

INTERANNULAR PROTON EXCHANGE IN PROTONATED LONG-CHAIN 1, ω -DIPHENYLALKANES

DIETMAR KUCK *, WOLFGANG BÄTHER and HANS-FR. GRÜTZMACHER

Fakultät für Chemie, Universität Bielefeld, D-4800 Bielefeld 1 (F.R.G.)

(Received 7 March 1985)

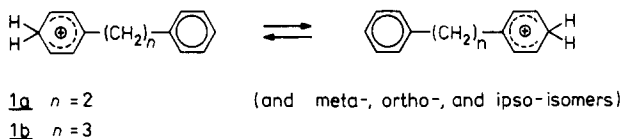
ABSTRACT

The interannular proton exchange in (ω -phenylalkyl)-benzenium ions, **1**, ($2 \leq n \leq 20$) is an extremely fast process. It gives rise to the statistical distribution of the eleven protons at the two rings within the microsecond time scale even if twenty methylene groups are located between the rings. **1** ions and various deuterium-labelled analogues have been generated by EI-induced fragmentation of the corresponding 1-(ω -phenylalkyl)-1,4-dihydrobenzoic acids, **2**, and/or by CI-(*i*-butane) of the corresponding 1, ω -diphenylalkanes, **3**. Proton randomization is not affected by the internal energy of the ions. The results suggest that an association complex is formed gaining energy from the interaction of the benzenium and the benzene ring. Whereas the 2-butyne-1,4-diyl moiety in **5** ions mediates the fast proton transfer between the rings in spite of its steric rigidity, the *trans*-cyclohexane-1,4-diyl unit in **7** ions suppresses the proton exchange almost completely. Kinetic model calculations yield rate constants for the interannular proton transfer in the order of $k_{\text{H}} \geq 1 \times 10^6 \text{ s}^{-1}$ for metastable **1** ions, but $k_{\text{H}} \approx 5 \times 10^4 \text{ s}^{-1}$ for metastable **7** ions. A kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 5$ seems to operate during the interannular proton transfer in sterically hindered (ω -phenylalkyl)-benzenium ions.

INTRODUCTION

The structure and reactivity of protonated arenes (arenium ions) have been a matter of great interest [1,2]. In particular, the isomerization reactions of arenium ions have been investigated by nuclear magnetic resonance [3] and by mass spectrometry [4] as well as by radiolytic [5] and computational [6] methods. Arenium ion intermediates have been found to govern the course of electrophilic substitution of aromatic substrates in the liquid and gas phases. In turn, the course of gas-phase reactions, mostly mass spectrometric fragmentation reactions of e.g. alkylbenzenes, depend strongly on the

* To whom correspondence should be addressed.



Scheme 1.

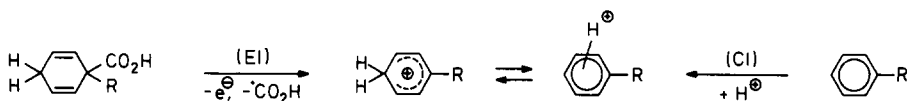
formation of arenium ion intermediates [7]. In order to study their unimolecular reactivity in more detail, we have generated arenium ions by selected ionization or fragmentation reactions of suitable precursor molecules in the ion source of a double focussing mass spectrometer.

(2-Phenylethyl)-benzenium ions (**1a**) and (3-phenylpropyl)-benzenium ions (**1b**, Scheme 1) undergo a fast, degenerate intramolecular exchange reaction of the eleven protons at the two benzene rings yielding a random distribution within the lifetime of microseconds [8]. The hydrogen atoms of the aliphatic chain are not involved in this process.

Two reactions have been used to generate gaseous benzenium ions (e.g. **1b** [8]): (i) electron impact ionization (EI) of the corresponding 1,4-dihydrobenzoic acid followed by rapid loss of $\cdot\text{CO}_2\text{H}$ [4(e),8], and (ii) chemical ionization (CI) of the corresponding arene (Scheme 2). Both methods have been shown to give benzenium ions of the same reactivity [9]. Therefore, the EI and the CI methods are equivalent but the initial site of protonation is only defined by using the first approach. This can be a valuable advantage especially if other basic groups are present in the conjugate arene [10].

In order to investigate the effect of the length of the polymethylene chain on the proton exchange, we generated a series of (ω -phenylalkyl)-benzenium ions **1a–1h** (Scheme 3) with $2 \leq n \leq 20$ and the deuterium-labelled analogues ($[D_5]$ -**1a** to $[D_5]$ -**1e**, $[D_6]$ -**1g** and $[D_6]$ -**1h**) mostly using the CI method.

In addition, two analogues with less flexible links between the benzenium and the benzene rings and two deuterium-labelled isotopomers have been studied using the EI method, i.e. (Scheme 4) (4-phenyl-2-butyn-1-yl)-benzenium ions, **5**, and $[D_5]$ -**5**, as well as [(*trans*-4-phenyl)-cyclohex-1-yl-methyl]-benzenium ions, **7**, and $[D_5]$ -**7**.



Scheme 2.

6 kV; electron energies, 70 eV (EI), 100 eV (CI); trap current, 0.1 mA (EI); emission current, 0.5 mA (CI); source temperature, 180–200°C; source pressures (nominal), $1.5\text{--}3 \times 10^{-5}$ Pa (EI), $3\text{--}7 \times 10^{-3}$ Pa (CI), $[\text{C}_4\text{H}_9^+]/[\text{C}_3\text{H}_7^+]$ was in the range 2–5). The dihydrobenzoic acids **2c–2f** and the hydrocarbons **3g** and **3k** were introduced by using the air-cooled solid probe: the lower homologues were introduced via the septum inlet system heated to 200–250°C.

Isobutane used for the CI measurements was obtained from Matheson (purity > 99.5%). In some cases, methane (Linde, purity > 99.95%) was used, too, without significant changes in the MIKE spectra.

The synthesis of the compounds is described in the appendix.

