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Intramolecular Ring-to-Ring Proton Transfer in Gaseous (ω-Phenylalkyl)benzenium Ions

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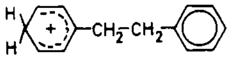
Abstract: Gaseous (2-phenylethyl)benzenium and (3-phenylpropyl)benzenium ions **1** and **2** are generated easily by mass spectrometric loss of $\cdot CO_2H$ from the positive molecular ions of the corresponding 1-(ω-phenylalkyl)-1,4-dihydrobenzoic acids **4** and **5**. The major secondary fragmentation is loss of benzene from **1** and **2**. It is shown by deuterium labeling that **1** and **2** ions undergo repeated ring-to-ring proton transfer reactions, equilibrating all of the 11 "aromatic" hydrogen atoms within ~10^{-5} s without involving those from the aliphatic chain. A competition between the ring-to-ring (quasi-*inter*molecular) proton transfer and proton shifts within the ring ("ring walks") is discussed.

Introduction

Since arenium ions have been found to play a central role as intermediate in electrophilic aromatic substitution, their properties have been investigated intensively. In particular, the relative stabilities of isomeric arenium ions and their reactivity toward isomerization have been of considerable interest.[1-3] Contrary to proton addition complexes generated in strongly acidic media,[2] arenium ions formed in the gas phase[3] are not influenced by solvation effects, thus offering the possibility to study their intrinsic reactivity.

In this contribution we report on the intramolecular proton transfer occurring in gaseous (2-phenylethyl)- and (3-phenylpropyl)benzenium ions, **1** and **2**, respectively. The approach used to obtain **1** and **2** is generally applicable to generate gaseous arenium ions. The positive molecular ions of C-3-substituted cyclohexa-1,4-dienes (formed upon ionization by electron impact) readily lose one of the groups at the diallylic C-3 position, yielding the corresponding arenium ions. These primary ions are assumed to be formed, at least originally, as 3-substituted benzenium ions (Scheme I).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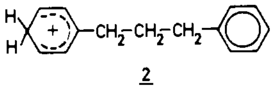
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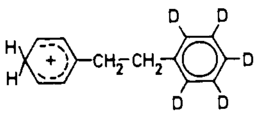
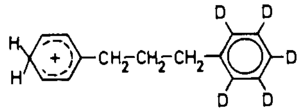

1a


2a

Results and Discussion

1 (m/z 183) and **2** (m/z 197) are generated by loss of CO_2H from the molecular ions of 3-(2′-phenylethyl)-1,4-dihydrobenzoic acid (**4**) and 3-(3′-phenylpropyl)-1,4-dihydrobenzoic acid (**5**), respectively, as indicated in their 70-eV mass spectra (Figures 1a and 1c). In both cases this fragmentation is remarkably favored (apparent activation energies 5 and 7 kcal mol^{-1}, respectively[4]). Contrary to $4^{+\cdot}$ and $5^{+\cdot}$, their benzyl homologue $3^{+\cdot}$[5] exhibits predominant cleavage of the *benzylic* C^3–C bond at 70 eV, thereby suppressing the loss of $\cdot CO_2H$.[6]

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The most abundant secondary fragmentation of both **1** and **2** is by far elimination of benzene, generating $C_8H_9^+$ (*m/z* 105) and $C_9H_{11}^+$ (*m/z* 119), respectively. After a lifetime of $\bar{\tau} \sim 10^{-5}$ s, metastable ions **1** and **2** yield ~100% $C_8H_9^+$ and ~90% $C_9H_{11}^+$, respectively, as illustrated in Figure 2a for $\mathbf{2} \rightarrow C_9H_{11}^+ + C_6H_6$. This fragmentation behavior may be considered characteristic for benzenium-type ions as it corresponds to the well-known dealkylation of alkylbenzenes upon protonation in solution[1b,2b,7] as well as in the gas phase.[8]

