ACTA CHEMICA SCANDINAVICA 26 (1972) 205–212

Mass Spectra of *S*-(Alkoxythiocarbonyl)thiohydroxylamines

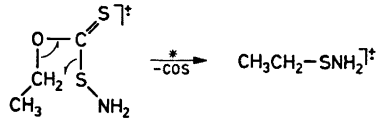
ARNE HOLM and GUNNAR MYRUP JENSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

The mass spectra of eight *S*-(alkoxythiocarbonyl)thiohydroxylamines have been obtained and interpreted by means of high-resolution mass measurements and of the defocusing technique. Important fragmentation paths occur by rearrangement of the molecular ion and elimination of COS with formation of alkyl thiohydroxylamine ions.

The thermal and acidic cleavage of certain *S*-(alkoxythiocarbonyl)thiohydroxylamines have been studied.[1,2] In this connection, the mass spectra of eight homologues were recorded. These compounds have been found to undergo characteristic skeletal rearrangements with loss of COS upon electron impact, and thus resemble a number of similar sulfur compounds. Comprehensive reviews concerning skeletal rearrangements and mass spectrometry of sulfur compounds in general have been published recently.[3–5] Although the title compounds are unstable and slowly decompose at room temperature it proved feasible to obtain mass spectra of them except of the *tert*-butyl homologue. In this case the compound decomposed in the inlet system, and only the superimposed mass spectra of the decomposition products, carbonyl sulfide, isobutene, sulfur, and ammonia were obtained. *S*-(Ethoxythiocarbonyl)-thiohydroxylamine exhibits most of the characteristic fragmentations and rearrangements exhibited by this class of substances and is chosen as model substance in the discussion of the mass spectra.

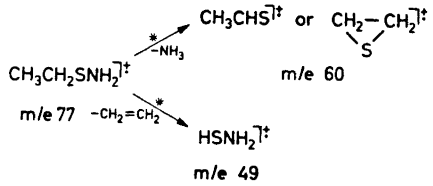
The fragmentations of S-*(ethoxythiocarbonyl)thiohydroxylamine.* The molecular ion (*m/e* 137) is observed with an intensity of 6.9 % $\sum_{29}$. The ion at *m/e* 77, C_2H_7NS (14.4 % $\sum_{29}$) is formed directly from the molecular ion by rearrangement and loss of COS:



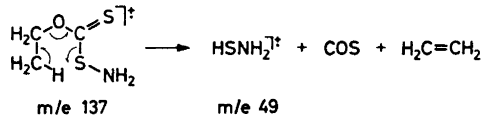
m/e 137 m/e 77

This process is similar to those observed with certain thio- and dithiocarbonates.[6]

The $[M-COS]^{+\cdot}$ ion rearranges in two ways; with elimination of ammonia to give $[C_2H_4S]^{+\cdot}$ and with elimination of ethylene to give $[H_3NS]^{+\cdot}$:



The two possible formulations of $[C_2H_4S]^{+\cdot}$ correspond to abstraction of an α- and a β-hydrogen in the formation of NH_3. The peak of *m/e* 49, formulated as due to the thiohydroxylamine radical ion, is abundant (16.1 % $\sum_{29}$). It may also have been formed from the molecular ion in a six-centre process but no



metastable peak has been observed, not even by utilizing the defocusing technique. The $[M-COS]^{+\cdot}$ ion further loses the methyl radical with formation of $[CH_4NS]^+$ (*m/e* 62). α-Cleavages are observed, and are responsible for the peaks at *m/e* 92, 89, 48, and 45 as depicted on the spectrum. The peak at *m/e* 48 may, of course, also arise from the *m/e* 49 ion by hydrogen abstraction, or from the *m/e* 77 ion by loss of the ethyl radical.

The peak at *m/e* 60 was shown to be a triplet by high resolution measurements. The triplet consists of the ions $[COS]^{+\cdot}$, $[CH_2NS]^+$ and $[C_2H_4S]^{+\cdot}$ in the ratios 8:2:2. Only the formation of the ion $[CH_2NS]^+$ remains to be explained. By application of the defocusing technique it was shown that decomposition of ions with *m/e* 92 produces ions with *m/e* 60 corresponding to loss of a sulfur atom. The *m/e* 76 ion is a singlet and found to be $[CS_2]^{+\cdot}$ by high resolution measurements. The origin of the ion with *m/e* 105 has not been established, but it is most likely *O*-ethylthiocarbamate present as an impurity. The relative intensity is not changed if either the inlet or the ion source temperature is lowered but it varies somewhat with different samples.

