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METAL CHELATING AGENTS IV: ELECTRON IONIZATION AND CHEMICAL IONIZATION MASS SPECTRA OF 2-PHENYL ACETOPHENONE SEMICARBAZONE.

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ABSTRACT

The electron ionization (EI) and ammonia chemical ionization [CI (NH_3)] mass spectral studies on 2-phenyl acetophenone semicarbazone are reported. The EI spectrum shows a clearly identifiable molecular ion peak of weak intensity at m/z 253 and the base peak is observed at m/z 77. The CI (NH_3) spectrum is characterized by strong MH^+ signal at m/z 254.corresponding to the base peak. The primary fragmentations of significance include the loss of NH_3, H_2NCO, H_2NCONH, $H_2NCONHN$ and $C_6H_5CH_2$. Fragmentation processes are discussed and rationalized.

KEY WORDS: 2-phenyl acetophenone, semicarbazone, electron ionization, chemical ionization, fragmentation.

INTRODUCTION

Semicarbazones are novel chelating agents both in solution and solid state. The use of semicarbazones for selective and sensitive determination of metal ion have been reviewed (Singh and Ishii 1991). The semicarbazone complexes of transition metal ions have been characterized by spectral methods and reviewed (Padhye and Kauffman 1985). Magnetic and spectral studies on copper(II) complexes of semicarbazone derived from isatin, benzoin and 2-hydroxy –1-naphthaldehyde have been reported (Akinchan et al 1994). Stereochemistry and biochemical aspects of some difluoroboron complexes of the types BF_2 (NO) with ligands having nitrogen-oxygen (NO) donor atoms have been described. Based on IR, ^1H NMR, ^{13}C NMR, ^{19}F NMR ^{11}B NMR spectral studies a tetracoordinated boron center has been established. (Saxena et al, 1994). Crystal and molecular structures of tetrachloro palladate salt complex with picolinaldehyde N-Oxide semicarbazone cation have been also been reported (Gong et al 1994) Besides, semicarbazone have been found to participate as the key intermediates in the syntheses of biologically active 1, 3, 4,-oxadiazoles (Pathak et al 1993, Andotra et al, 1992) and 1, 2, 4-triazines (Pathak et al 1993). The electron impact, chemical ionization, fast- atom bombardment and collision-induced mass spectra of semiccarbazone derivatives of benzoin and 2-hydroxy–1-naphthaldehyde have been reported. (Akinchan 2002). The mass spectral studies on the semicarbazone of isatin has also been reported (Akinchan 2001). The present article decribes electron ionization (EI) and ammonia chemical ionization [CI(NH_3)] mass spectral studies on 2-phenyl acetophenone semicarbazone abbreviated as PAPSCH.

MATERIALS AND METHODS

Materials.

Semicarbazide hydrochloride (AnalaR BDH) 2-phenyl acetophenone (LR Aldrich) and sodium acetate (AnalaR BDH) were used as supplied. The other chemicals were chemically pure laboratory reagents.

Preparation of 2-phenyl acetophenone semicarbazone (PAPSCH).

The semicarbazone was prepared by condensing semicarbazide hydrochloride (1.12g, 10 mmol) with 2-phenyl acetophenone (1.96g, 10 mmol) in the presence of sodium acetate (0.82g, 10 mmol) using ethanol as solvent.

MEASUREMENTS

The electron ionization (EI) mass spectrum of 2-phenyl acetophenone semicarbazone was recorded on a JEOL D-300/JMA-2000 mass spectrometer/data system. The sample was introduced via a direct inlet system, ionization energy 70 ev, ionization current 100 μA, source temperature

