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Intramolecular Aromatic Substitution and Amino-Claisen Rearrangement in Substituted *N*-(2-Propynyl)anilines on Electron Impact

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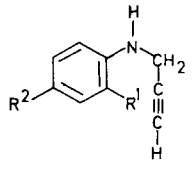
N*-(2-Propynyl)anilines undergo amino-Claisen rearrangement to a minor extent in the ion source, losing a molecule of HCN under electron impact conditions. However, metastable molecular ions with energies closer to threshold undergo Claisen rearrangement giving rise to more abundant $[M - HCN]^{+\cdot}$ ions in the first field-free region. Loss of a hydrogen from the molecular ion gives rise to the base peak in the mass spectrum of *N*-(2-propynyl)aniline. The hydrogen that is expelled for the formation of the $[M - H]^+$ ion is observed to be from the amino nitrogen, propargylic carbon and the *ortho*-carbon of the ring. The last process leads to a cyclic fragment involving intramolecular aromatic substitution. Double oxygen migration from the nitro group to the triple bond, due to the *ortho* effect, yields an abundant ion at *m/z* 105 in *N*-(2-propynyl)-*o*-nitroaniline. The proposed fragmentation pathways and ion structures are substantiated by high-resolution data, *B/E* and B^2/E linked-scan spectra, collisionally activated dissociation–*B/E* linked-scan spectra and deuterium isotopic labelling.

INTRODUCTION

Claisen rearrangement is a 3,3-sigmatropic rearrangement of an allyl vinyl ether to a homoallylic carbonyl compound.[1] Such a phenomenon is also observed[2] in phenyl allyl ethers, phenyl propargyl ethers, etc. In recent years, the investigation of the occurrence of Claisen rearrangements in the gas phase has gained importance. Very few reports of amino-Claisen rearrangements in solution have been published.[3–5] Such a rearrangement is reported to be insignificant in the ion source of the mass spectrometer but gains importance along the flight path in *N*-allylaniline under both electron impact (EI)[6] and chemical ionization (CI)[7] conditions. Claisen rearrangement is observed as a major fragmentation pathway in phenyl allenyl ethers,[8] whereas such a decomposition mode is not predominant in phenyl propargyl ethers.[9] Phenyl allenyl sulphides and phenyl propargyl sulphides do exhibit[10] fragment ions of low abundance corresponding to thio-Claisen rearrangement in their EI mass spectra.

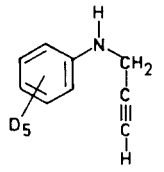
The nitro group and methoxy substituent are known to interact very efficiently with the *ortho* substituent in aromatic systems by transferring oxygen atoms and hydrogen respectively to multiple bonds[11,12] or heteroatoms.[13,14] The *ortho* effect of the nitro group with aromatic primary amines[15] and secondary amines[16] has been well documented. However, there are no reports of the *ortho* interaction of nitro and methoxy groups with a side-chain containing both an amino function and a triple bond.

The study of the EI mass spectral decomposition of *N*-(2-propynyl)anilines (**1–12**, cf. Table 1) were under-



Compound No.	R^1	R^2
1	H	H
2	OCH_3	H
3	H	OCH_3
4	CH_3	H
5	H	CH_3
6	Cl	H
7	H	Cl
8	NO_2	H
9	H	NO_2

10



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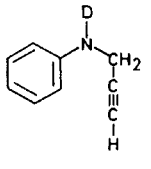

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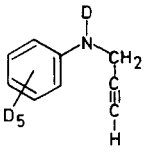

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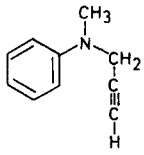

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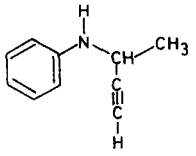

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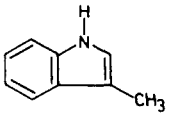

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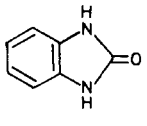

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Table 1. Partial mass spectra of compounds 2–9

