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Gaseous $[M - H]^+$ ions of α,ω-diphenylalkanes: cyclization to $[M + H]^+$ type ions of benzocycloalkanes as recognized by chain-length dependent proton exchange*

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ABSTRACT

Metastable $[M - H]^+$ ions of α,ω-diphenylalkanes $C_6H_5(CH_2)_xC_6H_5$ where $x = 3$–6 (structures **3**–**6** respectively), generated by hydride abstraction in the chemical ionization (*i*-butane) source, eliminate benzene after proton exchange between the aromatic rings. The proton exchange is slow for ions $[\mathbf{3} - H]^+$ and $[\mathbf{4} - H]^+$, but fast and apparently complete for ions $[\mathbf{5} - H]^+$ and $[\mathbf{6} - H]^+$. These observations, combined with collision activation experiments, suggest the cyclization of the $[M - H]^+$ ions to isomeric protonated 1-phenylbenzocycloalkane and 1-benzylbenzocycloalkane derivatives, i.e. to $[M^1 + H]^+$ type ions, with a preference for protonated tetralin structures. Hydrogen exchange between the aliphatic chain and the rings is absent or negligible for $[M - H]^+$ ions of **3**–**5** but is significant for ions $[\mathbf{6} - H]^+$.

Keywords: diphenylalkanes; proton exchange; mechanisms; cyclization; gas phase.

INTRODUCTION

The gas-phase ion chemistry of protonated alkylbenzenes [1] has been investigated in much detail during the past decades, to an extent approaching that of the studies of alkylbenzene radical cations [2]. By contrast to these $[M + H]^+$ and $[M]^{\cdot +}$ ions, the corresponding $[M - H]^+$ ions have gained only little attention. In early papers, Field and co-workers [3] reported on chemical ionization (CI) mass spectrometry of simple alkylbenzenes [4], mainly aiming at a comparison with electron impact (EI)-induced fragmentation. More complex $[M - H]^+$ ions have not been studied since. As extended benzyl type ions, the $[M - H]^+$ ions of α,ω-diphenylalkanes represent interesting gas-phase species. Moreover, from an organic chemistry point of view, the $[M - H]^+$ ions of diphenylalkanes are of general interest because they

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*Dedicated to Professor Charles H. DePuy on the occasion of his 65th birthday.

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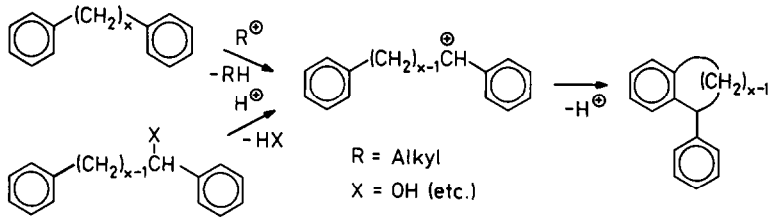
correspond to the key intermediates of many carbocyclization reactions, for example, the acid-catalysed cyclohydration of arylaliphatic alcohols and related compounds (Scheme 1) [5–9].



Scheme 1.

In this paper we report on the unimolecular cyclization of the gaseous $[M - H]^+$ ions of several α,ω-diphenylalkanes (**3–6**). It is shown that these quasi-molecular ions, generated by hydride abstraction from the neutral hydrocarbons by alkyl ions of the CI(*i*-butane) plasma, isomerize to cyclic structures with the typical reactivity of protonated alkylbenzenes, and hence to $[M' + H]^+$ type ions. The probe for this isomerization is the interannular proton exchange known to occur in the "true" $[M + H]^+$ ions of α,ω-diphenylalkanes [2, 10, 11].

The interannular proton transfer is rather slow in protonated diphenylmethane ions, $[\mathbf{1} + H]^+$ [10]. This leads to limited extent of H/D exchange in [*ring*-D_5]-labelled analogues $[\mathbf{1a} + H]^+$ and the observation of "concave" abundance distributions of the $[\mathbf{1a} + H - C_6(H,D)_6]^+$ fragment ions (Fig. 1). In contrast, in protonated 1,2-diphenylethane, $[\mathbf{2} + H]^+$, and all higher homologous $[M + H]^+$ ions as well as in branched congeners, the interannular proton transfer is fast, leading to complete equilibration of the 11 protons within the ions' lifetime (1–30 μs) [11]. This is reflected by "convex" patterns of $[M + H - C_6(H,D)_6]^+$ fragment ions generated from [*ring*-D_5]-labelled ions, e.g. $[\mathbf{2a} + H]^+$. In the cases of slow proton transfer, the

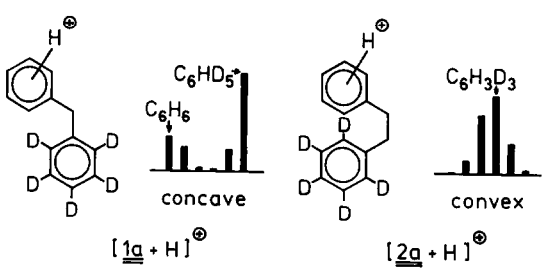
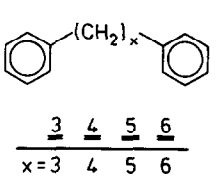
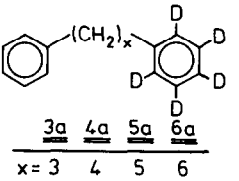


Fig. 1. Typical peak patterns for loss of $C_6(H,D)_6$ from protonated [*ring*-D_5] labelled diphenylmethane and 1,2-diphenylethane (metastable ions [10]).

