SOME REARRANGEMENT REACTIONS IN NEGATIVE ION MASS SPECTROMETRY

A THESIS

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CONTENTS

Summary

The purpose of this work is to investigate the occurrence and mechanisms of particular rearrangement reactions in negative-ion mass spectrometry. This work is divided into three sections.

In Chapter 2, the first examples of the retro-Diels-Alder reaction occurring from negative-ions for nitrochromans, nitro-1,3-benzodioxans and nitro-1,4-benzodioxans are described. The extent of the retro reaction in the nitrochromans and nitro-1,3-benzodioxans is dependent upon the position of the nitro group relative to the oxygenated ring. Mechanisms of this reaction are discussed in the light of results from labelling studies, use of model compounds and collision-induced dissociation investigations.

Chapter 3 deals with the proximity effects of salicylates and anthranilates. The molecular anions of methyl and phenyl 5-nitro-salicylates and 4-nitroanthranilates eliminate ROH (R = Me or Ph) by an ortho rearrangement. The molecular anions of phenyl 3-hydroxy-5-nitrobenzoate and phenyl 3-amino-5-nitrobenzoate lose PhOH to a lesser extent, and collision excitation studies indicate the operation of simultaneous two-stage cleavage reactions. The competitive ortho effects observed when the nitro group is adjacent to either the ester or hydroxyl functions are described.

Chapter 4 describes the unimolecular decompositions of nitrophenyl-1,3-oxathianes. These compounds give intense molecular anions which undergo both simple and complex cleavage processes. Evidence is presented which suggests that the decomposing molecular anions have low internal energies. The spectra contain an unusual scrambling process for the p-nitro isomer and a characteristic proximity effect for the o-nitro isomer. In contrast, the isomeric nitrophenyl-1,3-dioxans give similar spectra and show no hydrogen scrambling or proximity effects.

Statement

Except where due reference is made in the text, the material contained in this thesis has neither been submitted for a degree in any university nor to the best of my knowledge or belief previously been published or written by another person.

A. C. HO

Acknowledgements

I thank Dr. J.H. Bowie for his encouragement and guidance throughout the course of this work. I am indebted to Mr. T. Blumenthal for his assistance with the recordings of mass spectra. I also extend my thanks to my colleagues and other members of the department for their discussions and criticisms.

Finally, I wish to thank the University of Adelaide who saw fit to extend a research grant to make possible this work.

Publications

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

1) "Negative-ion mass spectra of 2-aryl-1,3-oxathianes and 1,3-dioxans", J.H. Bowie and A.C. Ho, Aust.J.Chem., 1973, 26, 2009.

2) "Proximity Effects in the Negative-ion Spectra of Salicylates and Anthranilates", J.H. Bowie and A.C. Ho, Org.Mass Spectrom., 1974, 10, 1009.

3) "The Retro-Diels-Alder reaction in Negative-ion Mass Spectrometry", J.H. Bowie and A.C. Ho., J.Chem.Soc. Perkin II, in press.

Chapter 1. Introduction

1.1 General

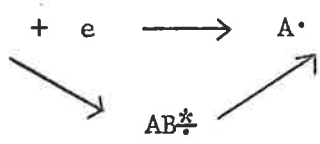
The conception of negative ions dates back to the ionic theory of electrolysis.[1] This theory explains how the charge is carried by particles of molecular mass in solution. It was shown subsequently that this theory can also be applied to the gas phase.[2] However the properties of negatively charged entities were not investigated prior to 1900 because of a lack of appropriate equipment. It was not until 1910 that J.J. Thomson[3] was able to identify negatively charged molecules using the mass spectrograph.

Negative ions may be produced by many different processes.[4] This thesis is concerned with the formation of negative ions by electron impact.

1.2 The mechanisms and Energetics of Negative-Ion Formation

There are basically two ways in which negative ions may be produced by the interaction of electrons with neutral molecules.[5] The former involves an electron capture process, while the latter is a collision or non-capture process. The more important processes are listed below.

i) Dissociative Resonance Capture



ii) Electron Resonance Capture

$$AB + e \longrightarrow AB^{\cdot -} \qquad (2\text{-}10 \text{ ev})$$

iii) Ion-Pair Production

$$AB + e \longrightarrow A^{+} + B^{-} + e \qquad (>15 \text{ ev})$$

1.2.1 Electron Capture Processes

The simplest way of producing a negative ion is by the direct capture of a low-energy electron. If such an electron is captured by a neutral molecule a transition can be regarded as taking place between two electronic levels of the negative molecular ion. In the initial state the extra electron occupies an unbound orbital and hence the potential energy curve is simply that of the neutral molecule. The nature of the negative ion formed, depends upon the position and shape of the electronic state of the negative molecular ion. In other words it depends

upon the shape and position of the upper potential energy curve. Possible cases for a diatomic molecule AB, are considered in the following potential energy diagrams (see figs. 1a, 1b and 1c).

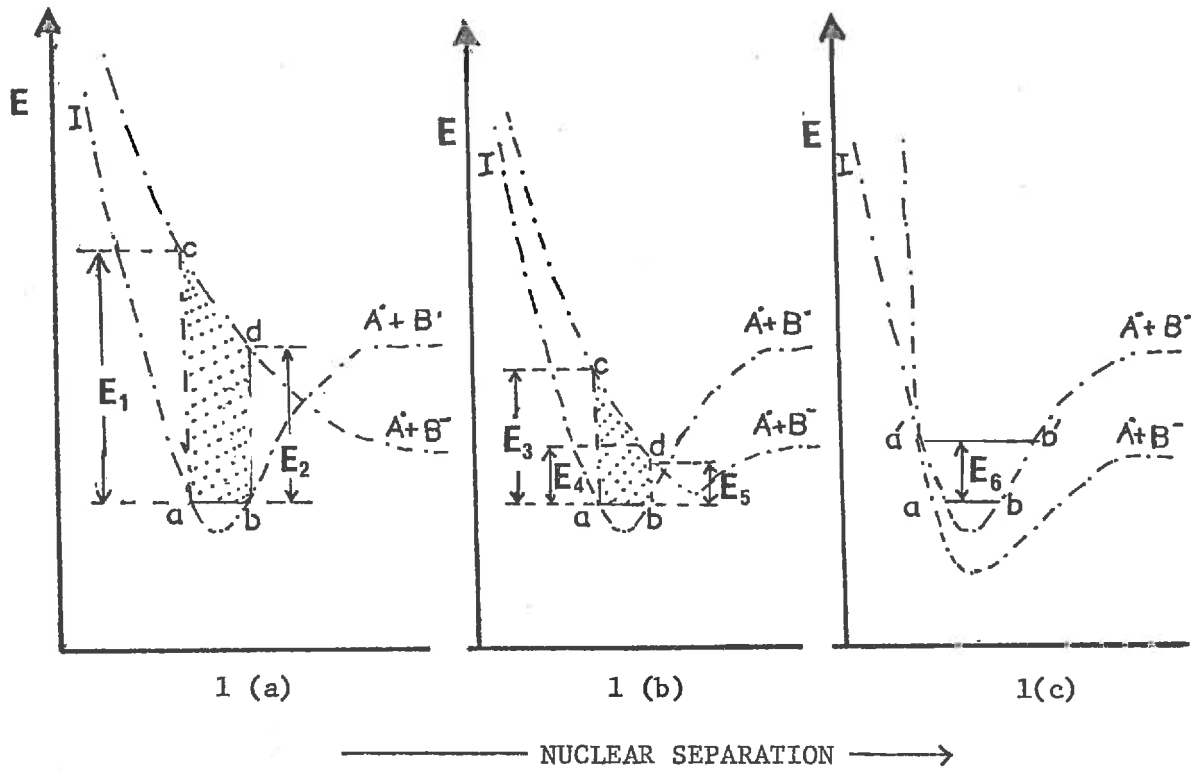


Fig. 1a, 1b, 1c. Potential Energy Curves for Negative Ion Formation by Capture Processes.

Electronic Transitions Region

In all three cases, curve I is the potential energy curve of the initial state of the neutral molecule, while the second curve represents that of the negative molecular ion. The nuclear separation in the ground vibrational level will lie effectively between the limits a and b in all cases. Applying the Franck-Condon principle,[6] which states that the electronic transition is much faster than the vibration of the atomic nuclei, the nuclear separation must still lie within these limits after the transition. The transitions will be confined within the shaded areas a b c d. The final state will therefore be confined to the region c and d.

In case (1a), the upper potential energy curve shows a repulsive situation. Hence the negative ion state will lie within the continuum of nuclear levels. In addition, the final state will have an energy in excess of that expected at infinite nuclear separation. If a molecule AB captures an electron into this state, it can dissociate into $A^{\cdot} + B^{-}$. The Franck-Condon principle predicts that the capture process will occur between the electron energy range of E_1 and E_2. The transitory molecular anion formed can dissociate into fragment ions ($A^{\cdot} + B^{-}$), or revert back to the neutral molecule by ejecting the captured electron. The latter process is generally referred to as autodetachment.[7] The fate of the molecular anion will therefore depend upon the relative rates of dissociation and autodetachment.

In case (1b), the energies of some of the possible states of the molecular anion are less than that at infinite separation. If a molecule captures an electron with an energy between E_3 and E_4, then the molecular anion will have the properties as those outlined above for case (1a). On the other hand, capture of an electron with an energy between E_4 and E_5 will produce a vibrationally excited molecular anion. This molecular anion is unstable, and will undergo autodetachment unless it can release its excess energy by either radiative emission or collision stabilisation.[7]

Case (1c) is not a Franck-Condon process as the potential energy curve AB^{-} does not cross the Franck-Condon region. This process will occur only if the neutral molecule is first excited to a vibrational level (a'b') where the probability of electron capture is high. It can be visualised as the electron first exciting the molecule to the appropriate state and then being captured. The fate of the vibrationally excited molecular anion is similar to that described for case (1b).

1.2.2 Summary

Case (1a). Diatomic molecule (AB) with Repulsive States

Electrons with energies (2-10 ev) between E_1 and E_2 are captured

and dissociation may follow. No stable molecular species $AB^{-\cdot}$ can be formed.

Case (1b). Diatomic molecule (AB) with Attractive and Repulsive States.

Electrons with energies (2-10 ev) between E_3 and E_4 are captured to give $AB^{*-\cdot}$ as for (1a). Capture of electrons with energies (0-2 ev) between E_4 and E_5 will give vibrationally excited $AB^{*-\cdot}$ Stable $AB^{-\cdot}$ can be formed if excess energy can be released.

Case (1c). Diatomic Molecule (AB) with Attractive and Repulsive States.

Electrons with energies (0-2 ev) around E_6 will be captured to form $AB^{*-\cdot}$. Its fate is similar to (1b).

1.2.3 Ion-Pair Production

This is a non-capture process. The electron provides the energy necessary for the electronic transition to occur. The excited molecule (AB*) formed may undergo spontaneous dissociation into $A^+ + B^-$.

This process is expected to occur at high electron energies (>15 ev). The probability of the operation of this process generally

increases with increasing electron energy.

1.2.4 Negative-Ion Formation by Secondary Electrons

Negative molecular ions may be formed by capture of secondary electrons[8-11] (analogous to section 1.2.1). The secondary electron is a de-energized electron produced from the electrode surfaces or by one of the processes shown;

1) Excitation of a molecule above its ground state

$$AB + ep \longrightarrow AB^* + es$$

2) Autoionisation

$$AB + ep \longrightarrow AB^{**} \longrightarrow AB^* + es$$

3) Positive ionisation

$$AB + ep \longrightarrow AB^{+\cdot} + 2es$$

where ep and es are primary and secondary electrons respectively.

2. Complications in Negative-Ion Studies

In principle, mass spectrometry offers an ideal method for the study of negative ions, since all ions formed in a particular system may be readily identified. In addition, the properties of these ions can be examined over a range of electron energies. There are, however, a variety of problems associated with the formation and detection of negative ions. These problems are outlined in detail below.

2.1 Control of the Ionising-electron Beam Current

When examining ionisation processes, it is desirable to either maintain a constant number of electrons or make corrections for any necessary variations. The number of electrons in the beam is indicated by the electron trap current. Thynne et al[12] have shown that the electron trap current varies with electron energy using the Bendix model 3015 time-of-flight mass spectrometer. It is desirable therefore either to have some method of regulating the trap current, or alternatively to have a knowledge of the variation of ion current with trap current.

2.2 Appearance Potential Measurements

The ionising electrons should be as homogeneous in energy as possible if reliable appearance potential data are to be obtained and if fine structure in the ionisation efficiency curves is to be seen. In mass spectrometric studies, the source of electrons is generally a heated filament and the emitted electrons consequently have appreciable thermal energies with a spread of 1-2 ev.[13] Clearly some method which allows the selection of a narrow band of energies is required.

One of the most widely used methods is the retarding potential difference (RPD) technique devised by Fox.[14] This method has been used successfully in positive-ion studies. Thynne et al[13] have applied this method with success in negative-ion studies. However the method leads to a reduction in the electron beam intensity and therefore the ion current. This is particularly important in view of the relatively low abundance of some negative ions formed upon electron impact. As a consequence, analytical methods which utilise the full electron distribution are normally reported. Such methods include i) the deconvolution process, introduced by Morrison[15] for positive-ion studies, which has been applied by Thynne et al[16,17] to studies of negative ions, and ii) the electron distribution

difference method,[18] an analytical technique which allows for the effect of a broad energy spread.

2.3 Intensity

Many negative ions are produced upon electron impact in much lower yields than the corresponding positive ions (often 10^3 times less than positive ions[19]). The low yields are claimed[19] to make detection difficult. Furthermore, metastable ions, which are produced in very low abundance, will be harder to detect than conventional negative ions.

The intensity problem may be overcome either by improving the detection sensitivity of the spectrometer, or alternatively by increasing the abundance of negative ions by some suitable method. The use of the electron multiplier detector in positive ions usually increases the detection sensitivity by several thousand fold over conventional electrometer techniques.[20] However its use for negative-ion detection does not necessarily increase the detection sensitivity, because the first dynode of the electron multiplier is maintained at a high negative potential and hence repels negative ions.[20] As a consequence, the negative-ion accelerating potential must be maintained at a higher value than that of the first dynode of the electron multiplier.

The abundances of some negative ions may be increased by an increase in the source pressure.[19] This technique requires the use of special high pressure sources which are generally not available in conventional mass spectrometers. von Ardenne and co-workers[21] have developed a high pressure method for producing slow electrons by low voltage discharge in Argon at a pressure of about 10^{-2} Torr. The applications of this technique are described in Sections 3.2 and 4.10.

2.4 The Modes of Negative-Ion Formation

The various modes of negative-ion formation (Section 1) are not well understood for polyatomic molecules. It has been shown[22-26] that these modes of formation depend markedly upon both electron energy and source pressures.

Variation of the electron-beam energy may cause the modes of formation to change. This is reflected in the relative intensities of some peaks measured at different energies of the electron-beam. A particular example is the formation of F^- from perfluorocyclobutane.[23] The ionisation efficiency curve for the formation of F^- (over a 10 ev electron energy range) contains four maxima, clearly demonstrating the operation of different processes at various electron energies. The processes listed below have been suggested as a rationale for the formation of F^-.

$$C_4F_8 + e \longrightarrow F^- + F^\cdot + C_4F_6$$
$$\longrightarrow F^- + CF_2 + C_3F_5^\cdot$$
$$\longrightarrow F^- + C_2F_3^\cdot + 2CF_2$$
$$\longrightarrow F^- + CF^\cdot + 3CF_2$$

3. Negative-Ion Studies

3.1 General

The subject of gaseous negative ions has been extensively studied in the past ten years. This is because an understanding of the formation processes for negative ions and the roles that negative ions play in various chemical processes is of fundamental importance in describing the nature of radiation phenomena,[27] the formation of ions in the ionosphere,[28] and the production of ions in flames.[29] Negative-ion studies carried out prior to 1960 have been reviewed.[19] Since then several books[7,27,31] and reviews[10,28,32-39] have been published. The majority of these reports place stronger emphasis on the theoretical aspects rather than on the practical applications of negative ion mass spectrometry. A notable exception is the work of von Ardenne and co-workers[31] on natural products (Section 3.2 and 4.10). Since 1965 there has been an ever increasing effort to develop negative-ion mass spectrometry as an aid to structure determination. A survey of progress in this area is outlined in section 4.

3.2 Instrumentation

The mass spectrometers used for negative-ion studies include

1) time-of-flight (TOF) mass spectrometers,

2) ion cyclotron resonance (ICR) spectrometers,

3) conventional mass spectrometers, and

4) high pressure source instruments.

TOF Instruments are particularly useful for appearance potential measurements[10,32,39] and for the determination of autodetachment lifetimes of negative ions.[39,40] ICR Spectrometers[41-44] are largely used for the study of ion-molecule reactions.

Most conventional mass spectrometers can be used to measure negative-ion mass spectra if the appropriate potentials and fields can be reversed. The use of a double focusing instrument enables the focusing of metastable ions,[45] determination of negative-ion kinetic energy spectra[45] and collision-induced decompositions.[45] The various problems associated with conventional spectrometers have been outlined earlier (section 2).

A high pressure source has been specially designed by von Ardenne and coworkers[21] for producing slow electrons by a low-voltage gas discharge at a pressure of about 10^{-2} Torr. These electrons are then captured by the molecules in question to give molecular anions and fragment ions. Using this technique they have obtained many useful spectra of organic compounds, in particular of certain natural products[31,46,47] (see section 4.10). This approach has a

major disadvantage in that the use of high source pressures frequently produce peaks which originate from ion-molecule reactions. Consequently some spectra contain anomalous peaks sometimes of mass greater than that of the molecular anion, and such spectra are of limited application for structural determination.[19]

3.3 The Quasi-Equilibrium Theory and its Applications to Negative Ions.

The quasi-equilibrium theory (QET) of mass spectra was developed in order to rationalise the general features observed in positive-ion mass spectra.[48-52] The two principal assumptions of the QET are:-[48-52]

1) a mass spectrum can be considered to be formed by a series of competing, consecutive unimolecular decomposition reactions, and

2) the rates of each of these reactions can be calculated using the absolute rate theory.

In the absolute rate theory,[53] the reaction rate is assumed to depend upon the concentration and nature of the activated complex in equilibrium with the reactants. The average rate constant of a unimolecular reaction can be represented by the simplified form [54]

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

where k(E) represents the rate constant at total energy E with activation energy Eo, ν is the frequency factor and s is the number of effective oscillators. Because of unknown parameters, viz. ν, E and s, the QET is currently limited to relatively simple molecules. Nevertheless it has been widely used to provide a qualitative rationale for many reactions.

For simple bond cleavages, the "frequency factors" are high (approximately 10^{14}), while for rearrangements the values are several orders of magnitude lower, reflecting a restricted geometry in the transition state for the reaction.[55] A simple method for assessing frequency factors involves comparison of spectra at high and low electron beam energy.[56] Since a rearrangement reaction generally has a lower frequency factor and often a lower activation energy than a competing direct cleavage reaction, the rate of increase of k with E will generally be lower for a rearrangement than for a direct cleavage reaction. As a consequence direct cleavage reactions will generally dominate at higher internal energies of the decomposing species while rearrangement reactions will become more important at lower internal energies (see fig. 2).

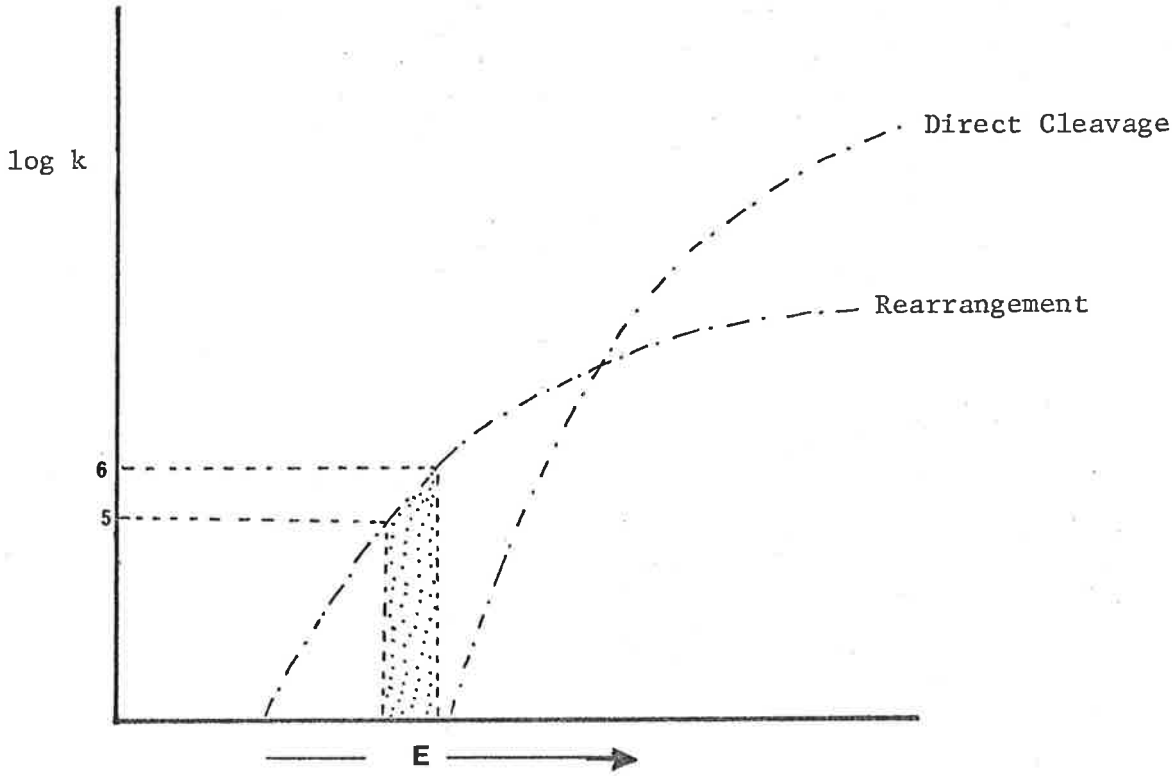


Fig. 2. Typical k vs E curves for a direct cleavage and rearrangement reaction. The shaded area represents the energy segment corresponding to a metastable transition.

The QET was first applied to negative ions by Winters and Kiser.[57] The materials chosen for study were nickel carbonyl, iron pentacarbonyl and the hexacarbonyls of chromium, molybodenium and tungsten. The negative-ion spectra of these compounds were

measured and compared with the theoretical spectra calculated using the QET. The observed spectra agree quite well with the calculated values, hence demonstrating the applicability of the QET to the negative-ion spectra of such compounds.

3.4 Metastable Ions

"Metastable ions" are formed by the spontaneous decomposition of ions that have been accelerated out of the ion source.[58] There are three distinct regions of a double focusing mass spectrometer where such fragmentations may be detected.

Ions of mass m_1 with a lifetime of about 1 μsec or less will decompose to give a daughter ion m_2 in the source.[59] The ion m_2, if not energetic enough to decompose, will be recorded as a "normal" sharp signal at m_2/e. Ions of mass m_1 with slightly longer lifetime (about 2-11 μsec) will decompose into daughter ions m_2' before entering the electrostatic analyser. The velocity of m_2' is determined by the velocity of the heavier precursor ion m_1. The velocity of m_2' will be less than that of ions of equal mass m_2 formed in the source. Under normal operating conditions m_2' does not fulfil the conditions required to pass through the electric sector and therefore does not appear on the spectrum. Ions of mass m_1 with even longer lifetimes

(>11 μsec) decompose to daughter ions m_2' in the field-free region between the electric and magnetic analysers. The ions m_2'' have the same mass and velocity as m_2' but they are not energy focused. These ions (m_2'') are recorded as the familiar diffuse, low intensity peaks at a mass equal to m_2^2/m_1.

The presence of metastable peaks provide direct evidence for the occurrence of particular fragmentation pathways. However recent advances[60] demonstrate that more useful information concerning mass spectral processes and ion structures can be obtained from metastable peaks. Some of these applications include:-

i) ion structure determination by comparison of metastable abundances,

ii) identification of rearrangement reactions,

iii) determination of kinetic energy released in metastable transitions,

iv) determination of atom scrambling in labelled ions,

v) elucidation of isotope effects, and

vi) measurement of collision-induced reactions.

The progress made in the application of metastable transitions is largely due to advances in the QET, and to the development of the double defocusing technique.[60] The QET predicts that metastable

transitions will occur from low energy precursor ions within a narrow energy segment controlled by narrow rate constant limits ($\log_{10} k$ = 5-6).[61] The way in which the shape of k vs E curves influences metastable abundances has been described.[61]

Use of the 'defocusing' technique[62-64] allows sensitive measurement of metastable ions. There are two ways of focusing these "metastable" transitions. The first is to raise the acceleration voltage while keeping the electrostatic voltage constant.[62,63] For the process $m_1 \longrightarrow m_2$, the acceleration voltage is raised by a value of m_1/m_2 in order to enable the metastable ions to traverse the electric sector. The second method lowers the electrostatic voltage (by a value of m_2/m_1) while keeping the acceleration voltage constant.[64]

3.4.1 Metastable Decompositions

By lowering the electrostatic potential to an appropriate value E_2, the daughter ions (m_2') in the field-free region before the electric sector can be recorded. The value E_2 is related to E_1 at normal operating conditions by the expression,

$$\frac{E_2}{E_1} = \frac{m_2}{m_1}$$

At sector potential E_2, the ions m_2' appear in the spectrum as a sharp energy-focused signal at the mass value $m^* = m_2^2/m_1$. If m_2' decompose further in the drift region between the electric and magnetic sectors, then these ions (m_3) will be recorded as diffuse transitions at the mass value $m^{**} = m_3^2/m_1$. Similarly for a three step fragmentation, the metastable ion will be recorded at a value equal to m_4^2/m_1. Hence the metastable defocusing technique provides an elegant method for the observation of multistep processes in the mass spectrometer.[59]

3.4.2 Ion Kinetic Energy Spectroscopy.

A variation of the metastable focusing method has been used to give a spectrum of ion energies corresponding to decompositions in the first field-free region of the mass spectrometer. The ion beam passing through the energy-resolving (β) slit (between the two analysers) is monitored while continuously varying the electrostatic voltage. The resulting ion kinetic energy (IKE) spectrum[65] i.e. a pure 'metastable' ion spectrum can detect low abundance reactions which are often obscured in the normal spectrum. IKE Spectra give detailed "finger-prints" of organic compounds. Such spectra are particularly sensitive to small structural differences,[66] and as such are useful structural aids, especially as normal mass spectra

are often insensitive to stereochemical differences.

3.4.3 Collision-Induced Dissociations of Positive Ions

There are many fragmentation processes, particularly those of high activation energy, where the appropriate metastable ions are either absent or only formed in low abundance. These reactions commonly involve simple cleavages, and it is desirable to obtain metastable-type information for such reactions.

The collision with neutral molecules provides a convenient way of increasing the internal energy of ions in the drift regions of the spectrometer.[67,68] The neutral molecules (target gas) are introduced into the drift region preceding the electric sector through a leak valve. The target gases used include H_2, He and Ar. The optimum conditions for collision activation depend upon several factors,[68] namely

1) length of the drift tube,
2) kinetic energy of the incident ion,
3) pressure of target gas,
4) type of target gas.

The pressure of the target gas is particularly important, because of the possible loss of ions through collisional scattering. The optimum pressure is usually about 10^{-4} Torr.[68]

The collision of ions with neutral molecules introduced into the drift region of the mass spectrometer converts part of the translational energy of the ions to internal energy.[69,70] The increase in internal energy may be quite considerable (more than 12 ev in one particular example[69]) when ions of high kinetic energy (>1 kev) collide with neutral molecules. These higher-energy ions undergo dissociations which may be observed in the drift regions as collision-induced decompositions. These decompositions in the drift region between the two sectors are detected as diffuse peaks at a mass value equal to m_2^2/m_1 for the process $m_1 \longrightarrow m_2$. Those decompositions occurring in the drift region preceding the electric sector can be measured using the "metastable defocusing technique".[64] In particular, the use of a Hitachi Perkin Elmer RMU-7 double-focusing mass spectrometer of reverse geometry[71] (i.e. an instrument that has the relative positions of the electric and magnetic sectors reversed) enables the collision-induced spectrum of any ion to be obtained. The ion in question is selected by the magnetic sector. Subsequent decompositions of the ion between the two sectors can be measured by scanning the electric sector. The resulting ion kinetic energy spectrum obtained shows all products from that particular ion.

Jennings[69] has investigated the collision-induced dissociations in the positive mode of a variety of aromatic compounds. The collision-induced spectra are very similar to the electron impact

spectra obtained under normal operating conditions. This suggests that there is little difference between energy transfer by electron impact or by collision followed by fragmentation. In other words, the collisional energy is randomised prior to fragmentation.[69]

McLafferty et al[68,72-75] have carried out intensive investigations of the behaviour of positive-ion collision-induced decompositions. The results show the collision-induced decompositions can be predicted by QET. Furthermore, an important generalisation has been made regarding the minimisation of rearrangements by employing collisional activation. Higher energy ions frequently decompose preferentially via direct cleavage rather than via rearrangement.[56,76] Consequently, collision-induced transitions (which generally occur from higher energy precursors than do unimolecular metastable transitions) should decompose preferentially by direct cleavage. A collision-induced process will provide a lower probability for a rearrangement reaction only if a competitive pathway of high frequency is operative.[73] This feature has been applied to the structure determination of some peptide derivatives, where the collision-induced transitions involving sequence peaks (direct cleavage) are absent in the corresponding electron impact spectra.[77] A particular example is provided by the oligopeptide derivative Ac-Gly-Ala-Leu-OCH_3. The electron

impact spectrum contains a metastable peak for the sequence process $Ac\text{-}Gly\text{-}Ala^{+} \longrightarrow Ac\text{-}Gly^{+}$, but the collision-induced spectrum gives sufficient peaks for elucidation of the entire sequence.[75]

Collision-induced dissociations frequently give more product ions than do the corresponding unimolecular metastable spectra.[68-69] Collision-induced spectra therefore provide additional information concerning both the mechanism of ion formation and the structures of organic molecules.

3.4.4 Negative Metastable Ions

Metastable transitions are common in negative-ion spectra.[45,78,79] Most metastable peaks produced in the drift region between the two sectors are gaussian in shape, but some may be broad and flat topped. An example of the latter type is found for the loss of NO· from substituted nitrobenzene molecular anions.[79,80] In particular, the loss of NO· from p-dinitrobenzene involves the loss of 0.89 ev of kinetic energy.[80]

The metastable ions formed in the drift region between the two sectors can be detected by the usual magnetic scan. Those formed in the drift region preceding the electric sector are detected by the 'metastable defocusing' technique.[64] Using the decreasing electric

sector potential method;[64,81] and operating at maximum sector potential (180 volts) on the Hitachi Perkin Elmer RMU-7D instrument, the metastable ions in the drift region preceding the electric sector are intensified about 10 times over those formed in the region between the two sectors.[45] This enhancement is usually not sufficient for the sensitive measurement of metastable transitions in negative-ion spectra. A metastable defocusing unit requiring a sector voltage greater than that used by the commercial instrument was devised;[45] this unit gives metastable ions approximately 100 times more intense than those mentioned above.

3.4.5 Negative Metastable Ion Decompositions

The metastable defocusing technique not only allows the assignment of fragmentation pathways for negative ions but also permits the detection of multistep sequences of metastable ions. Bowie and Hart[45] first reported two-step metastable decompositions in 1-(acetoxy-$^2H_3$)-3-acetoxyflavone and 3-nitrophthalic anhydride. The negative-ion spectrum of the flavone shows the processes $[M-CD_2CO-CH_3CO^{\cdot}]$ (m/e 341 $\longrightarrow$ 297 $\longrightarrow$ 254). These decompositions are analogous to those of the acetoxyquinones.[78,82] When the electric sector potential is reduced to 87.1% of its normal value (i.e. m_2/m_1 = 297/341 = 0.8710) and a magnetic scan carried out, the

metastable ion (m*) at m/e 258.7 for the process [M-CD_2CO] is accompanied by a peak (m**) for the two-step process [M-(CD_2CO + $CH_3CO^{\cdot}$)]. These fragmentations are shown in fig. 3.