Compound No.	*m/z* (relative abundance, %)							
	$M^{+\cdot}$	$[M-H]^+$	$[M-R]^+$	$[M-HCN]^{+\cdot}$	*c*	*d*	*e*	Other ions
2	161 (100)	160 (37)	130 (33)	134 (2)	103 (4)	122 (8)	123 (3)	146 (69), 118 (26), 117 (20)
3	161 (100)	160 (7)	130 (3)	134 (1)	103 (2)	122 (89)	123 (12)	146 (57), 118 (4), 117 (10)
4	145 (100)	144 (68)	130 (53)	118 (8)	103 (7)	106 (86)	107 (7)	117 (10), 115 (16), 79 (23)
5	145 (100)	144 (75)	130 (45)	118 (4)	103 (5)	106 (37)	107 (6)	117 (5), 115 (10), 79 (26)
6	165 (72)	164 (57)	130 (100)	138 (8)	103 (16)	126 (13)	127 (5)	129 (17), 99 (36)
7	165 (100)	164 (59)	130 (79)	138 (7)	103 (12)	126 (37)	127 (9)	129 (15), 128 (29), 99 (45)
8	176 (52)	175 (1)	130 (18)	149 (1)	103 (100)	137 (1)	138 (1)	129 (78), 128 (24), 105 (85), 102 (48), 101 (28), 91 (24)
9	176 (100)	175 (24)	130 (35)	149 (1)	103 (32)	—	—	129 (53), 128 (11), 146 (27), 102 (14), 91 (27)

taken in this work in order to investigate the possible occurrence of amino-Claisen rearrangements and *ortho* effects of methoxy and nitro groups with the triple bond and amino function.

RESULTS AND DISCUSSION

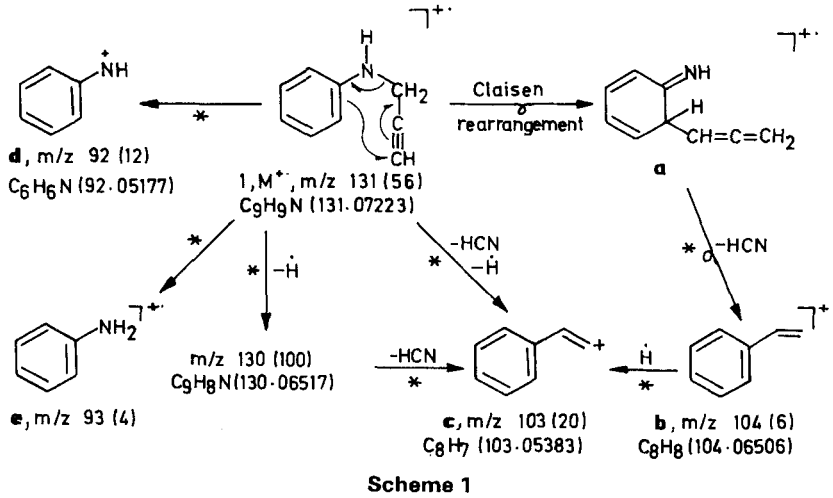
The expected amino-Claisen rearrangement in the $M^{+\cdot}$ of *N*-(2-propynyl)aniline (**1**) is observed for the formation of ion *b* at *m/z* 104 (Scheme 1, Fig. 1). An accurate mass measurement study revealed the elemental composition of ion *b* to be C_8H_8, corresponding to the expulsion of HCN from the molecular ion. The *B/E* linked-scan spectral data for the molecular ion of **1** and B^2/E linked-scan spectral data for ion *b* indicate the direct formation of ion *b* from the molecular ion. A styrene radical cation structure has been assigned to ion *b* based on the earlier studies.[8–10,17] This hypothesis is confirmed from the fact that the collisionally activated dissociation (CAD)–*B/E* linked-scan spectrum of the ion at *m/z* 104 from **1** is found to be identical with that of the $M^{+\cdot}$ of styrene, taken as the reference compound (Fig. 2).

