

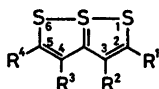
Mass Spectrometric Studies of 1,6,6a λ^4 -Trithiapentalenes Bearing Functional Groups or Alkyl Substituents

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The fragmentation taking place upon electron impact of benzoyl substituted 1,6,6a λ^4 -trithiapentalenes is strongly dependent on the substitution pattern. The loss of a 2-benzoyl group gives rise to a highly stable ion, whereas the stability of the ion formed by loss of a 3-benzoyl group is lower as seen from the more pronounced fragmentation. This difference is not observed in alkyl or methoxycarbonyl substituted trithiapentalenes.

The geometry of the 1,6,6a λ^4 -trithiapentalene nucleus is strongly dependent on substitution as indicated by CNDO calculations¹ and observed experimentally in X-ray studies.^{2,3} Furthermore it is known from chemical evidence, *e.g.* 3-amino-1,6,6a λ^4 -trithiapentalenes show basic properties in contrast to the 2-amino-compound, which is acidic rather than basic,⁴ that the 3 and 4 positions are more electron deficient than the 2 and 5 positions although this difference is not reflected in *ab initio* calculations.⁵ Accordingly the fragmentation upon electron impact of a series of previously studied aryl substituted trithiapentalenes⁶ was found to be dependent on the sub-



stitution pattern. However, significant differences which primarily may be ascribed to the influence of substitution and electron distri-

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bution on the fragmentation patterns of 2- and 3-monophenyl substituted isomers, are smaller than might be anticipated. The predominant difference, the elimination of the phenyl group from the molecular ions, takes place preferentially in the case of 2-substituted compounds, giving rise to an $[M - C_6H_5]^+$ ion of 20 % (in the case of the 3-substituted compound only 3 %).

X-Ray studies⁷ have shown that the introduction of functional groups in the trithiapentalene nucleus gives rise to a higher degree of asymmetry than observed with simple substituents. Therefore it was found of interest to study whether this was reflected in the electron impact induced fragmentation of trithiapentalenes with various groups in the 2 or 3 position.

RESULTS

Three groups of compounds were studied.

1. Benzoyl substituted trithiapentalenes.
2. Alkoxy carbonyl substituted trithiapentalenes.
3. Methyl substituted trithiapentalenes.

1. Benzoyl substituted trithiapentalenes

	R ¹	R ²	R ³	R ⁴
I	COC ₆ H ₅	H	H	H
II	H	COC ₆ H ₅	H	H
III	COC ₆ H ₅	H	H	C ₆ H ₅
IV	H	COC ₆ H ₅	H	C ₆ H ₅
V	COC ₆ H ₅	C ₆ H ₅	H	C ₆ H ₅
VI	C ₆ H ₅	COC ₆ H ₅	H	C ₆ H ₅

