SOME STUDIES IN ORGANIC MASS SPECTROMETRY

A THESIS

PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

THE UNIVERSITY OF ADELAIDE

BY

BRIAN NUSSEY, B.Sc.(HONS)

DEPARTMENT OF ORGANIC CHEMISTRY

JANUARY 1974.

TO HAZEL

with heartfelt thanks.

INDEX

INDEX (continued)

INDEX (continued)

INDEX (continued)

INDEX (continued)

INDEX (continued)

STATEMENT

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

Brian Nussey.

ACKNOWLEDGEMENTS

I wish to thank Dr. J.H. Bowie most sincerely for his enthusiastic encouragement and guidance throughout the course of this work.

I am greatly indebted to the following people: Dr. A.D. Ward for his interest and stimulating help during the absence of Dr. Bowie, to Mr. T. Blumenthal for his skilful technical assistance and to Mr. P.J. Tildesley for his help with computational problems during the Linear Free-Energy Determinations.

I am grateful to the other members of Staff and to my research colleagues for many helpful discussions.

Part of this research was carried out during the tenure of a University Research Grant, which I gratefully acknowledge.

PUBLICATIONS

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

1. "Hydrogen Randomization in Negative Ions", Bowie, J.H., Nussey, B., Chem.Commun., 18 (1970).

2. "Novel Rearrangements Occurring during the Thermolysis of 2,3-Diphenyl-2H-azirine", Bowie, J.H., Nussey, B., Chem.Commun., 1565 (1970).

3. "The Formation of $[C_{13}H_9^+]$ in the Mass Spectra of Benzyl Phenyl Ketoxime and 2,3-Diphenyl-2H-Azirine", Simons, B.K., Nussey, B., Bowie, J.H., Org. Mass Spec., 3, 925 (1970).

4. "Skeletal Rearrangement and Hydrogen Scrambling Processes in the Positive and Negative Ion Mass Spectra of Phenyl Derivatives of Elements of Group IV and V", Bowie, J.H., Nussey, B., Org.Mass Spec., 3, 933 (1970).

5. "Substituent Effects in the Negative Ion Spectra of Nitroaryl Esters", Bowie, J.H., Nussey, B., Org.Mass Spec., 6, 429 (1972).

6. "The Thermal Rearrangements of 2,3-Diphenyl-2H-azirine", Bowie, J.H., Nussey, B., J.Chem.Soc. Perkin I., 1693 (1973).

7. "The Reaction Between 2,3-Diphenyl-2H-azirine and Phenyldiazomethane", Bowie, J.H., Nussey, B., Ward, A.D., Aust.J.

Chem., 26, 2547 (1973).

8. "Substituent Effects in the Negative-Ion Mass Spectra of Aryl Esters", Bowie, J.H., Nussey, B., Org.Mass.Spec., in press.

PART I - SUBSTITUENT EFFECTS IN NEGATIVE-ION MASS SPECTRA

SUMMARY

The field of negative-ion mass spectrometry is relatively unexplored. The purpose of this study was to continue the search for information concerning the type of molecule that will produce simple negative-ion mass spectra. It is shown that some simple aromatic esters produce negative-ion mass spectra, and that these spectra exhibit enhanced stabilization when a nitro group or a cyano group is present in the molecule. A mechanism is proposed for the fragmentation pathway, and it is shown that these molecules exhibit a substituent dependence between the Hammett sigma constant and the parameters defined by McLafferty and Harrison for positive-ion mass spectral fragmentations. This substituent dependence must be interpreted cautiously and does not provide any useful information about the mechanism of fragmentation.

CHAPTER 1. INTRODUCTION

1.1 History

The beginning of mass spectrometry originates with the discovery of positively charged electrical entities (canal rays) by E. Goldstein[1] in 1886, but a quantitative study of ions was not attempted until about 1910 when J.J. Thompson[2] developed the mass spectrograph. The mass spectrograph produces a focussed mass spectrum on a photographic plate and is able to detect both positively and negatively charged ions with equal ease.

The term mass spectrometer was not introduced until 1926 when Smythe and Mattauch used it to describe an instrument which brought a focussed beam of ions to a fixed collector[3]. This type of instrument is primarily designed to accelerate and detect positively charged ions, but negative-ions may also be examined by reversing the magnetic field.

Positive-ion mass spectrometry has undergone extensive development and refinement in the sixty years since the first report of the mass spectrograph, while negative-ion mass spectrometry in comparison has undergone significantly less development.

1.2 Complications in Negative-ion Studies

The reasons for the slow development of negative-ion mass spectrometry have been outlined[4], and can be classified under the following headings:

1) Poor intensity of negative-ions.

2) Complicating ion-molecule reactions.

3) The various modes of negative-ion formation.

4) Collection efficiency of ions.

5) Lack of sensitive instrumentation.

1.2 (i) Intensity

The intensity of ions produced in a negative-ion mass spectrum are reported[5,6] to be generally of much lower abundance (*c.a.* 1000 times) than the corresponding positive-ions. This makes detection of negative-ions more difficult and results in the production of weaker spectra than for the corresponding positive-ion spectra. Decompositions occurring in flight between the acceleration plates and the collector ('metastable' decompositions) are correspondingly difficult to measure.

1.2 (ii) Ion-molecule Reactions

A conventional mass spectrometer operates at a low pressure (*c.a.* 10^{-7}-10^{-6} Torr.). At these pressures the probability of collisions between ions and molecules is small. In many of the negative-ion studies carried out so far much higher pressures

(*e.g.* 10^{-2}-10^{-3} Torr.) have been used to obtain reasonable spectra[eg.7] and, at these pressures, the probability of ion-molecule reactions occurring in the ion source is greatly increased. These ion-molecule reactions may deplete or enhance the intensity of some peaks in the spectrum and, in addition, new peaks may appear as a result of such reactions. The abundances of peaks that result from ion-molecule reactions are strongly pressure dependent and such peaks may therefore be detected by observing the changes in peak abundance with increasing source pressure. The abundance of peaks produced by ion-molecule reactions will increase as the source pressure is increased.

1.2 (iii) Modes of Negative-ion Formation

The modes of negative-ion formation (see section 1.3) are not well established, but they are dependent upon both the electron energy and the source pressure[4,5].

An alteration in the electron-beam energy may result in a change in the type of negative-ion formation and such an effect is reflected by a change in the intensity of certain peaks in the spectrum. Some modes of formation are only observed at particular electron-beam energies. The various mechanisms of negative-ion production are pressure dependent in specific ways, and variation of the source pressure produces well defined changes in the relative intensities of peaks[8,9].

1.2 (iv) Collection Efficiency[5]

Since the first dynode of the electron multiplier detector is maintained at a high negative potential (2-6keV) it will repel negative ions and thus lower the collection efficiency. Hence the negative-ion accelerating potential must always be maintained at a value $\geqslant$ 2kV higher than that of the first dynode.

1.2 (v) Sensitive Instrumentation

Because the ions produced in a negative-ion mass spectrum are of weak intensity and are sensitive to small variation in ion source conditions, it is desirable to equip the mass spectrometer with some special features:

1) A high detection sensitivity is required because negative-ion production by ionizing electrons is much less than positive-ion production.

2) Many of the negative-ions produced are extremely reactive and consequently a corrosion-resistant filament is desirable.

3) If the appearance potential of a given ion is to be measured, a very precise control of the ionizing radiation is required.

4) As many negative-ion studies must be carried out at high pressures ($\geqslant 10^{-4}$ Torr.) in the ionization chamber, a

differential pumping unit is required to reduce any excessive loss of ions by charge transfer and elastic scattering[5]. The differential pumping is applied between the ionizing chamber and the analyzer tube.

Many of these instrument modifications have only been developed in the past decade, and their absence was a contributing factor to the slow development of negative-ion mass spectrometry.

1.3 Ion Formation

When an electron is fired at a stationary neutral molecule a high-energy collision results. If the projectile removes an electron, a positively charged ion is formed. However, if the neutral molecule absorbs the electron, the product is a negatively charged ion[4].

While it is true that a negative-ion is simply a neutral molecule or fragment that has captured an electron, the mechanism for capture cannot be represented in simple terms. Negative-ions are formed by the interaction of electrons with neutral molecules through basically three different processes:

1.3 (i) Ion-pair Production[3-5]

Ion-pair production occurs from an excited state of the molecule. The reaction sequence can be represented as a two step

process:

$$AB + e \rightarrow AB^{*} + e_{s} \qquad (1\text{-}1)$$

$$AB^{*} \rightarrow A^{+} + B^{-} \qquad (1\text{-}2)$$

where AB^{*} is the excited state and e_{s} is an inelastically scattered electron. The kinetic energy of the ions produced will probably be distributed in accord with the ratio of their respective degrees of freedom.

1.3 (ii) Dissociative Capture[3-5]

The most general type of electron capture by a diatomic molecule is dissociative capture.

$$AB + e \rightarrow A^{\cdot} + B^{-} \qquad (1\text{-}3)$$

Dissociative capture may occur to a bound state of the negative-ion which then undergoes internal conversion to a repulsive state that gives a dissociative ionization.

1.3 (iii) Nondissociative capture[3-5]

This broad category can be further subdivided into the following classifications[4]:

(a) Temporary Nondissociative Attachment

This is the simplest type of nondissociative electron-capture process.

$$AB + e \rightleftharpoons (AB^{-})^{*} \qquad (1\text{-}4)$$

The electron is captured into discrete states of AB to give a vibrationally excited AB molecular anion. If the vibrationally excited molecular-anion does not emit a photon or undergo a collision stabilization reaction, the electron will be ejected by autodetachment (Auger process) within a time comparable to vibration. Such diatomic molecular negative-ions have never been detected at low pressure because of their short life times. However, at high pressure these negative-ion states may play an important role in the interaction of low-energy electrons with molecules.

(b) Radiative Nondissociative Attachment

Stable negative-ions can be formed in an atom of a molecule by subsequent radiation of the excess energy of formation from $(AB^-)^*$.

$$AB + e \rightleftharpoons (AB^-)^* \rightarrow AB^- + h\nu \qquad (1\text{-}5)$$

(c) Dielectric Attachment

Dielectric attachment is an attachment process in which the incoming electron excites an atom or molecule and is simultaneously captured into a doubly excited state of the negative-ion.

$$AB + e \rightleftharpoons (AB^-)^{**} \rightarrow AB^- + h\nu \qquad (1\text{-}6)$$

The excited negative-ion may then undergo two possible

reactions:

(i) eject the electron by autodetachment,

or (ii) become stabilized by the emission of radiation.

1.3 (iv) Energetics

The pressure dependence of negative-ions produced by the three major ionization processes (1.3 (i)-(iii)) is more complicated than is the case for positive-ions[4]. Caution must therefore be applied to any interpretation of the mode of formation of negative-ions from pressure studies.

When an electron collides with a molecule in the gas phase, the molecule can undergo one of two possible reactions. Firstly, the electron can be absorbed by nondissociative capture and, since there is no other particle produced in the collision process, the molecular anion must retain as internal energy all the electron energy. If the excess energy is not removed either by radiative decay or by collision with other molecules (unlikely at low source pressures) the molecular anion will fragment. Secondly, if the electron is absorbed either by dissociative capture or ion-pair production, the excess energy can be dissipated during the formation of the two product species.

It is desirable to use electrons of low-energies if a molecular anion is required, but high currents of slow electrons

cannot easily be produced in a normal ion source. Nevertheless, a number of papers have been published recently[10] reporting the observation of molecular negative-ions at high electron energies. This behaviour has been accounted for[11-13,15] in terms of slow moving secondary electrons produced either during positive-ion formation or, alternatively, by emission from electrode surfaces. This argument is strengthened by the observation that sulphur hexafluoride[14], hexafluoroacetone[13,15] and nitrobenzene[12] all accept slow electrons to produce molecular anions of low internal energy.

1.3 (v) Metastable Ions[3,16,17]

A schematic representation of a double-focussing mass spectrometer of Nier-Johnson geometry is shown in Figure (1-1). There are three distinct regions in the double focussing mass spectrometer, where fragmentation can be observed; these are the source, the first and second field free regions. The lifetime of the decomposing ion will determine where in the flight path the decomposition is observed.

Ions of mass m_1 with a lifetime of about 1 μsec or less will decompose to yield a daughter ion m_2 in the source[18]. The ion m_2, if sufficiently stable, will be accelerated, and will be recorded as a "normal" sharp signal at m_2/e. Ions of mass m_1 with

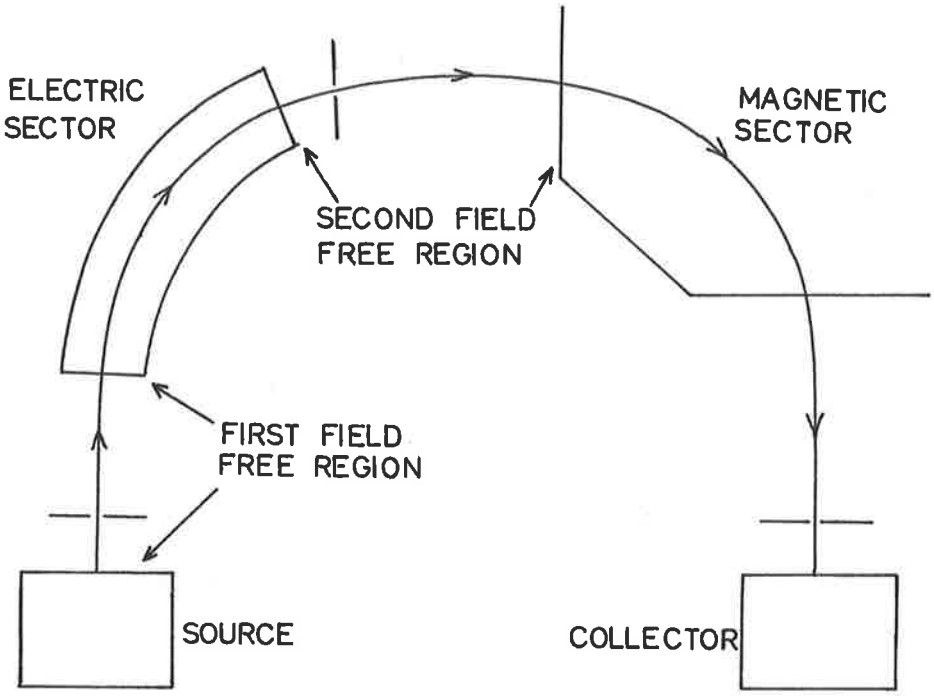


Figure 1-1. A schematic drawing of a Nier-Johnson double focussing mass spectrometer.

a slightly longer lifetime (2-11 μsec) will be accelerated, and will decompose into daughter ions m_2^1 before entering the electrostatic analyser. Since the velocity of m_2^1 is determined by the velocity attained by the heavier ions 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_2^1 does not fulfil the conditions required to pass through the electric sector field and therefore does not appear in the spectrum. Ions of mass m_1

with even longer lifetimes (> 11μsec) decompose to daughter ions m_2^{11} in the second field-free region between the electrostatic and magnetic analysers. The ions m_2^{11} have the same mass and velocity as m_1^1, but, since they are not energy focussed, they are recorded in the spectrum as diffuse, low intensity peaks at a value equal to m_2^2/m_1 [19].

If the ratio of the acceleration voltage to the electric sector voltage is increased above its normal value to the value m_2/m_1, the main ion beam will be deflected, and the daughter ions m_2^1 will pass through the electric sector[20]. This process is called "double defocussing" and the daughter ions produced are called "defocussed metastable transitions". A "defocussed metastable transition" may be produced in two ways; *viz.*

(i) by raising the acceleration voltage while keeping the electrostatic voltage constant[21], or

(ii) by lowering the electrostatic voltage while keeping the acceleration voltage constant[22].

Defocussed metastable transitions reported in the discussion were obtained using the second method. The development of metastable defocussing has allowed each metastable transition to be determined uniquely and sensitively. These metastable transitions can be explained in terms of the Q. E. T. (see section 1.4

(i)) as decomposition occurring from low-energy percursor ions within a narrow energy segment controlled by the narrow rate constant limits (Log_{10} k ≃ 5-6) of a typical mass spectrometer[23]. Metastable transitions have been used to provide valuable information concerning mass spectral processes[17], and a summary of various applications follows.

The presence, absence or relative abundance of the metastable transitions for various processes can provide valuable information about their relative activation energies[24]. A comparison of the abundances of the appropriate metastable transitions and their normal ions can yield information about rearrangement reactions[25]. The ratio of metastable transitions for competing reactions from an energetic ion provides information about the identity or non-identity of the structures[26], whereas a study of metastable transitions will provide more relevant information about scrambling reactions than a study of normal decomposition in the ion source[23]. This approach can be extended to isotope effects where larger variations are observed for metastable transitions than normal decompositions[27].

Most of the information published about metastable transitions has been obtained from investigations in the positive-ion mode. It has been shown[10] that the same rules also apply to metastable transitions in the negative-ion mode.

1.4 Theoretical Aspects

Excellent reviews of the ionization of molecules and of dissociation processes that occur from molecular cations produced in a mass spectrometer are available[3-5,16,17,28-37], and brief descriptions of those areas relevant to the subject matter of this thesis are enumerated below.

1.4 (i) The Quasi-Equilibrium Theory[3-5,16,17,38-40]

In 1952, the first attempt was made to place the fragmentation processes of polyatomic molecules after ionization and their resultant mass spectrum on a theoretical basis[38]. This theory has become known as the quasi-equilibrium theory of mass-spectra (Q.E.T.), and is based on several assumptions, *viz.*

(1) The ionization of a polyatomic molecule by an electron is generally assumed to be a vertical or Franck-Condon transition to one or another of the potential curves of the ion.

(2) The time required for dissociation of the initial molecular ion is relatively long compared with the time of interaction leading to its formation.

(3) The rate of dissociation of the ion is slow relative to the rate of redistribution of energy of the internal degrees of freedom, both electronic and vibrational of the ion.

(4) The observed mass spectrum is formed by a series of competing consecutive, unimolecular decomposition reactions starting with those molecular ions containing sufficient internal energy to fragment, concentrated in the necessary degrees of freedom.

The dependence of the rate constant for the decomposition of a unimolecular ion on the internal energy is a feature common to several alternative unimolecular rate theories (e.g. Eyring *et al*[41] and the R.R.K.M. theory[42-44]).

The Q.E.T. has been used in varying degrees of complexity. The full Q.E.T. requires certain information that is not easy to acquire, including the energy distribution in ions and their correct vibrational frequencies. Consequently, the theory has developed relatively slowly, and those papers that have appeared contain large amounts of complex mathematics. At a much less sophisticated level the Q.E.T. can be reduced to the simple equation (1-7)[16] for the unimolecular rate constant k(E) for any dissociation.

$$k(E) = \nu\left(\frac{E - E_o}{E}\right)^{s-1} \qquad (1\text{-}7)$$

where k(E) represents the rate constant at total energy E with activation energy E_o. ν may be regarded as a frequency factor, with low frequency factors usually reflecting a restricted geometry in the transition state[16].

The activated complex of a rearrangement reaction involves new bond formation and hence some vibrational frequencies will increase and some internal rotation will be restricted. This type of activated complex is called a "tight complex". In a direct cleavage reaction, the activated complex (known as a loose complex) involves stretching of a bond along the reaction co-ordinate. Some vibrational frequencies will decrease and certain torsional and skeletal vibrations might change to internal rotations in the activated complex[45].

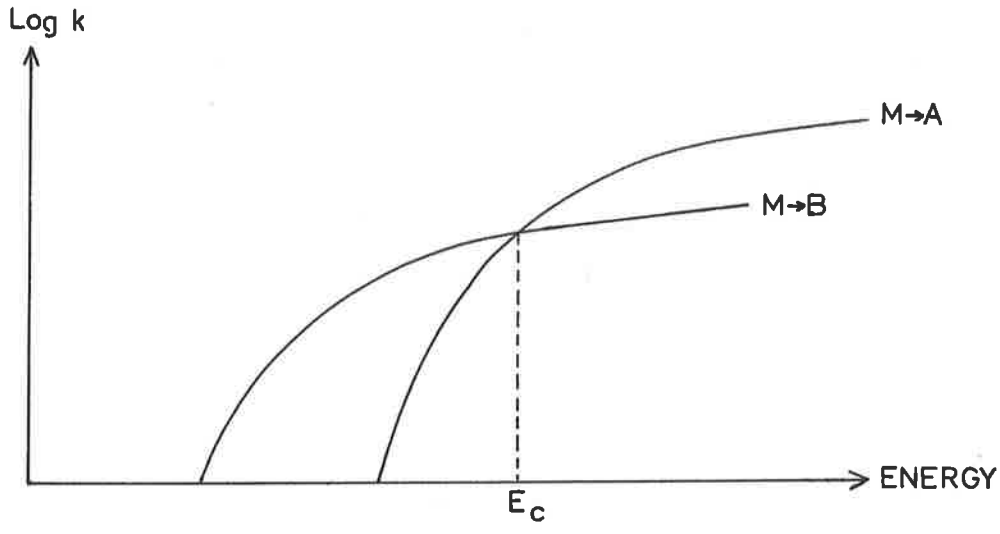


Figure 1-2. Log k vs E plots (see section 1.4 (ii)) of a competing simple cleavage (A) and a rearrangement (B).

Consider a molecular ion that can undergo two competing reactions (see Figure 1-2). The Q.E.T. predicts that M → A is a simple cleavage while M → B represents a rearrangement[46]. From the diagram it is obvious that the abundance of the rearrangement ion B increases relative to that of the direct cleavage ion A as the electron-beam energy is lowered. These results clearly show that a rearrangement reaction proceeds with a slower rate constant ($< 10^{10}$ sec^{-1}) than a direct cleavage reaction (*c.a.* 10^{13} sec^{-1}).

These results agree well with those recently reported[10] for the negative-ion mass spectra of 2-(4-nitrophenyl)-1,3-oxathiane. This paper reports the formation of the molecular anion by two different processes using a nominal electron beam energy of 70eV (see Figure 1-3).

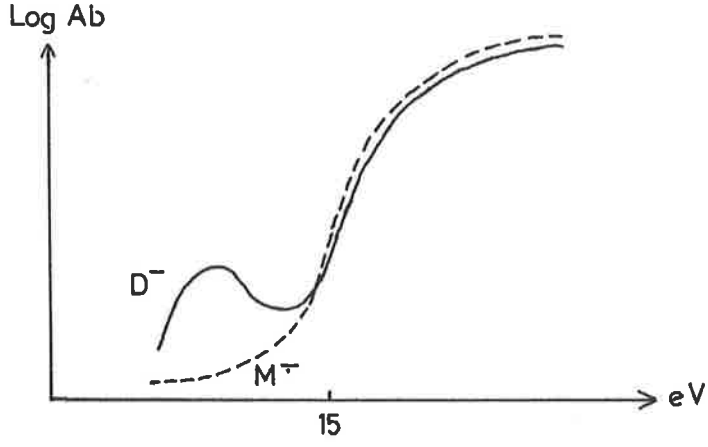


Figure 1-3. A plot showing the log abundance of the molecular ion and a daughter ion with electron beam energy ($M^{-} \rightarrow D^{-}$).

A daughter ion is produced by decomposition of molecular anions whose energies are near thermal, when the electron beam energy is above 15eV, while below this value the daughter ions are produced from a high-energy species which fragments rapidly. These conclusions are supported by deuterium-labelling studies[10] which show the high-energy molecular ion (below 15eV) produces a daughter ion without prior hydrogen scrambling while the low-energy molecular ion (above 15eV) produces a daughter ion which shows almost complete hydrogen-deuterium scrambling. These observations, although unusual at first glance, are in complete agreement with those reported for positive-ions. In both cases the *low energy* molecular ion is decomposing with prior rearrangement rather than by simple cleavage.

Equation (1-7) is so oversimplified that it is not surprising to find that calculations based upon it have needed to adjust one, or more of the parameters to obtain even modest correlation between the calculated and observed spectra[40].

The Q.E.T. was postulated and developed as a model for the fragmentation reactions of molecular cations. However, a recent paper[47] reports the successful application of the Q.E.T. to negative-ions formed in the mass spectrometer.

1.4 (ii) Ionization Efficiency Curves

An ionization efficiency curve is a plot of the ion current

of a given ion as a function of the energy of the ionizing beam[3]. A striking property of these curves (see Figure 1-4) is the relative insensitivity of the ion current to the electron energy in the region of 50eV to about 150eV. For this reason most conventional mass spectrometers are operated at an electron energy of 70eV.

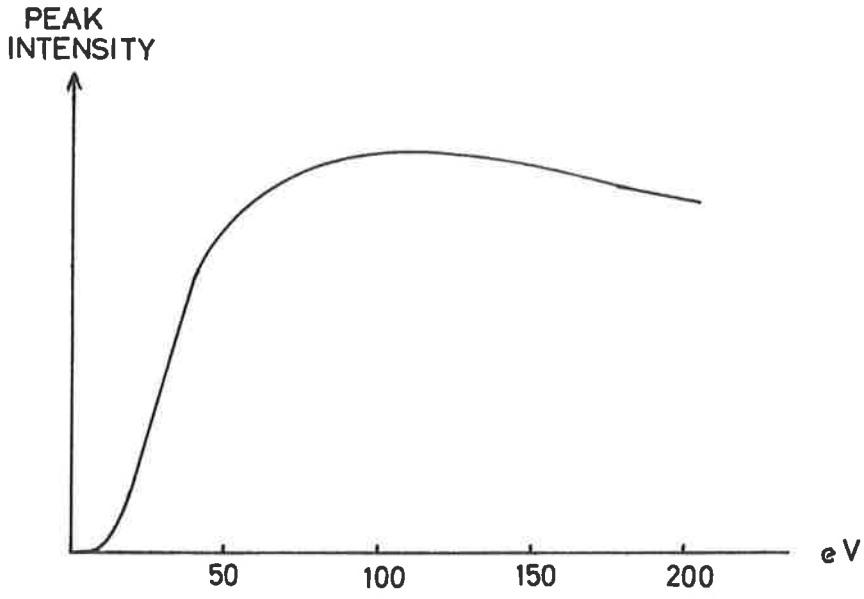


Figure 1-4. A typical ionization efficiency curve.

1.4 (iii) Ionization Potentials[3,39]

The ionization potential of a molecule is defined[3] as the minimum energy required to remove an electron from a neutral molecule. The determination of Ionization Potentials (I.P.) and

Appearance Potentials (A.P.) (see section 1.4 (iv)) can be accomplished experimentally by interpretation of ionization efficiency curves. It should be noted that Franck-Condon vertical 0-0 excitations of an electron are not always possible so the I.P. determined from electron impact values are usually considered to constitute upper limits to the adiabatic values[3].

The standard method of determining I.P's (and A.P's) of various ions is to compare the ionization efficiency curve of the unknown ion with some reference molecule whose I.P.(and A.P.) have been accurately determined by other methods (e.g. fitting spectroscopic data to a Rydberg series)[e.g. 48,49]. The ionization potential may be determined by applying appropriate techniques to the ionization curves described above. The most useful procedure is the Semi-Logarithmic Plot Method described by Lossing *et al*[49]. Other methods that have been used to determine ionization potentials include linear extrapolation[50], extrapolated voltage differences[51], critical slope[52] and energy compensation techniques[56], but all of these methods have some short comings and are not of general use. Ionization potentials can also be calculated on a theoretical basis using either the Equivalent Orbital Method[54,55] or the Group Orbital Method[58], but these determinations are of a semi-empirical nature and require tedious calculations[3].

1.4 (iv) Appearance Potentials

The appearance potential is the minimum energy required to produce a given ion and its accompanying neutral fragments (if any) from a given molecule, ion or radical. It considers both the ionization and dissociation processes.

For the reaction

$$M + e \rightarrow F^+ + N_i + 2e \qquad (1\text{-}8)$$

where F^+ is a fragment ion and N_i is/are the neutral fragment(s), the appearance potential of F^+ is:

$$A.P.(F^+) = \Delta H_f(F^+) + \underset{i}{\varepsilon}\Delta H_f(N_i) - \Delta H_f(m) \qquad (1\text{-}9)$$

providing that the appearance potential experimentally determined corresponds to the species in their ground states, and that there is no excess kinetic energy involved in the process given by equation (1-8)[3].

In principle, the appearance potentials can be obtained from the ionization efficiency curves by the same general methods applied to ionization potentials (1.4 (iii)). The methods that can produce reasonable results include the extrapolated voltage differences[51], semi-logarithmic plots[49], critical slope[52] and the energy compensation technique[53].

In a study of ionization and dissociation processes, it is often necessary to study the appearance potential of negative-ions[15,56,57] in order to fully understand the processes producing these ions. There are several problems associated with the measurement of negative-ion appearance potentials. Firstly, some negative-ion ionization efficiency curves are more complex than those for positive-ions. Secondly, the precise determination of appearance potentials was unreliable until Fox *et al*[58] devised a method for reducing electron energy spread, which is called the "Method of retarding potential differences".

From an examination of log k vs E curves (see Figure 1-5) it is apparent that the measured appearance potential is not necessarily equal to the minimum energy that must be imparted to a neutral molecule M to form a daughter ion F^+ (see equation 1-8). A number of factors are responsible for this observed inaccuracy. These are:

1.4 (iv) (a) The Kinetic Shift

The Kinetic Shift[59] arises because an ion must be formed with a unimolecular rate constant greater than $\sim 10^6$ sec^{-1} before it can be detected in the ion source[17]. The Kinetic Shift is then the excess energy (above the minimum energy for the reaction) necessary to allow the ions to decompose with this rate constant (see Figure 1-5).

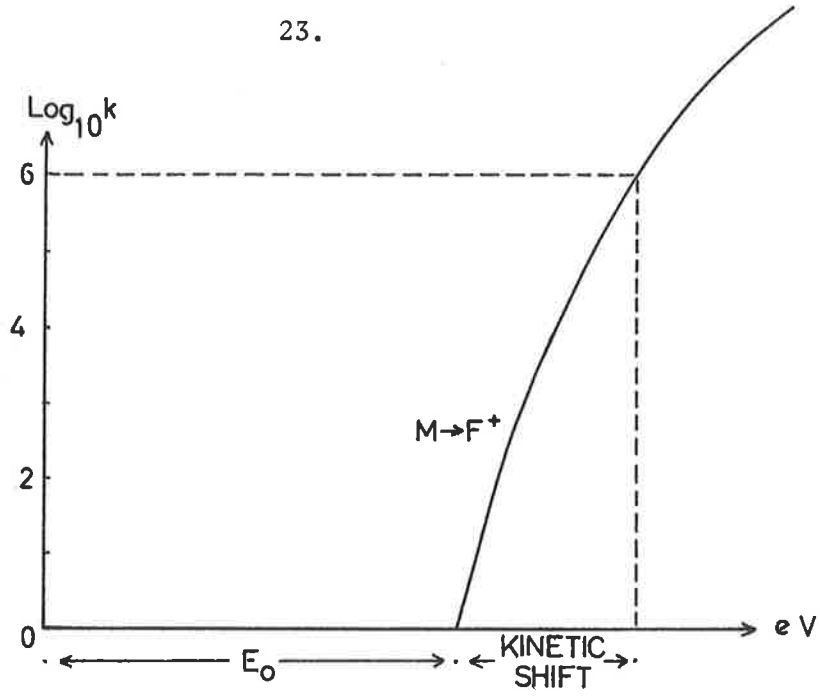


Figure 1-5. A log k vs E curve indicating appearance potential of the daughter ion.

The main consequence of the Kinetic Shift is that the observed appearance potential for a fragment F^+ will be too high. It has been suggested that the Kinetic Shift can be estimated[60] by comparing the appearance potentials of metastable and normal ions. Theoretically this concept seems sound, but, as applied experimentally[61], the results can be very misleading[28] because of inadequacies in the experimental methods used.

Reactions that possess tight transition states (restricted internal rotation, e.g. rearrangements) will exhibit larger kinetic

shifts from those having loose complexes (i.e. direct cleavage reactions) owing to a slower increase of the constant k with internal energy E[62].

The insensitivity of mass-spectral detecting systems is another contributing factor in many observed "Kinetic Shifts"[40].

1.4 (iv) (b) The Competitive Shift

When an ion decomposes by competing pathways, a further complication is introduced for all but the lowest energy decomposition[63]. This additional factor is called the "Competitive Shift"[62,64] and causes the measured appearance potential(s) for the higher energy decomposition(s) (e.g. $M^+ \rightarrow B^+$ in Figure 1-6) to be even higher than expected from the Kinetic Shift. A typical log k vs E curve is illustrated in Figure 1-6. At the threshold for the production of ion A^+ the rate constant for the lowest energy decomposition (to form A^+) is substantially greater than the rate constant for the competing decomposition (to form B^+). Hence, the molecular ion decomposes exclusively to A^+. However, if the reaction $M^+ \rightarrow B^+$ has a higher activation energy and a higher frequency factor, B^+ will appear at an energy somewhere between E_K^B and E_C and k_B will be considerably greater than 10^6 sec^{-1}, moreover decomposition to B^+ will be preferred at energies above E_C. In an alternative case where the k(E) curves do not cross the Competitive Shift may be very large indeed.

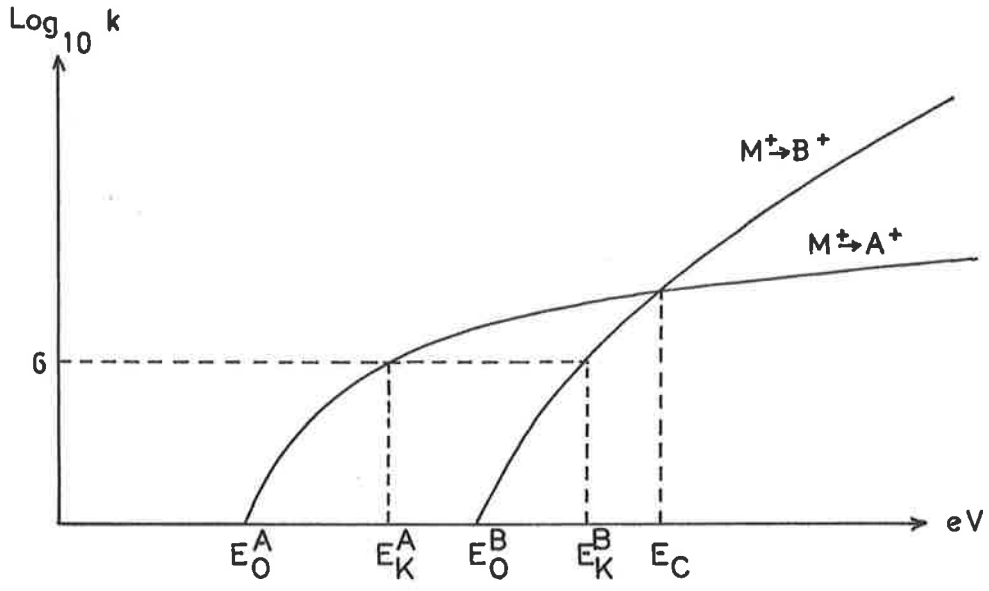


Figure 1-6. Rate curves for competing reactions, illustrating the competitive shift.

The Competitive Shift effect will always operate, whether or not the Kinetic Shift effect is involved, since it depends solely on the relative magnitudes of the rate constants for the competing decompositions.

1.4 (iv) (c) The Thermal Shift

Another factor that may compromise the ionization potential and appearance potential measurement is the presence in a molecule of thermal energy prior to ionization[65]. This means (neglecting other factors) that the energy required to produce an ion at its threshold is less than the true critical potential by the amount of

thermal energy present. This Thermal Shift acts in the opposite direction to the Kinetic Shift. In a large molecule the thermal energy is significant relative to the average internal energy gained upon electron impact with 70eV electrons[62].

1.4 (iv) (d) Stevenson's Rule

Stevenson has reported[66] that the fragmentation pattern of alkanes in the mass spectrometer always proceed to leave the positive charge on the more substituted fragment (i.e. the one with lower ionization potential). This led to the postulation of Stevenson's Rule, which states that in the dissociation of the ion AB^{+}, the positive charge will remain on the fragment (A or B) of lower ionization potential (see Figure 1-7).

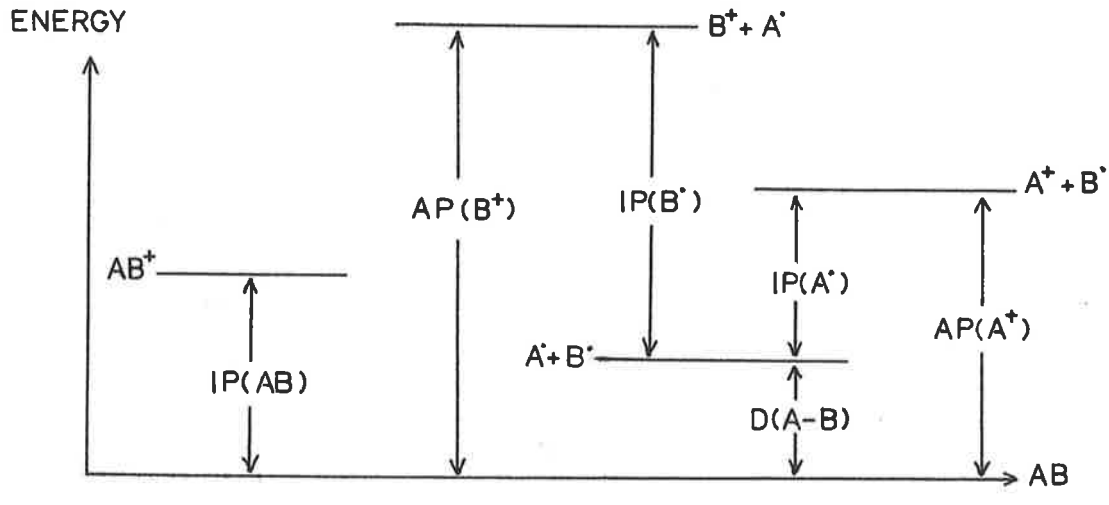


Figure 1-7. The energy changes involved in the ionization and dissociation of a molecule AB.

In Figure 1-7 the formation of A^+ has the lower energy requirement and $A^\cdot$ has the lower ionization potential. The rule will only predict which way the charge will go for the scission of a given bond. It cannot predict which bond is the most likely to fragment.

1.4 (iv) (e) Ion Cyclotron Resonance

Ion-cyclotron resonance spectrometry was developed as an alternative method of mass analysis by Wobschall *et al*[67] in 1963. Since that time it has been developed and applied to many problems of physical and chemical interest[68-70]. One of the more important current developments is the use of an I.C.R. spectrometer to improve the accuracy of ionization and appearance potentials[71,72]. I.C.R. has two major advantages over the conventional mass spectrometer when ionization or appearance potential measurements are required. Firstly, the kinetic energy possessed by the electron will not be distorted by the small electric fields[73]. Secondly, the ions have a much longer residence time in the ion source. As a result rate constants of the order of 10^2 to 10^3 sec^{-1} are required and appearance potentials are much less sensitive to the "Kinetic Shift"[71,72].

1.5 Substituent Effects

Since the original observation of the effect of different substituents on the mass-spectra of aromatic molecules[74], research

relating to substituent effects has been active, and many reviews[16,17,28,34,36,63,75] of this subject have been published. There has been an increasing awareness[34,37] of the application of the Q.E.T. in the interpretation of mass spectra, and some recent papers have used this theory to clarify the effects of substituents on ion intensities[62,76,77].

Early workers[e.g.78] found that linear relationships could be obtained by using a modification of the Hammett equation[79].

