 277 (100), 235 (40), 161 (31), 147 (33), 131 (16), 117 (30), 91 (25), 57 (16); IR (KBr): $\bar{\nu}$ (cm^{-1}) 2966, 2872, 1653, 1605, 1588, 1238, 1224, 1194, 1108, 1034, 813. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.27 H 8.25.

3-(4-*tert*-Butylphenyl)-1-(2,5-dimethylphenyl) prop-2-ene-1-one (20)

From 4-*tert*-butylbenzaldehyde and 2,5-dimethylacetophenone; yield 60%; yellow solid, m_p 77–78.5 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.33 (*s*, 9 H), 2.36 (*s*, 3 H), 2.38 (*s*, 3 H), 7.09 and 7.44 (*AB*, ^3J 16.0 Hz, 2 H), 7.17–7.18 (*m*, 2 H), 7.27 (s_{br}, 1 H), 7.43 and 7.52 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 292 (57, $M^{\cdot+}$), 291 (11), 277 (51), 235 (57), 145 (100), 133 (38), 131 (32), 105 (60), 91 (38), 77 (54), 57 (65); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3036, 2968, 2870, 1657, 1593, 1332, 1171, 1024, 994, 820, 653. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.02 H 8.24.

3-(4-*tert*-Butylphenyl)-1-(2-methyl-5-[D_3]methylphenyl)prop-2-ene-1-one (20a)

From 2-methyl-5-[D_3]methylacetophenone and 4-*tert*-butylbenzaldehyde; yield 39%, yellow solid, m_p 72–75 °C (MeOH/H_2O). ^{1}H NMR ($CDCl_3$): δ 1.33 (*s*, 9 H), 2.38 (*s*, 3 H), 7.09 and 7.44 (*AB*, ^3J 16.2 Hz, 2 H), 7.17–7.18 (*m*, 2 H), 7.27 (s_{br}, 1 H), 7.42 and 7.51 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 295 (99, $M^{\cdot+}$), 294 (26), 280 (67), 238 (67), 162 (23), 161 (22), 148 (100), 147 (76), 133 (45), 131 (36), 119 (16), 117 (20), 115 (19), 108 (33), 91 (21), 57 (53).

3-(4-*tert*-Butylphenyl)-1-(2,5-di[D_3]methylphenyl)prop-2-ene-1-one (20b)

From 4-*tert*-butylbenzaldehyde and 2,5-di[D_3]methylacetophenone; yield 42%, yellow crystals, m_p 77.5–78.5 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.33 (*s*, 9 H), 7.09–7.44 (*AB*, ^3J 16.0 Hz, 2 H), 7.15–7.21 (*m*, 2 H), 7.27–7.28 (*m*, 1 H), 7.43 and 7.51 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 298 (100, $M^{\cdot+}$), 297 (26), 283 (85), 241 (90), 165 (25), 151 (67), 150 (42), 149 (35), 148 (37), 147 (28), 134 (30), 132 (26), 129 (25), 128 (21), 111 (42), 91 (14), 81 (13), 80 (14), 57 (51).

3-(4-*tert*-Butylphenyl)-1-(2,5-di[D_3]methyl[D_3]phenyl)prop-2-ene-1-one (20c)

From 2,5-di[D_3]methyl-[3,4,6-D_3]acetophenone and 4-*tert*-butylbenzaldehyde; yield 59%, yellow needles, m_p 78–79 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.33 (*s*, 9 H), 7.09 and 7.44 (*AB*, ^3J 16.1 Hz, 2 H), 7.43 and 7.52 (*AA′BB′*, ^3J 8.5 Hz, 4 H); mass spectrum (EI): *m/z* (%) 301 (100, $M^{\cdot+}$), 300 (29), 286 (72), 258 (11), 244 (79), 168 (21), 154 (55), 153 (41), 148 (34), 147 (24), 134 (27), 132 (22), 120 (16), 114 (32), 82 (17), 57 (44).

1-(4-*tert*-Butylphenyl)-3-(2,6-dimethylphenyl)prop-2-ene-1-one (21)

From 2,6-dimethylbenzaldehyde and 4-*tert*-butylacetophenone; yield 40% after kugelrohr distillation and recrystallization, pale yellow needles, m_p 101–103 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.36 (*s*, 9 H), 2.41 (*s*, 6 H), 7.09–7.17 (*m*, 3 H), 7.19 and 7.95 (*AB*, ^3J 16.1 Hz, 2 H), 7.52 and 7.96 (*AA′BB′*, ^3J 8.6 Hz, 4 H); mass spectrum (EI): *m/z* (%) 292 (12, $M^{\cdot+}$), 277 (100), 235 (57), 161 (34), 147 (28), 131 (13), 117 (26), 91 (24), 57 (16); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3063, 2968, 2872, 1658, 1600, 1306, 1218, 1009, 987, 772. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.19 H 8.44.

3-(4-*tert*-Butylphenyl)-1-(2,6-dimethylphenyl)prop-2-ene-1-one (22)

From 2,6-dimethylacetophenone and 4-*tert*-butylbenzaldehyde; yield 44%, yellow oil, bp 155 °C/0.015 mbar. ^{1}H NMR ($CDCl_3$): δ 1.32 (*s*, 9 H), 2.22 (*s*, 6 H), 6.93 and 7.16 (*AB*, ^3J 16.1 Hz, 2 H), 7.06–7.22 (*m*, 3 H), 7.41 and 7.47 (*AA′BB′*, ^3J 8.7 Hz, 4 H); mass spectrum (EI): *m/z* (%) 292 (56, $M^{\cdot+}$), 277 (62), 235 (37), 163 (42), 145 (100), 133 (58), 105 (43), 91 (43), 77 (30), 57 (58); IR (film): $\bar{\nu}$ (cm^{-1}) 3034, 2966, 2872, 1647, 1621, 1603, 1270, 1107, 1060, 828. $C_{21}H_{24}O$ (HRMS) calcd 292.1827, found 292.1822.

1-(4-*tert*-Butyl-2,6-dimethylphenyl)-3-phenylprop-2-ene-1-one (23)

From 4-*tert*-butyl-2,6-dimethylacetophenone and benzaldehyde; yield 55%, yellow crystals, m_p 71 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.33 (*s*, 9 H), 2.23 (*s*, 6 H), 6.95 and 7.23 (*AB*, ^3J 16.2 Hz, 2 H), 7.07 (*s*, 2 H), 7.38–7.40 (*m*, 3 H), 7.51–7.55 (*m*, 2 H); mass spectrum (EI): *m/z* (%) 292 (57, $M^{\cdot+}$), 277 (25), 235 (8), 201 (100), 131 (23), 91 (10), 77 (12), 57 (10); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3028, 2965, 2867, 1653, 1626, 1270, 1139, 1058, 975, 870, 766, 704, 681. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.11 H 8.30.

3-(4-*tert*-Butyl-2,6-dimethylphenyl)-1-phenylprop-2-ene-1-one (24)

From 4-*tert*-butyl-2,6-dimethylbenzaldehyde (2.86 g, 15.0 mmol) and acetophenone (1.90 g, 16.0 mmol), with dioxane (6 mL) and further KOH (2 g) in MeOH (8 mL) added to the reaction mixture; yield 55%, yellow crystals, m_p 70–71 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.33 (*s*, 9 H), 2.44 (*s*, 6 H), 7.13 (*s*, 2 H), 7.18 and 7.98 (*AB*, ^3J 16.0 Hz, 1 H), 7.48–7.62 (*m*, 3 H), 7.98–8.00 (*m*, 2 H); mass spectrum (EI): *m/z* (%) 292 (26, $M^{\cdot+}$), 291 (1), 277 (100), 235 (10), 171 (15), 129 (12), 128 (13), 115 (15), 105 (50), 77 (59), 57 (16); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3065, 2960, 2868, 1661, 1604, 1445, 1298, 1227, 1214, 1012, 980, 692. $C_{21}H_{24}O$ (292.42), calcd C 86.26 H 8.27, found C 86.18 H 7.99.

