PART I: ELECTRON IMPACT AND FIELD IONIZATION MASS SPECTROMETRY OF SULFUR ANALOGUES OF CARBOXYLIC ACID ESTERS. PART II: ELECTRON IMPACT AND FIELD IONIZATION DEFOCUSING STUDIES OF 1- AND 2-ADAMANTYL ESTERS.

BERNARD TURYAGENDA. KIREMIRE
University of Windsor

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PART I

ELECTRON IMPACT AND FIELD IONIZATION MASS SPECTROMETRY
OF SULFUR ANALOGUES OF CARBOXYLIC ACID ESTERS

PART II

ELECTRON IMPACT AND FIELD IONIZATION DEFOCUSING STUDIES
OF
1- AND 2-ADAMANTYL ESTERS

by

© Bernard Turyagenda Kiremire

A Dissertation
submitted to the Faculty of Graduate Studies
through the Department of
Chemistry in Partial Fulfillment
of the requirements for the Degree
of Doctor of Philosophy at
The University of Windsor,
Windsor, Ontario, Canada
1979
To My Parents
ABSTRACT

PART I

Electron impact and field ionization mass spectra of 5 thiolacetates (CH$_3$COSR), 5 thionacetates (CH$_3$CSOR), 5 thiolbenzoates (PhCOSR) and 7 thionbenzoates (PhCSOR) were studied. On electron impact, most thiolacetates display the acetyl ion [CH$_3$CO]$^+$ as the base peak while most thionacetates display [R-H]$^+$ as the base peak. All thiolbenzoates and thionbenzoates display the benzoyl fragment [PhCO]$^+$ as the base peak. In thionbenzoates this peak arises by a rearrangement reaction while in thiolbenzoates it arises by a simple cleavage. Characteristic features for thiolesters and thionesters are discussed, along with their field ionization mass spectra. With the aid of metastable studies, fragmentation schemes are proposed and discussed.

PART II

Electron impact and field ionization mass spectra of 1- and 2-adamantyl esters were studied. All the esters display ions corresponding to olefin (adamantene) as the base peak. The fragment at m/z 135 corresponding to direct cleavage is a significant peak. With the help of deuterium labelling and field ionization defocusing techniques, the rearrangement giving rise to the presumed olefin is shown to be a gas phase process. Further, these studies strongly suggest that the product corresponds to ionized 1,2-dehydroadamantane.
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I am greatly indebted to my advisor, Dr. G.W. Wood, for his guidance, patience and concern during the course of this work.

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<tr>
<td>a.m.u.</td>
<td>atomic mass units</td>
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<td>A.P.</td>
<td>Appearance potential</td>
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<tr>
<td>α</td>
<td>alpha</td>
</tr>
<tr>
<td>β</td>
<td>beta</td>
</tr>
<tr>
<td>base peak</td>
<td>peak representing the most abundant ion in the spectrum</td>
</tr>
<tr>
<td>but.</td>
<td>butyl</td>
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<tr>
<td>daughter ion</td>
<td>ionic reaction product</td>
</tr>
<tr>
<td>e.i.</td>
<td>electron impact</td>
</tr>
<tr>
<td>Et.</td>
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<tr>
<td>eV</td>
<td>electron volt</td>
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<tr>
<td>f.i.</td>
<td>field ionization</td>
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<td>f.i.k.</td>
<td>field ionization kinetics</td>
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<td>f.i.m.s.</td>
<td>field ionization mass spectrometry</td>
</tr>
<tr>
<td>γ</td>
<td>gamma</td>
</tr>
<tr>
<td>g.l.c.</td>
<td>gas liquid chromatography</td>
</tr>
<tr>
<td>hex.</td>
<td>hexyl</td>
</tr>
<tr>
<td>I.P.</td>
<td>ionization potential</td>
</tr>
<tr>
<td>i.r.</td>
<td>infra red</td>
</tr>
<tr>
<td>isobaric ions</td>
<td>ions of the same nominal mass but of different elemental compositions</td>
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<tr>
<td>K.E.</td>
<td>Kinetic Energy</td>
</tr>
<tr>
<td>LAD</td>
<td>lithium aluminium deuteride</td>
</tr>
<tr>
<td>Me.</td>
<td>methyl</td>
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<td>m.s.</td>
<td>mass spectrometry</td>
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<td>m/z</td>
<td>mass to charge ratio</td>
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M⁺ the ionized molecule
pent.
pentyl
Ph Phenyl
Py Pyridine
% RA Percent relative abundance
+ Radical ion (for example M⁺)
→ (full arrow) Transfer of an electron pair
→ (fish hook) Transfer of a single electron
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PART I

ELECTRON IMPACT AND FIELD IONIZATION MASS SPECTROMETRY OF SULFUR ANALOGUES OF CARBOXYLIC ACID ESTERS
Chapter 1

INTRODUCTION

In its simplest form, the mass spectrometer is designed to perform three basic functions. These are (a) to vaporize the compounds, (b) to produce ions from the neutral molecules, and (c) to separate the ions according to their mass-to-charge ratios (m/z) and to record them. The devices used to perform these functions will be described briefly in Chapter 2.

The most common technique used for the production of ions is electron bombardment. Bombardment of a polyatomic molecule with a beam of electrons results in a variety of positive ions of various relative intensities. Mass analysis of these ions results in a mass spectrum.

Numerous surveys of the spectra of classes of organic compounds have been published and correlations between mass spectra and structure established. In addition, simple rules for predicting fragmentation reactions have been presented. Application of these correlations and rules requires knowledge of the fundamental physics and chemistry of the processes by which ions are formed and decomposed to give the mass spectrum. Such processes are described in Chapter 2.

The behaviour of esters $R^1\text{-C-Y-R}^2$ under electron impact has been the subject of numerous studies within the last two decades. A substantial amount of work has been published on the normal esters ($X = Y = O$). Specific rearrangements have been widely, but apparently inconclusively, studied by deuterium labelling of various esters and the behaviour of long chain esters has been reviewed.

The analogous sulfur esters, however, have received scant attention.
The electron impact studies on these esters were initiated in 1965 with an extensive paper by McFadden in which the fragmentation patterns of S-alkyl thioesters (thioesters) \((X = 0, Y = S)\) were compared with those of the analogous normal esters. In general the fragmentation patterns of the two esters were similar. The molecular ions were considerably greater than in the analogous normal esters, but the relative abundances for rearrangement reactions were found to be lower than those of the normal esters. Of particular significance was the loss of 60 a.m.u. from the molecular ion in the thioesters. Such a reaction does not occur in the normal esters. It was shown by using esters substituted in the first and second position of the alcohol chain that the reaction occurred by a six centered transition state in which part of the alcohol portion was transferred to the carbonyl group.

\[\text{CH}_2\text{R} \quad \text{CH}_2\text{S} \quad \text{CH}_2 \quad \text{R}^1\text{C}=\text{O} \quad \text{CH}_2\text{R} \]

Recently these studies were extended to thion esters \((X = S, Y = O)\) and to the dithioesters. Ohno et al have reported electron impact spectra of simple thionbenzoates (O-alkyl thionbenzoates) \((R^2 = \text{Me, Et})\) and drawn attention to the differences in fragmentation patterns between these esters and the thioesters. The main differences lie in the rearrangement reactions observed in the two types of esters. An uncommon hydrogen rearrangement is observed in thion esters; migration of hydrogen to the thiocarbonyl group followed by \(\text{\textalpha}-\text{cleavage}\) produced a peak at \(m/z 122\) in thionbenzoates. As opposed to the
McLafferty rearrangement the hydrogen migration is observed in methyl thionbenzoate. Further, such a fragment may lose a hydrogen radical to contribute to the base peak which corresponds to the thiobenzoyl fragment \([\text{PhCS}^+]\).

\[
\begin{align*}
\text{PhC} \quad \text{CH}_2 & \quad \xrightarrow{+} \quad [\text{PhC} = \text{SH}]^+ + \text{CH}_2 = 0 \\
\text{PhC} \quad \text{O} & \quad \text{H} \quad \xrightarrow{-\text{H}^+} \quad [\text{PhC} = \text{S}]^+
\end{align*}
\]

Another interesting rearrangement observed is the migration of alkyl group to the thiocarbonyl group prior to \(\alpha\)-cleavage thus yielding a fragment corresponding to the benzoyl fragment \([\text{PhCO}]^+\).

\[
\begin{align*}
\text{PhC} \quad \text{O} & \quad \xrightarrow{\text{SR}} \quad \text{PhC} \quad \text{O} \quad \xrightarrow{-e} \quad [\text{PhCO}]^+ + \text{SR} \\
\text{S} \quad \text{R}^+ & \quad \xrightarrow{+} \quad \text{S} \quad -\text{R}^+.
\end{align*}
\]

Both these rearrangements were confirmed by metastable studies and in the case of alkyl migration, further evidence comes from the fact that \([\text{SR}]^+\) was detected.

In order to have a more complete comparison of thioesters and thionesters, these studies have been extended in the present work to include longer alkyl groups and both acetates and benzoates were investigated.
Chapter 2

PHYSICAL BASIS OF MASS SPECTROMETRY

A. Instrumentation

In a mass spectrometer, the sample to be analysed is introduced into an ionization chamber in which ions characteristic of the molecules are produced. The ions are sorted according to their mass-to-charge ratios by the action of electric and magnetic fields and a plot of the relative abundances of the ions against these ratios constitutes the mass spectrum.

Various types of mass spectrometers, many built for special applications, have been described (1,2). A typical electron impact ion source is shown in Fig. 1.1. This type of ion source, first introduced by Dempster in 1921, has since been improved in the later designs of other workers, notably by Nier(3).

Figure 1.1.
Electrons are produced from an incandescent filament or ribbon usually made from tungsten or rhenium. The electrons are accelerated towards the ionization chamber and enter it through a system of collimating slits (not shown in the figure). The kinetic energy of the electrons can be varied by changing the potential difference between the filament and the ionization chamber. The space within the ionization chamber is essentially free of electric fields and the electrons traverse it at a constant velocity. Electrons which pass through a slit at the far end of the ionization chamber are accelerated towards an electrode (trap) at a potential higher than that of the chamber and collected. The current flowing to the trap can be used to regulate the filament current to maintain a constant rate of ion production. One or two repeller electrodes are usually located within the ionization chamber. Application of a positive voltage to the repeller electrodes causes the positive ions to be repelled towards the slit A. Ions which do not escape through this slit lose their charge on the walls of the chamber.

(1) The ion accelerator

The ions which leave the ionization chamber under the influence of the repeller electrodes have very small kinetic energies. Outside the ionization chamber, they are accelerated towards a plate containing a slit (source slit) by a strong electric field. The ion accelerator contains some focusing plates designed to concentrate the ion beam on the source slit and is arranged in such a way as to minimize penetration of the accelerating field into the ionization chamber.

The kinetic energy of an ion of mass \( m \) and charge \( z \) accelerated
through a potential drop $V$ is given by $\frac{mv^2}{2}$ where $v$ is the velocity after acceleration and $\frac{1}{2}mv^2 = zV$ \hspace{1cm} (1-1)

Thus, the more massive ions will travel more slowly than the lighter ones.

(2) The magnetic analyser

\begin{figure}[h]
  \centering
  \includegraphics[width=0.5\textwidth]{magnetic_analyser.png}
  \caption{Focusing action of a 180° magnetic analyser on a monoenergetic beam containing ions of two different mass-to-charge ratios.}
\end{figure}

In a magnetic field of strength $H$, any ion will experience a force of $Hzv$, producing an acceleration of $\frac{v^2}{r}$ in a circular path of radius $r$. Hence, from Newton's second law of motion

$$Hzv = \frac{mv^2}{r} \hspace{1cm} (1-2)$$

From equations (1-1) and (1-2) one obtains

$$\frac{m}{z} = \frac{H^2r^2}{2V} \hspace{1cm} (1-3)$$

From the above equation, it is evident that ions of a given $m$ value will follow a particular path of radius $r$, and that ions of various $m$ values can be swept past the collector slit by either varying $H$ at constant $V$, or by varying $V$ at constant $H$. The former mode of operation is called magnetic scanning and the latter electric (or voltage) scanning.
(3) The electrostatic analyser

In order to reduce the image spread in the focused beam issuing from the magnetic sector, focusing energy analysers are used to ensure that the beam entering the magnetic field is as homogeneous in energy as possible. The arrangement shown in Figure 1.3 has been used successfully in this respect.

![Diagram of electrostatic analyser]

**Figure 1.3**

In the electrostatic analyser, the outer plate is at a positive potential with respect to the inner plate. If a beam of ions of various energies is injected midway between the plates and perpendicular to the direction of the electric field, some ions will describe a circular trajectory along a curve of radius $r_e$. This condition is met when the kinetic energy of these ions $\frac{mv^2}{2}$ is such that the electrostatic force $\frac{xzF}{r_e}$ is balanced by the centrifugal force $\frac{mv^2}{r_e}$, thus $\frac{mv^2}{r_e} = xzF \quad \cdots \cdots (1-4)$

where $F$ is the field strength and $x$ the number of charges carried by the ions. From equation (1-1) we have

$$\frac{mv^2}{r_e} = 2xzV \quad \text{thus} \quad r_e = \frac{2V}{F} \quad \cdots \cdots (1-5).$$

Hence ions of all masses carrying any number of charges will follow the same radius through the electrostatic analyser, provided that they are
accelerated through the same voltage $V$. Only ions with the predetermined energies $x\xi V$ will describe the radius $r_e$. Ions of greater or smaller energies will describe greater or smaller radius so that they are essentially focused out.

B. Ion formation and decomposition processes

1. Ionization and ionization potentials

It has been pointed out (4) that a 50eV electron has a velocity of $4.2 \times 10^8$ cm/sec. and will traverse molecular diameters of the order of $10^{-7}$ cm in a time of $2.4 \times 10^{-16}$ sec. If such an electron passes sufficiently close to one of the electrons in a molecule, it will repel the electron out of the molecule to give a positively charged molecular ion within this order of time. Such a period is $10^2$ faster than the fastest vibrations in organic molecules (C-H stretching vibration). Thus we may consider all the atoms to be effectively at rest during ionization. That is, the transition will follow the Franck-Condon rule, which requires that the configuration and momenta of the nuclei do not alter during the transition. Such a process is illustrated in Figure 1.4 for diatomic molecules.
The lowest energy process that can occur corresponds to removal of an electron from the highest molecular orbital. This corresponds to the vertical ionization potential (transition A in Fig. 1.4). In contrast, the adiabatic ionization potential is the energy required to remove an electron from a molecule in its lowest vibrational level, leaving the resultant ion in its lowest vibrational level (transition B in Fig. 1.4). Adiabatic ionization potentials can be measured by methods such as ultraviolet, photoionization, and photo-electron spectroscopy. These adiabatic ionization potentials are lower than vertical ionization potentials (determined by electron impact methods \(^5,6\)) by up to 0.5eV and sometimes more \(^7\).

It is important to note that simple relationships exist between molecular structure and ionization potentials \(^8\). For example in monosubstituted aromatic compounds \(C_6H_5X\), it is observed that substituents with strong electron withdrawing groups increase the ionization potentials relative to benzene while electron donating groups reduce the ionization potential relative to benzene. A good correlation is also observed between the ionization potential and the \(6^+\)-value for the substituents in both monosubstituted benzenes and substituted toluenes. A general decrease in the ionization potentials is observed as the number of \(\pi\)-electrons increases in polynuclear aromatic compounds.

It should also be mentioned that if sufficient energy is transferred to the neutral molecule during electron impact a doubly charged molecular ion \(M^{2+}\) may be generated and recorded at half the m/z value for the molecular ion. The minimum energy required to generate \(M^{2+}\) is known as the second ionization potential. Such doubly charged molecular ions
are only important in large aromatic compounds. In small compounds
where the two repulsive positive charges are in proximity doubly charged
molecular ions may not be observed.

2. Energy distribution in molecular ions

Within a few eV of the threshold for the production of positive
ions, the rate at which the positive ions are produced increases rap-
idly. This is attributed to the presence of electrons in the beam with
energies in excess of the ionization potentials of the particular
molecule. Such electrons can cause ionization by giving up most or all
of their energy, in which case the orbiting electron may be ejected from
a lower-lying molecular orbital of ionizing species.

\[
\begin{array}{cccc}
| & | & | & |\\
A & B & C & D
\end{array}
\]

Figure 1.5

Consider a neutral molecule in which the three highest occupied
molecular orbitals are represented by A(Fig. 1.5). Energy equal to the
ionization potential will be necessary to produce the molecular ion in
its ground state B, while more energetic bombarding electrons may pro-
duce the electronically excited molecular ion C. As the energy of the
electron beam is increased further, higher excited states of M⁺ such
as D may be generated. In the ionization process the energy of the
impacting electron is not imparted completely to the molecule but rather a distribution of energies is produced, with a small fraction of the molecular ions having internal energies in excess of 10 eV. Indeed there is experimental evidence to show that at 20 eV the most probable energy transfer is between 1-8 eV in excess of the ionization potential (9). The internal energy of the ions produced, is much less than the formal limits defined as 0 to \((E_{el} + E_{ch} - I.P.)\), where \(E_{el}\) is the electron beam energy and \(E_{ch}\) the maximum initial thermal energy of the molecules. The energy distribution of the molecular ions (i.e. the fractions of ions having specific energies) is not known exactly (8).

3. Residence time and ion lifetime

The period of time between the initial formation of an ion and its arrival at the collector (residence time) varies with both instrument type and conditions under which it is operated. For example, the accelerating voltage and the repeller voltage are either controllable or built-in variables from instrument to instrument. Since \(eV = \frac{1}{2}mv^2\) where \(v\) is the velocity after acceleration through a voltage difference \(V\), it follows that \(v = \sqrt{V}\) and therefore the time to reach any point on the flight path is such that \(t \approx 1/\sqrt{V}\). This time can be related to rate constant \(k\) for a particular fragmentation reaction. It has been shown (8) that ions decomposing with a rate constant of \(10^6 \text{s}^{-1}\) will give rise almost exclusively to the daughter ion while those with rate constants less than \(10^4 \text{s}^{-1}\) will almost all be recorded as parent ions. Rate constants in between, i.e. \(10^4-10^6 \text{s}^{-1}\) contribute to metastable transitions.

C. The quasi-equilibrium theory (Q.E.T.)

1. Fundamental assumptions
The quasi-equilibrium theory attempts a mathematical expression of the molecular ion decomposition in terms of the excess of vibrational energy distributed throughout the oscillators, and aims to allow calculation of the mass spectrum (10). In this discussion it is intended to emphasize that some fundamental assumptions of Q.E.T. are helpful in understanding the mass spectra of complex organic molecules. This discussion by no means covers the more detailed aspects of the approach (11,12,13) nor the R R K M version (14,15,16) of the statistical theory which, though formally different from (Q.E.T.), contains all its essential physical features.

The most important fundamental assumption is that the molecular processes leading to the formation of a mass spectrum consist of a series of competing, and consecutive unimolecular decomposition reactions of energetically excited parent ions. It is further assumed that the initial excitation energy is randomly distributed among the vibrational degrees of freedom of the ground electronic state of the parent ions at a rate which is faster than the rate of dissociation. That is, although a certain amount of energy may be produced in a specific bond at the time of ionization, this energy will flow into other bonds in times comparable to molecular vibrational periods; and decomposition results only when sufficient energy has concentrated in the particular bond(s).

Since there is a distribution of energies in the parent ions, in order to calculate the extent of competition between any two or more reactions it is necessary to calculate the rate constants (k) for any given value of internal energy (E) sufficient to bring about the various reactions. It is important to note that the operating pressure in the
mass spectrometer (ca $10^{-6}$ Torr) effectively precludes collisions so that the internal energies of the ions remain in a non-equilibrium distribution from the instant of ionization. This is in contrast to the common kinetic situation where continual energization and de-energization of the molecules by collisions results into a Maxwell-Boltzmann distribution of energies defined by temperature.

In the simplest form of the quasi-equilibrium theory, the rate constant $k$ is related to the internal energy $E$ by the following equation

$$k = \sqrt{(E - E_o)}S$$  \hspace{1cm} (1-6)

where $E_o$ is the activation energy of the reaction in question, $\sqrt{}$ is the frequency factor and $S$ is the effective number of oscillators. It can be seen from the above equation that if $(E \gg E_o)$ then the rate constant approaches the frequency factor. Thus for a simple single bond cleavage reaction in the hypothetical case where the internal energy is very large, the reaction will occur in one vibration and $k = \sqrt{} = \text{vibrational frequency of the bond in question} \left(10^{13} - 10^{14} \text{ s}^{-1}\right)$. If $E$ is slightly greater than activation energy so that $(E - E_o)/E < 1$ then the reaction will only occur when the requisite number of vibrational quanta (equal to the activation energy) have gathered in the reaction co-ordinate. The time taken for this will depend on the total number of vibrational quanta available, activation energy $E_o$, and the molecular size. The derivation of equation (1-6) involves numerous approximations. In addition, for energies near threshold the effective number of oscillators is usually taken as a fraction of the total for example $(\frac{3n - 6}{3})$, resulting in a rapid rise of $k$ with $E$. 
In rearrangement reactions, it is not a sufficient condition for the reaction to take place merely that the energy of activation for the reaction be collected in the appropriate co-ordinates. In addition, it is necessary that in the transition state a proper alignment of the atoms involved be achieved. For instance, in the loss of acetic acid from adamantyl acetate, the hydrogen atom which is to rearrange with formation of a new bond, must take up a specific orientation with respect to the atom which is to receive it (O in C=O).

![Diagram of molecular structure]

The relatively low probability of attaining such a specific orientation lowers the reaction rate, and therefore the rates of such rearrangement reactions do not approach bond vibrational frequencies even when the internal energy is very large. Rather will be lowered by some characteristic amount and this amount will be larger the more precise the geometrical orientation which is necessary for reaction.

2. Reaction competition

In terms of the Q.E.T. the abundance of fragment ions can be determined by the competition between the various fragmentation pathways. The competition depends on the relative rate coefficients for the relevant fragmentation routes and the internal energy of the fragment ions. In some reactions the competition is determined by activation energy differences and in others by the frequency factor.

Consider the k vs E curves in Fig. 1.6 for a 12 atom molecule.
If the effective number of oscillators is taken to be \( \frac{1}{3} \) of the total, then \( s = 10 \).

\[
\begin{align*}
1 \ J &= 10^{13} \ s^{-1}, E_o = 2 \text{eV} \\
2 \ J &= 10^9 \ s^{-1}, E_o = 1 \text{eV} \\
3 \ J &= 10^9 \ s^{-1}, E_o = 2 \text{eV}
\end{align*}
\]

Figure 1.6

If reactions corresponding to curves 1 to 3 are competing unimolecular reactions from a given molecular ion, then at any given value of internal energy, sufficient to cause decomposition on the mass spectrometer time-scale, reaction 3 is much slower than reaction 1, and also much slower than 2 except at very high internal energies. Hence such a reaction would not compete effectively since the abundance of the daughter ion \( (\log_{10} k > 6) \) will be negligible.

