

Short Communication

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ELECTRON IMPACT STUDIES ON SOME ETHYL 2,3-DIOXOBUTYRATE-2-PHENYLHYDRAZONES

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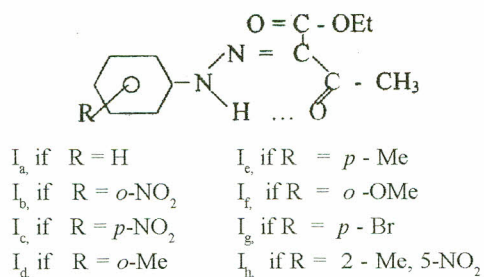
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The present communication deals with the electron impact studies on ethyl 2,3-dioxobutyrates-2-phenylhydrazones and related substituted phenylhydrazones containing electron releasing as well as electron withdrawing substituents on the phenyl nucleus. The formation of base peaks were greatly influenced by the nature of substituent in the phenyl nucleus. Neutral and radical loss from the aromatic substituents were also found to depend upon the nature of groups. These hydrazones undergo thermal isomerisation to azo form which fragments subsequently to daughter ions in accordance with the azo structure having very low relative intensity and Σ %.

Survey of literature (Prasad *et al* 1984; Prasad and Sahay 1993) indicates that the structure of coupling products obtained by the coupling of benzenediazonium salt with active methylene compound has generated in fact so much argument and speculation as hardly any other topic in the whole realm of organic chemistry has done so far since the normal hydrazone (coupling product) is capable of tautomerising to the azo

(Ar-N = N - $\begin{matrix} \text{H} & \text{R}_2 \\ | & / \\ \text{C} & - \text{C} \\ | & | \\ \text{R}_1 & \text{H} & \text{R}_3 \end{matrix}$) and enehydrazine ($\begin{matrix} \text{R}_2 \\ | \\ \text{C} = \text{C} - \text{NH-NH-AR} \\ | \\ \text{R}_1 \end{matrix}$) form.

The present study deals with mass spectral investigations on coupling product (1) which is related to the previous work (Prasad *et al* 1984) Fig 1.



(Scheme - 1)

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The object of the present work is to distinguish between the hydrazono and azo or any other structure. Ethyl 2,3-dioxobutyrates-2-phenylhydrazone was prepared according to the method given elsewhere (Prasad *et al* 1990).

a) Examination of molecular (M)⁺, (M+1)⁺, (M+2)⁺, (M-1)⁺ and (M-2)⁺ and their abundance. In *p*-bromo derivative (I_g), molecular ion peak M⁺ was found to be absent probably due to the fact that the activation energy for decomposition was quite low and no M⁺ ion survive to reach the collector. In all other cases M⁺ appeared as the highest mass ion peak. On comparing the relative M⁺ intensities of *o*- and *p* derivatives (for same substituents), it was found that the ortho-isomer gave M⁺ of lower intensity than that from the corresponding *p*-isomer. It must be due to interaction between the hydrazono group and ortho situated groups which altered the energy profile made the formation of daughter ions more facile and consequently lowers the M⁺ intensity.

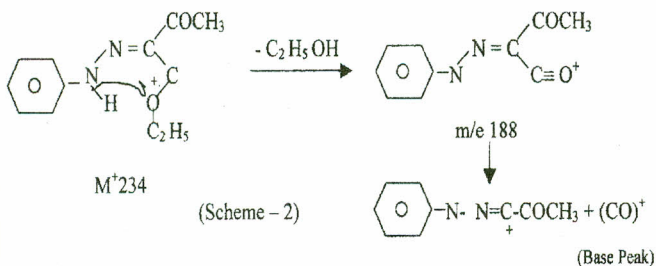
Although the parent compound (I_a) has comparatively low I.P. and expected to form M⁺ ion of high intensity a low value for parent compound was obtained. It may be due to the easy fragmentation to daughter ion [A⁺] because of low energy of activation, a high frequency factor as well as the smaller size of the molecule on which large value of A⁺/M⁺ depends. The molecular ion intensities were found greater in the case of electron releasing groups (I_d , I_e and I_f) compared to electron withdrawing groups (I_b and I_c) proving the contention that electron releasing groups lower the I.P. whereas electron withdrawing groups increase it.