A Claisen rearrangement in the $M^{+\cdot}$ of **1**, leading to the allenic species *a*, is envisaged for the formation of *b* (Scheme 1). Expulsion of HCN from ion *a* followed by skeletal rearrangement yields *b*.

It is noteworthy that the Claisen rearrangement yielding $[M-HCN]^{+\cdot}$ ion becomes more predominant along the flight path in the first field-free region, which is seen from the investigation of metastable molecular ions of **1**–**9** (Table 2). However, the increase in the abundance of the $[M-HCN]^{+\cdot}$ ion along the flight path reveals that Claisen rearrangement competes with other fragmentation pathways in the molecular ions with internal energies closer to the threshold.

The base peak in the mass spectrum of **1** is at *m/z* 130 (Fig. 1), formed by expulsion of a hydrogen radical from $M^{+\cdot}$. Deuterium labelling of the ring hydrogens (**10**), amino hydrogen (**11**) and both ring hydrogens and amino group (**12**) was carried out and their mass spectral decompositions (Fig. 1) were studied to examine the origin of the hydrogen that is lost during the formation of the ion at *m/z* 130 in **1**. It can be seen from Fig. 1 that the loss of hydrogen in **1** occurs from all three centres. An intramolecular aromatic substitution followed by the loss of the *ortho*-hydrogen yields the quinolinium ion *f* (Scheme 2). The expulsion of amino hydrogen leads to the ion structure *g* whereas elimination of hydrogen from the propargylic carbon gives rise to the propargylic species *h* (Scheme 2). However, the ejection of the hydrogen from the propargylic carbon seems to make a greater contribution towards the formation of the $[M-H]^+$ ion, as revealed by the mass spectra of the deuterium-labelled compounds **10**, **11** and **12**.

Comparison of the CAD–*B/E* linked-scan spectrum of the ion at *m/z* 130 from **1** with those from **6**, **7**, **13**, **14**



Scheme 1

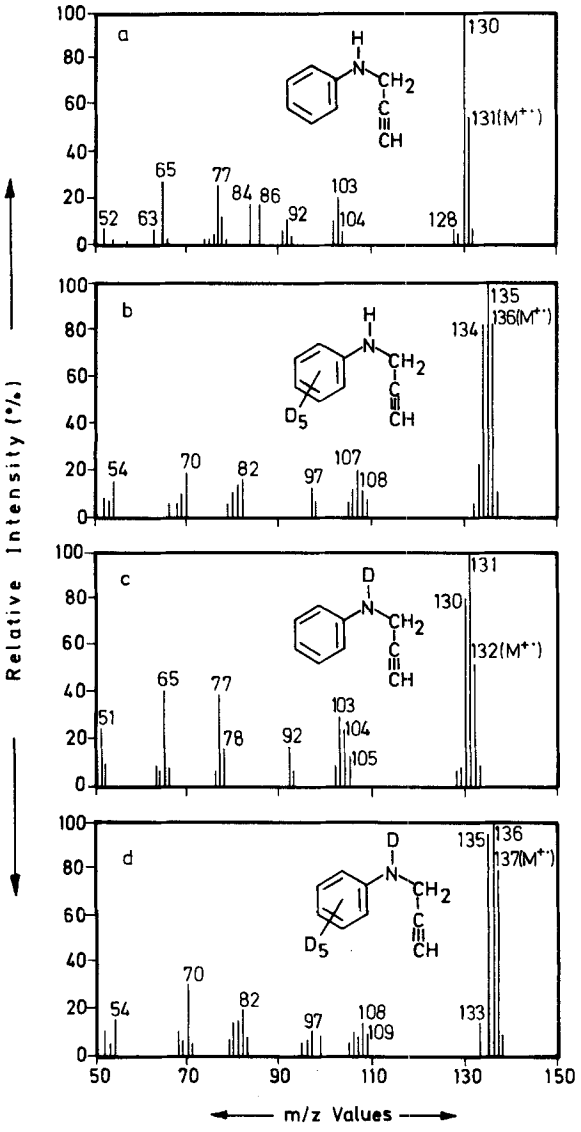


Figure 1. EI mass spectra at 70 eV of (a) *N*-propargylaniline (1), (b) *N*-propargyl[$^2H_5$]aniline (10), (c) *N*-propargyl-*N*-deuteroaniline (11) and (d) *N*-propargyl-*N*-deutero[$^2H_5$]aniline (12).

