

Part of the work was aided by a grant from the Swedish Natural Science Research Council (Contract No. 2318).

1. Yen, Ai-chen, and Dyrssen, D. *Acta Chem. Scand.* To be published.
2. Cavalca, L., Nardelli, M. and Braibanti, A. *Gazz. Chim. Ital.* **23** (1954) 1239.
3. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1952, 2nd Ed.

Received October 23, 1967.

N-Isothiocyanatoamines

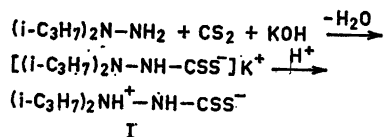
V. Conversion of

N-Isothiocyanatodiisopropylamine to Seleno- and Tellurothiocarbazic Acid Derivatives

U. ANTHONI, CH. LARSEN and
P. H. NIELSEN

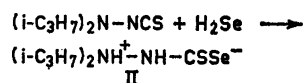
Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

Recently,¹ the synthesis and infrared spectra of several dithio- and diseleno-carbazic acids have been described and their dipolar structure established. *N,N*-Diisopropyldithiocarbazic acid (I), which became of interest in connection with our studies on *N*-isothiocyanatodiisopropylamine,² proved to be readily available from *N,N*-diisopropylhydrazine and carbon disulfide by a closely related method.



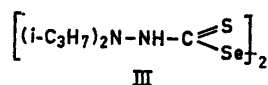
Replacement of carbon disulfide in this synthesis by CSSe or CSeTe would furnish the title compounds. Both these starting materials, however, are unstable and dif-

ficult to prepare. To circumvent these preparative difficulties, we decided to investigate the reaction between *N*-isothiocyanatodiisopropylamine and H₂Se or H₂Te. The first reaction proceeds according to the following scheme.



The assignment to I and II of the dipolar structures shown followed from their infrared spectra (KBr). In the high frequency region, the strong bands originating from the NH⁺ stretching vibrations were observed in the 2500–3000 cm⁻¹ range and the NH stretching vibrations are (as a result of the neighbouring positive charge) characteristically¹ around 3100 cm⁻¹. The lower frequency regions were nearly identical, apart from two absorptions in the regions 1000–1050 cm⁻¹ and 600–700 cm⁻¹. These bands have been assigned to the antisymmetrical and symmetrical CSS⁻ stretching vibrations for dithiocarbazic acids.¹ Consistently with this, we assign the bands at 1048 and 1017 cm⁻¹ in I and II, respectively, to the antisymmetrical CXS⁻ vibrations and the bands at 680 or 650 and 660 or 624 cm⁻¹ to the corresponding symmetrical modes.

If an ethanolic solution of II is oxidized for some time with air, the corresponding diselenide (III) is formed.



By treating *N*-isothiocyanatodiisopropylamine with hydrogen telluride we obtained, instead of the expected tellurothiocarbazic acid, the tellurium analogue of III (IV). The reason for the failure to observe the intermediate tellurothiocarbazic acid is at present obscure, especially if the strongly reducing properties of hydrogen telluride are taken into account. It cannot *a priori* be decided whether III and IV have the diselenide and ditelluride structures, respectively, instead of being disulfides, though chemical reasoning argues for the former alternative. However, the infrared spectra support the

above formulation, being almost identical in the whole range between 3500 and 400 cm^{-1} . It is probably not safe to comment on the small differences between the spectra, but it is pertinent to point out that if III and IV were disulfides, we should, by analogy to the differences between the spectra of thio- and selenocarbonyl compounds,¹ expect differences in the location of the skeletal bands at 1310 and 1009 cm^{-1} . Since these are identical in III and IV, it may be concluded that they arise from the same grouping, *i.e.* the *N,N*-diisopropylthiocarbonyl radical, or, in other words, that III and IV should be formulated as a diselenide and a ditelluride, respectively.

The reaction of *N*-isothiocyanatodiisopropylamine with hydrogen sulfide proceeds to give bis-(*N,N*-diisopropylthiocarbonyl)-sulfide and will be treated in full in part VI of this series.