1-(4-*tert*-Butylphenyl)-3-(2,4,5-trimethylphenyl) prop-2-ene-1-one (25)

From 2,4,5-trimethylbenzaldehyde and 4-*tert*-butylacetophenone; yield 57%, yellow crystals, m_p 122 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.36 (*s*, 9 H), 2.26 (*s*, 3 H), 2.28 (*s*, 3 H), 2.42 (*s*, 3 H), 7.01 (s_{br}, 1 H), 7.49 (s_{br}, 1 H), 7.45 and 8.09 (*AB*, ^3J 15.6 Hz, 2 H), 7.52 and 7.99 (*AA′BB′*, ^3J 8.6 Hz, 4 H); mass spectrum (EI): *m/z* (%) 306 (62, $M^{\cdot+}$), 305 (6), 291 (100), 249 (28), 161 (30), 147 (32), 124 (26), 115 (20), 91 (18), 57 (16); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3020, 2965, 2871, 1650, 1605, 1584, 1318, 1265, 1222, 1193, 1108, 1009, 984. $C_{22}H_{26}O$ (306.45), calcd C 86.23 H 8.55, found C 86.39 H 8.85.

3-(4-*tert*-Butylphenyl)-1-(2,4,5-trimethylphenyl) prop-2-ene-1-one (26)

From 2,4,5-trimethylacetophenone and 4-*tert*-butylbenzaldehyde; yield 47%, yellow crystals, m_p 98 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.33 (*s*, 9 H), 2.27 (*s*, 3 H), 2.29 (*s*, 3 H), 2.39 (*s*, 3 H), 7.05 (s_{br}, 1 H), 7.29 (s_{br}, 1 H), 7.13 and 7.48 (*AB*, ^3J 16.0 Hz, 2 H), 7.42 and 7.52 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 306 (88, $M^{\cdot+}$), 305 (25), 291 (57), 249 (51), 173 (30), 159 (100), 147 (30), 133 (25), 131 (27), 119 (31), 91 (36), 57 (31); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3020, 2970, 1658, 1591, 1328, 1217, 1100, 993, 824. $C_{22}H_{26}O$ (306.45), calcd C 86.23 H 8.55, found C 86.24 H 8.49.

3-(4-*tert*-Butylphenyl)-1-(2,4,6-trimethylphenyl) prop-2-ene-1-one (27)

From 4-*tert*-butylbenzaldehyde and 2,4,6-trimethylacetophenone; yield 40%, yellow oil, bp 145 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 1.32 (*s*, 9 H), 2.18 (*s*, 6 H), 2.32 (*s*, 3 H), 6.88 (s_{br}, 2 H), 6.91 and 7.17 (*AB*, ^3J 16.2 Hz, 2 H), 7.40 and 7.46 (*AA′BB′*, ^3J 8.6 Hz, 4 H); mass spectrum (EI): *m/z* (%) 306 (69, $M^{\cdot+}$), 291 (53), 249 (29), 159 (100), 147 (58), 131 (26), 119 (29), 91 (43), 77 (22), 57 (32); IR (film): $\bar{\nu}$ (cm^{-1}) 3034, 2965, 2871, 1673, 1606, 1561, 1460, 1413, 1364, 1325, 1275, 1166, 1065, 983, 832. $C_{22}H_{26}O$ (HRMS), calcd 306.1984, found 306.1987.

A2. tert-Butylated 1,3-diphenylpropanones (tert-butyldihydrochalcones)

1-(4-*tert*-Butylphenyl)-3-(3,4-dimethylphenyl)propane-1-one (28)

By hydrogenation of **15**; yield 68%, colorless oil, bp 150 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.34 (*s*, 9 H), 2.23 (*s*, 3 H), 2.25 (*s*, 3 H), 2.99 (*t*, ^3J 7.8 Hz, 2 H), 3.26 (*t*, ^3J 7.9 Hz, 2 H), 6.96–7.09 (*m*, 3 H), 7.46 and 7.91 (*AA′BB′*, ^3J 8.7 Hz, 4 H); mass spectrum (EI): *m/z* (%) 294 (26, $M^{\cdot+}$), 279 (12), 237 (42), 161 (100), 133 (29), 119 (41), 91 (25), 57 (19); IR (film): $\bar{\nu}$ (cm^{-1}) 3043, 2966, 1682, 1606, 1407, 1363, 1269, 1189, 1107, 979, 878. $C_{21}H_{26}O$ (HRMS), calcd 294.1984, found 294.1985.

3-(4-*tert*-Butylphenyl)-1-(3,4-dimethylphenyl)propane-1-one (29)

By hydrogenation of **16**; yield 65%, colorless solid, m_p 56–58 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 2.30 (*s*, 3 H), 2.31 (*s*, 3 H), 3.02 (*t*, ^3J 7.8 Hz, 2 H), 3.27 (*t*, ^3J 7.9 Hz, 2 H), 7.18–7.21 (*m*, 1 H), 7.20 and 7.33 (*AA′BB′*, ^3J 8.4 Hz, 4 H), 7.68–7.74 (*m*, 2 H); mass spectrum (EI): *m/z* (%) 294 (47, $M^{\cdot+}$), 279 (73), 237 (7), 133 (100), 105 (32), 91 (14), 57 (10); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3055, 2970, 2870, 1677, 1606, 1407, 1301, 1207, 1161, 1022, 818, 778. $C_{21}H_{26}O$ (294.44), calcd C 85.67 H 8.90, found C 85.57 H 9.09.

1-(4-*tert*-Butylphenyl)-3-(2,4-dimethylphenyl)propane-1-one (30)

By hydrogenation of **17**; yield 79%, colorless crystals, m_p 73–75 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.34 (*s*, 9 H), 2.30 (*s*, 3 H), 2.31 (*s*, 3 H), 3.00 (*t*, ^3J 7.8 Hz, 2 H), 3.21 (*t*, ^3J 7.7 Hz, 2 H), 6.96–7.10 (*m*, 3 H), 7.47 and 7.91 (*AA′BB′*, ^3J 8.6 Hz, 4 H); mass spectrum (EI): *m/z* (%) 294 (30, $M^{\cdot+}$), 279 (8), 237 (20), 161 (100), 133 (11), 119 (45), 118 (41), 91 (24), 57 (8); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3010, 2964, 2870, 1678, 1605, 1406, 1360, 1192, 975, 810. $C_{21}H_{26}O$ (294.44), calcd C 85.67 H 8.90, found C 85.76 H 9.22.

3-(4-*tert*-butylphenyl)-1-(2,4-dimethylphenyl)propane-1-one (31)

By hydrogenation of **18**; yield 95%, pale yellow oil, bp 120 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.30

(*s*, 9 H), 2.33 (*s*, 3 H), 2.47 (*s*, 3 H), 2.99 (*t*, ^3J 7.7 Hz, 2 H), 3.21 (*t*, ^3J 7.6 Hz, 2 H), 7.01–7.04 (*m*, 2 H), 7.16 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H), 7.55–7.57 (*m*, 1 H); mass spectrum (EI): *m/z* (%) 294 (22, $M^{\cdot+}$), 279 (35), 135 (24), 133 (100), 105 (28), 91 (17), 57 (9); IR (film): $\bar{\nu}$ (cm^{-1}) 2967, 2871, 1681, 1611, 1448, 1363, 1268, 1202, 979, 816. $C_{21}H_{26}O$ (HRMS), calcd 294.1984, found 294.1986.

1-(4-*tert*-Butylphenyl)-3-(2,5-dimethylphenyl)propane-1-one (32)

By hydrogenation of **19**; yield 65%, colorless oil, bp 160 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.34 (*s*, 9 H), 2.30 (*s*, 6 H), 3.03 (*t*, ^3J 7.7 Hz, 2 H), 3.22 (*t*, ^3J 7.7 Hz, 2 H), 6.94–7.07 (*m*, 3 H), 7.47 and 7.92 (*AA′BB′*, ^3J 8.6 Hz, 4 H); mass spectrum (EI): *m/z* (%) 294 (38, $M^{\cdot+}$), 279 (6), 276 (4), 237 (16), 161 (100), 119 (39), 118 (53), 117 (26), 91 (28), 57 (12); IR (film): $\bar{\nu}$ (cm^{-1}) 2968, 2872, 1682, 1605, 1460, 1407, 1363, 1269, 1190, 1107, 807. $C_{21}H_{26}O$ (HRMS), calcd 294.1984, found 294.1982.