Before discussing the fragmentation of **1** and **2** in more detail it seems necessary to check for eventual isomerization processes occurring on the level of the molecular ions. Since the formation of **1** and **2** represents highly favorable fragmentation pathways for $\mathbf{4}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$, respectively, a closer inspection of the 70-eV mass spectra of the deuterated analogues **4a** and **5a** will be appropriate (Figures 1a–d). Firstly, loss of $\cdot CO_2H$ is accompanied by only minor amounts of $\cdot CO_2D$ (3% from $\mathbf{4a}^{+\cdot}$ and 8% from $\mathbf{5a}^{+\cdot}$). Secondly, the McLafferty rearrangement product $C_7H_8O_2^{+\cdot}$ (*m/z* 124) is observed only in the case of the β-phenylethyl compounds— probably owing to the localized activation of the β-C–H bonds in $\mathbf{4}^{+\cdot}$ and $\mathbf{4a}^{+\cdot}$. No deuterium label is incorporated into this fragment, suggesting that no H/D exchange occurs prior to the rearrangement.[9] Finally, high amounts of $C_9H_4D_5^+$ (*m/z* 110) are formed from $\mathbf{4a}^{+\cdot}$ (in addition to a separate set of variously deuterated $C_9(H,D)_9^+$ ions at *m/z* 105–110, vide infra) indicating again that the β-phenylethyl moieties of the molecular ions $\mathbf{4}^{+\cdot}$ and $\mathbf{4a}^{+\cdot}$ are *not* involved in hydrogen exchange processes. Similarly, a significant fraction of $C_7H_2D_5^+$ (*m/z* 96) is generated directly from $\mathbf{5a}^{+\cdot}$ (in addition to a separate set of various deuterated $C_7(H,D)_7^+$ ions in the range of *m/z* 91–96). From these observations it follows that there are essentially no isomerization reactions occurring on the level of the molecular ions prior to fragmentation.[10]

Contrary to the molecular ions, the benzenium ions **1** and **2** do undergo unimolecular isomerization. The pentadeuterated analogues **1a** and **2a** do not eliminate C_6H_6 and C_6HD_5 exclusively (the latter may be expected to result from a single proton transfer to the originally unprotonated C_6D_5 ring). Instead **1a** and **2a** eliminate all of the six possible isotopomers $C_6H_{6-x}D_x$ ($0 \leq x \leq 5$), as can be seen from Figures 1b, 1d, and 2b. By using metastable defocusing techniques[11a] the individual contributions for $\mathbf{1a} \rightarrow C_8(H,D)_9^+ + C_6(H,D)_6$ and $\mathbf{2a} \rightarrow C_9(H,D)_{11}^+ + C_6(H,D)_6$ can be resolved for long-lived, metastable ions. They are found to be equal for both homologues within the limits of experimental error (Table I).

Comparing these experimental intensity distributions with those calculated for various H/D scrambling models reveals that, prior to elimination of benzene, all of the 11 "aromatic" H and D atoms are completely randomized over both rings (model A, Table I). Agreement is very good within experimental error and does not allow for other possibilities. For example, scrambling cannot involve any H atoms from the aliphatic methylene groups (e.g., the four H^α and H^γ atoms, model B), which was found to occur in the case of the (open-shell) molecular positive ions of 1,3-diphenylpropane.[12] Moreover, the results strictly exclude a transfer of any aliphatic H atom to the unprotonated $C_6(H,D)_5$ group as the final step of $C_6(H,D)_6$ elimination (model C, Table I). Hence it follows that the eliminated benzene consists exclusively of the original ring (carbon and) hydrogen atoms.[13]

Indeed, even the *unstable* benzenium ions (those eliminating $C_6(H,D)_6$ within the ion source, $\bar{\tau} \ll 10^{-6}$ s) undergo considerable H/D exchange which, however, is not complete. Thus the 70-eV mass spectrum of **4a** (Figure 1b) shows a distribution of $C_8H_{9-x}D_x^+$ ions ($0 \leq x \leq 5$) the maximum corresponding to loss of $C_6H_3D_3$ from **1a** (*m/z* 107, cf. Table I). Similarly, loss of $C_6H_3D_3$ from **2a** is found to be most abundant (*m/z* 121) in the 70-eV spectrum of **5a** (Figure 1d).[14]

