

The Gas-phase Amino–Claisen Rearrangement of Protonated *N*-Allylaniline

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Metastable molecular protonated ions of *N*-allylaniline dissociate with significant losses of ethene and ammonia in the flight path of a mass spectrometer. The structures of the daughter ions formed on the loss of ethene have been elucidated using collision-induced dissociation and it is postulated that two isomeric structures are formed, one corresponding to molecular protonated ions which have undergone an amino–Claisen rearrangement. The relative proportion of this rearranged species is dependent on the exothermicity of the proton-transfer reaction between the sample molecule and the chemical ionization reagent gas ion. It is proposed that the two isomeric parent species differ in the site of protonation.

INTRODUCTION

Recently, we have presented evidence for the occurrence of the amino–Claisen rearrangement in molecular ions of *N*-allylaniline (**1**).¹ Although the reaction makes only a small contribution to the ion source fragmentation pathways, it competes much more effectively when metastable molecular ions of **1** are examined.

The gas-phase Claisen rearrangement of protonated allyl phenyl ether has been examined in detail.² The reaction occurs in both the ion source and flight path and is followed, predominantly, by the loss of ethene and, to a lesser extent, carbon monoxide. This present work with **1**, the nitrogen analogue of allyl phenyl ether, was undertaken to see whether its behaviour under chemical ionization conditions would be similar.

The observation of a weak thermal Claisen rearrangement of **1** in 3-methyl-2-butanol has been reported.³ In the same work, however, it was also reported that the acid-catalysed Claisen rearrangement of **1** ($2N-0.1N$ H_2SO_4 , 145–170°C) proceeds cleanly. The driving force for this acid-catalysed Claisen rearrangement was attributed to the delocalization of the positive charge in the transition state, but solvent effects also seemed to play a role.³

RESULTS AND DISCUSSION

Major peaks in the chemical ionization (CI) mass spectra of **1**, using hydrogen, methane, propane or isobutane as reagent gas, are given in Table 1. The full CI(methane) spectrum of **1** is shown in Fig. 1. The presence of peaks at m/z 134, m/z 133 and m/z 132 show

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three possible forms of ionization occurring. They are, respectively, protonation to form an MH^+ , charge exchange to form an M^{++} , and hydride abstraction to form an $[M - H]^+$. The latter ions may, however, be formed from the M^{++} ions as is observed in the electron ionization (EI) mass spectrum of **1**.

Reaction within the ion source

A significant peak is observed at m/z 106, for propane, methane or hydrogen as reagent gas. These ions could be formed by the loss of ethene from the MH^+ and/or the loss of a vinyl radical from the M^{++} . This latter pathway is already well known from the EI mass spectrum.¹ A high-resolution mass measurement of the m/z 106 ions formed by CI(methane) shows that they are >99% due to $[C_7H_8N]^+$.

The structure of these m/z 106 ions formed in the ion source was investigated using collision-induced dissociation (CID). Figure 2(a) shows the mass-analysed ion kinetic energy (MIKE) spectrum resulting from the collision of the m/z 106 ions (from the source) with nitrogen gas in the third field-free region of our three-sector ZAB-2F mass spectrometer.⁴ Two reference compounds which generated isomeric $[C_7H_8N]^+$ structures in their EI mass spectra were chosen. Figure 2(b) shows the CID/MIKE spectrum of the m/z 106 ions from *N*-ethylaniline which have the anilinomethene structure (a), while Fig. 2(c) shows that of the m/z 106 ions from *o*-toluidine which have the *o*-aminobenzyl structure (b).



