# A MASS SPECTROMETRIC STUDY

# OF SOME PESTICIDES

# A Mass Spectrometric Study of Some Pesticides

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B R O C K  U N I V E R S I T Y

St. Catharines, Ontario

1 9 7 1

To

Prof. Martin Stuart Gibson,

A Kind "Friend, Philosopher and Guide"

And Above All A Good Teacher

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The study of pesticides by mass spectrometry presented in this thesis has been carried out in the Department of Chemistry, Brock University, during the period, September 1970 - August 1971.

Words alone cannot describe the author's sense of gratitude to his supervisor, Prof. J. M. Miller, for the suggestion of the problem, for the guidance and for the help he rendered in ways more than one. But for the timely service rendered so kindly by Mr. Jim Ross and Mr. Tony Biernacki, this work would have taken longer to complete. Thanks to them are still due. It is a pleasure to acknowledge Mrs. E. Blair who has taken immense care and pains in typing out this manuscript.

The financial assistance from the Department of Chemistry, Brock University, which made this work possible is gratefully placed on record.

## ABSTRACT

The fragmentation processes in the mass spectra of a series of organophosphorus, organochlorine, thio and dithiocarbamate as well as a number of miscellaneous pesticides have been studied in detail by using the Bendix time-of-flight, MS-12 single-focussing and MS-30 double-focussing mass spectrometers. Interpretation of all the spectra have been presented; their modes of dissociation elucidated, aided by metastable transitions wherever possible and the structures of the various fragmentation species postulated wherever feasible. The fragmentation mechanisms are based on the concepts of inductive, resonance and steric effects. Multiple bond cleavages accompanied by simultaneous bond formation and rearrangement reactions involving cyclic transition states have clarified the formation of various ions. Due emphasis has been placed on the effect of the functional groups or substituents in altering the mass spectral behaviour of the pesticides as they form the basis for the identification of the otherwise identical pesticides.

The organophosphorus pesticides which have been studied include i) the phosphates (eg: DDVP and Phosdrin); ii) phosphorothionates (eg: Parathion, O-2, 4 dichloro phenyl O, O-diethyl thionophosphate); iii) phosphorothioites (eg: Tributyl phosphorotrithioite); iv) phosphorothioates (eg: Ethion) and v) phosphorodithioates (eg: Carbophenolthion). Cleavages and rearrangements of the ester moiety

dominate the spectrum of phosdrin while that of DDVP is dominated by the fragmentation modes of the $(CH_3O)_2\overset{+}{P}=O$ moiety. Fragmentation of the $(CH_3O)_2\overset{+}{P}=S$ characterises the spectrum of $(CH_3O)_2\overset{S}{\overset{\|}{P}}-Cl$ while cleavages of the $(C_2H_5O)_2\overset{+}{P}=S$ species mark the spectra of parathion and O-2, 4-dichlorophenyl O, O-diethyl thiophosphate. The $\alpha$ and $\beta$ cleavages of the thioether function rather than cleavages of the $(C_2H_5O)_2\overset{+}{P}=S$ signify the spectrum of carbophenolthion. Tributyl phosphorotrithioite behaves more like an aliphatic hydrocarbon than like the corresponding phosphites.

The isopropyl and butyl esters of 2, 4 dichlorophenoxy acetic acid show cleavage and rearrangement ions typical of an ester. In spite of its structural similarity to pp' - DDT and pp' - DDD, Kelthane has a completely different mass spectral behaviour due to the influence of its hydroxyl function.

The thiocarbamate pesticides studied include Eptam and Perbulate. Both are structurally similar but having different alkyl substituents on nitrogen and sulphur. This structural similarity leads to similar types of (N-C), (C-S) and (S-alkyl cleavages). However, perbulate differs from Eptam in showing a rearrangement ion at m/e 161 and in forming an isocyanate ion as the base peak. In Eptam the base peak is the alkyl ion. The dithiocarbamate, Vegadex, resembles the thiocarbamates in undergoing simple cleavages

but it differs from them in having a weak parent ion; in the formation of its base peak and in undergoing a series of rearrangement reactions.

The miscellaneous pesticides studied include 1-Naphthalene acetic acid - methyl ester, Piperonyl butoxide and Allethrin. The ester is stable to electron impact and shows only fewer ions. Piperonyl butoxide, a polyether, shows characteristics of an ether, alcohol and aldehyde. Allethrin is regarded as an ester of the type R-C-O-R' with R being a substituted cyclopropane moiety and $\overset{O}{\overset{\|}{\text{C}}}$ R', a substituted cyclopentenone moiety. Accordingly it shows cleavage ions typical of an aliphatic ester and undergoes bond ruptures of the cyclic moieties to give unusual ions. Its base peak is an odd electron ion, quite contrary to expectations.

## Chapter 1

## INTRODUCTION

## i) Study of Fragmentation Processes By Mass Spectrometry

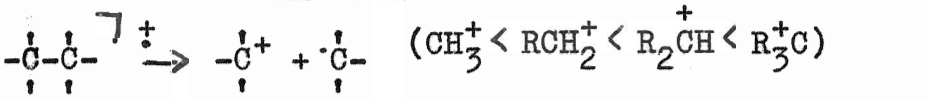
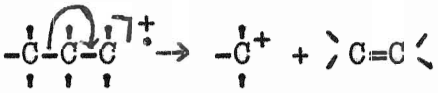
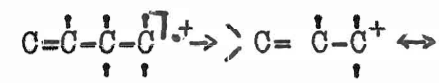
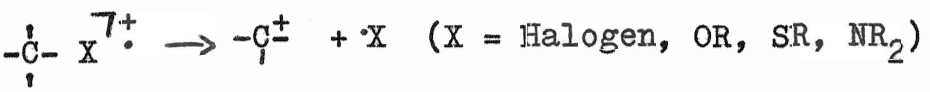
Physical organic chemistry has made great strides in the study of ions from organic compounds. Carbonium ions, carbanions, oxonium ions and quarternary ions are typical examples. In fact, these ions assume special importance as intermediates in many reactions. Such studies, however, have necessarily been in solution. In contrast, Mass Spectrometry offers a unique opportunity for the study of the chemistry of excited organic ions without the influence of neighbouring molecules or solvent effects.

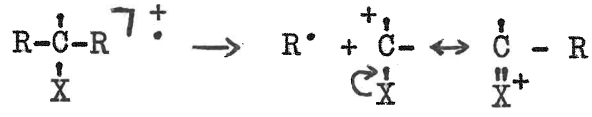
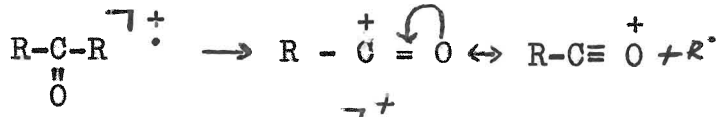
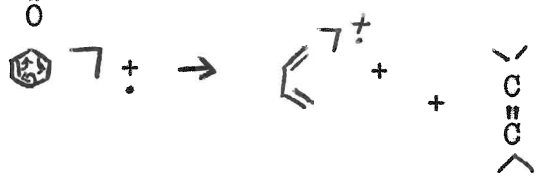
The mass spectrum of a compound usually results from its bombardment by electrons (usually 70 ev) and consists, in general, of a series of peaks which can be directly related by fragmentation (or dissociation) and rearrangement processes to the structure of the molecule. Explanation of these processes involves the application of such basic principles of physical organic chemistry as polarisability, hyperconjugation, resonance, steric, inductive and field effects. Many books[1-4] describe the general fragmentation behaviour of the various groups of compounds based on the above principles and a general picture of fragmentations based on charge localization on a particular bond has been outlined by Mclafferty[5,6] and Budziekiewics and co-authors[3]. A well-documented review has been written on the general classification of mass spectral

fragmentation mechanism[7]. A treatment of the mechanism of the fragmentation behaviour of organic molecules, is, thus, perhaps redundant here. Suffice it to say that the favoured decomposition pathways are determined by i) the bond lability of the precursor ion; ii) bond stability of the product ion and iii) steric requirements for the transition state. In addition, ion-decomposition paths involving multiple bond cleavages and/or rearrangements in complex molecules are also evident. A detailed account of the latter process has been given by Cooks[8] in a recent review.

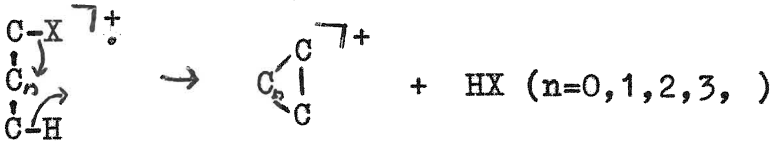
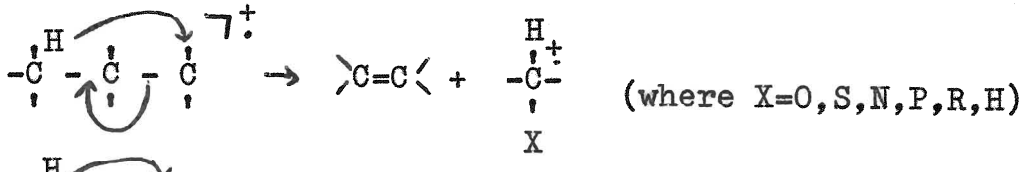
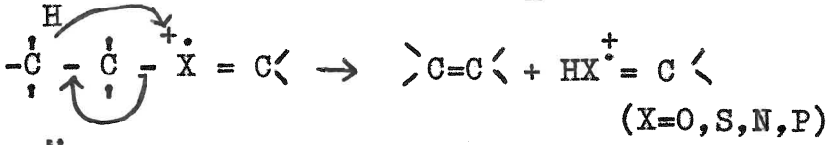
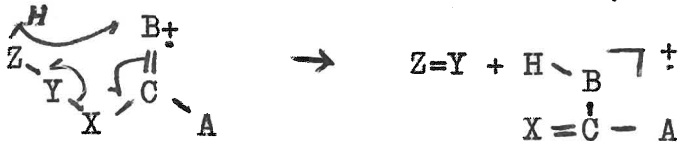
However, the fragmentation processes leading to intense peaks in the mass spectrometer may be summarized below: The fragmentation behaviour of an organic compound falls into two main categories: (i) Bond-cleavages (ii) Rearrangements.

Bond cleavages consist of the following types:[1]

| Type | Process |
|---|---|
| $A_1$ |  |
| $A_2$ |  |
| $A_3$ |  |
| $A_4$ |  |
| $A_5$ |  |

| Type | Process |
|---|---|
| B |  |
| C |  |
| D |  |

Rearrangements:

| | |
|---|---|
| $E_1$ |  |
| $E_2$ |  |
| F |  (where X=O,S,N,P,R,H) |
| G |  (X=O,S,N,P) |
| H |  |

Simple cleavages which are accompanied by new bond formations are particularly favoured (e.g. oxonium ion, acylium ions etc.). Rearrangements are invariably associated with new bond formation. Cyclisation of the ion to form favourable transition states is evident in many molecular systems. The 6-membered

ring transition state expected on steric grounds is heavily favoured for a number of rearrangements.[6,9]

Mass spectrometry, in its present stage, is not able to determine molecular structures independently. But a lot of correlations observed between mass spectral features and molecular structures[10] permit conclusions to be drawn in many cases. Use of high resolution mass spectrometry, appearance potential determinations, isotopic labelling studies, metastable transitions, negative ions, field and chemical ionizations and preparation of a derivative of the compound in question may further aid such conclusions. Ultimately, it may even be possible in future to gather, calculate, store, interpret and report all the data for each spectrum, thereby enabling the prediction of the structure of a given compound from its spectrum. We hope that the work on pesticides set out in the following pages, is, at least, one step forward in achieving this goal, although in a modest way.

## ii) Pesticides

Of the many control mechanisms presently in use for changing the face of the landscape, the various pesticidal chemicals may be regarded as of critical importance. The subject of pesticides however, is too vast for a detailed presentation here. Several books[11-21] give generalized accounts of pesticides while many technical and trade journals[22-28] devote their attention to the nature, production, marketing, use and hazards of these chemicals.

Pesticides have been classified in several ways based on targets of applications; on structure; botanical origin; psysiological action or even on the purpose of application. Based on structure, these chemicals may be grouped into (1) Organic chlorine pesticides which have been the most widely used; (2) Organic phosphorus pesticides which form the second major group and perhaps comprise the largest number of new materials that are being tested and synthesised; (3) carbamates, thiocarbamates and dithiocarbamates which form a new class of chemicals, stimulated by the development of insect resistance to the chlorinated hydrocarbons and organophosphorous compounds and by the search for control agents which are relatively non-toxic to warm-blooded animals and which do not accumulate as residues in animal tissues; and (4) several miscellaneous pesticides such as those belonging to the pyrethrum group, the triazines, ureas, organo mercurials and a host of inorganic chemicals.

Although pesticides are effective controlling agents of the environment, they are at the same time a potential source of environmental pollution, because, by their very nature, they are toxic and are thus harmful to living organisms other than their intended targets. This is particularly so, because, the pesticide having done the job, does not disappear but becomes a factor of the environment in the form of a "residue". (Residues are reduced portions or metabolites of the original substance). In fact, all the pesticidal compounds in common use produce residues that survive for noticeable periods in soil, water or air. These residues are normally transferred to the living systems by physical or biological means. The exact effects of the pesticides on the human system are not yet understood. It is only known that the organo chlorine pesticides are toxic, persistent and resistant to decomposition by microbial organisms and normally affect the central nervous system. The phosphorus compounds, though toxic, can be metabolised to less toxic residues but they are generally potential inhibitors of the neural enzyme, cholinstearase, thereby paralysing the transmission of impulses to glands and muscles. Carbamates are the least toxic while their physiological action is similar to that of the phosphorus compounds.

The toxicity of these pesticides and pesticide residues and the harmful effects they cause to living organisms certainly calls for safe limits to which they can be applied so that they are brought under effective environmental control.

An analysis of the compound or its residue through its identification and determination, thus, becomes imperative. It is further important that a method be available which is as insensitive to impurities as possible and which requires a minimum amount of the sample. Of the four methods of analysis viz; biological, chemical, chromatographic and spectroscopic, the use of gas liquid chromatography has certainly revolutionised the pesticide residue analysis over the past decade but it can be used only for volatile materials. Infra-red spectroscopy certainly provides a finger-print index of the pesticide and its residue but it lacks sensitivity and is effective only for a single pesticide at any time and the presence of even small amounts of impurities can invalidate the data. But the development of mass spectroscopy and the coupling of gas chromatography to mass spectrometers for its application to pesticide research has overcome the above limitations and it will not be wrong to anticipate its increasing use in future to the advancement of pesticide analysis and the detection of such low levels will, no doubt, give an idea as to the permitted dose in any mammal.

The present work on the organo phosphorus, organo chlorine and carbamate and thiocarbamate pesticides with the mass spectrometer is but a pointer to the future.

iii) Study of Organo Phosphorus Pesticides by Mass Spectrometry

The study of organo phosphorus pesticides by mass spectrometry is a sequel to the study of organo phosphorus compounds in general and a brief introduction to the mass spectra of the latter thus seems appropriate. The methyl phosphines,[29-33] whose mass spectra were the first to be examined, were completely different from each other in their behaviour. For example, where the ion produced by the loss of $CH_3$ gave the base peak for $(CH_3)_3P$ it was of low abundance for $(CH_3)_2PH$ and almost negligible for $CH_3PH_2$. A series of rearrangement ions involving loss of the ethylene molecule marked the spectra of the ethyl phosphines,[29, 30] while bond-forming reactions involving atoms other than hydrogen was a feature in the case of the aromatic phosphines[34-38]. Simple cleavages of the (P - O) bond dominated the lower trialkyl phosphite spectra[39] but a series of hydrogen rearrangements with migration of the hydrogen from the alkyl to the electrophilic phospate entity, subsequent to a prior alkyl chain fission was of importance to the higher alkyl phosphites[40]. Migrations of the hydrogen atom was found to occur to the oxygen atoms as well. Interestingly enough, all the higher phosphites (higher than ethyl) had a common base peak at m/e = 83 ($H - \overset{+}{P}(OH)_3$). In comparison, the triphenyl phosphites,[40] showed fewer rearrangement ions. Ions of importance in the spectra were the simple cleavage species. Rearrangement ions

also dominated the spectra of the homologous phosphinic acids ($R - \overset{O}{\overset{\|}{P}}(R) - OH$), di- and tri-alkyl phosphinates[40] ($\begin{matrix} R \\ H \end{matrix}\!\!>\!P\!<\!\begin{matrix} O \\ OR \end{matrix}$ and $\begin{matrix} R \\ R \end{matrix}\!\!>\!P\!<\!\begin{matrix} O \\ OR \end{matrix}$ respectively) and the diphenyl phosphinates[41-45]. In all these cases, the formation of the base peak involved loss of an olefin with subsequent migration of a hydrogen atom from the $(M - R)^+$. The dialkyl hydrogen phosphorates (also called dialkyl phosphites, of the general formula, $H - \overset{O}{\overset{\|}{P}}\!<\!\begin{matrix} OR \\ OR \end{matrix}$)[46,47] were similar in their behaviour to the corresponding trialkyl phosphites. The general mode of fragmentation involved cleavages of the (C - O) and (P - O) linkages. In general, the migratory aptitude was found to increase with increasing size of the alkyl group and accordingly the m/e value of the rearranged base peak increased. This would help confirm the structure of the compound as well as distinguish the dialkyl phosphites from the trialkyl phosphites and phosphates as the base peak in the two latter cases involved to $P^+(OH)_3$ and $P^+(OH)_4$ moieties respectively. Breakdown of the carbon chain was the major mode of cleavage for the higher phosphonates. The occurrence of $\beta$ -cleavage to the ether linkage, scission of the (P - O) bond and migration of the hydrogen was the interesting phenomenon in the spectra of the dialkyl $\beta$ -alkoxy ethyl phosphonates[47]. The diaryl, aryl phosphorates[34, 42] had abundant molecular ions and suffered a number of unusual rearrangements. Decreasing intensity of the molecular ion with increasing alkyl size, and shifting of one or two hydrogens from the substituent groups to the strongly

electrophilic phosphate central body dominated the phosphate spectra.[45,47,48,49] All the phosphates had a common base peak in the resonance-stablised $P^{+}(OH)_4$ species in which the phosphorus is pentacovalent. As for the tri aryl phosphates,[49,50] the parent ion itself was the base peak and the spectra were marked by a series of polyphenyl rearrangement peaks with or without oxygen. The dialkyl aryl phosphates[50] also showed extensive rearrangements. Compounds having the (P = S) bond have received recent attention.[51] Simple cleavage reactions, molecular ion rearrangements of the type

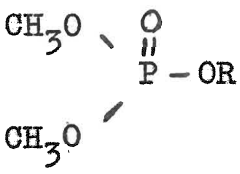
$$-\underset{\underset{S}{\|}}{P}-OR \longrightarrow -\underset{\underset{O}{\|}}{P}-SR$$

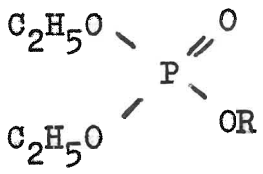
aryl and alkyl migrations to sulphur as shown by the formation of ions such as $\emptyset S^{+}$, $MeS^{+}$ etc., bond-formations between substituents on phosphorus, loss of $\dot{S}H$ from the molecular ions in which the H was derived from the alkyl or aryl group and hydrogen rearrangements to give a phenol ion or an isomer in compounds having a phenoxy substituent were characteristic of several O-alkyl and S-alkyl phosphorothioates[51,52].

The organo phosphorus pesticides may be broadly classified into five main divisions: (i) The Phosphates; (ii) The Phosphorothionates; (iii) The Phosphorothioates; (iv) The Phosphorothiolates and (v) The Phosphorodithioates. Their spectra may be treated accordingly as follows.

(i) The Phosphates

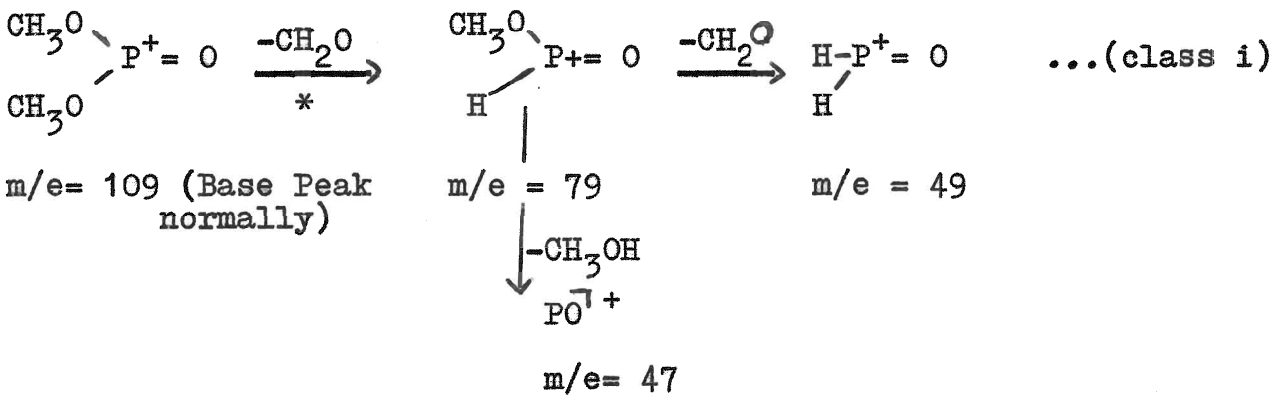
All the phosphate pesticides possess one of the following structures:

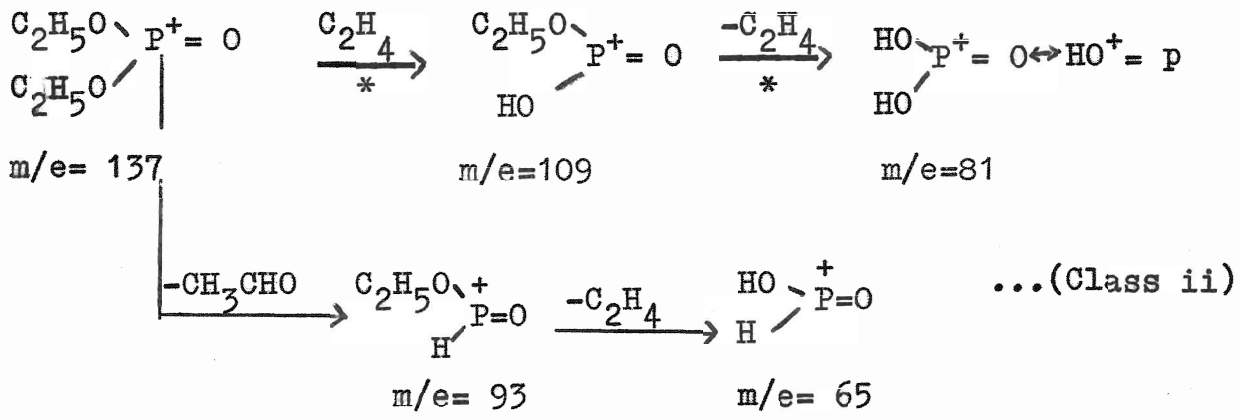
i) 

ii) 

where R represents a substituent which is different for different compounds

DDVP, Phosdrin, DMMEP, Phosphamidon and Trimethyl phosphate belong to class (i); DEMMP, Paraoxon and the oxygen analogue of diazinon belong to class (ii). All compounds belonging to class i) were found to exhibit the same dissociation pattern for the common structural moiety $(CH_3O)_2P^+ = O$ and similarly in the case of class ii), identical behaviour was observed for the common $(C_2H_5O)_2 P^+ = O$ species. The dissociation of both is given in scheme - 1.



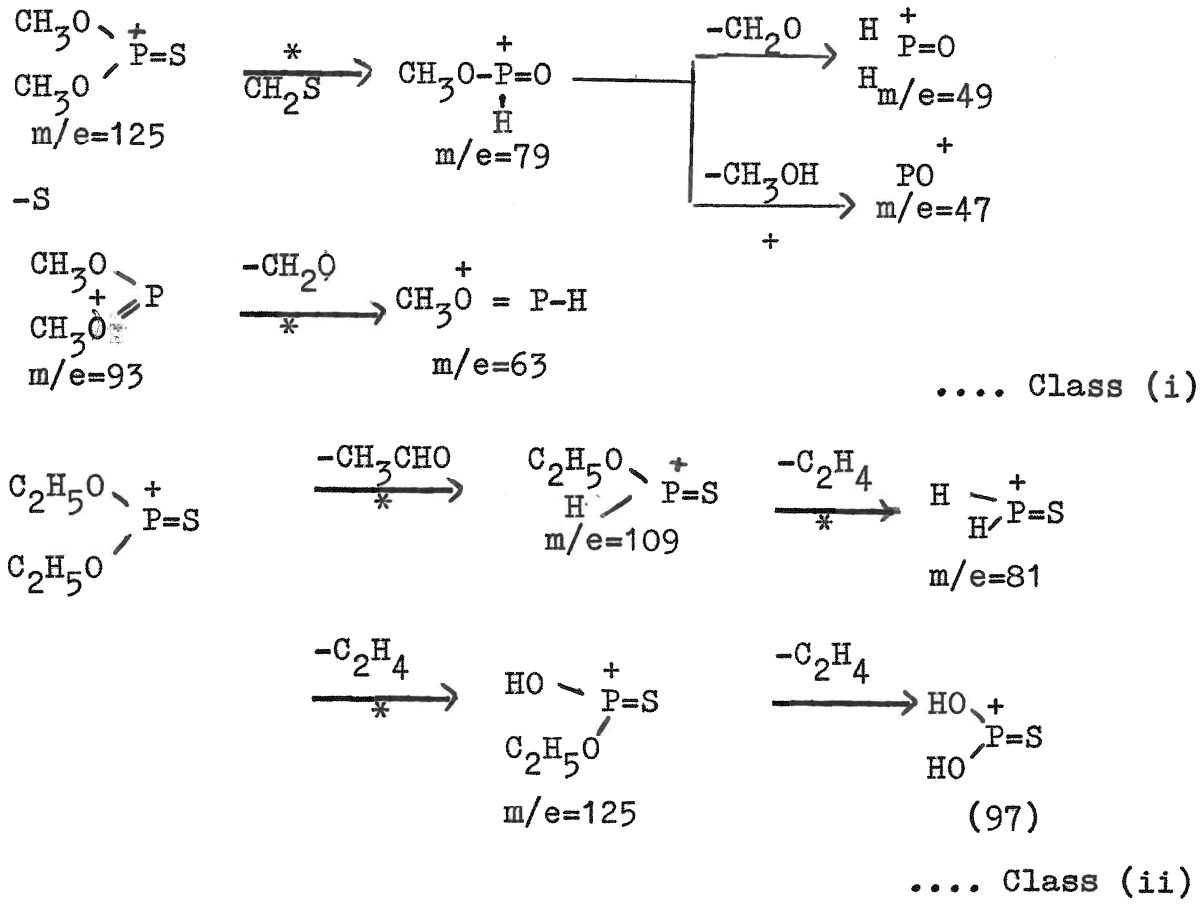



In Class (i), loss of a molecule of formaldehyde with the subsequent transfer of a hydrogen to the phosphorus atom gives rise to the ions of m/e - 79 and 49 resp'ly.while in class (ii) ions of m/e = 109 and 81 are formed by loss of a molecule of ethylene in a Mclafferty rearrangement process.

Details regarding the modes of fragmentation of the (OR) part of the above phosphate pesticides are lacking in earlier works[53-57]. As for Paraoxon only the field ionizations spectrum has been reported[57] and this indicates only the molecular ion.

(ii) <u>The Phosphorothionates</u>[51-56]

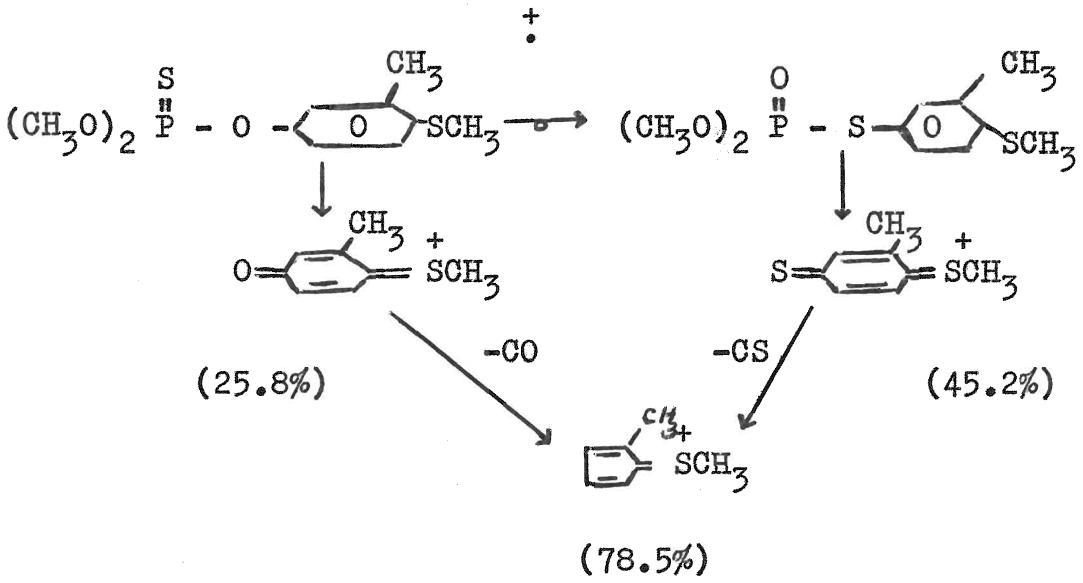
Just as in the case of the phosphates, the phosphorothionate pesticides possess either the $(CH_3O)_2$ P(=S) - OR or the $(C_2H_5O)_2$ P(=S) - OR structures. Sulfotepp, methyl parathion, Ronnel etc. belong to class (i) while parathion, delnav, diazinon etc. belong to class (ii). As before, the dissociation common to compounds in each class is depicted in Scheme - 2.




As seen from the scheme, two competing modes of fragmentation behaviour seem to dominate the spectra of these compounds: (i) eliminations of an alkyl substituent with subsequent migration of hydrogen and (ii) cleavage of the (P-O) bond with or without subsequent hydrogen rearrangement. Besides, they may also lose a sulphur atom or a sulphydryl radical (SH ):

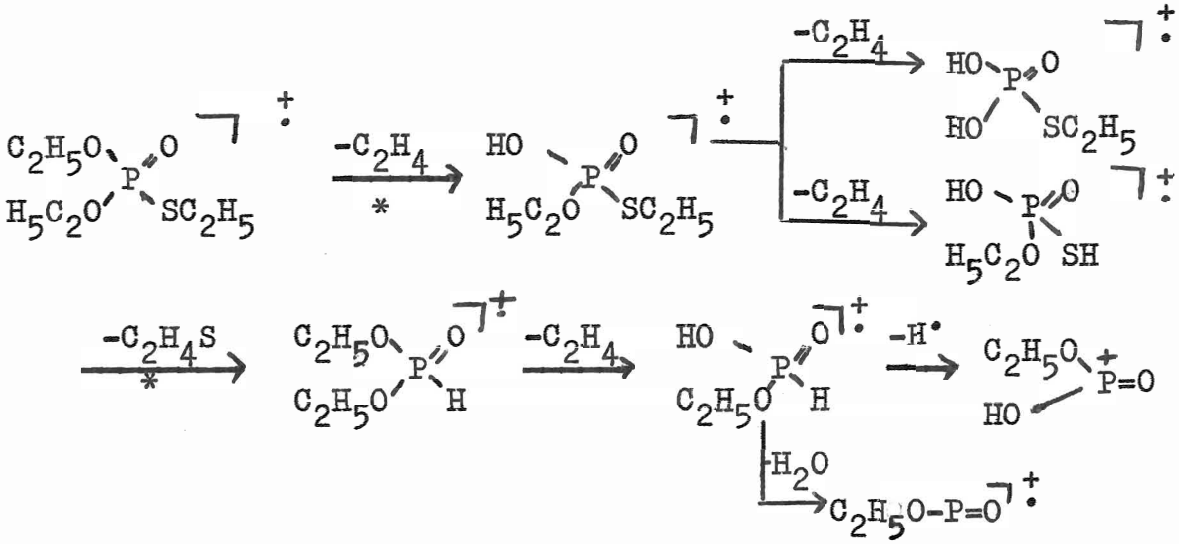
Isomerization of the thiono compound to the thiolo compound has also been observed as peaks were found characteristic of

the $(CH_3O)_2P^+ = O$ or $(C_2H_5O)_2 P^+= O$ dissociation pattern. This isomerization is believed to be an electron-impact induced phenomenon.[51] In these cases also, characterisation of the R part of the molecule has not yet been achieved excepting in Fenthion[56] which suffered a ring contraction involving loss of CO or CS as the case may be:

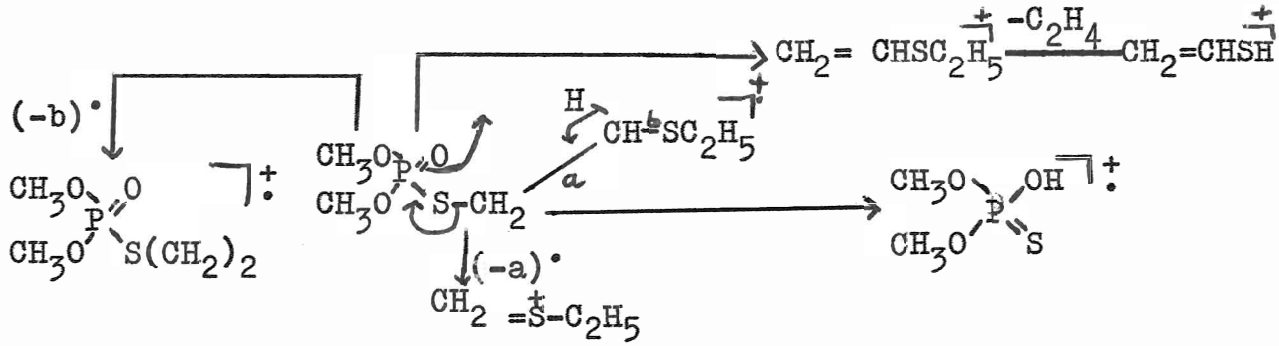



(iii) Phosphorothiolates[54]

The phosphorothiolates are isomeric with the thionates. Accordingly they may be represented as $(CH_3O)_2\overset{O}{\underset{SR}{P}}$ and $(C_2H_5O)_2\overset{O}{\underset{SR}{P}}$. Thus, in their common structural moiety they resemble the phosphates and the dissociation scheme given therein for the species holds here too. The only interesting feature in these molecules is the dissociation pattern of the compound as a whole: (Scheme 3)



The R part of only Meta-Systox[52] has been characterised.



Bar graphs alone of the field ionization and electron-impact spectra of the oxygen analogues of Malathion and Dimethoate are given in the literature[55].

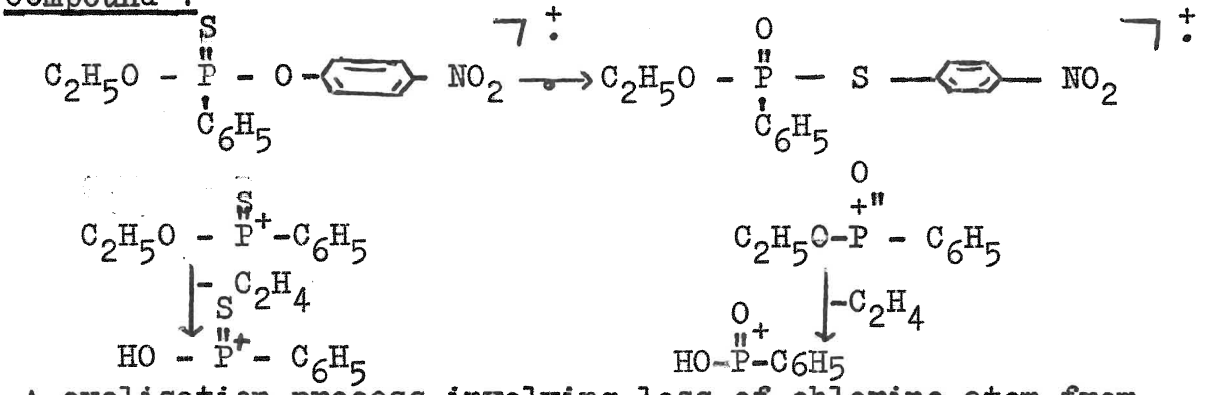
(iv) Phosphorothioates

The phosphorothioates which have been examined by mass spectrometry include the following compounds:

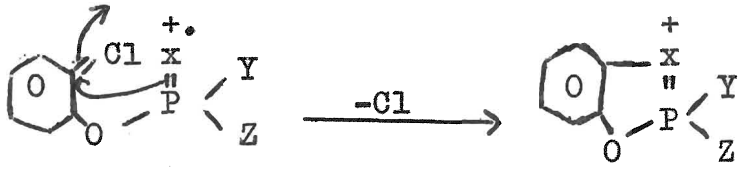
1) O-ethyl, o, p-nitro phenyl phosphorothioate[52,53]
2) o-p cyano phenyl O-ethyl phenyl phosphorothioate[54]
3) O-ethyl, o-2,4,5 trichlorophenyl ethyl phosphorothioate[54]
4) Zytron (DOWCO-118)[52,53]
5) Dimethoate[54]

Bar graphs of the spectra of (2, 3 and 5) have been published without any discussion of their fragmentation. The fragmentation patterns of (1 and 4) were however, in agreement with the other groups of phosphorus pesticides. Besides undergoing simple cleavages, they revealed interesting rearrangement reactions involving loss of ethylene, e.g.:

Compound 1



A cyclisation process involving loss of chlorine atom from the aromatic ring of DOWCO-118 set it apart from the other compounds of its group. Thus,

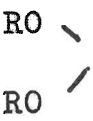


where x = O or S

and Y, Z = $-\dot{O}CH_3$ or $-\dot{O}C_2H_5$

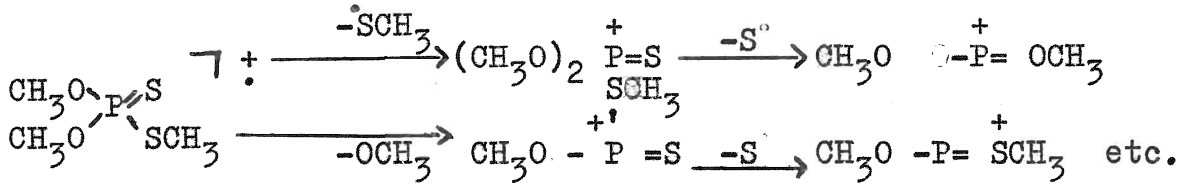
(v) Phosphorodithioates

Dithioates are characterised by the general formula,



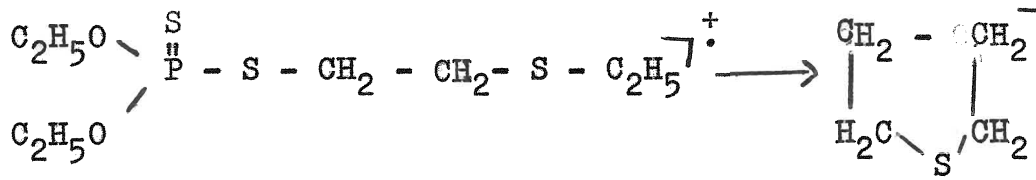
where RO = $OCH_3$ (class i) or $OC_2H_5$ (class ii)

and R' is any substituent. Dimethoate, Malathion, Methyl-trithion, Imidan and Guthion belong to class (i) while Disyston, Ethion, Delnav, Trithion, Disystonsulfoxide, Thometon, Thimet and Phenkapton belong to class (ii). All these pesticides have been examined by mass spectrometry but the discussion presented is of a very fragmentary nature.[52-55] Due to their structural similarity to other classes of phosphorus compounds they exhibit a number of characteristics similar to those observed for the phosphates or phosphorothionates. Thus they suffered simple cleavages, involving loss of OR or SR' and subsequent hydrogen rearrangement or loss of an olefin: e.g.:[54]



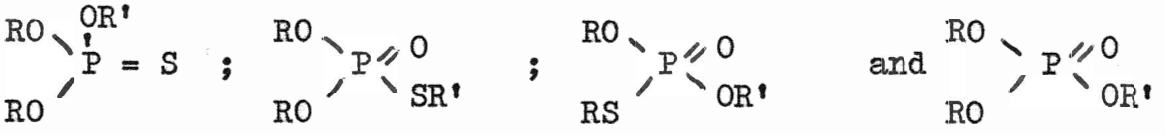
O, o-dimethyl s-methyl Phosphorodithioate (TMDTP)

The corresponding diethoxy compound (TEDTP) underwent elimination of $C_2H_4$ to give a series of rearrangement ions. The $(HO^+)_2PO$ rearrangement ion accounted for the base peak in (m/e = 97) ethion and Delnav and intense peaks in Disyston and Trithion[54]. The ion-configuration of the base peak of dimethoate (m/e = 87) was not readily apparent. Formation of a cyclic ion accounted for the base peak in Di-syston[53].



A number of unusual rearrangements involving hydrogen migrations were observed in the spectra of Trithion, Methyl trithion, Malathion, Imidan and Guthion[52,53]. The base peaks in these cases were formed by β-cleavage.

Thus, in conclusion, we see that the various organophosphorus pesticides which have been investigated hitherto have the following four common structural patterns:



(1) (2) (3) (4)

Their spectra, therefore, were similar to each other in many ways with differences occurring only in the OR' or SR' part of the molecule. Detailed mass spectral analysis of the OR' or SR' entity thus seems to be important in elucidating their characteristics and subsequently their identification. In the past, individual phosphorus pesticides were identified mainly from the mass of their molecular ion and isotopic pattern. The unique behaviour of the OR' or SR' part of each individual pesticide should serve equally well in aiding such identification. Detailed studies of this nature are however lacking in the literature. The mass spectra of organo phosphorus pesticides which form part of the subject matter of this dissertation have been interpreted with particular emphasis on the

OR' or SR' part of the molecule and it is hoped that this would lead to a more unambiguous identification of a given pesticide.

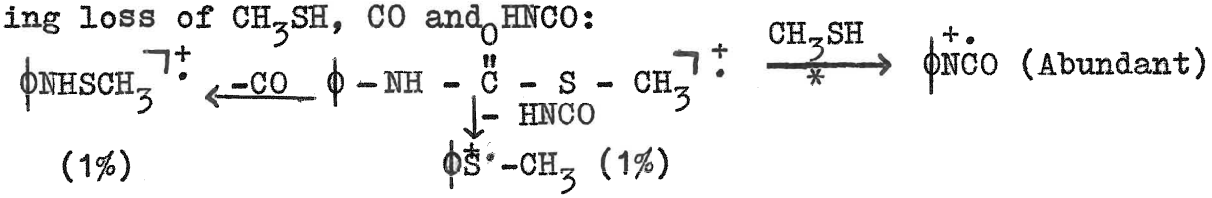
## iv) Mass Spectra of Thio and Dithio Carbamate Pesticides

As in the case of organo phosphorous pesticides, a brief but general introduction to the mass spectra of thiocarbamates and dithiocarbamates is useful to the study of the mass spectral properties of the pesticides belonging to this group.

Studies on thio- and dithiocarbamates seem to have received little attention.[58,59] More work appears to have been done on carbamates[58-63]. The dialkyl substituted carbamates, as a rule, suffered simple changes involving loss of R , RO and ROC(=O) etc., while the mono aryl substituted compounds showed a number of interesting rearrangement reactions involving transfer of hydrogen from the nitrogen atom to the oxygen of the alkoxy group and vice versa. Skeletal rearrangements involving loss of $CO_2$ were also common. The analogous sulphur compounds (i.e., the thiocarbamates), as studied by Thomson et al[59] showed considerable variations in their behaviour. No generalisations were thus possible. A formal discussion alone of the various individual compounds seems appropriate:

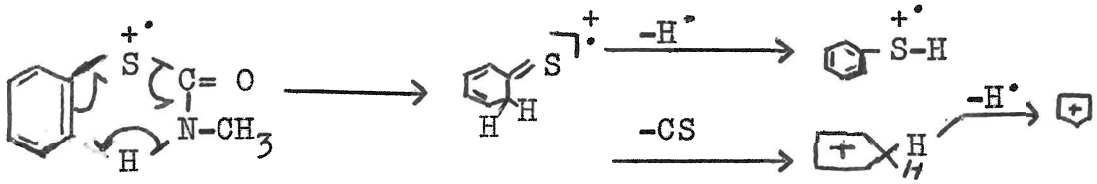
### (i) S-methyl phenyl thiocarbamate[58]

This compound differed from the corresponding carbamate in undergoing a series of rearrangement reactions involving loss of $CH_3SH$, CO and HNCO:

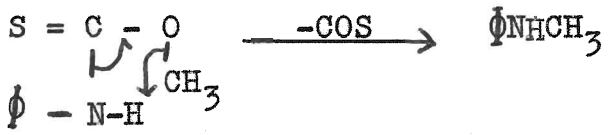


(ii) S-phenyl N, N-dimethyl thiocarbamate[58] gave the $\phi SN\langle^{CH_3}_{CH_3}$ ion arising through the loss of CO as before but did not show losses of $CH_3SH$ or HNCO. Loss of $CH_3S\phi$, however, led to the formation of the unique $\phi\overset{+}{S}CH_3$ ion.

(iii) S-phenyl methyl thiocarbamate[58] showed a peak resulting from the elimination of HNCO but no peaks involving elimination of CO or $CH_3SH$. A skeletal rearrangement involving transfer of hydrogen from nitrogen to the aromatic ring in a four-membered transition state was a feature of its spectrum:




(iv) Methyl phenyl thiocarbamate[58] eliminates a molecule of COS with subsequent migrations of a methyl group from oxygen to nitrogen:




It does not show loss of $CH_3SH$, CO or HNCO.

The substitution of one hetero atom (viz. sulphur) for another (viz. oxygen) in otherwise identical compounds affects the fragmentation behaviour, thereby preventing the "a priori"prediction of fragmentation modes in such compounds.

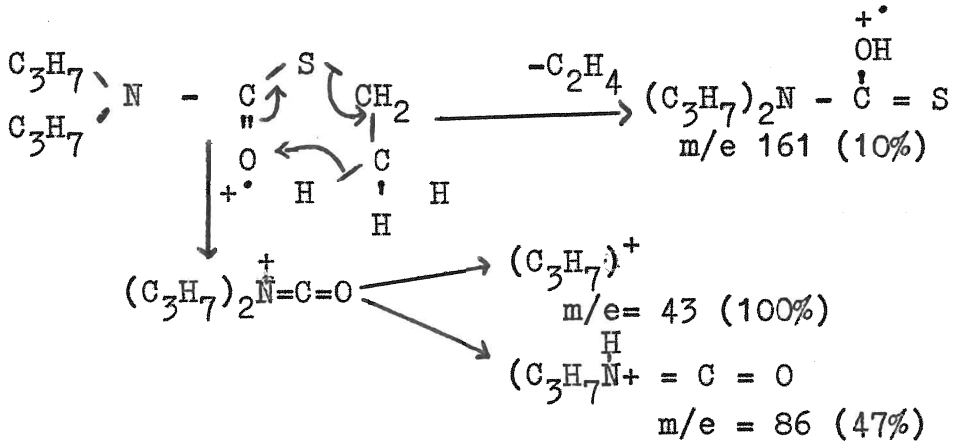
As for the dithio carbamates, methyl phenyl dithio carbamate[58] was found to behave much the same way as methyl

phenyl thiocarbamate but without undergoing any rearrangement reactions. The phenyl methyl dithiocarbamate dissociated in the same way as its oxygen analogue with $\phi S^+$ and $CH_3\overset{+}{N}CS$ being the most abundant ions. No further studies on dithiocarbamates were reported.