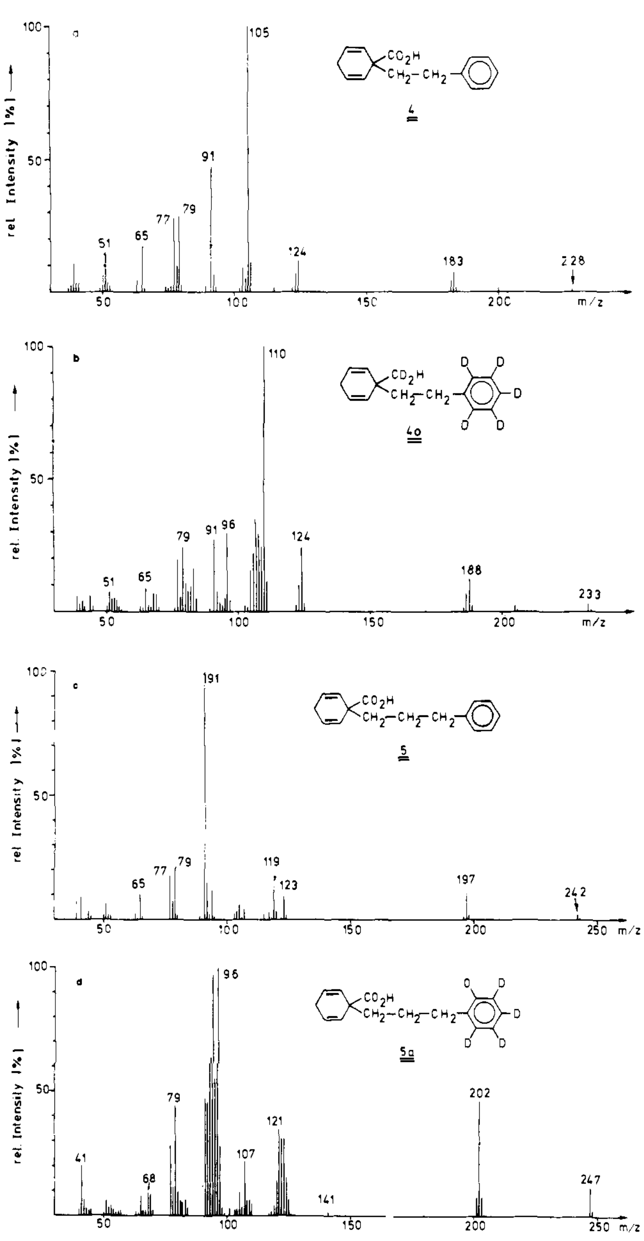
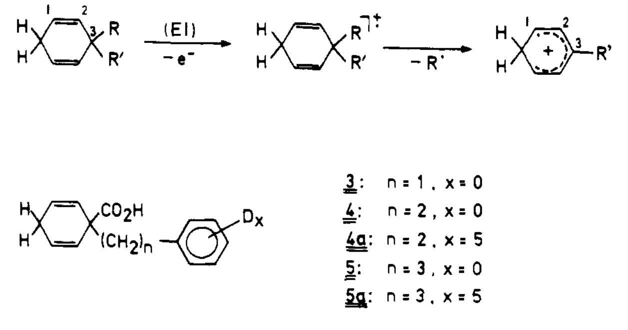


Figure 1. 70-eV mass spectra of (a) **4**, (b) **4a**, (c) **5**, and (d) **5a**.

