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Large gaseous alkylbenzenium ions. The apparently simultaneous loss of two molecules of benzene from protonated tri- and tetrabenzylmethane

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Abstract

The consecutive loss of two molecules of benzene from several protonated oligophenylisoalkylbenzenium ions has been studied by chemical ionization/mass analyzed ion kinetic energy (CI/MIKE) and CI/collision induced dissociation (CID)/MIKE spectrometry. The twofold elimination of benzene is most pronounced for protonated tribenzylmethane (**1**) and tetrabenzylmethane (**2**). In the latter case, this process represents ~98% of the fragmentation, even of the metastable ions dissociating in the second field-free region of a double focusing mass spetrometer. In contrast, the higher homologues of **1** (**3**–**6**) dissociate predominantly or almost exclusively by single benzene loss. The mechanism and origin of the unprecedented, and apparently simultaneous, expulsion of two neutral arenes from alkylbenzenium ions is discussed in terms of the competition of cyclization and 1,2-H and 1,2-C shifts in β-branched protonated alkylbenzenes. Collision (CID/MIKE) spectrometry has been performed to elucidate the structures of the $[M + H - 2\ C_6H_6]^+$ ions ($C_{10}H_{11}^+$ from **1** and $C_{17}H_{17}^+$ from **2**). The results suggest that homobenzylic and benzylic carbenium ions (indanyl- and/or tetralyl-type ions) are formed whereas the intermediate $[M + H - C_6H_6]^+$ ions represent *arenium ions*, viz. protonated 2-benzylindane (**7**) and protonated 2,2-dibenzylindane (**8**). Protonated 2,2′-spirobiindane (**9**) can be excluded as the product of twofold benzene loss from **2**. The role of the highly mobile protons and ion/molecule complexes in large oligophenylalkylbenzenium ions has been considered. Whereas high proton mobility represents a mechanistically salient feature for the fast twofold loss of benzene, the relevance of protonated arene heterodimers to the apparent simultaneity of the elimination of two benzene neutrals cannot be corroborated. (Int J Mass Spectrom 179/180 (1998) 147–163) © 1998 Elsevier Science B.V.

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1. Introduction

Alkylbenzenium ions, or more generally, protonated alkylarenes, are known to undergo heterolytic cleavage of the C(α)–C(*ipso*) bond [1,2]. This reaction is archetypical for *tert*-butylbenzenes but also for other σ complexes bearing less branched alkyl sidechains [3–7]. In the liquid phase, proton-induced alkyl group shifts occur, giving rise to thermodynamically controlled isomerization, and directed Friedel–Crafts alkylation reactions using Lewis acids are

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Dedicated to Professor Fulvio Cacace with all best wishes.

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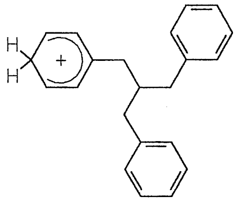

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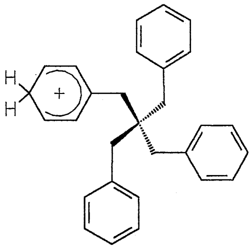

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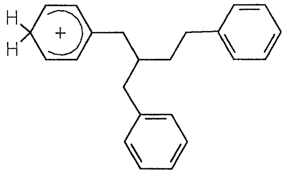

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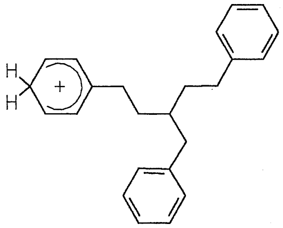

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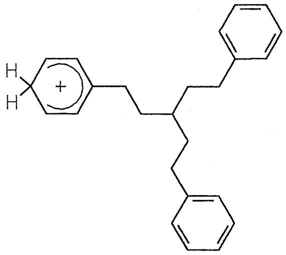

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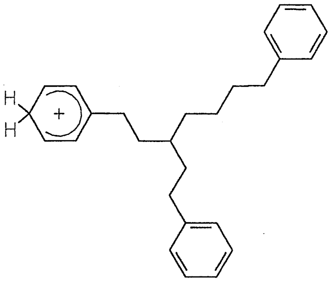

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usually disturbed by interference of skeletal isomerization of aliphatic moiety [8]. Owing to its general importance to synthetic organic chemistry, a large body of knowledge on the chemistry of protonated aromatic compounds, in particular of alkylbenzenium ions, has been accumulated in the past four decades [9]. Besides extended studies in superacidic solutions, in particular those by Olah et al. [10], a vast range of gas-phase investigations have contributed to this central topic of organic chemistry [11,12]. These include classical mass spectrometric techniques employing truly in vacuo conditions and focusing on the unimolecular behaviour of alkylbenzenium ions [13–18], but also investigations in the dense gas phase such as high pressure chemical ionization [5,19], flowing afterglow [20], and radiolysis [21]. Over several decades, Cacace and his school have been protagonists to explore and demonstrate the potential of radiolysis for the investigation of gaseous alkylbenzenium ions and the fundamental mechanisms of Friedel–Crafts chemistry [22].

Although originating from opposite starting points, mass spectrometric investigations, dealing largely with excited alkylbenzenium ions, and radiolytic techniques, generating in most cases thermalized alkylbenzenium ion intermediates [23], have met in recent years in several instances [24,25]. One basis for such an interplay, often ignored in physical organic chemistry, is the high variability of chemical structures. In this respect, our studies on protonated diphenylalkanes have raised the possibility of introducing an intramolecular probe into the arenium ion under investigation [26,27]. This has enabled insights into the quasibimolecular reactivity of arenium species with neutral arenes and has revealed, in particular, the almost ubiquitous ring-to-ring proton exchange in such species. Thus, protonated diphenylalkanes may be considered arenium ions containing one solvent, or “bath” molecule in an effectively close vicinity. In fact, an additional aromatic ring within the same protonated arenium ion has opened detailed insights on the internal solvation and the chemistry of gaseous ion/neutral complexes [28], including the spectator ring effect demonstrated recently both by applying radiolytic techniques [24] and metastable ion spectrometry [29].

In a preceding article [30], we demonstrated the particularly fast interannular proton exchange of large oligophenylisoalkylbenzenium ions such as protonated tribenzylmethane **1** and protonated tetrabenzylmethane **2**, that has been traced to the extremely close packing of several aromatic rings within the same quasimolecular ion. (Only one of the tautomeric σ complexes is shown in each case.) Besides the complete equilibration of up to 21 protons within the lifetime of the ions, protonated oligophenylisoalkylbenzenium ions have revealed unprecedented fragmentation behaviour, namely the apparently simultaneous elimination of two molecules of benzene even within the same field-free region of a double-focusing mass spectrometer. This fragmentation reaction was first observed in 1982 [31], and is given in summa for the most prominent cases of protonated tribenzylmethane (**1**) and protonated tetrabenzylmethane (**2**) in Eqs. (1) and (2):

$$C_{22}H_{23}^{+} \rightarrow C_{10}H_{11}^{+} + 2\ C_6H_6 \tag{1}$$

$$C_{29}H_{29}^{+} \rightarrow C_{17}H_{17}^{+} + 2\ C_6H_6 \tag{2}$$

The case of **2** is most peculiar since the elimination of a single molecule of benzene ($C_{29}H_{29}^{+} \rightarrow C_{23}H_{23}^{+} + C_6H_6$) is a negligible reaction path only [30].

Consecutive fragmentation reactions of metastable ions, involving an intermediate product ion that itself is metastable, were first observed by Jennings [32] and, later on, studied in detail by Beynon et al. [33,34]. Attempts to understand the apparently simultaneous double benzene loss raised some speculation about the role of ion-neutral complexes during the fragmentation of ionic species that contain a number of fast-moving, “mobile” protons [35–37]. Therefore, we have investigated the structure of possible intermediate and fragment ions of **1** and **2** by MIKE and CID-MIKE spectrometry. At the same time, the article demonstrates another junction between two of the three well-known branches of the gas-phase ion chemistry of alkylbenzenes [11], viz. alkylbenzenium ions (i.e. the $[M + H]^{+}$ type species) and the phenylalkyl cations (i.e. the $[M - H]^{+}$ type species) [38]. Further, this article may be regarded as demonstrating an extremal case of unimolecular gas-phase chemistry of excited (nonthermalized) ions in which internal solvation, or spectator ring effects, may be the governing factor for unimolecular fragmentation.

