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EIMS STUDIES OF ACETOPHENONE DERIVED AZINES : PART 1*

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ABSTRACT

Many studies have shown that azines are good synthones for obtaining the heterocyclic compounds like pyrazoles, purines and pyrimidines etc. A series of acetophenone derived azines were prepared and EI mass spectral studies were carried out. Formation of cyclic intermediates are strongly indicated for a number of fragments produced. Fragmentation patterns for most of the major ions are discussed. These pathways involve the initial loss of hydrogen and/or methyl group with subsequent migration of various groups like phenyl or methyl. The ortho nitro compounds undergoes the loss of the nitro group prior to the cyclization and migration of various groups. Vapor - phase FT-IR were recorded and selective data are included in our report.

INTRODUCTION

Recent studies [1-4] have shown that azines can be good and reliable intermediates and can be easily synthesized and used as synthones for the heterocyclic compounds like pyrazoles, purines and pyrimidines and these in turn are used for new drug synthesis. Some of the above mentioned targets were studied in two of our previous works [5,6]. We have initiated a program for the synthesis of acetophenone derived azines. We report the synthesis and EI mass spectral analysis of acetophenone azine derivatives.

RESULTS AND DISCUSSION

Earlier mass spectral studies have shown that electron impact (EI) induces hydrogen, alkyl and aryl migration within the molecule in the azines [7-10]. In our series of compounds, compound **(I)** has been investigated[7,9]

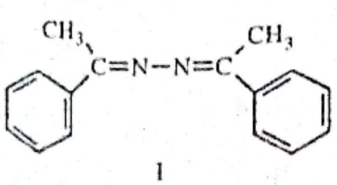
. It has been shown to fragment via the alkyl, aryl migration through the plausible aromatic cyclization (Scheme A or Scheme B). The spectra and the fragments of compound **(I)** reported in the literature[1] agree with the one we obtained with our instrument.

The compounds **(II-III)** showed some unique features in the fragmentation pattern. Both have M-CH_3 as the base peak and the subsequent loss of CH_3CN. loss of halogen only is not indicated. However, both of them show the loss of Ar-X where X= Cl and Br (m /z 111/113 for compound **II** and m/z 155 /157 for compound **III**).

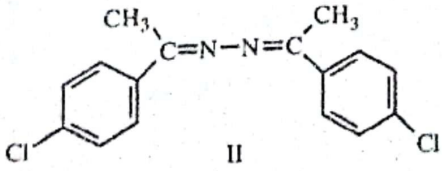
Both of these compounds also fragment between the azine nitrogens and form the m/z 152/154 fragment in **II** and m/z 196/198 fragment in **III.**

Compound **IV** showed a familiar fragmentation pattern with the formation of M-CH_3, M-CH_3-CH_3 as well as M-CH_3CN fragments. Like compounds **II** it also fragments between the azine nitrogens m/z 148). The m/z 107 is probably the p-methoxyphenyl .

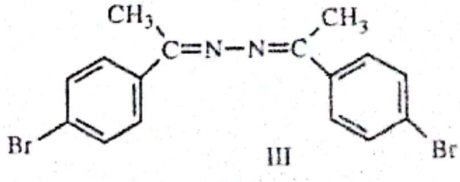
These compounds are mixed azines and contain different side chains on each side of the azine nitrogens. We observed some additional features in the fragmentation pattern. Compounds **V** has a unique feature of having m/z 42 as the base peak. As the molecule has small alkyl groups attached to one side of the azine linkage, the hydrogen, alkyl migration within the molecule is perhaps easier. The fragmentation does not seem to go through most of the cyclization Schemes A or B but probably proceeds by the following pathway:



I



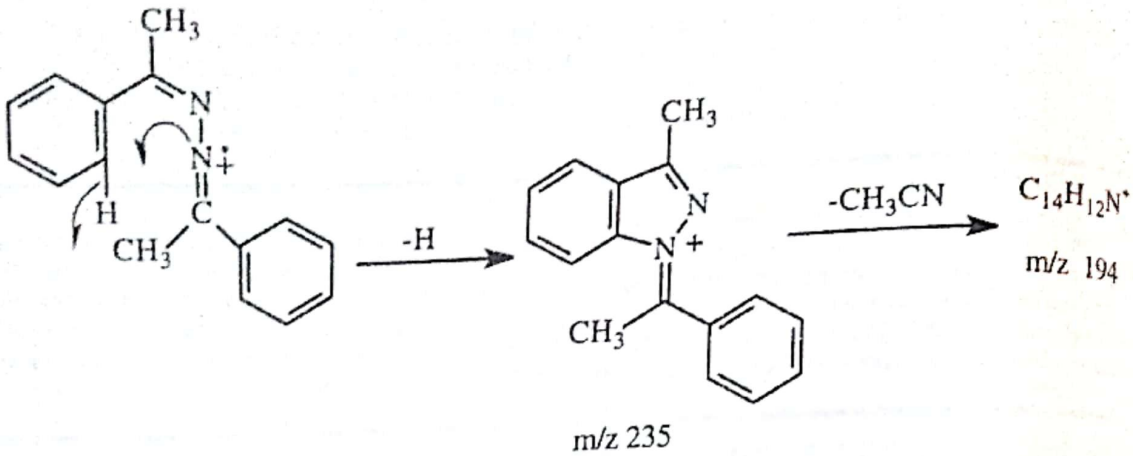
II



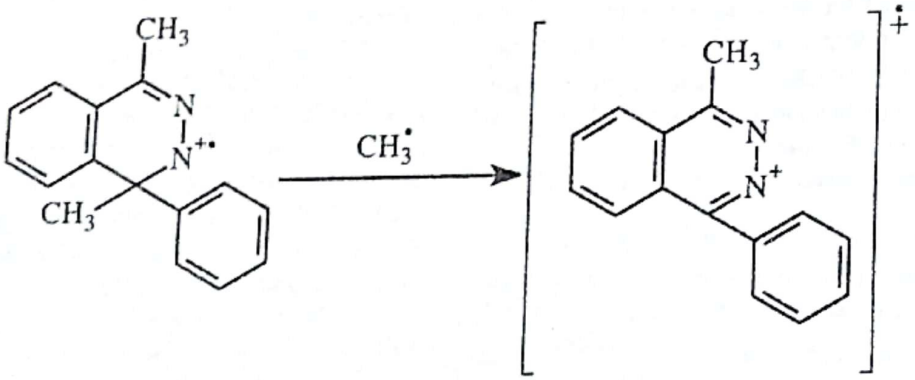
III

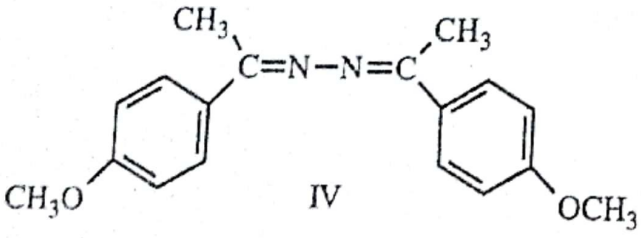
*The present investigation has been presented in the 4th Ibn Sina international Symposium On Pure and Applied Heterocyclic Chemistry, 19-22 December, Cairo (1992) PIII a-7, page 156.