$[M + H - C_6(H,D)_6]^+$ peak pattern also reflects the kinetic isotope effect operating during the ring-to-ring proton transfer step. The prototype behaviour of the $[\mathbf{1a} + H]^+$ and $[\mathbf{2a} + H]^+$ ions with respect to slow and fast H^+/D^+ transfer will be used in the present paper to characterize the structure of the $[M - H]^+$ ions of the α,ω-diphenylalkanes **3–6**.





EXPERIMENTAL

The syntheses of the labelled diphenylalkanes **3a–6a** and **4b**, **5b**, **5c**, and **6b** (isotopic purities 97–99%) have been described [11(c), 12]. The $[D_{10}]$-labelled 1,4-diphenylbutane **4c** was prepared from 2-$[D_5]$phenylethyl magnesium bromide by oxidation with Ag(I), in analogy to the synthesis of **4a** [12(a)]. The 1-phenylindans **7** and **7a** and 1-benzylindan **9** were prepared by reacting 1-indanone with the appropriate Grignard reagent to give the corresponding 1-phenylindenes or 1-benzylindenes which were hydrogenated in a usual shaker to give the saturated benzocycloalkane. 1-Phenyltetralins **8** and **8a** as well as 1-benzyltetralin **10** were obtained by performing similar Grignard reactions with benzylmagnesium bromide, giving the corresponding 1-tetralols, which were subjected to hydrogenolysis with $H_2/Pd/C$ in a Parr apparatus at 4 bar and room temperature. The compounds were purified by bulb-to-bulb distillation; their identity and purity were checked by ^1H NMR and mass spectrometry.

The mass spectrometric measurements were performed with a ZAB-2F double focusing mass spectrometer (VG Analytical Ltd., Manchester, UK) [13]. In the mass-analysed ion kinetic energy (MIKE) spectrometry scanning mode [14] the $[M - H]^+$ ions of interest were selected with the first, magnetic sector of the instrument, and their fragments formed in the field-free region (FFR) following the magnet were analysed by scanning the field of the second, electrostatic sector. The B/E linked scan spectra [14] were obtained by simultaneous scanning of the magnetic and the electrostatic field in the appropriate, constant ratio to register exclusively those fragment ions which are formed within the FFR preceding the magnetic field. The data given in Tables 1 and 2 represent averaged values of at least five scans. It is noted, however, that the MIKE spectra of ions $[\mathbf{3a} - H]^+$ and $[\mathbf{4a} - H]^+$ depend markedly on the ion source pressure of the reactant gas. The following typical ion source conditions were used: accelerating voltage 5600 V, electron energy 100 V,

TABLE 1

Fragmentation of metastable $[M - H]^+$ ions of 1,3-diphenylpropane and 1,4-diphenylbutane (MIKE spectra)

Compound	Label	Loss of [% Σ]						
		C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5	C_6D_6
3	D_0	100.0						
3a	*ring*-D_5	0.0	31.5	9.0	9.2	7.9	42.4	
4	D_0	100.0						
4a	*ring*-D_5	1.0	32.1	13.1	11.8	13.3	28.8	
4b	2,2,3,3-D_4	100.0	0.0	0.0	0.0	0.0		
4c	*ring*, *ring*-D_{10}	0.0	0.0	0.0	0.0	0.0	0.0	100.0

emission current 200 μA, ion source temperature 180–200°C, ion source pressure (nominal) (7–11) × 10^{-3} Pa, isobutane (Matheson, stated purity ⩾99.5%). The samples were introduced via an air-cooled direct inlet probe with gentle heating where appropriate. Collision activation (CA) spectra were measured by introducing helium in the second FFR collision cell until the main beam intensity is attenuated by about 50%. Owing to the relatively high abundance of the corresponding $M^{\cdot +}$ ions, the peaks at the mass of the $[M + H]^+$ ions of the phenylindans and phenyltetralins (**7–8a**) and, to a minor extent, those of benzylindan (**9**) and of benzyltetralin (**10**) represented mainly

TABLE 2

Fragmentation of metastable $[M - H]^+$ ions of 1,5-diphenylpentane and 1,6-diphenylhexane (MIKE and B/E linked scan spectra)

Compound	Label	Scan	Loss of [% Σ]					
			C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5
5	D_0		100.0					
5a	*ring*-D_5	MIKES	0.0	3.1	24.5	46.9	23.1	2.4
		B/E	0.0	3.8	25.4	45.8	22.1	2.9
5b	2,2,4,4-D_4		98.2	1.8	0.0	0.0	0.0	
5c	3,3-D_2		100.0	0.0	0.0			
Calculated for exchange of 5H/5D (**5a** and **6a**)			0.0	2.4	23.8	47.6	23.8	2.4
6	D_0		100.0					
6a	*ring*-D_5	MIKES	1.5	11.1	32.2	38.3	15.1	1.8
		B/E	1.4	9.9	31.1	38.7	16.0	2.9
6b	3,3,4,4-D_4	MIKES	81.6	14.9	3.2	0.3	0.0	
		B/E	79.5	17.7	2.7	< 0.3	0.0	

the naturally occurring $^{13}C_1$ satellites of the $M^{\cdot+}$ ions. Therefore, the collision-induced dissociation of the true $[M + H]^+$ ions had to be evaluated with great care, and only partial spectra are reproduced in Figs. 4 and 7.