2. Experimental details

2.1. Materials

The general methodology and synthesis of the oligophenylisoalkanes used as CI precursors of ions **1**–**5** has been described in a preceding article [30]. The synthesis of the precursor of ion **6** is given below. Syntheses of the reference compounds used in the CID measurements were carried out according to procedures given in the literature, if not stated otherwise.

The 1,7-Diphenyl-3-(2-phenylethyl)heptane was synthesized by Grignard reaction of δ-phenylbutyl bromide and α,α'-dibenzylacetone to give the corresponding carbinol, 1,7-diphenyl-3-(2-phenylethyl) heptan-3-ol (73%) as a clear, pale-yellow oil, that remained after Kugelrohr evaporation of volatile components and appeared to be pure by spectroscopy; mass spectrometry (70 eV) m/z 372 (<0.2%, $[M]^{+\cdot}$), 354 (19, $[M - H_2O]^{+\cdot}$), 267 (32), 250 (3), 249 (3), 239 (19), 221 (5), 181 (4), 171 (12), 145 (6), 143 (3), 131 (15), 129 (6), 118 (6), 117 (42), 115 (3), 105 (24), 104 (14), 92 (19), 91 (100), 79 (7), 78 (6), 77 (10), 65 (12); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (*m*, 6 H), 7.18 (9 H), 2.64 (*m*, 6 H), 1.82 (*m*, 4 H), 1.66 (*m*, 2 H), 1.61 (*m*, 2 H), 1.43 (3 H). The alcohol was subjected to dehydration in dimethyl sulfoxide (DMSO) at 170°C to give a mixture of isomeric olefins (65%) as a yellow oil (b.p. 180°C/0.1 mbar); mass spectrometry (70 eV) m/z 354 (5, $[M]^{+\cdot}$), 263 (2), 250 (2), 249 (1), 222 (1), 221 (1), 145 (5), 144 (3), 143 (4), 131 (22), 130 (5), 129 (9), 128 (5), 117 (32), 115 (8), 105 (14), 104 (17), 92 (23), 91 (100), 79 (8), 78 (6), 77 (11), 65 (17), 63 (5). Subsequent hydrogenation with Pd/C in EtOH furnished the triphenylisoalkane (95%) as a colourless oil, bp 195°C/0.1 mbar; MS (70 eV) m/z 356 (9, $[M]^{+\cdot}$), 265 (1.5), 264 (1.2), 145 (3), 131 (9), 130 (1), 129 (1), 117 (8), 115 (1), 105 (16), 104 (10), 103 (2), 92 (100), 91 (85), 79 (2), 78 (2), 77 (3), 65 (4); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.0–7.4 (*m*, 15 H), 2.50–2.70 (*br m*, 6 H), 1.25–1.75 (*br m*, ~11 H).

Most of the compounds **A**–**I** and **J**–**P** used as precursors for reference ions $C_{20}H_{11}^{+}$ and $C_{17}H_{17}^{+}$, respectively (cf. Tables 2–4), were synthesized according to routine procedures and compared to data given in the literature. 2-Methylindene (**A**) [39] was prepared from 2-methyl-2-indanol (**E**, see below) by heating at 170 °C in DMSO for 20 h. Workup with water/pentane and Kugelrohr distillation of the crude product gave pure **A** as a colourless oil (bp 117 °C/48 mbar) in 49% yield. 3-Methylindene (**B**) [39] was prepared in the same way from 1-methyl-1-indanol (**D**, see below) as a colourless oil (bp 117 °C/48 mbar) in 48% yield. 2-(Hydroxymethyl)indane (**C**) [40] was synthesized via indane 2-carboxylic acid [41], that was reduced with $LiA1H_4$ in diethyl ether. Workup and Kugelrohr distillation gave **C** as a colourless oil (bp 92 °C/0.07 mbar) in 75% yield. 1-Methyl-1-indanol (**D**) [42] was prepared by Grignard reaction of methyl iodide and 1-indanone. Workup with aqueous NH_4Cl followed by Kugelrohr distillation (bp 90 °C/0.13 mbar) furnished a colourless solid (mp 56–57 °C) in 64% yield. 2-Methyl-2-indanol (**E**) [43] was synthesized by Grignard reaction of methyl iodide with 2-indanone. Workup as noted for **D** and distillation (bp 87 °C/0.15 mbar) gave a colourless solid (mp 55 °C) in 46% yield. 1,2-Dihydronaphthalin (**F**) [44] was prepared by heating 1-tetralol (**G**) in DMSO at 170°C for 20 h, followed by extraction with water/pentane and Kugelrohr distillation to give a colourless oil (bp 102 °C/27 mbar) in 80% yield. 1-Tetralol (**G**) [45] and 2-tetralol (**H**) were prepared in 85% yields by reduction of the corresponding tetralones with $LiA1H_4$ as pale-yellow oils (**G**: bp 94 °C/0.15 mbar, **H**: bp 95 °C/0.14 mbar). 2-Benzyl-indane **I** was available from a previous study [46]. 2-Benzyl-3,4-dihydronaphthalin (**J**) [47] was obtained by heating 2-benzyl-1-tetralol (**M**) at 170 °C in DMSO for 20 h, workup and Kugelrohr distillation as a colourless oil (bp 130 °/0.17 mbar) in 63% yield. In a similar way, 1-benzyl-3,4-dihydronaphthalin (**K**) [48] was prepared from 1-benzyl-1-tetralol (**N**) as a colourless oil (bp 135 °/0.14 mbar) in 65% yield. The product contained ~20% of 1-benzylidenenaphthalin (by ^{1}H NMR spectrometry).

Synthesis of 2-phenylmethyl-1,2,3,4-tetrahydro-2-hydroxynaphthalin (2-benzyl-2-tetralol, **L**): Into a suspension of magnesium turnings (386 mg, 16.0 mmol) in anhydrous diethyl ether (5.0 ml) was slowly dropped a solution of benzyl chloride (2.01 g, 16.0 mmol) in the same solvent (5 ml). After heating to reflux for 1 h, a solution of 2-indanone (1.80 g, 13.6 mmol) in diethyl ether (10 ml) was added slowly, and the mixture was heated for another 2 h. The solution was allowed to cool and worked up by adding water and aqueous NH_4Cl, extraction with diethyl ether, and drying of the extracts with Na_2SO_4. Removal of the solvent furnished the crude product (1.06 g) that was purified by Kugelrohr distillation; subsequent recrystallization from hexane gave colourless crystals of mp 88°C (910 mg, 28%). Mass spectrometry (70 eV): m/z 238 (2%, $M^{+\cdot}$), 147 (74), 146 (100), 129 (46), 119 (10), 117 (17), 115 (6), 105 (12), 104 (23), 92 (27), 91 (29). ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 7.26$ (mc, 5 H), 7.11 (mc, 4 H), 2.6–3.0 (m, 6 H), 1.65–1.95 (2 H), 1.50 (s, 1 H).

2-Benzyl-1-tetralol (**M**) [46] was prepared by aldol condensation of 1-tetralone and benzyldehyde, giving 2-benzylidene-1-tetralone (mp 105 °C, 81%) [49], and subsequent reduction with $LiA1H_4$ in diethyl ether. Workup and recrystallization of the crude product from ethanol gave the alcohol (mp 118 °C) as long, colourless needles in 36% yield. 1-Benzyl-1-tetralol (**N**) [47] was prepared by reaction of benzylmagnesium chloride and 1-tetralone as described above for **L**. Workup furnished a crude product that was purified by Kugelrohr distillation to give the alcohol as a colourless oil (bp 152 °C/0.14 mbar) in 81% yield.

