MECHANISTIC STUDIES IN ORGANIC MASS SPECTROMETRY

A Thesis
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by

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SUMMARY.

The behaviour upon electron impact of a number of different classes of organic compounds have been examined with the aid of deuterium and ^{13}C-labelling and metastable ion techniques, with particular reference to the investigation of hydrogen and carbon scrambling processes.

It is shown that the elimination of a methyl radical from the diphenylmethyl cation and the diphenylmethane molecular ion is preceded by hydrogen and carbon scrambling. Evidence is also presented for the possible intermediacy of the radical ions derived from phenyltropylidene and o-methylbiphenyl in the $M-CH_3\cdot$ rearrangement process in the spectrum of diphenylmethane.

Similarly, considerable randomisation of hydrogen and carbon atoms occurs in the stilbene molecular ion prior to the loss of a methyl radical. This observation may be rationalised in terms of either the simultaneous occurrence of (at least) two separate mechanisms for methyl loss (with the major loss occurring from a scrambled molecular ion) or the decomposition via a single mechanism of a molecular ion which is predominantly scrambled, but which contains some partially scrambled material. In contrast, the process $M - C_6H_6$ in the spectrum of stilbene occurs mainly via a specific mechanism.

The simple fragmentations which are observed in the spectra of 1,3-dithianes involve specific cleavage and/or hydrogen rearrangement, but the mechanism of the rearrangement process $M - S_2H\cdot$, which is characteristic of the 1,3-dithiane system, is complex. The $(M - S_2H\cdot)$

Summary (contd.)

ions undergo complete hydrogen scrambling before subsequent fragmentation, and in particular the corresponding ion in the spectrum of 2-phenyl-1,3-dithiane scrambles both carbon and hydrogen.

It has been further demonstrated that 2-aryl-1,3-dithianes give satisfactory negative-ion spectra which contain molecular anions and which, in some cases at least, may contain the extra electron localised on a sulphur atom. An unusual hydrogen scrambling process is observed in the negative-ion spectra of 2-phenyl- and 2-(p-nitrophenyl)-1,3-dithiane, which is absent in the corresponding positive-ion spectra. Furthermore, a unique double hydrogen rearrangement is observed in the spectrum of 2-(o-nitrophenyl)-1,3-dithiane.

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STATEMENT.

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

PETER Y. WHITE.

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PUBLICATIONS.

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

"The Mass Spectra of 2-Aryl-1,3-dithianes and -1,3-dithiolanes", J.H. Bowie and P.Y. White; J.Org. Mass Spectrometry, 1969, 2, 611.

"Hydrogen Randomisation in the Stilbene Molecular Ion", P.F. Donaghue, P.Y. White, J.H. Bowie, B.D. Roney, and H.J. Rodda, J. Org. Mass Spectrometry, 1969, 2, 1061.

"Hydrogen and Carbon Scrambling in the Molecular Ions of Diphenylmethane Derivatives", T.K. Bradshaw, J.H. Bowie, and P.Y. White, Chem. Comm., 1970, 537.

"The Loss of C_6H_6 from the Stilbene Molecular Ion", J.H. Bowie and P.Y. White, Austral. J. Chem., 1971, 24, 205.

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INTRODUCTION.

The principle of the mass spectrograph has been known since the beginning of this century, its main application then being to determine accurately isotopic abundances, relative masses of nuclides, and atomic weights. Mass spectrometry, however, is no longer the exclusive domain of the physicist, and today mass spectrometers are used in all branches of physical, chemical, geophysical, and biological research. The discipline of mass spectrometry has expanded enormously over the past few years, and its importance is steadily growing. This has been the result of both fast progress in instrumental techniques and significant advances in basic research.

Mass spectrometry has provided the chemist with a unique area of research in that it is one of the few spectral methods which deals directly with chemical reactions.[1] A mass spectral reaction involves at least two steps: (i) ionisation of the molecule, followed (in general) by (ii) unimolecular decomposition of the ion; and the aim of much recent research has been a better understanding of the structural and energetic properties of the ions formed, and the mechanisms of fragmentation. The rapid expansion of mass spectrometry first began, however, about ten years ago when it became a field of intense interest for the organic chemist. The characteristic breakdown pattern of a molecular ion was recognised as a valuable aid in elucidating the structure of chemical compounds, particularly organic compounds. As a consequence, the basic fragmentations which occur upon electron impact in the mass spectrometer have been systematically investigated for most classes of organic compounds. In particular, many examples of specific elimination and rearrangement reactions, substituent and proximity effects, and various stereoisomeric and steric effects have been documented.[2-5]

Analysis and Interpretation.

The analysis of an electron impact induced reaction involves, like the reaction itself, two basic steps: (i) obtaining the data in the form of a mass spectrum, and (ii) subsequently interpreting the information obtained. The latter provides the challenge and stimulation to the mass spectrometrist. The former, however, is an unrewarding process which can be very tedious and time-consuming. This dilemma is a result of the demonstration by Biemann[6] of the utility of total high resolution spectra, whereby the elemental compositions of ions in the spectrum can be determined from known precise masses. Various methods of presenting the large amount of elemental data have been proposed.[6-8] Biemann[7] and McLafferty[8] have suggested "element mapping" techniques; the "hetero-atomic plotting" method proposed by Burlingame[9] has also been shown to be useful.

Despite these innovations, the fact remains that measurement of total high-resolution spectra by conventional means is a near impossible task. More recently, the development of systems[10] comprising a fast-scanning, high-resolution mass spectrometer linked to a gas chromatograph has compounded the problem of data handling. Thus, the necessity to acquire, reduce, and present mass spectrometric data efficiently and rapidly has led inevitably to the rapid development of high-speed computer techniques. Various data-acquisition systems are available, and depend on the type of mass spectrometer and the requirements of the user. The considerable advances in this area have been reviewed.[11,12]

The second problem is that of interpretation. Traditionally, the mass spectrometrist has sought to interpret mass spectral data in terms of chemical structure.[2,3,13] His understanding of this aspect has progressed remarkably, but most interpretative reasoning is still based on empirical correlations. In the light of the ever-growing volume of mass spectral information to be processed, it is obvious that the high-speed computer is best suited to the task of data analysis.

Not surprisingly, progress in the efficient use of this vast amount of data has lagged behind progress in the acquisition techniques. Nevertheless, more research has recently been directed towards this end. Two general approaches have been followed: (i) examination by the computer of an individual mass spectrum, utilising knowledge of the general fragmentation patterns for the various types of compounds,[14-16] and (ii) direct comparison of the spectrum with a large number of other spectra, in the hope that it can be matched with an identical (or almost identical) spectrum, and thus be identified.[17] A notable advance in this field has been the sequence analysis of peptides,[18-20] and it is expected that research in this most important area will expand in the next few years.

Rearrangements.

At present, disadvantages inherent in "conventional" mass spectrometric methods, which use an electron impact - positive ion (EI) source, have placed restrictions on the rapid development of computer techniques to mass spectral analysis. For example, many compounds do not produce stable molecular ions, the recognition of which is one of the first requirements in a structure determination. Similarly, many ions undergo rearrangement reactions which involve groups other than hydrogen. These so-called skeletal rearrangements[21] are generally of the form

$$ABC \longrightarrow AC + B$$

or alternatively they can occur by reorganisation of the molecular ion,[22] e.g. a→b.

a b

Some such reactions may be very useful diagnostically (e.g. the McLafferty rearrangement[23]); often, however, their occurrence leads to confusion in interpretation. Thus, a prerequisite for the first of the two general approaches to the computerised interpretation of mass spectra is a complete knowledge of all classes of compounds which undergo rearrangement reactions, and a clear understanding of the reaction pathways involved. This has stimulated the re-studying of simple fragmentations in greater depth by labelling, metastable and kinetic techniques, and many rearrangement processes have been uncovered.

Rearrangement processes which involve migration of groups other than hydrogen are no longer rare, and the field has been extensively documented.[21,24-27] In a recent review, McLafferty[27] has thoroughly discussed the properties of rearrangements; a convenient summary of many rearrangement reactions is also available.[5] For example, internal reorganisations are observed for a large number of aliphatic compounds, for fluoro- and N-O substituted compounds, and complex rearrangements occur for aromatic and heterocyclic systems. Sulphur-containing compounds, in particular, exhibit unusual and varied rearrangement reactions,[26] and part of the work presented in this thesis covers the investigation of rearrangement processes in the spectra of substituted 1,3-dithianes.

Brown and Djerassi, in their review[24] of the field up to 1966, observed that fragmentation pathways may be rationalised by the formation of product species capable of stabilising the positive charge, and by invoking the preferential elimination of a radical from a radical ion (or a neutral molecule from an ionic species) to form a cationic intermediate. Cooks[21] has since made a detailed review of bond formation on electron impact, and he has extended the concept of charge localisation to classify and rationalise a large number of rearrangements.

The recent adoption in organic mass spectrometry of the quasi-equilibrium theory (QET)[28,29] has led to a better understanding of the kinetic properties of rearrangement reactions, and the conditions under which they may be minimised. The QET recognises that rates of unimolecular fragmentation processes depend on their energies and entropies of activation, and the rate constant (k) for a fragmentation reaction is most simply related to the internal energy (E) of the decomposing ion, the number of effective oscillators (s) in the ion and the activation energy (E_a) for the reaction, by the expression

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

where ν is a frequency factor.[30] For simple bond cleavages, the "frequency factors" are high (approximately 10^{14}), while for rearrangements the values are several orders of magnitude lower, reflecting a restricted geometry of the transition state for the reaction.[21] A simple method for assessing frequency factors has been developed, which involves comparison of spectra at high and low beam energy (E_{el}).[31] Since a rearrangement reaction has a lower frequency factor and (often) a lower activation energy than a (competing) direct cleavage reaction, then the rate of increase of k with E will be lower for the rearrangement reaction. Hence the direct cleavage will dominate at higher internal energies, and conversely, the rearrangement will be predominant at low values of E (see Fig. 1). As an example, scrambling[≠] reactions, being rearrangements, would be expected to have low frequency factors and therefore to compete more successfully with direct cleavage reactions at lower internal energies. This has been demonstrated by Howe and McLafferty,[32] who have

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[≠] The phenomenon of scrambling is considered below in the context of isotopic labelling.

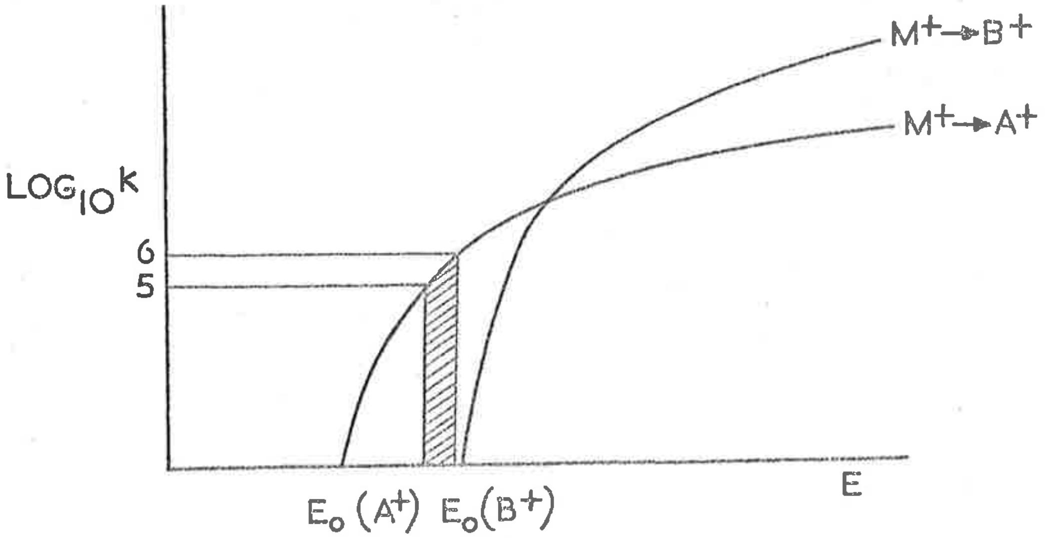


Fig. 1

Typical k *vs.* E curves for (a) a rearrangement reaction $M^+ \to A^+$, and (b) a normal cleavage reaction $M^+ \to B^+$. The shaded area represents the energy segment corresponding to a metastable transition.

shown a variation in the extent of hydrogen scrambling for certain definable energy segments of the molecular ion.

The low activation energies frequently observed for rearrangement reactions result from combined bond formation and bond breaking,[21,33] the energy released as a new bond is formed being available to break the old bond. It is common, therefore, to invoke "concerted" rearrangement pathways, usually via the favourable four- or six-membered "tight" transition states (e.g. the McLafferty rearrangement). However, three- and five-membered transition states are not uncommon in mass spectrometry;

e.g. the concerted elimination of CO from benzophenone[34] probably occurs via a three-membered transition state. Seven-membered[35] and larger[36] intermediates have also been suggested. The fact that the transition state and products are likely to be energetically similar for mass spectral processes (normally endothermic reactions) has given rise to the widely used generalisation that the importance of a given process can be estimated by the stability of the ionic and neutral products formed. Therefore, since a rearrangement reaction is often associated with the expulsion of a stable neutral molecule[37] e.g. CO, H_2O, NO, this product stability may provide a "driving force" for the reaction. The above rule is probably less useful for rearrangements, however, where varying entropy factors must be considered, and where appreciable energies of activation for the reverse reaction can be expected.[21]

Many skeletal rearrangements are accompanied by relatively abundant "metastable" ions[33] (see below). This is interpreted in the QET as a consequence of a low frequency factor and the correspondingly low rate of increase of k with E for the rearrangement. Thus, the observation of (i) a relative increase in the importance of a particular reaction at low energies and (ii) an abundant "metastable" ion for the process is strong evidence for the occurrence of a rearrangement reaction.

Metastable Ions.

The mass spectra of most compounds contain weak, diffuse peaks usually occurring at non-integral mass numbers. These are due to the decomposition of metastable ions along their flight path through the mass spectrometer, and are generally referred to as "metastable peaks", or "metastables".[3] Their position of maximum intensity occurs at the m/e value of m_2^2/m_1, where m_1 and m_2 are the masses of the precursor and daughter ions respectively, for the process $m_1 \rightarrow m_2$, and thus, for a long time, "metastables" have provided the only direct evidence for the occurrence of particular fragmentation pathways. Although the neutral part lost in the process is not necessarily present in the molecule as a structural entity,[38] the mass of the precursor related to a particular fragment is determined unequivocally.

The "metastable peak" no longer serves merely to identify a one-step transition and has been attracting increasing interest as a potential means for investigating the kinetic aspects of mass spectral processes. Some of the recent applications of metastable transitions are: (i) ion structure elucidation by comparison of metastable abundances (ii) identification of rearrangement reactions (see above) (iii) determination of kinetic energy released in metastable transitions (iv) the determination of scrambling in labelled ions, and (v) elucidation of isotope effects. The enormous progress in the application of metastable transitions is a result of two factors.[39] (i) The QET predicts that metastable transitions will occur from low energy precursor ions within a narrow energy segment controlled by narrow rate constant limits ($\log_{10}k = 5 - 6$,[33] represented by the shaded area in Fig. 1). Furthermore, the way in which the shape of k vs. E curves influences metastable abundances is widely known. (ii) The development of the metastable defocusing[40] technique and its widespread use has allowed sensitive metastable abundances measurements to be made. Each metastable is determined uniquely in the defocused mode and this technique is therefore particularly useful in scrambling investigations.

Depending on the life-time of the decomposing ions, there are three distinct regions of a double focusing mass spectrometer in which fragmentations are observed. Ions of mass m_1 with life-times of about 1 μsec or less decompose in the source to yield a daughter ion m_2, before acceleration. The ion m_2 will, if sufficiently stable, be recorded as a "normal" sharp signal at the value m_2/e. Ions of mass m_1 with a slightly longer life-time (about 2 - 11 μsec) will be accelerated, and will decompose into daughter ions m'_2 before entering the electrostatic analyser. Since the velocity of m'_2 is determined by the velocity attained by the heavier ions m_1, m'_2 will be slower than the ions of equal mass m_2 formed in the source. Under normal operating conditions, m'_2 does not fulfil the conditions to pass the electric sector field and does not appear in the spectrum. Ions of mass m_1 of even longer life-time (more than 11 μsec) decompose into daughter ions m''_2 in the field-free region between the electrostatic and magnetic analysers. The ions m''_2 have the same mass and velocity as m'_1, but they are recorded in the spectrum as the familiar diffuse, low intensity peaks at a mass equal to m_2^2/m_1. Seibl[41] has termed these transition signals, to distinguish them from precursors which are the true metastable ions, and this distinction will be adhered to in this thesis.

Ions formed by a metastable decomposition possess a fraction only of the kinetic energy imparted to the precursor, and this fraction is determined by the relative masses of the ions. By lowering the potential of the electric sector to a suitable value, the ions m'_2 formed in the first field-free region can be made to follow a path suitable for registration, while at the same time the main ion beam is filtered out, and all "normal" peaks are suppressed. The critical potential E_2 is determined by the mass ratio $m_2/m_1 = \gamma_m$ and is related to the value E_1 at normal operating conditions by the same ratio as the masses:

$$E_2/E_1 = m_2/m_1.$$

At sector potential E_2 the daughter ions m'_2 appear in the spectrum as a sharp signal at the mass value $m^* = m_2^2/m_1$. Further fragmentations of m'_2 which occur in the second field-free region can be observed as diffuse transition signals at the mass value $m^{**} = m_3^2/m_1$ for the two-stage sequence $m_1 \rightarrow m_2 \rightarrow m_3$. Thus, in addition to the accurate and sensitive detection of metastable transitions in the first field-free region, the technique of metastable defocusing provides an elegant method for the observation of multi-step processes occurring in the mass spectrometer.[41]

A variation of the metastable defocusing method has been used to give a spectrum of ion energies corresponding to decompositions in the first drift region. The main ion beam passing through the energy resolving (β) slit (between the two analysers) is monitored while continuously varying the electrostatic voltage. The resulting ion kinetic energy (IKE) spectrum[42] can detect low abundance reactions which are often obscured in normal spectra. Consequently, IKE spectra give detailed "fingerprints" of organic compounds, and are sensitive to small structural differences.[43] This is an important achievement, since the insensitivity to stereochemical differences of normal mass spectral methods is a serious disadvantage with respect to structure elucidation.

The basis for the wide application of metastable characteristics is the reasonable assumption[33] that ions identical in structure and energy distribution will behave identically, and that this will be reflected by the daughter and metastable ions they form. The shapes of transition signals are characteristic for a particular process; they are often observed to be broader than the usual Gaussian shape, and the width of these "flat-topped" peaks has been shown to be a measure of the kinetic energy released in the decomposition of the metastable ion.[44,45] Furthermore, if the abundances of metastable ions (formed from various precursors) relative to the precursor $[P^+]$ or the daughter $[D^+]$ abundances are equal, the precursors must be identical in structure and energy.[33,46] However, it is possible that structurally identical ions may give very different abundance ratios due to differing energy distributions. Thus, a fragment ion P^+ may be formed with excess energy at its appearance potential, compared with an ion formed by direct ionisation of P, while the "degrees-of-freedom" effect[47] is also responsible for a variation in internal energy of common ions P^+ formed from different precursors of an homologous series. In spite of the variety of factors influencing energy distributions of common ions, studies of metastable ion characteristics in a number of compounds, including the pairs phenetole/phenol, tropolone/phenol, and diphenyl carbonate/diphenyl ether have been made,[48] in which the results were consistent with identical structures for the relevant ions in each pair.

A more useful technique is available for application to ion structural problems, in which it is possible to ignore the energy distributions of ions.[49] When two competing fragmentations from the same ion both give reasonably abundant metastable ions m_1^* and m_2^*, the abundance ratio of these metastables $[m_1^*]/[m_2^*]$ may be used directly to characterise the ion structure. Occolowitz,[50] however, has indicated that this ratio may be susceptible to changes in the potential energy curve of P^+ prepared in different ways, if one of the two processes considered has a broader energy segment giving rise to metastable transitions. In other words, in order for the method to be completely satisfactory the two metastable transitions should have similar k _vs._ E curves.

The collision of ions with neutral molecules introduced into a drift region of a mass spectrometer enhances the internal energy of the ions, and a metastable decomposition results. These collision-induced metastable transitions[51] correspond closely to those observed in the normal mass spectrum, so it would appear that there is very little difference between energy transfer by electron impact or by collision followed by unimolecular decomposition. Furthermore, since collision-induced metastable transitions arise from higher energy precursors than do unimolecular metastable transitions, rearrangements will be minimised and decomposition should occur preferentially via direct cleavage. This is confirmed in the spectra of peptide derivatives,[52] where sequence peaks (direct cleavage) which are observed in the presence of a target gas are absent at low pressure.

Energetic Considerations and Substituent Effects.

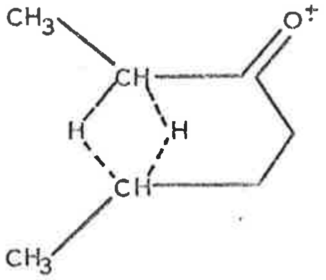
Some workers have presented plausible evidence for ion structures from the consideration of the ionisation potential (IP) of a molecule and the appearance potential (AP) of the fragments.[33,39] The method suffers from the disadvantage, however, of considerable sources of error, and it is possible for opposite conclusions to be reached from AP data.[39] The study of the effect on IP (and hence on the activation energy and rate for a particular fragmentation) of altering a substituent has been a more successful method of obtaining information about fragmentation mechanisms and ion structures. The so-called "kinetic approach", developed initially by Bursey and McLafferty,[53] is based upon a steady state approximation, in which the rates of mass spectral reactions are measured in terms of the relative abundances at the collector of the daughter and parent ions. The change in rate, brought about by alteration of a substituent, for a particular reaction $M^+ \rightarrow A^+$ is measured by the parameter $\log_{10} Z/Z_o$ (where $Z = [A^+]/[M^+]$). Thus, for example, the observation[53] of a linear relationship of $\log_{10} Z/Z_o$

values for the formation of benzoyl and acetyl ions from substituted benzophenones and acetophenones with Hammett σ values suggests a correlation of structure with the species reacting in solution. Bursey[54] has reviewed the earlier work in this area, and Cooks[33] _et al_. have made further observations. Recently, Chin and Harrison[55] have made a quantitative formulation of the factors governing the value of Z, and using this have confirmed earlier results. No direct information on the rate of a specific reaction is possible, however.

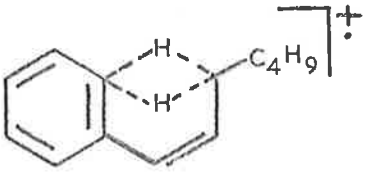
Isotopic Labelling and Scrambling.

Probably the most useful technique in mechanistic studies in mass spectrometry is the use of isotopically labelled molecules.[33] The common isotopes are deuterium, ^{13}C, ^{15}N, ^{18}O; recently, however, the _para_-fluoro substituent[56] has been developed as an effective label in aromatic systems. On the assumption that the position of the labelled atom in a molecular ion corresponds to that in the neutral molecule from which the ion is formed, reasonable ion structures and fragmentation mechanisms can be proposed from a knowledge of the fate of the label in subsequent fragmentations. However, great care must be exercised in interpreting labelling results as it is becoming apparent that under certain conditions positional identity of the isotopic labels is frequently lost. This phenomenon is loosely termed "scrambling".[5,21,33,39] Recent research has amply illustrated that hydrogen and carbon scrambling reactions are common in mass spectrometry. In view of the fact that the occurrence of scrambling reactions may lead to erroneous structural conclusions, there is justification for the extensive research in this area; part of the work described in this thesis includes the investigation of the scrambling processes observed in the molecular ions of diphenylmethane, stilbene, and other ions.

Hydrogen atom scrambling in aliphatic hydrocarbons[57] and in compounds with long alkyl chains[58] has been known for some time. Recently, randomisation within alkyl chains has been observed for alkyl alcohols,[59-61] ketones,[62-64] and ethers.[65] Hydrogen randomisation in aliphatic systems generally occurs only at low energies of the electron beam, and this is in accord with the expectation of low activation energies and frequency factors for rearrangement processes.[21] Various models have been proposed to explain this type of randomisation. For example, hydrogen interchange without alteration to the carbon skeleton may occur as in c;[64] scrambling between remote aryl and alkyl hydrogens might be envisaged proceeding via d.[66]



c



d

In addition to H randomisation, extensive carbon scrambling has been observed in some butyl systems.[67,68]

Both hydrogen and carbon randomisation appear to be widespread in aromatic systems. The equivalence of the hydrogen atoms in the benzene molecular ions[69] has been known for some time; recently, Williams et al.[70,71] have elegantly demonstrated that hydrogen and carbon scrambling occur simultaneously and independently, prior to the expulsion of acetylene from the molecular ion of benzene. The mechanisms of these processes are unclear, although possible isomerism through prismane and benzvalene structures has been suggested, by analogy with photochemical isomerisations.[72] The problem of the structure of the benzene molecular ion remains unsolved; molecular orbital calculations suggest that a cyclic molecular ion would be much less aromatic than the neutral species,[73] while the doubly charged ion is almost certainly linear.[74] There is wide acceptance, however, for the intermediacy of a tropylium ion species to explain the scrambling in ions derived from toluene and benzyl derivatives.[75] Such a simple model is insufficient to explain the randomisation observed in more complex systems,[5] e.g. diphenyl, benzothiophen, diphenylmethane, and stilbene.

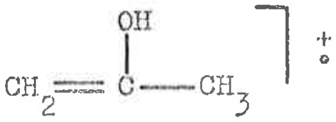
The metastable-defocusing technique[40,41] is well suited to the study of scrambling processes. The defocused metastable ion uniquely determines the process under investigation, and the relative contributions to the particular process from variously labelled species in the spectrum of a labelled compound can be measured easily in the defocused mode. Measurements of the corresponding daughter ion abundances are often complicated by competing fragmentations and isotopic impurities.

Ions of different lifetimes have been observed to undergo scrambling to varying degrees: the longer the lifetime of the ion, the higher the degree of scrambling.[63,76,77] This effect seems to be more pronounced in aliphatic systems than aromatic. In this respect, results obtained from observation of the longer lifetime metastable ions should be interpreted with care.

The occurrence of a primary deuterium isotope effect[39] can be a further complication in labelling studies. Howe and McLafferty[32] have shown that the magnitude of the deuterium isotope effect for the loss of a hydrogen atom from the toluene molecular ion decreases with increasing energy. An isotope effect can therefore be expected to influence the extent of scrambling processes (which are also energy dependent[32]), and hence the results of labelling experiments must be analysed carefully.

Alternatives to EI.

Although investigations involving "conventional" instrumentation continue to contribute the majority of research in mass spectrometry, alternative techniques[78] are being used increasingly. These include, (i) field ionisation (FI), (ii) chemical ionisation (CI), and (iii) negative ion spectroscopy, and (iv) ion cyclotron resonance (ICR). The first three provide alternative methods of ion production, and their particular characteristics may help solve some of the difficulties encountered in spectra produced by an electron impact-positive ion (EI) source. ICR is a different method of analysis. Its importance lies in its ability to measure the reactivity of ions, as applied to the study of ion-molecule reactions. It has already yielded useful information concerning ion structures, e.g. the structure of both the "single" and "double" McLafferty rearrangement products, from hexan-2-one and nonan-5-one respectively, has been shown to have the same structure, perhaps the enol form e.[79,80]



$[CH_2{=}C(OH){-}CH_3]^{+\cdot}$

e

The nature of ionisation by a powerful electric field in FI ensures that very little energy is transferred to the ionised molecule, which is then quickly accelerated into the analyser region. These two factors give a high probability that a molecular ion will be formed, and since the lifetime of ions in the source is of the order of 10^{-14} - 10^{-12} sec., any fragmentation which occurs should be via direct cleavage. Thus, a rearrangement or multi-step process taking place upon electron impact will be absent (or in very low abundance) in the FI spectrum.[81] On the other hand, metastable transitions from the low energy molecular ions produced by FI should occur preferentially via rearrangement. Similarly, CI[82] (in which low energy ions are produced via interactions with ions derived from a reactant gas, e.g. methane) and negative ion spectroscopy[83] have been shown to produce molecular ions in cases where the molecular ion is absent in EI spectra. Negative ion spectroscopy is potentially useful in this respect since the spectra usually contain few fragment ions, but the optimum conditions for the general production of negative ions of organic compounds have yet to be defined. This technique is at present the most readily accessible of the alternatives to EI, and although it has not been generally accepted as an analytical method in organic chemistry it is receiving increasing attention.[5,78] A more detailed discussion of the technique is given below in the introduction to Chapter 4, which deals with the study of the negative ion spectra of some substituted 1,3-dithianes.

This brief review of recent developments in the theory and practice of organic mass spectrometry has been an attempt to give a general impression of the climate in which the organic mass spectrometrist is working today and the tools he has at his disposal, and to provide some rationalisation of the directions which research in the field is taking. The most significant characteristics of this picture are the great enthusiasm for discovery and, as a consequence, the enormous rate of development. The work reported in this thesis contributes in a small way to the ever-increasing accumulation of knowledge which is the field of mass spectrometry. It was prompted by the necessity to gain as full an understanding as possible of mass spectral processes and the mechanisms of fragmentation, and if possible of the reacting species themselves in terms of ion structures and energies.

The thesis falls into two distinct sections. The first section deals with the investigation of the rearrangement processes occurring on electron impact in diphenylmethyl derivatives (Chapter 1) and stilbene (Chapter 2), including randomisation of the hydrogen and carbon atoms. Some of the results discussed in this section have been incorporated previously in theses[84,85] presented for degrees in the University of Adelaide. These relate to some deuterium labelled diphenylmethyl derivatives,[84] and deuterium labelled stilbenes.[85] The inclusion of these results, which are acknowledged here and in the appropriate sections of the Discussion (below), has been considered necessary to ensure that the additional work discussed in Chapters 1 and 2 is viewed in its correct perspective. The second section is a study of the fragmentation processes of some substituted 1,3-dithianes and 1,3-dithiolanes, in both the positive (Chapter 3) and negative (Chapter 4) ion modes. The nomenclature used throughout is that suggested by Budzikiewicz,[86] which is based on the earlier proposals of Shannon[87] and Djerassi.[3] The spectra of compounds referred to in the text which are recorded as bar-graphs are in a fold out format at the end of the appropriate chapter. Those spectra not recorded graphically and which have not been previously published are tabulated in the Appendix.

Chapter 1. Scrambling processes in the mass spectra of diphenylmethyl systems.

1.1 Introduction.

The mass spectra of aromatic hydrocarbons have been intensively investigated for many years, and their general characteristics are well known.[3] In contrast to the complex fragmentations of aliphatic and acyclic hydrocarbons, aromatic hydrocarbons in general undergo very few fragmentations upon electron impact. This simplicity is no doubt due to the ability of the aromatic nucleus to stabilise a positive charge. Furthermore, a stable ionised species is frequently generated by fragmentation. In this respect, the observation in the spectra of toluene and alkyl benzenes of an abundant ion $C_7H_7^+$ (m/e 91), corresponding to the benzyl cation has been of much interest. On the basis of a study of deuterium labelled toluenes and ethylbenzenes, Grubb and Meyerson showed that the interpretation of $C_7H_7^+$ as a benzyl ion was incorrect.[1,75,88] They postulated instead the symmetrical tropylium ion e, in which the seven hydrogen atoms are indistinguishable. The simplest mechanism for

e, $C_7H_7^+$, m/e 91

the ring expansion, viz. the insertion of the α-carbon between ring carbons 1 and 2, and migration of an α-hydrogen to carbon 1, was ruled out by the subsequent observation of complete hydrogen scrambling prior to the formation of $C_5H_5^+$ from e.[89] More recently, Rinehart et al.

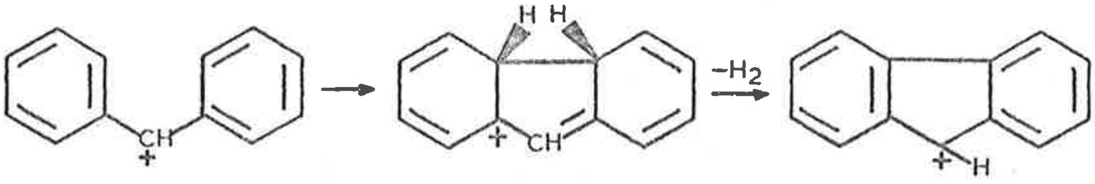
have measured the spectrum of $[\alpha, 1\text{-}^{13}C_2]$ toluene, and they have demonstrated that the tropylium ion is produced essentially by the α-carbon inserting equally between all the carbons of the original benzene ring.[90] Thus, both hydrogen and carbon atoms in the $C_7H_7^+$ ion formed from toluene are completely scrambled.

The initial interest in toluene derivatives prompted the study by many workers of diphenylmethane (1) and its derivatives, and other related systems. The important fragmentations in the spectrum of (1) (Fig. 2) are outlined in Scheme 1. The loss of a hydrogen atom from the molecular ion gives rise to the diphenylmethyl cation (<u>f</u>, <u>m/e</u> 167),

$$\begin{tikzcd}
C_6H_5{-}CH_2{-}C_6H_5 \arrow[r, "-e", "-H\cdot"'] & C_6H_5{-}\underset{+}{C}H{-}C_6H_5 \arrow[r, "-H_2"] & C_{13}H_9^+ \\
(1) \arrow[d, "-e"', "-CH_3\cdot"] & \underline{f},\ \underline{m/e}\ 167 \arrow[d, "-CH_3\cdot"] & \underline{g},\ \underline{m/e}\ 165 \\
C_{12}H_9^+ & [C_{12}H_8]^{+\cdot} & \\
\underline{h},\ \underline{m/e}\ 153 & \underline{i},\ \underline{m/e}\ 152 &
\end{tikzcd}$$

Scheme 1.

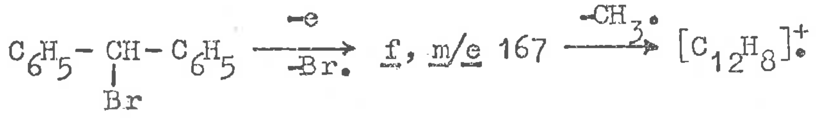
the structure of which may be a phenyl tropylium species, by analogy with alkyl benzenes. The further loss from <u>f</u> of two hydrogen atoms produces the ion $C_{13}H_9^+$, <u>m/e</u> 165. This ion appears in the spectra of a wide variety of aromatic heterocyclic compounds and hydrocarbons,[91] and evidence has been presented[92] which suggests that in many cases $C_{13}H_9^+$ shares the characteristics of the ion derived by loss of a hydrogen atom from the fluorene molecular ion (see Chapter 2). It has been suggested[93] that the formation of $C_{13}H_9^+$ from *f* occurs via the cyclisation of the diphenylmethyl cation followed by a *cis* elimination of a molecule of hydrogen to form the fluorenyl cation *g*. This mechanism may well be correct, since the ion *g* has the same characteristics as the fluorenyl cation.[92] However, deuterium labelling studies have shown that the hydrogen atoms in *f* are completely scrambled prior to the formation of *g*,[94] and this demands that *m/e* 167 have (or have passed through) a structure in which the hydrogen atoms can become equivalent.



f, *m/e* 167

g, *m/e* 165

Both the molecular ion of (1) and the (M - H•) ion fragment by loss of a methyl radical, to produce the ions at *m/e* 153 and 152 respectively. The process M - CH_3• in the spectrum of (1) was first commented on by Meyerson in a study of methyl substituted diphenylmethanes.[95] Eland and Danby subsequently observed M - CH_3• fragments in the spectra of a number of aromatic compounds including (1), *cis*-stilbene, diphenylacetylene, dihydrophenanthrene, and phenanthrene, and these authors implied that the methyl radical eliminated from the molecular ion of (1) originated from the central CH unit.[96] In 1966, Johnstone and Millard[97] reported a study of the expulsion of a methyl radical from the diphenylmethyl ion *f*, produced from diphenylmethyl bromide (2) (Fig. 3, Scheme 2).



