

## Mass Spectra of Some Monosubstituted Benzophenone Oximes

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The mass spectra of six benzophenone oximes substituted in the para-position with  $-\text{NH}_2$ ,  $-\text{OCH}_3$ ,  $-\text{CH}_3$ ,  $-\text{Cl}$ ,  $-\text{Br}$  and  $-\text{NO}_2$  have been studied. Introduction of a substituent into one of the aromatic rings enables the molecule to fragment by a variety of different reaction pathways. The influence of substitution on hydrogen and hydroxyl migration has been investigated. It is shown that electron-donating substituents enhance, while the electron-withdrawing substituents reduce both of these rearrangement reactions.

### INTRODUCTION

Various oximes have been a subject of mass spectral study in a number of papers that have recently appeared in the literature. The mass spectra of aromatic oximes<sup>1-5</sup> are of particular interest and reveal many fragmentation processes, among which rearrangement reactions are very pronounced.

In this paper we report on the mass spectral investigation of various *p*-monosubstituted benzophenone oximes in order to establish the influence of substituents on the degradation pattern of such molecules under electron impact.

### EXPERIMENTAL

Low resolution mass spectra were recorded using a Varian CH-7 instrument operated at 70 eV, 100  $\mu\text{A}$  and 3 kV. Accurate mass determinations and measurements of the metastable peaks by refocusing technique were made on a CEC 21-110 C instrument at the »J. Stefan« Institute, Ljubljana, Yugoslavia.

Substituted benzophenone oximes were prepared by reaction of the corresponding substituted benzophenones with hydroxylamine hydrochloride.

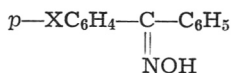
### RESULTS AND DISCUSSION

The mass spectrum of unsubstituted benzophenone oxime together with the discussion of the origin of some selected ions has been reported earlier<sup>1,2</sup>. In order to investigate the mass spectra, we have prepared the monosubstituted benzophenone oximes with the following *para*-substituents:  $-\text{NH}_2$  (I),  $-\text{OCH}_3$  (II),  $-\text{CH}_3$  (III),  $-\text{Cl}$  (IV),  $-\text{Br}$  (V) and  $-\text{NO}_2$  (VI). No attempt has been made to obtain pure geometrical isomers, which in many cases gave identical<sup>6-8</sup> or very similar<sup>5</sup> mass spectra.

The normalized and uncorrected 70 eV mass spectra of I—VI are listed in Table I. Only peaks with an intensity of 3% or more relative to the base

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TABLE I  
The mass spectra of substituted benzophenone oximes

I (X = NH<sub>2</sub>)

50(6)	51(20)	52(7)	63(7)	64(8)	65(43)	66(10)
76(7)	77(29)	78(7)	84(4)	90(10)	91(19)	92(30)
93(88)	94(5)	104(8)	108(5)	109(7)	118(15)	119(18)
120(15)	151(6)	152(7)	153(4)	165(6)	166(4)	167(7)
168(4)	178(6)	179(6)	180(19)	181(8)	182(4)	194(7)
195(90)	196(41)	197(6)	211(5)	212(100)	213(15)	

II (X = OCH<sub>3</sub>)

50(9)	51(24)	52(5)	63(4)	64(15)	65(20)	66(7)
76(11)	77(54)	78(7)	90(7)	91(6)	92(21)	93(4)
107(4)	108(90)	109(11)	127(5)	151(6)	152(15)	153(10)
154(4)	165(6)	166(6)	167(14)	168(4)	180(7)	181(8)
182(4)	195(15)	196(6)	210(66)	211(19)	226(5)	227(100)
228(16)						

III (X = CH<sub>3</sub>)

50(7)	51(19)	63(9)	65(17)	75(4)	76(6)	77(30)
78(3)	90(7)	91(25)	92(27)	94(6)	104(5)	108(9)
109(5)	116(6)	118(7)	119(8)	165(16)	166(8)	178(8)
179(8)	180(8)	181(5)	182(8)	194(88)	195(23)	196(5)
210(14)	211(100)	212(16)				

