A Study of Gaseous Benzenium and Toluenium Ions generated from 1,4-Dihydro- and 1-Methyl-1,4-dihydro-benzoic Acids[1]

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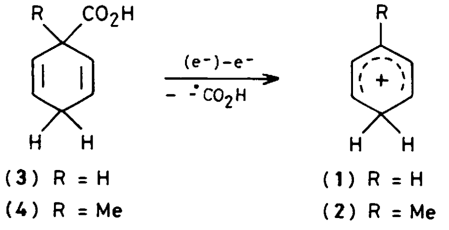
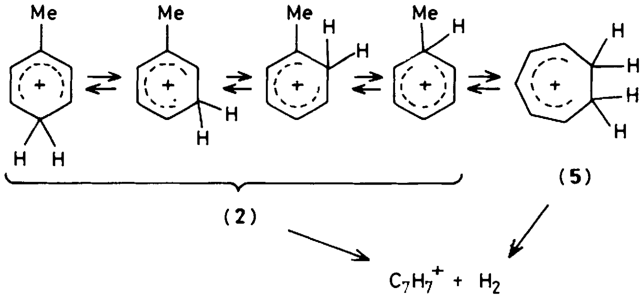
Gaseous benzenium $C_6H_7^+$ (1) and toluenium $C_7H_9^+$ (2) ions have been generated by mass spectrometric loss of $^{\bullet}CO_2H$ from the corresponding 1,4-dihydrobenzoic acids (3) and (4), and their fragmentations after *ca.* 10 μs have been investigated by means of mass-analysed ion kinetic energy (MIKE) spectrometry of some ^2H and ^{13}C labelled analogues. Metastable $C_6H_7^+$ ions eliminate H_2 after proton randomization, whereas metastable $C_7H_9^+$ ions expel both H_2 and CH_4 after *incomplete* proton equilibration. In particular, 40% of $C_7H_9^+$ ions randomize all their carbon and hydrogen atoms prior to loss of CH_4, and 60% of $C_7H_9^+$ ions lose the original methyl group along with a hydrogen atom from the (proton-equilibrated) benzenium ring, accompanied by a slow and incomplete exchange between the hydrogen atoms of the ring and the methyl group. It is suggested that loss of *both* CH_4 and H_2 occur *via* the (*ipso*-)toluenium ion (2). The role of a non-classical $C_7H_9^+$ isomer, phenylmethonium ion (6), is discussed since striking similarities are found compared with $[C_6H_6{\cdot}CH_3^+]^{\bullet}$ adducts from ion–molecule reactions described in the literature.

Among protonated aromatic molecules, benzenium ions (1) and toluenium ions (2) have attracted considerable interest.[2–5] They are formed not only by liquid[4] and gas-phase[5] protonation of the conjugate hydrocarbons but also by dissociative ionization of a number of aromatic[6,7a] and olefinic[7] compounds in the ion source of a mass spectrometer. Toluenium ions, in particular, have also been generated by ion–molecule reactions between methyl cations and benzene under various conditions in the liquid[8] as well as in the gas phase[8b,9] and by gas-phase ion–molecule reactions between phenyl cations and methane.[10]

A recent controversy[9c,11] concerning the chemical nature of $C_7H_9^+$ and related ions formed by such bimolecular reactions stimulates us to present our results for ions (1) and (2) generated by a well defined unimolecular reaction. This is the loss of a $^{\bullet}CO_2H$ radical from the radical cations of 1,4-dihydrobenzoic acids (3) and (4), respectively (Scheme 1), formed upon electron-impact ionization in the ion source of a mass spectrometer.[12] If isotopically labelled dihydrobenzoic acids are used the arenium ions formed can be assumed to have mainly retained the original position of the methylene group (*i.e.* site of 'protonation') and isotope incorporation.



Scheme 1.



Scheme 2.

A more detailed study of ions (1) and (2) seems to be important for another reason. Williams and Hvistendahl[13] proposed an attractive explanation for the extremely different kinetic energies released during the elimination of H_2 from these homologous arenium ions. As suggested by Field[5a] they inferred that the dihydrotropylium ions (5) are formed from ions (2) by a skeletal rearrangement and represent the reactive species for elimination of H_2.[13] The present work will show that the isomerization behaviour of $C_7H_9^+$ (2) is more complex than supposed earlier, but that elimination of H_2 may nevertheless occur from the toluenium ion structure (2) rather than from the dihydrotropylium ion structure (5).

Mass Spectrometric Fragmentation.—Dihydrobenzoic acid (3) and 1-methyl-1,4-dihydrobenzoic acid (4) were prepared from the corresponding benzoic acids by reduction and reductive methylation, respectively, using lithium in ammonia, as described in the literature.[14] Six labelled analogues of (3) and (4) have been synthesized and investigated. The 70 eV mass spectra of (3) and (4) are shown in Figure 1.† The relative low abundances of the molecular ions $(3)^{+\bullet}$ (m/z 124) and $(4)^{+\bullet}$ (m/z 138) reflect the ease of $^{\bullet}CO_2H$ loss giving rise to the intense base peaks at m/z 79 and 93, respectively, indicating the formation of $C_6H_7^+$ (1) and $C_7H_9^+$ (2) ions as the products of primary fragmentation. Secondary fragmentation of ions (1) is elimination of H_2 exclusively, giving rise to $C_6H_5^+$ ions (m/z 77). Ions (2) also eliminate H_2 generating $C_7H_7^+$ ions (m/z 91), but, in addition, they expel CH_4 to give $C_6H_5^+$ ions (m/z 77). Formation of ions (1) and (2) and their elimination products represent more than 95% of the total fragmentation of ionized acids (3) and (4) within the ion source.

By magnetic selection of the ions m/z 79 and 93, respectively, which leave the ion source prior to secondary fragmentation,

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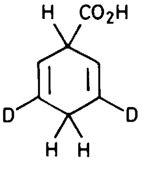
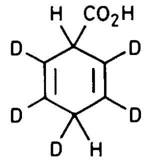
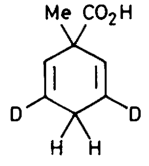
† Contrary to its 1-substituted homologue, (3) undergoes slow dehydrogenation in the heated inlet system of the mass spectrometer giving rise to m/z 122, 105, and 77 ions from benzoic acid (see Experimental section).



