Acta Chemica Scandinavica B 28 (1974) 97—101

# Mass Spectra of Substituted 1,2,3,4-Thiatriazoles

KAI ARNE JENSEN, SVEND TREPPENDAHL,* CARSTEN CHRISTOPHERSEN and GUSTAV SCHROLL

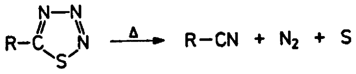
Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

The mass spectra of 14 1,2,3,4-thiatriazoles have been recorded and interpreted with the aid of high resolution mass measurements and by the application of the metastable defocusing technique. The observed electron impact induced fragmentations are compared with the known thermal decompositions of these compounds.

The electron impact induced decompositions of heterocyclic compounds have received appreciable attention during the last decade, and mass spectrometry has as a result of these investigations become an important tool in the structure elucidation of this type of compounds.[1–3]

Although several classes of heterocyclic compounds thus have been investigated no detailed studies dealing with the mass spectra of thiatriazoles ** have been published. In connection with the study of the fragmentations of 1,2,3-thiadiazoles the mass spectrum of 5-phenylthiatriazole has been scrutinized.[4]

Thiatriazoles are known to be rather unstable compounds,[5] decomposing upon heating by the loss of $N_2$ and S according to the scheme:



The purpose of this investigation is twofold, partly to examine whether mass spectrometry can be used for the identification of this type of heterocyclic compounds, partly to compare the electron impact induced fragmentations with the known thermal decompositions of thiatriazoles.

Comparisons of thermally and electron impact induced processes are often complicated by the possibility of pyrolysis of the sample in the inlet system of the mass spectrometer. In order to prevent such decompositions prior to ionization the thiatriazoles were introduced through the direct inlet at a temperature below 100°C. Applying this technique it was possible to obtain a mass spectrum (Fig. 4) of 5-mercaptothiatriazole (XI) (known to explode at 50 – 60°C at atmospheric pressure) with a molecular ion peak of *ca.* 40 % relative abundance. The presence of an abundant molecular ion peak indicates that some of the sample has evaporized unchanged into the ion source, but it does not exclude that pyrolysis has also taken place. As the pyrolysis of the thiatriazoles leads to the formation of sulfur, the presence of peaks in the mass spectra at *m/e* n·32 corresponding to $S^{+\cdot}$ (n = 2, 3,...8) can be taken as evidence for a thermal destruction of the sample. Thus in the case of 5-mercaptothiatriazole (XI) the mass spectrum (Fig. 4) contains peaks at *m/e* 128 and 64, indicating that some of the sample decomposes during the evaporation.

This investigation deals with the mass spectra (Figs. 1 – 4) of 14 thiatriazoles (I – XIV). Depending on the substituent in the 5-position the compounds can be divided into three groups:

*A*: 5-Arylthiatriazoles (I – II)
*B*: 5-Aminothiatriazoles (III – X)
*C*: 5-Thiothiatriazoles (XI – XIV)

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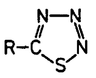
* Present address: Institute for Chemistry, Faculty of Medicine, University of Copenhagen, Rådmandsgade 71, DK-2200 Copenhagen, Denmark.

** The positional numerals are for the sake of brevity omitted.



A:

I. R=$-C_6H_5$

II. R=$-C_6H_4-\underline{p}-CH_3$

B:

III. R=$-NH_2$

IV. R=$-NHCH_3$

V. R=$-NHCH_2CH_3$

VI. R=$-NHCH_2CH_2CH_3$

VII. R=$-NHCH(CH_3)_2$

VIII. R=$-NHC_6H_5$

IX. R=$-N(CH_3)_2$

X. R=$-N(CH_2CH_2CH_3)_2$

C:

XI. R=$-SH$

XII. R=$-SCH_3$

XIII. R=$-SCH_2CH_3$

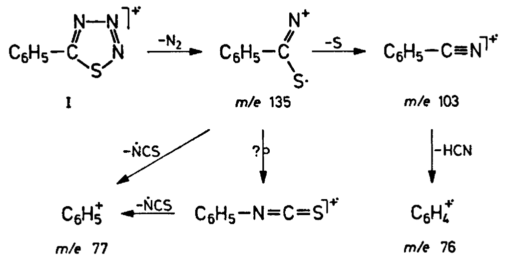
XIV. R=$-SC_6H_5$

## DISCUSSION

### A. 5-Arylthiatriazoles

The base peak (*m/e* 103) in the mass spectrum (Fig. 1) of 5-phenylthiatriazole (I) is due to ionized benzonitrile and the peaks at *m/e* 76 and 75 correspond to the known decomposition products of $C_6H_5CN^{+\cdot}$ [6] (I) is known to decompose into benzonitrile upon heating,[5] and in order to ascertain whether $103^+$ was the result of a pyrolysis prior to ionization or due to an electron impact induced process metastable defocusing technique (MDT) was applied. It was found that $103^+$ is formed by the decomposition of $135^+$ (by the loss of S) as suggested by Zeller *et al.*[4]