## The Pesticides

The mass spectra of several N-methyl, N-phenyl, N, N-dimethyl, N-aryl and a number of heterocyclic carbamate pesticides have been discussed[59,62]. But the mass spectra of only one thiocarbamate pesticide and five dithiocarbamate pesticides[59] have been so far reported. The interpretation given is, further, very brief and fragmentary.

Thus di-n-propyl s-ethyl thiocarbamate ("Eptam") was found to undergo two major rearrangements - one involving loss of ethylene and the other involving loss of propylene. Simple cleavage of the $C_3H_7$-N bond gave the base peak ($C_3H_7^+$ , m/e = 43) in the spectrum:



The monomeric dithiocarbamate pesticides[59] (Ferbam-dimethyl dithiocarbamic acid, $Fe^{+3}$ salt, Ziram - the corresponding $Zn^{+2}$ salt and Thiram $\left[(CH_3)_2N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-N(CH_3)_2\right]$ decomposed the same way as the aryl N. N-dimethyl carbamates.[60,61]

$$\left[(CH_3)_2\,N-\overset{S}{\overset{\|}{C}}-S\right]_X \text{Metal}^{\cdot+} \longrightarrow (CH_3)_2\,N=C=S^{+}$$

The Zinc salt also suffered a simple cleavage of the molecular ion to give

$$\left[(CH_3)_2N-\overset{S}{\overset{\|}{C}}-S\right]_2Zn^{\cdot+} \xrightarrow{-(CH_3)_2NCS_2} (CH_3)_2N-\overset{S}{\overset{\|}{C}}-S-Zn^{\cdot+}$$

$$(CH_3)_2NCS_2^{+} \longrightarrow (CH_3)_2N^{+}$$

The two fungicidal polymeric dithiocarbamates (Zineb and Maneb ) did not give the parent ion and they fragmented in a way similar to those of ethylene bis dithiocarbamates:

$$(-S-\overset{S}{\overset{\|}{C}}-\overset{H}{\underset{|}{N}}-\underset{H\ H}{C}-\overset{H}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-S-ZN)_X-S-\overset{S}{\overset{\|}{C}} \xrightarrow[-2H]{-ZnS} S=C=N-CH_2^{+}$$

$$S=C=N-CH_2 \quad m/e=144\ (77\%)$$

$$S=C=N=CH_2 \quad m/e=72\ (100\%)$$

It would thus appear that more studies are needed in order to draw any generalised conclusions as to the mass spectral properties of the thio and dithio carbamate pesticides. It may be observed that these pesticides are of recent origin and are rapidly replacing the halogenated and organo-phos-phosphorus pesticides because of their less toxic nature and lower persistence. As a rule, considerable amount of research

must be done in order to ascertain the composition of the residue under ordinary circumstances. But mass spectrometry would give quick information as to the nature of the residue (i.e., whether it is the original compound or its metabolite) if a reference spectrum is available. The need for extensive study and generalisation on these pesticides is thus obvious.

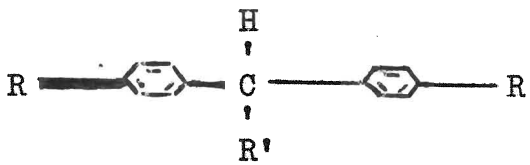
## v) Mass Spectra of Chlorinated Pesticides

As most of the chlorinated pesticides contain the chlorine atom either in the aromatic ring or in the side chain, a brief introduction to the mass spectral behaviour of such compounds may precede the study of pesticides.

In the case of ring-substituted chlorinated aromatic hydrocarbons loss of ring chlorine, often leads to a prominent peak[64]. When the alkyl group is larger than methyl, ions arising from the $\beta$ -cleavage ( $\beta$ w.r. to the ring) of the alkyl group also tend to predominate. When cleavage or more than one bond is possible, loss of HCl or $CH_3Cl$ may act as a driving force to yield stable abundant ions and this would be particularly the case when the chlorine and methyl are ortho with respect to each other ("ortho effect"). When the chlorine atom is in the side chain (e.g.: $Ar\text{-}CH_2\text{-}CH_2\text{-}Cl$) the (C-C) bond $\beta$ to the ring will cleave preferentially (e.g. loss of $CH_2Cl$ in the above example) due to the formation of the resonance stabilised tropylium ion[65]. Formations of a phenyl ion may be favoured whenever it can be stabilised (e.g.: poly alkyl ring substituted compounds). In conclusion, aromatic chlorinated compounds give simple and straightforward spectra which are easy to identify, except for the relative positions of the substituents. The identification is further facilitated by the characteristic isotopic patterns of chlorine and by the presence of fewer or no rearrangement ions.

## The Pesticides

The chlorinated pesticides may be thought to fall under two broad categories: (i) chlorinated aromatic pesticides; (ii) bridged polycyclic chlorinated pesticides. The chlorinated aromatic pesticides may be subdivided into 1) substituted diphenyl derivatives of methane; 2) of ethene and 3) of methanol[52,67]. Class (i) includes pp' and op' DDT, pp' and op' DDD, pp'-DDA, perthane and methoxychlor. Compounds of this group have the common structure



where R = p-Cl and R' = $CCl_3$ for pp'DDT; one of the R = O-Cl for O, p' DDT; R' = $CHCl_2$ and R = p-Cl for pp'DDD; R = p-$C_2H_5$ and R' = $CHCl_2$ for perthane and R = p-$OCH_3$ of R' = $CCl_3$ for methoxychlor.

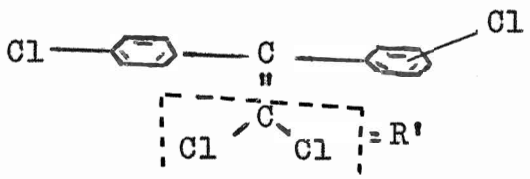
A substituted phenyl tropylium ion (i.e. the $(M-R)^+$ ion) was a common feature of all the compounds. Loss of the remaining two chlorine atoms led to the second largest peak in DDT and DDD isomers while this was less significant for methoxychlor and perthane. The structure of this species was confirmed to be the fluorenyl ion by comparing the spectra with that of 9-DCMF (i.e., 9-dichloromethyl fluorene) and hydrogen scrambling experiments.

A method of distinguishing pp'-DDT from Op'-DDT was proposed[67] making use of the greater significance of the

$(M-2Cl)^+$ in the former case. The DDD isomers could not be distinguished by mass spectrometry alone. Possibilities of identification of DDT isomers from a mixture of pesticides by making use of the characteristic molecular ion composition and isotopic pattern of the pesticide and of the residue in human adipose tissue[57], liver tissue[67] and bald eagles[68] were explored using a combined gas chrometographic-mass spectrometric technique.

Diphenyl ethene derivatives

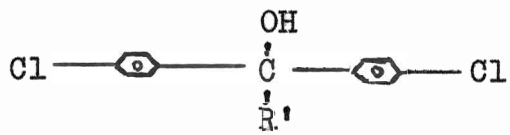
pp' and op' DDE, having the following structure are the representatives of this class.




Unlike in the previous cases, the (M-R') peak was absent for obvious reasons. Loss of the two ring chlorines gave the base peak in the spectra. The formulation of this ion is still not clear[67]. A method for distinguishing the DDE isomers was proposed[67] based on the significant differences in the abundances of ions of m/e = 316, 246, 210 and 176.

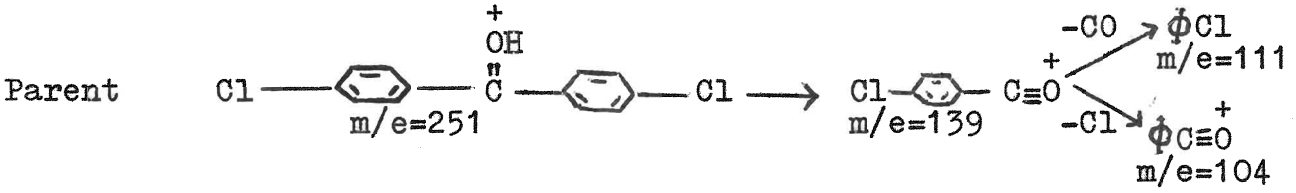
Diphenyl methanol derivatives

Pesticides of this group are represented by,



Where R' = $CH_3$ in Dimite; $-CH_2O\ C_2H_5$ in Etoxinol; $-\overset{|}{\underset{|}{C}}-OC_2H_5$ in chlorobenzilate and $-CCl_3$ in Kelthane[67].

The presence of the hydroxyl function in these compounds was found to alter the fragmentation patterns completely. For example, although Kelthane was structurally similar to pp'-DDT, the $(M-R')^+$ did not lose the R substituents (i.e., the two chlorine atoms). Thus




In conclusion, it may be mentioned that apart from giving pathways for the formation of some significant ions in the spectra of the aforementioned pesticides, no detailed discussions were presented by the authors[66] concerned. Such a discussion is, however, essential for a complete correlation of the spectral data with structure.

The bridged polycyclic chlorinated pesticides

A host of bridged polycyclic chlorinated pesticides such as Aldrin, Isodrin, Dieldrin, Endrin (all are dimethano naphthalene derivatives), Chlordane, Heptachlor, Heptachlor-epoxide, Trichlordane and Nonachlor (all are methano indene derivatives) were examined and pathways for the formations of the major ions were proposed[66]. Ions resulting from the Diels-Alder process accompanied by the subsequent loss of Cl· or

HCl; from the retro-Diels-Alder process; from losses of Cl$^{\bullet}$, HCl or both and ions involving the epoxide group were found to dominate the spectra of these compounds.

Definitive studies on these pesticides thus seem to be lacking. It may be mentioned that chlorinated pesticides are widely used as insecticides, fumigants, fungicides, herbicides and plant-growth regulators. Most of the pesticides, are, however, very toxic and persistent and are thus harmful. This calls for caution and a means of establishing their identity. A complete characterisation of each halogenated pesticide is thus needed and because of its high sensitivity and potential for determining organic compounds of known structure, mass spectrometry appears to be a suitable tool towards this end.

## Chapter 2

## EXPERIMENTAL

## i) Techniques

### (a) The AEI-MS 12 Mass Spectrometer

The mass spectra of the various pesticides reported here (excepting Parathion, Ethion and O, O-dimethyl phosphoro-Chloridothionate) were obtained using the AEI-MS 12 single focusing mass spectrometer located at Trent University. (Details regarding the mass spectrometer can be found in the manual, "MS-12 Mass Spectrometers", Picker-AEI Scientific Apparatus, 1969). The ion source potential was adjusted for maximum ion beam current at 8 kv accelerating voltage. The 70 ev. spectra were scanned magnetically. The resolution used was 1,000 and the mass range 1 m/e - 900 m/e. The spectra were read from a 3-channel UV-recorder fitted in with three 5 KHZ galvanometers at sensitivity ratios of 1 : 10 : 100.

Samples were admitted into the ion source region via the direct insertion probe. The sample was mounted in a glass probe-tip and was introduced through a vacuum lock into the ion-chamber. The sample was heated and volatilised at the lowest practical temperature possible to keep thermal degradation to a minimum. The temperatures ranged from 35°C - 80°C depending on the volatility and thermal stability of each compound. Thus tributylphosphorotrithioite, Perbulate and O-2,4 dichlorophenyl O, O-diethyl thiophosphate were introduced at 35°C; eptam at 45°C; isopropyl ester of 2,4-D and phosdrin at 50°C;

butyl ester of 2, 4-D and 1-naphthalene acetic acid methyl ester at 60°C; Vegadex, Allethrin and Carbophenolthion at 65°C; Kelthane at 70°C; Piperonyl butoxide at 75°C and DDVP at 80°C.

(b) AEI-MS 30 Mass Spectrometer

Parathion, Ethion and O, O-dimethyl phosphorochloridothionate were examined in the AEI-MS 30 double beam double focusing mass spectrometer. (For details, reference may be made to the manual, "MS-30 Double Beam Mass Spectrometers", Picker AEI-Scientific Apparatus, 1970). In this mass spectrometer two ion beams are produced by two independent ion sources. Adjustments of the electrostatic sector and ion source potentials were made at an accelerating voltage of 4 kv. The ion source was maintained at 100°C. The resolution used at 4 kv was nominally 1000 (but actually 1300) and the mass range m/e2 - m/e700. The 70 ev spectra were scanned magnetically from the high to low mass end. As the sample and reference beams pass side by side through a common mass analyser, they have the same mass scales and were therefore recorded simultaneously on the same chart paper. The sample spectrum was recorded at three different sensitivities of 1:10:100 while the reference (Perfluorokerosene) was recorded logarithmically in a single channel. Samples were admitted into the ion chamber through an all-glass heated inlet system, called the "Aghis". Ethion was introduced at ambient temperature without

any external heating due to its thermal instability while Parathion and $(CH_3O)_2P\langle^{S}_{Cl}$ were heated to 35°C. The reference sample, perfluorokerosene, was admitted into the second ion source through a heated direct probe inlet system, designed for volatile liquids and gases.

A Pye Model 104 gas liquid chromatograph was interfaced to Beam-Two via a silicone membrane separator housed in a separate oven. The total ion monitor was used as the GC-detector.

(c) The Bendix Time of Flight Mass Spectrometer

The samples (excepting those run in the MS-30 mass spectrometer and Vegadex were also run in the Bendix (Basic Model 12) Time-of-Flight Mass Spectrometer. (For details see the "Instruction Manual for Models 1003 and 1005 (Basic Model 12), Bendix TOF, 1963). Maximum ion current was obtained at 2.8 kv accelerating voltage while the resolution at this voltage was only 250. The 70 ev spectra were read from a UV-recorder at three different galvanometer sensitivities of 1:10:50.

Samples were injected (as all were liquids) through a rubber septum into a heated metal inlet system maintained at 40°C.

## ii) Source of Pesticides

All the pesticides included in this study were obtained commercially from the "Chem Service, Inc. West Chester, Pa. U.S.A. The pesticides were contained in the "Chem-Supply", pesticide kit, Model PS-100-N (1968).

The pesticides had been purified by Chem-Service using methods of column chromatography, fractional crystallisation and redistillation wherever feasible. All the materials were above 99% pure and were thus used without any further purification.

The chemical names, trade names and chemical structures of the various pesticides are given in Appendix A. The mass spectral data of these compounds are tabulated in Appendix B. All peaks with relative abundances of 1% and above have been considered. The tabulation has been done relative to the base peak whose abundance is taken as 100%. The mass spectral data have also been presented in the form of bar graphs and have been included in the appropriate sections dealing with the different classes of pesticides.

# Chapter 3

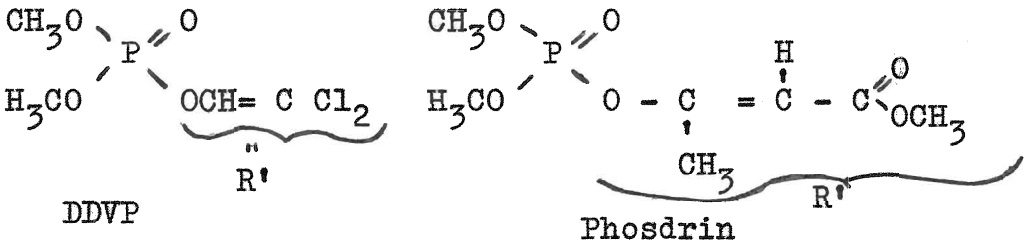
# RESULTS AND DISCUSSION

## Part i) The Mass Spectra of Organophosphorus Pesticides*

*Appendix B gives the m/e values and the % relative abundances of the various ions.

(a) DDVP and Phosdrin (Phosphate Group)

DDVP and phosdrin belong to the phosphate group of pesticides. Their structures are given below:




Jörg et.al.[52] have given the bar graph spectrum of DDVP and phosdrin and have suggested pathways for the $(CH_3O)_2P^+=O$ fragmentation, as involving a loss of $CH_2O$ to give an ion of m/e 79 and a loss of $CH_3OH$ to give an ion of m/e 47. Apart from this, both the spectra remained unexplained. Further, the fragmentation modes proposed require reconsideration in the light of recent investigations on the mass spectra of phosphorus compounds. The mass spectra of DDVP and Phosdrin are therefore discussed here in detail and pathways for the formation of the various ions are postulated. The fragmentation pattern of these pesticides have been considered as involving (i) fragmentation of the common $(CH_3O)_2\overset{+}{P}=O$ moiety; ii) simple cleavages at specific bond sites and iii) rearrangement reactions.

(i)

Fragmentation of the $(CH_3O)_2\overset{+}{P}=O$ Moiety

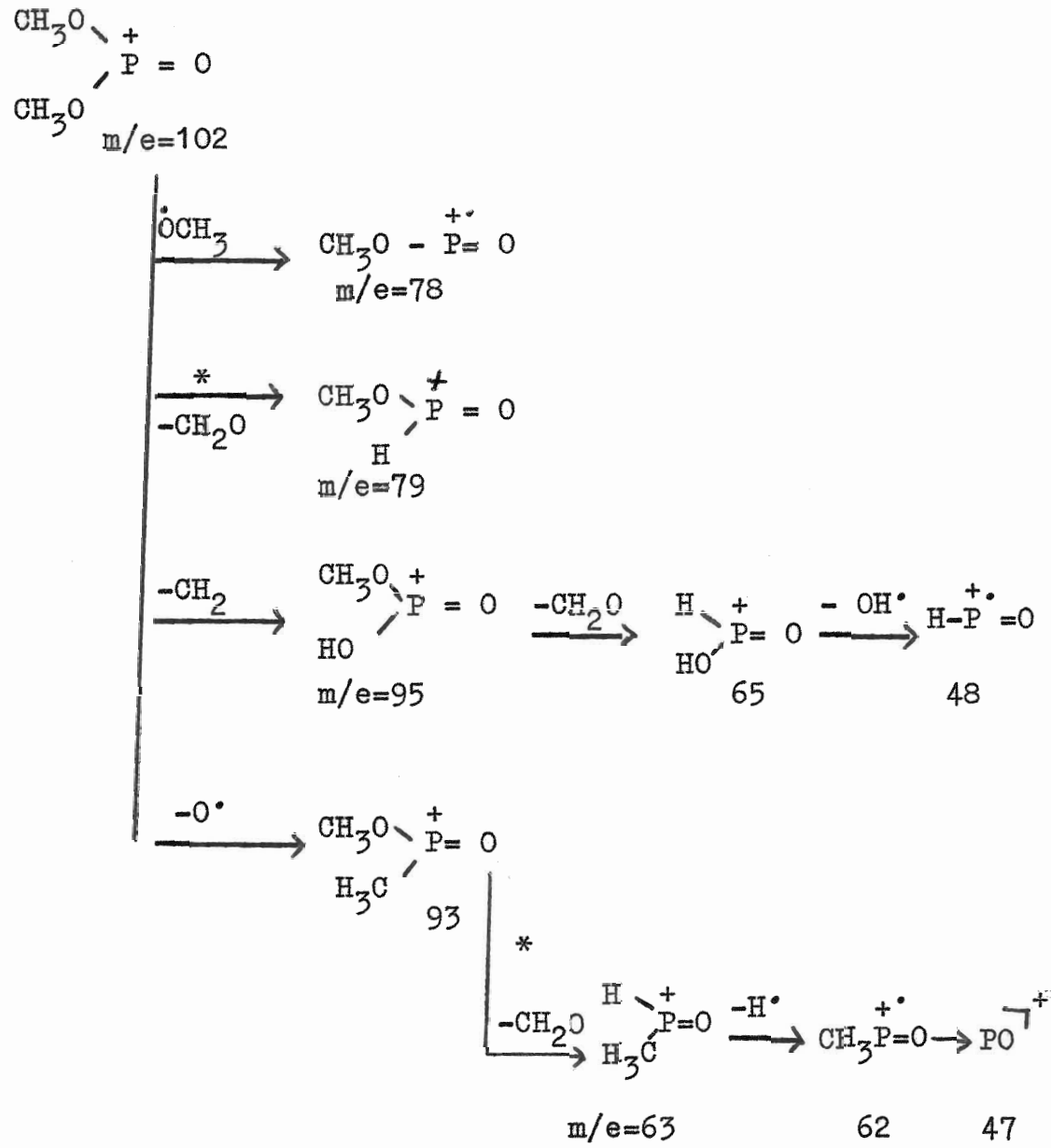
The $(CH_3O)_2\overset{+}{P}=O$ dissociates by simple rupture of bonds and by rearrangement processes as depicted in Scheme-1a. But all these ions are detectable only in the spectrum of DDVP while in phosdrin only ions of m/e 109, 79 and 47 are evident. The absence of the other ions in the phosdrin spectrum is due to the much more favoured cleavages involving the ester part of the molecule (Scheme-2). Ways for such cleavages are absent in the OR' part of the molecule in DDVP. Accordingly cleavages involving breakeage of the (P-C) linkage dominate the spectrum. Thus the lower mass end of the DDVP spectrum contains many ions while relatively few ions are present in the phosdrin spectrum (Figs. 1 and 2), since ions representing the dissociation of the $(CH_3O)_2\overset{+}{P}=O$ are not prominant.

(ii) Simple Cleavages

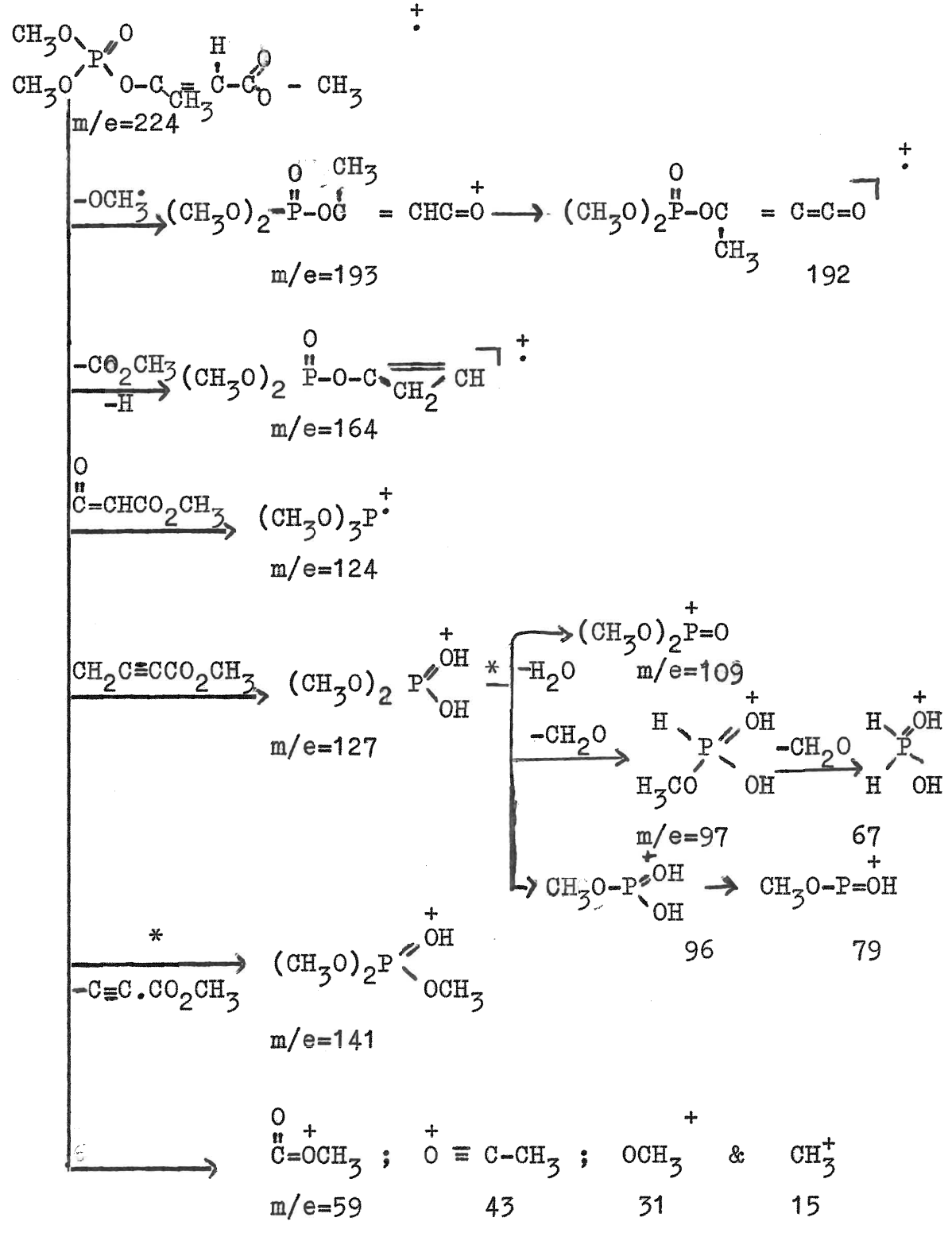
The ester moiety (i.e., R') in phosdrin gives the expected cleavage ions, viz, $CH_3^+$, $OCH_3^+$, $COCH_3^+$, $CO_2CH_3^+$, and $(CH_3O)_2\overset{O}{\overset{\|}{P}}-OCCH_3 = CHCO^+$ (See Scheme 2).

(m/e=193)

m/e 193 is abundant and it gives rise to a more intense ion of m/e=192 by the loss of a H°. Ion of m/e 192 contains multiple bonds and as a rule, species having multiple bonds give abundant ions in the mass spectra[74]. Loss of CO from m/e 193




Scheme 1-a Fragmentation Pattern of $(CH_3O)_2\overset{+}{P} = O$ moiety




Scheme 2 Cleavages and Rearrangements of Phosdrin

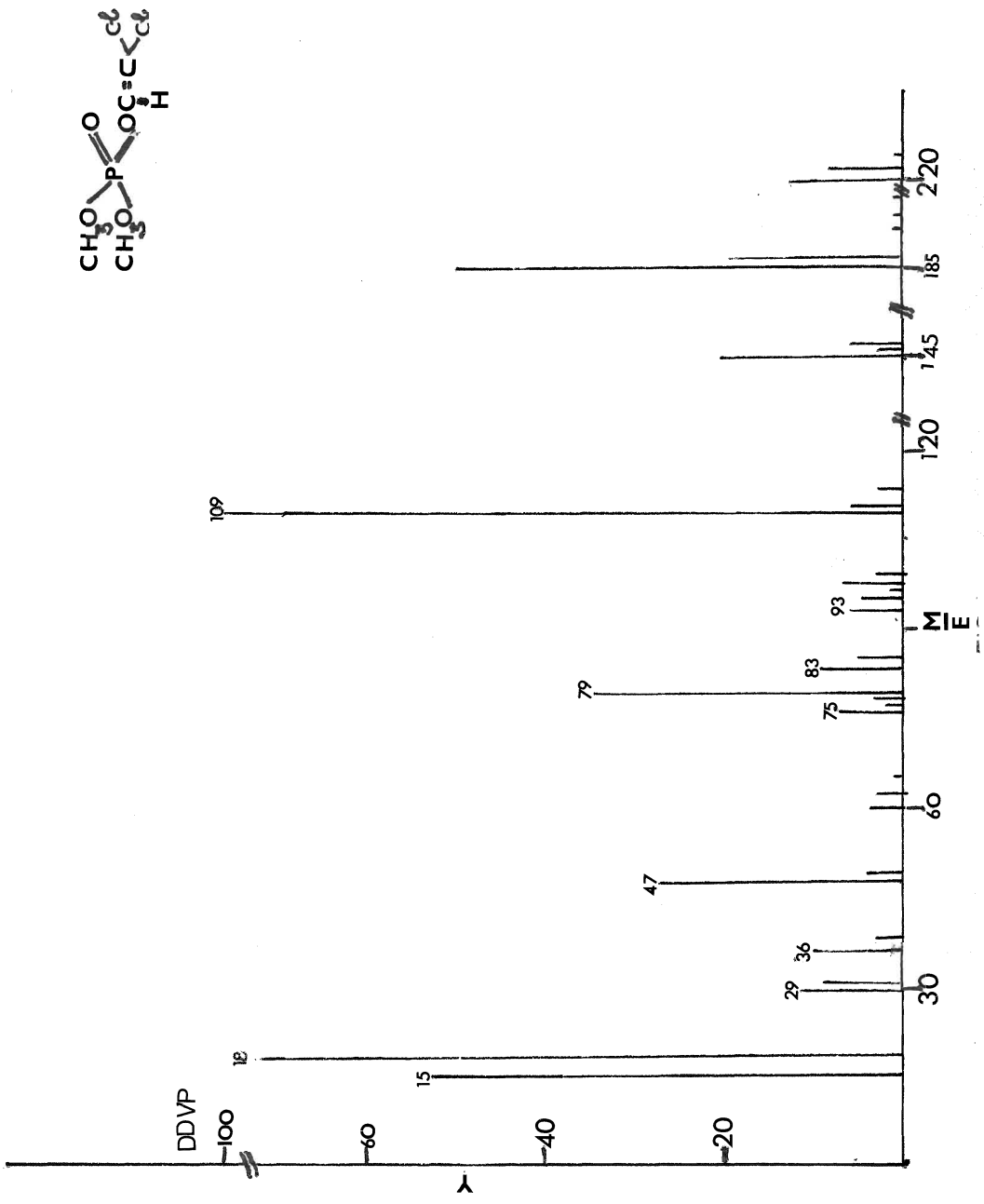



fig.I. mass spectrum of DDVP (AEI.MS.I2.)

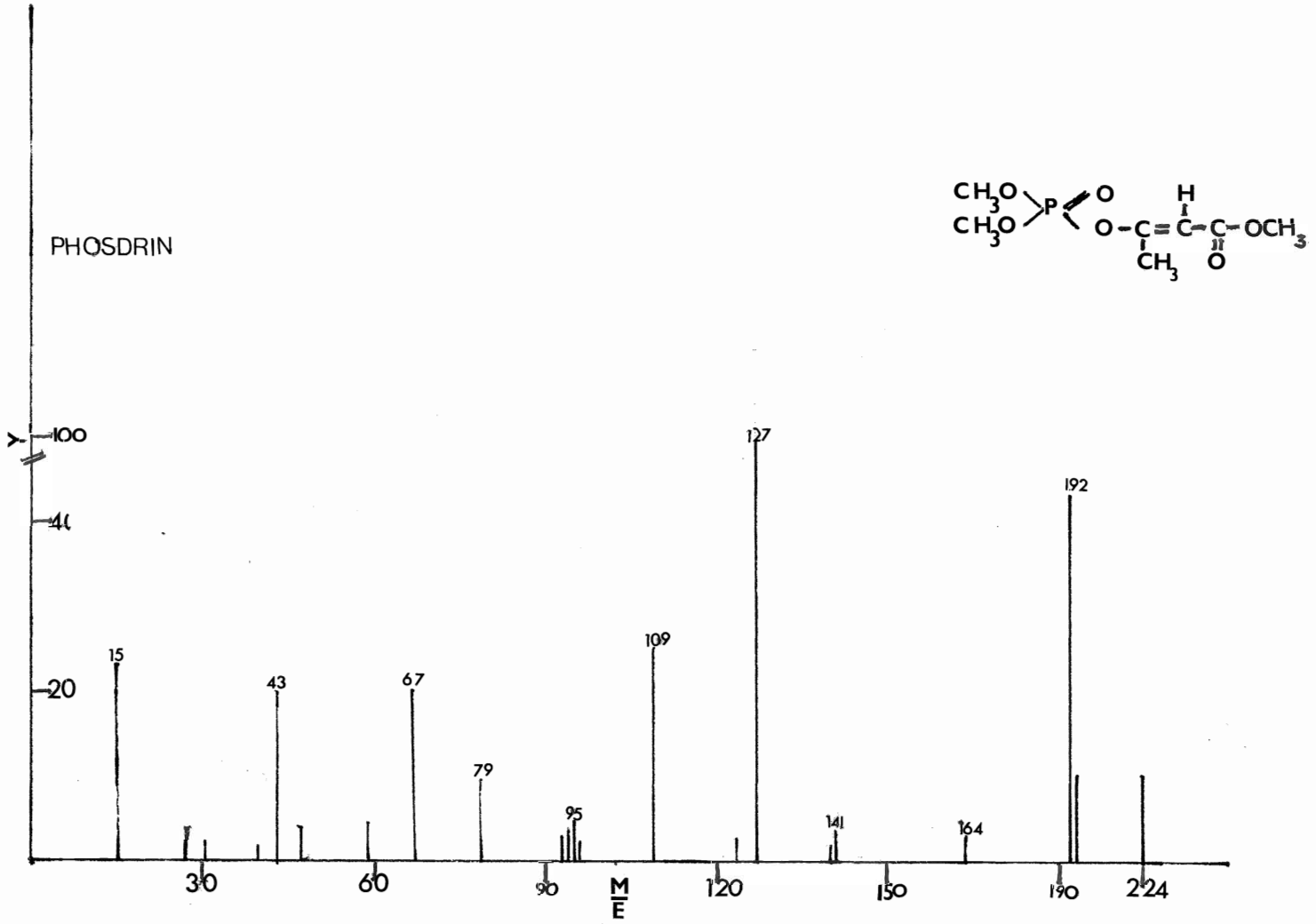


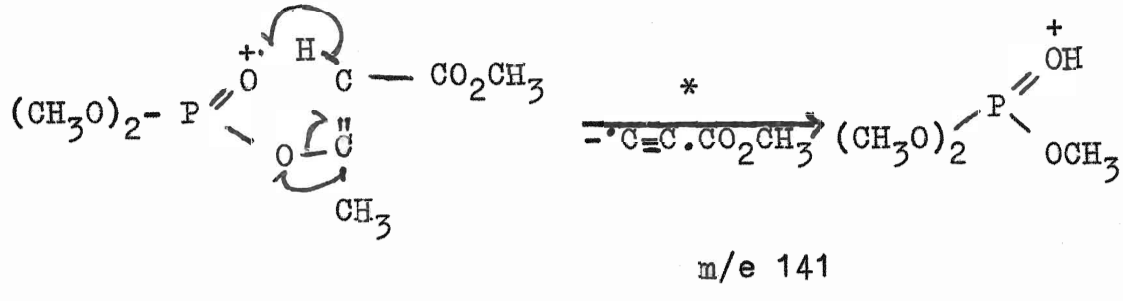

fig.2. mass spectrum of PHOSDRIN (AEI.MS.I2)

leads to the species of mass 165 which then, by loss of a H• yields the ion of m/e 164. The formation of a cyclopropene ring is assumed in this ion. Such cyclisations have been postulated in many other compounds by earlier workers[75].

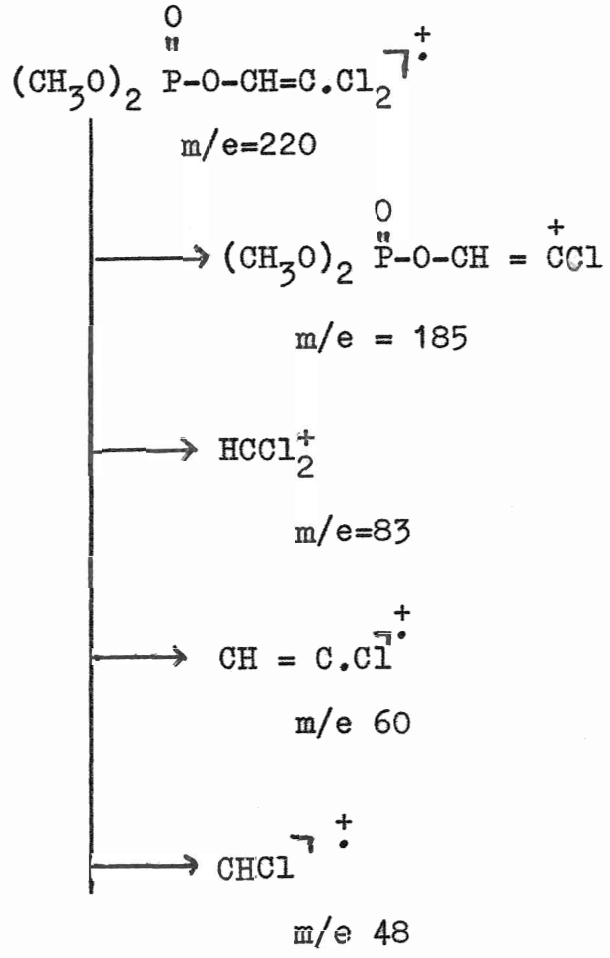
Cleavages of the (C-Cl) and the (O-C) bonds (in which the oxygen is also linked to the central phosphorus atom) are evident in the spectrum of DDVP as illustrated in Scheme 3-a. The lability of the (C-Cl) bond relative to that of the (C-H) bond accounts for the greater abundances of these ions[76]. The fragment ions exhibit isotopic patterns typical of one chlorine atom or two chlorine atoms as the case may be.

(iii) Rearrangement Ions

Rearrangement ions dominate the spectrum of phosdrin. Examples can be found in the ions of m/e 141, 127, 124, 97, 67 and 60 (Scheme 2). Ion of m/e 141 may arise in a concerted process involving the simultaneous migration of $CH_3^•$ and H• from the OR' part to the two oxygen atoms linked to the central phosphorus:



m/e 141

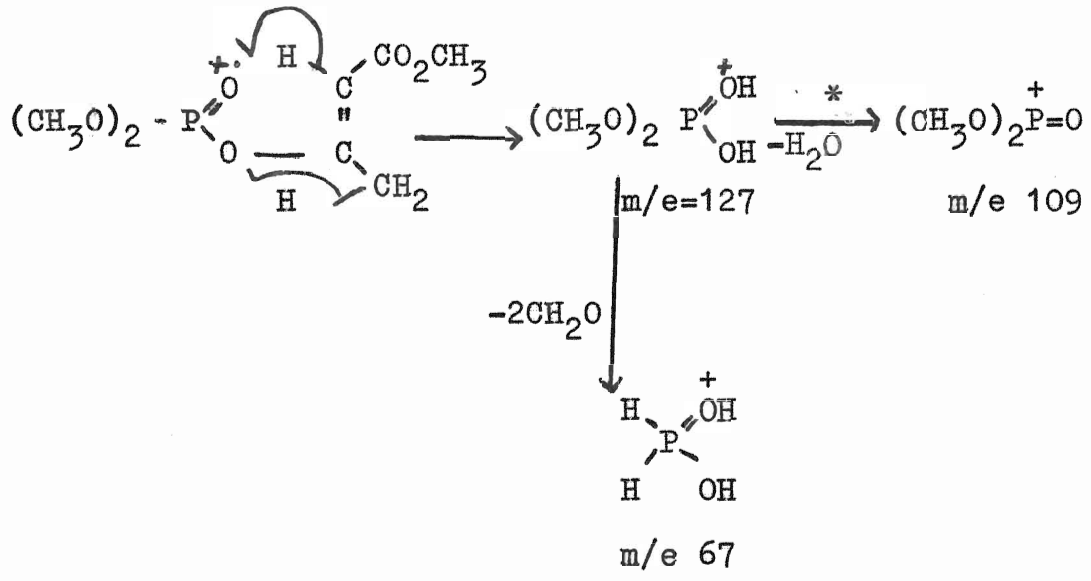



Scheme 3-a Fragmentation pattern of DDVP

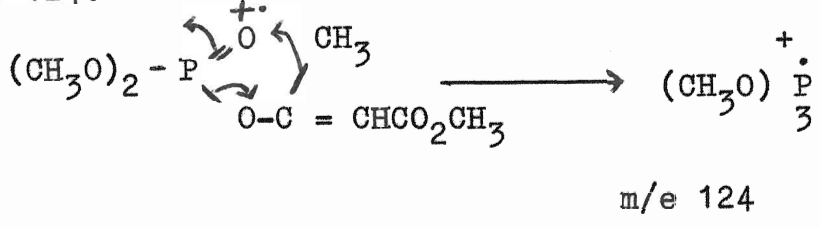
The formation of this ion involves a 6-membered cyclic transition state and is supported by a metastable transistion. Further, although migrations of $CH_3^{\cdot}$ [69,70] or $H^{\cdot}$ [69,71] or two hydrogens at the same time (i.e., a double hydrogen rearrangement)[71,72] have been reported by previous workers, the simultaneous migration of a $CH_3^{\cdot}$ and $H^{\cdot}$ does not seem to have been observed by earlier authors.

Migrations of the two hydrogens to the two oxygen atoms bonded to phosphorus gives rise to the base peak in the spectrum of phosdrin (Ion of m/e=127). This ion is resonance-stabilised. In many of the phosphate compounds, ion of m/e 109 is the base peak. But the preference, in this case for the ion of m/e 127 could be due to the tendancy for phosphorus to remain in the pentacovalent state rather than the tetracovalent state in which form it is present in ion 109. This specific tendancy of phosphorus to remain in the pentavalent state has been noted by earlier workers[39,40,73] in their studies of other phosphorus-containing compounds. Successive loss of two ($CH_2O$) molecules from ion 127 yields the species of m/e=67. The low abundance of the intermediate ion of m/e 97 (0.25%) could be due to the greater stabilities of ion 127 from which it is derived and ion 67 which it gives rise to.

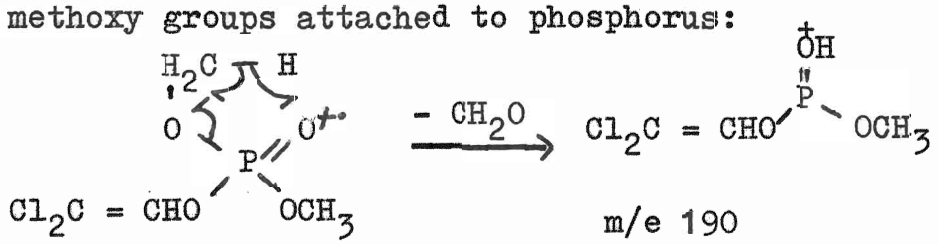
Thus




Migration of the $CH_3^{\cdot}$ would yield the rearranged ion of m/e=124:




DDVP, on the other hand, gives only a weak rearrangement ion (0.2%). It may arise by the loss of $CH_2O$ from one of the methoxy groups attached to phosphorus:



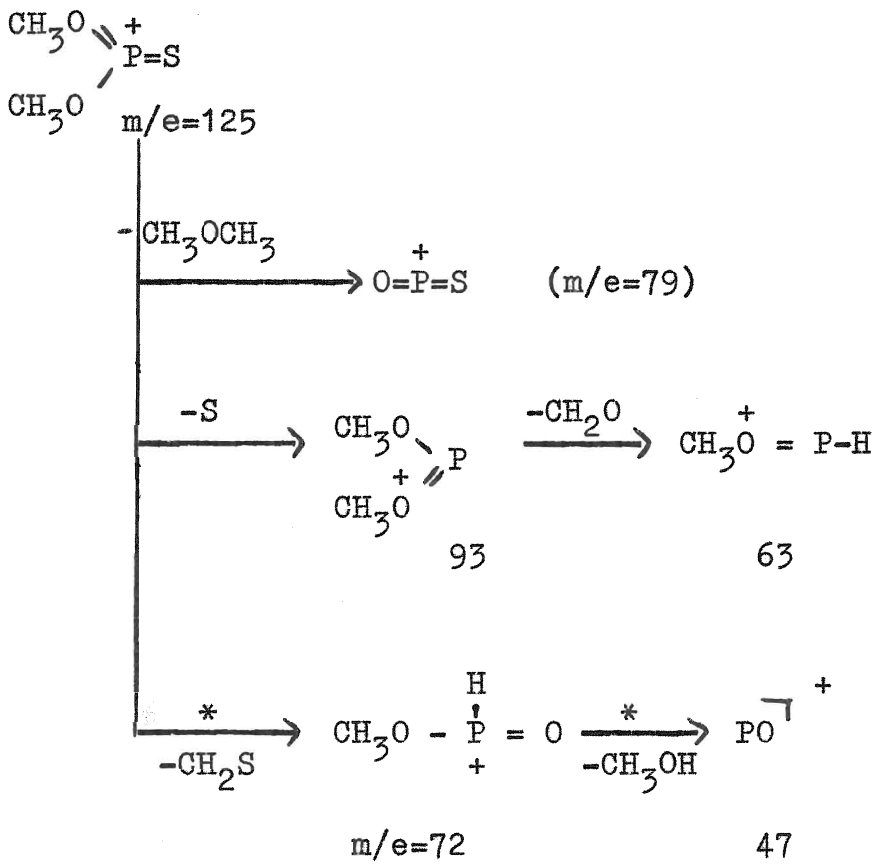

In summary, the spectrum of phosdrin is characterised by a series of cleavage and rearrangement ions involving the ester entity while that of DDVP is characterised by those derived from the $(CH_3O)_2\overset{+}{P}=O$ moiety. Further, DDVP gives

a number of isotopic peaks indicating one chlorine atom or two chlorine atoms as the case may be. These unique features of phosdrin and DDVP should serve to distinguish them from one another and also help their identification in pesticide residues.