RESULTS AND DISCUSSION

EI and CI mass spectra

The 70 eV EI mass spectrum of 1-(5-phenylpentyl)-1,4-dihydrobenzoic acid, **2d**, and the CI-(*i*-butane) mass spectrum of 1,5-diphenylpentane, **3d**, are shown in Fig. 1. The extremely low abundance of the molecular ions in the EI mass spectrum [Fig. 1(a)] of the acid ($\sim 0.1\%$ of total ion current) points to the ease of fragmentation reactions, in particular those occurring at the quaternary carbon (C^1). Thus, the m/z 225 peak corresponds to the formation of (5-phenylpentyl)-benzenium ions, **1d**, by loss of $\cdot\text{CO}_2\text{H}$, and the m/z 123 peak indicates the formation of protonated benzoic acid via loss of the ω -phenylalkyl group. Ions m/z 147 are due to the key reaction of this study, i.e. elimination of C_6H_6 from **1d** ions. Unfortunately, the relative abundance of these secondary fragment ions decreases with increasing length of the polymethylene chain. In contrast to the EI mass spectrum, the CI-(*i*-butane) spectrum [Fig. 1(b)] shows the $[\text{M} + \text{H}]^+$ ions (**1d**, m/z 225) to be the most abundant ones, again losing C_6H_6 to give m/z 147 ions of similar abundance. Unfortunately, besides **1** ions, the CI method produces ions having two mass units less $\{[\text{M} + \text{H} - (\text{C}_6\text{H}_6 - \text{H}_2)]^+\}$, e.g. m/z 145 ions, Fig. 1(b)). This effect is found to be typical for the CI mass spectra of diphenylalkanes and obscures the interpretation of the spectra of the deuterium-labelled analogues. Thus, in general, the normal EI and CI mass spectra of these compounds give only qualitative information about the extent of the proton exchange. More reliable, quantitative data have been obtained from the metastable **1** ions, measuring their fragmentation reactions in the field-free region(s) (FFR) of the mass spectrometer.

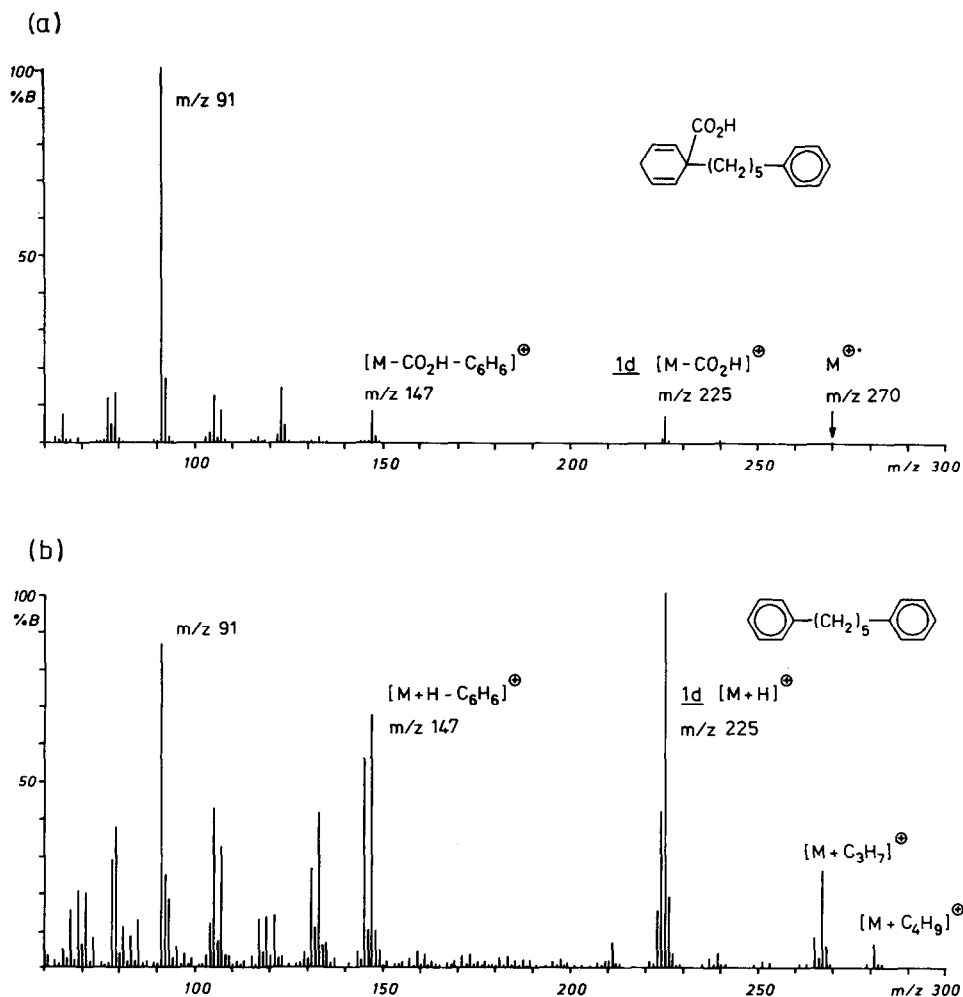


Fig. 1. (a) EI mass spectrum (70 eV) of 1-(5-phenylpentyl)-1,4-dihydrobenzoic acid, **2d**, and (b) CI-(*i*-butane) mass spectrum of 1,5-diphenylpentane, **3d**.

Metastable (ω -phenylalkyl)-benzenium ions, **1a–1h**

As found in the previous work [8] for the lower homologues **1a** and **1b**, the elimination of C_6H_6 is the dominant (> 90%) fragmentation reaction of long-chain metastable (ω -phenylalkyl)-benzenium ions.

Table 1 gives the distribution of benzene isotopomers eliminated from the ring- d_5 -labelled (ω -phenylalkyl)-benzenium ions $[D_5]$ -**1a** to $[D_5]$ -**1e**, fragmenting in the second FFR. Within the limits of experimental error, the relative abundances of the $C_6(H,D)_6$ isotopomers lost correspond to that

TABLE 1

Loss of benzene isotopomers ^a from metastable [*D*₅]-(*ω*-phenylalkyl)-benzenium ions (MIKE spectra)

Entry	Ion	Precursor	C ₆ H ₆	C ₆ H ₅ D	C ₆ H ₄ D ₂	C ₆ H ₃ D ₃	C ₆ H ₂ D ₄	C ₆ HD ₅
1	[<i>D</i> ₅]- 1a	[<i>D</i> ₅]- 2a ^b	< 0.4	5.7	35.6	42.8	14.4	1.1
2		[<i>D</i> ₅]- 2a' ^c	0.3	7.5	29.9	43.8	17.1	1.4
3		[<i>D</i> ₅]- 3a	0.2	6.6	32.8	43.0	16.0	1.4
4	[<i>D</i> ₅]- 1b	[<i>D</i> ₅]- 2b ^b	< 0.3	3.8	31.0	45.8	17.3	1.8
5		[<i>D</i> ₅]- 3b	0.3	6.9	32.7	42.8	16.0	1.5
6	[<i>D</i> ₅]- 1c	[<i>D</i> ₅]- 3c	~ 0.1	6.5	32.4	43.3	16.3	1.4
7		[<i>D</i> ₅]- 3d	0.3	6.7	32.1	43.0	16.3	1.7
8	[<i>D</i> ₅]- 1e	[<i>D</i> ₅]- 2e	0.3	7.5	29.9	43.8	17.1	1.4
9		[<i>D</i> ₅]- 3e	< 0.4	7.5	32.9	42.5	15.1	1.5
10	statistical ^d		0.2	6.5	32.5	43.3	16.2	1.3

^a In % Σ.

^b Taken from the previous work [8] (Varian MAT 311A); rel. error for small peaks ≤ 20%.

