NEGATIVE ION MASS SPECTROMETRY OF THE CARBONYL GROUP

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CONTENTS

SUMMARY

The negative ion spectra of carbonyl compounds were studied in order to investigate the fragmentation of this group in the negative mode. The work is divided in four sections.

In Chapter 2,we are concerned with carbonyl compounds of the general types aryl-CO-alkyl and aryl-CO-aryl. Parent anions are formed by secondary electron capture and have low internal energies. Fragmentation is only observed for aryl-CO-alkyl systems under collision excitation. In contrast, aryl-CO-aryl and α-dicarbonyl systems yield pronounced rearrangement peaks, produced by cyclizations between the adjacent substituent: Such reactions are particularly pronounced in the spectra of o-nitrobenzil, o-nitrobenzoyl benzoyl methane and o-nitrobenzoyl acetyl methane.

In Chapter 3, we describe studies of nitroaryl-$(CH_2)_n$-CO-alkyl and nitroaryl-$(CH_2)_n$-aryl systems (n=1,2). Fragmentation occurring by α-cleavage to the carbonyl group is noted for the compounds n=1, whereas β-cleavage to the carbonyl group is observed for the compounds n=2.

Pronounced rearrangement peaks occur in the spectra of o-nitrophenyl-CH_2-CO-R compounds, but similar reactions are not noted for o-nitrophenyl-CH_2-CH_2-CO-R systems. Labelling studies indicate the identity of the eliminated species, but the mechanisms of the rearrangements are complex.

Chapter 4 deals with unsaturated compounds of the type nitroaryl-$(CH=CH)_n$-CO-R (n=1 to 3). Proximity effects are observed for o-nitroaryl unsaturated compounds but are not noted when the nitro group is replaced by the carboxyl group. Rearrangement peaks are produced by cyclization reactions; when n = 1, reactions proceed mainly through 6- and 7- membered transition states to produce fragment ions corresponding to 1,2-

dicarbonyl radical anions. When n = 2, reactions proceed through 5- and 6-membered transition states to produce 1,4- dicarbonyl-2-ene (n = 2) and 1,6-dicarbonyl-2,4-diene (n=3) radical anions as the major fragment ions.

In Chapter 5, we discuss the negative ion spectra of oximes of the carbonyl compounds described in the previous chapters. The fragment ion $[M^{\cdot -}-H_2O]^{\cdot -}$ is noted in the spectra of α-carbonyl monoxime compounds and in those of simple oxime compounds of the types $O_2N\text{-}C_6H_5\text{-}C(NOH)\text{-}R$ and $O_2N\text{-}C_6H_5\text{-}CH_2\text{-}C(NOH)\text{-}R$. Rearrangements involving cyclization reactions are noted for nitroaryl-$(CH{=}CH)_n$-C(NOH)-R systems and these are generally analogous to those described in Chapter 4 for the analogous carbonyl precursors.

STATEMENT

This Thesis contains no material submitted for a degree in any University, and to the best of my knowledge, contains no material previously written or published, except where due reference is included in the text.

SOMPONG JANPOSRI

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PUBLICATIONS

Part of the work described in this thesis has been published in the following papers:

1. Negative-Ion Mass Spectra of the Carbonyl Group. The Aryl-CO--CO-Systems, J.H. Bowie and S. Janposri, *Australian J. Chem.*, 1975, 28, 2169-74.

2. Negative-Ion Mass Spectra of the Carbonyl Group. The Aryl-CH_2-CO- and Aryl-$(CH_2)_2$-CO-Systems, J.H. Bowie and S. Janposri, *Organic Mass Spectrometry*, 1975, 10, 1117-1124.

3. Negative-Ion Mass Spectra of the Carbonyl Group. Unsaturated Carbonyl Compounds, J.H. Bowie and S. Janposri, *J. Chem. Soc. Perkin II*, 1976, (in press).

4. Negative-Ion Mass Spectra of Oximes. Monoximes derived from α-Dicarbonyl System, J.H. Bowie and S. Janposri, *Organic Mass Spectrometry*, Submitted for publication.

CHAPTER 1.

INTRODUCTION

1.1 General

The existence of negative ions in the gas phase was first recognised by J.J. Thomson,[1] who identified a number of simple negatively charged atoms and molecules using the mass spectrograph. Since then negative ions have been extensively studied in many fields; for example, atomic negative ions,[2-5] inorganic systems,[6] negative ion-molecule reactions,[5] negative ion-neutral reactions,[7] field ionization[8] and the formation of negative ions on metallic surfaces.[9-12] The majority of investigations carried out with negative ions between 1950 and 1965 were concerned with the theoretical rather than the practical applications of negative ion mass spectrometry. Since 1965 there has been a continuing interest in the development of negative ion mass spectrometry as an aid to structure determination.

1.2 Mode of Formation

Negative ions are formed by the interaction between electrons and neutral molecules.[13,14] There are basically three different processes. For a diatomic molecule AB, these processes are conventionally classified as resonance capture, dissociative resonance capture and ion-pair production.

Resonance capture and dissociative resonance capture are electron-capture processes, but ion-pair production is a collision or non-capture process. Resonance capture forms a parent ion near 0 eV. Dissociative resonance capture occurs in the range 0-15 eV and ion-pair production is noted above 10 eV.

1.2.1 Ion-Pair Processes

Ion-pair processes are produced by electron or by photon impact. The electron may excite the molecule to an unstable state from which it dissociates spontaneously into positive and negative ions.

$$\begin{array}{lcl} AB + e & \longrightarrow & AB^{*} \\ AB^{+} & \nearrow & A^{+} + B^{-} \\ & \searrow & A^{-} + B^{+} \end{array}$$

1.2.2 Dissociative Attachment

This is the most general type of electron-capture process viz.,

$$AB + e \begin{array}{l} \nearrow A^- + B \\ \\ \searrow A + B^- \end{array}$$

Dissociative attachment occurs to a bound state of the negative ion, which then undergoes internal conversion to produce a repulsive state that undergoes dissociative ionisation.

1.2.3 Nondissociative Attachment

Electron capture gives a vibrationally excited molecular ion $[AB^{-*}]$ If the vibrationally excited molecular ion does not emit a photon or undergo collisional stabilization,[15] the electron will be ejected by autodetachment (Auger electron).

$$AB^{-*} \longrightarrow AB^* + e$$

Another possible electron capture process is the process which produces a temporary negative ion. This capture process might occur if the interaction time between the electron and the molecule is long enough to allow the nuclei to change from their normal configuration.

1.2.4 Negative-Ion Formation by Secondary Electrons.

Negative molecular ions may be formed by capture of secondary electron[16-18] (analogous to section 1.2.2). The secondary electron is a de-energized electron produced either from the electrode surfaces or from the ionisation process of the molecular cation.

1.3 Instrumentation

Mass spectrometers used for negative ion studies are:-

a) Conventional mass spectrometers,
b) Time of flight mass spectrometers,
c) Ion cyclotron resonance spectrometers,
d) Quadrupole mass spectrometers, and
e) Spectrometers with high-pressure sources.

1.3.1 Conventional Mass Spectrometers [19,20]

There are two types; single and double focusing mass spectrometers. Some conventional mass spectrometers have a negative ion capability which is produced by the reversal of the polarities of the electric, magnetic fields and the accelerating voltage. Double-focusing mass spectrometers have much higher resolving power than single focusing instruments, and they may also be used to measure metastable decompositions,[21] negative ion kinetic energy spectra [21] and collision induced dissociations. [21]

1.3.2 Time of Flight Mass Spectrometers [22,23]

The principle of mass separation is that ions of different mass, accelerated to uniform kinetic energy, have different velocities, and hence different times of flight over a given distance. These spectrometers are generally used for the determination of appearance potentials and autodetachment lifetimes. [24-26]

1.3.3 Ion Cyclotron Resonance Spectrometers [27,28]

An ICR spectrometer is suitable for the observation of collision processes, because of the long ion lifetime in the cell (up to a millisecond). Such spectrometers are suitable for the study of ion-molecule reactions at low pressures, studies which are of value for ion-structure elucidation.

1.3.4 Quadrupole Mass Spectrometers [29]

In a quadrupole instrument, the gaseous sample is ionized by electron impact and the ions are extracted electrostatically from the ion source. In order to separate mass, the radiofrequency (rf) and dc voltages are scanned while being kept in the same ratio. Quadrupole mass spectrometers are capable of mass resolution up to about 1000. These mass spectrometers are commonly used with a gas-chromatography attachment.

1.3.5 Spectrometers with High Pressure Sources

A modified spectrometer, developed by von Ardenne, and coworkers [30,31] produces slow electrons by a low-voltage argon-gas discharge at a pressure of about 10^{-2} Torr. The slow electrons are then captured by suitable molecules to produce molecular anions which may undergo further decomposition to yield fragment ions. This technique has proved useful for the study of certain natural products. [32-36]

1.4 Negative Ion Production

The following methods are used to produce negative ions in the mass spectrometer. They are: low energy electron beams, [37-40] higher energy electron beams in conventional ion sources using secondary electron attachment [37-40] and plasma sources of slow-electrons [41]. A further method for the production of negative ions is the process

$$M^{+} + N \longrightarrow M^{-} + N^{2+}$$

where N is a neutral collision gas which has been introduced into the first field free region of the mass spectrometer [42].

1.5 Fragment Ions

Molecular anions formed by secondary electron capture often undergo unimolecular - fragmentation,[40] to produce fragment ions. The fragment ions may contain an odd or an even number of electrons. The processes can be represented by

$$M^{\dot{-}} \longrightarrow F^{-} + N\cdot$$

when the daughter ion is an even-electron species or by

$$M^{\dot{-}} \longrightarrow F^{\dot{-}} + N$$

when the daughter ion is an odd electron species.

The fragment ion F^{-}, formed by a unimolecular decomposition, may exist in a vibrationally excited state [43,44] and decompose further.

Fragment ions can also be formed by the process of "pair production" in which both a positively and negatively charged fragment arise simultaneously. This process has been noted [45] in halogenated compounds.

1.5.1 Stable Ions, Unstable Ions and Rearrangement Ions

If an ion formed in the ionisation chamber, travels from the ionisation chamber to the collector without further decomposition, then such an ion is defined as a stable ion. The peaks in a mass spectrum are due almost entirely to stable ions.

An unstable ion is one that is formed with sufficient internal energy to enable decomposition to occur.

Rearrangement ions are those fragment ions which have been produced by some transfer of atoms prior to or during the breaking of bonds. Rearrangement reactions often tend to lead to products of high stability [44] (see later).

1.6 The Quasi-Equilibrium Theory [31,45-48]

The quasi-equilibrium theory assumes the applicability of the Franck-Condon principle, i.e. the ionization via electron impact is assumed to be a vertical process. According to the Franck-Condon principle [49], ionization is extremely rapid, occurring at a rate faster than those of bond vibrations (10^{-14} to 10^{-12} sec.). The molecular ion thus formed will have the same nuclear configuration as the neutral molecule and all the internuclear distances remain essentially unchanged in the conversion of the neutral excited molecule to the molecular ion. For a simple diatomic molecule, the Franck-Condon principle [49] can be illustrated in terms of an energy diagram as shown in Fig. 1-1.

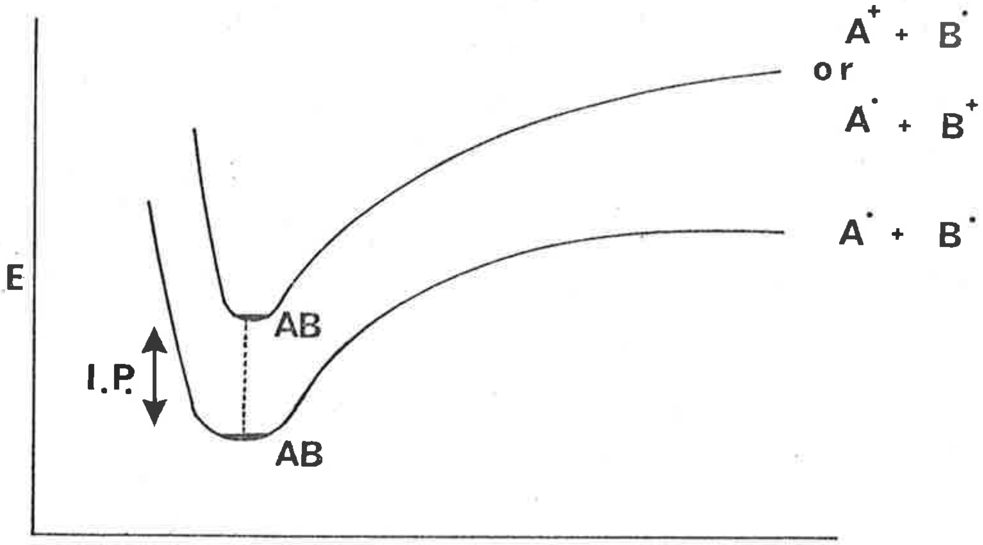


FIG 1-1

The excited parent molecular ion, formed by the electron-impact process, will have a certain amount of excitational energy. It is assumed that the various fragment ions are not formed immediately from the excited parent-molecular ion, but rather undergo several vibrations prior to decomposition. The molecular ions can usually decompose in more than one way, leading to several fragment ions. The quasi-equilibrium theory[45-48] can be used to rationalise how a series of competing unimolecular reactions can occur.

The simplest form of the quasi-equilibrium theory (QET) of mass spectra relates the unimolecular reaction rate constant k to internal energy E, activation energy E_0, frequency factor ν and effective number of oscillators s, in the following equation.[31]

$$k = \nu \left(\frac{E-E_o}{E}\right)^{s-1}$$

From a consideration of this expression, it has been demonstrated[50] that a simple bond cleavage reaction will be pronounced if the internal energy (E) of the ion is very much larger than the activation energy (E_o).

The value of $(E-E_o)/_E$ tends to unity and the rate constant k will be equal to the frequency factor ν or to the vibrational frequency of the bond (10^{13} - 10^{14} s^{-1}).

For a rearrangement process, [50-52] the activated complex ('tight' complex) will increase the vibrational frequency, some internal rotations will consequently be restricted and the rates of such rearrangement reactions will not approach bond vibrational frequencies.

Application of the quasi-equilibrium theory leads [53] to k (E) vs E curves as shown in Fig. 1-2. Curve C represents a high activation energy process (typically simple cleavage [50]), whereas curve R represents a low frequency factor and low activation energy process (typically rearrangements reactions [50]).

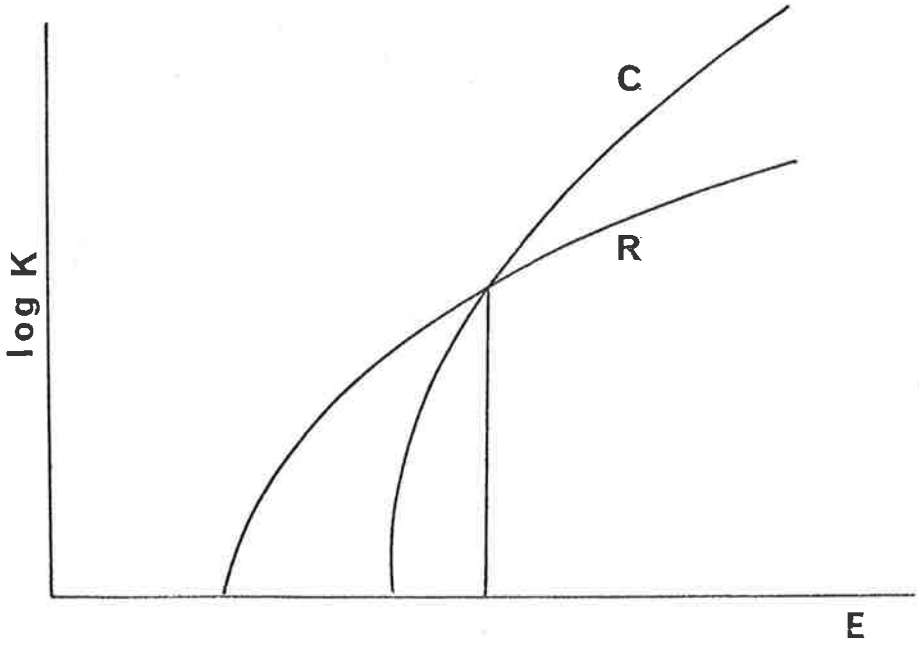


FIG 1-2

log k vs E Curves for hypothetical competing rearrangement (R) and simple cleavage (C) reactions

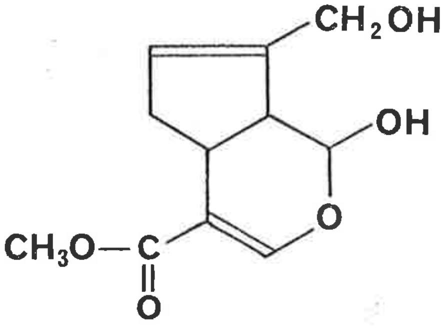
It has been shown [50, 54-58] that [R]/[C] increases with decreasing electron energy. It appears that generally, the rearrangement reaction has the lower activation energy and often gives rise to an abundant metastable ion [59]. At high internal energies of the decomposing ion, simple cleavage reactions have higher frequency factors than rearrangement reactions yield more abundant daughter ions [59], but often the metastable-ion abundances for such reactions are low. Thus the observation of an abundant "metastable - ion" suggests the possibility of a rearrangement reaction.

1.7 Metastable Ions

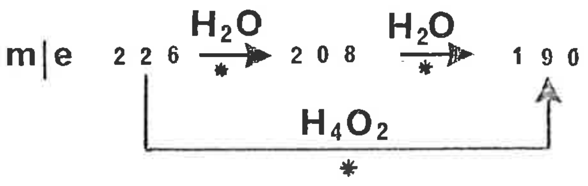
If a singly-charged ion of mass m_1 fragments after acceleration such an ion is termed [60] "metastable". The majority of "metastable" decompositions occur between the ion source and the magnetic sector. The position of daughter ions resulting from the decomposition $m_1 \rightarrow m_2$ of a metastable ion is:

$$m^* = m_2^2 / m_1$$

Metastable decompositions may occur by one step or multistep pathways. Many multistep fragmentations of positive ions occurring between the ion source and collector have been reported. [61-71] For example a simple two step fragmentation is observed in the spectrum of genipin [72] (sec a). The three metastable decompositions are observed by the defocusing technique (see below).



a



Metastable peaks are usually readily identifiable in the normal mass spectrum because

a) they need not occur at integral m/e values

b) they are often diffuse, broad peaks, extending several mass units and

c) they are of weak intensity (10^{-2} or less of the abundance of the parent and daughter ions in 70 eV spectra).

1.7.1 Metastable Defocusing Technique [73-77]

The products of metastable transitions which occur in the field free-region in front of the electric sector of a double focusing mass spectrometer usually possess kinetic energies lower than that which enable the ions to be transmitted through the sector. There are two methods which have been used to enable the measurement of daughter ions produced in the first field-free region of the mass spectrometer, viz.

a) By increasing[73-76] the accelerating voltage while keeping the electrostatic analyser voltage constant.

b) by lowering[77] the electrostatic voltage while keeping the acceleration voltage constant.

If method a) is used, the accelerating voltage must be increased from its normal value (V_o) to V_1 such that $V_1/V_0 = m_1/m_2$. As m_2 is known and the ratio V_1/V_0 is measured experimentally, it is possible to determine all values of the precursor m_1 ions [78].

The advantages of the use of the focusing technique for the study of metastable transitions are that:-

a) each transition is unequivocally identified in terms of the masses of parent and daughter ions.

b) all the precursor ions of m_2 may rapidly be found using one scan of the accelerator voltage.

c) normal ions do not interfere, and

d) in the absence of normal ions, the sensitivity of the electron multiplier can be increased and so minor processes may be detected.

1.7.2 The Shapes and Applications of Metastable Peaks

The shapes of metastable peaks vary from gaussian through a flat-topped[79] peak, to one with a double maximum. Factors which influence the shapes of metastable peaks have been discussed by Beynon and Fontaine.[80] The value of the metastable peaks are:-

(a) an aid to the interpretation of mass spectral fragmentations,

(b) the measurement of kinetic energy released in the fragmentation, which yields both thermodynamic and structural information, and

(c) to classify the types of decomposing ions generated from the precursors. For example,

if an ion of given composition generated from different precursors decomposes by two reactions which give metastable peaks in the same abundance ratio over a given internal energy range than this is an indication that the ions from the two sources either have the same structure, or alternatively consis of the same mixture of structures.[81] This technique was used by Shannon and McLafferty to study[82] the types of decomposing $C_2H_5O^+$ ions generated from compounds CH_3OCH_2Y, $HOCH_2CH_2Y$, $CH_3CH(OH)Y$ and CH_3CH_2OY, where Y, corresponds to one of a variety of groups.

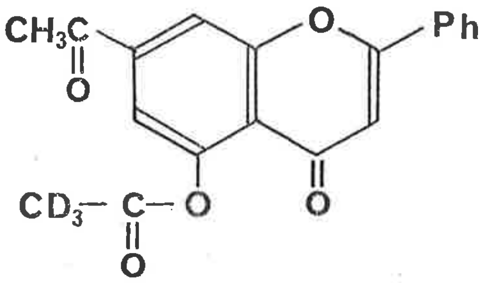
1.7.3 Metastable Negative Ions

Abundant metastable negative decompositions may be studied[83] in both the first and second field-free regions of a double focusing mass spectrometer. Those formed in the field-free region in front of the electric sector may be detected by the metastable focusing technique.[74, 84] In the case of competing unimolecular reactions, metastable ions are generally more abundant for re-arrangement processes than those observed for simple cleavage processes.

Many metastable negative ions are gaussian in shape but some may be very broad and flat-topped.[44,85,86] An example of the latter type is found for the loss of $NO\cdot$ from substituted nitrobenzene molecular anions.

Bowie and his coworkers [87] have studied metastable decompositions in negative ion spectra in the first field free region of the mass spectrometer by the decreasing electric sector potential technique, using the maximum sector potential (180 volts) of RMU 7D instrument. This technique gave an enhancement of ca. 10:1 in the abundances of metastable ions when compared with those produced in the second field free region. Bowie and Hart [83] modified the instrument by developing an external unit which utilized a sector voltage greater than that available using the commercial instrument. This unit increased the sensitivity of metastable ion measurement approximately 100 times that mentioned above.

Two step fragmentations of metastable ions are observed in some negative ion spectra.[83] The spectrum of 1- (acetoxy - d_3) - 3 - acetoxyflavone (see b) exhibited a daughter ion (m*) at m/e 258.7 for the process $[M^{\overline{\cdot}} - CD_2CO]^{\overline{\cdot}}$ which was accompanied by a peak (m**) for the two step process $[M^{\overline{\cdot}} - CD_2CO - CH_3CO\cdot]^{\overline{\cdot}}$.



b

Further examples of two step fragmentations of a metastable negative ion can be seen in the spectrum of 3 - nitrophthalic anhydride which is shown in Fig. 1-3. The spectrum shows peaks from metastable decomposition at m/e 115.0 (m*), m/e 57.7 (m**) and 75.9 (m**) for the two step fragmentations $[M^{\overline{\cdot}}-CO_2-CO_2]^{\overline{\cdot}}$ and $[M^{\overline{\cdot}}-CO_2-CO]^{\overline{\cdot}}$ respectively.

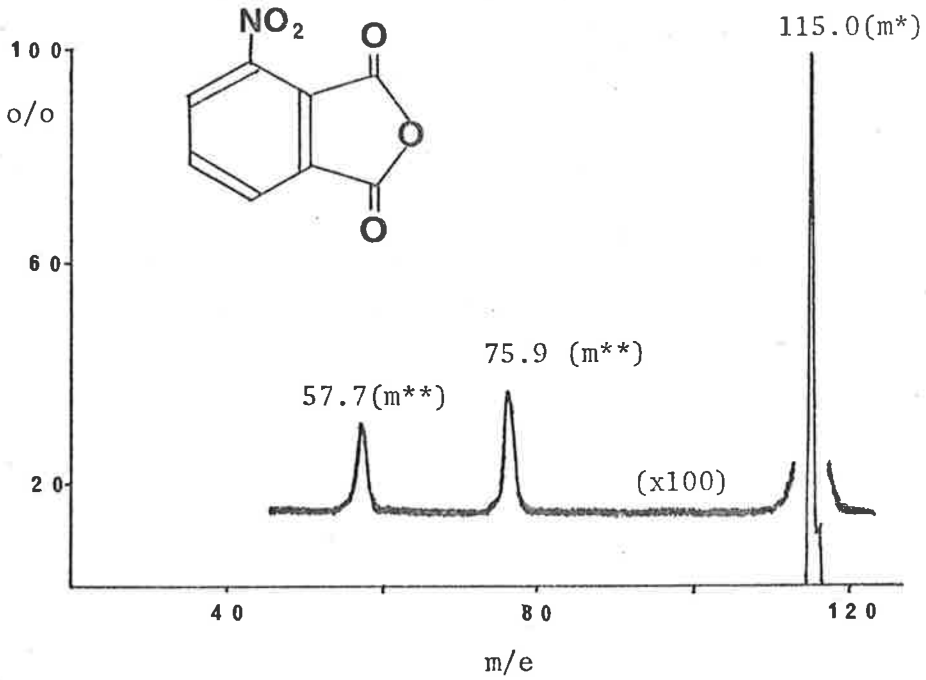


FIG 1-3

1.7.4 Ion Kinetic Energy Spectroscopy [84,88,89]

When ions m_1 decompose to ions m_2 in the field-free region preceding the electrostatic sector, the m_2 ions entering the electrostatic sector will have a spectrum of kinetic energies. If an electron multiplier detector is placed at the energy-resolving (β) slit at the exit from the electrostatic analyser, and the electrostatic voltage is continuously varied, a spectrum of ion kinetic energies can be obtained.

IKE spectroscopy has been used extensively for the study of positive ion decompositions. The technique may be used to provide a fingerprint for organic compounds, [90] to detect low-abundance reactions [91] and to aid the determination of ion structure [92].

The negative ion kinetic energy spectra of phenyl p-nitrophenyl-acetate and o-nitroacetanilide have been reported [83], and were measured using the decreasing electric sector potential method at a source pressure of 2 x 10^{-6} Torr.

1.7.5 Collision-Induced Dissociation

Many molecular anions formed by electron impact are very stable and do not fragment. [93] A low-energy molecular anion can be given higher internal energy if a collision process occurs between that ion and a neutral molecule (i.e. a target gas) in the region before the electric sector. The target gas is usually argon, helium and nitrogen and is introduced into the first field free region of the mass spectrometer through an additional gas inlet system. The optimum collision pressure has been found to be about 5 x 10^{-5} torr. Increasing the pressure to more than 10^{-4} torr should be avoided as collisional scattering occurs at these pressures. However the optimum pressure varies with such factors as the nature of the target gas, the length of the drift tube and the kinetic energies of the incident ions.

After collision activation, the anions may undergo fragmentation.[94-95] The resulting collision-induced spectra may be observed in both the first or second field free region of the mass spectrometer.

Collision-induced processes have the following applications:-

a) They provide a detailed picture of fragmentation processes, not only from molecular ions but also fragment ions.

b) Many more reactions occur on collision than occur unimolecularly.

c) Collisional activation minimizes [96] the occurrence of rearrangement reactions (see e.g. Fig 1-2).

The enhancement of internal energies of molecular ions when they collide with a neutral gas, can be considered to be due to the conversion of translational into internal (vibrational) energy. Fig. 1-4 depicts the situation of a molecular ion undergoing decomposition after collision.

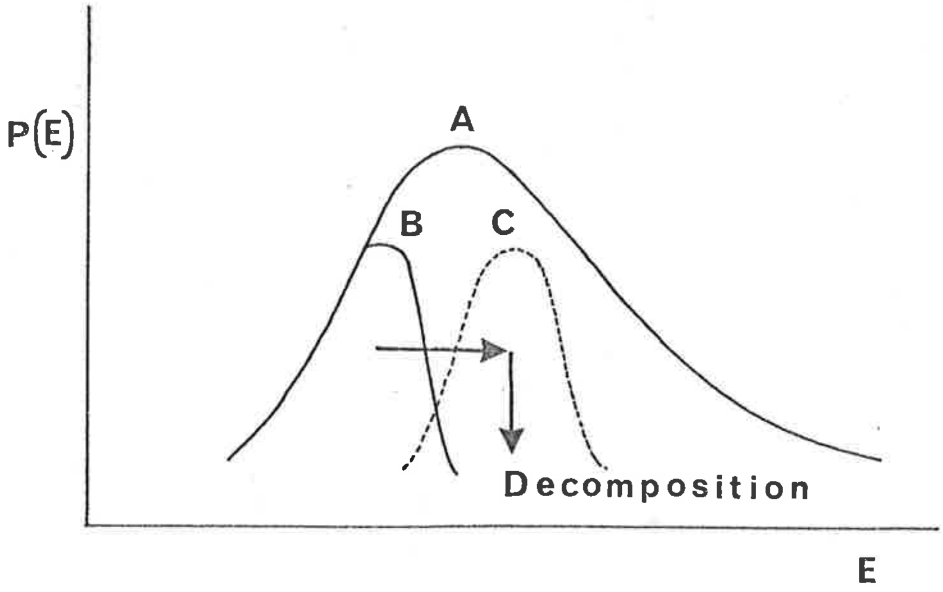


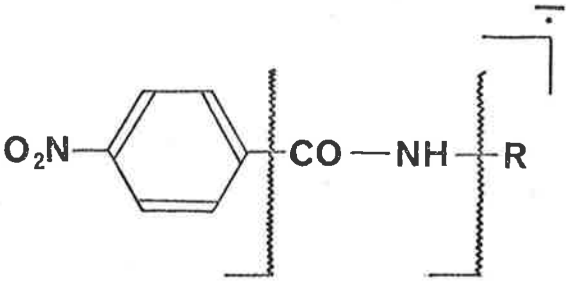
FIG 1-4

Curve A represents the hypothetical energy distribution of a molecular ion after electron impact. Curve B represents the lower energy ions which leave the source. Curve C represents the higher energy ions after collision with the neutral gas. Molecular ions with sufficient internal energies then decompose in less than a microsecond.[97]

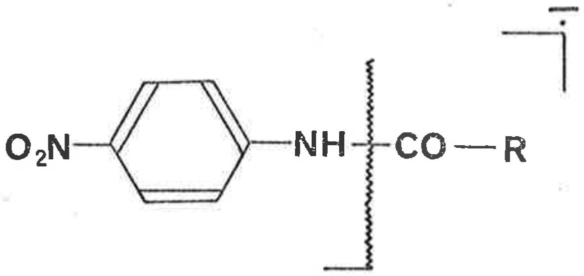
Collision activation (C.A.) positive ion spectra have been widely investigated by McLafferty.[98-101] This technique was used for the determination of ion structure and for studies of decomposition pathways. For example, the structures of ions $C_2H_5O^+$, $C_3H_6O^+$, and $C_{13}H_9^+$ were studied[100] by matching their collision activation spectra with those of known reference ions. The resemblance of decomposition pathways in collision activation spectra to those observed in conventional positive ion mass spectra makes possible the structural identification of unknown ions. The C.A. technique was also found to be useful for oligopeptides.[100] The conventional positive ion spectrum of Ac-Gly-Ala-Leu-OCH_3 only showed the sequence m/e 142→100 (corresponding to Ac-Gly-Ala^+→Ac-Gly^+), while the C.A. spectra gave sufficient peaks for elucidation of the complete sequence.

The C.A. technique is equally applicable to negative ions and has been used to force the fragmentations of anhydrides[93,102] ketones[103], amides[104] and carboxylic acids.[105] For example, the conventional negative ion spectra of phthalic anhydride and maleic anhydride showed no fragmentation at 70eV, however the fragment ions $[M^{\cdot-}-CO]^{-}$ and $[M^{\cdot-}-C_2O_2]^{\cdot-}$ were observed[93] in the negative C.A. spectrum of phthalic anhydride, and $[M^{\cdot-}-CO]^{-}$ for maleic anhydride.

Molecular anions of simple amides produced by secondary electron capture do not undergo fragmentation. The collision induced spectra of c and d (R = Me or Ph) show[104] the fragmentations indicated below.



c



d

Molecular anions of some aromatic carboxylic acids also do not undergo fragmentation under normal conditions. After collision activation the p-nitrobenzoic acid[83] and p-cyanobenzoic acid[83] molecular anions eliminate $HCO_2^{\cdot}$; but the corresponding ions from the anthraquinone monocarboxylic acids eliminate CO_2.

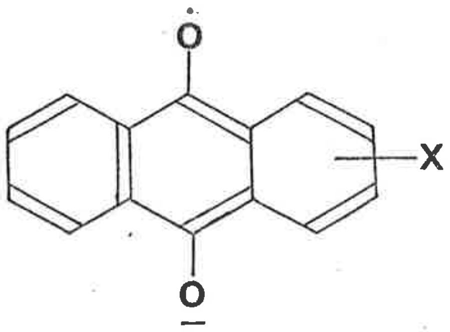
Some molecular anions are extremely stable even after collision activation. An example is the α-dicarbonyl group,[103] which will be discussed later.

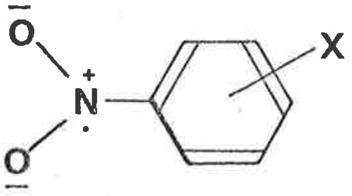
1.8 Negative Ion Studies

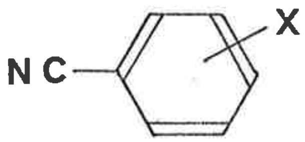
As explained previously (1.3.1) negative ion mass spectra can be obtained by reversing the polarities of the electric and magnetic fields, the accelerating potential and the drift potentials in the source of a conventional mass spectrometer. In some cases there are considerably more (10^3 to 10^5) positive ions formed than negative ions, but certain types of organic compound yield intense negative ion mass spectra. Those elements with high electron affinities (oxygen, sulfur and the halogens) tend to promote negative ion formation. Thus negative ions are formed in considerable abundance from the simple compounds SO_2, PCl_5 and ClO_3F.[106] Organic compounds containing electron withdrawing groups, for example, halides,[107-132] ester,[86-133] anhydrides[102,134], cyanides[135-140], ketones[86,103,141-146], carboxylic acids[105,147-149], nitro-compounds[350-158] and organometallic compounds[159-165] exhibit negative ions. Some compounds such as N-oxides[166], azoxy-compounds[166], nitrones[166], amides[104,142,158,167], amines[168,169], carbamates[170], as well as sulphur[171] and phosphorous compounds[118,119,170,174-175] and some heterocyclic compounds[176] yield intense molecular anions. The molecular anions are thought to be produced by the capture of low energy secondary electrons which originate either from the ionization process of the molecular cation or from electrode surfaces.[177]

It has been stated[87] that negative ion spectra are not generally as useful as positive ions for structure determination, primarily because of the low abundances of negative ions and because of experimental difficulties in obtaining suitable conditions in the ion source. These disadvantages certainly apply to the majority of aliphatic compounds and some aromatic and inorganic compounds which do not yield molecular anions. The real value of negative ion mass spectra lies in the area of fluorocarbon chemistry, for compounds containing π systems with electron withdrawing groups, and for organometallic compounds.[159-165]

Bowie and his colleagues[87] have used the organic compounds RX, where R is quinonyl,[86-178] nitrophenyl[44,133,140] or cyanophenyl[140] (the electron-capture moieties) in order to investigate the fragmentations of functional groups (X) in the negative mode.





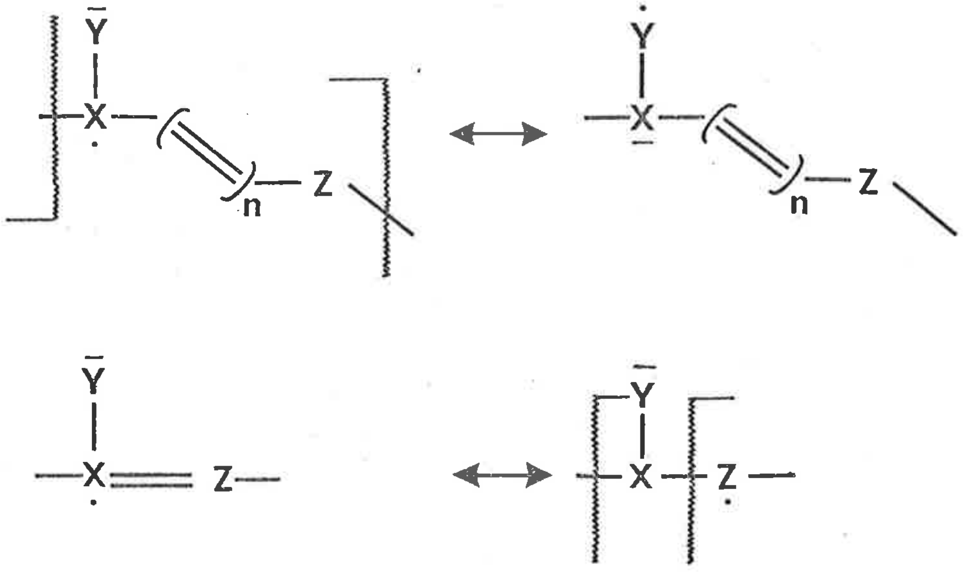


1.8.1 Type of Fragmentations

There are two general types of fragmentation of molecular anions, i.e. simple cleavage and rearrangement reactions.[87]

1.8.1a Simple Cleavage Reactions

Simple cleavages of negative ions generally occur α to the charge - containing unit or α to some atom or group which is in conjugation with the centre of charge as shown in the general scheme 1.



SCHEME 1

1.8.1b Rearrangement Reactions

The quasi-equilibrium theory indicates that rearrangement reactions of positive ions will be dominant at low electron beam energies (see Fig.1.2 and section 1.5.1). In negative ion spectra, the molecular anions are formed by secondary electron capture,[87] and have low internal energies. When a molecular anion undergoes fragmentation, rearrangement reactions will predominate if competitive rearrangement and cleavage processes occur.

β-Cleavage with accompanying γ-hydrogen rearrangement (the McLafferty rearrangement[179]) is prevalent in the positive ion spectra of carbonyl compounds. Such rearrangements are not observed in negative ion spectra.[148,180-182]

Rearrangement reactions often occur when two functional groups are adjacent or ortho to each other. A brief survey of various rearrangement processes of negative ions is given below.

The spectrum of 1-acetoxyanthraquinone shows the base peak due to the fragment ion $[M^{\overline{\cdot}}-CH_2CO]^{\overline{\circ}}$ [178]. This hydrogen rearrangement can be rationalized as illustrated in *e*. †

When the acetoxy group is at the 2-position (see *f*) the proximity effect $[M^{\overline{\circ}}-CH_2CO]^{\overline{\cdot}}$ is not observed. Fragmentation of 2-acetoxy anthraquinone proceeds as shown in *f*. †

The fragment ion $[M^{\overline{\cdot}}-PhOH]^{\overline{\circ}}$ is observed[140] in the spectrum of phenyl *p*-nitrophenylacetate. This fragment ion is produced as shown in *g*.†

Another hydrogen rearrangement process observed in the spectra of thioglycollic acids[183], involves the formation of $\cdot CH_2COO^{-}$ and $RSH^{\overline{\cdot}}$. A suggested mechanism is shown in *h*.†

The fragment ion $[M^{\overline{\cdot}}-NO^{\circ}]^{-}$ from *o*-nitroacetanilide eliminates ketene (see *i*).[44] †

The *o*-nitrobenzoic acid molecular anion eliminates $NO\cdot$ to yield *j*, which then decomposes by loss of CO_2 (see *j*) †

Proximity effects involving migration of groups other than hydrogen are also observed in the negative ion spectra of many *o*-substituted arylnitro compounds.[87] For example, the molecular anion of 3-nitrophthalic anhydride[102] eliminates two molecules of carbon dioxide with the first loss involving one of the nitrogen oxygens (see *k*).*

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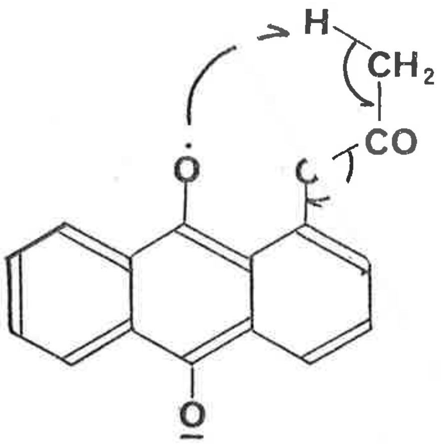
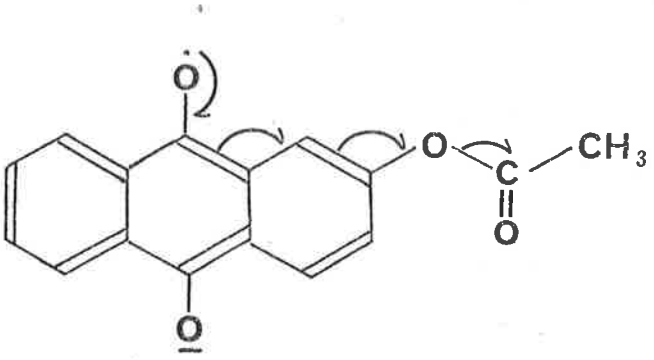
† See Page 20

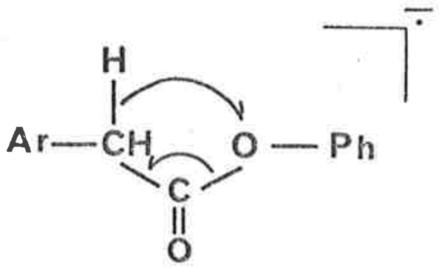
* See Page 22.