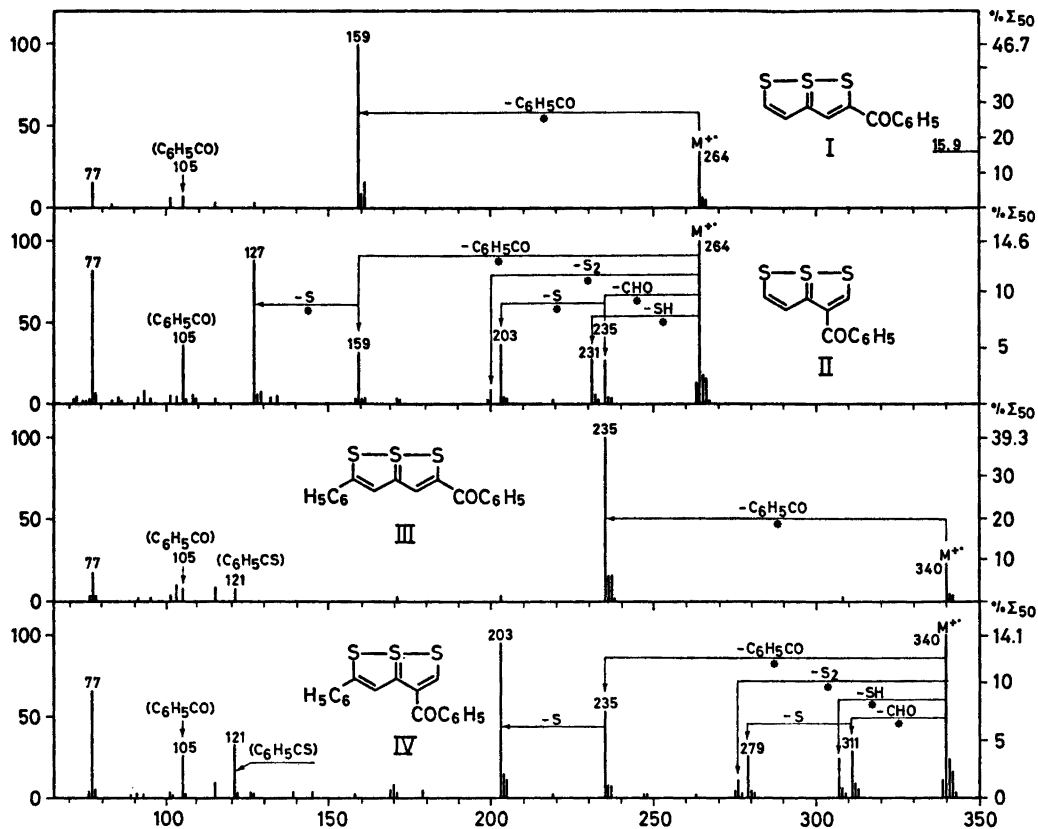


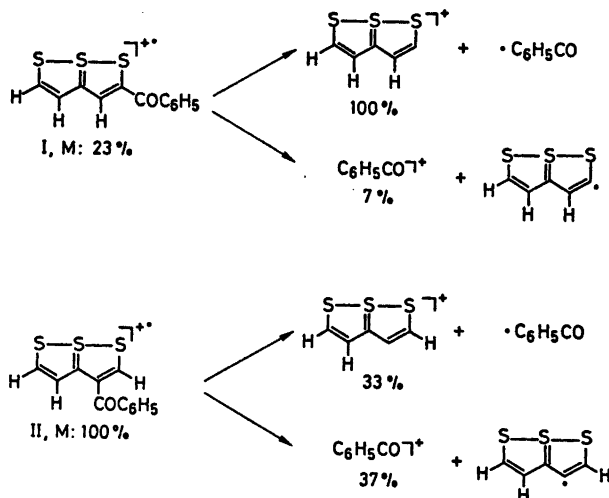
Fig. 1. MS of compound I–IV.

If the phenyl group is replaced by a benzoyl group the position dependent differences in the fragmentation pattern are increased drastically, *cf.* Fig. 1. The only fragmentation mode of importance for I is loss of the 2-benzoyl group with charge retention preferentially on the trithiapentalene moiety yielding the base at m/e 159. The corresponding $[M - C_6H_5CO]^+$ ion possesses a considerable stability carrying 47 % of the total ion current (\sum_{50}).

The corresponding loss of the 3-benzoyl group also takes place in the fragmentation of II. However, in this case charge localization on the benzoyl moiety competes effectively giving rise to a $[C_6H_5CO]^+$ ion (m/e 105) of relatively high abundance (Scheme 1). The $[M - C_6H_5CO]^+$ ion is readily decomposed by elimination of a sulfur atom and is only responsible for 5 % of \sum_{50} .

In addition, other marked differences between I and II exist. Loss of $\cdot CHO$, requiring a skeletal rearrangement, followed by elimination of a sulfur atom takes place only from the molecular ion of II. The same difference was observed for the losses of $\cdot SH$ and S_2 (Fig. 1).