RESULTS AND DISCUSSION

The molecular ion region of a typical CI(*i*-butane) mass spectrum of alkylbenzenes consists of the peak triplet $[M - H]^+$, $[M]^{\cdot+}$ and $[M + H]^+$. The relative abundances of these ions strongly depend on the pressure of the reactant gas and on the "branching" at the α (ω) position [15]. Both the $[M + H]^+$ and the $[M - H]^+$ ions expel benzene as the predominant ion-source fragmentation reaction, whereas the $M^{\cdot+}$ ions undergo this reaction only in special cases [2, 16].

The $[M - H]^+$ ions of deuterium-labelled 1,3-diphenylpropanes and 1,4-diphenylbutanes are discussed first. Figure 2 shows the CI(*i*-butane) mass spectrum of [*ring*-D_5] labelled 1,4-diphenylbutane **4a**. In this case, the peak intensities at *m/z* 131–137 qualitatively show that the main fragmentation is due to the loss of the benzene isotopomers $C_6H_{6-x}D_x$ ($1 \leqslant x \leqslant 5$) from the ions $[\mathbf{4a} - H]^+$, whereas the loss of benzene isotopomers $C_6H_{6-y}D_y$ ($0 \leqslant y \leqslant 5$) from ions $[\mathbf{4a} + H]^+$ [11(c)] represents only a minor fraction. The abundance pattern of the $[\mathbf{4a} - H - C_6(H,D)_6]^+$ is concave, with a clearly dominant loss of the heaviest and lightest of the benzene isotopomers giving rise to ions with *m/z* 131 and *m/z* 135 respectively. Notably, only five protons

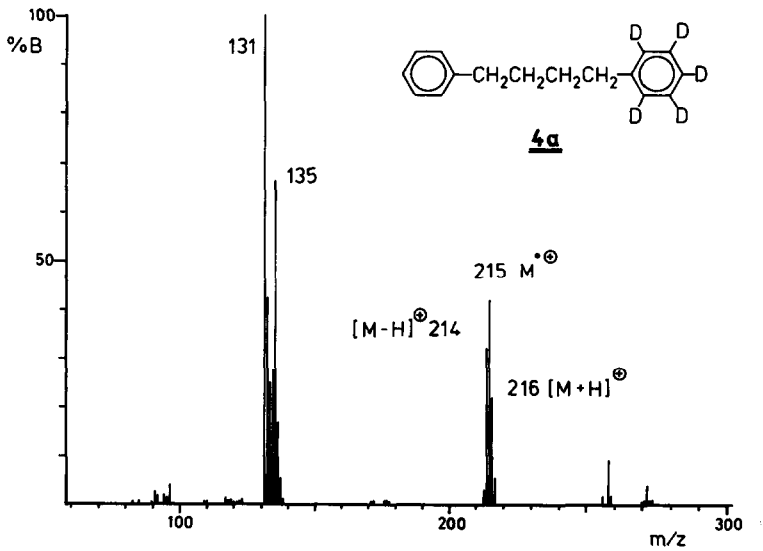
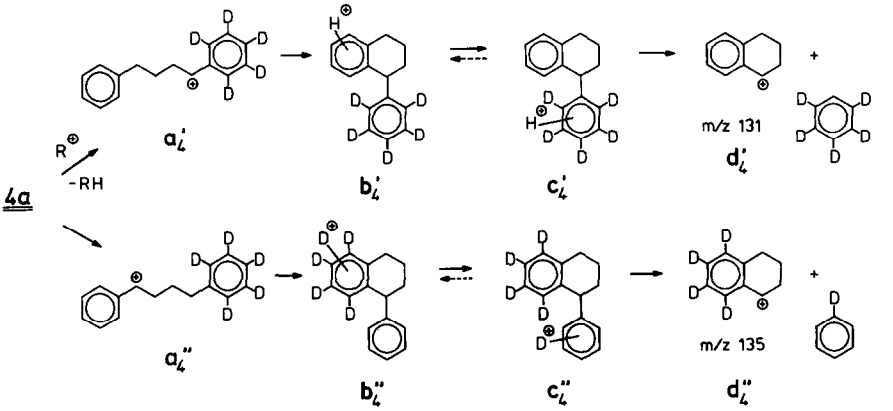


Fig. 2. Standard CI(*i*-butane) mass spectrum of [*ring*-D_5] labelled 1,4-diphenylbutane **4a**.

are involved in the H/D exchange of the [*ring*-D_5] labelled $[M - H]^+$ ions, in contrast with six isotopomers being lost from the corresponding $[M + H]^+$ ions (cf. Fig. 1) [2, 10, 11]. Both the incomplete H/D exchange and the kinetic isotope effect discriminating against the loss of C_6H_5D parallel the fragmentation behaviour of protonated [*ring*-D_5] diphenylmethane $[\mathbf{1a} + H]^+$.



Scheme 2.

An obvious mechanism to explain the fragmentation of ions $[\mathbf{4a} - H]^+$ is shown in Scheme 2. Electrophilic cyclization of the initially formed benzylic structures $\mathbf{a}'_4$ and $\mathbf{a}''_4$ gives protonated (or deuteronated) 1-phenyltetralins (ions $\mathbf{b}'_4$ and $\mathbf{b}''_4$). These isomers represent diphenylmethane derivatives, which should decompose preferably by elimination of C_6HD_5 and C_6H_5D, respectively, after rate-limiting proton or deuteron transfer to the phenyl ring ($\mathbf{b}_4 \rightarrow \mathbf{c}_4$). The latter isomerization and hence the H/D exchange should be slow owing to the relatively rigid and unfavourable orientation of the two arene units in 1-phenyltetralin (**8**, see below). Because of the rigidity imposed by the additional six-membered ring, the steric hindrance towards interannular proton transfer in protonated 1-phenylbenzocycloalkane ions such as $\mathbf{b}_4$ and $\mathbf{c}_4$ should be even stronger than in $[\mathbf{1} + H]^+$, and the final protonolysis step ($\mathbf{c}_4 \rightarrow \mathbf{d}_4$) should be more facile.