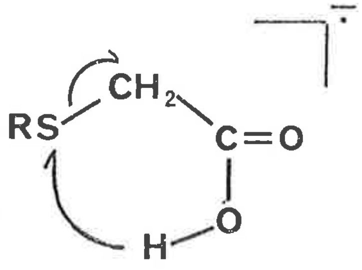
e



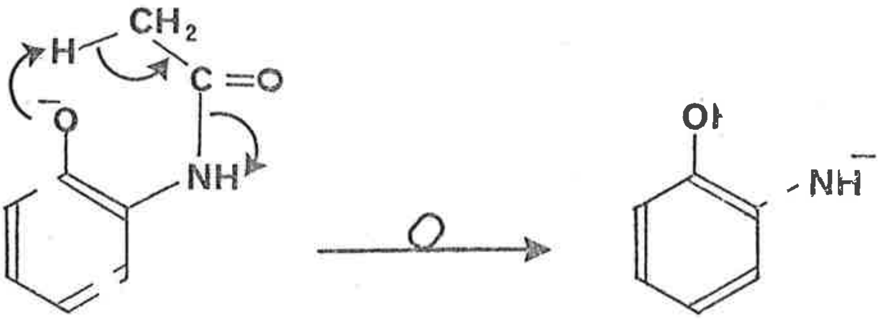
f

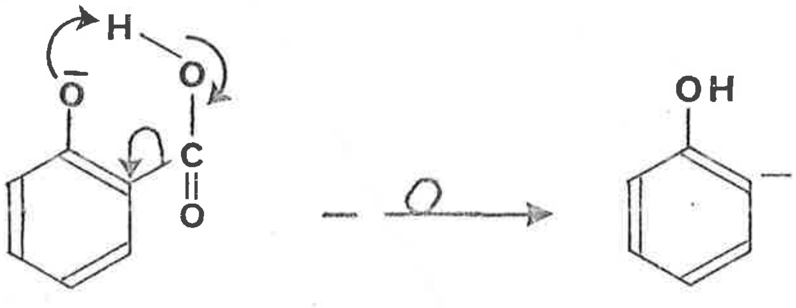


g



h





j

$[\mathrm{M}^{\cdot-}-\mathrm{HO}\cdot]^{-}$ ions are noted[44,158,167] in the spectra of amides of type 1. †

The negative ion spectrum of phenyl o-nitrobenzoate,[133,140] shows a base peak due to an $[\mathrm{M}^{\cdot-}-\mathrm{PhCO_2}\cdot]^{-}$ ion (see m). †

The negative ion spectrum of o-nitrophenyl phenyl ether shows an $[\mathrm{M}^{\cdot-}-\mathrm{PhO}\cdot]^{-}$ ion, formed as shown in n[172]. †

A fragment ion $[\mathrm{M}^{\cdot-}-\mathrm{EtO}\cdot]^{-}$ is produced from 1-ethoxycarbonyl anthraquinone[86] as shown in o.‡ When the ethoxycarbonyl group is at position 2, this fragment ion is not observed.

$[\mathrm{M}^{\cdot-}-\mathrm{NO}\cdot]^{-}$ ions are observed for nitroaryl compounds,[44] and are considered to occur by rearrangement to the nitrite ester followed by loss of $\mathrm{NO}\cdot$ to yield p.‡

Some "apparent" rearrangement processes involve two groups remote from each other. Typical processes are observed in the spectra of p-nitrobenzoic acid and p-cyanobenzoic acid[83]. The spectra of these compounds exhibit elimination of $\mathrm{HNO_2}$ and HCN from their respective molecular anions (see q and r).‡

Other rearrangement reactions of carbonyl compounds are discussed in the Discussion Section of this thesis.

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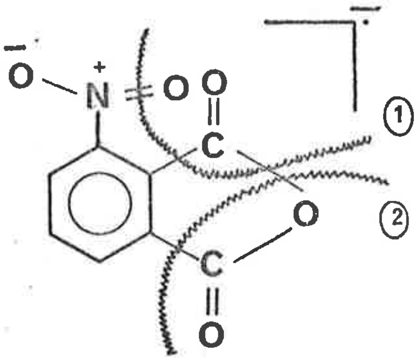
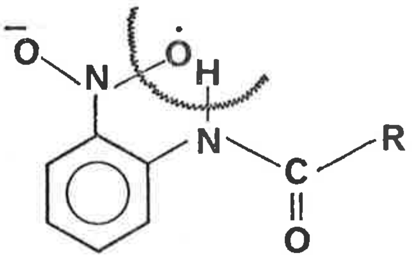
† See Page 22.

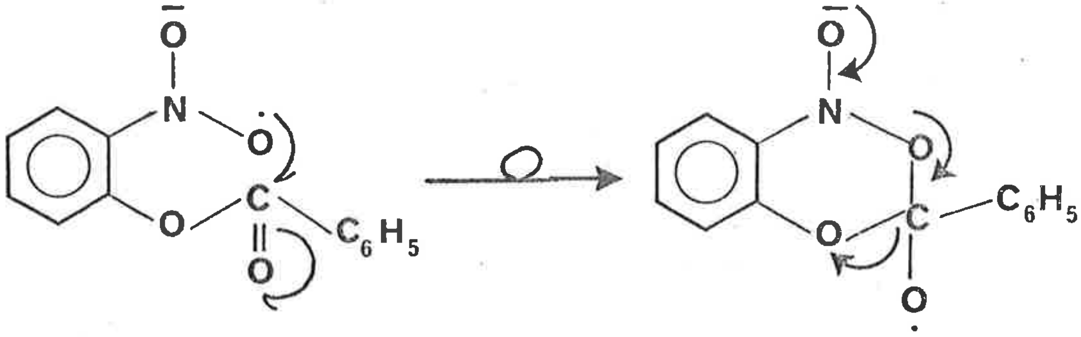
‡ See Page 23.



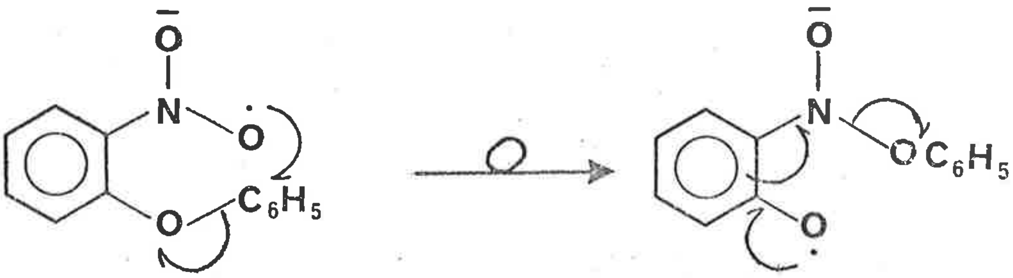
k



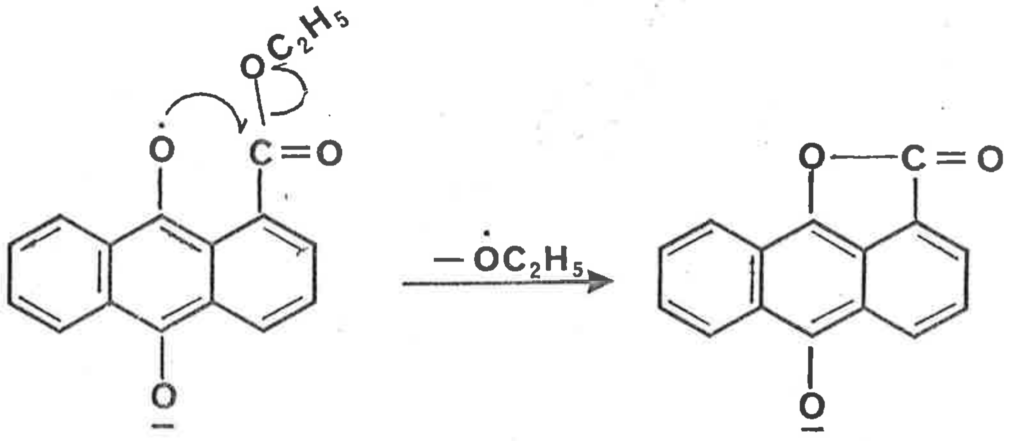
l



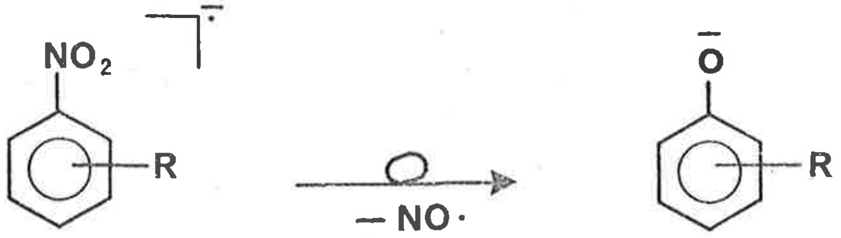
m



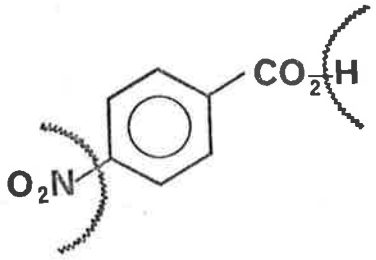
n



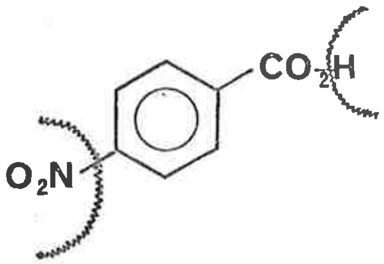
o



p



q



r

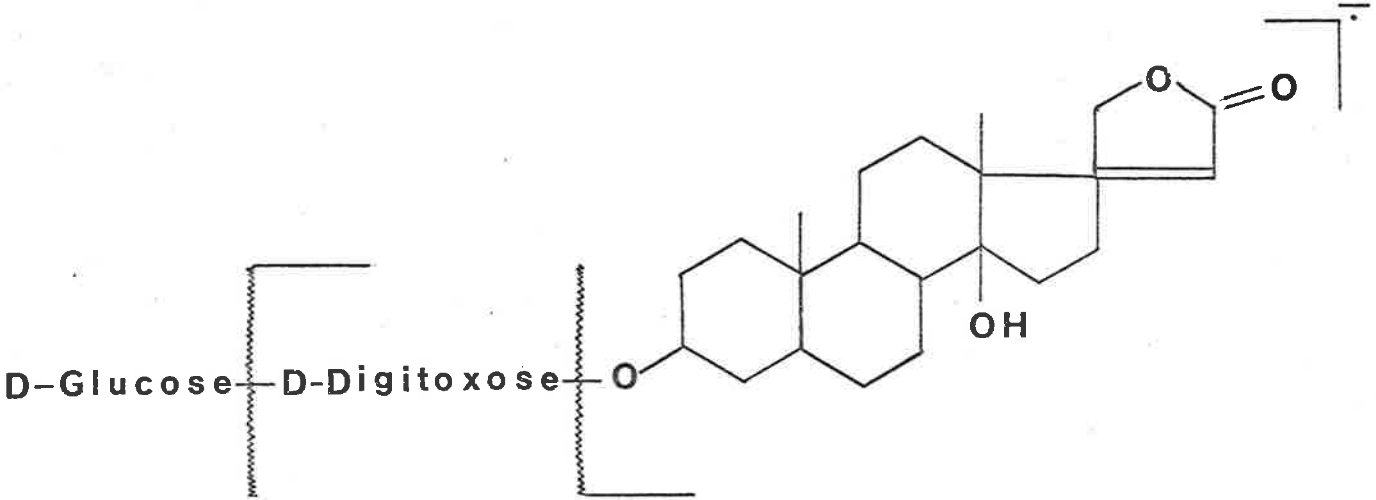
1.8.2. Some Applications of Negative-Ion Mass Spectra

Negative ion mass spectra appear to be useful for molecular weight determination and for structural problems when the corresponding positive ion spectra are either devoid of molecular ions or undergo very complex fragmentations.

As mentioned above, negative ion mass spectra are of value in the area of fluorocarbon chemistry. The molecular anions of fluoro compounds are relative stable at low electron energies, (e.g. perfluorocyclobutane,[109,116,117] perfluorocyclobutene[118] perfluorobenzene[118] and perfluorotoluene[118]) while positive molecular ions usually decompose by loss of a fluorine atom. At 70eV, most fluorocompounds produce the dominant ions F^- and $[M^{\bullet -}-F]^-$.

The *o*-, *m*-, *p*-nitrophenyl trifluoroacetanilides[167] could be identified by their negative ion mass spectra. The *o*-isomer eliminates $HO^{\bullet}$ from the molecular anion, the *m*-isomer fragments by the process $[M^{\bullet -}-HF-HO^{\bullet}]^-$ and the *p*-isomer decomposes by loss of HF. The positive ion mass spectra of the three isomers are almost identical.[167]

The high pressure technique of von Ardenne [30, 31, 184, 185] (see 1.3.5) has been used mostly for natural products and this area has been reviewed recently.[186, 187] The method proved to be particularly useful for the structural elucidation of the cardiac glycosides.[32-36] These complex glycosides give no molecular cations but produce pronounced molecular anions, [M-1] peaks, and undergo fragmentation at the glycoside ether positions. For example, bulloside[36] fragments as shown in *s*.



s

p-Nitrophenyl ester derivatives of long chain alcohols (t)[188] and p-nitrophenyl esters of carboxylic acids (u)[188] may be used for structural purposes. The negative ion spectra of t and u† produce intense molecular anions, whereas the positive ion spectra generally lack molecular ions. The basic fragmentations are simple and are shown in t and u.

Negative ion mass spectrometry has been used in the field of organometallic and co-ordination chemistry.[159,165,189-191] Some organometallic compounds produce pronounced molecular anions and simple fragmentation patterns.

A series of cyclopentadienyl metal carbonyls[192], viz. $[C_6H_5V(CO)_4]$; $[C_5H_5Cr(CO)_3]_2Hg$; $[C_5H_5Mn(CO)_3]$; $[C_5H_5Fe(CO)_2]$; $[C_5H_5Mo(CO)_3]_2$ produce pronounced molecular anions (by secondary electron capture), which then undergo fragmentation by successive losses of CO. A series of π-arene chromium tricarbonyls of formulae (v)† give intense negative ion mass spectra with the principle fragmentations $M^{\cdot-} \rightarrow [M^{\cdot-}-CO] \rightarrow [M^{\cdot-}-2CO] \rightarrow [M^{\cdot-}-3CO] \rightarrow [M^{\cdot-}-4CO]$.

The Schiffs base complexes w produce intense molecular anions and ligand ions.[193] Metastable evidence has been found in all cases for the process $[Cu(ligand)_2]^- \rightarrow [ligand]^-$.

The best illustration of the use of negative ion mass spectra for structure determination of organometallic systems is for the acetylacetonate type complex x[194]. †

Abundant molecular anions and the ligand radical anion $(L^{\cdot-})$ are produced and a comparison of a negative with a positive ion spectrum is shown in (Fig. 1-5)* for copper hexafluoroacetyl acetonate.

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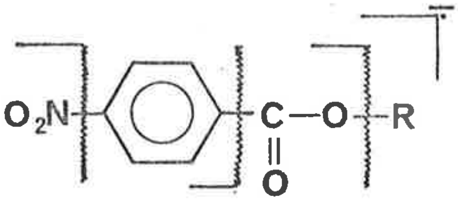
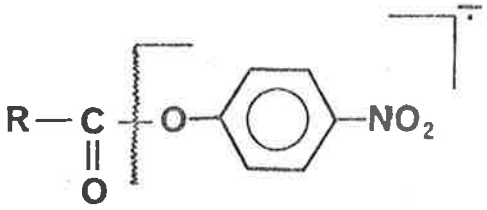
† See Page 27.

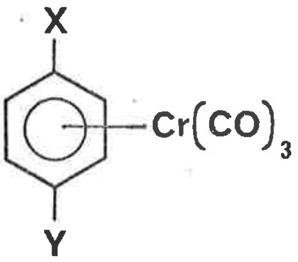
* See Page 28.



t



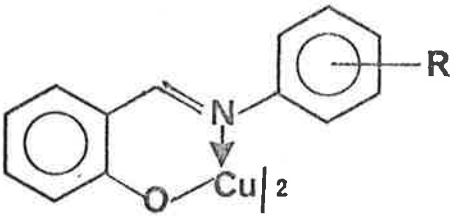
u



v

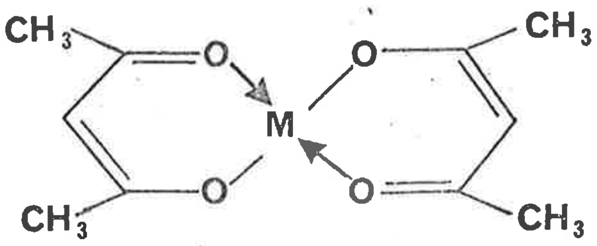
X = H, COOH, COOMe
CH_2COOMe

Y = H, Cl, Br, OCH_3
CH_3, NH_2, NO_2



w

R = H, o-, m-, p- Me, o-, m-, p- OMe, o-, m-, p- Cl
o-, m-, p- CF_3 and m-, p- CO_2Me

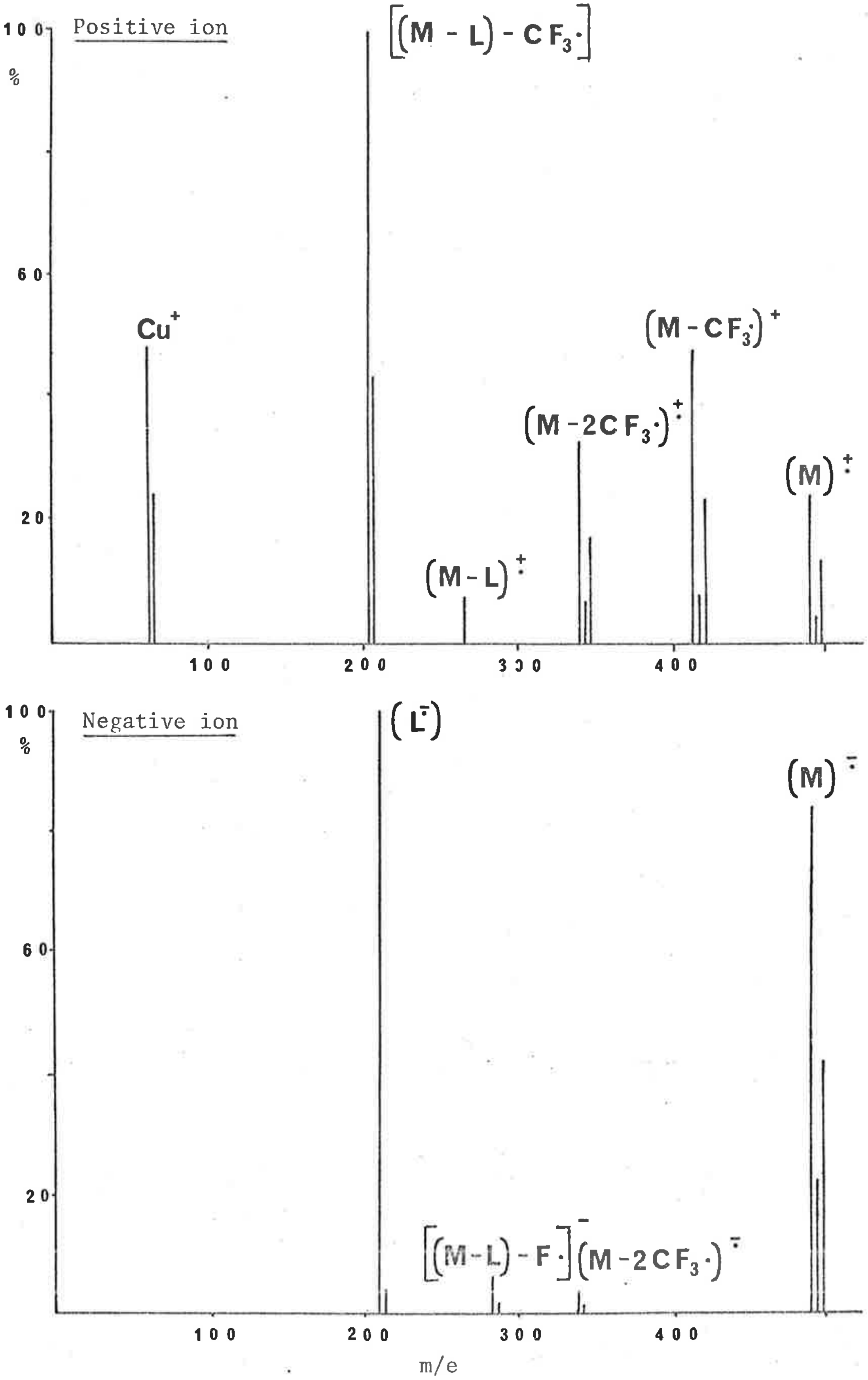


x

M = Cu, Co

FIGURE 1-5

Positive- and negative- ion spectra of copper hexafluoroacetylacetonate.



CHAPTER 2.

Negative-Ion Mass Spectra of The Aryl-CO-, Aryl-CO-CO- and Aryl-CO-CH_2-CO- Systems.

Page

INTRODUCTION

Certain types of organic compounds will accept electrons by secondary electron capture[38,39,173] to produce molecular anions.[41,87,195] The molecular anions may decompose by unimolecular processes involving either simple cleavage or rearrangement[89]. Processes are often substantiated by metastable peaks which can be detected in the field-free regions of the mass spectrometer.[13,74,83] Metastable peaks may be observed in the field-free region between the electric and magnetic sectors. In addition, the de-focussing technique[43,74,83] may be used to detect metastable ions produced in the field-free region before the electric sector.

Fragmentations may occur by one-step or multi-step pathways. A number of reports concerning the multi-step fragmentations of positive ions occurring between the ion source and collector have been reported.[62-69] Two step fragmentations of metastable ions are also observed in many negative ion spectra.[83]

Molecular anions formed by secondary electron capture processes at 70eV [41,87,195] usually undergo unimolecular decomposition. There are some molecular anions which do not have enough internal energy to enable fragmentation to occur, and as a consequence, there are particular functional groups which will not decompose under these conditions. A collision process based upon that developed for positive ions[96,98,196] has been used to increase the internal energy of a low energy molecular anion produced by secondary electron capture. The collision gas is usually nitrogen and is introduced into the first field-free region of the mass spectrometer to give a pressure of 10^{-5} Torr. Sample pressures of $1\text{-}2\times10^{-6}$ Torr are used in the source (with differential pumping). The low energy molecular anions are activated by collision in the first field-free region and then undergo decomposition. This technique may also be used to observe the fragmentations of initially un-reactive fragment anions.

Collision-induced dissociations produce daughter ions which have properties similar to the products of metastable ion fragmentations and may be observed in either field-free region of a double-focussing mass spectrometer. The collision-induced peaks are detected either by metastable focussing[13,94,83] or the related ion kinetic energy technique.[83]

The collision-induced dissociations of anthraquinone carboxylic acids,[148] p-nitrobenzoic acid,[105] p-cyanobenzoic acid,[105] nitroanilides,[104] maleic anhydride[93] and phthalic anhydride[102] have been investigated using this method.

Because of the low internal energy of molecular anions, rearrangement processes are generally observed to yield more abundant fragment anions than those produced by competing cleavage reactions. Skeletal rearrangement reactions are often observed when two functional groups are adjacent.[87] Hydrogen rearrangement occurs where a hydrogen transfer can proceed through a favourable transition state; e.g. phenyl p-nitrophenyl-acetate,[140] o-nitroacetanilide[44] and thioglycollic acid[183].

The molecular anions of aromatic aldehydes or ketones formed by secondary electron capture processes at 70eV, have low internal energies and show no fragmentation near the carbonyl centre. Quinones[86] and p-nitroacetophenones[44,93] give intense molecular anions. Fragmentation of the quinone chromophore and of the -COMe group does not occur under normal conditions. Collision activation of the 1,4-naphthoquinone molecular anion yields the ions $[M^{\cdot -} - CHO]$ and $[M^{\cdot -} - (CHO^{\cdot} + CO)]^{-}$ Similar treatment of p-nitroacetophenone[93] produced $[(M^{\bullet -}-NO)-Me^{\bullet}]^{\bullet -}$, $[(M^{\bullet -}-NO^{\bullet}-Me^{\bullet})-CO]^{\bullet -}$, $[(M^{\bullet -}-NO^{\bullet})-MeCO]^{\bullet -}$ and $[(M^{\bullet -}-NO^{\bullet})-CH_2CO]^{-}$ ions. Pentafluorobenzaldehyde[120] produces the fragment ion $C_6F_5^{-}$ and the rearrangement ion $[(M^{\bullet -}-NO)-CO]^{-}$ is observed in the conventional negative ion spectrum of o-nitrobenzaldehyde.[38] However, only simple fragmentation is noted in the negative ion spectrum of o-nitroacetophenone.[44]

Acetone[4] yields $M^{\bullet -}$, $[M^{\bullet -}-H^{\bullet}]^{-}$, $MeCO^{-}$ and H^{-} ions at 10^{-3} Torr. The 70eV spectrum of hexa-fluoroacetone[11,38,199] gives $M^{\bullet -}$, $[M^{\bullet -}-F^{\bullet}]^{-}$, CF_3^{-} and F^{-} ions. Long chain aldehydes[142] do not produce molecular anions but yield $[M-H]^{-}$ ions at 55eV and 10^{-5} Torr. Ketene,[198] at low energy gives C_2HO^{-}, $C_2O^{\bullet -}$ and C_2H^{-} ions.

From the above observations, it would appear that α-cleavage to the carbonyl group is the basic decomposition of ketones and aldehydes in the negative mode. No systematic investigation of ketones and aldehydes has yet been reported, so the negative ion spectra of Aryl-CO-, Aryl-CO-CO- and Aryl-CO-CH_2-CO- compounds have been surveyed in order to:-

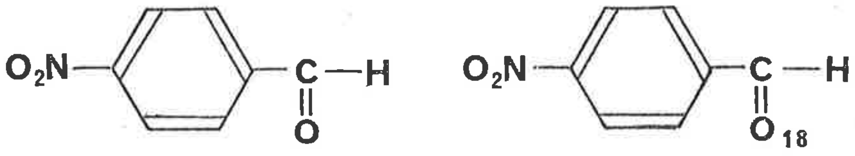
(a) determine the basic collision-induced dissociations of the carbonyl group of aryl ketones and aldehydes,

(b) determine the extent of any hydrogen transfer reactions and

(c) examine possible ortho effect in o-nitrophenyl carbonyl systems.

2.2 RESULTS AND DISCUSSION

2.2.1 The Aryl-CHO Group

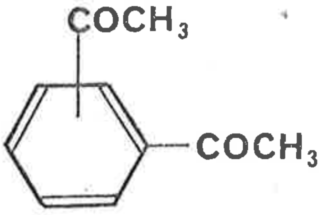


(1)

The conventional negative ion spectrum of p-nitrobenzaldehyde exhibits a pronounced molecular anion and the additional fragment ions $[M^{\cdot-}-NO^{\cdot}]^{-}$ and $NO_2^{\,-}$; fragmentation at the carbonyl centre is not observed. When collision gas (nitrogen) is introduced into the first field-free region of the mass spectrometer to a pressure of 3 x 10^{-5} Torr; a collision excitation spectrum is obtained. The collision induced dissociation of p-nitrobenzaldehyde $[^{18}O]$ yields the ions $[M^{\cdot-}-NO^{\cdot})-CH^{18}O^{\cdot}]^{\cdot-}$ $[M^{\cdot-}-(NO^{\cdot}+CH^{18}O^{\cdot})]^{\cdot-}$, $[M^{\cdot-}-NO_2^{\cdot}]^{-}$, $[M^{\cdot-}-(NO^{\cdot}+CH^{18}O^{\cdot})]^{\cdot-}$, $[M^{\cdot-}-O]^{\cdot-}$, $[(M^{\cdot-}-O)-NO^{\cdot}]^{-}$ and $[(M^{\cdot-}-O)-(NO^{\cdot}+CH^{18}O^{\cdot}]^{\cdot-}$.

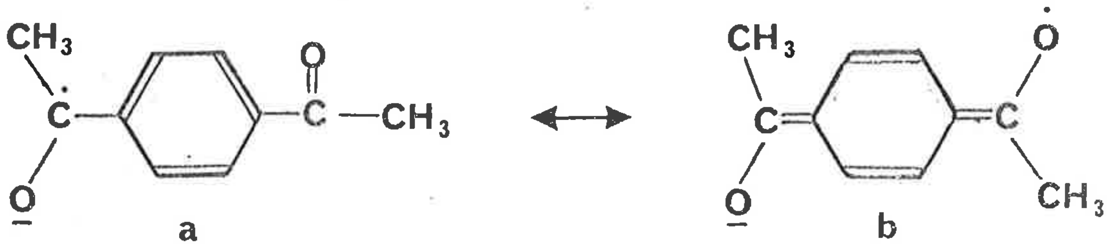
In this case α-cleavage to the formyl group may occur either by simple cleavage from a fragment anion, or by a two stage cleavage from the molecular anion.

2.2.2 THE ARYL-CO-ALKYL AND ARYL-CO-ARYL SYSTEMS



COMPOUND	$COCH_3$
(2)	*o*
(3)	*m*
(4)	*p*

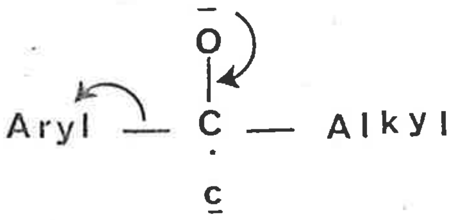
The 70eV spectra of *o*- and *p*-diacetylbenzene (2) and (4) show pronounced molecular anions which produce high ion currents, while that of *m*-diacetylbenzene (3) gives a lower ion current. The α-cleavage ion $[M^{\cdot -}-CH_3CO^{\cdot}]^-$ is not noted, because the molecular anions have low internal energies and high stabilities when the two functional groups are in conjugation (see e.g. *a* and *b*).



a

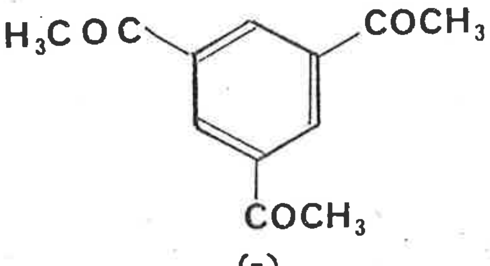
b

However fragmentation α- to the carbonyl group does occur under collision-excitation conditions. The collision-induced peaks $[M^{\cdot -}-MeCO]^-$ are noted in the spectra of (2), (3), (4). The formation of $[M^{\cdot -}-MeCO^{\cdot}]^-$ may be rationalized as shown in *c*.



The abundance of the fragment ion $[M^{\bar{\cdot}}\text{-MeCO}^{\cdot}]^-$ increases as the pressure of the collision gas is increased because of an increase in the internal energy of the decomposing molecular anion.

The fragment ion $[(M^{\bar{\cdot}}\text{-NO}^{\cdot})\text{-CH}_2\text{CO}]^-$, produced by a hydrogen rearrangement process, has been observed previously in the negative ion spectrum of p-nitroacetophenone.[44] Fragment ions of this type have not been encountered in the collision-excitation spectrum determined in this study.



(5)

1, 3, 5 - Triacetylbenzene (5) shows no fragmentation in the conventional negative ion spectrum, but the collision-excitation spectrum shows the formation of the simple cleavage ion $[M^{\bar{\cdot}}\text{-MeCO}^{\cdot}]^-$ and an ion $[M^{\bar{\cdot}}-(\text{MeCO}^{\cdot} + \text{MeCO}^{\cdot})]^{\bar{\cdot}}$ (see Fig 2-1).†

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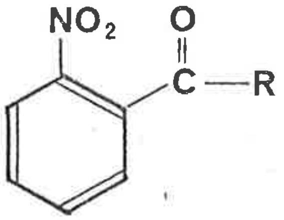
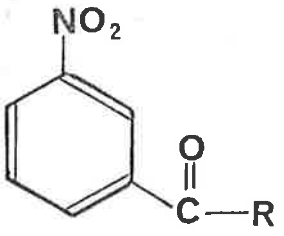
† Figures are shown in lift-out format at the end of the appropriate chapter.



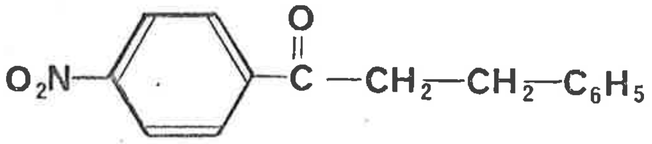
(6) R = Et

(7) R = Pr



(8) R = Et

(9) R = Pr



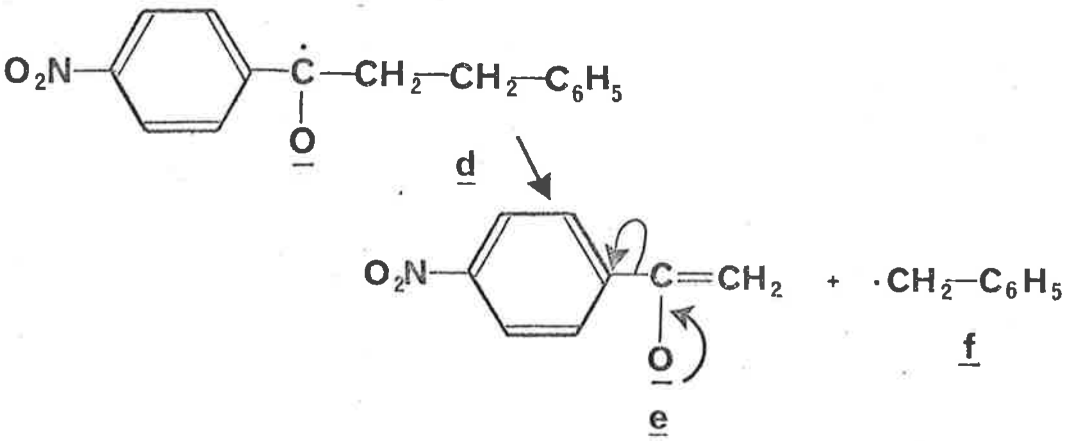
(10)

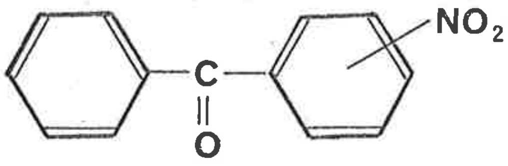
The conventional negative ion spectra of the nitrophenyl ketones (6) - (10) exhibit the normal $M^{\overline{\cdot}}$, $[M^{\overline{\cdot}}-NO^{\cdot}]^{-}$ and NO_2^{-} ions. Fragment ions $[M^{\overline{\cdot}}-RCO^{\cdot}]^{-}$ are noted in the collision-excitation spectra of (6) - (9). These fragment ions are produced by α-cleavage to the carbonyl centre as illustrated in c. Proximity effects are not observed in the negative ion spectra of o-nitropropiophenone (6) and o-nitrobutyrophenone (7). Hydrogen rearrangement processes are also not observed in any spectra (see also above).

α-cleavage to the carbonyl group is not noted in the collision-excitation spectrum of (10). Instead, β-cleavage to the carbonyl group produces the ion $[M^{\overline{\cdot}}-PhCH_2^{\cdot}]^{-}$ which then eliminates ketene (see Table 2-1).[†] The mechanisms of these fragmentations may be rationalized as shown in d and e.

[†] Tables are shown at the end of the chapter.

The elimination of the benzyl radical f from the molecular anion (10) should be contrasted with the non-observance of H• or CH_3· loss from (6)-(9); a feature undoubtedly due to the stability of benzyl radical.

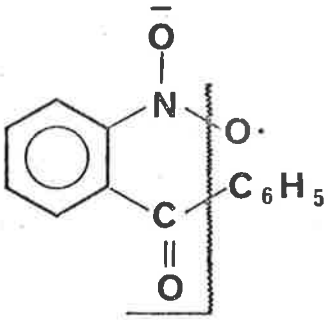




(11)	NO_2	o
(12)	NO_2	m
(13)	NO_2	p

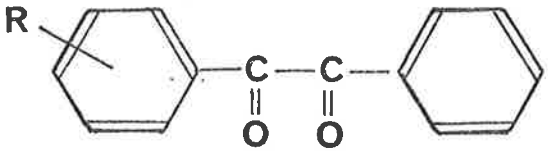
The basic fragmentations of m- and p-nitrobenzophenone (12) and (13) yield $[M^{\cdot-}-NO^{\cdot}]^{-}$ and NO_2^{-} ions. α-cleavage to the carbonyl group is not noted in the collision-excitation spectra. The conventional negative in spectrum of a o-nitrobenzophenone (11) shows the following peaks: $M^{\cdot-}$ (100%), $[M^{\cdot-}-NO^{\cdot}]^{-}$(12%) $[M^{\cdot-}-PhO^{\cdot}]^{-}$(6%) and NO_2^{-}(8%).

The elimination of the phenoxide radical from the molecular anion of *o*-nitrobenzophenone is thought to occur by an unusual ortho rearrangement (see Fig 2.2). This is a general process which occurs for organic compounds of type *o*-$NO_2C_6H_4$ X C_6H_5,[172] where X is either oxygen or sulphur. It has been shown that the oxygen involved in the rearrangement process $[M^{\bar{\cdot}}-PhO^{\cdot}]$ was the oxygen from the nitro group. The rearrangement process is illustrated in *g*.



g

2.2.3 The Aryl-CO-CO-Aryl System

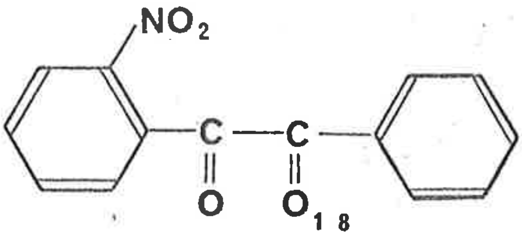


(14) R = H

(15) R = *o*-NO_2

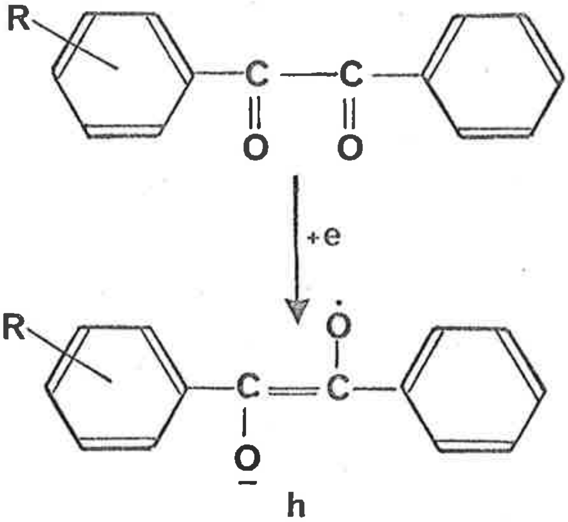
(16) R = *m*-NO_2

(17) R = *p*-NO_2



(18)

The 70eV spectra of α-dicarbonyl systems exhibit stable molecular anions (e.g. h).