Ions with internal energies \((1.5 - 2.0 \text{eV})\) in excess of ionization potential of the molecule will undergo reaction 2 exclusively with rate
constants in the range $\log_{10} k = 4 - 6$ (metastable region). Thus the molecular ion will display a metastable peak for reaction 2. Reaction 1 will occur with the same rate constants in a narrower range of internal energies because of the higher frequency factor which causes a sharper rise of $k$ with $E_{17}$. However, in this range of internal energies it can be seen that reaction 1 proceeds much more slowly than 2 and therefore the intensity of the metastable peak due to 1 should be lower. At slightly higher internal energies eg. 2.7eV reaction 1 will occur much faster than 2 and consequently will display a more abundant daughter ion.

In general, for competing reactions, activation energies play an important part in determining the relative abundances in the low eV spectra and metastable transitions. In ions of high internal energies however, the relative reaction rates are largely influenced by the relative values of the frequency factors (Fig. 1.6). Fragmentation reactions of normal frequency factors ($10^{14} \text{ s}^{-1}$) correspond to simple bond cleavages. The relative abundance of such cleavages increases with the electron beam energy. Conversely, rearrangement reactions which are considered to have low frequency factors are often dominant in the low energy (eg. 10 - 12eV) spectra. That is, reactions with low frequency factors will only compete successfully if they have lower activation energies (see reaction 2 vs. 1).

D. Energetics of ion decompositions

In the discussion so far of the rate processes occurring in the mass spectrometer, it has been assumed that decompositions occur from the ground state of the ion which is given by the ionization potential
(I.P.). It has been argued (8) that the extra energy which must be added just to produce daughter ions \( F^+ \) in the ion source for the reaction \( M^{++} \rightarrow F^+ \) corresponds to the vibrational activation energy \( (E_o) \) for the reaction from the ground state of \( M^{++} \).

The minimum energy required to produce \( F^+ \) in the ion source is known as the appearance potential (A.P.) of \( F^+ \). Thus it is assumed that A.P. - I.P. = \( E_o \). The problem with this assumption is that A.P. - I.P. does not merely represent the energy necessary to attain the transition state, but rather the energy required to make the reaction occur with a rate constant approaching \( 10^5 \text{ s}^{-1} \), since the daughter ion \( F^+ \) must be produced within a few ps in the ion source to be detected as such. Consequently, A.P. - I.P. is generally larger than the true activation energy by an amount which corresponds to the energy necessary to raise the rate constant from zero to \( 10^5 \text{ s}^{-1} \). This extra energy is known as the kinetic shift.

1. Heats of formation

Appearance potential measurements may be employed for heat of formation determinations provided account is taken of the fact that the ion and the neutral products of a decomposition may be formed with excess kinetic and/or internal energy. For the reaction \( M + e \rightarrow F^+ + N + 2e \) we may write:

\[
\text{A.P.}(F^+) = \Delta H_f(F^+) + \Delta H_f(N) - \Delta H_f(M) + E
\]

where A.P. \((F^+)\) is the appearance potential of \( F^+ \) and the term \( E \) accounts for the fact that \( F^+ \) and/or the neutral particle \( N \) may be produced with excess energy at the threshold, i.e. \( F^+ \) and \( N \) may not be in the ground electronic states, or may be vibrationally excited, or may possess
excess K.E. when produced at the A.P.

If the heats of formation of M and N are known, then the heat of formation of F⁺ can be calculated if the excess energy can be reliably assumed to be zero, or calculated or estimated. This requires an assumption of the structure of N and knowledge of the structure of F⁺. Usually the structure of F⁺ may not be known, and indeed the purpose of the measurement may be to obtain information about the structure of F⁺ at the threshold.

It is common practice to compare the heat of formation of F⁺ obtained in the above manner with that obtained by direct ionization of a molecule (or radical) F⁺ of the same elemental composition in order to deduce the structure of F⁺. Ideally, identical heats of formation indicate identical structures at the instant of formation of the ions.

In summary, the origin of mass spectra can be explained in terms of the quasi-equilibrium theory. In this approach the reactions leading to the different fragments in the spectrum are considered as series of competing and consecutive unimolecular fragmentation reactions from the molecular ion. The abundances of the fragments observed are determined by the relative rates of these competing and consecutive reactions. The rates of the various reactions depend on the internal energy, the activation energy and on the "frequency factor" term in the rate expression. Fragmentation reactions of low activation energy will be favoured and should lead to abundant ions in the spectrum. This allows generalizations concerning the factors that stabilize fragment ions which are frequently used in interpretation of mass spectra of organic compounds.
Chapter 3

BACKGROUND STUDIES OF ESTERS $R^1-C-Y-R^2$

A. Mass spectra of alkyl esters $R^1-C-O-R^2$

Over the past two decades, a vast amount of work has appeared in the literature on esters, especially those of simple acids (18, 19, 20, 21, 22). Since it is difficult to obtain mass spectra of the acids without causing thermal degradation, acids are usually converted to the more volatile esters for examination (23, 24). The parent ions in the spectra of aliphatic esters are generally of low abundance while those of aromatic esters are usually significant, especially in short chain alkyl groups. Aliphatic esters of general formula $R^1-C-O-R^2$ usually display peaks due to the following fragments: $[R^1]^+$, $[R^1-\text{CO}]^+$, $[\text{COOR}^2]^+$, $[\text{OR}^2]^+$ and $[R^2]^+$ which result from direct cleavage, and fragments $[R^1-\text{COOH}]^+$, $[R^1-\text{COOH}_2]^+$, $[R^2-\text{H}]^{++}$ (when $R^2$ is greater than methyl), $[\text{CH}_2\text{C(OH)OR}^2]^+$ (when $R^1$ is greater than methyl) which result from rearrangement reactions (25). Specific rearrangements have been studied with the aid of deuterio compounds (20, 26, 27, 28) and the spectra of long chain esters have been reviewed by Ryhage and Stenhagen (29, 30).

The fragmentation of esters can be divided into two major classes: simple cleavage reactions and rearrangement reactions; elimination reactions being less significant.

(1) Simple cleavage reactions:

Fragmentation reactions which involve only the cleavage of a single bond in the odd-electron molecular ion ($M^+$) are classified as simple
cleavages. Such cleavages result in even-electron fragments and neutral radical species. Odd-electron species are generally less stable than even-electron. The two fragments produced by cleavage of the odd-electron molecular ion compete for the unpaired electron and their relative abundance is therefore determined by their combined stabilities, although the fragment of lower ionization potential is commonly favoured as the ionic product.

Ion stabilization through electron sharing of non-bonding electrons is a primary force in many reactions; for example the stability of an even-electron oxonium ion $\text{R}_4\text{C}=\text{O} -> \text{R}^{-}\text{C}=\text{O}^+$ is increased because ionization at the hetero atom creates a new bonding orbital. Product ion abundance is also influenced by the lability of the bond(s) cleaved and the stability of the bonds formed; decreasing bond strength in the molecular ion may be reflected in an increased relative abundance of the cleavage products. If formation of a new bond in possible, it helps to compensate for the energy required for the bond cleavage in the decomposition.

In esters of above formula, some of the direct cleavage fragments may not be primary products of a single bond cleavage in $\text{R}^{-}\text{CO}^+$, for example $[\text{R}^1]^+$ may arise by loss of carbon monoxide from $[\text{R}^1\text{CO}]^+$ and both $[\text{R}^2]^+$ and $[\text{R}^1]^+$ may give rise to smaller fragments by direct cleavage. Of the above possible fragments, those corresponding to $[\text{R}^2]^+$ and especially $[\text{COOR}^2]^+$ are usually low or negligible in the spectra of long straight chain esters (29,30). On the other hand the fragment $[\text{R}^1\text{CO}]^+$ assumes general importance depending on $\text{R}^1$; in benzoates where $\text{R}^1$ is a phenyl group (Table 1) the same fragment is usually the base peak (31). In aliphatic esters, the relative abundance of $[\text{R}^1\text{CO}]^+$
Table 1

Mass spectra of alkyl benzoates

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Ethyl</th>
<th>i-Propyl-</th>
<th>Butyl-</th>
<th>Pentyl-</th>
<th>Hexyl-</th>
</tr>
</thead>
<tbody>
<tr>
<td>[M]+</td>
<td>25.0</td>
<td>13.0</td>
<td>2.0</td>
<td>0.1</td>
<td>2.0</td>
</tr>
<tr>
<td>[R]+</td>
<td>3.0</td>
<td>11.0</td>
<td>2.0</td>
<td>5.0</td>
<td>2.0</td>
</tr>
<tr>
<td>[R-H]+</td>
<td></td>
<td>2.0</td>
<td>19.0</td>
<td>85.0</td>
<td>22.0</td>
</tr>
<tr>
<td>[PhCOOH]+</td>
<td>33.0</td>
<td>20.0</td>
<td>17.0</td>
<td>7.0</td>
<td>16.0</td>
</tr>
<tr>
<td>[PhCOOH₂]+</td>
<td>3.0</td>
<td>31.0</td>
<td>68.0</td>
<td>30.0</td>
<td>93.0</td>
</tr>
<tr>
<td>[PhCO]+</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>[M-OH]+</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ph]+</td>
<td>33.0</td>
<td>32.0</td>
<td>38.0</td>
<td>37.0</td>
<td>39.0</td>
</tr>
<tr>
<td>[PhO]+</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

a: Selected from Appendix 1(I)
decreases as the alcohol chain increases.

(2) Rearrangement reactions:

Mass spectral reactions can produce ions whose atoms have not retained the structural relationships of the original molecule. Some of these rearrangement reactions may be useful in structure elucidation but most of them give ambiguous structure information. These are termed random because extensive molecular scrambling occurs or because no specific mechanism is apparent; random rearrangements are exhibited mainly by ions whose bonds are relatively difficult to cleave and which do not have reactive radical or charge sites. Common examples include hydrocarbons, for example, \((\text{CH}_3)_3\text{CH}\) shows a \([\text{C}_2\text{H}_5]^+\) ion in its spectrum, which must arise by some complicated mechanism. Perhaps the most common random rearrangement is 'hydrogen scrambling', an example of this occurs in the mass spectrum of methyl cyclohexane where the base peak is due to \([\text{M-CH}_3]^+\), however, the labelled compound \(\text{C}_6\text{H}_{11}\text{CD}_3\) displays peaks due to \([\text{M-CHD}_2]^+\) and \([\text{M-CH}_2\text{D}]^+\) at higher relative abundance than the expected \([\text{M-CD}_3]^+\). Similar effects may be observed in the spectra of other molecules at very low electron impact energies (33). Other rearrangements occur through specific mechanisms which are well understood. Product ions from such rearrangements may be valuable in structure determination; a good example of this is the well-known McLafferty rearrangement.

(3) McLafferty rearrangement:

This rearrangement can be defined as the transfer of a gamma hydrogen to a doubly bonded atom through an energetically and sterically favoured six-membered transition state, with a beta bond cleavage (eq. 1)
The most prominent characteristic of this rearrangement is the highly specific source of the hydrogen transferred to the doubly bonded atom. In straight chain aliphatic ketones and in esters at high internal energies (70eV), various deuterium labelling experiments and experiments in compounds lacking a gamma hydrogen indicate that the transferred hydrogen migrates exclusively from the gamma position (19). In some cases, however, the participation of other sites has been reported; for example at low internal energies (34, 35) and at high internal energies in certain branched chain aliphatic ketones (35, 37) and in benzoates (38, 39). In earlier works (34-38), the participation of other sites has been attributed to a disguised randomization of hydrogens following an exclusive transfer of a gamma hydrogen. Recent experiments with n-propyl benzoate, however, indicate that the rearrangement involves direct hydrogen transfer from each position of the alkyl group without significant H/D interchange within the alkyl chain (39). Field ionization kinetic studies (f.i.k.) have shown that the lack of specificity under e.i. conditions results from competing rearrangements via different ring sizes in the transition state (40). There is substantial evidence to show that the overall reaction is stepwise (41, 42). In principle, therefore, after the initial hydrogen transfer, two competing reactions are possible (Scheme 1).
Scheme 1. Mechanism for McLafferty rearrangement

The factors that affect this rearrangement have been amply discussed by Kingston and Bursey (19). This discussion will therefore summarise facts which apply mainly to esters. It should be pointed out here that some of these factors may not be applicable in thionesters, since they are based on the presence of a carbonyl group:

(i) formation of stable ionic products provides substantial driving force for the reaction. If the olefin product is very stable, the charge will be retained on this fragment (Scheme 1). It has been shown that the charge resides preferentially on the product of lower ionization potential (43) and in general the ionization potentials for terminal olefins decrease as the alkyl group increases (44).

(ii) secondary hydrogen atoms are more readily transferred than primary hydrogen atoms.

(iii) Hydrogen atoms are more readily transferred than deuterium atoms.

(iv) the maximum interatomic distance between the hydrogen transferred and the oxygen to which it migrates is 1.8 Å; examples where the interatomic distance exceeds the maximum value can be explained by alternative mechanisms (45,46).
v) The rearrangement may be suppressed by non-interacting sites of low ionization potential in the molecule but in general the carbonyl group competes effectively with other functional groups.

Rearrangement of two hydrogen atoms:

"McLafferty + 1" reaction, sometimes called double McLafferty rearrangement is also characteristic of esters in which \( R^2 \) is larger than ethyl (22). Labelling experiments on various esters indicate that reaction is not as site-specific as the single McLafferty rearrangement (26,38,47,48,49,50). Some hydrogen scrambling may precede the formation of the product ions in some cases (48) but in general one hydrogen atom migrates more or less specifically from the gamma position, while the second hydrogen atom is abstracted randomly from the available positions. The mechanisms in Scheme 2 have been proposed (38,41). The driving force for this reaction is the stability of the neutral radical and

![Scheme 2: Proposed mechanisms for double McLafferty rearrangement.](image-url)

the resonance stabilization of the even-electron product ion. For propyl and higher esters the above rearrangement reaction is predominant over the single hydrogen rearrangement. This may be reflected in
the ratio of the product ions \((\text{R}^1\text{CXHY})_2 / (\text{R}^1\text{CXHY})\). Such an increase may be attributed to the cyclopropyl or allylic stabilization of the resulting neutral radical \((\text{R}^2\text{CHCH}=\text{CH}_2 \rightarrow \text{R}^2\text{CH}=\text{CH-CH}_2)\).

\(\beta\)-Phenethyl esters \((\text{Ph-CH}_2\text{CH}_2\text{OCR})\) on the other hand display fragmentation similar to normal aliphatic esters despite the phenyl ring. This can be attributed to the fact that the electron-rich carboxyl group is insulated from the phenyl ring by the methylene groups. It is not surprising therefore that these compounds show a definite lack of the molecular ion and the presence of the following major fragments: \([\text{R}^1]^+, [\text{R}^1\text{CO}]^+, [\text{PhCH}_2]^+, [\text{PhCH}_2\text{CH}_2] \text{ and } [\text{PhCH}=\text{CH}_2]^+\) (51). The formation of a styryl ion \([\text{PhCH}=\text{CH}_2]^+\) via McLafferty rearrangement in these esters is influenced by the nature of the alkyl group in the acyl portion of the molecule \((\text{R}^1)\). Absence of the fragment corresponding to double McLafferty rearrangement is not surprising since structurally, these esters are similar to ethyl esters which seldom undergo rearrangement of a second hydrogen (31).

B. Mass spectra of thioesters. \(\text{R}^1\text{C}^\cdot\text{Y-R}^2\)

A number of groups (52,53) have speculated on the involvement of sulfur 3d-orbitals in the fragmentation of S-alkyl thioesters \((\text{X}=\text{O}, \text{Y}=\text{S})\) to explain differences between their behaviour and that of alkyl esters \((\text{X}=\text{Y}=\text{O})\). Such speculations may be extended to explain the differences in behaviour of S-alkyl thioesters and O-alkyl thioesters \((\text{X}=\text{S}, \text{Y}=\text{O})\) in terms of the differences in electronic structures of the stabilities of the thiocarbonyl group and the carbonyl group. Like oxygen, sulfur has two unshared valence-shell pairs in its lowest valence state, but unlike oxygen, sulfur has a large atomic core.
Such a large core accounts for the low ionization potential of the unshared electrons on sulfur (compared to oxygen) and for the larger volume of thiocarbonyl groups. Further, unlike oxygen, sulfur has a strong tendency to expand its electron shell by using the vacant 3d-orbitals (54). There exists about 40 Kcal/mole of difference between (C=S) and (C=O)π-bond energies (54,55) which can be attributed to the low efficiency of (2p-3p)π-overlapping in comparison with that of 2p-2p. Ionization potential measurements in ureas and thioureas $\text{R}_1^1\text{N}=\text{C}=\text{N}\text{R}_2^2$ indicate that the ionization takes place from the nitrogen in urea (X=O) while it takes place from the sulfur in thiourea (X=S) (56). It can therefore be inferred from these data that thiocarbonyl and carbonyl groups have the following characteristic features (54):

i) The π-electrons in a thiocarbonyl group are more localized than those in a carbonyl group; therefore the thiocarbonyl carbon bears more positive charge than the carbonyl carbon.

ii) The non-bonded electrons on the thiocarbonyl sulfur are more ionizable than those on the carbonyl oxygen.

Evidently these characteristics are very important in mass spectrometry where the compounds are ionized first before unimolecular decomposition takes place and throughout this work note will be taken of how these differences interact in the electron impact induced fragmentation of S-alkyl thioesters and O-alkyl thioesters.

a) S-alkyl thioesters (X=O, Y=S)
Although a substantial amount of work done on aliphatic S-alkyl thioesters (57) reveals fragmentation patterns similar to that of the alkyl esters (X=Y=O), all rearrangements observed have been assumed to follow the same mechanisms; for example no labelling experiments have been performed to justify the hydrogen rearrangements such as the McLafferty rearrangement or loss of elements of thioethylene oxide. As for aromatic esters, the meagre information available is limited to short chain alkyl groups. In general, simple cleavage on electron impact produces fragments analogous to those of alkyl esters. \([R^1CO]^+, [R^1]^+, [R^1COS]^+, [COSR^2]^+, [SR^2]^+\) and \([R^2]^+\) (Table 2); of these fragments, \(COSR^2\), \(SR^2\) and \(R^2\) carry very negligible ion current and may be absent in higher molecular weight thioesters. The ions \([R^1]^+\) and \([R^1COS]^+\) are minor for small alkyl groups except in branched chain thioesters. When the molecular ion is very low, however, \(R^1COS\) may be a valuable indication of sulfur, the presence of which is confirmed by the isotopic \(^{34}\)S ion fragment. The fragment \([R^1CO]^+\) is usually prominent and frequently the base peak in both aliphatic thioesters (57) and thiobenzoates (53, 58).

Rearrangement reactions similar to those in the alkyl esters have been observed (57). The fragments \([CH_2COSHR^2]^+\) and \([R^2-H]^+\) due to McLafferty rearrangements are much weaker in aliphatic thioesters than in alkyl esters. The fragments \([R^1COSH]^+\) and \([R^1COSH_2]^+\) formed when \(R^2\) is ethyl or larger, are relatively important. As \(R^1\) increases in size, however, this mode of ionization decreases. In thioesters where the acyl portion is aliphatic, the above fragments occur at masses 76 to 77, 90 to 91, 104 to 105, etc., fragments which might correspond to benzene and alkyl substituted benzene fragments; thus the fragments
Table 2

Mass spectra of thioacetates ($^{13}C_{SR}^2$)...

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Methyl-</th>
<th>Propyl-</th>
<th>Butyl-</th>
<th>Pentyl-</th>
<th>Hexyl-</th>
</tr>
</thead>
<tbody>
<tr>
<td>($[M]^+$</td>
<td>49.1</td>
<td>17.1</td>
<td>15.7</td>
<td>8.4</td>
<td>7.4</td>
</tr>
<tr>
<td>($[R^1CO]^+$</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>($[R^1]^+$</td>
<td>(3.7)$^b$</td>
<td>1.0</td>
<td>0.7</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>($[R^1COS]^+$</td>
<td>3.9</td>
<td>3.3</td>
<td></td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>($[COSR^2]^+$</td>
<td>15.8</td>
<td>3.3</td>
<td>2.7</td>
<td>10.9</td>
<td>15.9</td>
</tr>
<tr>
<td>($[R^2]^+$</td>
<td>3.7</td>
<td>(100)</td>
<td>3.0</td>
<td>2.8</td>
<td>3.1</td>
</tr>
<tr>
<td>($[R^2-H]^+$</td>
<td>9.6</td>
<td>17.5</td>
<td>16.8</td>
<td>17.3</td>
<td></td>
</tr>
<tr>
<td>($[R^1COSH]^+$</td>
<td>4.9</td>
<td>2.5</td>
<td>3.1</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>($[R^1COSH_2]^+$</td>
<td>2.2</td>
<td>4.8</td>
<td>4.8</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>($[M-60]^+$</td>
<td>1.6</td>
<td>8.9</td>
<td>7.6</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>($[M-74]^+$</td>
<td>1.1</td>
<td></td>
<td>3.6</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>($[M-88]^+$</td>
<td></td>
<td></td>
<td>1.3</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>($[M-SH]^+$</td>
<td>0.7</td>
<td>1.2</td>
<td>1.4</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>($[M-H_2O]^+$</td>
<td>0.8</td>
<td>0.2</td>
<td>0.5</td>
<td>1.3</td>
<td>0.3</td>
</tr>
<tr>
<td>($[SH_3]^+$</td>
<td>0.7</td>
<td>0.5</td>
<td>0.5</td>
<td>1.3</td>
<td>0.3</td>
</tr>
<tr>
<td>($[CH_3S]^+$</td>
<td>15.8</td>
<td>6.5</td>
<td>6.1</td>
<td>4.1</td>
<td>3.7</td>
</tr>
<tr>
<td>($[M-RCHO]^+$</td>
<td>7.2</td>
<td>10.4</td>
<td>3.4</td>
<td>4.1</td>
<td>2.6</td>
</tr>
</tbody>
</table>

a Underlined entries are the most abundant ions.

b Entries in brackets are isobaric, with other modes of ionization and the figure given may be due to that other mode entirely.

c Blank entries designate modes of ionization not observed or unimportant.

* See reference (57).
should be regarded carefully in samples that contain these partial structures.

