MASS SPECTRA OF SOME
SULFUR AND SELENIUM COMPOUNDS

THE MASS SPECTRA OF SOME MONOCYCLIC, BICYCLIC, AND TRICYCLIC SULFUR AND SELENIUM COMPOUNDS

By

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SCOPE AND CONTENTS:

The mass spectra of disubstituted 1,4-dithiane, 1,4-oxathiane, and 1,4-oxaselenane, as well as the mass spectra of some disubstituted bicyclic and tricyclic sulfur and selenium compounds, were studied. The exact composition of the major ions of many of these compounds was determined. Fragmentation mechanisms are proposed to account for the major peaks in their spectra.

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GENERAL INTRODUCTION

The mass spectra of many aromatic sulfur compounds, and aliphatic thiols and sulfides have been studied but little has been done on sulfur-bridged carbocyclic systems. The work reported in this thesis involves an investigation of the mass spectral fragmentation of some mono-, bi-, and tricyclic sulfur compounds, all of which are disubstituted. In the monocyclic compounds the effect of changing the heteroatom is studied. The differences, which result when the substituents and bridging atom are varied, are examined for the bicyclic compounds. The effects of the oxidation of sulfur on the fragmentation of the tricyclic compounds has also been studied.

The object of this work was to determine if there were common fragmentation patterns in the three classes of compounds. The use of high resolution mass spectrometry enabled the composition of the ions to be determined and thus simplified the interpretation of the spectra. It is proposed that a sulfonium ion is formed and stabilizes the positive charge. Fragmentation mechanisms are suggested but one must keep in mind that there is as yet no way of determining the structures of ions produced upon electron impact.

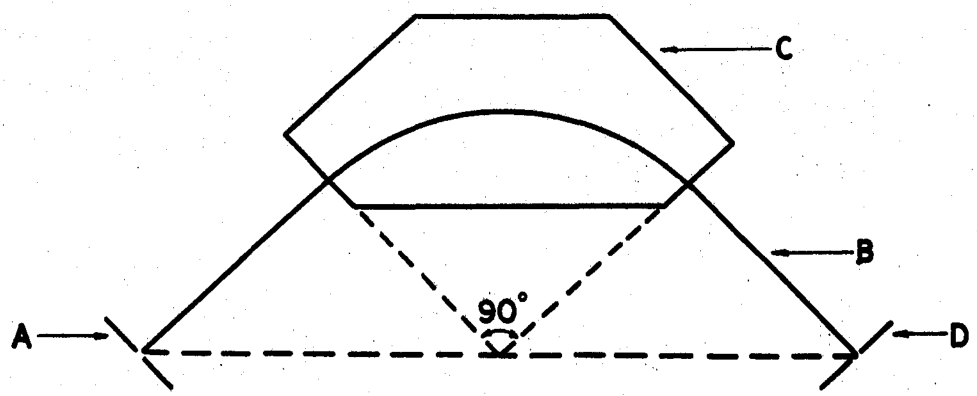
HISTORICAL INTRODUCTION

Theory and Instrumentation of Mass Spectrometry

The first crude mass spectrometers were produced by Wien (1) and Sir J.J. Thompson (2). Modern instruments are based on the design of the mass spectrometers developed by Dempster (3) in 1918 and Aston (4) in 1919. Since their time improvements have occurred producing specialized mass spectrometers which are used in various fields today.

When the petroleum industry discovered that mass spectrometry was a fast and efficient way to analyze complex hydrocarbon mixtures (5) serious development of this technique began. Later it was found that the spectra of organic compounds containing heteroatoms were even more easily interpreted and interest increased rapidly. The development of instrumentation, applications, and theory of mass spectrometry is traced in many books, among which are those by Duckworth (6), Kiser (7), Beynon (8), and McLafferty (9).

A common design of a mass spectrometer for organic applications is shown in Figure 1a. Molecules of mass M are introduced into the ion source (Figure 1b) where they are ionized by an electron beam whose energy is usually 70 electron volts (eV) although this beam can range between the ionization potential and 150 eV. Energy above the minimum required for ionization may be imparted to the molecule by this beam, and if the excess energy is large enough, decomposition of the molecule into smaller fragment ions will occur. Both positive and negative ions



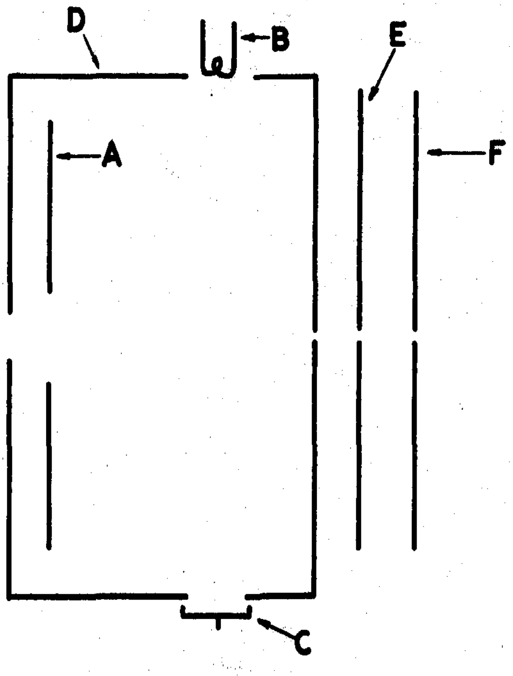
A: Source Slit

B: Ion Beam

C: Magnet

D: Detector Slit

Figure 1a: 90° Sector Magnetic Analyzer



A: Repelling Electrodes

B: Electron Source

C: Electron Target

D: Chamber

E: Lens Electrodes

F: Accelerating Electrodes

Figure 1b: Ion Source

are produced. Most spectrometers measure only positive ions but a few have been built to measure negative ions. The positive ions are moved towards the accelerating region by repeller plates which have a small positive potential with respect to the source. The ion source is held at a positive potential, V, giving the ions a potential energy eV. After the ions are accelerated through a potential drop V, the ions of mass m have a kinetic energy given by:

$$eV = \tfrac{1}{2}mv^2 \qquad 1)$$

where e is the ionic charge and v is the velocity.

On passing through the magnetic field of strength H, the ions will follow a circular path whose shape is due to the counterbalancing of a centripetal force, Hev, and a centrifugal force, $\frac{mv^2}{r}$. Equation 2) expresses this balance in mathematical form.

$$Hev = \frac{mv^2}{r} \qquad 2)$$

The mass spectrometer equation 3) results when v is eliminated from equations 1) and 2).

$$\frac{m}{e} = \frac{H^2r^2}{2V} \qquad 3)$$

Ions of different mass to charge ratio may be focused on the collector and a spectrum obtained by either electric scanning (V is changed) or magnetic scanning (H is changed). From equation 3) it can be seen that the mass to charge ratio varies as the square of the magnetic field and inversely with the accelerating voltage. Therefore, a large mass range can be covered by a scan of the magnet. With electrical scanning, resolution at high mass is reduced since contributions of initial thermal or kinetic energy become significant at low accelerating potential. However, electrical scanning is still sometimes used because it is easier to achieve electronically and because, for 180° instruments, the magnetic field in the source can be kept constant.

A variable slit is situated after the magnet at the focal point of the ion beam and behind this slit is positioned a collector. At the collector the ion current may be amplified by an electron multiplier and recorded by an oscillograph recorder on photographic paper. This method will cover a wide range of peak intensities and covers a spectrum in a fairly short time. Biemann (10) has described this arrangement in detail.

Besides peaks corresponding to molecular ions and peaks corresponding to fragment ions many mass spectra contain small diffuse peaks generally in positions corresponding to non-integral masses. Their intensities vary with the exit slit width and ion repeller voltage (11). These peaks, referred to as metastable peaks, are due to metastable ions which have decomposed after leaving the ionization chamber and before reaching the collector. Some of these metastable ions (of original mass m_1) will reach the collector without dissociation. Others will decompose, to an ion of mass m_2, before leaving the ionization chamber. Thus, the peaks corresponding to both the initial and final masses of the metastable ion will appear in the mass spectrum. A metastable ion, which gives a metastable peak, has been accelerated as an ion of mass m_1 and deflected in the magnetic field as an ion of mass m_2; therefore, it will be observed at a mass different from that of either ion. Following is a derivation of the expression for m*, the mass at which the metastable peak is found.

The kinetic energy of the parent ion is $eV = \frac{1}{2}m_1v^2$. After decomposition the kinetic energy of the new ion is given by equation 4).

$$\frac{m_2eV}{m_1} = \frac{1}{2}m_2v^2 \qquad 4)$$

Upon entering the magnetic field the centripetal and centrifugal forces on this daughter ion will be counterbalanced.

$$Hev = \frac{m_2v^2}{r} \qquad 5)$$

By eliminating v from equations 4) and 5), equations 6) and 7) are obtained.

$$H^2e^2 = \frac{m_2{}^2 2eV}{m_1r^2} \qquad 6)$$

$$\text{i.e.,} \quad \frac{m_2{}^2}{m_1e} = \frac{H^2r^2}{2V} = \frac{m^*}{e} \qquad 7)$$

It was assumed that all dissociations occurred after the parent ion left the ionization chamber and before it entered the magnetic field. This assumption is valid as the chance of metastables being collected is low outside of this region.

The type of mass spectrometer considered up until now has been a single or direction focusing instrument used for low resolution work. Metastable peaks may also be seen on a double focusing instrument (which is used for high resolution), the ions most likely collected being those which fragment between the electrostatic and magnetic analyzers. Metastable peaks are of considerable importance in qualitative organic analysis as they supply a useful tool in determining the decomposition scheme of a molecule. The presence of a metastable peak for a transition m_1 to m_2 can usually be regarded as evidence that that fragmentation occurs in one step and that the neutral fragment of mass, $(m_1 - m_2)$, is ejected as a single moiety.

For a single focusing instrument only low resolution is obtained. If the ions have the same mass to charge ratio and the same energy as they leave the source slit at a small divergent angle α, they will be refocused at a point (labelled as D in Figure 1a) after deflection by the magnetic field. The problem is that if there is a spread in the kinetic or thermal energies of the ions before acceleration, this spread contributes to the total kinetic energy after acceleration and results in a spread of r for a given value of $\frac{m}{e}$ and a broadening of the peak. This broadening means a loss of resolving power. High resolution, using the double focusing principle, is obtained by compensating for the velocity dispersion by means of an electric field and is briefly described below.

When an ion passes through a radial electric field, the field behaves as an energy separator and an energy spectrum is produced in a focal plane after the electric field. Ions with identical energies will be found at the same point in the plane. A slit is positioned in this plane such that only a small energy range will pass through into the magnetic sector and therefore the magnetic field will receive essentially a monoenergetic beam. Then, ions having different velocities will undergo different deflections (as explained previously) and mass dispersion will result. After passing through the magnetic field ions with the same mass to charge ratio will be brought to a point focus and since the beam entering the magnetic field is monoenergetic very sharp lines (high resolution) result.

The use of high resolution mass spectrometry in organic chemistry was pioneered by Beynon and he has described this application in his book (8). By using high resolution mass spectrometry one can obtain the exact mass of an ion found in the mass spectrum of a compound and from this mass determine the elemental composition of the ion. A mass spectrometric design that is very useful in these organic structural studies is that of Mattauch and Herzog (12, 13) shown in Figure 2.

There are two methods of measuring the exact mass of an ion using Mattauch's double focusing design. One method is the "peak matching" technique originally described by Nier et al (14) and the other is by use of a photographic plate. In the "peak matching" technique the voltage across the plates of the electric sector is varied causing the ion beam to bend until an unknown ion peak coincides with a known ion peak, both of which are displayed on the screen of an oscilloscope. The voltage needed to bring the two peaks together can be measured with

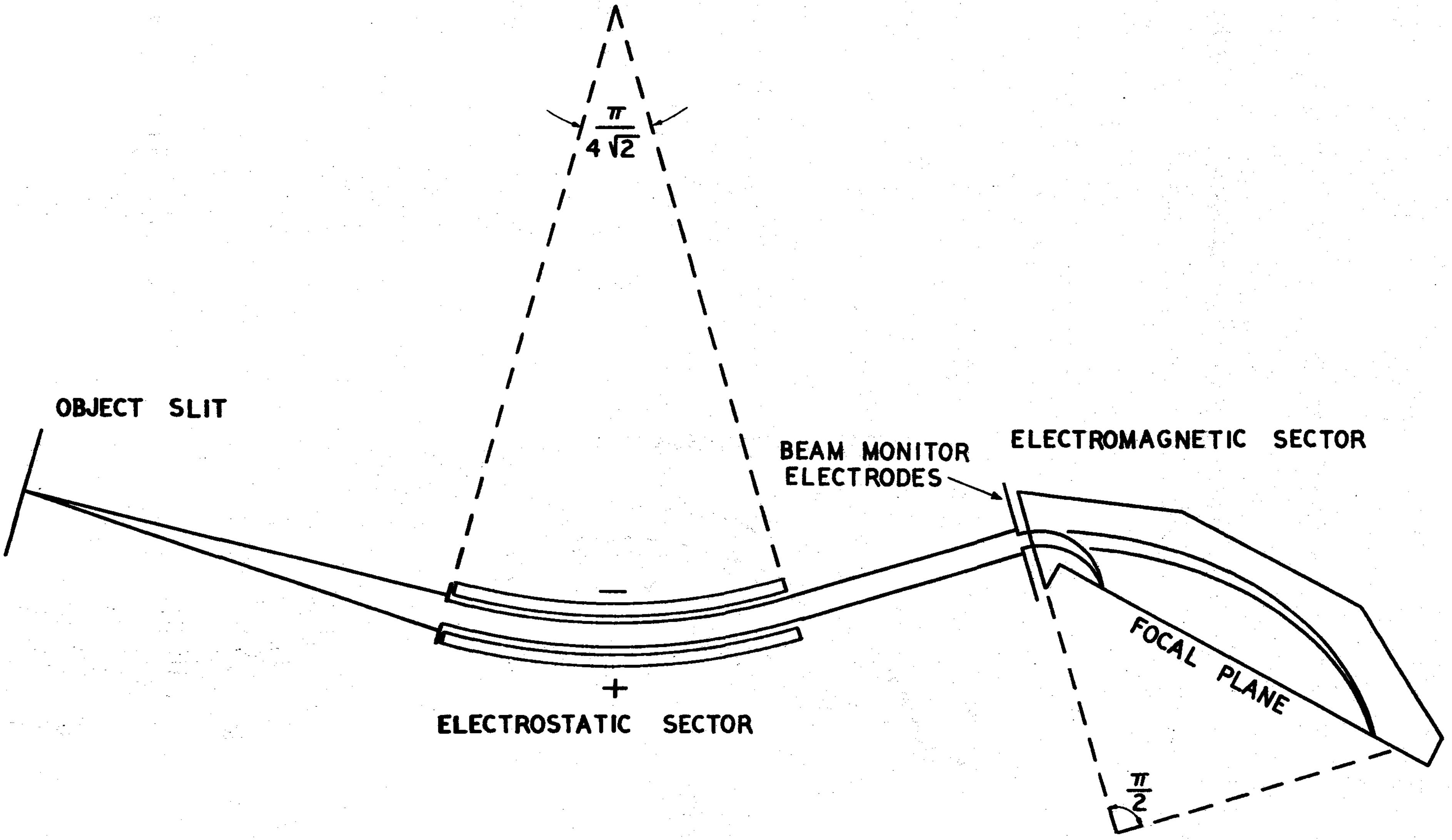


Figure 2: Double Focusing Design of Mattauch and Herzog

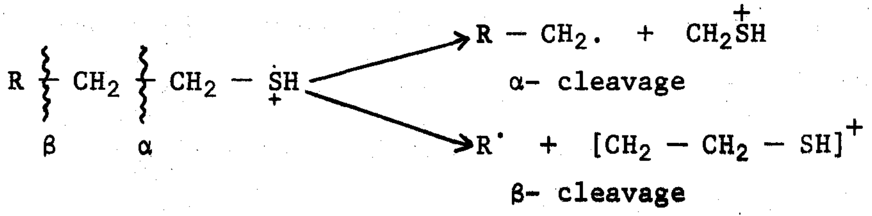
great accuracy and this voltage difference is related to the mass difference between these two peaks. Using this difference in mass, the mass of the unknown may be calculated. The ion with the known mass is from a standard such as perfluorokerosene, which is introduced into the spectrometer along with the compound under study. Only one peak at a time can be measured using this technique and it is extremely time-consuming and requires a fairly large sample. In the other method a photographic plate is placed in the focal plane, where all the masses are focused, and the whole spectrum is recorded at one time and with a small sample. Ions of different masses show up as parallel lines when the plate is developed. A standard compound is introduced at the same time as the sample so that the distance of a sample ion from a standard ion can be measured and the exact mass of the unknown calculated. The distances are measured with great accuracy with a comparator and the line densities (peak intensities) are measured approximately with a densitometer. Because a complete spectrum contains many lines the line positions and densities are often recorded on magnetic tape and a computer used to calculate the exact masses and compositions.

Mass Spectrometry of Aliphatic Sulfur Compounds

Many organic sulfur compounds are present in crude oil and because of this fact the petroleum industry has encouraged research into the behavior of sulfur compounds under electron impact. Therefore, many studies of the mass spectra of organic sulfur compounds have been done. A good general review of the mass spectrometry of the main organic groups, including sulfur compounds, is to be found in the book by Budzikiewicz, Djerassi, and Williams (15). Some types of organic sulfur compounds related to my work, such as aliphatic thiols, sulfides, sulfoxides, sulfones, and disulfides, are discussed below.

Thiols have significant molecular ions except for the higher molecular weight tertiary compounds such as 2-methyl-2-undecanethiol (16). Dissociations of thiol molecular ions are strongly influenced by the presence of the sulfur atom and usually occur α, β, or γ to this atom, often with rearrangement. According to Levy and Stahl the major ions of thiol fragmentation can be classified into four series: M-14N-1, M-14N-6, M-14N-5, and M-14N-7, where N is an integer and M is the molecular ion (16). When determining whether a compound is a thiol or not only the first two series are usually considered.

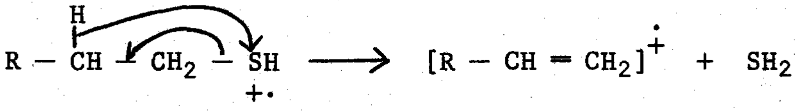
The first series results from loss of the alkyl portion of the molecular ion, as shown in equation 8), mainly by α- and β- cleavage.



$$R \underset{\beta}{\wr} CH_2 \underset{\alpha}{\wr} CH_2 - \overset{\cdot}{\underset{+}{S}}H \begin{cases} \rightarrow R - CH_2\cdot + CH_2\overset{+}{S}H & \alpha\text{- cleavage} \\ \rightarrow R^\cdot + [CH_2 - CH_2 - SH]^+ & \beta\text{- cleavage} \end{cases} \quad 8)$$

For primary unbranched thiols α- cleavage is preferred over β- cleavage and usually predominates with primary branched thiols. When the α bond of any thiol breaks the largest alkyl group on the α carbon is usually lost. The most intense peak in the M-14N-1 series for both secondary and tertiary thiols usually results from cleavage of the largest branch at the α carbon.

The formation of the M-14N-6 series is due to the loss of $SH_2(CH_2)n$ where n = 0,1,2, ... The charged portion is an olefin formed by the transfer of a hydrogen atom to the sulfur and the breaking of a bond in the chain. An example is given in equation 9).



$$R - \overset{H}{CH} - CH_2 - \underset{+\cdot}{SH} \longrightarrow [R - CH = CH_2]^{\dot{+}} + SH_2 \qquad 9)$$

Generally for primary and secondary thiols, the peak intensities are strong for even N and weak for odd N. One of the exceptions is di-β-branched primary thiols for which the alternation in peak intensities is reversed. Tertiary thiols have low intensity fragment ions in the M-14N-6 series and do not show the strong, weak, strong variation.

The M-14N-5 series arises from cleavage of $SH(CH_2)n$, where n = 0,1,2, ... , from the molecular ion with the alkyl portion retaining the positive charge. For secondary and tertiary thiols the fragment ions in this series are formed by carbon-sulfur bond cleavage and α- cleavage. The peaks are typical of an alkane type of molecule.

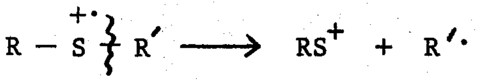
The fourth series is M-14N-7, which is formed by the loss of $SH_3(CH_2)n$, where n = 0,1,2, ... , from the thiol molecule. This series produces peaks typical of an olefin minus a hydrogen atom.

Very rarely does a thiol base peak contain sulfur. The ion usually has an olefinic or paraffinic structure. Both Cook and Foster (17) and Cook and Dineen (18) discovered this when they examined a large number of thiols. Primary thiols usually have more intense olefinic ions than alkyl ions. The reverse is true for secondary and tertiary thiols.

Thus, alkanethiol spectra resemble hydrocarbon spectra more than they resemble the spectra of other types of sulfur compounds.

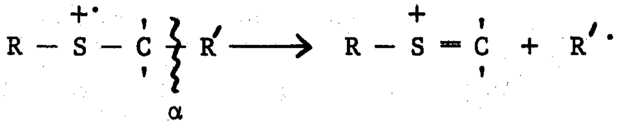
Like the thiols, sulfides have significant molecular ions. The sulfur atom greatly affects the dissociations undergone by the molecule. Bond breaking usually occurs at the bond next to, or α or β to the sulfur atom, often with rearrangement. The aliphatic sulfides show a fragment ion series similar to those of the thiols plus two additional types, M-14N and M-14N+1.

The M-14N-1 fragment ions result from C-S bond cleavage, α-cleavage, and α- cleavage followed by C-S bond cleavage with hydrogen rearrangement. These three types of cleavage are outlined in equations 10), 11), and 12), respectively.



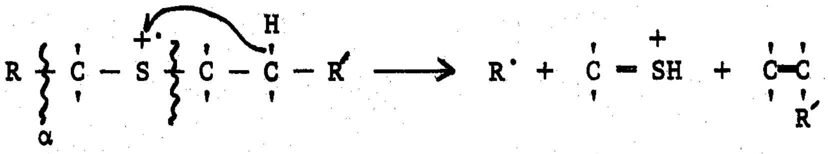
$$R-\overset{+\cdot}{S}\wr R' \longrightarrow RS^{+} + R'\cdot$$

10)



$$R-\overset{+\cdot}{S}-\underset{\alpha}{C\wr}R' \longrightarrow R-\overset{+}{S}=C + R'\cdot$$

11)

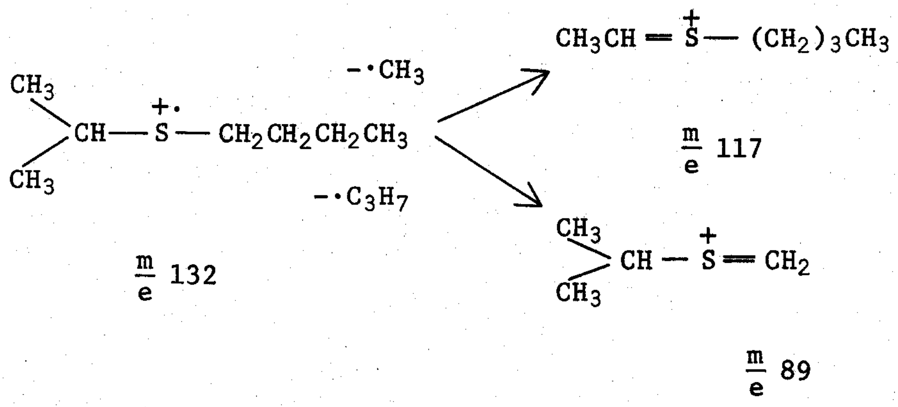


$$R\underset{\alpha}{\wr}C-\overset{+\cdot}{S}\wr C-\overset{H}{C}-R' \longrightarrow R\cdot + C=\overset{+}{S}H + C=\underset{R'}{C}$$

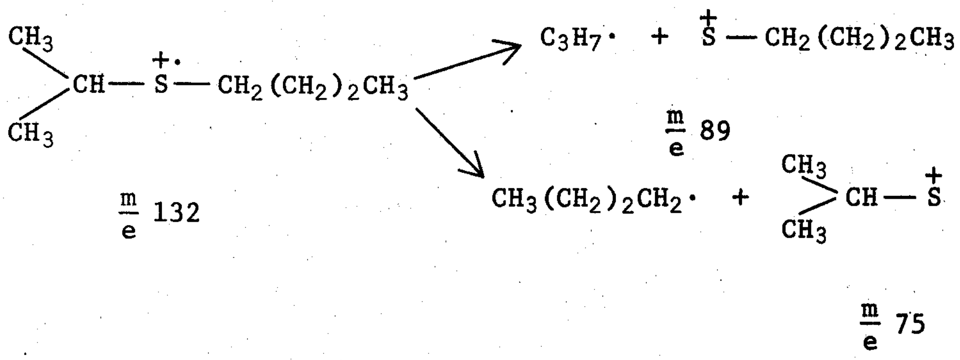
12)

Djerassi and Sample found that isopropyl n-butyl sulfide fragmented in all three ways (<u>19</u>).

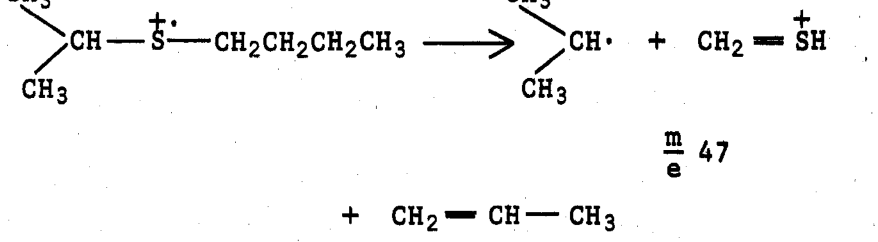
α- cleavage



C-S bond cleavage

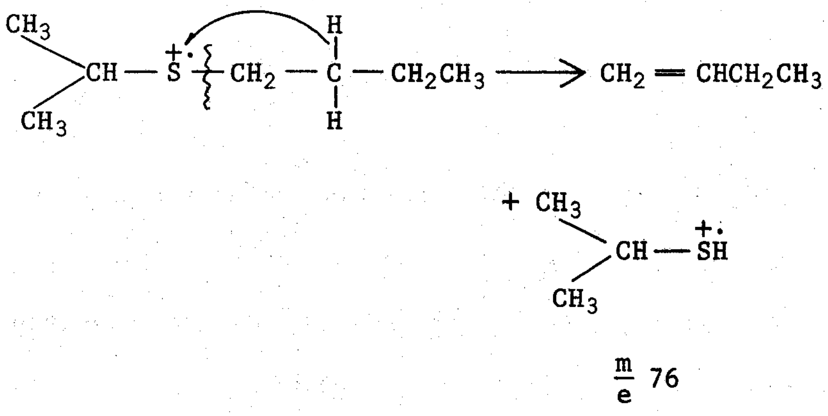


α- cleavage and C-S bond cleavage with H rearrangement



Which one of these three mechanisms will predominate depends on the length and branching of the alkyl chains.

Carbon-sulfur bond cleavage is the most common kind of cleavage in the M-14N-5, M-14N, and M-14N+1 series. In the first series the hydrocarbon fragment retains the positive charge. In the last two series hydrogen transfer to the charged sulfur atom occurs and the charge is retained by the sulfur fragment. Isopropyl n-butyl sulfide provides a good example, in equation 13), of C-S bond cleavage with hydrogen rearrangement (<u>19</u>).



13)

Fragment ions where hydrogen rearrangement has occurred are among the more abundant in the mass spectra of organic sulfides. The M-14N, M-14N+1, and M-14N-5 series are the ones commonly used for structure correlation of aliphatic sulfides. The larger alkyl group attached to the sulfur atom is determined by using the largest olefin peak in the spectrum. This olefinic ion will have the same number of carbon atoms as the larger alkyl group.

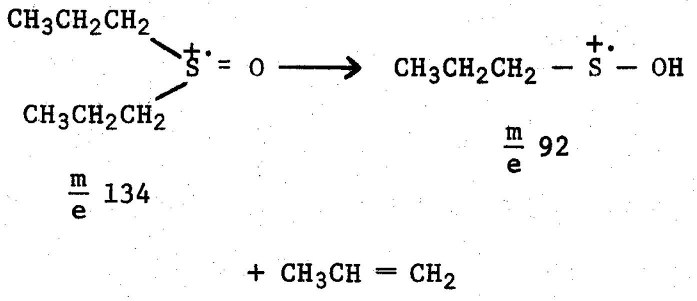
There are three ways in which bonds cleave to produce the base peaks in aliphatic sulfide spectra. The C-S bond can break, sometimes with hydrogen rearrangement. Isopropyl n-amyl sulfide, isopropyl n-butyl sulfide, and n-amyl isoamyl sulfide form their base peaks in this manner (19). A second group of sulfides forms their base peaks by α-cleavage. The charge is usually retained by the sulfur-containing fragment. The formation of the base peak of ethyl n-hexyl sulfide is an example of this (19). In the third group the base peaks are formed by rearrangement or consecutive reactions (18). The charge can be on either the sulfur fragment or alkyl fragment. Primary sulfides usually prefer to fragment at an α bond whereas secondary and tertiary sulfides, which are those with secondary and tertiary carbon atoms, respectively, attached to the sulfur atom, would rather cleave at a C-S bond (17). There are many exceptions to this generalization so that the usefulness of a base peak in predicting the structure of a sulfide is limited.

Cyclic sulfides form base peaks via one of the three ways shown in equation 14).

a Molecule ⟶ molecular ion (base peak)
b Molecule ⟶ molecular ion ⟶ R· + base peak　　14)
c Molecule ⟶ molecular ion ⟶ base peak by ring cleavage with loss of part of the ring.

The molecular ion of thiacyclohexane is also the base peak (18). The base peak of trans-2,5-dimethylthiacyclopentane is formed as in 14b) (18). The base peak of tetrahydrothiophene results from ring cleavage to eliminate ethylene (20). It is not yet possible to tell by looking at the structure of a cyclic sulfide what the base peak will be. The intensity of the molecular ion of a cyclic organic sulfide is always large and therefore the molecular weight can be determined easily.

Not much work has been done on the mass spectra of aliphatic sulfoxides and thus it is impossible to make general statements on their method of fragmentation. Bowie et al. found that saturated aliphatic sulfoxides behave fairly simply on electron impact (21). Some lose the hydroxyl radical. If R in R-SO-R is greater than CH_3, they undergo olefin elimination as is illustrated by the loss of propylene from dipropyl sulfoxide (21) in equation 15).