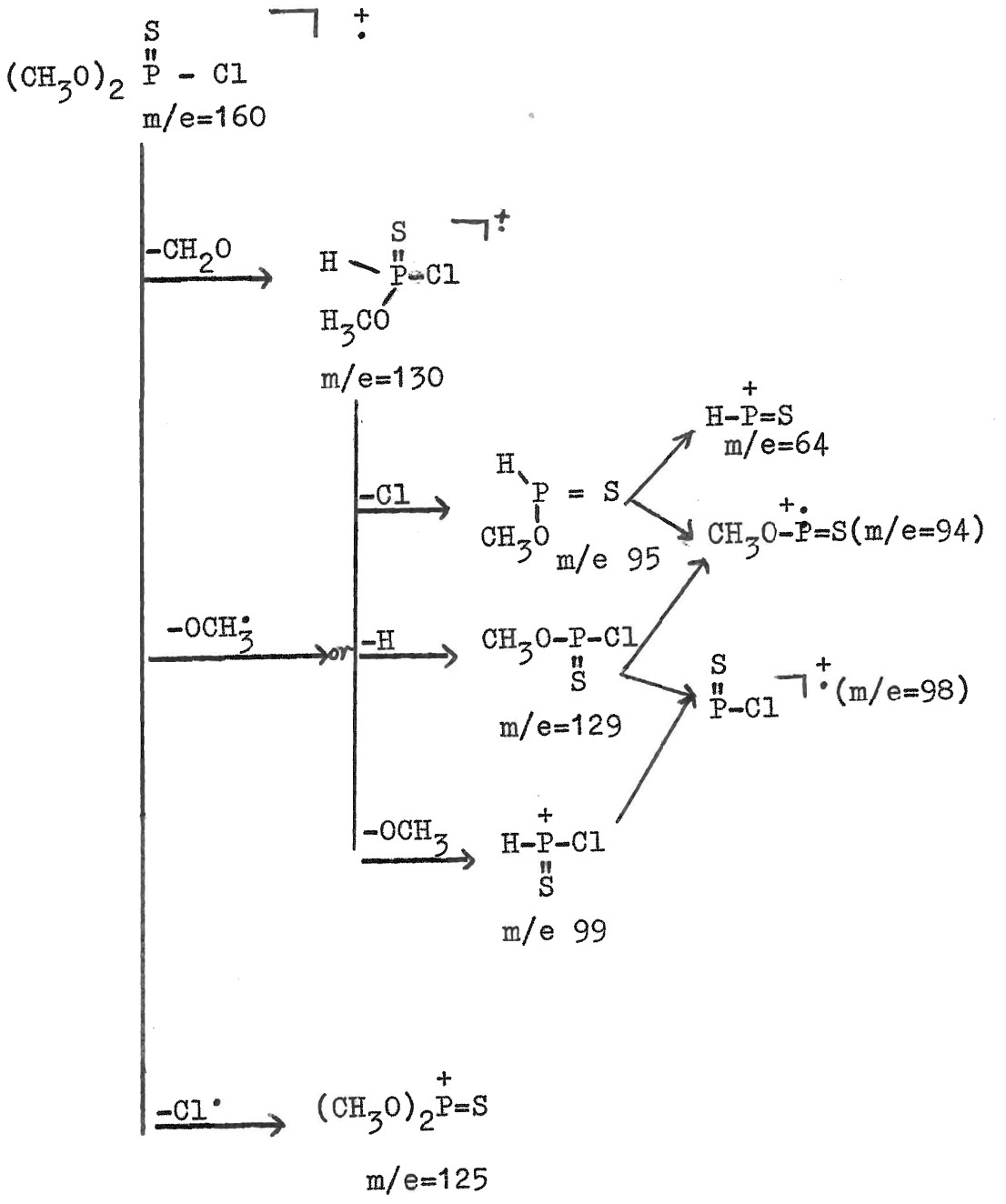
The Phosphorothionate Group

a) $(CH_3O)_2\text{-}P\overset{S}{\underset{Cl}{}}$

O, O-dimethyl phosphoro chloridothionate contains the $(CH_3O)_2\overset{+}{P}=S$ moiety and exhibits a fragmentation pattern (Scheme 1-b) analogous to that of the $(CH_3O)_2\overset{+}{P}=O$ species (Scheme 1-a) found in DDVP and Phosdrin. However, ions arising from this cleavage dominate the spectrum of $(CH_3O)_2P\overset{S}{\underset{Cl}{}}$ while the corresponding ions arising from the fragmentation of the $(CH_3O)_2$ P=O moiety are least significant in the spectrum of phosdrin. This difference in behaviour arises essentially through differences in the nature of the substituents present in these compounds. The (P-Cl) bond in the phosphoro chloridothionate is labile and the influence of the chlorine atoms on the fragmentation modes of the $(CH_3O)_2\overset{+}{P}=S$ moiety is therefore little. Consequently the dissociation of the $(CH_3O)_2\overset{+}{P}=S$ tends to be significant. In fact ions containing the chlorine atom are very few in its spectrum (Scheme 3-b and Fig. 3).




Scheme 1-b Fragmentation Pattern of the $(CH_3O)_2\overset{+}{P}=S$ moiety




Scheme 3-b Fragmentation of $(CH_3O)_2$ S=P-Cl

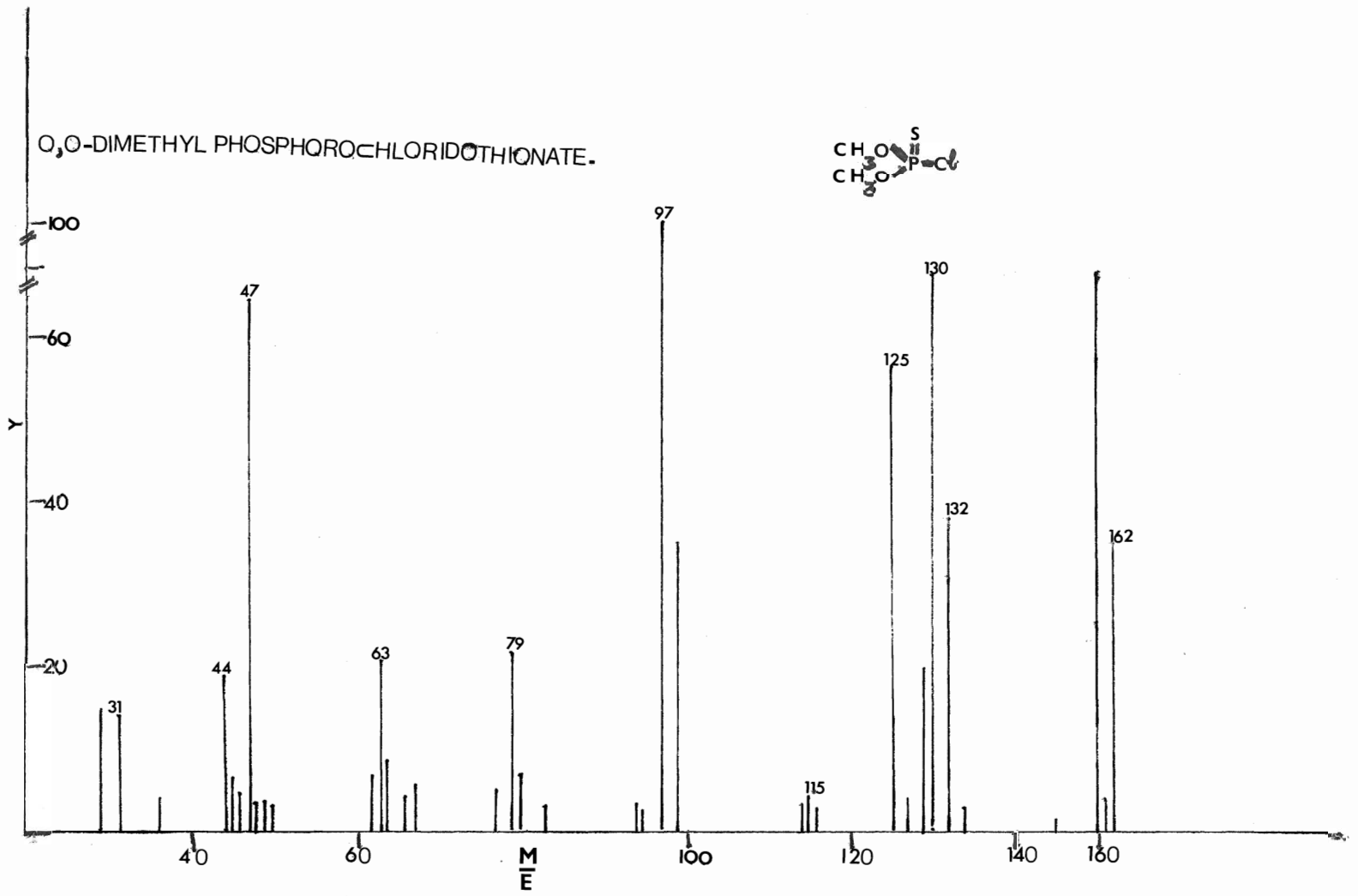
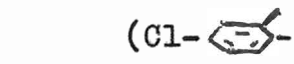



fig.3. mass spectrum of O,O-DIETHY CHLORIDOTHIONATE. (AEI.MS.I2.&30.

Phosdrin, on the other hand, contains an allylic ester substituent. As is known, esters suffer cleavages and rearrangements more easily under electron impact. The pattern due to the dissociation of the ester moiety, therefore, assumes more significance. Similarly the chloro allyl substituent in DDVP competes with the $(CH_3O)_2\overset{+}{P} = O$ moiety but less effectively than the allylic ester substituent in phosdrin. For this reason, ions arising from cleavages of the $(CH_3O)_2\overset{+}{P}=O$ moiety as well as those containing the chlorine atom tend to be equally important. These facts imply that in the presence of a favoured alternate pathway in a particular compound, the normally expected fragmentation behaviour of a common structural moiety would become less and less significant.

b) <u>o-2,4 dichlorophenyl O, O- diethyl thiophosphate</u>

o-2,4 dichlorophenyl O, O-diethyl thiophosphate



belongs to the phosphorothioate group of pesticides.

As in the case of DDVP and phosdrin, its spectrum may be discussed in terms of the (i) cleavage and rearrangement processes of the $(C_2H_5O)_2\overset{+}{P} = S$ species; (ii) simple cleavages of the molecular ion and (iii) rearrangement reactions of the moleculer ion and other daughter species.

(i) <u>Cleavages and Rearrangements of the $(C_2H_5O)_2\overset{+}{P}=S$ Moiety</u>

The pathways for the formation of the various ions

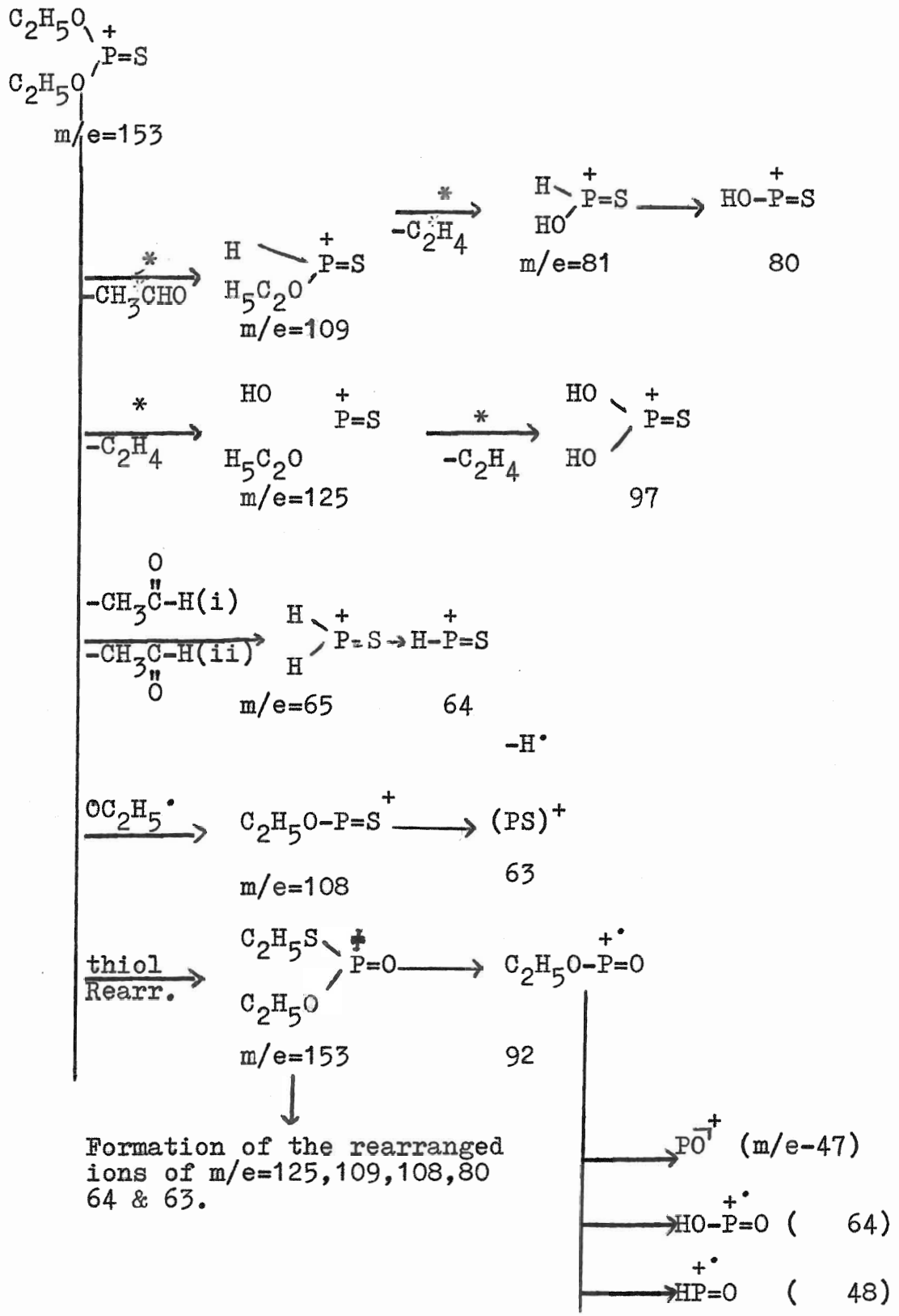
from the $(C_2H_5O)_2\overset{+}{P}=S$ species are given in Scheme 4. Eliminations of a molecule of $CH_3CHO$ from one of the ethoxy groups bonded to phosphorus in the $(C_2H_5O)_2\overset{+}{P}=S$ ion with transfer of the hydrogen to the central phosphorus atom leads to the ion of m/e=109. The formation of this ion is supported by a metastable transition. A similar process from ion 109 gives rise to the species of m/e 65. Another rearrangement process involves loss of a molecule of ethylene from the $(C_2H_5O)_2\overset{+}{P}=S$ species (m/e 153) to give the ion, 125 which then undergoes a similar process to yield the base peak (m/e 97) in the spectrum. These are the Mclafferty rearrangements and are supported by metastable transitions. Further the ion of m/e 153 isomerises to yield the thiol $(C_2H_5O\text{-}\overset{+}{P}(=O)SC_2H_5)$ which subsequently suffers rupture of the (P-S) and (P-O) linkages to yield the above ions (m/e 125, 97 etc.) in their isomeric forms.

(ii) Simple Cleavages

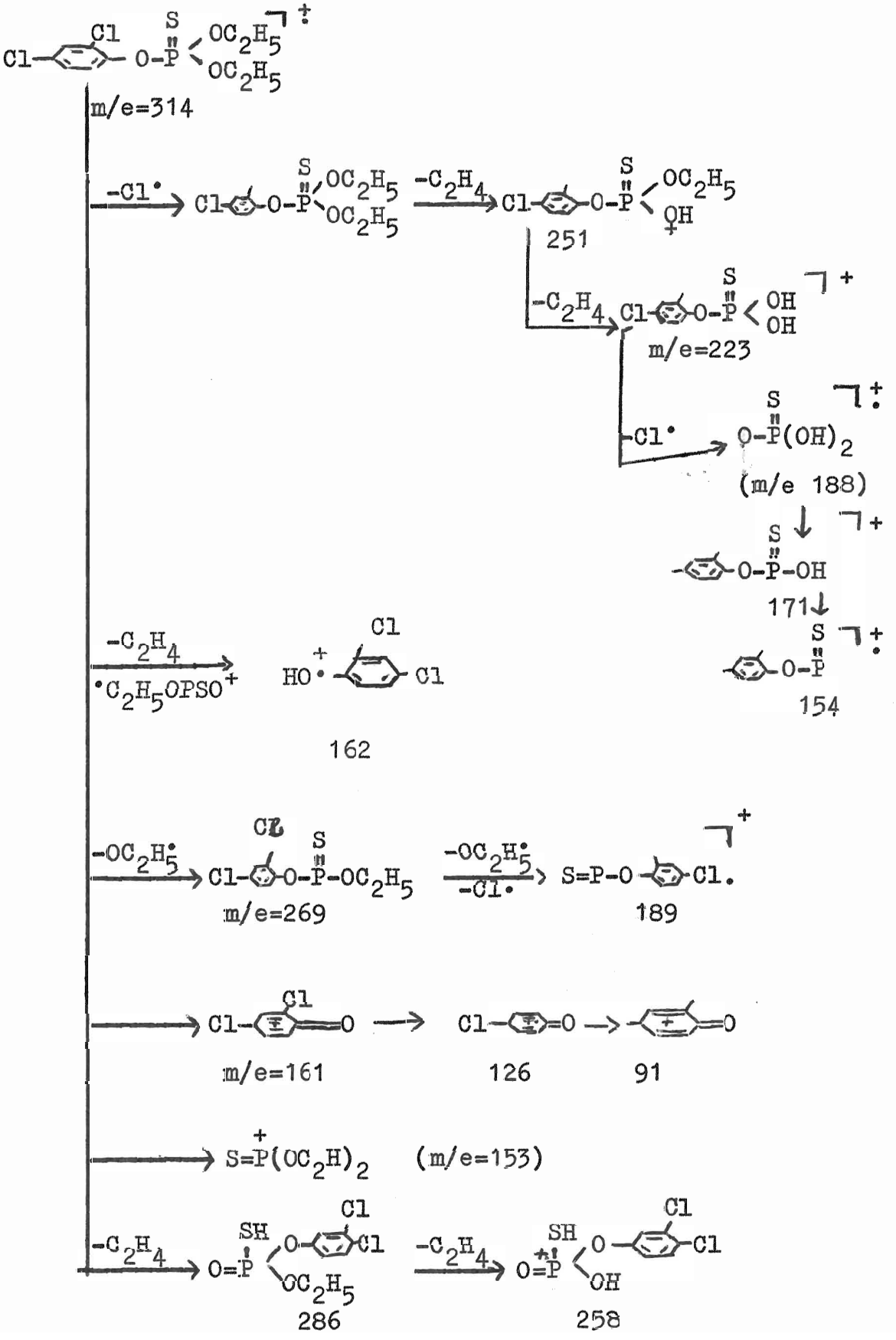
Breakages of the (P-O) and the (C-Cl) bonds lead to the various fragment ions depicted in Scheme 5. Ions of m/e 279, 269 and 153 are typical examples.

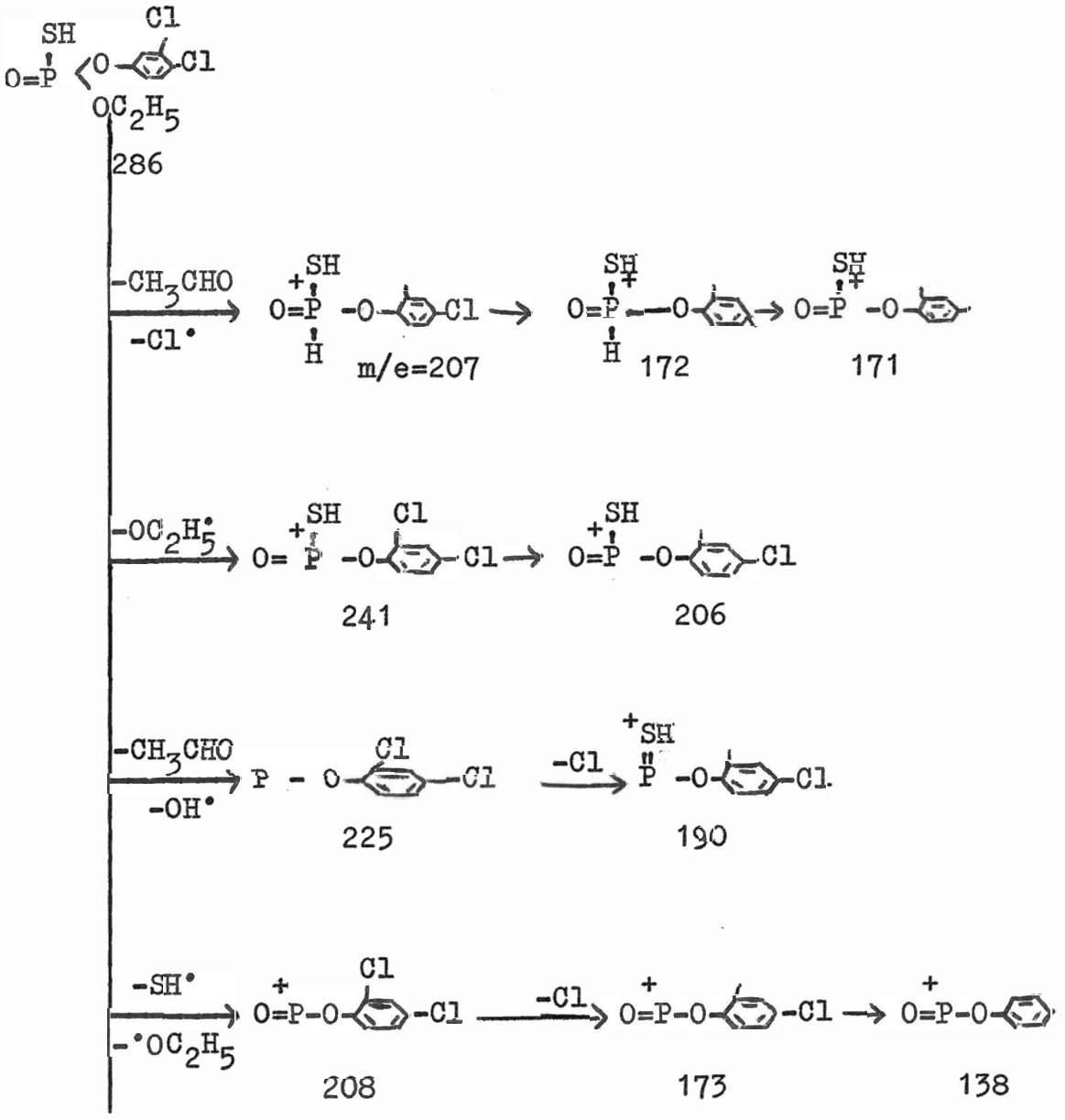
(iii) Rearrangements

The molecular ion undergoes two interesting rearrangement reactions. One process involves formation of either of the two odd electron ions through the loss of molecule of



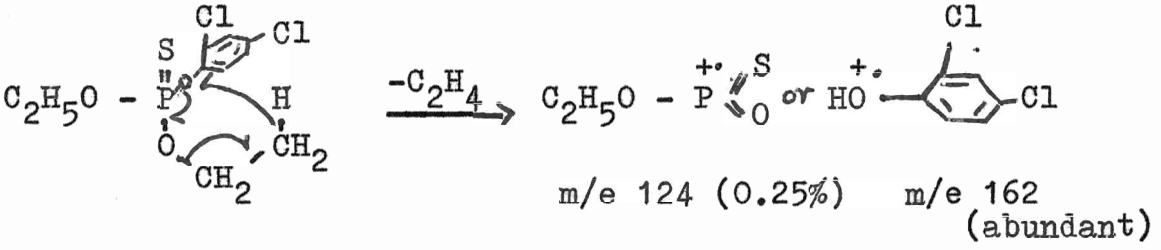

Scheme 4 Fragmentation pattern for the $(C_2H_5O)_2P{=}S$ Species


m/e=314
-Cl•
-C2H4
251
-C2H4
m/e=223
-Cl•
(m/e 188)
171
154
-C2H4
•C2H5OPSO+
162
-OC2H5•
m/e=269
-OC2H5•
-Cl•
189
m/e=161
126
91
(m/e=153)
-C2H4
286
-C2H4
258




Scheme 5 Fragmentation Scheme for O-2, 4 dichlorophenyl O, O-diethyl thiophosphate

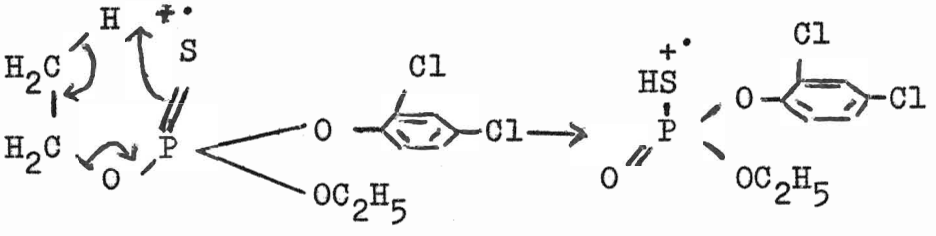
ethylene and the migration of a hydrogen from one of the ethoxyl groups either to the aryl oxygen or to the phosphorus atom.



m/e 124 (0.25%) m/e 162 (abundant)

(The ion of m/e 162 is abundant in view of its resonance stability).

Rearrangements of this type have been postulated in many dimethoxy phosphorothionates[55]. The second rearrangement also involves loss of a molecule of ($C_2H_4$) but this time it is a skeletal process involving a 6-membered ring transition state.



m/e 286 (0.25%)

The ion is very weak and undergoes cleavages and rearrangements to give the various ions illustrated in Scheme 5. Formations of the major ions of m/e 251, 225, 223 and 171 may be taken as typical examples. In fact, ion 223 constitutes another base peak and is formed by two successive Mclafferty rearrangements involving the loss of two $C_2H_4$

molecules followed by the departure of a Cl· from the parent ion or vice versa. The species is resonance stabilised and the central phosphorus atom is in the pentavalent state. Formation of the less abundant ion of m/e 190 may be postulated to involve the successive eliminations of a molecule of $CH_3CHO$ and OH· from the rearrangement ion of m/e 286. The possibility of an isomeric structure for this ion (in which one may have either the $P{=}\overset{+}{S}H$ or $P{=}\overset{+}{O}H$ ) is not ruled out.

In summary, o-2, 4 dichloro phenyl O, O-diethyl thiophosphate has a fairly abundant molecular ion; has two resonance stabilised base peaks formed by rearrangement reactions of the daughter species; gives two odd molecular ions in a single step and shows the typical chlorine isotopic patterns. (See Fig.4). These unusual features in its spectrum may aid its identification in pesticide residues.

c) <u>Parathion</u> <u>$(C_2H_5O)_2-P(=S)(=O)-C_6H_4-NO_2$)</u>

Damico[53] has published the bar-graph spectrum of parathion and observed that ion 109 is the base peak and that it resembles *p*-nitrophenol in the formation of ions of m/e 139, 123, 93, 81 and 65. Further, the molecular ion did not lose a molecule of NO, although it is to be expected on general considerations. Parathion is discussed here with a view to clarify some of its features noted by earlier authors[53]. As expected, cleavage and rearrangement ions arising from the $(C_2H_5O)_2\overset{+}{P}{=}S$ fragmentation are present (Scheme 4 and Fig. 5).

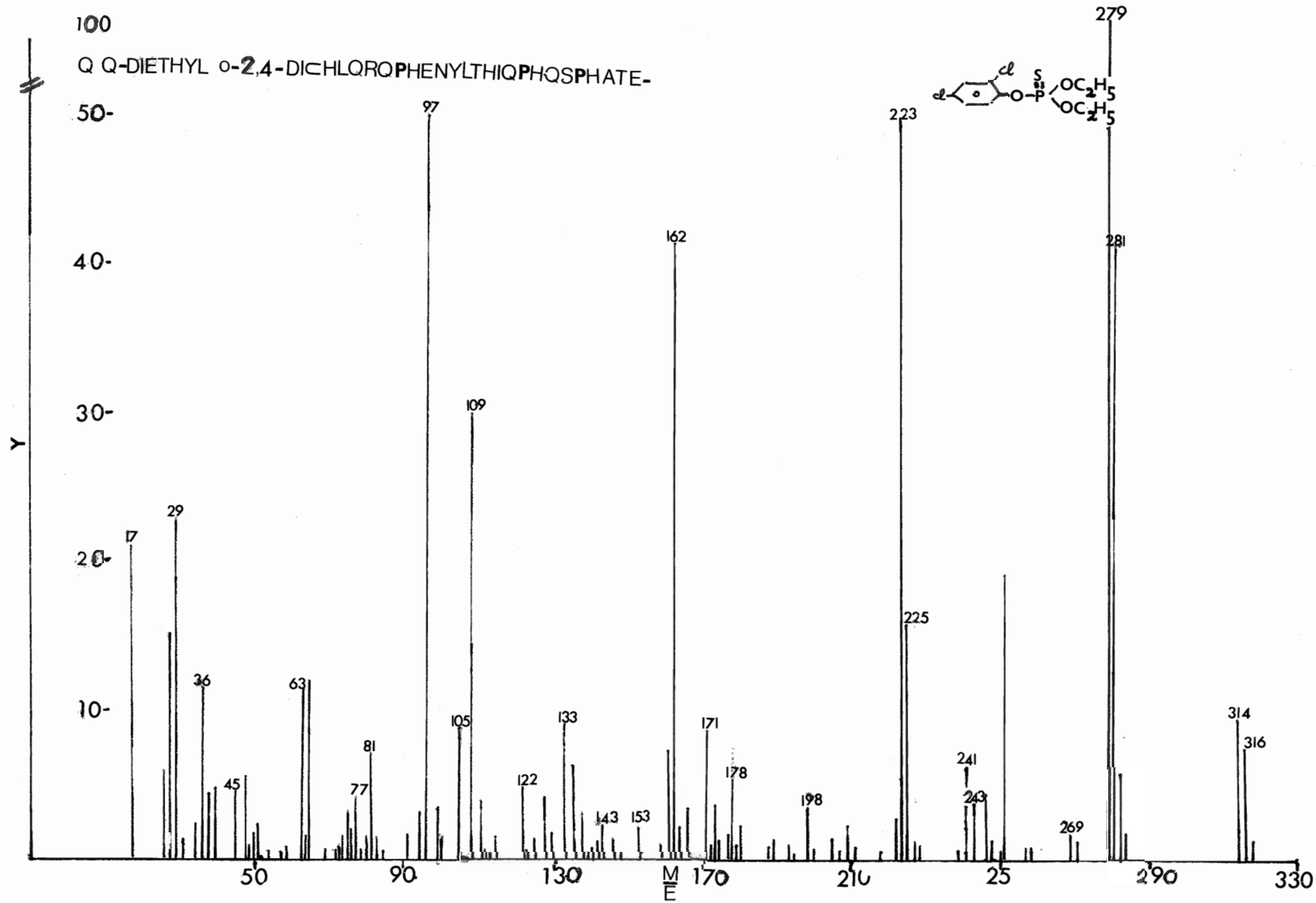
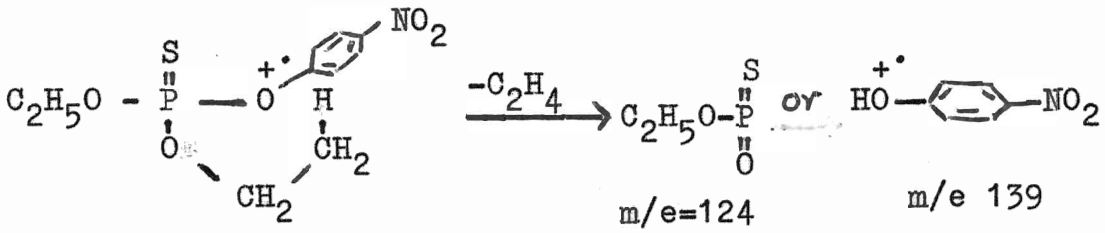
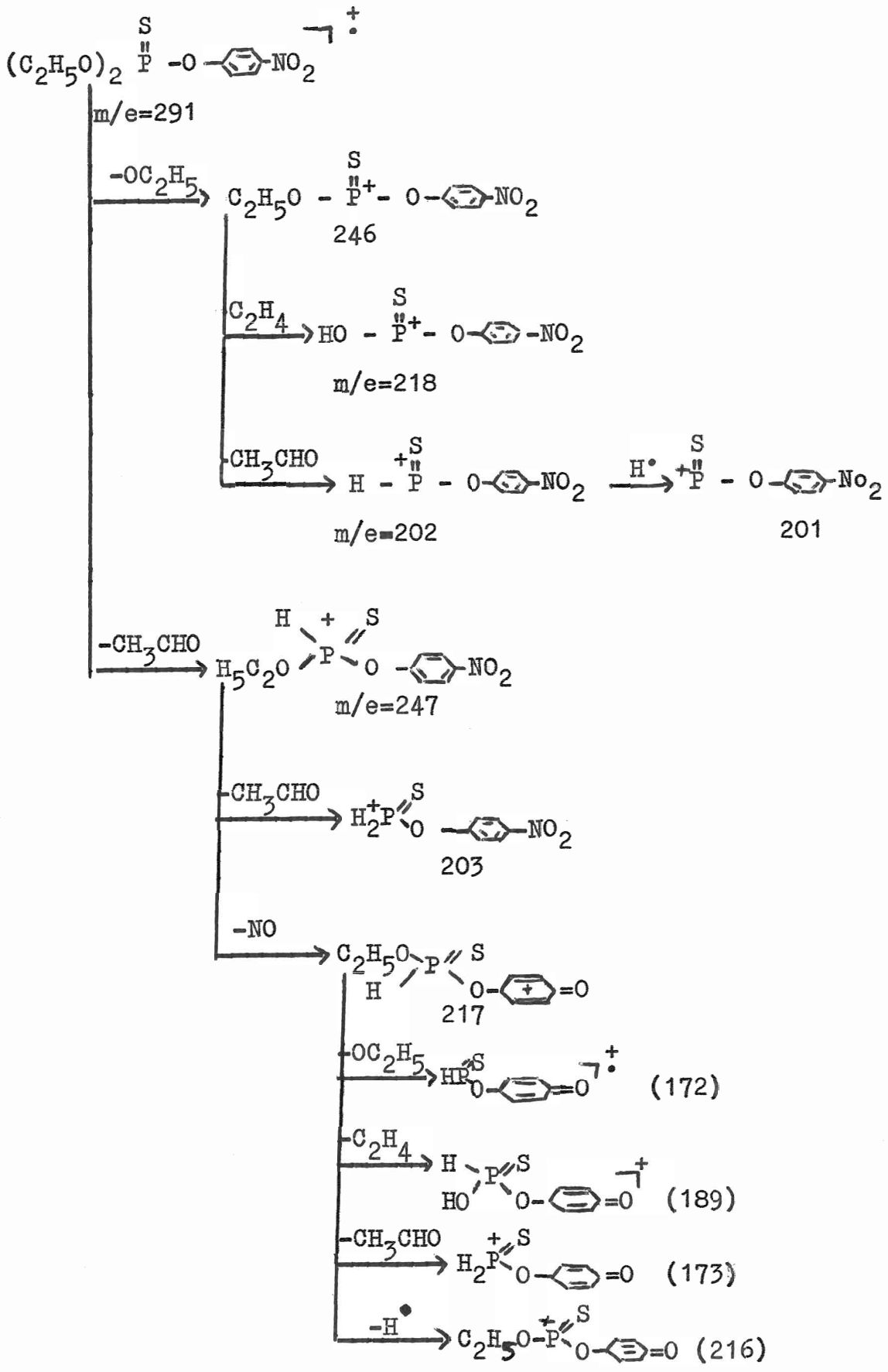


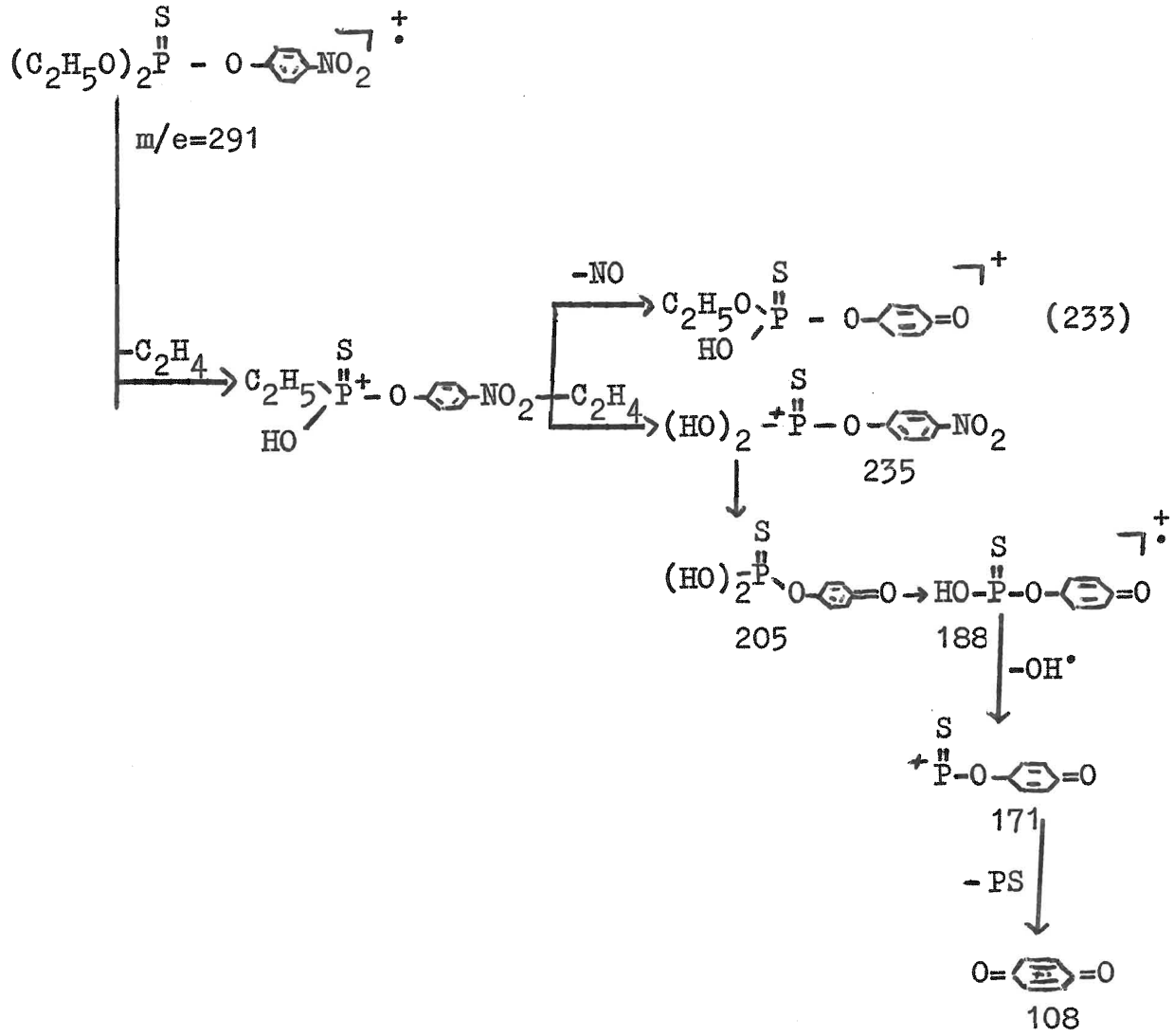

fig.4. mass spectrum of 0,2,4-DICHLOROPHENYL O,O-DIETHYL THIOPHOSPHATE. (AEI.MS.I2.)

Hydrogen migration from the ethoxy group to the oxygen atom linked to the central phosphorus atom gives either the p-nitrophenol ion of m/e 139 or another odd electron ion at m/e 124.




The p-nitrophenol ion then cleaves as expected.[53] Damico has reported[53] the base peak of the spectrum at m/e=109. In the present work, however, this ion is only 70% abundant and the base peak is at m/e 97. In general, organophosphorus compounds containing the $(C_2H_5O)_2\overset{+}{P}=S$ moiety have their base peak at m/e 97 due to the greater resonance stability of this ion.[48,49,51] The parent ion eliminates a molecule of nitric oxide (NO) as expected to give an ion at m/e 261 (12%) which was absent in Damico's report[53]. The loss of NO from aromatic nitro compounds is however well-known((See for example reference 3 (pages 515-520) and reference 4 (pages 39-85)). In addition, ions of m/e 275, 263, 247, 235 and 219 involving the p-nitro phenoxy moiety are present in the spectrum (Scheme 6). Ion 263 is particularly abundant in view of its stable structure. Formation of other ions in the spectrum follows an exactly analogous pathway as given for the dissociation of the $(C_2H_5O)_2\overset{+}{P}=S$ moiety and is illustrated in Scheme 6. Particular mention


m/e=291
-OC2H5
246
C2H4
m/e=218
CH3CHO
m/e=202
H•
201
-CH3CHO
m/e=247
CH3CHO
203
-NO
217
OC2H5
(172)
C2H4
(189)
CH3CHO
(173)
-H•
(216)




Scheme 6 Fragmentation Scheme for Parathion

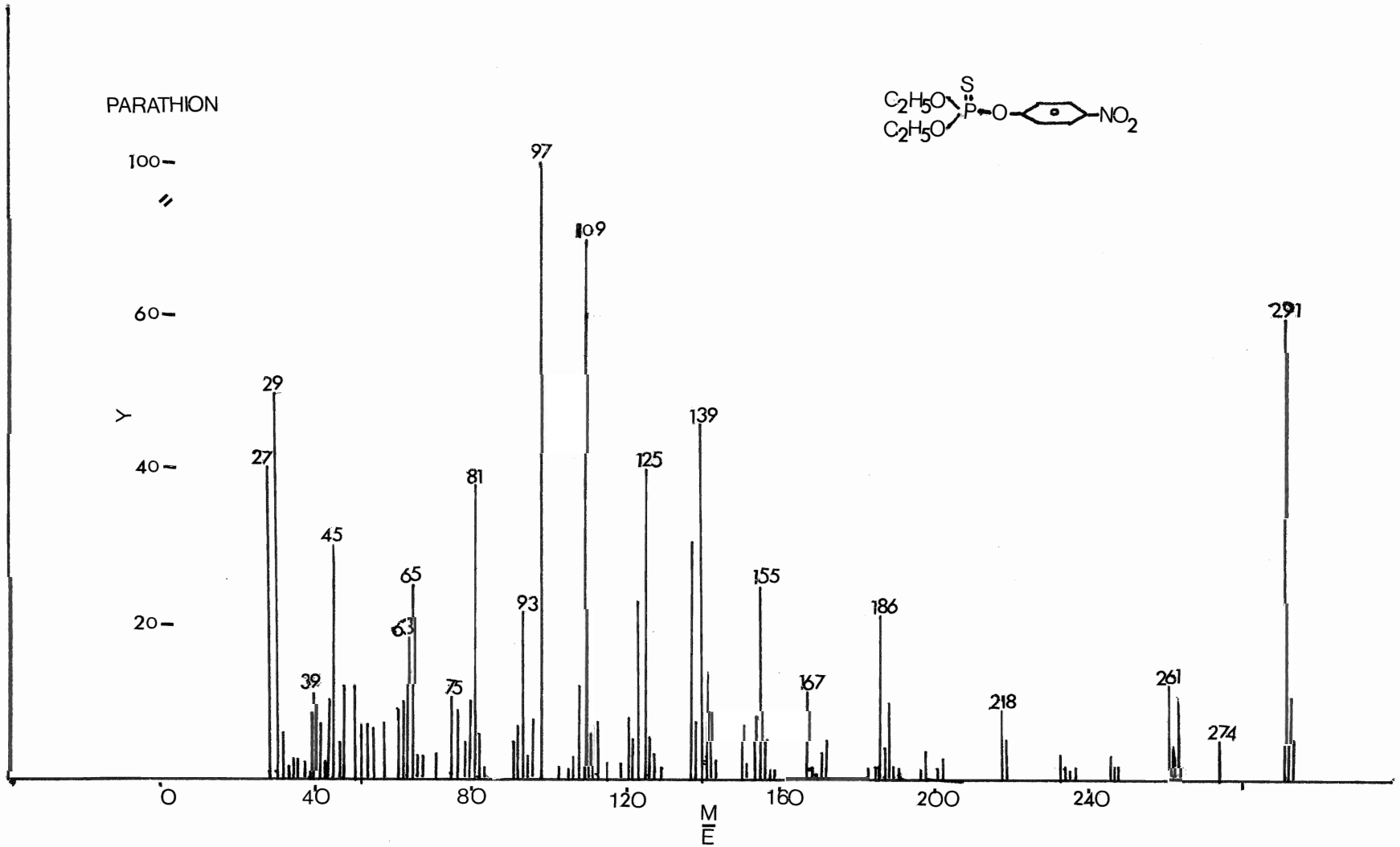
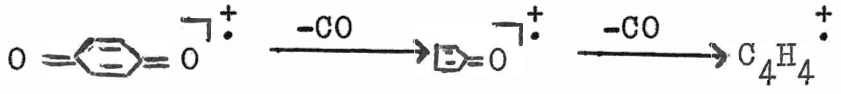



fig.5.mass spectrum of PARATHION.(AEI.MS.I2.&30.)

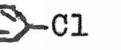
may be made of the ion of m/e 108 which is assigned a p- quinonoid structure and is postulated to arise from m/e 171 by the loss of (PS·). Subsequent loss of a molecule of CO from m/e 108 leads to the cyclopentenone structure of m/e 80 which then loses another molecule of CO to give m/e 52. This ion may have the cyclobutene structure:




m/e 108 m/e 80 m/e 52

The spectrum of Parathion is thus characterised by the formation of ions resulting from the loss of $C_2H_4$, $CH_3CHO$, NO and CO from the various daughter species. The spectrum is straightforward and hence its identification in a pesticide residue should not be very difficult.

The Phosphorodithioate Group

a) Carbophenolthion $(C_2H_5O)_2-\overset{S}{\overset{\|}{P}}-S-CH_2-S-$ 

As in the case of the thionophosphate pesticides (viz. o-2, 4 dichlorophenyl O, O-diethyl thiono phosphate and parathion), carbophenolthion contains the $(C_2H_5O)_2\overset{+}{P}=S$ moiety and dissociates to yield the expected ions of m/e 125, 109, 97 and 65 (See Scheme 4.). However, the following differences are noteworthy. (1) In carbophenolthion, the $(C_2H_5O)_2\overset{+}{P}=S$ series ( m/e 153) is very intense whereas in the thiono phosphorus compounds it is weak. This is due to the greater stability of

the OR' part of the molecule in the latter case (e.g. the o-2,4 dichloro phenoxy moiety and p-nitro phenoxy moiety) (2) In the thiono group, ion of m/e 97 is the base peak whereas it is less important in carbophenolthion. This is because the parent ion (ion 125) from which it arises is very abundant in carbophenolthion; but very weak in the case of the thiono phosphates. Further, a more favourable pathway leading to ions of greater stability is possible in carbo penolthion whereas it is absent in the thionophosphates. Thus as in the case of DDVP and phosdrin, the influence of the substituent in determining the relative abundances of the same species in different compounds is evident here also. This change in abundance implies that the intensity is not merely determined by the structural stability of the product ion alone but that it depends to a considerable extent, on the stability of the precursor ion as well. The stability of the precursor ion is, in turn, influenced by the nature of the substituent present in the compound. It is thus evident that by changing the substituent, one can enhance or decrease the abundances of the various fragment ions in the spectra and this may be valuable from a mechanistic point of view.

