Fragmentation Processes of Some Thiocarbonyl Compounds on Electron Impact*

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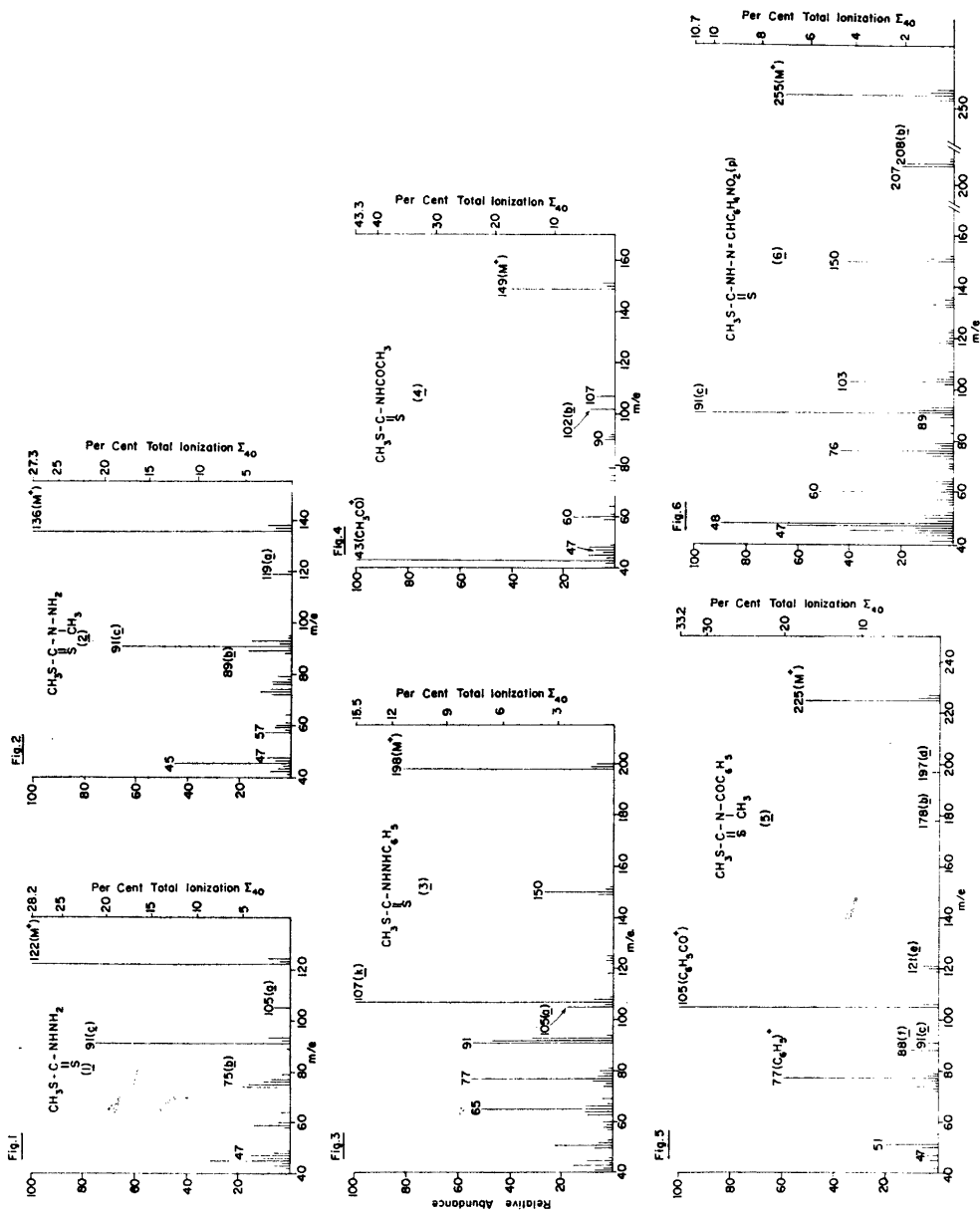
J. SANDSTRÖM

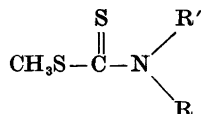*Department of Organic Chemistry, University of Lund, Lund, Sweden*

The mass spectra of fourteen thiocarbonyl compounds are reported and discussed. The fragmentation of these compounds was generally explicable in terms of simple bond cleavage processes with and without hydrogen rearrangement although in several instances unexpected skeletal rearrangements did occur.