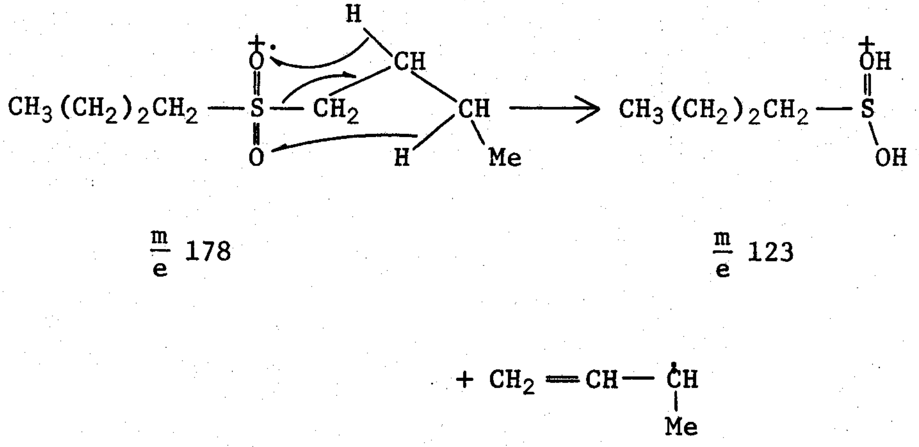
$$\underset{\frac{m}{e}\ 134}{(CH_3CH_2CH_2)_2\overset{+\cdot}{S}=O} \longrightarrow \underset{\frac{m}{e}\ 92}{CH_3CH_2CH_2-\overset{+\cdot}{S}-OH} + CH_3CH=CH_2 \qquad 15)$$

$CH_2=\overset{+\cdot}{S}-OH$ ($\frac{m}{e}$ 63) is another common ion which may form from the M-olefin ion as shown in equation 16).

$$\underset{\frac{m}{e}\ 92}{CH_3CH_2 \wr CH_2-\overset{+\cdot}{S}-OH} \longrightarrow CH_3CH_2\cdot + \underset{\frac{m}{e}\ 63}{CH_2=\overset{+}{S}-OH} \qquad 16)$$

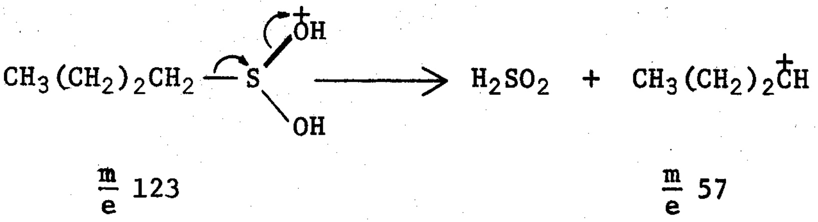
The most abundant ions are hydrocarbon ions. If R is aryl then rearrangement occurs so that R-SO-R′ loses SO, CO, O, and CS (21, 22, 23).

A survey of aliphatic sulfones has been done and a few common fragmentation routes have emerged. Aliphatic sulfones have a tendency to lose one of the alkyl groups with double hydrogen rearrangement to the charged fragment (21). An example of this is given in equation 17).



17)

This tendency seems to increase as the size of the alkyl groups increases. H_2SO_2 is then usually lost from this $[RSO_2H_2]^+$ fragment (<u>24</u>) as illustrated in equation 18).



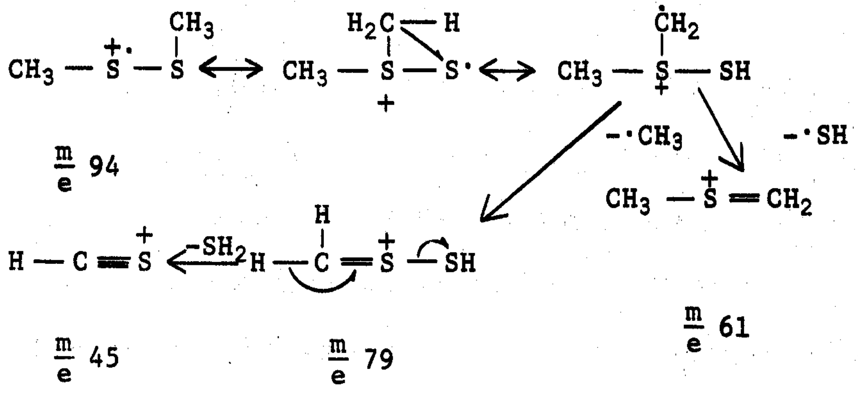
18)

An $[M\text{-}RO]^+$ peak is also seen with these sulfones. The base peak of many alkyl sulfones examined by Aplin and Bailey (<u>24</u>) was the ion corresponding to the alkyl group. Sulfones with large alkyl groups, such as di-n-butyl sulfone, di-n-hexyl sulfone, and di-n-heptyl sulfone, lose ·OH from the molecular ion (<u>24</u>). Many aliphatic sulfones even lose O (<u>24</u>). Upon electron impact sulfolane loses fragments containing sulfur and two oxygens, while 2-sulfolene undergoes a rearrangement in which CHO is lost as well as SO_2 and HSO_2 (<u>25</u>). Just as for aliphatic sulfones, where the base peak is a hydrocarbon ion, so for sulfolane the base peak is an alkyl ion. Because charge retention by the hydrocarbon appeared favourable Weinberg et al. suggested that the sulfone functional group was a poor fragment director (25). This is not so much the case with aryl sulfones since they undergo extensive rearrangement to lose SO_2, CO, SOR, SO, CHO, and O (21, 22, 23, 26, 27, 28). The mass spectra of both sulfolane and aliphatic sulfones are dominated by hydrocarbon fragment ions.

The common dissociation which aliphatic disulfides undergo is the elimination of an olefin, formed by loss of an alkyl group with hydrogen rearrangement to sulfur (29).

$$R'S\overset{+\cdot}{S}R \longrightarrow R'S\overset{+\cdot}{S}H + \text{olefin}$$

This fragmentation cannot occur when both groups are methyl. If both alkyl groups are larger than methyl then usually a large H_2S_2 peak occurs in the spectrum (18). Skeletal rearrangement ions are observed in the spectrum of dimethyl disulfide but it is one of a very few aliphatic disulfides which undergo rearrangement (29). Dimethyl disulfide cannot eliminate an olefin and so instead it eliminates HS· from the molecular ion or H_2S from the M-CH_3 ion. An example of how these two reactions can occur is given in equation 19).



19)

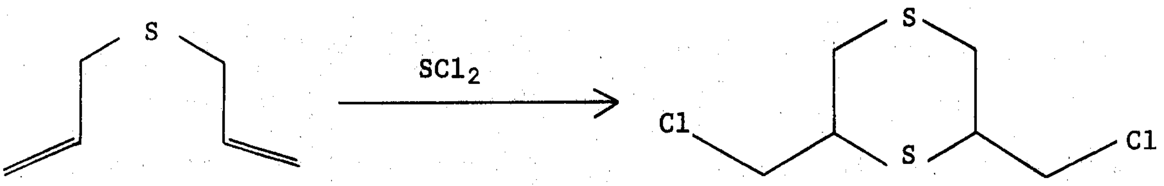
The base peaks of most aliphatic disulfides are usually formed by breaking a carbon-sulfur bond. An alkyl ion is the most abundant ion in a large number of the disulfides examined by Cook and Dinneen (18).

The Synthesis of the Sulfur and Selenium Compounds

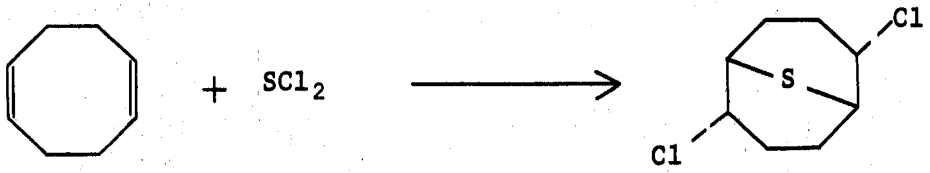
The reaction of sulfur monochloride with an olefin leads to a β, β′-dichlorosulfide as shown below in the preparation of mustard gas (30).

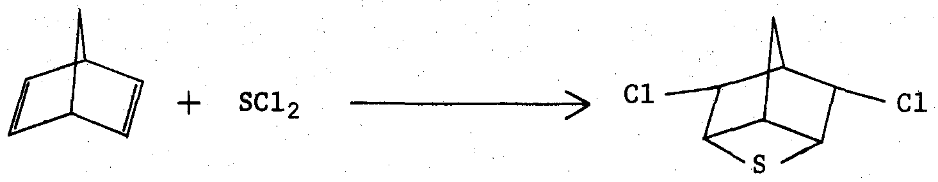
$$2CH_2 = CH_2 + S_2Cl_2 \text{——} ClCH_2CH_2SCH_2CH_2Cl + S$$

A similar reaction using sulfur dichloride instead of sulfur monochloride was applied by Lautenschlaeger to linear diolefins to form cyclic β, β′-dichlorosulfides such as 2,6-dichloromethyl-1,4-dithiane and 3,5-dichloromethyl-1,4-oxathiane (31).

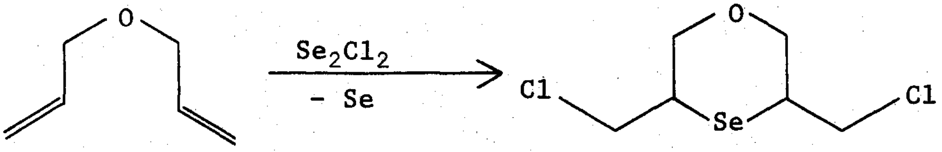


This reaction was applied to the formation of β, β′-disubstituted sulfur-bridged bicyclic and tricyclic products as illustrated below (32, 33, 34, 35.).





Lautenschlaeger found that selenium monochloride reacted with diolefins to form selenium analogues of the sulfur compounds (36).



Other substituents besides chlorine are obtained by simple substitution reactions (34). The sulfides are oxidized readily to sulfoxides and sulfones (32, 33, 34).

The mass spectra of β, β′-dichlorosubstituted sulfur-bridged bi- and tricyclic compounds have not been studied before; therefore, it was of interest to examine their spectra and attempt to discover characteristic fragmentations. The monocyclic compounds investigated here serve as models because they contain the β, β′-dichlorosulfide unit.

DISCUSSION OF RESULTS

Section 1:

The Mass Spectra of Some Disubstituted Monocyclic Sulfur and Selenium Compounds

a) 2,6-Dichloromethyl-1,4-Dithiane

2,6-Dichloromethyl-1,4-dithiane (I) was examined using low and high resolution mass spectrometry. The low resolution spectrum appears in Figure 3, the exact compositions of the major ions and some of the minor ions are listed in Table 1, and a list of metastable peaks is found in Table 2. The most intense peak or base peak occurs at $\frac{m}{e}$ 45 of composition CHS. Possible pathways of fragmentation are outlined in Schemes 1.1, 1.2, 1.3, and 1.4 below.

Several possible ways in which the molecular ion may fragment are presented in Scheme 1.1. Ions a and b are formed by loss of all or part of the substituent without ring opening while c and d are formed by ring fission. A metastable peak is found only for the formation of a. The relative intensities of a and b are large (26% and 53%, respectively) and their further dissociation is dealt with in Schemes 1.2, 1.3, and 1.4 Ion c is also intense but its opportunities for further breakdown are limited. The decomposition of d, a minor ion, is outlined in Scheme 1.3. Both c and d may result from paths other than those in Scheme 1.1 and it is not known whether these pathways are their primary modes of formation.

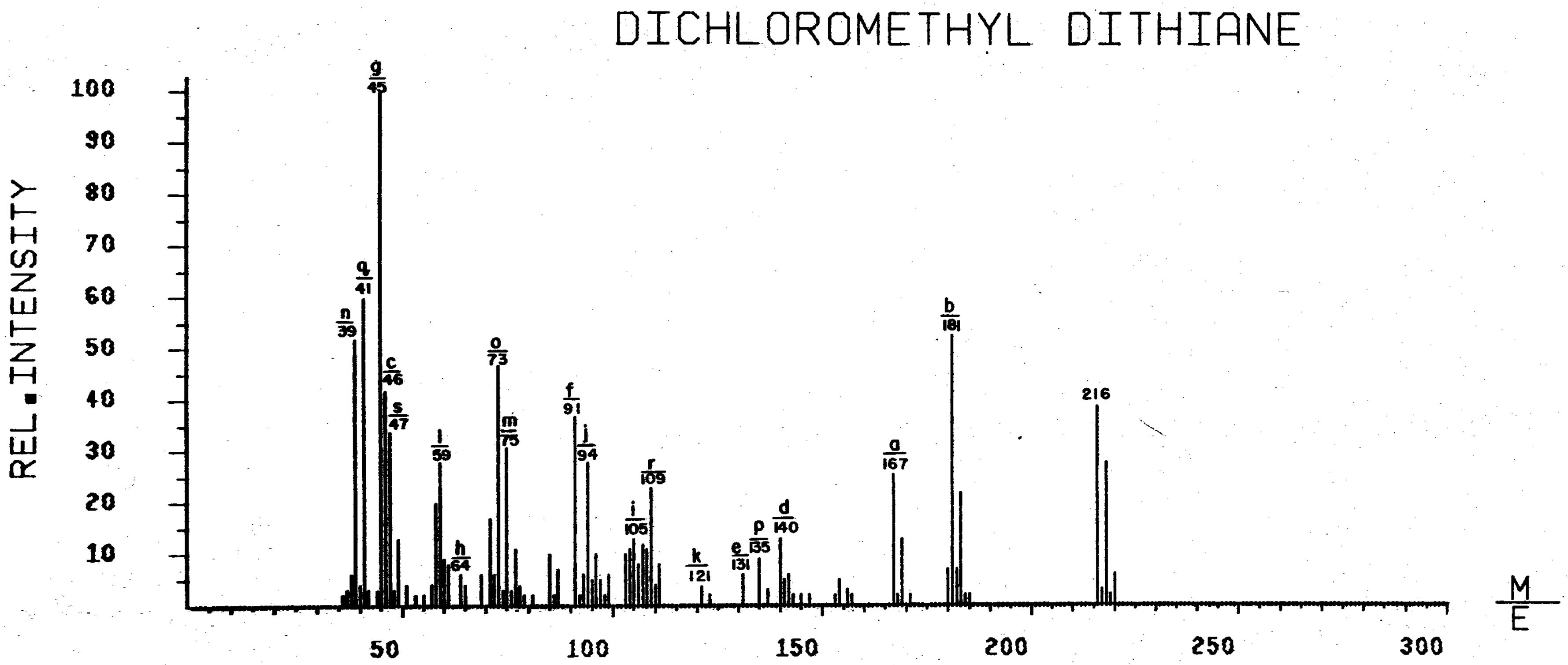


Figure 3: The Mass Spectrum of 2,6-Dichloromethyl-1,4-Dithiane

TABLE 1*

Compositions of the Major Ions in the Mass Spectrum of 2,6-Dichloromethyl-1,4-Dithiane

$\frac{m}{e}$	Composition	$\frac{m}{e}$	Composition
39	C_3H_3	86	C_4H_6S
41	C_3H_5	91	$C_2H_3S_2$
45	CHS	94	C_2H_3ClS
46	CH_2S	95	C_2H_4ClS
47	CH_3S	105	$C_3H_5S_2$
58	C_2H_2S	107	C_3H_4ClS
59	C_2H_3S	108	C_3H_5ClS
61	C_2H_5S	109	C_3H_6ClS
64	S_2	121	C_4H_6ClS
71	C_3H_3S	135	C_5H_8ClS
73	C_3H_5S	140	$C_3H_5ClS_2$
75	C_3H_4Cl	167	$C_5H_8ClS_2$
76	C_3H_5Cl	181	$C_6H_{10}ClS_2$
85	C_4H_5S	216	$C_6H_{10}Cl_2S_2$

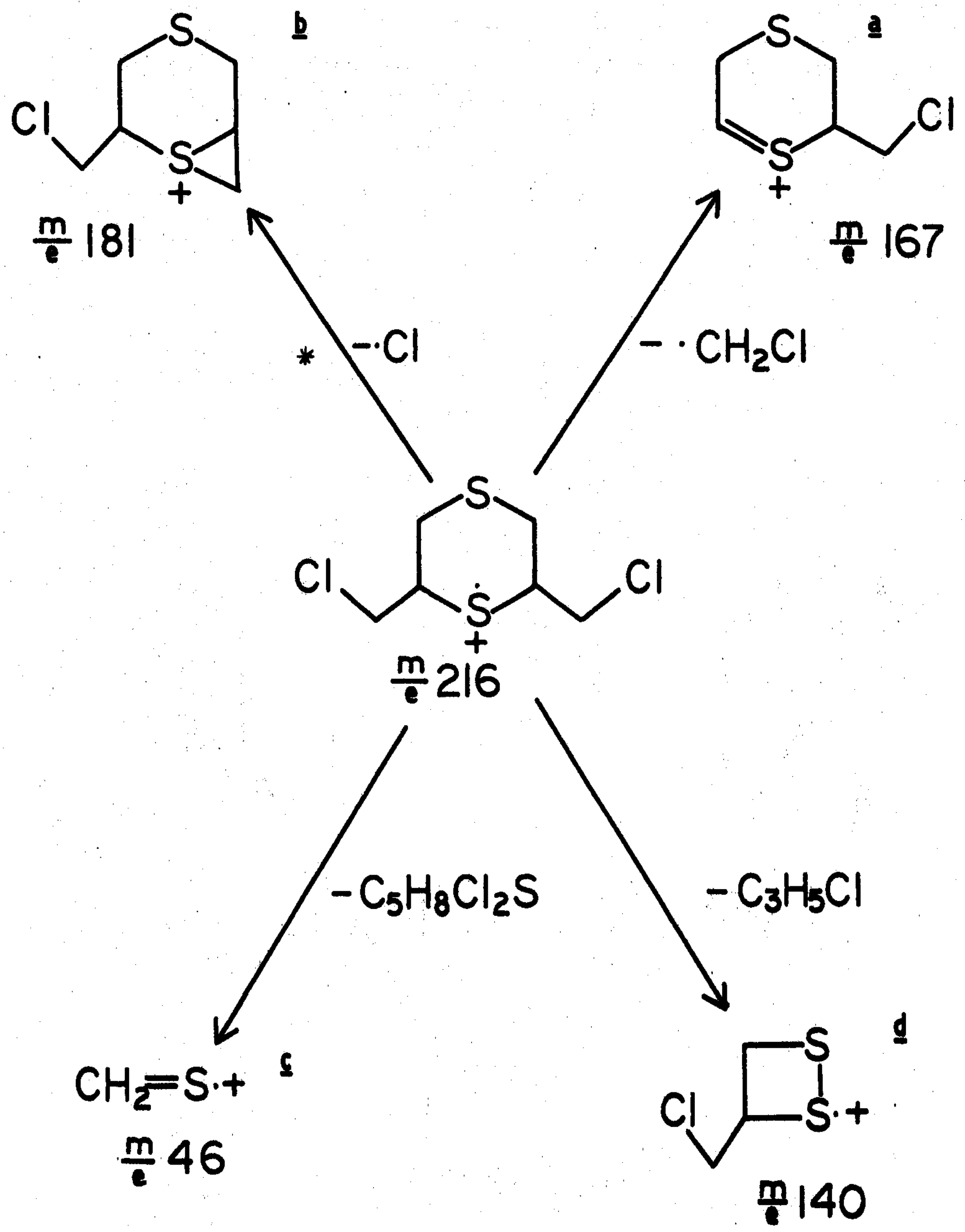
---

*In this and subsequent tables only the compositions of ions containing major isotopes are given unless otherwise specified.

TABLE 2

Metastable Transitions of 2,6-Dichloromethyl-1,4-Dithiane

Observed	Transformation	Calculated
151 ± 1	216 → 181	151.67
117.1 ± .3	167 → 140	117.37
102.6 ± .4	167 → 131	102.76
100.6 ± .2	181 → 135	100.69
78.8 ± .2	140 → 105	78.75
72.9 ± .1	121 → 94	73.02
49.5 ± .1	167 → 91	49.59
37.1 ± .1	94 → 59	37.03
	41 → 39	37.10
29.5 ± .1	181 → 73	29.44
27.8 ± .1	73 → 45	27.74
25.8 ± .1	135 → 59	25.79
20.4 ± .2	109 → 47	20.27
	75 → 39	20.28
	181 → 61	20.56


b
m/e 181
a
m/e 167
* −·Cl
− ·CH₂Cl
m/e 216
−C₅H₈Cl₂S
−C₃H₅Cl
CH₂=S·+
c
m/e 46
d
m/e 140

SCHEME 1.1

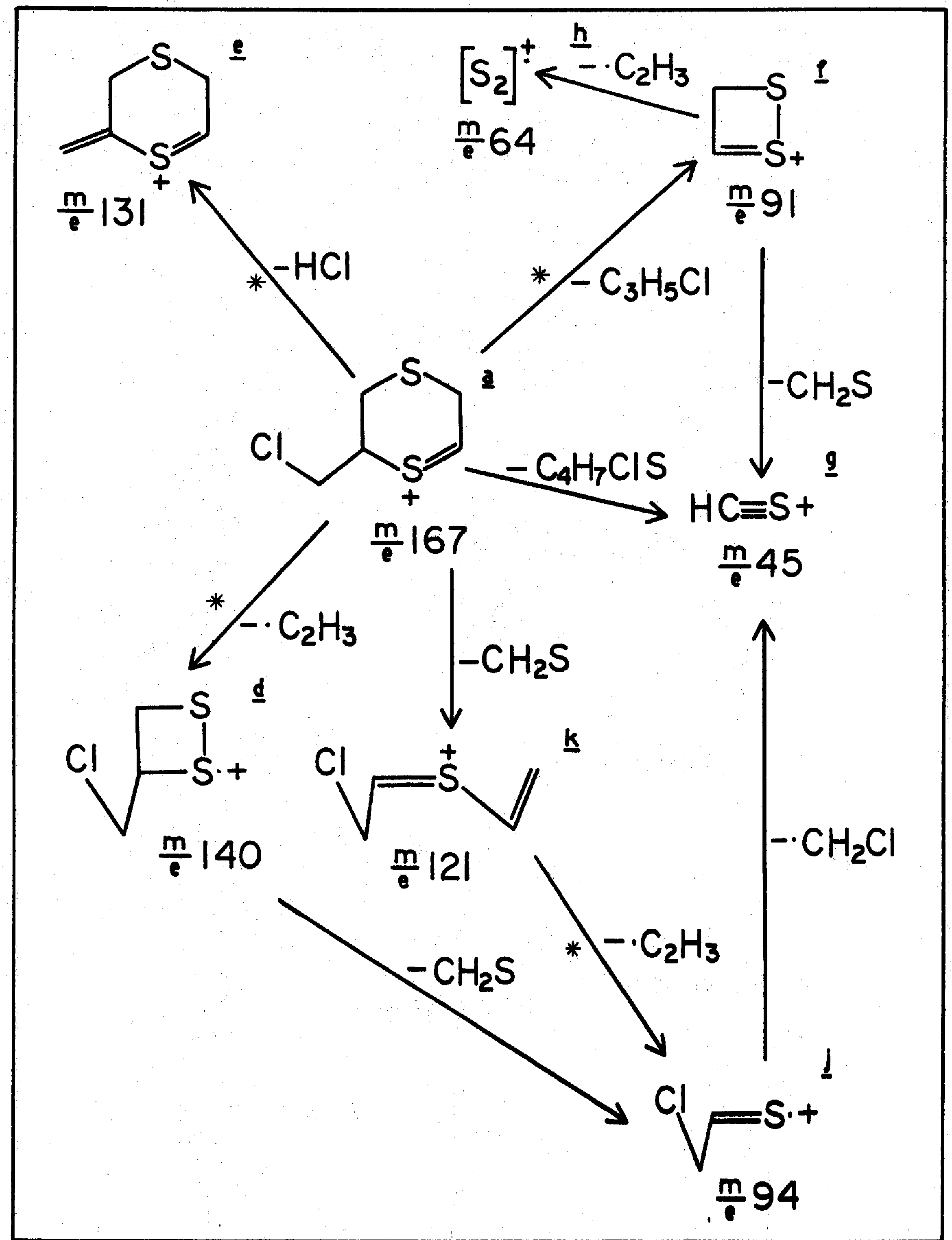
Of all the dissociations of *a* outlined in Scheme 1.2, only those producing *e*, *f*, and *d* are verified by metastable peaks. Unfortunately it was not possible to mass match the ion at $\frac{m}{e}$ 131 (*e*) since its mass is very similar to that of the perfluorokerosene ion at $\frac{m}{e}$ 131. It is likely, however, that its composition is $C_5H_7S_2$ since no chlorine isotope peak was observed at $\frac{m}{e}$ 133. Ion *f*, a major ion, may fragment to *g* or *h* neither of which is likely to fragment further. Ion *h* has been observed by others in disulfide and dithiane spectra where a cyclic intermediate such as *f* may form (*29*, *37*). By a retro Diels-Alder fragmentation *a* is converted to *k* which in turn can lose $\cdot C_2H_3$ to form *j*. The latter ion can also arise from *d*.

Pathways for the further fragmentation of *d* are found in Scheme 1.3. The loss of $\cdot Cl$ and $\cdot CH_2Cl$ to form even electron ions is expected. Fragmentation of the dithiacyclobutane ring of *d* to give the sulfur-containing ion *j* and the sulfur-free ion *m* is proposed. Since cyclic disulfides are reported to lose $HS_2\cdot$ (*29*) it is likely that *d* dissociates to *m*. Ion *j* can decompose further through loss of $\cdot Cl$ to *l* and *m* through loss of $\cdot Cl$ to *n* at $\frac{m}{e}$ 39. Metastable peaks may be present* for these two transitions. Both *l* and *n* are prominent in the low mass region of the spectrum.

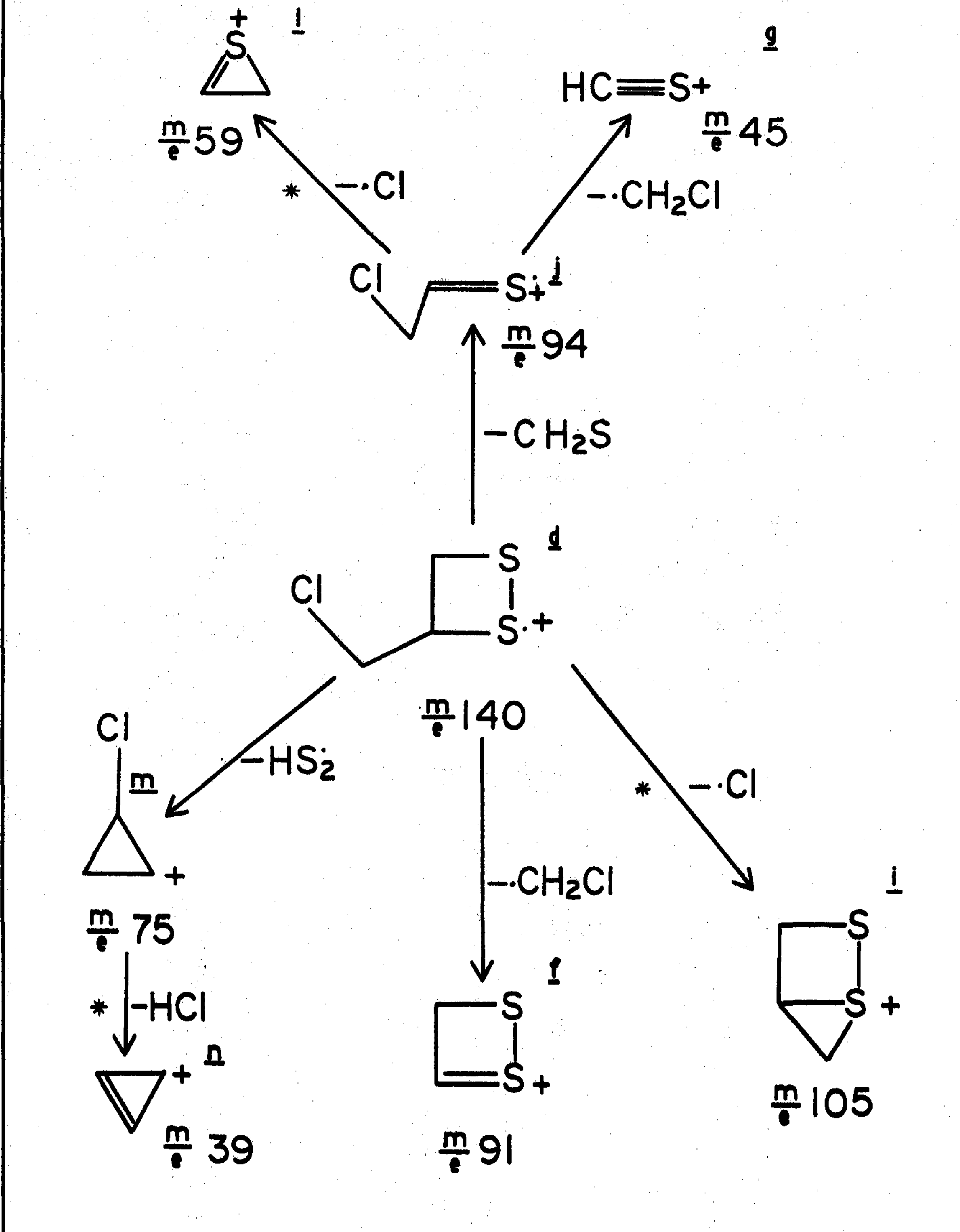
Routes by which *b* may fragment are found in Scheme 1.4. Three of the decompositions involve loss of a chlorine-containing neutral fragment and three loss of fragments containing no chlorine. Metastable peaks are

---

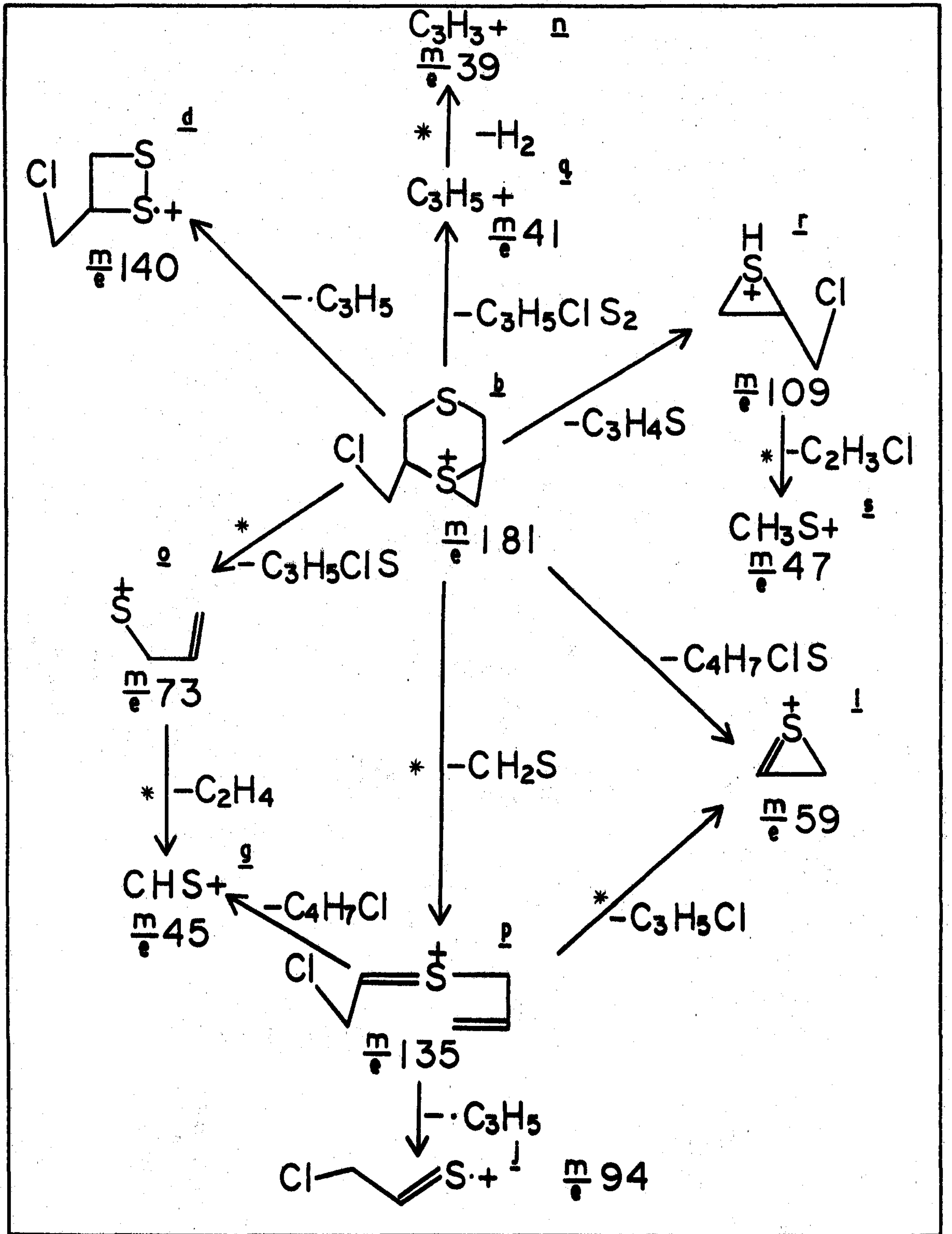
* Several possible transitions can lead to a metastable peak whose calculated $\frac{m}{e}$ is within the error range of the observed $\frac{m}{e}$.