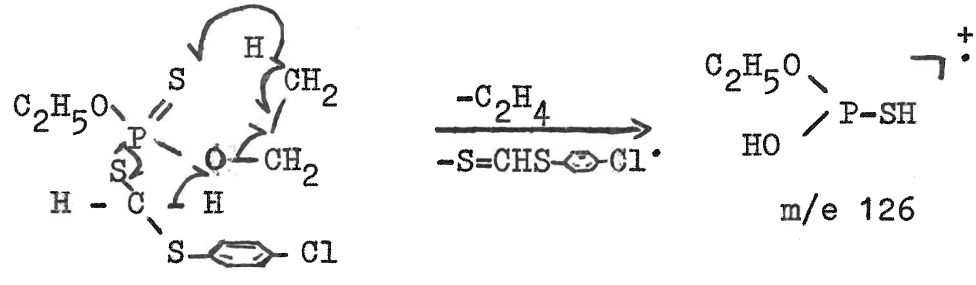
Simple Cleavage Ions

Carbophenolthion may also be regarded as a bis-thioalkane conforming to the general formula, $R\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}R'$. As is characteristic of such compounds, it has an abundant

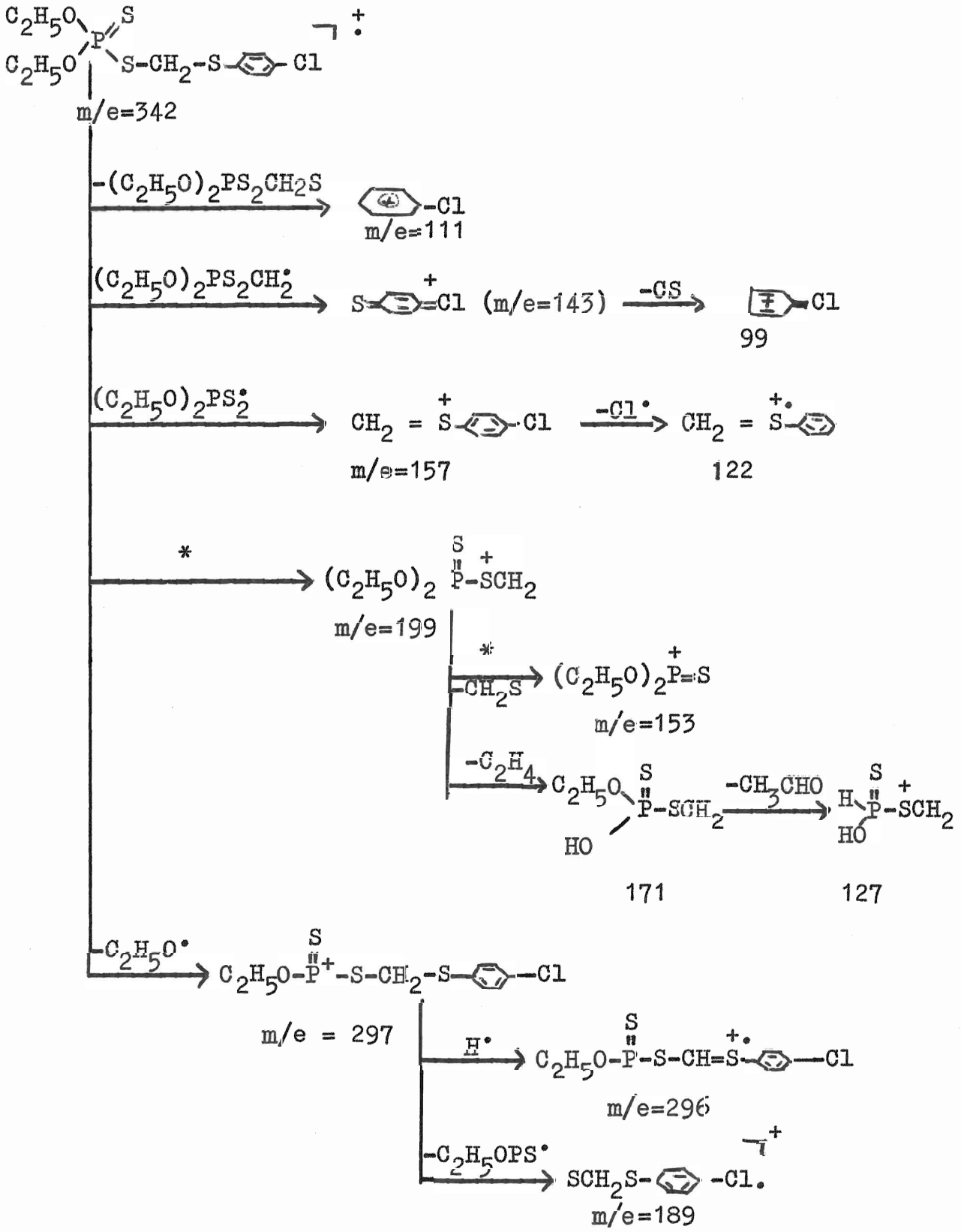
parent ion (72.7%); gives a base peak by cleavage at a bond $\beta$ to the sulphur atom (m/e 153); undergoes $\alpha$-cleavage to give ions of m/e 153 and 143 ($\alpha$ with respect to both the sulphur atoms) and also a double fragmentation involving cleavages of bonds $\alpha$ and $\beta$ on either side of the sulphur atom. In general, it shows considerable similarity to the corresponding oxygenated compounds. All these features are summarised in Scheme 7. In particular, mention may be made of ions of m/e 109 and 122. Two structures are possible for the species of m/e 109. It can have either the $S{=}P{-}S{-}CH_2^+$ structure or the $C_2H_5O{-}\overset{+}{P}(H){+}S$ structure. The latter structure is preferred on evidences of metastable transition and isotopic abundances. Ion of m/e 122 may be formed either by loss of sulphur from the $SCH_2S{-}\phi$ species or by loss of chlorine from the $CH_2S$-  -Cl species. In either case, the species will have the structure $CH_2{=}\overset{+\cdot}{S}{-}$ .

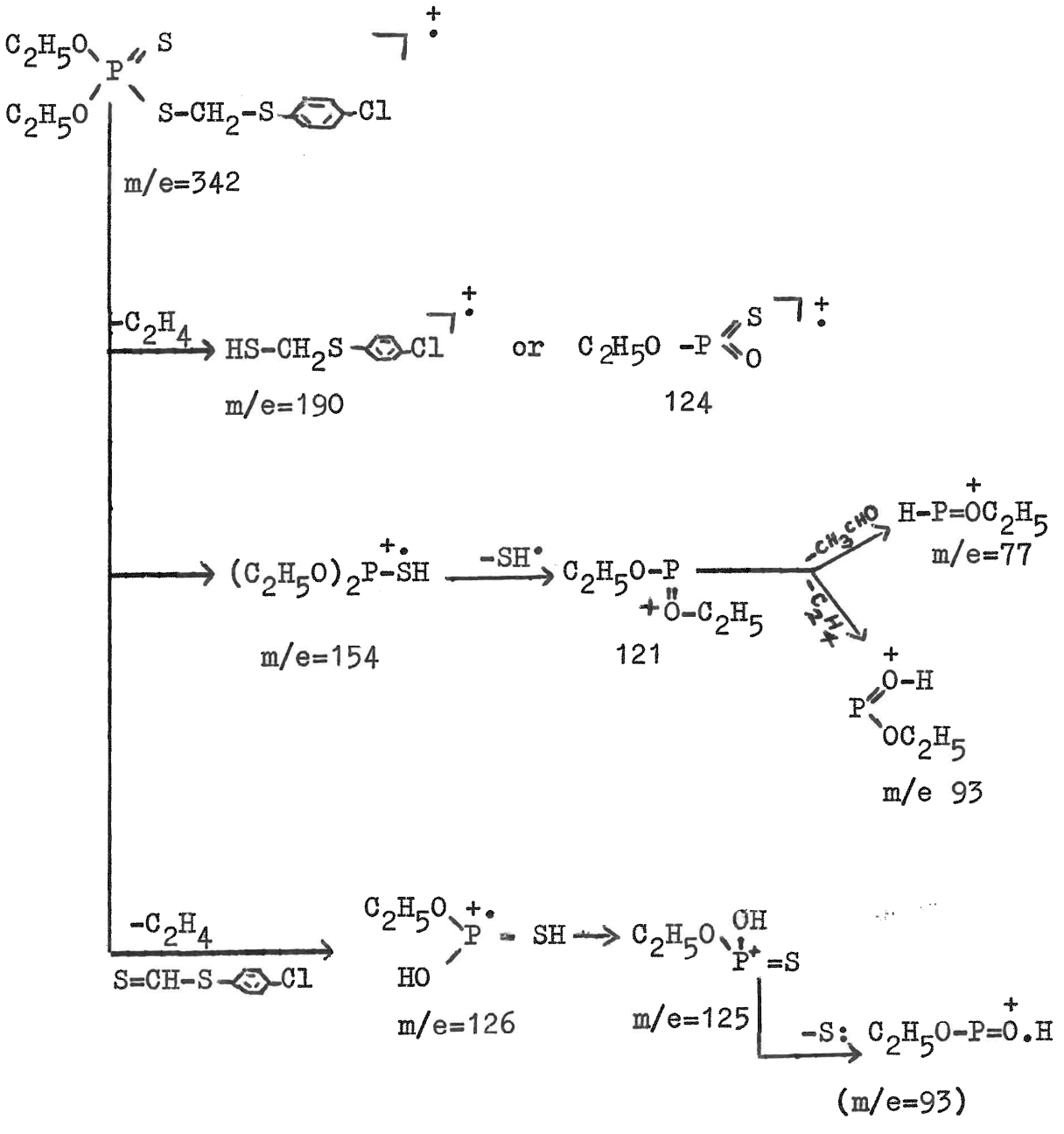
Rearrangement Ions

i) The parent ion eliminates a molecule of $C_2H_4$ and an $S{=}CH{=}S{-}$  $\dot{C}l$ to yield an ion of m/e 126:



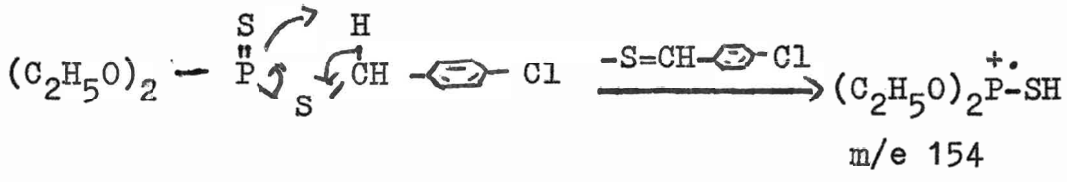

Subsequent loss of H· from m/e 126 yields m/e 125 which then eliminates the sulphur atom to give the species of m/e 93 (Scheme 7).


m/e=342
-(C2H5O)2PS2CH2S
m/e=111
(C2H5O)2PS2CH2•
(m/e=143)
-CS
99
(C2H5O)2PS2•
m/e=157
-Cl•
122
*
m/e=199
-CH2S
m/e=153
-C2H4
-CH3CHO
171
127
-C2H5O•
m/e = 297
H•
m/e=296
-C2H5OPS•
m/e=189



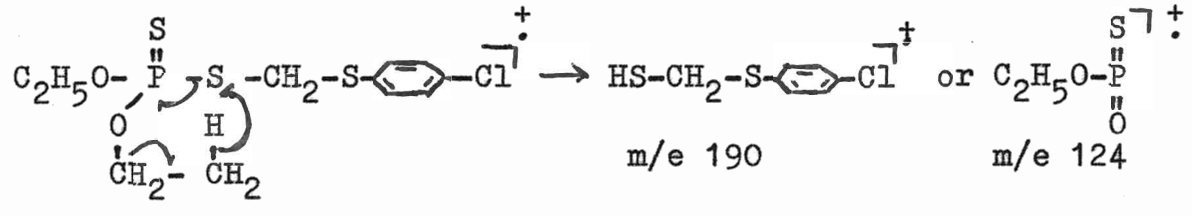

Scheme 7 Fragmentation pattern for Carbophenolthion

ii) A skeletal rearrangement of the parent ion involving loss of S=CH- $\Phi$-Cl gives the ion of m/e 154:

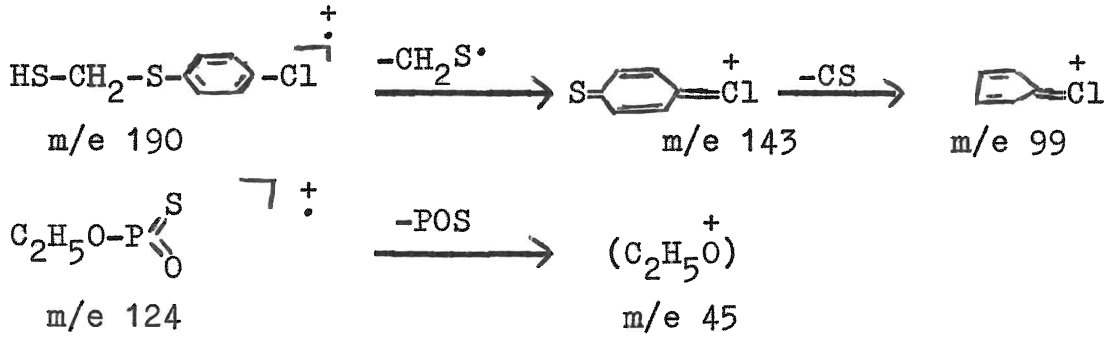


Ion 154 then may eliminate the sulphydryl radical (SH•) to yield the species of m/e 121. This ion now rearranges by loss of $C_2H_4$ to form m/e 93 (supported by metastable transition) and by loss of acetaldehyde to form m/e 77. The structures of the various species are indicated in Scheme 7.

iii) As in the case of the thionophosphates, the parent ion eliminates a molecule of ethylene involving rupture of the (P-S) and (O-$CH_2$) bonds to give either of two odd electron ions:



Both the odd ions are very weak as they readily dissociate by simple rupture to give the more abundant ions of m/e 143 and 45 respectively:




It may be mentioned that loss of the SH• from m/e 190 can yield the ion of m/e 157, the base peak in the spectrum. However, its formation from the parent ion by simple cleavage is the favoured pathway.

Thus the spectrum of carbophenolthion may be summed up in the statement that it has a stable parent ion and fewer fragment ions (See Fig. 6). It behaves more like a dithioether as is exemplified from the formation of its base peak at m/e 157 instead of the expected ion at m/e 97. The reason for this could be that ion 157 is formed by a simple rupture of bonds and that it is much more resonance stabilised through extended conjugation than the ion of m/e 97. This unique feature, incidentally, may aid its identification in a pesticide residue.

b) <u>Ethion</u> $(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-S-CH_2-S-\overset{S}{\overset{\|}{P}}(OC_2H_5)_2$

Damico[53] has given the bar graph spectrum of ethion and has explained the formation of the base peak at m/e 97. No further comments were made on its other spectral features.

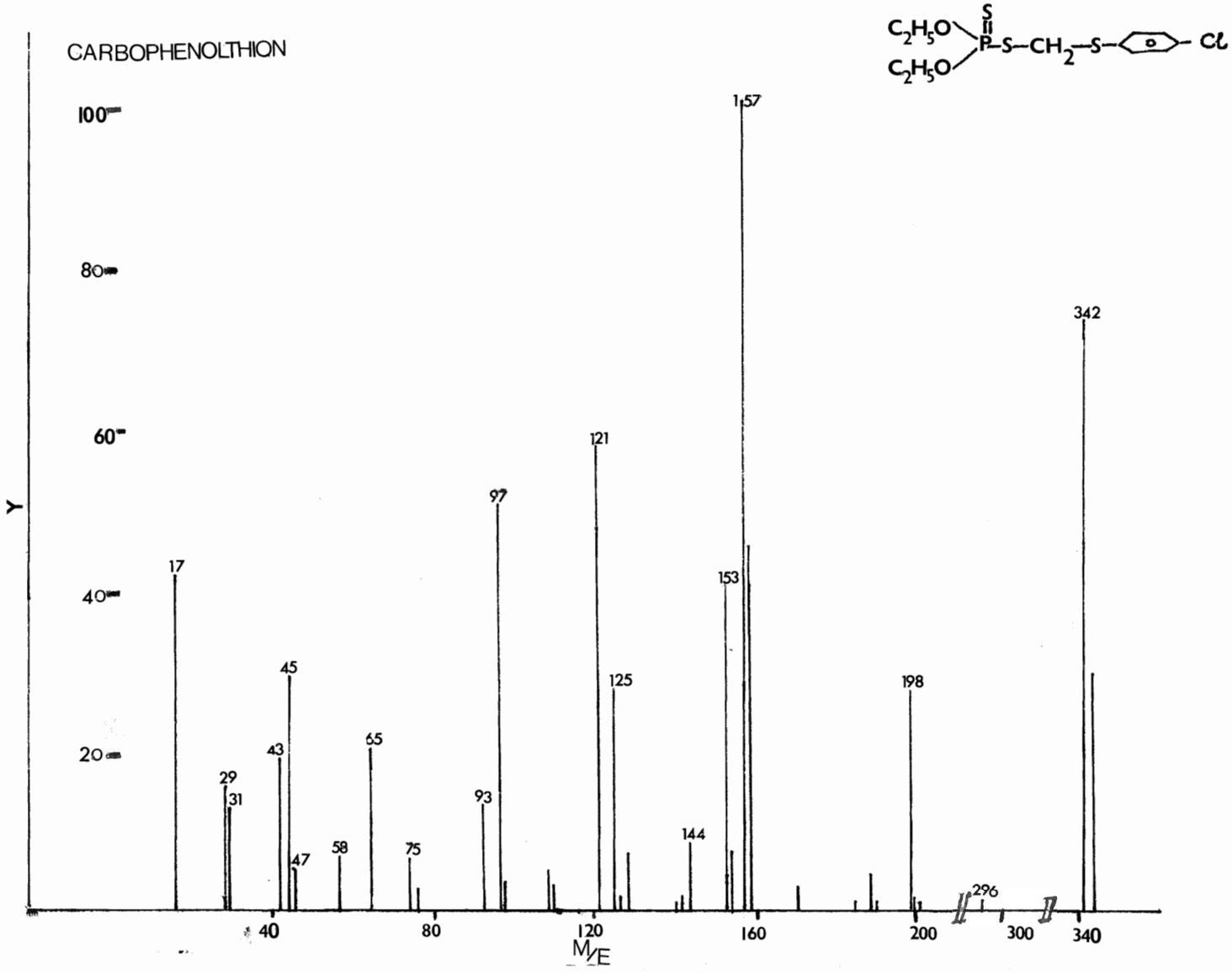



fig.6.mass spectrum ofCCARBOPHENOLTHIN.(AEI.MS.I2.)

Ethion is structurally close to carbophenolthion and this similarity in structure gives rise to the same ionic species at m/e 171, 158, 154, 142, 141, 130, 129, 122, 121, 113 and 112. However it differs from carbophenolthion in the following respects:

(1) Ions resulting from the dissociation of the $(C_2H_5O)_2\overset{+}{P}=S$ are dominant in the spectrum of ethion whereas they are less significant in carbophenolthion.

(2) The base peak in ethion is the species of m/e 97 whereas it is less important for carbophenolthion.

In both the above respects, ethion resembles the phosphorothionates such as parathion (See Fig. 7). But it differs from them in exhibiting peaks at m/e 231, 186 and 140. Their formation and structures are indicated in Scheme 8. (These ions result from simple cleavage on rearrangement reactions and thus need no further elaboration). Owing to the above factors, the identification of ethion from a given pesticide residue should be feasible.

Phosphorothioite Group

Tributyl phosphorotrithioite: $(C_4H_9S)_3P$

No serious attempt has been made to elucidate the mass spectral behaviour of the phosphorotrithioites, $P(SR)_3$ which are structurally analogous to the trialkyl phosphites, $P(OR)_3$ , although evidence does exist on the study of other

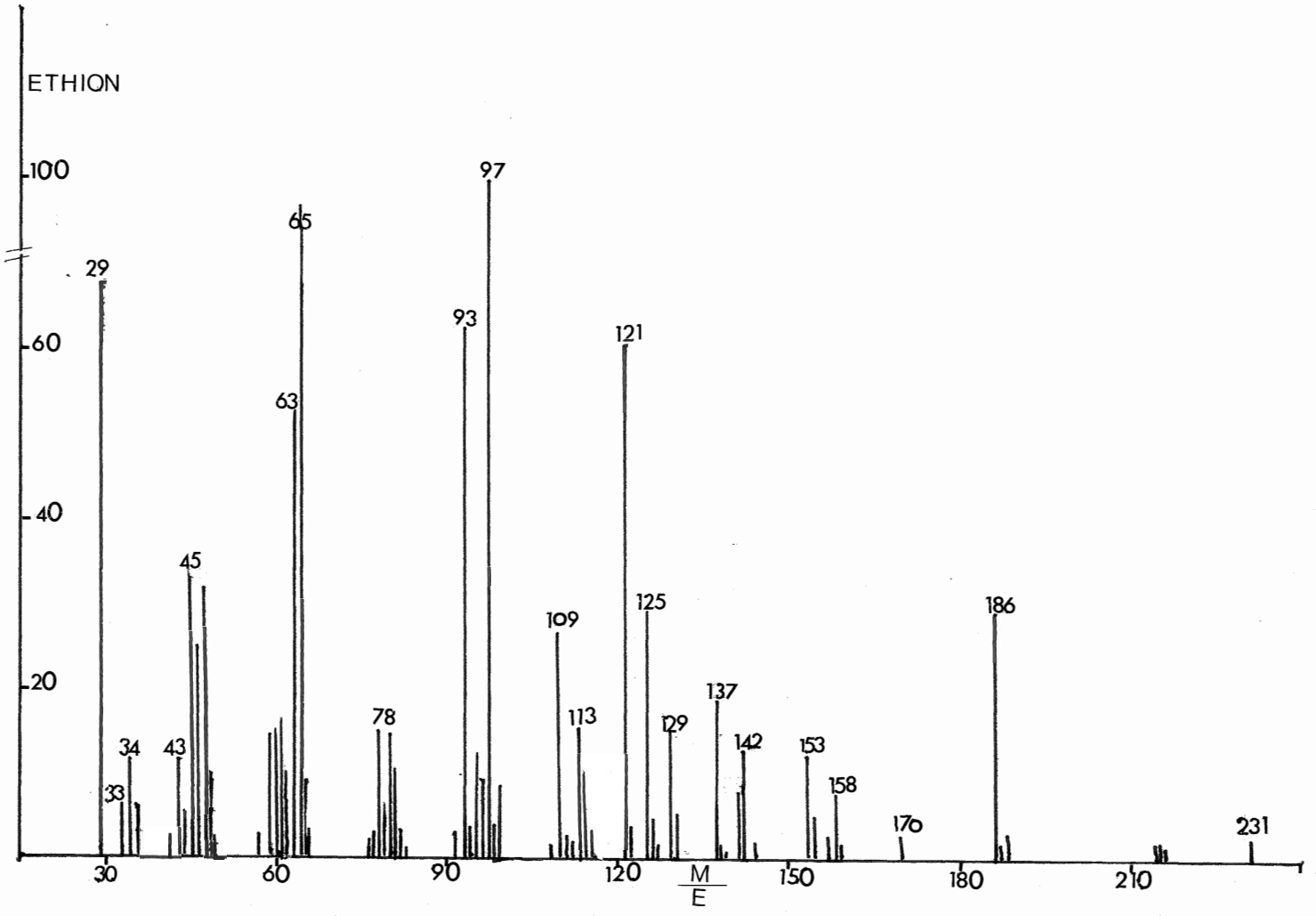
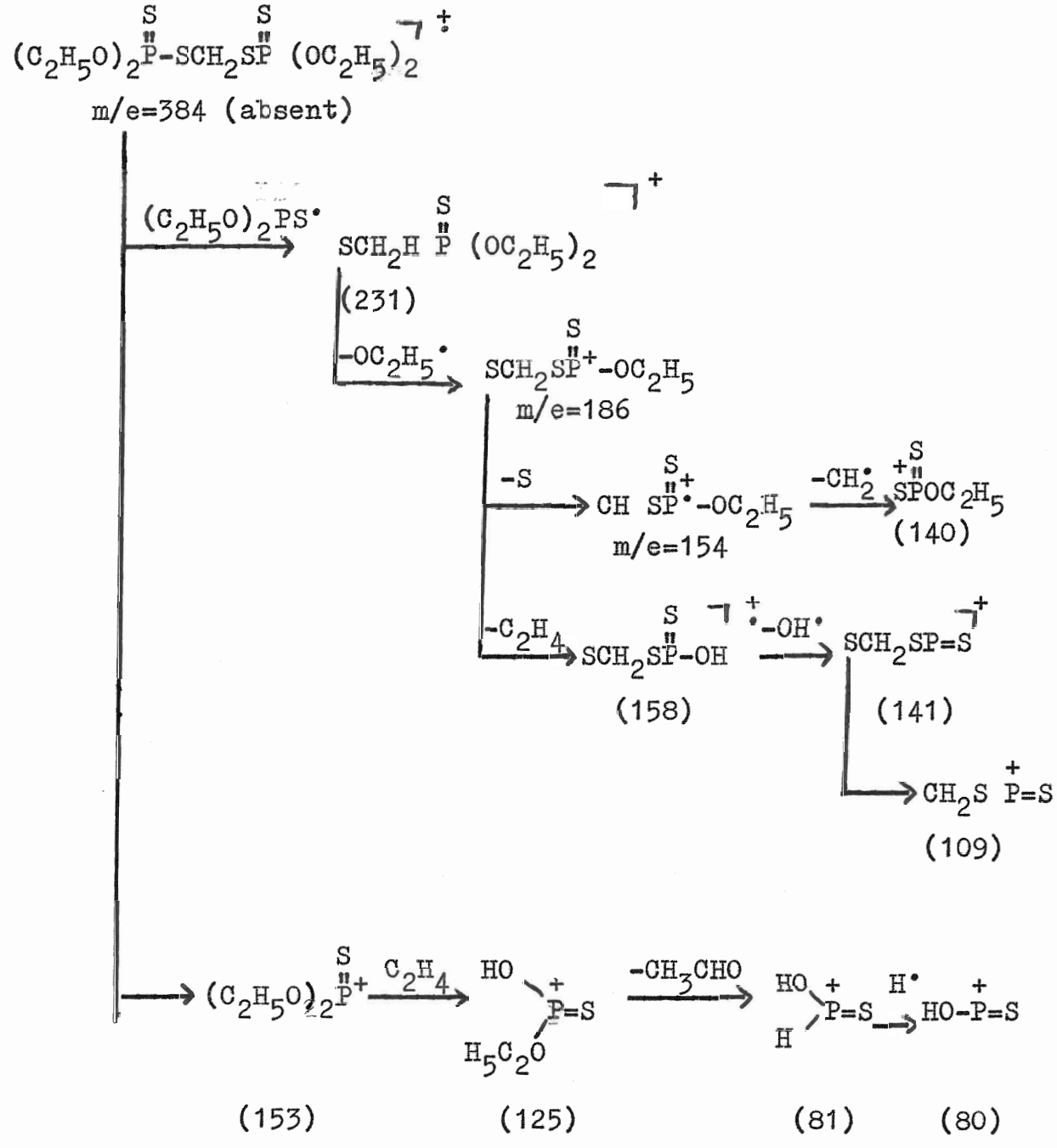



fig.7.mass spectrum of ETHION.(AEI.MS.30.)



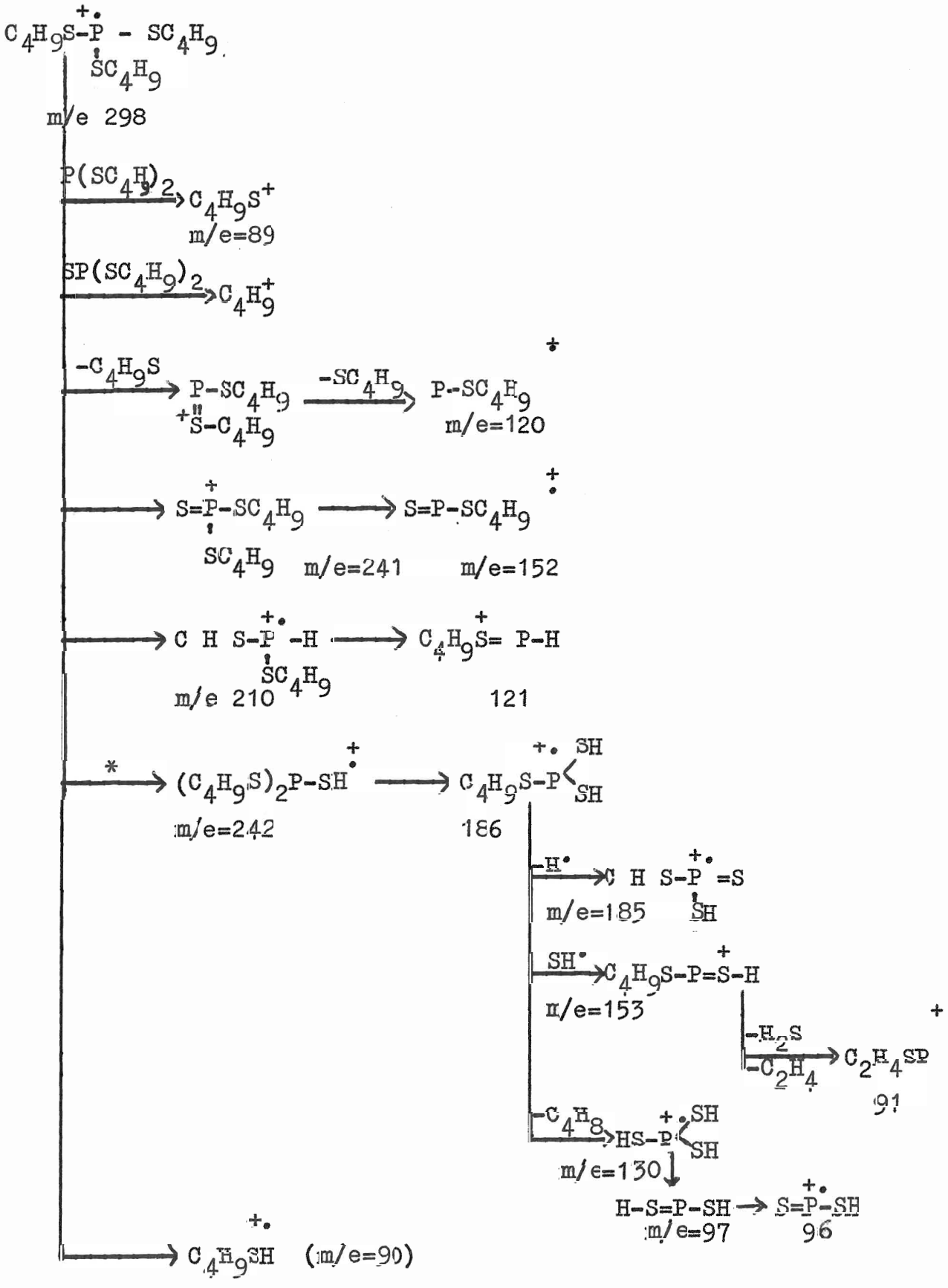

Scheme 8 Fragmentation Pattern for Ethion

compounds having (P-S) linkages such as on the thionates [46,51-55], thiolates[55], thioates[52-55] and dithioates[52,53]. Further Harless[39] and Occolowitz et al[40] have generalised on the mass spectral properties of the trialkyl and triaryl phosphites. It is, therefore, of interest, to examine the behaviour of the corresponding sulphur analogues and to note the points of similarities and dissimilarities for the two groups of compounds. Tributyl phosphorotrithioite, a defoliant, is chosen as a typical representative.

As in the case of the phosphites, the fragmentation pattern is a combination of simple cleavage ions and a series of rearrangement ions involving hydrogen transfers.

(i) Simple cleavages:

Simple cleavage ions are formed mostly by rupture of bonds $\alpha$ to the sulphur atom on either side. $\beta$ -cleavages, characteristic of ethers are less significant in this spectrum. In fact, the fragmentation pattern is closer to that of an aliphatic hydrocarbon as seen from the successive hydrogen losses and the decreasing abundances of ions at every 14 mass units below m/e 90. Also the formation of the two most intense ions in the spectrum (m/e 209 and the base peak at m/e 57) is typical of a hydrocarbon cleavage. These features are incorporated in Scheme 9 and Fig. 8.




Scheme 9 Fragmentation pattern for Tributyl phosphorotrithioite

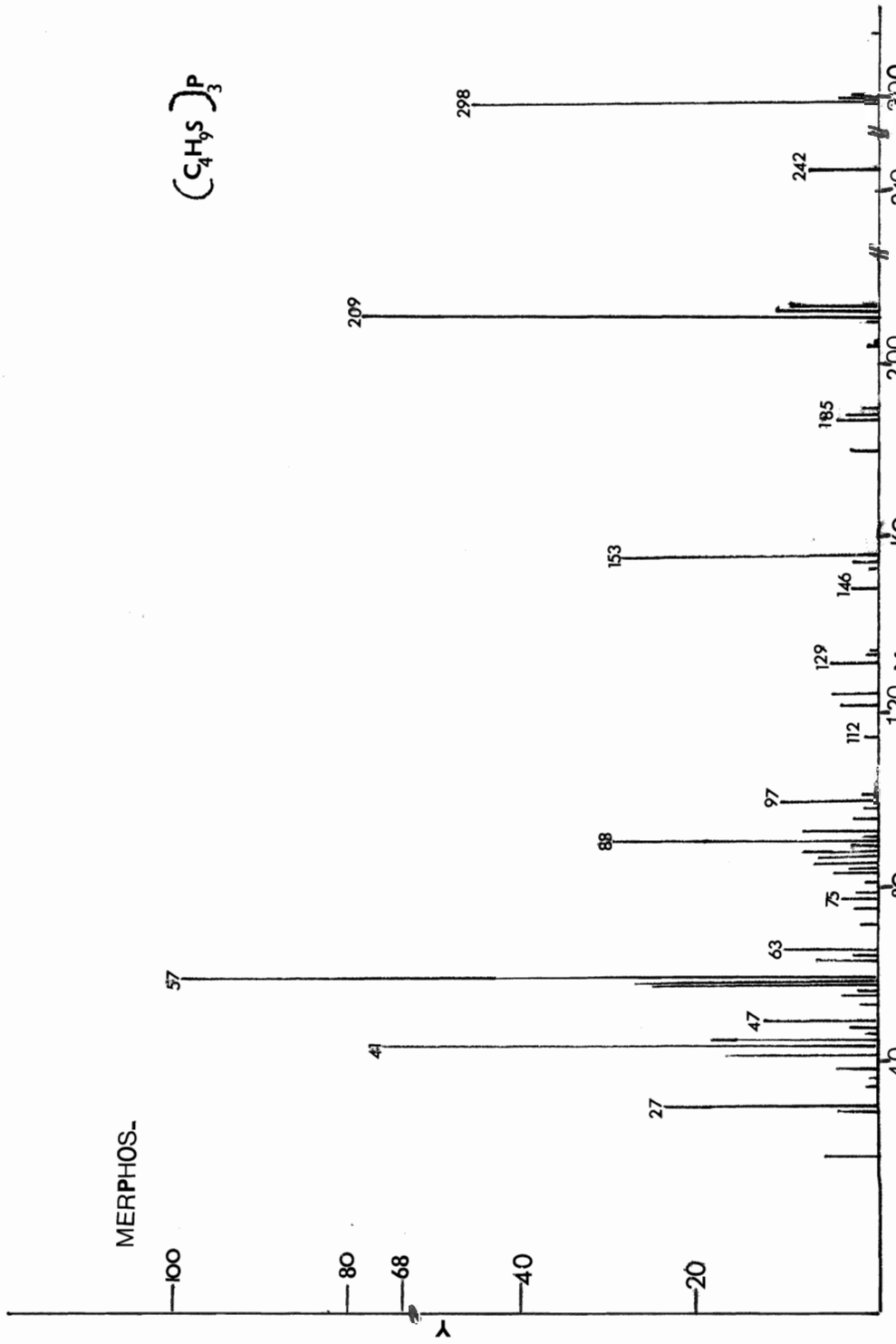
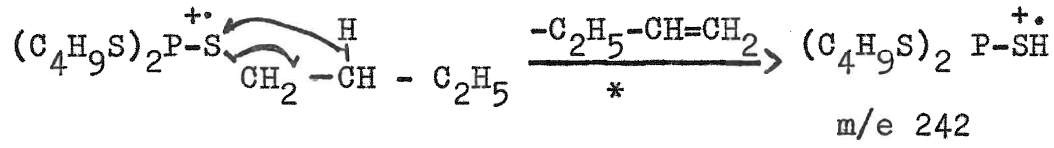


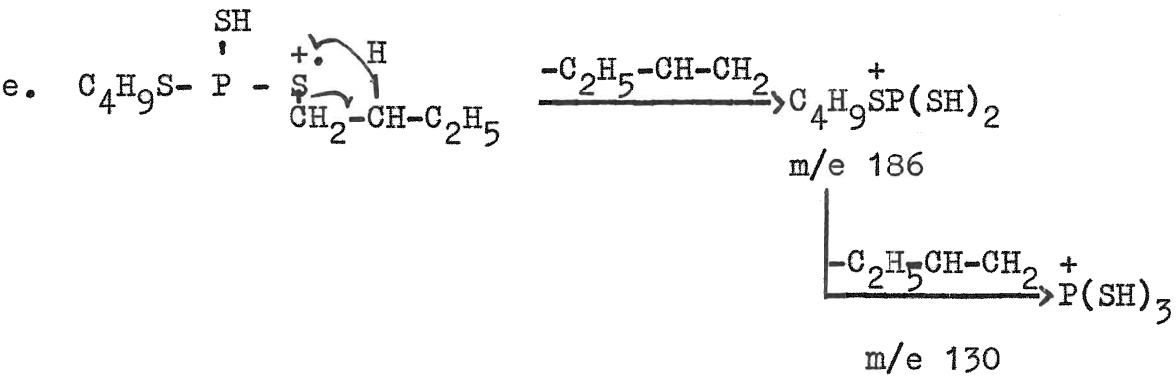

fig.8.mass spectrum of MERPHOS.(AEI MS.I2&3)

(ii) Rearrangement ions:

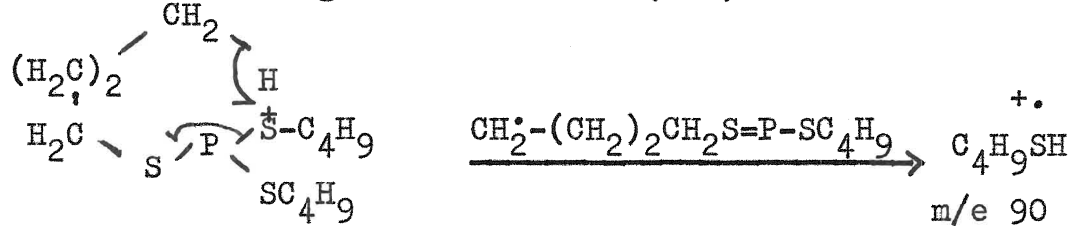
Rearrangements in tributyl phosphorotrithioite may involve hydrogen transfer either to the sulphur or to the phosphorus atom. Thus transfer of a $\beta$-hydrogen ( $\beta$ to the sulphur) to the sulphur atom in a 4-membered cyclic transition state may be postulated for the formation of ion of m/e 242. The rearrangement involves loss of a butene molecule and is supported by a metastable transition.



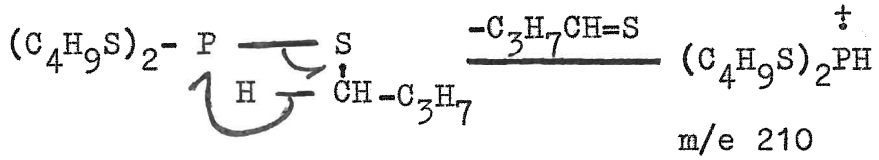
Ion 242 may rearrange in an analogous way to give m/e 186



(ii) Formation of a butyl mercaptan ion (m/e 90) may result by transfer of a hydrogen to the sulphur with the simultaneous breakage of one of the (P-S) bonds:



(iii) Migration of hydrogen to the phosphorus atom involving a four membered transition state may be envisaged in the formation of ion of m/e 210:




The tributyl phosphorotrithioite spectrum differs from the corresponding tributyl phosphite spectrum[39,40] in the following respects:

(1) The parent ion in phosphorotrithioite is very abundant whereas it is weak in the phosphite.

(2) The base peak of tributyl phosphite is the $HP(\overset{+}{O}H)_3$ species whereas the analogous $HP(\overset{+}{S}H)_3$ ion is least important in the trithioite spectrum.

(3) Rearrangement ions such as $HP(OC_4H_9)_2\overset{+}{O}H$ and $HP(OC_4H_9)(\overset{+}{O}H)_2$ are very significant for the phosphite while the analogous sulphur containing species are very insignificant.

(4) Simple cleavage ions dominate the spectrum of tributyl phosphorotrithioite but they are less important for the tributyl phosphate.

In short, the tributyl phosphorotrithioite spectrum shows little similarity to its oxygen analogue and tend to behave more like an aliphatic hydrocarbon.

## Part ii) The Mass Spectra of Thiocarbamate and Dithiocarbamate Pesticides*

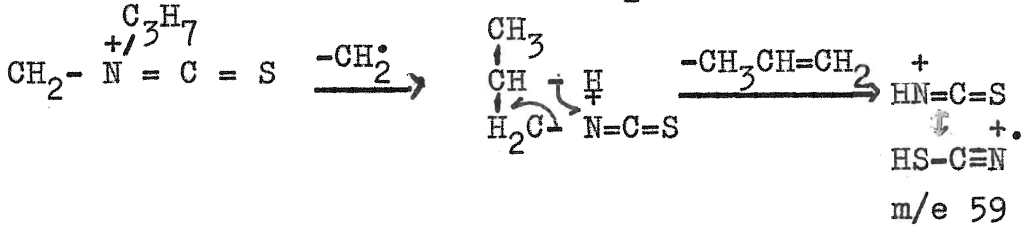
*Appendix B gives the m/e values and relative abundances of the variations.

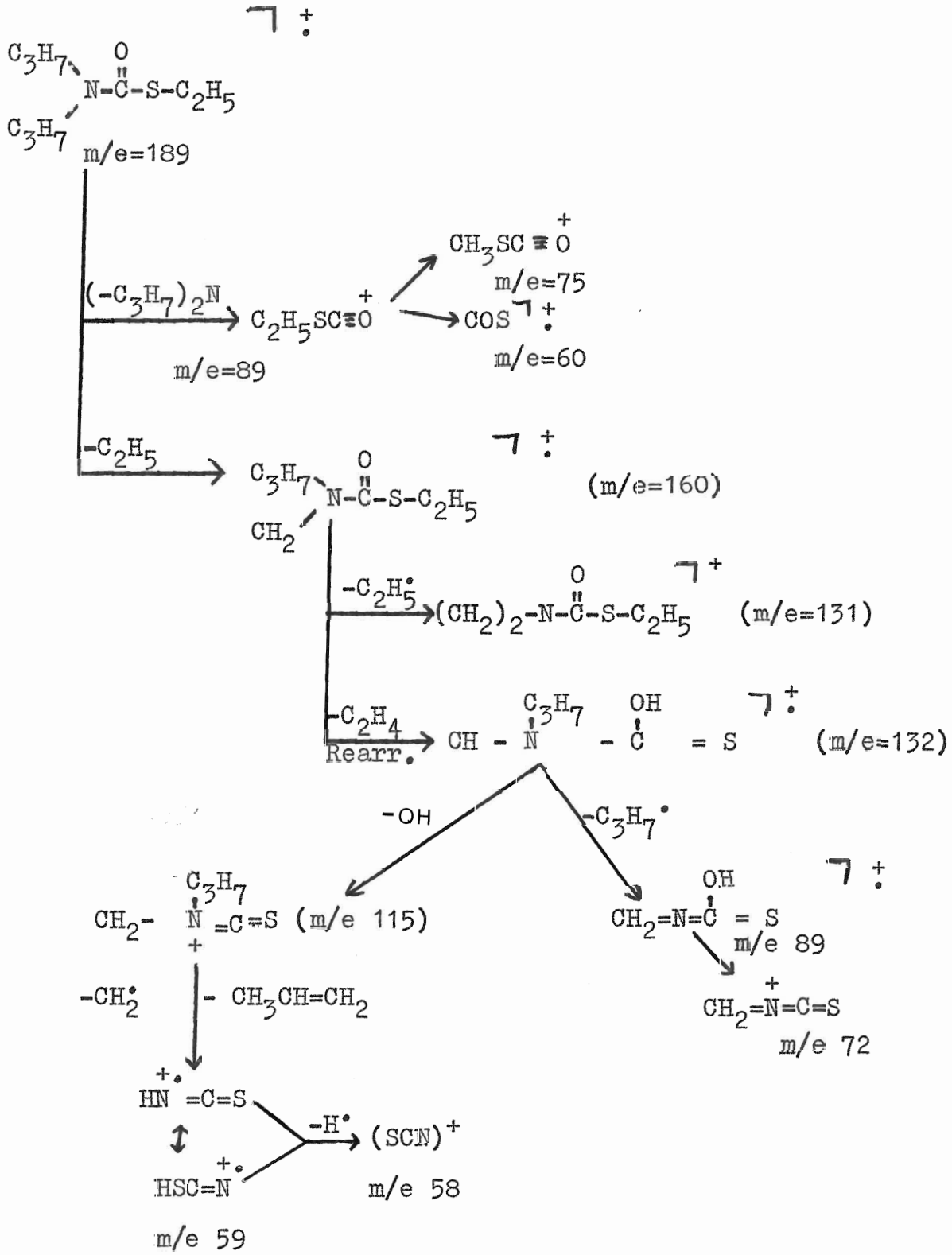
Thiocarbamate Pesticides

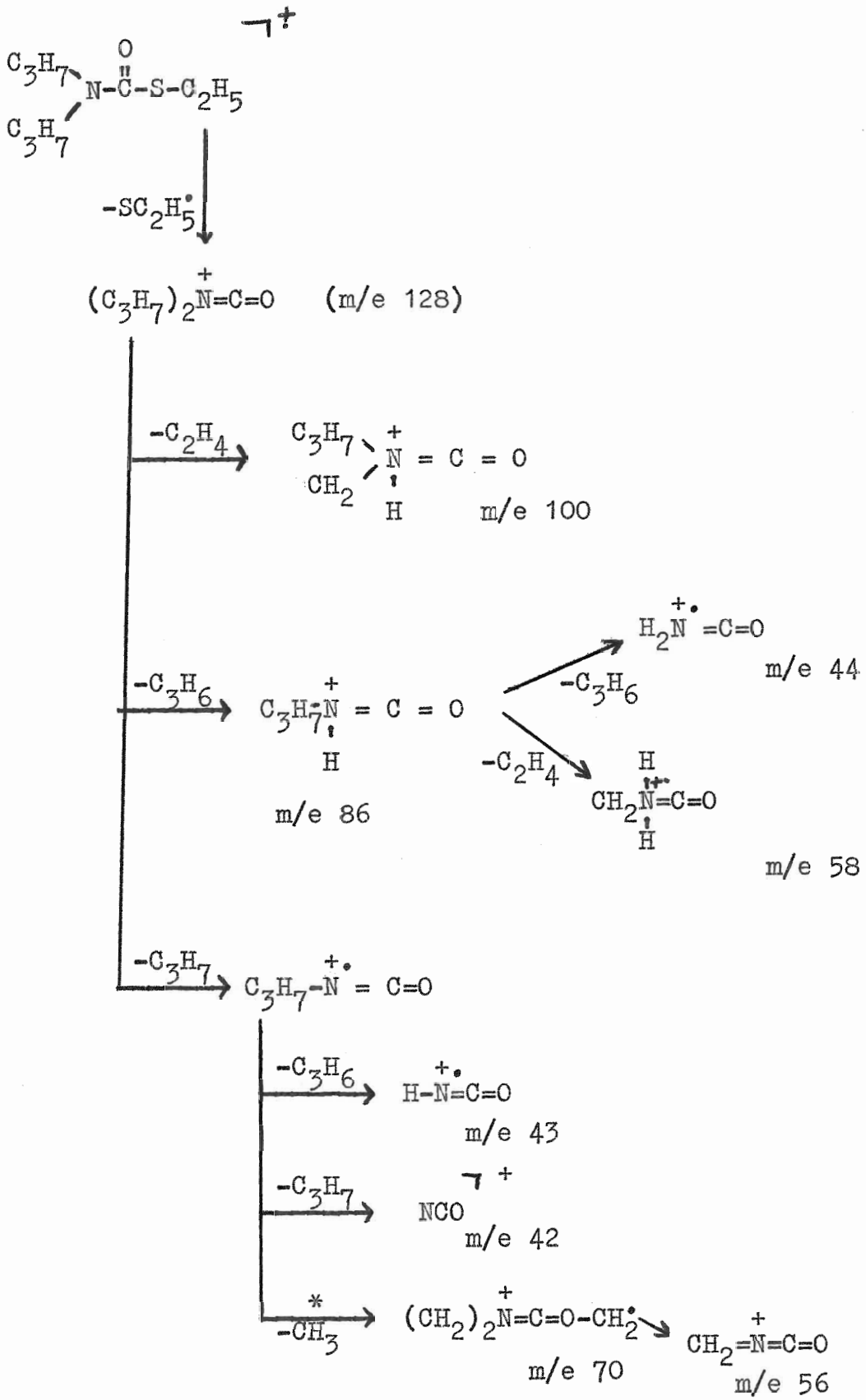
(a) Eptam $(C_3H_7)_2\text{-N-}\overset{\overset{O}{\|}}{C}\text{-S-}C_2H_5$

Damico et.al.[59] have reported the bar-graph spectrum of 'Eptam' and have elucidated pathways for the formation of ions of m/e 161, 128, 86, and 43. Apart from this the spectrum remained unexplained. A detailed discussion of the mass spectrum of Eptam therefore seems appropriate.