By additional phenyl substitution in the trithiapentalene nucleus it is found that these differences (except for the $\cdot SH$ and S_2 losses, not observed in the spectrum of VI) are repeated and thus primarily may be due to the position of the benzoyl group. In no case is direct elimination of a phenyl group from the molecular ion observed.



Scheme 1.

2. Alkoxy carbonyl substituted trithiapentalenes

	R ¹	R ²	R ³	R ⁴
VII	CO ₂ CH ₃	H	H	H
VIII	H	CO ₂ CH ₃	H	H
IX	CO ₂ CH ₃	H	H	C ₆ H ₅
X	H	CO ₂ CH ₃	H	C ₆ H ₅
XI	CO ₂ CH ₃	C ₆ H ₅	H	H
XII	C ₆ H ₅	CO ₂ CH ₃	H	H
XIII	CO ₂ C ₂ H ₅	H	H	C ₆ H ₅
XIV	H	CO ₂ C ₂ H ₅	H	C ₆ H ₅
XV	CO ₂ CH ₃	C ₆ H ₅	H	C ₆ H ₅
XVI	C ₆ H ₅	CO ₂ CH ₃	H	C ₆ H ₅

The influence of the alkoxy carbonyl group on the fragmentation mode is completely different from that of the benzoyl group and none of the differences found between 2- and 3-benzoyl substituted compounds are reproduced with correspondingly substituted alkoxy carbonyl trithiapentalenes as seen from Fig. 2 where the spectra of compounds VII and VIII are given.

The predominant fragmentation process is also in this group of compounds elimination of the functional group. The resulting [M-COOCH₃]⁺ ions in VII and VIII formally correspond to the [M-C₆H₅CO]⁺ ions in the spectra of I and II, respectively. The [M-COOCH₃]⁺ ions, however, in the case of VII loses a sulfur atom whereas the corresponding loss from [M-C₆H₅CO]⁺ in I is not observed.

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The sulfur loss is considerably reduced in VIII as compared with II.

The position of the methoxycarbonyl group affects the fragmentation pattern in another way, however. Thus, instead of losing the OCH₃ group as observed for VIII, a hydrogen rearrangement with loss of CH₂O takes place in VII. CH₃CH₂O and CH₃CHO, respectively, are eliminated from the molecular ions of XIV and XIII. Apart from this difference, the fragmentation modes of the methyl and ethyl esters are analogous. Furthermore the spectrum of VIII exhibits a peak at *m/e* 158 not present in that of VII. It corresponds to the loss of a hydrogen atom from the [M-CO₂CH₃]⁺ ion and since a corresponding ion is completely absent in the spectra of XII and XVI but present in that of X and XIV it is likely that the hydrogen lost in this process originates from the 2 position. Apart from this loss, additional phenyl substitution on the trithiapentalene nucleus in the spectrum of XI only, gives rise to different behaviour (Fig. 3). In this case, the loss of CH₂O from the molecular ion is completely absent. Instead, the loss of a hydrogen atom from the molecular ion gives rise to an abundant peak. This process is probably due to the proximity of the phenyl group and the carbonyl oxygen which enables the ejection of a phenyl hydrogen under formation of the following ion.

