

Mass Spectra of Dimethyl- and Ethylsubstituted Thietanes

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Abstract

The mass spectra of dimethyl- and ethylsubstituted thietanes (totally six isomers) have been investigated. They all show fragmentations due to four center cleavage, specific rearrangements and loss of substituent(s). The fragmentation patterns divide them into three different groups, each group with its own characteristics: one group with 2- and 3 ethylthietane, a second group with 2,2-dimethyl- and 3,3-dimethylthietane and a third group with 2,3-dimethyl- and 2,4-dimethylthietane. The resemblance between the spectra in each group is evident, but each of the six isomers has a unique mass spectrum.

INTRODUCTION

A variety of methods to synthesize thietanes has been given in a review article by Trost et al.¹⁾ We have chosen the method described by Searles et al.^{2,3)} to synthesize the dimethyl- and ethylthietanes.

Only a few mass spectral analysis of thietane and substituted thietanes have been made previously^{1,4,5)}. The data presented here is the first systematical study of all thietane isomers with the molecular formula $C_5H_{10}S$. Scala and Colon⁴⁾ have presented a four center cleavage for the thietane ring ($m/z = 74$) based upon earlier knowledge of fragmentation of fourmembered ring organic compounds. In the case of our thietane isomers ($m/z = 102$) the described four center cleavage gives rise to dominant peaks, though not always to the base peak (see below).

The molecules studied were: 3-ethylthietane, 2-ethylthietane, 2,4-dimethylthietane, 2,3-dimethylthietane, 3,3-dimethylthietane and 2,2-dimethylthietane, all with the empirical formula $C_5H_{10}S$ ($m/z = 102$). The mass spectra of 2,4-dimethylthietane¹⁾ and 2,2-dimethylthietane⁵⁾ have been presented earlier. A comparison with the mass spectra of methylsubstituted tetrahydrothiophene and thiane, which also have the empirical formula $C_5H_{10}S$, has been made observing earlier presented data⁶⁾.

The reason to investigate the thietanes was raised when observing mass spectra from GC-MS investigations of anal gland secretions from species of the Mustelidae family (Dr Göran Odham, University of Lund, Sweden, personal communication). Several natural occurring substances showed in several cases mass spectra similar to that of 2,2-dimethylthietane, but not identical⁵⁾.

RESULTS AND DISCUSSION

It is evident from Figures 1-6 that the fragmentation patterns of the isomers can be divided into three separate groups each with two isomers. The presentation of the data will therefore follow accordingly.

Ethylsubstituted thietanes: Four center cleavage, loss of methyl and ethyl radicals are the dominating fragmentation modes. The other peaks in the spectra can be explained by loss of alkyl, alkenyl and sulfur containing radicals from the rearranged molecular ion or by loss of hydrogen sulfide, ethene and propene (see Schemes and Figures 1 and 2).

2,4- and 2,3-dimethylthietane: Also here the four center cleavage is the dominating fragmentation mode and most of the ion current is carried by the fragments containing the sulfur atom. Losses of a methyl radical and, after rearrangement, alkyl, alkenyl and sulfur containing radicals are observed. In both mass spectra the $m/z = 60$ is the base peak (see Schemes and Figures 3 and 4). The mass spectra of 2,4-dimethylthietane and 2,3-dimethylthietane have been taken on a mixture of isomers (optical isomers and cis-trans isomers). The cis and trans isomers of 2,4-dimethylthietane have been shown to be superimposable in MS¹).

3,3- and 2,2-dimethylthietane: Four center cleavage is still the most important fragmentation mode, but here only a limited part of the ion current is carried by the sulfur containing fragment. The limited possibilities for rearrangement of 3,3-dimethylthietane strongly contributes to the dissimilarities in the mass spec-

tra of these two compounds. As in the case with the other thietanes also these lose a methyl radical from the molecular ion. The rearranged molecular ion fragmentates both by loss of alkyl and sulfur containing radicals. Fragmentation of hydrogen sulfide and ethene occurs only from 2,2-dimethylthietane (see Schemes and Figures 5 and 6).