## IV (X = Cl)

50(17)	51(42)	65(8)	76(56)	77(67)	78(10)	89(7)
94(14)	102(8)	103(6)	104(9)	112(13)	114(4)	119(20)
128(10)	130(3)	151(8)	152(5)	153(12)	164(8)	165(32)
166(14)	167(6)	168(6)	177(8)	178(10)	179(6)	180(6)
199(9)	201(7)	202(7)	203(6)	214(83)	215(15)	216(28)
217(5)	230(12)	231(100)	232(17)	233(34)	234(5)	

## V (X = Br)

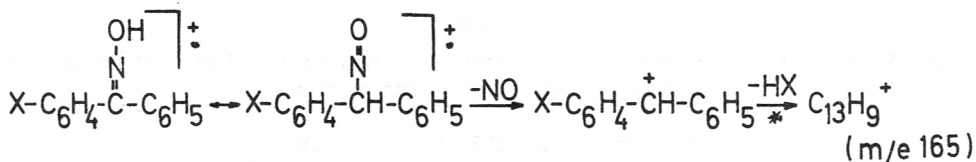
50(33)	51(50)	63(11)	65(9)	74(12)	75(36)	76(43)
77(91)	78(8)	89(21)	91(21)	94(11)	96(11)	102(15)
103(11)	104(14)	119(19)	139(8)	155(20)	156(10)	157(20)
158(10)	163(16)	164(13)	165(41)	166(20)	167(10)	168(12)
172(6)	174(6)	177(7)	178(10)	179(31)	180(19)	181(7)
195(7)	196(9)	197(9)	199(7)	243(8)	245(8)	246(8)
247(8)	248(8)	258(57)	259(13)	260(57)	261(13)	274(10)
275(100)	276(19)	277(99)	278(18)			

VI (X = NO<sub>2</sub>)

50(8)	51(16)	63(8)	76(24)	77(15)	78(28)	94(30)
103(8)	104(10)	139(11)	151(8)	152(10)	163(4)	164(8)
165(20)	166(10)	167(18)	168(9)	178(14)	179(48)	180(11)
195(12)	196(4)	213(8)	214(5)	225(31)	226(9)	241(9)
242(100)	243(16)					

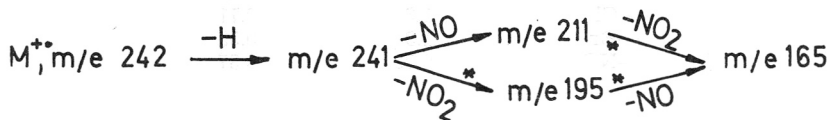
peak are tabulated. The molecular peak serves as a base peak in the spectra of all substituted benzophenone oximes studied. These compounds follow the general fragmentation scheme given for the unsubstituted benzophenone oxime<sup>1,2</sup> and reactions common with it (*e.g.* loss of OH, CO, HNOH *etc.*) can easily be recognized by inspection of their spectra. For the fragment ions containing only one of the phenyl rings, two forms, *i.e.* the unsubstituted one and the one bearing a substituent, usually appear in the spectrum, but their relative abundances may differ to a great extent. In the discussion which follows the fragmentation reactions associated only with the presence of a substituent in the molecule, will be emphasized. These reactions have been studied by means of accurate mass measurement and of refocusing of the corresponding metastable ions in the first drift region.

An ion at  $m/e$  165 has often been reported in the literature as fluorenyl cation and can be encountered in the mass spectra of a variety of compounds having two phenyl rings in the molecule. It is formed directly from the molecular ion of unsubstituted benzophenone oxime by expulsion of HNOH<sup>2</sup>. However this stable ion is also generated during a degradation of substituted aromatic oximes. Thus, in I, II, IV and V the  $m/e$  165 ion (elemental composition  $C_{13}H_9$  by accurate mass determination) is formed by the consecutive loss of NO and HX (X = substituent) from the molecular ion, probably from its tautomeric nitroso form<sup>1</sup>, as shown in Scheme 1. In III the  $[M-NO]^+$  ion first



Scheme 1.

losses H and then X (HX is not eliminated as  $\text{CH}_4$ ), while in VI the process for the formation of  $m/e$  165 proceeds according to Scheme 2.

