Regioselective hydride abstraction and proton transfer in gaseous ion/molecule complexes: methyl substituent effects on the fragmentation of protonated 1-(4-*tert*-butylphenyl)-3-phenylpropanes

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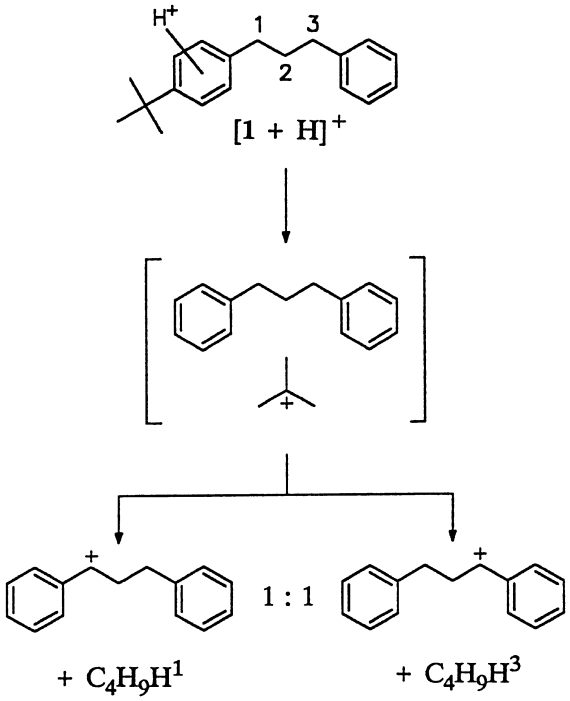
Gas-phase protonolysis of 1-(4-*tert*-butylphenyl)-3-phenylpropanes bearing a methyl substituent at one of the arene rings gives rise to competing losses of isobutane and isobutene via intermediate, purely hydrocarbon, ion/molecule complexes [Me_3C^+ C_6H_5–$CH_2CH_2CH_2$–$C_6H_4CH_3$]. The hydride transfer within the complexes occurs preferentially from the CH_2 group of the methylated benzyl unit (in the order *p*-CH_3 > *m*-CH_3 > *o*-CH_3 ≈ H) and irrespective of the ring from which the *tert*-butyl group has been released originally. The reciprocal proton transfer gains importance with increasing proton affinity of the substituted benzene nucleus (*p*-CH_3 < *o*-CH_3 < *m*-CH_3), again independent of the original substitution pattern. Thus, the reactivity of the *tert*-butyl cation within the complex (as a Lewis and a Brønsted acid) is governed by the whole of the electrostatically bound 1,3-diarylpropane neutral.

Introduction

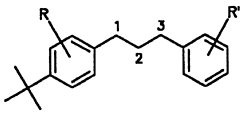
The investigation of ion/neutral complexes during unimolecular decompositions of gaseous organic ions has attracted much attention because of analytical implications and the possibility to gain insight into the "intrinsic" chemistry of (fragment) ions solvated exclusively by the corresponding (fragment) radicals or molecules.[1–5] Whereas, in most cases, the intermediacy of ion/neutral complexes is suggested for the fragmentation of polar species, we recently reported on evidence that ion/neutral complexes [Me_3C^+ Ph–$(CH_2)_n$–Ph)] (n = 1–10), consisting of relatively large and non-polar, purely *hydrocarbon* components, are formed during the elimination of isobutane from protonated *t*-butyl substituted α,ω-diphenylalkanes, e.g. ions [**1** + H]$^+$ (n = 3, Scheme 1).[6,7] In these complexes the *t*-butyl cation acts as a Lewis acid upon a symmetrical α,ω-diphenylalkane by random hydride abstraction from both of the benzylic methylene groups and irrespective of the length of the polymethylene chain.

To elucidate the effect of electronic activation of the formerly remote benzylic hydride donor by ring substituents, we synthesised the three isomeric 1-(*p*-*t*-butylphenyl)-3-(methylphenyl)propanes and some related hydrocarbons as well as several deuterium labelled analogues and studied the gas-phase protonolysis of the cor-



Scheme 1.

Table 1. Regioselectivity of isobutane loss from the $[M + H]^+$ ions of methyl-substituted, deuterium-labelled 1-(4-*t*-butylphenyl)-3-phenylpropanes.

Neutral precursor			[1,1-D_2]-Isotopomers	[3,3-D_2}-Isotopomers	Regioselectivity of hydride abstration
			$\frac{[C_4H_{10}\ \text{loss}]}{[C_4H_9D\ \text{loss}]}$	$\frac{[C_4H_9D\ \text{loss}]}{[C_4H_{10}\ \text{loss}]}$	$\frac{[\text{from}\ C^3H_2]}{[\text{from}\ C^1H_2]}$
	R	R′			
1[a]	H	H	**1a** 1.6 : 1.0	**1b** 1.0 : 1.6	1.0 : 1.0
2	H	*p*-CH_3	**2a** 5.3 : 1.0	**2b** 2.1 : 1.0	3.3 : 1.0
3	H	*m*-CH_3	**3a** 2.7 : 1.0	**3b** 1.1 : 1.0	1.7 : 1.0
4	H	*o*-CH_3	**4a** 1.8 : 1.0	**4b** 1.0 : 1.8	1.0 : 1.0[b]
5	*o*-CH_3	H	**5a** 1.8 : 1.0	**5b** 1.0 : 1.8	1.0 : 1.0[b]
6	*o*-CH_3	*o*-CH_3	**6a** 1.9 : 1.0	**6b** 1.0 : 1.9	1.0 : 1.0

[a]Data taken from Reference 4.

[b]See text.

responding metastable $[M + H]^+$ ions by CI(CH_4)/MIKE spectrometry.

Results and discussion

Hydride abstraction

Similar to the parent ions $[\mathbf{1} + H]^+$, the *para*-methyl substituted arenium ions $[\mathbf{2} + H]^+$ (R′ = *p*–Me) react exclusively by loss of isobutane. The origin of the hydride incorporated into the isobutane neutral was deduced from the fragmentation of the deuterium labelled ions $[\mathbf{2a} + H]^+$, $[\mathbf{2b} + H]^+$ and $[\mathbf{2c} + H]^+$ (Figure 1). As shown by the spectrum of ions $[\mathbf{2c} + H]^+$, the ring and methyl hydrogens do not participate in the hydride transfer reaction. Also, the participation of the homobenzylic positions can be safely excluded as has been shown explicitly for the case of the parent system.[6] How does the methyl group at the remote arene ring affect the hydride donor activity of the two benzylic methylene groups? In contrast to the unsubstituted $[M + H]^+$ ions labelled in one of the benzylic positions, the isotopomers $[\mathbf{2a} + H]^+$ and $[\mathbf{2b} + H]^+$ eliminate C_4H_9D and C_4H_{10} with clearly different ratios (Table 1). Obviously, the hydride abstraction within the complex occurs predominantly at the benzylic methylene group of the substituted—and originally remote—arene ring. Assuming the same kinetic isotope effect (k_H/k_D = 1.6) which was found to operate for the parent ions $[\mathbf{1} + H]^+$,[6,8] the hydride abstraction at the remote benzylic position of ions $[\mathbf{2} + H]^+$ is 3.3 times faster than that at the formerly adjacent benzylic position.

Comparison of these data with those obtained from the deuterium-labelled analogues of the corresponding *meta*- and *ortho*-methyl substituted isomers **3** and **4** (Table 1) demonstrates that the preference of the hydride abstraction from the remote donor position decreases in the order *para* > *meta* > *ortho*. This correlates, only in part, with the relative thermodynamic stability expected for the corresponding methylbenzyl cations.[9] Obviously, activation towards hydride abstraction from the remote benzylic C–H bonds is decreased in the case of the *meta*-methyl isomer for electronic reasons and in that of the *ortho*-methyl isomer mainly because of steric hindrance.

Ortho-substitution is particularly informative and has required extended investigation. Besides compound **4** and its [1,1-D_2] and [3,3-D_2] isotopomers (**4a** and **4b**, respectively), the isomer **5** bearing the *tert*-butyl and the *ortho*-methyl substituent *at the same ring* and the corresponding dideuterated analogues (**5a** and **5b**) were studied (Table 1), as well as the [D_3]methyl isotopomer **4c**. Furthermore, the *ortho*,*ortho*-dimethyl congener **6** and the respective dideuterated analogues (**6a** and **6b**) were subjected to MIKE spectrometry.

