

REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS. V*.
ADDITION AND SUBSEQUENT DECOMPOSITION REACTIONS OF
N-METHYLHEXAMETHYLDISILAZANE AND -DISTANNAZANE TO
CARBON DISULFIDE AND PHENYL ISOTHIOCYANATE

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Even though the addition reactions of N-alkylhexamethyldisilazane (Me_3Si)₂N-Me, with phenyl isocyanate had been well established¹⁻³, there was no confirming study on the reaction of N-methylhexamethylmetallazane (Me_3M)₂N-Me (M=Si and Sn) with carbon disulfide and phenyl isothiocyanate. In this publication, we report the addition reactions of N-methylhexamethyldisilazane I, or -distannazane II, to carbon disulfide as well as to phenyl isothiocyanate, and the induced decomposition of the adducts.

Reaction with Carbon Disulfide

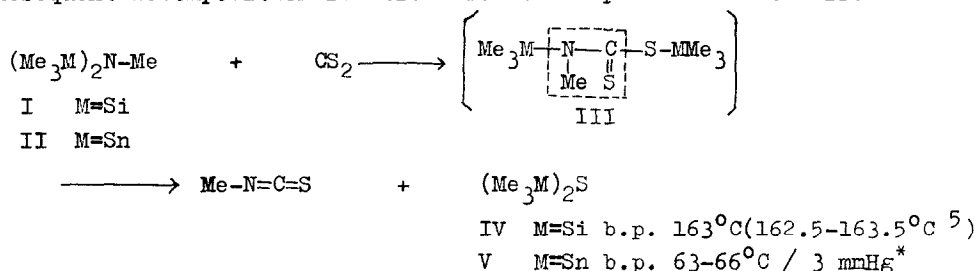
Breederveld⁴ found that trimethylsilyldiethylamine added reversibly to carbon disulfide at room temperature, giving corresponding dithiocarbamate $\text{Me}_3\text{Si-S-C(=S)NEt}_2$. The mixture of I (3.5g) and carbon disulfide (3.0g) did not react at room temperature, however, did when heated in a sealed tube at 150°C for seven days. After the removal of unreacted carbon disulfide, methyl isothiocyanate (80%) and bis(trimethylsilyl)sulfide (80%) were obtained by distillation. Analogous reaction between II (3.6g) and carbon disulfide (1.5g) took place much more vigorously than I, and occurred exothermally at

* Part IV, K. Itoh, Y. Kato, S. Sakai, and Y. Ishii, J. Chem. Soc. Japan, (industrial chemistry section), in press

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room temperature. When the reaction product was distilled under reduced pressure, methyl isothiocyanate and bis(trimethylstannyl)sulfide V, were obtained in 61% and 71% yield, respectively.

Above results predict the following scheme, including addition reaction and subsequent decomposition reaction from the expected adduct III.