The synthesis of 2,2-di(phenylmethyl)indane (dibenzylindane) **O** was described in a preceding article [30]. 2,2′-Spirobiindane **P** was synthesized as described in the literature [50].

2.2. Measurements

All CI mass spectra, CI/MIKE, and CI/CID/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 or, in the case of volatile liquids, the heated inlet system held at

Table 1
MIKE spectra of protonated oligophenylalkylbenzenium ions **1**–**6**[a]

Precursor ion	Fragment ion[b] $[M + H - 2\ C_6H_6]^+$	Fragment ion[b] $[M + H - C_6H_6]^+$	$\{[M + H - 2\ C_6H_6]^+\}/\{[M + H - C_6H_6]^+\}$
1	81.5	18.5	4.4 (±0.5)
2	98.6	1.4	70 (±20)
3	0.5	99.5	0.005 (±0.001)
4	1.2	98.8	0.012 (±0.001)
5	12.3	87.7	0.14 (±0.01)
6	10.7	89.3	0.12 (±0.01)

[a] $[M + H]^+$ ions were generated by CI(iC_4H_{10}) under similar conditions.
[b] Fraction (in % Σ) of total fragment ion abundance.
[c] Error limits were estimated from repeated runs.

~200 °C. 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.

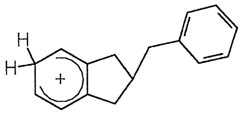
Mass spectral data represent averaged data from at least 5–10 spectra. CID/MIKE spectra were obtained with helium as the collision gas by 50% attenuation of the main beam signal and were evaluated according to signal intensity rather than signal area; error limits were estimated to be <5% (rel.).

3. Results and discussion

3.1. Single versus double benzene loss from oligophenylalkanes

Among protonated oligophenylisoalkanes bearing three rings at the outermost sites of the branched aliphatic chain, the twofold loss of benzene from the $[M + H]^+$ ions is particularly pronounced for protonated tribenzylmethane **1**. The MIKE spectrum of **1** shows that only a 19% fraction of the $[M + H]^+$ ions fragmenting in the second field-free region (2nd ffr) undergo the usual loss of a single molecule of benzene to give ions $C_{16}H_{17}^+$ (m/z 209). The major fraction (81%) of the metastable $[M + H]^+$ ions lose the mass of 156 Da to form ions $C_{10}H_{11}^+$ (*m/z* 131), indicating the expulsion of two molecules of benzene rather than any single neutral fragment of the elemental composition $C_{12}H_{12}$. This follows (1) from thermochemical arguments that disfavour the formation of a $C_{12}H_{12}$ neutral bearing, necessarily, only one single aromatic π-electron sextet, and (2) from the fact that the loss of 78 Da, i.e. elimination of a single molecule of benzene being ubiquitous for protonated alkylbenzenium ions, does compete with the double loss in the case of **1**. As shown in Table 1, all of the higher homologues of protonated tribenzylmethane, **3**–**6**, also undergo the twofold benzene loss within the 2nd ffr, albeit to a far lesser extent. Thus, substitution of one benzyl group for a β-phenylethyl group in **3** almost completely suppresses the twofold elimination, whereas the presence of two phenethyl groups in **4** give rise to a slight increase of the ratio $\{[M + H - 2\ C_6H_6]^+\}/\{[M + H - C_6H_6]^+\}$. Interestingly, the most symmetrical homologue of this series, protonated tris(phenylethylmethane) **5**, exhibits a relative maximum of this ratio but the single loss of benzene clearly dominates. The twofold elimination appears to vanish slowly with even higher homologues (cf. **6**).

Another extreme was found when protonated tetrabenzylmethane **2** was studied. This highly symmetrical, large oligophenylisoalkylbenzenium ion undergoes the twofold elimination process almost exclusively, even within the same field-free region—the single benzene loss representing an almost negligible (≤2%) fraction. As already discussed in a preceding article [30], the twofold loss of benzene from the quasimolecular ions **1**, **2**, and **5** is also observed in the normal CI(CH_4) or CI(iC_4H_{10}) mass spectra and the corresponding *B/E* linked scan spectra. The ion-abundance ratios $\{[M + H - 2\ C_6H_6]^+\}/\{[M + H - C_6H_6]^+\}$ are even higher for the more



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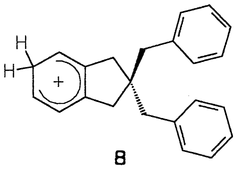

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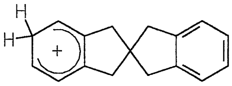

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highly excited $[M + H]^+$ ions already fragmenting in the CI ion source. At the same time, the fast interannular proton exchange is still statistical in all of these ions [30].

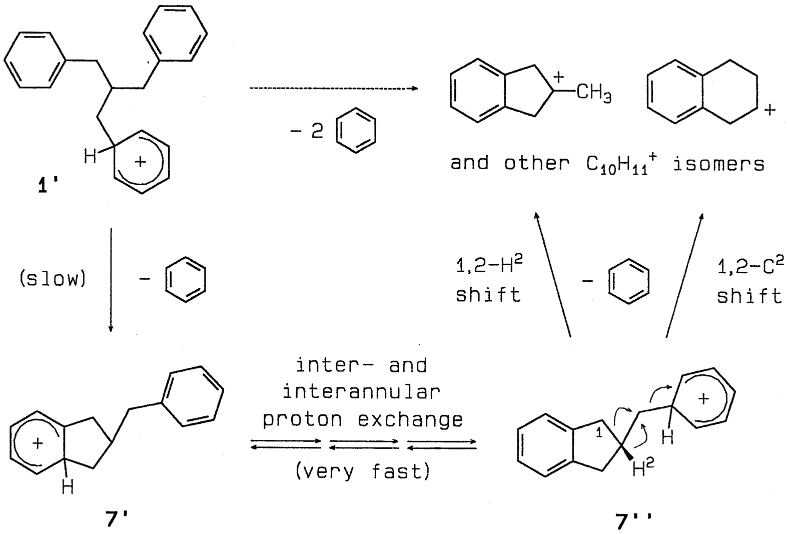
Three more particular, and at the same time cyclic *and* branched alkylbenzenium-type ions have been included in this study, viz. protonated 2-benzylindane **7**, protonated 2,2-dibenzylindane **8**, and protonated 2,2′-spirobiindane **9**.

Both **7** and **8** undergo the fast interannular proton exchange, and they both eliminate a single molecule of benzene as the only fragmentation channel [30]. Notably, twofold loss of benzene does not take place in the case of **8**. In contrast, the bicyclic congener, protonated 2,2-spirobiindane **9**, does expel benzene albeit in competition with major elimination channels (cf. Table 3).

