Asian Journal of Chemistry Vol. 7, No. 4 (1995), 714–721

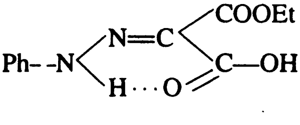
Studies on Arylhydrazones, Part-X: Electron Impact Studies on Ethyl Hydrogen Mesoxalate Phenylhydrazone and 2,3-Dioxo-2-Phenylhydrazono Butyric Acid

N. PRASAD, A. SAHAY*, J. PRASAD† and N.P. SINGH
Department of Chemistry
Bihar University, Muzaffarpur-842 001, India

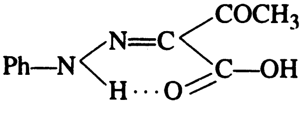
Mass spectral studies on ethylhydrogen mesoxalate phenylhydrazone and 2,3-dioxo-2-phenylhydrazono butyric acid have been carried out and their fragmentation patterns have been rationalised. None of the products shows the ion of highest abundance, *i.e.* the base peak as the molecular ion. The base peak of ethyl hydrogen mesoxalate phenylhydrazone is at m/e 91 whereas in case of 2,3-dioxo-2-phenylhydrazono butyric acid, base peak is at m/e 43.

INTRODUCTION

As a part of our investigation on arylhydrazones, the action of perchloric acid-formic acid on diethyl mesoxalate phenylhydrazone and 2,3-dioxo-2-(phenylhydrazono) butyrate have been reported in our earlier communication[1]. Thus, in continuation of our investigations, the electron impact studies on ethyl hydrogen mesoxalate phenylhydrazone(I) and 2,3-dioxo-2-phenylhydrazono butyric acid(II) have been carried out and their fragmentation patterns are reported in this communication.



(I)



(II)

EXPERIMENTAL

The details regarding the experimental procedure have been described in our earlier paper.[1]

RESULTS AND DISCUSSION

The relative intensity (R.I.) of the ions (excluding ions of low abundance) in case of compound(I) are as follows:

m/e	44	63	64	65	72	77	91 (B.P.)	92
R.I. (%)	16.25	4.68	9.37	30.0	4.65	18.75	100	27.5
m/e	93	105	118	145	162	190	236	237
R.I. (%)	18.75	2.5	20.62	3.12	22.18	17.5	43.12	5.62

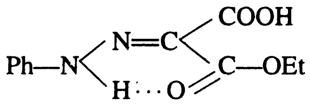
The M^+ appears at 236 amu having relative intensity of 43.12%. In the high

---

*Department of Chemistry, S.R. Sandhaya College, Raja Bazar, Patna-800 014, India.
†Department of Chemistry, M.S. College, Motihari, India.

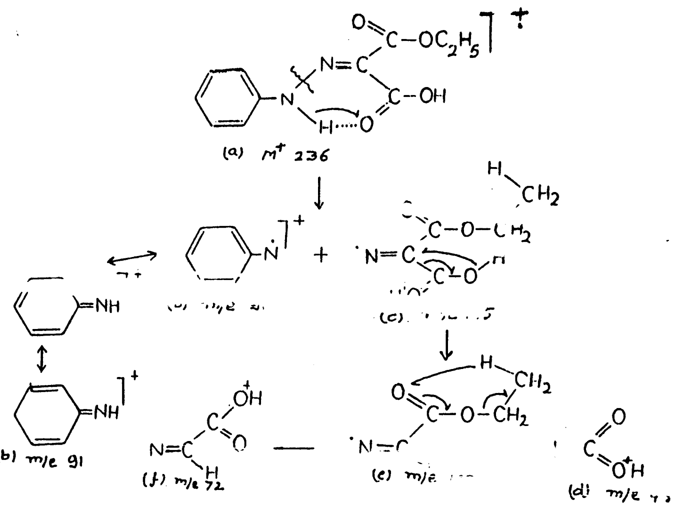
resolution electron impact, the observed mass of M^+ was found to be 236.0800 which is in agreement with theoretical mass 236.0797 (Δm 0.0003) and confirming the molecular formula of the product (I) to be $C_{11}H_{12}N_2O_4$. This also gave a peak at 237 of $(M + 1)^+$ ion, but no peak for $(M + 2)^+$ was observed in this case indicating the non-resolution of peak due to isotopic abundance of oxygen atoms present in the molecule.