Scheme I



Similar evidence is provided independently by investigating the fragmentation of the benzenium ion **2b** formed by chemical ionization[15] of the D_9-labeled 1,3-diphenylpropane **6**[12] using CH_4 as reagent gas (Scheme II). **2b** ions, consisting necessarily of at least two primary tautomers, eliminate $C_6(H,D)_6$ with the same distribution as does **2a** (Table I, Figure 3). Within experimental error, agreement with scrambling model A is again excellent, demonstrating that, indeed, aliphatic hydrogen

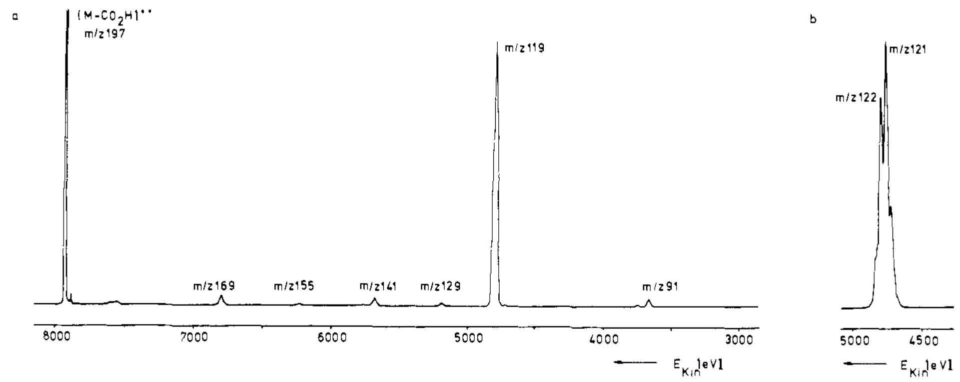


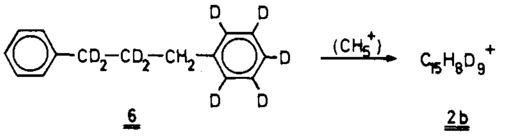
Figure 2. DADI (MIKE) spectra[11] of (3-phenylpropyl)benzenium ions: (a) **2**; (b) **2a** (partial spectrum).

Table I. Deuterium Distribution in Loss of $C_6(H,D)_6$[a]

	C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5
$[C_6H_6CH_2CH_2C_6D_5]^+$ (**1a**)	<0.4	5.7	35.6	42.8	14.4	1.1
$[C_6H_6CH_2CH_2CH_2C_6D_5]^+$ (**2a**)	<0.3	3.8	31.0	45.8	17.3	1.8
scrambling model A[b]	0.2	6.5	32.5	43.3	16.2	1.3
scrambling model B[b]	4.2	25.2	42.0	24.0	4.5	0.2
scrambling model C[b]	1.3	16.2	43.3	32.5	6.5	0.2
$[C_6H_5CD_2CD_2CH_2C_6D_5 + H]^+$ (**2b**)	<0.1	8.5	31.3	39.3	19.0	1.8

[a] Values in % $\sum {}^{12}C_8(H,D)_9^+$ and % $\sum {}^{12}C_9(H,D)_{11}^+$, respectively. [b] See text.

Scheme II



atoms are not transferred to the aromatic nuclei prior to or during elimination of benzene.

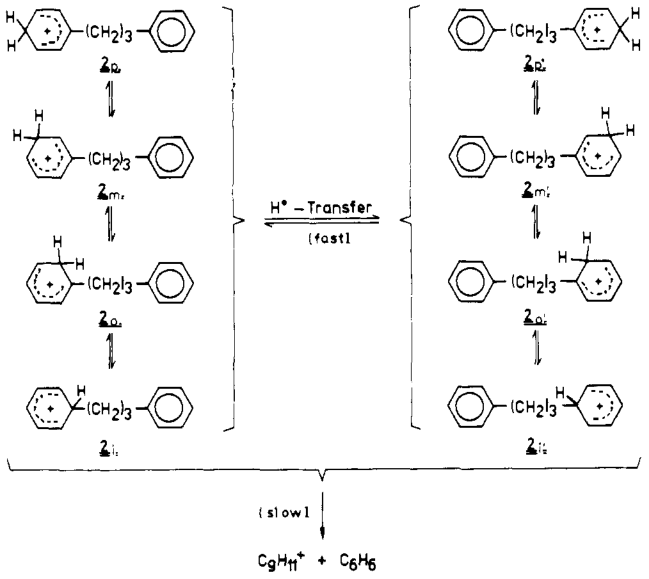
The results clearly show that fast repetitive proton transfer reactions occur *between* the aromatic nuclei of **1** and **2** (e.g., $2_p \rightleftharpoons 2_{m'}$, Scheme III). They may be accompanied by competitive proton shifts *within* the protonated ring[3d] (e.g., $2_p \rightleftharpoons 2_m$, etc.). Assuming this "ring walk" tautomerization to be much faster than the ring-to-ring proton transfer, the minimum number of proton-transfer steps necessary to achieve randomization as found for **1** and **2** is calculated to be 14.

