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REACTION OF GROUP IV ORGANOMETALLIC COMPOUNDS VIII
FORMATION OF BIS(TRIMETHYLTIN)SULFIDE FROM THE REACTION OF N-METHYLHEXAMETHYLDISTANNAZANE WITH VARIOUS C=S COMPOUNDS

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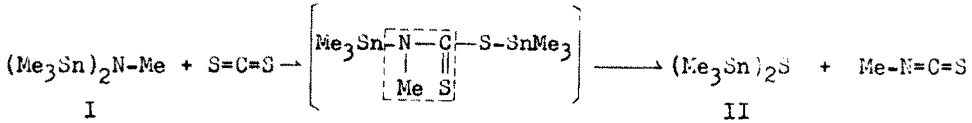
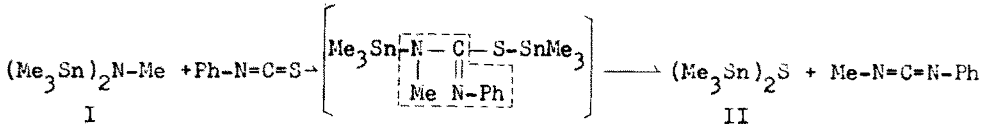
In the preceeding publication[1], reaction of N-methylhexamethyldistannazane (I) with carbon disulfide or phenyl isothiocyanate was found to give bis(trimethyltin)sulfide(II) and methyl isothiocyanate or methyl phenyl carbodiimide, respectively.



$$\underset{\text{I}}{(Me_3Sn)_2N\text{-}Me} + S{=}C{=}S \rightarrow \left[\begin{array}{l} Me_3Sn-N-C-S-SnMe_3 \\ \qquad\quad | \quad \| \\ \qquad\; Me \;\; S \end{array} \right] \longrightarrow \underset{\text{II}}{(Me_3Sn)_2S} + Me\text{-}N{=}C{=}S \tag{1}$$



$$\underset{\text{I}}{(Me_3Sn)_2N\text{-}Me} + Ph\text{-}N{=}C{=}S \rightarrow \left[\begin{array}{l} Me_3Sn-N-C-S-SnMe_3 \\ \qquad\quad | \quad \| \\ \qquad\; Me \;\; N\text{-}Ph \end{array} \right] \longrightarrow \underset{\text{II}}{(Me_3Sn)_2S} + Me\text{-}N{=}C{=}N\text{-}Ph \tag{2}$$

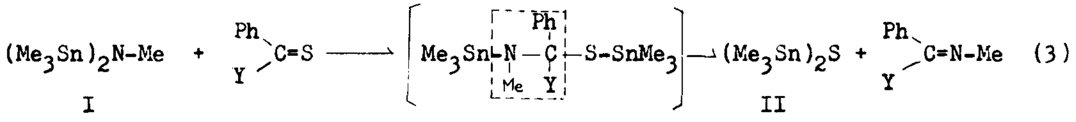
Extensive study with other C=S compounds as carbonyl sulfide, thiobenzophenone, or N,N-dimethylthiobenzamide is described here and formation of II is found to occur in general.

When carbonyl sulfide was bubled into the solution of I(1.51grams) in 10 ml of n-hexane at -72°, methyl isocyanate (50%) was shown by the infra-red spectrometry of the reaction mixture. After the removal of excess carbonyl sulfide, methyl isocyanate, and n-hexane, II could be isolated in 80% yield. This result suggested that I gave unstable adduct with carbonyl sulfide not across C=O bond, but across C=S bond, which decomposed readily in an analogous manner as eq. 1 and 2.

Addition of I(3.66 millimoles) to thiobenzophenone(3.53 millimoles) caused slight evolution of heat at room temperature and characteristic blue color vanished, affording II(57%) and benzophenone methylimine(62%) which are identified by comparison with authentic materials^2.