e
m/e 131
h
$[S_2]^{+\cdot}$
$-\cdot C_2H_3$
m/e 64
f
m/e 91
* −HCl
* $-C_3H_5Cl$
a
m/e 167
$-CH_2S$
$-C_4H_7ClS$
g
$HC{\equiv}S^+$
m/e 45
* $-\cdot C_2H_3$
$-CH_2S$
d
m/e 140
k
m/e 121
$-\cdot CH_2Cl$
$-CH_2S$
* $-\cdot C_2H_3$
j
m/e 94

SCHEME 1.2


l
m/e 59
g
HC≡S+
m/e 45
* −·Cl
−·CH2Cl
j
m/e 94
−CH2S
d
m/e 140
−HS2
m
m/e 75
* −HCl
n
m/e 39
−·CH2Cl
f
m/e 91
* −·Cl
i
m/e 105

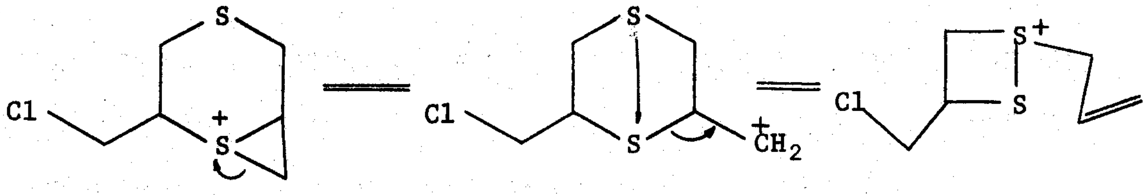
SCHEME 1.3

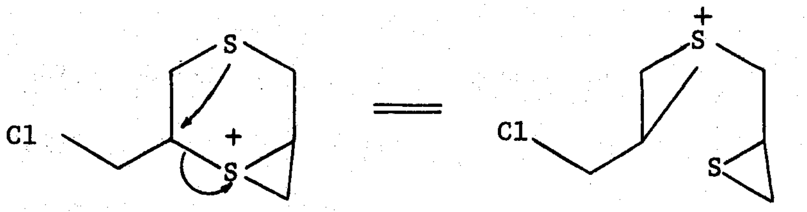

C3H3+ n
m/e 39
* −H2
C3H5+ q
m/e 41
Cl
S
S·+
d
m/e 140
−·C3H5
−C3H5ClS2
H
S
+
Cl
r
m/e 109
* −C2H3Cl
CH3S+ s
m/e 47
S
b
Cl
+
S
m/e 181
−C3H4S
* −C3H5ClS
o
+
S
m/e 73
* −C2H4
CHS+ g
m/e 45
−C4H7Cl
* −CH2S
−C4H7ClS
+
S
l
m/e 59
* −C3H5Cl
Cl
+
S
p
m/e 135
−·C3H5
Cl
S·+ j
m/e 94

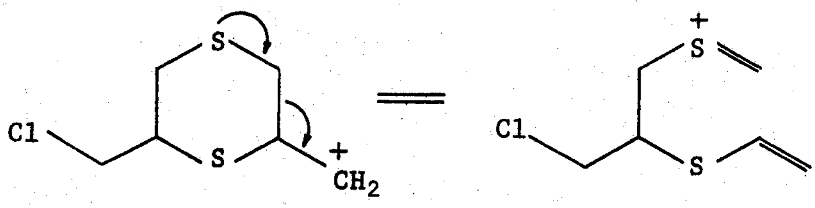
SCHEME 1.4

observed for the transitions b to o to g and b to p to l. The transitions b to q, b to d, b to l, b to r, r to g, and r to j may occur as shown in Scheme 1.4 but there is no proof that they do.

Some of the transformations of Scheme 1.4 are difficult to visualize. One must remember, however, that it is possible by electron shifts to derive other structures for b, which, by simple bond cleavages, will lead to most of the ions found in Scheme 1.4. Some rational structures of b are shown below.







Most of the ions discussed in Schemes 1.1, 1.2, 1.3, and 1.4 will ultimately dissociate to g, n, or l and therefore it is impossible to specify the major route, if there is one, by which these ions are formed.

b) 3,5-Dichloromethyl-1,4-Oxathiane

Since oxygen is in the same group as sulfur it would be expected that 3,5-dichloromethyl-1,4-oxathiane (II) and compound I would fragment in a similar manner as indeed they do. Thus, one finds that the initial fragments lost from I and II are similar and that the low mass end of the spectra of I and II (Figures 3 and 4) are nearly the same. Oxygen has a higher ionization potential than sulfur (37) and, therefore, when II becomes ionized the charge is very likely localized on the sulfur atom. The metastable peaks listed in Table 3 verify that some of the transitions which occur when II dissociates are identical with those proposed for I. The possible routes by which II may fragment are outlined in Schemes 1.5, 1.6, and 1.7.

The molecular ion (Scheme 1.5) may fragment to ions t and u in a manner exactly analogous to I. The ion at $\frac{m}{e}$ 46, however, cannot arise directly from the molecular ion of II as it does from I and its abundance is relatively lower in the spectrum of this compound than in that of I. Another noticeable difference is the failure of II to form ions analogous to d and f. Condê-Caprace and Collin reported that dithiane and oxathiane formed $[C_2H_4S_2]^+$ and $[C_2H_4OS]^+$, respectively, and proposed that these ions had a cyclic structure (37). However, the contribution of $[C_2H_4OS]^+$ to the total ionization was small compared with the contribution of $[C_2H_4S_2]^+$. Thus it appears that upon electron impact the formation of sulfur-sulfur bonds is favoured over the formation of oxygen-sulfur bonds in a cyclic system. This result agrees with the findings for I and II.

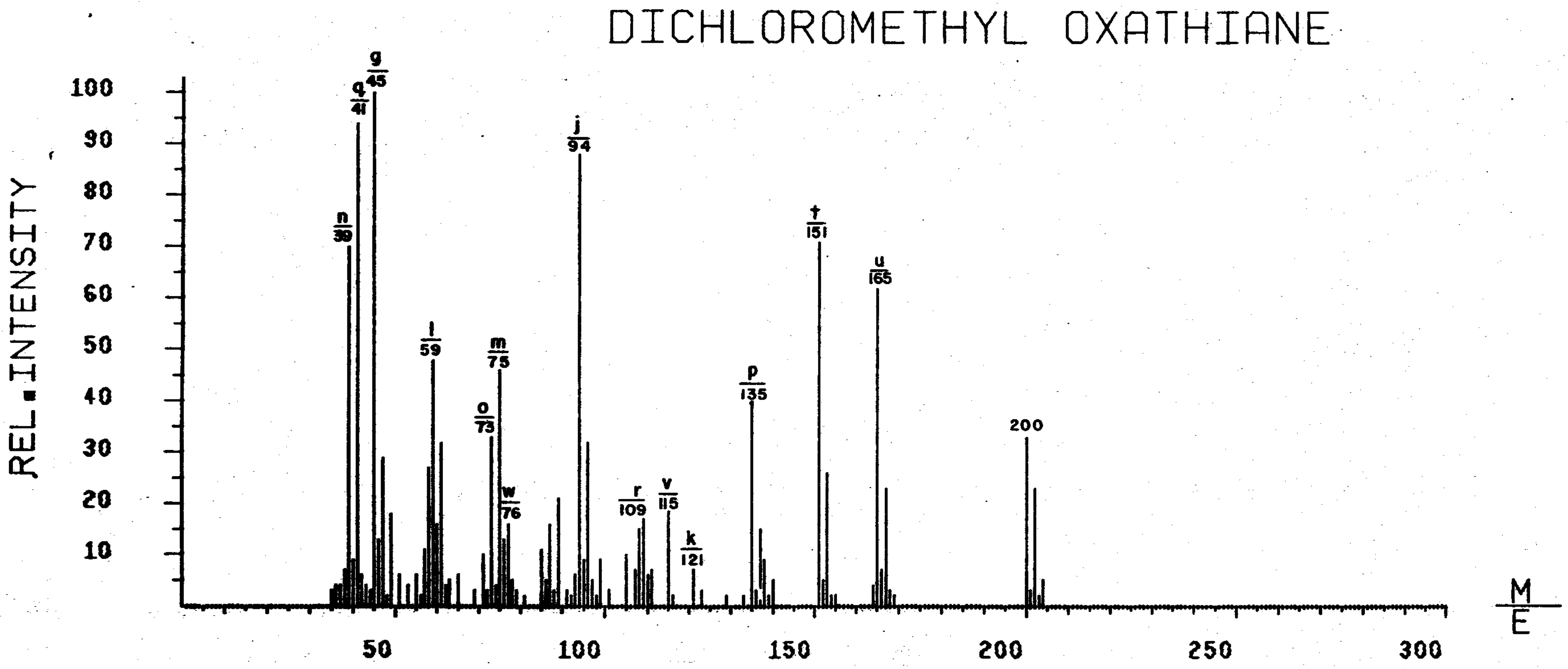
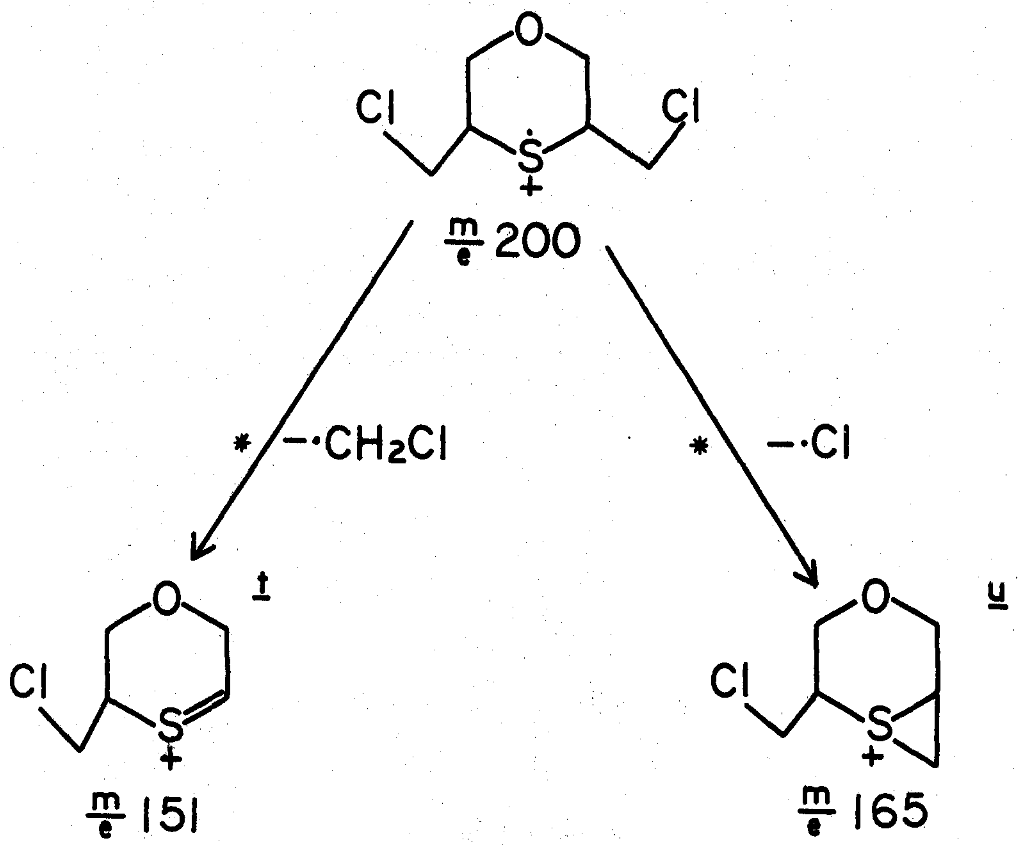


Figure 4: The Mass Spectrum of 3,5-Dichloromethyl-1,4-Oxathiane

TABLE 3

Metastable Transitions of 3,5-Dichloromethyl-1,4-Oxathiane

Observed	Transformation	Calculated
136.5 ± .5	200 → 165	136.13
114.5 ± .5	200 → 151	114.01
110.5 ± .1	165 → 135	110.45
87.5 ± .5	151 → 115	87.58
66.1 ± .6	135 → 94	65.45
37.2 ± .2	94 → 59	37.03
	41 → 39	37.10
32.4 ± .1	165 → 73	32.30
27.7 ± .1	73 → 45	27.74
22.3 ± .2	76 → 41	22.12
21.7 ± .2	94 → 45	21.54



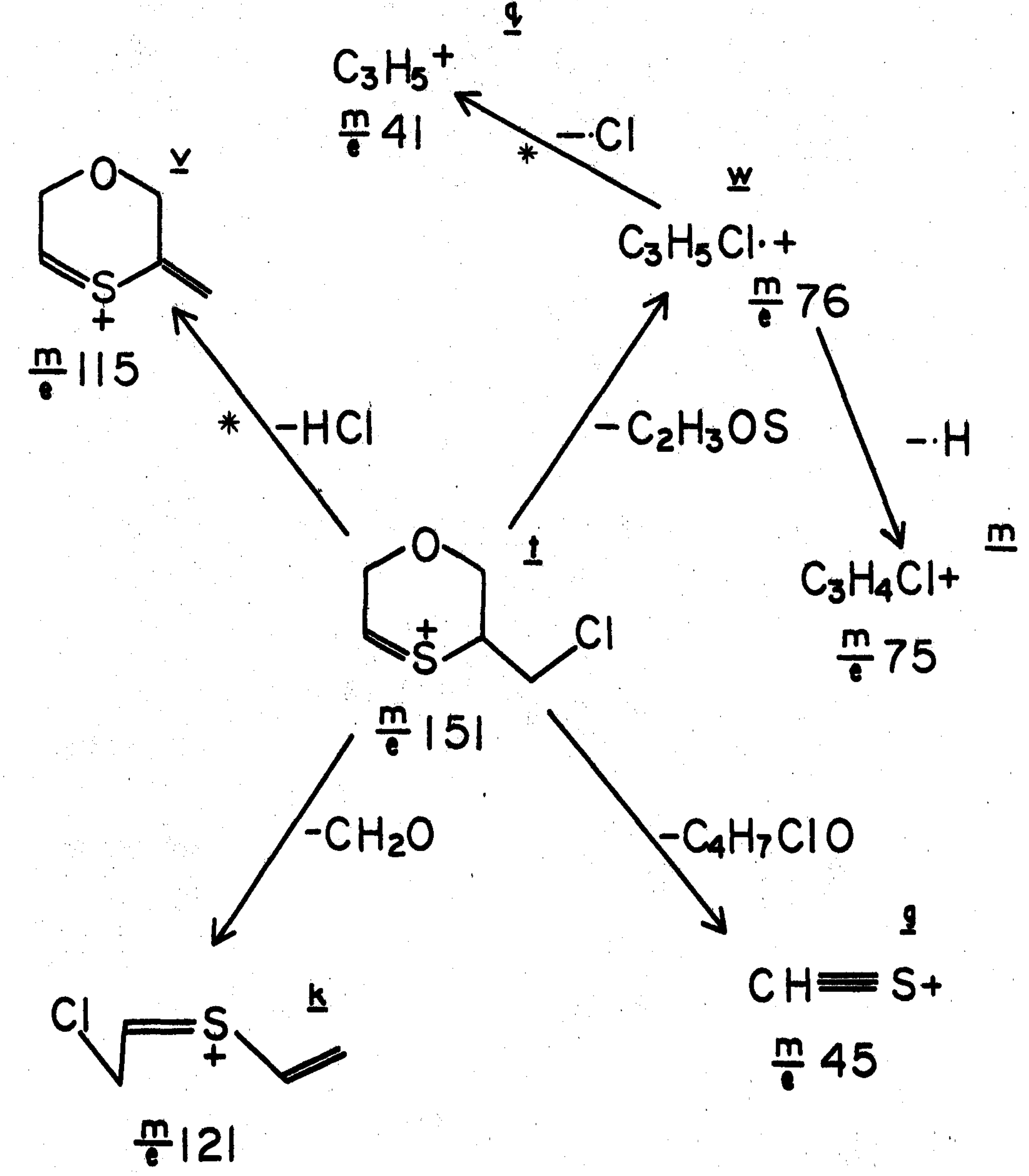
SCHEME 1.5

The further fragmentation of ion t (Scheme 1.6) parallels that of ion a. Again ions corresponding to d and f are not observed. Ion w of composition C_3H_5Cl is an ion of medium intensity in this spectrum but absent in I. It may form from t as shown or direct from the molecular ion. It is significant that the neutral fragment expelled in the formation of d from I has this composition. In I the charge is retained by d, in II by ion w. By loss of ·H and ·Cl ion w is converted to m and q, respectively, whose further fragmentation was discussed previously. The composition of ion m, a major ion, is deduced from the fact that the relative intensities of $\frac{m}{e}$ 75 and $\frac{m}{e}$ 77 are in the ratio three to one, the expected values for the two ions containing isotopes of chlorine.

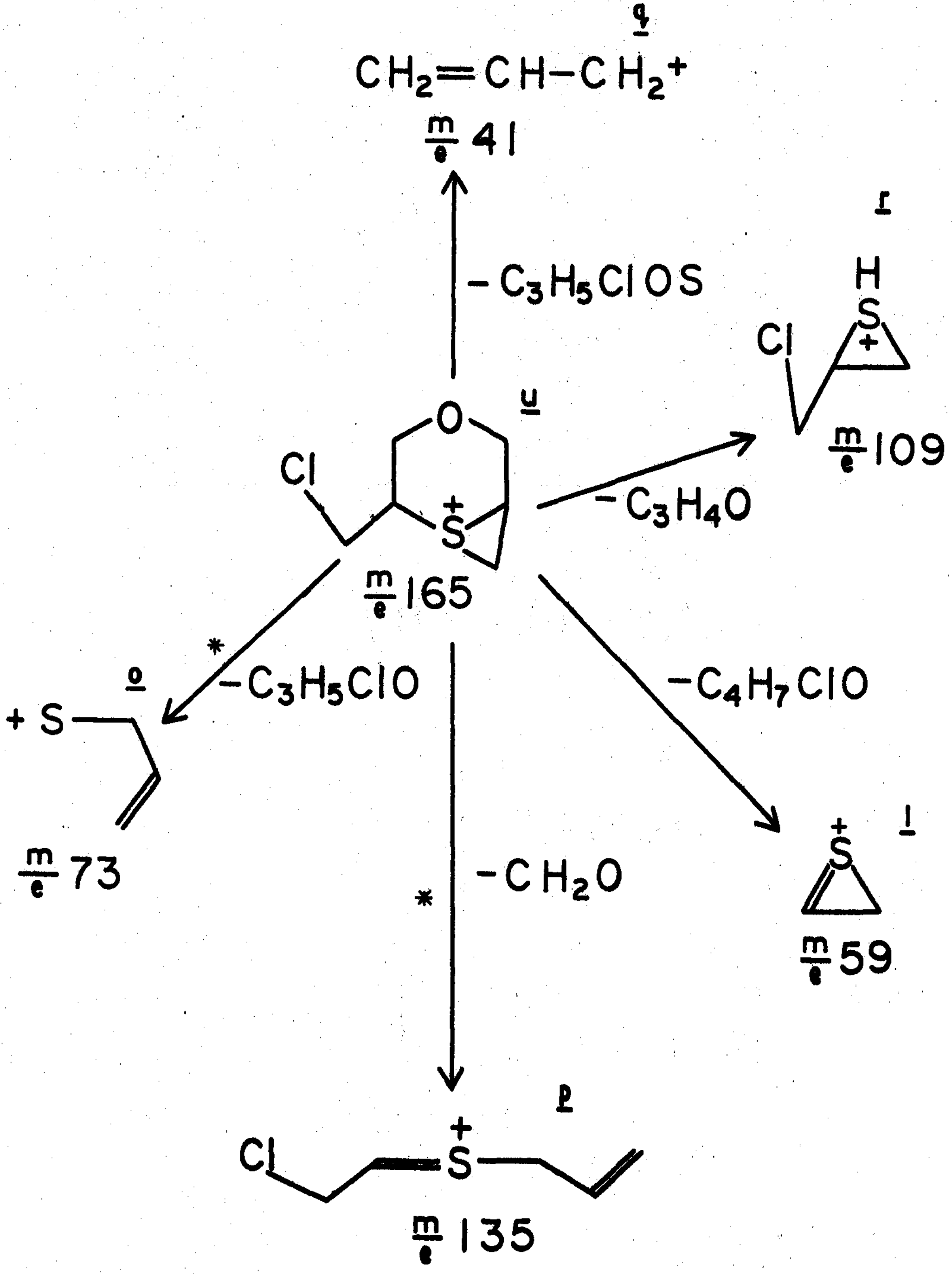
Finally the behavior of ion u (Scheme 1.7) parallels that of b except no cyclic ion analogous to d forms. It is of interest that the sulfur atom directs the fragmentation of this compound. It is probably its position β to the two chlorines which accounts for its directive effect since the loss of ·Cl or ·CH_2Cl from the molecular ion leads to stable sulfonium ions. The oxygen is not suitably situated to form the corresponding oxonium ions.

c) 3,5-Dichloromethyl-1,4-Oxaselenane

Selenium has six isotopes (Se^{74}, Se^{76}, Se^{77}, Se^{78}, Se^{80}, and Se^{82}) whose natural abundances are in the ratio of 0.87:9.02:7.58:23.52:49.82:9.19, respectively. The large number of isotopes makes it difficult to identify the ions which comprise a peak and to tell whether the peak intensity is due to one ion or a number of minor isotopic ions. When


q
$C_3H_5^+$
m/e 41
*
−·Cl
w
$C_3H_5Cl\cdot+$
m/e 76
−·H
m
C_3H_4Cl+
m/e 75
v
m/e 115
*
−HCl
−C_2H_3OS
t
Cl
m/e 151
−CH_2O
−C_4H_7ClO
g
CH≡S+
m/e 45
k
Cl
m/e 121

SCHEME 1.6


q
$CH_2=CH-CH_2^+$
m/e 41
$-C_3H_5ClOS$
r
H
S
+
Cl
m/e 109
$-C_3H_4O$
u
O
Cl
S
+
m/e 165
*
$-C_3H_5ClO$
o
+ S
m/e 73
$-C_4H_7ClO$
l
S
+
m/e 59
*
$-CH_2O$
p
Cl
S
+
m/e 135

SCHEME 1.7

giving the composition of ions only the major isotope of selenium, Se^{80}, is considered. Selenium has a lower ionization potential than sulfur and a much lower one than oxygen (38); thus, when 3,5-dichloromethyl-1,4-oxaselenane (III) is ionized the charge is localized on the selenium atom. Compound III fragments similarly to its analogues I and II but the mass spectrum of III has most of its intense ions in the high mass region in contrast with I and II where the most intense ions are in the low mass region (compare Figures 3, 4, and 5). The exact compositions of some of the important ions are recorded in Table 4 and the likely fragmentation routes are found in Schemes 1.8, 1.9, 1.10, and 1.11. No metastable peaks are observed in the mass spectrum of III.

The molecular ion of III fragments to ions x, y, and z (Scheme 1.8) in a manner analogous to I. The ion at $\frac{m}{e}$ 95 which is the analogue of c cannot arise directly from the molecular ion as in the case of I. Its abundance is relatively lower in the spectrum of III than c is in that of I.

The fragmentation of ion y parallels that of ion a as can be seen by comparing Schemes 1.9 and 1.2. The only difference is that the ion analogous to h does not form in III. I is unique in that an $[S_2]^{+\cdot}$ ion (h) is present in its spectrum but neither II nor III appear to have the corresponding $[SO]^{+\cdot}$ and $[SeO]^{+\cdot}$ ions. The ion at $\frac{m}{e}$ 169 in the mass spectrum of III is weak and since its mass is quite close to that of the $\frac{m}{e}$ 169 ion of perfluorokerosene it is not possible to verify its composition.

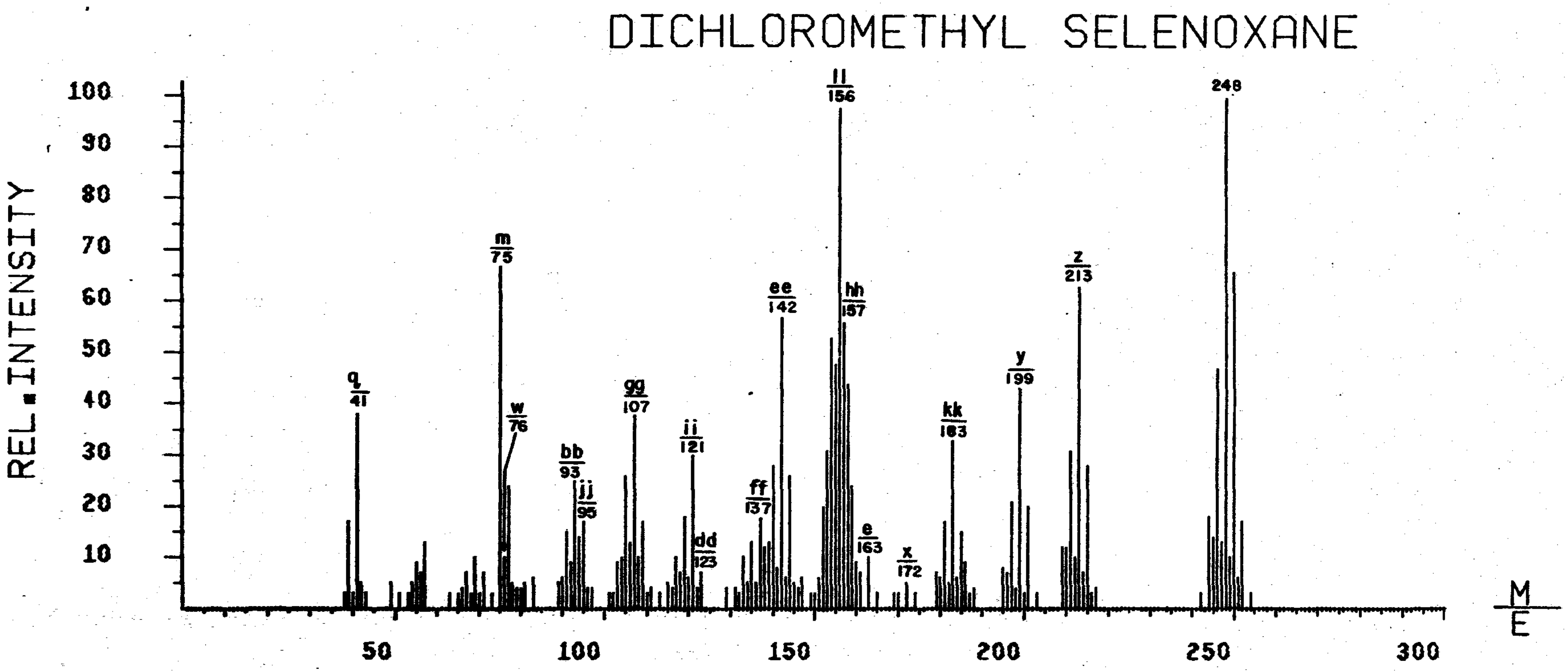
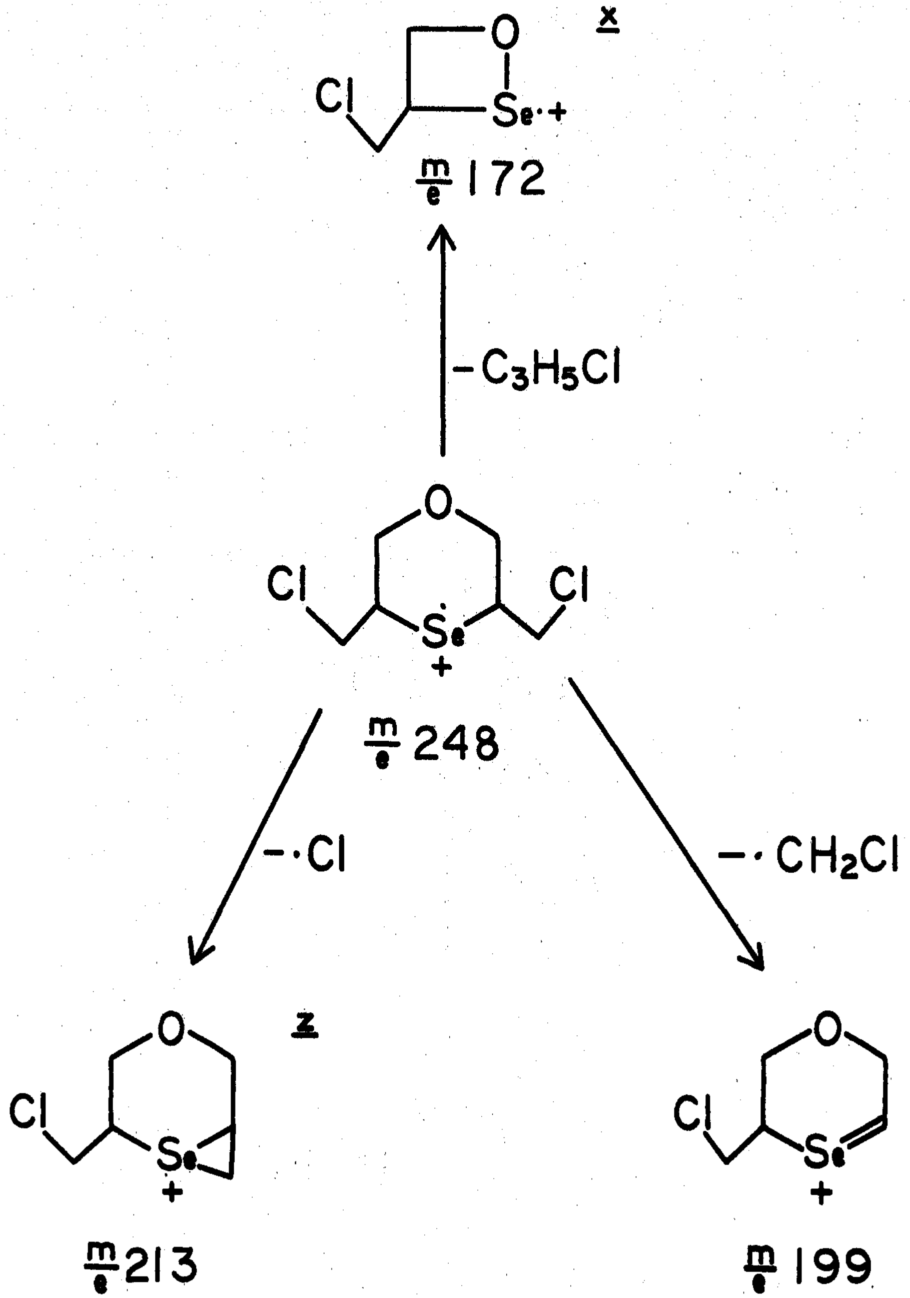