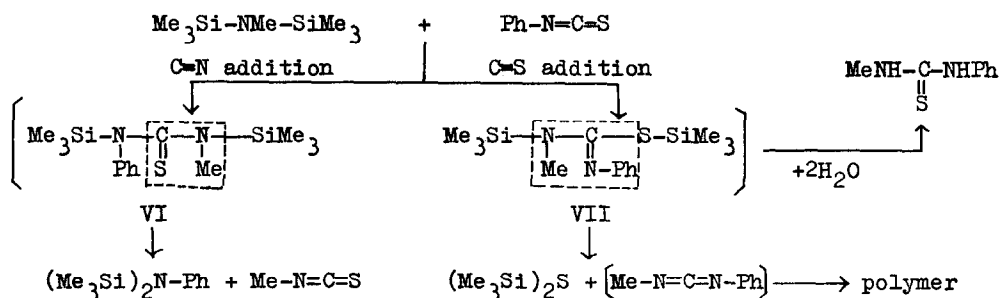
Reaction with Phenyl Isothiocyanate

Klebe *et al.*² studied the reaction between I and phenyl isothiocyanate and presumed reversible addition of I to C=N bond in isothiocyanate in the same way as in carbon disulfide⁴, only from IR absorption at 1710 cm^{-1} . We found that phenyl isothiocyanate had much lower reactivity toward I than phenyl isocyanate. After heating the mixture of I and phenyl isothiocyanate at 150°C for ten days, the characteristic absorption at 2058 cm^{-1} of isothiocyanate remained considerably. Distillation of the reaction mixture under reduced pressure gave methyl isothiocyanate (46%), unreacted I and IV (47%) in a cold trap (-78°C), unreacted phenyl isothiocyanate and 30% of N-phenylhexamethyldisilazane** as distillate, and the distillation residue was identified as the polymer of N-methyl-N'-phenylcarbodiimide from its IR and nmr spectra⁷. When the mixture of I and phenyl isothiocyanate was exposed in air for a day at room temperature, the hydrolysis with moisture occurred quantitatively, giving a white crystal of N-methyl-N'-phenylthiourea (m.p. 112.8-114.0°C. Anal. Calc. as $\text{C}_8\text{H}_{11}\text{N}_2\text{S}$ C 57.79, H 6.07, N 16.85. Obs. C 57.74, H 5.92, N 16.91).

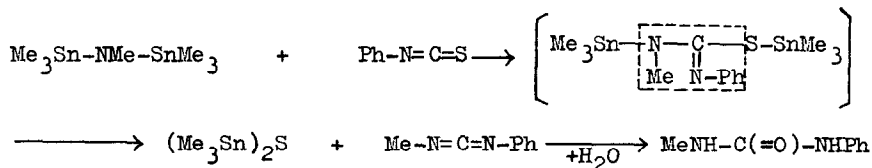
* Identified with the authentic sample prepared from trimethylstannyl chloride and sodium sulfide⁶.

** Identified with the authentic sample⁸.

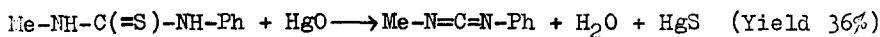
From these facts, the following two types of addition reaction of I both to C=N and C=S bonds of phenyl isothiocyanate, and the subsequent decomposition reactions could be formulated.



The reaction between phenyl isothiocyanate and N-methylhexamethyldi-stannazane II occurred exothermally even at -50°C . This reaction mixture showing a strong IR absorption at 2160 cm^{-1} , gave N-methyl-N'-phenyl-carbodiimide* (63%) and bis(trimethylstannyl)sulfide V (83%) at b.p. $52-57^\circ\text{C}$ under 0.4 mmHg on vacuum distillation. The distillation residue was also the polymer of N-methyl-N'-phenylcarbodiimide (20%). The hydrolysis product either of the reaction mixture or of the distillate was N-methyl-N'-phenylurea (m.p. 145°C . Anal. Calc. as $\text{C}_8\text{H}_{11}\text{N}_2\text{O}$ C 63.98, H 6.71, N 18.65. Obs. C 63.81, H 6.63, N 18.57). The fact that no fission products were obtained expectable from the addition compound $\text{Me}_3\text{Sn-NMe-C(=S)-NPh-SnMe}_3$, shows the absence of the addition of II to C=N bond of isothiocyanate. Therefore, in the case of II, the addition of II across C=S bond of isothiocyanate would occur exclusively and easily followed by the decomposition reaction as shown below.



* Identified by comparing with the product of the following reaction⁷.



In conclusion, N-methylhexamethyldisilazane I reacts very slowly, but -distannazane II, does vigorously, with carbon disulfide or phenyl isothiocyanate. Subsequent decomposition reaction of the adducts proceeds easily. A distinct difference in the mode of addition reaction was found for the reaction of phenyl isothiocyanate with I or II, that is, although I added to both C=S and C=N bond in nearly 1 : 1 ratio, II added exclusively to C=S bond. This result is a clear cut proof of C=S addition. For the addition reactions of Sn-O^{9,10} or Sn-N¹¹ bond to isocyanate, ambiguity has remained which bond in -N=C=O was attacked by addenda.

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