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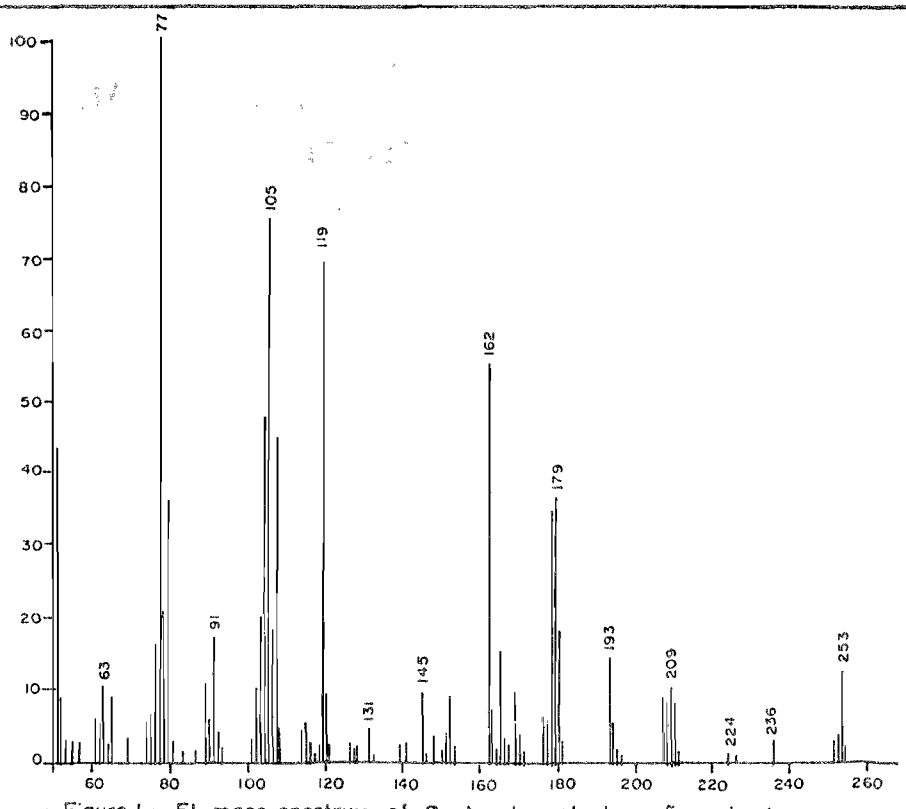