As a first result, the spectra of ions $[\mathbf{4} + H]^+$ and $[\mathbf{5} + H]^+$ were found to be identical (*cf.* Figure 3). Second, the ratios of C_4H_{10} vs C_4H_9D losses for the $[M + H]^+$ ions

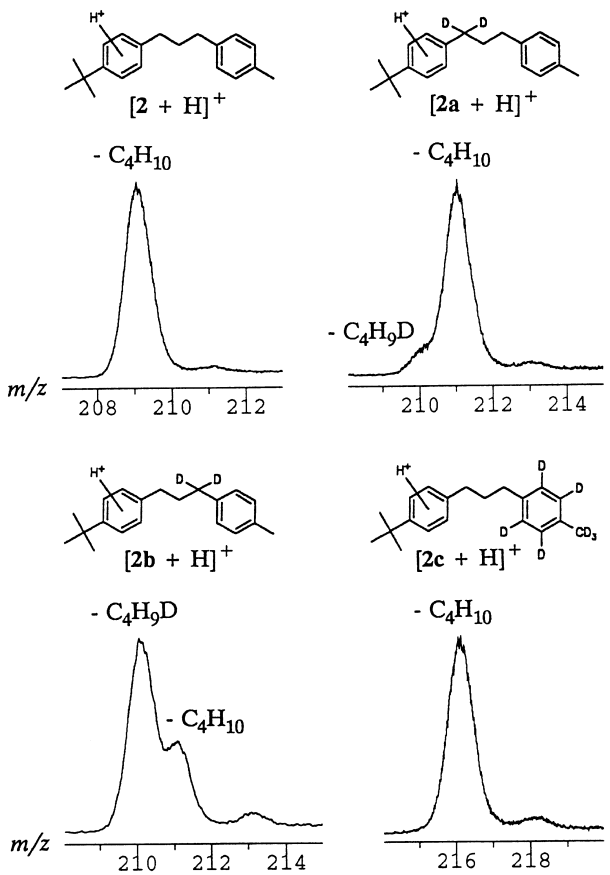


Figure 1. Partial MIKE spectra of $[M + H]^+$ ions of 2 and deuterium labelled analogues 2a–2c. Note that contributions at *m/z* 211 (2), *m/z* 213 (2a and 2b) and *m/z* 218 (2c) correspond to the fragmentation of molecular radical ions $[M^{+\bullet}]$ which contain naturally occurring ^{13}C.

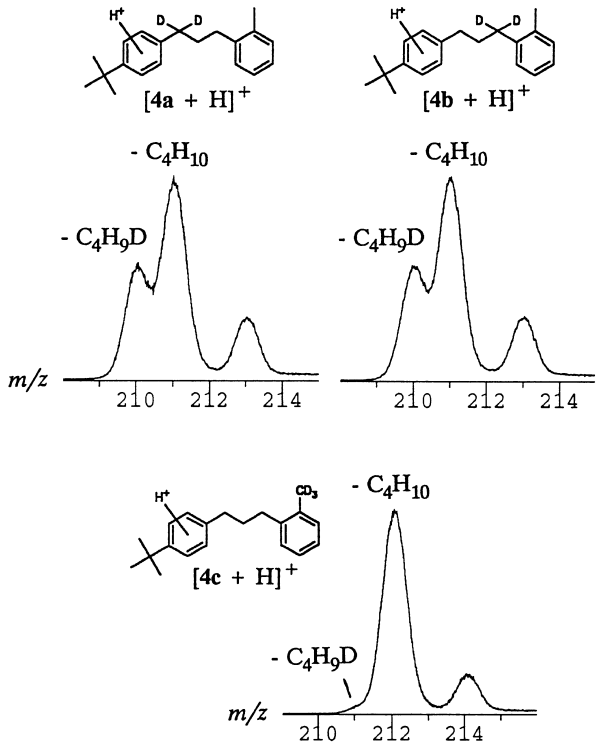


Figure 2. Partial MIKE spectra of $[M + H]^+$ ions of labelled analogues 4a–4c.

within the set of the $[D_2]$-labelled monomethyl-substituted ions (**4a**, **4b**, **5a** and **5b**) were also indistinguishable, as were those of the two $[D_2]$-labelled dimethyl-substituted ones (**6a** and **6b**). As an illustration, the partial MIKE spectra of ions $[\mathbf{4a} + H]^+$ and $[\mathbf{4b} + H]^+$ are reproduced in Figure 2. Taken together with the results obtained for the labelled *para*- and *meta*-substituted isomers, this demonstrates that the site from which the *t*-butyl group is released from the $[M + H]^+$ ions of **2–6** does not affect the fragmentation of the intermediate complex. On the contrary, only the structure of the neutral component, be it a symmetrically or unsymmetrically substituted diphenylalkane, determines the intrinsic reactivity in the ion/molecule complex. This holds also for the competing loss of isobutene (*vide infra*).

As a third, and somewhat puzzling point, we found that the ratios of C_4H_{10} vs C_4H_9D losses measured for the $[M + H]^+$ ions of the *ortho*-monomethylated hydrocarbons **4** and **5** are slightly increased (by *c.* 10%, Table 1), when compared to that measured for the parent ions $[\mathbf{1a} + H]^+$ and $[\mathbf{1b} + H]^+$. The ratio found for the *ortho,ortho′*-dimethyl analogues is increased even more (by *c.* 20%). At first glance, this finding might simply be attributed to a sterically-induced increase of the kinetic isotope effect that operates on the H^- and D^- abstraction, that is, to a steric shielding of the benzylic position by an *ortho*-methyl substituent. This implies that no other C–H bonds act as hydride donors, as has been confirmed in the case of the *para*-methyl substituted ions $[\mathbf{2c} + H]^+$. Warned, however, by the fragmentation behaviour of related deuterium-labelled $[M + H]^+$ ions bearing more than one methyl substituent at the *same* arene ring,[10] we synthesized the *ortho*-CD_3-substituted precursor **4c** to unravel if the *ortho*-methyl group acts as an additional hydride donor in ions $[\mathbf{4} + H]^+$. In fact, we found that the MIKE spectrum of ions $[\mathbf{4c} + H]^+$ shows a very small but significant peak at *m*/*z* 211, indicating a C_4H_9D loss of *c.* 3.0% abundance relative to that of C_4H_{10} (Figure 2)! Assuming that the deuteride abstraction from the methyl group of ions $[\mathbf{4c} + H]^+$ is attenuated by the same kinetic isotope effect ($k_H/k_D = 1.6$), which has been found for *tert*-butylalkylbenzenenium ions in general,[6,8,10] we estimate that a *c.* 5% contribution of the overall hydride transfer originates from the *ortho*-methyl group (Scheme 2). Further, the benzylic methylene groups react at equal rates (i.e. nonselectively) in ions $[\mathbf{4} + H]^+$ and they *both* display again the kinetic isotope effect of $k_H/k_D = 1.6$. This latter result may be considered rather normal for the unshielded

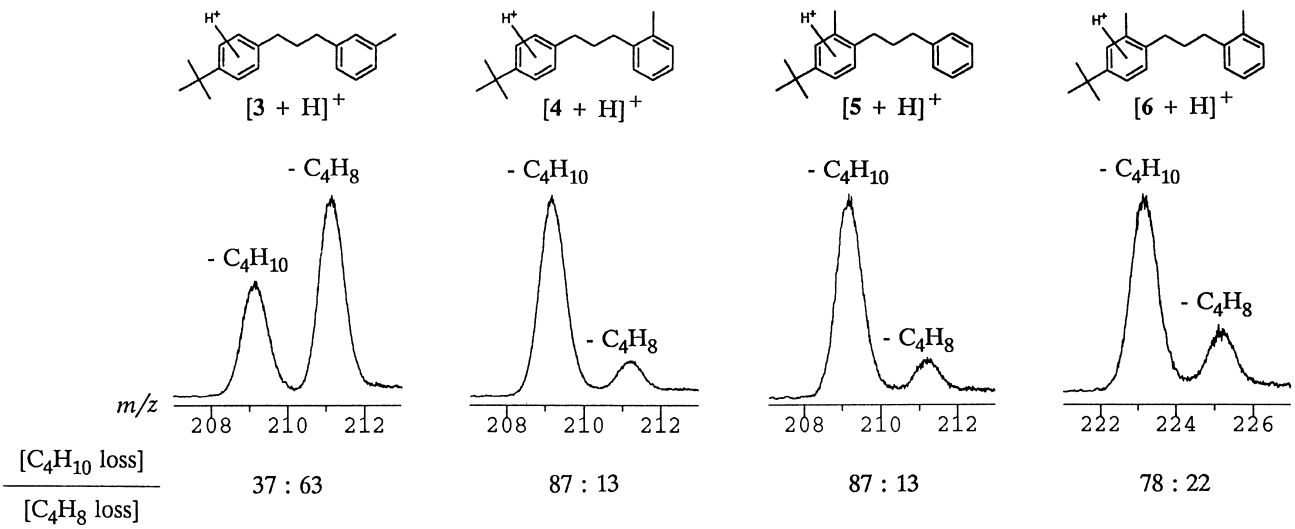
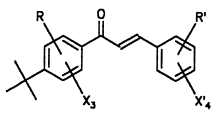
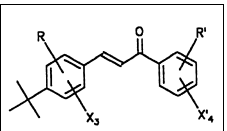
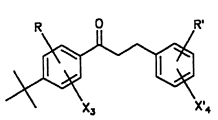
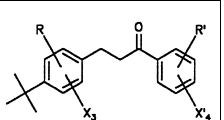