The peaks at $(M - 1)^+$ and $(M - 2)^+$ are formed in case of arylhydrazones of aldehydes and ketones by the loss of N—H and aromatic protons.[2] In this case neither $(M - 1)^+$ at m/e 235 nor $(M - 2)^+$ at m/e 234 was observed presumably due to ready scrambling of N—H proton which is strongly bonded to either carbonyl oxygen of carboxylic group(I) or ester group(III) taking precedence over its loss in electron impact process. It could also be possible that the intensities of $(M - 1)^+$ and $(M - 2)^+$ are very low and computerised bar graph may be unable to show their features.



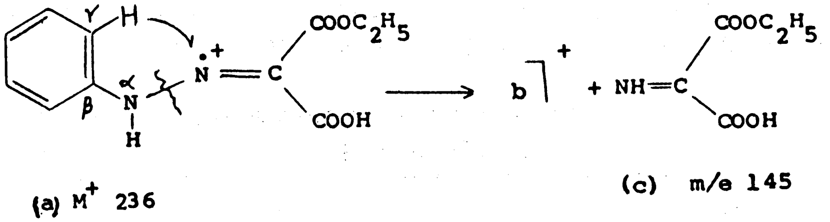
(III)

The base peak (b), at m/e 91 (R.I. 100%) could not be obtained directly from M^+ (a) without H-scrambling (Scheme-1). Normal bond cleavage at N—N could not provide this fragment. The formation of base peak could only be explained by migration of N—H-hydrogen to carbonyl with which it is bonded followed by normal bond cleavage at N—N bond. The base peak (b) is further stabilised by its resonance. This assignment is further substantiated by the formation of fragment (c) at m/e 145 of R.I. 3.12% which loses the fragment (d) at m/e 45 by 1:4 rearrangement and gives the ion (e) at m/e 100 which undergoes Me-Lafferty rearrangement to give ion (f) at m/e 72.



Scheme 1

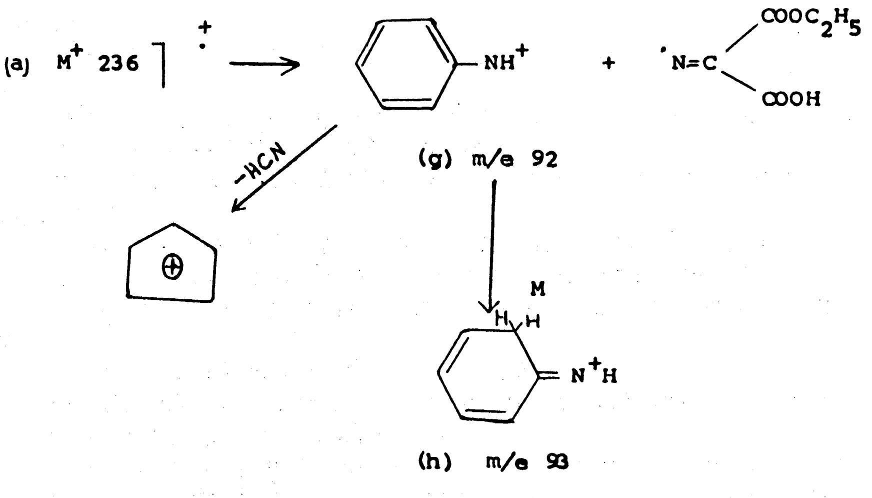
Alternatively the base peak (b) at m/e 91 may form by scrambling of *ortho*-hydrogen of phenyl nucleus followed by N—N-fission (Scheme-2). Such γ-scrambling is known in the case of hydrazones of aldehydes.[2]