3-(4-*tert*-Butylphenyl)-1-(2,5-dimethylphenyl)propane-1-one (33)

By hydrogenation of **20**; yield 76%, pale yellow oil, bp 170 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 2.32 (*s*, 3 H), 2.43 (*s*, 3 H), 3.00 (*t*, ^3J 7.7 Hz, 2 H), 3.21 (*t*, ^3J 7.6 Hz, 2 H), 7.10–7.19 (*m*, 2 H), 7.17 and 7.32 (*AA′BB′*, ^3J 8.3 Hz, 4 H), 7.39 (s_{br}, 1 H); mass spectrum (EI): *m/z* (%) 294 (46, $M^{\cdot+}$), 279 (44), 133 (100), 117 817), 105 (37), 91 (21), 77 (19), 57 (12); IR (film): $\bar{\nu}$ (cm^{-1}) 3027, 2967, 2871, 1686, 1567, 1362, 1267, 1170, 816. $C_{21}H_{26}O$ (HRMS), calcd 294.1984, found 294.1980.

1-(4-*tert*-Butylphenyl)-3-(2,6-dimethylphenyl)propane-1-one (34)

By hydrogenation of **21**; yield 77%, colorless crystals, m_p 76–77.5 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.34 (*s*, 9 H), 2.34 (*s*, 6 H), 3.07–3.11 (*m*, 4 H), 7.03 (s_{br}, 3 H), 7.47 and 7.91 (*AA′BB′*, ^3J 8.6 Hz, 4 H); mass spectrum (EI): *m/z* (%) 294 (19, $M^{\cdot+}$), 279 (6), 276 (13), 161 (100), 119 (45), 118 (67), 117 (27), 91 (30), 57 (13); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3022, 2967, 2872, 1678, 1605, 1463, 1403, 1361, 1210, 1189, 974, 770. $C_{21}H_{26}O$ (294.44), calcd C 85.67 H 8.90, found C 85.43 H 8.89.

3-(4-*tert*-Butylphenyl)-1-(2,6-dimethylphenyl)propane-1-one (35)

By hydrogenation of **22**, yield 68%, colorless oil, bp 135 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.30 (*s*, 9 H), 2.15 (*s*, 6 H), 3.03 (s_{br}, 4 H), 6.98–7.01 (*m*, 2 H), 7.12–7.17 (*m*, 1 H), 7.17 and 7.31 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 294 (15, $M^{\cdot+}$), 279 (19), 133 (100), 117 (11), 105 (30), 91 (12), 77 (13), 57 (9); IR (film): $\bar{\nu}$ (cm^{-1}) 3028, 2965, 2872, 1697, 1514, 1462, 1363, 1268, 822, 770. $C_{21}H_{26}O$ (HRMS), calcd 294.1984, found 294.1981.

1-(4-*tert*-Butyl-2,6-dimethylphenyl)-3-phenylpropane-1-one (36)

By hydrogenation of **23**; yield 85%, colorless oil, bp 165 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 1.28 (*s*, 9 H), 2.15 (*s*, 6 H), 3.02–3.05 (*m*, 4 H), 7.00 (*s*, 2 H), 7.18–7.30 (*m*, 5 H); mass spectrum (EI): *m/z* (%) 294 (5, $M^{\cdot+}$), 279 (12), 189 (100), 146 (13), 105 (15), 91 (22), 77 (9); IR (film): $\bar{\nu}$ (cm^{-1}) 3032, 2967, 2871, 1698, 1605, 1453, 1362, 1238, 975, 868, 698. $C_{21}H_{26}O$ (HRMS), calcd 294.1984, found 294.1981.

3-(4-*tert*-Butyl-2,6-dimethylphenyl)-1-phenylpropane-1-one (37)

By hydrogenation of **24**; yield 66%, colorless oil, bp 150 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 2.35 (*s*, 6 H), 3.01–3.07 (*m*, 2 H), 3.11–3.17 (*m*, 2 H), 7.06 (s_{br}, 2 H), 7.43–7.48 (*m*, 2 H), 7.54–7.57 (*m*, 1 H), 7.95–7.98 (*m*, 2 H); mass spectrum (EI): *m/z* (%) 294 (30, $M^{\cdot+}$), 279 (100), 237 (6), 175 (93), 174 (92), 159 (90), 145 (40), 105 (90), 91 (28), 77 (81), 57 (40); Contamination by overhydrogenated products was detected in low amounts by mass spectrometry (*m/z* 300, 285); IR (film): $\bar{\nu}$ (cm^{-1}) 3065, 2966, 2869, 1687, 1448, 1361, 1288, 1203, 740, 689. $C_{21}H_{26}O$ (HRMS), calcd 294.1984, found 294.1983.

1-(4-*tert*-Butylphenyl)-3-(2,4,5-trimethylphenyl) propane-1-one (38)

By hydrogenation of **25**; yield 63%, colorless crystals, m_p 75 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.34 (*s*, 9 H), 2.21 (*s*, 6 H), 2.28 (*s*, 3 H), 2.97 (*t*, ^3J 8.0 Hz, 2 H), 3.20 (*t*, ^3J 8.2 Hz, 2 H), 6.95 (s_{br}, 1 H), 6.97 (s_{br}, 1 H), 7.47 and 7.91 (*AA′BB′*, ^3J 8.6 Hz, 4 H); mass spectrum (EI): *m/z* (%) 308 (46, $M^{\cdot+}$), 293 (9), 251 (14), 161 (100), 147 (31), 133 (72), 132 (79), 117

(26), 91 (25), 57 (11); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3003, 2973, 2934, 1680, 1605, 1407, 1361, 1290, 1210, 1192, 976, 843. $C_{22}H_{28}O$ (308.47), calcd C 85.66 H 9.15, found C 85.65 H 9.11.

3-(4-*tert*-Butylphenyl)-1-(2,4,5-trimethylphenyl) propane-1-one (39)

By hydrogenation of **26**; yield 50%, colorless crystals; m_p 60–63 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 2.23 (*s*, 3 H), 2.25 (*s*, 3 H), 2.44 (*s*, 3 H), 2.99 (*t*, ^3J 7.7 Hz, 2 H), 3.21 (*t*, ^3J 7.8 Hz, 2 H), 7.01 (s_{br}, 1 H), 7.18 and 7.33 (*AA′BB′*, ^3J 8.2 Hz, 4 H), 7.42 (s_{br}, 1 H); mass spectrum (EI): *m/z* (%) 308 (17, $M^{\cdot+}$), 293 (21), 147 (100), 131 (11), 119 (14), 91 (14), 57 (5); IR (KBr): $\bar{\nu}$ (cm^{-1}) 3019, 2966, 2867, 1672, 1446, 1355, 1267, 1208, 1105, 937, 820. $C_{22}H_{28}O$ (308.47), calcd C 85.66 H 9.15, found C 85.63 H 8.93.

3-(4-*tert*-Butylphenyl)-1-(2,4,6-trimethylphenyl) propane-1-one (40)

By hydrogenation of **27**; yield 73%, colorless oil, bp 150 °C/0.05 mbar. ^{1}H NMR ($CDCl_3$): δ 1.30 (*s*, 9 H), 2.12 (*s*, 6 H), 2.26 (*s*, 3 H), 3.01 (s_{br}, 4 H), 6.80 (*s*, 2 H), 7.16 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 308 (7, $M^{\cdot+}$), 293 (14), 147 (100), 131 (15), 119 (24), 91 (22), 77 (11), 57 (9); IR (film): $\bar{\nu}$ (cm^{-1}) 2965, 2870, 1697, 1611, 1514, 1462, 1363, 1268, 977, 849, 821. $C_{22}H_{28}O$ (HRMS), calcd 308.2140, found 308.2132.