Identification of the mass spectra within each group: As outlined above, there are striking resemblance between the mass spectra within each group. Still each isomer has a unique mass spectrum. The easiest way to confirm this is to study the differences in four center cleavage between each pair of isomers (belonging to the same group). Only 2-ethylthietane and 2,2-dimethylthietane have the fragment of $m/z = 74$ in the mass spectra, due to loss of ethene. The fragment $m/z = 56$ is seen in the mass spectrum of 2,3-dimethylthietane but not in the case of 2,4-dimethylthietane due to the configurational differences. Also other fragments can be used to distinguish between the isomers in each group, but these are the most obvious and infallible.

Little attempts have been made to explain the structures of the fragments between $m/z = 40$ and $m/z = 59$ as there are several structure possibilities for each fragments.

EXPERIMENTAL

The methods to synthesize the compounds discussed in this work are known in the literature^{2,3)}. In spite of the low yield in some cases, we have chosen to synthesize the thietanes starting from the corresponding saturated five-carbon diols to make substituted 1,3-dioxane-2-ones with dimethylcarbonate followed by

treatment with dry KSCN under a slow stream of nitrogen giving the thietane. An other method with higher yield has been presented recently^{7,8)} starting with dihalides (corresponding to the diols above). However we found it more convenient to use the diols as they were cheaper to buy or easier to synthesize.

The purity of the thietanes was checked on GC (1% OV-17, column temperature 40 °C), and in single cases also by NMR (JEOL C -60 HL) according to the data given by Trost et al.¹⁾

When investigating the thietanes described above on capillary GC, the values of the retention times for all isomers, except the ethyl substituted thietanes, are close to each other. The values of the retention times of the ethyl substituted thietanes are also close to each other but well separated from the other isomers (longer retention times).

Mass spectral analysis was made on a Varian MAT, model 112 GC-MS equipped with a SCOT column 34 m I.D. 0.5 mm with SE -30 as stationary phase. (Column temperature 60 °C.) Ion source temperature was 240 °C and temperature in separator and interface 230 °C. All the mass spectra were recorded at 70 eV.

The background spectra from column and gas in MS has been subtracted in all cases. However, some small peaks due to impurities can still be seen between $m/z = 80$ and $m/z = 100$ in the case of 2-ethylthietane. This was caused by a non-sulfur containing compound lying close to 2-ethylthietane in GC-MS.

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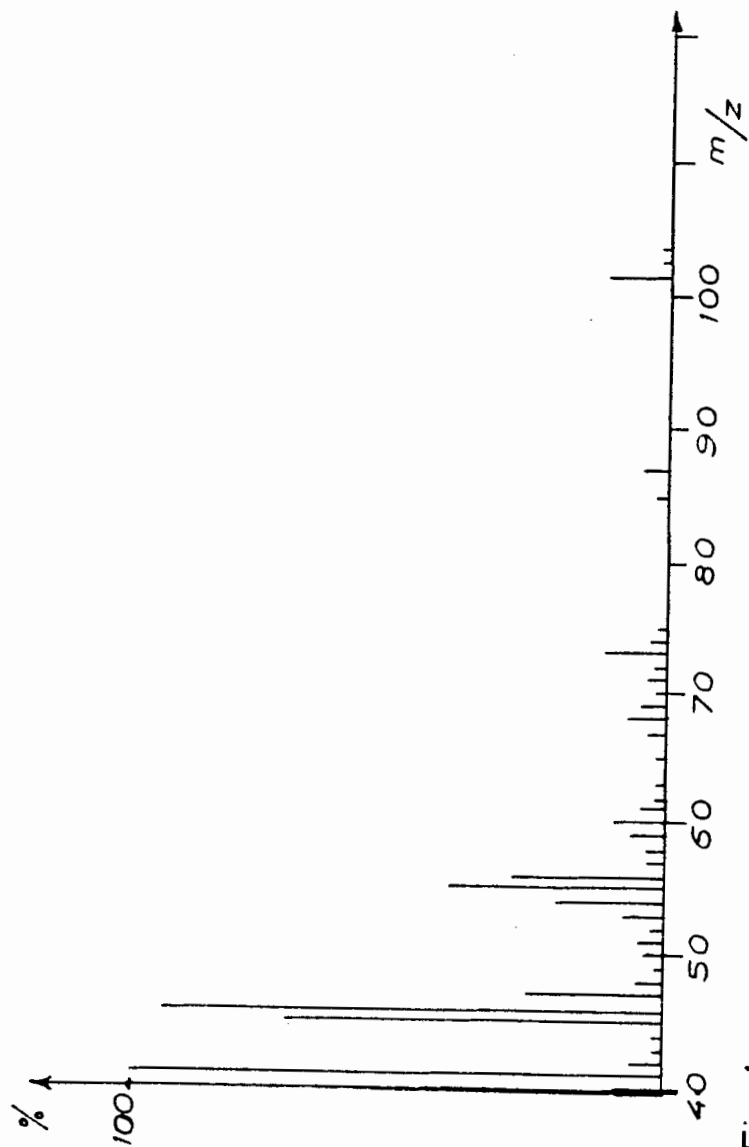
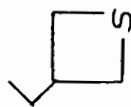


