



MASS SPECTROSCOPY OF SOME COMPLEX ARYLHYDRAZONES

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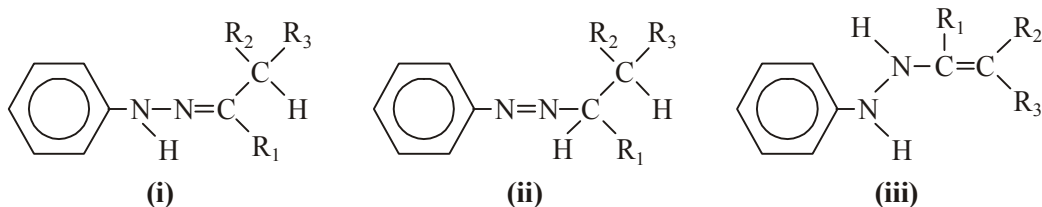
ABSTRACT

The technique of mass spectrometry could be used in resolving the controversy regarding structure of some complex arylhydrazones. The objective of the work was to resolve the controversy regarding azo and hydrazo structure of some complex arylhydrazones.

Key words: Arylhydrazones, Fragmentation, Coupling products

INTRODUCTION

The complex arylhydrazones are obtained by reacting aryldiazonium salts with active methylene compounds (acetylacetone, in this case), conventionally represented in the hydrazone form; however, these are also reported as isomeric azo form (II) or ene-hydrazine form (III).



EXPERIMENTAL

Ten such compounds were prepared by diazotizing o-, m- and p- substituted benzene and then coupled with acetylacetone.

Literature survey concerning mass spectral behaviour of azo compounds, containing the azo grouping, showed that they undergo typical fragmentation and invariably lose a neutral nitrogen molecule of mass 28^{1,2}.

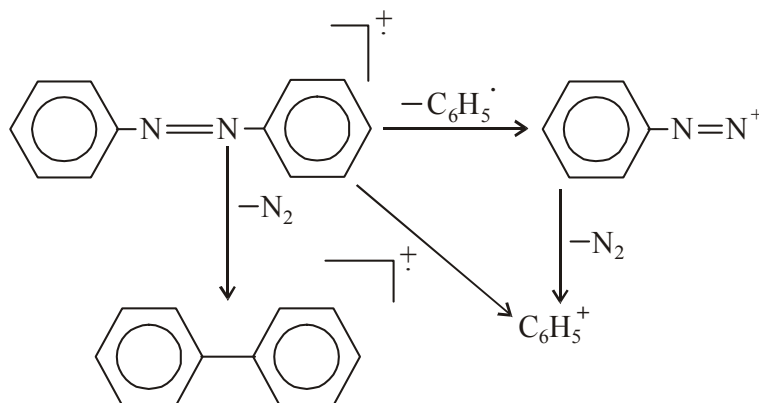


Fig. 1

A neutral molecule is lost in each of the fragmentation pathway. The decomposition product after loss of N₂ molecule undergo further changes after rearrangement and bond cleavages.

RESULTS AND DISCUSSION

None of our coupling products gave (M - 28)⁺ peak indicating initial loss of N₂ molecule. From this evidence, it could be concluded that the coupling products i.e. the complex hydrazones did not possess the azo structure and -N=N- grouping was not present in them.

As already seen, loss of N₂ molecule from the azo structure occurs by simultaneous cleavage of C-N bond on both sides of the -N=N- grouping. If we consider cleavage of C-N bond to occur on only one side of the -N=N- grouping, then azo compounds could undergo fragmentation without losing N₂; a possible fragmentation mode for the coupling product in the azo form could be as follows (Fig. 2).

The above mode of fragmentation would initially give rise to several ions viz. (A), (B), (C), (D) etc., which may undergo further cleavages involving breaking of C-N bond on either side of -N=N- grouping. Absence of these ions in mass spectra of the compounds would easily eliminate such possibilities. The bar graph and print out data of the ten such compounds were examined and it was found that all the coupling products gave peaks though

of small intensities with m/e values 127 and 99 corresponding to ions (A) and (B). Only the amino compounds did not show any peak of m/e 127, although it had a peak at m/e 99.

Again all the compounds gave peaks for the respective (D) ions of small intensities with the exception of p-nitro compound. Only a few compounds gave m/e peaks at 98 corresponding to the ion (C). Isotopic clusters in the case of p-bromo and p-chloro compounds substantiated the structure of (D) ions whereas the p-bromo compound gave peaks with m/e 183 (4.5%) and 185 (4.0%) and p-chloro had peaks with m/e 139 (4.8%) and 141 (1.6%).

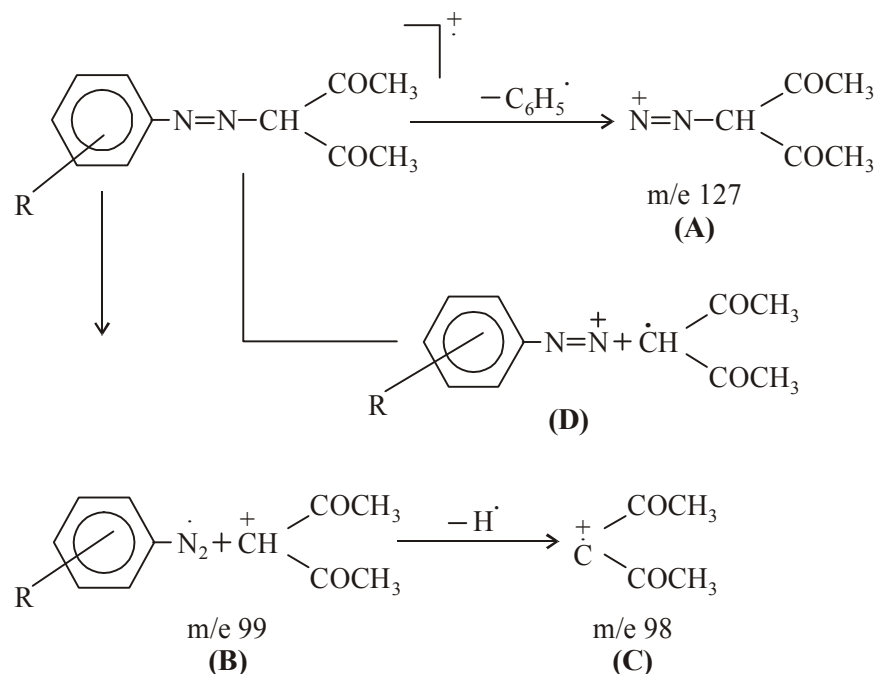


Fig. 2: Fragmentation pattern

CONCLUSION

The foregoing evidence thus pointed to the presence of azo grouping, -N=N- in the coupling products. The apparent anomaly in evidences was resolved by further literature survey. There is spectroscopic evidence to show that hydrazones may undergo thermal isomerization to azo compounds i.e. change from -NH-N=C to -N=N-CH, prior to fragmentation³. Simple phenyl hydrazones have been found to undergo thermal rearrangement to the azo form under electron impact⁴, which then fragment by cleavage of

C-N bond on either side of the azo linkage. The rearrangement is a facile, low energy process and occurs much below 70 eV.

It was, therefore, reasonable to argue that our coupling products which are in the hydrazono form, also undergo similar rearrangement to the azo form and then behaving like azo compounds, suffer cleavage of the C-N bond on either side of the $-N=N-$ grouping.

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