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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS. XVI[1]
REACTIONS OF BENZOYL HETEROCUMULENS WITH TRIMETHYLSTANNYLALKYLAMINES

KENJI ITOH, ISAMU MATSUDA, AND YOSHIO ISHII

Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University. Furo-cho, Chikusa-ku, Nagoya, Japan

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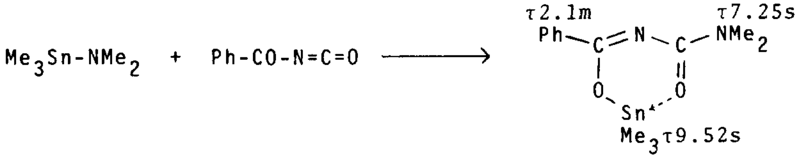
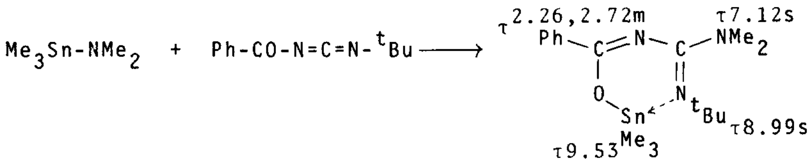
Benzoyl isocyanate and isothiocyanate were previously reported to be novel acceptors for organosilylamines[2].

In this publication, reactions of benzoyl isocyanate, isothiocyanate, and t-butylcarbodiimide with trimethylstannylamines are presented.

Benzoyl isocyanate or t-butylcarbodiimide gave quantitatively stable 1:1 adducts with trimethylstannyldimethylamine. These reactions took place exothermally at room temperature. Infrared spectra of these adducts showed surprisingly no $\nu_{C=O}$ absorption expected from usual addition reaction with common isocyanates or carbodiimides[3] around 1650 cm^{-1}. Strong and broad absorptions were observed at 1601, 1570, and 1550 cm^{-1} for the adduct with benzoyl t-butylcarbodiimide and at 1545 cm^{-1} for that with benzoyl isocyanate, respectively. From these results, structures of the adducts containing intramolecular co-ordination between tin and oxygen, or nitrogen atoms would be prefered.

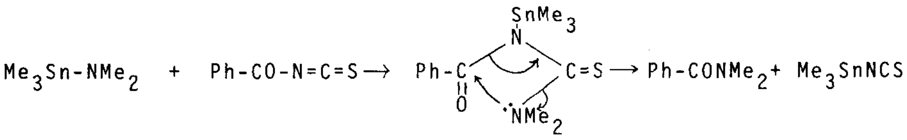


(1)



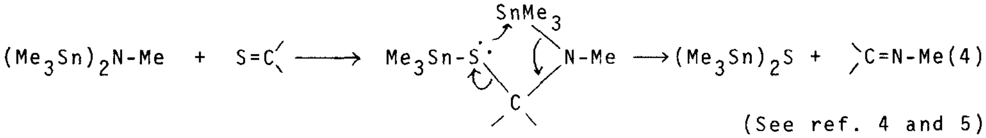
(2)

However, in the case of the reaction with benzoyl isothiocyanate, no 1:1 adduct was isolated and the products isolated were trimethyltin isothiocyanate (89%) and N,N-dimethylbenzamide(67%).



(3)

N-Methylhexamethyldistannazane which was known to be an effective desulfurization agent as eq. 4, could react exothermally with benzoyl isothiocyanate.



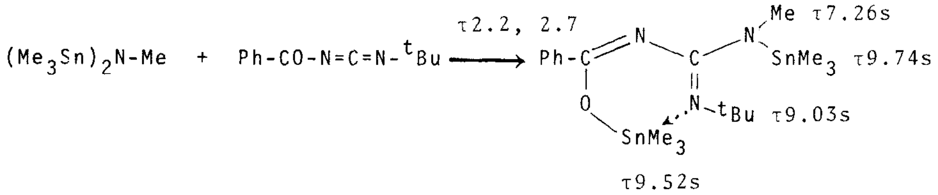
(See ref. 4 and 5)

One of the reaction products, bis(trimethylstannyl)sulfide, was isolated in 44% yield by distillation. The other product would be benzoyl methylcarbodiimide(eq. 4), however, it could not be detected at all.