Fig. 1

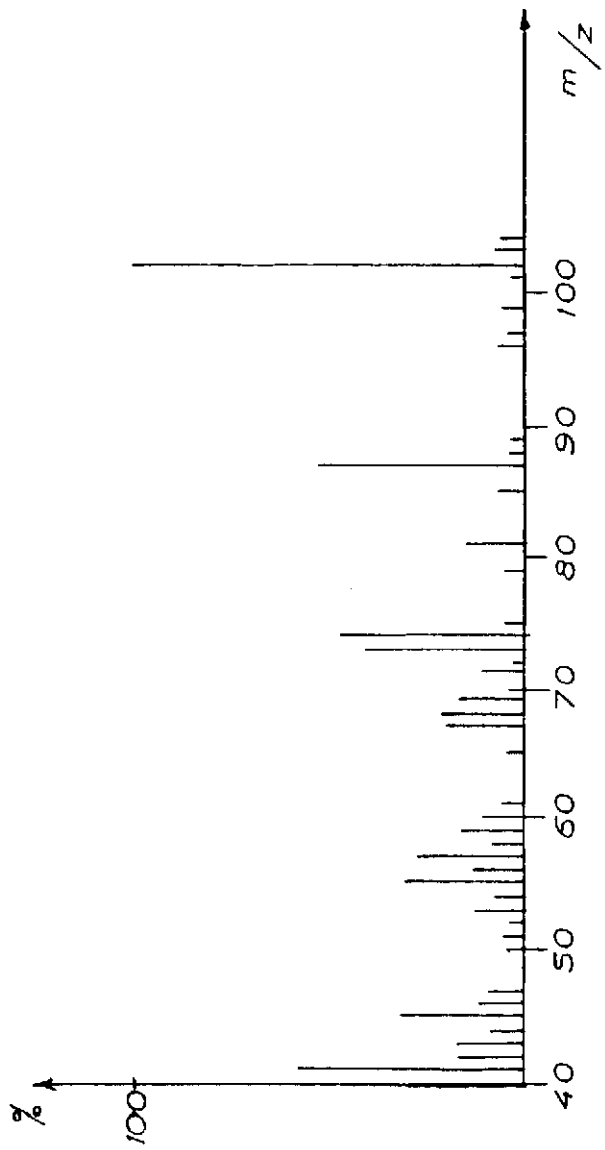
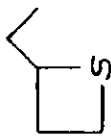


