ELSEVIER

International Journal of Mass Spectrometry 179/180 (1998) 129–146

International Journal of Mass Spectrometry

Mobile protons in large gaseous alkylbenzenium ions. The 21-proton equilibration in protonated tetrabenzylmethane and related "proton dances"

Dietmar Kuck[a,b,*], Allan Petersen[c], Uwe Fastabend[a]

[a]*Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, D-33501 Bielefeld, Germany*
[b]*Fachbereich Chemie und Chemietechnik, Universität-Gesamthochschule Paderborn, Warburger Straße 100, D-33098 Paderborn, Germany*
[c]*Department of Chemistry, The H.C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark*

Received 27 March 1998; accepted 3 June 1998

Abstract

The proton transfer between the protonated arene (arenium) and the neutral arene rings of protonated tribenzylmethane (**8**), tetrabenzylmethane (**9**), several higher triphenylisoalkylalkanes (**10**–**12**) as well as of protonated 2-benzylindane (**13**) and 2,2-dibenzylindane (**14**) has been studied in detail. In all regimes of the ions' lifetimes (ion source, first and second field-free region), the interannular proton exchange leads to complete equilibration. As an extreme, 21 protons are randomized in protonated tetrabenzylmethane **9** prior to fragmentation within ~1 μs. The hydrogens of the aliphatic or alicyclic spacer do not participate in the exchange process. The interannular proton exchange is independent of the fragmentation path; both single and twofold loss of benzene from **8** and protonated tris(β-phenylethyl)methane **12** are preceded by complete proton equilibration between all of the rings. The individual proton transfer rate for **9** is estimated to be $>10^8$ s^{-1}, and the readiness of proton equilibration is assigned to the efficient internal solvation, or spectator ring effects, in these large alkylbenzenium ions, possibly giving rise to a merge between the numerous inter- and intra-annular proton transfer steps during the ions' lifetime. (Int J Mass Spectrom 179/180 (1998) 129–146) © 1998 Elsevier Science B.V.

Keywords: Mobile protons; Proton transfer; Alkylbenzenes, protonated; Arenium ions; Alkylbenzenes, branched

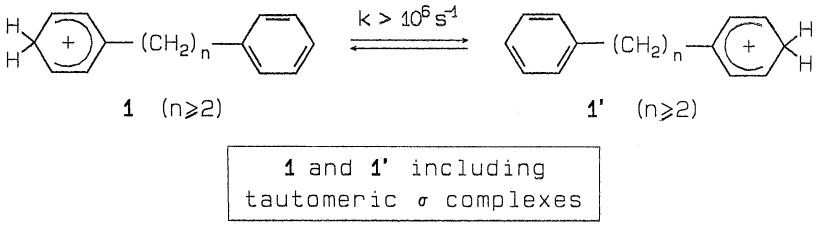
1. Introduction

Proton transfer processes make part of the most fundamental processes of matter. Acid-base pairs determine the driving force of numerous reactive systems and represent a key element of stability and information in static chemical arrangements, including both natural and nonnatural compounds. Of particular interest are proton transfer reactions that may be so fast that they enable the reactants to exchange a set or even all of the hydrogens within the time window of observation. Among these, proton equilibration of heteroatomic functionalities, such as X–H (X = O, NR, CO_2, SO_3) are well known, as are hydrogen/deuterium (H/D) exchange processes involving acidic C–H bonds and heteroatomic X–H groups [1]. Proton transfer or proton exchange pro-

* Corresponding author. kuck@chema.uni-bielefeld.de

Dedicated to Professor Fulvio Cacace in long-standing admiration.

PII S1387-3806(98)14168-4



Scheme 1.

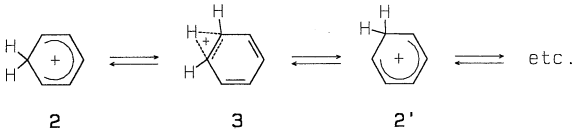
cesses *between* carbon sites, i.e. those involving both C–H donors and C–H acceptors are much less common, although they are very important in synthetic organic chemistry where lithium or other organometallic reagents are employed [2].

In a series of studies over the past two decades we have investigated gas-phase proton transfer processes occurring between protonated arenes (arenium ions) and arenes [3]. Most of this work was carried out on unimolecular reaction systems such as diphenylalkane-derived ions (**1**) formed by protonation ($[M + H]^+$ ions) [4,5] or by hydride abstraction ($[M - H]^+$ ions isomerizing to $[M' + H]^+$ type ions by cyclization) [6]. In a few cases, bimolecular arenium ion/arene reactions were carried out by us [7] and by others [8] and showed that the bimolecular proton transfer between carbon sites is, in fact, slow in the dilute gas phase. A recent study by DePuy et al. [9] employing a *dense* gas-phase technique, viz. flowing afterglow, demonstrated that low energy, long-lived arenium ion/arene complexes may be forced to undergo extensive proton exchange leading to a nevertheless incomplete equilibration of all arene protons between the partners.

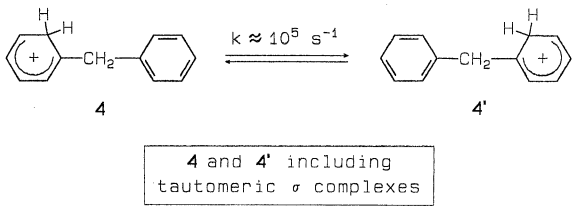
The surprising feature of intramolecular proton exchange is the high rate of the process, leading to the *complete* equilibration of, for example, 11 ring protons in protonated α,ω-diphenylalkanes **1** (Scheme 1) within $\sim$1 μs, i.e. the mean lifetime of an $[M + H]^+$ ion in the chemical ionization source of a mass spectrometer.

In a recent study, Cacace et al. [10] have determined the activation energies of the interannular proton (H^+ and D^+) transfer in **1** by obtaining kinetic information on thermally equilibrated ions by the use of a radiolytic technique [11]. It turned out that, strikingly, the Arrhenius activation energies of the interannular transfer of a proton ($E^a_{\text{inter}} = 6.3 \pm 0.2$ kcal mol^{-1}) or a deuteron ($E^a_{\text{inter}} = 8.0 \pm 0.2$ kcal mol^{-1}) is very similar to the activation energy of the well-known *intra*-annular process, i.e., the proton and deuteron "ring walks" in isolated arenium ions. The latter elementary process has been a long-standing topic of fundamental interest and debate [12–16]. Nevertheless, experimental studies in the liquid phase [17,18] *and* in the gas phase [9,19] as well as various computational approaches [14–16] have settled the view that the edge-protonated species **3** represents the transition state of the intra-annular proton shift (Scheme 2) at an energy of 7.0 $\pm$ 1.0 kcal mol^{-1} above the ground state of **2**. To date, the report by Cacace et al. [19] for the intra-annular ring walk ($E^a_{\text{intra}} = 7.6 \pm 0.2$ kcal mol^{-1}) is unique in providing the only experimentally determined energy data for the gas-phase process.

Whereas the Arrhenius activation energies of the intra- and interannular proton transfer steps are very close, the preexponential factor of the interannular proton transfer was found to fall short of that of the intra-annular process by one order of magnitude [10,19]. Although this difference appears less than expected, the ring-to-ring proton transfer clearly requires a relatively high degree of orientation of the



Scheme 2.

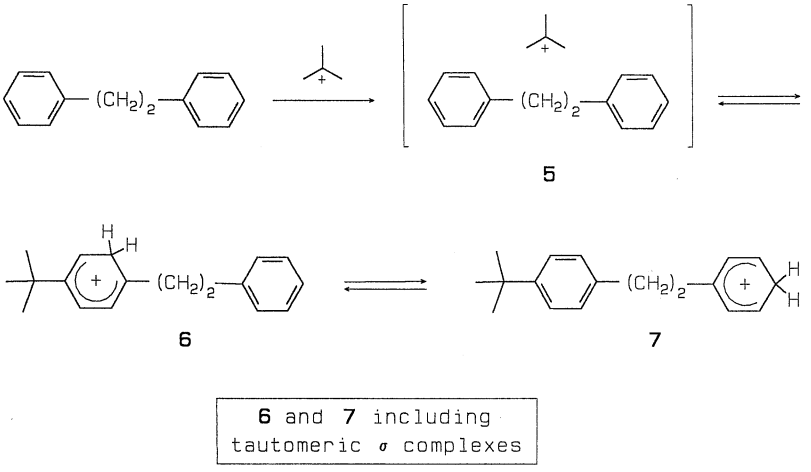


Scheme 3.

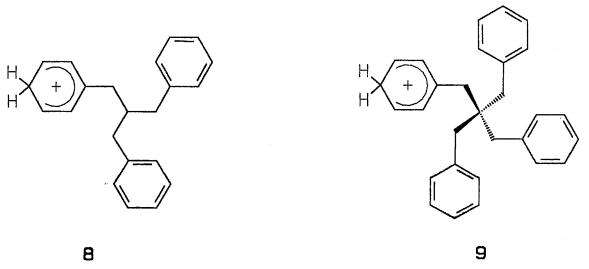
acid and base partners that increases the activation entropy of the process with increasing length of the aliphatic chain. Nevertheless, we reported that even in homologues as high as protonated 1,20-diphenyleicosane (**1**, $n = 20$) the proton exchange between the formally very remote arene rings is complete, i.e. "statistical," prior to fragmentation of the metastable ions [4b].

One of the few systems in which the inter- and intra-annular proton-exchange pathways were observed as separated processes, i.e., as reactions occurring at different relative rates, represents protonated diphenylmethane (**4**). Owing to the particularly low energy of fragmentation towards loss of benzene on the one hand, and to the steric hindrance on the other, both operating against rapid interannular proton exchange, the ring-to-ring proton transfer in **4** is slowed down to $k_{inter} \approx 10^5$ s^{-1}, whereas the ring walk process is still fast ($k_{intra} \geq 10^6$ s^{-1}) for metastable ions (Scheme 3) [20,21].

