CROATICA CHEMICA ACTA
CCACAA, ISSN-0011-1643, ISSN-1334-417X
Croat. Chem. Acta **82** (1) (2009) 7-19.
CCA-3291

Original Scientific Paper

Gaseous [$C_nH_{2n+1}^+$ ··· 1,3-Diphenylpropane] Ion/Neutral Complexes Containing Alkyl Cations of Different Acidities and Hydride Ion Affinities*

Carsten Matthias and Dietmar Kuck**

Department of Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany

RECEIVED JUNE 16, 2008; REVISED AUGUST 8, 2008; ACCEPTED AUGUST 9, 2008

Abstract. Gaseous ion/neutral (I/N) complexes [R^+ ··· $C_6H_5CH_2CH_2CH_2C_6H_5$] with R = *t*-$C_4H_9^+$, *s*-$C_4H_9^+$ and *s*-$C_3H_7^+$ have been generated by protonation of the corresponding precursor compounds, R-$C_6H_4CH_2CH_2CH_2C_6H_5$, in the chemical ionisation (CI) source of a sector-field mass spectrometer. The fragmentation of these I/N complexes and several deuterium-labelled isotopologues on the metastable ions' timescale (20−30 μs), as studied by MIKE spectrometry, revealed that (i) the initial ring position (*meta*- or *para*-) of R = *t*-$C_4H_9^+$ does not affect their intra-complex reactivity, (ii) the fragmentation of the *s*-$C_3H_7^+$ and *s*-$C_4H_9^+$ ions is dominated by proton transfer to the 1,3-diphenylpropane neutral but hydride ion abstraction in the reverse direction competes to a minor extent, (iii) the secondary alkyl cations exhibit the same regioselectivity ($k_{\alpha\text{-H}}/k_{\omega\text{-H}}$ = 1.0) and kinetic isotope effect (k_H/k_D = 1.6) in the hydride transfer channel as do tertiary alkyl cations, (iv) the *s*-$C_4H_9^+$ ions do not undergo skeletal isomerisation to *t*-$C_4H_9^+$ ions within the I/N complex. Attempts to characterise the trimethylsilyl complex, [$Si(CH_3)_3^+$ ··· $C_6H_5CH_2CH_2CH_2C_6H_5$], by CI/MIKE spectrometry under analogous conditions failed.

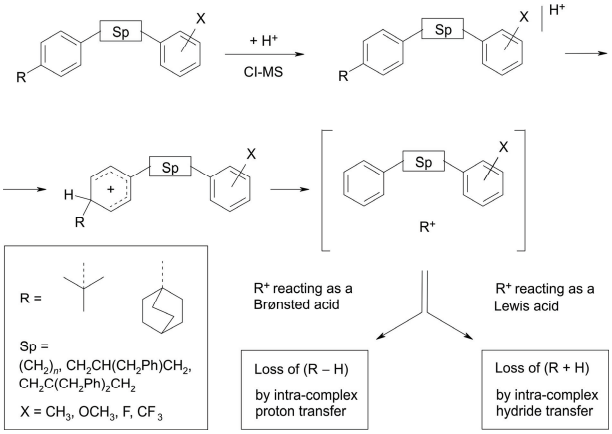
Keywords: proton transfer, hydride ion transfer, alkyl cations, ion/neutral complexes (gaseous), mass spectrometry, metastable ions

INTRODUCTION

It has been well established during the past two decades that unimolecular fragmentation reactions occurring in the highly dilute gas-phase of a mass spectrometer often occur *via* ion/neutral (I/N) complexes.[1–4] In most cases, the existence of such species may be hidden because the mere observation of the fragmentation products does not provide an indication of the formation of the I/N complexes. However, many examples of mass spectrometric fragmentation reactions have been found which necessarily require the intermediacy of I/N complexes because simple dissociation or elimination mechanisms cannot explain the occurrence of a particular fragmentation.[5,6] As a consequence, such highly "complex" fragmentation behaviour may cause problems for the analytical application of mass spectrometry, since unexpected peaks can easily give rise to misinterpretation. In most cases, suitable isotopic labelling has helped decisively to unravel the occurrence of I/N complexes.[5,7–15] Considered with even more consequence, organic synthesis and suitable mass spectrometric techniques can be combined in a way to generate "targeted" gaseous ions that are prone to form "tailored" gaseous ion/neutral complexes. Hence, pinpointed unimolecular fragmentation of (possibly isotope-labelled) model compounds can be utilized to study ion/molecule and ion/radical reactions by conventional mass spectrometry. Other groups[1–4] and largely we ourselves have used this "organic-synthesis" approach to study the reactivity of carbenium ions within their I/N complexes with a large variety of aromatic molecules, such as α,ω-diphenylalkanes[16–22] and related alkylbenzene hydrocarbons including exceedingly large[21] and small ones,[19] and alkyl benzyl ethers.[23–26] A recent report, triggered by analytical work, on the fragmentation of various protonated benzylamines represents a nice confirmation of this concept.[27] Most of our own work has been invested into studies on I/N molecules consisting of a *t*-$C_4H_9^+$ ion and various diphenylalkanes, and variations of this theme led us to model I/N complexes such as [*t*-$C_4H_9^+$ ··· tetrabenzylmethane][21] and {2.2.2[bicyclooct-1-yl]$^+$ ··· 1,3-diphenylpropane},[22] among others (Scheme 1). In all cases, the reactivity of the I/N complexes was characterised by competing intra-complex hydride and proton transfer reactions, in contrast to extended radio-

* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

** Author to whom correspondence should be addressed. (E-mail: dietmar.kuck@uni-bielefeld.de)



Scheme 1. Formation and fragmentation reactions of ion/neutral complexes from various *tert*-alkyl-substituted α,ω-diphenylalkanes.

lytic studies based on deprotonation reactions in the dense gas-phase under thermalising conditions.[28–30] Besides the variations of the spacer unit ("Sp" in Scheme 1), which proved to be structurally stable in all cases except one, substituent effects on the competing fragmentation reactions of the I/N complexes were studied in particularly great detail with respect to the regioselectivity of the hydride transfer and relative rates of the two fragmentation channels.[18–20]

This contribution is focused on still another part of this extended project, namely the effect of the acidity and hydride ion affinity of the ionic partner within the I/N complex and the mobility of the *tert*-butyl group within the protonated precursor 1,3-diarylpropane. To this end, we synthesised compounds **1**–**4** (Chart 1) and the labelled analogues **1a**–**3b** (Chart 2) and subjected them to methane chemical ionisation [CI(CH_4)]. The fragmentation of the corresponding $[M + H]^+$ ions within the ion source and, in particular, in the 2nd field-free region of a double-focusing mass spectrometer was used to determine the effect of the different acidities of the alkyl cations on the regioselectivity of the hydride ion transfer and on the competition between hydride transfer and proton transfer. As found previously throughout our studies with all of the *para*-*tert*-butyl-substituted α,ω-diarylalkanes,[16–22] the results all point to

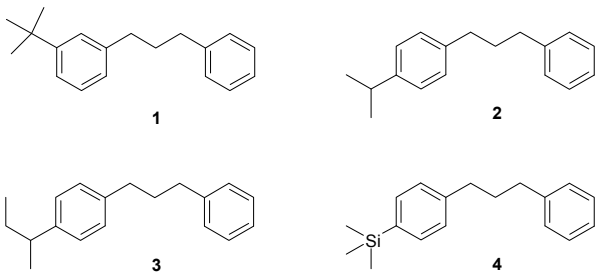


Chart 1. Neutral precursors of the $[M + H]^+$ ions studied in this work.

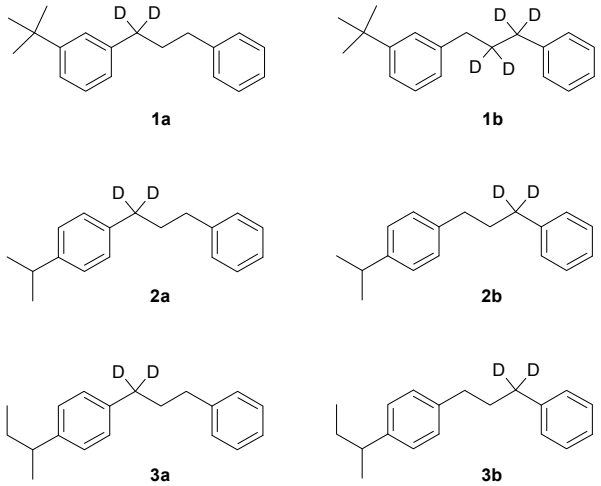


Chart 2. Neutral precursors of the deuterium-labeled $[M + H]^+$ ions studied in this work.

the existence of well-behaved ion/neutral complexes as reactive intermediates.

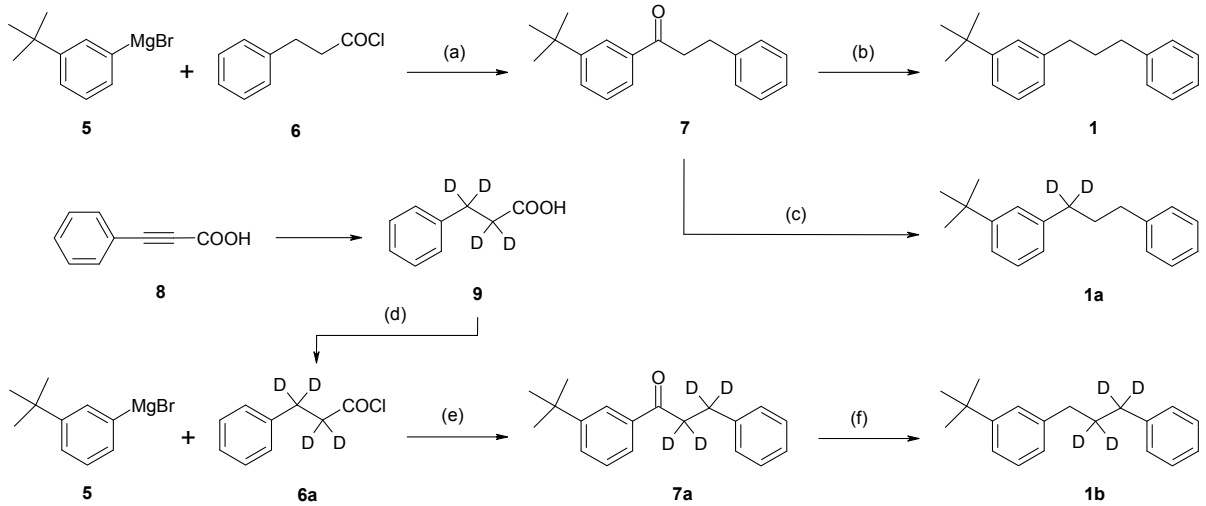
EXPERIMENTAL

Mass Spectrometry

All measurements were carried out on a double-focussing instrument, AutoSpec (Fisons, Manchester/UK) with a three-sector, EBE geometry. The compounds were introduced into the CI source *via* the heatable inlet rod. Methane was used as the reactant gas at a (nominal) pressure of $4 \cdot 10^{-5} \le p \le 1 \cdot 10^{-4}$ mbar. The electron energy was set at 70 eV, the trap current at 200 μA, the accelerating voltage at 8000 V, and the source temperature at 160−200 °C. Fragmentation of the metastable ions in the third field-free region was registered by selecting the precursor ion by the magnetic field and scanning the field of the second electrostatic analyzer. The MIKE spectra are representative examples for several independent measurements and averaged from at least ten consecutive scans.

