# ELECTRON IMPACT INDUCED FRAGMENTATION OF Β-NITROAMINES

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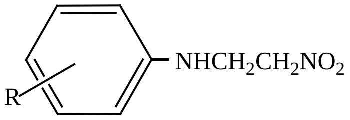
## Abstract

One of the most characteristic electron impact induced fragmentation processes of β-nitroamines, investigated here, is loss of nitromethane and/or nitromethylene radical to produce an imine or imonium ion. Through the comparison of an imine spectrum with that of β-nitroamine derived from, it was possible to shed additional light on the course of most significant fragmentation reaction of β-nitroamines. The other two most characteristic fragmentation processes of β-nitroamines upon electron impact are i) loss of aniline or an aniline moiety with expulsion of a nitroalkene. Similer steps are also noted in fragmentation of amines, aliphatic ethers and thioethers. ii) Fragmentation with loss of $NO_2$ or $HNO_2$ followed by a series of fragmentation processes yielding low m/e species. Other features of the mass spectrometric fragmentation of β-nitroamines are also discussed in the light of the spectra of the specific compounds discussed here.

**Keywords:** β-Nitroamines, Imines, Nitromethane, Nitromethylene radical

## Introduction

β-Nitroamines of type **I** were recently synthesized from paraformaldehyde, aniline or its ring substituted derivatives and nitromethane by a silica catalized one-pot nitro-Mannich reaction [Ali S. Mahasneh et all, 2006]. As part of characterization of these compounds their mass spectra were recorded. The most characteristic electron impact fragmentation processes of β-nitroamines of this type will be studied regarding those spectra.