A3. tert-Butylated 1,3-diphenylpropanes

1-(4-*tert*-Butylphenyl)-3-(3,4-dimethylphenyl) propane (5)

By catalytic hydrogenolysis of **29**; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.93 (quin, ^3J 7.8 Hz, 2 H), 2.22 (*s*, 3 H), 2.23 (*s*, 3 H), 2.59 (*t*, ^3J 7.8 Hz, 2 H), 2.62 (*t*, ^3J 7.8 Hz, 2 H), 6.92–6.97 (*m*, 2 H), 7.03–7.05 (*m*, 1 H), 7.12 and 7.30 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 280 (68, $M^{\cdot+}$), 265 (77), 133 (36), 120 (100), 105 (35), 92 (27), 91 (26), 57 (29); IR (film): $\bar{\nu}$ (cm^{-1}) 3007, 2967, 2862, 1515, 1503, 1459, 1363, 1268, 1108, 1019, 831, 815. $C_{21}H_{28}$ (HRMS), calcd 280.2191, found 280.2181.

1-(4-*tert*-Butylphenyl)-3-(3,4-dimethylphenyl)-[1,1-D_2]propane (5a)

By chloralane reduction of **28** using $LiAlD_4/AlCl_3$; colorless oil, bp 140 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.91 (*t*, ^3J 7.7 Hz, 2 H), 2.23 (*s*, 3 H), 2.24 (*s*, 3 H), 2.59 (*t*, ^3J 7.7 Hz, 2 H), 6.91–6.97 (*m*, 2 H), 7.03–7.06 (*m*, 1 H), 7.12 and 7.30 (*AA′BB′*, ^3J 8.5 Hz, 4 H); mass spectrum (EI): *m/z* (%) 282 (82, $M^{\cdot+}$), 267 (88), 133 (68), 121 (100), 119 (82), 106 (30), 93 (28), 91 (34), 57 (52). Some elimination product was detected in small amounts by mass spectrometry (*m/z* 279, 264, 222). D contents (mass spectrometry): 88% (79% d_2, 19% d_1, 2% d_0).

1-(4-*tert*-Butylphenyl)-3-(3,4-dimethylphenyl)-[3,3-D_2]propane (5b)

By chloralane reduction of **29** using $LiAlD_4/AlCl_3$; colorless oil, bp 140 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.91 (*t*, ^3J 7.7 Hz, 2 H), 2.23 (*s*, 3 H), 2.24 (*s*, 3 H), 2.62 (*t*, ^3J 7.8 Hz, 2 H), 6.91–6.97 (*m*, 2 H), 7.03–7.06 (*m*, 1 H), 7.13 and 7.30 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 282 (65, $M^{\cdot+}$), 267 (77), 133 (15), 131 (35), 122 (100), 107 (24), 105 (26), 93 (37), 91 (35), 57 (28). Some elimination product was detected in small amounts by mass spectrometry (*m/z* 279, 264, 222). D contents (mass spectrometry): 98% (97% d_2, 2% d_1, 1% d_0).

1-(4-*tert*-Butylphenyl)-3-(3,4-di[D_3]methyl[D_3]phenyl)propane (5c)

By catalytic hydrogenation/hydrogenolysis of **16a**; colorless oil, bp 155 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.93 (quin, ^3J 7.7 Hz, 2 H), 2.60 (*t*, ^3J 7.8 Hz, 2 H), 2.62 (*t*, ^3J 7.7 Hz, 2 H), 7.12 and 7.30 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 289 (79, $M^{\cdot+}$), 274 (100), 142 (25), 141 (18), 129 (82), 128 (77), 117 (24), 111 (19), 93 (12), 92 (22), 91 (18), 57 (33); D contents (mass spectrometry): 96% (75% d_7, 22% d_6, 3% d_5).

1-(4-*tert*-Butylphenyl)-3-(2,4-dimethylphenyl)propane (6)

By hydrogenolysis of **31**; colorless oil, bp 150 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.88 (quin, ^3J 7.8 Hz, 2 H), 2.24 (*s*, 3 H), 2.28 (*s*, 3 H), 2.60 (*t*, ^3J 7.8 Hz, 2 H), 2.66 (*t*, ^3J 7.9 Hz, 2 H), 6.92–6.95 (*m*, 2 H), 7.02–7.04 (*m*, 1 H), 7.13 and

7.30 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 280 (86, $M^{\cdot+}$), 265 (100), 159 (23), 133 (55), 131 (37), 119 (91), 105 (28), 91 (37), 57 (37); IR (film): $\bar{\nu}$ (cm^{-1}) 3007, 2966, 2868, 1503, 1462, 1363, 1269, 831, 817. $C_{21}H_{28}$ (HRMS), calcd 280.2191, found 280.2188.

1-(4-*tert*-Butylphenyl)-3-(2,4-dimethylphenyl)-[1,1-D_2]propane (6a)

By chloralane reduction of **30** using $LiAlD_4/AlCl_3$; colorless oil, bp 135 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.87 (*t*, ^3J 7.9 Hz, 2 H), 2.24 (*s*, 3 H), 2.28 (*s*, 3 H), 2.60 (*t*, ^3J 7.9 Hz, 2 H), 6.92–7.09 (*m*, 3 H), 7.13 and 7.31 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 282 (79, $M^{\cdot+}$), 267 (100), 133 (75), 121 (46), 119 (99), 94 (23), 93 (16), 91 (26), 57 (45). Low amounts of elimination product(s) was detected both by ^{1}H NMR spectrum [δ 1.30 (*s*), 3.49 (*d*), 6.28 (*t*)] and by mass spectrometry (*m/z* 279, 264, 222). D contents (by mass spectrometry): 92% (85% d_2, 14% d_1, 1% d_0).

1-(4-*tert*-Butylphenyl)-3-(2,4-dimethylphenyl)-[3,3-D_2]propane (6b)

By chloralane reduction of **31** using $LiAlD_4/AlCl_3$; colorless oil, bp 150 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.87 (*t*, ^3J 7.8 Hz, 2 H), 2.24 (*s*, 3 H), 2.28 (*s*, 3 H), 2.66 (*t*, ^3J 7.8 Hz, 2 H), 6.92–6.95 (*m*, 2 H), 7.02–7.04 (*m*, 1 H), 7.13 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 282 (82, $M^{\cdot+}$), 267 (100), 161 (31), 135 (41), 121 (79), 119 (22), 93 (29), 91 (24), 57 (42). An elimination product was detected in very low amounts by mass spectrometry (*m/z* 279, 264, 222). D contents (mass spectrometry): 87% (75% d_2, 24% d_1, 1% d_0).

1-(4-*tert*-Butylphenyl)-3-(2,5-dimethylphenyl)propane (7)

By catalytic hydrogenolysis of **33**; colorless oil, bp 120 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.89 (quin, ^3J 7.9 Hz, 2 H), 2.23 (*s*, 3 H), 2.29 (*s*, 3 H), 2.61 (*t*, ^3J 7.9 Hz, 2 H), 2.67 (*t*, ^3J 7.8 Hz, 2 H), 6.89–6.92 (*m*, 1 H), 6.96 (s_{br}, 1 H), 7.00–7.03 (*m*, 1 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 280 (64, $M^{\cdot+}$), 265 (65), 145 (15), 133 (32), 131 (34), 120 (100), 119 (54), 105 (30), 91 (33), 57 (25); IR (film): $\bar{\nu}$ (cm^{-1}) 3004, 2966, 2868, 1503, 1462, 1363, 1268, 1108, 831, 806. $C_{21}H_{28}$ (HRMS), calcd 280.2191, found 280.2189.