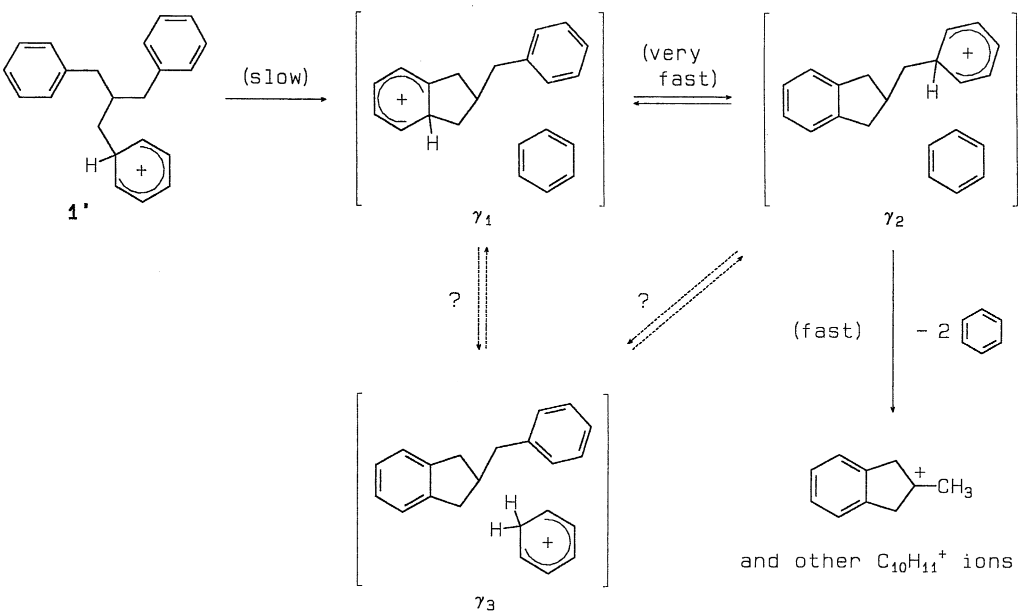
3.2. Mechanistic implications—mobile protons pro and contra ion/neutral complexes

The apparently simultaneous loss of two molecules of benzene within the same field-free region of a sector field mass spectrometer is most intriguing because of the generally accepted fact that the formation of a pair of (ionic and neutral) fragmentation products requires less energy than the formation of a triple of fragments, i.e. one ion and *two* neutrals. Further, the simultaneous expulsion of two neutrals, and two arene molecules, in particular, appears to be mechanistically highly improbable. Since the formation of a $C_{12}H_{12}$ molecule has to be discarded, two hypotheses have been raised to approach our understanding of the twofold benzene loss.

(1) The rate of the release of the second benzene molecule exceeds that of the first one, as expressed by Scheme 1. This situation parallels that of the double CO loss from ionized anthraquinones [32,33]. The energy requirements for the elimination of two ben-



Scheme 1.



Scheme 2.

zene molecules have to be in the same range as that of the release of a single one; that is, the critical energy for the release of the second neutral cannot significantly exceed that of the first one but could well be considerably lower. This holds in particular for protonated tribenzylmethane **1** and tetrabenzylmethane **2**, the latter being presumably a case where the second benzene loss is considerably faster than the first one, even for the metastable ions.

As suggested in Scheme 1, the first molecule of benzene is eliminated during the cyclization of the incipient primary carbenium ion to form protonated 2-benzylindane (**7′**). Subsequent to a fast interannular proton transfer step (**7′** → **7″**) [30], a 1,2-H or 1,2-C shift (Wagner–Meerwein rearrangement) in ions **7″** during the second loss of benzene gives rise to indanyl- or tetralyl-type $C_{10}H_{11}^+$ ions, respectively. Heterolytic cleavage of the C^{ipso}–C^{α} bonds of simple (mononuclear) alkylbenzenium ions [8,51–53] and lower ω-phenylalkylbenzenium ions [26a,54,55] has been suggested to occur with concomitant 1,2-H or 1,2-C shifts in particular with β-branched isomers [56].

In this view, the elimination of the second molecule of benzene from the homologous $[M + H]^+$ ions **3**–**6** should require significant, albeit small, amounts of additional energy as compared to the single loss of benzene (see below).

(2) As a second hypothesis, we considered the possibility that the first molecule of benzene would remain coordinated with the ion generated by the primary fragmentation, $[M + H - C_6H_6]^+$, within an ion-molecule complex, "await" the formation of the second benzene fragment, and would eventually be released *ensemble* (i.e. simultaneously) with the first one (Scheme 2). This idea was raised in view of the fact that the ring protons in **1**, **2**, and **5** were found to be highly mobile [30,31,35], and that the mobility of 16 or 21 protons could contribute a significant entropy term ($T\cdot\Delta S$) to the free enthalpy of the overall fragmentation process. The idea of an extra "entropic stabilization" of the complex $\{[M + H - C_6H_6]^+ C_6H_6]\}$ (cf. γ_1, γ_2 in Scheme 2) by fast proton exchange within, and possibly between, its aromatic components (cf. γ_3) was encouraged in part by the temporary assumption that fast-moving protons in arenium ions can give rise to unusually high entropy effects [36,37]. Notwithstanding this aspect, the inter-

mediacy of ion/neutral complexes such as $\boldsymbol{\gamma_1}$–$\boldsymbol{\gamma_3}$ cannot be excluded [57]. Protonated arene dimers (or heterodimers) are known to be stable species [58] and, therefore, we would like to consider their possible formation in the course of the twofold benzene elimination [59].

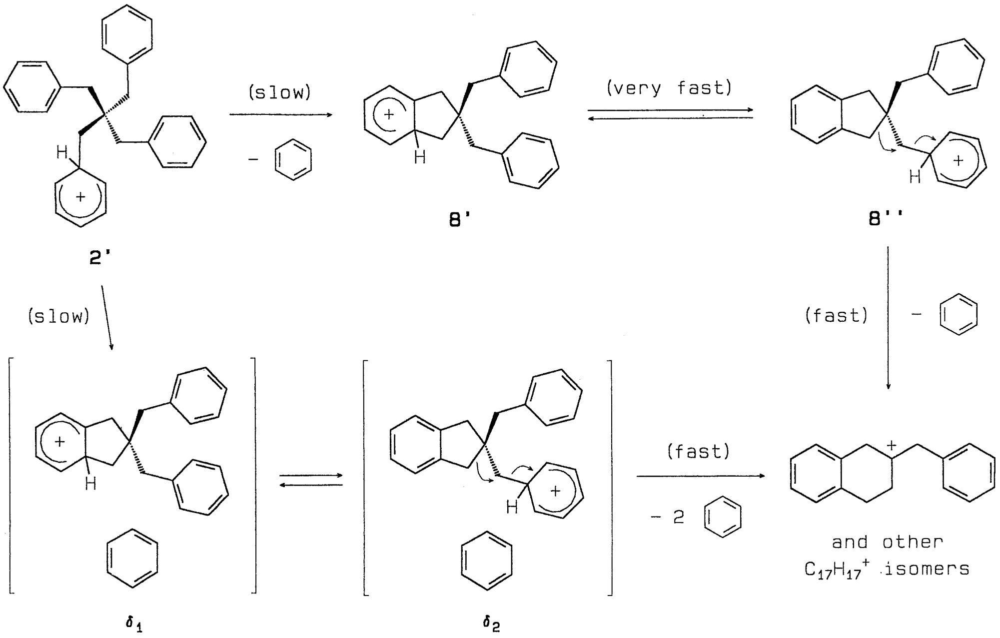
As mentioned above, both protonated 2-benzylindane **7** and protonated 2,2-dibenzylindane **8** undergo the fast interannular proton equilibration and loss of benzene is the exclusive fragmentation channel for both of these ions, too. Cyclization of the charge-bearing ω-phenylalkyl moiety during release of the benzene neutral appears to be highly probable for most of the protonated diphenylalkanes [12b] and has been demonstrated to operate in the corresponding $[M - H]^+$ ions formed by hydride abstraction [38]. For all these reasons, the protonated indanes **7** and **8**, respectively, were considered the best candidates for the $[M + H - C_6H_6]^+$ species formed upon release of the first molecule of benzene from **1** and **2**.

