ELECTRON-IMPACT-INDUCED REARRANGEMENTS OF ORGANIC IONS

VI*—UNIMOLECULAR REACTIONS OF ISOMERIC [C₈H₉]⁺ IONS

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Abstract—Metastable ion spectra and deuterium labelling have been used to investigate a series of gaseous $[C_{a}H_{a}]^{+}$ ions of isomeric structures. The similarity of the intensities of their metastable loss of hydrogen, acetylene and ethylene molecules and metastable reactions of specifically labelled ions, suggests that the $[C_{a}H_{a}]^{+}$ reacting ions, formed initially with different structures, isomerise to a common structure or mixture of structures via deep-seated rearrangement reactions which render all hydrogen atoms equivalent. The isomerisation process involved is controlled by a conversion of a vinyl bond into an allyl-type bond, thus destroying the aromatic moiety.

ISOMERISATION processes of gaseous cations appear to be reactions commonly encountered in organic mass spectrometry. In particular, aromatic compounds decompose on electron-impact to yield ions which undergo extensive rearrangement prior to fragmentation processes. Hydrogen migrations have been shown to occur with or without competing skeletal reorganisation of several aromatic ions.² Carbon atoms may be involved in randomisation reactions.^{2.3} Several aliphatic ions undergo hydrogen and/or carbon scrambling prior to or concurrent with the elimination of neutral molecules; thus the mass spectra of isomeric compounds may show close similarities.

Different functional groups have shown marked ability to influence fragmentation reactions in aliphatic chains⁴ and therefore have a profound effect on the appearance of the mass spectra. Similar effects on isomerisation processes have been observed when simple functional groups are introduced into aliphatic or aromatic compounds. The presence of a hetero atom reduces hydrogen scrambling and rearrangement reactions in oxonium⁵ and immonium^{1.6} ions. Randomisation of hydrogen atoms occurs in various analogues of benzene, but is restricted in polysubstituted $[C_9H_{11}]^+$ benzenoid ions⁷ and does not take place in *p*-chloroaniline molecular ions prior to HNC elimination.⁸

In agreement with these data and results, the above observations may be interpreted on the basis that the functional group induces specific fragmentation reactions with lower activation energies than those of the isomerisation processes which therefore cannot compete so effectively; thus, specific decomposition⁹ and retention of structure^{1.6} might be a direct consequence of the presence of appropriate groups, as found in the similar behaviour of ionic species in condensed phase.

Correlation of similar decomposition pathways from homologous ions may facilitate the understanding of unimolecular fragmentation mechanisms of organic ions. A comparison of hydrogen migration and rearrangement to identical structure or mixture of structures in isomeric $[C_8H_9]^+$ (m/e 105) ions with that of homologous ions $[C_9H_{11}]^+$ (m/e 119)⁷ should lead to the interpretation of the mass spectrometric

^{*} For Part 1, see Ref. 1.

behaviour of benzenoid ions and may offer a better insight into the energetics and mechanistic implications of isomerisation reactions.

A discussion of the decomposition path of organic ions requires information on the possible modification of structures of the reacting ions. Metastable ions may be of great utility for the assignment of structural identity or non-identity of gaseous positive ions.^{1,2,5-7,10-14}

The metastable ion technique, 5-7,10-12 dealing with ions which fragment in the mass spectrometer at low internal energy, investigates decomposition pathways of ionic species which are more likely to undergo skeletal reorganisation. However, field ionisation experiments indicate that rearrangement processes, in spite of restrictions due to their entropy requirements occur at a fast rate, e.g. within 10^{-11} s.¹⁵

In addition to the investigation of metastable decomposition of isomeric $[C_8H_9]^+$ ions, specifically labelled systems were also studied in detail in order to elucidate hydrogen rearrangements prior to further fragmentation processes involving the loss of neutral molecules.

Isomeric $[C_8H_9]^+$ ions were chosen to investigate the effect of the aromatic ring in rearrangement processes and decomposition reactions of alkyl substituted aryl cations. Although the formation, together with their decomposition by loss of acetylene,¹⁹ of $[C_8H_9]^+$ ions through aryl participation via an ethylenebenzenium ion structure¹⁶ or classical ion structure, i.e. the β -phenylethyl cation,^{17,18} has received attention recently, competing metastable transitions and possible isomerisation processes from different precursors have not been discussed.

