ever, the rate of the second reaction is sufficiently slow not to interfere with the kinetic measurements of reaction 1.

Since $Co(CN)_5SCN^{3-}$ is more stable than $Co(CN)_5NCS^{3-}$, it is perhaps surprising that the nitrogen-bonded isomer is the primary product of reaction 1. However, it must be noted that the nature of the product of reaction 1 will be governed by the relative nucleophilicities of the nitrogen and sulfur ends of thiocyanate ion. In organic reactions, where isothiocyanates are considerably more stable than thiocyanates, the ratio of attack by the sulfur end to attack by the nitrogen end varies between 10^3 and 2.5.[17] Attack by the nitrogen end becomes more favorable as the stability of the carbonium ion increases, presumably because the affinity of the electrophilic center for the hard nitrogen end increases relatively to the soft sulfur end.[17] A similar explanation might be used to account for the primary formation of $Co(CN)_5NCS^{3-}$ in reaction 1: the relatively stable $Co(CN)_5^{2-}$ intermediate displays a kinetic discrimination in favor of the hard nitrogen end although the sulfur-bonded isomer is thermodynamically favored. An analogous (but inverse) situation was previously reported for the thiocyanate linkage isomers of pentaamminerhodium(III) and pentaammineiridium(III);[15] reaction of $Rh(NH_3)_5OH_2^{3+}$ or $Ir(NH_3)_5OH_2^{3+}$ with thiocyanate ion yields the sulfur-bonded isomer in the first step of the reaction and is followed by rearrangement to the more stable nitrogen-bonded isomer.

[17] A. Fava in "The Chemistry of Organic Sulfur Compounds," Vol. II, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press Inc., New York, N. Y., 1966, Chapter 3.

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The Preparation of Hexamethyldisilthiane

BY EDWIN LOUIS AND GRANT URRY

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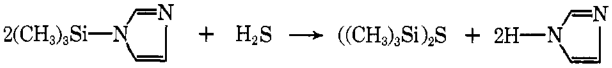
The many methods for the preparation of hexamethyldisilthiane that appear in the literature suffer from inconvenience, high cost of materials, or low yields, or they require equipment not ordinarily available in the laboratory.[1-6]

A novel method reported here utilizes the reaction between two readily available materials, H_2S and trimethylsilylimidazole.



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[4] G. Champetier, Y. Etienne, and R. Kullmann, *Compt. Rend.*, **234**, 1985 (1962).

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A solvent was not used in this reaction because of added problems of purification and because in one experiment, using benzene as a solvent, no hexamethyldisilthiane was produced.

The reaction can be effected in ordinary glassware with filtration carried out in a dry bag followed by atmospheric distillation of the filtrate or in a vacuum apparatus with separation of liquids from solid by vacuum condensation followed by high-vacuum distillations.

The yield of fully purified material was 68% in the bench-top preparation. Better yields often are obtained in the vacuum apparatus preparation.

Experimental Section

Apparatus and Reagents.—The work described here can be performed in a laboratory bench setup. It was found to be more convenient in our work to utilize some type of standard high-vacuum apparatus. Other times a bench-top vacuum assembly constructed from rubber tubing, a 1-l. bulb, mercury-bubbler manometer, and round-bottom flask was used. This was connected by means of a three-way stopcock to a vacuum pump, dry nitrogen tank, and dry H_2S source. The atmosphere within the system could thus be alternated between vacuum, H_2S, or dry nitrogen as needed.

Hydrogen sulfide (CP) was used from a tank as received from the Matheson Chemical Co.

Trimethylsilylimidazole was prepared according to the method of Birkofer and Ritter.[7] The material used displayed a boiling point of 92° (12 mm).

Hexamethyldisilthiane.—In one experimental run using a standard vacuum apparatus, 22.7 g (0.162 mol) of trimethylsilylimidazole was placed in a 50-ml one-necked flask fitted with an O-ring joint which contained a magnetic stirring bar. This operation was carried out in a nitrogen dry bag. The flask then was connected to a vacuum apparatus and evacuated. An approximately stoichiometric amount of H_2S was allowed to fill the evacuated apparatus. The reaction flask was cooled to 0° and stirred. The trimethylsilylimidazole reacted with the H_2S as evidenced by the drop of pressure in the system. The reaction mixture was stirred for about 12 hr. Reaction was accompanied by precipitation of solid white imidazole. The volatile portion of the reaction mixture was separated by passing it through a series of cold baths at 0, −30, and −196°. Hexamethyldisilthiane stopped in the −30° bath and upon repeated fractionation gave a vapor pressure of 3–4 mm at room temperature (25–27°). The yield was determined by condensing the purified hexamethyldisilthiane into a preweighed flask, corrected for buoyancy, and reweighing. The yield of the repurified product was calculated to be 67.8%.

The reaction mixture was sometimes purified by fractional distillation to a boiling point of 162°. This however, required several distillations.

Anal. Calcd for $C_6H_{18}Si_2S$: C, 40.44; H, 10.11; S, 17.96. Found: C, 40.31; H, 10.40; S, 17.70.

