

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.

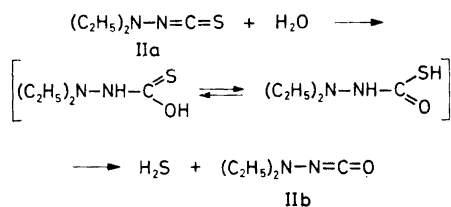


Fig. 3.

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 μ A. The gas chromatograph was a Varian Aerograph 204 B using a 1.4 m \times 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 C₁₁H₁₇N₃O: C 63.74; H 8.27; N 20.27).

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Thermal Fragmentations

IV.* On the Existence of Alkoxy Isocyanates

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In a recent paper Binder¹ 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.

this work to alkoxythioureas. In this paper we give the results of the pyrolysis of 1-ethoxy-3-phenylthiourea when its solution in acetone is injected into a combined gas chromatograph-mass spectrometer fitted with a heated metal block inlet system. By analogy to Ref. 1 it was expected that cleavage should occur on both sides of the thiocarbonyl group with formation of ethoxyl isothiocyanate (II),⁴ aniline, phenyl isothiocyanate, and ethoxyamine (Fig. 1).

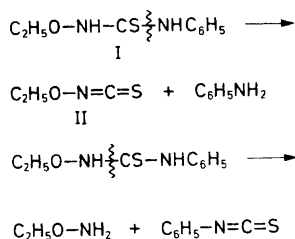


Fig. 1.

Fig. 2 shows the total ion current trace from a typical experiment with (I). The peaks were scanned at the point indicated by the numbers 1 to 5.

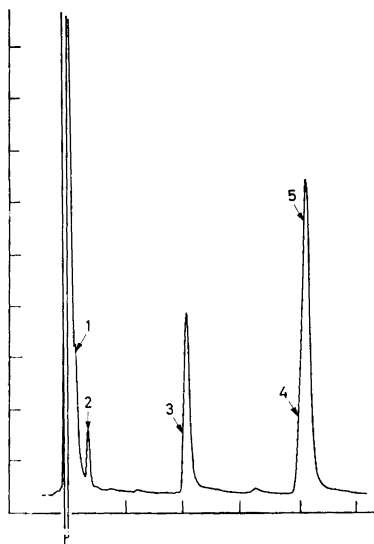


Fig. 2.

Scan 1 shows apart from the mass spectra of acetone and water, peaks at m/e 87 (40%), m/e 72 (15%), and m/e 59 (100%). The compound giving rise to this spectrum must contain an odd number of nitrogen atoms, no sulfur atoms (absence of an $M+2$ ion), and no more than three carbon atoms (isotope peak at $M+1$ less than 4% of M^+). This shows that the $\text{C}_6\text{H}_5\text{NH}$ -moiety has been eliminated (as aniline, see scan 3) and indicates a molecular formula of $\text{C}_3\text{H}_5\text{NO}_2$ for the unknown compound. From the results given in paper III of this series,³ it is proposed that this compound is ethoxyl isocyanate (III) formed *via* the isothiocyanate II by the following sequence of reactions:

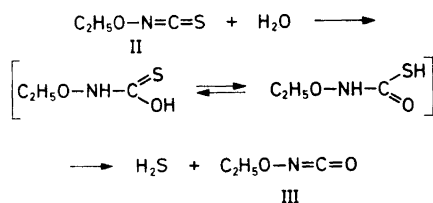
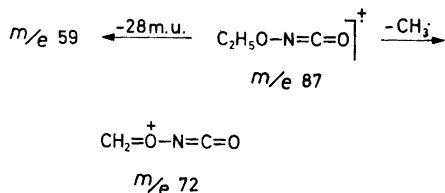


Fig. 3.

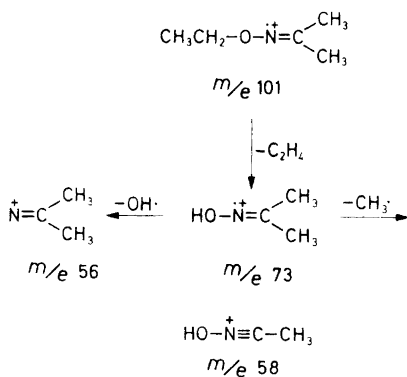
The first steps in the fragmentation of III can then be represented as shown in Scheme 1. The loss of 28 mass units from m/e 87 may be due to C_2H_4 or CO. However, as no high-resolution measurements have been carried out, and as both fragmentation pathways are known for aliphatic isocyanates⁵ upon electron impact, (though elimination of CO in only a few cases) it cannot be said which reaction actually occurs.



Scheme 1.

Scan 2 shows, in addition to peaks in the low region, peaks at m/e 101 (49%), 73 (100%), 58 (65%), 56 (63%), and 43

(38 %). From the ratio of the abundances of the m/e 58 and m/e 43 peaks it is clear that not all of the m/e 58 peak can be ascribed to acetone. All the details of the spectrum are in close agreement with the supposition that this spectrum is due to acetone *O*-ethylxime, formed from acetone and ethoxyamine. The mass spectrum of an authentic sample of acetone *O*-ethylxime⁶ verified this supposition, and the fragmentation can then be envisaged as illustrated in Scheme 2.



Scheme 2.