The MIKE spectra of the $[M - H]^+$ ions of **4a** and the lower homologue, **3a** (Fig. 3 and Table 1), as well as those of the higher homologues **5a** and **6a** (Fig. 6 and Table 2) corroborate the cyclization reaction. In spite of the longer lifetime of the metastable ions, the H/D exchange in both $[\mathbf{3a} - H]^+$ and $[\mathbf{4a} - H]^+$ is far from being random; thus the proton transfer in these ions

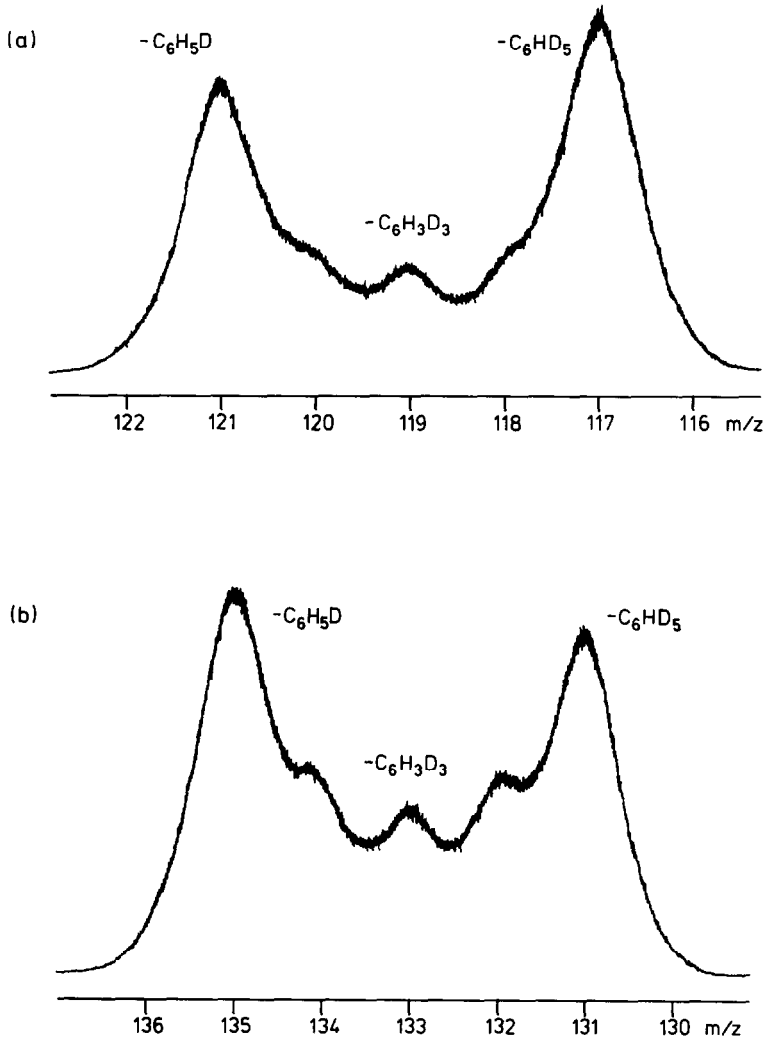
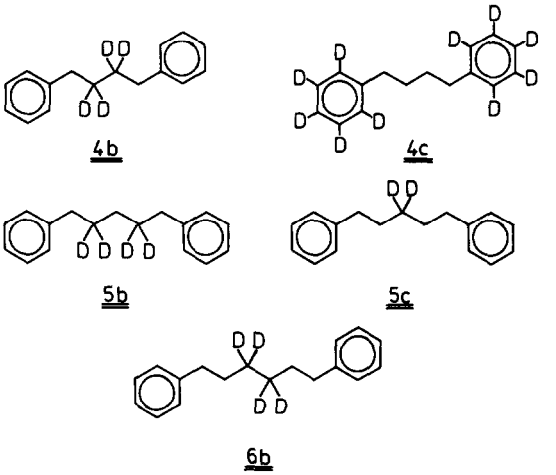
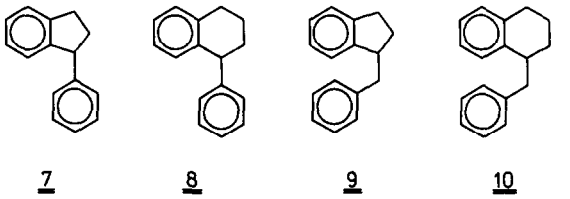


Fig. 3. MIKE spectra of the $[M - H]^+$ ions of (a) [*ring*-D_5] labelled 1,3-diphenylpropane **3a**, *m/z* 200, and (b) 1,4-diphenylbutane **4a**, *m/z* 214.

is slow. Again, only five protons are involved in the H/D exchange. This observation shows that the hydrogen atoms of the aliphatic chain of $[\mathbf{3a} - H]^+$ and $[\mathbf{4a} - H]^+$ do not participate in the hydrogen exchange, in line with the spectra of the [2, 2, 3, 3-D_4] and [*ring*-D_{10}] labelled analogues $[\mathbf{4b} - H]^+$ and $[\mathbf{4c} - H]^+$, which exclusively show loss of C_6H_6 and C_6D_6 respectively (Table 1).