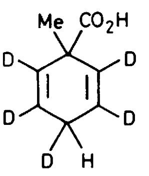
(3a)



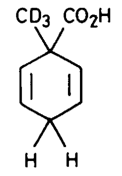
(3b)



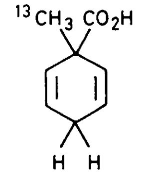
(4a)



(4b)



(4c)



(4d)

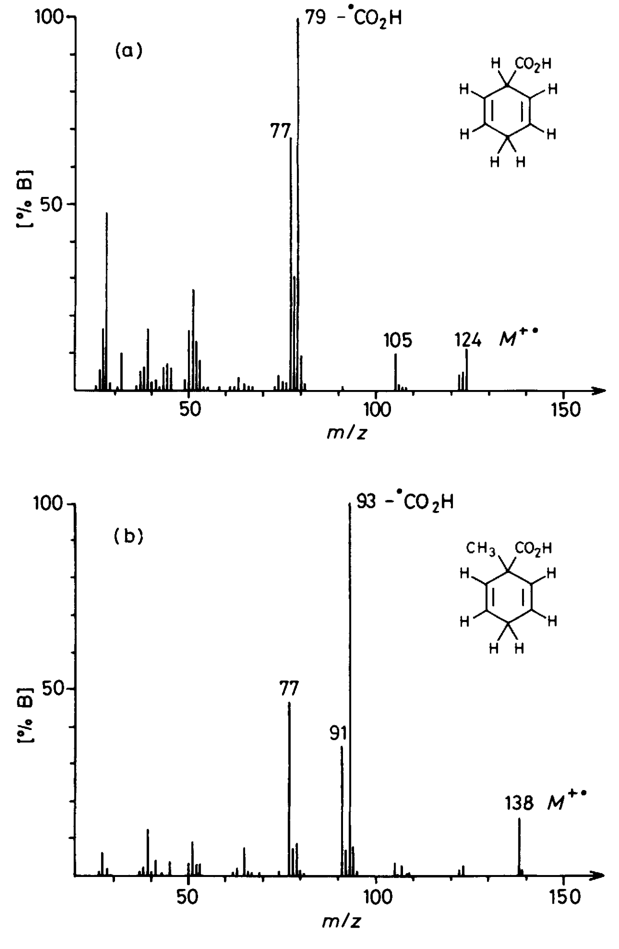
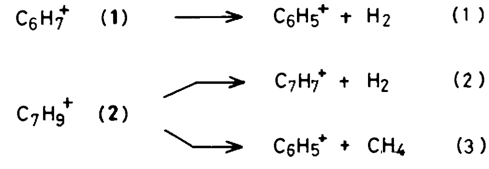


Figure 1. 70 eV Mass spectrum of (a) 1,4-dihydrobenzoic acid (3) and (b) 1-methyl-1,4-dihydrobenzoic acid (4)

and by scanning the deflection voltage of the electric sector following the magnet, the fragmentation of long lived 'metastable' ions (1) and (2) can be investigated. These mass-analysed ion kinetic energy (MIKE) spectra are given in Figure 2.*



Scheme 3.

Although a number of studies describe the gas-phase fragmentation behaviour of $C_7H_9^+$,[5a,13] part of them ignore the elimination of CH_4 competing with that of H_2. However, this reaction channel [reaction (3)] enables more insight to be gained into the isomerization behaviour of ions (**2**) than reaction (2). Loss of CH_4 along with loss of H_2 is a characteristic feature of $C_7H_9^+$ (*m*/*z* 93) ions in normal (70 eV) mass spectra of, *e.g.*, monoterpene hydrocarbons.[7b,15] Furthermore, both H_2 and CH_4 are produced by ion–molecule reactions (4)[9c] and (5)[10] (Scheme 4) in triple-stage quadrupole (t.s.q.) mass spectrometers.

Energy Requirements for Loss of H_2 *and* CH_4 *from* $C_7H_9^+$ *Ions.*—It is of interest to note that reactions (2) and (3) compete also for metastable ions (**2**) (Figure 2b).[16,17] As a consequence, the activation barriers of these fragmentation channels must be of similar heights.[18] However, a thermochemical estimation shows that the reaction enthalpies $\Delta H_{r(3)}$ and $\Delta H_{r(4)}$ are exceedingly different favouring the elimination of H_2 (Figure 3).[16] Assuming a benzyl cation (or, alternatively, a tropylium ion) to be formed, $\Delta H_{r(2)}$ is estimated to be +104 (+80) kJ mol^{-1} whereas for reaction (3) $\Delta H_{r(3)}$ is +260 kJ mol^{-1}.[16] If the course of fragmentation of ions (**2**) were governed by these thermodynamic energy requirements, CH_4 elimination could not compete successfully with loss of H_2. However, the latter reaction gives rise to a large amount of kinetic energy carried away with the fragments (kinetic energy release $T_{(2)}^{50}$ = 0.99 eV = 96 kJ mol^{-1}), in accord with the $C_7H_9^+$ ions from all other origins.[12,17,†] $T_{(2)}^{50}$ represents a lower limit to the reverse energy of activation (*i.e.* the addition barrier of H_2 to $C_7H_7^+$ ions, $E_{(2)}^{\mathrm{o.rev}}$); therefore, the activation barrier of H_2 loss from ions (**2**) is $E_{(2)}^{\mathrm{o}} \geq 200$ (176) kJ mol^{-1}. Since the elimination of CH_4 is accompanied by a relatively small kinetic energy release ($T_{(3)}^{50}$ = 34 meV = 3.3 kJ mol^{-1}) and the peak shape is Gaussian its reverse activation energy ($E_{(3)}^{\mathrm{o.rev}}$) can be assumed to be negligibly small.[17] Thus, the general observation that both H_2 and CH_4 are eliminated from low energy, metastable $C_7H_9^+$ ions is mostly due to a particularly high activation barrier towards the loss of H_2.