The fragmentation of S-*(alkoxythiocarbonyl)thiohydroxylamines.* Table 1 shows the occurrence and intensities of the common ion in the mass spectra of *S*-(alkoxythiocarbonyl)thiohydroxylamines. All compounds exhibit a molecular ion varying in abundance from 14.1 % $\sum_{29}$ (methyl) to 0.3 % $\sum_{29}$ (isobutyl). The peak corresponding to $[RSNH_2]^{+\cdot}$, formed from $M^{+\cdot}$ by a skeletal rearrangement process with loss of COS, is most abundant in the spectra of the methyl and ethyl compounds, falls off rapidly in the higher homologues and is absent in the neopentyl compound.

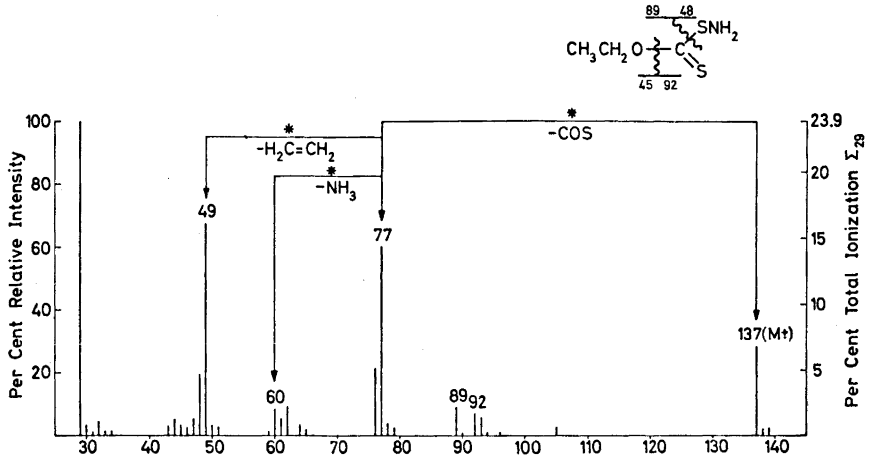
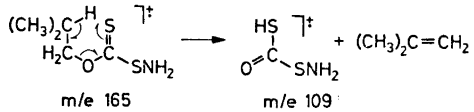


Fig. 1.

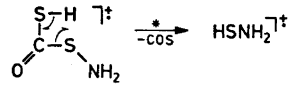
All compounds with the exceptions of the methyl and the neopentyl compounds form abundant thiohydroxylamine radical ions (*m/e* 49, 17.1 – 7.1 % $\sum_{29}$). In the mass spectrum of the neopentyl compound the abundance is only 0.5 % $\sum_{29}$ and in the case of the methyl compound no such peak was found. The fact, that the peak at *m/e* 49 is absent in the spectrum of the methyl compound and very small in the spectrum of the neopentyl compound, may be rationalized on the basis of the mechanisms suggested above for *S*-(ethoxythiocarbonyl)thiohydroxylamine, since these compounds lack an appropriate *β*-hydrogen atom.

Most of the compounds form an ion with *m/e* 109, which is formed in a McLafferty rearrangement in the molecular ion, *e.g.:*



m/e 165 m/e 109

An additional route to $[HSNH_2]^{+\cdot}$ is loss of COS from the ion at *m/e* 109. This process is established for the isobutyl compound by a metastable defocusing measurement.



m/e 109 m/e 49

α-Cleavage, with the formation of $S=C=\overset{+}{S}NH_2$, *m/e* 92, occurs in all of the compounds, the peak intensity of this ion being almost independent of the alkyl group and varying between 0.4 and 1.7 % $\sum_{29}$. The α-cleavage ion