Again, unlike **4**, the more flexible higher homologues of **1** may gain a driving force in favour of the intra-annular proton transfer from internal solvation effects. Although introduced in the 1960's already [22–24], the role of internal solvation in gas-phase ion chemistry has remained unclear for a long time. By recurring to protonated α,ω-diphenylalkanes as the model substrates, the effect of the second neutral arene ring on the course, and readiness of electrophilic aromatic substitution in the gas phase has been studied by the "La Sapienza" group [25]. It has been shown [26] that not only the gas-phase basicity of the higher diphenylalkanes is subject to subtle effects of the "spectator ring," but also that the presence of additional aromatic spectator rings renders the encounter of a *tert*-butyl cation to form the ion-neutral complex **5** irreversible. The electrophilic attack is followed by interannular proton exchange (**6** ⇌ **7**, Scheme 4) [27,28]. However, ion-molecule complexes such as **5** are formed, in reverse, by dissociation of excited (metastable) alkylbenzenium ions such as **6** [29], but also from simpler gaseous σ complexes of alkylbenzenes [30–33]. Also, spectator-ring effects were observed upon fragmentation of protonated 1,3-diphenylpropanes bearing a *tert*-



Scheme 4.

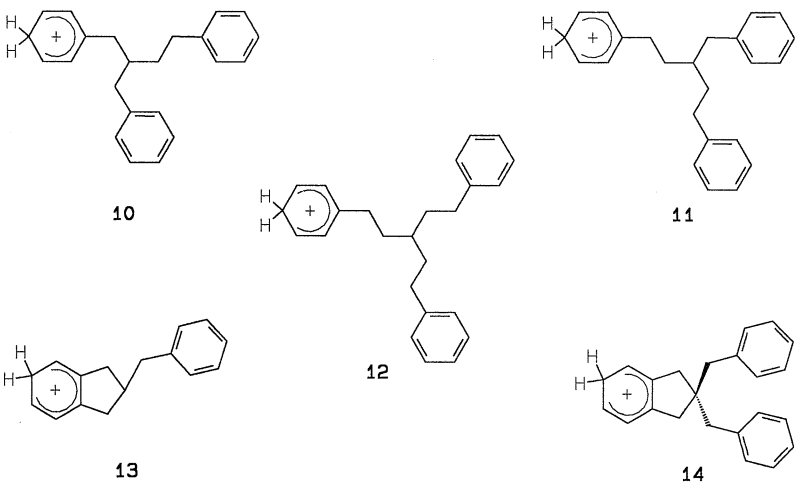


8 and **9** including tautomeric σ complexes

butyl and methyl substituents each at separate rings [34].

Thus, the variety of phenomena connected with the gas-phase chemistry of protonated arenes, and protonated diphenylalkanes in particular, points to an interesting interplay of both energy and entropy effects. This article and the following one [35] demonstrate this in a particular way, in that two phenomena are being carried to an extreme. The key systems under investigation are branched congeners of **1** containing three or even four arene rings, viz. protonated tribenzylmethane [1,3-diphenyl-2-(phenylmethyl)propane], **8**, and protonated tetrabenzylmethane [1,3-diphenyl-2,2-bis(phenylmethyl)propane], **9**. Also, some additional protonated triphenylisoalkanes, **10**–**12**, as homologues of **8**, and two isocyclic congeners, protonated 2-benzylindane, **13**, and protonated 2,2-dibenzylindane, **14**, were investigated.

The present article is focused on the interannular proton transfer in these large phenylisoalkylbenzenium ions, whereas the following one concentrates on the unprecedented and intriguing fragmentation of these species. In preliminary communications [36] on gaseous protonated tri- and tetrabenzylmethane, we already stated that ions **8**, **9**, and **12** exhibit not only a fast, and again complete ("statistical") proton exchange involving in these cases 16 and, respectively, 21 protons prior to fragmentation. Protonated tri- and tetrabenzylmethane, in particular, also show an unprecedented twofold loss of benzene, in competition with, or instead of, the single loss of benzene usually observed [3–5]. Notably, the twofold loss of benzene from **8** and **9** was found to occur *within the same field-free region* of a double-focusing mass spectrometer, a fragmentation behaviour that parallels the relatively rare cases of consecutive "metastable transitions" [37], i.e. twofold elimination of other stable



10 – **14** including tautomeric σ complexes

neutrals such as carbon monoxide from ionized anthraquinones, in particular [38–40]. Whereas the mechanistic details of the unusual double benzene loss from **8**, **9**, and related species will be discussed in the following article, the present one reports in detail on the fast proton exchange in various deuterium labeled analogues of ions **8**–**14**.

2. Experimental details

2.1. Materials

General: Identity and purity of the synthetic intermediates and products were analyzed by ^{1}H NMR spectroscopy (500 MHz: Bruker DRX 500; 300 MHz: Bruker AM 300; 80 MHz: Bruker WP 80; 60 MHz: Varian EM 360 A) and mass spectrometry [electron ionization (EI), 70 eV; Finnigan MAT 311 A and CH4-2F]; the label contents were obtained by evaluating the $M^{+\cdot}$ peak groups of 70 eV EI mass spectra. Oily products were purified (if necessary) by repeated Kugelrohr distillation. Most of the syntheses were carried out on a 1–2 gram scale and yields of the final products were not optimized.

Tribenzylmethanes: The chemical ionization (CI) precursor of **8**, 1,3-diphenyl-(2-phenylmethyl)propane, was synthesized by twofold benzylation of acetophenone according to Conia et al. [41], followed by reduction of the product, ω,ω-dibenzylacetophenone, with hydroiodic acid (HI) and red phosphorus according to Hill et al. [42]. However, this method is not suitable for the synthesis of [D_5]phenyl-labeled isotopomers due to considerable loss of the label. Alternatively, dibenzyl ketone was reacted with benzyl Grignard to give tribenzylmethanol [43]; mass spectrometry (70 eV) *m*/*z* 211 (100, $[M - C_7H_7]^+$), 210 (24), 193 (46), 92 (42), 65 (52); ^{1}H NMR (60 MHz, $CDCl_3$) δ = 7.18 (15 H), 2.72 (s, 6 H), 1.46 (s, 1 H). The carbinol was converted to 2-benzyl-1,3-diphenylpropene [44] by dehydration in dimethyl sulfoxide (DMSO) at 170 °C (yield 73%); mass spectrometry (70 eV) *m*/*z* 284 (34, $[M]^{+\cdot}$), 193 (82), 191 (10), 178 (19), 165 (10), 152 (4), 115 (100), 91 (77), 65 (23); ^{1}H NMR (60 MHz, $CDCl_3$): δ = 7.13 (s, 15 H), 6.48 (s, 1 H), 3.51 (s, 2 H), 3.32 (s, 2 H). Catalytic hydrogenation (Pd/C in EtOH) of the olefin furnished the [D_0]tribenzylmethane (88%); colourless solid, mp 85.5 °C; mass spectrometry (70 eV) *m*/*z* 286 (17, $[M]^{+\cdot}$), 195 (2), 194 (5), 193 (2), 117 (24), 115 (4), 92 (29), 91 (100), 78 (2), 77 (2), 65 (9), 63 (2); ^{1}H NMR (60 MHz, $CDCl_3$): δ = 7.20 (br s, 15 H), 2.55 (m, 7 H). The CI precursor of **8a**, 1,3-diphenyl-2-([D_5]phenylmethyl)propane, was prepared from [ring-D_5]benzyl bromide via the [ring-D_5] carbinol, 1,3-diphenyl-2-([D_5]phenylmethyl)-2-propanol; mass spectrometry (70 eV) *m*/*z* 216 (40, $[M - C_7H_7]^+$), 215 (13, $[M - C_7H_3D_4]^+$), 211 (20, $[M - C_7H_2D_5]^+$), 198 (6), 197 (5), 193 (6), 96 (38), 95 (19), 94 (10), 93 (10), 92 (25), 91 (100); ^{1}H NMR (60 MHz, $CDCl_3$) δ = 7.16 (m, 10 H), 2.71 (s, 6 H), 1.42 (s, 1 H). Subsequent dehydration gave the corresponding mixture of [ring-D_5]-labeled 2-benzyl-1,3-diphenylpropenes; mass spectrometry (70 eV) *m*/*z* 289 (53, $M^{+\cdot}$), 198 (90), 197 (18), 196 (10), 195 (8), 194 (16), 193 (49), 120 (14), 119 (28), 118 (10), 117 (11), 116 (27), 115 (100), 96 (34), 95 (10), 94 (3), 93 (5), 92 (18), 91 (78); ^{1}H NMR (80 MHz, $CDCl_3$) δ = 7.10–7.20 (m, 10 H), 6.56 (br s, 1 H), 3.55 (s, 2 H), 3.36 (d, J = 1.1 Hz, 2 H). Hydrogenation of the olefin furnished the [ring-D_5]tribenzylmethane; colourless solid, mp 85 °C; mass spectrometry (70 eV) *m*/*z* 291 (20, $[M]^{+\cdot}$), 200 (2), 199 (2), 198 (2), 197 (0.5), 196 (0.5), 195 (1), 194 (1.5), 193 (1), 121 (5), 120 (2), 119 (2), 118 (5), 117 (21), 116 (2), 115 (5), 96 (46), 95 (5), 94 (1), 93 (3), 92 (27), 91 (100), 65 (15); ^{1}H NMR (60 MHz, $CDCl_3$): δ = 7.18 (br s, 10 H), 2.58 (m, 7 H). The CI precursor of **8b**, [1,2-D_2]-1,3-diphenyl-2-(phenylmethyl)propane, was obtained by catalytic hydrogenation of the [D_0]olefin using deuterium gas (>99%) and $RhCl(PPh_3)_3$ in benzene [45]; mass spectrometry (70 eV) *m*/*z* 288 (42, $[M]^{+\cdot}$), 197 (5), 196 (8), 195 (6), 120 (10), 119 (40), 118 (27), 93 (34), 92 (100), 91 (88); ^{1}H NMR (60 MHz, $CDCl_3$): δ = 7.18 (br s, 15 H), 2.58 (m, 5 H). Label contents were >98% in both cases.