Scheme A

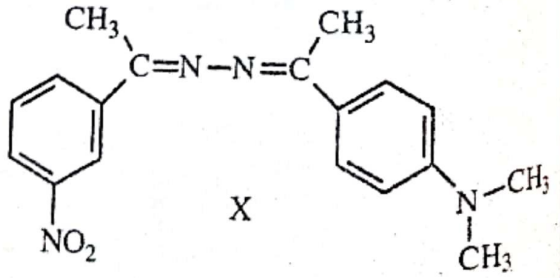


Scheme B





IV



X

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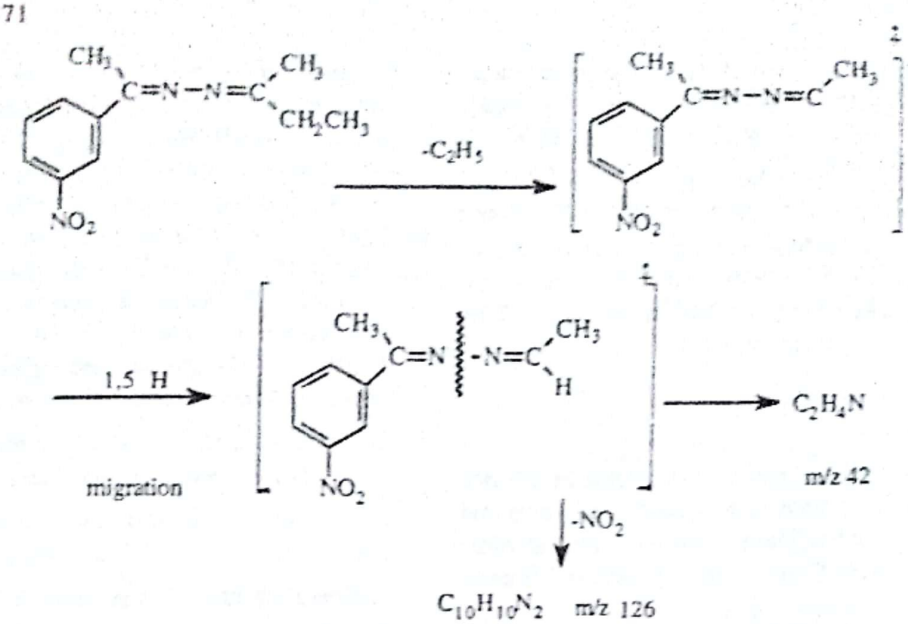


Possible pathway for compound V fragmentation:

In addition, the usual M-CH_3, M-CH_3CN fragments are present while M-$C_2H_5$is also observed. The presence of m/z 117 is due to the phenylacetonitrile fragment.

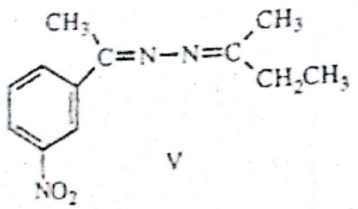
Compound VI: It has the usual M-CH_3 as the base peak and M-CH_3, CH_3 . CN fragment is also formed. Thecompound breaks between the azine nitrogens and m /z 56 is due to the formation of C_3H_6N m/z 158 is probably due to the M-CH_3CO_2 fragment; m/z 117 which is again due to the formation of phenylacetonitrile fragment.

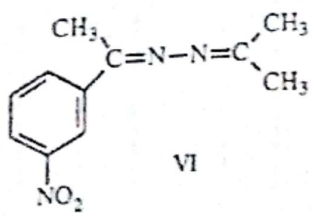
Compound VII: The spectra of this compound shows complete absence of M-1. This perhaps indicates that the compound is not fragmenting through the aromatic cyclization Scheme A or through Scheme B.

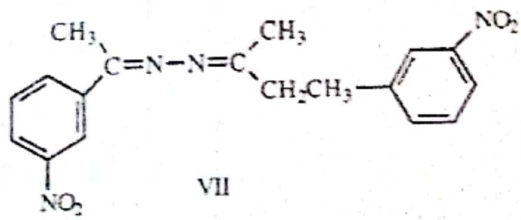
The compound probably fragments between the azine nitrogens (m/z 163) and immediately loses the NO2 group and forms m/z 117 which is the phenylacetonitrile fragment.

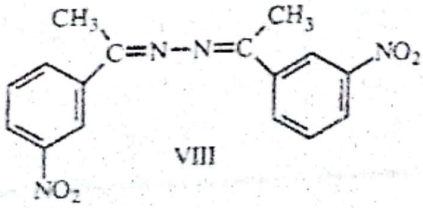
The fragmentation of these two compounds present a good case of comparison . Compound **VIII** has a meta substituted nitro group whereas **IX** has the nitro group as o-substituded. In **VIII**, the case peak is M-CH_3 and the presence of m/z 270 indicates the subsequent loss of M-CH_3NO_2 . Again the presence of m/z of 163 indicates that the molecule fragments between the azine nitrogens.

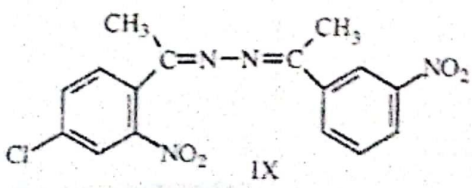
Compound IX is unique in more than one way. The complete absence of the molecular ion, M-1 and M-CH_3 fragments is indicative that the compound perhaps fragments by a different pathway. M-NO_2 (m/z 280) is the first peak in the spectra. Also m/z 163 is totally absent indicating that the molecule doesn't fragment between the azine nitrogens. The absence of the molecular ion and presence of the M-NO_2 fragment has been shown to be the pattern for ortho substituted nitro compounds [11]


V


VI


VII


VIII


IX

Compound X : This compound shows the presence of the molecular ion which is also the base peak Fragmentation proceeds with the formation of M-CH_3(m/z 309) M-C_3H_6 (m/z 294) as well as M-CH_3NO_2 (m/z 263) .The presence of m/z 120 is due to the formation of the N,N-dimethylaniline fragment. Presence of m/z 161 indicates that the molecule fragments between the azine nitrogens. The phenylacetonitrile fragment (m/z 117) is absent.