For a fragmentation reaction:

$$M \rightarrow A \rightarrow B + C + \ldots\ldots\ldots \qquad (1\text{-}10)$$

where A is the species of interest, a steady-state approximation was invoked and a term "Z" was defined (see equation (1-11) in terms of the relative intensities of parent ($M^{+\cdot}$) and daughter ions (A^+).

$$Z = \frac{(A^+)}{(M^{+\cdot})} \qquad (1\text{-}11)$$

The Z values for each parent ion were then compared by equating the term $Z/Z_o^{\neq}$ with k/k_o. Fair correlations between log (Z/Z_o) and the Hammett sigma constants (σ) were observed for some aromatic compounds[75]. Recent work has criticised this approach on both empirical[80] and theoretical[81] grounds. It has been suggested[76] that these correlations probably arise because of a correlation

$Z = Z_o$ when X = H.

between the ionization potential and the sigma constants (σ) and as a consequence it is unwise to attach too much importance to the correlation of $\log(Z/Z_o)$ with σ.

The rest of this section outlines the major factors responsible for substituent effects in mass spectra and is intended as a background to the observations reported in the discussion.

1.5 (i) Substituent Effects on Decomposition Pathways

Changing the substituent in a molecule can induce several important changes in the fragmentation pattern of an ion. Firstly, in the extreme case, new competing fragmentation pathways may be introduced. Secondly, the rates of some existing competing fragmentations may be altered to varying degrees by different substituents. To avoid these irregular substituent effects a careful choice of substrate is required.

1.5 (ii) Substituent Effects on Internal Energy and Rate Constants

When only regular effects of substituents on a particular decomposition pathway are operating, the relative ion intensities reflect the internal energy distribution functions P(E) and the rate constant functions k(E) for all decomposing ions. The observed dependence of ion intensities on substituent effects will then be determined by the effect of the substituents on these functions.

Consider the following[16] hypothetical, but plausible situation (see Figure 1-8) where a molecule has an ionization potential of E_I and two daughter ions which have appearance potentials E_A and E_B. If 70eV electrons are used then the energy distribution might be as shown in Figure 1-8.

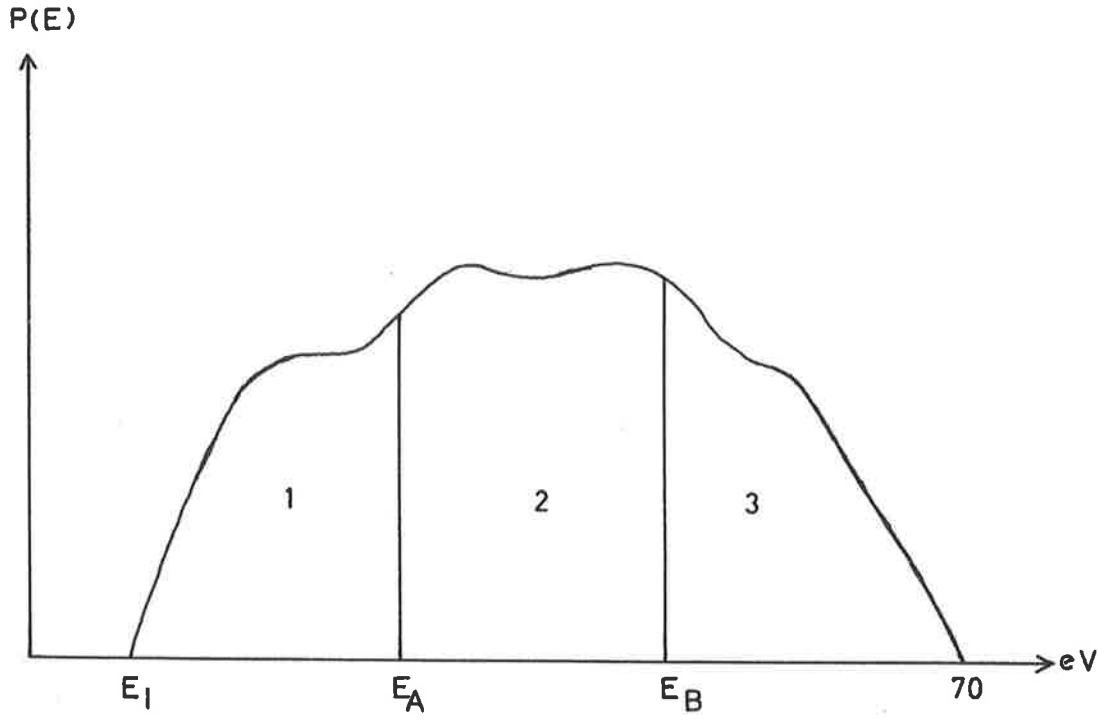


Figure 1-8. A hypothetical energy distribution in a molecular ion.

The portion of ions represented by area one do not have sufficient energy to fragment and therefore reach the detector as molecular ions. Those ions in energy region two have sufficient

energy to produce fragment A^+ while those in region three have sufficient energy to produce A^+ and B^+.

If we consider A^+ as the main fragment in a substituent effect study and B^+ is then any competing fragmentation from the molecular ion, the appearance potentials of A^+ and B^+ will be important influencing factors on the ratio $(A^+)/(M^{\cdot+})$. For example, even if the appearance potential (E_A) of A^+ remains constant with varying substituents, the amount of ion current carried by B^+ will increase as the appearance potential E_B decreases. As a consequence, the amount of ion current carried by A^+ will decrease. In other words, competition becomes more effective in region three and the effect is magnified if the frequency factor for the B^+ reaction is greater than for the A^+ reaction. If E_B falls below E_A then fragmentation becomes weighted in favour of B^+. In many cases, there is more than one fragmentation pathway that may compete with the formation of A^+. Substituents may also change the shape of the P(E) curve[63] of the molecule-ion through their influence on ionization transition probabilities. Changing the substituent may also alter the rate constant k(E), mainly through their effect on the activation energy and the frequency factor for a decomposition[63].

There is also an upper energy limit, above which the ion A^+ has sufficient energy to fragment further. Secondary decomposi-

tion must therefore also be considered[36,76,82] irrespective of whether A^+ retains the substituent.

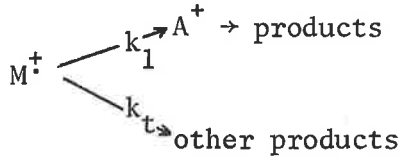
The effect of the substituent on the ionization potential of the parent molecular-ion can also play a significant role in any fragmentation pathway[16]. As a substituent becomes more electron-donating the ionization potential in a series of compounds is lowered and the percentage of molecular cations with insufficient energy to fragment is increased[eg. 83].

It is possible that (A^+) and ($M^{\cdot+}$) ions will decompose to different extents in flight from the ion source to the detector. If this happens the ratio (A^+)/($M^{\cdot+}$) will be a function of the time of flight and hence dependent upon the acceleration potential. This effect has been shown to be small[84-86].

1.5 (iii) Improved Substituent Effect Relationships

A theoretically more sound, quantitative formulation of the factors determining the effect of substituents on ion intensities[36,82], using the above arguments as a basis, has been given by Chin and Harrison[76]. Their treatment uses the quasi-equilibrium theory (see section 1.4 (i)) and includes many simplifications which make the kinetic analysis of the ion decompositions more tractible (e.g. rate constants are averaged values).

If we consider the fragmentation scheme:



The fraction f of the total molecular ions (M_o^+) produced during the initial ionization with insufficient energy to fragment is taken to be equivalent to the abundance ($M^{+\cdot}$) of the molecular ion recorded at the collector.

$$\text{i.e. } (M^{+\cdot}) = f(M_o^+) \qquad (1\text{-}12)$$

As the decomposition of $M^{+\cdot}$ is assumed to occur *via* competing unimolecular reactions, the total abundance, (A_o^+) of A^+ ions initially formed from $M^{+\cdot}$ is given by:

$$(A_o^+) = \frac{k_1}{k_t}\left\{(M_o^+) - (M^{+\cdot})\right\} \qquad (1\text{-}13)$$

where k_1 is the rate constant for the formation of A^+ from $M^{+\cdot}$ and k_t is the sum total of all competing reactions from $M^{+\cdot}$.

It is possible that a fraction f' of the ions A_o^+ will have sufficient energy to fragment further, therefore the measured abundance of A^+ is given by:

$$(A^+) = f' \quad (A_o^+) \qquad (1\text{-}14)$$

A combination of equations (1-12)-(1-14) leads to an

alternative definition of Z:

$$Z = \frac{(A^+)}{(M^{+\cdot})} = f' \frac{k_1}{k_t}\left(\frac{1-f}{f}\right) \qquad (1\text{-}15)$$

Equation (1-15) indicates that the substituent may exert its effect in three different ways:

(1) A change in the fraction f of $M^{+\cdot}$ with insufficient energy to fragment.

(2) A change in the fraction f' of A^+ ions with insufficient energy to fragment.

(3) The fraction k_1/k_t of fragmenting molecular ions that initially form A^+. This point illustrates the dependence of the Z value on competing unimolecular decompositions from $M^{+\cdot}$ ions. The observation is contrary to that reached from a steady-state approach[76].

If the energy of the electron beam is reduced, further fragmentation of A^+ may be eliminated and, in these circumstances, $f' = 1$. Furthermore, if competing fragmentation can be removed then $k_1/k_t=1$ and equation (1-15) is greatly simplified, exhibiting a substituent effect entirely due to changes in f.

An alternative equation[76] (1-16) can be derived from equations (1-12)-(1-14).

$$\frac{(A^+)}{(M_o^+)} = f \frac{k_1}{k_t} (1-f) \qquad (1\text{-}16)$$

and a linear dependence of log (k_1/k_t) with σ can be demonstrated[76] in many cases.

A note of warning must be sounded when drawing conclusions from the effect of substituents on ion abundance ratios. Direct information concerning the rate of a specific fragmentation cannot be obtained using this method[16] and care must be exercised when drawing conclusions concerning ion structures or fragmentation mechanisms[36,76,80].

1.5 (iv) Substituent Effects in Negative-Ion Mass Spectra

The first observation of substituent effects in negative-ion mass spectrometry have been reported recently[87]. Linear correlations were obtained for both the function proposed by McLafferty[74] and also Harrison[76] (see sections 1.5 and 1.5 (iii)). This paper reports[87] part of the work examined in the following discussion.

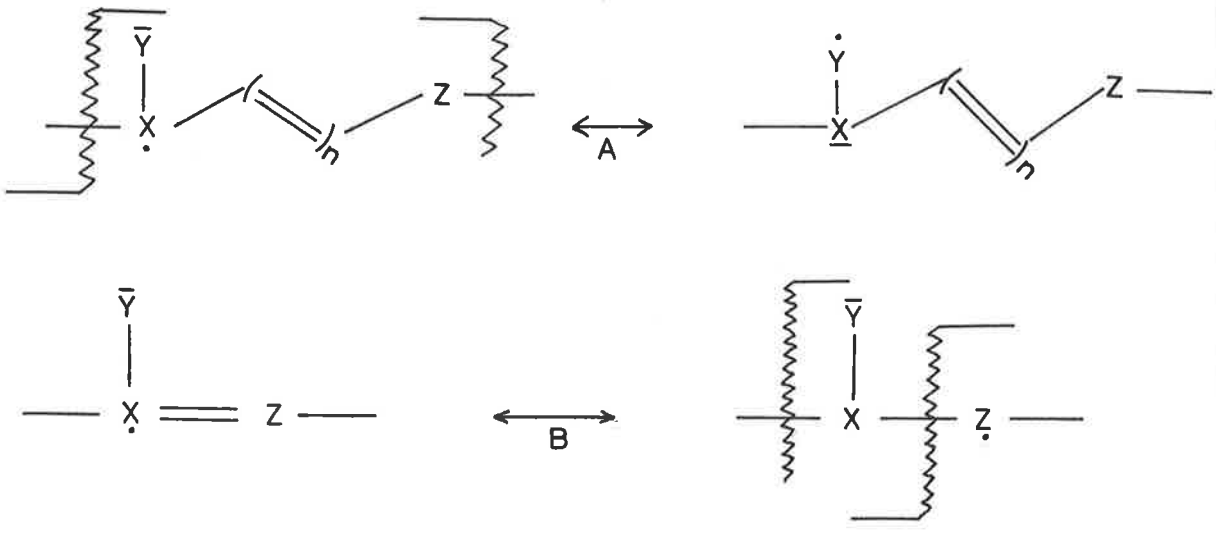
1.6 Formation of Negative-ion Mass Spectra

The general methods of negative-ion formation in the mass-spectrometer have already been discussed (see section 1.3). This section is intended to be a brief review of the general type of system that will accept an extra electron and produce a stable

molecular anion using electron beam energies up to 70eV.

It has been shown[10,15,56,57] that many organic compounds will accept an electron to produce a molecular anion capable of fragmentation by either simple cleavage or rearrangement reactions.

At the present time there is insufficient knowledge available concerning cleavage and rearrangement reactions in negative-ion spectra to confidently propose general mechanisms for these processes[cf. 11]. However, it is tempting to summarize the available results by a scheme such as Scheme 1.



Scheme 1. Possible fragmentation pathways in negative-ion mass spectra.

Simple cleavages have been observed[10] to occur mainly *via* the processes shown in Scheme 1. These fragmentations are not all common to all compounds studied, although each decomposition will generally be one or more of those indicated. The bond cleaved is generally α to the charge containing system or α to an atom (or atoms) linked to the centre of charge by a conjugated system (e.g. A).

As mentioned earlier (1.3 (iv)), the production of negative-ion mass spectra at 70eV is probably due to the capture of secondary electrons[12] which produce a molecular anion of near thermal energy. This view is reinforced by the observation[10] of simple spectra, which commonly exhibit only a molecular anion and a small number of fragmentations produced either by simple cleavage or rearrangement. These ions are normally accompanied by intense metastable decompositions. The abundance of rearrangement reactions is good evidence for molecular ions of near thermal energies; and is predicted[38] by the Q.E.T. (see section 1.4 (i)).

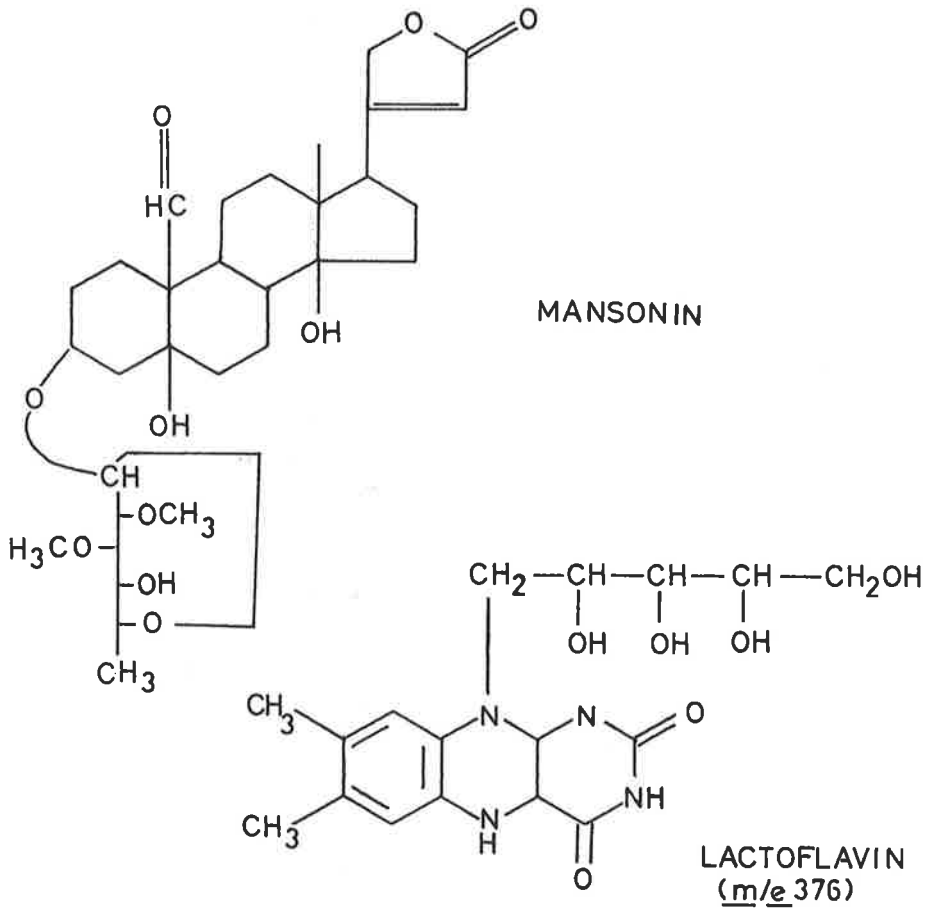
The compounds that exhibit these simple spectra appear to be ones that contain unfilled, low lying, non-bonding orbitals, and therefore can readily accept low energy electrons[88].

1.7 Some Uses of Negative-ion Mass Spectra

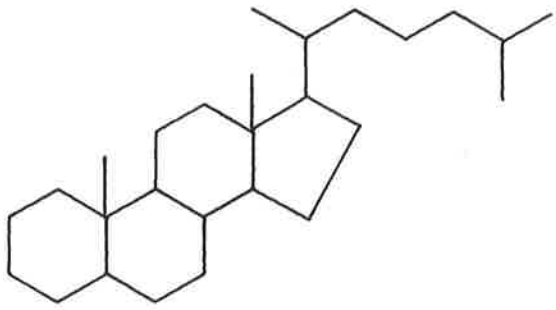
Negative-ion mass spectra have been applied with some success to structure elucidation problems. Von Ardenne and his co-workers have applied this technique with particular success in the field of natural products[89-93]. The pioneering work in this area[89,90,92] was developed using fairly high source pressures (e.g. 10^{-2} torr) in the presence of an inert support gas (Argon). The negative-ions were generated by low energy electrons (3-4eV) produced from a low voltage discharge in Argon.

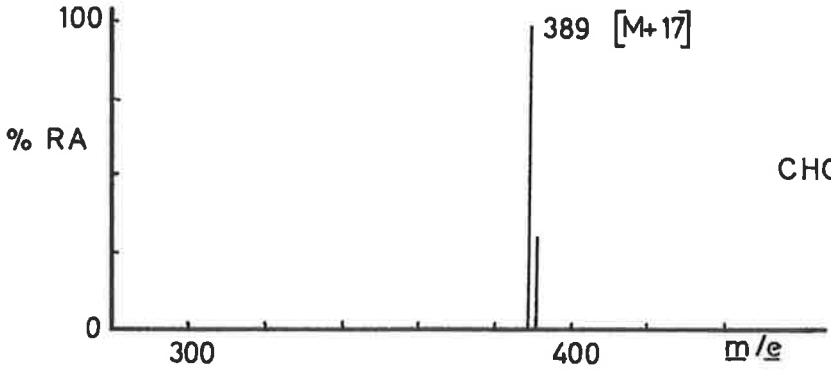
Molecular anions are often observed in the negative-ion spectra of large natural product molecules when their corresponding molecular cations are absent. This observation has been employed in the structure elucidation of many biologically useful compounds such as the cardiac glycoside Mansonin[91], and riboflavin derivatives such as lactoflavin.

The presence of electron rich centres within the molecule under study can influence the observed fragmentation pattern considerably. Consider the series Cholestane (1-1), Cholest-5-ene(1-2) and Cholesta-3,5-diene(1-3) (see below)[93]; Cholestane shows no molecular anion but exhibits a peak at *m/e* 389 produced by an ion-molecule reaction. When one double bond is introduced into the "A" ring (Cholest-5-ene) an [M-1] peak appears

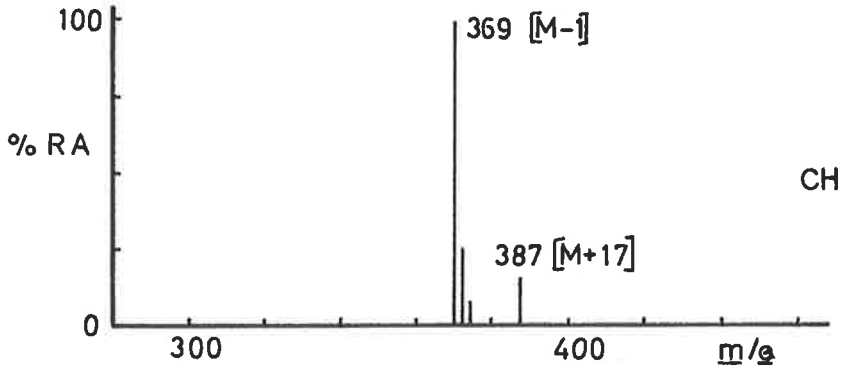


and the abundance of the peak produced *via* an ion-molecule reaction decreases. When two double bonds are introduced into the "A" ring (Cholesta-3,5-diene), then the peak due to the ion-molecule reaction disappears entirely, leaving only an [M-1] peak. This trend, however, must be treated with due care since the introduction of full aromatization into ring A may lead to the production of a large number of peaks attributable to ion-molecule reactions[93] (c.f. 1-4).

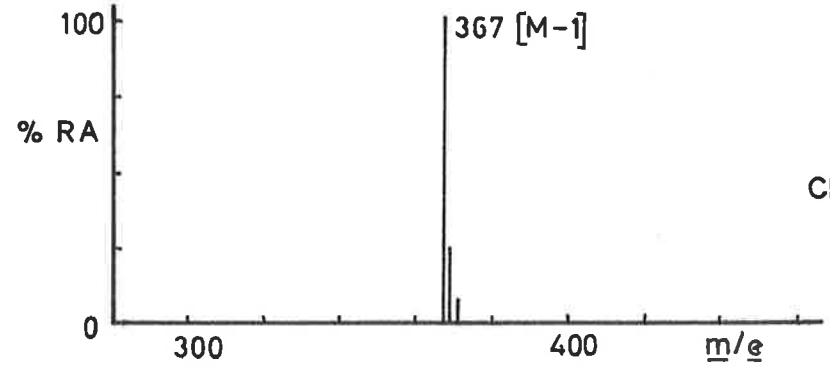




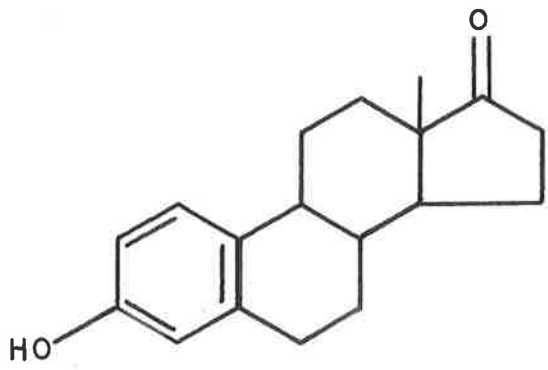
CHOLESTANE (1-1)
[M^{+} = 372]



CHOLEST - 5-ENE (1-2)
[M^{+} = 370]

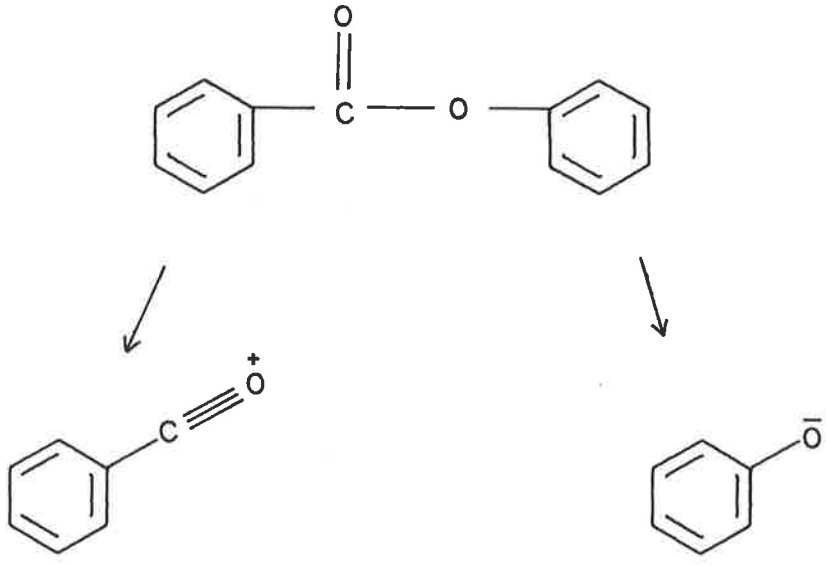


CHOLESTA -3,5- DIENE
(1-3)
M^{+} = 368



(1-4)

In a report pertinent to the ensuing discussion, it was shown that phenylbenzoate fragments in the negative-ion mode to produce the phenoxide anion (*m/e* 93) as the most intense peak in the spectrum[92]. This peak is more intense than the most intense peak (benzoyl-*m/e* 105) in the positive-ion spectrum[93].



The procedure is obviously one of much merit, and as such provided a useful impetus for the work discussed in chapters two and three. It does, however, suffer from two serious drawbacks. Firstly, since the source is maintained at such a high pressure the recorded spectra are prone to complication as a result of ion-molecular reactions, *c.f.* the production of a peak at *m/e* 389 in the spectrum of cholestane[90]. Secondly, most positive-ion mass spectra are recorded at *c.a.* 2×10^{-6} Torr and consequently the conventional mass-spectrometer is not equipped to handle pressures as high as 1×10^{-2} Torr.

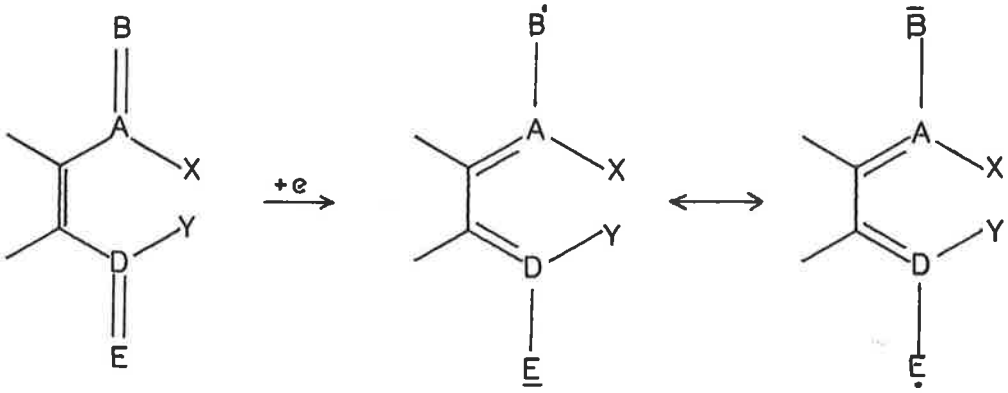
1.8 Summary

Much of the work presented in the introduction is based either entirely or substantially on results obtained using the positive-ion mode of mass spectrometry. The purpose of the study outlined in the discussion was twofold, *viz.* (1) to continue the search for information concerning the type of molecule likely to form simple negative-ion mass spectra; (ii) to see if these compounds exhibit the same type of substituent dependence that has been observed in positive-ion mass spectra, and to investigate any mechanistic implications found in these results.

CHAPTER 2. THE NEGATIVE-ION MASS SPECTRA OF SOME SUBSTITUTED ARYL NITRO ESTERS

2.1 Introduction

The interest in negative-ion mass spectrometry has been re-awakened by some recent reports[10] concerning the formation of negative-ion mass spectra of systems such as (2-1). Using 70eV electrons these systems readily accept an electron (probably into low lying unoccupied, non-bonding orbitals[88]) to form a stable molecular anion (e.g. 2-2 or 2-3).

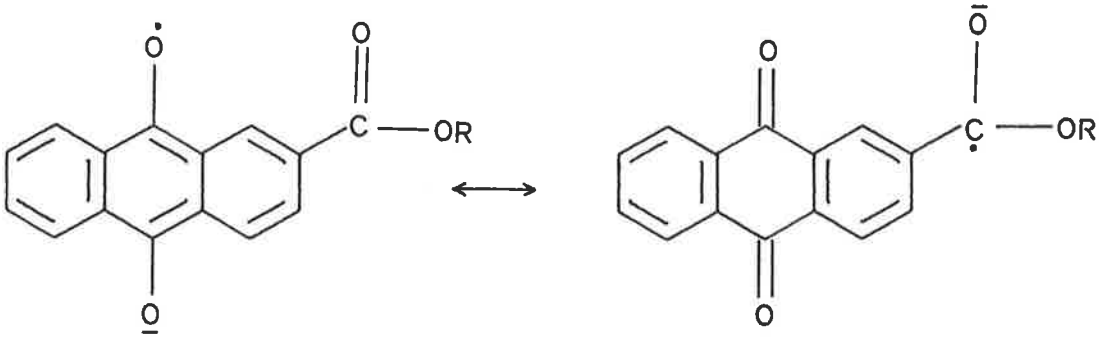


(2-1) (2-2) (2-3)

The compounds studied exhibit intense molecular anions (see section 1.6) and fragment *via* characteristic pathways. The studies were conducted at low pressure (2×10^{-7} torr) in order to reduce the

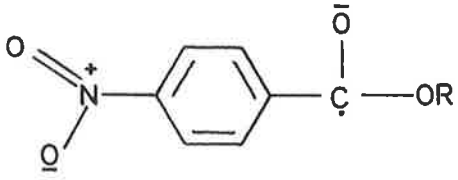
possibility of ion-molecular reactions taking place[94,95≠].

The first study published[95] involved some anthraquinone esters and the results were rationalized by fragmentation *via* species (2-4). It was subsequently shown[96] that 3- and 4-alkyl nitrobenzoates fragment by essentially the same pathway as these anthraquinone esters. These observations pose a major mechanistic problem, because, although a conjugate elimination may occur from the 4-nitrobenzoates (e.g. 2-6), this type of mechanism is not possible for the 3-nitrobenzoates (e.g. 2-7).

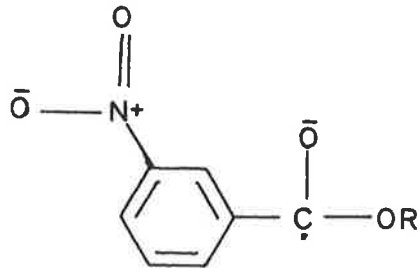


(2-4) (2-5)

≠ If the pressure is allowed to rise to 2×10^{-6} torr then ion-molecule reactions occur in some systems[7,96].



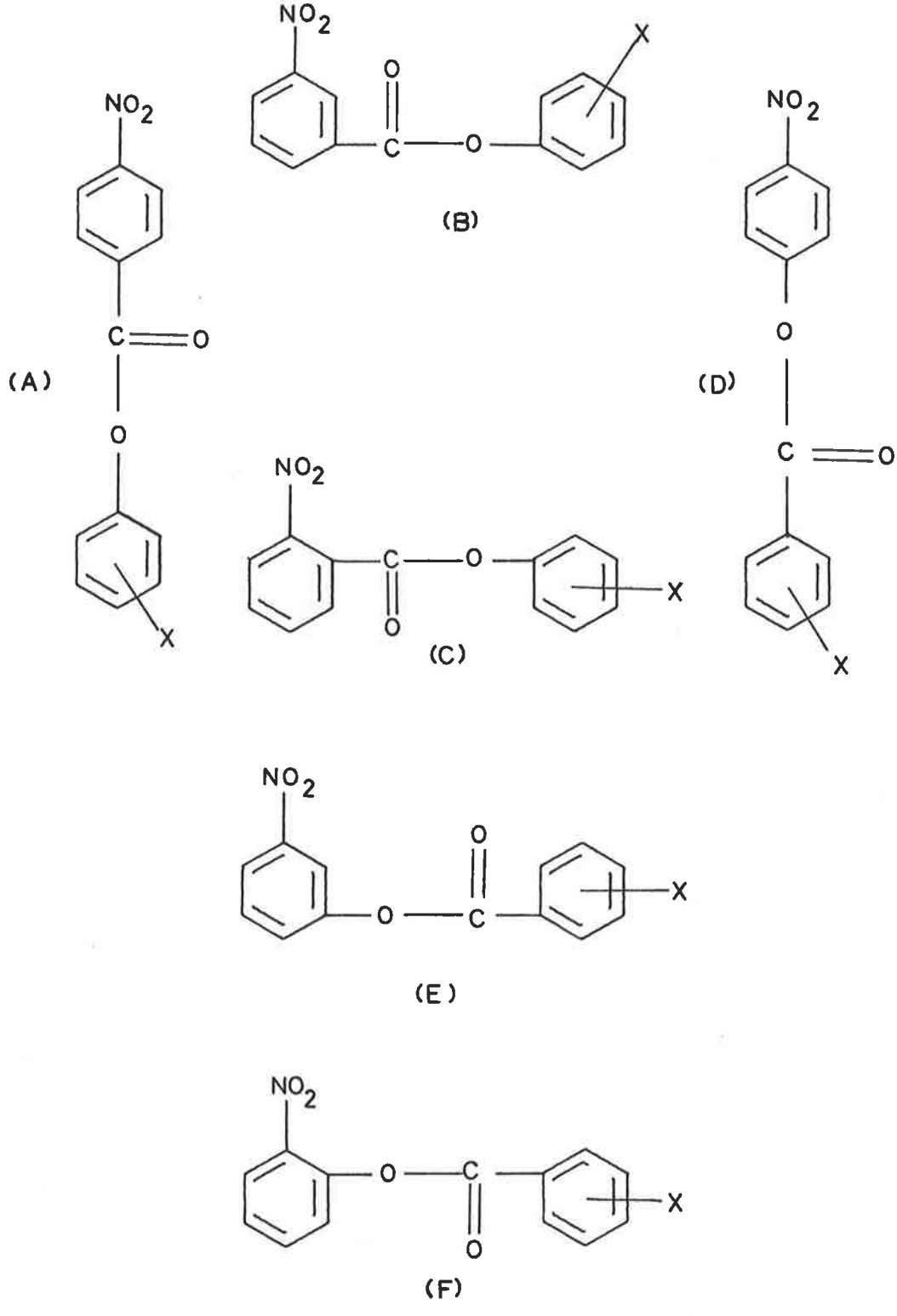
(2–6)



(2–7)

There are two plausible explanations for this apparent anomaly: (1) If the 3- and 4- alkyl nitrobenzoates undertake valence isomerism to the same structure prior to or during decomposition, the same fragmentation pattern would be expected for each isomer. (2) If the charge is localized specifically on the carbonyl group of the ester (e.g. (2-6) and (2-7) or in the case of the anthraquinones (2-5) a canonical form of (2-4)), similar fragmentation patterns will be expected.

In an attempt to clarify the reaction pathway, the six series of nitro substituted arylbenzoates (A → F) were studied.


NO2
C
O
X
(A)
(B)
(C)
(D)
(E)
(F)

The results will be presented in the following order; first, a fragmentation mechanism will be proposed; second, all of the major fragmentations of series A → F will be discussed in terms of the mechanism; and, lastly, the effect of substituents on the various fragmentations will be examined.

The spectra of the compounds examined in each of these series are recorded in tables (2.1A → 2.1F).

TABLE (2-1A).≠ 4-nitrobenzoates

Compound	Substit.	$M^{\bar{}}$	*m/e*166	*m/e*122	$X\text{-}C_6H_4O^{\ominus}$	M-NO·	M-O·	$NO_2^{\ominus}$
2-14	*p* NO_2	8.5	52	3.6	100	0.4	0.1	0.02
2-15	*m* NO_2	52	10	2.3	100	2.0	1.0	0.06
2-16	*p* $COCH_3$	100	3.3	1.3	68	6.0	1.2	0.07
2-17	*m* Br	100	3.5	1.05	16.7	4.5	2.1	0.14
2-18	*m* Cl	100	3.9	0.97	16.5	4.9	2.5	0.13
2-19	*p* Br	100	1.25	0.71	10.0	5.3	2.3	0.15
2-20	*p* Cl	100	1.50	0.72	12.0	4.7	2.6	0.16
2-21	*m* OCH_3	100	0.59	0.42	5.1	6.2	3.2	0.23
2-8	H	100	0.45	0.35	3.0	5.0	2.0	0.36
2-22	*m* CH_3	100	0.27	0.24	2.2	4.8	3.0	0.65
2-23	*p* CH_3	100	0.20	0.25	1.3	6.3	2.1	1.1
2-24	*p* OCH_3	100	0.12	0.19	0.81	4.8	2.0	1.6

≠ All spectra recorded in these tables are an average of three measurements and are correct to ± 2% (of the peak in question, NOT the base peak).

TABLE (2-1B). 3-nitrobenzoates

Compound	Substit.	$M^{\ddagger}$	*m/e*166	*m/e*122	$X\text{-}C_6H_4O^{\oplus}$	M-NO·	M-O·	$NO_2^{\oplus}$
2-25	*p* NO_2	5.2	3.5	0.32	100	0.02	0.1	0.35
2-26	*m* NO_2	100	11.5	0.75	99	0.21	1.1	0.15
2-27	*p* $COCH_3$	100	2.9	0.29	55	0.28	0.71	0.20
2-28	*m* Br	100	0.98	0.20	8.1	0.21	0.42	0.81
2-29	*p* Br	100	0.60	0.11	5.5	0.42	0.30	0.93
2-30	*p* Cl	100	0.53	0.091	5.2	0.38	0.14	0.64
2-31	*m* OCH_3	100	0.23	0.065	2.6	0.82	0.33	1.2
2-9	H	100	0.10	0.061	1.22	0.26	0.15	1.5
2-32	*m* CH_3	100	0.068	0.045	0.84	0.13	0.15	1.6
2-33	*p* CH_3	100	0.050	0.030	0.65	0.11	0.16	2.0
2-34	*p* OCH_3	100	0.050	0.020	0.30	0.09	0.09	1.0

TABLE (2-1C). 2-nitrobenzoates

Compound	Substit.	$M^{\cdot-}$	*m/e*150	*m/e*106	$X\text{-}C_6H_4O^{\ominus}$	$NO_2^{\ominus}$
2-35	*p* NO_2	0.07	11.8	0.90	100	0.30
2-36	*m* NO_2	0.15	82	2.0	100	0.30
2-37	*p* $COCH_3$	0.12	82	2.0	100	0.09
2-38	*m* Cl	0.185	100	3.0	35.5	0.10
2-39	*p* Cl	0.42	100	5.1	33.0	0.15
2-40	*m* OCH_3	0.40	100	3.5	5.5	0.60
2-10	H	0.45	100	4.0	3.3	0.20
2-41	*p* CH_3	0.50	100	3.2	2.3	0.10
2-42	*p* OCH_3	0.65	100	3.0	2.5	0.20

TABLE (2-1D). 4-nitrophenylbenzoates

Compound	Substit.	$M^{\cdot-}$	$X\text{-}C_6H_4CO_2^{\ominus}$	*m/e*138	*m/e*166
2-43	*p* NO_2	8.5	52≠	100	52≠
2-44	*m* NO_2	4.2	0.35≠	100	8.0≠
2-45	*p* Br	0.07	0.38	100	5.2
2-46	*p* Cl	0.06	0.27	100	2.0
2-47	*m* OCH_3	0.08	0.15	100	-
2-11	H	0.11	0.25	100	-
2-48	*m* CH_3	0.14	0.25	100	-
2-49	*p* CH_3	0.15	0.18	100	-
2-50	*p* OCH_3	0.25	0.23	100	-

≠ These species can be formed from both ends of the molecule.

TABLE (2-1E). 3-nitrophenylbenzoates

Compound	Substit.	$M^{-\cdot}$	$X\text{-}C_6H_4CO_2^{\ominus}$	*m/e*138
2-51	*p* NO_2	52	10	100
2-52	*m* NO_2	100	11.5	90
2-53	*m* Br	20	1.2	100
2-54	*p* Br	24	1.6	100
2-55	*p* Cl	26	2.2	100
2-56	*m* OCH_3	27	0.4	100
2-12	H	28	0.27	100
2-57	*m* CH_3	30	0.36	100
2-58	*p* CH_3	38	0.40	100
2-59	*p* OCH_3	52	0.60	100

TABLE (2-1F). 2-nitrophenylbenzoates

Compound	Substit.	$M^{\cdot}$	*m/e*138	*m/e*46	$XC_6H_4CO^{\oplus}$	$X\text{-}C_6H_4^{\oplus}$
2-60	*p* Br	0.12	1.7	0.08	100	0.60
2-61	*p* Cl	0.10	1.2	0.06	100	0.55
2-62	*m* OCH_3	0.09	1.6	0.07	100	0.65
2-13	H	0.10	1.3	0.06	100	0.55
2-63	*m* CH_3	0.09	2.0	0.08	100	0.52
2-64	*p* CH_3	0.10	1.8	0.06	100	0.55
2-65	*p* OCH_3	0.11	1.3	0.05	100	0.50

Inspection of table 2-1 indicates that series A and series B fragment essentially *via* the same pathways. The major difference between these two series is that a compound from series A shows a much more intense spectrum than does the corresponding isomer from series B. The fragmentation pathways exhibited in series C are completely different from those observed in series A or B.

