Table I

Infrared Spectra of $(C_2H_5)_4NMFe_2(CO)_{12}$ (M = Tc, Mn, or Re)

Element	Absorption frequency, cm^{-1}							
Tc	2077 w	2008 m	1987 s		1943 m	1903 w	1815 w	1783 w
Mn[2]	2063 vw	1999 m	1990 s	1972 m	1944 m	1903 w	1827 w	1785 w
Re[3]	2075 w	2006 m	1991 s		1946 m	1903 w	1814 w	1785 w

solution changed color very dramatically: from almost colorless to yellow to orange to red in less than 5 min, then to a very deep red-violet after extended irradiation. After irradiation, excess (1 mmol) tetraethylammonium bromide in ethanol was added to stabilize the anion, and the solvent was removed under high vacuum. The residue was extracted several times with *n*-hexane to remove the unreacted carbonyls. The infrared spectrum in the carbonyl stretch region of a THF solution of the salt is remarkably similar to the spectra of the analogous manganese and rhenium compounds; the infrared absorption bands for the three anions are given in Table I.

The first group VIIb diiron dodecacarbonyl anion reported was prepared by the reaction of the pentacarbonylmanganese anion with iron pentacarbonyl in diglyme.[2] It is not known whether this reaction is general for all of the group VIIb elements. The photochemical reaction, however, of a group VIIb carbonyl with iron pentacarbonyl is a general reaction—all members of this series have now been prepared by this method. The products of this preparation depend on the particular group VIIb element and the solvent employed; the principal products being a neutral linear $M_2Fe(CO)_{14}$ species and a triangular anionic $MFe_2(CO)_{12}^-$ species. The usual differences in properties of transition elements within a group are not very apparent in the structures of their metal carbonyls,[5] but the typical difference between elements of the first transition series and those in the second and third series is quite obvious in the reactions of their carbonyls. The formation of the neutral linear species is favored by manganese and *n*-hexane as the solvent, and the triangular anionic species is favored by technetium and rhenium and polar solvents, such as THF or diethyl ether; the element and solvent dependence is summarized in Table II.

Table II

Yield Dependence on Group VIIb Element and Solvent

Element	THF or ether: Linear	THF or ether: Triangular	*n*-Hexane: Linear	*n*-Hexane: Triangular
Tc	None	High	Trace	Moderate
Mn	Moderate	Moderate[a]	High	None
Re	None	High	Low	Moderate

[a] Required prolonged (4-hr) irradiation.

The striking similarity of the infrared carbonyl stretch spectra of the manganese and rhenium compounds to that of triiron dodecacarbonyl led previous workers[2,3] to propose an $Fe_3(CO)_{12}$-like structure in which the apical *cis*-$Fe(CO)_4$ moiety is replaced by a *cis*-$M(CO)_4^-$ group, where M = Mn or Re; the same structure is also proposed for the technetium iron carbonyl anion.

All known isotopes of technetium are radioactive, and the isotope used in this work was ^{99}Tc (a fission product available from Oak Ridge National Laboratory, Oak Ridge, Tenn). This isotope can be safely used with standard radiochemical precautions[6] in ordinary laboratory glassware and equipment because of its long half-life (2.1×10^5 years) and its decay mode involves only a low-energy β particle (maximum energy, 0.29 MeV).[7] Since the average β-particle energy is about 0.1 MeV, the β radiation and attendant bremsstrahlung are attenuated to dose rates of 1 mr/hr, and less, at a distance of 1 ft by ordinary laboratory glassware.[8] Personnel and equipment were monitored with a thin (1.4-mg/cm^2) end-window Geiger portable survey meter.

Acknowledgment.—This work was supported by the U. S. Atomic Energy Commission under Contract At-40-2434 with Florida State University. The authors are grateful to the U. S. Atomic Energy Commission for obtaining the technetium carbonyl and for the support of this research while M. W. L. served as an Oak Ridge Associated Universities research participant at the Savannah River Laboratory, which is operated for the USAEC by E. I. du Pont de Nemours and Co. under Contract At(07-2)-1.

---

[5] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965).

[6] R. T. Overman and H. M. Clark, "Radioisotope Techniques," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 153–154.