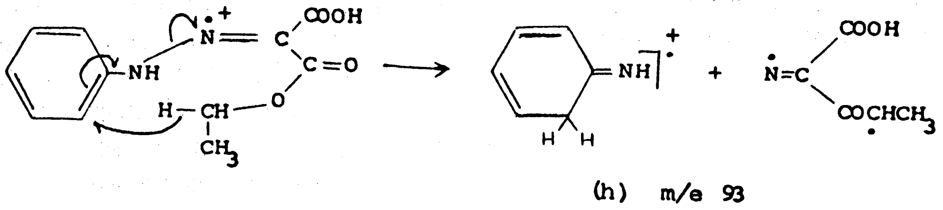
Scheme-2

In both the methods discussed above for the formation of base peak (b) at m/e 91, H-scrambling takes place prior to scission at N—N bond and the hydrogen of N—H group or aromatic nucleus can take part in scrambling; of course, it could be pin-pointed whether the hydrogen of N—H or aromatic nucleus is taking part in the rearrangement by obtaining the mass spectra of deuterated sample, but the same could not be available to us.

The peak (g) at m/e 92 and peak (h) at m/e 93 are of greater intensity than expected for isotopic content of C, H and N of base peak (b). The peak (h) at m/e 93 can form either by simple cleavage to form the ion $C_6H_6N^+$ (g, below) followed by reaction with the molecule (Scheme-3) or by H-scrambling in molecular ion followed by N—N cleavage (Scheme-4). Scheme-4 involves a 1:8 transition over a large distance but hydrogen-scrambling at even larger distances is known.[3]

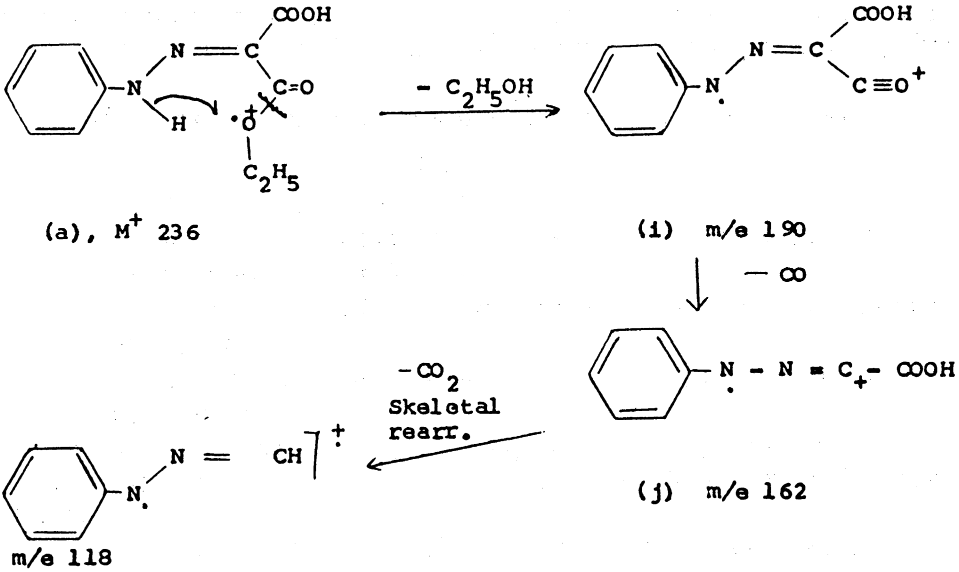


Scheme-3



Scheme-4

Compound (I) contains —COOH and —$COOC_2H_5$ functional groups apart from hydrazono group and hence fragmentation in this case can also be expected from far end of the molecule containing —COOH and —$COOC_2H_5$ functional groups. Loss of —OH (mass 17) and H_2O (mass 18) from (a) containing —COOH group is expected but no such fragmentation was observed in this case ruling out the possibility of cleavage of —COOH group with or without H-rearrangement. Significant peaks (i) at m/e 192 and (j) at m/e 162 are observed in this case. These arise by effective charge localisation at alkyl oxygen followed by H-scrambling from N—H and subsequent α-cleavage (Scheme-5). The fragment (j) at m/e 162 then produces ion at m/e 118 by the loss of CO_2.