The simple cyclization mechanism of Scheme 2 has been checked by studying the fragmentation of the $[M + H]^+$ ions of 1-phenylindan **7** and 1-phenyltetralin **8** as well as of their [phenyl-D_5] analogues **7a** and **8a**. In fact, the MIKE and CA spectra of ions $[\mathbf{7} + H]^+$ are identical with those of $[\mathbf{3} - H]^+$ [17]. The same holds for ions $[\mathbf{8} + H]^+$ and $[\mathbf{4} - H]^+$. Interestingly, the CA spectrum of the $[M + H]^+$ ions generated by protonation of 1-benzylindan **9** is only qualitatively similar to the spectra of ions $[\mathbf{8} + H]^+$ and $[\mathbf{4} - H]^+$. In particular, the relatively intense peaks at *m/z* 91 and *m/z* 117 in the spectrum of ions $[\mathbf{9} + H]^+$ may reflect the 1,2-diphenylethane substructure of these isomers (Fig. 4). Also, the kinetic energy released during the loss of benzene from ions $[\mathbf{9} + H]^+$ is different from that observed with ions $[\mathbf{4} - H]^+$ and $[\mathbf{8} + H]^+$ [18].

These results further corroborate the simple cyclization mechanism of Scheme 2. Surprisingly, however, the [phenyl-D_5] labelled ions $[\mathbf{7a} + H]^+$ and $[\mathbf{8a} + H]^+$ exhibit no significant H/D exchange (Fig. 5). This finding suggests that the critical energy of the interannular proton transfer in $[\mathbf{7} + H]^+$ and $[\mathbf{8} + H]^+$ is higher than that of the benzene loss. This is in line with the enhanced steric hindrance of the proton transfer and of the decreased energy requirements of the final elimination step, as compared to ions $[\mathbf{1} + H]^+$.

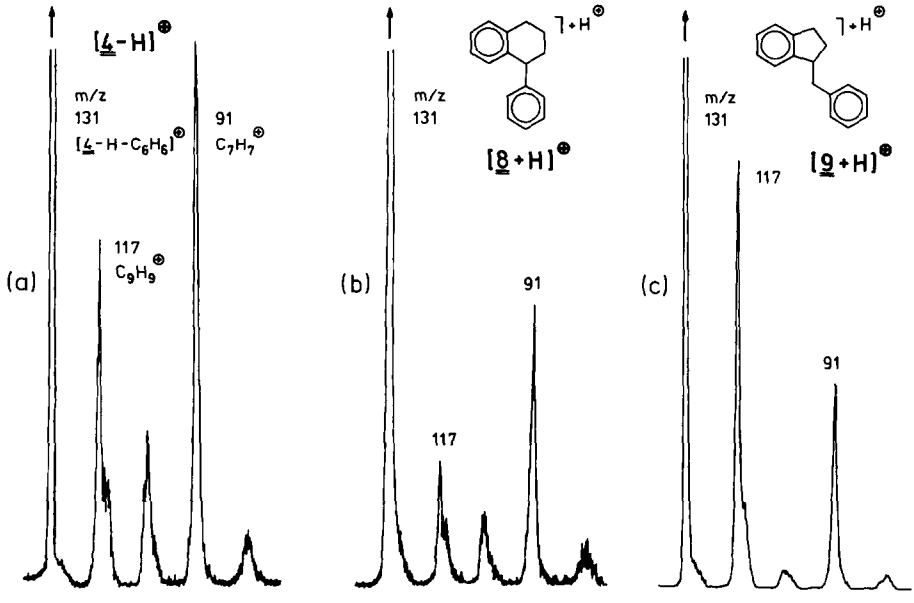


Fig. 4. Partial CA spectra (a) of the $[M - H]^+$ ions of 1,4-diphenylbuane **4** and (b and c) of the $[M + H]^+$ ions of 1-phenyltetralin **8** and 1-benzylindan **9**. About 35% of the *m/z* 91 peak intensity in the spectrum of $[\mathbf{8} + H]^+$ originates from $[^{13}C_1]$-$\mathbf{8}^{\cdot+}$ ions.

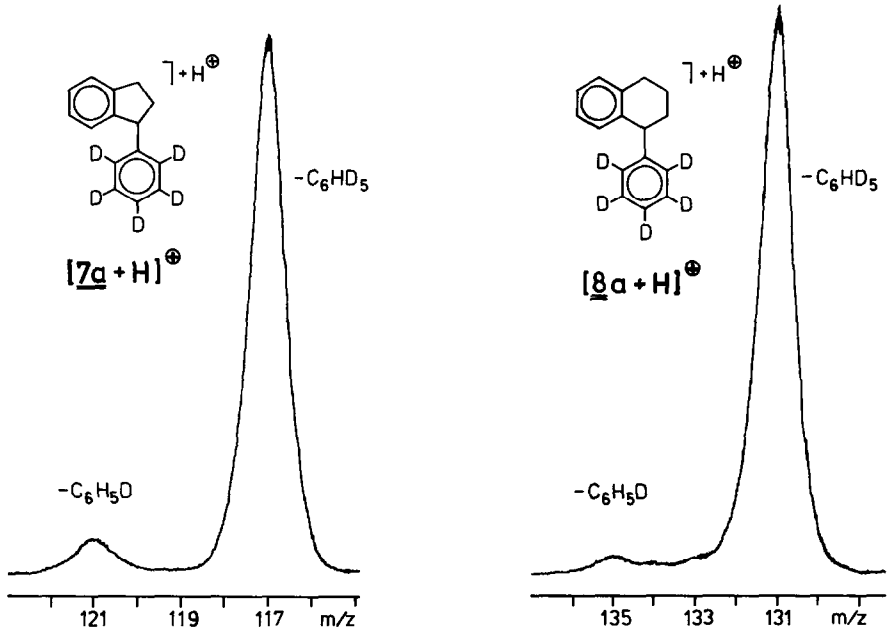
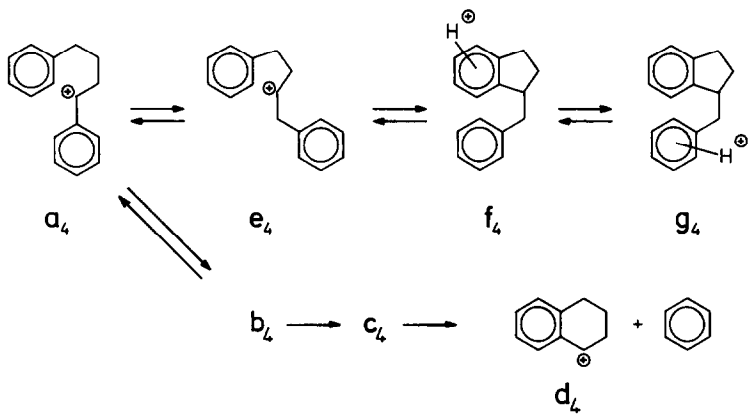