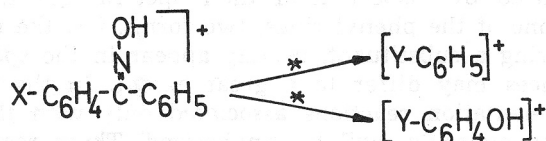


Scheme 2.

The substituent X is lost directly from the molecular ion in compounds IV, V and VI only. In II the methoxy group adds to the variety of fragmentation pathways starting from the molecular ion. The expulsion of  $\text{CH}_2\text{O}$  has been observed, as well as the loss of methoxy group together with the carbon atom to which it was bound ( $\text{COCH}_3$ ). In II and VI there is also a possibility that a part of the substituent ( $\text{CH}_3$  and NO, respectively) is eliminated, followed by the loss of CO.

The influence of the substituents in the *m*- and *p*-substituted benzaldoximes on both hydrogen and hydroxyl migration has been studied<sup>4</sup>. Five and four membered cyclic transition states were postulated for the hydrogen and hydroxyl transfer, respectively. It was found that the hydrogen transfer was

favoured in the *p*-isomer, while the hydroxyl transfer was predominant in the *m*-isomer. We have compared the intensity ratios of ions resulting from the hydrogen or hydroxyl transfer in the molecular ion, either to the unsubstituted or to the substituted ring (Scheme 3).



X = substituent, Y = H or X

Scheme 3.

*i. e.* the intensity of  $[\text{C}_6\text{H}_6]^+$  versus  $[p\text{-XC}_6\text{H}_5]^+$  and of  $[\text{C}_6\text{H}_5\text{OH}]^+$  versus  $[p\text{-XC}_6\text{H}_4\text{OH}]^+$ . These rearrangement reactions are supported by metastable peaks. It must be noted that the hydrogen transfer to one of the phenyl rings may take place both in the molecular ion and in the  $[\text{M}-\text{O}]^+$  ion (the molecular ion of benzophenone imine, formed from benzophenone oxime by thermal loss of oxygen prior to ionization<sup>2</sup>). To avoid these thermal processes, we kept the source temperature below 130 °C<sup>2</sup>. The results of the intensity measurement are given in Table II. It is obvious that the electron-donating

TABLE II

Relative abundances of ions resulting from the hydrogen and hydroxyl transfer in substituted benzophenone oximes

Substituent <i>p</i> -X	$\frac{[p\text{-XC}_6\text{H}_5]^+}{[\text{C}_6\text{H}_6]^+}$	$\frac{[p\text{-XC}_6\text{H}_4\text{OH}]^+}{[\text{C}_6\text{H}_5\text{OH}]^+}$
—NH <sub>2</sub>	13.5	1.5
—OCH <sub>3</sub>	13.1	1.1
—CH <sub>3</sub>	9.0	1.6
—Cl	1.3	0.71
—Br	1.3	0.59
—NO <sub>2</sub>	0.02	0.37

*p*-substituents strongly favour the hydrogen transfer due to the stabilization of the unpaired electron at the transfer site. Hydroxyl migration is also enhanced by these substituents, although only to a minor extent. The influence of the electron-withdrawing substituents is just the opposite. In the halogen-*p*-substituted benzophenone oximes there seems to be no influence of the substituent on the hydrogen transfer, while the hydroxyl transfer is somewhat reduced. The *p*-nitro substituent practically precludes the hydrogen transfer to the aromatic ring.

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## SAŽETAK

## Spektri masa monosupstituiranih benzofenonoksima

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Ispitivani su spektri masa monosupstituiranih benzofenon-oksima sa slijedećim *para*-supstituentima:  $-\text{NH}_2$ ,  $-\text{OCH}_3$ ,  $-\text{CH}_3$ ,  $-\text{Cl}$ ,  $-\text{Br}$  i  $-\text{NO}_2$ . Uvođenjem supstituenata u jedan od aromatskih prstenova povećava se broj reakcija kojima se cijepaju molekularni ion i fragmenti. Studiran je utjecaj supstitucije na putovanje vodika i hidroksilne skupine na benzenski prsten. Nađeno je da se te obje reakcije pregrađivanja mogu ubrzati supstituentima koji daju elektrone, dok supstituenti koji privlače elektrone imaju suprotno djelovanje.

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