THE INTERACTIONS
OF
THE GROUP IV METAL-NITROGEN BONDS
WITH
HETEROCUMULENES

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Preface

This dissertation covers several studies on "The Interactions of the Group IV Metal-Nitrogen Bonds with Heterocumulenes" under the direction of Professor Yoshio Ishii during 1969/1972.

In this thesis, some insertions followed by the β-elimination or cyclization reactions of N-(trimethylsilyl)-, -(germyl), and -(stannyl)amines as well as N-(trimethylsilyl)imine were investigated. The intramolecular 1,3-transfer of trimethylmetal group in the insertion products, which played important roles to decide the processes, was also studied in detail for several cases.

The author is greatly indebted to Professor Yoshio Ishii for his direction and significant advices and to Dr. Kenji Itoh for his encouragement and suggestions throughout this work. He also expresses his gratitude to Professor Shizuyoshi Sakai and Dr. Yasutaka Takahashi for their interest and discussions.

He thanks his coworkers for their helpful experiments; Mr. Tsuguo Katsuura in the insertion reactions of thiobenzoyl isocyanate as well as asymmetric metallazanes, Mr. Hiroharu Suzüki in the degradation reactions and Miss Mihoko Ogimura for measurements of n.m.r. spectra. He extends his gratitude to all other members in the Ishii's Laboratory.

The author thanks his parents who satisfied his will to study as a doctor course student.

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CONTENTS

CHAPTER 1

Introduction

The chemical behaviours of group IVB organometallic compounds have attracted much attentions in recent years 1∿6), since they have shown remarkable differences in their carbon analogues. There are also appreciable differences in the chemical and physical properties among the group IVB organometallic compounds. Although they have the same outest electronic configurations $\{(ns)^2(np)^2\}$, the reason why such different behaviours are induced by changing the group IVB elements are presumably due to the following characteristic properties.

(1) Difference in electronegativities among group IVB elements:

Various values are proposed 7∿12) and it is recently supported that the electronegativity sequence is compatible with the original one which would be expected by the positions of each element in the Periodical Table, *i.e.* $C > Si > Ge > Sn$ 13, 14).

(2) Possibility of $(p\rightarrow d)\pi$ overlapping:

Despite of much controversy 15∿18) it is widely accepted that there are significant $(p\rightarrow d)\pi$ contributions to the Si-N bonds in such compounds as the planar trisilylamine 19) or siloxanes. In particular, a surprisingly high stability of Si-O bonds can be explained by the strong $(p\rightarrow d)\pi$ interaction.

Since the electrophilicity of the metal moieties is very weak in the group IVB compounds (Me_3M-X), their reactions are mainly controlled by the nucleophilicity of X, which was expected to be the sum of the above two factors. As the measure of the nucleophilicity, the basicity of several group IVB organometallic compounds determined by $CDCl_3$ as a reference acid is most useful one 20, 21).

The insertion reactions of the polar unsaturated bonds into M-X bonds were recently reviewed 22, 23). In some cases, different types of unsaturated compounds were given by the subsequent β-elimination of the primary insertion products (eq. 1.2) in the following manner [23)]

$$\begin{tikzcd}
\text{M—X} + \text{A=B} \arrow[r, "(1.1)"] & \text{M-A-B-X} \arrow[r, "(1.2)", "\text{X=Y=M}"'] \arrow[d, "(1.3)"', "+\ \text{Y=Z}"] & \text{M-A-M} + \text{B=Y} \\
& \text{M-Y-Z-X} + \text{A=B} &
\end{tikzcd}$$

Another insertion reactions, so-called "acceptor exchange" (eq. 1.3) is frequently induced with the interaction of other acceptor to an insertion product [24)]. On these basis brilliant success to the utilities on the organic synthesis are explored by considering the distinct difference in the affinity of metal atoms to the particular hetero atoms [24∿28)].

On the other hand, the conception of the partial double bond character is quite generally explained by the resonance method. In this context, the considerable interest was directed to N,N-dialkylacylamide in n.m.r. spectroscopy [29)]. The silylamide⇌silylimidate [30)] and amine⇌imine [31, 32)] tautomerisms were understood in terms of the "elementotropy" which was analogous to a symmetry forbidden 1,3-sigmatropic shift of the hydrogen atom [33)].

From these points of view, the individual character of group IVB elements should be more clearly determined by the comparison of the reactivity and the affinity order even in the qualititative sence. Compounds with a metal-nitrogen bond seem to be most convenient for the above comparison, because they have moderate reactivity to the addition reaction for every group IVB element.