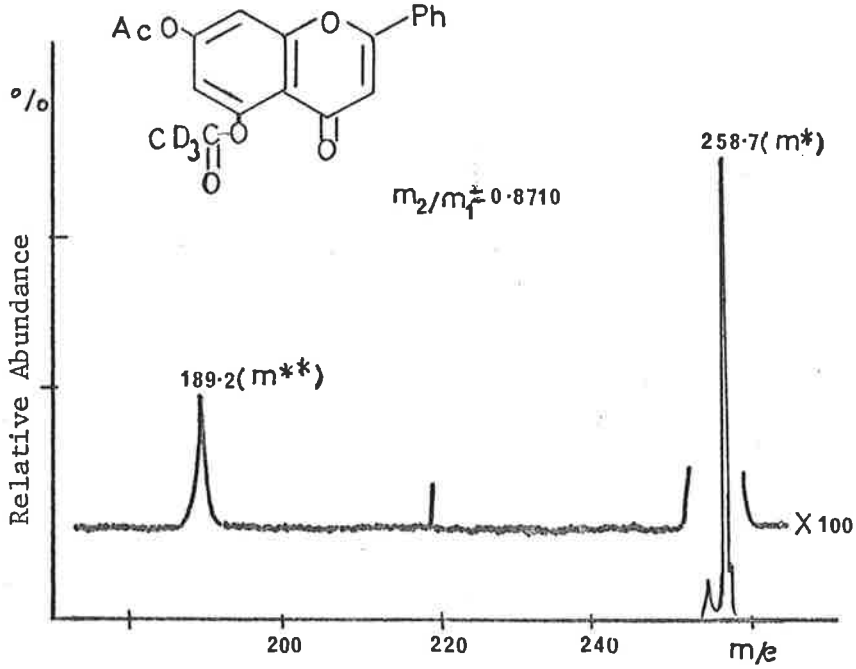


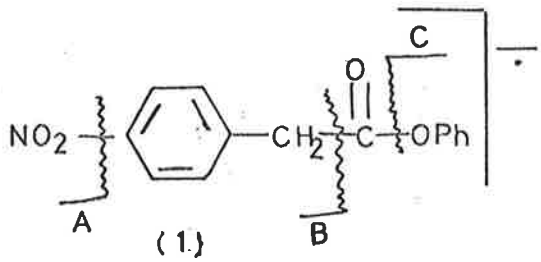
Fig. 3. Metastable Decompositions in the Negative-ion spectrum of 1-(acetoxy-$^2H_3$)-3-acetoxyflavone.

Three step metastable decompositions are rare in negative ions. Nevertheless this has been observed in emodin triacetate (1,6,8-triacetoxy-3-methylanthraquinone).[45]

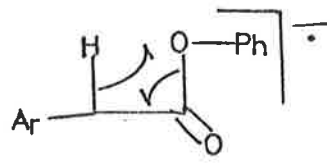
3.4.6 Negative Ion Kinetic Energy Spectroscopy.

Negative ion kinetic energy (NIKE) spectra can be obtained by monitoring the ion beam passing through the electric sector when the

sector voltage is varied continuously at constant accelerating potential (cf. section 3.4.2). The NIKE spectrum provides an accurate measure of all the metastable ions present. This is demonstrated for the case of phenyl-(p-nitrophenyl)acetate[45] (fig. 4). The molecular anion undergoes simple cleavage processes (as shown in (1)) and the rearrangement reactions [M-PhOH] and [M-NO$^{\bullet}$]. A possible mechanism for the loss of PhOH is shown in (2)



(1)



(2)

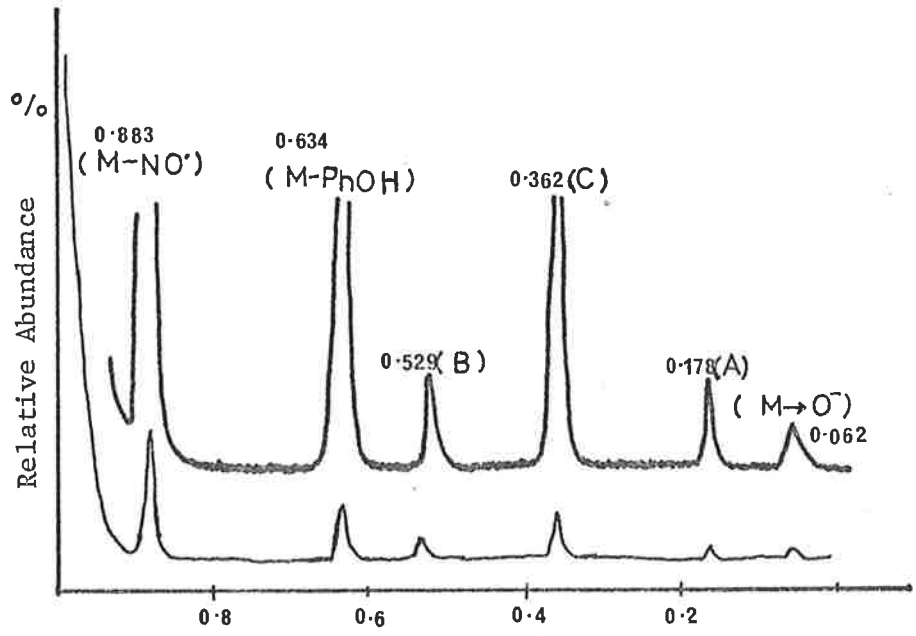


Fig. 4. NIKE spectrum of phenyl-(p-nitrophenyl)-acetate

3.4.7 Collision-Induced Dissociations of Negative Ions

The molecular anions produced by secondary electron capture have low internal energies (see Results and Discussion, Chap. 4); consequently certain molecular anions do not have enough energy to allow fragmentation to proceed. There are also functional groups which do not fragment in the negative mode. It is therefore necessary to increase the internal energy of these ions if they are to decompose.

The internal energy of a decomposing positive ion can be enhanced by increasing the energy of the ionising electrons. However this method is not applicable for molecular anions produced by secondary electron capture.

Collision has been used to increase the internal energy of molecular anions.[45,83,85] A sample pressure of about 10^{-6} Torr is used. The collision gas is introduced through a separate inlet system into the drift region preceding the electric sector to a pressure of about 10^{-5} Torr. Differential pumping is maintained in the source and analyser regions. The gas used should

i) not produce negative ions under the operating conditions; and

ii) not undergo ion-molecule reactions.

The gases used include krypton, nitrogen, benzene and toluene.

Aliphatic hydrocarbons (e.g. methane[86]) have been avoided because of the risk of ion-molecule reactions. The collision-induced dissociations produce daughter anions which have similar properties to the products of metastable ion decompositions,[45,83] and they can be detected in both field-free regions of the mass spectrometer.

Collision activation has been used to force fragmentations of quinones,[83] anhydrides,[83] ketones, amides[84] and carboxylic acids.[85] As an example, the molecular anion of p-nitroacetanilide fragments to give only an NO_2^- ion.[79] The collision-induced spectrum of this compound contains additional peaks corresponding to the processes [M-NO·] (m* = 125.0), (M-MeCO·) (m* = 104.3) and [M-HNO_2] (m* = 98.3).[84] The collision-induced spectrum of p-nitroacetanilide obtained in the drift region between the two sectors by a magnetic scan is shown in fig. 5.

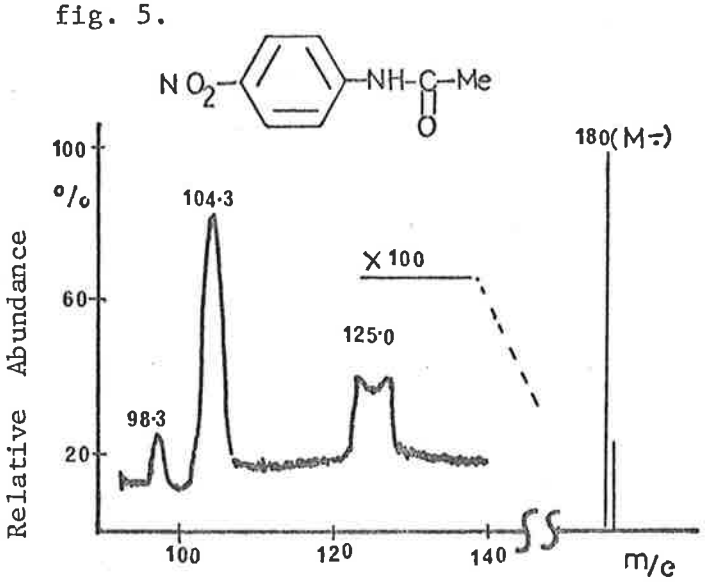


Fig. 5. Collision-Induced spectrum of p-nitroacetanilide (the conventional molecular anion is shown to allow comparison of relative abundances)

3.4.8 Behaviour of various Reactions with Varying Pressures of Target Gas.

The internal energy of an anion undergoing collision increases with increasing pressure of the target gas.[45] The relative rates of various reactions with respect to increasing internal energy of the decomposing ion have been investigated.[45] The generalisations from their results have been useful especially in classifying the various types of reactions.

There are essentially three types of fragmentations which a molecular anion can undergo. These are:-

1) simple cleavage reactions[87]

2) rearrangement reactions (both hydrogen and skeletal)[36,88]

3) "apparent rearrangement" reactions.[45]

The relative rates of these reactions may be determined by measuring the relative abundances of collision-induced peaks with increasing gas pressure. It has been demonstrated that if a molecular anion fragments by competing cleavage and rearrangement processes, the rate of the simple cleavage process generally increases more rapidly than that of the competing rearrangement.[45] (Cf. the same effect for positive ions, 3.4.3). An elegant example, is provided by phenyl-(p-nitrophenyl)-acetate. The molecular anion undergoes both simple and rearrangement reactions[45] (see section 3.4.6). Both

rearrangement reactions ([M-NO·] and [M-PhOH]) proceed via tight transition states. As the internal energy of the decomposing molecular anion increases (with increasing gas pressure), both rearrangement ions suffer pronounced relative decreases in abundance, while the simple cleavage ions increase in relative abundance. These variations are shown in fig. 6.

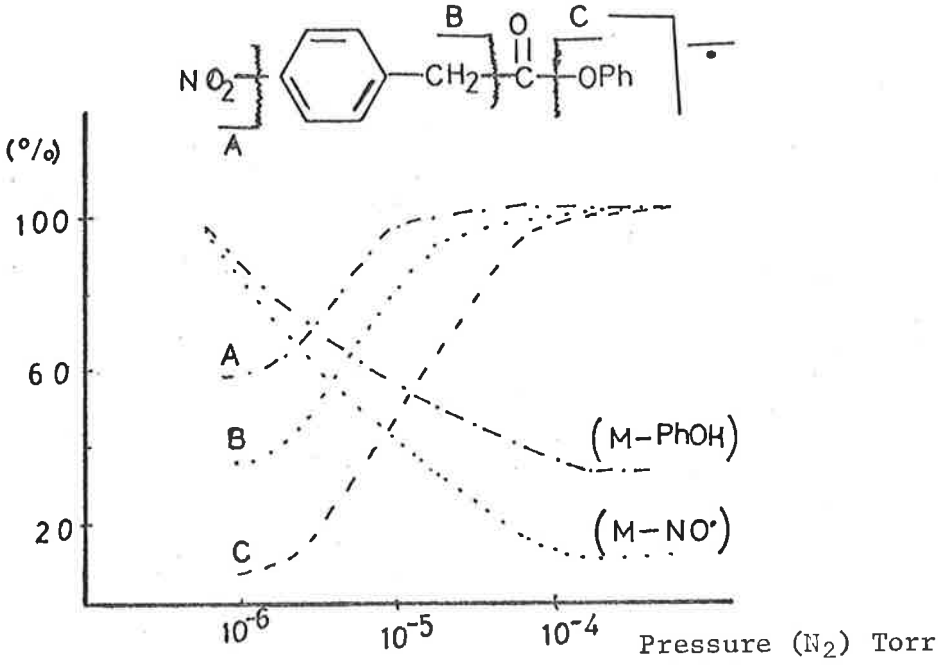
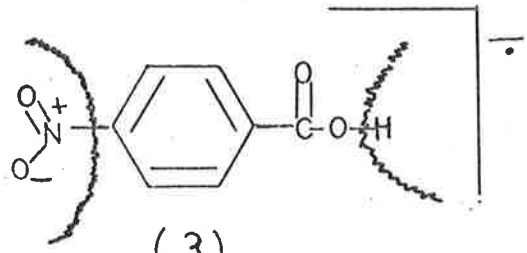


Fig. 6. Variation of Abundances of metastable ions in the NIKE spectrum of phenyl-(p-nitrophenyl)-acetate with pressure of collision gas (N_2).

In the "apparent rearrangement" reactions, the two reacting groups are remote from each other. A typical example involves the loss of the elements of HNO_2 from the molecular anion of p-nitrobenzoic acid.[79] The species involved in the loss of HNO_2

are shown in (3).



(3)

The collision-induced NIKE spectra of p-nitrobenzoic acid (measured using different pressures of collision gas) show that the $[M-HNO_2]^{-\cdot}$ peak increases with the increasing pressure of collision gas. The energetics of this type of reaction resemble those of a simple cleavage reaction. It is therefore probable that the observed metastable ions for such processes are due to simultaneous two-stage cleavage reactions rather than complex rearrangement processes.

Further examples of the application of this technique will be given in the discussion.

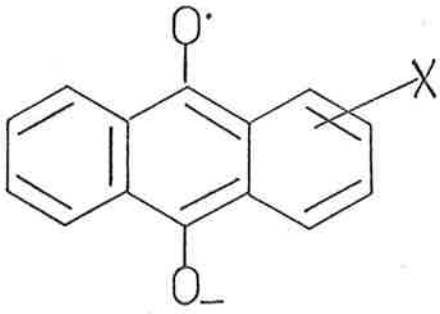
4. Negative-Ion Mass Spectra

The mass spectrum is usually described in terms of the relative proportions of the different ions produced when a molecule is bombarded with ionising electrons. When the electron energy is greater than 30-40 ev, the relative abundances of positive ions are usually independent of the electron energy. Consequently the positive-ion spectra of many compounds have been obtained under such conditions. Negative-ion spectra cannot be similarly tabulated because of the complications (section 2) associated with their formation. The disadvantages encountered explain why negative-ion mass spectrometry has not been generally accepted as a viable analytical technique.

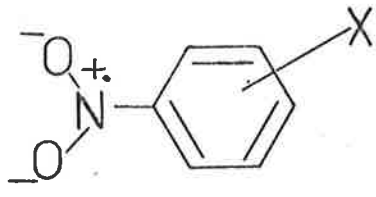
The sensitivity of negative ion production is largely related to the type of molecules under investigation. Those molecules with a high electron affinity will tend to capture a low-energy electron.

The majority of aliphatic compounds, some aromatic and inorganic compounds do not form stable molecular anions.[28,36] On the other hand, organometallics with vacant metal orbitals or with a suitable ligand, may accept an electron.[28,34] Similarly, aromatic compounds (and some aliphatics) with at least one electron

withdrawing group (e.g. NO_2, CN) generally give molecular anions under normal operating conditions of the mass spectrometer (1-3 x 10^{-6} Torr, 40-80 ev). These compounds often produce larger negative-ion currents than the corresponding positive-ion currents.[36] These molecular anions are believed to be produced by the capture of secondary electrons.[11,87,89] (See section 1.2.4). Bowie and co-workers[36,78] have used such compounds to investigate the fragmentations of various functional groups in the negative mode. By selecting the appropriate molecule RX where R can accept an electron to give $RX^{\cdot-}$, they were able to determine decompositions of X. The moiety R was chosen such that it will form a stable molecular anion under normal operating conditions of the spectrometer. The quinonyl[78] (4) and nitrophenyl[79](5) moieties were initially chosen for these studies. Quinones form long-lived negative ions by capture of thermal electrons via electron- and/or nuclear-excited Feshbach resonances.[90,91] The nitrophenyl group is an efficient electron capture group because of the electron withdrawing power of nitro group and the low-energy vacant π levels in the molecule.[92] Christophorou and co-workers[93] have demonstrated that many nitroaryl compounds form long-lived molecular anions via nuclear-excited Feshbach resonance.



(4)



(5)

The results of these, and other studies are given below in a brief survey of the negative-ion spectra of various classes of compounds.

4.1 Hydrocarbons

The majority of hydrocarbons investigated do not give molecular anions between 0 and 70 ev. The most important ion at low energies is H^-[94-99] which may be formed by dissociative processes[96-98] or by ion-pair production.[96,98] The other fragment ions are usually produced by the loss of $H^\cdot$, H_2 or $CH_3^\cdot$ etc.

Aromatic hydrocarbons behave in a similar way to aliphatic hydrocarbons.[95] More complex hydrocarbons do form molecular anions

by capture of low-energy electrons.[26,100,101]

In general, negative-ion mass spectrometry is not particularly useful for the identification of hydrocarbons.

4.2 Halo-compounds

Halo-compounds have been widely studied because of the variety and abundance of negative ions formed. Most investigations have been concerned with the determination of physical parameters; viz. capture cross-section, ion lifetimes and electron affinities.

Fluorocarbons do not generally give molecular anions, but yield fragment ions, the most important of which at both 70 ev and low energies is F^-.[40,102-110] Molecular anions have, however, been detected in select cases at low electron energies (e.g. perfluorobenzene[111]), and at 70 ev (e.g. perfluorocyclobutane).[40,110,112] Alkyl[22,92,97,99,111,113-121] and aryl chlorides[22,92] rarely give molecular anions. The major ions observed at both 70 ev and at low energies, are Cl^- and $[M-Cl^{\cdot}]^-$.

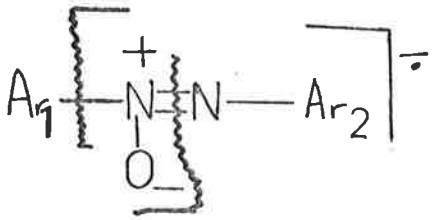
The negative-ion spectra of halo-compounds are of limited value for structural investigations.

4.3 Nitro compounds, Nitrones and N-oxides

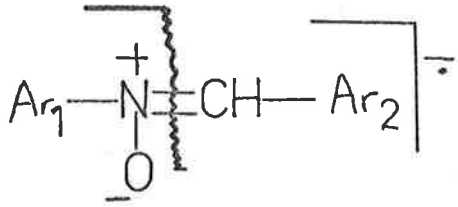
The most intense ion in the negative-ion spectra of nitroalkanes is NO_2^-.[25,122-124] Molecular anions are detected in some cases (e.g. nitromethane[25]).

In contrast, aryl nitro compounds give intense negative-ion spectra.[36] The parent compound, nitrobenzene, affords a pronounced molecular anion by direct electron capture at less than 1 ev[22,122] or by secondary electron capture at electron energies greater than 15 ev.[11] The characteristic fragment ions in the 70 ev spectra of aryl nitro compounds are NO_2^- and $[M-NO^{\cdot}]^-$ ions.[79,80,125-127] The loss of $NO^{\cdot}$ is believed to proceed by rearrangement to the nitrite followed by fragmentation.[80,127] Proximity effects are common in o-substituted nitrobenzenes, and the spectra of such compounds are often diagnostic for structural purposes, even though the mechanisms of particular proximity effects may be complex.

Aromatic N-oxides, aromatic azoxy compounds and nitrones, give intense molecular anions together with fragment ions arising by simple cleavage processes.[128] The 70 ev spectra of aromatic N-oxides contain molecular anions and $[M-O]^{\cdot-}$ ions. Aromatic azoxy compounds and nitrones undergo characteristic fragmentations as shown in (6) and (7) respectively.



(6)

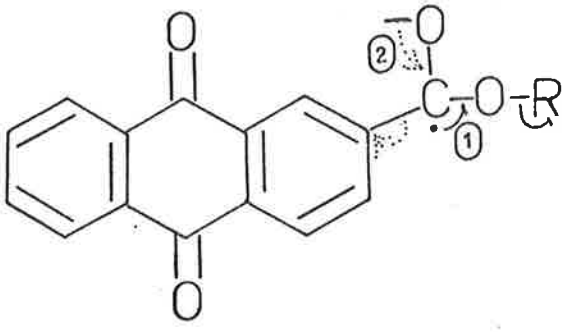


(7)

These negative-ion spectra are more informative than the corresponding positive-ion spectra. The positive-ion spectra of aromatic azoxy compounds,[129] aromatic N-oxides[130] and nitrones[131] are complicated by fragment ions formed by complex rearrangements.

4.4 Esters and Anhydrides

The characteristic fragmentations of esters have been examined by high pressure methods,[31] and by the use of secondary electron capture groups such as quinonyl,[78] nitrophenyl,[79,132,133] and p-cyanophenyl.[133] The alkyl esters undergo the characteristic reactions [M-R$^{\cdot}$-CO_2] as shown in (8).[78] Proximity effects may be observed if the ester group is adjacent to the charge-containing centre. For example the ester (9) undergoes the process [M-RO$^{\cdot}$].[78]



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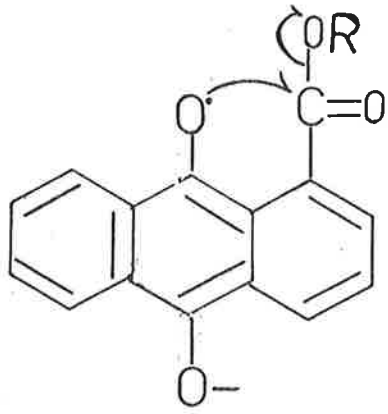
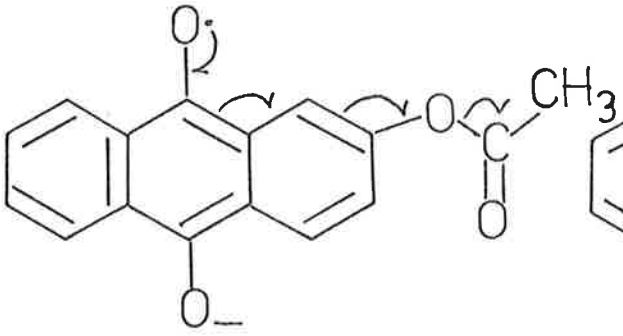
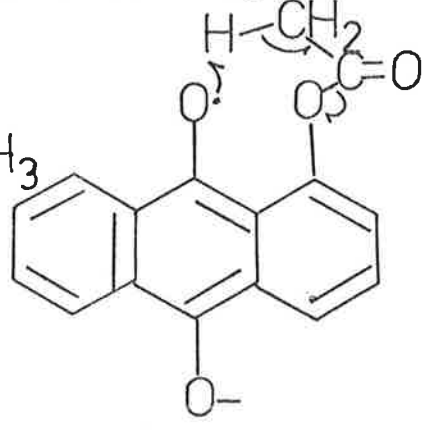


(9)

Acetates decompose by the simple cleavage process [M-MeCO$^{\cdot}$][78] except when the acetate group is adjacent to a quinoid oxygen. In this case the acetate fragments exclusively by a hydrogen rearrangement process [M-CH_2CO].[78] The operation of the former process (M-MeCO$^{\cdot}$) is demonstrated for the molecular anion of 2-acetoxyanthraquinone (10), and the latter (M-CH_2O) for 1-acetoxyanthraquinone (11).

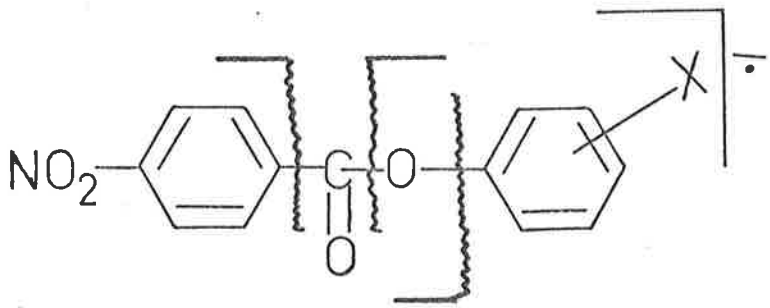


(10)



(11)

Phenyl esters undergo more fragmentations than the simple alkyl esters. This is illustrated for the phenyl p-nitrobenzoate molecular anion (12).[145]



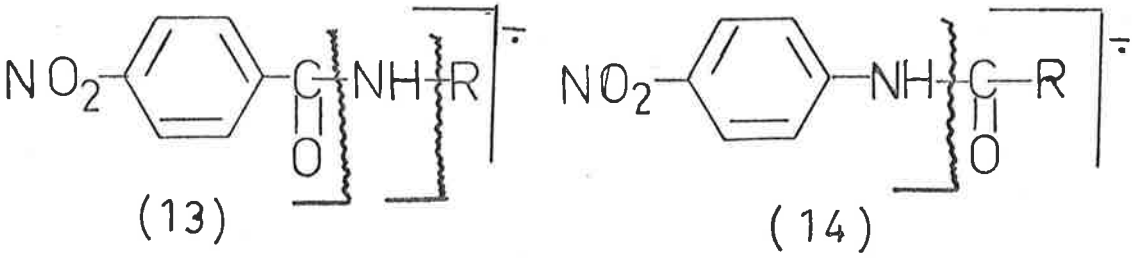
(12)

Rearrangement ions are common in the negative-ion spectra of o-nitrophenyl esters, and often constitute the base peaks in the spectra. A typical example is provided by the molecular anion of phenyl o-nitrobenzoate which undergoes the major process [M-PhO$^{\bullet}$]. This elimination is believed to be preceded or accompanied by cyclisation between a nitro oxygen and the carbonyl centre.[132]

Maleic and phthalic anhydrides form molecular anions by direct electron capture between 0 and 2 ev[134-136] and by secondary electron capture at electron energies greater than 15 ev.[135] The molecular anions formed in this manner do not fragment, but they can be made to decompose using collision activation.[83] For example the collision activated molecular anion of maleic anhydride decomposes by loss of carbon monoxide.

4.5 Amides

The molecular anions of simple aromatic amides fragment after collision activation, e.g. see (13) and (14).[79]



(13) (14)

The o-nitro isomer of (14) shows a proximity effect involving the elimination of a hydroxy radical.[79,127] The three isomers of nitrophenyltrifluoroacetanilide give entirely different negative-ion spectra.[137] In contrast, the positive-ion spectra of these isomers are very similar.

4.6 Carboxylic acids

The negative-ion spectra of aliphatic mono-[138] and dicarboxylic acids[139] usually contain pronounced [M-H$^{\cdot}$] ions. Aliphatic dicarboxylic acids give molecular anions of low abundance together with fragment ions produced by the processes [M-H_2O] and [M-$HCO_2^{\cdot}$].[139]

The molecular anions of aryl carboxylic acids generally do not decompose. However collision activated molecular anions decompose by the process [M-HCO_2·]. This has been observed for anthraquine carboxylic acids, p-nitrobenzoic acid and p-cyanobenzoic acid.[85]

Proximity effects have been detected for some o-substituted benzoic acids. For example the molecular anion of phthalic acid eliminates water, a reaction which does not occur for the corresponding m- and p-isomers.[139] A further example is provided by the molecular anion of o-nitrobenzoic acid which undergoes the eliminations M-NO·-CO_2.[79]

4.7 Aldehydes, Ketones and Quinones

Long chain aldehydes give useful negative-ion spectra for structure characterisation.[140] Ketene[141] and acetone[97,142] yield only fragment ions. However hexafluoroacetone forms a molecular anion at 70 ev together with simple fragment ions.[9,106,143]

The molecular anions of aromatic aldehydes or ketones are generally stable except when collision activated. This is demonstrated by the collision activation spectrum of p-nitroacetophenone, which shows the decompositions for the COMe group in the

negative mode by the processes [(M-NO·)-Me·], [(M-NO·-Me·)-CO], [(M-NO·)-MeCO·] and [(M-NO·)-CH_2CO].[83]

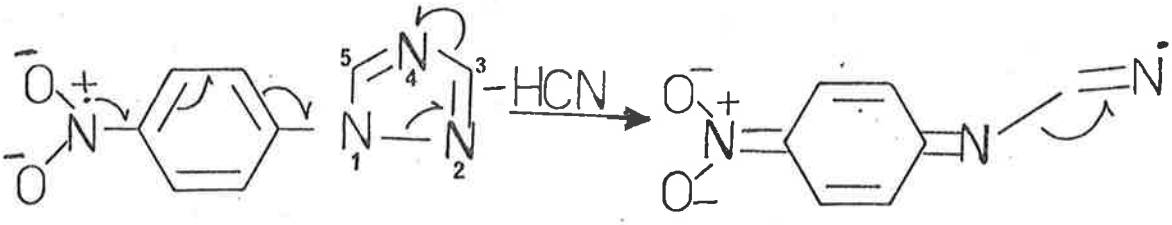
Quinones form intense molecular anions at low electron energies (<5 ev)[90,144] and by secondary electron capture.[78] The quinone moiety does not fragment under normal operating conditions, but collision activation induces decompositions of the ring system. For example the collision activated 1,4-naphthoquinone molecular anion undergoes the eliminations [M-CHO·] and [M-(CHO· + CO)].[83]

4.8 Nitriles and heterocyclic compounds

Cyanogen[145,147] and alkyl cyanides[124] produce CN^- but no parent anions. Intense molecular anions are obtained near 0 ev for tetracyanoethylene[148] and dicyanoacetylene.[146] Benzonitrile[92] and other aryl nitriles[45,135] form molecular anions near 0 ev and by secondary electron capture.

The negative-ion spectra of pyrrole,[149] indole,[149] pyridine,[149,151] alkyl pyridines[151] and pyridazine[151] contain peaks corresponding to [M-H·] processes. The nitrophenyl moiety can be used to direct fragmentations of a heterocyclic system and this is demonstrated by the negative ion spectrum of 1-(p-nitrophenyl)-1,2,4-triazole.[152] The molecular anion undergoes consecutive elimination

of 2 molecules of HCN as shown in Scheme (1). If the nitrophenyl group is at positions 4 or 5, the triazole ring does not decompose.

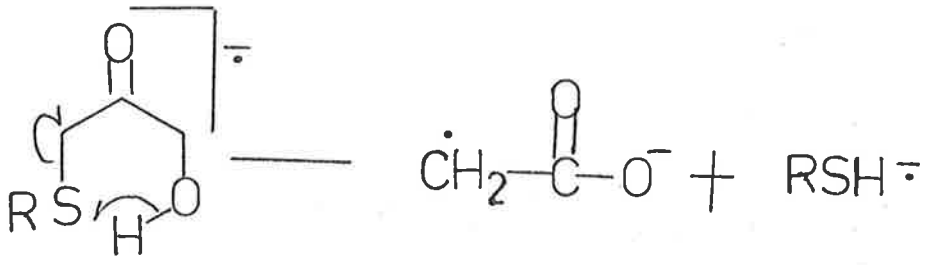


Scheme 1

4.9 Organosulphur compounds

Negative-ion mass spectral studies of organosulphur compounds are rather limited. Nevertheless some studies provide useful information.

Aryl thiols form molecular anions near 0 ev.[153] Thioethers also give molecular anions which undergo simple cleavage of the C-S bond to give fragment ions.[153,154] The 70 ev spectra of thioglycollic acids contain parent ions and fragment ions produced by hydrogen rearrangement[155] as shown in Scheme (2).



Scheme 2

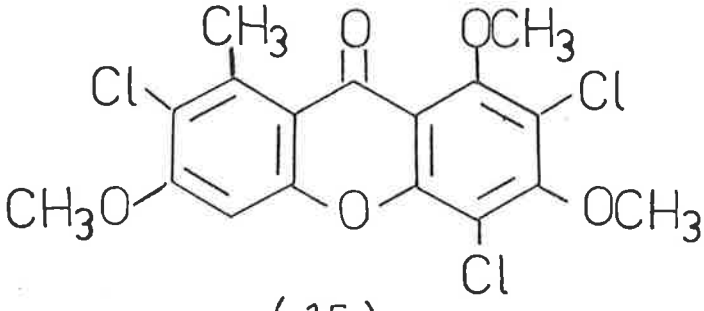
β-Thioketothiol esters produce molecular anions at 70 ev which decompose by both simple cleavage and rearrangement processes.[156] Dialkyl and diarylsulphoxides, aryl sulphones, sulphonamides, sulphonyl chlorides and sulphonate esters give simple but characteristic negative-ion spectra.[154]

4.10 Natural Products

Most of the work with natural products has been carried out using the special high pressure source of von Ardenne[21,46,47] (cf. section 3.2). These studies have been reviewed.[31 157 158] A wide range of natural products has been investigated, and several examples have been selected in order to demonstrate the applicability of this approach.