^c **2a'** is [2,3,4,5,6-*D*₅]-1-(2-phenylethyl)-1,4-dihydrobenzoic acid, cf. Scheme 3.

^d Calculated for randomization of 6 H and 5 D at the benzene rings exclusively.

expected for the statistical distribution (entry 10) of the eleven protons and deuterons over the two rings. The same pattern is obtained irrespective of the original site of the extra proton in, e.g. [*D*₅]-**1a** ions: the regiospecifically labelled ions C₆H₆⁺-(CH₂)₂-C₆D₅ and C₆HD₅⁺-(CH₂)₂-C₆H₅ (by EI of acids [*D*₅]-**2a** and [*D*₅]-**2a'**, respectively) or a ca. 1 : 1 mixture of both (by CI of **3a**) yield the same distribution of C₆(H,D)₆ isotopomers. Figure 2 shows the MIKE spectra of [*D*₅]-**1a** and [*D*₅]-**1e** generated by CI-(*i*-butane).

Loss of benzene from **1** ions is found to be associated with $T^{0.5} = 22 \pm 1$ meV (2.1 ± 0.1 kJ mol⁻¹) independently of the length of the aliphatic chain. Hence, the MIKE spectra of the high mass homologues [*D*₆]-**1g** (*m/z* 343) and [*D*₆]-**1h** (*m/z* 441) show a single, mass-unresolved signal for loss of several C₆(H,D)₆ isotopomers. In these cases, the [M + H - C₆(H,D)₆]⁺ ions formed in the first FFR were analyzed by using the B/E linked scan technique [11]. Figure 3 shows the well-resolved pattern thus obtained for the labelled (20-phenyleicosyl)-benzenium ion [*D*₆]-**1h**, and Table 2 gives the relative abundances of C₆(H,D)₆ isotopomers lost from [*D*₆]-**1g** and [*D*₆]-**1h** ions which again agrees well with the statistical distribution calculated for randomization of the eleven protons and deuterons at the two rings. Thus, the interannular proton exchange is fast enough to equilibrate the protons over a distance of 20 methylene units!

Hydrogen atoms at the aliphatic chain are not involved in the exchange process since this would severely affect the distribution of the C₆(H,D)₆ isotopomers lost [8,12]. Moreover, metastable (*ω*-phenylalkyl)-benzenium

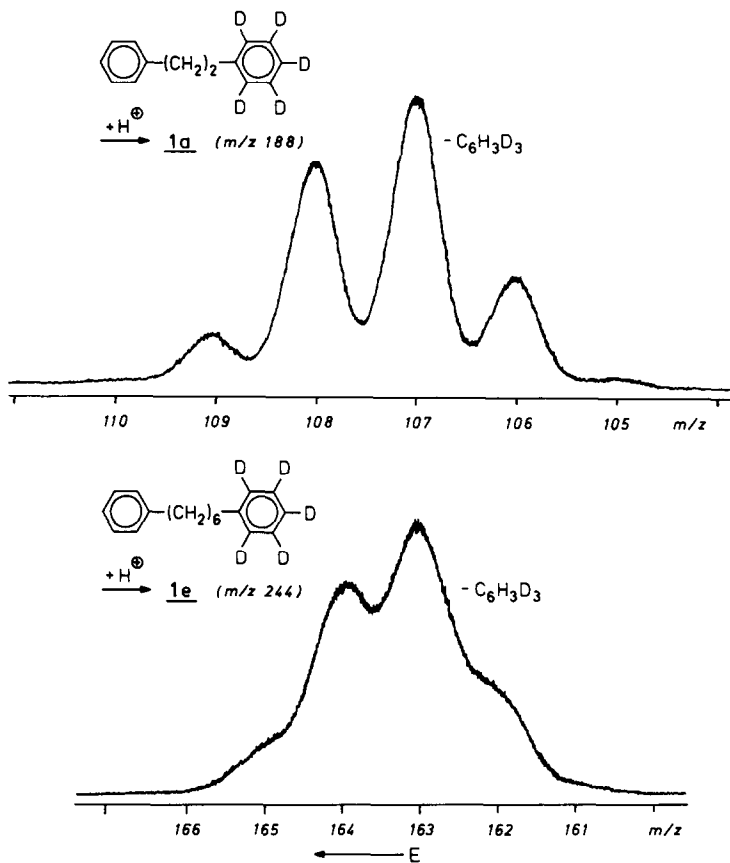


Fig. 2. MIKE spectra of (a) $[D_5]$ -**1a** and (b) $[D_5]$ -**1e** ions generated by CI(*i*-butane) of the hydrocarbons $[D_5]$ -**3a** and $[D_5]$ -**3e**, respectively.

ions obtained by CI of various chain-deuterated 1, ω -diphenylalkanes (e.g. [2,2,4,4- D_4]-**1d** and [3,3- D_2]-**1d** [13]) do not eliminate isotopomers other than C_6H_6 , in accordance with earlier results [8].

Several attempts have been made [14] to increase the barrier towards interannular proton transfer in (ω -phenylalkyl)-benzenium ions. Among these are phenyl-protonated 1, ω -diphenylalkynes [15] as ion **5** and benzyl-protonated *trans*-1-benzyl-4-phenylcyclohexane, **7** (Scheme 4). The central triple bond in the former ion was expected to suppress the interannular proton transfer by holding the two rings apart from each other. However, as can be seen from Fig. 4(a), the pattern observed for loss of $C_6(H,D)_6$ isotopomers from the labelled ion $[D_5]$ -**5** corresponds to an almost complete proton exchange. Because of its relatively high proton affinity [16] the acetylene moiety seems to mediate the proton transfer between the aromatic rings rather than to suppress it. It is worth noting that the isomeric

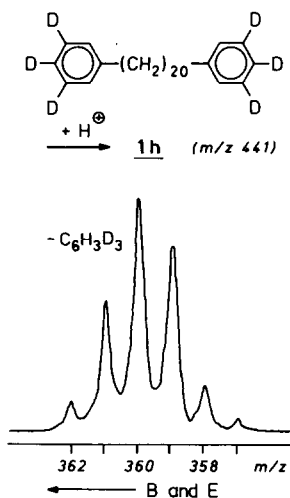


Fig. 3. Linked scan spectrum (B/E constant) of $[D_6]$ -**1h** ions generated by CI-(*i*-butane) of hydrocarbon $[D_6]$ -**3h**.

TABLE 2

Loss of benzene isotopomers ^a from metastable $[D_6]$ -(ω -phenylalkyl)-benzenium ions (B/E linked scan spectra)

Ion	Precursor	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5	C_6D_6
$[D_6]$ - 1g	$[D_6]$ - 3g	2.9	20.7	39.5	29.2	6.9	0.8
$[D_6]$ - 1h	$[D_6]$ - 3h	3.7	19.0	39.0	30.0	7.4	1.4
statistical ^b		1.3	16.2	43.3	32.5	6.5	0.2

^a In % Σ .