Fig. 2

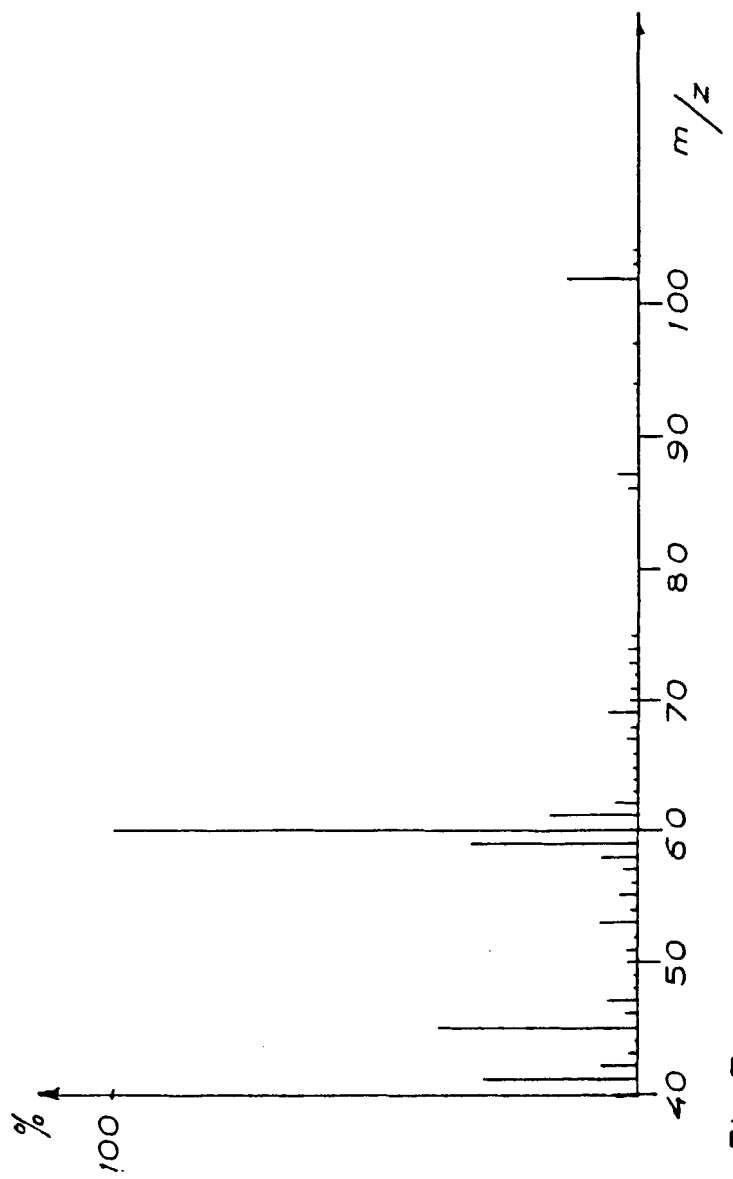