The abundant molecular ion cleaves at the (N-C), (C-S) and the S-alkyl) bonds to give some of the major ions in the spectrum as exemplified in Scheme 10. Ions of m/e 128, 160, 89 and 29 are all abundant as each one is a stable entity. The 93% abundance of ion 128 is understandable in view of its resonance stability. The species of m/e 160 undergoes a Mclafferty rearrangement eliminating a molecule of ethylene. Subsequent loss of an OH• from this rearranged species leads to an isothiocyanate ion of m/e 115. Cleavages typical of an isothiocyanate ion (such as the loss of SH• ; loss of $C_2H_4$ leading to cyclisation and loss of NCS•) are absent in the spectrum. These cleavages are, however, favoured only under specific conditions[77]. Nevertheless the isothiocyanate ion yields m/e 72 by loss of $C_3H_7$• and m/e 59 by loss of propylene and $CH_2^•$ (Scheme 10).



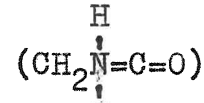

m/e=189
(-C3H7)2N
C2H5SC≡O+
m/e=89
CH3SC≡O+
m/e=75
COS+·
m/e=60
-C2H5
(m/e=160)
-C2H5·
(CH2)2-N-C-S-C2H5
(m/e=131)
-C2H4
Rearr.
CH - N - C = S
(m/e=132)
-OH
-C3H7·
CH2- N =C=S (m/e 115)
-CH2·
- CH3CH=CH2
CH2=N=C = S
m/e 89
CH2=N=C=S
m/e 72
HN =C=S
HSC=N
-H·
(SCN)+
m/e 58
m/e 59




Scheme 10 Fragmentation pattern for Eptam

Although, formation of ion 59 is found to be important for isothiocyanates[77], in the present case, it is of lower significance. The ion at m/e 128 is an isocyanate ion, having the structure, $(C_3H_7)_2\overset{+}{N}=C=O$. This is the second largest peak in the spectrum due to the charge stabilisation on the nitrogen atom by the electron donating propyl groups. As expected of an isocyanate, it yields the base peak ($C_3H_7^+$) by cleavage of the N-alkyl bond. $\alpha$ -cleavage of the alkyl group ($\alpha$ w.r. to nitrogen) in the isocyonate gives m/e 56 and $\beta$ -cleavage of the same alkyl group yields m/e 70. Ion 56 is, however, of lower significance in contrast to its high abundance in normal isocyanates. Rearrangements involving loss of $C_2H_4$ and $C_3H_6$ from the isocyanates leads to ions of m/e 100 and 86 respectively.

On the basis of Lewis[60] postulation one might expect the ion of m/e 100 to have the $(C_3H_7)_2\overset{+}{N}$ structure formed by the simple cleavage of the (N-C) bond, and with nitrogen in the divalent state. But in the present case (where the ion is postulated to have been formed by a rearrangement process) nitrogen is in the much more preferred quinquivalent state. On a similar basis ion 86 may lose a molecule of $C_2H_4$ to yield the species of m/e 58 in which nitrogen is quinquivalent and this structure



m/e 58

may be preferred to the $(SCN)^+$ species.

m/e 58

Also one can envisage loss of a propylene molecule from the same ion to give m/e 44 having the $H_2\overset{+}{N}=C=O$ structure. Two possible formulations are possible for the ion of m/e 89. It can be formed by direct cleavage of the (C-N) bond to give the $C_2H_5SC\equiv\overset{+}{O}$ structure or may be formed from the ion of m/e 160 by loss of $C_2H_4$ followed by breakage of the $C_3H_7^{\bullet}$ to give the $CH_2=N-\overset{OH}{\overset{|}{C}}=S$ structure. Isotopic ratio measurements confirm the $(C_2H_5S\overset{+}{C}O)$ structure for this species.

In conclusion, the spectrum of Eptam is the sum total of the fragmentation patterns of the carbamate molecular ion, the isothiocyanate ion and the isocyanate ion (see Fig. 9).

(b) <u>Perbulate</u> $\left(\begin{matrix}C_2H_5\\C_4H_9\end{matrix}\right)N-\overset{O}{\overset{\|}{C}}-S-C_3H_7$

Perbulate has not been examined by mass spectrometry. However, it is structurally close to Eptam and accordingly has similar mass spectral properties as depicted in Scheme 11 and Fig. 10. Ions of m/e 128, 160, 43 and 29 are intense as expected. The species of m/e 128 is the base peak in the spectrum. In this respect, it differs from Eptam whose base peak is at m/e 43 ($C_3H_7^+$). In analogy with this, one would have expected either $C_4H_9^+$ or $C_2H_5^+$ to be the base peak in Perbulate. It could be that the isocyanate ion at m/e 128 is much more stable than the corresponding ion

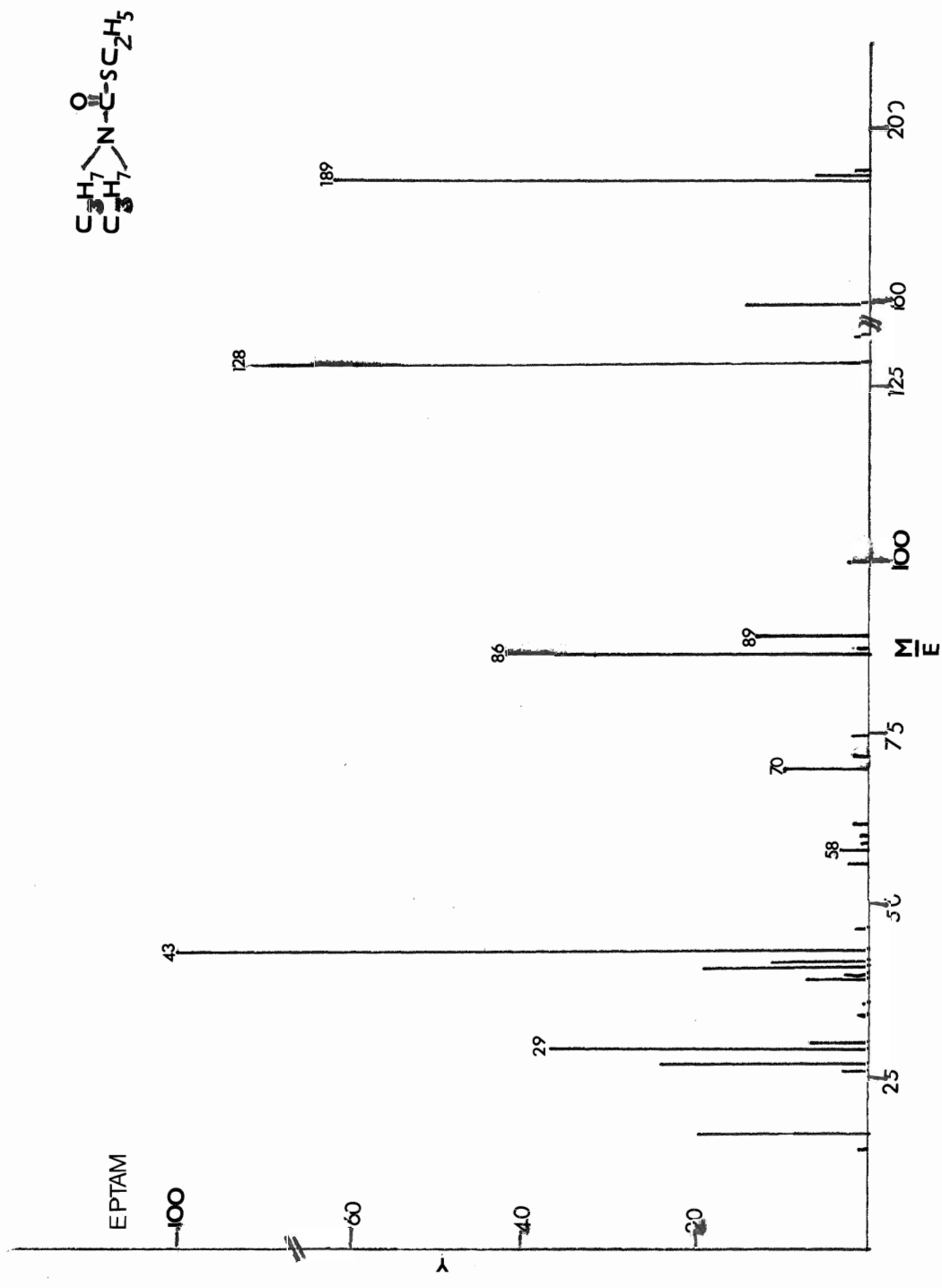
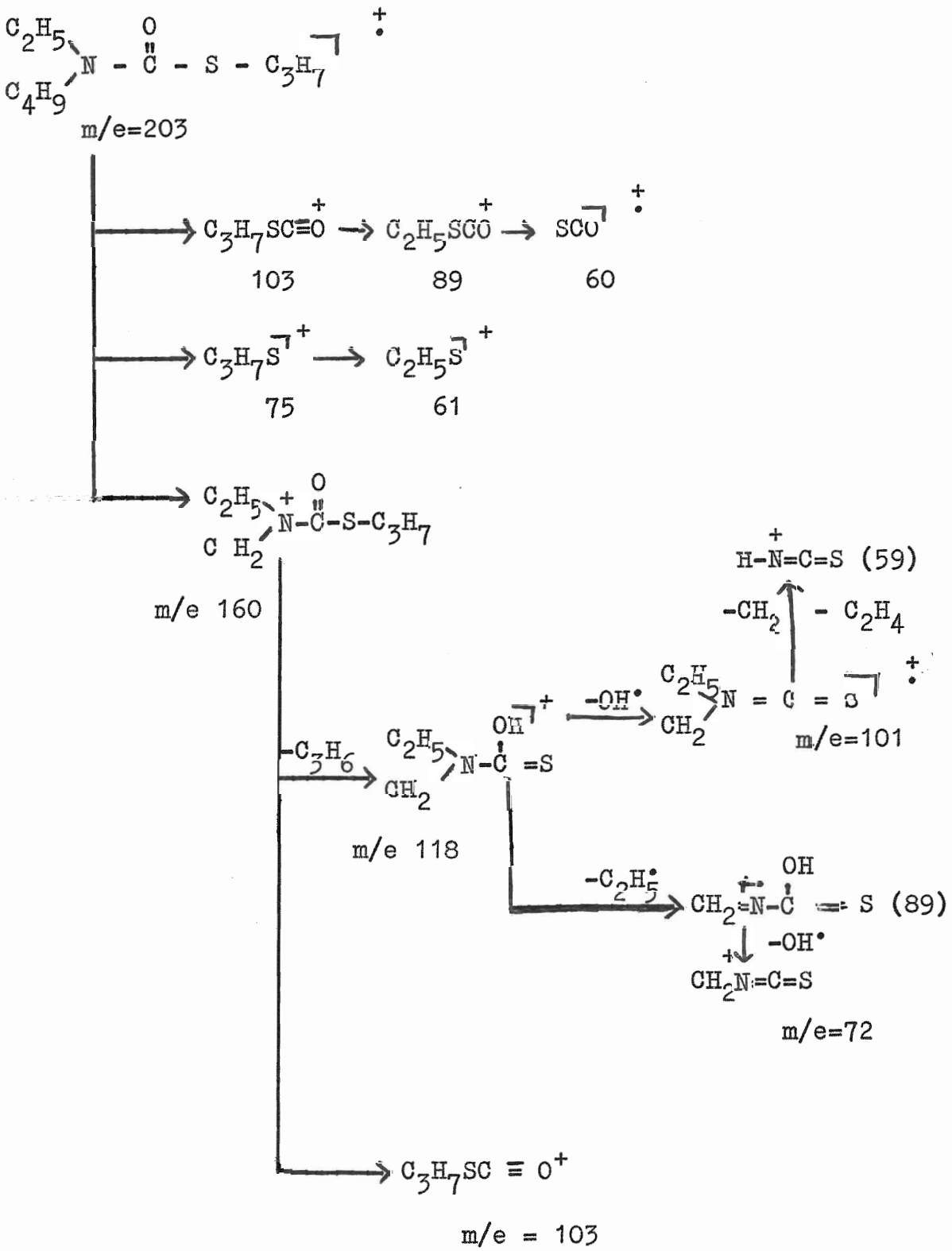
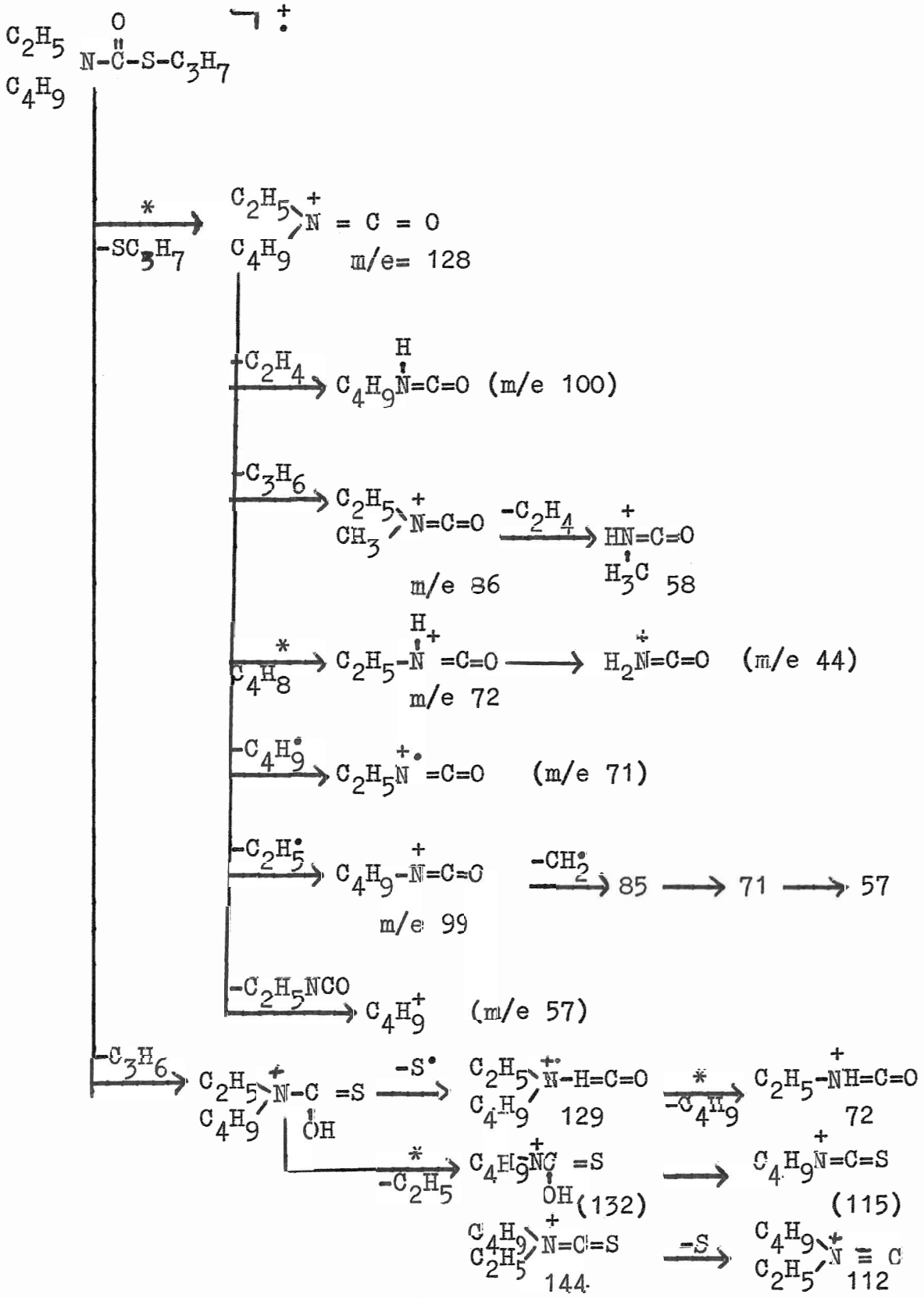



fig.9.mass spectrum of EPTAM.(mol.wt.189.)


m/e=203
103
89
60
75
61
m/e 160
m/e 118
m/e=101
(59)
(89)
m/e=72
m/e = 103




Scheme 11 Fragmentation Pattern for Perbulate

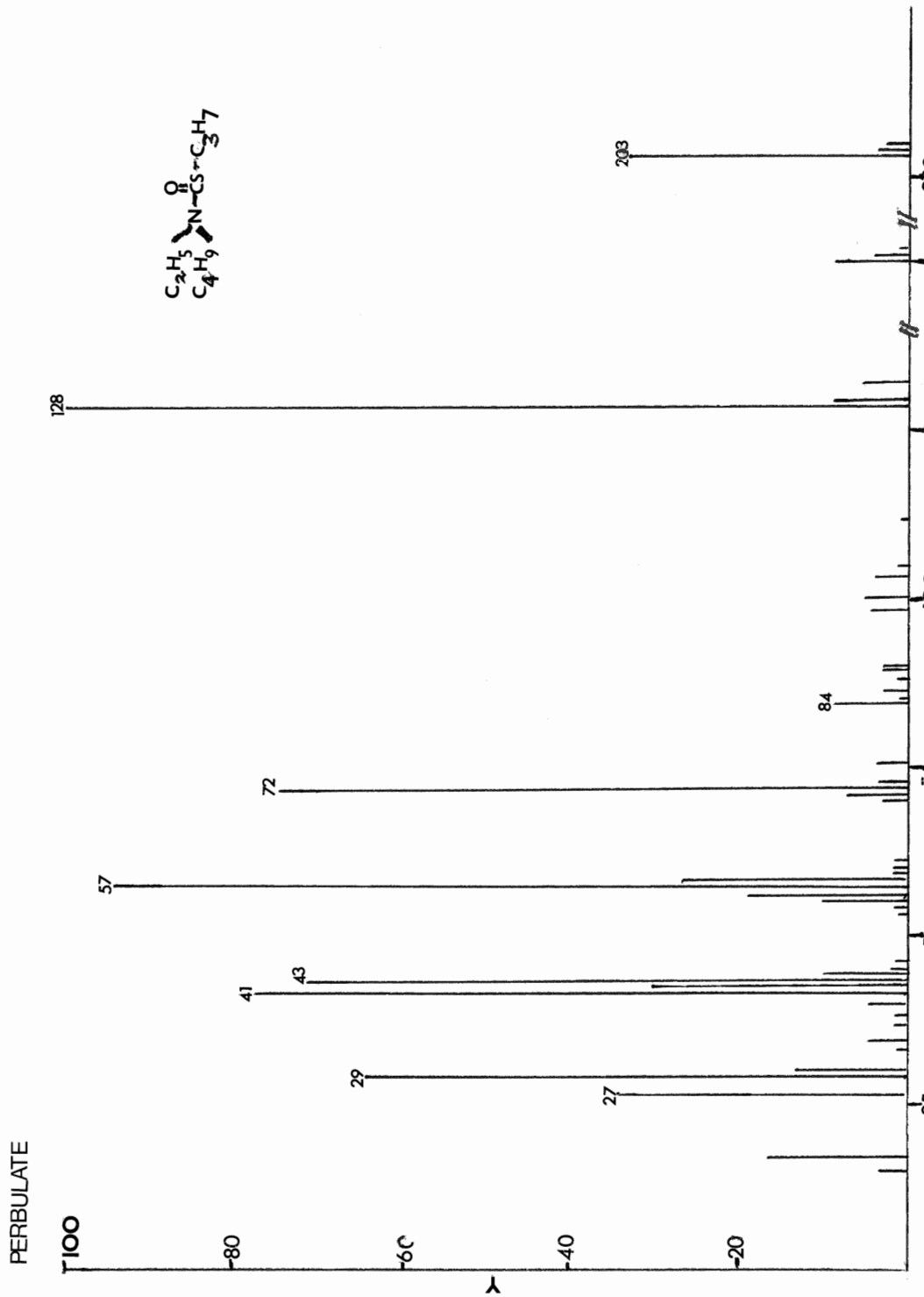
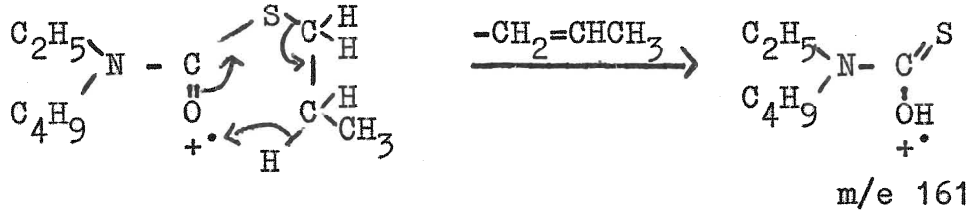



fig.10.mass spectrum of PERBULATE.(AEI.MS.12.)

in Eptam as the butyl group in the former may stabilise the charge on the nitrogen atom more than the isopropyl group in the latter. This is understandable in view of its 94% abundance in Eptam and 100% abundance in Perbulate. Apart from this, both the spectra show identical behaviour. Thus, for reasons same as in the case of Eptam, the species of m/e 100 is assigned the $C_4H_9\text{-}\overset{+}{\underset{H}{N}}=C=O$ structure rather than the $C_4H_9\text{-}\overset{+}{N}\text{-}C_2H_5$ formulation and the species of m/e 44 is formulated as $H_2N^+=C=O$ rather than $(CS)^{+\bullet}$. Similarly ion 72 is given the $C_2H_5\overset{+}{N}H=C=O$ structure instead of the $CH_2=\overset{+}{N}=C=S$ formulation. This is based on isotopic ratio measurements (m/e 73/72) and on the formation of the ion of m/e 44 by loss of $C_2H_4$, supported by a metastable transition. This, incidentally, seems to substantiate the structure of the ion 44 as well.

Unlike in the case of Eptam, Perbulate undergoes a rearrangement reaction involving loss of propylene to give an ion of m/e 161 by the following path:




m/e 161

This ion is very significant in the spectrum of Perbulate. Also are important the fragment ions derived from it (see Scheme 11).

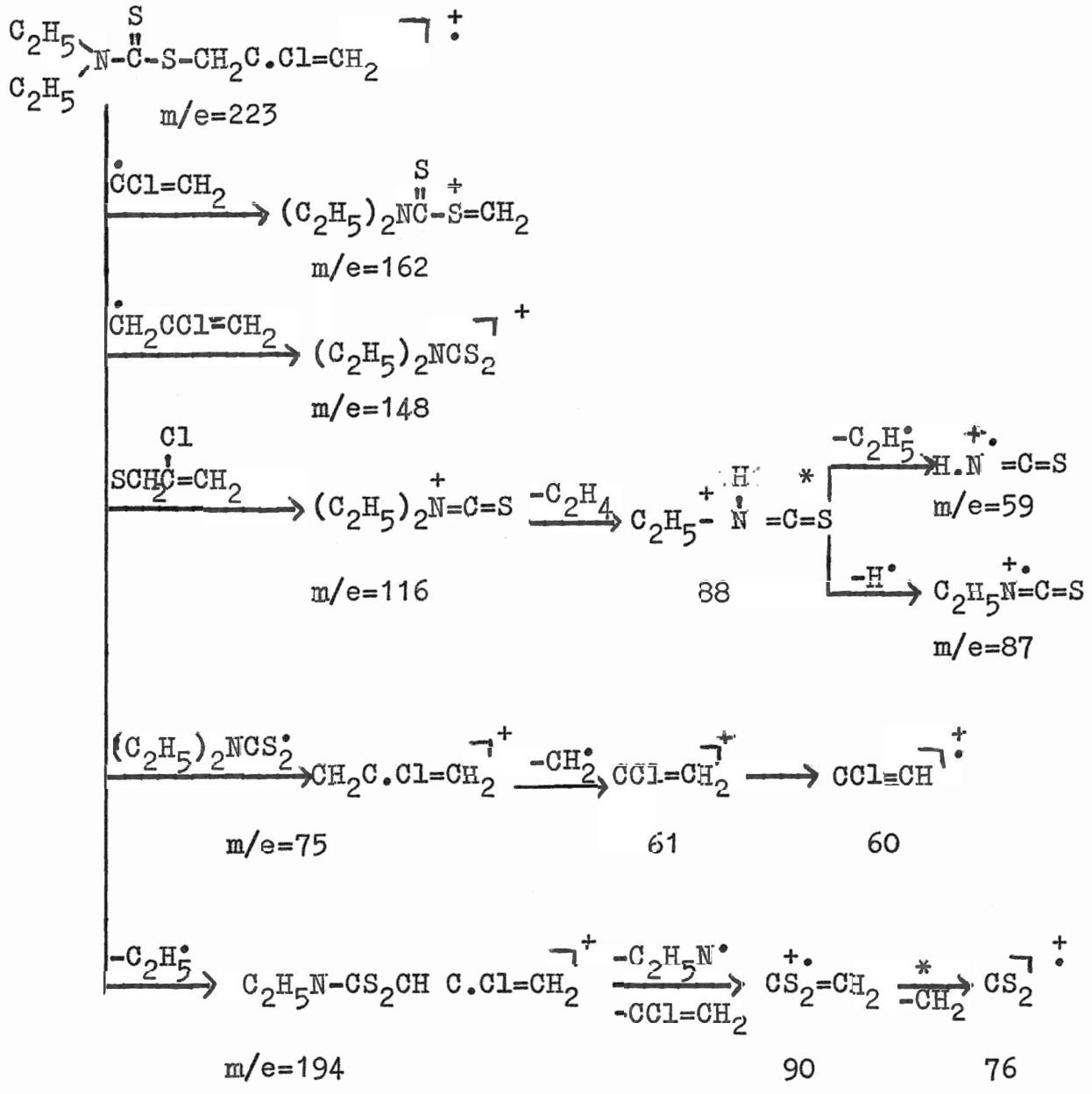
In conclusion, Perbulate differs from Eptam in exhibiting the above rearrangement peak and the base peak at m/e 128. These facts may enable its identification in a pesticide residue.

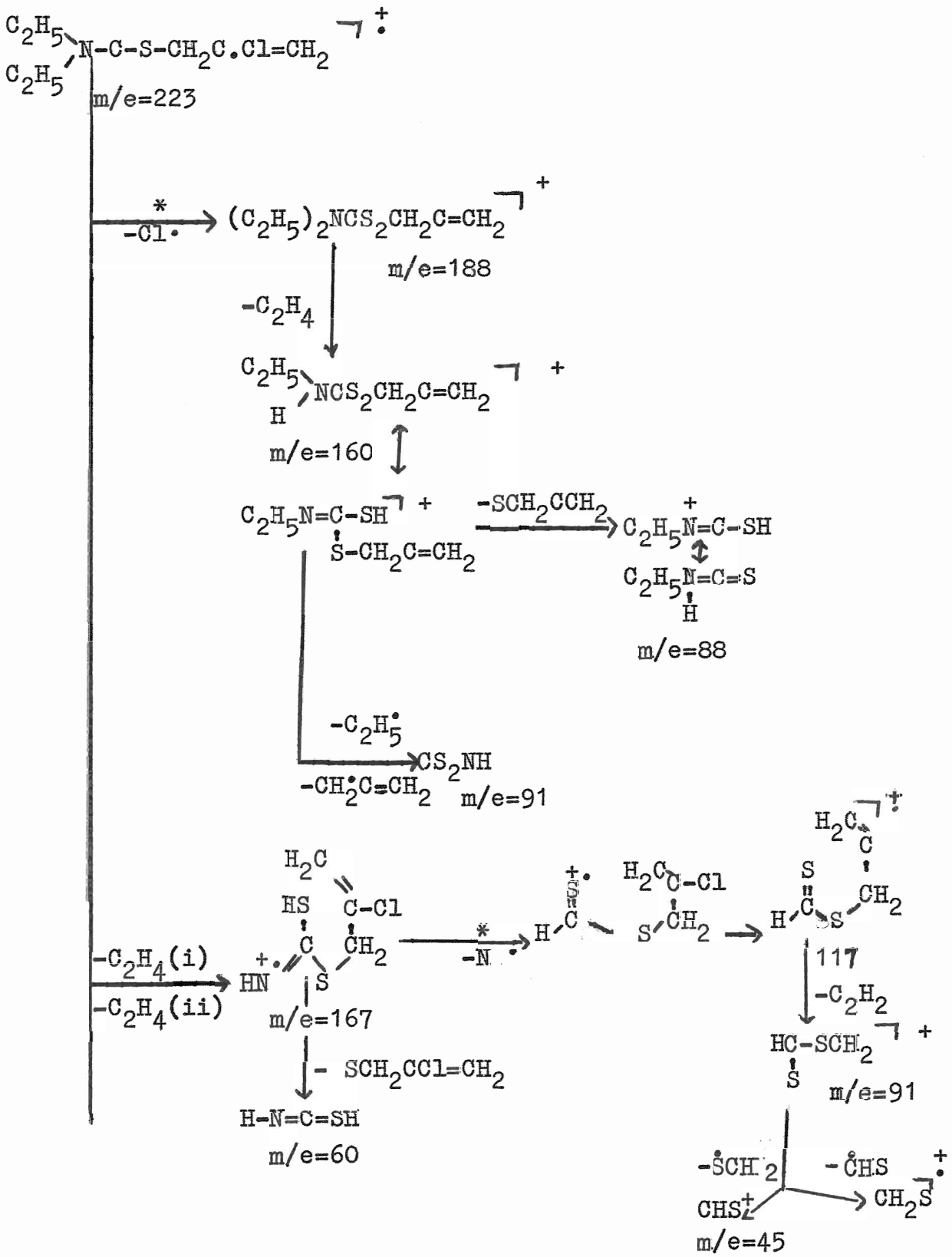
Dithiocarbamate Pesticides

i) Vegadex $(C_2H_5)_2$-N-C(=S)-S-$CH_2$-C Cl = $CH_2$

In general, the dithiocarbamates have received little attention. Only the $Zn^{+2}$ and $Fe^{+3}$ salts of dimethyl dithiocarbamic acid have so far been reported[59]. Vegadex is the 2-chloroallyl ester of diethyl dithiocarbamic acid and it is of interest to study the influence, in particular, of the chloro allyl substitutent on the mass spectral behaviour of this compound which has not yet been examined by earlier workers.

Unlike in the case of the thiocarbamates, the molecular ion is weak. But it resembles them in undergoing simple cleavages (See Scheme 12 and Fig. 11). Thus ions of m/e 148 and 116 are abundant as expected on the basis of the abundances of the corresponding ions in Eptam and Perbulate. The abundance of the species of m/e 75 is due to the resonance stability of the allylic bond. Ions of m/e 151, 162 and 194 are, however, insignificant. This implies that cleavages of the (C-S), ($CH_2$- C Cl) and (N-alkyl) bonds are not favoured. The reason for this could be that the cleavage


m/e=223
m/e=162
m/e=148
m/e=116
88
m/e=59
m/e=87
m/e=75
61
60
m/e=194
90
76




Scheme 12 Fragmentation Pattern for Vegadex

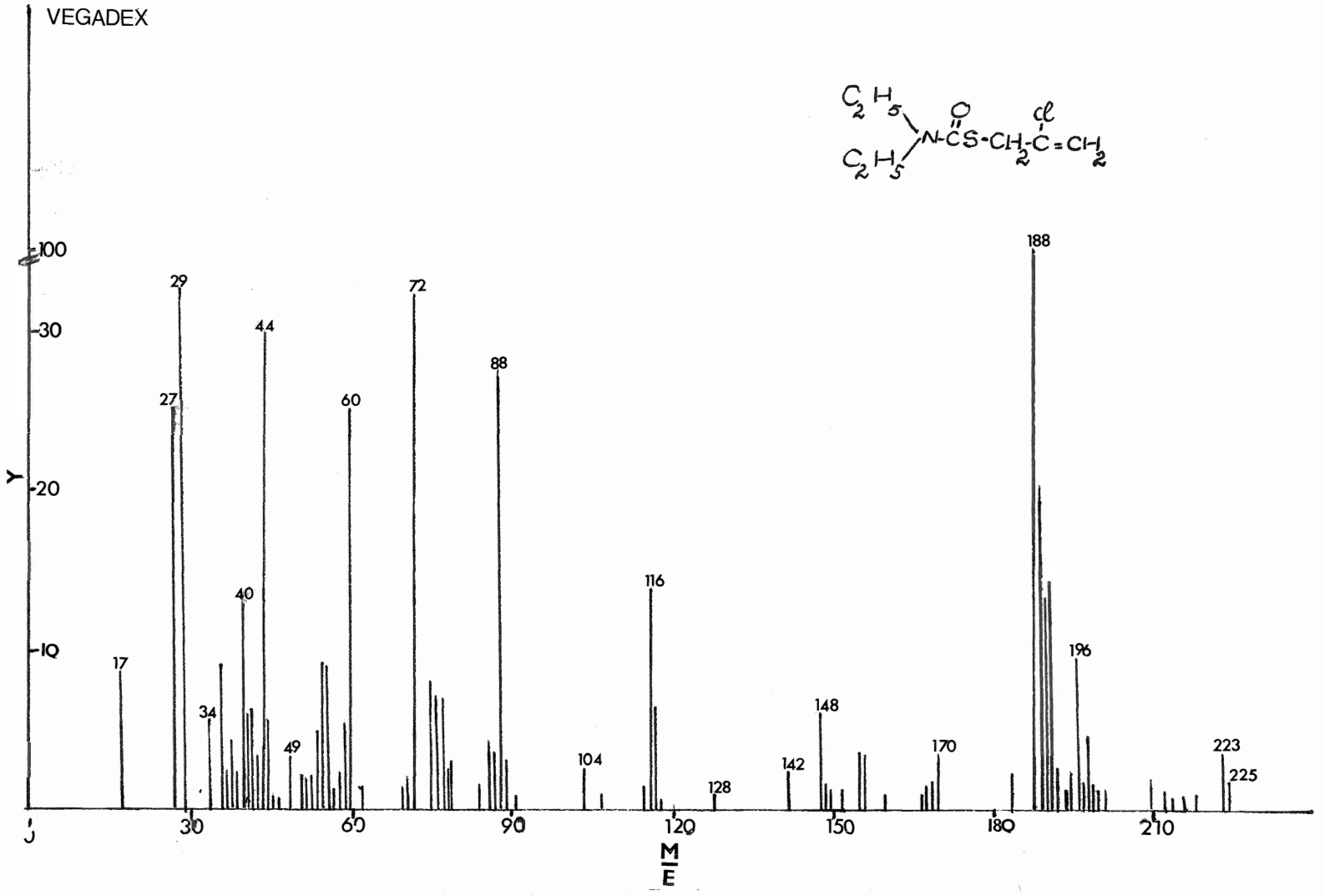



fig.II.mass spectrum of VEGADEX.(AEI.MS.12.0

of the ($S-CH_2$) results in the resonance stablised isocyanate (m/e 116) and isothiocyanate (m/e 148) ions. The pathway leading to the formation of these ions therefore overshadows other possible cleavages and this is substantiated by the abundances of the ions of m/e 148 and 116. The isocyanate and isothiocyanate ions suffer the expected cleavages as in the case of Eptam and Perbulate to give the various ions as illustrated in Scheme 12.

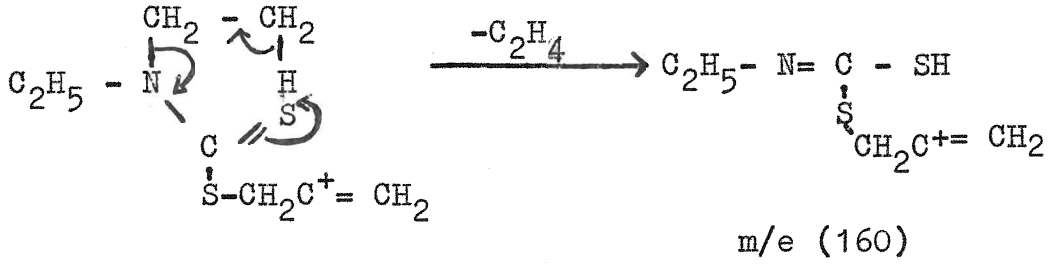
The allylic ester, differs from the thiocarbamates in the following respects:

(1) The base peak is formed by the loss of the allylic Chlorine.

$$(C_2H_5)_2\ NCS_2CH_2C\ Cl{=}\ CH_2^{\ddagger\cdot} \xrightarrow[*]{-Cl^{\cdot}} (C_2H_5)_2N\ CS_2CH_2\overset{+}{C} = CH_2$$

m/e 188

The lability of (C-Cl) bond in the parent ion may explain the high abundance of this ion of m/e 188. In the case of Eptam, the base peak results by cleavage of the N-alkyl bond as expected while in Perbulate, it is formed by the cleavage of the (C-S) bond. These facts suggest that the base peak is formed by the most favoured pathway. (i.e., by cleavage of the most labile bond under the circumstances). The ion of m/e 188 may now eliminate a molecule of $C_2H_4$ in a 6-membered cyclic transition state to yield m/e 160.

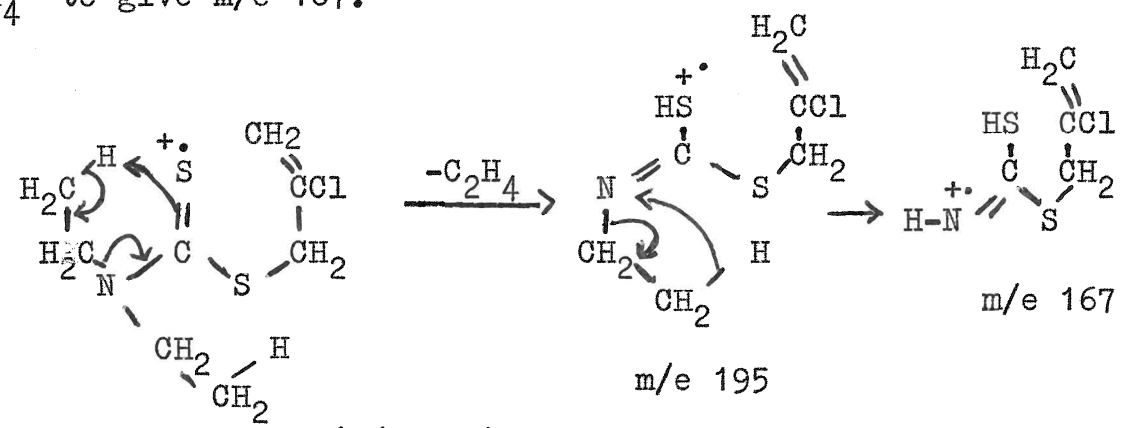


m/e (160)

The rearranged ion now eliminates the ($^{\bullet}SCH_2C{=}CH_2$) to give the species of m/e 88 which is formulated as

Also loss of $N\text{-}C_2H_5^{\bullet}$ from ion 160 yields ion 117.

(2) The parent ion itself undergoes the above rearrangement to give an ion of m/e 195 which then eliminates $C_2H_4$ to give m/e 167.



Parent ion (m/e 223)

Loss of($\dot{N}H$) from ion 167 yields the species of m/e 152. The formation of this ion is supported by a metastable transition. These features of its spectrum may help in its identification in pesticide residues.

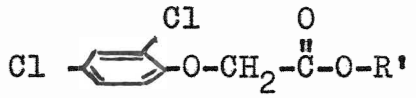
## Part iii) The Mass Spectra of Chlorinated Pesticides*

*See Appendix B for the m/e value and the % selective abundances of the various ions

Halogenated Pesticides

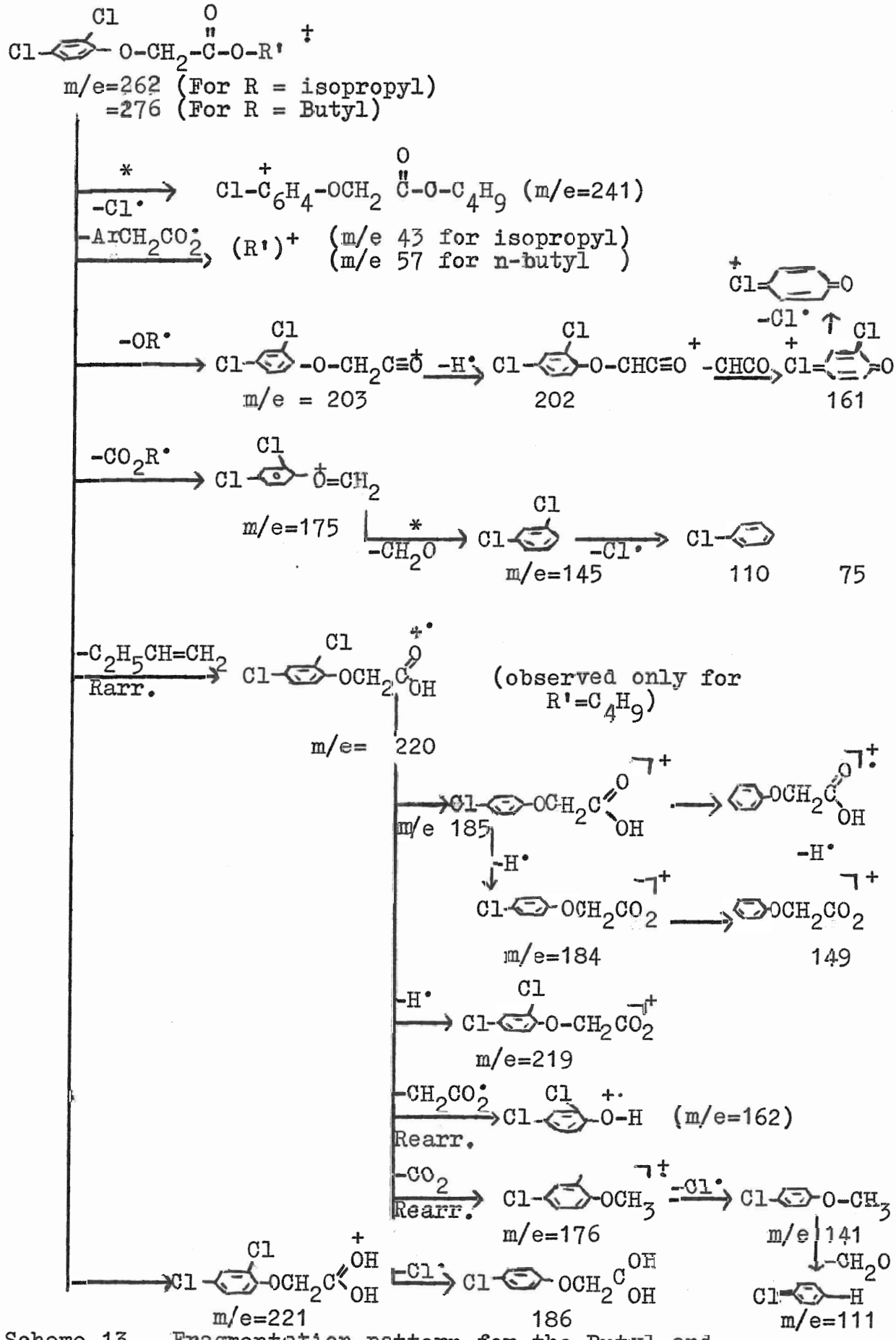
a) 2,4 dichlorophenoxy acetic acid, isopropyl and butyl esters

The isopropyl and butyl esters of 2, 4 dichloro phenoxy acetic acid are ring chlorinated aromatic herbicides. The acid portion of these esters are the same and they differ only in their alcohol position. Accordingly, they may be represented by the common structure,



where R' is isopropyl in isopropyl ester and n-$C_4H_9$ in the butyl ester

For the same reason, they yield identical fragment ions for the acid portion and different ions for the alcohol portion of the ester. As is typical of an aromatic ester, both the compounds yield abundant parent ions; but, that of the butyl ester is more abundant as it is more stable than the labile isopropyl ester. Also the cleavage ion $R^+$ (m/e 175) is more abundant for the isopropyl ester than for the butyl ester for similar reasons. Besides $R^+$, ions such as $(R')^+$ and $RCO^+$ expected of an ester are also present in the spectra, as illustrated in Scheme 13. The $(R')^+$ species ($CH\langle^{CH_3}_{CH_3}$ for isopropyl and $C_4H_9$ for butyl esters) is the base peak. This is contrary to general observations because in aromatic esters, the $RCO^+$ constitutes the base peak while in aliphatic esters, ions arising from the McLafferty rearrangement for the base peak. The reason for this anomalous behaviour is

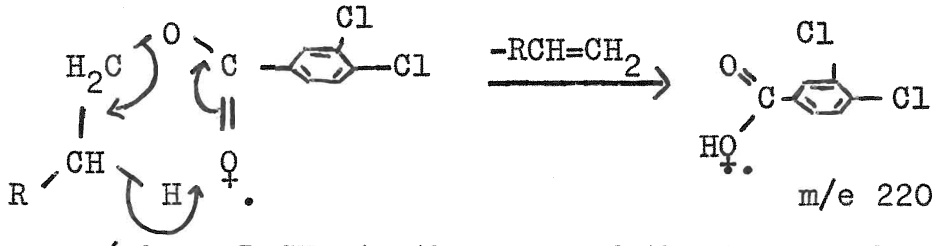



Scheme 13. Fragmentation pattern for the Butyl and Isopropyl esters of 2,4 dichlorophenoxy acetic acid

not clear. Particular mention may be made of ion of m/e 161 which is formed from the $RCO^+$ (m/e 203) ion by loss of a H• followed by the departure of the (CHCO)•. This ion is assigned a para-quinonoid type structure in which one of the p-oxygen atoms is replaced by a p-chloronium ion. In other words, the charge is presumed to be located on the chlorine atom. The structures of the other ions are indicated in Scheme 13 and Fig. 12 represents the bar graphs of the spectra.

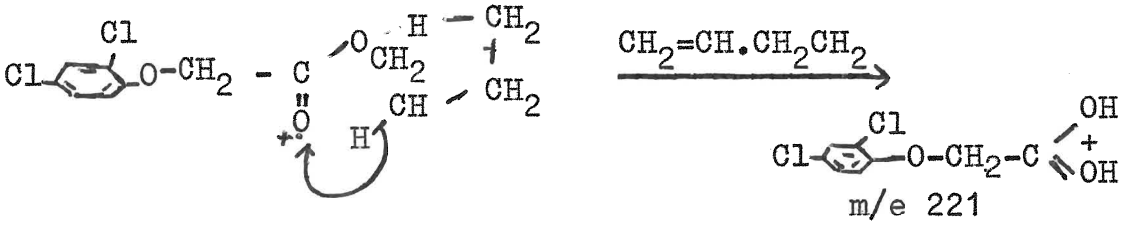
Both the esters undergo rearrangement reactions expected of them as given below:

(1) A Mclafferty rearrangement to give the 2, 4 dichloro phenoxy acetic acid ion (m/e 220)




(where R=$CH_3$ in the case of the isopropyl and $C_2H_5$ in the case of the butyl esters)

(2) A double hydrogen rearrangement to give an ion of m/e 221.