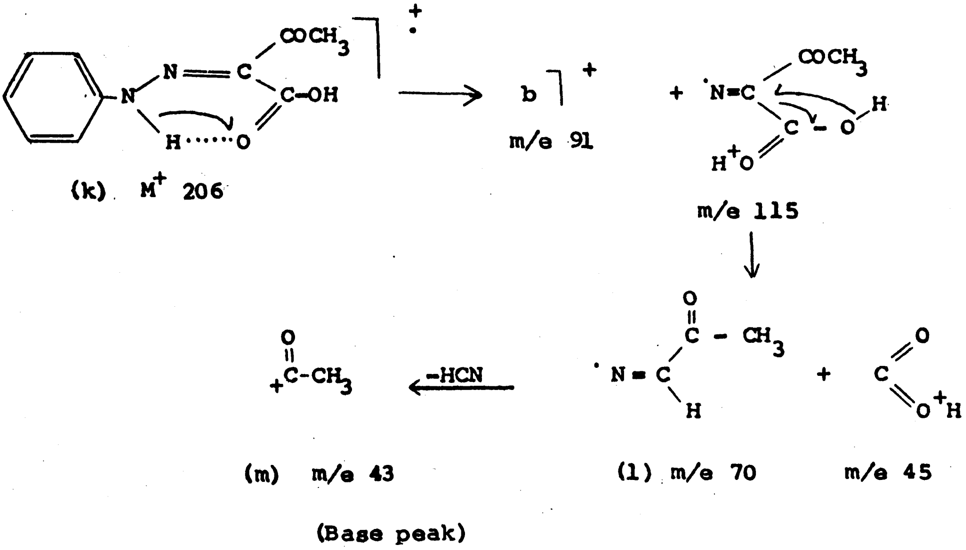
Scheme-5

In case of compound (II), the relative intensity of major ions (excluding ions of low abundance) are as follows:

m/e	43 (B.P.)	45	63	64	65	77	91	
R.I. (%)	100	3.12	8.75	11.87	49.37	46.25	36.25	
m/e	92	93	105	118	160	188	206	207
R.I. (%)	46.25	72.5	6.25	60	16.25	3.75	76.87	9.37

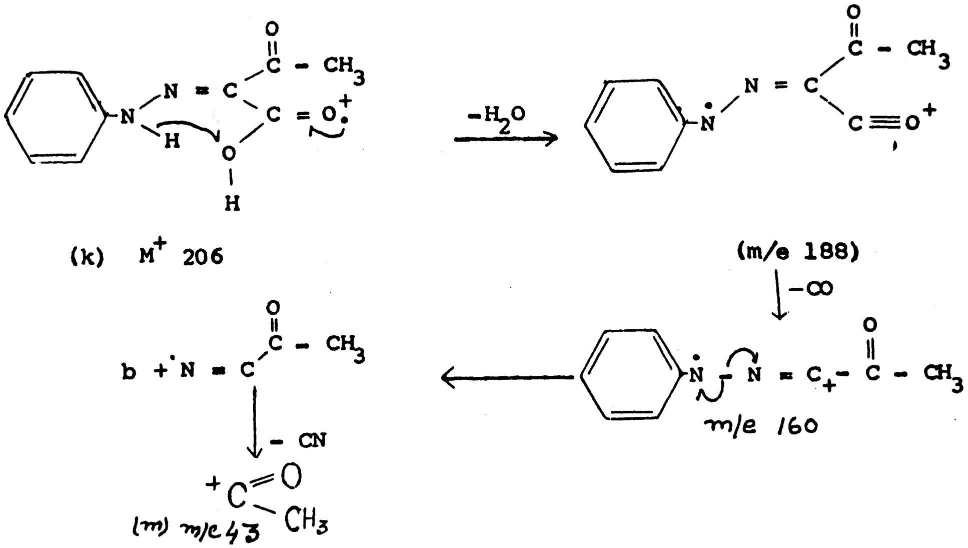
The M^+ appears at 206 amu having relative intensity of 76.87%. In the high resolution electron impact, the observed mass of M^+ was found to be 206.0691 which is in agreement with theoretical mass 206.0692 (Δm 0.0001) and confirming the molecular formula of the product (II) to be $C_{10}N_2H_{10}O_3$. Keto acids show $(M + 1)^+$ at m/e 207 and $(M + 2)^+$ at m/e 208 ions due to the isotopic elements ^{13}C and ^{15}N (A + 1 element) and ^{16}O (A + 2 element) present in them. Again in this case neither $(M - 1)^+$ at m/e 205 nor $(M - 2)^+$ at m/e 204 was observed.