The mass spectrometric fragmentation of carbonyl compounds has been extensively investigated [1] especially with regard to hydrogen transfer processes of which the principal mode is the well-documented McLafferty rearrangement.[2] More recently the elimination of carbon monoxide and carbon dioxide from various carbonyl compounds has been observed [3] while sulphur compounds have shown some facility in suffering skeletal rearrangements under electron impact conditions.[4] Thus it was of interest to examine the mass spectra of a series of thiocarbonyl compounds that had been prepared recently [5] in order to ascertain whether this class of compounds might undergo rearrangements of groups other than hydrogen upon electron impact and if possible to define the scope and limitations of these processes.

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Fig. 1

$CH_3-S-C-NHNH_2$

Fig. 2

$CH_3-S-C-N-NH_2$

Fig. 3

$CH_3-S-C-NHNHC_6H_5$

Fig. 4

$CH_3-S-C-NHCOCH_3$

Fig. 5

$CH_3-S-C-N-COC_6H_5$

Fig. 6

$CH_3-S-C-NH-N=CHC_6H_4NO_2(p)$

AMIDES OF DITHIOCARBONIC ACID

$$\text{CH}_3\text{S}-\overset{\overset{\text{S}}{\|}}{\text{C}}-\text{N}\underset{\text{R}}{\overset{\text{R}'}{\diagup}}$$

(1)   R = H, R′ = NH$_2$
(2)   R = CH$_3$, R′ = NH$_2$
(3)   R = H, R′ = NHC$_6$H$_5$
(4)   R = H, R′ = COCH$_3$
(5)   R = CH$_3$, R′ = COC$_6$H$_5$
(6)   R = H, R′ = N:CHC$_6$H$_4$NO$_2$-(p)

All six substituted amides of dithiocarbonic acid (1—6) have mass spectra (Figs. 1—6) in which the molecular ion is of appreciable intensity. An interesting fragmentation in the case of compounds 1 and 2 is the elimination of ammonia from the molecular ion (the appropriate metastable ion is observed in both instances) and this process can be rationalized by 1→a. The elimination of ammonia from organic compounds upon electron impact is not a common process although it has been observed in the fragmentation of salicylamide.[6] Substitution of one of the terminal amino hydrogen atoms by phenyl as in 3 does not change this mode of fragmentation since a peak at m/e 105 in Fig. 3 now points to the elimination of the elements of aniline rather than of ammonia.


a, R = .H,   m/e 105
R = CH$_3$, m/e 119
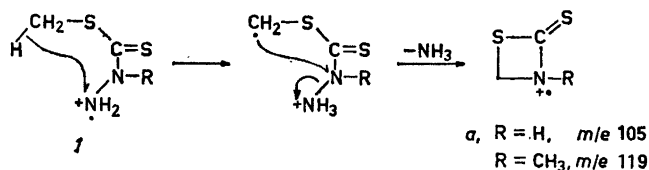
A peak occurs at M—47 in compounds 1, 2, 4, 5, and 6 which corresponds to the elimination of CH$_3$S such that the general form of the charged entity is depicted by b. It is noteworthy that in this fragmentation a portion of the ion yield can also be accomodated by the thiomethyl species yielding peaks at m/e 47 (CH$_3$S$^+$) in all spectra. These conclusions are not valid for 3 and no readily apparent reason for this exception can be seen.

$$\overset{+}{\text{S}}{\equiv}\text{C}-\text{N}\underset{\text{R}}{\overset{\text{R}'}{\diagup}}$$

b
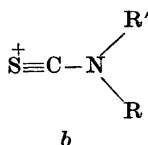
The alternate α-cleavage to the carbonyl sulphur atom promotes the ubiquitous m/e 91 peak in the spectra of compounds 1—6 and this can be represented by c, m/e 91.

$$\text{CH}_3\text{S}-\text{C}{\equiv}\overset{+}{\text{S}}$$

c, m/e 91
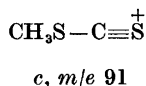
An interesting fragmentation, found only in compound *5*, is the loss of carbon monoxide from the molecular ion generating the peak at m/e 197 in the spectrum (Fig. 5) of compound 5. This fragmentation remained at low electron voltage (14 eV) and high resolution mass spectrometry verified that this ion did indeed arise from the expulsion of carbon monoxide from the molecular ion. A rationalization for the genesis of this ion would be transfer of a phenyl group through a five-membered intermediate to the carbonyl sulphur atom (*5→d*, m/e 197). It is noteworthy that the mass spectrum (Fig. 7) of the methoxy thiocarbonyl amide *7* contains a peak at m/e 105 (M−CO) which must arise from a similar decomposition as depicted by *5→d* except that the migrating entity is now a methyl radical.