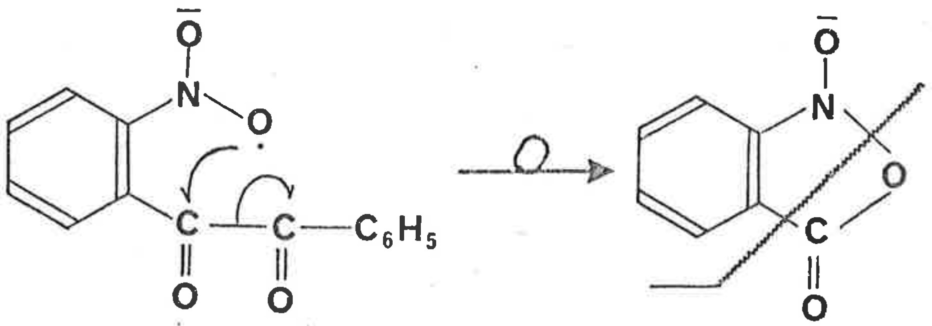


h

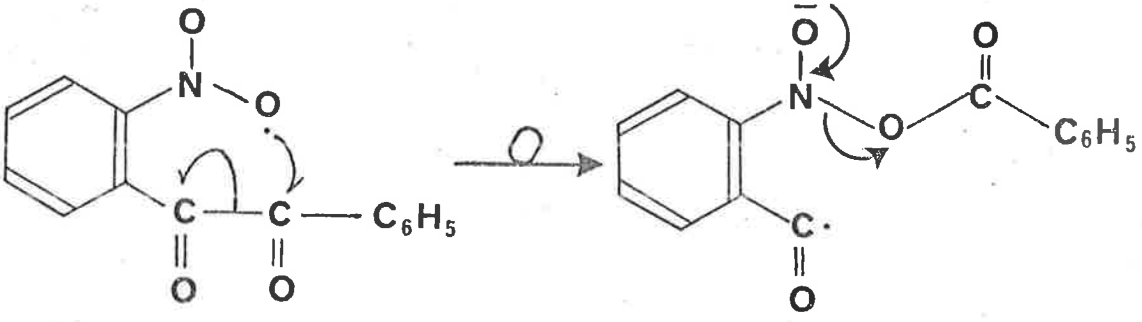
Neither benzil (14) nor the m- and p-nitro-derivatives (16) and (17) undergo cleavage of the aryl-CO-CO- system upon collision-excitation, negative ion spectra of m- and p-nitro-derivatives (16) and (17) show only the basic fragment ions [M-NO•]$^-$ and NO_2^- (see Table 2-1).

Pronounced peaks due to ortho effects are observed in the negative ion spectrum of o-nitrobenzil (15). The spectrum (Fig 2-3) was measured in the absence of collision gas and various fragmentations are observed (see Table 2-1).

The fragment ions yield peaks at m/e 225, m/e 209, m/e 150, m/e 121, m/e 106 and m/e 46 which correspond to $[M-NO\cdot]^-$, $[M-NO_2\cdot]^-$, $[M-PhCO\cdot]^-$, $[M-C_7H_4NO\cdot]^-$, $[(M-PhCO\cdot)-CO_2]^-$ and NO_2^- respectively. In order to investigate the formation of these fragment ions, the ^{18}O-labelled species (18) was prepared. The corresponding spectrum shows the ions $[M-C_6H_5C^{18}O\cdot]^-$ and $PhC^{18}OO^-$ for (18). These rearrangement ions are probably produced by competitive cyclizations of the nitro group to each carbonyl centre through five and six membered transition states respectively. The reactions may be rationalized as shown in i → j and k → l respectively.

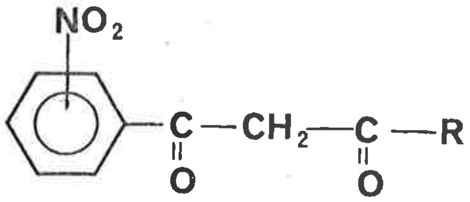


i j



k l

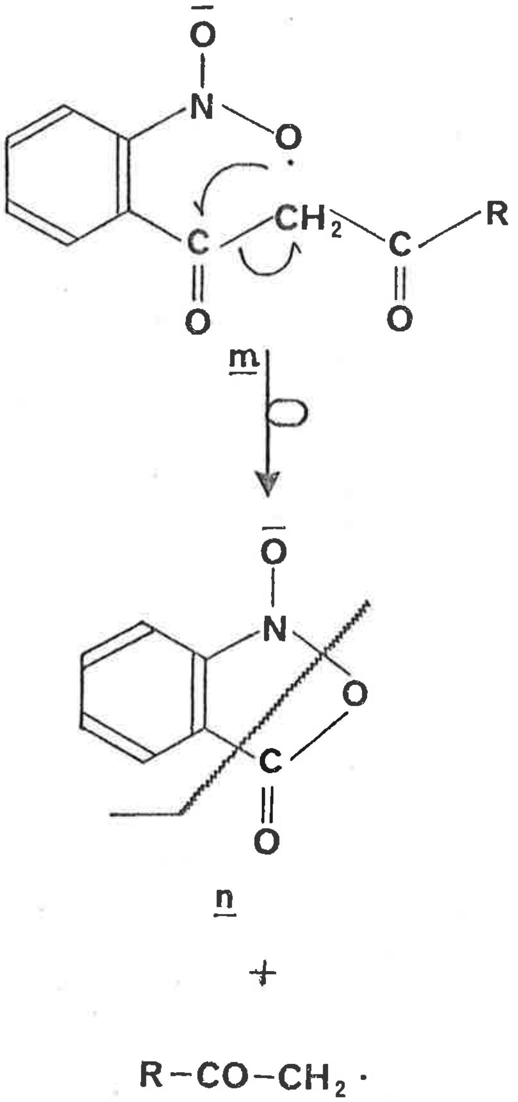
2.2.4 The Aryl-CO-CH_2-CO-Alkyl and Aryl-CO-CH_2-CO-Aryl Systems



COMPOUND	NO_2	R
(19)	o	CH_3
(20)	m	CH_3
(21)	p	CH_3
(22)	o	C_6H_5
(23)	m	C_6H_5
(24)	p	C_6H_5

The conventional negative ion spectra of the nitrophenyl β-diketone derivatives (20), (21), (23) and (24) produce the molecular anion as the base peak and the fragment ions $[M-HO^\bullet]^-$, $[M-NO^\bullet]^-$ and NO_2^- (see Table 2-2). The fragment ions $[M-CH_2COR^\bullet]^-$ and $[M-COR^\bullet]^-$ are not observed. However the negative ion spectra of o-nitrophenyl β-diketone derivatives (19) and (22) show prominent peaks due to the ion $[M-CH_2-COR^\bullet]^-$ (see Fig 2-4 and 2-5). Other fragment ions are shown in Table 2-2.

The rearrangement ions $[M-CH_2COR^\bullet]^-$ must be produced by the effect of the o-nitro group, which may cyclize to the nearer carbonyl centre through a five membered transition state (see m → n). The ion n fragments further by loss of carbon dioxide.


m
n
+
R–CO–CH₂·

2.3 CONCLUSIONS

(1) The basic collision-induced fragmentation of Aryl-CO-R is α-cleavage to the carbonyl centre when R = alkyl. When R = $(CH_2)_2Ph$ loss of $PhCH_2^{\bullet}$ (by β-cleavage to the carbonyl group) is noted. No fragmentation occurs when R = aryl.

(2) Decomposition with accompanying hydrogen rearrangement has only been observed for p-nitroacetophenone.

(3) ortho-Rearrangements are noted for the systems o-nitrophenyl-CO-aryl, o-nitroaryl-CO - CO-aryl, o-nitroaryl-CO-CH_2-CO-alkyl and o-nitroaryl-CO-CH_2-CO-aryl.

TABLE 2-1

Conventional Negative Ion Mass Spectra of (6)-(7)

(6)	m/e	46	149	178	179(M$^{-\cdot}$)	180		
	I %	27	22	6	100	14		
	m*	179 → 149						
(7)	m/e	46	145	163	193(M$^{-\cdot}$)	194		
	I %	58	2	10	100	10		
	m*	193 → 163,	193 → 145					
(8)	m/e	46	149	163	164	179(M$^{-\cdot}$)	180	
	I %	47	5	1.5	2	100	2	
	m*	179 → 149						
(9)	m/e	46	163	193(M$^{-\cdot}$)	194			
	I %	25	1	100	10			
	m*	193 → 163						
(10)	m/e	46	164	225	255(M)$^{-\cdot}$	256		
	I %	20	1	3	100	18		
	m*	255 → 225,	255 → 164					
(11)	m/e	46	134	179	180	197	227(M$^{-\cdot}$)	288
	I %	9	4	2	1.5	13	100	15
	m*	227 → 197,	227 → 180,	227 → 179,	227 → 134			
(12)	m/e	46	197	227(M$^{-\cdot}$)	228			
	I %	20	4	100	15			
	m*	227 → 197						
(13)	m/e	46	197	227(M$^{-\cdot}$)	228			
	I %	10	9	100	18			
	m*	227 → 197						

(15)

m/e	46	106	118	121	148	150	151	163	166
I%	45	14	14	22	32	42	5	10	5

m/e	167	193	209	225	255($M^{\cdot-}$)	256
I%	6	7	15	5	100	18

m* 255 → 225, 255 → 209, 255 → 150 → 106, 255 → 121

(16)

m/e	46	225	255($M^{\cdot-}$)	256
I%	13	6	100	14

m* 255 → 255

(17)

m/e	46	225	255($M^{\cdot-}$)	256
I%	17	15	100	18

m* 255 → 225

TABLE 2-2

Conventional Negative Ion Mass Spectra of (19)-(24)

(19)

m/e	46	106	150	151	177	190	206	207($M^{\cdot-}$)	208
I%	20	5	100	8	6	4	25	80	5

m* 207 → 190, 207 → 177, 207 → 150 → 106

(20)

m/e	46	177	190	206	207($M^{\cdot-}$)	208
I%	15	5	45	45	100	20

m* 207 → 190, 207 → 177

(21)

m/e	46	92	122	159	177	178	206	207($M^{\cdot-}$)	208
I%	4	3	9	3	20	4	10	100	18

m* 207 → 177, 207 → 122

(22)

m/e	46	106	122	134	150	151	223	252	268	269($M^{\cdot-}$)
I%	4	3	2	2	100	8	2	3	10	7

m* 269 → 252, 269 → 150 → 106

(23)

m/e	46	254	255	270	271($M^{\overline{\cdot}}$)	272
I%	3	16	6	3	100	22

m* 271 → 254

(24)

m/e	46	271($M^{\overline{\cdot}}$)	272
I%	2	100	18

FIGURE 2-1

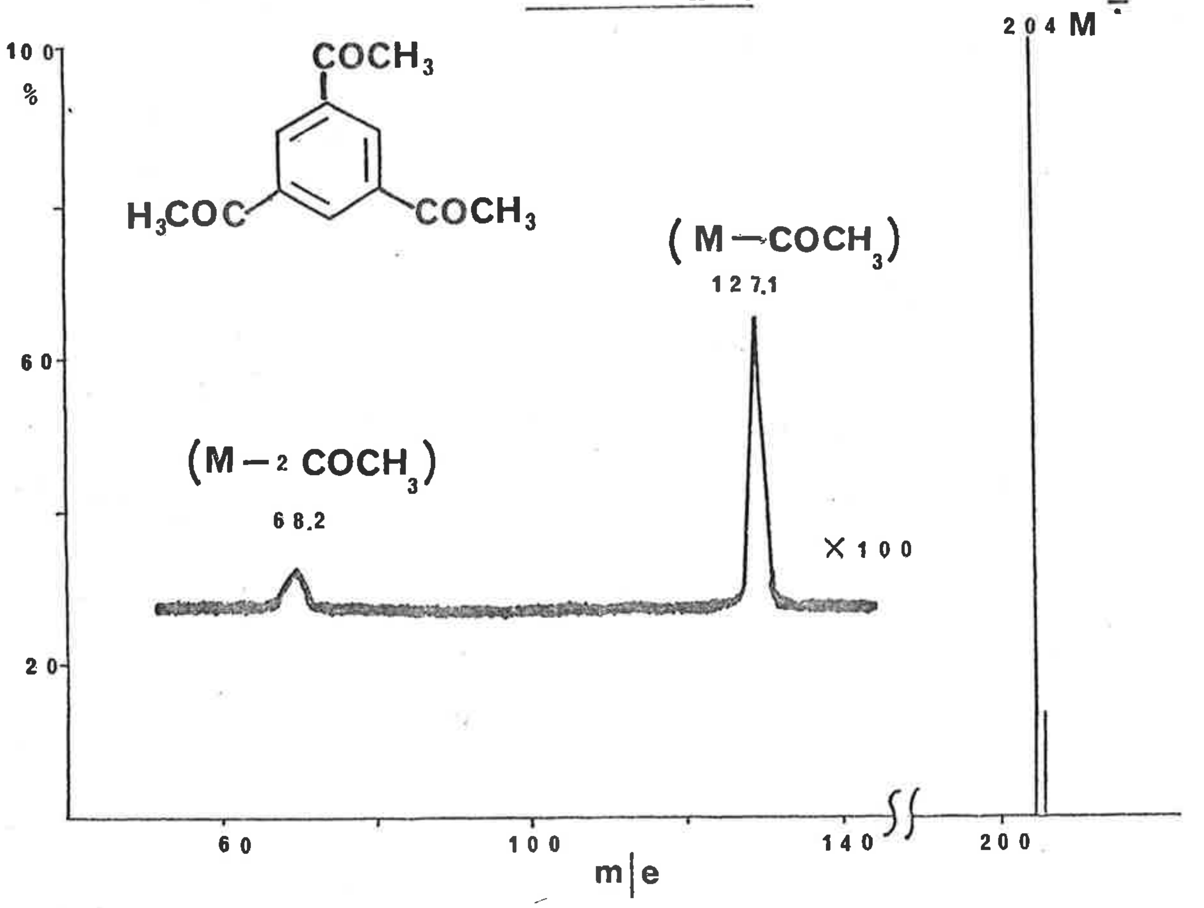


FIGURE 2-2

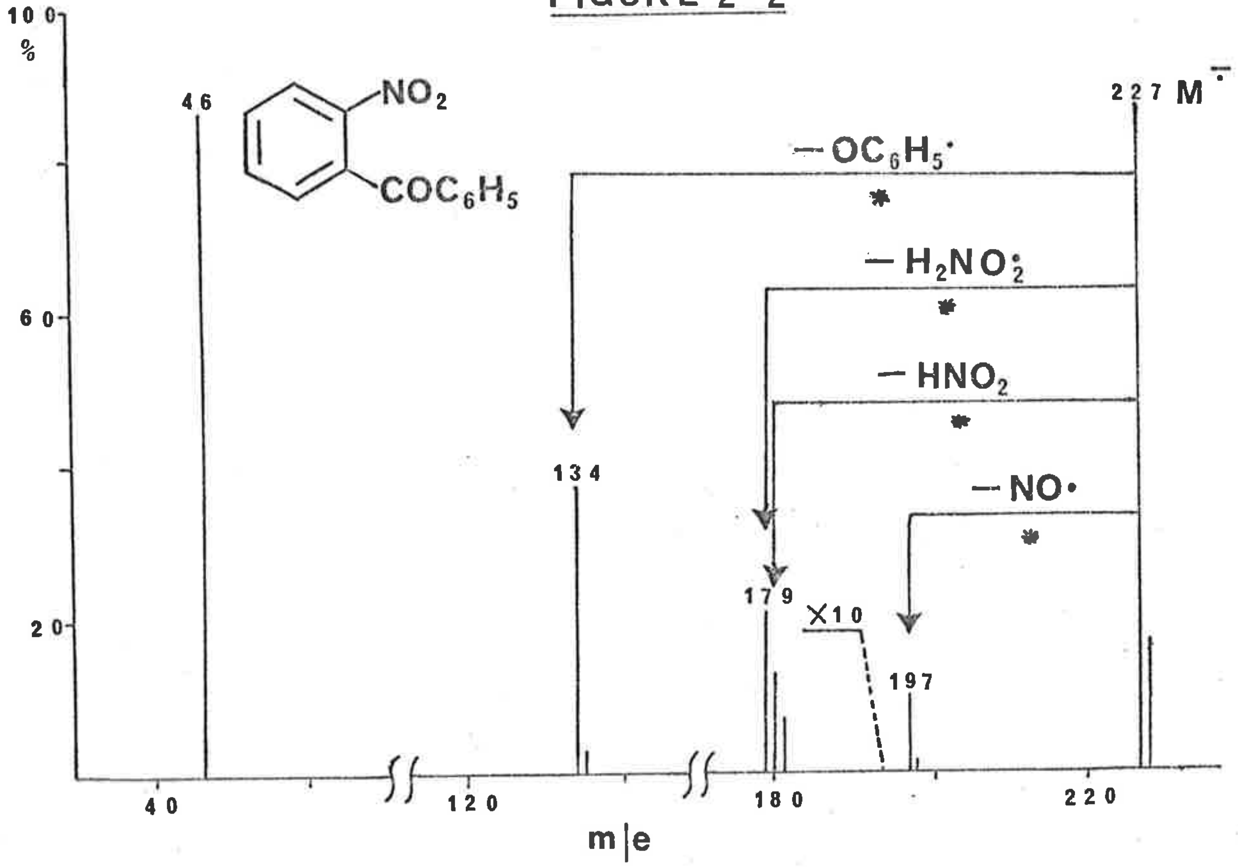


FIGURE 2—3

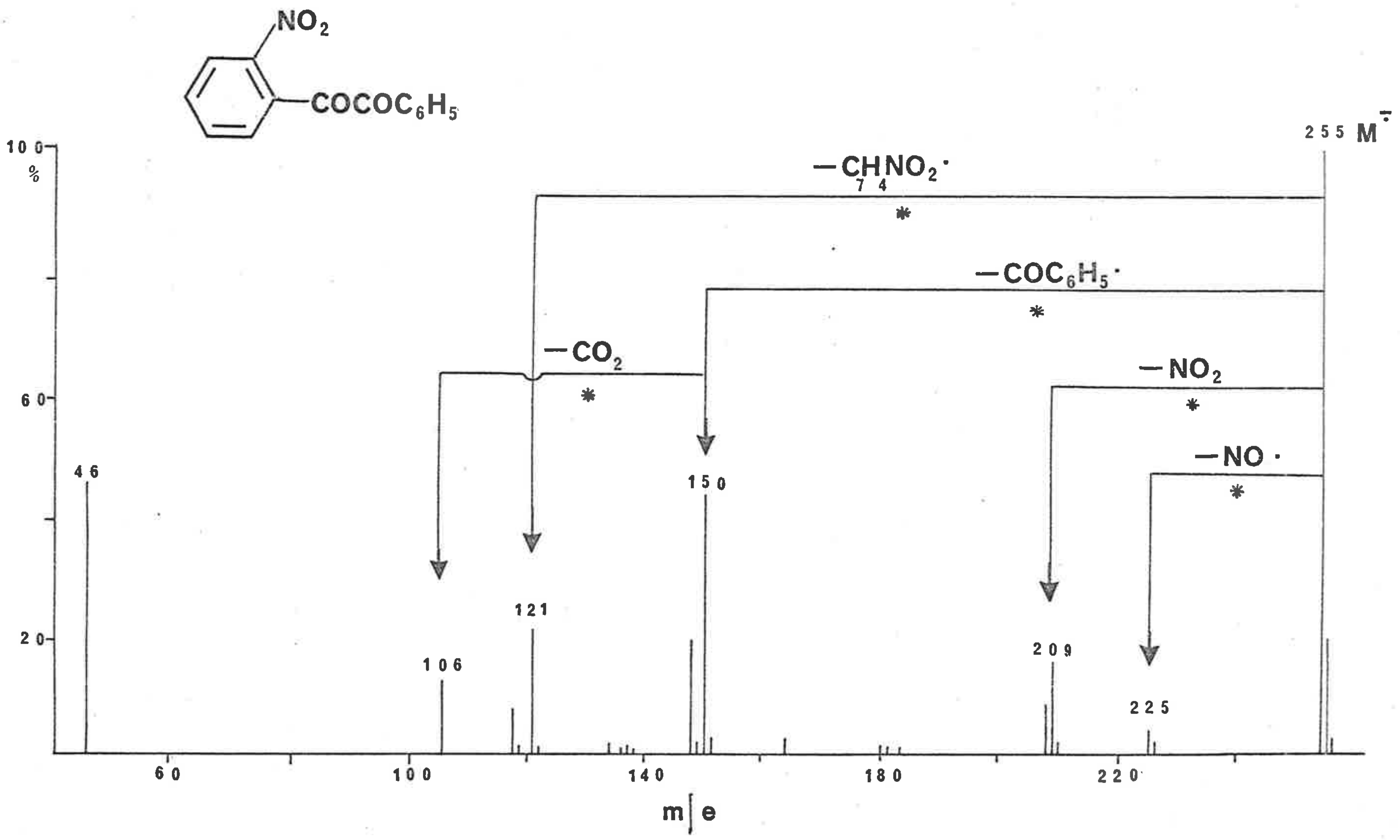
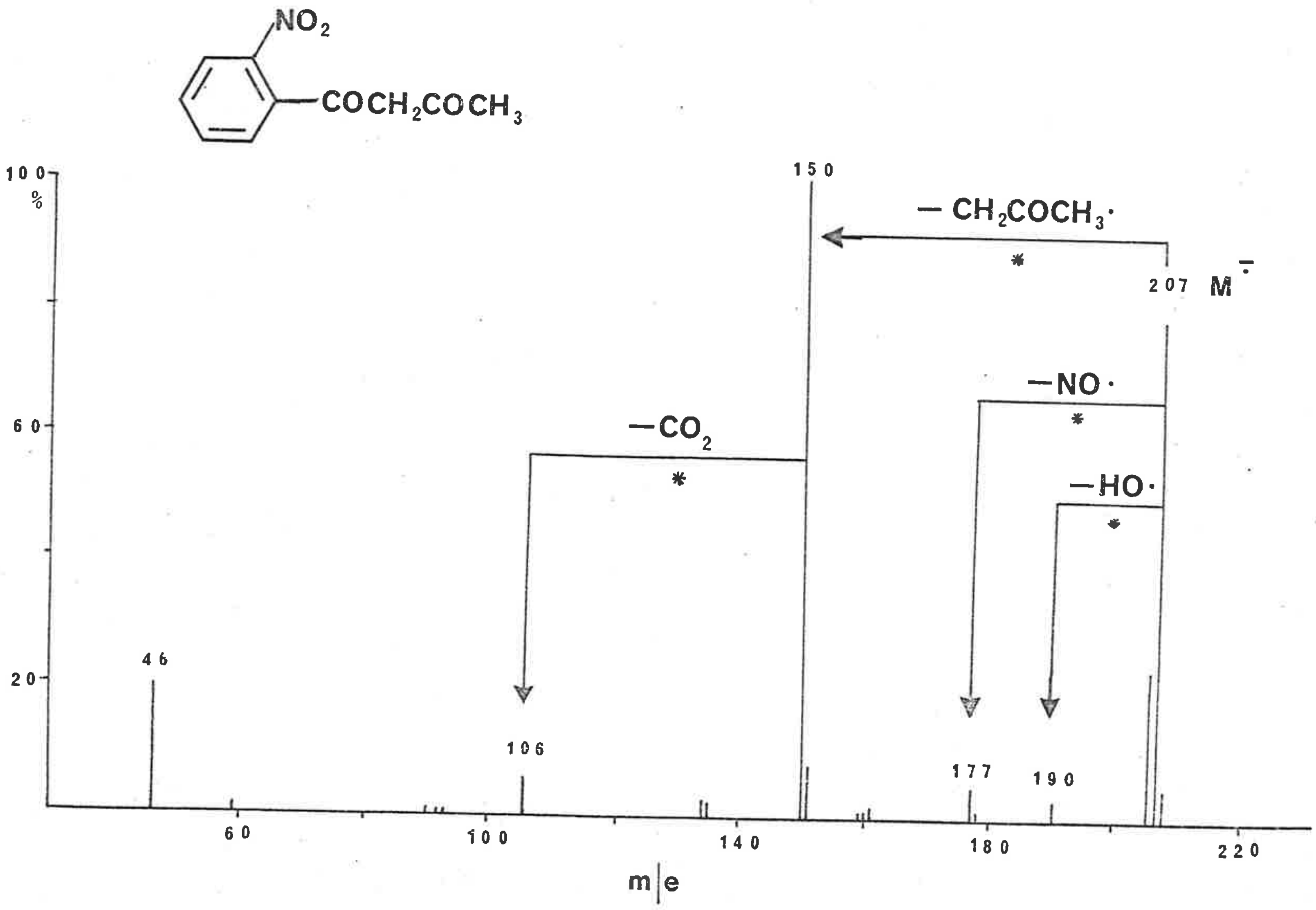
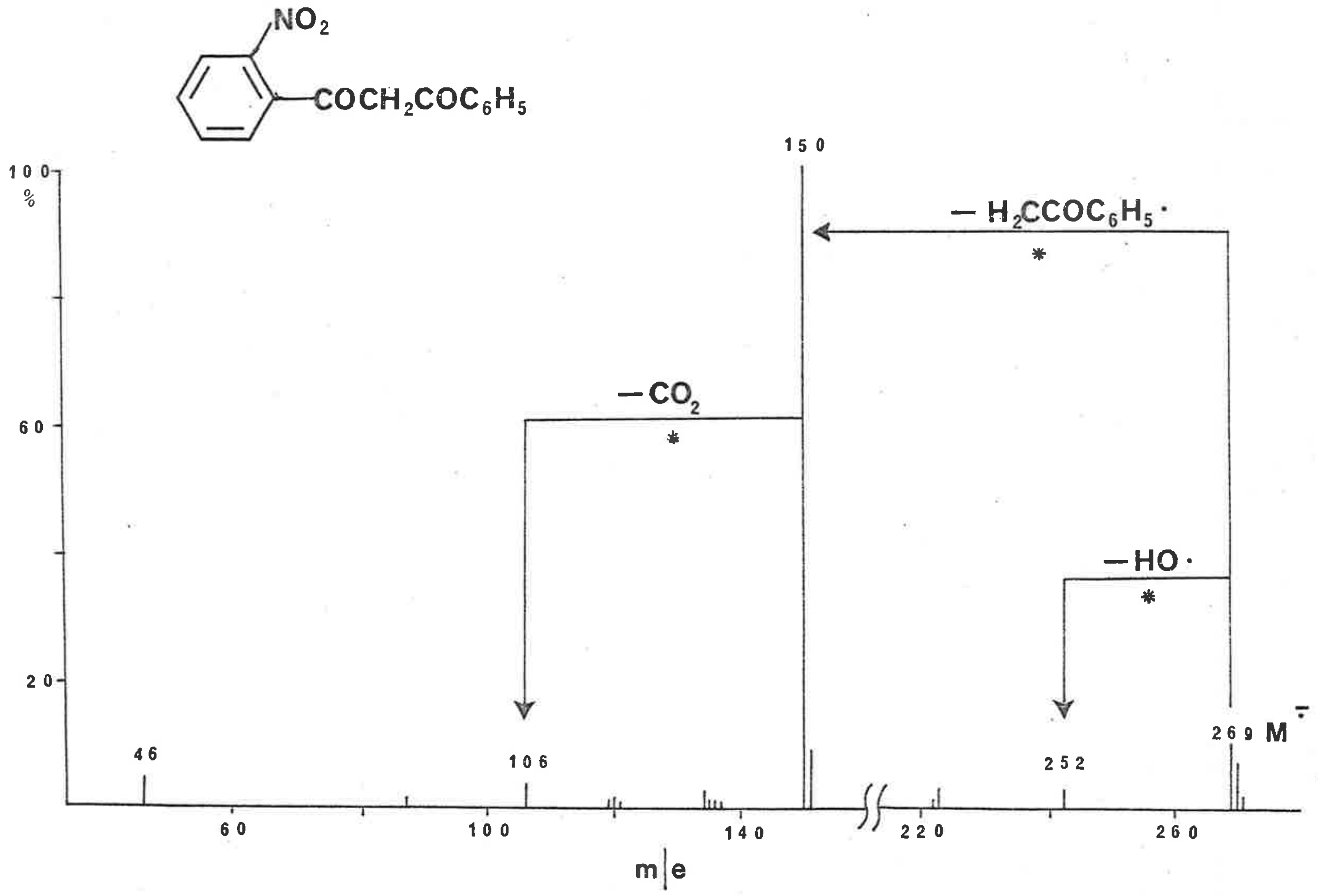

NO2
COCOC6H5
100 %
60
20
46
106
121
150
209
225
255 M
—CHNO2·
74
—COC6H5·
—CO2
—NO2
—NO·
*
60
100
140
180
220
m/e

FIGURE 2—4



NO2
COCH2COCH3
100 %
60
20
150
46
106
177
190
207 M-·
— CH2COCH3·
—NO·
—HO·
—CO2
*
60
100
140
180
220
m|e

FIGURE 2—5


NO2
COCH2COC6H5
100 %
60
20
150
— H2CCOC6H5·
*
—CO2
*
—HO·
*
46
106
252
269 M+·
60
100
140
220
260
m|e

CHAPTER 3.

Negative-Ion Mass Spectra of The Aryl-CH_2-CO- and Aryl-$(CH_2)_2$-CO-Systems.

Page

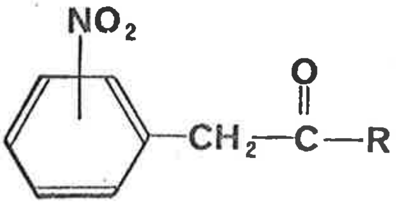
3.1 INTRODUCTION

In Chapter 2, the behaviour of fragmentation of the carbonyl systems Aryl-CO-, Aryl-CO-CO- and Aryl-CO-CH_2-CO- was discussed. α-Cleavage to the carbonyl centre was observed in the collision-excitation spectra of compounds of the general formula Aryl-CO-alkyl. The Aryl-CO-Aryl group was stable under these conditions. Parent ions from α-dicarbonyl systems did not generally fragment, but in the case of o-nitrobenzil and o-nitrophenyl-CO-CH_2-CO- derivatives, fragment ions were produced after cyclization of the nitro group to the carbonyl centres.

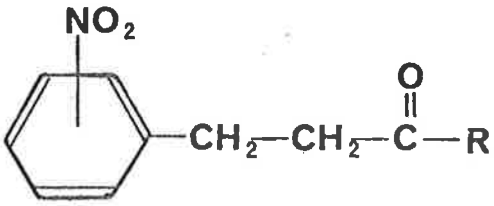
Systematic studies of Aryl-$(CH_2)_n$-CO-, (n=1,2) systems were carried out next, in order to ascertain the basic cleavages of the carbonyl containing units of these compounds.

3.2 RESULTS AND DISCUSSION

3.2.1 THE ARYL-$(CH_2)_n$-CO-R SYSTEMS (n=1 or 2)



COMPOUND	NO_2	R
(25)	*m*	CH_3
(26)	*p*	CH_3
(27)	*m*	C_6H_5
(28)	*p*	C_6H_5



COMPOUND	NO_2	R
(29)	*o*	CH_3
(30)	*p*	CH_3
(31)	*o*	C_6H_5
(32)	*p*	C_6H_5

The conventional negative ion spectra of compounds (25)-(32) exhibit intense molecular anions. Nitrobenzyl anions, produced by α-cleavage to the carbonyl group are noted for compounds (27) and (28). This result should be compared with that obtained for (25) and (26), whose negative ion spectra contain no nitrobenzyl anions. Collision induced dissociations of the molecular anions derived from (25) and (26) do yield nitrobenzyl anions (the use of nitrogen as collision gas has been described in Chapter 2). All decompositions mentioned in the text have been substantiated by the presence of metastable or collision induced decompositions occurring in both field-free regions of the mass spectrometer. The appropriate metastable or collision induced daughter ions for these processes [and for all other mentioned in this chapter] are gaussian in shape, except for [M-NO$^{\bullet}$] processes (flat-topped)[93] . The collision induced negative ion spectrum of (25) produces a dished flat-topped peak (see Fig 3-1) and the energy release† (at half height)[199] is 0.075eV.

The driving force for the α-cleavage reactions, observed for (25)-(28), may be due to initiation of fragmentation from either the charged nitro or carbonyl groups. The processes may be depicted formally as shown in a and b respectively.

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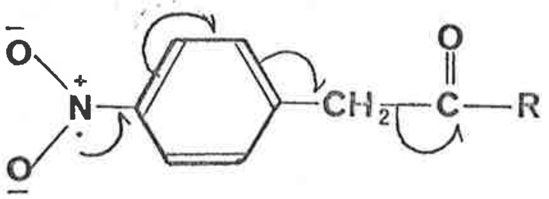
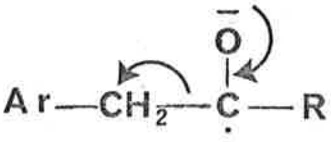
† The methods used for the determination of kinetic energy release have been previously described, see J.H. Bowie, S.G. Hart and T. Blumenthal, Int. J. Mass Spectrom. Ion Phys., in press.



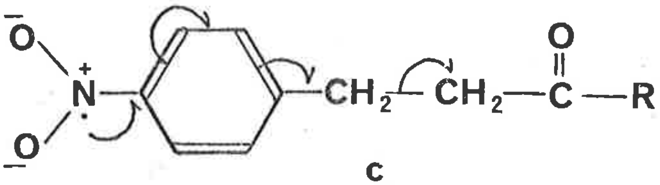
a



b

The mechanism shown in b should operate for the m-isomers (25) and (27). Compounds (29)-(32) fragment by β-cleavage to give the species aryl-CH_2^- (see Table 3-1). As an illustration, the spectrum of (31) shows the following peaks; $M^{\cdot -}$(100%), $[M^{\cdot -}-NO^{\cdot}]^-$ (2%), $[M^{\cdot -}-PhCOCH_2^{\cdot}]^-$ (8%), NO_2^-(35%).

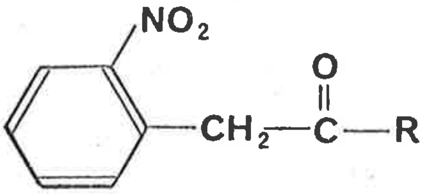
The initiation of fragmentation by a charged nitro group (a) has been discussed above and is well illustrated for the β-cleavage process as shown in c. The driving force for such a reaction is the formation of the very stable nitrobenzyl anion.



c

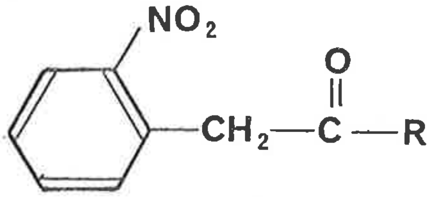
Processes involving re-arrangement reactions are not noted in the negative ion spectra of the p-nitro derivatives (29) and (31). Fragment ions are produced solely by simple fragmentation (see Table 3-1).

3.2.2 REARRANGEMENT PROCESSES OF *o*-NO$_2$-C$_6$H$_4$-CO-R

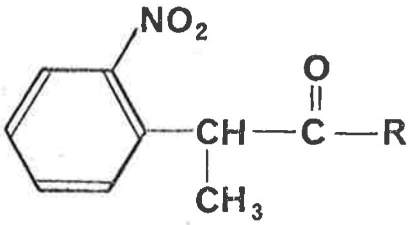


	R
(33)	H
(34)	CH$_3$
(35)	Ph

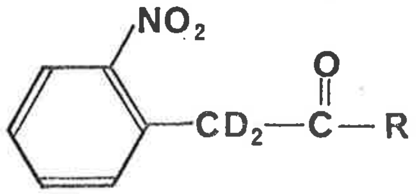
Rearrangement reactions are prevalent in the negative ion mass spectra of *o*-substituted nitrophenyl compounds, and such processes have been reviewed recently.[87,200] Ketone compounds which exhibit rearrangement peaks are *o*-nitrobenzophenone (11), *o*-nitrobenzil (15), *o*-nitrobenzoyl acetyl methane (19) and *o*-nitrobenzoyl benzoyl methane (22); these have been discussed in Chapter 2. The negative ion mass spectra of *o*-nitrophenylacetaldehyde (33), *o*-nitrophenylacetone (34) and *o*-nitrophenylacetophenone (35) also undergo rearrangement processes and these complex reactions are discussed below.



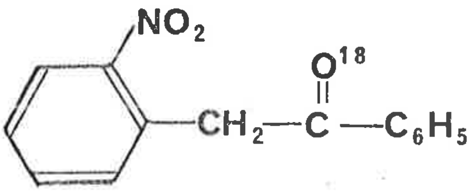
COMPOUND	R
(36)	$\underline{p}$-MeOC$_6$H$_4$
(37)	$\underline{p}$-MeC$_6$H$_4$
(38)	$\underline{m}$-O$_2$NC$_6$H$_4$



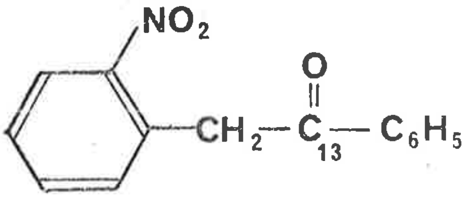
(39)



COMPOUND	R
(40)	CD$_3$
(41)	Ph



(42)



(43)

The substituted derivatives (36)-(39) and the labelled derivatives (40)-(43) were prepared in order to investigate, clarify and rationalize the mechanisms of the rearrangement processes.

The major peaks observed in the spectra of (33)-(35) (see Figs 3-2, 3-3 and Table 3-2)[†] are due to the ions $[M^{\overline{\cdot}}-HO\cdot]^-$, $[M^{\overline{\cdot}}-NO\cdot]^-$, $[(M^{\overline{\cdot}}-HO\cdot)-CO]^-$, $[M^{\overline{\cdot}}-CO_2H\cdot]^-$, $[M^{\overline{\cdot}}-RCH_2O\cdot]^-$ and $[(M^{\overline{\cdot}}-HO\cdot)-RCHO]^-$

The relative abundances of the metastable ions for the processes noted above, decrease with respect to that of the collision-induced peak NO_2^- (a simple cleavage process), as the pressure of collision gas is increased; indicating that the processes have low activation energies, and are thus probably true rearrangement reactions.[83]

3.2.2.a The Process $[M^{\overline{\cdot}} \rightarrow (M^{\overline{\cdot}}-RCH_2O\cdot)^-]$

The negative ion spectra of (33)-(38) show prominent peaks at m/e 134 (see Table 3-2 and Figs 3-2, 3-3)[†] which correspond to the fragment ion $[M^{\overline{\cdot}}-RCH_2O\cdot]^-$. Corresponding peaks due to loss of $RCH_2O\cdot$ from the molecular anions of (31) and (39) are not observed, thus indicating that this rearrangement reaction does not operate for compounds (31) and (39). The necessary pre-requisites for the rearrangement are therefore:

(a) An *o*-nitrobenzyl system with the benzylic carbon bearing two hydrogen atoms.

(b) The presence of a carbonyl group α to the benzylic position.

[†] Tables and Figures are shown at the end of the chapter.

3.2.2.a.1 Substituent Effects

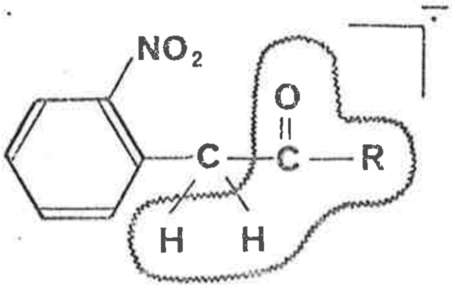
Substituent effects in the negative ion spectra of phenyl m-and p-nitrobenzoates, m- and p- nitrophenylbenzoates, phenyl p-cyanobenzoates, benzyl p-nitrobenzoates and phenyl p-nitrophenyl-acetates have been studied by Bowie and Nussey,[133,140] They used both the McLafferty approach[201,202] [$\log Z/Zo = \rho\sigma$], based upon the quasi-equilibrium theory; and the Chin and Harrison equation[203] [$Z = \frac{[A]}{[M]} = \frac{k1}{kt}(\frac{1}{f} - 1)$] to examine the correlation between the abundance of fragmenting ions and the Hammett constant σ. Straight line correlations were often obtained when $\log Z/Zo$ was plotted against σ or for $\log [A]/[M]\ (1-f)$ against σ. Correlations obtained from the McLafferty or Harrison expression were extremely good for substituted phenyl m- and p-nitrobenzoates. For simple cleavage reactions, ρ was found to be 1.5-5.0, and for cleavages involving proximity or ortho effects ρ was found to be 0-0.8. It is generally possible therefore to distinguish between an ortho rearrangement and a simple cleavage reaction by determining the value of ρ[133,140,158].