It is clear that the structure of the stable m/z 106 ions generated by CI(methane) of **1** is the anilinomethene

Table 1. CI mass spectra of *N*-allylaniline (**1**)

Reagent gas	Proton Affinity ^a	<i>m/z</i>	190	176	162	135	134	133	132	106
C ₄ H ₁₀	823		6	—	—	11	100	13	3	1
C ₃ H ₈	773		—	16	—	18	100	57	11	11
CH ₄	545		—	—	14	12	100	43	13	14
H ₂	421		—	—	—	14	44	100	28	62

^a PA (kJ mol⁻¹) of the conjugate base of the reagent gas ions (from A. G. Harrison, *Chemical Ionization Mass Spectrometry*, CRC Press, Florida (1983)).

structure (**a**). In Fig. 2(a), the increased abundance of the *m/z* 91 fragment when compared with that in Fig. 2(b) suggests that there is a weak contribution from [C₈H₁₀]⁺⁺ ions to the *m/z* 106 ions formed in the ion source.¹ Since the loss of a [CH₂N][•] radical from the MH⁺ ion is of low probability, it can be assumed that the precursor of these [C₈H₁₀]⁺⁺ ions is the molecular ion, M⁺⁺.

The behaviour of the M⁺⁺ ions formed in the CI source appears to be very similar to those M⁺⁺ ions formed in an EI source and which have already been the subject of a detailed study.¹ It seems likely that the *m/z* 106 ions which are present in the CI mass spectra are formed solely from the M⁺⁺ ions at *m/z* 133, predominantly by cleavage and vinyl radical loss, but also by a much lower probability rearrangement reaction which is followed by HCN loss to form [C₈H₁₀]⁺⁺ ions of low abundance.

Reactions along the flight path

The behaviour of the metastable MH⁺ ions of **1** was examined. Figure 3(a) shows the unimolecular MIKE spectrum of metastable MH⁺ ions formed by CI(methane) of **1**. In addition to the peaks shown in this figure, a small peak corresponding to ions of *m/z* 56 is seen. A peak is observed at *m/z* 117, corresponding to the loss of 17 mass units from metastable MH⁺ ions.

No peaks due to consecutive fragmentation processes could be observed for these MH⁺ ions losing 2 mass units and then 15 mass units, or vice versa, when the appropriate dissociations were sought in consecutive field-free regions, so the loss of 17 mass units is deduced to correspond to the loss of ammonia. Loss of this neutral fragment is clear evidence that some of these metastable MH⁺ ions have undergone a skeletal rearrangement.

The peak corresponding to the loss of 28 mass units (*m/z* 106) is seen to be composite in shape (Fig. 4(a)). It is proposed that both of these components result from the loss of ethene, but by two different pathways. Any molecular ions which contain a ¹³C atom and therefore make a contribution to *m/z* 134 cannot make a significant contribution to the *m/z* 106 ions seen in the MIKE spectrum. To do this, these ¹³C molecular ions would have to lose ¹³CCH₃ or HN¹³C. In either case, these ions would have to generate a much larger peak at *m/z* 107 owing to the loss of the unlabelled C₂H₃ or HNC. The absence of significant peak at *m/z* 107 indicates that the contribution of molecular ions with the heavy ¹³C isotope to the MIKE spectrum of Fig. 3(a) is not great. This observation also rules out the likelihood of the *m/z* 117 ions observed above having come solely from ¹³C molecular ions (the loss of NH₃ being an abundant peak¹ in the MIKE spectrum of M⁺⁺ ions of **1**).

Metastable MH⁺ ions, formed by the protonation of **1** by reactions of different exothermicity, were examined. Figure 3(b-d) shows the resulting unimolecular