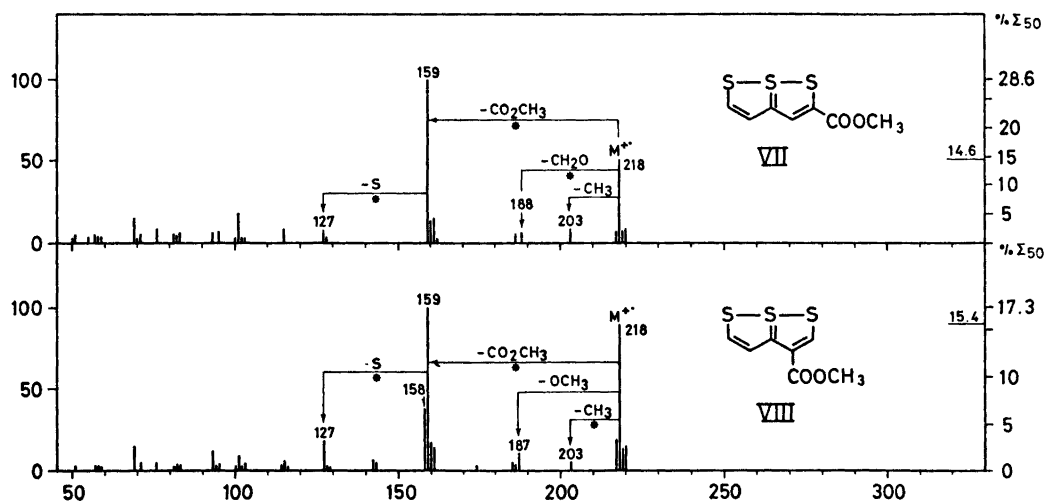


Fig. 2. MS of compound VII and VIII.

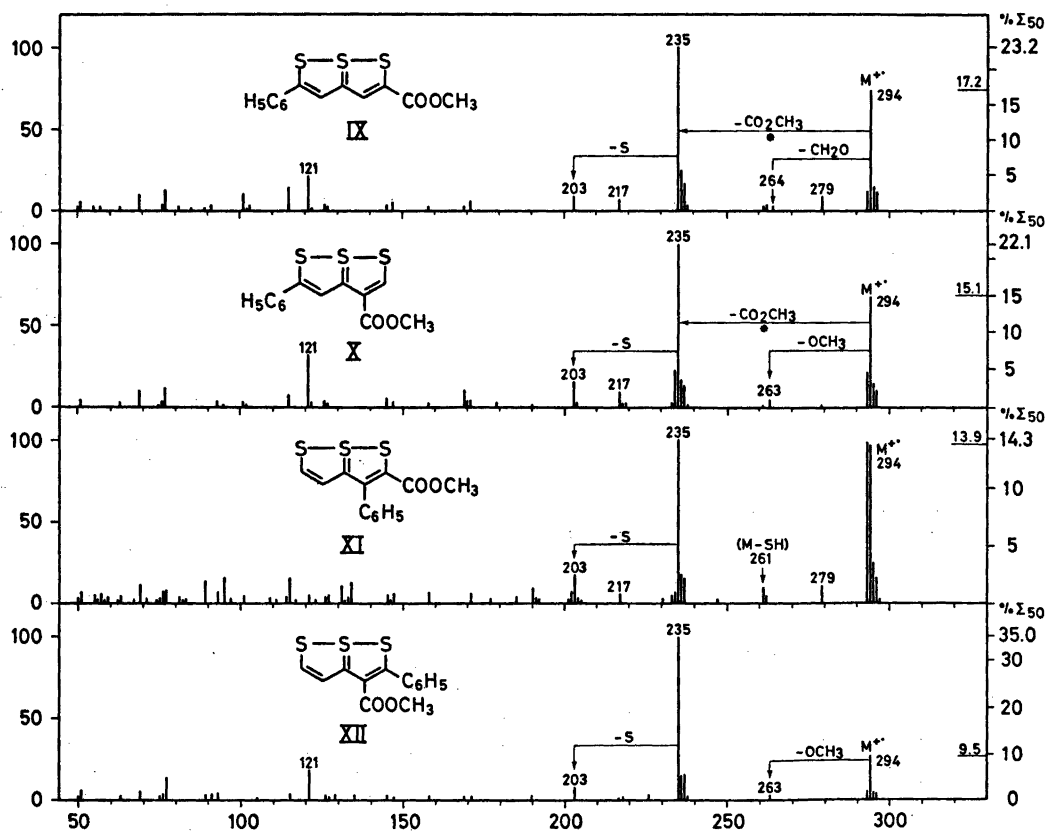
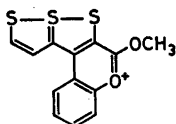


Fig. 3. MS of compound IX–XII.



An analogous ion is not formed from XII in accordance with the previous observation⁶ that a phenyl group in position 2 or 5 does not participate in the expulsion of a hydrogen atom.