Since benzoyl carbodiimide behaved as an effective acceptor towards trimethylstannylamine as already described in eq. 2, unstable benzoyl methylcarbodiimide reacted rapidly with the remaining N-methylhexamethyldistannazane to give a guanidine derivative. This fact was confirmed by 10% formation of N-benzoyl-N',N''-dimethylguanidine picrate(m. p. 194°; Anal. Found C, 45.52; H, 3.54; N, 19.88. Calcd. C, 45.72; H, 3.84; N, 19.94) , when the mixture was treated with picric acid.

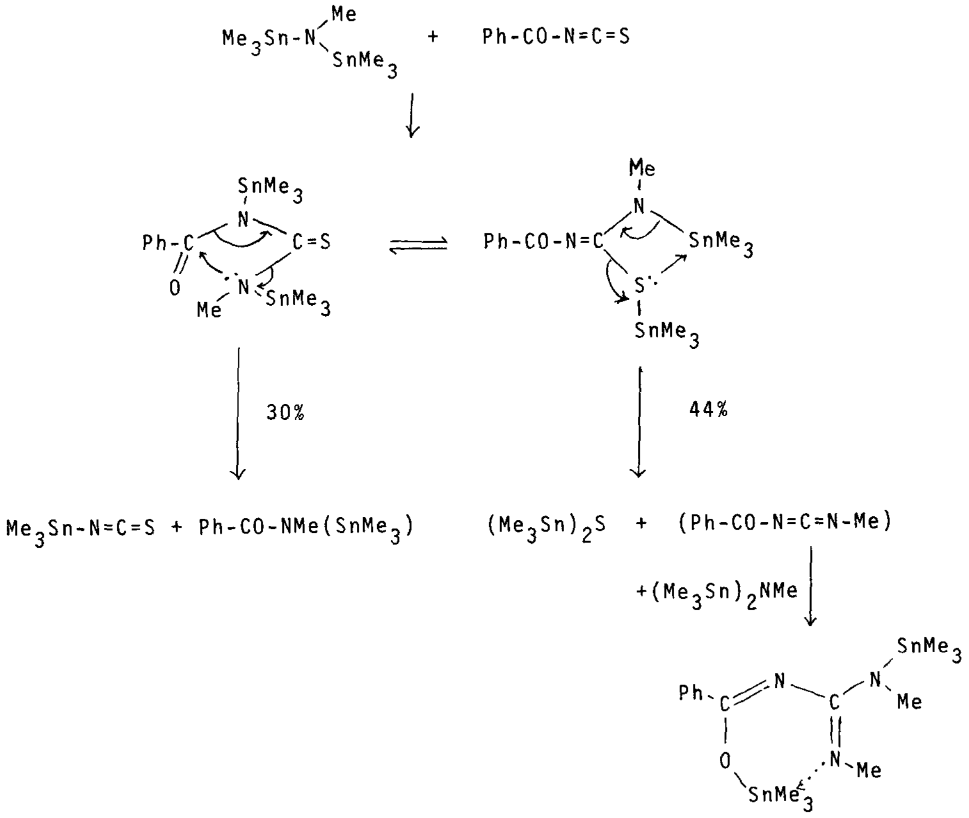
Other products were trimethyltin isothiocyanate and N-methyl-N-trimethylstannylbenzamide in 30% yield, which were formed in an analogous way as eq. 3.

Similar addition reaction occurred quantitatively at room temperature between benzoyl t-butylcarbodiimide and N-methylhexamethyldistannazane.



(5)

These results suggested the following pathway in the case of N-methylhexamethyldistannazane.



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