The situation is the same in the reverse series, where D and E fragment *via* essentially the same pathways, while series F fragments *via* a different pathway. Again a compound in series D exhibits a more intense spectrum than its corresponding isomer from series E.

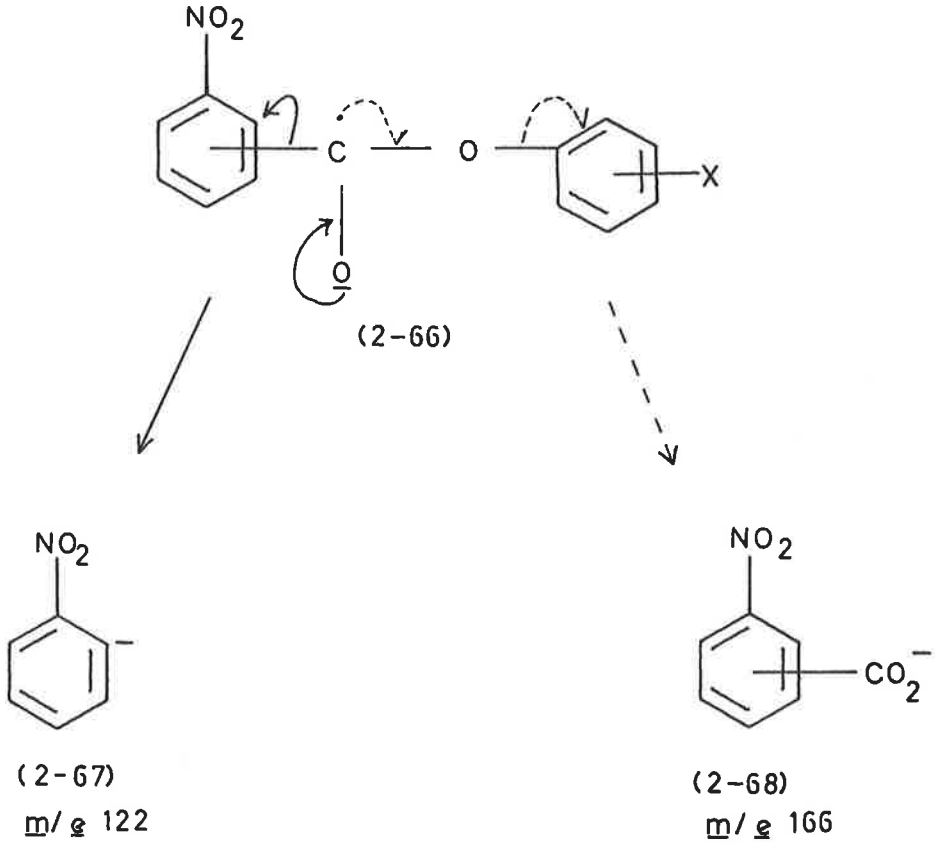
2.2 A suggested mechanism for fragmentation

A comparison of the spectra of phenyl-4-nitrobenzoate (2-8) (see figure 2-1[≠]) and phenyl-2-nitrobenzoate (2-10) (see figure 2-2) clearly shows that these two compounds are fragmenting *via* different pathways. Observation of the spectra of 4-nitrophenylbenzoate (2-11) (see figure 2-3) and 2-nitro phenylbenzoate (2-13) (see figure 2-4) indicates that these isomers also are fragmenting *via* different routes. Thus the possibility of valence isomerism occurring prior to or during fragmentation can be discounted.

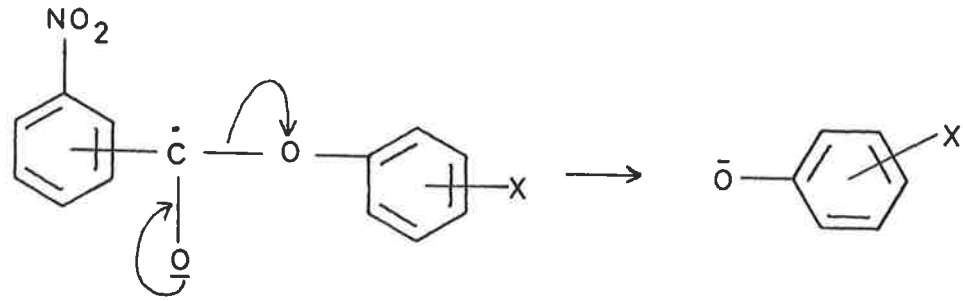
The observed differences in the major fragmentation pathways reported in tables 2-1A → 2-1F are consistent with a localization of the added electron in the carbonyl group of the ester function. This leads to a proposal of the following mechanism for the production of all major fragments [see schemes (2-1), (2-2) and (2-3)] in series A → F.

≠ All figures are together in a lift-out section at the end of each chapter.

Scheme 2-1



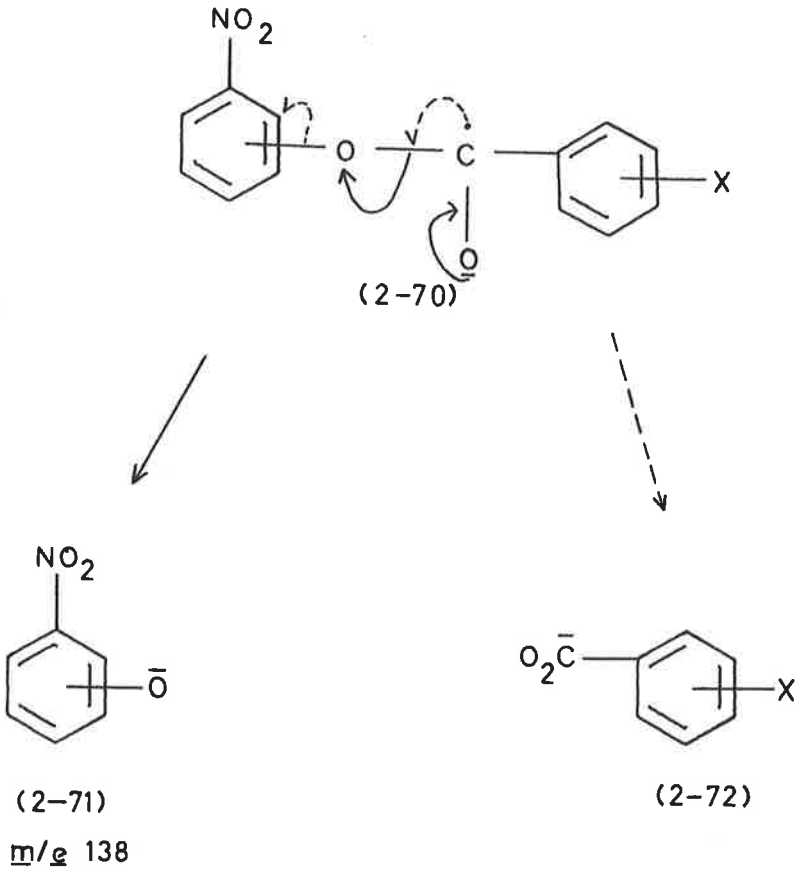
or Scheme 2-2



(2-66) (2-69)

A completely analogous mechanism can be proposed to explain the fragmentation of series D-F.

Scheme 2-3

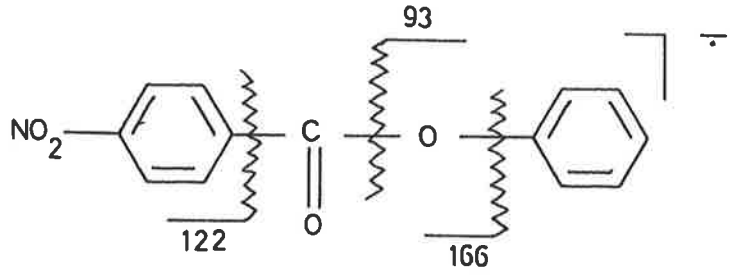


2.3 Negative-ion mass spectra of the aryl esters

2.3 (i) Aryl nitrobenzoates

The fragmentation of phenyl-4-nitrobenzoate (2-8) [(figure (2-1) and scheme (2-4)] is representative (see tables 2-1A and 2-1B) of the fragmentations found in series A and series B.

Scheme 2-4



(2-8)

The spectrum is dominated by a series of simple cleavage reactions (see scheme 2-4), each substantiated by a defocussed metastable transition (see section 1.3 (v)). In addition, two other species $[M^{\bullet-}-NO^{\bullet}]$ and $[M^{\bullet-}-O^{\bullet-}]$[cf.94] are observed in the spectrum. These fragments result from two rearrangement reactions normally associated with the presence of an aromatic nitro group[97], and are supported by the appropriate defocussed metastable decompositions.

It is possible that the fragment at *m/e*122 could be produced by loss of CO_2 from *m/e*166 as well as directly from the molecular

anion. There is no metastable decomposition in either field-free region of the mass spectrometer to substantiate this decomposition. There is no evidence for the further decomposition of *m/e*122 or $C_6H_5O^-$.

The final fragmentation product is a species at *m/e*46 (NO_2^-). The I.K.E. spectrum of this compound (see Appendix A) shows that at least a portion of this ion arises directly from the molecular anion (2-8).

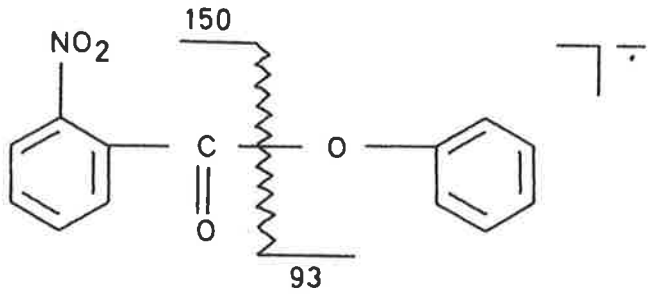
Information concerning the internal energy of the molecular anion produced can be obtained by plotting the relative abundance of both the fragment ion *m/e*93 (see scheme 2-4) and the molecular anion of phenyl-4-nitrobenzoate (2-8) against the nominal electron-beam energy [see figure (2-5)]. No delectable molecular anion is produced at electron beam energies below 15eV, while the fragment ion is still clearly produced. At these low electron-beam energies (3-8eV) the fragment ion is produced by ion-pair formation (see section 1.3 (i)), dissociative attachment (see section 1.3 (ii))or by temporary ion-dissociative attachment (see section 1.3 (iii)), while at normal electron-beam energies (15-70eV) the fragment ion is produced by decomposition of a low energy molecular ion (probably formed by absorption of secondary electrons (see section 1.3 (iv)).

These results indicate that molecular anions formed by capture of secondary electrons have less internal energy and are longer lived than the higher energy, more reactive molecular anions formed between

3 and 8 eV. This implies that a spectrum obtained using electron-beam energies above 15eV is produced by decomposing molecular anions whose range of internal energies are near thermal[c. f. 10] (see also section 1.3 (iv)).

The fragmentation pattern observed for phenyl-2-nitrobenzoate (2-10) is shown in figure (2-2) and scheme (2-5). It is quite different from that observed for phenyl-4-nitrobenzoate (2-8) [figure (2-1)].

Scheme 2-5



(2-10)

The major cleavage observed is cleavage "α" to the carbonyl group producing an ion at *m/e*150. This is followed by the elimination of a molecule of CO_2. Both of these processes are supported by the appropriate defocussed metastable decomposition.

The elimination of CO_2 from *m/e*150 demonstrates that "proximity or ortho effects[98]" can also operate on negative-ion mass spectral decompositions.

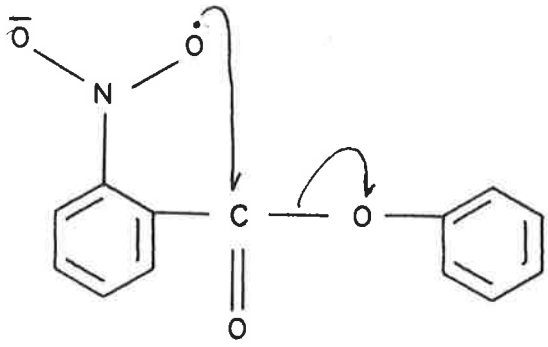
The species of *m/e*150 is probably best represented as a cyclic structure (2-73) formed by condensation of the nitro group and the ester carbonyl group with concomitant elimination of a phenoxy radical. This implies that a second form of the molecular anion (2-74) may exist (cf. 2-66) where the electron is localized in the nitro function and not in the ester carbonyl group.

Further evidence for a cyclic structure such as (2-73) is obtained from the elimination of CO_2 from *m/e*150. One of the constituent oxygen atoms in the CO_2 molecule must originate from the nitro group and hence a cyclic intermediate is suggested.

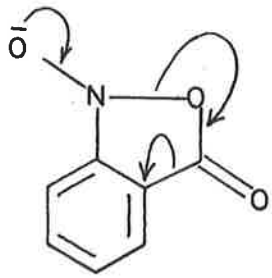
2.3 (ii) Nitroarylbenzoates

The fragmentation patterns observed for series D and series E are very similar (see tables 2-1D and 2-1E). In general, a compound from series D will exhibit a more intense spectrum than its corresponding isomer from series E.

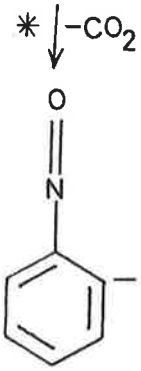
The fragmentations shown in figure (2-3) and scheme (2-6) are representative of series D and series E.



(2-74)

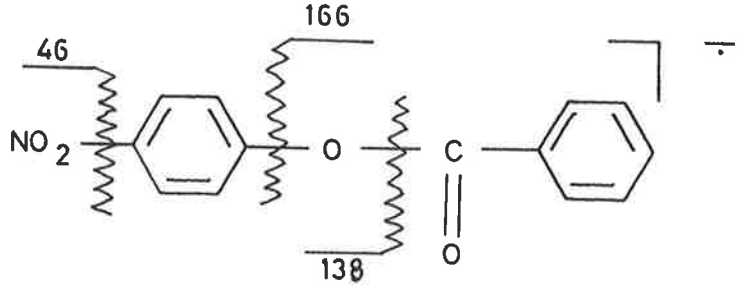


(2-73) m/e 150



(2-75) m/e 106

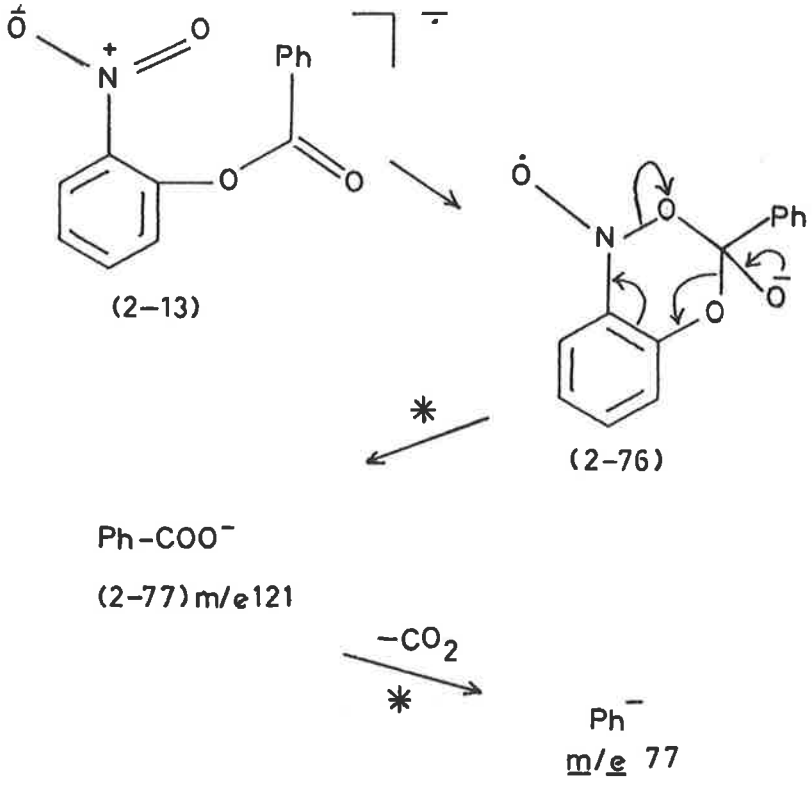
Scheme 2-6



(4)

The major fragment produced is a phenoxide anion (*m/e*138), a species strongly stabilized by a nitro group [see section 2.3 (iii)]. A competing reaction forms the benzoate anion (*m/e*121) in much smaller abundance. A fragmentation to produce the characteristic NO_2^- fragment at *m/e*46 also exists, showing that a small amount of the molecular anion probably exists with the charge localized on the nitro group. All fragments are supported by the appropriate defocussed metastable decompositions. The spectrum of 2-nitrophenylbenzoate (2-13) [see figure (2-4)] contains the same peaks as the spectrum of 4-nitrophenylbenzoate (2-11) [see figure (2-3)], but they are easily distinguished as different peaks dominate each spectrum. The major fragment ion in the spectrum of (2-13) is the benzoate anion (*m/e*121) while the nitrophenoxide (*m/e*138) anion represents < 2% of the base peak (c.f. table 2-1D).

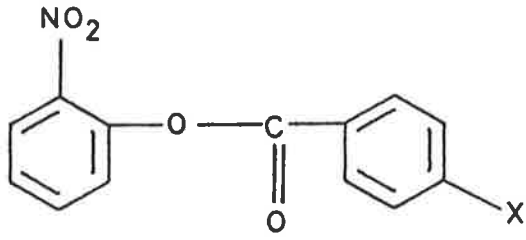
The benzoate anion fragments further by expulsion of a molecule of CO_2. Defocussed metastable transitions are observed for each of these processes. The change in fragmentation pattern is due to a proximity effect[98] influencing fragmentation of the 2-nitrophenylbenzoate (2-13). The nitro group condenses with the ester carbonyl group (c.f. (2-73)) to form a rearranged cyclic molecular anion (2-76) which can fragment to produce the benzoate anion (*m/e*121, (2-77).



The benzoate anion (2-77) then eliminates a molecule of carbon dioxide.

If the proposed cyclic structure (2-76) is correct, then the daughter benzoate anion will contain one oxygen atom from the ester group plus a second oxygen atom originating from either the nitro group or the ester group.

Using the assumption that the benzoate anion is produced by a "proximity effect" the ^{18}O labelled compound (2-78) was synthesised≠.



(2-13) X = H

(2-78) X = OCH_3

≠ (2-78) was synthesised rather than (2-13) because (2-13) is a low melting compound which is difficult to purify.

The ion corresponding to the benzoate compound (in this case *m/e*151) was observed not to contain any ^{18}O. This demands a cyclization of the molecular ion [with the charge localized on either the nitro group or the carbonyl group] to form a cyclized species (e.g. (2-78)), which must then fragment to the benzoate species (e.g. (2-77)) in the manner shown.

2.3 (iii) Phenyl-4-Cyanobenzoates (Series G)

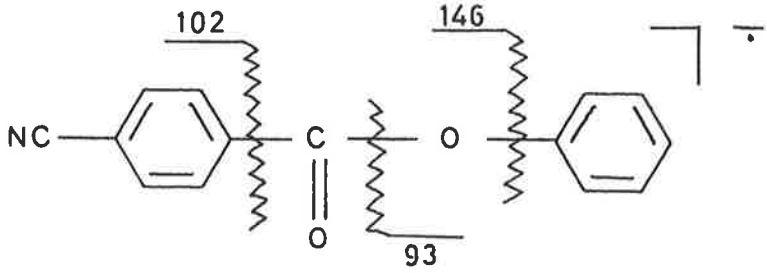
The electron withdrawing nitro group has been shown [see sections 2.3 (i) and 2.3 (ii)] to provide a good stabilizing function for the production of negative-ion mass spectra formed at electron-beam energies of 70eV. The nitro substituent was replaced by a cyano (i.e. - CN) substituent in order to observe the effect of a less efficient electron withdrawing group on the overall negative-ion mass spectrum. The results are recorded in Table (2-2).

TABLE 2-2. Negative-Ion Mass Spectra of Phenyl 4-Cyanobenzoates (Series G)

Compound	Substituent	$[M^{\cdot-}]$	*m/e* 102	$XC_6H_4O^-$	*m/e* 146
2-80	*p* NO_2	0.65	100	61	0.1
2-81	*m* NO_2	0.3	2.4	100	42.0
2-82	*p* $COCH_3$	9.0	6.0	100	2.0
2-83	*m* Br	100	24.0	68	1.7
2-84	*m* Cl	76	14.0	100	36.0
2-85	*p* Br	100	8.6	2.7	0.1
2-86	*p* Cl	100	36.0	88.0	48.0
2-87	*m* OCH_3	100	1.9	0.6	0.2
2-79	H	100	0.2	2.0	0.4
2-88	*p* CH_3	100	1.2	0.2	0.2
2-89	*p* OCH_3	100	1.5	0.6	0.6

Phenyl-4-cyanobenzoate (2-79) is representative of this series [see figure (2.6) and scheme (2-7)].

Scheme 2-7



(2-79)

The basic fragmentations observed are similar to those reported for the corresponding phenyl-4-nitrobenzoates [see scheme (2-4)] and are supported by defocussed metastable decompositions.

A substantial reduction in the overall intensity of any spectrum was observed when the nitro stabilizing group was replaced by a cyano stabilizing group. However, the intensity of this spectrum is still enhanced when compared with the case where no stabilizing group is present at all. Thus, it would appear that as the electron withdrawing power of a substituent increases the ability of a molecule to form a stabilized molecular anion also increases[e.g.83] (c.f. section (1.5 (ii)).

2.4 Substituent Effects

The quasi-equilibrium theory of mass spectrometry [see section 1.4 (i)] has been used extensively as a kinetic basis for mass spectral decompositions observed in positive-ion mass spectra[87] and references cited therein.

This theory was originally employed by McLafferty[74] to modify the Hammett equation[79] to give equation (2-1) (see section 1.5).

$$\text{Log } \left(\frac{Z}{Z_o}\right) = \rho\sigma$$

Log $\left(\frac{Z}{Z_o}\right)$ is found to be a linear function of the Hammett sigma constant and a plot of Log $\left(\frac{Z}{Z_o}\right)$ against the appropriate substituent constant (σ) results in a straight line whose slope (ρ) is a function of the fragmentation under consideration.

A coherent paper by Chin and Harrison[76] has shown that equation (2-1) is oversimplified and an alternative expression (equation (2-2)) [see section 1.5 (iii)] was proposed to replace it.

$$\frac{[A^+]}{[M_o^+]} = f' \frac{k_1}{k_t} (1 - f) \qquad (2\text{-}2)$$

A plot of Log $\left(\frac{A^+}{M_o^+(1 - f)}\right)$ against the Hammett sigma constant again results in the product of a straight line. This indicates that Log $\left(\frac{k_1}{k_t}\right)$ is a linear function of sigma and slope of the straight

line is a function of the fragmentation under consideration.

A study of substituent effects was initiated for two reasons. First, to discover if compounds in the negative-ion mode will exhibit linear relationships similar to those observed in the positive-ion mode when treated with equations (2-1) and (2-2). Second, to determine if such linear correlations will provide any precise information concerning the nature of the transition state for a particular reaction of a negative ion.

It was assumed that under the conditions employed in the mass spectrometer (see experimental section), the daughter anions do not contain sufficient internal energy to fragment further, therefore f' = 1 and equation (2-2) can be further simplified to equation (2-3).

$$\frac{[A^+]}{[M_o^+]} = \frac{k_1}{k_t}(1 - f) \qquad (2\text{-}3)$$

The substituent effect can be studied by plotting log $\left(\frac{[A^+]}{[M_o^+]\ (1 - f)}\right)$ against the appropriate sigma value of the substituent.

2.4 (i) Arylnitrobenzoates

The spectra of the arylnitrobenzoates are reported in tables (2-1A → C). A plot of the log $(\frac{Z}{Z_o})$ values against the corresponding substituent Hammett sigma value for each fragmentation (tables 2-3A → C) reveals that extremely good linear relationships exist for most of

the daughter ions produced. The only fragments whose log $(\frac{Z}{Z_o})$ value deviates markedly from the straight line plots are those compounds whose substituents are successively *p* NO_2 and *m* NO_2. This deviation was expected since the esters now contain two stabilizing nitro groups.

TABLE 2-3A. 4-nitrobenzoates

Fragment ion	$\rho^{\neq}$	Slope*
m/e 166	2.2 ± 0.3	0.9 ± 0.5
m/e 122	1.3 ± 0.2	0.0 ± 0.3
$X\text{-}C_6H_4O^{\oplus}$	2.6 ± 0.7	1.3 ± 0.7
$M\text{-}NO^{\cdot}$	-0.08 ± 0.15	-1.4 ± 0.4
$M\text{-}O^{\cdot}$	-0.1 ± 0.3	-1.4 ± 0.6
$NO_2^{\oplus}$	-1.9 ± 0.3	-3.2 ± 0.6

≠ The slopes are calculated in the form[97]

$$\text{Slope} = b \pm t\sigma(b)$$

with a confidence level set at 95%.

---

* Slope = the gradient obtained from a linear plot of equation (2-3).

TABLE 2-3B. 3-nitrobenzoates

Fragmentation	ρ	Slope*
m/e 166	2.6 ± 0.2	0.8 ± 0.3
m/e 122	1.5 ± 0.2	-0.3 ± 0.4
$X\text{-}C_6H_4O^{\ominus}$	2.6 ± 0.3	0.7 ± 0.2
$M\text{-}NO^{\bullet}$	0.4 ± 0.7	-1.4 ± 1.0
$M\text{-}O^{\bullet}$	1.0 ± 0.4	-0.81 ± 0.4
$NO_2^{\ominus}$	-1.1 ± 0.5	-2.9 ± 0.8

TABLE 2-3C. 2-nitrobenzoates

Fragmentation	ρ	Slope*
m/e 150	0.7 ± 0.3	- 0.4 ± 0.2
m/e 106	0.5 ± 0.3	- 0.5 ± 0.4
$X\text{-}C_6H_4O^{\ominus}$	2.7 ± 0.7	1.7 ± 0.6
$NO_2^{\ominus}$	0.7 ± 0.7	- 0.3 ± 0.9

* Slope = the gradient obtained from a linear plot of equation (2-3).

Plots derived from equations (2-1) and (2-3) reveal good linear relationships (see tables 2-3A → 2-3C) for all daughter ions (see for example figures (2-7) and (2-8) except those produced by rearrangement reactions, *viz.* $[M^{\bar{\cdot}} - NO^{\cdot}]$ and $[M^{\bar{\cdot}} - O^{\cdot}]$. In all cases observed a broader scatter of points is obtained from using equation (2-3) than from using equation (2-1).

There are a number of interesting observations to be drawn from tables 2-3A → 2-3C. (1) When a sequence of equivalent daughter ions are produced from corresponding isomers in series A and B, the slope obtained from equations (2-1) and (2-3) display remarkable similarity.

e.g. the formation of $^{\oplus}O\text{-}C_6H_4\text{-}X$:-

Series	ρ	Slope*
A	2.6 ± 0.7	1.3 ± 0.7
B	2.6 ± 0.3	0.7 ± 0.2

Despite the warning issued by Harrison[76] concerning mechanistic interpretations drawn from mass spectral Linear Free-Energy Relationships, it is tempting to interpret this result as a suggestion that the meta and para isomeric series are fragmenting *via* essentially the same or similar mechanisms.

---

* Slope = the gradient obtained from equation (2-3).

(2) When the fragment ion produced is the same ion for all compounds in series A and B (i.e. when the fragment ion does not contain the substituent, for example *m/e* 166 and 122) good linear dependence is observed using both equations (2-1) and (2-3) [see for example figures 2-7 and 2-8]. This behaviour is opposite to that shown in positive-ions[76] where no correlations are observed under these circumstances.

When the fragment ion produced is different for all compounds in series A and B [e.g. $^{-}O\text{-}C_6H_5\text{-}X$] excellent linear relationships are obtained for all cases.

(3) Consider the fragmentations within either series A or series B. Both meta and para oriented substituents produce points that fall about the same line and consequently produce only one plot (see for example figures 2-7 and 2-8). This behaviour is different to that observed for positive-ions where two separate plots can usually be drawn for meta and para orientated substituents[76].

(4) The term $\frac{k_1}{k_t}$ (see equation 2-2 or 2-3) represents the fraction of fragmenting molecular ions that produce the daughter ion under consideration. Calculation of this ratio for each fragment peak in each spectrum reveals that in all cases the phenoxide ion is produced by greater than 95% of all fragmenting molecular anions. This calculation is reflected in the observed

spectra (see tables 2-1A and 2-1B) where the phenoxide ion is either the base peak of the spectrum or the most abundant peak after the molecular anion.

(5) The abundance of the NO_2^- species is generally very small, however linear correlations do exist (tables 2-3A and 2-3B) and the slopes are seen to be reverse slopes. In a conventional Hammett plot the presence of a reverse slope is taken as evidence that the transition state contains a higher degree of positive charge (or conversely a smaller degree of negative charge) than the parent molecule[75]. It is not clear what the observation of a reverse slope implies about the formation of NO_2^- in series A or B, but it must add weight to the assertion by Harrison[76] that considerable caution should be exercised when formulating conclusions concerning ionic structures or fragmentation mechanisms from the observation of substituent effects on ion abundances.

Alternative plots of equations (2-1) and (2-3) using modified sigma constants[99] such as Tafts' σ^*, σ^+ and σ^- were attempted. In all cases studied the original Hammett sigma values produced the linear relationship of best fit, therefore all subsequent correlations were performed using these values.

Plots of equations (2-1) and (2-3) for the phenyl-2-nitro-benzoates (series C - table 2-3C) reveal good linear relationships for most of the daughter ions produced in this series. A marked deviation from the linear plot is only observed when the substituent

is a nitro group (e.g. (2-35) and (2-36) c.f. Series A and Series B). This is expected since these molecules now contain two stabilizing nitro groups instead of the customary one found for the rest of the series. The results reported in this section reveal that a molecular anion displays strong stabilization when the carbonyl group and the nitro group are both attached directly to the same aryl ring.

2.4 (ii) Nitroarylbenzoates

In series D, E and F (tables 2-3D→2-3F) the nitro group and the carbonyl group are attached to different aryl rings and consequently correlation between the abundances of fragment ions and the Hammett sigma values for the varying substituent are not expected to be as good as those observed for the aryl nitrobenzoates (section 2.4 (i)).

Plots of equations (2-1) and (2-3) for the fragmentations in series D and E proved this to be the case. Some linear relationships were observed, but these were not as numerous or as close as those produced by series A-C (see tables 2-3D and 2-3E).

The 2-nitroarylbenzoates (series F) are almost completely devoid of linear relationships and graphs at best show nothing more than a trend (see table 2-3F). These results are unusual since the fragment ions produced (i) all contain a substituent, and (ii) fragment further by expulsion of CO_2. Thus formation of the fragment species appears to be almost independent of the substituent.

TABLE 2-3D. 4-nitrophenylbenzoates

Fragment ion	ρ	Slope$^{\neq}$
$XC_6H_4CO_2^{\ominus}$	2.71 ± 2.7	1.5 ± 1.3
m/e 138	1.2 ± 0.3	-0.04 ± 0.02
m/e 166	1.2 ± 0.3	0.6 ± 0.4

TABLE 2-3E. 3-nitrophenylbenzoates

Fragment ion	ρ	Slope$^{\neq}$
$X\text{-}C_6H_4CO_2^{\ominus}$	1.3 ± 0.7	1.5 ± 0.8
m/e 138	0.6 ± 0.3	-0.04 ± 0.03

TABLE 2-3F. 2-nitrophenylbenzoates

Fragment Ion	ρ	Slope$^{\neq}$
m/e 138	-0.2 ± 1.2	-0.2 ± 0.9
$NO_2^{\ominus}$	0.1 ± 1.1	0.1 ± 0.8
$X\text{-}C_6H_4CO_2^{\ominus}$	0.04 ± 0.3	0.0 ± 0.01
$X\text{-}C_6H_4^{\ominus}$	0.1 ± 0.5	0.0 ± 0.2

$\neq$ Slope = the gradient obtained from a linear plot of equation (2-3).

The spectra of compounds in Series D → F all exhibit extremely small molecular anions (see tables 2-1D → 2-1F). Thus, the values employed to evaluate equations (2-1) and (2-3) are prone to large error limits and a consequent increase in the spread of points is expected. As with previous cases, when the substituent is a nitro group, the points lie well away from the line of best fit.

2.4 (iii) Phenyl-4-cyanobenzoates

Since the nitro substituent has a very marked effect on the stability of negative-ion mass spectra the effect of introducing a less efficient electron withdrawing group was studied in the series phenyl-4-cyanobenzoates (series G).

TABLE 2-4. Fragmentation of Phenyl 4-Cyanobenzoates (Series G). Values of ρ and the Slope from the Chin-Harrison Expression

Process	McLafferty	Chin-Harrison
m/e 102	3.0 ± 0.6	no correlation
$\bar{O}$-C_6H_5-X	5.0 ± 1.3	no correlation
m/e 146	4.0 ± 1.5	no correlation

Straight line plots (see table 2-4) are readily obtained from equation (2-1) (figure 2-9). These linear correlations obtained for the phenyl-4-cyanobenzoates (table 2-4) show a much larger scatter of points than do the corresponding linear correlations found for the phenyl-4-nitrobenzoates (table 2-3A) and therefore

the slope of the correlation graph (ρ) contains a greater error factor. In contrast to earlier observations (section 2.4 (i)) no correlations could be found for any cleavage using equation 2-3 (see figure 2-10).

2.5 Appearance Potentials

Correlations between σ, calculated $\log(\frac{Z}{Z_o})$ values and observed appearance potentials have been reported for some positive-ion mass spectra[16].

An unsuccessful attempt was mounted to explore any such relationships found in negative-ion mass spectra.

Some difficulty was expected in this task since (1) negative-ions are often produced by more than one process (see section 1.2) and consequently the appearance potential is more difficult to measure and (2) no suitable internal standard is available for ions produced by secondary-electron capture. Despite these difficulties, it was expected that a linear relationship between sigma and the measured relative appearance potential would be observed.

The failure to measure suitable appearance potentials however resulted from an unexpected complication. The mass spectrometer employed during this study proved to be particularly unstable in the negative-ion mode at electron voltages below 20eV, consequently any attempted appearance potential measurements were not reproducible and successive concordant determinations could not be obtained. The

reason for the machine instability was clearly electrical and further work is being conducted in this area in an attempt to uncover the problem.

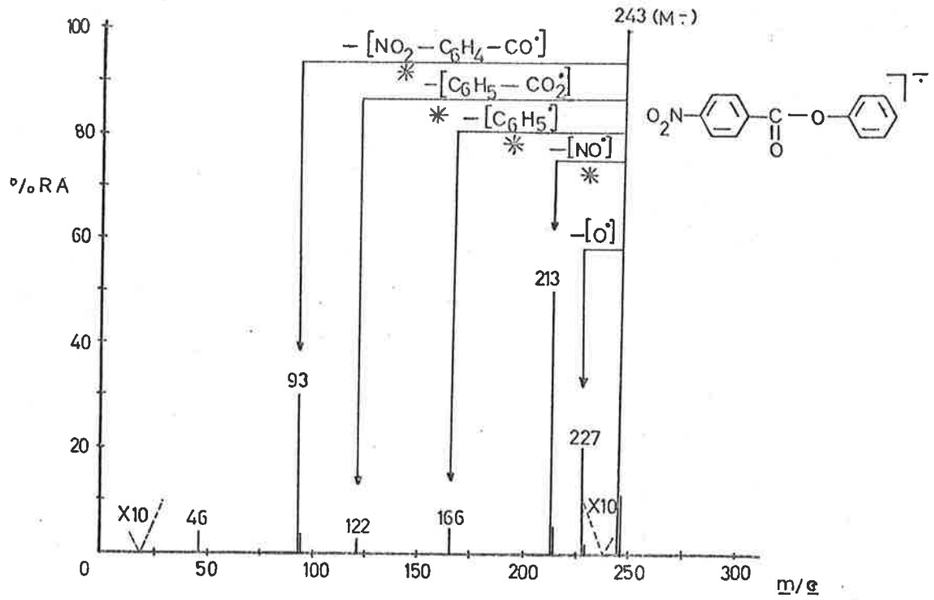


FIGURE (2-1): The negative-ion mass spectrum of phenyl-4-nitrobenzoate (2-8).

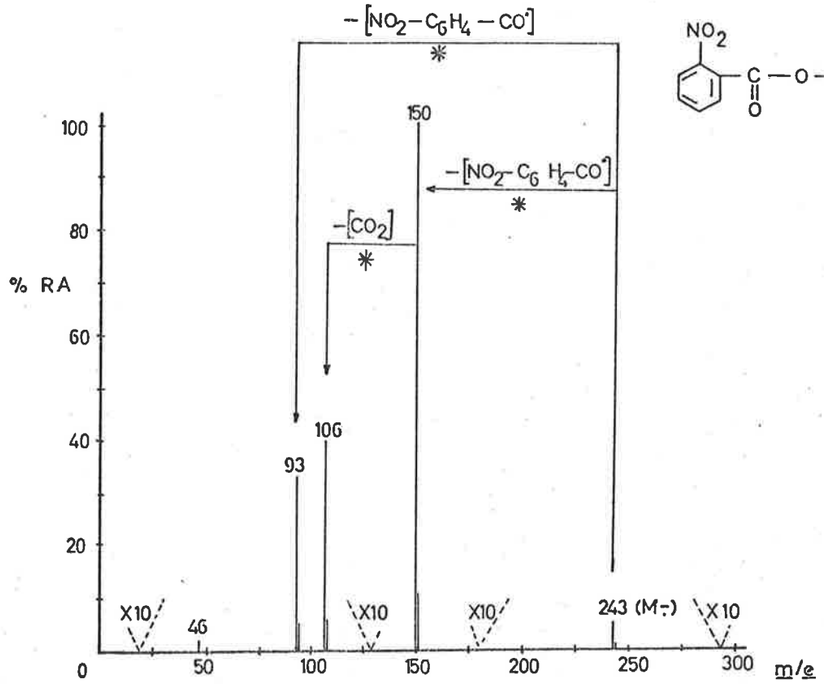


FIGURE (2-2): The negative-ion mass spectrum of phenyl-2-nitrobenzoate (2-10)

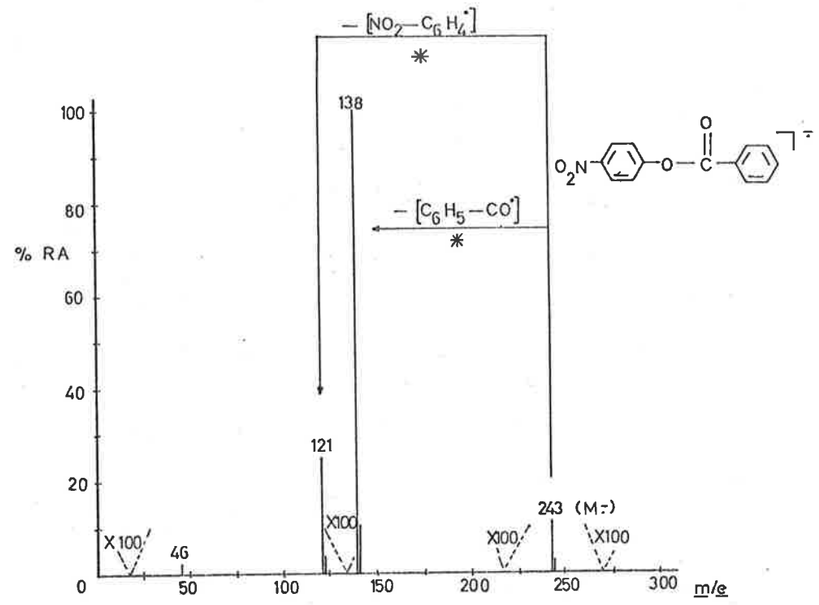


FIGURE (2-3): The negative-ion mass spectrum of 4-nitrophenylbenzoate (2-11).