Fig. 5. MIKE spectra of the $[M + H]^+$ ions of (a) 1-([D_5]-phenyl)indan **7a**, *m/z* 200, and (b) 1-([D_5]-phenyl)tetralin **8a**, *m/z* 214.

Therefore, the slow H/D exchange observed with the ions $[\mathbf{3a} - H]^+$ and $[\mathbf{4a} - H]^+$ may actually not occur via **b** ⇄ **c**, as shown in Scheme 2, but rather via the corresponding ring-contracted protonated 1-benzylbenzocycloalkanes (**f** ⇄ **g**, Scheme 3). These isomers may be formed by a 1,2-hydride shift (e.g. $\mathbf{a}_4 \rightarrow \mathbf{e}_4$) and subsequent cyclization and should undergo a fast interannular proton exchange because of their 1,2-diphenylethane substructure (cf. $[\mathbf{2} + H]^+$). However, owing to the increased steric strain of the four- and five-membered rings (in particular of the initially generated ipso-protonated forms of species **f**) these benzocycloalkane isomers should be only short-lived. In fact, the CA spectra of ions $[\mathbf{4} - H]^+$, $[\mathbf{8} + H]^+$ and $[\mathbf{9} + H]^+$ seem to reflect the intermediacy of 1-benzylindan type ions $\mathbf{f}_4$ and $\mathbf{g}_4$ but they rule out their predominance. In summary, owing to the contrasting effects of short lifetime and fast proton exchange of intermediates **f** and **g**, the extent of the interannular H/D exchange observed with ions $[\mathbf{3a} - H]^+$ and $[\mathbf{4a} - H]^+$ is low.



Scheme 3.

The behaviour of the higher homologues, ions $[\mathbf{5} - H]^+$ and $[\mathbf{6} - H]^+$, is in two ways different from that found for ions $[\mathbf{3} - H]^+$ and $[\mathbf{4} - H]^+$, but it nevertheless fits in the "extended" cyclization mechanism of Scheme 3. Most importantly, the interannular proton exchange is fast and apparently complete in both cases. Secondly, with increasing formal distance between the arene units, the hydrogen atoms of the aliphatic chain increasingly participate in the hydrogen exchange reactions.

In the case of $[M - H]^+$ of 1,5-diphenylpentane (**5**), the participation of hydrogen atoms from the chain is negligible. The [3,3-D_2] labelled ions $[\mathbf{5c} - H]^+$ lose exclusively C_6H_6, and only a very small fraction of C_6H_5D is expelled from the [2,2,4,4-D_4] analogues $[\mathbf{5b} - H]^+$ (Table 2). In contrast to the lower homologues, both the MIKE and B/E linked scan spectra of the