Experimental. Conditions and equipment used for the physical measurements were those described in part II of this series.³

N,N-Diisopropylthiocarbonyl acid (I). *N,N*-Diisopropylhydrazine (2.3 g) was stirred vigorously for 3 h with KOH (1.1 g) and CS_2 (1.6 g) in water. On addition of concentrated hydrochloric acid, an oil precipitated which soon crystallized. It was washed with dry ether, dried, dissolved in methylene chloride and precipitated with pentane. A 40 % yield of colourless crystals with m.p. 112–113°C (decomp.) was obtained. (Found: C 43.87; H 8.52; N 14.55. Calc. for $\text{C}_7\text{H}_{16}\text{N}_2\text{S}_2$: C 43.71; H 8.39; N 14.57). *IR-spectrum*: 3070s, 2998m, 2983m, 2968s, 2920s br, 2770s br, 1467m, 1457s, 1404m, 1387m, 1373m, 1357m, 1328s, 1308s, 1294vs, 1218s, 1168s, 1136m, 1111m, 1090m, 1048vs, 991m, 949w, 930m, 893m, 840w, 796s, 680s, 650m br, 577m, 548w, 490s, 475w.

N,N-Diisopropylselenothiocarbonyl acid (II). A slow stream of hydrogen selenide (generated from aluminium selenide and 4 N HCl) was bubbled through a 10 % ethanolic solution of *N*-isothiocyanatodiisopropylamine.² After 10 min, ochre-yellow crystals began to deposit and by saturating the solution with hydrogen selenide a total yield of 74 % could be obtained after filtration and washing with ethanol. The compound melts at 103–104°C with decomposition. (Found: C 34.85; H 6.69; N 11.72.

Calc. for $\text{C}_7\text{H}_{16}\text{N}_2\text{SSe}$: C 35.14; H 6.74; N 11.71). *IR-spectrum*: 3050s, 2980m, 2960m, 2920s br, 2770s br, 1468m, 1458s, 1406m, 1388m, 1373m, 1363m, 1328s, 1310s, 1293s, 1220s, 1170s, 1136s, 1108m, 1088m, 1017vs, 992m, 944w, 930m, 924m, 890m, 792s, 660m br, 624m, 578w, 528m, 517w, 490m, 463m.

Bis-(*N,N*-Diisopropylthiocarbonyl)ditelluride (IV). This compound was prepared in the same way as II, using hydrogen telluride instead of hydrogen selenide. It is important that the stream of hydrogen telluride is fast; if it is not, a yellow solution is formed which cannot be brought to deposit any crystals even on prolonged scratching with a spatula. The brick-red crystals, obtained in 70 % yield, produce elemental tellurium on exposure to air for any extended time. On heating, the compound decomposes at 110–113°C without melting. (Found: C 29.9; H 5.3; N 10.1. Calc. for $\text{C}_{14}\text{H}_{30}\text{N}_4\text{S}_2\text{Te}_2$: C 29.3; H 5.3; N 9.8). *IR-spectrum*: 3070s, 2965s, 2920s br, 2867s sh, 2800s br, 1488m, 1468m, 1458m, 1388m, 1368m, 1324m, 1308s, 1208w, 1183w sh, 1170s, 1138s, 1124m sh, 1100w, 1007s, 992m, 940w, 923w, 897m, 850w, 770s, 704m br, 611m, 570w, 520m, 510m, 475w, 460w.

Bis-(*N,N*-diisopropylthiocarbonyl)diselenide (III). This compound separated as yellow crystals from an ethanolic solution of II. After washing with ethanol and drying, it had a m.p. of 139–140°C. (Found: C 35.58; H 6.38; N 11.60. Calc. for $\text{C}_{14}\text{H}_{30}\text{N}_4\text{S}_2\text{Se}_2$: C 35.30; H 6.35; N 11.77). *IR-spectrum*: 3105s, 2969s, 2937s, 2910 m sh, 2867m, 1490s, 1461m, 1388m, 1368m, 1326m, 1311s, 1208w, 1184w, 1170s, 1139s, 1120m, 1101w, 1008s, 996 m sh, 940w, 920w, 896m, 849w, 770s, 681m br, 614m, 532m, 518m, 470w.

Acknowledgement. We wish to thank Dr. M. Ettlinger for stimulating discussions during the course of the study.

1. Anthoni, U. *Acta Chem. Scand.* **20** (1966) 2742.
2. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **21** (1967) 2061.
3. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **21** (1967) 1201.

Received October 31, 1967.