Tetrabenzylmethanes: The CI precursor of **9**, 1,3-diphenyl-2,2-bis(phenylmethyl)propane [43,46], was synthesized by threefold benzylation of acetophenone with sodium *tert*-amylate (3.0 equiv) in benzene to

give ω,ω,ω-tribenzylacetophenone (82%) or, as described previously by Conia [40], by benzylation of ω,ω-dibenzylacetophenone (see above). Again, reduction with HI and red phosphorus [45] is unfavourable in the case of [ring-D] labeling. Instead, the phenone was reduced by hydrogenolysis with Pd/C in ethanol (5 bar, 40 °C) or by treatment with $LiAlH_4/AlCl_3$ in diethyl ether [47]. The latter method gives the far better yields (90%) since hydrogenolysis is accompanied by significant hydrogenation of the aromatic rings. The hydrocarbon forms colourless crystals, mp 163.5 °C; mass spectrometry (70 eV): *m*/*z* 376 (2%, $M^{+\cdot}$), 284 (13), 207 (71), 193 (14), 181 (25), 117 (17), 115 (19), 105 (12), 103 (4), 91 (100), 79 (7), 78 (4), 77 (10), 65 (22); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.23 (s, 20 H), 2.71 (s, 8 H). The CI precursor of **9a**, 1-[D_5]phenyl-3-phenyl-2,2-bis(phenylmethyl)propane (label contents >98%), was synthesized from ω,ω-dibenzylacetophenone by benzylation with [ring-D_5]benzyl bromide to give 3-[D_5]phenyl-1-phenyl-2,2-bis(phenylmethyl)propan-1-one (label contents >99%) in 77% yield, mp 128 °C; mass spectrometry (70 eV): *m*/*z* 395 (<0.1%, $M^{+\cdot}$), 304 (33, [M − C_7H_7]$^+$), 303 (3), 300 (4), 299 (17, [M − $C_7H_2D_5$]$^+$), 298 (2), 201 (12), 198 (7), 197 (6), 196 (25), 186 (13), 185 (3), 184 (2), 183 (2), 182 (3), 181 (5), 117 (5), 115 (10), 106 (10), 105 (100), 97 (5), 96 (47), 95 (7), 94 (2), 93 (2), 92 (11), 91 (80), 82 (2), 78 (5), 77 (45), 65 (10); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.05–7.35 (m, 15 H), 3.28 (s, 6 H). Subsequent reduction of the ketone furnished the [phenyl-D_5]-labeled hydrocarbon (85%) as colourless crystals, mp 164 °C; mass spectrometry (70 eV): *m*/*z* 381 (0.2%, $M^{+\cdot}$), 289 (5), 285 (1), 284 (2), 212 (11), 211 (12), 210 (4), 209 (3), 208 (8), 207 (20), 193 (14), 198 (4), 193 (5), 186 (11), 181 (11), 117 (10), 115 (7), 96 (34), 95 (5), 94 (1), 93 (2), 92 (13), 91 (100), 69 (5), 65 (8); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.18 (s, 15 H), 2.70 (s, 8 H); label contents >99%. The CI precursor of **9b**, [1,1,3,3-D_4]-diphenyl-2,2-bis(phenyl[D_2]-methyl)propane (label contents >99.3) was prepared by threefold benzylation of acetophenone with [α,α-D_2]benzyl bromide to give [3,3-D_2]-1,3-diphenyl-2,2-bis([α,α-D_2]-phenylmethyl)propan-1-one (yield 74%) as colourless crystals, mp 128.5–129 °C; mass spectrometry (70 eV): *m*/*z* 396 (<0.1%, $M^{+\cdot}$) 303 (49%, [M − $C_7H_5D_2$]$^+$), 213 (11), 209 (2), 198 (26), 196 (6), 184 (9), 182 (2), 181 (3), 180 (3), 119 (3), 118 (7), 117 (5), 116 (2), 115 (2), 105 (96), 94 (13), 93 (100), 79 (2), 78 (4), 77 (33), 67 (6), 66 (6), 65 (2); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 704–7.19 (m, 6 H), 7.13–7.33 (m, 14 H). Subsequent reduction furnished the [D_8]-labeled hydrocarbon as colourless crystals (70%), mp 165–165.5 °C; mass spectrometry (70 eV): *m*/*z* 384 (<1%, $M^{+\cdot}$), 289 (5), 213 (45), 198 (3), 197 (3), 184 (14), 121 (8), 118 (5), 117 (3), 94 (12), 93 (100), 67 (4), 66 (4); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (m, 20 H), 2.72 (s, <0.05 H).

Other triphenylisoalkanes: The CI precursor of **10**, 1,4-diphenyl-2-(phenylmethyl)-butane, was synthesized by Grignard reaction of β-phenylethyl bromide with dibenzyl ketone to give the carbinol (73%) [48]. Subsequent dehydration in DMSO at 170 °C gave a mixture of the corresponding olefins (54%); hydrogenation of this material with Pd/C in EtOH gave the triphenylisopentane as a colourless oil (bp 160 °C/0.1 mbar); mass spectrometry (70 eV): *m*/*z* 300 (9%, $M^{+\cdot}$), 131 (50), 117 (25), 116 (2), 115 (6), 105 (8), 104 (2), 103 (3), 92 (25), 91 (100), 79 (2), 78 (2), 77 (4), 65 (10), 63 (1); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 6.95–7.35 (m, 15 H), 2.50–2.72 (m, 6 H), 2.05 (m, 1 H), 1.45–1.75 (m, 2 H). In analogy, the CI precursor of **10a**, 1-[D_5]phenyl-4-phenyl-2-(phenylmethyl)butane (label contents >98%), was synthesized starting with β-[D_5]phenylethyl bromide and dibenzyl ketone to give the corresponding [D_5]carbinol (68%), followed by dehydration in DMSO to give a mixture of olefins (50%) and hydrogenation with Pd/C in EtOH yielding a colourless oil (bp 160 °C/0.1 mbar); mass spectrometry (70 eV): *m*/*z* 305 (32%, $M^{+\cdot}$), 179 (1), 178 (1), 145 (2), 135 (33), 134 (20), 133 (12), 132 (11), 131 (19), 118 (11), 117 (38), 115 (10), 110–103 (<10 each), 96 (71), 95 (15), 94 (4), 93 (5), 92 (53), 91 (100). The CI precursor of **11**, 1,5-diphenyl-3-(phenylmethyl)pentane, was synthesized by Grignard reaction of benzyl bromide and α,α′-dibenzylacetone to give the corresponding carbinol (75%), which was subjected to dehydration in DMSO to give a mixture of isomeric olefins (73%) as a yellow oil (bp 190 °C/0.05 mbar); mass spectrometry (70 eV): *m*/*z* 312

(14%, $[M]^{+\cdot}$), 222 (11), 221 (31), 143 (17), 131 (22), 130 (15), 129 (55), 128 (28), 127 (8), 118 (19), 117 (88), 115 (34), 105 (38), 104 (18), 103 (12), 92 (46), 91 (100). Subsequent hydrogenation with Pd/C in EtOH gave a colourless oil (bp 187 °C/0.14 mbar); mass spectrometry (70 eV): *m*/*z* 314 (7%, $M^{+\cdot}$), 222 (2), 145 (16), 133 (8), 131 (19), 118 (4), 117 (8), 116 (1), 115 (2), 105 (21), 104 (10), 103 (3), 92 (25), 91 (100), 79 (5), 78 (6), 77 (10), 65 (12), 63 (3); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.00–7.35 (m, 15 H), 2.55–2.80 (m, 6 H), 1.50–1.75 (m, 5 H). In the same way, the CI precursor of **11a**, 1-[D_5]phenyl-5-phenyl-3-(phenylmethyl)pentane (label contents >98), was synthesized starting from [ring-D_5]benzyl bromide and α,α'-dibenzylacetone to give the corresponding carbinol (68%) that was subjected to dehydration in DMSO to give a mixture of isomeric olefins (79%). Subsequent hydrogenation with Pd/C in EtOH gave the hydrocarbon as a colourless oil (bp 190 °C/0.15 mbar). Mass spectrometry (70 eV): *m*/*z* 319 (62%, $M^{+\cdot}$), 239 (3), 238 (4), 223 (2), 222 (3), 191 (5), 147 (9), 146 (28), 145 (69), 133 (12), 132 (15), 131 (63), 116 (9), 117 (15), 105 (26), 104 (17), 96 (39), 95 (7), 94 (4), 93 (10), 92 (53), 91 (100). 1,5-Diphenyl-3-(2-phenylethyl)pentane **12** was prepared by Grignard reaction of β-phenylethyl bromide and α,α'-dibenzylacetone to give the corresponding carbinol (78%) [49]. Dehydration in DMSO at 170 °C furnished the corresponding olefin (68%), 1,5-Diphenyl-3-(2-phenylethyl)pent-2-ene; mass spectrometry (70 eV): *m*/*z* 326 (2%, $M^{+\cdot}$), 222 (7), 131 (21), 130 (7), 129 (9), 128 (4), 118 (8), 117 (20), 105 (18), 104 (18), 103 (7), 92 (29), 91 (100); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.00–7.30 (m, 15 H), 5.38 (t, ^3J = 7.3 Hz, 1 H), 3.28 (d, ^3J = 7.2 Hz, 2 H), 2.30–2.85 (m, 8 H). This product was subjected to hydrogenation with Pd/C in ethanol (bp 155 °C/0.1 mbar); mass spectrometry (70 eV): *m*/*z* 328 (3%, $M^{+\cdot}$), 237 (1), 159 (6), 145 (6), 131 (6), 117 (10), 105 (15), 104 (9), 92 (66), 91 (100), 65 (15); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.05–7.40 (m, 15 H), 2.52–2.76 (m, 6 H), 1.54–1.69 (m, 7 H). In analogy, the CI precursor of **12a**, 1-[D_5]phenyl-5-phenyl-3-(2-phenylethyl)pentane (label contents >98), was synthesized by Grignard reaction of β-[D_5]phenylethyl bromide and α,α'-dibenzylacetone to give the corresponding carbinol (82%); mass spectrometry (70 eV): *m*/*z* 331 (11%, $[M - H_2O]^{+\cdot}$), 244 (10), 239 (6), 238 (4), 222 (4), 117 (12), 105 (23), 104 (11), 103 (5), 96 (21), 95 (11), 94 (6), 93 (7), 92 (25), 91 (100). A mixture of olefins was obtained by dehydration in DMSO (72%); mass spectrometry (70 eV): *m*/*z* 331 (12%, $[M]^{+\cdot}$), 235–240 ($\leq$2 each), 117 (21), 103–110 ($\leq$11 each), 96 (40), 95 (13), 94 (3), 93 (4), 92 (18), 91 (100). It was subjected to hydrogenation with Pd/C in ethanol (bp 160 °C/0.1 mbar). Mass spectrometry (70 eV): *m*/*z* 333 (15, $[M]^{+\cdot}$), 243 (2), 242–239 (1 each), 238 (2.5), 110 (9), 109 (5), 108 (2.5), 107 (3), 106 (4.5), 105 (23), 97 (25), 96 (48), 95 (15), 94 (9), 93 (22), 92 (67), 91 (100); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.05–7.35 (m, 10 H), 2.50–2.75 (m, 6 H), 1.57–1.70 (m, 7 H).