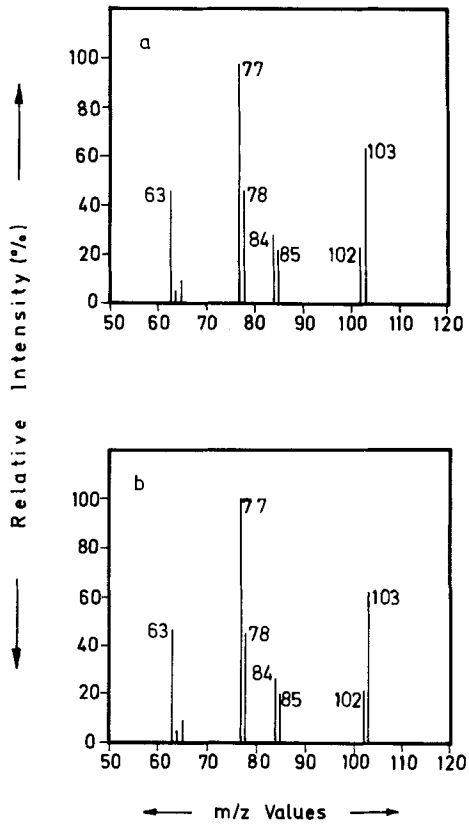


Figure 2. CAD-*B/E* linked-scan spectra of the ions at (a) *m/z* 104 from *N*-propargylaniline and (b) $M^{+\cdot}$, *m/z* 104 of styrene.

and **15** (Fig. 3) reveals that the ion at *m/z* 130 from **1** has characteristic fragment ions in all the spectra. This observation indicates that the ion at *m/z* 130 from **1** is a mixture of structures *f*, *g* and *h*, suggesting that these cations do not rearrange to a common structure.

Losses of hydrogen and the substituents are predominant modes of fragmentations in these compounds forming quinolinium ion structures (Table 1). The proposed quinolinium ion structure for the ions at *m/z* 130 in these compounds is confirmed from the fact the CAD spectra of the ions at *m/z* 130 from **6** and **7** are identical with that from **15**[18] (Fig. 3). The formation of quinolinium ion by the expulsion of the substituent from the $M^{+\cdot}$ of **7** indicates that substituent scrambling may be involved in the para-substituted compounds (**3**, **5**, **7** and **9**) during the ejection of the substituent from the molecular ions.

