

Studies on Complex Arylhydrazones, Part XI: Electron Impact Studies on Some Diethyl Mesoxalate Phenylhydrazones

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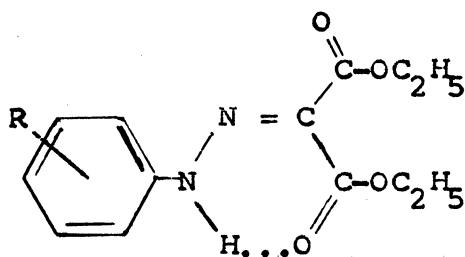
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The potential use of the technique of mass spectrometry as a tool to elucidate the hydrazone structure of diethyl mesoxalate phenylhydrazones has been discussed in this communication. The possibility of their rearrangement to the azo form in the mass spectrometer inlet system at the probe condition has also been examined. Base peak formation by electron impact on diethyl mesoxalate phenylhydrazones was greatly influenced by the nature of substituents in the aromatic nucleus.

INTRODUCTION

The present communication deals with mass spectral studies on diethyl mesoxalate phenylhydrazones (I) obtained by coupling of aryldiazonium salts with diethyl malonate and known as complex hydrazones due to existence of H-bonding between anilino N—H and carbonyl of ester group in the side chain



(I)

where

Ia, if R = H; Ib, if R = *o*-NO₂

Ic, if R = *p*-NO₂; Id, if R = *o*-Cl,

Ie, if R = *p*-Cl; If, if R = *p*-Br,

Ig, if R = *o*-CH₃; Ih, if R = *o*-OCH₃

The object of the present work was, therefore, to subject the complex hydrazones to such studies as these were¹ expected to clearly distinguish between the hydrazone and azo or any other structure.¹

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EXPERIMENTAL

In order to carry out mass spectral investigations on complex hydrazones we particularly chose the coupling products of aryl diazonium salts with diethyl malonate since Fernandes *et al.*² studied such compounds and proposed azo structures for them. The coupling products were synthesised under the same experimental conditions as adopted by Fernandes *et al.*² in order to avoid any change in structural features with change in experimental conditions.

RESULTS AND DISCUSSION

Examination of Molecular Ions (M^+), $(M + 1)^+$, $(M + 2)^+$, $(M - 1)^+$, and $(M - 2)^+$ and Their Abundances

The abundance of the molecular ion depends upon the ionisation potential (I.P.) of the molecule which is related directly to the substituents of functional group present. These groups can stabilise or destabilise the odd electron species by delocalisation of electron and thereby affect the stability of the formed M^+ . The formation of daughter ions (A^+) with ease or difficulty, which is dependent upon appearance potential (A.P.), is yet another factor which is related to the intensity of M^+ . The decreased value of $[A^+]/[M^+]$ is due to increase in A.P. – I.P. whereas enhanced value is on account³ of low A.P. – I.P. The appearance potential is dependent upon the nature of substituents in the molecule. Since the aromatic nucleus and the hydrazono function are common to all the coupling products, differences in the intensities of M^+ of these products are clearly due to different substituents present.⁴

Although the parent compound (Ia) has comparatively low I.P. and so expected to form molecular ion of high intensity, a low value for this is obtained. This may be due to its easy fragmentation to daughter ion (A^+) because of low activation energy, a high frequency factor as well as the smaller size of the molecule on which large value of A^+/M^+ depends. In Ig and Ih, the molecular ion abundances are quite high probably due to the fact that the I.P.s of the molecules are decreased in these cases as both methyl and methoxy substituents are electron-releasing groups. In case of Ib and Ic the M^+ abundances are less than those of Ig and Ih. The nitro group being a powerful electron-withdrawing group raises the I.P. of the molecule and thus lowers the intensities of M^+ in these compounds. The M^+ of If is found to have the highest intensity among all the compounds examined. The I.P. of bromobenzene is lower than nitro-substituted phenyl compounds and a little higher than methoxy-substituted phenyl compounds. It, therefore, would be expected to give more intense M^+ than Ib and Ic but a feebler peak than Ig and Ih on the basis of I.P. values. The greater intensities of M^+ peak observed in the case of If must, therefore, also depend upon its stability, *i.e.*, the rate of its decomposition into daughter ions. Since bromine is essentially an electron withdrawing group it is expected to impede the process of fragmentation by cleavage of the N—N bond. The large size of the bromine atom as well as the increased C—Br distance, however, reduce considerably the mesomeric effect of

bromine and hence its decomposition into daughter ions. Thus reactions governed by higher A.P. largely determined the intensity of M^+ in this case.