3. Methyl substituted trithiapentalenes

	R ¹	R ²	R ³	R ⁴
XVII	CH ₃	H	H	H
XVIII	H	CH ₃	H	H
XIX	CH ₃	H	H	CH ₃
XX	H	CH ₃	CH ₃	H
XXI	CH ₃	H	H	C ₆ H ₅

The fragmentation patterns of these compounds (Fig. 4) are similar to those of the corresponding phenyl substituted compounds.⁶ Ions corresponding to losses of a hydrogen atom and of ·SH from the molecular ions are characteristic features for both groups of compounds.

However, the difference in ability for elimination of the substituent from the 2 and 3 position is much less pronounced. While *m/e* 159 corresponding to [M - C₆H₅]⁺ in the mono phenyl substituted compounds was 20 and 3% for the 2 and 3 substituted isomer, respectively, the corresponding [M - CH₃]⁺ ions appear with abundance of 52 and 33% in the spectra of XVII and XVIII, respectively.

The resemblance of the influence of a methyl and a phenyl group in the 2-position on the fragmentation modes of the molecular ions is clearly demonstrated in the spectrum of XXI. The [M - C₆H₅]⁺ ion (*m/e* 173) and the [M - CH₃]⁺ ion give rise to peaks with approximately the same abundances. (Ca. 10% of *m/e* 173 corresponds to the loss of CS from the [M - SH]⁺ ion in accordance with the behaviour of XVII to XX). Furthermore the peaks corresponding to [C₆H₅CS]⁺ and [CH₃CS]⁺ appear with similar abundances.

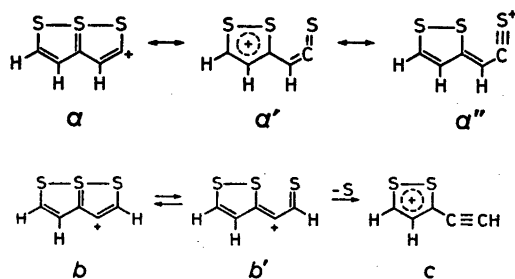
DISCUSSION

Not only was the behaviour of the molecular ions found to vary with the substituents

and their positions but also the further fragmentation of formally identical fragment ions such as the trithiapentalenyl ions *a* and *b* formed by elimination of the substituents were found to be strongly dependent on the original substituent pattern of the molecular ions.

These differences in behaviour might be explained in terms of different amounts of excess energies for *a* and *b* in the various spectra. Thus *b* might for some reason be generated with a large amount of excess energy in case of II as compared with VIII and XVIII, and *a* with a minimum of excess energy in I relative to VII and XVII. However, this explanation did not find any support in the low voltage spectra, since the characteristic differences observed at 70 eV were maintained even at the lowest obtainable ionizing energy.

An alternative explanation of the differences in fragmentation can be expressed in terms of resonance stabilization of *a* and *b* (Scheme 2). Thus, *a* is stabilized by the resonance (*a* ↔ *a'* ↔ *a''*) without further fragmentation whereas this mode of stabilization is not open in the case of *b*. Additional loss of a sulfur atom therefore appears to be more likely from *b* (to yield *c*) than from *a*. The very high selectivity between the 2 and 3 position in the case of benzoyl substituents can be explained by the assumption that this substituent favours the thiocarbonyl form *b'* and thus facilitates the loss of sulfur, when other modes of stabilization are not open.



Scheme 2.