^b Calculated for randomization of 5H and 6D at the benzene rings exclusively.

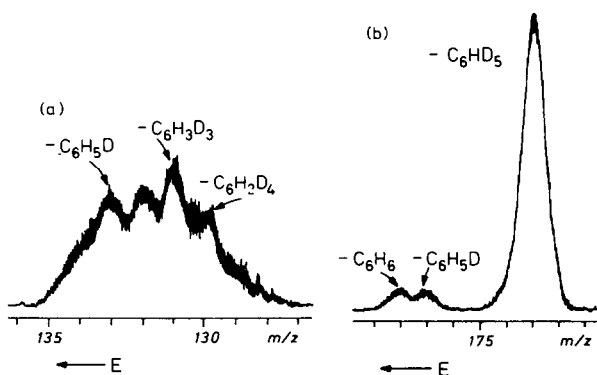
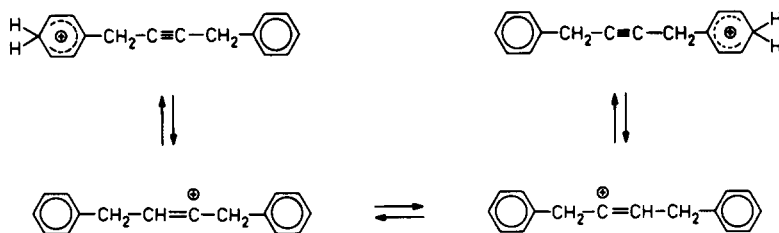


Fig. 4. MIKE spectra of (a) $[D_5]$ -**5** ions (m/z 212) and (b) $[D_5]$ -**7** ions (m/z 256).



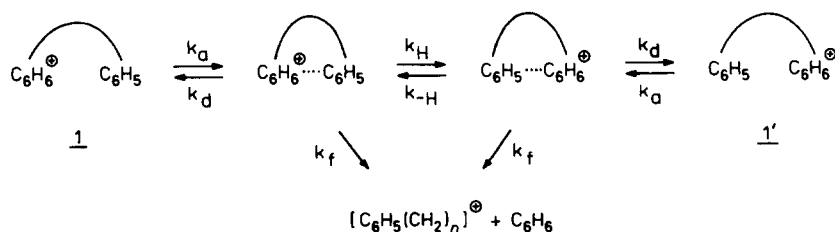
Scheme 5.

(4-phenyl-3-butyn-1-yl)-[D_5]-benzenium ions (**8**) exhibit a completely different (asymmetric) pattern for loss of $C_6(H,D)_6$ [17]. Thus, the triple bond in ions **5** is fixed in its central position and does not give rise to skeletal isomerization prior to loss of benzene as observed in the lower homologues of **8** [15]. A possible mechanism for the proton exchange in **5** ions is depicted in Scheme 5.

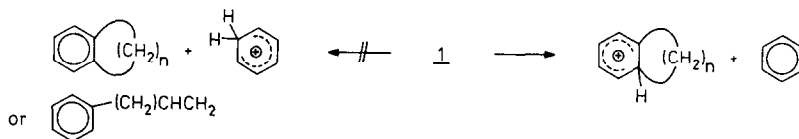
In contrast to the 2-butyne moiety, a cyclohexane ring does hinder the interannular proton transfer. The MIKE spectrum of protonated *trans*-1-benzyl-4-phenyl-cyclohexane (**7**) shows only loss of benzene as found for **1** ions. However, in contrast to the latter, the aromatic moieties of **7** remain different. The MIKE spectrum of [D_5]-**7** [Fig. 4(b)] shows that the benzylic benzene nucleus is mostly lost prior to interannular proton transfer. A minor portion ($\sim 12\%$) of [D_5]-**7** ions undergoes the interannular proton exchange giving rise to loss of C_6H_6 , C_6H_5D and $C_6H_2D_4$ (ca. 2% of C_6HD_5 being obscured). Obviously, the steric restrictions conferred by the *trans* orientation of the two rings in **7** reduce the proton transfer rate constant by at least two orders of magnitude as compared to the long-chain ions **1**.

In order to explain the pattern of $C_6(H,D)_6$ loss quantitatively, an isotope effect has to be assumed, favouring the interannular transfer of a proton over that of a deuteron by a factor of $k_H/k_D \approx 5$. This follows from a kinetic model calculation described in the following section.

The competing isomerization and fragmentation pathways of (ω -phenyl-alkyl)-benzenium ions, **1**, are outlined in Scheme 6. The ring-associated



Scheme 6.



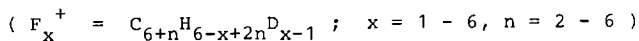
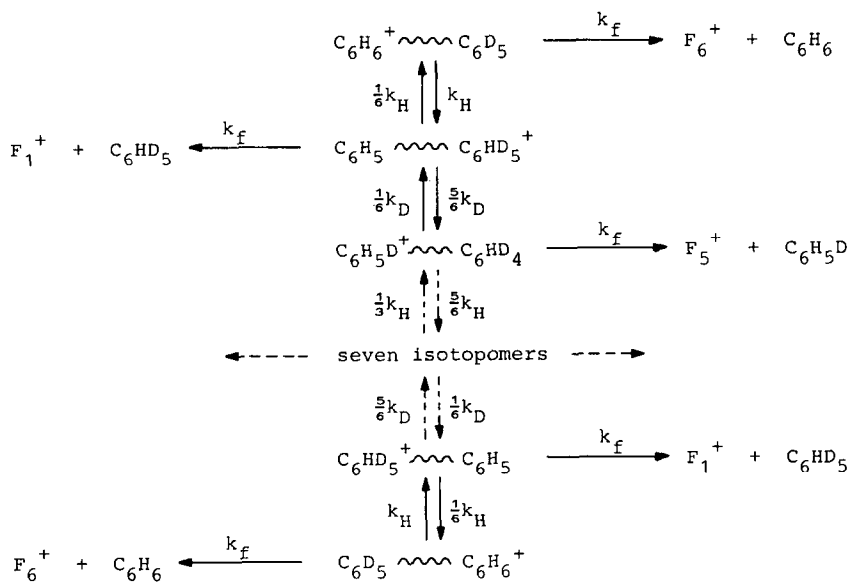
Scheme 7.

