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Intramolecular aromatic substitution and ortho interactions in substituted 1-phenyl ethanone and diphenylmethanone oximes on electron Impact+

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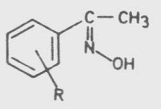
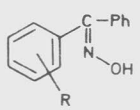
The formation of the ions at m/z 133 and 195 from the molecular ions of substituted 1-(phenyl)ethanone oximes and diphenylmethanone oximes has been identified to be due to the expulsion of RH, wherein R is the substituent present in the phenyl ring, for which are assigned 3-methylbenz-1,2-isoxazole and 3-phenylbenz-1,2-isoxazole radical cation structures respectively based on CAD spectral study. A mechanism involving an initial intramolecular aromatic substitution of the oxygen atom of the oxime hydroxyl group on the *ortho* carbon leading to the distonic ion from which a 1,2-elimination of the *ortho* substituent along with the hydrogen of the hydroxyl group is proposed for the elimination of RH. Substituent scrambling in the distonic ion has been invoked for the loss of RH from certain *para* substituted derivatives. An important fragment ion at m/z 181 has been noticed in the mass spectra of (2-methoxyphenyl)phenyl-methanone oxime due to *ortho* interaction during the secondary fragmentation process. The proposed mechanism for these processes and the ion structures are supported by high-resolution data, B/E and B^2/E linked-scan spectra and CAD/B/E spectra.

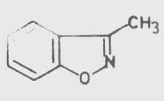
The mass spectral decompositions of aromatic aldoximes and ketoximes have been extensively studied[1-4]. The major fragmentation pathways in aromatic aldoximes are due to the expulsions of $^{\bullet}OH$, HCN, HCNO and the *ortho* substituent from their molecular ions. The isomerization of the molecular ion of 1-(2- methylphenyl)ethanone oxime to its nitrone has been identified by Vijfhuizen and Terlouw[5]. Elimination of HNO is the major fragmentation reported[6] in the mass spectrum of 1-(2- nitrophenyl)ethanone oxime.

The important fragment ions[7] noticed in the mass spectrum of diphenylmethanone oxime are due to the eliminations of $^{\bullet}OH$, CO, $H^{\bullet}$ and $^{\bullet}NHOH$ species from the molecular ion. Kallury *et al*[8] in their electron-impact-induced decomposition studies of a series of aryl heteryl ketoximes have observed fragment ions corresponding to the related anilide for which they visualized a Beckmann rearrangement in





Compound	R	Compound	R
1	H	10	H
2	o-NH_2	11	o-OCH_3
3	p-NH_2	12	p-OCH_3
4	o-OH	13	o-CH_3
5	p-OH	14	p-CH_3
6	o-OCH_3	15	o-Cl
7	p-OCH_3	16	p-Cl
8	o-NO_2	17	p-NO_2
9	p-NO_2		



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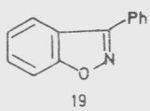

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Scheme I

+Presented in part at 6th AGMS meeting, June 1995, Tubingen, Germany

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the molecular ions. However, several reports[9-11] subsequently proved that transformation of oxime to anilide is purely a thermal decomposition in the ion source and not an electron impact isomerization. In the present paper the study of various substituted 1-(phenyl)ethanone **1-9** and diphenylmethanone oximes **10-17** (Schemes I) has been undertaken to investigate the *ortho* interactions of several interacting groups like amino, hydroxy, methoxy, nitro and methyl with the oxime function in the molecular ions of these substrates.

Results and Discussion

The presence of substituents in the *ortho* position is found to markedly influence the fragmentation process in both 1- (phenyl)ethanone and diphenylmethanone oximes (Table I). The mass spectrum of 1-(2-aminophenyl)ethanone oxime **2** exhibits abundant ions at m/z 149, 134, 133 and 132 (Table I) due to the explusions of $H^{\bullet}$, N_2, $^{\bullet}OH$ and H_2O from the molecular ion. The fragment ion at m/z 133 is identified to be a mixture of two ions in the intensity ratio of 7 : 3 at a resoltuion of 12000. It is noticed from the high- resolution measurements that the expected loss of hydroxyl radical from the molecular ion leads to the more abundant ion. The accurate mass of the less intense ion is found to be 133.05146 which corresponds to an elemental composition C_8H_7NO. This observation reveals the interesting elimination of NH_3 from the molecular ion of **2**.