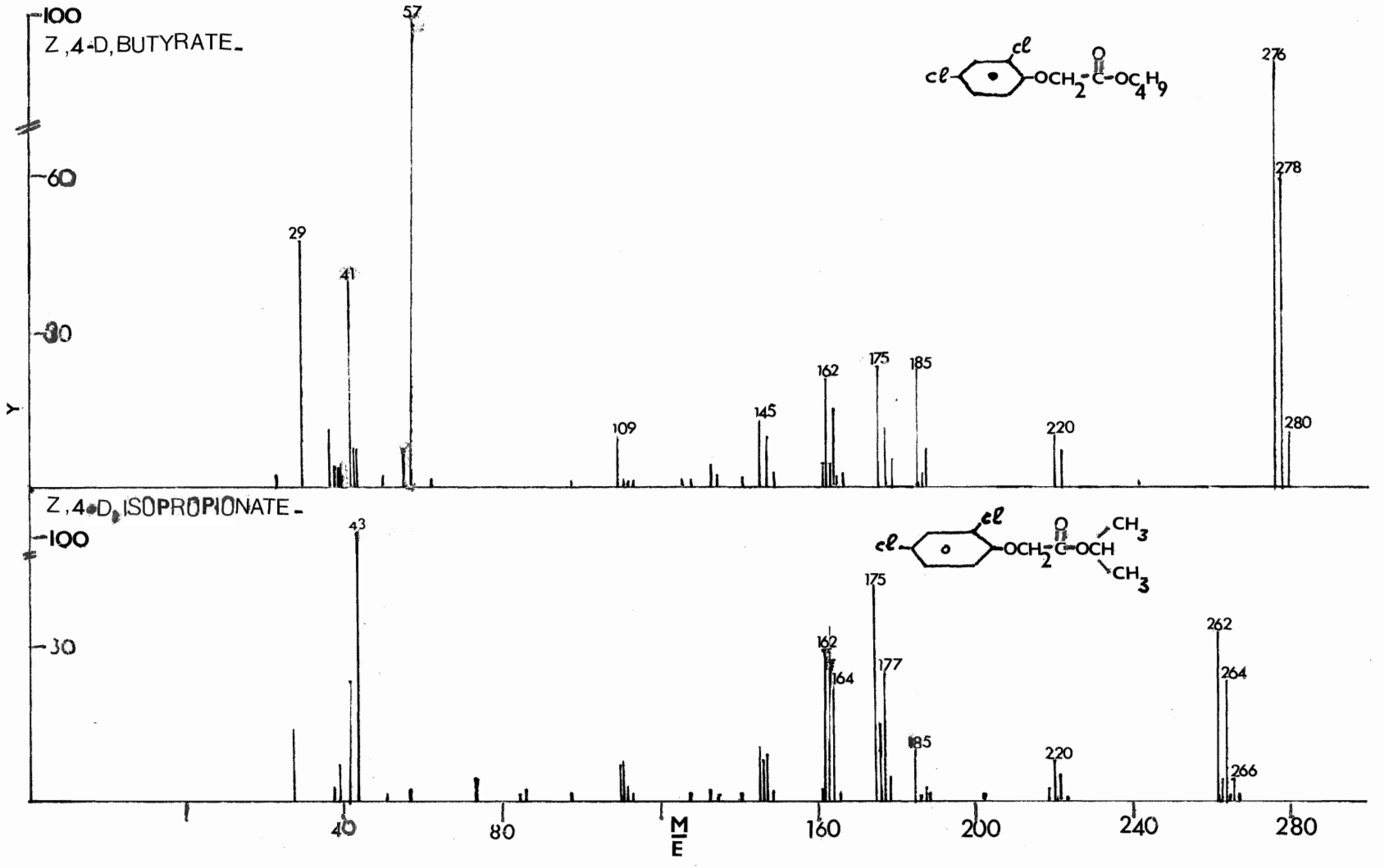
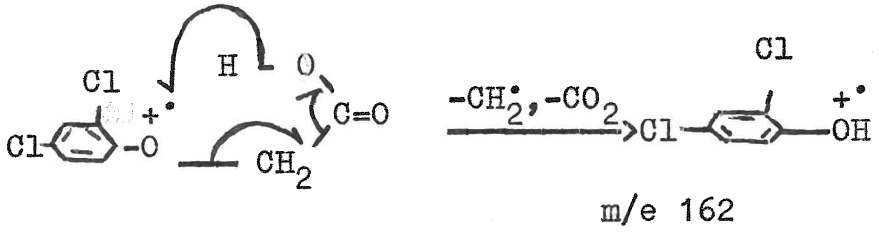



fig.I2.mass spectrum of 2,4-D,ISOPROPYL& BUTYL ESTERS.(AEI.MS.I2.)

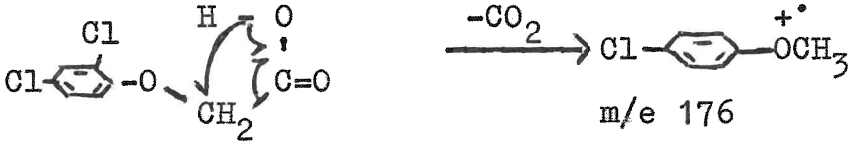
The acid ion produced in (1), rearranges in two different ways to give ions of m/e 162 and 176.

(3)




m/e 162

(4)



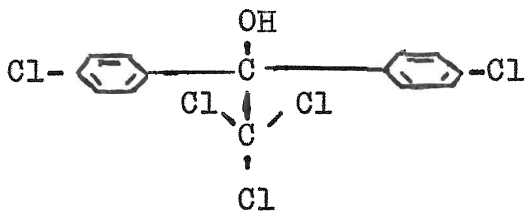

m/e 176

In (4) the migration terminus is carbon.

All these rearrangement ions are intense and involve only migration of hydrogen from the butyl or isopropyl group.

Thus, to conclude, these compounds show characteristics of both aromatic and aliphatic esters; but differ from both in giving the hydrocarbon moiety as the base peak and this may differentiate them from the other esters and hence ease their identification in a pesticide residue.

Kelthane




Kelthane, a halogenated insecticide, is a diphenyl derivative of methanol. Sphon and Damico[66] have given the bar-graph spectrum of the pesticide and have indicated pathways for the formation of ions of m/e 251, 139, 111 and 104. A detailed interpretation of the mass spectrum of any compound leads to a better understanding of the mechanistic pathways by which the various fragment ions are formed. The mass spectrum of Kelthane has therefore been examined in detail.

Kelthane is structurally similar to pp'-DDT with the difference that the hydrogen in DDT is replaced by the hydroxyl in Kelthane. Nevertheless, the two spectra (viz. that of DDT and Kelthane) are considerably different as can be seen from the ways of cleavage of the molecule at the (C-Cl), (C-OH), ($C-CCl_3$) and the (C-C) (involving the ring C and the side chain carbon)bonds (Scheme 14 and Fig. 13.)

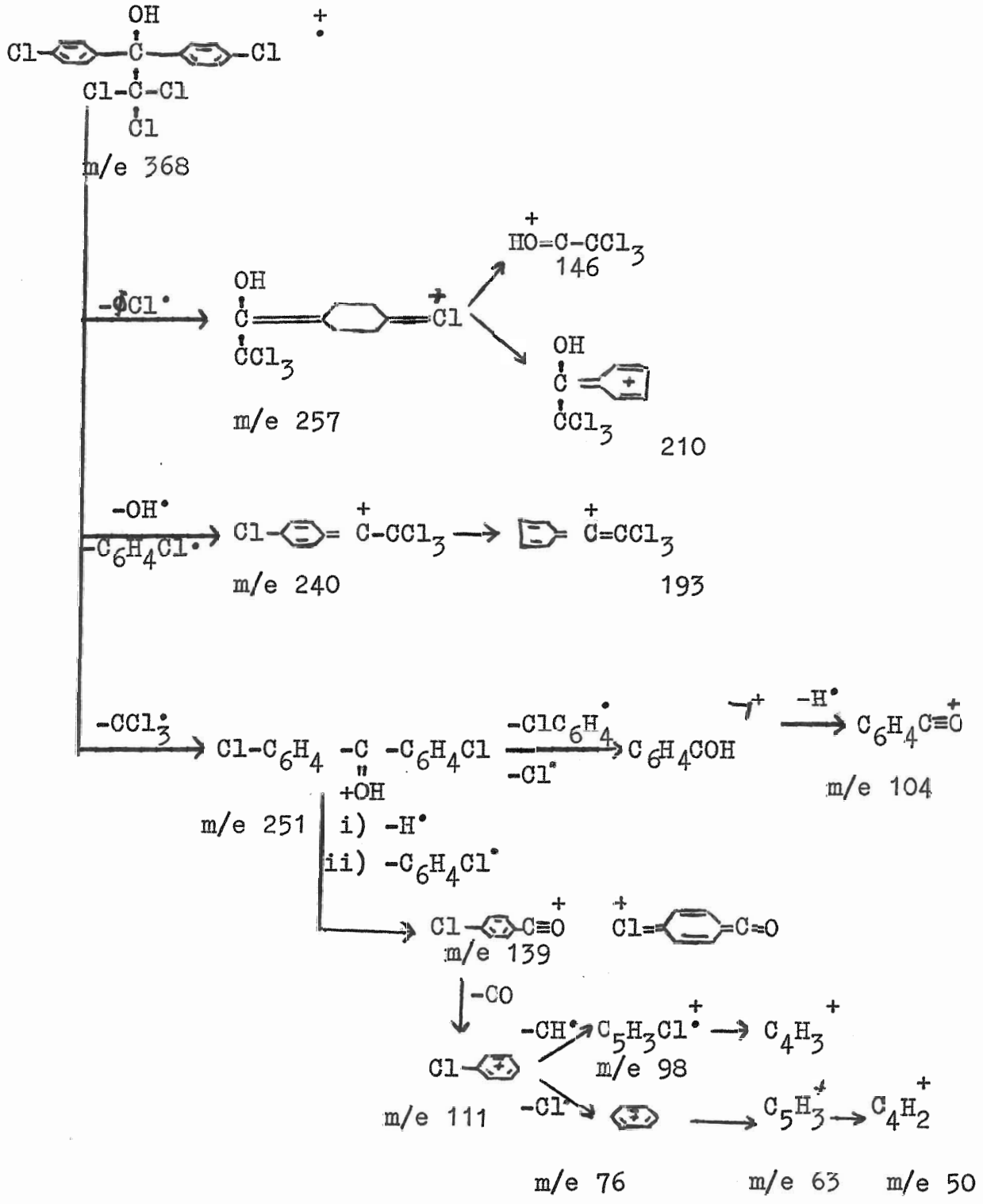
(1) Rupture of the (C-Cl) bond:

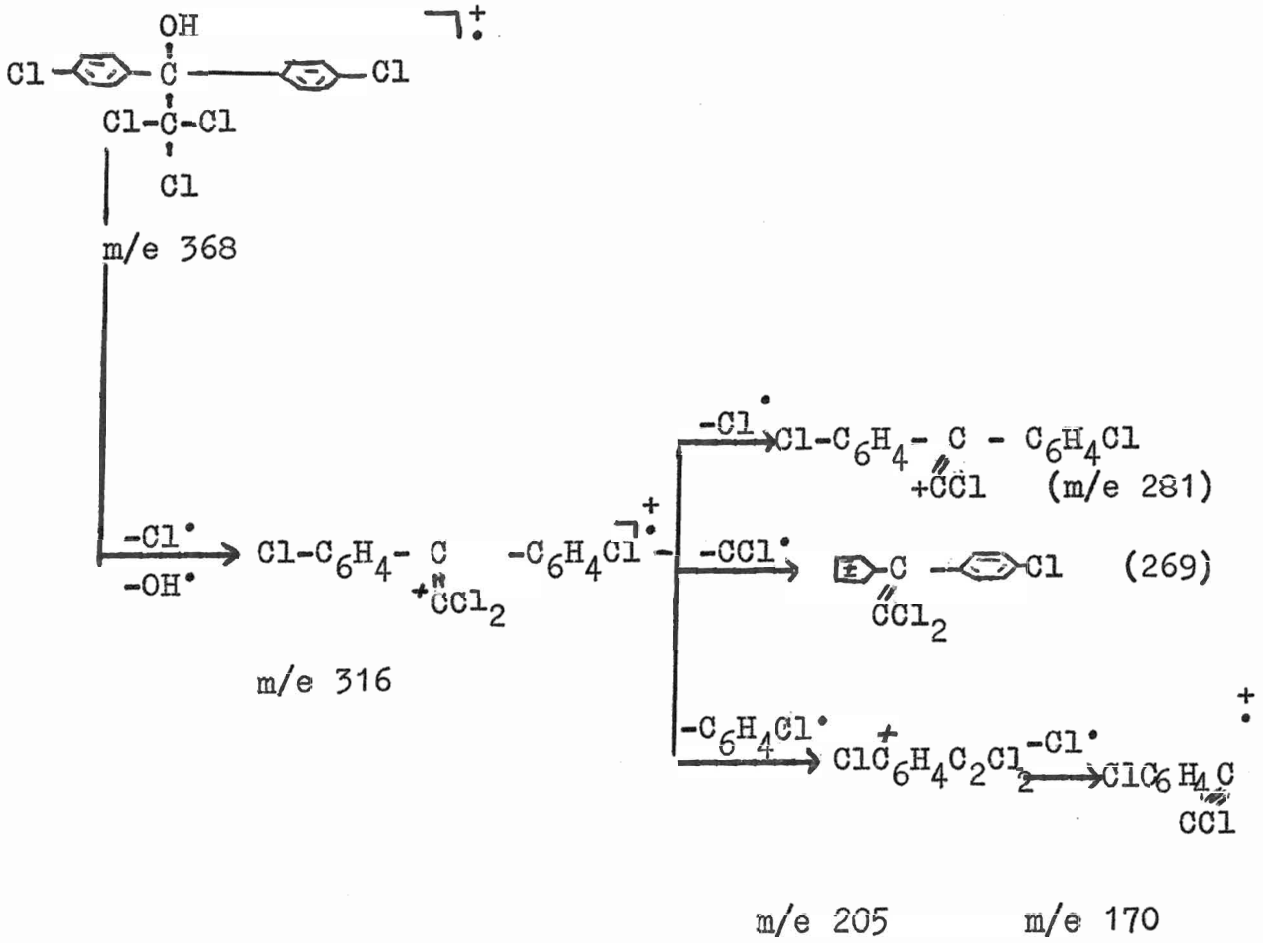
The initial cleavage of the (C-Cl) bond followed by loss of the hydroxyl radical leads to the diphenyl derivative of 1, 1 dichloroethylene ion of m/e 316. This ion eliminates

a $(CCl)^{\cdot}$ from the ring to yield the 2-cyclopentene, 2-phenyl substituent derivative of 1, 1 dichloroethylene (m/e 269). The ion 316 may also break at the (C-C) bond (involving carbon of ethylene and of the aromatic ring) to yield a weak ketene derivative (m/e 205) which subsequently loses a chlorine to give the stable phenyl acetylene derivative at m/e 170. This type of cleavage of the (C-Cl) bond breakage is absent in the spectrum of DDT[66]. The labile nature of the (C-Cl) bond in Kelthane is due to influence of the hydroxyl group.

(2) Rupture of the $(C\text{-}Cl_3)$ bond:

Cleavage of the $(C\text{-}Cl_3)$ bond leads to the major ions in the spectrum. Thus the substituted diphenyl derivative of m/e 251 formed by this breakage is the second largest peak. In DDT, this leads to the base peak[66]. The difference in behaviour in the two cases is again due to the presence of the hydroxyl function in Kelthane. In its presence, a new pathway leading to a resonance stabilised product ion (at m/e 139) becomes possible from ion 251. In fact this constitutes the base peak in the spectrum. The base peak, in its turn, yields two intense ions at m/e 104 (by loss of chlorine) and at m/e 111 (by loss of CO, supported by a metastable transition). Subsequent fragmentation of the species of m/e 111 leads to the significant ions at m/e 98, 76, 63, 51 and 50. (See Scheme 14). Mention may be made


OH
Cl
Cl
Cl-C-Cl
Cl
m/e 368
-ϕCl•
OH
C
CCl3
Cl
m/e 257
HO=C-CCl3
146
OH
C
CCl3
210
-OH•
-C6H4Cl•
Cl
C-CCl3
m/e 240
C=CCl3
193
-CCl3•
Cl-C6H4
-C
-C6H4Cl
-ClC6H4•
-Cl•
C6H4COH
-H•
C6H4C≡O
m/e 104
m/e 251
+OH
i) -H•
ii) -C6H4Cl•
Cl
C≡O
m/e 139
Cl
C=O
-CO
-CH•
C5H3Cl•
m/e 98
C4H3
Cl
m/e 111
-Cl•
C5H3
C4H2
m/e 76
m/e 63
m/e 50




Scheme 14 Fragmentation pattern for Kelthane

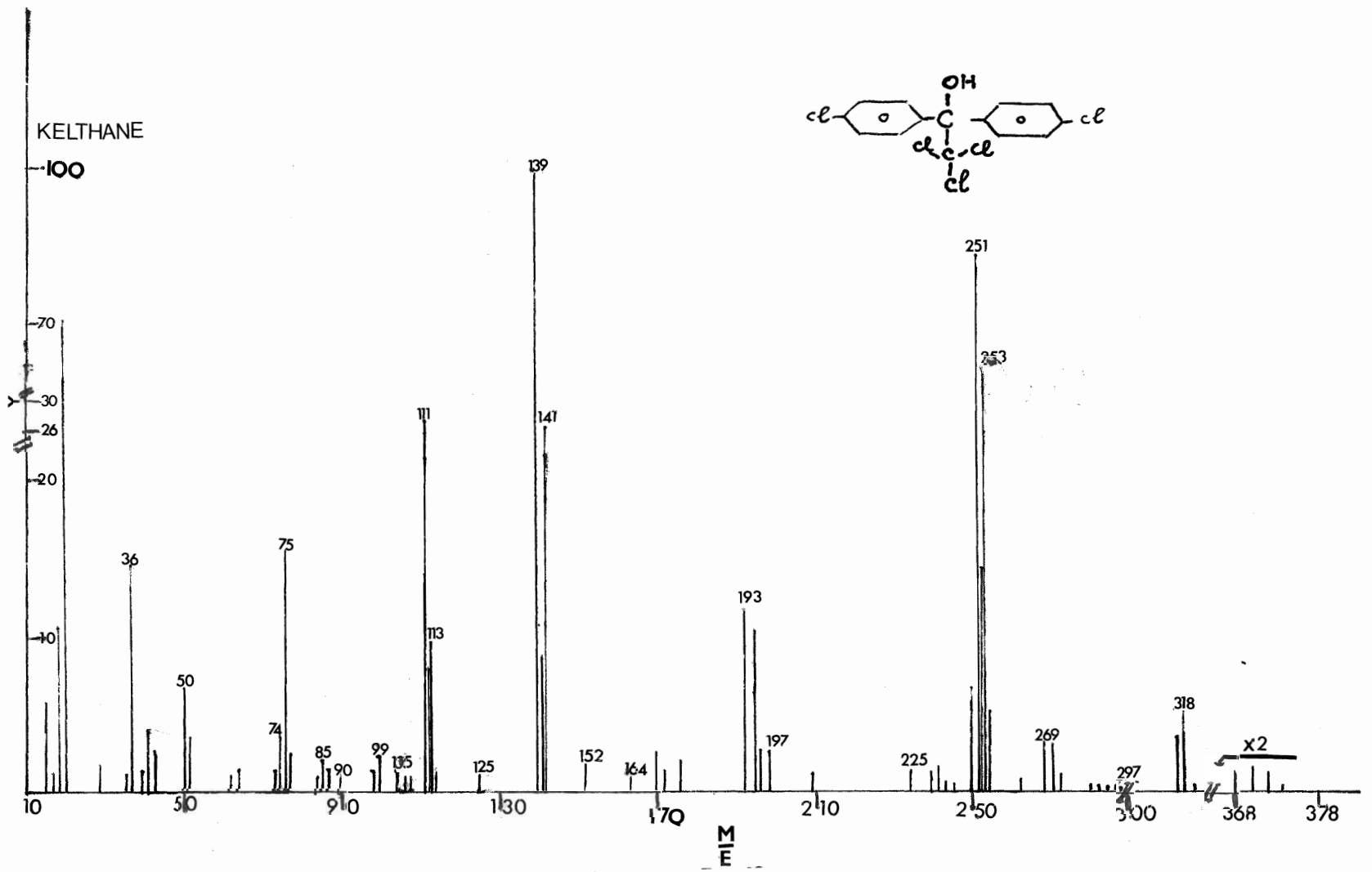



fig.13.mass spectrum of KELTHANE.(AEI.MS.12.)

Part iv) The Mass Spectra of Miscellaneous Pesticides*

*See Appendix B for the m/e values and the % Relative abundances of the various ions

of the formulation of a chlorocyclopentene moiety (with chlorine retaining the charge) for ion of m/e 98. This may be justified in view of the postulation of the cyclopentene species from the phenyl ion[78,79]. Further, unlike in the case of DDT, the rupture of the $CCl_3$ linkage is not followed by the loss of a chlorine atom. The influence of the hydroxyl function in altering the mass spectral properties of Kelthane is thus clear.

Loss of Hydroxyl

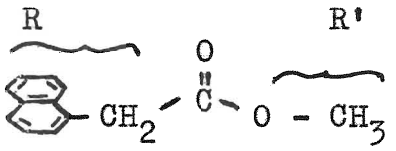
Loss of the hydroxyl radical leads to a weak ion at m/e 351 which then fragments to give ions of m/e 240 and 193 - (the former involving loss of O Cl' and the latter involving loss of ring CCl'). The structure of ion of m/e 193 is analogous to that of m/e 98. (Scheme 14).

In conclusion, the spectrum of Kelthane is formed by the simple cleavages of different bonds. This is a compound containing chlorine in the ring as well as in the side chain. From separate studies of ring chlorinated and side chain chlorinated aromatic hydrocarbons, Mclafferty[64] concluded that the base peak in the former case results from loss of ring chlorine while in the latter case, it results by breakage of the (C-C) bond $\beta$ to the ring. This holds good for DDT[66] but in Kelthane loss of ring chlorine is insignificant and loss of side-chain substituted chlorine (i.e. C-$CCl_3$ rupture) leads only to the second largest peak.

This anomalous behaviour arises from the influence of the hydroxyl function. This would mean that the presence of functional groups in compounds may alter their mass spectral behaviour completely and accordingly give a characteristic spectrum for each compound. This may be of value for identification purposes.

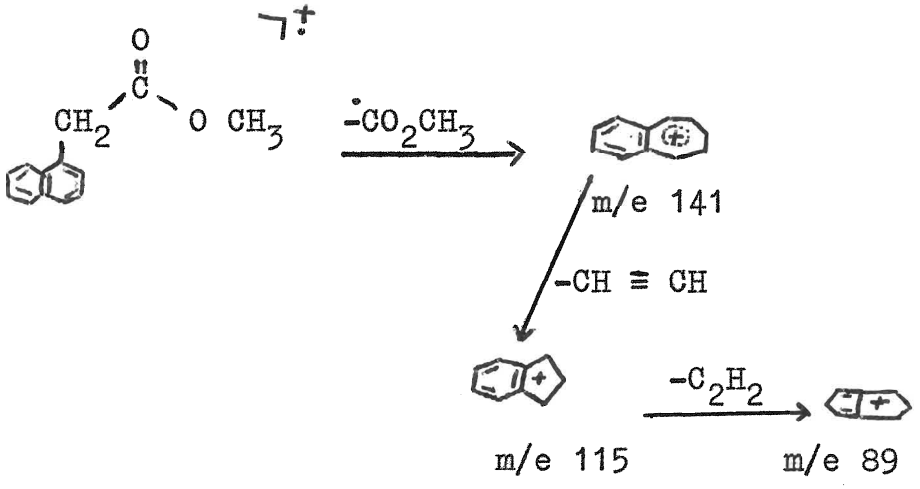
Miscellaneous Pesticides

a) 1-Naphthalene acetic acid, methyl ester



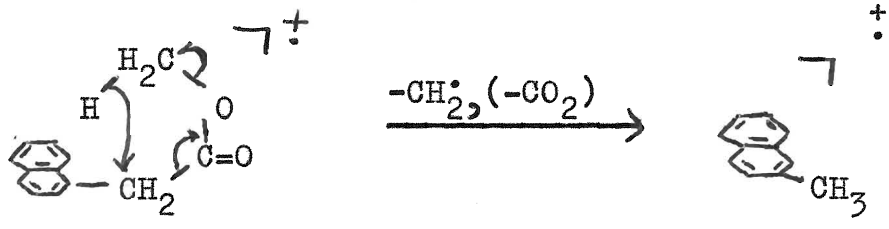
Although a number of aromatic and aliphatic esters[80,81] have been studied, those of naphthalenic acids and higher fused ring compounds seem to have defied attention. The mass spectral study of 1-naphthalenic acid, methyl ester is therefore appropriate. The ester is a herbicide.

Owing to the increasing resonance stability of the ring, only fewer ions are present. Thus, cleavage ions of the type $RCO^+$, $RCOO^+$, $ROCO^+$, $R'O^+$ and $R'^+$, characteristic of an ester, are absent in the spectrum. The only cleavage ion present is the $R^+$ion. This is the resonance stabilised tropylium ion (m/e 141) and is the base peak in the spectrum:



The tropylium ion subsequently loses a molecule of acetylene to yield the ion of m/e 115 (formulated as above) which then by a similar process gives m/e 89, having the above structural postulation.

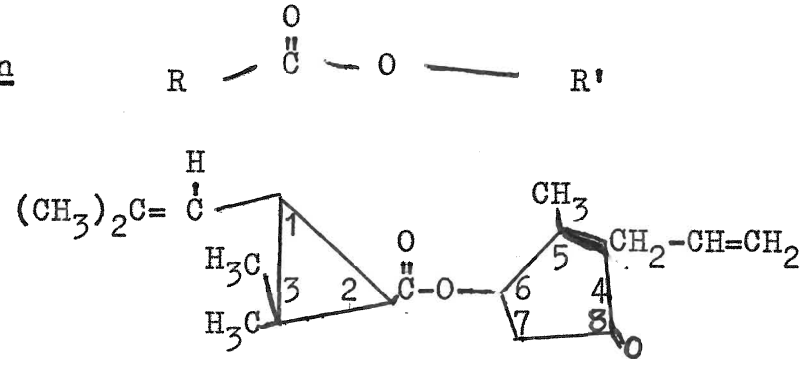
Also the Mclafferty rearrangement and the double hydrogen rearrangement are absent. But the migration of hydrogen from the methyl to the methelene carbon attached to the side chain of the ring occurs.




m/e 142

The methyl ester of 1-naphthalene acetic acid is thus stable to electron impact and accordingly gives rise to a simple and straightforward spectrum, as seen from Fig. 14.

b) <u>Allethrin</u>




Allethrin is a contact insecticide and belongs to the Pyrethrum group of pesticides. From its structure, Allethrin may be regarded as an ester of the type R-C-O-R' with R and
O

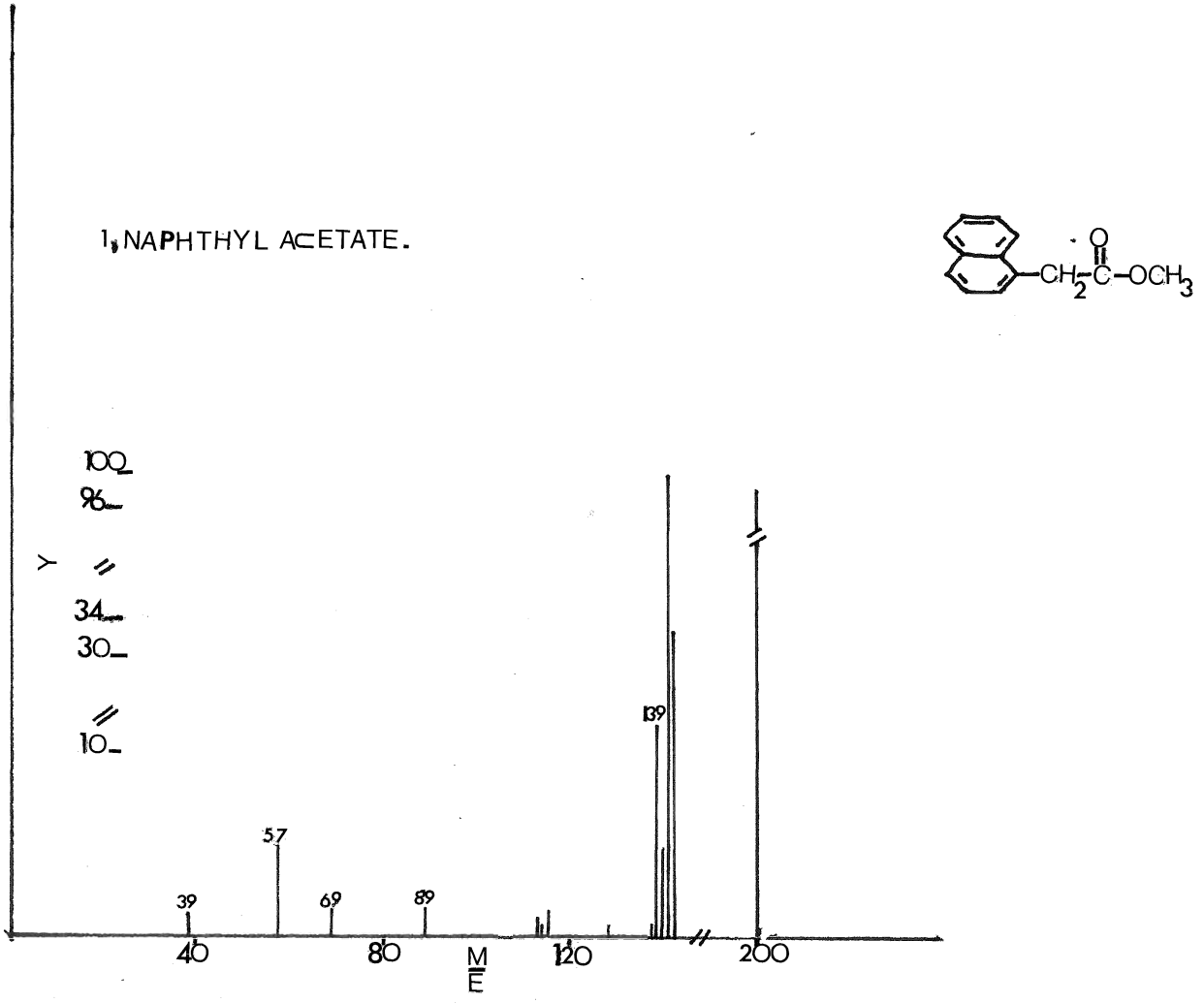



fig.I4.mass spectrum of I,NAPHTHYLACETICACID METHYLESTER.(AEI.MS.I2.)

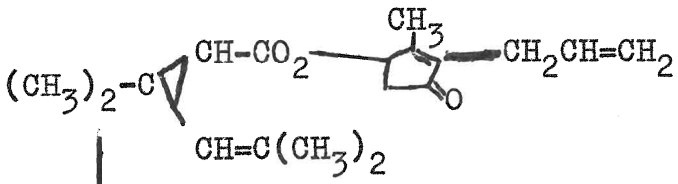
R' representing the substituted cyclopropane and cyclopentenone moieties respectively. As expected of such an ester, it suffers cleavage of bonds $\alpha$ to either side of the carbonyl group to give fragment ions of the type $R^+$, $RCO^+$, $R'OCO^+$, $(OR)^+$ and $(R')^+$ (Scheme 15-a). As in the case of the isopropyl and butyl esters of 2, 4 dichloro-phenoxy acetic acid, the base peak in the spectrum is the $R^+$ ion (m/e 123). Successive losses of H' from $C_1$ and $C_2$ in the $R^+$ ion leads to m/e 121 forming a double bond between the two carbon atoms ($C_1$ and $C_2$). Ions $RCO^+$ (m/e 151), $(R')^+$ (m/e 135) and $R'OCO^+$ (m/e 179) are all weak due to their greater tendency for further dissociation. A number of ions result from the fragmentation of the species of m/e 179 $(R')^+$. Mention may be made of the following ions.

(1) Cleavage of the ($C_4$- $C_5$) and ($C_7$- $C_8$) bonds in $(R')^+$ leads to the ion of m/e 81 which is assigned an allylic substituted ketene type of structure, (i.e. $O=C=\overset{+}{C}-CH_2CH=CH_2$). Subsequent loss of the ($^{\bullet}CH=CH_2$) from this may lead to ($CH_2=C=C=O^{+}$) of m/e 54.

(2) Breakeage of the 5-membered ring between $C_5$ and $C_6$ as well as $C_7$ and $C_8$ leads to the spcies of m/e 71, having the structure ($\overset{+}{O}\equiv C-OCH=CH_2$). Successive losses of hydrogen from the double bonded carbons yield m/e 69 having the triply bonded ($\overset{+}{O}\equiv C-OC=CH$) structure.

All the above structural assignments are purely tentative.

R - $CO_2$ - R'



$CH=C(CH_3)_2$

(m/e=302)

$-R'CO_2^{\bullet}$ → $R^+$ (m/e=123) $\xrightarrow{-H^{\bullet}}$ $(R-H)^{+\bullet}$ 122 $\xrightarrow{-H^{\bullet}}$ $(R-2H)^+$ 121 → $C_5H_8$ (68) → $C_5H_6$ (66)

$-R'O_2$ → $RCO^+$ 151 → $C_5H_7O^+$ (83) → $C_5H_6O^{+\bullet}$ (82) → $C_4H_4$ (52) → $C_4H_3^+$ (51)

$-RCO_2^{\bullet}$ → $(R')^+$ m/e 135 → $(R'-1)^+$

$-R'$ → $R'OCO^+$ m/e 179

$(R'-H)^{\bullet}$ → $RCO_2H^{+\bullet}$ m/e 168

→ $(CH_3)_2C=CH-CH=C(CH_3)_2^+$ $\xrightarrow[-H^{\bullet}]{-CH_3^{\bullet}}$ $CH_3C\equiv CCH=C(CH_3)_2^{+\bullet}$

↓ m/e 94

$C_4H_7^+$ → $CH\equiv C-CH_3^{+\bullet}$

m/e 55 m/e 40

→ $(H_3C)_2C=CHCO_2CH=CH_2$ $\xrightarrow{-CH_3^{\bullet}}$ $CH_3\overset{+}{C}=CH\ CO_2CH=CH_2$

$-H^{\bullet}$ ↓ m/e 111

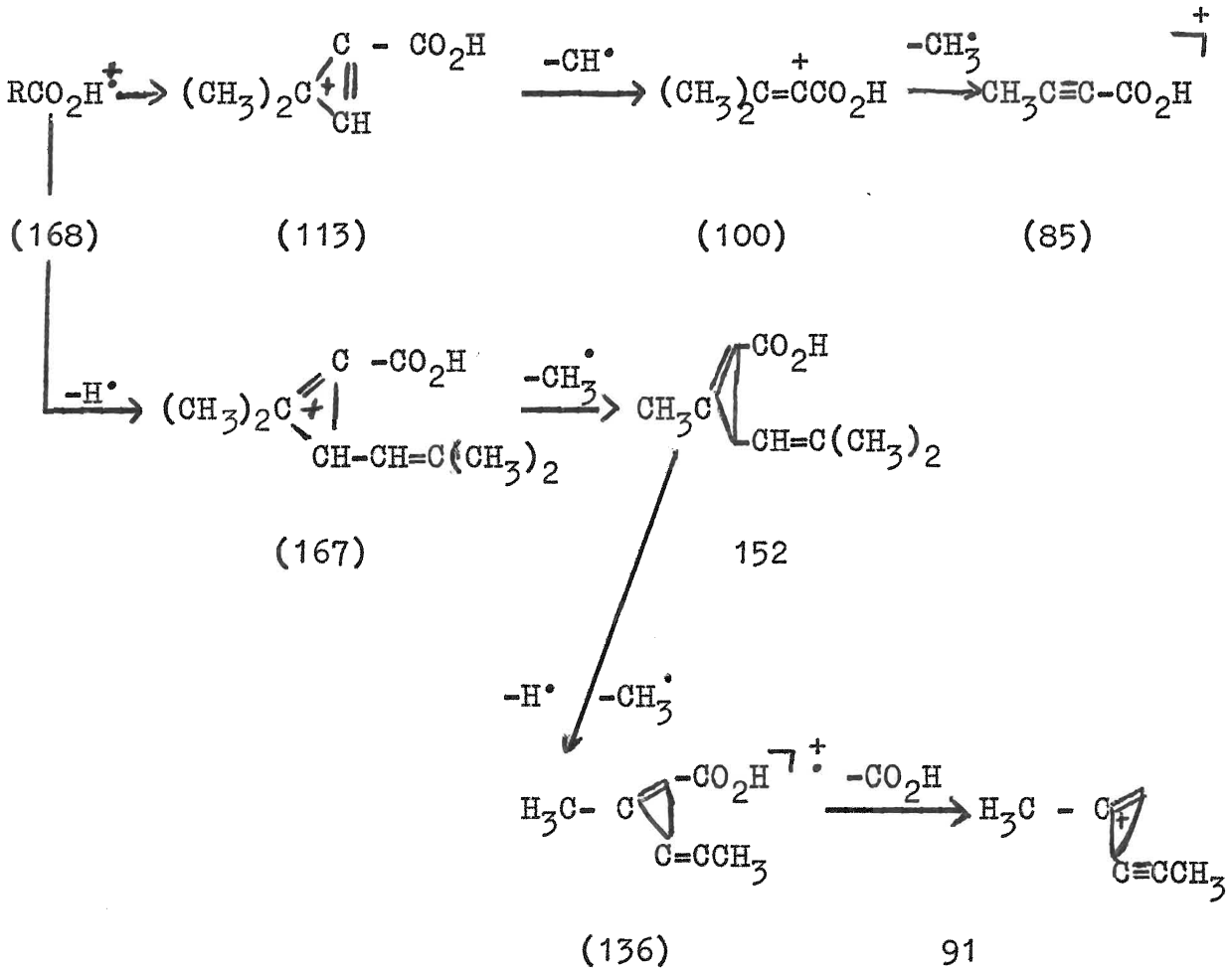
$CH_3C\equiv C-CO_2CH=CH_2^{+\bullet}$ $\xrightarrow{-H^{\bullet}}$ $^{+\bullet}$

↓ (110) m/e 109

$OC_2CH=CH_2^+$ → $C_2H_3^+$ $\xrightarrow{-H^{\bullet}}$ $CH\equiv CH^{+\bullet}$

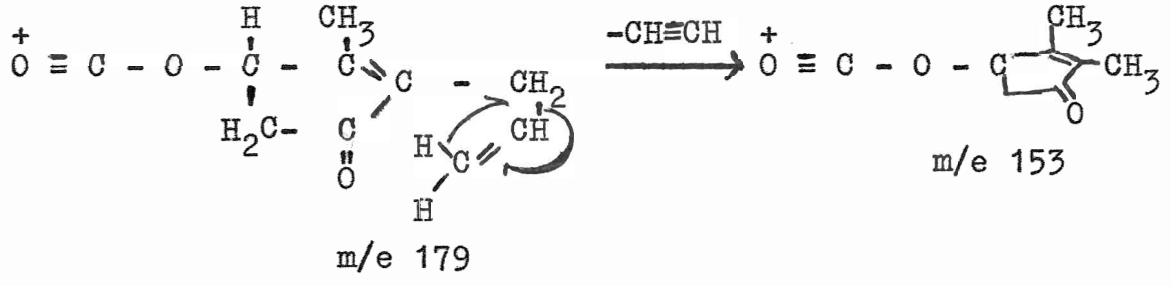
(71) (27) (26)

Further Fragmentations of Species of m/e=168




Scheme 15-a Fragmentation Pattern for Allethrin

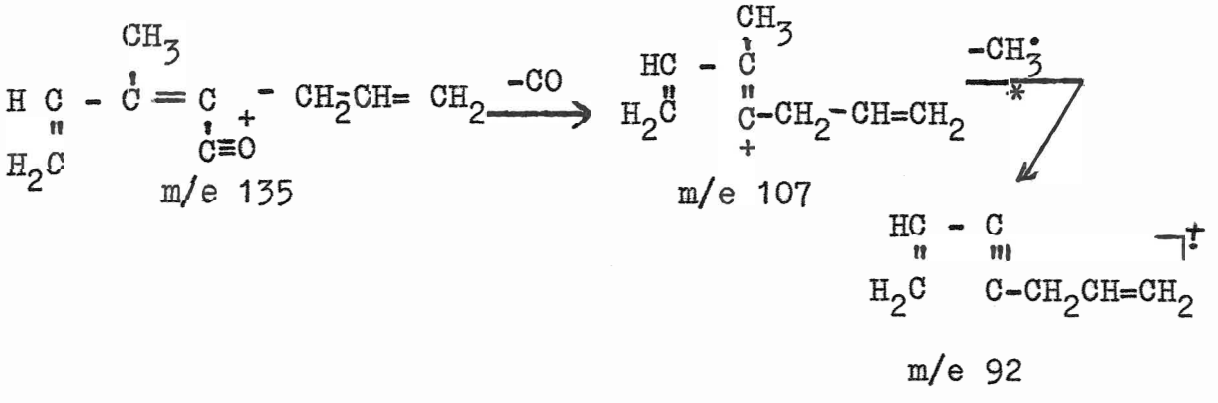
(3) The species of m/e 179 rearranges to the ion of m/e 153 by the loss of a molecule of acetylene:



m/e 179 m/e 153

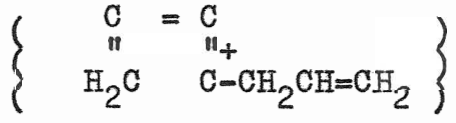
Structures for the other ions are indicated in Scheme 15-b.

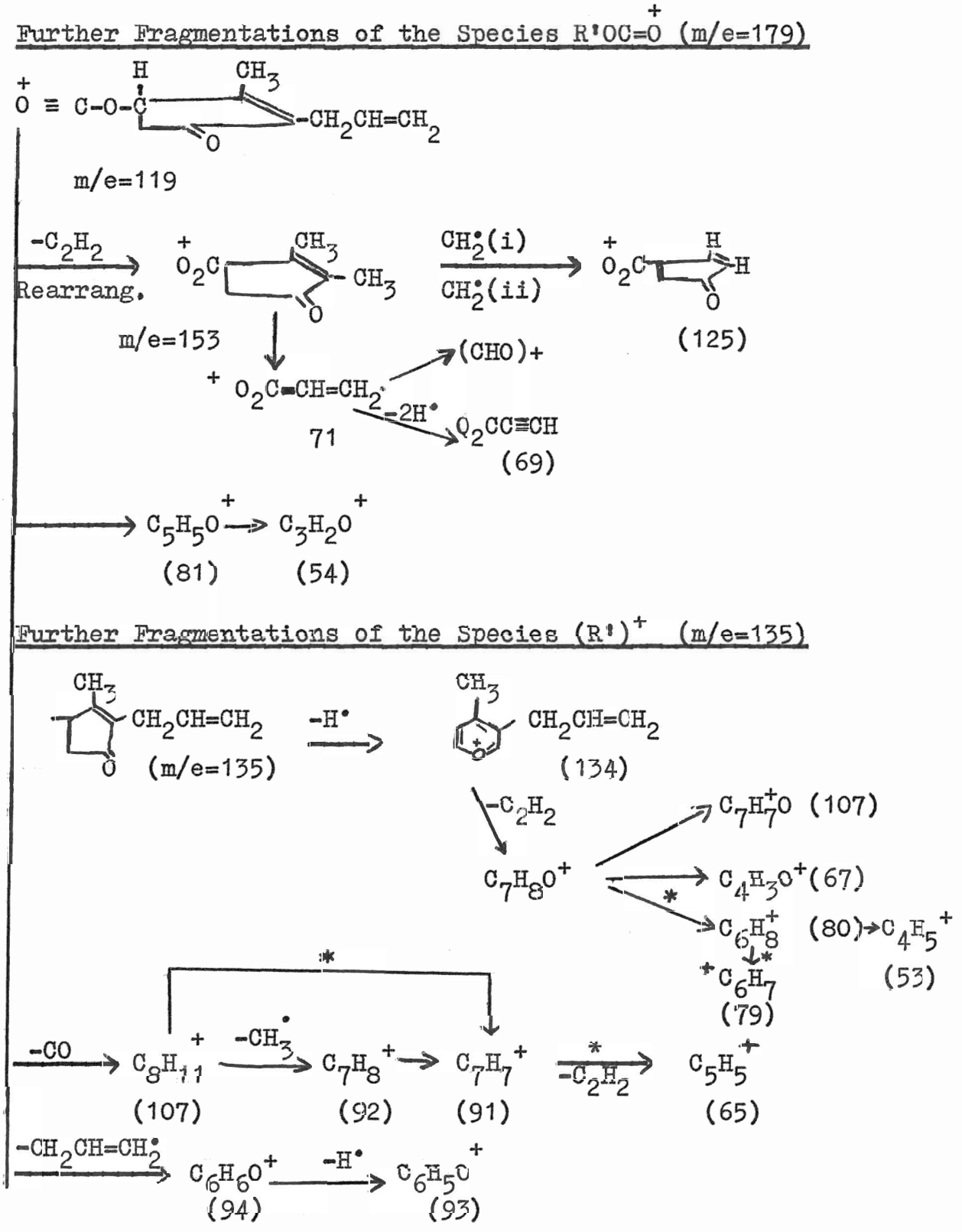
As in the case of the ion of m/e 179, ion 135 also dissociates to give a variety of ions. (See Scheme 15-b). Mention may be made of ions 107, 92 and 91. Ion 107, formed from m/e 135 by loss of CO, eliminates the $CH_3^{\bullet}$ to give m/e 92 forming a triple bond between $C_4$ and $C_5$:



m/e 135 m/e 107 m/e 92

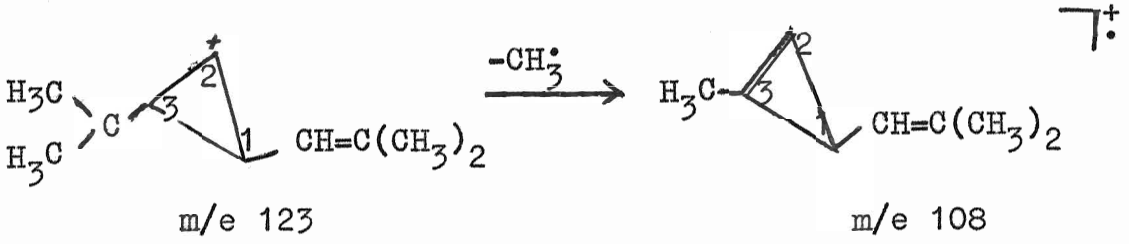
Ion 92 loses the methine hydrogen ($C_6$) with a subsequent reorganization of bonds to give m/e 91, having the

 structure.