**I**

**IA R = H**
**IB R = *p*-$CH_3$**
**IC R = *p*-Br**

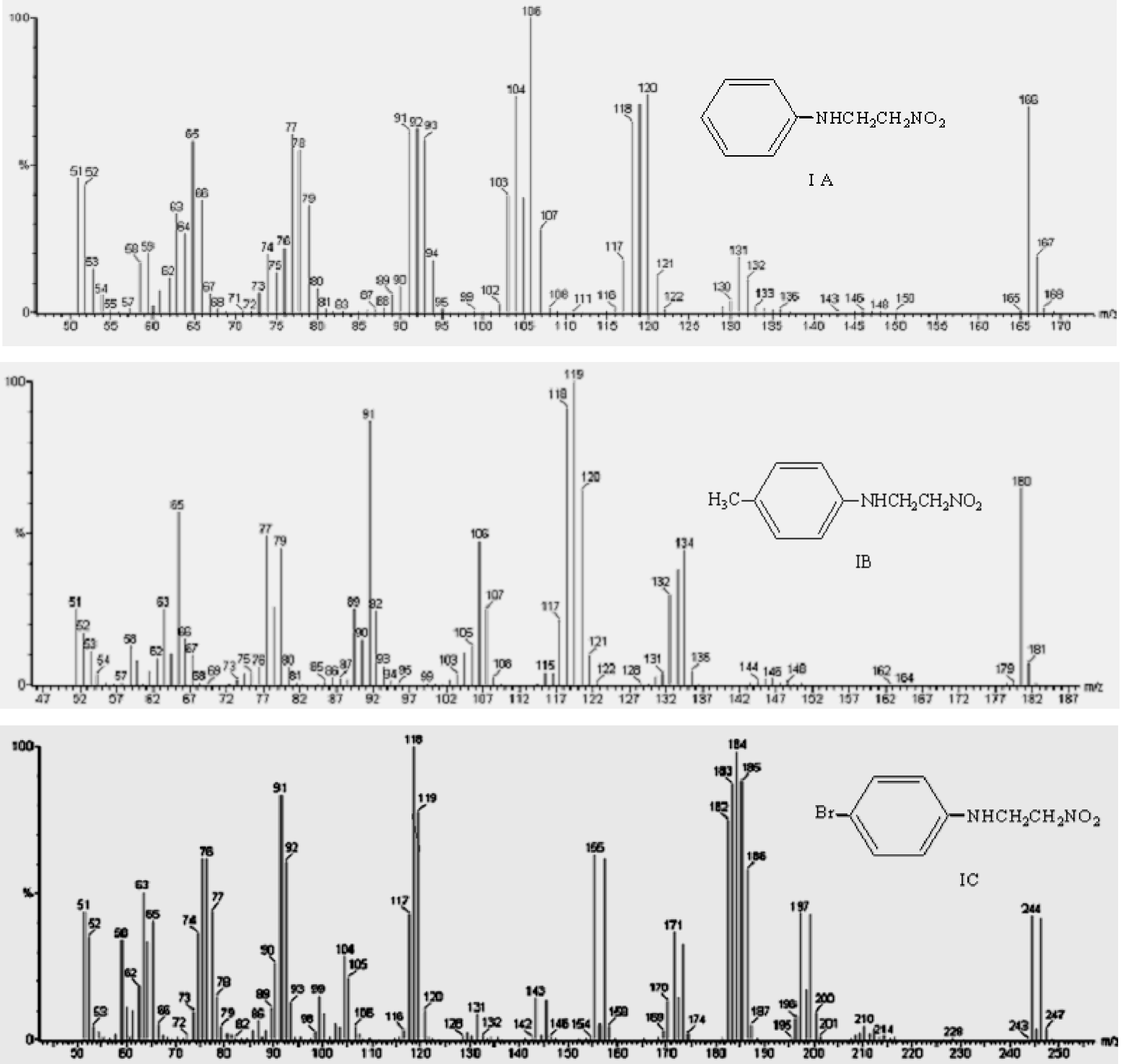
## Results and Discussions

Table 1. Shows all ions having abundance greater than 2% of the base peak. The molecular ion peak intensities of compounds **I** are high; for **IA** as an example m/e 166 is more than 90% of the base peak and M+H peaks are also present figure 1. Table 2 contains the data extracted from table 1 and shows some of the fragmentation behavior.

**Table 1.**

| **Compound** | **m/e (*I*%)** |
|---|---|
| **IA** | 51(72) 52(66) 53(30) 54(12) 58(39) 59(45) 62(23) 63(62) 65(105) 66(61) 67(15) 73(13) 74(35) 76(40) 77(37) 78(67) 79(62) 80(19) 89(15) 90(19) 91(89) 92(88) 93(77) 94(34) 103(62) 104(88) 105(70) 106(54) 107(50) 117((34) 118(38) 119(88) 120(100) 121(22) 130(10) 131(40) 132(26) 166 M(96) 167(13) |
| **IB** | 51(12) 52(8) 58(10) 63(14) 65(33) 73(2) 77(19) 79(12) 89(12) 91(100) 92(11) 105(5) 106(20) 107(27) 117(9) 118(58) 119(78) 120(40) 121(7) 133(10) 134(15)135(2) 180 M(15) 181(2) |
| **IC** | 51(41) 52(35) 58(31) 63(47) 64(30) 65(37) 73(9) 74(34) 75(57) 76(56) 77(41) 78(16) 89(10) 90(25) 91(78) 92(56) 93(12) 9915) 104(28) 105(20)117(42) 118(98) 119(75) 120(10) 131(12) 143(15) 145(14) 155(58) 157(57) 168(6) 170(13) 171(33) 172(15) 173(30) 182(75) 183(92) 184(100) 185(94) 186(56) 196(8) 197(39) 198(18) 199(38) 200(11) 244 M(43) 246(42) |

**Figure 1**



Compounds **I** fragment upon electron impact by formation of aniline or its derivatives and nitroethylene both fragments appear as radical cations in the spectra, having masses M-73 and 73 respectively, as shown in scheme 1.