Ab initio calculations[16a] indicate, in accordance with experimental observations,[12] that the intrinsic activation energy for the proton shift in gaseous benzenium ions is 20–30 kcal mol^{-1}. This activation barrier[16] should be too high to allow for an effective ring walk isomerization to occur in **1** and **2**, because the activation energy of the rate-determining step, i.e., elimination of benzene, is measured to be of equal height (24 ± 5 kcal mol^{-1}). As a consequence, isomerization of **1** and **2** prior to elimination of benzene is assumed to take place by ring-to-ring proton transfer *without* significant participation of the proton ring walk mechanism. The number of transfer steps to achieve total proton randomization by this mechanism must be $\gg 14$.

The high entropy requirements for the ring-to-ring proton transfer in **1** and **2** might be compensated by an energy gain due to formation of *intra*molecular association intermediates between the protonated and the unprotonated phenyl ring. This is supported by the recent finding[17] that association complexes like $[C_6H_6 \cdot C_6H_7^+]$ exhibit a stabilization of ~11 kcal mol^{-1}. On the other hand, such "internal solvation"[18] might be expected to decrease the activation barrier of proton shifts within the protonated ring, thus approaching the value found for arenium ions in superacidic solution.[2a,b]

Presently, investigations are in progress to further elucidate the mechanism and scope of these ring-to-ring intramolecular proton-transfer reactions.

Scheme III



Experimental Section

Mass Spectrometric Measurements. The 70-eV mass spectra (Figure 1) were measured with a Varian MAT 311A double-focusing instrument ($\pi/2$ magnetic sector followed by $\pi/2$ electric sector) and represent the average of at least three scans. Operating conditions follow: emission current, 2 mA; accelerating voltage, 3 kV; ion source temperature, ~250 °C. Samples were introduced by a water-cooled direct inlet system using aluminum crucibles closed by a cap with a very small hole The crucible was heated to 80–95 °C in order to achieve a nominal ion source pressure of $\lesssim 1.5 \times 10^{-6}$ Torr. Measurements were repeated with a Vacuum Generators MM 12B single-focusing instrument (accelerating voltage 4 kV). Only minor changes of the relative peak heights were observed.

The fragmentation of the metastable $(M - CO_2H)^+$ ions **1**, **1a**, **2**, and **2a** given in Table I was measured with the MAT 311A instrument by selecting the *m/z* values of the secondary fragment $(M - CO_2H - C_6(H,D)_6)^+$ by the magnetic sector field and increasing the ac-

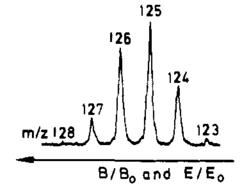


Figure 3. B/E linked scan spectrum[11a] of benzenium ion **2b**.

celerating voltage (U_0 = 1 kV) at constant electric sector field. The mean deviation is estimated to be $\leq \pm 10\%$ from three independent measurements. The MIKE spectra of the metastable $(M - CO_2H)^+$ ions (cf. Figure 2 for **2** and **2a**) were measured with a Vacuum Generators ZAB-2F double-focusing instrument (55° magnetic sector followed by 81° electric sector) as well as with the MAT 311A instrument by selecting the desired *m/z* value at fixed accelerating voltage (ZAB-2F, 8 kV; MAT 311A, 3 kV) and magnetic sector field and decreasing the electric sector field (DADI technique[11]). Samples were introduced to the ZAB-2F ion source (140 °C, trap current 200 μA) by the direct inlet rod using a quartz crucible without external cooling (~70°C), affording a nominal pressure of ~2×10^{-7} Torr. All measurements on metastable ions were performed using 70-eV electrons.