The base peak (m) at m/e 43 (R.I. 100%) could be obtained from (k), M^+ through Scheme-6. The formation of fragment (b) at m/e 91 (R.I. 36.25%) could again be explained by migration of N—H hydrogen to carbonyl with which it is bonded followed by normal bond cleavage of N—N bond. This assignment is further substantiated by the formation of fragment (1) at m/e 70 of R.I. 9.37% which gives the fragment (m) (the base peak at m/e 43 of R.I. 100%) by the loss of HCN.



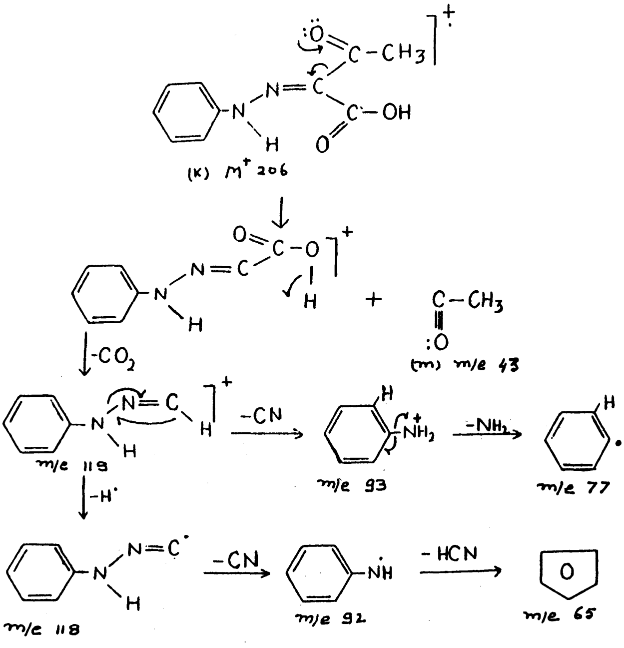
Scheme-6

Alternatively the base peak can also arise due to fragmentation from far end of the molecule containing —COOH functional group (Scheme-7). Loss of mass 18 can be attributed to loss of water from cleavage of —COOH functional group after H-rearrangement.



Scheme 7

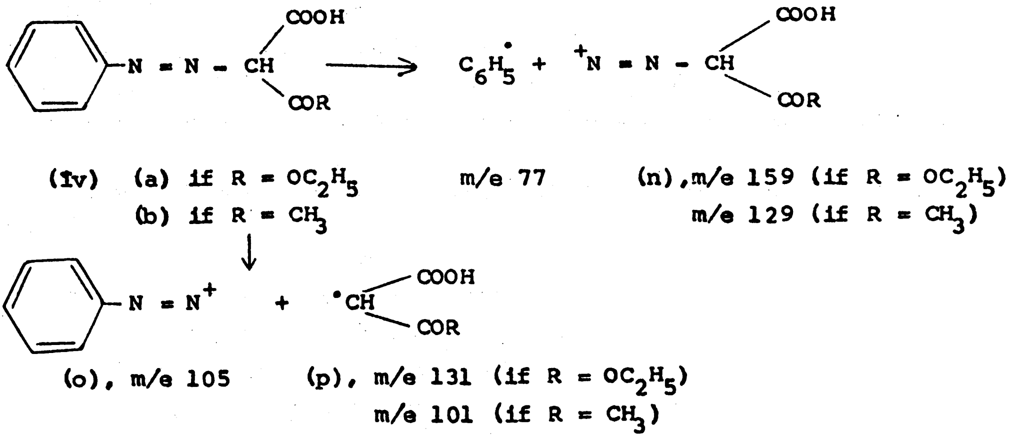
The base peak (m) at m/e 43 may also be due to $CH_3—C≡O^+$ group by cleavage of C—C bond of β-keto methyl function from the molecular ion (Scheme-8).