Xanthones[159] and flavones[160] give negative-ion spectra containing both parent and simple fragment ions. A particular

example is thuringion methyl ether (15), which forms a molecular anion together with an $[M-Me^{\cdot}]^{-}$ ion.



(15)

Depsides and depsidones also give molecular anions and simple fragment ions.[161,162] Similarly, riboflavin type systems have been demonstrated to give useful negative-ion spectra.[163-165]

Steroids[166-168] and triterpenes[169,170] yield negative-ion spectra but ion-molecule reactions frequently produce ions which give peaks of mass higher than the molecular anions. Hence these spectra must be interpreted with caution.

Perhaps the most elegant application of this technique is its use for the structure determination of the caridac glycosides.[171-175] These glycosides do not give molecular cations, but yield pronounced molecular anions together with simple fragment ions.

4.11 Organometallics

Negative-ion spectra have been reported for compounds containing other non-metal elements and for some metal containing materials. In particular many investigations of the group IV elements, especially silicon and tin, have been carried out.[176-181] The spectra of tetramethylsilane and tetramethylstannane show large $[M-H^{\cdot}]^{-}$ ions. The stability of these ions has been attributed to the $p\pi$-$d\pi$ bonding of the central atom (Si, Sn) d orbitals with p orbitals on carbon.[176]

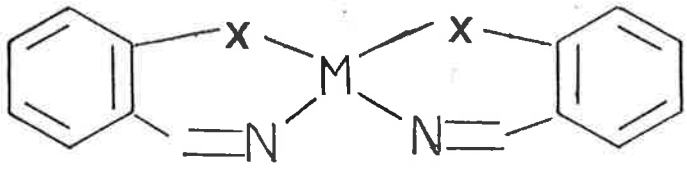
Bowie and Nussey[180] have studied the phenyl derivatives of elements of groups IV and V. The negative-ion spectra of these compounds contain parent ions together with $[M-Ph^{\cdot}]^{-}$ ions.

A series of metallocenes has been investigated.[182] The cyclopentadienyl anion was observed in all spectra, and molecular anions were recorded in some cases. For example nickelocene forms long-lived parent ions between 0 and 1 ev.[182]

Transition metal carbonyls with the exception of $V(CO)_6$ do not give molecular anions. Their spectra show the ions $M(CO)_n$ $(n = 1\text{-}5)$.[57,183-187]

The negative-ion spectra of Shiffs base complexes (16) [M = Ni, Co, Cu; X = O or NH) have been reported.[188] Molecular

anions were detected together with fragment ions of small abundances (except for the cases when M = Ni, Cu and X = O). The formation of the molecular anion is believed to be accomplished by electron capture by the metal and not the ligand.[188]

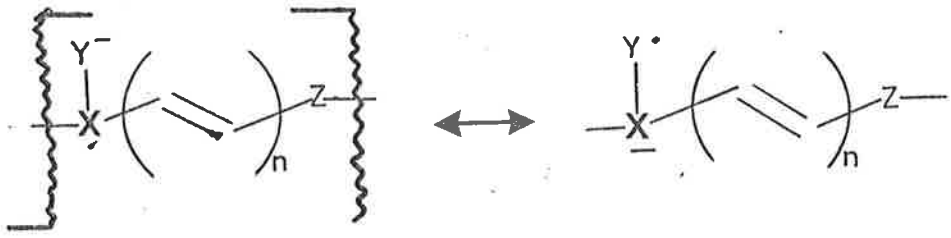


(16)

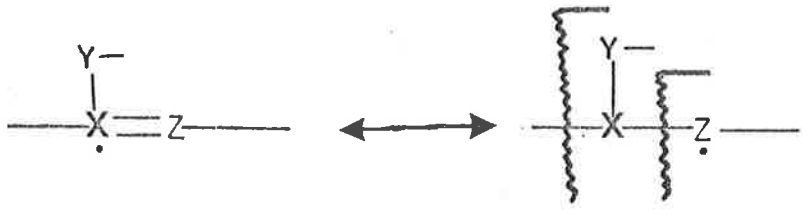
5. Types of Fragmentations - A Summary

5.1 Simple Cleavage Reactions

Molecular anions undergo both simple cleavage and complex reactions. Many of these simple cleavage reactions can be rationalised[87] by schemes (4) and (5) as shown.



Scheme 4



Scheme 5

Not all molecular anions undergo all the fragmentations shown but decompositions may be one or more of those indicated. Simple

cleavages generally occur α to the negative or radical centre, or α to some atom (or group of atoms) in conjugation with the negative/radical centre.

5.2 Rearrangement Reactions

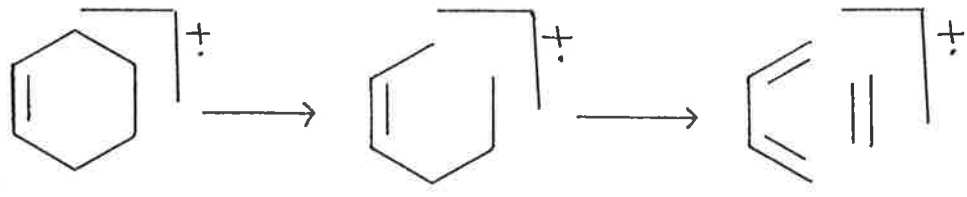
Many rearrangement reactions are known in negative ions, but it is not possible at this stage to write general mechanisms for these reactions. It is the purpose of this work described in this thesis to investigate the occurrence and mechanisms of particular rearrangement reactions. We have chosen to examine those reactions which have counterparts in positive-ion mass spectrometry. In Chapter 2, we describe the first retro-Diels-Alder reactions reported for negative ions. Chapter 3 deals with the proximity effects of salicylates and anthranilates while Chapter 4 is devoted to a discussion of more complicated reactions which occur for organosulphur compounds.

Chapter 2. The Retro-Diels-Alder Reaction in Negative-Ion Mass Spectrometry.

1. General

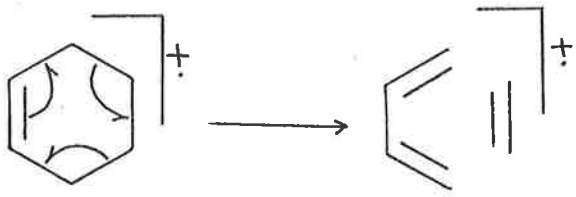
The electron-impact induced retro-Diels-Alder reaction is one of the most important processes occurring in the positive-ion spectra of organic compounds containing the cyclohexene moiety.[189-192] This process is diagnostic for the structural determination of polycyclic compounds including many terpenoids, steroids and other natural products.[193]

There have been two suggestions made concerning the possible mechanism of the retro process occurring in positive ions. The stepwise process shown in Scheme (2-1) is favoured by Budzikiewicz, Brauman and Djerassi,[189] and is based upon the charge distribution between fragmentation products and on energetic considerations.



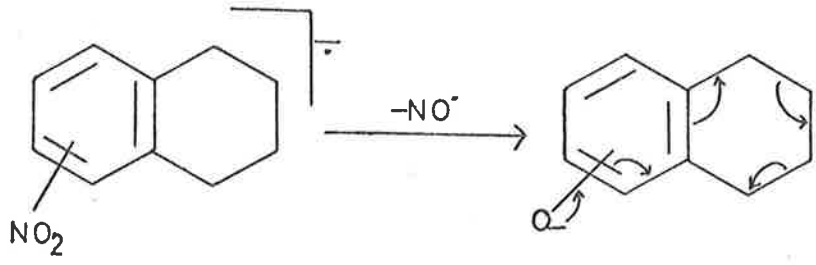
Scheme (2-1)

On the other hand, Dougherty,[194] on theoretical grounds preferred the concerted mechanism depicted in Scheme (2-2).



Scheme (2-2)

The widespread occurrence and application of this reaction in positive-ion mass spectrometry, has prompted us to investigate whether similar decompositions occur in the negative mode. The first system to examine is one containing the cyclohexene unit. However such compounds do not give molecular anions under normal operating conditions of the mass spectrometer (70 ev, 1 x 10^{-6} torr) without the presence of a suitable electron-capture group in the molecule. The nitrotetralin system was chosen for the initial study for two reasons. Firstly, the nitrophenyl substituent will function as an electron-capture group. Secondly, it is conceivable that the initial loss of NO$^{\cdot}$ from the molecular anion will yield a phenoxide anion which may decompose further by a "retro-Diels-Alder" reaction as shown in Scheme (2-3).



Scheme (2-3)

Both the 5- and 6-nitrotetralins yield intense molecular anions together with pronounced NO_2^- ions. The retro process is absent in both spectra. Furthermore, losses of NO· are very small in both spectra (< 1% of the base peak), hence reducing the possibility of any "retro-Diels-Alder" decompositions from $[M-NO\cdot]^-$ ions. These results are not surprising, as the retro process in cyclohexene type systems will involve cleavages of several C-C bonds. Decompositions involving cleavages of C-C bonds are generally not favourable for molecular anions which have low internal energies (see Chapter 4). On the other hand, the aryl O-C bond fragments with relative ease in the negative mode.[79] Consequently it was anticipated that the corresponding benzopyran systems may fulfil the conditions required for the occurrence of the retro process. The nitrochromans (see below) were thus chosen for investigation.

2. The Nitrochromans.

The negative-ion spectra of the nitrochromans (2-1) - (2-4) are recorded in table (2-1).

	NO_2
(2-1)	5
(2-2)	6
(2-3)	7
(2-4)	8

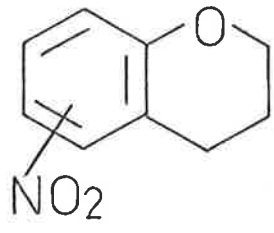


Table (2-1). Negative-ion mass spectra of the Nitrochromans.

	M	M-HO$^{\cdot}$	M-C_2H_4	M-NO$^{\cdot}$	M-(C_2H_4 + NO$^{\cdot}$)	M-(C_2H_4 + NO$^{\cdot}$ + CO)	NO_2^-
(2-1)	100	1.7	0.3	1.2	2	0.1	78
(2-2)	100		7		1	0.1	11
(2-3)	100		0.4		0.5	0.1	10
(2-4)	100		7		5	5	77

The spectra of the nitrochromans are intense and rather similar except for the variations in relative abundances of the fragment ions. The molecular anions of the 5- and 7-nitrochromans ((2-1), (2-3)) undergo the decompositions [M-C_2H_4-NO$^{\cdot}$-CO] to a comparable extent.

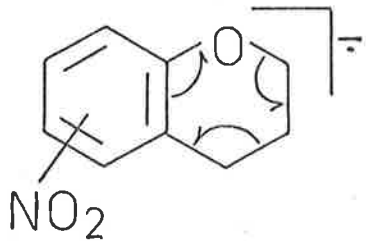
The spectrum of (2-1) contains additional peaks produced by the processes [M-HO$^{\bullet}$] and [M-NO$^{\bullet}$]. The decomposition [M-HO$^{\bullet}$] must therefore be associated with the proximity of the nitro group to the reaction site (i.e. heterocyclic ring). No metastable transitions were detected for any of these decompositions.

The molecular anions of 6- and 8-nitrochromans (2-2 and 2-4) undergo the decompositions [M-C_2H_4-NO$^{\bullet}$-CO] to a comparable extent. The retro process [M-C_2H_4] is substantiated by a metastable transition in both spectra.

2.1. The Process [M-C_2H_4].

The fragment ion produced by the retro-Diels-Alder process [M-C_2H_4] is more prominent in the spectra of the 6- and 8-nitrochromans (≃ 7% of the base peak) than that of the 5- and 7-nitrochromans (≃ 0.3% of the base peak). In other words, the process is favoured in compounds where the nitro group is in conjugation with the phenolic oxygen. It seems therefore that the nitro substituent is acting more than an electron-capture group and appears to play a definite role in the retro process. As a consequence, it seems unlikely that the retro process is proceeding via the simple

electrocyclic mechanism depicted in a.†



a

Collision excitation studies have been carried out with compounds (2-2) and (2-4) in an attempt to determine the nature of the retro process. The other isomers, (2-1) and (2-3), were not similarly studied because of the absence of metastable transition for the retro process. The NIKE spectra of both compounds (2-2 and 2-4) were measured using pressures of added collision gas (N_2) ranging from 1×10^{-6} - 3×10^{-5} torr. in the first drift region of the mass spectrometer. The abundances of the ions produced by the

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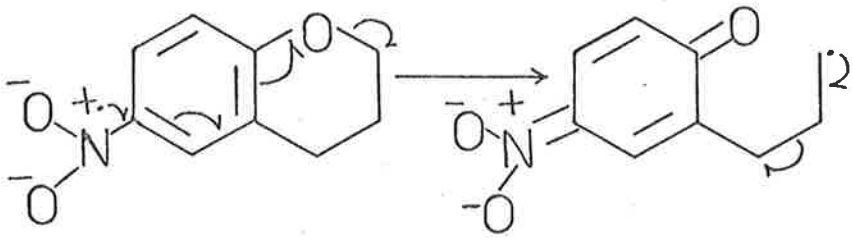
† Labelling studies have not been carried out in this system to substantiate the fragment loss from positions C_2 - C_3 , but such studies have been undertaken for the nitro-1,3-benzodioxans (see section 4).

collision induced process [M-C_2H_4] were compared with those of the direct cleavage process [M→NO_2^-]. The results show in both cases that the abundances of the ions produced by the collision-induced process [M-C_2H_4] increase dramatically with respect to the competing simple cleavage process [M→NO_2^-] with increasing pressure of the collision gas. This behaviour resembles that of a direct cleavage reaction[45] (see Chapter 1, section 3.4.8) and suggests a stepwise mechanism for the elimination of C_2H_4 from the molecular anions of 6- and 8-nitrochromans (see scheme (2-4) for the case of (2-2)).

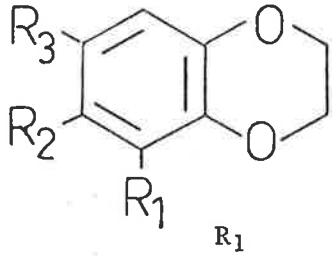


Scheme (2-4)

In order to further clarify the effect of the nitro group on the extent of the retro process, it was decided to study systems which would undergo such processes by the cleavage of two C-O bonds. The nitro-1,4- and 1,3- benzodioxans were chosen for the purpose.

3. The Nitro-1,4-benzodioxans

The spectra of (2-5) and (2-6) are recorded in table (2-2) while that of (2-7) is illustrated in fig. (2-1).†



	R_1	R_2	R_3
2-5	NO_2	H	H
2-6	H	NO_2	H
2-7	H	NO_2	NO_2

Table (2-2) Negative-ion mass spectra of (2-5) and (2-6).

	M	$M-C_2H_4$	$M-NO^{\cdot}$	$M-(C_2H_4 + NO^{\cdot})$	$M-(C_2H_4 + NO^{\cdot} + CO)$	NO_2^-
2-5	100	15	2	1	0.3	40
2-6	100	15	3	1	0.2	10

The spectra of (2-5) and (2-6) show the decompositions $[M-C_2H_4-NO^{\cdot}-CO]$ and $[M-NO^{\cdot}]$ to a comparable extent, with the abundances of the $[M-C_2H_4]^{\bar{\cdot}}$ peaks forming 15% of the base peak in

† All figures are placed in a lift out section at the end of each chapter

both cases. The spectrum (fig. 2-1) of the dinitro compound (2-7) again shows the similar decompositions [M-C_2H_4-NO$^{\cdot}$-CO] and [M-NO$^{\cdot}$] as for the mononitro compounds. The molecular anion of (2-7), in contrast to those of (2-5) and (2-6), undergoes the retro process to furnish the base peak of the spectrum, hence demonstrating the effect of the number of nitro substituents upon the extent of the retro process.

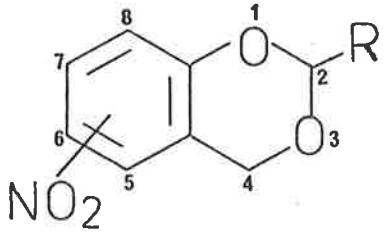
In summary, the spectra of the nitro-1,4-benzodioxans show;

1) that the extent of the retro process is dependent upon the number of nitro groups, and

2) that the distance of the nitro group from the oxygen atoms does not appear to affect the extent of the retro reaction if the nitro group is in conjugation with one of the ring oxygens.

4. The Nitro-1,3-benzodioxans

The nitro-1,3-benzodioxans chosen for study are listed below.



	NO_2	R
2- 8	5	H
2- 9	6	H
2-10	7	H
2-11	8	H
2-12	5	Me
2-13	6	Me
2-14	7	Me
2-15	8	Me

The spectra of 5-, and 6- and 7-nitro-1,3-benzodioxans (2-8, 2-9, and 2-10) are shown in figs. (2-2) - (2-4), while that of the 8-nitro isomer (2-11), which is very similar to the spectrum of (2-9), is recorded in table (2-3). The spectra of the 2-methyl-nitro-1,3-benzodioxans are also recorded in table (2-3).

Table (2-3). Negative-ion spectra of (2-11) - (2-15).

	M	M-CH_2O	M-(CH_2O + HO$^\cdot$)	M-(CH_2O + NO$^\cdot$)	M-(CH_2O + NO + CO)	NO_2^-
2-11	100	10		0.8		43
2-12	100	90	11	12	4	30
2-13	100	9		3		8
2-14	82	100		3		33
2-15	100	5		1		30

The spectra of (2-8) - (2-11) show the peaks at m/e 151, 121, 93 corresponding to [M-30-30-CO], which could arise from either the processes [M-NO$^\cdot$-CH_2O-CO] or [M-CH_2O-NO$^\cdot$-CO]. In the absence of high resolution data, it is only possible to unequivocally distinguish between the two possibilities by labelling studies. However the spectra of the 2-methyl-1,3-benzodioxans show the fragmentations [M-MeCHO-NO$^\cdot$-CO] which would tend to indicate the operation of the processes [M-CH_2O-NO$^\cdot$-CO] for the compounds (2-8) - (2-11). The extent of the retro process [M-RCHO] varies markedly for the different isomers. As a consequence, there are a number of questions to be answered concerning the nature of this reaction. Among these questions are; what is

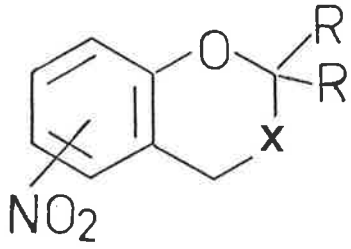
1) the origin of the entity RCHO?

2) the specificity of the reaction?

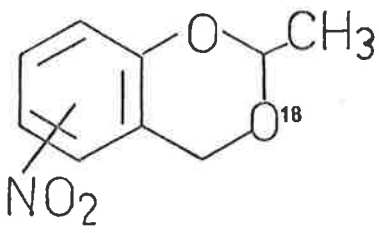
3) the role of the nitro group? and

4) the mechanism(s) of the process?

A study of the labelled derivatives listed below was carried out in order to establish the origin of the species eliminated (RCHO), and hence the specificity of the reaction.



	NO_2	R	X
2-16	5	D	^{16}O
2-17	6	D	^{16}O
2-18	7	D	^{16}O
2-19	5	H	^{18}O
2-20	6	H	^{18}O
2-21	7	H	^{18}O
2-22	5	D	^{18}O
2-23	6	D	^{18}O
2-24	7	D	^{18}O



	NO_2
2-25	5
2-26	6
2-27	7

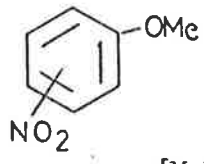
The spectra of the D_2-derivatives, (2-16) - (2-18), show the retro processes to correspond to $[M-CD_2O]$, hence demonstrating that the peaks at m/e 151 in the spectra of (2-8) - (2-11) were <u>not</u> produced by the process $[M-NO^{\cdot}]$. Furthermore, these spectra show that the two deuterium atoms are specifically eliminated from C_2, hence dismissing the possibility of any hydrogen scrambling occurring prior to or accompanying these decompositions.

The spectra of the ^{18}O-derivatives, (2-19) - (2-21), show the operation of the retro processes $[M-CH_2{}^{18}O]$. Again no atom scrambling was detected in these decompositions. The species eliminated (CH_2O) must therefore originate from the 2-3 positions, and this is confirmed by the spectra of the $D_2,{}^{18}O$-derivatives, (2-22) - (2-24) which show the decompositions $[M-CD_2{}^{18}O]$. Similarly, the spectra of the ^{18}O-2-methyl-

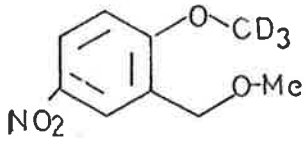
nitro-1,3-benzodioxans, (2-25) - (2-27), show the eliminations $[M-MeCH^{18}O]$.

The spectra of the unlabelled compounds, (2-8) - (2-11), show that the relative abundances of the peaks produced by the retro processes depend markedly upon the position of the nitro group. The order observed is $7\text{-}NO_2 > 5\text{-}NO_2 >> 6\text{-}NO_2 \simeq 8\text{-}NO_2$.

In order to determine the role that the nitro group plays in the retro process, it was decided to determine the relative extents of the initial aryl O-C and benzyl C-O bond cleavages by resorting to a study of the spectra of some model compounds. The compounds listed below were selected for this purpose.



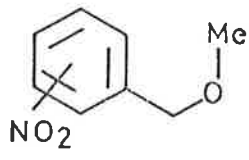
		$[M-Me^{\cdot}]^-$
(2-28)	o	10%
(2-29)	m	1%
(2-30)	p	30%



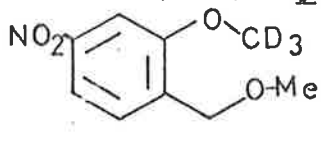
(2-34)

$M^{\cdot-}$ = 22%

$(M-CD_3)^-$ = 100%



		$[M-MeO]^-$
(2-31)	o	5%
(2-32)	m	0.5%
(2-33)	p	12%



(2-35)

$M^{\cdot-}$ = 100%

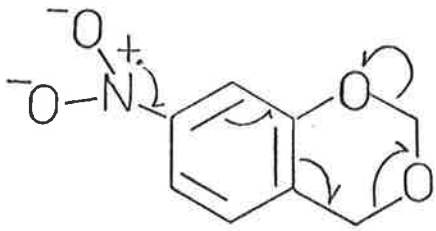
$[M-MeO^{\cdot}]^-$ = 3%

$[M-CD_3^{\cdot}]^-$ = 6%

The spectra[79] of the nitroanisoles, (2-28) - (2-30), show the abundances of the fragment ions $[M-Me^{\cdot}]^{-}$ in the order para>ortho>>meta (exact abundances measured with respect to the molecular anions (base peak) are shown above). The spectra of the nitrobenzyl methyl ethers, (2-31) - (2-33), show a similar trend for the abundances of the $[M-MeO^{\cdot}]^{-}$ ions. The results demonstrate that the position of the nitro group relative to the reaction site markedly affects the abundance of the fragment anion. The relative ease of cleavage of the aryl O-C and benzyl C-O bonds can be determined from the spectra of (2-34) and (2-35). The spectrum of (2-34) contains a molecular anion together with the fragment ion $[M-CD_3^{\cdot}]^{-}$ as the base peak. The model compound (2-35) was anticipated to show precisely the reverse situation to that of (2-34). Here the CH_2OMe group would be expected to be the more favoured fragmentation site. Contrary to expectation, the molecular anion decomposes competitively to yield the fragment ions $[M-CD_3^{\cdot}]^{-}$ and $[M-MeO^{\cdot}]^{-}$ with the relative abundances of 6 and 3%.

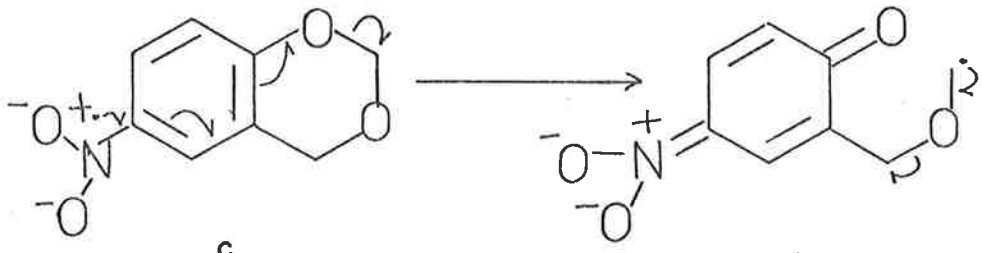
The results from the study of the model compounds indicate that the cleavage of the aryl O-C bond is favoured in systems where the nitro group is in conjugation with the phenolic oxygen, viz.for the 6- and 8- nitro compounds. If the initial cleavage of the aryl O-C bond is controlling the rate of the reaction, then the extent of the retro process should be more prominent in the 6- and 8-nitro compounds. However the spectra show more pronounced retro processes

for the 5- and 7-nitro isomers. It appears therefore that the cleavage of the second bond must be rate determining. The facile cleavage of the 1-2 bond of the 5- and 7-nitro isomers points to the operation of a low activation energy process, e.g. a concerted reaction is in b (for the case of the 7-nitro isomer).



b

On the other hand, the relatively difficult 3-4 bond cleavage of the 6- and 8- nitro isomers suggests a process of higher activation energy, e.g. a stepwise process c → d (for the case of the 6-nitro isomer).



c d

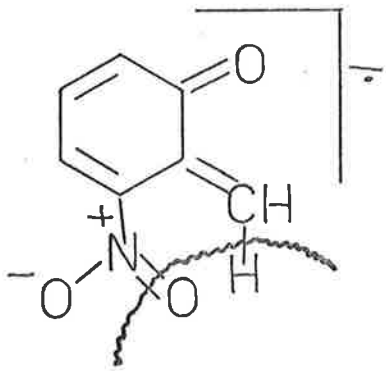
Collision-induced studies on these compounds were carried out in order to clarify the nature of the retro processes. The NIKE spectra of the compounds were measured using pressures of added collision gas (N_2) ranging from 5 x 10^{-6} - 10^{-4} torr. in the first drift region of the mass spectrometer. The abundances of the ions produced by the

collision-induced retro process [M-RCHO] were compared with those of the direct cleavage process [$M \rightarrow NO_2^-$]. The NIKE spectra of (2-8), (2-10), (2-12) and (2-14) (the 5- and 7-nitro compounds) showed that $K_{[M \rightarrow NO_2^-]} > K_{[M-RCHO]^-}$ with increasing collision gas pressure, whereas those of (2-9), (2-11), (2-13) and (2-14) (the 6- and 8-nitro compounds) showed the reverse behaviour, i.e. $K_{[M-RCHO]^-} > K_{[M \rightarrow NO_2^-]}$ with increasing collision gas pressure. If it is assumed that the rates of NO_2^- formation are comparable in these cases, then the former retro process is one of low activation energy (i.e. it resembles a rearrangement reaction[45]) and the latter process is one of higher activation energy (i.e. it resembles a direct cleavage reaction[45]). This evidence supports the earlier suggestions but it does not allow unequivocal differentiation between the concerted and stepwise mechanisms.

In order to have concrete evidence for the operation of the various mechanisms, it would be necessary to know activation energies of the retro processes together with the bond dissociation energies of the aryl O-C and benzyl C-O bonds of these compounds. However we have been unable to determine the activation energies because of the difficulty involved in the accurate measurement of the appearance potentials of the species formed by secondary electron capture.[133]

4.1. Proximity Effects

The spectra of the 5-nitro compounds, (2-8) and (2-12), contain an additional peak (at m/e 134) produced by the process [(M-RCHO)-HO·]. Its formation is diagnostic of the 5-nitro substituent and must therefore be associated with the proximity of the nitro to the reaction site. The elimination of an hydroxyl radical from the $[M-RCHO]^{\cdot}$ ion is depicted in e.



e

5. A Summary

It has been shown that the molecular anions of nitrochromans, nitro-1,3-benzodioxans and nitro-1,4-benzodioxans undergo retro-Diels-Alder reactions. The extent of the reaction is dependent upon the position of the nitro group relative to the oxygenated ring in the nitrochromans and nitro-1,3-benzodioxans. Labelling studies demonstrate the process to be specific for the nitro-1,3-benzodioxans. Furthermore it has been shown by collision excitation studies that the retro processes occurring in the 5- and 7-nitro-1,3-benzodioxans have lower activation energies than those of the 6- and 8-nitro-1,3-benzodioxans. It seems that these retro processes, although "apparently simple" and diagnostic for structural purposes, are in fact mechanistically complex.