Synthesis (General)

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



Scheme 2. Syntheses of 1-(3-*tert*-butylphenyl)-3-phenylpropanes **1**, **1a** and **1b**. Reagents, conditions and yields: (a) $Fe(acac)_3$/THF, 0 °C, 67 %; (b) H_2, Pd/C, HOAc, 20 °C, 4 bar, 50−80 %; (c) $LiAlD_4/AlCl_3$, Et_2O, 0 °C, then Δ, 2 h, 60−80 %; (d) $SOCl_2$, Δ, 96 %; (e) $Fe(acac)_3$/THF, 0 °C, 31 %; (f) $LiAlH_4/AlCl_3$, Et_2O, 0 °C, then Δ, 2 h, 60−80 %.

*1-(3-*tert*-Butylphenyl)-3-phenylpropane (**1**)*

A solution of 3-phenylpropionyl chloride (**6**) (5.00 g, 30.0 mmol) in anhydrous THF (50 mL) was stirred and cooled to 0 °C and iron(III)-acetylacetonate (53 mg, 0.15 mmol) was added. A freshly prepared solution of 3-*tert*-butylphenylmagnesium bromide (**5**) (0.9 M) (38 mL, 34 mmol) was added within 30 min and stirring was continued at 0 °C for 10 min. The mixture was poured on ice and dilute HCl and the product was extracted with diethyl ether. Workup followed by chromatography (CH_2Cl_2/*n*-hexane) and kugelrohr distillation furnished 1-(3-*tert*-butylphenyl)-3-phenylpropan-1-one (**7**) (5.33 mg, 67 %) as a colourless liquid. B.p. 120 °C/0.01 mbar; ^{1}H NMR δ/ppm: 1.34 (s, 9H), 3.07 (t, ^3J = 7.7 Hz, 2H), 3.31 (t, ^3J = 7.8 Hz, 2H), 7.20−7.40 (m, 6H), 7.58−7.61 (m, 1H), 7.74−7.78 (m, 1H), 8.00−8.01 (m, 1H); MS *m*/*z* (%): 266 (9, $M^{+\bullet}$), 251 (4), 209 (20), 161 (100), 133 (8), 117 (5), 105 (12), 91 (35), 77 (8), 57 (6); IR ν_{max}/cm^{-1}: 3031, 2966, 2931, 2855, 1687, 1580, 1453, 1364, 1196, 749, 696; accurate mass (EI-MS): $C_{19}H_{22}O$, calcd.: 266.1671; found: 266.1669.

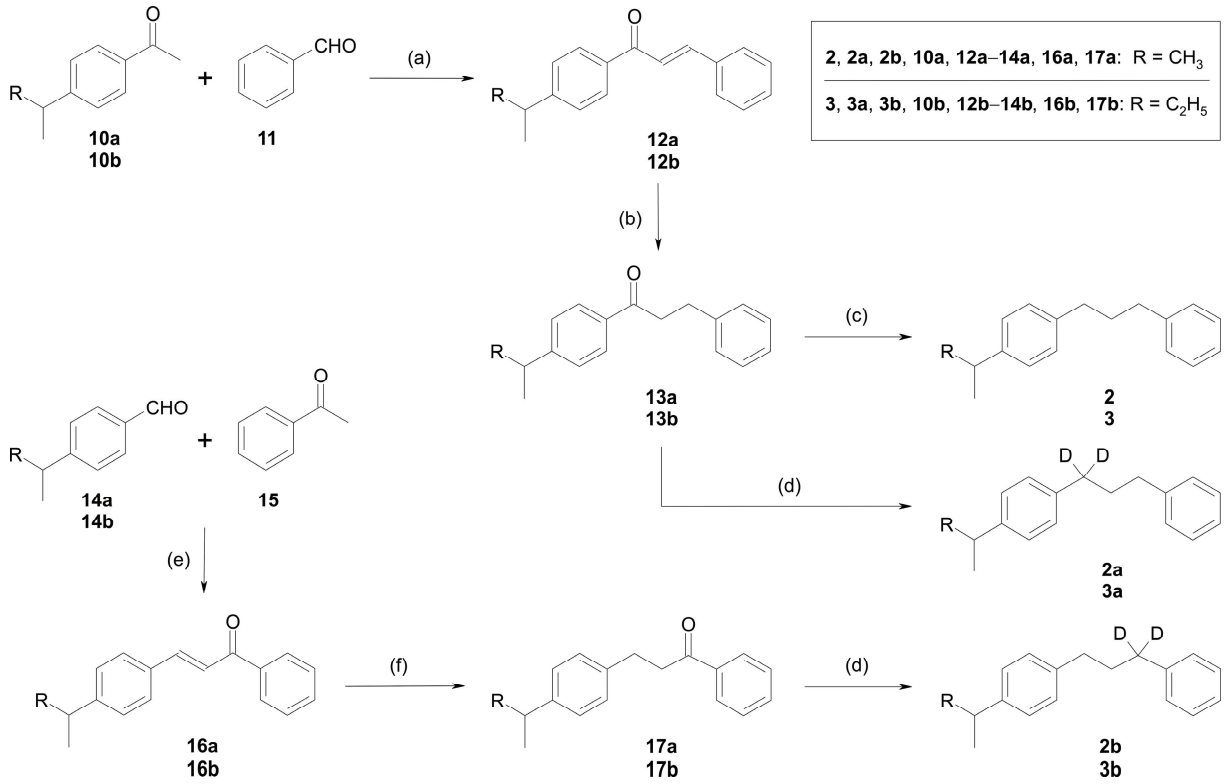
Hydrogenolysis of **7** (266 mg, 1.0 mmol) in acetic acid (5.0 mL) in the presence of Pd/C (10 %) (40 mg) under hydrogen (4 bar) gave compound **1** (yield 50−80 %), b.p. 100 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 1.31 (s, 9 H), 1.97 (qui, ^3J = 7.7 Hz, 2 H), 2.65 (t, ^3J = 7.7 Hz, 2 H), 2.66 (t, ^3J = 7.7 Hz, 2 H), 7.02 (m, 1 H), 7.21−7.31 (m, 8 H). MS *m*/*z* (%): 252 (54, $M^{+\bullet}$), 237 (86), 163 (21), 161 (13), 148 (32), 133 (34), 131 (35), 117 (33), 105 (41), 92 (74), 91 (100), 77 (23), 57 (74). IR ν_{max}/cm^{-1}: 3031, 2967, 2864, 1603, 1494, 1453, 1364, 1273, 1201, 1091, 1029, 787, 745, 697; accurate mass (EI-MS): $C_{19}H_{24}$, calcd.: 252.1878; found: 252.1879.

*[1,1-D_2]-1-(3-*tert*-Butylphenyl)-3-phenylpropane (**1a**)*

A suspension of lithium aluminium deuteride (Merck) in anhydrous diethyl ether (5 mL) was stirred and cooled to 0 °C. Stirring and cooling was continued while a solution of aluminium chloride (3.0 mmol) in the same solvent (5 mL) was added quickly, followed by a solution of compound **7** (266 mg, 1.0 mmol), again in diethyl ether (5 mL). The mixture was heated to reflux for 2 h and then hydrolysed with ice/water and aqueous HCl. Work-up furnished compound **1a** (60−80 %), b.p. 100 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 1.31 (s, 9 H), 1.95 (t, ^3J = 7.9 Hz, 2 H), 2.66 (t, ^3J = 7.7 Hz, 2 H), 6.99−7.03 (m, 1 H), 7.19−7.32 (m, 8 H); MS *m*/*z* (%): 254 (57, $M^{+\bullet}$), 239 (90), 150 (32), 149 (24), 135 (34), 133 (32), 132 (20), 119 (32), 118 (34), 117 (24), 116 (26), 107 (23), 105 (30), 94 (60), 93 (57), 92 (59), 91 (92), 77 (22), 57 (100). D content (MS): 93 % (87 % d_2, 12 % d_1, 1 % d_0). The product of elimination was found to be present by signals at δ/ppm: 1.32 (s), 3.56 (d) and 6.36 (t) (^{1}H NMR) and by peaks at *m*/*z*: 251, 236 and 194 (MS).

*[2,2,3,3-D_4]-1-(3-*tert*-Butylphenyl)-3-phenylpropane (**1b**)*

Phenylpropiolic acid (**8**) was converted to 3-phenyl-[2,2,3,3-D_4]propionic acid (**9**) and further to 3-phenyl-[2,2,3,3-D_4]propionic acid chloride (**6a**), b.p. 135 °C/30 mm, by standard procedures. The acid chloride (910 mg, 4.1 mmol) was then reacted with 3-*tert*-butylphenylmagnesium bromide (**5**) (7.0 mL of a 0.84 M solution) in analogy to the procedure described above for **1**. Workup afforded 1-(3-*tert*-butylphenyl)-3-phenyl-[2,2,3,3-D_4]propan-1-one (**7a**) (440 mg, 31 %) as a colourless liquid. B.p. 130 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 1.34 (s, 9H), 7.19−7.41 (m, 6H), 7.58−7.62 (m, 1H), 7.75−7.78 (m, 1H), 7.99−8.00 (m,



Scheme 3. Syntheses of 1-(4-isopropylphenyl)-3-phenylpropanes **2**, **2a** and **2b** and 1-(4-*sec*-butylphenyl)-3-phenylpropanes **3**, **3a** and **3b**. Reagents, conditions and yields: (a) KOH/H_2O, 12 h, 20 °C, 45 % (**12a**), 47 % (**12b**); (b) H_2, Pt, EtOAc, 20 °C, 59 % (**13a**), 68 % (**13b**); (c) H_2, Pd/C, HOAc, 20 °C, 4 bar, 50−80 %; (d) $LiAlD_4/AlCl_3$, Et_2O, 0 °C, then Δ, 2 h, 60−80 %; (e) KOH/H_2O, 12 h, 20 °C, 68 % (**16a**), 52 % (**16b**); (f) H_2, Pt, EtOAc, 20 °C, 58 % (**17a**), 72 % (**17b**).

1H); MS *m*/*z* (%): 270 (14, $M^{+\bullet}$), 255 (3), 213 (13), 161 (100), 93 (28), 92 (5), 91 (9).

Reduction of dihydrochalcone **7a** (200 mg, 0.77 mmol) in analogy to the procedure as described above for **7** but by use of $LiAlH_4/AlCl_3$ in diethyl ether afforded compound **1b** (yield 60−80 %), b.p. 110 °C/0.01 mbar (kugelrohr); ^{1}H NMR *δ*/ppm: 1.31 (s, 9H), 2.63 (br s, 2H), 7.00−7.02 (m, 1H), 7.17−7.35 (m, 8H); MS *m*/*z* (%): 256 (38, $M^{+\bullet}$), 241 (61), 147 (9), 134 (14), 133 (7), 132 (9), 131 (11), 120 (7), 119 (6), 118 (7), 117 (10), 116 (5), 115 (6), 106 (10), 105 (7), 94 (27), 93 (100), 92 (31), 91 (16), 57 (44); D content (MS): 90 % (67 % d_4, 26 % d_3, 4 % d_2, 2 % d_1, 1 % d_0). The product of elimination was recognised by signals at *δ*/ppm 4.80 (s) (^{1}H NMR) and peaks at *m*/*z* 253 and 238 (MS).