Figure 1 : EI mass spectrum of 2-phenyl acetophenone semicarbazone

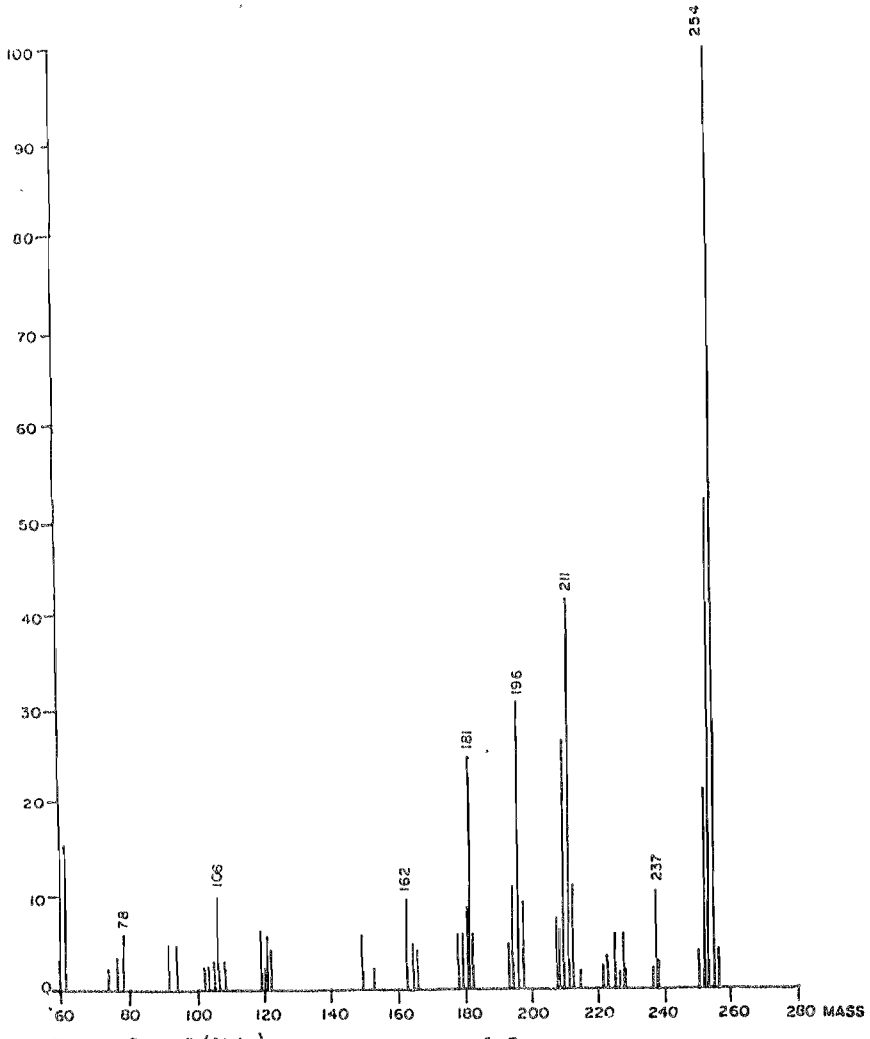


Figure 2 : $CI(NH_3)$ mass spectrum of 2-phenyl acetophenone semicarbazone

Table 1:Major fragment ions in the EI and CI(NH_3) mass spectra of 2-phenlacetophene semicarbazone

Ion	EI		CI(NH_3)		Groups lost
	M/Z	Rel. abun	M/Z	Rel abun	
MH$^+$	...	..	254	100.00	...
[M]	253	11.20	..	...	...
[MH-17]	..	....	237	10.30	NH_3
[M-17]	236	2.50	...	..	NH_3
[MH-43]	...	..	211	41.50	NHCO
[M-44]	209	10.30	...	...	NHCO
[MH-58]	..	..	196	32.40	NHCO, NH
[M-60]	193	14.20	...	...	NH_2CONH, H
[MH-73]	.	...	181	26.10	NH_2CONH,
[M-73]	180	28.30	...	...	NH_2CONH,
[M-74]	179	38.20	...	..	NH_2CONH, H
[M-75]	178	35.40	...	...	NH_2CONH, 2H
[MH-92]	..	..	162	9.00	$C_6H_5CH_2$, H
[M-91]	162	56.10	..	..	$C_6H_5CH_2$
[M-108]	145	10.20	...	..	$C_6H_5CH_2$, NH_3
[M-134]	119	70.20	...	...	H_2NCO, C_6H_5CH
C_6H_5CHO	..	.	106	10.00	----
C_6H_5CO	105	76.10	...	...	----
$C_6H_5CH_2$	91	17.20	..	...	----
C_6H_6	.	...	78	5.50	----
C_6H_5	77	100.00	...	...	---

200^{0}C. The CI(NH_3) mass spectrum was obtained with a VG 70-250 mass spectrometer.