1-(4-*tert*-Butylphenyl)-3-(2,5-dimethylphenyl)-[1,1-D_2]propane (7a)

By chloralane reduction of **32** using $LiAlD_4/AlCl_3$; colorless oil, bp 135 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.88 (*t*, ^3J 7.9 Hz, 2 H), 2.22 (*s*, 3 H); 2.28 (*s*, 3 H), 2.60 (*t*, ^3J 7.9 Hz, 2 H), 6.89–6.92 (*m*, 1 H), 6.95 (s_{br}, 1 H), 7.00–7.03 (*m*, 1 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 282 (49, $M^{\cdot+}$), 267 (62), 146 (16), 133 (56), 121 (100), 120 (40), 119 (78), 106 (22), 93 (15), 91 (29), 57 (37). Some elimination product was detected in low amounts by mass spectrometry (*m/z* 279, 264, 222). D contents (mass spectrometry): 87% (76% d_2, 22% d_1, 2% d_0).

1-(4-*tert*-Butylphenyl)-3-(2,5-dimethylphenyl)-[3,3-D_2]propane (7b)

By chloralane reduction of **33** using $LiAlD_4/AlCl_3$; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.88 (*t*, ^3J 7.8 Hz, 2 H), 2.22 (*s*, 3 H), 2.29 (*s*, 3 H), 2.67 (*t*, ^3J 7.8 Hz, 2 H), 6.90–6.92 (*m*, 1 H), 6.95 (s_{br}, 1 H), 7.00–7.03 (*m*, 1 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H), mass spectrum (EI): *m/z* (%) 282 (86, $M^{\cdot+}$), 267 (81), 147 (29), 145 (29), 131 (50), 122 (100), 121 (88), 105 (33), 91 (39), 57 (42). Some elimination product and a chlorinated product were detected in low amounts by mass spectrometry (*m/z* 279, 264, 222 and *m/z* 317/315, 302/300, respectively). D contents (mass spectrometry): 82% (66% d_2, 31% d_1, 3% d_0).

1-(4-*tert*-Butylphenyl)-3-(2-methyl-5-[D_3]methylphenyl)propane (7c)

By catalytic hydrogenation/hydrogenolysis of **20a**; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.89 (quin, ^3J 7.9 Hz, 2 H), 2.23 (*s*, 3 H), 2.61 (*t*, ^3J 7.9 Hz, 2 H), 2.67 (*t*, ^3J 7.8 Hz, 2 H), 6.89–6.92 (*m*, 1 H), 6.95 (s_{br}, 1 H), 7.00–7.03 (*m*, 1 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.2 Hz, 4 H); mass spectrum (EI): *m/z* (%) 283 (51, $M^{\cdot+}$), 268 (59), 159 (9), 147 (8), 145 (11), 136 (20), 135 (10), 134 (11), 133 (7), 132 (9), 123 (100), 122 (56), 121 (15), 108 (10), 105 (14), 92 (16), 91 (17), 57 (25). D contents (mass spectrometry): 92% (80% d_3, 16% d_2, 3% d_1, 1% d_0).

1-(4-*tert*-Butylphenyl)-3-(2,5-di[D_3]methylphenyl)propane (7d)

By catalytic hydrogenation/hydrogenolysis of **20b**; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.89 (quin, ^3J 7.8 Hz, 2 H), 2.60 (*t*, ^3J 7.9 Hz, 2 H), 2.67 (*t*, ^3J 7.8 Hz, 2 H), 6.89–6.92 (*m*, 1 H), 6.95–6.96 (*m*, 1 H), 7.00–7.02 (*m*, 1 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 286 (64, $M^{\cdot+}$), 271 (73), 147 (11), 145 (14), 139 (26), 131 (32), 126 (100), 125 (63), 117 (27), 108 (15), 92 (17), 91 (20), 57 (30). D contents (mass spectrometry): 97% (86% d_6, 12% d_5, 2% d_4, 1% d_3).

1-(4-*tert*-Butylphenyl)-3-(2,5-di[D_3]methyl[D_3]phenyl)propane (7e)

By catalytic hydrogenation/hydrogenolysis of **20c**; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.89 (quin, ^3J 7.9 Hz, 2 H), 2.60 (*t*, ^3J 7.9 Hz, 2 H), 2.67 (*t*, ^3J 7.8 Hz, 2 H), 7.13 and 7.30 (*AA′BB′*, ^3J 8.2 Hz, 4 H); mass spectrum (EI): *m/z* (%) 289 (66, $M^{\cdot+}$), 274 (70), 142 (20), 129 (100), 128 (71), 117 (22), 111 (16), 92 (12), 91 (15), 57 (24). D contents (mass spectrometry): 98% (84% d_9, 14% d_8, 2% d_7, 0% d_6).

1-(4-*tert*-Butylphenyl)-3-(2,6-dimethylphenyl)propane (8)

By catalytic hydrogenolysis of **34**; colorless oil, bp 145 °C/0.04 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.78 (quin, ^3J 7.8 Hz, 2 H), 2.26 (*s*, 6 H), 2.61 (*t*, ^3J 7.8 Hz, 2 H), 2.71 (*t*, ^3J 7.8 Hz, 2 H), 6.97 (s_{br}, 3 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 280 (77, $M^{\cdot+}$), 265 (91), 159 (42), 145 (23), 133 (70), 131 (61), 120 (64), 119 (100), 117 (54), 105 (45), 91 (63), 77 (25), 57 (55); IR (film): $\bar{\nu}$ (cm^{-1}) 3025, 2966, 2871, 1509, 1466, 1362, 1268, 829, 766. $C_{21}H_{28}$ (HRMS), calcd 280.2191, found 280.2188.

1-(4-*tert*-Butylphenyl)-3-(2,6-dimethylphenyl)-[1,1-D_2]propane (8a)

By chloralane reduction of **34** using $LiAlD_4/AlCl_3$; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.78 (*t*, ^3J 7.7 Hz, 2 H), 2.26 (*s*, 6 H), 2.61 (*t*, ^3J 7.8 Hz, 2 H), 6.97 (s_{br}, 3 H), 7.15 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 282 (57, $M^{\cdot+}$), 267 (78), 160 (24), 146 (19), 133 (86), 121 (39), 120 (32), 119 (100), 118 (44), 105 (21), 93 (15), 91 (42), 57 (53). The compound was contaminated by ~25% of an elimination product [^{1}H NMR: δ 1.29 (*s*), 3.53 (*d*); mass spectrometry (*m/z* 279, 264, 222)]. D contents (mass spectrometry): 85% (74% d_2, 22% d_1, 4% d_0).

1-(4-*tert*-Butylphenyl)-3-(2,6-dimethylphenyl)-[3,3-D_2]propane (8b)

By chloralane reduction of **35** using $LiAlD_4/AlCl_3$; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.77 (*t*, ^3J 7.7 Hz, 2 H), 2.26 (*s*, 6 H), 2.72 (*t*, ^3J 7.7 Hz, 2 H), 6.98 (s_{br}, 3 H), 7.15 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 282 (72, $M^{\cdot+}$), 267 (100), 161 (44), 147 (23), 145 (21), 135 (58), 131 (50), 122 (47), 121 (94), 117 (48), 105 (29), 93 (18), 91 (40), 57 (63). The compound was contaminated by ~20% of an elimination product [^{1}H NMR: δ 1.32 (*s*), 3.57 (*d*); mass spectrometry (*m/z* 279, 264, 222)]. D contents (mass spectrometry): 93% (86% d_2, 14% d_1, 0% d_0).

1-(4-*tert*-Butyl-2,6-dimethylphenyl)-3-phenylpropane (9)

By catalytic hydrogenolysis of **37**; colorless oil, bp 135 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.28 (*s*, 9 H), 1.79 (quin, ^3J 7.6 Hz, 2 H), 2.25 (*s*, 6 H), 2.59 (*t*, ^3J 7.6 Hz, 2 H), 2.74 (*t*, ^3J 7.6 Hz, 2 H), 6.99 (*s*, 2 H), 7.19–7.31 (*m*, 5 H); mass spectrum (EI): *m/z* (%) 280 (68, $M^{\cdot+}$), 265 (100), 175 (83), 162 (25), 145 (40), 119 (34), 105 (30), 91 (88), 57 (21). IR (film): $\bar{\nu}$ (cm^{-1}) 3031, 2956, 2867, 1605, 1486, 1453, 1361, 867, 744, 698. $C_{21}H_{28}$ (HRMS), calcd 280.2191, found 280.2194.