5.   *d,* m/e **197**
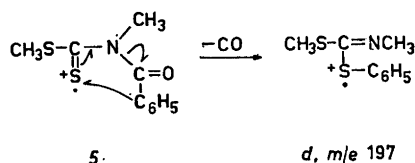
High resolution mass spectrometry established the composition C_7H_5S (25 %) and $C_3H_7NS_2$ (75 %) for the ion of mass 121 in the spectrum (Fig. 5) of compound *5*. The minor component of the doublet must arise from a skeletal rearrangement process and one possibility would be decomposition of the species *d* although no reasonable mechanistic rationalization is apparent for what must be a very bizarre process. The major constituent of mass 121 could arise from either loss of benzyne from *d* or by the elimination of C_6H_4CO from the molecular ion. No metastable ion was found to confirm the occurrence of either process but it was observed that at low electron energy (14 eV) the peak at m/e 121 did become markedly less abundant than other fragment ions suggesting that it arose by a secondary decomposition process such as that represented by *d→e* (m/e 121).


d   *e,* m/e **121**
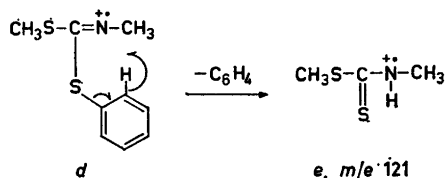
The ion of mass 88 (C_3H_6NS by high resolution mass measurement) in the spectrum (Fig. 5) of compound *5* remained prominent at low electron energy (14 eV) suggesting that it arose from a primary decomposition of the molecular ion. One such rationalization is depicted by *5→f* (m/e 88).

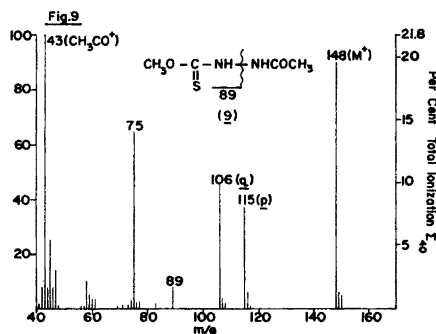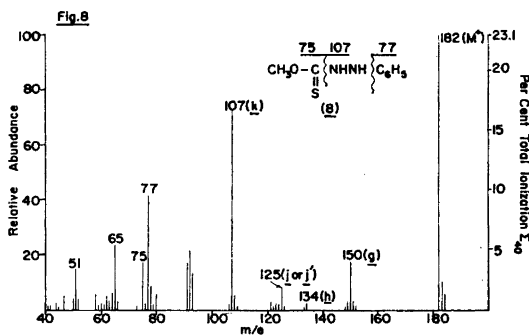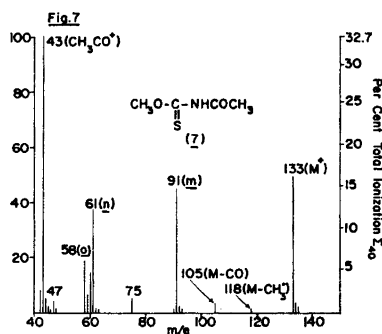*5*   *f,* m/e **88**
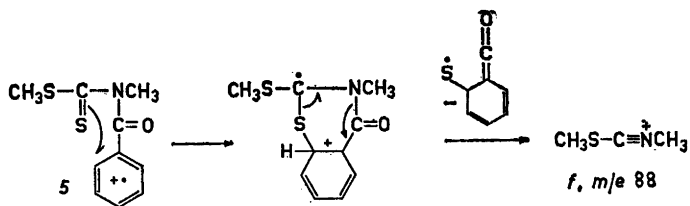
The presence of the benzoyl cation $(C_6H_5CO^+)$ at mass 105 and the phenyl ion at mass 77 in the spectrum (Fig. 5) of compound *5* require no comment.