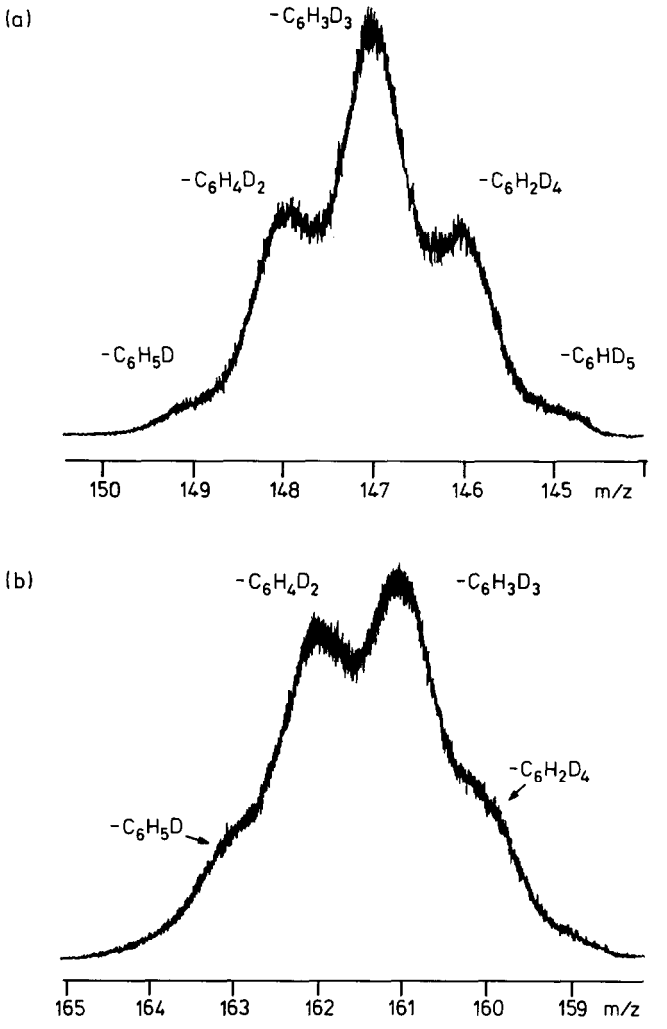


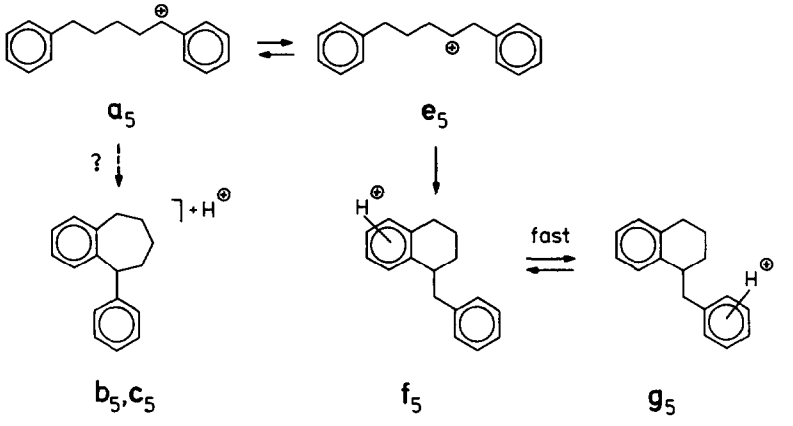
Fig. 6. MIKE spectra of the $[M - H]^+$ ions of (a) [*ring*-D_5] labelled 1,5-diphenylpentane **5a**, *m/z* 228, and (b) 1,6-diphenylhexane **6a**, *m/z* 242.

[*ring*-D_5] labelled ions $[\mathbf{5a} - H]^+$ show a convex ion abundance pattern (Fig. 6(a)), which agrees perfectly with the statistical distribution calculated for equilibration of five protons and five deuterons prior to loss of benzene (Table 2).

The [*ring*-D_5]-labelled ions of 1,6-diphenylhexane, $[\mathbf{6a} - H]^+$, show a convex pattern for loss of $C_6(H,D)_6$ as well. In this case, however, the distribution is shifted markedly in favour of the loss of lighter benzene isotopomers (Fig. 6(b)), indicating considerable participation of the "aliphatic" hydrogen atoms in the overall H/D exchange. Correspondingly, significant portions of

C_6H_5D and $C_6H_4D_2$ are lost from the [3,3,4,4-D_4]-labelled ions **[6b** – H]$^+$ (Table 2). A quantitative evaluation is not possible without further isotopomers, but the data clearly show that the interannular proton exchange in ions [**6** – H]$^+$ is fast and leads to randomization of the ten protons at the aromatic rings [19].

On the basis of these observations we propose that the [M – H]$^+$ ions of α,ω-diphenylalkanes **3–6** isomerize by electrophilic cyclization to form the protonated benzocycloalkane derivatives. These [M′ + H]$^+$ type ions may undergo intraannular and interannular proton exchange, and loss of benzene finally occurs from the tautomer bearing the "extra" proton at the ipso position of the phenyl group. The convex abundance distribution found for the [*ring*-D_5]-labelled ions of the higher homologues **5a** and **6a** clearly indicates that, in these cases, the cyclized isomers are derivatives of protonated 1,2-diphenylethane, [**2** + H]$^+$, rather than of protonated diphenylmethane [**1** + H]$^+$. It is postulated that ions [**5** – H]$^+$ isomerize to species $\mathbf{f_5} \rightleftarrows \mathbf{g_5}$ after 1,2-hydride shift ($\mathbf{a_5} \rightarrow \mathbf{e_5}$, Scheme 4). In fact, metastable ions generated by protonation of 1-benzyltetralin **10** lose only benzene, and the CA spectrum of ions [**5** – H]$^+$ and [**10** + H]$^+$ are identical (Fig. 7). Benzocycloheptane ions ($\mathbf{b_5}$,$\mathbf{c_5}$) may be formed only during the final fragmentation step. Obviously, the ring closure of gaseous [M – H]$^+$ ions of α,ω-diphenylalkanes to protonated tetralin derivatives is particularly favourable.



Scheme 4.

Finally, it is noted that the 1,2-hydride shifts within the aliphatic chain are directly detectable only with longer chain lengths. In the case of ions [**6** – H]$^+$, the 1,2-hydride shift $\mathbf{a_6} \rightleftarrows \mathbf{e_6}$ activates the "inner" (C-3 and C-4) methylene groups towards a sterically favourable chain-to-ring proton

