



## ELECTRON IMPACT STUDIES ON SOME ARYLHYDRAZONES

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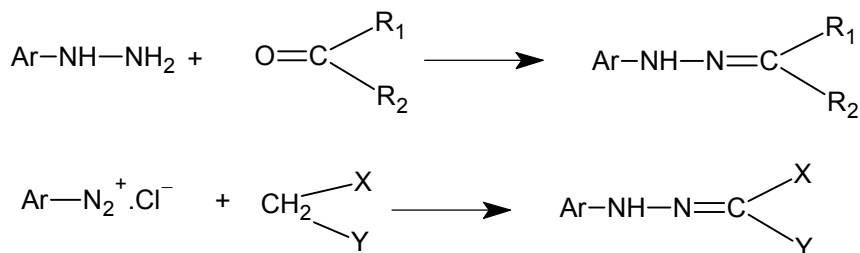
### ABSTRACT

The versatile technique of mass spectrometry could be used successfully in resolving the controversy with regard to the structure of diethyl mesoxalate phenylhydrazones upon which electron impact studies were not made earlier. Ten compounds were prepared. The objective of the work was to end the controversy regarding azo and hydrazo structure.

**Key words :** Electron impact, Arylhydrazones, Coupling, Fragmentation

### INTRODUCTION

Condensation product of aldehydes and ketones with arylhydrazines and coupling products of aryldiazonium salts with active methylene compounds are called arylhydrazones.



Where X and Y are activating groups.

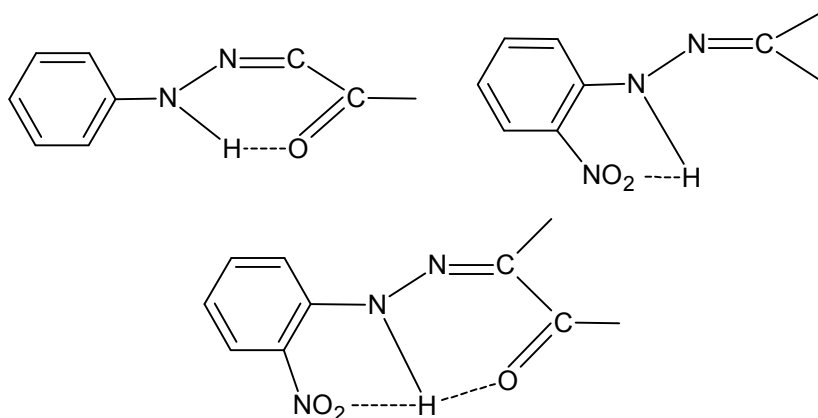
These hydrazones find important use as intermediates in the synthesis of various types of heterocyclic compounds; many of them are physiologically active compounds. In

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addition hydrazones have gained importance in analytical chemistry and chemotherapy.

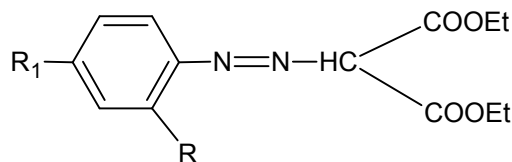
In complex hydrazones, hydrogen of N-H is bonded to suitable substituent either in the side chain or O- to the hydrazone group.



In both classes of hydrazones, simple and complex, the structural controversies, whether they exist in normal hydrazone, azo, enehydrazine or azoenol, have been debated extensively. Extensive studies on structure elucidation of arylhydrazones have been done<sup>1-11</sup>. In case of hydrazones of symmetrical and unsymmetrical ketones and aldehydes, the structural controversies as well as their stereochemistry have been settled by Karabatsos<sup>12</sup> by <sup>1</sup>H NMR in favour of hydrazones.

In case of complex hydrazones, extensive studies both; chemical and physicochemical studies have been made. Spectral work includes IR, UV, <sup>1</sup>H NMR, <sup>15</sup>N NMR and X-ray crystallography and <sup>13</sup>C NMR study was done in this laboratory with a view to find the structure of such complex hydrazones. Bulk of these evidences point in favour of hydrazone structure.

Fernandes et al.<sup>13</sup> couples o-and p-nitrobenzene diazonium salt with diethylmalonate to utilize the coupled products for the synthesis of cinnolines and assigned azo-structure to coupled products on inadequate evidences.