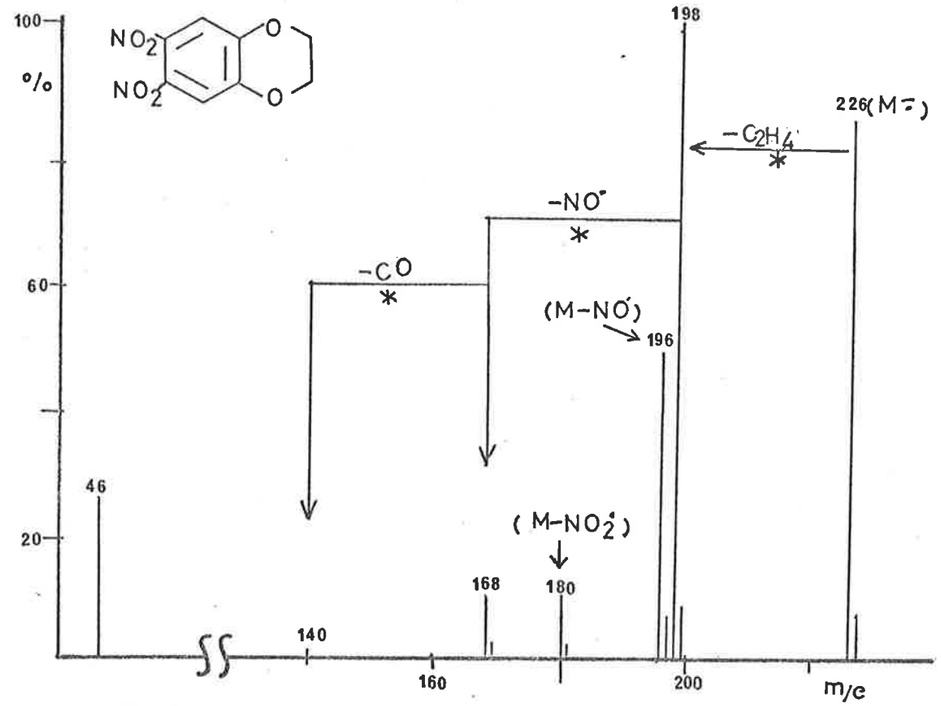

100
%
60
20
NO_2
NO_2
O
O
198
226(M⁺)
$-C_2H_4$
*
$-NO^{\cdot}$
*
-CO
*
(M-NO)
196
46
$(M-NO_2^{\cdot})$
168
180
140
160
200
m/e

Fig. (2-2)

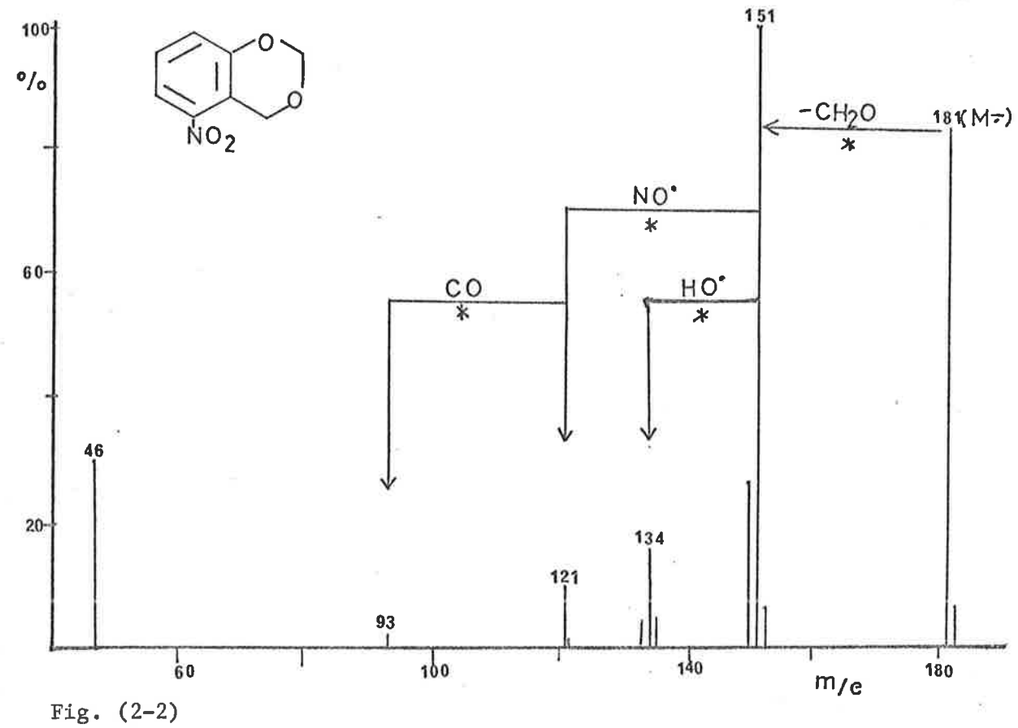

100
%
60
20
O
O
NO_2
151
$-CH_2O$
181(M⁺)
*
$NO^{\cdot}$
*
CO
*
$HO^{\cdot}$
*
46
134
121
93
60
100
140
180
m/e

Fig. (2-2)

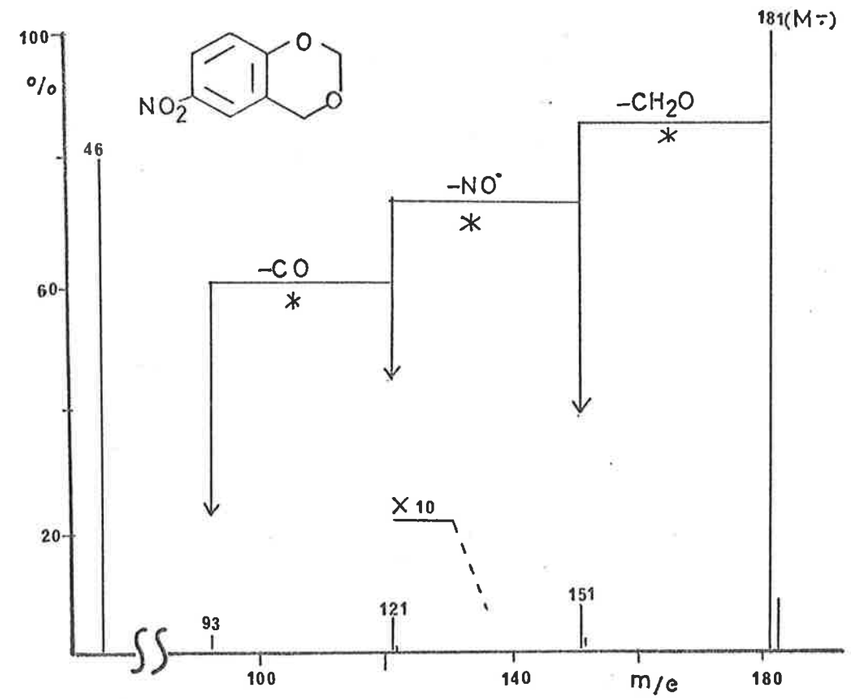

100
%
60
20
46
93
121
151
181(M⁺)
X 10
-CH2O
*
-NO°
*
-CO
*
100
140
180
m/e

Fig. (2-3)

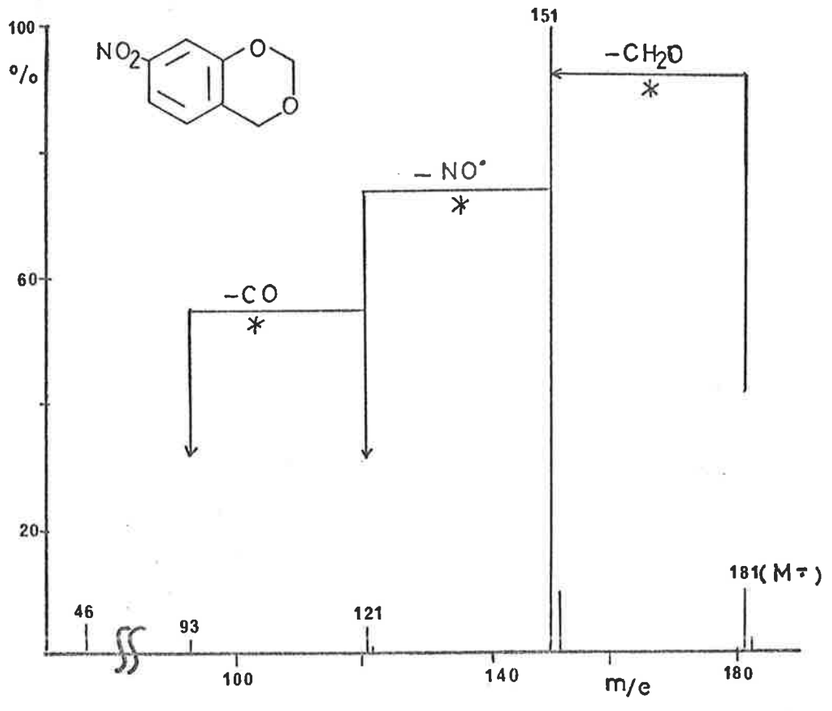
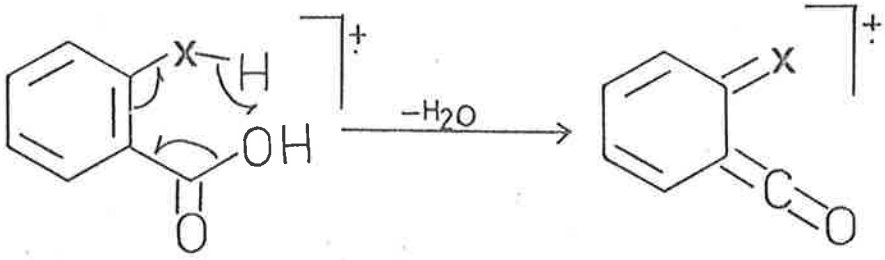

100
%
60
20
151
-CH2O
*
- NO°
*
-CO
*
181(M⁺)
46
93
121
100
140
180
m/e

Fig. (2-4)

Chapter 3. Proximity Effects in the Negative-Ion Mass Spectra of Salicylates and Anthranilates.

1. General

Proximity effects are common in the positive mode when two or more groups are adjacent to one another. Perhaps one of the most widely studied of all is that which occurs for benzoic acid derivatives.[195-199] This ortho effect is highly diagnostic and is illustrated in scheme (3-1).



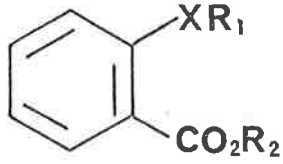
X = O, NH or S.

Scheme (3-1)

Because of the widespread occurrence of such ortho effects in positive ions, it was of interest to investigate whether similar rearrangements occur for negative ions. Negative-ion studies of salicylates, anthranilates and thiosalicylates are described in the following sections.

2. Salicylates, Anthranilates and Thiosalicylates.

The following salicylates, anthranilates and thiosalicylates were selected for a preliminary investigation.



COMPOUND	X	R_1	R_2
3-1	O	H	Me
3-2	O	H	Ph
3-3	O	H	CH_2Ph
3-4	NH	H	Ph
3-5	S	H	Me
3-6	S	H	Ph
3-7	S	D	Ph

The 70 eV spectra of compounds (3-1) - (3-7) are listed in table (3-1).‡ The spectra of (3-1) - (3-4) are very weak and contain molecular anions of low abundance together with peaks corresponding to the ions $[M-R_2OH]^-$ and $[M-R_2^{\bullet}]^-$. No metastable transitions substantiate these decompositions and consequently the peak at $[M-R_2OH]$ may be produced by a concerted process or a stepwise route, e.g. $[M-R_2^{\bullet}-HO^{\bullet}]$. The spectra of the sulphur analogues, (3-5) and

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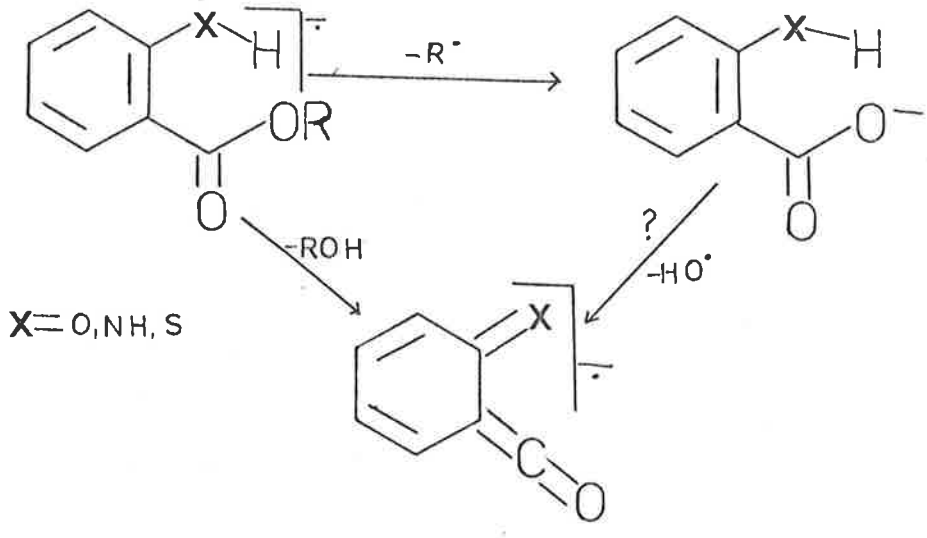
‡ All tables are placed at the end of this Chapter.

(3-6) are more intense but again contain no metastable peaks to substantiate the fragmentations. The spectrum of the methyl ester (3-5) shows no peak at a mass value equal to [M-MeOH]. In contrast, the $[M-PhOH]^{\cdot}$ ion from (3-6) forms the base peak of the spectrum. The spectrum of the deuterated derivative (3-7) contains the peak at [M-PhOD], hence demonstrating that the hydrogen attached to sulphur is specifically involved in the elimination. Nonetheless the process may be concerted [M-PhOH], or stepwise, viz. [M-H$^{\cdot}$-PhO$^{\cdot}$], [M-PhO$^{\cdot}$-H$^{\cdot}$] or [M-Ph$^{\cdot}$-HO$^{\cdot}$].

The major fragmentations of the molecular anion from (3-1 - (3-7) may be summarised in scheme (3-2).

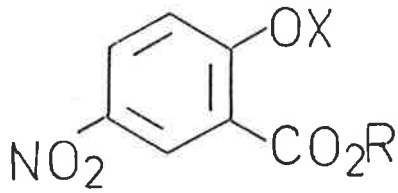


Scheme (3-2)

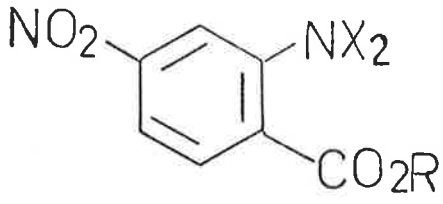
The most interesting process is [M-ROH], which may be achieved in either a concerted or stepwise manner. The stepwise process requires consecutive eliminations of R$^{\cdot}$ and an hydroxyl radical from the molecular anion. Such eliminations are not favourable on energetic grounds and this has been demonstrated by the negative-ion spectra of anthraquinone acetates.[78] On the other hand the molecular anion may decompose in a one-step process but there is no evidence to substantiate such a process. Consequently more intense spectra containing metastable peaks are required in order to determine the decomposition pathway(s) of the molecular anions. The nitro derivatives of the above compounds are thus appropriate for further investigations.

3. 5-Nitrosalicylates and 4-Nitroanthranilates.

The nitrosalicylates and nitroanthranilates produce intense negative-ion spectra containing metastable peaks. The nitro group which enhances the stability of the molecular anion must be isolated from the reaction site because of the possibility of ortho eliminations taking place between the nitro group and another substituent. As a consequence, the following compounds were chosen for this study.



	X	R
3- 8	H	Me
3- 9	D	Me
3-10	H	Ph
3-11	D	Ph
3-12	Me	Ph
3-13	H	p$MeOC_6H_4$
3-14	H	pMeC_6H_4
3-15	H	pClC_6H_4
3-16	H	p$MeCOC_6H_4$
3-17	H	pNO_2



	X	R
3-18	H	Me
3-19	H	Ph
3-20	D	Ph

The spectra (fig. 3-1 and 3-2) of the methyl and phenyl esters (3-8 and 3-10) are characteristic of the compounds in this series. The spectrum (fig. 3-1) of the methyl ester (3-8) shows the major decompositions of the molecular anion corresponding to $[M-Me^{\cdot}-CO_2]$ and $[M-MeCO^{\cdot}]$. These eliminations are characteristic of the ester group.[78,132] Furthermore, the spectrum also contains a large $[M-H^{\cdot}]^-$ fragment ion, an ion frequently observed in the spectra of phenols.[79] The peak at m/e 46 (NO_2^-) demonstrates the presence of the nitro group. The loss of MeOH from the molecular anion to yield a small peak at m/e 165 is substantiated by the appropriate metastable transition. The $[M-MeOH]^-$ ion decomposes further by two consecutive losses of carbon monoxide.

The spectrum (fig. 3-2) of the phenyl ester (3-10) is much simpler than that of the methyl ester (3-8). In contrast to (3-8),

the molecular anion of (3-10) fragments by loss of PhOH to furnish the base peak in the spectrum. The other characteristic eliminations, [M-Ph$^{\cdot}$], [M$\rightarrow$PhO^{-}] and [M$\rightarrow$NO$_2^{-}$] are present to a lesser extent. The spectra of the nitroanthranilates (3-18, 3-19) exhibit similar decompositions and are recorded in table (3-2).

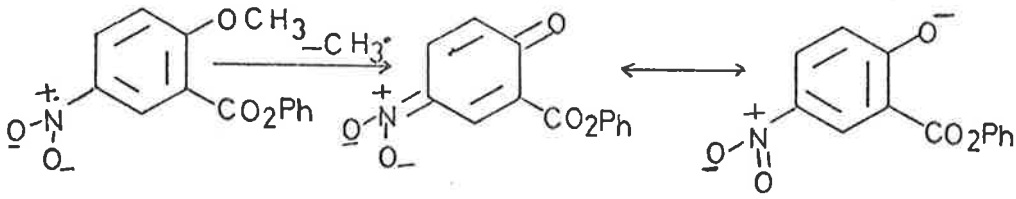
3.1. The Process [M-ROH]

The occurrence of the process [M-ROH] in the spectra of the nitrosalicylates and nitroanthranilates has been substantiated by the appropriate metastable transition in all cases. The spectra of the deuterated derivatives (3-9, 3-11, 3-20), show the operation of the process [M-ROD], hence demonstrating that the elimination specifically involves the hydroxyl or amino hydrogens.

If the hydroxyl hydrogen is replaced by a substituent, the ortho elimination does not occur. This is shown by the spectrum (table 3-2) of phenyl 2-methoxy-5-nitrobenzoate (3-12) which contains the molecular anion and a major fragment ion (base peak) due to loss of Me$^{\cdot}$. No peak is observed for the ortho elimination.

The large abundance of the [M-Me$^{\cdot}$]$^{-}$ ion together with the lack of other obvious competing fragmentations affords some indication of the relative ease of this process. It is probable that the driving force for this decomposition is provided to some extent by the resonance

stabilisation of the product anion as depicted in scheme (3-3).



Scheme (3-3)

The complete absence of the rearrangement process [M-PhOMe] is expected in view of the occurrence of the competing direct cleavage reaction. Furthermore, this rearrangement process, in contrast to the elimination of PhOH from the molecular anion of (3-10), will be even less favoured in terms of geometrical and perhaps electronic requirements for the reaction, as it is well known that the hydrogen atom migrates faster than a methyl group and can form bonds in all directions.[54]

It is interesting to note that the molecular anions from the corresponding acids do not undergo the ortho elimination [M-H_2O]. For example the molecular anion of 5-nitrosalicylic acid decomposes largely by the processes [M-H$^{\bullet}$] and [M-$\dot{O}$H] which are characteristic of a substituted m-nitrobenzoic acid.[79] In a further attempt to investigate the nature of the ortho elimination, a study of the effect of varying the substituent on the aryl group was undertaken.

3.2. The Hammett Plots

For the reaction M $\longrightarrow$ A, the Hammett equation[200] has been modified by McLafferty and Bursey[201,202] into the form

$$\log {}^{z}/zo = \sigma\rho$$

where z = [A]/[M] and z = zo when the substituent = H, [A] is the intensity of the daughter ion and [M] is the intensity of the parent ion. The theoretical basis of this approach depends on the QET[48-52] of mass spectra. Initially z was equated to k (rate constant for the reaction M $\longrightarrow$ A) and the results were rationalised in terms of the effect of the substituent upon the rate of the reaction. However it was shown[203] later that z depends not only upon the rate of the reaction concern but also upon the rates of all other competing reactions, and the proportion of both parent and daughter ions which are able to fragment. In spite of its limitations, this approach has been widely used in positive-ion mass spectrometry for the study of substituent effects on ion decompositions. The applications and limitations of the method have been reviewed.[202,204] This approach has also been recently applied in negative-ion mass spectrometry.[132,133]

We have applied the method in an attempt to study the effect of substituents on the relative abundances of fragment anions produced by simple cleavage and rearrangement reactions. Since the ortho process is most prominent in the phenyl esters (e.g. 3-10),

the derivatives ((3-10, (3-12) - (3-17)) were chosen for study. The partial negative-ion spectra of those compounds were recorded in table (3-3).

The plots of the log ($^{z}/_{zo}$) values against the corresponding Hammett sigma values for the simple cleavage process and for the ortho rearrangement reaction for compounds ((3-10), (3-12) - (3-17)) are shown in fig. (3-3).

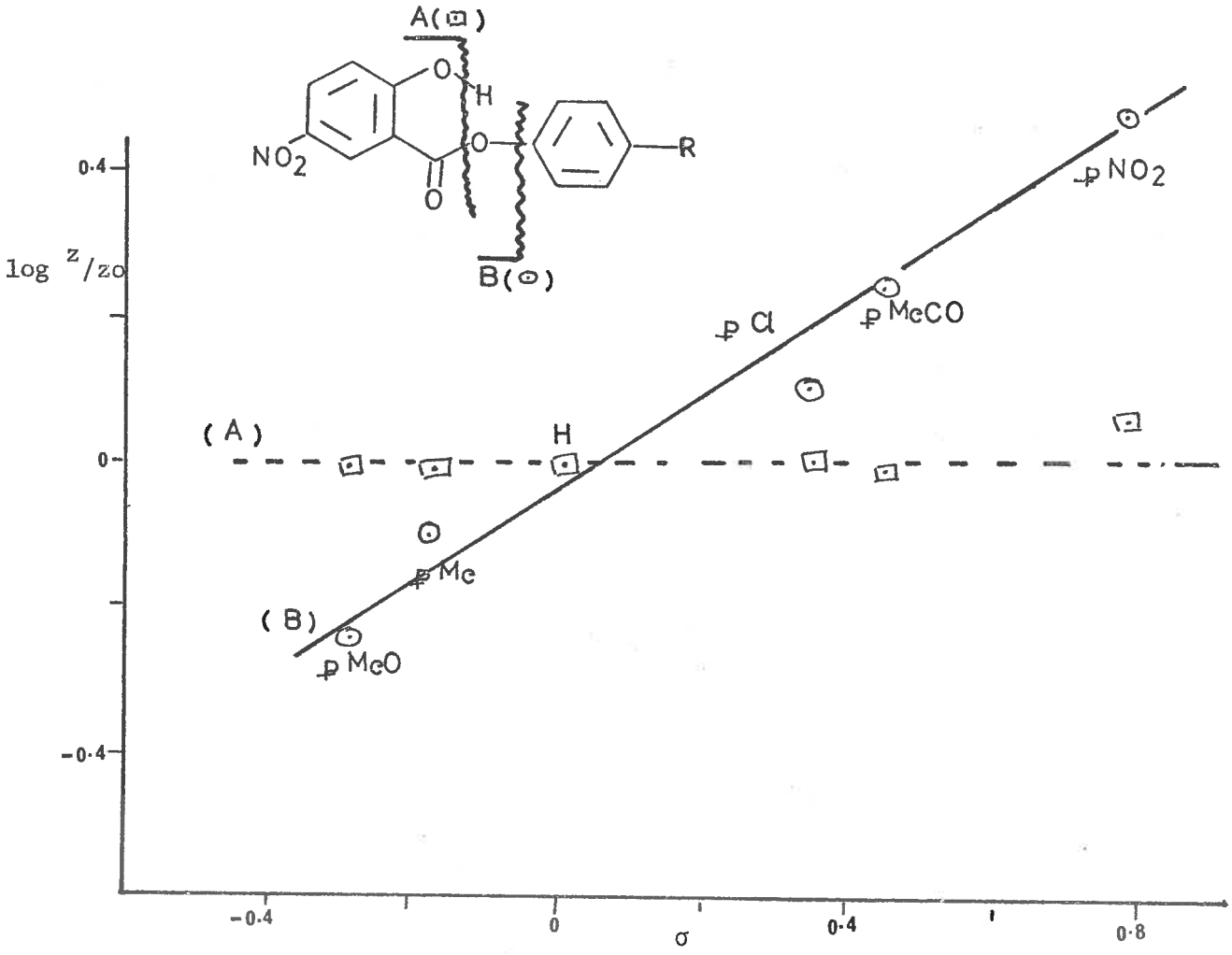
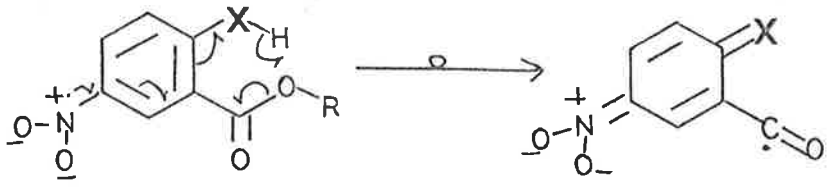


Fig. (3-3)

The slope of the plot from the simple cleavage process (B) demonstrates the effect of the substituents on the decomposition. Its value ($\rho = 0.75 \pm 0.2$) is within the range (-1.6 to 5.0) of that observed for simple cleavage reactions in earlier studies.[132,133] On the other hand, the ortho rearrangement process has a ρ value of zero, hence indicating that the process is independent of the nature of the substituents.

3.3. The Mechanism for the Process [M-ROH].

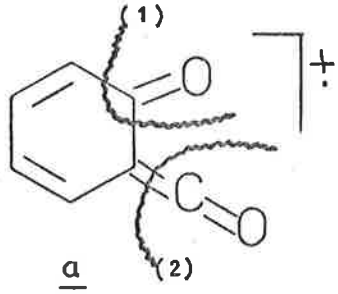
We have shown that the ortho elimination is a rearrangement reaction which can be best represented by the general process depicted in scheme (3-3).



Scheme (3-3)

The radical anion $[M-ROH]^{\cdot -}$ from the salicylates decomposes by consecutive losses of two units of carbon monoxide. The origins of these losses are not known even though it appears from scheme (3-3) that the loss of carbon monoxide should involve the carbonyl unit of the original ester group. It is of interest in this context to describe the behaviour of salicylates in the positive mode. The molecular cation of salicylic acid undergoes ortho elimination

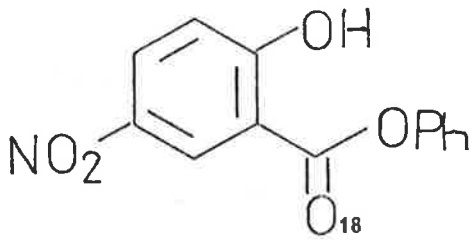
of water to give a cation a which fragments by consecutive losses of two molecules of carbon monoxide.



a

Occolowitz[205] has shown by ^{14}C labelling that the first loss of carbon monoxide involves a ring carbon (see a).

We have synthesed the ^{18}O-phenyl ester (3-21) in order to determine the origins of the losses of carbon monoxide in the negative mode.

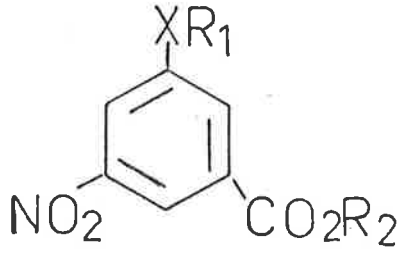


(3-21)

The negative-ion spectrum of (3-21) shows the decompositions [M-PhOH-C^{18}O-CO], hence demonstrating that the first loss of carbon monoxide originates from the carbonyl of the original ester group. It also shows that the fragment ions [M-ROH] decompose differently in the positive and negative modes.

4. 3-Hydroxy-5-nitrobenzoates and 3-Amino-5-nitrobenzoates

In continuing our investigations on ortho effects, it was necessary to examine the decompositions of compounds where all three substituents are remote from one another. The following compounds were selected for this study.



	X	R_1	R_2
3-22	O	H	Me
3-23	O	H	Ph
3-24	O	D	Ph
3-25	NH	H	Me
3-26	NH	H	Ph
3-27	NH	D	Ph

The spectra of (3-22) and (3-23) are illustrated in figs. (3-4) and (3-5) while those of (3-25) and (3-26) are listed in table (3-4).

The spectrum of the methyl ester (3-22) is characterised by the molecular anion (base peak), a large [M-1] peak, and a number of

other fragment ions of low abundance. Analyses of these decompositions show that they are characteristic of the presence of three isolated substituents, viz. nitro ([M-NO$^{\bullet}$], [M$\rightarrow$NO$_2^-$], [M-HNO$_2$]);[79] methoxycarbonyl, ([M-Me-CO$_2$]);[78] and hydroxyl, ([M-H$^{\bullet}$]).[79] In contrast to the spectrum (fig. 3-1) of methyl nitrosalicylate (3-8), no peak corresponding to the elimination [M-ROH] was detected.

The spectrum (fig. 3-5) of the phenyl ester (3-23) contains the molecular anion (base peak), a large [M-H$^{\bullet}$] peak and a small peak at m/e 165 corresponding to the [M-PhOH]$^{\bullet-}$ ion. The decomposition leading to the formation of the [M-PhOH]$^{\bullet-}$ ion, although unexpected, is substantiated by a metastable transition. This process corresponds to [M-PhOD] in the spectrum the deuterated derivative (3-24), hence demonstrating that the hydrogen atom involved in the elimination originates specifically from the hydroxyl function.

The amino analogues ((3-25) - (3-27)) exhibit similar decompositions to the hydroxy esters although there are some minor differences. In particular, the methyl ester (3-25) affords an intense molecular anion (base peak) and a small [M-MeCO$_2^{\bullet}$]$^-$ ion. No peak corresponding to the [M-MeOH] process was detected. The phenyl esters (3-26 and 3-27) show the major decompositions [M-PhOH-CO].

4.1. The Process [M-PhOH].

There are two possible mechanisms for the elimination of PhOH in compounds (3-23) and (3-26), viz.

1) valence isomerism, and

2) simultaneous two-stage cleavage reactions.

Valence isomerism of the benzenoid system to give the corresponding ortho compound would explain the occurrence of the process. However no example of valence isomerism of molecular anions of substituted benzenoid systems has yet been observed.

Simultaneous two-stage decompositions, although uncommon, have been detected in some disubstituted benzenes[45] (see Chapt. 1, section 3.4.8). An example is the loss of HCN from the molecular anion of p-cyanobenzoic acid.[45]

Bowie and Hart[45] have demonstrated that it is possible to distinguish between a rearrangement reaction and a two-stage cleavage process or so called "apparent rearrangement" reaction by studies of collision-induced dissociations (see Chapt. 1, section 3.4.8). They have shown that the relative rate of an "apparent rearrangement" reaction increases with increasing internal energy of the decomposing anion (i.e. with increase pressure of the added collision gas) while that of a competing rearrangement process decreases.

The compounds (3-10 and 3-23) were initially selected for this investigation in view of the large difference in the elimination of PhOH from the molecular anions of these compounds. The NIKE spectra of these compounds have been measured using pressures of added collision gas (N_2) ranging from 1 x 10^{-6} - 10^{-4} torr. in the first drift region of the mass spectrometer. The plots of the relative abundances of the collision-induced peaks for the process [M-PhOH] against the pressure of the pressure of collision gas are shown in fig. (3-6).

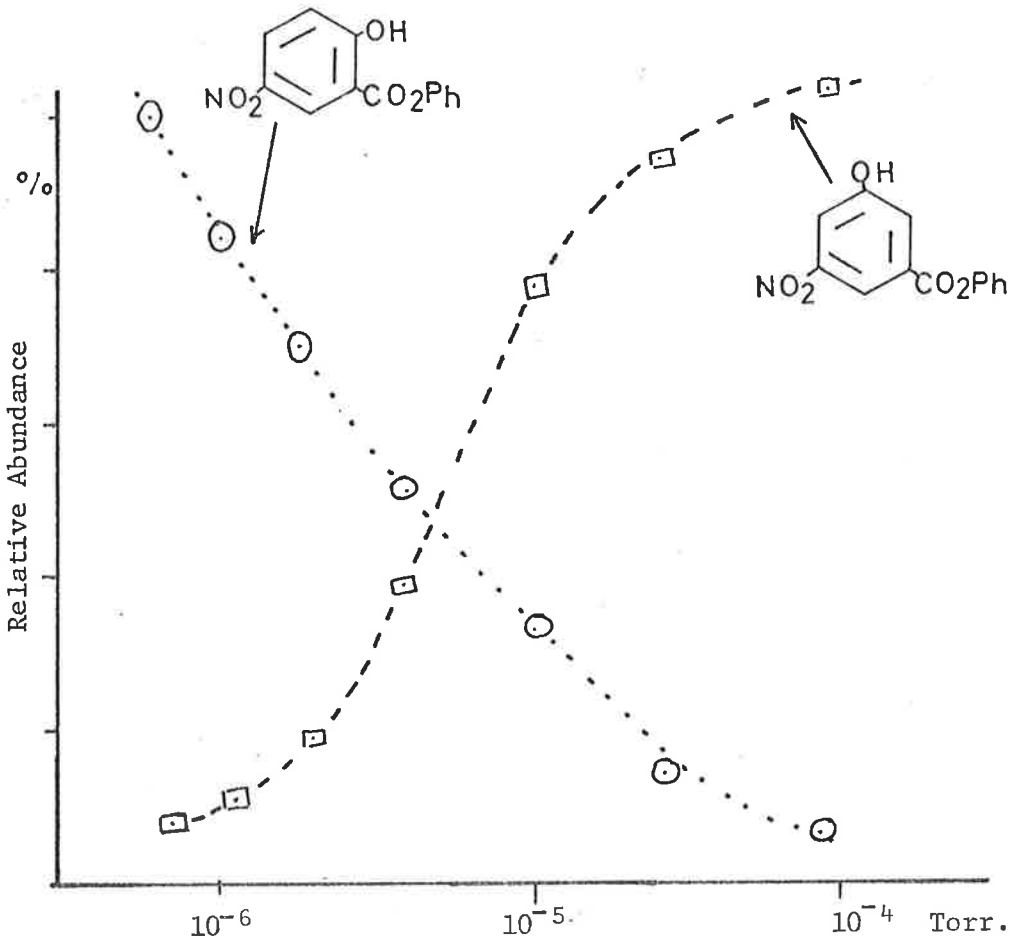


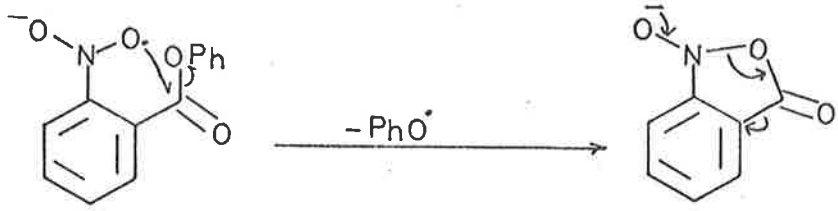
Fig. (3-6) Variation of the relative abundance of the collision-induced $[M-PhOH]^-$ ion for 3-10 and 3-23 with collision gas (N_2) pressure.