**Scheme 1**

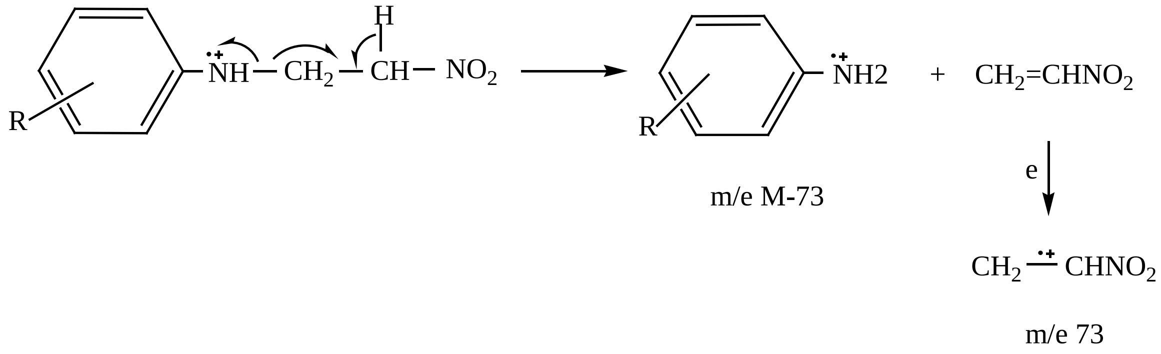
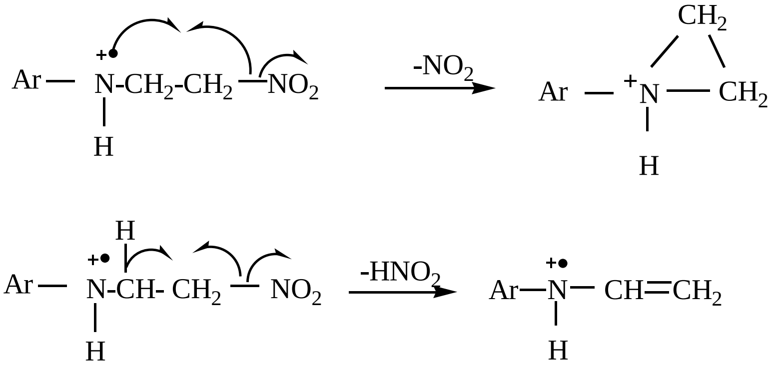


**Table 2**

| Comp. | M | M-aniline | M-CH2=CHNO$_2$ | M-NO$_2$ | M-HNO$_2$ | M-$CH_3NO_2$ | M-$CH_2NO_2$ | M+H-$CH_2NO_2$ |
|---|---|---|---|---|---|---|---|---|
| **IA** | 166(96) | 73(13) | 93(77) | 120(100) | 119(88) | 105(70) | 106(54) | 107(50) |
| **IB** | 180(15) | 73(2) | 107(27) | 134(15) | 133(10) | 119(78) | 120(40) | 121(40) |
| **IC** | 244(43) | 73(9) | 171(33) | 198(18) | 197(39) | 183(93) | 184(100) | 185(93) |
|  | 246 |  | 173 | 200 | 199 | 185 | 186 | 187 |

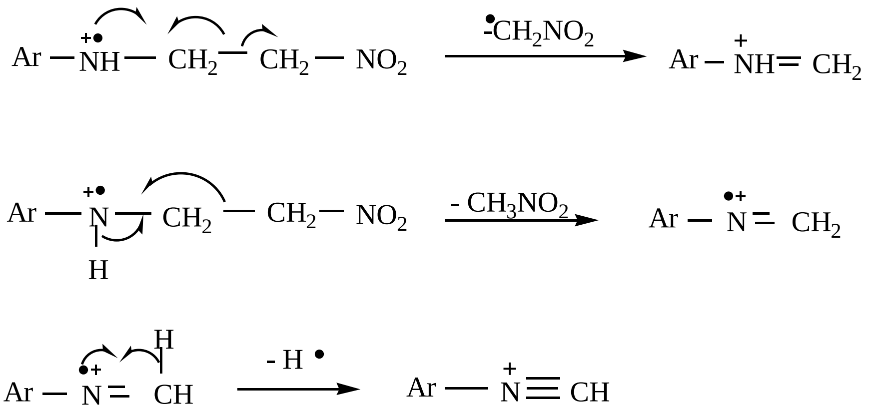
Loss of $NO_2$ and $HNO_2$ occurs as illustrated in the proposed mechanisms scheme 2. Both M ion or M+H ion may lose $NO_2$ and $HNO_2$ in the same fashion forming the aziridinium cation or the enamine radical cation below [J. A. Gilpin, 1959].