EXPERIMENTAL

A) Synthesis:

Typically, 1 mmole of acetophenone in ethanol was mixed with 0.5 mmole of anhydrous hydrazine and heated for ten minutes. The yellow (different shades) crystals obtained were filtered and recrystallized from in ethanol.

In the case of o-nitroacetophenone, the mixture was refluxed for three hours followed by the same work-up as above.

m-Nitroacetophenone hydrazone: 1 mmole of m-nitroacetophenone in Eton 10 ml ethanol was mixed with 1 mmole anhydrous hydrazine.

The mixture was heated for thirty minutes followed by the same work -up as before.

Mixed azines (azines where different functional groups are attached on each side of the azines nitrogens): The corresponding ketones (0.1 mmole)was heated with 0.1 mmole was heated with 0.10 mmole 3-nitroacetophenone hydrazones and anhydrous solution of hydrazine in ethanol for ten minutes. The same work-up as mentioned above.

B) Instrumentation:

Mass spectra were obtained one Hewlett -Packard Quadruple mass spectrometer (model 5970) interfaced with Hewlett- Packard gas chromatograph (model 5890, Series II) which in turn is interfaced with Hewlett- Packard Fourier- transform infrared spectrometer (model 5970A). An autosampler is attached to the gas chromatogrph to run the multiple samples. Mass spectrometer ion- source temperature is kept at 200°C and at a constant voltage of 70 e.v.

Gas chromatograph: Injection port temperature is kept at 250°C and nitrogen is used as purge gas. Helim is the carrier gas. For all the runs, the oven temperature ramp for gc was: 60°C/3 min, 10 °C/min. 280 °C/ (3min.). Methanol was used as a solvent to dissolve the samples. HP-5 capillary column (25 m x0.32 mm x0.53 um) was used to put the samples through. Overhead pressure was 15 psi and the carrier gas flow was maintained at 30 cc/min. Any impurity that may been present got separated on the capillary columnn.

Infrared spectrometer: Transfer line temperature was maintained at 250 °C and the flow cell temperature was kept at 280°C. Spectra were recorded at optical resolution of $8cm^{-1}$. Table -1 lists the selective data for gc/ir.

Table -1 : Selective data for gc and ir data

No	. Formula	GC.R_t (in min.)	IR Absorptions (cm^{-1})		
			C-H	C=N[1]	aromatic
I	$C_{16}H_{16}N_2$	23.05	2931	1610	3070
II	$C_{16}H_{14}C_{12}N_2$	26.90	2931	1608	2038
III	$C_{16}H_{14}C\,Br_2N_2$	29.06	2932	1610	3037
IV	$C_{18}H_{20}N_2O_2$	28.57	2946	1605	3009
V	$C_{12}H_{15}N_3O_2$	21.50	2981	1632	3003
VI	$C_{11}H_{13}N_3O_2$	20.55	2927	1639	3034
VII	$C_{18}H_{14}N_3O_2$	27.28	2930	1624	3074
VII	$C_{16}H_{14}N_4O_4$	32.75	2934	1611	3036
IX	$C_{16}H_{14}N_4O_4$	28.37	2939	1621	3035
X	$C_{20}H_2N_4O_2$	33.03	2934	1607	3034

Note1: The -C=N- band shows an IR absorption in the range of 1690-1650-1 (10). However the moderate to weak phenyl bending mode also shows absorption in the range 1600 -1500 Cm -1. (10). Hence the -C=N assignment in this paper may include the phenyl bending modes also.

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دراسة طيف الكتله لبعض مشتقات الاسيتوفينون :
الجزء الأول : مشتقات الأزين

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***كلية الهندسة -جامعة عين شمس- القاهرة .

تم فى هذا البحث دراسة طيف الكتلة لعشرة أزينات مشتقة من الأسيتوفينون واتضح أن أسلوب التكسير يمكن أن يتم بين ذرتى النيتروجين للآزين أو من خلال تعدل وتكوين حلقة سداسة.