1-(4-*tert*-Butyl-2,6-dimethylphenyl)-3-phenyl-[1,1-D_2]propane (9a)

By chloralane reduction of **36** using $LiAlD_4/AlCl_3$; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.28 (*s*, 9 H), 1.78 (*t*, ^3J 7.6 Hz, 2 H), 2.25 (*s*, 6 H), 2.74 (*t*, ^3J 7.6 Hz, 2 H), 6.99 (*s*, 2 H), 7.20–7.29 (*m*, 5 H); mass spectrum (EI): *m/z* (%) 282 (63, $M^{\cdot+}$), 267 (100), 177 (83), 161 (48), 147 (48), 120 (25), 105 (19), 91 (64), 57 (10). Some elimination product was detected in minor amounts both by ^{1}H NMR and mass spectrometry [δ 1.30 (*s*), 3.50 (*d*) and *m/z* 279, 264, 222]. D contents (mass spectrometry): 97% (95% d_2, 3% d_1, 2% d_0).

1-(4-*tert*-Butyl-2,6-dimethylphenyl)-3-phenyl-[3,3-D_2]propane (9b)

By chloralane reduction of **37** using $LiAlD_4/AlCl_3$; colorless oil, bp 140 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.28 (*s*, 9 H), 1.77 (*t*, ^3J 7.7 Hz, 2 H), 2.25 (*s*, 6 H), 2.56–2.62 (*m*, 2 H), 6.99 (*s*, 2 H), 7.19–7.29 (*m*, 5 H); mass spectrum (EI): *m/z* (%) 282 (54, $M^{\cdot+}$), 267 (100), 175 (98), 163 (16), 159 (29), 145 (39), 119 (33), 105 (19), 93 (41), 92 (34), 91 (33), 57 (26). Small amounts of some elimination product and a chlorinated product were detected by mass spectrometry (*m/z* 279, 264, 222 and *m/z* 317/315, 302/300, respectively). D contents (mass spectrometry): 90% (84% d_2, 13% d_1, 3% d_0).

1-(4-*tert*-Butylphenyl)-3-(2,4,5-trimethylphenyl) propane (10)

By catalytic hydrogenolysis of **39**; colorless oil, bp 135 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.88 (quin, ^3J 7.8 Hz, 2 H), 2.19 (*s*, 3 H), 2.20 (*s*, 6 H), 2.58 (*t*, ^3J 7.9 Hz, 2 H), 2.67 (*t*, ^3J 7.8 Hz, 2 H), 6.91 (s_{br}, 2 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 294 (60, $M^{\cdot+}$), 279 (32), 147 (41), 134 (100), 133 (80), 119 (29), 117 (29), 91 (26), 57 (22); IR (film): $\bar{\nu}$ (cm^{-1}) 3005, 2967, 2867, 1506, 1459, 1363, 1268, 1018, 831. $C_{22}H_{30}$ (HRMS), calcd 294.2348, found 294.2346.

1-(4-*tert*-Butylphenyl)-3-(2,4,5-trimethylphenyl)-[1,1-D_2]propane (10a)

By chloralane reduction of **38** using $LiAlD_4/AlCl_3$; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.86 (*t*, ^3J 7.9 Hz, 2 H), 2.19 (*s*, 3 H), 2.20 (*s*, 6 H), 2.57 (*t*, ^3J 7.9 Hz, 2 H), 6.90 (s_{br}, 2 H), 7.13 and 7.30 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 296 (83, $M^{\cdot+}$), 281 (41), 147 (49), 135 (100), 134 (53), 133 (99), 119 (32), 117 (27), 93 (17), 91 (28), 57 (45). Some elimination product was detected in small amounts by mass spectrometry (*m/z* 293, 278, 236). D contents (mass spectrometry): 87% (77% d_2, 20% d_1, 3% d_0).

1-(4-*tert*-Butylphenyl)-3-(2,4,5-trimethylphenyl)-[3,3-D_2]propane (10b)

By chloralane reduction of **39** using $LiAlD_4/AlCl_3$; colorless oil, bp 140 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.87 (*t*, ^3J 7.7 Hz, 2 H), 2.20 (*s*, 9 H), 2.66 (*t*, ^3J 7.8 Hz, 2 H), 6.91 (s_{br}, 2 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 296 (64, $M^{\cdot+}$), 281 (35), 149 (32), 136 (100), 135 (92), 117 (27), 93 (17), 91 (20), 57 (25). Some elimination product was detected in very small amounts by mass spectrometry (*m/z* 293, 278, 236). D contents (mass spectrometry): 92% (85% d_2, 14% d_1, 1% d_0).

1-(4-*tert*-Butylphenyl)-3-(2,4,6-trimethylphenyl) propane (11)

By chloralane reduction of **40** using $LiAlH_4/AlCl_3$; colorless oil, bp 130 °C/0.02 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.77 (quin, ^3J 7.7 Hz, 2 H), 2.22 (*s*, 6 H), 2.23 (*s*, 3 H), 2.60 (*t*, ^3J 7.7 Hz, 2 H), 2.71 (*t*, ^3J 7.7 Hz, 2 H), 6.81 (*s*, 2 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 294 (100, $M^{\cdot+}$), 279 (23), 174 (47), 159 (55), 147 (49), 133 (75), 117 (27), 105 (15), 91 (19), 57 (25); IR (film): $\bar{\nu}$ (cm^{-1}) 2965, 2868, 1513, 1483, 1464, 1363, 1268, 849, 829. Some elimination product was detected in very small amounts by mass spectrometry (*m/z* 291, 276, 234). $C_{22}H_{30}$ (HRMS), calcd 294.2348, found 294.2344.

1-(4-*tert*-Butylphenyl)-3-(2,4,6-trimethylphenyl)-[3,3-D_2]propane (11b)

By chloralane reduction of **40** using $LiAlD_4/AlCl_3$; colorless oil, bp 145 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.75 (*t*, ^3J 7.7 Hz, 2 H), 2.22 (*s*, 6 H), 2.23 (*s*, 3 H), 2.70 (*t*, ^3J 7.7 Hz, 2 H), 6.81 (*s*, 2 H), 7.14 and 7.30 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 296 (50, $M^{\cdot+}$), 281 (26), 161 (60), 149 (53), 147 (53), 135 (100), 119 (30), 117 (31), 91 (31), 57 (42). The compound was contaminated by ~25% of some elimination product, as detected by ^{1}H NMR and mass spectrometry [δ 1.32 (*s*), 3.55 (*d*) and *m/z* 293, 278, 236, respectively). D contents (mass spectrometry): 89% (86% d_2, 7% d_1, 7% d_0).

A4. 1-tert-Butyl-4-ethylbenzenes

1-*tert*-Butyl-4-ethylbenzene (12)

By catalytic hydrogenolysis of 4-*tert*-butylacetophenone (1.88 g, 10.7 mmol); yield 69%, colorless liquid, bp 95 °C/44 mbar (102–105 °C/23 mbar [27]). ^{1}H NMR ($CDCl_3$): δ 1.23 (*t*, ^3J 7.6 Hz, 3 H), 1.31 (*s*,

9 H), 2.62 (*q*, ^3J 7.6 Hz, 2 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.2 Hz, 4 H); mass spectrum (EI): *m/z* (%) 162 (19, $M^{\cdot+}$), 147 (100), 119 (17), 105 (5), 91 (16), 79 (7), 77 (5).

1-(4-*tert*-Butylphenyl)-[1-D_1]ethanol (41)

By reduction of 4-*tert*-butylacetophenone (7.63 g, 43.3 mmol) with $LiAlD_4$; yield 77%, colorless solid, m_p 67 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.32 (*s*, 9 H), 1.49 (*s*, 3 H), 1.75 (*s*, 1 H), 7.31 and 7.39 (*AA′BB′*, ^3J 8.5 Hz, 4 H); mass spectrum (EI): *m/z* (%) 179 (22, $M^{\cdot+}$), 164 (100), 161 (7), 149 (11), 146 (26), 134 (7), 122 (9), 118 (11), 106 (13), 92 (15), 91 (18), 78 (10), 77 (10), 57 (43), 43 (51).