In alkenyl and aryl thioacetates (S9) transfer of a hydrogen from the acetyl group leads to the elimination of a ketene. This transfer of a hydrogen presumably occurs through a six-centred transition state in which case the hydrogen migrates to the benzene ring (in aryl thioacetates) and to the double bond in alkenyl thioacetates rather than to the carbonyl group.

\[
\begin{array}{c}
\text{R'} \\
\text{S} \\
\text{R''} \\
\text{H} \\
\text{R'''}
\end{array}
\rightarrow
\begin{array}{c}
\text{R'} \\
\text{S} \\
\text{R''}
\end{array}
+ \text{CH}_2\text{CO}
\]

In aliphatic thioesters, a prominent elimination reaction is loss of thioethylene oxide (\(\text{SCH}_2\text{CH}_2\)); the mechanism proposed for its formation involves a six-membered transition state (Scheme 3). The only evidence available to support the mechanism is the observation of corresponding fragments in \(\alpha\)-branched chain thioesters; it should be noted however, that the mechanism could be more complicated than that proposed, since, in addition to elimination of \(\text{SCH}_2\text{CH}_2\), loss of \(\text{S(CH}_2\text{)}_3\) and \(\text{S(CH}_2\text{)}_4\) fragments in equally substantial amounts are observed in \(\text{S-pentyl thioesters and S-hexyl thioesters respectively. There is no equivalent elimination in the mass spectra of alkyl esters, although the mechanism may be comparable to the weak mode of ionization leading to loss of (OCH}_2\text{), since both fragments are lost from the centre of the molecule by an acyclic mechanism.}

\[
\begin{array}{c}
\text{R} \\
\text{C} \\
\text{S}
\end{array}
\rightarrow
\begin{array}{c}
\text{R'} \\
\text{C} \\
\text{S}
\end{array}
+ \text{R'}\text{C}O\text{CH}_2\text{R}
\]

Scheme 3: Proposed mechanism for elimination of \(\text{SCH}_2\text{CH}_2\)
Other eliminations noted in aliphatic thioesters, for example loss of a sulfhydryl radical (SH) and elements of water (H₂O) are negligible. Elimination of water (H₂O) appears to require at least five carbons in the mercaptan chain of the aliphatic thioesters.

(b) O-Alkyl thioesters (X=S, Y=O) and dithioesters (X=Y=S).

In contrast to both the carboxylic acid esters and S-alkyl thioesters, little is known on the mass spectrometry of O-alkyl thioesters (20,60,61,62) and the dithiocarboxylate acid esters (63). Studies on the O-alkyl thioesters were initiated to shed some light on the stability of the thioacyl cation and on the effect of sulfur in a thiocarbonyl group on the fragmentation. Thus Ohno et al (60,61) compared the mass spectra of simple O-alkyl and S-alkyl thioesters (R=Me, Et) and established that simple O-alkyl thioesters give fragments analogous to their oxygen counterparts. (Table 3).

The base peak in the spectrum of O-alkyl thioesters corresponds to a thioacyl fragment [RCS]⁺ produced by α-cleavage, and the second highest peak is the molecular ion, which is in contrast to the thioesters. Other significant peaks correspond to [Ph]⁺ and [C₄H₃]⁺ ions respectively at m/z 77 and 51 for thiobenzoates. Thus successive fragmentations 1, 2 and 3 are most important for simple O-alkyl thioesters as has been reported for alkyl esters (31).

\[
\text{[Ph-S-OR]}^+ \rightarrow_1 \text{[Ph-C=S]}^+ \rightarrow_2 \text{[Ph]}^+ \rightarrow_3 \text{[C₄H₃]}^+
\]

Although transitions 2 and 3 were justified by metastable studies, the metastable transition for step 1 was observed neither in O-alkyl thiobenzoates nor in dithioesters (X=Y=S). The differences between S-alkyl thioesters and O-alkyl thioesters are displayed mainly in rearrangement ions: At low internal energies in O-alkyl thioesters,
Table 3.

Mass spectra of thion and thiolbenzoates (PhCYR)*

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Methyl-</th>
<th>Ethyl-</th>
<th>Methyl-</th>
<th>Ethyl-</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhCS]⁺</td>
<td>100</td>
<td>100</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>[PhCO]⁺</td>
<td>5.5</td>
<td>90.9</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>[PhGSH]⁺⁺⁺</td>
<td>21.6</td>
<td>44.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PhCOSH]⁺⁺⁺</td>
<td></td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PhCH₂]⁺</td>
<td>7.8</td>
<td>1.0</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>[Ph]⁺</td>
<td>27.9</td>
<td>64.0</td>
<td>65.2</td>
<td>56.4</td>
</tr>
<tr>
<td>[PhS]⁺</td>
<td>5.7</td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[RO]⁻</td>
<td></td>
<td>4.6</td>
<td>0.1</td>
<td>2.1</td>
</tr>
<tr>
<td>[RS]⁺</td>
<td>1.8</td>
<td>1.6</td>
<td>3.4</td>
<td>1.5</td>
</tr>
<tr>
<td>[M-SH]⁺⁺⁺</td>
<td>6.0</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[M-OH]⁺⁺⁺</td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>[M]⁺⁺⁺</td>
<td>63.0</td>
<td>67.6</td>
<td>15.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

* See reference (61)
the base peak shifts from \( R^1-C≡S \) to \( R^1-C≡O \) suggesting alkyl migration to the thiocarbonyl group prior to \( \alpha \)-cleavage. (Scheme 4). This rearrangement was confirmed by metastable studies, and the presence of a fragment corresponding to \([SR]^+\) in the mass spectra of the O-alkyl thioesters.

\[
\begin{align*}
\text{R} & \quad \text{C} & \quad \text{O} & \quad \text{SR}^2
\end{align*}
\]

Scheme 4: Mechanism for migration of alkyl group

A similar rearrangement was observed in S-alkyl thioesters, although to a very negligible extent. A control experiment confirmed that thermal alkyl-migration did not occur under the experimental conditions. Thus this rearrangement is similar in one respect to Schonberg rearrangement which will be discussed later. While in both rearrangements sulfur is necessary for the four-centred transition state, in Schonberg rearrangement the sulfur must be in a thiocarbonyl function.

Another rearrangement which seems to be unique to O-alkyl thioesters is the migration of a single hydrogen atom to the thiocarbonyl moiety

\[
\begin{align*}
\text{H} & \quad \text{R}^2 & \quad \text{S} \\
\text{R} & \quad \text{C} & \quad \text{O} & \quad \text{R}^1-C≡\text{SH} & \quad \text{R}^2\text{CH}=\text{O} & \quad 1
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{R}^1 & \quad \text{S} \\
\text{R} & \quad \text{C} & \quad \text{O} & \quad [\text{RCS}]^+ & \quad \text{H}^+ \\
\text{R}^2 \quad \text{C} & \quad \text{S} & \quad [\text{RCSH}]^+ & \quad \text{R}^2\text{CH}=\text{O} & \quad 2
\end{align*}
\]

Scheme 5: Rationalization for the formation of \([\text{RCSH}]^+\).
followed by \( \alpha \)-cleavage (Scheme 5). As opposed to McLafferty rearran-
gement, this rearrangement takes place even in O-methyl thioesters.

It is difficult to ascertain whether mechanism 1 or 2 or both are
correct. However, studies on dipole moments of thioesters in liquid
phase strongly suggest that the alkyl group exists almost completely in
the syn-position to the thiocarbonyl sulfur and it is also known that
under electron impact, a hydrogen atom migrates to a hetero atom more
frequently than to a carbon, which seems to favour mechanism 1 over
2 (61).

The elimination of a sulfhydryl radical is very prominent and in
simple thioesters it is much more significant than the analogous
elimination of a hydroxyl radical observed in S-alkyl thioesters (Table
3).

(c) Dithioesters (X=Y=S) (63).

The mass spectra of dithioesters show definite similarities to
those of alkyl esters (X=Y=O). In simple benzoates studied so far, the
base peak corresponds to the thiobenzoyl fragment which is produced by
\( \alpha \)-cleavage. The second largest peak [Ph]\(^+\) also corresponds to \( \alpha \)-cleavage
while the other significant peak corresponds to [C\(_4\)H\(_3\)]\(^+\). The last two
peaks may not be primary fragment ions but may arise from the first
fragment by successive fragmentations.

\[
\text{[Ph-C-SR]}^+ \xrightarrow{\alpha} \text{PhC=S}^+ \xrightarrow{\alpha} \text{[Ph]}^+ \xrightarrow{\alpha} \text{[C\(_4\)H\(_3\)]}^+
\]

\( R = \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{n-C}_4\text{H}_9 \).

Unlike alkyl benzoates but similar to O-alkyl thiobenzoates, a meta-
stable transition for step (\( \bar{a} \)) is not observed. This may imply that
the fragment [PhCS]\(^+\) is formed only in ion source. McLafferty
rearrangement fragments [PhCSSH]\(^+\), [PhCSSH\(_2\)]\(^+\) are observed. [PhCSSH]\(^+\)
contributes to the base peak [PhCS]⁺ by loss of a sulfhydryl radical. This behaviour is again similar to that observed in 0-alkyl thioesters. The double hydrogen rearrangement product [PhCSSH₂]⁺ does not seem to be very significant in these esters (Table 4) probably because θ-cleavage is a much more favoured process here. The migration of hydrogen to the thiocarbonyl group observed in 0-alkyl thioesters (Scheme 5) is not observed here.

C. Skeletal rearrangements in thioesters

Skeletal rearrangements are often quite abundant in the mass spectra of sulfur compounds (64). Recently Tomer et al (52, 58, 65) have reported rearrangements which involve sulfur migrations. In alkyl phenoxy thioacetate, for example (52), fragmentation through a three-centred transition state (Scheme 6), initiates the expulsion of PhO and CO to give CH₂=S–CH₂CH₃. It is postulated that the 3d orbitals on sulfur influence this fragmentation since the driving force for such a reaction is not obvious.

Scheme 6  Mechanism for formation of CH₂=S–CH₂CH₃

In thiophenoxy thioacetates (65), the sulfur in the thioacetate migrates to the benzene ring by a six-membered cyclic transition state (Scheme 7) to give the fragments [PhS–CH₂CH₃]⁺ and [C₆H₅S(SCH₂CH₃)]⁺.
Scheme 7  Mechanism for formation of $[\text{PhSCH}_2\text{CH}_3]^+$ and $[\text{C}_6\text{H}_5\text{S}(\text{SCH}_2\text{CH}_3)]^+$

In S-ethyl thiobenzoate, migration of sulfur to the benzene ring by a four-membered cyclic transition state (Scheme 8) leads to a fragment at $m/z$ 109 corresponding to $[\text{PhS}]^+$. The mechanism for formation of this fragment involves elimination of a (CHO) fragment from a McLafferty rearrangement product ion. Migration of sulfur to the ring has been confirmed by carbon-13 labelling experiments (58). In addition, expulsion of fragments (CHO) and (CHS) has been observed from the molecular ion of thiobenzoic acid. (66)
Table 4

Mass spectra of dithioesters<sup>a</sup> (PhCSR)

<table>
<thead>
<tr>
<th>m/z</th>
<th>Methyl-</th>
<th>Ethyl-</th>
<th>Propyl-</th>
<th>Butyl-</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ph].&lt;sup&gt;+&lt;/sup&gt;</td>
<td>4.5</td>
<td>19.2</td>
<td>28.6</td>
<td>16.3</td>
</tr>
<tr>
<td>[M].&lt;sup&gt;++&lt;/sup&gt;</td>
<td>69.9</td>
<td>40.0</td>
<td>21.0</td>
<td>24.0</td>
</tr>
<tr>
<td>[PhS].&lt;sup&gt;+&lt;/sup&gt;</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PhSH].&lt;sup&gt;++&lt;/sup&gt;</td>
<td>2.4</td>
<td>2.9</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>[PhCS].&lt;sup&gt;+&lt;/sup&gt;</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>[PhCSH]&lt;sup&gt;++&lt;/sup&gt;</td>
<td>9.1</td>
<td>8.8</td>
<td>8.5</td>
<td>8.4</td>
</tr>
<tr>
<td>[PhCSSH].&lt;sup&gt;++&lt;/sup&gt;</td>
<td>7.2</td>
<td>17.5</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>[PhCSSH&lt;sub&gt;2&lt;/sub&gt;].&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.7</td>
<td>1.8</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>[R].&lt;sup&gt;+&lt;/sup&gt;</td>
<td>3.0</td>
<td>2.7</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>[R-H].&lt;sup&gt;+&lt;/sup&gt;</td>
<td>5.6</td>
<td>2.3</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>[R-2H].&lt;sup&gt;+&lt;/sup&gt;</td>
<td>5.2</td>
<td>6.3</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> See appendix 1 (II)
Perhaps the most common skeletal rearrangement is the migration of the alkyl group to sulfur in a thion function by a four-membered transition state (60,61,67,68,69). In O-alkyl thioesters (Scheme 4), the alkyl group migrates to the thiocarbonyl group prior to α-cleavage (60,61). Heating samples of O-alkyl thioesters does not induce this rearrangement, indicating that the rearrangement is induced by electron impact. In thioncarbonates, alkyl migration to thiocarbonyl group causes rearrangement to thiolcarbonates. Chemical precedent for this transition exists in the Schonberg rearrangement (67). When heated to 250°-300° for 0.5 hr. to 3 hr. diaryl thioncarbonates rearrange to the corresponding thiolcarbonates in an intramolecular, four-centre process (68) and this provides an efficient way of converting phenols to thiophenols.

\[
\text{PhO-C} \xrightarrow{\Delta} \text{PhS-C-Ph} \xrightarrow{\text{H}_2\text{O}, \text{OH}} \text{PhSH}
\]

That the rearrangement taking place in the mass spectrometer for the same compounds is a true electron impact-induced process was shown by heating thioncarbonates at conditions more vigorous thermally than in the mass spectrometer (69). The infrared spectrum of the product was identical with that of the starting material (no >CO absorption), indicating that the rearrangement is electron impact-induced in the mass spectrometer. This isomerization has been attributed to the difference in dissociation energies of (C-S) bond and the (C-O) bond, and the relative stabilities of the acyl fragments \([R^1CS]^+\) and \([R^1CO]^+\) in thiolcarbonates (70).

D. Photochemical and thermolytic analogies to the mass spectral process.

Mass spectral processes are usually described as 'analogous' or 'parallel', to reactions occurring under conventional chemical conditions.
such as thermal processes, photolysis and other processes. However, because species in the mass spectrometer often contain one electron less than the analogous species and because their structure remain largely unknown, similarities between the two processes can at best be described as apparent. Two processes which have received attention in this respect are photochemical and thermochemical. Numerous studies of the inter-relationship between mass spectrometry and photochemistry have been carried out in the hope that the photochemical process will be a useful guide to the prediction of mass spectrometric ones and vice-versa.

Perhaps the most frequently cited analogy in the case of carbonyl compounds is the Norrish type II rearrangement. The apparent similarity between McLafferty rearrangement and the Norrish type II photochemical process in solution and in the gas phase was first noted by Nicholson (71) and by Martin and Pitts (72).

The photochemical process follows the reaction path shown in Scheme 9, for 2-pentanone.

![Scheme 9](image)

**Scheme 9** Mechanism for Norrish type II photochemical process.

Assuming, by analogy with the photochemical process, that the mass spectrometric process was not concerted, it was possible to explain puzzling features of the mass spectra of certain $\Delta^2$-unsaturated esters, 3-chloroalkanoic acids, and ketones (73). However, Bentley and Johnstone (7) have argued that such reasoning by "analogy" is not reliable
since the products and mechanism of the mass spectrometric and other apparently similar chemical processes are usually different. Early comparisons of the parallels between Norrish type II process and McLafferty rearrangement have been reviewed by Meyerson and McCollum (74). In carbonyl compounds, the Norrish type II process has been extensively studied for ketones, aldehydes, carboxylic acids and esters (75,76); a gamma hydrogen is transferred to the carbonyl group to give an enolic product in a stepwise manner (77). Like the McLafferty rearrangement, this process does not take place when the migrating hydrogen is vinylic (78). Both rearrangements are absent in isopropyl pyruvate, which instead yields the products in (Scheme 10), while gas phase photolysis of pyruvic acid yields identical products to those observed in the mass spectrum (Scheme 11) (79).

\[
\begin{align*}
\text{CH}_3\text{C} & \equiv \text{C} \text{OCH(CH}_3)_2 \quad \text{hv} \quad \text{CH}_3\text{COCH}_3 + \text{CO} \\
 & \quad \text{e} \quad [\text{CH}_3\text{CO}]^+ + [\text{C} \equiv \text{OCH(CH}_3)_2]^+
\end{align*}
\]

**Scheme 10** Photochemical and e.i. induced decomposition of isopropyl pyruvate.

\[
\begin{align*}
\text{CH}_3\text{C} & \equiv \text{C} \text{OH} \quad \text{hv} \quad \text{CH}_3\dot{\text{C}}: + \text{CO}_2 \\
 & \quad \text{e} \quad \text{CH}_3\dot{\text{C}}=\text{OH} + \text{CO}_2
\end{align*}
\]

**Scheme 11** Photochemical and e.i. induced decomposition of pyruvic acid.

On the other hand there are several cases where the photochemical and mass spectrometric reactions do not parallel each other, for example certain macrocyclic ketones undergo McLafferty rearrangement but do not
parallel each other, for example certain macrocyclic ketones undergo McLafferty rearrangement but do not form type II cleavage products (80). Similarly, a comparison of the mass spectral (81) and photochemical (82) behaviour of some amino ketones concludes that correlations of mass spectral and photochemical behaviour is limited because electronic excitation is more localised in the lowest excited states of molecules than is charge in electron impact produced molecular ions. Thus, although the two reactions resemble each other in many respects caution should be exercised in extrapolating from one to the other. Similar studies have been carried out with thion and thiol esters over the past few years. Photolysis of O-alkyl thioesters Ph-CO(\(\text{CH}_2\))\(_2\) R yields olefins and thiobenzoic acid in quantitative yields if R is capable of conjugation with the resulting olefin. Low yields are obtained if R is not capable of conjugation with the resulting olefin (83, 84).

![Chemical structure](image)

A comparison of the photochemical behaviour of the alkyl benzoates and S-alkyl thiobenzoates to their behaviour in mass spectrometry (52) shows that the major product in alkyl benzoates is benzoic acid while \(\alpha\)-cleavage in S-alkyl thiobenzoates makes the photochemical reaction difficult. This preference for sulfur-acyl bond cleavage in photo-decomposition also observed in thiocarboxylates (85) can be attributed to the low dissociation energy of the (C-S) bond compared to (C-O) bond.
The mass spectrum of S-pentyl thiobenzoate also indicates preference for \( \sim \)-cleavage leading to the benzoyl fragment as a base peak, either directly or as a result of decomposition of thiobenzoic acid fragment \([\text{PhCOSH}]^+\); inefficiency in the formation of thiobenzoic acid following gamma hydrogen abstraction may be attributed to the interaction of the sulfur 3d-orbitals with the carbonyl group which decreases the ability of the carbonyl oxygen to abstract hydrogen.

\[
\begin{array}{c}
\text{PhC} \quad \text{S} \quad \text{R} \\
\text{O} \\
\end{array}
\quad \leftrightarrow \quad 
\begin{array}{c}
\text{PhC} \quad \text{S} \quad \text{R} \\
\text{O}^- \\
\end{array}
\]

Although product ions to support such an assumption are not observed in thiol benzoates, ionization at sulfur in presence of a carbonyl group is not uncommon (Schemes 6 and 7).

Although less documented, the thermochemical behaviour of thioesters is equally important and may produce the same products as the McLafferty rearrangement. S-methyl xanthates undergo the Chugaev reaction to produce olefins and xanthic acid, specifically by a cis-elimination mechanism (87,88,89,90).

\[
\begin{array}{c}
\text{Z} \quad \text{X} \quad \text{H} \quad \text{Y} \quad \text{R'} \\
\end{array}
\quad \rightarrow \quad 
\begin{array}{c}
\text{Z} \quad \text{X} \quad \text{H} \\
\text{Y} \\
\end{array}
\quad + \quad 
\begin{array}{c}
\text{Z} \quad \text{Y} \quad \text{R'} \\
\end{array}
\]

\( Z = \text{SCH}_3 \)

\( Y = \text{O} \)

\( X = \text{S} \)

A similar preference for cis-elimination is found in the mass spectrometric behaviour of the same compounds (89,91,92), and in S-alkyl thioacetates (92).
It is noted that thermolysis of thioesters could offer an attractive way of eliminating elements of hydrogen sulfide ($H_2S$) from thiols since direct thermolysis and mercaptans to alkenes has a much higher activation energy. The behaviour of thionacetates on pyrolysis is similar to that of the thiolacetates (93). The major products correspond to olefins and thiocacetic acid, in addition this elimination is accompanied by isomerization to the thiolacetate (53).

The corresponding acetates, however, undergo the elimination at a much slower rate, a fact which can be attributed to the bond strength of the ($C=S$) and ($C=O$); in the transition state above, the relatively weaker ($C=S$) is breaking while the stronger ($C=O$) is forming from ($C=O$); such a favourable process ($D(C=O)-(C=S)$ ca $40 \text{ Kcal mol}^{-1}$) is not available to the normal acetates. Further, sulfur is more nucleophilic than oxygen and may be expected to attack the $\beta$-hydrogen more readily.

E. The Metastable Ion Techniques

Metastable ions arising from ion decompositions outside the mass spectrometer ion source, are used routinely in the interpretation of
mass spectra and for the elucidation of ion structures, reaction pathways and decomposition energetics in mass spectrometry. Their use has been the subject of a large number of papers, several reviews (94,95) and a major book (1) and needs no elaboration here. Different mass spectrometers have different metastable characteristics, determined mainly by the geometry of their ion optics; the work described here takes advantage of both metastable scanning modes of a Varian CH-5 DF mass spectrometer with reverse Nier-Johnson geometry.

(1) Formation of metastable.

Fragmentation processes do not take place exclusively in the ion source but also over part of the path of flight within the mass spectrometer. The ion velocity \( v \) for each mass spectrometer is given by the relationship:

\[
v = \sqrt{\frac{2eV}{M}} = \sqrt{\frac{2 \times \text{charge} \times \text{Accelerating potential}}{\text{mass}}}
\]

Thus in an instrument with an accelerating potential of 3000 V, a particle of around 100 a.m.u. attains a velocity of \( 7 \times 10^4 \) m/sec. Such a particle will traverse the distance from the ion source to the detector (1.5 m in a double-focusing instrument such as varian-MAT CH-5 DF) in ca \( 10^{-5} \) sec. Ions with a mean lifetime of this order can therefore decompose during their journey to the detector; these are described as metastable. The K.E. of the mother ion \( M_1 \) achieved during acceleration in the ion source is divided between the daughter ion \( M_2 \) and the neutral particle \( N \) which continue their journey in accordance with their reduced K.E. If these ions originate in the region of an electrical or magnetic field, they are deflected to different extents depending on their point of origin. Therefore such ions cannot be focused and do not give an
evaluable peak in the detector. If, however, the origin of a specific
type of ion is in the field-free region, all of them are similarly
influenced by the next field and can be effectively focused into a peak
(metastable peak) at the detector.