AMIDES OF METHOXYTHIOCARBONIC ACID

$$\underset{\underset{\displaystyle\overset{\|}{CH_3O-C-NHR}}{S}}{}$$
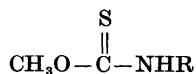
(7) R = COCH_3
(8) R = NHC_6H_5
(9) R = NHCOCH_3

Fig.7

Fig.8

Fig.9

The mass spectra (Figs. 7—9) of the three amides of methoxy thiocarbonic acid (compounds 7—9) all display abundant molecular ion peaks. The most interesting fragmentation pattern is produced by compound 8 and its mass spectrum will be discussed in some detail.

The peak at m/e 150 ($C_7H_6N_2S$ by high resolution) in the spectrum (Fig. 8) of 8 arises from the elimination of methanol from the molecular ion (metastable ion at mass 123.6; $150^2/182 = 123.6$). Such a process can be rationalized by 8→g, (m/e 150) and this is supported by the occurrence of a weak peak at m/e 116 (M—CH_3OH) (larger than the ^{13}C isotope contribution from m/e 115) in the spectrum (Fig. 9) of the amide 9. Significantly, the thiocarbonyl derivative 7, in which no hydrazine-type hydrogen is located for the transfer envisaged in 8→g, lacks a peak (Fig. 7) corresponding to the elimination of methanol.

8   g, m/e 150
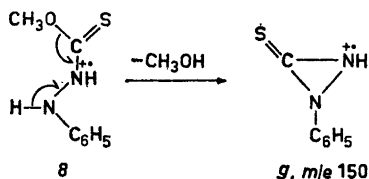
It is noteworthy that the thiocarbonyl compounds 1—6 which contain the SCH_3 group all showed loss of this entity in their mass spectra (ion b) while none of the methoxy substituted derivatives 7—9 displays any loss of OCH_3 from the molecular ion.
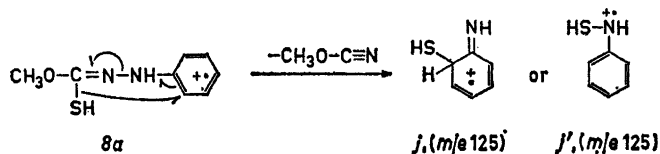
A weak peak at m/e 134 (M—48) in the spectrum (Fig. 8) of the amide 8 must arise from the expulsion of CH_3SH from the molecular ion. Such a process may be rationalized by the sequence 8→h, (m/e 134), which assumes the intervention of a tautomeric species 8a.

8   8a   h, m/e 134
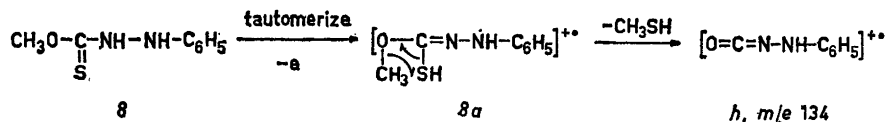
High resolution mass spectrometry established the composition C_6H_7NS for the ion of mass 125 in Fig. 8. A metastable ion at mass 85.9 ($125^2/182 = 85.9$) indicated that this fragment arose from a one step decomposition from the parent ion while at low electron energy this fragment was still present. Furthermore, the spectra (Figs. 12 and 13) of the thiocarbonyl compounds 12 and 13 (see below) which contain the common grouping $\overset{S}{\overset{\|}{C}}$—$NHNHC_6H_5$ exhibit an ion (C_6H_7NS) of mass 125. Consequently, it must arise by a skeletal rearrangement process and one rationalization is depicted through the tautomer 8a giving j (m/e 125). The alternative possibility of the transfer of the sulphydryl

radical in *8a* through a four-membered ring with the production of *j'* (*m/e* 125) is, of course, not excluded.

$$-CH_3O-C\equiv N$$

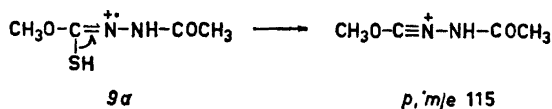*8a*   *j,* (*m/e* 125)   *j',* (*m/e* 125)