Infrared analysis showed the same spectrum described by Kriegsman[8] with peaks at 3.3, 3.4, 6.9, 7.1, 8.0, 9.95, 11.85, 12.1, 13.2, and 14.5 μ.

Vapor density measurements gave an average molecular weight of 176.9 as compared to the calculated value of 178.5.

Vapor pressure data are given below.

	Temp, °C					
	29.2	36.4	56.8	68.1	84.9	102.0
Obsd	7.150	11.38	24.47	36.81	68.10	119.18
Calcd	7.162	10.03	24.07	37.39	68.23	119.20

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[7] L. Birkofer and A. Ritter, *Angew. Chem. Intern. Ed.*, **4**, 417 (1965).

[8] H. Kriegsman, *Z. Elektrochem.*, **61**, 1088 (1957).

The calculated vapor pressures were obtained using

$$\log P_{\mathrm{mm}} = (-1903.2/T) + 7.1490$$

The normal boiling point extrapolated from these data is 170.4°. The reported atmospheric distillation temperature is 162–163°.

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Poly(carbon diselenide)[1a]

BY A. J. BROWN[1b] AND E. WHALLEY

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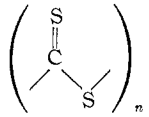
Carbon disulfide can be polymerized to a black solid at high pressures which has the structure[2]



Carbon diselenide[3] spontaneously precipitates a black solid at the rate of about 1%/month at room temperature whose structure has not been investigated. It is probably similar to that of poly(carbon disulfide), and its structure has therefore been investigated by infrared spectroscopy.

Experimental Methods and Results

The carbon diselenide was kindly supplied by Noranda Research Centre, Pointe Claire, Quebec. It was allowed to polymerize spontaneously for several months. The monomer was removed by vacuum distillation, and the solid was evacuated at 100°. Like poly(carbon disulfide) it is amorphous to X-ray diffraction.

The infrared spectra were taken as mulls in Nujol and, less satisfactorily, as dispersions in potassium bromide or polyethylene wax pellets. The frequency range 4000–50 cm^{-1} was covered with a Perkin-Elmer 301 spectrophotometer. The spectrum, with allowance for the scattering, is shown in Figure 1. There is a strong band at 885 cm^{-1} and there are weak bands at 940 and 775 cm^{-1}, all due to the polymer. In addition there is a band near 1260 cm^{-1} of variable intensity relative to the other bands, presumably caused by the ν_3 vibration of the residual monomer,[4] and weaker bands near 1460, 1355, and 1316 cm^{-1} of unknown origin. The 885-cm^{-1} band is too strong relative to the 1260-cm^{-1} band for it to be associated with the 925-cm^{-1} band[4] of the monomer.

The thermodynamics of polymerization of carbon disulfide and diselenide are of some interest. It has been reported[5] that carbon and sulfur will react at 37 kbars and 800° to give poly(carbon disulfide). This seems unlikely to be correct on thermodynamic grounds (see Discussion) and several attempts to repeat this observation have failed, in agreement with observations reported by Butcher, Weston, and Gebbie.[6]

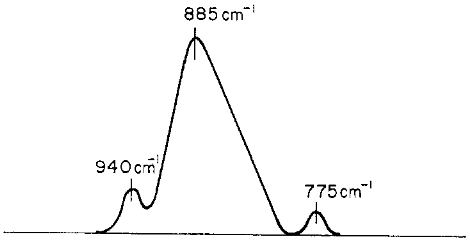
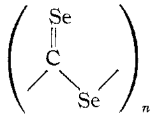


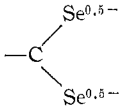
Figure 1. Infrared spectrum of poly(carbon diselenide).

Discussion

Poly(carbon disulfide) has a strong absorption at 1062 cm^{-1},[2] which is due to the C=S stretching vibration. If black carbon diselenide has an analogous structure, a strong infrared band due to the C=Se stretching vibration would be expected in the region 800–900 cm^{-1}. The 885-cm^{-1} band can probably be associated with this vibration. It seems very likely therefore that black carbon diselenide has essentially the structure



and is thus poly(carbon diselenide). Diselenocarboxylate ions, which contain the unit



have strong bands in this region.[7] Furthermore, the frequency ratio of the asymmetric stretching band of the monomer (1270 cm^{-1})[4] to the strong band of the polymer is 1.44 for carbon diselenide and 1.437 for carbon disulfide,[2] which provides further evidence for the assignment. The 775-cm^{-1} band can perhaps be associated with the C–Se stretching motion. Minor departures from the proposed structure would of course not be detectable by the techniques used and could cause some of the unassigned bands. Since the polymerization proceeds spontaneously at room temperature, the stable form of carbon diselenide is not the triatomic molecule but the polymer.

The thermodynamic relations between the monomer, the polymer, and the elements of both carbon disulfide and carbon diselenide are of some interest. Liquid carbon disulfide at room temperature is unstable relative to the elements by 15 kcal mol^{-1} in the Gibbs energy.[8] Carbon disulfide can be polymerized at pressures as

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(1) (a) NRC No. 10160; (b) NRC Postdoctoral Fellow, 1963–1965.

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