Figure 5: The Mass Spectrum of 3,5-Dichloromethyl-1,4-Oxaselenane

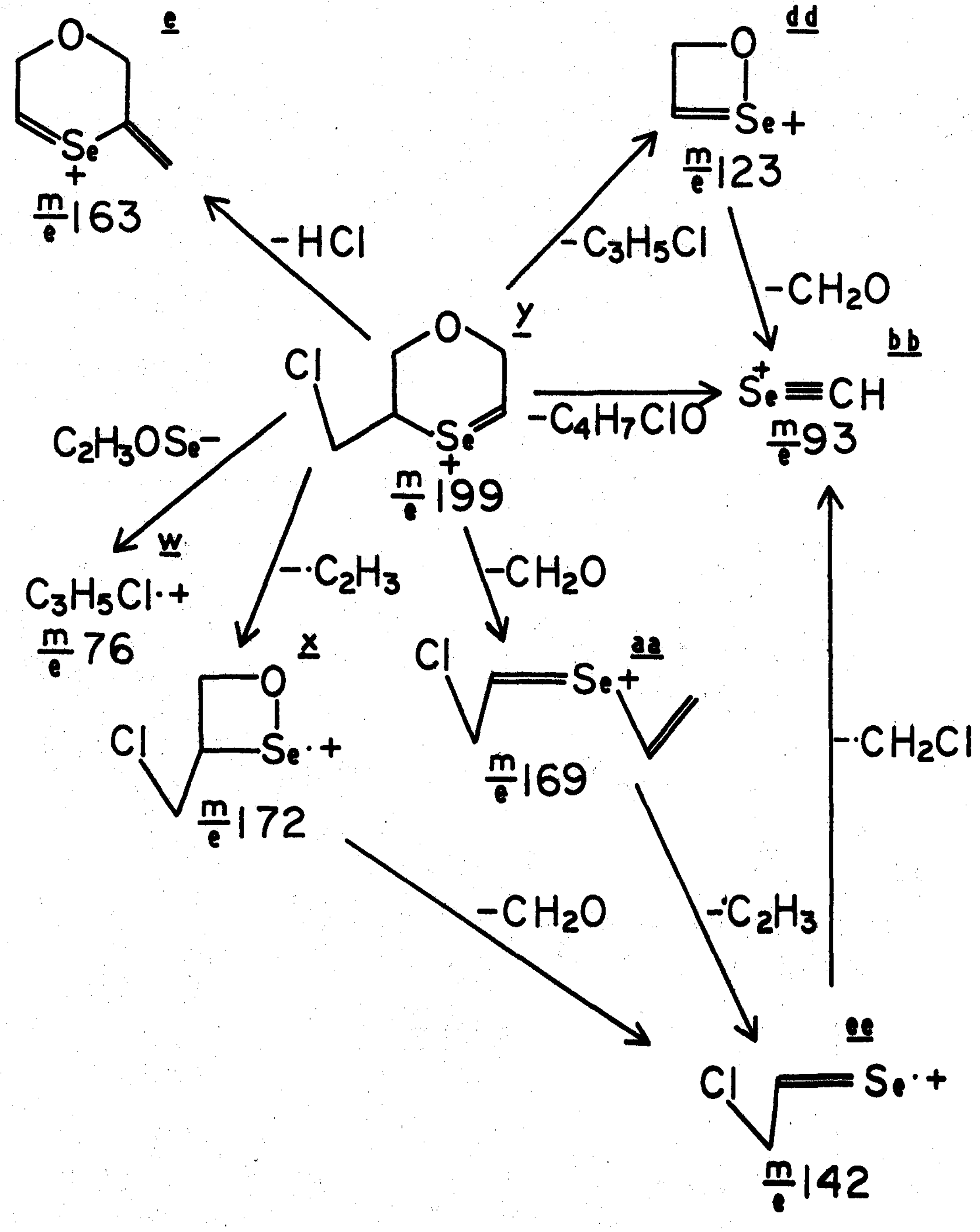
TABLE 4

Compositions of the Major Ions in the Mass Spectrum of 3,5-Dichloromethyl-1,4-Oxaselenane

$\frac{m}{e}$	Composition
75	C_3H_4Cl
76	C_3H_5Cl
93	$CHSe$
95	CH_3Se
96	CH_4Se, $C_2H_2Cl_2$, C_6H_8O
107	C_2H_3Se
121	C_3H_5Se
123	C_2H_3OSe
137	C_3H_5OSe
142	C_2H_3ClSe
155	C_3H_4ClSe
156	C_3H_5ClSe
157	C_3H_6ClSe
163	C_5H_7OSe
172	C_3H_5ClOSe
183	C_5H_8ClSe
199	C_5H_8ClOSe
213	$C_6H_{10}ClOSe$
248	$C_6H_{10}Cl_2OSe$



SCHEME 1.8


e
m/e 163
-HCl
dd
Se+
m/e 123
-C3H5Cl
-CH2O
y
Cl
Se
+
m/e 199
-C4H7ClO
bb
Se≡CH
m/e 93
C2H3OSe-
w
C3H5Cl·+
m/e 76
-·C2H3
x
Cl
Se·+
m/e 172
-CH2O
aa
Cl
Se+
m/e 169
-·CH2Cl
-CH2O
-·C2H3
ee
Cl
Se·+
m/e 142

SCHEME 1.9

Unlike II, compound III forms ions similar to d and f. Ion x, as shown in Scheme 1.10, fragments analogously to ion d (Scheme 1.3).

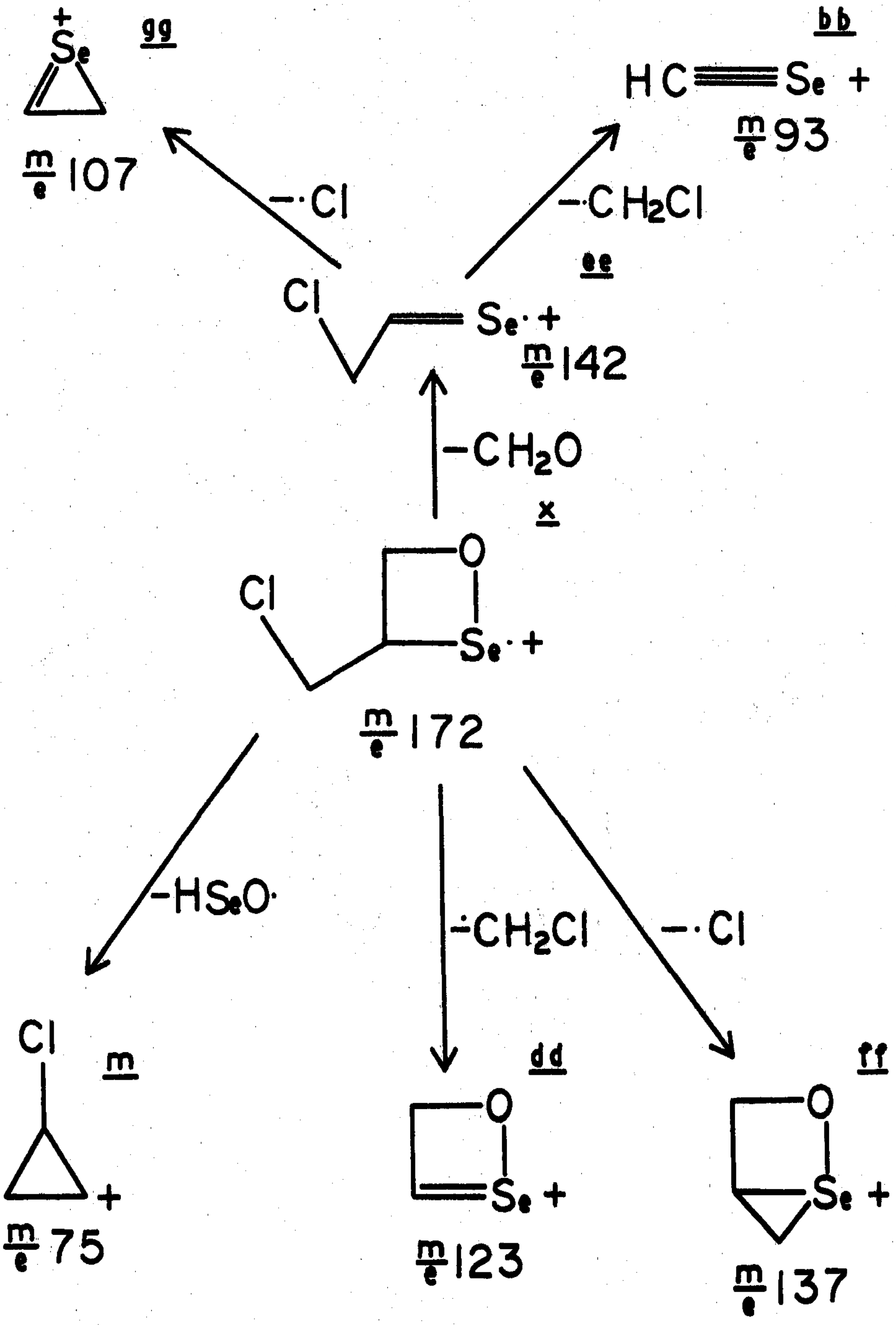
Ion z (Scheme 1.11) and its analogue b dissociate along similar routes. The only difference between the fragmentation paths of Scheme 1.4 and Scheme 1.11 (besides the heteroatoms involved) is the additional path showing that ion z loses C_3H_5O then $\cdot CH_2Cl$ to form ll and gg, respectively.

The selenium ion holds the same position in III as the sulfur atom, which directs the fragmentation, does in I and II. This is of interest since the selenium, not the oxygen, has the directive effect in III. It would appear that the heteroatom β to the two chlorines guides the dissociation of the molecule since the loss of all or part of a substituent will result in the formation of a stable sulfonium ion or its selenium analogue.

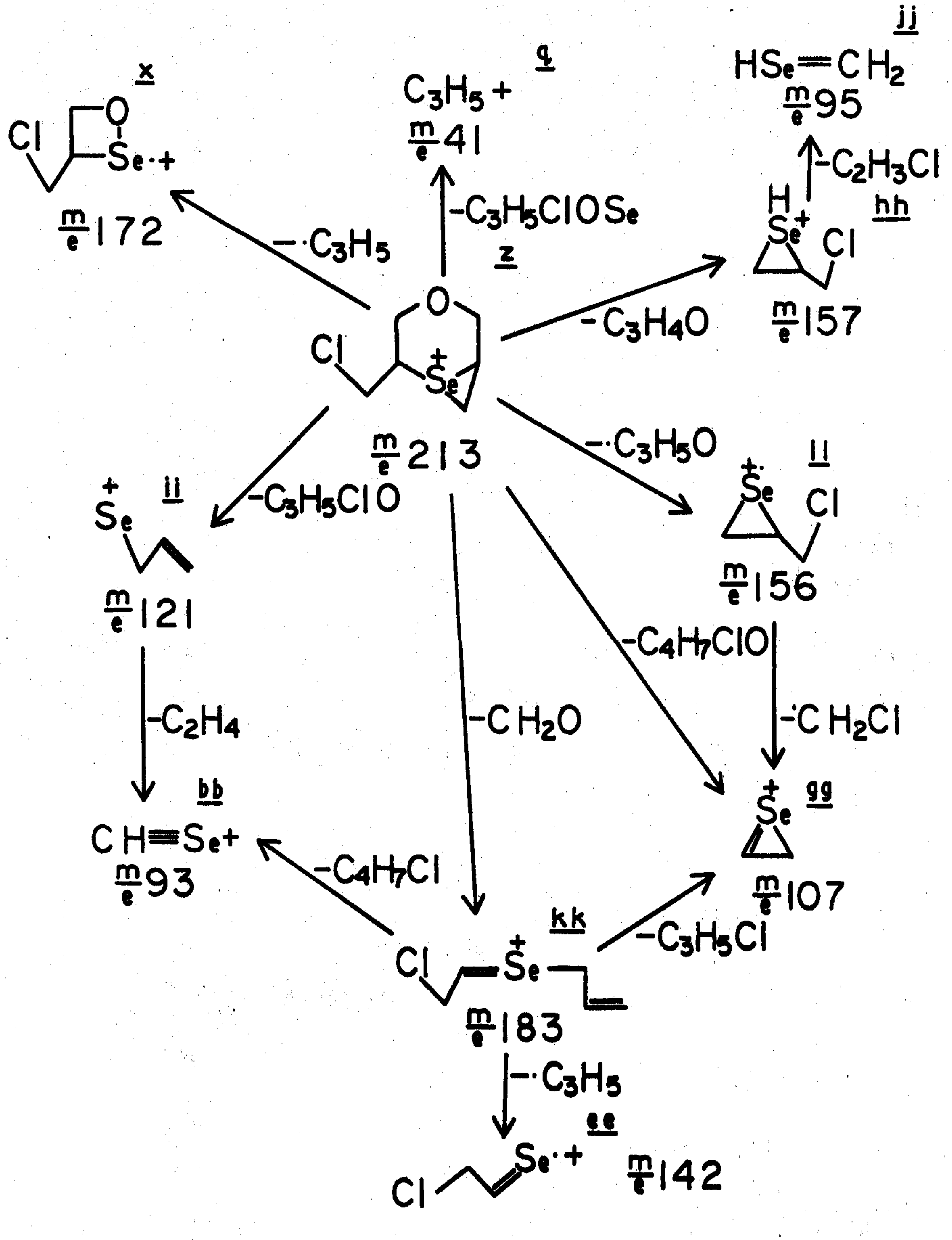
Section 2:

The Mass Spectra of Some Disubstituted Bicyclic Sulfur and Selenium Compounds

Although mass spectrometric analysis of sulfur heterocycles has been reported in the literature (17, 18, 20, 23, 25, 28, 37, 39, 40, 41, 42, 43, 44, 45), very little has been done on compounds where the sulfur acts as a bridging group. Here, the mass spectra of five bicyclo[3,3,1]-9-thianonanes (IV), one bicyclo[3,3,1]-9-selenonane (V), one bicyclo[3,3,1]-9-thianonane-9,9-dioxide (VI), one bicyclo[3,3,1]-9-thianonadi-2,6-ene (VII), and one bicyclo[3,2,1]-8-thiaoct-2-ene (VIII) are examined. All compounds are substituted at the 2 and 6 positions except for VII


gg
m/e 107
−·Cl
bb
HC≡Se +
m/e 93
−·CH2Cl
ee
Cl
Se· +
m/e 142
−CH2O
x
Cl
O
Se· +
m/e 172
−HSeO·
−·CH2Cl
−·Cl
Cl
m
+
m/e 75
dd
O
Se +
m/e 123
ff
O
Se +
m/e 137

SCHEME 1.10


x
m/e 172
−·C3H5
C3H5+
q
m/e 41
−C3H5ClOSe
z
jj
HSe=CH2
m/e 95
−C2H3Cl
hh
m/e 157
−C3H4O
m/e 213
−·C3H5O
ll
m/e 156
ii
m/e 121
−C3H5ClO
−C2H4
−CH2O
−C4H7ClO
−·CH2Cl
bb
CH≡Se+
m/e 93
−C4H7Cl
gg
m/e 107
kk
−C3H5Cl
m/e 183
−·C3H5
ee
m/e 142

SCHEME 1.11

and VIII; thus, 2,6-dichloro, 2,6-dibromo, 2,6-diiodo, 2,6-dimercapto, and 2,6-dicyano derivatives of IV, 2,6-dichloro V , 2,6-dichloro VI, 4,8-dichloro VII, and 4,7-dichloro VIII are studied. Their mass spectra are located in Figures 6 to 14 inclusive. Fragmentation routes for IV to VIII are outlined in Schemes 2.1 to 2.8 while the exact compositions of the major ions are found in Tables 6, 7, 10, and 12, and the metastable peaks observed are listed in Tables 5, 8, 9, 11, and 13.

a) Some 2,6-Disubstituted Bicyclo[3,3,1]-9-Thianonanes

A general scheme for the fragmentation of compounds of structure I, except for the dicyano compound which behaves differently, is outlined in Schemes 2.1 and 2.2. For the dihalo and dimercapto compounds one substituent is lost as the radical (·X) followed by the loss of the other substituent as HX to form the stable sulfonium ion, a. Most of the spectra have metastable peaks (Table 5) verifying these two transitions. When X = I the ion of highest mass which is observed is an ion corresponding to the loss of iodine from the molecular ion. The ion at $\frac{m}{e}$ 139 (a) may then eliminate H_2S yielding the hydrocarbon ion b. Ion b also forms from the (M-X) ion by loss of H_2S and then HCl. The compositions of the major ions of the dichloro, dimercapto, and dicyano compounds are listed in Table 6.

In Scheme 2.2 the fragmentations of a and b are followed further. Ion b eliminates C_2H_2 with the formation of c which yields the phenyl ion e upon loss of H_2. The subsequent fragmentation of the $C_6H_5^+$ species to ions at $\frac{m}{e}$ 51, $\frac{m}{e}$ 50, and $\frac{m}{e}$ 39 is well documented (46). The sulfur-containing ion d can form directly from a (metastable observed) or step-

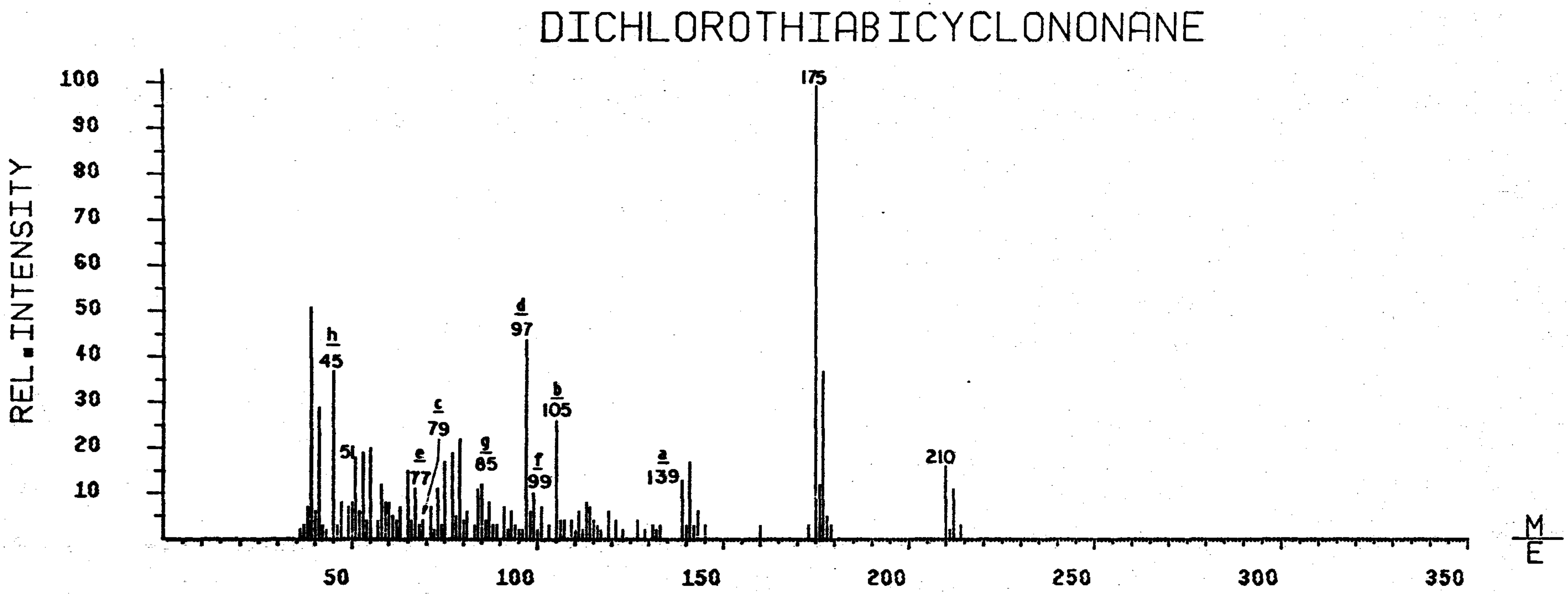


Figure 6: The Mass Spectrum of 2,6-Dichlorobicyclo[3,3,1]-9-Thianonane

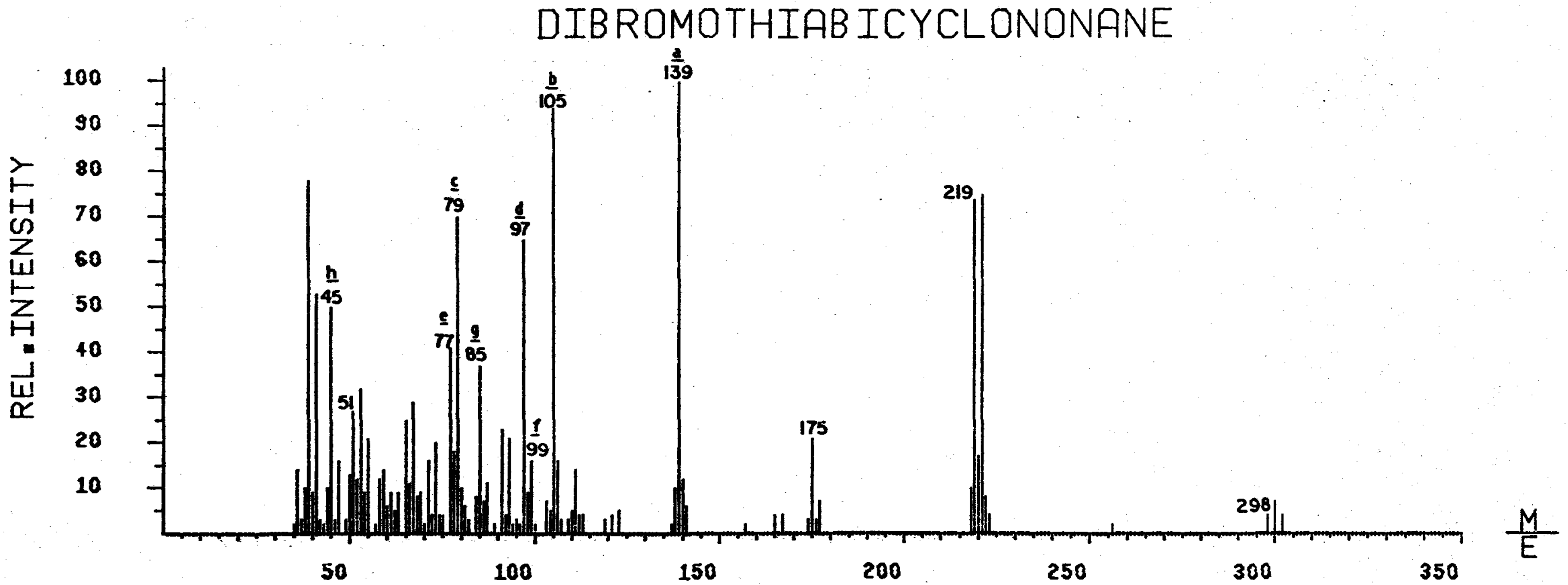


Figure 7: The Mass Spectrum of 2,6-Dibromobicyclo[3,3,1]-9-Thianonane

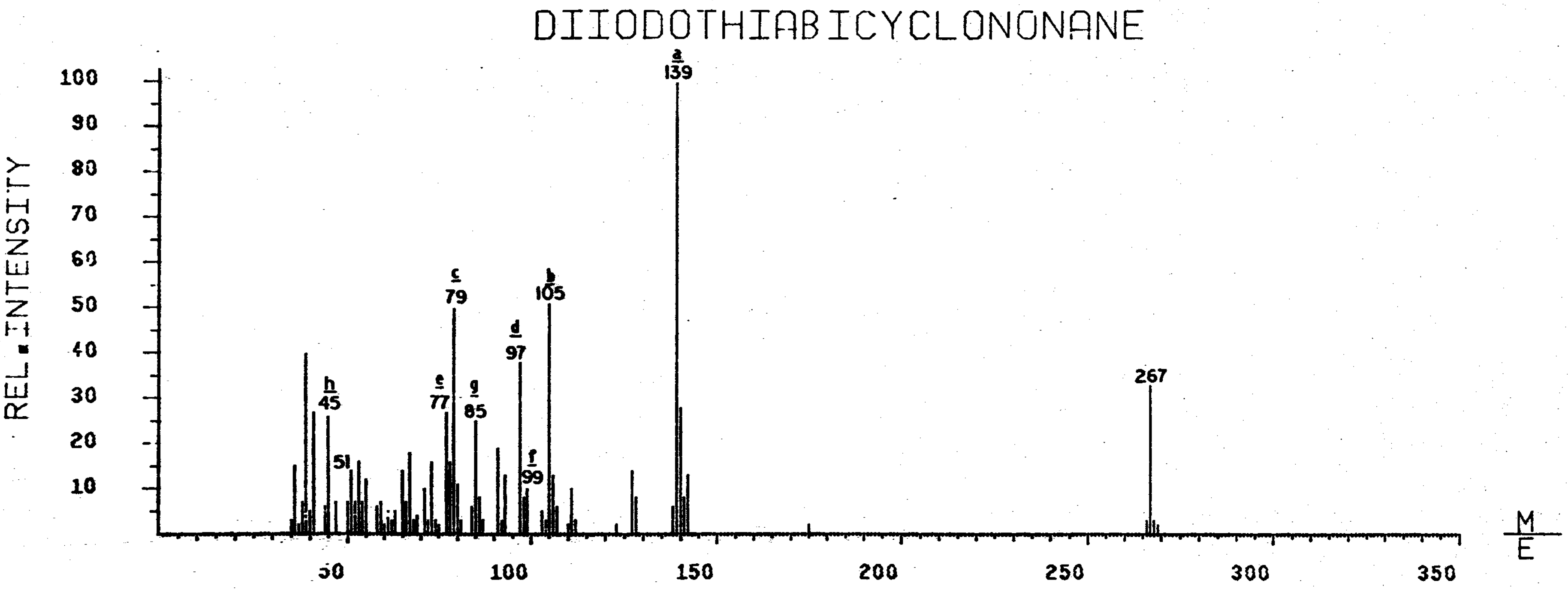


Figure 8: The Mass Spectrum of 2,6-Diiodobicyclo[3,3,1]-9-Thianonane

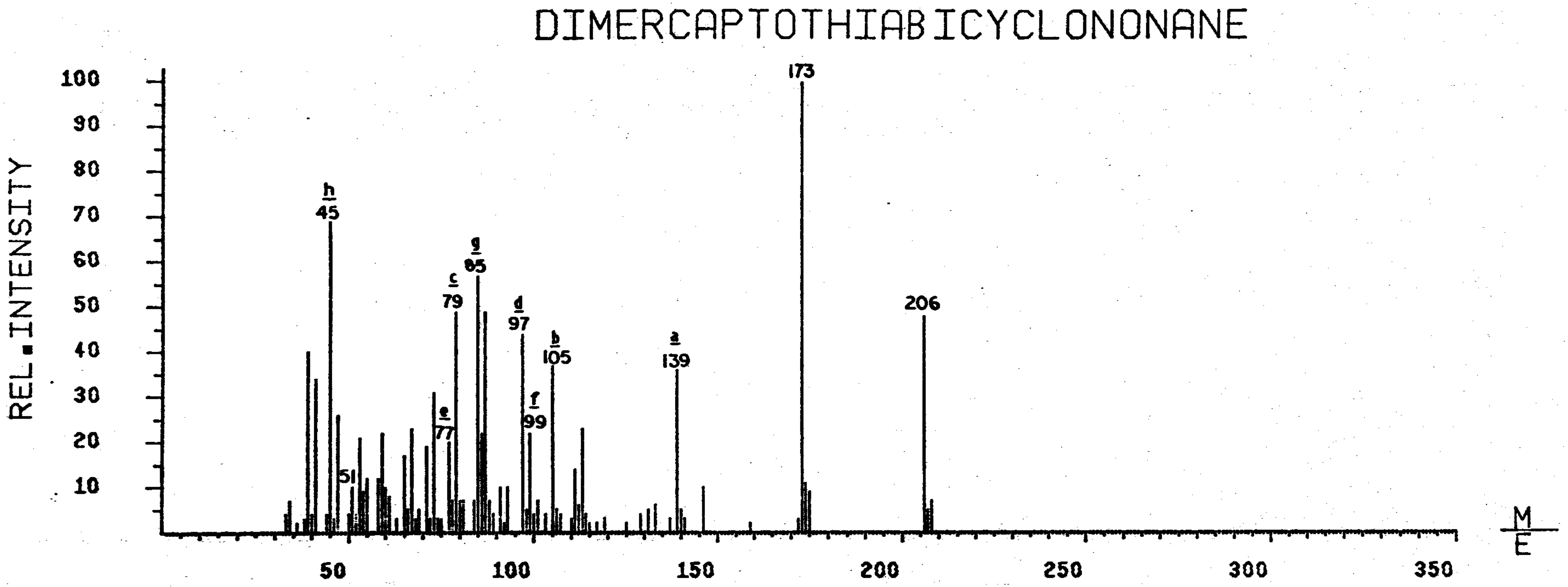


Figure 9: The Mass Spectrum of 2,6-Dimercaptobicyclo[3,3,1]-9-Thianonane

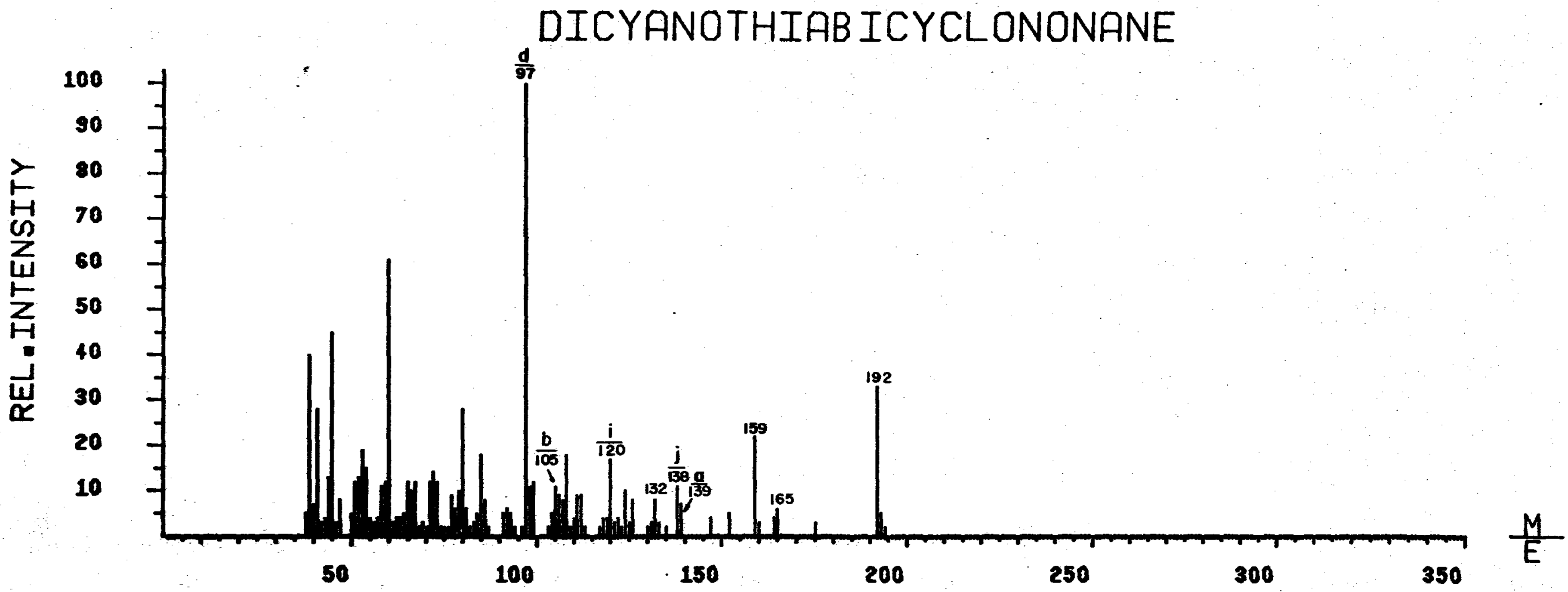


Figure 10: The Mass Spectrum of 2,6-Dicyanobicyclo[3,3,1]-9-Thianonane

TABLE 5

Metastable Transitions of Some 2,6-Disubstituted Bicyclo [3,3,1]-9-Thianonanes

Compound	Observed	Transformation	Calculated
2,6-Dichlorobicyclo [3,3,1]-9-Thianonane	145.8 ± .2	210 ⟶ 175	145.8
	79.4 ± .2	139 ⟶ 105	79.3
2,6-Dibromobicyclo [3,3,1]-9-Thianonane	88.1 ± .1	219 ⟶ 139	88.2
	79.4 ± .1	139 ⟶ 105	79.3
	59.4 ± .1	105 ⟶ 79	59.4
	67.7 ± .1	139 ⟶ 97	67.7
2,6-Diiodobicyclo [3,3,1]-9-Thianonane	79.4 ± .1	139 ⟶ 105	79.3
	59.5 ± .1	105 ⟶ 79	59.4
	67.8 ± .2	139 ⟶ 97	67.7
	33.8 ± .1	77 ⟶ 51	33.8
2,6-Dimercaptobicyclo [3,3,1]-9-Thianonane	145.4 ± .2	206 ⟶ 173	145.2
	111.9 ± .2	173 ⟶ 139	111.7
	67.8 ± .2	139 ⟶ 97	67.7
	79.4 ± .1	139 ⟶ 105	79.3
	59.5 ± .1	105 ⟶ 79	59.4
2,6-Dicyanobicyclo [3,3,1]-9-Thianonane	141.8 ± .2	192 ⟶ 165	141.8
	57.8 ± .2	165 ⟶ 97	57.0