(2) Defocusing techniques

There are two metastable defocusing techniques which can be used
to define all the transitions leading to a particular daughter ion occurring
in the field free regions.

These are:

(a) Scanning the accelerating voltage at a fixed ESA voltage (96)

and

(b) Scanning the ESA voltage at a fixed accelerating voltage which

is described under DADI technique (96).

Both techniques were used in this work although the first one was
preferred because our instrument is equipped with an accelerating voltage
which can be externally controlled.

a) In this defocusing technique, a selected daughter ion \( M_2 \) is

focused at the collector at a reduced accelerating voltage \( V_o \), the

magnetic current is also set to observe \( M_2 \), the accelerating voltage is

then increased to focus the main beam and transmit the precursor ion \( M_1 \)
at an accelerating voltage \( V \). The precursor ion \( M_1 \) is related to the
daughter ion by the equation:

\[
M_2 = M_1 \times \frac{V}{V_o}
\]

Thus, knowing the initial voltage \( V_o \), \( M_1 \) can be calculated by determining \( V \).

b) DADI technique

Direct analysis of daughter ions (DADI) was first put forward by
Maurer et al. in 1971. Later in the same year Beynon and Cooks published the same method under the names MAIKES (mass analysed ion kinetic energy spectrometry) (97). Recently this method has been used in structural elucidation problems where classical mass spectrometry would be useless (97,98).

In principle a metastable ion may decompose not only in the first field-free region but also anywhere in its path within the mass spectrometer, particularly in the second field-free region of a double focusing instrument. (Fig. 1.7). In this case the daughter products from these metastable ions can be focused on the detector by decoupling and alteration of the second deflection field and so measured. There is an appreciable difference from the process in the first field-free region. The second field-free region contains only those particles that have already passed the first deflection field, the others having been discharged. Thus if decomposition of metastable particles is observed in the second field-free region, they must have originated from ions selected by the first deflection field. If it were possible to select a single ionic species by means of the first deflection field, then the assignment of the products of decomposition in the second field-free region would be simple. Such conditions are met in the double focusing instruments with reverse Nier-Johnson geometry where the magnetic field precedes the electrostatic field. Here the first field achieves mass separation so that only those ions having a mass fixed by the magnet reach the second field-free region.

Decomposition of this species generates daughter ions whose origin is characterised physically, i.e. the genetic connection between the precursor ion fixed by the magnet and its daughter products is ensured. In practice the electric field is decoupled first and then varied. The
magnetic field is tuned for a particular precursor ion of interest at full accelerating voltage, the decoupled ESA voltage is then decreased starting from the coupled value $E_0$. Each peak occurring at ESA voltages $E$ represents a daughter ion from decomposition of the preselected ion.

Information regarding metastable transitions will be represented by the voltages at which the particular peaks are observed. $E_0 (V_o)$ corresponds to the initial value set for a particular peak of interest and $V_n$ corresponds to the mother ion(s), while $E_n$ corresponds to the daughter ion(s) derived from the known fragment peak of interest (See appendix 4).

F. Field ionization mass spectrometry of esters

In field ionization, molecules are subjected to field strengths of the order of $10^8$ V/cm. With such high fields, the most loosely bound electron in the molecule is removed to give a ground state ion having little excess vibrational energy. Ions are then collected very soon after ionization because of the high accelerating voltage used so that within this short time very few bond vibrations are likely to occur. Because of these two factors, the likelihood of much fragmentation occurring is small. Consequently, molecular ions are always abundant with very few fragments.

Because simple bond cleavages have a higher frequency factor than rearrangement reactions, the former reactions are favoured in those ions decomposing in the ion source in f.i.m.s., due to their shorter lifetimes ($10^{-9} - 10^{-12}$ sec.), as compared to $10^{-6}$ sec. for e.i. It is not surprising, therefore, that even prominent rearrangements such as McLafferty rearrangement, are of very low intensity in f.i.m.s., and indeed the first searches for this rearrangement were futile (99). Later studies started to uncover peaks of low relative abundance due to this rearrangement
Fig. 1.7 Schematic diagram of a DADI mass spectrometer.

(Reverse Nier-Johnson geometry)

a: Ion source

b: First field-free region, M: Magnetic analyser,

c: Second field-free region, E: Electrostatic analyser (Energy filter)

d: Detector.
despite the fact that the metastable peak for this rearrangement was easy to detect (100, 101). Subsequently the explanation advanced for the observation of the fragment ions was that the rearrangements occurred in the condensed phase on the surface of the anode (102, 103). However, later it was shown in a study of temperature effects on field ionization mass spectrum of methene (104) and aliphatic acid esters (105) that the McLafferty rearrangement was more significant than the comparable direct bond cleavages; and in some of the esters the rearrangement yielded the base peak. In butyl acetate other workers found surface reactions very predominant (106). McLafferty rearrangement peaks have also been observed in ions of long life-time produced by f. of hexanal, and the point is made that the ions decompose in similar ways to those generated by e.i. (107).

It would seem therefore, that while one cannot rationalize the absence of rearrangement peaks on the basis of the time scale alone as outlined above, one should eliminate the possibility of surface reactions in order to confirm rearrangement reactions. The temperature behaviour of fragments in dispute usually helps in deciding whether they are due to decomposition in the gas phase or due to surface or layer influences. In the case of surface reactions the effect of temperature on the formation of the fragments should be small and their relative abundance should decrease as soon as the layer is removed at higher temperatures. In the case of decomposition in the gas phase the relative abundance of the fragments should show temperature dependence similar to that of fragments due to single bond cleavages, since the observed fragments are due to very fast rearrangement reactions with a small activation energy.
Also the behaviour of ions in defocused f.i. spectra can help in distinguishing between gas phase fragmentations and surface related fragmentations. Gas phase fragmentations are characterized by an extended tail on the current vs voltage plot. Surface-related fragmentations on the other hand display a narrow symmetrical peak.

G. **Statement of Problem**

It would appear from the above discussion, that while a considerable amount of work has been done on thermochemical and photochemical behaviour of thioesters, their behaviour in mass spectrometry is poorly investigated. For example, alkyl migration to a thiocarbonyl group in O-alkyl thioesters deserves further investigation. Ohno et al (60,61) came to the conclusion that such a migration was not thermally induced in the mass spectrometer. Such a conclusion was reached by heating samples outside the mass spectrometer to higher temperatures than those used in the ion source. However, such results are inconclusive since they do not preclude the possibility of metal surface catalysis. More significantly, the influence of alkyl group on such rearrangement has not been investigated. The field ionization mass spectrometry of these esters has not been investigated and the hydrogen migration observed in O-alkyl thioesters leading to the fragment [PhCSH]** deserves further study. In general, the influence of sulfur in a thiocarbonyl group on fragmentation of these esters has not been compared to that of oxygen in a carbonyl group.

Accordingly, we set out to investigate the two sets of thioesters with longer chain alkyl groups. Longer alkyl groups would allow observation of interesting rearrangements such as the McLafferty
rearrangement, which are not observed in short chain alkyl groups. Variation of ion source temperature would yield results which can prove or disprove the fact that alkyl migration is thermally induced. Low electron impact energy studies would give an indication of fragments that are formed by low energy processes and field ionization studies would give an indication of fragments that arise by direct cleavage and those formed by rearrangement reactions. The behaviour of β-phenethyl esters would allow observation of influence of fragment stability on fragmentation behaviour. Further, it is hoped that such a study will serve as a basis for future work on mechanism of specific reactions observed in thioesters.

The results obtained will be discussed in Chapter 5 and where necessary compared to those obtained by earlier workers.
CHAPTER 4

EXPERIMENTAL

A. Instrumental

Proton n.m.r. spectra were obtained with a JEOL C60 HL spectrometer using T.M.S. as an internal reference. The n.m.r. chemical shifts are reported in $\delta$ units downfield from the reference. The splitting pattern of each resonance is reported using the following code system: s=singlet; d=doublet; m=multiplet and b=m=broad multiplet. The infrared spectra were obtained by using Beckman IR-12 spectrophotometer. The specific infrared absorptions are reported in cm$^{-1}$ and their intensities are expressed using the following code system: w=weak (100-75% transmission), m=medium (75-40% transmission) and strong (40-0% transmission).

Mass spectra were obtained on a Varian MAT CH-5DF mass spectrometer equipped with a combined f.d./f.i./e.i. source. Samples were introduced through the bath inlet system. All spectra were recorded through an INCOS Model 2000 computer interfaced with the mass spectrometer. Nominal resolution was 1000 and 1500 (10% valley definition) for oscillographic and computer recording respectively. The ion source temperature was kept within the range of 200-250$^\circ$ for e.i. and for f.i. the temperature varied between 70-150$^\circ$. Examples of f.i. spectra run at various ion source temperatures for some of the compounds indicated that some of the ions may be formed by surface related reactions. Metastable spectra were obtained by either of the methods described in Chapter 2 and recorded with a galvanometer recorder.
B. Chemicals

(1) Alkyl thiolacetates:

Alkyl thiolacetates were prepared by the method of Wenzel and Reid (108). A mixture of mercaptan (0.05 mole), acetic anhydride (0.06 mole) and anhydrous sodium acetate (0.02 mole) was refluxed in a flask for 1 hour by means of an oil bath which was kept at 140°C. The cooled mixture was poured into water and the upper layer was washed free of acid, dried over anhydrous sodium sulfate and distilled. The following thiolacetates were prepared.

\[ n\text{-propyl} \quad \text{bp} \quad 140^\circ, \quad \text{lit}^{108} \quad 139.8^\circ \]
\[ n\text{-butyl} \quad \text{bp} \quad 159-61^\circ, \quad \text{lit}^{108} \quad 163.4^\circ \]
\[ n\text{-pentyl} \quad \text{bp} \quad 90^\circ \quad (30\text{mm}), \quad \text{lit}^{108} \quad 185.1^\circ \]
\[ \beta\text{-phenethyl} \quad \text{bp} \quad 130^\circ \quad (11\text{mm}), \quad \text{lit}^{109} \quad 135-138^\circ \quad (14\text{mm}) \]

(2) Alkyl thionacetates and thionbenzoates:

The thionesters were prepared (110) by bubbling hydrogen sulfide through a stirred suspension of the appropriate imidate hydrochloride* in dry pyridine for 9 hours. The resulting solution was poured into cold water to which excess acid was added. Extraction with methylene chloride gave a yellow solution which was dried over anhydrous sodium sulfate and fractionally distilled. The following benzoates and acetates were prepared:

Thionbenzoates

\[ n\text{-propyl} \quad \text{bp} \quad 122^\circ \quad (8\text{mm}), \quad \text{lit}^{110} \quad 127-32^\circ \quad (29\text{mm}) \]
\[ n\text{-butyl} \quad \text{bp} \quad 138^\circ \quad (7\text{mm}), \quad \text{lit}^{112} \quad 160^\circ \quad (23\text{mm}) \]
\[ \beta\text{-phenethyl} \quad \text{bp} \quad 114^\circ \quad (0.2\text{mm}), \quad \text{lit}^{113} \quad 0.1^\circ \quad (0.1\text{mm}) \]

*In all cases the imidate hydrochlorides were prepared by the method of Reynaud and Moreau (111) and used in their crude form.
p(Meo) phenethyl - mp 83°, lit[113] 78-81°
n-pentyl - bp 128° (3.4mm)
iso-pentyl - bp 129-130° (3.4mm)

Thiomacetates

n-propyl - bp 126-129°, lit[110] 125-130°
n-butyl - bp 145-148°, lit[110] 146-149°
n-pentyl - bp 73° (55mm), lit[110] 72-4° (55mm)
β-phenethyl - bp 98° (1.8mm)

(3) Alkyl thiolbenzoates

A modification of the procedure described by Wenzel and Reid (108) was used to prepare the thiolbenzoates.

To the mercaptan (0.05 mole) in 20ml. of concentrated sodium hydroxide was added benzoic anhydride (0.06 mole) with stirring. The stirring was continued for 0.25 hr. and the mixture was poured into water. The organic layer was separated and the aqueous layer washed with ether (3x50ml). The ether layer was combined with the organic layer, washed with water, 10% HCL, saturated sodium bicarbonate solution and then water, dried over anhydrous sodium sulfate and distilled. The following thiolbenzoates were prepared:

n-propyl - bp 130° (15mm), lit[114] 144° (13mm)
n-butyl - bp 160° (22mm), lit[112] 160° (23mm)
n-pentyl - bp 130° (1.2mm), lit[110] 130° (1.5mm)
n-hexyl - bp 156° (1.8mm)
β-phenethyl - bp 176-178° (1.6mm)

n-pentyl thionbenzoates

n-Pentyl thionbenzoate was prepared as in 2 above. An orange liquid bp 128° (3.4mm) was obtained (30% yield)
Anal. calculated for C_{12}H_{16}OS: C, 69.20; H, 7.74; S, 15.36.
Found: C, 69.32; H, 7.72; S, 15.39

i.r. (CHCl₃, 5%) 3100, 3020 (s, C₆H₅); 2900 (m, CH₃)
1610 (m, C₆H₅); 1460, 1400 (s, CH₂); 1290, 1270 (s, C=S) cm⁻¹.

n.m.r. (CDCl₃, 10%): δ 8.25-7.5 (m, 5); 4.7 (t, 2); 2.1 (m, 6); 1.95 (m, 3)

**Iso-Pentyl thionbenzoate**

Iso-pentyl thionbenzoate was prepared as in 2 above. An orange liquid bp 129-130° (3.4mm) was obtained (35% yield).

Anal. calculated for C_{12}H_{16}OS: C, 69.20; H, 7.74; S, 15.36
Found: C, 69.38; H, 7.79; S, 15.40

i.r. (CHCl₃, 5%) 3010, 3080 (s, C₆H₅); 2895 (m, CH₃);
1595 (m, C₆H₅); 1455 (s, CH₂); 1310, 1295 (s, C=S) cm⁻¹.

n.m.r. (CDCl₃, 10%) δ 8.25-7.5 (m, 5); 4.72 (t, 2); 1.82 (m, 3);
2.0 (d, 6).

**β-Phenethyl thionacetate**

β-Phenethyl thionacetate was prepared as in 2 above. A light orange liquid bp 98° (1.8mm) was obtained (30% yield).

Anal. calculated for C_{10}H_{12}O: C, 66.6; H, 6.71; S, 17.75
Found: C, 66.51; H, 6.84; S, 17.75

i.r. (CHCl₃, 5%) 3100, 3040 (s, C₆H₅); 2980 (s, CH₃); 1505, 1460 (s, CH₂);
1610 (s, C₆H₅); 1370, 1295 (s, C=S) cm⁻¹.

n.m.r. (CDCl₃, 10%) δ 7.15 (s, 5); 4.6 (t, 2); 3.0 (t, 2); 2.5 (s, 3).

**β-Phenethyl thiolbenzoate**

β-Phenethyl thiolbenzoate was prepared as in 3 above. A colourless liquid bp 176-178° (1.6mm) was obtained (85% yield).

Anal. calculated for C_{15}H_{14}O: C, 74.35, H, 5.82; S, 13.20*

*A high resolution mass measurement shows the correct molecular ion.
Found: C, 74.95; H, 6.02; S, 11.02

i.r. (CHCl₃, 5%) 3075 (m, C₆H₅); 1600, 1580 (m, C₆H₅); 1660 (s, C=O);
                    1480, 1450 (s, CH₂) cm⁻¹.

n.m.r. (CDCl₃, 10%) 7.85-7.35 (m, 5); 7.20 (s, 5); 3.16 (m, 2);
                    2.75 (m, 2).

n-Hexyl thiolbenzoate

n-Hexyl thiolbenzoate was prepared as in 3 above. A colourless
liquid bp 156° (1.8mm) was obtained (80% yield).

Anal. calculated for C₁₃H₁₈O₂S: C, 70.23; H, 8.16; S, 14.39
Found: C, 70.28; H, 8.12; S, 13.88

i.r. (CHCl₃, 5%) 3090, 3020 (s, C₆H₅); 1610, 1590 (m, C₆H₅0);
                    2960, 2920 (m, CH₃); 1665 (s, C=O); 1450 (m, CH₃) cm⁻¹.

n.m.r. (CDCl₃, 10%) 7.9-7.4 (m, 5); 4.7 (t, 2); 1.8-1.2 (bm, 8);
                    0.98 (t, 3).

All thionoesters were purified by column chromatography on a silica
gel column (45 cm. x 1 cm.). The thiolestes were purified by glc
(20% SE 30, 10' x 0.375'). The purity of all the thioesters was
checked by n.m.r. and i.r.
CHAPTER 5

RESULTS AND DISCUSSION

In preparation for electron impact studies on thioesters, 20 compounds were synthesized (Chart 1). The thioester studies can be divided into 2 major classes: thionesters (commonly known as O-alkyl thioesters) and thioesters (S-alkyl thioesters). The two names are used interchangeably in this work. For the sake of discussion the thioesters are divided into the 3 classes: benzoates, acetates and \( \beta \)-phenethyl esters. The spectra for the esters are presented in tabular form in the appendix. Only fragments (> 1.0% RA) are reported unless the fragment is reported for comparative purposes. In all cases the detection limit was 0.1% and all spectra were reliably reproduced. Unless otherwise stated, the spectra presented in the tables and appendices are not corrected for \(^{13}\text{C}\) isotope contribution. Metastable peaks quoted are reported in Appendix 4.

A. Thiobenzoates

An examination of the mass spectra of various thiobenzoates (Appendix 1, 2, 3) reveals a wealth of information. The molecular ion in both types of esters is very significant and of higher relative abundance in thion esters (24-47% RA) than in thioesters (6-11% RA) Table 5a.

The greater relative abundance of the molecular ion is probably due to the ease of ionization of the thiocarbonyl group as opposed to the carbonyl group in thioesters. A decrease in relative abundance of the molecular ion as the alkyl group increases is observed in the analogous
<table>
<thead>
<tr>
<th>Ester Type</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>Mol. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 = \text{Ph} )</td>
<td>( \text{CH}_3(\text{CH}_2)_2 )</td>
<td>( \text{CH}_3(\text{CH}_2)_3 )</td>
<td>180.06</td>
</tr>
<tr>
<td>( X = \text{S} )</td>
<td>( \text{CH}_3(\text{CH}_2)_4 )</td>
<td>( \text{CH}_3\text{CH}(\text{CH}_3)(\text{CH}_2)_2 )</td>
<td>208.09</td>
</tr>
<tr>
<td>( Y = \text{O} )</td>
<td>( \text{CH}_3(\text{CH}_2)_5 )</td>
<td>( \text{CH}_3\text{C}_6\text{H}_4(\text{CH}_2)_2 )</td>
<td>222.10</td>
</tr>
<tr>
<td>( \text{Ph}(\text{CH}_2)_2 )</td>
<td></td>
<td></td>
<td>272.08</td>
</tr>
<tr>
<td>( R_1 = \text{Ph} )</td>
<td>( \text{CH}_3(\text{CH}_2)_2 )</td>
<td></td>
<td>180.06</td>
</tr>
<tr>
<td>( X = \text{O} )</td>
<td>( \text{CH}_3(\text{CH}_2)_3 )</td>
<td></td>
<td>194.07</td>
</tr>
<tr>
<td>( Y = \text{S} )</td>
<td>( \text{CH}_3(\text{CH}_2)_4 )</td>
<td>( \text{CH}_3(\text{CH}_2)_5 )</td>
<td>208.09</td>
</tr>
<tr>
<td>( \text{Ph}(\text{CH}_2)_2 )</td>
<td></td>
<td></td>
<td>222.10</td>
</tr>
<tr>
<td>( R_1 = \text{CH}_3 )</td>
<td>( \text{CH}_3(\text{CH}_2)_2 )</td>
<td></td>
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<tr>
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<tr>
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<td>( \text{Ph}(\text{CH}_2)_2 )</td>
<td>146.07</td>
</tr>
<tr>
<td>( R_1 = \text{CH}_3 )</td>
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<td>( \text{CH}_3(\text{CH}_2)_3 )</td>
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</tr>
<tr>
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<td>( \text{Ph}(\text{CH}_2)_2 )</td>
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<tr>
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<tr>
<td></td>
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<td>146.07</td>
</tr>
<tr>
<td>Fragment</td>
<td>Propyl-</td>
<td>Butyl-</td>
<td>Pentyl-</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------</td>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>([\text{Ph}]^+)</td>
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</tr>
<tr>
<td>([\text{PhS}]^+)</td>
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<td></td>
</tr>
<tr>
<td>([\text{PhCO}]^+)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>([\text{PhCS}]^+)</td>
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<td></td>
</tr>
<tr>
<td>([\text{PhCSH}]^+)</td>
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<td>1.6</td>
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<td>4.2</td>
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<td>0.3</td>
</tr>
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<td>10.8</td>
<td>9.3</td>
<td>6.6</td>
</tr>
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</table>
alkyl esters. The relative abundance of most prominent fragments varies in a predictable manner with the alkyl group and depends to a very large extent on whether the ester is thiolester (X=O, Y=S), or a thionester (X=S, Y=O).

1. Direct cleavage fragments

In S-alkyl thiobenzoates, the benzoyl fragment (m/z 105) is the base peak. Like alkyl benzoates, this fragment arises by α-cleavage on the alkyl side. Metastable studies show that it can also arise by loss of sulfhydryl radical from the thiobenzoic acid fragment [PhCOSH]\(^{+}\). A similar cleavage on the acyl side of the carbonyl group gives rise to the peak at m/z 77 due to the phenyl fragment [Ph]\(^{+}\). In S-alkyl thioesters the phenyl radical is the second largest peak in the spectra. Besides arising by α-cleavage, however, this peak also arises from the benzoyl fragment by loss of carbon monoxide as in alkyl benzoates.