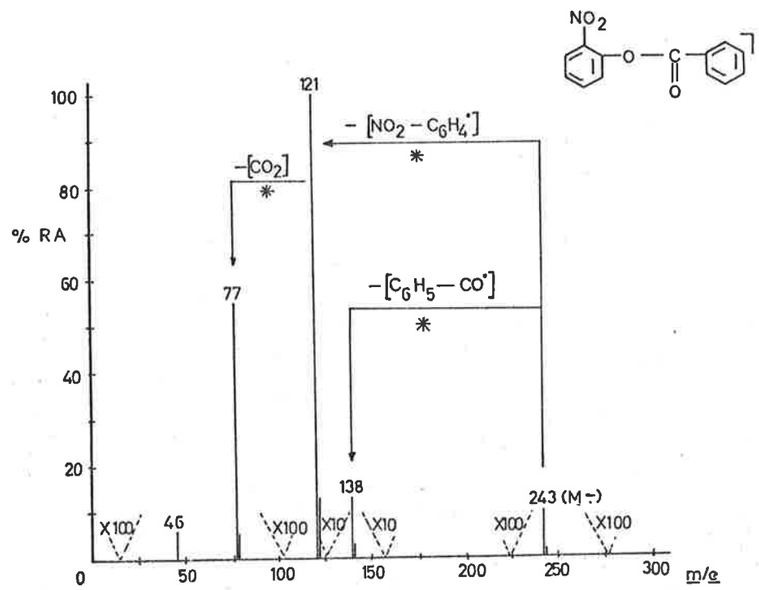


FIGURE (2-4): The negative-ion mass spectrum of 2-nitrophenylbenzoate (2-13).

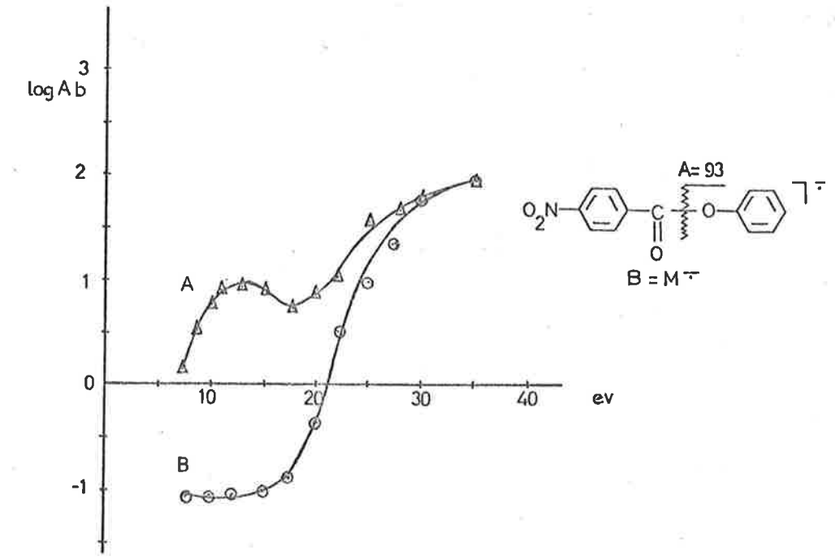


FIGURE (2-5): The plot of relative abundance of the ion m/e 93 and the molecular anion of phenyl 4 nitrobenzoate (2 8) against nominal electron beam energy.

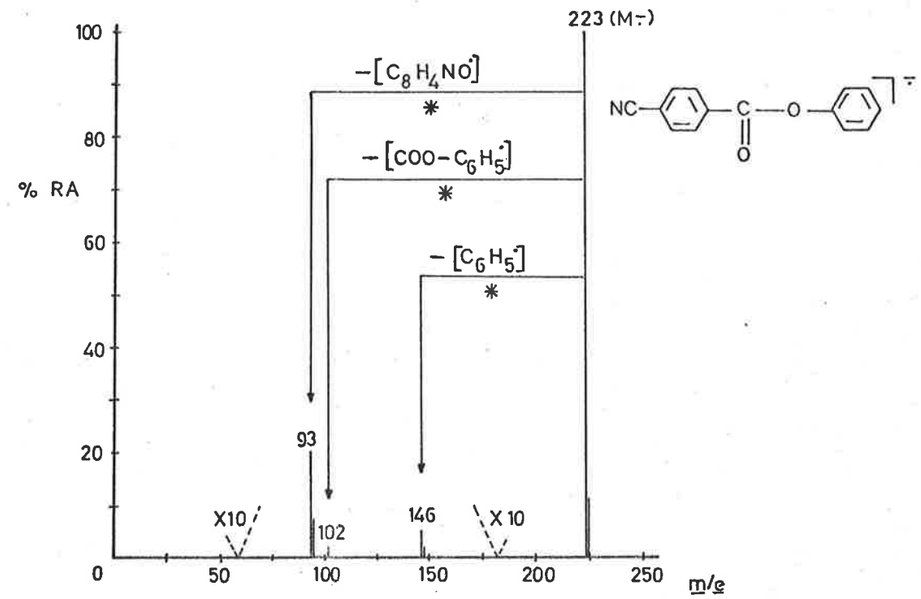


FIGURE (2-6): The negative-ion mass spectrum of phenyl -4-cyanobenzoate (2-79).

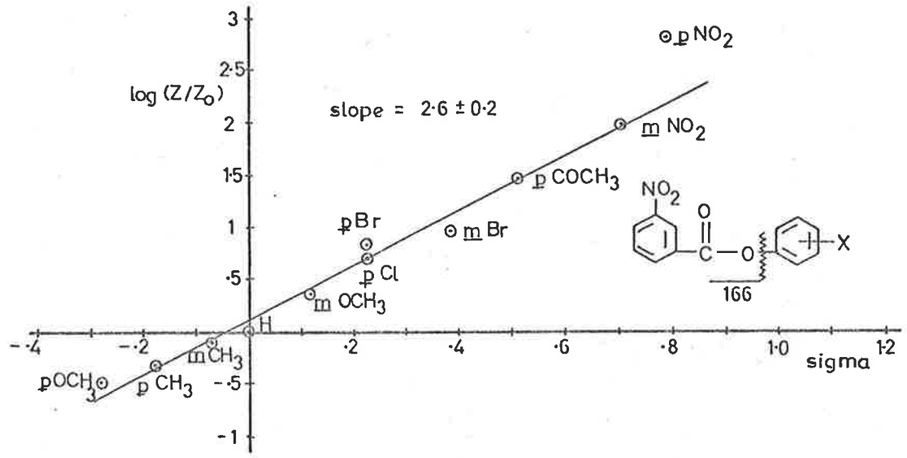


FIGURE (2-7): The plot of log (Z/Z_o) against sigma for the phenyl-3-nitrobenzoates (Series B).

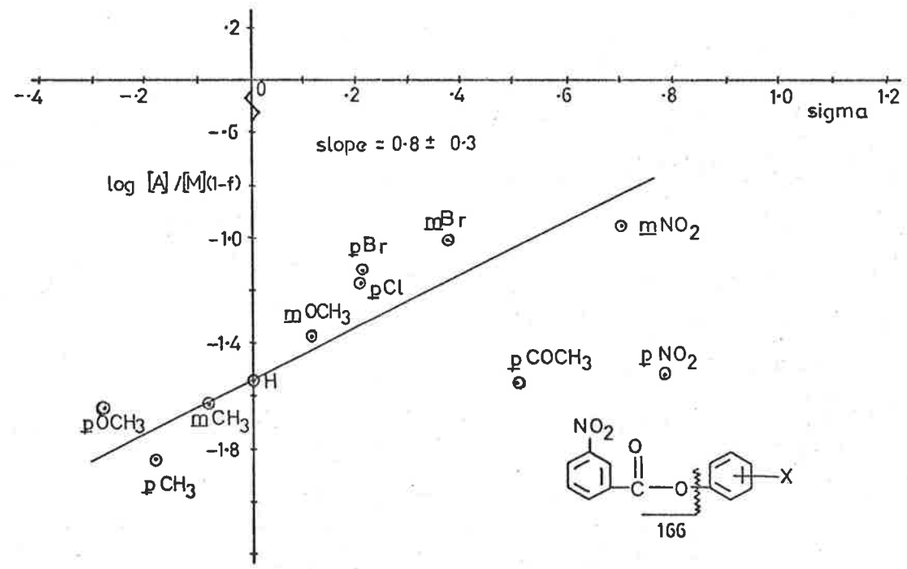


FIGURE (2-8): The plot of log [A]/[M] (1-f) against sigma for the phenyl-3-nitrobenzoates (Series B).

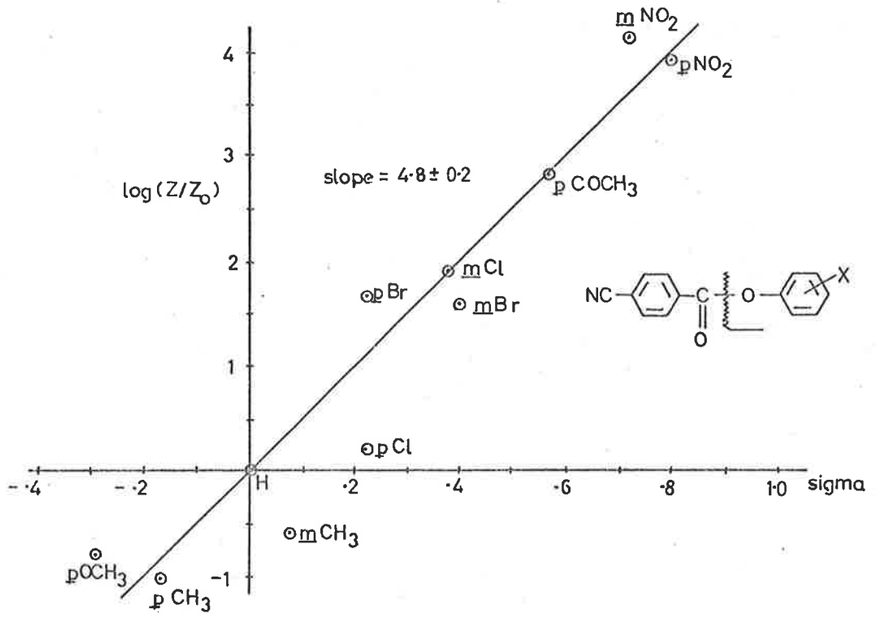


FIGURE (2-9): The plot of log (Z/Z_o) against sigma for the formation of the phenoxide anion from phenyl-4-cyanates.

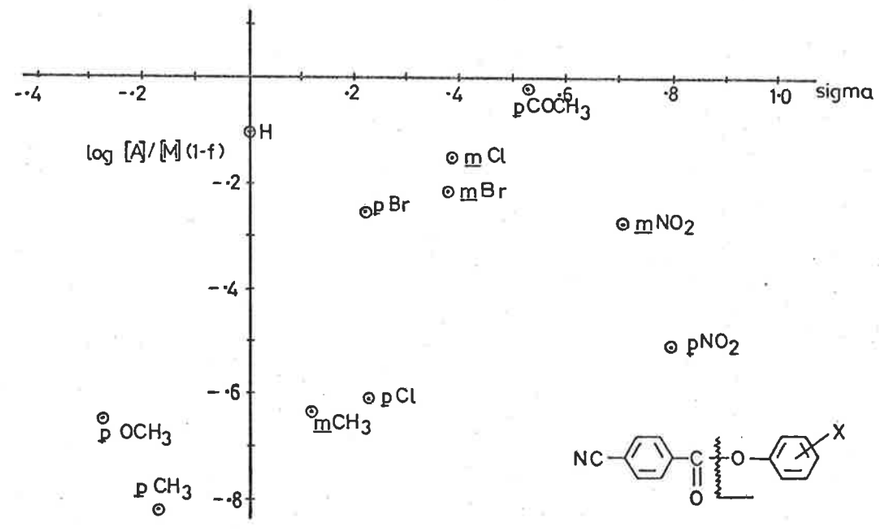
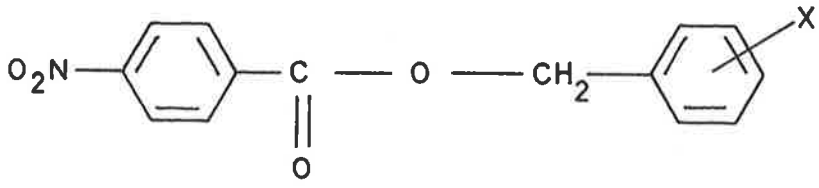


FIGURE (2-10): The plot of log [A]/[M](1-f) against sigma for phenyl 4 cyanobenzoates. (no correlation is seen)

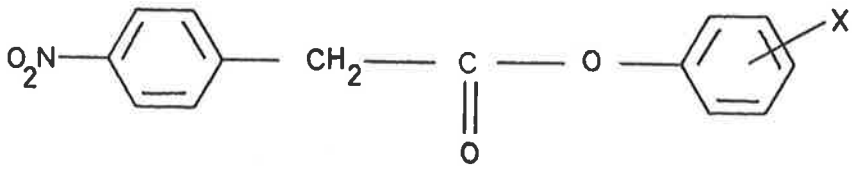
CHAPTER 3. THE EFFECT OF AN INTERPOSED METHYLENE GROUP

3.1 Introduction

Extremely good linear relationships have been observed for the fragment ions of simple aryl esters when the ester function is attached directly to two phenyl rings (see tables 2-3A → 2-3F). The effect of isolating the ester function by interposing a methylene bridge between the ester and each phenyl ring was studied in the series benzyl-4-nitrobenzoates (series H) and phenyl (4-nitrophenyl) acetates (series I). The arylnitrobenzoates provide better examples of linear relationships (see section 2.4 (i))than do nitroaryl-benzoates (see section 2.4 (ii)) therefore they are the obvious choice for modification. Study of the 4-nitro series in each case was considered to be adequate since isomers from series A and series B fragment to produce the same daughter ions (see section 2.3 (i)), and a compound from series A always shows a much more intense spectrum than its corresponding isomer from series B. Similar results are obtained for series D and series E. The 2-nitro series was not considered since its spectra are complicated by rearrangement peaks (2.3 (i) and 2.3 (ii)).



SERIES H



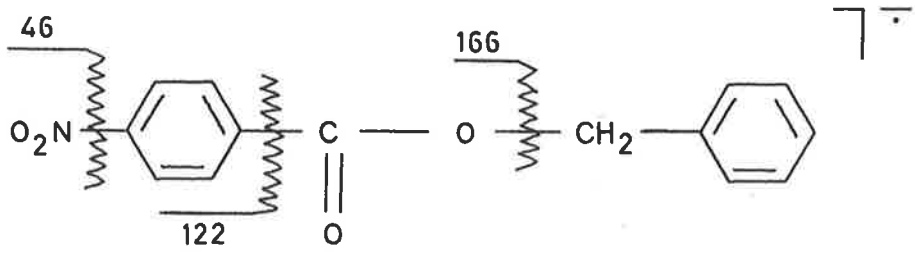
SERIES I

3.2 Negative-ion spectra of the methylene compounds

3.2. (i) Benzyl-4-nitrobenzoates

The methylene bridge was first inserted between the ester function and the phenyl ring containing the variable substituent. The spectra are recorded in table (3-1) and the fragmentation of benzyl-4-nitrobenzoate (3-1) [see figure 3-1 and scheme 3-1] is representative of this series.

Scheme 3-1



(3-1)

TABLE 3-1. Negative-Ion Mass Spectra of Benzyl-4-nitrobenzoates

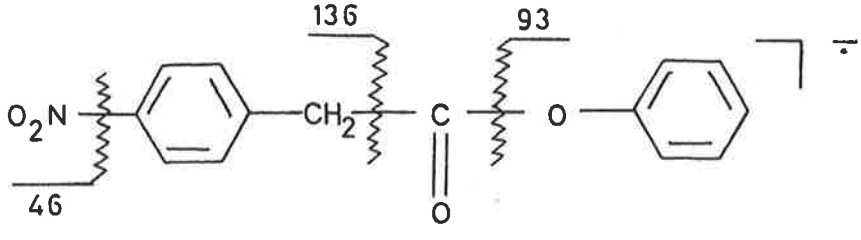
Compound	Substituent	$M^{\bar{\cdot}}$	*m/e* 166	*m/e* 122	*m/e* 46
3-2	*p* NO_2	0.66	100	2.6	0.9*
3-3	*m* Br	0.52	100	10.0	0.9
3-4	*m* Cl	1.2	100	6.1	6.0
3-5	*p* Br	0.27	100	0.6	0.5
3-6	*m*OCH_3	5.6	100	1.7	0.5
3-7	*m* CH_3	3.2	100	7.9	0.3
3-1	H	2.5	100	2.1	1.9
3-8	*p* CH_3	3.4	100	4.8	1.9
3-9	*p*OCH_3	3.2	100	5.3	0.7

* This peak may contain contributions from both nitro groups.

Introduction of the methylene group resulted in the disappearance from the spectrum of the peak due to the phenoxide ion. This observation is reasonable since any such fragment produced in this case would be an alkoxide rather than a phenoxide and the resonance stabilization of the negative charge would be destroyed. All other fragmentation pathways are essentially the same as those reported for the aryl nitrobenzoates (c.f. figure (2-1) and scheme (2-4)).

3.2 (ii) Phenyl-(4-nitrophenyl) acetates

If the methylene group is introduced between the nitro substituted ring and the ester group, the fragmentation pattern is substantially altered. The spectra are reported in table 3-2 and the spectrum of phenyl-(4-nitrophenyl)-acetate (3-10) (see figure (3-2) and scheme (3-2)) is representative of this series.



(3-10)

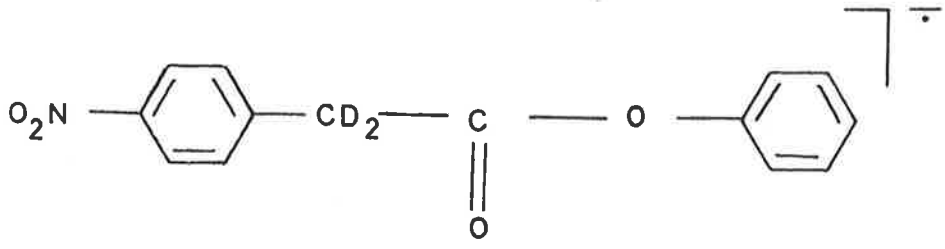
TABLE 3-2. Negative-Ion Spectra of Phenyl-(4-nitrophenyl) acetates

Compd.	Substituent	M^-	*m/e*179	*m/e*163	*m/e*136	$XC_6H_4O^-$	*m/e*46
3-11	*p* NO_2	1.8	5.6	0.8	3.5	100	55*
3-12	*m* NO_2	3.6	100	32	8.0	73	1.0*
3-13	*p* $COCH_3$	12.0	85	1.7	1.6	100	0.8
3-14	*p* Cl	4.5	5.5	100	0.9	14	3.3
3-10	H	100	17	60	8.1	19	22.0
3-15	*m* CH_3	100	18	92	5.7	7.1	4.1
3-16	*p* CH_3	100	19	72	12.0	19	17.0
3-17	*p* OCH_3	100	5.8	40	7.0	1.0	1.4

The spectrum (figure 3-2) reveals a series of simple cleavage reactions which produce fragment ions at *m/e* 46, 93 and 136. The major fragment ions however are produced by the rearrangement pathways $[M^- - C_6H_5OH]$ and $[M^- - C_6H_6]$ to produce daughter ions of *m/e* 163 and 179 respectively. The spectrum of the d_2 labelled ester (3-18) reveals that the hydrogen atom involved in the rearrangement reactions originates exclusively from the benzylic position.

---

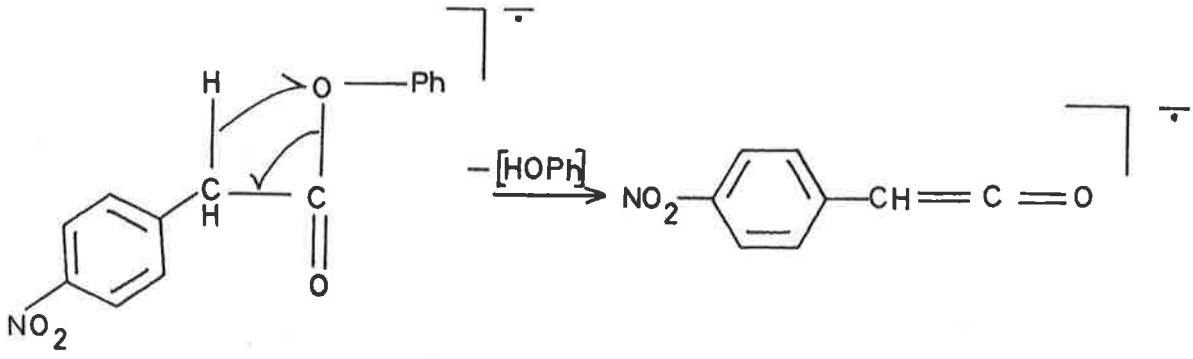
* These peaks may contain contributions from both nitro groups.



(3-18)

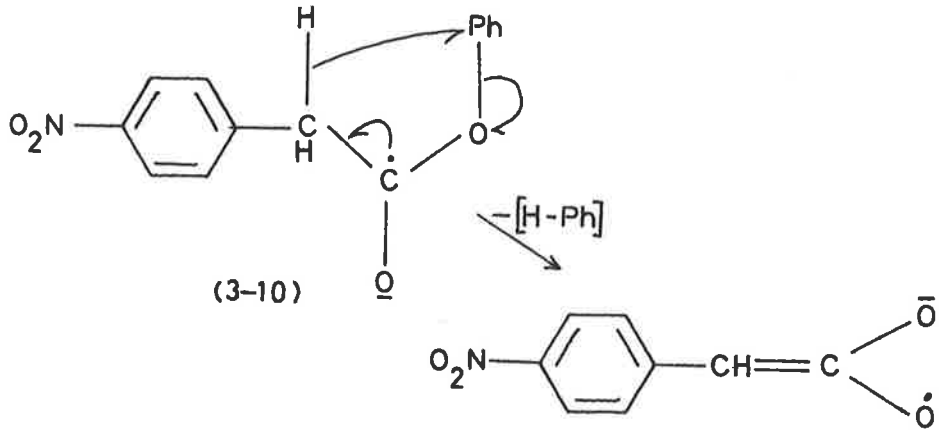
The products can be rationalized in terms of a 4-centre rearrangement [see scheme (3-3)] for [$M^{\bar{\cdot}}$ - C_6H_5OH] and a 5-centre rearrangement [see scheme (3-4)] for [$M^{\bar{\cdot}}$ - C_6H_6]. Additional support for the rearrangement reactions is presented in Appendix A.

Scheme 3-3



(3-10) (3-19)

Scheme 3-4

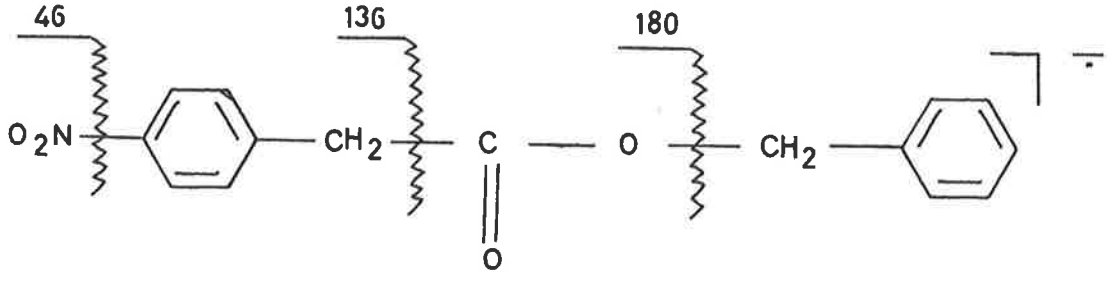


(3-20)

3.2 (ii) Benzyl-(4-nitrophenyl)acetate (3-21)

It is interesting to note that if a methylene group is inserted on both sides of the ester group (e.g. (3-21)) the rearrangement reactions disappear and are replaced by the simple cleavages shown in figure (3-3) and scheme (3-5) (c.f. schemes (2-4) and (3-1) respectively).

Scheme 3-5



(3-21)

3.3 Substituent Effects

Insertion of a methylene group between the ester function and a phenyl ring effectively separates these groups from each other. One effect of this separation should be a deterioration in the dependence of any fragmentation on the substituent. Therefore, any treatment of the spectra of benzyl-4-nitrobenzoates and phenyl-(4-nitrophenyl)acetates with equations (2-1) or (2-3) is expected to show a much wider scatter of points than was observed in the case of fragmentations where the methylene group was absent (c.f. section 2.4 (i)).

3.3 (i) Benzyl-4-nitrobenzoates

When a methylene group is inserted between the ester function and the ring containing the substituent (see table 3-3) the effect is quite pronounced. The plots obtained from equation (2-1) still show a general trend of increasing fragmentation with increasing sigma values, but the scatter of points is much larger than was the case for the aryl-4-nitrobenzoates (see table 2-1A), thus producing much larger errors in the slopes. The plots from equation (2-3) show no correlation at all.

TABLE 3-3. Fragmentation of Benzyl-4-nitrobenzoates. Values of ρ and the slope from the Chin-Harrison Expression

Process	McLafferty (ρ)	Chin-Harrison (slope)
m/e 166	1.9 ± 1.2	no correlation
m/e 122	1.8 ± 1.4	no correlation
m/e 46	1.9 ± 1.5	no correlation

3.3 (ii) Phenyl-(4-nitrophenyl)acetates

When the methylene group is inserted between the ester function and the second aromatic ring, the stabilizing nitrophenyl group has been essentially isolated. In this case, fragmentations show reasonable correlations for plots obtained from equation (2-1) (see table 3-4). Those peaks due to simple cleavage reactions (i.e. *m/e* 46, 136 and O^{-}-C_6H_5-X) exhibit a smaller scatter of points than those due to rearrangement reactions (i.e. M-C_6H_5-X and M-XC_6H_4OH) (see scheme 3-2). Again it was not possible to obtain any linear correlations from equation (2-3) (see table 3-4).

Careful observation of tables 2-3A, 2-4 and 3-4 reveals that each series forms essentially the same sequence of daughter ions [i.e. $\overline{O}$-C_6H_4-X]. A comparison of the linear free-energy relationship parameters for each series (see table 3-5) unfortunately

TABLE 3-4. Fragmentation of Phenyl (4-nitrophenyl)acetates. Values of ρ and the slope from the Chin-Harrison Expression

Process	McLafferty (ρ)	Chin-Harrison (slope)
m/e 136	1.4 ± 0.5	no correlation
$\overline{O}$-C_6H_5-X	3.3 ± 0.7	no correlation
m/e 46	0 .9 ± 0.4≠	no correlation
M-C_6H_5X	2.3 ± 1.0	no correlation
M-XC_6H_4OH	1.9 ± 1.3	no correlation

shows no trend and therefore does not provide any useful information about the processes involved in fragmentation.

TABLE 3-5. A comparison of the ρ value for the formation of $^{\theta}O$-C_6H_4-X in several different series

Series	ρ
Phenyl-4-nitrobenzoates	2.6 ± 0.2
Phenyl-(4-nitrophenyl)acetates	3.3 ± 0.7
Phenyl-4-cyanobenzoates	5.0 ± 1.3

3.4 Conclusions

The results presented in chapters 2 and 3 reveal several important inferences.

≠ Compounds (3-11) and (3-12) were not included in this determination.

(1) The presence of quite different fragmentation patterns, or substantial differences in peak intensities allows a facile differentiation of all isomeric compounds from among the series studied. This trend should be compared with the positive-ion spectra where *ortho*, *meta* and *para* isomers fragment *via* essentially the same pathway.

(2) In both cases studied the spectrum of the *ortho* isomer is totally different from those of its corresponding *para* and *meta* isomers. This strongly suggests that valence isomerism of the benzanoid system does not occur either prior to or during fragmentation of the molecular anions.

(3) The major fragmentations of all compounds are best rationalized by a fragmenting molecular anion with the charge retained on the carbonyl group of the ester function, although some localization of charge on the nitro group may precede the formation of NO_2^- and $[M^{\bar{\cdot}} - NO^{\cdot}]$ ions. No information was obtained about the "structures" of the molecular anions that undergo "proximity effects" during the decomposition of the *ortho* isomers.

(4) Inserting a methylene group between the ester function and the substituent containing ring does not materially affect the fragmentation pattern, whereas placing a methylene group between the ester function and the nitro containing ring introduces a completely new mode of fragmentation.

(5) The presence of a nitro group in either phenyl ring has a pronounced effect on the stability of the molecular anion, and hence the nature of the fragment ions produced. If the nitro group is replaced by a less efficient electron withdrawing group (e.g. cyano group) the stability of the molecular ion is reduced, although it still remains considerably above the level found when no stabilizing substituent is present.

(6) Linear correlations between parameters involving the abundance of the fragmentation and the appropriate substituent constant (σ) were observed for most of the negative-ion spectra recorded. Alternative substituent constants values were tested, but the correlations produced were not as satisfactory as those obtained using the original Hammett substituent constants.

The values of the slopes obtained from such plots vary considerably and therefore they should not be used to infer information about the actual transition states or the mechanisms of the reactions.

(7) The expression derived by Chin and Harrison (equation 2-3) has a much stronger theoretical foundation than the expression derived by McLafferty (equation 2-1), nevertheless plots of log $(\frac{Z}{Z_o})$ against σ result in closer linear correlations than do plots of log $\frac{A}{M(1-f)}$ against σ for all the cleavages studied.

(8) It has been shown that the isomeric *meta* and *para* nitro

series studied fragment to produce essentially the same products. One outstanding feature exhibited by these series is the remarkable correspondence between the fragmentation parameters from one series to the other (compare series A and B or series D and E). This observation suggests that the mechanism of the fragmentation processes for each of these two isomers could be essentially the same.

(9) When a methylene group is inserted between the ester group and either aryl ring linear plots are observed between log $(\frac{Z}{Z_o})$ and σ. In general, the substituent effects are not as pronounced as those observed in aryl-4-nitrobenzoates or aryl-4-cyanobenzoates. No correlation was observed between sigma and the Chin-Harrison expression.

(10) When the stabilizing group is a less efficient electron withdrawing group such as a cyano group, linear correlations are obtained between log $(\frac{Z}{Z_o})$ and sigma for the fragmentation of the ester group, while no correlation between log $\frac{A}{M(1-f)}$ and sigma could be found.

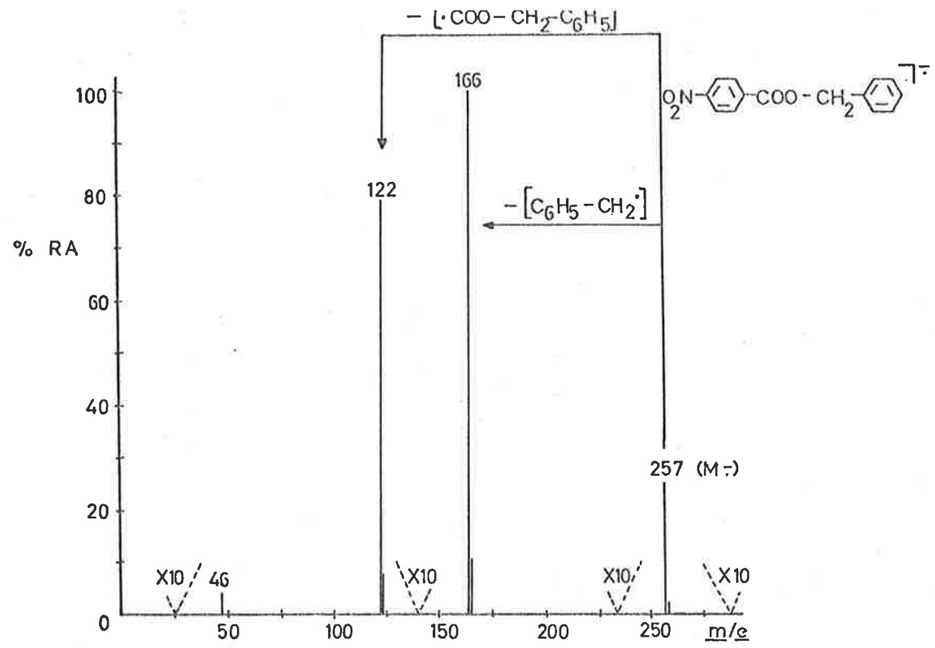


FIGURE (3-1): The negative-ion mass spectrum of benzyl-4-nitrobenzoate (3-1).

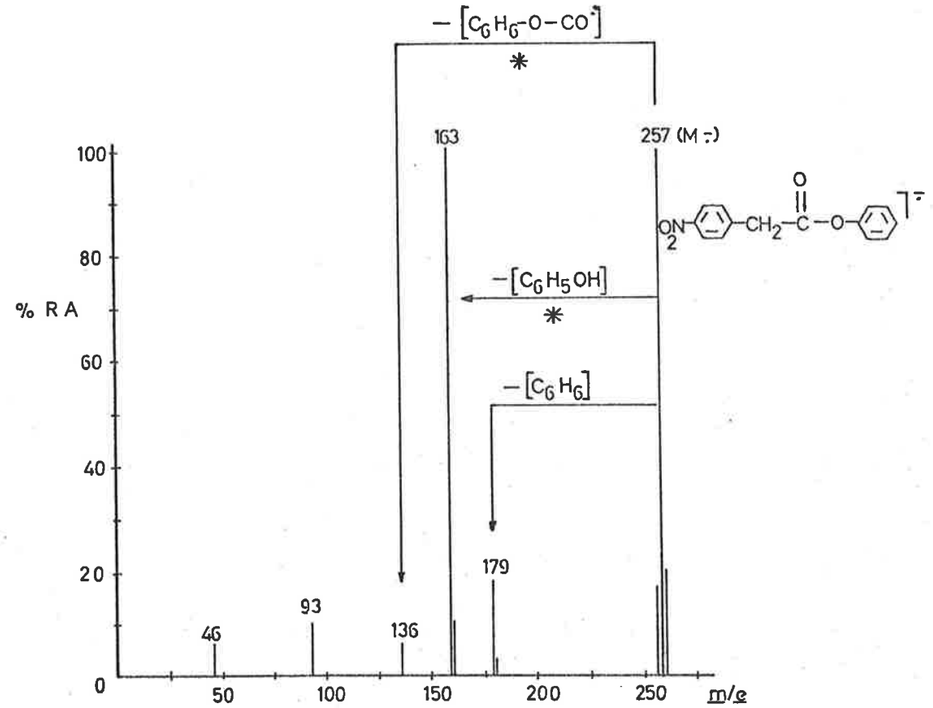


FIGURE (3-2): The negative-ion mass spectrum of

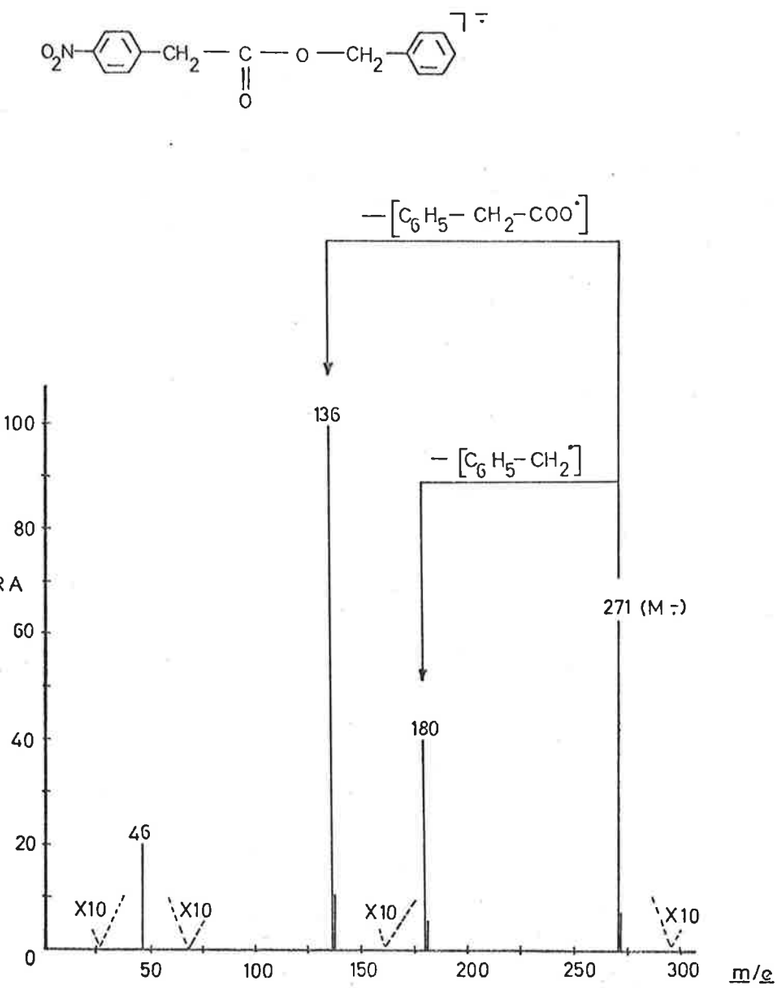


FIGURE (3-3): The negative-ion mass spectrum of benzyl -(4-nitrophenyl)-acetate (3-21).

APPENDIX A. ION KINETIC ENERGY STUDIES (I.K.E.S.)

The work outlined in this appendix was originally planned as an integral part of the work discussed in chapters 2 and 3. However, due to a delay in the construction of the equipment necessary to observe and record the I.K.E. spectra, it was not possible to conduct these studies concurrently with the work for chapters 2 and 3. It is reproduced here with the kind permission of Dr. J.H. Bowie in an attempt to produce a greater sense of completeness to the discussion.

-- * --

When an ion collides with a neutral molecule in a mass spectrometer, the internal energy of the ion may be enhanced and decomposition may follow[100]. The daughter ions produced have properties similar to the products of metastable decompositions (see section 1.3 (v)[102-104]. The effect of increasing the pressure of the neutral molecule (nitrogen) on the collision-induced spectrum is equivalent to increasing the electron-beam energy on a normal spectrum. This leads to enhancement of the internal energy of the molecular anions by collisional excitation, and may lead to the subsequent decomposition of functional groups that under normal conditions do not fragment[101] (c.f. section 1.3 (v)). This approach has been used to study the properties

of collision-induced dissociations in both positive-ion spectra[102-104] and negative-ion spectra[96,100,101]. A description of the device constructed to measure the I.K.E. spectra is set out below.

The Metastable Defocussing/Ion Kinetic Energy Device

The unit was designed to operate with the maximum accelerating potential of 3.6 kV of the R.M.U. 7D mass spectrometer. A variable power supply 360 ± 15 V) provides the electric sector potential. The unit, together with specifications, is shown in Fig. A-1.