TABLE 6

Compositions of the Major Ions in the Mass Spectra of Some 2,6-Disubstituted Bicyclo[3,3,1]-9-Thianonanes

a) 2,6-Dichlorobicyclo [3,3,1]-9-Thianonane

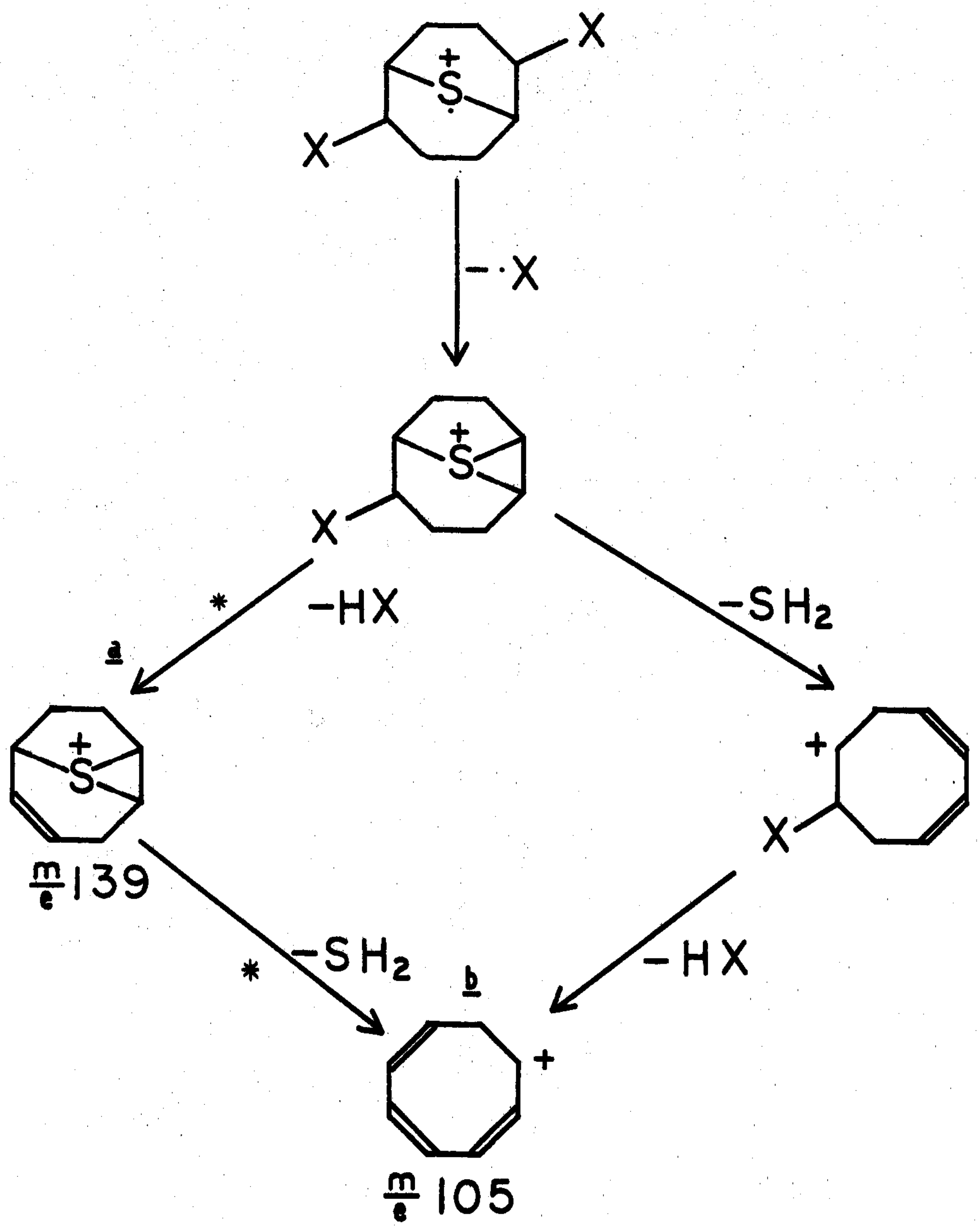
$\frac{m}{e}$	Composition
210	$C_8H_{12}Cl_2S$
175	$C_8H_{12}ClS$
141	$C_8H_{10}Cl$
139	$C_8H_{11}S$
105	C_8H_9
99	C_5H_7S
97	C_5H_5S
85	C_4H_5S
79	C_6H_7
77	C_6H_5
60	C_2H_4S
53	C_4H_5
45	CHS
41	C_3H_5
39	C_3H_3

b) 2,6-Dimercaptobicyclo [3,3,1]-9-Thianonane

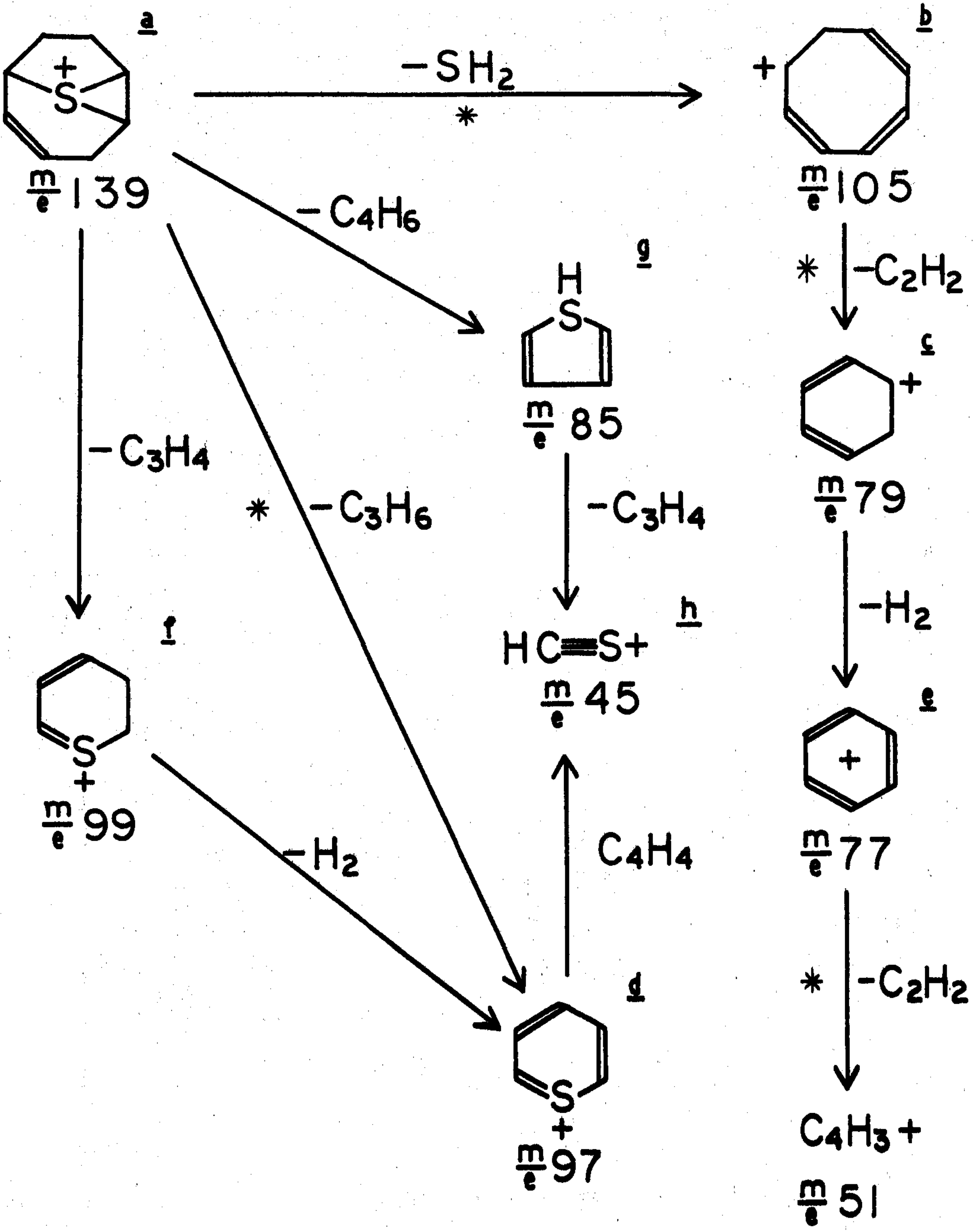
$\frac{m}{e}$	Composition
206	$C_8H_{14}S_3$
173	$C_8H_{13}S_2$
139	$C_8H_{11}S$
113	C_6H_9S
105	C_8H_9
99	C_5H_7S
97	C_5H_5S
87	C_4H_7S
86	C_4H_6S
85	C_4H_5S
79	C_6H_7
77	C_6H_5
73	C_3H_5S
71	C_3H_3S
67	C_5H_7
65	C_5H_5
59	C_2H_3S
53	C_4H_5
47	CH_3S
45	CHS
41	C_3H_5
39	C_3H_3

c) 2,6-Dicyanobicyclo [3,3,1]-9-Thianonane

$\frac{m}{e}$	Composition
192	$C_{10}H_{12}N_2S$
165	$C_9H_{11}NS$
159	$C_{10}H_{11}N_2$
139	C_7H_9NS, $C_8H_{11}S$
138	C_7H_8NS
132	$C_9H_{10}N$, $C_8H_8N_2$
120	$C_8H_{10}N$
108	$C_6H_8N_2$
105	C_8H_9
97	C_5H_5S
85	C_4H_5S
80	C_5H_6N
60	C_2H_4S
45	CHS
39	C_3H_3



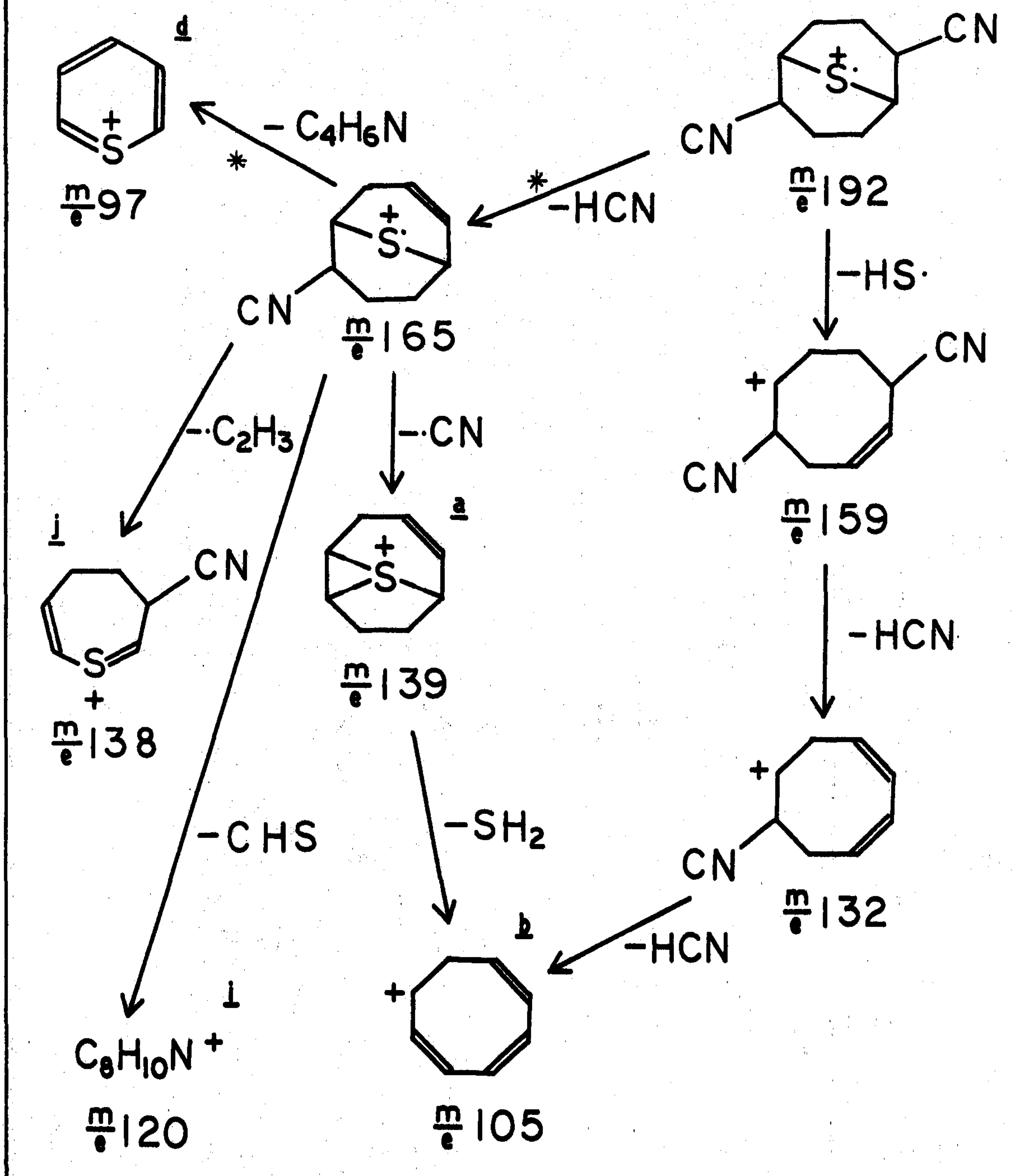
SCHEME 2.1


a
m/e 139
−SH2
*
b
m/e 105
−C4H6
g
m/e 85
*
−C2H2
c
m/e 79
−C3H4
*
−C3H6
−C3H4
−H2
f
h
HC≡S+
m/e 45
e
m/e 99
−H2
C4H4
m/e 77
*
−C2H2
d
m/e 97
C4H3+
m/e 51

SCHEME 2.2

wise through f. Similarly the ion g of $\frac{m}{e}$ 85 can be formed directly from a. Both d and g will dissociate to h at $\frac{m}{e}$ 45. Except for differences in the relative intensities of the ions, the fragmentation of the dibromo, diiodo, and dimercapto compounds is similar to that of the dichloro compound.

On a casual glance the mass spectrum of the dicyano compound appears very different from those already examined but this is not entirely true. The dicyano compound can fragment along paths similar to those followed by the other compounds. The molecular ion loses HCN to form $\frac{m}{e}$ 165 and then HS· to give an ion at $\frac{m}{e}$ 132 (Scheme 2.3). This ion at $\frac{m}{e}$ 132 may then lose HCN to give $\frac{m}{e}$ 105 (b) which behaves as outlined in Scheme 2.2. The ion at $\frac{m}{e}$ 165 may also lose ·CN to yield $\frac{m}{e}$ 139 (a) which behaves as discussed previously. The ions at $\frac{m}{e}$ 139, $\frac{m}{e}$ 132, and $\frac{m}{e}$ 105 are weak. The loss of HCN from the molecular ion is different from the fragmentation shown in Scheme 2.1 since the other compounds lose the first substituent as a radical from the molecular ion. The molecular ion of the dicyano compound can also lose HS· to form $\frac{m}{e}$ 159 which loses HCN to give $\frac{m}{e}$ 132. The sulfur ion d ($\frac{m}{e}$ 97) is the base peak in the mass spectrum and it appears to be a product of the dissociation of the ion at $\frac{m}{e}$ 165. Superimposed on these fragmentation routes are other paths involving rearrangements directed by the nitrogen to form ions such as $\frac{m}{e}$ 120 (i). No attempt will be made to explain these. Cyano compounds generally undergo extensive rearrangement (15).


d
$\frac{m}{e}$ 97
$- C_4H_6N$
*
CN
$\frac{m}{e}$ 192
*
$-HCN$
CN
$\frac{m}{e}$ 165
$-HS\cdot$
CN
CN
$\frac{m}{e}$ 159
$-\cdot C_2H_3$
$-\cdot CN$
a
j
CN
$\frac{m}{e}$ 139
$\frac{m}{e}$ 138
$-HCN$
CN
$\frac{m}{e}$ 132
$-CHS$
$-SH_2$
$-HCN$
b
i
$C_8H_{10}N^+$
$\frac{m}{e}$ 120
$\frac{m}{e}$ 105

SCHEME 2.3

b) 2,6-Dichlorobicyclo[3,3,1]-9-thianonane-9,9-Dioxide

The mass spectrum of the sulfone is different from those already studied because sulfur in the oxidized state is lost much more readily than the sulfide sulfur. The mass spectrum of the sulfone (V) is dominated by hydrocarbon ions and sulfur-containing ions are virtually absent in the low mass end of the spectrum. Possible fragmentation routes are outlined in Schemes 2.4 and 2.5 while the exact composition of the major ions and the observed metastable peaks are listed in Tables 7 and 8, respectively.

The molecular ion (Scheme 2.4) loses a chlorine atom or $HSO_2\cdot$ to form ions k and l, respectively. Ion k can lose SO_2 to yield n or O and SO successively to yield m and n. The loss of oxygen from sulfones has been observed by others (24). Both n and l can yield ion o as shown.

The further fragmentation of n and o is outlined in Scheme 2.5. They can both lose HCl to form p and b, respectively, and o can also lose HCl in a stepwise manner to give ions q and b. These three ions b, q, and p each lose C_2H_2 to form $\frac{m}{e}$ 79 (c), $\frac{m}{e}$ 80, and $\frac{m}{e}$ 81 (s), respectively. Besides these fragmentations ion p probably decomposes to yield an ion at $\frac{m}{e}$ 67 as has been reported for cyclooctadiene (47). A metastable peak may be present for the loss of CH_2 from b to form r. This loss of CH_2 is easily explained if ion b is a homotropylium ion.

The change from a bridging sulfur atom in IV to a bridging SO_2 group in V affects the mass spectrum greatly. It is primarily a hydrocarbon spectrum. The high mass end of the spectrum of the sulfone is

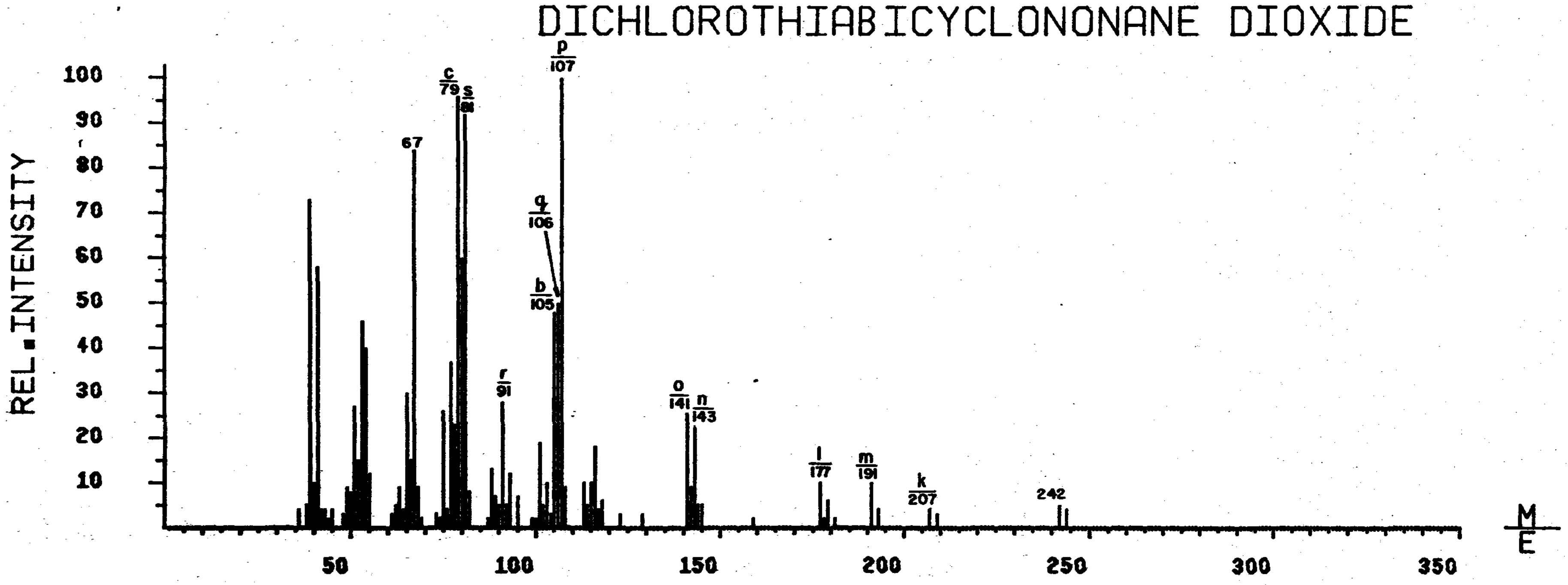


Figure 11: The Mass Spectrum of 2,6-Dichlorobicyclo[3,3,1]-9-Thianonane-9,9-Dioxide

TABLE 7

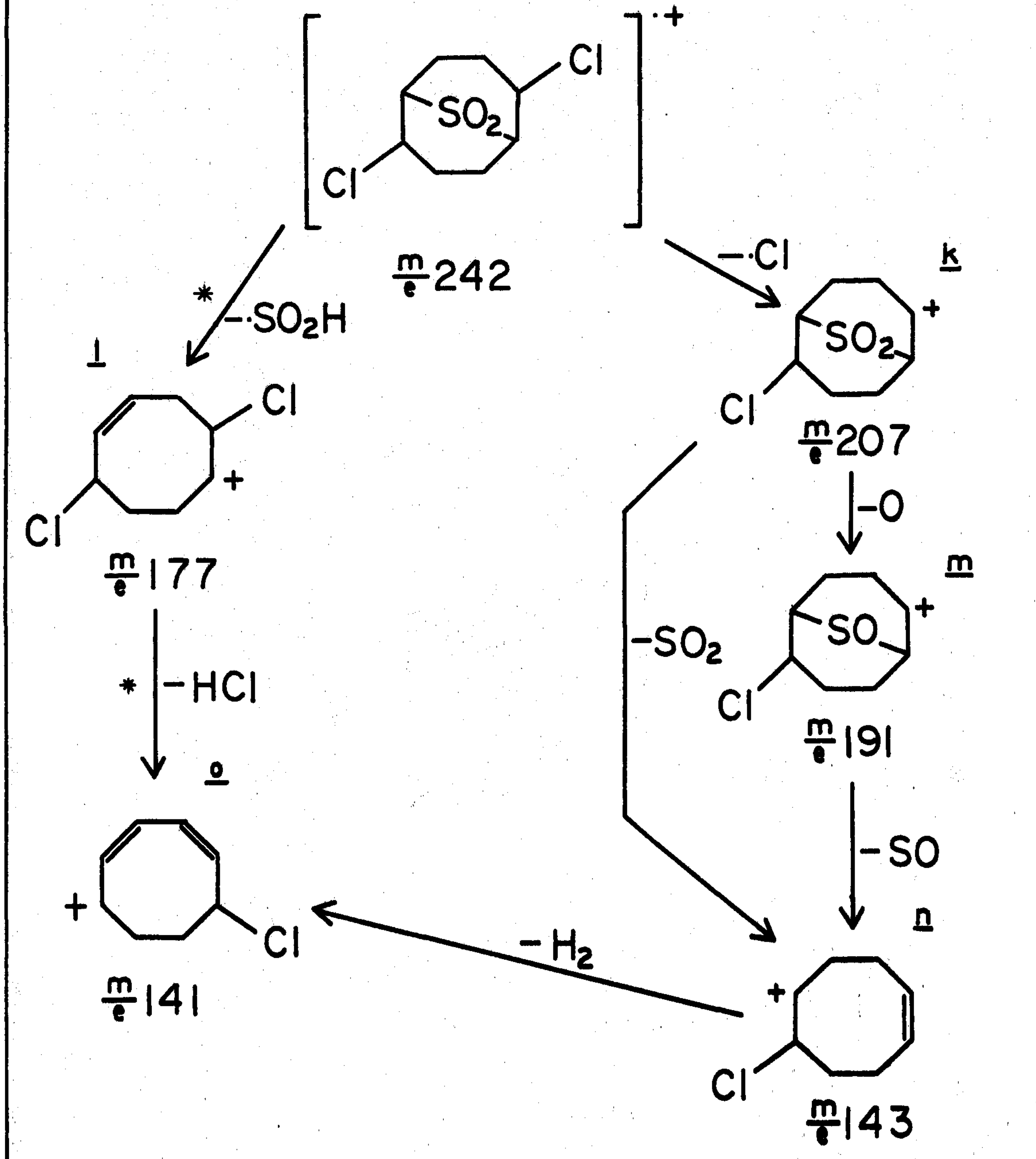
Compositions of the Major Ions in the Mass Spectrum of 2,6-Dichlorobicyclo[3,3,1]-9-Thianonane-9,9-Dioxide

$\frac{m}{e}$	Composition	$\frac{m}{e}$	Composition
242	$C_8H_{12}Cl_2OS_2$	79	C_6H_7
207	$C_8H_{12}ClO_2S$	78	C_6H_6
191	$C_8H_{12}ClOS$	77	C_6H_5
177	$C_8H_{11}Cl_2$	75	C_3H_4Cl
143	$C_8H_{12}Cl$	67	C_5H_7
141	$C_8H_{10}Cl$	65	C_5H_5, HSO_2
107	C_8H_{11}	54	C_4H_6
106	C_8H_{10}	53	C_4H_5
105	C_8H_9	51	C_4H_3
91	C_7H_7	41	C_3H_5
81	C_6H_9	39	C_3H_3
80	C_6H_8		

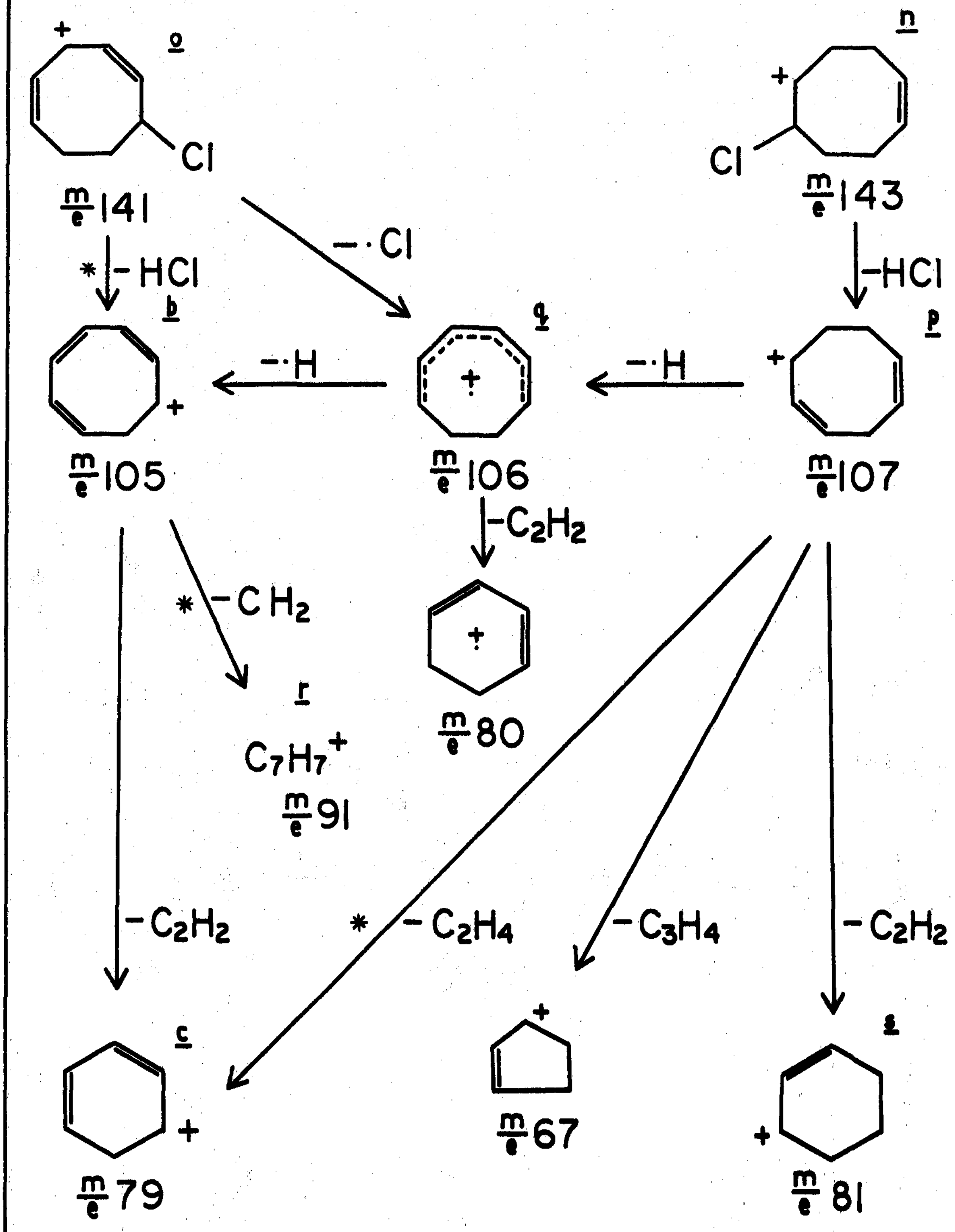
TABLE 8

Metastable Transitions of 2,6-Dichlorobicyclo[3,3,1]-9-Thianonane-9,9-Dioxide

Observed	Transformation	Calculated
129.6 ± .2	242 → 177	129.5
112.5 ± .2	177 → 141	112.3
78.5 ± .5	141 → 105	78.2
	105 → 91	78.9
58.5 ± .1	107 → 79	58.4