Benzylindanes: The CI precursor of **13a**, 2-([D_5]phenylmethyl)indane (label contents >99%), and of **13b**, 2-(phenylmethyl)-[1,1,2,3,3]indane (label contents >97%), were prepared as described previously [50]. 2,2-Dibenzylindane **14** was prepared from 2,2-dibenzylindane-1,3-dione [51] by hydrogenolysis with Pd/C in ethanol/glacial acetic acid (100:1) in a Parr shaker (25°, 5 bar), as colourless crystals (mp 64–65 °C) in 85% yield; mass spectrometry (70 eV): *m*/*z* 298 (14, $[M]^{+\cdot}$), 207 (43), 206 (35), 205 (5), 204 (5), 203 (3), 202 (3), 129 (16), 128 (9), 127 (3), 115 (15), 92 (21), 91 (100), 65 (16); ^{1}H NMR (60 MHz, $CDCl_3$): δ = 7.15–7.35 (m, 14 H), 2.78 (br s, 8 H). The CI precursor of **14a**, 2-phenylmethyl-2-([D_5]phenylmethyl)indane (label contents >97%), was prepared from 2-benzylindane-1,3-dione [52] by benzylation with [ring-D_5]benzyl bromide to give 2-phenylmethyl-2-([D_5]phenylmethyl)indane-1,3-dione as yellowish crystals, mp 157.5 °C; ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.14–7.30 (m, 9 H), 2.75 (br s, 8 H). Subsequent hydrogenolysis with Pd/C in a Parr shaker (25°, 5 bar) furnished the [D_5] hydrocarbon as colourless crystals (mp 64.5–65.5 °C); mass spectrometry (70 eV): *m*/*z* 303 (25, $[M]^{+\cdot}$), 212 (40), 211 (35), 210 (12), 209 (26), 207 (45), 206 (38), 205 (5), 204 (4), 202 (3), 97 (15), 96 (90), 95 (10), 94 (14), 93 (17), 92 (27), 91 (100); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.15–7.30 (m, 9 H), 2.77 (br s, 8 H).

2.2. Measurements

All CI mass spectra including the (B/E = constant) linked scan and mass-analyzed ion kinetic energy (MIKE) spectra were measured with a double focusing mass spectrometer ZAB-2F (VG Micromass, Manchester, UK) using isobutane as the reagent gas. Samples were introduced by using a thermally controlled solids probe with appropriate heating. Ion source conditions, T = 180–200 °C, $p \approx 10^{-3}$ Pa (nominal); accelerating voltage, 6000 V; electron energy, 100 V; emission current 500 mA.

Mass spectral data concerning the proton exchange represent averaged data from 5–10 spectra. B/E linked scanning measurements were optimized for the appropriate mass interval to minimize artefact contributions. MIKE spectra were evaluated by manual fitting; error limits were estimated to be <5% (rel.) for most abundant isotopomers and <20% (rel.) for the least abundant isotopomers.

3. Results and discussion

3.1. Protonated tri- and tetrabenzylmethane

Protonated tribenzylmethane **8** and protonated tetrabenzylmethane **9** are derivatives of isobutylbenzenium and neopentylbenzenium ions, respectively. Therefore, it is not surprising that the normal CI(CH_4) and CI(iC_4H_{10}) mass spectra of the neutral hydrocarbons exhibit the corresponding $[M + H]^+$ ions at low relative abundances only. Surprisingly, the CI mass spectra show no significant peaks for the loss of a single benzene molecule, $[M + H - C_6H_6]^+$ that is usually observed for simpler α,ω-diphenylalkanes and related ions formed in the CI plasma. Instead, the major high-mass fragment ion peaks correspond to the intriguing loss of 156 Da (i.e. to the apparent loss of a $C_{12}H_{12}$ neutral) or, more likely, to *two* molecules of benzene. A typical CI(iC_4H_{10}) mass spectrum also containing contributions due to charge transfer and EI-induced fragmentation of **9** is shown in Fig. 1(a).

The metastable ion spectra of **8** and **9** are much simpler than their normal CI mass spectra. In the case of protonated tribenzylmethane fragmenting in the second field-free region (2nd ffr) the elimination of a single benzene molecule represents a minor process only (~20%); the twofold loss of benzene is still clearly dominating (Scheme 5). The higher analogue, metastable protonated tetrabenzylmethane **9** fragments almost exclusively by loss of two molecules of benzene within the same field-free region (Scheme 6). The MIKE spectrum of **9** gives a peak ratio $[M + H - 2\ C_6H_6]^+/[M + H - C_6H_6]^+ = 70\ (\pm 10)$, i.e. more than 98% of the low energy ions **9** undergo the double benzene loss within the same field-free region. As an illustration, the MIKE spectrum of protonated tetrabenzylmethane **9** is reproduced in Fig. 1(b). Similar effects were found in the B/E linked scan spectra of **8** and **9** representing the fragmentation of ions of slightly higher internal energies in the first field-free region (1st ffr).

When [ring-d_5] labeled tri- or tetrabenzylmethane are subjected to CI(iC_4H_{10}), the peaks at m/z 131 and m/z 221 in the spectra of the unlabeled species, corresponding to the double benzene losses, are split into peak clusters in the ranges of m/z 131–136 and m/z 221–226, respectively (after correction for natural ^{13}C contributions), both showing a "convex" pattern of relative abundances. The pattern obtained from the normal CI(iC_4H_{10}) spectrum of protonated [ring-D_5]-tetrabenzylmethane **9a**, is shown in Fig. 2.

Whereas the relative abundances of the $[M + H - C_6(H,D)_6]^+$ ions are generally disturbed by contributions from other origins, such as in the case of **8a** [53], the pattern obtained for the isotopomeric $[M + H - 2\ C_6(H,D)_6]^+$ ions **8a** and **9a** are quite close to the distribution of ion abundances calculated for the complete equilibration of the 11 or 16 ring protons, respectively, and five ring deuterons. Thus, equilibration of 16 or 21 ring protons in **8** and **9**, respectively, is apparently complete within the ions' lifetime in the CI source and prior to elimination of two molecules of benzene (cf. Table 1, entries 5 and 8, and Table 2, entries 1 and 3).

More reliable data on the relative abundances of the isotopomeric ions formed by benzene losses from **8a** and **9a** were obtained for the fragmentation of the metastable $[M + H]^+$ ions. The MIKE and B/E =

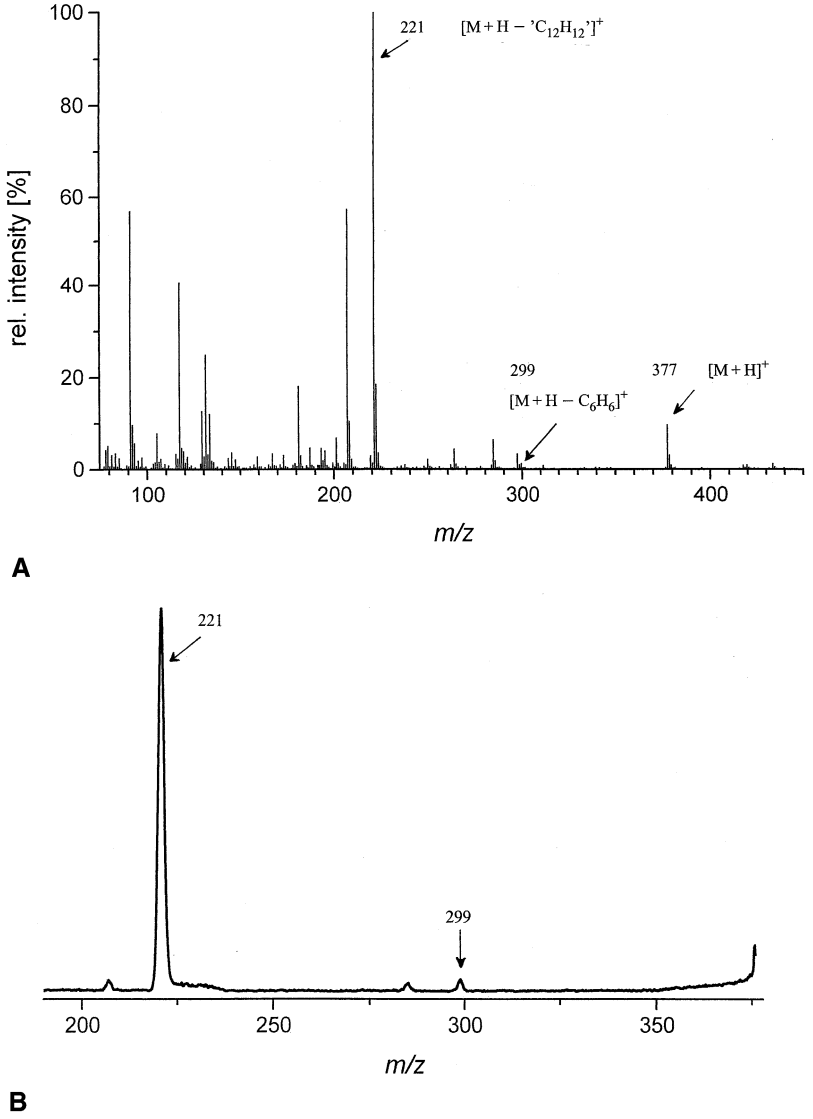
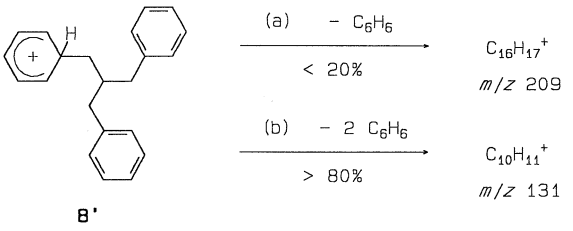
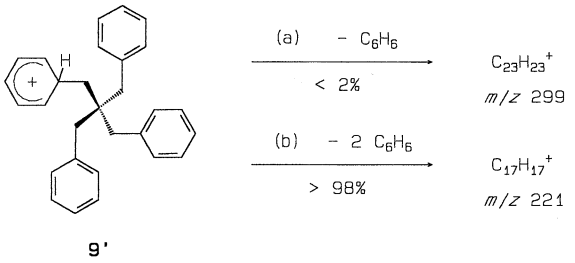