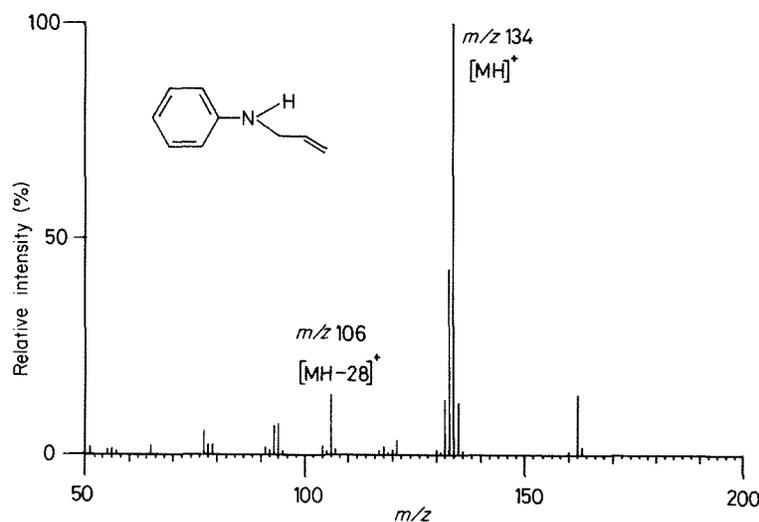


Figure 1. CI(methane) mass spectrum of *N*-allylaniline.