The prominent peak at *m/e* 107 (M—75) in the spectrum (Fig. 8) of compound *8* corresponds to the ion *k* resulting from fission of the carbon-nitrogen bond. It is noteworthy that in this fragmentation the charge can also be retained by the other cleavage product yielding an ion of mass 75 (C_2H_3SO) in Fig. 8 and Fig. 9. This ion also occurs in the spectra (Figs. 7 and 9) of the analogous compounds *7* and *9*.
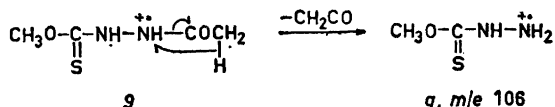

$$-CH_3O-CS$$

8   *k, m/e* 107
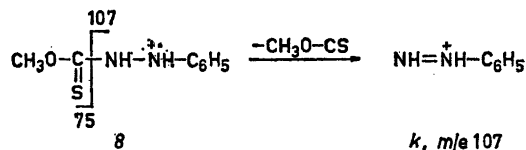
The McLafferty rearrangement [2] (*7→m/e* 91) is probably responsible for the peak at *m/e* 91 (M—42) in the spectrum (Fig. 7) of the methoxy thiocarbonyl derivative *7* although a four centered transition state with hydrogen transfer to the nitrogen atom is not excluded (*cf. 9→q*) while the further loss of formaldehyde from the species *m* would yield *n*, (*m/e* 61). An alternative fragmentation mode for the species *m* is the loss of the sulphydryl radical and production of *o*, (*m/e* 58).

$$-CH_2CO \qquad -CH_2O$$

m, m/e 91   *n, m/e* 61

7

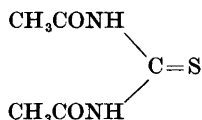$$-\dot{S}H$$

$$CH_3O-C\equiv\overset{+}{N}H$$

o, m/e 58
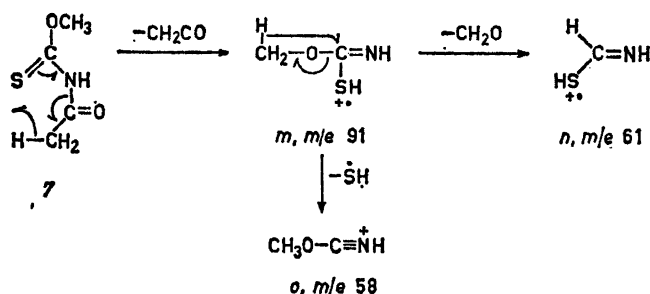
The mass spectrum (Fig. 9) of the N-acetyl hydrazine derivative *9* contains an abundant peak at *m/e* 115 (M—33) which arises directly from the molecular ion (a metastable ion at mass 89.4 was recognized; $115^2/148 = 89.4$) by loss of a sulphydryl radical. Intervention of the tautomeric molecular ion *9a* is a likely explanation for the production of *p*

$$CH_3O-\overset{..+}{\underset{\underset{SH}{|}}{C}}=\overset{+}{N}-NH-COCH_3 \longrightarrow CH_3O-C\equiv\overset{+}{N}-NH-COCH_3$$

$$9\alpha \qquad\qquad\qquad p,\ m/e\ 115$$

Elimination of 42 mass units from the molecular ion of *9* yields the ion of mass 106 in Fig. 9. A plausible rationalization for the formation of this ion would be by loss of ketene from the molecular ion as envisaged in *9→q*, (*m/e* 106).

$$CH_3O-\overset{+.}{\underset{\underset{S}{\|}}{C}}-NH-\overset{}{NH}-COCH_2 \quad\xrightarrow{-CH_2CO}\quad CH_3O-\overset{+.}{\underset{\underset{S}{\|}}{C}}-NH-\overset{+.}{NH}_2$$