2b ions were obtained with the ZAB-2F instrument by chemical ionization[15] of 1-phenyl-3-[$^2H_5$]phenyl[1,1,2,2-$^2H_4$]propane (**6**)[12] using CH_4 (nominally 1×10^{-5} Torr) as the reagent gas. The fragmentation of metastable **2b** ions (Table I) was analyzed at fixed accelerating voltage (8 kV) by simultaneously scanning the magnetic and electric sector fields keeping their ratio constant (B/E linked scan technique[11a,19]). **6** was introduced by the septum inlet at 220 °C and was a mixture of 88.1% d_9, 6.6% d_8, and 4.1% d_{10} isotopomers. However, D correction was not necessary since other than isobaric ions (i.e., ~1% [$^2H_8$, $^{13}C_1$]**2b**) are filtered out. The mean deviation of several scans was $\leq \pm 15\%$.

Ionization and appearance energies were measured semiautomatically with a Vacuum Generators MM 12B single-focusing instrument at an emission current of 20 μA. The samples were introduced via the direct inlet system (80–90 °C) to give a nominal pressure of $\lesssim 1.0 \times 10^{-6}$ Torr at a source temperature of ~200 °C. The data were obtained from three independent runs for both **4** and **5**.

Preparation of Compounds. Melting points are uncorrected. ^1H NMR and IR spectra were recorded with a Varian EM 360 and a Perkin-Elmer Model 377 instrument, respectively.

1-Phenylalkyl-1,4-dihydrobenzoic acids **3**,[5b] **4**, **4a**, **5**, and **5a** were obtained by alkylation of 1,4-dihydrobenzoic acid using a procedure similar to that given by Plieninger and Ege.[5b] Ammonia (180 mL) (dried over KOH) was condensed into a 250-mL three-necked flask. After a small amount of sublimed $FeCl_3$ was suspended, 1.76 g (45 mmol) of potassium metal was added in small pieces to the stirred mixture at −33 °C. After each addition the solution was allowed to decolorize (3–5 min). The mixture was cooled to −70 to −75 °C under N_2 atmosphere and, during very fast stirring, a solution of 2.48 g (20 mmol) of 1,4-dihydrobenzoic acid[5a] in 10 mL of dry, peroxide-free diethyl ether was added in one portion, generating a deeply yellow precipitate. The appropriate ω-phenylalkyl bromide (24 mmol) (vide infra) in 10 mL of ether was added under stirring within 3 min, decolorizing the suspension quickly. The ammonia was allowed to evaporate and the reaction mixture worked up by adding a few milliliters of H_2O and 10 mL of concentrated NaOH and extracting twice with ether. The aqueous layer was acidified with concentrated HCl and extracted with ether. The extract was washed with a small amount of water dried over $MgSO_4$, and freed of solvent, yielding a pale yellow or colorless oil (55–65%) which was recrystallized twice from *n*-hexane. **4**: mp 94–95 °C; IR (KBr) 3300–2400, 1690–1670, 1600, 1490, 1410, 1290, 1265, 1250, 1080, 1065, 960, 940, 760, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.95 (m, 2 H), 2.54 (m, 2 H), 2.67 (m, 2 H), 5.82 (m, 4 H), 7.17 (s, 5 H), 11.64 (s, 1 H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.02; H, 7.08. **5**: mp 81–82 °C; IR (KBr) 3300–2400, 1690, 1490, 1450, 1410, 1270, 1220, 940, 745, 705 cm^{-1}; NMR ($CDCl_3$) δ 1.64 (m, 4 H), 2.57 (m, 4 H), 5.77 (m, 4 H), 7.14 (s, 5 H), 11.67 (s, 1 H). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.63; H, 7.64.

The deuterium content of acids **4a** and **5a** was determined by mass spectrometry (9 eV) and was found to be 98–99%.