Fig. 1. (A) CI(isobutane) mass spectrum of tetrabenzylmethane. Peaks at *m*/*z* 284 and 207, among others, are due to fragmentation reactions of the $M^{+\cdot}$ ions. (B) MIKE spectrum of protonated tetrabenzylmethane, ions **9** (*m*/*z* 377), generated by CI(isobutane).

constant linked scan spectra of deuterium labeled, protonated tribenzylmethane **8a** and the B/E linked scan spectra of tetrabenzylmethane **9a** [54] are very close to the distributions calculated for the complete equilibration of 16 and 21 protons and deuterons within the lifetime of the ions (Tables 1 and 2). As an example, the partial B/E linked scan spectra showing the twofold benzene loss from ions **8a** and **9a** is illustrated in Fig. 3. Thus, the extent of the interan-



Scheme 5.



Scheme 6.

nular proton exchange is independent of the lifetime of the ions and of the fragmentation channel, i.e. single or twofold benzene loss (Table 1 and 2).

It is also of importance to note that the interannular proton exchange includes all of the arene rings in a *common* interchange. There is no evidence for what could be termed a "biannular" proton exchange which, as an extreme, would occur separately within each of three individual pairs of rings in the case of **8**, or within six individual pairs of rings in the case of **9**, prior to fragmentation. This follows clearly by contrasting the experimental pattern for the single loss of $C_6(H,D)_6$ from protonated tribenzylmethane **8a** with that calculated for such a "biannular" exchange, which would be recognizable by a prominent loss of C_6H_6 (Table 1, entry 4).

The almost perfect agreement between the experimental and calculated abundances for the single and twofold benzene losses also indicates that the hydrogens from the aliphatic (isoalkane) moiety spacer between the rings neither participate in the hydrogen exchange, nor are they incorporated during the final elimination step(s). Independent evidence for the inertness of the aliphatic hydrogens is provided by inspection of the B/E linked scan and MIKE spectra of the deuterium labeled analogues of **8b** and **9b**. Only unlabeled benzene is formed during the single and twofold losses of benzene (Scheme 7).

This finding parallels the general behaviour of less complex protonated α,ω-diphenylalkanes **1** and **4** studied previously [3,4,20]. It is of interest since limited exchange between the arene and side-chain protons is known to occur in ion/molecule complexes formed during the fragmentation of simple alkylbenzenium ions [30–32,55]. In the case of ions **8** and **9**, the reactivity of the aliphatic C–H bonds could be enhanced as compared to **1** if heterolysis of the C^{α}–C^{aryl} bonds is coupled with rearrangement of the

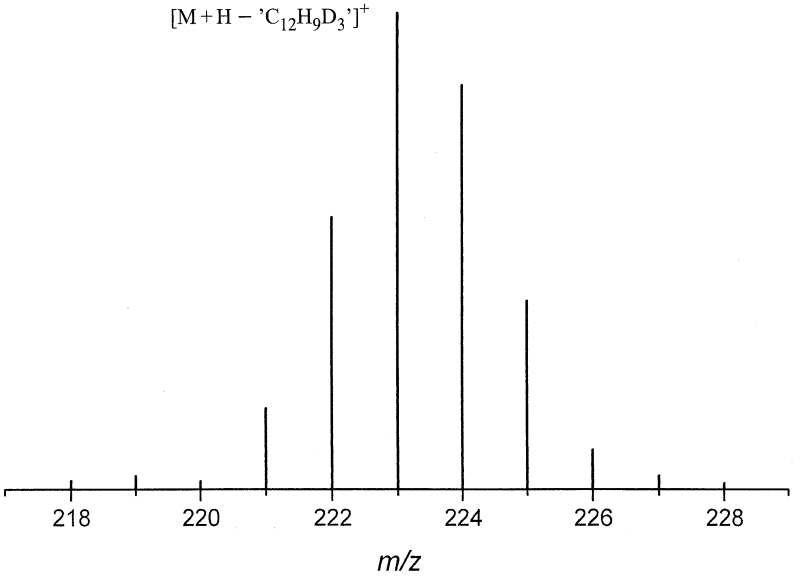


Fig. 2. Partial CI(isobutane) mass spectrum of [ring-D_5]-tetrabenzylmethane, ions **9a** (m/z 382), generated by CI(isobutane).

Table 1
Loss of benzene isotopomers from [ring-D_5]-labeled protonated tribenzylmethane **8a** [a,b]

Single loss	C_6HD_5	$C_6H_2D_4$	$C_6H_3D_3$	$C_6H_4D_2$	C_6H_5D	C_6H_6
Mass-to-charge ratio	209	210	211	212	213	214
1st ffr [c]	0.3	3.5	19.9	39.8	29.6	6.8
2nd ffr [d]	0.4	3.3	18.7	39.5	29.9	8.0
Statistical (all 3 rings)	0.1	3.4	20.6	41.2	28.9	5.8
Statistical (3 couples of rings) [e]	0.9	10.8	28.9	21.7	4.3	33.5
Double loss	"$C_{12}H_7D_5$"	"$C_{12}H_8D_4$"	"$C_{12}H_9D_3$"	"$C_{12}H_{10}D_2$"	"$C_{12}H_{11}D$"	"$C_{12}H_{12}$"
Mass-to-charge ratio	131	132	133	134	135	136
Ion source	15.5	36.1	29.5	12.1	5.1	1.7
1st ffr [c]	15.3	42.4	32.8	8.7	0.8	0.0
2nd ffr [d]	13.3	39.2	34.5	10.8	1.4	<0.1
Statistical (all 3 rings)	18.1	45.3	30.2	6.0	0.3	—

[a] In % Σ.
[b] $[M + H]^+$ ions were generated by CI(iC_4H_{10}).
[c] Measured by linked scanning (B/E = constant).
[d] Measured by MIKE spectrometry.
[e] See text.

aliphatic (isobutyl or neopentyl) cores, allowing for reversible C–C bond formation or, at least, a partial H^+/D^+ exchange in ion/molecule complexes formed between the putative diphenylalkyl cation and the benzene neutral released. However, even the tertiary hydrogen of **8**, which appears to be prone to undergo such an intracomplex proton exchange, is not involved in the overall exchange process, as evident from the fragmentation of ions **8b**.

3.2. Higher protonated triarylisoalkanes

Mainly with regard for the mechanistic implications of the double benzene loss from protonated tri- and tetrabenzylmethane **8** and **9**, which will be discussed in the following article [35], we also studied the interannular proton exchange in some higher homologues of **8**, i.e. protonated "long-chain" triarylisoalkanes **10**–**12**, as well as in two alicyclic congeners that were envisaged as reasonable products of the single benzene loss from **8** and **9**, viz. protonated 2-benzylindane **13** and protonated 2,2-dibenzylindane **14**.

Interestingly, metastable protonated triphenylisoalkanes **10**–**12** undergo mainly the single benzene loss. Whereas twofold elimination of benzene still represents a minor fragmentation channel in the "symmetrical" homologue **12**, this process is almost completely suppressed in **10** and **11** [35].

As may have been expected, labeling of one of the

Table 2
Twofold loss of benzene isotopomers from [ring-D_5]-labeled protonated tetrabenzylmethane **9a** [a,b]

Double loss[c]	"$C_{12}H_7D_5$"	"$C_{12}H_8D_4$"	"$C_{12}H_9D_3$"	"$C_{12}H_{10}D_2$"	"$C_{12}H_{11}D$"	"$C_{12}H_{12}$"
Mass-to-charge ratio	221	222	223	224	225	226
Ion source	6.7	20.8	35.5	25.9	10.0	1.0
1st ffr [d]	3.1	19.1	36.5	29.2	10.7	1.5
Statistical (all 4 rings)	3.9	21.9	38.9	27.2	7.4	0.6

[a] In % Σ.
[b] $[M + H]^+$ ions were generated by CI(iC_4H_{10}).
[c] See text.
[d] Measured by linked scanning (B/E = constant).