$$9 \qquad\qquad\qquad q,\ m/e\ 106$$

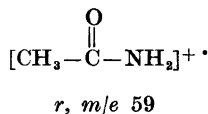## N,N'-DIACETYL THIOUREA

$$\begin{array}{c} CH_3CONH \\ \diagdown \\ \qquad\qquad C=S \\ \diagup \\ CH_3CONH \end{array}$$
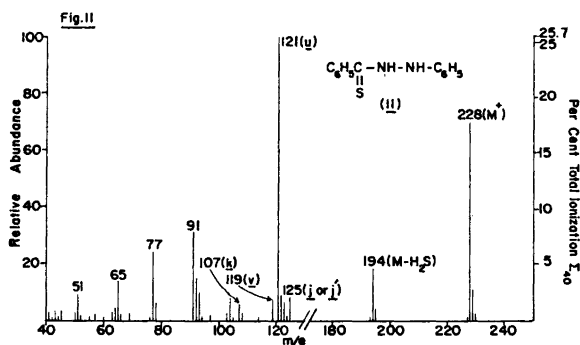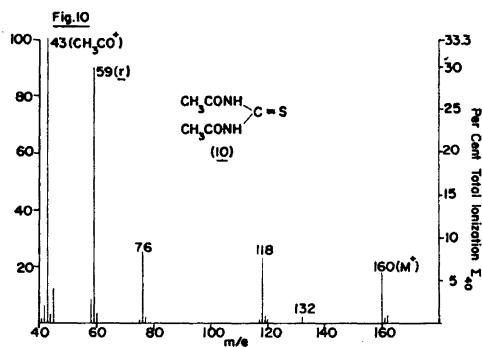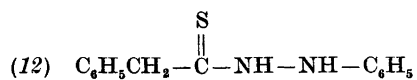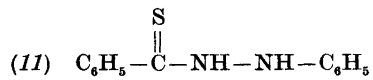
10

N,N'-Diacetyl thiourea (*10*)[7] yields a mass spectrum (Fig. 10) which can easily be rationalized by well established fragmentation modes. Thus the most intense peak (*m/e* 43) corresponds to CH_3CO^+ and the strong peak at *m/e* 59 to the species *r*, (*m/e* 59) since this ion lacks sulphur as no ^{34}S isotope peak at *m/e* 61 was observed. Peaks at *m/e* 118 and 76 have the compositions $C_3H_6N_2OS$ and CH_4N_2S and the genesis of these ions can be rationalized by successive McLafferty rearrangements[2] or by successive four-centered intermediates such as *9→q*. The appropriate metastable ions for these decompositions were observed at mass 87.0 ($118^2/160 = 87.0$) and 48.9 ($76^2/118 = 48.9$).

$$\begin{array}{c} O \\ \| \\ [CH_3-C-NH_2]^{+\,\cdot} \end{array}$$

r, m/e 59

A weak peak at *m/e* 132 (M—28) in the spectrum (Fig. 11) of N,N'-diacetylthiourea (*10*) corresponds by high resolution mass spectrometry to the elimination of carbon monoxide. Recognition of a metastable ion at mass 108.9 ($132^2/160 = 108.9$) verified that this ion resulted from an electron impact promoted fragmentation which must involve a methyl migration and is thus analogous to the loss of carbon monoxide from compound *7* (*m/e* 105 in Fig. 7).
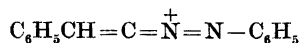
Fig. 10

Fig. 11

Fig. 12

N-PHENYLTHIOHYDRAZIDES

$$
\text{(11)} \quad C_6H_5 - \overset{\overset{\textstyle S}{\|}}{C} - NH - NH - C_6H_5
$$

$$
\text{(12)} \quad C_6H_5CH_2 - \overset{\overset{\textstyle S}{\|}}{C} - NH - NH - C_6H_5
$$
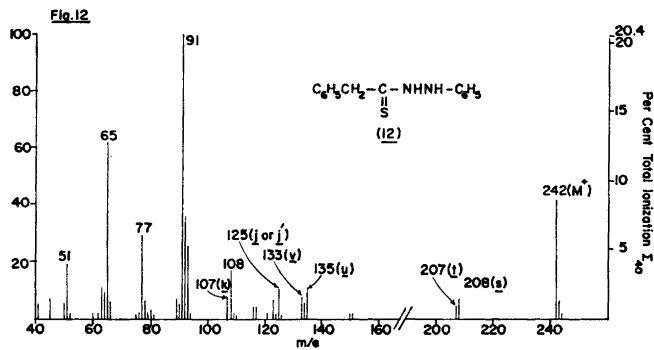
The mass spectra (Figs. 11 and 12) of the phenylhydrazine derivatives *11* and *12* contain strong peaks due to the respective molecular ions while the loss of hydrogen sulphide surprisingly yields peaks of appreciable intensity in each instance. The composition of the ion (high resolution mass spectrometry) of mass 208 in the spectrum (Fig. 12) of compound *12* was indeed compatible with the elimination of hydrogen sulphide from the molecular ion such that the charged entity might be written as *s*, *m/e* 208. The facile loss of a hydrogen atom from an $M-H_2S$ precursor in the benzyl derivative *12* (metastable ion at mass 206; $207^2/208 = 206$) can be interpreted in terms of the formation of the highly conjugated even-electron species *t*, (*m/e* 207).