[7] D. Strominger, J. M. Hollander, and G. T. Seaborg, *Rev. Mod. Phys.*, **30**, 585 (1958).

[8] "Radiological Health Handbook," revised ed, U. S. Department of Health, Education, and Welfare, Washington, D. C., 1960, p 155.

Contribution from the Departments of Chemistry,
University of Southern California,
Los Angeles, California, and
State University of New York, Stony Brook, New York

The Synthesis of Potassium Isothiocyanatopentacyanocobaltate(III)[1a]

By Ingo Stotz, W. K. Wilmarth, and Albert Haim[1b]

Received February 16, 1968

In our previous study of the substitution of water in the aquopentacyanocobaltate(III) ion by thiocyanate ion[2] we did not isolate the reaction product and, therefore, could not establish whether the sulfur- or nitrogen-

---

[1] (a) This work was supported by Grant GP-6528 from the National Science Foundation and by Grant AT(11-1)-113(PA4) from the Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation.

[2] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

bonded isomer was produced. Subsequently, Burmeister[3] isolated the product of the redox reaction between $Co(NH_3)_5NCS^{2+}$ and $Co(CN)_5^{3-}$ and concluded, on the basis of infrared evidence, that the sulfur-bonded isomer $Co(CN)_5SCN^{3-}$ is formed in this reaction. Recently, Halpern and Nakamura,[4] in a study involving the detection of various metastable linkage isomers produced by redox reactions, indicated that no evidence for an intermediate could be obtained in the $Co(NH_3)_5NCS^{2+}$–$Co(CN)_5^{3-}$ reaction and also concluded that the initial reaction product is the sulfur-bonded isomer. In the present note, we wish to report that the initial product of the $Co(CN)_5OH_2^{2-}$–SCN^- reaction is the nitrogen-bonded isomer $Co(CN)_5NCS^{3-}$.

Experimental Section

Materials.—Isothiocyanatopentaamminecobalt(III) sulfate was prepared by the method of Werner and Muller[5] and converted to the perchlorate by treatment with sodium perchlorate. Potassium azidopentacyanocobaltate(III) was prepared by reaction of azidopentaamminecobalt(III) chloride[6] with potassium cyanide.[7] Solutions containing the aquopentacyanocobaltate(III) ion were prepared by reaction of $Co(CN)_5N_3^{3-}$ with nitrous acid.[7] Potassium thiocyanatopentacyanocobaltate(III) was prepared by the method of Burmeister,[3] except that the perchlorate salt of $Co(NH_3)_5NCS^{2+}$ was used instead of the sulfate. All other chemicals were reagent grade.

Preparation of Potassium Isothiocyanatopentacyanocobaltate(III).—One hundred milliliters of a neutral solution 0.01 *M* in $K_2[Co(CN)_5OH_2]$ and 0.5 *M* in KSCN was concentrated in a rotary evaporator to *ca.* 5 ml at 40° within 2–3 hr. The precipitate of $KClO_4$ was removed, and then 5–10 ml of 95% ethanol was added to the solution. The precipitate of $K_3[Co(CN)_5NCS]$ was filtered out, washed with ethanol and ether, and then dried under vacuum; yield 75%. *Anal.* Calcd for $K_3[Co(CN)_5NCS]$: C, 19.78; N, 23.07; S, 8.80; Co, 16.17. Found: C, 19.61; N, 22.76; S, 8.75; Co, 16.06.

Measurements.—Visible and ultraviolet spectra were measured with a Cary 14 recording spectrophotometer. Infrared spectra were measured with a Beckman IR-7 spectrophotometer. Samples were mulls in Nujol or hexachlorobutadiene.

Results

The $Co(NH_3)_5NCS^{2+}$–$Co(CN)_5^{3-}$ Reaction.—The reaction of $Co(NH_3)_5NCS^{2+}$ (2.1×10^{-3} *M*) with cyanide ion (1.5×10^{-2} *M*) catalyzed by a trace of cobalt(II) was allowed to proceed to completion (a few seconds), and the resulting solution was examined spectrophotometrically from 550 to 220 nm. Maxima were observed at 377 and 263 nm with molar absorptivities of 196 and 18,400, respectively. These values are characteristic of the sulfur-bonded isomer $Co(CN)_5SCN^{3-}$ since a sample of $K_3[Co(CN)_5SCN]$ prepared following the procedure of Burmeister[3] was also found to exhibit maxima at 377 and 263 nm.[8]