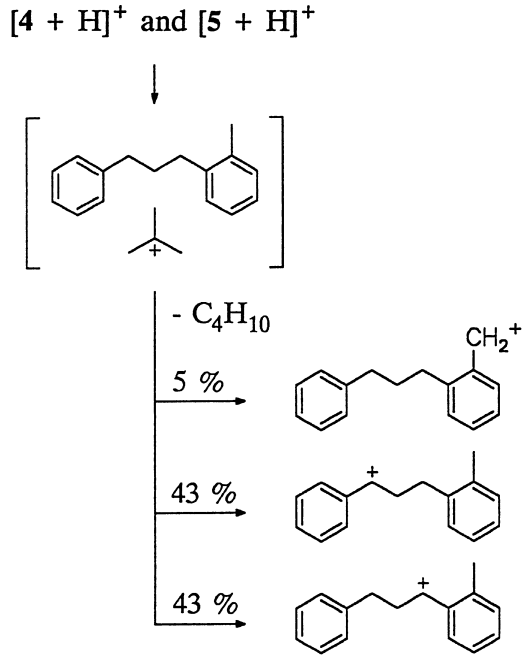
Figure 3. Partial MIKE spectra of $[M + H]^+$ ions of methyl substituted precursors 3–6 (for ions $[2 + H]^+$, see Figure 1).

methylene group (C^1H_2) with regard to the data obtained for the other isomers; however, it appears to be accidental for the shielded one (C^3H_2). Also, the remarkable equivalence of the benzylic methylene groups as hydride donors in ions $[\mathbf{4} + H]^+$ appears to be the result of a compensation of the electronic and steric effects, as stated above.

Having recognised that the *ortho*-methyl group contributes to the overall elimination of isobutane from ions $[\mathbf{4} + H]^+$ and $[\mathbf{5} + H]^+$, we have to assume a similar effect in ions $[\mathbf{6} + H]^+$. Therefore, the relatively high ratio of C_4H_{10} vs C_4H_9D loss observed for the doubly *ortho*-methyl-substituted ions $[\mathbf{6a} + H]^+$ and $[\mathbf{6b} + H]^+$ is attrib-

Table 2. Chalcones 7–16 and dihydrochalcones 17–26 synthesised.

	R	X	R′	X′	
7	H	H	*p*-CH_3	H	**8**
	H	H	*p*-CD_3	D	**8a**
9	H	H	*m*-CH_3	H	**10**
11	H	H	*o*-CH_3	H	**12**
	H	H	*o*-CD_3	H	**12a**
13	*o*-CH_3	H	H	H	**14**
15	*o*-CH_3	H	*o*-CH_3	H	**16**
	R	X	R′	X′	
17	H	H	*p*-CH_3	H	**18**
19	H	H	*m*-CH_3	H	**20**
21	H	H	*o*-CH_3	H	**22**
23	*o*-CH_3	H	H	H	**24**
25	*o*-CH_3	H	*o*-CH_3	H	**16**



Scheme 2.

uted to the presence of *two* additional hydride donors, rather than to an increased kinetic isotope effect.

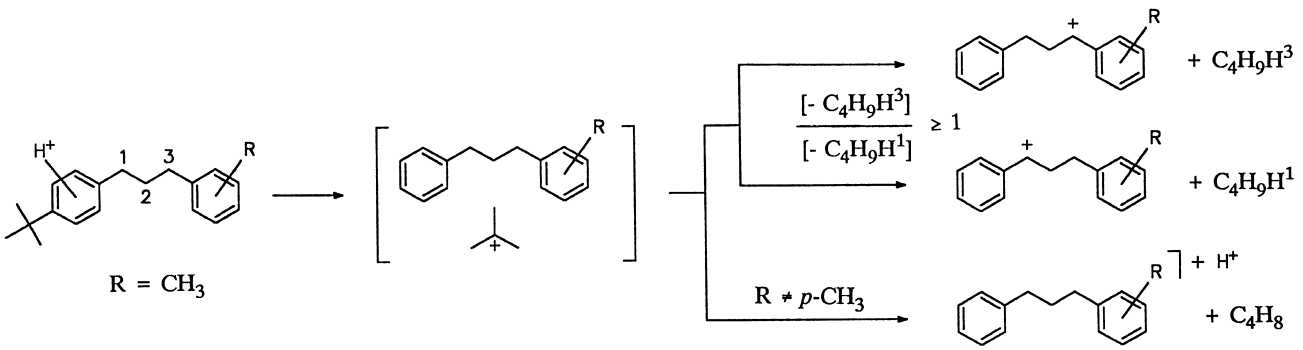
To summarise, at this point, we may state that the regioselectivity of hydride abstraction in the $[M + H]^+$ ions of **2–6** suggest that the *t*-$C_4H_9^+$ cation bound within the ion/molecule complex can move relatively freely along the substituted 1,3-diphenylpropane neutral and undergo highly regioselective hydride abstraction. Regioselectivity is not only governed by the electronic stabilization of the resulting benzylic cations, but also by steric hindrance, as shown from the behaviour of the *ortho*-methyl-substituted ions. The finding that the *ortho*-methyl group acts as a hydride donor itself, whereas the *para*-methyl group does not, is quite intriguing. Further efforts are required to elucidate the origin of this phenomenon.[10]

Proton transfer

As stated in the beginning, the *para*-methyl-substituted ions $[\mathbf{2} + H]^+$ undergo exclusively elimination of isobutane. Introduction of methyl substituents at positions other than *para* opens another fragmentation channel of the $[M + H]^+$ ions. Owing to the increased proton affinity of the diphenylpropane neutral in the ion/molecule complex, the Me_3C^+ cation may not only abstract a hydride from the neutral but also transfer, in the opposite direction, a proton to the neutral, giving rise to the loss of isobut*ene*. This process is clearly predominant (Figure 3) with ions $[\mathbf{3} + H]^+$, which generate a 1,3-diphenylpropane bearing the most basic arene ring within this series [*cf.* PA(*m*-xylene) = 820 kJ mol^{-1}].[9b,11] In turn, with *ortho*-methyl-substitution in ions $[\mathbf{4} + H]^+$ to $[\mathbf{6} + H]^+$, isobutene loss falls short of isobutane loss owing to the relatively low proton affinity of the *ortho*-dialkyl group contained in the neutral partner of the complex [PA(*o*-xylene) = 809 kJ mol^{-1}]. [9b] The lack of isobutene loss in ions $[\mathbf{2} + H]^+$ is in accordance with the particularly low proton affinity of the *para*-dialkyl unit [PA(*o*-xylene) = 803 kJ mol^{-1}][9b] and the particular ease of hydride transfer in this case (*vide supra*). Remarkably, the competition between hydride abstraction and proton transfer is strictly the same for the two "regioisomeric" ions $[\mathbf{4} + H]^+$ and $[\mathbf{5} + H]^+$, showing again that the entire 1,3-diarylpropane neutral reacts as a solvating species within the ion/molecule complex. Finally, and again in accordance with this overall view, the *ortho,ortho′*-dimethyl substituted ions $[\mathbf{6} + H]^+$ exhibit significantly more isobutene loss than ions $[\mathbf{4} + H]^+$ and $[\mathbf{5} + H]^+$.[12]

Conclusion

The results clearly demonstrate that the unimolecular fragmentation of protonated 1-(4-*t*-butylphenyl)-3-



Scheme 3.

(methylphenyl)propanes takes place via ion/molecule complexes [Me_3C^+ Aryl–$CH_2CH_2CH_2$–Aryl′], in which the *tert*-butyl cation is allowed to react both as a Brønsted and a Lewis acid, exhibiting, as the latter, a marked regioselectivity (Scheme 3). Both the hydride abstraction and proton transfer channels are independent of the origin of the *tert*-butyl group, and reflect the presence of an ion/neutral complex in which the Me_3C^+ cation is apparently free to move along and interact with the whole of the 1,3-diarylalkane molecule.