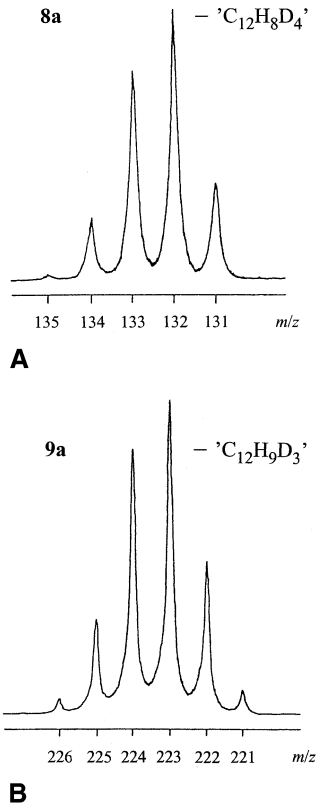
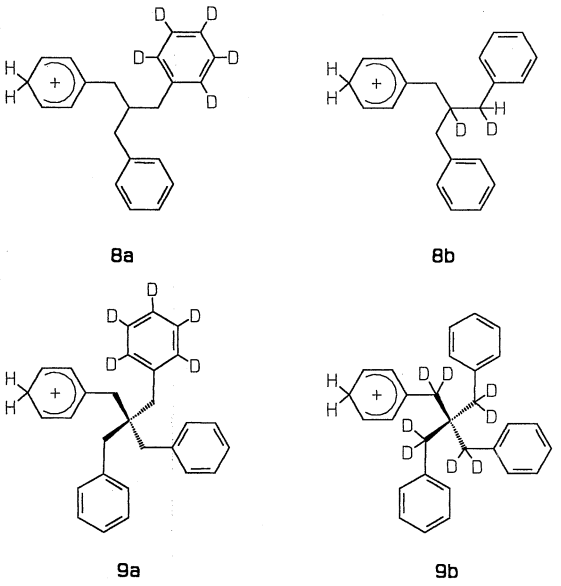


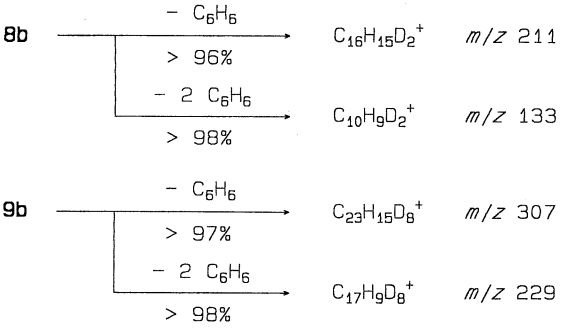
Fig. 3. Partial linked scan (*B*/*E* = constant) spectra of (A) [ring-D_5]-tribenzylmethane, ions **8a** (*m*/*z* 292) and (B) [ring-D_5]-tetrabenzylmethane, ions **9a** (*m*/*z* 382), generated by CI(isobutane).

phenyl rings of **10**–**12** reveals again the fast interannular proton exchange in the metastable ions. Both the single and twofold elimination of benzene from metastable [phenyl-D_5]-labeled ions **12a** are preceded by the complete equilibration of 16 protons and deuterons, as is evident from the data collected in Table 3. Likewise, the relative ion abundances for the single loss of $C_6(H,D)_6$ from the lower [phenyl-D_5]-labeled homologues, **10a** and **11a**, perfectly agree with the pattern calculated for the fast ring-to-ring proton interchange (Table 4). Thus, the gradual elongation of the aliphatic links between the three arene rings in the series **8**, **10**, **11**, and **12** does not result in incomplete or "biannular" proton exchange.

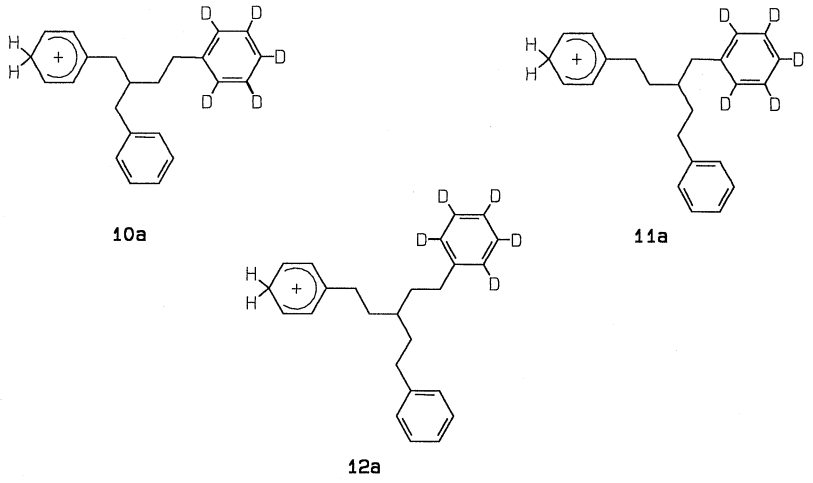


3.3. Protonated 2-benzylindanes

Protonated 2-benzylindane **13** and protonated 2,2-dibenzylindane **14** represent alicyclic counterparts of protonated 1,3-diphenylpropane **1** ($n = 3$) and protonated tribenzylmethane **8**. Again, elimination of benzene is the only fragmentation channel of **13**, but also of **14**, in spite of the presence of three arene rings in the latter ions. Both [phenyl-D_5]-labeled protonated 2-benzylindane **13a** and [phenyl-D_5]-labeled protonated 2,2-dibenzylindane **14a** were studied by B/E linked scanning and by MIKE spectrometry. In addition, the isotopomer **13b** containing a [D_5]-labeled



Scheme 7.



cyclopentene ring was studied. Both **13a** and **13b** were available from previous investigations on the intramolecular hydrogen exchange of the radical cations of 2-benzylindane [50].

Again, fast and complete equilibration of the 10 and 15 protons and deuterons at the aromatic rings of **13a** and **14a** was found (Table 5). In the case of **13a**, the equal numbers of protons and deuterons participating in the exchange give rise to a nicely symmetrical abundance pattern of the $[M + H - C_6(H,D)_6]^+$ ions, whereas in the case of **14a** the protons and five deuterons involved lead to an unsymmetrical pattern. In both cases, the experimentally obtained distributions of isotopomers are almost identical to those calculated for the complete proton equilibration between the aromatic rings. In further agreement with the behaviour of protonated tri- and tetraphenylisoalkanes **8b** and **9b**, the exchange in protonated [1,1,2,3,3-D_5]-2-benzylindane **13b** does not involve hydrogens from the tertiary and benzylic positions of the alicyclic moiety (Scheme 8).

The data show that, in fact, the aliphatic chain or alicyclic spacer in diphenylalkane-derived arenium ions do not participate in the intra-annular proton

Table 3
Loss of benzene isotopomers from [ring-D_5]-labeled protonated tris(β-phenylethyl)methane **12a** [a,b]

Single loss	C_6HD_5	$C_6H_2D_4$	$C_6H_3D_3$	$C_6H_4D_2$	C_6H_5D	C_6H_6
Mass-to-charge ratio	251	252	253	254	255	256
1st ffr [c]	0.4	4.1	19.3	39.3	29.1	7.8
2nd ffr [d]	<0.2	2.5	20.5	39.9	30.5	6.7
Statistical (all three rings)	0.1	3.4	20.6	41.2	28.9	5.8
Double loss[e]	"$C_{12}H_7D_5$"	"$C_{12}H_8D_4$"	"$C_{12}H_9D_3$"	"$C_{12}H_{10}D_2$"	"$C_{12}H_{11}D$"	"$C_{12}H_{12}$"
Mass-to-charge ratio	173	174	175	176	177	178
1st ffr [c]	16.4	43.4	30.5	8.9	0.6	0.3
2nd ffr [d]	15.4	41.1	33.1	9.6	0.8	<0.1
Statistical (all three rings)	18.1	45.3	30.2	6.0	0.3	—

[a] In % Σ
[b] $[M + H]^+$ ions were generated by CI(iC_4H_{10}).
[c] Measured by linked scanning (B/E = constant).
[d] Measured by MIKE spectrometry.
[e] See text.

Table 4
Loss of benzene isotopomers from [ring-D_5]-labeled protonated triphenylisoalkanes **10a** and **11a** [a,b]

Loss of	C_6HD_5	$C_6H_2D_4$	$C_6H_3D_3$	$C_6H_4D_2$	C_6H_5D	C_6H_6
Mass-to-charge ratio	223	224	225	226	227	228
10a, 1st ffr [c]	0.7	4.7	20.0	37.9	28.1	8.7
10a, 2nd ffr [d]	0.7	3.7	19.0	38.8	29.9	7.9
Mass-to-charge ratio	237	238	239	240	241	242
11a, 1st ffr [c]	0.7	3.6	19.2	38.5	29.4	8.6
11a, 2nd ffr [d]	0.5	4.1	19.0	39.2	28.8	8.4
Statistical (all three rings)	0.1	3.4	20.6	41.2	28.9	5.8

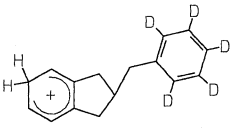
[a] In % Σ.
[b] $[M + H]^+$ ions were generated by CI(iC_4H_{10}).
[c] Measured by linked scanning (B/E = constant).
[d] Measured by MIKE spectrometry.

exchange. In particular, there is no significant H/D exchange or proton transfer *after* protonolysis of the C^{α}–C^{phenyl} bond of the protonated indanes **13** and **14**, a process that would be conceivable if intermediate ion/molecule complexes had long enough lifetimes to undergo acid-base reactions. Also, the proton affinities of indenes [56,57] and dialins, as the conjugate base of the most likely ionic fragment generated by benzene loss [35], and of benzene are too far apart to allow for intracomplex proton exchange. Obviously, similar arguments hold for the more complex systems such as protonated tri- and tetrabenzylmethane **8** and **9** as well as for the higher protonated triphenylisoalkanes **10**–**12**.

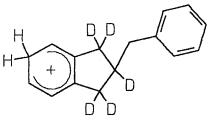
3.4. The readiness of the interannular proton exchange

The fact that protonated 2-benzyl- and 2,2-dibenzylindane undergo complete interchange of the arene protons is again telling. Inspection of the steric situation by molecular modeling suggests that the two aromatic rings of **13** cannot approach each other such that the proton transfer could occur freely between all of the ring positions. Rather, only the *ortho* positions of the benzyl group are sufficiently close to allow proton transfer to one of the ring junctions (C-3a and C-7a) of the indane moiety. Nevertheless, the *intra-annular* proton shifts (cf. Scheme 2) combined with the spatially restricted interannular proton transfer are sufficiently fast to enable complete proton equilibration (Scheme 9). A factor operating in favour of the interannular proton exchange may be the preorientation of the benzyl group in **13** relative to the indane moiety. This preorientation may decrease the entropic barrier towards the inter-annular proton exchange, and may be even more efficient in the case of the more crowded 2,2-dibenzyl-substituted analogue **14**.