The M⁺ intensity of disubstituted compound (I_h) was less than those of methyl and methoxyl derivatives (I_d , I_e and I_f) but greater than that of corresponding nitro compounds (I_b and I_c). Since the nitro group was present in the meta position with respect to hydrazono group, it has little effect on the delocalisation of electrons. The electron releasing methyl group exert much greater influence on electron delocalisation. The I.P. of the compound was lowered and consequently M⁺ intensity was enhanced.

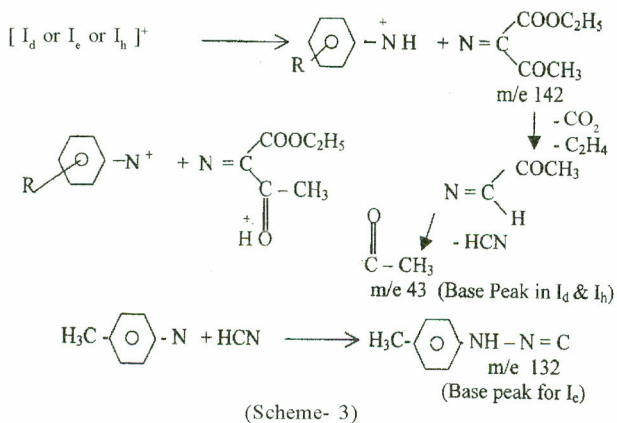
All coupling product show (M+1)⁺ ions due to the isotopic elements ¹³C and ¹⁵N present in them. Few of them (I_a , I_e , I_g and I_h) also show (M+2)⁺ ion due to ¹⁸O element. Except the compound (I_b), neither (M-1)⁺ nor (M-2)⁺ ions was observed presumably due to ready scrambling of N-H proton which was strongly bonded to carbonyl oxygen taking precedence over its loss in electron impact. Presence of (M-1)⁺ ion in compound (I_b) must clearly be attributed to the interaction involving the nitro group and the hydrazono group in ortho position.

b) Formation of base peak. Methoxyl group was more electron releasing than any other group therefore, (I_f) shows

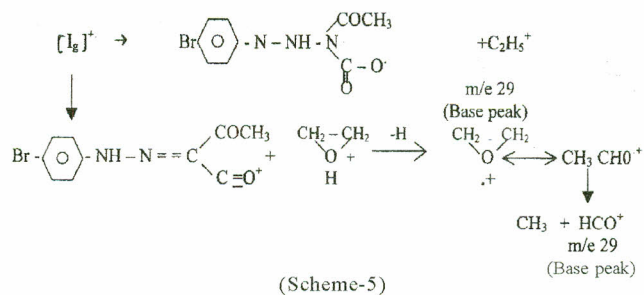
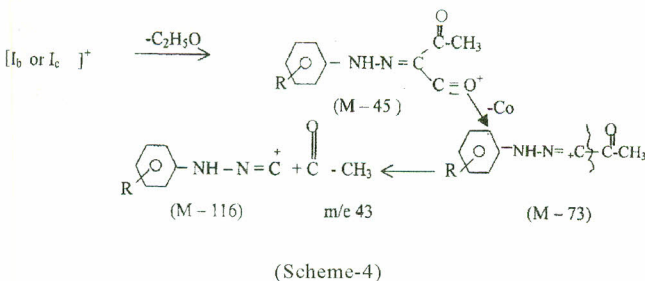
the ion of highest abundance i.e. base peak as the molecular ion. None of the other coupling product show the base peak as the molecular ion. In I_a the base peak was at m/e 28. In this case base arise peak may arise by effective charge localisation at alkyl oxygen followed by H- scrambling from N-H and subsequent α - cleavage (scheme-2).



Coupling products containing electron releasing groups (I_d , I_e and I_h) gave base peak by the cleavage of N-N bond (Williams and Howe 1972) with and without H- scrambling (Scheme- 3). In I_e derivative, base peak at m/e 132 could be due to ion molecule interaction