1-*tert*-Butyl-4-[1-D_1]ethylbenzene (12a)

By catalytic hydrogenolysis of **41** (1.00 g, 5.58 mmol); yield 89%, colorless liquid, bp 89 °C/15–20 mbar. ^{1}H NMR: δ 1.22 (*dt*, ^3J 7.5 Hz, $^3J^{H,D}$ 1.0 Hz, 3 H), 1.31 (*s*, 9 H), 2.57–2.65 (*m*, 1 H), 7.14 and 7.31 (*AA′BB′*, ^3J 8.3 Hz, 4 H); mass spectrum (EI): *m/z* (%) 163 (12, $M^{\cdot+}$), 148 (100), 120 (20), 91 (15), 79 (9). D contents (mass spectrometry): 94%.

1-*tert*-Butyl-4-[1,1-D_2]ethylbenzene (12b)

By chloroalane reduction of 4-*tert*-butylacetophenone (420 mg, 2.4 mmol) using $LiAlD_4/AlCl_3$; yield 71%, colorless liquid, bp 105 °C/41 mbar. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.22 (*s*, 3 H), 1.31 (*s*, 9 H), 7.13 and 7.31 (*AA′BB′*, ^3J 8.4 Hz, 4 H); mass spectrum (EI): *m/z* (%) 164 (21, $M^{\cdot+}$), 149 (100), 121 (14), 119 (6), 93 (6), 92 (5), 91 (9). Minor amounts of the elimination product were detected by mass spectrometry (*m/z* 161, 146). D contents (mass spectrometry): 95% (90% d_2, 9% d_1, 1% d_0).

1-*tert*-Butyl-4-ethyl-3-methylbenzene (13)

By catalytic hydrogenolysis of 4-*tert*-butyl-2-methylacetophenone (1.63 g, 8.6 mmol); yield 92%, colorless liquid, bp 102–107 °C/41 mbar (71–72 °C/4 mbar [28]); ^{1}H NMR ($CDCl_3$): δ 1.20 (*t*, ^3J 7.6 Hz, 3 H), 1.30 (*s*, 9 H), 2.30 (*s*, 3 H), 2.59 (*q*, ^3J 7.6 Hz, 2 H), 7.08–7.10 (*m*, 1 H), 7.16 (s_{br}, 1 H), 7.16–7.20 (*m*, 1 H); mass spectrometer (EI): *m/z* (%) 176 (18, $M^{\cdot+}$), 161 (100), 133 (10), 115 (6), 105 (12), 91 (8).

1-(4-*tert*-Butyl-2-methylphenyl)-[1-D_1]ethanol (42)

By reduction of 4-*tert*-butyl-2-methylacetophenone (8.10 g, 42.6 mmol) with $LiAlD_4$, yield 57%, pale yellow liquid, bp 148 °C/27 mbar. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9 H), 1.45 (*s*, 3 H), 1.81 (*s*, 1 H), 2.34 (*s*, 3 H), 7.15 (s_{br}, ^4J 2.0 Hz, 1 H), 7.25 (*d*, ^3J 8.2 Hz, ^4J 1.8 Hz, 1 H), 7.42 (*d*, ^3J 8.2 Hz, 1 H); mass spectrum (EI): *m/z* (%) 193 (26, $M^{\cdot+}$), 178 (100), 175 (20), 160 (46), 148 (8), 134 (12), 132 (12), 120 (19), 116 (14), 115 (13), 106 (15), 105 (17), 94 (20), 92 (19), 91 (19), 78 (12), 77 (13), 57 (61), 43 (49).

1-*tert*-Butyl-4-[1-D_1]ethyl-3-methylbenzene (13a)

By catalytic hydrogenation of **42** (1.00 g, 5.2 mmol); yield ~70%, colorless liquid, bp 96–100 °C/27 mbar. ^{1}H NMR ($CDCl_3$): δ 1.19 (quasi *d*, ^3J 7.6 Hz, 3 H), 1.30 (*s*, 9 H), 2.30 (*s*, 3 H), 2.54–2.63 (*m*, 1 H), 7.08–7.11 (*m*, 1 H), 7.16–7.23 (*m*, 2 H); mass spectrum (EI): *m/z* (%) 177 (21, $M^{\cdot+}$), 162 (100), 134 (10), 105 (11), 93 (7), 91 (6), 57 (34), 56 (32), 43 (26), 41 (38). D contents (mass spectrometer): 96%.

1-*tert*-Butyl-4-[1,1-D_2]ethyl-3-methylbenzene (13b)

By chloroalane reduction of 4-*tert*-butyl-2-methylacetophenone (460 mg, 2.4 mmol) using $LiAlD_4/AlCl_3$; yield 72%, colorless liquid, bp 115 °C/41 mbar. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.19 (*s*, 3 H), 1.30 (*s*, 9 H), 2.30 (*s*, 3 H), 7.07–7.10 (*m*, 1 H), 7.15 (s_{br}, 1 H), 7.15–7.19 (*m*, 1 H); mass spectrum (EI): *m/z* (%) 178 (20, $M^{\cdot+}$), 163 (100), 135 (7), 133 (6), 107 (5), 105 (7), 93 (6), 91 (4). A minor contamination by the elimination product was detected by mass spectrometry (*m/z* 175, 160). D content (mass spectrometry): 96% (92% d_2, 8% d_1, 0% d_0).

1-*tert*-Butyl-3,5-dimethyl-4-ethylbenzene (14)

By chloroalane reduction 4-*tert*-butyl-2,6-dimethylacetophenone (500 mg, 2.4 mmol) using $LiAlH_4/AlCl_3$; yield ~60%, colorless liquid, bp 130 °C/41 mbar (125 °C/27 mbar [29]). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.11 (*t*, ^3J 7.6 Hz, 3 H), 1.29 (*s*, 9 H), 2.32 (*s*, 6 H), 2.62 (*q*, ^3J 7.6 Hz, 2 H), 7.01 (*s*, 2 H); mass spectrum (EI): *m/z* (%) 190 (19, $M^{\cdot+}$), 175 (100), 147 (7), 119 (7), 107 (6), 105 (4), 91 (6). Some elimination product was detected by mass spectrometry (*m/z* 188, 173).

1-(4-*tert*-Butyl-2,6-dimethylphenyl)-[1-D_1]ethanol (43)

By reduction of 4-*tert*-butyl-2,6-dimethylacetophenone (9.71 g, 47.6 mmol) with $LiAlD_4$, yield 53%, colorless solid, m_p 115 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.29 (*s*, 9 H), 1.53 (*s*, 3 H), 1.63 (s_{br}, 1 H), 2.45 (*s*,

6 H), 7.00 (*s*, 2 H); mass spectrum (EI): *m/z* (%) 207 (13, $M^{\cdot+}$), 192 (100), 189 (23), 174 (70), 134 (13), 116 (7), 108 (10), 91 (8), 57 (30), 43 (15), 41 (12).

4-*tert*-Butyl-2,6-dimethyl-[α-D_1]styrene (44)

A mixture of **43** (2.0 g, 9.7 mmol), anhydrous copper(II) sulfate (30 mg) and *n*-nonane (20 mL) was heated to reflux for 3 h in a 100 mL flask equipped with a water separator (TLC control, CH_2Cl_2). The product was separated by fractionate distillation into a bulb containing a crystal of hydroquinone. Yield 32%, colorless liquid, bp 80 °C/27 mbar. ^{1}H NMR ($CDCl_3$): δ 1.30 (*s*, 9 H), 2.32 (*s*, 6 H), 5.24–5.27 (*m*, 1 H), 5.49–5.51 (*m*, 1 H), 7.06 (*s*, 2 H); mass spectrum (EI): *m/z* (%) 189 (25, $M^{\cdot+}$), 174 (100), 146 (7), 134 (14), 129 (7), 116 (7), 57 (13).