The high-resolution study of the ion at m/z 133 in 1-(4- aminophenyl)ethanone oxime **3**, the *para* isomer of **2**, reveals that the ion is formed only due to the loss of OH radical and is not contributed by NH_3 ejection from the molecular ion. This observation clearly indicates that an *ortho* interaction between the *o*-NH_2 group and the oxime function occurs in the $M^{+\bullet}$ of **2** for the NH_3 ejection.

Table I - Partial mass spectral data of compounds **1- 17**

Comp.	M^+	$[M-H]^+$	$[M-R]^+$	$[M-OH]^+$	$[M-RH]^+$	m/z values with relative abundances (%) in parentheses of other ions
1	135(85)	134(13)	-	118(18)	-	119(5), 94(33), 77(100)
2	150(80)	149(30)	134(19)	133(100)	133(100)	132(16), 118(30), 92(39)
3	150(100)	-	-	133(50)	-	118(36), 92(59)
4	151(100)	150(13)	134(37)	134(37)	133(44)	105(80)
5	151(100)	-	134(21)	134(21)	-	110(10), 94(30)
6	165(68)	-	134(12)	148(16)	133(100)	107(8), 105(70), 104(12), 77(40)
7	165(100)	-	134(12)	148(48)	133(25)	107(20), (105(6), 77(49)
8	180(5)	-	134(8)	-	133(8)	149(100), 139(6), 118(5), 117(24), 106(10), 105(8)
9	180(100)	179(10)	134(6)	163(12)	133(13)	118(52), 105(71), 92(14), 64(21).
10	197(44)	196(8)	-	180(89)	195(7)	181(26), 179(34), 165(26), 104(38), 94(20), 77(100)
11	227(59)	-	196(39)	210(11)	195(100)	212(14), 181(13), 180(20), 167(46), 165(21), 107(5), 77(64)
12	227(100)	-	196(5)	210(44)	195(20)	212(14), 179(11), 167(7), 152(8), 133(15), 108(15)
13	211(100)	-	196(79)	194(38)	195(100)	179(11), 178(15), 167(4), 165(11), 91(40), 77(38)
14	211(100)	210(14)	-	194(92)	195(24)	179(8),,178(7), 167(11), 165(21), 91(38), 77(27)
15	231(100)	-	196(68)	214(78)	-	179(12), 165(22), 111(18), 94(20), 77(84)
16	231(85)	-	196(7)	214(100)	-	179(11), 178(4), 165(9), 128(13), 111(17), 77(88)
17	242(100)	24(9)	-	225(44)	195(17)	226(10), 179(48), 178(14), 167(13), 165(11), 105(4), 94(6), 77(18)

Table II — B/E linked scan spectral data

Comp	Parent ion m/z	m/z values of the daughter ions with relative abundances in parentheses
2	$M^{+\bullet}$, 150	149(100), 134(10), 133(61), 132(11), 93(6), 92(14)
	133	118(8), 105(100), 92(11), 76(14)
4	$M^{+\bullet}$, 151	150(100), 134(18), 133(36), 92(12)
6	$M^{+\bullet}$, 165	164(15) 148(100) 134(22) 133(16) 76(10)
	148	147(9), 133(100), 118(14)
7	$M^{+\bullet}$, 165	164(30), 148(100), 134(22), 133(24), 107(6)
	148	147(16), 133(100), 118(14)
11	$M^{+\bullet}$, 227	226(15), 212(14), 210(13), 196(17), 195(100)
	210	195(85), 181(100), 107(6), 77(18)
12	$M^{+\bullet}$, 227	226(19), 212(26), 210(100), 196(11), 195(33)