Indeed, by measuring the appearance energies (AE)[19] of $C_7H_7^+$ and $C_6H_5^+$ ions formed *via* reactions (2) and (3), respectively, from metastable ions (**2**) we find a relatively small difference $AE_{(3)} - AE_{(2)} = +0.39\ (\pm 0.1)$ eV = +37 (±10) kJ mol^{-1}. This value is remarkably close to the difference of the thermodynamic energy requirements of reactions (2) and (3), assuming a benzyl ion being formed and correcting for $E_{(2)}^{\mathrm{o.rev}}$ ($\geq T_{(2)}^{50}$): $\Delta H_f(C_6H_5^+) + \Delta H_f(CH_4) - [\Delta H_f(C_7H_7^+) + T_{(2)}^{50}] = 60$ kJ mol^{-1}. This in turn suggests that the major part of the reverse activation energy of reaction (2) is reflected by the kinetic energy release.

Elimination of Hydrogen from Labelled $C_6H_7^+$ *and* $C_7H_9^+$ *Ions.*—The labelled analogues of ions (**1**) and (**2**) generated by loss of $^{\bullet}CO_2H$ from the ionized acids (**3a**)—(**4d**) (Scheme 1) in the ion source show elimination of hydrogen and methane isotopomers in the second field-free region of the mass

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* The MIKE spectra of ions (**2**) from all *n*-methyl-1,4-dihydrobenzoic acids (*n* = 1—4) have been found to be very similar.

† See also ref. 7*b*. However, the values for kinetic energy release given there differ significantly from those found generally.

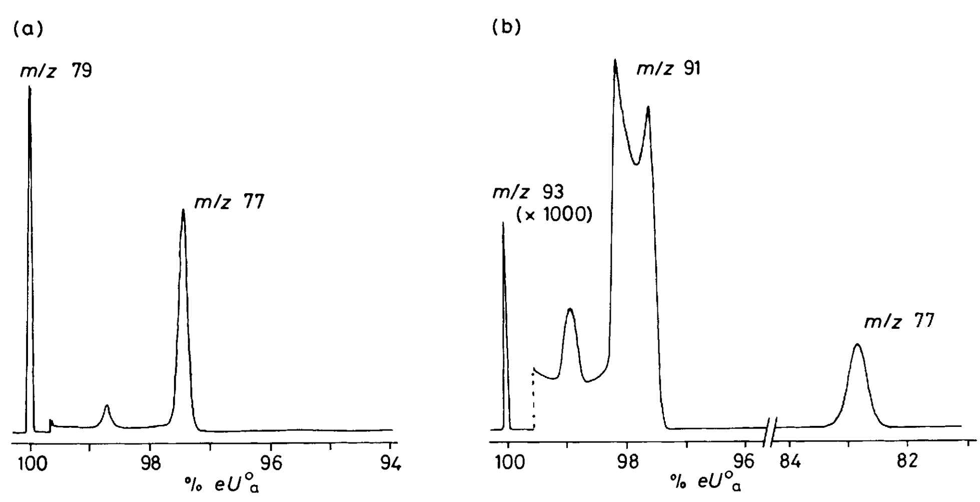
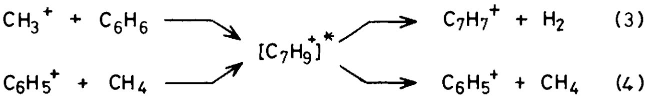


Figure 2. MIKE spectrum of (a) benzenuim ions (**1**), *m/z* 79, from acid (**3**), and (b) toluenium ions (**2**), *m/z* 93, from acid (**4**)



Scheme 4.

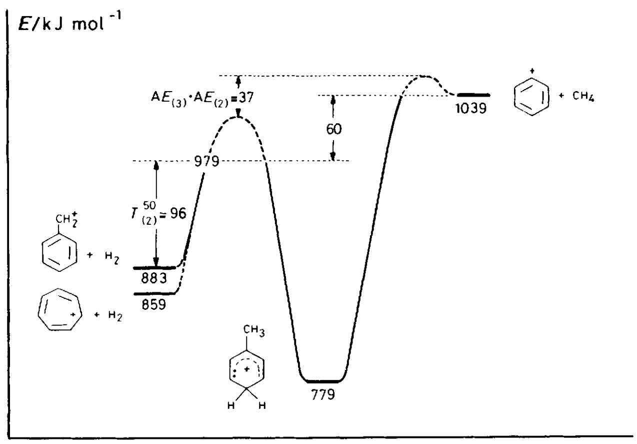


Figure 3. Energy profile for the competing fragmentation reactions of toluenium ions (**2**)

spectrometer. The relative amounts of $(H,D)_2$ eliminated are shown in Table 1.

As expected from prior work by Bruins and Nibbering[6a] and by Olah and his co-workers,[4] scrambling of the seven hydrogen atoms in (**1**) is found. Since the energy barrier for proton ring walk tautomerization in benzenium ions (**1**) is *ca.* 42 kJ mol⁻¹ (as measured in superacidic medium [2d,4]) and, in the same range, up to 86 kJ mol⁻¹ (as computed by semiempirical methods for the gas phase)[3] it is by far lower than the enthalpy of fragmentation ($\Delta H_{r(1)}$ 272 kJ mol⁻¹).[16,20] Therefore, the deviation of the measured pattern for $C_6(H,D)_5^+$ from that calculated for statistical distribution of hydrogen and deuterium atoms must be due to a kinetic isotope effect operating during the expulsion of the $(H,D)_2$ molecules from ions (**1**).

The same arguments hold for the loss of H_2 from $C_7(H,D)_9^+$ ions (**2**)—(**2c**) (see Figure 3). Again a marked isotope effect discriminates against elimination of HD and D_2 [*cf.* loss of H_2 from ions (**2b**)].

Table 1. Loss of hydrogen isotopomers[a] from $C_6(H,D)_7^+$ and $C_7(H,D)_9^+$ ions in the second field-free region (MIKE spectra)

Ion			$-H_2$	-HD	$-D_2$
(**1a**)	$C_6H_5D_2^+$	exp.	60.4	36.5	3.1
		stat.[b]	47.6	47.6	4.8
(**1b**)	$C_6H_2D_5^+$	exp.	8.6	57.1	34.3
		stat.[b]	4.8	47.6	47.6
(**2a**)	$C_7H_7D_2^+$	exp.	74.0	21.5	4.4
		stat.[b]	58.1	38.9	2.9
(**2b**)	$C_7H_4D_5^+$	exp.	35.9	55.2	8.8
		stat.[b]	16.7	55.6	27.8
(**2c**)	$C_7H_6D_3^+$	exp.	24.3	69.4	6.3
		stat.[b]	41.5	50.0	8.5

[a] Σ%. [b] Calculated for scrambling of all H and D atoms.