The results show a rapid decrease in the abundance of the ion for the ortho rearrangement (for 3-10), and a dramatic enhancement of the abundance of the ion from (3-23) with increasing collision pressure. The latter behaviour is characteristic of a direct cleavage reaction, thus suggesting the operation of a simultaneous two-stage cleavage reaction rather than a rearrangement reaction. The evidence does not indicate the operation of the valence isomerism mechanism.

Collision excitation studies have also been carried out with compounds (3-8), (3-18), (3-19) and (3-26). The results are similar to those from compounds (3-10) and (3-23). The nitrosalicylate (3-8) and nitroanthranilates (3-18, 3-19) show a similar decrease in the abundance of the collision peak corresponding to the process [M-ROH] with increasing pressure of the collision gas. On the other hand, the nitrobenzoate (3-26) exhibits the reverse effect as observed for (3-23).

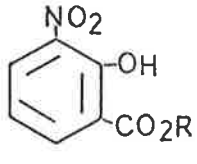
5. Competitive Ortho Effects

The proximity of the nitro group to the fragmenting centre has frequently caused drastic changes in the decomposition pathway of many anions. An elegant example is illustrated by the molecular anion of phenyl o-nitrobenzoate which undergoes the processes $[M-PhO^{\cdot}-CO_2]$[132] as depicted in scheme (3-4). These decompositions are entirely different from those of the meta and para nitro isomers.

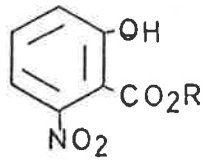


Scheme (3-4)

Since the proximity of the nitro group usually affects the "normal" reaction pathway, it would therefore be interesting to examine whether such effects occur in the nitrosalicylates and nitroanthranilates. The compounds appropriate for this study are listed below.



	R
3-28	Me
3-29	Ph



	R
3-30	Me
3-31	Ph

The molecular anions of the 3-nitrosalicylates (3-28 and 3-29) may decompose by two competing ortho processes, viz. [M-ROH] and [M-$\dot{O}$H]. The latter process is the major decomposition for the molecular anion of o-nitrophenol.[79] In addition, the molecular anions may undergo the characteristic fragmentations of the various substituents. The two possible ortho eliminations from the molecular anions of the 6-nitrosalicylates (3-30, 3-31) are [M-ROH] and [M-PhO$^{\bullet}$].

The spectra of (3-28) and (3-30) are listed in table (3-5) while those of (3-29) and (3-31) are illustrated in figs. (3-7) and (3-8).

The spectrum of (3-28) contains the molecular anion (base peak) which undergoes the major competitive decompositions [M-$\dot{O}$H] (m/e 180) and [M-NO$^{\bullet}$] (m/e 167) and a minor decomposition [M-Me$^{\bullet}$] (m/e 182). There is also a large [M-H$^{\bullet}$] peak which is characteristic of phenols.[79] The ortho process [M-MeOH], is absent, in marked contrast to that observed for (3-8).

The spectrum (fig. 3-7) of the phenyl ester (3-29) shows similar decompositions as observed for the methyl ester (3-28), i.e. the molecular anion decomposes competitively by the processes [M-$\dot{O}$H], [M-NO$^{\bullet}$] and [M-Ph$^{\bullet}$]. In addition, the molecular anion undergoes the characteristic ortho eliminations [M-PhOH-CO]. The ortho processes

[M-$\dot{O}$H] and [M-PhOH] appear to occur to a comparable extent.

The spectrum of (3-30) again shows the usual decompositions [M-Me$^{\cdot}$] and [M-H$^{\cdot}$]. However, in contrast to its isomeric ester (3-28), the major elimination corresponds to the ortho process [M-MeOH]. The [M-MeOH]$^{\cdot}$ ion decomposes further by loss of carbon dioxide to yield a peak at m/e 121. This unusual decomposition is substantiated by metastable defocusing in the first drift region of the mass spectrometer. It is noted that the other anticipated ortho process [M-MeO$^{\cdot}$] occurs to a substantial extent.

The spectrum (fig. 3-8) of the isomeric phenyl ester (3-31) shows two major peaks at m/e 165 and 166, which are produced by the processes [M-PhOH] and [M-PhO$^{\cdot}$] respectively. The anion at m/e 166 decomposes further by competitive eliminations of carbon monoxide and carbon dioxide. The loss of carbon dioxide from this ion appears to indicate that the process [M-PhO$^{\cdot}$] may be operating to some extent by the mechanism depicted in scheme (3-4). Again as in the corresponding methyl ester (3-30), the [M-PhOH]$^{\cdot}$ ion fragments by an unusual loss of carbon dioxide.

6. Summary

The negative-ion mass spectra of methyl and phenyl 5-nitrosalicylates and 4-nitroanthranilates show intense [M-ROH] peaks which are produced by rearrangement processes.

Methyl 3-hydroxy- and 3-amino-5-nitrobenzoate show fragmentations through each substituent. The corresponding phenyl esters eliminate PhOH from the respective molecular anions by simultaneous 'two-stage cleavage reactions'.

Competitive ortho rearrangements occur when the nitro group is adjacent to either the ester or hydroxyl substituent of the methyl or phenyl salicylates.

Table (3-1). Negative ion mass spectra of (3-1) - (3-7)

(3-1)	m/e	92	120	121	136	137	138	152	($M^{-\cdot}$)		
	%	2	100	8	5	22	2	2			
(3-2)	m/e	92	93	120	121	137	214	($M^{-\cdot}$)			
	%	3	3	100	8	8	4				
(3-3)	m/e	92	120	137	138	238	($M^{-\cdot}$)				
	%	2	5	100	8	2					
(3-4)	m/e	92	93	118	119	120	136	212	213	($M^{-\cdot}$)	
	%	3	15	16	100	8	28	5	3		
(3-5)	m/e	108	152	167	($M^{-\cdot}$)	168	169				
	%	1	1	100		8	5				
(3-6)	m/e	93	108	136	138	139	153	229	230	($M^{-\cdot}$)	
	%	3	5	100	8	4	3	19	19		
(3-7)	m/e	93	108	136	137	138	139	140	154	239	231 ($M^{-\cdot}$)
	%	3	5	100	8	70	7	3	3	18	20

Table (3-2) Negative-ion spectra of (3-12), (3-18), (3-19)

(3-12)	m/e	46	93	137	258	259	260	273	($M^{\bar{\cdot}}$)	274
	%	0.1	2	3	100	15	2	23		3
(3-18)	m/e	46	137	164	181	196	($M^{\bar{\cdot}}$)	197		
	%	16	3	3	3	100		10		
(3-19)	m/e	46	136	164	165	258	($M^{\bar{\cdot}}$)	259		
	%	3	3	60	6	100		16		

Table (3-3)

Compound	Substit.	$M^{\bar{\cdot}}$	m/e 182	m/e 165
(3-13)	p-MeO	0.4	1.8	100
(3-14)	p-Me	0.4	1.4	100
(3-10)	p-H	0.4	4.0	100
(3-15)	p-Cl	0.3	1.8	100
(3-16)	p-$COCH_3$	0.3	2.3	100
(3-17)	p-NO_2	0.8	6.5	100

Table (3-4). Negative-ion spectra of (3-25) and (3-26)

(3-25)	m/e	46	136	197	$(M^{\bar{\cdot}})$	198		
	%	10	2	100		10		
(3-26)	m/e	46	93	136	164	258	$(M^{\bar{\cdot}})$	259
	%	9	4	1	2	100		17

Table (3-5). Negative-ion spectra of (3-28) and (3-30)

(3-28)	m/e	46	120	135	138	139	150	166	167	168
	%	1	2	5	22	2	3	3	25	3
		179	180	181	182	196	197	$(M^{\bar{\cdot}})$	198	
		5	78	8	3	40	100		10	
(3-30)	m/e	46	121	122	135	138	165	166	182	196
		5	26	3	2	1	100	25	3	21
		197	$(M^{\bar{\cdot}})$	198						
		25		3						

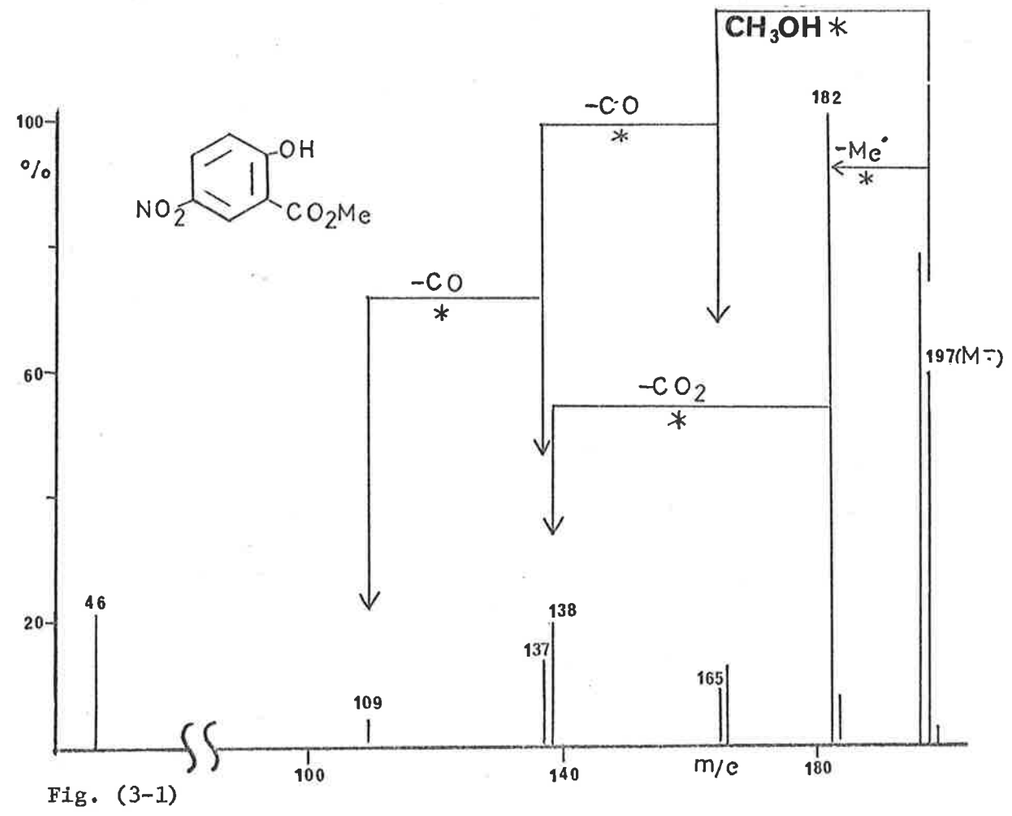

100
%
60
20
OH
NO2
CO2Me
CH3OH*
-CO
*
182
-Me·
*
-CO
*
197(M·)
-CO2
*
46
138
137
165
109
100
140
m/e
180

Fig. (3-1)

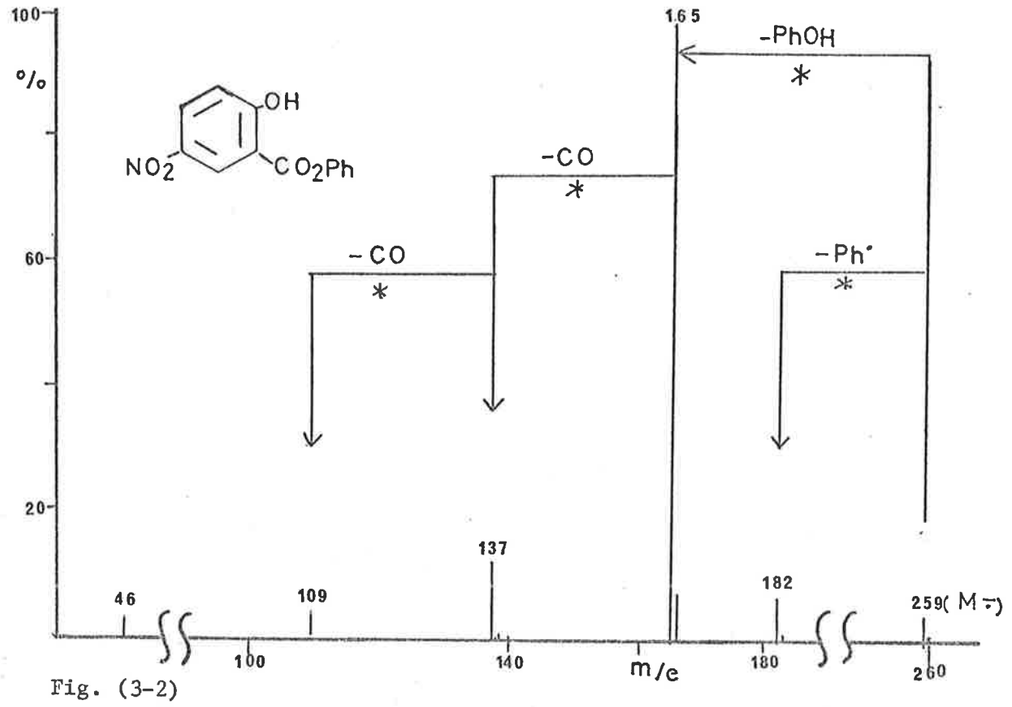

100
%
60
20
OH
NO2
CO2Ph
165
-PhOH
*
-CO
*
-CO
*
-Ph·
*
137
46
109
182
259(M·)
100
140
m/e
180
260

Fig. (3-2)

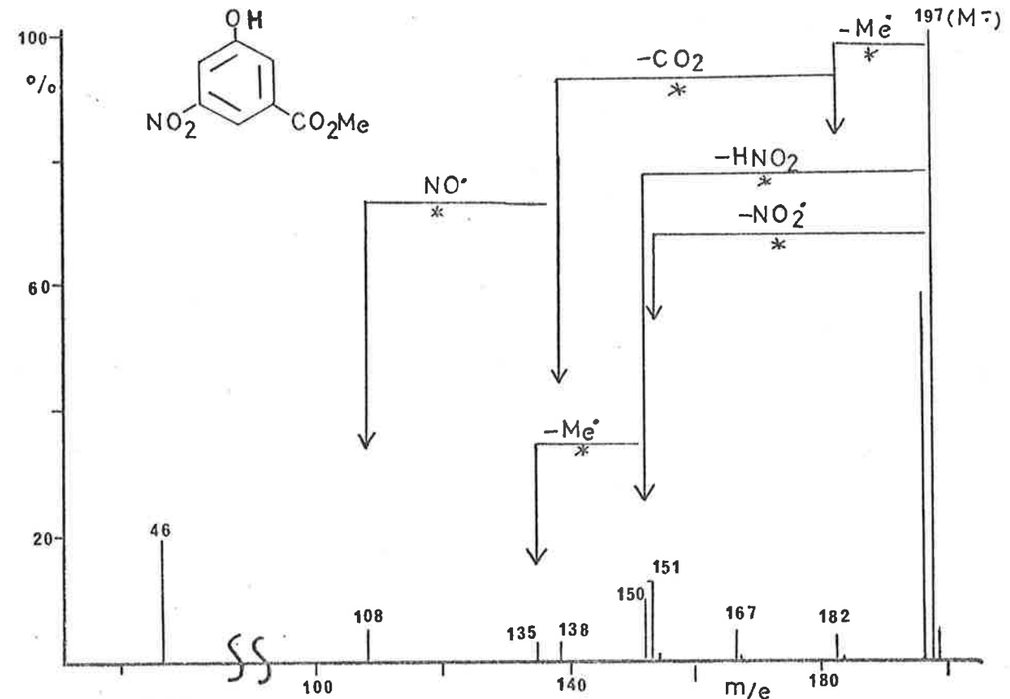

OH
NO2
CO2Me
100
%
60
20
-Me·
197(M+·)
-CO2
-HNO2
NO·
-NO2·
-Me·
46
108
135
138
150
151
167
182
100
140
m/e
180

Fig. (3-4)

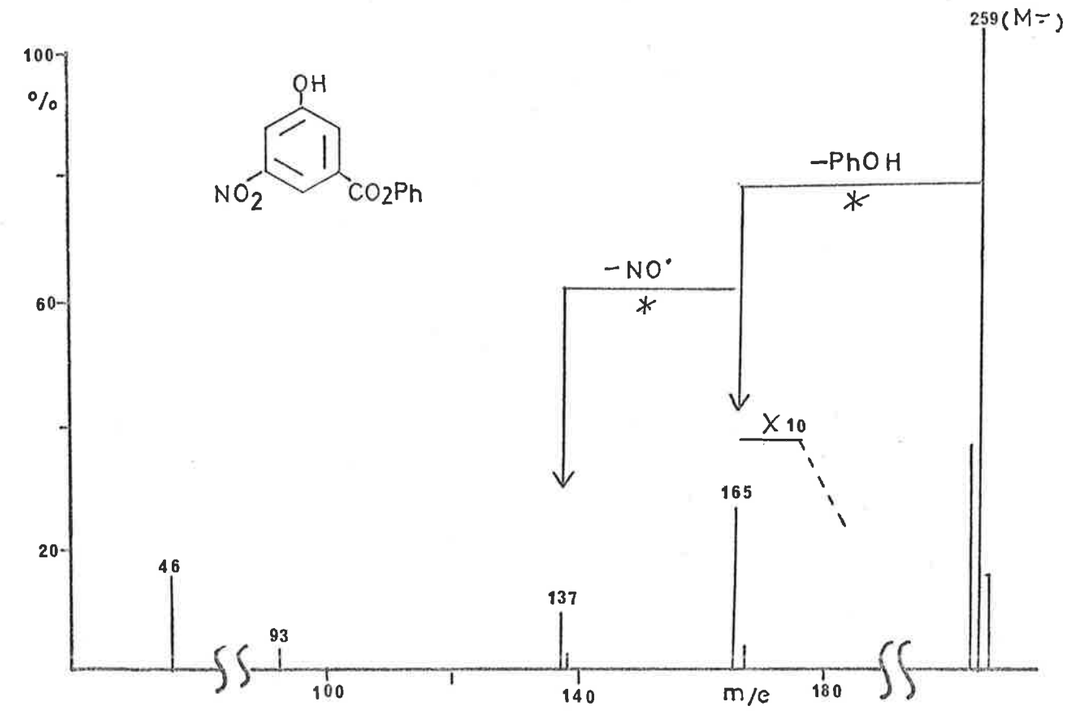

259(M+·)
100
%
OH
NO2
CO2Ph
-PhOH
-NO·
X10
165
60
20
46
137
93
100
140
m/e
180

Fig. (3-5)

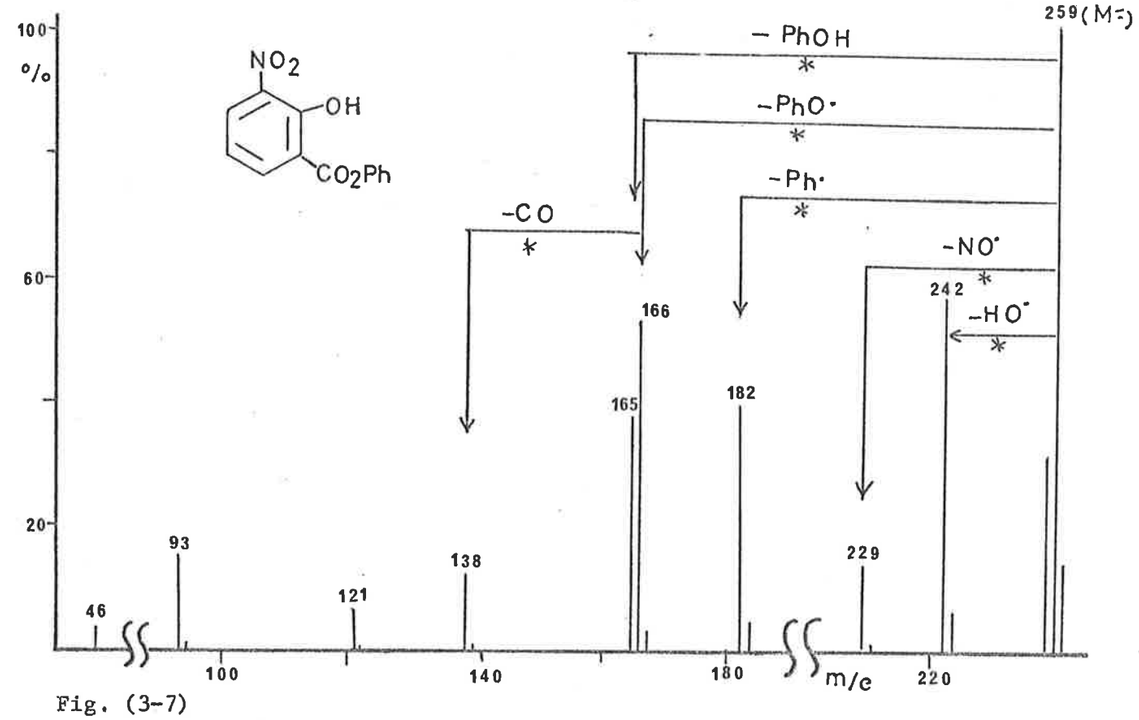

100
%
60
20
NO2
OH
CO2Ph
259(M+)
- PhOH
-PhO·
-Ph·
-CO
-NO·
242
-HO·
166
165
182
229
93
121
138
46
100
140
180
m/e
220

Fig. (3-7)

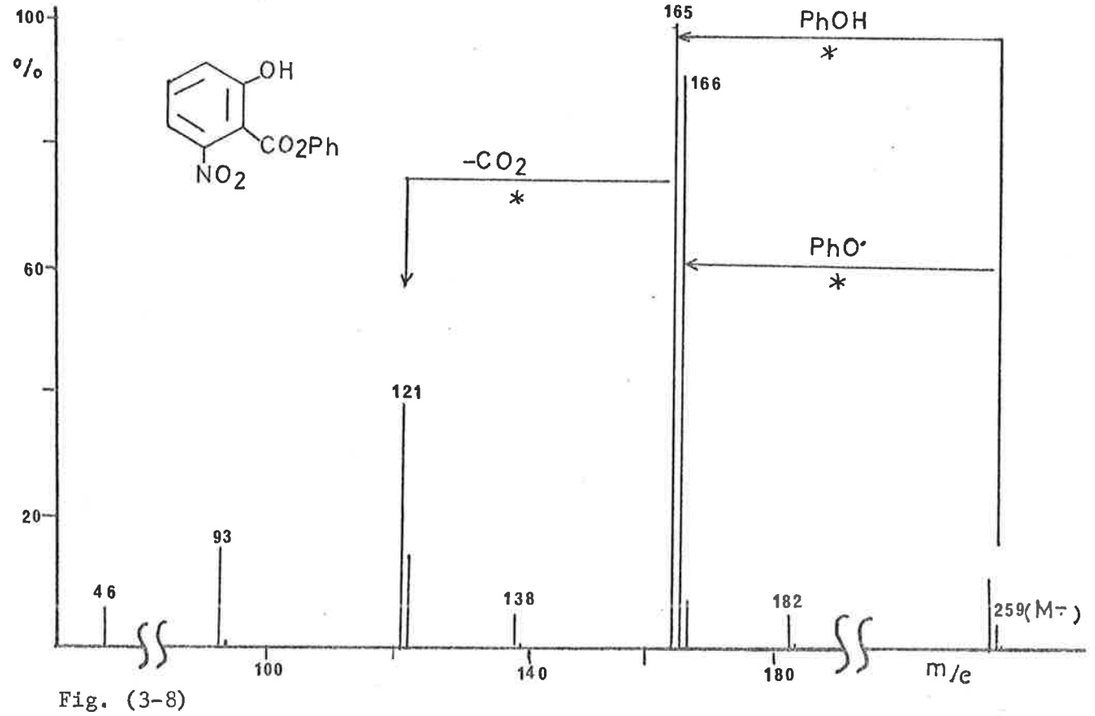
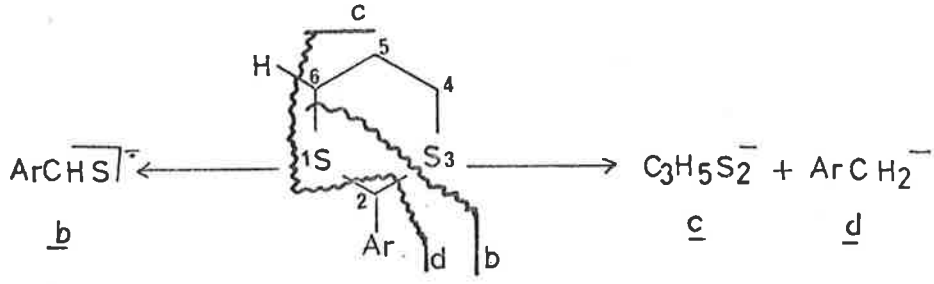

100
%
60
20
OH
CO2Ph
NO2
165
PhOH
166
-CO2
PhO·
121
93
46
138
182
259(M+)
100
140
180
m/e

Fig. (3-8)

Chapter 4. Negative-Ion Spectra of 2-Aryl-1,3-oxathianes and 1,3-Dioxans.

1. Introduction

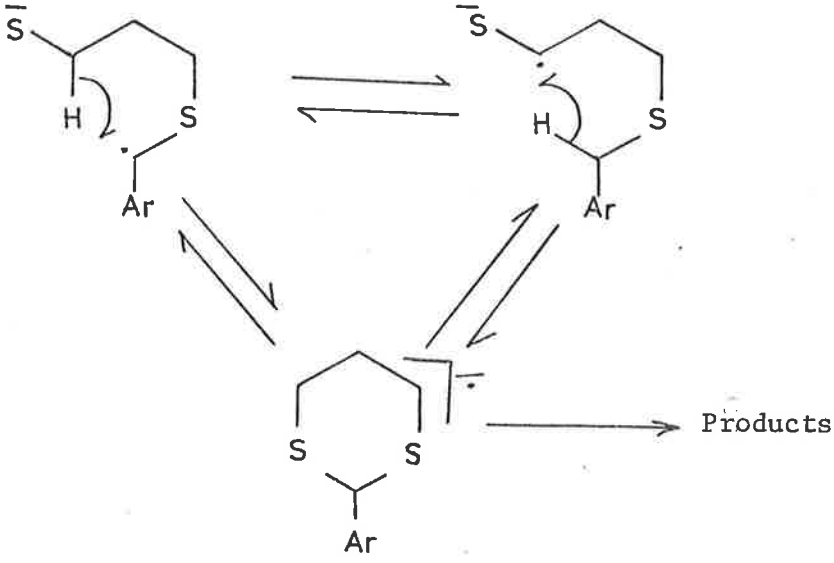
Aryl-1,3-dithianes have been investigated in detail by Bowie and White.[206] In general these compounds yield molecular anions which undergo the fragmentations indicated in a.



a

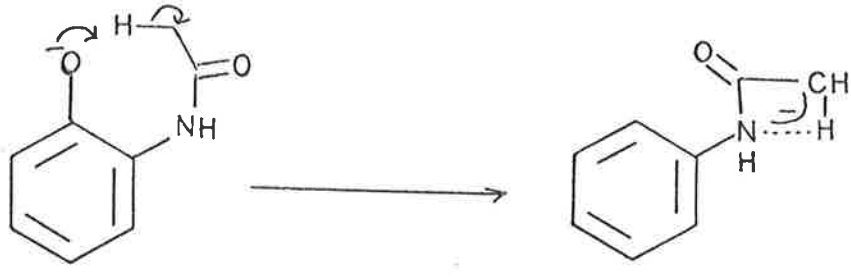
They have shown that the fragment ions b and c (when Ar = Ph or p-nitrophenyl), and d (when Ar = p-nitrophenyl) were produced after almost complete equilibration of the five hydrogens occupying the 2, 4 and 6 positions. To explain this phenomenon, it was proposed that the molecular anion undergoes initial cleavage of the C-S bond, followed by a series of hydrogen transfers through six-membered transition states prior to fragmentation (see scheme (4-1)).

Few examples of hydrogen-scrambling processes are known in negative-ion mass spectrometry. Indeed the first hydrogen scrambling process for negative ions was reported in some organometallic systems



Scheme (4-1)

by Bowie and Nussey[179] in 1970. The next example of this phenomenon is provided by the negative-ion spectrum of o-nitroacetanilide.[79] The molecular anion of this compound decomposes by loss of NO$^{\bullet}$ to give an anion e which eliminates ketene after equilibration of the three hydrogens depicted in f.



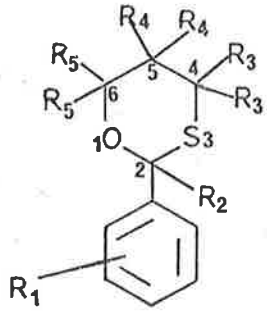
e f

There are several reasons why hydrogen scrambling in any particular system should be investigated as thoroughly as possible. A knowledge of the nature of the scrambling process is important in the interpretation of the mass spectrum. Perhaps more important is the fact that many fragmentation mechanisms are determined with the help of labelling studies. As a consequence, unless the positional identity of the label(s) in a particular system prior to fragmentation is known, incorrect conclusions may be obtained from such data. Hence a study of the nature of hydrogen scrambling is not only necessary, but also challenging from a mechanistic view point. Such a study may yield information on the ion structure, energetics and lifetimes of the decomposing ions. However the study of hydrogen scrambling may not always be possible for negative ions, e.g. scrambling in molecular anions which do not fragment, or loss of a fragment containing no hydrogens.

The following discussion describes the nature of hydrogen scrambling of those systems where the sulphur atoms of the dithiane system have been successively replaced by oxygen atoms. The compounds selected for this study were the 2-aryl-1,3-oxathianes and 2-aryl-1,3-dioxans.

2. 2-(nitrophenyl)-1,3-oxathianes.

The oxathianes synthesised for this study are listed below.



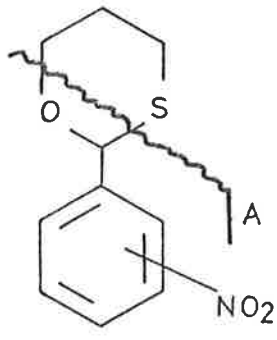
Compound	R_1	R_2	R_3	R_4	R_5	X
4-1	p-NO_2	H	H	H	H	^{16}O
4-2	p-NO_2	H	H	D	H	^{16}O
4-3	p-NO_2	H	H	H	D	^{16}O
4-4	p-NO_2	H	D	H	D	^{16}O
4-5	m-NO_2	H	H	H	H	^{16}O
4-6	m-NO_2	D	H	H	H	^{16}O
4-7	o-NO_2	H	H	H	H	^{16}O
4-8	o-NO_2	H	H	H	H	^{18}O
4-9	o-NO_2	D	H	H	H	^{16}O
4-10	o-NO_2	H	H	D	H	^{16}O
4-11	o-NO_2	H	H	H	D	^{16}O
4-12	o-NO_2	H	D	H	D	^{16}O

The spectra of the unlabelled oxathianes (4-1, 4-5 and 4-7) all illustrated in figs. (4-1) - (4-3), while the spectra of the labelled derivatives are listed in table (4-1).†

These spectra are intense and contain pronounced metastable peaks. The spectra of the m- and p-isomers are essentially the same except for variations in the relative abundances of particular peaks. In contrast, that of the o-isomer contains many more peaks. Consequently, all three isomers can be differentiated by negative-ion mass spectrometry.

2.1. Process (A) [M-C_3H_6S].

This process is common to all three isomers and is illustrated in g.



g

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† Table (4-1) is placed at the end of this Chapter.

The fragment ion A (m/e 151) produced by this process constitutes the base peak in the p-nitro isomer whereas in the o- and m-isomers, it is of lower abundance. In order to determine whether the ion A is produced with any hydrogen scrambling, the spectra (table 4-1) of the labelled derivatives (4-2) - (4-4), (4-6), (4-9) - (4-12), are examined. The results are summarised in table (4-2).