Experimental

Mass spectrometry

A Fisons VG Autospec double-focussing mass spectrometer with an E/B/E sequence of sector fields was used under CI conditions (reagent gas CH_4, electron energy 70 eV, emission current 200 μA, acceleration voltage 8 kV, ion-source temperature 200°C, nominal ion-source pressure *c*. 10^{-4} mbar). Samples were introduced by using the solids probe with slight external heating. Mass-analysed ion kinetic energy (MIKE) spectra were recorded by scanning the second electrostatic analyser to show the fragmentation of the metastable $[M + H]^+$ ions in the (third) field-free region following the magnetic sector (general error limits ± 2%).

Syntheses (general)

NMR spectra (300 MHz): Bruker AM 300; solvent $CDCl_3$/TMS; δ (ppm). Analytical mass spectra: VG Autospec; EI (70 eV); IR spectra: Perkin-Elmer 841; solids were measured in KBr pellets, liquids as films. Melting points (uncorrected): Electrothermal melting point apparatus (open capillaries). Combustion analysis: Leco CHNS-932. High resolution mass spectrometry (HRMS): VG Autospec (peak matching at $m/\Delta m \approx 8000$).

All unlabelled and labelled 1-(4-*t*-butylphenyl)-3-phenylpropanes were synthesised via the respective, previously unknown, chalcones **7–16** and dihydrochalcones **17–26** shown in Table 2. Unlabelled hydrocarbons **2–6** were obtained from the corresponding dihydrochalcones by catalytic hydrogenolysis at medium pressure and isotopomers **2c** and **4c** were prepared in the same way from the labelled chalcones (**8a** and **12a**); all other labelled hydrocarbons were obtained by chloroalane reduction using $LiAlH_4/AlCl_3$ in diethyl ether. Typical procedures are given in the following.

Chalcones

An aqueous solution of KOH (20 mL, 20%) was added dropwise to a stirred solution of the corresponding acetophenone and benzaldehyde (20 mmol each) in methanol (20 mL). Stirring was continued for 12 h, the precipitate was collected by suction and washed with small volumes of ice-cold methanol and then with water. Recrystallization from ethanol gave the pure chalcone derivatives. If the product formed an oil instead of a solid precipitate, the reaction mixture was neutralised with acetic acid and then extracted with diethyl ether and isolated. Chalcones which remained oily were purified by kugelrohr distillation.

Dihydrochalcones

The corresponding dihydrochalcones **17–26** were prepared from the chalcones **7–16** by hydrogenation at normal pressure in ethyl acetate solution, typically on a 10.0 mmol scale, using platinum (from *c*. 30 mg of PtO_2 hydrate) as the catalyst. Equimolar amounts of hydrogen were absorbed in *c*. 4 h. Usual workup gave solid products which were recrystallised from ethanol, or liquids which were purified by kugelrohr distillation.

1-(4-t-Butylphenyl)-3-phenylpropanes by catalytic hydrogenolysis

A solution of the corresponding dihydrochalcone or chalcone (1.00 mmol) in glacial acetic acid (5 mL) was shaken with palladium-on-charcoal (10%, 40 mg) under hydrogen (5 bar, 25°C) in a Parr apparatus for 4 h. The catalyst was removed by filtration, the same volume of water was added, and the mixture was extracted thrice with 10 mL portions of *n*-hexane. Drying with sodium sulphate and evaporation of the solvent furnished oily residues which were purified by kugelrohr distillation to give the pure hydrocarbons in good yields (50–80%).

Labelled 1-(4-t-Butylphenyl)-3-phenylpropanes by reduction with $LiAlD_4AlCl_3$

A suspension of lithium aluminium deuteride (1.0 mmol) in dry diethyl ether (5 mL) was cooled to 0°C and a solution of aluminium chloride (3.0 mmol) in diethyl ether (5 mL) was added quickly. Cooling was continued while a solution of the substituted dihydrochalcone (1.0 mmol) in diethyl ether (5 mL) was added slowly. The mixture was heated to reflux temperature and monitored by TLC (silica gel, CH_2Cl_2, *c*. 2 h) until the conversion was completed. The mixture was allowed to cool, hydrolysed with ice/water, and the precipitate formed was dissolved by adding some hydrochloric acid (33%). Usual workup by extraction with diethyl ether gave the crude product which was purified by kugelrohr distillation. The hydrocarbons were obtained in good yields (60–80%); in several cases, however, minor amounts of the corresponding 1,3-diphenylpropene (formed by 1,2-elimination) were present as impurities. In a few cases, the corresponding 1-chloro-1,3-diphenylpropane was also formed in extremely low amounts.

1 - (4-*t*-Butylphenyl) - 3 - (4-methylphenyl)prop - 2 - en - 1-one 7 was obtained by kugelrohr distillation

(175°C/0.004 mbar) and recrystallisation in 73% yield as yellow crystals, m.p. 105–106°C (EtOH); ^{1}H NMR: δ 1.37 (s, 9H), 2.40 (s, 3H), 7.23 and 7.55 (AA′BB′, ^3J = 8.1 Hz, 4H), 7.51 and 7.80 (AB, ^3J = 15.8 Hz, 2H), 7.52 and 7.98 (AA′BB′), ^3J = 8.6 Hz, 4H); MS: *m/z* (%) 278 (74, $M^{\bullet+}$), 277 (42), 263 (100), 221 (75), 161 (19), 145 (39), 115 (57), 91 (57), 57 (18); IR: $\tilde{\nu}$ 3029, 2967, 2872, 1654, 1591, 1308, 1181, 1009, 812 cm^{-1}. $C_{20}H_{22}O$ (278.40); calcd C 86.29 H 7.97; found C 86.26, H 7.98.

3 - (4-*t*-Butylphenyl) - 1 - (4-methylphenyl)prop - 2 - en - 1 -one 8 was obtained in 45% yield as a yellow solid, m.p. 82°C (EtOH); ^{1}H NMR: δ 1.34 (s, 9H), 2.44 (s, 3H), 7.31 and 7.94 (AA′BB′, ^3J = 8.1 Hz, 4H), 7.44 and 7.59 (AA′BB′, ^3J = 8.4 Hz, 4H), 7.51 and 7.80 (AB, ^3J = 15.7 Hz, 2H); MS: *m/z* (%) 278 (56, $M^{\bullet+}$), 277 (27), 263 (72), 221 (100), 119 (41), 91 (45), 57 (14); IR: $\tilde{\nu}$ 3032, 2967, 2869, 1657, 1592, 1332, 1183, 989, 814 cm^{-1}. $C_{20}H_{22}O$ (278.40); calcd C 86.29, H 7.97; found C 86.25, H 7.86.

3 - (4-*t*-Butylphenyl) - 1 - (4-[D$_3$]methyl-[D$_4$]phenyl)-prop-2-en-1-one 8a was obtained in 48% yield as a yellow solid, m.p. 80.5–82.5°C (EtOH); ^{1}H NMR: δ 1.34 (s, 9H), 7.44 and 7.59 (AA′BB′, ^3J = 8.3 Hz, 4H), 7.51 and 7.80 (AB, ^3J = 15.7 Hz, 2H); MS: *m/z* (%) 285 (34, $M^{\bullet+}$), 284 (31), 270 (75), 228 (100), 126 (33), 98 (38), 57 (14).

1 - (4-*t*-Butylphenyl) - 3 - (3-methylphenyl)prop - 2 - en - 1-one 9 was obtained in 72% yield as a yellow, highly viscous oil, b.p. 160°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.35 (s, 9H), 2.37 (s, 3H), 7.18–7.31 (m, 2H), 7.42–7.44 (m, 2H), 7.50 and 7.98 (AA′BB′, ^3J = 8.5 Hz, 4H), 7.53 and 7.78 (AB, ^3J = 15.7 Hz, 2H); MS: *m/z* (%) 278 (47, $M^{\bullet+}$), 277 (46), 263 (100), 221 (50), 161 (31), 145 (34), 115 (42), 91 (42), 57 (16); IR: $\tilde{\nu}$ 3042, 2968, 2872, 1662, 1609, 1317, 1109, 1011, 783 cm^{-1}. $C_{20}H_{22}O$; calcd 278.1671; found 278.1660 (HRMS).

