Structure Determination of Ions Formed by the Decomposition of Metastable Ions. $C_8H_9^+$ Ions from *p*-Bromoethylbenzene[1]

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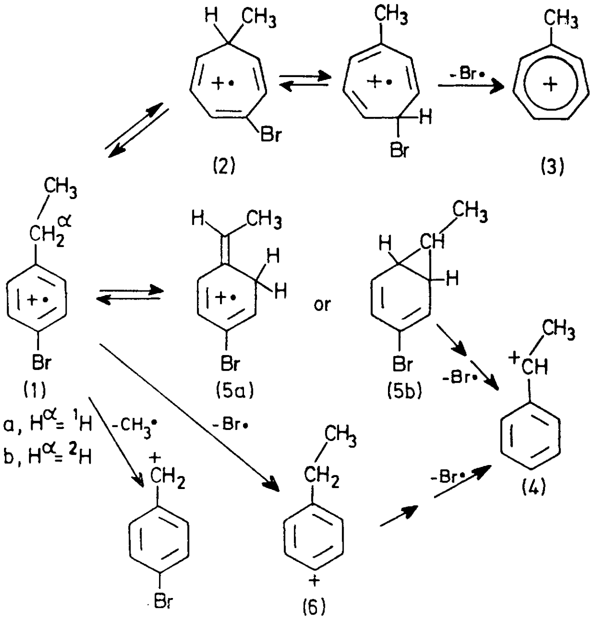
Summary Collisional activation spectra are useful for structure determination of ions produced by metastable decomposition, showing that only half of the $C_8H_9^+$ ions from *p*-bromoethylbenzene have the methyltropylium structure, contrary to previous conclusions.

A well known source of ambiguity in the study of unimolecular decompositions of gaseous organic ions is the possibility of competing rearrangement reactions of the precursor ion, so that an observed decomposition product can actually originate from an isomeric precursor. Because such rearrangement reactions are relatively more competitive for precursor ions of lower energy, the extent of rearrangement is maximized for metastable ions undergoing decomposition.[2,3] For studies involving the latter an isotope effect method recently proposed by Howe and Williams[4] appears to offer unique advantages. For example,[5] for *p*-bromoethylbenzene (**1**) there is a deuterium isotope effect reducing the loss of Br *vs.* that of CH_3 when comparing the behaviour of (**1b**) and (**1a**) (see Scheme). This was explained[5] as arising from the hydrogen migration (**1**) → (**2**) accompanying ring expansion which precedes the loss of Br to form the methyltropylium ion (**3**). There is ample precedent for this rearrangement,[5,6] and it is supported by the reduction in $[M^+ - \text{Br}]/[M^+ - CH_3]$ observed in the normal mass spectrum with reduction in ionizing electron energy.[5]

However, in a separate study[7] we have found that $C_8H_9^+$ ions formed in the ion source from 7-methylcycloheptatriene, which have the structure (**3**), show a characteristic metastable ion (M.I.) decomposition for loss of methyl, m^* ($105^+ \rightarrow 90^+$); this is *not* observable for $C_8H_9^+$ ions formed from (**1**) in the ion source. Further, the latter $C_8H_9^+$ ions yield a collisional activation (C.A.) spectrum[1,7–9] which is consistent only with the presence of ethylphenyl (**5**) and α-phenylethyl (**4**) ions (their C.A. spectra are closely similar)[7] even at low electron energies. As a possible explanation, the observed[5] isotope effect could have been caused instead by a molecular ion isomerization that does not involve ring expansion through intermediates such as (**5a**) or (**5b**), for which there is also precedent.[6]

As an approach to such problems, we report here that

C.A. spectra can also be employed to characterize the structures of ions produced from metastable ions. In this case $C_8H_9^+$ ions formed thus from (**1**) in the first field-free region of a reversed-geometry double-focussing mass spectrometer[9] are allowed to pass through the magnetic field by adjusting it to a value corresponding to *m/e* = $(105)^2/184$. The separated ions then undergo collision with helium, and the resulting C.A. spectrum is determined in the usual manner.[9] Reference C.A. spectra of (**3**) and (**4**) ions† were determined using an ion accelerating potential of 105/184 of the normal (7·8 kV) value to make the ion kinetic energies equivalent to those formed by the decomposition of metastable ions of (**1**). In the C.A. spectrum of such ions from (**1**) the *m/e* 51 abundance shows that 50 $\pm 15\%$ of these $C_8H_9^+$ ions have the (**3**) structure; the balance presumably are (**4**) and (**6**), although these C.A. data do not exclude the possibility of other isomers. The C.A. *m/e* 90 peak abundance, which should be affected by ion internal energy, is equivalent to 13 ± 7% of (**3**) in the reference spectrum. Further, the M.I. spectrum‡ of the $C_8H_9^+$ ions produced in this manner from (**1**) shows the *m/e* 90 peak uniquely characteristic of the ring-expanded isomer (**3**), with the peak abundance equivalent to 4 ± 2% of (**3**) in the reference M.I. spectrum. Because the ions of the reference spectra are of higher average internal energy, the C.A. and M.I. *m/e* 90 abundances indicate the actual proportion of (**3**) ions to be $>13\%$ and $>>4\%$.[3,10]§ Thus the isotope effect method has correctly predicted one of the major pathways for $C_8H_9^+$ formation from (**1**) by decomposition of metastable ions, but the qualitative nature of its predictive capabilities should be noted.



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† $C_8H_9^+$ ions formed in the ion source from *p*-xylene (low electron energy) for (**3**) and from (**1**) for (**4**) (ref. 7).

‡ The ionic products of metastable decompositions occurring between the magnetic and the electrostatic analyser, measured in the same way as the C.A. spectrum (ref. 9).

§ The reference M.I. spectrum of (**3**) formed in the ion source at 70 eV shows an *m/e* 90 abundance nearly three times that at 13 eV.

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