**Scheme 2.**



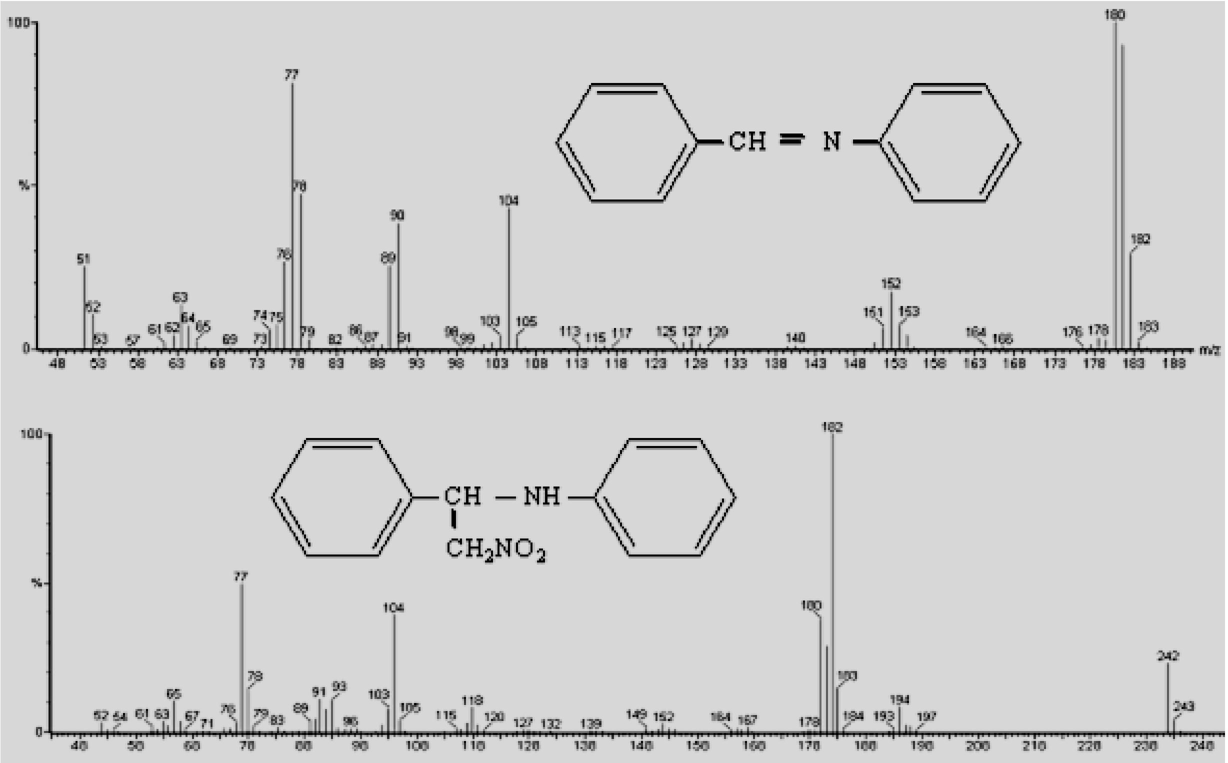
Perhaps the most prominent diagnostic fragmentation process of β-nitroamines is the α-bond cleavage to the Nitro group leading to loss of $CH_2NO_2$ radical and/or $CH_3NO_2$ molecule giving a group of intense peaks that differ by one atomic mass unit. This fragmentation occurs in both M and M+H ion. Loss of H radical from the main radical cation is a common behavior as illustrated in scheme 3.