3 - (4-*t*-Butylphenyl) - 1 - (3-methylphenyl)prop - 2 - en - 1-one 10 was obtained in 55% yield as a yellow viscous oil, b.p. 165°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.34 (s, 9H), 2.44 (s, 3H), 7.38–7.40 (m, 2H), 7.44 and 7.60 (AA′BB′, ^3J = 8.4 Hz, 4H), 7.50 and 7.80 (AB, ^3J = 15.7 Hz, 2H), 7.81–7.83 (m, 2H); MS*: m/z* (%) 278 (25, $M^{\bullet+}$), 277 (20), 221 (100), 119 (32), 91 (50), 57 (20); IR: $\tilde{\nu}$ 3034, 2967, 2871, 1662, 1599, 1328, 1163, 1027, 984, 827, 745 cm^{-1}. $C_{20}H_{22}O$; calcd 278.1671, found 278.1660 (HRMS).

1 - (4-*t*-Butylphenyl) - 3 - (2-methylphenyl)prop - 2 - en - 1-one 11 was obtained in 50% yield as a yellow oil, b.p. 160°C/0.015 mbar (kugelrohr); ^{1}H NMR: δ 1.36 (s, 9H), 2.48 (s, 3H), 7.22–7.31 (m, 3H), 7.48 and 8.12 (AB, ^3J = 15.8 Hz, 2H), 7.52 and 7.99 (AA′BB′, ^3J = 8.7 Hz, 4H), 7.69–7.71 (m, 1H); MS*: m/z* (%) 278 (26, $M^{\bullet+}$), 277 (15), 263 (100), 221 (52), 161 (42), 147 (32), 115 (45), 91 (42), 57 (24); IR: $\tilde{\nu}$ 3065, 2967, 2872, 1661, 1610, 1329, 1220, 1108, 1010, 767 cm^{-1}. $C_{20}H_{22}O$; calcd 278.1671, found 278.1658 (HRMS).

3 - (4-*t*-Butylphenyl) - 1 - (2-methylphenyl)prop - 2 - en - 1-one 12 was obtained in 65% yield as a yellow, viscous oil, b.p. 160°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.32 (s, 9H), 2.43 (s, 3H), 7.10 and 7.45 (AB, ^3J = 16.5 Hz, 2H), 7.23–7.28 (m, 2H), 7.34–7.47 (m, 2H), 7.41 and 7.50 (AA′BB′, ^3J = 8.5 Hz, 4H); MS: *m/z* (%) 278 (77, $M^{\bullet+}$), 277 (21), 263 (99), 221 (95), 147 (77), 131 (100), 119 (59), 91 (88), 57 (49); IR: $\tilde{\nu}$ 3029, 2968, 2872, 1667, 1644, 1601, 1327, 1269, 1215, 1016, 828, 742 cm^{-1}. $C_{20}H_{22}O$; calcd 278.1671, found 278.1657 (HRMS).

3 - (4-*t*-Butylphenyl) - 1 - (2-[D$_3$]methylphenyl)prop - 2 - en-1-one 12a was obtained in 34% yield as a yellow oil, b.p. 160°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.33 (s, 9H), 7.10 and 7.44 (AB, ^3J = 15.9 Hz, 2H), 7.25–7.29 (m, 2H), 7.35–7.49 (m, 2H), 7.42 and 7.50 (AA′BB′, ^3J = 8.4 Hz, 4H); MS: *m/z* (%) 281 (89, $M^{\bullet+}$), 280 (22), 266 (96), 224 (100), 148 (42), 147 (31), 134 (45), 133 (21), 132 (22), 122 (33), 120 (23), 94 (66), 91 (15), 77 (10), 57 (36).

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - phenylprop - 2 - en - 1 - one 13 was obtained in 55% yield as yellow needles, m.p. 72°C (EtOH); ^{1}H NMR: δ 1.34 (s, 9H), 2.49 (s, 3H), 7.18 and 7.53 (AB, ^3J = 16.0 Hz, 2H), 7.27–7.29 (m, 2H), 7.35–7.38 (m, 3H), 7.49–7.56 (m, 3H); MS: *m/z* (%) 278 (90, $M^{\bullet+}$), 277 (19), 263 (73), 221 (39), 187 (100), 131 (55), 117 (44), 103 (66), 91 (45), 77 (52), 57 (47); IR: $\bar{\nu}$ 3066, 2965, 2869, 1664, 1598, 1448, 1339, 1223, 1113, 997, 826, 772, 681 cm^{-1}. $C_{20}H_{22}O$ (278.40); calcd C 86.29, H 7.97; found C 86.10, H 7.73.

3 - (4-*t*-Butyl-2-methylphenyl) - 1 - phenylprop - 2 - en - 1 - one 14 was obtained in 58% yield as a yellow oil, b.p. 165°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.33 (s, 9H), 2.49 (s, 3H), 7.25–7.29 (m, 2H), 7.45 and 8.12 (AB, ^3J = 15.6 Hz, 2H), 7.50–7.68 (m, 4H), 8.01–8.04 (m, 2H); MS: *m/z* (%) 278 (28, $M^{\bullet+}$), 277 (4), 263 (100), 221 (35), 105 (33), 77 (30), 57 (16); IR: $\tilde{\nu}$ 3032, 2968, 2872, 1660, 1600, 1331, 1224, 1016, 734, 694, 648 cm^{-1}. $C_{20}H_{22}O$; calcd 278.1671, found 278.1664 (HRMS).

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - (2-methylphenyl)prop - 2-en-1-one 15 was obtained in 65% yield as a yellow oil, b.p. 135°C/0.05 mbar (kugelrohr); ^{1}H NMR: δ 1.35 (s, 9H), 2.42 (s, 3H), 2.52 (s, 3H), 7.15 and 7.89 (AB, ^3J = 15.9 Hz, 2H), 7.20–7.31 (m, 5H), 7.54–7.57 (m, 1H), 7.62–7.65 (m, 1H); MS: *m/z* (%) 292 (82, $M^{\bullet+}$), 291 (8), 277 (55), 235 (30), 187 (100), 117 (59), 105 (38), 91 (48), 57 (53); IR: $\tilde{\nu}$ 3028, 2968, 2872, 1665, 1596, 1479, 1460, 1322, 1218, 1112, 1011, 982, 768, 747 cm^{-1}. $C_{21}H_{24}O$; calcd 292.1827, found 292.1817 (HRMS).

3 - (4-*t*-Butyl-2-methylphenyl) - 1 - (2-methylphenyl)prop - 2-en-1-one 16 was obtained in 65% yield as a yellow oil, b.p. 170°C/0.01 mbar (kugelrohr); ^{1}H NMR: δ 1.32 (s, 9H), 2.39 (s, 3H), 2.46 (s, 3H), 7.06 and 7.79 (AB, ^3J = 15.9 Hz, 2H), 7.22–7.30 (m, 4H), 7.36–7.38 (m, 1H), 7.49–7.52 (m, 1H), 7.59–7.61 (m, 1H); MS: *m/z* (%) 292 (35, $M^{\bullet+}$), 291 (5), 277 (100), 235 (45), 161 (47), 119 (47), 105 (19), 91 (70), 57 (33); IR: $\tilde{\nu}$ 3027, 2968, 2872, 1666, 1593, 1322, 1224, 1015, 981, 740, 647 cm^{-1}. $C_{21}H_{24}O$; calcd 292.1827, found 292.1812 (HRMS).

1 - (4-*t*-Butylphenyl) - 3 - (4-methylphenyl)propan - 1 - one 17 was obtained from **7** in 70% yield after kugelrohr distillation (140°C/0.02 mbar) and subsequent recrystallisation as colourless platelets; m.p. 37.5–38.5°C (EtOH); ^{1}H NMR: δ 1.33 (s, 9H), 2.32 (s, 3H), 3.02 (t, ^3J = 7.7 Hz, 2H), 3.26 (t, ^3J = 7.8 Hz, 2H), 7.11 and 7.15 (AA′BB′, ^3J = 8.2 Hz, 4H), 7.46 and 7.90 (AA′BB′, ^3J = 8.6 Hz, 4H); MS: *m/z* (%) 280 (32, $M^{\bullet+}$), 265 (7), 223 (47), 161 (100), 105 (67), 91 (38), 77 (23), 57 (14); IR: $\tilde{\nu}$ 3030, 2968, 2872, 1682, 1608, 1515, 1406, 1363, 1190, 1107, 809 cm^{-1}. $C_{20}H_{24}O$ (280.41); calcd C 85.67, H 8.63; found C 85.66, H 8.72.