The $Co(CN)_5OH^{2-}$–SCN^- Reaction.—A solution 1.58×10^{-3} *M* in $Co(CN)_5OH_2^{2-}$ and 1.0 *M* in SCN^- at 40° was scanned in the wavelength range 500–300 nm every 10–15 min for 100 min. Under these conditions the calculated half-life of the reaction is 29 min. Isosbestic points were observed at 413 and 370 nm. The absorbance at 363 nm (an absorption maximum) in a 1-cm cell was 0.414 at 150 and 300 min. This absorbance corresponds to a molar absorptivity of 260. At long times the absorbance at 363 nm decreased very slowly, and the maximum shifted to longer wavelengths. For example, after 30 and 72 hr the absorbance values were 0.408 and 0.398, respectively, and the maximum occurred at 365 nm. In another experiment, the absorbance at 263 nm was followed as a function of time. The measurements were carried out at 40° with a solution 3.80×10^{-3} *M* in $Co(CN)_5OH_2^{2-}$ and 0.50 *M* in SCN^- (ionic strength was maintained at 1.0 *M* with sodium perchlorate). Under these conditions the calculated half-life for the reaction is 50 min. Values of the absorbance in a 1-cm cell (after 100-fold dilution) were 0.490, 0.512, 0.524, and 0.525 at 160, 217, 285, and 350 min, respectively. The last value corresponds to a molar absorptivity of 13,800. At long times, a very slow increase in absorbance was observed; thus, after 24, 48, and 72 hr the absorbance values were 0.530, 0.534, and 0.540, respectively. Clearly these results demonstrate the occurrence of two consecutive reactions. The product of the first reaction, isolated in the manner described in the Experimental Section, is the nitrogen bonded isomer $Co(CN)_5NCS^{3-}$. The infrared evidence to support this assertion is summarized in Table I. As seen in column 1, the C–S stretching frequency appears at 810 cm^{-1}, a value which falls within the range 780–860 cm^{-1}, characteristic of nitrogen-bonded complexes.[9] The nature of the second reaction has not been established. However, the increase in absorbance at 263 nm, the decrease in absorbance at 363 nm, and the shift of the latter maximum toward longer wavelengths are consistent with linkage isomerization of $Co(CN)_5NCS^{3-}$ to $Co(CN)_5SCN^{3-}$.

TABLE I

INFRARED SPECTRA OF $Co(CN)_5NCS^{3-}$ AND $Co(CN)_5SCN^{3-}$ IN THE CN AND CS STRETCHING REGIONS[a]

Frequency, cm^{-1}			
$K_3[Co(CN)_5NCS]$	$K_3[Co(CN)_5SCN]$[b]	$K_3[Co(CN)_5SCN]$[c]	Assignment
2131 s, 2124 s	2145 s, 2135 s, 2129 s, 2121 s	2147 s, 2137 m, 2129 s, 2122 s	Cyanide C–N str
2065 br	2110 s	2110 s	Thiocyanate C–N str
810 w	718 w	719 w	Thiocyanate C–S str

[a] Mulls in nujol or hexachlorobutadiene; s, strong; m, medium; w, weak; br, broad. [b] Prepared by heating $K_3[Co(CN)_5NCS]$ at 150° for 6 hr. [c] From ref 3.

The Isomerization of $Co(CN)_5NCS^{3-}$ to $Co(CN)_5SCN^{3-}$.—When a solid sample of $K_3[Co(CN)_5NCS]$ is heated for 6 hr at 150° or allowed to stand for 3–4 months at room temperature, it is found that the infrared absorption at 810 cm^{-1} disappears and a new band at 718 cm^{-1} appears. This latter value falls

---

[3] J. L. Burmeister, *Inorg. Chem.*, **3**, 919 (1964).

[4] J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).

[5] A. Werner and H. Muller, *Z. Anorg. Allgem. Chem.*, **22**, 101 (1900).

[6] M. Linhard and H. Flygare, *ibid.*, **262**, 328 (1950).

[7] R. Barca, J. Ellis, M. S. Tsao, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 243 (1967).