RESULTS AND DISCUSSION

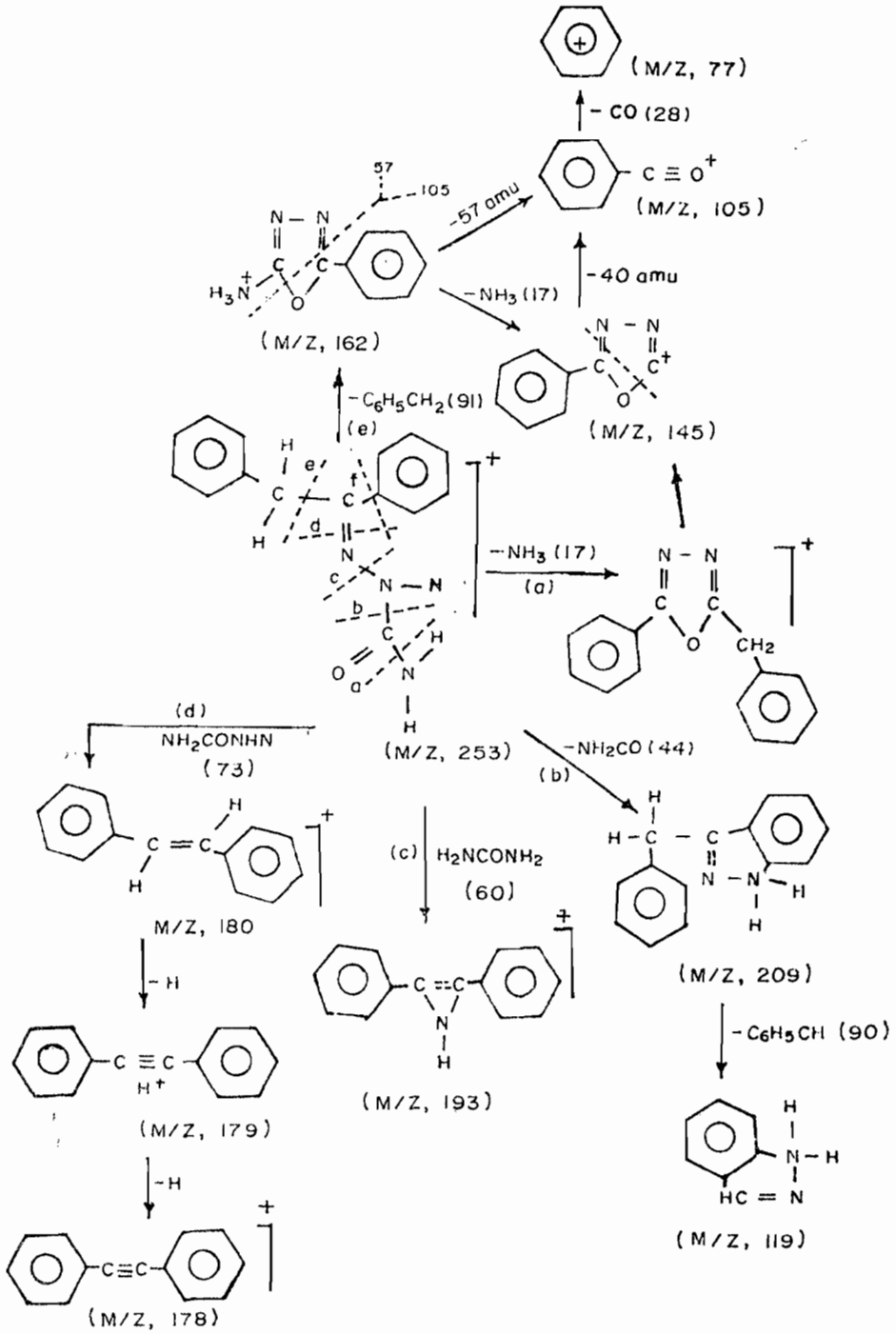
EI mass spectrum

The EI mass spectrum of 2-phenyl acetophenone semicarbazone (PAPSCH) shows (Table 1, Figure 1) a clearly identifiable molecular ion peak at m/z 253 of relatively low abundance. Relatively strong ion peak corresponding to loss of $C_6H_5CH_2$ at m/z 162 and weak ion peak at m/z 236 corresponding to loss of NH_3 are present in the mass spectrum of PAPSCH. A cyclization to a five membered ring has been suggested to account for this process (Rezk et al 2002). The secondary fragment ion of lower abundance at m/z 145 could be formed either by loss of NH_3 from $[M-C_6H_5CH_2]^+$ with m/z 162 or loss of $C_6H_5CH_2$ from $[M-NH_3]^+$ with m/z 236 fragment ion. The ion formed dissociates successively to give m/z 105 and m/z 77 as shown in scheme 1. Thus it appears that the formation of ion peak at m/z 77, which is the base peak involves process a, e and f as shown in scheme -1.

The formation of signal at m/z 180 can be rationalizated as shown in scheme 1. Further, successive hydrogen losses from this ion peak may lead to the formation of ions with m/z 179 and m/z 178 having higher relative intensities. Relatively weak signal at m/z 209 corresponding to loss of NH_2C0 has been observed. It is being stabilized by intramolecular aromatic substitution reaction suggested for accounting EI mass spectral fragmentation of substituted diphenylamines (Rezk et al 2002) and N-phenyl-2-aminobenzamidines (Mendes et al 2002). The ion formed is susceptible to secondary fragmentation and produces ion peak at m/z 119 of relatively higher abundance. (scheme 1).Finally the mass spectrum of semicarbazone under investigation exhibits ion peak at m/z 193, which is formed probably as a result of N-N bond cleavage of semicarbazone moiety. (process c, scheme 1)