3 - (4-*t*-Butylphenyl) - 1 - (4-methylphenyl)propan - 1 - one 18 was obtained from **8** in 41% yield as colourless crystals, m.p. 53.5°C (EtOH); ^{1}H NMR: δ 1.31 (s, 9H), 2.41 (s, 3H), 3.03 (t, ^3J = 7.8 Hz, 2H), 3.28 (t, ^3J = 7.9 Hz, 2H), 7.19 and 7.33 (AA′BB′, ^3J = 8.4 Hz, 4H), 7.25 and 7.87 (AA′BB′, ^3J = 8.1 Hz, 4H); MS: *m/z* (%) 280 (39, $M^{\bullet+}$), 265 (85), 223 (9), 147 (11), 131 (47), 119 (100), 91 (71), 57 (13); IR: $\tilde{\nu}$ 3029, 2956, 2867, 1676, 1605, 1517, 1363, 1185, 810 cm^{-1}. $C_{20}H_{24}O$ (280.41); calcd C 85.67, H 8.63; found C 85.60, H 8.45.

1 - (4-*t*-Butylphenyl) - 3 - (3-methylphenyl)propan - 1 - one 19 was obtained from **9** in 72% yield as a slightly yellow liquid, b.p. 150°C/0.03 mbar (kugelrohr); ^{1}H NMR: δ 1.33 (s, 9H), 2.33 (s, 3H), 3.01 (t, ^3J = 7.7 Hz, 2H), 3.27 (t, ^3J = 7.7 Hz, 2H), 7.01–7.07 (m, 3H), 7.16–7.23 (m, 1H), 7.46 and 7.91 (AA′BB′, ^3J = 8.5 Hz, 4H). MS: *m/z* (%) 280 (21, $M^{\bullet+}$), 265 (10), 223 (43), 161 (100), 105 (36), 91 (30), 77 (22), 57 (16). IR: $\tilde{\nu}$ 3029, 2967, 2872, 1681, 1605, 1406, 1363, 1269, 1190, 1107, 979, 781, 700 cm^{-1}. $C_{20}H_{24}O$; calcd 280.1827, found 280.1829 (HRMS).

3 - (4-*t*-Butylphenyl) - 1 - (3-methylphenyl)propan - 1 - one 20 was obtained from **10** in 82% yield as a colourless liquid, b.p. 135°C/0.01 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 2.38 (s, 3H), 3.02 (t, ^3J = 7.7 Hz, 2H), 3.28 (t, ^3J = 7.8 Hz, 2H), 7.19 and 7.33 (AA′BB′, ^3J = 8.6 Hz, 4H), 7.18–7.34 (m, 2H), 7.74–7.77 (m, 2H); MS: *m/z* (%) 280 (55, $M^{\bullet+}$), 265 (100), 223 (8), 147 (45), 131 (44), 119 (89), 91 (72), 57 (24); IR: $\tilde{\nu}$ 3029, 2966, 2871, 1685, 1604, 1362, 1268, 1156, 689 cm^{-1}. $C_{20}H_{24}O$; calcd 280.1827, found 280.1823 (HRMS).

1 - (4-*t*-Butylphenyl) - 3 - (2-methylphenyl)propan - 1 - one 21 was obtained from **11** in 67% yield as a colourless liquid, b.p. 130°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.33 (s, 9H), 2.35 (s, 3H), 3.04 (t, ^3J = 8.1 Hz, 2H), 3.23 (t, ^3J = 8.0 Hz, 2H), 7.14–7.19 (m, 4H), 7.47 and 7.92 (AA′BB′, ^3J = 8.6 Hz, 4H); MS: *m/z* (%) = 280 (32, $M^{\bullet+}$), 265 (9), 223 (24), 161 (100), 105 (34), 91 (24), 77 (16), 57 (13); IR: $\tilde{\nu}$ 3025, 2968, 2873, 1682, 1605, 1461, 1407, 1363, 1269, 977, 840, 754, 741 cm^{-1}. $C_{20}H_{24}O$; calcd 280.1827, found 280.1821 (HRMS).

3 - (4-*t*-Butylphenyl) - 1 - (2-methylphenyl)propan - 1 - one 22 was obtained from **12** in 75% yield after kugelrohr distillation (120°C/ 0.02 mbar) and recrystallisation as a colourless solid m.p. 47–48°C (EtOH); ^{1}H NMR: δ 1.31 (s, 9H), 2.47 (s, 3H), 3.01 (t, ^3J = 7.8 Hz, 2H), 3.22 (t, ^3J = 7.9 Hz, 2H), 7.17 and 7.32 (AA′BB′, ^3J = 8.3 Hz, 4H), 7.19–7.25 (m, 2H), 7.35–7.38 (m, 1H), 7.59–7.62 (m, 1H); MS: *m/z* (%) 280 (31, $M^{\bullet+}$), 265 (59), 147 (11), 131 (25), 119 (100), 91 (52), 57 (15); IR: $\tilde{\nu}$ 3027, 2966, 2871, 1686, 1570, 1455, 1362, 1267, 970, 822, 749 cm^{-1}. $C_{20}H_{24}O$ (280.41); calcd C 85.67, H 8.63; found C 85.67, H 8.55.

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - phenylpropan - 1 - one 23 was obtained from **13** in 71% yield as a colourless liquid, b.p. 130°C/0.01 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 2.51 (s, 3H), 3.03 (t, ^3J = 7.6 Hz, 2H), 3.22 (t, ^3J = 7.8 Hz, 2H), 7.19–7.29 (m, 7H), 7.59–7.62 (m, 1H); MS: *m/z* (%) 280 (4, $M^{\bullet+}$), 265 (9), 223 (36), 175 (100), 132 (18), 117 (15), 105 (20), 91 (34), 77 (15), 57 (13); IR: $\tilde{\nu}$ 3032, 2968, 2872, 1681, 1605, 1453, 1362, 1293, 1210, 1112, 976, 825, 699 cm^{-1}. $C_{20}H_{24}O$; calcd 280.1827, found 280.1821 (HRMS).

3 - (4-*t*-Butyl-2-methylphenyl) - 1 - phenylpropan - 1 - one 24 was obtained from **14** as a colourless liquid (yield 52%); b.p. 130°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 2.35 (s, 3H), 3.02 (t, ^3J = 8.7 Hz, 2H), 3.26 (t, ^3J = 8.8 Hz, 2H), 7.06–7.19 (m, 4H), 7.35–7.56 (m, 3H), 7.95–7.99 (m, 1H); MS: *m/z* (%) 280 (25, $M^{\bullet+}$), 265 (100), 161 (49), 145 (72), 131 (42), 105 (70), 91 (41), 77 (72), 57 (58). IR: $\tilde{\nu}$ 3030, 2966, 2869, 1688, 1598, 1449, 1362, 1203, 822, 741, 700 cm^{-1}. $C_{20}H_{24}O$; calcd 280.1827, found 280.1815 (HRMS). The partially over-hydrogenated product is present in small amounts as shown by MS (*m/z* 286, 271).

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - (2-methylphenyl) propan-1-one 25 was obtained from **15** as a yellowish liquid (yield 75%); b.p. 145°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.32 (s, 9H), 2.33 (s, 3H), 2.54 (s, 3H), 3.01 (t, ^3J = 7.6 Hz, 2H), 3.18 (t, ^3J = 7.8 Hz, 2H), 7.10–7.17 (m, 4H), 7.23–7.26 (m, 2H), 7.61–7.64 (m, 1H); MS: *m/z* (%) 294 (18, $M^{\bullet+}$), 279 (9), 237 (33), 175 (100), 132 (17), 117 (25), 105 (26), 91 (22), 57 (19); IR: $\tilde{\nu}$ 3025, 2968, 2872, 1681, 1606, 1492, 1459, 1362, 1294, 1208, 1112, 975, 827,

751, 621 cm^{-1}. $C_{21}H_{26}O$; calcd 294.1984, found 294.1979 (HRMS).

3 - (4-*t*-Butyl-2-methylphenyl) - 1 - (2-methylphenyl) propan-1-one 26 was obtained from **16** as a colourless liquid (yield 48%); b.p. 140°C/0.01 mbar (kugelrohr); ^{1}H NMR: δ 1.30 (s, 9H), 2.33 (s, 3H), 2.50 (s, 3H), 2.99 (t, ^3J = 8.6 Hz, 2H), 3.18 (t, ^3J = 8.7 Hz, 2H), 7.08–7.25 (m, 5H), 7.34–7.37 (m, 1H), 7.61–7.64 (m, 1H); MS: *m/z* (%) 294 (34, $M^{\bullet+}$), 279 (72), 161 (28), 145 (35), 131 (16), 119 (100), 91 (45), 57 (31); IR: $\tilde{\nu}$ 3025, 2967, 2872, 1687, 1600, 1454, 1362, 1271, 969, 824, 749 cm^{-1}. $C_{21}H_{26}O$; calcd 294.1984, found 294.1980 (HRMS).