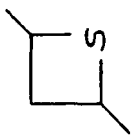
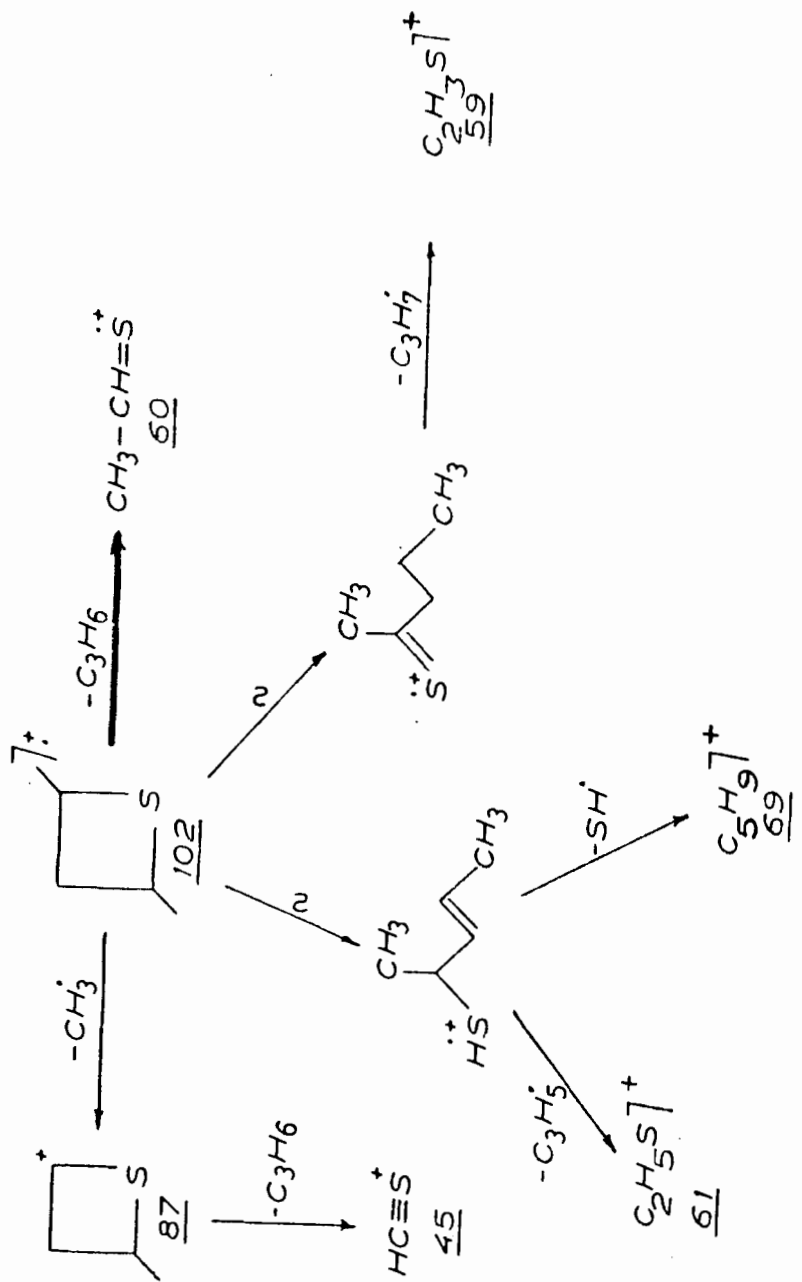