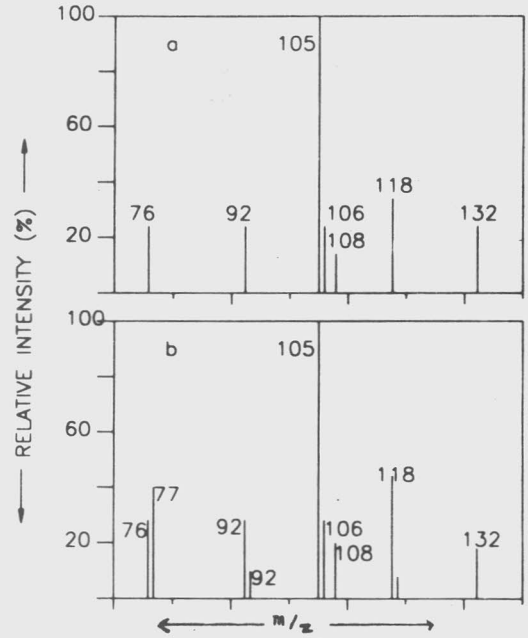
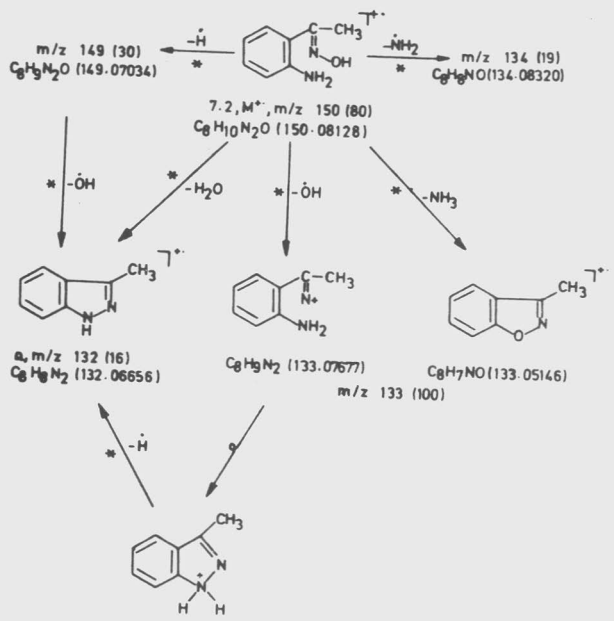


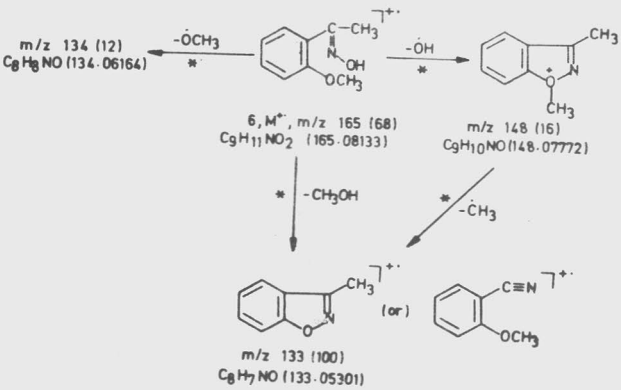
Figure 1 - CAD/B/E linked scan spectra of the ions at m/z 133(a) M^+ of 18(b) from M^+ ion of 2



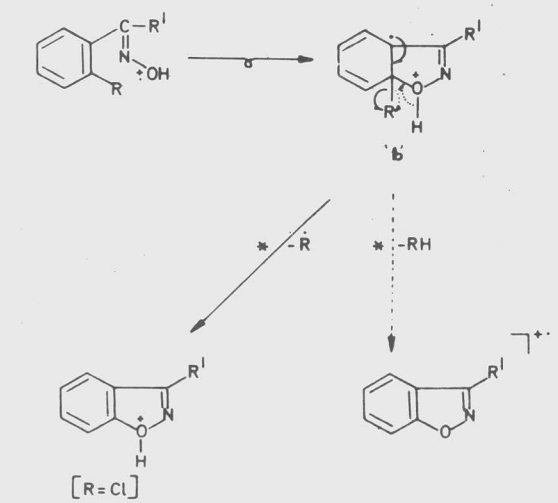
Scheme II

The ion at m/z 133 are observed in the mass spectra of o- NO_2 **4**, *o*-OCH_3 **(6)** and *o*-NO_2 **(8)** derivatives (Table I) in good intensities. The ion is formed both by direct and stepwise process as adduced from the linked scan spectral data of the respective ions (Table II). High resolution study reveals that the eliminations of H_2O, CH_3OH and HNO_2 are involved in the formation of the ion **a** from the molecular ions of **4,6** and **8**.