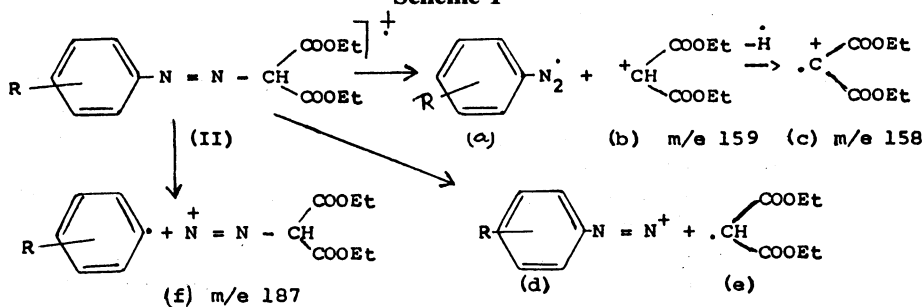
As compared to If, Id and Ie show only very small M^+ intensities although the I.P. of chlorobenzene is slightly higher than bromobenzene. Cl, being smaller in size than Br, is capable of causing delocalisation of electrons more effectively. The effect is felt on the hydrazono group and the appearance potential for the formation of daughter ions by cleavage of the N—N bond is lowered. M^+ intensity in this case is therefore decreased. Moreover, H loss is more evident in these compounds as $(M-1)^+$, $(M-2)^+$ and even $(M-3)^+$ ions are formed by loss of 1, 2 and 3 hydrogens only in these cases and in none others. On comparing the relative M^+ intensities of Id and Ie, it is found that *ortho*-isomer gives M^+ of lower intensity. This must be due to interaction between the hydrazono groups and *ortho*-substituted groups which alters the energy profiles and makes the formation of daughter ions more facile and consequently lowers the M^+ intensity as noticed earlier also with other *ortho*-substituted derivatives.

All the coupling products show $(M+1)^+$ and $(M+2)^+$ ions due to the isotopic elements ^{13}C and ^{15}N ($A+1$ element) and ^{16}O ($A+2$ element) present in them. In case of chloro (Id and Ie) and bromo derivatives (If) isotopic clusters in ratio 3:1 and approximately 1:1 respectively were observed. The molecular formulae of the coupling products were calculated from the intensities of M^+ , $(M+1)^+$ and $(M+2)^+$ ions and these were in agreement with the theoretical value.

Distinction between Hydrazo- and Azo- Structures of the Coupling Product

Loss of neutral nitrogen molecule of mass 28, accompanied by skeletal rearrangement is a common feature of this type of azo compounds.⁵ None of the coupling products shows $(M-28)^+$ peak due to loss of neutral nitrogen. The ion $(M-28)^+$ may also form by loss of neutral $\text{CH}_2=\text{CH}_2$ from fragmentation of ester function but this possibility is also excluded. From this evidence it may be concluded that the coupling products do not exist in the azo form. However, other possible modes of fragmentation (Scheme-1) have also to be considered for the coupling products so that the possibility of their existence in the azo structure may be eliminated.

