plate, previously dried 30 min at 100°C. The plate was first developed with chloroform and then with benzene-ethyl acetate 10:1.[3] The silica gel layer was divided into squares of 1–4 cm², and each of these was scraped into a counting vial and analysed with a liquid scintillation spectrometer (Packard Tri-Carb, Model 3314). One spot, separate from pentachlorophenol, was detected, corresponding to 3–4 % of the activity.

The purity of inactive pentachlorophenol, synthesized as described above, was checked by gas chromatography after methylation with diazomethane. An Aerograph Hy-Fi Fractometer, Model 600, supplied with an Electron Capture Detector was used. The column was packed with 20 % SE 30 on Chromosorb W and the temperature was 200°C. The only impurity found was 2,3,4,6-tetrachlorophenolether, corresponding to 1 % of the product.

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Thermal Fragmentations

II.* *N*-Isothiocyanatoamines from 4,4-Disubstituted Thiosemicarbazides

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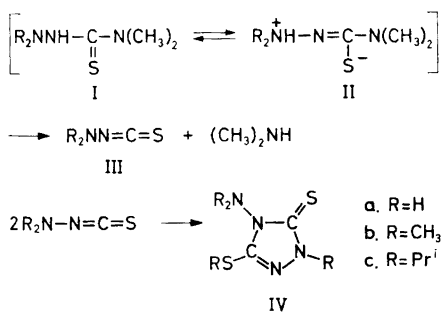
In part I[1] of this series it was shown that heating 4,4-dimethylthiosemicarbazide (Ia) resulted in the evolution of dimethylamine, together with hydrogen sulfide. The residue was shown to consist partly of the dimethylammonium salt of 4-amino-3,5-dimercapto-1,2,4-triazole, from which 4-amino-3-mercapto-1,2,4-triazol-2-ine-5-thione (IVa) was liberated on treatment with acid. It has previously been found[2] that the closely related 4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione (IVb) is the most stable product from dimerization of the unstable *N*-isothiocyanatodimethylamine (IIIb). This suggested that IVa was formed *via* the unknown isothiocyanatoamine (IIIa) by dimerization, *i.e.*



Preliminary experiments showed that detection of IIIa by gas chromatography or mass spectrometry of the gaseous products from pyrolysis of Ia could not be achieved with certainty, the main problem being that if Ia was heated at 10^{-3} mm Hg sublimation occurred prior to fragmentation. Attempts to solve this problem by heating the inlet system to the pyrolysis temperature were unsuccessful presumably because, under these conditions, any IIIa formed would dimerize immediately.

From infrared and NMR spectroscopic investigations,[3] it can be concluded that Ia and Ib exist in the non-polar form both in the solid state and in solution. Therefore, if pyrolysis of Ib can be shown to yield IIIb and dimethylamine it is reasonable to assume that Ia on pyrolysis breaks down into IIIa and dimethylamine.

When Ib was pyrolyzed in a reaction vessel directly connected to the inlet system of the mass spectrometer, a mass spectrum was obtained consisting of the mass spectrum of IIIb (molecular ion at *m/e* 102) on which was superimposed the mass spectrum of varying amounts of a substance $C_5H_9N_3S_2$ [*m/e* 175]. The

* Ref. 1 "The Decomposition of 4,4-Dialkyl-substituted Thiosemicarbazides" should be considered part I.

authentic mass spectrum of IIIb was obtained from a product prepared by pyrolysis of 1-(*N*,*N*-dimethylthiocarbazoyl) -imidazole.[2] The formula for the byproduct was deduced from the isotopic composition and the shift from *m/e* 175 to *m/e* 184 caused by deuteration. The same by-product has also been observed in some of the authentic mass spectra of IIIb and investigations on the structure will be reported later.

This observation shows that *N*-isothiocyanatomines are formed on pyrolysis of thiosemicarbazides. The analogous reaction for thioureas has received some attention lately [4] and has been shown to give isothiocyanates. The connection between thermal and mass spectrometric fragmentation has also been discussed.[5] In contrast to Ia, 1,1-diisopropyl-4,4-dimethylthiosemicarbazide both in the solid state and in solution has been shown to adopt the dipolar form IIc.[3] This form would, by analogy to the results obtained with thiocarbazoylimidazoles [6] with the same structure, be expected to give the stable *N*-isothiocyanatodiisopropylamine (IIIc) on pyrolysis.

When IIc was dissolved in absolute ethanol and injected in a gas chromatograph with the injection block heated to *ca.* 230°C, thermal cleavage was quantitative and instantaneous. The retention time of the main fragment proved to be identical with the retention time of authentic IIIc prepared from 1-(*N*,*N*-diisopropylthiocarbazoyl)imidazole.[7] A definitive proof that IIIc can be formed on pyrolysis of IIc was obtained by submitting the fragmentation products to a mass-spectrometric analysis. The mass spectrum obtained was in nearly every detail identical with that of authentic IIIc with the exception that the mass spectrum of dimethylamine was superimposed from *m/e* 45 and downwards.

This result is of special interest in so far as it shows that thiocarbazoyl compounds other than imidazolides can form *N*-isothiocyanatoamines on heating. A systematic investigation of the behaviour of such compounds on pyrolysis has been undertaken and will be published in subsequent papers. Also, representatives of the hitherto unknown classes of compounds, $RO-N=C=O$ and $R_2N-N=C=O$, have been prepared by analogous methods (*cf.* the following papers).

Experimental. An improved method for the preparation of Ib [8] and the preparation of IIc will be reported later from this laboratory [3] as well as IR and NMR studies on these compounds.

The gas chromatographical analyses were carried out on a Perkin-Elmer 116 instrument, using a two meter O-column at 140°C with helium as carrier gas. The injection block was held at 230°C. The flow rate was 73 ml/min. The retention time was 8.0 min for IIIc, and in addition an unidentified peak appeared at 16.5 min.

The mass spectra were obtained with an Atlas CH-4 instrument operating at 70 eV. The inlet system was kept at 40°C. The temperature in the ion source was *ca.* 150°C, and the ionizing current 35 μA.

The following apparatus proved convenient for the preparation of *N*-isothiocyanatodimethylamine from 1-(*N*,*N*-dimethylthiocarbazoyl)imidazole. A 400 mm long, 10 mm bore horizontal closed glass tube was connected to a receiver immersed in liquid nitrogen which, in turn, was connected to the inlet system of the mass spectrometer, the pump of which was used for diminishing the pressure of the system to 10^{-3} mm Hg. The 100 mm length of the glass tube furthest from the receiver served as the reaction chamber and was electrically heated. The long air-cooled part of the glass tube was essential for condensation of the subliming imidazole formed from the reaction.

The thiosemicarbazides were pyrolyzed at 160°C in a stainless steel vessel connected directly to the inlet system.

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