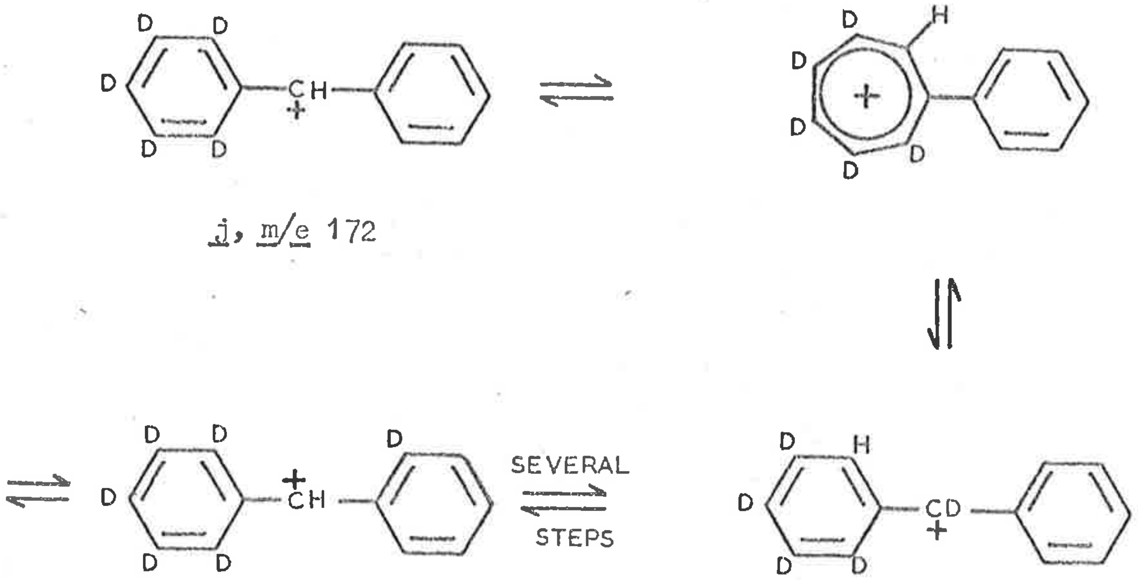
$$C_6H_5-\underset{\displaystyle Br}{\underset{|}{CH}}-C_6H_5 \xrightarrow[-Br\cdot]{-e} f,\ m/e\ 167 \xrightarrow{-CH_3\cdot} [C_{12}H_8]^{+\cdot}$$

(2) *i*, *m/e* 152

Scheme 2.

On the basis of the spectra of the labelled compounds (2-*d*-phenyl)phenylmethyl bromide and (2,4,6-d_3-phenyl)phenylmethyl bromide (4), they proposed mechanisms for the rearrangement involving the central CH unit, together with specific loss of *ortho* hydrogen atoms. The methyl radical expelled in the spectrum of (4) had the composition CH_3, 33.4%; CH_2D, 48.1%; CHD_2, 18.5%. They concluded from these results that two mechanisms were operating simultaneously, *viz.* one involving two *ortho* positions in the same ring, the other an *ortho* position in each ring.

In a subsequent paper Williams *et al.*[98] showed that, in contrast to the earlier work, the expulsion of methyl from the d_5-diphenylmethyl cation (*j*, *m/e* 172, formed from (d_5-phenyl)phenylmethyl chloride) occurred in a random manner with respect to the hydrogen and deuterium atoms. They proposed that the observed hydrogen scrambling could be explained by rapid reversible equilibration between the diphenylmethyl cation and a phenyl tropylium ion (Scheme 3).



Scheme 3.

Furthermore, in an independent study of the properties of the tropylium ion $C_7H_7^+$, e, Meyerson reported that the processes M - H•, M - CH_3•, and M - C_2H_3• in the spectrum of (1) occurred with complete hydrogen scrambling.[94] Although the evidence of randomisation in diphenylmethyl systems seemed more reasonable than non-random processes (in view of the extensive scrambling observed in aromatic compounds,[39] and benzyl systems[75] in particular), other workers have nevertheless postulated specific processes in the spectra of triptycene,[99,100] triphenylmethane,[101] and o-terphenyl[102] and, in the light of their own results, have made comparisons with and comments on the corresponding process in diphenylmethane. In order to clarify the conflicting evidence and comment concerning the fragmentations of diphenylmethane and its derivatives, it was decided to investigate more fully the processes in question, using deuterium and ^{13}C labelling.

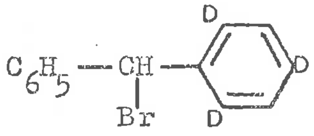
1.2 Results and Discussion:

1.2.1. The loss of methyl from m/e 167.

The diphenylmethyl cation (f, m/e 167), is a common feature of the mass spectra of diphenylmethyl derivatives, including dimethylmethyl ethers, nitriles, halides, and diphenylmethanol.[84] The most convenient of these as precursors of f are the halides, since m/e 167 is formed directly from the molecular ion by the elimination of a halogen atom, and no competing reactions are observed. Thus, the spectrum of diphenylmethyl bromide (2) (Fig. 3) shows no molecular ion, and the base peak corresponds formally to the diphenylmethyl cation f. The percentage composition of the methyl radicals lost from the (M - Br•) species in the 25 eV spectra of the deuterium labelled compounds (3)-(5) is listed

$C_6H_5-\underset{\overset{|}{Br}}{CD}-C_6H_5$

(3)



(4)

$C_6H_5-\underset{\overset{|}{Br}}{CH}-C_6D_5$

(5)

in Table 1, together with the values expected for random loss of hydrogen and deuterium.[103] The observed values show good agreement with the calculated values, and confirm the earlier suggestion[98] of Williams et al. that complete hydrogen scrambling precedes the elimination of a methyl radical from m/e 167. It is of interest to compare the values observed for the elimination of methyl from the d_3-diphenylmethyl ion derived from (4) (Table 1) with the previously published results[97] (see 1.1, above). Although Johnstone did not observe the small proportion of methyl which

Table 1.

Composition[a] of the methyl species eliminated in the process $[(M - Br^\bullet) - CH_nD_{3-n}^\bullet]$ for (3)-(5)[b] at 25 eV.

Compound		CH_3	CH_2D	CHD_2	CD_3
(3)	Obs.	70	30	-	-
	Calc.	73	27	-	-
(4)	Obs.	34	49	15.5	1.5
	Calc.	34	51	14	1
(5)	Obs.	14	42	34.5	9.5
	Calc.	12	46	36	6

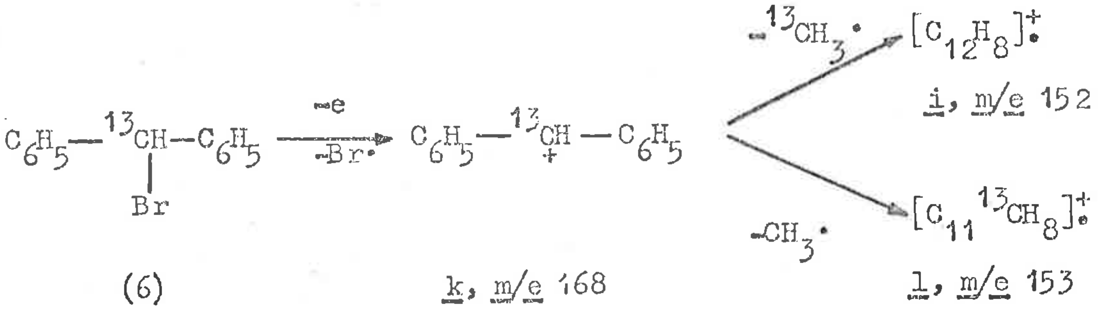
a The values observed for fragment ions and metastable ions are almost identical.

b These values have been reported before.[84,103]

is eliminated as $CD_3^\bullet$, the figures he obtained for (4) agree closely with those recorded in Table 1, and are not inconsistent with complete randomisation. It would appear, therefore, that the earlier proposal[97] is invalid, at least with respect to the hydrogen atoms involved in the process.

Although there are numerous examples known of the simultaneous occurrence of hydrogen and carbon scrambling, hydrogen randomisation can also proceed without rearrangement of the carbon skeleton.[5,39] It was considered necessary, therefore, to measure the spectrum of bromodiphenylmethane-1-^{13}C (6), in order to establish unequivocally the origin of the carbon atom involved in the rearrangement.

No specific loss of carbon was observed;[103] hence, the methyl group does not arise specifically from the central CH unit. Metastable ions for the processes m/e 168 → 153 and m/e 168 → 152 (k → i and k → l) were observed at m* = 139.5 and 137.5 respectively. The ratio of the



abundance of the metastable ions in the first field-free region for the two processes were 92.8 : 7.2 and 93.7 : 6.3 at 70 and 15 eV respectively. The ratio expected for a random loss of carbon is 92.3 : 7.7. Since the accuracy of measurement of the observed peak heights is probably no better than ± 1%, the slight deviations from the calculated ratio are most likely insignificant. The observed values, therefore, strongly suggest that complete randomisation[≠] of the carbon atoms has occurred

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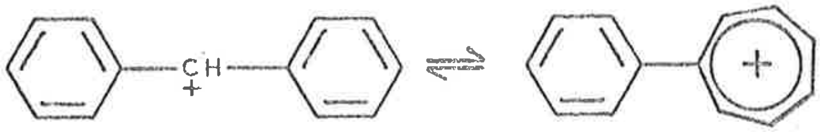
[≠] It is recognized that the labelling results do not allow differentiation of (i) complete randomisation prior to fragmentation, and (ii) the loss of a methyl radical in a completely random manner. The second possibility is intuitively less attractive, however, since it is unlikely that formally non-equivalent atoms will react in an exactly similar manner, unless some process of equilibration (i.e. scrambling) has taken place. Furthermore, in a completely scrambled species, the distinction between a random and specific process is not possible.

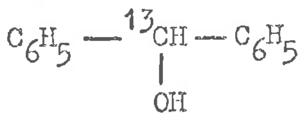
in the ion m/e 167 before the formation of m/e 152.[≠]

Computations have been carried out which show that the model (Scheme 3) which Williams proposed to explain hydrogen scrambling between the phenyl rings would require at least 300 cycles (each of which involves several ring expansions and contractions) to achieve a random distribution in the ion. Rearrangement reactions and scrambling processes in particular are, in general, relatively slow processes in the mass spectrometer, and hence Williams' model is unlikely to randomise completely on the time-scales involved. If, however, all atoms in the postulated expanded ring became equivalent (by analogy with the tropylium species e) before subsequent contraction and re-expansion, then a random distribution of both hydrogen and carbon atoms would be achieved after approximately 30 ring expansions and contractions (e.g. f → m).



f m

[≠] The analogous elimination of methyl from the (M – OH•) ion (m/c 167) in the spectrum of 1-^{13}C-diphenylmethanol (7) also proceeds with complete carbon scrambling. The abundances of the defocused metastable ions for m/e 168 → 153 and 152 indicate a ^{13}C label retention of approximately 93% (value expected for randomisation = 92.3%).



$$C_6H_5-{}^{13}\underset{\displaystyle OH}{\underset{|}{CH}}-C_6H_5$$

(7)

If the deviation from the calculated values for the loss of the methyl carbon atom is significant, then apparently slightly more of the methyl radical is being lost from the phenyl rings than expected for complete randomisation. This can be rationalised in terms of the methyl radical originating from the rings of a diphenylmethyl cation which is predominantly scrambled, but which also contains an amount of partially scrambled material. Accordingly, calculations of the compositions of the various labelled methyl species, assuming (i) that x% of <u>f</u> is completely randomised, and (ii) that the remaining (100 - x)% of methyl is lost from the rings of a cation <u>f</u> which shares the central hydrogen atom with one ring. This model assumes no particular mechanism for the scrambling process, but is invoked in an attempt to illustrate the effect of incomplete scrambling.

The values calculated for x = 85,90,95,100 (together with the observed values from Table 1) are given in Table 2. The observed and calculated values show best agreement when x = 95. Thus, on the model proposed the observed values can be explained in terms of at least 95% randomisation of hydrogen and carbon. Whatever the mechanism of scrambling may be, it must be recognised that the degree of scrambling in the diphenylmethyl cation <u>f</u> is high, prior to the elimination of a methyl radical.

Table 2.

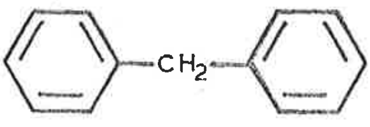
Composition[a] of the methyl species eliminated in the process $[(M - Br\cdot) - CH_nD_{3-n}^{\bullet}]$ for (3)-(6).

Compound	x	$^{13}CH_3$	CH_3	CH_2D	CHD_2	CD_3
(3)	85	-	73.3	26.7	-	-
	90		73.2	26.8		
	95		73.1	26.9		
	100		73.0	27.0		
	Obs.		70.0	30.0		
(4)	85	-	36.6	46.1	15.8	1.5
	90		35.7	47.8	15.2	1.3
	95		34.9	49.4	15.0	1.0
	100		34.0	51.0	14.0	1.0
	Obs.		34.0	49.0	15.5	1.5
(5)	85	-	18.8	38.6	32.9	10.7
	90		15.9	40.9	34.1	9.1
	95		14.0	43.2	35.2	7.6
	100		12.0	46.0	36.0	6.0
	Obs.		14.0	42.0	34.5	9.5
(6)	85	6.5	93.5	-	-	-
	90	6.9	93.1			
	95	7.3	92.7			
	100	7.7	92.3			
	Obs.	7.2	92.8			

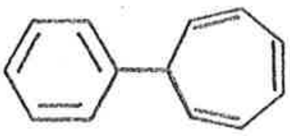
[a] Calculated for x% random loss, (100 - x)% loss from rings, 6H, 5H.

1.2.2. The loss of methyl from *m/e* 168.

At 70 eV, the processes M - $CH_3\cdot$ and (M - H$\cdot$) - $CH_3\cdot$ in the mass spectrum of diphenylmethane (1) (Fig. 2) produce the ions *h*, *m/e* 153 and *i*, *m/e* 152 respectively. Meyerson has studied the processes M - H$\cdot$, M - $CH_3\cdot$, and M - $C_2H_3\cdot$ in the spectrum of (1) at 70 eV, and has concluded from the spectra of α-*d*-diphenylmethane and α-d_2-diphenylmethane that each process occurred after the hydrogen atoms in the molecular ion had scrambled.[94] It was of interest, therefore, to investigate the possibility of carbon randomisation and if possible to clarify the scrambling mechanism(s) involved. The isomeric compounds (1), (8), and (9) were chosen for this purpose, for the following reasons. (i) The high mass regions of the spectra of each are very similar (Figs. 2 and 4). (ii) The process (M - H$\cdot$) - $CH_3\cdot$ in each spectrum does not occur at 15 eV. Hence, the M - $CH_3\cdot$ process can be conveniently studied at 15 eV, without interference from the corresponding loss of methyl from the (M - H$\cdot$) species. (iii) In view of the scrambling process already established (see 1.2, above) for the loss of a methyl radical from the even-electron species *f*, *m/e* 167 (presumably via the phenyltropylium intermediate *m*) it seemed likely that any scrambling process in the molecular ion of (1) could occur via an



(1)



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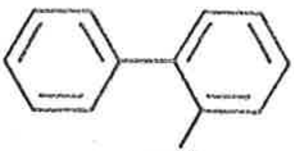
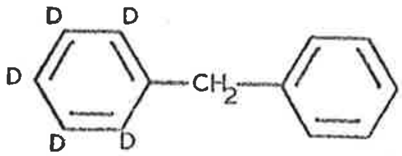


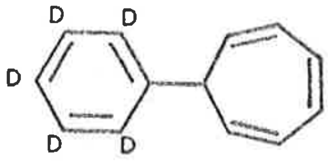
(9)

analogous intermediate, viz. the molecular ion n of phenyltropylidene (8). Furthermore, since an o-methylbiphenyl cation had been suggested[97] as an intermediate in the expulsion of a methyl radical from f, m/e 167, the radical ion o derived from (9) could also be envisaged as participating in the $M - CH_3^{\bullet}$ process in the spectrum of (1).

The composition of the methyl radicals eliminated from the molecular ions of the deuterium labelled compounds (10)-(14), measured



(10)



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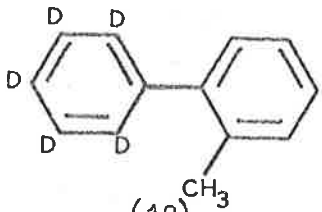

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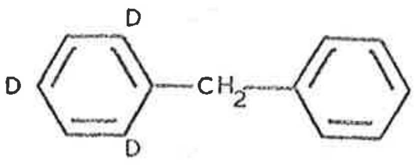

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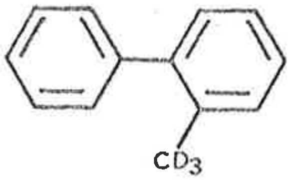


(14)

by the abundances of the appropriate metastable ions in the first field-free region at 15 eV, is given in Table 3, together with the values calculated for random loss of hydrogen and deuterium.

There is a fair correlation between the observed and calculated values in the table. This demonstrates that randomisation of the hydrogen atoms has occurred to a large extent before the loss of a methyl radical,

Table 3.

Composition[a] of the methyl species eliminated in the process M – $CH_nD_{3-n}^{\bullet}$ for (10)-(14) at 15 eV.

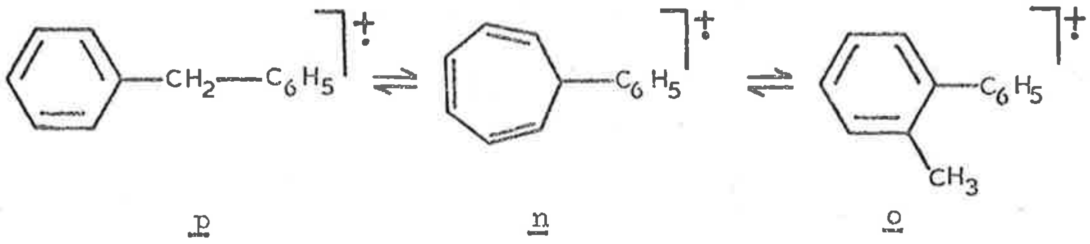
Compound		CH_3	CH_2D	CHD_2	CD_3
[b] (10)	Obs.	21.0	38.0	31.5	9.5
[b] (11)	Obs.	20.0	37.0	33.0	10.0
(12)	Obs.	18.0	39.0	32.0	11.0
(10)-(12)	Calc.	15.0	48.0	32.0	5.0
(13)	Obs.	42.5	44.8	11.5	1.2
(14)	Obs.	41.1	44.6	12.2	2.0
(13)-(14)	Calc.	38.2	49.0	12.3	0.5

[a] The values observed for fragment ions and metastable ions are almost identical.

[b] These values have been reported before.[84,103]

and confirms the earlier contention[94] of Meyerson, whose conclusions were based only on daughter ion abundances at 70 eV which were likely to have been complicated by competing processes. Nevertheless, a deviation from the expected values, similar to that observed in the diphenylmethyl cation f (see 1.2, above) is noticeable; this is discussed further below.

The striking similarity in the values observed for (10)-(12), and (13) and (14) strongly supports the suggestion that both phenyl tropylidene and o-methylbiphenyl species are implicated in the rearrangement. These results suggest either that all three species n, o, and p are implicated in the scrambling and subsequent rearrangement of the diphenylmethane ion (e.g. p ⇌ n ⇌ o), or that the three species share a common "structure" which may or may not bear a resemblance to the ground state structures of the individual ions.



Measurement of the spectrum of diphenylmethane-1-^{13}C (15) (^{13}C incorporation 60.1%) at 15 eV shows a 55.3% incorporation of ^{13}C in the

$$C_6H_5 — {}^{13}CH_2 — C_6H_5$$

(15)

M - CH_3• daughter ion.[103] This is very close to the figure calculated for the random loss of carbon from the molecular ion, viz. 55.5%. The abundances of metastable ions in the first field-free region for the processes M - CH_3• and M - $^{13}CH_3$• (m/e 169 → 154 and m/e 169 → 153, m* = m/e 143.9 and 138.5 respectively) occur in the ratio 93.7 : 6.3 at 15 eV;[103] randomisation requires 92.3 : 7.7. Both observed values rule out any specific loss of the methyl carbon, and favour a completely random process.

The field ionisation mass spectrum of diphenylmethane, which was measured through the courtesy of Professor H.D. Beckey, reveals that the elimination of a methyl radical from the molecular ion of (1) is a relatively slow reaction.[104] There is no field induced dissociation peak ($\tau = 10^{-14} - 10^{-12}$ sec) and no fast metastable peak ($\tau = 10^{-12} - 10^{-7}$ sec), but a normal metastable peak ($\tau = 10^{-7} - 3\text{x}10^{-3}$ sec) is observed. Therefore the likelihood of scrambling processes in the molecular ion of (1), prior to loss of methyl, is high, and this is borne out by the experimental observations above.

In this context, it is of interest to consider several reports of non-random rearrangement processes in the spectra of compounds related to diphenylmethane. Berlin and Shupe[101] observed an "almost quantitative" ^{13}C label retention of 94% for the process M - CH_3. in the spectrum of triphenylmethane-1-^{13}C. They interpreted this observation as a contradiction of previous "implications" that the central unit was involved in the elimination, and mechanisms were proposed in which the carbon eliminated as methyl from both triphenylmethane and (1) is derived solely from the rings. In view of the scrambling in diphenylmethyl systems described above, it seems likely that the "almost quantitative" retention is better interpreted as a loss of carbon from a randomised molecular ion of triphenylmethane (retention expected for random loss = 94.7%). Similarly, Copet and Facchetti[102] do not consider the possibility of complete carbon randomisation in the spectrum of o-terphenyl-2-^{13}C, although their reported incorporations of ^{13}C label for successive eliminations of a methyl radical would suggest this.

If the deviation from the expected values for carbon randomisation for the M-CH_3• process in the spectrum of diphenylmethane is significant, then the ^{13}C labelling evidence and the data in Table 3 support the possibility that more methyl than anticipated for complete scrambling arises from the phenyl rings. A similar possibility arose for the elimination of methyl from the diphenylmethyl cation f.

Accordingly, calculations similar to those made for the diphenylmethyl cation (above) have been carried out, assuming (i) that x% of p is decomposing after complete randomisation, (ii) that the remaining (100 - x)% of methyl is lost from the rings of an intermediate which shares one of the two central hydrogen atoms with one of the rings, and (iii) that this model, based on diphenylmethane, can apply also to (8) and (9). As before, no particular scrambling mechanism is assumed. The values calculated for x = 80,85,90,100 (together with the observed values from Table 3) are given in Table 4.

In general, the correlation between the observed and calculated values is best when x = 85 (Table 4). Therefore, on the basis of the proposed model (which is very similar to that used for the calculations in Table 2), the observed values can be explained in terms of a diphenylmethane molecular ion, approximately 85% of which has randomised. The difference in the percentage scrambling deduced for the two systems f and p (95% and 85% respectively) may be relevant. The species m and n have been suggested as intermediates through which the ions (f and p

Table 4.

Composition[a] of the methyl species eliminated in the process M – $CH_nD^{\bullet}_{3-n}$ for (10)-(15).

Compound	x	$^{13}CH_3$	CH_3	CH_2D	CHD_2	CD_3
(10)-(12)	75	–	22.5	36.0	30.3	10.2
	80		22.0	38.4	30.6	9.0
	85		20.2	40.8	31.0	8.0
	90		18.5	43.2	31.3	7.0
	100		15.0	48.0	32.0	5.0
(10)	Obs.	–	21.0	38.0	31.5	9.5
(11)	Obs.		20.0	37.0	33.0	10.0
(12)	Obs.		18.0	39.0	32.0	11.0
(13),(14)	75	–	41.5	41.5	15.7	1.3
	80		40.8	43.0	15.0	1.2
	85		40.2	44.5	14.3	1.0
	90		39.5	46.0	13.7	0.8
	100		38.2	49.0	12.3	0.5
(13)	Obs.	–	42.5	44.8	11.5	1.2
(14)	Obs.		41.2	44.6	12.2	2.0
(15)	75	5.8	94.2	–	–	–
	80	6.1	93.9			
	85	6.5	93.5			
	90	6.9	93.1			
	100	7.7	92.3			
	Obs.	6.3	93.7	–	–	–

[a] Calculated for x% random loss, (100 – x)% loss from rings (6H, 5H).

respectively) pass, during the scrambling process. In this context, the cation m would be a more stable intermediate than the radical ion n which might be expected to fragment more quickly, before scrambling had reached completion. Nevertheless, regardless of the validity of the calculations in Table 4, or the relevance of their interpretation, it is apparent from the experimental results that considerable, if not complete, scrambling takes place in the molecular ion of (1) before the loss of a methyl radical.

In contrast, the simple dissociation process M - $C_6H_5^{\bullet}$, which produces the tropylium ion (e, m/e 91) in the spectrum of (1) (Fig. 2), occurs with negligible scrambling. Meyerson has observed a high retention of deuterium label in the formation of the M - C_6H_5. ion from α-d- and α-d_2-diphenylmethane.[94] This specific process is confirmed in the spectra of (10) and (13). For example, the spectrum of d_3-diphenylmethane (13) shows two daughter ions at m/e 91 and 94, of almost equal intensity, corresponding to the d_0- and d_3-tropylium ions respectively. The presence of minor amounts of d_1- and d_2- species (at m/e 92 and 93) indicates that a limited amount of scrambling occurs, and as might be expected this increases as the energy of the electron beam decreases. This is illustrated in Table 5; the abundances of the ions at m/e 91-94 have been corrected for naturally occurring isotopes, but no correction has been made for further losses of hydrogen (and deuterium) which occur from the various labelled tropylium ions. Therefore, the abundances of the d_1- and d_2-tropylium ions (m/e 92 and 93) are inflated. Nevertheless,

Table 5.

Relative abundances[a] of m/e 91-94 in the spectrum of (13), compared with values calculated for randomisation.

eV	m/e 91	m/e 92	m/e 93	m/e 94
70	40	8	9	43
25	34	16	12	38
12.5	27	20	18	35
Calc.	4	32	48	16

[a] The observed values are uncorrected for losses of hydrogen (and deuterium) from the tropylium species.

it is apparent that hydrogen scrambling has occurred to a limited extent only, even at low ionising voltages. Similarly, the retention of ^{13}C label in the m/e 91 ion (at 15 eV) in the spectrum of (15) is 97.5% (retention expected for random loss = 53.9%). Therefore, the cleavage reaction M - C_6H_5. in the spectrum of diphenylmethane occurs with no carbon scrambling, and very little hydrogen randomisation.≠ This is not

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≠ The loss of a phenyl radical is also observed from the molecular ion of diphenylmethanol, to produce the ion C_7H_7O (m/e 107). The spectrum of (7) shows that no carbon scrambling precedes the formation of the (M - C_6H_5.) ion; the subsequent elimination of CO from m/e 107 is also a specific process. Furthermore, the observation in the spectrum of (7) that the formation (and decomposition by loss of CO) of the benzoyl cation involves no carbon scrambling is consistent with the report[98] of Williams that a limited amount of hydrogen scrambling is associated with the M - C_6H_7. process.

surprising, since dissociation reactions in the mass spectrometer are rapid processes ($\tau = 10^{-14}$ sec), whereas rearrangement (and scrambling) processes are slow ($\tau = 10^{-7}$ sec).

In summary, hydrogen and carbon scrambling have been shown to occur before the elimination of a methyl radical from both the diphenylmethyl cation and the diphenylmethane molecular ion. The randomisation is essentially complete in the former, but slightly less than complete scrambling is observed in the latter. The radical ions derived from phenyltropylidene and _o_-methylbiphenyl are implicated in the rearrangement and scrambling processes observed in the spectrum of diphenylmethane. As expected, the scrambling and subsequent rearrangement reactions proceed (relatively) slowly, whereas the competing (fast) cleavage reaction $M - C_6H_5\cdot$ in the spectrum of (1) occurs with little or no scrambling. In general, fragmentations which involve rearrangement do not appear to be specific processes in the diphenylmethyl and related systems, as suggested previously, but occur in a random manner with respect to both hydrogen and carbon.

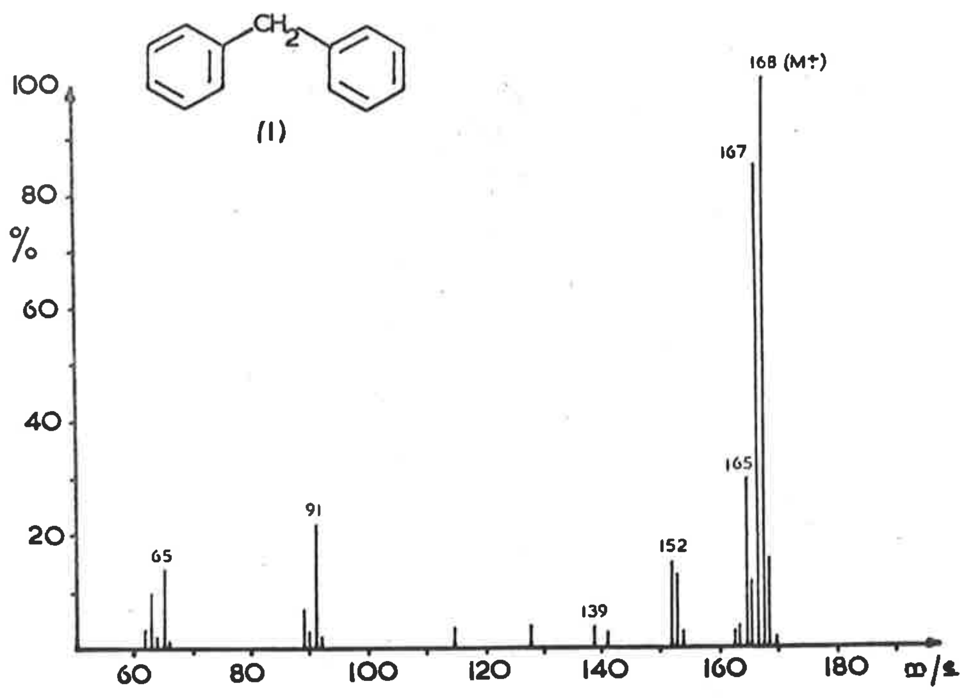


FIG. 2

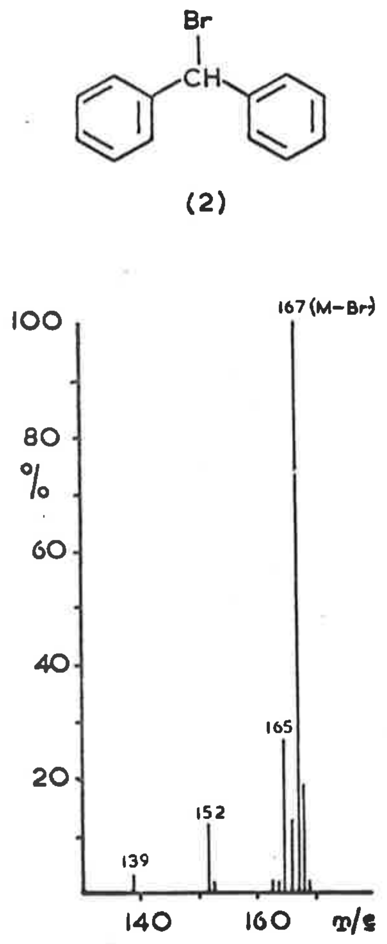


FIG. 3

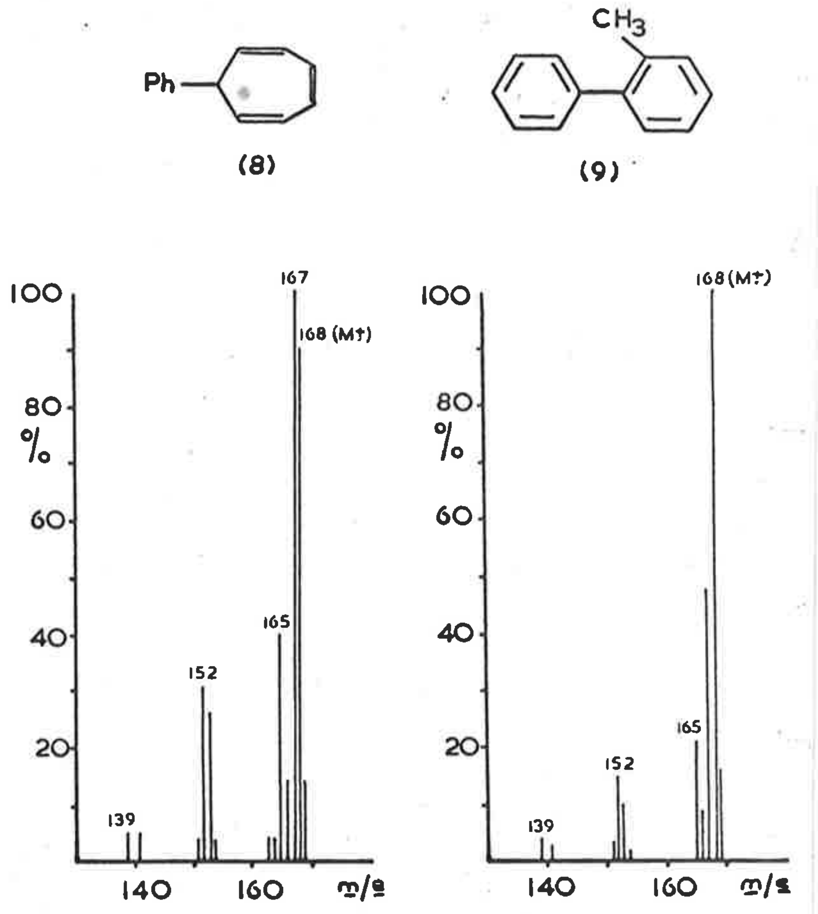


FIG. 4

Chapter 2. Fragmentations of the Stilbene Molecular Ion.

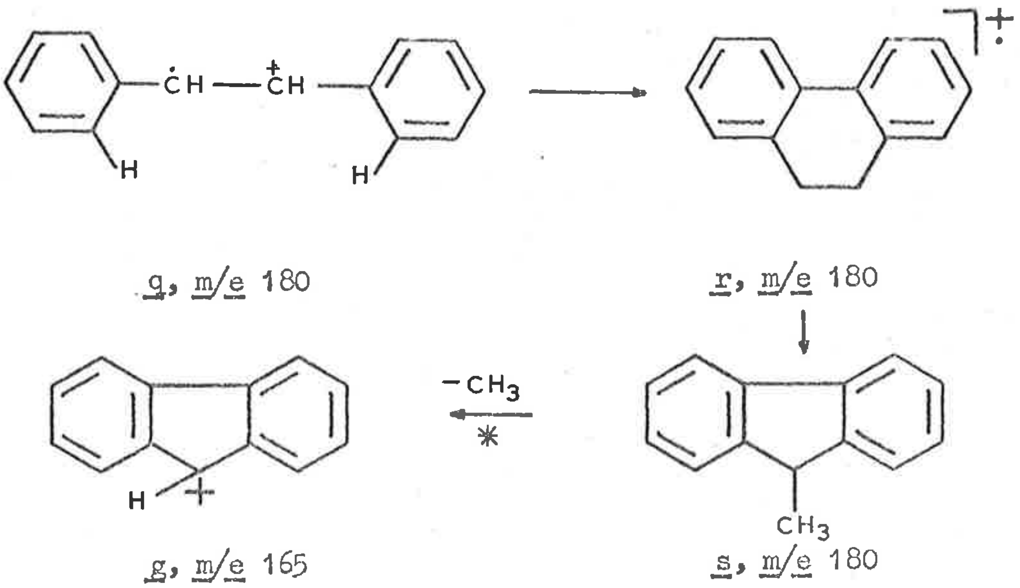
2.1 Introduction.