In O-alkyl thiobenzoates, cleavage on the alkyl side gives rise to the thiobenzoyl fragment [PhCS]\(^{+}\), the third largest peak in the spectra. This is in sharp contrast to the simple (R=Me, Et) thionbenzoates (60, 61), where this peak constitutes the base peak. It has been shown by metastable studies that this peak arises also by loss of a hydrogen radical from the fragment at m/z 122 due to [PhCOSH]\(^{+}\). In principle the same fragment may be expected to arise by loss of a hydroxyl radical (OH) from thiobenzoic acid ion (analogous to loss of (SH) observed in both S-alkyl thiobenzoates and O-alkyl thiobenzoates) since McLafferty rearrangement of O-alkyl thiobenzoates should produce the thiobenzoic acid fragment in both tautomeric forms (eq. 2).
However, such a transition was not observed in either S-alkyl thiobenzoates or O-alkyl thiobenzoates. This may be attributed to the stability of (C-O) single bond relative to (C-S) but also may indicate that McLafferty rearrangement in O-alkyl thionbenzoates is more energetically favoured than alkyl migration to the thiocarbonyl function. It is known (58) that in form (a) rather than form (b), sulfur migrates to the ring leading to other competitive modes of fragmentations (Scheme 8). It also may imply that ionization takes place at sulfur rather than the carbonyl group in which case the thiobenzoic acid formed by rearrangement is predominantly in form (b). Such ionization as sulfur would lead to at least a four-membered transition state (eq. 3), depending on the source of hydrogen abstracted.
Another cleavage fragment of considerable significance in thio-
benzoates is \([R]^+\). The relative abundance of this peak decreases as
the length of \((R)\) increases, in fact \([R]^+\) is not observed in O-hexyl
thiobenzoate, and is negligible in S-hexyl thiobenzoate. Other direct
cleavage fragments namely, \((OR), (SR)\), are significant in higher alkyl
thioesters, while contrary to aliphatic thioesters (57), the fragments
\((COSR)\) and \((CSOR)\) are not detected.

(2) **Rearrangement fragments**

Perhaps the most important rearrangement in O-alkyl thioesters is
the migration of the alkyl group to the thiocarbonyl group prior to
\(\alpha\)-cleavage (Scheme 4). Such a rearrangement leads to the benzoyl
fragment which is the base peak in all thionesters investigated; the
same peak has been observed at low electron impact energies in simple
thionbenzoates (61). Metastable studies have shown that the same peak
arises by loss of a sulfhydryl group from the thiobenzoic acid fragment
and by loss of hydrogen sulfide \((SH_2)\) from the protonated thiobenzoic
acid fragment \([PhCOSH_2]^+\).

In S-alkyl thiobenzoates, one might expect the same rearrangement
to give rise to the thiobenzyol fragment \([PhCS]^+\) and in fact such a
fragment and the complementary fragment \([OR]^+\) have been observed in
simple thiol benzoates (60,61). However, in the results we obtained with
larger alkyl groups (propyl-hexyl), such fragments were not detected.
This difference may be attributed to lack of competitive modes of frag-
mentation in the simple molecules, such as the energetically favoured
McLafferty rearrangement, and also, as discussed above, to the fact
that once formed, the McLafferty rearrangement product \([PhCOSH]^+\) may be
predominantly in form \((b)\) so that the subsequent cleavage is loss of
of sulfhydryl rather than hydroxyl radical. In addition, the facility of such a migration may be hampered in the case of bulky or larger alkyl groups.

The transition from the thiobenzoyl fragment \([\text{PhCS}]^+\) as the base peak in simple O-alkyl thioesters to the benzoyl fragment \([\text{PhCO}]^+\) in higher O-alkyl thioesters, may be attributed to two major factors: one, that in simple O-alkyl thiobenzoates direct cleavage competes effectively with rearrangements such as alkyl-migration and McLafferty rearrangement, which give rise to the benzoyl fragment; and two, that as the alkyl group increases in length cleavage becomes effectively less favoured relative to rearrangements which include both the 'McLafferty' and 'McLafferty + 1' rearrangements. These rearrangements do not take place in methyl esters and the 'McLafferty + 1' rearrangement seldom takes place in ethyl esters. Consequently one would expect a lower relative abundance of the benzoyl fragment in such simple O-alkyl thioesters.

This type of rearrangement has been compared to the well known Schonberg rearrangement, which as discussed earlier requires a thiocarbonyl group and is both thermally and electron impact induced (69). Ohno et al investigated the possibility of thermal induction with the mass spectrometer, by heating the samples at various higher temperatures than those used in the ion source. Analysis by i.r. showed lack of isomerisation to S-alkyl thioesters within this range of temperatures. Thus it was concluded that the difference between the Schonberg rearrangement and the observed alkyl migration is that the former requires a thiocarbonyl function while the latter takes place in compounds with a carbonyl group since it was also observed in S-alkyl thioesters. Johnstone and Bentley (7) argue that while preheating samples prior to electron impact studies
<table>
<thead>
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<th>Fragment</th>
<th>Relative abundance at given ion source temperature</th>
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</thead>
<tbody>
<tr>
<td></td>
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</tr>
<tr>
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</tr>
<tr>
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<td>10.3</td>
</tr>
<tr>
<td>[PhCO]⁺</td>
<td>483.0</td>
</tr>
<tr>
<td>[PhCS]⁺</td>
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</tr>
<tr>
<td>[PhCSH]⁺</td>
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</tr>
<tr>
<td>[PhCOSH]⁺</td>
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</tr>
<tr>
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</tr>
<tr>
<td>[M-SH]⁺</td>
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</tr>
<tr>
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</tr>
<tr>
<td>[C₃H₇]⁺</td>
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</tr>
<tr>
<td>[R-H⁺]⁺</td>
<td>49.8</td>
</tr>
<tr>
<td>[M]⁺⁺</td>
<td>100</td>
</tr>
<tr>
<td>[\frac{[PhCO]}{[PhCS]}]</td>
<td>3.9</td>
</tr>
</tbody>
</table>

* Spectra have been normalized to the molecular ion.
may prove that thermal rearrangements do not take place, such a method fails to preclude the possibility of metal-surface catalysis within the mass spectrometer. Thus we decided to investigate the effect of ion source temperature on the rearrangement. As one would expect, an increase in all the fragments is observed. However, the increase in the ratio (PhCO) / (PhCS) as the temperature increases, which would result from thermally induced rearrangement, is not observed (Table 5b). Thus our results confirmed that the thion to thiol rearrangement observed in the mass spectrum of O-alkyl thiobenzoates is not thermally induced within the mass spectrometer. Although this rearrangement is not detected in thiobenzoates, our results on aliphatic thiol esters indicate that it is not limited to thions, in agreement with Ohno's results.

(3) Hydrogen rearrangements

Two types of hydrogen rearrangement are observed in thiobenzoates; one is the McLafferty type of rearrangement which requires that the alkyl group be ethyl or higher, and the other is the hydrogen migration specifically to a thio carbonyl group (Scheme 2 and 5, pages 25 and 33 respectively). McLafferty rearrangement gives rise to fragments [R-H]+ and [PhCOSH]+, the relative abundances of which are determined by the stabilities of the individual fragments. In S-alkyl thiobenzoates the relative abundances of [PhCOSH]+ are small and relatively unaffected by the increase in the alkyl group. In S-pentyl thiobenzoate the above fragment is not observed. Although a definite pattern cannot be drawn from the data as to the variation with the alkyl group, a relatively small increase is observed as the alkyl group increases. In S-propyl thiobenzoate, the olefinic product [R-H]+ is not observed while in S-pentyl thiobenzoate the same fragment is significant. The absence of
[R-H]^+ in S-propyl thiobenzoates may be expected since as discussed earlier the ionization potential of terminal olefins may be expected to be higher in short alkyl groups, causing the charge to be preferentially retained on the thioacid fragment. On the other hand, a more or less definite pattern in O-alkyl thiobenzoates allows the following generalization to be drawn:

a) For all O-alkyl thiobenzoates investigated (Table 5a), the thioacid products give rise to intense peaks. In contrast, the intensities of the olefinic products are lower;

b) The relative intensities of the olefinic products increase with increasing alkyl group chain length while the relative intensity of the thioacid product shows a general decrease.

The higher relative abundance of the olefinic product and the thioacid product in O-alkyl thiobenzoates is consistent with a lower ionization potential of a thiocarbonyl group compared to a carbonyl group. Conclusions a and b are also consistent with, and can be understood in terms of, charge competition between the olefinic product and the thioacid product. The decrease of the thioacid product as the alkyl group chain length increases may also be attributed partly to other competing reactions, for example, direct cleavage to give rise to the thiobenzoyl fragment and the double McLafferty rearrangement.

The double McLafferty rearrangement is indicated by the peak at m/z 139 corresponding to the protonated thiobenzoic acid [PhCSOH₂]^+ (Table 5a). Examination of the spectra of S-alkyl thiobenzoates shows that the rearrangement is not detected in O-propyl thiobenzoate while in the other compounds a more or less constant relative abundance is observed. In principle one may statistically expect an increase in this fragment as the
alkyl group increases in length since the site of the second hydrogen is not specific. The levelling off of the fragment is probably caused by competition with other modes of fragmentation.

In O-alkyl thiobenzoates on the other hand, the expected increase in the double rearrangement product is observed. The results show that the double rearrangement is much more favoured than the single rearrangement. This may be attributed to the stability of the protonated thiobenzoic acid by resonance stabilization and to allylic stabilization of the resulting neutral radical. Loss of hydrogen sulphide from this fragment contributes to the base peak at m/z 105 corresponding to the benzoyl fragment [PhCO]⁺. The mechanism below is proposed for overall reaction. The possibility of both hydrogens migrating to the thiocarbonyl group is supported by absence of transition 3 from the protonated thiobenzoic acid fragment derived from the S-alkyl thiobenzoates. The latter fragment presumably has only one hydrogen on sulfur.

Scheme 12 Proposed mechanism for loss of hydrogen sulfide from PhCOSH₂

If the protonated thiobenzoic acid (resonance forms as below) were formed by either of the mechanisms in (Scheme 2, page 25), then elimination
of hydrogen sulfide from this fragment would imply tautomerism as represented by the right-hand structure below. In this case the S-alkyl thioesters would also be expected to show transition 3 in (Scheme 12). However, such a transition was not observed, indicating that the transfer of the two hydrogens must take place directly to the thiocarbonyl group.

\[
\begin{align*}
\text{Ph} - & \text{C} \quad \text{OH} \\
\text{SH} & \quad \leftrightarrow
\end{align*}
\]

\[
\begin{align*}
\text{Ph} - & \text{C} \quad \text{OH} \\
\text{SH} & \quad \leftrightarrow
\end{align*}
\]

\[
\begin{align*}
\text{Ph} - & \text{C} \quad \text{S} \\
\text{H}^+ & \quad \leftrightarrow
\end{align*}
\]

The driving force for the loss of hydrogen sulfide probably consists of three factors:

(1) formation of a stabilized allylic radical;
(2) formation of a neutral fragment of hydrogen sulfide and
(3) the stability of the benzoyl fragment.

Transitions 2 and 3 in the scheme above were confirmed by metastable studies. In O-hexyl thiobenzoate, the metastable peaks are observed at \( V_o = 3.25, V = 5.19 \) and \( V_o = 3.27, V = 4.32 \) for the transitions 222 → 139 and 139 → 105 respectively, thus confirming that this mode of fragmentation contributes to the base peak.

Loss of (CHO) fragment from the protonated thiobenzoic acid leads to a peak at m/z 110 corresponding to the fragment \([\text{PhSH}]^+\). This may be formed by migration of sulfur to the benzene ring in a mechanism similar to that proposed by Tomer and Djerassi (58) in Scheme 8, page 36 for the peak at m/z 109.
Scheme 13  Proposed mechanism for formation of peak at m/z 110

At high internal energies (70eV ionization), the peak at m/z 110 has a higher relative intensity than the peak at m/z 109 derived from PhCOSH fragment. At low internal energies, the peak at m/z 109 is not observed. Metastable studies confirmed transition step 3 above. A metastable peak for m/z 119→110 was observed at V_0=6.5, V=8.21. It would seem that a thiocarbonyl group is necessary for the migration of sulfur to the ring prior to expulsion of (CHO). The rearrangement can likewise be expected to be absent in lower 0-alkyl thioesters which do not undergo double hydrogen rearrangement. The requisite of a thiocarbonyl is fulfilled in S-alkyl thiobenzoates where the thiobenzoic acid formed after McLafferty rearrangement attains the thiocarbonyl structure and in higher alkyl chain O-alkyl thiobenzoates where the protonated thiobenzoic acid is capable of attaining the thiocarbonyl function by tautomerism.

The other important hydrogen rearrangement which occurs in O-alkyl thiobenzoates only, is the migration of hydrogen to the thiocarbonyl group (Scheme 5), page 33. Such migration followed by cleavage on the
alkyl side of the thiocarbonyl group leads to a peak at m/z 122 corresponding to the fragment \([\text{PhCSH}]^+\). Examination of the spectra of O-alkyl thiobenzoates shows that this peak has a substantial relative abundance which shows a gradual decrease as the length of the alkyl group increases. Such a decrease may be expected since other competing fragmentations come into effect as the length of the alkyl group increases. One such rearrangement is the energetically favoured McLafferty rearrangement. That the McLafferty rearrangement is favoured over this type of hydrogen rearrangement can be deduced from spectra at low internal energies (12eV, 10eV ionization). The fragment due to this rearrangement \([\text{PhCSH}]^+\) is not observed while the McLafferty rearrangement product \([\text{PhCOSH}]^+\) is observed as low as 12eV and the 'McLafferty + 1' rearrangement-product is observed to be substantial even at 10eV.

(4) Elimination reactions

In S-alkyl thiobenzoates the major elimination reaction is due to loss of thioethylene oxide \((\text{SCH}_2\text{CH}_2)\) fragment (Table 5a). As discussed earlier the reaction was first observed in aliphatic thioesters (57) and the mechanism in (Scheme 3, page 30) was proposed. However, loss of \(\text{S(CH}_2)\_3\) fragment in S-pentyl and \(\text{S(CH}_2)\_4\) in S-hexyl thiobenzoates is not observed. The relative abundance of the former fragment does not show any significant change as the length of the alkyl group increases. One may expect a decrease as the alkyl group increases due to an increased number of competing modes of fragmentation.

In O-alkyl thioesters this elimination is not detected. Since O-alkyl thiobenzoates rearrange to S-alkyl thiobenzoates under electron impact one may expect such an elimination to take place. Lack of such a reaction in O-alkyl thiobenzoates may be taken as partial evidence that
alkyl migration to the thiocarbonyl group is not a major contributor to the benzoyl fragment, or it may be interpreted to mean that the elimination reaction is a very slow reaction compared to the α-cleavage after alkyl migration to the thiocarbonyl group.

In O-alkyl thiobenzoates, the most prominent elimination corresponds to elimination of a sulfhydryl radical (SH). This elimination was first observed in aliphatic S-alkyl thioacetates (Table 2) (57), and later was observed in simple O-alkyl thiobenzoates (60,61) (Table 3). An analogous loss of a hydroxyl radical was noted in simple S-alkyl thiobenzoates. However, no attempt has been made to determine the source for the hydrogen eliminated or the mechanism for the formation of the fragment.

In higher O-alkyl thiobenzoates it can be seen that the elimination of SH shows a definite increase as the alkyl group increases in length. Examination of the mass spectral data (Table 5a) indicates that this elimination is not detected in S-alkyl thiobenzoates. In thiobenzoates therefore, the reaction shows preference for a thiocarbonyl group. This is in sharp contrast to published data on aliphatic thiolesters (Table 2) where this reaction was found to be significant. A mechanism for this reaction in the case of O-alkyl thioesters involves hydrogen migration to the thiocarbonyl group followed by elimination of (SH) radical, a step which may involve a cyclisation reaction in which 4 to 7 membered ring fragments may be formed depending on the source of hydrogen in the initial step. Subsequent fragmentation of this product ion leads to a neutral olefin product and a benzoyl ion [PhCO]⁺ which constitutes the base peak. Although there is no evidence to show that the [M-SH]⁺ fragment is cyclic, the relative abundance of this peak indicates significant stability. Also, metastable studies confirmed that the same
fragment contributes to the base peak.

\[
\text{RCH=CH}_2 + [\text{PhCO}]^+ \quad \rightarrow \quad [\text{PhCS}]^+ \quad \rightarrow \quad \text{SH}
\]

Scheme 14  Proposed mechanism for elimination of (SH) radical.

(5) Low energy electron impact studies

In general, rearrangement processes have low energies of activation and should be favoured in molecular ions formed with only a small amount of excess internal energy. Such conditions can be obtained by reducing the electron impact energy in the mass spectrometer to threshold values.

Previously Ohno et al (61) observed that at low electron impact energies McLafferty rearrangement in thionesters was favoured and led to the predominance of the benzoyl fragment [\text{PhCO}]^+ over the thiobenzoyl fragment [\text{PhCS}]^+ in O-alkyl thiobenzoates.

Low electron impact energy studies which were carried out for O-butyI thiobenzoate (Table 5c) reveal the following information:

Near threshold energies (12eV, 10eV ionization) direct cleavage fragments such as [\text{Ph}]^+ and [\text{PhCS}]^+, which are due to \(\alpha\)-cleavage on either side of the thiocarbonyl group, are not detected. Hydrogen migration to the thiocarbonyl group prior to \(\alpha\)-cleavage, which gives rise to the fragment [\text{PhCSH}]^+, is not observed, while the comparable McLafferty rearrangement is observed at 12eV. These results indicate
### Table 5c

**Selected ions O-Butyl thiobenzoate**

<table>
<thead>
<tr>
<th>Fragment</th>
<th>10eV</th>
<th>12eV</th>
<th>15eV</th>
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<th>25eV</th>
<th>29.5eV</th>
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<td>[Phh]⁺</td>
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<td></td>
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<td>12.1</td>
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</tr>
<tr>
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<td>6.6</td>
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<td>31.6</td>
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<td>126.5</td>
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<td>26.9</td>
<td>18.6</td>
<td>18.7</td>
<td>26.8</td>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

* - Spectra have been normalized to the molecular ion.
that the rearrangement which involves α-cleavage is energetically less favoured than the McLafferty rearrangement which involves β-cleavage.

Both the double hydrogen rearrangement product and the benzoyl fragment are significant even at 10eV. This suggests that the double hydrogen rearrangement is a more energetically favoured reaction than the single hydrogen rearrangement. It may also imply that near threshold energies, the single hydrogen rearrangement does not contribute to the benzoyl ion but rather that the major contributors are the molecular ions, the double hydrogen rearrangement product and the \([M-SH]^+\) fragment.

The fragment due to \([M-SH]^+\) is very significant but shows a more or less constant relative abundance from 12eV to 29.5eV. This shows that the process is not sensitive to internal energies within this range of electron impact energies. Both the double hydrogen rearrangement product \([\text{PhCOSH}_2]^+\) and the \([M-SH]^+\) fragment are major precursors to the benzoyl fragment, which constitutes the base peak at high internal energies as confirmed by metastable studies. The metastable peaks were observed at \(V_0=3.27\), \(V_1=4.325\), \(V_2=5.90\) and \(V_3=6.92\), corresponding to the transitions 139 → 105, 189 → 105 and 222 → 105, in O-alkyl thiobenzoate (PhCOSH\(_2^+\) → PhCO\(^+\), M-SH\(^+\) → PhCO\(^+\), M\(^+\) → PhCO\(^+\)).

(6) **Field ionization mass spectrometry of thiobenzoates**

The field ionization spectra of S-alkyl thiobenzoates and O-alkyl thiobenzoates are summarized in (Table 5d). In these spectra the base peak corresponds to the molecular ion. This is expected since in this mode of ionization, the molecules generally do not acquire sufficient energy to lead to extensive fragmentation. Both types of esters show a peak at m/z 105 corresponding to the benzyol ion \([\text{PhCO}]^+\).
<table>
<thead>
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<th>Fragment</th>
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<th>Butyl-</th>
<th>i-Pentyl-</th>
<th>Pentyl-</th>
<th>Hexyl-</th>
<th>Propyl-</th>
<th>Butyl-</th>
<th>Pentyl-</th>
<th>Hexyl-</th>
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</thead>
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<tr>
<td>[M]+</td>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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</tr>
</tbody>
</table>

Table 5d

Selected fragments f.i. Mode (PhCYR)
Table 5e

f.i. spectra of butyl thiobenzoates at various ion source temperatures

<table>
<thead>
<tr>
<th>m/z</th>
<th>PhCSO(CH₂)₃CH₃</th>
<th></th>
<th></th>
<th>PhCOS(CH₂)₃CH₃</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>52 °C</td>
<td>70 °C</td>
<td>150 °C</td>
<td>70 °C</td>
<td>150 °C</td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>0.4</td>
<td>0.2</td>
<td>-</td>
<td>0.4</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>166</td>
<td>0.7</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>178</td>
<td>0.1</td>
<td>0.8</td>
<td>-</td>
<td>0.6</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>194</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>195</td>
<td>15.4</td>
<td>11.5</td>
<td>11.7</td>
<td>11.2</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>196</td>
<td>6.5</td>
<td>4.7</td>
<td>4.9</td>
<td>5.1</td>
<td>4.8</td>
<td></td>
</tr>
</tbody>
</table>
In the case of S-alkyl thiobenzoates this fragmentation results from direct α-cleavage but in the case of O-alkyl thiobenzoates the fragment results from the initial migration of alkyl group to the thiocarbonyl group followed by α-cleavage. The analogous fragment at m/z 121 corresponding to [PhCS]⁺ is not observed in either case.

Two other peaks at m/z 166 and m/z 182 are observed in the spectra of O-alkyl thiobenzoates. However, in spectra obtained at higher ion source temperatures (Table 5a), the peaks were not detected. This indicates that the two fragments are not formed by true gas phase reactions but may be surface related fragments. Similarly the same results indicate that alkyl migration to the thiocarbonyl group in the thionoesters may not be a true gas phase process in field ionization spectra of the same compounds.

B. Thioacetates \( \text{R} \equiv \text{C-yr} \)

The mass spectra of S-alkyl thioacetates have been reported and their characteristics are discussed in the background section. The mass spectra of simple O-alkyl thioacetates (\( \text{R}^1 = \text{Me, Et} \)) have also been discussed. In order to compare the behaviour of S-alkyl thioacetates to that of O-alkyl thioacetates, under electron impact, analogous thioacetates (\( \text{R}^1 = \text{propyl-pentyl} \)) were synthesized. The individual spectra are presented in the appendix and a summary of major fragments is presented in Table 5.