EXPERIMENTAL

The mass spectra were obtained on an MS 902 mass spectrometer using the direct sample insertion system with the lowest feasible ion source temperature. 70 eV electrons were used. Peaks corresponding to doubly charged ions

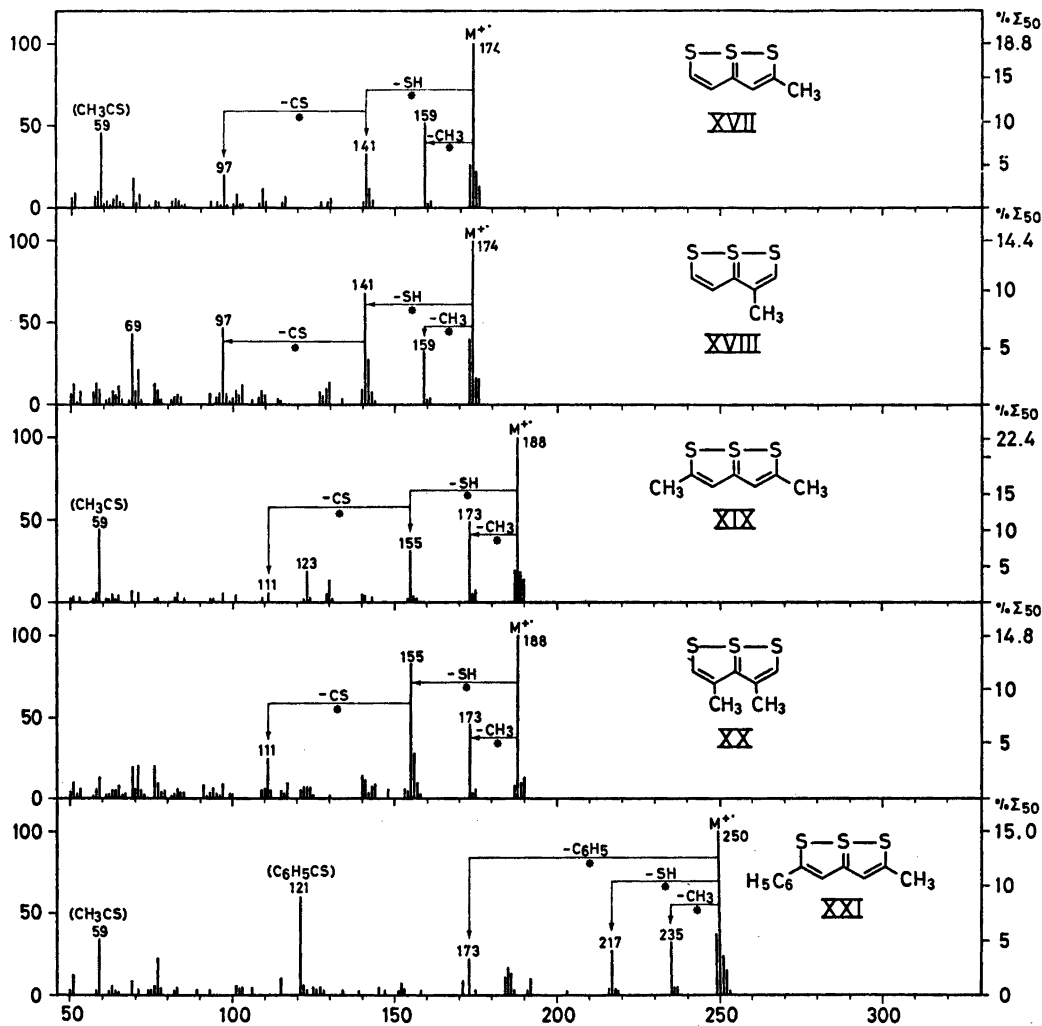


Fig. 4. MS of compound XVII–XXI.

appearing at half mass numbers as well as peaks of abundance lower than 2 % were omitted from the spectra shown.

Benzoyl, alkoxy carbonyl and monomethyl substituted 1,6,6aλ⁴-trithiapentalenes were prepared as described by Davy⁸ from 1,2-dithiole-3-thiones and acetylenes with subsequent isomerization.

2,5-Dimethyl-1,6,6aλ⁴-trithiapentalene was prepared according to Arndt *et al.*⁹

3,4-Dimethyl-1,6,6aλ⁴-trithiapentalene was prepared according to Dingwall *et al.*¹⁰

2-Methyl-5-phenyl-1,6,6aλ⁴-trithiapentalene was prepared according to Pedersen.¹¹

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