$$R-C \overset{+\cdot}{=} N$$

$$\underset{\overset{|}{C_6H_5}}{N}$$

$$C_6H_5CH = C = \overset{+}{N} = N - C_6H_5$$
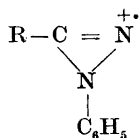
t, m/e 207

s, (R = C_6H_5, *m/e* 194)
(R = $C_6H_5CH_2$, *m/e* 208)

The ion of mass 125 in the spectra (Figs. 11 and 12) of the N-phenyl-thiohydrazides *11* and *12* has been shown (see above) to involve a skeletal rearrangement in its formation and has been assigned structure *j* or *j'*.

Cleavage of the molecular ion α to the thiocarbonyl group can be noted in both *11* and *12* and the resulting species assigned structure *u*. This cleavage is much more pronounced in *11* (*m/e* 121 in Fig. 11) as compared to *12* (*m/e* 135 in Fig. 12), presumably because of the latter's competitive fission to the tropylium ion (*m/e* 91).

$$R-C \equiv \overset{+}{S}$$
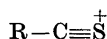
u, (R = C_6H_5, *m/e* 121)
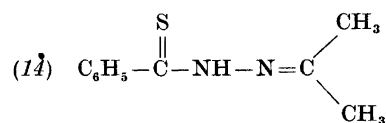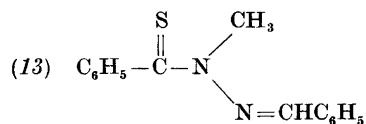
(R = $C_6H_5CH_2$, *m/e* 135)

Ions of low abundance at mass 119 and 133 in the spectra of compounds *11* and *12* correspond to the unexpected elision of C_6H_5S from the respective molecular ions and this was verified by high resolution mass spectrometry in the case of the benzyl thiocarbonyl derivative *12*. One representation for these ions is depicted by *v*.

$$R-C \overset{+}{=} NH$$

$$\underset{\overset{|}{H}}{N}$$
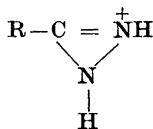
v, (R = C_6H_5, *m/e* 119)
(R = $C_6H_5CH_2$, *m/e* 133)

A peak at m/e 107 in the spectra (Figs. 11 and 12) of both the phenyl hydrazine derivatives *11* and *12* corresponds to the ion *k* and requires no comment, while that at m/e 108 in these spectra is almost certainly the phenyl hydrazine ion radical.
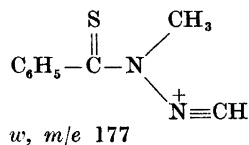
THIOHYDRAZONES

$$(13) \quad C_6H_5-\overset{\overset{\text{S}}{\|}}{C}-N\overset{\nearrow CH_3}{\underset{\searrow N=CHC_6H_5}{}}$$

$$(14) \quad C_6H_5-\overset{\overset{\text{S}}{\|}}{C}-NH-N=C\overset{\nearrow CH_3}{\underset{\searrow CH_3}{}}$$

The mass spectra (Figs. 13 and 14) of the two thiohydrazones *13* and *14* contain intense ions (*w* in the case of *13*) arising from the elimination of a phenyl and methyl radical, respectively, from the molecular ion even though
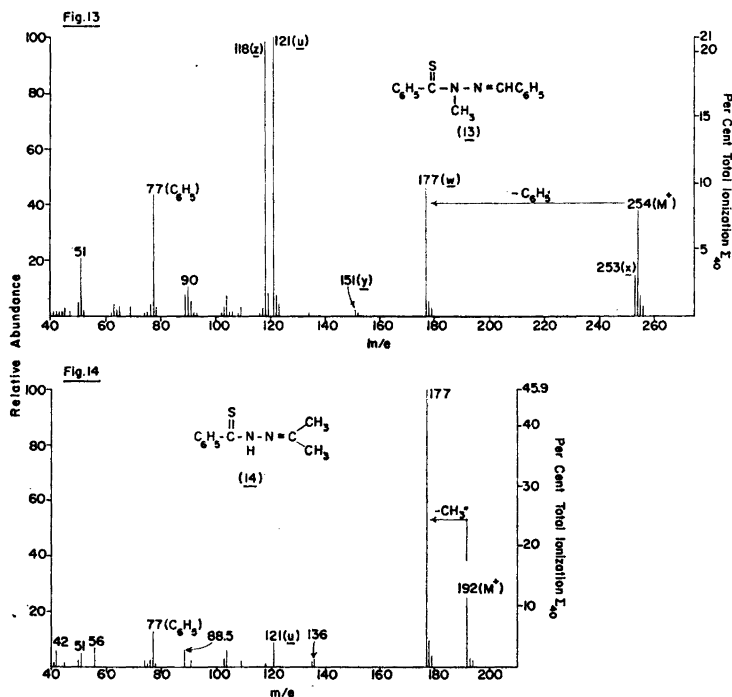
this genesis involves the breaking of a vinylic bond. These ions remained prominent at low electron energy and the driving force for this fragmentation must be the stability of the even-electron species w.