As a result of its completely conjugated system, the mass spectrum of stilbene (16) (Fig. 5) is characterised by very little fragmentation of the molecular ion (q, m/e 180), and a number of doubly charged ions. Apart from successive losses of hydrogen atoms from the molecular ion, the most pronounced fragmentation in the spectrum corresponds to the elimination of a methyl radical from the molecular ion (q → g), and this important rearrangement has been the

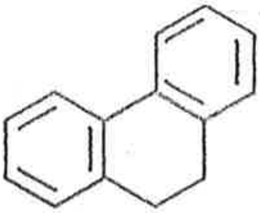
$$\underset{(16)}{C_6H_5-CH=CH-C_6H_5} \xrightarrow{-e} \underset{\underline{q},\ \underline{m/e}\ 180}{[C_6H_5-CH=CH-C_6H_5]^{+\cdot}} \xrightarrow[*]{-CH_3^{\cdot}} \underline{g},\ \underline{m/e}\ 165$$

subject of a number of studies.[91,92,97,105,106] In addition, the nature of the product ion, usually depicted as the fluorenyl cation g, has been extensively investigated.

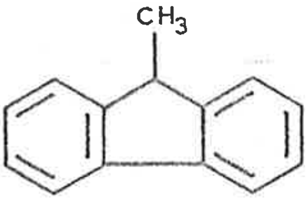
In a study of the M - $CH_3^{\cdot}$ process in stilbene, Johnstone and Millard reported[97] that the methyl radical originated from the olefin bridge, together with two ortho hydrogen atoms, and the mechanism which they proposed for the rearrangement is outlined in Scheme 4. In particular, the ions r and s, which represent the molecular ions of 9,10-dihydrophenanthrene (17) and 9-methylfluorene (18) respectively, are invoked as intermediates in the expulsion of a methyl radical from q.



Scheme 4.



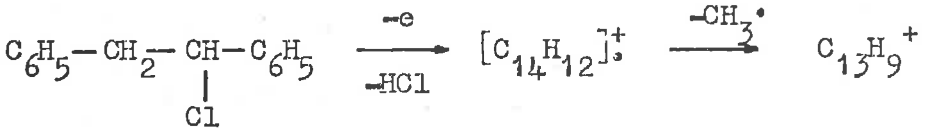
(17)



(18)

These authors based their conclusions on the spectra of 2,2'-d_2-stilbene (only partially labelled in each ring), several deuterium labelled 2,2'-diphenylethyl chlorides, and 1-^{13}C-1,2-diphenylethyl chloride. 1,2-Diphenylethyl chloride (19) eliminates the elements of HCl from the molecular ion to produce a species q', m/e 180, which is isomeric with the stilbene molecular ion (q), and which in turn ejects a methyl radical to produce m/e 165. The formation of m/e 165 in the spectrum of (19), however, can occur by various pathways, e.g.

(19) → *q*' → *g*, $M - H^{\cdot} - Cl^{\cdot} - CH_3^{\cdot}$, $M - Cl^{\cdot} - CH_3^{\cdot} - H^{\cdot}$, not all of



$$C_6H_5{-}CH_2{-}\underset{\underset{\displaystyle Cl}{|}}{CH}{-}C_6H_5 \xrightarrow[-HCl]{-e} [C_{14}H_{12}]^{+\cdot} \xrightarrow{-CH_3^{\cdot}} C_{13}H_9^{+}$$

(19) *q*', *m/e* 180 *g*, *m/e* 165

which pass through the "stilbene molecular ion" *q*' at *m/e* 180. Thus, although the reaction *q*' → *g* occurring in the first field-free region could be examined unequivocally by metastable defocusing, the daughter ion abundances used in this case may well not be representative of a reaction occurring specifically from *m/e* 180. Furthermore, in the absence of any information about its metastable characteristics, the structure and energy distribution of *q*' may be quite different from that obtaining in the molecular ion of stilbene *q*.

It was subsequently found[91,107] that the formation of the "fluorenyl cation" in systems which have adjacent phenyl substituents was preceded by hydrogen scrambling, and indeed hydrogen scrambling is a common feature in the spectra of many aromatic systems, including biphenyl,[108] diphenylmethane,[94,103] and diarylacetylenes.[109,110] It seemed probable, therefore, that the previous description[91] of the formation of *m/e* 165 in the spectrum of stilbene could be invalid. In view of the uncertainty surrounding the rearrangement of the stilbene molecular ion, it was decided to investigate the mass spectral properties of stilbene, 9,10-dihydrophenanthrene, and 9-methyl fluorene, using deuterium and ^{13}C labelling, and metastable techniques.

2.2 Results and Discussion:

2.2.1. The loss of methyl from the stilbene molecular ion.

In an attempt to obtain a definite answer to the problem outlined above, the spectra of the stilbenes (16) and (20)-(26), the 9,10-dihydrophenanthrenes (17) and (27), and the 9-methylfluorenes (18) and (28) have been measured.

The spectra of (16) and (17) show almost identical fragmentation patterns.[85,91,105] In addition to the pronounced rearrangement ion at m/e 165, the process M - H• - H• is present in both spectra at 70 eV. At 15 eV, however, only one hydrogen atom is eliminated, and the 15 eV spectra of (20)-(23) show that the stilbene molecular ion loses hydrogen in a completely random manner. In contrast, the molecular ion of (17) loses a greater than random proportion of hydrogen from the aromatic nucleus.[85] These results suggest that the molecular ions of stilbene and 9,10-dihydrophenanthrene do not behave in the same manner, at least with respect to the process M - H• .

The spectra of (16)-(18) (Figs. 5 and 6) each contain a peak at m/e 165, and the shape of the transition signal ($m^* = m/e\ 151.5$), corresponding to the metastable transition in the second field-free region for the process M - CH_3•, is very similar in the three spectra.[85,105] The ratios of the abundances of m/e 165 and m^* for (16)-(18) at varying energies of the electron beam are given in Table 6.[105] The ratios for (16) and (17) are very similar at all energies of the electron beam,

Table 6.

Values of [m/e 165]/[m*] in the spectra of (16)-(18).

eV	(16)[a]	(17)[a]	(18)
70	147	149	222
45	145	145	217
35	142.5	143	212.5
25	135	137	192.5
15	108	106.5	145

[a] These values have been reported before.[85]

but no correlation exists between (16) [and (17)], and (18). Since ions identical in structure and energy distribution must show identical fragmentations and metastable characteristics, then a reasonable interpretation of the results in Table 6 is that (i) g is produced from a common intermediate $\mathrm{A}^{+\cdot}$ in the spectra of (16) and (17), but that (ii) the decomposing species in the spectrum of (18) does not have the properties of $\mathrm{A}^{+\cdot}$. This does not necessarily preclude the participation

$$\begin{tikzcd}
(16) \arrow[dr, "-e"] & & \\
& \mathrm{A}^{+\cdot} \arrow[r, "-CH_3^{\cdot}", "*"'] & g,\ m/e\ 165 \\
(17) \arrow[ur, "-e"'] & &
\end{tikzcd}$$

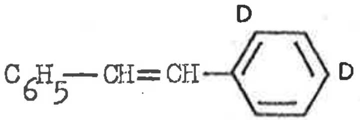
of a 9-methylfluorene species in the rearrangement, since it is possible that the different metastable characteristics observed in the spectrum of (18) are a result of different energy distribution in the decomposing ion.

$C_6H_5-CD=CH-C_6H_5$

(20)

$C_6H_5-CD=CD-C_6H_5$

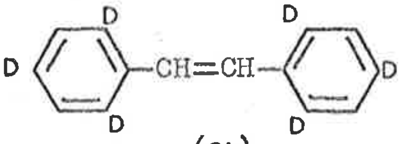
(21)



(22)

$C_6H_5-CH=CH-C_6D_5$

(23)



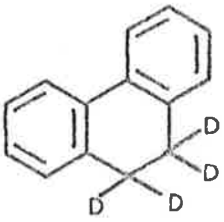
(24)

$C_6H_5-CH=CD-C_6D_5$

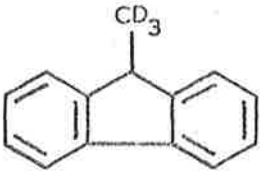
(25)

$C_6H_5-{}^{13}CH=CH-C_6H_5$

(26)



(27)



(28)

The composition of the various methyl species eliminated in the spectra of (20)-(25) and (27), measured by the abundances of the daughter ions formed at 15 eV, is given in Table 7, together with the values calculated for random loss of hydrogen and deuterium.

The ratios observed for the labelled stilbenes (20) and (24) are in excellent agreement with the calculated values, but the other results show a significant deviation from the values expected for random loss. The deviation (which corresponds to a greater loss of deuterium than hydrogen) appears to increase as the deuterium content increases;[85] this is unlikely to be the result of a "reverse" isotope effect (favouring loss of deuterium) since the primary deuterium isotope effect for the C—H/C—D bond cleavage in the M - H· process (see above) is

Table 7.

Composition[a] of the methyl species eliminated in the process M – $CH_nD^{\bullet}_{3-n}$ for (20)-(25), and (27) at 15 eV.

Compound		CH_3	CH_2D	CHD_2	CD_3
(20)	Obs.	75	25	-	-
	Calc.	75	25	-	-
(21)	Obs.	56	33	11	-
	Calc.	54	41	5	-
(22)	Obs.	43	37	17	3
	Calc.	38	49	12.5	0.5
(23)	Obs.	26	31	28	15
	Calc.	16	47.5	32	4.5
(24)	Obs.	11	41	39	9
	Calc.	9	41	41	9
(25)	Obs.	14	31	34	20
	Calc.	9	41	41	9
(27)	Obs.	23	36	32	9
	Calc.	25	51	22	2

[a] The values for the compounds (20)-(23), and (27) have been reported before.[85,105]

approximately 1.0.[85,105] Consideration of the values obtained for the two $\underline{d}_6$-labelled compounds (24) and (25), however, reveals that the symmetrically labelled compound (24) expels methyl statistically, but the unsymmetrical $\underline{d}_6$-compound (25) does not. Therefore, the divergence from a statistical distribution increases rather as the asymmetry of the molecule increases;[111] the implications of this possibility are discussed further below. The scrambling and/or rearrangement process is obviously complex, and the mechanism(s) unclear. Nevertheless, the data listed in Table 7 show that considerable randomisation of hydrogen and deuterium must occur in the molecular ions of the various labelled stilbenes, prior to the loss of a methyl radical.

Incomplete scrambling is also observed for (27)[105] (Table 7). The values obtained agree closely with results reported by Maquestiau *et al.*,[112] in an independent deuterium labelling study of 9,10-dihydrophenanthrene. These authors concluded that a methyl radical is eliminated from the bridge after scrambling has occurred. Whether the common intermediate $A^{+}_{\bullet}$ [which produces *g* in the spectra of (16) and (17)] has a "dihydrophenanthrene" structure which loses methyl from the bridge is unknown. However, since this ion has undergone considerable hydrogen scrambling, there must be at least one other form of the molecular ion in order to account for the enhanced loss of a hydrogen atom in the M - H./M - D. process in (27).[105]

At a nominal 8 eV, the M - H. process in the spectrum of (16) is no longer observed. At this energy of the electron beam, the spectrum of (26) shows peaks at *m/e* 180 and 181, the abundances of which are in the ratio 67.1 : 32.9 (corrected for isotope peaks). The ratio of abundances of *m/e* 165 and 166 in the same spectrum is 69.0 : 31.0. This value remains unchanged between 70 eV and the appearance potential of *g*, and corresponds to a retention of ^{13}C label of 94.3% (retention expected for random loss of ^{13}C = 92.9%). Since the accuracy of the observed value is probably no better than ± 1%, it would appear either that the carbon atom eliminated as a methyl radical in the rearrangement originates randomly from the whole molecule, or alternatively that complete carbon scrambling has occurred.[105,111] The statistical loss of carbon from two separately scrambled seven-membered units is a further possibility, but this model would not explain the inter-ring hydrogen scrambling which is observed. There is no evidence to suggest that methyl is lost specifically from the bridge.

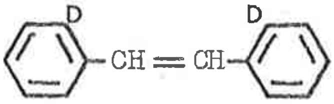
The question remains of the possible intermediacy in the rearrangement of a 9-methylfluorene species s. As might be expected, the elimination of methyl from s occurs almost exclusively from the 9-position. The processes M - $CD_3^{\bullet}$ and M - $CHD_2^{\bullet}$ occur in the ratios 95 : 5, 90 : 10, and 80 : 20 at 70, 15, and 10 eV respectively, in the spectrum of (28). A limited amount of scrambling is observed but is relatively unimportant, even at low internal energies when the low frequency factor scrambling process should compete most effectively with simple cleavage reactions. It is possible that the facile simple cleavage process effectively prevents any rearrangement of the molecular ion, thereby precluding the formation of the ion $A^{+\bullet}$ which is (according to the metastable evidence in Table 5) common to the M - $CH_3^{\bullet}$ processes in (16) and (17), but not (18). The non-correlation of metastable characteristics, however, is not proof of different ion structures, since different energy distributions may be involved. It is conceivable, therefore, that rearrangement (with scrambling) of the stilbene molecular ion could yield an ion $A^{+}_{\bullet}$ with a 9-methylfluorene structure, in which the hydrogen and carbon atoms are randomised, but in which the energy characteristics are different from those of the ion s produced from 9-methylfluorene.

A study[92] of the product ion in the rearrangement, $C_{13}H_9^{+}$, has provided evidence which supports the implications of the labelling results. The ion at m/e 165 is present in the spectra of many different classes of compounds,[92] including (1), (2), (16)-(18), phenalene, a large variety of di- and triphenyl heterocyclic compounds, 2,3-diphenylazirine, benzyl phenyl ketoxime, thiobenzophenone,[113] and 2,2-diphenyl-1,3-dithiane (see Chapter 3). Metastable ions resulting from the loss of acetylene (m_1^*) and C_4H_2 (m_2^*) $C_{13}H_9^{+}$ are observed in the first field-free region, and the parameter m_2^*/m_1^* has been used to classify the $C_{13}H_9^{+}$ ions formed from different precursors. In this manner, it has been shown that the $C_{13}H_9^{+}$ ions from fluorene and phenalene do not have the same properties. Furthermore, the ions at m/e 165 in the spectra of diphenylmethane (1), bromodiphenylmethane (2), stilbene (16), 9,10-dihydrophenanthrene (17), and 9-methylfluorene (18) all correspond to the ion produced by the loss of a hydrogen atom from the fluorene radical ion. (Although its actual structure cannot be assigned, this ion is nevertheless conveniently represented as the fluorenyl cation g.) Thus the formation of a common product ion at m/e 165 in the spectra of (16) and (17) supports the proposal made above that a common "molecular ion"

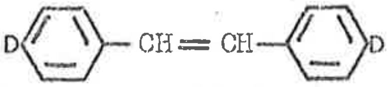
($A^{+}_{\bullet}$) is involved. Whether a 9-methylfluorene intermediate participates in the rearrangement of the stilbene molecular ion is no further clarified. Since the M - $CH_3^{\bullet}$ ion in the spectrum of (18) has the same properties as the rearrangement ions from (16) and (17), the involvement of s is certainly possible. However, the formation of such an intermediate must be preceded by carbon and hydrogen scrambling and therefore the intermediacy of s is not proven.

In summary, the results discussed above lead to the following proposals. The loss of a methyl radical may proceed from a common "molecular ion" in the spectra of stilbene and 9,10-dihydrophenanthrene to form an ion $C_{13}H_9^+$ which in each case has the same properties as the fluorenyl cation. Although the structure of the intermediate is unknown, it is unlikely to correspond to either the intact stilbene or 9,10-dihydrophenanthrene molecular ions, and the intermediacy of a 9-methylfluorene species is possible. Complete randomisation of hydrogen atoms occurs in the stilbene molecular ion prior to elimination of a hydrogen atom, and the M - $CH_3^{\bullet}$ process occurs after almost complete scrambling of the carbon and hydrogen atoms.

In a recent communication, Güsten et al.[106] have questioned the assumption[85,105] that a complete scrambling process precedes the loss of methyl from q. They suggest instead that randomisation takes place primarily within each half of the molecule and to a lesser extent between the rings. Their conclusion is based on the spectra of (21), (23), (25), and (29)-(31), and they advance the following arguments: (i) Negligible



(29)



(30)

$C_6D_5-CH=CH-C_6D_5$

(31)

hydrogen scrambling between the phenyl rings and the olefin bridge is observed for the processes $M - C_6H_5^{\bullet}$ and $M - C_6H_6$. (ii) The relative proportions of the methyl species eliminated in the spectra of (29) and (30) are identical, but different from those of (21), although each compound has two deuterium atoms in the molecule. (iii) The observed values for the $M - CH_3^{\bullet}$ process in the above deuterated stilbenes differ from the values calculated for complete randomisation.

Negligible hydrogen scrambling has been observed previously for the loss of the elements of benzene from the molecular ions of 9[114] (see following section). However, the contention that this specific process provides evidence in favour of the absence of inter-ring scrambling during the loss of methyl is not necessarily valid.[111] The $M - CH_3^{\bullet}$ rearrangement is a low energy process, and it is possible that the loss of C_6H_6 occurs from a high energy molecular ion which does not undergo scrambling between the rings and the bridge. In support of this suggestion is the fact that the metastable ion for the $M - CH_3^{\bullet}$ process is more than 100 times more intense than that for the process $M - C_6H_6$.

Similarly, it has been recognised (see above) that the deviation from the expected values for the elimination of methyl from the deuterated stilbenes (Table 7) suggests that the rearrangement and scrambling processes are both complex, and the mechanism(s) unclear. Furthermore, Güsten *et al.* make the contradictory observations that methyl loss appears to be favoured from either the rings or the bridge; significantly, they have not advanced a specific mechanism for the rearrangement.

As described above, the daughter ion in the rearrangement process in the spectrum of the ^{13}C-labelled stilbene (26) retains 94.3% of the ^{13}C label.[≠] This value has been assumed to represent a random loss of carbon (expected retention = 92.9%). If, however, the observed value is exactly correct and randomisation is not occurring completely, then the origin of the carbon atom in the loss of methyl may be one of the following possibilities: (i) Approximately 90% originates from the phenyl rings with 10% coming from the olefin bridge. (ii) Approximately 25% originates from the phenyl rings, with 75% from *either* a completely scrambled intermediate *or* from two separately-scrambled 7-carbon units.

A number of calculations have been made in order to test the various possible explanations of the observed scrambling, and some of these are given in Table 8. The calculations are contrasted with the observed values for the distribution of deuterated methyl species

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[≠] This is supported by defocusing. Although a precise measurement of the retention figure was not possible (since the residual metastable ion for the process m/e $180 \rightarrow 165$ overlaps that of the process m/e $181 \rightarrow 165$ at $E/E_o = 165/181$), greater than 90% retention of the label is indicated.

Table 8.

Observed and calculated values for the composition of methyl species eliminated in the process M − $CH_nD_{3-n}^{\bullet}$ for (20)-(25), and (29)-(31)*.

a Observed abundances of defocused metastable ions, at 70 eV.

b As for a, reproduced from Ref. 106.

c Values calculated for random loss.

Compound		CH_3	CH_2D	CHD_2	CD_3	A				B				C			
(20)	a	76	24	-	-	57	43	-	-	75	25	-	-	70	30	-	-
	c	75	25	-	-												
(21)	a	50	35	15	-	28	57	15	-	43	43	4	-	48	45	7	-
	b	55	28	17	-												
	c	54	41	5	-												
(22)	a	41	40	13	6	55	26	17	2	42	42	15	1	43	43	13	1
	c	38	49	12	1												
(23)	a	24	33	30	13	50	7	29	14	25	36	30	9	25	37	31	7
	b	31	31	24	14												
	c	16	47	32	5												
(24)	a	12	42	38	8	11	51	34	4	9	42	42	9	9	44	39	8
	c	9	41	41	9												
(25)	a	11	32	38	19	29	21	21	29	19	31	31	19	14	36	36	14
	b	19	30	32	19												
	c	9	41	41	9												
(29)	b	44	48	8	-	57	43	-	-	47	47	6	-	47	46	7	-
	c	44	47	9	-												

Continued...

Table 8 (contd.)

Compound		CH_3	CH_2D	CHD_2	CD_3	A	B	C
(30)	b	42	49	9	–	57 43 – –	42 49 9 –	43 48 9 –
	c	38	49	13	–			
(31)	b	–	15	31	54	– 14 57 29	– 4 42 54	– 7 45 48

A Calculated values for statistical loss of methyl from two "sets" of 7 hydrogen atoms.

B Calculated values for 75% random loss of methyl, with 25% from the phenyl rings, including the adjacent olefinic hydrogen atom.

C Calculated values for 75% random loss of methyl, with 25% from the phenyl rings, but with one of the methyl hydrogen atoms originating from either of the olefinic hydrogen atoms.

* The observed and calculated values for (29)-(31) are reproduced from Ref. 106. Similarly, the values in B and C for these compounds are based on the reported calculations for random loss.

eliminated from (20)-(25), and (29)-(31), measured by the abundances of the appropriate defocused metastable ions.≠ The values observed by Güsten *et al.* are included for comparison.

As suggested above, the possibility that the methyl radical is lost entirely from two independently randomised halves of the molecule, either from the phenyl rings or from 7-carbon units, does not explain the inter-ring scrambling which is observed. Furthermore, there is an *apparent* enhanced loss of hydrogen from the olefin bridge which must be allowed for in any mechanism. The calculations in columns A, B, and C attempt to include this factor. Column A shows the values expected for statistical methyl loss from either phenyl ring, with which are included both olefinic hydrogen atoms; there is no correlation, because again no accommodation is made for inter-ring scrambling. The calculations which show the best correlation with the observed values are recorded in columns B and C. These allow for inter-ring scrambling by assuming 75% randomisation; the remaining 25% loss is proposed to arise from independently-scrambling phenyl rings either with one bridge hydrogen atom considered with the ring hydrogen atoms (column B), or with one of the methyl hydrogen atoms actually originating from either olefin hydrogen atom (column C).

≠ It is of interest that the ratios obtained from abundances of defocused metastable ions (Table 8) are largely consistent with the daughter ion ratios (Table 7). This tends to favour a single mechanism for the loss of methyl and also supports complete (or nearly complete) hydrogen scrambling.

In conclusion, it seems likely that the experimental observations described in this section concerning the loss of a methyl radical from the stilbene molecular ion can be rationalised in either of two ways. These are:- (i) The loss of methyl involves (at least) two mechanisms with the major loss occurring from a scrambled molecular ion. The minor loss (or losses) originate from the phenyl rings, together with some participation of the hydrogens of the olefin unit. (ii) The close correspondence of metastable and daughter-ion ratios may be interpreted in terms of a single mechanism. If this is the case, the results may be interpreted as the decomposition of a predominantly scrambled molecular ion which also contains some partially scrambled material. If this molecular ion corresponds to stilbene itself, and if the methyl group originates from the phenyl rings together with participation from the olefin bridge, then the rationalisations in (i) and (ii) above are essentially equivalent.

2.2.2. The loss of benzene from the stilbene molecular ion.

The elimination of a hydrogen atom from the molecular ion of stilbene has been shown to be preceded by complete hydrogen scrambling.[85,105] Similarly, the rearrangement process $M - CH_3^\bullet$ proceeds, as described above, after randomisation of the hydrogen and carbon atoms. A third process which is observed in the spectrum of stilbene corresponds to the loss of the elements of benzene from the molecular ion,[111] to form the ion $[C_8H_6]^{+\cdot}$ (m/e 102), the abundance of which is 10% of the base peak at 70 eV. This decomposition is substantiated by a weak metastable ion (at m/e 57.8) formed in the first field-free region of the mass spectrometer. In contrast to the losses of H• and CH_3•, the M - C_6H_6 process does not involve any major hydrogen or carbon scrambling either between the phenyl rings, or between a phenyl ring and the olefin bridge. This observation is not without precedent, since scrambling has been observed previously[115] for some daughter ions, but not others formed by different processes from the same molecular ion. For example, whereas the losses of H•, CH_3• (and C_2H_3•) in diphenylmethyl systems are preceded by randomisation,[94] the M - C_6H_5• process involves little or no scrambling[103] (see above).

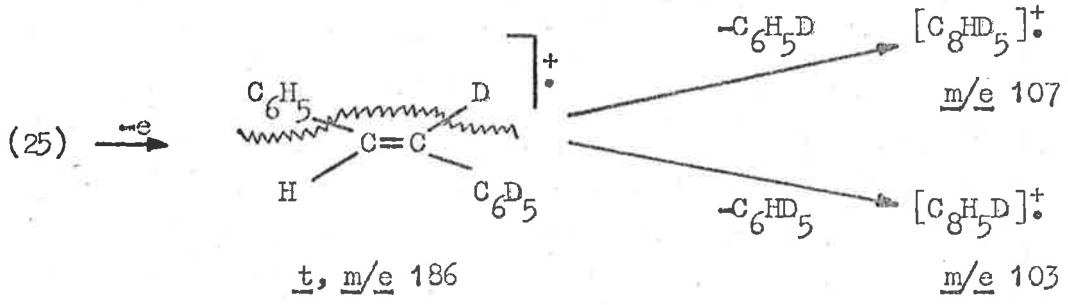
The partial spectra, at 25 eV, of stilbene (16) and the labelled derivatives (22)-(25) in the region m/e 100-110 are recorded in Fig. 7. The spectra are corrected for incomplete labelling (where appropriate) and for the small abundance of an M - C_6H_5• ion. The latter correction is justified on the grounds that the abundance of the ion [m/e 103 in the spectrum of (16)] is only 13% of that of the M - C_6H_6 ion at 25 eV, there is no metastable ion for its formation from the molecular ion in the first field-free region, and it does not appear to lose a hydrogen atom to produce m/e 102. After correction, the spectrum of each compound in this region is virtually identical between 15 and 70 eV.

The spectrum of d_3-stilbene (22) reveals that the phenyl rings are specifically involved in the M - C_6H_6 process, viz. the species

$C_6H_3D_3$ and C_6H_6 are eliminated, to produce ions at m/e 102 and 105 respectively. This specificity is confirmed in the spectrum of d_5-stilbene (23), in which the corresponding fragment ions are observed at m/e 102 and 105, in almost equal abundance. A slight preference for the loss of the labelled ring is noticeable in both spectra, the preference being greater in the spectrum of (23). This secondary isotope effect [^{k}(M-unlabelled)]/[^{k}(M-labelled)] has the value 0.97 for (22) and 0.91 for (23). The opposite effect might be expected to operate, since the greater "electron introducing" nature of deuterium compared with hydrogen (in solution chemistry)[116] would presumably strengthen the C-C bond adjacent to the labelled ring, and also stabilise the deuterium-containing fragment ion, thereby favouring the formation of the labelled species. Although similar reverse isotope effects have been reported previously,[117] the phenomenon is nevertheless unusual and not readily explicable.

The spectra of (22),(23),(24) show clearly that the sixth hydrogen atom arises from the olefin bridge. The mode of removal of the olefinic hydrogen atom is revealed by the spectrum of the d_6-stilbene (25). The major peaks at m/e 103 and 107 correspond to the loss of C_6HD_5 and C_6H_5D respectively, and this indicates that the departing phenyl group takes with it the hydrogen atom from the opposite end of the olefinic bridge (Scheme 5).

Despite the preference for the transfer of the non-adjacent olefinic hydrogen atom, the adjacent hydrogen atom is lost to a small



Scheme 5.

extent to give the ions at m/e 102 and 108 in the spectrum of (25). This might be the result of a limited degree of randomisation of the olefinic hydrogen atoms. However, scrambling processes have been shown to be energy dependent,[33,39] the randomisation increasing as the internal energy of the decomposing ion decreases.[32] Since there is negligible change in the relative distribution of the product species in the spectrum of (25) between 70 and 15 eV, the possibility of randomisation is unlikely.

It is noticeable that the abundance of the ion at m/e 108 is greater than that of the ion at m/e 102, and therefore a small primary isotope effect must be operating in favour of the loss of a hydrogen atom, rather than a deuterium atom. The direction of this isotope effect is as expected,[118] and an analogous effect has been observed before for the loss of C_6H_6 in the spectra of other aromatic compounds.[119] Neither the relative amount of hydrogen transferred from either position on the bridge, nor the magnitude of the deuterium isotope effect could be accurately estimated, since the two effects cannot be separated. However, the approximate ratio of loss of β-hydrogen to α-hydrogen is 4 : 1.

Since the molecular ion of 9,10-dihydrophenanthrene (17) has been shown to participate (in some way) in the M - CH_3• rearrangement process in stilbene,[105] it is of interest that the spectrum of (17) also shows a peak at m/e 102 (3% of the base peak) corresponding to the process M - C_6H_6. Although this process presumably involves a rearrangement of the molecular ion of (17), no metastable ion occurs for the decomposition in the first field-free region. Nevertheless, it is conceivable that a low energy, 9,10-dihydrophenanthrene species might slowly isomerise (with concurrent scrambling) to a stilbene molecular ion, before eliminating C_6H_6. In fact, the spectrum of (27) shows the losses of C_6H_6, C_6H_5D, $C_6H_4D_2$, $C_6H_3D_3$, and $C_6H_2D_4$ in the relative proportions of 9 : 43 : 23 : 17 : 8. The distribution required for completely random loss is 3 : 24 : 46 : 24 : 3. Therefore, a complex mechanism (which presumably involves some hydrogen randomisation) is operating; however, the possibility that 9,10-dihydrophenanthrene has undergone complete scrambling and reverted to a scrambled stilbene molecular ion which eliminates C_6H_6 is unlikely.

On the basis of the spectra of the d_3- and d_5-stilbenes, it was concluded (above) that a phenyl unit of stilbene is specifically involved in the M - C_6H_6 process. This assumption is supported by ^{13}C labelling evidence. The incorporation of ^{13}C in the molecular ion of (26) is

32.9%, and the corrected spectrum of (26), measured at 25 eV, shows the peaks m/e 102 and 103 in the ratio 67.6 : 32.4. The observed ratio is essentially unchanged over all energies of the electron beam, and represents (within experimental error) complete retention of the label.

In summary, the elimination of the species C_6H_6 from the stilbene molecular ion occurs predominantly via specific participation of a phenyl group and the non-adjacent olefinic hydrogen atom. The hydrogen and carbon scrambling which precedes the losses of a hydrogen atom and a methyl radical from the molecular ion of stilbene is not observed for the M - C_6H_6 process.

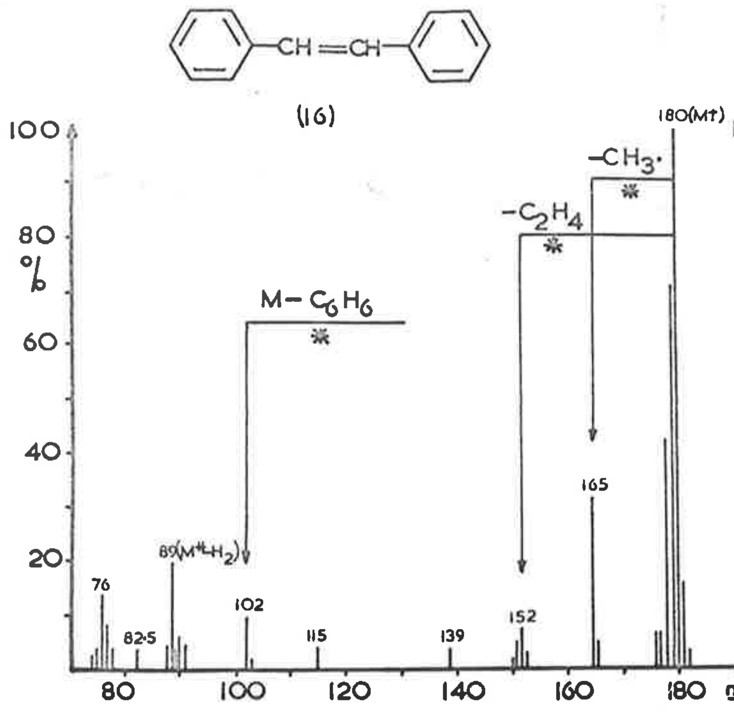


FIG. 5

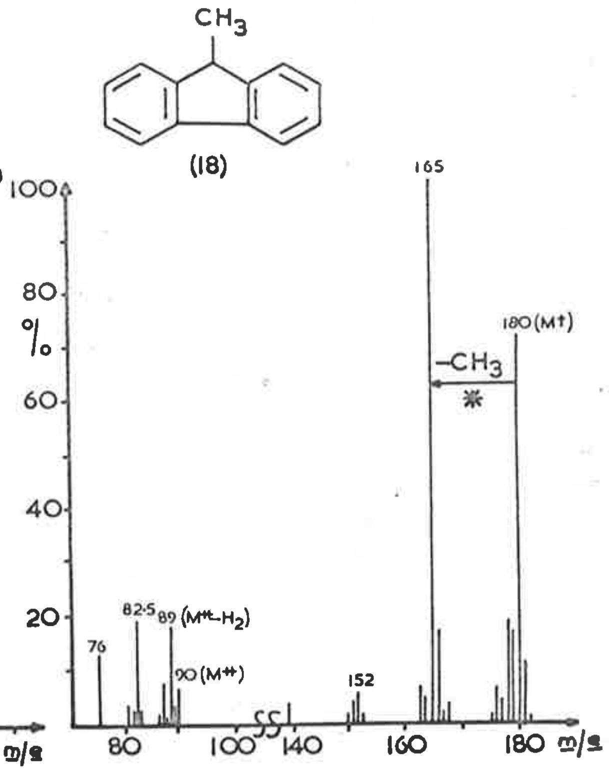


FIG. 6

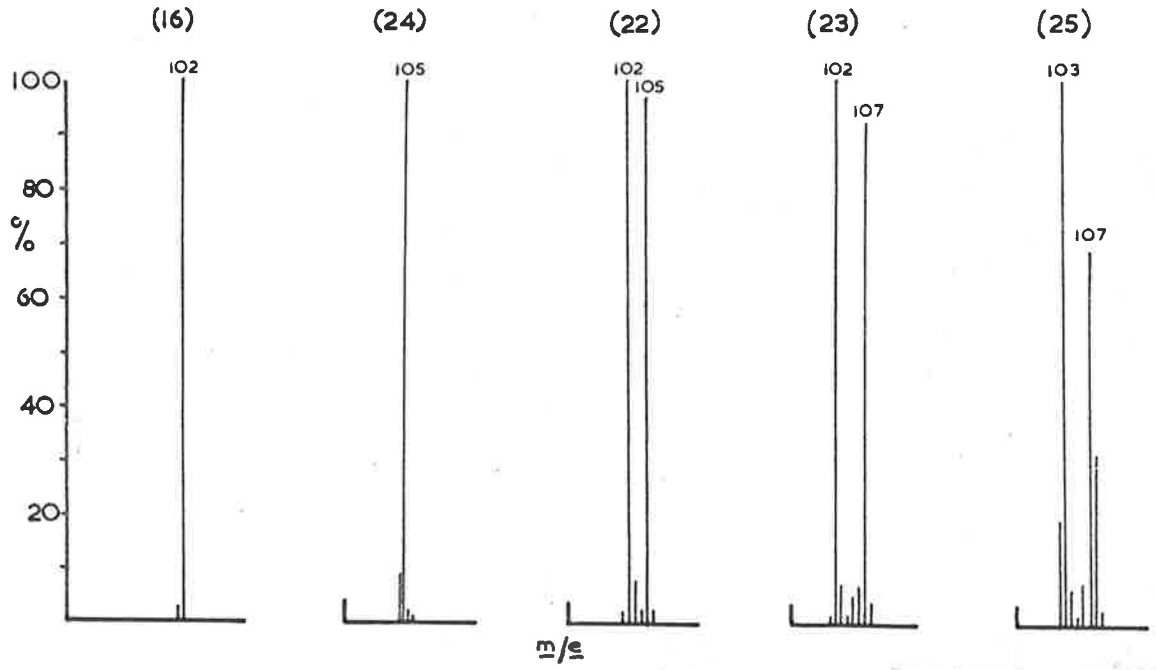


FIG. 7

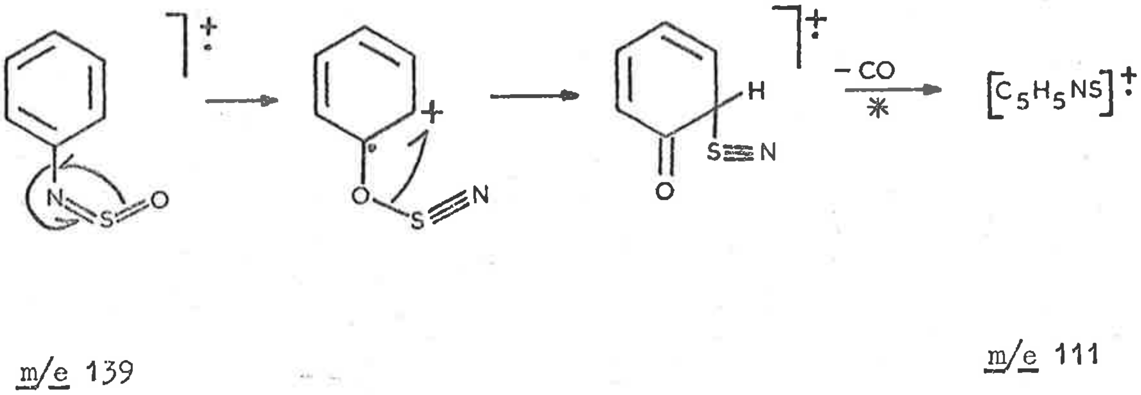
Chapter 3. The Mass Spectra of 1,3-Dithianes and Related Compounds.