The formation of the fragment ion $[M^{\bar{\cdot}}-RCH_2O^{\cdot}]^-$ (m/e 134), produced by the decomposition of the molecular anions of (36)-(38) was studied using the McLafferty approach.[201,202] Substituted derivatives of (35) are difficult to synthesize and we were only able to prepare (36)-(38). The following $\log Z/Zo$ values were obtained for the $[M^{\bar{\cdot}}-R-CH_2O^{\cdot}]^-$ ions, (36), -0.10, (37), -0.05 and (38), 0.50. This gives $\rho = 0.57 \pm 0.1$, a value falling within the range obtained previously for ortho rearrangements.[133,140]

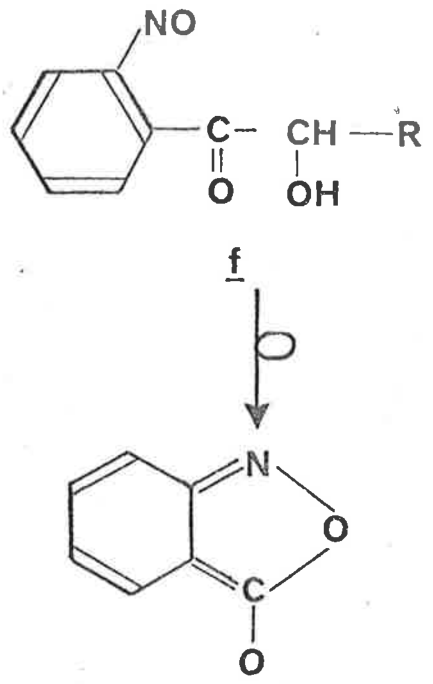
3.2.2.a.2. The Evidence from Isot-opic Labelling and Metastable Characteristics.

Decompositions of the molecular anions of the labelled compounds (40)-(43) give the unlabelled ion $C_7H_4NO_2^-$ at m/e 134. The elimination therefore involves the specific loss of those atoms illustrated in d. The ion produced, $C_7H_4NO_2^-$ at m/e 134, decomposes further by elimination of CO and CO_2 to $C_6H_4NO^-$ (m/e 106) and $C_6H_4N^-$ (m/e 90) respectively (see Fig 3-2). Similar fragmentations are encountered for o-nitrosobenzoate derivatives (see Fig 3-5 and Table 3-3). Comparison of the fragmentation processes in the negative ion spectra of o-nitrophenylacetophenone (35) and methyl o-nitrosobenzoate (46) (see Fig 3-5 and 3-3) together with a study of the appropriate metastable characteristics, show that the fragmentations at m/e 134 from (35) and (46) behave identically. This indicates that the fragment ion (m/e 134) from o-nitrophenyl-acetophenone (35) must have the structure as shown in e (o-nitrosobenzoate derivatives produce the fragment ion m/e 134, see details in the appendix to Chapter 3).

A plausible way to rationalize the formation of e from (35) is to suggest fragmentation through f.



d

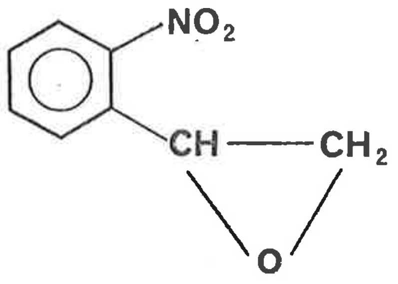


f

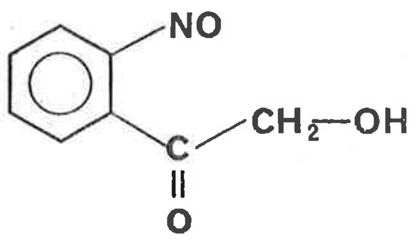
e

The nitroso compound (45) is the appropriate analogue of the aldehyde (33) and this has been prepared from the o-nitro epoxide (44) by treatment with concentrated formic acid.[204] Compound (45) is unstable and undergoes ready polymerisation at room temperature. The negative ion spectrum of (45) shows no molecular anion but produces the fragment ion at m/e 134 as the base peak. It is also interesting to observe that the major fragment ions observed in the negative ion mass spectra of the aldehyde (33) and the nitro-epoxide (44) are very similar (see Figs 3-3 and 3-4). We conclude that f may be fragment to e and a possible reaction sequence is shown in d → f → g → e.

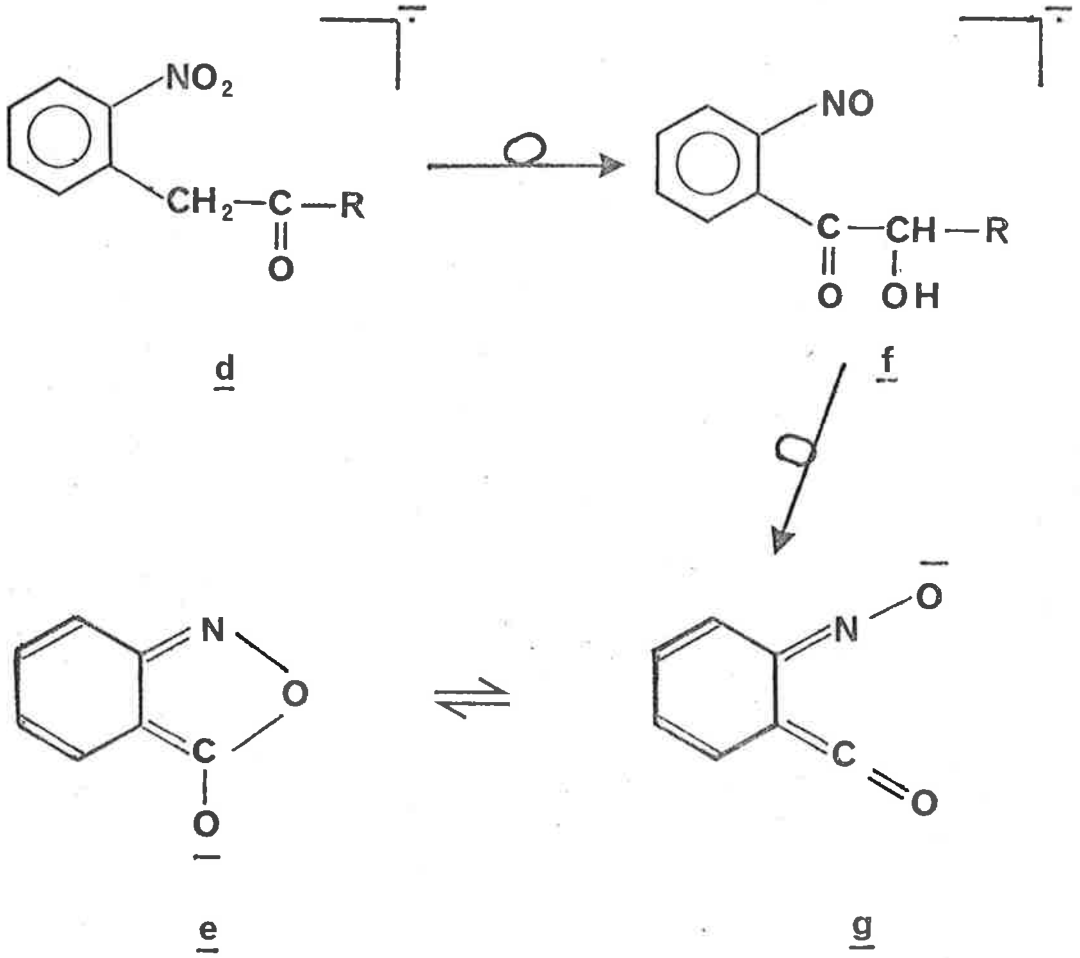
A double hydrogen transfer from the benzyl position to the nitro group may precede the formation of f, as hydrogen rearrangements (including double hydrogen rearrangements) are known to occur to nitro oxygens from ortho positions.[158,173,174]


NO₂
CH
CH₂
O

(44)


NO
CH₂—OH
C
O

(45)


NO₂
CH₂—C—R
O
d
O
NO
C—CH—R
O OH
f
O
O
N
C
O
e
⇌
N
O
C
O
g

3.2.2.b The $[M^{\bullet -}-HO^{\bullet}]$ and Related Fragmentations

The rearrangement ions $[M^{\bullet -}-HO^{\bullet}]^-$, $[M^{\bullet -}-HO^{\bullet}-CO]^-$, $[M^{\bullet -}-CO_2H^{\bullet}]^-$ and $[M^{\bullet -}-HO^{\bullet}-RCHO]^-$ found in the negative in spectra of (33)-(35), see Table 3-2, are produced by the losses of atoms shown in h, i and j* [as evidenced by the spectra the labelled compounds (40)-(43)]. The ions produced as shown in h, i, j do not fragment when subjected to collision excitation. It is therefore not known whether R migrates to C, N or O in the case of i and j.

The fragment ion $[(M^{\bullet -}-HO^{\bullet})-RCHO]^-$ (see k)* decomposes further by eliminating CO (see Fig 3-2) to an ion probably corresponding to l or to a ring-opened form where oxygen is bound to carbon.

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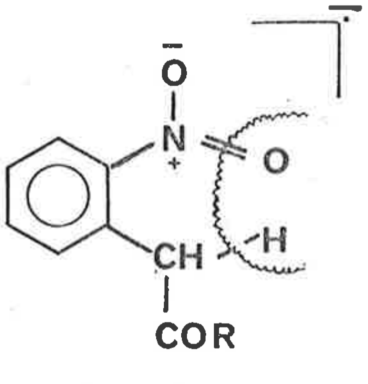
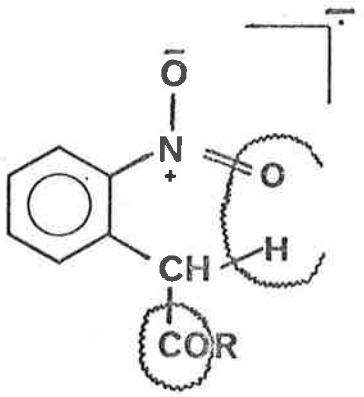
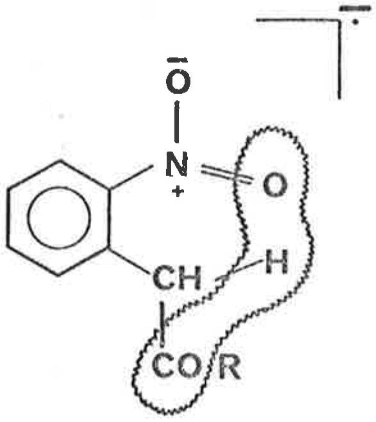
* See the following page.



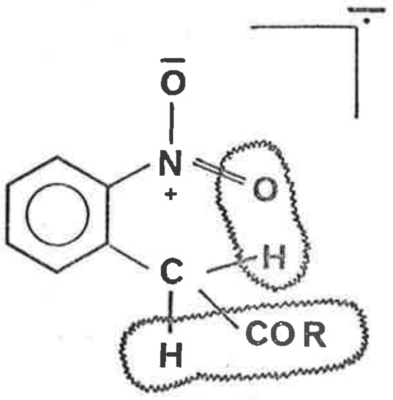
h



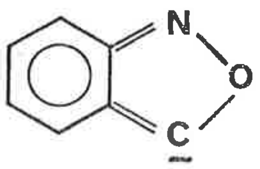
i



j



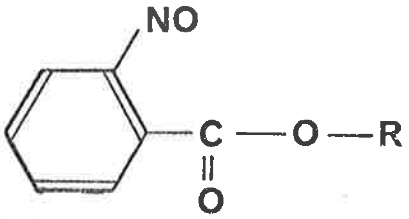
k



l

3.3. APPENDIX TO CHAPTER 3

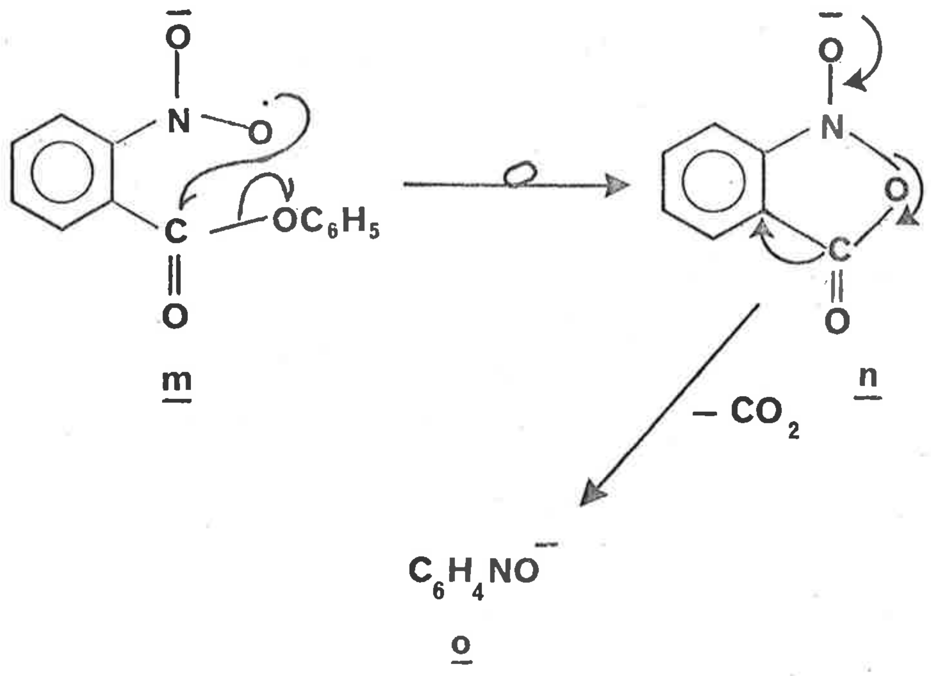
3.3.1 The Behaviour of o - Nitrosobenzoate Derivatives

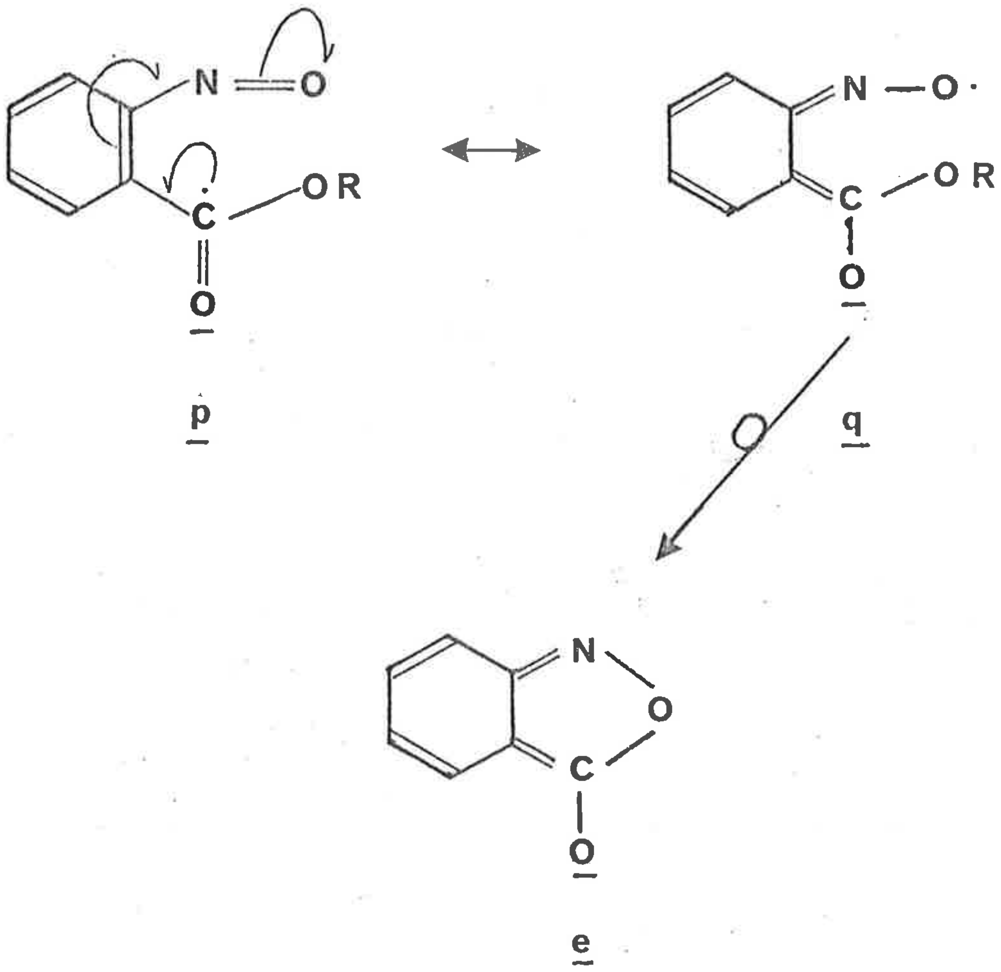


COMPOUND	R
(46)	CH_3
(47)	C_2H_5
(48)	$CH_2C_6H_5$

Methyl o-nitrosobenzoate (46), ethyl o-nitrosobenzoate (47) and benzyl o-nitrosobenzoate (48) show similar fragmentations. The 70eV negative ion spectra of o-nitrosobenzoate derivatives produce the fragment ions $[M^{\cdot -}-OR^{\cdot}]^{-}$ at m/e 134 as the base peak and other peaks $[(M^{\cdot -}-OR^{\cdot})-CO]^{-}$ and $[(M^{\cdot -}-OR^{\cdot})-CO_2]^{-}$ (see Table 3-3). The fragmentations of o-nitrosobenzoate derivatives should be compared with those of o-nitrobenzoate,[133,140] which also show the major peaks due to the ions $[M^{\cdot -}-OR^{\cdot}]^{-}$ and $[(M^{\cdot -}-OR^{\cdot})-CO_2]^{-}$. The cleavages have been rationalized as shown in m, n, and 0 respectively.

We reasoned that the molecular anions of o-nitrosobenzoate derivatives should cyclise to yield e as illustrated in p → q → e respectively (see also 3.2.2.b).


m
n
− CO$_2$
C$_6$H$_4$NO$^-$
o


p
q
e

3.4 CONCLUSIONS

(1) The negative ion mass spectra of compounds of the general type m- and p- O_2N-C_6H_4-CH_2-COR produce nitrobenzyl anions by α-cleavage to the carbonyl group

(2) β-Cleavage to the carbonyl group produces nitrobenzyl anions in the negative ion mass spectra of compounds of the general type o- and p- O_2N-C_6H_4-CH_2-CH_2-COR.

(3) Molecular anions of o- O_2N-C_6H_4-CH_2-COR compounds produce pronounced rearrangement ions which are often produced by complex pathways.

TABLE 3-1

NEGATIVE ION MASS SPECTRA OF (25)-(32)

(25)

m/e	46	179(M)	180
I%	13	100	12

(26)

m/e	46	178	179(M)	180
I%	25	2	100	13

(27)

m/e	46	136	241(M)	242
I%	27	2	100	17

m* 241 → 136

(28)

m/e	46	136	211	240	241(M)	242
I%	29	2	1	76	100	13

m* 241 → 211, 241 → 136

(29)

m/e	46	57	136	163	193(M)	194
I%	61	3	6	5	100	12

m* 193 → 163, 193 → 136, 193 → 57

(30)

m/e	46	136	193(M)	194
I%	46	11	100	11

m* 193 → 136

(31)

m/e	46	136	255 (M)	256
I%	35	8	100	18

m* 255 → 136

(32)

m/e	46	136	225	255(M)	256
I %	36	8	3	100	16

m* 255 → 225, 255 → 136

TABLE 3-2

NEGATIVE ION MASS SPECTRA OF (33)-(39), (44)

(33)	m/e	46	90	91	92	106	107	108	118	119	120	121
	I %	28	8	6	7	3	15	2	11	2	62	7
	m/e	134	135	136	148	149	164	165 (M$^{\cdot-}$)	166			
	I %	100	41	6	79	7	56	60	6			
	m*	165 → 148 → 120, 165 → 135; 165 → 134 → 90										
(34)	m/e	46	59	90	91	92	106	118	119	134	135	149
	I %	38	4	10	18	8	2	22	5	96	8	50
	m/e	150	162	163	178	179(M)	180					
	I %	6	38	34	18	100	12					
	m*	179 → 162 → 134; 179 → 149, 179 → 134 → 90 162 → 118 → 90, 134 → 106.										
(35)	m/e	46	77	90	91	92	106	118	119	121	122	134
	I %	20	7	10	8	10	4	45	5	8	4	100
	m/e	135	136	193	194	195	196	197	211	212	223	224
	I %	5	8	8	7	5	47	6	65	7	6	72
	m/e	225	240	241(M)	242							
	I %	8	13	83	8							
	m*	241 → 224 → 196, 241 → 211, 241 → 134 → 90 241 → 196, 224 → 118 → 90, 134 → 106										
(36)	m/e	46	90	91	92	106	108	118	121	134	135	136
	I %	43	5	3	4	9	3	21	9	82	5	11
	m/e	223	227	237	238	241	242	254	254	271(M)		272
	I%	64	9	5	17	81	10	100	16	96		20
	m*	271 → 254, 271 → 241, 271 → 226, 271 → 134, 134 → 106, 134 → 90										

(37)

m/e	46	90	91	92	106	118	119	134	135	136	155	207
I%	13	10	9	8	3	23	4	92	8	6	11	5

m/e	210	225	226	238	239	255(M)	256
I%	13	27	5	34	6	100	20

m* 255 → 238 → 210, 255 → 225, 255 → 134 → 90

238 → 118 → 90, 134 →106

(38)

m/e	90	91	92	93	106	107	108	109	118	119	121
I%	10	6	8	13	4	8	4	4	39	5	23

m/e	122	134	135	136	150	240	241	254	256	268
I%	12	100	8	14	48	2	5	5	10	7

m/e	269	285	286(M)	287
I%	26	7	24	3

m* no metastable ions detectable

(39)

m/e	46	121	207	208	225	238	239	255(M)	256
I%	60	3	10	22	11	18	3	100	19

m* 255 → 238. 255→225; 255 → 208

(44)

m/e	46	90	91	92	105	106	107	118	120
I%	50	8	17	4	16	6	12	6	9

m/e	134	135	148	164	165(M)
I%	100	17	19	5	4

m* 165 → 148 → 120, 165 → 148 → 118, 165 → 134 → 90

165 → 118 → 90, 134 → 106

TABLE 3-3

NEGATIVE ION MASS SPECTRA OF (46)-(48)

(46)

m/e	26	90	91	106	134	135	165(M)	166
I %	1	2.5	1.6	1.5	100	8	10	2

m* 165 → 134 → 90; 134 → 106

(47)

m/e	26	90	91	92	106	121	134	135	179(M)	180
I %	0.8	2.5	5.5	1	2	2.5	100	12	7	2

m* 179 → 134 → 90; 134 → 106

(48)

m.e	26	90	91	106	121	134	135	150	194
I %	6	12	18	6	3	100	15	15	3

m/e	210	211(M)
I %	4	3

m* 211→ 134 → 90; 134 → 106; 150 → 106; 135 → 91

FIGURE 3—1

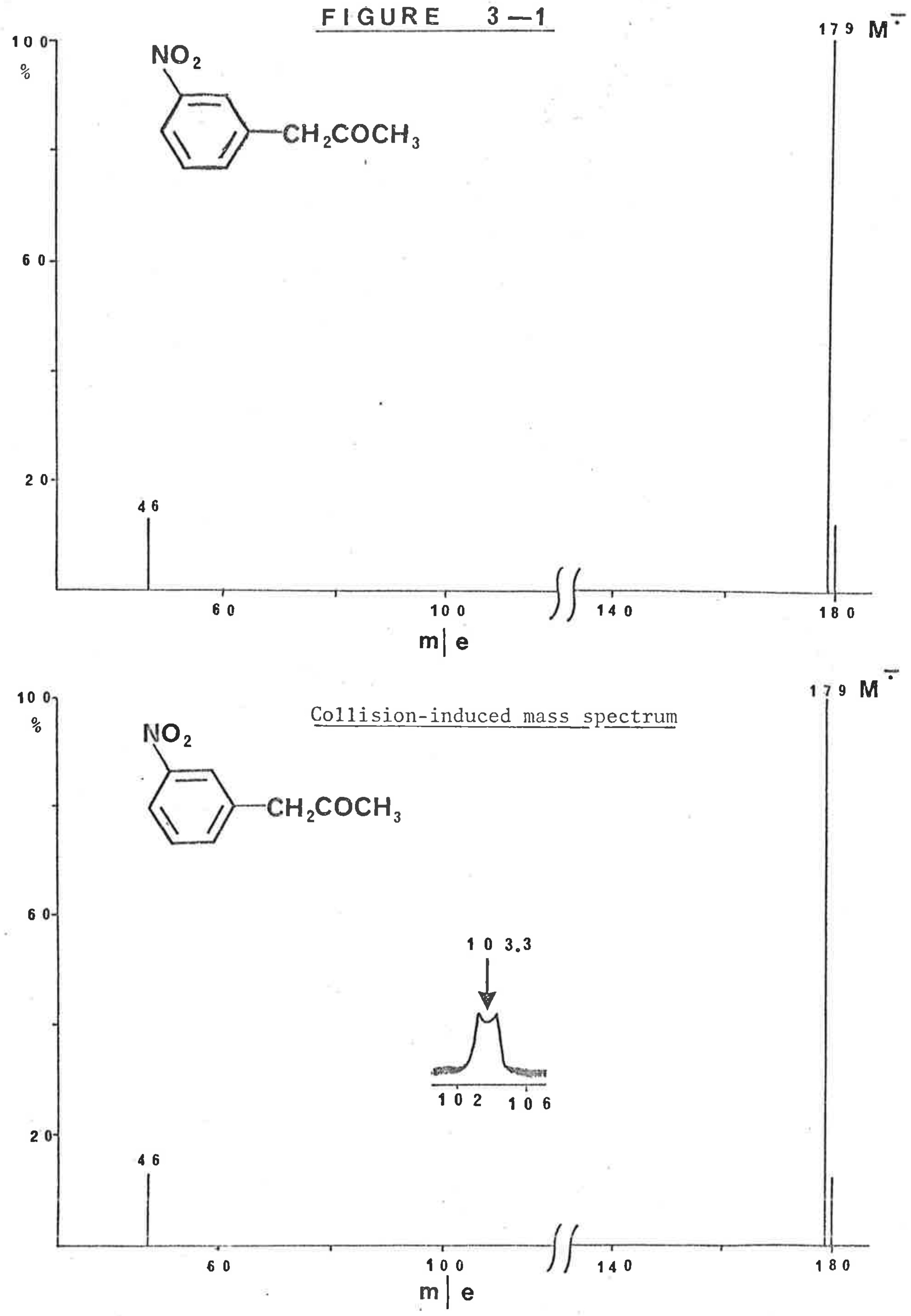

100
%
60
20
NO_2
CH_2COCH_3
46
179 $M^{\bar{\cdot}}$
60
100
140
180
m|e
Collision-induced mass spectrum
103.3
102
106

FIGURE 3—2

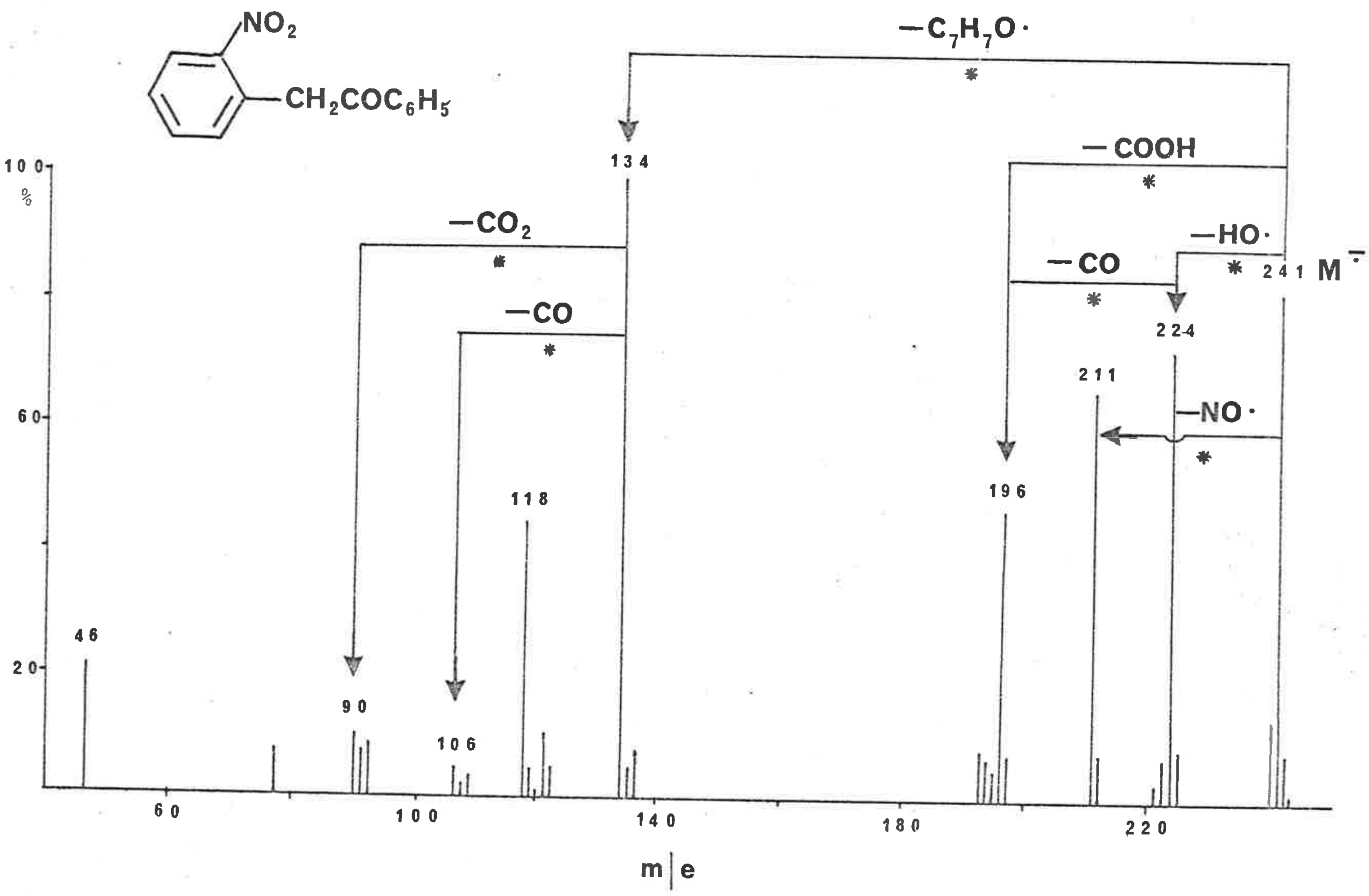

NO2
CH2COC6H5
100 %
60
20
−C7H7O·
−COOH
−HO·
−CO2
−CO
−CO
−NO·
134
241 M−·
224
211
196
118
106
90
46
60
100
140
180
220
m|e

FIGURE 3—3

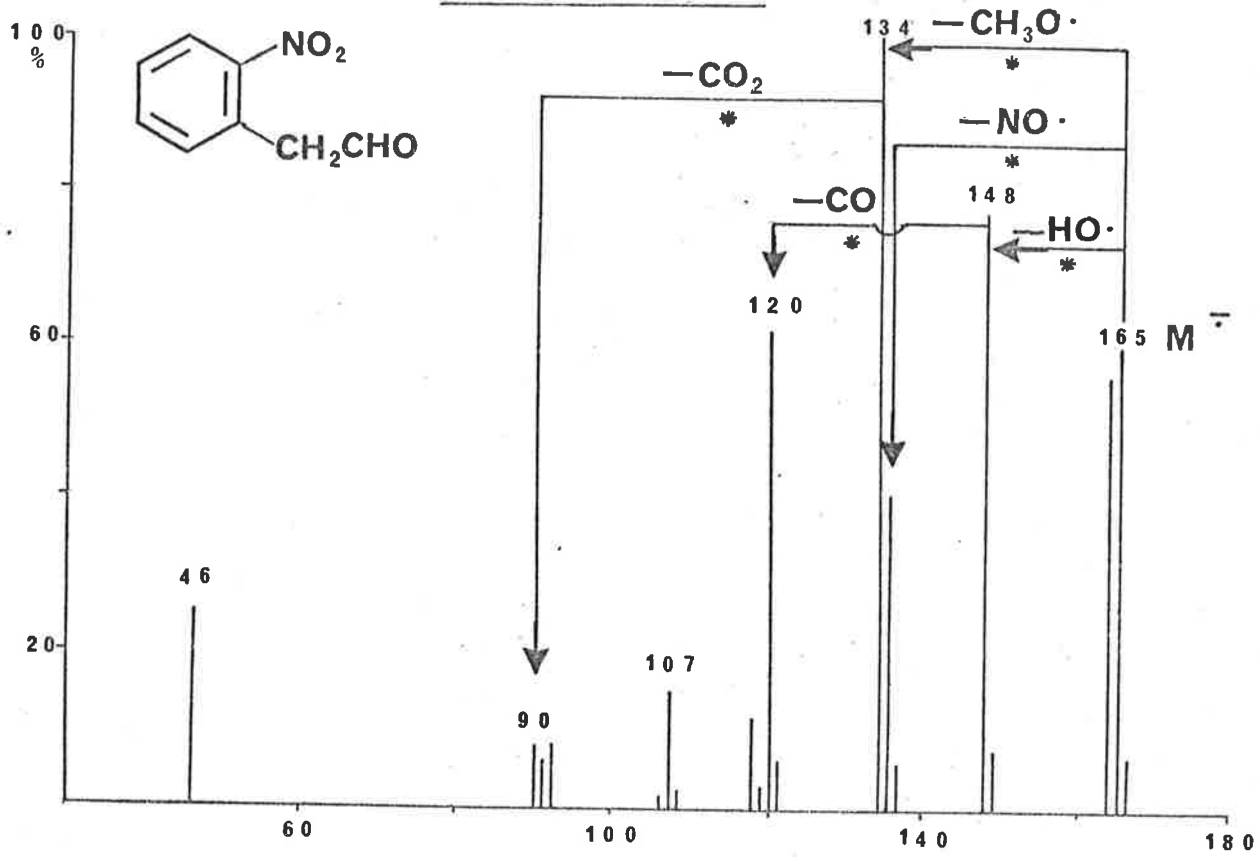


FIGURE 3—4

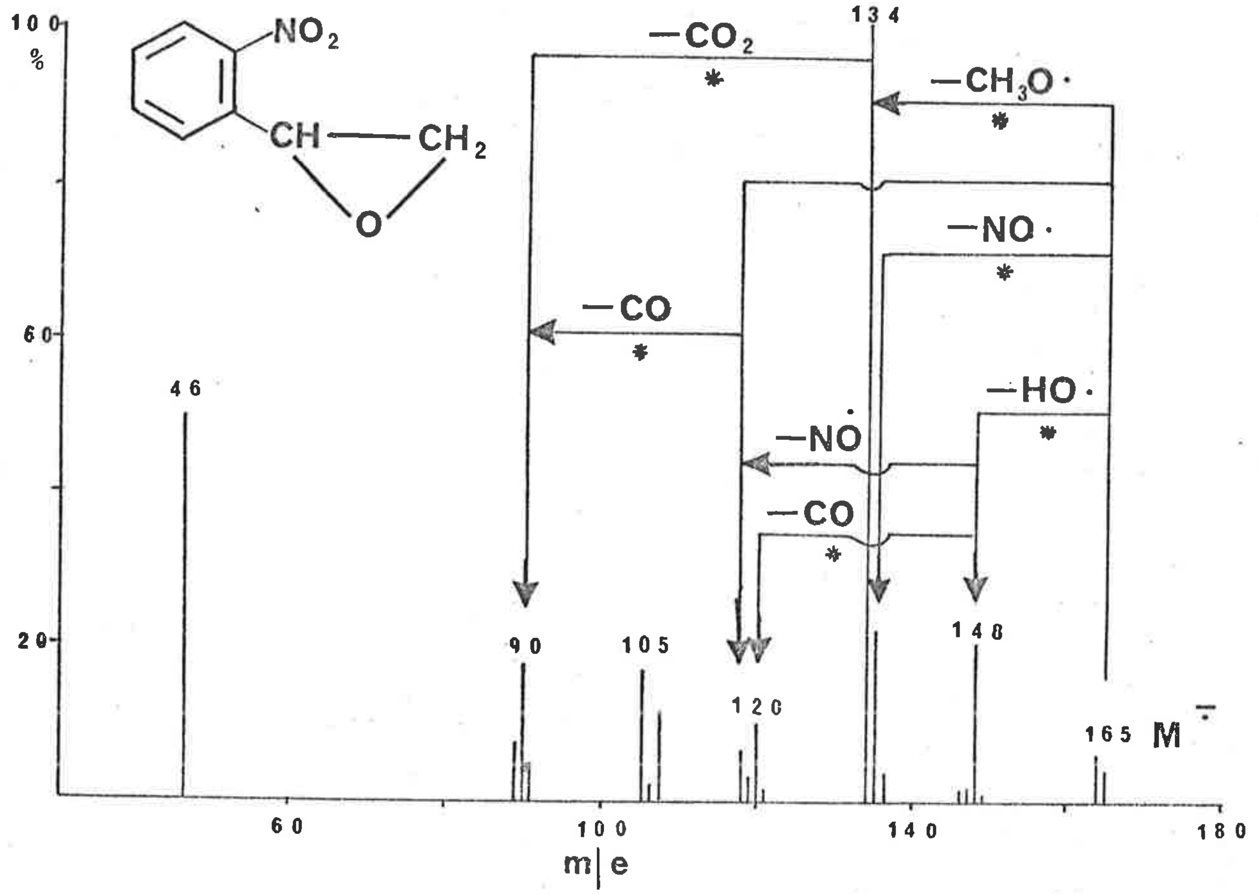
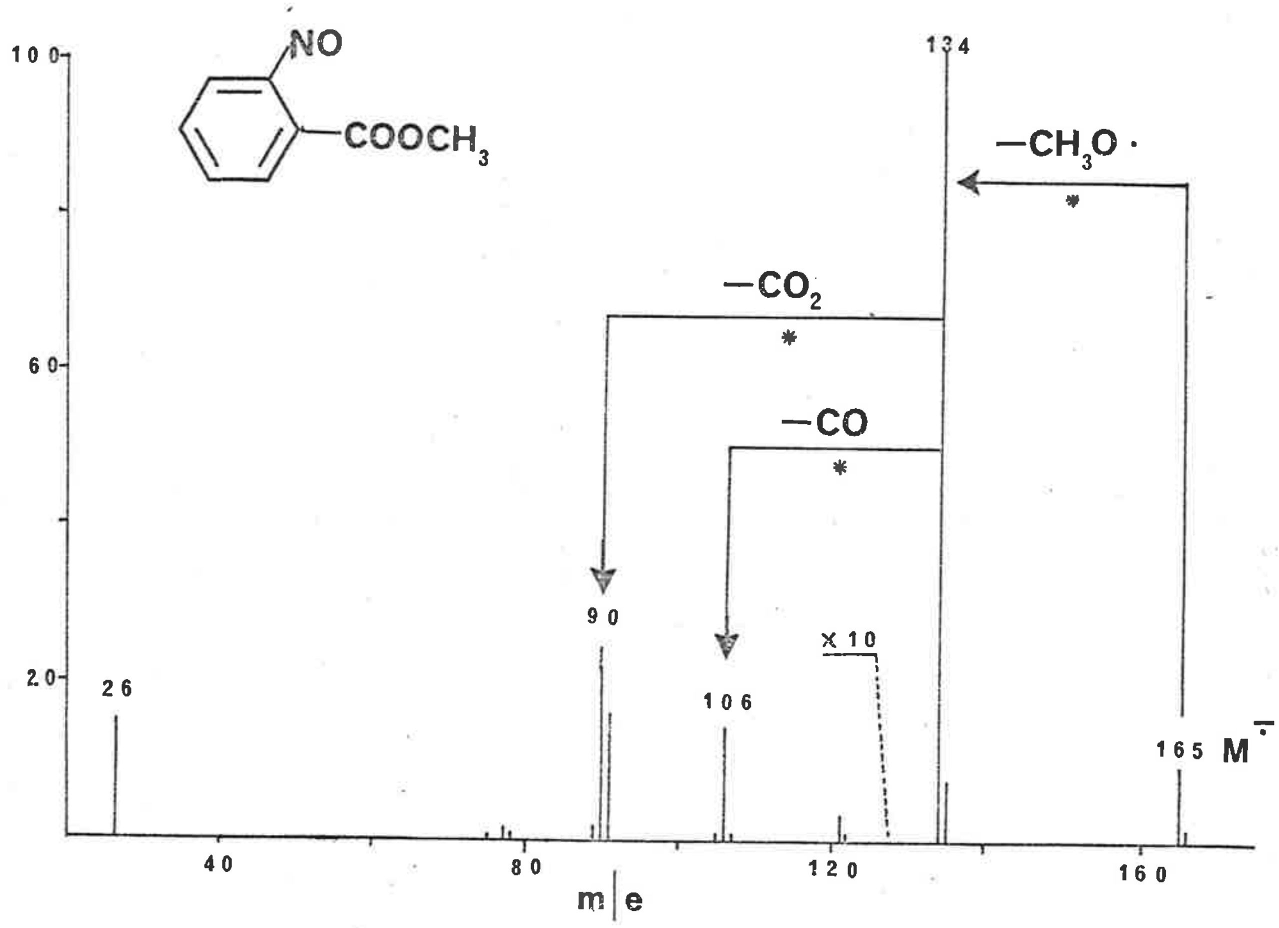


FIGURE 3—5


NO
COOCH$_3$
100
60
20
26
90
106
134
165 M$^{+\cdot}$
×10
−CH$_3$O·
−CO$_2$
−CO
*
40
80
120
160
m|e

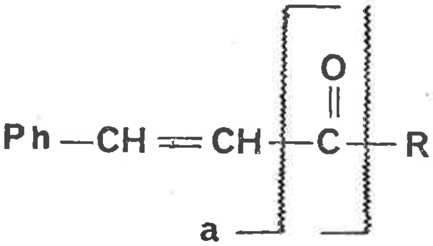
CHAPTER 4.