The unit is operated in the negative mode by first turning S_3 to N. With S_1 in position F and VR = VR max., the main beam of ions is then adjusted to give a maximum ion current at a sector potential of approximately 360 V. The D.V.M. is adjusted to read 1.0000 (100%) at this maximum value. To operate in the metastable defocussing mode, S_1 remains in position F and the sector potential is adjusted to the required value by manual alteration of VR (when $VR = VR_{max}$, $E_{IN} = E_{OUT}$). If an automatic scan is required (i.e. an I.K.E. spectrum), S_1 is moved to G, S_2 switched on, and the unit produces an almost linear scan from 0-360V (D.V.M. reading 0-1.0000 (0-100%)). The I.K.E. signals are collected by a modified ion monitor positioned after the energy-focussing β slit. The signal from the collector goes directly to an amplifier (Keithley 410 A picoammeter) and thence to the recorder (Honeywell 1508 visicorder) of the mass spectrometer.

The unit gives metastable ions approximately 100 times more intense than those obtained using a conventional metastable defocusser. Negative I.K.E. spectra are run routinely using the 0.3×10^{-10} A range of the amplifier (maximum sensitivity 0.3×10^{-12}A). The energy resolution for the positive I.K.E. spectrum of *n*-decane was compared with published spectra obtained using R.M.U. 7 and R.M.H. 2 instruments[20] and was found to be intermediate in value between the two recorded spectra.

The sample is introduced at a pressure of 2×10^{-6} torr in the normal manner, while the collision gas (nitrogen) is introduced into the field free region between the ion source and the electric sector.

It has been shown that induced decompositions due to simple cleavage reactions increase in intensity as the pressure of the collision gas is increased, while those resulting from rearrangement processes decrease in intensity[98,100].

When the defocussed negative-ion metastable spectrum (Ion Kinetic Energy Spectrum) of (3-10) is measured using varying pressures of collision gas (see figure A-2), five pressure dependent fragmentations were observed. Each peak was assigned a nominal value of 100% at its maximum intensity and the abundance relative to this value was monitored as the collision gas pressure was altered.

As the internal energy of the molecular anion increases the abundance of the two peaks $[M^{\bullet-}-PhOH]$ and $[M^{\bullet-}-NO^{\ominus}]$ is seen to decrease while at the same time the abundance of the peaks (*m/e* 46, 93 and 136) is seen to increase. This observation confirms earlier suggestions (section 3.2 (ii)) that the former are produced *via* rearrangement reactions while the latter are produced *via* simple cleavage reactions. This observation is consistent with other reported rearrangement/simple cleavage competitions discussed above (see section 1.4 (ii)).

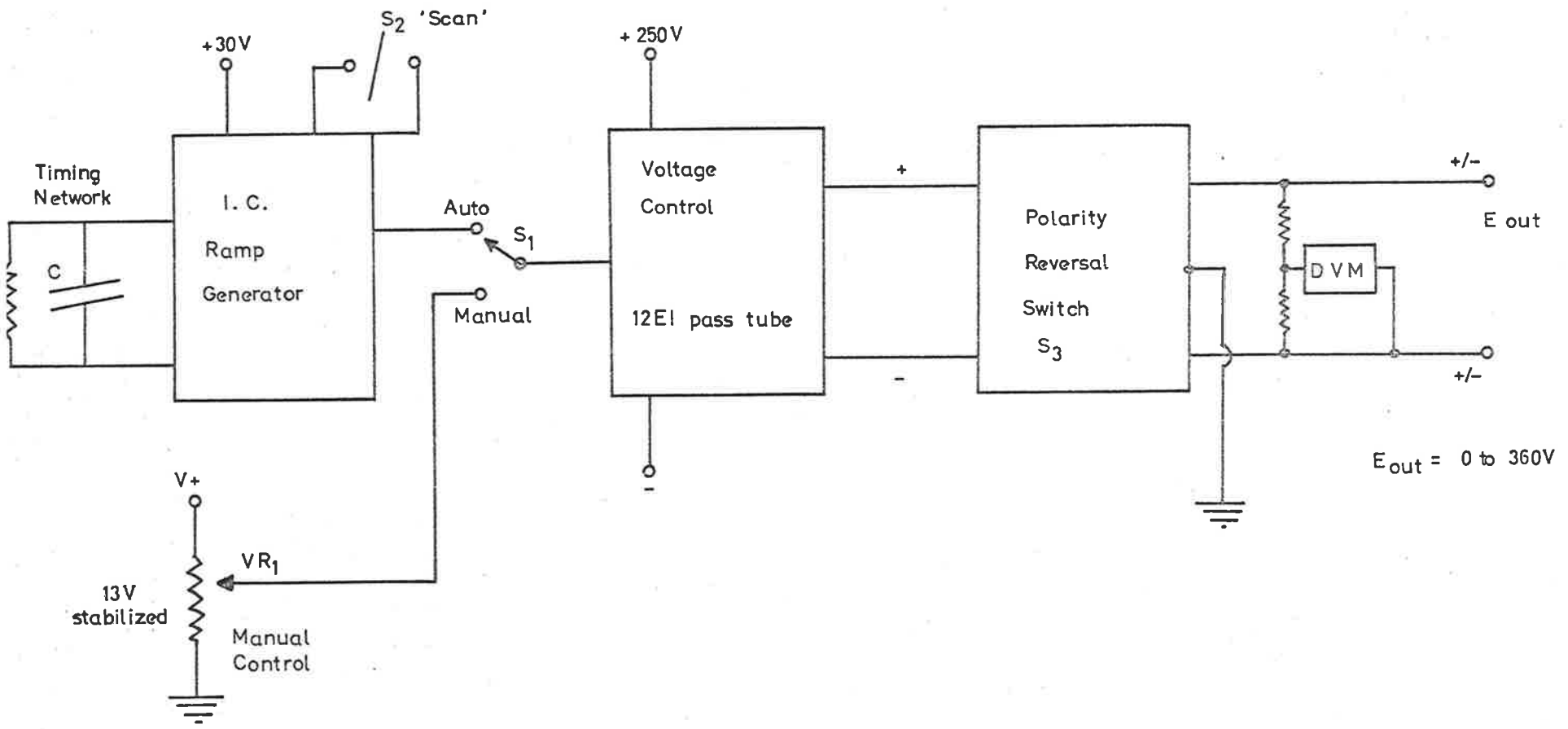
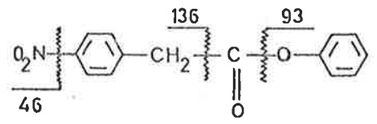


FIGURE (A-I): Circuit diagram of the Metastable Defocussing / Ion Kinetic Energy Device



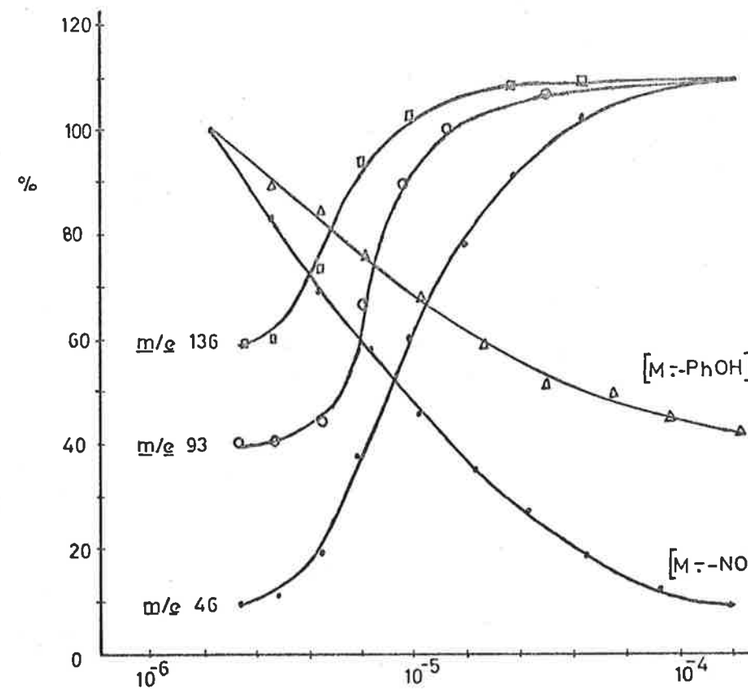


FIGURE (A-2): The defocussed negative-ion metastable spectrum of phenyl-(4-nitrophenyl)-acetate (3-10).

CHAPTER 4. EXPERIMENTAL

4.1 General Procedures

All mass spectra were determined with an Hitachi Perkin-Elmer RMU-7D mass spectrometer operating at 70eV (unless otherwise specified) with a source temperature of approximately 150°. Samples were introduced through an all glass inlet system at a temperature between 50° and 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 70eV (unless otherwise stated) and 1-3 x 10^{-7} Torr; all peaks were checked against internal standards. (These spectra are reproducible to a factor of less than 2% in abundance ratios of major peaks). The metastable defocussing device was modified electronically to allow the measurement of negative-ions.

The nuclear magnetic resonance spectra were measured with either a Varian DA-60-IL or Varian T60 spectrometer, operating at 60MHz, using carbon tetrachloride as a solvent with tetramethylsilane as an internal standard. Infrared spectra were recorded as Nujol mulls or liquid films, on either a Perkin Elmer 337 or a Unicam SP.200 infrared spectrophotometer. Ultraviolet spectra were recorded with a Unicam SP.700 U.V. spectrophotometer.

All gas chromatographic separations were conducted on a Perkin Elmer 881 gas chromatograph, while all liquid phase chromatographic separations were achieved using Mallenkrodt 100 greater mesh silicic acid. The term light petroleum refers to the fraction of B.pt 55-65°. All compounds were purified by crystallization, distillation or chromatography as required.

Melting points were determined on a Kofler hot-stage microscope, and are uncorrected. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

The lines of best fit for the linear free energy relationship graphs and the errors inherent in these estimations[105] were calculated by the C.D.C. 6400 computer at the University of Adelaide computing centre, using their library Least Squares Plot Routine written in Fortran IV.

4.2 Preparation of aryl esters

The aryl esters reported in the discussion were prepared by one of the four general procedures outlined below. All routes start with the appropriate carboxylic acid and all acids used were purified commercial samples.

The carboxylic acid was first converted into its acid chloride using a standard procedure[106]. This was followed by:

(A) The phenol (0.5 gm) was dissolved in dry pyridine (5 ml), the acid chloride (1.3 gm) added and stirred for 1 hr. The reaction mixture was poured into hydrochloric acid (2N, 40 mls). The supernatant liquid was decanted from the precipitated solid or oil, which was then stirred with sodium carbonate (1N, 10 mls). The solid derivative was filtered off, washed with water (2 x 50 mls) and purified by elution over a 20 x 2 cm column of silicic acid with light petroleum-diethyl ether followed by crystallization from ethanol or glacial acetic acid.

OR (B) The acid chloride (1.2 gm) was dissolved in dry benzene (25 mls), the phenol (0.5 gm) added and the mixture treated under reflux in an atmosphere of nitrogen for 14 hrs. The solution was cooled and the benzene removed *in vacuo*. The resulting solid was purified by column chromatography using silicic acid as adsorbent and diethyl ether as eluent. The product was recrystallized from a chloroform/*n*-hexane mixture to a constant m.pt.

OR (C) The phenoxide (2.0 gm) was dissolved in water (50 mls) and the acid chloride (1.0 gm) added over 10 minutes. The mixture was heated at 50° for 45 mins. The solid was separated and recrystallized from chloroform/*n*-hexane to a constant m.pt.

OR (D) The acid (0.5 gm) was dissolved in water, containing phenolphthalein (2 drops), sodium hydroxide (15%) was added until the solution was neutral. Hydrochloric acid (1N, 2 drops) was added, followed by the appropriate *para* substituted benzyl-bromide (0.5 gm) dissolved in ethanol (5 mls). The mixture was heated under reflux for 1 hr and allowed to cool. The solid was separated, washed with water (2 x 10 ml) and crystallized from ethanol/water (1:1).

Starting materials for ester synthesis

(a) Carboxylic acids: 4-nitrobenzoic acid, 3-nitrobenzoic acid, 2-nitrobenzoic acid, 4-nitrophenylacetic acid, 4-cyanobenzoic acid, 4-bromobenzoic acid, 3-bromobenzoic acid, 4-chlorobenzoic acid, 3-chlorobenzoic acid, 4-methylbenzoic acid, 3-methylbenzoic acid, 4-methoxybenzoic acid, 3-methoxybenzoic acid and benzoic acid were all purified commercial samples.

(b) Phenols: 4-nitrophenol, 3-nitrophenol, 2-nitrophenol, 4-hydroxyacetophenone, 4-bromophenol, 4-chlorophenol, 4-methylphenol, 3-methylphenol and phenol were purified commercial samples. 3-bromophenol and 3-chlorophenol were prepared *via* a standard Sand-meyer reaction[107] starting from the 3-haloaniline, while 4-methoxyphenol and 3-methoxyphenol were prepared by the mono-alkylation of quinol and resorcinol respectively using the method of Robinson and Smith[108].

(c) Alcohols: 4-nitrobenzyl alcohol, 4-methoxybenzyl alcohol and benzyl alcohol were purified commercial samples. 4-methylbenzyl alcohol, 3-methylbenzyl alcohol and 3-methoxybenzyl alcohol were all prepared by reduction of the corresponding carboxylic acid using a standard Lithium Aluminium Hydride reduction procedure[109].

(d) Bromides: 4-bromobenzyl bromide, 3-bromobenzyl bromide and 4-chlorobenzyl bromide were all purified commercial samples.

The following esters have been reported previously. The column headed "General Method" refers to the general method employed to synthesize that ester. (The compound numbers refer to those given in chapters 2 and 3).

Compound	m.pt.	Lit.	Ref.	General Method
4-nitrobenzoates				
2-14	157	159	110	A
2-15	176-178.5	174-175	111	A
2-18	99-100	101	112	A
2-19	181-182	181	113	A
2-20	170-172	168	111	A
2-21	123-125	126	115	A
2-8	129-130	129	116	A
2-22	86-88	85.5, 90	(110) (117)	A
2-23	97-98	97-98	117	A
2-24	113-115	113-115	114	A

Compound	m.pt.	Lit.	Ref.	General Method
3-nitrobenzoates				
2-25	144-145	145.5	118	A
2-26	135-136	129	119	A
2-29	122-123	122	113	A
2-30	125	124.5	120	A
2-9	97-98	97-98	118	A
2-32	63-65	63-64	117	A
2-33	75-77	77-78	117	A
2-nitrobenzoates				
2-35	111-112	111	110	A
2-10	49-50	52-53	121	A
2-41	78-79	78-79	117	A
4-nitrophenylbenzoates				
2-43	157-159	158-159	110	A
2-44	144-145	144.5	119	A
2-45	138-140	137	111	A
2-11	143-144	145-146	122	A
2-49	121-122	124	123	A
2-50	164-165	167-168	122	A

Compound	m.pt.	Lit.	Ref.	General Method
3-nitrophenylbenzoates				
2-51	176-178	174-175	111	A
2-52	135-136	129	119	A
2-53	130-132	132	124	A
2-55	134-136	135-136	125	A
2-12	94-95	95	126	A
2-58	106-107	106-107	125	A
2-nitrophenylbenzoates				
2-13	103-105	105	124	A
4-cyanobenzoates				
2-86	139-141	142-142.5	127	B
2-79	86-89	87-89	128	B
Benzyl-4-nitrobenzoates				
3-2	169-170	171-172	129	B
3-1	82-84	82-82.5	130	B

The following compounds have not been reported (the compound numbers are those allocated in chapters 2 and 3).

Compound	m.p. °C	Composition	Found (%)			Calc. (%)			Gen. Meth.
			C	H	N	C	H	N	
3-nitrobenzoates									
2-34	91-91.5	$C_{14}H_{11}NO_5$	61.4	4.1	4.9	61.5	4.1	5.1	A
2-31	91-92	$C_{14}H_{11}NO_5$	61.6	4.1	5.0	61.5	4.1	5.1	A
2-28	101-102	$C_{13}H_8NO_4Br$	48.7	2.6	4.1	48.5	2.5	4.35	A
2-27	129-131	$C_{15}H_{11}NO_5$	62.9	3.9	5.0	63.2	3.9	4.9	A
4-nitrobenzoates									
2-17	108-109.5	$C_{13}H_8BrNO_4$	48.4	2.4	4.3	48.5	2.5	4.35	A
2-16	199-200	$C_{15}H_{11}NO_5$	63.1	4.0	4.8	63.2	3.9	4.9	A
2-nitrobenzoates									
2-42	71-73	$C_{14}H_{11}NO_5$	61.6	4.2	5.1	61.5	4.1	5.1	A
2-40	66-67	$C_{14}H_{11}NO_5$	61.6	4.2	5.1	61.5	4.1	5.1	A
2-39	70-71	$C_{13}H_8ClNO_4$	56.1	3.0	4.8	56.2	2.9	5.0	A
2-38	84-85	$C_{13}H_8ClNO_4$	56.2	2.9	5.0	56.2	2.9	5.0	A
2-37	94-96	$C_{15}H_{11}NO_5$	63.1	4.0	4.7	63.2	3.9	4.9	A
2-36	114-115	$C_{13}H_8N_2O_6$	54.2	2.7	9.5	54.2	2.8	9.7	A
3-nitrophenylbenzoates									
2-59	124-125	$C_{14}H_{11}NO_5$	61.5	4.2	5.1	61.5	4.1	5.1	A
2-57	70-72	$C_{14}H_{11}NO_4$	65.4	4.4	5.6	65.4	4.3	5.5	A
2-56	92-93	$C_{14}H_{11}NO_4$	61.9	4.1	5.1	65.4	4.3	5.5	A
2-54	124-126	$C_{13}H_8BrNO_4$	48.6	2.5	4.2	48.5	2.5	4.35	A

Compound	m.p. °C	Composition	Found (%)			Calc. (%)			Gen. Meth.
			C	H	N	C	H	N	
4-nitrophenylbenzoates									
2-48	95-96	$C_{14}H_{11}NO_4$	65.5	4.5	5.4	65.4	4.3	5.45	A
2-47	114-115	$C_{14}H_{11}NO_5$	61.5	4.3	5.4	61.5	4.1	5.1	A
2-45	153-154	$C_{13}H_8BrNO_4$	48.7	2.6	4.1	48.5	2.5	4.35	A
2-nitrophenylbenzoates									
2-65	90-93	$C_{14}H_{11}NO_5$	61.2	4.0	5.2	61.5	4.1	5.1	A
2-64	75-76	$C_{14}H_{11}NO_4$	65.6	4.3	5.5	65.4	4.3	5.45	A
2-63	73-74	$C_{14}H_{11}NO_4$	65.7	4.3	5.3	65.4	4.3	5.45	A
2-62	66-67	$C_{14}H_{11}NO_5$	61.3	4.1	5.1	61.5	4.1	5.1	A
2-60	106-107	$C_{13}H_8BrNO_4$	48.5	2.7	4.3	48.5	2.5	4.35	A
4-cyanobenzoates									
2-80	196.5-198.5	$C_{14}H_8N_2O_4$	62.8	3.2	10.8	62.7	3.0	10.5	B
2-81	171-173	$C_{14}H_8N_2O_4$	62.5	3.1	10.3	62.7	3.0	10.5	B
2-82	164.5-165.5	$C_{16}H_{11}NO_3$	72.2	4.2	5.1	72.4	4.2	5.3	B
2-83	112-113	$C_{14}H_8NO_2Br$	55.6	2.6	4.5	55.7	2.6	4.6	B
2-84	109-111	$C_{14}H_8NO_2Cl$	65.1	3.0	5.3	65.3	3.1	5.4	B
2-85	90-92	$C_{14}H_8NO_2Br$	56.0	2.7	4.8	55.7	2.6	4.6	B
2-87	110-112	$C_{15}H_{11}NO_3$	71.1	4.5	5.3	71.1	4.5	5.5	B
2-88	102-104	$C_{15}H_{11}NO_2$	75.6	4.8	5.8	75.9	4.7	5.9	B
2-89	126-127	$C_{15}H_{11}NO_3$	70.9	4.5	5.3	71.1	4.5	5.5	B

Compound	m.p. °C	Composition	Found (%)			Calc. (%)			Gen. Meth.
			C	H	N	C	H	N	
Benzyl-4-nitrobenzoates									
3-3	90-92	$C_{14}H_{10}NO_4Br$	50.0	3.1	4.2	50.0	3.0	4.2	D
3-4	94-95	$C_{14}H_{10}NO_4Cl$	57.5	3.6	4.6	57.6	3.5	4.8	B
3-5	121-122	$C_{14}H_{10}NO_4Br$	49.9	3.0	4.4	50.0	3.0	4.2	D
3-6	169-171	$C_{15}H_{13}NO_5$	62.6	4.5	4.6	62.7	4.6	4.8	B
3-7	89-90	$C_{15}H_{13}NO_4$	66.5	5.0	5.1	66.4	4.8	5.2	B
3-8	130-132.5	$C_{15}H_{13}NO_5$	66.2	4.8	5.2	66.4	4.8	5.2	B
3-9	94.5-95	$C_{15}H_{13}NO_5$	62.9	4.6	4.9	62.7	4.6	4.8	B
Phenyl-(4-nitrophenyl)acetates									
3-11	121-122	$C_{14}H_{10}N_2O_6$	55.7	3.4	9.2	55.6	3.3	9.3	C
3-12	109-110	$C_{14}H_{10}N_2O_6$	55.4	3.2	9.4	55.6	3.3	9.3	C
3-13	107-109	$C_{16}H_{13}NO_5$	64.0	4.4	4.8	64.2	4.4	4.7	C
3-14	109-110	$C_{14}H_{10}NO_4Cl$	57.8	3.5	4.5	57.6	3.5	4.8	C
3-15	58-60	$C_{15}H_{13}NO_4$	66.4	4.8	5.1	66.4	4.8	5.2	C
3-10	89-91	$C_{14}H_{10}NO_4$	65.5	4.5	5.3	65.4	4.3	5.4	C
3-16	49-51	$C_{15}H_{13}NO_4$	66.6	5.0	5.0	66.4	4.8	5.2	C
3-17	85-87	$C_{15}H_{13}NO_5$	62.5	4.5	4.9	62.7	4.6	4.9	C
Benzyl-(4-nitrophenyl)acetate									
3-21	90-92	$C_{15}H_{13}NO_4$	66.1	4.9	5.2	66.4	4.8	5.2	B

Labelled compounds

The ^{18}O labelled Ester (2-78)

Benzene diazonium fluoborate was heated under reflux with a solution of HCl in $H_2{}^{18}O$ (^{18}O = 10%) for $1\frac{1}{2}$ hrs, giving a 70% yield of phenol ^{18}O (^{16}O = 90%, ^{18}O = 10%). Nitration[131] of the labelled phenol followed by chromatography over silicic acid using light petroleum as eluent gave the labelled 2-nitrophenol (30%) which was treated with 4-methoxybenzoyl chloride in pyridine[109] to produce the labelled ester 2-78 (m.pt. 91-93°) (^{18}O - 10%).

Mass spectrum: *m/e* 77 (8%), 92 (6), 107 (4), 135 (100), 136 (10), 151 (1.2), 169 (1.4), 171 (0.5), 273 (1.5), 275 (0.15).

The ^{2}H labelled ester (3-18)

Phenyl-(4-nitrophenyl)acetate (3-10) (0.5 gm) was heated under reflux in D_2O (25 ml) in a nitrogen atmosphere for 48 hrs. The solution was cooled and the solid separated. The solid was again heated under reflux in D_2O (25 mls) in a nitrogen atmosphere for a further 48 hrs. The solution was extracted with diethylether (LAH dried, 2 x 50 mls), extracted with sodium carbonate (10% in D_2O, 10 mls), washed (D_2O, 2 x 10 mls) and vacuum dried. M.pt. = 88-91° (d_2 = 67.8%, d_1 = 26.3%, d_o = 5.9%).

Mass spectrum: *m/e* 46 (6%), 93 (7), 136 (5), 137 (11), 138 (15), 163 (17), 164 (45), 165 (5), 179 (3), 180 (8), 181 (3), 256 (5),257 (15), 258 (54), 259 ($M^{\bar{}}$, 100), 260 (17).

CHAPTER 5. REFERENCES

1. Goldstein, E., Berl.Ber., 39, 691 (1886)
2. Thompson, J.J., "Rays of Positive Electricity and their Applications to Chemical Analysis", Longmans, Green & Co., London, 1913.
3. Kiser, R.W., "INtroduction to Mass Spectrometry and its Applications" Prentice-Hall Inc., Englewood Cliffs, N.J., 1965.
4. Melton, C.E., "Principles of Mass Spectrometry and Negative-Ions", Marcel Dekker Inc., N.Y., 1970.
5. Melton, C.E., in "Mass Spectrometry of Organic Ions", Edited by McLafferty, F.W., Academic Press, N.Y., 1963, Chapter 3.
6. Aplin, R.T., Budzikiewicz, H., and Djerassi, C., J.Am.Chem.Soc., 87, 3180 (1965).
7. Brown, C.L., and Weber, W.P., J.Am.Chem. Soc., 92, 5775 (1970).
8. Tsuda, S., Yokhata, A., and Kawai, M., Bull.Chem.Soc.Japan, 42, 607, 614, 1515, 2514, 3115 (1969).
9. Dougherty, R.C., and Weisenberger, C.R., J.Am.Chem.Soc., 90, 6570 (1968).
10. Bowie, J.H., and Ho, A.C., Aust.J.Chem., 26, 2009 (1973), and references 1-15 cited therein.
11. Alexander, R.G., Bigley, D.B., and Todd, J.F.J., Org.Mass Spectrom., 7, 643 (1973).
12. McAllister, T., Chem.Commun., 245 (1972).
13. Thynne, J.C.J., Chem.Commun., 1075 (1968).

14. Jacobs, G., Henglein, A., in "Advances in Mass Spectrometry", Ed., Mead, W.L., Institute of Petroleum, London, 1966, p. 286.

15. Harland, P.W., MacNeil, K.A.G., and Thynne, J.C.J., "Studies of Negative-Ion Formation at Low Electron Energies" in "Dynamic Mass Spectrometry", Heyden, London and Sadler Research Laboratories, Inc., Philadelphia, Pa., Vol. 1, chapt. 8 (1970).

16. Howe, I., "Energetics, Kinetics and Ion Structures", in "Mass Spectrometry", Ed., Williams, D.H., Chemical Society Specialist Periodical Reports, 1, 31 (1971).

17. Howe, I., "Energetics, Kinetics and Ion Structures", in "Mass Spectrometry", Ed., Williams, D.H., Chemical Society Specialist Periodical Reports, 2, 33 (1973).

18. Tajima, E., and Seibl, J., Int.J.Mass Spectrom.Ion Phys., 3, 245 (1969).

19. Hipple, J.H., Fox, R.E., and Condon, E.U., Phys.Rev., 69, 347 (1946).

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

21. Barber, M., and Elliott, R.M., 12th Annual Conference on Mass Spectrometry and Applied Topics, Committee E14, ASTM, Montreal, 1964.

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

23. Shapiro, R.H., Tomer, K.B., Caprioli, R.M., and Beynon, J.H., Org.Mass Spectrom., 3, 1333 (1970).

24. Hickling, R.D., and Jennings, K.R., Org.Mass Spectrom., 3, 1499 (1970).

25. Shannon, T.W., and McLafferty, F.W., J.Am.Chem.Soc., 88, 5021 (1966).

26. Williams, D.H., Cooks, R.G., and Howe, I., J.Am.Chem.Soc., 90, 6759 (1968); Yeo, A.N.H., and Williams, D.H., J.Am.Chem.Soc., 93, 395 (1971).

27. Löhle, U., and Ottinger, Ch., J.Chem.Phys., 51, 3097 (1969); Vestal, M., and Futrell, J.H., J.Chem.Phys., 52, 978 (1970); Sternberg, L., Internat.J.Mass Spectrom.Ion Phys., 2, 303, (1969); Howe, I., and Williams, D.H., Chem.Commun., 1195 (1971).

28. Bentley, T.W., and Johnstone, R.A.W., Adv.in Phys.Org.Chem., 8, 151 (1970).

29. Rosenstock, H.M., and Krauss, M., in "Mass Spectrometry of Organic Ions", Ed., McLafferty, F.W., Academic Press, New York, 1963, p. 1.

30. Krauss, M., and Diebler, V.H., Adv.in Phys.Org.Chem., 8, 117 (1970).

31. Wachs, M.E., in "Modern Aspects of Mass Spectrometry", Ed. Reed, R.I., Plenum Press, New York (1968), p. 323.

32. Collins, J.E., Adv.in Phys.Org.Chem., 8, 231 (1970).

33. Wahrhaftig, A.L., in "Mass Spectrometry", Ed., Reed, R.I., Academic Press, New York, 1965, p. 137.

34. McLafferty, F.W., in "Topics in Mass Spectrometry", Ed., Burlingame, A.L., Wiley-Interscience, New York, 1970, p. 223.

35. Harrison, A.G., in "Topics in Mass Spectrometry", Ed., Burlingame, A.L., Wiley-Interscience, New York, 1970, p. 121.

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

37. Williams, D.H., in "Advances in Mass Spectrometry", Ed., Quayle, A., Institute of Petroleum, London, 5, 569 (1971).

38. (a) Rosenstock, H.M., Wallenstein, M.B., Wahrhaftig, A.L., and Eyring, E., Proc.Nat.Acad.Sci., 38, 667 (1952).

(b) Rosenstock, H.M., "Advances in Mass Spectrometry", Vol. 4, The Institute of Petroleum, London, 1968.

39. Wahrhaftig, A.L., "Theory of Mass Spectra" in "International Review of Science, Mass Spectrometry, Physical Chemistry Series One, Volume 5", Ed., Maccoll, A., Butterworths University Press, London (1972), p. 1, and references cited therein.

40. Johnstone, R.A.W., and Mellon, F.A., J.Chem.Soc.(B), Annual Reports, 68, 5 (1971).

41. Glasstone, S., Laidler, K.J., and Eyring, H., "The Theory of Rate Processes", McGraw-Hill, New York (1941).

42. Marcus, R.A., and Rice, O.K., J.Phys. and Colloid Chem., 55, 894 (1951).

43. Marcus, R.A., J.Chem.Phys., 20, 359 (1952).

44. Marcus, R.A., J.Chem.Phys., 43, 2658 (1965).

45. Tou, J.C., J.Phys.Chem., 75, 1903 (1971).

46. Brown, P., Org.MassSpectrom., 3, 1175 (1970).

47. Lifshitz, C., Peers, A.M., Grajower, R., and Weiss, M., J.Chem.Phys., 53, 4605 (1970).

48. Catalan, M.A., and Rico, F.R., Anales real soc. espan. fis y quin, Ser. A., 54A, 5 (1958). Through Chem.Abstracts, 52, 10711h (1958).

49. Lossing, F.P., Tickner, A.N., and Bryce, W.A., J.Chem.Phys., 19, 1254 (1951).

50. Vought, R.H., Phys.Rev., 71, 93 (1947).

51. Warren, J.W., Nature, 165, 810 (1950).

52. Honig, R.E., J.Chem.Phys., 16, 105 (1948).

53. Kiser, R.N., and Gallegos, E.J., J.Phys.Chem., 66, 947 (1962).

54. Hall, G.G., Proc.Roy.Soc.(London), 205A, 541 (1951); Trans. Faraday Soc., 49, 113 (1953).

55. Lennard-Jones, J., and Hall, G.G., Proc.Roy.Soc., 213A, 102 (1952).

56. Thynne, J.C.J., in "Dynamic Mass Spectrometry", Vol. 3, 1972, Heyden & Son Ltd., London (Ed. Price, D.), chapter 2.

57. Thynne, J.C.J., MacNeil, K.A.G., and Caldwell, K.J., in "Time of Flight Mass Spectrometry", Pergamon Press (1969), p. 117-170.

58. Fox, R.E., Hickman, W.M., Grove, D.J., and Kjedaas, T., Rev.Sci. Instr., 26, 1101 (1955); Phys.Rev., 84, 859 (1951).

59. Chupka, W.A., J.Chem.Phys., 30, 191 (1959).

60. Hertel, I., and Ottinger, Ch., Z.Naturforsch, 22a, 40 (1967).

61. Beynon, J.H., Hopkinson, J.A., and Lester, G.R., Internat.J.Mass Spectrom.Ion Phys., 2, 291 (1969).

62. McLafferty, F.N., Wacks, T., Lifshitz, C., Innorta, G., and Irving, P., J.Am.Chem.Soc., 92, 6867 (1970).

63. McMasters, B.M., Ph.D. Thesis, University of Canberbury, Christchurch, New Zealand, 1972.

64. Lifshitz, C., and Long, F.A., J.Chem.Phys., 41, 2468 (1964).

65. Chupka, W.A., J.Chem.Phys., 54, 1936 (1971).

66. Stevenson, D.P., Discuss.Faraday Soc., 10, 35 (1951).

67. Wobschall, D., Graham, J.R., and Malone, D.P., Phys.Rev., 131, 1565 (1963).

68. Baldeschwider, J.D., Science, 159, 263 (1968).

69. Gray, G.A., Advan.Chem.Phys., 19, 141 (1971).

70. Drewery, C.J., Goode, G.C., and Jennings, K.R., "Ion Cylotron Resonance Mass Spectrometry" in "International Review of Science, Mass Spectrometry, Physical Chemistry Series one, Vol. 5", Ed., Maccoll, A., Butterworths University Park Press, London (1972), chapt. 6.

71. Gross, M.L., and Wilkins, C.L., Analyt.Chem., 43, 1624 (1971).

72. Gross, M.L., Org.Mass Spectrom., 6, 827 (1972).

73. Wilson, J.M., "Alternative Methods of Ionization and Analysis" in "Mass Spectrometry", Ed., Williams, D.H., Chemical Society Specialist Periodical Reports, 2, 33 (1973).

74. McLafferty, F.W., Anal.Chem., 31, 477 (1959).

75. Bursey, M.M., Org.Mass Spectrom., 1, 31 (1968).

76. Chin, M.S., and Harrison, A.G., Org.Mass Spectrom., 2, 1073 (1969).

77. Howe, I., and Williams, D.H., J.Am.Chem.Soc., 91, 7137 (1969).

78. Bursey, M.M., and McLafferty, F.W., J.Am.Chem.Soc., 88, 529, 4484 (1966); 89, 1 (1967).

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

80. Bentley, T.W., Johnstone, R.A.W., and Payling, D.W., J.Am.Chem. Soc., 91, 3978 (1969).

81. Ward, R.S., Cooks, R.G., and Williams, D.H., J.Am.Chem.Soc., 91, 2727 (1968).

82. McLafferty, F.W., Chem.Commun., 956 (1968).

83. Yeo , A.N.H., and Williams, D.H., J.Chem.Soc.(C), 2666 (1968).

84. Howe, I., and Williams, D.H., J.Chem.Soc.(B), 1213 (1968).

85. Bursey, M.M., and Rosenthal, D., Chem.Commun., 1010 (1968).

86. Howe, I., and Williams, D.H., Org.Mass Spectrom., 2, 1141 (1969).

87. Bowie, J.H., and Nussey, B., Org.Mass Spectrom., 6, 429 (1972).

88. Christophorou, L.G., Carter, J.G., and Christodoulides, A.A., Chem.Phys.Letters, 3, 237 (1969).

89. von Ardenne, M., Z.angew.Phys., 11, 121 (1959).

90. Tümmler, R., and Steinfelder, K., Z.Chem., 7, 1 (1967).

91. Allgeier, H., Weiss, Ek,and Reichstein,W.,Helv Chim.Acta., 50, 431, 456, (1967).

92. Huneck, S., Djerassi, C., Becher, D., Barber, M., von Ardenne, M., Steinfelder, K., and Tümmler, R., Tetrahedron, 24, 2707 (1968).

93. von Ardenne, M., Steinfelder, K., and Tümmler, R., "Elektronenanlagerungs-Massenspektrographie organisher Substanzen", Springer-Verlag, Berlin/Heidelberg, 1971, and references cited therein.

94. Bowie, J.H., Org.Mass Spectrom., 5, 945 (1971).

95. Ho Ac, Bowie, J.H., and Fry, A., J.Chem.Soc.(B),530 (1971).

96. Bowie, J.H., Aust.J.Chem., 24, 989 (1971).

97. Budzikiewicz, H., Djerassi, C., and Williams, D.H., "Mass Spectrometry of Organic Compounds", Holden-Day Inc., San Francisco, 1967, p. 515, and references cited therein.

98. Budzikiewicz, H., Djerassi, C., and Williams, D.H., "Mass Spectrometry of Organic Compounds", Holden-Day Inc., San Francisco, 1967, p. 130-134.

99. (a) Shorter, J., "Correlation Analysis in Organic Chemistry. An Introduction to Linear Free-Energy Relationships", Oxford Chemistry Series, Oxford University Press (1973).

(b) Shorter, J., Chem.in Britain, 5, 269 (1969).

100. Bowie, J.H., and Hart, S., Internat.J.Mass Spectrom.Ion Phys., in press.

101. Bowie, J.H., J.Am.Chem.Soc., 95, 5795 (1973).

102. Jennings, K.R., Internat.J.Mass Spectrom.Ion Phys., 1, 227 (1968).

103. Haddon, W.F., and McLafferty, F.W., J.Am.Chem.Soc., 90, 4745 (1968).

104. McLafferty, F.W., and Schuddemage, H.D.R., J.Am.Chem.Soc., 91, 1866 (1969).

105. Anderson, R.L., and Bancroft, T.A., "Statistical Theory in Research", McGraw-Hill, New York, 1952, p. 157.

106. Adams, R., and Jenkins, R.L., Org.Synthesis, Coll.Vol.I, 394 (1944).

107. Ungnade, H.E., and Orwoll, E.F., Org.Synth., Coll.Vol.III, 131 (1955).

108. Robinson, R., and Smith, J.C., J.Chem.Soc., 392 (1926).

109. Nystrom, R.F., and Brown, W.G., J.Am.Chem.Soc., 69, 2548 (1947).

110. Barnett, E. de B., and Nixon, I.G., Chem.News,129, 190 (1924).

111. Matsukawa, T., Ban, S., and Imada, T., J.Pharm.Soc.Jap., 71, 477 (1951).

112. Tadkod, R.S., Satlur, P.B., Kulkarni, S.N., and Nargund, K.S., J.Karnatak.Univ., 2, 29 (1957).

113. Jadhav, G.V., and Rangwala, Y.I., Proc.Indian Acad.Sci., 1A, 616 (1935).

114. Forrest,J., Tucker, S., and Whalley, M., J.Chem.Soc., 303 (1951).

115. Forbes, N.F., and Sheratte, M.B., Can.J.Chem., 33, 1829 (1955).

116. Raiford, L.C., Taft, R., and Tankelma, H.P., J.Am.Chem.Soc., 46, 2051 (1924).

117. Hanggi, E., Helv, 4, 23 (1921).

118. Bernoulli, A.L., and St. Goar, A., Helv, 9, 730 (1926).

119. Neumann, G., Ber., 19, 2018 (1881).

120. Wohlleben, W.J., Ber., 42, 4369 (1909).

121. Heacock, R.A., and Hey, H.D., J.Chem.Soc., 2481 (1954).

122. Cilento, G., J.Am.Chem.Soc., 75, 3748 (1953).

123. Satchell, D.P.N., and Secemski, I.I., J.Chem.Soc.(B), 130 (1969).

124. Jadhov, G.V., and Rangwala, Y.I., J.Indian Chem.Soc., 12, 89 (1935).

125. Kirsch, J.F., Clewell, W., and Simon, A., J.Org.Chem., 33, 127 (1968).

126. Neumann, G., Ber., 19, 2979 (1886).

127. Chow, A.W., and Gisvold, O., J.Am.Pharm.Assoc.Sci.Ed., 41, 202 (1952).

128. Kazmirowski, H.G., Newland, P., Landmann, H., and Markwardt, M., Pharmazie, 22, 465 (1967).

129. Tischtschenko, A.W., and Gushow, C.D., J.Rus.Phys-Chem.Gess., 38, 516 (1906).

130. Yates, P., and Shapiro, L.B., J.Org.Chem., 23, 759 (1958).

131. Vogel, A.I., "Practical Organic Chemistry", Third Edn., Longmans, London, 1956, p. 677.

PART II - THE THERMAL REARRANGEMENT OF 2,3-DIPHENYL-2H-AZIRINE. A PRODUCT DETERMINATION STUDY

SUMMARY

2,3-Diphenyl-2H-azirine rearranges in the heated inlet system of a mass spectrometer to produce 2-phenylindole. The sealed tube thermolysis of 2,3-diphenyl-2H-azirine gives as main products, 2-phenylindole, 2,4,5-triphenylimidazole, N-Benzyl-2,4,5-triphenyl-imidazole and 2,3,4,5-tetraphenylpyrrole.