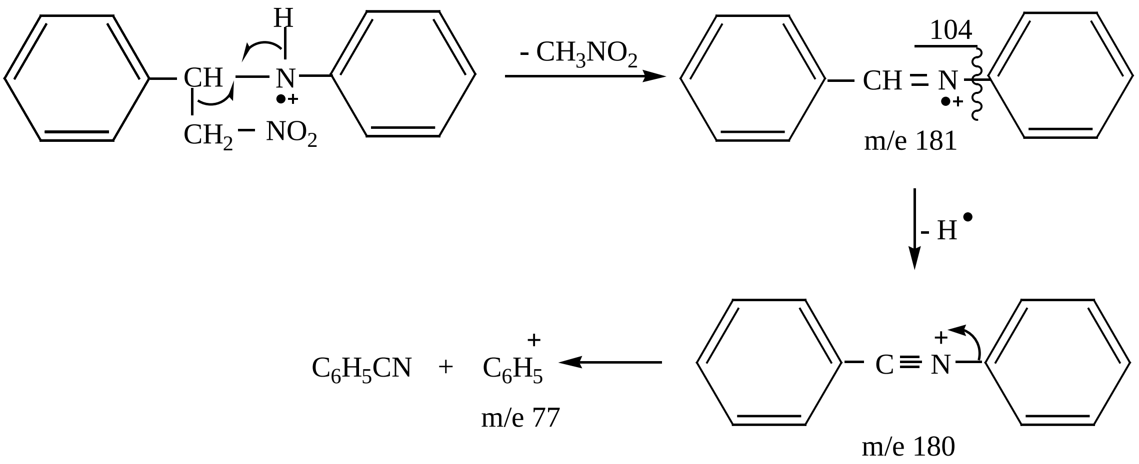
**Scheme 3.**



For the purpose of finding an evidence for fragmentation of scheme 3, the spectra of 2-anilino-2-phenyl-1-nitroethane, taken as a β-nitroamine, and the imine from which it was synthesized were recorded figure 2. Examining both spectra it is obvious that the β-nitroamine fragments to the imine by loss of $CH_3NO_2$ and or $CH_2NO_2$ radical from both M and M+H species giving fragments m/e 181, 182, and 183 (182 is the base peak). Compared to the spectrum of imine itself, the same fragments are found around M region of the imine; 181, 182 and 183.The intense peak at m/e 180 in both spectra is due to the loss of H radical from the imine radical cation. The most significant conclusion to be derived from both spectra of figure 2 pertains to the loss of nitromethane molecule and nitromethylene radical, the imine is involved in the genesis of the species m/e 104 and m/e 77 which are common fragments in both spectra [R. M. Teeter, 1965].

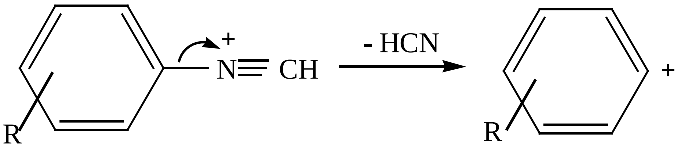
**Figure 2**





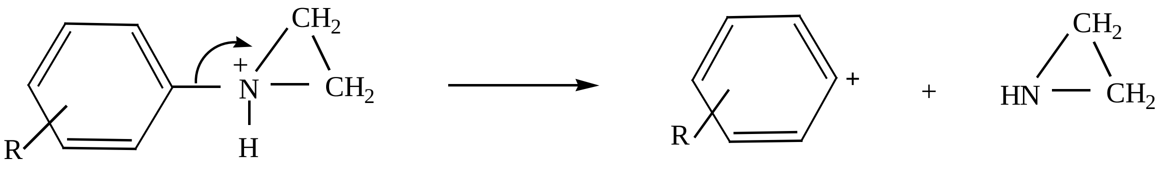
Peaks ascribed to the fragmentation of some of the species in scheme 3 constitute a remarkable feature in the spectra of compounds **I.** Loss of HCN from the last species of scheme 3, for example, will produce the aromatic cations m/e 77 in **IA** spectrum, m/e 91 in **IB** spectrum and m/e 155, 157 in **IC** spectrum. This fragmentation process is illustrated in scheme 4.