Cl
SO₂
Cl
·+
m/e 242
* –·SO₂H
l
Cl
+
Cl
m/e 177
* –HCl
o
+
Cl
m/e 141
–H₂
–·Cl
k
SO₂
+
Cl
m/e 207
–O
m
SO
+
Cl
m/e 191
–SO₂
–SO
n
+
Cl
m/e 143

SCHEME 2.4

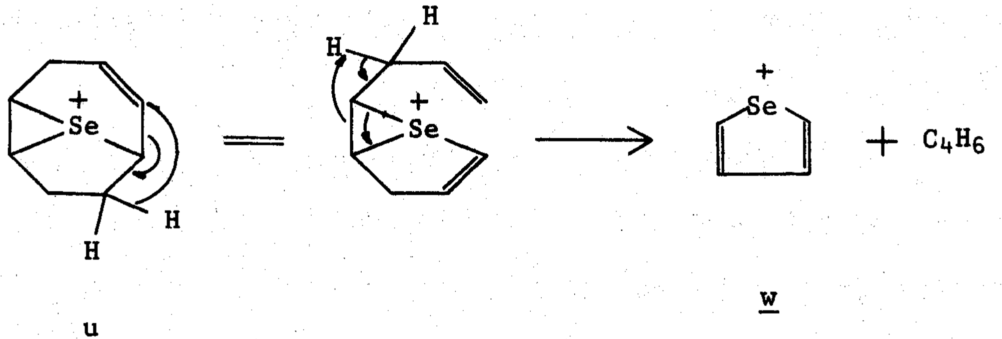

o
Cl
m/e 141
n
Cl
m/e 143
* – HCl
– ·Cl
–HCl
b
q
p
–·H
–·H
m/e 105
m/e 106
m/e 107
–C2H2
* –CH2
r
C7H7+
m/e 91
m/e 80
–C2H2
* –C2H4
–C3H4
–C2H2
c
s
m/e 79
m/e 67
m/e 81

SCHEME 2.5

much weaker than that of the sulfide. Ions d and g are not present in the sulfone spectrum and ion h is very weak. These differences occur because the sulfone sulfur is lost much more easily than the sulfide sulfur. An important difference between the spectra of IV and V lies in the relative intensity of p. When SO_2 is substituted for S as the bridging group the SO_2 is lost as such but S carries with it two hydrogens. Thus, ion p is very intense in V but weak in IV.

c) 2,6-Dichlorobicyclo[3,3,1]-9-Selenonane

Compound VI is the selenium analogue of IV. Its fragmentation is outlined in Scheme 2.6 and the metastable peaks found in its spectrum are listed in Table 9. The molecular ion loses a chlorine atom to give t, a transition which is verified by the presence of a metastable peak. Ion t loses HCl and SeH_2 to form u and b, respectively, or SeH_2 and HCl to form o and b, respectively. Analogous behavior was observed for the (M-X) ion of IV. Ions b and o will dissociate as described earlier. Ion u may lose C_3H_6 and C_4H_6 to give v and w, respectively. Once again analogous dissociations occurred for IV. Possible mechanisms by which the two ions, w and v, can form are depicted in Equations 20) and 21).



20)

u

w

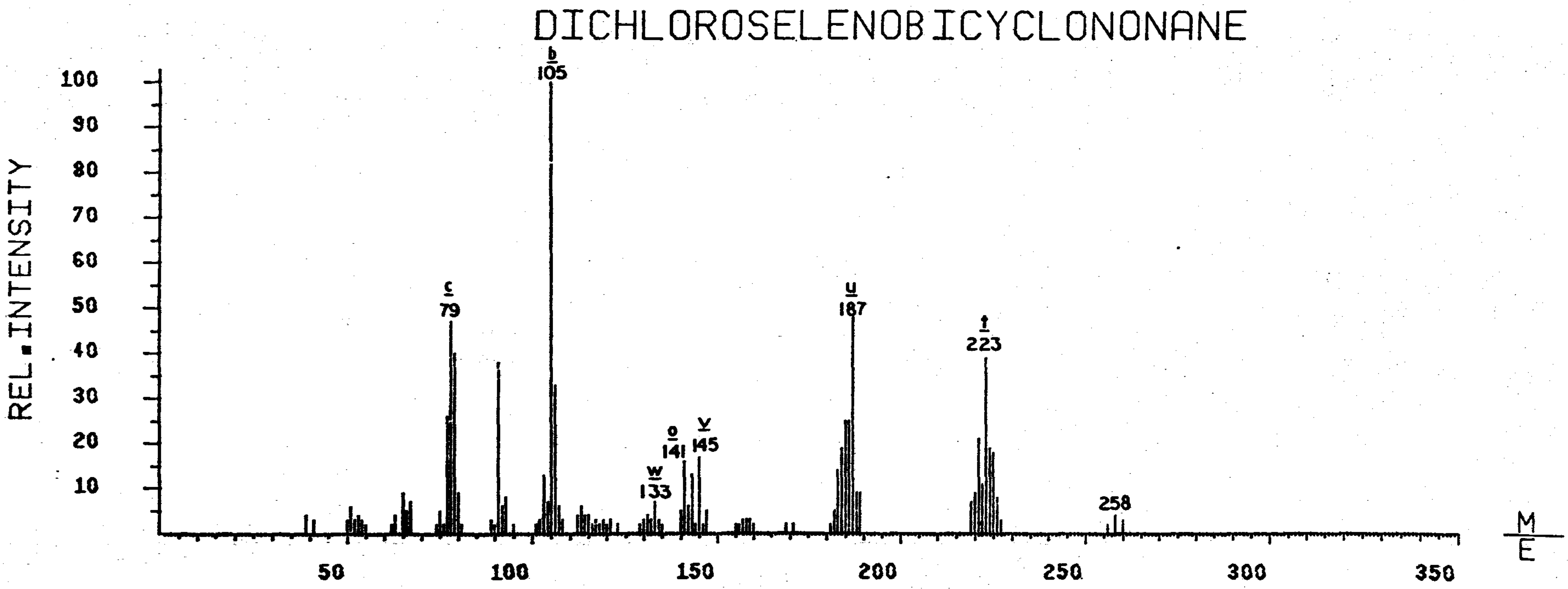
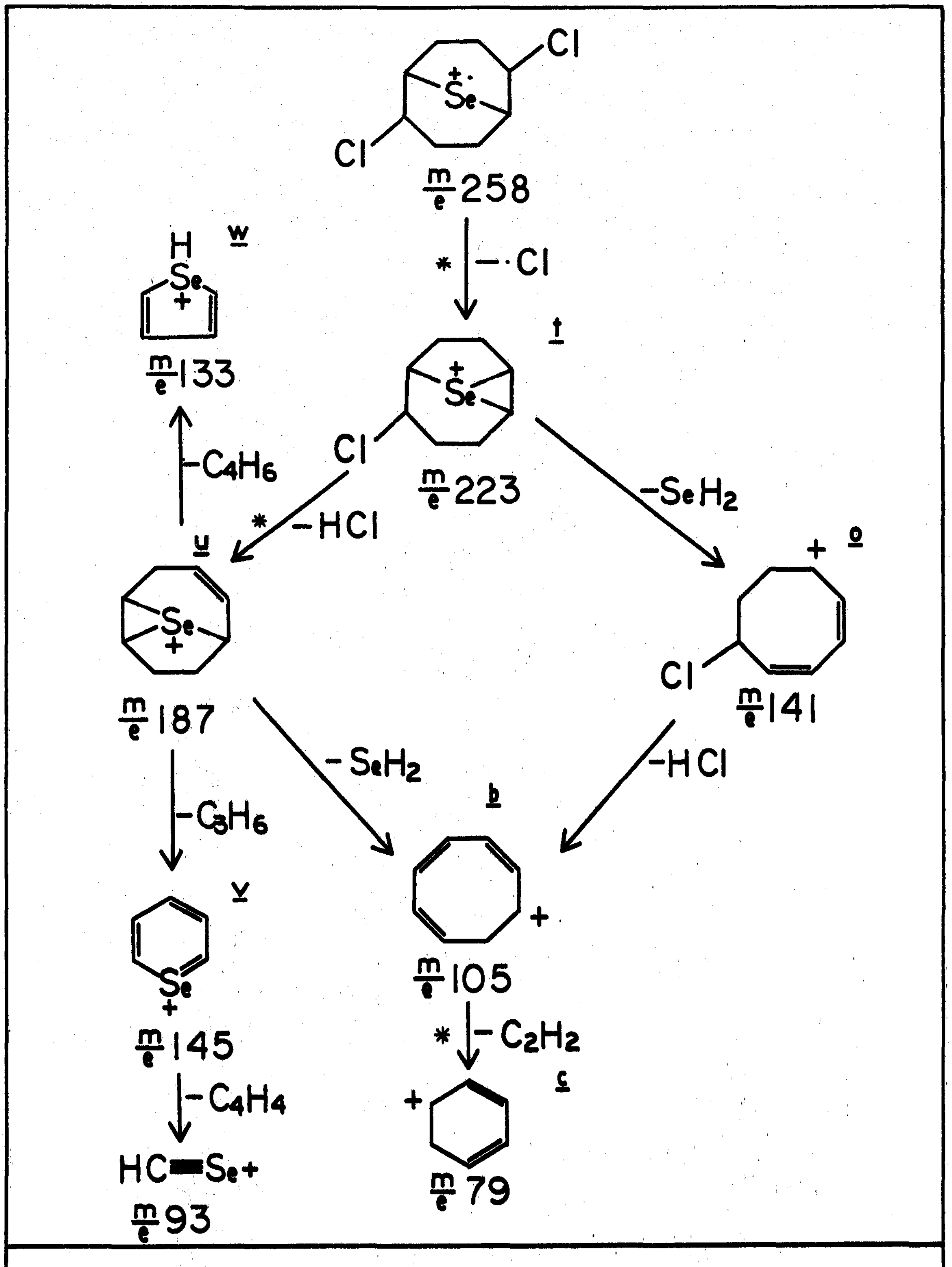


Figure 12: The Mass Spectrum of 2,6-Dichlorobicyclo[3,3,1]-9-Selenonane

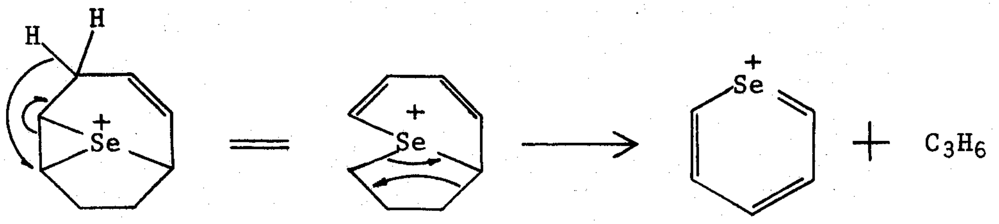
TABLE 9

Metastable Transitions of 2,6-Dichlorobicyclo[3,3,1]-9-Selenonane

Observed	Transformation	Calculated
192.5 ± .5	258 → 223	192.7
156.5 ± .5	223 → 187	156.0
59.5 ± .2	105 → 79	59.4


m/e 258
* −·Cl
t
m/e 223
* −HCl
−SeH2
u
m/e 187
o
m/e 141
−C4H6
w
m/e 133
−SeH2
−HCl
b
m/e 105
−C3H6
v
m/e 145
−C4H4
HC≡Se+
m/e 93
* −C2H2
c
m/e 79

SCHEME 2.6



u v

21)

The behavior of IV and VI under electron impact is very similar but selenium is lost more readily than sulfur. This accounts for the fact that selenium-containing ions corresponding to d, g, and h are not prominent.

d) 4,8-Dichlorobicyclo[3,3,1]-9-thianonadi-2,6-ene

Compound VII differs from IV in that it contains two centres of unsaturation and it was, therefore, of interest to compare its behavior with that of its saturated analogue. Its fragmentation is outlined in Scheme 2.7 and the compositions of the major ions of the spectrum are found in Table 10. The molecular ion loses ·Cl as expected (metastable peak listed in Table 11) yielding ion x which then loses SH_2, ·Cl, HCl, and C_3H_3Cl to form y, z, aa, and d, respectively.

The loss of HCl and SH in that order or in the reverse order from the (M-X) ion occurs also to IV and VI. The unsaturation of VII is probably the reason why ion aa does not lose SH_2 easily but instead loses

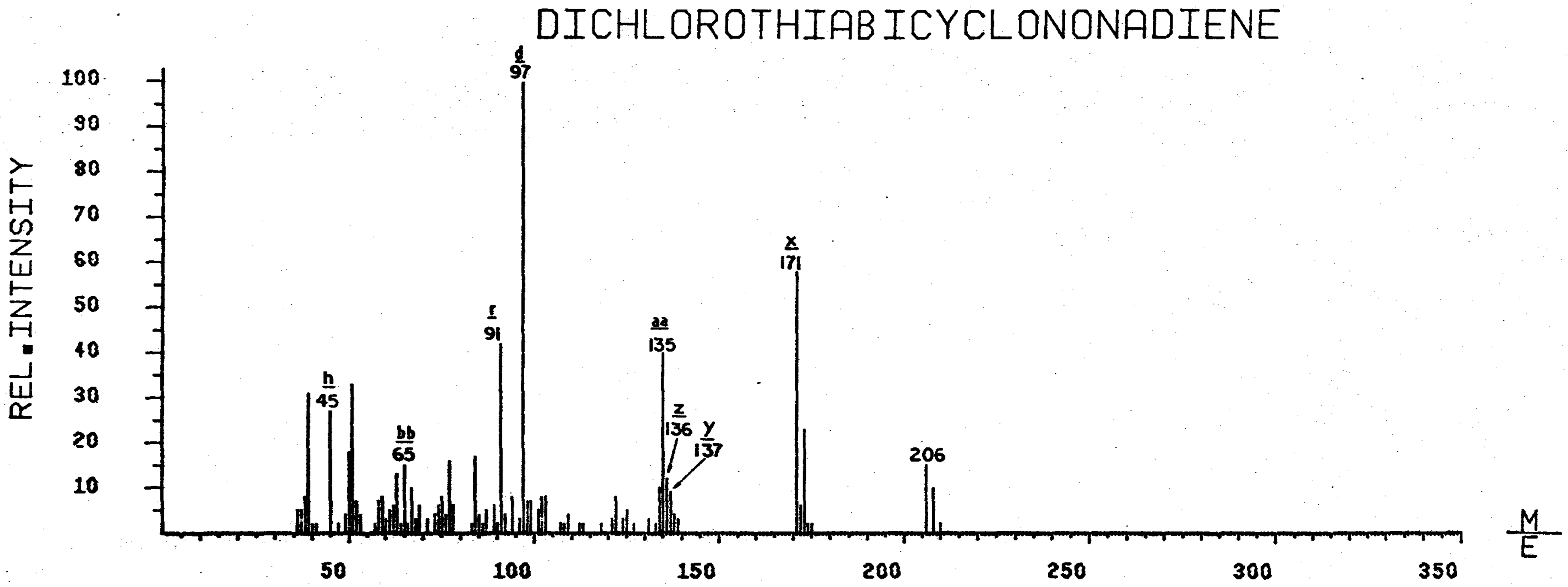


Figure 13: The Mass Spectrum of 4,8-Dichlorobicyclo[3,3,1]-9-Thianonadi-2,6-ene

TABLE 10

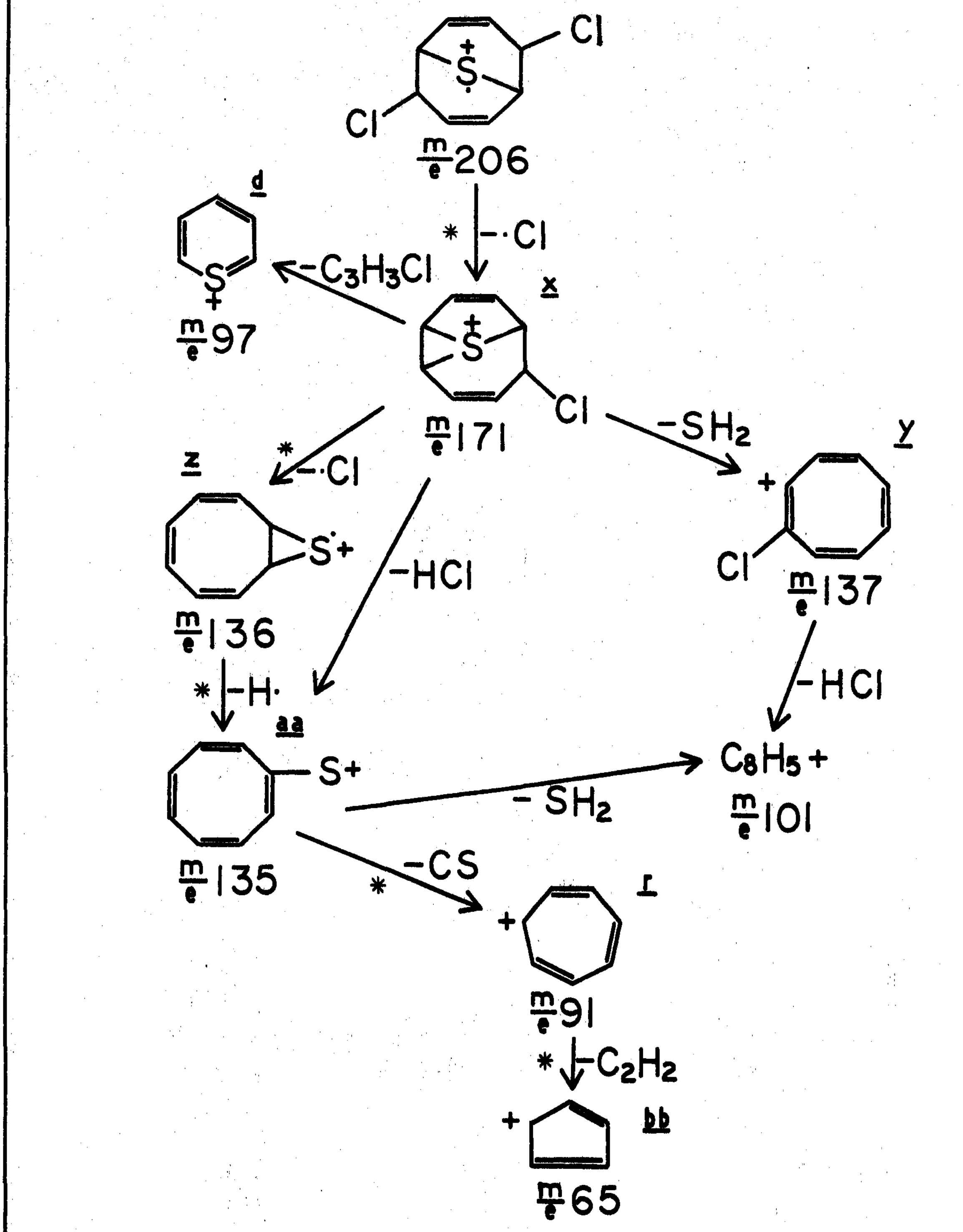
Compositions of the Major Ions in the Mass Spectrum of 4,8-Dichlorobicyclo[3,3,1]-9-Thianonadi-2,6-ene

$\frac{m}{e}$	Composition	$\frac{m}{e}$	Composition
206	$C_8H_8Cl_2S$	84	C_4H_4S
171	C_8H_8ClS	77	C_6H_5
137	C_8H_6Cl	65	C_5H_5
135	C_8H_7S	51	C_4H_3
101	C_8H_5	50	C_4H_2
97	C_5H_5S	45	CHS
91	C_7H_7	39	C_3H_3

TABLE 11

Metastable Transitions of 4,8-Dichlorobicyclo[3,3,1]-9-Thianonadi-2,6-ene

Observed	Transformation	Calculated
142.0 ± .2	206 → 171	141.9
108.3 ± .2	171 → 136	108.2
134.2 ± .2	136 → 135	134.0
61.4 ± .1	135 → 91	61.3
46.5 ± .1	91 → 65	46.4


m/e 206
* -·Cl
x
m/e 171
d
-C3H3Cl
m/e 97
* -·Cl
z
m/e 136
-HCl
-SH2
y
m/e 137
* -H·
aa
m/e 135
-HCl
C8H5+
m/e 101
- SH2
* -CS
r
m/e 91
* -C2H2
bb
m/e 65

SCHEME 2.7

CS. The loss of CS is an important dissociation for this unsaturated compound but is not for the saturated compounds.

e) 4,7-Dichlorobicyclo[3,2,1]-8-thiaoct-2-ene

Compound VIII, dichlorobicyclothiaoctene, has been examined since the corresponding nonene was unavailable and also because it is isomeric with dichlorotricyclothiaoctane (see Section 3). The route proposed for the fragmentation of VIII is found in Scheme 2.8 and the compositions of the major ions are listed in Table 12. The molecular ion loses a chlorine atom to yield ion dd as is verified by the presence of a metastable peak (Table 13). The (M-Cl) ion then fragments in a similar manner to that already observed for the sulfides and selenide, which is the loss of H_2S and HCl in either order. Ion dd may also lose HS· and Cl· to give r which behaves in a manner characteristic of the tropylium ion (48). In analogy with the behavior of the diene, ion dd loses C_2H_3Cl to form d, the most intense peak in the spectrum, and ion gg loses CS to yield c whose further fragmentation is characteristic of the $\frac{m}{e}$ 79 ion (49). The dissociation of both c and d was discussed earlier. Ion gg may fragment to d but there is no direct evidence that it does.

Ion d is the base peak for both unsaturated compounds (VII and VIII). It is interesting that although VIII has both five- and six-membered rings the six-membered ring is favoured on fragmentation. The ion at $\frac{m}{e}$ 85 ($C_4H_5S^+$) has a low intensity. Both the 4,8-dichlorobicyclo[3,3,1]-9-thianonadi-2,6-ene and 4,7-dichlorobicyclo[3,2,1]-8-thiaoct-2-ene lose CS. The reason that CS instead of SH_2 is lost may be that the C:H ratio is low and not many hydrogens are available for loss with sulfur.

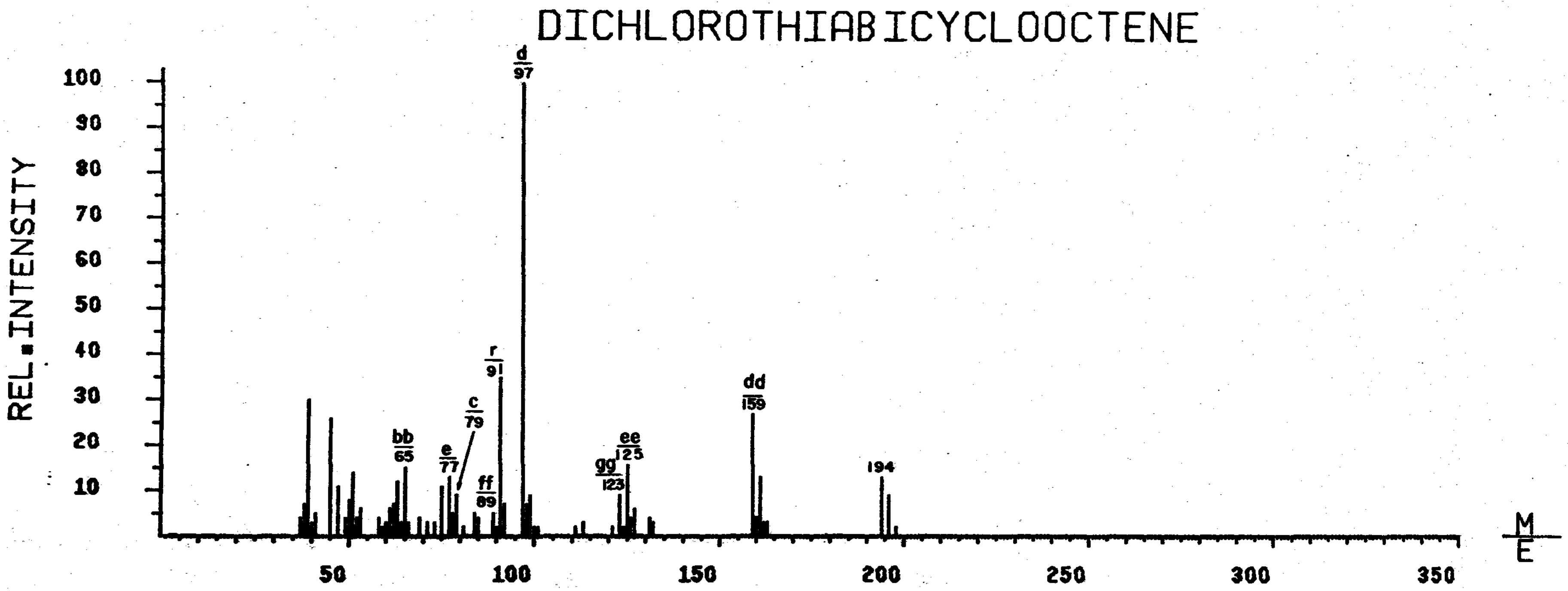


Figure 14: The Mass Spectrum of 4,7-Dichlorobicyclo[3,2,1]-8-Thiaoct-2-ene

TABLE 12

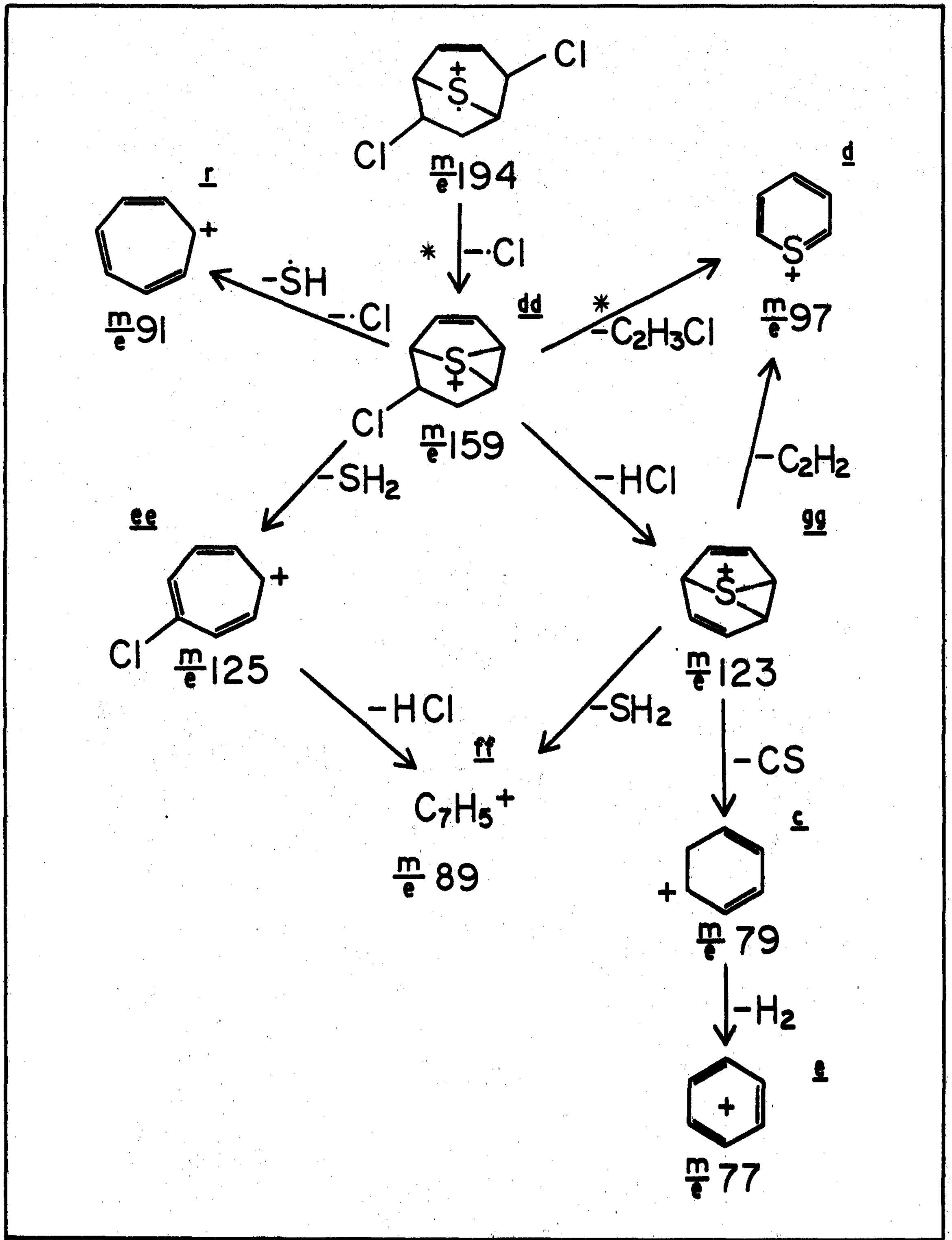
Compositions of the Major Ions in the Mass Spectrum of 4,7-Dichlorobicyclo[3,2,1]-8-Thiaoct-2-ene

$\frac{m}{e}$	Composition	$\frac{m}{e}$	Composition
194	$C_7H_8Cl_2S$	89	C_7H_5
159	C_7H_8ClS	65	C_5H_5
125	C_7H_6Cl	63	C_5H_3
123	C_7H_7S	45	CHS
97	C_5H_5S	39	C_3H_3
91	C_7H_7		

TABLE 13

Metastable Transitions of 4,7-Dichlorobicyclo[3,2,1]-8-Thiaoct-2-ene

Observed	Transformation	Calculated
130.3 ± .2	$194 \longrightarrow 159$	130.3
59.1 ± .2	$159 \longrightarrow 97$	59.2
46.5 ± .1	$91 \longrightarrow 65$	46.4


Cl
Cl
m/e 194
* −·Cl
r
m/e 91
−ṠH
−·Cl
dd
m/e 159
Cl
* −C2H3Cl
d
m/e 97
−C2H2
−SH2
−HCl
ee
gg
Cl
m/e 125
m/e 123
−HCl
−SH2
ff
C7H5+
m/e 89
−CS
c
m/e 79
−H2
e
m/e 77

SCHEME 2.8

The spectra of all the compounds examined in this section are characterized by the loss of a substituent from the molecular ion. With the loss of the substituent, IV, VII, and VIII formed stable sulfonium ions while VI formed the selenium analogue of the sulfonium ion. The sulfone (V), which can lose SO_2 from the molecular ion, is the only compound which loses something other than a substituent from the molecular ion. The (M-X) ions of all the compounds except V lose SH_2 and HCl in either order. The (M-X) ion of the sulfone loses SO_2 then HCl. The unsaturated compounds have a fragmentation path not found in the mass spectra of the saturated compounds and this is the loss of CS from the (M-HCl_2) ion.