The peak at *m/e* 135 is due to ions formed by the loss of $N_2$ from the molecular ion. A similar thermal process is not known for this compound. The composition of the $M-N_2$ ion corresponds to that of phenylisothiocyanate and phenylthiocyanate. From the mass spectra of $C_6H_5NCS$ [7] and $C_6H_5SCN$ [8] we are most inclined to assign the $M-N_2$ ion to ionized phenylisothiocyanate. The formation of this ion requires a phenyl migration from C(5) to N(4).



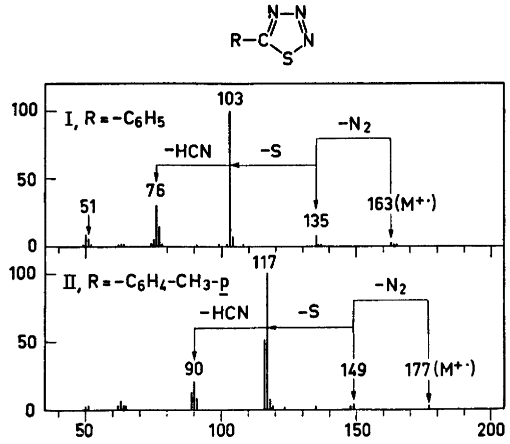


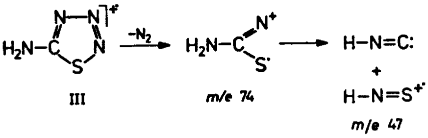
*Fig. 1.*

If the phenyl group is substituted by *p*-tolyl, the decomposition pattern observed for (I) is expanded by the loss of a hydrogen atom from $M-N_2$ as well as from $M-N_2S$, probably leading to the formation of isothiocyano- and cyanotropylium ions, respectively.[6]

### B. 5-Aminothiatriazoles

The mass spectrum (Fig. 2) of 5-aminothiatriazole (III) displays rather abundant peaks at *m/e* 102, 74, 47, and 42, corresponding to $M^{+\cdot}$, $M-N_2$, $HNS^{+\cdot}$, and $H_2N-CN^{+\cdot}$, respectively. The molecular ion has an abundance of *ca.* 16 % $\sum_{40}$; in the mass spectrum of the methylamino analogue (IV) the abundance of $M^{+\cdot}$ is 18.5 % $\sum_{40}$, whereas the remaining compounds (V – X) from this group display molecular ion peaks with abundances less than 5 % $\sum_{40}$. The decrease of molecular ion intensity with increasing size of the alkyl substituent is a well known phenomenon, but the situation is normally reversed when the alkyl group is replaced by an aromatic moiety such as phenyl. In the mass spectrum (Fig. 3) of 5-phenylaminothiatriazole (VIII), however, the abundance of the molecular ion is only 0.8 % $\sum_{40}$.

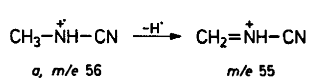
The decrease in molecular ion abundance with increasing size of the alkyl is normally due to the possibility for new reactions when the side chain is enlarged, and this is also the case here, as seen from below.



The $M-N_2$ ion from 5-aminothiatriazole (III) has the composition $CH_2N_2S$ and this fragment decomposes into the ion $HNS^{+\cdot}$ and neutral HCN. In the mass spectra of the two 5-arylthiatriazoles (I – II) the $M-N_2$ ions corresponded to ionized arylisothiocyanates, but an analogous skeletal rearrangement (leading to $H_2N-N=C=S^{+\cdot}$) is neither reasonable from a mass spectrometric point of view, nor in agreement with the further loss of HCN and formation of $HNS^{+\cdot}$. The genesis of $HNS^{+\cdot}$ requires the formation of a S – N bond.