1-(4-Isopropylphenyl)-3-phenylpropane (2)

A solution of 4-isopropylacetophenone (**10a**) (2.43 g, 15.0 mmol) and benzaldehyde (**11**) (1.59 g, 15.0 mmol) in methanol (20 mL) was reacted with a solution of aqueous KOH (20 mL) at ambient temperature for 12 h. Work-up and recrystallisation gave 1-(4-isopropylphenyl)-3-phenylprop-2-en-1-one (**12a**) (2.23 g, 45 %) as yellow needles. M.p. 62−63 °C (EtOH) (64−65 °C (MeOH));[31,32] ^{1}H NMR *δ*/ppm: 1.29 (d, ^3J = 6.9 Hz, 6H), 2.99 (sep, ^3J = 6.9 Hz, 1H), 7.41−7.44 (m, 3H), 7.36 and 7.98 (AA'BB', 4H), 7.55 and 7.82 (AB, 2H), 7.63−7.67 (m, 2H); MS *m*/*z* (%): 250 (88, $M^{+\bullet}$), 249 (99), 235 (27), 207 (100), 147 (51), 131 (48), 117 (20), 103 (59), 91 (27), 77 (51); IR *ν*/cm^{-1}: 3068, 2966, 2874, 1654, 1590, 1448, 1333, 1223, 1177, 1013, 985, 838, 769, 742, 677.

Chalcone **12a** (1.70 g, 6.8 mmol) was subjected to catalytic hydrogenation in ethyl acetate (20 mL) in the presence of Adam's catalyst (from $PtO_2 \cdot xH_2O$, 20 mg) at ambient temperature and pressure. Work-up gave 1-(4-isopropylphenyl)-3-phenylpropan-1-one (**13a**) (1.02 g, 59 %) as a colourless liquid. B.p. 150 °C/0.02 mbar (kugelrohr); ^{1}H NMR *δ*/ppm: 1.26 (d, ^3J = 6.9 Hz, 6H), 2.95 (sep, ^3J = 6.9 Hz, 1H), 3.05 (t, ^3J = 7.7 Hz, 2H), 3.28 (t, ^3J = 7.8 Hz, 2H), 7.17−7.31 (m, 5H), 7.30 and 7.90 (AA'BB', 4H); MS *m*/*z* (%): 252 (16, $M^{+\bullet}$), 209 (36), 147 (100), 105 (10), 104 (15), 91 (36), 77 (17); IR: *ν*/cm^{-1}: 3032, 2966, 2875, 1681, 1606, 1453, 1414, 1291, 1183, 1056, 978, 699; accurate mass (EI-MS): $C_{18}H_{20}O$, calcd.: 252.1514; found: 252.1506.

Hydrogenolysis of dihydrochalcone **13a** (370 mg, 1.5 mmol) under 4 bar, as described above for compound **7**, gave hydrocarbon **2** (yield 50−80 %) as a colourless liquid. B.p. 110 °C/0.03 mbar (kugelrohr); ^{1}H NMR *δ*/ppm: 1.24 (d, ^3J = 6.9 Hz, 6H), 1.95 (qui, ^3J =

7.8 Hz, 2H), 2.62 (t, ^3J = 7.8 Hz, 2H), 2.66 (t, ^3J = 7.8 Hz, 2H), 2.88 (sep, ^3J = 6.9 Hz, 1H), 7.10−7.30 (m, 9H); MS *m/z* (%): 238 (83, $M^{+\bullet}$), 223 (46), 147 (26), 133 (53), 119 (47), 117 (48), 105 (57), 92 (93), 91 (100), 77 (23); IR ν/cm^{-1}: 3030, 2964, 2863, 1604, 1514, 1496, 1453, 1055, 832, 743, 698; accurate mass (EI-MS): $C_{18}H_{22}$ calcd.: 238.1722; found: 238.1715.

*[1,1-D$_2$]-1-(4-Isopropylphenyl)-3-phenylpropane (**2a**)*
This hydrocarbon was obtained by reduction of dihydrochalcone **13a** (250 mg, 1.0 mmol) with $LiAlD_4/AlCl_3$ in analogy to the procedure given above for compound **1a** as a colourless liquid (60−80 %). B.p. 100 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 1.24 (d, ^3J = 6.9 Hz, 6H), 1.94 (t, ^3J = 7.7 Hz, 2H), 2.66 (t, ^3J = 7.7 Hz, 2H), 2.88 (sep, ^3J = 6.9 Hz, 1H), 7.10−7.31 (m, 9H); MS *m/z* (%): 240 (88, $M^{+\bullet}$), 225 (58), 194 (22), 149 (23), 135 (69), 119 (75), 105 (54), 94 (61), 93 (100), 92 (54), 91 (82), 79 (21), 77 (25); D content (MS): 92 % (86 % d_2, 12 % d_1, 2 % d_0). The product of elimination was recognised as a very minor contamination by peaks at *m/z* 237, 222 and 194 (MS).

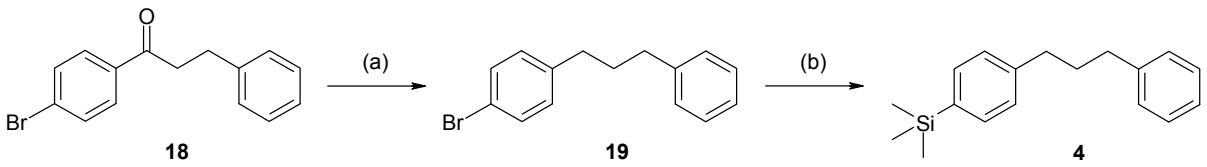
*[3,3-D$_2$]-1-(4-Isopropylphenyl)-3-phenylpropane (**2b**)*
Condensation of 4-isopropylbenzaldehyde (**14a**) (3.60 g, 26.0 mmol) and acetophenone (**15**) (3.30 g, 26.0 mmol) in analogy to the procedure given above for chalcone **12a** furnished 3-(4-isopropylphenyl)-1-phenylprop-2-en-1-one (**16a**) (4.43 g, 68 %) as a yellow oil. B.p. 165 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 1.27 (d, ^3J = 6.9 Hz, 6H), 2.95 (sep, ^3J = 6.9 Hz, 1H), 7.28 and 7.59 (AA'BB', 4 H), 7.47−7.60 (m, 3H), 7.50 and 7.81 (AB, ^3J = 15.7 Hz, 2H), 8.00−8.03 (m, 2H); MS *m/z* (%): 250 (41, $M^{+\bullet}$), 249 (41), 235 (45), 207 (100), 131 (35), 115 (15), 105 (40), 91 (15), 77 (45); IR ν/cm^{-1}: 3064, 2966, 2874, 1662, 1332, 1214, 1017, 827, 778, 693, 652; accurate mass (EI-MS): $C_{18}H_{18}O$ calcd.: 250.1358; found: 250.1355.

Chalcone **16a** (3.60 g, 14.4 mmol) was subjected to catalytic hydrogenation in ethyl acetate (40 mL) in the presence of Adam's catalyst (from $PtO_2 \cdot xH_2O$, 40 mg) at ambient temperature and pressure. Work-up gave 3-(4-isopropylphenyl)-1-phenylpropan-1-one (**17a**) (2.08 g, 58 %) as a colourless liquid. B.p. 130 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 1.24 (d, ^3J = 6.9 Hz, 6H), 2.89 (sep, ^3J = 6.9 Hz, 1H), 3.04 (t, ^3J = 7.7 Hz, 2H), 3.30 (t, ^3J = 7.7 Hz, 2H), 7.13−7.21 (m, 4H), 7.43−7.49 (m, 2H), 7.53−7.58 (m, 1H), 7.95−7.98 (m, 2H); MS *m/z* (%): 252 (75, $M^{+\bullet}$), 237 (47), 209 (28), 147 (21), 133 (52), 117 (38), 105 (100), 91 (35), 77 (65), 51 (13), 43 (15); IR ν/cm^{-1}: 3059, 3027, 2964, 2873, 1687, 1448, 1203, 822, 743, 690; accurate mass (EI-MS): $C_{18}H_{20}O$ calcd.: 252.1514; found: 252.1491.

Reduction of dihydrochalcone **17a** (250 mg, 1.0 mmol) with $LiAlD_4/AlCl_3$ in analogy to the procedure given above for compound **1a** furnished hydrocarbon **2b** as a colourless liquid (yield 60−80 %). B.p. 135 °C/0.02 mbar (kugelrohr); ^{1}H NMR δ/ppm: 1.24 (d, ^3J = 6.9 Hz, 6H), 1.93 (t, ^3J = 7.7 Hz, 2H), 2.62 (t, ^3J = 7.8 Hz, 2H), 2.88 (sep, ^3J = 6.9 Hz, 1H), 7.09−7.38 (m, 9H); MS *m/z* (%): 240 (91, $M^{+\bullet}$), 225 (57), 147 (37), 133 (88), 119 (73), 118 (63), 117 (76), 116 (64), 107 (34), 105 (66), 94 (71), 93 (100), 92 (87), 91 (81), 77 (29). D content (MS): 92 % (85 % d_2, 15 % d_1, 0 % d_0). The product of elimination was observed by signals at δ/ppm 1.24 (d), 3.52 (d) and 6.35 (t) and the 3-chloropropane derivative was seen at δ/ppm 2.20−2.50 (m) and 2.65−2.80 (m) (^{1}H NMR). Both contaminations were also identified by peaks at *m/z* 237, 222 and 194 and at *m/z* 275/273 and 260/258, respectively (MS).

*1-(4-*sec*-Butylphenyl)-3-phenylpropane (**3**).*
4-*sec*-Butylacetophenone (**10b**) (3.52 g, 20.0 mmol) and benzaldehyde (**11**) (2.12 g, 20.0 mmol) were reacted in analogy to the condensation described above for chalcone **12a**. Work-up and recrystallisation gave 1-(4-*sec*-butylphenyl)-3-phenylprop-2-en-1-one (**12b**) (2.46 g, 47 %) as a yellow oil. B.p. 155 °C/0.005 mbar (kugelrohr); ^{1}H NMR δ/ppm: 0.83 (t, ^3J = 7.4 Hz, 3H), 1.26 (d, ^3J = 6.9 Hz, 3H), 1.63 (qui, ^3J = 7.4 Hz, 2H), 2.68 (sex, ^3J = 7.0 Hz, 1H), 7.31 and 7.98 (AA'BB', 4H), 7.39−7.43 (m, 3H), 7.55 and 7.82 (AB, 2H), 7.62−7.66 (m, 2H); MS *m/z* (%): 264 (73, $M^{+\bullet}$), 263 (85), 235 (56), 207 (100), 161 (33), 117 (19), 103 (66), 91 (34), 77 (54); IR ν/cm^{-1}: 3064, 3032, 2966, 2933, 2877, 1664, 1610, 1449, 1332, 1305, 1219, 1181, 1033, 1012, 767; accurate mass (EI-MS): $C_{19}H_{20}O$ calcd.: 264.1514; found: 264.1511.

Chalcone **12b** (1.66 g, 6.3 mmol) was subjected to catalytic hydrogenation in ethyl acetate (20 mL) in the presence of Adam's catalyst (from $PtO_2 \cdot xH_2O$, 20 mg) at ambient temperature and pressure. Work-up gave 1-



Scheme 4. Syntheses of 1-(4-trimethylsilylphenyl)-3-phenylpropane (**4**). Reagents, conditions and yields: (a) $N_2H_4 \cdot H_2O$, KOH, DEG (20 °C → 120 °C → 195 °C, 8 h); (b) *n*-BuLi/Et_2O (−20 °C, 15 min), then $(CH_3)_3SiCl$ (−20 °C → +20 °C, 30 min), 70 %.