rotamers of **1** ions are certainly more stable than the non-associated ones (and hence $k_a/k_d \gg 1$), since the proton-bound dimer of benzene, $[\text{C}_6\text{H}_7^+ \cdot \text{C}_6\text{H}_6]$, is stabilized by $\Delta H = -46 \text{ kJ mol}^{-1}$ as compared to C_6H_7^+ and C_6H_6 [18]. The internal energy gained by association of the two rings increases the proton transfer rate constants k_H and k_{-H} , and the ring-to-ring proton exchange takes place mainly within these proton-bound association complexes ($k_H = k_{-H} \gg k_d$) [19]. The protonolysis of the $\text{C}^\alpha\text{-C}^{\text{ipso}}$ (or $\text{C}^\omega\text{-C}^{\text{ipso}}$) bond should, in the first step, give rise to ion/molecule complexes $[\text{F}^+ \cdot \text{C}_6\text{H}_6]$ as has been shown for **1a**-type ions [20]. In long-chain **1** ions ($n \geq 3$), benzocycloalkanes should be formed within the complexes giving rise to proton-bound pairs of arenes which finally separate into the products, i.e. the protonated benzocycloalkane and benzene (Scheme 7) [21]. It may be noted that the fragmentation of simple alkylbenzenium ions [4(d),9,22] differs from that of **1** ions in that the latter do not form benzenium (C_6H_7^+) ions and the corresponding alkene (Scheme 7). Obviously, the second benzene nucleus suppresses this fragmentation by the favourable interaction with the benzenium ring, as outlined above.

A kinetic model for H^+/D^+ exchange

In the case of the $[\text{D}_5]$ - and $[\text{D}_6]$ -labelled ions **1a–1e** and **1g–1h**, respectively, twelve isotopomers equilibrate via the interannular proton transfer with rate constants k_H and k_D . Neglecting secondary isotope effects, the relative abundances of these isotopomeric reactand ions and of the products F_x^+ and $\text{C}_6(\text{H},\text{D})_6$ can be calculated for a given set of the three rate constants k_H , k_D and k_f [17,23] (Scheme 8).

Due to the instrumental parameters of the mass spectrometer used, ions fragmenting with $k_f = 5 \times 10^{-4} \text{ s}^{-1}$ contribute most to the loss of benzene in the second FFR [17]. The kinetic calculations show, that metastable $[\text{D}_5]$ -**1** ions undergo the interannular proton and deuteron transfer with rate constants $k_H \approx k_D \geq 1 \times 10^6 \text{ s}^{-1}$. This follows from the kinetic model calculations, some results of which are shown in Fig. 5. It is evident that with transfer rates k_H and k_D in the order of 10^5 s^{-1} , the statistical distribution of the eleven protons and deuterons cannot be achieved for metastable ions fragmenting within the time frame corresponding to the second FFR (i.e. for $[\text{D}_5]$ -**2a** ions, m/z 188: $t = 1.2\text{--}2.4 \times 10^{-5} \text{ s}$).



Scheme 8.

With $k_{\text{H}} = k_{\text{D}} = 1 \times 10^6 \text{ s}^{-1}$ [Fig. 5(b)], the pattern corresponding to the complete proton exchange is fully evolved. Since this is the pattern found experimentally for all metastable (ω -phenylalkyl)-benzenium ions [D_3]-**1a** to

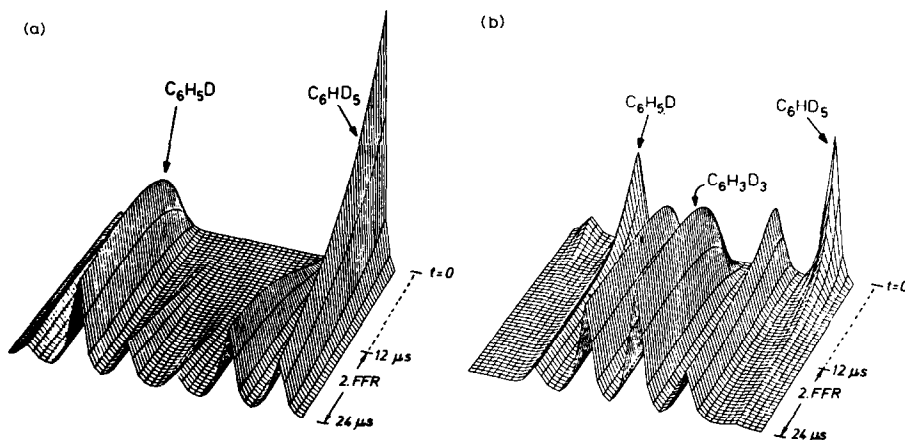


Fig. 5. Relative abundances of benzene isotopomers from [D_3]-**1a** ions (from acid **2a'**) vs. ion lifetime, calculated for: (a) $k_{\text{H}} = k_{\text{D}} = 1 \times 10^5 \text{ s}^{-1}$ and $k_f = 5 \times 10^4 \text{ s}^{-1}$; and (b) $k_{\text{H}} = k_{\text{D}} = 1 \times 10^6 \text{ s}^{-1}$ and $k_f = 5 \times 10^4 \text{ s}^{-1}$.

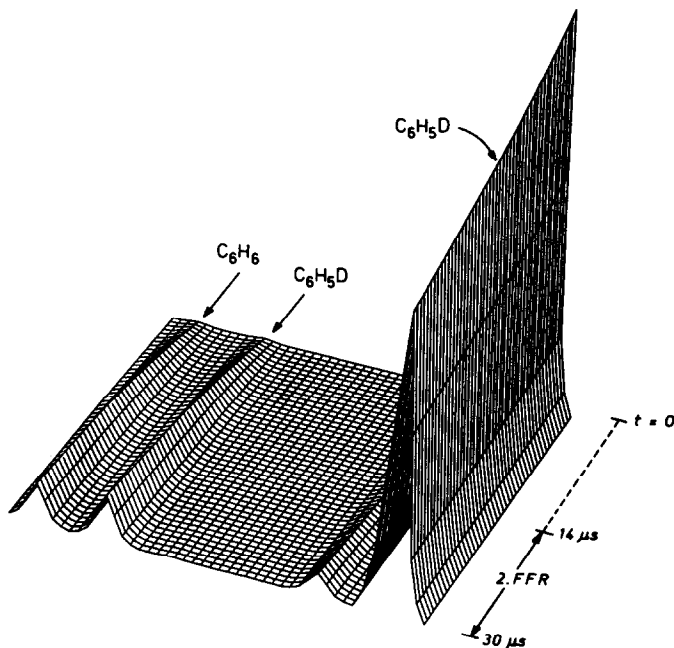


Fig. 6. Relative abundances of benzene isotopomers from $[D_5]$ -7 ions vs. ion lifetime, calculated for $k_H = 5 \times 10^4 \text{ s}^{-1}$, $k_D = 1 \times 10^4 \text{ s}^{-1}$, and $k_f = 5 \times 10^4 \text{ s}^{-1}$.

$[D_6]$ -1h as well as for metastable $[D_5]$ -5 ions, the rates for proton transfer and loss of benzene must be in the ratio $k_H/k_f \geq 20$. This corresponds to the previous estimation [8] of at least 14 ring-to-ring proton transfer steps necessary for randomization. The actual rate constant for the interannular proton transfer is probably considerably higher than $1 \times 10^6 \text{ s}^{-1}$ since the proton exchange is complete even in unstable ions for which $k_f \geq 1 \times 10^6 \text{ s}^{-1}$ [24].