Scheme 8

Distinction between hydrazo- and azo- structure of these hydrolysed products.

Loss of neutral nitrogen molecule of mass 28 is a common feature of this class of azo compounds[4]. None of the hydrolysed products (I or II) shows $(M-28)^+$ peak due to loss of neutral nitrogen. The ion $(M-28)^+$ may also form by loss of neutral $CH_2{=}CH_2$ from fragmentation of ester function (in case of (I)) but this possibility is also excluded. From this evidence it may be concluded that the hydrolysed products do not exist in the azo form. However, other possible modes of fragmentation, such as one shown in Scheme-9 which occurs by cleavage of C—N bonds on either side of the azo linkage have also to be considered for these products so that the possibility of their existence in the azo structure may be eliminated. Various ions from azo-structure of the hydrolysed products may possibly arise according to charge delocalisation on the two nitrogens.



(IV) (a) if R = OC_2H_5
(b) if R = CH_3

m/e 77

(n), m/e 159 (if R = OC_2H_5)
m/e 129 (if R = CH_3)

(o), m/e 105

(p), m/e 131 (if R = OC_2H_5)
m/e 101 (if R = CH_3)

Scheme-9

The peak (o), at m/e 105 of small intensity, was present in both the compounds. The peaks at m/e 159 for fragment (n) and m/e 131 for fragment (p) were absent in the spectra of (IVa) but lines of small intensity at m/e 129 and 101 due to fragment (n) and (p) respectively were detected in the spectra of (IVb). Although the intensity of ions is low, the fragmentation mode shows that these products may exist in the azo form (IV). These are, however, spectroscopic evidences,[5, 6] to show that hydrazones may undergo thermal isomerisation to azo-compounds prior to fragmentation.

Thus on the basis of arguments put forward above, the hydrolysed products exist in the hydrazo (I and II) rather than the azo form (IV) as the main fragmentation pattern of azo-compounds characterising loss of neutral N_2 molecule of mass 28 was not observed in any case. The R.I. of ions (n), (o) and (p) are very low indicating that isomerization of the hydrazo to azo compounds occurs to some extent in the inlet source of mass spectrometer prior to fragmentation under the probe conditions.

ACKNOWLEDGEMENT

The authors are thankful to Prof. R.J. Ferrier, Victoria University, Wellington, New Zealand for mass spectral measurements.

REFERENCES

1. N. Prasad, R.M. Prasad, A. Sahay, A.K. Srivastava and J. Prasad, *Asian J. Chem.*, **6**, 901 (1994).
2. K.G. Das, P.S. Kulkarni and C.A. Chinchwadkar, *Indian J. Chem.*, **7**, 144 (1969) and references therein.
3. D.G.I. Kingston, H.P. Tannebaum, G.B. Baker, J.R. Dimmock and W.G. Taylor, *J. Chem. Soc. (C)*, 2574 (1970).
4. J.H. Bowie, G.E. Lewis and R.G. Cooks, *J. Chem. Soc. (B)*, 621 (1967).
5. M.P. Grammaticakis, *Bull. Soc. Chi. Fr.*, **14**, 438 (1947).
6. A.V. Cherenova, R.R. Shagidullin and Yu.P. Kitaev, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, **8**, 1555 (1964).

(*Received*: 17 October 1994; *Accepted*: 10 February 1995) AJC-944