(4-*sec*-butylphenyl)-3-phenylpropan-1-one (**13b**) (1.13 g, 68 %) as a colourless liquid. B.p. 120 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 0.81 (t, ^3J = 7.4 Hz, 3H), 1.24 (d, ^3J = 6.9 Hz, 3H), 1.61 (qui, ^3J = 7.3 Hz, 2H), 2.66 (sex, ^3J = 7.0 Hz, 1H), 3.06 (t, ^3J = 7.7 Hz, 2H), 3.29 (t, ^3J = 7.7 Hz, 2H), 7.18−7.33 (m, 5H), 7.26 and 7.90 (AA'BB', 4H); MS *m/z* (%): 266 (21, $M^{+\bullet}$), 237 (10), 209 (48), 176 (10), 161 (100), 147 (8), 132 (12), 117 (10), 105 (23), 91 (37), 77 (18); IR ν/cm^{-1}: 3066, 3032, 2966, 2932, 2877, 1681, 1605, 1453, 1415, 1291, 1212, 1183, 978, 698; accurate mass (EI-MS): $C_{19}H_{22}O$ calcd.: 266.1671; found: 266.1672.

Hydrogenolysis of dihydrochalcone **13b** (266 mg, 1.0 mmol) under 4 bar, as described above for compound **7**, gave hydrocarbon **3** (yield 50−80 %) as a colourless liquid**.** B.p. 115 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 0.82 (t, ^3J = 7.4 Hz, 3H), 1.22 (d, ^3J = 7.0 Hz, 3H), 1.57 (qui, ^3J = 7.2 Hz, 2H), 1.95 (qui, ^3J = 7.7 Hz, 2H), 2.56 (sex, ^3J = 7.0 Hz, 1H), 2.63 (t, ^3J = 7.8 Hz, 2H), 2.66 (t, ^3J = 7.8 Hz, 2H), 7.07−7.13 (m, 4H), 7.15−7.20 (m, 3H), 7.26−7.31 (m, 2H); MS *m/z* (%): 252 (60, $M^{+\bullet}$), 237 (6), 223 (100), 161 (6), 147 (12), 131 (17), 119 (24), 117 (29), 105 (28), 91 (52), 77 (11); IR ν/cm^{-1}: 3030, 2964, 2933, 2861, 1513, 1495, 1453, 828, 743, 698; accurate mass (EI-MS): $C_{19}H_{24}$ calcd.: 252.1878; found: 252.1876.

*[1,1-D$_2$]-1-(4-*sec*-Butylphenyl)-3-phenylpropane (**3a**)*
This hydrocarbon was obtained by reduction of dihydrochalcone **13b** (266 mg, 1 mmol) with $LiAlD_4/AlCl_3$ in analogy to the procedure given above for compound **1a** as a colourless liquid (60−80 %). B.p. 120 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 0.82 (t, ^3J = 7.4 Hz, 3H), 1.22 (d, ^3J = 6.9 Hz, 3H), 1.57 (qui, ^3J = 7.3 Hz, 2H), 1.94 (t, ^3J = 7.7 Hz, 2H), 2.56 (sex, ^3J = 7.1 Hz, 1H), 2.65 (t, ^3J = 7.7 Hz, 2H), 7.09−7.30 (m, 9H); MS *m/z* (%): 254 (53, $M^{+\bullet}$), 225 (100), 149 (13), 133 (16), 132 (22), 119 (31), 118 (45), 117 (29), 105 (38), 93 (33), 92 (45), 91 (74), 77 (21); D content (MS) 80 % (65 % d_2, 27 % d_1, 9 % d_0). The product of elimination was observed by the signals at δ/ppm: 3.54 (d) and 6.32 (t) (^{1}H NMR) and by the peaks at *m/z* 251, 222 and 194 (MS).

*[3,3-D$_2$]-1-(4-*sec*-Butylphenyl)-3-phenylpropane (**3b**)*
Condensation of 4-*sec*-butylbenzaldehyde (**14b**) (0.40 g, 2.5 mmol) and acetophenone (**15**) (0.30 g, 2.5 mmol) in analogy to the procedure given above for chalcone **12a** furnished 3-(4-*sec*-butylphenyl)-1-phenylprop-2-en-1-one (**16b**) (0.35 g, 52 %) as a yellow oil. B.p. 170 °C/0.02 mbar (kugelrohr); ^{1}H NMR δ/ppm: 0.84 (t, ^3J = 7.4 Hz, 3H), 1,26 (d, ^3J = 6.9 Hz, 3H), 1.62 (qui, ^3J = 7.3 Hz, 2H), 2.65 (sex, ^3J = 7.0 Hz, 1H), 7.24 and 7.59 (AA'BB', 4H), 7.48−7.61 (m, 3H), 7.50 and 7.81 (AB, ^3J = 15.7 Hz, 2 H), 8.00−8.04 (m, 2H); MS *m/z* (%): 264 (42, $M^{+\bullet}$), 263 (31), 249 (8), 235 (80), 207 (100), 178 (11), 131 (21), 129 (21), 128 (21), 115 (20), 105 (48), 91 (22), 77 (55), 57 (8); IR ν/cm^{-1}: 3063, 2966, 2932, 2877, 1663, 1602, 1331, 1216, 1016, 777, 693; accurate mass (EI-MS): $C_{19}H_{20}O$ calcd.: 264.1514; found: 264.1509.

Chalcone **16b** (300 mg, 1.14 mmol) was subjected to catalytic hydrogenation in ethyl acetate (7 mL) in the presence of Adam's catalyst (from $PtO_2 \cdot xH_2O$, 10 mg) at ambient temperature and pressure. Work-up gave 3-(4-*sec*-butylphenyl)-1-phenylpropan-1-one (**17b**) (210 mg (72 %) as a colourless liquid. B.p. 150 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 0.82 (t, ^3J = 7.4 Hz, 3H), 1.22 (d, ^3J = 7.0 Hz, 3H), 1.58 (qui, ^3J = 7.4 Hz, 2H), 2.57 (sex, ^3J = 7.0 Hz, 1H), 3.04 (t, ^3J = 7.7 Hz, 2H), 3.30 (t, ^3J = 7.8 Hz, 2H), 7.11 and 7.18 (AA'BB', 4H), 7.42−7.47 (m, 2H), 7.53−7.58 (m, 1H), 7.95−7.98 (m, 2H); MS *m/z* (%): 266 (59, $M^{+\bullet}$), 237 (100), 147 (12), 131 (18), 117 (42), 105 (72), 91 (24), 77 (47); IR ν / cm^{-1}: 3026, 2965, 2932, 2877, 1687, 1449, 1203, 742, 698; accurate mass (EI-MS): $C_{19}H_{22}O$ calcd.: 266.1671; found: 266.1664.

Reduction of dihydrochalcone **17b** (150 mg, 0.56 mmol) with $LiAlD_4/AlCl_3$ in analogy to the procedure given above for compound **1a** furnished hydrocarbon **3b** as a colourless liquid (yield 60−80 %). B.p. 130 °C/0.01 mbar (kugelrohr); ^{1}H NMR δ/ppm: 0.82 (t, ^3J = 7.4 Hz, 3H), 1.22 (d, ^3J = 7.0 Hz, 3H), 1.58 (qui, ^3J = 7.1 Hz, 2H), 1.94 (t, ^3J = 7.7 Hz, 2H), 2.56 (sex, ^3J = 7.1 Hz, 1H), 2.62 (t, ^3J = 7.8 Hz, 2H), 7.10−7.35 (m, 9H); MS *m/z* (%): 254 (69, $M^{+\bullet}$), 225 (100), 147 (29), 131 (35), 118 (45), 117 (58), 107 (27), 105 (41), 93 (65), 92 (54), 91 (65), 77 (17). D content (MS): 92 % (84 % d_2, 15 % d_1, 1 % d_0). The product of elimination was observed by signals at δ/ppm 3.52 (d) and 6.36 (t) (^{1}H NMR) and by peaks at *m/z* 251, 222 and 194 (MS), and the chloropropane derivative was recognized at *m/z* 289/287 and 260/258 (MS).

*1-Phenyl-3-(4-trimethylsilylphenyl)propane (**4**)*
A mixture of 1-(4-bromophenyl)-3-phenylpropan-1-one (**18**)[33] (1.55 g, 5.4 mmol), hydrazine hydrate (85 %) (1.0 mL, 16 mmol) and powdered KOH (1.18 g, 21 mmol) in diethylene glycol (10 mL) was stirred and heated to 120 °C for 2 h and then to 195 °C for 8 h. Work-up by extraction of the product with diethyl ether gave an oily residue, which was purified by kugelrohr distillation affording 1-(4-bromophenyl)-3-phenylpropane (**19**) in good yield as a colourless liquid. B.p. 140 °C/0.01 mbar (220 °C/30 mm);[34] ^{1}H NMR δ/ppm: 1.91 (qui, ^3J = 7.7 Hz, 2H), 2.58 (t, ^3J = 7.7 Hz, 2H), 2.61 (t, ^3J = 7.7 Hz, 2H), 7.03 and 7.38 (AA'BB', 4H), 7.14−7.20 (m, 3H), 7.25−7.30 (m, 2H); MS *m/z* (%): 274/276 (38/41, $M^{+\bullet}$), 193 (22), 185 (16), 183 (17), 171 (26), 169 (26), 115 (30), 105 (56), 92 (100), 91 (72), 77 (27), 65 (27),

51 (20). IR ν/cm^{-1}: 3030, 2940, 2862, 1603, 1487, 1453, 1072, 1010, 747, 698.

A solution of compound **19** (520 mg, 1.9 mmol) in anhydrous diethyl ether (5 mL) was stirred and cooled to −20 °C and a solution of *n*-butyllithium (1.6 M in *n*-hexane) (1.25 mL, 2.0 mmol) was added. Stirring was continued for 15 min at the same temperature and then a solution of trimethylsilyl chloride (300 mg, 2.80 mmol) in anhydrous diethyl ether (2.0 mL) was added. The mixture was allowed to warm to ambient temperature within *ca*. 30 min and then hydrolysed by addition of water. Work-up by extraction with diethyl ether gave a liquid residue, which was purified by kugelrohr distillation affording compound **4** as a colourless liquid (355 mg, 70 %). B.p. 90 °C/0.01 mbar; ^{1}H NMR δ/ppm: 0.25 (s, 9H), 1.96 (qui, ^3J = 7.7 Hz, 2H), 2.64 (t, ^3J = 7.6 Hz, 2H), 2.65 (t, ^3J = 7.6 Hz, 2H), 7.14−7.19 (m, 3H), 7.18 and 7.44 (AA'BB', 4 H), 7.25−7.30 (m, 2H); MS *m/z* (%): 268 (18, $M^{+\bullet}$), 253 (100), 161 (6), 148 (6), 91 (11), 73 (10); IR ν/cm^{-1}: 3068, 3032, 2957, 2861, 1601, 1496, 1453, 1247, 1108, 857, 838, 751, 697; accurate mass (EI-MS): $C_{18}H_{24}Si$ calcd.: 268.1647; found: 268.1643.