Fig. 3

2,4-DIMETHYLTHIETANE:



SCHEME 3

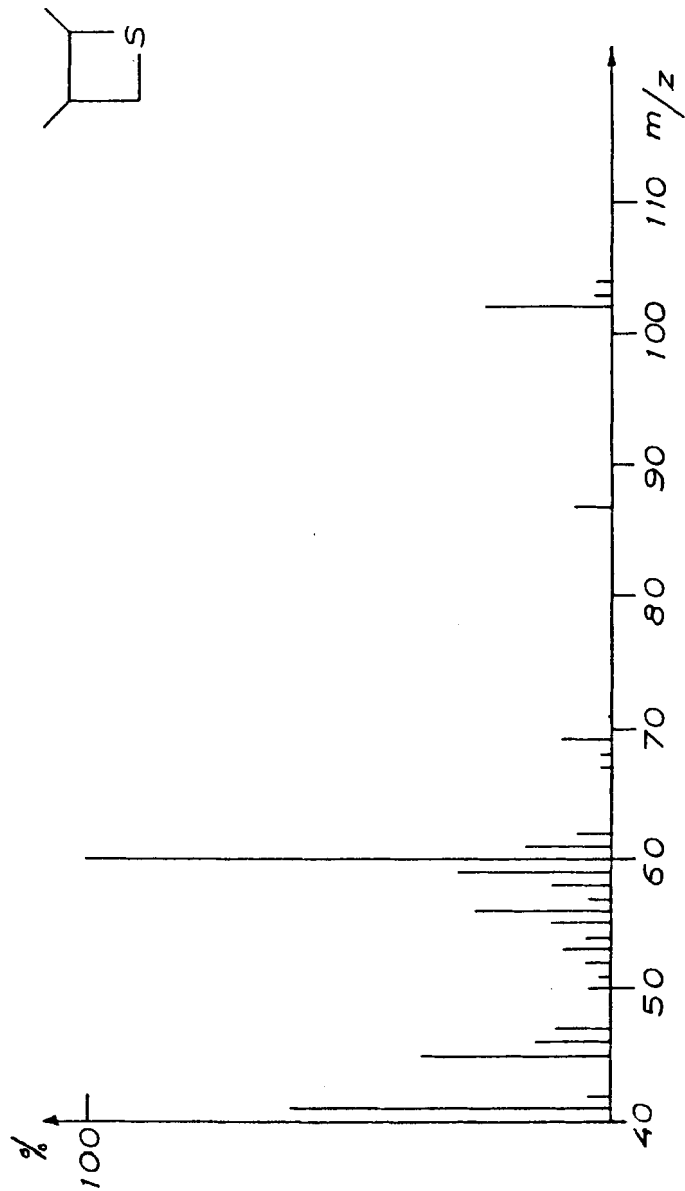