3.1 Introduction.

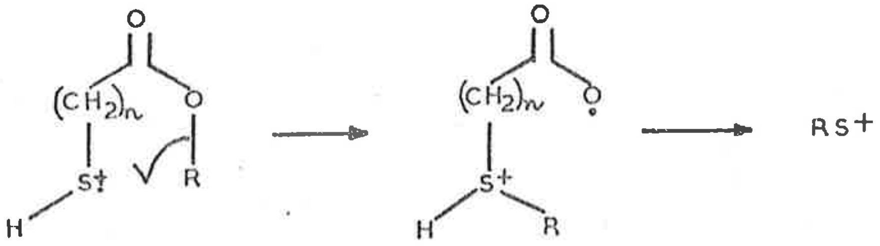
In view of the exceptional importance which the study of rearrangement processes in mass spectrometry has recently assumed, the mass spectral processes of organo-sulphur compounds, which exhibit a large number and variety of skeletal rearrangements, provide both an attractive and a rewarding area of investigation. The rearrangement reactions which are observed in the mass spectra of sulphur-containing compounds fall into three general groups: (i) rearrangements of the type ABC → AC + B, (ii) reorganisation of the molecular ion, and (iii) migration of a functional group to an electron deficient centre (e.g. a charged sulphur atom or a carbonium ion).

Rearrangement ions of the type M - S•, M - SH•, M - H_2S, and M - CHS• observed in the spectra of sulphides, thioethers, and disulphides illustrate the first group.[26] For example, the process M - SH• is important in the spectrum of thioanisole, and the results from deuterium-labelling studies have been interpreted in terms of an elimination of SH• from a rearranged molecular ion.[119] Similarly, the rearrangement ions M - S•, M - SH•, and M - CHS• are present in the spectra of ethylarylthioethers,[120] while diphenyldisulphide[121] exhibits pronounced losses of S•, SH•, and S_2 from the molecular ion. On the other hand, skeletal rearrangement processes are rare in the spectra of cyclic sulphides.[26] The process M - S• is common, but this is not a rearrangement in the strict sense because of the cyclic nature of the compound. However, hydrogen rearrangements are observed.[5]

The spectra of arylsulphoxides contain peaks which arise by both group (i) and (ii) rearrangements.[26] Thus, the processes M - SO [group (i)] and M - CO [group (ii)] are observed in the spectrum of diphenylsulphoxide.[122] Similarly, the initial fragmentation M - CO (see m/e 139 → m/e 111, below) in the spectrum of sulphonylaniline[123,124]



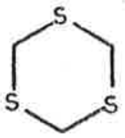
presumably arises by a rearrangement of the molecular ion involving C-O bond formation. The spectra of thioglycollates and β-thiopropionates contain RS^+ ions, and these are examples of specific migration to an electron-deficient sulphur atom [group (iii)][5,26] (see diagram, below).



S - Alkylthioglycollates undergo similar rearrangements under electron impact.[5,26]

A further characteristic of the mass spectral behaviour of organo-sulphur compounds is that the tendency to rearrangement is often not reflected in the analogous oxygen-containing compounds. For example, the familiar ion $C_{13}H_9^+$ (m/e 165), which is the product of the rearrangement process M - SH• in the spectrum of thiobenzophenone,[113] is absent in that of benzophenone.[34] The many other examples of the unusual and often unique behaviour in the mass spectrometer of compounds containing sulphur are extensively documented.[5,26]

During the course of a labelling study of proximity effects in the spectra of some aromatic aldehydes[125] and other carbonyl compounds,[126] it was observed that the spectrum of 2-phenyl-1,3-dithiane (46) contained abundant fragment ion (37% of the base peak) which corresponded to the elimination of the elements of S_2H• from the molecular ion, a process which is substantiated by the presence of a pronounced metastable peak.[122] Since the sulphur atoms are non-adjacent, the occurrence of the M - S_2H• process implies that a reorganisation of the molecular structure has taken place. Furthermore, this unusual rearrangement was not observed in the spectrum of the homologue of (46), 2-phenyl-1,3-dithiolane (67) (see below). Previous reports of the occurrence of an M - S_2H• fragmentation are rare, and are limited to the spectra of cyclic sulphides. For example, the ion is present in small abundance in the spectrum of 1,3,5-trithiane (32),[26] while it constitutes the base peak in the spectrum of 1,2-dithiane (33).[128] In the latter case, no formal rearrangement of the molecular structure is necessary. It is of interest that the spectrum of 1,4-dithiane (36), reported more recently,[129] contains no M - S_2H• fragment.



(32)

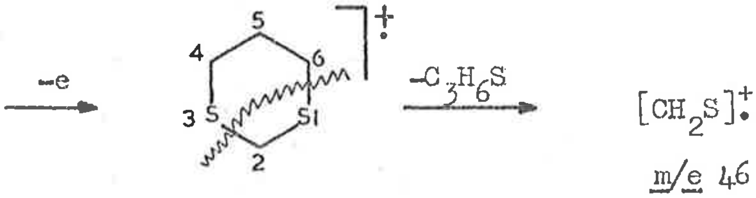
(33)

(34)

Previous studies of 1,3-dithio systems have been limited to two reports[129,130] of aliphatic bis-1,3-dithianes and -1,3-dithiolanes, in which α-cleavage reactions (with hydrogen transfer) are discussed. Since very little information about the mass spectral properties of the 1,3-dithiane system (and related systems) was available it was decided to investigate the general fragmentations of this system, with a view to gaining further understanding of the nature and scope of the $M - S_2H\cdot$ rearrangement process.

3.2 Results and Discussion.

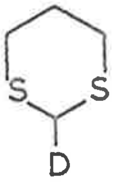
1,3-Dithiane (35) and derivatives substituted in the 2-position[≠] form abundant molecular ions when subjected to electron impact, and their spectra display a variety of fragment ions (Figs. 8-13). The decompositions of the 1,3-dithianes involve simple cleavage of the dithiane ring [e.g. (35) → m/e 46] and cleavage with hydrogen rearrangement, and processes which require skeletal reorganisation. The general cleavage

(35)


reactions are discussed below (3.2.1.) while the latter type, viz. M − SH• and M − S_2H•, are discussed separately (3.2.2. and 3.2.3.). The discussion below is based on the spectra (Figs. 8-14) of the parent compound (35), the substituted dithianes (39), (43), (46), (52), and (53), and the various labelled derivatives (36)-(38), (40)-(42), (44), (45), (47)-(51), and (54) (Appendix A). The molecular formulae of the compounds (35)-(53) are illustrated on the following page, and in a fold-out format at the end of this chapter, p.103. All fragmentations discussed below have been established by isotopic labelling, metastable defocusing, and/or exact mass measurement.

[≠] The carbon atoms of the dithiane ring are numbered in relation to the hetero atoms, which define the ring system (i.e. 1,3-dithiane or *meta*-dithiane).

(35)



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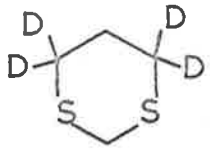

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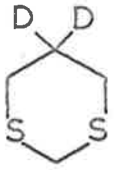

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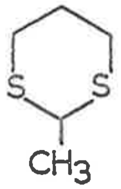

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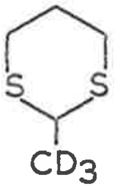

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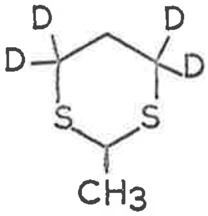

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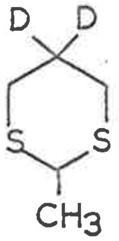

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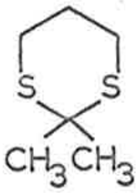

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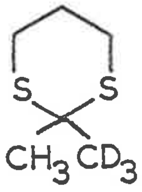

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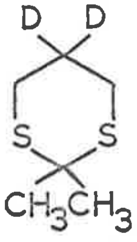

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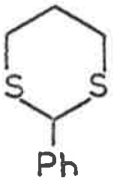

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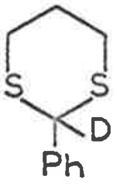

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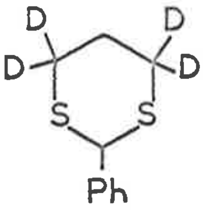

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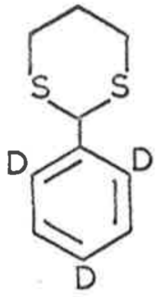
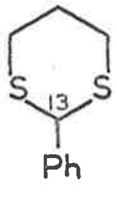
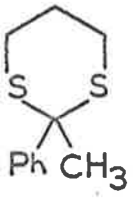
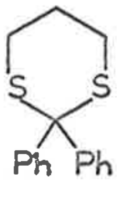


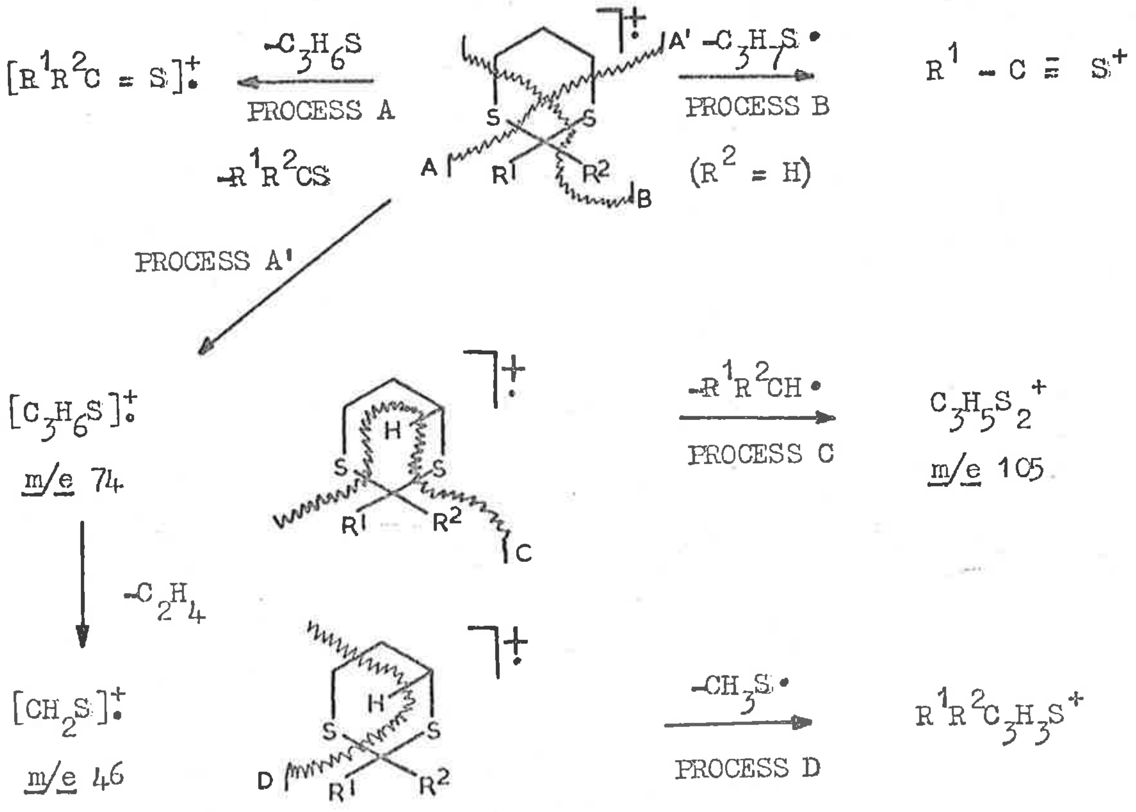






3.2.1. Simple cleavage processes in the spectra of 1,3-dithianes.

The fragmentation pathways of simple cleavage processes which are characteristic of the dithiane ring system are outlined in Scheme 6.



Scheme 6.

General fragmentations (cleavage type) of the 1,3-dithiane ring system.

A dominant fragmentation observed in all spectra (often yielding the base peak), corresponds to the cleavage of the dithiane ring with elimination of the species C_3H_6S from the molecular ion (Scheme 6, Process A), a process which is always accompanied by a metastable transition.

Charge retention by C_3H_6S also occurs (Process A') and the abundance of this ion (at m/e 74) varies with the nature of the substituent. In addition to the characteristic M - C_3H_6S fragmentation, the spectra of those compounds having a hydrogen atom attached to C-2 [e.g. (35), (39), and (46) in Figs. 8, 9, and 11] show the additional fragmentation M - $C_3H_7S\cdot$ (Process B). The hydrogen atom involved in this cleavage and transfer process originates from C-2 (deuterium labelling) for (35), (39), and (46). An equivalent process has been noted[129,130] in the spectra of bis-1,3-dithianes and -1,3-dithiolanes. Furthermore, a lesser amount of the ion current in the spectra of the majority of 1,3-dithianes is carried by the cation $C_3H_5S_2^+$ (m/e 105), which corresponds to the elimination of C-2 and its substituent(s), together with a hydrogen atom transfer (Process C). In every case, the hydrogen atom transferred in this process originates from the equivalent positions C-4,6.

The substitution at C-2 affects the general modes of fragmentation in a variable manner, and provides further fragmentation pathways. The specific fragmentations in the spectra of the various substituted compounds are discussed most conveniently in the terms of aliphatic and aromatic substitution. The spectra of the parent compound (35), 2-methyl-1,3-dithiane (39), and 2,2-dimethyl-1,3-dithiane-5,5-d_2 (45) are illustrated in Figs. 8-10, and Table 9 lists the major processes occurring from the molecular ions of (35), (39), (43), and the deuterium labelled derivatives (36)-(38), (40)-(42), (44), and (45). In addition

Table 9.

Major processes in the spectra of (35)-(45). (Figures in brackets refer to percentages determined by defocusing.)

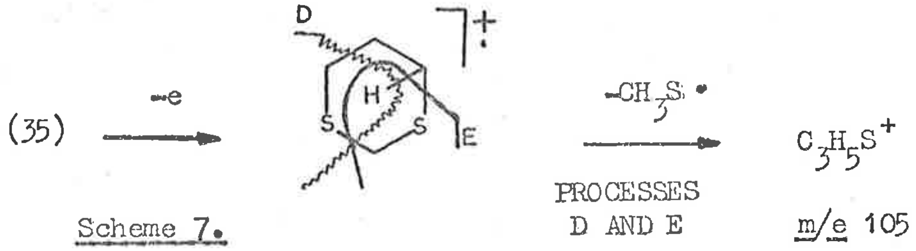
Compound	Process (M - X)				
(35)	CH_3	CH_2S	CH_3S		C_3H_6S
(36)	CH_2D	CHDS	CH_3S (50) CH_2DS (50)		C_3H_6S
(37)	CH_2D	CH_2S	CH_2DS (60) CD_3S (40)		$C_3H_2D_4S$
(38)	CH_3	CH_2S	CH_3S		$C_3H_4D_2S$
(35)	C_3H_7S	SH	S_2H		
(36)	C_3H_6DS (50) C_3H_7S (50)	SH (90) SH (10)	S_2H		
(37)	$C_3H_3D_4S$	SH (65) SD (35)	S_2H (60) S_2D (40)		
(38)	$C_3H_5D_2S$	SH (80) SD (20)	S_2H (58) S_2D (42)		
(39)	CH_3	CH_3S	C_2H_5	C_2H_4S	C_3H_6
(40)	CD_3	CH_3S	$C_2D_3H_2$	C_2HD_3S	C_3H_6
(41)	CH_3	CD_3S	C_2H_4D	C_2H_4S	$C_3H_2D_4$
(42)	CH_3	CH_3S	C_2H_5	C_2H_4S	$C_3H_4D_2$

Continued.

Table 9 (contd.)

Compound			Process (M − X)	
(39)	C_3H_6S	C_3H_7S	SH	S_2H
(40)	C_3H_6S	C_3H_7S	SH	S_2H
(41)	$C_3H_2D_4S$	$C_3H_3D_4S$	SH (40) SD (60)	S_2H (65) S_2D (35)
(42)	$C_3H_4D_2S$	$C_3H_5D_2S$	SH (80) SD (20)	S_2H (68) S_2D (32)
(43)	CH_3	CH_3S	C_2H_4S	C_3H_6
(44)	CH_3 (55) CD_3 (45)	CH_3S	C_2H_4S	C_3H_6
(45)	CH_3	CH_3S	$C_2H_2D_2S$	$C_3H_4D_2$
(43)	C_3H_6S	SH	S_2H	
(44)	C_3H_6S (60) $C_3H_3D_3S$ (40)	SH (60) SD (40)	S_2H	
(45)	C_3H_6S (40) $C_3H_4D_2S$ (60)	SH (90) SD (10)	S_2H (45) S_2D (55)	

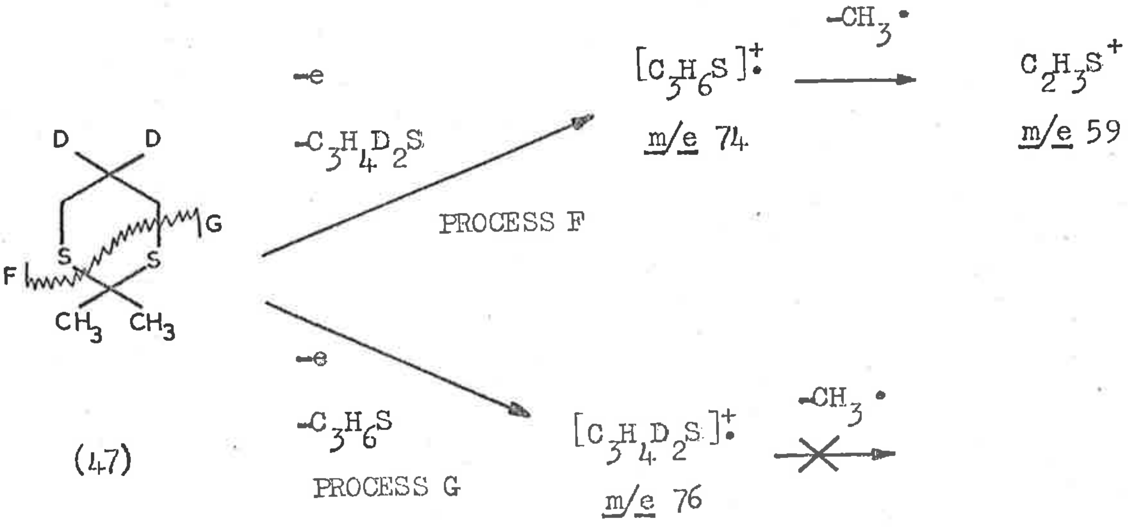
to the general processes of the dithiane ring (Scheme 6), the spectra show variations according to the substitution pattern. For example, all dithianes eliminate $CH_3S\cdot$ in the manner indicated in Scheme 6, Process D, but the spectrum of the parent compound (35) shows that the process M − $CH_3S\cdot$ occurs by two mechanisms, the alternative route being via C-2 (Scheme 7, Process E).



Scheme 7.

An additional process M - CH_2S in the spectrum of (35) (see Table 9), also occurs in the same manner as the M - $CH_3S\cdot$ process. Similarly, the elimination of $CH_3\cdot$ from the molecular ion of (35) specifically involves C-2, but the losses of methyl from the molecular ions of the methyl substituted compounds (39) and (43) occur exclusively from the methyl substituents. Furthermore, it is of interest that all simple cleavage processes in these spectra occur specifically, i.e. no randomisation of the hydrogen atoms is observed. Even the ion $[C_3H_6S]^{+\cdot}$ (m/e 74) eliminates the elements of ethylene (C_2H_4) (Scheme 6) in a specific manner, i.e. the corresponding ions in the spectra of the d_2- and d_4- derivatives (37) and (38) both lose $C_2H_2D_2$. Similarly, although both ionised "halves" of the molecule contribute almost equally to the (M - C_3H_6S) ion at m/e 74 in the spectrum of (45), the further loss of $CH_3\cdot$ from m/e 74 occurs only from the "half" originally containing the 2,2-dimethyl substitution [see the spectrum of (47), Fig. 10, and Process F, Scheme 8].

The spectrum (Fig. 11) of 2-phenyl-1,3-dithiane (46) and the information listed in Table 10 illustrate the main processes occurring from the molecular ions of (46) and the deuterium labelled compounds (47)-(50). The aromatic substituent tends to reduce the complexity of



Scheme 8.

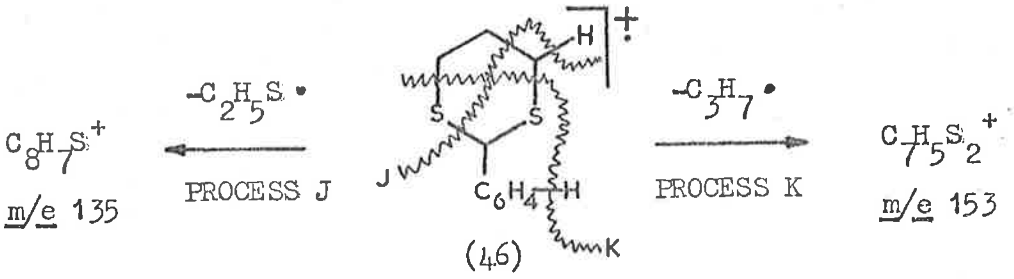
the fragmentation pattern of the dithiane ring by stabilising certain of the fragment ions. As a consequence, the M - C_3H_6S and M - $C_3H_7S{}^\bullet$ fragments (Scheme 6, Processes A and B) dominate the spectrum, the product ions being presumably the stable thiobenzaldehyde and thiobenzoyl species respectively. The remaining "general" fragmentations (Scheme 6) occur in relatively low abundances. [This is further illustrated in the spectra of (52) and (53) (Figs. 12 and 13).] For example, in the spectrum of (46), (Fig. 11) the loss of CH_3S from the molecular ion in the usual specific manner produces m/e 149 (8% of base peak). On the other hand, the facile elimination of $C_7H_7{}^\bullet$ yields $C_3H_5S_2{}^+$ (m/e 105) in the expected manner, in greater abundance than observed in the spectra of the aliphatic substituted derivatives (35), (39), and (43). The latter ion may be produced via a rearrangement process and not via simple cleavages, since it is the major fragment in the spectrum of (46) at 10 eV.

Table 10.

Major processes in the spectra of (46)-(50). (Figures in brackets refer to percentages determined by defocusing.)

Compound	Process (M − X)			
(46)	CH_3S	C_2H_5S	C_3H_7	C_3H_6S
(47)	CH_3S	C_2H_5S	C_3H_7	C_3H_6S
(48)	CD_3S	$C_2H_2D_3S$	$C_3H_3D_4$	$C_3H_2D_4S$
(49)	CH_3S	$C_2H_3D_2S$	$C_3H_5D_2$	$C_3H_4D_2S$
(50)	CH_3S	C_2H_5S	C_3H_7 (60) C_3H_6D (40)	C_3H_6S
(46)	C_3H_7S	C_7H_7	S_2H	
(47)	C_3H_6DS	C_7H_7	S_2H	
(48)	$C_3H_3D_4S$	C_7H_6D	S_2H (70) S_2D (30)	
(49)	$C_3H_5D_2S$	C_7H_7	S_2H (52) S_2D (48)	
(50)	C_3H_7S	$C_7H_4D_3$	S_2H	

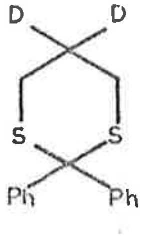
Additional low abundance ions common to the aromatic substituted 1,3-dithianes, corresponding to the processes M − $C_2H_5S\cdot$ and M − $C_3H_7\cdot$, are observed at m/e 135 and 153 respectively. These ions are formed by the specific processes shown in Scheme 9 (Processes J and K). The pathway of the M - C_3H_7• fragmentation (Process K) is of interest, since it is the only cleavage of the dithiane ring in the spectrum of 2-phenyl-1,3-dithiane in which a hydrogen atom from the phenyl ring is utilised.



Scheme 9.

This can be seen in the spectrum of 2-($\underline{d}_3$-phenyl)-1,3-dithiane (51) which exhibits ions at m/e 155 and 156, corresponding to the processes M - C_3H_6D• and M - C_3H_7• respectively. These two processes occur in the approximate ratio of 60 : 40, indicating that the additional hydrogen atom arises from the phenyl substituent, either in a random manner or after randomisation of the aromatic hydrogen atoms has taken place.

The characteristic fragment ions produced by the processes M - C_3H_7•, M - CH_3S•, M - C_2H_5S•, and M - C_3H_6S are all observed in the spectra of 2-methyl-2-phenyl-1,3-dithiane (52) and 2,2-diphenyl-1,3-dithiane (53) (Figs. 12 and 13). The spectrum of 2,2-diphenyl-1,3-dithiane-5,5-$\underline{d}_2$ (54) confirms the reaction pathways of these



(54)

processes for (53) (see Schemes 6 and 9). The fragment ion produced by the M - C_3H_6S process in the spectrum of (53) corresponds formally to the thiobenzophenone radical ion, from which the formation (by removal of SH•) of the cation $C_{13}H_9^+$ (m/e 165) has been reported.[113] The metastable characteristics of the abundant ion $C_{13}H_9^+$ in the spectrum of (53) (Fig. 13) have been examined. Elimination of C_2H_2 and C_4H_2 from m/e 165 in the first field-free region produce the ions m/e 139 and 115 respectively, and the appropriate defocusing data is given below:

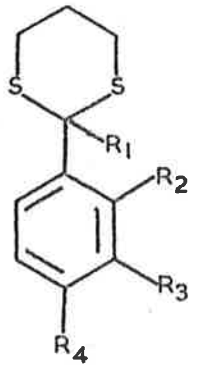
m/e 165 → m/e 115	E/E_o = .6970	m_1^* = m/e 80.1
m/e 165 → m/e 139	E/E_o = .8424	m_2^* = m/e 117.1

$$[m_1^*]/[m_2^*] = 1.10 \pm .03 \text{ (at 70 eV)}$$
$$= 1.13 \pm .04 \text{ (at 35 eV)}$$

The corresponding values of the parameter $[m_1^*]/[m_2^*]$ in the spectrum of stilbene (16), in which the ion $C_{13}H_9^+$ at m/e 165 has been shown to have the same properties as the ion derived by the loss of a hydrogen atom from fluorene, are 1.14 and 1.12, at 70 and 35 eV respectively. These values are in good agreement with those obtained for (53) above, and hence, the ion at m/e 165 in the spectrum of 2,2-diphenyl-1,3-dithiane (53) corresponds to the "fluorenyl" cation g (see Chapters 1 and 2).

The presence of a substituent on the aromatic ring influences the initial fragmentations of the 2-aryl-1,3-dithianes. The cleavage process M - C_3H_6S is generally pronounced in the dithiane system, but a strongly electron-withdrawing group on the aromatic substituent appears to destabilise the (M - C_3H_6S) ion, which is in very low abundance in the spectra of the nitrophenyl derivatives (62) and (63). The majority of the ion current in these spectra is carried by $[C_3H_6S]^{+\cdot}$ (m/e 74). On the other hand, the spectra of the p-$N(CH_3)_2$- phenyl derivative (67) and even the chlorophenyl derivatives (64)-(66) show the (M - C_3H_6S) ion as the base peak.

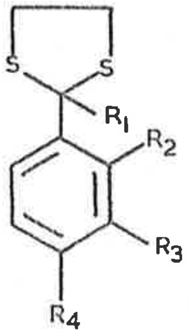
Ortho-effects,[3] which are observed in the spectra of a variety of aromatic compounds containing adjacent substituents, and which are often characteristic of the particular substitution pattern, are also a feature of 2-aryl-1,3-dithianes. The spectra of the two o-methoxy derivatives (57) and (58) (Figs. 14 and 15) illustrate this effect. The initial cleavage (M - C_3H_6S) is followed by the loss of SH•, the hydrogen atom of which arises from the o-methoxy substituent [i.e. SD• is eliminated in the spectrum of (57), Fig. 14]. The o-ethoxy derivative (59) also undergoes an equivalent fragmentation when subjected to electron impact, and these ortho-effects are similar to those observed in the spectra of o-alkoxybenzaldehydes.[125,126] The spectrum of the p-methoxy analogue (58) (Fig. 15) does not show the corresponding (M - C_3H_6S - SH•) ion. Similar ortho-effects are observed in the spectra of the nitrophenyl and chlorophenyl derivatives (61) and (64). For example, the spectrum of (61) shows an (M - OH•) peak (m/e 224) which is not present in the spectra of (62) and (63), while in the spectra of the chlorophenyl derivatives (64)-(66), an M - Cl• fragmentation is unique to that of the o-chloro derivative (64). An M - Cl• process is usually favourable in the spectra of aryl chlorides, and furthermore



	R_1	R_2	R_3	R_4
(55)	H	OCH_3	H	H
(56)	D	OCH_3	H	H
(57)	H	OCD_3	H	H
(58)	H	H	H	OCH_3
(59)	H	OC_2H_5	H	H
(60)	D	OC_2H_5	H	H
(61)	H	NO_2	H	H
(62)	H	H	NO_2	H
(63)	H	H	H	NO_2
(64)	H	Cl	H	H
(65)	H	H	Cl	H
(66)	H	H	H	Cl
(67)	H	H	H	$N(CH_3)_2$

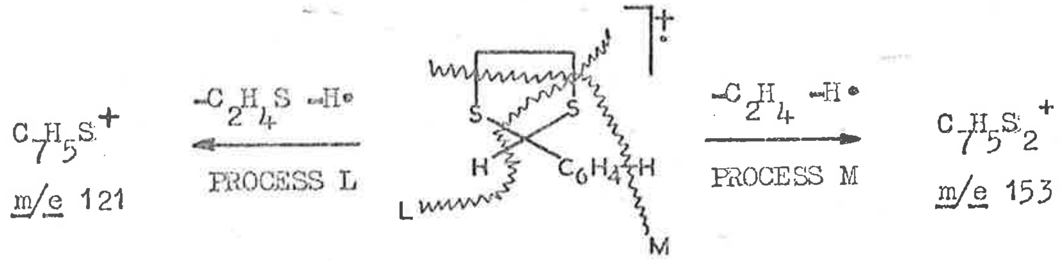
the position of substitution (i.e. o-, m-, or p-) of the halogen atom on the aromatic nucleus generally has little effect upon the fragmentation pattern for the particular series of isomeric compounds.[131] Hence, it is of some interest that an M - Cl• ion [m/e 195, 15% of the base peak in the spectrum of (54)] is observed only as the result of an ortho effect.

It is also of interest to compare the spectra of the aryl-1,3-dithianes with those of the homologous -1,3-dithiolanes (68)-(75).

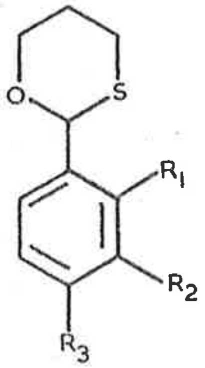


	R_1	R_2	R_3	R_4
(68)	H	H	H	H
(69)	D	H	H	H
(70)	H	OCH_3	H	H
(71)	H	H	H	OCH_3
(72)	H	NO_2	H	H
(73)	H	H	NO_2	H
(74)	H	H	H	NO_2
(75)	H	H	H	CH_3

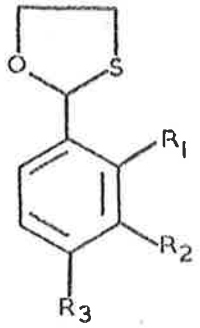
The basic fragmentations, viz. M - C_2H_4S - H• - CS, of 2-phenyl-1,3-dithiolane (68) (Fig. 16) are analogous to those observed in the spectrum of (46). In addition, the elements of ethylene and C_2H_5• are eliminated from the molecular ion to a significant extent. The spectrum of (69) confirms that the hydrogen atom which is eliminated after the initial M - C_2H_4S cleavage arises from C-2 (Scheme 10, Process L). Furthermore, the process (M - C_2H_4) - H• is observed in the spectra of both (68) and (69). Therefore, the (M - C_2H_5•) ion arises by participation with the aromatic ring (Scheme 10, Process M). The mechanism of this process is entirely analogous to that of the M - C_3H_7• process in the spectrum of (46). In addition, ortho-effects similar to those seen in the spectra of the 1,3-dithianes, operate in the spectra of the substituted phenyl derivatives (70)-(74). For example, the process M - C_2H_4S - SH• occurs in the spectrum of 2-(o-methoxyphenyl)-1,3-dithiane (70) but not in that of the para isomer (71). Similarly, the initial M - C_2H_4 process in the spectra of the m- and p-NO_2 derivatives (72) and (73) is entirely replaced by an M - NO• fragmentation in the spectrum of the ortho isomer (74).



Scheme 10.



	R_1	R_2	R_3
(76)	H	H	H
(77)	NO_2	H	H
(78)	H	NO_2	H
(79)	H	H	NO_2

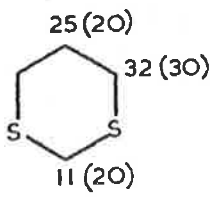


	R_1	R_2	R_3
(80)	NO_2	H	H
(81)	H	NO_2	H
(82)	H	H	NO_2

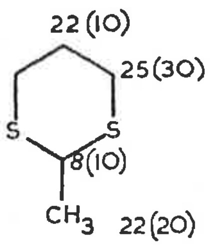
The spectrum of 2-phenyl-1,3-oxathiane (76) is similar to that of (46), in that the major fragmentation corresponds to M - $C_3H_7S\cdot$ while the process M - $C_3H_7O\cdot$ occurs to a smaller extent (the abundance ratio of the ions (M - $C_3H_7S\cdot$) and (M - $C_3H_7O\cdot$) is approximately 75 : 25). Similarly, the spectra of the nitrophenyl derivatives (77)-(79) resemble those of the analogous dithianes. Almost all the ion current in the spectra of (78) and (79) is carried by $[C_3H_6S]^{+\cdot}$ (m/e 74), but the molecular ion of (77) fragments through the o-nitro substituent (e.g. M - $OH\cdot$), and the spectrum is quite complex. The characteristics of the spectra of the nitrophenyl 1,3-oxathiolanes (80)-(82) are similar to those above. The ring cleavage product $[C_2H_4S]^{+\cdot}$ (m/e 60) is the only significant fragment in the spectra of (81) and (82), but the spectrum of (80) is complicated by ortho processes.