The achievement of the statistical distribution in the deuterium-labelled benzenium ions is certainly complicated by a kinetic isotope effect, i.e. $k_H/k_D > 1$, which is obscured, of course, in ions $[D_5]$ -1a to $[D_6]$ -1h and $[D_5]$ -5 because $k_H \approx k_D \gg k_f$. However, in contrast to all of these ions, the experimental pattern for loss of $C_6(H,D)_6$ from $[D_5]$ -7 ions is not in accord with any of the distributions calculated with $k_H = k_D$ (Fig. 5); but it can be explained by assuming $k_H = 5 \times 10^4 \text{ s}^{-1}$ ($= k_f$) and $k_D = 1 \times 10^4 \text{ s}^{-1}$ (Fig. 6). Obviously, the steric hindrance of the interannular proton transfer in 7 ions decreases the rate of this process by two orders of magnitude. Hence, loss of benzene competes with proton transfer, and the kinetic isotope effect, $k_H/k_D = 5$, becomes observable. A similar situation has been found for protonated diphenylmethane [12,25].

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Dr. N.M.M. Nibbering, University of Amsterdam, for many discussions and his active engagement in the research project. Thanks are also due to Mr. E. Gärtner for technical assistance in mass spectrometry, Mr. G. Lipinski for measuring $^1\text{H-NMR}$ spectra and Mr. H. Siffczyk for performing elemental analysis of the compounds.

Financial support by the Fonds der Chemischen Industrie and by the "Forschungsprojekt 2196" der Universität Bielefeld is gratefully acknowledged.

REFERENCES

- 1 The present results were reported in part at the EUCHEM Conference, Chemistry of Ion Beams, Lunteren, The Netherlands, April 4, 1980.
- 2 (a) V.A. Koptuyug, *Top. Curr. Chem.*, 122 (1984) 1. (b) V.G. Shubin, *Top. Curr. Chem.*, 116/117 (1984) 267. (c) P. Ahlberg, G. Jönsall and C. Engdahl, *Adv. Phys. Org. Chem.*, 19 (1983) 223. (d) D. Fărcașiu, *Acc. Chem. Res.*, 15 (1982) 46.
- 3 (a) D.M. Brouwer, E.L. Mackor and C. MacLean, in G.A. Olah and P.v.R. Schleyer (Eds.), *Carbonium Ions*, Vol. 2, Wiley, New York, 1970, Chap. 20. (b) G.A. Olah, R.H. Schlosberg, R.D. Porter, Y.K. Mo, D.P. Kelly and G.D. Mateescu, *J. Am. Chem. Soc.*, 94 (1972) 2034. (c) G.A. Olah, J.S. Staral, G. Asencio, G. Liang, D.A. Forsyth and G.D. Mateescu, *J. Am. Chem. Soc.*, 100 (1978) 6299. (d) D. Fărcașiu, M.T. Melchior and L. Craine, *Angew. Chem. Int. Ed. Engl.*, 16 (1977) 315.
- 4 (a) A.P. Bruins and N.M.M. Nibbering, *Org. Mass Spectrom.*, 11 (1976) 950. (b) D.H. Williams and G. Hvistendahl, *J. Am. Chem. Soc.*, 96 (1974) 6755. (c) J.L. Devlin, III, J.F. Wolf, R.W. Taft and W.J. Hehre, *J. Am. Chem. Soc.*, 98 (1975) 1990. (d) J.A. Herman and A.G. Harrison, *Org. Mass Spectrom.*, 16 (1981) 423. (e) D. Kuck, J. Schneider and H.F. Grützmacher, *J. Chem. Soc. Perkins Trans. 2*, (1985) 689.
- 5 (a) P. Giacomello and F. Cacace, *J. Am. Chem. Soc.*, 98 (1976) 1823. (b) M. Attina, F. Cacace, G. Ciranni and P. Giacomello, *J. Am. Chem. Soc.*, 99 (1977) 2611. (c) See also, F. Cacace and M. Speranza, *J. Am. Chem. Soc.*, 98 (1976) 7305.
- 6 (a) W.J. Hehre and J.A. Pople, *J. Am. Chem. Soc.*, 72 (1972) 6901. (b) D. Heidrich and M. Grimmer, *Int. J. Quant. Chem.*, 9 (1975) 923. (c) D. Heidrich, M. Grimmer and B. Sommer, *Tetrahedron*, 32 (1976) 2027. (d) T. Sordo, J. Bertran and E. Canadell, *J. Chem. Soc. Perkin Trans. 2*, (1979) 1486. (e) D. Heidrich, U. Göring, W. Förster and C. Weiss, *Tetrahedron*, 35 (1979) 651. (f) M.J.S. Dewar and C.H. Reynolds, *J. Am. Chem. Soc.*, 104 (1982) 3244.
- 7 (a) D. Kuck and H.F. Grützmacher, *Org. Mass Spectrom.*, 13 (1978) 81, 90. (b) D. Kuck and H.F. Grützmacher, *Adv. Mass Spectrom.*, 8 (1980) 867.
- 8 D. Kuck, W. Bäter and H.F. Grützmacher, *J. Am. Chem. Soc.*, 101 (1979) 7154.
- 9 D. Kuck, G. Prior and H.F. Grützmacher, *Extended Abstracts of the 14th Meeting of the British Mass Spectrometry Society, Edinburgh, September, 1984.*
- 10 W. Bäter, D. Kuck and H.F. Grützmacher, *Org. Mass Spectrom.*, in press.
- 11 R.K. Boyd and J.H. Beynon, *Org. Mass Spectrom.*, 12 (1977) 163.
- 12 D. Kuck, *Int. J. Mass Spectrom. Ion Phys.*, 47 (1983) 499.
- 13 D. Kuck and H.F. Grützmacher, *Z. Naturforsch. Teil B*, 34 (1979) 1750.