Fig. 4

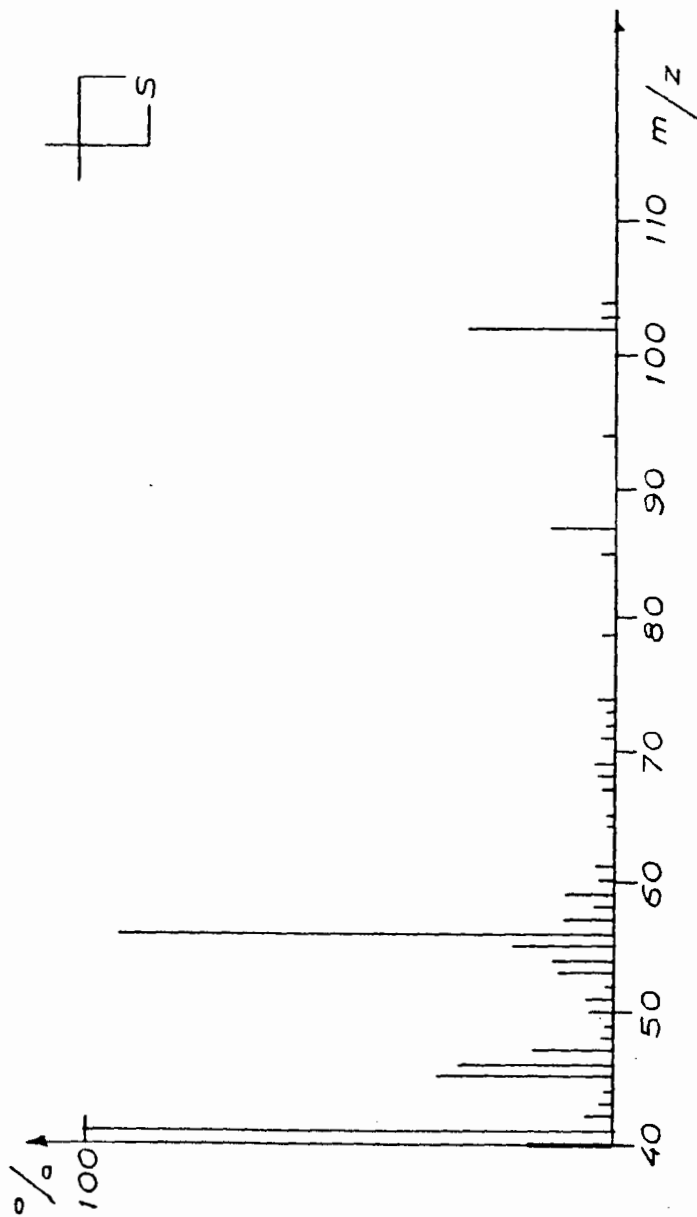


Fig. 5

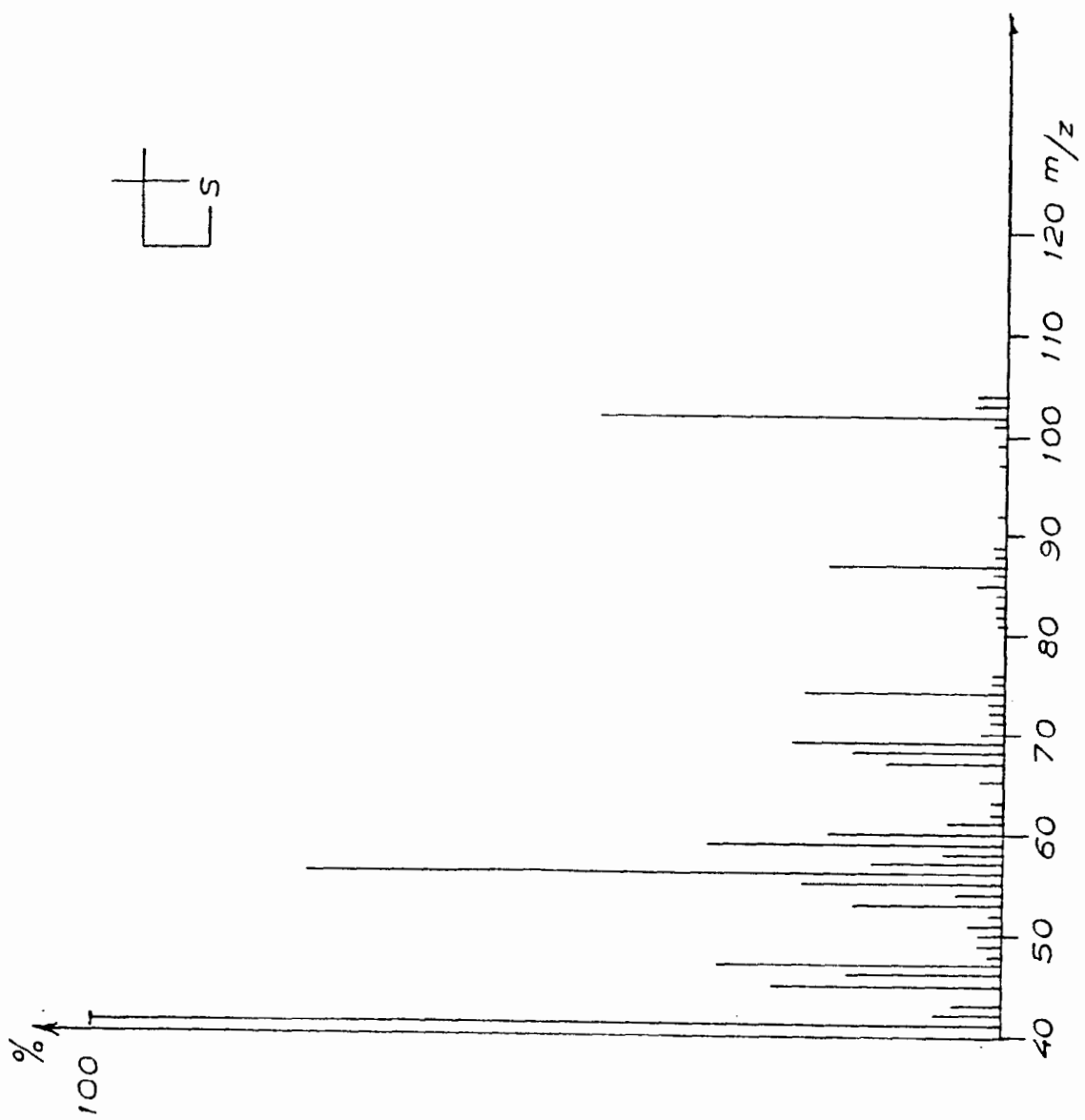