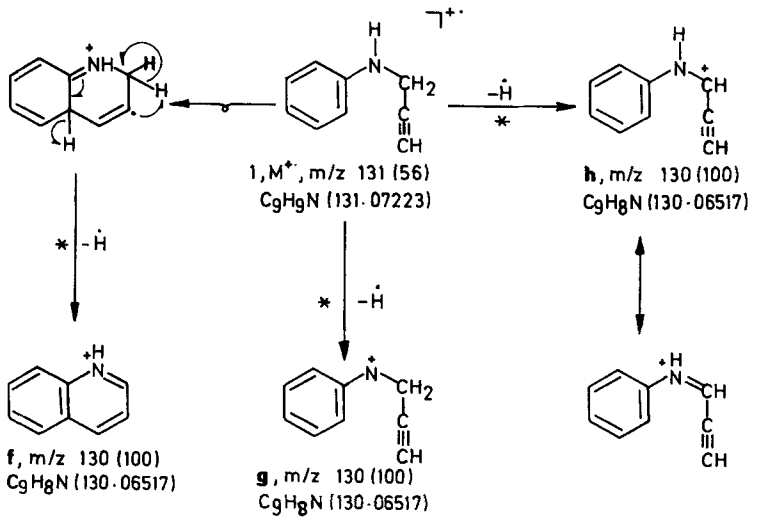
Ortho effect

No fragment ion corresponding to the *ortho* interaction of the methoxy group with the triple bond is observed. However, *ortho* interaction of the methoxy group during secondary fragmentation leads to the ion at *m/z* 94 in **2** (Scheme 3). A methyl migration from the oxygen to the amino function in the ion at *m/z* 122 followed by the elimination of CO is proposed for the formation of the ion at *m/z* 94 (Scheme 3).

In contrast, *ortho* interaction of the nitro group with the triple bond yields the interesting fragment ion *k* at *m/z* 105 in *N*-(2-propynyl)-*o*-nitroaniline (**8**). The elemental composition of the ion *k* as determined by the high-resolution technique is $C_6H_5N_2$, indicating the

Table 2. Relative abundances of $[M - HCN]^{+\cdot}$ ions from compounds 1–9

	m/z (relative abundance, %)								
In	1	2	3	4	5	6	7	8	9
Ion source	104	134	134	118	118	138	138	149	149
	(6)	(2)	(1)	(8)	(4)	(8)	(7)	(1)	(1)
First field-free region	104	134	134	118	118	138	138	149	149
	(24)	(17)	(7)	(49)	(14)	(24)	(17)	(7)	(8)