Examination of these spectra shows that in thiolacetates, the base peak at m/z 43 corresponds to the acetyl ion [CH₃CO]⁺, which is formed by α-cleavage. The same peak is very significant in thionacetates where it is formed by alkyl migration to the thiocarbonyl group followed by α-cleavage. As in the thionbenzoates, α-cleavage on the alkyl side does not lead to the base peak, except in short chain alkyl groups. This can
Table 6

Selected fragments for thiol and thion acetates (RCCTR⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻{-

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Propyl-</th>
<th>Butyl-</th>
<th>Pentyl-</th>
<th>Propyl-</th>
<th>Butyl-</th>
<th>Pentyl-</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RS]⁺</td>
<td>3.4</td>
<td>2.7</td>
<td>2.4</td>
<td>14.6</td>
<td>1.8</td>
<td>1.0</td>
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<tr>
<td>[RCO]⁺</td>
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<td>100</td>
<td>100</td>
<td>20.0</td>
<td>77.6</td>
<td>74.2</td>
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<td>10.2</td>
<td>43.6</td>
<td>27.2</td>
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<tr>
<td>[RCOSH]⁺⁺⁺</td>
<td>0.8</td>
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<td>2.3</td>
<td>10.2</td>
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<td>0.3</td>
<td>0.9</td>
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<td>3.4</td>
<td>10.6</td>
<td>28.0</td>
<td>11.7</td>
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<tr>
<td>[RCOSH₂]⁺⁺⁺</td>
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<td>6.2</td>
<td>11.8</td>
<td>84.3</td>
<td>56.6</td>
<td></td>
</tr>
<tr>
<td>[R¹⁺⁺⁺]</td>
<td>(100)b</td>
<td>1.6</td>
<td>2.9</td>
<td>(20.0)</td>
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<td>12.9</td>
</tr>
<tr>
<td>[R¹⁺⁺⁺]</td>
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<td>1.4</td>
<td>(2.2)</td>
<td>3.2</td>
<td>2.3</td>
</tr>
<tr>
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<td>1.5</td>
<td>14.6</td>
<td>(2.2)</td>
<td>3.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>
| [R¹⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-

b entries in brackets could be due to other fragments entirely.

a Blank entries represent ions below list threshold (0.1) or ions not detected.

* Base peak is due to solvent.
be observed in O-propyl thioacetate, where the acetyl ion constitutes the
base peak. The molecular ion [M]+ is significant and carries at least
5% of the total ion current. In S-alkyl thioacetates other direct
cleavage fragments R, R', R'S are significant. Most of the fragments
could be either from the acyl side or from the alkyl side. For example,
the fragment [R']+ could arise by either α-cleavage on the acyl side or
cleavage of the terminal CH3 in the alkyl group. The base peak could be
due to [R']+ or [RCO]+. α-Cleavage on the alkyl side of the S-propyl
thioacetate leads to [R'S]+ which is equivalent in mass to the fragment
[RCOS]+. Clearly in the case of S-propyl thioacetate high resolution
mass spectrometry is necessary to resolve most of the cleavage peaks.
In O-alkyl thioacetates direct cleavage fragments are more abundant than
in S-alkyl thioacetates.

The presence of the fragment corresponding to [R'-H]+ reflects the
ability of the olefin formed to carry the charge which implies that the
olefin has a lower ionization potential than the thioacetic acid formed
in the competing reaction (Scheme 1), page 24.

As the alkyl group increases in length, the charged olefin formed
in the McLaugherty rearrangement becomes more stable, possibly because
of inductive effect. In thionacetates (X=S, Y=O), the base peak
corresponds to the [R-H]+ fragment in contrast to thiolacetates. This
may reflect the higher ability of a thiocarbonyl group to abstract a
hydrogen atom as compared with a carbonyl group. Since sulfur-hydrogen
single bonds are typically much longer than oxygen-hydrogen single bonds,
hydrogen migration to the thion sulfur may occur over longer distances
than migration to the carbonyl oxygen.

On the other hand, the relative abundance of [R-2H]+ is of the same
order of magnitude as that of the counter ion $[\text{CH}_3\text{COSH}_2]^+$. This may indicate an even competition for charge retention and ionization potentials which are within the same range. However, it is possible that $[\text{R-2H}]^+$ results from loss of a hydrogen radical from the $[\text{R-H}]^+$ ion.

$[\text{R-H}]^+ - \text{H}^+ \rightarrow [\text{R-2H}]^+$. Both thiolacetates and thionacetates show a significant peak at m/z 47 which corresponds to $[\text{CH}_3\text{S}]^+$. Formation of such a fragment is difficult to rationalize in terms of simple mechanisms. The methyl group may come from either acyl or the alkyl portion of the thioester.

Alkyl migration to the thiocarbonyl group prior to $\alpha$-cleavage is observed in thionacetates as indicated by the fragments $[\text{RCO}]^+$ and $[\text{SR}]^+$. In thiolacetates, the same migration is indicated by presence of the fragment $[\text{RCS}]^+$ and $[\text{OR}]^+$ both of which are minor peaks indicating that the alkyl migration is not as energetically favoured here as in thionacetates.

The major elimination reactions in thioacetates are the loss of sulfhydryl radical and expulsion of thioethylene oxide. Elimination of a sulfhydryl group seems to be much more significant in thionacetates than in thiolacetates. In fact the fragment was only detected in S-butyl thioacetate. On the other hand the expulsion of $(\text{SCH}_2\text{CH}_2)$ is much more significant in thiolacetates but is observed even in thionacetates.

Formation of such a fragment $[M-60]^-$ in thionacetates may entail alkyl migration prior to the expulsion of the $(\text{SCH}_2\text{CH}_2)$ fragment by the mechanism in Scheme 3, page 30, in which case one would not expect this mode of fragmentation to compete effectively with $\alpha$-cleavage leading to the acetyl fragment. Observation of this fragmentation mode is contrary to what is observed in thionbenzoates. One may attribute the failure to
show this fragmentation to the stability of the benzoyl fragment which is formed in a competing reaction.

Also in thioacetates an analogous elimination of ethylene oxide \((\text{CCH}_2\text{CH}_2)\) is observed; both propyl thiolacetate and propyl thionacetate show a peak at m/z 74 which can be rationalized as loss of ethylene oxide, and a similar fragment is observed in the butyl thioacetates at m/z 88. In pentyl thioacetates such a peak is not observed. However, such a fragment may in either case be rationalized as loss of carbon monosulfide \((\text{C}=\text{S})\) from the molecular ion. This type of ambiguity can easily be resolved by labelling experiments or by high resolution measurements.

Clearly, one cannot distinguish between thiolacetates and thionacetates on the basis of fragments other than the base peak, which, in the case of propyl thioacetates cannot be assigned unambiguously without the use of either high resolution measurements or labelling experiments. Fragments such as \([\text{M}-60]^+\), \([\text{RS}]^+\) etc., which in the case of thiobenzoates are distinctive features of a particular functional group \((\text{C}=\text{S} \text{ and not } \text{C}=\text{O})\) are in most cases equally abundant in both thion and thiolacetates. Because all the alkyl groups have a terminal methyl group one can only speculate that \((\text{R})\) comes from the acyl or alkyl side of the carbonyl or thiocarbonyl group. One example of such a peak is at m/z 47, which corresponds to \([\text{CH}_3\text{S}]^+\). However, one can make the following generalizations which could help in distinguishing between the thioacetates:

For the same alkyl group, both McLafferty rearrangements are much more prominent in thionacetates, the base peak in thiolacetates corresponds to \([\text{RCO}]^+\) while in thionacetate the base peak may correspond to the alkene formed in the McLafferty rearrangement, depending on the length
of the alkyl group, while the corresponding \([R-H]^+\) peak in thiolacetate is relatively smaller. Both the fragments \([\text{RCS}]^+\) and \([\text{RCSH}]^+\) are much more predominant in thionesters and have a much lower relative abundance in thiolacetates, and the molecular ion peak is more prominent in thionacetates.

C. \(\beta\)-Phenethyl thioesters 

\[
\begin{array}{c}
\text{R} \quad \bigcirc \quad \text{Y} \quad \text{CH}_2\text{CH}_2 \quad \bigcirc \quad \text{R} \\
\end{array}
\]

In general, the fragmentation of \(\beta\)-phenethyl esters occurs in the alcohol portion rather than the acyl portion, thus making the fragmentation pattern rather similar to that of aliphatic esters. In this work \(\beta\)-phenethyl thiobenzoates and \(\beta\)-phenethyl thioacetates were investigated. Thus one may expect that the \(\beta\)-phenethyl thioacetates should behave more like aliphatic thioesters while the \(\beta\)-phenethyl thiobenzoates are expected to behave more like the alkyl thiobenzoates investigated.

Examination of the spectra of \(\beta\)-phenethyl thioesters reveals a noticeably low abundance molecular ion, even less significant than that observed in aliphatic alkyl thioesters. In \(\beta\)-phenethyl thioesters the molecular ion is much more significant in both thiolacetate and thiobenzoate rather than in the analogous thions (Table 7a). This is in contrast to alkyl thioesters where the thions show a higher \(M^+\) than the thioesters. The fragments can be divided into two major categories.

Direct cleavage fragments:

In the thiobenzoate \((X=O, Y=S, R=H)\), \(\alpha\)-cleavage on the alkyl side produces the benzoyl fragment \([\text{PhCO}]^+\) as the base peak at \(m/z\) 105. However, the fragment \([\text{CH}_2\text{CH}_2\text{Ph}]^+\) would appear at the same mass number. Thus in order to make the correct assignment, it was necessary to use high resolution mass spectrometry. Under high resolution, a doublet was
observed corresponding to the two fragments. Measurement of the area under the two peaks revealed that approximately 95% of this peak corresponds to the benzoyl fragment [PhCO]⁺, which indicates that the base peak is mainly due to α-cleavage with a very small contribution from the hydrocarbon fragment [PhCH₂CH₂]⁺. The phenyl fragment [Ph]⁺ is fairly abundant and could be derived from either the acyl or the alkyl portion of the molecule. However, the fact that this ion is of the same order of magnitude in both acetates and benzoates (10%) may suggest that it arises mainly from the alkyl portion. High resolution measurements discount the fragment [CH₃COSH₂]⁺ as a component of this peak.

In the thionbenzoates (X=S, Y=O, R=H), the base peak is due to the olefin formed by McLafferty rearrangement. This particular behaviour may be compared with the thionacetates investigated. The thionbenzoate also displays isobaric fragments, [R¹CO]⁺ and [PhCH₂CH₂]⁺, the relative abundance of which is the second largest in the spectrum. An attempt to resolve these two peaks by substitution does not positively show which of the two fragments is important in the unsubstituted molecule. Taking the isotope peak into consideration, the hydrocarbon fragment accounts for about 40% which is slightly higher than the relative abundance of the acyl fragment and may therefore be the major component of the peak at m/z 105.

In the thioacetates, the base peak is due to the styryl ion. The acetyl fragment in thiolactate is the second largest peak in the spectrum (38%) and in thionacetate where it is formed by alkyl migration followed by α-cleavage, the relative abundance of this peak is much smaller (3.7%). α-Cleavage in thionesters is not very significant. Other direct cleavage fragments include [PhCH₂CH₂]⁺, [PhCH₂]⁺ and [PhCOS]⁺.
Table 7a

Mass Spectra of thiol and thion analogues of B-phenethyl benzoates and acetates (R¹ – CH₃ – CH₂ – CO – R)

<table>
<thead>
<tr>
<th>Fragment</th>
<th>R¹ = Ph</th>
<th>R¹ = Ph</th>
<th>R¹ = CH₃</th>
<th>R¹ = Ph</th>
<th>R¹ = CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R = H</td>
<td>R = CH₃</td>
<td>R = H</td>
<td>R = H</td>
<td>R = H</td>
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<tr>
<td>[M]⁺</td>
<td>1.3</td>
<td>0.2</td>
<td>1.2</td>
<td>4.6</td>
<td>13.5</td>
</tr>
<tr>
<td>[R¹CO]⁺</td>
<td>(29.4)ᵇ</td>
<td>3.7</td>
<td>(100)*</td>
<td>38.3</td>
<td></td>
</tr>
<tr>
<td>[R¹CS]⁺</td>
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<td>11.9</td>
<td>0.4</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>[R¹CSH]⁺</td>
<td>1.0</td>
<td>1.1</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[R¹CO₅]⁺</td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>0.6</td>
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</tr>
<tr>
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<td>0.8</td>
<td>4.4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>[Ph]⁺</td>
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<td>10.6</td>
<td>11.4</td>
<td>27.6</td>
<td>9.3</td>
</tr>
<tr>
<td>[R – CH₂ – CH₂]⁺</td>
<td>(29.4)ᵇ</td>
<td>20.3</td>
<td>37.2</td>
<td>(100)*</td>
<td>13.5</td>
</tr>
<tr>
<td>[R – CH₅ – CH₂]⁺</td>
<td>5.7</td>
<td>3.8</td>
<td>9.7</td>
<td>2.8</td>
<td>4.6</td>
</tr>
<tr>
<td>[R – CH₆ – CH₂]⁺</td>
<td>1.8</td>
<td>8.7</td>
<td>12.8</td>
<td>4.9</td>
<td>32.6</td>
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<tr>
<td></td>
<td><strong>100</strong></td>
<td><strong>100</strong></td>
<td><strong>100</strong></td>
<td>51.3</td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

ᵇ entries in brackets could be due to one or the other fragment partly or entirely

* base peak is mainly due to [R¹CO]⁺
which corresponds to the alkyl fragment, is much more abundant here than in either the alkyl thiobenzoates or the alkyl thioacetates investigated. In β-phenethyl thiobenzoates, however, it presents problems of assignment as discussed above. The fragment due to [Ph-CH₂]⁺ is much more abundant in thioacetates than in benzoates indicating the influence of the acyl group on the fragmentation pattern of β-phenethyl thioesters. The same fragment may be derived from the fragment at m/z 105 due to [PhCH₂CH₂]⁺.

Rearrangement fragments:

In the β-phenethyl thioacetates, the fragment due to McLafferty rearrangement [R'\text{COSH}]⁺ is observed but is not as significant as in the alkyl thioacetates. The complementary fragment [PhCH=CH₂]⁺, however, is stable enough to make the base peak. This behaviour is similar to that observed in the aliphatic thionesters where the olefin fragment forms the base peak. However, while in β-phenethyl thioacetates, both the thion and the thiol acetate produce the olefin as the base peak, in the aliphatic thioacetate this behaviour is only displayed by the thionacetates. Thus in β-phenethyl thioacetate this behaviour must be influenced by the stability of the styryl ion. In β-phenethyl thionbenzoate the fragment due to [R'\text{COSH}]⁺ is not detected. A clear reversal of charge placement is observed here, the charge being preferentially placed on the olefin fragment rather than the complementary thioacid. This is expected because of the stability of the styryl ion fragment and a higher ionization potential for thioacetic acid and thiobenzoic acid compared to the olefin. The peak at m/z 103 which corresponds to the fragment [PhCHCH]⁺ may result from the styryl ion by loss of a hydride radical rather than from double hydrogen rearrangement since the title compounds seldom undergo
double hydrogen rearrangement. The fragment \([R^1 \text{COSH}_2]^+\) corresponding to the double McLafferty rearrangement product is not detected in any of the thioesters. Formation of the peak at m/z 103 can be rationalized as in Scheme 15, below. The transition corresponding to step 1 was confirmed by a metastable peak at \(V_0=3.275, V=7.62\), for O-phenethyl thiobenzoate. The metastable corresponding to step 2 however, was not observed.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{Y} & \quad \text{X}
\end{align*}
\]

\[\overset{1}{\rightarrow} \quad [\text{PhCHCH}_2]^+ \quad + \quad \begin{align*}
\text{Ph} & \quad \text{Y} \\
\text{X} & \quad \text{H}
\end{align*}
\]

\[
\overset{2}{\downarrow} \quad [\text{PhCHCH}]^+
\]

**Scheme 15** Rationalization of the formation of m/z 103

Both alkyl migration and hydrogen migration prior to \(\alpha\)-cleavage occur in \(\beta\)-phenethyl thioesters as in the other thioesters investigated, although here these reactions seem to occur to a much lesser extent.

Migration of the alkyl group followed by \(\alpha\)-cleavage leads to the thioacyl fragment \([R^1 \text{CS}]^+\) in \(S\)-alkyl thioesters and to the acyl fragment \([R^1 \text{CO}]^+\) in \(O\)-alkyl thioesters. The migration is more noticeable in the thionesters. Migration of hydrogen prior to \(\alpha\)-cleavage is again specific to the thiocarbonyl group.

(1) **Field ionization spectra of \(\beta\)-phenethyl esters**

The field ionization spectra of the above compounds are presented in Table 7b. The base peak corresponds to the molecular ion \([M]^+\) in both thionesters and thioesters. The thionesters \(R^1 \text{COR}^2 \quad (X=S, \; Y=O)\) show a significant peak corresponding to the alkyl group \([R^2]^+\) and a peak corresponding to \([R^2-\text{H}]^{++}\) which could arise by McLafferty rearrangement.
Table 7b

Field ionization spectra of β-phenethyl thioesters

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Benzoates (PhCYR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R=CH₂CH₂Ph(oMe)</td>
</tr>
<tr>
<td></td>
<td>X=S, Y=O</td>
</tr>
<tr>
<td>[R]⁺</td>
<td>1.0</td>
</tr>
<tr>
<td>[R-H]⁺</td>
<td>4.3</td>
</tr>
<tr>
<td>M²⁺</td>
<td>79.7</td>
</tr>
<tr>
<td>M⁺⁺</td>
<td>100</td>
</tr>
</tbody>
</table>

* Isobaric with PhCO

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Acetates (CH₃CYR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R=CH₂CH₂Ph</td>
</tr>
<tr>
<td></td>
<td>X=S, Y=O</td>
</tr>
<tr>
<td>[R]⁺</td>
<td>7.3</td>
</tr>
<tr>
<td>[R-H]⁺</td>
<td>14.5</td>
</tr>
<tr>
<td>[CH₃CO]⁺</td>
<td>7.3</td>
</tr>
<tr>
<td>M²⁺</td>
<td>7.7</td>
</tr>
<tr>
<td>M⁺⁺</td>
<td>100</td>
</tr>
</tbody>
</table>
in which the charge is retained by olefin or by loss of hydrogen radical from the alkyl group fragment \([R^2]^+\). The thionacetates \((X=S, Y=O)\) and thiolacetates \((X=O, Y=S)\) display a peak due to the acetyl ion \([R^1CO]^+\). A corresponding benzoyl fragment is not observed in the thiobenzoates.

The thionesters \((X=S, Y=O)\) display a peak corresponding to a doubly charged molecular ion \(M^{2+}\) which is not observed in thiolesters. The fragment due to \(M^{2+}\) is especially important in the substituted esters where the substituent \((CH_3O)\) makes ionization at the phenyl ring easier.
CHAPTER 6

CONCLUSIONS

At high internal energies (70eV ionization) both thionbenzoates and thiolbenzoates show analogous direct cleavage fragments. In thionbenzoates these include (PhCO)$^+$ as the base peak; in thionbenzoates this base peak is due to rearrangement which involves alkyl migration followed by direct cleavage. More rearrangements are observed in thionbenzoates than in thiolbenzoates. In thionbenzoates fragments due to rearrangement reactions include (PhSH)$^{2+}$, (PhCSH)$^{+}$, (M-SH)$^+$ and (PhS)$^+$. The fragments PhS and PhSH arise from the McLafferty, and the 'McLafferty + 1' rearrangement products, respectively, by migration of sulfur to the benzene ring followed by the loss of (CHO). The fragment (PhCSH)$^+$ results from hydrogen migration from the alcohol side to the thiocarbonyl group followed by \( \alpha \)-cleavage. At low internal energies (10-20eV ionization) all direct cleavage fragments are not observed but rearrangement reactions are significant. Both the single and double hydrogen rearrangements are observed. The double hydrogen rearrangement reaction is more significant than the single hydrogen rearrangement. Field ionization spectra indicate the molecular ion as the base peak. Although the fragment due to alkyl migration prior to \( \alpha \)-cleavage may be observed, there are indications that it is not a true gas phase reaction but may be formed by surface related processes.

In the thiolbenzoates both the single and the double hydrogen rearrangements are observed, with the double hydrogen rearrangement more relatively abundant. A rearrangement corresponding to loss of
thioethylene oxide ($\text{SCH}_2\text{CH}_2$) is observed to be very significant. Such a rearrangement was not observed in the thionbenzoates. The thioacetates on the other hand are difficult to differentiate in terms of rearrangement reactions. The fragment due to loss of thioethylene oxide for example, is observed in both the thionacetates and the thiolacetates. A fragment at $(M-44)^+$ is observed in both types of thioacetates. The fragment lost in this reaction could be carbon monosulfide but may also be ethylene oxide. Fragments $(\text{RCS})^+$ and $(\text{RCSH})^{++}$ are observed in thionacetates and thiolacetates although they are much more prominent in the thionacetates. In butyl and pentyl thionacetates the base peak corresponds to the olefin produced in a McLafferty rearrangement while in the thiolacetates the base peak corresponds to the $\alpha$-cleavage fragment $(\text{RCO})^+$ . The field ionization spectra of the thioacetates show predominance of the molecular ion as the major fragment and the acetyl ion as the other major fragment.

In conclusion, this work has uncovered some interesting rearrangement reactions that need further investigation. In the case of thiobenzoates labelling experiments are necessary to justify some of the mechanisms observed. In the case of thioacetates a thorough understanding of the fragmentation patterns will need both labelling experiments and high resolution measurements.
REFERENCES


87. For leading references and an excellent review of pyrolytic processes, see:
   b) H.R. Nace, Org. Reactions, 12, 57, (1962).


PART II

ELECTRON IMPACT AND FIELD IONIZATION DEFOCUSING STUDIES

OF

1- AND 2-ADAMANTYL ESTERS
CHAPTER 1

INTRODUCTION

Adamantane (I), a highly symmetrical diamondoid hydrocarbon was first isolated from petroleum in 1933 (1). However, widespread investigation did not start until 1957, when Schleyer et al. (2) reported its synthesis by rearrangement of tetrahydrodicyclopentadien (II) catalysed by aluminum halides. Since the initial discovery (3) that amantadine (III, 1-adamantylamine hydrochloride) displays antiviral activity towards certain influenza strains, the yearly growth in the number of papers dealing with adamantane and its related homologues has been exponential.

\[ \text{AlX}_3 \text{ Br, Cl} \]

The early literature dealing with the synthetic aspects of adamantane chemistry has been summarized by Stetter (4,5). More recent reviews (6-9) indicate a continued rapid growth of interest in adamantane chemistry.

A. Electron impact studies of adamantanes

Adamantane is a typical example of compounds in which a small number of carbon atoms form a relatively high number of cycles. Consequently,
its mass spectrum is very complex since its molecular ion may decompose or isomerise into fragment ions with a large number of multiple bonds. The earliest electron impact studies on derivatives of adamantane revealed that the substituents markedly influence the mechanism of cleaving the basic adamantane skeleton (10). Study of a large number of 1-adamantyl derivatives indicated two types of fragmentation patterns: The first type was observed when alkyl substituents and functional groups were eliminated from the molecular ions as neutral species (equation 1.1).

\[ \text{X=alkyl, NO}_2, \text{Cl, Br, COOH, COCH}_3 \]

The fragment \([\text{C}_{10}\text{H}_{15}]^+\) formed from different compounds shows similar further fragmentations for all the compounds studied. The major fragments formed from \([\text{C}_{10}\text{H}_{15}]^+\) include \([\text{C}_8\text{H}_{11}]^+, [\text{C}_7\text{H}_9]^+, [\text{C}_6\text{H}_7]^+, [\text{C}_5\text{H}_7]^+, \) and \([\text{C}_5\text{H}_9]^+\).

