Thermal Fragmentations

III.* Precursors to *N*-Isocyanatoamines

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In a paper [1] of this series the formation of *N*-isothiocyanatodialkylamines from 1,1-dialkyl-4-phenylthiosemicarbazides will be established by gas chromatography and mass spectrometry. As a part of this investigation the products from pyrolysis of 1,1-diethyl-4-phenylthiosemicarbazide (Ia)[2] were examined on a combined gas chromatograph-mass spectrometer with a heated metal block inlet system. Injection of Ia dissolved in acetone was expected [1] to lead to complete degradation of the sample, and result in peaks corresponding to *N*-isothiocyanatodiethylamine (IIa), aniline, and phenyl isothiocyanate.

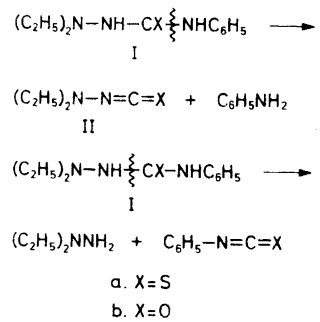


Fig. 1.

Fig 2 shows the total ion current trace obtained in a typical experiment. The peaks were scanned at the points indicated by the numbers 1 to 7 of which scan 1 is the solvent.

Beyond *m/e* 50 scan 2 only showed peaks at *m/e* 114, 99, 71, 58, and 56. The low intensity of the peak at *m/e* 43 served to verify that the peak at *m/e* 58 was due to acetone only to a negligible

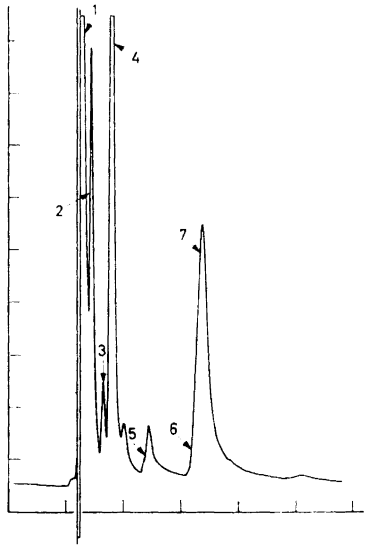


Fig. 2.

extent. Here it suffices to mention that the compound giving rise to this spectrum contained no sulfur (absence of an M+2 ion). The intensity of the isotope peak at M+1 was 6.3% of that of M^+ which is in accordance with the isotopic content of a molecule having 5 carbon and 2 nitrogen atoms. We suggest this compound to be $(C_2H_5)_2N-N=C=O$ (IIb) for reasons given below.

Scan 3 showed, apart from peaks in the low region, only peaks at *m/e* 98 (M^+), 83, and 55, with intensities of 24 %, 27 % and 100 %, respectively. We assign this spectrum to isocyanodiethylamine, produced by thermal induced loss of sulfur from *N*-isothiocyanatodiethylamine (IIa).[3] The assignment is supported by the fact that one of the fragmentation pathways in the mass spectrum of IIa [3] also is characterized by peaks at *m/e* 98, 83, and 55, with nearly identical relative intensities (25 %, 27 %, and 100 %, respectively). A possible fragmentation is given in Scheme 1.

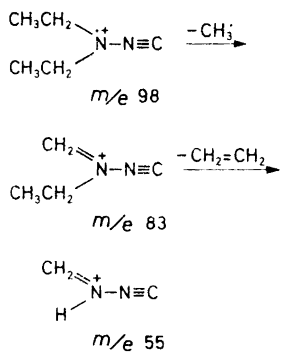
Scan 4 was identical to the mass spectrum of aniline.[4]

Scan 5 represented the spectrum of an aromatic compound containing only three peaks above mass 77, the molecular ion at *m/e* 133, the base peak at *m/e* 118, and a peak at *m/e* 93. These characteristics [4]

* For Part II, see preceding communication.

Table 1. Abundances of important peaks in % relative to M−15

	$(C_2H_5)_2N-NCS$	$(C_2H_5)_2N-NCO$ from scan 2	$(C_2H_5)_2N-NCO$ from Ib
M	89	35	37
M−15	100	100	100
M−15−28	27	33	27
m/e 58	–	33	30
m/e 56	–	42	39



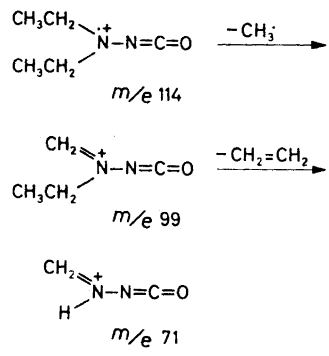
Scheme 1.

are not inconsistent with those expected from *N*-isopropylideneaniline formed from acetone and aniline, either in the injection chamber or on the first part of the column. Comparison with a mass spectrum obtained from authentic *N*-isopropylideneaniline shows identity apart from minor differences in the intensities of the peaks at *m/e* 77.