Negative-Ion Mass Spectra of Unsaturated Carbonyl Compounds.

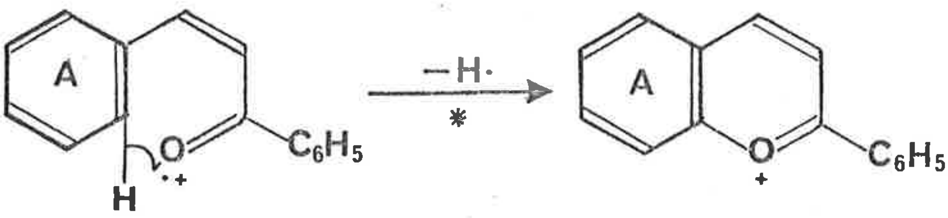
Page

4.1 INTRODUCTION

The positive ion fragmentations of benzalacetone, benzalacetophenone and their labelled derivatives have been studied[205] by Williams and Coworkers. The characteristic fragmentation of the unsaturated ketone is shown in a. Apart from exhibiting α-cleavage to the carbonyl group (see a), the spectrum of benzalacetophenone (R = Ph) shows a pronounced [M-1] ion. This fragment ion is formed by loss of a hydrogen atom from ring A to form a stable oxonium ion as shown in b.



a

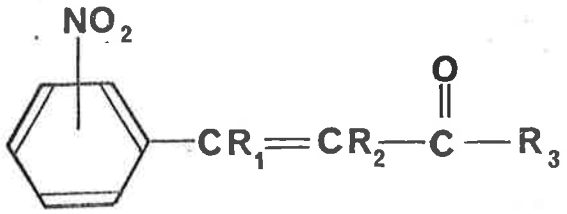


b

In Chapters 2 and 3, we discussed the behaviour of negative ions derived from the systems Aryl-CO-, Aryl-CO-CO-, Aryl-CO-CH_2-CO- and Aryl-$(CH_2)_n$-CO-. In this chapter we describe the negative ion spectra of unsaturated nitroaryl carbonyl compounds, a study which constitutes a logical extension of the previous work.

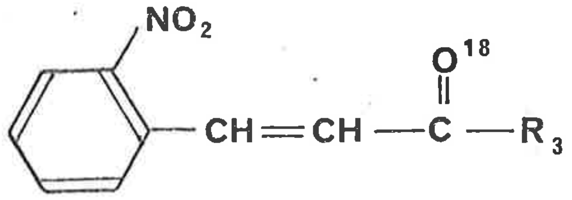
4.2 RESULTS AND DISCUSSION

4.2.1 The Nitrobenzal Carbonyl Derivatives



COMPOUND	NO_2	R_1	R_2	R_3
(49)	o	H	H	H
(50)	o	H	CH_3	H
(51)	m	H	H	H
(52)	p	H	H	H
(53)	o	H	H	CH_3
(54)	o	H	CH_3	CH_3
(55)	m	H	H	CH_3
(56)	p	H	H	CH_3
(57)	o	H	H	Ph
(58)	o	H	H	p-CH_3Ph
(59)	m	H	H	Ph
(60)	p	H	H	Ph
(61)	o	D	H	H

COMPOUND	NO_2	R_1	R_2	R_3
(62)	*o*	H	H	D
(63)	*o*	D	H	Ph
(64)	*o*	H	D	Ph



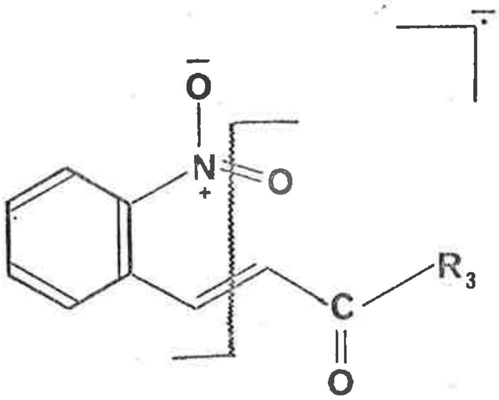
COMPOUND	R_3
(65)	H
(66)	Ph

The 70eV spectra of the compounds listed above were determined and are listed in Table 4-1.[†] The labelled derivatives (61)-(66) were synthesized in order to clarify the fragmentation pathways. All fragmentations mentioned in the text, are substantiated by metastable peaks, the decompositions of which are detected in both field-free regions of the mass spectrometer.

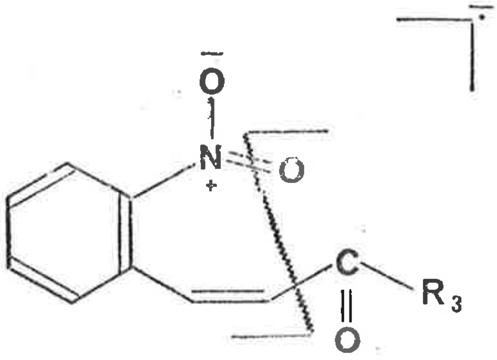
[†] Tables are shown at the end of the chapter.

The negative ion spectra of the *o*-nitrobenzal derivatives (49), (50), (53), (54), (57) and (58) produce the following fragment ions viz, $[M^{\cdot -}-HO^{\cdot}]^{-}$, $[M^{\cdot -}NO^{\cdot}]^{-}$, $[M^{\cdot -}-R^{3}CO^{\cdot}]^{-}$, $[M^{\cdot -}-CO_{2}H^{\cdot}]^{-}$, $[C_{7}H_{4}NO_{2}]^{-}$, $[M^{\cdot -}-C_{7}H_{5}NO^{\cdot}]^{-}$, $[C_{7}H_{5}NO]^{-}$, $[R^{3}CO_{2}]^{-}$ and $[M^{\cdot -}-R^{3}CO_{2}^{\cdot}]^{-}$. The *m* and *p*-nitrobenzal derivatives (51), (52), (55), (56), (59) and (60) show only $M^{\cdot -}$ and the fragment ions $[M^{\cdot -}-NO^{\cdot}]^{-}$ and NO_{2}^{-} in their spectra (see Table 4-1). A number of fragment ions observed in the spectra of *o* - nitrobenzal derivatives are produced by re-arrangements or processes occurring because of the proximity of the two substituents. The spectra of the labelled compounds (61) - (66) demonstrate that the atoms eliminated from the molecular anions to form the fragment ions $[M^{\cdot -}-C_{7}H_{5}NO^{\cdot}]^{-}$, $[C_{7}H_{5}NO]^{-}$, $[M^{\cdot -}-R^{3}CO_{2}^{\cdot}]^{-}$ and $[R^{3}CO_{2}]^{-}$ are as shown in *c* and *d* respectively.

The formation of these re-arrangement ions is discussed below.



c



d

4.2.1. a The Processes $[M^{\cdot-} \rightarrow (R^3CO_2)^-]$ and $[M^{\cdot-} \rightarrow (M^{\cdot-} - R^3CO_2^{\cdot})^{-}]$

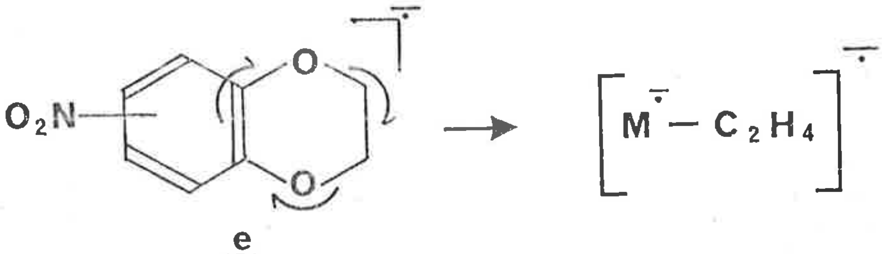
The species eliminated from the molecular anion to produce the carboxylate ion $[R^3CO_2]^-$ and the $[M^{\cdot-} - R^3CO_2]^-$ ion are shown in d. The abundances of carboxylate anions range from 7 to 33% of the base peak ($M^{\cdot-}$) in each spectrum, and these anions are observed in the negative ion spectra of all the o-nitrobenzal derivatives studied (see Table 4-1). The carboxylate anion may be produced by a radical attack of the nitro group at the carbonyl centre through a seven membered transition state as illustrated in Scheme 1.

This fragmentation is similar to the fragmentation of the o-nitrophenyl benzoate molecular anion[125] (see Scheme 2).

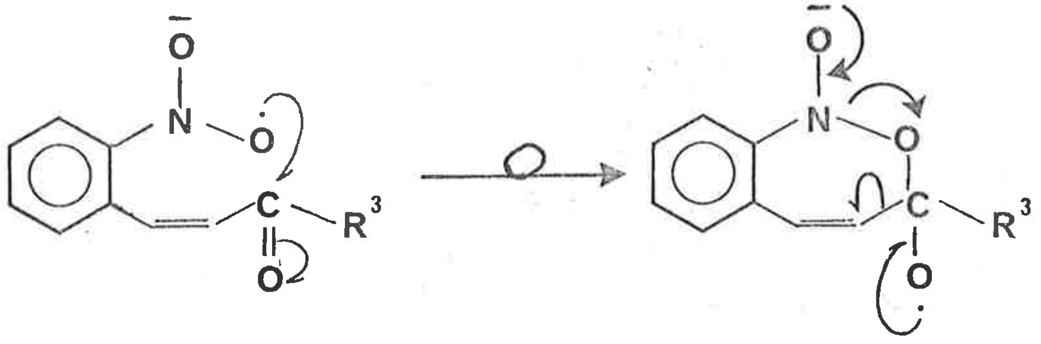
A fragment ion $[M^{\cdot-} - R^3CO_2^{\cdot}]^-$ is produced by a similar mechanism to that shown in Scheme 1, except that in this case anionic attack of the nitro group at the carbonyl centre may occur through seven membered transition state (see Scheme 3).

4.2.1.b The Processes $[M^{\cdot-} \rightarrow (M^{\cdot-} - C_7H_5NO^{\cdot})^{-}]$ and $[M^{\cdot-} \rightarrow (C_7H_5NO)^-]$

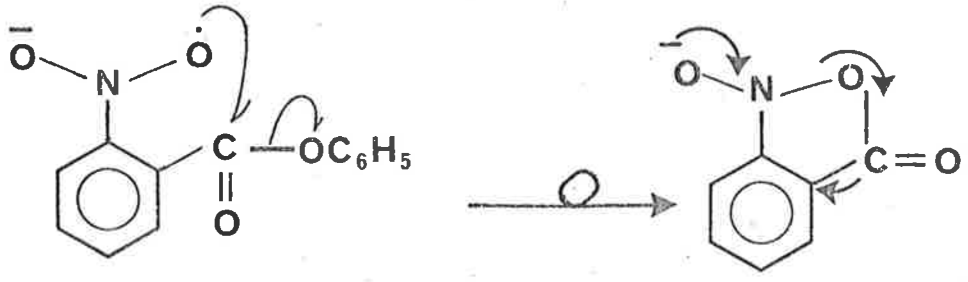
The retro-Diels-Alder reaction occurs commonly in the positive ion mass spectra of cyclohexene type molecules.[206-209] This process is diagnostic for certain polycyclic compounds, particularly some terpenoids and steroids.[210] Related retro-Diels-Alder processes are also noted in the negative ion spectra of nitrochromans,[211] nitro-1,3-benzodioxans and nitro-1,4-benzodioxans.[212] For example, the fragment ion $[M^{\cdot-} - C_2H_4]^{\cdot-}$ is observed for nitrochromans (see e).



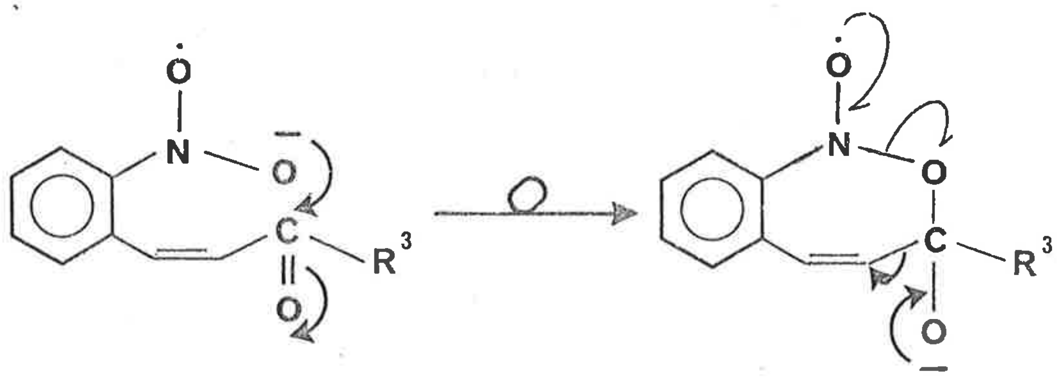
e



SCHEME 1

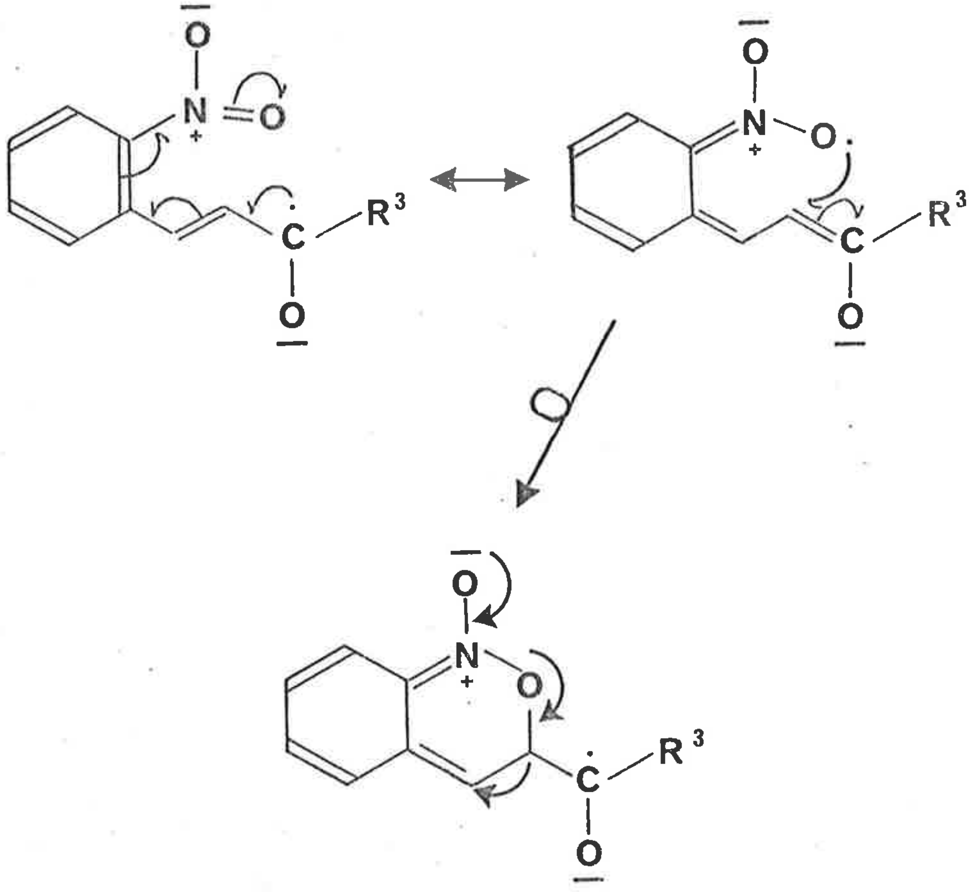


SCHEME 2



SCHEME 3

The fragment ions $[M^{\cdot-}-C_7H_5NO^{\cdot}]^-$ and $[C_7H_5NO]^-$ derived from the o-nitrophenyl carbonyl compounds (see above) are both produced by retro processes. The abundances of the ions $[M^{\cdot-}-C_7H_5NO^{\cdot}]^-$ range from 9 to 46% of the base peak $(M^{\cdot-})$. The product anion radical probably corresponds to the non-decomposing α-dicarbonyl species,[212] [H -CO-CO-R]$^{\cdot-}$. The formation of these ions may be rationalized by attack of a nitro-oxygen at the carbon α to the carbonyl group through the intermediary of a six-membered transition state, followed by a retro cleavage of the six-membered ring system (see Scheme 4).



SCHEME 4

An alternative process produces charge retention on the other fragment to yield an ion $[C_7H_5NO]^-$, which is generally of low abundance (see Table 4-1).

4.2.1. c The Process $[M^{\cdot -} \rightarrow (M^{\cdot -}-R^3CO^{\cdot})^-]$

An ion $[M^{\cdot -}-R^3CO^{\cdot}]^-$ is observed in low abundance in the spectra of the *o*-nitrobenzal derivatives (see Table 4-1). This fragment ion is not noted in the conventional negative ion spectra of *m* and *o*-nitrobenzal derivatives, but may be produced by collision-activation. The formation of this ion in the spectra of the *o*-compounds could be rationalized as shown in *f*.

4.2.1. d The Processes $[M^{\cdot -} \rightarrow (M^{\cdot -}HO^{\cdot})^-]$ and $[M^{\cdot -} \rightarrow (M^{\cdot -}-HCO_2^{\cdot})^-]$

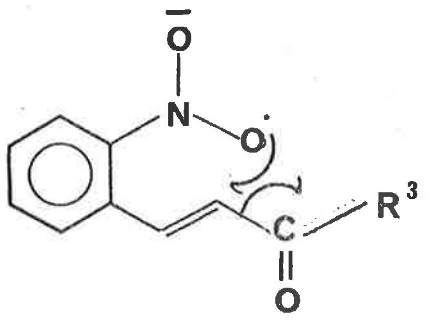
Other rearrangement processes found in the spectra of *o*-nitrobenzal derivatives yield the fragment ions $[M^{\cdot -}-HO^{\cdot}]^-$ and $[M^{\cdot -}-HCO_2^{\cdot}]^-$. The species involved in elimination of both $HO^{\cdot}$ and $HCO_2^{\cdot}$ from the molecular anions were determined from the spectra of (61)-(66), and are illustrated in *g* and *h* respectively. The overall mechanisms must be complex.

4.2.1. e The Process $[M^{\cdot -} \rightarrow (M^{\cdot -}-NO^{\circ})^-]$

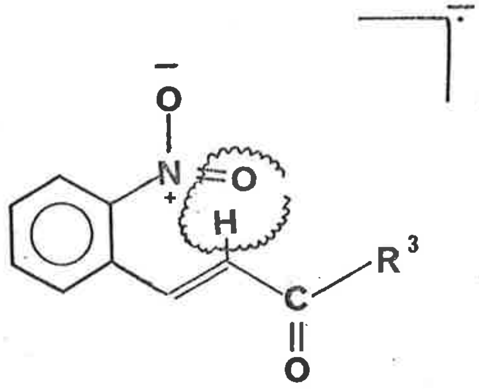
The loss of NO° from the molecular anion is a general process of fragmentation of arylnitro compounds.[44]

4.2.1. f The Process $[M^{\cdot -} \rightarrow (C_7H_4NO_2)^-]$

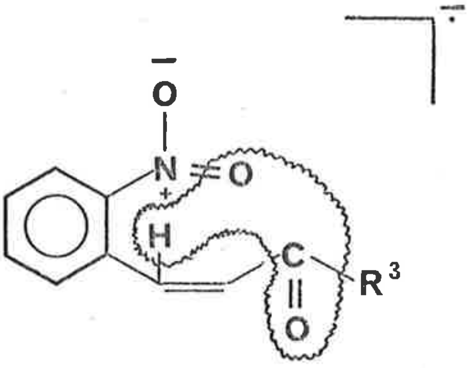
An ion $[C_7H_4NO_2]^-$ (m/e 134) (see Table 4-1), is produced by the loss shown in *i*. The abundances of the ions are low, ranging from 1-3% of the base peaks ($M^{\cdot -}$) and correspond to the structure *k* (see below). This fragment ion (*k*) has been observed in the negative ion spectra of *o*-nitroaryl-CH_2-CO-R and *o*-nitrosobenzoate derivatives (see Chapter 3). The $[C_7H_4NO_2]^-$ ions from *o*-nitrobenzal derivatives (49), (50), (53), (54), (64), (65) and *o*-nitrosobenzoate (*j*) decompose further by elimination of CO and CO_2[145] with kinetic energy releases at half height[199] (using V=3600 volts) in the range 48-57 and 21-28 meV respectively. This indicates that the ion $[C_7H_4NO_2]^-$ from the *o*-nitrobenzal derivatives has the same structure as that formed from *o*-nitrosobenzoates.



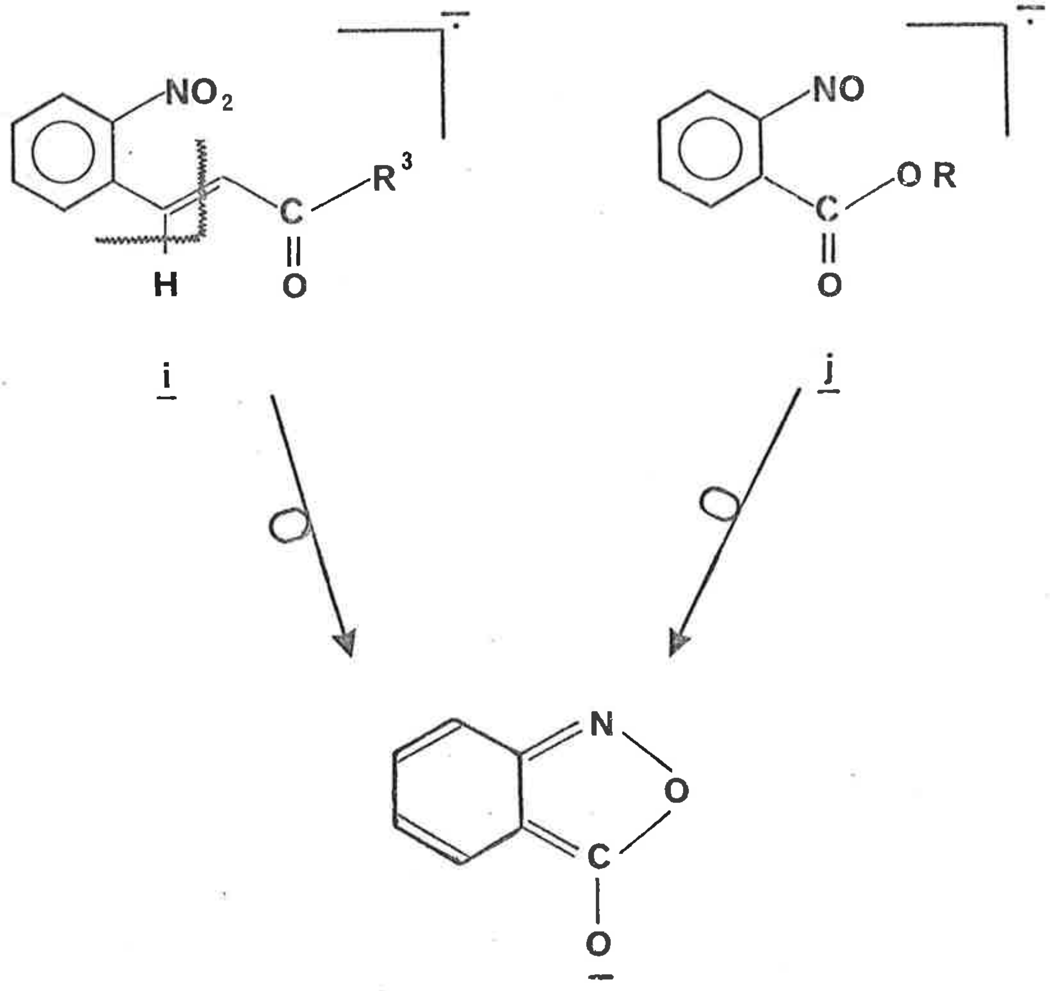
f



g



h

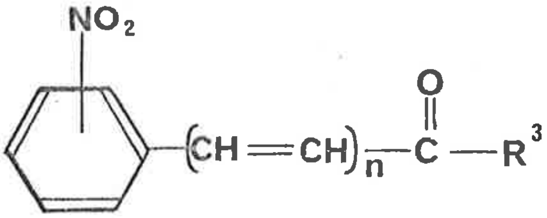


i

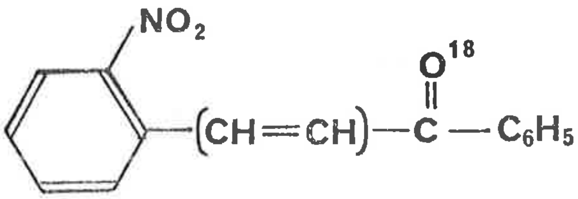
j

k

4.2.2 THE O_2N-C_6H_5 - $(CH=CH)_n$ - COR SYSTEM



COMPOUND	NO_2	R	n
(67)	o	H	2
(68)	m	H	2
(69)	p	CH_3	2
(70)	o	CH_3	2
(71)	m	CH_3	2
(72)	p	CH_3	2
(73)	o	Ph	2
(74)	o	p-CH_3Ph	2
(75)	m	Ph	2
(76)	p	Ph	2
(77)	o	CH_3	3



(78)

When the number of olefinic bonds is increased to 2 (67)-(76) and 3 (77) as listed above, the major fragmentations in the negative ion spectra (Table 4-2) of the *o*-nitro derivatives (67), (70), (73), (74) and (77) are similar to those described above for the *o*-nitrobenzal derivatives (see section 4.2.1).[*] However $[M^{\cdot-}-R^3CO^{\cdot}]^-$ and $[R^3CO]^-$ ions are not observed in these spectra. This is to be expected, since their formation (cf. *f*)[†] would now involve nine and eleven-membered transition states for n=2 and 3 respectively.

The major reaction in this series is $M^{\cdot-} \rightarrow [M^{\cdot-}-C_7H_5NO]^-$, and this produces the base peak in the spectra of (73), (74) and (77). These fragment ions may correspond to the 1,4-dicarbonyl-2-ene (n=2) and 1,6-dicarbonyl 2,4-diene (n=3) moieties respectively (see Table 4-2 and Figs 4-2, 4-3). The process may be depicted as shown in Scheme 5.

Fragment ions $[C_7H_4NO_2]^-$ (*k*)[†] are also formed in these spectra (see Table 4-2), this formation is the same as that shown in *i*, but the overall mechanism is not known. No rearrangement peaks except for the usual process $(M^{\cdot-}-NO^{\cdot})^-$, are observed in the spectra of the *m*- and *p*-nitro analogues (see Table 4-2).

Compound (79) was prepared in order to ascertain whether rearrangement reactions corresponding to those shown in *c* and *d*, will occur when a nitro group is replaced by a carbonyl substituent. The negative ion spectrum of (79) shows only a molecular anion and an $[M^{\cdot-}-CO_2]^{\cdot-}$ peaks in 5% abundance. Rearrangement processes involving proximity effects do not occur.

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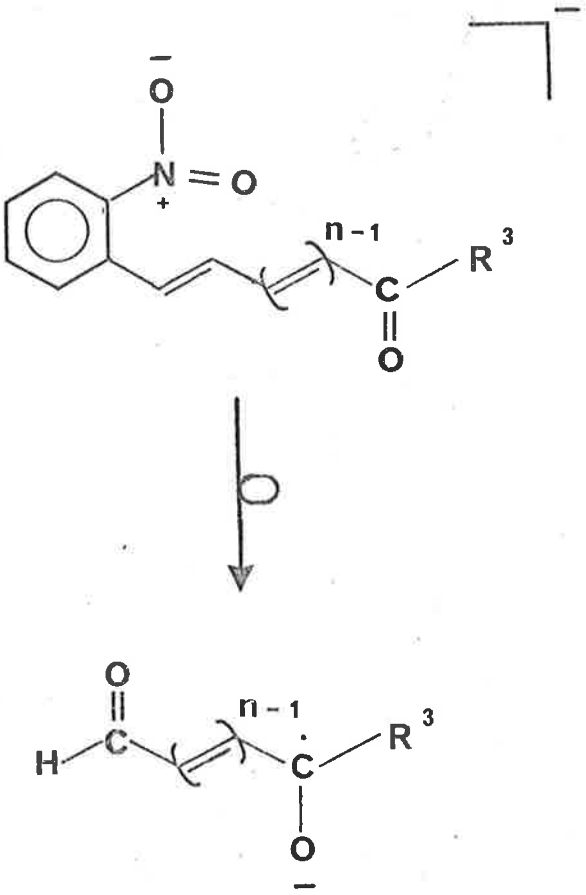
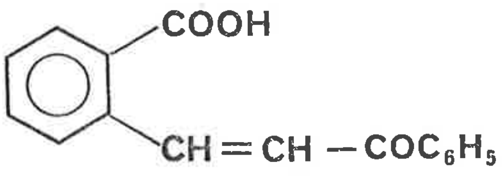
[*] See page 75

[†] See page 82, 83



SCHEME 5



(79)

4.3 CONCLUSIONS

(1) The negative ion mass spectra of compounds of the general type *o* - $O_2NC_6H_4$-$(CH{=}CH)_n$-COR (n=1 to 3) exhibit re-arrangement peaks which are formed by cyclisation reactions between the adjacent substituents, followed by retro-cleavages to yield non-decomposing dicarbonyl radical anions.

(2) No re-arrangement peaks are observed for the corresponding *m*- and *p*- nitro derivatives.

TABLE 4-1

NEGATIVE ION MASS SPECTRA OF (49)-(60)

COMPOUND	$M^{\cdot -}$	$[M^{\cdot -}-HO^{\cdot}]^{-}$	$[M^{\cdot -}-NO^{\cdot}]^{-}$	$[M^{\cdot -}-R^3CO^{\cdot}]^{-}$	$[M-CO_2H^{\cdot}]^{-}$
(49)	100	4	27	-	6
(50)	100	3	4	4	3
(51)	100	-	6	-	-
(52)	100	-	10	-	-
(53)	100	-	16	3	-
(54)	100	2	4	8	-
(55)	100	-	3	=	=
(56)	100	-	4	-	-
(57)	100	-	5	3	2
(58)	100	-	2	-	2
(59)	100	-	4	-	-
(60)	100	-	12	-	-

COMPOUND	$[C_7H_4NO_2]^{-}$	$[M^{\cdot -}-C_7H_5NO^{\cdot}]^{-}$	$[C_7H_5NO]^{-}$	$[R^3CO_2]^{-}$	$[M^{\cdot -}-R^3CO_2^{\cdot}]$	NO_2^{-}
(49)	6	17	2	12	6	50
(50)	10	15	-	7	3	22
(51)	-	-	-	-	-	10
(52)	-	-	-	-	-	20
(53)	6	9	1	14	-	38
(54)	8	10	1	23	-	26
(55)	-	-	-	-	-	10
(56)	-	-	-	-	-	12
(57)	2	46	-	30	-	13
(58)	2	33	1	33	-	24
(59)	-	-	-	-	-	18
(60)	-	-	-	-	-	46

TABLE 4-2

NEGATIVE ION MASS SPECTRA OF (67) - (78)

COMPOUND	$M^{\bar{\cdot}}$	$[M^{\bar{\cdot}}-HO\cdot]^-$	$[M^{\bar{\cdot}}NO]^-$	$[M^{\bar{\cdot}}-R^3CO\cdot]^-$	$[M-CO_2H\cdot]^-$
(67)	100	3	3	-	3
(68)	100	-	3	-	-
(69)	100	-	2	-	-
(70)	100	-	3	-	-
(71)	100	-	6	-	-
(72)	100	-	4	-	-
(73)	71	3	2	-	-
(74)	88	1	2	-	-
(75)	100	-	2	-	-
(76)	100	-	3	-	-
(77)	82	-	-	-	-

COMPOUND	$[C_7H_4NO_2]^-$	$[M^{\bar{\cdot}}-C_7H_5NO\cdot]^-$	$[C_7H_5NO]^{\bar{\cdot}}$	NO_2
(67)	77	92	11	31
(68)	-	-	-	36
(69)	-	-	-	34
(70)	34	22	13	21
(71)	-	-	-	22
(72)	-	-	-	21
(73)	30	100	8	11
(74)	39	100	8	18
(75)	-	-	-	29
(76)	-	-	-	25
(77)	51	100	-	31

FIGURE 4—1

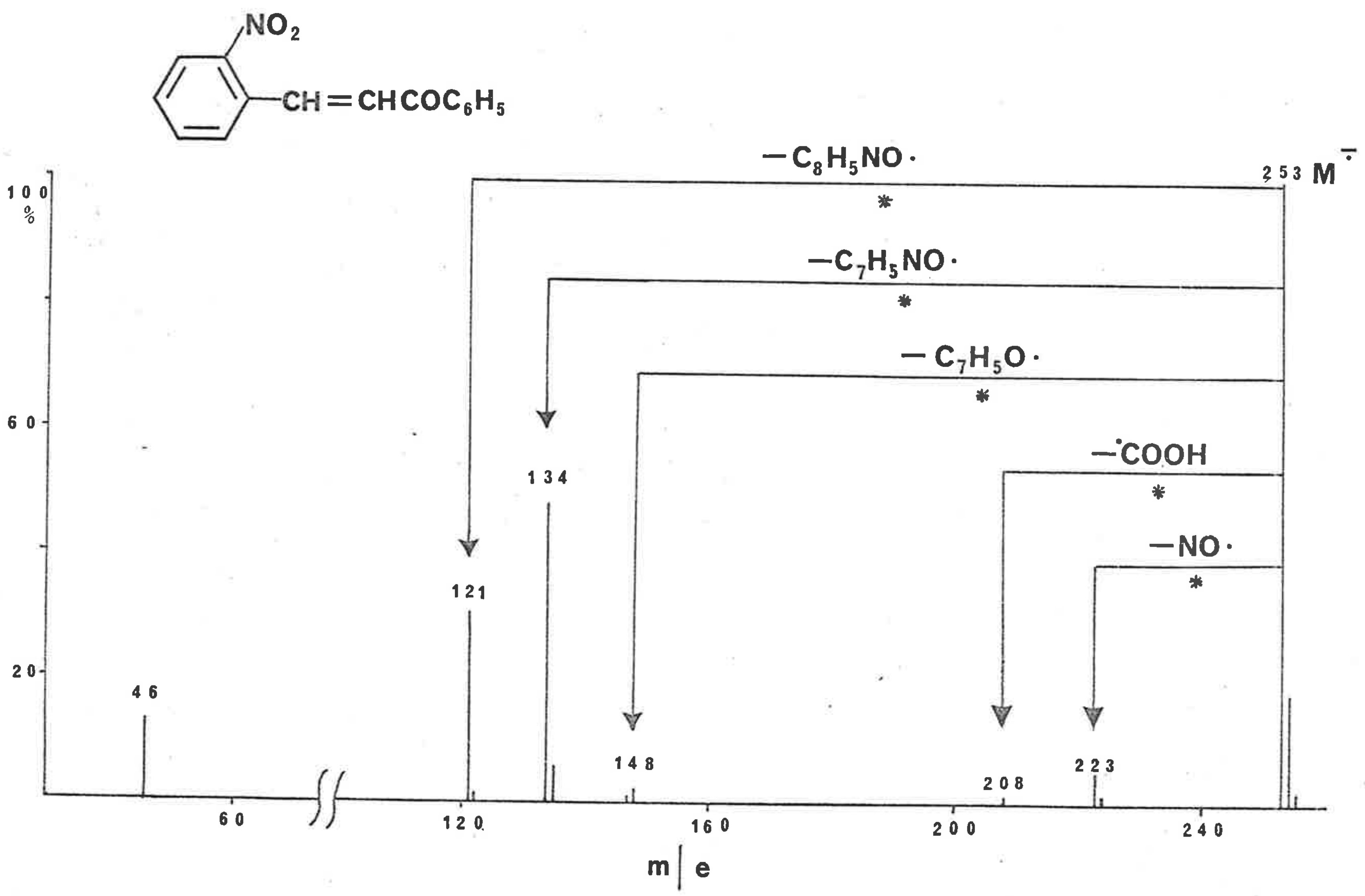

NO2
CH=CHCOC6H5
—C8H5NO·
—C7H5NO·
— C7H5O·
—·COOH
—NO·
*
253 M⁺·
134
121
148
208
223
46
100
%
60
20
60
120
160
200
240
m|e