However, the methyl hydrogen atoms are involved only partially in the exchange with those at the benzenium ring. This follows from the loss of D_2 from (**2a** and **b**) and, in particular, from the loss of H_2 from ions (**2c**). Since the latter reaction should be favoured by an isotope effect but, nevertheless, falls short of the value expected for randomization the methyl group preserves its entity to a considerable extent. Thus, in contrast to $C_6H_7^+$ ions, $C_7H_9^+$ ions do not equilibrate all of their protons prior to elimination of H_2 within *ca.* 10 μs.

Elimination of Methane from Labelled $C_7H_9^+$ *Ions.*—The relative amounts of methane isotopomers eliminated from deuterium labelled ions (**2a**—**c**) and from the ^{13}C labelled ions (**2d**), generated from acids (**4a**—**d**) (Scheme 1), are given in Table 2. The elimination of methane from ions (**2**) occurs neither by specific loss of the elements of the original methyl group nor by randomization of all the hydrogen and carbon atoms. As can be seen qualitatively from Table 2, the methane isotopomer eliminated with greatest abundance reflects the original position of the label in each case, but all the possible isotopomers are formed.

Quantitative inspection of the data reveals a complicated situation. The elimination of methane occurs *via* two main pathways: (i) randomization of all the hydrogen and carbon atoms prior to fragmentation and (ii) specific loss of the original methyl carbon atom preceded by partial hydrogen exchange between the methyl group and the benzenium ring. From the fact that 34.6% $^{13}CH_4$ is expelled from ions (**2d**) we assume that (7/6) × (34.6) = 40.4% of the ions have passed through the

Table 2. Loss of methane isotopomers[a] from $C_7(H,D)_9^+$ ions in the second field-free region (MIKE spectra)

Ion			$-CH_4$	$-CH_3D$	$-CH_2D_2$	$-CHD_3$	$-CD_4$
(**2a**)	$C_7H_7D_2^+$	exp.	45.7	45.7	8.6		
		stat.[b]	27.8	55.6	16.6		
(**2b**)	$C_7H_4D_5^+$	exp.	6.1	40.8	36.7	14.3	2.0
		stat.[b]	0.8	15.8	47.8	31.6	3.8
(**2c**)	$C_7H_6D_3^+$	exp.	4.9	21.9	32.5	40.6	
		stat.[b]	11.9	47.6	35.7	4.8	
			$-CH_4$	$-^{13}CH_4$			
(**2d**)	$^{13}C^{12}C_6H_9^+$	exp.	34.6	65.4			
		stat.[c]	85.7	14.3			

[a] Σ%. [b] Calculated for scrambling of all H and D atoms. [c] Calculated for scrambling of all C atoms.

Table 3. Loss of methane isotopomers as a combination of random and specific elimination from labelled $C_7H_9^+$ ions

(**2d**) $C_6H_6{}^{13}CH_3^+$	$-CH_4$	$-^{13}CH_4$	Σ
Experimental	34.6	65.4	100.0
i calculated for randomization of all C (and H) atoms	34.6[a]	5.8[a]	40.4
ii calculated for specific loss of C^{methyl} with partial H exchange		59.6	59.6

(**2c**) $C_6H_6CD_3^+$	$-CH_4$	$-CH_3D$	$-CH_2D_2$	$-CHD_3$	Σ
Experimental	*4.9*	*21.9*	32.5	40.6	100.0
i[b]	*4.8*	*19.2*	14.4	1.9	40.3
ii[e]	0.1	2.7	18.1	38.7	59.6

(**2b**) $C_6HD_5CH_3^+$	$-CH_4$	$-CH_3D$	$-CH_2D_2$	$-CHD_3$	$-CD_4$	Σ
Experimental	6.1	40.8	36.7	*14.3*	*2.0*	100.0
i[c]	0.3	6.4	19.3	*12.8*	*1.5*	40.3
ii[e]	5.8	34.4	17.4	1.5	0.5	59.6

(**2a**) $C_6H_4D_2CH_3^+$	$-CH_4$	$-CH_3D$	$-CH_2D_2$	Σ
Experimental	45.7	45.7	*8.6*	100.0
i[d]	11.2	22.5	*6.7*	40.4
ii[e]	34.5	23.2	1.9	59.6

[a] 6/7 and 1/7, respectively. [b–d] Calculated as a 40.4% fraction of the statistical distribution for (**2c**, **b**, and **a**), respectively, in Table 2. [e] Calculated differences of values in entries Experimental and i.

dihydrotropylium ion structure (**5**) which has been suggested to be an intermediate for the loss of H_2 from ions (**2**).

Because of the considerable energy requirements of the elimination of methane it is reasonable to assume a fast equilibration of the nine hydrogen atoms in (**5**) rendering all carbon atoms equivalent, too. By re-contracting the seven-membered ring a 40.4% fraction of ions (**2**) is produced with randomization of all the carbon and hydrogen atoms which are expelled, in the case of (**2a**—**c**), as $C(H,D)_4$ with statistical distributions. The calculated fractions are given in Table 3 (entries i). Indeed, the experimental portions for loss of CH_4 and CH_3D from ions (**2c**) and for loss of CD_4 and CHD_3 from (**2b**) (italic numbers in Table 3) agree well with those expected from this conception. Accordingly, loss of CH_2D_2 from ions (**2a**) is found to be close to the calculated value.