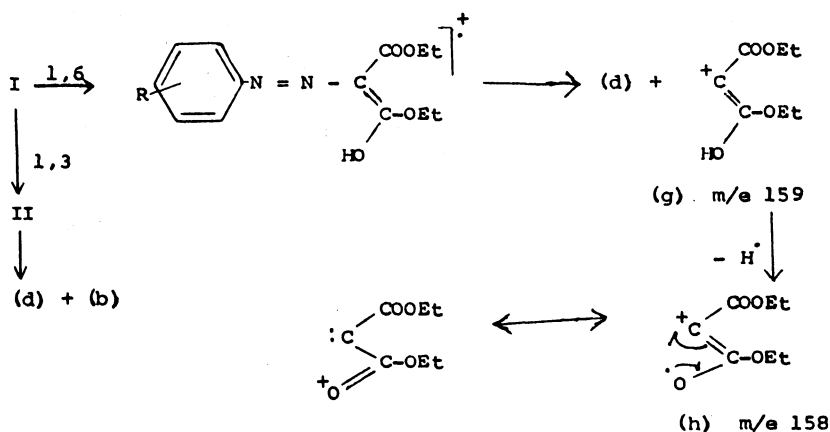
Scheme-1



The peak at m/e 159 (b) of small intensity was found in all cases accompanied by a peak at m/e 158 (c). In case of Id and Ie the peak (b) was not observed but peak (c) were present in both the compounds. The peak (f) at m/e 187 which could result by α -cleavage of the phenyl C—N bond was absent in the spectra of all the coupling products, but lines of small intensity due to fragment (d) were detected.

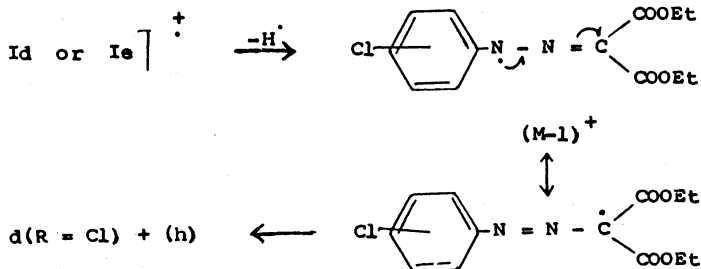
Although the intensity of ions is quite low, the fragmentation mode (Scheme-1) shows that the coupled products may exist in the azo form (II). These are, however, spectroscopic evidences^{6,7} to show that hydrazones may undergo thermal isomerisation to azo compounds prior to fragmentation. H-scrambling in the coupled products could be either 1,3- or 1,6-centred (Scheme-2).

Scheme-2



The absence of any peak at m/e 159 but its presence at m/e 158 in the case of Id and Ie must clearly be due to the formation of $(M-1)^+$ primarily by loss of hydrogen from the N—H group, followed by C—N cleavage (Scheme-3).

Scheme-3

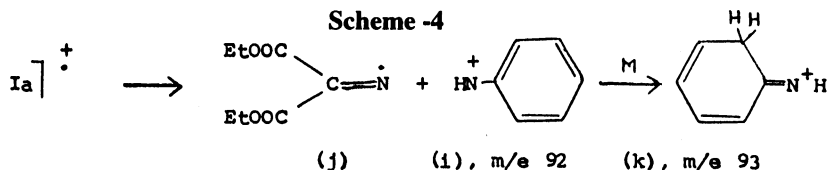


Thus on the basis of arguments put forward above, the coupling products exist in hydrazo (I) rather than the azo (II) form as the main fragmentation pattern of azo compounds characterising loss of neutral N_2 (mass 28) was not observed in any case. Moreover, the parent ion does not fragment to give (f) and the abundance of ions (b), (c), (g) and (h) is very low indicating that isomerisation of hydrazo

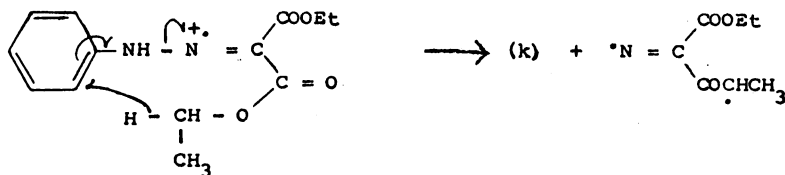
to azo compounds occurs to some extent in the inlet source of mass spectrometer prior to fragmentation under the probe conditions.

Examination of the Formation of Base Peak

Base peak formation by electron impact on (I) was greatly influenced by the nature of substituents in the aromatic nucleus. The base peak of parent compound Ia is at m/e 93 which can form either by simple cleavage to form the ion $C_6H_6N^+$ followed by reaction with the molecule (Scheme-4) or by H-scrambling in the molecular ion followed by N—N cleavage (Scheme-5).