CI (NH_3) Mass Spectrum

The CI(NH_3) mass spectrum displays (Table 1, Figure 2) an ion of m/z 254 of relatively higher abundance constituting the base peak. This indicates the greater stability of the pseudomolecular ion due to effective delocalized protonation. Other abundant ions are observed at m/z 237, m/z 211, m/z 181 and m/z 162 involving primary fragmentation processes a, b, d and e respectively (scheme 2). The peak observed at m/z 196 appears to be secondary fragmentation from m/z 211. The ions at m/z 106 and m/z 78 are also as a result of secondary fragmentation of m/z 162. Similar

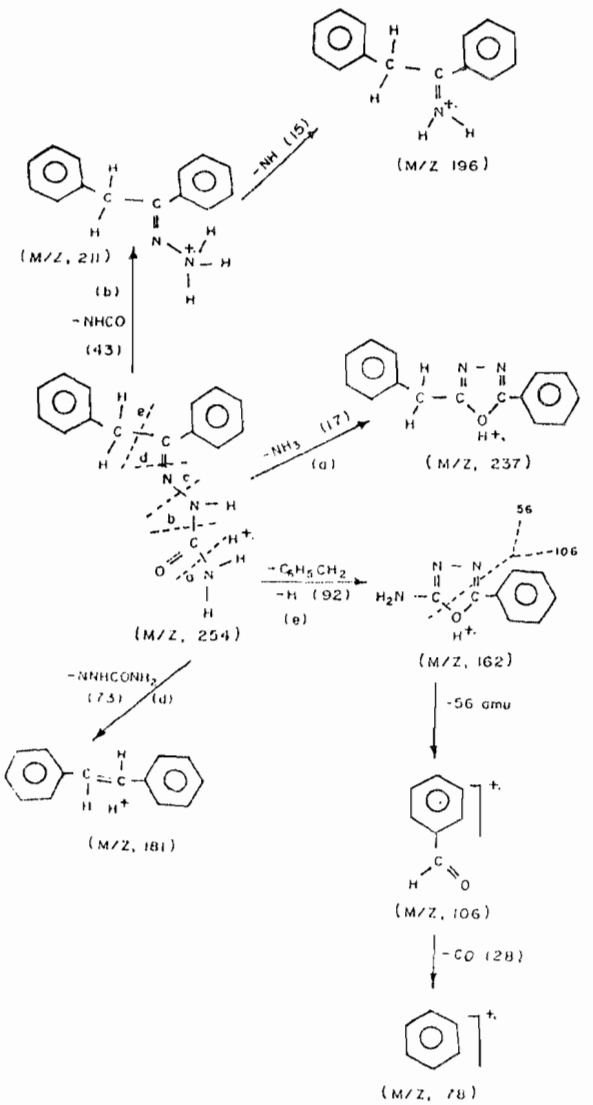


Scheme I : Electron ionization mass spectral fragmentation of 2-phenyl acetophenone semicarbazone (PAPSCH)

observation have been reported on benzoin semicarbazone (Akinchan 2002). The loss of NH_3 could be due to the loss of NH_2 and the hydrazino NH hydrogen from the pseudo molecular ion [MH']. The fragmentations are rationalized as shown in scheme 2.

CONCLUSION

Electron ionization (EI) mass spectra of semicarbazone under investigation and for other semicarbazones reported earlier (Akinchan 2001, 2002) are unable to provide definite characteristic feature if the nature of



Scheme 2. Chemical ionization (NH_3) mass spectral fragmentation of 2-phenyl acetophenone semicarbazone (PAPSCH)

most abundant ion is compared. But by far the most structurally diagnostic fragment ion is $[M+H]^+$ with m/z 254, which is formed abundantly and nearly exclusively in the ammonia chemical ionization mass spectrum of 2-phenyl acetophenene semicacarbone. Almost similar observations were made during earlier investigations on other semicarbazones (Akinchan 2001, 2002).

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