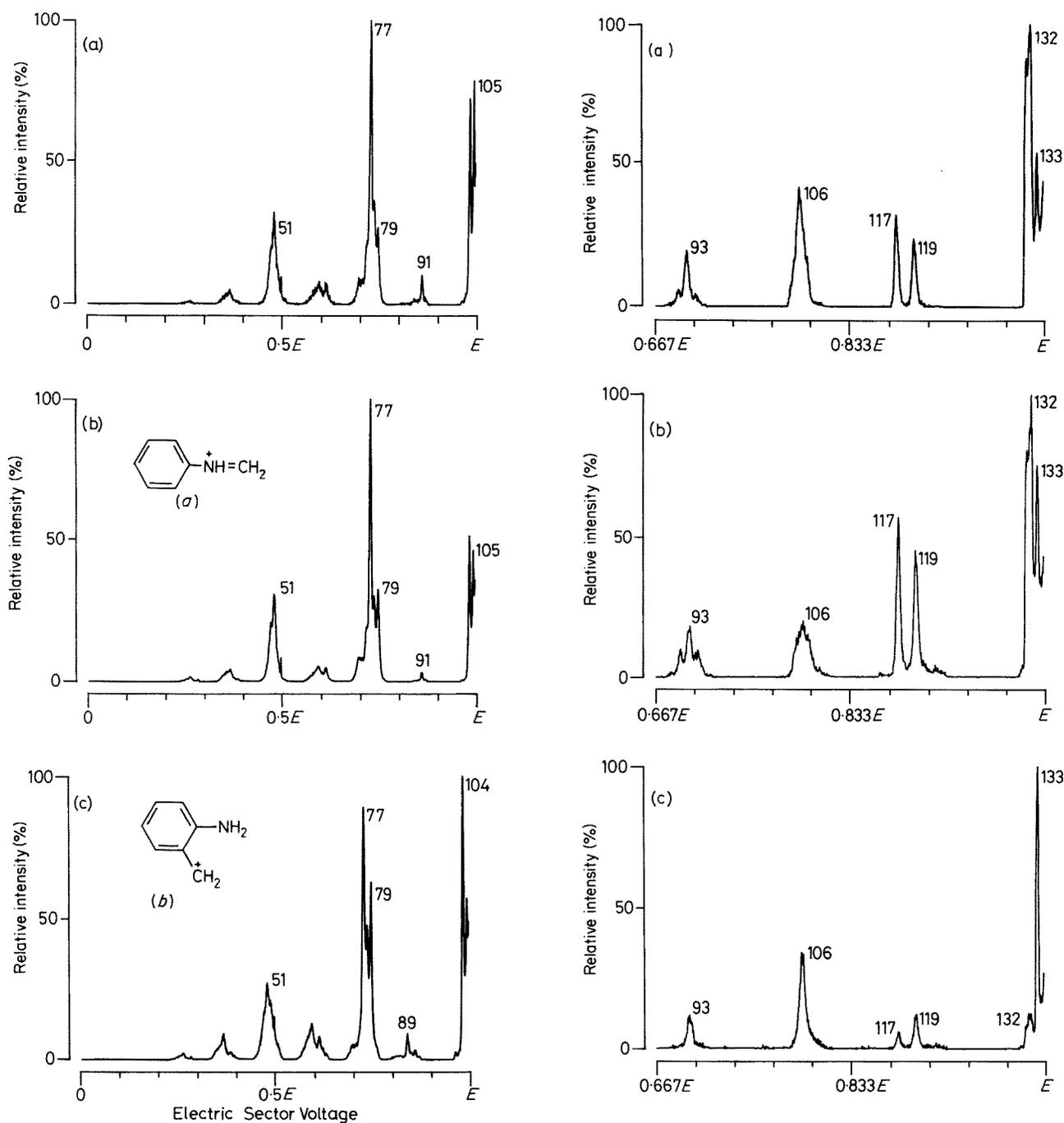


Figure 2. (a) CID/MIKE spectrum of m/z 106 ions from CI (methane) of *N*-allylaniline. (b) CID/MIKE spectrum of m/z 106 ions from EI of *N*-ethylaniline. (c) CID/MIKE spectrum of m/z 106 ions from EI of *o*-toluidine.

MIKE spectra when the CI reagent gas is hydrogen (b), propane (c), or isobutane (d). Details of the peaks corresponding to the m/z 134 \rightarrow m/z 106 transition are seen in Fig. 4(b–d). Table 2 gives kinetic energy release (T) measurements for these peaks. For the metastable peak associated with the loss of ethene (Fig. 4), the composite profile is dependent on the exothermicity of the protonation reaction which is employed to generate the MH^+ ions in the ion source. The broad component is favoured when methane and hydrogen are used as reagent gas (Fig. 4(a) and (b)). These two gases, which have the lowest proton affinities of those gases used, also lead to a relative increase in the abundance of the

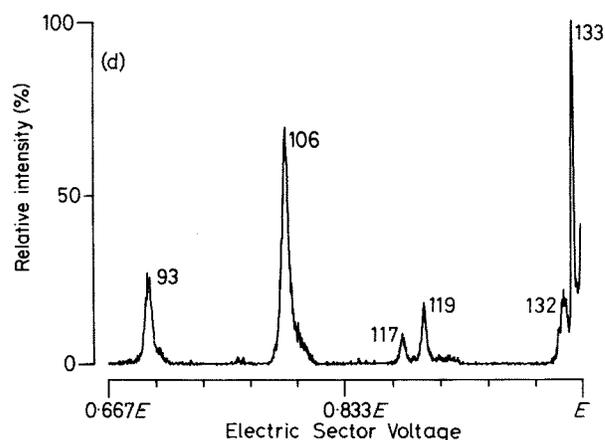


Figure 3. MIKE spectrum of metastable MH^+ ions, m/z 134, generated from *N*-allylaniline with (a) methane, (b) hydrogen, (c) propane or (d) isobutane as reagent gas.