Scheme 2

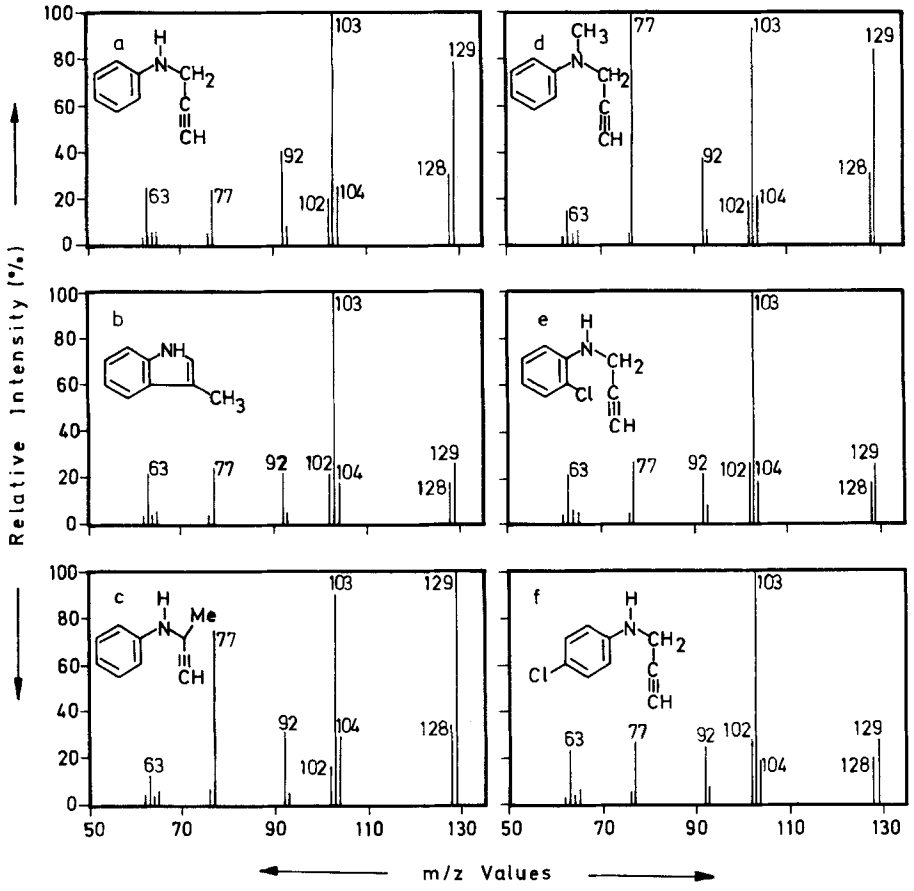
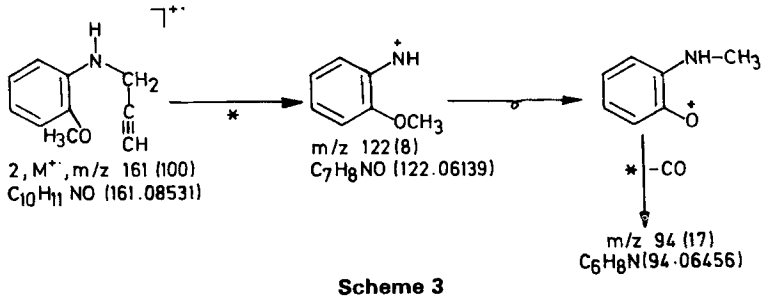
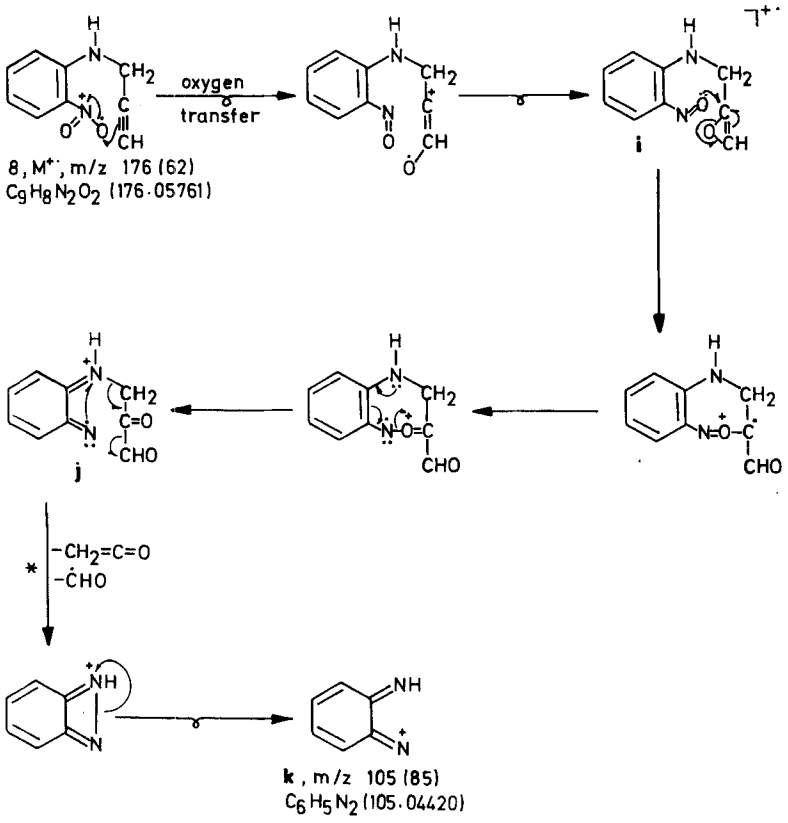


Figure 3. CAD–*B*/*E* linked-scan spectra of the ions at *m*/*z* 130 from (a) **1**, (b) **15**, (c) **14**, (d) **13**, (e) **6** and (f) **7**.