**Scheme 4**



Alternatively these fragments could arise according to scheme 5 via the formation of aziridene ring after loss of $NO_2$ (see also scheme 2).

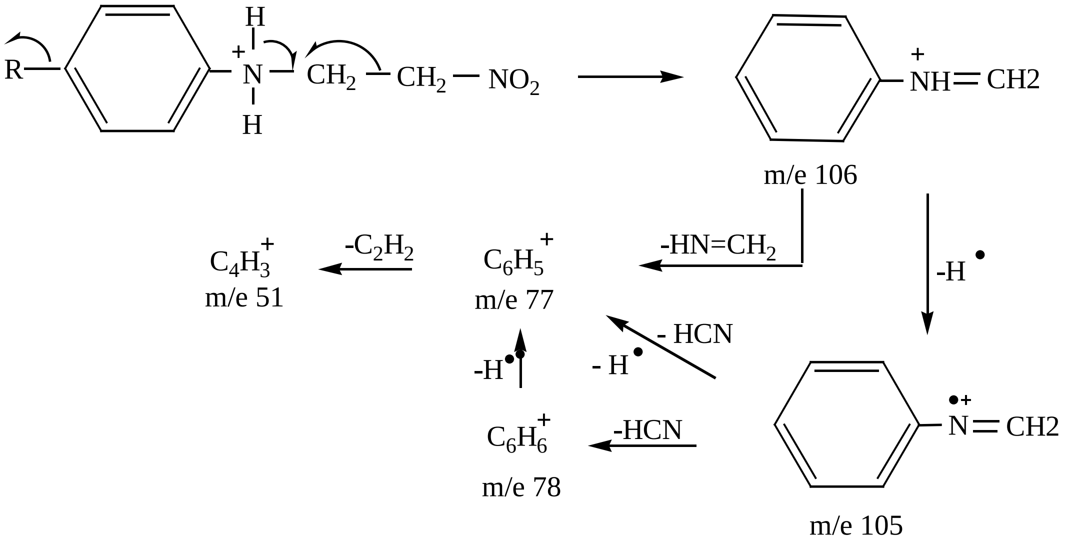
**Scheme 5**



R=H m/e 77
R =$CH_3$ m/e 91
R=Br m/e 155,157

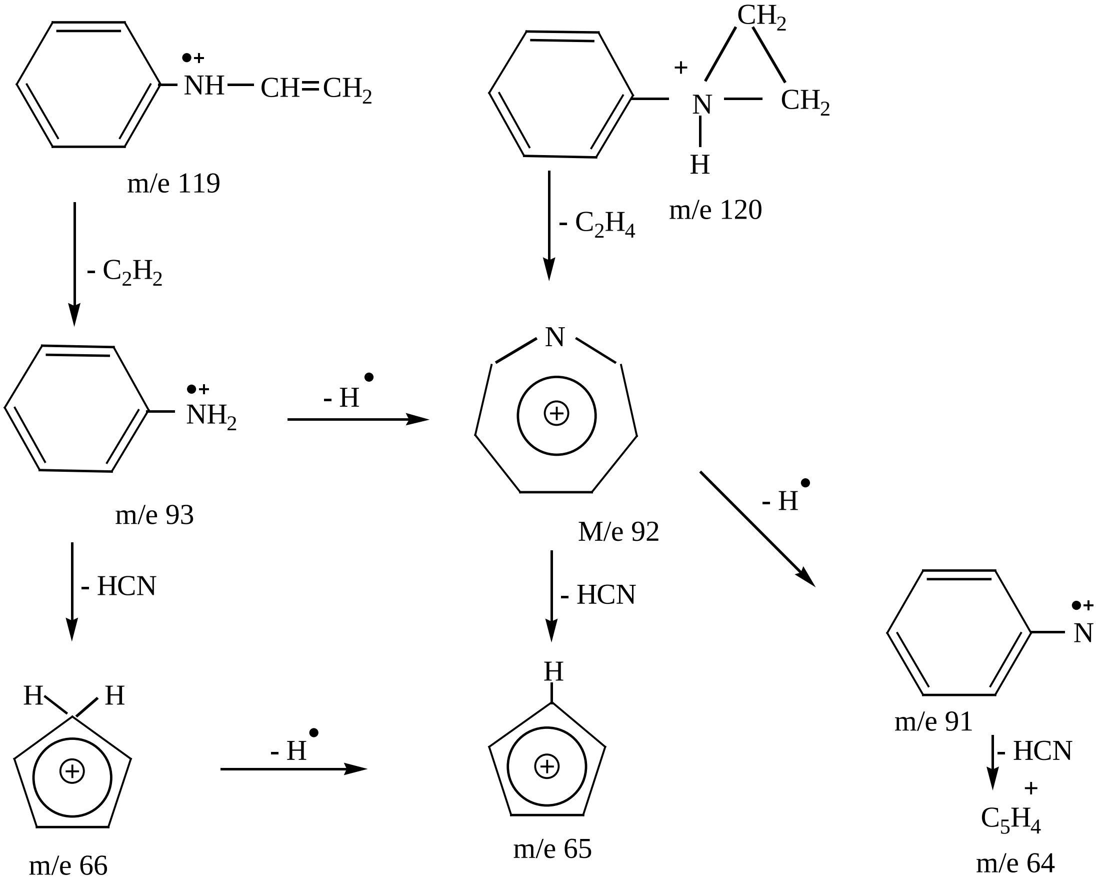
The peak m/e 106, found in all spectra of compounds **I** in variable intensities, is formed after loss of $CH_2NO_2$ radical from the M+H species and the expulsion of the ring constituent as radical [H. M. Grubb et all, 1963]. The mechanism of this fragmentation process and the following fragmentation steps is illustrated in scheme 6.

**Scheme 6.**



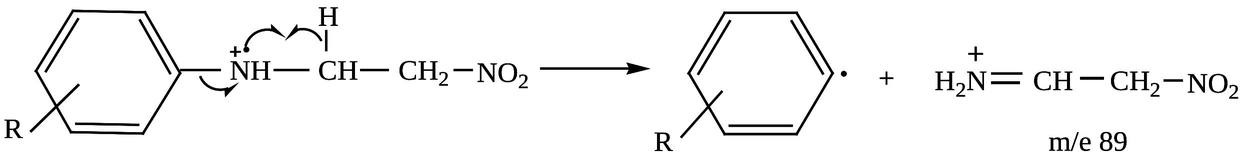
Peaks of m/e 93, 92 and 91 arise from the fragmentation of the products m/e 119 and 120, in spectrum of **IA** as an example. Plausible rationalization for the formation of these fragments and the steps to follow are as shown in scheme 7. The stable azatropylium ion m/e 92 is a characteristic fragment. Similar fragmentation mechanism could be proposed for compounds **IB** and **IC** [S. Meyerson et all, 1966].

**Scheme 7.**



Finally a common fragment in the mass spectra of compounds **I** is the β-nitroethylene imonium ion having m/e 89 which is formed as the result of fragmentation of the molecular ion suggested in scheme 8.

**Scheme 8**



## Conclusion

The common features of the mass spectra of both types of β-nitroamines studied here could be summarized in the following points:

- Loss of aniline moiety and formation of a nitroalkene cation from the remainder of the molecule.
- Loss of $NO_2$ and or $HNO_2$ leading to an eniminium or cyclic amine carbocation.
- The process that is perhaps the most characteristic feature of the mass spectra of these compounds is the loss of nitromethane molecule and/or nitromethylene radical and thereby forming an imine carbocation.
- Fragmentation by formation of β-nitrethylene ammonium ion, which has a m/e 89.
- Fragmentation processes, suggested here, can be confirmed by a series of meta stable ion peaks that can be observed in the individual spectra.

## Experimental

The electron impact mass spectra were recorded on an on a Klarus 500 instrument at 70 ev.

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