RESULTS AND DISCUSSION

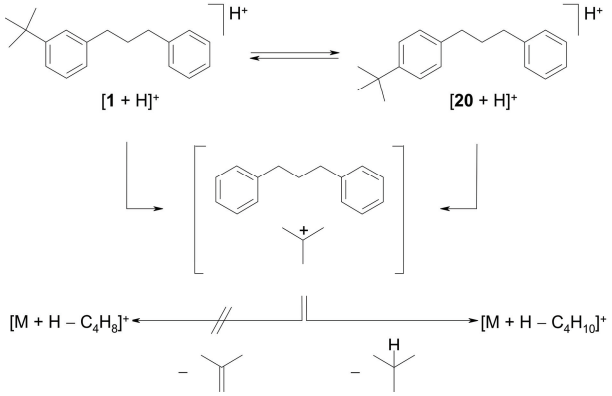
The *tert*-butyl cation represents the most stable isomer among the $C_4H_9^+$ ions and its protonolytic release from the $[M + H]^+$ ions of *tert*-butyl-substituted α,ω-diarylalkanes is particularly facile.[8,35–38] In addition, α,ω-diphenylalkanes (higher than diphenylmethane) are known to be considerably more basic than simple monoalkylbenzenes.[39–42] Nevertheless, one of the simplest $[M + H]^+$ ions studied so far, protonated 1-(4-*tert*-butylphenyl)-3-phenylpropane (**20**, *cf.* Scheme 5) exclusively undergoes hydride abstraction (*i.e.*, loss of isobutane) and no proton transfer (*i.e.*, loss of isobutene).[16,17] Thus, the Lewis acidity of *t*-$C_4H_9^+$ ions prevails and hydride transfer is the lowest energy path of long-lived $[\mathbf{20} + H]^+$ ions. As compared to the *para*-substituted ions, protonated 1-(3-*tert*-butylphenyl)-3-phenylpropane $[\mathbf{1} + H]^+$, was expected to form the same I/N complex but possibly with a somewhat higher internal excitation energy. The *meta*-position of the *tert*-butyl group should give rise to an increased activation barrier towards protonolysis since *ipso*-protonation of a *meta*-dialkylbenzene is less favourable than *ipso*-protonation of the respective *para*-isomer, an assumption based on the wealth of local proton affinities of aromatic compounds available nowadays.[43–47] This could result in a "hotter" I/N complex when formed from ions $[\mathbf{1} + H]^+$, instead of $[\mathbf{20} + H]^+$, and a lower selectivity of fragmentation (Scheme 5). The difference of the proton affinities of the two isomers could well lie in the range of PA(**1**) − PA(**20**) ≈ 15−20 kJ mol^{-1}.[48]

However, we found that the fragmentation of long-lived $[\mathbf{1} + H]^+$ ions is identical with that of the isomeric ions $[\mathbf{20} + H]^+$ studied previously. The *meta*-isomer undergoes almost exclusive loss of isobutane on the metastable ions' timescale (Figure 1); isobutene loss is negligible in strict parallel to the fragmentation behaviour of the *para*-isomer.[16,17] Moreover, the regioselectivity ($k_{\alpha\text{-H}}/k_{\omega\text{-H}}$) and the kinetic isotope effect (k_H/k_D) associated with the hydride transfer are virtually the same with both isomers. Thus, long-lived [α,α-D_2]- and the [β,β,γ,γ-D_4]-labeled isotopologues $[\mathbf{1a} + H]^+$ and $[\mathbf{1b} + H]^+$ were found to eliminate C_4H_{10} and C_4H_9D in the same ratios, 1.60 ± 0.05 (Figure 2).[17]

Obviously, the conceivable difference in the heats of formation of the isomeric ions $[\mathbf{1} + H]^+$ and $[\mathbf{20} + H]^+$ does not affect the fragmentation behaviour of the I/N complexes. Rather, we have to assume a rapid equilibrium between ions $[\mathbf{1} + H]^+$ and $[\mathbf{20} + H]^+$ (Scheme 5), with the former being the predominant isomer in analogy to protonated *meta*- *vs*. *para*-xylene.[49,50] In any case, the $C_4H_9^+$ ion can move freely between the aromatic moieties of the 1,3-diphenylpropane molecule and abstract a hydride from either of the two benzylic methylene groups with the same probability, *i.e.*, the regioselectivity $k_{\alpha\text{-H}}/k_{\omega\text{-H}}$ = 1.0. The results confirm the conclusion that the barrier of protonolysis is considerably lower than that of the hydride transfer from the I/N complex. The kinetic isotope effect k_H/k_D = 1.60 is identical with those found for the isobutane elimination from numerous other $[M + H]^+$ ions of *tert*-butyl-substituted α,ω-diarylalkanes bearing electronically similar aryl groups.[20] Notably, the same or very similar k_H/k_D values were also found for long-lived simple 4-(*tert*-butyl)-1-ethylbenzenium ions.[19,50,51]

At variance from all previous studies on the I/N complex formation from the $[M + H]^+$ ions of *tert*-butyl-substituted α,ω-diphenylalkanes and related hydrocarbons studied so far, we also investigated the fragmentation of two sets of protonated α,ω-diphenylalkanes bearing *secondary* alkyl groups, *viz.* the *para*-isopropyl and the *para*-*sec*-butyl analogues, $[\mathbf{2} + H]^+$ and $[\mathbf{3} + H]^+$, respectively. The corresponding [α,α-D_2]- and [ω,ω-D_2]-labeled isotopomers $[\mathbf{2a} + H]^+$, $[\mathbf{2b} + H]^+$ and $[\mathbf{3a} + H]^+$, $[\mathbf{3b} + H]^+$ were studied as well.

In contrast to the *tert*-butyl-substituted analogue, the fragmentation of long-lived ions $[\mathbf{2} + H]^+$ is dominated by the proton transfer, *i.e.*, by the loss of propene (87 % Σ, Figure 3). Only a minor fraction of the ions eliminates propane (10 % Σ), and a still minor fraction (3 % Σ) undergoes consecutive loss of propane and benzene, giving rise to ions $C_9H_9^+$ (*m/z* 117). Thus, in the case of the isopropyl cation released into the I/N



Scheme 5. Identical unimolecular fragmentation of the ion/neutral complex generated from protonated 1-(4-*tert*-butylphenyl)-3-diphenylpropane, [**20** + H]$^+$,[16,17] and its *meta*-isomer, [**1** + H]$^+$ (this work).

complex, intra-complex proton transfer clearly prevails over hydride abstraction. It is obvious that the increased Brønsted acidity of the *s*-$C_3H_7^+$ ion is the origin of the drastic change of the fragmentation behaviour. From well established thermodynamic data, *viz.* the proton affinities PA($CH_3CH{=}CH_2$) = 751.6 kJ mol^{-1} and PA[$(CH_3)_2C{=}CH_2$] = 802.1 kJ mol^{-1},[41,42,52] it can be deduced that, as compared to *tert*-butyl analogues [**1** + H]$^+$, the proton transfer channel is by 50.5 kJ mol^{-1} more favourable in the case of ions [**2** + H]$^+$. However, the hydride ion affinity of the *s*-$C_3H_7^+$ ion is also higher than that of the *t*-$C_4H_9^+$ ion, *viz.* by *ca*. 61 kJ mol^{-1},[53] thus facilitating the hydride transfer channel as well. Obviously, the minor thermodynamic difference ($\Delta\Delta_r H$ = −10 kJ mol^{-1}) should operate in favour of the hydride transfer but not of the proton transfer, a result which cannot account for the drastic change in the ratios of alkane-to-alkene losses observed for ions [**1** + H]$^+$ and [**2** + H]$^+$. Therefore, we have to assume that the hydride transfer channels are disfavoured by considerable activation energies as compared to the proton transfer channels, in contrast to the results of recent computational work.[54]

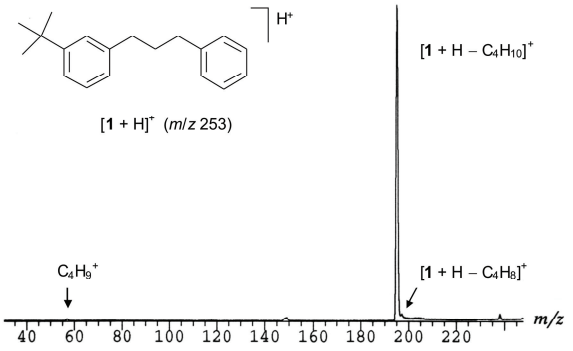


Figure 1. MIKE spectrum of ions [**1** + H]$^+$ (*m*/*z* 253) showing almost exclusive loss of C_4H_{10} (*m*/*z* 195). All peaks except that at *m*/*z* 57 (≤ 1 %) originate from the fragmentation of isobaric molecular radical cations [$^{13}C_1$]-**1**$^{+\bullet}$.

As mentioned above, it is well known that the protolytic release of secondary alkyl groups from *sec*-alkylbenzenium ions are energetically more demanding than that of tertiary alkyl groups from *tert*-alkylbenzenium ions. This is also reflected in the standard CI(CH_4) spectra of **1** and **2**. In the case of **1** (and **20**), the free *t*-$C_4H_9^+$ ions (*m*/*z* 57) give rise to the base peak, whereas the peak indicating free *s*-$C_3H_7^+$ ions (*m*/*z* 43) from **2** has minor relative intensity. However, the increased reactivity of the *s*-$C_3H_7^+$ ion, once being released into the complex, is reflected by the formation of ions $C_9H_9^+$ (*m*/*z* 117) produced by the consecutive loss of benzene from the [**2** + H − C_3H_8]$^+$ ions. I/N complexes bearing the *tert*-butyl cation undergo such secondary reactions only in special cases, *e.g.*, with tri- and tetrabenzylmethanes as the neutral constituent.[21]

Notwithstanding the finding that the hydride transfer is of minor importance in the fragmentation of long-lived ions [**2** + H]$^+$, the mobility of the *s*-$C_3H_7^+$ ions within the complex can be probed. In fact, the MIKE spectra of [D_2]-labeled ions [**2a** + H]$^+$ and [**2b** + H]$^+$ exhibit the losses of C_3H_8 and C_3H_7D in again identical ratios (Figure 4). Moreover, in spite of the low signal-to-noise ratio, it appears that the ratio of hydride *vs.* deuteride abstraction has remained unchanged with respect to the previous cases (*e.g.* [**1a** + H]$^+$ and [**1b** + H]$^+$), being again $k_H/k_D \approx 1.6$, and that the regioselectivity is again unity ($k_{\alpha\text{-H}}/k_{\omega\text{-H}} = 1$). Thus, in fact, the *s*-$C_3H_7^+$ ions released into the I/N complex can move freely to abstract a hydride from either of the two benzylic methylene groups, just as do the *t*-$C_4H_9^+$ ions in their respective I/N complexes, and the activation barrier towards hydride transfer is similar to the previous cases.

A quite similar fragmentation behaviour was found for protonated 1-(4-*sec*-butylphenyl)-3-phenylpropane [**3** + H]$^+$ and its deuterium-labeled analogues [**3a** + H]$^+$ and [**3b** + H]$^+$ (Figures 5 and 6), confirming the formation of I/N complexes consisting of a secondary alkyl cation and 1,3-diphenylpropane. The MIKE spectrum of ions [**3** + H]$^+$ is dominated by the peak corresponding to the loss of butane(s) (95 % Σ) and only very minor amounts of C_4H_{10} elimination is indicated. As compared to ions [**2** + H]$^+$, the hydride abstraction is diminished even further to *ca*. 5 % of the total fragmentation, and the consecutive elimination of benzene is negligible (< 0.2 %).