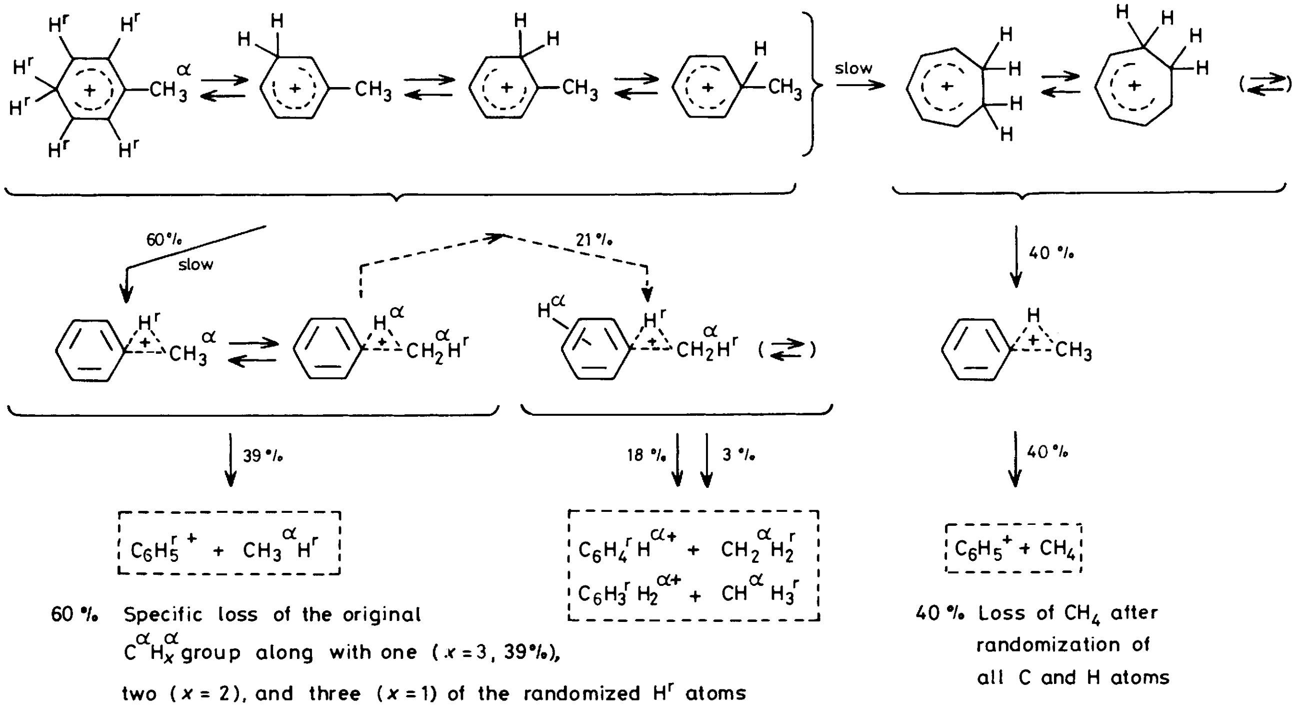
59.6% of methane eliminated contains the carbon atom of the original methyl group but, as can be seen from Table 3 (entries ii), *more* than one H (or D) atom from the benzenium ring is incorporated on the average. Only two thirds of this fraction [38.7/59.6 for (**2c**) and roughly (5.8 + 34.4)/59.6 for (**2b**)] contain the three original hydrogen atoms of the methyl group and one hydrogen atom from the ring. Roughly three-tenths [(**2c**): 18.1/59.6 = 0.30] of the $C(H,D)_4$ fraction are expelled after one interchange of H(D) atoms between the ring and the methyl group; one-tenth is lost after even two or more such interchanges. A closer inspection of the values (entries ii) corroborates this picture since it is consistent for all the three isotopomers (**2a**—**c**).

On the basis of these results, we can formulate the various isomerization pathways preceding the elimination of methane from $C_7H_9^+$ (**2**) as shown in Scheme 5.

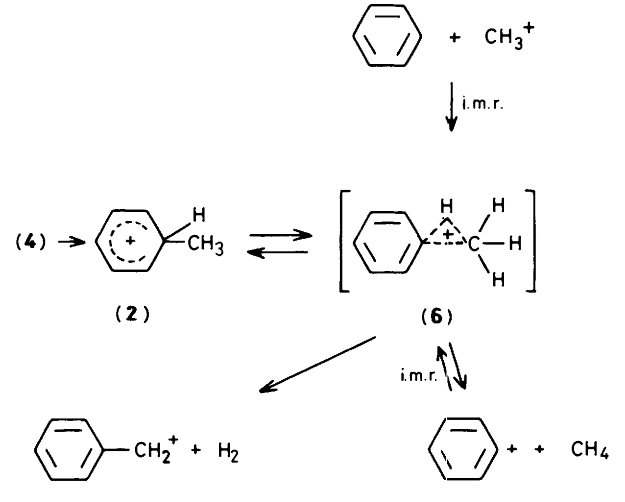
Isomerization of $C_7H_9^+$ *Ions*.—It follows from the results presented here that gaseous $C_7H_9^+$ ions exhibit a complex unimolecular reactivity. Due to the high energy barriers towards fragmentation (Figure 3), there are several isomerization channels, as shown in Scheme 5. It is of particular interest to note that $C_7H_9^+$ ions investigated here retain in part the toluenium ion structure and reactivity but, on the other hand, undergo ring expansion and re-contraction to a considerable extent. Thus, the reactivity of gaseous $C_7H_9^+$ ions corresponds to that of a protonated arene but also resembles the well known isomerization behaviour of $C_7H_7^+$ and $C_7H_8^{+\bullet}$ ions.[21]

The major part of metastable $C_7H_9^+$ ions (*ca.* 60%) eliminate methane without prior ring expansion and re-contraction. We assume that protonolysis occurs *via* a phenylmethonium ion (**6**) formed by protonation of the C^{ipso}–C^{α} bond. Ion (**6**) represents the simplest of the penta-co-ordinate carbonium ions postulated by Olah and his co-workers[2d] to be intermediates in the isomerization and dealkylation reactions of higher alkylbenzenes in superacidic media.[20] A slow interchange between the *four* protons at C^{α} and those at the phenyl 'substituent', as observed for isotopomers (**2**), seems to be reasonable.

From the present results it has to be assumed that elimination of hydrogen, likewise, occurs *via* the (*ipso*-)toluenium and the phenylmethonium ion (**6**), not (or not only) from the



Scheme 5.



Scheme 6. i.m.r. = ion–molecule reaction

dihydrotropylium ion (5), as postulated by Williams and Hvistendahl.[13] However, there is no compelling evidence available strictly to exclude the latter pathway.