1-(4-*t*-Butylphenyl)-3-(4-methylphenyl)propane 2 was obtained from **17** by hydrogenolysis as a colourless liquid, b.p. 135°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.93 (quin, ^3J = 7.8 Hz, 2H), 2.32 (s, 3H), 2.62 (t, ^3J = 7.8 Hz, 4H), 7.09 (s, 4H), 7.12 and 7.30 (AA′BB′, ^3J = 8.3 Hz, 4H); MS: *m/z* (%) 266 (66, $M^{\bullet+}$), 251 (100), 131 (22), 119 (24), 117 (26), 105 (54), 92 (30), 91 (27), 57 (29); IR: $\tilde{\nu}$ 3025, 2965, 2864, 1514, 1460, 1363, 1268, 1108, 1020, 831, 806 cm^{-1}. $C_{20}H_{26}$; calcd 266.2035, found 266.2029 (HRMS).

1 - (4-*t*-Butylphenyl) - 3 - (4-methylphenyl) - [1,1-D_2] - propane 2a was obtained from **17** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 140°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.92 (t, ^3J = 7.7 Hz, 2H), 2.32 (s, 3H), 2.62 (t, ^3J = 7.7 Hz, 2H), 7.09 (s, 4H), 7.12 and 7.30 (AA′BB′, ^3J = 8.4 Hz, 4H); MS: *m/z* (%) 268 (56, $M^{\bullet+}$), 253 (100), 133 (18), 119 (35), 105 (44), 93 (15), 91 (16), 57 (51); D content (MS) 94% (89% d_2, 10% d_1, 1% d_0). The eliminination product is present in very low amounts, as shown by MS (*m/z* 265, 250, 208).

1 - (4-*t*-Butylphenyl) - 3 - (4-methylphenyl) - [3,3-D_2] - propane 2b was obtained from **18** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 150°C/0.01 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.92 (t, ^3J = 7.7 Hz, 2H), 2.32 (s, 3H), 2.61 (t, ^3J = 7.8 Hz, 2H), 7.09 (s, 4H), 7.12 and 7.30 (AA′BB′, ^3J = 8.4 Hz, 4H); MS: *m/z* (%) 268 (53, $M^{\bullet+}$), 253 (100), 131 (30), 117 (28), 107 (68), 93 (25), 91 (30), 57 (23); D content (MS) 98% (96% d_2, 3% d_1, 1% d_0). The eliminination product is present in very low amounts, as shown by MS (*m/z* 265, 250, 208).

1 - (4-*t*-Butylphenyl) - 3 - (4-[D_3]methyl - [D_4]phenyl) - propane 2c was obtained from **8a** by hydrogenolysis as a colourless liquid, b.p. 115°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.93 (quin, ^3J = 7.7 Hz, 2H), 2.62 (t, ^3J = 7.7 Hz, 4H), 7.12 and 7.30 (AA′BB′, ^3J = 8.3 Hz, 4H); MS: *m/z* (%) = 273 (58, $M^{\bullet+}$), 258 (100), 147 (35), 126 (46), 112 (44), 92 (34), 91 (32), 57 (38); D content (MS) 96% (77% d_7, 20% d_6, 3% d_5).

1-(4-*t*-Butylphenyl)-3-(3-methylphenyl)propane 3 was obtained from **20** by hydrogenolysis as a colourless liquid, b.p. 110°C/0.01 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.94 (quin, ^3J = 7.8 Hz, 2H), 2.33 (s, 3H), 2.62 (t_{br}, ^3J = 7.8 Hz, 4H), 6.98–7.01 (m, 3H), 7.11–7.19 (m, 1H), 7.13 and 7.31 (AA′BB′, ^3J = 8.3 Hz, 4H); MS: *m/z* (%) 266 (60, $M^{\bullet+}$), 251 (100), 145 (22), 131 (37), 117 (43), 106 (80), 105 (69), 91 (49), 77 (25), 57 (32); IR: $\tilde{\nu}$ 3026, 2965, 2863, 1609, 1517, 1461, 1363, 1268, 1108, 831, 699 cm^{-1}. $C_{20}H_{26}$; calcd 266.2035, found 266.2022 (HRMS).

1 - (4-*t*-Butylphenyl) - 3 - (3-methylphenyl) - [1,1-D_2] - propane 3a was obtained from **19** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 130°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.93 (t, ^3J = 7.8 Hz, 2H), 2.33 (s, 3H), 2.62 (t, ^3J = 7.8 Hz, 2H), 6.98–7.01 (m, 3H), 7.11–7.17 (m, 1H), 7.13 and 7.31 (AA′BB′, ^3J = 8.4 Hz, 4H); MS: *m/z* (%) 268 (62, $M^{\bullet+}$), 253 (100), 149 (16), 133 (30), 119 (43), 108 (27), 107 (74), 106 (42), 105 (54), 93 (25), 91 (29), 57 (42); D content (MS) 89% (81% d_2, 17% d_1, 2% d_0). The eliminination product is present in low amounts, as shown by MS (*m/z* 265, 250, 208).

1 - (4-*t*-Butylphenyl) - 3 - (3-methylphenyl) - [3,3-D_2] - propane 3b was obtained from **20** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 130°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.93 (t, ^3J = 7.8 Hz, 2H), 2.32 (s, 3H), 2.62 (t, ^3J = 7.8 Hz, 2H), 6.98–7.01 (m, 3H), 7.11–7.19 (m, 1H), 7.12 and 7.30 (AA′BB′, ^3J = 8.3 Hz, 4H); MS: *m/z* (%) 268 (62, $M^{\bullet+}$), 253 (100), 147 (13), 131 (24), 117 (27), 108 (68), 107 (56), 106 (25), 105 (22), 93 (23), 91 (25), 57 (26); D content (MS) 93% (86% d_2, 13% d_1, 1% d_0). The eliminination product is present in low amounts, as shown by MS (*m/z* 265, 250, 208).

1-(4-*t*-Butylphenyl)-3-(2-methylphenyl)propane 4 was obtained from **22** by hydrogenolysis as a colourless liquid, b.p. 110°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.91 (quin, ^3J = 7.9 Hz, 2H), 2.27 (s, 3H), 2.65 (t, ^3J = 8.0 Hz, 2H), 2.67 (t, ^3J = 7.9 Hz, 2H), 7.10–7.16 (m, 4H), 7.14 and 7.31 (AA′BB′, ^3J = 8.5 Hz, 4H); MS: *m/z* (%) 266 (44, $M^{\bullet+}$), 251 (100), 131 (30), 117 (29), 105 (55), 91 (42), 57 (24); IR: $\tilde{\nu}$ 3024, 2966, 2868, 1604, 1517, 1461, 1363, 1268, 1108, 1018, 832, 739 cm^{-1}. $C_{20}H_{26}$; calcd 266.2035, found 266.2030 (HRMS).

1 - (4-*t*-Butylphenyl) - 3 - (2-methylphenyl) - [1,1-D_2] - propane 4a was obtained from **21** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 120°C/0.03 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.89 (t, ^3J = 7.9 Hz, 2H), 2.27 (s, 3H), 2.64 (t, ^3J = 8.0 Hz, 2H), 7.10–7.16 (m, 4H), 7.13 and 7.31 (AA′BB′, ^3J = 8.5 Hz, 4H); MS: *m/z* (%) 268 (55, $M^{\bullet+}$), 253 (100), 133 (35), 119 (46), 105 (68), 93 (21), 91 (31), 57 (40); D content (MS) 89% (81% d_2, 17% d_1, 2% d_0). The elimination product is present in low amounts, as shown by MS (*m/z* 265, 250, 208).

1 - (4-*t*-Butylphenyl) - 3 - (2-methylphenyl) - [3,3-D_2] - propane 4b was obtained from **22** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 110°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.89 (t, ^3J = 7.8 Hz, 2H), 2.27 (s, 3H), 2.67 (t, ^3J = 7.8 Hz, 2H), 7.10–7.15 (m, 4H), 7.14 and 7.31 (AA′BB′, ^3J = 8.5 Hz, 4H); MS: *m/z* (%) 268 (58, $M^{\bullet+}$), 253 (100), 131 (43), 117 (41), 107 (62), 93 (29), 91 (40), 57 (42); D content (MS) 92% (84% d_2, 15% d_1, 1% d_0). The elimination product is present in low amounts, as shown by MS (*m/z* 265, 250, 208).