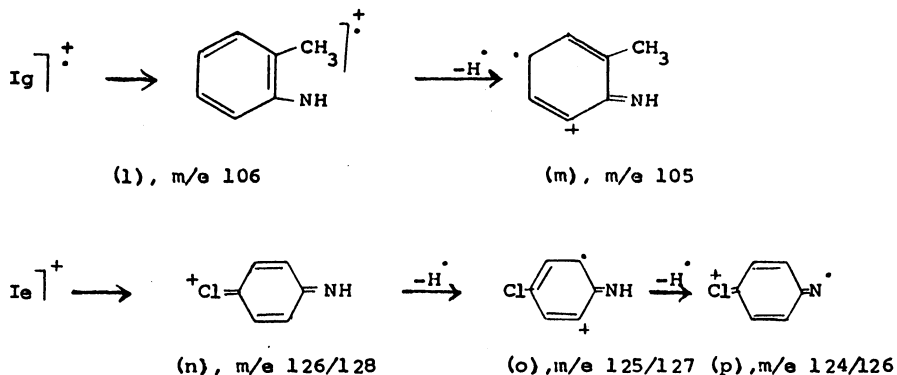


Scheme-5



Electron releasing groups such as Cl, CH_3 and $-OCH_3$ gave base peak by the cleavage of N—N bond of hydrazo group, to give $(M-172)^+$ and subsequent loss of H-atoms (Scheme-6).

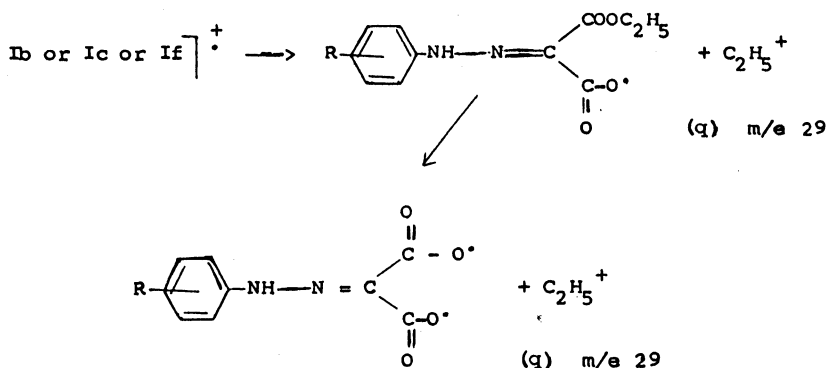
Scheme-6



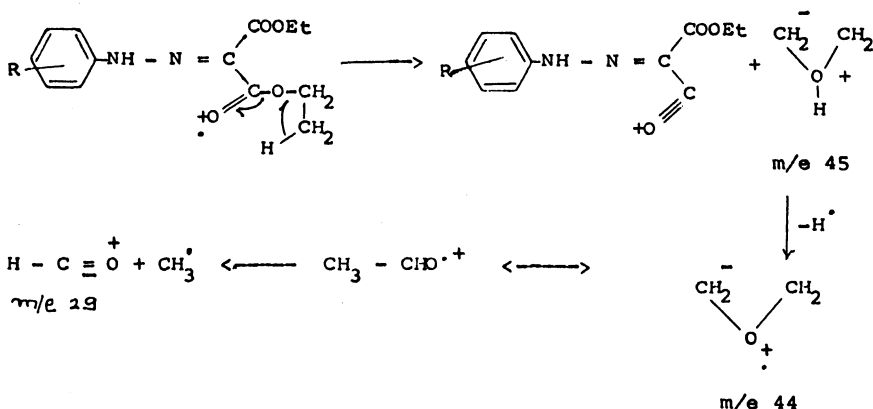
The base peak in the case of electron withdrawing groups ($-NO_2$ and $-Br$) arose from ester function either by direct cleavage leading to $C_2H_5^+$ (m/e 29)

(Scheme-7) or through loss of $C_2H_5O^+$ and subsequent formation of CHO^+ at m/e 29 (Scheme-8).

Scheme-7

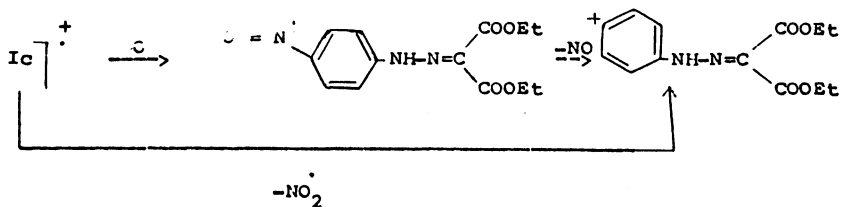


Scheme-8



Rationalisation of Neutral and Radical loss from the Substituents in Aromatic Nucleus

For Ic, the fragments observed were $(M-O)$ at m/e 293 and $(M-NO_2)$ at m/e 263 but no fragment at m/e 279 corresponding to $(M-NO)$ was found. It appears that neutral NO loss follows after the removal of oxygen from the molecular ion.