It is striking that two mechanisms, a randomizing (i) and a specific one (ii), compete in the $C_7H_9^+$ system. Although a detailed insight into the potential hypersurface is not available the results suggest a particularly high barrier of the skeletal isomerization (2)⟶(5). This subject will be a matter for further investigation. Since the phenylmethonium ion (6) represents one of the possible $C_7H_9^+$ intermediates generated by bimolecular reactions (4)[9b,c] and (5)[10] (Schemes 4 and 6) their fragmentation behaviour seems worth comparing with that of the $C_7H_9^+$ ions formed by unimolecular dissociation from ionized acids (4) (Table 4). The distributions of $(H,D)_2$ eliminated from deuteriated $[C_6H_6{\cdot}CH_3^+]^*$ adducts formed in an ion cyclotron resonance spectrometer[9b] and in a triple-stage quadrupole mass spectrometer[9c] are similar to those reported in the present work and far from being statistical (*cf.* Table 1). However, no conclusion can be drawn concerning the extent of 'isomerization' within the $[C_6H_6{\cdot}CH_3^+]^*$ adduct from these data. In contrast, the distribution of methane isotopomers observed from reaction (5) in the t.s.q. instrument[9c] is strikingly similar to the fragmentation behaviour of comparable ions (2) from the present work (**2c** and **b**), if the contribution from the unscrambled $C_7(H,D)_9^+$ ions (pathway ii) is considered alone (Table 4). In both cases double or multiple H–D exchange prior to elimination of methane are very slow as compared with single exchange. Thus, the adducts $[C_6H_6{\cdot}CH_3^+]^*$ generated by collision in the t.s.q. mass spectrometer do not isomerize to the dihydrotropylium structure (5) but rather react as an interconverting mixture of short lived phenylmethonium (6) and toluenium ions (2) (Scheme 6) with high internal energies (Figure 3).

Experimental

Mass Spectrometry of Dihydrobenzoic Acids.—70 eV Mass spectra were measured at an accelerating voltage of 3 kV, emission current of 300 mA, and ion-source temperature of *ca.* 200 °C on a Varian MAT 311A double-focusing instrument. Samples were introduced to the ion source by a water-cooled inlet probe without external heating. MIKE spectra were measured with a ZAB-2F (Vacuum Generators) double-focusing instrument, the magnet sector preceding the electrostatic sector, at an accelerating voltage of 6 kV, trap current of 200 μA, ion-source temperature of 215 °C, and nominal ion-source pressure of 1×10^{-7} mbar. The samples were introduced *via* the septum inlet system heated to 190 °C.

Contrary to their 1-methyl derivatives (4)—(**4d**) the 1,4-dihydrobenzoic acids (3)—(**3b**) undergo significant dehydrogenation in the inlet system over 1 h. For example, acid (3) was converted into benzoic acid under the above conditions to 50% after 1.5 h. Since mass selection is used to record the MIKE

Table 4. Fragmentation[a] of $C_7H_9{}^+$ species formed by bimolecular and unimolecular reactions

Species	Origin	$-H_2$	$-HD$	$-D_2$	$-CH_4$	$-CH_3D$	$-CH_2D_2$	$-CHD_3$	$-CD_4$
$[C_6H_6{\cdot}CD_3{}^+]^*$	t.s.q.[b]	26.0	55.0	19.0			16.0	84.0	
$[C_6H_6{\cdot}CD_3{}^+]^*$	i.c.r.[c]	13.0	72.0	15.0					
$[C_6H_6{-}CD_3]^+$ (**2c**)	This work[d]	24.3	69.4	6.3	0.2	4.5	30.4	64.9	
$[C_6D_6{\cdot}CH_3{}^+]^*$	t.s.q.[b]	23.0	59.0	18.0		79.0	21.0		
$[C_6HD_5{-}CH_3]^+$ (**2b**)	This work[d]	35.9	55.2	8.8	9.7	57.7	29.2	2.5	0.8
$[C_6D_6{-}CH_3]^+$	This work[e]					65.0	30.0	4.5	~0.5

[a] $\%\Sigma\ (H,D)_2$ and $\%\Sigma\ C(H,D)_4$, respectively. [b] Ref. 9*c*. [c] Ref. 9*b*. [d] From Tables 1 and 3, respectively. For loss of $C(H,D)_4$, data of entries ii in Table 3 are normalized to 100%. [e] Data for this hypothetical ion have been extrapolated from those of (**2b** and **c**).

spectra, however, the main consequence of the dehydrogenation reaction is loss of ion intensity during the measurements.

MIKE spectra were measured in at least five consecutive runs for each of two different days. The inaccuracy of the relative abundances is estimated to be $< \pm 10\%$. Low relative abundances of $C_7(H,D)_7{}^+$ ions formed by reaction (2) (Scheme 3) are somewhat less accurate ($< \pm 20\%$) because of overlapping of an artefact peak and/or the influence of the main beam noise. Kinetic energy release values measured at half-height of the peak and corrected for the width of the main beam signal. The difference of appearance energies of ions $C_7H_7{}^+$ and $C_6H_5{}^+$ formed from metastable $C_7H_9{}^+$ ions (**2**) (fragmenting in the second field-free region of the ZAB-2F instrument) was measured according to the procedure given in ref. 19 and represents the average of eight runs.

Materials.—1,4-Dihydrobenzoic acid (**3**) and 1-methyl-1,4-dihydrobenzoic acid (**4**) and their labelled analogues were obtained by reduction of the corresponding benzoic acid with lithium in liquid ammonia and quenching with either ammonium chloride or (labelled) methyl iodide, according to procedures given in the literature.[14] The purity of the dihydrobenzoic acids was monitored by thin-layer chromatography (Kieselgel-60, Merck, ethanol as eluant), i.r. (Perkin-Elmer 377), and n.m.r. (Bruker WP 80) spectroscopy, and by mass spectrometry (Varian MAT 311A).

Labelled 1,4-*Dihydrobenzoic Acids* (**3a**) *and* (**3b**).—Benzoic acid, 3,5-dideuteriobenzoic acid (2.0 g, 16 mmol) or, respectively, 2,3,4,5,6-pentadeuteriobenzoic acid (Merck, 99% isotopic purity) was dissolved in liquid ammonia (200 ml) at *ca.* −50 °C under nitrogen. Lithium (*ca.* 0.29 g, 47 matom) was added slowly in small pieces with continuous stirring until the deep blue colour of the solution just persisted. Subsequently, ammonium chloride (1.4 g, 25 mmol) was added slowly, decolourizing the mixture completely, and stirring was continued for 30 min. The mixture was then allowed to warm up and the ammonia was evaporated by a slow stream of nitrogen overnight.