At first glance, the still increased dominance of the proton transfer in ions [**3** + H]$^+$, as compared to ions [**2** + H]$^+$, came to us as a surprise. However, a strict thermochemical assessment in analogy to that made above

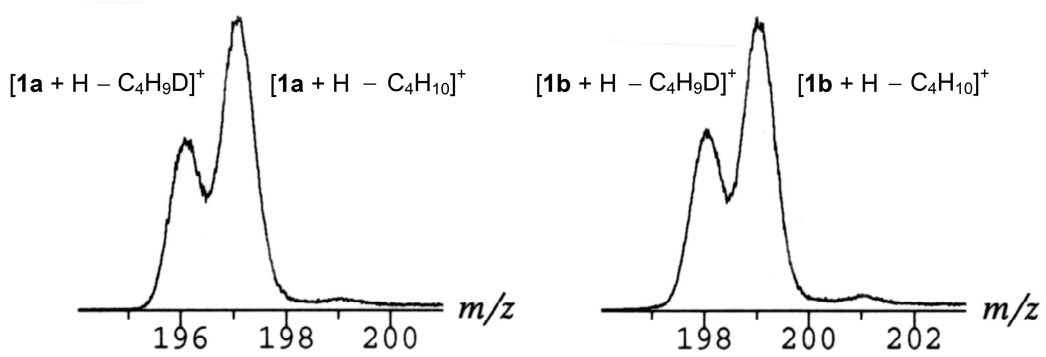


Figure 2. Partial MIKE spectra of ions [**1a** + H]$^+$ (*m/z* 255) and [**1b** + H]$^+$ (*m/z* 257) showing the competing losses of C_4H_{10} and C_4H_9D in virtually identical ratios.

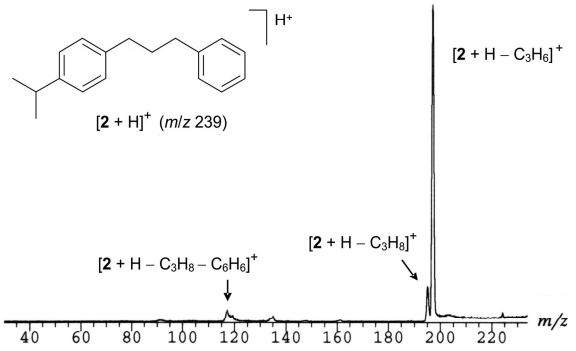


Figure 3. MIKE spectrum of ions [**2** + H]$^+$ (*m/z* 239) showing competing losses of C_3H_6 (*m/z* 197) and C_3H_8 (*m/z* 195). The peak at *m/z* 117 is due to the consecutive losses of C_3H_8 and C_6H_6. All other peaks originate from the fragmentation of isobaric molecular radical cations [$^{13}C_1$]-**2**$^{+\bullet}$.

provides a satisfying rationalisation for the further suppression of the hydride transfer in ions [**3** + H]$^+$ as compared to proton transfer. A comparison of the proton transfer channels for ions [**3** + H]$^+$ and ions [**1** + H]$^+$ results in a difference of 55 kJ mol^{-1} operating in favour of the *sec*-butyl ion [PA(*E*-$CH_3CH{=}CHCH_3$) = 747 kJ mol^{-1} and PA[$(CH_3)_2C{=}CH_2$] = 802.1 kJ mol^{-1}].[41] (Note that *s*-$C_4H_9^+$ is by 3 kJ mol^{-1} more acidic than *s*-$C_3H_7^+$ as (*E*)-2-butene is less basic than propene by this amount.)[41] However, the hydride ion affinity of the *s*-$C_4H_9^+$ ion surpasses that of the *t*-$C_4H_9^+$ ion by only 46 kJ mol^{-1}.[55] Therefore, in the case of the I/N complex formed from ions [**3** + H]$^+$, the thermodynamic energy requirements for the hydride transfer channel are even larger than in the case of the ions [**2** + H]$^+$ discussed above. The minor thermodynamic difference calculated above for the latter ions ($\Delta\Delta_rH$ = − 10 kJ mol^{-1}) is now reversed, giving a stronger facilitation for the proton transfer ($\Delta\Delta_rH$ = + 9 kJ mol^{-1}). Thus, the kinetic barrier towards the hydride transfer should be more efficient

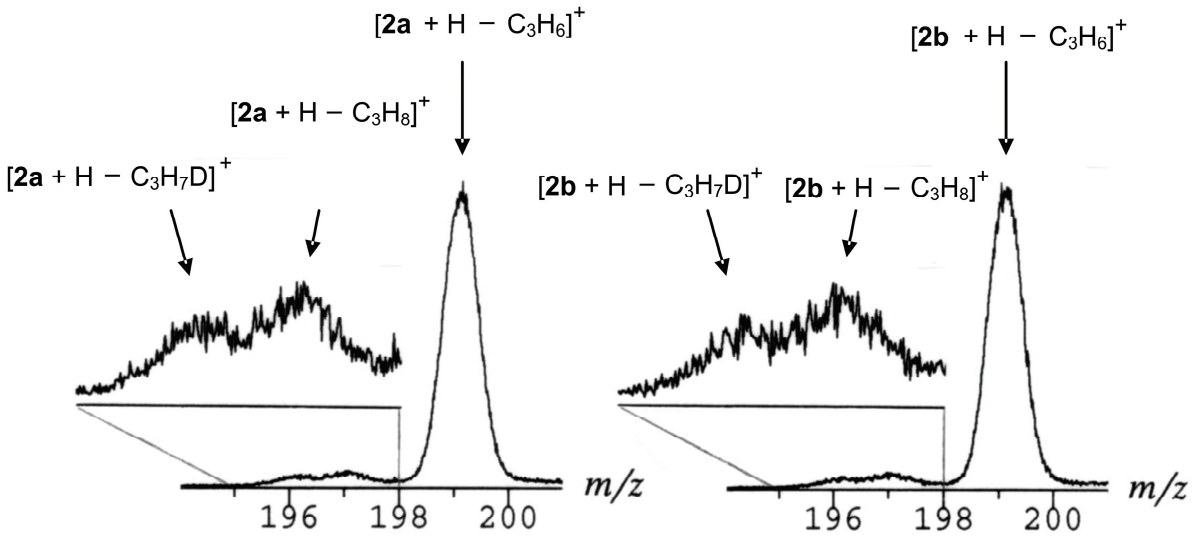


Figure 4. Partial MIKE spectra of ions [**2a** + H]$^+$ and [**2b** + H]$^+$ (*m/z* 241 both) showing the competing losses of C_3H_8 and C_3H_7D in virtually identical ratios, besides the dominating loss of C_3H_6.

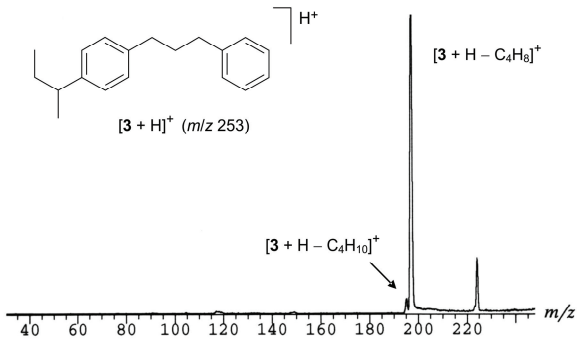


Figure 5. MIKE spectrum of ions $[\mathbf{3} + H]^+$ (*m*/*z* 253) showing competing losses of C_4H_8 (*m*/*z* 197) and C_4H_{10} (*m*/*z* 195). The peak at *m*/*z* 224 originates from the fragmentation of isobaric molecular radical cations $[^{13}C_1]$-$\mathbf{3}^{+\bullet}$.

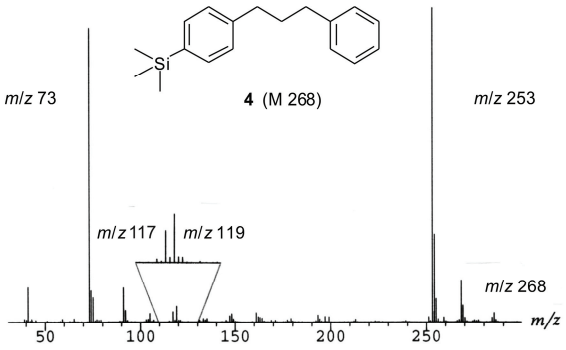


Figure 7. CI(CH_4) spectrum of protonated 1-phenyl-3-(4-trimethylsilylphenyl)propane (**4**). Note that the spectrum is dominated by the fragmentation of the molecular radical cations $\mathbf{4}^{+\bullet}$.

with ions $[\mathbf{3} + H]^+$ than with ions $[\mathbf{2} + H]^+$. In other words, the observed further decrease of the alkane loss from long-lived ions $[\mathbf{3} + H]^+$ is mainly due to the lower hydride ion affinity of the *s*-$C_4H_9^+$ ion as compared to that of the *s*-$C_3H_7^+$ ion in their respective I/N complexes.

Despite the very low relative abundance of the $[\mathbf{3} + H - C_4H_{10}]^+$ ions, the MIKE spectra of the deuterium-labeled analogues $[\mathbf{3a} + H]^+$ and $[\mathbf{3b} + H]^+$ confirm the overall picture (Figure 6). Once again, the equivalency of the benzylic methylene groups is evident from the identical relative rates of the C_4H_{10} and the C_4H_9D losses. And, within admittedly relatively large limits of experimental error, the ubiquitous kinetic isotope effect, $k_H/k_D = 1.6$ (± 0.2), is again recognised from the spectra, yielding the regioselectivity $k_{\alpha\text{-H}}/k_{\omega\text{-H}} = 1$.