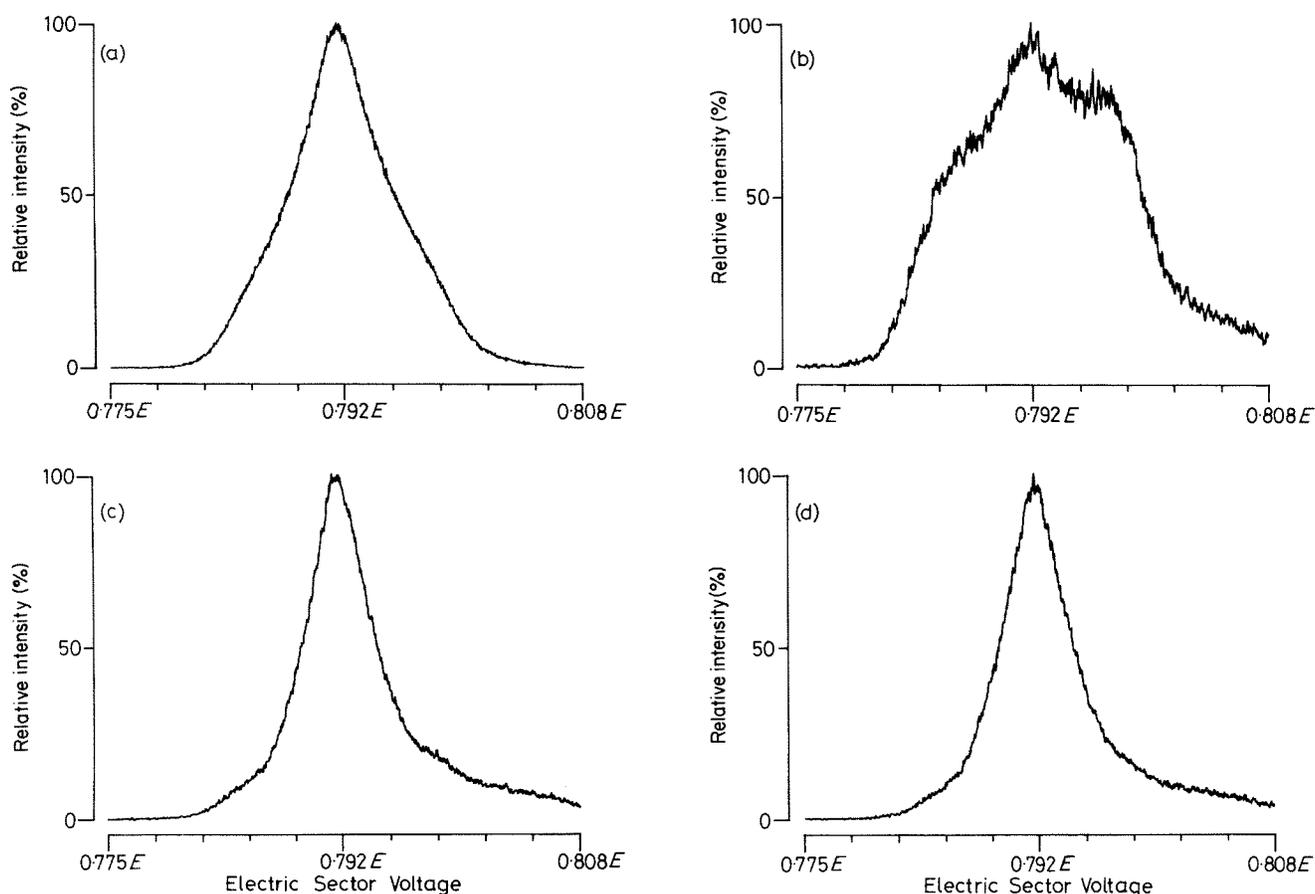


Figure 4. Detail of metastable ion transitions corresponding to m/z 134 \rightarrow m/z 106 (a-d).

daughter ions which contribute to the peak at m/z 117, corresponding to the loss of ammonia (Fig. 3(a) and (b)).

These studies suggest that the protonation of **1** generates two isomeric MH^+ species, both of which eliminate ethene. The isomer which is contributing to the broad component at m/z 106 is also undergoing a competitive reaction to form m/z 117 by the loss of ammonia. It is proposed that this MH^+ isomer undergoes the amino-Claisen rearrangement before fragmentation.

Information of the structure of the m/z 106 ions formed from metastable MH^+ ions of **1** can be obtained by generating the CID/MIKE spectra of these daughter ions in a multi-sector mass spectrometer. Table 3 gives these spectra obtained on a three-sector MS902 mass spectrometer. Owing to low signal intensities in the case of **1** (generated using a CI source), only the most intense peaks have been recorded. The relative abundances of the peaks at m/z 79–77 are similar to those obtained for aminobenzyl ions (b) formed in the field-free region.