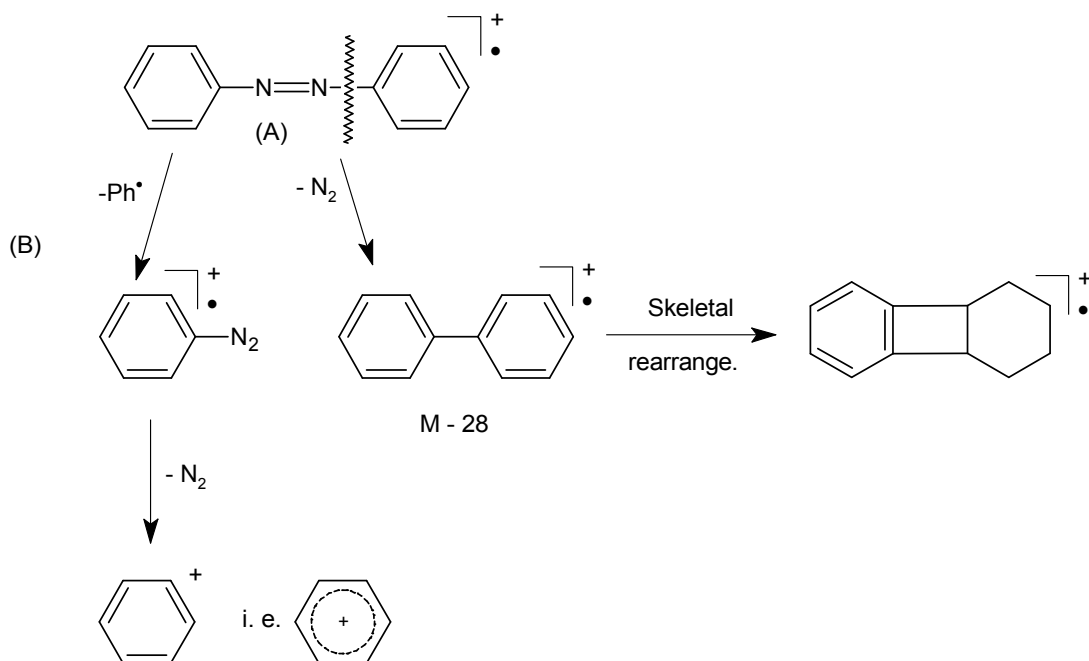


Mass spectrometry technique has been applied to simple hydrazones, oximes semicarbazones, anils etc. Hence, we thought it appropriate to apply this technique to pin point the structure of the coupling products of aryl diazonium salt, with diethyl malonate with different substituents, both; electron releasing and withdrawing groups in aromatic nucleus.

## EXPERIMENTAL

Ten such compounds were prepared following the procedure of Fernandes et al.<sup>13</sup>, who proposed the azo structure of o-and p-nitro derivatives.

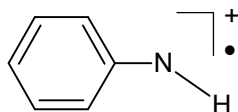
Azo compounds are characterized by mass loss of  $N_2$  due to  $[M - 28]^+$  peak.



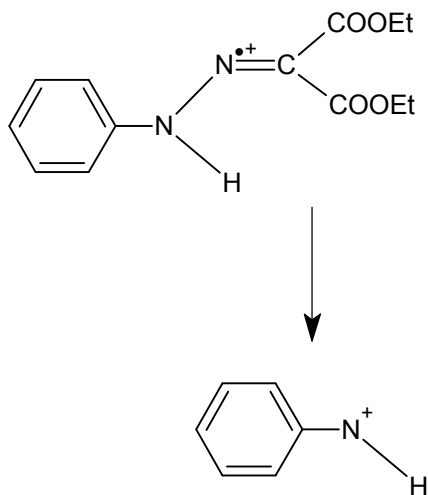
## RESULTS AND DISCUSSION

No M - 28 peak was observed in any of the coupling products excluding the possibility of the coupling products existing in azo form. However, fragments of very low intensities taking the path B were observed from the intensities and total ion % of these fragments and, hence it can be deduced that the coupling products undergo rearrangement to some extent in azo form in mass instrument. Examples of thermal isomerization of

hydrazone to azo form are known.



Anilino fragment in all the coupling products are formed in appreciable abundance proving that hydrazone group must be present as such in all the coupling products.



Moreover normal fragmentation from two ester groups including skeletal rearrangement characteristics to  $\alpha$ ,  $\beta$ -unsaturated ester was observed proving that two –COOEt groups are intact.

## CONCLUSIONS

Adding the two observations together, one can safely conclude that the coupling products of aryldiazonium with diethylmalonate exist in hydrazone form and the technique of mass spectrometric analysis can be applied to find out the structure of such type of complex hydrazones.

Thus, it can be concluded that the hydrazone structure exists for the coupling products as evidenced by electron impact studies. These compounds undergo some rearrangement but the intensity of fragments obtained by such rearrangement is very low and

does not hamper in any way in pinpointing the structure.

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