- 14 For example, the CI mass spectra of stereoisomeric diphenylcyclohexanes have been studied. However, the abundances of the $[M+H]^+$ ions have been found to be extremely low. In general, 1, ω -branched protonated 1, ω -diphenylalkanes, e.g. $C_6H_5CH(CH_3)(CH_2)_4CH(CH_3)C_6H_6^+$, eliminate benzene much more rapidly than the corresponding unbranched ions, e.g. **1e**: D. Kuck, unpublished results.
- 15 W. Bather, D. Kuck and H.F. Grutzmacher, *Org. Mass Spectrom.*, in press.
- 16 (a) D.H. Aue and M.T. Bowers, in M.T. Bowers (Ed.), *Gas Phase Ion Chemistry*, Vol. 2, Academic Press, New York, 1979, p. 35. (b) G. Melloni, G. Modena and U. Tonellato, *Acc. Chem. Res.*, 14 (1981) 227.
- 17 W. Bather, Ph.D. Thesis, Bielefeld, 1984.
- 18 M. Mautner, P. Hamlet, E.P. Hunter and F.H. Field, *J. Am. Chem. Soc.*, 100 (1978) 5466.
- 19 The intermolecular proton exchange in the collision complex $[C_6H_7^+ \cdot C_6H_6]^*$ has been investigated: D. Kuck, S. Ingemann, L.J. de Koning, H.F. Grutzmacher and N.M.M. Nibbering, in press.
- 20 W. Bather and H.F. Grutzmacher, *Int. J. Mass Spectrom. Ion Processes*, 64 (1985) 193.
- 21 This is the energetically more favourable fragmentation channel, assuming $PA(\text{benzocycloalkane}) = PA(o\text{-xylene}) = 817 \text{ kJ mol}^{-1}$; $PA(\text{benzene}) = 777 \text{ kJ mol}^{-1}$, cf. ref. 16(a), p. 33.
- 22 (a) H.W. Leung and A.G. Harrison, *Org. Mass Spectrom.*, 12 (1977) 582. (b) C. Wesdemiotis, H. Schwarz, C.C. Van de Sande and F. Van Gaever, *Z. Naturforsch. Teil B*, 34 (1979) 495.
- 23 The time-dependence of the relative abundances of the fragment ions F_x^+ (Scheme 8) has been calculated [17] by expressing the concentrations y_k of the twelve interconverting isotopomers of $[D_5]\text{-1a}$ as well as of F_x^+ ions in a system of interdependent differential equations, viz.
- $$y_1' = a_{11}y_1 + a_{12}y_2 + \dots + a_{1m}y_m$$
- $$y_2' = a_{21}y_1 + a_{22}y_2 + \dots + a_{2m}y_m$$
- $$\vdots$$
- $$y_m' = a_{m1}y_1 + a_{m2}y_2 + \dots + a_{mm}y_m \quad (y_m' = dy_m/dt)$$
- a_{ik} corresponds to the rate constants k_H , k_D and k_f including the isotope contents of the individual benzenium rings. Transformation and integration of the equation system as well as the graphic representation of the results were performed by means of a computer using standard software (Rechenzentrum der Universitat Bielefeld).
- 24 The complete interannular proton exchange is not limited to metastable **1** ions. In spite of the interfering effects mentioned above, the completeness of the exchange can be recognized also for the more excited, unstable ions fragmenting in the ion source. Thus, the proton randomization is achieved even in ions with lifetimes $\gg 1 \mu\text{s}$. According to the CID spectra of the deuterated **1** ions, stable ions undergo the complete proton exchange as well. Therefore, the energy barrier towards the interannular proton transfer seems to be quite low. Concerning the CID spectra, however, post-collision proton exchange in the originally stable ions cannot be ruled out.
- 25 (a) D. Kuck and W. Bather, to be published. (b) E.E. Kingston, J.S. Shannon, V. Diakiw and M.J. Lacey, *Org. Mass Spectrom.*, 16 (1981) 428.
- 26 R.P. Morgan, J.H. Beynon, R.H. Bateman and B.N. Green, *Int. J. Mass Spectrom. Ion Phys.*, 28 (1978) 171.
- 27 H. van Bekkum, C.B. van den Bosch, G. van Minnenpathuis, J.C. de Mas and A.M. van Wijk, *Recl. Trav. Chim. Pays-Bas*, 90 (1971) 137.
- 28 L.F. Fieser and J. Szmuszkowicz, *J. Am. Chem. Soc.*, 70 (1948) 3352.
- 29 (a) L. Horner, H. Oedinger and H. Hoffmann, *J. Liebigs Ann. Chem.*, 626 (1959) 26. (b) D.R. Hepburn and H.R. Hudson, *J. Chem. Soc. Perkin Trans. 1*, (1976) 754.

- 30 K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, 94 (1972) 4374.
31 M. Schlosser, *Angew. Chem. Int. Ed. Engl.*, 13 (1974) 701.
32 W.J. Bailey and E. Fujiwara, *J. Am. Chem. Soc.*, 77 (1955) 165.
33 VG Analytical Ltd., Manchester, Gt. Britain, Model ZAB-2F.

APPENDIX

The identity and purity of all compounds were determined by IR, ^1H -NMR, and mass spectrometry, as well as by elemental analysis, giving satisfactory data in each case. The melting points given are uncorrected.

1-(ω -Phenylalkyl)-1,4-dihydrobenzoic acids, 2c–2f

The synthesis of acids **2c–2f**, [D_5]-**2a'** and [D_5]-**2e** was carried out by reductive alkylation of benzoic acid or [D_5]-benzoic acid with lithium or sodium in liquid ammonia, using the corresponding ω -phenylalkyl bromide. A similar procedure using lithium has been described for simpler 1,4-dihydrobenzoic acids [27].

The synthesis of [2,3,4,5,6- D_5]-1-(2-phenyl-ethyl)-1,4-dihydrobenzoic acid [D_5]-**2a'**, is given here. The reaction apparatus was dried carefully by flushing it with nitrogen at 300–350°C. After cooling, 0.5 mmol of the appropriate benzoic acid was placed in the bulb and dissolved at –55 to –60°C in liquid ammonia which had been dried over KOH and then over sodium. Lithium was then added in small portions until the deep-blue colour just persisted, avoiding any considerable excess of the metal. Subsequently, 2.5–5 mmol of 1-bromo-2-phenylethane was added in one portion, changing the colour of the solution to yellow and then to white. The solvent was allowed to evaporate overnight, and the residue was dissolved in 100 ml 10% NaCl and 50 ml CCl_4 . The aqueous layer was extracted several times with CCl_4 to remove the excess organic halide, acidified with conc. HCl, and extracted thrice with 30 ml CH_2Cl_2 . After drying and evaporation of the solvent, the oily residue was recrystallized from petroleum ether (50/70) containing some drops of methanol, giving white crystals of m.p. 94–95°C (yield 90%). The EI mass spectrum (70 eV) gave: m/z 233 (M^+ , 2%), 188 (5), 129 (14), 110 (3), 109 (12), 108 (22), 107 (27), 106 (29), 105 (100), 91 (25). The higher homologues were synthesized in a similar way, but sodium was used instead of lithium as reduction reagent, and the phenylalkyl bromide was added at –60 to –70°C within 30 min. The following acids were obtained as viscous oils: 1-(4-phenylbutyl)-1,4-dihydrobenzoic acid, **2c**, (35%), EI-MS m/z 256 (M^+ , 0.5%), 211 (2.5), 133 (18), 124 (10), 123 (10), 91 (100); 1-(5-phenylpentyl)-1,4-dihydrobenzoic acid, **2d**, (25%), for EI-MS, see Fig. 1; 1-(6-phenylhexyl)-1,4-dihydrobenzoic acid, **2e**, (28%), EI-MS m/z 284 (M^+ , 0.3%),