The second pattern consisted of 1-adamantanes with functional groups which were not lost during the fragmentation. These follow the fragmentation pattern of equation (1.2).
\[ X = \text{C}_6\text{H}_5, \text{OH, NH}_2, \text{NHCOCH}_3 \]

In this group the decomposition of adamantane skeleton is easier than the simple elimination of the substituent. Such a decomposition is effected by dissociation of the \( \text{C}(1)\text{C}(2) \) bond which is weakened by substituents capable of localising the positive charge.

Upon electron impact, 1-adamantylacetone did not undergo McLafferty rearrangements that have been noted for simple ketones with \( \sigma \) hydrogens (equation (1.3))(11).

\[ \begin{array}{c}
+ \\
\text{O} \\
\text{C=C=CH}_2 \\
\text{CH}_3
\end{array} \rightarrow
\begin{array}{c}
+ \\
\text{CH}_3
\end{array} \text{C}=\text{CH}_2 \]

Instead, direct cleavage led to elimination of acetylnyl radicals and the appearance of an intense peak at \( \text{m/z} \ 135 \ (\text{C}_{10}\text{H}_{15}^+) \) consistent with the fragmentation pattern of equation (1.1).

Electron impact studies on 2-substituted adamantanes (V) (12-15) revealed two types of fragmentation patterns (13-16), with the molecular
ions undergoing either loss of HX or X' depending on the C-X bond strength or the stability of the radical X' (12).

The relative ease for loss of HX and X' for some 2-adamantane derivatives is tabulated in Table 1.

Table 1. Relative ease of loss of HX and X' from the molecular ion (12)*

<table>
<thead>
<tr>
<th>Substituent (X)</th>
<th>Loss of HX/loss of X</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>0.0</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>290.0</td>
</tr>
<tr>
<td>OCOCH$_3$</td>
<td>44.0</td>
</tr>
<tr>
<td>OCOCF$_3$</td>
<td>8.0</td>
</tr>
<tr>
<td>Cl</td>
<td>6.5</td>
</tr>
<tr>
<td>Br</td>
<td>0.016</td>
</tr>
<tr>
<td>I</td>
<td>0.004</td>
</tr>
</tbody>
</table>

* calculated from the m/z 134 and 135 peaks after correcting latter for isotopic contribution of the former.

In cases where loss of HX was dominant, the presence of appropriate metastables indicated that the reaction occurred in a concerted fashion. A most likely primary fragmentation product from loss of HX in a series of derivatives (e.g. V, X = COOH, COOCH$_3$, CONH$_2$) was thought to be 2-4,dehydroadamantane (VI). Previously such a structure had been postulated in the fragmentation of V, X = OH and NH$_2$, compounds which had shown a
striking similarity in fragmentation of the \([M-HX]^+\) ion (14). In these compounds the fragment \([M-HX]^+\) is thought to form by a 1,3-elimination for which the spatial relationship is favourable. In V, \((X=OH)\), such a mechanism has been confirmed by deuterium labelling experiments (15).

![Image](image)

VI

However, the similarity in the fragmentation patterns of protoadamantene, and 2-adamantyl and 4-protoadamantyl derivatives has been taken as an indication that the \([M-HX]^+\) ions formed from 2-adamantyl compounds possess a structure corresponding to the protoadamantene radical cation VII rather than that of dehydroadamantane (16) Fig. 1.1. In most cases, the difference in fragmentation patterns of 1- and 2-substituted adamantanes is distinctive enough to allow easy identification. However, the 1- and 2-adamantanethiols give almost identical spectra with loss of the sulfhydryl radical producing the most abundant ion (14). Unexpectedly, 1-adamantanethiol does not follow the fragmentation pattern of equation (1.2) but that of equation (1.1). This behaviour is surprising since sulfur is known to participate readily in the type of new bond formation that would lead to IV \((X=SH)\).
Recent experiments (17) using the criteria of competing metastable transitions (18) for 2,4-dehydro adamantane, 2-adamantanol, 2-endoproto adamantanols, and both exo and endo-4-protopadamantanols, have shown these compounds to have similar ratios for competing metastable transitions. This may be taken to indicate that 2,4-dehydro adamantane radical cation VI rather than VII, is formed by loss of HX (17).
However, other adamantoid compounds which require a skeletal rearrangement and/or hydride shift in order to achieve the structure VI, such as 4-protoadamantene, 9-homonoradamantene, 9-homonoradamantanol and 10-endo-protoadamantanol may form 4-protoadamantene radical cation VII on electron impact. The differences in the intensity ratio of the competing metastable transitions for the two types of compounds were too small to allow such classification of structure. It was therefore concluded that various possible isomeric structures of \([C_{10}H_{14}]^+\) ions generated from both types of adamantoid compounds interconvert to a mixture of common ions before undergoing further degradation in the field-free region of a mass spectrometer.

In the mass spectra of some 1-substituted adamantanes \((X = \text{OCOCH}_3, \text{OCOC}_2\text{H}_5, \text{CN})\) the elimination of \(HX\) was also observed (19) but no structure was assigned to the resulting ion. An indication of the possible occurrence of the adamantene (VIII) ion was noted in the mass spectra of some disubstituted adamantanes (20).

\[
\text{VIII}
\]

B. The search for adamantene

The possibility of existence of 1,2-dehydroadamantane or adamantene is an intriguing question in chemistry (7). Adamantene is expected to be highly strained because the \(p\)-orbitals of the 1,2-double bond cannot overlap without considerable deformation of the rigid skeleton. Partly due to this inherent strain and partly to the great interest in adamantane
chemistry, adamantene has been extensively sought (23-31). These efforts reveal not only the intrinsic interest of this olefin and its reactions, but reflect as well a continuing controversy over the properties of the olefin in the various methods used to generate it. Although most of these attempts were futile (14, 23-25), various groups have produced unequivocal results which indicate the existence of adamantene (26-31).

For example, dimers of the formula C_{20}H_{28} were isolated in very high yields from treatment of either 1,2-diiodoadamantane or 1-bromo-2-iodo adamantane, with butyl lithium (26) (Fig. 1.3).

It was specifically noted that furan could not form a Diels-Alder adduct with VIII.

![Diagram](image)

**Fig. 1.3**

Two routes to adamantane were published following the isolation of the dimers. Adamantene produced by photolysis of 1- or 2-adamantyl phenylacetate (27), was trapped in methanol to yield 1-methoxyadamantane Fig. 1.4. In addition, Wynberg and co-workers heated adamantane 1,2-di-tert-butyl perester to 70° in dimethylfuran and isolated a Diels-Alder adduct (28). No dimers
were found in either case.

Fig. 1.4

Recently (31) evidence has been presented for formation of adamantene by ring expansion of carbene XI produced by pyrolysis of XII in presence of butadiene. Isolation of IX is taken as evidence for formation of adamantene during the pyrolysis.

\[
\text{XI} \quad R = \text{CH} \\
\text{XII} \quad R = \text{CHNNLiTs}
\]
The picture therefore remains hazy. As Wynberg et al (28) note, it is possible that dimer formation from 1,2-dihaloadamantanes (Fig. 1.3) does not involve adamantene since coupling is possible under the same experimental conditions (32, 33). This raises the possibility also of similar processes operating in the formation of IX. Schleyer et al (31) argue that isolation of an adduct with dimethylfuran by Wynberg could be misleading since a stepwise process is not impossible in this reaction.

It seemed appropriate therefore to investigate the possibility of formation of adamantene by electron impact studies (conditions which preclude formation of the dimer) and by field ionization kinetics (conditions which allow distinction between surface related processes and gas phase processes).

Although earlier studies on esters (19) have noted the presence of the peak corresponding to [M-HX]⁺, the possibility that adamantene radical cation might be the structure remaining after loss of HX from both isomers does not appear to have been considered. In esters such a fragment would form by McLafferty rearrangement, a process related to the Norrish type II cleavage (one of the modes which has been used to form adamantene).

Consequently, a number of adamantyl esters which included those labelled with deuterium in the position 1 were synthesized and their mass spectra are presented in Appendix 5.

C. Kinetics and mechanisms of decomposition of field induced ions in the gas phase

Field ionization mass spectrometry is a powerful technique for the elucidation of the mechanisms of decomposition of organic ions from kinetic data. The f.i. technique offers a time-resolved view of the
reactions in the time range $10^{-12}$ to $10^{-5}$ sec after the ionization process.

On the other hand, ionization by electron impact leads to a time integrated view of all processes occurring in the time range of $5 \times 10^{-14}$ to $10^{-6}$ sec. (34). In the proximity of a field anode, the field strength is high enough to ionize molecules, and also can induce decomposition reactions. But the field strength decreases with the distance from the anode and rapidly falls to relatively low values at which unimolecular decompositions are virtually uninfluenced. The field strengths in the space between the anode and the cathode (counter-electrode) are however, still high enough to allow differentiation between fragments formed at different lifetimes because of the differences in potentials at their points of origin. Differences in lifetimes as short as several $10^{-12}$ to $10^{-11}$ sec. can be detected. The use of a double focusing f.i. mass spectrometer for the study of unimolecular decomposition affords an advantage over the single focusing mass spectrometer, particularly when isotopic labelling techniques are employed (35-37). Here, the ions are energy selected by the electric sector analyser (ESA) before entering the magnetic analyser (in conventional mass spectrometers) and after passing through the magnetic analyser in "reverse geometry" mass spectrometers. Under normal conditions, ions with reduced kinetic energy will not reach the detector at all. Such ions can be detected by either of two defocusing techniques. In one technique the accelerating (anode) voltage is raised and in the other the electric sector potential is lowered. Both methods measure ion currents as a function of ion kinetic energy for ions of any selected mass, without interference from ions of nearby masses. The first technique was first reported by Schultze et al (38, 39) who detected the kinetic energy deficient fragment ions resulting from gas
phase decompositions by increasing the f.i. emitter voltage. The second method was first used by Chait and Kitson (40). Reported kinetic measurements based on this latter method have been demonstrated to be erroneous (37, 41) which led to the conclusion that this technique is not suited for kinetic measurements as it may lead to serious energy discriminations. It was argued that fragments formed on their path from the emitter to the counter electrode at a potential appreciably lower than that of the anode (possessing a considerably smaller kinetic energy) are discriminated against as the source is focused only for fragments formed at or in the near vicinity of the anode (37). The first technique is also more convenient since the magnetic field is kept constant (43). By focusing the magnet on a fragment ion of interest and progressively increasing the anode voltage, the kinetic energy lost during fragmentation at greater distances from the anode is restored, and fragment ions pass through the analyser and are collected at their normal m/z value but at a higher potential (39, 44). In this way, a curve of ion current against anode potential for a particular ion is measured. This procedure amounts to a defocusing experiment in (a) a high field region (anode to cathode) and (b) the first field free region. Following calculation of potential maps and ion trajectories (40, 45, 47) for an f.i. source, the ion current vs potential curves can be transformed into ion current vs time plots (48, 49). Typical ion lifetimes in a Mattauch–Herzog double focusing f.i. mass spectrometer are (48): anode–cathode $10^{-11}$ to $10^{-9}$ s; focus slit $10^{-8}$ s; first field-free region $10^{-6}$ s; second field-free region $10^{-5}$ s. The first region provides a continuum of ion current readings, whereas the others provide only a single point. In all these regions only gas phase formation of fragment ions is involved. At very short times
ions can be formed on the anode surface as well (normal f.i. spectrum). Double focusing mass spectrometers with "reversed geometry" i.e. with the electric sector following the magnet, have also been used in the studies of kinetics of field ionized molecules (50, 51, 52).

Although it is necessary to convert curves of ion current vs emitter voltage to curves of ion current vs parent ion life-time in order to obtain quantitative kinetic information, the initial experimental curves of ion current vs emitter voltage can provide some useful information without further calculation. For example, gas phase fragmentations are readily identified by comparison of the extended tail on the current vs voltage plot with the narrow, symmetrical peak obtained for an ion formed only at the surface (e.g. M+).
CHAPTER 2

EXPERIMENTAL

A. Instrumental

Proton n.m.r. spectra were obtained by means of a JEOL C60 HL spectrometer using TMS as internal reference. The infrared spectra were obtained using a Beckman IR-12 spectrophotometer. Melting points were determined with a Fisher-Johns apparatus and are uncorrected. All the e.i. spectra and normal f.i. spectra were obtained by methods and conditions described in the experimental section of Part I of this thesis.

Identification of all compounds was accomplished by using infrared spectra, n.m.r. spectra and mass spectrometry. Spectra obtained in the defocused mode were obtained by either of the two modes described in Chapter 1:

(1) by scanning the anode voltage from 2KV to 3KV (at - 8KV extraction plate), for a selected fragment ion. The spectra were recorded on chart paper with a Fisher S5000 recorder.

(2) by a stepwise increase of accelerating voltage and scanning the magnet at a fixed accelerating voltage.

For measuring the accelerating voltages at which defocused peaks appear, a digital voltmeter (measuring 0 to +10V) was connected to the socket U_B on unit BHA of the instrument so that a read-out of 10V corresponds to an accelerating voltage of 3KV.

B. Chemicals

Adamantyl esters

1- and 2-adamantyl acetates and trifluoroacetates were prepared according to the procedure of Schleyer (54). The following esters were
prepared:

1-adamantylacetate XXIII, i.r. (CHCl₃, 5%) 1720 (s, C=O); 1265 (s, C-O-C) cm⁻¹, n.m.r. (CDCl₃) δ 2.05 (9H, m); 1.85 (3H, s); 1.75 (6H, m).

1-adamantyl trifluoroacetate XXIV, i.r. (CHCl₃, 5%) 1775 (s, C=O); 1265 (s, C-O-C) cm⁻¹, n.m.r. (CDCl₃) δ 2.20 (9H, m); 1.70 (6H, m).

2-adamantylacetate XIV, i.r. (CHCl₃, 5%) 1780 (s, C=O); 1235, 1185 (s, C-O-C) cm⁻¹, n.m.r. (CDCl₃) δ 2.50-1.30 (14H, bm); 4.85 (1H, m).

2-adamantyl trifluoroacetate XV, i.r. (CHCl₃, 5%) 1780 (s, C=O); 1240, 1185 (s, C-O-C) cm⁻¹, n.m.r. (CDCl₃) δ 1.5-2.01 (14H, bm); 4.85-5.01 (1H, m).

All the compounds were isolated by g.l.c. and the purity confirmed by n.m.r. and i.r.

4-Protoadamantanone, XVII (53)

Benzene, 250 mL, was purified by distilling the first 100 mL from a 350 mL sample. To the cooled (room temperature) benzene was added 1-admantanol (Aldrich), 10.1 g, 66.3 mmole, lead tetraacetate (Aldrich), 32.6 g, 1.1 mmole, and iodine, 18.6 g, 1.1 mmole. The mixture was stirred vigorously with a mechanical stirrer at 50° (carefully controlled) for 80 minutes. The cooled solution was filtered and the solid washed with benzene and then ether. The filtrate and washings were stirred with 115 g of sodium bisulfite in 1000 mL of water until the benzene layer remained colourless upon standing, washed with water, then with 93 g of sodium bicarbonate in 1000 mL water, and finally dried (MgSO₄).

Evaporation at 50° at aspirator pressure gave an oil which crystallised from 100 mL of methanol at -70°. The crystals which formed were filtered cold and washed with a small amount of cold methanol to yield 8.7 g (the yields varied) of 7-iodomethyl bicyclo (3.3.1) nonan-3-one, mp 76°-78° (lit. 53 mp 78-79°); n.m.r. (CDCl₃) δ 3.1 (2H, d), 1.0 (1H, t),
and 1.7-2.8 (12H, m).

The crude iodo-ketone was stirred in 10 mL of dry pyridine at 55° for 4 hours. The cooled solution was poured into 900 mL of ice water. The mixture was then filtered to remove small amounts of a brown, oily residue. The filtrate was extracted with 350 mL of ether, and the ether layer washed with 4 x 50 mL of 5% phosphoric acid, and then water. The ether layer was dried (Na₂SO₄), filtered, and evaporated to leave 4.1 g (41% from 1-adamantanol; yields varied) of 4-protoadamanlanone:

mp 208-209° (lit. 55 mp 210-212°); i.r. (CCl₄) 2930, 2840, 1725, 1710, and 1235 cm⁻¹; n.m.r. (benzene-d₆) δ 2.7 (1H, sextet) and 1.1-2.4 (15H, m).

Reduction of 4-Protoadamanlanone XVII with LiAlD₄ (54)

Lithium aluminum deuteride (Aldrich), 0.2 g., 4.76 mmole in 20 mL of absolute ether was placed in a round bottomed flask equipped with a reflux condenser and a calcium chloride drying tube. 4-protoadamanlanone, 1.0 g., 6.66 mmole in 20 mL of absolute ether was added with a dropping funnel to maintain gentle boiling. The mixture was then refluxed for 15 hours and cooled. Dilute hydrochloric acid 20 mL was added dropwise to destroy excess lithium aluminum deuteride. The mixture was extracted with ether and washed with water. The ether layer was dried (Na₂SO₄), filtered, and evaporated to leave 0.9 g. (89%) of a mixture of the epimeric alcohols (XVIII, XIX) Scheme 1. The mixture was separated by column chromatography on a silica gel column (53) to give 0.22 g. of 4-exoprotoadamanlanol-4d (XVIII), gas chromatographically identical with unlabelled (XVIII) (by co-injection). The exact deuterium content could not be determined because of complications introduced by the strong (M-1) and (M-2) peaks. n.m.r. (CDCl₃) shows complex pattern of
signals centered at $\delta$ 1.25, 1.4, 1.9 and 2.3. The broad signal for C$_4$-H at $\delta$ 4.4 is not observed indicating a deuterium content 95%.

Also obtained from the silica gel chromatography was 0.43 g. of 4-endo-protoadamantan-4-d$_4$ (XIX) shown to be gas chromatographically identical with unlabelled (XIX) by co-injection. The n.m.r. spectrum of the product showed a complex pattern of signals centered at $\delta$ 1.5, 1.75, and 2.3 and no signal was observed at 4.05 (4-exo-H).

2-Adamantanol-1-d XX (55)

To the mixture of epimeric alcohols XVIII and XIX 0.5 g. in 30 mL of aqueous acetone (60%) was added 5 drops of sulfuric acid. The mixture was refluxed for 3 hours, reduced in volume (aspirator pressure) and extracted with ether. The ether layer was washed with water and dried (Na$_2$SO$_4$). Evaporation of ether (aspirator pressure) left 0.385 g. of 2-adamantanol-1-d mp 223-225° (sublimes). XX was shown to be chromatographically identical with authentic 2-adamantanol by co-injection. n.m.r. (CDCl$_3$) $\delta$ 3.88 (1H,m) and 2.6-1.1 (14H,m) on a 10' x 0.375' SE 30 column, the products XVIII, XIX, and XX, could be distinguished by their different retention times.

2-Adamantyl-1-d acetate XXI (54)

2-adamantanol-1-d 0.5 g., 3.3 mmoles in 4 mL of pyridine was refluxed with 4 mL of acetic anhydride for 4 hours. The mixture was poured into cold water and extracted with ether. Evaporation of the ether left a crude ester 0.45 g. which was purified by g.l.c.

n.m.r. (CDCl$_3$) $\delta$ 4.85 (1H,m), 1.2-2.1 (13H,m) and 2.2 (3H,s).

2-Adamantyl-1-d trifluoroacetate XXII

To 2-adamantanol-1-d 0.5 g., 3.3 mmoles in 10 mL of ether, in
a flask fitted with a reflux condenser and a dropping funnel, was added 5 mL of trifluoroacetic anhydride dropwise. After the reaction subsided the mixture was poured into cold water and extracted with ether, washed with water and dried (Na₂SO₄). Evaporation of the ether left an orange liquid which was purified by g.l.c.

n.m.r. (CDCl₃) δ 1.7-2.20 (bm)

i.r. (CHCl₃) 1775 (C=O) 1250 (C-OC) cm⁻¹
CHAPTER 3

RESULTS AND DISCUSSIONS

In preparation for mass spectrometric studies on adamantyl esters, the compounds in Chart 2 were synthesized. The labelled adamantyl esters (XXI, XXII) were synthesized according to Scheme 1. Mass spectra of the esters are presented in Appendix 5. The relative intensities of the major fragments are summarized in Table 2. Examination of the spectra of 1- and 2-adamantyl acetates XXIII and XIV, respectively shows that the relative intensities of most fragments are higher in 1-adamantyl acetate than in 2-adamantyl acetate, in some cases by two-fold. In one case (C_{11}H_{11}) the fragment is not observed in 2-adamantyl acetate. However, the 1- and 2-adamantyl trifluoroacetates display the reverse order, that is, most major fragments have higher relative intensities in 2-adamantyl trifluoroacetate than in 1-adamantyl trifluoroacetate. For example, the fragments (C_{7}H_{7}), (C_{9}H_{10}), C_{6}H_{7} and (C_{8}H_{7}) range between 5 and 14 times higher in 2-adamantyl trifluoroacetate. The fragments at m/z 69, 78, 79, and 97 in Appendix 5-I show higher relative intensities in trifluoroacetates than in the acetates, which may reflect a contribution from the fragments [CF_{3}]^{+}, [CF_{2}CO]^{+}, [CF_{2}COH]^{+} and [CF_{3}CO]^{+}. The adamantyl esters undergo a primary loss of HX and X to form the fragments at m/z 134 and 135 respectively. The relative ease of loss of HX and X have been measured for 2-adamantyl esters and expressed as the ratio HX/X. It has been reported that for 2-adamantyl acetate HX/X = 44.0 and for 2-adamantyl trifluoroacetate the ratio is 8.0. The smaller ratio for 2-adamantyl trifluoroacetate may indicate that the (C-O) bond to adamantane is easier to cleave in 2-adamantyl trifluoroacetate than in the acetate.