 $[C_8H_9]^+$ (m/e 105) cations of formal structure a to e (Table 1) have been conveniently generated, as indicated in (1), by bromine loss from alkyl substituted benzenes (II to VI) (Table 1), while ions a have also been formed by methyl radical loss by electron-impact on compound I.

$$[C_8H_9 - X]^+ \rightarrow [C_8H_9]^+ + X \quad (X = Br \text{ or } Me)$$
(1)

Ions *a*, *c* and *d* may be assumed to be structurally distinct at the threshold of their formation, since bromine expulsion is a fast process which occurs without interference with the initial molecular ion structure in the case of unimolecular reactions of ionised compounds (II), (IV) and (V), where a benzylic carbon-bromine bond is involved. Evidence from collision-activated spectra for the formation of a single isomeric product have been reported in the case of ion a.¹⁸

The $[C_8H_9]^+$ cations, produced by electron-impact-induced elimination of bromine radical from compound III, may be formed in a mixture of isomers, i.e. ethylenebenzenium ions *a* and *b*, whose composition is dependent on the energy content of the reacting precursors, as indicated by collision activated experiments,¹⁸ or may have partially isomerised prior to collision with the neutral molecule of the target gas.¹

As far as ions of formal structure e are concerned (compound VI $\rightarrow e$), it should be noted that the unimolecular process (1) takes place with a rearrangement to a 7-membered ring system, which precedes bromine elimination and therefore structure e might be considered to be formed initially.²⁰

 $[C_8H_9]^+$ ions of formal structures *a* to *e* have been found to decompose in both first and second drift regions of a double focusing mass spectrometer via three competing unimolecular processes (2) to (4) which involve the elimination of hydrogen, acetylene and ethylene molecules with metastable peaks at m/e 101·3, 41·6 and 39·6,

Table 1. Ratios of competing metastable transitions of some $[C_8H_9]^+$ ions^

]	H ₂	C2	H ₂	C2	H4
	Compound	Ion	¹ m*	² <i>m</i> *	¹ m*	² m*	¹ <i>m</i> *	² m*
(I)		(<i>a</i>)	51	63	47	32	2	5
(II)	Br	(<i>a</i>)	49	60	48	34	3	6
(111)	Br	(b)	42	42	54	53	4	5
(IV)	Br	(c)	54	56	43	42	3	2
(V)	Br	(d)	56	53	41	46	3	1
(VI)	Br	(e)	46	39	50	55	4	6

* The symbols ${}^{1}m^{*}$ and ${}^{2}m^{*}$ refer to measurements in the first and second drift regions, respectively.

respectively. The ratios of metastable ion intensities observed in the first and second drift regions for reactions (2) to (4) occurring from m/e 105 ions of the five nominal structures a to e are reported in Table 1.

$$[C_{8}H_{7}]^{+} + H_{2}$$
(2)
 $\nearrow m/e \ 103$

$$[C_8H_9]^+ \longrightarrow [C_6H_7]^+ + C_2H_2$$

$$m/e \ 105 \longrightarrow m/e \ 79$$
(3)

$$\sum_{\substack{[C_6H_5]^+ + C_2H_4 \\ m/e \ 77}} (4)$$

Independent of the precursor ions, all the $[C_8H_9]^+$ ions studied fragment by two major processes, i.e. loss of H₂ and C₂H₂, appear to proceed at the energies accessible for metastable transitions with similar rate constants, as shown by their intensity ratios which are close to unity. The metastable loss of ethylene is of much lower abundance than for those of hydrogen and acetylene, although these species provide a higher number of degrees of freedom for the partitioning of excess vibrational energy involved in the unimolecular processes.