In case of Ib, neither the loss of $(M-O)$ nor of $(M-NO)$ was observed. Absence of any $(M-OH)$ peak in this case indicates clearly that the *ortho*-effect,

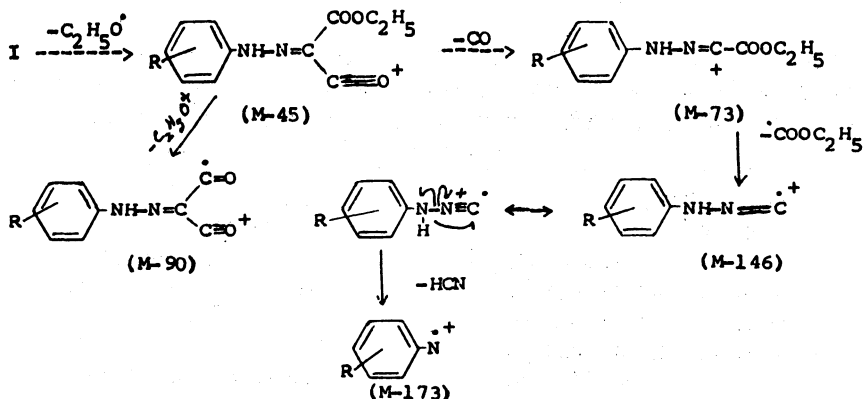
as observed with *o*-nitroaniline and other *o*-nitro substituted compounds is not operating here.

Loss of NO_2 is a significant process⁸ and involves lower energy than the cleavage at N—N bond. However, the loss of mass 46 can also be attributed to the loss of EtOH from the ester function after H-transfer and indeed this mode of fragmentation is also taking place because the ion further produces fragments which are consistent with its structure and (M - 46) ion is present in the case of the other coupling products also. Failure of Ib to exhibit *ortho*-effect may be attributed to the involvement of N—H in H-bonding both with N—O and oxygen function of the ester carbonyl or with alcoholic oxygen part which allows H-scrambling more readily to occur with them rather than with the oxygen of the nitro group. It gave (M—Br) ion. The relative abundances of these ions were low. No neutral and radical loss in cases of compounds containing electron-releasing groups was observed proving the contention that cleavage at N—N bond of the hydrazono group is a lower energy process than the occurrence of neutral and radical loss. Neither (M—H) nor (M—CH₃) ions were observed in methyl derivative nor (M—CHO), (M—CH₂O) and (M—CH₃) were found in the case of methoxy derivative which are the characteristic modes of fragmentation of aromatic methyl and methoxy substituted compound.

Fragmentation of Hydrazono and Ester Functions in the Aliphatic chain of the Coupling Products

The fragmentation from hydrazono and ester functions could be rationalised as far as possible with the help of useful guides.^{9, 10} Fragmentation from the two ester groups depends upon effective charge localisation on either carbonyl oxygen or alkyl oxygen and also to some extent on imino nitrogen ($-\text{N}=\text{C}<$). Loss of mass 45 due to ethoxy radical and appearance of (M - 45) peaks are observed in all the cases except Ia where the abundance is very low. Effective charge localisation at ester carbonyl followed by α -cleavage (Scheme-9) gives this ion.