Table 2. Kinetic energy release for the loss of ethene from the molecular protonated ions of *N*-allylaniline (**1**)

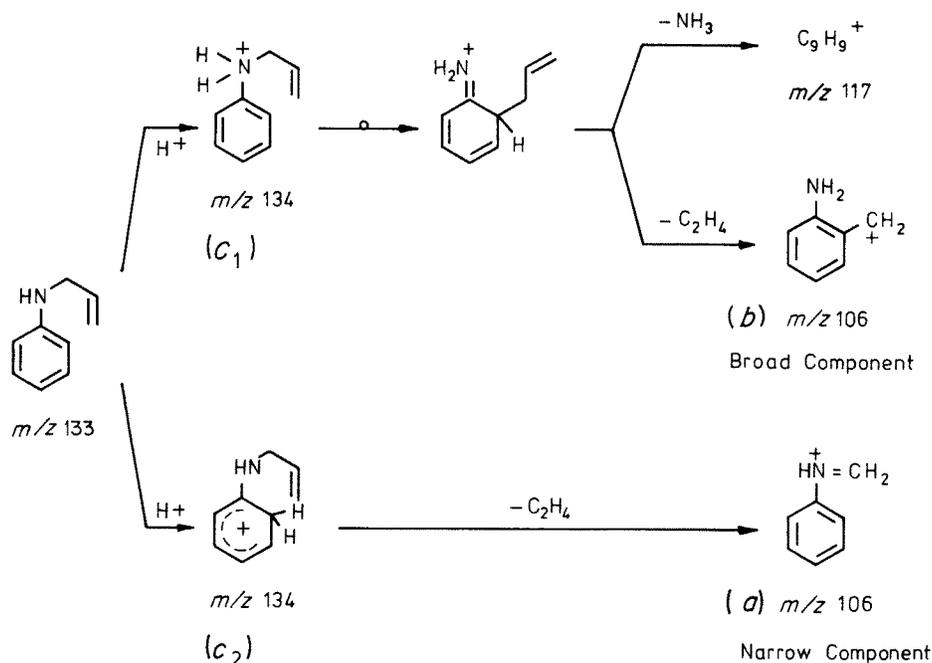
Reagent gas	T_{50} meV	T_{22} meV
C_4H_{10}	110 (165) ^a	300 (435)
C_3H_8	110	300
CH_4	240 (283)	800 (734)
H_2	800	1300

^a Values obtained with a triple-sector (modified MS902) mass spectrometer.

The reduced abundance of the peak at m/z 104 would appear, however, to indicate the presence of anilino-methene ions (a). It seems likely, therefore, that the m/z 106 ions formed from metastable MH^+ ions of **1** consist of both of these structures. The higher abundance of m/z 91 ions with respect to the two reference structures was observed previously¹ when there was a small contribution of $[C_8H_{10}]^{++}$ ions to the m/z 106 ions being investigated. This $[C_8H_{10}]^{++} \rightarrow m/z$ 91 ions is very facile under CID, so only a small proportion of $[C_8H_{10}]^{++}$ ions are required. The source of these $[C_8H_{10}]^{++}$ ions could be $(^{13}C)M^{++} (m/z$ 134) \rightarrow m/z 106 + $HN^{13}C$ in the field-free region or, more likely, interference from the process $M^{++} (m/z$ 133) \rightarrow m/z 106 + HNC, which is also occurring along the flight path.

An attempt to obtain the CID spectra of the broad and narrow components of the m/z 106 peaks and therefore determine the structure of the $[C_7H_8N]^+$ ions which make up these components was unsuccessful, owing to the very low signal levels obtained.

Recent studies have shown the possibility of protonation on the ring or on the nitrogen atom for aniline derivatives, the relative abundances of the two protonated species being dependent on the type of substitution.^{5,6} For non-substituted aniline, it has been demonstrated⁶ that the ring has higher basicity when compared with the amine function. A Brønsted acid of sufficient strength is necessary to allow protonation of the nitrogen to compete with protonation of the ring. If a similar situation applies to *N*-allylaniline, the experimental results can be interpreted as follows (Scheme 1):



(i) For the basic reagent gases, the reagent ions $[C_2H_9]^+$ or $[C_3H_7]^+$ protonate principally on the ring. The elimination of ethene from these metastable MH^+ ions (c_2) gives an m/z 106 peak which contains mainly anilino-methene ions (a).