According to the metastable abundance ratios for all the $[C_8H_9]^+$ cations, listed in Table 1, those initially distinct ions which possess sufficient excitation energy for unimolecular decomposition with rate constants 10^4 to 10^6 s^{-1} , have extensively isomerised to a common structure or mixture of structures prior to fragmentation with loss of 2, 26 and 28 mass units. Differences of intensity ratios are experimentally observed among ions of formal structures *a* to *e*, but these variations are not sufficiently large to allow any clearcut interpretation.^{3,5e}

The isomerisation of ions a and b to a common structure might involve [1,2]hydrogen migration, probably to the most stabilised structure a, in accord with the rearrangement proclivity in solution where formation of β -phenylethyl cations has been shown to occur from compound III.²¹ However, from previous ¹³C labelling studies a partial skeletal reorganisation may be also postulated to be operative in metastable decompositions of [C₈H₉]⁺ ions of formal structure a and b.¹⁹

The close similarity in the abundance ratios of fragmentation reactions from metastable ions a to b and c to d implies a rearrangement, probably via ring expansion to the methyltropylium structure e [see (5)] by insertion of hydrogen and carbon atoms into the aromatic skeleton.

The ring expansion of ions when formed from benzyl-type derivatives and the subsequent decompositions are among the most widely found examples of bond migrations in organic chemistry of condensed and gas phase systems. This type of process has been evidenced in the formation of ions e,²⁰ which show a similar mode of decomposition path to ions a to d.

It must be pointed out that all these isomerisation reactions are expected to involve extensive hydrogen rearrangements prior to fragmentation, with loss of hydrogen, acetylene and ethylene molecules.

To confirm the previous proposal, the metastable spectra of some deuterium labelled compounds which produce specifically labelled analogues of ions a to e have been examined.

Elimination of molecular hydrogen (2) occurs from isomeric $[C_8H_9]^+$ metastable ions in which the hydrogen atoms have lost their positional identity, as is clearly



shown by the data reported in Table 2. Consider the results from ions of formal structure a, produced by decomposition of the ionised compound VII (see Table 2). It is apparent that the statistical ratios 42:50:8 calculated for complete randomisation of the loss of $H_2:HD:D_2$, respectively, are very close to the observed values (Table 2). The preference for H_2 loss may reflect a relatively large kinetic isotope effect discriminating against deuterium elimination. Similar results are observed in relation to hydrogen loss from isomeric ions b to e, formed by bromine radical loss from compounds VIII to XII. In these cases, complete interchange of hydrogen atoms among the carbon atoms should produce a random elimination of $H_2:HD:D_2$ in the ratio 58:39:3, respectively. Preferential H_2 expulsion has also been observed for deuterated analogues of ions b to e, in agreement with the results obtained from the labelled ions a discussed above, and is interpreted in a similar manner with the occurrence of more facile C—H bond breaking in the rate-determining step of the reaction involved, i.e. reaction (2).

The results from labelling experiments for ions of formal structures a to e from compounds VII to XII thus prove that in all cases fragmentation of $[C_8H_9]^+$ cations with loss of molecular hydrogen occurs with extensive scrambling of hydrogen atoms within the carbon skeleton. In fact, the calculated ratios for hydrogen and labelled hydrogen loss involving only the hydrogens of the original alkyl groups for the deuterated ions a and b only would be 50:50 for a and 17:66:17: for b, which are very different from the experimental data (Table 2).

Data for the metastable decompositions of $[C_8(H, D)_9]^+$ ions pertinent to the investigation of acetylene and labelled acetylene losses are given in Table 2. The transitions observed using the refocusing technique in the first drift region of a double focusing mass spectrometer show a random distribution of the eliminated labelled acetylene molecules from each of the $[C_{s}(H, D)_{s}]^{+}$ metastable ions resulting from electron-impact decomposition of compounds VII to XII. The calculated statistical ratios for acetylene loss are the same as that reported above for hydrogen elimination, since in both cases two hydrogen atoms are involved. However, comparison of the data shown in Table 2 with that reported previously,¹⁹ indicates that the distributions of the deuterium label found within the C₈ ions from compounds VII, VIII and IX are similar to those observed in the present study. The above observations suggest that in fact acetylene is lost, involving a process associated with complete hydrogen/ deuterium shift without any isotope effect being observed. This randomisation process could occur in the metastable ions of the benzenoid species prior to fragmentation once they are thought to experience no isotope effect since the ratedetermining step in the decomposition involving acetylene loss is a carbon-carbon