In great contrast to the product ions of the primary fragmentation, [**1** $- C_6H_6]^+$, those of the secondary fragmentation, [**1** $- 2\ C_6H_6]^+$ and the $C_{10}H_{11}^+$ (*m*/*z* 131) ions generated by loss of benzene from protonated 2-benzylindane **7**, cannot undergo fast intramolecular proton shifts. We can safely assume that (homobenzylic) 2-indanyl- or 2-tetralyl-type ions shown in Schemes 1 and 2 as well as the corresponding benzylic isomers (see below) represent the most stable $C_{10}H_{11}^+$ congeners. This is because of the high local proton affinity of the corresponding conjugate bases (e.g. 2-methyl-1H-indene or 1,2-dialine) at the styrylic double bond [60,61]. Thus, protonation at these sites is highly favourable and interchange with other tautomers should be suppressed. Therefore, we assume that the release of the first molecule of benzene from protonated tribenzylmethane **1** leads to a protonated arene (benzenium ion), viz. protonated 2-benzylindane **7**, which contains ten mobile "aromatic" protons, whereas the second loss of benzene from **7** generates "simple" secondary or, by subsequent 1,2-hydride shift, tertiary carbenium ions, that no longer bear mobile protons. As a consequence, any entropic stabilization, if present at all in complexes $\boldsymbol{\gamma_1}$–$\boldsymbol{\gamma_3}$, would vanish at this point. Thus, the release of the two molecules of benzene would be "simultaneous."

According to the mechanistic concepts displayed for protonated tribenzylmethane in Schemes 1 and 2, the loss of the first molecule of benzene from protonated tetrabenzylmethane **2** could occur in a similar way, generating protonated 2,2-dibenzylindane **8** within a complex ($\boldsymbol{\delta}$, Scheme 3). The arenium ion **8**, $C_{23}H_{23}^+$ (m/z 299), containing 15 mobile protons in total (cf. $\boldsymbol{\delta_1} \rightleftharpoons \boldsymbol{\delta_2}$), has two possibilities to release another benzene fragment. A 1,2-C shift would generate benzyl-substituted tetralyl ions $C_{17}H_{17}^+$ (*m*/*z* 221), in analogy to the secondary loss of benzene from **1**. Alternatively, a second cyclization would produce protonated 2,2′-spirobiindane **9** aggregated to two benzene molecules ($\boldsymbol{\epsilon}$, Scheme 4). Protonated 2,2′-spirobiindane, $C_{17}H_{17}^+$ (*m*/*z* 221), represents an arenium ion on its own that, however, should not undergo direct interannular proton exchange because of its skeletal rigidity. In the first case (Scheme 3), ion-molecule complex $\boldsymbol{\delta_2}$ would "isomerize" into a terbody complex—the ionic component of which no longer bears mobile protons and thus would be relatively short-lived. In the second case (Scheme 4), a terbody complex $\boldsymbol{\epsilon}$ would form, which represents a proton-bound triple of arenes, and thus may have a somewhat longer lifetime as long the 2,2′-spirobiindane partner persists. Also shown in Scheme 4 is the possibility that protonated 2,2′-spirobiindane **9′** is formed via **8″** without being solvated by a benzene molecule. In either case, isomerization of **9′** by a 1,2-C shift into tetralyl-type ions appears to be possible. As will be shown in the next section, the intermediacy of ion/neutral complexes cannot be corroborated; however, the structural alternative concerning the $C_{17}H_{17}^+$ ions formed by the twofold benzene loss can be answered.

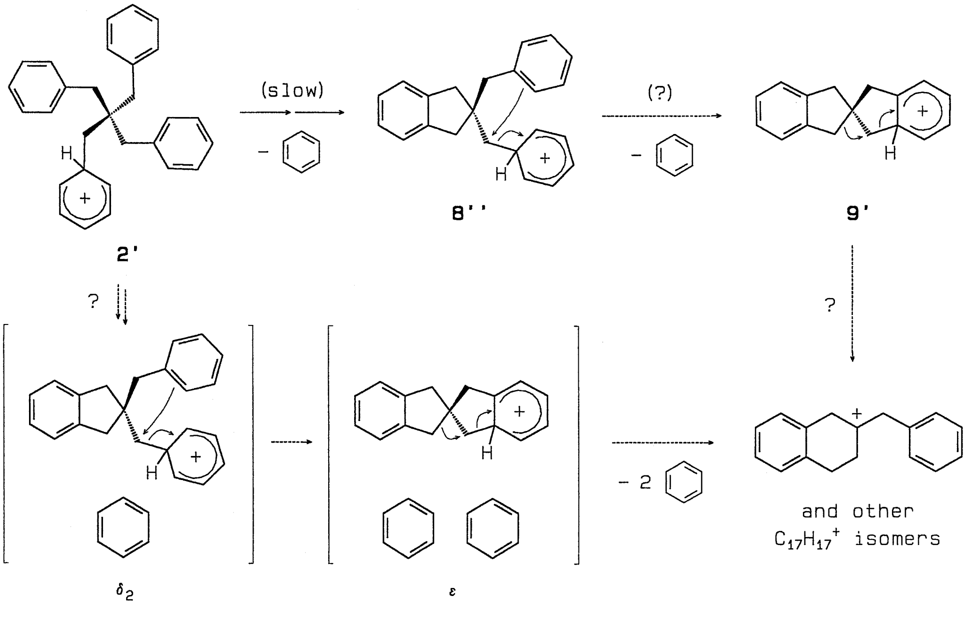
3.3. Identification of the product ions $[M + H - 2\ C_6H_6]^+$ of the twofold benzene loss

In order to substantiate the mechanisms of the twofold benzene loss from **1** and **2** and to elucidate the structures of the $[M + H - 2\ C_6H_6]^+$ ions, a series of $C_{10}H_{11}^+$ ions (*m*/*z* 131) and $C_{17}H_{17}^+$ ions (*m*/*z* 221),



Scheme 3. Mechanism for the twofold loss of benzene from ions **2**.

respectively, were generated by chemical ionization [CI(iC_4H_{10})] of authentic precursors. Both MIKE and CID/MIKE spectra were recorded. As reference species for ions [**1** − 2 C_6H_6]$^+$ (m/z 131), the [M + H]$^+$ ions of the cyclic styrenes **A**, **B**, and **F** and of the [M + H − H_2O]$^+$ ions generated from alcohols **C**–**E**,



Scheme 4. Alternative mechanism, which can be excluded by CID mass spectrometry (see text).

Table 2
CID/MIKE spectra of ions $[\mathbf{1} - 2\ C_6H_6]^+$ and $C_{10}H_{11}^+$ reference ions (*m*/*z* 131) generated from **A**–**I**[a]

Precursor CI(iC_4H_{10}) *m*/*z*	**A** $+H^+$	**B** $+H^+$	**C** $+H^+–H_2O$	**D** $+H^+–H_2O$	**E** $+H^+–H_2O$	**F** $+H^+$	**G** $+H^+–H_2O$	**H** $+H^+–H_2O$	**I** $-C_6H_6$	**1** $-2\ C_6H_6$
27	0.6	0.6	0.6	0.7	0.5	0.7	0.8	0.7	0.9	0.7
39	2.6	1.9	1.9	2.1	2.1	2.3	2.2	1.9	2.2	2.3
51	3.2	2.9	2.8	3.0	2.6	3.0	3.5	3.0	2.9	3.4
53	1.0	0.9	0.9	1.1	1.0	1.0	1.1	1.1	1.2	1.2
63[b]	3.3	2.6	2.6	2.8	2.8	2.7	3.1	2.9	2.6	3.1
74/75[c]	1.2	1.3	1.2	1.3	1.1	1.2	1.5	1.3	1.3	1.3
77	2.7	2.7	2.6	2.9	2.6	3.0	3.2	2.7	3.1	3.1
86	0.6	0.4	0.4	0.5	0.6	0.4	0.4	0.4	0.4	0.5
89	1.8	1.6	1.2	1.6	1.9	1.3	1.3	1.3	1.5	1.7
91	8.5	7.9	8.9	8.8	9.5	9.6	8.4	10.3	10.3	9.0
102/103[c]	1.4	1.4	1.4	1.5	1.4	1.6	1.7	1.5	1.8	1.5
115	14.8	15.5	12.7	15.4	18.3	10.8	12.2	12.0	12.7	13.3
116	6.3	5.8	5.6	6.2	9.1	5.4	5.6	5.7	6.3	5.8
127	5.1	5.2	5.9	5.1	5.0	5.7	5.9	5.5	5.3	5.1
128	12.5	12.3	14.1	12.1	12.4	14.2	14.5	13.4	12.2	13.6
129	15.2	15.2	17.1	14.5	15.4	17.4	16.5	17.3	15.9	16.1
130	19.2	21.8	20.2	20.4	13.6	19.7	18.1	19.0	19.3	18.2

[a] In %Σ.
[b] Charge-stripping peak(s) at ~*m*/*z* 65.5–64.0 have been omitted (see text).
[c] Combined intensity of overlapping signals.