Although the mass spectrum of 5-methylaminothiatriazole (IV) displays an abundant peak at *m/e* 88, corresponding to $M-N_2$, the peaks due to the subsequent decomposition by loss of HCN (*m/e* 61) or formation of $HNS^{+\cdot}$ (*m/e* 47) are not as significant as in the case of III. Further, the $M-N_2$ ion from IV is found to decompose by the loss of ·H (*m/e* 87) and $\cdot CH_3$ (*m/e* 73 = $CHN_2S$, H. R.) as indicated by the presence of the appropriate metastable peaks. These differences between the decompositions of the $M-N_2$ ions from III and IV makes the assignment of a general structure to the $M-N_2$ ions impossible.

As in the mass spectrum of III that of IV displays an abundant peak corresponding to $M-N_2S$. This ion is assigned to the structure *a*. The peak at *m/e* 55 is due to $M-HN_2S$, formed by α-cleavage in *a*:



$$\underset{a,\ m/e\ 56}{CH_3-\overset{+\cdot}{N}H-CN} \xrightarrow{-H^\cdot} \underset{m/e\ 55}{CH_2=\overset{+}{N}H-CN}$$

The dominating features in the mass spectra (Figs. 2 – 3) of the higher homologues are formation of *N*-alkyl cyanamides, which decompose further by α-cleavage, and formation of alkyl ions. Finally, these mass spectra display minor peaks corresponding to ionized alkylisothiocyanates ($M-HN_3$) and to the known fragments of these ions.[7]

The mass spectrum (Fig. 3) of 5-phenylaminothiatriazole (VIII) reveals that the formation of phenylisothiocyanate (*m/e* 135) and phenylcyanamide (*m/e* 118) are important processes. Peaks corresponding to the decomposition products of the two compounds are found in agreement with the mass spectra of $C_6H_5NCS$[7] and $C_6H_5NHCN$.[9]

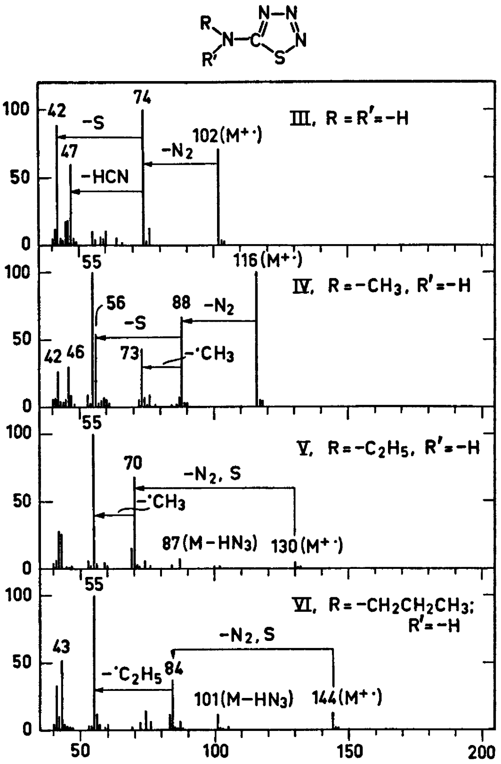
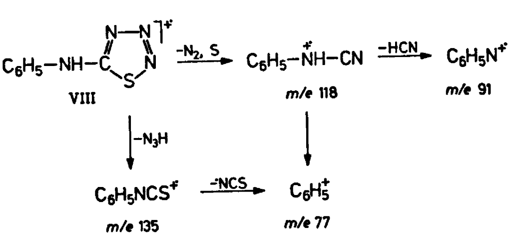
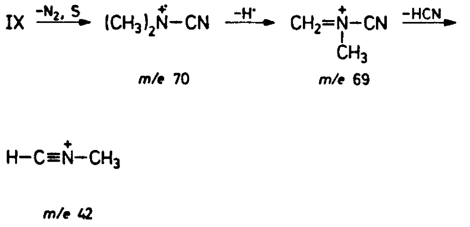


*Fig. 2.*

The mass spectra (Fig. 6) of dimethylamino (IX) and dipropylaminothiatriazole (X) display peaks corresponding to a fragmentation pattern very similar to that of the monoalkyl analogues (IV – VII), *i.e.* formation and decomposition of