The residue was dissolved in degassed water (100 ml), acidified with dilute sulphuric acid to pH 2—3, and extracted twice with degassed methylene dichloride (50 ml) under nitrogen. After drying ($MgSO_4$), the solvent was evaporated and the residue distilled by bulb-to-bulb distillation *in vacuo*, yielding 1,4-*dihydrobenzoic acid* (**3**) (95%), b.p. 91 °C at 0.25 mbar; δ_H (80 MHz; $CDCl_3$) 2.70 (2 H, d, ^5J 8.5 Hz, 4-CH_2), 3.80 (1 H, t, ^5J 8.5 Hz, 1-H), 5.90 (4 H, m, 2-, 3-, 5-, and 6-H), and 11.1 (1 H, br s, CO_2H); *m/z* (70 eV) 124 ($M^{+\bullet}$, 11%), 79 (100, $M^{+\bullet} - CO_2H$), 78 (30), and 77 (67). Using 3,5-dideuteriobenzoic acid as an educt, 3,5-*dideuterio*-1,4-*dihydrobenzoic acid* (**3a**) was obtained (1.9 g, 97%), b.p. 92 °C at 0.25 mbar; δ_H (80 MHz; $CDCl_3$) 2.70 (2 H, dt, ^5J 8.5 and ^4J 2.0 Hz, 4-CH_2), 3.78 (1 H, tt, ^5J 8.5 and ^3J 3.4 Hz, 1-H), 5.82br (2.057 H, s, 2- and 6-H plus residual 3- and 5-H), and 10.07br (1 H s, CO_2H); *m/z* (70 eV) 126 ($M^{+\bullet}$, 10%), 81 (100, $M^{+\bullet} - CO_2H$), 80 (30), 79 (45), and 78 (27). Alternatively, 2,3,4,5,6-pentadeuterio-1,4-dihydrobenzoic acid (**3b**)[22] was obtained (94%), b.p. 91 °C at 0.25 mbar; δ_H (80 MHz; $CDCl_3$) 2.65 (2 H, dt ^5J *ca.* 8.8 and $^2J_{HD}$ *ca.* 3.3 Hz, 4-H), 3.77 (2 H, d, ^5J 8.4 Hz, 1-H), *ca.* 5.9br (0.062 H, s, residual 2-, 3-, 5-, and 6-H), and 11.64br (1 H, s, CO_2H); *m/z* (70 eV) 129 ($M^{+\bullet}$, 10%), 84 (100, $M^{+\bullet} - CO_2H$), 83 (24), 82 (22), 81 (43), 80 (28), 79 (12), 78 (5), and 77 (5). According to the n.m.r. spectra, (**3a**) contained 3.5% of 3,5-dideuteriobenzoic acid whereas no 2,3,5,6-tetradeuteriobenzoic acid was indicated in the case of (**3b**). Therefore, (**3b**) is estimated to contain 3% of 2,3,4,5,6-pentadeuteriobenzoic acid at the most. Since some dehydrogenation occured in the inlet of the mass spectrometer, the benzoic acids mentioned above were found in both cases: *m/z* 124 [60% relative to *m/z* 126 ($M^{+\bullet}$) of (**3a**)] and 126 and 127 [23 and *ca.* 35% relative to *m/z* 129 ($M^{+\bullet}$) of (**3b**)]. The isotopic purity of (**3a** and **b**) was determined by n.m.r. to be 97.1 and 99.2%, respectively.

1-Methyl-1,4-dihydrobenzoic acids (**4**)—(**4d**) were obtained by adding methyl iodide, trideuteriomethyl iodide, and [^{13}C]methyl iodide, respectively, to the reaction mixtures containing the corresponding benzoic acids instead of ammonium chloride. A 1.5-fold molar excess was necessary to decolourize the solution completely. Ammonia was evaporated, the residue was dissolved in water and washed once with methylene dichloride to remove excess of methyl iodide.