3.2.2. M - $SH\cdot$ and M - $S_2H\cdot$ in the spectra of 1,3-dithianes.

Many sulphides and disulphides eliminate $SH\cdot$ from their molecular ions in a complex manner,[5,26] and this is also the case for the 1,3-dithianes (35), (39), (43), (46), and (52). In contrast to the cleavage reactions discussed above, the hydrogen atom involved in the M - $SH\cdot$ (and M - $S_2H\cdot$) processes observed in these spectra does not arise from a specific position in the molecule. In the spectrum of (46) the hydrogen atom originates equally from C-2 and the equivalent C-4,6 positions, and the elimination from the molecular ions of (35), (39), and (43) is more complex (see Tables 9 and 10). The origins of the hydrogen atoms in these cases are summarised below. The values in brackets are obtained from the abundances of the appropriate defocused



(35)



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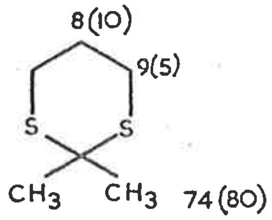


(43)

metastable ions, and the other figures from daughter ion abundances. Since it is likely that more than one mechanism is operating in each case, the variation between the two sets of values is not surprising. On the other hand, the operation of a partial hydrogen scrambling process could also explain the variation between the observed values.

The fragment M - $S_2H\cdot$, which is present in the spectra of all 1,3-dithianes reported here [except that of the diphenyl substituted compound (53)], is particularly interesting. This process, which appears to be characteristic of the dithiane system (the M - $S_2H\cdot$ ion is not observed in the spectra of 1,3-dithiolanes), is always accompanied by a pronounced metastable peak. The M - $S_2H\cdot$ peak is most abundant in the spectrum of (46) (Fig. 11), in which it corresponds to the cation $C_{10}H_{11}^+$ (m/e 131, 37% of the base peak), and since this ion remains significant in the 10 eV spectrum, some kind of skeletal reorganisation may be involved. Although a pronounced metastable ion is associated with the process, it is difficult to envisage the rearrangement as a one-step reaction, since at least five bonds must be broken and two reformed to produce the $M - S_2H•$ species. The process is obviously complex, and may be better considered as a multi-stage process involving a series of bond breaking and bond forming steps.

The abundance of the $M - S_2H•$ species decreases with substitution of the phenyl ring in the 2-aryl-1,3-dithianes. This does not appear due to a specific electronic effect, but merely the result of the introduction of alternative decomposition modes which discriminate against the rearrangement reaction. For example, the $M - S_2H•$ ion is in equally low abundance in the spectra of (63) and (67) (where the substituents have opposite electronic effects); on the other hand, the presence of a chloro substituent in the spectra of (64)-(66) does not significantly alter the abundance of the $M - S_2H•$ species. The absence of a $M - S_2H•$ peak in the spectrum of (53) is presumably the result of the domination of the facile cleavage ($M - C_3H_6S$), from which the equally facile rearrangement process (producing $C_{13}H_9^+$, m/e 165) occurs.

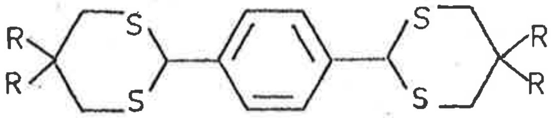
The abundances of the ions at m/e 132 and 133 corresponding to $M - S_2D•$ and $M - S_2H•$ in the spectrum of (49) are in the ratio 34 : 66 at 70 eV. This observation can be interpreted either as a random loss of hydrogen from C-4,5, and 6 or that the hydrogen atoms on C-4,5, and 6 have fully randomised prior to fragmentation. Although all other fragmentations which involve hydrogen atoms of the dithiane ring apparently proceed without hydrogen randomisation [with the possible exception of the M - SH• process (see above)], there are precedents for the occurrence of both random and non-random processes from the same initial molecular ion. It is also recognised that random processes become more pronounced as the internal energy of the decomposing ion decreases. However, the random nature of the elimination of $S_2H\cdot$ and $S_2D\cdot$ decreases as the energy of the ionising beam is lowered (see Table 11). Furthermore, the low energy process which is the result of the equivalent metastable transition in the second field-free region, reflects the same trend (Table 11), viz. the process appears to be less random at lower energies, where a preference for the loss of hydrogen from C-5 is apparent. This is further substantiated by the spectrum of the d_4-derivative (48) which shows relative daughter ion abundances at 70 eV for M - $S_2D\cdot$ and M - $S_2H\cdot$ of 51 : 49 (value for random loss = 80 : 20). The elimination of $S_2H\cdot$ is also pronounced in the spectrum of

Table 11.

Abundance ratios of the daughter and metastable ions for the processes M - $S_2D\cdot$ and M - $S_2H\cdot$, in the spectrum of (49).

	70 eV	25 eV	15 eV	10 eV
m/e 132 : m/e 133	34 : 66	35 : 65	37 : 63	39 : 61
m/e 88.0 : m/e 89.3	46 : 54	50 : 50	54 : 46	59 : 41

the bis-1,3-dithiane (83), in which it occurs from both the molecular ion, and the M - C_3H_6S ion, (with metastable ions substantiating both processes) and the spectrum of (84) shows almost exclusive loss of $S_2D\cdot$


(83) R = H

(84) R = D

in both processes. Overall, these observations are not consistent with the occurrence of a random process. This is further supported by the observed values for the losses of $S_2H\cdot$ and $S_2D\cdot$ from the molecular ions of the labelled derivatives (37), (38), (41), (42), and (45). The results for these compounds and for (48) and (49) are summarised in Table 12; these also indicate non-random behaviour. The observations may be rationalised in terms of (at least) two separate processes for the elimination of $S_2H\cdot$, with the loss of hydrogen from C-5 being more favoured than from $C_{4,6}$. The preference for the C_5 position is variable, being dependent on the substitution of the dithiane and the lifetime of the decomposing ion. At the same time, deuterium isotope effects are operating in favour of hydrogen loss. Furthermore, the process does not proceed via the M - SH· fragment, since the hydrogen involved in the formation of this ion is not the same as that of the M - $S_2H\cdot$ elimination.

The facility of a rearrangement process can be a function of, among other things, the ease of formation of the product ion, i.e. a stable product species is likely to be the result of a facile rearrangement. Hence, a plausible structure for the (M - $S_2H\cdot$) rearrangement

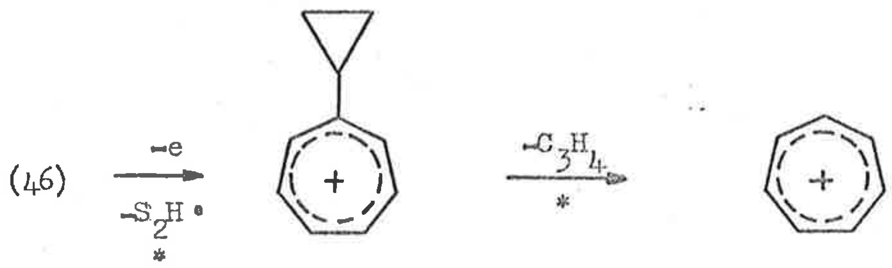
Table 12

Compositions of the $S_2H\cdot$ species eliminated from the molecular ions of (37), (38), (41), (45), (48), and (49) at 70 eV, measured by the abundances of (a) the daughter ions (b) the defocused metastable ions.

	(a)		(b)	
Compound	S_2H	S_2D	S_2H	S_2D
(37)	≠		60	40
(38)	≠		58	42
(41)	60	40	64	36
(42)	57	43	68	32
(45)	44	56	40	60
(48)	49	51	71	29
(49)	65	35	52	48

≠ The M - $S_2H\cdot$ regions in the conventional spectra of these compounds are complicated by the presence of other ions; accurate measurement of the daughter ion abundances was not possible.

ion $C_{10}H_{11}$ (m/e 131) in the spectrum of (46) might be the cyclopropyl tropylium ion (u). This ion can eliminate C_3H_4 to give the tropylium cation e, as is observed in the spectrum of (46) (Fig. 11). By analogy with the formation of tropylium species in the spectra of toluene derivatives, it might be expected that the molecular ion of the isomer of (46), 2-(p-tolyl)-1,3-dithiolane (75), would produce u also.



u, *m/e* 131   *e*, *m/e* 91

However, no M − S_2H• ion is observed in the spectrum of (75), and this suggests that the structure of $C_{10}H_{11}^+$ may not be *u*. A discussion of the properties of $C_{10}H_{11}^+$, and of those of the M − S_2H• ions in the spectra of (35), (39), and (43) is given in the following section.

3.2.3. Scrambling in the M − S_2H• ions.

Carbon and hydrogen scrambling processes are well known in both odd and even electron species derived from aliphatic and aromatic systems. In particular, it has been shown by ^2H and ^{13}C labelling that carbon and hydrogen scrambling precede the decomposition of the cations $C_4H_9^+$,[67,68] $C_7H_7^+$,[75,90] and $C_{13}H_{11}^+$ (Chapter 1, above), while ^2H labelling shows that hydrogen scrambling precedes or accompanies the decomposition of the cations $C_6H_5^+$,[69] $C_8H_9^+$,[132] and $C_{13}H_9^+$.[92] It was of interest, therefore, to investigate the properties of the cations formed by the elimination of $S_2H\cdot$ from the molecular ions of the dithianes (35), (39), (43), and (46), with particular regard to carbon and hydrogen scrambling.

The molecular ions of 1,3-dithiane (35) and the two methyl derivatives (39) and (43) eliminate $S_2H\cdot$ to form the ions $C_4H_7^+$ (m/e 55, Fig. 8) $C_5H_9^+$ (m/e 59, Fig. 9) and $C_6H_{11}^+$ (m/e 83) respectively. These ions decompose further in the first field-free region, eliminating the elements of acetylene (from $C_4H_7^+$) or ethylene (from $C_5H_9^+$ and $C_6H_{11}^+$) to form the ions $C_2H_5^+$ (m/e 29), $C_3H_5^+$ (m/e 41), and $C_4H_7^+$ (m/e 55) respectively. These processes are depicted in Scheme 11. The compositions of the neutral species eliminated from the

					E/E_o	m^*
(35)	$\xrightarrow[-S_2H\cdot]{-e}$	$C_4H_7^+$ m/e 55	$\xrightarrow{-C_2H_2}$	$C_2H_5^+$ m/e 29	.5273	15.3
(39)	$\xrightarrow[-S_2H\cdot]{-e}$	$C_5H_9^+$ m/e 69	$\xrightarrow{-C_2H_4}$	$C_3H_5^+$ m/e 41	.5942	24.4
(43)	$\xrightarrow[-S_2H\cdot]{-e}$	$C_6H_{11}^+$ m/e 83	$\xrightarrow{-C_2H_4}$	$C_4H_7^+$ m/e 55	.6627	36.4

Scheme 11.

Metastable decompositions of the $(M - S_2H\cdot)$ ions in the spectra of (35), (39), and (43) (e.g. for $C_4H_7^+$, $E/E_o = 29/55$, $m^* = 29^2/55$)

$(M - S_2H\cdot)$ ions in the spectra of (35), (39), (43), and the deuterium labelled compounds (36), (40), and (44) have been determined from the abundances of the appropriate defocused metastable ions and these values are recorded in Table 13. The observed distribution of the various

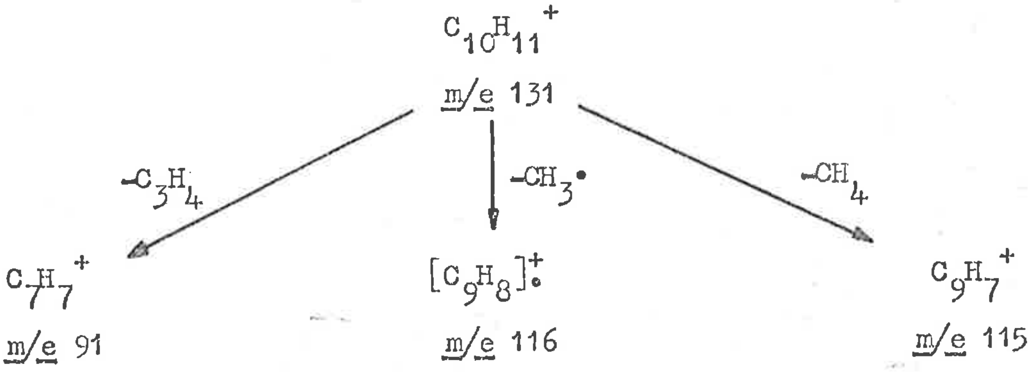
Table 13.

Compositions of the neutral species eliminated from the $(M - S_2H\cdot)$ ions in the spectra of (35), (36), (39), (40), (43), and (44), measured by the abundances of the defocused metastable ions.

Compound	Ion	Process							
		Observed				Calculated for Randomisation			
		C_2H_2	C_2HD			C_2H_2	C_2HD		
(35)	$C_4H_7^+$	100				100			
(36)	$C_4H_6D^+$	68	32			71	29		
		C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3
(39)	$C_5H_9^+$	100				100			
(40)	$C_5H_6D_3^+$	18	46	31	5	12	48	36	5
(43)	$C_6H_{11}^+$	100				100			
(44)	$C_6H_8D_3^+$	26	42	28	4	21	51	25	3

labelled species is very close in all cases to the distribution expected for random loss of hydrogen and deuterium. These results show that the low energy $(M - S_2H\cdot)$ ions which decompose in the first field-free region of the mass spectrometer have undergone almost complete hydrogen scrambling prior to or during further decomposition.

The cation $C_{10}H_{11}^+$ (m/e 131) has been found to arise by the elimination of $S_2H\bullet$ from the molecular ion of 2-phenyl-1,3-dithiane (46), via one or more non-random pathways (see 3.2.2., above), and this ion may have the cyclopropyl tropylium structure u. The three main decompositions of $C_{10}H_{11}^+$, viz. the losses of C_3H_4, $CH_3\bullet$, and CH_4, are shown in Scheme 12. These decompositions in the spectra of (47) and (50) have



E/E_o	.6946	E/E_o	.8855	E/E_o	.8778
m_1^*	63.2	m_2^*	102.7	m_3^*	100.9

Scheme 12.

Metastable ions for the decompositions of m/e 131.

been examined in the first field-free region, and the defocusing evidence is summarised in Table 14. The results show that all the hydrogen atoms in $C_{10}H_{11}^+$ are completely scrambled prior to or during the eliminations of C_3H_4 and $CH_3\bullet$.≠ Since the formation of $C_{10}H_{11}^+$ appears to proceed

---

≠ The calculation for the loss of $CH_3\bullet$ is complicated by the simultaneous loss of CH_4 (Scheme 11, $m_3^* : m_2^* = 23 : 77$). The values recorded in Table 2 are corrected for this process, which is assumed to proceed with hydrogen scrambling.

Table 14.

Compositions of the species $C_3H_nD_{4-n}$ and $CH_nD_{3-n}^{\bullet}$ eliminated from the $(M - S_2H\bullet)$ ions in the spectra of (47) and/or (50), at 70 eV.

Compound		CH_3	CH_2D	C_3H_4	C_3H_3D	$C_3H_2D_2$	C_3HD_3
(47)	Obs.	69	31	63	27	-	-
	Calc.	73	27	63	27		
(50)	Obs.	-	-	23	48	24	5
	Calc.			21	51	25	3

without scrambling (see 3.2.2., above), the randomisation observed in $C_{10}H_{11}^+$ occurs mainly after the elimination of $S_2H\bullet$ from the molecular ion of (46). Hence, the behaviour of the ion $C_{10}H_{11}^+$ with respect to hydrogen scrambling parallels that of the $M - S_2H\bullet$ ions derived from (35), (39), and (43).

Examination of the appropriate metastable ions in the spectrum of the ^{13}C-labelled compound (51) shows that the losses of $CH_3\bullet$ and C_3H_4 from $C_{10}H_{11}^+$ also occur with complete carbon scrambling. The metastable ions for the appropriate processes in the spectrum of (51) are tabulated in Table 15. The defocused metastable spectrum does not resolve m/e 62.8 and 63.2 at the correct E/E_0 values, but the ratio of the relative abundances of (m/e 62.8 + 63.2) and m/e 64.1 is found to be 59 : 41 (value calculated for random loss of carbon = 65 : 35). The metastable ions formed in the second field-free region were also examined. The

Table 15.

m/e values of the metastable ions for the elimination of $^{13}C_nC_{3-n}H_4$ (n = 0,1) from the (M - $S_2H\cdot$) ions in the spectrum of (51).

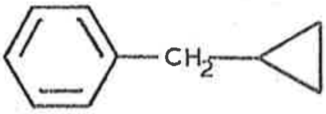
Process	m*
$^{13}CC_9H_{11}^+ - {}^{13}CC_2H_4$	62.8
$C_{10}H_{11}^+ - C_3H_4$	63.2
$^{13}CC_9H_{11}^+ - C_3H_4$	64.1

oscilloscope trace of the relevant region of the conventional mass spectrum of (51) (resolution 8000) is reproduced in Fig. 16, and clearly shows the presence of the three appropriate metastable ions.

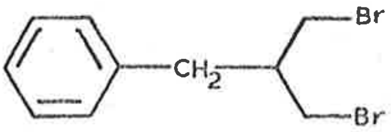
The defocused metastable ions for the processes $^{13}CC_9H_{11}^+ - CH_3\cdot$ and $^{13}CC_9H_{11}^+ - ({}^{13}CH_3\cdot + CH_4)$ are well resolved and occur in the ratio 67 : 33. After the known loss of CH_4 (see Footnote, p.96) is subtracted from the latter value, the ratio of the abundances of $({}^{13}CC_9H_{11}^+ - CH_3\cdot)$ and $({}^{13}CC_9H_{11}^+ - {}^{13}CH_3\cdot)$ is 84 : 16 (value calculated for random loss of carbon = 90 : 10.

It seems, therefore, that within the limitations imposed by the particular processes studied, and within experimental error, the carbon atoms in the $C_{10}H_{11}^+$ ion have randomised prior to further decomposition of the cation. This casts even more doubt on the possible intermediacy of the cyclopropyl tropylium ion. An intermediate of this nature would explain the fragmentation observed in $C_{10}H_{11}^+$ (i.e. loss of C_3H_4), but not the scrambling processes.

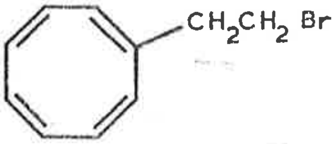
The molecular ion of benzylcyclopropane (85) fragments predominantly by the facile elimination of $C_3H_5\cdot$, to form the tropylium ion $C_7H_7^+$ with very little of the cation $C_{10}H_{11}^+$ (M - H•) being produced.



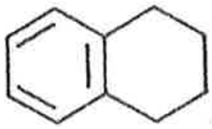
(85)



(86)



(87)



(88)

C_6H_5-CH=CH-CH$(CH_3)_2$

(89)

C_6D_5-CH=CH-CH$(CH_3)_2$

(90)

Therefore it was not possible to examine the properties of the benzyl cyclopropyl cation, which might be expected to isomerise to u. In view of this, it is of interest that the ion $C_{10}H_{11}^+$ is produced in the spectra of (86)-(89) (by the respective processes M - Br• - HBr, M - Br•, M - H•, and M - $CH_3\cdot$) and in the spectra of the isomeric dimethylindans[133] (by the process M - $CH_3\cdot$). The metastable characteristics of the various $C_{10}H_{11}^+$ ions formed in the spectra of (46) and (86)-(89) were compared by measuring the parameter m_1^*/m_2^* (see Scheme 12), and the values obtained are recorded in Table 16. The results indicate that the

Table 16.

Values of the parameter m_1^*/m_2^* for decomposition of $C_{10}H_{11}^+$ (Scheme 12), in the spectra of (46), and (86)-(89).

	(46)	(86)	(87)	(88)	(89)
m_1^*/m_2^* (70 eV)	1.92	2.00	1.88	1.95	2.05
m_1^*/m_2^* (25 eV)	1.85	1.73	1.70	1.75	1.58

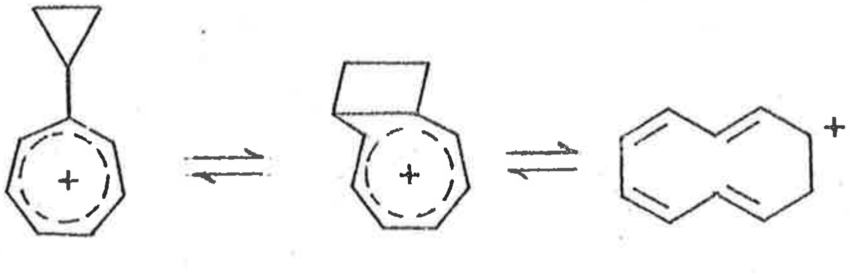
$C_{10}H_{11}^+$ ion formed in the spectrum of 2-phenyl-1,3-dithiane (46) has the same structural and energetic properties as the $C_{10}H_{11}^+$ ions produced in the spectra of (86)-(89). If this is the case, then these ions should all undergo complete scrambling prior to or during the elimination of $CH_3\cdot$ and C_3H_4. This is confirmed in the spectrum of trans-3-methyl-1-(d_5-phenyl)-but-1-ene (90). The molecular ion of (90) loses a methyl radical (without scrambling) to produce the cation $C_{10}H_6D_5^+$ (m/e 136). The ratios of the defocused metastable ion for the losses of the various $CH_3\cdot$ and C_3H_4 species from m/e 136 are tabulated below (Table 17). The agreement between the observed and calculated values in the table is excellent. Hence, there is good evidence for the existence in the spectra of (46) and (86)-(89) of a common ion $C_{10}H_{11}^+$, which is completely scrambled with respect to both carbon and hydrogen. The

Table 17.

Compositions of the $CH_nD_{3-n}\cdot$ and $C_3H_nD_{4-n}$ species eliminated from the $(M - CH_3\cdot)$ ion (m/e 136) in the spectrum of (90) at 70 eV, measured by the abundances of the defocused metastable ions.

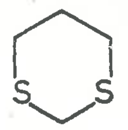
	CH_3	CH_2D	CHD_2	CD_3	
Obs.	14	46	35	5	
Calc.	12	46	36	6	
	C_3H_4	C_3H_3D	$C_3H_2D_2$	C_3HD_3	C_3D_4
Obs.	6	33	41	17	3
Calc.	5	30	45	18	2

structure of this ion is unknown, but the intervention of structures such as u - w may occur, in which the intermediacy of the substituted homotropylium ion v is involved. A structure of this nature would enable the carbon and hydrogen atoms to scramble through a series of expansion and contraction cycles (v ⇌ w), together with simultaneous hydrogen migrations.



u v w

In summary, the positive-ion mass spectra of 1,3-dithianes show a number of specific cleavage reactions which do not involve any hydrogen randomisation. The pathways of the rearrangement processes M - SH• and M - S_2H• (the latter of which is characteristic of 1,3-dithianes) are more complex, and each appears to occur by at least two mechanisms. The ions produced by the process M - S_2H• in the spectra of the parent compound (35), the two methyl derivatives (39) and (43), and the phenyl derivative (46) all undergo complete hydrogen scrambling before subsequent decomposition. In particular, the ion $C_{10}H_{11}^+$ from (46) scrambles both carbon and hydrogen, and this ion is common to the spectra of a number of other compounds. The structure of $C_{10}H_{11}^+$ is unknown, but it may correspond to a substituted homotropylium ion.



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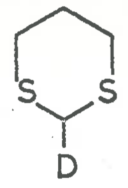
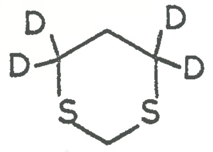


(36)



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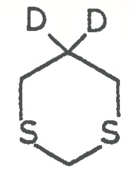

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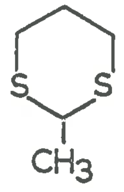

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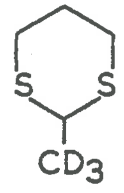

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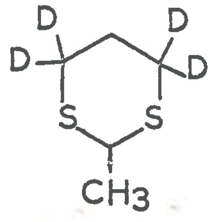

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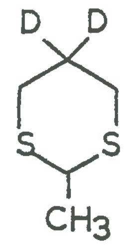

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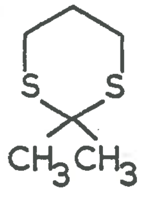

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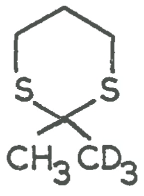

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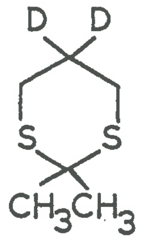

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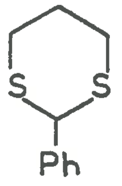

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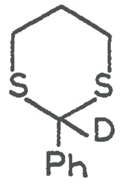

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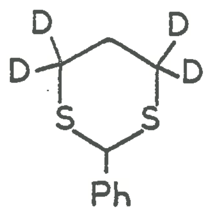

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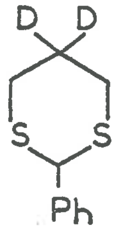

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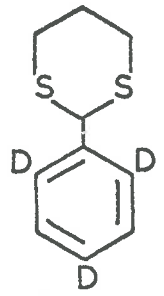

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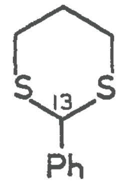

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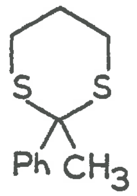

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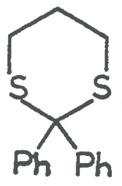

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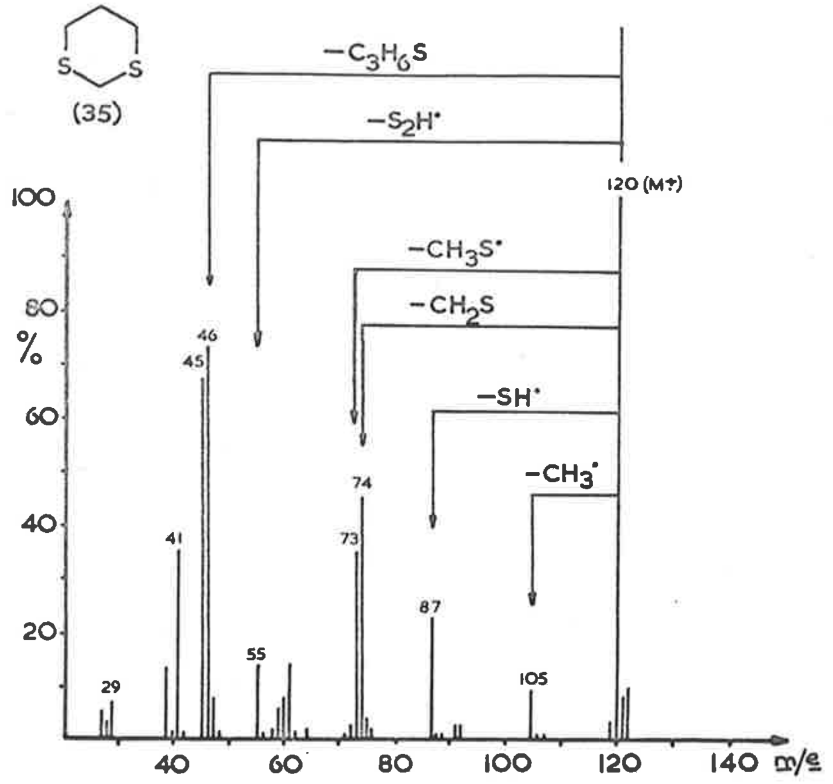

S S
(35)
$-C_3H_6S$
$-S_2H^\cdot$
120 (M+)
$-CH_3S^\cdot$
$-CH_2S$
$-SH^\cdot$
$-CH_3^\cdot$
100
80
%
60
40
20
29
41
45
46
55
73
74
87
105
40
60
80
100
120
140
m/e

FIG. 8

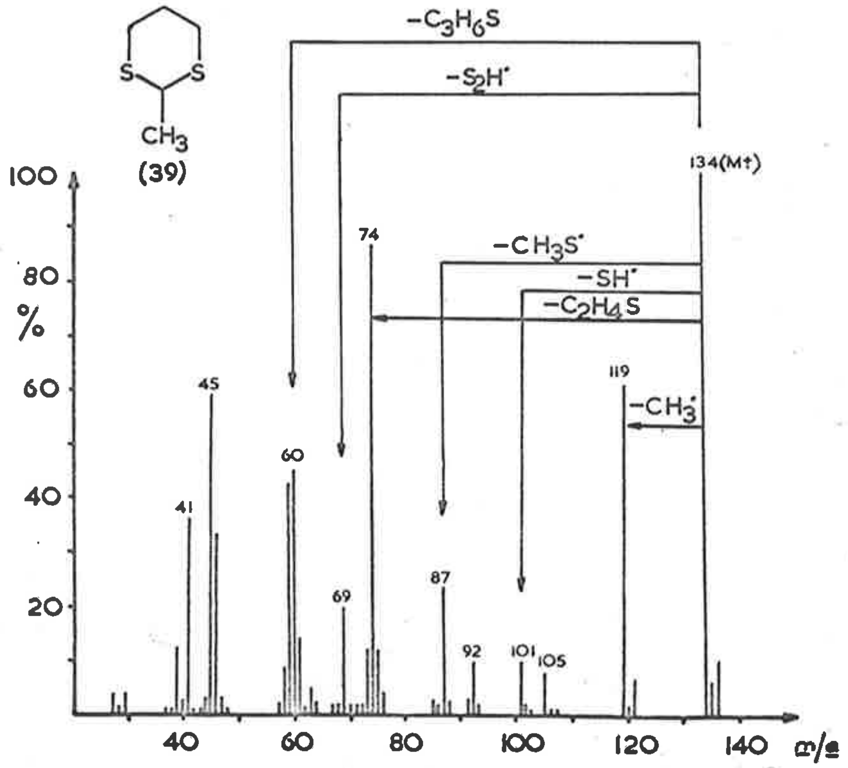

S S
CH_3
(39)
$-C_3H_6S$
$-S_2H^\cdot$
134(M+)
100
80
%
60
40
20
74
$-CH_3S^\cdot$
$-SH^\cdot$
$-C_2H_4S$
119
$-CH_3^\cdot$
45
60
41
69
87
92
101
105
40
60
80
100
120
140
m/e

FIG. 9

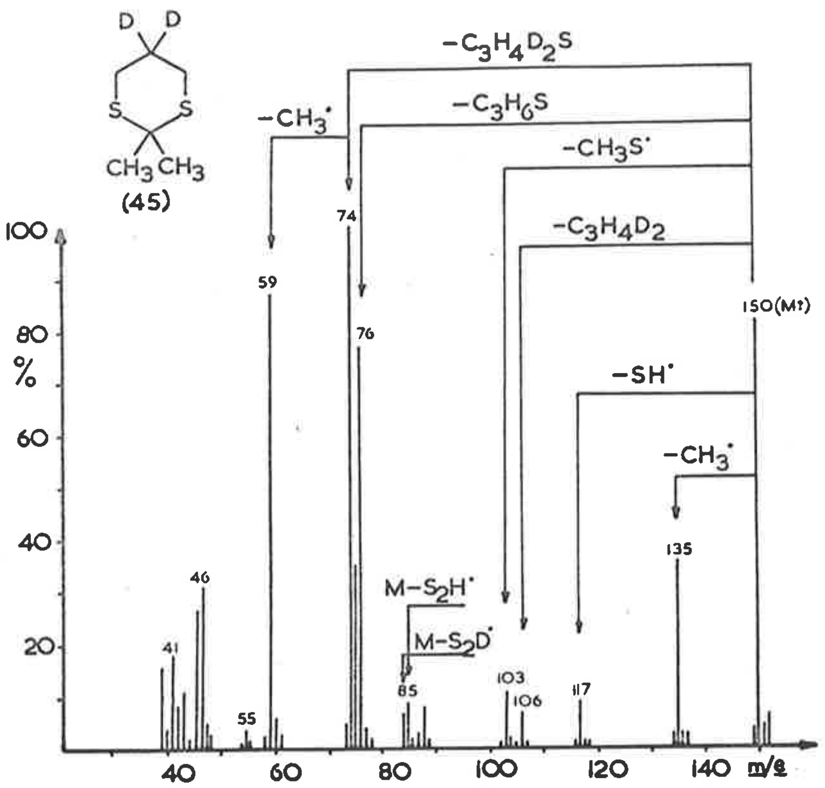

D D
S S
CH3 CH3
(45)
−C3H4D2S
−C3H6S
−CH3•
−CH3S•
−C3H4D2
74
59
76
150(M+)
−SH•
−CH3•
135
M−S2H•
M−S2D•
46
41
55
85
103
106
117
100
80
%
60
40
20
40
60
80
100
120
140
m/e

FIG. 10

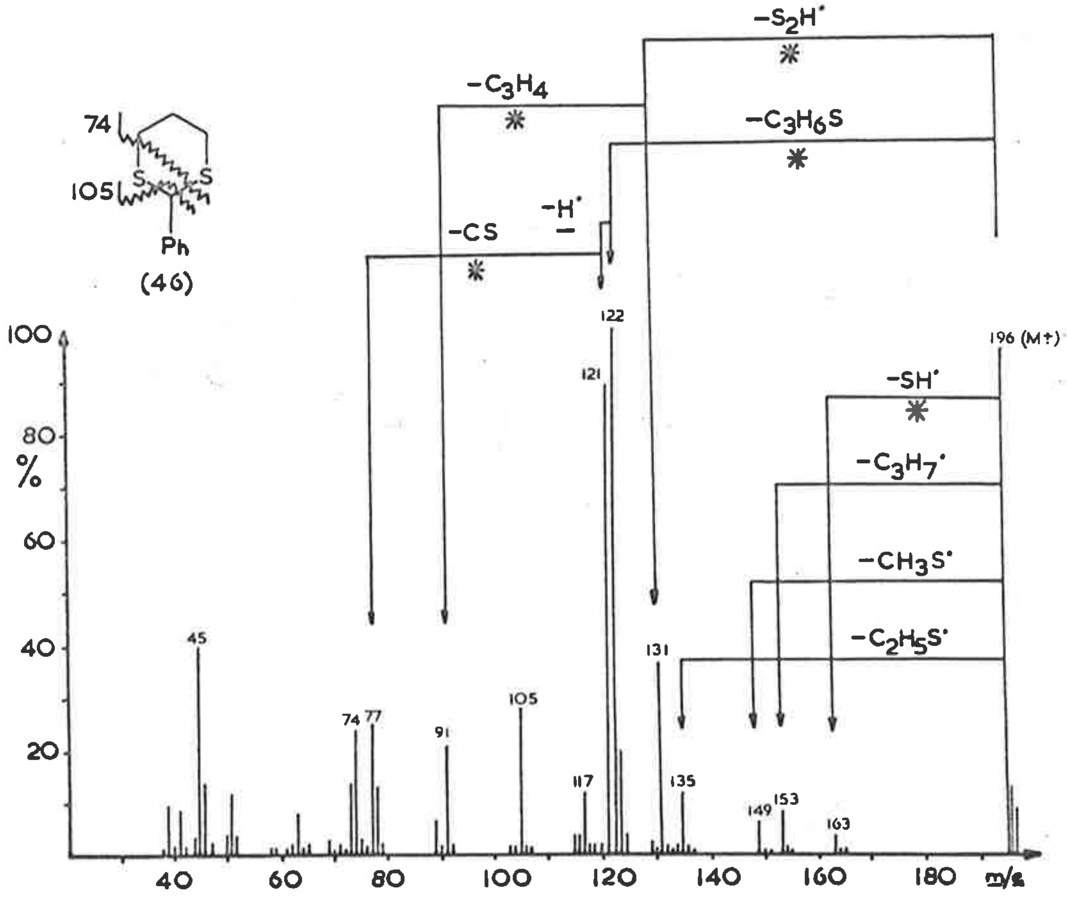

−S2H•
−C3H4
−C3H6S
−H•
−CS
74
105
S S
Ph
(46)
122
121
196 (M+)
−SH•
−C3H7•
−CH3S•
−C2H5S•
131
45
74 77
91
105
117
135
149
153
163
100
80
%
60
40
20
40
60
80
100
120
140
160
180
m/e