FIGURE 4 — 2

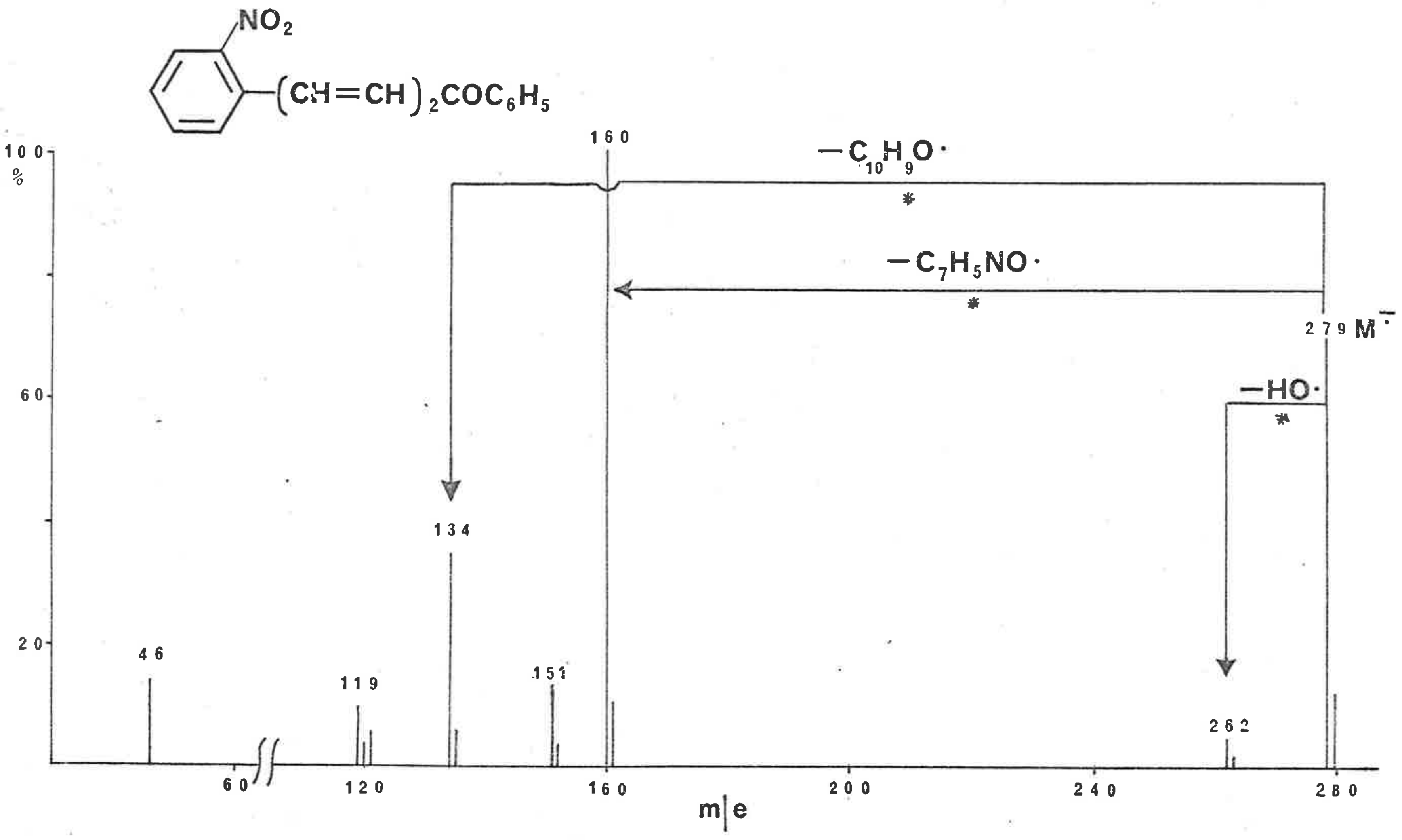
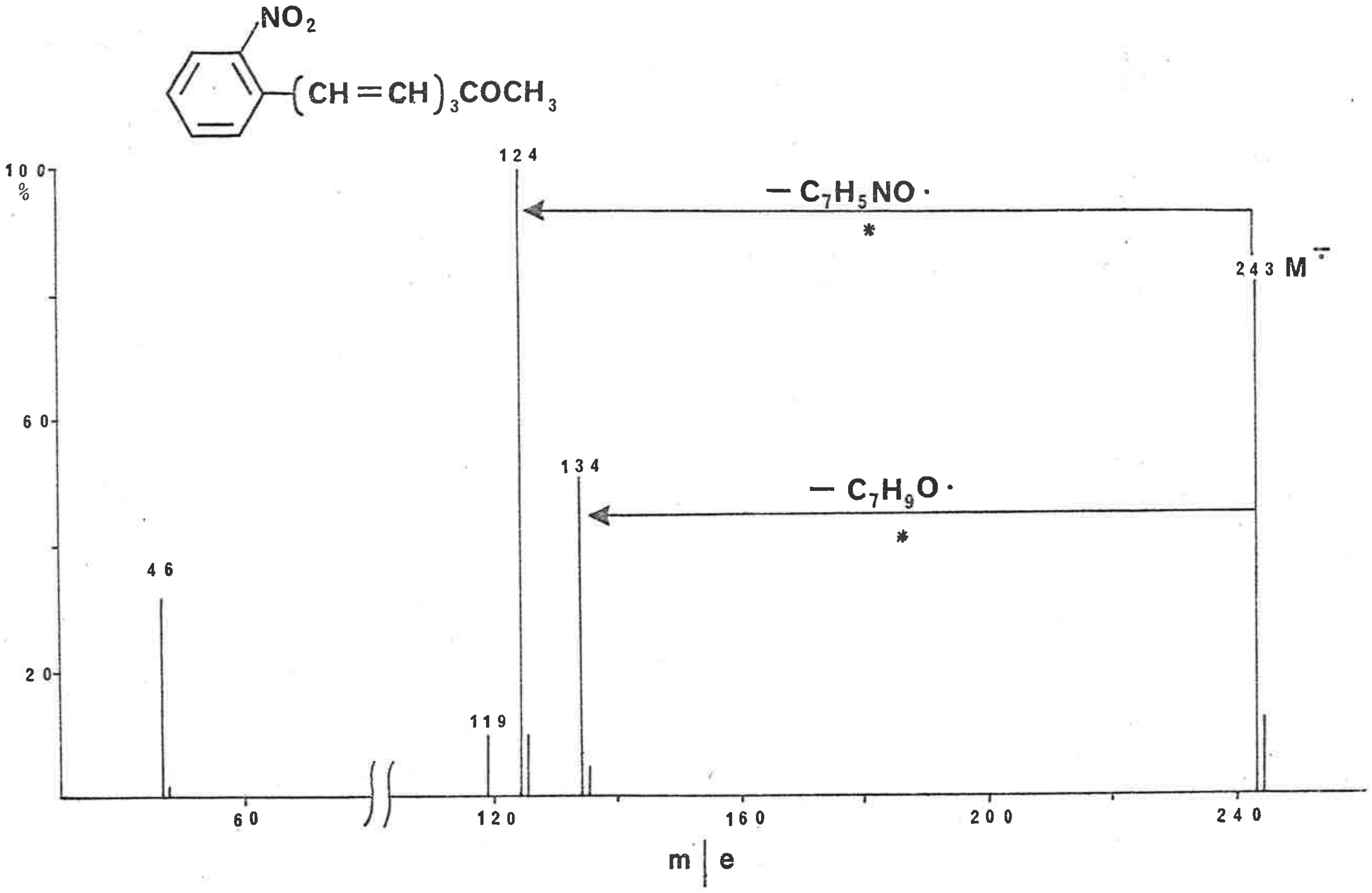
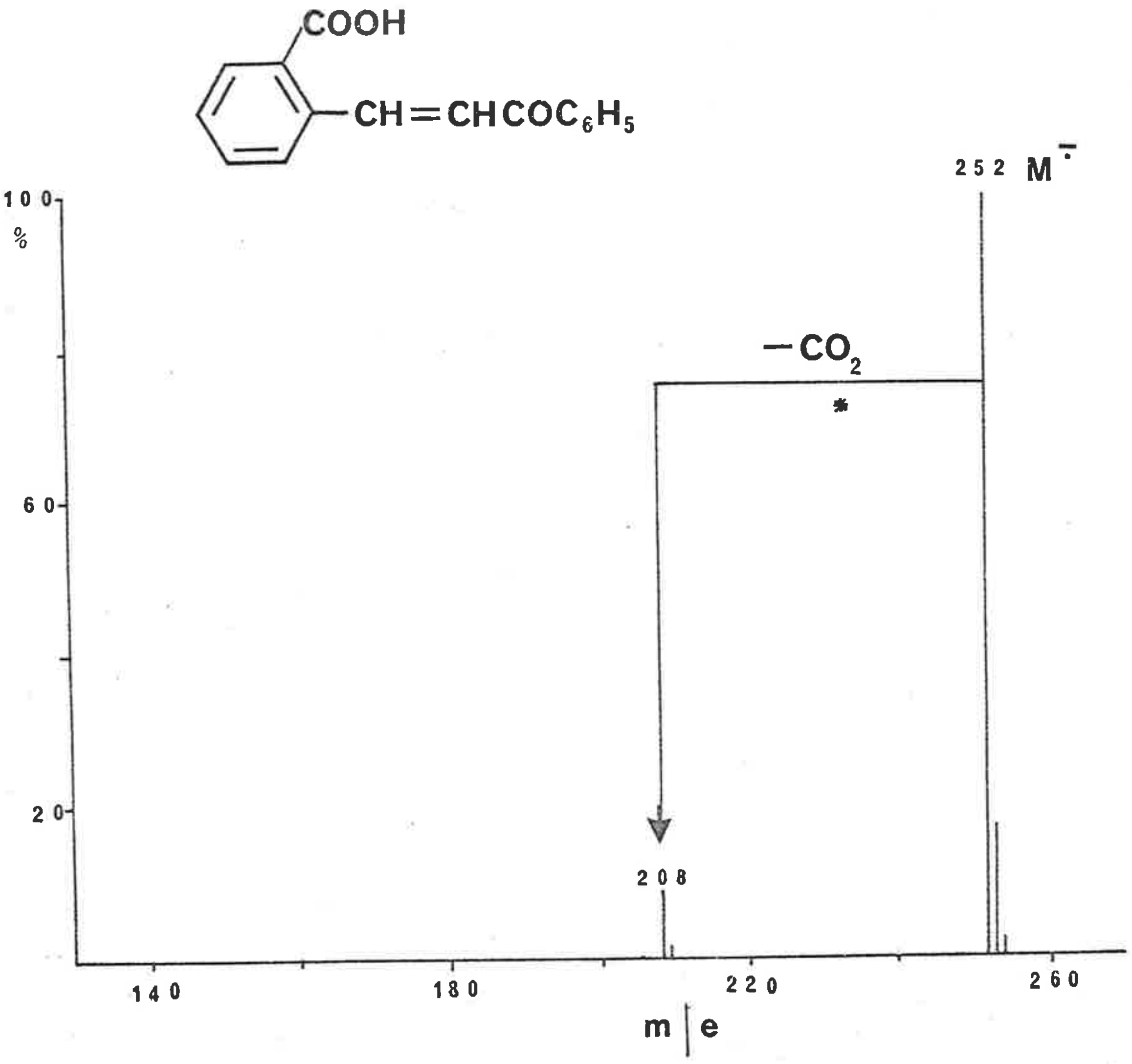

NO2
(CH=CH)2COC6H5
100
%
60
20
46
119
134
151
160
262
279 M+·
−C10H9O·
−C7H5NO·
−HO·
*
60
120
160
200
240
280
m|e

FIGURE 4—3



NO₂
(CH=CH)₃COCH₃
100 %
60
20
46
119
124
134
243 M⁺·
− C₇H₅NO·
*
− C₇H₉O·
*
60
120
160
200
240
m|e

FIGURE 4—4



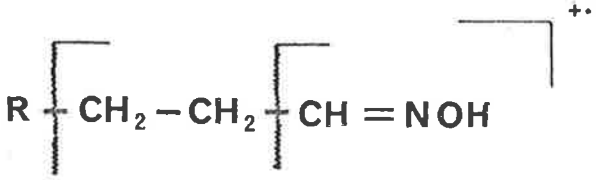
CHAPTER 5.

Negative-Ion Mass Spectra of Oximes.

5.1 Introduction

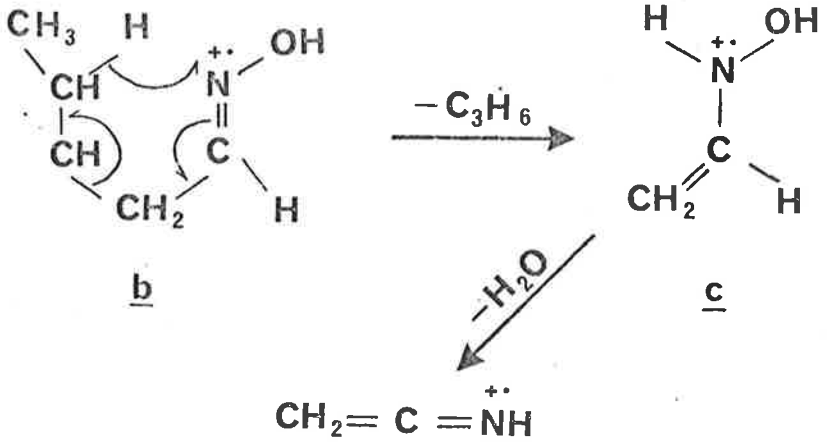
The positive ion spectra of aliphatic aldoximes[213,214] show weak molecular ions and few fragment ions.

Fragmentations which occur include α-cleavage and γ-cleavage to the oxime group as shown in a, and γ-hydrogen rearrangement (McLafferty rearrangement).



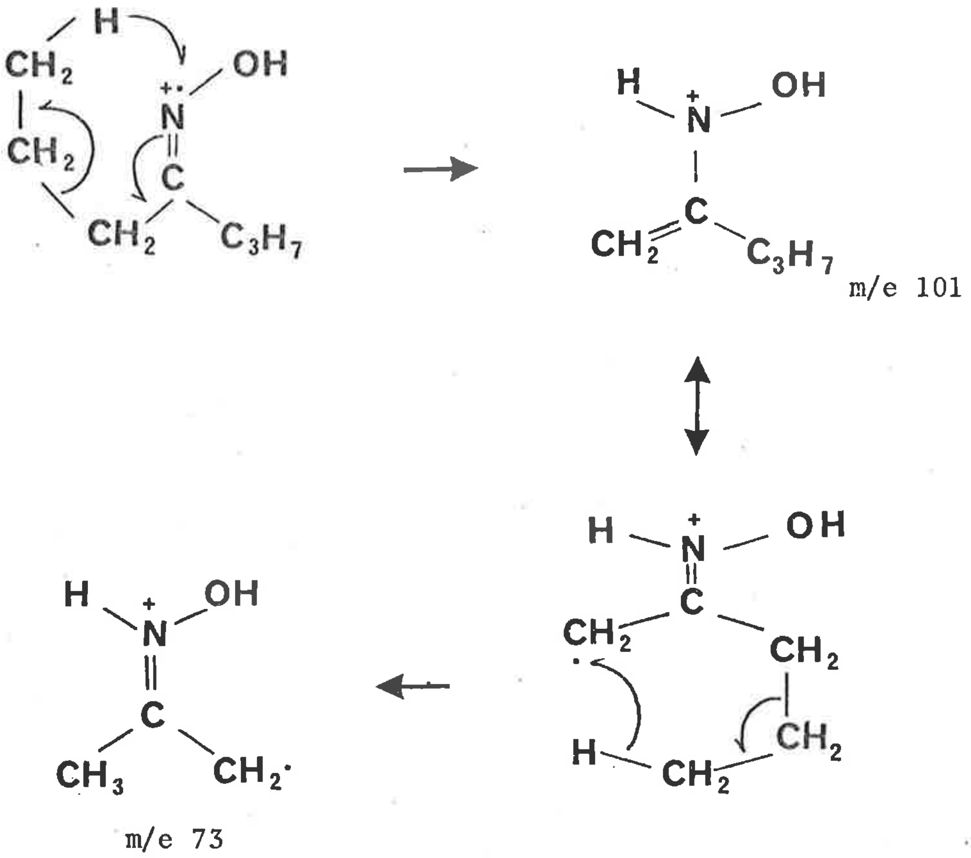
a

When R = $-CH_3$ or $-C_2H_5$ (see a), the positive ion spectra show base peaks at m/e 59 due to McLafferty rearrangements. An example of this process is shown in b → c.



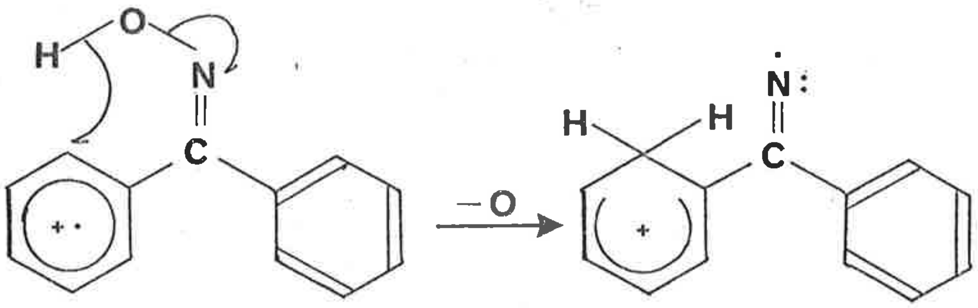
Similar fragmentations are noted for aliphatic ketoximes[213,214]. The fragmentation of di-n-propyl ketoxime is shown in Scheme 1.

Little published work is available for aromatic ketoximes[215]. The suggested occurrence of an electron-impact Beckmann rearrangement of benzopheno oximes was discounted.[213] The positive ion spectra of aromatic oximes[216] show abundant peaks due to molecular ions; fragmentations occur by α-fission to the oxime group, and loss of hydroxyl radicals from the respective molecular ions.


H
CH2
OH
N
C
CH2
CH2
C3H7
H
OH
N
C
CH2
C3H7
m/e 101
H
OH
N
C
CH2
CH2
CH2
H
CH2
H
OH
N
C
CH3
CH2
m/e 73

SCHEME 1

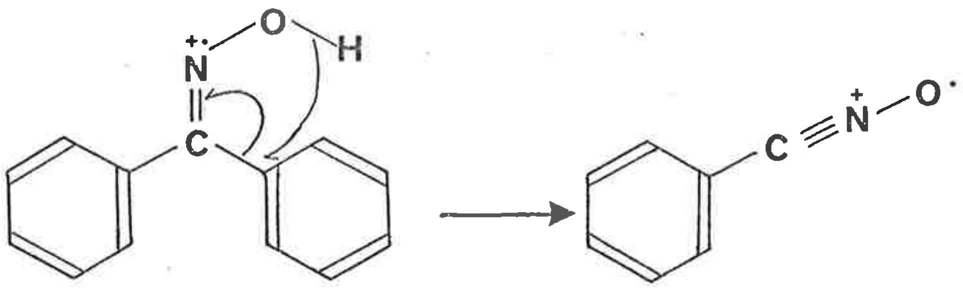
The loss of oxygen from the molecular ion is also noted, and this loss may be depicted by the transformation d → e.



d

e

Benzophenone monoxime undergoes α-fission to yield resonance stabilised f.

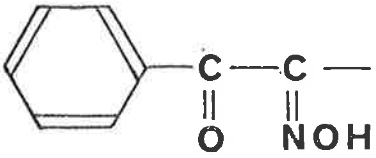


f

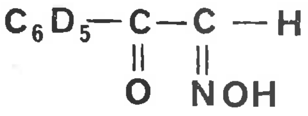
No survey of the negative ion spectra of aldoximes and ketoximes has been published. This chapter deals with the negative ion spectra of aldoximes and ketoximes of the carbonyl compounds described in Chapters 2,3 and 4.

5.2 RESULTS AND DISCUSSION

5.2.1. Benzilmonoxime, Isonitrosopropiophenone and Isonitrosoacetophenone.

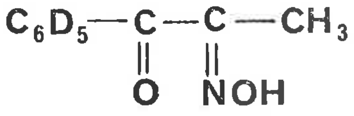


COMPOUND	R	FORM
(80)	H	α-
(81)	CH_3	α-
(82)	C_6H_5 †	α-
(83)	C_6H_5 †	β-



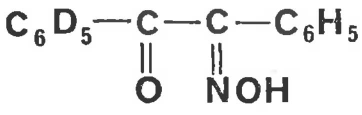
$\mathrm{C_6D_5{-}\underset{O}{\underset{\|}{C}}{-}\underset{NOH}{\underset{\|}{C}}{-}H}$

α-form (84)



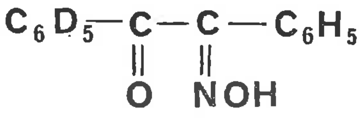
$\mathrm{C_6D_5{-}\underset{O}{\underset{\|}{C}}{-}\underset{NOH}{\underset{\|}{C}}{-}CH_3}$

α-form (85)



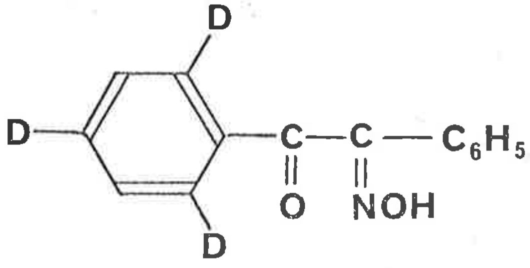
$\mathrm{C_6D_5{-}\underset{O}{\underset{\|}{C}}{-}\underset{NOH}{\underset{\|}{C}}{-}C_6H_5}$

α-form (86)



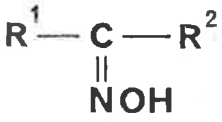
$\mathrm{C_6D_5{-}\underset{O}{\underset{\|}{C}}{-}\underset{NOH}{\underset{\|}{C}}{-}C_6H_5}$

β-form (87)



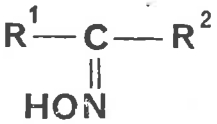
α-form (88)

Foot Note † α-form and β-form



$\mathrm{R^1{-}\underset{NOH}{\underset{\|}{C}}{-}R^2}$

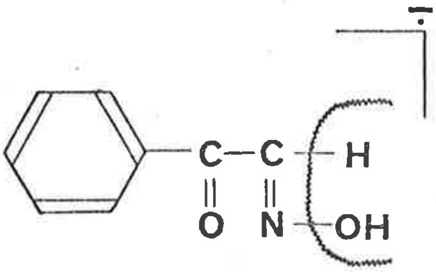
α-form



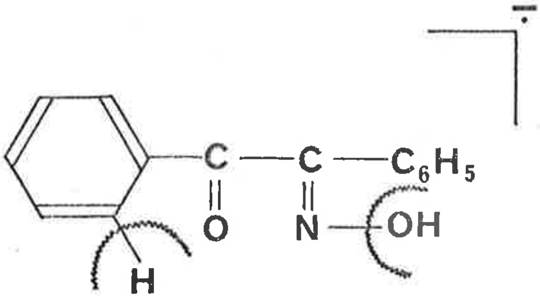
$\mathrm{R^1{-}\underset{HON}{\underset{\|}{C}}{-}R^2}$

β-form

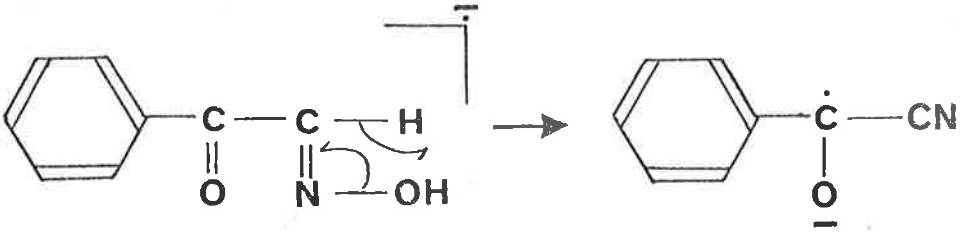
The negative ion spectra of (80)-(83) and of the labelled compounds (84)-(88) were studied and are listed in Table 5-1. The spectra of the unlabelled compounds exhibit pronounced molecular anions and $[M^{\cdot -}-H^{\cdot}]^{-}$ fragment ions. Other fragment ions noted are $[M^{\cdot -}-H_2O]^{\cdot -}$, $[C_7H_6O_2]^{\cdot -}$ and $C_7H_5O_2^{-}$ (see Table 5-1 and Figs 5-1, 5-2, 5-3). $[M^{\cdot -}-H_2O]^{\cdot -}$ ions produce the base peaks in the spectra of compounds (80) and (82). Losses of water from the molecular anions of (80) and (82) occur as depicted in g and h respectively, as evidenced by the spectra of the labelled derivatives (84), (86), (87) and (88). The fragmentation shown in g can be rationalised (Scheme 2) by the formation of an α-ketonitrile radical anion.



g



h



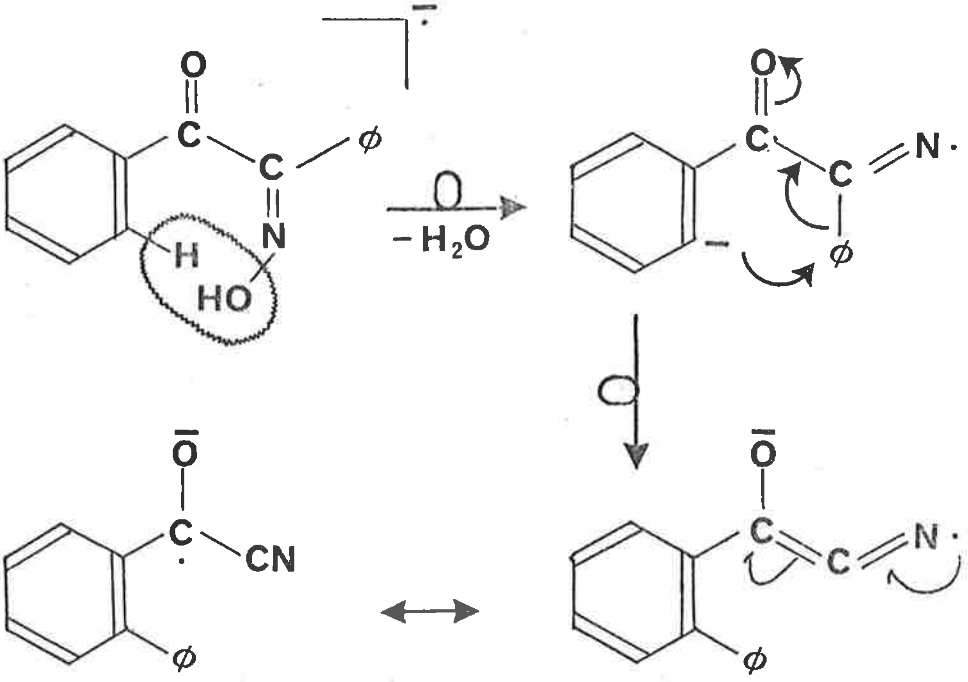
SCHEME 2

The fragmentation shown in h may occur as follows:-

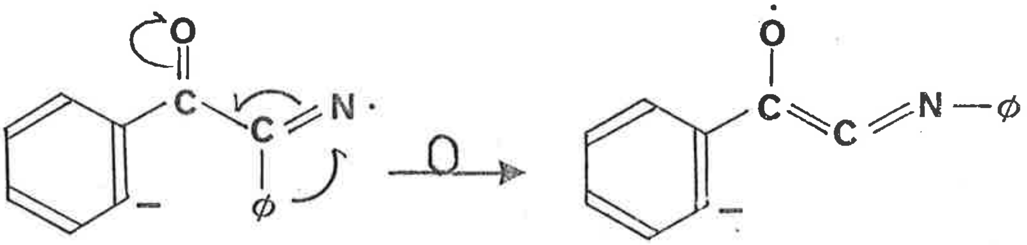
(a) Phenyl to phenyl migration as shown in Scheme 3.

(b) Phenyl to nitrogen rearrangement, as shown in Scheme 4.

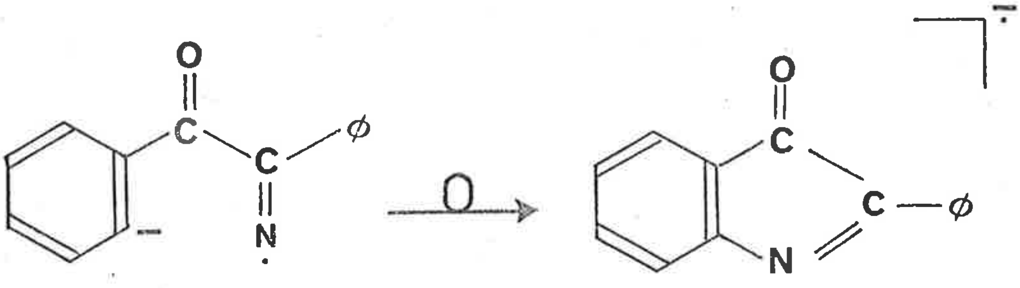
(c) Cyclization as shown in Scheme 5.



SCHEME 3



SCHEME 4



SCHEME 5

The three possibilities cannot be differentiated from the negative ion mass spectra, because no decomposition of the ion is observed. However, they could be differentiated if the positive ion decompositions of the M-18 ion could be determined. If the structure is a benzoyl cyanide derivative (as shown in Scheme 3), then the corresponding positive ion should show the fragmentations outlined in Scheme 6

$$[M\text{-}H_2O]^{+\cdot} \rightarrow [(M\text{-}H_2O)^{+\cdot}\text{-}CN^{\cdot}\text{-}CO\text{-}C_2H_2]^{+}$$

SCHEME 6

Positive ions derived from the product ions shown in Schemes 4 and 5 will not undergo the eliminations shown in Scheme 6.

Non-decomposing negative ions can be converted into decomposing positive ions by collision-induced charge stripping reactions to give +E spectra[217,218] The +E spectrum of negative ions derived from (82) shows no molecular cation, but does show a peak at m/e 207 which correspond to the fragment cation derived from $[M^{-\cdot}\text{-}H_2O]^{-\cdot}$. This fragment ion further fragments to produce peaks at m/e 181 and m/e 153 respectively, as shown in Scheme 7[†].

$$\begin{array}{ccccc} [M\text{-}H_2O]^{+\cdot} & \rightarrow & [(M\text{-}H_2O)\text{-}CN^{\cdot}]^{+} & \rightarrow & [(M\text{-}H_2O\text{-}CN^{\cdot})\text{-}CO]^{+} \\ m/e\ 207 & & m/e\ 181 & & m/e\ 153 \end{array}$$

SCHEME 7

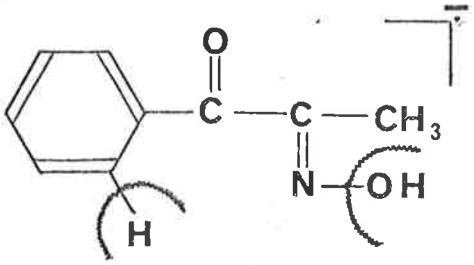
Similar fragmentations are observed in the +E spectrum of (80)[†]

This evidence suggests that the rearrangement ion $[M^{-\cdot}\text{-}H_2O]^{-\cdot}$ observed in the negative ion spectrum of (82) corresponds to the benzoyl cyanide radical anion shown in Scheme 2.

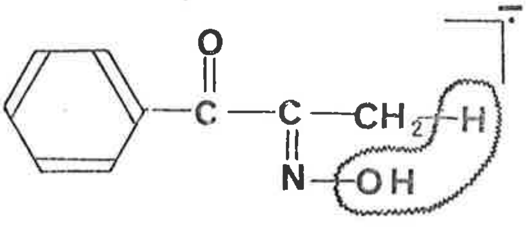
[†] The spectra were measured and interpreted by Dr J.H. Bowie.

The fragmentations observed for compound (81) are more complicated (see Table 5-1 and Fig 5-3). The spectrum shows peaks due to both $(M^{\overline{\cdot}}-H_2O)^{\overline{\cdot}}$, $[M^{\overline{\cdot}}-H_3O]^{\overline{\cdot}}$ The spectrum of the labelled compound (85) indicates that there are two different mechanisms operating for the loss of water, i.e. that shown in i (about 70%), and that shown in j (about 30%). The fragmentation shown in i probably yields k by analogy with the phenyl case (above).

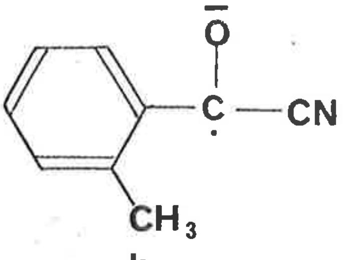
The formation of the $[M^{\overline{\cdot}}-H_3O\cdot]^{-}$ ion is not understood.



i

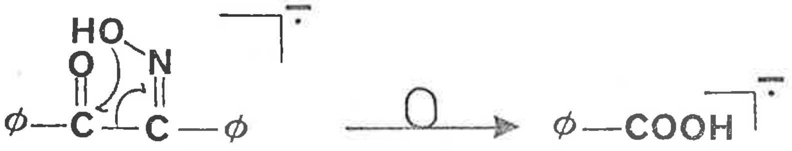


j



k

Fragment ions at m/e 121 $(C_7H_5O_2^-)$ are noted in all the spectra of unlabelled compounds in this series (see Table 5-1, Figs 5-1, 5-2 and 5-3). This fragment ion further decomposes by the elimination of CO_2 to yield m/e 77 $(C_6H_5^-)$. These results suggest that $C_7H_5O_2^-$ corresponds to the benzoate anion. Another peak observed in these spectra is that at m/e 122 (see Table 5-1, Figs 5-1, 5-2 and 5-3). This ion loses H· to form m/e 121 and is presumably due to the benzoic acid radical anion (see Scheme 8).



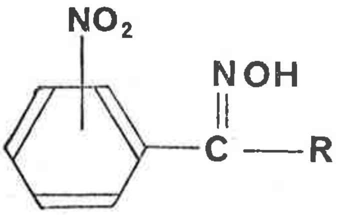
SCHEME 8

Finally, the spectra of the α and β-oximes (82) and (83) and (86) and (87) are identical.

As major fragmentations of some α-carbonyl oximes yield prominent rearrangement ions, we decided to investigate whether the fragmentations of simple aromatic, aliphatic and unsaturated oximes are similar to those mentioned above.

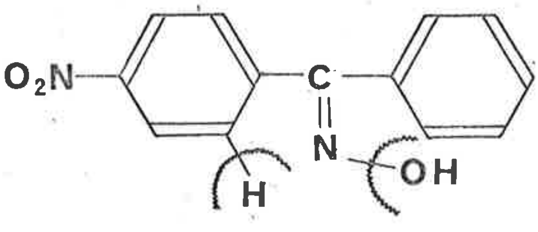
5.2.2 The $O_2N-C_6H_5-C(NOH)-R$ System

The oxime compounds (89) - (98) listed below were studied and their spectra are listed in Table 5-2.



COMPOUND	NO_2	R
(89)	p	H
(90)	m	H
(91)	o	H
(92)	p	CH_3
(93)	m	CH_3
(94)	o	CH_3
(95)	p	ϕ
(96)	m	ϕ
(97)	m	D
(98)	p	C_6D_5

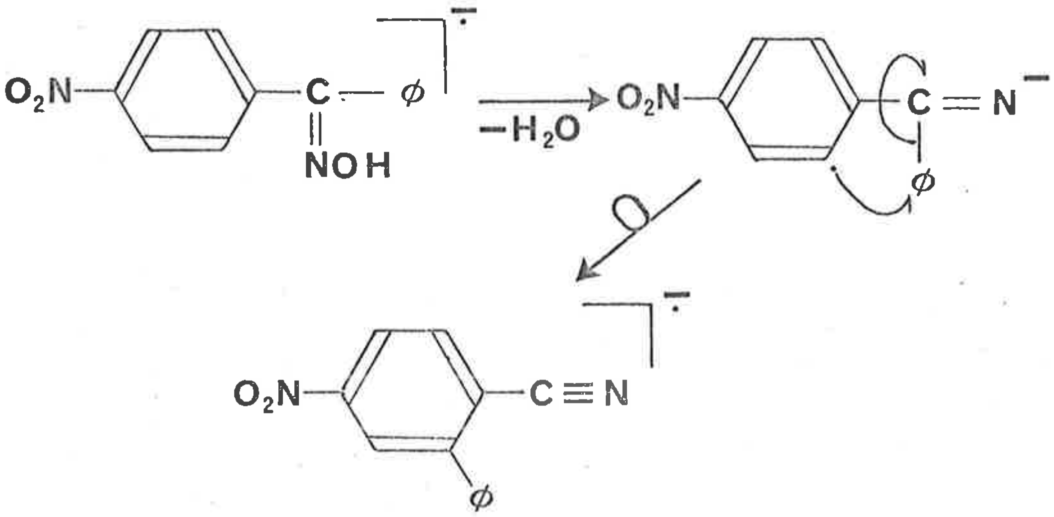
The negative ion spectra of compounds (89)-(98) yield pronounced molecular anions (see Table 5-2). The most characteristic fragmentation of these oxime compounds result in the formation of the ion $[M^{\cdot -}-H_2O]^{\cdot -}$



1

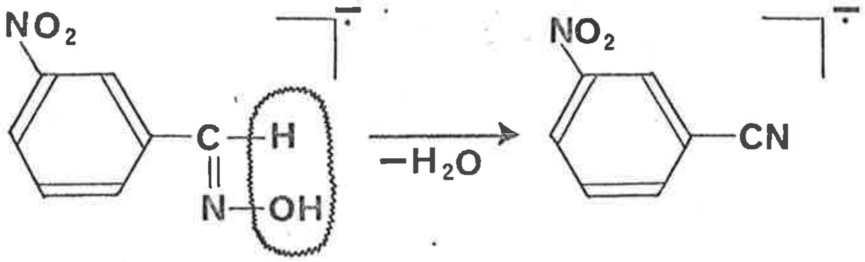
When R is a phenyl group, e.g. (95) and (96) the spectra exhibit the fragment ions $[M^{\cdot -}-H_2O]^{\cdot -}$ as base peaks (see Table 5-2, Fig 5-4). The spectrum of the labelled compound (98) shows that the eliminated water molecule originates as shown in 1.

This fragment ion may be formed by a rearrangement process in which the phenyl group migrates to the nitrophenyl ring. The mechanism of migration of the phenyl group to the nitrophenyl ring could be rationalized as shown in Scheme 9, a reaction analogous to that proposed above for the α-dicarbonyl monoximes (5.2.1). A similar mechanism may operate for the methyl derivatives (92) and (93).



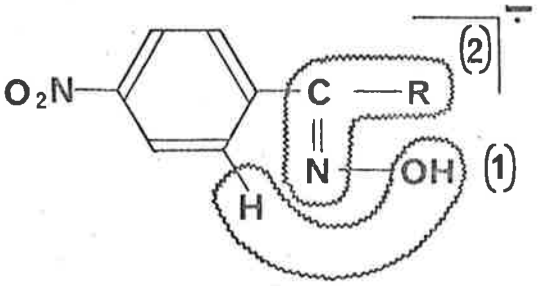
SCHEME 9

The spectra of the nitrobenzaldehyde oximes (89)-(91) and the labelled compound (97) show that the major loss of water occurs as shown in Scheme 10.



SCHEME 10

The fragment ions $[(M^{\overline{\cdot}}-H_2O)-RCN]^{\overline{\cdot}}$ are noted in the spectra of (92), (93), (95), (96) and (98) (see Table 5-2, Fig 5-4). This fragmentation could be rationalized as shown in m.

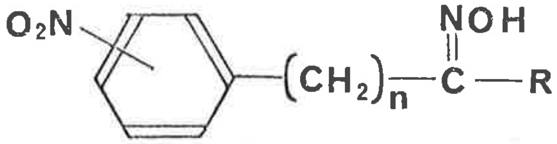


m

Other peaks observed in the spectra of (89)-(91) correspond to the process $[M^{\overline{\cdot}}-H_2O]^{\overline{\cdot}} \rightarrow [(M^{\overline{\cdot}}-H_2O)-NO\cdot]^{-}$.

Proximity effects are not noted in the spectra of the o-nitro oxime derivatives (91) and (94). (see Table 5-2).

5.2.3 The $O_2N-C_6H_5-(CH_2)_n-C(NOH)-R$ System.

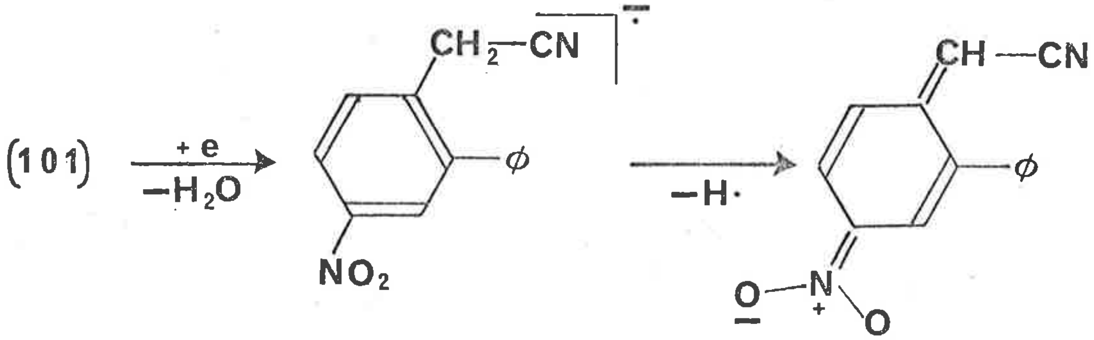


COMPOUND	NO_2	R	n
(99)	p	CH_3	1
(100)	o	CH_3	1

COMPOUND	NO_2	R	n
(101)	*p*	ϕ	1
(102)	*o*	ϕ	1
(103)	*p*	CH_3	2
(104)	*o*	CH_3	2
(105)	*p*	ϕ	2
(106)	*o*	ϕ	2
(107)	*p*	C_6D_5	1

Losses of water are observed in the negative ion spectra (Table 5-3) of the majority of compounds 99-105. Due to the lack of labelling evidence no conclusions can be reached concerning the intimate mechanisms for most of these processes. Processes of interest are those observed in the spectra of (101) and (107), *viz*, $M^{\bar{\cdot}}-H_2O-H^{\cdot}$ in both cases. We propose the processes (101) → *n* → *o* as a rationale for these reactions (see below).

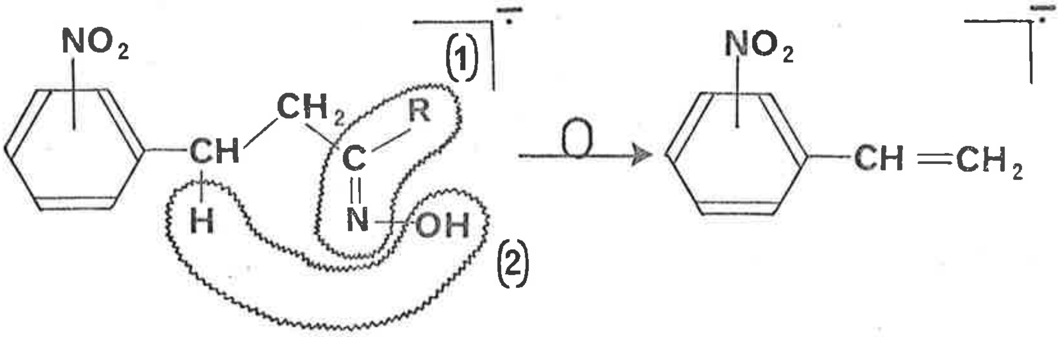
The spectra of (103)-(106) (where n=2) exhibit peaks at m/e 149.



n *o*

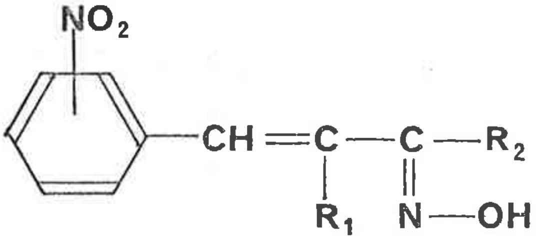
This species is probably produced as shown in Scheme 11 (see Table 5-3 and Fig 5-6).