Reaction of N,N-dimethylthiobenzamide and I(each 1.7 millimoles) required much drastic conditions, namely, kept at 130° for 8 hours in a sealed tube. Distillate boiling at 57-62°/ 0.1mmHg showed a strong infra-red absorption of C=N bond at 1620 cm^{-1}. Treatment of above distillate with picric acid gave yellow precipitate of N,N,N'-trimethylbenzamidine picrate in 65% yield; M.p. 137.2-137.5° (136-138°)^3, Anal., Calcd. for $C_{16}H_{17}N_4O_7$ C 48.78, H 4.26, N 17.88, Found C 49.11, H 4.38, N 17.90. After above filtrate was washed with conc. hydrochloric acid, II was isolated in 85% yield by distillation.

Above results suggest that II and N,N,N'-trimethylbenzamidine were formed.



$$\underset{\text{I}}{(Me_3Sn)_2N\text{-}Me} + \overset{Ph}{\underset{Y}{>}}C{=}S \longrightarrow \left[Me_3Sn\text{-}\underset{Me}{N}\text{-}\overset{Ph}{\underset{Y}{C}}\text{-}S\text{-}SnMe_3 \right] \longrightarrow \underset{\text{II}}{(Me_3Sn)_2S} + \overset{Ph}{\underset{Y}{>}}C{=}N\text{-}Me \quad (3)$$

Y= Ph and NMe_2

From the competitive reaction between I(2.82 millimoles) and the mixture of N,N-dimethylthiobenzamide as well as tetramethylthiourea(each 2.84 millimoles), the former gave predominantly N,N,N'-trimethylbenzamidine and the latter failed to react. Consequently, reactivity order was given as follows.

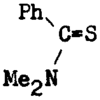
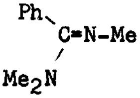
$$OCS \simeq CS_2 > Ph\text{-}NCS \gg Ph_2CS > Ph\text{-}C({=}S)NMe_2 \gg (Me_2N)_2CS$$

Generally, reactions of I with various C=S compounds were represented as eq. 4, and all results were summarized in TABLE I.

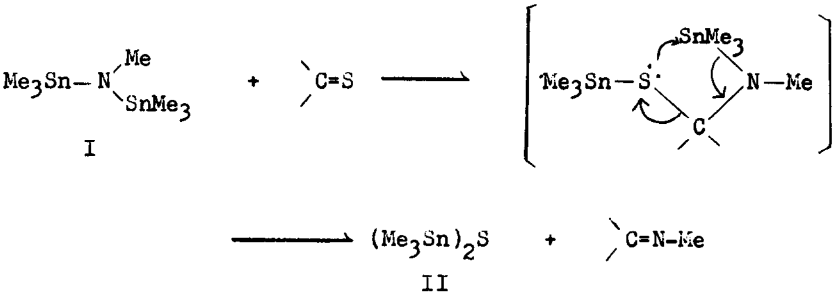
$$(Me_3Sn)_2N\text{-}Me + {>}C{=}S \longrightarrow (Me_3Sn)_2S + {>}C{=}N\text{-}Me \qquad (4)$$

TABLE I

REACTIONS OF N-METHYLHEXAMETHYLDISTANNAZANE WITH C=S COMPOUNDS

Starting Material	Reaction Product
$\mathrm{O{=}C{=}S}$	$\mathrm{Me{-}N{=}C{=}O}$
$\mathrm{S{=}C{=}S}$	$\mathrm{Me{-}N{=}C{=}S}$
$\mathrm{Ph{-}N{=}C{=}S}$	$\mathrm{Me{-}N{=}C{=}N{-}Ph}$
$\mathrm{Ph_2C{=}S}$	$\mathrm{Ph_2C{=}N{-}Me}$
 $\mathrm{Ph(Me_2N)C{=}S}$	 $\mathrm{Ph(Me_2N)C{=}N{-}Me}$

Elimination of II was presumed to take place through unstable 1:1 insertion addition product, which decomposed readily by the following four-centered transition state.



(5)

For the similar reaction between I with corresponding C=O compounds, namely, carbon dioxide or phenyl isocyanate, elimination of bis(trimethyltin)oxide did not occur and reaction products were usual insertion adducts which were analogous as reported by Lappert *et al*[4].

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