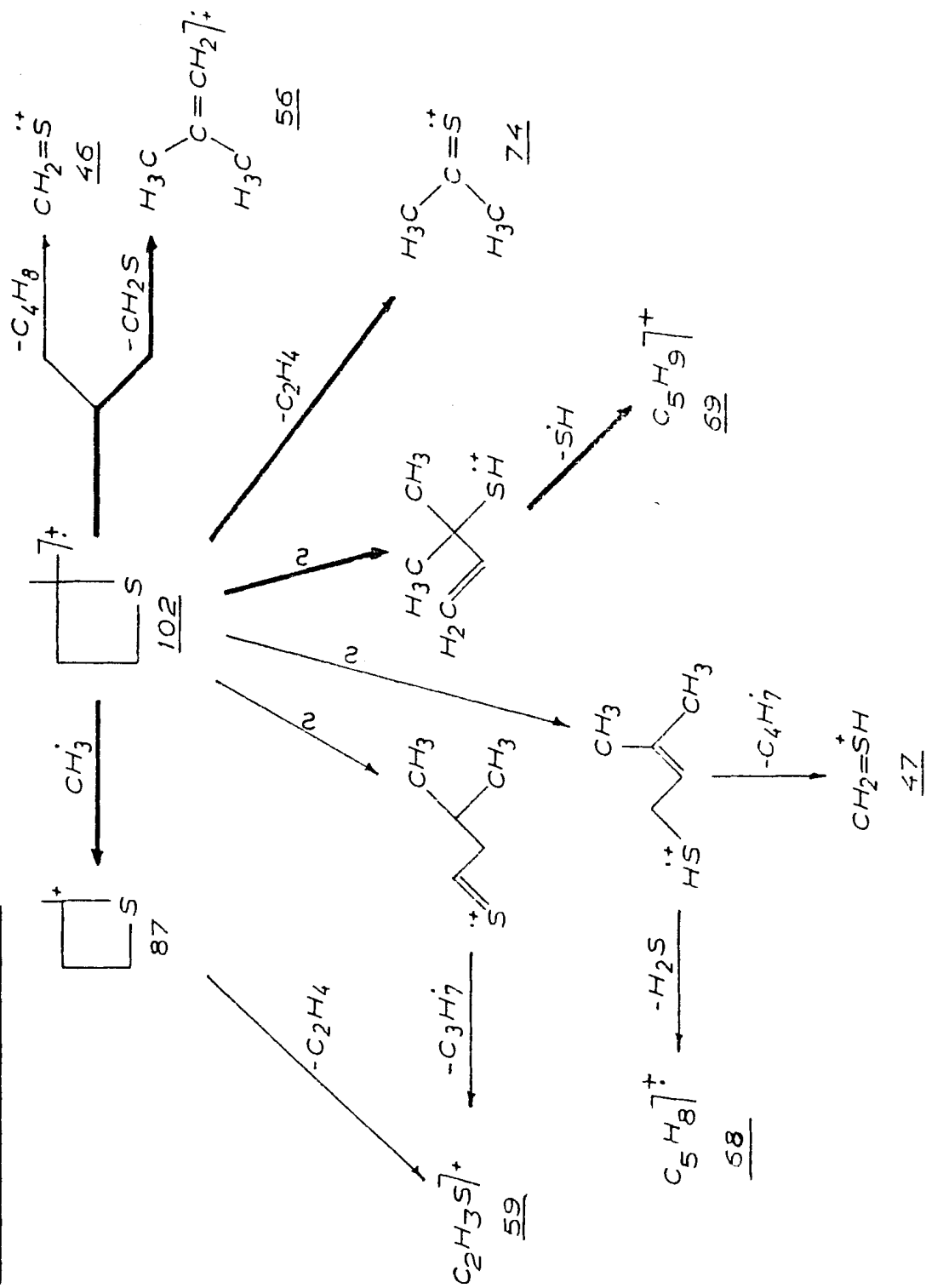


Fig. 6

2,2-DIMETHYLTHIETANE:



SCHEME 6