Proximity effects are not noted in the spectra of the *o*-nitro oxime derivatives (100), (102), (104) and (106).



SCHEME 11

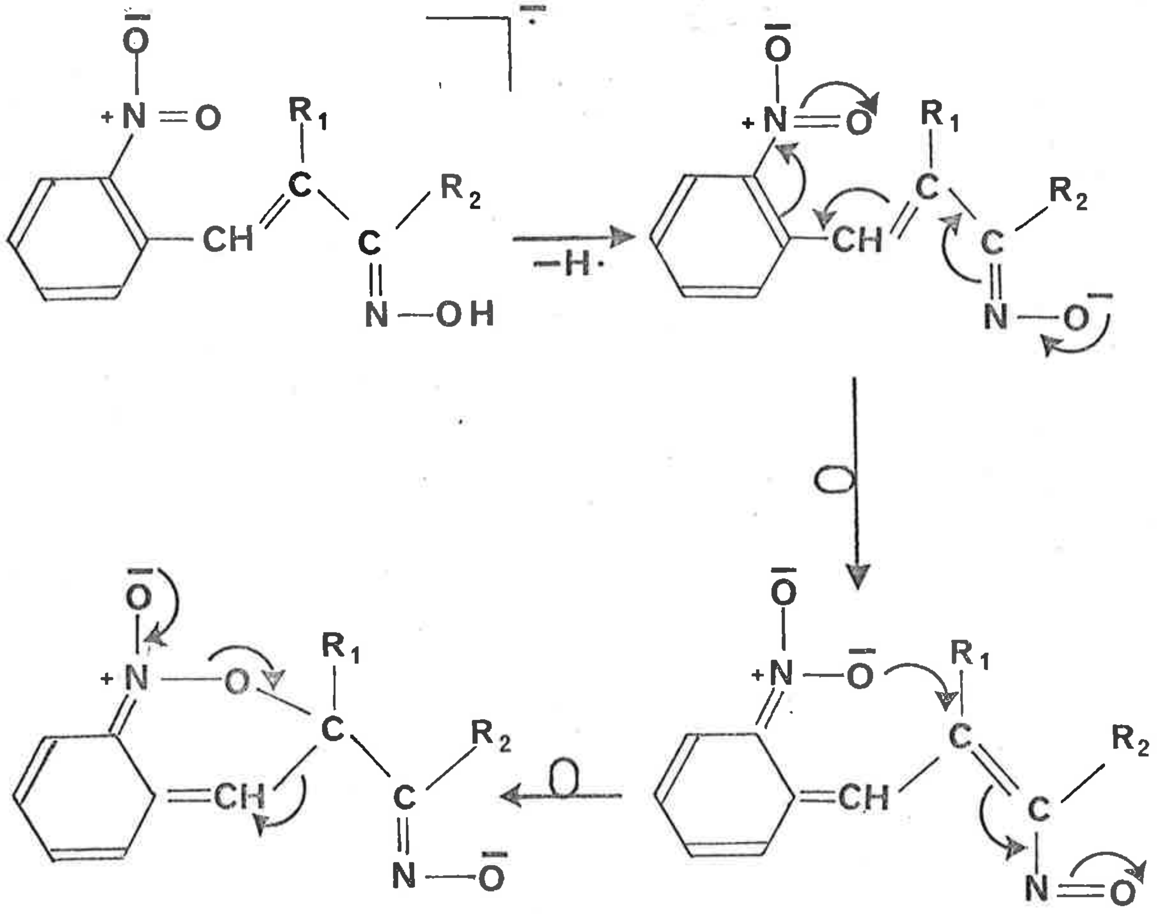
5.2.4 The Oximes of Unsaturated Compounds



COMPOUND	NO_2	R_1	R_2
(108)	o	H	H
(109)	m	H	H
(110)	o	CH_3	H
(111)	o	H	CH_3
(112)	o	CH_3	CH_3
(113)	p	H	CH_3
(114)	o	H	D

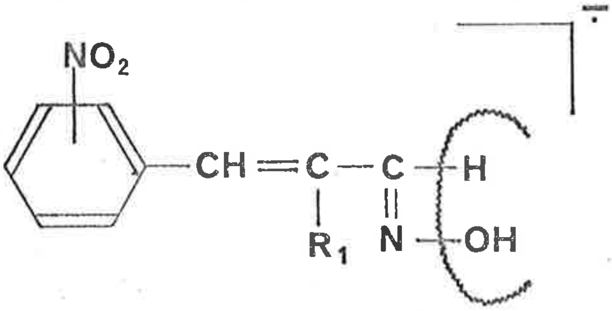
The 70eV spectra of the unsaturated oxime compounds listed above are listed in Table 5-4. The negative ion spectra of o-nitro unsaturated oxime derivatives (108), (110), (111), (112) and (114) yield the following fragment ions, viz: $[M^{-\cdot}-H_2O]^{-\cdot}$, $[M^{-\cdot}-NO\cdot]^{-}$, $C_7H_4NO_2^{-}$, $C_7H_6NO^{-}$, $[M^{-\cdot}-C_7H_6NO\cdot]^{-}$ and NO_2^{-}. The m and p-nitro oxime derivatives (109) and (113) show only the simple fragment ions $[M^{-\cdot}-NO\cdot]^{-}$ and NO_2^{-}. The ions $C_7H_4NO_2^{-}$, $C_7H_6NO^{-}$ and $[M^{-\cdot}-C_7H_6NO\cdot]^{-}$ from the o-nitrobenzal oxime derivatives are produced by rearrangement processes, analogous to those of the o-nitrobenzal ketone derivatives which were discussed in Chapter 4.

The abundances of $[M^{\cdot -}-C_7H_6NO\cdot]^-$ ions range from 20-100% (see Table 5-4, Figs 5-7, 5-8) of the base peak. The fragmentation mechanism may be rationalized as shown in Scheme 12.



SCHEME 12

The abundance of the $[M^{\cdot -}-H_2O]^{\cdot -}$ ion is small in the spectra of nitrobenzal oxime derivatives. (see Table 5-4, Figs 5-7, 5-8). This ion



p

is produced as shown in p, as demonstrated by the spectrum of (114).

5.3 Conclusions

(a) The characteristic negative ion fragmentation of oximes is $[M^{\cdot -}-H_2O]^{\cdot -}$. This elimination is specific for a particular molecule, and in some cases, may involve rearrangement reactions.

(b) Proximity effects are not observed for *o*-nitro aldoxime and ketoxime compounds except in the case of *o*-nitrobenzal oxime derivatives, which fragment in a similar manner to *o*-nitrobenzal carbonyl compounds. (see Chapter 4).

TABLE 5-1

Negative Ion Mass Spectra of (80) - (88)

(80)	m/e	26	46	121	131	132	148	149	$(M^{\cdot -})$
	I%	47	4	3	100	12	57	72	
	m^*	149 → 131, 149 → 121							
(81)	m/e	26	40	58	77	121	122	144	145
	I%	12	44	4	2	10	8	32	37
	m/e	162	163	$(M^{\cdot -})$					
	I%	100	92						
	m^*	163 → 145, 163 → 144, 163 → 121, 121 → 77							
(82)	m/e	26	77	102	121	122	207	208	224
	I%	2	4	4	11	5	100	17	14
	m/e	225	$(M^{\cdot -})$	226					
	I%	87		10					
	m^*	225 → 207, 225 → 122, 122 → 121, 121 → 77.							
(83)	m/e	26	77	102	121	122	207	208	224
	I%	2	4	4	11	5	100	17	14
	m/e	225	$(M^{\cdot -})$	226					
	I%	87		10					
	m^*	225 → 207, 225 → 122, 122 → 121, 121 → 77							
(84)	m/e	26	126	136	153	154	$(M^{\cdot -})$		
	I%	45	10	100	51	72			
	m^*	154 → 136, 154 → 126							
(85)	m/e	40	58	82	126	127	148	149	
	I%	51	3	4	6	6	12	22	
	m/e	150	167	168	$(M^{\cdot -})$	169			
	I%	8	80	100		17			
	m^*	168 → 149, 168 → 148, 168 → 126, 126 → 82							

(86)	m/e	26	82	102	126	127	211	212	229
	I%	2	2	4	15	9	70	10	11
	m/e	230 $(M^{-\cdot})$		231					
	I%	100		10					

m^* 230 → 211, 230 → 127, 127 → 126, 126 → 82

(88)	m/e	26	80	102	124	125	209	210
	I%	2	3	4	10	7	98	22
	m/e	227	228 $(M^{-\cdot})$		229			
	I%	14	100		19			

m^* 228 → 209, 228 → 125, 125 → 124, 124 → 80

TABLE 5-2

Negative Ion Mass Spectra of (89) - (98)

(89)	m/e	46	118	148	166	$(M^{\cdot -})$				
	I%	30	100	10	8					
	m^*	166 → 148,	166 → 118,	148 → 118						
(90)	m/e	46	118	148	166	$(M^{\cdot -})$				
	I%	80	100	87	84					
	m^*	166 → 148,	166 → 118,	148 → 118						
(91)	m/e	46	118	148	116	$(M^{\cdot -})$				
	I%	100	77	5	5					
	m^*	166 → 118								
(92)	m/e	46	121	132	138	162	179	180	$(M^{\cdot -})$	
	I%	25	4	3	3	34	16	100		
	m/e	181								
	I%	17								
	m^*	180 → 162,	180 → 138,	180 → 132,	180 → 121					
(93)	m/e	46	121	162	179	180	$(M^{\cdot -})$	181		
	I%	20	4	25	60	100		40		
	m^*	180 → 162,	180 → 121							
(94)	m/e	46	132	150	151	179	180	$(M^{\cdot -})$		
	I%	66	3	100	13	35	42			
	m^*	180 → 150,	180 → 132							
(95)	m/e	26	46	91	121	122	138	139	194	197
	I%	3	14	2	20	6	3	3	3	4
	m/e	224	225	226	241	242	$(M^{\cdot -})$	243		
	I%	100	20	15	8	80		12		
	m^*	242 → 224,	242 → 138,	242 → 121,	224 → 197,	224 → 194				

(96)	m/e	46	121	122	138	139	194	223	224	
	I%	8	8	2	3	3	10	80	85	
	m/e	241	242	$(M^{\cdot-})$	243					
	I%	80	100		11					
	m^*	242 → 224, 242 → 138, 242 → 121								
(97)	m/e	46	118	148	167	$(M^{\cdot-})$				
	I%	60	64	80	100					
	m^*	167 → 148, 167 → 118.								
(98)	m/e	46	91	121	122	138	127	128	129	130
	I%	13	3	28	10	6	16	50	100	20
	m/e	131	245	246	247	$(M^{\cdot-})$	248			
	I%	17	14	48	95		6			
	m^*	247 → 229, 247 → 121, 121 → 91								

TABLE 5-3

Negative Ion Mass Spectra of (99) - (106)

(99)	m/e	46	121	135	136	137	151	161	162	
	I%	25	2	5	35	5	9	56	8	
	m/e	193	194	$(M^{\cdot -})$	195					
	I%	13	100		17					
	m^*	194 → 161, 194 → 136								
(100)	m/e	46	118	131	135	136	145	159	161	
	I%	100	30	20	3	5	14	7	12	
	m/e	175	176	194	$(M^{\cdot -})$	195				
	I%	3	7	24		5				
	m^*	194 → 176, 194 → 161								
(101)	m/e	46	121	135	136	151	161	221	237	238
	I%	6	2	4	2	4	16	5	100	23
	m/e	256	$(M^{\cdot -})$	257						
	I%	33		5						
	M^8	256 → 238, 256 → 237, 238 → 221								
(102)	m/e	46	121	135	136	151	208	209	221	238
	I%	30	2	3	4	2	60	10	20	11
	m/e	255	256	$(M^{\cdot -})$	257					
	I%	4	100		19					
	m^*	256 → 238, 256 → 221, 256 → 208								
(103)	m/e	46	136	149	151	167	208	$(M^{\cdot -})$	209	
	I%	6	3	3	4	4	100		8	
	m^*	208 →149								
(104)	m/e	46	136	149	151	167	208	$(M^{\cdot -})$	209	
	I%	26	3	12	14	3	100		10	
	m^*	208 → 149								

(105)	m/e	46	136	149	150	151	167	252	270 (M$^{\cdot-}$)
	I%	15	4	32	3	3	2	29	100
	m^*	270 → 252, 270 → 149						271 15	

(106)	m/e	46	136	149	150	151	167	252	270 (M$^{\cdot-}$)
	I%	10	2	38	5	5	4	38	100
	m^*	270 → 252, 270 → 149						271 18	

TABLE 5-4

Negative Ion Mass Spectra of (108)-(114)

(108)	m/e	26	46	72	144	162	174	191	192 (M$^{\cdot-}$)
	I%	20	100	22	14	5	30	7	62
	m/e	193							
	I%	4							
	m^*	192 → 174, 192 → 162, 192 → 72, 174 → 144							

(109)	m/e	46	144	174	192 (M$^{\cdot-}$)	193
	I%	100	30	35	32	8
	m^*	192 → 174, 174 → 144				

(110)	m/e	26	46	86	120	121	158	163	176	188
	I%	17	74	100	21	5	12	6	12	7
	m/e	205	206 (M$^{\cdot-}$)	207						
	I%	4	98	11						
	m^*	206 → 188, 206 → 176, 206 → 163, 206 → 158, 206 → 120, 206 → 86								

(111)	m/e	26	46	86	120	158	176	188	205
	I%	3	39	19	6	4	5	3	3
	m/e	206 (M$^{\cdot-}$)	209						
	I%	100	7						
	m^*	206 → 188, 206 → 176, 206 → 158, 206 → 120, 206 → 86							

(112)	m/e	26	46	100	101	120	172	190	220	$(M^{\cdot -})$
	I%	2	42	100	9	22	3	4	72	
	m*	220 → 190, 220 → 120, 220 → 100, 190 → 172								

(113)	m/e	46	158	176	206	$(M^{\cdot -})$	207
	I%	86	60	30	100		10
	m*	206 → 176, 206 → 158					

(114)	m/e	26	46	73	144	163	174	192	193	$(M^{\cdot -})$
	I%	8	94	28	8	6	14	9	100	
	m*	193 → 174, 193 → 163, 193 → 73, 174 → 144								194 10

FIGURE 5-1

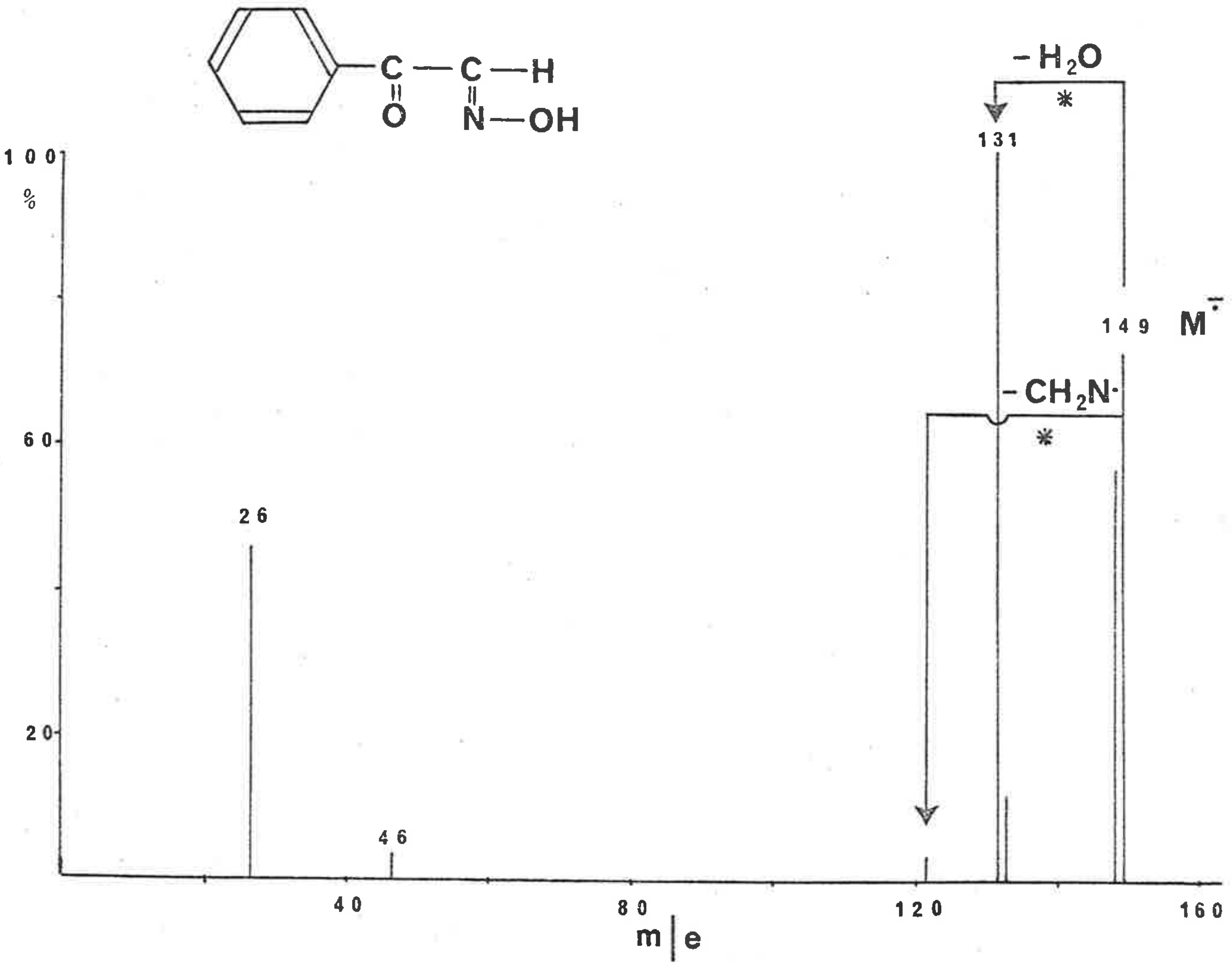


FIGURE 5-2

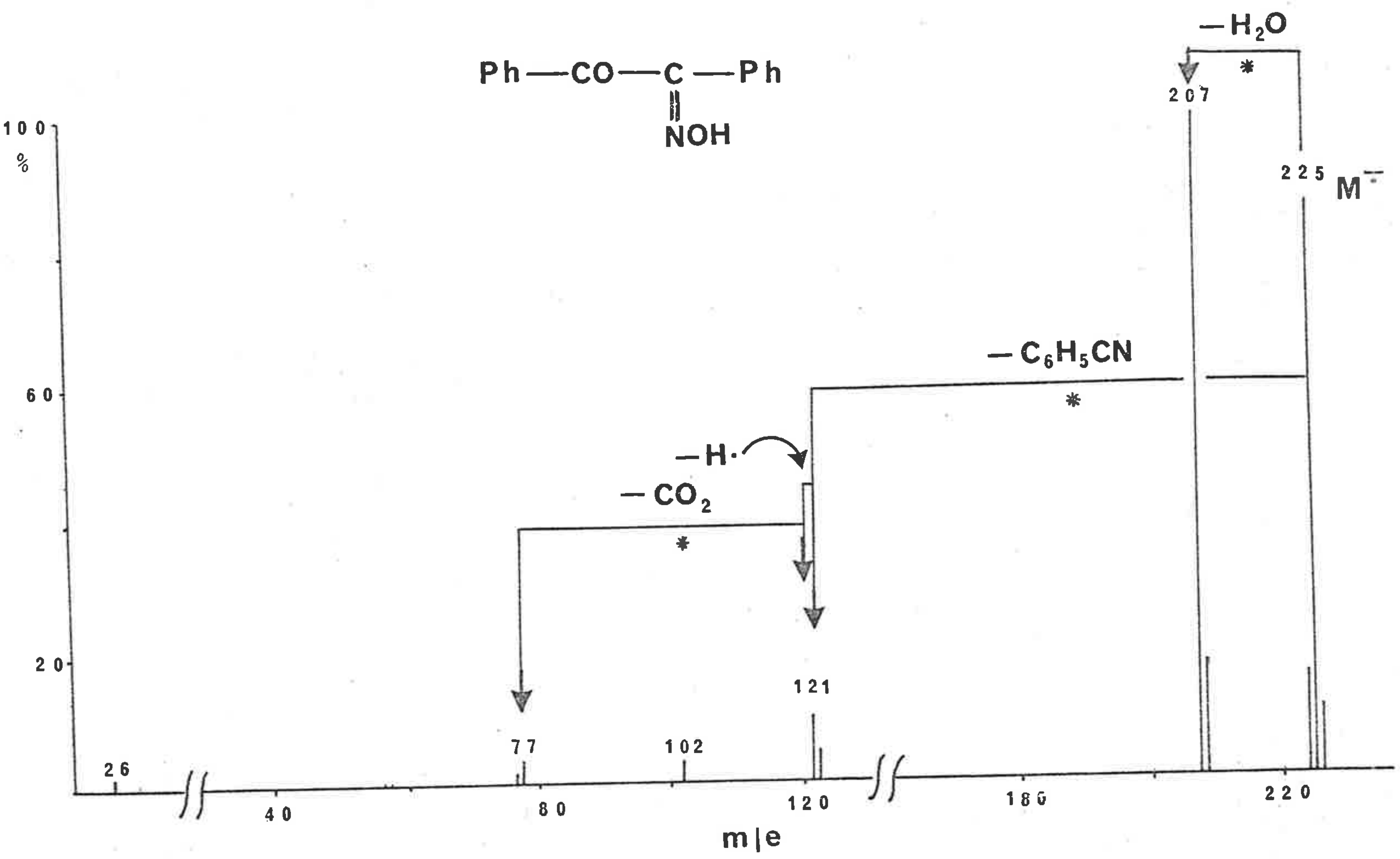

Ph—CO—C—Ph
NOH
−H₂O
*
207
225
M⁻·
100
%
60
20
−C₆H₅CN
*
−H·
−CO₂
*
121
77
102
26
40
80
120
180
220
m|e

FIGURE 5-3

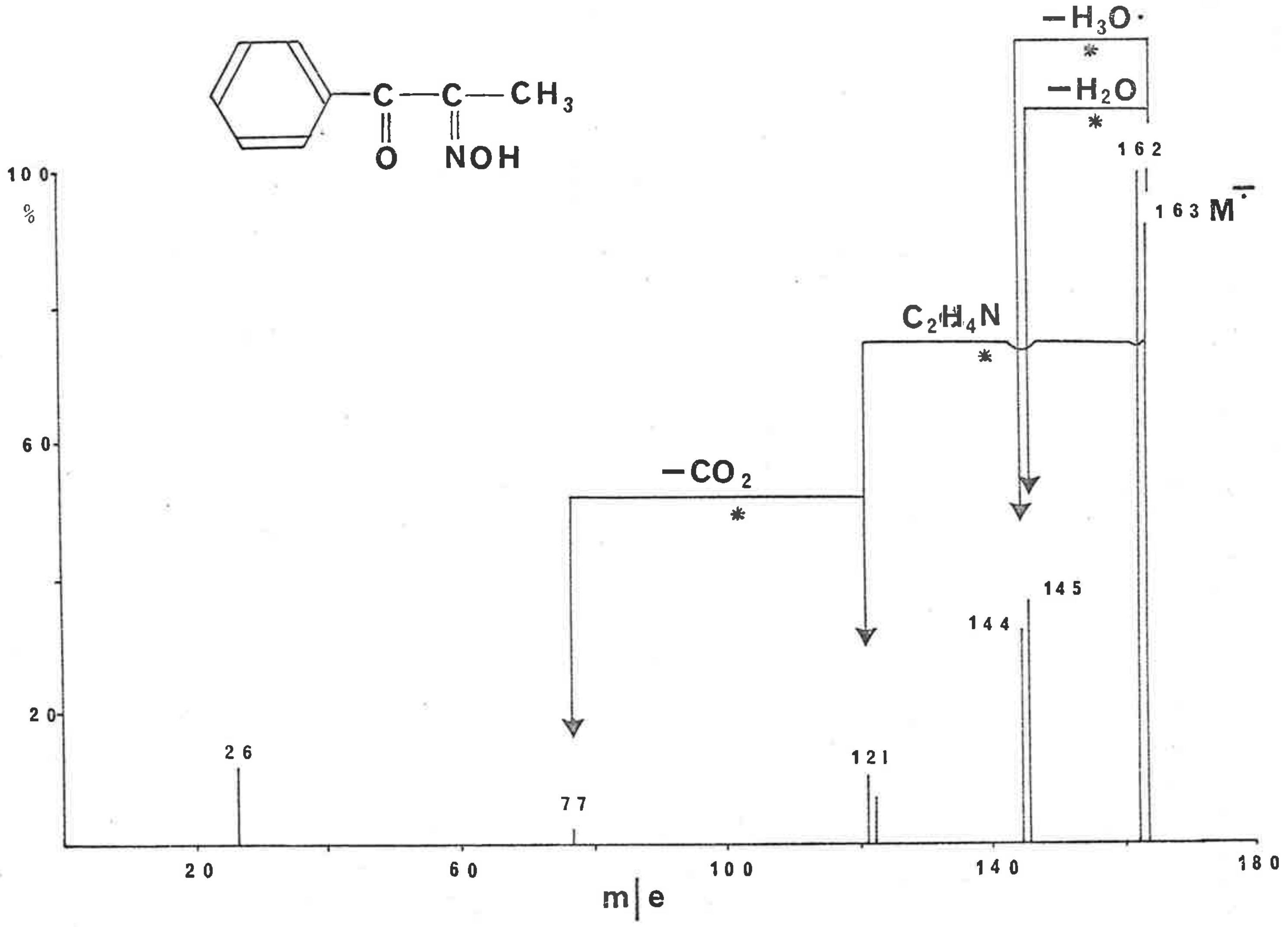
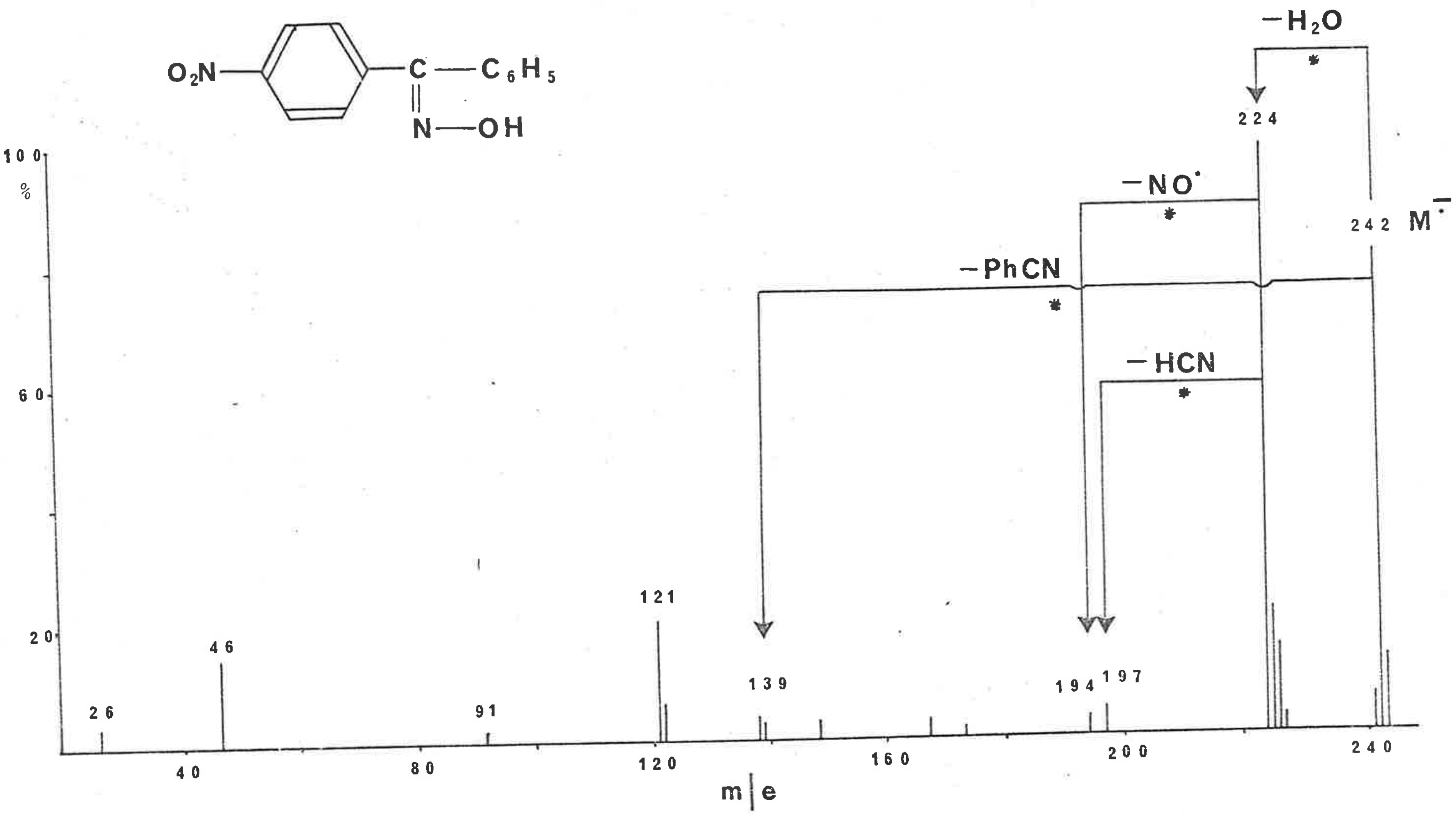
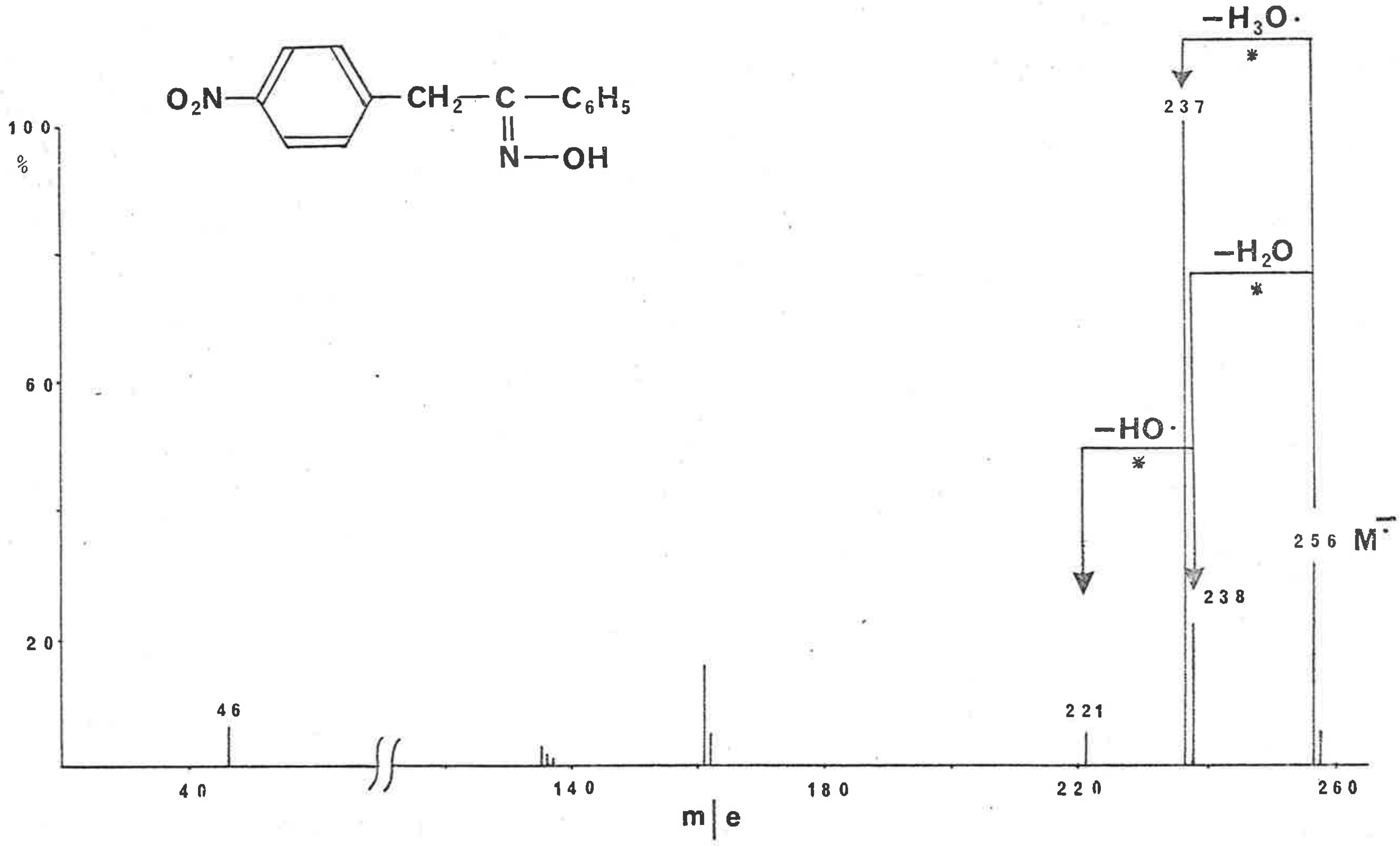

C—C—CH3
O
NOH
100
%
60
20
−H3O·
*
−H2O
*
162
163 M·
C2H4N
*
−CO2
*
145
144
26
121
77
20
60
100
140
180
m|e

FIGURE 5 – 4



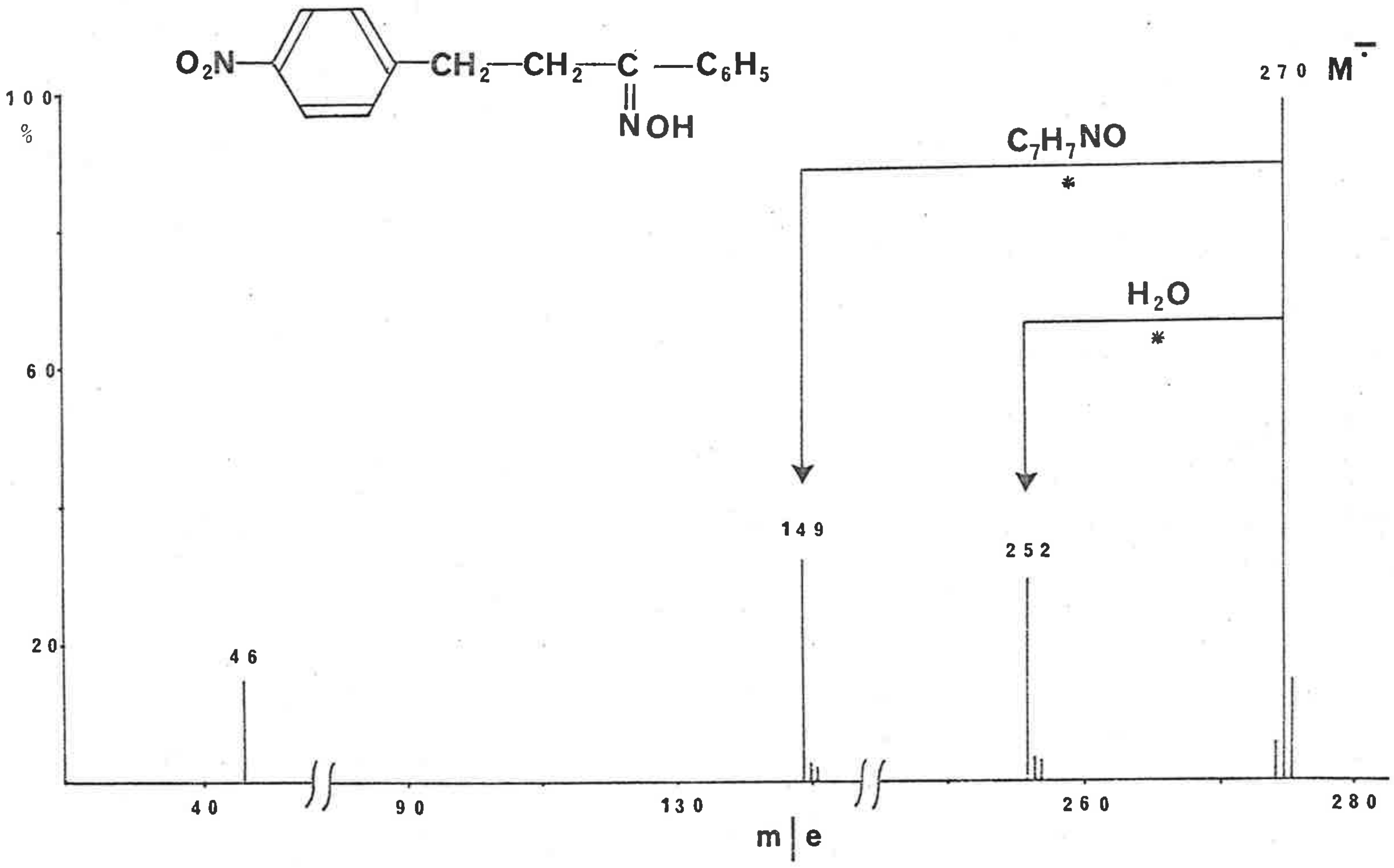
O_2N–C$_6$H$_4$–C(=N–OH)–C$_6$H$_5$
−H$_2$O
*
224
−NO·
*
242 M$^{-\cdot}$
−PhCN
*
−HCN
*
100
%
60
20
121
46
139
194
197
26
91
40
80
120
160
200
240
m|e

FIGURE 5 – 5



$O_2N-C_6H_4-CH_2-C(=N-OH)-C_6H_5$
100
%
60
20
46
221
237
238
256 M⁻
$-H_3O\cdot$
*
$-H_2O$
*
$-HO\cdot$
*
40
140
180
220
260
m|e

FIGURE 5 – 6



$O_2N-C_6H_4-CH_2-CH_2-C(=NOH)-C_6H_5$
100
%
60
20
46
149
252
270 M$^{\overset{-}{\cdot}}$
C_7H_7NO
*
H_2O
*
40
90
130
260
280
m|e

FIGURE 5 — 7

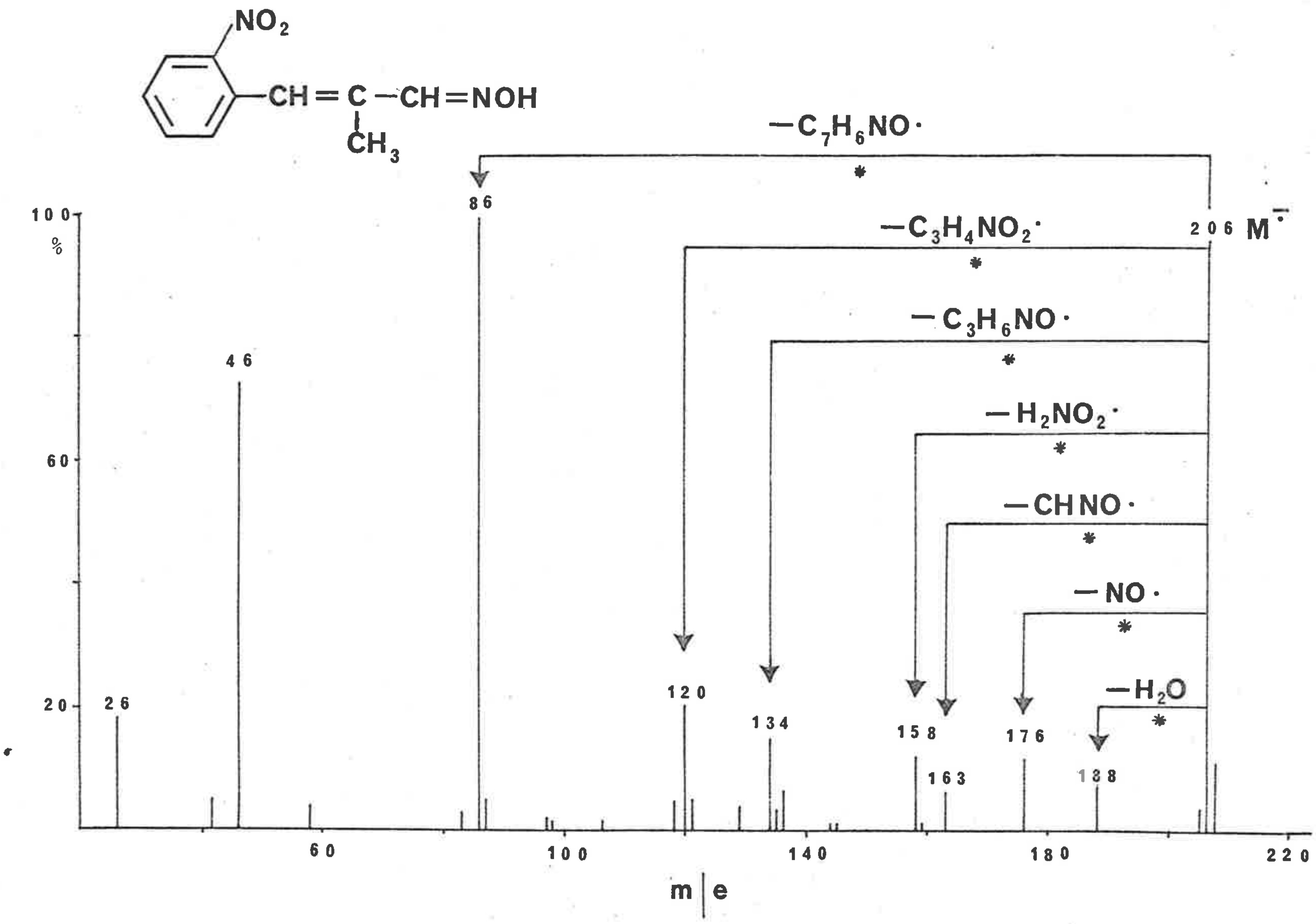
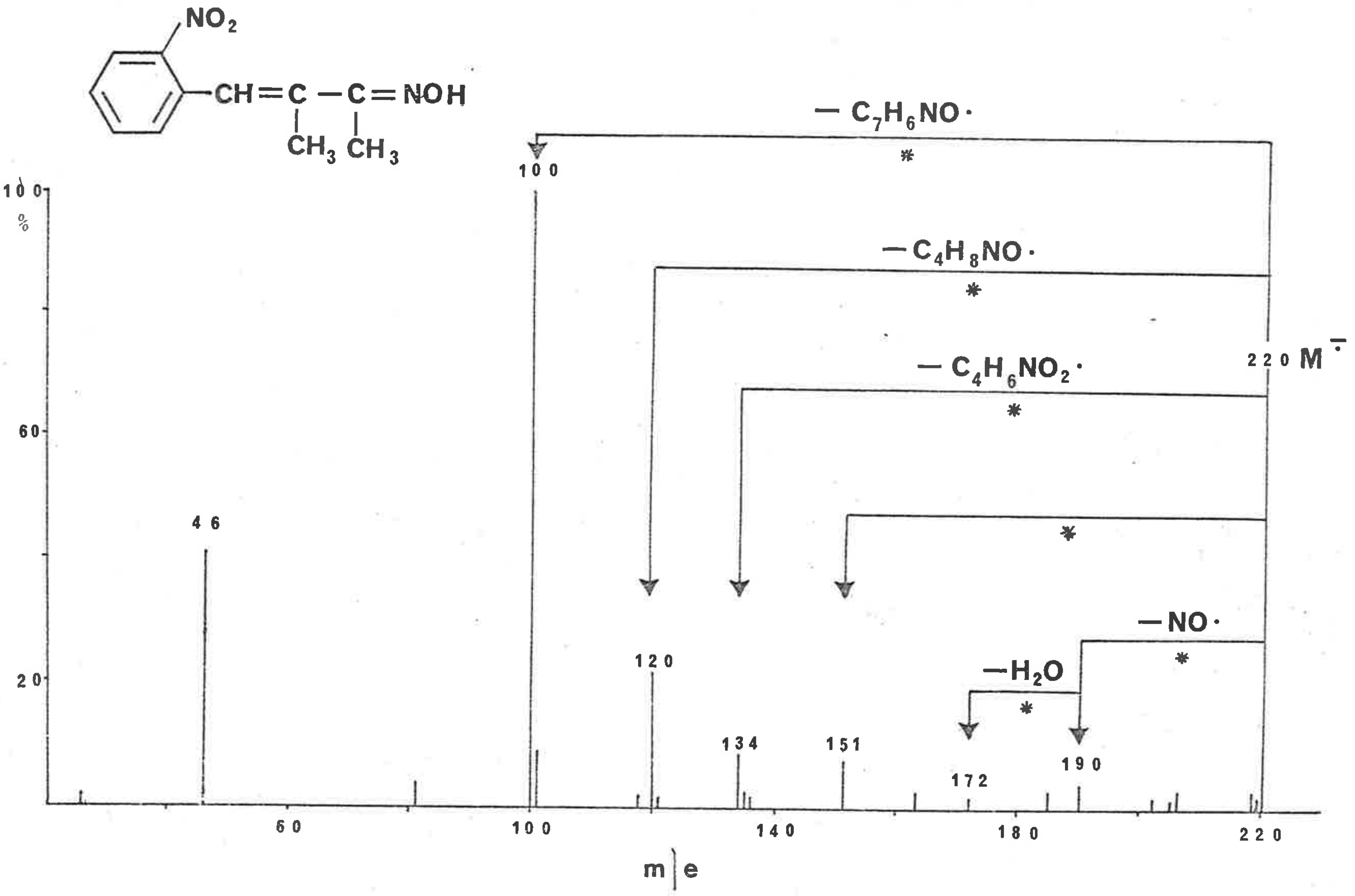

NO2
CH = C — CH = NOH
CH3
— C7H6NO·
— C3H4NO2·
— C3H6NO·
— H2NO2·
— CHNO·
— NO·
— H2O
206 M⁻·
100
%
60
20
26
46
86
120
134
158
163
176
188
60
100
140
180
220
m|e

FIGURE 5 – 8


NO2
CH=C–C=NOH
CH3 CH3
100 %
60
20
46
100
120
134
151
172
190
220 M
– C7H6NO·
– C4H8NO·
– C4H6NO2·
– NO·
– H2O
*
60
100
140
180
220
m/e

CHAPTER 6.