$$C_6H_5-\overset{\overset{\text{S}}{\|}}{C}-N\overset{\diagup CH_3}{\diagdown \overset{+}{N}\equiv CH}$$

w, m/e 177

In the case of compound *13* loss of a hydrogen atom from the molecular ion yields x (m/e 253). Consistent with this formulation is the observation that acetone thiobenzhydrazone contains an $M-15$ ion in its spectrum (Fig. 14).

$$C_6H_5-\overset{\overset{\text{S}}{\|}}{C}-N\overset{\diagup CH_3}{\diagdown \overset{+}{N}\equiv C-C_6H_5}$$

x, m/e 253
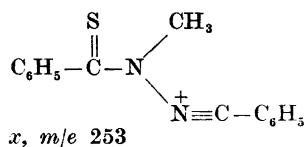
The base peak (m/e 121) in the spectrum (Fig. 13) of compound *13* is associated with the ion u, ($R = C_6H_5$), but at low electron energy this peak becomes virtually unrecognizable. This result indicates that u arises not directly from the molecular ion but rather from a fragment ion. A plausible genesis would be $w \rightarrow u$ (m/e 121) in which rupture of the carbon-nitrogen bond is facilitated by allylic activation. No metastable ions could be detected for either $M^+ \rightarrow m/e$ 121 or for the proposed fragmentation $w \rightarrow u$.
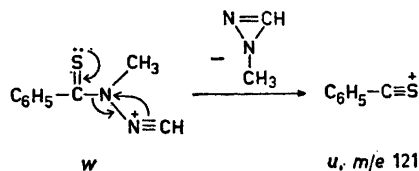
A weak peak at m/e 151 (M—103) in the spectrum (Fig. 13) of the thio-hydrazone *13* corresponds to expulsion of benzonitrile as envisaged (McLafferty rearrangement [2]) by *13* $\rightarrow y$ (m/e 151) or by a four-centered intermediate (see *9* $\rightarrow q$).

13 y, m/e 151 z, m/e 118
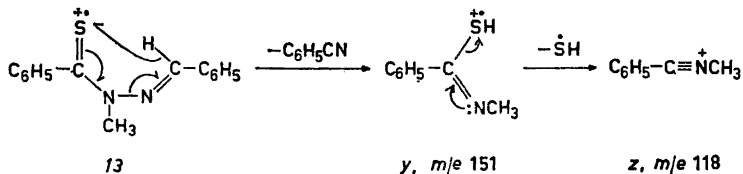
Further decomposition of y by loss of a sulphydryl radical can yield z, (m/e 118) the second most abundant ion in the spectrum (Fig. 13) of the thiohydrazone *13*. The results from high resolution mass spectrometry (C_8H_8N) agree with the empirical composition assigned to the ion z. No metastable ion for the transition $y \rightarrow z$ was found while at low voltage (19 eV) the ratio of the peaks at m/e 118 and 151 remained virtually identical to that found at 70 eV.

EXPERIMENTAL

The low resolution mass spectra were obtained with an Atlas CH-4 instrument using the TO-4 ion source (direct sample introduction into the ion source) operating at 70 eV. Attempts to determine the mass spectra of the compounds reported in this paper with a Consolidated Electrodynamics Model 21-103C mass spectrometer using an all-glass heated inlet system (200°) resulted in sample decomposition. High resolution mass measurements were performed by Mr. R. G. Ross using an A.E.I. MS-9 instrument. The thiocarbonyl compounds were of analytical purity.

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