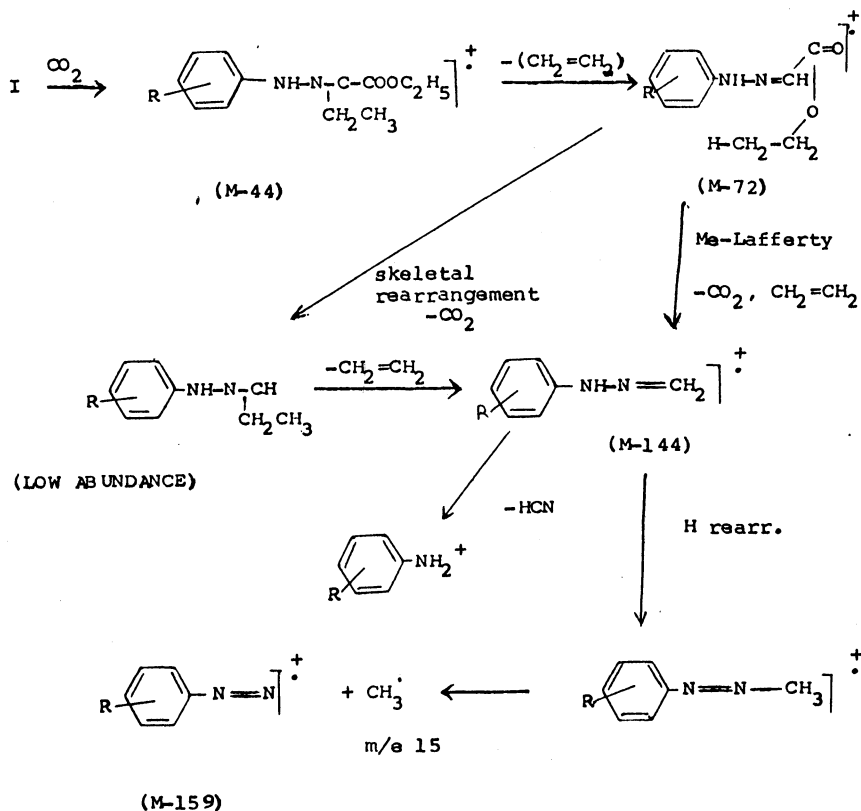
Scheme-9



The ion at m/e ($M - 90$) which is expected to form by loss of two ethoxy groups has been observed in appreciable intensity in Ic although a tiny peak at ($M - 90$) is present in the bar graph of the remaining cases. The ions at m/e ($M - 45$) and ($M - 73$) are confirmed by the presence of isotopic clusters in the cases of chloro derivatives (m/e 253/255 in the ratio 3:1) and the bromo derivative (m/e 297/299; 1:1). The peak at ($M - 146$), which is present in all cases, arises by the loss of the second ethoxy carbonyl radical from ($M - 73$) ion. The intensity of these peaks furnishes sufficient evidence against the ene-hydrazine structure¹ of these coupling products. The peak at ($M - 173$) is also present in all cases.

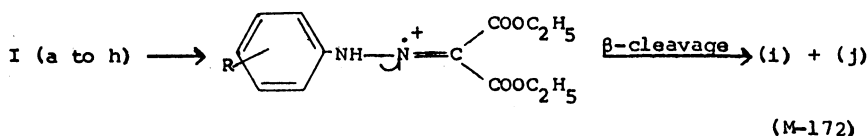
The peaks at moderate intensities at ($M - 44$) and ($M - 72$) are due to skeletal rearrangements of the molecular ion and are formed by localisation of charge on imino nitrogen (Scheme-10). Skeletal rearrangement accompanied by exclusion of CO_2 and the migration of the alcohol group in α,β -unsaturated esters are fairly general processes.¹¹ The ion ($M - 72$) can undergo a second skeletal rearrangement to form ($M - 116$) and ($M - 144$) ions, the latter ion can also arise by McLafferty rearrangement. This further undergoes fragmentation to give an ion at ($M - 171$) by loss of neutral HCN. The ion ($M - 159$) appears as a result of 1,4-H-rearrangement giving an intermediate azo compound followed by loss of CH_3 from the latter.

Scheme-10



It is necessary to point out here that the formation of (M - 159) ion has been postulated to be due to the cleavage of the fragment Ar—N=N arising as a result of rearrangement of the coupling products. The above route of fragmentation is in conformity with the hydrazo-structure for the coupling products.

Fragmentation of hydrazone group depends upon effective charge localisation at the imino nitrogen atom.



From a perusal of the relative intensity and total ion percentage of fragments (M - 45), (M - 73) and (M - 146) from the ester function and (M - 172) from the hydrazone function it is evident that electron-withdrawing groups in the benzene nucleus favour cleavage from the ester side first while electron-releasing groups favour cleavage from the hydrazone group. In spite of various rearrangements and H-scrambling effects the above correlation is found to hold true.

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