The strong predominance of the alkene elimination from the *sec*-alkyl-substituted ions $[\mathbf{2} + H]^+$ and $[\mathbf{3} + H]^+$ parallels the behaviour of simple mononuclear propyl- and butylbenzenium ions.[7,8] Beyond the intermediacy of I/N complexes en route to alkene (and benzene) elimination, it has been demonstrated that the alkyl cation may undergo skeletal isomerisation within the I/N complex. In particular, *sec*-butylbenzenium ions[8] have been shown to isomerise to *tert*-butylbenzenium ions and it has been argued that the latter isomer dissociates much faster than the former. Therefore, the fragmentation of long-lived, metastable $[C_6H_6C_4H_9]^+$ ions mostly reflects the fraction of *sec*-butylbenzenium ions that survive the flight to the field-free region, whereas the fraction of the *tert*-butylbenzenium ions mostly fragments already within the CI source. Similarly distinct fragmentation behaviour was found for protonated 1,1- and 1,2-diphenylethane.[56] Therefore, we believe that the loss of C_4H_{10} from ions $[\mathbf{3} + H]^+$ does *not* reflect a small fraction of I/N complexes containing a *t*-$C_4H_9^+$ ion formed

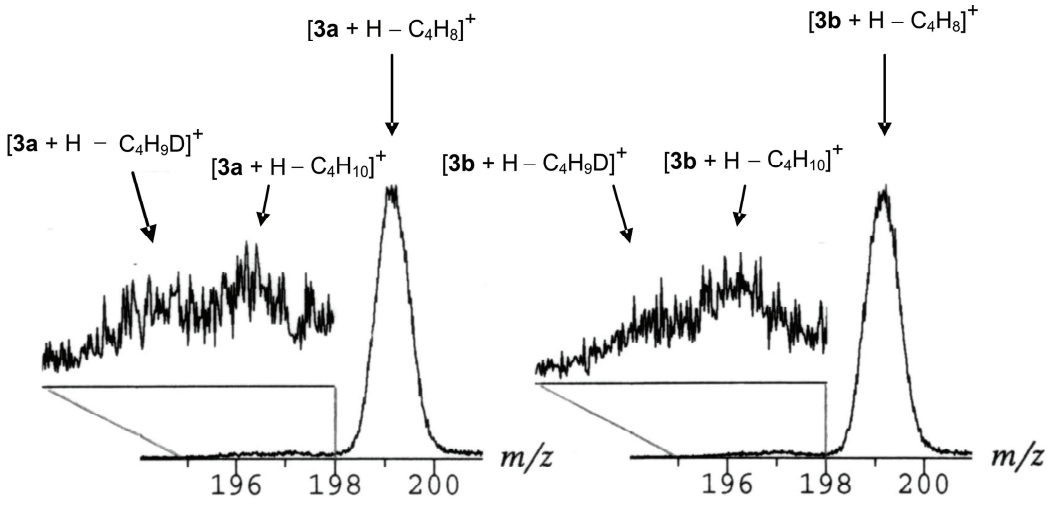
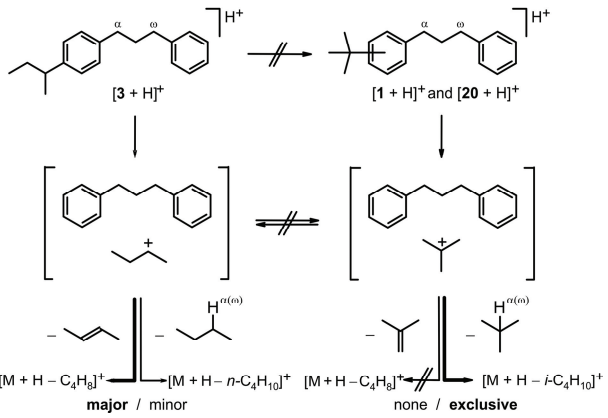


Figure 6. Partial MIKE spectra of ions $[\mathbf{3a} + H]^+$ and $[\mathbf{3b} + H]^+$ (*m*/*z* 255 both) showing the competing losses of C_4H_{10} and C_4H_9D in virtually identical ratios, besides the dominating loss of C_4H_8.

by isomerisation within the I/N complex.[57] Rather, we think that metastable ions $[\mathbf{3} + H]^+$ lose *n*-butane (not isobutane) *via* the I/N complex containing a *s*-$C_4H_9^+$ ion – although the striking similarity of the regioselectivity and kinetic isotope effects may suggest the presence of the *t*-$C_4H_9^+$ ion. In fact, and very notably, this view is corroborated by the finding that propane elimination from ions $[\mathbf{2} + H]^+$ shows the very same characteristics as does the C_4H_{10} elimination from ions $[\mathbf{1} + H]^+$, in spite of the fact that the *s*-$C_3H_7^+$ ion has to retain its secondary structure. Thus, the results presented here suggest that, in fact, gaseous secondary and tertiary carbenium ions solvated by 1,3-diphenylpropane undergo intra-complex hydride transfer independent of their secondary or tertiary constitution.

Finally, the reactivity of the tertiary and secondary alkyl cation within their I/N complexes with 1,3-diphenylpropane will be briefly contrasted to that of the trimethylsilyl cation. Protonated 1-phenyl-3-(4-trimethylsilylphenyl)propane (**4**) was synthesised and subjected to chemical ionisation under the same conditions that were used for the pure hydrocarbons **1**–**3**. The standard CI(CH_4) spectrum (Figure 7) exhibits an $[M + H]^+$ peak at *m*/*z* 269, the intensity of which only slightly exceeds that expected for the peak of the isobaric $[^{13}C_1]$-$M^{+\bullet}$ ions. Whereas the peak at *m*/*z* 253 corresponds to the typical primary fragmentation the molecular radical cation of a trimethylsilyl derivative giving $[M - CH_3]^+$ ions, the major peak at *m*/*z* 73 represents the $Si(CH_3)_3^+$ ion itself, which may well originate from both ions $\mathbf{4}^{+\bullet}$ and $[\mathbf{4} + H]^+$. However, the MIKE spectrum of the ions with *m*/*z* 269 was found to reflect mainly the fragmentation of the naturally occurring radical cations $[^{13}C_1]$-$\mathbf{4}^{+\bullet}$, and only a minor peak at *m*/*z* 73 points to the protonolysis of the $[^{12}C_1]$-$[\mathbf{4} + H]^+$ ions leading to the elimination of the intact 1,3-diphenylpropane. Thus, as may have been expected on thermochemical grounds, there is no indication for the formation a reactive I/N complex $[Si(CH_3)_3^+ \cdots C_6H_5(CH_2)_3C_6H_5]$ through loss of $(CH_3)_3SiH$ or $(CH_3)_2Si{=}CH_2$. Also, the long-lived $[\mathbf{4} + H]^+$ ions do not undergo consecutive losses, such as the conceivable formation of ions $[\mathbf{4} + H - (CH_3)_3SiH - C_6H_6]^+$ (*m*/*z* 117).



Scheme 6. Formation and distinct fragmentation of two isomeric non-interconverting I/N complexes, $[C_4H_9^+ \cdots C_6H_5CH_2CH_2CH_2C_6H_5]$, demonstrating the persistence of the *sec*-butyl cation within the complex formed from $[\mathbf{3} + H]^+$. As a consequence, butenes (most probable isomer shown) and *n*-butane are lost in this case.

Thus, the Brønsted acidity and the hydride ion affinity of the trimethylsilyl cation are by far too low to compete with the direct dissociation. Obviously, much more electron-rich hydride donor and proton acceptor sites are required to allow H^- and H^+ transfer process to occur in the putative $[Si(CH_3)_3^+ \cdots$ diarylalkane] complexes. It has to be noted here that, by contrast, radiolytic experiments run under thermalising conditions have shed much light on the chemistry of $[Si(CH_3)_3^+ \cdots$ arene] complexes, including $[Si(CH_3)_3^+ \cdots C_6H_5(CH_2)_2C_6H_5]$, formed by electrophilic attack.[30,58,59]

CONCLUSION

Our previous findings concerning the free mobility of the *tert*-butyl cation within long-lived gaseous ion/neutral complexes with α,ω-diphenylalkanes have been confirmed and extended to secondary alkyl cations (Scheme 6). It is obvious, and no surprise, that the initial position of the *tert*-butyl group prior to proton-induced release from the 1,3-diphenylpropane backbone into the I/N complex $[t\text{-}C_4H_9^+ \cdots C_6H_5CH_2CH_2CH_2C_6H_5]$ does not affect its reactivity. More remarkable, however, is the observation that the secondary alkyl cations in the analogous complexes $[s\text{-}C_3H_7^+ \cdots C_6H_5CH_2CH_2CH_2C_6H_5]$ and $[s\text{-}C_4H_9^+ \cdots C_6H_5CH_2CH_2CH_2C_6H_5]$ behave identical, as far as their Lewis acid character is concerned: The hydride ion transfer from the benzylic positions of the neutral partner is non-regioselective and the same kinetic isotope effect operates. The dominating Brønsted acidity observed is in line with the secondary structure of the alkyl cations. Moreover, the fact that the *sec*-butyl cation behaves analogous to the *sec*-propyl cation suggests that the even the hydride abstraction by the former ion is not preceded by (partial) skeletal isomerisation to *tert*-butyl cation. Therefore, it appears that all the characteristics found for the I/N complexes generated from *tert*-alkyl-substituted diarylalkanes pertain for such formed from *sec*-alkyl-substituted diarylalkanes as well. This is also worth considering with respect to the co-operation of the two aromatic moieties of the diphenylalkanes during both the proton and hydride transfer steps; such a co-operation obviously occurs but its details are hardly understood on the experimental grounds presented in this work.[60]

Therefore, it may be a great future challenge to extend such studies to larger alkyl (and cycloalkyl) cations solvated by an α,ω-diphenylalkane in the isolated state, and to model such prototypical cases of gaseous ion/neutral complexes by means of theory.