FIG. 11

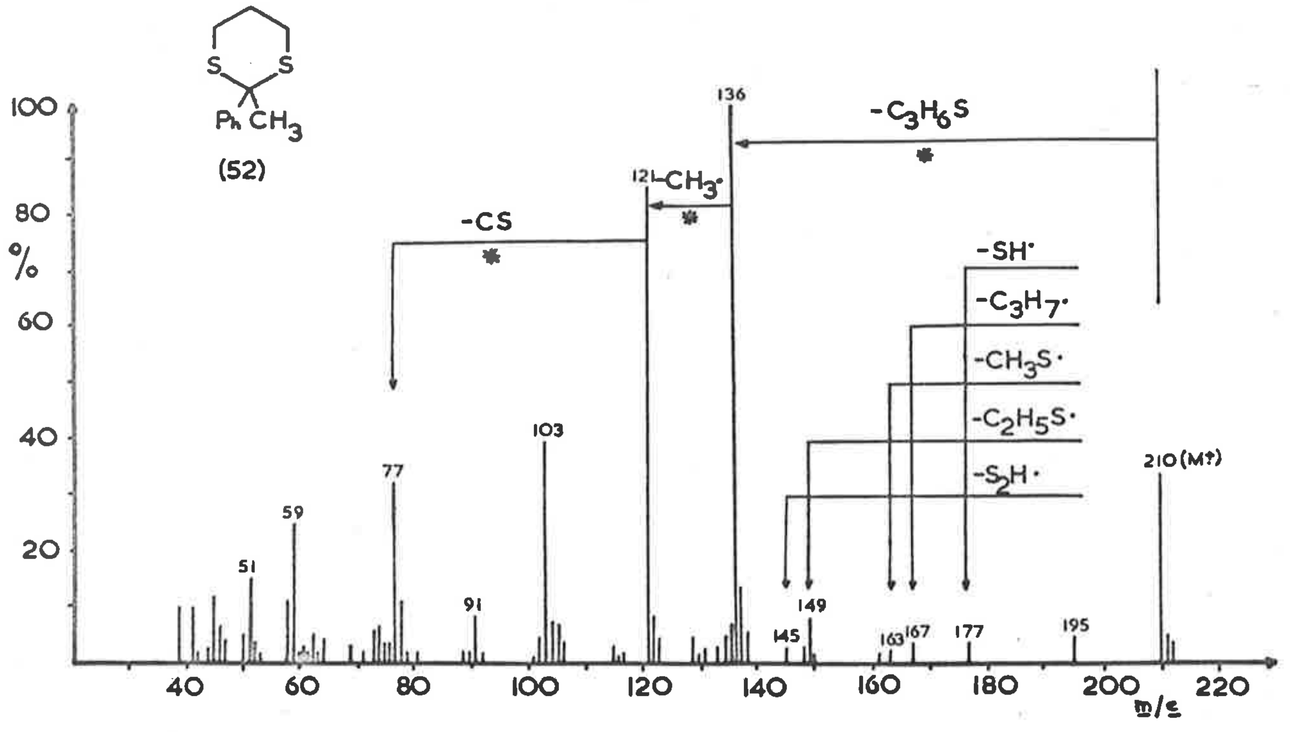

S
S
Ph
CH3
(52)
100
80
%
60
40
20
136
-C3H6S
121
-CH3·
-CS
-SH·
-C3H7·
-CH3S·
-C2H5S·
-S2H·
210(M+)
103
77
59
51
91
149
145
163
167
177
195
40
60
80
100
120
140
160
180
200
220
m/e

FIG. 12

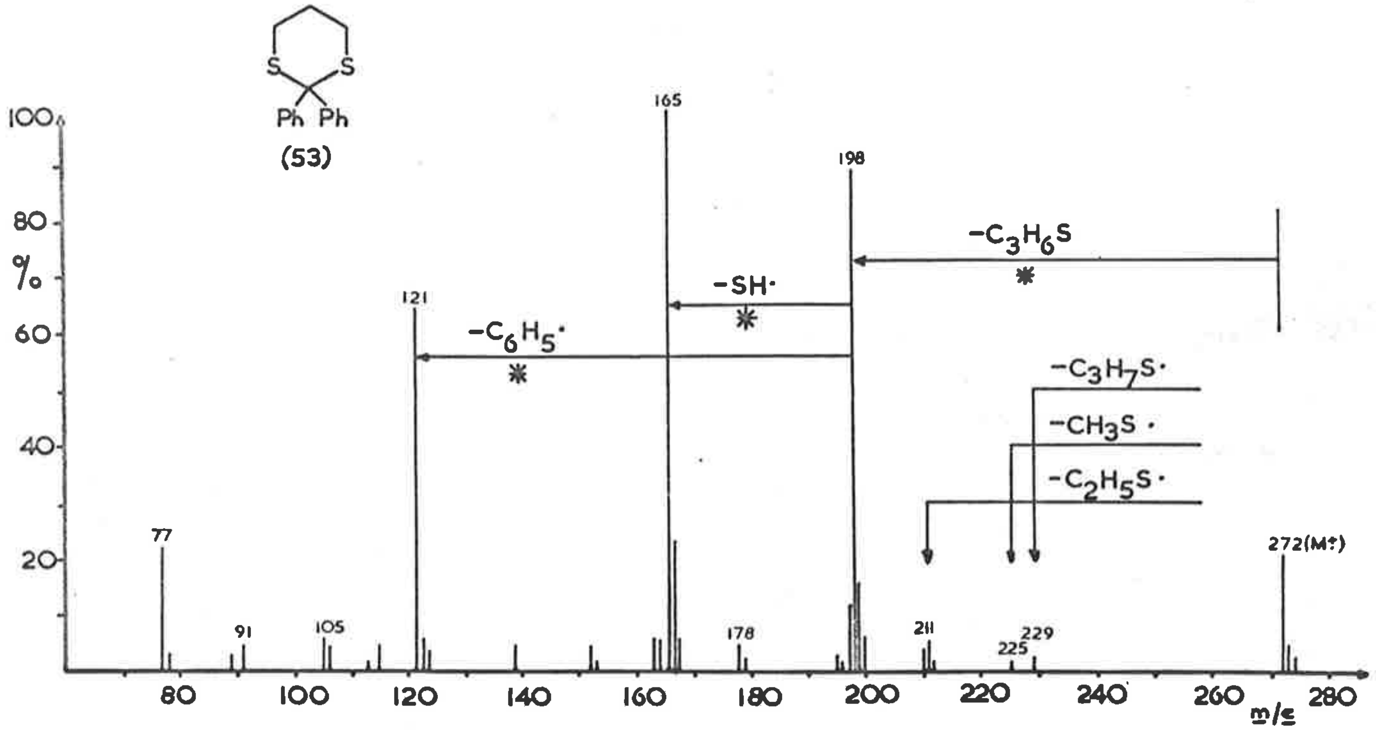

S
S
Ph
Ph
(53)
100
80
%
60
40
20
165
198
121
-C3H6S
-SH·
-C6H5·
-C3H7S·
-CH3S·
-C2H5S·
272(M+)
77
91
105
178
211
225
229
80
100
120
140
160
180
200
220
240
260
280
m/e

FIG. 13

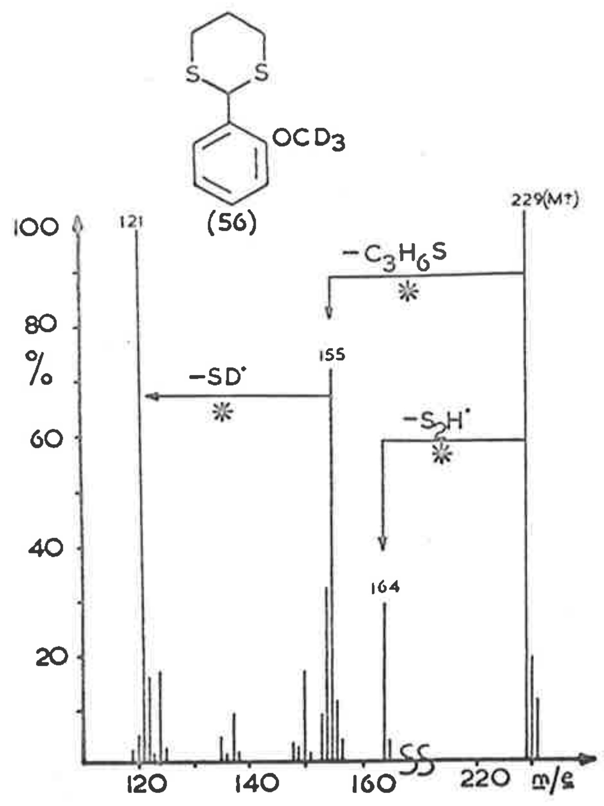


FIG. 14

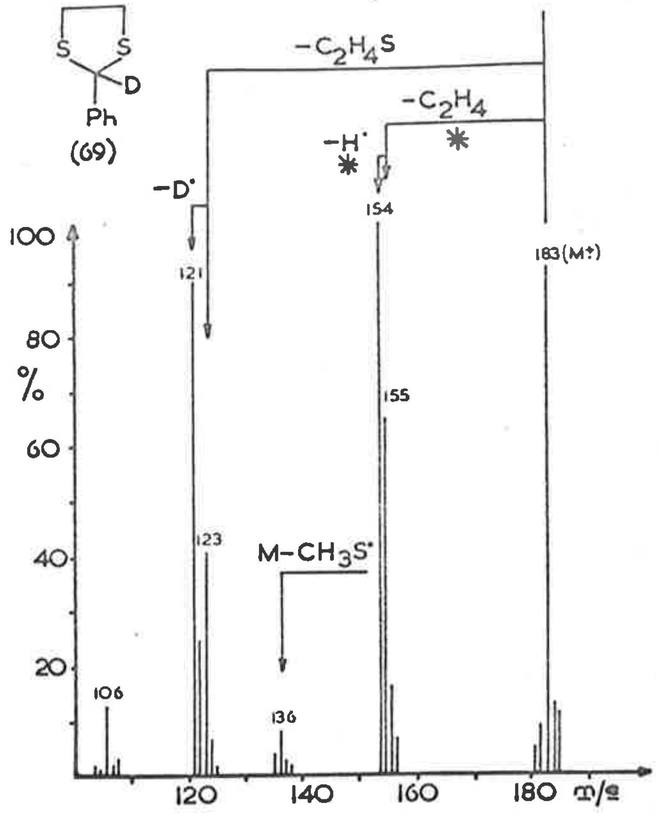
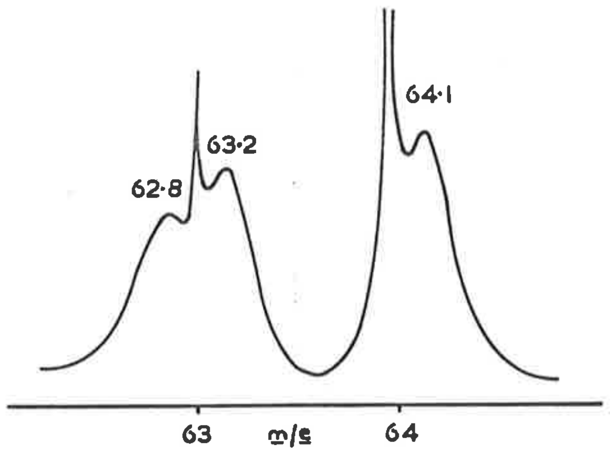


FIG. 15



METASTABLE IONS IN THE SPECTRUM OF (51)

FIG. 16

Chapter 4. The Negative-Ion Mass Spectra of 1,3-Dithianes and Related Compounds.

4.1 Introduction.

The existence of negative ions in the mass spectrometer has been recognised for many years,[134] and gas phase negative ions have found application in a number of areas.[135] For example, negative ions play an important role in the physics of the ionosphere, and they have been used to enhance the effective potential of ion accelerators. Negative ions allow the accurate measurement of isotopic abundances, and have also been shown to be important intermediates in the chemistry of polymerisation (and other) reactions. The possibility of applying negative-ion spectrometry to molecular structure determination has been discussed in detail by Melton,[83,135] and in particular, he has pointed out that rearrangement reactions should be rare in negative-ion spectra.[83] These spectra should therefore be particularly advantageous when the corresponding positive-ion spectra are complicated by rearrangement fragments.

Nevertheless, negative-ion mass spectrometry[136-8] has not been generally accepted as an analytical method for several reasons. The yield of negative ions upon electron impact is very low (often 1000 times less than that for positive ions), and the spectra are frequently found to be dependent on both the energy of the ionising beam and the pressure. This is a result of the variety of processes involved in the formation of negative ions, viz. electron capture (4.1), dissociative charge transfer (4.2), and ion-pair production (4.3), each of which is energy (and pressure) dependent. Furthermore, ions produced by ion-molecule reactions commonly occur at relatively high pressures in the

$$e + AB \rightarrow AB^{\overset{-}{\bullet}} \qquad (4.1)$$

$$AB^{\overset{-}{\bullet}} \rightarrow A^{-} + B\bullet \qquad (4.2)$$

$$AB^{\overset{-}{\bullet}} \rightarrow A^{+} + B^{-} + e \qquad (4.3)$$

mass spectrometer. As a consequence of these factors, negative-ion spectra are generally non-reproducible.

The simple electron capture process (4.1) is usually endothermic by approximately 2 eV.[78] The molecular anion must therefore retain all the electron energy as internal energy and unless it can stabilise the excess energy, either dissociative charge transfer (4.2) or ion-pair production (4.3) takes place, and no molecular anion is recorded. Similarly, the highly energetic nature of negative-ions reduces the efficiency of their collection by the mass spectrometer. These factors make desirable the use of ionising beams of very low energy, but these are difficult to maintain under the usual conditions in the source. Ion molecule reactions tend to predominate at relatively high pressures, and the resulting negative-ion spectrum is then complicated by ions which may bear no direct relation to the structure of the intact molecule. Despite the difficulties inherent in the mass spectrometric investigation of negative-ions, recent advances have been made in the field, in particular with respect to the study of the behaviour of organic compounds upon electron capture.

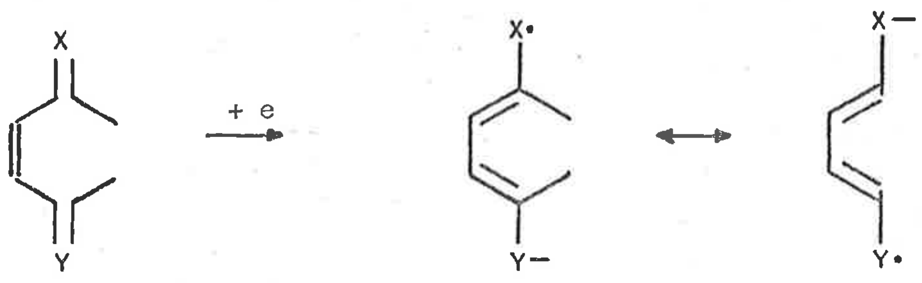
The large decrease in sensitivity in the production of negative ion compared with positive ions is largely related to the type of molecule under investigation. Not all molecules have a high affinity for accepting an electron, and those organic compounds with a high electron affinity will tend to capture an electron more efficiently. Consequently, it has been demonstrated[5,78] that some classes of compound give useful negative-ion spectra containing molecular anions, at normal pressures and ionising voltages (i.e. 10^{-7} Torr, and 70 eV). For example, polynitroaromatic compounds readily form negative ions in the mass spectrometer and the spectra obtained provide much structural information.[139] Aromatic azoxy-compounds, nitrones, and N-oxides, the positive-ion spectra of which[140-142] often undergo skeletal rearrangements involving C-O bond formation, also give negative-ion spectra in which only simple cleavages are observed.[143] Similarly, reproducible negative-ion spectra are obtained for many sulphur-containing compounds, including S-alkylthioglycollic acids,[144] β-thioketothiolesters,[145] and sulphonylanilines.[146] The positive-ion spectra[26] of these compounds all contain skeletal rearrangement fragments, whereas only simple cleavages (or cleavages with hydrogen rearrangement) are observed in the negative-ion spectra. For example, the molecular cation[26] of *m*-methoxysulphonyl-

$$[\underline{m}\text{-}CH_3O\ C_6H_5NSO]^{\underset{\bullet}{+}} \longrightarrow CO + [C_5H_5NS]^{\underset{\circ}{+}} \qquad (4.4)$$

$$[\underline{m}\text{-}CH_3O\ C_6H_4NSO]^{\underset{\circ}{-}} \longrightarrow M^{\dot{-}}\ ,\ [M - CH_3\bullet]^{-},\ [M - OCH_3\bullet]^{-},\ [M - SO]^{-} \qquad (4.5)$$

aniline undergoes the rearrangement process M - CO (4.4), but the corresponding molecular anion[146] exhibits only cleavage processes (4.5). Molecular anions have also been observed for fluoro-substituted compounds,[147,148] while skeletal-rearrangement processes have been reported[147] in the cases of perfluoro-3-heptanone and perfluoro-2-butyltetrahydrofuran. Furthermore, hydrogen scrambling in the (M - C_6H_5•) ion in the spectrum of triphenylsilane has been described in a recent report.[149]

More recent studies of substituted quinones[150,151] and anhydrides,[152] have demonstrated that reproducible negative-ion spectra may be obtained when a species a[≠] can accept an electron to yield a stabilised charged species, e.g. a → b.



a b c

In other words, the stability of the molecular anion may be due to the acceptance of the extra electron into an extended π system in the molecule, and further studies of the negative-ion spectra of esters,[150,151,153,154] ethers,[151] and variously substituted nitrobenzene derivatives[139,152-6] have lent support to this suggestion.

The work which is discussed in this chapter was prompted by the desire to study a system in which the acceptance of an electron into an

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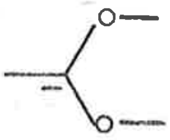
[≠] It should be noted that the anionic (and other) species denoted by the symbols a, b, etc. in this chapter bear no relation to those cationic (and other) species symbolised by similar notation in Chapters 1-3.

extended π system is unlikely, but which nevertheless might produce a stable molecular anion. Sulphur-containing compounds in general appear to give useful negative-ion spectra,[5,78] and substituted thioanisoles[157] in particular produce molecular anions. Furthermore, it is known in solution chemistry that, whereas the formation of a stable negatively charged acetal species (e.g. d) is difficult, a long-lived anionic thioacetal species (e.g. e) forms readily, the vacant d orbitals of the adjacent sulphur atoms stabilising the anionic centre (e.g. e ↔ e').[158]

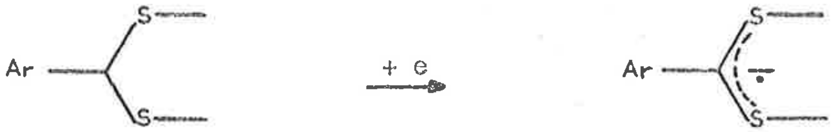


d

e

e'

Although this analogy is not strictly comparable with the formation of a molecular anion, it was nevertheless felt that a 1,3-dithio system would in general fulfil the above conditions, and the aryl dithioacetal system f was chosen in particular.

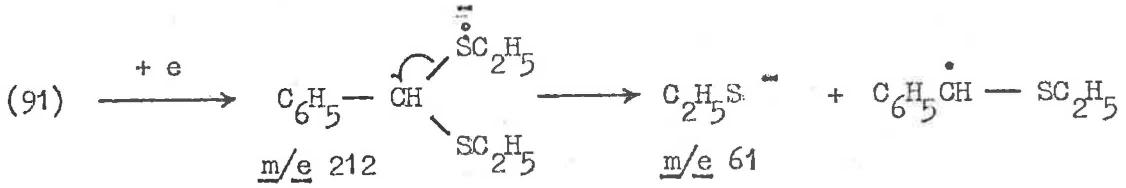


f

g

4.2 Results and Discussion.

For the negative-ion mode investigation, the di-ethylthioacetal (91) of benzaldehyde was chosen as a simple model for a 1,3-dithio-system. The negative-ion mass spectrum[≠] of (91) was measured (Fig. 17), and it shows a molecular anion (m/e 212) in small abundance, with a fragment ion at m/e 61, corresponding to the species $C_2H_5S^-$. This reaction proceeds presumably by the pathway outlined in Scheme 12, in which it is assumed that the extra electron in the molecular anion is localised on one of the sulphur atoms. Hence, the model system demonstrates the ability to produce a molecular anion.



Scheme 12.

This is supported by the behaviour towards electron capture of the di-ethylthioacetal (92) of p-nitrobenzaldehyde. The spectrum (Fig. 18) of this compound also shows a molecular anion (m/e 257), together with a simple fragmentation product h (Scheme 13). The ability of the nitro group to stabilise a molecular anion is well documented.[139,152-6] Aryl nitro anions in particular have been shown to have a sufficiently long lifetime ($\tau = 4 \times 10^{-5}$ sec.)[159] to be recorded in the mass

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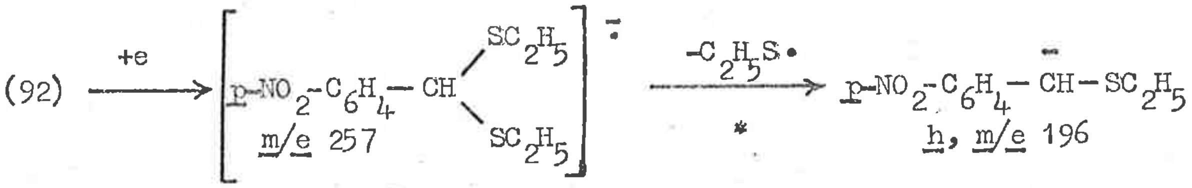
[≠] In this chapter, the term "mass spectrum" refers specifically to a negative-ion mass spectrum, unless otherwise indicated.

spectrometer before fragmentation ($\tau = 10^{-6}$ sec.), and to undergo metastable transitions ($\tau = 10^{-5}$ sec.). Consequently, it is not surprising that the molecular anion of (92) (m/e 257, Fig. 18) fragments to give the ethylthio-nitrobenzyl species h (m/e 196), which is presumably stabilised by the p-nitro substituent (Scheme 13). The process is substantiated by an appropriate metastable peak. It seems likely that the extra electron involved in the formation of the molecular anion is



Scheme 13.

localised on the nitro substituent, with the result that fragmentation to form the stabilised benzyl anion is favoured.

Having established a model system, the investigation was extended to the 2-aryl-1,3-dithiane system. The positive-ion spectra of this class of compounds contain examples of specific hydrogen rearrangements, skeletal rearrangement processes, and proximity effects (see Chapter 3). It was of interest to investigate the behaviour after electron capture of this class of compounds, in view of the fact that skeletal rearrangements observed in positive ion spectra are generally absent in the corresponding negative ion spectra.[5,78] The discussion below is based on the spectra of 2-phenyl-1,3-dithiane (46) (Fig. 19), the three nitrophenyl isomers (61)-(63) (Figs. 20-22), the three chlorophenyl isomers (64)-(66), and the labelled derivatives (47)-(51) and (93)-(100) (Fig. 20 and Appendix B). The molecular formulae of the compounds (46)-(51), (61)-(63), and (93)-(100) are illustrated on the following page, and also in a fold-out format at the end of this chapter, p.128. All fragmentations discussed below have been established by isotopic labelling and, where appropriate, metastable defocusing.

The spectra of the dithianes (46)-(51) were measured at 70 eV, using a source pressure of 1-2 x 10^{-7} Torr.≠ The spectra are relatively weak, and the molecular anions are sufficiently unstable that decomposition occurs only in the source, and no metastable ions are observed. Many additional peaks resulting from ion-molecule reactions are observed when the source pressure is increased to 3 x 10^{-6} Torr.

The spectrum of 2-phenyl-1,3-dithiane (46) (Fig. 19) shows a molecular anion in small abundance at m/e 196, and two fragment ions are observed at m/e 105 and m/e 122, corresponding to the processes M - C_7H_7• and M - C_3H_6S respectively. The spectra of the labelled compounds (47)-(51) show that these processes occur as indicated in Scheme 14. It is also apparent that both processes are preceded (or accompanied) by partial scrambling of the hydrogen atoms at C-2,4, and 6. The partial spectrum of the d_1-derivative (47) (Fig. 20) shows the processes M - C_3H_6S and M - C_3H_5DS (m/e 123 and 122, respectively) and

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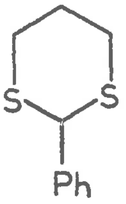
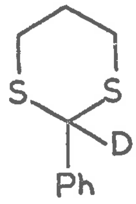
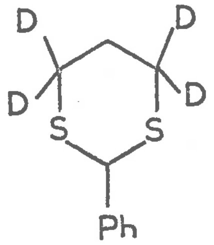
≠ It is of interest that 1,3-dithiane (35) does not give a spectrum under these conditions.



(46)



(47)



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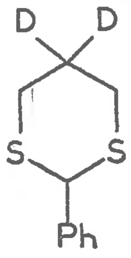

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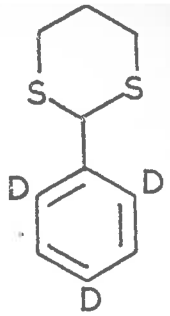

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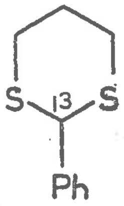

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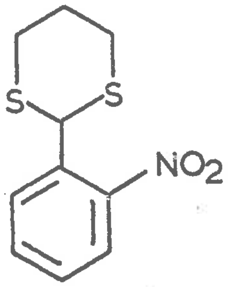

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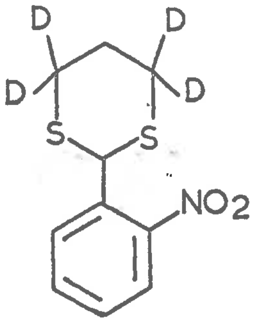

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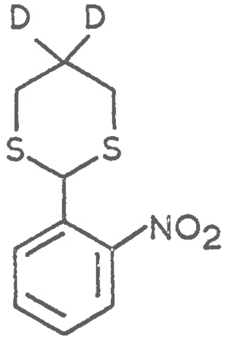

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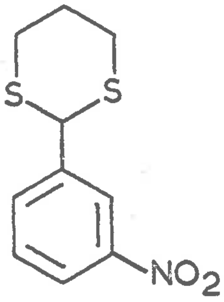

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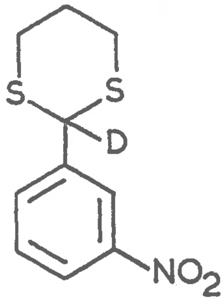

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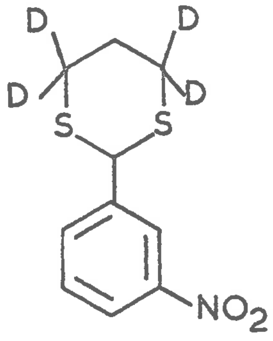

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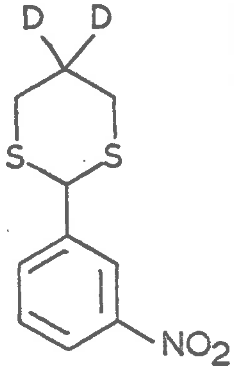

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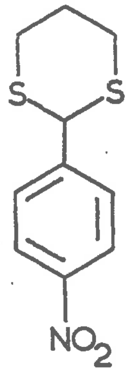
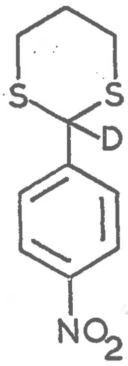
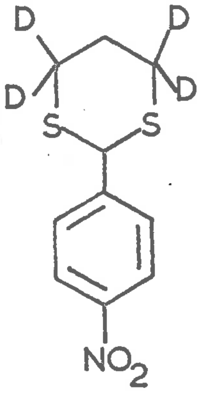


(63)



(98)



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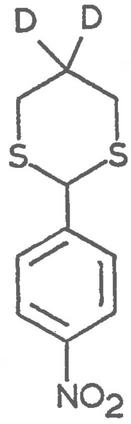
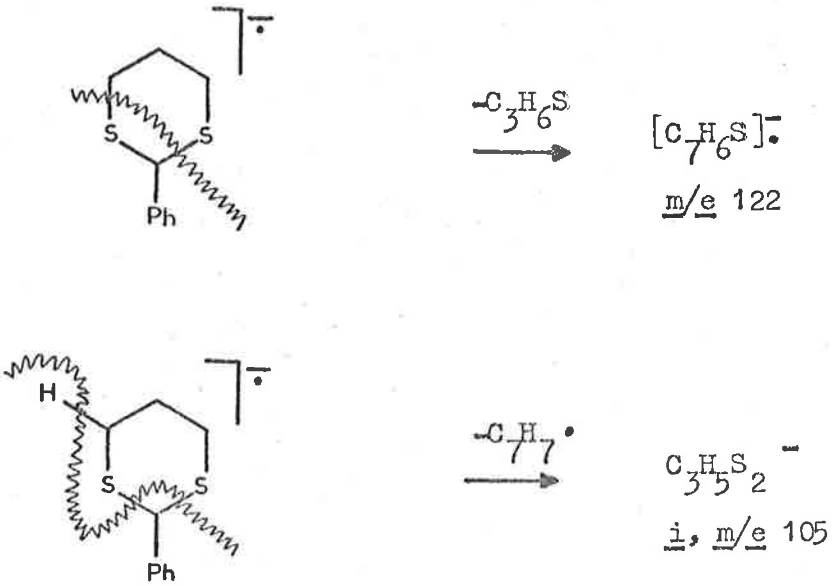


(100)



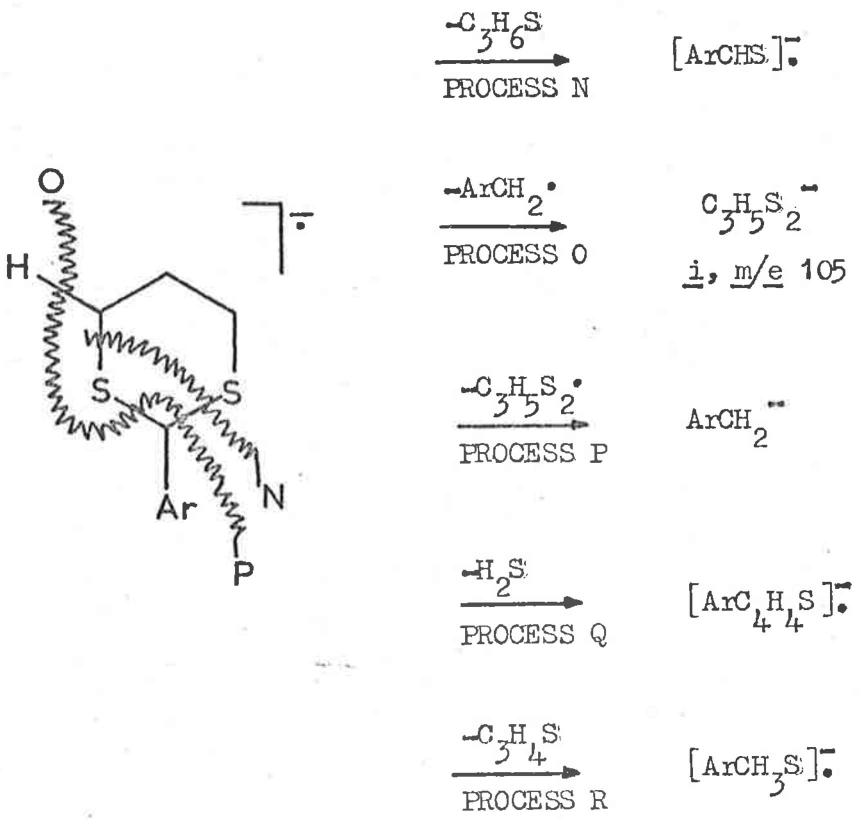
Scheme 14.

M - $C_7H_7{\cdot}$ and M - $C_7H_6D{\cdot}$ (m/e 106 and 105, respectively). This can only be the result of a randomisation of the hydrogen atoms between C-2 and C-4,6. (This randomisation is discussed more fully below.) The incorporation of ^{13}C in the molecular anion of (51) is 60.1%, and the observed retentions in the (M - C_3H_6S) and (M - $C_7H_7{\cdot}$) ions in the spectrum of (51) are 58.1% and 0%, respectively. Therefore, no carbon scrambling accompanies the observed hydrogen scrambling. Analogous ions at m/e 105 and 122 are formed in the positive-ion spectrum of (46), but those processes occur without hydrogen scrambling (see Chapter 3).

A careful study of the hydrogen rearrangement processes in the spectra of dithianes requires an intense spectrum containing metastable ions. It was considered that the introduction of an electron-withdrawing substituent on the phenyl ring would, by increasing the electron affinity of the molecule, yield more abundant molecular anions of longer lifetimes, capable of undergoing metastable transitions. The two substituents Cl and NO_2 were chosen for this purpose.

It was found that although spectra were obtained for the three isomeric chloro derivatives (64)-(66) the spectra were weak and devoid of metastable ions. No variation with substitution was observed, and each spectrum was similar to that of 2-phenyl-1,3-dithiane (46) itself. On the other hand, the spectra of the nitro derivatives (61)-(63) contain, in addition to the basic fragmentations outlined in Scheme 14, fragment ions which are characteristic of the particular substitution pattern. Consequently, the three isomers can be readily differentiated. The spectra of (61)-(63) are reproduced in Figs. 21-23, while those of the deuterium labelled derivatives (94)-(100) are recorded in Appendix B.

The fragmentations observed in the spectra of the 2-aryl-1,3-dithianes (46) and (61)-(63) are outlined in Scheme 15. (Only processes N and O are common to the spectra of all dithianes.) The spectra of all three nitrophenyl derivatives show ions at m/e 167 and 105, corresponding to the processes M - C_3H_6S and M - $C_7H_6NO_2^{\bullet}$ respectively (Processes N and O, Scheme 15) which are analogous to the fragmentations of 2-phenyl-1,3-dithiane (46) (see Scheme 14). These processes in the spectrum of the p-nitrophenyl isomer (63) are preceded by incomplete hydrogen scrambling similar to that observed in the spectrum of (46), but this phenomenon is not reflected in the spectra of the o- and m-nitrophenyl derivatives. A comparison of the scrambling processes in



Scheme 15.

(46) and (63) is made in Table 18 for the appropriate labelled compounds (47) and (48), and (98) and (99). The ratios of the fragment ions produced in the spectra of (47), (48), (98), and (99) (Table 18) show that complete scrambling has not occurred during the lifetime of the decomposing ion (i.e. up to 10^{-6} sec.). On the other hand, the same Process N in the spectra of (98) and (99), arising from the longer-lived metastable ions ($\sim 5 \times 10^{-5}$ sec.), occurs with almost complete randomisation of the hydrogen atoms on C-2,4, and 6. The hydrogen scrambling is likely to proceed with no reorganisation of the carbon

Table 18.

Hydrogen randomisation occurring during Processes N-Q (Scheme 15).