239 (7), 238 (4), 161 (4), 123 (13), 105 (20), 92 (30), 91 (100); 1-(6-([D_5]-phenyl)-hexyl)-1,4-dihydrobenzoic acid [D_5]-**2e** (22%), EI-MS m/z 289 (M^+ , 0.4%), 244 (6), 243 (3), 165/164/163/162 (0.5/1.5/1.8/0.5), 95 (100); 1-(12-phenyl-dodecyl)-1,4-dihydrobenzoic acid, **2f**, (20%), EI-MS m/z 368 (M^+ , 0.6%), 324 (4), 323 (12), 322 (5), 246 (2), 245 (0.8), 123 (25), 92 (49), 91 (100). Long-chain 1-bromo- ω -phenylalkanes ($\omega = 5,6,12$) required for the synthesis of these acids were obtained by addition of C_6H_5MgBr to the appropriate cycloalkanone (yields 75–79%), oxidation of the resulting 1-phenyl-cycloalkanol with CrO_3/CH_3CO_2H at 30°C to the corresponding ω -phenyl- ω -oxo-alkanoic acid [28] (yields 63–72%), two-step reduction of the keto acid with $H_2/Pd/BaSO_4$ in CH_3OH at 3 bar and room temperature and then with $LiAlH_4$ /ether (yields $\sim 75\%$), and subsequent conversion of the ω -phenylalkanol to the corresponding ω -phenylalkyl bromide using $(C_6H_5)_3PBr_2/CCl_4$ [29(a)] or $[(CH_3)_2NCHBr]^+ Br^-/CH_3CN$ [29(b)] (yields 73–85%). The physical constants of previously unknown compounds are: 12-oxo-12-phenyldodecanoic acid, m.p. 80°C, 12-phenyl-1-dodecanol, m.p. 38–40°C, b.p. 150–160°C/0.04 mbar, 1-bromo-12-phenyldodecane, b.p. 140–150°C/0.04 mbar. 1-Bromo-6-([D_5]-phenyl)-hexane was obtained in the same way starting from [D_5]-bromobenzene.

Deuterium-labelled 1, ω -diphenylalkanes [D_5]-3c to [D_6]-3h

The synthesis of the unlabelled 1, ω -diphenylalkanes has been described earlier [13], as well as that of [D_5]-**3b** [7(a)]. The other 1-([D_5]-phenyl)- ω -phenylalkanes [D_5]-**3a**, [D_5]-**3c**, [D_5]-**3d** and [D_5]-**3e** were synthesized by the Grignard reaction of the corresponding 1-bromo- ω -phenylalkane with [D_5]-benzaldehyde and reduction of the resulting alcohol with $H_2/Pd/BaSO_4$ in ethyl acetate at 5 bar and room temperature. No remarkable loss of deuterium label was found. [D_5]-**3c** and [D_5]-**3d** were also obtained in 45 and 38% yield, respectively, by refluxing [D_5]-bromobenzene and the corresponding ω -phenylalkyl-magnesium bromide in ether in the presence of 1 mol-% of $[Ni(dpp)_2Cl_2]$ [30] under N_2 for 48 h. The hexadeuterated analogues of **3g** and **3h** were obtained from 1,9-bis-(*p*-toluolsulfonyl)-nonane and 1,16-bis-(*p*-toluolsulfonyl)-hexadecane [13], respectively, and 2-([3,4,5- D_3]-phenyl)-ethylmagnesium bromide in the presence of $Li_2[CuCl_4]$ [13,31]. The corresponding 2-([3,4,5- D_3]-phenyl)-1-bromo-ethane was synthesized from [3,4,5- D_3]-bromobenzene [7(a)] by the conventional two-step sequence [8]. The melting and/or boiling points of the labelled hydrocarbons 1,13-di-([3,4,5- D_3]-phenyl)-tridecane [D_6]-**3g** and 1,20-di-([3,4,5- D_3]-phenyl)-eicosane [D_6]-**3h** agree with those reported for the unlabelled ones [13].

1-(4-Phenyl-2-butyne)-1,4-dihydrobenzoic acids, 4, and [D₅]-4

These acids were prepared in the way described above for the saturated analogues, using 1-bromo-4-phenyl-2-butyne. Yields were low (5–8%), and the samples contained some educt benzoic acids. **4** was obtained as a yellow oil, and [*D*₅]-**4** as a solid with m.p. 100–105°C.

The ¹H-NMR of **4** (CDCl₃) was: δ [ppm] 1.9–2.9 (m, 4H), 2.65 (m, 2H), 5.87 (m, 4H), 7.2 (s, 5H). The EI-MS of **4** (70 eV) gave: *m/z* 252 (M⁺, 2%), 207 (24), 129 (92), 128 (83), 115 (61), 91 (87), 79 (82), 77 (100). The deuterium content of [*D*₅]-**4** was > 95% (by ¹H-NMR). 1-Bromo-4-phenyl-2-butyne (b.p. 92–96°C/0.04 mbar) was obtained in 51% yield from 4-phenyl-2-butyne-1-ol [32] and (C₆H₅)₃PBr₂ in CCl₄ [29(a)].

1-[(trans-4-Phenylcyclohexyl)-methyl]-1,4-dihydrobenzoic acids, 6 and [D₅]-6

4-Phenylbenzoic acid was reduced to *trans*-4-phenyl-cyclohexanecarboxylic acid with sodium/3-methylbutanol (yield 47%, m.p. 198°C), which was then converted to *trans*-4-phenyl-cyclohexanol with LiAlH₄ (82%). Treatment of the alcohol with [(CH₃)₂NCHBr]⁺Br⁻ in acetonitrile afforded *trans*-1-(bromomethyl)-4-phenyl-cyclohexane in 78% yield, b.p. 138–143°C/0.4 mbar. Alternatively, 4-phenylcyclohexanone was converted to 1-methylene-4-phenyl-cyclohexane with CH₂P(C₆H₅)₃ in 42% yield: subsequent addition of HBr in CCl₄ gave the *trans*-bromide in 74% yield. Reductive alkylation of benzoic acid gave 1-[(*trans*-4-phenylcyclohexyl)-methyl]-1,4-dihydrobenzoic acid, **6**, in 18% yield, m.p. 144–146°C. The ¹H-NMR (CDCl₃) was: δ [ppm] 1.1–2.6 (m, 11H), 2.65 (s, 1H), 7.18 (s, 5H); and the EI-MS (70 eV) gave: *m/z* 301 (M⁺, 1%), 256 (19), 173 (19), 129 (24), 105 (16), 95 (18), 91 (100). Contamination of **6** and [*D*₅]-**6**, obtained in the same way from [*D*₅]-benzoic acid, with the *cis*-isomers were < 1% (by ¹H-NMR).