A 3-methylbenz-1,2-isoxazole radical cation structure has been assigned to the ion at m/z 133 formed from these compounds based on the comparison of CAD spectra of the ions **a** formed in the mass spectra of **2** (Fig.1), **4** and **6** with that of the molecular ion of 3-methylbenz-1,2-isoxazole **18**. The little dif-



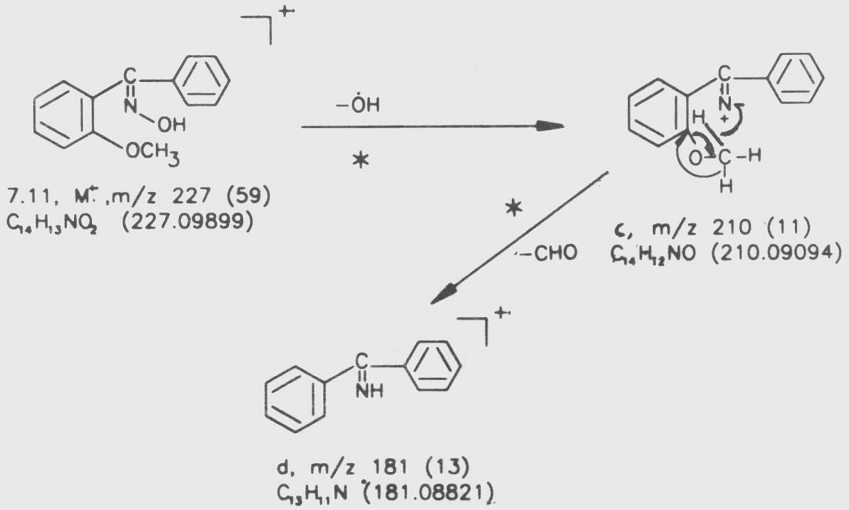
Scheme III



Scheme IV

ference in the CAD spectra of the ions **at** m/z 133 from **2** and **6** are due to the contribution from the alterntive ion-structures for m/z 133 in these compounds (Scheme II and III). Based on these observations, a mechanism involving the initial attack of the oxygen atom of the oxime hydroxyl group on the *ortho* carbon atom leading to a distonic ion **b** is proposed. A 1,2-elimination of RH in **b** (R = *ortho* substituent) results in the formation of 3- methylbenz-1,2-isoxazole radical cation (Scheme IV). Similarly, the expulsion of the *ortho* methoxy and the *ortho* methyl groups from the molecular ions of **11** and **13** with the hydrogen of the oxime function present abundant ions at m/z 195 (Table I) for which a 3-phenylbenz-1,2-isoxazole **19** structure is assigned based on CAD spectral studies (Fig. 2).

The mass spectrum of (2-methoxyphenyl) phenylmethanone oxime **(11)** exhibits an interesting ion at m/z 181(Table I). The origin of the ion is identified