Table 1. Selected peaks in the spectra of *S*-(alkoxy-

R	% Σ_{29} (% relative intensity)				
	M+·	[HSC(=O)SNH$_2$]+·	[RSNH$_2$]+·	[HSNH$_2$]+·	[RSNH$_2$−NH$_3$]+·
CH_3-	14.1(72)	–	12.9(65)	–	3.1(15.6)
CH_3CH_2-	6.9(28.8)	–	14.4(60)	16.1(68)	2.1 (8.6)
$CH_3CH_2CH_2$-	2.1 (7.8)	0.3 (1.1)	1.2 (4.4)	17.1(64)	1.6 (5.9)
$(CH_3)_2CH$-	0.5 (1.5)	0.4 (1.1)	2.5 (7.0)	11.8(33)	–
$CH_3CH_2CH_2CH_2$-	0.3 (1.7)	0.1 (0.5)	0.1 (0.3)	7.1(40)	0.3 (1.6)
$(CH_3)_2CHCH_2$-	0.3 (1.1)	3.2(13.8)	0.1 (0.5)	9.8(42)	0.2 (0.9)
$CH_3CH_2CH(CH_3)$-	0.7 (2.8)	0.4 (1.6)	3.4(14.6)	8.6(37)	0.2 (1.0)
$(CH_3)_3CCH_2$-	1.2 (4.1)	–	–	0.5 (1.9)	–

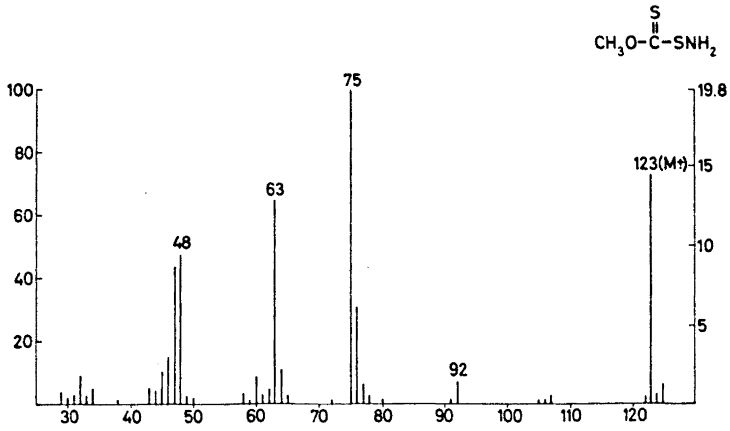


Fig. 2.

thiocarbonyl)thiohydroxylamines, $ROC(=S)SNH_2$.

% Σ_{29} (% relative intensity)						
$[S=C=\overset{+}{S}NH_2]$	$[ROC\equiv\overset{+}{S}]$	$[\overset{+}{S}NH_2]$	$[\overset{+}{R}O]$	$[COS]^{+\cdot}$ [a]	$[CS_2]^{+\cdot}$	$[CS]^{+\cdot}$
1.4 (7.2)	19.8(100)	9.4(48)	0.6 (3.1)	1.8 (9.0)	6.2(31)	1.0 (4.8)
1.7 (7.2)	2.3 (9.5)	4.7(19.8)	0.8 (3.5)	2.1 (8.6)	5.2(21.6)	1.2 (5.1)
1.2 (4.5)	–	2.7(10.2)	0.4 (1.5)	1.9 (6.9)	4.0(14.9)	1.0 (3.6)
1.2 (3.3)	0.6 (1.7)	3.0 (8.3)	0.7 (1.9)	3.0 (8.4)	1.7 (4.6)	1.2 (3.4)
0.4 (2.4)	–	1.1 (6.3)	–	1.7 (9.4)	2.9(16.3)	1.1 (6.0)
1.1 (5.0)	–	1.9 (8.3)	0.3 (1.2)	2.0 (8.5)	3.4(14.6)	0.4 (1.9)
1.6 (6.9)	0.3 (1.3)	1.6 (6.7)	0.3 (1.3)	6.3(26.9)	1.7 (7.4)	0.6 (2.6)
1.2 (4.1)	–	1.2 (4.3)	0.3 (1.0)	1.2 (4.3)	2.7 (9.5)	1.0 (3.4)

[a] This peak probably consists of both $[COS]^{+\cdot}$ and $[S=C=\overset{+}{N}H_2]$ (*cf.* $EtOC(=S)SNH_2$).