Scans 6 and 7 were identical to the mass spectrum of phenyl isothiocyanate.[5]

To confirm the suggested origin of scan 2, an authentic sample of IIb was needed. As *N*-isothiocyanatoamines are formed [1] from pyrolysis of 4-phenylthiosemicarbazides, it appeared possible that IIb in the same way could be prepared from Ib. The mass spectrum of pyrolysed 1,1-diethyl-4-phenylsemicarbazide (Ib) showed, in addition to fragmentation patterns corresponding to aniline and phenyl isocyanate,[6] peaks at *m/e* 114, 99, 71, 58, and 56 of very nearly the same intensity ratio (Table 1), as found in scan 2. Accordingly three of the four possible products expected from the reactions shown in Fig. 1 have been identified. As is the case for Ia,[1] diethylhydrazine is not detected by these methods because it is too unstable at the block temperature of 300°C. Since aliphatic *N*-isocyanatodialkylamines can be prepared by pyrolysis, the preparative possibilities of this method are at present being investigated.

The first steps in the fragmentation of IIb may be represented by the sequence shown in Scheme 2. However, as no high-resolution measurements has been carried out, the loss of 28 mass units from *m/e* 99 might also be due to the loss of CO or N_2.



Scheme 2.

The formation of IIb from Ia in acetone can now be explained as an exchange of a sulfur atom in the initially formed *N*-isothiocyanatodiethylamine (IIa), by an oxygen atom from water, formed by decomposition of a part of the acetone. This reaction (Fig. 3) will be described in a forthcoming paper, and proceeds even at 0°C. The possibility that the thiosemicarbazide Ia is instead converted to Ib can be ruled out by the fact that no trace of phenyl isocyanate is found in any of the scans 1 to 7.

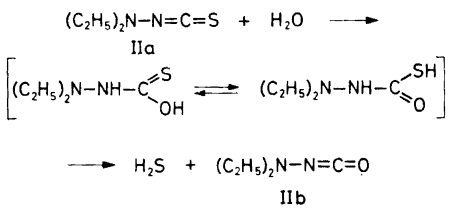


Fig. 3.

Experimental. Mass spectra of the pyrolysis products from Ia dissolved in acetone (scans 1 to 7) were obtained on a Varian MAT CH 7 combined gas chromatograph-mass spectrometer, equipped with a double-stage separator EHP of the Biemann-Watson type. The mass spectrometer was operated at 75 eV. The ion source temperature was 250°C, and the ionizing current 100 μA. The gas chromatograph was a Varian Aerograph 204 B using a 1.4 m × 3 mm column packed with 5 % SE 30 on Chromosorb W. Column and injector temperature was 105 and 300°C, respectively. The helium flow rate through the column was 20 ml/min. The GLC trace was given by the total ion current at 20 eV.

All other mass spectra were obtained with an Atlas CH-4 instrument. For operating conditions, see Ref. 1.

1,1-Diethyl-4-phenylsemicarbazide. This compound was conveniently prepared by adding a solution of phenyl isocyanate (0.1 mol) in dry ether (25 ml) dropwise to another solution of *N,N*-diethylhydrazine (0.1 mol) in dry ether (50 ml). The solution was left at room temperature for 24 h. A 60 % yield of colourless crystals, m.p. 126–127°C, were filtered off and washed with ether. After drying, the crude product was submitted for elemental analysis. (Found: C 64.02; H 8.26; N 20.49. Calc. for $C_{11}H_{17}N_3O$: C 63.74; H 8.27; N 20.27).

Acknowledgement. The authors are greatly indebted to the Varian Laboratories for supplying the spectra necessary to complete this project.

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IV.* On the Existence of Alkoxyl Isocyanates

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In a recent paper Binder[1] reported that substituted thioureas are cleaved into amines and isothiocyanates when injected into a gas chromatograph. Our investigations of the thermolysis of thiosemicarbazides[2,3] and related compounds suggested that this is a general reaction for compounds containing the group $>N-CX-$ (X=O or S), and we therefore extended

* For Part III, see Ref. 3.