115
Chart 2

XIV, \( X = \text{OCOCOCH}_3 \)

XV, \( X = \text{OCOCF}_3 \)

XXIII, \( X = \text{OCOCOCH}_3 \)

XXIV, \( X = \text{OCOCF}_3 \)

XXI, \( X = \text{OCOCOCH}_3 \)

XXII, \( X = \text{OCOCF}_3 \)
### Table 2

Variation of relative intensities of major fragments*

<table>
<thead>
<tr>
<th>Compound</th>
<th>XXIII</th>
<th>XIV</th>
<th>XXIV</th>
<th>XV</th>
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<tr>
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<td>Assignment</td>
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<td></td>
<td></td>
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<tr>
<td>41</td>
<td>C₃H₅</td>
<td>12.8</td>
<td>4.3</td>
<td>9.9</td>
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<tr>
<td>43</td>
<td>CH₃CO</td>
<td>18.9</td>
<td>19.2</td>
<td>-</td>
</tr>
<tr>
<td>55</td>
<td>C₄H₇</td>
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<td>4.1</td>
<td>4.4</td>
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<td>C₆H₅</td>
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<td>5.7</td>
<td>20.1</td>
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<td>C₆H₆</td>
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<td>7.3</td>
<td>58.7</td>
</tr>
<tr>
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<td>C₆H₇</td>
<td>20.9</td>
<td>16.9</td>
<td>19.4</td>
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<tr>
<td>91</td>
<td>C₇H₇</td>
<td>14.7</td>
<td>11.6</td>
<td>12.4</td>
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<td>C₇H₈</td>
<td>61.4</td>
<td>52.6</td>
<td>47.3</td>
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<tr>
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<td>C₇H₉</td>
<td>25.9</td>
<td>19.7</td>
<td>18.8</td>
</tr>
<tr>
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<td>C₈H₁₀</td>
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<td>5.4</td>
<td>3.2</td>
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<td>C₈H₁₁</td>
<td>3.9</td>
<td>1.6</td>
<td>2.0</td>
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<tr>
<td>134</td>
<td>C₁₀H₁₄</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
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<td>28.1</td>
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<td>136</td>
<td>C₁₀H₁₆</td>
<td>3.7</td>
<td>1.3</td>
<td>2.9</td>
</tr>
<tr>
<td>152</td>
<td>C₁₀H₁₅O</td>
<td>-</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>194</td>
<td>M⁺</td>
<td>13.9</td>
<td>12.8</td>
<td>-</td>
</tr>
<tr>
<td>195</td>
<td>[M + 3]⁺</td>
<td>-</td>
<td>2.1</td>
<td>-</td>
</tr>
<tr>
<td>248</td>
<td>M⁺</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>249</td>
<td>[M + 4]⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Blank entries represent ions below threshold of 0.1%.

Underlined entries represent base peaks.
It may also indicate that the trifluoroacetate radical \((X)\) is more stable than the acetate radical. The results obtained here follow this general trend although the ratios \((HX/X)\) are lower than those in the previous data. The ratios obtained after correcting both \(m/z\) 134 and 135 for \(^{13}\text{C}\) isotope contribution, in the present study are 27.0 and 1.4 respectively for 2-adamantyl acetate and trifluoroacetate. In 1-adamantyl esters, on the other hand, figures were obtained which are comparable for the two functional groups: Loss of \((HX/X) = 5.8\) for 1-adamantyl acetate, and 7.2 for 1-adamantyl trifluoroacetate. These low values indicate a close competition between direct cleavage and the rearrangement reaction.

In contrast with 2-adamantyl esters, the low values imply formation of a more stable carbonium ion, the tertiary 1-adamantyl cation. However, if one accepts the notion that carbonium ions prefer a coplanar arrangement of the groups attached to the central atom, a bridgehead cation which cannot achieve such a coplanar arrangement would be unstable. Consequently a cyclic allyl ion (XIII) has been proposed to arise by a further dissociation and hydrogen transfer (Scheme 2). Such a structure may be stabilised by the interaction of the positive charge with the double bond, and enables one to rationalize formation of some of the major fragments from the 1-adamantyl cation (10).

![Scheme 2](image)

XIII
The formation of a peak at m/z 93 may involve elimination of propene by hydrogen transfer followed by cleavage of the carbon bond next to the double bond in the side chain. Further elimination of molecular hydrogen would lead to formation of a tropylion ion.

The formation of a peak at m/z 78 involves hydrogen transfer to the double bond followed by elimination of butene.

A. Mass spectra of 2-adamantyl-1-d esters

Previously, it has been assumed that the base peak in the spectra of adamantyl esters at m/z 134 arises by a 1,3 elimination mechanism leading to 2,4-dehydroadamantane (VI) (12). In Norrish Type II photochemical cleavage of adamantyl esters sufficient evidence was given to suggest 1,2-dehydroadamantane (VIII) as the cleavage product (27). Since the photochemical process in analogous to McLafferty rearrangement, it is of interest to confirm the existence of 1,2-dehydroadamantane radical ion by studying the mass spectra of 2-adamantyl esters labelled in the position 1. If 2,4-dehydroadamantane is the product of elimination [M-HX]^+, it is expected that all the deuterium label will be retained on the adamantyl skeleton. If however, the elimination product is 1,2-dehydroadamantane
then a fraction of the label should be transferred to the acid fragment as in equation (2.1).

![Chemical Structures](img)

\[
\text{m/z 134} \quad \text{m/z 135}
\]

Table 3 displays the relative intensities of fragment ions (M), (M-1), and the fragment ions associated with the two major peaks m/z 135 and 134. The mass spectrum for the labelled acetate (XXI) shows a substantial (M-1) peak. Since such a peak is negligible in the unlabelled compounds, it may be taken as evidence for incomplete labelling of the acetate. For this reason the f.i. defocusing experiments were performed with 2-adamantyl-1-d trifluoroacetate (XXII). The fragments (HX) and (DX) represent McLafferty rearrangement with charge retention while (M-HX) and (M-DX) represent McLafferty rearrangement with charge transfer (Scheme 3).

Scheme 3
Table 3

Variation of relative intensities of selected fragments in labelled adamantyl esters\textsuperscript{a,b,c,d}.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>XXI</th>
<th>XXII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fragment</td>
<td>EI</td>
<td>FI</td>
</tr>
<tr>
<td>[H\text{X}]^{+*}</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>[D\text{X}]^{+*}</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>[M-D\text{X}]^{+*}</td>
<td>100</td>
<td>0.2</td>
</tr>
<tr>
<td>[M-H\text{X}]^{+}</td>
<td>39.8</td>
<td>0.4</td>
</tr>
<tr>
<td>[M-X]^{+}</td>
<td>2.2</td>
<td>0.3</td>
</tr>
<tr>
<td>M^{+}</td>
<td>0.8</td>
<td>100</td>
</tr>
<tr>
<td>[M-1]^{+}</td>
<td>2.9</td>
<td>77.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: Corrected for $^{13}$\text{C}.
\textsuperscript{b}: Relative intensities are expressed as percent of the base peak.
\textsuperscript{c}: List threshold = 0.1%
\textsuperscript{d}: XXI = 2-adamantyl-1-d acetate
XXII = 2-adamantyl-1-d trifluoroacetate
\textsuperscript{*}: [M-1]\textsuperscript{+} indicates unlabelled compound. The data for XXI is not reliable and hence will not be discussed.
From the relative intensities of the two fragments it is clear that transfer predominates over charge retention. The spectra for the adamantyl trifluoroacetates (XV, XXII and XXIV) Appendix 5-I display peaks at m/z 152 and 153 which are much more significant than those in the acetates. While the peak at m/z 152 could be attributed to the molecular ion of adamantanol, the peak at m/z 153 cannot be accounted for. Isotopic contribution only accounts for a minor fraction. Moreover it is expected that the same peak would be relatively more abundant in the labelled compounds. The spectra of the labelled compounds display the same peaks with much lower relative intensities. This suggests that the peaks may involve fluorine. On this basis, the most reasonable assignment for the peaks is (M-CF₂COOH⁻)⁺ for m/z 152 and (M-CF₂COOH)⁺ for m/z 153. This suggests fluorine scrambling prior to decomposition (Scheme 4). Fluorine and hydrogen scrambling have been observed in fluorobenzene (56).

Scheme 4
B. Field ionization mass spectrometry of adamantyl esters

The 'normal' f.i. mass spectra of adamantyl esters are presented in Appendix 5-II. The normal f.i. spectra are those which were measured with the potential applied to the anode (3kV) approximately equal to the accelerating potential necessary for ions to be transmitted through the electric sector analyzer. Thus these spectra display the ions formed within the very high electric field in the neighbourhood of the anode.

Table 4 displays defocused spectra of 1-adamantyl acetate. These spectra were obtained by raising the anode potential from the normal value 2kV in the defocused mode. The anode potential was then kept constant while the magnet was scanned. Examination of the spectra shows that as the anode potential is increased both the total ionization and the number of ions detected is severely cut down. Some of the ions observed at the normal anode potential, for example, (m/z 199, 208, 259) are difficult to rationalize in terms of simple mechanisms. However, as the anode potential is increased further, the same ions disappear indicating that they are either induced by high field or are formed at the anode surface. Table 5 shows that normal f.i. spectrum of 1-adamantyl trifluoroacetate along with defocused spectra (b & c) which were obtained with a potential of 2940V and 2970V respectively, applied to the emitter. Under these conditions the ions formed at the emitter have too much kinetic energy to pass through the electric sector and do not appear in the spectra. Fragment ion m/z 135 is formed by direct cleavage of acyl fragment, i.e. [M-CF₃COO]⁺. The fragments m/z 170 and 228 are formed by elimination of a ketene and hydrogen fluoride [M-CF₂CO]⁺ and [M-HF]⁺ respectively. The peak at m/z 249 is an isotope peak while the fragment ion [M-1]⁺ may be attributed to surface processes. The
fragment ions appearing in the defocused spectrum are formed by the decomposition of the molecular ions some distance from the anode as they are accelerated towards the cathode. These decompositions are pure gas-phase processes little influenced by external electric fields. From the spectra in Table 5 a, b, and c, it is evident that the complexity of the normal f.i. mass spectrum resulting from both surface and high field reactions is reduced by defocusing. Thus at an increased anode potential only fragments at m/z 152, 248, 250, 78 are observed. The fragment \([\text{CF}_2\text{CO}]^+\) at m/z 78 is complementary to that one at m/z 170 which is observed at a lower potential. However, as spectrum c shows, both fragments are only formed at high fields or may be formed by surface related processes. Spectrum c and spectra at higher emitter potentials indicate that the fragment m/z 134 is formed by true gas phase decomposition of the molecular ion. Defocused spectra such as those in Table 5 b, and c, and those presented in Appendix 5 were measured by maintaining the anode potential at some constant value above normal and sweeping the magnetic analyzer. Such spectra are useful for preliminary identification of the low-field gas phase processes induced by f.i., but as discussed in Chapter 1, for detailed kinetic investigation, the alternative method of focusing the magnetic analyzer on a particular fragment ion and sweeping the anode potential is more convenient.

Curves of ion current vs anode potential obtained by this technique are presented in Figures: 2.1 - 2.3. In Figure 2.1, the intensity profiles of the molecular ion (m/z 194) and of a major fragment (m/z 134) which corresponds to McLafferty rearrangement, are shown as a function of the voltage applied to the anode. The coincidence of the intensity maxima indicates that the formation of adamantene radical ion takes place partly in the vicinity of the anode. The figure also shows an extensive
Table 4
Spectra of 1-adamantyl acetate XXIII (defocused mode)

1. Accelerating voltage = 2,937 V
   Total ionization = 1385
   \[\begin{array}{ll}
   \text{m/z} & \% \text{ RA} \\
   134 & 7.5 \\
   135 & 5.4 \\
   194 & 100 \\
   195 & 3.1 \\
   208 & 5.9 \\
   \end{array}\]

2. Accelerating voltage = 2,943 V
   Total ionization = 50
   \[\begin{array}{ll}
   \text{m/z} & \% \text{ RA} \\
   194 & 100 \\
   195 & 10.0 \\
   259 & 0.5 \\
   \end{array}\]

3. Accelerating voltage = 2,955 V
   Total ionization = 320
   \[\begin{array}{ll}
   \text{m/z} & \% \text{ RA} \\
   134 & 100 \\
   199 & 0.8 \\
   \end{array}\]

4. Accelerating voltage = 2,961 V
   Total ionization = 514
   \[\begin{array}{ll}
   \text{m/z} & \% \text{ RA} \\
   134 & 100 \\
   135 & 6.9 \\
   \end{array}\]
Table 5

f.i. and f.i. defocused spectra of 1-adamantyl trifluoroacetate (XXIV)

<table>
<thead>
<tr>
<th>m/z</th>
<th>a %RA</th>
<th>b %RA</th>
<th>c %RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td></td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td></td>
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<tr>
<td>135</td>
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<tr>
<td>152</td>
<td>4.3</td>
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<td>153</td>
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<tr>
<td>170</td>
<td>0.5</td>
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<tr>
<td>194</td>
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<tr>
<td>228</td>
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<tr>
<td>247</td>
<td>0.2</td>
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</tr>
<tr>
<td>248</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>249</td>
<td>13.4</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>1.7</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

a= Normal f.i. spectrum

b= Defocused f.i. spectrum (Anode potential) 2940V

c= Defocused f.i. spectrum (anode potential) 2988V
retardation of this rearrangement as reflected in the marked tailing towards higher voltages. Evidently most of the fragment ions acquire insufficient kinetic energy because of formation at some distance further away from the anode (and thus from its absorption layer), proving that decomposition of molecular ions occurs in the gas phase. In Figure 2.2, an increased intensity is observed for the molecular ion and the fragment corresponding to adamantene radical ion. It is clear here that formation of this radical ion takes place in the gas phase. The differences observed in the two figures is probably a reflection of the physical properties of the two esters, adamantyl acetate (less volatile) showing a greater tendency for absorption than the more volatile adamantyl trifluoroacetate. In figure 2.3, the intensity profiles of the molecular ion (m/z 249) and of two major fragments (m/z 134 and 135) are displayed as a function of the voltage applied to the anode, for 2-adamantyl-trifluoroacetate. The peak at m/z 135 corresponds to loss of (CF₃COOH), while the peak at m/z 134 corresponds to loss of (CF₃COOD). Assuming that there are no significant differences in the collection efficiencies of the two fragment ions, the ion abundances provide a direct measure of the relative extents of H and D' loss from the partially deuterated molecular ion. Thus, the isotope effect $k_H/k_D$ is given by the relative abundance of (M-CF₃COOH)$^+$ and (M-CF₃COOD)$^+$ product ions. It is likely that the McLafferty rearrangement proceeds by a stepwise mechanism and therefore $k_H/k_D$ may be very large. Indeed the ratio of the areas under the two curves gives an approximate $k_H/k_D$ of 1.7 (not corrected for $^{13}$C isotope contribution). In any event, both peaks are formed by McLafferty rearrangement and exhibit the expected tailing and displacement of peak maxima toward higher emitter voltages justifying gas phase formation of adamantene (equation 2.1).
In conclusion, the above experimental results show that adamantene or 1,2-dehydro adamantane is the structure produced when adamantyl esters eliminate the acid fragment in the McLafferty rearrangement. The electron impact data display the peak due to adamantene (m/z 134) as the base peak, the fragment corresponding to retention of charge (RCOOH)⁺, is not detected in most cases. Defocusing experiments with both the unlabelled esters and the labelled esters show beyond reasonable doubt that the fragment ion at m/z 134 is formed by gas-phase decomposition of the molecular ion rather than by high field effects or surface related mechanisms.

For a more precise interpretation it is suggested that rate constants and lifetimes of the fragment ions (m/z 134 and 135) be investigated in future work. It is also conceivable that such rate constants may provide a clear distinction between the 1- and 2-adamantyl compounds.
REFERENCES


### APPENDIX 1-I

**Electron impact mass spectra of benzoates (PhCOR)**

<table>
<thead>
<tr>
<th>m/z</th>
<th>Ethyl-</th>
<th>i-Propyl-</th>
<th>Butyl-</th>
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<th>Hexyl-</th>
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<td>6.0</td>
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</tr>
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</tr>
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Source: Extracted from Anal. Chem. 31, 2076, (1959)
APPENDIX I-II

Electron impact mass spectra of dithioesters<sup>a</sup> (PhCSR)

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APPENDIX 2-I

Electron impact mass spectra of S-alkyl thiobenzoates

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Except for comparative purposes the list threshold recorded is 1% RA.
### APPENDIX 2-Il

**Electron impact mass spectra of O-alkyl thiobenzoates**

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APPENDIX 2-VI

Electron impact mass spectra of thiol and thion analogues of

\[
\text{R-phenethyl benzoates and acetates } \quad \text{Thions (X=S, Y=O)} \quad \text{Thiols (X=O, Y=S)}
\]

\[
\begin{array}{cccccc}
\text{R}^1=\text{Ph} & \text{R}^1=\text{Ph} & \text{R}^1=\text{CH}_3 & \text{R}^1=\text{Ph} & \text{R}^1=\text{CH}_3 \\
\text{R}=\text{H} & \text{R}=\text{MeO} & \text{R}=\text{H} & \text{R}=\text{H} & \text{R}=\text{H}
\end{array}
\]

\[
m/2 \\
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15 & 0.2 & 0.2 & 0.4 & & \\
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26 & 0.7 & & 0.9 & 1.0 & \\
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40 & 0.2 & 0.2 & 0.2 & 0.1 & \\
41 & 0.2 & 0.4 & 0.4 & 0.2 & 0.8 \\
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43 & 0.4 & 0.5 & 3.7 & 0.4 & 38.3 \\
44 & 0.7 & 0.1 & 0.8 & 0.5 & 1.5 \\
45 & 0.1 & 0.3 & 0.7 & 0.3 & 1.2 \\
49 & 0.3 & & 0.2 & 0.1 & \\
50 & 2.2 & 0.7 & 1.5 & 1.4 & 2.7 \\
51 & 4.1 & 2.7 & 4.9 & 6.1 & 5.7 \\
52 & 0.8 & 0.6 & 1.1 & 0.6 & 1.4 \\
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Blank entries represent ions below limit of detection (0.1) or ions not detected.
### APPENDIX 3-I

**Percent relative abundance for thio benzoates (PhCYR) F.I. mode**

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182 & 4.3 & 1.0 & 1.2 & & & & & & \\
194 & & 100 & & & & & & & 100 \\
195 & & 15.4 & & & & & & & 17.1 \\
196 & & 6.5 & & & & & & & 0.6 \\
197 & & 0.4 & & & & & & & 0.8 \\
202 & & & & & & & & & \\
207 & & & & & & & & & 0.3 \\
208 & & & 100 & 100 & & & & & -100 \\
209 & & & 14.4 & 13.4 & & & & & 11.6 \\
210 & & & 5.7 & 5.5 & & & & & 5.8 \\
222 & & & & 100 & & & & & 100 \\
223 & & & & 16.2 & & & & & 14.3 \\
224 & & & & 1.6 & & & & & 5.1 \\
225 & & & & 0.5 & & & & & 0.4 \\
227 & & & & & & & & & 0.5 \\
234 & & & & & & & & & 11.0 \\
235 & & & & & & & & & 1.7 \\
236 & & & & & & & & & 1.0 \\
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APPENDIX 3—II

Percent relative abundance for thioacetates ($\text{CH}_3\text{CyR}$) F.I. mode

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APPENDIX 3-III

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### APPENDIX 5-I

**EI spectra of adamantyl esters\(^a, b, c\)**

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*a:* relative intensities are expressed as percent of the base peak = 100%.

*b:* blank entries represent modes of ionization below threshold 0.1%.

*c:* See page 116-119 for compound names.
**APPENDIX 5-II**

Field ionization spectra of adamantyl esters\(^a,b,c\)

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\(^a\): Relative intensities are expressed as percent of the base peak = 100%.

\(^b\): Blank entries represent ions below the threshold limit of 0.1%.

\(^c\): See page 116-119 for compound names.
APPENDIX 5-III

f.i. spectra (defocused mode) for 1-adamantylacetates XXIII

1. $U_A/U_B$ ratio = 9.10
   Voltmeter reading = 9.79V
   Accelerating voltage = 2.937V
   Total ionization = 1385
   Ion source temperature = 72°
   LT = 0.5% RA

   m/z    % RA
   134    7.5
   135    5.4
   194    100
   195    3.1
   208    5.9

2. $U_A/U_B$ ratio = 9.15
   Voltmeter reading = 9.18V
   Accelerating voltage = 2.943V
   Total ionization = 50
   LT = 0.5% RA

   m/z    % RA
   194    100
   195    10.0
   259    0.5

3. $U_A/U_B$ ratio = 9.25
   Voltmeter reading = 9.85V
   Accelerating voltage = 2.955V
   Total ionization = 320
   LT = 0.5% RA

   m/z    % RA
   134    100
   199    0.8

4. $U_A/U_B$ ratio = 9.30
   Voltmeter reading = 9.87V
   Accelerating voltage = 2.961V
   Total ionization = 514
   LT = 0.5% RA

5. $U_A/U_B$ ratio = 9.35
   Voltmeter reading = 9.89V
   Accelerating voltage = 2.967V
   Total ionization = 835
   LT = 0.5% RA

   m/z    % RA
   134    100
   135    6.9

6. $U_A/U_B$ ratio = 9.40
   Voltmeter reading = 9.90V
   Accelerating voltage = 2.970V
   Total ionization = 880
   LT = 0.35% RA

   m/z    % RA
   134    100
   135    13.8

7. $U_A/U_B$ ratio = 9.50
   Voltmeter reading = 9.39V
   Accelerating voltage = 2.979V
   Total ionization = 526
   LT = 0.35% RA

   m/z    % RA
   134    100
   135    17.2

8. $U_A/U_B$ ratio = 9.55
   Voltmeter reading = 9.95V
   Accelerating voltage = 2.985V
   Total ionization = 526
   LT = 0.35% RA

   m/z    % RA
   134    100
   135    6.3
APPENDIX 5-IV

f.i. spectra (defocused mode) for 1-adamantyl trifluoroacetate (XXIV)

Ion source temperature = 70°

1. $U_A/U_B$ ratio = 9.10
   Voltmeter reading = 9.80V
   Accelerating voltage = 2,940V
   Total ionization = 3094
   LT = 0.1% RA

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<td>136</td>
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5. $U_A/U_B$ ratio = 9.50
   Voltmeter reading = 9.94V
   Accelerating voltage = 2982V
   Total ionization = 107
   LT = 0.1% RA

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<tbody>
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6. $U_A/U_B$ ratio = 9.55
   Voltmeter reading = 9.96V
   Accelerating voltage = 2988V
   Total ionization = 92
   LT = 0.1% RA

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7. $U_A/U_B$ ratio = 9.70
   Voltmeter reading = 10.00V
   Accelerating voltage = 3000V
   Total ionization = 33
   LT = 0.1% RA

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4. $U_A/U_B$ ratio = 9.45
   Voltmeter reading = 9.92V
   Accelerating voltage = 2,976V
   Total ionization = 203
   LT = 0.1% RA
VITA AUCTORIS

Born: July 30, 1947, Uganda

Son of Mr. and Mrs. Kiremire

Education:

1971 - 1973 Makerere University, Kampala, Uganda
B.Sc., (Hons. Chemistry and Biochemistry) 1973

1975 - 1979 University of Windsor, Windsor, Ontario
Candidate for the Degree of Doctor of Philosophy (Chemistry).

Awards:

1971 - 1973 Uganda Government Scholarship

1973 - 1975 Makerere Staff Development Program
Postgraduate Scholarship (merit)

1978 - 1979 University of Windsor Scholarship for Postgraduate study.