1 - (4-*t*-Butylphenyl) - 3 - (2-[D_3]methylphenyl)propane 4c was obtained from **12a** by hydrogenolysis as a colourless liquid, b.p. 130°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.31 (s, 9H), 1.91 (quin, ^3J = 7.8 Hz, 2H), 2.64 (t, ^3J = 7.9 Hz, 2H), 2.67 (t, ^3J = 7.9 Hz, 2H), 7.10–7.15 (m, 4H), 7.14 and 7.31 (AA′BB′, ^3J = 8.5 Hz, 4H); MS: *m/z* (%) 269 (56, $M^{\bullet+}$), 254 (100), 161 (6), 147 (13), 131 (30), 122 (18), 117 (27), 109 (31), 108 (46), 92 (21), 91 (26), 79 (8), 78 (7), 77 (8), 57 (29); D content (MS) 91% (78% d_3, 18% d_2, 3% d_1, 1% d_0).

1-(4-*t*-Butyl-2-methylphenyl)-3-phenylpropane 5 was obtained from **23** by hydrogenolysis as a colourless liquid, b.p. 115°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.30 (s, 9H), 1.91 (quin, ^3J = 7.8 Hz, 2H), 2.27 (s, 3H), 2.60 (t, ^3J = 7.9 Hz, 2H), 2.70 (t, ^3J = 7.7 Hz, 2H), 7.06–7.09 (m, 1H), 7.14–7.31 (m, 7H); MS: *m/z* (%) 266 (50, $M^{\bullet+}$), 251 (100), 175 (58), 161 (31), 131 (28), 105 (32), 91 (65), 57 (23); IR: $\tilde{\nu}$ 3030, 2965, 2867, 1604, 1495, 1453, 1362, 1029, 828, 746, 698 cm^{-1}. $C_{20}H_{26}$; calcd 266.2035, found 266.2025 (HRMS).

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - phenyl - [1,1-D_2] - propane 5a was obtained from **23** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 130°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.30 (s, 9H), 1.89 (t, ^3J = 7.7 Hz, 2H), 2.26 (s, 3H), 2.70 (t, ^3J = 7.7 Hz, 2H), 7.05–7.08 (m, 1H), 7.14–7.31 (m, 7H); MS: *m/z* (%) 268 (33, $M^{\bullet+}$), 253 (80), 163 (17), 162 (21), 161 (13), 133 (23), 105 (27), 91 (100), 57 (39); D content (MS) 91% (83% d_2, 15% d_1, 2% d_0). The eliminination product is present in considerable amounts, as shown by MS (*m/z* 265, 250, 208).

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - phenyl - [3,3-D_2] - propane 5b was obtained from **24** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 140°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.30 (s, 9H), 1.90 (t, ^3J = 7.8 Hz, 2H), 2.26 (s, 3H), 2.60 (t, ^3J = 7.9 Hz, 2H), 7.06–7.10 (m, 1H), 7.14–7.38 (m, 7H); MS: *m/z* (%) 268 (47, $M^{\bullet+}$), 253 (100), 161 (60), 131 (47), 107 (43), 91 (53), 57 (87); D content (MS) 76% (55% d_2, 40% d_1, 5% d_0). The elimination product and the chlorine-substituted product are present, as shown by MS (*m/z* 265, 250, 208 and *m/z* 303/301, 288/286, respectively).

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - (2-methylphenyl) propane 6 was obtained from **25** by hydrogenolysis as a colourless liquid, b.p. 130°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.30 (s, 9H), 1.86 (quin, ^3J = 7.9 Hz, 2H), 2.28 (s, 6H), 2.66 (t, ^3J = 7.8 Hz, 2H), 2.68 (t, ^3J = 7.8 Hz, 2H), 7.07–7.17 (m, 7H); MS: *m/z* (%) 280 (57, $M^{\bullet+}$), 265 (100), 161 (26), 131 (32), 119 (42), 105 (83), 91 (33), 57 (37); IR: $\tilde{\nu}$ 3022, 2967, 2869, 1605, 1492, 1461, 1362, 1053, 828, 740 cm^{-1}. $C_{21}H_{28}$; calcd 280.2191, found 280.2183 (HRMS).

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - (2-methylphenyl) - [1,1-D_2] propane 6a was obtained from **25** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 135°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.30 (s, 9H), 1.85 (t, ^3J = 7.9 Hz, 2H), 2.28 (s, 6H), 2.68 (t, ^3J = 7.9 Hz, 2H), 7.07–7.16 (m, 7H); MS: *m/z* (%) 282 (53, $M^{\bullet+}$), 267 (100), 163 (23), 133 (31), 119 (34), 107 (34), 105 (80), 91 (27), 57 (37); D content (MS) 85% (72% d_2, 25% d_1, 3% d_0). The elimination product is present in very low amounts, as shown by MS (*m/z* 279, 264, 222).

1 - (4-*t*-Butyl-2-methylphenyl) - 3 - (2-methylphenyl) - [3,3-D_2]propane 6b was obtained from **26** by reduction with $LiAlD_4/AlCl_3$ as a colourless liquid, b.p. 140°C/0.02 mbar (kugelrohr); ^{1}H NMR: δ 1.30 (s, 9H), 1.85 (t, ^3J = 8.0 Hz, 2H), 2.28 (s, 6H), 2.65 (t, ^3J = 8.0 Hz, 2H), 7.07–7.16 (m, 7H); MS: *m/z* (%) 282 (63, $M^{\bullet+}$), 267 (100), 161 (38), 131 (33), 119 (20), 107 (57), 91 (22), 57 (42). D content (MS) 87% (74% d_2, 25% d_1, 1% d_0). The elimination product and the chlorinated product are present, as indicated by MS (*m/z* 279, 264, 222 and *m/z* 317/315, 302/300, respectively).

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References

1. P. Longevialle, *Mass Spectrom. Rev.* **11**, 157 (1992).
2. (a) T.H. Morton, *Org. Mass Spectrom.* **27**, 353 (1992); (b) T.H. Morton, *Tetrahedron* **38**, 3195 (1982).
3. R.D. Bowen, *Acc. Chem. Res.* **24**, 364 (1991).
4. D.J. McAdoo, *Mass Spectrom. Rev.* **7**, 363 (1988).
5. S. Hammerum, *J. Chem. Soc., Chem. Commun.* 858 (1988).
6. (a) D. Kuck and C. Matthias, *J. Am. Chem. Soc.* **114,** 1901 (1992); (b) C. Matthias and D. Kuck, *Org. Mass Spectrom.* **28,** 1073 (1993).
7. (a) B. Chiavarino, M.E. Crestoni, S. Fornarini and D. Kuck, *Int. J. Mass Spectrom. Ion Processes* **148**, 215 (1995); (b) M.E. Crestoni, S. Fornarini and D. Kuck, *J. Chem. Phys.* **99,** 3144 (1995).

8. The same or a closely similar kinetic isotope effect was found for simpler alkylbenzenium ions ($k_H/k_D \approx 1.6$); see (a) H.E. Audier, C. Monteiro, P. Mourgues and D. Berthomieu, *Org. Mass Spectrom.* **25,** 245 (1990); (b) D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié and H.E. Audier, *J. Phys. Chem.* **99,** 712 (1995).
9. (a) From thermochemical data (Reference 9b), the abstraction of a hydride from the methylene position of 4-ethyltoluene (taken as a model substrate for the case of **2**) by t-$C_4H_9^+$ is exoergic by *c.* 38 kJ mol^{-1}. Using the relative heats of formation of the methylbenzyl cations, the corresponding reaction of 3- and 2-ethyltoluene should be significantly less exergonic (≥ 20 and ≥ 25 kJ mol^{-1}); (b) S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, *J. Phys. Chem. Ref. Data* **17**, *Suppl. 1* (1988). See also (c) J.E. Szulejko and T.B. McMahon, *J. Am. Chem. Soc.* **115**, 7839 (1993).
10. C. Matthias, *Doctoral Thesis.* University of Bielefeld, in preparation.
11. M.E. Crestoni, S. Fornarini and D. Kuck, *J. Chem. Phys.* **99,** 3150 (1995).
12. This finding suggests that PA[(*o*-CH_3)C_6H_4–$CH_2CH_2CH_2$–C_6H_4(*o*-CH_3)] > PA[C_6H_5–$CH_2CH_2CH_2$–C_6H_4(*o*-CH_3)]; see also Reference 11.

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