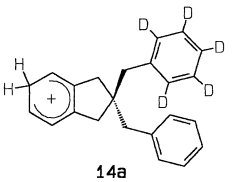
Returning to the particular case of tri- and tetrabenzylmethane, we can assume that an increasing degree of crowding in ions **8** and **9**, as compared to **1** (e.g. $n = 3$) and possibly **13**, increases the ease of proton transfer between the formally equivalent arene rings. Therefore, we may also expect the 16 and 21 ring protons in **8** and **9**, respectively, to be equilibrated *prior to* fragmentation. Although technically impossible at present, as far as the radiolytic tech-



13a



13b



14a

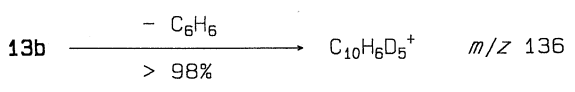
Table 5
Loss of benzene isotopomers from [ring-D_5]-labeled protonated 2-benzylindane **13a** and 2,2-dibenzylindane **14a** [a,b]

Loss of	C_6HD_5	$C_6H_2D_4$	$C_6H_3D_3$	$C_6H_4D_2$	C_6H_5D	C_6H_6
Mass-to-charge ratio	131	132	133	134	135	136
13a, 1st ffr [c]	3.5	23.2	45.7	24.0	3.3	0.3
13a, 2nd ffr [d]	2.6	21.9	46.7	24.6	3.8	0.4
Statistical	2.4	23.8	47.6	23.8	2.4	—
Mass-to-charge ratio	221	222	223	224	225	226
14a, 1st ffr [c]	2.5	5.2	23.8	40.9	23.3	4.4
14a, 2nd ffr [d]	2.3	6.9	25.2	40.1	22.2	3.3
Statistical	0.2	4.5	24.0	42.0	25.2	4.2

[a] In % Σ.
[b] $[M + H]^+$ ions were generated by CI(iC_4H_{10}).
[c] Measured by linked scanning (B/E = constant).
[d] Measured by MIKE spectrometry.

nique is concerned, it appears intriguing to determine the kinetic parameters of the interannular proton transfer in these "large" alkylbenzenium ions. X-ray single crystal structure analysis of (neutral) tetrabenzylmethane [58] confirms the close vicinity of the aromatic rings in this crowded neopentane derivative. Since kinetic simulations for the simple protonated α,ω-diphenylalkanes **1** have shown, at least for the energy range of the metastable ions, that an individual ring-to-ring proton-transfer step requires less than 1 μs ($k_{inter} \geq 10^6$ s^{-1}) [4b,20], we estimate that the proton interannular transfer rates in the much more preoriented, sterically crowded ions **8** and **9**, in particular, have to be at least two orders of magnitude higher, i.e. $k_{inter} \geq 10^8$ s^{-1}, to achieve complete equilibration of up to 21 protons within ~1 μs (Scheme 10).

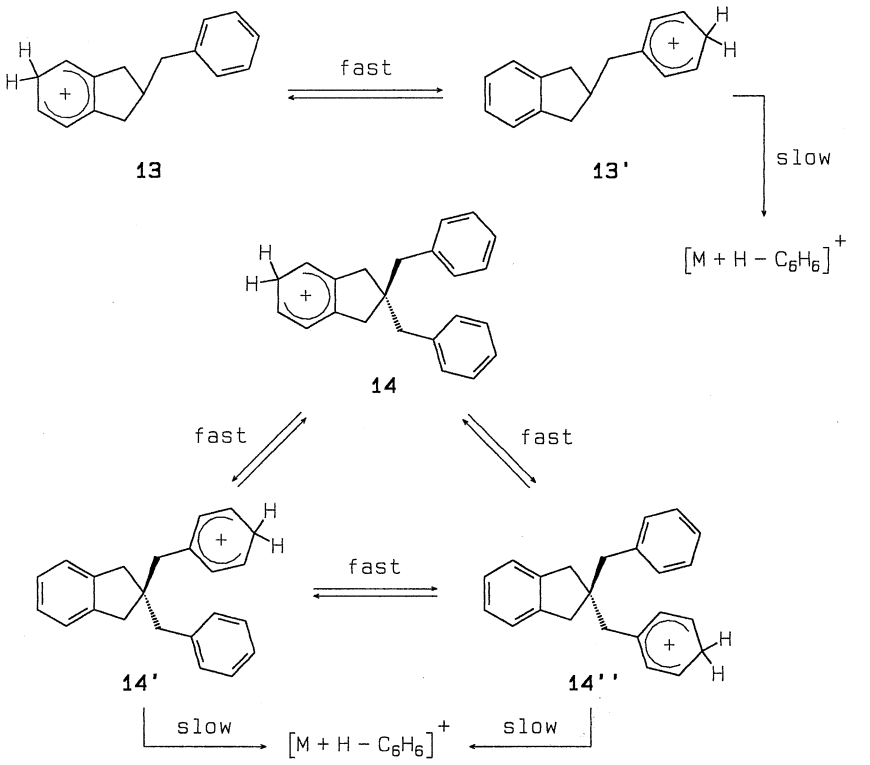
Kinetic model calculations for the multiple proton exchange presented here have not yet been achieved [59]. On a qualitative basis, we may speculate that, in protonated oligophenylisoalkanes such as **8** and **9**, the interannular proton transfer rate may even exceed that of the intrannular proton shifts, i.e., $k_{inter} \geq k_{intra}$. However, it appears extremely hard to assess the competition of these hydrogen exchange processes since the presence of several spectator rings may contribute efficiently to internal solvation. Thus, the effect of the high effective (intramolecular) density of aromatic nuclei in **9**, in particular, may also facilitate the ring-walk isomerization. In this view, the limits between intra- and interannular proton transfer may vanish in oligophenylisoalkylbenzenium ions such as **8** and **9** and it may be a particular challenge to determine the contribution of entropy to the ease of intramolecular proton mobility [60].



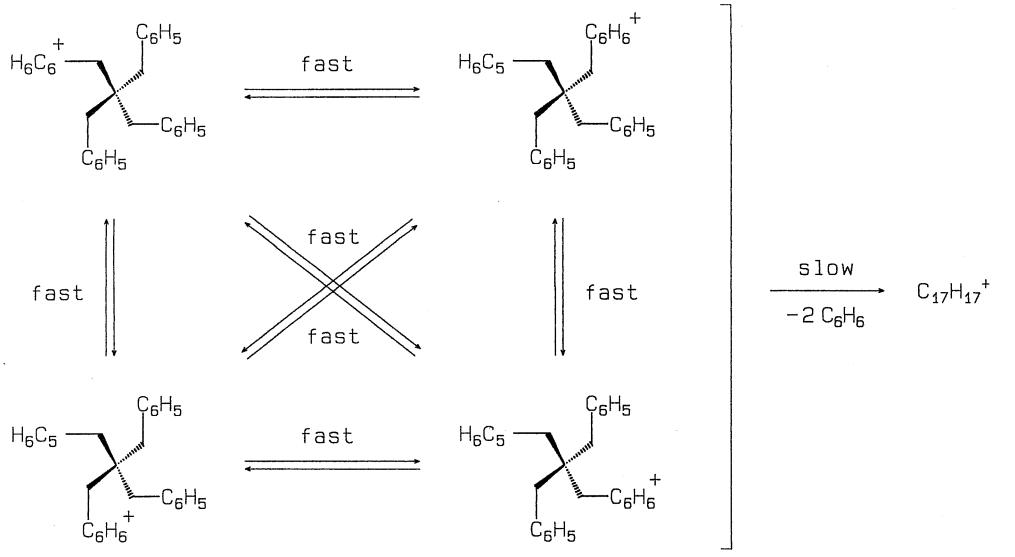
Scheme 8.

4. Conclusions

The general finding that gaseous protonated α,ω-diphenylalkanes undergo fast and complete proton equilibration between the aromatic rings prior to loss of benzene has been demonstrated to also occur in larger congeners containing three or even four benzene rings. Not only do the metastable ions undergo interannular proton exchange but the ions decomposing in the CI(iC_4H_{10}) source also reveal the complete equilibration, as shown for the case of protonated tetrabenzylmethane **9** containing 21 mobile ring protons. No evidence is found for a biannular exchange path that would include pairs of rings and exclude the remaining ones prior to benzene loss. Also, there is no interference of proton exchange between the aromatic



Scheme 9.



Scheme 10.

and aliphatic parts of the ions, and the interannular proton exchange precedes both the single and the twofold losses of benzene. Thus, the fast interannular "proton dance" appears to be a truly ubiquitous isomerization channel in di- and oligophenylalkylbenzenium ions and related ions, at least in those congeners that bear the phenyl rings at the extremal (α and ω) positions of the aliphatic chain, or alicyclic spacer. The mechanism of the intriguing twofold elimination of benzene from protonated tribenzylmethane **8** and protonated tetrabenzylmethane **9** will be investigated in the following article [35].

Acknowledgements

This work has been supported in part by the European Commission (HUCAMO Project No. CHRX-CT93 0291, "Fundamental Studies in Gas-Phase Ion Chemistry and Mass Spectrometry") and by the Fonds der Chemischen Industrie (FCI). We are grateful to Dr. Ulrich Neuert for valuable discussions and to Dipl.-Chem. Michael Mormann for assistance during the final part of this work.