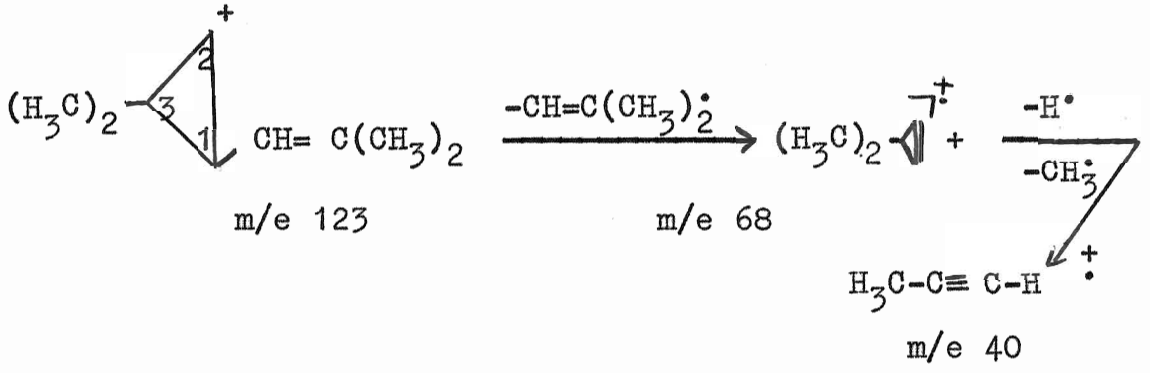

Scheme 15-b Fragmentation Pattern for Allethrin

All the above structural assignments are again tentative. The base peak (m/e 123) of Allethrin undergoes three interesting cleavage reactions. Loss of a $CH_3^{\bullet}$ (from $C_3$) results in the formation of a double bond between $C_2$ and $C_3$ in the ion of m/e 108:




m/e 123 m/e 108

Similarly loss of the substituent radical form $C_1$ leads to the formation of double bond between $C_1$ and $C_2$ in ion 68:




m/e 123 m/e 68 m/e 40

Elimination of a $CH^{\bullet}$ followed by a $CH_3^{\bullet}$ from m/e 68, yields a methyl acetylene ion of m/e 40. The formation of this species involves a simultaneous bond-breakeage and bond formation.

Loss of $CH^{\bullet}$ (from $C_2$) involving breakeage of bonds between $C_2$ and $C_3$ and $C_2$ and $C_1$ leads to a conjugated diene species of m/e 110; having the $(H_3C)_2\text{-}C = CH\text{-}CH = C(CH_3)_2$ $^{+\bullet}$. Loss of a methyl followed by loss of a $H^{\bullet}$ may give the

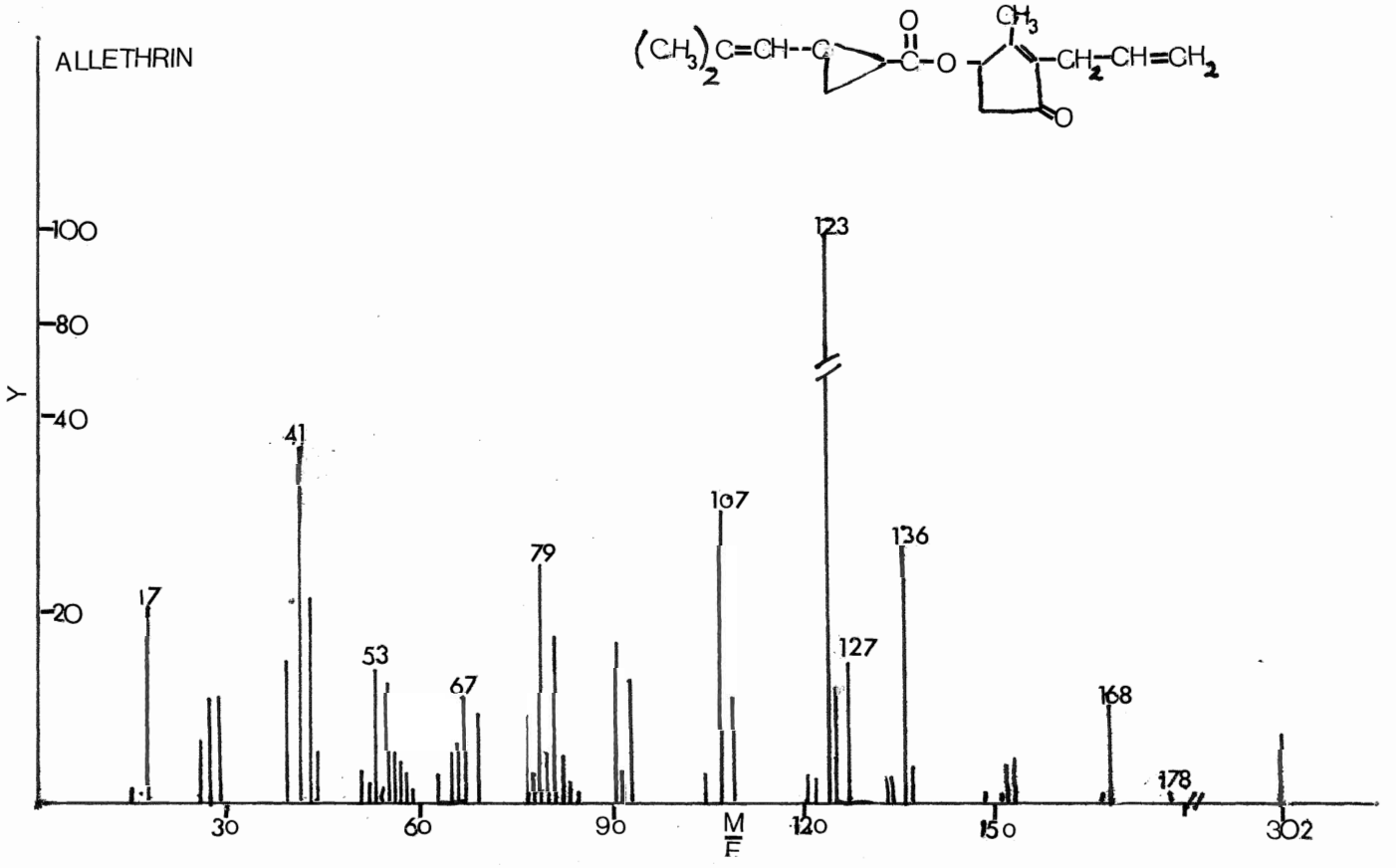
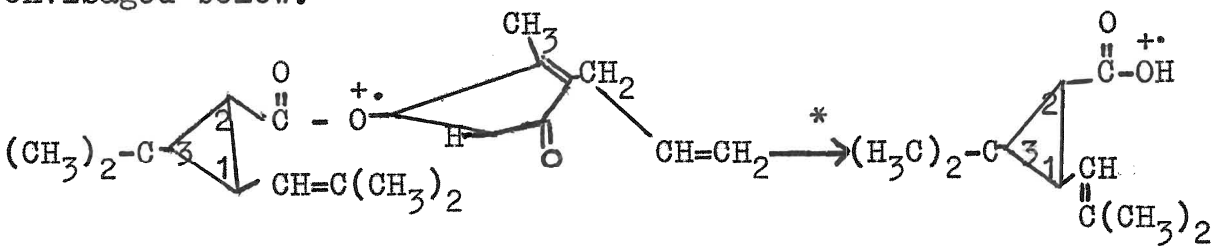



fig.I5.mass spectrum of ALLETHRIN.(AEI.MS.I2.)

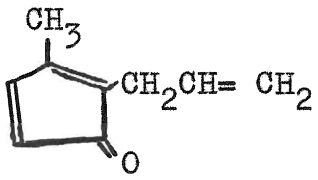
tentative ( $H_3C \equiv C-CH = C(CH_3)_2$ structure for the ion of m/e 94.

Apart from these simple cleavages, the ester also gives a rearrangement ion at m/e 168. Its formation may be envisaged below.

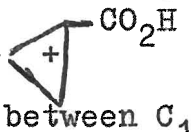
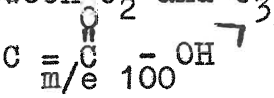


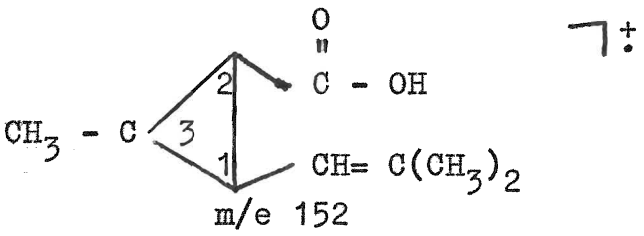
m/e 302 m/e 168

The formation of this ion involves elimination of the

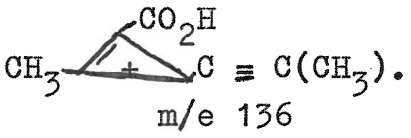


molecule.

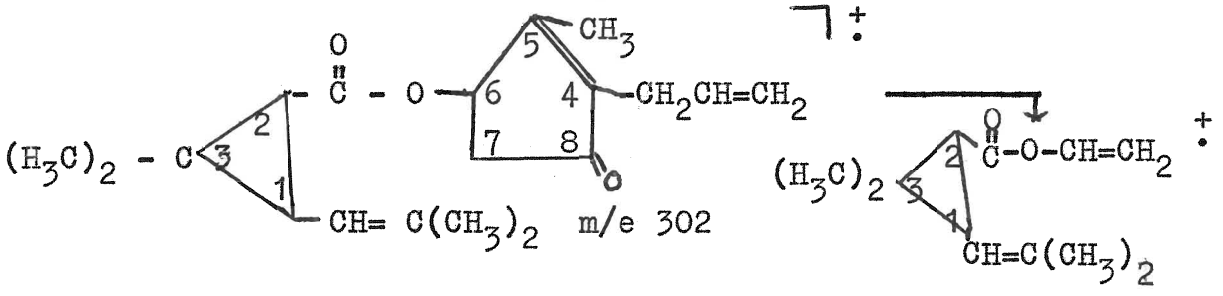
Loss of the substituent (from $C_1$) from this ion, then yields m/e 113 with the simultaneous formation of a double bond between $C_1$ and $C_2$, having the  structure. Similarly breakages of the bonds between $C_1$ and $C_2$ as well as $C_1$ and $C_3$ leads to an acid ion of m/e 100 with the formation of the double bond between $C_2$ and $C_3$ as may be seen from its structure:  m/e 100 . Also loss of $CH_3$ from $C_3$ and loss of H· from $C_2$ may lead to the ion of m/e 152 with the formation of a double bond between $C_3$ and $C_2$:



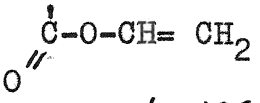

. This ion may now eliminate one of the methyl radical from the $C_1$ substituent and then by the loss of the olefinic methine hydrogen may give the ion of m/e 136 having the structure




Finally, the parent ion suffers cleavages at bonds between $C_5$ and $C_6$as well as $C_7$ and $C_8$ of the cyclopentenone moiety to give the species of m/e 194.



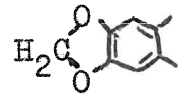

This species loses the substituent from $C_1$ to give m/e 139. The cyclopropane moiety of m/e 139 then suffers a bond-breakeage at $C_1$ and $C_3$ as well as at $C_1$ and $C_2$ to give m/e 126 which has the tentative $(CH_3)_2C=CH$




m/e 126.

Thus, Allethrin exhibits a number of unique features in its spectrum especially in giving rise to ions by breakeages

of (C-C) bonds of the cyclopropane and cyclopentenone rings. These ions may facilitate its identification in a pesticide residue.

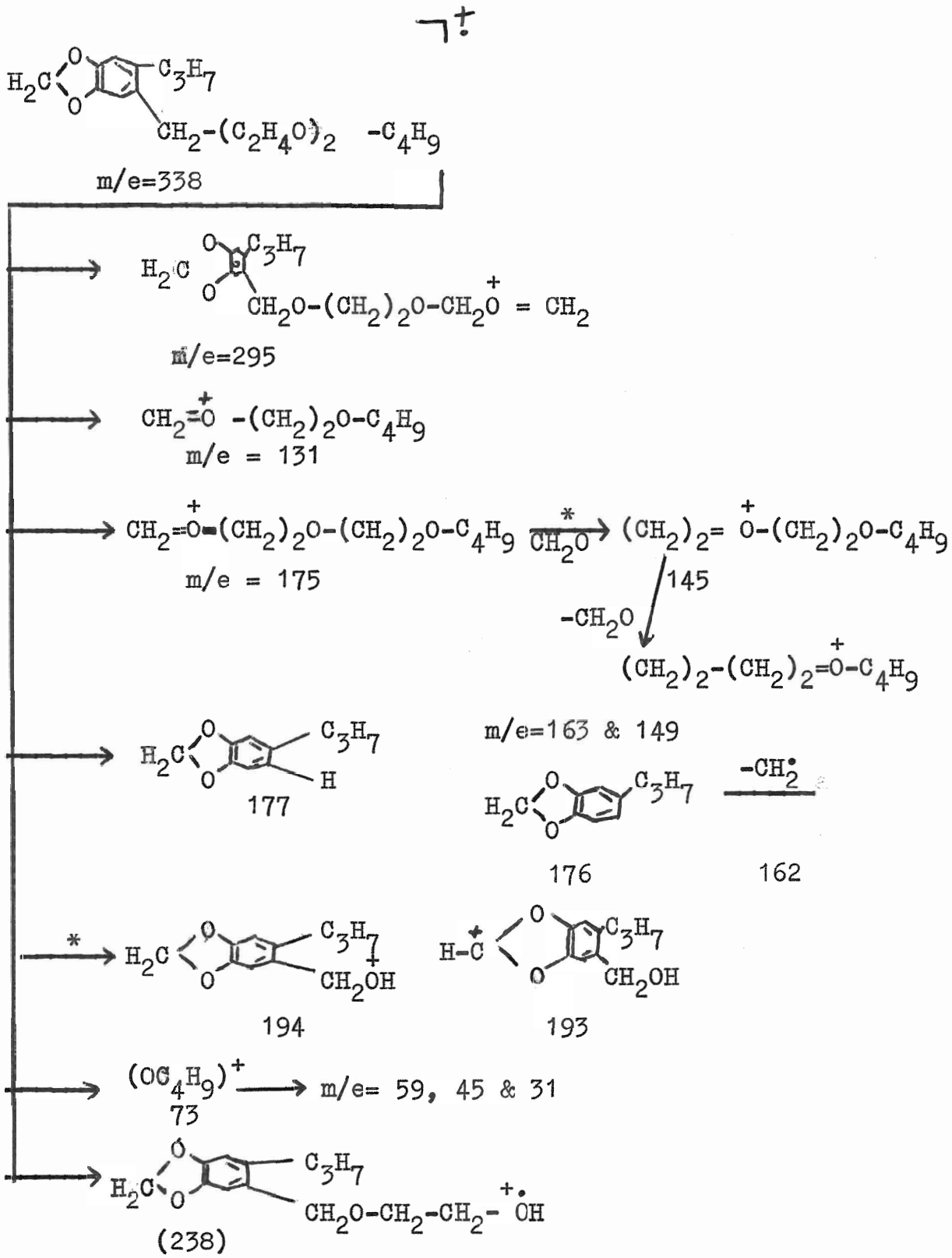
c) Piperonyl Butoxide:  $C_3H_7$

$CH_2O - (C_2H_4O)_2 - C_4H_9$

Piperonyl butoxide, as insecticide synergist, may be considered as a dioxy poly ether. The mass spectra of several aliphate, alicyclic and aromatic ethers have been investigated[1,3,4]. More recent articles have paid attention to the fragmentation modes of cyclic acetals[79], aryl-alkyl ethers[79] and various substituted dioxy benzenes[79]. Nevertheless, studies on poly ethers are lacking. A detailed discussion of piperonyl butoxide is, therefore attempted.

Pi peronyl butoxide shows the mass spectral features expected of an alcohol, aldehyde and ether.

As an ether, it fragments at the (C-C) bond $\beta$ to the oxygen ($\beta$ -cleavage) and at the (C-O) bond by $\alpha$ cleavage. However, all the (C-C) bonds $\beta$ to the different methenoxy oxygen atoms do not dissociate. Only the (C-C) bond linking the aromatic carbon and the adjacent methenoxy carbon as well as the (C-C) bond terminal to the butoxy group suffer cleavages to give abundant ions of m/e 175 and 295 respectively (Scheme 16-a). This implies that preferential charge localisation occurs on these two oxygen atoms involved in the cleavage. An exactly similar situation

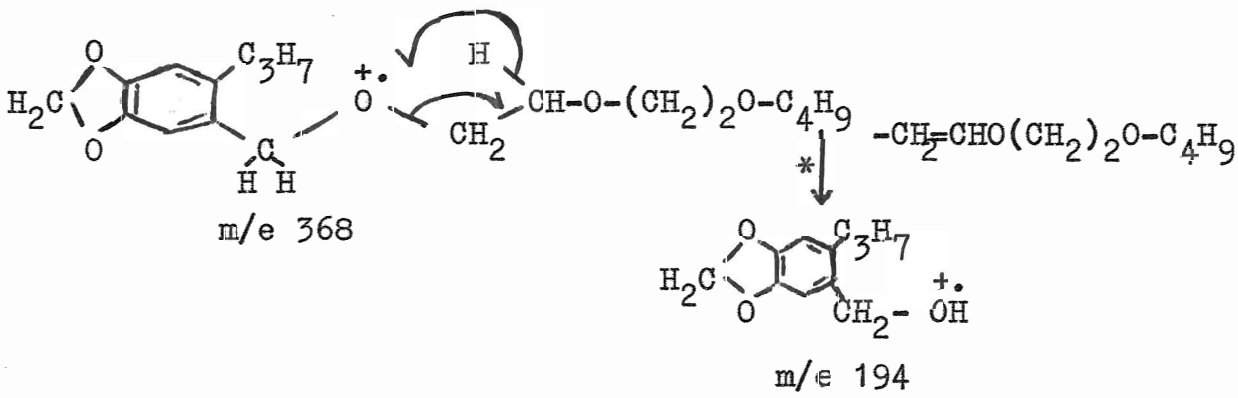



Scheme 16-a Fragmentation Pattern for Piperonyl butoxide

prevails with respect to the $\alpha$ -cleavage (see Scheme 16-a). Ion 177 formed by the (C-O) bond breakage in an analogous way as ion 175, is an abundant peak in the spectrum. In view of its aromatic stability, this species then rearranges by loss of H$^{\bullet}$ to give the resonance stabilised tropylium ion which naturally forms the base peak in the spectrum (m/e 176). Another $\alpha$ -cleavage ion of interest is the species of m/e 145 which by successive loss of the $CH_2^{\bullet}$ from the butyl group yields ions of m/e 131, 117, 103 and 89. Ion 117 then loses a ($^{\bullet}CH_2$-O-$CH_2$) radical to give $CH_2 = \overset{+\bullet}{O} - C_3H_7$ (m/e 59). The ion 89 leads to the methoxy aldehyde, $CH = \overset{+\bullet}{O}- (CH_2)_2O - CH_3$ (m/e 88) by loss of a H$^{\bullet}$.

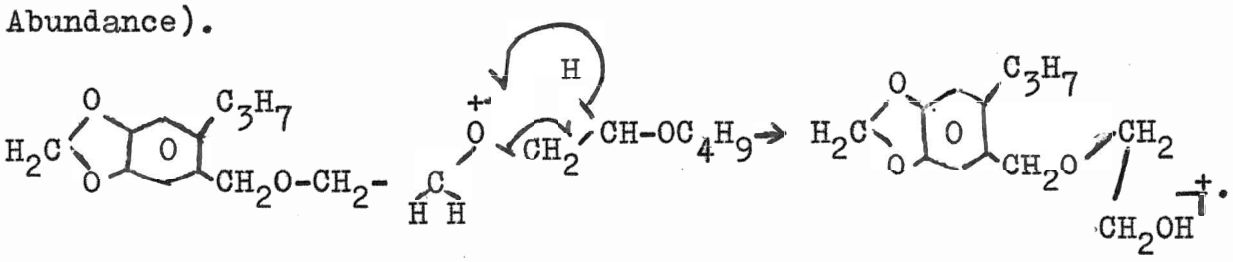
Apart from the above cleavage ions, piperonyl butoxide forms a series of rearrangement ions typical of an ether.

(1) The parent ion rearranges to an alcohol of m/e 194 in a four-membered cyclic transition state:



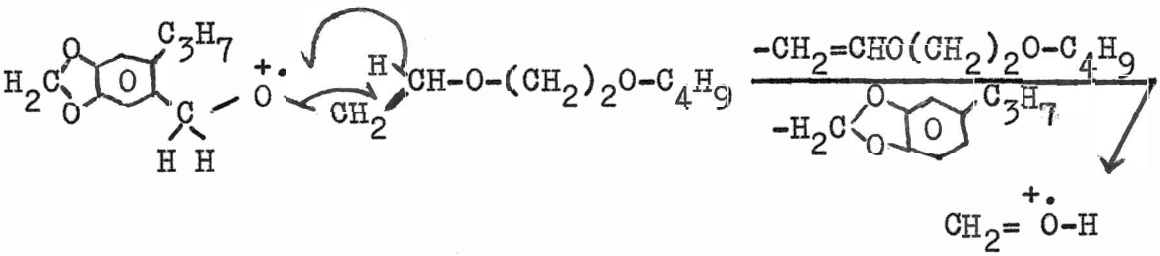

The formation of this rearrangement ion is supported by a metastable transition.

(2) An $\alpha$ - $\beta$ bond cleavage (w.r. to the butoxy oxygen) with transfer of hydrogen in exactly the same way as above, leads to another alcohol ion of m/e 238 (0.42% Relative Abundance).



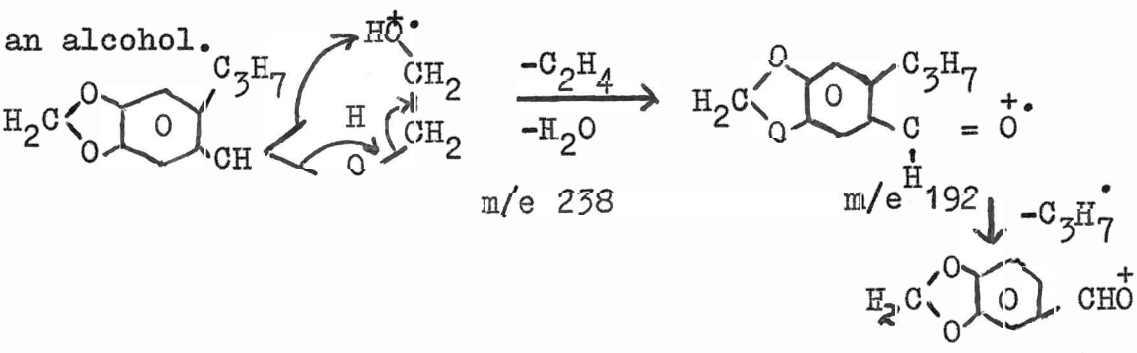
m/e 238

(3) Cleavage at the aromatic (C-C) bond of the parent ion yields the $CH_2=\overset{+}{O}H$ ion of m/e 31.

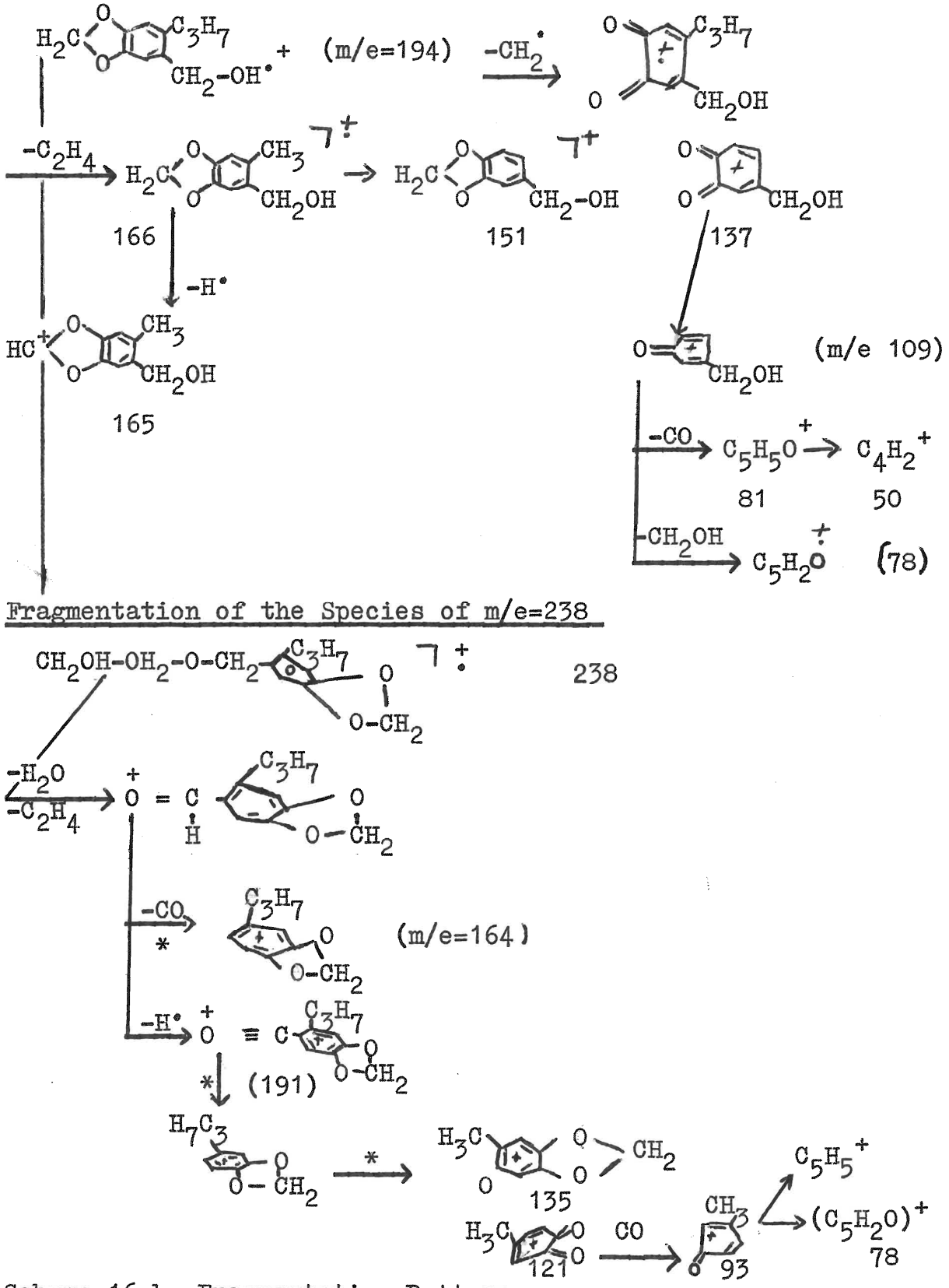


m/e 31

The weaker abundances of ions 238 and 31 are understandable in view of the preferential charge localisation on the end-oxygen atoms of the polyether side chain. Added to this is the fact that the ion 238 eliminates a molecule of $C_2H_4$ and $H_2O$ to give an aldehyde of m/e 192. This reaction is typical of an alcohol.



(149)




Scheme 16-b Fragmentation Pattern for Piperonyl butoxide

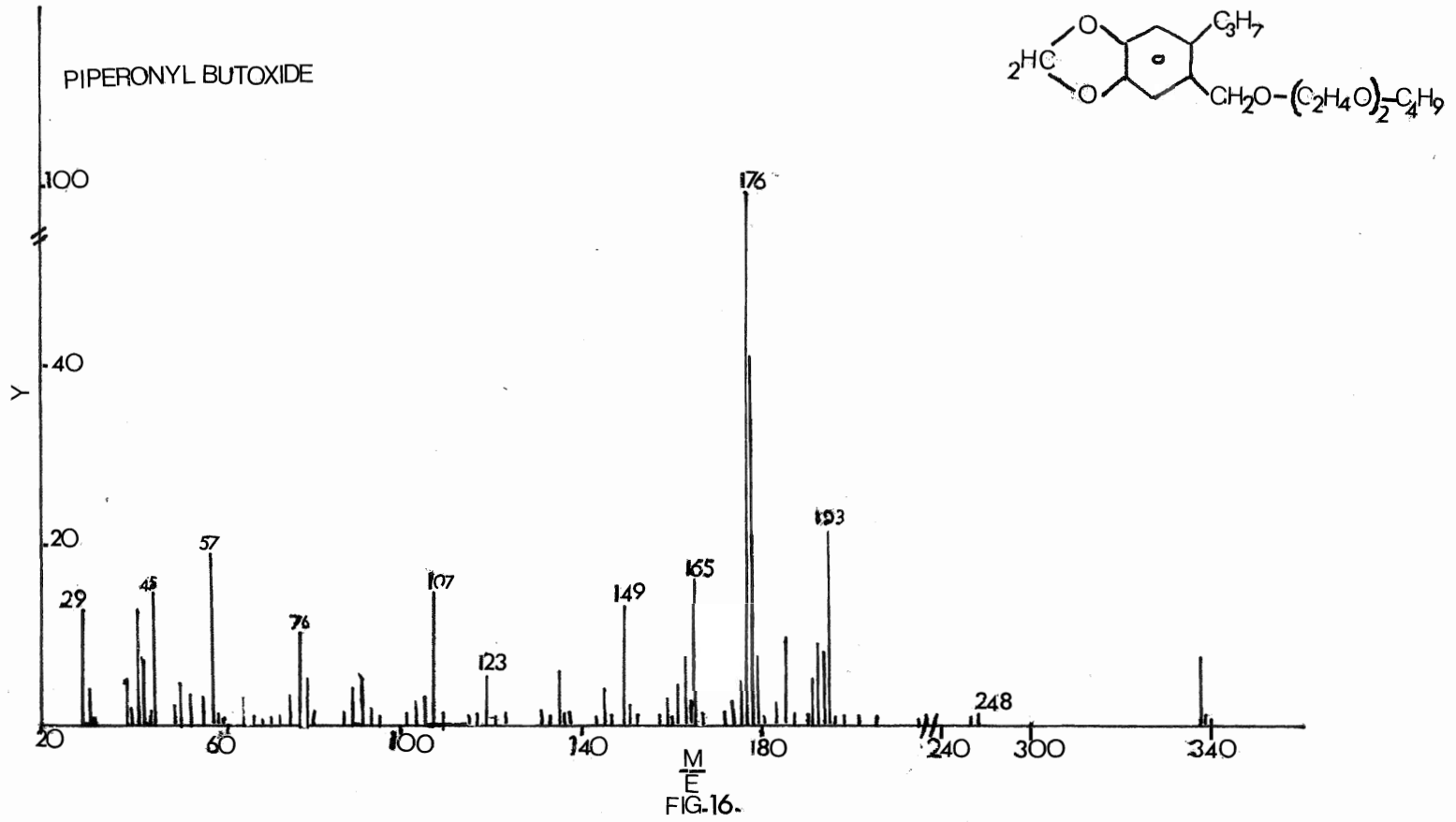
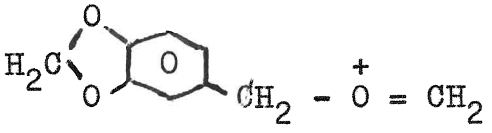



FIG.16.

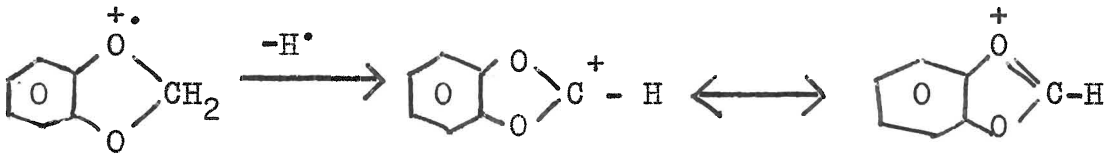
fig.I6.mass spectrum of PIPERONYL BUTOXIDE.(AEI.MS.I2.)

The ion 192 suffers a series of cleavages characteristic of an aldehyde to give the major ions in the spectrum. Thus loss of the aldehydic hydrogen yields the species of m/e 191 which subsequently eliminates the CO molecule to give m/e 163. The ion of m/e 163 leads to a metastable-transition-supported rearrangement species of m/e 135 by loss of $C_2H_4$. The structures of these ions are given in Scheme 16-b.

Ion 238 eliminates $C_3H_7^{\bullet}$ and $CH_2OH^{\bullet}$ to give m/e 164 having the  structure.

The alcohol ion of m/e 194 also undergoes a number of cleavages as illustrated in Scheme 16-b. Ion 137 (one of the daughter products) is assigned an orthoquinonoid structure in accordance with its abundance while ion 109 formed from it by the loss of CO is postulated to have the cyclopentadienone structure.

Finally, loss of the $C_3H_7^{\bullet}$ and the polyether substituent from the parent ion leads to the dioxybenzene moiety of m/e 120, having the following structure:




m/e 120 m/e 119

This, on subsequent loss of a H• leads to the species of m/e 119 which has been assigned a structure as suggested by Biemann et at[79] in their work on dioxy benzene compounds.

The spectrum of piperonyl butoxide is thus instructive as it shows characteristics of an ether, alcohol and aldehyde in the same molecule. Further, an odd electron ion is the base peak in the spectrum in contrast to an even ion, as this leads to the resonance stablised tropylium ion structure.

## Part v) Comparison of medium vs low resolution mass spectrometry in the study of pesticides

v) Comparison of medium vs. low resolution mass spectrometry in the study of pesticides

As mentioned in the experimental section, the various pesticides were studied using the low resolution ( 250) Bendix Time-of-Flight mass spectrometer with a view to test its applicability as a means of identification in comparison with medium resolution (1000) MS-12 single focusing mass spectrometer.

The results of this comparison for the organophosphorus, thio and dithiocarbamate, organochlorine and the miscellaneous pesticides are discussed separately below.

Organophosphorus Pesticides

The dimethoxy phosphorus pesticides, DDVP and Phosdrin had all the significant ions in their low resolution spectra. (Ions of m/e 220 (Parent Peak), 185, 145, 113, 109 (base peak) and 93 in the case of DDVP and m/e 224 (Parent ion), 192, 127 (base peak) 109, 93, 79 in the case of Phosdrin). Although the other ions observed in the MS-12 mass spectrometer were not prominent here, these major ions alone could characterise the spectra of these compounds. On the other hand, the molecular ions were absent in the spectra of the diethoxy phosphorus compounds as they had molecular ions of m/e > 250. Further in carbophenolthion only ions characteristic of the $(C_2H_5O)_2\overset{+}{P}{=}S$ species and the base peak at m/e 157 were evident. Ions of m/e 190, 154, 143 and 126 indicative of

its bisthioalkane nature were absent, thereby hampering the identification of this pesticide. Similarly, in the case of O-2, 4 dichlorophenyl O, o-diethylthiophosphate, ions resulting from the cleavages of the(P-O) and (C-Cl) bonds were absent,(e.g. ions of m/e 282, 281, 253, 246, 225) due to the low resolution of the instrument. Although the base peaks at m/e 223 and 97 as well as the species of m/e 171, 162, 161, 109 and 67 showed up in the spectrum, absence of the above ions at the high mass end would cause difficulty in the identification of this compound. All the major ions (excepting the parent ion) of m/e 209, 153, 97, 88, 63 and 57 (base peak) were detectable in the spectrum of tributyl-phosphorotrithioite, thus facilitating its identification.

The thiocarbamate pesticide, Eptam, showed up all the intense ions at m/e 189 (Parent peak), 160, 128, 89, 70 and 43 (base peak). The closely related pesticide, Perbulate, also had all the major ions (m/e 160, 132, 128 (base peak), 72, 57 and 43) in its spectrum. The parent ion which was weak in the MS-12 mass spectrometer was absent in the Bendix. But for this, the identification of these two compounds should be feasible in the Bendix.

The parent peaks in the spectra of the chlorinated butyl and isopropyl esters of 2,4 D were absent in the Bendix as the m/e values of their molecular ions were greater than 250. But the major ions of m/e 185, 175, 162, 145, 109 were present in both the spectra. The base peak at m/e 57

for the n-butyl ester and at m/e 43 for the isopropyl ester could distinguish the two in the absence of the molecular ion. In the spectrum of Kelthane again, the parent peak at m/e 368 as well as the ions at m/e 253, 252 and 251 was absent. Only the major isotopic peaks at m/e 193 and the base peak at m/e 139 were evident. The identification of this pesticide was therefore difficult in the Bendix.

The characteristic naphthalene spectrum and the major ions at m/e 200 (Parent ion) as well as 141 (base peak) in the case of the methyl ester of 1-naphthalene acetic acid enabled its identification with ease. The absence of many of the major ions in the spectra of Allethrin (from m/e 302 to m/e 168) and piperonyl butoxide (from m/e 368 to m/e 193) in the high mass end failed to characterise these compounds using the Bendix Time of flight mass spectrometer.

In conclusion, then, the Bendix Time of Flight Mass Spectrometer cannot be applied as a general purpose instrument for the identification of the various pesticides due to its low resolution, low sensitivity and absence of metastable ions. The AEI, MS-12 medium resolution mass spectrometer has the required sensitivity and also it gives the metastable ions. This instrument, may, therefore, be preferred in the qualitative identification of the several pesticides.

## CONCLUSION

The mass spectra of the organophosphorus; organochlorine; thiocarbamate; dithiocarbamate and the miscellaneous pesticides presented in this thesis had three major goals:

(1) to understand the various fragmentation processes which enables one to explain the formation of the various ions found in the spectra,

(2) to understand the various mass spectral features of a compound by a detailed interpretation of its spectrum,

and (3) to facilitate the identification of these pesticides in a mixture or redisue and thereby to serve as a reference index.

It is hoped that this work fulfills these aims, at least, in a modest way.

The use of high resolution measurements, isotope labelling studies and appearance potential determinations, perhaps, would have gone a long way in establishing and confirming several of the peak assignments made in this study. This is yet to be achieved. In addition, the combined use of the gas-chromatographic-mass spectrometric technique would have been of value in the analysis of several pesticide residues. As a preliminary to this study, the organophosphorus pesticides were examined in the GLC-MS combination. However, the spectral features remained the same as those obtained using the MS technique alone. Further

work in this direction may throw much light on the mass spectra of the organochlorine and thiocarbamate pesticides.

In spite of the above limitations, the work was concluded with the only belief that "it is better to complete an imperfect work than a perfect work".

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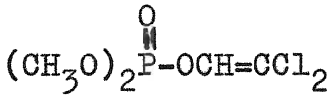
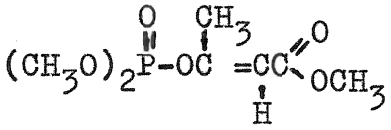
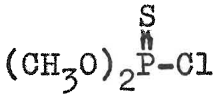
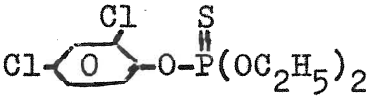
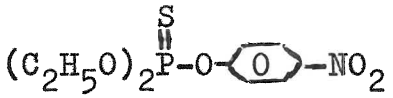
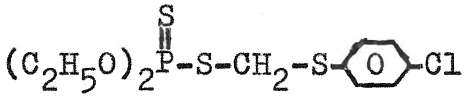
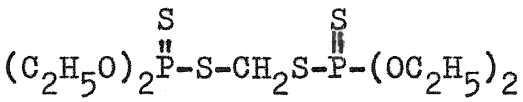
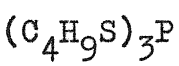
# APPENDIX

A) INDEX OF PESTICIDES

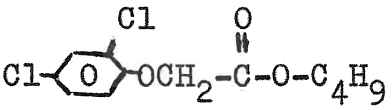
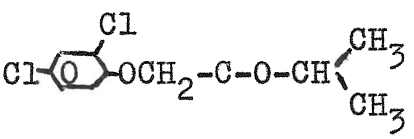
TABLE-1

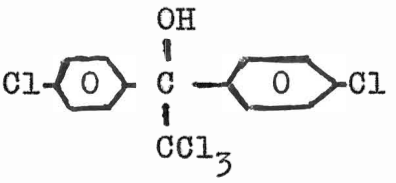
CHEMICAL NAMES AND STRUCTURES OF THE PESTICIDES EXAMINED IN THIS WORK

(a) Organo Phosphorus Pesticides

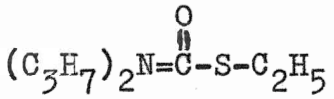
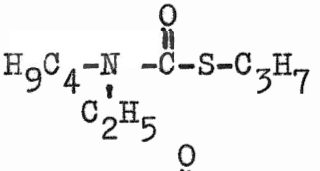
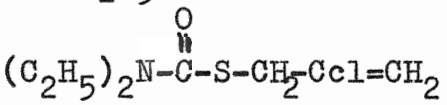
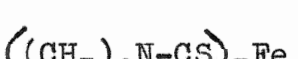
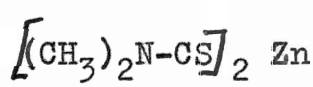
| Chemical Name | Trade Name | |
|---|---|---|
| 0,0-Dimethyl 2, 2-dichlorovinyl phosphate | DDVP |  |
| 0,0-Dimethyl 0-(2-carbomethoxy-1-methyl vinyl) phosphate | Phosdrin |  |
| 0,0-Dimethyl phosphorochloridothionate | — |  |
| 0,0-diethyl o-2,4 dichlorophenyl thiophosphate | — |  |
| 0,0-diethyl o,-p-nitro phenyl phosphorothioate | Parathion |  |
| 0,0-diethyl o,-p-chloro phenyl, s,s'-methylene bisphosphorodithioate | Carbephenolthion |  |
| 0, 0, 0',0'-tetra ethyl, S, S'-methylene bisphosphorodithioate | Ethion |  |
| Tributyl phosphoro trithioite | Merphos |  |

(b) Organochlorine Pesticides

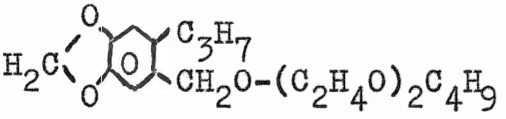
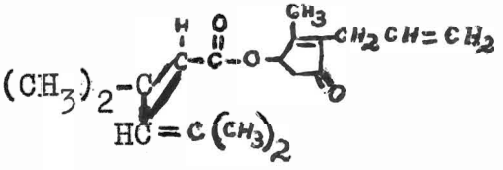
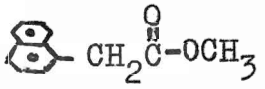
| | | |
|---|---|---|
| 2, 4 dichlorophenoxy acetic acid, butyl ester | 2, 4-D butyl ester |  |
| 2,4 dichlorophenoxy acetic acid, isopropyl ester | 2, 4-D isopropyl ester |  |

| | | |
|---|---|---|
| 1, 1-bis(4-chlorophenyl) 2,2,2,-trichloro ethanol | Kelthane |  |

(c) Thio and dithio Carbamates

| | | |
|---|---|---|
| S-ethyl,N,N-di-n-propyl thiocarbamate | Eptam (EPTC) |  |
| S-propyl N-ethyl N-butyl thiocarbamate | Perbulate |  |
| 2-Chloro allyl N, N-diethyl dithiocarbamate | Vegadex (CDEC) |  |
| Ferric dimethyl dithiocarbamate | Ferbam |  |
| Zinc dimethyl dithiocarbamate | Ziram |  |

Miscellaneous Pesticides

| | | |
|---|---|---|
| 3,4 methylene dioxy-6-propyl benzyl n-butyl diethelene glycol ether | Piperonyl Butoxide |  |
| dl-2-allyl-4-hydroxy-3-methyl-2-cyclopentam-1-one ester of al-cis trans-chrysanthum monocarboxylic acid | Allethrin |  |
| 1-Naphthalene acetic acid methyl ester | |  |

B) TABLES OF MASS SPECTRAL DATA

## Part i) Organo Phosphorus Pesticides

TABLE-2

DDVP

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 220,222,224 | 12.5,8.4,0.9 | $(CH_3O)_2\overset{O}{\overset{\|\|}{P}}-OCH=CCl_2^{+\cdot}$ |
| 185,187 | 50, 20 | $(CH_3O)_2\overset{O}{\overset{\|\|}{P}}-OCH\overset{+}{C}Cl$ |
| 109 | 100 | $(CH_3O)_2\overset{+}{P}=O$ |
| 95, 97, 99 | 6.5,4.5,2.5 | $CHCCl_2^+$ |
| 93 | 6.0 | $(CH_3O)_2P^+$ |
| 83, 85 | 8.5, 5.3 | $CHCl_2$ |
| 79 | 35.0 | $CH_3O\overset{+}{P}OH$ |
| 78 | 3.5 | $CH_3OPO^{+\cdot}$ and $OCHC^{37}Cl$ (2.6%) |
| 76 | 7.8 | $OCHC^{35}Cl$ |
| 65 | 1.4 | $H_2\overset{+}{P}O_2$ |
| 63 | 1.4 | $CH_3O\overset{+}{P}H$ |
| 62 | 2.8 | $CH_3OP^{+\cdot}$ |
| 60 | 6.3 | $CHOP^{+\cdot}$ and $CH=CCl$ |
| 49 | 4.0 | $H_2PO^+$ & $C^{37}Cl^+$ |
| 48 | 6.0 | $POH^{+\cdot}$ |
| 47 | 27.5 | $PO^+$ & $C^{35}Cl$ |
| 36, 38 | 10, 3 | $H^{35}Cl$, $H^{37}Cl$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 35, 37 | 1.5, 0.4 | $^{35}Cl$, $^{37}Cl$ |
| 31 | 8.5 | $(OCH_3)^+$ |
| 30 | 1.8 | $(OCH_2)^+$ |
| 29 | 11.3 | $(CHO)^+$ |
| 18 | 72.5 | $(H_2O)^+$ |
| 15 | 52.5 | $(CH_3)^+$ |

TABLE-3

PHOSDRIN

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 224 | 10.0 | $(CH_3O)_2\overset{O}{\overset{\|}{P}}-O-\overset{CH_3}{\overset{\|}{C}}=HC-\overset{O}{\overset{\|}{C}}-O-CH_3$ $^{+\bullet}$ |
| 193 | 10.0 | $(CH_3O)\overset{O}{\overset{\|}{P}}-OC(CH_3)=CHCO_2CH_3$ or $(CH_3O)_2PO_2C(CH_3)CHCO^+$ |
| 192 | 42.5 | $CH_2O-PO_2C(CH_3)CHCO_2CH_3^+$ |
| 164 | 3.4 | $(CH_3O)_2\overset{+}{P}O_2C_3H_3$ |
| 141 | 3.0 | $(CH_3O)_2\ P(\overset{+}{O}H)(OCH_3)$ |
| 140 | 2.0 | $(CH_3O)_2\ P(\overset{+}{O})(OCH_3)$ |
| 127 | 100.0 | $(CH_3O)_2\ P(\overset{+}{O}H)_2$ |
| 124 | 2.3 | $(CH_3O)_3P^{+\bullet}$ |
| 109 | 25.0 | $(CH_3O)_2\overset{+}{P}=O$ |
| 96 | 1.9 | $CH_3O - P(\overset{+}{O}H)_2$ |
| 95 | 4.3 | $CH_3O-PO_2^+$ |
| 93 | 3.0 | $P(\overset{+}{O}CH_3)_2$ or $CH_2O-\overset{+}{P}O_2$ |
| 79 | 8.3 | $CH_3\overset{+}{O}POH$ |
| 67 | 20.0 | $H_2P^+(OH)_2$ |
| 59 | 4.5 | $CO_2CH_3^+$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 55 | 9.5 | $C_3H_3O^+$ |
| 43 | 20.0 | $^+OCCH_3$ |
| 31 | 3.0 | $^+OCH_3$ |
| 15 | 22.5 | $CH_3^+$ |