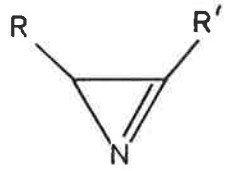
The major product of the reaction is either 2-phenylindole or 2,3,4,5-tetraphenylpyrrole. In all cases studied one is the major product while the other is present in trace amounts only. The formation of all products is rationalized in terms of known reactions.

During the investigation of possible product forming reactions, an unusual reaction was discovered. Addition of phenyldiazomethane to 2,3-diphenyl-2H-azirine followed by rearrangement of the addition species produced the unusually stable vinyl azide, 1-azido-1,2,3-triphenylprop-2-ene.

CHAPTER 1. INTRODUCTION

1.1 Preamble

Very little is known about the thermal stability of azirines (I). A few recent reports[1-5] suggest that the products of a thermal rearrangement may be explained by reaction of the azirine *via* a carbene or nitrene intermediate.



(I)

1.2 Carbenes and nitrenes

1.2 (i) Definition

Carbenes[6,7] are neutral, bivalent carbon intermediates in which the carbon atom has two covalent bonds to other groups and two non-bonding orbitals containing two electrons between them. If the two electrons are spin-paired, then the carbene is a singlet, whereas if the spin of the two electrons are parallel, then the carbene is a triplet.

A reasonable structure for a carbene is a bent sp^2 hybrid, although a triplet carbene or an excited singlet, may exist as a linear sp hybrid[8a]. Singlet carbenes are electron-deficient species, comparable to carbonium ions. On the other hand, they possess a non-bonding pair of electrons comparable with that of carbanions.

Triplet carbenes may be considered as di-radicals, although the location of the two unpaired electrons at the same carbon atom may lead to some peculiarities.

The term "carbene" was first introduced by Doering, Winstein and Woodward[9,10] and is well suited to describe this class of reactive divalent carbon compounds. The field of carbene chemistry has been reviewed[8,11] extensively. A second edition of "Carbene Chemistry" has been published[8b] and the formation of carbenes by thermal[12] or photochemical[13] extrusion reactions has been reviewed.

Nitrenes[7,11,14,15] are the nitrogen analogues of carbenes, they are neutral univalent nitrogen intermediates. They can exist in singlet and triplet states, with one of the covalent bonds of the carbene replaced by the nitrogen line pair of electrons. The nomenclature parallels that of carbenes[9,10].

1.2 (ii) Preparation of carbenes and nitrenes

The mechanisms by which carbenes are generated in many reactions have not been thoroughly investigated, consequently it is not possible

to adopt a rigid classification of the methods for carbene generation based on mechanism[11].

In principle, however, carbenes can be formed *via* a concerted elimination reaction, or *via* carbanion, radical or carbonium ion intermediates. Hence, methods of generating these intermediates may also be potential pathways for generating carbenes. Under normal conditions, carbanions, radicals and carbonium ions react *via* pathways that do not include carbenes; therefore, some special structural features must be included for carbene generation[≠]. These structural requirements can quite often be met in carbanions and radicals, while they are very rarely met in carbonium ions.

The chemistry of nitrenes has not been as fully investigated as that of carbenes. Until very recently, the only reaction in which nitrenes could be postulated as intermediates was the decomposition of azides, a route that parallels the formation of carbenes from diazoalkanes. Subsequently, it has been possible to find parallel reactions thought to involve nitrenes for most of the other reactions used to generate carbenes. Generally, these reactions have been less thoroughly explored and in many cases alternative mechanisms, not involving nitrenes, can be written[e.g.16-21]. Conversely, there are a few reactions thought to involve nitrenes that have no direct parallels in carbene chemistry, e.g. the oxidation of amines[22].

≠ For a review of the more common methods for carbene and nitrene generation see "Carbenes, Nitrenes and Arynes" by Gilchrist, T.L., and Rees, C.W., Nelson, Pitman Press, Bath 1969.

1.2 (iii) Carbenoids and Nitrenoids

gem-Dihalogeno compounds can be dehalogenated by metals or by metal alkyls and the products obtained are often typical of those from carbenes. Whenever the mechanism of one of these reactions has been investigated carefully[e.g. 11], the evidence is nearly always against free carbenes as intermediates[11]. The intermediates in these reactions have been termed "Carbenoid".

A similar series of "nitrenoid" reactions also exist.

1.2 (iv) Carbene or Nitrene Intermediates

The evidence that carbenes or nitrenes are intermediates in a particular reaction must be examined very critically. Only in a very few cases has a detailed kinetic analysis been carried out to definitely establish the presence of a carbene or nitrene intermediate. Usually the presence of such an intermediate is postulated by analogy with other well known reactions, or because two independent sources of the intermediate lead to the same product. Isolation of the expected adduct is not, by itself, sufficient evidence for the existence of an intermediate carbene or nitrene in a reaction.

1.2 (v) Spin states

The chemical behaviour of carbenes is determined by the relative energies of the singlet and triplet spin states. The most incisive information concerning the chemical characteristics of singlet and triplet carbenes comes from the study of addition reactions involving

carbon-carbon double bonds. Two approaches have been suggested by Doering[23a] and Skell[23b,24]. The first involves a study of relative reactivities of various olefinic substrates towards carbenes using the competitive method. Competitive experiments in the liquid phase[24] have shown that most carbenes do not select among olefinic substrates in the same way that a typical free radical does. The second criterion involved the stereo specificity of addition[23a,b]. If a carbene is in a single ground state it could add to a double bond in a single concerted step and hence retain the stereochemistry of the olefin. However, for a triplet carbene the cycloaddition should go through a triplet di-radical intermediate and the stereochemistry of the original olefin may not be retained in the product. This model correlates data in the carbene field rather well[25], even though some theoretical details of the interpretation might still have to be revised[26,27].

The same arguments are equally valid for addition reactions involving nitrenes, hence the Skell-Doering hypothesis can be applied to nitrenes in the same manner that it is applied to carbenes.

Unfortunately, there is no simple and obvious way to predict *a priori* the ground states of carbenes and nitrenes. There have been two approaches towards the solution of this problem: (1) direct detection of the ground state or excited state by spectroscopic means, and (2) by molecular orbital calculations. The results of experimental observations and of MO calculations indicate that many carbenes

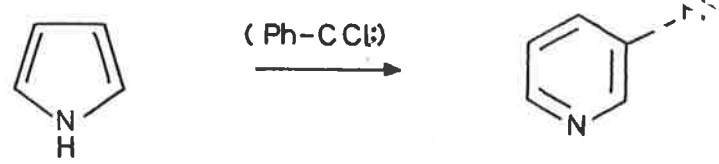
have a non-linear triplet ground state[28]. Even though the ground state of many carbenes has been defined, the state through which the reaction proceeds in most cases is still uncertain. For example, phenylcarbene has been shown by electron spin resonance spectroscopy to possess a triplet ground state[29,30], while separately it has been reported[31,33] that addition of phenylcarbene to *cis* and *trans*-2-butene is almost, but not entirely, stereospecific. Although the observation of a small degree of non-stereospecific addition to the 2-butene can be interpreted in terms of a corresponding proportion of the reaction proceeding through a triplet state and the remainder *via* the singlet state, the possibility of larger fractions, or even the entire reaction, proceeding through triplet intermediates cannot be excluded[32].

1.2 (vi) Insertion reactions

1.2 (vi) (a) Carbene insertion reactions

The insertion of carbenes into aromatic systems is well documented[31-33]. Gutsche[31], in an excellent paper on comparative *inter*molecular and *intra*molecular reactivities of carbenes to various types of bonds, showed that phenylcarbene exhibits approximately equal reactivities towards the C-C bonds of a benzene ring and to aliphatic CH_2-CH_2 bonds. In addition, phenylcarbene is approximately six times more reactive towards aliphatic -CH_2 bonds than towards aliphatic -CH_3 bonds, and is very unreactive towards aromatic C-H bonds.

Halo carbenes are generally less reactive than their non-halogenated analogues[33]. Even so, the chlorocarbenoid generated from benzylidine chloride by α-elimination will insert into the C_2-C_3 double bond of pyrrole (1-1) to produce 3-phenylpyridine (1-2)[34]a. Many other examples of carbene insertions into aromatic systems have been reported.

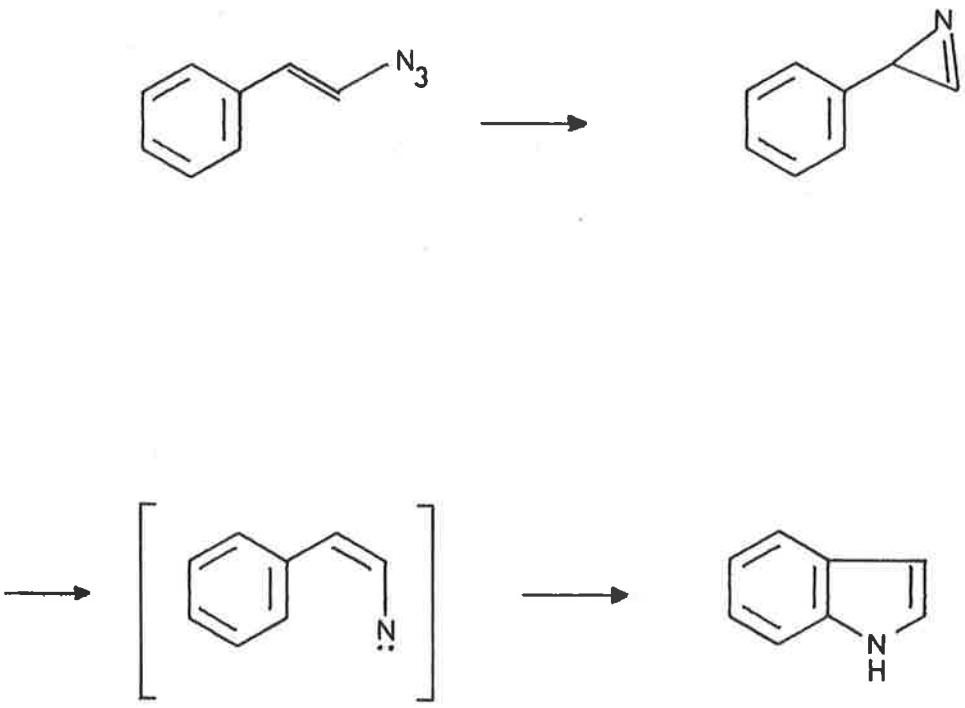


(1-1) (1-2)

1.2 (vi) (b) Nitrene insertion reactions

A common reaction of nitrenes is their insertion into an aromatic carbon-hydrogen bond[1,6,7,38-43] (c.f. carbenes [1.2 (vi) (a)].

For example, β-styrylazide produces indole[7] when pyrolysed in boiling *n*-hexadecane. The reaction is shown to proceed *via* 2-phenyl-2H-azirine; this intermediate is thought to rearrange to β-styrylnitrene followed by an *intra*molecular insertion of the nitrene into an *ortho* carbon-hydrogen bond of the phenyl ring.



The conversion of *o*-isocyanatobiphenyl to carbazole[40], the oxidation of *o*-aminodiphenylamine to phenazine[41,42], the thermal conversion of 2-methyl-3-phenyl-3H-azirine to 2-methylindole[7] and 3-methyl-2-phenyl-2-phthalimido-2H-azirine to 2-methy-3-phthalimido-indole[1,6] are all examples of this process.

Intra molecular insertion of a nitrene (or nitrene source) into an aromatic carbon-hydrogen bond occurs with much higher yields than insertion into a saturated carbon-hydrogen bond[44]. This has become the basis of a general synthesis of carbazoles from ortho substituted biphenyls[44].

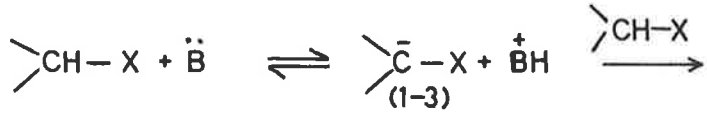
The most common biphenyl precursor for these carbazoles is an azide, however almost every other source of arylnitrenes have been successfully employed as alternative precursors.

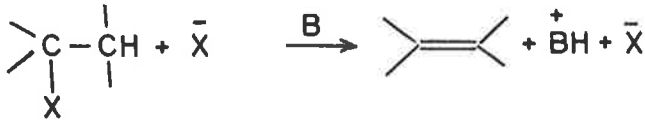
1.2 (vi) (c) Nitrene condensation

The *inter* molecular condensation of a nitrene with itself *via* a 1,3-dipolar addition reaction is an alternative reaction pathway. The conversion of α-styrylazide to 2,5-diphenylpyrrole[45,46] is an example of this mode of reaction.

1.2 (vi) (d) Dimer formation

Carbene and nitrene insertion reactions are frequently accompanied by the formation of apparent "dimers" of the hypothetical carbene or nitrene, e.g. stilbene in the case of phenylcarbene. The synthesis of such olefins from the appropriate halide and base has long been known. Early publications reported the formation of dinitrostilbenes from *o*- and *p*-nitrobenzylchloride[47,48]. The mechanism for this reaction has been a matter of considerable controversy. Nef[49] was the first to advocate a carbene intermediate and this was supported by other authors[50-52]. Later, in 1926, Bergmann[51] suggested that dimerization of the hypothetical carbene to form olefins did not take place. An alternate mechanism was advanced by Hahn[53] and Kleucker[54], this involved alkylation of the intermediate carbanion (1-3) by excess starting halide, followed by dehydrohalogenation of the resulting halide.



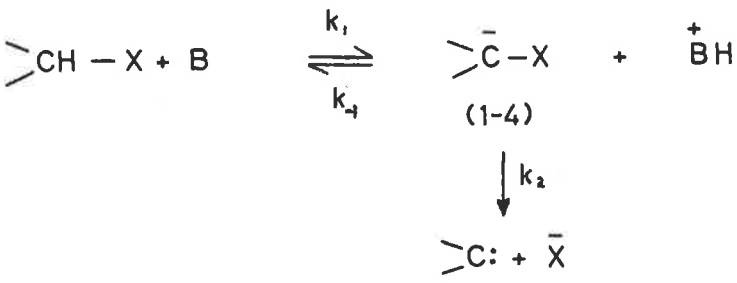


A recent kinetic study of the 9-bromofluorene-base system[55] provides additional support for this mechanism.

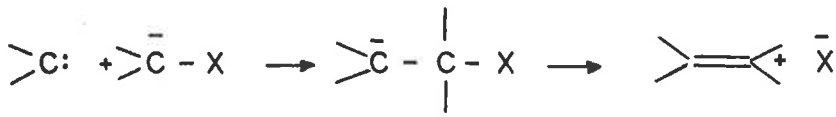
Recently, a modified carbene mechanism has been suggested[56] to replace that of Hahn[53] and Kleucker[54]. A reaction between the carbanion produced (1-4) and the carbene generated from it by elimination of halide ion[≠] could form the observed "dimeric" olefin.

≠ The evidence supporting this mechanism is rather tenuous and consequently it should be regarded with suspicion.

(a)



(b)



For further discussion of dimer formation see section 1.3 (ii) (photochemical dimerization in azirines).

1.2 (vii) Carbene-Carbene Rearrangements

Certin carbenes have been shown to undergo carbene-carbene rearrangements in the gas phase above 250°, i.e. migration of a group to the reaction site with generation of a new carbene prior to reaction[57]. As in the case of the more conventional rearrangements, this notation carries with it no mechanistic implications. For example, phenylcarbene undergoes facile rearrangement to cyclohepta-trienylidene in the gas phase[57].

Several multiple carbene-carbene reactions are also reported[57]. The conditions employed (40 mm and N_2 carrier gas in a flow through cell) are designed to facilitate such *intra* molecular reactions.

1.3 Reactions of Azirines

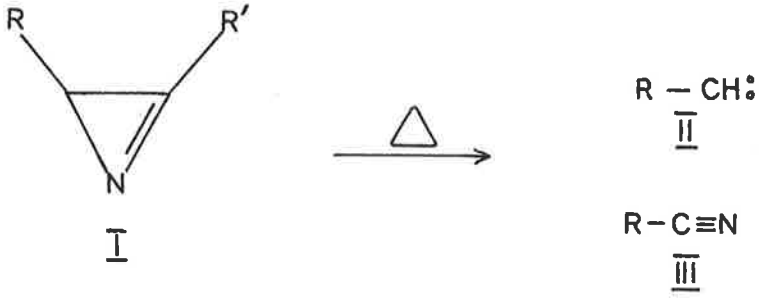
Much of the work presented in this section was published[1,6,60,65] either during the course of or after the completion of the work reported in the discussion. It is included here rather than later because the concepts developed are parallel to those outlined in the discussion and these concepts are vital to the justification of the product distribution observed.

1.3 (i) Thermal reactions of Azirines

Several different types of thermal rearrangements have been reported for azirines.

1.3 (i) (a) Rearrangement to carbenes

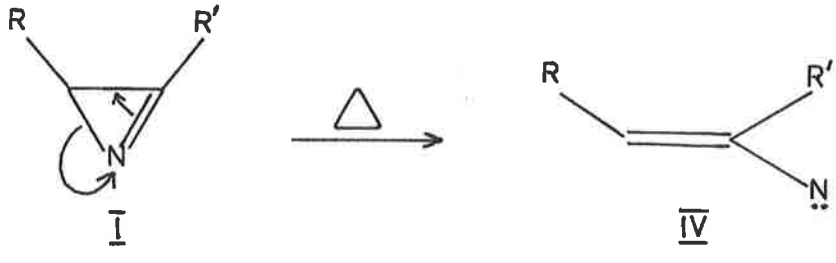
Under suitable reaction conditions an azirine (I) can thermally rearrange to form a carbene (II) and a nitrile (III)[1,6].



I II III

1.3 (i) (b) Rearrangement to nitrenes

Under different conditions an azirine can rearrange to form an isomeric nitrene[2,7,15,38-42,58,59].



I IV

For example, the conversion of 2-phenyl-2H-azirine into indole[7] is thought to proceed *via* the nitrene intermediate [for other examples see section 1.2 (vi) (b)].

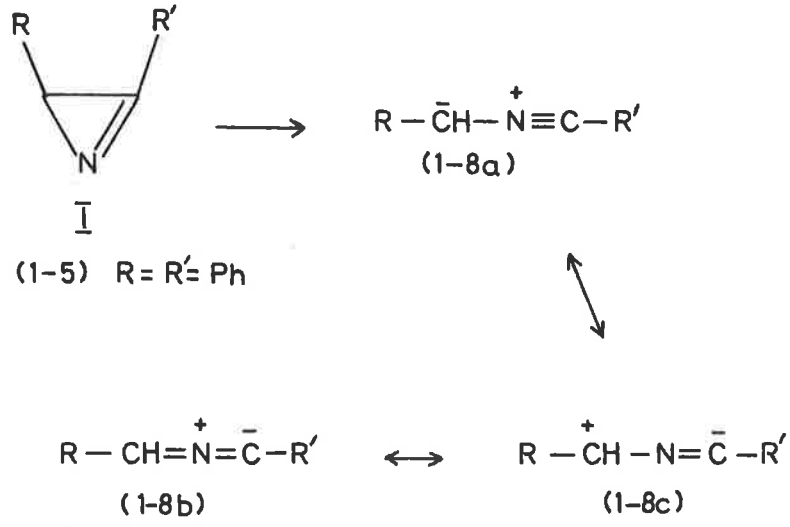
1.3 (i) (c) Rearrangement to imidazoles

Pyrolysis of 2,3-diphenyl-2H-azirine (1-5) in refluxing xylene has been reported[60a] to produce 2,4,5-triphenylimidazole (1-6)[c.f.61] among its reaction products. No attempt has been made to rationalize the formation of this product[60a].

1.3 (ii) Photochemical Reactions of azirines

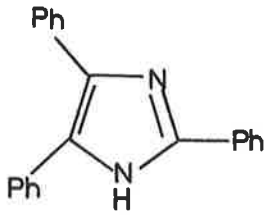
1.3 (ii) (a) Photodimerization[46,60,62,63]

The photochemical reactions of azirines have been studied by several groups. When 2,3-diphenyl-2H-azirine (1-5) is irradiated in a benzene solution, the observed products are either 2,4,5-triphenylimidazole (1-6)[60a,b,c] or 2,3,5,6-tetraphenylpyrazine (1-7)[60c,62]. The pyrazine (1-7)[62] was explained as the product of a simple nitrene dimerization reaction [see section 1.2 (iv) (d)], a reaction superficially analogous to the conversion of 3-phenyl-2H-azirine to 2,5-diphenyl-3,6-dihydropyrazine[63,64]. This mechanism has since been shown to be incorrect[65] (see below). When the reaction is carried out in degassed cyclohexane the reaction follows a more complex pathway. Under the influence of ultraviolet light, the azirine (1-5) first rearranges to the appropriate nitrile ylide (1-8a → c)[65a-c]. This intermediate nitrile ylide can in principle react in several different ways. In the presence of a dipolarophile, a 1,3-dipolar addition can occur and the cycloadducts Δ'pyrrolines are formed[c.f.60a]. If the irradiation is carried out in the presence of an olefin of low dipolarophilic activity, no photoadduct is observed, but tetraphenyl-

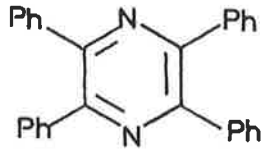


pyrazine (1-7) was isolated[60c,65b]. The reaction was shown[65b] to proceed by an addition of the nitrile ylide (1-8a → c) to the ground state azirine (1-5). Compounds (1-9a), (1-9b) and (1-10) were isolated and proved to be intermediates.

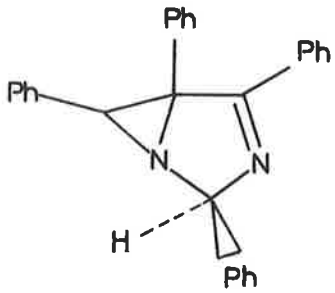
The two diastereoisomeric 1,3-diazabicyclo[3,1.0]hex-3-enes (1-9a & b) are plausibly formed by combination of the nitrile ylide (1-8a → c) with the ground state azirine (1-5).



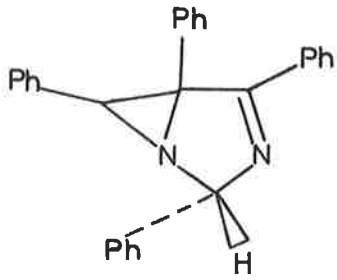
(1-6)



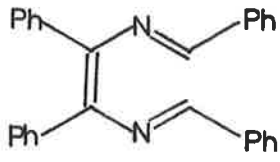
(1-7)



(1-9a)



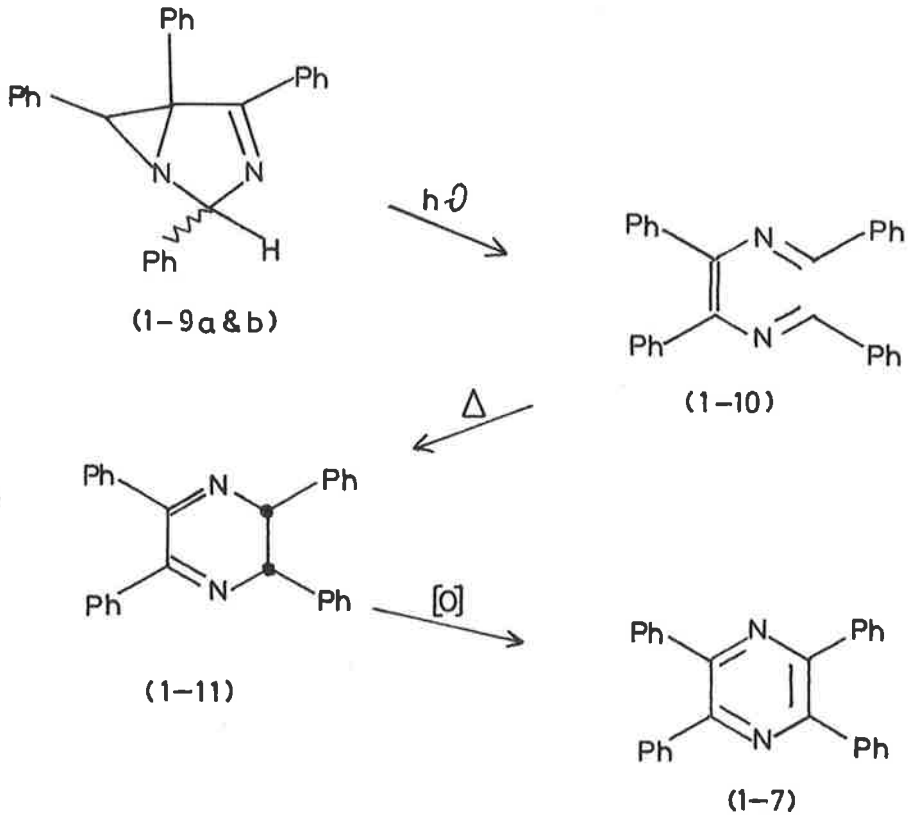
(1-9b)



(1-10)

The intermediates (1-9a & b) are converted to tetraphenylpyrazine (1-7) *via* the *cis*-2,3-dihydro-2,3,5,6-tetraphenylpyrazine (1-11) [see scheme 1].

Scheme 1



The mechanism is supported by a study of the variation of quantum yield of adduct formation as a function of the concentration of the added dipolarophile[65].

This mechanism readily accommodates the formation of triphenylimidazole (1-6) (*via* expulsion of phenylcarbene) and tetraphenylpyrazine (1-7) from the irradiation of 2,3-diphenyl-2H-azirine (1-5) as reported by Schmid[60] and Hassner[62].

Huisgen[66] was the first to suggest that a nitrile ylide was an intermediate during the participation of azirines in 1,3-dipolar addition reactions, since then Schmid *et al*[60] and Padwa *et al*[65] have also invoked the intermediacy of a nitrile ylide to rationalize photochemical 1,3-dipolar cycloaddition reactions of azirines.

1.3 (ii) (b) Photochemical rearrangements[5,67,68]

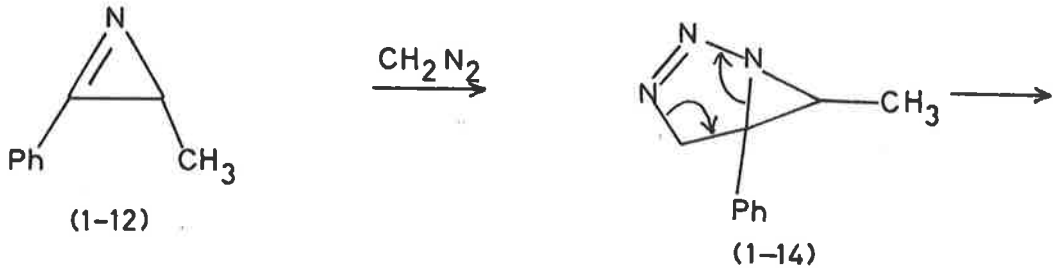
Azirines have been shown to be isolatable intermediates in the photochemical conversion of isoxazoles to oxazoles[5,66,67]. By varying the wavelength of irradiation the isolated intermediate azirine can be forced to revert to starting isoxazole or be converted into the product oxazole[67,68].

1.3 (iii) Carbene and carbenoid reactions with azirines

Experiments between azirines and carbene-like reagents have been somewhat limited.

(a) When diazomethane is allowed to react with 2-methyl-3-

phenyl-2H-azirine (1-12) a mixture of allyl azides (1-13a & b) are isolated[69,70]. The reaction presumably proceeds *via* a 1,3-dipolar addition reaction to give a species such as (1-14), which could then rearrange to the observed products.

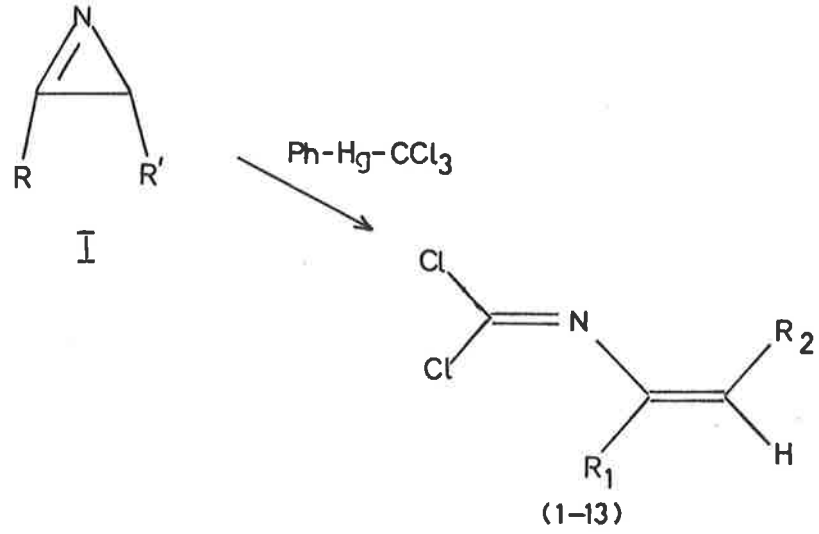


(1-12) (1-14)

(1-13a) (1-13b)

(b) If an azirine (I) is reacted in the presence of phenyl (trichloromethyl mercury)[71] an unusual reaction occurs. None of the expected azabicyclobutane formed by cycloaddition of dichlorocarbene to the C=N was found. Instead a corresponding enamine (1-13) was

isolated.



I

(1–13)

No evidence was presented for the mechanism of the initial addition of the dichlorocarbene to the azirine, but, in view of other known reactions, it seems likely to proceed *via* a carbenoid type of intermediate rather than a free carbene[72].

(c) Addition of dimethysulphonium methylide to 2-phenylazirine represents the first successful synthesis of an azabicyclobutane[73].

1.4 Summary

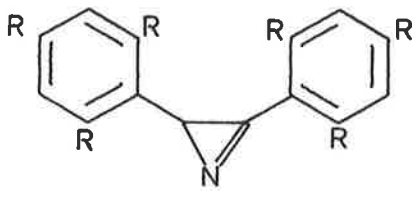
A review of the information presented indicates that azirines are capable of undertaking a variety of rearrangement reactions. This fact will be employed to explain the variety of products obtained from a thermal treatment of 2,3-diphenyl-2H-azirine in a sealed tube.

CHAPTER 2. RESULTS AND DISCUSSION

2.1 Introduction

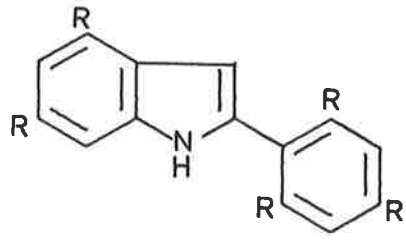
During a recent study[74] of the formation of deuterated fluorenyl cation at *m/e* 171 ($C_{13}H_3D_9^+$) in the mass spectrum of 2,3-diphenyl-(2,4,6-d_3-phenyl)-2H-azirine (2-1) a thermal rearrangement was observed in the heated inlet system of the mass spectrometer. The product was found to have lost a deuterium atom in the rearrangement process. Further investigation revealed that 2,3-diphenyl-2H-azirine (2-2) was rearranged to 2-phenylindole (2-4) in a 60% yield when passed through an apiezon vapour phase chromatography column maintained at 220°.

≠



(2-1) R = D

(2-2) R = H



(2-3) R = D

(2-4) R = H

≠ All figures included in the discussion are repeated in a fold-out section at the end of the chapter.

The indole products were formed by a rearrangement of the azirine to its valence isomeric nitrene[7,15,38-42,58,59] (see section 1.3 (i) (b)), followed by an insertion of the nitrene into one of the ortho C-H bonds in the β phenyl ring[74]. This was followed by exchange of the acidic deuterium in the case of the deuterated azirine (2-1) to produce the deuterated indole (2-3)[c.f. 1,6,7].

2.2 Sealed tube thermolyses

When a sealed tube containing 2,3-diphenyl-2H-azirine (2-2) is heated for 3 hrs in an oven pre-equilibrated to 250° the reaction follows a much more complex pathway. The products obtained from such a reaction were purified by column chromatography over silica acid followed by recyrstallization from ethanol. All products were known compounds (see table 1), except for tetraphenylpyrimidine (2-10). The major product obtained was either 2-phenylindole (2-4) or tetraphenylpyrrole (2-5). In all cases examined (see table 1) one of these was the major product while the other was present in trace amounts only.

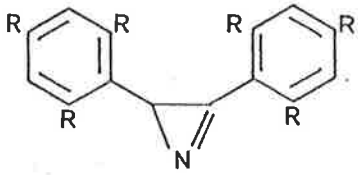
TABLE 1≠

Product	Run 1	Run 2	Run 3	Run 4
2-phenylindole (2-4)	0.8	44.5	trace	trace
2,4,5-triphenylimidazole (2-6)	46.2	14.8	31.5	28.8
N-Benzyl-2,4,5-triphenylimidazole (2-7)	trace	11.9	18.4	24.8
2,3,4,5-tetraphenylpyrrole (2-5)	35.5	trace	27.4	16.5
2,3,4,5,6-pentaphenylpyridine (2-8)	2.6	-	0.8	trace
2,3,5,6-tetraphenylpyrazine (2-9)	5.9	8.0	9.5	14.7
2,4,5,6-tetraphenylpyrimidine (2-10)	4.1	-	5.4	-
Benzamide (2-11)	-	5.9	2.3	10.0
Stilbene (2-12)	-	-	-	5.3
Benzonitrile (2-15)	trace	-	trace	-
Unidentified	4.8	14.8	4.7	-

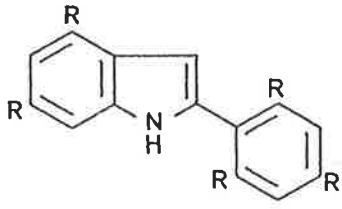
The structure of each product was confirmed by comparison of m pt, mm pt, mass and infrared spectra with authentic samples. Compounds (2-5) to (2-9), (2-11) and (2-12) have been reported in the literature (see experimental section). The pyrimidine (2-10) was synthesised by condensation of benzamidine (2-13) with 1,2-

---

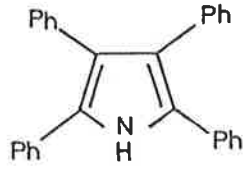
≠ The results recorded are expressed as a percentage of the total product recovered for that run. The average total product recovered was 84%.



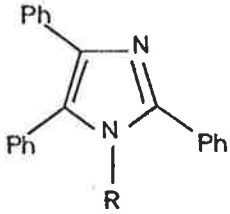
(2-1) R=D
(2-2) R=H



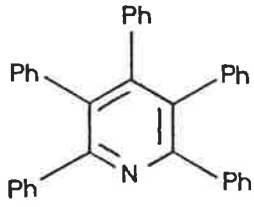
(2-3) R=D
(2-4) R=H



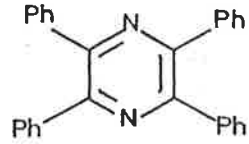
(2-5)



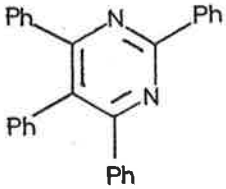
(2-6) R=H
(2-7) R=$-CH_2$-Ph



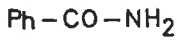
(2-8)



(2-9)

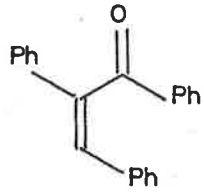


(2-10)

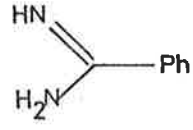


(2-11)

(2-12)

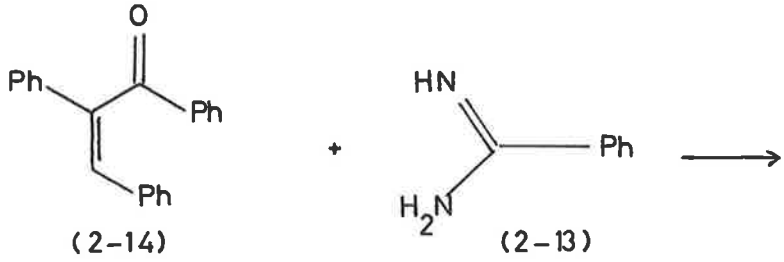


(2-14)

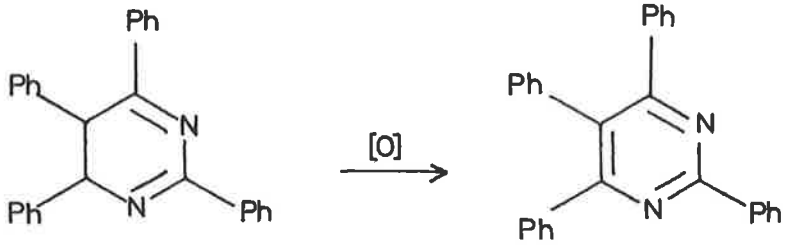


(2-13)

diphenylacrylophenone (2-14) followed by aerial oxidation≠.



(2-14) (2-13)



(2-10)

When the thermolysis was carried out at 470° for 3 hrs, the major product was 2-phenylindole (2-4)-(72%). Smaller amounts of triphenylimidazole (2-6)-(8.8%) and tetraphenylpyrazine (2-9)-(2.0%) were also found in the reaction mixture, while at 100° no detectable reaction occurred and unreacted azirine (2-2)-(92%) was recovered.

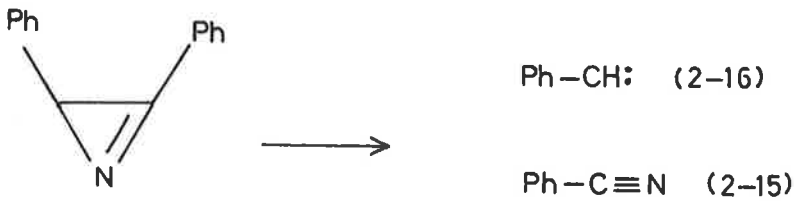
≠ Subsequent to this preparation a very similar sequence was published by Padwa *et al*[65a].

2.3 Product formation

Under the thermal conditions employed, an azirine could rearrange in several different ways.

2.3 (i) Rearrangement to carbenes

On heating, an azirine may rearrange to form a carbene and a nitrile[1,6] (see section 1.3 (i) (a)). If the conditions are appropriate then 2,3-diphenyl-2H-azirine (2-2) should rearrange to produce benzonitrile (2-15) and phenylcarbene (2-16).



(2–2)

Benzonitrile (2-15) was observed only in trace amounts in the pyrolyses reactions. Therefore, if this mechanism operates any benzonitrile formed must be completely utilized as an intermediate in the formation of other reaction products. A thermolysis conducted at 250° in the presence of 2,4,6-d_3-benzonitrile revealed no incorporation of deuterium into any of the products, while un-

reacted 2,4,6-d_3-benzonitrile was recovered. Thus benzonitrile does not appear to be an intermediate in the formation of the reaction products and therefore any dissociation of the azirine (2-2) into benzonitrile (2-15) and phenylcarbene (2-16) must be minimal.

2.3 (ii) Rearrangement to nitrenes

An alternative rearrangement is the valence isomerization of the azirine to a vinyl nitrene[7,15,38-42,58,59] (see section 1.3 (i) (b)).