[8] The molar absorbancy indices were somewhat smaller than those obtained in the *in situ* reaction because the solid contained some potassium perchlorate.

within the range 690–720 cm^{-1} characteristic of sulfur-bonded thiocyanate complexes.[9] This result suggests that linkage isomerization occurs in the solid state. Moreover, when the solid heated at 150° is dissolved in water, the absorption spectrum of the aqueous solution exhibits maxima at 377 and 265 nm with molar absorptivities of 195 and 18,000, respectively. These values are in good agreement with those for $Co(CN)_5SCN^{3-}$, and we conclude that heating the solid $K_3[Co(CN)_5NCS]$ at 150° for 6 hr results in linkage isomerization.

Attempts to measure the $Co(CN)_5{}^{3-}$-catalyzed linkage isomerization in solution were unsuccessful. The spectrum of a solution 1.9×10^{-3} M in $Co(CN)_5NCS^{3-}$ and 1.0×10^{-4} M in $Co(CN)_5{}^{3-}$ was unchanged for 2 hr and exhibited the characteristic absorption maximum of the nitrogen-bonded isomer at 363 nm. This result demonstrates that no rapid $Co(CN)_5{}^{3-}$-catalyzed isomerization obtains. At 1.0×10^{-3} M $Co(CN)_5{}^{3-}$ with $[Co(CN)_5NCS^{3-}] = 3.4 \times 10^{-3}$ M, an absorbance change of 0.015 occurred in 20 min, the calculated absorbance change for linkage isomerization being 0.27. This result again demonstrates that the catalyzed isomerization is a slow process. At 1.0×10^{-2} M $Co(CN)_5{}^{3-}$ and 3.4×10^{-3} M $Co(CN)_5NCS^{3-}$ a substantial decrease in absorbance was observed. The calculated absorbance decrease for linkage isomerization (0.27) occurred in 95 min, but the absorbance did not remain constant at that point. The absorbance continued decreasing, and after 18 hr the change was 0.820. No conclusive evidence for $Co(CN)_5{}^{3-}$-catalyzed isomerization can be obtained from these data. The situation is complicated by two competitive processes: the instability of $Co(CN)_5{}^{3-}$ solutions[10] and the $Co(CN)_5{}^{3-}$-catalyzed substitution of X^- by CN^- in complexes of the class $Co(CN)_5X^{3-}$.[11] The observed change in absorbance is consistent with the rate law $-d \ln [A_t - A_{18}]/dt = k[Co(CN)_5{}^{3-}]$, with $k \sim 10^{-2}$ M^{-1} sec^{-1} (A_{18} is the absorbance after 18 hr). Since the rate constant for the $Co(CN)_5{}^{3-}$-catalyzed substitution of SCN^- by CN^- in $Co(CN)_5SCN^{3-}$ is 5.0×10^{-2} M^{-1} sec^{-1},[11] our results do not provide a distinction between $Co(CN)_5{}^{3-}$-catalyzed isomerization to $Co(CN)_5SCN^{3-}$, followed by $Co(CN)_5{}^{3-}$-catalyzed substitution of SCN^- by CN^- in $Co(CN)_5SCN^{3-}$, and direct $Co(CN)_5{}^{3-}$-catalyzed substitution of SCN^- in $Co(CN)_5NCS^{3-}$ by CN^-.

Discussion

The present preparation of the isothiocyanato complex $Co(CN)_5NCS^{3-}$, coupled with the previous report[3] regarding the isolation of the thiocyanato complex $Co(CN)_5SCN^{3-}$, yields an additional example of linkage isomerism in thiocyanate complexes. The substitution of water in $Co(CN)_5OH_2{}^{2-}$ by SCN^- yields, as the primary product, the nitrogen-bonded isomer

$$Co(CN)_5OH_2{}^{2-} + SCN^- \longrightarrow Co(CN)_5NCS^{3-} + H_2O \quad (1)$$

whereas the reduction of $Co(NH_3)_5NCS^{2+}$ by $Co(CN)_5{}^{3-}$ yields, as the primary product, the sulfur-bonded isomer

$$Co(NH_3)_5NCS^{2+} + Co(CN)_5{}^{3-} \longrightarrow Co(CN)_5SCN^{3-} + Co^{2+} + 5NH_3 \quad (2)$$