(ii) For the less basic bases, the reagent ions ($[CH_5]^+$ and H_3^+) are able to protonate more competitively on the nitrogen atom. The metastable MH^+ ions formed by this reaction (c_1) undergo the amino-Claisen rearrangement and eliminate ethene (forming *o*-aminobenzyl ions (b)) and ammonia. Since protonation on the ring still takes place, the m/z 106 peak is seen to be a composite peak formed via the two competing pathways.

The occurrence of the rearrangement reaction is more a function of the reagent ion's ability to protonate the various sites of the molecule than it is a function of the metastable ion's internal energy.

CONCLUSIONS

As could be anticipated by the work which has been performed in the condensed phase, an acid-catalysed

amino-Claisen rearrangement of *N*-allylaniline can be induced in the gas phase. The behaviour of this protonated compound shows, however, significant differences from protonated allyl phenyl ether, which readily undergoes an acid-catalysed Claisen rearrangement in both the ion source and flight path. For *N*-allylaniline, the molecular ions formed by charge exchange in the CI source are the likely precursors of the m/z 106 peak observed in the mass spectrum. MH^+ ions, formed in a proton-transfer reaction with sufficient exothermicity to protonate the nitrogen atom, are observed to undergo an amino-Claisen rearrangement in the flight path, after which they lose ethene and ammonia competitively.

EXPERIMENTAL

Mass spectra were recorded on a VG-ZAB-2F mass spectrometer fitted with a combined EI/CI source. The spectrometer has been modified by the addition of a second electric sector⁴ and a collision cell in the third field-free region.

CI mass spectra were obtained using either hydrogen, methane, propane or isobutane as reagent gas at

Table 3. CID/MIKE spectra of m/z 106 ions formed in the first field-free region of an *E/B/E* (modified MS902) mass spectrometer^a

Precursors	<i>m/z</i>	104	92	91	89	79	78	77	67	65	63
<i>N</i> -ethylaniline	^b	104	8	4	—	25	29	100	—	8	6
<i>o</i> -ethylaniline	^b	185	6	6	12	47	43	100	3	10	10
<i>N</i> -allylaniline (1)	^{cd}	93		41		54	33	100		7	4
	^{ce}	95		35		58	32	100		6	4

^a The accelerating voltage of the metastable precursors was adjusted to obtain the same (6330 eV) kinetic energy for the fragment m/z 106 ions (Collision gas = He).

^b Dissociative ionization induced by electron impact (m/z 121 \rightarrow m/z 106).

^c Dissociative ionization induced by protonation (m/z 134 \rightarrow m/z 106).

^d Isobutane reagent gas.

^e Methane reagent gas.

source-housing pressures $2-5 \times 10^{-5}$ Torr. The electron energy was 100 eV, and filament emission was 1 mA. The source temperature was 200 °C and the inlet system for liquid samples was maintained at 200 °C. The source-accelerating potential was 6 kV.

EI mass spectra were obtained with an electron energy of 70 eV and a trap current of 100 μ A. The source and inlet-system temperatures were 160 °C and 200 °C, respectively. The source-accelerating voltage was 6 kV.

MIKE spectra were obtained by scanning the appropriate electric sector under the control of a data system. Where necessary, successive scans could be signal-averaged. CID spectra were obtained by introducing

nitrogen collision gas into either the second or third field-free region collision cell to an estimated pressure of 10^{-3} Torr (0.1 Pa).

Some data were also obtained on a three-sector MS902 mass spectrometer.⁷

Chemicals were obtained commercially or synthesized by conventional techniques.

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