G, and **H** were studied. Additionally, the $[M + H - C_6H_6]^+$ ions of 2-benzylindane **I** were investigated. In the second series, the reference ions for $[\mathbf{2} - 2\ C_6H_6]^+$ (*m*/*z* 221) were $[M + H]^+$ ions formed by protonation of the benzyldialins **J** and **K** and $[M + H - H_2O]^+$ ions generated from the benzyltetralols **L**–**N**. Finally, the $[M + H - C_6H_6]^+$ ions from 2,2-dibenzylindane **O** and the $[M + H]^+$ ions of 2,2′-spirobiindane **P** (≡ **9**) were measured by MIKE and CID/MIKE spectrometry.

The outcome of these measurements is clear-cut. In the case of the $C_{10}H_{11}^+$ ions (*m*/*z* 131), all reference ions give the same MIKE and CID/MIKE spectra and these spectra are identical to those measured for the $[M + H - 2\ C_6H_6]^+$ ions of protonated tribenzylmethane **1**. Spontaneous fragmentation of all these $C_{10}H_{11}^+$ ions was found to be relatively weak with major contributions consisting of losses of $H^\cdot$, H_2 and the combination thereof, and minor ones consisting of the losses of $CH_3^\cdot$, CH_4 (m/z 116 and 115), and C_3H_4 (*m*/*z* 91). In contrast, the collision-induced fragmentation was very pronounced and gave a rich pattern (Table 2) containing a characteristic charge-stripping peak [62] indicating the formation of $C_{10}H_{11}^{2+}$. The spectrum reproduced in Fig. 1 is representative of all the CID/MIKE spectra of these $C_{10}H_{11}^+$ ions.

Thus, the similarity between the CID/MIKE spectra of the reference ions and that of the $[M + H - 2\ C_6H_6]^+$ ions from protonated tribenzylmethane con-

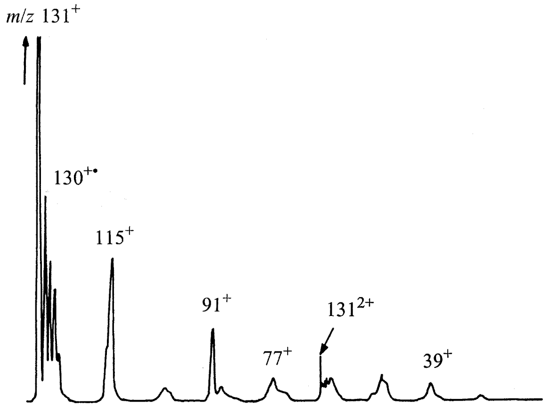
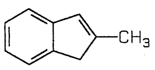
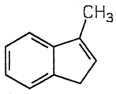


Fig. 1. Representative CID/MIKE spectrum of $C_{10}H_{11}^+$ ions (*m*/*z* 131) generated from precursors **A**–**I** (see text) and of ions $[\mathbf{1} - 2\ C_6H_6]^+$.



A



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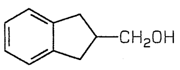

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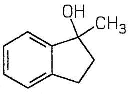

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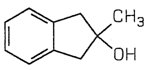

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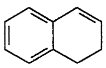

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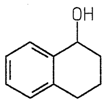
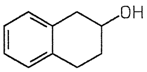


G



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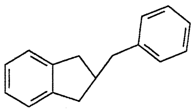


I

firms the structure of the product ions of the twofold benzene loss.

Of the $C_{17}H_{17}^{+}$ reference ions (*m/z* 221) measured in order to identify the structure of the $[M + H - 2\ C_6H_6]^+$ ions of protonated tetrabenzylmethane **2**, all but one (viz. **9**, see below) gave the same MIKE and CID/MIKE spectra. In fact, these spectra were also identical to those measured for the $[M + H - 2\ C_6H_6]^+$ ions of **2** and include those of the reference ions $[M + H - C_6H_6]^+$ of 2,2-dibenzylindane **O**. A representative example is reproduced in Fig. 2(a) and the data are collected in Table 3. The unimolecular fragmentation of all these $C_{17}H_{17}^{+}$ ions is characterized by the losses of C_6H_6 (note that this process does *not* occur in the same field-free region as the two preceding losses of benzene) and also of C_7H_8, C_8H_8, and $C_{10}H_{10}$. In these cases, elimination of C_8H_{10} (→ *m/z* 115) and C_9H_8 (→ m/z 105) does not occur. In fact, most of these fragmentation channels appear to be characteristic for the benzyltetralyl structure(s) suggested above. The CID/MIKE spectra of this set of $C_{17}H_{17}^{+}$ reference ions [Fig. 3(a)] exhibit only a minor charge-stripping peak, indicating the formation of $C_{17}H_{17}^{2+}$ ions.

The single exception among the $C_{17}H_{17}^{+}$ studied is protonated 2,2′-spirobiindane **9** (≡ [**P** + H]$^+$). Both the MIKE and CID/MIKE spectra of these ions exhibit characteristic differences from those of the other $C_{17}H_{17}^{+}$ ions [Figs. 2(b), 3(b), and Tables 3 and 4]. In this case, spontaneous loss of a C_8H_{10} does occur (cf. *m/z* 115) but even more so in C_9H_8 (cf. *m/z* 105), as evident from the MIKE spectrum. Correspondingly, the CID spectrum of **9** reveals a significantly different fragmentation pattern not only in the *m/z* 105–117 but also in the high mass region. Moreover, the charge-stripping peak at *m/z* 110.5 is much more pronounced in the CID spectrum of **9** than in those of the other $C_{17}H_{17}^{+}$ reference ions. Thus, it

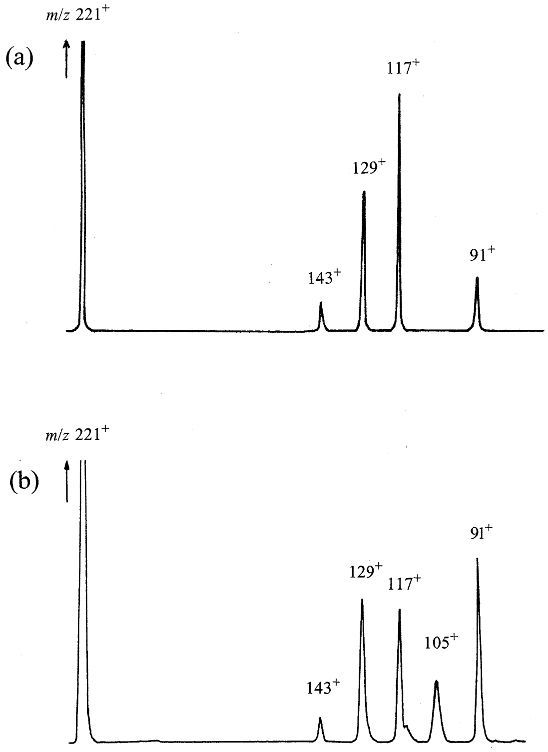


Fig. 2. (a) Representative MIKE spectrum of $C_{17}H_{17}^{+}$ ions (*m/z* 221) generated from precursors **J**–**O** (see text) and of ions $[\mathbf{2} - 2\ C_6H_6]^+$. (b) MIKE spectrum of protonated 2,2′-spirobiindane [**P** + H]$^+$ ≡ **9**.