The labeled acids **4a** and **5a** were obtained similarly by using $C_6D_5(CH_2)_2Br$ and $C_6D_5(CH_2)_3Br$, which were synthesized from C_6D_5Br (Merck) and $C_6D_5CH_2Br$,[20] respectively, and oxirane. The procedure given by Ramsden et al.[21] was modified by using ~100% excess of magnesium and adding the Grignard solution to an ~100% excess of oxirane in tetrahydrofuran. Thus 2-[$^2H_5$]phenylethanol and 3-[$^2H_5$]phenylpropanol were isolated in 60 and 62% yields, respectively. The alcohols were reacted with PBr_3 in CCl_4[22] yielding 2-[$^2H_5$]phenylethyl bromide (55%) and 3-[$^2H_5$]phenylpropyl bromide (65–71%), respectively. No significant loss of deuterium label had occurred (vide supra).

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(3) (a) Devlin III, J. L.; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1976,** *98*, 1990–1992. (b) Cacace, F.; Speranza, M. *Ibid.* **1976,** *98*, 7305–7307. (c) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, *Ibid.* **1977,** *99*, 2611–2615. (d) Bruins, A. P.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1976,** *11*, 950–954.

(4) The ionization and appearance energies (semilogarithmic plot method; see, e.g., Kiser, R. W. "Introduction to Mass Spectrometry and Its Applications"; Prentice-Hall: Englewood Cliffs, N.J., 1965; pp 166–198) are *I*(**4**) = 8.64, *I*(**5**) = 8.75 eV and *A*(1) = 8.84, *A*(**2**) = 9.03 (±0.05) eV.

(5) (a) Plieninger, H.; Ege, G. *Chem. Ber.* **1961,** *94*, 2088–2095. (b) *Ibid.* **1961,** *94*, 2095–2105.

(6) The 70-eV mass spectrum of **3** contains the following significant peaks: *m/z* 214 ($M^{+\cdot}$, 1.1%), 123 (11%), 105 (9.5%), 92 (100%), 91 (85%).

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(9) The fact that the McLafferty rearrangement ions from **4a**$^{+\cdot}$ do not contain any D atoms strictly excludes H/D scrambling in the neutral samples within the inlet system of the mass spectrometer. Correspondingly, the extent of H/D scrambling observed (see following) is governed by the mean lifetime ($\bar{\tau}$) of the decomposing ions but not by the temperature of the ion source.

(10) Admittedly, shifts of the allylic double bonds within the cyclohexadiene ring cannot be excluded strictly. However, they should exert no significant effect on the reactivity of the $(M - CO_2H)^+$ ions.

(11) (a) A systematic review of various mass spectrometric defocusing techniques is given: Boyd, R. K.; Beynon, J. H. *Org. Mass Spectrom.* **1977,** *12*, 163–165. (b) For the DADI or MIKES technique, in particular, see: Schlunegger, U. P. *Angew Chem., Int. Ed. Engl.* **1975,** *14*, 679, and references cited therein.

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(13) It was argued by a referee that the $(M - CO_2H)^+$ ions may rearrange to open-chain or other isomers rather than persist as cyclic arenium structures before elimination of benzene. It is generally accepted, however, that the excess energy of metastable ions in the transition state of fragmentation is small (see, e.g., Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lestér, G. R. "Metastable Ions"; Elsevier: Amsterdam, 1973; Chapter 4). Thus *skeletal* isomerization is very unlikely within the internal energy range of metastable **1** and **2** ions (24 ± 5 kcal). Furthermore, H/D scrambling in open-chain or ring-enlarged isomers of **1a** and **2a** (as well as of **2b**; see following) must be assumed to involve some or even all of the H atoms of the aliphatic chains (cf. scrambling models B and C).

(14) The second isotopomer cluster in the 70-eV mass spectrum of **5a** (*m/z* 91–96) is qualitatively similar; however, quantitative evaluation is not possible because of the tertiary fragmentation $C_9(H,D)_{11}{}^+ \rightarrow C_7(H,D)_7{}^+ + C_2(H,D)_2$.

(15) For reviews on chemical ionization mass spectrometry see: (a) Field, F. H. In "Ion Molecule Reactions", Vol. 1; Franklin, J. L., Ed., Butterworths: London, 1972; pp 261–313. (b) Richter, W. J.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1978,** *17*, 424.

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