TABLE-4

O, O-DIMETHYL PHOSPHOROCHLORIDOTHIONATE

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 160, 162 | 85.5, 35.2 | $(CH_3O)_2\overset{+}{P}S(Cl)$ |
| 134 | 3.8 | |
| 132 | 38.0 | $(OH)_2\overset{+}{P}SCl$ |
| 130 | 85.5 | $H\overset{+}{P}(OCH_3)(S)(Cl)$ |
| 129 | 20.0 | $CH_3O\overset{+}{P}(S)(Cl)$ |
| 127 | 4.3 | $CHO\overset{+}{P}SCl$ |
| 125 | 57.0 | $(CH_3O)_2\overset{+}{P}S$ |
| 116 | 2.9 | $H\overset{+}{P}(OH)(S)(Cl)$ |
| 115 | 4.3 | $\overset{+}{P}(OH)(S)(Cl)$ |
| 114 | 3.8 | $O\overset{+}{P}S(Cl)$ |
| 99 | 35.2 | $H\overset{+}{P}(S)Cl$ |
| 98 | 3.8 | $\overset{+}{P}(S)Cl$ |
| 94 | 3.8 | $CH_3O\overset{+}{P}S$ |
| 93 | 18.1 | $(CH_3O)_2\overset{+}{P}$ |
| 80 | 6.7 | $HO\overset{+}{P}S$ |
| 79 | 219 | $CH_3O\overset{+}{P}HO$ |
| 64 | 8.6 | $H\overset{+}{P}S$ |
| 63 | 21.0 | $(PS)^+$ |
| 62 | 6.7 | $(CH_3OP)^+$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 49, 48 | 3.8 | $(H_2PO)^+$ & $(HPO)^+$ |
| 47 | 64.6 | $(PO)^+$ |
| 46 | 4.3 | $(CH_2S)^+$ |
| 45 | 6.7 | $(CHS)^+$ |
| 44 | 19.0 | $(CS)^+$ |
| 31 | 14.3 | $(^+OCH_3)$ |
| 30 | 3.8 | $^+OCH_2$ |
| 29 | 15.2 | $^+OCH$ |

TABLE - 5

O-2, 4 DICHLOROPHENYL O,
O-DIETHYL THIOPHOSPHATE

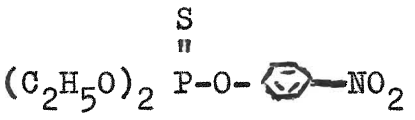
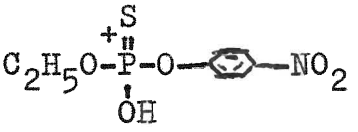
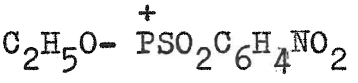
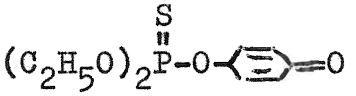
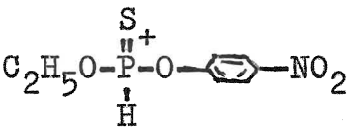
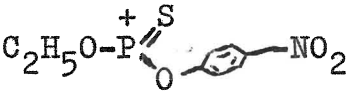
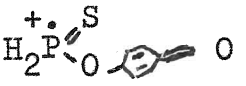
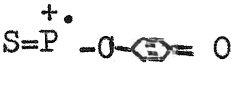
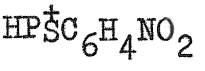
| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 314,316,318 | 9.6,7.5,1.2 | $Cl_2C_6H_3OP(S)(OC_2H_5)_2^{+\bullet}$ |
| 279,281 | 100, 41.6 | $ClCH_3^{+}OPS(OC_2H_5)_2$ |
| 269, 271 | 1.8, 1.2 | $Cl_2C_6H_3^{+}OPS(OC_2H_5)$ |
| 251, 253 | 15.4, 6.7 | $ClC_6H_3OPOC_2H_5(^{+}SH)(OH)$ |
| 246, 248 | 4.9, 7.3 | $ClC_6H_3OP(S)(OC_2H_5)(CH_2)$ |
| 243 | 3.8 | $C_6H_3OP(S)(OC_3H_9)(OC_2H_5)$ |
| 242 | 1.1 | $Cl_2C_6H_3OP(^{+}SH)(OH)$ |
| 241 | 5.8 | $Cl_2C_6H_3O^{+}P(=S)(OH)$ |
| 223, 225 | 50.0, 15.9 | $ClC_6H_3O^{+}P(=S)(OH)_2$ |
| 224,226,228 | 5.0,3.8,1.1 | $Cl_2C_6H_3OPS^{+\bullet}$ or $ClC_6H_3OP(OH)_2(^{+}SH)$ |
| 222 | 3.0 | $ClC_6H_3O_2P(OH)(S)$ |
| 209 | 2.3 | $Cl_2C_6H_3OP(^{+}OH)$ |
| 205 | 1.3 | $Cl_2C_6H_3O^{+}P=S(OH)$ |
| 198 | 3.8 | - |
| 190 | 1.0 | $ClC_6H_3OP^{+}SH$ |
| 189 | 1.2 | $ClC_6H_3O^{+}PS$ |
| 188 | 1.0 | $C_6H_3O^{+}P(S)(OH)_2$ |

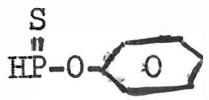
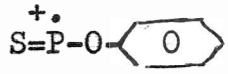
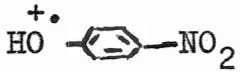
| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 173, 175 | 3.8, 1.3 | $ClC_6H_3\overset{+}{O}PO$ |
| 171 | 8.8 | $C_6H_3OP(OH)(\overset{+}{S}H)$ |
| 170 | 1.4 | $C_6H_3O\overset{+}{P}(OH)(S)$ |
| 162 | 41.7 | |
| 164,166 | 21.9, 3.8 | $Cl_2C_6H_3OH$ |
| 161 | 7.5 | $Cl_2C_6\overset{+}{H}_3O$ |
| 153 | 2.3 | $(C_2H_3O)_2\overset{+}{P}\text{-}S$ |
| 145 | 1.2 | $Cl_2C_6H_3$ |
| 143 | 2.8 | $(CH_3O)_2P(OH)(\overset{+}{S}H)$ |
| 142 | 2.3 | $(CH_3O)_2\overset{+}{P}(OH)(S)$ |
| 138 | 3.4 | $(C_2H_3O)_2\overset{+}{P}\text{-}OH$ or $C_6H_3O\overset{+}{P}{=}O$ |
| 135 | 6.1 | |
| 133 | 9.2 | $C_5\overset{+}{H}_3Cl_2$ |
| 128 | 4.6 | $(CH_9O)_2\overset{+}{P}SH$ |
| 125 | 1.7 | $C_2H_3O\text{-}\overset{+}{P}(OH)(S)$ or $(CH_3O)_2\overset{+}{P}S$ |
| 123 | 5.0 | $(CH_2O)_2\overset{+}{P}S$ |
| 111 | 3.9 | $C_2H_5O\ PH(\overset{+}{O}H)_2$ |
| 109 | 29.2 | $C_2H_5O\overset{+}{P}(O)(OH)$ or $C_2H_5O\overset{+}{P}(H)(S)$ |
| 97 | 50 | $(HO)_2\overset{+}{P}S$ |
| 96 | 1.3 | $HO\overset{+}{P}(O)(S)$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 94 | 3.1 | $CH_3OPS^+$ |
| 91 | 1.5 | $C_6H_3O^+$ |
| 81 | 7.1 | $(HO)_2P^+=O$ or $H-P^+(OH)(S)$ |
| 80 | 1.4 | $HP(O)(S)$ or $HOPS^+$ |
| 77 | 4.2 | $CH_2PS^+$ |
| 76 | 2.1 | $CHPS^+$ or $CS_2$ |
| 75 | 3.4 | $C_6H_3^+$ |
| 65 | 12.1 | $P(OH)_2^+$ |
| 64 | 1.5 | $HOP=O^{+\cdot}$ or $PHS^{+\cdot}$ |
| 63 | 11.7 | $(PS)^+$ or $C_5H_3^+$ |
| 51 | 2.2 | $C_4H_3^+$ |
| 47 | 5.4 | $(PO)^+$ |
| 45 | 4.6 | $^+OC_2H_5$ |
| 36,38 | 11.7, 4.1 | HCl |
| 35, 37 | 1.1, 0.4 | Cl |
| 34 | 1.5 | $H_2S^+$ |
| 31 | 1.5 | $^+OCH_3$ |
| 29 | 23.0 | $C_2H_5^+$ or $CHO^+$ |
| 27 | 15.0 | $C_2H_3^+$ |
| 26 | 7.1 | $C_2H_2^+$ |
| 17 | 21.1 | $OH^+$ |

TABLE - 6

PARATHION

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 291 | 60.0 |  |
| 274 | 5.0 | |
| 263 | 11.0 |  |
| 262 | 3.0 |  |
| 261 | 12.0 |  |
| 247 | 1.2 |  |
| 246 | 3.2 |  |
| 218 | 9.0 |  |
| 189 | 2.4 |  |
| 188 | 10.0 |  |
| 187 | 4.0 |  |
| 186 | 21.0 |  |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 185 | 1.5 | $PS\overset{+\cdot}{C}_6H_4NO_2$ |
| 172 | 5.2 |  |
| 170 | 3.7 |  |
| 167 | 11 | - |
| 156 | 4.6 | - |
| 155 | 25.0 | $POS\overset{+}{C}_6H_4$ |
| 153 | 8.0 | $(C_2H_5O)_2\overset{+}{P}=S$ |
| 150 | 7.0 | - |
| 142 | 8.0 | - |
| 140 | 11.0 | - |
| 139 | 46.0 |  |
| 138 | 7.0 | $O\overset{+}{C}_6H_4NO_2$ |
| 137 | 31.0 | Fragmentation of Para nitrophenol ion moiety |
| 127 | 3.5 | |
| 126 | 5.2 | |
| 125 | 40.0 | |
| 124 | 8.0 | |
| 123 | 23.0 | |
| 122 | 5.0 | |
| 121 | 8.0 | |
| 120 | 1.5 | |
| 115,114 | 3.1 | |
| 111, 110 | 7.0 | |

| m/e | % Relative Abundance | Ion Assignments |
|---|---|---|
| 109 | 70.0 | $H_5C_2O\overset{H}{\diagdown}\overset{+}{P}=S$ |
| 108 | 12.1 | $C_2H_5O-\overset{+\cdot}{P}=S$ |
| 99 | 6.3 | - |
| 97 | 100.0 | $(HO)_2\overset{+}{P}=S$ |
| 96 | 8.0 | $HO_2\overset{+\cdot}{P}S$ |
| 95 | 2.7 | $O_2\overset{+}{P}S$ |
| 93 | 22.0 | $C_2H_5O-P=\overset{+}{O}H$ |
| 92 | 7.0 | $C_2H_5O-\overset{+\cdot}{P}=O$ |
| 91 | 5.0 | - |
| 82 | 5.8 | - |
| 81 | 38.0 | - |
| 80 | 10.0 | - |
| 79 | 4.3 | $\overset{+}{P}OS$ |
| 78 | 1.5 | |
| 77 | 5.0 | |
| 76 | 9.0 | |
| 75 | 11.0 | |
| 71 | 3.1 | |
| 68 | 1.7 | |
| 67 | 2.9 | |
| 65 | 2.50 | $\overset{+}{P}(OH)_2$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 64 | 15.0 | |
| 63 | 21.0 | |
| 62 | 10.0 | |
| 61 | 9.0 | |
| 60 | 5.9 | |
| 59 | 4.5 | |
| 58 | 2.5 | |
| 57 | 6.9 | |
| 56 | 2.0 | |
| 55 | 6.5 | |
| 54 | 2.7 | Fragmentation of the aromatic moiety |
| 53-51 | 7.0 | |
| 50,47 | 12.0 | |
| 46 | 2.5 | |
| 45, 43 | 10.0 | |
| 44 | 30.0 | |
| 41 | 7.0 | |
| 39 | 11.0 | |
| 38 | 8.0 | |
| 35,34 | 3.0 | |
| 31 | 6.0 | |
| 30 | 10.0 | |
| 29 | 50.0 | |
| 27 | 4.0 | |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 122 | 5.5 | $CH_2\overset{+}{S}C_6H_4$ |
| 121 | 55.0 | $(C_2H_5\overset{+}{O})_2P$ |
| 113 | 1.8 | $HS_2\overset{+}{P}(OH)$ |
| 112 | 1.5 | $S_2P(OH)^+$ |
| 111 | 2.6 | $\overset{+}{C_6H_4}Cl$ |
| 109 | 5.0 | $C_2H_5O\ \overset{+}{P}H(S)$ |
| 99 | 3.4 | $\overset{+}{C_5H_4}Cl$ |
| 93 | 13.2 | $C_2H_5O\overset{+}{P}OH$ |
| 77 | 2.5 | $CHS_2^+$ or $PH(OC_2H_5)$ |
| 65 | 20.0 | $\overset{+}{H_2}PS$ or $P(\overset{+}{O}H)_2$ |
| 58 | 6.8 | |
| 47 | 4.8 | $CH_2^+SH$ |
| 45 | 29.1 | $\overset{+}{O}C_2H_5$ or CHS |
| 29 | 15.5 | $C_2H_5^+$ |

TABLE - 7

CARBOPHENOLTHION

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 342, 344 | 72.7, 29.5 | $(C_2H_5O)_2PS_2CH_2SC_6H_4Cl^+$ |
| 199 | 27.3 | $(C_2H_5O)_2PS_2CH_2^+$ |
| 189, 191 | 4.6, 1.5 | $SCH_2S\ C_6H_4Cl^+$ |
| 171 | 3.0 | $C_2H_5O\ P(OH)\ PS_2^+CH_2$ |
| 157, 159 | 100.0, 45.5 | $CH_2\overset{+}{S}\ C_6H_4Cl$ |
| 158 | 9.1 | $C_2H_5O\ PS_2H(OH)^+$ |
| 154 | 8.2 | $(C_2H_5O)_2P^+SH$ |
| 153 | 50.0 | $(C_2H_5O)_2\overset{+}{P}S$ |
| 146 | 2.3 | |
| 145 | 4.5 | $H_2S^+C_6H_4Cl$ |
| 144 | 8.2 | $HSC_6H_4Cl^{+\cdot}$ |
| 143 | 1.4 | $\overset{+}{S}C_6H_4Cl$ |
| 142 | 2.1 | $SCH_2SPSH$ |
| 141 | 1.1 | $C_2H_5OPS_2H^+$ |
| 129 | 6.8 | $(HO)_2P^+S_2$ |
| 127 | 2.0 | $HP(OH)\overset{+}{S}_2CH_2$ |
| 125 | 27.7 | $C_2H_5O\overset{+}{P}(OH)S$ |

TABLE - 8

*ETHION $(C_2H_5O)_2PS_2CH_2S\overset{S}{\overset{\|}{P}}(OC_2H_5)_2$

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 186 | 28.9 | $C_4H_{11}O_2PS_2^{+\cdot}$ |
| 170 | 2.7 | $C_3H_7O_2PS_2^{+}$ |
| 158 | 7.7 | $C_2H_7O_2PS_2^{+}$ |
| 157 | 3.20 | $C_2H_6O_2PS_2^{+}$ $_{+\cdot}$ |
| 154 | 5.3 | $(C_2H_5O)_2PSH$ |
| 153 | 11.9 | $(C_2H_5O)_2P{=}S^{+}$ |
| 142 | 13.6 | $CH_3PS_3^{+}$ |
| 141 | 8.0 | $C_2H_5OPS_2H^{+}$ |
| 137 | 18.7 | - |
| 130 | 5.3 | $(OH)_2PS_2H^{+\cdot}$ |
| 129 | 15.3 | $(OH)_2PS_2^{+}$ |
| 127 | 2.3 | $HP(OH)S_2CH_2^{+}$ |
| 126 | 4.6 | $(HO)PS_2CH_2^{+}$ |
| 125 | 28.9 | $(C_2H_5O)\overset{S}{\overset{\|}{P}}^{+}{}_{OH}$ |
| 122 | 3.6 | $C_7H_6S^{+}$ |
| 121 | 6.2 | $C_7H_5\overset{+}{S}$ or $C_2H_5O\text{-}P{=}\overset{+}{O}C_2H_5$ |
| 115 | 3.9 | - |

*Parent ion is absent

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 114 | 10.5 | - |
| 113 | 15.8 | $HS_2\overset{+}{P}(OH)$ |
| 112 | 2.6 | $\overset{+}{P}S_2(OH)$ |
| 109 | 27.2 | $C_2H_5O\overset{+}{P}H(S)$ |
| 108 | 2.4 | $C_2H_5O\overset{+}{P} = S$ |
| 99 | 8.5 | - |
| 97 | 100 | $(HO)_2\overset{+}{P}=S$ |
| 96 | 7.5 | $O=\overset{+}{P}(\overset{\cdot}{O}H)=S$ |
| 95 | 13.6 | $\overset{+}{P}O_2S$ |
| 93 | 62.1 | $C_2H_5OP=\overset{+}{O}H$ |
| 91 | 3.2 | $C_2H_3OP=\overset{+}{O}H$ |
| 81 | 11.5 | HO-H=S |
| 80 | 15.3 | $HO-\overset{+}{P}=S$ |
| 79 | 6.8 | $CH_3OP=\overset{+}{O}H$ |
| 78 | 15.3 | $H_2P(OC_2H_5)$ |
| 77 | 2.9 | $PH(OC_2H_5)$ |
| 76 | 2.2 | $\overset{+}{P}OC_2H_5$ |
| 65 | 96.6 | $H_2\overset{+}{P}S$ |
| 64 | 16.7 | $\overset{+}{H}PS$ |
| 63 | 53.4 | $\overset{+}{P}S$ |
| 62 | 10.9 | $\overset{+}{P}OCH_3$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 61 | 16.7 | $POCH_2^+$ |
| 60, 59 | 15.3 | |
| 49 | 3.4 | $H_2PO^+$ |
| 48 | 8.5 | $HP{=}O^{+\cdot}$ |
| 47 | 34.0 | $CH_2SH^+$ |
| 46 | 25.5 | $CHSH^+$ |
| 45 | 34 | $OC_2H_5^+$ |
| 44 | 5.1 | |
| 43 | 11.9 | |
| 42 | 2.6 | |
| 41 | 3.4 | Fragments from $OC_2H_5$ |
| 35 | 6.8 | |
| 34 | 11.9 | |
| 33 | 6.8 | |
| 29 | 68.0 | |

TABLE - 9

TRIBUTYL PHOSPHOROTRITHIOITE

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 298 | 46.2 | $(C_4H_9S)_3P^{+\cdot}$ |
| 242 | 8.5 | $(C_4H_9S)_2P^{+\cdot}SH$ |
| 210 | 11.5 | $(C_4H_9S)_2PH$ |
| 209 | 88.5 | $(C_4H_9S)^{+}_2P$ |
| 187 | 1.6 | $H-P(SC_4H_9)(SH)(SH^{+})$ |
| 186 | 3.9 | $C_4H_9SP(SH)^{+}_2$ |
| 185 | 4.8 | $C_4H_9SP^{+}(SH)(SH)$ |
| 155, 154 | 3.2 | $HP(^{+}SH)(SC_4H_9)$ & $P^{+}SH(SC_4H_9)$ |
| 153 | 30.0 | $(C_4H_9S)P^{+}SH$ |
| 152 | 3.5 | $C_4H_9SP^{+\cdot}S$ |
| 151 | 1.2 | $C_4H_8SP^{+}S$ |
| 131 | 1.5 | $HP(SH)^{+}_3$ |
| 129, 122 | 4.9 | $SP(SH)^{+}_2$ & $H_2P^{+}SC_4H_9$ |
| 121, 120 | 2.0 | $HP^{+}S-C_4H_9$ & $P^{+\cdot}SC_4H_9$ |
| 119 | 4.5 | $C_4H_8SP$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 112 | 1.7 | $HP^{+}_{SCH_3}$ SH |
| 99, 98 | 1.1 | $H_2\overset{+}{P}(SH)_2$ $HP(SH)_2$ |
| 97 | 11.5 | $\overset{+}{P}(SH)_2$ |
| 96 | 1.9 | $\overset{+\cdot}{HSPS}$ |
| 90 | 8.5 | $C_4H_9SH$ |
| 89 | 4.6 | $C_4H_9\overset{+}{S}$ |
| 88 | 30.8 | $C_4H_8S^+$ |
| 87 | 2.4 | |
| 86 | 9.2 | |
| 85 | 6.9 | |
| 84 | 2.3 | |
| 83 | 7.7 | Fragmentation of $C_4H_8S^+$ |
| 82 | 3.9 | |
| 81 | 4.9 | |
| 79 | 1.6 | |
| 77 | 2.3 | |
| 75 | 4.4 | |
| 74 | 1.3 | |
| 73 | 1.4 | |
| 69 | 2.0 | |
| 63 | 11.5 | |
| 62 | 3.1 | |
| 61 | 6.9 | |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 57 | 100 | $C_4H_9^+$ |
| 56 | 27.7 | |
| 55 | 24.6 | |
| 54 | 2.4 | |
| 53 | 4.1 | |
| 47 | 12.7 | |
| 46 | 3.4 | |
| 44 | 1.6 | Fragmentation of $C_4H_9^+$ |
| 43 | 22.3 | |
| 42 | 4.5 | |
| 41 | 76.9 | |
| 40 | 2.7 | |
| 39 | 16.2 | |
| 36 | 4.5 | |

## Part ii) Thiocarbamate and Dithiocarbamate Pesticides

TABLE - 10

EPTAM

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 189 | 62.50 | $(C_3H_7)_2NCOSC_2H_5^{+\cdot}$ |
| 160 | 14.5 | $C_3H_7N(CH_2)COSC_2H_5$ or $(C_3H_7)_2NCOS^{+}$ |
| 131 | 1.5 | $(CH_2)_2\overset{+\cdot}{N}COSC_2H_5$ or $C_3H_7$-$N(CH_2)COS$ |
| 128 | 93.8 | $(C_3H_7)_2\overset{+}{N}CO$ |
| 89 | 13.8 | $C_2H_5SCO^{+}$ |
| 86 | 42.5 | $C_3H_7\overset{+}{N}HCO$ |
| 75, 72 | 2.4 | $CH_3SCO^{+}$ & $CH_2NCS$ resply. |
| 70 | 10.0 | $(CH_2)_2\overset{+}{N}CO$ |
| 62 | 1.7 | |
| 59,60 | 1.1 | HNCS & $COS^{+}$ resply. |
| 58 | 3.6 | $CH_2NH_2CO$ |
| 56 | 2.4 | $CH_2\overset{+}{N}CO$ |
| 47 | 1.4 | |
| 44 | 3.1 | $H_2\overset{+}{N}CO$ |
| 43 | 100.0 | $\overset{+}{H}NCO$ or $C_3H_7^{+}$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 42 | 11.3 | |
| 41 | 20.0 | |
| 40 | 2.1 | |
| 39 | 7.5 | |
| 36, 34 | 1.1 | |
| 30 | 7.5 | Fragmentation of $C_3H_7^+$ |
| 29 | 37.5 | |
| 27 | 25.0 | |
| 26 | 3.1 | |

TABLE - 11

PERBULATE

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 203 | 33.3 | $C_2H_5\overset{C_4H_9}{\overset{\vert}{N}}-COSC_3H_7^+$ |
| 161 | 3.3 | $C_2H_5\overset{C_4H_9}{\overset{\vert}{N}} - C(OH)=S^+$ |
| 160 | 8.2 | $C_2H_5\overset{CH_2}{\overset{\vert}{N}} - COSC_3H_7^+$ |
| 132 | 5.4 | $C_4H_9N\overset{OH}{\overset{\vert}{C}} = S$ |
| 129 | 8.5 | $C_2H_5\overset{C_4H_9}{\overset{\vert}{N}}HCO$ |
| 128 | 100 | $C_2H_5\overset{C_4H_9}{\overset{\vert}{N}}CO^+$ |
| 112 | 0.7 | $C_2H_5\overset{C_4H_9}{\overset{\vert}{N}} \equiv C^+$ |
| 103 | 3.9 | $C_3H_7SCO^+$ |
| 100 | 4.8 | $C_4H_9\overset{+}{N}HCO$ |
| 98 | 4.0 | $C_4H_8\overset{+}{N}CO$ |
| 90, 89 | 2.7 | $CH_2\overset{+}{N}\overset{OH}{\overset{\vert}{C}}S$ & $C_2H_5-SCO^+$ |
| 84 | 8.6 | $C_3H_6\overset{+}{N}CO$ |
| 72 | 75.0 | $CH_2\overset{+}{N}CS$ & $C_2H_5\overset{+}{N}HCO$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 71 | 7.1 | $C_2H_5\overset{+}{N}CO$ |
| 70 | 2.5 | $C_2H_4\overset{+}{N}CO$ |
| 61 | 1.7 | $C_2H_5S^+$ |
| 60 | 1.5 | SCO & $C_2H_9S^+$ |
| 59 | 1.1 | $\overset{+}{H}NCS$ |
| 58 | 26.4 | $(NCS)^+$ |
| 57 | 94.3 | $CH_3\overset{+}{N}CO$ & $C_4H_9^+$ |
| 55 | 10.0 | $C_4H_7^+$ |
| 54 | 1.6 | $C_4H_6^+$ |
| 53 | 1.2 | $C_4H_5^+$ |
| 44 | 10.0 | $H_2NCO$ |
| 43 | 71.4 | $C_3H_7^+$ |
| 42 | 27.9 | |
| 41 | 78.6 | |
| 40 | 4.4 | |
| 39 | 19.3 | |
| 38 | 1.7 | Fragmentation of $C_3H_7^+$ |
| 37 | 1.1 | |
| 34 | 4.8 | |
| 33 | 1.3 | |
| 30 | 12.9 | |
| 29 | 64.3 | |
| 27 | 34.3 | |

TABLE - 12

VEGADEX

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 223, 225 | 3.5, 1.3 | $(C_2H_5)_2NCS_2CH_2CCl{=}CH_2^+$ |
| 195, 197 | 2.3, 1.5 | $C_2H_5\text{-}\overset{H}{\overset{\vert}{N}}CS_2CH_2CCl = CH_2^+$ |
| 194 | 1.3 | $C_2H_5\text{-}NCS_2CH_2CCl = CH_2^+$ |
| 191 | 14.3 | - |
| 190 | 11.3 | - |
| 189 | 20.0 | - |
| 188 | 100 | $(C_2H_5)_2NCS_2CH_2CCH_2^+$ |
| 167 | 1.0 | $NHCS_2HCH_2CClCH_2^+$ |
| 152, 150 | 1.1 | $HCS_2CH_2CCl{=}CH_2^+$ |
| 149 | 1.6 | $CS_2CH_2CCl{=}CH_2^+$ |
| 148 | 11.0 | $(C_2H_5)_2NCS_2^+$ |
| 142 | 2.3 | |
| 117 | 6.3 | $HCS_2CH_2C_2H_2^+$ |
| 104, 89 | 2.5 | $C_2HS_2^+$ |
| 88 | 27.5 | $C_2H_5NHCS$ |
| 87 | 3.5 | $C_2H_5NCS^+$ |
| 77, 76 | 6.8 | $CS_2H^+$, $CS_2$ resply. |
| 75 | 7.8 | $C_3H_4Cl^+$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 72 | 32.5 | $C_3H_4S^+$ or $CH_2NCS^+$ |
| 71 | 2.3 | $C_3H_3S^+$ |
| 70, 62 | 1.5 | $C_3H_2S^+$ |
| 60 | 25 | $NHCSH^+$ |
| 59 | 5.5 | $NHCSH^+$ |
| 58 | 2.5 | $NCS^+$ |
| 57 | 1.3 | $C_2H_5-\overset{+}{N}=CH_2$ |
| 56 | 9.0 | $C_2H_4\overset{+}{N}=CH_2$ |
| 55 | 9.3 | $C_2H_3\overset{+}{N}CH_2$ |
| 54 | 5.0 | $C_2H_2\overset{+}{N}CH_2$ |
| 45 | 5.8 | $CHS^+$ |
| 44 | 30 | $CS^+$ |
| 43 | 3.5 | $C_2H_5\overset{+}{N}$ |
| 42, 41 | 6.3 | $C_2H_9N$ & $C_2H_3N$ resply. |
| 34 | 5.8 | $H_2S^+$ |
| 29 | 32.5 | $C_2H_5^+$ |
| 27 | 25.0 | $C_2H_3^+$ or $HCN^+$ |

Part iii) Chlorinated Pesticides

TABLE - 13

2, 4-D, ISOPROPYL ESTER

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 262,264,266 | 32.2,23.2,3.5 | $Cl_2.C_6H_3O.CH_2.CO_2C_3H_7^+$ |
| 220,222,224 | 8.1,5.3,0.7 | $Cl_2.C_6H_3O.CH_2.CO_2H^+$ |
| 219,221,223 | 2.8,2.6,0.5 | $Cl_2.C_6H_3O.CH_2.CO_2^+$ |
| 185, 187 | 9.3, 3.0 | $Cl.C_6H_3O.CH_2.CO_2H^+$ |
| 176,178,180 | 7.0,4.2,0.5 | $Cl_2.C_6H_3O.CH_3^+$ |
| 175,177,179 | 39.4,25.5,3.5 | $Cl_2.C_6H_3O.CH_2^+$ |
| 162, 164 | 27.8, 23.2 | $Cl_2.C_6H_3O.H^+$ |
| 145,147,149 | 10.0,7.4,1.6 | $Cl_2.C_6H_3^+$ |
| 110, 112 | 7.2,2.5 | $Cl.C_6H_3^+$ |
| 74 | 4.4 | $C_6H_2^+$ |
| 57 | 2.1 | $CHCO_2^+$ |
| 51 | 0.7 | $C_4H_3^+$ |
| 43 | 100 | $C_3H_7^+$ |
| 41 | 23.2 | $C_3H_5^+$ |

TABLE - 14

2, 4-D, n-BUTYL ESTER

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 276,278,280 | 90.0, 60.0, 100 | $Cl_2.C_6H_3O.CH_2CO_2C_4H_9^+$ |
| 220,222,224 | 9.5, 6.5, 1.0 | $Cl_2.C_6H_3O.CH_2CO_2H^+$ |
| 185, 187 | 23.5, 9.5 | $Cl.\overset{+}{C}_6H_3O.CH_2CO_2H$ |
| 176,178,180 | 5.0, 4.5, 1.1 | $Cl_2.C_6H_3O.CH_3^+$ |
| 175,177,179 | 23.5, 17.0, 5.0 | $Cl_2.C_6H_3\overset{+}{O}.CH_2$ |
| 162,164,166 | 22.0, 15.0, 2.6 | $Cl_2.C_6H_3OH^+$ |
| 145,147,149 | 13.4, 10.0, 3.0 | $Cl_2.C_6H_3^+$ |
| 146 | 4.0 | - |
| 109 | 9.5 | - |
| 57 | 100 | $C_4H_9^+$ |
| 43 | 7.0 | $C_3H_7^+$ |
| 29 | 50.0 | $C_2H_5^+$ |

TABLE - 15

KELTHANE

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 368-378 | 0.6,1.0,0.6, 0.2, ... | $Cl.C_6H_4.\overset{\overset{CCl_3}{|}}{\underset{\underset{OH}{|}}{C}}-C_6H_4Cl^+$ |
| 316-324 | 3.4,5.3,2, 0.5, 0.1 ... | $Cl.C_6H_4-C(CCl_2)C_6H_4Cl^+$ |
| 269,271,273 | 3.4, 3.4, 1.0 ... | $C_5H_4.C(CCl_2).C_6H_4Cl^+$ |
| 250,252,254 | 11.8, 6.5, 1.1 | $Cl.C_6H_4.\overset{O}{\overset{\|}{C}}-C_6H_4Cl.^+$ |
| 240-248 | 1.2, 1.7, 0.9, 0.8, 0.5 ... | $C.Cl_3-C.C_6H_4Cl^+$ |
| 210 | 1.2 | $CCl_3\overset{\overset{+}{C}}{\underset{\underset{OH}{|}}{|}}-C_5H_4$ |
| 193-199 | 11.8, 10.6, 2.8, 2.8 | $CCl_3-\overset{+}{C}.C_5H_4$ |
| 170,172 | 2.7, 1.6 | $CCl_2.C.C_6H_4^+$ |
| 140, 142 | 6.5, 1.3 | $Cl.C_6H_4C.OH$ |
| 139, 141 | 100, 24.7 | $Cl.C_6H_4CO^+$ |
| 111, 113 | 29.4, 9.4 | $Cl.C_6H_4^+$ |
| 105 | 2.5 | $C_6H_4\overset{+}{C}.OH$ |
| 104 | 1.4 | $C_6H_4CO^+$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 99 | 2.4 | $C_5H_4Cl^+$ |
| 76 | 5.9 | $C_6H_4^+$ |
| 75 | 15.6 | $C_6H_3^+$ |
| 74 | 3.7 | $C_6H_2^{+\cdot}$ |
| 63 | 1.5 | $C_5H_3^+$ |
| 51 | 3.6 | $C_4H_3^+$ |
| 50 | 6.8 | $C_4H_2^{+\cdot}$ |

## Part iv) Miscellaneous Pesticides

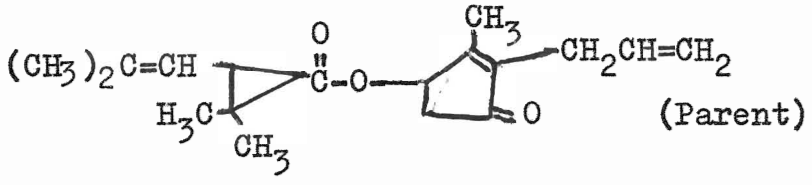
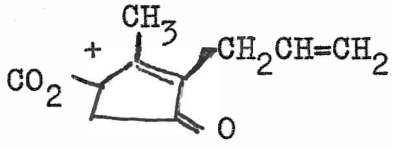
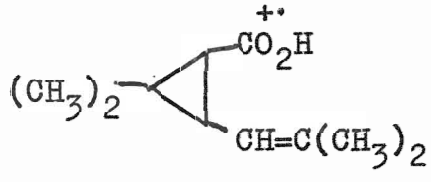
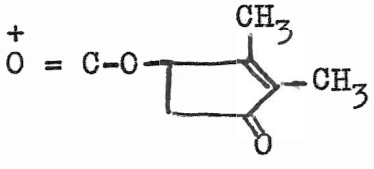
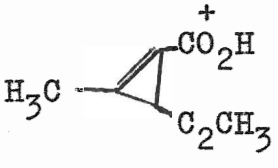
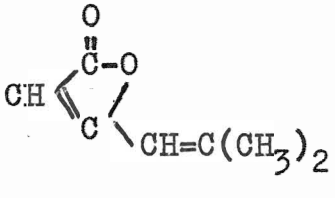
TABLE - 16

1-NAPHTHALENE ACETIC ACID, METHYL ESTER

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 200 | 96.7 | $C_{10}H_7CH_2CO_2CH_3^+$ |
| 142 | 33.3 | $C_{11}H_{10}^+$ |
| 141 | 100.0 | $C_{11}H_9^+$ |
| 140 | 5.0 | $C_{11}H_8^+$ |
| 139 | 11.7 | $C_{11}H_7^+$ |
| 138 | 1.0 | $C_{11}H_6^+$ |
| 128 | 1.0 | |
| 115 | 1.8 | |
| 114, 113 | 1.0 | |
| 89 | 1.8 | Fragmentation pattern |
| 71 | 7.0 | due to naphthalene |
| 70 | 1.4 | |
| 69 | 1.7 | |
| 57 | 5.0 | |
| 39 | 1.1 | |

TABLE - 17

ALLETHRIN

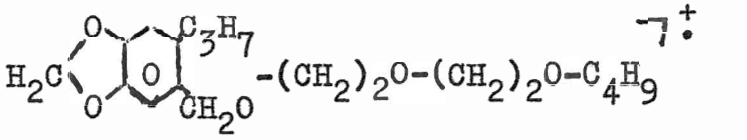
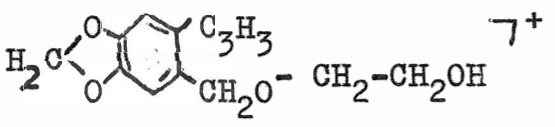
| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| | | R R' + |
| 302 | 7.7 |  (Parent) |
| 178 | 1.1 |  |
| 168 | 10.2 |  |
| 153 | 5.4 |  |
| 151 | 1.7 | $RC\equiv O^{+}$ |
| 136 | 27.7 |  |
| 125 | 4.6 |  |
| 123 | 100.0 | $R^{+}$ |
| 122 | 2.5 | $(R-H)^{+\cdot}$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 121 | 3.4 | $(R-2H)^+$ |
| 113 | 1.2 | $(CH_3)_2C$  |
| 111 | 3.7 | $CH_3C{=}\overset{+}{C}\ CO_2CH{=}CH_2$ |
| 110 | 3.1 | $(CH_3)_2C{=}CH{-}CH{=}C(CH_3)_2^{\cdot+}$ or $CH_3C = CCO_2CH{=}CH_2$ |
| 109 | 10.2 ) | |
| 108 | 4.0 ) | Successive loss of H$^\bullet$ from m/e 110 |
| 107 | 30.8 ) | |
| 94 | 1.9 | $C_7H_{10}^+$ |
| 93 | 12.9 | $C_7H_9^+$ |
| 92 | 3.1 | $C_7H_8^+$ |
| 91 | 17.2 | $C_7H_7^+$ |
| 85 | 1.4 | $C_5H_9O^+$ |
| 83 | 4.0 | |
| 82 | 4.6 | |
| 81 | 18.2 | Success.loss of H$^\bullet$ from $C_5H_9O^+$ |
| 80 | 4.0 | |
| 79 | 24.6 | |
| 78 | 2.8 | |
| 77 | 8.9 | |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 71 | 1.2 | $^{+}O_2CCH{=}CH_2$ |
| 69 | 9.5 | $C_5H_9^+$ or $^{+}O_2C.C{\equiv}CH$ |
| 68 | 1.7 | $C_5H_8^+$ |
| 67 | 11.4 | $C_5H_7^+$ or $C_4H_3O^+$ |
| 66 | 2.5 | $C_5H_6^+$ |
| 65 | 5.9 | $C_5H_5^+$ |
| 55 | 12.3 | $C_4H_7^+$ |
| 54 | 1.30 | $C_4H_6^+$ or $C_3H_2O^+$ |
| 53 | 10.2 | $C_4H_5^+$ |
| 44 | 5.2 | $C_2H_4O^+$ |
| 43 | 21.5 | $C_2H_3O^+$ |
| 41 | 36.8 | $C_3H_5^+$ |
| 40 | 2.8 | $C_3H_4^+$ |
| 39 | 15.1 | $C_3H_3^+$ |
| 29 | 11.7 | $CHO^+$ |
| 27 | 10.8 | $C_2H_3^+$ |
| 26 | 7.4 | $C_2H_2^+$ |

TABLE - 18

PIPERONYL BUTOXIDE

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 338 | 7.7 |  |
| 195 | 1.4 |  |
| 194 | 26.0 | $C_{10}H_{10}O_4^{+\cdot}$ |
| 193 | 8.0 | $C_{10}H_{15}O_3^{+}$ |
| 192 | 9.3 | $C_{12}H_{16}O_2^{+\cdot}$ |
| 191 | 5.2 | $C_{12}H_{15}O_2^{+}$ |
| 190 | 1.5 | $C_{12}H_{14}O_2^{+\cdot}$ |
| 183 | 2.6 | $C_{10}H_{15}O_3^{+}$ |
| 178 | 6.5 | $C_{11}H_{14}O_2^{+\cdot}$ |
| 177 | 41.0 | $C_{10}H_9O_3^{+}$ |
| 176 | 100 | $C_{11}H_{12}O_2^{+\cdot}$ |
| 175 | 5.0 | $C_{12}H_{15}O^{+}$ or $C\ H_{11}O_2^{+}$ |
| 173 | 2.1 | $C_{12}H_{13}O^{+}$ |
| 166 | 1.8 | $C_9H_{10}O_3^{+\cdot}$ |
| 165 | 16.6 | $C_9H_9O_3^{+}$ |
| 164 | 3.2 | $C_9H_8O_3^{+\cdot}$ |
| 163 | 7.7 | $C_{10}H_{11}O_2^{+}$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 162 | 3.2 | $C_{10}H_{10}O_2^{+\cdot}$ |
| 161 | 4.6 | $C_{11}H_{13}O^+$ |
| 159 | 3.2 | $C_8H_{15}O_3^+$ |
| 151 | 2.6 | $C_8H_7O_3^+$ |
| 150 | 2.1 | $C_8H_6O_3^{+\cdot}$ |
| 149 | 13.7 | $C_9H_{10}O_2^+$ |
| 145 | 4.1 | $C_7H_{13}O_3^+$ |
| 135 | 6.0 | $C_8H_7O_2^+$ |
| 131 | 2.1 | $C_7H_{15}O_2^+$ |
| 119 | 5.9 | $C_7H_3O_2^+$ |
| 115 | 1.7 | $C_6H_{11}O_2^+$ |
| 107 | 15.0 | $C_7H_7O^+$ |
| 105 | 3.6 | $C_7H_5O^+$ |
| 103 | 2.1 | $C_7H_3O^+$ |
| 101 | 1.4 | $C_6H_{13}O^+$ |
| 93 | 2.0 | $C_6H_5O^+$ |
| 91 | 5.9 | $C_6H_3O^+$ |
| 88 | 1.2 | $C_4H_8O_2^{+\cdot}$ |
| 87 | 1.7 | $C_5H_{11}O^+$ |
| 79 | 5.5 | $C_5H_3O^+$ |
| 77 | 10.0 | $O_2C_3H_9^+$ |
| 75 | 3.6 | $O_2C_3H_7^+$ |
| 73 | 1.3 | $O_2C_3H_5^+$ |
| 65 | 2.8 | $C_5H_5^+$ |

| m/e | % Relative Abundance | Ion Assignment |
|---|---|---|
| 58 | 1.6 | $OC_3H_6^+$ |
| 57 | 18.7 | $OC_3H_5^+$ |
| 45 | 15.0 | $OC_2H_5^+$ |
| 44 | 2.0 | $OC_2H_4^{+\cdot}$ |
| 43 | 6.3 | $OC_2H_3^+$ |
| 42 | 7.3 | $OC_2H_2^{+\cdot}$ |
| 41 | 12.7 | $C_3H_5^+$ |
| 31 | 1.8 | $CH_2^+OH$ |
| 29 | 12.3 | 12.3 |

## C) TABLES OF METASTABLE IONS

| Compound | $m_1$ | | $m_2$ | $m^*$ Observed | $m^*$ Calculated |
|---|---|---|---|---|---|
| i) Organophosphorus Pesticides | | | | | |
| (a) DDVP and Phosdrin | 109 | $\xrightarrow{-CH_2O}$ | 79 | 57.3 | 57.25 |
| | 79 | $\xrightarrow{CH_2O}$ | 49 | 30.4 | 30.39 |
| | 93 | $\xrightarrow{-CH_2O}$ | 63 | 42.7 | 42.68 |
| DDVP only | 220 | $\xrightarrow{-Cl^\bullet}$ | 185 | 155.4 | 155.56 |
| Phosdrin only | 224 | $\xrightarrow{-C\equiv CCO_2CH_3}$ | 141 | 88.9 | 88.90 |
| | 127 | $\xrightarrow{H_2O}$ | 109 | 93.5 | 93.55 |
| (b) O,O-dimethyl phosphoro-chloridothionate | 125 | $\xrightarrow{-CH_2S}$ | 79 | 49.9 | 49.90 |
| | 79 | $\xrightarrow{-CH_3OH}$ | 47 | 27.8 | 27.96 |
| (c) Transitions common to the O, O-diethyl phosphorus compounds | 153 | $\xrightarrow{-C_2H_4}$ | 125 | 102.1 | 102.11 |
| | 125 | $\xrightarrow{-C_2H_4}$ | 97 | 75.9 | 75.87 |
| | 153 | $\xrightarrow{-CH_3CHO}$ | 109 | 77.6 | 77.68 |
| | 109 | $\xrightarrow{-C_2H_4}$ | 81 | 60.2 | 60.18 |
| (d) Carbophenol-thion | 342 | $\xrightarrow{-C_6H_4SCl^\bullet}$ | 199 | 115.7 | 115.77 |
| | 199 | $\xrightarrow{-CH_2S}$ | 153 | 117.7 | 117.63 |
| | 121 | $\xrightarrow{-C_2H_4}$ | 93 | 71.4 | 71.48 |
| (e) Tributylphos-phorotrithioite | 298 | $\xrightarrow{-C_4H_8}$ | 242 | 196.6 | 196.52 |

| Compound | $m_1$ | | $m_2$ | m* Observed | m* Calculated |
|---|---|---|---|---|---|
| ii) Thio and dithio-carbamates | | | | | |
| (a) Eptam | 189 | $\xrightarrow{-C_2H_5^{\bullet}}$ | 160 | 135.4 | 135.45 |
| | 85 | $\xrightarrow{-CH_3^{\bullet}}$ | 70 | 57.6 | 57.64 |
| (b) Perbulate | 203 | $\xrightarrow{-C_3H_7S^{\bullet}}$ | 128 | 80.7 | 80.7 |
| | 128 | $\xrightarrow{-C_4H_8}$ | 72 | 40.5 | 40.5 |
| | 161 | $\xrightarrow{-C_2H_5^{\bullet}}$ | 129 | 103.3 | 103.38 |
| (c) Vegadex | 223 | $\xrightarrow{-Cl^{\bullet}}$ | 188 | 158.5 | 158.49 |
| | 167 | $\xrightarrow{-(NH)^{\bullet}}$ | 152 | 138.3 | 138.34 |
| | 90 | $\xrightarrow{-CH_2^{\bullet}}$ | 76 | 64.2 | 64.17 |
| | 88 | $\xrightarrow{-C_2H_5^{\bullet}}$ | 59 | 39.5 | 39.56 |
| iii) Chlorinated Pesticides | | | | | |
| (a) isopropyl and n-butyl esters of 2, 4-D | 175 | $\xrightarrow{-CH_2O}$ | 145 | 120.1 | 120.14 |
| | 145 | $\xrightarrow{-Cl^{\bullet}}$ | 110 | 83.5 | 83.45 |
| isopropyl ester only | 85 | $\xrightarrow{-C_2H_4}$ | 57 | 38.2 | 38.22 |
| n-butyl ester only | 276 | $\xrightarrow{-Cl^{\bullet}}$ | 241 | 210.5 | 210.43 |
| (b) Kelthane | 139 | $\xrightarrow{-CO}$ | 111 | 88.6 | 88.63 |

| Compound | $m_1$ | | $m_2$ | m* Observed | m* Calculated |
|---|---|---|---|---|---|
| iv) Miscellaneous Pesticides | | | | | |
| Piperonyl butoxide | 338 | $-(C_2H_3O-C_2H_4O-C_4H_9)$ | 194 | 111.4 | 111.35 |
| | 175 | $\xrightarrow{-CH_2O}$ | 145 | 120.1 | 120.14 |
| | 192 | $\xrightarrow{-CO}$ | 164 | 140.1 | 140.08 |
| | 163 | $\xrightarrow{-CO}$ | 135 | 111.9 | 111.82 |