Scan 3 was identical with the spectrum of aniline,⁷ and the scans 4 and 5 both gave the spectrum of phenyl isothiocyanate.⁸ Thus, with this evidence for the four possible fragments (or their derivatives) of (I), the tendency of the thioureide structure, XNH-CS-NHR , to undergo cleavage on both sides of the thiocarbonyl group has been demonstrated for the cases of X equal to alkyl,¹ aryl,¹ dialkylamino,² or alkoxy groups.

The experiment was repeated on another instrument (for details, see experimental part) with the same results as described above, but with an additional peak in the ion current trace. This very large peak appeared later than the peak representing phenyl isothiocyanate. The scan of this peak showed a mass spectrum of a compound, presumably aromatic, containing no sulfur, and with a molecular ion at m/e 118 which is also the base peak. In addition prominent peaks were observed at m/e 91 (53 %) and m/e 77 (36 %). The abundance of the peak at m/e 119 corresponded to

the isotopic content of a compound containing seven carbon and two nitrogen atoms. As this molecule must originate from (I), the only two compounds which reasonably fit these demands are benzimidazole and phenyl cyanamide. The mass spectrum of benzimidazole has been published by Nishiwaki,⁹ and shows several differences from the one obtained by us. For example, the peak at m/e 77 is absent in the mass spectrum of authentic benzimidazole. However, the mass spectrum of phenyl cyanamide proved indistinguishable from our scan. Since this compound is also known¹⁰ to be formed on heating (I) in solution, the identity of the scan in question seems to be adequately established. The formation of phenyl cyanamide from (I) may then proceed as shown in Fig. 4.

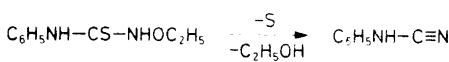


Fig. 4.

Experimental. Scans 1 to 5 were obtained from a Varian MAT CH 7 combined gas chromatograph-mass spectrometer equipped with a double-stage separator EHP of the Biemann-Watson type. Operating conditions were as described in Ref. 3.

The scan which is shown to be due to phenyl cyanamide was obtained using an LKB 9000 combined gas chromatograph-mass spectrometer with a two step jet separator of the Becker-Ryhage type. The mass spectrometer was operating at 70 eV. The ion source temperature was 270°C and the ionizing current was 60 μA . As the thermal degradation of the thioureide structure seems to be catalyzed by metals,¹ a small piece of nickel foil was placed in the flash heated injection port of the gas chromatograph, which usually is operated by an on column technique. The temperature in the injection port was 310°C. The separation was achieved on a 2.7 m \times 1.5 mm glass column packed with 5 % SE 30 on 80-100 mesh acid washed silanised Gas-Chrom Q. The column temperature was 120°C, and the helium flow rate through the column was 25 ml/min.

The starting materials. Ethoxyamine (b.p. 69°C¹¹) was obtained in 40 % yield with b.p. 69-70°C following the directions given for methoxyamine in the literature.¹²

1-Ethoxy-3-phenylthiourea. A solution of phenyl isothiocyanate (0.1 mol) in ether (25 ml) was added to another solution of ethoxyamine (0.1 mol) in ether (25 ml). A slightly exothermic reaction occurred on mixing. The solution was allowed to stand for 24 h. The colourless, crystalline precipitate was filtered off and washed with a small amount of ether. The crude product (yield 60 %; m.p. 98–99°C) was submitted to elemental analysis without further purification. (Found: C 54.90; H 6.14; N 14.27. Calc. for $C_9H_{12}N_2OS$: C 55.09; H 6.16; N 14.28).

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Note on the Structures of $M^{IV}P_2O_7$ ($M^{IV} = Ge, Zr, \text{ and } U$)

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In connection with studies on the geometry of anions of B_2X_7 , stoichiometry, such as diphosphates, several members of the extensive series of $M^{IV}P_2O_7$ compounds have been synthesized and characterized by X-ray techniques. This family of compounds was first investigated by Levi and Peyronel^{1,2} who reported the structure to be cubic (space-group $Pa\bar{3}$). The structure determination was performed on the basis of X-ray powder data of ZrP_2O_7 . The symmetry requires the P—O—P bridge of the P_2O_7 group to be linear.

While the existence of the linear P—O—P bridge has been questioned from several quarters as being not very likely from a theoretical point of view the first experimental evidence of deviations from the structure given by Levi and Peyronel was reported in 1963 by Völlenke, Wittmann and Novotny,³ who found from single-crystal data of GeP_2O_7 , that the actual cube axis of this compound is three times the one previously reported.

The compounds prepared within the present investigation include SiP_2O_7 , GeP_2O_7 , TiP_2O_7 , ZrP_2O_7 , SnP_2O_7 , ThP_2O_7 . Single crystals suitable for X-ray examinations have been obtained of the Ge, Zr, and U compounds.

X-Ray powder patterns of the various compounds were taken with a Guinier-Hägg camera using strictly monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) and with potassium chloride ($a = 6.2923 \text{ \AA}$ at 25°C)⁴ added to the specimen as an internal standard. The photographs of SiP_2O_7 and GeP_2O_7 were found to contain a large number of very weak lines not accounted for by the unit cells reported by Levi and Peyronel. Such lines were not observed in the patterns of the other specimens. All the extra lines could be indexed when the unit cell reported by Novotny and coworkers³ was assumed. This type of superstructure was also revealed by single-crystal rotation and Weissenberg photographs of GeP_2O_7 , ZrP_2O_7 , and UP_2O_7 . The dimensions of the super-