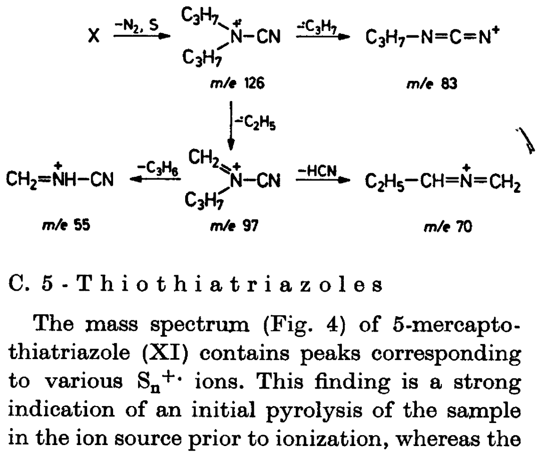


ionized cyanamides. In the case of IX the following sequence is observed:



The M − $N_2$ peak in the mass spectrum of IX is due to an ion undergoing subsequent decomposition through the expulsion of a methyl radical. A similar process was observed for the monomethyl analogue (IV).

The loss of $N_2S$ from the molecular ion of dipropylaminothiatriazole (X) leads to the formation of ionized dipropylcyanamide (*m/e* 126), undergoing α-cleavage by loss of $\cdot C_2H_5$ (*m/e* 97) followed by the elimination of $C_3H_6$ (*m/e* 55). Minor peaks in the mass spectrum of X are due to loss of a propyl radical from the ionized cyanamide (*m/e* 83) and to the elimination of HCN from the α-cleavage product (*m/e* 70), as depicted in the Scheme:



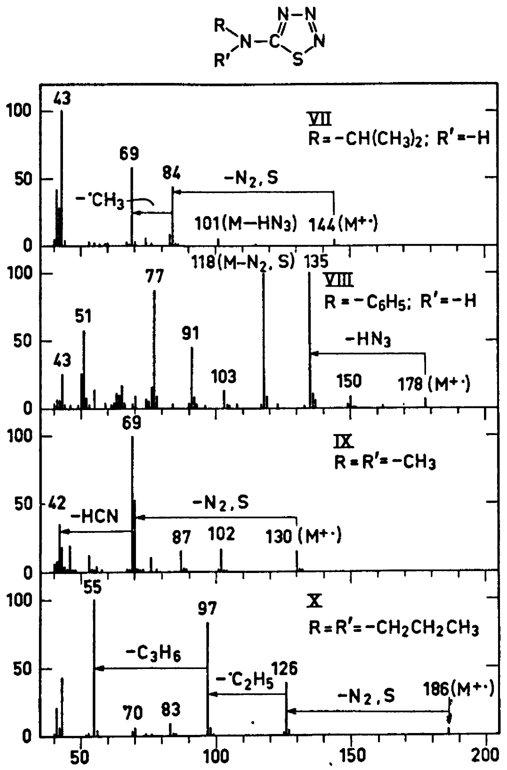
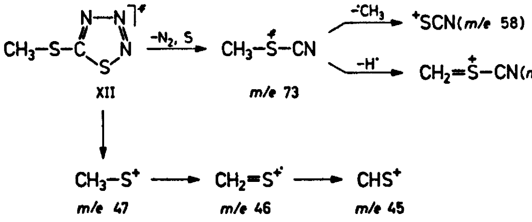


*Fig. 3.*

C. 5-Thiothiatriazoles

The mass spectrum (Fig. 4) of 5-mercaptothiatriazole (XI) contains peaks corresponding to various $S_n^{+\cdot}$ ions. This finding is a strong indication of an initial pyrolysis of the sample in the ion source prior to ionization, whereas the presence of a fairly abundant molecular ion peak clearly depicts that a large portion of the sample evaporizes unchanged from the probe tip. The peaks at *m/e* 76 and 59 are due to $CS_2^{+\cdot}$ and $HSCN^{+\cdot}$, respectively. These ions might be thermal in their origin.

The absence of any peaks, corresponding to $S_n^{+\cdot}$ in the mass spectra of the remaining compounds belonging to this class can be taken as evidence for the absence of thermal processes. The mass spectrum of methylthiothiatriazole (XII) displays peaks due to the processes listed below:



Processes of minor contribution to the total ion current include the loss of $\cdot CH_3$ ($m/e$ 118), loss of $N_2$ ($m/e$ 105), and a combined expulsion of $N_2$ and $\cdot CH_3$ leading to $S_2CN^+$ ($m/e$ 90). As in the case of the mercaptothiatriazole (XI) $CS_2^{+\cdot}$ gives rise to a fairly abundant peak ($m/e$ 76). The assignment of the $M-N_2S$ ion to the structure of ethylthiocyanate is supported by the decomposition pattern of this compound.[10]

The base peak ($m/e$ 135) in the mass spectrum of phenylthiothiatriazole (XIV) is due to ionized phenylthiocyanate, the decomposition of which is known.[8] Minor peaks are due to $M-N_2$ and $CS_2^{+\cdot}$.