(2-2) (2-17)

Such an isomerization of 2,3-diphenyl-2H-azirine (2-2) would produce the vinyl nitrene (2-17).

An *intra* molecular insertion of this nitrene into an *ortho* carbon-hydrogen bond of the β-phenyl ring would generate 2-phenyl-indole (2-4)[c.f.39b,43]. This mechanism is similar to the one advanced for the production of indole from 2-phenyl-2H-azirine[7].

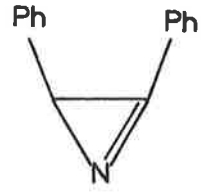
There are many such recorded examples of nitrene insertion into aromatic C-H bonds[7,15,38-42,44,58,59].

If, on the other hand, the nitrene (2-17) condensed by an *inter* molecular 1,3-dipolar addition to itself, the other major product, tetraphenylpyrrole (2-5) would result[c.f.62-64]. This mechanism is similar to the one proposed for the conversion of α-styrylazide into 2,5-diphenylpyrrole[45,46].

Hence, it is possible to rationalize the formation of both 2-phenylindole (2-4) and tetraphenylpyrrole (2-5) from the same nitrene intermediate (2-17). The former being produced by an *intra* molecular nitrene reaction, while the latter is produced *via* an *inter* molecular nitrene reaction.

2.3 (iii) Dimer products

A third type of rearrangement is possible. Several workers[62-65] have reported the isolation of a "dimeric" species from among the products of a nitrene forming reaction. Padwa and co-workers[65] have shown that under the influence of ultra-violet light this dimeric species is formed *via* the addition of a rearranged nitrile ylide (e.g. 2-18a → c) to a ground state azirine molecule to form a 1,3-diazabicyclo-[3,1,0]-hex-3-ene intermediate (e.g. 2-19a & b) followed by a rearrangement to the observed dimer (see section 1.2 (iv) (b)and 1.3 (ii) (a)) rather than by a simple dimerization of the intermediate vinyl nitrene[65].



(2-2)

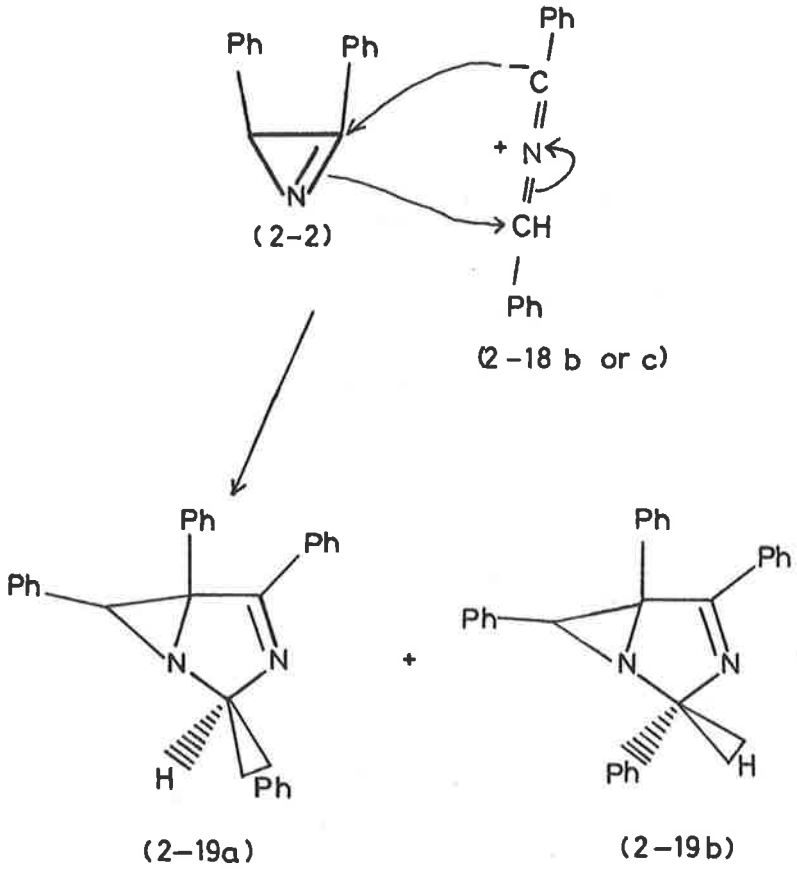
$Ph - \bar{C}H - \overset{+}{N} \equiv C - Ph$

(2-18a)

$Ph - CH = \overset{+}{N} = \bar{C} - Ph$ $\longleftrightarrow$ $Ph - \overset{+}{C}H - N = \bar{C} - Ph$

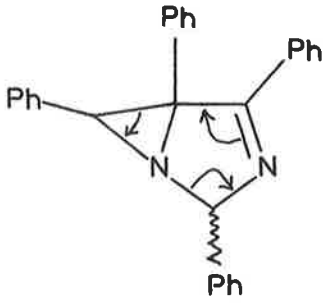
(2-18b) (2-18c)

Therefore, the azirine (2-2) could also thermally rearrange through an irreversible opening of the azirine ring to form an analogous nitrile ylide (2-18a → c) which could then be trapped by a suitable dipolarophile[66]. Hence, a thermally initiated 1,3-dipolar addition of the nitrile ylide (2-18a → c) to the ground state azirine (2-2) could produce the same diastereoisomeric 1,3-diazabicyclo-[3,1,0]-hex-3-ene intermediate [2-19a and b]. Although the diastereoisomers (2-19a & b) were not isolated, their intermediacy plausibly rationalizes the formation of several products.

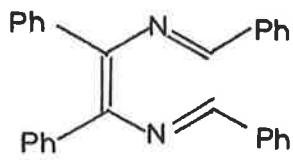


(2-19a) (2-19b)

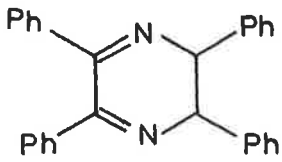
The application of heat should result in a ready rearrangement of these intermediates (2-19a & b) to the so called "dimeric species", tetraphenylpyrazine (2-9). This transformation would proceed *via* ring opening to the enediimine (2-20) followed by thermal cyclization to a dihydropyrazine (2-21) in a reaction similar to those observed for the related 1,3-diazabicyclohexanes[75-77].



(2-19 a & b)

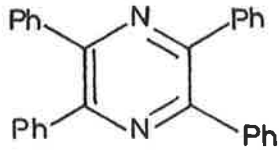


(2-20)



(2-21)

[O]

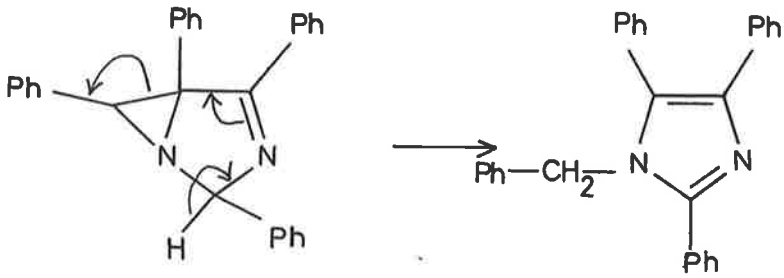


(2-9)

Oxidation of the dihydropyrazine (2-21) during the work-up procedure[c.f.65] leads to formation of the tetraphenylpyrazine (2-9).

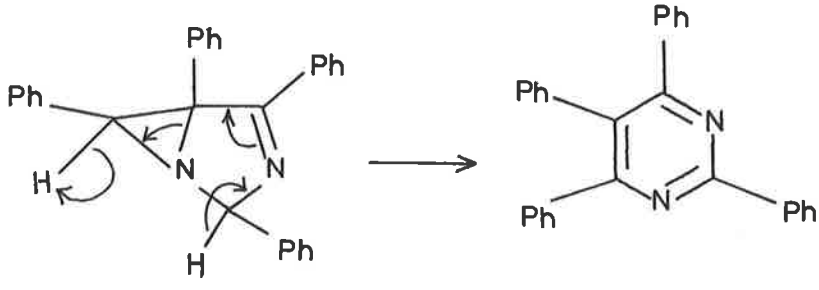
Since the intermediates (2-19) could not be isolated the possibility that the pyrazine (2-9) is formed by a thermal dimerization of the intermediate nitrene (2-17) cannot be exluded, but in light of other known reactions such a thermal dimerization is considered unlikely (see section 1.2 (vi) (d)).

It is possible to rearrange the isomeric intermediates (2-19a & b) in several different ways. If the intermediates (2-19a & b) could transfer a proton, then any subsequent aromatization could occur in three ways: (a) breakage of the C_5-C_6 bond accompanied by transfer of the C_2 proton to C_6 would produce N-benzyl-2,4,5-triphenylimidazole (2-7). It should be noted here that concerted suprafacial [1,5] hydrogen shifts are symmetry allowed under thermal conditions, and must occur with retention of the shifting centre[78]. Similar specific thermal [1,5] shifts have been observed in a number of cases[79].



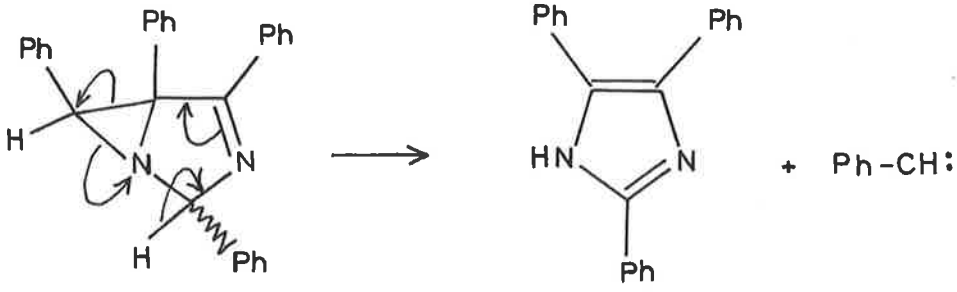
(2-19) (2-7)

(b) Breakage of the C_5-N_1 bond with concomitant oxidation would generate tetraphenylpyrimidine (2-10)[c.f.65a].



(2-19) (2-10)

(c) The final rearrangement pathway proceeds *via* elimination of phenyl carbene (2-16) to produce triphenylimidazole (2-6).



(2-19a & b) (2-6) (2-16)

This route is analogous to the one suggested by Schmid *et al*[60c] for the formation of triphenylimidazole (2-6) during a photolytic irradiation of 2,3-diphenyl-2H-azirine (2-2) conducted in benzene (see section 1.3 (ii) (a)). Schmid *et al*[60] also report the isolation of the imidazole (2-6) from a thermolytic irradiation of 2,3-diphenyl-2H-azirine (2-2),in this case no attempt was made to rationalize the product formation.

Structures such as (2-18a → c) or (2-19a & b) must be regarded as hypothetical since the reaction conditions employed are much too vigorous for their survival and isolation. It should be noted however that many suitable analogies do exist, and that many of

the observed reaction products can be rationalized satisfactorily *via* such structures.

2.4 Apparent anomalies

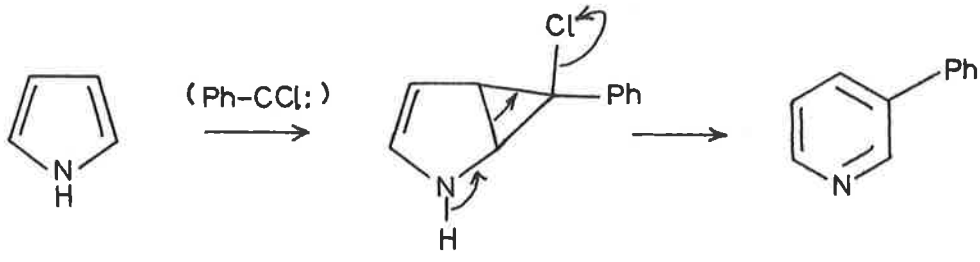
At first sight the results shown in table 1 are anomalous because successive reactions conducted under essentially the same conditions provide quite different results. This complexity arises from three major causes. Firstly, any species produced under thermoletic conditions should be highly reactive and hence the differences in the energies of activation towards a large number of compounds should be small. Secondly, many compounds formed by thermal processes are "hot", that is contain excess energy. One result of this excess energy is that in any particular system, many possible reactions occur with closely similar probabilities. Finally, because of the high exothermic nature of the reaction, many compounds formed initially contain enough energy to undergo further reaction and will do so unless stabilized by collision. In the gas phase this may lead to the yield of various products being pressure dependent in a manner found in very few other systems[c.f.80]. These arguments are analogous to those employed by Frey to explain the apparently anomalous reactions of methylene[80].

2.5 Carbene insertion reactions

An unusual feature of table 1 is the formation of 2,3,4,5,6-pentaphenylpyridine (2-8). The pyridine (2-8) was only observed among the reaction products when tetraphenylpyrrole (2-5) was a major product, thus suggesting a connection between these two products. The obvious method for the generation of pyridines from pyrroles is by insertion of a carbene or carbenoid species into a double bond of the pyrrole followed by a rearrangement of the intermediate 2-azabicyclo-[3,1,0]-hex-3-ene[36d]. There are many reported examples of this type of reaction[31-36].

2.5 (i) Phenylchlorocarbene

Alexander, Herrick and Roder[34a] demonstrated that a carbenoid species produced by α-elimination from benzylidine chloride could insert into the C_2-C_3 double bond of pyrrole (2-22) to form the 2-azabicyclohex-3-ene (2-23) which aromatizes by loss of hydrogen chloride to generate 3-phenylpyridine (2-24).

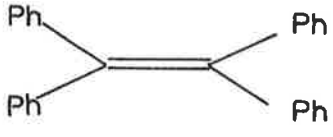


(2-22) (2-23) (2-24)

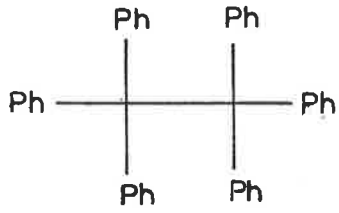
The intermediate (2-23) is similar in structure to intermediates (2-19 a & b) and the mechanism for the rearrangement of (2-23) to the pyridine (2-24) is analogous to that proposed for rearrangement of (2-19a & b) to form the pyrimidine (2-10).

When the Riemer-Tiemann Reaction was applied to tetraphenylpyrrole (2-5) using the carbenoid generated by α-elimination from benzylidine chloride under the conditions described by Alexander[34a], pentaphenylpyridine (2-8) was isolated in a 60% yield. Because this reaction employs a strong base to generate the carbenoid species the results are not directly comparable to the thermolysis results. However, the results do demonstrate that a carbene or carbene source can insert into tetraphenylpyrrole (2-5) to produce pentaphenylpyridine (2-8).

Two other products were isolated in this reaction. They are tetraphenylethylene (2-25) and hexaphenylethane (2-26).



(2-25)



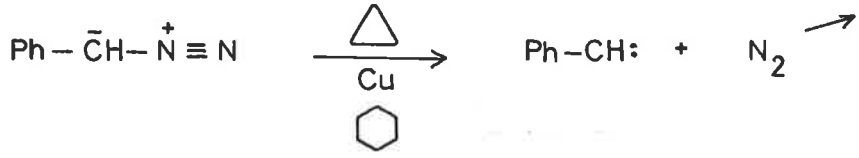
(2-26)

These products are artefacts produced by displacement at an intermediate organometallic site rather than by addition of carbenes[17-19].

2.5 (ii) Phenylcarbene

Reaction conditions more closely resembling the thermolysis conditions were sought[c.f. 81-83].

Using a modification of the Simmons-Smith procedure phenylcarbene (2-16) was generated by heating phenyldiazomethane (2-27) under reflux in a solution of cyclohexane containing a suspension of copper powder. The reaction was maintained in an atmosphere of nitrogen≠.



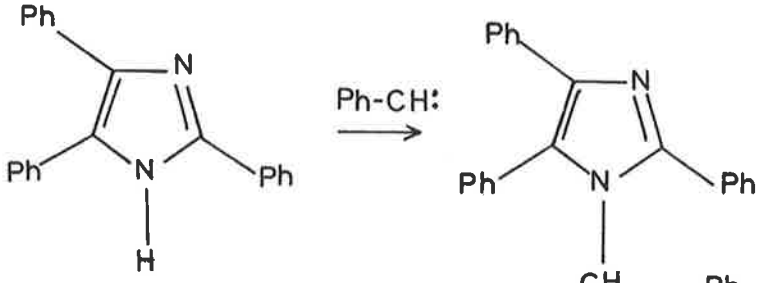
(2-27) (2-16)

≠ Copper-catalysed reactions of this type are thought[11,31-33] to involve complexed singlet carbenes. It is not clear whether the reactive species in the pyrolysis is singlet or triplet carbene, but it is known from e.s.r. studies[29,30] that phenyl carbene has a triplet ground state.

When the carbene (2-16) was generated in the presence of tetraphenylpyrrole (2-5) pentaphenylpyridine (2-8) (3%) was isolated from the reaction mixture. Stilbene (5%) and unreacted starting material (90%) were the other products isolated. These conditions more closely resemble the thermolysis conditions and indicate that insertion of a carbene or carbenoid species into a carbon-carbon double bond of tetraphenylpyrrole (2-5) is a feasible route to the formation of pentaphenylpyridine (2-8).

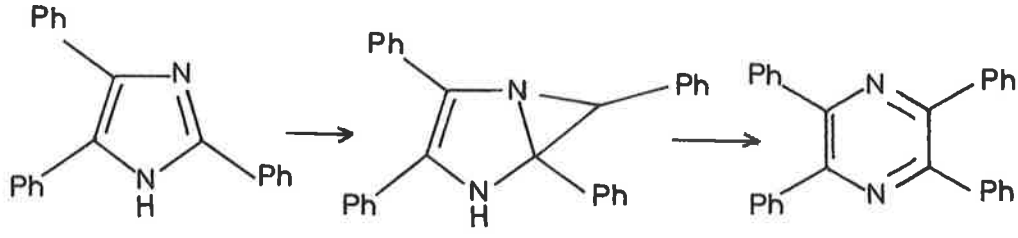
When the carbene (2-16) was generated in the presence of triphenylimidazole (2-6) three major products were obtained. These were N-benzyl-2,4,5-triphenylimidazole (2-7), tetraphenylpyrazine (2-9) and tetraphenylpyrimidine (2-10). Each of these products can be rationalized in terms of a carbene reaction with triphenylimidazole (2-6).

Insertion of the carbene into the nitrogen-hydrogen bond (see section 1.2 (vi) (a)) would produce N-benzyl-2,4,5-triphenylimidazole (2-7).



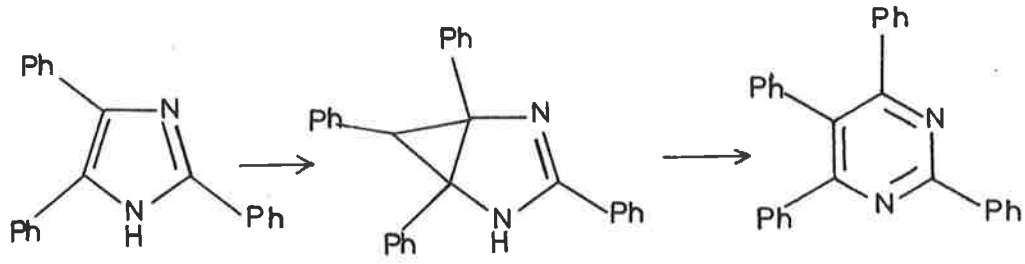
(2-6) (2-7)

Addition of the carbene (2-16) to a ring double bond (see section 1.2 (vi) (a)) can occur in two ways to produce two different diazabicyclo intermediates. Addition to the C_2-N_3 double bond would form an intermediate diazabicyclohex-3-ene (2-28), which would then aromatize to produce tetraphenylpyrazine (2-9).



(2-6) (2-28) (2-9)

However, if the addition occurs to the C_4-C_5 double bond a different diazabicyclohex-3-ene intermediate (2-29) is formed.



(2-6) (2-29) (2-10)

Rearrangement and aromatization of (2-29) would produce tetraphenylpyrimidine (2-10).

It is interesting to note the similarity between the intermediates (2-28, 2-29), the intermediate (2-19a & b) and the proposed mechanisms for their respective rearrangement.

When an attempt was made to generate the carbene (2-16) in the presence of 2,3-diphenyl-2H-azirine (2-2) anomalous reaction products were obtained. A product analysis revealed tetraphenylpyrrole (2-5) - 3%, a mixture of tetraphenylpyrazine (2-9) and tetraphenylpyrimidine (2-10) - 2%, plus a pale yellow solid

(73% - $C_{21}H_{17}N_3$) that was not found in the products of the other pyrolyses reactions (for a full discussion of the product see section 2.5 (iii)).

Phenylcarbene (2-16) has been reported[57] to undergo a "carbene-carbene" rearrangement (see section 1.2 (vii)) in a "flowthrough" gas phase reactor maintained above 250°C.

The pyrolysis reactions reported here contain no products attributable to such rearrangements. Intuitively this is a reasonable observation since the pyrolysis reactions reported here[2-4] would generate the carbene under an increased pressure in a sealed system containing many species capable of undertaking a reaction (c.f. section 1.2 (vii)).

Another group studying heterocyclic thermal rearrangement reactions have reported[84] that pyrazine will thermally rearrange to produce pyrimidine during flash pyrolysis conducted at 1270°K/ 2mm in a packed silica tube.

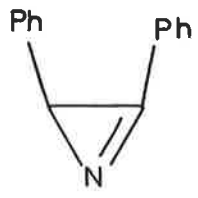
To test (1) the possibility that this type of rearrangement is occurring in the thermolyses reactions, and (2) the thermal stability of the other major products; 2-phenylindole (2-4), tetraphenylpyrrole (2-5), triphenylimidazole (2-6) and tetraphenylpyrazine (2-9) were each separately subjected to control thermal reactions. In each case, the starting material was recovered unchanged, indicating all of the major reaction products are stable under the pyrolysis conditions.

2.5 (iii) Reaction between phenyldiazomethane and 2,3-diphenyl-2H-azirine

When an attempt was made to generate phenylcarbene (2-16) in the presence of 2,3-diphenyl-2H-azirine (2-2) the major product was a pale yellow solid (73% - $C_{21}H_{17}N_3$). This product exhibited a strong *i.r.* absorption at 2150 cm^{-1} and contained no other peaks that would be readily assigned to another functional group. The proton magnetic resonance spectrum showed a broad multiplet representing 15 aromatic hydrogen atoms at δ6.9 and a sharp singlet representing 2 benzylic hydrogen atoms at δ5.3. This peak remained a singlet after addition of europium shift reagent indicating that the original singlet is not due to two coincident proton resonances with the same chemical shift. The mass spectrum contains no molecular ion but has peaks due to the processes $M^{+\cdot} - N_2$, $M^{+\cdot} - N_3^{\cdot}$, $(M^{+\cdot} - N_2) - C_6H_5^{\cdot}$ and $(M^{+\cdot} - N_2) - C_7H_7^{\cdot}$.

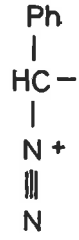
A closer examination of the molecular formula reveals that the product is formed by a 1:1 combination of the azirine (2-2) and phenyldiazomethane (2-27). The *i.r.* data strongly suggest that the nitrogen atoms are present as an azide grouping in the product. A combination of the reactants and the spectral data of the product leads to the postulation of 1-azido-1,2,3-triphenylprop-1-ene (2-30) as the most reasonable structure for the product[c.f.69,70]. The information available is not sufficient to deduce the geometry of the double bond.

A plausible reaction mechanism is the 1,3-dipolar addition of phenyldiazomethane (2-27) to the ground state azirine (2-2) to generate an intermediate (2-31) which is analogous to structures (2-19a & b). This mechanism is analogous to the one proposed[69,70] for the reaction of diazomethane with 3-methyl-2-phenyl-1-azirine, and similar to the mechanism suggested[65] for a photolytic rearrangement of 2,3-diphenyl-2H-azirine (2-2). The mechanism by which (2-31) rearranges to the vinyl azide (2-30) is much less obvious and the arrows depicted in scheme 1 outline only one possibility. The conversion of structure (2-32) into structure (2-31) represents the normal 1,3-dipolar addition of an azide to a double bond, a reaction that usually proceeds quite readily[85]. Recently, however, the first example of a cyclo reversion reaction involving a 1,3-dipole adduct from an azide group was reported[86]. Hence, the allylic rearrangement of

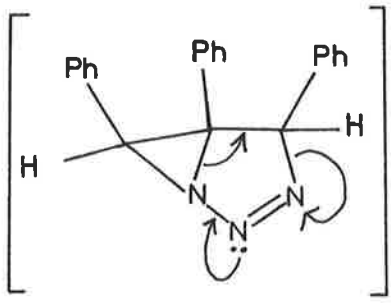


(2-2)

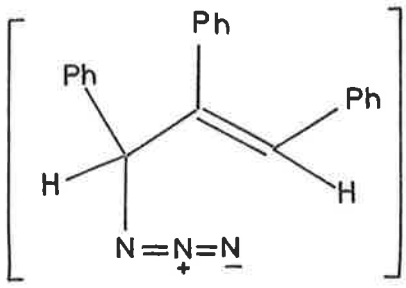
+



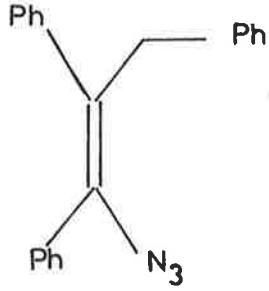
(2-27)



(2-31)



(2-32)

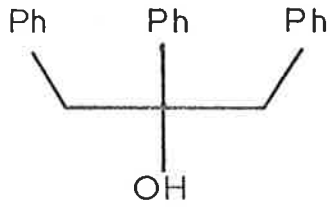


(2-30)

(2-32) to produce the vinyl azide (2-30) could well be facile, especially as the migrating group is diallylic and the reaction conditions should permit either radical or polar rearrangement reactions to occur. Since vinyl azides are relatively stable when compared to alkyl azides[87], the product vinyl azide (2-30) should not readily rearrange back to the allyl azide (2-32). In fact, (2-30) exhibits unusual stability properties; it was unaffected by boiling toluene and only slowly decomposed in boiling xylene (monitored by loss of ν_{max} at 2150 cm^{-1} ($-N_3$)). The minimum conditions required for complete loss of the azide absorption (2150 cm^{-1}) in the *i.r.* spectrum was flash pyrolysis at 350°. A thin layer chromatographic investigation of the pyrolysis product revealed no less than seven components.

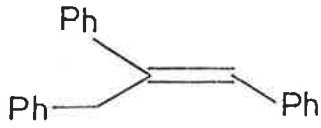
In order to confirm the structure proposed for (2-30), two synthetic routes were considered (see scheme 2).

The asymmetric olefin (E)-1,2,3-triphenylpropene (2-34) served as the starting point for both synthetic routes. This olefin was conveniently prepared by dehydration[88,89] of 1,2,3-triphenylpropan-2-ol (2-33). The stereochemistry of this elimination has been rigorously established by spectral means and produces only the (E) isomer[89] (2-34).

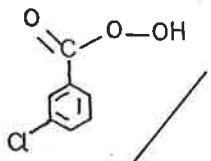


(2–33)

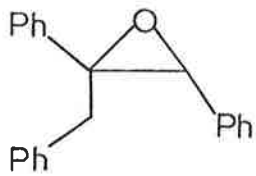
H_2SO_4



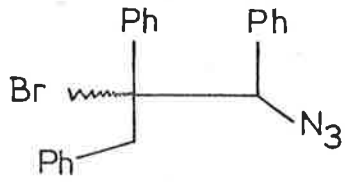
(2–34)



BrN_3/pentane / N_2



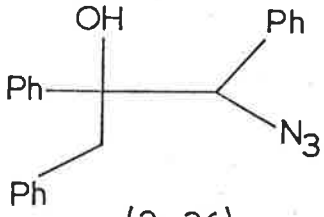
(2–35)



(2–38)

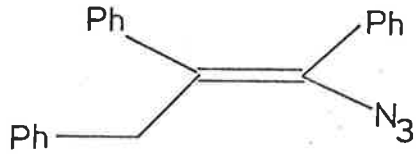
NaN_3

$Bu^t\ O^-K^+$



(2–36)

CH_3SO_2Cl
SO_2
Pyr
D.M.F.



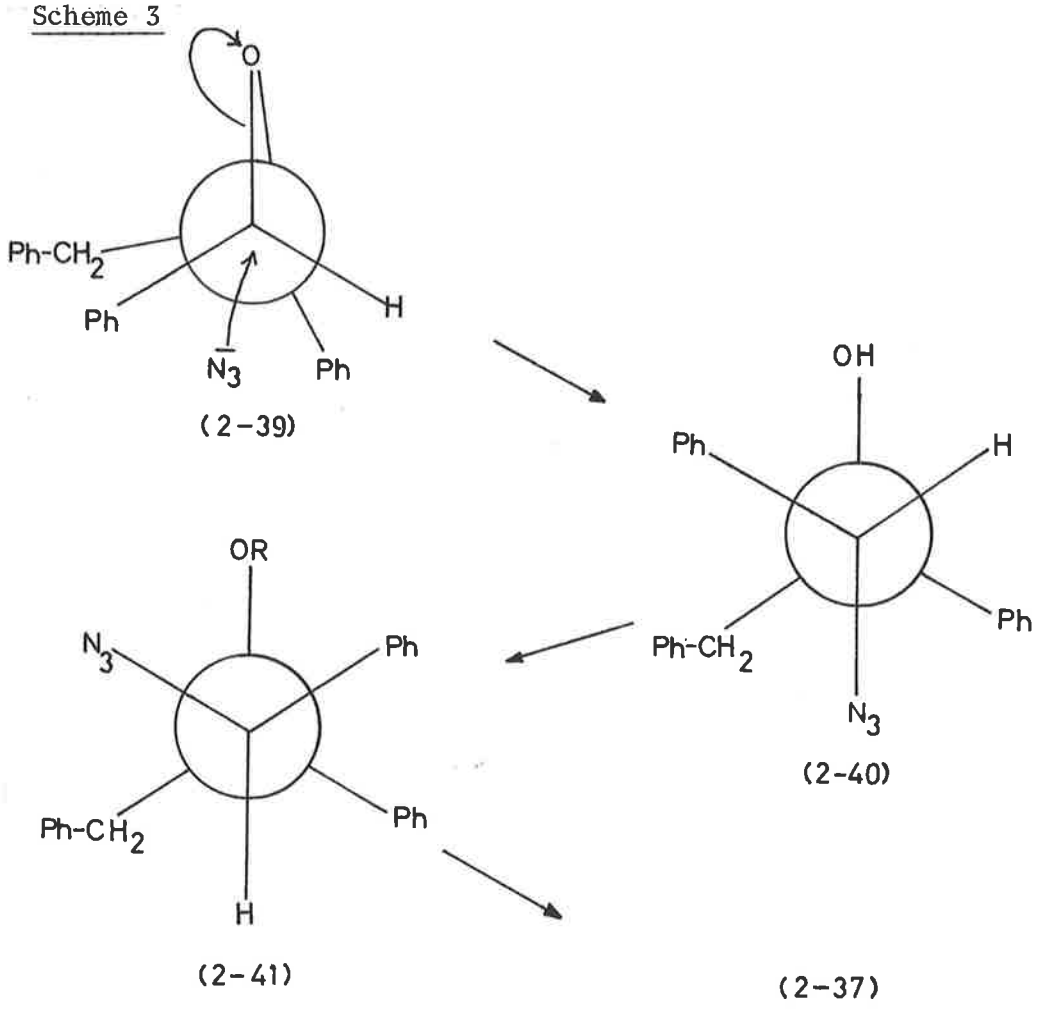
(2–37)

The olefin (2-34) was converted to its epoxide (2-35) by reaction with a buffered *m*-chloroperbenzoic acid solution. The reaction was conducted in a basic medium at 0°C, since a trace of acid or the presence of heat allowed the epoxide to rearrange to an unidentified carbonyl compound, a rearrangement analogous to the thermal rearrangement of 1,2-epoxy-1,1,3-triphenylpropane[90]. Since the treatment of an epoxide with sodium azide results in cleavage of the epoxide ring to form an hydroxy-azide[87], the epoxide (2-35) was treated with sodium azide in dimethylsulphoxide at room temperature to produce the hydroxyazide (2-36) [ν_{max} at 3450 cm^{-1} and 2145 cm^{-1}].

Epoxidation of the olefin (2-34) leads to a structure of rigid geometry (see scheme 3) which is ideally constructed (2-39) for ring cleavage *via* a backside attack of the azide anion to produce the more stable tertiary alcohol (2-40) with the configuration depicted in scheme 3.

Since the hydroxy-azide (2-36) decomposed on attempted chromatographic purification the ensuing dehydration reaction was carried out on the crude reaction product. This crude product was allowed to react with methanesulphonylchloride in pyridine - D.M.F. containing sulphur dioxide[91] to give 1-azido-1,2,3-triphenyl-propene (2-37). This product was found to be identical in all respects with the compound (2-30) formed from the reaction between

Scheme 3



phenyldiazomethane (2-27) and the azirine (2-2). If the elimination of methanesulphonic acid (2-41)→ (2-37) follows the expected *trans* pathway then the produce olefin (2-37) would have the (E)-configuration (see scheme 3). However, since the methanesulphonate group is situated at a benzylic carbon atom the possibility of an E1 elimination reaction occurring cannot be discounted. Hence,

the assignment of the double bond configuration in (2-37) cannot be regarded as proved.

An alternate approach to the vinyl azide (2-37) would be the regiospecific≠ addition of bromine azide to the olefin (2-34).

Hassner and co-workers have shown that bromine azide can undergo a facile free radical addition to olefins, leading to the opposite regiochemistry in the products when compared with the normal ionic addition[87,93-97]. Since the addition does proceed *via* a free radical intermediate, a regiospecific but non stereospecific addition is expected. This should lead to a mixture of diastereoisomers (2-38) which would ultimately produce both (E)- and (Z)-1-azido-1,2,3-triphenylpropene.

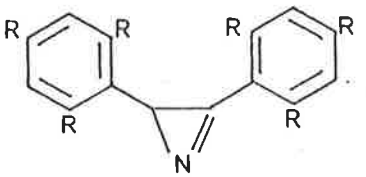
Free radical addition of bromine azide to the olefin (2-34) was achieved with some difficulty to produce a small amount (10%) of the desired bromoazide (2-38). All attempts to eliminate hydrogen bromide from the bromoazides (2-38) using a variety of bases to generate the vinyl azide (2-37) failed. In all cases, the resulting product mixtures contained at least six compounds. When the base was potassium-t-butoxide a small amount of unreacted bromo-azide

≠ The term regiospecific[92] describes orientational or directional preference in reaction specificity and selectivity involving bond making or breaking.

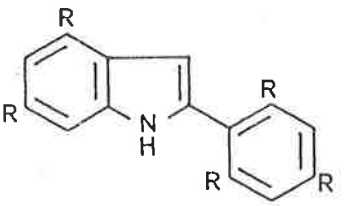
(2-38) was recovered from the products; this again illustrates the rather surprising stability of azides in this series. Since the required olefins could not be isolated from the reaction products this route was not investigated further.

2.6 Conclusion

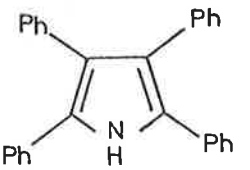
All of the reaction products have been rationalized in terms of observed experimental reactions or in terms of analogous reactions reported in the literature. The mechanism of formation for many of the products would be much clearer if the intermediate (2-19) could be isolated. However, the reaction conditions employed are sufficiently vigorous to make this impossible, and hence the product interpretation must rely heavily on analogy. However, the results obtained indicate that tetraphenylpyrrole (2-5) and 2-phenylindole (2-4) may be produced by nitrene insertion reactions, that triphenylimidazole (2-6) is possibly produced from a reactive intermediate (e.g. (2-19)), that N-benzyl-2,4,5-triphenylimidazole (2-7), tetraphenylpyrazine (2-9) and tetraphenylpyrimidine (2-10) can be formed by phenylcarbene insertion into triphenylimidazole (2-6), or by rearrangement of the reactive intermediate (2-19), and that pentaphenylpyridine (2-8) can be produced by reaction between phenylcarbene and tetraphenylpyrrole (2-5).



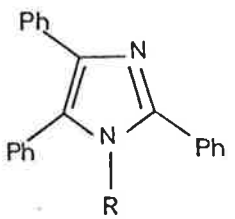
(2-1) R=D
(2-2) R=H



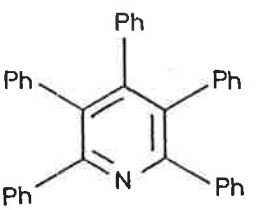
(2-3) R=D
(2-4) R=H



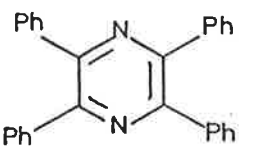
(2-5)



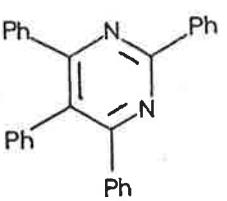
(2-6) R=H
(2-7) R=$-CH_2-Ph$



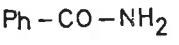
(2-8)



(2-9)

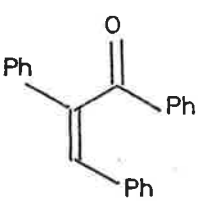


(2-10)

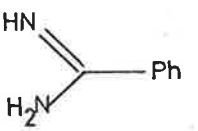


(2-11)

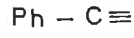
(2-12)



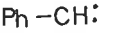
(2-14)



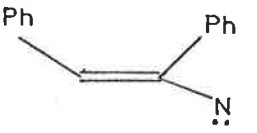
(2-13)



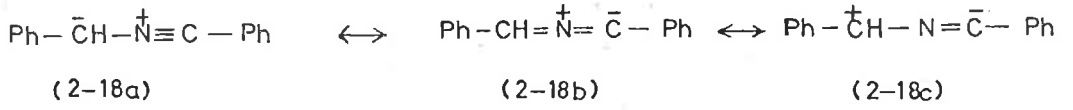
(2–15)



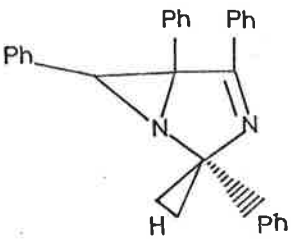
(2–16)



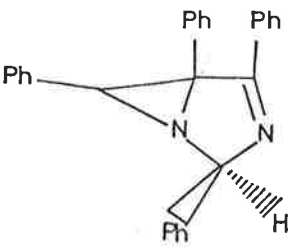
(2–17)



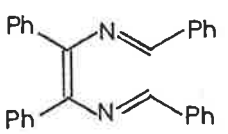
(2–18a) (2–18b) (2–18c)



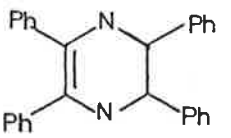
(2–19a)



(2–19b)

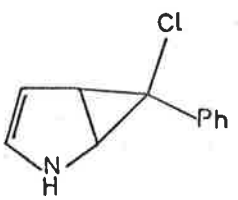


(2–20)

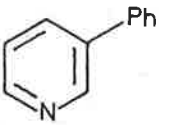


(2–21)

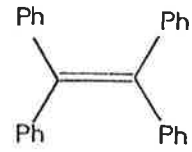
(2–22)



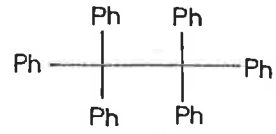
(2–23)



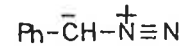
(2–24)



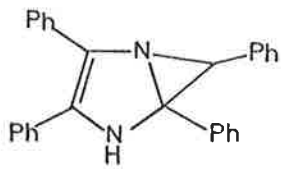
(2-25)



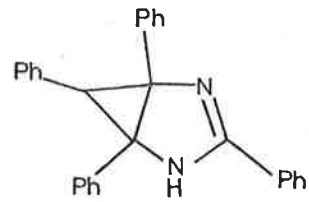
(2-26)



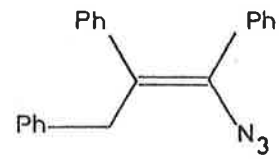
(2-27)



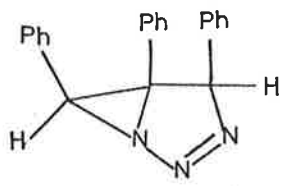
(2-28)



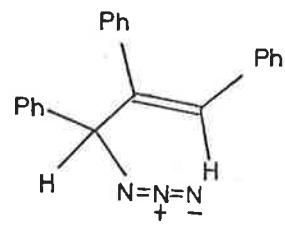
(2-29)



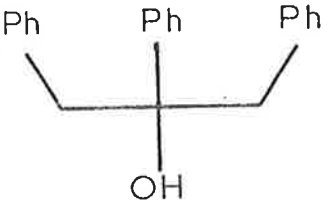
(2-30)



(2-31)

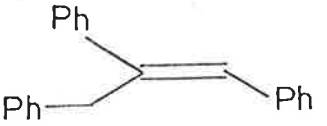


(2-32)

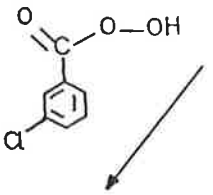


(2-33)

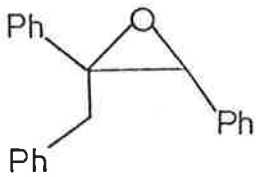
H_2SO_4



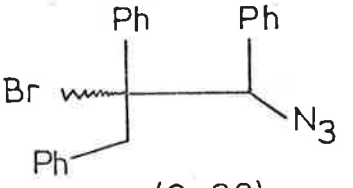
(2-34)



BrN_3/pentane / N_2



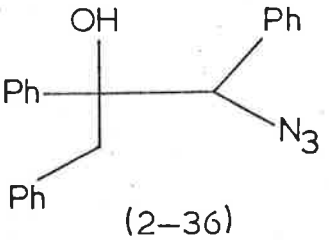
(2-35)



(2-38)

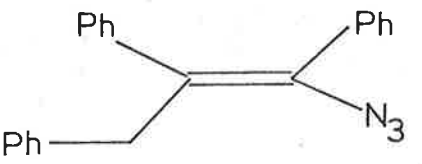
NaN_3

$Bu^t\ O^-K^+$

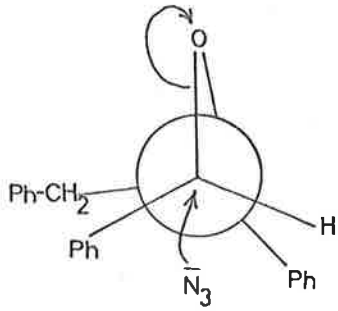


(2-36)

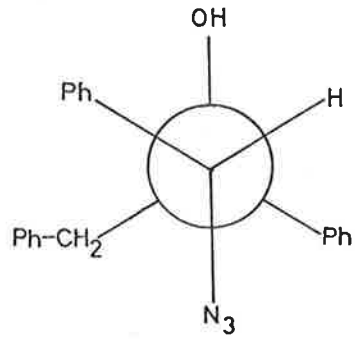
CH_3SO_2Cl
SO_2
Pyr
D.M.F.