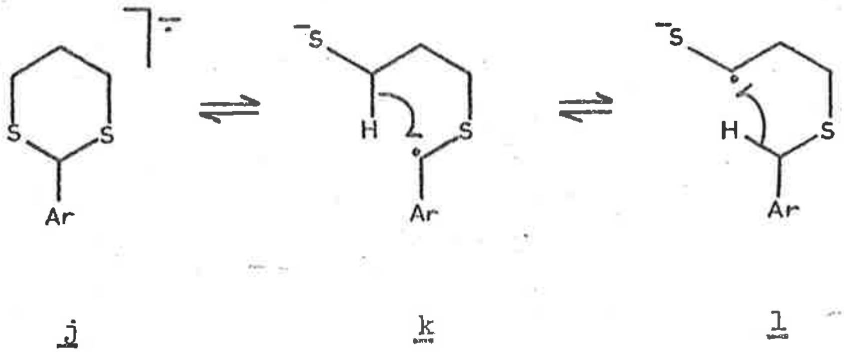
Compound	Process	m/e	Abundance Ratio		Calc.
			Fragment ions	m*	
(47)	N	122, 123	32 : 68	-	80 : 20
(48)	N	122, 123	74 : 26	-	20 : 80
(98)	N	167, 168	65 : 35	78 : 22	80 : 20
(99)	N	167, 168	45 : 55	26 : 74	20 : 80
(47)	O	105, 106	84 : 16	-	40 : 60
(48)	O	107, 108	15 : 85	-	60 : 40
(98)	O	105, 106	66 : 34	-	40 : 60
(99)	O	107, 108	37 : 63	-	60 : 40
(98)	P	136, 137	42 : 58	50 : 50≠	60 : 40
(99)	P	137, 138	65 : 35	50 : 50≠	40 : 60
(98)	Q	207, 208	45 : 55	42 : 58	40 : 60
(99)	Q	209, 210	60 : 40	57 : 43	60 : 40

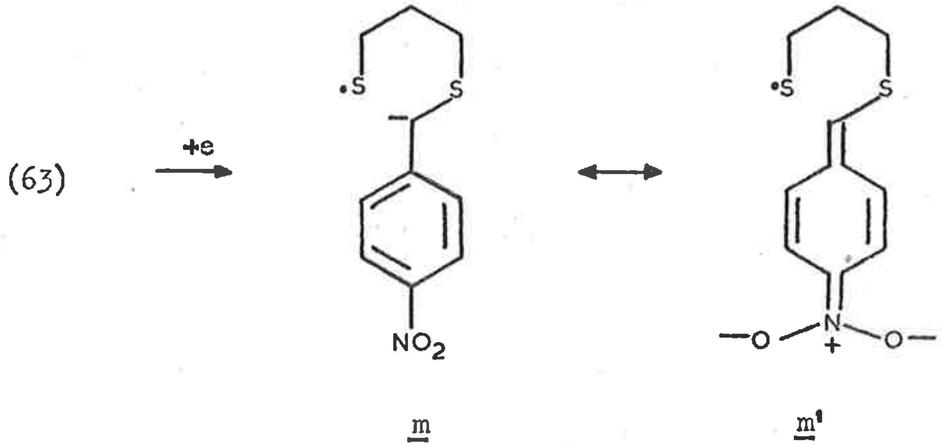
≠ The defocused metastables were weak, and this ratio is only correct to ± 10%.

skeleton, by analogy with the absence of carbon scrambling observed in the molecular anion of the ^{13}C labelled dithiane (51).

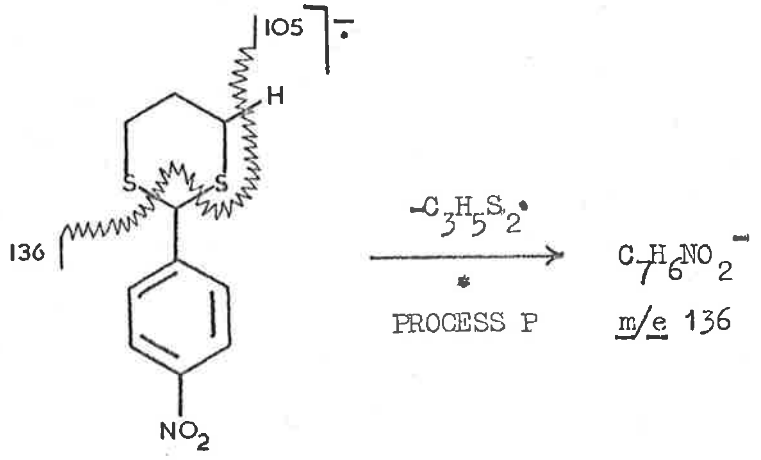
The following sequence (Scheme 16) is proposed to rationalise the hydrogen randomisation which occurs in the spectra of (46) and (97).

The initial cleavage of a C-S bond in the dithiane ring produces k, and a series of hydrogen transfers may proceed through six-membered transition states (e.g. k and l). This mechanism requires approximately six cycles (e.g. j → j) to attain a random distribution of the hydrogen atoms on C-2,4, and 6. The mode of ring opening depicted in k is based upon the fragmentations of the dithioacetals (91) and (92), each of which involves initial cleavage of the analogous C-S bond (see Schemes 12 and 13, above). The alternative formulation of k, with the radical and anion centres exchanged, is equally probable. Indeed, it may be that a ring opening (e.g. j ⇌ k) in the p-nitrophenyl derivative (63) would produce a species such as m (in which the benzylic anionic centre is stabilised by the nitro substituent) with a longer lifetime than might be expected in the absence of any stabilisation [e.g. in the molecular ion of the parent compound (46)]. Thus, the randomisation process would be able to proceed towards completion much further than that in the molecular anion of (46). In support of this suggestion is the fact that the degree of randomisation observed in the spectra of the





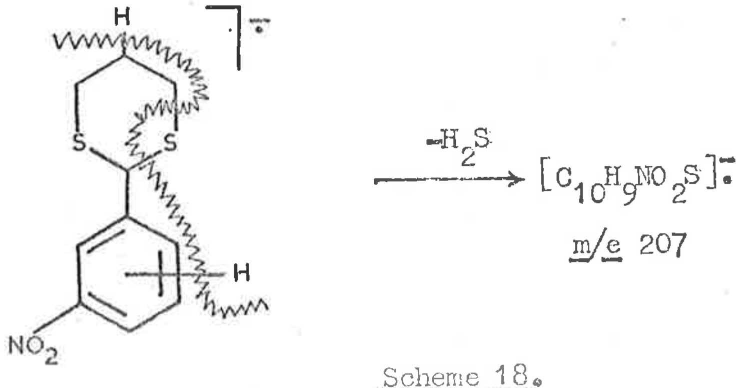
nitro-compounds (98) and (99) is greater than that in the spectra of (47) and (48) (see Table 18). The ion *i* ($C_3H_5S_2^-$, *m/e* 105) is present in the spectra of all dithianes [(46), (61), (62), and (63)], and its formation corresponds to Process O (Scheme 15). It is produced with incomplete hydrogen scrambling (of the type represented in *j* ⇌ *k*, Scheme 16) in the spectra of (46) and (63) (Fig. 20 and Table 18), just as Process N similarly proceeds with partial hydrogen scrambling (Table 18). The formation of *m/e* 105 in the spectra of *o*- and *m*-nitro derivatives (61) and (62) does not proceed with hydrogen scrambling. Process P (Schemes 15 and 17), which involves the loss of 105 mass units from the molecular anion $(M - C_3H_5S_2\cdot)^-$, is observed only in the spectrum of the *p*-nitro derivative (63) (Fig. 23). It is probable that this fragmentation is favoured by the stabilising influence of the *p*-nitro substituent on the substituted "benzyl anion" (*m/e* 136) which is produced. It also seems likely that the mechanism of formation



Scheme 17.

of *m/e* 136 is the same as that producing $C_3H_5S_2^-$ (*m/e* 105, Process O), with the charge residing on either fragment.

The spectra (Figs. 22 and 23) of the *m*- and *p*-nitrophenyl isomers (62) and (63) both exhibit (M - H_2S) ions (Process Q, Scheme 15), but these ions are produced by entirely different processes. In the case of the *m*-nitro compound, the *d*$_1$- and *d*$_4$- derivatives (95) and (96) each lose H_2S from the molecular anions, but the process M - HDS occurs exclusively in the spectrum of 2-(*m*-nitrophenyl)-1,3-dithiane-5,5-*d*$_2$ (97). Thus, one of the hydrogen atoms in the fragmentation arises from C-5, the second from the aromatic ring (Scheme 18). Examination of the

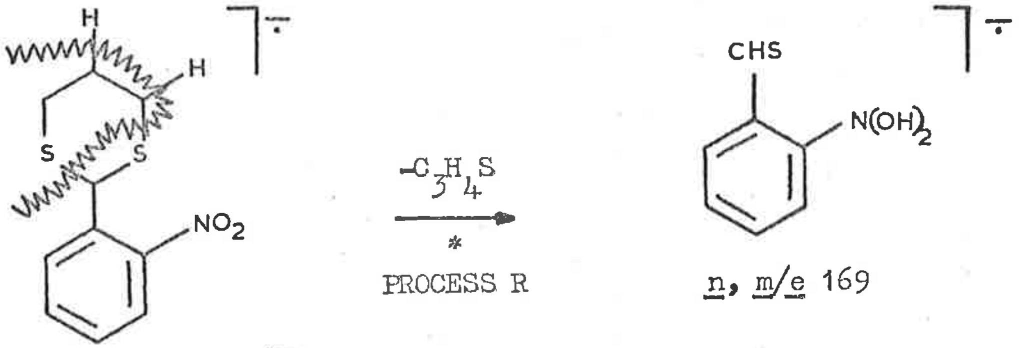


Scheme 18.

spectra of the d$_1$- and d$_4$- p-nitro derivatives (98) and (99) shows that the loss of H_2S in these cases involves two of the five hydrogens at C-2,4, and 6. The abundances of the appropriate ions (Table 18) indicate that the five hydrogen atoms in question have randomised before the elimination of H_2S.

Proximity effects (or ortho effects) are very common in positive-ion spectra,[3] and are relatively common even in negative-ion spectra. For example, the base peak in the spectrum[156] of o-nitrotrifluoroacetanilide corresponds to the elimination of OH• from the molecular anion. This peak is entirely absent in the spectra of the meta and para isomers. Similar specific effects have been observed in the spectra of o-nitrobenzanilide,[155] o-nitroacetanilide and their derivatives,[153] and polynitrobenzenes.[139]

Perhaps the most spectacular proximity effect is observed in the spectrum (Fig. 21) of 2-(o-nitrophenyl)-1,3-dithiane (61). The "normal" fragmentations of the dithiane ring, viz. M - C_3H_6S, and the formation of $C_3H_5S_2^-$ (i, m/e 105) (Processes N and O), occur in very small abundance in the spectrum of (91), whereas the base peak in the spectrum is produced by an M - C_3H_4S ion (Process R, Schemes 15 and 19). This process is unique to the spectrum of the o-nitro derivative, and presumably involves a transfer of two hydrogen atoms from the dithiane ring onto the ortho substituent, prior to (or during) fragmentation. The spectrum of the d$_4$-derivative (93) exhibits the process M - C_3HD_3S exclusively, i.e. one of the two hydrogen atoms transferred from the dithiane ring arises from C-4,6. Similarly, the process M - C_3H_3DS occurs exclusively in the spectrum of the d$_2$-derivative (94), and confirms that the second hydrogen atom involved in the transfer originates from C-5. The pathway of this unique fragmentation is depicted in Scheme 19. It is notable that no scrambling of the C-4,6 hydrogen atoms occurs, but nevertheless the mechanism of the reaction is obviously complex. The structure written in Scheme 19 for the product ion n (m/e 169) is purely conjectural, but since the o-nitro substituent clearly provides the "driving force" for this specific reaction it is not unreasonable to assume that the hydrogen atoms which are transferred from the dithiane ring before fragmentation are associated (in some way) with the nitro group. The double hydrogen rearrangement involved in the M - C_3H_4S process is the first of its type to be observed in a negative-ion spectrum.

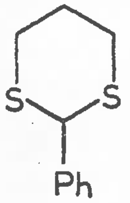


Scheme 19.

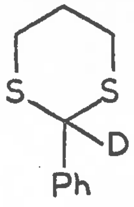
It is of interest that 2-phenyl-1,3-dithiolane (68) does not yield a molecular anion under the same conditions as the homologous dithiane (46); the spectrum of (68) consists of one peak (at m/e 122) which is produced by a M - C_2H_4S process. Since the molecular anion of (68) (if formed) fragments too quickly to be recorded in the mass spectrometer, then a hydrogen scrambling process between C-2,4, and 5 in the dithiolane ring, similar to that observed between C-2,4, and 6 in the spectra of the $\underline{d}_1$- and $\underline{d}_4$- derivatives [(47) and (48)] of 2-phenyl-1,3-dithiane, would be unlikely to take place. This is confirmed in the spectrum of 2-d-2-phenyl-1,3-dithiolane (69), in which a single peak is observed at m/e 123 (representing the process M - C_2H_4S). The o-, m-, and p-nitro derivatives (72)-(74) form very weak molecular anions, and the major fragment ion arises by a M - C_2H_4S process, which is substantiated by a metastable ion. This fragment decomposes further by the elimination of NO, but no variation of the fragmentations with substitution pattern is observed.

On the other hand, satisfactory negative-ion spectra (containing metastable peaks) are obtained from the nitrophenyl substituted 1,3-oxathianes (77)-(79), and 2-(p-nitrophenyl)-1,3-oxathiolane (82) (Appendix B). These spectra contain abundant molecular anions, and the major fragmentations correspond in general to the elimination of the sulphur-containing part of the hetero-ring, i.e. M - C_3H_6S and M - C_2H_4S respectively. As might be expected, the fragmentation pattern in the spectrum of 2-(o-nitrophenyl)-1,3-oxathiane (77) is entirely different from that of the m- and p- derivatives (78) and (79), and is complicated by numerous proximity effects. No further comment on these processes is possible in the absence of the appropriate labelling experiments.

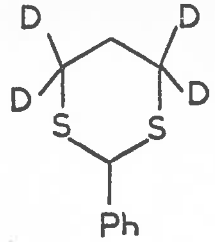
In summary, it has been demonstrated that 2-aryl-1,3-dithio compounds in general and 2-aryl-1,3-dithianes, in particular, give satisfactory negative-ion spectra containing molecular anions which, at least in some cases, may initially contain the extra electron localised on a sulphur atom. 2-Aryl-1,3-dithianes exhibit several cleavage processes, and all fragmentations of 2-phenyl- and 2-(p-nitrophenyl)-1,3-dithiane [(46) and (63)] take place after hydrogen scrambling has occurred between C-2,4, and 6 in the dithiane ring, with no alteration to the carbon skeleton. No such randomisation occurs for the o- and m-nitrophenyl isomers (61) and (62), indicating that these molecular ions are less stable (and shorter-lived) than those of the former pair. Furthermore, the spectra of the isomeric nitrophenyl dithianes (61)-(63) display fragmentations characteristic of the substitution pattern, and a unique double hydrogen rearrangement reaction is observed in the spectrum of 2-(o-nitrophenyl)-1,3-dithiane (61).



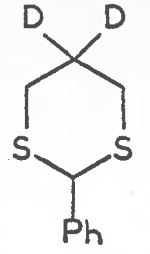
(46)



(47)



(48)



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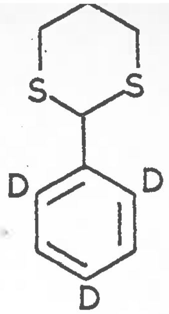

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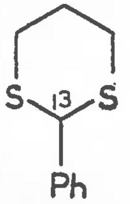

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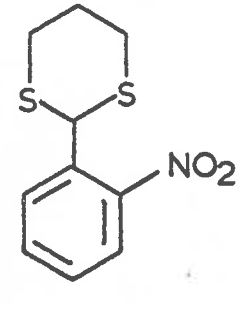
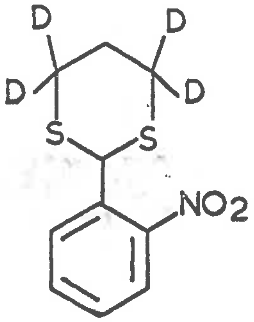
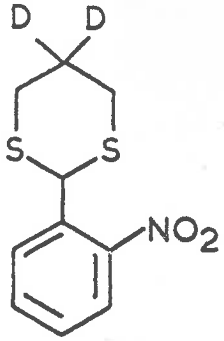


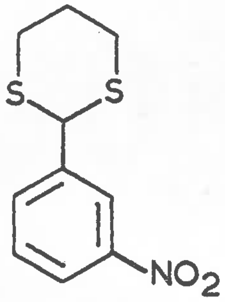
(61)



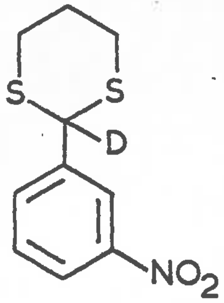
(93)



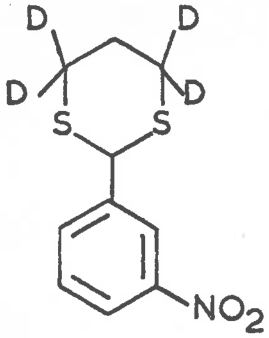
(94)



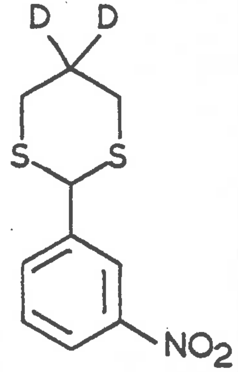
(62)



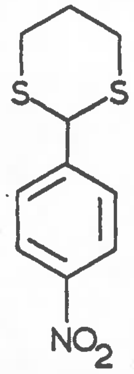
(95)



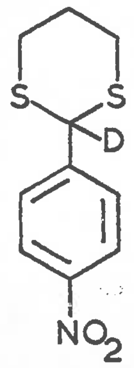
(96)



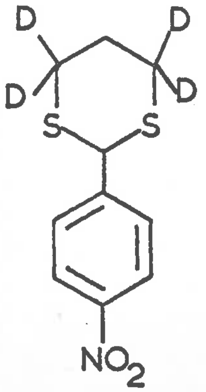
(97)



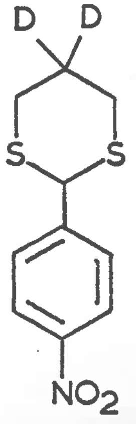
(63)



(98)



(99)



(100)

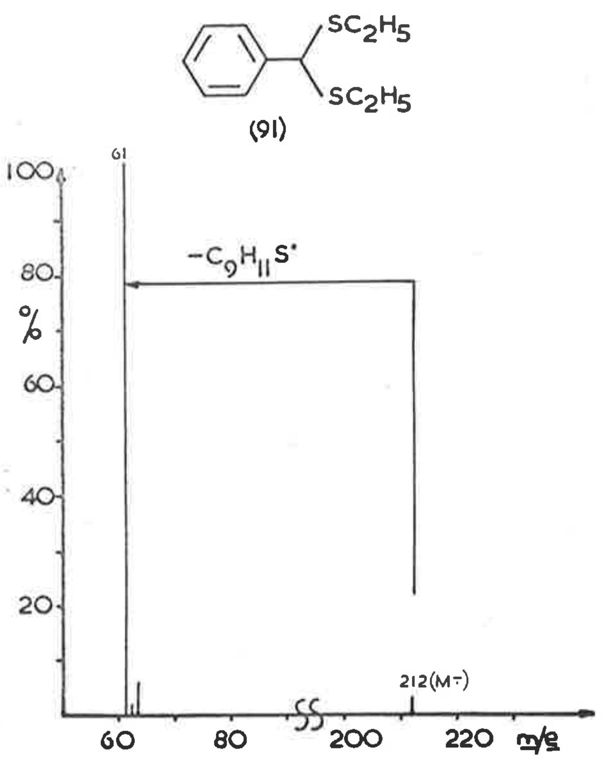


FIG. 17

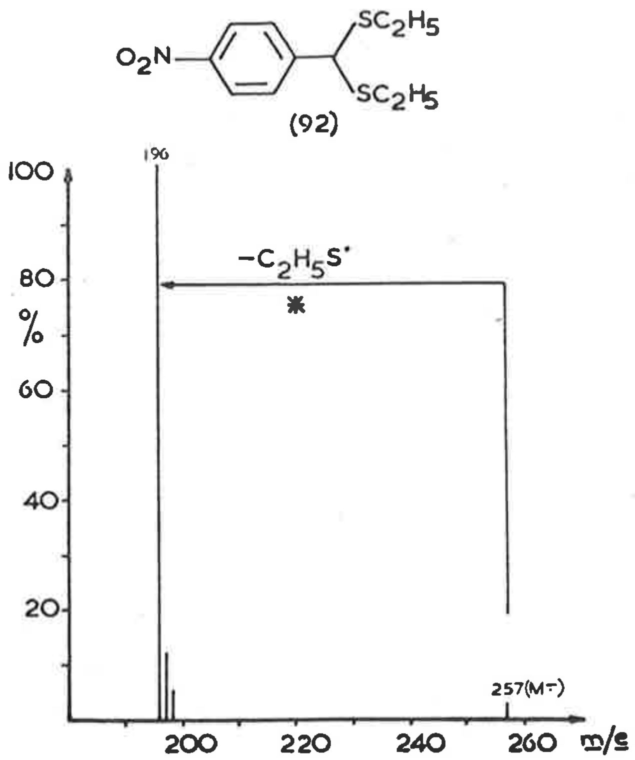


FIG. 18

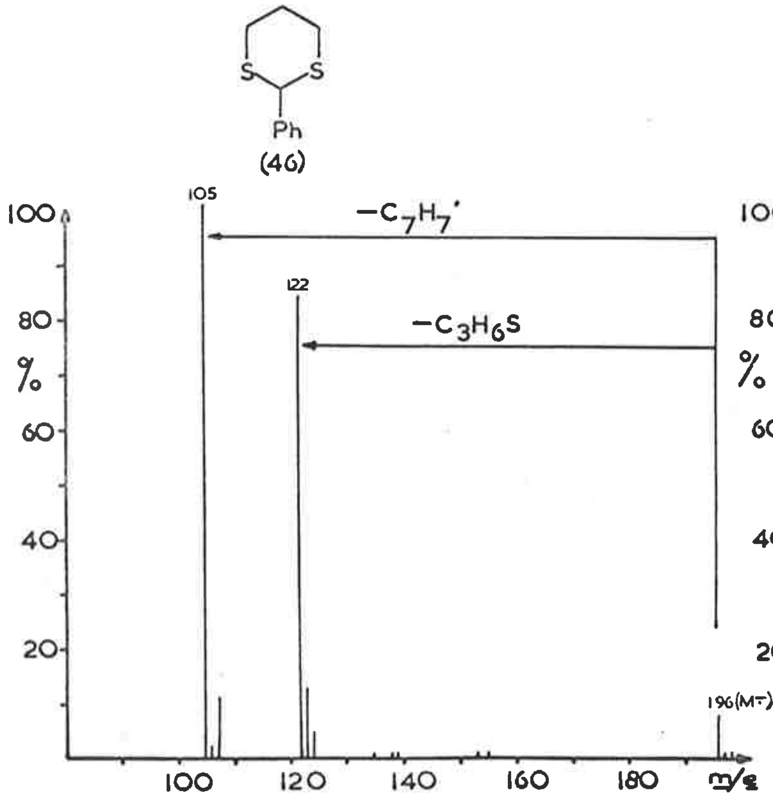


FIG. 19

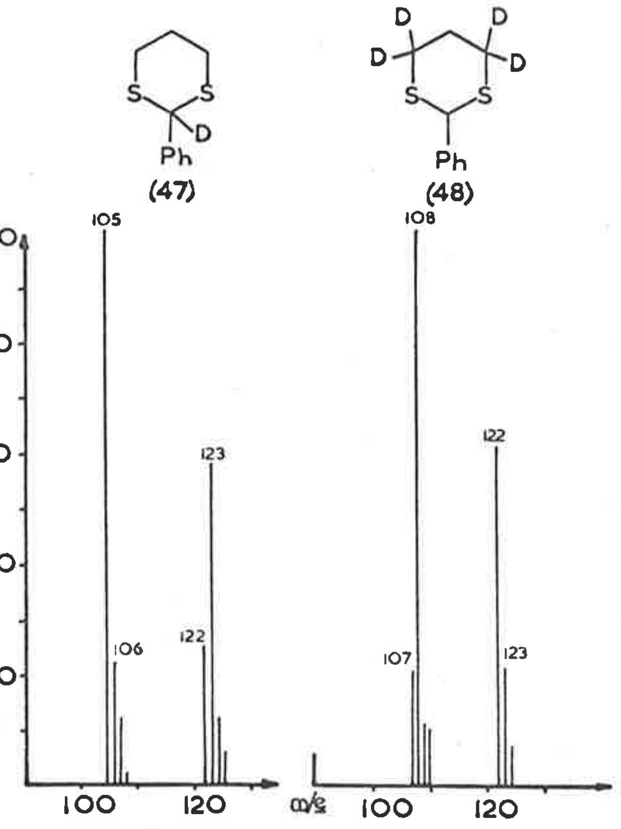


FIG. 20

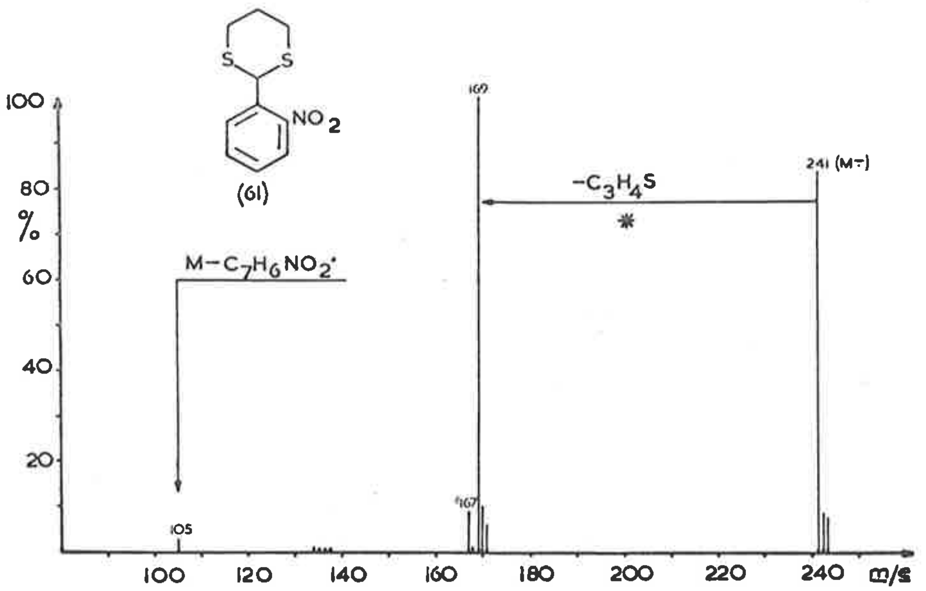


FIG. 21

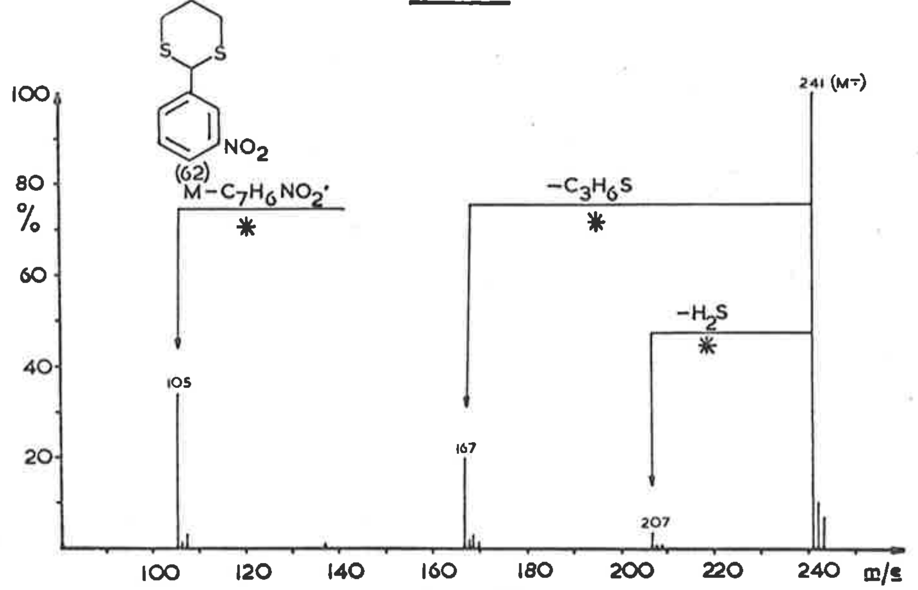


FIG. 22

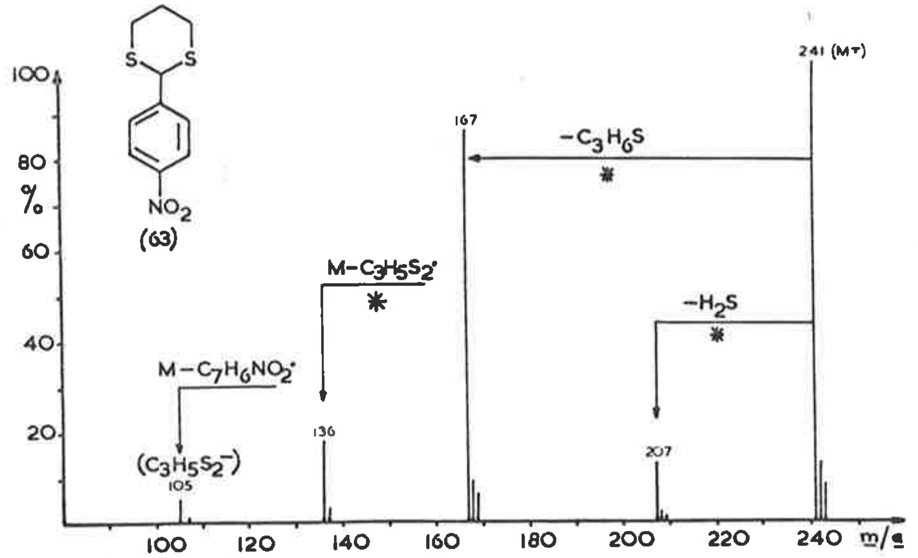


FIG. 23

Experimental.

General.

All mass spectra were determined with an Hitachi Perkin-Elmer RMU 6D double focusing mass spectrometer operating at 70 eV (unless otherwise specified). Samples were introduced through an all glass heated inlet system at 150°. Exact mass measurements were performed at a resolution of 10,000 (40% valley definition) using heptacosafluorotributylamine to provide reference masses. Defocused metastable ions were measured using a defocusing device of the type with variable electric sector voltage. All negative-ion spectra were determined at 70 eV and $1-3 \times 10^{-7}$ Torr, and all peaks were checked against internal standards. The metastable defocusing device was modified electronically to allow the measurement of negative ions.

The compounds examined were purified either by crystallisation or fractional distillation (where appropriate) and various chromatographic techniques, and were additionally checked by infrared and nuclear magnetic resonance spectroscopy, and mass spectrometry.

The nuclear magnetic resonance spectra were measured with either a Varian DA-60-IL or Varian T60 spectrometer (operating at 60 MHz), using carbon tetrachloride as solvent with tetramethyl silane as an internal standard. Infrared spectra were recorded as Nujol mulls or liquid films, on either a Perkin-Elmer 337 or a Unicam SP.200 infrared spectrophotometer. Melting points were determined on a Kofler hot-stage microscope, and are uncorrected. Analyses were carried out by the Australian Microanalytical Service, Melbourne.

The term light petroleum refers to the fraction of b.p. 55-65°.

Part A: Preparation of Diphenylmethane, Stilbene, and related Compounds.

Diphenylmethane (1), diphenylmethyl bromide (2), and stilbene (16) were purified commercial samples. The following compounds were available from previous studies: diphenylmethane-1-$\underline{d}_1$ (3), ($\underline{d}_3$-phenyl)phenylmethyl bromide (4), ($\underline{d}_5$-phenyl)phenylmethyl bromide (5), phenyl tropylidene (8), ($\underline{d}_5$-phenyl)phenylmethane (10), $\underline{d}_5$-phenyl tropylidene (11) (Ref. 84); dihydrophenanthrene (17), 1-$\underline{d}$-1-phenyl-2-phenylethylene (20), 1,2-$\underline{d}_2$-1,2-diphenylethylene (21), 1-($\underline{d}_3$-phenyl)-2-phenylethylene (22), 1-($\underline{d}_5$-phenyl)-2-phenylethylene (23) (Ref. 85); 1,2-diphenylethyl chloride (19), 9-($\underline{d}_3$-methyl)fluorene (28) (Ref. 105); 1,2-di($\underline{d}_3$-phenyl)ethylene (24) (Ref. 160). An impure sample of 9,10-$\underline{d}_2$-9,10-dideuterophenanthrene (27) was available,[85] and was purified by preparative g.l.c., using a 36 ft. 25% Apiezon M column. 9-Methylfluorene (18) was prepared by a reported procedure.[161]

2-Methylbiphenyl (9).

2-Methyl-1-phenylcyclohexanol.

An ethereal solution of phenylmagnesium bromide (360 mmoles) was treated at 0° with 2-methylcyclohexanone (0.200 g, 1.79 mmoles), and heated under reflux for one hour. The crude product obtained after the careful addition of saturated NH_4Cl solution was chromatographed on silica, and a small amount of the bi-product biphenyl was eluted in petroleum ether. 2-Methyl-1-phenylcyclohexanol was eluted in petroleum ether/ether (90 : 10), and was obtained, after recrystallisation from petroleum ether, as a colourless solid, m.p. 64-66°, in 72% yield.

6-Methyl-1-phenylcyclohexene.

The alcohol obtained above was dehydrated in aqueous oxalic acid (15%), by heating under reflux for four hours.[162] The product was obtained in 72% yield as a colourless liquid, b.p. 94-96°/2 mm, δ_{max} 6.0 (m, 1H, C=C$\underline{H}$), 1.0 (d, 3H, -C$\underline{H}_3$).

2-Methylbiphenyl (9).

6-Methyl-1-phenylcyclohexene was dehydrogenated with chloranil in xylene, using the procedure of Arnold and Collins.[163] 2-Methylbiphenyl (9)[164] was obtained as a pale yellow liquid, b.p. 106-108°/8 mm in 55% yield. Small amounts of unreacted olefin and biphenyl were separated by preparative g.l.c., using a 36 ft. 25% Apiezon M column.

Preparation of deuterium labelled compounds.

d_7-Benzyl bromide.

This was obtained by treatment of $\underline{d}_8$-toluene with bromine in the light.[165]

(2,4,6-d_3-Phenyl)phenylmethane (13).

(2,4,6-$\underline{d}_3$-Phenyl)phenylmethanol[84] (0.115 g, 0.615 mmoles) in ethanol (15 ml) was stirred for four hours with Pd/C (0.016 g) under an atmosphere of hydrogen. The solution was filtered through a pad of diatomaceous earth, the solvent removed *in vacuo*, and ($\underline{d}_3$-phenyl)phenylmethane (13) was obtained as a colourless oil in 95% yield. The product was sublimed at 80-90° (block temperature)/10 mm, and was pure by infrared spectroscopy and mass spectrometry.

2-Methylbiphenyl-d_5 (12).

This compound was prepared in the same manner as for (9), using d_5-bromo benzene (99.5% d_5) to form the Grignard reagent in the first step. 2-Methylbiphenyl-d_5 (12) was obtained in 30% overall yield as a pale yellow liquid, b.p. 108°/8 mm. The product was purified by preparative g.l.c. [as for (9)], and the mass spectrum measured at the appearance potential showed an isotopic incorporation of 99.5% d_5.

2-(d_3-Methyl)biphenyl (14).

This was prepared from 2-(d_3-methyl)cyclohexanone, by the same general procedure as for (9). The deuterium labelled methylcyclohexanone was obtained by alkylation of ethylcyclohexanone-2-carboxylate[166] with d_3-methyl iodide (99.5% d_3), followed by decarboxylation, using the method of House.[167] The n.m.r. spectrum of 2-(d_3-methyl)biphenyl indicated that approximately 40% of the deuterium label had been lost in the dehydration step. A study of the fragment ions in the spectrum of (14) was therefore impossible, but investigation of processes from the molecular ion was still possible by measurement of the appropriate defocused metastable ions.

1-d-1-(d_5-Phenyl)-2-phenylethylene (25).

The Grignard reagent prepared from d_7-benzyl bromide was treated with benzaldehyde, according to the method of Donaghue.[85] A small amount of bi-product ($\underline{d}_{14}$-bibenzyl) was separated from the crude alcohol by chromatography on silica, with petroleum ether as eluent. Elution with petroleum ether/ether (90 : 10) gave pure 1,1-$\underline{d}_2$-1-($\underline{d}_5$-phenyl)-2-phenylethanol as a colourless solid, m.p. 66-67°. Dehydration[168] of the alcohol in dimethylsulphoxide, and chromatography of the crude product on silica, eluting with petroleum ether, gave the $\underline{d}_6$-stilene (25) in 55% overall yield, as colourless crystals, m.p. 124-125° (lit.[168] m.p. 124°). The mass spectrum recorded at the appearance potential showed the deuterium incorporation to be 91% $\underline{d}_6$, 9% $\underline{d}_5$.