Table 3
MIKE spectra of ions [**2** − 2 C_6H_6]$^+$ and $C_{17}H_{17}^+$ reference ions (*m*/*z* 221) generated from **J**–**P**[a]

Precursor CI(iC_4H_{10}) *m*/*z*	**J** $+H^+$	**K** $+H^+$	**L** $+H^+-H_2O$	**M** $+H^+-H_2O$	**N** $+H^+-H_2O$	**O** $-C_6H_6$	**2** $-2\ C_6H_6$	**P** $+H^+$
91	18.8	16.4	5.9	3.9	33.1	6.4	5.3	30.1
105	.0	.0	.0	.0	.0	.0	.0	12.4
115	.0	.0	.0	.0	.0	.0	.0	9.1
117	41.4	44.4	53.1	53.9	28.9	59.2	54.7	21.8
129	31.1	27.5	33.7	36.5	28.3	26.1	32.8	21.0
143	8.8	11.8	7.4	5.8	9.7	8.3	7.2	5.7

[a] In %Σ.

appears obvious that protonated 2,2′-spirobiindane **9** *does not* (or does not predominantly) form during the twofold elimination of benzene from protonated tetrabenzylmethane **2**. A second cyclization step (**8″** → **9′** or $\boldsymbol{\delta}_2 \rightarrow \boldsymbol{\epsilon}$) appears to be unlikely or a transitory process only. Rather, benzyltetralyl ions, i.e. cyclic derivatives of protonated styrenes, represent the structures of the [M + H − 2 C_6H_6]$^+$ ions of **2**. This means that if the overall fragmentation of **2** takes place via ion/molecule complexes $\boldsymbol{\delta}$ and $\boldsymbol{\epsilon}$ at all, the eventual intermediate from which the benzene neutrals are lost is *not* a protonated triple of arenes. Thus, there is no positive evidence supporting the hypothesized favourable role of mobile protons.

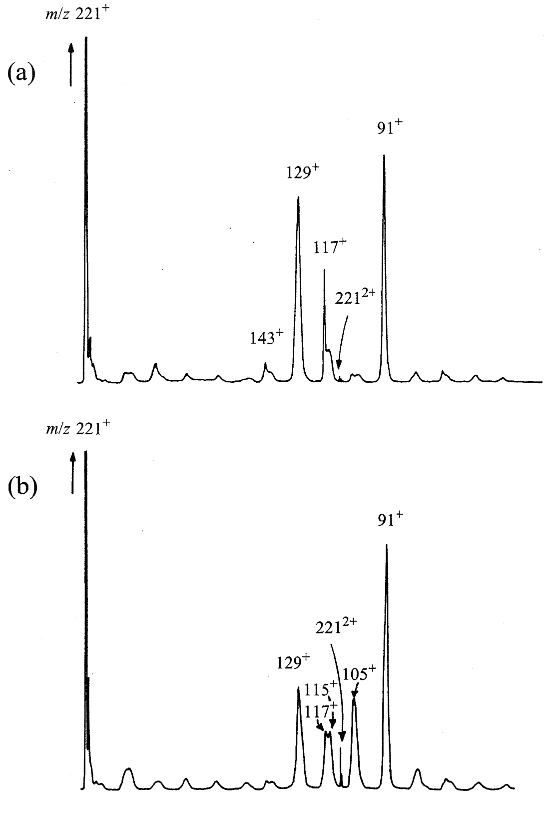
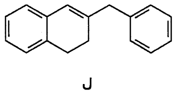


Fig. 3. (a) Representative CID/MIKE spectrum of $C_{17}H_{17}^+$ ions (*m*/*z* 221) generated from precursors **J**–**O** (see text) and of ions [**2** − 2 C_6H_6]$^+$. (b) CID/MIKE spectrum of protonated 2,2′-spirobiindane [**P** + H]$^+$ ≡ **9**.

3.4. Higher homologues: Suppression of the twofold benzene loss

The structural characterization of the [M + H − 2 C_6H_6]$^+$ ions, $C_{10}H_{11}^+$ and $C_{17}H_{17}^+$, discussed in the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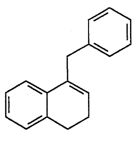
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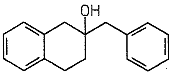

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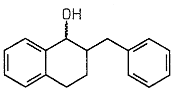
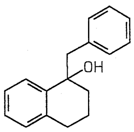


M



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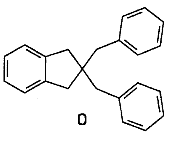
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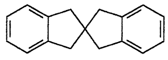

P

Table 4
CID/MIKE spectra of ions $[\mathbf{2} - 2\ C_6H_6]^+$ and $C_{17}H_{17}^+$ reference ions (*m*/*z* 221) generated from **J**–**O**[a]

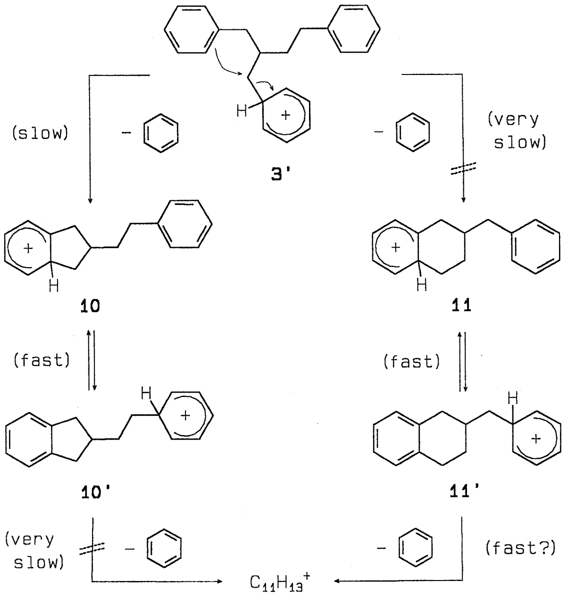
Precursor CI(iC_4H_{10}) *m*/*z*	**J** $+H^+$	**K** $+H^+$	**L** $+H^+–H_2O$	**M** $+H^+–H_2O$	**N** $+H^+–H_2O$	**O** $-C_6H_6$	**2** $-2\ C_6H_6$	**P** $+H^+$
27	0.5	0.4	0.5	0.5	0.3	0.6	0.5	0.5
39	1.6	1.6	2.1	2.3	1.5	2.1	2.2	2.2
51	2.9	2.7	3.2	3.3	2.2	3.0	3.3	2.8
63	2.5	2.7	3.2	3.4	2.2	2.6	3.2	2.8
65	4.6	3.2	5.0	5.0	3.1	4.0	4.6	3.2
77	4.3	3.3	4.7	4.5	3.0	4.0	5.0	6.8
91	*112*	*68*	*95*	*95*	*63*	*84*	*88*	*75*
102/103[c]	2.9	2.2	3.2	2.9	1.9	2.6	3.4	~2.
105	3.2	2.6	4.1	3.4	2.5	5.6	3.4	28.
~110[d]	2.5	1.3	2.0	1.8	1.2	1.5	1.6	4.8
~110.5d[d]	(5.0)	(3.2)	(2.2)	(1.6)	(2.4)	(2.9)	(3.3)	(19)
115	13.1	9.1	14.3	13.0	9.3	12.8	15.1	*17.9*
117	*39*	*25*	*49*	*44*	*23*	*57*	*49*	*18.9*
129	*74*	*39*	*78*	*74*	*38*	*64*	*69*	*32*
141	5.5	4.6	4.3	4.1	3.7	4.0	4.0	2.8
143	*8.0*	*10.6*	*8.2*	*7.8*	*9.5*	*11.1*	*8.2*	*3.1*
151/152[c]	2.3	2.4	1.8	1.6	2.5	2.0	1.5	2.5
165	2.9	3.6	2.6	2.5	3.7	2.8	2.4	3.0
178	2.8	4.0	3.5	3.7	4.5	3.5	3.4	3.5
192	4.4	5.9	7.8	8.3	6.1	5.4	7.8	3.0
202/203[c]	3.7	3.4	3.8	3.9	6.2	3.8	3.7	6.3
205	3.7	3.6	4.4	4.3	3.8	4.8	4.1	6.3
214/215[c]	1.6	1.1	1.4	1.6	3.3	1.2	1.4	2.3
217	1.9	1.9	1.6	1.8	1.5	1.6	1.6	2.8
219	5.8	6.1	7.4	7.5	6.5	8.0	7.2	6.3
220	27.3	34.3	19.1	20.6	31.0	24.1	20.6	36.1