Subsequently, the aqueous phase was acidified with dilute sulphuric acid and extracted thrice with methylene dichloride. The combined extracts are washed with 10% aqueous sodium thiosulphate. After drying ($MgSO_4$), the solvent was evaporated, and the residue was purified by bulb-to-bulb distillation *in vacuo* yielding 1-*methyl*-1,4-*dihydrobenzoic acid* (**4**) (90%), b.p. 85 °C at 0.017 mbar; δ_H (80 MHz; $CDCl_3$) 1.38 (3 H, s, 1-Me), 2.68 (2 H, m, 4-CH_2), 5.83 (4 H, m, 2-, 3-, 5-, and 6-H), and 11.0br (1 H, s, CO_2H); *m/z* (70 eV) 138 ($M^{+\bullet}$, 16%), 93 (100, $M^{+\bullet} - CO_2H$), 92 (7), 91 (36), 79 (9), 78 (7), and 77 (47). Using 3,5-dideuteriobenzoic acid, 3,5-*dideuterio*-1,4-*dihydro*-1-*methylbenzoic acid* (**4a**) was obtained (89%), b.p. 85 °C at 0.02 mbar; δ_H (80 MHz; $CDCl_3$) 1.38 (3 H, s, 1-Me), 2.67 (2 H, t, ^4J 2.1 Hz, 4-CH_2), 5.83br (2.09 H, s, 2- and 6-H plus residual 3- and 5-H), and 11.13br (1 H, s, CO_2H); *m/z* (70 eV) 140 ($M^{+\bullet}$, 7%), 95 (100, $M^{+\bullet} - CO_2H$), 94 (13), 93 (40), 92 (16), 91 (2), 81 (12), 80 (9), 79 (36), 78 (22), and 77 (4). In the same manner, 2,3,4,5,6-*pentadeuterio*-1,4-*dihydro*-1-*methylbenzoic acid* (**4b**) was obtained (91%), b.p. 86 °C at 0.02 mbar; δ_H (80 MHz; $CDCl_3$) 1.35 (3 H, s, 1-Me), 2.55—2.75 (1 H, m, 4-H), 5.83br (0.03 H, s, residual 2-, 3-, 5-, and 6-H), and 10.62br (1 H, s, CO_2H); *m/z* (70 eV) 143 ($M^{+\bullet}$, 4%), 98 (100, $M^{+\bullet} - CO_2H$), 97 (15), 96 (10), 95 (16), 94 (5), 84 (5), 83 (4), 82 (8), 81 (24), 80 (13), and 79 (4). Using trideuteriomethyl iodide (Merck, >99% isotopic purity), 1-*trideuteriomethyl*-1,4-*dihydrobenzoic acid* (**4c**) was obtained (85%), b.p. 85 °C at 0.02 mbar; δ_H (80 MHz; $CDCl_3$) 2.67 (2 H, m, 4-CH_2), 5.82 (4 H, s, 2-, 3-, 5-, and 6-H, and 11.55br (1 H, s, CO_2H); *m/z* (70 eV) 141 ($M^{+\cdot}$, 5%), 96 (100, $M^{+\cdot} - CO_2H$), 95 (13), 94 (18), 93 (23), 92 (4), 81 (2), 80 (4), 79 (18), 78 (16), and 77 (47). [^{13}C]Methyl iodide (Merck, Sharp and Dohme; 90% isotopic purity) was used to synthesize 1-([^{13}C]*methyl*)-1,4-*dihydrobenzoic acid* (**4d**) (84%). b.p. 84 °C at 0.015 mbar; δ_H (80 MHz; $CDCl_3$) 1.38 (3 H, 90.3% d, $^1J_{HC}$ 130.5 Hz, 9.7% s, 1-Me), 2.68 (2 H, m, 4-CH_2), 5.84br (4 H, s, 2-, 3-, 5-, and 6-H), and 11.09br (1 H, s, CO_2H); *m/z* (70 eV) 139 ($M^{+\cdot}$, 9%), 94 (100, $M^{+\cdot} - CO_2H$), 93 (16), 92 (46), 79 (12), 78 (16), and 77 (64). The isotopic purity of the isotopomers was determined by n.m.r. and mass spectrometry to be 95% (**4a**), > 98% (**4b**), >99% (**4c**), 90.3% (**4d**).

No conclusive evidence concerning the stereoisomers of 1-methyl-1,4-dihydrobenzoic acids was provided from the n.m.r. spectra (*cf.* ref. 22). However, varying amounts (up to 15%) of labelled 1-methyl-1,2-dihydrobenzoic acids were generated during the synthetic procedure. As a control experiment, (**4**) was converted into 1-methyl-1,2-dihydrobenzoic acid (**5**) by heating a solution of (**4**) in 10% aqueous potassium hydroxide. After working up in the usual manner, (**5**) (97%), b.p. 96 °C at 0.02 mbar, was subjected to spectroscopic analysis, showing exactly the same mass spectrometric fragmentation behaviour as for (**4**): *m/z* (70 eV) 138 ($M^{+\cdot}$, 16%), 93 (100, $M^{+\cdot} - CO_2H$), 92 (7), 91 (36), 79 (9), 78 (7), and 77 (47). The same holds for the MIKE spectra of (**5**) and (**4**). For (**5**), δ_H (80 MHz; $CDCl_3$) 1.32 (3 H, s, 1-Me), 2.27, 2.79 (2 H, AB, ^2J 18.0 Hz, A resonance d, *J* 4.0 Hz, B resonance m; 2-CH_2), 5.9 (4 H, m, 3-, 4-, 5-, and 6-H), and 11.3br (1 H, s, CO_2H).[23]

Synthesis of 3,5-*Dideuteriobenzoic Acid*.—4-Bromoaniline (25 g, 0.12 mol), deuterium oxide (30 g, 1.5 mol), and 35% deuterium chloride (8 g) were placed in an oven-dried 100 ml bulb. The loosely stoppered bulb was heated to 100 °C with stirring, then stoppered tightly, and kept at this temperature with vigorous stirring for 24 h. After cooling the solvent was evaporated carefully, and the exchange procedure was repeated twice. 3,5,NNN-*Pentadeuterio*-4-*bromoanilinium chloride* was obtained as a quite pure (by t.l.c.) bluish solid (23.7 g, 95%). The salt is dissolved in some water, the solution is neutralized with saturated aqueous $NaHCO_3$, and extracted with methylene dichloride. After drying ($MgSO_4$) and evaporation of the solvent, 3,5-*dideuterio*-4-*bromoaniline* was obtained (22.5 g, 90%), m.p. 62—63 °C; δ_H (80 MHz; $CDCl_3$) 3.65br (2 H, s, NH_2) and 7.22 (2 H, s, 3- and 5-H); *m/z* (70 eV) 173/175 ($M^{+\cdot}$, 100/99), 172 (3.2), 94 (48, $M^{+\cdot}$ – Br), 67 (74), and 66 (34); the isotopic purity (by mass spectrometry) was 98.4%. 60% Aqueous hypophosphoric acid (28 g, 0.17 mol) was refluxed with 3,5-dideuterio-4-bromoaniline for 5 min. After cooling to –10 °C sodium nitrite (4.3 g, 62 mmol) was added very slowly to the stirred solution, the reaction temperature being kept within –5 to 0 °C, and stirring was continued at 0 °C for 3 h. The mixture was poured on ice and extracted with methylene dichloride. After drying ($MgSO_4$) and evaporation of the solvent the residue was distilled through a short Vigreux column, yielding pure 3,5-*dideuteriobromobenzene* (7.2 g, 80%), b.p. 51 °C at 27 mbar. This compound was treated with magnesium and solid carbon dioxide in the usual manner to give 3,5-dideuteriobenzoic acid (5.6 g, 84%), m.p. 123 °C; δ_H (80 MHz; $CDCl_3$) 6.35br (1 H, s, CO_2H), 7.64br (1 H, s, 4-H), and 8.15br (2 H, s, 2- and 6-H); *m/z* (70 eV) 124 ($M^{+\cdot}$, 92%), 107 (100, $M^{+\cdot}$ – OH), and 79 (89, $M^{+\cdot} - CO_2H$); isotopic purity (by mass spectrometry) 98.5%.

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