Section 3:

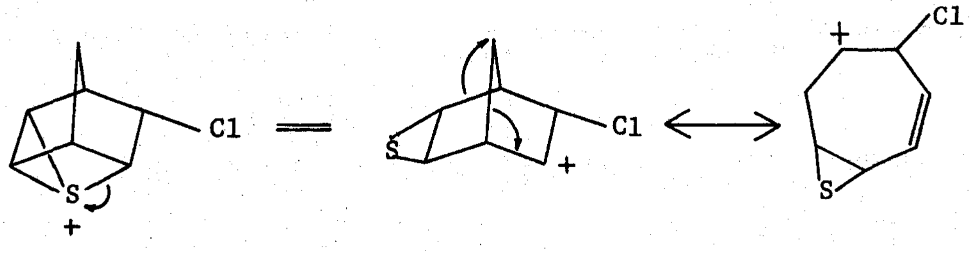
The Mass Spectra of Some Disubstituted Tricyclic Sulfur Compounds

Work has been done on the mass spectral fragmentation pattern of norbornyl and norbornenyl halides (50, 51, 52) but nothing has been reported on the behavior of sulfur-bridged norbornyl chlorides. Here, the behavior under electron impact of three such compounds is studied. The compounds examined are 3,5-dichlorotricyclo[2,2,1,$1^{2,6}$]-8-thiaoctane (IX), 3,5-dichlorotricyclo[2,2,1,$1^{2,6}$]-8-thiaoctane-8-oxide (X), and 3,5-dichlorotricyclo[2,2,1,$1^{2,6}$]-8-thiaoctane-8,8-dioxide (XI), and their mass spectra are found in Figures 15, 16, and 17, respectively. Fragmentation routes for these compounds are proposed in Schemes 3.1 to 3.8. In all cases the loss of chlorine from the molecular ion is observed but the sulfoxide and sulfone also lose SO and SO_2, respectively, from their molecular ions.

a) 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane

Like many of the compounds discussed in the previous section, compound IX is a β,β'-dichlorosubstituted sulfide which loses a chlorine atom from its molecular ion to form a, a stable sulfonium ion, as illustrated in Scheme 3.1. The exact composition of a and other major ions is listed in Table 14, while the metastable peaks observed in the spectrum of IX are found in Table 15.

The dissociations undergone by a are outlined in Scheme 3.2. It may lose C_2H_2S and then HCl to form c and e, respectively, or, lose them in the reverse order to form d and e, respectively. Ring expansion of a, as illustrated below, may take place before it dissociates to c and d.



a

It is apparent that this expanded ring could readily lose HCl and C_2H_2S in either order. Alternatively, e may form without ring expansion. Thus, e or f, depending on which fragment retains the charge, is the product of the reaction detailed in equation 22).

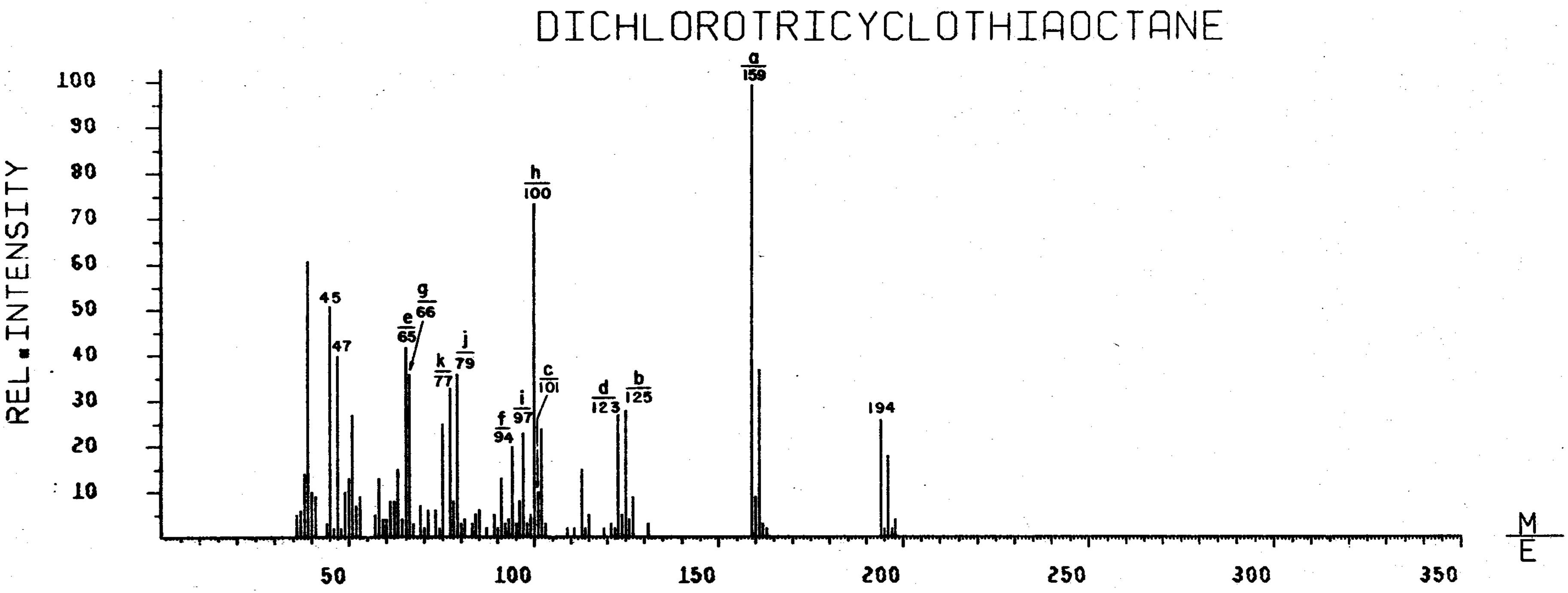


Figure 15: The Mass Spectrum of 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane

TABLE 14

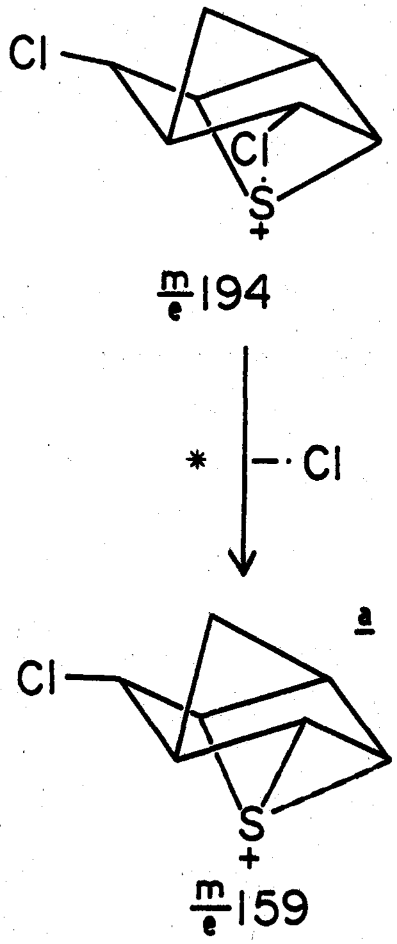
Compositions of the Major Ions in the Mass Spectrum of 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane

$\frac{m}{e}$	Composition	$\frac{m}{e}$	Composition
194	$C_7H_8Cl_2S$	79	C_6H_7
159	C_7H_8ClS	77	C_6H_5
125	C_7H_6Cl	75	C_3H_4Cl
123	C_7H_7S	66	C_5H_6
115	$C_6H_6Cl^{37}$	65	C_5H_5
102	$C_5H_5Cl^{37}$	51	C_4H_3
97	C_5H_5S	47	CH_3S
94	C_2H_3ClS	45	CHS

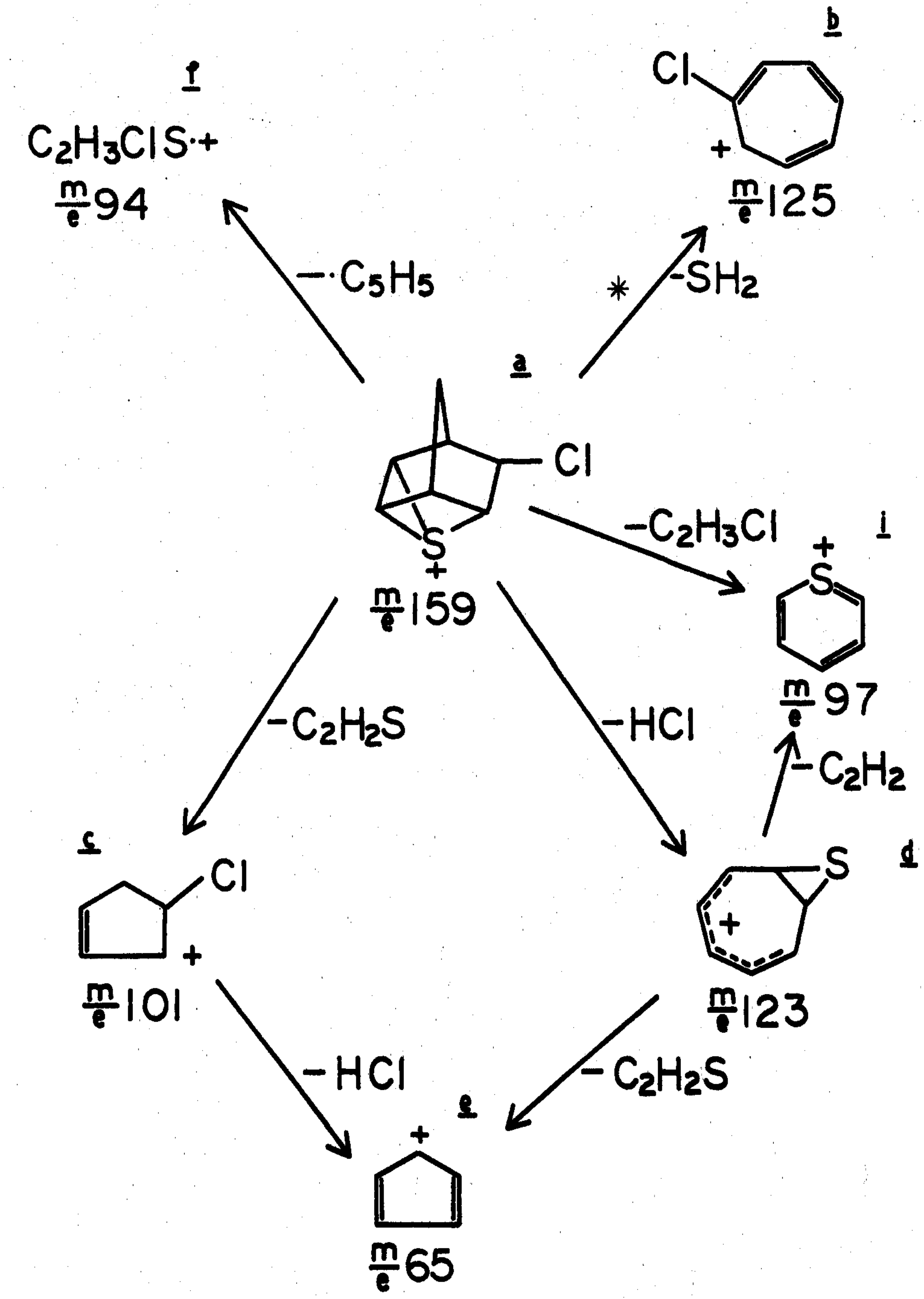
TABLE 15

Metastable Transitions of 3,5-Dichlorotricyclo $[2,2,1,1^{2,6}]$-8-Thiaoctane

Observed	Transformation	Calculated
130.4 ± .1	194 → 159	130.3
98.4 ± .1	159 → 125	98.3
42.4 ± .1	100 → 65	42.3

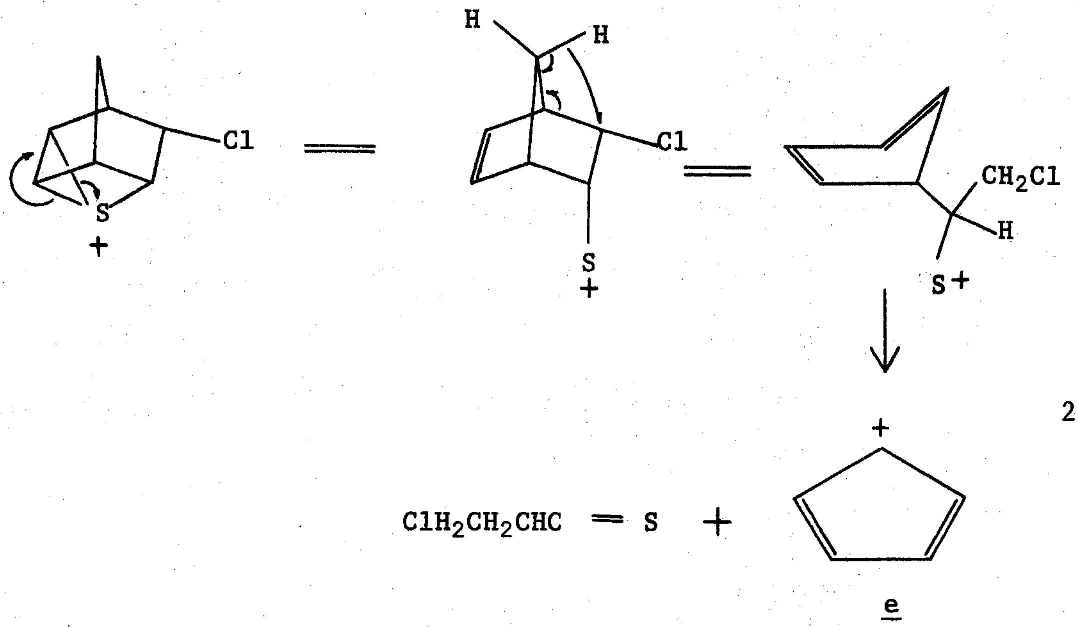


SCHEME 3.1



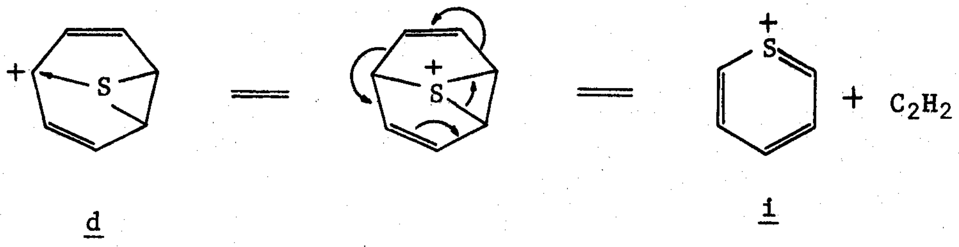
f
$C_2H_3ClS^{\cdot+}$
m/e 94
−·C_5H_5
b
Cl
+
m/e 125
∗
−SH_2
a
Cl
S
+
m/e 159
−C_2H_3Cl
i
+
S
m/e 97
−C_2H_2S
−HCl
−C_2H_2
c
Cl
+
m/e 101
d
S
+
m/e 123
−HCl
−C_2H_2S
e
+
m/e 65

SCHEME 3.2

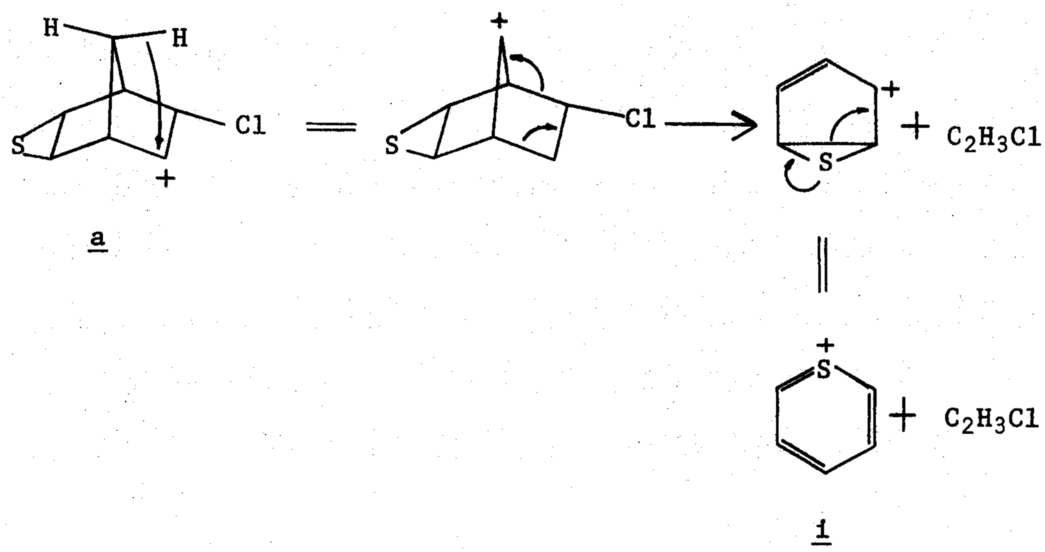


22)

Ion a also loses SH_2 to yield ion b as verified by a metastable peak. The loss of C_2H_2 from d or C_2H_3Cl from a yields i as illustrated in equations 23) and 24), respectively. These same losses were also observed for compound VIII, the isomer of IX.



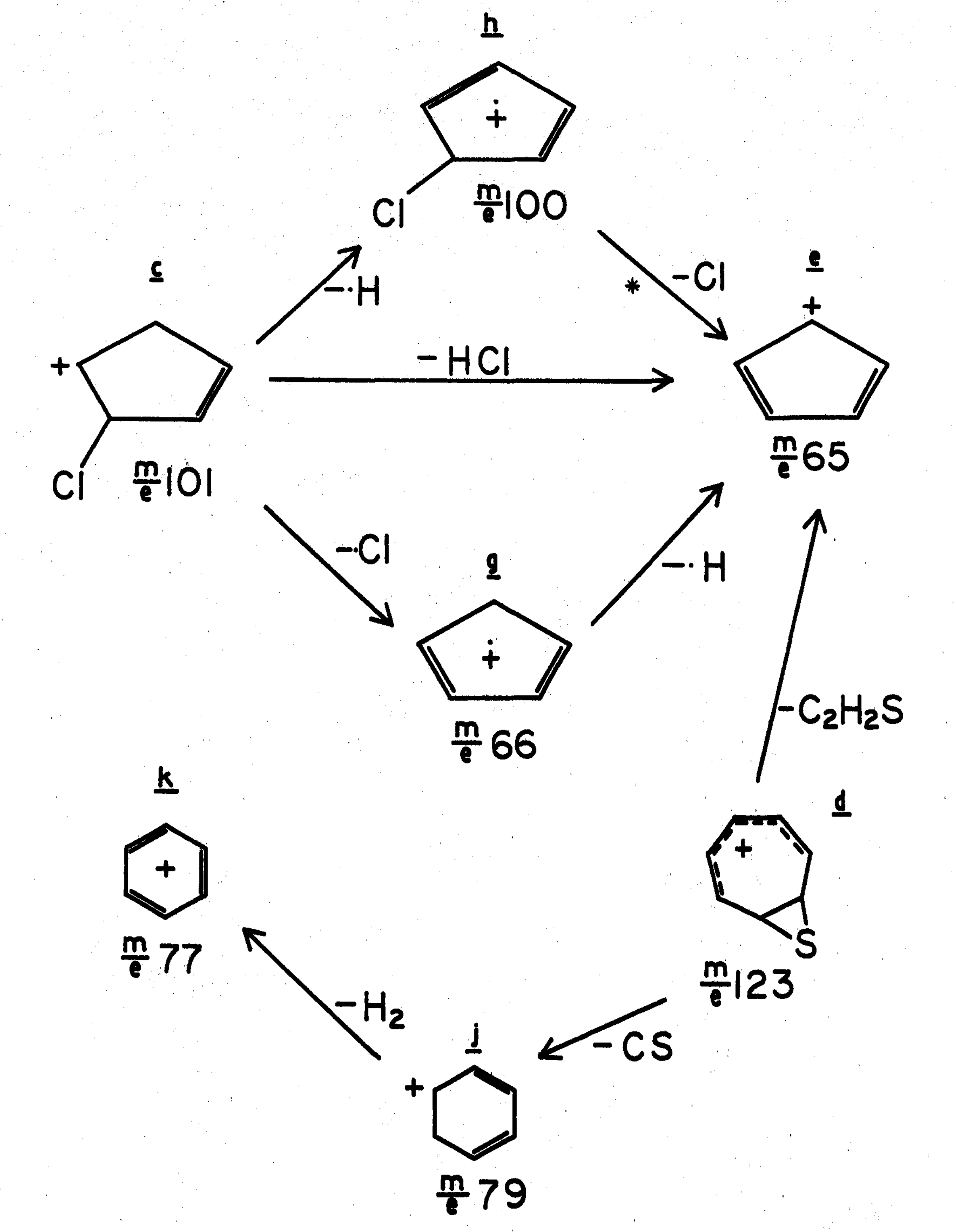
23)



24)

The further fragmentation of *c*, *d*, and *e* is outlined in Scheme 3.3. Ion *c* loses HCl all at once or stepwise to form ions *e*, *g*, and *h*. Ion *d* may lose CS to give *j* which behaves in a manner characteristic of the ($C_6H_7^+$) ion (9). It was found in Section 2 that compounds with a low C:H ratio lost CS readily and, therefore, this loss from *d* ($C_7H_7S^+$) is not surprising. The ions at $\frac{m}{e}$ 45 and $\frac{m}{e}$ 47 are probably formed by several routes involving the breakdown of higher mass ions containing sulfur.

Compounds VIII and IX are isomers. They undergo some similar fragmentations and their spectra have many peaks in common. The molecular ion of both compounds ($\frac{m}{e}$ 194) loses a chlorine atom to give a peak at $\frac{m}{e}$ 159. This ion (M^+-Cl) then loses HCl to form an ion at $\frac{m}{e}$ 123 or SH_2 to give an ion found at $\frac{m}{e}$ 125. Both compounds lose CS from the


h
Cl
m/e 100
c
−·H
−Cl
∗
e
−HCl
Cl
m/e 101
m/e 65
−Cl
g
−·H
m/e 66
−C₂H₂S
k
d
S
m/e 77
m/e 123
−H₂
j
−CS
m/e 79

SCHEME 3.3

(M-HCl_2) ion to give the ($C_6H_7^+$) ion, and C_2H_3Cl from the (M-Cl) ion to form ($C_5H_5S^+$). The two compounds (VIII and IX) do not fragment identically since the sulfur atom in VIII is lost mostly as SH_2 while the sulfur in IX is lost mostly as C_2H_2S. In the mass spectrum of VIII the peaks at $\frac{m}{e}$ 65, $\frac{m}{e}$ 66, $\frac{m}{e}$ 77, $\frac{m}{e}$ 79, and $\frac{m}{e}$ 100 are very weak while these same peaks in the mass spectrum of IX are intense. This would seem to indicate that in their fragmentation the two isomers VIII and IX do not pass through a common structural ion.

b) 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane-8-Oxide

In order to determine the effect upon the fragmentation pattern of changing the oxidation state of the bridging sulfur atom the sulfoxide analogue of IX, 3,5-dichlorotricyclo[2,2,1,$1^{2,6}$]-8-thiaoctane-8-oxide (X), was studied. Like IX the sulfoxide can lose a chlorine atom from its molecular ion, but it can also lose SO from the molecular ion to form ion o as shown in Scheme 3.4. The compositions of the major ions were verified by high resolution mass spectrometry (Table 16) but unfortunately it was not possible to mass match ion o ($\frac{m}{e}$ 162) since its mass is very similar to that of the perfluorokerosene ion at $\frac{m}{e}$ 162.

The fragmentation of ion p, as shown in Scheme 3.5, is analogous to that of the (M-Cl) ion of compound IX. Ion p loses C_2H_2SO and HCl in either order to form the final ion e in a manner similar to that of a. It also loses $C_5H_5\cdot$ to form ion v, which is analogous to ion f in the spectrum of IX. In analogy with the loss of CS from the (M-HCl_2) ion of IX, the (M-HCl_2) ion of X may lose CSO to form ion j.

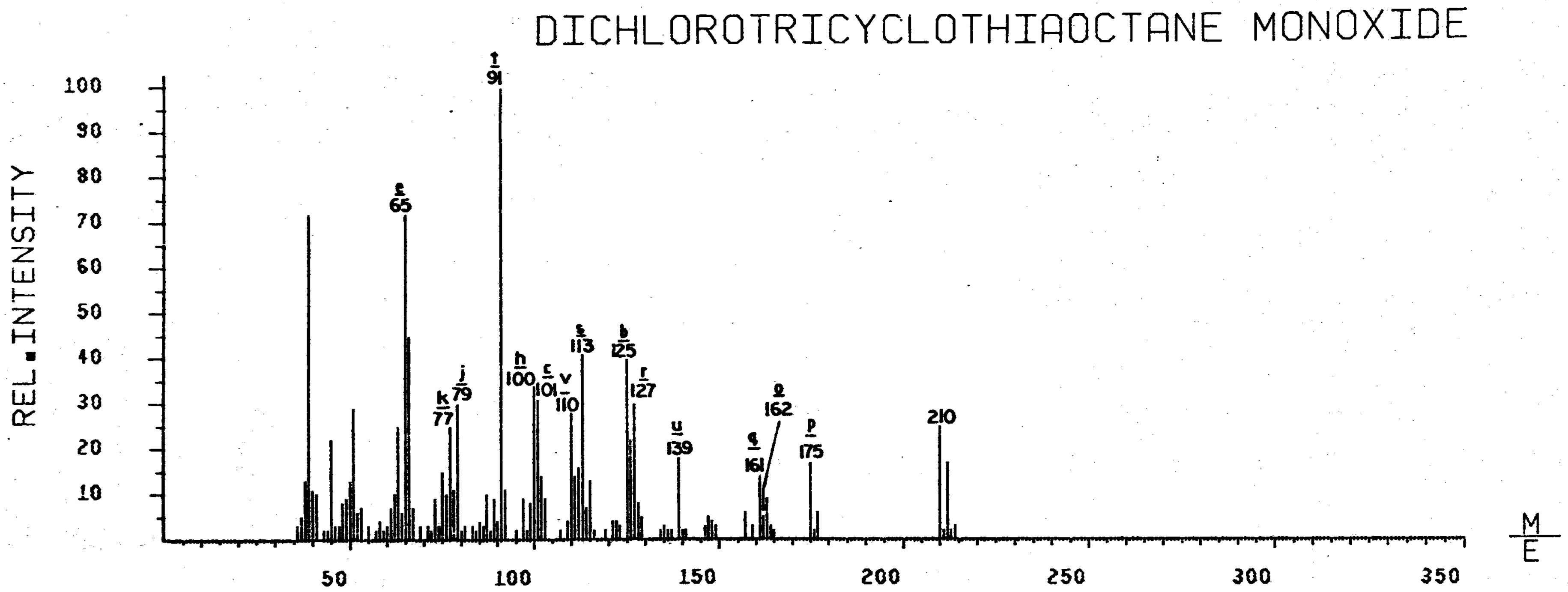
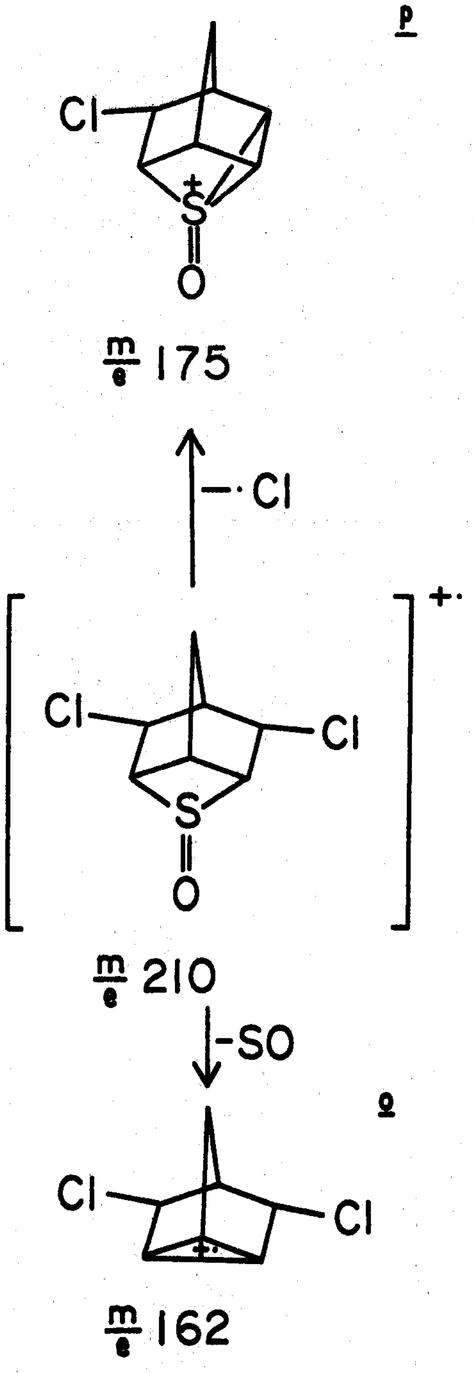


Figure 16: The Mass Spectrum of 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane-8-Oxide