EXPERIMENTAL

Page

6.1 GENERAL

Conventional negative ion spectra were measured with a modified Perkin Elmer R.M.U. 7D mass spectrometer, operating at 70eV using source pressures of 1-2 x 10^{-6} Torr, and accelerating potential 3.6kV. Samples were introduced through the all glass inlet system at 150°C. Collision excitation spectra[94-95] were measured under identical conditions, except that collision gas (N_2) was introduced into the region before the electrostati sector through a separate inlet system until the pressure in that region was 3 x 10^{-5} Torr. The source and analyser regions were differentially pumped. All fragmentations were substantiated by metastable focussing and the negative i.k.e. technique.

The nuclear magnetic resonance spectra were measured with a Varian T60 Spectrometer, operating at 60MHz, using tetramethylsilane as the internal standard. The data are reported in the order: value, integral, multiplicity and assignment. Multiplicity in this text is expressed as follows: s, singlet; d, doublet and t for triplet, etc.,

Infrared spectra were recorded with a Perkin Elmer 337 grating Spectrometer or a Unicam SP 200 infrared spectrometer, using Nujol mulls for solids and liquid films for liquids.

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

Whatman sorbsil (for column chromatography) and Merck Kieselgel G and HF 254 (for thin layer chromatography) were used as adsorbents.

6.2 PART I, WORK DESCRIBED IN CHAPTER 2

o-Nitrobenzaldehyde and benzil were purified commercial products. The following compounds were synthesised by reported methods: o-diacetylbenzene (2)[219], m-diacetylbenzene (3)[220], p-diacetylbenzene (4)[221], 1,3,5-triacetylbenzene (5)[222], o-nitropropiophenone (6)[223-224], m-nitropropiophenone (8)[223-224], p-nitrophenyl β-phenylethyl ketone (10)[225], o-nitrobenzophenone (11)[226], m-nitrobenzophenone (12)[227], p-nitrobenzophenone (13)[228], o-nitrobenzil (15)[229], m-nitrobenzil (16)[230], p-nitrobenzil (17)[231], o-nitrobenzoyl acetyl methane (19)[232], m-nitrobenzoyl acetyl methane (20)[232], p-nitrobenzoyl acetyl methane (21)[232], o-nitrobenzoyl benzoyl methane (22)[233], m-nitrobenzoyl benzoyl methane (23)[234] and p-nitrobenzoyl benzoyl methane (24)[234].

o- and m- Nitrobutyrophenone [(7) and (9)]

Butyrophenone (15 g.) was added dropwise over a 30 minutes period to nitric acid (100 ml, d.1.5), maintained at -30°. After a further 10 minutes at -10°, the mixture was poured on to ice (500g), the crude solid filtered, and crystallized from ethanol giving m-nitrobutyrophenone [7.7g. (40% yield)] as colourless needles, m.p. 59-60° Found: C, 62.4; H, 5.8; N. 7.3%, $C_{10}H_{11}NO_3$ requires: C, 62.2; H. 5.7; N. 7.2%; I.R. ν_{co} = 1685cm^{-1}., N.M.R., ($CDCl_3$) δ 7.2-8.8 (4H, m, aryl); 3·1.

(2H, t, $-CO-\underline{CH_2}-CH_2-CH_3$); 1.83 (2H, sextet, $-CO-CH_2-\underline{CH_2}-CH_3$), 1.1 (3 H, t, $-CO-CH_2-CH_2-\underline{CH_3}$).

The filtrate was made alkaline with solid sodium carbonate, extracted with ether (100 ml), and the extract washed with aqueous sodium hydroxide (10%, 50 ml) and dried over anhydrous sodium sulphate. Evaporation of the solvent in vacuo, followed by distillation of the residue gave o-nitrobutyrophenone [3.0g., (15% yield)] as a colourless liquid, b.p.

118-122°/1 m.mHg. Found: C, 62.4; H, 5.8; N, 7.5%. $C_{10}H_{11}NO_3$ requires: C, 62.2; H, 5.7; N, 7.2%, I.R. ν_{CO} = 1700cm^{-1}, N.M.R: ($CDCl_3$)δ7.35-8.4 (4H, m, aryl), 2.78 (2H, t, CO-<u>CH</u>$_2$-CH_2-CH_3), 1.8 (2H sextet, CO-CH_2-<u>CH</u>$_2$-CH_3), 1.05 (3H, t, CO-CH_2-CH_2-<u>CH</u>$_3$).

p-Nitrobenzaldehyde -^{18}O (1)

p-Nitrobenzaldehyde -^{18}O (^{18}O = 12%) was prepared by allowing p-nitrobenzaldehyde (100 mg) to stir at 25° in dry dioxan (5 ml) containing $H_2{}^{18}O$ (^{18}O = 20%, 200 mg) and trifluoroacetic acid (1 drop) for two days. Removal of the solvent gave the labelled aldehyde (^{18}O = 12%).

Benzoyl (^{18}O) o-nitrophenyl ketone (18)

o-Nitrophenylacetyl chloride (1.84 g.) in dry dimethoxyethane (15 ml) was hydrolysed with $H_2{}^{18}O$ (^{18}O = 20%, 200mg) to give a quantitative yield of labelled o-nitrophenyl acetic acid (^{18}O = 10%), which was reconverted to the acid chloride with thionyl chloride.[235] Anhydrous aluminimum trichloride (3.0g) was added in portions to a solution of benzene (5 ml) and o-nitrophenylacetyl chloride (1.8g). The mixture was heated under reflux for 5 minutes, then cooled and poured into a mixture of ice (30g.) and concentrated hydrochloric acid (5 ml). The benzene layer was separated and the aqueous layer was extracted with a mixture of benzene (20 ml) and ether (20 ml). The combined extract was washed once with water (30 ml) and then dried over calcium chloride (10g). Evaporation the solvent gave the crude product which was crystallized from diethyl ether to yield o-nitrophenylacetophenone (1.6g, 65%). The ketone was oxidized[239] to produce benzil-^{18}O which was crystallized from ethanol as pale yellow needles (0.8g., 50%) m.p. 94-95° (^{18}O = 10%).

6.3 PART II Work described in Chapter 3

The following compounds were synthesized by reported methods: o-nitrobenzylacetone (29)[236], p-nitrobenzylacetone (30)[236], o-nitrobenzylacetophenone (31)[237], p-nitrobenzylacetophenone (32)[238], o-nitrophenylacetaldehyde (33)[239], o-nitrophenylethylene oxide (44)[204], o-nitrosobenzoyl carbinol (45)[204], methyl o-nitrosobenzoate (46)[240], ethyl o-nitrosobenzoate (47)[240], and benzyl o-nitrosobenzoate (48)[240].

o-Nitrophenylacetone (34)

o-Nitrophenylacetyl chloride (3.67g., 0.02 mole) was treated with ethoxy-magnesium diethyl malonate [from magnesium (0.48g.), diethyl malonate (3.2g.) and absolute ethanol (1.0g.)]. The reaction product was hydrolysed with dilute sulphuric acid and decarboxylated under the conditions used in the synthesis of o-nitroacetophenone.[241] Compound (34) was extracted with diethyl ether (2 x 50 ml) and dried over anhydrous sodium sulphate. Removal of the solvent, followed by vacuum distillation yielded (34) (b.p. 200^0 at 1.5mm Hg.) as a pale yellow oil (2.0g., 60%).

m Nitrophenylacetone (25)

This was prepared by the same method used for (34). m- Nitrophenylacetyl chloride (3.67g., 0.02 mole) was treated with ethoxy-magnesium diethyl malonate (3.2g.) and absolute ethanol (1.0g.). The crude product was purified by column chromatography, using sorbsil as an adsorbant and diethyl ether: petroleum ether (b.p. 40-60^0) (1:4) as an eluant. m-Nitrophenylacetone (2.2g., 70%) was obtained as a viscous pale yellow oil.[cf. 242]

p-Nitrophenylacetone (26)

This was prepared by the same method used for (34). p-Nitrophenylacetyl chloride (3.67g., 0.02 mole) was treated with ethoxymagnesium diethyl malonate (3.2g.) and absolute ethanol (1.0g.). The crude product was crystallized from diethyl ether to yield p-nitrophenylacetone (2.8g., 80%) as yellow needles,m.p. 63-64° (Lit.[242] 62°.)

o-Nitrophenylacetophenone (35)

Anhydrous aluminium trichloride (5.3g., 0.04 mole) was added in portions to a solution of benzene (15 ml) and o-nitrophenylacetyl chloride (6.0g., 0.03 mole). The mixture was heated under reflux for 15 minutes, then cooled and poured on-to a mixture of ice (100g.) and concentrated hydrochloric acid (15 ml). The benzene layer was separated and the aqueous layer was extracted with a mixture of benzene (25 ml) and diethyl ether (25 ml). The combined extract was washed once with water (50 ml) and then dried over calcium chloride (10g.). Evaporation of the solvent gave the crude product, which was crystallized from diethyl ether to yield o-nitrophenylacetophenone (5.1g., 65%), as pale brown needles, m.p. 73-74° (Lit.[243] 72-74°).

m-Nitrophenylacetophenone (27)

This was prepared by the procedure outlined above for o-nitrophenylacetophenone (35). Crystallization of the crude product from acetone gave (27) as pale yellow needles (83% yield) m.p. 81-82° (Lit.[244] 82°).

p-Nitrophenylacetophenone (28)

This was prepared by the procedure outlined above for o-nitrophenylacetophenone (35). The crude product was crystallized from ethanol as pale yellow needles (71% yield), m.p. 140-141° (Lit.[243] 138-140°).

α-(o-Nitrophenyl) ethyl p-anisyl ketone (36)

This was prepared by the method used for (35). Treatment of o-nitrophenylacetyl chloride (6.0g., 0.03 mole) in anisole (10 ml) with anhydrous aluminium trichloride (5.3g., 0.04 mole) gave a crude product which was crystallized from methanol to yield (36) as pale yellow needles (6.3g., 78%), m.p. 116-117°. Found: C, 66.2; H, 4.85; N, 5.15%; $C_{15}H_{13}O_4$ requires: C, 66.4; H, 4.8; N, 5.15%, I.R., ν_{CO} = 1680cm^{-1}; N.M.R.

($CDCl_3$), δ 6.83-8.24 (4H, m, aryl), 4.63 (2H, s, O_2N-C_6H_4-CH2-CO-), 3.86 (3H, s, OCH_3).

α-(o-Nitrophenyl) ethyl p-tolyl ketone (37)

This was prepared by the method used for (35). Treatment of o-nitrophenylacetyl chloride (6.0g., 0.03 mole) in toluene (10 ml) with anhydrous aluminium trichloride (5.3g., 0.004 mole) gave (37) which was crystallized from diethyl ether as yellow brown needles (5.9g., 77%), m.p. 77-78°. Found: C, 70.5; H, 5.4; N, 5.5%; $C_{15}H_{13}NO_4$ requires: C, 70.6; H, 5.1; N, 5.5%; I.R. ν_{CO} = 1680 cm^{-1}; N.M.R. δ ($CDCl_3$), 7.21-8.22 (4H, m, aryl), 4.64 (2H, s, O_2N-C_6H_4-CH2-CO-), 2.41 (3H, s, $-CH_3$).

α-(o-Nitrophenyl) ethyl m-nitrophenyl ketone (38)

o-Nitrophenylacetophenone (1.0g.) was added in portions, over a twenty minute period to fuming nitric acid (10 ml) maintained at -40°. The mixture was allowed to stand at -40° for an additional 15 minutes, poured into ice water (100 ml), and filtered. The crude product (0.8g.) was purified by thick layer chromatography on Kieselgel G/HF 254 using diethyl ether-light petroleum (30-40°) (3:7), yielding (38) (0.44g., 40%) which crystallized from chloroform as yellow needles, m.p. 154-156°. Found: C, 58.7; H, 3.7; N, 10.0%; $C_{14}H_{10}N_2O_5$ requires: C, 58.75; H, 3.5; N, 9.8%; I.R. ν_{CO} = 1680 cm^{-1}.

2-(o-Nitrophenyl) propiophenone (39)

A mixture of o-nitrophenylacetophenone (1.7g.) and sodium ethoxide (0.4g.) in absolute ethanol (20 ml) was allowed to stir at 25°C for 15 minutes. To the solution was added methyl iodide (1.0g.), the mixture was allowed to stir for an additional 15 minutes, then diluted with water (100 ml) and extracted with diethyl ether (3 x 20 ml). The ether extract was concentrated to yield a brown oil (1.9 g.) which was chromatographed on sorbsil using light petroleum (30-40°): diethyl ether

(9:1). Compound (39) was obtained as a viscous red brown liquid (1.2g., 60%), (n_D 1.5972 at 17.5°). Found: C, 70.65; H, 5.15; N, 5.35%; $C_{15}H_{13}NO_3$ requires: C, 70.6; H, 5.1; N, 5.5%; I.R. ν_{CO} = 1680 cm^{-1}, N.M.R., δ ($CDCl_3$), 7.0-8.4 (4H, m, aryl), 5.2-5.6 (H, q, O_2N-C_6H_4-<u>CH</u>(CH_3)-CO-, 1.5-1.7 (3H, d, O_2N-C_6H_4-CH(<u>CH_3</u>)-CO-).

LABELLED COMPOUNDS

2α-d_2-o-Nitrophenylacetophenone (41)

A solution of o-nitrophenylacetophenone (0.5g.) in methanol-O-$^2H_1$ (5 ml, 100% $^2H_1$) and deuterium oxide (5 ml, 100% $^2H_2$) containing a trace of sodium metal was allowed to reflux for six hours. Removal of the solvent yielded (41) [$^2H_0$= 25, $^2H_1$ = 50, $^2H_2$= 25%], m.p. 73-74°.

5α-d_5-o-Nitrophenylacetone (40)

The $^2H_1$ -labelled compound (40) was prepared by allowing (34) to react with methanol-O-$^2H_1$ (5 ml, $^2H_1$ = 100%), containing a trace of sodium methoxide, under reflux for 30 minutes. Removal of the solvent gave (40) [$^2H_1$ = 2, $^2H_2$= 10, $^2H_3$= 32, $^2H_4$ = 35, $^2H_5$ = 29%].

o-Nitrophenylacetophenone-^{18}O (42)

Hydrolysis of o-nitrophenylacetyl chloride (1.84g.) in dry dimethoxy ethane (15 ml) with $H_2{}^{18}O$ (^{18}O = 20%, 200 mg), gave a quantitative yield of labelled o-nitrophenylacetic acid, which was reconverted to the acid chloride with thionyl chloride.[235] The Friedel-Crafts reaction[245] between the acid chloride and benzene gave (42) (1.6g., 65%) (^{18}O = 10%), m.p. 73-74°.

o-Nitrophenylacetophenone-α ^{13}C (43)

Benzyl chloride (1.27g.) was allowed to react[246] with $Na^{13}CN$ (0.5g., ^{13}C = 65.4%) in dimethylsulphoxide (5 ml) at room temperature to yield the labelled benzyl cyanide (1.0g., 90%) (^{13}C = 65.4%), which was converted to phenylacetic acid by hydrolysis[247] with diluted sulphuric acid. The acid (0.8g.) was converted to the acid chloride using thionyl chloride[235]. The crude acid chloride was allowed to condense with benzene by the Friedel -Craft reaction[245] to yield the labelled desoxybenzoin (1.1g., 80%) which was nitrated[243] at room temperature. The resulting solid (1.2g.) was extracted with cold diethyl ether (25 ml), the o-nitro compound dissolving, and the p-nitro compound remaining. The o-derivative (43) was purified by crystallization first from benzene-light petroleum (b.p. 60-80°) (1:1) and then from ethanol, to yield pale yellow needles (0.5g., 42%), m.p. 72-74° (^{13}C = 65.4%).

6.4 PART III Work described in Chapter 4

The following compounds were prepared by reported procedures: o-nitrocinnamaldehyde (49)[248], α-methyl o-nitrocinnamaldehyde (50)[249], m-nitrocinnamaldehyde (51)[250], p-nitrocinnamaldehyde (52)[251], o-nitrobenzylideneacetone (53)[252], α-methyl o-nitrobenzylidene-acetone (54)[249], m-nitrobenzylideneacetone (55)[252], p-nitrobenzylideneactone (56)[252], 1-o-nitrophenyl-3-p-tolyl propenone-3 (58)[253], 4-nitrochalcone (60)[254], m-nitrocinnamylideneacetaldehyde (68)[255], m-nitrocinnamylideneacetone (71)[256], p-nitrocinnamylideneacetone (72)[256], m-nitrocinnamylideneacetophenone (76)[257], and p-nitrocinnamylideneacetophenone (77)[257].

2-Nitrochalcone (57)

A solution of o-nitrobenzaldehyde (3.02g., 0.02 mole) and acetophenone (2.4g., 0.02 mole) in acetic acid (50 ml) containing concentrated sulphuric acid (7.5g., 0.08 mole) was allowed to stir for 24 hours at room temperature. The reaction mixture was diluted with water (100 ml) and neutralized with sodium carbonate. The crude product was filtered and then crystallized from methanol as pale yellow needles (4.0 g., 80%), m.p. 125-126° (Lit.[258] 125°).

3-Nitrochalcone (59)

This was prepared by the same method used for (57). Treatment of m-nitrobenzaldehyde (3.02g., 0.02 mole) and acetophenone (2.4g., 0.02 mole) in acetic acid (50 ml) containing concentrated sulphuric acid (7.5g., 0.08 mol gave (59) which crystallized from ethanol as pale yellow needles (4.0g., 80%) m.p. 145-146° (Lit.[259] 145-146°).

o-Nitrocinnamylacrolein (67)

A solution of formylmethylenetriphenylphosphorane[260] (0.610g., 0.002 mole) and o-nitrocinnamaldehyde (0.354g., 0.002 mole) in dry benzene (20 ml) was heated under reflux for 25 hours. The solvent was removed, the residue adsorbed from dichloromethane solution on-to silica gel and then chromatographed over silica gel using ethyl acetate - light petroleum ether (5-20%) as eluant, to yield (67) which crystallized from ethyl acetate as yellow needles (0.24g., 60%), m.p. 152-153° (Lit.[255] 153-154°) .

o-Nitrocinnamylideneacetone (70)

A solution of triphenylphosphineacetylmethylene[261] (0.638g.) and o-nitrocinnamaldehyde (0.354g.) in tetrahydrofuran (25 ml) was heated under reflux for 24 hours. The solvent was removed, the residue was pre-adsorbed from dichloromethane solution on-to silica gel and chromatographed over silica gel using ethyl acetate-light petroleum 5-20% as eluant. Compound (70) (0.25g., 60%) crystallized from ethyl acetate as pale yellow needles m.p. 72-73° (Lit.[262] 73.5°).

o-Nitrocinnamylideneacetophenone (73)

This was prepared by the same method as used for (67) using triphenylphosphinebenzoyl methylene[261] (0.762g.) and o-nitrocinnamaldehyde (0.354g.). Compound (73) (0.375g., 65%) crystallized from ethyl acetate as pale yellow needles, m.p. 138-139° (Lit.[263] 139°).

1-(2-Nitrophenyl)-5-(4-tolyl)penta-1,3-dien -5-one (74)

To a mixture of o-nitrocinnamaldehyde (0.8g.) and p-methylacetophenone (0.8g.) in ethanol (25 ml) was added aqueous sodium hydroxide (10%) dropwise until the colour changed from yellow to dark brown. The mixture was then allowed to stand at 20° for 8 hours, the product (82) (0.7g., 60%) filtered off and crystallized from ethanol as yellow needles, m.p. 118-119°. Found: C, 73.86; H, 5.29; N, 4.41%; $C_{18}H_{15}NO_3$ requires: C, 73.7; H, 5.2; N, 4.8%; I.R., ν_{CO} = 1655 cm^{-1}, N.M.R.,($CDCl_3$) δ 6.95-7.95 [8H and 4H, m, aryl, $-(\underline{CH=CH})_2-$], 2.22 (3H, s, $-\underline{CH}_3$).

1-(2-Nitrophenyl) octa-1,3,5-trien -7-one (77)

This was prepared from 5-(2-nitrophenyl) penta-2,4-dienal (67) (0.40g.) and acetone (1.0 ml) by the method outlined above for (74). The product was crystallized from ethanol as yellow needles (0.34g., 70%), m.p. 112-113°. Found: C,69.0; H, 5.5; N, 5.5%; $C_{14}H_{13}NO_3$ requires: C, 69.1; H, 5.4; N, 5.8%; I.R. ν_{CO} = 1680 cm^{-1}.

o-Carboxybenzalacetophenone (79)

A solution of triphenylphosphinebenzoylmethylene [261] (1.2g.) and o-phthaladehydric acid (0.5g.) in dry benzene (50 ml), under nitrogen, was heated under reflux for 24 hours. Removal of the solvent, followed by extraction of the residue with diethyl ether (2 x 50 ml), and removal of the ether solvent, gave the crude product, which was purified over sorbsil, using diethyl ether: light petroleum (1:4) as eluant. (79) was crystallized from this solvent as colourless needles, m.p. 140-141°, (yield 0.50g., 61%) Found: C, 76.6; H, 4.8%; $C_{16}H_{12}O_3$ requires: C, 76.2; H, 4.8%.

LABELLED COMPOUNDS

A. ^{18}O-Labelled Compounds

o-Nitrocinnamaldehyde-^{18}O (65)

A solution of o-nitrocinnamaldehyde (50 mg) in dry dioxan (2 ml) containing $H_2{}^{18}O$ (^{18}O=24.2%, 25 mg.) and trifluoracetic acid (1 drop) was allowed to stir at 25° for 48 hours. Removal of the solvent *in vacuo* yielded (65) (50 mg., ^{18}O = 12%) which crystallized from ethanol as yellow needles, m.p. 126-127°.

o-Nitrobenzalacetophenone-^{18}O (66)

Treatment of o-nitrocinnamoyl chloride (200 mg.) with $H_2{}^{18}O$ (50 mg., ^{18}O = 24.2%) in dry dimethoxyethane (5 ml) gave the labelled o-nitrocinnamic acid (180 mg.), which was reconverted to the labelled acid chloride (190 mg., ^{18}O = 12.1%) using thionyl chloride[235]. The Friedel-Crafts reaction[245] between the acid chloride and benzene yielded (66) [175 mg.,(75%), ^{18}O = 12.1%] which crystallized from ethanol as yellow needles m.p. 124-125°.

1-(2-Nitrophenyl)-5-phenylpenta-1,3-dien -5-one-^{18}O (78)

Ethyl β-(2-nitrostyryl) acrylate was prepared as for (67), using ethoxycarbonylmethylidenetriphenylphosphorane[264] (1.585g., 0.005 mole) and o-nitrocinnamaldehyde (0.895g., 0.005 mole). β-[2-Nitrostyryl] acrylic acid was obtained by hydrolysis[265] of the ester product in 85% yield. Compound (78) (^{18}O = 12.1%)was then prepared by the method used for (66). Treatment of β-[2-nitrostyryl] acrylic acid chloride (0.88g.) with $H_2{}^{18}O$ (0.25g.,^{18}O = 24.2%) in dry dimethoxyethane (15 ml) gave the labelled β-[2-nitrostyryl] acrylic acid in a quantitative yield, which was reconverted to the labelled acid chloride using thionyl chloride[235]. The Friedel-Crafts reaction[245] between the acid chloride (0.8g., ^{18}O = 12.1%) and benzene yielded (78) which was crystallized from ethanol as yellow needles (1.0g., 75%), m.p. 140-141° (^{18}O = 12.2%).

B. ^{2}H-Labelled Compounds

1-(2-Nitrophenyl) prop-1-en-3al-1-$^{2}H_1$ (61)

A solution of benzaldehyde-α-$^{2}H_1$[266] (0.65g., $^{2}H_1$ = 100%) and formylmethylenetriphenylphosphorane[260] (2.0g.) in dry benzene (50 ml) was heated under reflux for 24 hours. Removal of the solvent, followed by extraction of the residue with diethyl ether (2 x 25 ml) gave the labelled cinnamaldehyde (0.7g., 53%) which was nitrated[248] to yield (61) (0.4g., 45%), which crystallized from ethanol as yellow needles, m.p. 126-127° ($^{2}H_1$ = 100%).

1-(2-Nitrophenyl)prop-1-en-3-al-3-$^2H_1$ (62)

Cinnamaldehyde-α-$^2H_1$ was prepared from the dithiane by the same method [266] as that used for benzaldehyde-α-$^2H_1$. Nitration[248] gave (62) (40% yield), which crystallized from ethanol as yellow needles, m.p. 126-127° ($^2H_1$ = 100%).

1-(2-Nitrophenyl)-3-phenylprop-1-en-3-one-1-$^2H_1$ (63)

Benzaldehyde-α-$^2H_1$ [266] (1.7g.) was converted to the labelled cinnamic acid [267] which was nitrated [248] by the same method used for cinnamaldehyde, to yield the labelled o-nitrocinnamic acid (2.2g., 72% yield). The Friedel-Crafts reaction[245] between the acid chloride and benzene yielded (63) (2.2g., 75% yield), which crystallized from ethanol as pale yellow needles, m.p. 123-124° ($^2H_1$ = 100%).

1-(2-Nitrophenyl)-3-phenylprop-1-en-3-one-2-$^2H_1$ (64)

This was prepared by the same method [254] used for chalcone. Treatment of o-nitrobenzaldehyde (1.5g., 0.01 mole) and methyl ($^2H_3$) phenyl ketone [268] (1.2g., $^2H_3$ = 68%) gave (64) (2.1g., 80%) which was crystallized from ethanol as pale yellow needles, m.p. 124-125° ($^2H_0$ = 32, $^2H_1$ = 68%).

6.5 PART IV Work described in Chapter 5

The following compounds were synthesized by reported methods: isonitrosoacetophenone (80)[269], isonitrosopropiophenone (81)[270], α-benzilmonoxime (82)[271], β-benzilmonoxime (83)[271], *p*-nitrobenzaldehyde oxime (89)[272], *m*-nitrobenzaldehyde oxime (90)[272], *o*-nitrobenzaldehyde oxime (91)[272], *p*-nitroacetophenone oxime (92)[273], *m*-nitroacetophenone oxime (93)[274], *o*-nitroacetophenone oxime (94)[273], *p*-nitrobenzophenone oxime (95)[275], *m*-nitrobenzophenone oxime (96)[275], *p*-nitrobenzophenone-d_5 oxime (98)[276], *p*-nitrophenylacetone oxime (99)[277], *o*-nitrophenylacetone oxime (100)[278], *p*-nitrophenylacetophenone oxime (101)[229], *p*-nitrobenzylacetone oxime (103)[236], *o*-nitrobenzylacetone oxime (104)[236], *o*-nitrocinnamaldehyde oxime (108)[279], *m*-nitrocinnamaldehyde (109)[279], and α-methyl *o*-nitrocinnamaldehyde oxime (110)[219].

p-Nitrobenzylacetophenone oxime (105)

p-Nitrobenzylacetophenone (0.6g.) was prepared by the reported method[238] and was converted to compound (105) using hydroxylamine hydrochloride[280]. The crude product was crystallized from ethanol as pale yellow needles (0.56g., 86%), m.p. 130-131°. Found: C, 66.67; H, 5.19; N, 10.42%; $C_{15}H_{14}N_2O_3$ requires: C, 66.65; H, 5.22; N, 10.37%.

o-Nitrobenzylacetophenone oxime (106)

o-Nitrobenzylacetophenone (0.6g.)[237] was converted to compound (106) by the standard method[280]. Crystallization of the crude product from ethanol gave (106) (0.51g., 81%) as pale yellow needles, m.p. 125-126° Found: C, 66.64; H, 5.22; N, 10.37%; $C_{15}H_{14}N_2O_3$ requires: C, 66.65; H, 5.22; N, 10.37%.

o-Nitrocinnamyl methyl ketone oxime (111)

o-Nitrocinnamyl methyl ketone (1.0g.)[252] was converted to compound (111) by the standard method[280]. The crude product was crystallized from ethanol to yield (111) (0.98g., 85%) as pale yellow needles, m.p. 160-161°. Found: C, 58.10; H, 4.95; N, 13.69%; $C_{10}H_{10}N_2O_3$ requires: C, 58.25; H, 4.89; N, 13.58%.

α-Methyl o-nitrocinnamyl methyl ketone oxime (112)

α-Methyl o-nitrocinnamyl methyl ketone (1.0g.)[249] was converted to compound (112) by the standard method [280]. The product was crystallized from ethanol as yellow needles (0.9g., 80%), m.p. 153-154°. Found: C, 59.96; H, 5.48; N, 12.95; $C_{11}H_{12}N_2O_3$ requires: C, 59.99; H, 5.49; N, 12.95%.

p-Nitrocinnamyl methyl ketone oxime (113)

p-Nitrocinnamyl methyl ketone (1.0g.)[252] was converted to compound (113) by the standard method[280]. The product was crystallized from ethanol as pale yellow needles (1.0g., 86%), m.p. 199-200°. Found: C, 58.36; H, 4.87; N, 13.55%; $C_{10}H_{10}N_2O_3$ requires: C, 58.25; H, 4.89; N, 13.58%.

LABELLED COMPOUNDS

Isonitrosoacetophenone-d_5 (84)

Acetophenone-d_5($^2H_5$= 100%) was prepared in 40% yield from bromobenzene-d_5 (0.01 mole), magnesium turnings (0.01 mole) and acetonitrile (0.009 mole)[281]. Acetophenone-d_5 was allowed to react with isoamylnitrite (2.0g.) and dry hydrogen chloride gas[269] to yield isonitrosoacetophenone-d_5 (0.4g., 26%) ($^2H_1$ = 100%) which crystallized from ethanol as pale pink needles, m.p. 127-128°.

Isonitrosopropiophenone-d_5 (85)

Propiophenone-d_5 ($^2H_5$ = 100%) was prepared in 80% yield from bromobenzene-d_5 (0.01 mole), magnesium turnings (0.01 mole) and propionitrile (0.009 mole).[281] Propiophenone-d_5 was allowed to react with isoamylnitrite (2.0g) and dry hydrogen chloride gas[270] to yield isonitrosopropiophenone-d_5 (0.6g., 38% yield), which crystallized from ethanol as a colourless powder, m.p. 113-114°. ($^2H_5$ = 100%).

α-Benzilmonoxime-d_5 (86)

Benzoic acid-d_5 ($^2H_5$ = 100%) was prepared in 85% yield from brom obenzene-d_5 (0.03 mole), magnesium turnings (0.03 mole) in diethyl ether (50 ml) followed by addition of solid carbon dioxide.[282] Benzoic acid-d_5 was converted to benzoyl chloride-d_5 in quantitative yield by reaction with thionyl chloride.[235] Benzoyl chloride was then converted to benzamide-d_5 in 80% yield by reaction with concentrated ammonia solution.[283] The reaction[284] between benzamide-d_5 (1.89g., 0.015 mole) and benzyl magnesium chloride (0.06 mole) yielded desoxybenzoin-d_5 (1.6g., 76%) which crystallized from diethyl ether as pale yellow needles, m.p. 55-56°. A solution of dry ethanol (15 ml) containing sodium metal (0.23g.) was added to a solution of desoxybenzoin-d_5 (0.5g.), isoamylnitrite (1.0g.) and dry ethanol (15 ml), and the mixture was allowed to stir at room temperature for six hours. Diethyl ether (50 ml) was added to the reaction mixture which was then extracted with aqueous sodium hydroxide (2%, 2 x 25 ml). The combined sodium hydroxide extract was acidified with hydrochloric acid (10%) and extracted with diethyl ether (2 x 30 ml) to yield the crude oxime, which was purified by thick layer chromatography on Kieselgel G/HF 254, using diethyl ether: petroleum ether (30-40°) (4:6) as eluant. α-Benzilmonoxime-d_5 which crystallized from diethyl ether as pale yellow needles (0.4g., 71%) m.p. 137-138° ($^2H_5$ = 100%).

β-Benzilmonoxime-d_5 (87)

Activated charcoal (0.2g.) was added to a refluxing solution of α-benzilmonoxime-d_5 (0.4g.) and dry benzene (10 ml). The solution was filtered to yield the β-isomer (87) (0.16g., 80%) which crystallized from benzene as pale yellow needles m.p. 111-112^0 ($^2H_5$ = 100%).

α-Benzilmonoxime-2,4,6-d_3 (88)

Aniline was treated [285] with deuterium oxide to yield aniline-2,4,6-d_3 ($^2H_2$ = 3, $^2H_3$ = 97%) in quantitative yield, which was converted to benzonitrile-2,4,6-d_3 (65% yield) using the Sandmeyer reaction[286]. Hydrolysis[287] of benzonitrile-2,4,6-d_3 gave benzamide-2,4,6,-d_3 (50% yield), which was converted [284] into desoxybenzoin-2,4,6-d_3, and then to α-benzilmonoxime-2,4,6-d_3 as described above for (86). α-Benzilmonoxime-2,4,6-d_3 crystallized from diethyl ether as pale yellow needles, m.p. 137-138^0 (overall yield from benzamide-2,4,6-d_3 = 70%).

m-Nitrobenzaldehyde-α-d_1 oxime (97)

Nitration[288] of benzaldehyde-α-d_1[266] gave m-nitrobenzaldehyde-α-d_1 in 82% yield, which was converted to the labelled oxime (97) by treatment with hydroxylamine hydrochloride [280] (yield 76%). m-Nitrobenzaldehyde-α-d_1-oxime (97) crystallized from ethanol as yellow needles, m.p.120-121^0 ($^2H_1$ = 100%).

o-Nitrocinnamaldehyde-α-$^2H_1$ oxime (114)

Cinnamaldehyde-α-$^2H_1$ was prepared from the dithiane in 78% yield by the same method [266] as that used for benzaldehyde-α-$^2H_1$ (40% yield), which was converted to the oxime (114) with hydroxylamine hydrochloride.[280] The crude product was crystallized from ethanol to yield (114) as pale yellow needles, m.p. 140-141^0 ($^2H_1$ = 100%), (85% yield).

p- Nitrobenzyl phenyl - d_5 ketone oxime (107)

p-Nitrobenzyl phenyl - d_5 ketone was prepared by the Friedel-Crafts reaction[245], using p-nitrophenylacetyl chloride (0.6g., 0.003 mole), benzene - d_6 (0.3g., 0.003 mole) and anhydrous aluminium trichloride (0.6g., 0.004 mole). The crude produce was crystallized from ethanol as pale yellow needles (71% yield), m.p. 140-141°. The ketone was converted to the oxime (107) with hydroxylamine hydrochloride.[280] The crude produce was crystallized from ethanol to yield (107) as pale yellow needles m.p. 105-106°.

[$^2H_2$ = 12, $^2H_3$= 33, $^2H_4$= 37, $^2H_5$ = 18%].

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