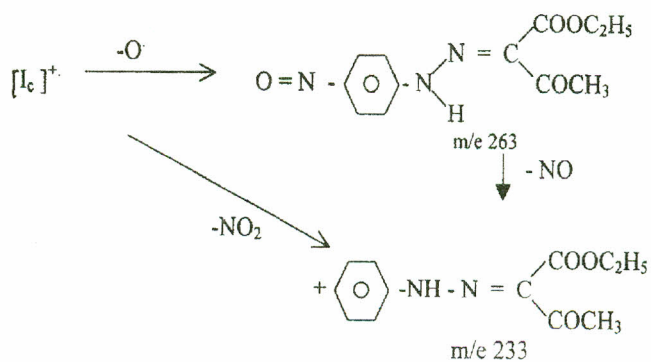


On the other hand, the base peak in the cases of hydrazones containing electron withdrawing group (I_b , I_c and I_g) arose from ester function by cleavage of C-O linkage. In I_b and I_c derivative, the loss of 45 mass unit can be attributed to the loss of ethoxy ion and formation of base peak at m/e 43 takes place (Scheme-4). In I_g derivative, the base peak at m/e 29 may be due to $C_2H_5^+$ ion and / or CHO^+ ion formed from the ethyl ester (Kumar 1986) group by cleavage of C-O bond. (Scheme-5)



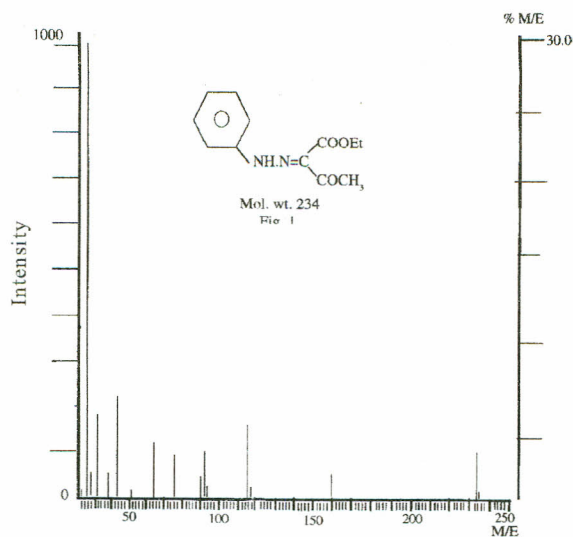
c) Distinction between hydrazo and azo structure. The coupling product I_a to I_n exist in the hydrazono form rather than azo form as the main fragmentation pattern of azo compounds characterising loss of neutral nitrogen of mass 28 ($M-28$)⁺ was not observed (Parasad *et al* 1995) in any case. However in some cases appearance of low abundance peak at $m/129, 157$ and ($M-129$)⁺ ion indicate that isomerisation of the hydrazo to azo compounds occur to some extent in the inlet source of mass spectrometer prior to fragmentation under the probe conditions (Parasad *et al* 1995; Sahay *et al* 2000)

d) Rationalisation of neutral and radical loss from the substituent on aromatic nucleus. NO ($M-CHO$) ($M-CH_2O$) and ($M-CH_3$) fragments were observed in I_f derivative and / or I_d , I_e and I_h derivative indicating that these requires high activation energy compared to N-N cleavage. In I_c derivative, the fragments observed were ($M-O$) at m/e 263 and ($M-NO_2$) at m/e 233 but no fragment at m/e 249 corresponding to ($M-NO$) was found. Thus it appears (Williams and Howe 1972) that neutral NO loss followed after the removal of oxygen from M^+ . In I_b , only ($M-NO_2$) was observed.



Absence of peak at m/e 17 and / or m/e 18 in ortho substituted derivative ruled out the possibility of ortho effect. Failure of ortho effect may be attributed to the involvement of N-H in H-bonding which allows H- scrambling more readily to occur with them rather than with the oxygen of nitro and methoxy.

e) Fragmentation of hydrazono, ester and ketomethyl functions in aliphatic chain of the coupling products. The total ion % of fragments were ($M-45$), ($M-73$). From



Mass spectrum, 3; Sample, 12 DR. Nagendra Prasad; R.T., 0 16; RIC, 961.5; Base Peak, M/E 28.0; Int., 445.9.

Fig 1. Real mass spectra of first compound.

ester (M-116) and from hydrazono (M-142), the favour cleavage from the ester side first electron withdrawing groups in the benzene nucleus and the favour cleavage from the hydrazono side the electron releasing groups in the benzene nucleus. In spite of various rearrangements and H-scrambling effects, the above correlations between different hydrazo and azo compounds is found true.

Keywords: Electron impact, phenylhydrazones, Benzenediazonium salt

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