Preparation of ^{13}C-labelled compounds.

Diphenylmethanol-1,^{13}C (7).

The Grignard reagent prepared from bromobenzene (0.741 g, 4.73 mmoles) and magnesium (0.118 g, 4.85 mmoles) in ether was treated at 0° with an ethereal solution of benzaldehyde-7,^{13}C (0.250 g, 2.34 mmoles, 60.8 atom %) [which had been purified by rapid elution with petroleum ether/ether (97 : 3) through silica, with removal of the solvent under reduced pressure and nitrogen at room temperature]. The mixture was stirred until room temperature was attained, heated under reflux for one hour, and stirred for a further three hours. After careful addition of saturated NH_4Cl solution, the ethereal layer was dried (Na_2SO_4) and concentrated _in vacuo_. The resultant solid was recrystallised from petroleum ether, and diphenylmethanol-1,^{13}C (7) was obtained as colourless crystals, yield 0.298 g (1.55 mmoles, 66%), m.p. 66-67° (lit.[169]

m.p. 68°). The mass spectrum measured at the appearance potential showed an isotopic incorporation of 60.5% ^{13}C.

Diphenylbromomethane-1,^{13}C (6).

Carbon tetrachloride (5 ml) was added to a mixture of diphenylmethanol-1,^{13}C (7) (0.132 g, 0.713 mmoles) and phosphorus tribromide (0.220 g, 0.813 mmoles) and the solution was stirred overnight. Water (5 ml) was added with vigorous stirring and the organic layer was separated and filtered through anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and diphenylbromomethane-1,^{13}C (6) was obtained as a colourless oil which solidified on standing. The product was recrystallised from pentane, and obtained as colourless crystals, yield 0.133 g (0.535 mmoles, 75%) m.p. 40-44° (lit.[170] m.p. 45°). The product was pure by infrared spectroscopy and mass spectrometry, and the mass spectrum showed an isotopic incorporation of 60.5% ^{13}C.

Diphenylmethane-1,^{13}C (15).

This was prepared from (7) by the same method as the deuterium labelled compound (13), and was obtained in 95% yield. The isotopic incorporation was found to be 60.5% ^{13}C.

1,2-Diphenylethylene-1,^{13}C (26).

Prepared from benzaldehyde-7,^{13}C (32.8 atom %), as for (25).

Part B: Preparation of 1,3-Dithiane, and related Compounds.

1,3-Dithiane (35),[171] 2-methyl-1,3-dithiane (39),[172] 2-phenyl-1,3-dithiane (46),[173] benzylcyclopropane (85),[174] and 2-benzyl-1,3-dibromopropane (86)[175] were prepared by reported procedures. A sample of 2-cyclooctatetraenylethyl bromide (87) was kindly donated by Dr. G. E. Gream. Tetralin (88) was a purified commercial sample.

General method for the preparation of 1,3-dithianes.

A solution of the appropriate aldehyde or ketone (1.0 mmole) and propane-1,3-dithiol (1.2 mmoles) in chloroform (10 ml) was saturated with dry hydrogen chloride, and allowed to stand for 0.5 hr. The solution was washed (2 x 2 ml), with water, aqueous sodium hydroxide (10%), and water, and the chloroform layer was separated and filtered through anhydrous Na_2SO_4. After removal of the solvent, the 1,3-dithiane was obtained in good yield (60-95%), and was purified by recrystallisation (from methanol), or fractional distillation (where appropriate).

With the exception of (35)[171] and (39),[172] all dithianes were prepared by the above procedure. 2,2'-p-Phenylene-bis-1,3-dithiane (83) was recrystallised from nitrobenzene. Before the conversion of o-, m-, and p-nitrobenzaldehyde to the corresponding dithianes, small amounts of isomeric contaminants were removed by preparative g.l.c., using a 36 ft. 25% Apiezon column. The purity of the nitrobenzaldehydes was checked by analytical g.l.c., using a MPGS/XE60 column at 235°, and was found to be greater than 99.5% in each case.

All 1,3-dithiolanes were prepared by the same general method as for the 1,3-dithianes, using ethane-1,2-dithiol. All 1,3-oxathianes and 1,3-oxathiolanes were similarly prepared, using 3-mercaptopropanol and 2-mercaptoethanol respectively, with the exception that the reaction mixtures were washed with 1% aqueous sodium hydroxide.

The 1,3-dithianes (35),[171] (39),[172] (43),[176] (46),[173] (52),[177] (53),[177] and (66),[177] and 1,3-dithiolanes (68),[178] (71),[178] (73),[178] (75),[179] 2-phenyl-1,3-oxathiane (76),[180] and 2-(p_-nitrophenyl)-1,3-oxathiolane (82)[181] have been reported previously.

Compounds (55), (58), (59), (61)-(65), (67), (70), (72), (74), (77)-(81), and (83) have not been reported previously, and the physical data for these compounds are tabulated below. Satisfactory analyses were not obtained for (72), (74), (77)-(81), but these compounds were pure by infrared and n.m.r. spectroscopy, and mass spectroscopy.

trans-3-Methyl-1-phenylbut-1-ene (89).

The reaction between benzaldehyde and iso-butyl magnesium bromide afforded 3-methyl-1-phenylbutan-1-ol[182] in 70% yield, b.p. 120-122°/12 mm. The alcohol was dehydrated in dimethylsulphoxide,[168] and the crude product was fractionally distilled. trans-3-Methyl-1-phenylbut-1-ene (89)[182] was obtained in 60% yield, b.p. 92-93°/15 mm (lit.[182] b.p. 91-92.5°/17 mm).

Compound	m.p. (or b.p.)	Composition	Found %			Calculated %		
			C	H	S(or N)	C	H	S(or N)
(55)	127.5-128°	$C_{11}H_{14}O\ S_2$	58.34	6.23	28.37	58.37	6.23	28.33
(58)	117-117.5°	$C_{11}H_{14}O\ S_2$	58.53	6.29	28.46	58.37	6.23	28.33
(59)	100-101°	$C_{12}H_{16}O\ S_2$	60.31	6.78	26.64	59.96	6.71	26.68
(61)	119-120°	$C_{10}H_{11}NO_2S_2$	49.49	4.66	26.76	49.79	4.6	26.54
(62)	117-118°	$C_{10}H_{11}NO_2S_2$	50.01	4.82	26.25	49.79	4.6	26.54
(63)	140-142°	$C_{10}H_{11}NO_2S_2$	49.82	4.68	(N)5.83	49.79	4.6	(N)5.80
(64)	92-93°	$C_{10}H_{11}Cl\ S_2$	51.75	4.87	27.7	52.07	4.81	27.75
(65)	63-64°	$C_{10}H_{11}Cl\ S_2$	52.14	4.93	27.82	52.07	4.81	27.75
(67)	119-120°	$C_{12}H_{17}N\ S_2$	60.50	6.83	(N)5.75	60.71	6.37	(N)5.90
(70)	b.p.135°/0.35 mm	$C_{10}H_{12}O\ S_2$	56.49	5.69	29.98	56.56	5.70	30.20
(72)	62.5-63°	$C_9H_9NO_2S_2$						
(74)	76-78°	$C_9H_9NO_2S_2$						
(77)	90-91°	$C_{10}H_{11}NO_3S$						
(78)	61-62°	$C_{10}H_{11}NO_3S$						
(79)	101-102°	$C_{10}H_{11}NO_3S$						
(80)	59-61°	$C_9H_9NO_3S$						
(81)	43-43.5°	$C_9H_9NO_3S$						
(83)	285-288°	$C_{14}H_{18}S_4$	53.26	5.87	40.68	53.46	5.77	40.77

Preparation of deuterium labelled compounds.

2-d-1,3-Dithiane (36)[183] and 2-d-2-phenyl-1,3-dithiane (46)[173] were prepared by reported procedures.

The d_1-labelled compounds 2-d-2-(o-methoxyphenyl)-1,3-dithiane (56), 2-d-2-(o-ethoxyphenyl)-1,3-dithiane (60), and 2-d-2-(p-nitrophenyl)-1,3-dithiane (98) were prepared by treatment of the lithium salt derived from the corresponding dithianes (55), (59), and (63), according to the method of Seebach et al.[173]

2-d-2-Phenyl-1,3-dithiolane (68).

Obtained from the reaction between d_1-benzaldehyde[173] and 1,2-ethanedithiol in the standard manner (100% d_1).

2-d-2-(m-Nitrophenyl)-1,3-dithiane (95).

Nitration of d_1-benzaldehyde[173] gave m-nitrobenzaldehyde-d_1. This was separated from a small amount of the ortho isomer by preparative g.l.c., as for the unlabelled nitrobenzaldehydes (see above). Treatment of the pure ($>$99.5% by g.l.c.) m-nitrobenzaldehyde-d_1 with propane-1,3-dithiol in the usual manner gave 2-d-2-(m-nitrophenyl)-1,3-dithiane (100% d_1).

2-(d_3-Methyl)-1,3-dithiane (40).

1,3-Dithiane (35) in anhydrous tetrahydrofuran (THF) was treated at -70° with n-butyl lithium, and the resultant lithio-derivative was alkylated with d_3-methyl iodide (99.5% d_3), according to the general method of Seebach.[172] 2-(d_3-Methyl)-1,3-dithiane (40) was obtained in

60% yield as a colourless liquid, b.p. 80°/11 mm (lit.[172] b.p. 84°/17 mm). The incorporation of deuterium was found to be 99.5% $\underline{d}_3$.

2-(d_3-Methyl)-2-methyl-1,3-dithiane (44).

2-Methyl-1,3-dithiane (39) was alkylated with $\underline{d}_3$-methyl iodide, by the same method as for the preparation of (40), and 2-($\underline{d}_3$-methyl)-2-methyl-1,3-dithiane (44) was obtained as a colourless liquid, b.p. 88°/15 mm (lit.[176] b.p. 79-81°/10 mm).

2-(2,4,6-d_3-Phenyl)-1,3-dithiane (50).

Prepared from 2,4,6-$\underline{d}_3$-benzaldehyde[160] and propane-1,3-dithiol. The mass spectrum showed an isotopic incorporation of 96% $\underline{d}_3$, 4% $\underline{d}_2$.

1,1,3,3-d_4-Propane-1,3-dithiol.

Malonic acid (2.72 g, 26.2 mmoles) in THF (50 ml) was added slowly to a stirred solution of lithium aluminium deuteride (2.2 g, 52.4 mmoles) in THF (150 ml). After the addition was complete, the mixture was heated under reflux for 8 hr, cooled, and treated carefully with water (2.2 ml) and aqueous sodium hydroxide (15%, 2.2 ml). The resultant slurry was stirred for 2 hr, after which the solid was filtered off at the pump, and the solvent removed *in vacuo*. Crude 1,1,3,3-$\underline{d}_4$-propane-1,3-diol was obtained as a colourless liquid (0.55 g). The granular precipitate obtained from work-up of the reduction mixture was continuously extracted with THF for 48 hr, giving a further 0.62 g of $\underline{d}_4$-diol, total yield 1.17 g (55%). The $\underline{d}_4$-diol was converted into 1,1,3,3-$\underline{d}_4$-

propane-1,3-dibromide in 57% yield by treatment[184] with HBr/H_2SO_4. The d_4-dibromide was subsequently treated[185] with thiourea, and the di-isothiuronium dihydrobromide was isolated in 93% yield. Treatment of this salt with aqueous potassium hydroxide[186] gave 1,1,3,3-d_4-propane-1,3-dithiol (0.59 g, 73%), b.p. 69-70°/19 mm (lit.[186] b.p. 92-98°/56 mm). The isotopic incorporation was found to be 96% d_4, 4% d_3.

2,2-d_2-Propane-1,3-dithiol.

The repeated equilibration of malonic acid with deuterium oxide in dioxan[187] gave d_4-malonic acid, and reduction of this material with lithium aluminium hydride yielded 2,2-d_2-propane-1,3-diol. The d_2-diol was converted into 2,2-d_2-propane-1,3-dithiol as for 1,1,3,3-d_4-propane-1,3-dithiol. Two separate runs gave the d_2-dithiol with deuterium incorporations of 94% d_2, 6% d_1, and 90% d_2, 10% d_1, respectively. The d_4-labelled dithianes (37), (41), (48), (93), (96), and (98) and the d_2-labelled dithianes (38), (42), (49), (54), (94), (97), and (100) were prepared from the appropriate aldehyde or ketone and the appropriate labelled dithiol, by the standard procedure.[173]

2,3,4,5,6-d_5-Benzaldehyde.

Prepared from d_5-bromobenzene and ethyl orthoformate by the method of Smith and Bayliss.[188]

trans-3-Methyl-1-(d_5-phenyl)but-1-ene (90).

Prepared from d_5-benzaldehyde and iso-butyl magnesium bromide, as for (89). Incorporation of deuterium was found to be 99.5% $\underline{d}_5$.

2-Phenyl-1,3-dithiane-2-^{13}C (51).

Prepared from benzaldehyde-7,^{13}C (60.5 atom %).

Appendix. All peaks greater than 5% of the base peak (arbitrarily 100%) and certain others of diagnostic value are recorded.

PART A: Positive-Ion Spectra.

Bromodiphenylmethane-1,^{13}C (6).

m/e	82.5	83	83.5	152	153	165	166	167	168 (M-Br)	169
%	8	10	7	11	14	21	37	73	100	16

Diphenylmethanol-1,^{13}C (7).

m/e	51	77	79	105	106	107	108	152	153	155	165	166	167
%	13	55	38	64	100	18	14	5	5	5	8	12	6

m/e	168	183	184	185(M)	186
%	5	12	47	49	8

2-Methylbiphenyl-d_5 (12).

m/e	154	155	156	157	158	166	167	168	169	170	171	172
%	6	14	23	17	8	3	4	8	17	13	21	39

m/e	173(M)	174
%	100	16

(d_3-Phenyl)phenylmethane (13).

m/e	89	90	91	92	93	94	116	117	118	129	130	131	140	141
%	5	4	14	7	4	12	4	6	4	3	4	3	2	4

m/e	142	143	144	153	154	155	156	166	167	168	169	170
%	3	3	2	6	15	16	10	5	17	22	24	73

m/e	171(M)	172
%	100	17

2-(d_3-Methyl)biphenyl (14).

m/e	83	84	91	104	117	129	130	143	152	153	154	155	156	157	166	167	168	169	170	171(M)	172
%	5	9	9	5	5	10	9	9	6	10	23	19	11	6	5	15	16	22	64	100	14

Diphenylmethane-1,^{13}C (15).

m/e	89	90	91	92	152	153	154	165	166	167	168	169(M)	170
%	5	7	15	18	12	22	13	18	28	47	100	71	9

1-d-1-(d_5-Phenyl)-2-phenylethylene (25).

m/e	78	91	91.5	92	93	156	168	169	170	171	182	183	184	185	186(M)	187
%	8	5	11	8	7	5	8	13	13	8	11	27	46	53	100	16

9-(d_3-Methyl)fluorene (28).

m/e	151	152	153	154	155	163	164	165	166	167	176	177	178	179	180	181	182	183(M)	184
%	3	4	4	3	2	8	6	100	20	3	2	3	6	8	20	18	32	44	8

4,4,6,6-d_4-1,3-Dithiane (37).

m/e	41	42	44	45	46	48	62	64	74	76	78	90	91	108	123	124(M)	125	126
%	8	5	8	21	31	21	5	8	13	11	32	9	6	5	10	100	8	10

5,5-d_2-1,3-Dithiane (38).

m/e	39	40	41	42	43	45	46	47	48	55	56	57	59	60	61	64
%	5	8	6	11	13	39	48	10	6	5	6	8	6	9	11	6

m/e	74	75	76	77	78	79	88	89	92	107	108	121	122(M)	123
%	9	29	34	6	11	5	7	16	6	9	6	18	100	19

m/e	124
%	21

2-(d_3-Methyl)-1,3-dithiane (40).

m/e	39	41	43	44	45	57	58	59	60	61	62	70	71	72	73	74
%	12	17	32	26	8	7	7	7	26	32	11	14	10	60	10	6

m/e	86	87	91	101	115	116	117	137(M)	138	139
%	16	8	6	7	48	6	5	100	8	10

4,4,6,6-d_4-2-Methyl-1,3-dithiane (41).

m/e	41	42	43	44	45	46	47	48	49	50	58	59	60	61	62	64
%	12	11	13	20	35	29	8	47	9	5	11	48	54	14	9	11

m/e	72	73	75	76	77	78	79	80	87	88	89	92	108	123	125
%	8	12	5	10	11	72	11	5	6	22	5	8	5	59	6

m/e	137	138(M)	139	140
%	7	100	10	10

5,5-d_2-2-Methyl-1,3-dithiane (42).

m/e	40	41	42	43	45	46	47	58	59	60	61	64	70	71	74	75
%	6	10	11	12	34	32	9	8	32	34	10	7	7	8	8	16

(42) - continued.

m/e	76	77	89	92	107	120	121	135	136(M)	137	138
%	54	8	16	6	6	6	46	14	100	9	10

2,2-Dimethyl-1,3-dithiane (43).

m/e	27	39	41	44	45	46	47	55	56	58	59	60	61	71	73	74
%	6	18	25	5	19	16	10	9	6	8	60	5	7	5	12	100

m/e	75	76	83	88	101	106	115	133	148(M)	149	150
%	19	8	10	7	11	9	8	29	68	7	8

2-(d_3-Methyl)-2-methyl-1,3-dithiane (44).

m/e	41	43	44	45	46	58	59	60	61	62	73	74	75	76	77	78
%	11	6	8	13	15	7	34	6	5	36	10	54	9	14	79	18

m/e	79	86	91	104	105	109	118	133	134	136	151(M)	152	153
%	5	12	6	14	5	7	7	21	7	24	100	9	11

2-d-2-Phenyl-1,3-dithiane (47).

m/e	27	28	39	40	41	44	45	46	47	51	52	63	64	69	73	74
%	5	7	15	5	16	8	30	48	5	12	5	6	7	5	20	32

m/e	76	77	78	79	90	91	92	105	106	116	117	118	121	122
%	5	16	11	23	7	6	24	40	5	7	7	14	66	19

m/e	123	124	125	132	133	136	150	154	197(M)	198	199
%	100	18	6	39	5	12	7	9	50	7	5

4,4,6,6-d_4-2-Phenyl-1,3-dithiane (48).

m/e	44	45	46	48	51	63	76	77	78	79	87	88	89	91	92	93
%	5	16	9	12	9	6	10	21	36	5	5	5	8	8	10	6
m/e	107	108	118	119	121	122	123	124	134	135	136	137	150			
%	5	23	10	5	84	100	18	10	18	19	6	7	5			
m/e	153	200(M)														
%	10	21														

5,5-d_2-2-Phenyl-1,3-dithiane (49).

m/e	39	41	42	43	45	46	51	63	75	76	77	78	89	91	92	107
%	7	5	5	9	29	16	10	7	13	21	23	16	7	14	7	30
m/e	108	117	118	119	121	122	123	124	132	133	135	151	153			
%	6	5	6	12	81	97	19	6	14	25	13	8	11			
m/e	197	198(M)	199	200												
%	9	100	15	11												

2-d_3-Phenyl-1,3-dithiane (50).

m/e	28	39	40	41	45	46	47	52	53	64	65	73	74	79	80	81
%	7	9	5	12	40	18	5	7	10	5	5	16	26	6	22	21
m/e	92	93	94	105	106	118	119	120	123	124	125	126	127	133		
%	6	6	22	32	5	6	6	13	10	86	100	21	6	5		
m/e	134	135	137	138	152	155	156	199(M)	200	201						
%	36	5	6	10	9	6	7	84	12	10						

2-Phenyl-1,3-dithiane-2,^{13}C (51).

m/e	39	41	45	46	51	63	73	74	75	77	78	90	91	92	105	116
%	5	6	15	16	7	5	17	28	5	19	20	5	14	15	36	6
m/e	117	118	121	122	123	124	131	132	135	136	150	153	154			
%	10	11	39	100	80	16	18	28	7	10	6	5	8			
m/e	196	197(M)	198	199												
%	42	67	11	7												

5,5-d$_2$-2,2-Diphenyl-1,3-dithiane (54).

m/e	77	105	121	165	166	167	197	198	199	200	211	274(M)	275
%	11	7	33	65	16	5	8	100	16	6	6	32	7

2-(o-Methoxyphenyl)-1,3-dithiane (55).

m/e	39	41	45	50	51	63	65	69	73	77	78	91	92	105	107	108
%	15	10	28	6	16	6	16	10	10	18	8	78	8	11	18	10
m/e	109	118	119	120	121	135	137	147	151	152	153	161	226(M)			
%	7	6	100	13	28	7	10	13	31	64	15	24	100			
m/e	227	228														
%	14	10														

2-d-2-(o-Methoxyphenyl)-1,3-dithiane (56).

m/e	39	41	45	46	51	52	66	69	73	77	78	79	91	92	93	106
%	7	8	16	10	8	6	10	7	10	7	10	6	16	52	6	11
m/e	107	108	119	120	121	122	136	138	148	151	152	153	154			
%	9	15	21	84	18	19	6	8	14	27	18	66	15			
m/e	161	162	226	227(M)												
%	7	29	18	100												

2-(p-Methoxyphenyl)-1,3-dithiane (58).

m/e	39	45	51	65	77	107	121	147	151	152	153	161	179	193
%.	6	12	7	7	7	8	22	20	60	100	14	13	3	3
m/e	226(M)													
%	58													

2-(o-Ethoxyphenyl)-1,3-dithiane (59).

m/e	39	41	45	51	65	77	87	91	105	107	109	119	121	131	133
%	8	6	17	9	10	14	7	7	32	13	7	7	7	10	100
m/e	134	135	137	165	166	175	211	240(M)	241	242					
%	13	12	25	11	9	6	6	52	8	5					

2-d-2-(o-Ethoxyphenyl)-1,3-dithiane (60).

m/e	45	46	66	78	87	92	106	107	108	110	120	133	134	135
%	10	8	7	11	7	3	29	6	13	6	6	9	100	14
m/e	136	138	165	167	176	212	241(M)	242	243					
%	13	20	9	9	8	6	67	12	6					

2-(o-Nitrophenyl)-1,3-dithiane (61).

m/e	39	40	45	46	51	63	64	65	69	73	74	76	77	78	79	90
%	5	13	9	5	7	5	9	6	6	10	6	6	16	6	14	6
m/e	91	92	104	105	106	107	108	109	119	120	121	134	135			
%	9	12	7	8	100	14	15	5	14	10	9	8	24			
m/e	147	161	166	167	224	241(M)										
%	18	10	26	10	28	7										

2-(m-Nitrophenyl)-1,3-dithiane (62).

m/e	39	41	45	46	63	73	74	75	76	77	105	119	120	121	130
%	6	10	17	22	5	10	100	8	8	12	15	5	8	15	8
m/e	166	167	241(M)	242	243										
%	7	10	39	6	5										

2-(p-Nitrophenyl)-1,3-dithiane (63).

m/e	39	41	45	46	51	63	65	69	73	74	75	76	77	105	120
%	14	21	41	44	9	7	6	7	9	100	9	9	23	14	6
m/e	121	130	166	167	241(M)										
%	9	6	5	5	14										

2-(o-Chlorophenyl)-1,3-dithiane (64).

m/e	39	41	45	46	47	51	63	69	73	74	75	77	89	105	112	120
%	8	10	30	12	5	5	6	5	13	20	8	10	6	27	8	6
m/e	121	125	130	135	151	153	155	156	157	158	159	165	183			
%	9	12	5	8	5	10	43	100	27	38	5	12	5			
m/e	195	230(M)	231	232												
%	14	63	9	28												

2-(m-Chlorophenyl)-1,3-dithiane (65).

m/e	39	41	45	46	47	51	63	69	73	74	75	76	77	89	105	106
%	11	16	43	27	6	5	7	6	27	100	17	8	10	7	48	5
m/e	107	111	112	119	120	121	125	127	130	135	151	153	155			
%	5	7	10	7	5	8	13	5	5	8	8	10	53			

(65) - continued.

m/e	156	157	158	165	167	169	183	187	230(M)	231	232	233
%	61	27	23	26	9	5	6	5	91	14	39	6

2-(p-Chlorophenyl)-1,3-dithiane (66).

m/e	39	41	45	46	73	74	75	77	89	105	107	111	112	120	121
%	5	8	22	11	15	35	9	7	6	37	5	6	10	6	8

m/e	125	127	130	135	151	153	155	156	157	158	159	165	167
%	14	6	5	9	15	14	74	100	41	39	7	29	10

m/e	183	187	230(M)	231	232	233
%	7	5	99	14	43	6

2-(p-Dimethylaminophenyl)-1,3-dithiane (67).

m/e	39	41	42	45	51	63	65	77	95	97	119	120	121	134	147
%	12	10	12	21	6	6	7	16	6	7	7	9	9	20	12

m/e	148	160	164	165	166	239(M)
%	11	18	46	100	15	23

2-Phenyl-1,3-dithiolane (68).

m/e	39	45	50	51	60	65	70	77	78	89	91	105	121	122	123
%	6	28	8	18	6	8	6	34	18	6	8	7	100	42	9

m/e	135	153	154	155	181	182(M)	183	184
%	7	90	72	15	13	84	12	8

2-(o-Methoxyphenyl)-1,3-dithiolane (70).

m/e	45	51	65	69	77	78	89	91	92	93	105	106	107	108	109
%	7	7	12	7	20	10	7	68	13	8	12	8	23	20	10
m/e	117	118	119	120	121	122	123	135	137	151	152	153	169		
%	26	10	40	10	26	17	8	26	14	100	23	78	23		
m/e	183	184	185	186	211	212(M)	213	214							
%	18	64	10	6	12	100	14	9							

2-(p-Methoxyphenyl)-1,3-dithiolane (71).

m/e	41	45	50	51	63	65	69	77	78	91	105	108	109	121	135
%	16	21	7	17	11	22	11	19	7	7	7	24	8	10	6
m/e	136	151	152	153	154	155	169	181	183	184	185	211			
%	10	100	45	56	7	5	11	1	30	46	7	6			
m/e	212(M)	213	214												
%	48	7	6												

2-(o-Nitrophenyl)-1,3-dithiolane (72).

m/e	56	62	67	68	69	76	77	78	80	81	82	86	93	94	96	108
%	9	17	7	15	6	9	5	9	9	9	8	9	8	23	8	9
m/e	109	110	111	113	121	122	125	126	136	137	138	151	152			
%	41	8	6	5	9	6	14	5	20	9	5	9	12			
m/e	168	169	170	171	172	173	184	197	227(M)	228						
%	5	100	13	56	9	6	28	14	38	5						

2-(m-Nitrophenyl)-1,3-dithiolane (73).

m/e	39	45	50	51	59	60	61	63	69	76	77	89	91	105	107
%	8	31	6	10	13	20	10	10	10	6	28	5	5	25	7

m/e	108	109	120	121	122	134	151	152	153	154	166	167	168
%	5	5	18	27	5	7	5	37	15	8	32	22	6

m/e	180	182	183	184	198	199	200	201	226	227(M)	228	230
%	5	63	7	7	18	45	6	5	5	100	13	10

2-(p-Nitrophenyl)-1,3-dithiolane (74).

m/e	40	46	51	52	58	59	60	61	62	63	64	66	70	77	78	79
%	8	32	7	11	5	5	14	20	8	5	9	7	12	7	30	5

m/e	92	104	106	108	109	110	121	122	124	135	149	153	154
%	7	5	15	9	6	8	17	19	5	7	5	51	13

m/e	155	167	168	169	180	182	183	184	198	199	226	227(M)
%	7	21	20	6	6	84	10	9	7	33	5	100

m/e	228	229
%	13	11

2-(p-Tolyl)-1,3-dithiane (75).

m/e	45	46	51	65	77	78	89	91	92	105	105	121	134	135	136
%	6	6	5	8	9	6	5	24	9	5	10	6	12	84	32

m/e	137	153	154	155	168	169	170	181	195	196(M)	197	198
%	8	100	11	11	23	23	5	16	11	97	16	11

2-Phenyl-1,3-oxathiane (76).

m/e	39	41	42	44	45	46	47	50	51	52	59	63	73	74	75	76
%	13	36	6	5	18	41	6	7	20	5	5	5	6	100	11	7
m/e	77	78	79	89	91	105	106	107	121	122	180(M)					
%	35	9	16	5	6	26	5	10	8	5	23					

2-(o-Nitrophenyl)-1,3-oxathiane (77).

m/e	27	28	29	30	39	41	42	43	45	46	47	48	50	51	52	57	59
%	11	6	7	5	26	99	8	5	39	91	14	6	17	37	11	7	12
m/e	61	62	63	64	65	69	71	73	74	75	76	77	78	79	90	91	92
%	7	5	10	9	22	7	5	43	87	15	27	34	9	20	33	21	17
m/e	93	104	105	106	107	108	109	119	120	121	122	123	131	132			
%	14	33	14	6	6	7	7	34	11	36	14	6	34	5			
m/e	134	135	136	137	138	145	149	150	151	152	153	166	167				
%	44	100	62	14	8	5	5	18	35	11	6	33	7				
m/e	178	208	209(M-OH)														
%	10	53	53														

2-(m-Nitrophenyl)-1,3-oxathiane (78).

m/e	39	41	45	46	51	73	74	75	76	77	105	121	225(M)
%	5	25	9	22	6	6	100	8	9	8	7	5	25

2-(p-Nitrophenyl)-1,3-oxathiane (79).

m/e	39	41	42	45	46	51	73	74	75	76	77	105	150	225(M)
%	6	28	5	10	37	7	6	100	7	8	9	5	5	25

2-(o-Nitrophenyl)-1,3-oxathiolane (80).

m/e	39	45	50	51	52	58	59	60	61	62	63	64	65	75	76	77
%	5	17	10	20	6	5	32	82	16	7	7	6	13	5	16	24
m/e	78	79	89	91	92	93	104	105	108	109	118	120	121	122		
%	5	6	5	7	6	10	12	5	9	5	8	35	6	5		
m/e	133	134	135	136	137	150	151	163	165	193(M-H_2O)						
%	9	9	43	6	7	100	11	9	12	10						

2-(m-Nitrophenyl)-1,3-oxathiolane (81).

m/e	45	50	51	59	60	61	62	77	89	105	151	211(M)
%	11	5	7	16	100	10	6	7	5	5	12	14

2-(p-Nitrophenyl)-1,3-oxathiolane (82).

m/e	45	51	59	60	61	62	77	211(M)
%	11	6	15	100	9	6	5	12

2,2'-p-Phenylene-bis-1,3-dithiane (83).

m/e	73	74	77	91	105	106	119	121	122	135	136	137	149	165
%	14	31	6	11	36	12	12	30	7	10	12	8	13	20
m/e	166	167	175	176	240	241	242	249	314(M)	315	316			
%	45	8	50	6	60	11	12	12	100	20	22			

5,5,5',5'-d_4-p-Phenylene-bis-1,3-dithiane (84).

m/e	80	89	91	93	107	108	120	121	122	123	124	131	134	135
%	5	10	11	6	37	15	7	37	11	20	5	5	9	11

(84) - continued.

m/e	136	137	144	145	147	149	150	151	153	165	166	167	168
%	6	7	5	6	8	11	9	7	5	22	54	10	8
m/e	176	177	178	241	242	243	244	252	271	285	318(M)	319	320
%	45	12	6	6	64	12	9	10	2	2	100	22	21

2-Benzyl-1,3-dibromopropane (86).

m/e	39	51	65	91	92	115	117	129	130	131 (M-HBr$_2$)	132
%	6	5	12	100	12	8	8	5	6	17	6

trans-3-Methyl-1-phenylbut-1-ene (89).

m/e	91	92	103	105	115	116	117	128	129	131	132	145	146(M)
%	42	5	6	6	13	11	7	7	10	100	12	5	48
m/e	147												
%	7												

trans-3-Methyl-1-(d$_5$-phenyl)but-1-ene (90).

m/e	27	29	39	40	41	42	43	52	53	54	55	65	66	67	68	69
%	7	6	6	5	9	6	5	8	9	15	6	5	6	5	11	9
m/e	80	81	82	83	84	93	94	95	96	97	107	108	109	110	111	
%	8	10	18	9	17	7	14	21	75	5	5	5	7	16	13	
m/e	112	119	120	121	122	132	133	134	135	136	137	151(M)	152			
%	7	9	10	6	6	5	7	5	6	100	13	43	6			

PART B: Negative-Ion Spectra.

5,5-d_2-2-Phenyl-1,3-dithiane (49).

m/e	106	107	108	109	122	123	124	198(M)
%	6	100	7	9	84	13	6	6

2-(d_3-Phenyl)-1,3-dithiane (50).

m/e	105	106	107	125	126	127	199(M)
%	100	6	10	79	12	5	6

2-Phenyl-1,3-dithiane-2,^{13}C (51).

m/e	105	106	107	122	123	124	196	197(M)
%	100	4	10	35	50	8	2	3

2-(o-Nitrophenyl)-1,3-dithiolane (72).

m/e	137	139	167	168	169	227(M)
%	3	1	100	9	5	2

2-(m-Nitrophenyl)-1,3-dithiolane (73).

m/e	46	137	167	168	169	227(M)
%	8	1	100	8	4	1

2-(p-Nitrophenyl)-1,3-dithiolane (74).

m/e	46	137	151	167	168	169	225	226	227(M)
%	7	1.5	.6	100	9	5	.03	.01	.02

2-(o-Nitrophenyl)-1,3-oxathiane (77).

m/e	46	59	91	134	135	136	151	152	153	225(M)	226	227
%	19	2	8	98	70	8	55	6	10	100	11	5

2-(m-Nitrophenyl)-1,3-oxathiane (78).

m/e	46	89	121	151	152	191	192	225(M)	226	227
%	10	5	2	32	2	.6	.1	100	10	5

2-(p-Nitrophenyl)-1,3-oxathiane (79).

m/e	121	151	152	191	225(M)	226	227
%	3	100	8	2	90	8	5

2-(p-Nitrophenyl)-1,3-oxathiolane (82).

m/e	121	151	152	167	209	210	211(M)	212
%	2	100	9	.2	.4	.2	.5	.1

4,4,6,6-d$_4$-2-(o-Nitrophenyl)-1,3-dithiane (93).

m/e	108	134	167	168	169	170	171	172	244	245(M)	246	247
%	2	4	12	1	2	100	9	5	3	95	10	9

5,5-d$_2$-2-(o-Nitrophenyl)-1,3-dithiane (94).

m/e	107	134	167	169	170	171	172	241	242	243(M)	244	245
%	2	4	9	9	100	8	5	1	9	80	9	8

2-d-2-(m-Nitrophenyl)-1,3-dithiane (95).

m/e	105	107	168	169	170	208	242(M)	243	244
%	30	3	20	3	4	3	100	9	8

4,4,6,6-d$_4$-2-(m-Nitrophenyl)-1,3-dithiane (96).

m/e	105	106	167	168	169	170	211	244	245(M)	246	247
%	30	3	20	2	2	4	3	4	100	9	8

5,5-d$_2$-2-(m-Nitrophenyl)-1,3-dithiane (97).

m/e	105	107	167	168	169	170	208	242	243(M)	244	245
%	26	3	20	3	2	4	3	7	100	10	9

2-d-2-(p-Nitrophenyl)-1,3-dithiane (98).

m/e	105	106	136	137	167	168	169	207	208	241	242(M)	243	244
%	4	2	7	11	42	22	4	5	6	8	100	10	8

4,4,6,6-d$_4$-2-(p-Nitrophenyl)-1,3-dithiane (99).

m/e	107	108	137	138	167	168	169	170	209	210	244	245(M)	246	247
%	2	4	13	7	34	40	5	5	5	5	4	100	10	8

5,5-d$_2$-2-(p-Nitrophenyl)-1,3-dithiane (100).

m/e	107	136	137	167	168	169	209	241	242	243(M)	244	245
%	6	22	2	80	9	5	12	2	12	100	10	8

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