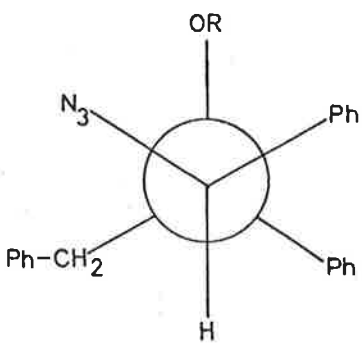
(2-37)



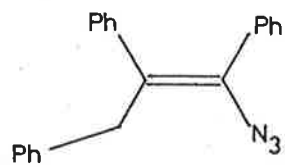
(2-39)



(2-40)



(2-41)



(2-37)

CHAPTER 3. EXPERIMENTAL SECTION

For the general experimental procedures, see Part I, chapter 4.

The following compounds were purified commercial samples; 2-phenylindole (2-4), Benzamide (2-11), Benzonitrile (2-15), Stilbene (2-12), Tetraphenylethylene (2-25) and Hexaphenylethane (2-26): while 2,3-diphenyl-2H-azirine (2-2)[98], 2,4,5-triphenyl-imidazole (2-6)[99]; N-benzyl-2,4,5-triphenylimidazole (2-7)[100], 2,3,4,5-tetraphenylpyrrole (2-5)[101], 2,3,4,5,6-pentaphenylpyridine (2-8)[102], 2,3,5,6-tetraphenylpyrazine (2-9)[103], benzamidine (2-13)[104] and 1,2-diphenylacrylophenone (2-14)[105] were prepared by reported procedures.

2,4,5,6-tetraphenylpyrimidine (2-10)

The pyrimidine (2-10) was prepared by a modification of the method of Cook *et al*[105]:

A mixture of 284 mgm of 1,2-diphenylacrylophenone (2-14)[105] and 122 mgm of benzamidine(2-13)[104] in 25 mls of ethanol and 20 mls of sodium hydroxide (10%) was stirred at 20°C for 4 days. The solution was diluted with excess acetic acid (200 mls) and set aside for one week. The solid precipitate was filtered off and recrystallized from ethanol as colourless needles. Yield 382 mgm = 93% mpt 196° (Lit.[107] 199°); $C_{28}H_{20}N_2$ requires C : 87.47, H : 5.24 found C : 87.52, H : 5.30%≠. *i.r.* (Nujol mull) 1615, 1600, 1560

≠ Subsequent to this preparation a very similar sequence was published by Padwa *et al*[65a].

1440, 1400, 1375, 760, 750, 740, 680 cm^{-1}. *N.M.R.* ($CDCl_3$) Broad multiplet, aromatic hydrogens centre δ7.33.

Thermal rearrangement of 2,3-diphenyl-2H-azirine (2-2) during vapour phase chromatography

15 mgm of 2,3-diphenyl-2H-azirine (2-2) was injected into a 10%-Poly(ethylene glycol)carbowax 1500 column (5 foot x 0.25 ins) maintained at 220°. The product isolated (9.3 mgm - 63%) mpt 187° was shown to be 2-phenylindole (2-4) by a comparison between the infrared spectrum of the V.P.C. product and authentic 2-phenylindole, and by mixed melting point determinations (mpt authentic sample 187-188°,mmpt 185-186°). The retention time of the indole was approximately 30 mins when the carrier gas (nitrogen) flow rate was 30 cm/min.

General Thermolysis Procedure

The heterocycle (2.0 gms) was sealed in a stainless steel bomb (volume = 103 cc) and heated for 3 hrs in an oven pre-equilibrated at the required temperature (100, 250 or 470°). The cooled products dissolved in diethylether (100 mls) were added to silicic acid (Mallinkrodt greater mesh; 10 gm); the ether was removed *in vacuo* and the dried material was applied to a column of silicic acid (120 x 3 cm) prepared in light petroleum. The column was eluted with mixtures of light petroleum diethyl ether and methanol of increasing polarity and fractions of 50 mls were

collected. Each fraction was evaporated *in vacuo* and the residue crystallized from either methanol or glacial acetic acid.

Thermolysis of 2,3-diphenyl-2H-azirine (2-2)

(a) When the arizine (2-2) (2 gms) was pyrolysed at 250° under the general reaction conditions the products were eluted from the chromatography column in the following order:

Compound	Solvent Polarity	mpt	mmpt	%≠
1. Stilbene (2-12)[108]	X4	124°	123-125°	1.3
2. Tetraphenylpyrrole (2-5)[101]	X4:15%Et_2O	214-215°	211-215°	20.0
3. 2-Phenylindole (2-4)[109]	X4:20%Et_2O	188-189°	186-189°	11.4
4. Tetraphenylpyrazine (2-9)[103]	X4:30%Et_2O	248-251°	245-251°	9.5
5. Tetraphenylpyrimidine (2-10)[107]	X4:30%Et_2O	195-197°	194-198°	2.4
6. Pentaphenylpyridine (2-8)[102]	X4:50%Et_2O	247-249°	244-249°	0.65
7. N-Benzylimidazole (2-7)[100]	X4:75%Et_2O	164-166°	163-166°	13.8
8. Triphenylimidazole (2-6)[99]	Et_2O	279-280°	276-280°	30.3
9. Benzamide (2-11)[110]	Et_2O:5%MeOH	129-130°	127-130°	4.6

(b) When the azirine (2-2) was pyrolysed at 470° the products eluted from the chromatography column were:

≠ These % results are an average of 4 thermolyses (see Results and Discussion). The average total product recovered was 84% and the percentages recorded are of the total recovered product.

Compound	Solvent	mpt	mmpt	%≠
1. 2-phenylindole (2-4)[109]	X4:20%Et_2O	186-189°	184-189°	75.4
2. tetraphenylpyrazine (2-9)[103]	X4:30%Et_2O	247-250°	245-251°	2.0
3. Black Tar	X4:60%Et_2O	-	-	13.8
4. Triphenylimidazole (2-6)[100]	Et_2O	278-280°	276-281°	8.8

(c) When the azirine (2-2) was pyrolysed at 100° the products isolated from the chromatography column were:

Compound	Solvent	mpt	mmpt	%≠
1. tetraphenylpyrrole (2-5)[101]	X4:15%Et_2O	213-215°	211-215°	6.1
2. diphenylazirine (2-2)[98]	X4:20%Et_2O	68-70°	67-70°	91.5
3. tetraphenylpyrazine(2-9)[103]	X4:30%Et_2O	248-250°	245-250°	2.4

In all cases, the structure of each product was confirmed by comparison of mpt, mmpt, infrared spectrum and mass spectrum with an authentic sample.

Thermolysis of other hetro cycles

2-phenylindole (2-4), triphenylimidazole (2-6), tetraphenylpyrrole (2-5) and tetraphenylpyrazine (2-9) were each individually submitted to control thermolyses reactions at 250°. In each case only unreacted starting material (> 95%) was obtained from column chromatography.

≠ These percentages are the result of a single thermolysis and are the percentage of the recovered product (95% and 88% respectively).

Benzalazine[cf.82]

A solution of hydrazinehydrate (20 gm) stirred under N_2 was cooled to 0° and freshly distilled benzaldehyde (21 gm) added over a period of 1 hr; the stirring was continued at 0° for 30 mins. The excess hydrazine hydrate was removed by distillation leaving a yellow crystalline residue. The product was recyrstallized from ethanol as yellow needles. Yield = 20 gms (95%). mpt = 91-93° (Lit.[111] - 92-93°). $C_{14}H_{12}N_2$ requires C : 80.7, H : 5.8 found C : 80.8, H : 5.7%. *i.r.* (Nujol mull) 3050, 1612, 1528, 1500, 1455, 1310, 1290, 1210, 1075, 1020, 960, 860, 760, 795, 785 cm^{-1}. *N.M.R.* : δ 8.6 [1H, Singlet], 7.6 [5H, broad multiplet].

Benzalhydrazine[122]

Benzalazine (20 gms) was dissolved in hydrazine hydrate (70 mls - 5 molar excess) and heated under reflux for 15 hrs. The solution was cooled and the two layers separated. The crude benzalhydrazine[cf.111] was used satisfactorily without further purification (attempted distillation or chromatographic purification resulted in disproportionation of the benzalhydrazine).

Pentaphenylpyridine (2-8) from 2,3,4,5-tetraphenylpyrrole (2-5)

(a) From phenylchlorocarbene

A solution of tetraphenylpyrrol-1-yl-lithium was prepared from tetraphenylpyrrole (3.5 gm), phenyl lithium (from lithium - 0.9 gm)

and bromobenzene (106 gm) in dry diethylether (20 mls) using the procedure of Alexander *et al*[34a]. Benzylidene chloride (106 gm) in dry diethylether (20 mls) was added and the mixture was stirred under an atmosphere of nitrogen for 1 week. The lithium salts were filtered off and the ether-benzene solvent mixture removed *in vacuo* to leave a red oil. Passage through a 120 x 3 cm chromatography column containing silicic acid using light petroleum-diethlether as eluant and collecting 50 ml samples led to isolation of the following solids which were recrystallized from ethanol as colourless needles: tetraphenylethylene(2-25) [0.079g, 2%; (X4:5%Et_2O)mpt 225-227°, Lit.[113] 214°], hexaphenylethane (2-26) [0.19g, 4.4%; (X4:10%Et_2O) mpt 145-146°, Lit.[114] 145-147°], pentaphenylpyridine (2-8) [2.5g, 59%; (X4:50%Et_2O) mpt 245-247°, Lit.[102] 249°, mmpt 244-249°].

The products were identified by comparison of infrared and mass spectra, mpt and mmpt with an authentic sample.

A control reaction was repeated in the absence of 2,3,4,5-tetraphenyl;yrrole (2-5). Chromatography of the products yielded tetraphenylethylene (2-25)(1.44g, 37.5%), hexaphenylethane (2-26) (1.95g, 40.5%), benzylidene chloride (7.98g, 22%) as the only products.

(b) From phenylcarbene

Phenyldiazomethane (2.2gm) [prepared from benzalhydrazine by the method of Mohrbacher and Cromwell[81]] in cyclohexane (150 mls) was

slowly added under nitrogen to a stirred suspension of copper powder (0.1gm) and 2,3,4,5-tetraphenylpyrrole (1gm) in cyclohexane (150 mls) heated under reflux. After a further 2 hrs the solvent was removed *in vacuo* and the residue chromatographed over silicic acid (120 x 3 cm), with light petroleum-ether as an eluant. The products isolated were: stilbene (2-12) (100 mgm) [mpt 120-123°, Lit.[108] 124°], 2,3,4,5-tetraphenylpyrrole (2-5) (910 mgm) [mpt 212-214°, Lit.[101] 214.5] and 2,3,4,5,6-pentaphenylpyridine (2-8) (56 mgm) [mpt 246-249°, Lit.[102] 249°]. The structures were confirmed by comparison of mpt, mmpt, infrared and mass spectra with an authentic sample.

Reaction of 2,4,5-triphenylimidazole (2-6) with phenylcarbene (2-16)

The reaction procedure and chromatographic techniques used were identical to those reported for the reaction of 2,3,4,5-tetraphenylpyrrole (2-5) and phenylcarbene (2-16).

When phenylcarbene [from phenyldiazomethane 12.2 gms][cf.81] was generated in the presence of 2,4,5-triphenylimidazole (300 mgm) in cyclohexane (150 mls), the following products were isolated: stilbene (2-12) [204 mgm, mpt 122-124°, Lit.[108] 124°], 2,4,5-triphenylimidazole (2-6) [101 mgm, mpt 271-274°, Lit.[99] 274°], N-benzyl-2,4,5-triphenylimidazole (2-7) [105 mgm, mpt 164-165°, Lit.[100] 165°], 2,3,5,6-tetraphenylpyrazine (2-9) [40 mgm, mpt 244-246°, Lit.[103] 244°], 2,4,5,6-tetraphenylpyrimidine (2-10) [15 mgm, mpt 197-199°,

Lit.[107] 199°].

Condensation of 2,3-diphenyl-2H-azirine (2-2) and phenyldiazomethane (2-27)

Phenyldiazomethane (2-27) (1.9 gm) [prepared by the method of Mohrbacher and Cromwell[81]] in cyclohexane (150 mls) was added dropwise to a solution of 2,3-diphenyl-2H-azirine (2-2) (0.5 gms) in diethylether (25 mls). The mixture was heated under reflux in an atmosphere of nitrogen for 72 hrs. The solvent was removed *in vacuo* and the crude reaction mixture was separated by chromatography over silicic acid (60 x 3 cm). Elution with light petroleum-diethylether (95:5) gave 1-azido-1,2,3-triphenylprop-1-ene (2-30) (0.56 gm, 71%) which was crystallized from hexane as yellow plates mpt 64.5-65° (Found: C, 81.4; H, 5.6; N, 13.6. $C_{21}H_{17}N_3$ requires C, 81.6; H, 5.5; N, 13.5%). ν_{max} (nujol mull) 3050, 2150, 1600, 1495, 1280, 1257, 875, 760, 700 cm^{-1}. *N.M.R.* δ6.9 (15H, broad multiplet, aromatic hydrogens); 5.31 (2H, singlet, benzylic hydrogens). *N.M.R.* with added Eu $(dpm)_3$: δ7.0 (15H, broad multiplet); 5.42 (2H, singlet). Mass spectrum: *m/e* 77 (8%), 89(4), 91 (6), 128 (5), 150 (3), 151 (4), 152 (8), 165 (13), 166 (5), 167 (7), 176 (6), 177 (6), 178 (34), 179 (24), 180 (10), 193 (3), 204 (9), 205 (6), 206 (74), 207 (15), 269 (2), 280 (12), 281 (12), 282 (91), 283 (100).

2,3,4,5-tetraphenylpyrrole (2-5), 2,3,5,6-tetraphenylpyrazine (2-9) and 2,4,5,6-tetraphenylpyrimidine (2-10) (all less than 1%) were

isolated from the column (see isolation procedure for general thermal reactions) and characterized by comparison of mpt, mmpt, infrared and mass spectra with authentic samples.

(E)-1,2,3,-triphenylprop-1-ene (2-34)

1,2,3-triphenylpropan-2-ol (2-33) [88] (1 gm) was dissolved in sodium dried benzene (100 mls) and heated under reflux in the presence of conc sulphuric acid (1 ml) in a Dean-Stark water separator for 14 hrs.

The benzene layer was separated, washed with water (2 x 10 mls), dried (magnesium sulphate) and the benzene removed by distillation. The resulting oil was distilled (160°/0.1 mm) and then recrystallized from petrol ether to give the alkene as colourless needles. Yield = 0.89g, 94%, mpt 61-62° (Lit.[89,115] 62-63°). *N.M.R.* δ7.05 (16H, broad multiplet, aromatic and vinyl hydrogens); 3.95 (2H, singlet, benzylic hydrogens).

G.l.c. analysis showed only one peak on the following columns: A) 3 ft by $\frac{1}{8}$ in Apiezon (10%) on Chromosorb W (80-100 mesh), column temperature 170°; B) 6 ft by $\frac{1}{8}$ in FFAP (1%) on Chromosorb W (80-100 mesh), column temperature 170°.

1,2-epoxy-1,2,3-triphenylpropane (2-35)

m-Chloroperbenzoic acid (0.86 mgm 85%) and sodium bicarbonate (1.1 gm) were added to dry methylene chloride (7 mls) and stirred

vigorously under nitrogen at 20° for 15 mins. The equilibrated per acid-buffer was added rapidly to 1,2,3-triphenylprop-1-ene (2-34) (1.35 gm) in dry methylene chloride (5 mls) and stirred under nitrogen for 10 hrs. The reaction mixture was washed with aqueous sodium hydroxide (10%, 2 x 5 ml), water (2 x 5 ml) and dried(magnesium sulphate). Evaporation of the methylene chloride and chromatography of the residue over silic acid (30 x 3 cm) in benzene revealed the epoxide as colourless needles (1.04 gm, 73%). A sample was distilled twice for analysis. Bpt 120°/0.6 mm, mpt 48-49°. [Found: C, 88.3; H, 6.4. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%]. ν_{max} (nujol mull): 3050, 1605, 1500, 1360, 1025, 805, 760, 700 cm^{-1}. *N.M.R.* δ6.9 (15H, broad multiplet, aromatic hydrogens); 2.81 (2H, singlet, benzylic hydrogens); 3.76 (1H, singlet, epoxy hydrogen).

1-azido-1,2,3-triphenylprop-2-ene (2-37)

Sodium azide (325mgm) and ethanol (46 mgm) were added to 1,2-epoxy-1,2,3-triphenylpropane (2-35) (286 mgm) in dimethylsulphoxide (10 ml) with stirring under a nitrogen atmosphere at room temperature[39a, 116]. The reaction mixture was then heated at 68°C for 14 hrs, cooled, diluted with water (50 mls) and extracted with diethylether (3 x 10 mls). The etherial solution was washed with water (10 x 5 mls) and dried (magnesium sulphate). Evaporation of the ether *in vacuo* yielded 1-azido-1,2,3-triphenylpropan-2-ol (2-36) as a colourless

oil (250 mgm) which exhibited strong ν_{max} at 2145 cm^{-1} (azide) and 3450 cm^{-1} (hydroxyl).

Using the method of Hazen and Rosenburg[91] the crude hydroxyazide (2-36) (200 mgm) was dehydrated in D.M.F. (20 ml) and pyridine (8 mls). The solution was cooled to 10° and methanesulphonylchloride (5 mls) containing sulphur dioxide (250 mgm) was added over a period of 2 minutes[91]. After an additional 5 mins, water (3 ml) was added dropwise, the temperature being maintained below 25°. Water (50 ml) was then added and the mixture extracted with methylene chloride (2 x 10 ml). The extract was washed with cold sulphuric acid (5 mls, 10%), cold sodium carbonate (5 mls, 10%), water (2 x 5 mls) and dried (magnesium sulphate). The methylene chloride was evaporated to dryness and the resulting oil was chromatographed on silicic acid. Elution with X 4:5%Et_2O gave 1-azido-1,2,3-triphenylprop-1-ene (2-37). The product was recrystallized from *n*-hexane as yellow plates [Yield = 105 mgm, 56% mpt 64-65°].

ν_{max} (Nujol mull), 2150 cm^{-1} (- azide). *N.M.R.* (CCl_4): δ6.9, (15H, broad multiplet, aromatic H), 5.3 (2H, singlet, benzylic H). *N.M.R.* (CCl_4 with added $Eu(dpm)_3$: δ7.0 (15H, broad multiplet, aromatic H), 5.42 (2H, singlet, benzylic H). A mixed mpt of 64-65° was observed with the product obtained (2-30) from the reaction between 2,3-diphenyl-2H-azirine (2-2) and phenyldiazomethane (2-27). The infrared and mass spectra of both compounds were identical.

Reaction of Bromine Azide with 1,2,3-Triphenylprop-1-ene (2-34)

Adapting the procedure of Hassner *et al*[93,94] 1,2,3-triphenylprop-1-ene (2-34)-(200 mgm) was added to a solution of bromine azide (from 3.0 gm of bromine) in pentane (50 mls) containing benzoyl peroxide (5 mgm) and stirred in an atmosphere of nitrogen and in the presence of light for 27 hrs. Most of the solvent was evaporated *in vacuo* at room temperature and the residue was purified by preparative thick layer chromatography (using an 8 x 8 x 0.5 cm plate of silicic acid HF_{254} and eluting with light petroleum/diethyl ether (1:1)). Recrystallization from *n*-hexane produced 1-azido-2-bromo-1,2,3-triphenylpropane (2-38) as white needles (30 mgm - 10%) as the only one crystalline fraction. mpt = 141-141.5 (Found: C, 64.2; H, 4.6; N, 11.0%. $C_{21}H_{18}BrN_3$ requires C, 64.3; H, 4.6; N, 10.7%. ν_{max}: 3050, 2120, 1600, 1500, 1280, 1080, 800, 780, 740, 650 cm^{-1}. *N.M.R.*: δ7.0 (15H, broad singlet, aromatic hydrogens); 2.95 (2H, singlet, benzylic hydrogens); 4.12 (1H, singlet, $CH\text{-}N_3$).

The bromoazide (2-38) (200 mgm) was dissolved in dry diethyl-ether (7 mls) and cooled to 3°. Potassium *t*-butoxide [600 mgm, 20% excess] was added and the solution stirred at 3° for 14 hrs. The reaction mixture was washed with water (2 x 5 mls), dried (magnesium sulphate) and the ether removed *in vacuo*. The resulting oil contained at least six compounds [by thin layer chromatography]. The only crystalline material obtained from preparative plate

chromatography on silicic acid was shown to be unchanged bromoazide (2-28).

The bromoazide (2-28) was also treated in a similar manner with other bases (sodium ethoxide, triethylamine, phenyl lithium and *n*-butyl lithium). Crystalline products could not be isolated from any of these reactions using a variety of chromatographic techniques.

CHAPTER 4. REFERENCES

1. Anderson, D.J., Gilchrist, T.L., Gymer, G.E., and Rees, C.W., Chem.Commun., 1518 (1971).
2. Bowie, J.H., and Nussey, B., Chem.Commun., 1565 (1970).
3. Bowie, J.H., Nussey, B., and Ward, A.D., Aust.J.Chem., 26, 2547 (1973).
4. Bowie, J.H., and Nussey, B., J.Chem.Soc.Perkin I, 1693 (1973).
5. Bauer, W., and Hafner, K., Angew Chem.Internat. Edn.Engl., 8, 772 (1969).
6. Gilchrist, T.L., Gymer, G.E., and Rees, C.W., Chem.Commun., 1519 (1971).
7. Isomura, K., Kobayashi, S., and Taniguchi, H., Tet.Lett., 3499 (1968).
8. (a) Kirmse, W., "Carbene Chemistry" (Academic), New York (1964).
   (b) Kirmse, W., "Carbene Chemistry" (Academic), New York (1971), 2nd Edn.
   (c) Sharp, J.T., J.Chem.Soc.(B), Annual Reports, 68, 217 (1971).
9. Doering, W.E., Winstein, S., and Woodward, H., in "119th Meeting of the American Chemical Society", 1951.
10. Doering, W.E., and Knox, L.H., J.Am.Chem.Soc., 78, 4947 (1956).
11. Gilchrist, T.L., and Rees, C.W., "Carbenes, Nitrenes and Arynes", Nelson, Pitman Press, Bath (1969).
12. Hoffmann, R.W., Angew Chem.Internat.Edn.Engl., 10, 529 (1971).
13. Griffin, G.W., Angew Chem.Internat.Edn.Engl., 10, 537 (1971).

14. Lwowski, W., "Nitrenes", Interscience, New York, 1970.

15. Gilchrist, T.L., Rees, C.W., and Stanton, E. J.Chem.Soc.(C), 3036 (1971).

16. Kirmse, W., "Carbene Chemistry" (Academic), New York (1964), p. 79.

17. Engler, C., and Bethge, H., Ber, 7, 1125 (1874).

18. Löb, W., Ber, 36, 3059 (1903).

19. Staudinger, H., and Kupfer, O., Ber, 44, 2194 (1911).

20. Staudinger, H., and Kupfer, O., Ber, 44, 2197 (1911).

21. Melkanovitskaya, S.G., and Tsukervanik, I.P., Zhur.Obshchei Khim, 28, 11 (1958).

22. Nagata, W., Hirai, S., Kawata, K., and Aoki, T., J.Amer.Chem.Soc., 89, 5045 (1967).

23. (a) Doering, W.E., and LaFlamme, P., J.Am.Chem.Soc., 78, 5447 (1956).

(b) Skell, P.S., and Woodworth, R.C., J.Am.Chem.Soc., 78, 4496 (1956).

24. Skell, P.S., and Garner, A.Y., J.Am.Chem.Soc., 78, 5430 (1956).

25. Gaspar, P.P., and Hammond, G.S., in "Carbene Chemistry", Ed. Kirmse, W., (Academic), New York (1964), chapter 12.

26. Hoffmann, R., Trans.N.Y.Acad.Sci.2, 28, 75 (1966).

27. Hoffmann, R., J.Am.Chem.Soc., 90, 1475 (1968).

28. Anastassiou, A.G., and Simmons, H.E., J.Am.Chem.Soc., 89, 3177 (1967).

29. Murray, R.W., Trozzolo, A.M., Wasserman, E., and Yager, W.A., J.Am.Chem.Soc., 84, 3213 (1962).

30. Brandon, R.W., Closs, G.L., and Hutchison, C.A., J.Chem.Phys., 37, 1878 (1962).

31. Gutsche, C.D., Backman, G.L., and Coffey, R.S., Tetrahedron, 18, 617 (1962).

32. Closs, G.L., and Moss, R.A., J.Am.Chem.Soc., 86, 4042 (1964).

33. Closs, G.L., and Coyle, J.J., J.Am.Chem.Soc., 87, 4270 (1965).

34. (a) Alexander, F.R., Herrick,A.B., and Roder, T.M., J.Am.Chem. Soc., 72, 2760 (1950).

(b) Closs, G.L., and Schwartz, G.M., J.Org.Chem., 26, 2609 (1961).

(c) La lancette, E.A., and Benson, R.E., J.Am.Chem.Soc., 85, 2853 (1963).

(d) Katz, T.J., and Garratt, P.J., J.Am.Chem.Soc., 85, 2852 (1963).

35. (a) Scott, L.T., and Cotton, W.D., J.Am.Chem.Soc., 95, 2708 (1973).

(b) Scott, L.T., and Cotton, W.D., J.Am.Chem.Soc., 95, 5416 (1973).

36. (a) Bocchi, O., Gazz.Chim.Ital., 30, 89 (1899).

(b) Ciamician, G.L., and Sibler, P., Ber, 20, 191 (1887).

(c) Ciamician, G.L., and Dennstedt, M., Ber, 14, 1153 (1881).

(d) Klingberg, E., "Pyridine and its derivatives" (Interscience),

New York, Part 1 (1960), p.226.

37. Kirmse, W., "Carbene Chemistry", (Academic), New York (1964), p. 85.

38. Hemetsberger, H., Knittel, D., and Weidmann, H. Montash, 101, 161 (1970).

39. (a) Smolinsky, G., and Pryde, C.A., J.Org.Chem., 33, 2411 (1968).

(b) Sundberg, R.J., and Yamazaki, T., J.Org.Chem., 32, 290 (1967).

40. Swenton, J.S., Tet.Lett., 2855 (1967).

41. Fischer, O., and Heiler, O., Ber, 26, 378 (1893).

42. McCombie, H., Scarborough, H.A., and Waters, W.A., J.Chem.Soc., 353 (1928).

43. Sundberg, R.J., J.Org.Chem., 30, 3604 (1965).

44. Smith, P.A.S., in "Nitrenes" by Lwowski, W. (Interscience), New York, (1970), p. 130, and references cited therein.

45. Boyer, J.H., Krueger, W.E., and Medler, R., Tet.Lett., 5979 (1968).

46. Woerner, F.P., and Reimlinger, H., Ber, 103, 1908 (1970).

47. Bischoff, C.A., Ber, 21, 2071 (1888).

48. Walden, P.A., and Kernbaum, A., Ber, 23, 1958 (1890).

49. Nef, J.U., Ann, 298, 202 (1897).

50. Michael, A., J.Am.Chem.Soc., 42, 820 (1920).

51. Bergmann, E., and Hervey, J., Ber, 62, 893 (1929).

52. Ingold, C.K., and Jessop, J.A., J.Chem.Soc.,709 (1930).

53. Hahn, G., Ber, 62, 2485 (1929).

54. Kleucker, E., Ber, 62, 2587 (1929).

55. Bethell, D., J.Chem.Soc., 666 (1963).

56. Trippett, S., Proc.Chem.Soc., 19 (1963).

57. Jones, W.M., Joines, R.C., Myers, J.A., Mitsuhashi, T., Kroyia, K.E., Waali, E.E., Davis, T.L., and Turner, A.B., J.Am.Chem.Soc., 95, 826 (1973) and references cited therein.

58. Saunders, W.H., and Caress, E.A., J.Am.Chem.Soc., 86, 861 (1964).

59. Arcus, C.L., Marks, R.E., and Coombs, M.M., J.Chem.Soc., 4064 (1957).

60. (a) Giezendanner, H., Märky, M., Hansen, H.J., and Schmid , H., Helv Chim.Acta, 55, 745 (1972).

(b) Märky, M., Hansen, H.J., and Schmid , H., Helv Chim.Acta, 54, 1275 (1971).

(c) Gakis, N., Märky, M., Hansen, H.J., and Schmid, H., Helv Chim.Acta, 55, 748 (1972).

61. Angadiyavar, C.S., Sukumaran, K.B., and George, M.V., Tet.Lett., 633 (1971).

62. Hassner, A., and Levy, L.A., J.Am.Chem.Soc., 87, 4203 (1965).

63. Horner, L., Christmann, A., and Gross, A., Ber, 96, 399 (1963).

64. (a) Smolinsky, G., J.Org.Chem., 27, 3557 (1962).

(b) Smolinsky, G., and Feuer, B.I., J.Org.Chem., 31, 1423 (1966).

65. (a) Padwa, A., Clough, S., Dharan, M., Smolanoff, J., and Wetmore, S.I., J.Am.Chem.Soc., 94, 1395 (1972).

(b) Padwa, A., Okaran, M., Smolanoff, J., and Wetmore, S.I., J.Am.Chem.Soc., 95, 1945, 1954 (1973).

66. Huisgen, R., Stangl, H., Sturm, H.J., and Wagenhofer, H., Angew.Chem.Internat.Edn.Engl., 1, 50 (1962).

67. Ullman, E.F. and Singh, B., J.Am.Chem.Soc., 88, 1844 (1966); 89, 6911 (1967).

68. Singh, B., Zweig, A., and Gallivan, J.B., J.Am.Chem.Soc., 94, 1199 (1972).

69. (a) Nair, V., J.Org.Chem., 33, 2121 (1968).

(b) Nair, V., Tet.Lett., 4831 (1971).

70. Yogothetis, A.L., J.Org.Chem., 29, 3049 (1964).

71. Hassner, A., Currie, J.O., Steinfeld, A.S., and Atkinson, R.F., J.Am.Chem.Soc., 95, 2982 (1973).

72. (a) For a review see: Gilchrist, T.L., and Rees, C.W., "Carbenes, Nitrenes and Arynes", Nelson, Pitman Press, Bath, (1969).

(b) For a specific example see, Kölrich, G., Angew.Chem.Internat. Edn., 6, 41 (1967).

73. Hortmann, A.G., and Robertson, D.A., J.Am.Chem.Soc., 89, 5974 (1967).

74. Simons, B.K., Nussey, B., and Bowie, J.H., Org.Mass Spectrom., 3, 925 (1970).

75. Padwa, A., and Glazer, E., Chem.Commun., 838 (1971).

76. Padwa, A., Clough, S., and Glazer, E., J.Am.Chem.Soc., 92, 1778 (1970).

77. DoMinh, T., and Trozzolo, A.M., J.Am.Chem.Soc., 92, 6997 (1970).

78. Woodward, R.B., and Hoffmann, B., "The Conservation of Orbital Symmetry" (Academic), Verlag Chemie GmbH, Germany (1970), p. 114.

79. Glass, D.S., Boikess, R.S., and Winstein, S., Tet.Lett., 999 (1966) and references therein.

80. Frey, H.M., in "Carbene Chemistry", by Kirmse, W. (Academic), New York,(1964), p. 217.

81. Mohrbacher, R.J., and Cromwell, N.H., J.Am.Chem.Soc., 79, 401 (1956).

82. Lock, G., and Stack, K., Ber, 76, 1252 (1943).

83. Smith, L.I., and Howard, K.L., Org.Synth., 24, 53 (1944).

84. Crow, W.D., and Wentrup, Tet.Lett., 3115 (1968).

85. Huisgen, R., Angew Chem.Internat.Edn., 2, 565 (1963).

86. Vandensavel, J.M., Smets, G., and L'Abbé, G., J.Org.Chem., 38, 675 (1973).

87. Hassner, A., and L'Abbé, G. Angew Chem.Internat.Edn.Engl., 10, 98 (1971).

88. Evantova, M.S., and Shapchenko, N.I., Vestn Mosk. gos.Univ. (Khim.), 16, 71 (1961) (Chem.Abstr.,57, 7143f (1962)).

89. Mulvaney, J.E., and Savage, D., J.Org.Chem., 36, 2592 (1971).

90. Lagrave, R., Ann.Chim., 8, 363 (1927).

91. Hazen, G.G., and Rosenburg, D.W., J.Org.Chem., 29, 1930 (1964).

92. Hassner, A., J.Org.Chem., 33,2684 (1968).

93. Hassner, A., and Boerwinkle, F.P., J.Am.Chem.Soc., 90, 216 (1968).

94. Hassner, A., and Boerwinkle, F.P., Tet.Lett., 3309 (1969).

95. Hassner, A., Boerwinkle, F.P., and Levy, A.B., J.Am.Chem.Soc., 92, 4879 (1970).

96. Hassner, A., and Teeter, J.S., J.Org.Chem., 36, 2176 (1971).

97. Hassner, A., Acc.Chem.Res., 4, 9 (1971).

98. Fowler, F.W., Hassner, A., and Levy, L.A., J.Am.Chem.Soc., 89, 2077 (1967).

99. Bredereck, H., Gompper, R., and Hayer, D., Ber, 92, 338 (1955).

100. Japp, F.R., and Davidson, W.B., J.Chem.Soc., 67, 35 (1895).

101. Davidson, D., J.Org.Chem., 3, 364 (1938).

102. Knoevenagel, E., and Weissgerber, R., Ber, 26, 440 (1893).

103. Winans, C.F., and Adkins, H., J.Am.Chem.Soc., 55, 2051 (1933).

104. Ronzio, A.R., and Ekeley, J.B., Org.Synth.Coll.Vol.I, 6 (1944).

105. Thiele, J., and Ruggli, P., Ann, 393, 61 (1912).

106. Anker, R.M., and Cook, A.H., J.Chem.Soc., 323 (1941).

107. Rio, G., Ranjon, A., and Pouchot, O., C.R.Acad.Sci.Paris, 263, 634 (1966).

108. Brackman, D.S., and Plesch, P.H., J.Chem.Soc., 2188 (1952).

109. Schrimer, R.L., Ashley, W.C., and Welch, E., Org.Synth., 22, 98 (1942).

110. Kao, C.H., and Ma, S.Y., J.Chem.Soc., 2788 (1930).

111. Hatt, H.H., Org.Synth., 16, 51 (1936).

112. Day, A.C., Raymond, P., Southam, R.M., and Whiting, M.C., J.Chem.Soc.(C), 467 (1966).

113. Mackenzie, J.E., J.Chem.Soc., 121, 1697 (1922).

114. Gomberg, M., and Schoepple, C.S., J.Am.Chem.Soc., 39, 1658 (1917).

115. Ruggli, P., Ann, 414, 128 (1916).

116. (a) Ponsold, K., Ber, 95, 1727 (1962).

(b) Ponsold, K., and Schubert, G., J.Prakt.Chem., 311, 919 (1969).

Bowie, J. H. & Nussey, B. (1970). Hydrogen randomisation in negative ions. *Journal of the Chemical Society D: Chemical Communications, 1*, 17-18.

Bowie, J. H. & Nussey, B. (1970). Novel rearrangements occurring during the thermolysis of 2,3-diphenyl-2*H*-azirine. *Journal of the Chemical Society D: Chemical Communications, 1*, 1565-1566.

Simons, B. K., Nussey, B. & Bowie, J. H. (1970), Electron-impact studies—LIV: The formation of $[C_{13}H_9]^+$ in the mass spectra of benzyl phenyl ketoxime and 2,3-diphenyl-2-H-azirine. *Organic Mass Spectrometry*, *3*(7), 925–931.

Bowie, J. H. & Nussey, B. (1970), Electron-impact studies—LV: Skeletal rearrangement and hydrogen scrambling processes in the positive and negative-ion mass spectra of phenyl derivatives of elements of group IV and V. *Organic Mass Spectrometry, 3*(7), 933-940.

Bowie, J. H. & Nussey, B. (1972), Electron-impact studies—LXX: Substituent effects in the negative-ion spectra of nitroaryl esters. *Organic Mass Spectrometry*, *6*(4), 429-442.

Bowie, J. H. & Nussey, B. (1973). Thermal rearrangements of 2,3-diphenyl-2*H*-azirine. *Journal of the Chemical Society, Perkin Transactions 1*, 1693-1696.

Bowie, J. H., Nussey, B. & Ward, A. D. (1973). The reaction between 2,3-diphenyl-2*H*-azirine and phenyldiazomethane. *Australian Journal of Chemistry, 26*(11), 2547-2551.