References

[1] A.F. Thomas, Deuterium Labeling in Organic Chemistry, Appleton-Century-Crofts, New York, 1971.
[2] (a) M. Schlosser, Pure Appl. Chem. 60 (1988) 1627; (b) L. Brandsma, H. Verkruijsse, Preparative Organometallic Chemistry 1, Springer, Heidelberg, 1987; (c) L. Brandsma, Preparative Organometallic Chemistry 2, Springer, Heidelberg, 1990; (c) R. Haag, B. Ohlhorst, M. Noltemeyer, R. Fleischer, D. Stahlke, A. Schuster, D. Kuck, A. de Meijere, J. Am. Chem. Soc. 117 (1995) 10474, and papers cited therein.
[3] (a) D. Kuck, Mass Spectrom. Rev. 9 (1990) 583; (b) D. Kuck, Mass Spectrom. Rev. 9 (1990) 181.
[4] (a) D. Kuck, W. Bäther, H.-Fr. Grützmacher, J. Am. Chem. Soc. 101 (1979) 7154; (b) D. Kuck, W. Bäther, H.-Fr. Grützmacher, Int. J. Mass Spectrom. Ion Processes 67 (1985) 75; (c) W. Bäther, D. Kuck, H.-Fr. Grützmacher, Org. Mass Spectrom. 20 (1985) 589.
[5] D. Kuck, D. Thölmann, H.-Fr. Grützmacher, J. Chem. Soc., Perkin Trans. 2 (1990) 251.
[6] D. Kuck, Int. J. Mass Spectrom. Ion Processes 117 (1992) 441.
[7] D. Kuck, S. Ingemann, L.J. de Koning, H.-Fr. Grützmacher, N.M.M. Nibbering, Angew. Chem. Int. Ed. Engl. 24 (1985) 693.
[8] P. Ausloos, S.G. Lias, J. Am. Chem. Soc. 103 (1981) 3641.
[9] (a) C.H. DePuy, R. Gareyev, S. Fornarini, Int. J. Mass Spectrom. Ion Processes 161 (1997) 43; (b) B. Chiavarino, M.E. Crestoni, S. Fornarini, C.H. DePuy, R. Gareyev, J. Phys. Chem. 100 (1996) 16 201.
[10] F. Cacace, M.E. Crestoni, S. Fornarini, D. Kuck, J. Am. Chem. Soc. 115 (1993) 1024.
[11] F. Cacace, Acc. Chem. Res. 21 (1988) 215.
[12] E. del Rio, R. López, T.L. Sordo, J. Phys. Chem. A 101 (1997) 10 090.
[13] R.S. Mason, C.M. Williams, P.D.J. Anderson, J. Chem. Soc. Chem. Commun. (1995) 1027.
[14] S. Siever, P.v.R. Schleyer, J. Am. Chem. Soc. 115 (1993) 6987.
[15] M.N. Glukhovtsev, A. Pross, A. Nicolaides, L. Radom, J. Chem. Soc. Chem. Commun. (1995) 2347.
[16] For a comprehensive citation of previous experimental and computational work on the chemistry benzenium ion, see [3a] and [15].
[17] (a) G.A. Olah, R.H. Schlosberg, D.P. Kelly, G.D. Mateescu, J. Am. Chem. Soc. 92 (1970) 2546; (b) G.A. Olah, R.H. Schlosberg, R.D. Porter, Y.K. Mo, D.P. Kelly, G.D. Mateescu, J. Am. Chem. Soc. 94 (1972) 2034; (c) G.A. Olah, J.S. Staral, G. Asencio, G. Liang, D.A. Forsyth, G.D. Mateescu, J. Am. Chem. Soc. 100 (1978) 6299.
[18] (a) D. Fărcaşiu, M.T. Melchior, L. Craine, Angew. Chem. Int. Ed. Engl. 16 (1977) 315; (b) D. Fărcaşiu, Acc. Chem. Res. 15 (1982) 46.
[19] F. Cacace, M.E. Crestoni, S. Fornarini, J. Am. Chem. Soc. 114 (1992) 6776.
[20] D. Kuck, W. Bäther, Org. Mass Spectrom. 21 (1986) 451.
[21] D. Kuck, H.E. Audier, C. R. Acad. Sci. Paris, Sér. II 324 (1997) 717.
[22] S. Meyerson, L.C. Leitch, J. Am. Chem. Soc. 93 (1971) 2244.
[23] P. Bommer, K. Biemann, Ann. Rev. Phys. Chem. 16 (1965) 481.
[24] J.T. Bursey, M.M. Bursey, D.G.I. Kingston, Chem. Rev. 73 (1973) 191.
[25] S. Fornarini, Mass Spectrom. Rev. 15 (1996) 365.
[26] M.E. Crestoni, S. Fornarini, D. Kuck, J. Phys. Chem. 99 (1995) 3150.
[27] M.E. Crestoni, S. Fornarini, D. Kuck, J. Phys. Chem. 99 (1995) 3144.
[28] (a) M.E. Crestoni, J. Phys. Chem. 97 (1993) 6197; (b) B. Chiavarino, M.E. Crestoni, S. Fornarini, D. Kuck, Int. J. Mass Spectrom. Ion Processes 148 (1995) 215.
[29] (a) D. Kuck, C. Matthias, J. Am. Chem. Soc. 114 (1992) 1901; (b) C. Matthias, D. Kuck, Org. Mass Spectrom. 28 (1993) 1073; (c) C. Matthias, K. Weniger, D. Kuck, Eur. Mass Spectrom. 1 (1995) 445.
[30] H.E. Audier, C. Monteiro, P. Mourgues, D. Berthomieu, Org. Mass Spectrom. 25 (1990) 245; (b) D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié, H.E. Audier, J. Phys. Chem. 99 (1995) 712; (c) D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié, H.E. Audier, J. Am. Chem. Soc. 115 (1993) 2505.

[31] R.W. Holman, M.L. Gross, J. Am. Chem. Soc. 111 (1989) 3560.
[32] J.A. Herman, A.G. Harrison, Org. Mass Spectrom. 16 (1981) 423.
[33] F. Cacace, M.E. Crestoni, G. de Petris, S. Fornarini, F. Grandinetti, Can. J. Chem. 66 (1988) 3099.
[34] (a) C. Matthias, Doctoral thesis, Universität Bielefeld, 1996; (b) C. Matthias, D. Kuck (unpublished).
[35] D. Kuck, U. Fastabend, Int. J. Mass Spectrom. Ion Processes 179/180 (1998) 147.
[36] (a) D. Kuck, Int. J. Mass Spectrom. Ion Phys. 47 (1983) 499; (b) D. Kuck, U. Fastabend, Adv. Mass Spectrom. 11A (1989) 904.
[37] K.R. Jennings, J. Chem. Soc. Chem. Commun. (1966) 283.
[38] (a) J.H. Beynon, A.E. Williams, Appl. Spectrosc. 14 (1960) 156; (b) C.J. Proctor, B. Kralj, E.A. Larka, C.J. Porter, A. Maquestiau, J.H. Beynon, Org. Mass Spectrom. 16 (1981) 312.
[39] L.W. Hall, R.W.A. Oliver, Org. Mass Spectrom. 2 (1969) 801.
[40] (a) C.J. Proctor, B. Kralj, A.G. Brenton, J.H. Beynon, Org. Mass Spectrom. 15 (1980) 619; (b) C.J. Proctor, B. Kralj, Org. Mass Spectrom. 15 (1980) 326; (c) C.J. Proctor, E.A. Larka, Z.V.I. Zaretskii, J.H. Beynon, Org. Mass Spectrom. 17 (1982) 131.
[41] J.-M. Conia, C. Névot, P. Gosselin, Bull. Soc. Chim. Fr. (1959) 1511.
[42] A. Hill, M.A. Little, S. Wray Jr., R.J. Trimbley, J. Am. Chem. Soc. 56 (1934) 911.
[43] A. Klages, S. Heilmann, Ber. 37 (1904) 1447.
[44] E.R. Trotman, J. Chem. Soc. 127 (1925) 88.
[45] See, for example: D. Kuck, Z. Naturforsch. B 39 (1984) 369.
[46] A. Hill, A.J. Cofrancesco, J. Am. Chem. Soc. 57 (1935) 2426.
[47] D. Kuck, E. Neumann, H.-F. Grützmacher (unpublished).
[48] A. Orechov, R. Konowaloff, Ber. 45 (1912) 861.
[49] K. Heß, W. Weltzien, Ber. 54 (1921) 2511.
[50] (a) D. Kuck, H.-Fr. Grützmacher, Adv. Mass Spectrom. 8 (1980) 867; (b) D. Kuck (unpublished).
[51] (a) D. Kuck, Chem. Ber. 127 (1994) 409; (b) D. Kuck, Angew. Chem. Int. Ed. Engl. 23 (1984) 508.
[52] See, for example: T. Okukawa, K. Suzuki, M. Sekiya, Chem. Pharm. Bull. 22 (1974) 448.
[53] The peaks of the fragment ions [**8a** − $C_6(H,D)_6$]$^+$ originating from the $[M + H]^+$ ions overlap with those corresponding to the twofold loss of $C_6(H,D)_6$ from the $[M - H]^+$ ions formed by hydride abstraction. For the case of **9**, see Fig. 1(a) (m/z 297 versus m/z 299).
[54] The MIKE spectrum of **9a** does not allow one to evaluate the individual contributions of [**9a** − 2 $C_6(H,D)_6$]$^+$ due to severe peak overlapping.
[55] (a) D. Berthomieu, H.E. Audier, C. Monteiro, J.-P. Denhez, Rapid Commun. Mass Spectrom. 5 (1991) 415; (b) D. Berthomieu, H.E. Audier, J.-P. Denhez, C. Monteiro, P. Mourgues, Org. Mass Spectrom. 26 (1991) 271.
[56] (a) E.P. Hunter, S.G. Lias, in W.G. Mallard, P.J. Linstom (Eds.), Proton Affinity Evaluation in NIST Standard Reference Database No. 69, National Institute of Standards and Technology, Gaithersburg, MD, 1997 (hppt://webbook.nist.gov); (b) S.A. Kafafi, M. Meot-Ner (Mautner), J.F. Liebman, J. Struct. Chem. 1 (1989) 101.
[57] D. Kuck, A. Mehdizadeh, Org. Mass Spectrom. 27 (1992) 443.
[58] D. Kuck, H. Bögge, A. Müller, (unpublished).
[59] Kinetic simulations for **8a** and **9a** would include the participation of twelve or, respectively, 16 distinct sets of isotopomers, e.g., for **8a**, C[$(CH_2C_6H_{6-x}D_x)(CH_2C_6H_{5-y}D_y)(CH_2C_6H_{5-z}D_z)$], where $x + y + z = 5$ and the *intra-annular* H^+/D^+ exchange is assumed to be "infinitely" fast.
[60] (a) R.S. Mason, M.T. Fernandez, K.R. Jennings, J. Chem. Soc., Faraday Trans. 83 (1987) 89; (b) M.T. Fernandez, K.R. Jennings, R.S. Mason, J. Chem. Soc., Faraday Trans. 83 (1987) 159; (c) A. Parry, M.T. Fernandez, M. Garley, R. Mason, J. Chem. Soc., Faraday Trans. 88 (1992) 3331.