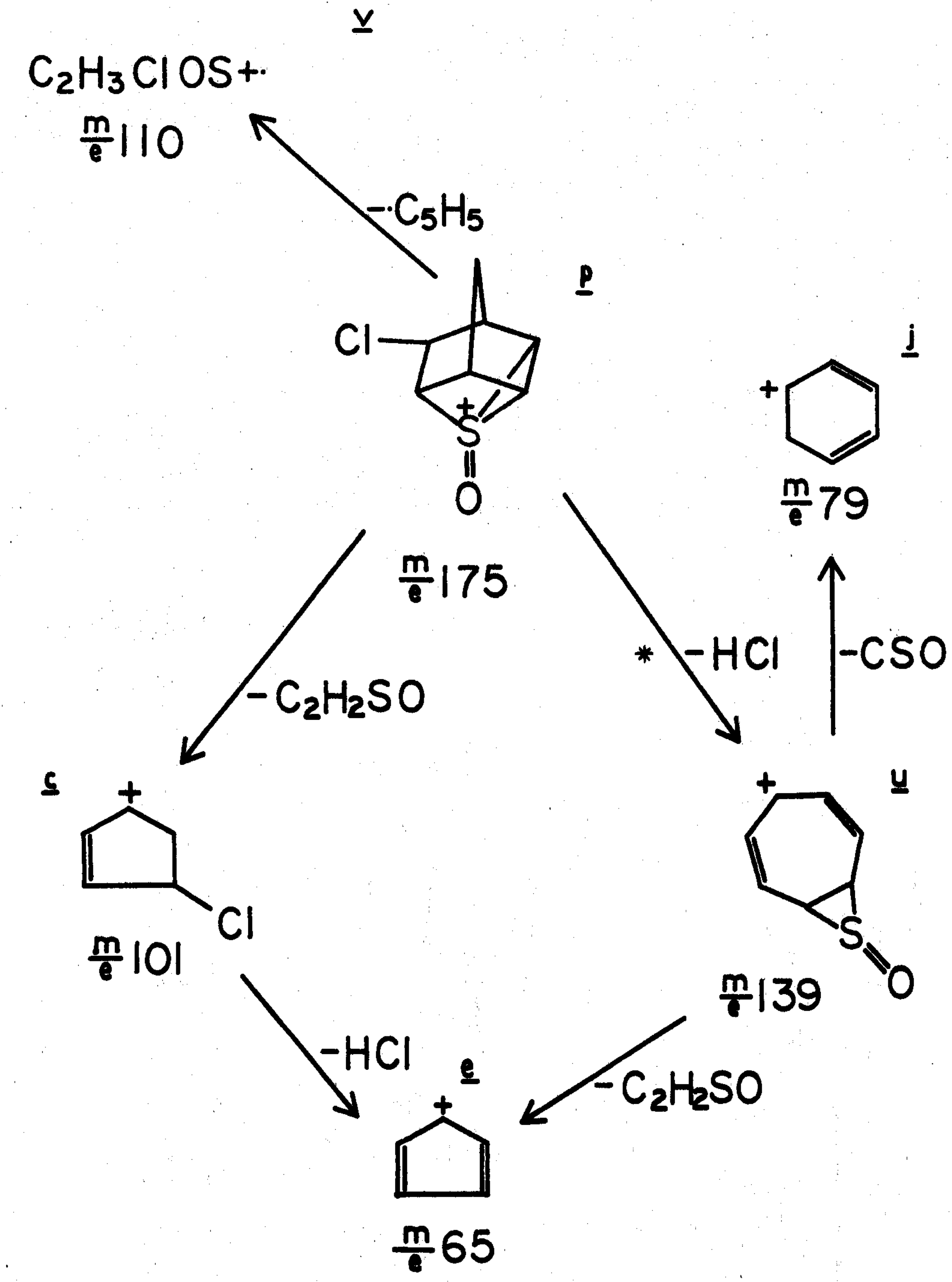
TABLE 16

Compositions of the Major Ions in the Mass Spectrum of 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane-8-Oxide

$\frac{m}{e}$	Composition	$\frac{m}{e}$	Composition
210	$C_7H_8Cl_2OS$	102	$C_5H_5Cl^{37}$
175	C_7H_8ClOS	91	C_7H_7
161	$C_7H_7Cl_2$	79	C_6H_7
139	C_7H_7OS	77	C_6H_5
129	$C_7H_8Cl^{37}$	65	C_5H_5
126	C_7H_7Cl	63	C_5H_3
125	C_7H_6Cl	51	C_4H_3
115	$C_6H_6Cl^{37}$	45	CHS
110	C_2H_3ClOS	39	C_3H_3
103	$C_5H_6Cl^{37}$		

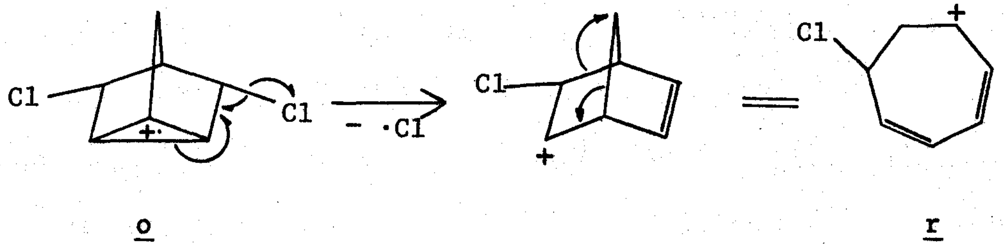


SCHEME 3.4


v
$C_2H_3ClOS^{+\cdot}$
m/e 110
$-\cdot C_5H_5$
p
Cl
S
O
m/e 175
j
m/e 79
* −HCl
−CSO
$-C_2H_2SO$
c
Cl
m/e 101
u
S
O
m/e 139
−HCl
e
$-C_2H_2SO$
m/e 65

SCHEME 3.5

Besides fragmenting by routes which are common to IX, the tricyclic sulfoxide also loses SO from the molecular ion to yield ion o which dissociates as shown in Scheme 3.6. Ion o probably has a nortricyclyl structure which undergoes ring expansion as shown below with loss of H· and Cl· to form ions q and r, respectively.

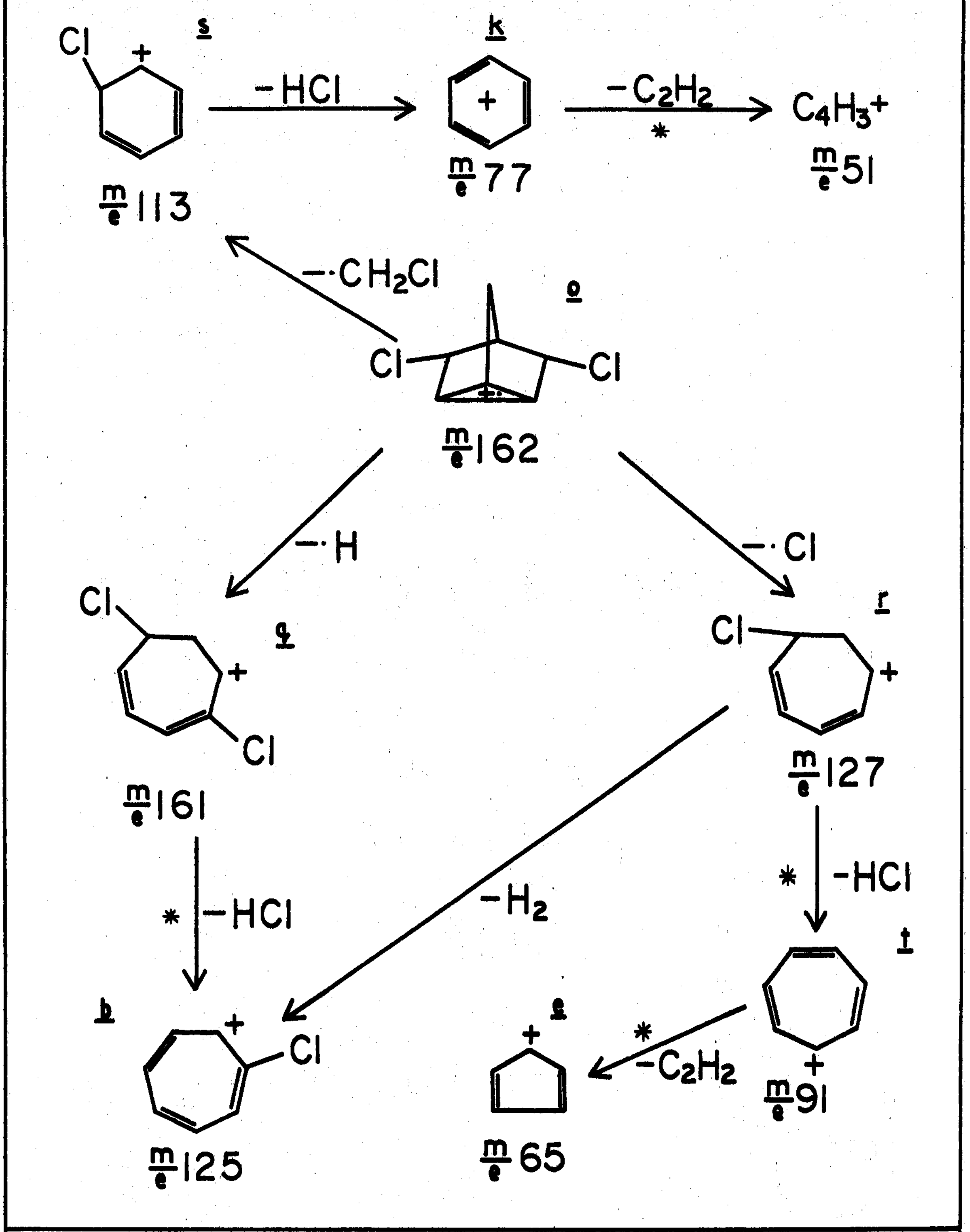


Both q and r lose HCl to give b and t, respectively. The transition r to t to e is supported by the presence of metastable peaks (Table 17). Just as t is a major ion in the spectrum of nortricyclyl chloride (52) and nortricyclyl bromide (53), so it is a major ion in the spectrum of X. Ion o also loses $\cdot CH_2Cl$ to form s just as nortricyclyl chloride can lose $\cdot CH_2Cl$ (52) and nortricyclyl bromide can lose $\cdot CH_2Br$ (53). Ion s then loses HCl to form k, a phenyl ion, whose fragmentation was discussed in Section 2. These two similarities between nortricyclyl chloride, nortricyclyl bromide, and X support the belief that, on losing SO from the molecular ion, X can assume a nortricyclyl structure.

TABLE 17

Metastable Transitions of 3,5-Dichlorotricyclo [2,2,1,$1^{2,6}$]-8-Thiaoctane-8-Oxide

Observed	Transformation	Calculated
110.5 ± .5	175 → 139	110.4
98.0 ± 1.0	161 → 125	97.0
	101 → 100	99.0
65.2 ± .2	127 → 91	65.2
46.5 ± .1	91 → 65	46.4
33.9 ± .1	77 → 51	33.8

s
Cl
+
m/e 113
−HCl
k
+
m/e 77
−C2H2
*
C4H3+
m/e 51
−·CH2Cl
o
Cl
Cl
m/e 162
−·H
−·Cl
Cl
q
+
Cl
m/e 161
r
Cl
+
m/e 127
*
−HCl
−H2
*
−HCl
t
h
+
Cl
m/e 125
e
+
m/e 65
*
−C2H2
+
m/e 91

SCHEME 3.6

c) 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane-8,8-Dioxide (XI)

The fragmentation of XI has features similar to those of both the sulfide and sulfoxide. The molecular ion of the sulfone eliminates a chlorine atom as do the molecular ions of the sulfide and sulfoxide, and it loses SO_2 in analogy with the loss of SO by the sulfoxide. Ion o, which is formed by the loss of SO_2 as illustrated in Scheme 3.7, behaves in a manner analogous to that observed when it was formed from compound X. The compositions of the major ions were verified by high resolution mass spectrometry and are listed in Table 18.

The dissociations undergone by ion x as shown in Scheme 3.8 resemble those of the sulfide. The (M-Cl) ion loses $C_2H_2SO_2$ and HCl to form ions c and e, respectively. If XI behaved in a manner completely analogous to that of IX and X then the (M-Cl) ion would lose HCl and $C_2H_2SO_2$ in that order. It doesn't undergo this loss, however, because SO_2 is ejected too readily. Instead the (M-Cl) ion loses SO_2 to form r which then loses HCl to give t, a tropylium ion. The loss of C_2H_2 by t to give e is verified by the presence of a metastable peak (Table 19). The ion at $\frac{m}{e}$ 91 (t) is the base peak in the spectra of both X and XI.

The formation of y probably involves extensive rearrangement with oxygen migration and the subsequent loss of SO and HCl. Ion y may then lose CO to form j. Oxygen migration has been reported in the spectra of dimethyl sulfone (21), aryl sulfones (21, 23, 26, 28) and sulfolene (25).

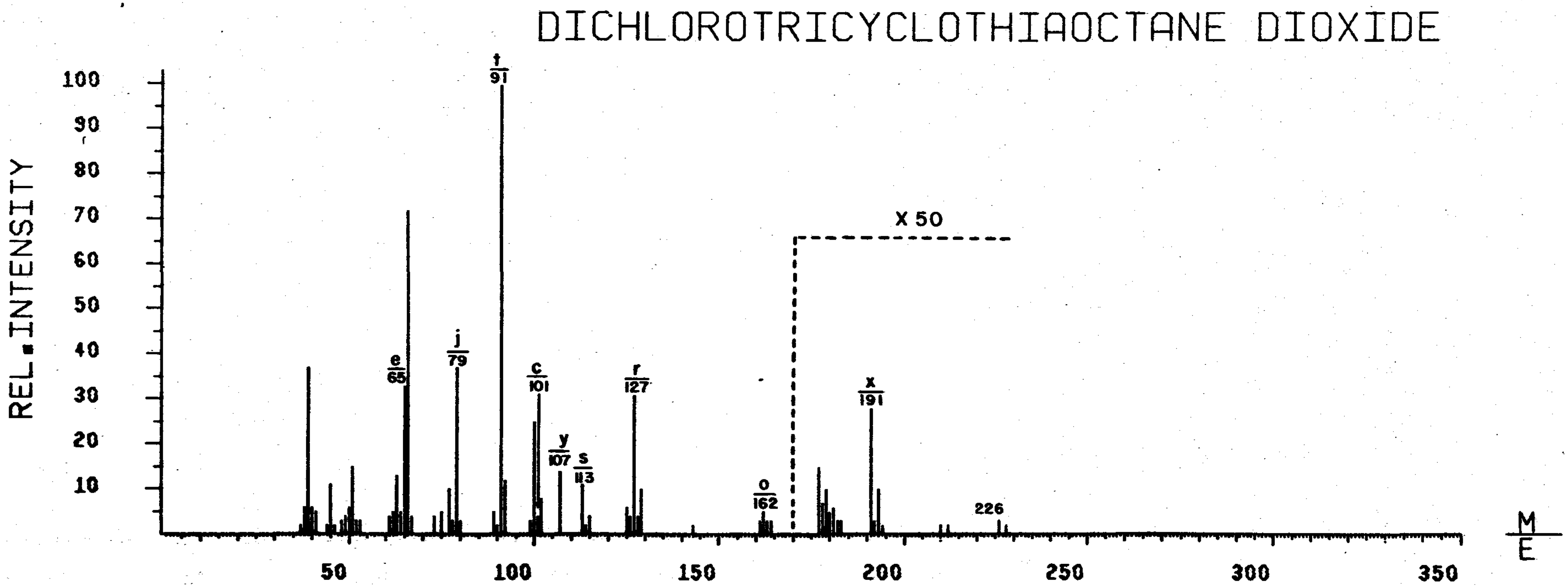


Figure 17: The Mass Spectrum of 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane-8,8-Dioxide

TABLE 18

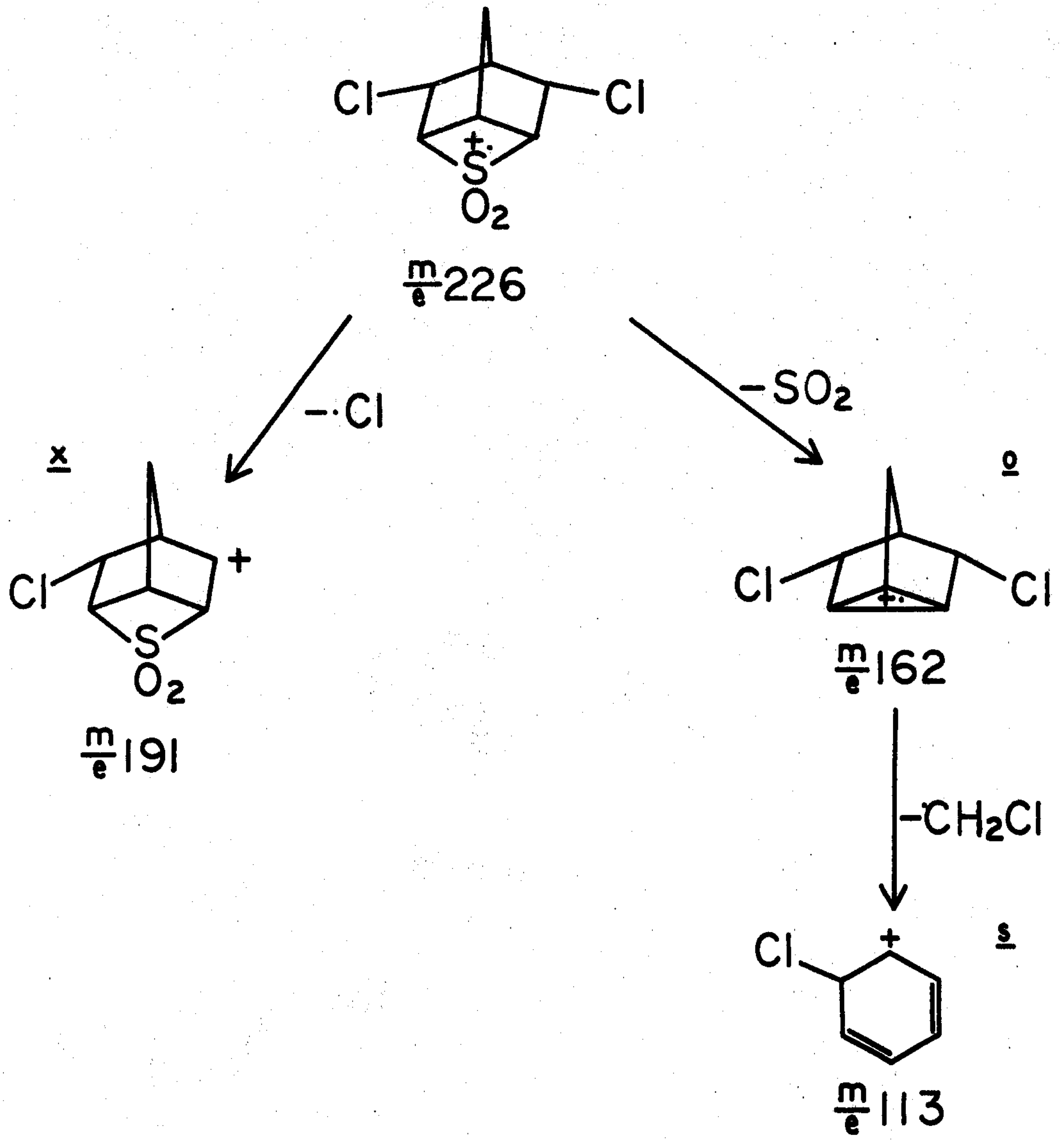
Compositions of the Major Ions in the Mass Spectrum of 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$]-8-Thiaoctane-8,8-Dioxide

$\frac{m}{e}$	Composition	$\frac{m}{e}$	Composition
191	$C_7H_8ClO_2S$	100	C_5H_5Cl
164	$C_7H_8Cl^{35}Cl^{37}$	91	C_7H_7
127	C_7H_8Cl	79	C_6H_7
113	C_6H_6Cl	66	C_5H_6
107	C_7H_7O	65	C_5H_5
101	C_5H_6Cl	39	C_3H_3

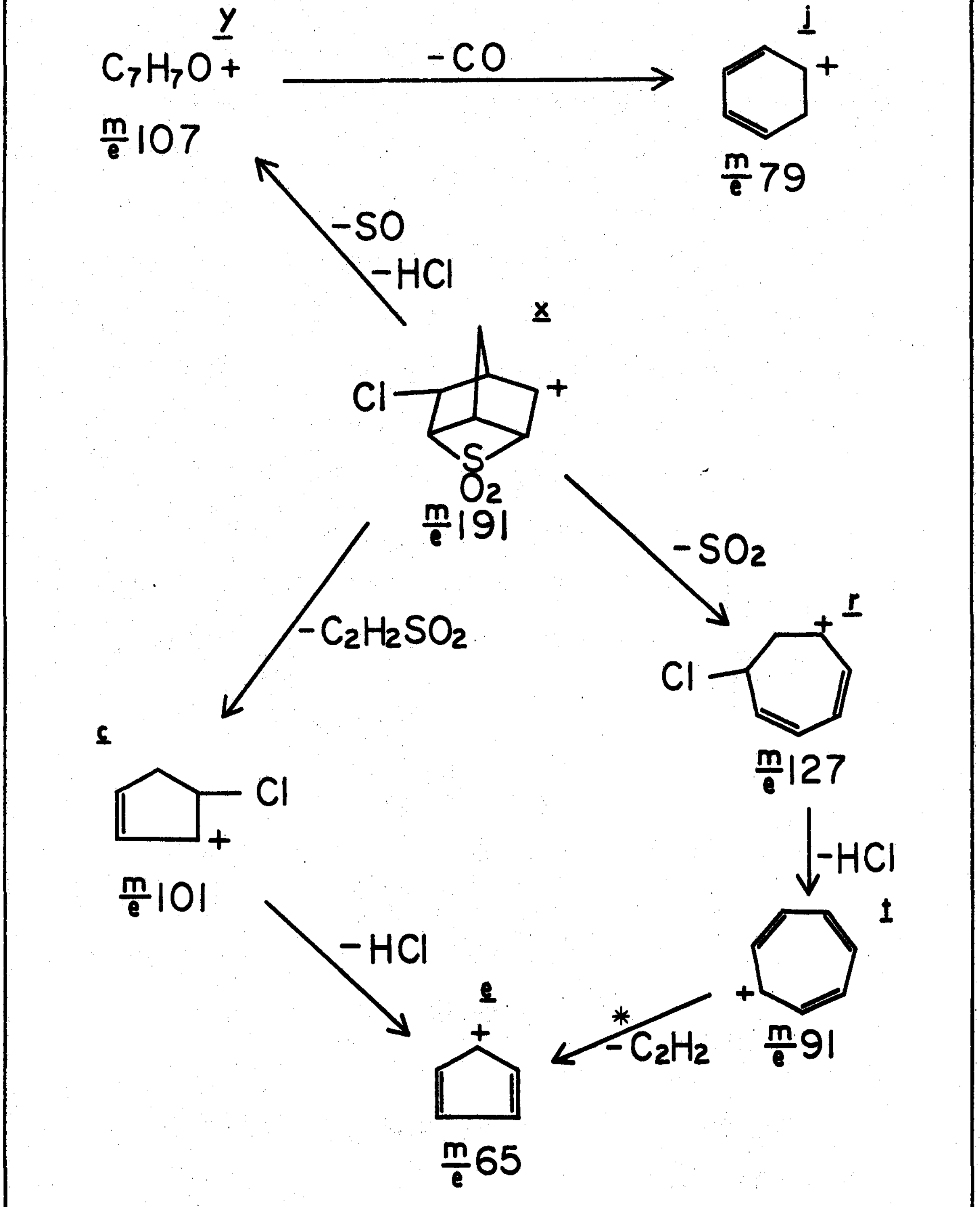
TABLE 19

Metastable Transitions of 3,5-Dichlorotricyclo[2,2,1,$1^{2,6}$] -8-Thiaoctane-8,8-Dioxide

Observed	Transformation	Calculated
46.5 ± .1	$91 \longrightarrow 65$	46.4



SCHEME 3.7


y
C₇H₇O+
m/e 107
-CO
j
m/e 79
-SO
-HCl
x
Cl
S
O₂
m/e 191
-SO₂
r
Cl
m/e 127
-C₂H₂SO₂
c
Cl
m/e 101
-HCl
-HCl
t
m/e 91
*
-C₂H₂
e
m/e 65

SCHEME 3.8

The high mass end of the spectrum of XI is very weak; in fact, the molecular ion is too weak to determine its exact mass. The differences between the mass spectra of XI and the other tricyclic compounds are due to the ease with which sulfur leaves the molecule when this sulfur atom is in the form of a bridging sulfone. For X and XI there are no major ions containing sulfur, oxygen, or chlorine below $\frac{m}{e}$ 100 except for $\frac{m}{e}$ 45; the $C_7H_7^+$ ion is the base peak for both compounds. The major hydrocarbon ions, except the (M-X) ion ($\frac{m}{e}$ 93), of nortricyclyl chloride (<u>52</u>) and nortricyclyl bromide (<u>53</u>) are identical with those of the norbornyl sulfone and sulfoxide; therefore, it appears likely that they all pass through a common ion structure. The three compounds all lose a chlorine atom from the molecular ion and the heteroatoms are then lost as stable molecules to form hydrocarbon ions.

Section 4:

Conclusions:

The mass spectra of three groups of β,β'-disubstituted sulfur and selenium compounds have been studied. The molecular ion of each compound, except for the diiodo compound in Section 2, is visible in its low resolution mass spectrum. Each loses a substituent as a radical from the molecular ion, although the sulfoxide and sulfones can also lose a sulfur-containing fragment before a substituent leaves. The substituents, except for the cyano group, have little effect on the fragmentation path. When a substituent leaves, it is proposed that the sulfides and selenides form a third bond so that the positive charge is localized on the bridging heteroatom and stable sulfonium and selenonium ions are created. Changing the heteroatom from sulfur to selenium has little effect on the fragmentation routes. When the sulfide becomes a sulfoxide new routes of dissociation are also observed. The fragmentation pattern is noticeably different when a sulfone replaces a sulfide. This difference occurs because SO_2 in a sulfone is lost more easily than the sulfur in a sulfide.

The compounds of Section 1 contain two heteroatoms in a six-membered ring. Compound I is the only compound in this group that has a major ion containing both Group 6 atoms in the low mass end of its spectrum. Analysis of the spectra shows that the heteroatom β to the two chlorine atoms is lost much less easily than the other heteroatom in the ring.

The compounds in Sections 2 and 3 contain sulfur and selenium bridges. These bridging sulfides and the selenide lose SH_2 and SeH_2, respectively. Also, the sulfides in Section 3 easily lose sulfur as part of a carbon-containing fragment. For the sulfoxide and sulfones sulfur is lost directly as SO and SO_2 or accompanied by a carbon fragment. On losing SO and SO_2 the tricyclic sulfoxide and sulfone, respectively, appear to form a nortricyclyl ion. Ring expansion may occur during the dissociation of the compounds in Section 3. The compounds in Sections 2 and 3 have few major sulfur-containing ions at low $\frac{m}{e}$ values. To explain the formation of some of the ions of the sulfur-bridged compounds it is necessary to invoke hydrogen rearrangement.

EXPERIMENTAL

The compounds used in this investigation were obtained from F. Lautenschlaeger of the Dunlop Research Centre, Sheridan Park, Ontario, Canada.

The low resolution spectra were run on the Hitachi Perkin-Elmer RMU-6A Mass Spectrometer at 80 eV. The high resolution work was done on the Consolidated Electrodynamics Corporation Mass Spectrometer 21-110B. In this instrument the spectrum is focused on a photographic plate or on a slit. If the spectrum is focused on a slit the ion peaks can be displayed on the screen of an oscilloscope. The compounds were introduced by solid introduction into a reservoir kept at about 180°C. The source was about 200°C; the ionizing voltage was 70 eV and the ionizing current was 150 microamperes. The high resolution spectra were recorded on type Q2 thin glass photographic plates manufactured by Ilford Photographic Materials, Ilford Ltd., Ilford, England. The following method was used for developing the plates.

1) Rinse developing tank (see diagram).
2) Turn N_2 bubbles on.
3) Put plate into tank.
4) Add developer (Kodak Microdol X) for 10 minutes then drain off.
5) Add Stop bath (5% HOAc) for 1 minute then drain off.
6) Add Fixer (Kodak Rapid Fixer) for 5 minutes then drain off.

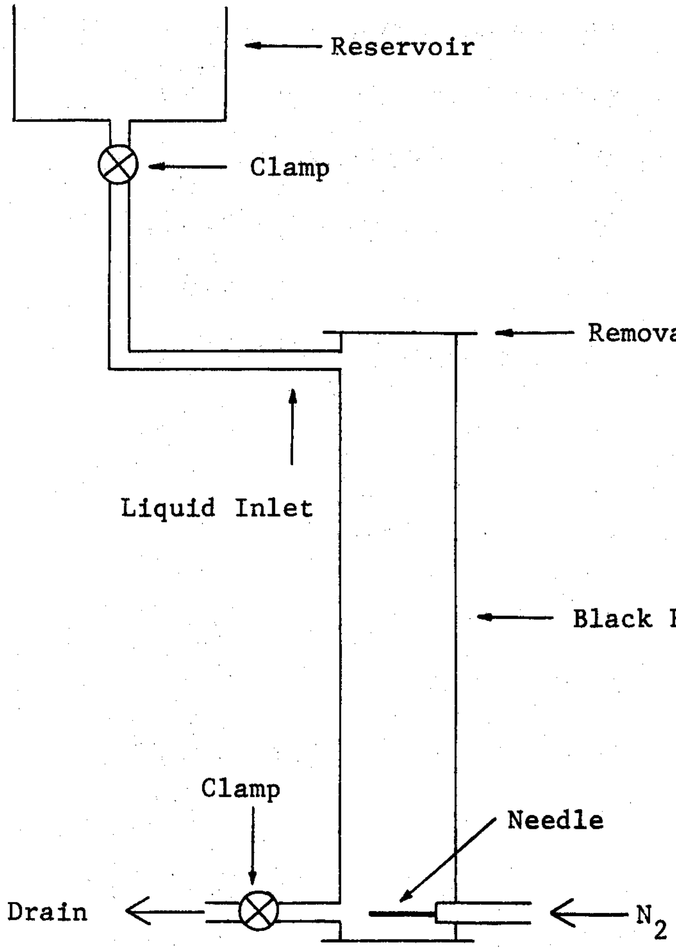
7) Add Hypo Clearing agent (1 part concentrated stock solution of Kodak Hypo Clearing Agent and 4 parts water) for 5 minutes then drain off.

8) Add distilled water for 2 minutes then drain off.

9) Turn off N_2.

10) Remove plate and rinse with distilled water and allow to dry.

<u>Diagram of Developing Tank</u>



The line distances on the photographic plate were examined using a Gaertner Special Spectrum Linear Comparator and recorded by a Datex APR-I Automatic Plate Reader System. The Automatic Plate Reader System automatically collects the data from the comparator and records it on magnetic tape in IBM compatible format. When the data from the comparator was not recorded automatically the most intense point of each line was determined using an Electronics Associates Inc. Digital Voltmeter and the distances were read from the comparator. A computer program developed by Dr. L. Baczynskyj was used to determine the compositions of the lines whose positions were manually recorded. The standard used in all cases was perfluorokerosene obtained from K and K Laboratories, Plainview, New York.

SUMMARY

The mass spectra of a disubstituted dithiane, oxathiane, and oxaselenane, and of some disubstituted sulfur-bridged cyclooctanes and norbornanes have been determined. High resolution mass spectrometry has been used to examine the spectra of most of the compounds in order to determine the composition of the major fragment ions. Some common fragmentation patterns of these compounds under electron impact have been proposed.

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