

using filtered copper radiation. Only the strong lines with 2θ less than 50° are listed.

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N-Isothiocyanatoamines

I. On the Existence of Monomeric *N*-Isothiocyanatodialkylamines (Dialkylaminoisothiocyanates)

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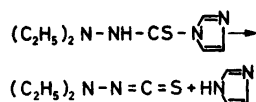
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In a recent communication, Podgornaya *et al.*¹ reported that *N*-piperidinedithiocarbamic acid on heating in ethanol will eliminate hydrogen sulfide to give piperidinoisothiocyanate (*N*-isothiocyanatopi-

peridine). This compound was characterized by its m.p. and by N and S analysis. Our work has provided strong evidence that the substance formed is, in fact, *N,N*-pentamethylenehydrazinium *N,N*-pentamethylenedithiocarbazate. A recent postulation² of aminoisothiocyanate being an intermediate in the reaction between dithiocarbamic esters with amines to form thiosemicarbazides prompts us to give a preliminary account of our findings.

We believe this report provides the first recognized case entailing thermal decomposition of thiocarbazoylimidazoles to species exhibiting the properties expected from a monomeric *N*-isothiocyanatoamine. The corresponding *N*-isocyanatoamines have been claimed by a similar method by Staab³ and reported to dimerize immediately.

These studies have primarily been conducted with *N,N*-diethylthiocarbazoylimidazole. This compound has been chosen because of its ready availability and the relative ease of characterisation of the products from the thermolysis reaction:



The *N*-isothiocyanatodiethylamine thus formed may be stored for some time in liquid air, and shows the expected reactions with, for example, amines to form thiosemicarbazides and hydrazines to give thiocarbonylhydrazides.

Further work on this interesting new group of compounds will be presented later in subsequent articles. Without citing specific examples, it can be stated that the application of the method outlined below (as well as thermolysis of dithiocarbazates) offers very promising preliminary results with other (monomeric and dimeric) aliphatic and aromatic *N*-isothiocyanatoamines.

Experimental. The analyses were carried out at the microanalysis department of this laboratory. The infrared spectra ($400-4000\text{ cm}^{-1}$) were recorded using a Perkin-Elmer model 337 grating infrared spectrophotometer.

N,N-Diethylthiocarbazoylimidazole. The preparation of this compound followed essentially the procedure by Staab and Walther⁴ for

N,N-diethylthiocarbonylimidazole. This yielded white crystals, m.p. 123–124°C, from dilute ethanol. (Found: C 48.30; H 7.17. Calc. for $C_8H_{14}N_4S$: C 48.47; H 7.12).

N-Isothiocyanatodiethylamine monomer. The following apparatus proved convenient for the small-scale preparation (50–250 mg) of the monomer. A 400 mm long horizontally adjusted closed glass tube with a tubing of 10 mm was connected with a receiver ("cold finger"), immersed in liquid air, which, in turn, was connected to a vacuum system capable of pumping to 10^{-4} mm pressure. The 100 mm length of the glass tube furthest from the cold finger 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. By careful control of the electrical heating, contamination of the monomer, collected in the cold finger, could be avoided.

In a typical experiment, 100 mg of the *N,N*-diethylthiocarbonylimidazole prepared above was evenly spread out in the reaction chamber. The apparatus was evacuated and heating applied. The reaction began just below the m.p., and became apparent by the formation of a circular, yellowish zone in the cold finger 5 mm over the surface of the liquid air. Immediately thereafter, crystals of imidazole began to settle in the unheated part of the glass tube, and heating was now carefully adjusted to a slow rate. Reaction was complete within ca. 15 min, when the temperature in the reaction chamber had reached 130°C. At this time it was often observed that some of the starting material had sublimed with the imidazole. To ensure complete reaction the heating zone was accordingly extended ca. 50 mm before the heating mantle was removed. The *N*-isothiocyanatodiethylamine was stored under nitrogen in the cold finger.

The yield of imidazole (identified by the infrared spectrum (KBr) and mixed m.p. with an authentic sample) was nearly quantitative. The crude *N*-isothiocyanatodiethylamine, m.p. –103 to –105°C, was obtained as a yellowish oil, which rapidly dimerised on heating to room temperature. It was analytically pure, which was shown by elemental analysis of the dimer formed (see below).

The low m.p. and high volatility of the crude compound points to this being a monomer, as does the rapid reaction with added amines or hydrazines. Convincing evidence was obtained by recording the infrared spectrum in methylene chloride at –78°C. The prominent features are (in cm^{-1}): 2990 s,

2950 m, 2040 s, 2010 vs, 1490 m, 1475 m, 1450 s, 1408 m, 1388 s, 1348 w, 1167 m, 1140 m, 1110 w, 1078 m, 1066 s, 1051 s, 1009 m, 847 m, 529 m. The presence of a very intense doublet near 2000 cm^{-1} can only be assigned to the antisymmetrical NCS stretching vibration⁶ and was accordingly found to be absent in the dimeric substance. Dimerisation could easily be followed by the appearance of a new peak at 1630 cm^{-1} . A consideration of the intensities showed the amount of dimer present in the crude monomer to be negligible.

N-Isothiocyanatodiethylamine dimer. This colourless crystalline substance, m.p. 56–58°C, was shown by mass spectrometry to be a dimeric form of *N*-isothiocyanatodiethylamine ($M = 260$). (Found: C 46.13; H 7.80; N 21.90; S 24.46. Calc. for $C_{10}H_{20}N_4S_2$: C 46.14; H 7.75; N 21.53; S 24.59). The structure of this compound is at present under investigation.

Compound claimed to be piperidinoisothiocyanate. This somewhat unstable colourless crystalline compound was prepared several times according to the directions given by Podgornaya *et al.*¹ with m.p. varying between 109 and 116°C. The infrared spectrum very clearly indicated this to be a hydrazinium salt (strong lines at 3200 cm^{-1} and a broad strong band at 2240 cm^{-1}) and we therefore decided to prepare *N,N*-pentamethylenedithiocarbazate for comparison. This was made from 2 mole *N*-aminopiperidine and 1 mole carbon disulfide in ether cooled to 0°C. The compound isolated proved to be identical with Podgornaya's compound (no mixed melting point depression and identical infrared spectra). Incidentally, this compound has nitrogen and sulfur values close to those calculated for piperidinoisothiocyanate, which explains the confusion between the two substances. (Found: C 47.98; H 8.52; N 19.62; S 23.07. Calc. for $C_{11}H_{24}N_4S_2$: C 47.81; H 8.75; N 20.28; S 23.16. Calc. for piperidinoisothiocyanate, $C_6H_{10}N_2S$: C 50.69; H 7.09; N 19.71; S 22.51).

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