The structural assignment is based on the infrared evidence summarized in Table I. As already indicated, $Co(CN)_5NCS^{3-}$ exhibits a weak band at 810 cm^{-1}, a value characteristic of a C–S stretching frequency for isothiocyanate complexes. $Co(CN)_5SCN^{3-}$ exhibits a band at 718 cm^{-1} characteristic of thiocyanate complexes. Additional evidence for this assignment comes from the positions of the first electronic absorption bands for the two isomers. The maxima for $Co(CN)_5SCN^{3-}$ and $Co(CN)_5NCS^{3-}$ are at 377 and 363 nm, respectively. As was found in the chromium(III) isomers,[12] sulfur-bonded thiocyanate has a weaker crystal field strength than nitrogen-bonded thiocyanate.

The *in situ* detection of $Co(CN)_5SCN^{3-}$ in the reaction of $Co(NH_3)_5NCS^{2+}$ with $Co(CN)_5{}^{3-}$, together with the observations regarding the very slow rate of linkage isomerization of $Co(CN)_5NCS^{3-}$ (either spontaneous or catalyzed by $Co(CN)_5{}^{3-}$), shows that the sulfur-bonded isomer is the primary product of reaction 2 and therefore that remote attack is featured in this electron-transfer reaction. This situation is similar to the one previously found in the *trans*-$Co(en)_2OH_2NCS^{2+}$–Cr^{2+} reaction, where $CrSCN^{2+}$ is produced.[12] There is, however, one notable difference between the two systems. In the chromium(III) system, the sulfur-bonded isomer is unstable and isomerizes (either spontaneously or by catalysis with Cr^{2+}) to the stable $CrNCS^{2+}$.[12] In the cobalt(III) cyanide system, on the other hand, the sulfur-bonded complex appears to be the stable isomer.[3] In this context, it is noteworthy that the difference in the order of stabilities of nitrogen- and sulfur-bonded thiocyanate for chromium(III) and pentacyanocobaltate(III) was previously invoked to rationalize some rate comparisons in the reductions of $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5N_3{}^{2+}$ by Cr^{2+} and $Co(CN)_5{}^{3-}$.[13] Moreover, it is interesting to note that a useful criterion for placing a given acid in the soft- or hard-acid category[14,15] relates to the point of attachment of the ambidentate ligand SCN^-. The stability of $Co(CN)_5SCN^{3-}$ as compared to that of $Co(CN)_5NCS^{3-}$ shows that the cobalt(III) center is behaving as a soft acid. An identical conclusion was previously reached[16] by considering the order of stabilities of the halogenopentacyanocobaltate(III) complexes ($I^- > Br^- > Cl^-$).

The present spectrophotometric study of the interaction between $Co(CN)_5OH_2{}^{2-}$ and SCN^- shows that two consecutive reactions occur in this system. The earlier kinetic studies[2] pertain to the first reaction represented by eq 1. As already indicated, the nature of the second reaction has not been established. How-

---

[9] A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

[10] M. G. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc., A*, 800 (1957).

[11] J. P. Birk and J. Halpern, *J. Am. Chem. Soc.*, **90**, 305 (1968).

[12] A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

[13] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

[14] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[15] H. H. Schmidtke, *Inorg. Chem.*, **5**, 1682 (1966).

[16] R. Grassi, A. Haim, and W. K. Wilmarth, *ibid.*, **6**, 237 (1967).

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.

CONTRIBUTION FROM THE
RICHARD BENBRIDGE WETHERILL LABORATORY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

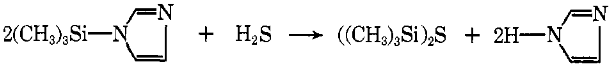
The Preparation of Hexamethyldisilthiane

BY EDWIN LOUIS AND GRANT URRY

Received March 1, 1968

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.



(1)

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

---

[1] C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

[2] C. Eaborn, *Nature*, **165**, 685 (1950).

[3] E. Larsson and R. Marin, *Acta Chem. Scand.*, **5**, 964 (1951).

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

[5] E. A. Abel, *J. Chem. Soc.*, 4933 (1961).

[6] M. Fild, W. Sundermeyer, and O. Glemser, *Chem. Ber.*, **97**, 620 (1964).

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

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