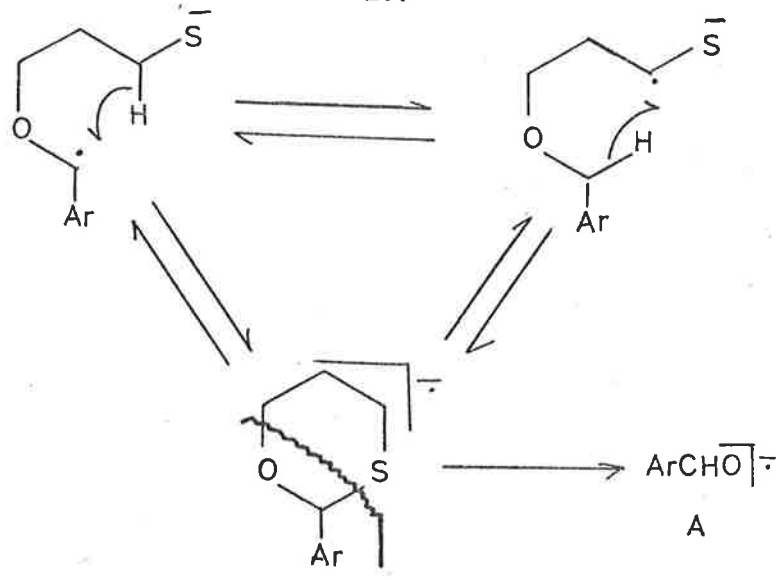
Table (4-2)

Compound	[M-C_3H_6S]	Hydrogen Scrambling
4-2	$C_3H_4D_2S$	NO
4-3	$C_3H_4D_2S$	NO
4-4*	$C_3H_2D_4S$; $C_3H_3D_3S$	YES
4-6	C_3H_6S	NO
4-9	C_3H_6S	NO
4-10	$C_3H_4D_2S$	NO
4-11	$C_3H_4D_2S$	NO
4-12	$C_3H_2D_4S$	NO

* Compound	Process	m/e	Ratio	Ratio M*	Calc for Random
4-4	A	151,152	90:10	70:30	67:33

The data show that no hydrogen scrambling occurs during the elimination of C_3H_6S from the molecular anions of the o- and m-isomers. Partial scrambling of the hydrogens at the C_2 and C_4 positions is observed for the p-isomer. The spectrum of 4-4 shows the ratios of the abundance of the ions $[M-C_3H_2D_4S]^{\cdot}$ and $[M-C_3H_3D_3S]^{\cdot}$ to be 90:10 for the daughter ions and 70:30 for metastable ions (in the first drift region of the mass spectrometer). For complete scrambling to occur, the ratio should be 67:33. The extent of the scrambling observed in both the metastable and daughter ions are anticipated because the decomposing molecular anion would have more time to undergo scrambling in the first drift region ($\tau \simeq 500\mu sec$) than in the source ($\tau = 10\mu sec$) of the mass spectrometer.

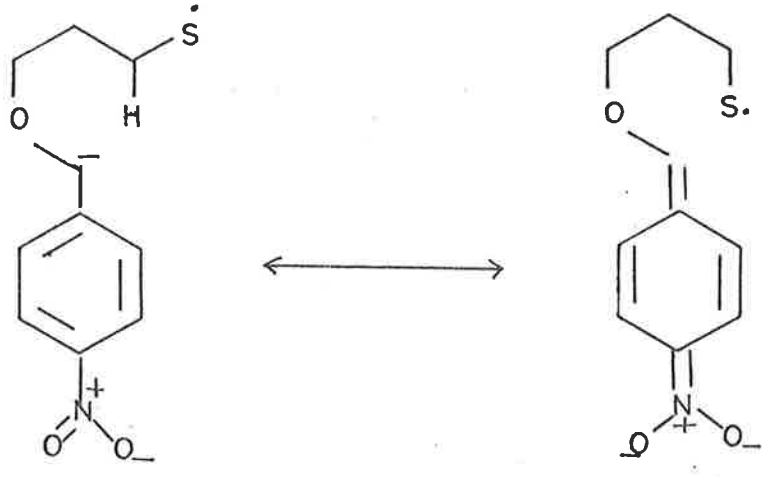
To account for the specific hydrogen scrambling process, a model is proposed, similar to that previously suggested for the dithiane system.[206] The model requires initial C_2-S bond cleavage of the oxathiane ring, followed by a series of hydrogen transfers through six-membered transition states as illustrated in scheme (4-2).



Scheme (4-2)

The structure (A) corresponds to the aryl aldehyde radical anion. This ion eliminates NO$^{\bullet}$ followed by carbon monoxide, behaviour which is characteristic of the o-nitrobenzaldehyde radical anion.[79]

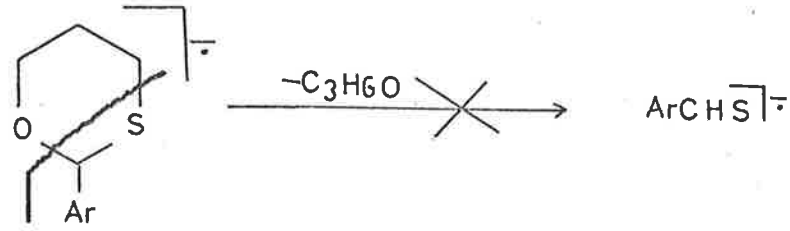
The ring opening depicted in scheme (4-2) is based on the assumption that the extra electron is initially localised on the sulphur atom. This has been substantiated for the case of the di-ethylthioacetal of benzaldehyde.[206] The alternative formulation of this ion structure, with the radical and anion centres exchanged is also possible. The radical anion so formed from the initial cleavage of the C_2-S bond would be stabilised by the nitro substituent as shown in h.



h

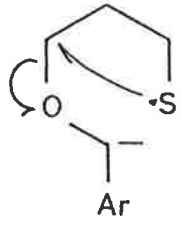
This resonance stabilisation is not possible for the m-isomer. This may make the molecular anion less stable than that of the p-isomer, and may explain why no scrambling is observed for the m-isomer. Such stabilisation is also possible for the o-isomer, but the absence of hydrogen scrambling in this case is probably due to the occurrence of the more facile, competitive ortho eliminations (see 2-3).

It is interesting to note that the alternative decomposition shown in i does not occur.



i

The energetics of this fragmentation would be similar to that of the process $[M-C_3H_6S]$. Consequently the question arises as to why the molecular anion decomposes exclusively by the $[M-C_3H_6S]$ and not $[M-C_3H_6O]$ process. The answer may be that the molecular anion is decomposing from the open ring form as depicted in scheme (4-2) or h. Because of the low bond dissociation energy of the C-S bond (ΔH = 65 kcal/mole), the initial cleavage of this bond would be favoured (see j).



j

Studies concerning the effect of the variation of the electron beam energy on the decompositions of the p-nitro isomer (4-1) have been carried out. The results are illustrated in a plot of the relative abundance of the fragment ion A and the molecular anion of 2-(p-nitrophenyl)-1,3-oxathiane against the norminal energy of the electron beam (see fig. (4-4)).

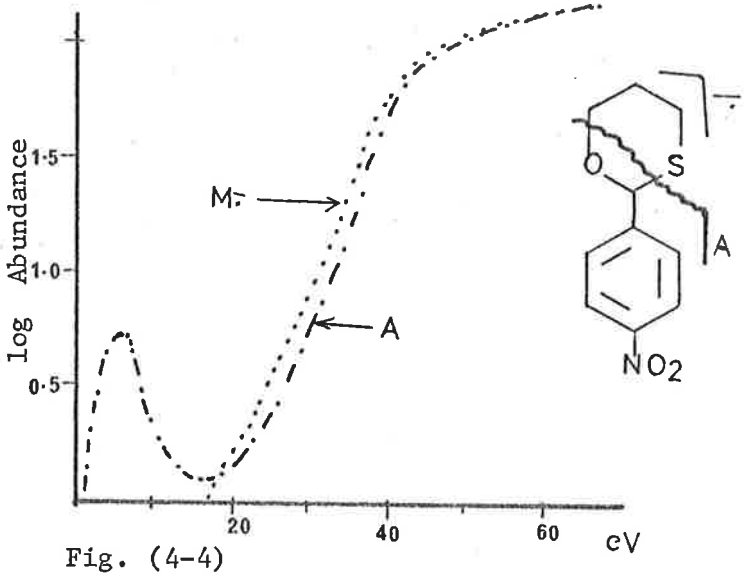


Fig. (4-4)

The plot shows that whereas no molecular anion is formed when the electron-beam energy is less than 15 eV, the fragment ion is produced below this value. The fragment ion (A) must therefore be produced either by ion-pair production or dissociative attachment between 3-8 eV, and by decomposition of a low-energy molecular anion above 15 eV. The molecular anions formed above 15 eV (n.b. the value of the electron beam), must be longer lived and therefore have less

internal energy than the species (not detected) which produce the fragment ion between 3 and 8 eV. Consequently, the spectrum obtained above 15 eV is that of a decomposing molecular anion with low internal energies.

The low-energy molecular anions must be produced by capture of thermal electrons (or secondary electrons) which may originate from the electrode surfaces or by one of the processes described in Chapt. 1, section 1.2.4.

There is some evidence to suggest that molecular anions observed at 30-70 eV are produced by the capture of secondary electrons. Thynne[9,10] reported that the molecular anion formation of hexafluoroacetone at 70 eV is strongly pressure dependent. Similarly, Dougherty[26] observed an increase in the abundances of the molecular anions of anthracene, napthalene and benzene with increasing pressure of nitrogen. Ion cyclotron resonance studies[11] show a dramatic enhancement of the intensity of the molecular anion of nitrobenzene when the electron energy is raised above the ionisation potential of the molecular cation of nitrobenzene. The above evidence suggests that secondary electrons are responsible for molecular anion formation above 15 eV. In our case, the molecular anion is only produced when the electron-beam energy is above ionisation potential of the molecular cation. Nonetheless, this

cannot be taken as rigorous proof that the captured electrons come from the positive ionisation process.

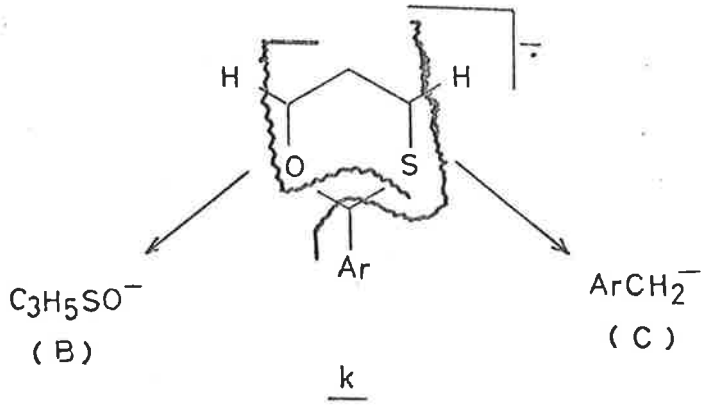
To study the effect of variation of the internal energy of the decomposing ions on the hydrogen scrambling process, we measured the negative-ion spectrum (fig (4-5)) of 2-(p-nitrophenyl)-1,3-oxathiane [4,4,6,6-$^2H_4$] at 6 eV. The spectrum is essentially similar to that at 70 eV (see fig 4-1) except that it contains no molecular anion and that the fragment ion A is produced with no prior hydrogen scrambling. This is in direct contrast to the formation of (A) at 70 eV. In order for ions to undergo hydrogen scrambling, they must be sufficiently long-lived and have low-internal energies.[207] The above evidence supports the results from the ionisation efficiency studies (fig. 4-4), viz. that the molecular anions formed at 70 eV have internal energies whereas fragment ions produced at less than 15 eV are formed by higher energy processes. This scrambling behaviour should be compared with that of positive ions,[207] the extent of which always increases with decreasing energy of the primary electron beam.

Since it has now been demonstrated that these molecular anions formed at 70 eV have low internal energies, we can now attempt to rationalise many of the characteristic features of negative-ion

spectra. The low-energy molecular anions generally undergo fewer fragmentations than the corresponding molecular cations. For example the molecular anions of anthraquinone esters decompose principally by loss of $R^{\bullet}$ to be followed by loss of CO_2.[78] On the other hand, the corresponding molecular cations fragment by elimination of $RO^{\bullet}$ to be followed by three successive losses of CO. Intense metastable ions[45,78] are frequently obtained in negative-ion spectra and should be contrasted with the less abundant species from positive ions. This is in accord with the QET[48-52] which predicts that the decomposing ions of lower internal energy should give more pronounced metastable ions.

2.2. Processes (B), (C) and M-H_2S.

The processes (B) and (C) are illustrated in k.



k

Process (B) is common to both m- and p-isomers, while process (C) only occurs for the p-isomer. The fragment ion (C) corresponds to the p-nitrobenzyl anion which is resonance stabilised. Furthermore, in process C, the hydrogen atom that migrates to C_2 comes from C_4 and this occurs only after equilibration of the three hydrogens at C_2 and C_4. On the other hand the ion (B) is produced together with specific elimination of the hydrogen atom at C_6. These results suggest that the molecular anion of the p-isomer is more stable and hence longer lived than that of the m-isomer.

The ions (B) and (C) may also be produced by decompositions of higher energy precursor ions (see fig. (4-5)). These ions are, however, produced with no prior hydrogen scrambling, a situation directly comparable with that described for the formation of fragment ion A.

The loss of H_2S occurs to a small extent in the p- and m-isomers. In the case of the p-isomer, the elimination is specific and involves one hydrogen at C_4 and the other at C_6. Although substantiated by the appropriate metastable ions, such eliminations are generally complex and hence no attempt is made to rationalise them mechanistically.

2.3. Proximity Effects in the Spectrum of 2-(o-nitrophenyl)-1,3-oxathiane.

The spectrum (fig. 4-3) of the o-isomer is much more complicated than that of the p- or m-isomers, and is characterised by prominent peaks at m/e 134 and 135. These peaks correspond to the processes $[M-C_3H_7SO^{\bullet}]$ and $[M-C_3H_6SO]$ respectively and must therefore be associated with the proximity of the nitro group. These processes may be complex but are highly diagnostic from a structural viewpoint. In addition, the molecular anion undergoes the characteristic eliminations observed for the p-and m-isomers, i.e. $[M-C_3H_6S-NO^{\bullet}]$ and also the processes $[(M-C_3H_6S-N\dot{O})-CO]$ and $[M-C_3H_4S]$.

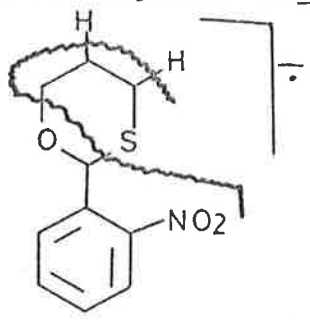
The spectra (table (4-1)) of the D-[(4-9) - (4-12)] and ^{18}O-derivative show the origin of the atoms or groups eliminated and demonstrate that the decompositions proceed with no prior hydrogen scrambling in the molecular anion.

The elimination of C_3H_4S is analogous to the major decomposition of the molecular anion of 2-(o-nitrophenyl)-1,3-dithiane,[206] and presumably involves the transfer of two hydrogen atoms from the oxathiane ring to the ortho substituent. In other words the nitro group acts as a hydrogen atom acceptor site for the process. Table (4-3) summarised the results from the spectra of (4-9) - (4-12).

Table (4-3)

Compound	[M-C_3H_4S]	[M-$C_3H_7SO^{\cdot}$]	[M-C_3H_6SO]
4-8	C_3H_4S	$C_3H_7S^{18}O^{\cdot}$	$C_3H_6S^{18}O$
4-9	C_3H_4S	$C_3H_6DSO^{\cdot}$	C_3H_6SO
4-10	C_3H_3DS	$C_3H_5D_2SO^{\cdot}$	$C_3H_4D_2SO$
4-11	C_3H_4S	$C_3H_5D_2SO^{\cdot}$	$C_3H_4D_2SO$
4-12	C_3H_3DS	$C_3H_3D_4SO^{\cdot}$	$C_3H_2D_4SO$

The information in table (4-3) demonstrates that the two hydrogens specifically retained originate from the C_4 and C_5 positions, and that no hydrogen scrambling occurs prior to or during this process. This ortho elimination is depicted in 1.

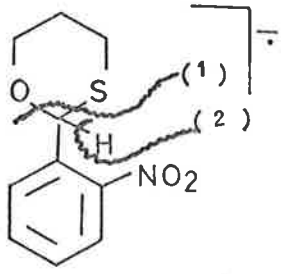


1

The structure of the product ion is not known, but it is not unreasonable to assume that the two hydrogen atoms transferred from the oxathiane ring during the process must be associated in some way with the nitro group as it is clearly providing the "driving

force" for this rearrangement reaction.

The spectra of (4-8) - (4-12) show the origins of the atoms or groups lost in the eliminations of $C_3H_7SO^{\bullet}$ and C_3H_6SO from the molecular anion of the o-isomer. The results from these spectra are summarised in table (4-3) and show that these eliminations occur with no prior hydrogen scrambling in the molecular anion. The process $[M-C_3H_7SO^{\bullet}]$ may occur in either a concerted manner or by a stepwise route $[M-C_3H_6SO-H^{\bullet}]$. These processes are depicted in m.



(1) ··· $(M - C_3H_6SO)$

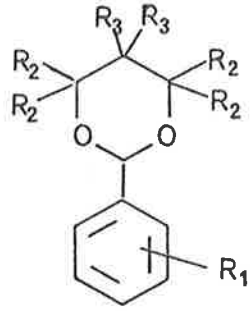
(2) ··· $(M - C_3H_7SO^{\bullet})$

m

Again the nitro substituent must be providing the driving force for these eliminations. No attempt is made to write mechanisms for these complicated processes but it appears that the nitro group undergoes cyclisations during or prior to these decompositions.

3. The 2-(nitrophenyl)-1,3-dioxans.

As a continuation of our investigations on the nature of hydrogen scrambling processes of systems related to aryl-1,3-dithianes the corresponding dioxans were examined. The following compounds listed were selected for this investigation.



Compound	R_1	R_2	R_3
4-13	o-NO_2	H	H
4-14	o-NO_2	D	H
4-15	o-NO_2	H	D
4-16	m-NO_2	H	H
4-17	p-NO_2	H	H
4-18	p-NO_2	D	H
4-19	p-NO_2	H	D

The spectrum of (4-13) is illustrated in fig. (4-6) while those of (4-14) - (4-17) are listed in table (4-4).†

The 70 eV spectra of the o-, m- and p-isomers are similar except for variations in the relative abundances of the fragment ions. The base peak in these spectra is the molecular anion which undergoes the major decomposition [M-C_3H_6O]. The extent of this process is most prominent in the o-isomer (15% of the base peak) and diminishes in the m- (0.5%) and p-isomers (1%). The small abundance of the fragment ion produced from the process [M-C_3H_6O] is conceivable in view of the strength of C-O bonds compared with the C-S bonds in the oxathianes or dithianes. It seems therefore probable that a large proportion of the molecular anions do not have sufficient energy to undergo decompositions. It is interesting to note that no proximity effects are present in the spectrum of the o-isomer. The absence of ortho effects demonstrates that such processes depend not only upon the spatial arrangements of the appropriate atoms or groups, but also upon the nature of the atoms participating in the reaction. The results of the spectra of the labelled derivatives (4-14), (4-15), (4-18) and (4-19) are summarised in table (4-5).

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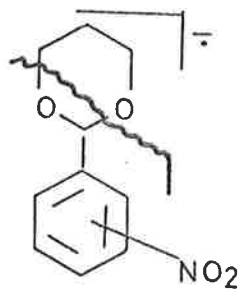
† Table (4-4) is placed at the end of this Chapter.

Table (4-5)

Compound	Process [M-C_3H_6O]
4-14	$C_3H_2D_4O$
4-15	$C_3H_4D_2O$
4-18	$C_3H_2D_4O$
4-19	$C_3H_4D_2O$

The labelling results demonstrate that no hydrogen scrambling occurs prior to or during the decomposition [M-C_3H_6O] for the p- and o-isomers. Although no labelling studies were carried out for the m-isomer, it seems unlikely that scrambling will occur by analogy from the work on dithianes and oxathianes. The process [M-C_3H_6O] is depicted in n.



n

Since no metastable transition accompanies this process, the possibility of other mechanisms operating cannot be ruled out; viz. dissociative capture and ion-pair production.

4. Summary

It has been shown that the extent of hydrogen scrambling diminishes in the progression from the dithianes to dioxans. The complex proximity effects observed for the o-nitro isomer of dithianes and oxathianes are absent in the spectra of the corresponding dioxans. Perhaps most important of all, we have provided evidence that a molecular anion formed at 70 eV (presumably by capture of a secondary electron) has a low internal energy range.

Table (4-1) Negative-ion spectra of (4-2) - (4-4), (4-6) and (4-8) - (4-12).

m/e	(4-2)	(4-3)	(4-4)	(4-6)	(4-8)	(4-9)	(4-10)	(4-11)	(4-12)
46	2	3	2	10	21	15	13	18	14
89				5					
91	2	2			5		4		
92			2		1	2		6	3
93					1		,	2	
121	2	3	2		4	3	2	2	2
122				2					
123					0.5				
134					100	100	100	100	100
135					70	8	72	75	66
136	2	2	0.6		8	75	4	7	5
137			2			7			
151	100	100	100		58	60	55	63	56
152	8	8	19	35	6	6	6	6	6
153				3	17	11		10	
154					1	1	7	1	7
155							1		1

cont'd

Table (4-1) Negative-ion spectra of (4-2) - (4-4), (4-6) and (4-8) - (4-12) cont'd.

m/e	(4-2)	(4-3)	(4-4)	(4-6)	(4-8)	(4-9)	(4-10)	(4-11)	(4-12)
192		2							
194			2						
225					80				
226	26			100	8	95	26		
227	97	96		8	15	8	98	95	
228	10	8		5	1	5	10	8	
229	6	5	97				6	5	86
230			10						8
231			6						5

Table (4-4)

Compound	m/e 46	121	151	209	210	211	212	213	214
14	9	1	3				30	100	10
15	10	3	14		5	100	15		
16	3		0.5	100	10				
17	5		1	100	10				
18		0.2	2				4	100	14
19	1.5	0.2	2		4	100	10		

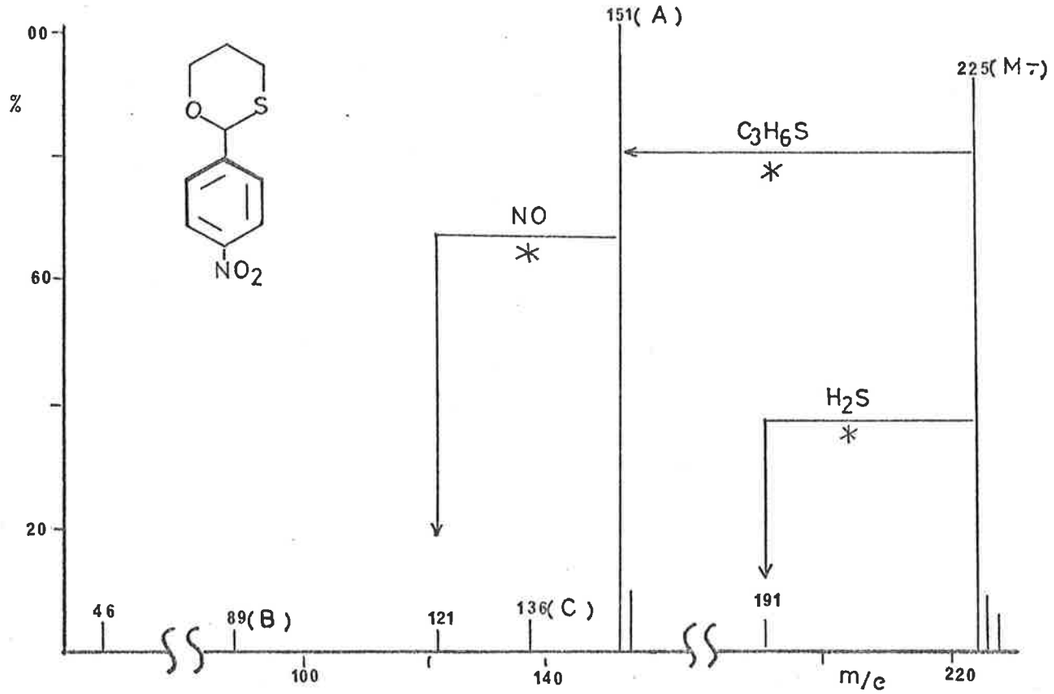

00
%
60
20
O
S
NO2
151(A)
225(M+)
C3H6S
*
NO
*
H2S
*
191
46
89(B)
121
136(C)
100
140
m/e
220

Fig. (4-1)

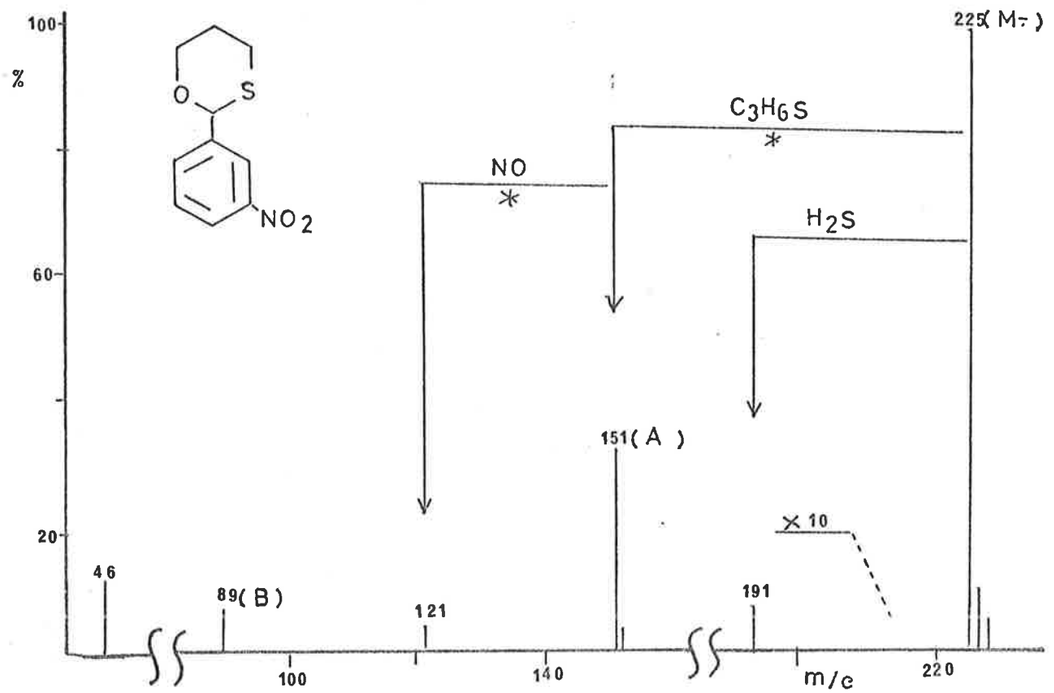

100
%
60
20
O
S
NO2
225(M+)
C3H6S
*
NO
*
H2S
151(A)
× 10
46
89(B)
121
191
100
140
m/e
220

Fig. (4-2)

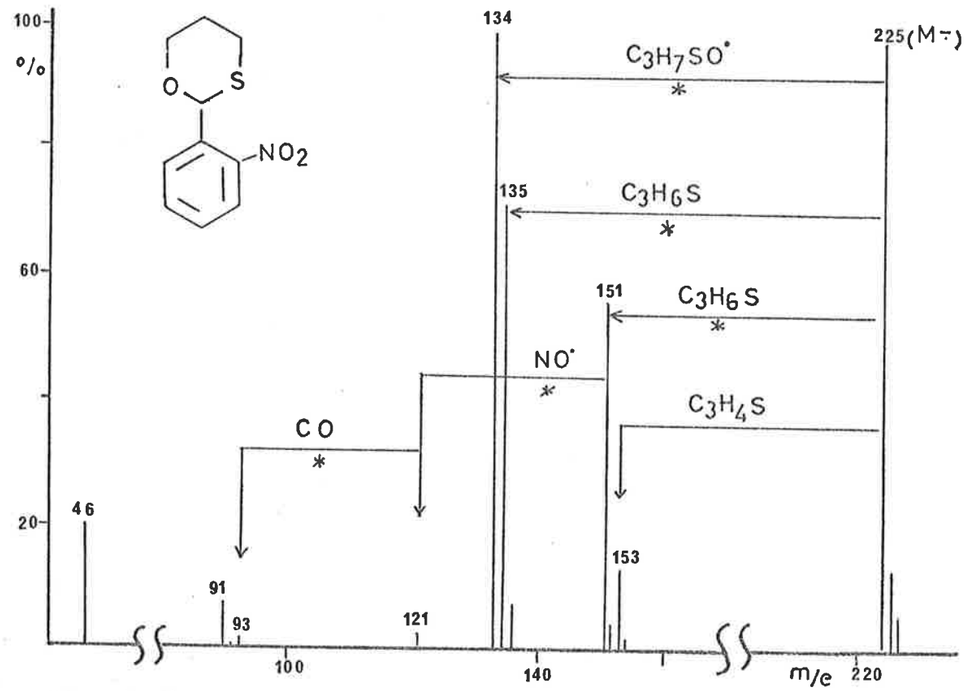

100
%
60
20
O
S
NO2
134
225(M+)
C3H7SO·
*
135
C3H6S
*
151
C3H6S
*
NO·
*
C3H4S
CO
*
46
91
93
121
153
100
140
m/e
220

Fig. (4-3)

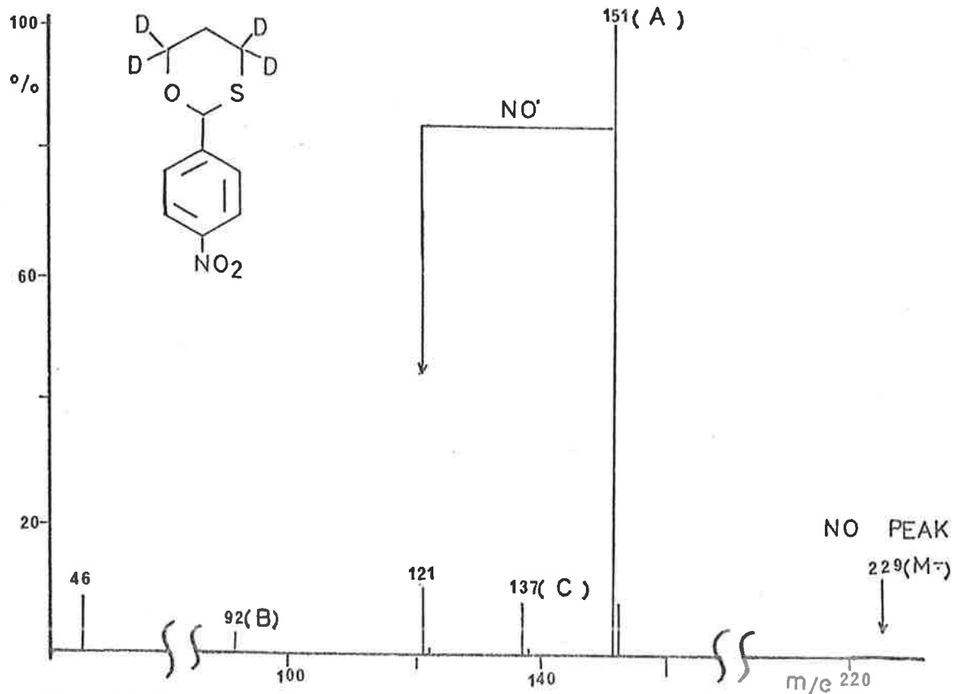

100
%
60
20
D
D
D
D
O
S
NO2
151(A)
NO·
NO PEAK
229(M+)
46
92(B)
121
137(C)
100
140
m/e
220

Fig. (4-5)

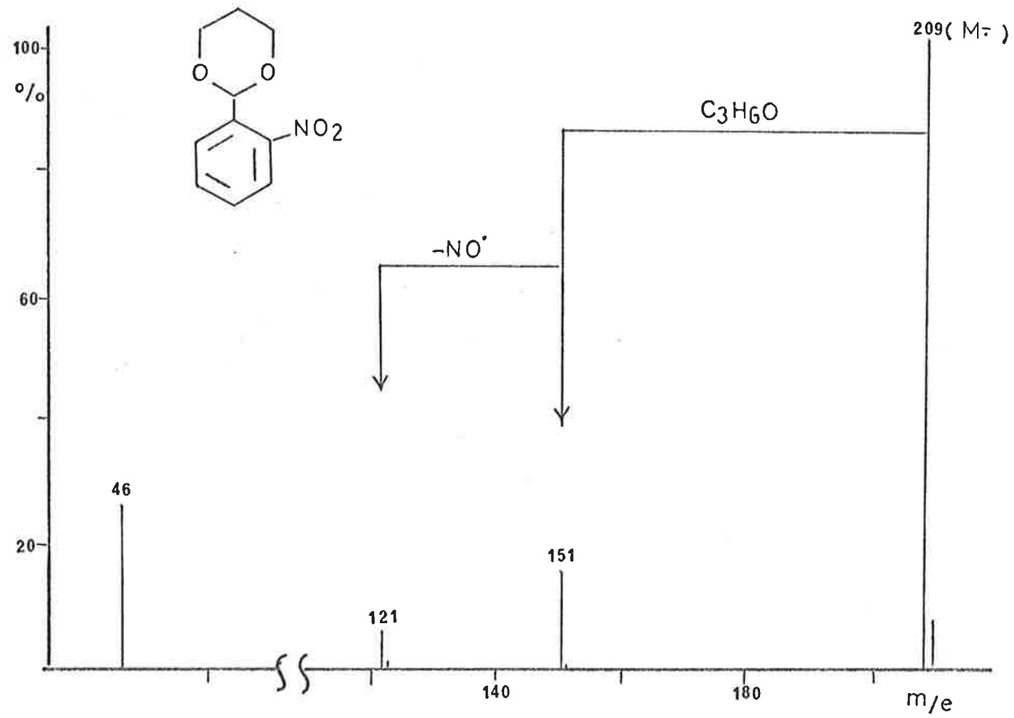


Fig. (4-6)

Chapter 5. Experimental

General

All mass spectra were determined with an Hitachi Perkin-Elmer RMU 7-D mass spectrometer operating at 70 eV (unless otherwise specified) with a source temperature of approximately 150°. Samples were introduced through an all glass inlet system at a temperature of 150-200°. Defocussed metastable ions were measured using a defocussing device of the type with variable electric sector voltage. All negative-ion spectra were determined at 70 eV and 1 - 3 x 10^{-7} torr (unless otherwise specified); all peaks were checked against internal standards. The instrument has been electronically modified[45] to allow the accurate measurements of defocussed metastable ions and negative-ion kinetic energy spectra.