1-*tert*-Butyl-3,5-dimethyl-4-[1-D_1]ethylbenzene (14a)

By hydrogenation of **44** (410 mg, 2.2 mmol); colorless liquid, bp 130 °C/27 mbar. ^{1}H NMR ($CDCl_3$): δ 1.10 (d, ^3J 7.6 Hz, 3 H), 1.29 (*s*, 9 H), 2.32 (*s*, 6 H), 2.56–2.65 (*m*, 1 H), 7.02 (*s*, 2 H); mass spectrum (EI): *m/z* (%) 191 (17, $M^{\cdot+}$), 176 (100), 148 (13), 119 (10), 107 (11), 91 (7). D contents (mass spectrometry): 97%.

1-*tert*-Butyl-3,5-dimethyl-4-[1,1-D_2]ethylbenzene (14b)

By chloroalane reduction of 4-*tert*-butyl-2,6-dimethylacetophenone (500 mg, 2.4 mmol) using $LiAlD_4/AlCl_3$; yield 60%, colorless liquid, bp 130 °C/41 mbar. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.09 (*s*, 3 H), 1.29 (*s*, 9 H), 2.32 (*s*, 6 H), 7.01 (*s*, 2 H); mass spectrum (EI): *m/z* (%) 192 (19, $M^{\cdot+}$), 177 (100), 147 (7), 119 (5), 107 (6). Some elimination product was detected by mass spectrometry (*m/z* 189, 174). D contents (mass spectrometry): 96% (95% d_2, 3% d_1, 2% d_0).

References

[1] H.E. Audier, C. Monteiro, P. Mourgues, D. Berthomieu, Org. Mass Spectrom. 25 (1990) 245.

[2] D. Kuck, C. Matthias, J. Am. Chem. Soc. 114 (1992) 1901.

[3] For a review, see: D. Kuck, Mass Spectrom. Rev. 9 (1990) 583.

[4] M.S.B. Munson, F.H. Field, J. Am. Chem. Soc. 89 (1967) 1047.

[5] (a) A.G. Harrison, P.-H. Lin, H.-W. Leung, Adv. Mass Spectrom. 7 (1978) 1394; (b) J.A. Herman, A.G. Harrison, Org. Mass Spectrom. 16 (1981) 423; (c) A.G. Harrison, Chemical Ionization Mass Spectrometry, 2nd ed., CRC, Boca Raton, FL, 1992, p. 120.

[6] C. Wesdemiotis, H. Schwarz, C.C. Van de Sande, F. Van Gaever, Z. Naturforsch. B 34 (1979) 495.

[7] (a) H.E. Audier, C. Monteiro, D. Robin, New. J. Chem. 13 (1989) 621; (b) J.P. Denhez, C. Monteiro, P. Mourgues, H.E. Audier, D. Berthomieu, *ibid*. 15 (1991) 273; (c) D. Berthomieu, H.E. Audier, J.P. Denhez, C. Monteiro, P. Mourgues, Org. Mass Spectrom. 26 (1991) 271; (d) D. Berthomieu, H.E. Audier, C. Monteiro, J.P. Denhez, Rapid Commun. Mass Spectrom. 5 (1991) 415.

[8] (a) R.W. Holman, M.L. Gross, J. Am. Chem. Soc. 111 (1989) 3560; (b) R.W. Holman, T. Eary, E. Whittle, M.L. Gross, J. Chem. Soc., Perkin Trans. 2 (1998) 2187.

[9] (a) D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié, H.E. Audier, J. Phys. Chem. 99 (1995) 712; (b) J.P. Denhez, H.E. Audier, D. Berthomieu, Rapid Commun. Mass Spectrom. 9 (1995) 1210.

[10] (a) H.E. Audier, D. Berthomieu, T.H. Morton, J. Org. Chem. 60 (1995) 7198; (b) H.E. Audier, G.K. Koyanagi, T.B. McMahon, D. Thölmann, J. Phys. Chem. 100 (1996) 8220; (c) H.E. Audier, T.B. McMahon, J. Mass Spectrom. 21 (1997) 201; (d) H.E. Audier, F. Dahhani, A. Milliet, D. Kuck, J. Chem. Soc. Chem. Commun. (1997) 429; (e) D. Kuck, F. Dahhani, A. Milliet, H.E. Audier Agnew. Chem. 112 (2000) 129.

[11] H.-F. Grützmacher, S. Dohmeier-Fischer, Int. J. Mass Spectrom. Ion Processes 179/180 (1998) 207.

[12] For papers on hydride transfer reactions involving nonaromatic tertiary carbenium ions, see (a) M.E. Crestoni, S. Fornarini, M. Lentini, M. Speranza, J. Phys. Chem. 100 (1996) 8285; (b) M.E. Crestoni, S. Fornarini, M. Lentini, M. Speranza, J. Chem. Soc., Chem. Commun. (1995) 121; (c) P. Ausloos, S.G. Lias, J. Am. Chem. Soc. 92 (1970) 5037.

[13] D.K. Sen Sharma, S. Ikuta, P. Kebarle, Can. J. Chem. 60 (1982) 2325.

[14] D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié, H.E. Audier, J. Am. Chem Soc. 115 (1993) 2505.

[15] C. Matthias, Doctoral thesis, Universität Bielefeld, 1996.

[16] (a) C. Matthias, D. Kuck, Org. Mass Spectrom. 28 (1993) 1073; (b) C. Matthias, K. Weniger, D. Kuck, Eur. Mass Spectrom. 1 (1995) 445.

[17] M.E. Crestoni, S. Fornarini, D. Kuck, J. Phys. Chem. 99 (1995) 3144.

[18] M.E. Crestoni, S. Fornarini, D. Kuck, J. Phys. Chem. 99 (1995) 3150.

[19] (a) E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413; (b) W.G. Mallard, P.J. Linstrom (Eds.), NIST Chemistry Webbook, NIST Standard Reference Database No. 69; March 1998; National Institute of Standards and Technology: Gaithersburg, MD 20899 (http://webbook.nist.gov).

[20] (a) J.L. Devlin III, J.F. Wolf, R.W. Taft, W.J. Hehre, J. Am. Chem. Soc. 98 (1976) 1990; (b) M. Eckert-Maksić, M. Klessinger, Z.B. Maksić, J. Phys. Org. Chem. 8 (1995) 435; (c) M. Eckert-Maksić, M. Klessinger, Z.B. Maksić, Chem.

Eur. J. 2 (1996) 1251; (d) Z.B. Maksić, B. Kovačević, D. Kovaček, J. Phys. Chem. A 101 (1997) 7446.
[21] For a recent short review commenting on the additivity of substituent effects on the basicity of gaseous aromatic species, see D. Kuck, Angew. Chem. Int. Ed. Engl. 39 (2000) 125.
[22] D. Kuck, Int. J. Mass Spectrom. Ion Processes 117 (1992) 441.
[23] Extended calculations using slightly varied kinetic isotope effects yield moderately diverging contributions f_i, e.g. $k_H/k_D = 1.5$ leads to $f_\alpha:f_\gamma:f_o = 15:68:18$ and $k_H/k_D = 1.8$ gives $f_\alpha:f_\gamma:f_o = 17:72:11$.
[24] D. Kuck, W. Bäther, Org. Mass Spectrom. 21 (1986) 451.
[25] The high-mass side of the MIKES signals are subject to some artefact increase of the baseline due to a slight tailing; corrections for this effect have been made.
[26] Considered strictly, we cannot exclude that the minute (1%) isobutane loss from ions [**14** + H]$^+$ may originate from an isomeric impurity in the neutral precursor.
[27] E. Rothstein, R.W. Saville, J. Chem. Soc. (1949) 1950.
[28] M. Tashiro, T. Yamato, J. Chem. Soc., Perkin Trans. 1 (1979) 176.
[29] R.C. Fuson, J.J. Denton, J.W. Kneisley, J. Am. Chem. Soc. 63 (1941) 2652.