[a] In %Σ.
[b] Ions whose mass-to-charge and intensity data are given in italics are also formed by unimolecular fragmentation (cf. Table 3).
[c] Combined intensity of overlapping signals.
[d] Charge-stripping products (see text).

previous section also provides strong support for the cyclization process suggested to occur during the first elimination step. The preference of cyclized isomers from protonated (and also from ionized) unsaturated alkylbenzenes has been documented, [63,64]. In particular, it has been demonstrated that intramolecular cyclization yielding five- and six-membered rings is a characteristic isomerization path for the α,ω-diphenylpropyl cations [38]. Therefore, the formation of protonated indane derivatives from **1** and **2** during the loss of benzene is a reasonable fragmentation route and of general importance for protonated diphenylalkanes and oligophenylisoalkanes.

Nevertheless, the heterolysis of the C^{ipso}–C^{α} bond of "primary" alkylbenzenium ions requires appreciable activation energies. Heterolysis of β-branched isoalkylbenzenium ions occurs much more readily [56]. Therefore, the mechanisms suggested in Schemes 1–3 are in line with the finding that the second benzene loss occurs at a similar (cf. **1**) or even higher (cf. **2**) rate as compared to the first one. In the case of protonated benzylindanes **7** and **8**, both 1,2-H and/or 1,2-C shifts should be very favourable processes since the cyclic framework of these alkylbenzenium ions offers a favourable pre-orientation of the migrating atom or group. The particular readiness of the elimination of benzene from protonated 2-benzylindanes such as **7** and **8** as compared to the cyclization process follows also from the finding that the latter ion does not form protonated 2,2′-spirobiindane **9** but preferably benzyltetralyl ions (cf. Schemes 3 and 4). Thus, a concerted heterolysis/1,2-C shift, as formulated for **8″** or complex $\boldsymbol{\delta}_2$ (Scheme 3) should be particularly favourable. Although reliable thermochemical data for such large reactants are lacking, we may safely assume that the origin for the fast secondary loss of benzene lies in the ease of this heterolysis, notwithstanding the fact that the interannular proton exchange in ions **1–8** is still a much faster process [30].

The mechanistic concept proposed for the unusual fragmentation of protonated tri- and tetraphenylisoalkanes is also in accordance with the (originally intriguing) observation that the twofold benzene loss is only a minor process for the higher homologues of **1**. Obviously, the entropic and/or enthalpic requirements of the competiting cyclizations to generate either a protonated indane or a protonated tetralin differ drastically. As shown in Table 1, the ratio $\{[M + H - 2\ C_6H_6]^+\}/\{[M + H - C_6H_6]^+\}$ is least in protonated 2-benzyl-1,4-diphenylbutane **3** and only slightly higher in protonated 3-benzyl-1,5-diphenylpentane **4**. This can be explained by assuming that the first elimination of benzene occurs preferably by cyclization to the five-membered isomer, as shown for the case of **3** in Scheme 5 (cf. **3′** $\rightarrow$ **10** $\rightleftharpoons$ **10′**), rather than by formation of the six-membered isomer (cf. **3′** $\rightarrow$ **11** $\rightleftharpoons$ **11′**). Whereas the first sequence implies a high energy barrier towards the second benzene loss from ion **10′**, representing a γ-branched alkylbenzenium ion only, the alternative route should be slow because of its first step. In the series of the higher homologues **4–6**, the first elimination of benzene becomes gradually less favourable since the size of the rings to be formed increases and the energy requirements should approach those for the second benzene loss. The reluctance of forming rings larger than six-membered ones in such cyclization reactions has been demonstrated recently [38]. Fig. 4 shows a schematic and qualitative representation of the energy profiles for the single and twofold benzene losses for **1**, **2**, and **3**.



Scheme 5

4. Conclusion

The gas-phase chemistry of protonated alkylbenzenes, higher α,ω-diphenylalkanes, and the highest congeners studied so far, protonated oligophenylisoalkanes, is characterized by three common features: (1) They all undergo fast intra-annular proton shifts (the proton ring walk); (2) if two or several benzene rings are present, they undergo a fast interannular (ring-to-ring) proton transfer leading to complete equilibration of up to 21 protons within the microseconds' lifetime of the ions; and (3) they all dissociate by elimination of benzene. If the structural conditions are suitable, as is the case for protonated tri- and tetrabenzylmethane, the fast interannular proton exchange enables the consecutive elimination of two molecules of benzene, with the second loss being considerably faster than the first one. This gives rise to the apparently simultaneous loss of two molecules of benzene, even from the long-lived, metastable ions. Mechanistically, the twofold loss provides evidence for the formation of benzylindane intermediates during the first step by electrophilic cyclization, as suggested earlier. This is confirmed by CID studies that reveal the formation of

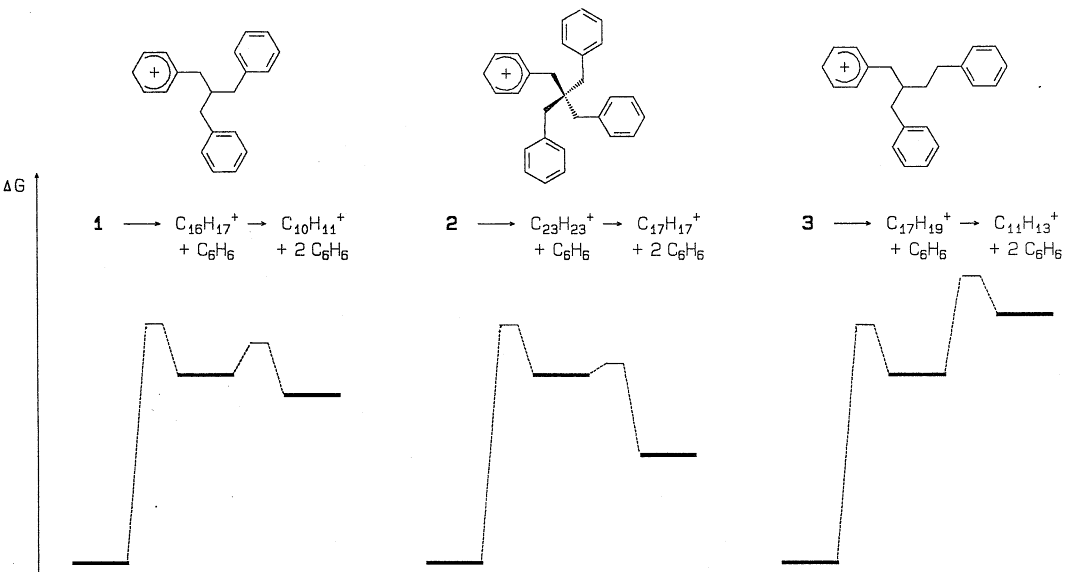


Fig. 4. Tentative and simplified energy profile for single and twofold loss of benzene from ions **1**, **2**, and **3**.

indanyl- and/or tetralyl-type ions as the final products of the twofold benzene elimination. The intriguing possibility that ion/molecule complexes (i.e. ionic aggregates consisting of protonated arene heterodimers or even heterotrimers) may play a major role during the twofold benzene has been considered but cannot be corroborated. Rather, the unusually fast, consecutive twofold loss of benzene has to be traced to structural peculiarities of the highly crowded oligophenylisoalkylbenzenium ions. In any case, both the fast interannular proton transfer and the twofold loss of benzene should also govern the fragmentation of other "large" protonated oligophenylalkanes such as polystyrene-derived fragments.

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