## CONCLUSIONS

As it will be evident from the discussion above the electron impact induced decompositions of the thiatriazoles resemble the pyrolytic loss of $N_2S$. In all cases the $M-N_2S$ ion together with the fragmentation products from the $M-N_2S$ ion are responsible for the major part of the total ion current.

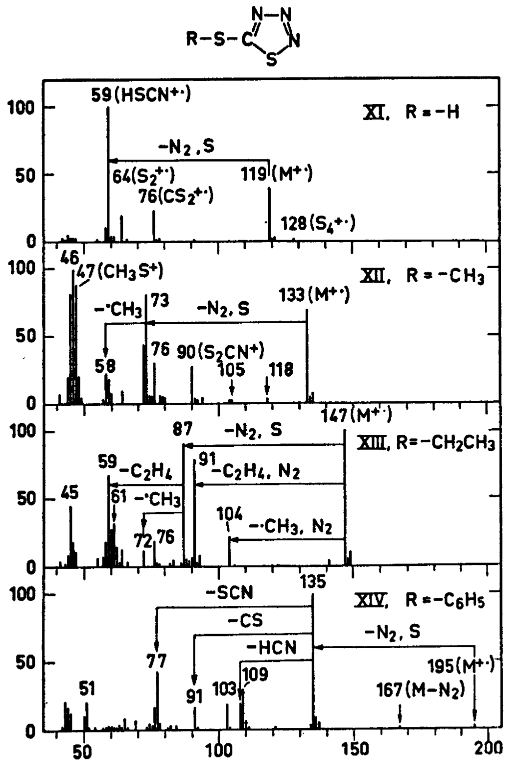
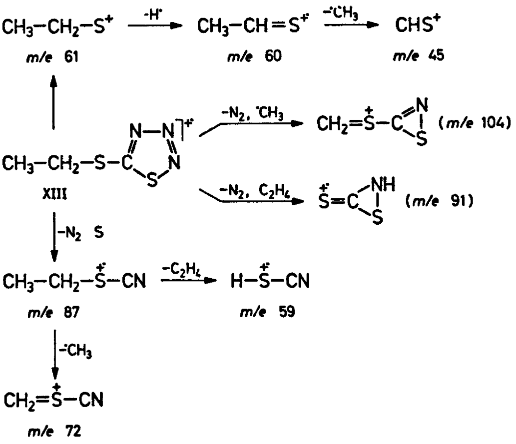


*Fig. 4.*



Rearrangement processes not observed upon pyrolysis include the formation of $M-N_2$ ions (observed in most spectra) and elimination of $HN_3$ (observed for some of the aminothiatriazoles).

## EXPERIMENTAL

The mass spectra were recorded at an AEI MS902 mass spectrometer. The samples were introduced through the direct inlet at a temperature below 100°C. All thiatriazoles were prepared in accordance with previously published procedures.[5]

## REFERENCES

1. Budzikiewicz, H., Djerassi, C. and Williams, D. H. *Structure Elucidation of Natural Products by Mass Spectrometry*, Holden-Day, San Francisco 1964.
2. Budzikiewicz, H., Djerassi, C. and Williams, D. H. *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco 1967.
3. Porter, Q. N. and Baldas, J. *Mass Spectrometry of Heterocyclic Compounds*, Wiley-Interscience, New York 1971.
4. Zeller, K.-P., Meier, H. and Müller, E. *Tetrahedron 28* (1972) 1353.
5. Jensen, K. A. and Pedersen, C. *Advan. Heterocycl. Chem. 3* (1964) 263.
6. Ref. 2, p. 418.
7. Kjær, A., Ohashi, M., Wilson, J. M. and Djerassi, C. *Acta Chem. Scand. 17* (1963) 2143.
8. Agenäs, L. B. *Ark. Kemi 30* (1969) 465.
9. *Unpublished results of this laboratory.*
10. Jensen, K. A., Holm, A., Wentrup, C. and Møller, J. *Acta Chem. Scand. 20* (1966) 2107.

Received August 18, 1973.