The nuclear magnetic resonance spectra were measured with a Varian T60 spectrometer, operating at 60 MHz, 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 as Nujol mulls for solids and as liquid films for liquids, with a Perkin-Elmer 337 grating spectrometer or a Unicam SP. 200 infrared spectrometer. Melting points were determined on a Kofler hot-stage microscope, and are uncorrected.

Analyses were carried out by the Australian Microanalytical Service, Melbourne.

Whatman sorbsil (for column chromatography) and Merck Kieselgel G and HF 254 (for qualitative (t.l.c.) and preparative (p.t.l.c.) thin layer chromatography) were used as adsorbants. The term light petroleum refers to the fraction of b.p. 55-65°

Part I. Work described in Chapter 2.

3-Nitrosalicylic acid is commercially available. The following compounds were prepared by reported procedures: 5- and 6-nitrotetralin,[208] 6-nitrochroman (2-2),[209] 6-nitro-1,4-benzodioxan (2-6),[210] 6,7-dinitro-1,4-benzodioxan (2-7),[211] 5-nitro-1,3-benzodioxan (2-8),[212] 6-nitro-1,3-benzodioxan (2-9),[213] 7-nitro-1,3-benzodioxan (2-10),[214] 2-, 3- and 4-nitrobenzylmethyl ether,[215] and 4-nitro-2-hydroxybenzyl alcohol.[216]

3-(m-Nitrophenoxy)-1-propanol

A mixture of m-nitrophenol (1 g, 7.2 mmole), 3-bromo-1-propanol (1 g, 7.2 mmole) and potassium carbonate (1.1 g, 7.9 mmole) in acetone (10 ml) was heated under reflux for 10 hr, cooled, diluted with water (20 ml) and then extracted with ether (3 x 30 ml). The ethereal extracts were dried with $MgSO_4$ and the solvent removed in vacuo to give a dark yellow oil. The crude product was purified by chromatography in chloroform over silicic acid (Mallincrockt greater mesh, 50 g) to give a pale yellow oil, and distilled at 172-174°/2.5 mm to yield 3-(m-nitrophenoxy)-1-propanol (1.1 g, 77.5%). Found: C, 54.8; H, 5.7; N, 7.4%; $C_9H_{11}NO_4$ requires: C, 54.8; H, 5.6; N, 7.1%; ν_{max} (film) 3350 cm^{-1}; n.m.r. ($CDCl_3$) δ2.12 (2H, quintet, O-CH_2-CH_2-CH_2OH), 2.83 (1H, s, -OH), 3.87 (2H, t, -CH_2-OH), 4.21

(2H, t, -O-$\underline{CH_2}$-CH_2-), 7.1-7.9 (4H, m, aryl).

5- and 7-Nitrochromans (2-1 and 2-3).

A mixture of 3-(m-nitrophenoxy)-1-propanol (1 g, 5.1 mmole) and polyphosphoric acid (5 g) was manually stirred for 4 hr. at 100 -110°C, cooled, and diluted with water (20 ml). The reaction mixture was extracted with ether (2 x 20 ml), dried, the solvent removed in vacuo to yield a light brown oil which was chromatographed in benzene over silicic acid to give 5-nitrochroman (180 mg, 20%) as a yellow oil and 7-nitrochroman (120 mg, 13%) as a pale yellow solid. 5-Nitrochroman was fractionated at 90-92°/0.1 mm to furnish a pale yellow oil. Found: C, 60.6; H, 5.2; N, 8.1%; $C_9H_9NO_3$ requires: C, 60.3; H, 5.0; N, 7.8%; n.m.r. ($CDCl_3$) δ2.03 (2H, quintet, -OCH_2-$\underline{CH_2}$-CH_2-), 3.05 (2H, t, Ar$\underline{CH_2}$-), 4.22 (2H, t, -O$\underline{CH_2}$), 6.90-7.73 (3H, m, aryl). 7-Nitrochroman was recrystallised from aqueous ethanol as white plates, m.p. 90-91°. Found: C, 60.5; H, 5.1; N, 7.7; $C_9H_9NO_3$ requires: C, 60.3; H, 5.0; N, 7.8; n.m.r. ($CDCl_3$) δ2.05 (2H, quintet, -OCH_2-$\underline{CH_2}$-CH_2), 2.87 (2H, t, Ar$\underline{CH_2}$), 4.24 (2H, t, -O$\underline{CH_2}$-), 7.05-7.82 (3H, m, aryl).

6- and 8-Nitrochromans (2-2 and 2-4).

To a cooled solution of chroman[209] (200 mg, 1.49 mmole) was added concentrated nitric acid (0.08 g, S. G. 1.4) dropwise. The

reaction mixture turned light brown to dark red in less than five minutes. The reaction mixture was stirred for another 10 min. before diluting with ice-water (10 ml). The mixture was extracted with chloroform (3 x 5 ml), the chloroform extracts were washed twice with $NaHCO_3$ solution, dried with $MgSO_4$, and the solvent removed *in vacuo*. The resulting red oil was purified by p.t.l.c. (eluting with benzene) to yield 6-nitrochroman (102 mg, 39%) as a pale yellow solid and 8-nitrochroman (96 mg, 36%) as a pale yellow oil. 6-Nitrochroman was crystallised from aqueous ethanol as pale yellow needles, m.p. 100 101° (lit.[209] 100-102°). 8-Nitrochroman was fractionated at 117-118°/ 0.02 mm to give a pale yellow oil. Found: C, 60.5; H, 5.2; N, 8.0%; $C_9H_9NO_3$ requires: C, 60.3; H, 5.0; N, 7.8%; n.m.r. ($CDCl_3$) δ2.10 (2H, quintet, $-OCH_2\underline{CH_2}-CH_2-$), 2.90 (2H, t, $Ar\underline{CH_2}-$), 4.35 (2H, t, $-O\underline{CH_2}-$), 6.75-7.75 (3H, m, aryl).

5-Nitro-1,4-benzodioxan (2-5)

Treatment[211] of 3-nitrocatechol[217] (500 mg, 3.22 mmole) with ethylene bromide (2.19 g, 11.7 mmole) and potassium carbonate in ethylene glycol (5 ml) gave a yellow solid. This was purified by p.t.l.c. (elution with benzene) and crystallisation from aqueous ethanol to yield 5-nitro-1,4-benzodioxan (192 mg, 33%) as yellow needles, m.p. 60-61°. Found: C, 53.3; H, 4.0; N, 7.5%. $C_8H_7NO_4$ requires: C, 53.1;

H, 3.9; N, 7.7%; n.m.r. ($CDCl_3$) δ4.4 (4H, s, $-OCH_2-$), 6.85-7.60 (3H, m, aryl).

4-Nitro-2-hydroxybenzyl bromide

A mixture of 7-nitro-1,3-benzodioxan (2-10) (500 mg, 2.76 mmole) and aqueous hydrogen bromide (5 ml, 48%) was heated under reflux for one hr., cooled, and the solid removed and crystallised from benzene/light petroleum to yield 4-nitro-2-hydroxybenzyl bromide (500 mg, 79%) as pale yellow needles, m.p. 112-114°. Found: C, 36.5; H, 2.7; N, 6.1%; $C_7H_6BrNO_3$ requires: C, 36.2; H, 2.6; N, 6.0%; ν_{max} (nujol) 3400 cm^{-1}; n.m.r. ($CDCl_3$) δ4.57 (2H, s, $ArCH_2Br$), 5.64 (1H, s, -OH), 7.21-7.85 (3H, m, aryl).

6-Nitro-2-hydroxybenzyl bromide

Treatment of 5-nitro-1,3-benzodioxan (2-8) (500 mg, 2.76 mmole) with aqueous hydrogen bromide (5 ml, 48%) as for 4-nitro-2-hydroxybenzyl bromide gave 6-nitro-2-hydroxybenzyl bromide (510 mg, 80%) which was crystallised from benzene/light petroleum as yellow needles, m.p. 140-141°. Found: C, 36.5; H, 2.62; N, 6.0%; $C_7H_6BNO_3$ requires: C, 36.2; H, 2.6; N, 6.0%; ν_{max} (nujol) 3350 cm^{-1}; n.m.r. ($CDCl_3$) δ4.80 (2H, s, $ArCH_2Br$), 6.82 (1H, s, -OH), 7.05-7.55 (3H, m, aryl).

3-Nitro-2-hydroxybenzyl alcohol.

3-Nitrosalicylic acid (500 mg, 2.73 mmole) in anhydrous tetrahydrofuran (THF) was treated at room temperature with diborane (3 ml, 2.7 M, 8.1 mmole) under a nitrogen atmosphere. The reaction mixture was stirred for 3 hr before quenching with aqueous acetic acid (1 ml, 50%). Removal of the solvent *in vacuo* gave a yellow solid which crystallised from water gave 3-nitro-2-hydroxybenzyl alcohol (300 mg, 64%) as yellow needles, m.p. 73-74° (lit.[217a] 75°).

6-Nitro-2-hydroxybenzyl alcohol

6-Nitro-2-hydroxybenzyl bromide (150 mg, 0.65 mmole) was heated under reflux with water (5 ml) for 2 hr to yield 6-nitro-2-hydroxybenzyl alcohol (90 mg, 82%), which was crystallised from water as yellow needles, m.p. 96-98°. Found: C, 49.7; H, 4.1; N, 8.0%; $C_7H_7NO_4$ requires; C, 49.7; H, 4.1, N, 8.3%.

8-Nitro-1,3-benzodioxan (2-11)

To a mixture of 3-nitro-2-hydroxybenzyl alcohol (200 mg, 1.18 mmole) and aqueous formaldehyde (100 mg, 1.33 mmole, 40%) was added concentrated sulphuric acid (1 ml). The mixture was stirred at

room temperature for 1 hr, diluted with water (10 ml), and then extracted with chloroform (2 x 5 ml). The chloroform extracts were washed with water, dried with magnesium sulphate and the solvent removed *in vacuo* to yield a yellow solid. This solid was purified by p.t.l.c. (elution with benzene) to give 8-nitro-1,3-benzdioxan (40 mg, 18%) which was crystallised from ethanol as colourless needles, m.p. 115-116°. Found: C, 53.1; H, 3.9; N, 7.7%. $C_8H_7NO_4$ requires: C, 53.0; H, 3.9; N, 7.7%; n.m.r. ($CDCl_3$) δ5.0 (2H, s, $ArCH_2$-), 5.43 (2H, s, O-CH_2-O), 7.0-7.95 (3H, m, aryl).

The 2-Methyl-nitro-1,3-benzodioxans (2-12) - (2-15).

General Method of preparation

A mixture of the nitro-2-hydroxybenzyl alcohol (100 mg, 0.59 mmole), acetaldehyde (5 ml) and a catalytic amount of p-toluene-sulphonic acid was heated under reflux for 10 hr. Removal of the acetaldehyde *in vacuo* gave a solid which was purified by p.t.l.c. (elution with benzene). All products were crystallised from ethanol as colourless needles.

2-Methyl-6-nitro-1,3-benzodioxan has been reported.[218] The other isomers have not been reported previously. The table below shows the physical data of these compounds.

Compound	m.p. (°C)	Yield %	Found (%) C	H	N	Requires (%) C	H	N
5-Nitro-(2-12)	82-83	82	55.3	4.6	7.2	55.4	4.6	7.2
7-Nitro-(2-14)	126-127	87	55.3	4.8	7.2	55.4	4.6	7.2
8-Nitro-(2-15)	74-75	63	55.2	4.9	7.0	55.4	4.6	7.2

The labelled compounds (2-16) - (2-27)

4-, 5- and 6-Nitro-2-hydroxybenzyl alcohol-1-^{18}O.

Treatment of 4-nitro-2-hydroxybenzyl bromide, 5-nitro-2-hydroxybenzyl chloride[219] or 6-nitro-2-hydroxybenzyl bromide (500 mg) by heating under reflux with $H_2{}^{18}O$ (0.1 ml, 0 = 20%), silver oxide (500 mg) and dioxan (5 ml) for 10 hr. gave the appropriate alcohol-1-^{18}O. [4-nitro- (300 mg, 82%); 5-nitro- (305 mg, 67%); 6-nitro- (290 mg, 80%)], which were crystallised from water as yellow needles m.p. 126-127°, 125-126° and 95-96° respectively [all ^{16}O = 80%, ^{18}O = 20%].

5-, 6- and 7-nitro-1,3-benzodioxan-2,2-$^2H_2$ (2-16) - (2-18).

Treatment of the appropriate benzyl alcohol (50 mg, 0.296 mmole) with aqueous formaldehyde -$^2H_2$ (35 mg, 0.35 mmole, 30%; $^2H_2$ = 100%) and concentrated sulphuric acid (1 ml) (as described for (2-11)) gave the $^2H_2$-nitro-1,3-benzodioxan which was purified by p.t.l.c. (elution

with benzene) followed by crystallisation from aqueous ethanol to give colourless needles. The physical data of these compounds are tabulated below.

5-, 6- and 7-Nitro-1,3-benzodioxan-3-^{18}O (2-19) - (2-21)

These were prepared from the three ^{18}O-labelled alcohols by the general procedure outlined above for (2-16) - (2-19). The physical data of these compounds are tabulated below.

5-, 6- and 7-Nitro-1,3-benzodioxan-2,2-$^{2}H_2$-3-^{18}O (2-22) - (2-24).

These were prepared from the three ^{18}O-labelled alcohols and formaldehyde-$^{2}H_2$ by the general procedure outlined above for (2-16) - (2-19). The physical data of these compounds are summarised in the table below.

The 2-Methyl-nitro-1,3-benzodioxan-3-^{18}O (2-25) - (2-27)

These were prepared from the three ^{18}O-labelled alcohols and acetaldehyde by the general procedure outlined above for (2-16) - (2-19). The physical data of these compounds are tabulated below.

Compound	m.p. (°C)	Yield (%)	Incorporation (%)
(2-16)	76-77	53	$^{2}H_2$ = 100
(2-17)	148-150	46	$^{2}H_2$ = 100
(2-18)	92-93	70	$^{2}H_2$ = 100
(2-19)	76-77	47	^{18}O = 20
(2-20)	148-150	51	^{18}O = 20
(2-21)	92-93	84	^{18}O = 20
(2-22)	76-77	60	$^{2}H_2$ = 100; ^{18}O = 20
(2-23)	148-150	41	$^{2}H_2$ = 100; ^{18}O = 20
(2-24)	92-93	68	$^{2}H_2$ = 100; ^{18}O = 20
(2-25)	82-83	87	^{18}O = 20
(2-26)	113-114	65	^{18}O = 20
(2-27)	126-127	87	^{18}O = 20

Model Compounds (2-34) and (2-35)

2-Hydroxy-5-nitrobenzyl methyl ether

A mixture of 2-hydroxy-5-nitrobenzyl chloride[219] (500 mg, 2.77 mmole), silver oxide (500 mg) and methanol (8 ml) was heated under reflux for 4 hr, cooled and then filtered through celite. Removal of the solvent *in vacuo* gave a yellow solid which was

purified by p.t.l.c. (elution with chloroform) to yield 2-hydroxy-5-nitrobenzyl methyl ether (400 mg, 82.5%) which was crystallised from benzene/light petroleum as pale yellow plates, m.p. 108-110° (lit.[215] 109-110°).

2-Hydroxy-4-nitrobenzyl methyl ether.

This was prepared by the procedure outlined above for the 5-nitro compound. 2-Hydroxy-4-nitrobenzyl bromide (300 mg, 1.29 mmole), silver oxide (300 mg) and methanol (5 ml) gave the benzyl methyl ether (174 mg, 73.5%) which was crystallised from benzene/light petroleum as yellow needles, m.p. 79-80°. Found: C, 52.5; H, 5.0; N, 7.6%; $C_8H_9NO_4$ requires: C, 52.5; H, 4.9; N, 7.6%; ν_{max} ($CHCl_3$) 3300 cm^{-1}; n.m.r. ($CDCl_3$) δ 3.50 (3H, s, -O<u>Me</u>), 4.75 (2H, s, Ar<u>CH</u>$_2$), 7.10-7.90 (3H, m, aryl), 8.2 (1H, s, -O<u>H</u>).

2-Methoxy-5-nitrobenzyl methyl ether

A mixture of 2-hydroxy-5-nitrobenzyl methyl ether (100 mg, 0.546 mmole), methyl iodide (0.051 ml, 0.819 mmole) and silver oxide (100 mg) in acetone (5 ml) was heated under reflux for 10 hr., cooled, and then filtered through celite. Removal of the solvent <u>in vacuo</u> gave a pale yellow solid. This was purified by p.t.l.c. (elution with chloroform) to yield 2-methoxy-5-nitrobenzyl methyl ether (98 mg,

91%) which was crystallised from light petroleum to yield colourless plates, m.p. 67-8°. Found: C, 54.8; H, 5.5; N, 6.9%; $C_9H_{11}NO_4$ requires: C, 54.8; H, 5.6; N, 7.1%; n.m.r. ($CDCl_3$) δ 3.50 (3H, s, $-CH_2-O\underline{Me}$), 3.94 (3H, s, $Ar\underline{OMe}$), 4.50 (2H, s, $ArC\underline{H_2}-$), 6.8-8.3 (3H, m, aryl).

2-Methoxy-4-nitrobenzyl methyl ether

This was prepared by the procedure outlined above for the 5-nitro compound. The reaction between 2-hydroxy-4-nitrobenzyl methyl ether (100 mg, 0.546 mmole) and methyl iodide (0.051 ml, 0.819 mmole), in acetone (5 ml) gave 2-methoxy-4-nitrobenzyl methyl ether (100 mg, 92.5%) which was crystallised from light petroleum to give colourless needles, m.p. 78-80°. Found: C, 55.0; H, 5.8; N, 6.9%; $C_9H_{11}NO_4$ requires: C, 54.8; H, 5.6; N, 7.1%; n.m.r. δ 3.50 (3H, s, $-CH_2-O\underline{Me}$), 3.95 (3H, s, $Ar\underline{OMe}$), 4.55 (2H, s, $ArC\underline{H_2}$), 7.50-7.95 (3H, m, aryl).

2-(Methoxy-$^2H_3$)-5-nitrobenzyl methyl ether (2-34).

This was prepared as for the corresponding unlabelled compound by the procedure outlined above. The reaction between 2-hydroxy-5-nitrobenzyl methyl ether (50 mg, 0.274 mmole) and methyl iodide-$^2H_3$ (50 mg, 0.345 mmole, $^2H_3$=100%) in acetone (5 ml) gave the $^2H_3$-benzyl methyl ether (48 mg, 88%, $^2H_3$=100%) which was crystallised from light petroleum to yield colourless plates, m.p. 65-67°.

2-(Methoxy-$^2H_3$)-4-nitrobenzyl methyl ether (2-35).

This was prepared as for (2-34). Treatment of 2-hydroxy-4-nitrobenzyl methyl ether (50 mg, 0.27 mmole) with methyl iodide-$^2H_3$ (50 mg, 0.345 mmole, $^2H_3$=100%) in acetone (5 ml) gave 2-(methoxy-$^2H_3$)-4-nitrobenzyl methyl ether (50 mg, 91.5%) which was crystallised from light petroleum to give colourless needles, m.p. 79-80°.

Part II. Work described in Chapter 3.

The following were purified commercial samples: 3-nitrosalicylic acid, 5-nitrosalicylic acid, 4-nitroanthranilic acid, thiosalicylic acid, methyl salicylate (3-1), phenyl salicylate (3-2) and benzyl salicylate (3-3). The following compounds were prepared by reported procedures: 6-nitrosalicylic acid,[220] 3-amino-5-nitrobenzoic acid[221] and 3-hydroxy-5-nitrobenzoic acid.[221]

The methyl esters were prepared by the reactions between the appropriate carboxylic acid and methanol/sulphuric acid. The following esters have been reported: methyl thiosalicylate (3-5),[222] methyl 5-nitrosalicylate (3-8),[223] methyl 4-nitroanthranilate (3-18),[224] methyl 3-hydroxy-5-nitrobenzoate (3-22),[221] methyl 3-amino-5-nitrobenzoate (3-25),[225] and methyl 3-nitrosalicylate (3-28).[226] The physical data for methyl 6-nitrosalicylate (3-30) are tabulated below.

The aryl esters were prepared from the carboxylic acids by the method of Gaylord and Kamath.[227] The esters, phenyl anthranilate (3-4),[228] phenyl thiosalicylate (3-6),[222] phenyl 5-nitrosalicylate (3-10),[229] p-nitrophenyl 5-nitrosalicylate (3-17),[230] phenyl 3-nitrosalicylate (3-29) [229] have been reported. Compounds (3-13) - (3-16), (3-19), (3-26) and (3-31) were prepared by the general method,[227] purified by column chromatography on silicic acid, and crystallised

from aqueous ethanol. Their physical data are tabulated below.

Compound	Yield %	m.p. (°C)	Composition	Found			Requires		
				C	H	N	C	H	N
3-13	25	135-136	$C_{14}H_{11}NO_6$	58.2	4.0	4.8	58.1	3.8	4.8
3-14	67	145-146	$C_{14}H_{11}NO_5$	61.5	5.1	5.2	61.5	4.0	5.1
3-15	34	155-156	$C_{13}H_8ClNO_5$	53.3	2.9	4.7	53.2	2.7	4.8
3-16	35	161-162	$C_{15}H_{11}NO_6$	59.8	3.8	4.4	59.8	3.7	4.7
3-19	57	135-136	$C_{13}H_{10}N_2O_4$	60.4	4.2	10.8	60.5	3.9	10.8
3-23	35	161-162	$C_{13}H_9NO_5$	60.4	3.5	5.4	60.2	3.5	5.4
3-26	68	144-145	$C_{13}H_{10}N_2O_4$	60.5	3.9	10.8	60.5	3.9	10.8
3-30	70	88-90	$C_8H_7NO_5$	48.8	3.6	7.3	48.7	3.6	7.1
3-31	64	98-99	$C_{13}H_9NO_5$	60.3	3.6	5.2	60.2	3.5	5.4

Phenyl 2-methoxy-5-nitrobenzoate (3-12)

A mixture of phenyl 5-nitrosalicylate (3-10) (100 mg, 0.386 mmole), methyl iodide (0.05 ml, 0.819 mmole) and potassium carbonate (100 mg, 0.725 mmole) in acetone (5 ml), was heated under reflux for 10 hr, filtered and the solvent removed in vacuo to give the crude product. This was purified by p.t.l.c. (elution with benzene) to yield phenyl 2-methoxy-5-nitrobenzoate (50 mg, 47%) which crystallised from aqueous ethanol as pale yellow plates, m.p. 129-130°. Found: C, 61.4; H, 4.1; N, 5.0%; $C_{14}H_{11}NO_5$ requires: C, 61.5; H, 4.0;

N, 5.1%; n.m.r. ($CDCl_3$) δ 4.10 (3H, s,-O-Me).

The deuterated compounds, (3-7), (3-9), (3-11), (3-20), (3-24) and (3-27) were formed in situ by exchange with deuterium oxide in the inlet system of the mass spectrometer.[231] In all cases the incorporation was in excess of 80%.

The ^{18}O labelled ester (3-11) was prepared by converting 5-nitrosalicylic acid to its acid chloride which was then reconverted to the labelled carboxylic acid with $H_2{}^{18}O$ (^{18}O = 40%). The acid was then treated[227] with phenol and phosphorus oxychloride to furnish (3-21) (^{18}O = 20%).

Part III. Work described in Chapter 4.

The unlabelled aryl-1,3-oxathianes

3-Bromopropionyl chloride

Treatment[232] of 3-bromopropionic acid with phosphorus trichbride gave the acid chloride in 81% yield, b.p. 68/18 mm (lit.[232] 65-70°/25-30 mm).

3-Bromo-1-propanol

Method 1

This was prepared by a modification of Nystrom's method.[233]

A solution of 3-bromopropionyl chloride (17.1 g, 0.1 mole) in diethyl ether (150 ml) was added dropwise at -75° to diethyl ether (200 ml) containing lithium aluminium hydride (3.8 g, 0.1 mole). The reaction mixture was then allowed to stir for a further 30 mins, then treated with water (3.8 ml) and aqueous sodium hydroxide (3.8 ml, 15%). The mixture was filtered and the solvent removed *in vacuo* to give the the crude product which was distilled at 81-82°/15 mm to yield 3-bromo-1-propanol (17.8 g, 75%) (lit.[233] 71-72°/10 mm).

Method 2

This was prepared by the method of Bogert.[234] Treatment[234] of propane-1,3-diol with dry hydrogen bromide gave the bromo alcohol in 78% yield, b.p. 82-86°/20 mm (lit.[233] 71-72°/10 mm).

3-Thiol-1-propanol

Treatment[235] of 3-bromo-1-propanol with thiourea gave the isothiuronium bromide (m.p. 88-90°, 90% yield) which upon hydrolysis[236] with aqueous sodium hydroxide yields 3-thiol-1-propanol in 48% yield, b.p. 86-88°/15 mm (lit.[235] 75-80°/7 mm).

General method for the preparation of aryl-1,3-oxathianes

A solution of the appropriate aldehyde (1.0 mmole) and 3-thiol-1-propanol (1.2 mmole) in chloroform (10 ml) was saturated with dry hydrogen chloride, and allowed to stand for ½hr at room temperature. The solution was washed with water (2 x 2 ml), aqueous sodium hydroxide (2 x 2 ml, 10%) and water (2 x 2 ml), dried with magnesium sulphate, and the solvent then removed *in vacuo* to yield the crude oxathiane, which was purified by column chromatography on silicic acid (elution with benzene), followed by crystallisation from methanol.

The unlabelled oxathianes [(4-1), (4-5) and (4-7)] were prepared by the above method. The physical data for these compounds are tabulated below.

Compound	Yield %	m.p. (°C)	Composition	Found (%) C	H	N	Calculated (%) C	H	N
(4-1)	48	110-111	$C_{10}H_{11}NO_3S$	54.4	5.1	5.8	53.3	4.9	6.2
(4-5)	33	64-65	$C_{10}H_{11}NO_3S$	53.1	5.0	6.2	53.3	4.9	6.2
(4-7)	51	88-90	$C_{10}H_{11}NO_3S$	53.6	5.0	6.0	53.3	4.9	6.2

The Labelled Aryl-1,3-oxathianes

3-Thiol-1-propanol-1,1-$^2H_2$

Reduction of 3-bromopropionyl chloride with lithium aluminium deuteride (as described for 3-bromo-1-propanol, method 1) gave the $^2H_2$-bromo alcohol (b.p. 74-76°/15 mm; 84% yield; $^2H_2$ = 100%) which was treated[235] with thiourea to yield the isothiuronium bromide (m.p. 89-91°, 78.5% yield). Treatment[236] of this salt with aqueous sodium hydroxide gave 3-thiol-1-propanol-1,1-$^2H_2$ (b.p. 86-88°/15 mm; 44% $^2H_2$ = 100%).

3-Thiol-1-propanol-2,2-$^2H_2$

Malonic acid-$^2H_4$† (3.65 g, 33.8 mmoles; $^2H_3$ = 10, $^2H_4$ = 90%)

† Available from previous studies.[237]

in tetrahydrofuran (THF; 100 ml) was added slowly to a stirred solution of lithium aluminium hydride (2.0 g, 52.5 mmoles). After the addition was complete, the mixture was heated under reflux for 4 hr, cooled, and treated with water (2 ml) and aqueous sodium hdyroxide (2 ml, 15%). The reaction mixture was stirred for another hr, after which the solid was filtered off, and the solvent removed in vacuo to yield crude propane-1,3-diol-2,2-$^2H_2$ (0.73 g) as a colourless liquid. The precipitate obtained from the work-up of the reduction mixture was continuously extracted with THF for 24 hr yielding a further 0.31 g of the diol-$^2H_2$ [(total yield 1.04 g, 39%); b.p. 108-110°/15 mm; $^2H_1$ = 22, $^2H_2$ = 78%]. The propane-1,3-diol-$^2H_2$ was treated[234] with anhydrous hydrogen bromide to give the $^2H_2$-bromo alcohol in 35% yield. This was subsequently converted[235] into the isothiuronium salt (92%) which upon hydrolysis[236] with aqueous sodium hydroxide gave 3-thiol-1-propanol-2,2-$^2H_2$ (b.p. 86-88°/15 mm; 50%; $^2H_1$ = 22, $^2H_2$ = 78%).

3-Thiol-1-propanol-1,1,3,3-$^2H_4$

Reduction of malonic acid with lithium aluminium deuteride (as described above) gave the tetradeutero diol (b.p. 108-110°/15 mm, 50%, $^2H_4$ = 100%) which was converted (as above) into 3-thiol-1-propanol-1,1,3,3-$^2H_4$ (b.p. 86-88°/15 mm, overall yield from the diol 21%, $^2H_4$ = 100%).

The deuterated oxathianes

The deuterated oxathianes, (4-2) - (4-4), (4-9) - (4-12) were prepared from the appropriate aldehyde and labelled 3-thiol-1-propanol by the general procedure described earlier. The physical data for these compounds are tabulated below.

Compound	Yield (%)	m.p. (°C)	Incorporation (%)
(4-2)	88	108-110	$^2H_1$ = 22; $^2H_2$ = 78
(4-3)	80	108-110	$^2H_2$ = 100
(4-4)	70	108-110	$^2H_4$ = 100
(4-10)	97	88-90	$^2H_1$ = 22; $^2H_2$ = 78
(4-11)	80	90-91	$^2H_2$ = 100
(4-12)	92	89-90	$^2H_4$ = 100.

2-(m-Nitrophenyl)-1,3-oxathiane-2-$^2H_1$ (4-6)

Benzaldehyde-α-$^2H_1$ was prepared by the method of Seebach et al.[238] Nitration[239] of benzaldehyde-α-$^2H_1$ gave m-nitrobenzaldehyde-α-$^2H_1$ (80% yield) which was treated in the usual way with 3-thiol-1-propanol to yield 2-(m-nitrophenyl)-1,3-oxathiane-2-$^2H_1$ (m.p. 64-65°, 30% yield; H = 100%).

2-(o-Nitrophenyl)-1,3-oxathiane-2-$^{2}H_1$ (4-9).