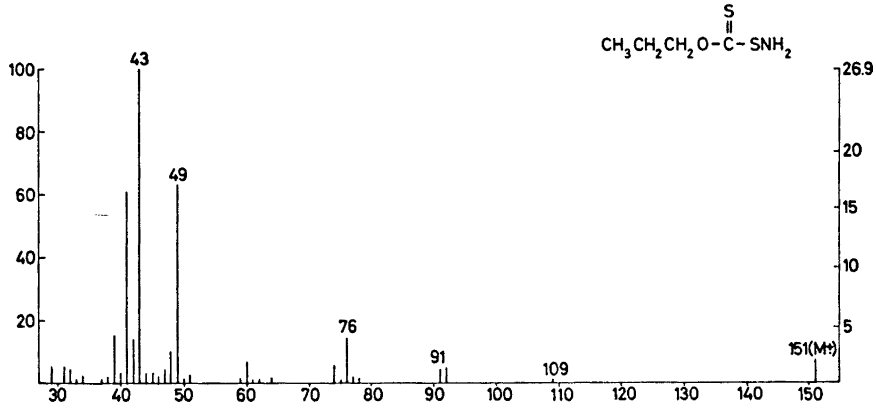


Fig. 3.

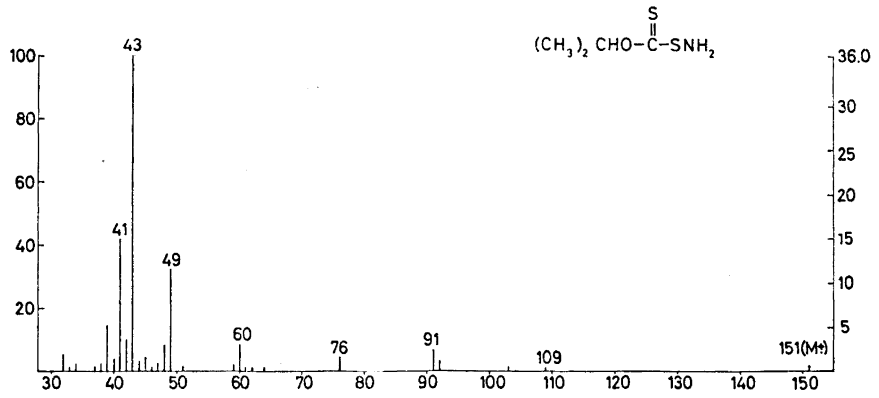


Fig. 4.

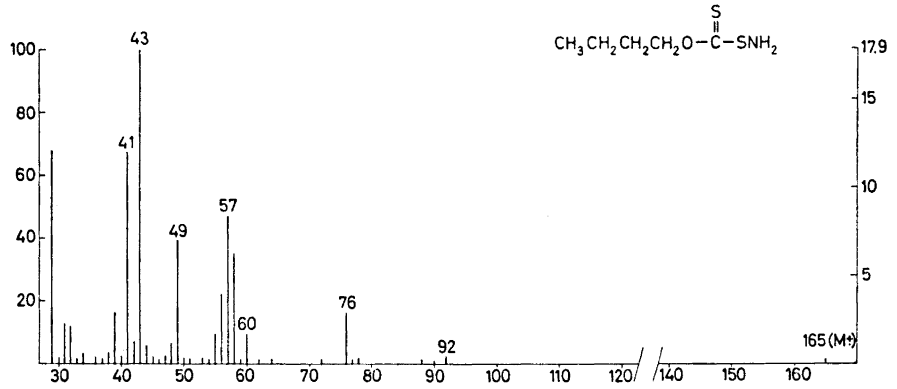


Fig. 5.

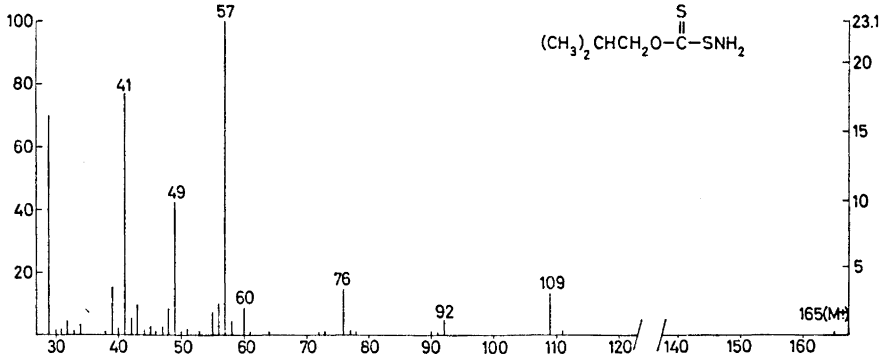


Fig. 6.