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Compound	Structure	${ m H}_2$	ЦIJ	D_2	$C_{2}H_{2}$	C ₂ HD	$C_2D_2^{th}$	$C_2H_4^{a}$	C_2H_3D	$C_2H_2D_2$	C ₃ HD ₃
(VII) PhCHBrCD ₈	(a) <i>m/e</i> 108	51	43	9	41	52	7	36	36	24	4
(VIII) PhCD _a CH _a Br	(b) <i>m/e</i> 107	68	27	2	50	38	12	53	36	11	
(IX) PhCH ₂ CD ₂ Br	(b) <i>m/e</i> 107	65	31	4	53	38	8	38	46	16	
(X) p-CH ₃ C ₆ H ₄ CD ₂ Br	(c) <i>m</i> / <i>e</i> 107	69	29	7	53	38	6	35	51	14	
(XI) m-CH ₃ C ₆ H ₄ CD ₂ Br	(d) <i>m/e</i> 107	62	34	4	55	37	œ	32	53	15	
(XII) <i>p</i> -CH ₃ CD ₂ C ₆ H ₄ Br	(e) <i>m</i> / <i>e</i> 107	70	27	3	49	38	13	43	36	21	
^a C ₂ D ₂ and C ₈ H ₄ eliminatio	n corresponds to	loss of	28 mass 1	inits and	l overlaps	in the same	e metastabl	e peak. T	his interfere	nce is more i	mportant in

OF SOME DEUTERATED ANALOGUES	
) FOR THE DECOMPOSITION	
(FIRST DRIFT REGION)	а то <i>е</i> ат 70 еV
) FOR SOME METASTABLE TRANSITIONS (US IONS
Table 2. Relative abundance ($\%$	

ethylene loss which is a low abundance process.

bond rupture (vide infra). The amount of loss of 28 mass units from the $[C_8(H, D)_9]^+$ cations is consistent with the overlapping of two distinct processes, i.e. loss of dideuteroacetylene and unlabelled ethylene.

Before detailed analysis of the data shown in Table 2 relative to ethylene expulsion is undertaken, it should be noted that the transitions observed from deuterated *a* to *e* cations suffer from the overlapping discussed above, which interferes to a greater extent in (4) than (3) since the average ratio $\{[C_8H_9 - C_2H_2]^+\}/\{[C_8H_9 - C_2H_4]^+\}$ is 15.

The interpretation of the predominant products in the metastable decomposition to m/e 80 from ions m/e 108 (a) and to ions of m/e 79 from ions m/e 107 (b to e) is therefore extremely facile, thus excluding preferential loss of unlabelled ethylene which would require a noncompetitive transition (4) with the other fragmentations. Considering the conclusion drawn above, the H/D scrambling reaction over the $[C_8(H, D)_9]$ systems must occur with a rate constant higher than hydrogen and acetylene losses in the metastable region. Therefore, a random elimination of ethylene and deuterated ethylene should occur if this reaction competes with the other two observed metastable processes. The data for compounds VII to XII support the above deduction, allowance being made for the concomitant loss of dideuteroacetylene.

All the data seem to be consistent with the $[C_8H_9]^+$ metastable ions reacting from the same structure (or mixture of structures) and involving an extensive randomisation process of the hydrogen atoms. Thus, on the basis of the above argument, a possible mechanism can be suggested for the interconversion of ions *a* and *b* through [1, 2] hydrogen migration, as indicated by (6), in addition to the ring expansion and contraction postulated in (5) to account for the isomerisation of ions *a*, *c*, *d* and *e*.