Scheme V

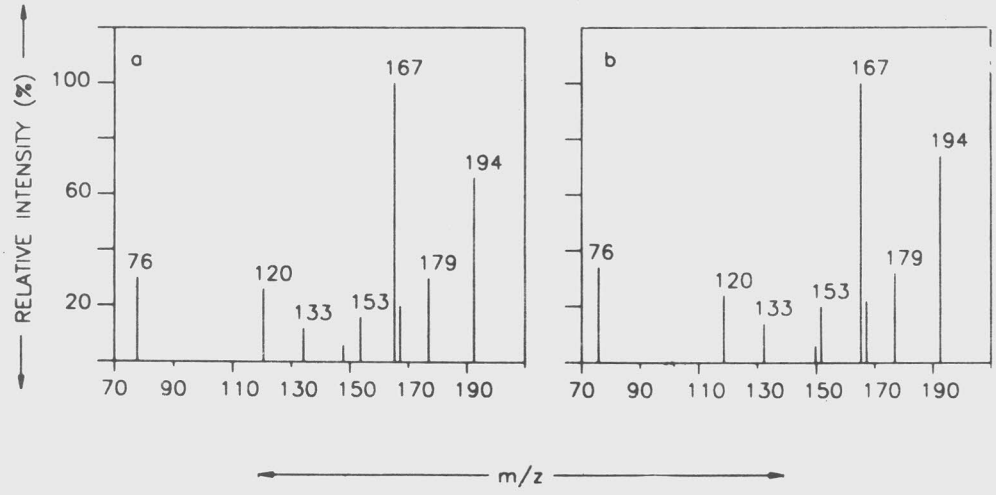


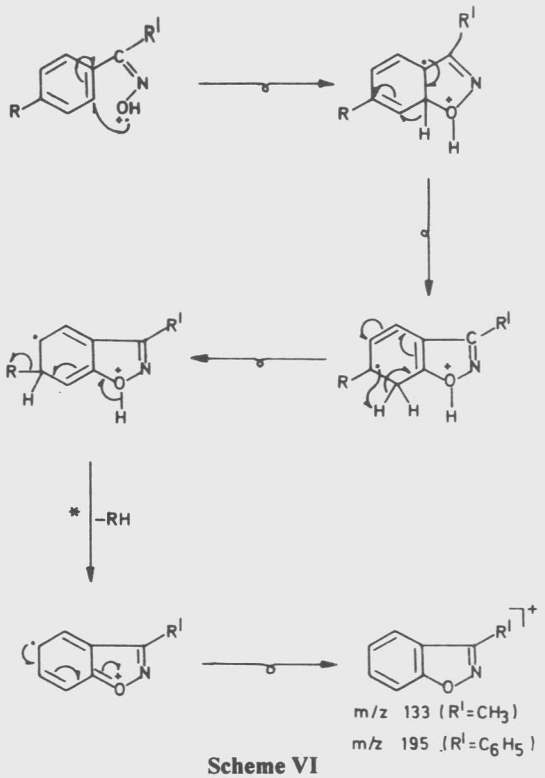
Figure 2 - CAD-B/E linked-scan spectra of the ions at m/z 195(a) M^+ ions of 19)b) from M^+ ion of 11

to be from the $[M-OH]^+$ ion by metastable studies (Table II). The accurate mass of the ion at m/z 181, as determined by high resolution technique, is 181.08821 which corresponds to an elemental composition of $C_{13}H_{11}N$ indicating the loss of CHO in its formation. An *ortho* interaction during a secondary fragmentation process is invoked for the formation of the ion at m/z 181 in **11**. Thus, the loss of $^{\bullet}OH$ from the $M^{+\bullet}$ of **11** forms ion **c** in which a double hydrogen migration from the methoxy group to the imine nitrogen and also to the *ipso* carbon results in the elimination of $^{\bullet}CHO$ to yield **d** (Scheme V).

The expulsion of $^{\bullet}Cl$ from the molecular ion of (2- chlorophenyl)phenylmethanone oxime **15** is predominant instead of the expected $[M-HCl]^+$ ion (Table I). The elimination of $^{\bullet}Cl$ is energetically more favourable than the 1,2-elimination of HCl in the distonic ion intermediate. Such a unique behaviour of chloro derivative is reported in electron impact study[9] of substituted cinnamic acids.

The formation of the ions at m/z 133 and 195 corresponding to the loss of CH_3OH from the molecular ions are noticed in the mass spectra of 1-(4-methoxyphenyl)ethanone oxime **7** and (4-methoxyphenyl)phenylmethanone oxime **12**. Similarly, the explusion of HNO_2 from the molecular ions are observed in the *p*-nitrosubstituted derivatives **9** and **17**. The ejection of CH_4 leading to an intense ion at m/z 195 is noticed in the mass spectrum of (4-methylphenyl)phenylmethanone oxime **14**. These fragmentation process are corrobated with the help of linked scan spectra, high resolution data and the ion-structures are identified by CAD spectra (Figs 1 and 2). The substituent scrambling as depicted in Scheme VI is envisaged for the formation of 3-substituted-1, 2-isoxazole radical cation in the *para* substituted oximes.

It can be concluded from the present study that the *ortho* interactions resulting in cyclisations and formation of diagnostically important fragments are observed in 1-(phenyl)ethanone and diphenylmethanone oxime.



Scheme VI

Experimental Section

Compounds **1 - 17** were obtained adopting literature method[12] for the preparation of aldoximes and ketoximes. The reference samples 3-methyl-**(18)** and 3-phenylbenz-1,2-isoxazole **(19)** were prepared by well-known methods. All the compounds examined were recrystallized to constant melting points and their purity was checked by TLC. Their structures were confirmed by IR and ^1H NMR spectral data. The mass spectra were obtained on a Finnigan MAT 8230 model mass spectrometer at 70 eV with an emission current of 100 μA. All the compounds were introduced into the mass spectrometer through direct inlet system at 30°C. Accurate mass measurements were carried out at a resolution of 12000 (10% valley) at an ionization energy of 70 eV and accelerating voltage of 3 kV and perfluorokerosene was used as the reference. The CAD-B/E linked scan spectra were investigated at an ionization energy of 70eV and an accelerating voltage of 3 kV using helium as the collision gas which was introduced into the collision chamber until the main beam is attenuated to 30% in intensity.

Acknowledgement

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