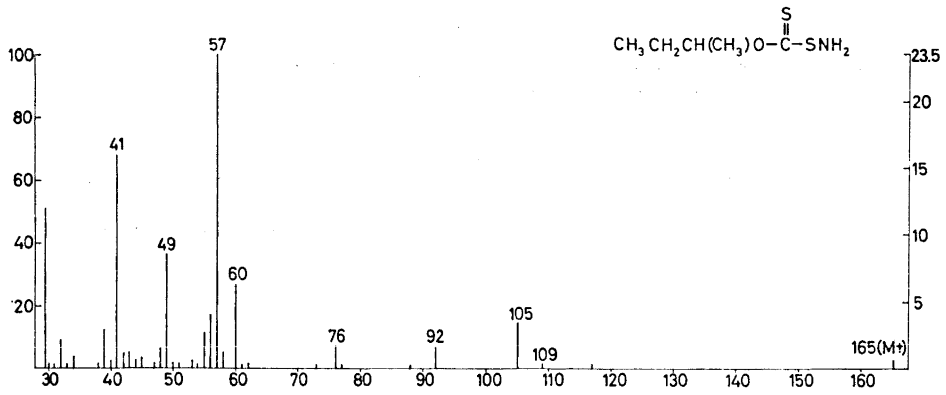


Fig. 7.

ROC≡S$^+$ gives rise to the base peak in the spectrum of the methyl compound, but the peak intensity in the higher homologues drops sharply in abundance to between 0 and 2.3 % Σ_{29}.

Except for the methyl compound, the base peaks in all cases are due to the formation of alkyl ions and alkyl fragment ions.

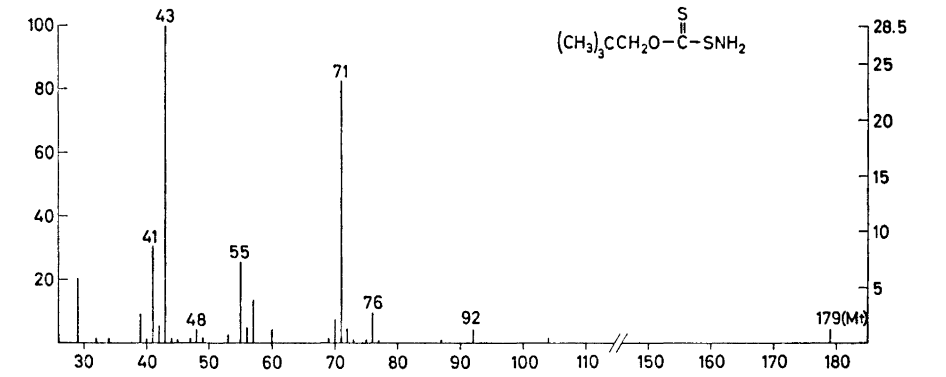


Fig. 8.

Experimental. The spectra were obtained with an AEI MS 902 mass spectrometer operating at 70 eV. The samples were introduced through the glass inlet system. The temperature of the ion source was between 80 and 100°C.

Acknowledgements. The authors are indebted to J. Møller and G. Schroll for helpful discussions. Acknowledgement is also made to Mrs. E. Wolff-Jensen for recording the spectra.

REFERENCES

1. Holm, A. and Myrup Jensen, G. *Acta Chem. Scand.* **25** (1971) 339.
2. Jensen, K. A., Holm, A. and Myrup Jensen, G. *To be published.*
3. Bowie, J. H., Simons, B. K. and Lawesson, S. -O. *Rev. Pure Appl. Chem.* **19** (1969) 61.
4. Cooks, R. G. *Org. Mass Spectrom.* **2** (1969) 481.
5. Brown, P. and Djerassi, C. *Angew. Chem.* **79** (1967) 481.
6. Thomson, J. B., Brown, P. and Djerassi, C. *J. Am. Chem. Soc.* **88** (1966) 4049.

Received April 5, 1971.