REFERENCES

1. P. Longevialle, *Mass Spectrom. Rev.* **11** (1992) 157−192.
2. (a) T. H. Morton, *Tetrahedron* **38** (1982) 3195−3243; (b) T. H. Morton, *Org. Mass Spectrom.* **27** (1992) 353−368; (c) T. H. Morton, *Via Ion-Neutral Complexes*, in: P. B. Armentrout (Ed.), *Encyclopedia of Mass Spectrometry*, Vol. 1, Elsevier, Amsterdam, 2003, pp. 467−479; (d) T. H. Morton, *Theoretical Models for Ion-Neutral Complexes in Unimolecular Ion Decompositions*, in: N. M. M. Nibbering (Ed.), *Encyclopedia of Mass Spectrometry*, Vol. 4, Elsevier, Amsterdam, 2005, pp. 165−173.
3. R. D. Bowen, *Acc. Chem. Res*. **24** (1991) 364−371.
4. (a) D. J. McAdoo, *Mass Spectrom. Rev.* **7** (1988) 363−393; (b) D. J. McAdoo and T. H. Morton, *Acc. Chem. Res.* **26** (1993) 295−302.
5. Among the most striking examples is the fragmentation of 3,20-difunctionalised steroids under EI conditions, *e.g.*: P. Longevialle and R. Botter, *J. Chem. Soc., Chem. Commun.* (1980) 823−825. For more, see refs. 1−4.
6. D. Kuck and U. Filges, *Org. Mass Spectrom.* **23** (1988) 643−653.
7. D. Berthomieu, H. E. Audier, J. P. Denhez, C. Monteiro, and P. Mourgues, *Org. Mass Spectrom.* **26** (1991) 271−275.
8. D. Berthomieu, H. E. Audier, C. Monteiro, and J. P. Denhez, *Rap. Commun. Mass Spectrom.* **5** (1991) 415−420.
9. D. Berthomieu, V. Brenner, G. Ohanessian, J. P. Denhez, P. Millié, and H. E. Audier, *J. Phys. Chem*. **99** (1995) 712−720.
10. S. Hammerum and H. E. Audier, *J. Chem. Soc., Chem. Commun.* (1988) 860−861.
11. S. Dohmeier-Fischer, N. Kramer, and H. F. Grützmacher, *Eur. Mass Spectrom*. **1** (1995) 3−10.
12. C. E. Hudson and D. J. McAdoo, *Int. J. Mass Spectrom. Ion Proc.* **59** (1984) 325−332.
13. J. P. Denhez, H. E. Audier, and D. Berthomieu, *Rap. Commun. Mass Spectrom.* **9** (1995) 1210−1212.
14. D. Kuck, *J. Labelled Comp. Radiopharm.* **50** (2007) 360−365.
15. J. L. Holmes, K. J. Jobst, and J. K. Terlouw, *J. Labelled Comp. Radiopharm*. **50** (2007) 1115−1123.
16. D. Kuck and C. Matthias, *J. Am. Chem. Soc.* **114** (1992) 1901−1903.
17. C. Matthias and D. Kuck, *Org. Mass Spectrom.* **28** (1993) 1073−1081.
18. C. Matthias, K. Weniger, and D. Kuck, *Eur. Mass Spectrom.* **1** (1995) 445−455.
19. C. Matthias, S. Anlauf, K. Weniger, and D. Kuck, *Int. J. Mass Spectrom.* **199** (2000) 155−187.
20. C. Matthias, A. Cartoni, and D. Kuck, *Int. J. Mass Spectrom.* **255**−**256** (2006) 195−212.
21. C. Matthias and D. Kuck, *Int. J. Mass Spectrom.* **217** (2002) 131−151.
22. C. Matthias, B. Bredenkötter, and D. Kuck, *Int. J. Mass Spectrom.* **228** (2003) 321−339.
23. H. E. Audier, F. Dahhani, A. Milliet, and D. Kuck, *J. Chem. Soc., Chem. Commun.* (1997) 429−430.
24. U. Filges and H. F. Grützmacher, *Org. Mass Spectrom.* **21** (1986) 673−680.
25. G. Thielking, U. Filges, and H. F. Grützmacher, *J. Am. Soc. Mass Spectrom.* **3** (1992) 417−426.
26. H. E. Audier, F. Dahhani, A. Milliet, and D. Kuck, unpublished work.
27. J. Bialecki, J. Ruzicka, and A. B. Attygalle, *J. Mass Spectrom.* **41** (2006) 1195−1204.
28. B. Chiavarino, M. E. Crestoni, S. Fornarini, and D. Kuck, *J. Phys. Chem. A* **107** (2003) 4619−4624.
29. B. Chiavarino, M. E. Crestoni, S. Fornarini, and D. Kuck, *Int. J. Mass Spectrom. Ion Processes* **148** (1995) 215−228.
30. M. E. Crestoni, S. Fornarini, and D. Kuck, *J. Phys. Chem.* **99** (1995) 3144−3149.
31. K. Bowden, A. Dal Pozzo, and C. K. Duah, *J. Chem. Res.* (1990) 2801−2830.
32. R. E. Lyle and L. P. Paradis, *J. Am. Chem. Soc.* **77** (1955) 6667−6668.
33. J. R. Johnson, T. L. Jacobs, and A. M. Schwartz, *J. Am. Chem. Soc.* **60** (1938) 1885−1889.
34. D. N. Kursanov, N. M. Loim, V. A. Baranova, L. V. Moiseeva, L. P. Zulakaev, and Z. N. Parnes, *Synthesis* (1973) 420−422.
35. D. K. Sen Sharma, S. Ikuta, and P. Kebarle, *Can. J. Chem.* **60** (1982) 2325−2331.
36. (a) A. G. Harrison, P. H. Lin, and H. W. Leung, *Adv. Mass Spectrom.* **7B** (1978) 1394−1401; (b) J. A. Herman and A. G. Harrison, *Org. Mass Spectrom.* **16** (1981) 423−427.
37. J. P. Denhez, H. E. Audier, and D. Berthomieu, *Org. Mass Spectrom.* **28** (1993) 704−706.
38. For reviews on gaseous alkylbenzenium and protonated arenes, see: (a) D. Kuck, *Mass Spectrom. Rev.* **9** (1990) 583−630; (b) D. Kuck, *Protonated Aromatics and Arenium Ions*, in: N. M. M. Nibbering (Ed.), *Encyclopedia of Mass Spectrometry*, Vol. 4, Elsevier, Amsterdam, 2005, pp. 229−242.
39. (a) M. Meot-Ner (Mautner), L. W. Sieck, and P. Ausloos, *J. Am. Chem. Soc.* **103** (1981) 5342−5348; (b) M. Mautner, *Acc. Chem. Res.* **17** (1984) 186−193.
40. M. E. Crestoni, S. Fornarini, and D. Kuck, *J. Phys. Chem.* **99** (1995) 3150−3155.
41. E. P. L. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data* **27** (1998) 413−656.
42. *NIST Standard Reference Database Number 69*, March 2005 Release; National Institute of Standards and Technology, Gaithersburg, MD 20899; (http://webbook.nist.gov/chemistry).
43. J. L. Devlin III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.* **98** (1976) 1990−1992.
44. M. Eckert-Maksić, M. Klessinger, and Z. B. Maksić, *J. Phys. Org. Chem.* **8** (1995) 435−441.
45. M. Eckert-Maksić, M. Klessinger, and Z. B. Maksić, *Chem. Eur. J.* **2** (1996) 1251−1257.
46. Z. B. Maksić, B. Kovačević, and D. Kovaček, *J. Phys. Chem. A* **101** (1997) 7446−7453.
47. Z. B. Maksić and M. Eckert-Maksić, *Intrinsic Proton Affinity of Substituted Aromatics*, in: C. Párkányi (Ed.), *Theoretical and Computational Chemistry*, Vol. 5, *Theoretical Organic Chemistry*, Elsevier, Amsterdam,1998, pp. 203−231.
48. The differences between the proton affinities of *meta*- and *para*-xylene give a good approximation: PA(*m*-xylene) − PA(*p*-xylene) = (812.1 − 794.4) kJ mol^{-1} = 17.7 kJ mol^{-1} (refs. 41 and 42).
49. Also note that a *meta*-methyl group in 1,2-diphenylethane gives rise to a similar stabilisation: GB(*m*-$CH_3C_6H_4CH_2CH_2C_6H_5$) − GB($C_6H_5CH_2CH_2C_6H_5$) = 25 kJ mol^{-1} (ref. 40).
50. H. E. Audier, C. Monteiro, P. Mourgues, and D. Berthomieu, *Org. Mass Spectrom.* **25** (1990) 245−246.
51. The ubiquity of the isotope effect in alkylbenzene-type $[M + H]^+$ ions is remarkable and not well understood yet. With electron-rich aryl groups (*e.g.* 4-$MeOC_6H_4$), this value is markedly decreased (k_H/k_D = 1.07), whereas electron-poor aryl groups (*e.g.* 3-FC_6H_4) give rise to a considerable increase (k_H/k_D = 2.30) (ref. 20).

52. Use of the ΔPA value is preferred to here over ΔGB to compare better with the difference of the hydride ion affinities. The corresponding ΔGB value is 52.9 kJ mol^{-1} for isobutene *vs* propene and 55.7 kJ mol^{-1} for isobutene *vs* (*E*)-2-butene (refs. 41 and 42).
53. This difference reflects the exothermicity of the hydride ion transfer reaction
$(CH_3)_2CH^+ + (CH_3)_3CH \rightarrow (CH_3)_2CH_2 + (CH_3)_3C^+$ (1)
the reaction enthalpy of which is $\Delta_r H(1) = \Delta_f H[(CH_3)_2CH_2] + \Delta_f H[(CH_3)_3C^+] - \Delta_f H[(CH_3)_2CH^+] - \Delta_f H[(CH_3)_3CH] = [-104.7 + 711 - 801 - (-134.2)]$ kJ mol^{-1} = −61 kJ mol^{-1} (data taken from ref. 42).
54. For a recent and extensive theoretical treatment of hydride ion transfer reactions, see: S. Gronert and J. R. Keeffe, *J. Am. Chem. Soc.* **127** (2005) 2324−2333.
55. The hydride ion transfer reaction
$CH_3CH_2CH^+CH_3 + (CH_3)_3CH \rightarrow CH_3(CH_2)_2CH_3 + (CH_3)_3C^+$ (2)
is exothermic by $\Delta_r H(2) = \Delta_f H[CH_3(CH_2)_2CH_3] + \Delta_f H[(CH_3)_3C^+] - \Delta_f H[(CH_3CH_2CH^+CH_3] - \Delta_f H[(CH_3)_3CH] = [-125.6 + 711 - 766 - (-134.2)]$ kJ mol^{-1} = −46 kJ mol^{-1} (data taken from ref. 42).
56. D. Kuck and H. E. Audier, *C. R. Acad. Sci. Paris, Sér. II* **324** (1997) 717−724.
57. The kinetic energy release observed for the alkane and alkene losses are minor only (*e.g.*, T^{50} = 20 meV for the C_4H_{10} loss and T^{50} = 22 meV for the C_4H_8 loss from [**3** + H]$^+$). Therefore, there is no hint for the peak shapes pointing to preceding isomerisation of the *s*-C_4H_9 ions (*cf*. ref. 13).
58. (a) S. Fornarini, *J. Org. Chem*. **53** (1988) 1314−1316; (b) F. Cacace, M. E. Crestoni, and S. Fornarini, *J. Am. Chem. Soc*. **114** (1992) 6776−6784; (c) M. E. Crestoni and S. Fornarini, *Angew. Chem.* **106** (1994) 1157−1159, *Angew. Chem. Int. Ed*. **33** (1994) 1094−1096.
59. B. Chiavarino, M. E. Crestoni, S. Fornarini, J. Lemaire, L. Mac Aleese, and P. Maître, *ChemPhysChem* **6** (2005) 437−440.
60. The authors thank two referees for mentioning the importance of the co-operation of the two aromatic rings and their (common) action on the alkyl cation bound within the I/N complex. However, the details of the overall scenario are very difficult to clarify. Even the structure of the [M + H − alkane]$^+$ ions is not known here – is it an acyclic, benzylic ion or a protonated 1-phenylindane formed by cyclization [*cf.* D. Kuck, *Int. J. Mass Spectrom. Ion Processes* **117** (1992) 441−455].

SAŽETAK

Plinoviti [$C_nH_{2n+1}^+$ ··· 1,3-difenilpropan] ion/neutralni kompleksi koji sadrže alkil katione različitih kiselosti i afiniteta prema hidridnom ionu

Carsten Matthias i Dietmar Kuck

Department of Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany

Plinoviti ion/neutralni (I/N) kompleksi [R^+ ··· $C_6H_5CH_2CH_2CH_2C_6H_5$] s R = *t*-$C_4H_9^+$, *s*-$C_2H_2^+$ i *s*-$C_4H_9^+$ priređeni su protoniranjem odgovarajućih prekursor spojeva, R-$C_6H_4CH_2CH_2CH_2C_6H_5$, u kemijsko ionizacijskom (CI) izvoru sector-field masenog spektrometra. Fragmentacija ovih I/N kompleksa i nekih deuterijski-obilježenih izotopoanaloga na vremenskoj skali metastabilnih iona (20-30 μs), studirana pomoću MIKE spektrometrije, otkriva da (i) početni položaj supstituenta R = *t*-$C_4H_9^+$ (*meta*- ili *para*-) u prstenu ne utječe na njihovu intra-kompleksnu reaktivnost, (ii) u reakciji fragmentacije *s*-$C_3H_7^+$ i *s*-$C_4H_9^+$ iona dominira transfer protona na neutralni 1,3-difenilpropan, ali oduzimanje hidridnog iona u suprotnom smjeru je samo djelom kompetitivno, (iii) sekundarni alkil kationi pokazuju istu regioselektivnost ($k_{\alpha-H}/k_{\omega-H}$ = 1.0) i kinetički izotopni efekt (k_H/k_D = 1.6) u kanalu za transfer hidrida kao i tercijarni alkil kationi, (iv) *s*-$C_4H_9^+$ ioni ne podliježu izomerizaciji kostura do *t*-$C_4H_9^+$ ione unutar I/N kompleksa. Pokušaji karakterizacije trimetilsilil kompleksa, [$Si(CH_3)_3^+$ ··· $C_6H_5CH_2CH_2CH_2C_6H_5$], pomoću CI/MIKE spektrometrije u analognim uvjetima bili su neuspješni.