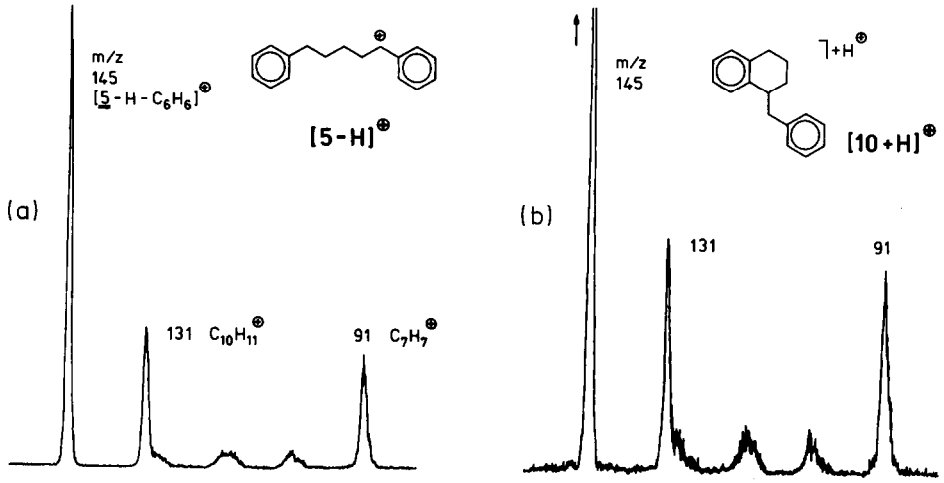
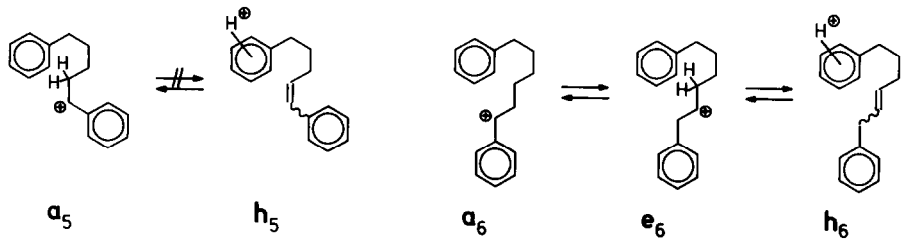


Fig. 7. Partial CA spectra (a) of the $[M - H]^+$ ions of 1,5-diphenylpentane **5** and (b) of the $[M + H]^+$ ions of 1-benzyltetralin **10**.

transfer $\mathbf{e}_6 \rightleftarrows \mathbf{h}_6$ (Scheme 5). In the case of ions $[\mathbf{5} - H]^+$, the proton transfer step $\mathbf{e}_5 \rightarrow \mathbf{h}_5$ seems to be suppressed, possibly because of the relatively high proton affinity of the conjugate styrene C–C double bond in $\mathbf{h}_5$.



Scheme 5.

The H/D exchange between the chain and the aromatic rings in $[\mathbf{6} - H]^+$ indicates, in agreement with the above suggestions, that the hydrogen atoms in the aliphatic chain of the $[M - H]^+$ ions are also more or less mobile. The observation (Fig. 6) that ions $[\mathbf{7a} + H]^+$ and $[\mathbf{8a} + H]^+$ expel minor amounts of unlabelled benzene may be taken as another consequence of the hydride shifts within the chain [20]. Covalently linked (intramolecular) π-complex type bonding between the carbenium centre in the chain and the aromatic nucleus may play an important role in these processes [21–23]. Investigations are underway in this laboratory to elucidate further the extent of skeletal rearrangements in $[M - H]^+$ type ions of α,ω-diphenylalkanes and $[M + H]^+$ type ions of protonated benzocycloalkanes.

CONCLUSION

The $[M - H]^+$ ions of α,ω-diphenylalkanes, generated by hydride abstraction in the plasma of a CI(*i*-butane) ion source, undergo cyclization followed by proton transfer between the aromatic rings and the elimination of benzene. This process is accompanied by interannular proton exchange, which is slow during the fragmentation of the shorter homologues, ions $[\mathbf{3} - H]$ and $[\mathbf{4} - H]^+$, but fast and apparently complete with the higher ones, ions $[\mathbf{5} - H]^+$ and $[\mathbf{6} - H]^+$. The hydrogen atoms of the aliphatic chain are interchanged at least partially, in addition to those of the rings and probably via (intramolecular) π complexes, giving rise to homobenzylic carbenium ions. The latter intermediates undergo ring closure to form protonated 1-benzylbenzocycloalkanes rather than 1-phenylbenzocycloalkanes which result from direct cyclization of the initially generated benzylic $[M - H]^+$ ions. Significant coupling between the ring/ring and the ring/chain hydrogen exchange occurs only in the highest homologues, ions $[\mathbf{6} - H]^+$.

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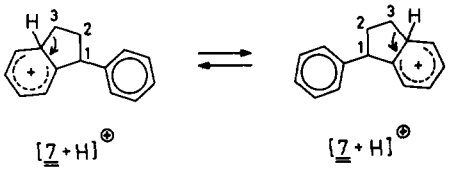
17 The CA spectra of ions $[7 + H]^+$ and $[8 + H]^+$ contain considerable contributions of the fragment ions originating from ions $[^{13}C_1]\text{-}M^{\cdot +}$.
18 (a) Kinetic energy releases [14(b)] T^{50}_{kin} (from precursor ion), for losses of benzene: 87.4 meV ($[3 - H]^+$) ≈ 85.1 meV ($[7 + H]^+$); 69.1 meV ($[4 - H]^+$) ≈ 67.1 meV ($[8 + H]^+$); 53.7 meV ($[9 + H]^+$).
19 Complete randomization of all H and D atoms in $[\mathbf{6b} - H]^+$ would lead to losses of $C_6H_{6-x}D_x$ ($x = 0$–4) in ratio of 22.0 : 44.1 : 25.4 : 4.8 : 3.6.
20 An alternative possibility is the protonolysis of the "primary" C^{ipso}–C^{α} in $[7 + H]^+$ and $[8 + H]^+$, leading to a degenerate skeletal rearrangement, as shown below:



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