Treatment[239] of benzaldehyde-α-$^{2}H_1$[238] (500 mg, $^{2}H_1$ = 100%) with acetic anhydride (5 ml) followed by addition of concentrated nitric acid (1.25 ml, S.G. 1.4) gave a mixture of nitrobenzylidene diacetates (99%), which were hydrolysed[239] with magnesium hydroxide (20 ml of an aqueous suspension of magnesium hydroxide (2.5%)) to yield a mixture of nitrobenzaldehydes-α-$^{2}H_1$ (90% yield). The aldehydes were converted into a mixture of oxathianes by treatment with 3-thiol-1-propanol (described earlier) and chromatography over silicic acid (Mallinckrodt, 100 mesh) eluting with benzene-light petroleum (1:1) gave 2-(o-nitrophenyl)-1,3-oxathiane-2-$^{2}H_1$ (m.p. 98-90°; 72%, $^{2}H_1$ = 100%).

2-(o-Nitrophenyl)-1,3-oxathiane-1-^{18}O

Hydrolysis of 3-bromopropionyl chloride (4.7 g) with $H_2{}^{18}O$ (0.5 ml, ^{18}O = 20%) gave the labelled 3-bromopropionic acid (4.06 g, 95.5%; m.p. 58-60°) which upon treatment[232] with phosphorus trichloride (2 ml) gave 3-bromopropionyl chloride-1-^{18}O (2.92 g, 65%; b.p. 70-72°/ 32 mm; ^{18}O = 10%) as a colourless liquid. Reduction of the acid chloride (2.0 g) with lithium aluminium hydride (0.45 g) gave 3-bromo-1-propanol (0.93 g, 57%; 90-02°/35 mm), which was converted through the isothiuronium bromide (as above) to give 3-thiol-1-propanol-1-^{18}O (b.p. 86-88°/15 mm, 70% yield from the bromo alcohol; ^{18}O = 10%).

The reaction between o-nitrobenzaldehyde and 3-thiol-1-propanol -1-^{18}O gave 2-(o-nitrophenyl)-1,3-oxathiane-1-^{18}O (m.p. 90-91°, 50% yield; ^{18}O = 10%) which was crystallised from methanol to yield pale yellow needles.

The aryl-1,3-dioxans

The aryl-1,3-dioxans, (4-13), (4-16) and (4-17) were prepared by the following general method.

A mixture of the aryl aldehyde (1 mmole), propane-1,3-diol (1.5 mmole) and a catalytic amount of p-toluenesulphonic acid in benzene (20 ml), was heated under reflux in a Dean-Stark water separator for 10 hr. The benzene layer was separated and then washed with water (10 ml), saturated aqueous solutions of sodium bisulphite (2 x 10 ml) and then again with water (10 ml), dried with magnesium sulphate and the solvent removed in vacuo. The crude acetal was purified by column chromatography on silicic acid (eluted with benzene). Solids were crystallised from ethanol while the liquids were distilled. The physical data for the compounds, (4-13), (4-16) and (4-17) prepared by the above procedure are tabulated below.

Compound	Yield (%)	m.p./b.p. (°C)	lit. m.p./b.p.
(4-13)	65	140-142/0.5 mm	188-189/16.5 mm[240]
(4-16)	70	52-53	53.5[240]
(4-17)	71	110-111	111.5[241]

The labelled Dioxans

The labelled compounds, (4-14), (4-15), (4-18) and (4-19) were prepared by the procedure used for the unlabelled compounds (as above) from the appropriate aryl aldehyde and propane-1,3-diol-2,2-$^2H_2$ or propane-1,3-diol-1,1,3,3-$^2H_4$. The physical data for these compounds are tabulated below.

Compound	Yield	m.p./b.p. (°C)	Incorporation (%)
(4-14)	60	140-142/0.5 mm	$^2H_4$ = 100
(4-15)	55	140-142/0.5 mm	$^2H_1$ = 22; $^2H_2$ = 78
(4-18)	48	106-109	$^2H_4$ = 100
(4-19)	62	106-109	$^2H_1$ = 22; $^2H_2$ = 78

References

1. W.J. Moore, "Physical Chemistry", Longmans Green Co. Ltd., 1963, p. 330.

2.(a) L.B. Loeb, "Fundamental Processes of Electron Discharge in Gases", Braunworth Press, U.S.A., 1939, Chap. VI, p. 258.

(b) L.B. Loeb, "Basic Processes of Gaseous Electronics", University of California Press, 1965, Chap V, p. 375.

3. J.J. Thomson and G.P. Thomson, "Conduction of Electricity Through Gases", Cambridge University Press, Fetter Lane, London, 1928, Vol. 1, Chap. 7, p. 291.

4. H.S.W. Massey "Negative Ions", Cambridge University Press, London and New Yord, 1950, p. 83.

5. H.S.W. Massey, E.H.S. Burhop and H.B. Gilbody, "Electronic and Ionic Impact Phenomena", Oxford University Press, 1966, Vol. II, Chap. 12, p. 801.

6. Ref. 1, p. 598.

7. C.E. Melton, "Principles of Mass Spectrometry and Negative Ions", Marcel Dekker, Inc., N.Y., 1970, p. 196.

8. G. Jacobs and A. Henglein, "Advances in Mass Spectrometry", ed. W.L. Mead, Institute of Petroleum, 1966, p. 287.

9. J.C.J. Thynne, Chem. Commun., 1968, 1075

References

10. J.C.J. Thynne, K.A.G. MacNeil and M.J. Caldwell, "Time-of-Flight Mass Spectrometry", ed. D. Price and J.E. Williams, Pergamon Press, London, 1969, p. 141.

11. T. McAllister, Chem.Commun., 1972, 245.

12. Ref. 10, p. 126.

13. Ref. 10, p. 132.

14. R.E. Fox, W.M. Hickam, D.J. Grove and T.J. Kjeldaas, Rev.Sci.Instru., 1955, 26, 1011.

15. J.D. Morrison, J.Chem.Phys., 1963, 39, 200.

16. K.A.G. MacNeil and J.C.J. Thynne, Int.J.Mass Spectrom. Ion Phys., 1969, 3, 35.

17. K.A.G. MacNeil and J.C.J. Thynne, Int.J.Mass Spectrom. Ion Phys., 1970, 4, 434.

18. R.E. Winters, J.H. Collins and W.L. Courchene, J.Chem.Phys., 1966, 45, 1931.

19. C.E. Melton, "Mass Spectrometry of Organic Ions", ed. I.W. McLafferty, Academic Press, N.Y., 1963, Chap. 4, p. 163.

20. M.G. Ingram and R.J. Hayden, "Mass Spectroscopy", National Academy of Sciences, National Research Council, Washington D.C., 1954, p. 44.

21. M. von Ardenne, Z. Angew.Phys., 1959, 11, 121.

22. L.G. Christophorou, R.N. Compton, G.S. Hurst and P.W. Reinhardt, J.Chem.Phys., 1966, 45, 536.

23. L.G. Christophorou and R.N. Compton, Heath Phys., 1967, 13, 1277.

24. T. Sugiura, T. Seguchi and K. Arakawa, Bull.Chem.Soc.Japan, 1967, 40, 4992.

25. S. Tsuda, A. Yokohata and M. Kawai, Bull.Chem.Soc.Japan, 1969, 42, 607, 614, 1515, 2514, 3115.

26. R.C. Dougherty and R. Weisenberger, J.Amer.Chem.Soc., 1968, 90, 6570.

27. L.G. Christophorou, "Atomic and Molecular Radiation Physics", London, Wiley Interscience, 1971.

28. J.G. Dillard, Chem.Rev., 1973, 73, 589.

29. H.F. Calcote, "Ion Molecule Reactions", ed. J.L. Franklin, London, Butterworths, 1971, Vol. 2, 485.

31. M. von Ardenne, K. Steinfelder and R. Tummler, "Electron Transfer mass spectrography of organic substances", Springer-Verlag, Berlin, 1971.

32. P.W. Harland, K.A.G. MacNeil and J.C.J. Thynne, "Dynamic Mass Spectrometry", Heyden, London and Sadtler Research Laboratories, Philadelphia 1970, Vol. 1, p. 105.

33. G. Briegleb, Ang.Chem.Int.Ed., 1964, 3, 617.

34. J. Wilson, "Mass Spectrometry", Specialist Reports, The Chemical Society, London, 1970, 1, 12.

35. J.H. Bowie, "Mass Spectrometry", Specialist Reports, The Chemical Society, London, 1970, 1, 91.

36. J.H. Bowie, "Mass Spectrometry", Specialist Reports, The Chemical Society, London, 1972, 2, 90.

37. R.W. Kiser, "Recent Developments in Mass Spectrometry", ed. K. Ogata and T. Hayakawa, Proc.Int.Conf.Kyoto, Japan, Baltimore, University Park Press, Sept. 1969, p. 844.

38. R.S. Berry, Chem.Rev., 1969, 69, 533.

39. J.C.J. Thynne, "Dynamic Mass Spectrometry", ed. D. Price, London, Heyden and Son, 1972, Vol. 3, Chapter 2.

40. P.W. Harland and J.C.J. Thynne, Int.J.Mass Spectrom. Ion Phys., 1972, 10, 11.

41. J.D. Balderschwieler and S.S. Woodgate, Accounts Chem.Res., 1971, 4, 114.

42. F.H. Futtrell, "Dynamic Mass Spectrometry", ed. D. Price, London, Heyden and Son, 1971, 2, 97.

43. J.M.S. Henis, "Ion-Molecule Reactions" ed. J.L. Franklin, London, Butterworths, 1971, 2, 395.

44. C.J. Drewery, G.C. Goode and K.R. Jennings, "MTP Internat.Rev. of Science Phys. Chem.", ed. A. Macoll, London, Butterworths, 1972, 5, 123.

45. J.H. Bowie and S.G. Hart, Int.J.Mass Spectrom.Ion Phys., 1974, 13, 1.

46. M. von Ardenne, K. Steinfelder, R. Tummler and K. Schreiber, Experientia, 1963, 19, 178.

47. M. von Ardenne, K. Steinfelder and R. Tummler, Z.Chem., 1965, 5, 287.

48. H.M. Rosenstock, M.B. Wallenstein, A.L. Wahrhaftig and H. Eyring, Proc.Nat.Acad.Sci., U.S.A., 1952, 38, 667.

49. H.M. Rosenstock and M. Krauss, "Mass Spectrometry of Organic Ions", ed. F.W. McLafferty, Academic Press, New York and London, 1963, p. 1.

50. H.M. Rosenstock and M. Krauss, "Advances in Mass Spectrometry", Oxford Pergamon Press, 1963, 2, 251.

51. H.M. Rosenstock, "Advances in Mass Spectrometry", ed. E. Kendrick, Institute of Petroleum, London, 1968, 4, 523.

52. A.L. Wahrhaftig, "MTP Internat.Rev. of Science Phys.Chem.", ed. A. Macoll, London, Butterworths, 1972, 5, 1.

53. S. Glasstone, K.H. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941, p. 184.

54. See e.g. I. Howe, "Mass Spectrometry", Specialist Reports, The Chemical Society, London, 1970, 1, 33.

55. R.G. Cooks, Org.Mass Spectrom., 1969, 2, 481.

56. D.H. Williams and R.G. Cooks, Chem.Commun., 1968, 663.

57. R.E. Winters and R.W. Kiser, J.Chem.Phys., 1966, 44, 1964.

58. Ref. 7, p. 113.

59. E. Tajima and J. Seibl, Int.J.Mass Spectrom.Ion Phys., 1969, 3, 245.

60. See e.g. I. Howe, "Mass Spectrometry", Specialist Reports, The Chemical Society, London, 1970, 1, 44.

61. R.G. Cooks, I. Howe and D.H. Williams, Org.Mass Spectrom., 1969, 2, 137.

62. A.H. Stuck and H.W. Major, Paper presented to the ASTM E14 Meeting, Dallas, 1969.

63. M. Barber and R.M. Elliot, 12th Annual Conference on Mass Spectrometry and Allied Topics, Committee E14, ASTM, Montreal.

64. J.H. Futrell, K.R. Ryan and L.W. Sieck, J.Chem.Phys., 1965, 43, 1832; K.R. Jennings, J.Chem.Phys., 1965, 43, 4176.

65. J.H. Beynon, J.W. Amy and W.E. Baitinger, Chem.Commun., 1969, 723.

66. J.H. Beynon, R.M. Caprioli, W.E. Baitinger and J.W. Amy, Org. Mass Spectrom., 1970, 3, 455, 817.

67. Ref. 60, p. 50.

68. F.W. McLafferty, P.E. Bente III, R. Kornfeld, S.C. Tsai and I. Howe, J.Amer.Chem.Soc., 1973, 95, 2120.

69. K.R. Jennings, Int.J.Mass Spectrom.Ion Phys., 1968, 1, 227.

70. J.H. Beynon, M. Bertrand, E.G. Jones and R.G. Cooks, Chem. Commun., 1972, 341.

71. T. Wachs, P.F. Bente III and F.W. McLafferty, Int.J.Mass Spectrom.Ion Phys., 1972, 9, 333.

72. W.F. Haddon and F.W. McLafferty, J.Amer.Chem.Soc., 1968, 90, 4745.

73. W.F. Haddon and F.W. McLafferty, Anal.Chem., 1969, 41, 31.

74. F.W. McLafferty and H.D.R. Schuddemage, J.Amer.Chem.Soc., 1969, 91, 1866.

75. F.W. McLafferty, R. Kornfeld, W.F. Haddon, K. Levsen, I. Sakai, P.F. Bente III, S.C. Tsai and H.D.R. Schuddemage, J.Amer.Chem. Soc., 1973, 95, 3887.

76. F.W. McLafferty and R.B. Fairweather, J.Amer.Chem.Soc., 1968, 90, 5915.

77. I. Howe, F.W. McLafferty and R.A. Kornfeld, Paper presented at the 18th Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, June 1970.

78. A.C. Ho, J.H. Bowie and A. Fry, J.Chem.Soc.B, 1971, 530.

79. J.H. Bowie, Org.Mass Spectrom., 1971, 5, 945.

80. C.L. Brown and W.P. Weber, J.Amer.Chem.Soc., 1970, 92, 5775.

81. J.H. Bowie and T.K. Bradshaw, Austral.J.Chem., 1970, 23, 1431.

82. J.H. Bowie and A.C.Ho, Austral.J.Chem., 1971, 24, 1093.

83. J.H. Bowie, J.Amer.Chem.Soc., 1973, 95, 5795.

84. J.H. Bowie, Austral.J.Chem., 1973, 26, 2719.

85. J.H. Bowie, Org.Mass Spectrom., 1974, 9, 304.

86. R.C. Dougherty, J. Dalton and F.J. Biros, Org.Mass Spectrom., 1972, 6, 1171.

87. J.H. Bowie and A.C. Ho, Austral.J.Chem., 1973, 26, 2009.

88. R.G. Alexander, D.B. Bigley and J.F.J. Todd, Org.Mass Spectrom., 1973, 7, 643.

89. R.N. Compton, L.G. Christophorou, G.S. Hurst and P.W. Reinhardt, J.Chem.Phys., 1966, 45, 4634.

90. L.G. Christophorou, J.G. Carter and A.A. Christodoulides, Chem.Phys.Lett., 1969, 3, 237.

91. P.M. Collins, L.G. Christophorou, E.L. Chaney and J.G. Carter, Chem.Phys.Lett., 1970, 4, 646.

92. W.T. Naff and R.N. Compton, J.Chem.Phys., 1971, 54, 212.

93. A. Hadjiantoniou, L.G. Christophorou and J.G. Carter, J.Chem. Soc. Faraday II, 1973, 69, 1691.

94. L. von Trepka and H. Nessert, Z.Naturforsch, 1963, 18a, 1295.

95. R.T. Aplin, H. Budzikiewicz and C. Djerassi, J.Amer.Chem.Soc., 1965, 87, 3180.

96. C.E. Melton and W.H. Hamill, J.Chem.Phys., 1964, 41, 546.

97. F.H. Dorman, J.Chem.Phys., 1966, 44, 3856.

98. R. Locht, Bull.Soc.Roy.Sci.Liege, 1966, 35, 764.

99. R. Locht and J. Monigny, Chem.Phys.Lett., 1970, 6, 273.

100. E.L. Chaney, L.G. Christophorou, P.M. Collins and J.G. Carter, J.Chem.Phys., 1970, 52, 4413.

101. Ref. 19, p. 218-220.

102. J.C.J. Thynne and K.A.G. MacNeil, J.Phys.Chem., 1971, 75, 2584.

103. M.M. Bibby and G. Carter, Trans.Faraday Soc., 1963, 59, 2455.

104. K.A.G. MacNeil and J.C.J. Thynne, Int.J.Mass Spectrom.Ion Phys., 1969, 2, 1.

105. J.C.J. Thynne and K.A.G. MacNeil, Int.J.Mass Spectrom.Ion Phys., 1970, 5, 329.

106. P. Harland and J.C.J. Thynne, J.Phys.Chem., 1970, 74, 52.

107. J. Ju and L. Kevan, J.Phys.Chem., 1973, 77, 148.

108. L.H. James and G. Carter, J.Electron Contr., 1962, 13, 213.

109. R.K. Asundi and J.D. Craggs, Proc.Phys.Soc.London, 1964, 83, 611.

110. R. Grawjer and C. Lifshitz, Isr.J.Chem., 1968, 6, 847.

111. W.T. Naff, C.D. Cooper and R.N. Compton, J.Chem.Phys., 1968, 49, 2784.

112. C. Lifshitz and R. Grawjer, Int.J.Mass Spectrom.Ion Phys., 1972, 10, 25.

113. W.M. Hickam and D. Berg, J.Chem.Phys., 1959, 29, 517.

114. W.M. Hickam and D. Berg, Adv.Mass Spectrom., 1959, 1, 458.

115. R.E. Fox and R.K. Curran, J.Chem.Phys., 1961, 34, 1595.

116. C.E. Brion and G.E. Thomas, Int.J.Mass Spectrom.Ion Phys., 1968, 1, 25.

117. K.A.G. MacNeil and J.C.J. Thynne, Trans.Faraday Soc., 1968, 64, 2212.

118. S. Tsuda, Y. Yokohata and M. Kawai, Bull.Soc.Chem.Japan, 1970, 43, 1649.

119. J.J. de Corpo, D.A. Bafus and J.L. Franklin, J.Chem.Phys., 1971, 54, 1592.

120. J.J. de Corpo and J.L. Franklin, J.Chem.Phys., 1971, 54, 1885.

121. A. Ito, K. Matsumoto and T. Takenchi, Org.Mass Spectrom., 1972, 6, 1045.

122. K. Jager and A. Henglein, Z.Naturforsch, 1967, 22a, 700.

123. J.T. Larkins, J.M. Nicholson and F.E. Saalfeld, Org.Mass Spectrom., 1971, 5, 265.

124. T. Shiga, H. Yamaoka, K. Arakawa and T. Suguina, Bull.Soc. Chem.Japan, 1972, 45, 2065.

125. J. Yinon and H.G. Boettger, Int.J.Mass Spectrom.Ion Phys., 1972, 10, 161.

126. J.F.J. Todd, R.B. Turner, B.C. Webb and C.H.J. Wells, J.Chem. Soc. Perkin II, 1973, 1167.

127. J.H. Bowie, T. Blumenthal and I. Walsh, Org.Mass Spectrom., 1971, 5, 777.

128. J.H. Bowie, S-O. Lawesson, B.S. Larsen, G.E. Lewis and G. Schroll, Austral.J.Chem., 1968, 21, 2031.

129. J.H. Bowie, R.G. Cooks and G.E. Lewis, Austral.J.Chem., 1967, 20, 1601.

130. J.H. Bowie, R.G. Cooks, N.C. Jamieson and G.E. Lewis, Austral.J.Chem., 1967, 20, 2545.

131. B.S. Larsen, G. Schroll, S-O. Lawesson, J.H. Bowie and R.G. Cooks, Tetrahedron, 1968, 24, 5193.

132. J.H. Bowie and B. Nussey, Org.Mass Spectrom., 1972, 6, 429.

133. J.H. Bowie and B. Nussey, Org.Mass Spectrom., 1974, 9, 310.

134. C.D. Cooper, R.N. Compton, H.C. Schweinler and V.E. Anderson, 20th Conference Mass Spectrometry and Allied Topics, ASTM, E14, Dallas, 1972, p. 35.

135. J.H. Bowie and B.D. Williams, Int.J.Mass Spectrom.Ion Phys., in press.

136. T. Blumenthal and J.H. Bowie, Austral.J.Chem., 1971, 24, 1853.

137. J.H. Bowie, Austral.J.Chem., 1971, 24, 989.

138. G.A. Ropp and C.E. Melton, J.Amer.Chem.Soc., 1958, 80, 3509.

140. P.C. Rankin, Lipids, 1971, 5, 825.

141. J.E. Collin and R. Locht, Int.J.Mass Spectrom.Ion Phys., 1970, 3, 465.

142. B.C. de Souza and J.H. Green, J.Chem.Phys., 1967, 46, 1421.

143. E.M. Chait, N.B. Askew and B.C. Matthews, Org.Mass Spectrom., 1969, 2, 1135.

144. A.L. Faragher and F.M. Page, Trans.Faraday Soc., 1966, 62, 3072.

145. J.T. Herron and V.H. Dibeler, J.Amer.Chem.Soc., 1960, 82, 1555.

146. V.H. Dibeler, R.M. Reese and J.L. Franklin, J.Amer.Chem.Soc., 1961, 83, 1813.

147. M. Inoe, J.Chem.Phys., 1966, 63, 1061.

148. C.E. Brion and L.A.R. Olsen, Int.J.Mass Spectrom.Ion Phys., 1972, 9, 413.

149. V.I. Klovostenko, I.I. Furlei, A.N. Kost, V.A. Budylin and L.G. Yudin, Dokl.Phys.Chem., 1969, 189, 778.

150. R.H. Huebner, R.N. Compton and H.C. Schweinler, Chem.Phys.Lett., 1968, 2, 407.

151. W.W. Pandler and S.A. Humphrey, Org.Mass Spectrom., 1970, 2, 407.

152. J.H. Bowie and A.J. Blackman, AustralJ.Chem., 1972, 25, 1335.

153. K. Jager and A. Henglein, Z.Naturforsch, 1966, 219, 1251.

154. C. Nolde, J.Ø.Madsen, S-O. Lawesson and J.H. Bowie, Arkiv.Kemi., 1969, 31, 481.

155. J.H. Bowie, F. Duus, S-O. Lawesson, F.C.V. Larsson and J.Ø. Madsen, Austral.J.Chem., 1969, 22, 153.

156. F. Duus, G. Schroll, S-O. Lawesson, J.H. Bowie and R.G. Cooks, Arkiv.Kemi, 1969, 30, 347.

157. R. Tummler and K. Steinfelder, Z.Chem., 1967, 7, 1.

158. R. Tummler, Wiadomosci Chemiczne, 1970, 23, 245.

159. S. Huneck and J. Santesson, Z.Naturforsch, 1969, 24b, 756.

160. Ref. 31, p. 301, 302.

161. S. Huneck, C. Djerassi, D. Becker, M. Barber, M. von Ardenne, K. Steinfelder and R. Tummler, Tetrahedron, 1968, 24, 2707.

162. Ref. 31, p. 244, 245.

163. M. von Ardenne, K. Steinfelder and R. Tummler, Z.Chem., 1965, 5, 287.

164. R. Tummler, K. Steinfelder, E.C. Owen and D.W. West, Org.Mass Spectrom., 1971, 5, 41.

165. Ref. 31, p. 177.

166. M. von Ardenne, G. Osski, K. Schreiber, K. Steinfelder and R. Tummler, Kulturpflanze, 1965, 13, 101, 115.

167. G. Adam, D. Voigt and K. Schreiber, J.Prakt.Chem., 1970, 312, 1063.

168. G. Adam, D. Voigt, K. Schreiber, M. von Ardenne, R. Tummler and K. Steinfelder, J.Prakt.Chem., 1973, 315, 125.

169. W. Stoeklin, Helv.Chim.Acta, 1967, 50, 491.

170. S. Huneck and R. Tummler, J.Prakt.Chem., 1968, 38, 233.

171. G. Adam, K. Schreiber, R. Tummler and K. Steinfelder, J.Prakt.Chem., 1971, 313, 1051.

172. R. Brandt, H. Kaufmann and T. Reichstein, Helv.Chim.Acta, 1966, 49, 1814.

173. S. Hoffmann, E.K. Weiss and T. Reichstein, Helv.Chim.Acta, 1966, 49, 1855.

174. H. Allglier, E.K. Weiss and T. Reichstein, Helv.Chim.Acta., 1967, 50, 431, 456.

175. Ref. 31, p. 179.

176. R.G. Kostyanosky, Tetrahedron.Lett., 1968, 2721.

177. B.C. Pant and R.E. Sacher, Inorg.Nucl.Chem.Lett., 1969, 5, 549.

178. R. Muller and H.J. Frey, Z.Anorg.Allg.Chem., 1969, 368, 113.

179. J.H. Bowie and B. Nussey, Chem.Commun., 1970, 17.

180. J.H. Bowie and B. Nussey, Org.Mass Spectrom., 1970, 3, 933.

181. P.A. Preston and N.A. Weir, Inorg.Nucl.Chem.Lett., 1968, 4, 279.

182. G.M. Begun and R.N. Compton, J.Chem.Phys., 1973, 58, 2271.

183. R.W. Kiser, R.E. Sullivan and M.S. Lupin, Anal.Chem., 1969, 41, 1958.

184. R.E. Winters and R.W. Kiser, J.Phys.Chem., 1965, 69, 1618.

185. S. Pignatoro, A. Foffani, F. Grasso and B. Cantone, Z.Phys.Chem.(Frankfurt), 1965, 47, 106.

186. R.E. Sullivan and R.W. Kieser, J.Chem.Phys., 1968, 49, 1978.

187. R.E. Sullivan, M.S. Lupin and R.W. Kiser, Chem.Commun., 1969, 655.

188. W.C. Gilbert, L.T. Taylor and J.G. Dillard, J.Amer.Chem.Soc., 1973, 95, 2477.

189. H. Budzikiewicz, J.I. Bauman and C. Djerassi, Tetrahedron, 1965, 21, 1855.

190. K. Bieman, "Mass Spectrometry", McGraw-Hill, New York, N.Y., 1962, p. 102.

191. H. Budzikiewicz, D.H. Williams and C. Djerassi, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, California, 1967, p. 67.

192. F.W. McLafferty, "Interpretation of Mass Spectra", W.A. Benjamin, New York, N.Y. 1966, p. 118.

193. H. Budzikiewicz, C. Djerassi and D.H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry", Holden-Day, San Francisco, California, 1964, Vol. 1 and 2, See Index (Retro-Diels-Alder decompositions).

194. R.C. Dougherty, J.Amer.Chem.Soc., 1968, 90, 5788.

195. K. Biemann, Angew.Chem., 1962, 74, 102.

196. E.M. Emery, Analyt.Chem., 1960, 32, 1495.

197. J.H. Beynon, B.E. Job and A.E. Williams, Z.Naturforsch, 1965, 20A, 388.

198. S. Meyerson and J.L. Corbin, J.Amer.Chem.Soc., 1965, 87, 3045.

199. S-O. Lawesson, J.Ø. Madsen, G. Schroll, J.H. Bowie and D.H. Williams, Acta Chem.Scand., 1966, 20, 2333.

200. L.P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, 1940, Chapter 7.

201. M.M. Bursey and F.W. McLafferty, J.Amer.Chem.Soc., 1966, 88, 529.

202. M.M. Bursey, Org.Mass Spectrom., 1968, 1, 31.

203. M.S. Chin and A.G. Harrison, Org.Mass Spectrom., 1969, 2, 1073.

204. R.G. Cooks, I. Howe and D.H. Williams, Org.Mass Spectrom., 1969, 2, 137.

205. J.L. Occolowitz, Chem.Commun., 1968, 1226.

206. J.H. Bowie and P.Y. White, Org.Mass Spectrom., 1972, 6, 75.

207. See e.g. I. Howe, "Mass Spectrometry", Specialist Reports, The Chemical Society, London, 1970, 1, 53.

208. G. Schroeter, E. Kindermann, C. Dietrich, C. Beyschlag, C.L. Fleischauer, E. Riebansahm and C. Oesterlin, Annalen, 1922, 426, 17.

209. L.W. Deady, R.D. Topsom and J. Vaughan, J.Chem.Soc., 1965, 5718.

210. D. Vorländer, Annalen, 1894, 280, 205.

211. B.N. Ghosh, J.Chem.Soc., 1915, 107, 1588.

212. D.R. Mehta and P.R. Ayyar, J.Univ Bombay, 1939, 8, 176; Chem.Abs., 1949, 34, 2814.

213. F.D. Chattaway and R.M Geopp, J.Chem.Soc., 1933, 699.

214. C.A. Beuhler, G.F. Deebel and R. Evans, J.Org.Chem., 1941, 6, 216.

215. J.R. Knowles and R.O.C. Norman, J.Chem.Soc., 1961, 2938.

216. B.C. Subba Rao and G.P. Thakar, Current Science (India) 1960, 29, 389; Chem.Abs., 1961, 55, 9362.

217. D.H. Rosenblatt, J. Epstein and M. Levitch, J.Amer.Chem.Soc., 1953, 75, 3277.

217a. J.B. Fishman, J.Amer.Chem.Soc., 1920, 42, 2295.

218. R.F. Collins, M. Davis and J. Rosenbaum, J.Science Food and Agriculture, 1969, 20, 690; Chem.Abs., 1970, 72, 55356.

219. C.A. Buehler, F.K. Kirchner and G.F. Deebel, Org.Synth.Coll., Vol. 3, p. 468.

220. S. Seki, K. Taya and K. Yamada, Chem.Abs., 1963, 59, 501a.

221. E. Epstein and M. Meyer, J.Amer.Chem.Soc., 1955, 77, 4059.

222. F. Mayer, Chem.Ber., 1909, 42, 1134.

223. H.C. Barany and M. Pianka, J.Chem.Soc., 1946, 965.

224. A. Dasettimo and M.F. Saettone, Tetrahedron, 1965, 21, 1923.

225. E.P. Sergeant, Austral.J.Chem., 1969, 22, 1189.

226. H. Hoyer and R. Macdonald, Chem.Abs., 1962, 57, 3352d.

227. N.G. Gaylord and P.M. Kamath, Organic Synthesis, 32, 25.

228. R.P. Staiger and E.B. Miller, J.Org.Chem., 1959, 24, 1214.

229. J. Knebel, J.Prakt.Chem., 1891, 43, 381.

230. M.L. Bender, F.J. Kezdy and B. Zerner, J.Amer.Chem.Soc., 1963, 85, 3017.

231. J.S. Shannon, Austral.J.Chem., 1962, 15, 265.

232. C.S. Hamilton and C.L. Simpson, J.Amer.Chem.Soc., 1929, 51, 3158.

233. N.F. Nystrom, J.Amer.Chem.Soc., 1959, 81, 610.

234. M.T. Bogert and E.M. Slocum, J.Amer.Chem.Soc., 1924, 46, 763.

235. R.O. Clinton, C.M. Suter, S.C. Laskowski, M. Jackman and W. Huber, J.Amer.Chem.Soc., 1945, 67, 594.

236. C.H. Crogan, L.M. Rice and E.E. Reid, J.Org.Chem., 1955, 20, 50.

237. P.Y. White, Ph.D. Thesis, University of Adelaide, South Australia, 1971.

238. D. Seebach, B.W. Erickson and G. Singh, J.Org.Chem., 1966, 31, 4303.

239. W. Davey and J.R. Gwilt, J.Chem.Soc., 1950, 204.

240. E.J. Salmi and K. Kyrki, Chem.Abs., 1947, 41, 5480.

241. H.H. Hibbert and M.G. Sturrock, J.Amer.Chem.Soc., 1928, 50, 3374.

Bowie, J. H. & Ho, A. C. (1973). Electron impact studies: LXXIX. Negative-ion mass spectrometry of functional groups, 2-Aryl-1,3-oxathians and 1,3-dioxans. *Australian Journal of Chemistry, 26*(9), 2009-2018.

Bowie, J. H. & Ho, A. C. (1974). Electron-impact studies: LXXXVII - *Ortho* effects in the negative ion mass spectra of salicylates and anthranilates. *Organic Mass Spectrometry*, *9*(10), 1006-1016.