The information obtained for $[C_8H_9]^+$ cations of formal structures *a* to *e* seems well suited to offer an interesting comparison with the previously reported results concerning the $[C_9H_{11}]^+$ homologues.⁶ In the latter case it was possible to distinguish two groups of ions, i.e. mono- and polysubstituted benzenoid systems, according to their metastable ion spectra and deuterium labelling experiments.⁶

Two different processes involved in the loss of neutral molecules from substituted aromatic cations, i.e. $[C_8H_9]^+$ and $[C_9H_{11}]^+$ ions, have been observed (see above and Ref. 6). In fact, the occurrence of extensive rearrangement prior to unimolecular decomposition in the case of $[C_8H_9]^+$ metastable ions and the partial isomerisation observed without loss of identity of the aromatic moiety for monosubstituted $[C_9H_{11}]^+$ ions,⁷ predict the existence of a crucial step which would account for the complete skeletal reorganisation of some alkyl substituted aryl ions $[C_8H_9]^+$, while others $[C_9H_{11}]^+$ do not isomerise in the same way. In particular, loss of neutral molecules from isomeric $[C_8H_9]^+$ ions requires a more complex pathway than in the case of monosubstituted $[C_9H_{11}]^+$ ions where a mere rearrangement of the alkyl groups takes place, while such a mechanism is precluded even for monosubstituted $[C_8H_9]^+$ ions of formal structures a and b. In accord with previous data,¹⁹ the nature of the decomposition path for ions a and b suggests that while the expulsion of a C₂ fragment from $[C_9H_{11}]^+$ ions may involve the rupture of a type of benzyl bond,²² $[C_8H_9]^+$ ions fragment via a transition state which is characterised by a higher energy barrier, i.e. a vinyl bond breaking in the case of ethylene loss.



Therefore (7) competes more effectively than ethylene loss, although requiring a larger hydrogen migration which converts the initial vinyl bond into an allyl structure which requirement may thus account for the extensive randomisation of the hydrogen atoms.

EXPERIMENTAL

All mass spectra were determined on an AEI MS-9 double focusing mass spectrometer with an electron beam energy of 70 eV and a source temperature below 100 °C. Samples were introduced via the heated inlet system at a temperature below 80 °C. Unimolecular metastable transitions in the second drift region were observed at a nominal 8 kV. The first drift region transitions were obtained using the metastable refocusing technique.²³ The n.m.r. spectra were recorded on a Varian EM-360 spectrometer with CDCl₃ as solvent. All final products were purified by preparative v.p.c. or thick-layer chromatography. Unlabelled compounds were either available commercially or synthesised by unexceptional methods.

1-Bromo-1-phenyl-[2,2,2- ${}^{2}H_{3}$]-ethane (VII). Acetophenone (2 mmol) was deuterated by treatment with K₂CO₃ in refluxing D₂O to yield the corresponding deuterated compound (1.7 mmol). The deuterated product (1.0 mmol) in dry ether solution was added with stirring to a slurry of lithium aluminium hydride (1.0 mmol) in dry ether (20 ml). The reaction mixture was heated under reflux for 30 min and the excess hydride was destroyed by adding a saturated solution of ammonium chloride. The product was extracted, dried and the solvent removed. The corresponding bromide was obtained by adding phosphorous tribromide to a petrol (b.p. 40 to 60) solution of the alcohol, obtained from the above procedure, and the reaction mixture was stirred overnight. Water was then added and the petrol solution separated and dried. The product was isolated and purified to yield the expected 1-bromo-1-phenyl-[2,2,2- ${}^{2}H_{3}$]-ethane (70%, [${}^{2}H_{3}$], 96%; [${}^{2}H_{2}$], 3%; [${}^{2}H_{1}$], 1%).

 $C_8H_7D_2Br$ analogues (VII to XI). A general procedure was devised in order to obtain the specifically labelled precursor compounds from methyl esters. A dry ether (5 ml) solution of methyl ester (3 mmol) was added with stirring to a slurry of LiAlD₄ (2 mmol) in dry ether (20 ml). The reaction mixture was heated under reflux for 2 h. The excess aluminium deuteride was destroyed by adding a saturated solution of NH₄Cl. The product was extracted with ether, dried (MgSO₄) and the solvent removed. The corresponding bromide was obtained as described above. On average, 70% yield of the expected [²H₄]-bromoarene was obtained with a deuteration > 98%.

p-Chloro- $[\alpha^2 H_2]$ -ethylbenzene (XII). The procedure previously described²⁰ was followed in order to obtain the product ($[{}^{2}H_{2}], 98\%$; $[{}^{2}H_{1}], 2\%$; 53%).

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