Scheme 3



Scheme 4

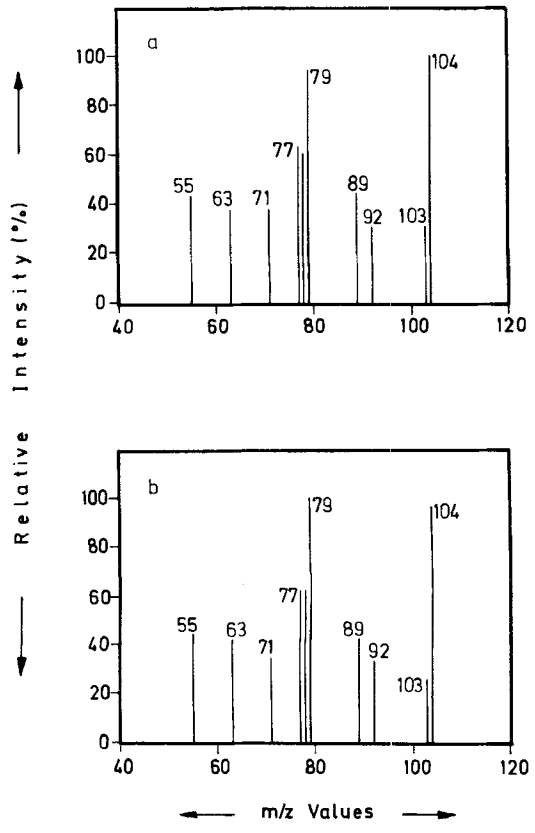


Figure 4. CAD-*B/E* linked-scan spectra of the ions at *m/z* 105 from (a) 2-benzimidazolone and (b) *N*-propargyl-*o*-nitroaniline.

expulsion of a ketene molecule and a formyl radical from the molecular ion. The direct formation of ion *k* from $M^{+\cdot}$ of **8** is deduced from the metastable spectral studies (Table 2).

Double oxygen transfer from the nitro group to the acetylenic triple bond is envisaged for the formation of the ion *k*. An initial oxygen transfer from the nitro group to the *β*-carbon of the triple bond yields the fragment *i* (Scheme 4). Another oxygen transfer in *i* affords *j*. Simultaneous ejections of a ketene molecule and the formyl radical from *i* give rise to the ion *k* at *m/z* 105. The comparison of the CAD-*B/E* linked-scan spectrum (Fig. 4) of ion *k* at *m/z* 105 from **8** and that from 2-benzimidazolone[19] reveals that they are identical, confirming the proposed structure for *k*.

It can be seen from this study that the Claisen rearrangement leading to $[M - HCN]^{+\cdot}$ ion is not a favourable process in the ion source, whereas such a decomposition mode is observed to a greater extent along the flight path. One of the pathways for the formation of the $[M - H]^{+}$ ion is intramolecular aromatic substitution followed by expulsion of the *ortho*-hydrogen from the aromatic ring, yielding a quinolinium ion.

EXPERIMENTAL

Compounds **1–10** and **13** were prepared from the appropriately substituted aniline and propargyl

bromide by stirring at room temperature for 6 h in *N*,*N*-dimethylformamide as the solvent in the presence of sodium hydride according to the general procedure reported in the literature.[20] Compounds **11** and **12** were prepared by refluxing **1** and **10**, respectively, with D_2O and K_2CO_3 as the base for 2 h. Compound **14** was prepared from the α-methylpropargyl tosylate under similar conditions. Compounds **15** and **16** were prepared according to literature procedures.[21,22] All the compounds were purified by column chromatography using silica gel (60–120 mesh) with hexane–benzene (10:1) as the eluent and their purities were checked by TLC. The structures were confirmed by ^1H NMR and IR spectral data.

The mass spectra were recorded on a Finnigan MAT 8230 double-focusing mass spectrometer. The mass spectra were run at 70 eV with an emission current of 100 μA and an accelerating voltage of 3 kV. All the compounds were introduced into the mass spectrometer through either the reference inlet at 110 °C or the direct insertion probe at 25 °C. Accurate mass measurements were carried out at the resolution of 8000 (10% valley) and perfluorokerosene was used as the reference. *B*/*E* and B^2/E linked-scan spectra were recorded on a Finnigan MAT 8230 double-focusing mass spectrometer at an ionization energy of 70 eV and an accelerating voltage of 3 kV. The CAD–*B*/*E* linked-scan spectra in the first field-free region were investigated using helium as the collision gas, which was introduced until the main beam was attenuated to 30%.

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