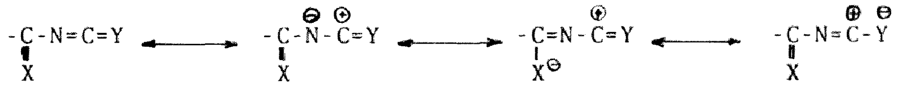
This dissertation consists of three main subjects. The first part is the 1:1 insertion and the subsequent elimination reactions of heterocumulene compounds to M-N bond (M=Si, Ge, and Sn). Secondly, the novel cyclization reactions which gave different six membered rings depending on the group IVB elements are described. Finally, the intramolecular 1,3-transfer of trimethylmetal groups in the organometallylurea and -guanidine derivatives are discussed in detail.

CHAPTER 2

The Reactions of Benzoyl and Thiobenzoyl Heterocumulenes

2.1. General Consideration of (Thio)Benzoyl Heterocumulenes

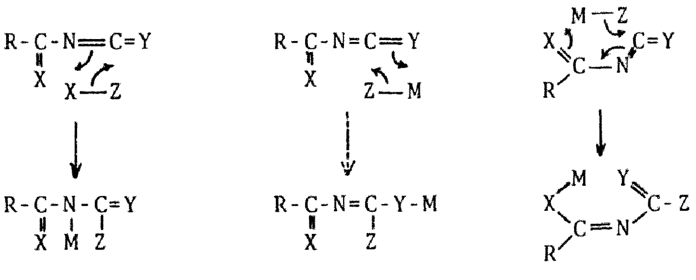
(Thio)Acyl heterocumulene compounds are strongly electrophilic because of the existence of the electron withdrawing (thio)acyl group. Since these compounds have been found to be conveniently prepared 34∿37), they have been used with interests in the aspect of organic synthesis 38). The following canonical structures can be visualized for (thio)acyl heterocumulenes, corresponding to the possible modes of addition.



(1a) (1b) (1c) (1d)

X=O and S, Y=O, S, and >N-Bu^t

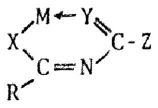
When organometallic compounds (M-Z) are added to (thio)acyl heterocumulene, the following three 1:1 insertion products are expected.



(A) (B) (C)

Path A (1,2-addition across the C=N bond) corresponds to the type of addition reaction most often observed when organometallic compounds add to the simple heterocumulenes 39∿45). No example has been found of reactions occurring by path B (1,2-addition across the C=Y bond).

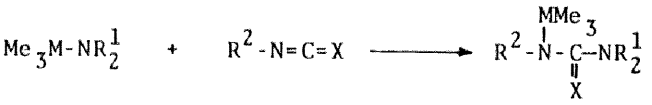
In organic chemistry, many compounds add to acyl or thioacyl isocyanates by path C (1,4-addition), *e.g.* isocyanides [46∿49], diazomethane [50], norbornadiene [51, 52], enolether [49, 53], and benzamidine [54], to give the corresponding cyclic products. For organometallic compounds 1,4-adducts can be stabilized to some extent by means of intramolecular co-ordination (D).


(D)

2.2 The Insertions of Benzoyl Isocyanate and n.m.r. Behaviour of the Insertion Products.

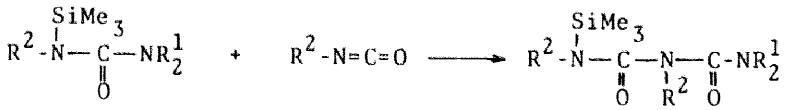
2.2.1. N-(Trimethylmetal)dialkylamines

There are many reports that organometalamines can form stable 1:1 adducts [39∿45] with isocyanates and isothiocyanates by an addition across the C=N bond (eq. 2.1). Further stepwise insertions of isocyanates across these adducts were also found to occur to give biuret derivatives [40] (eq. 2.2). However, the structures of these 1:1 and 1:2 adducts have not been established satisfactorily.



$$\mathrm{Me_3M\text{-}NR^1_2} + \mathrm{R^2\text{-}N{=}C{=}X} \longrightarrow \mathrm{R^2\text{-}\overset{MMe_3}{N}\text{-}\underset{X}{\overset{}{C}}\text{-}NR^1_2} \qquad (2.1)$$

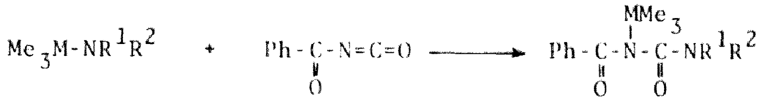
(X=O and S)



$$\mathrm{R^2\text{-}\overset{SiMe_3}{N}\text{—}\underset{O}{C}\text{—}NR^1_2} + \mathrm{R^2\text{-}N{=}C{=}O} \longrightarrow \mathrm{R^2\text{-}\overset{SiMe_3}{N}\text{—}\underset{O}{C}\text{—}\underset{R^2}{N}\text{—}\underset{O}{C}\text{-}NR^1_2} \qquad (2.2)$$

Since few studies on the reaction of acyl iso(thio)cyanates towards organometallic compounds are known 55), the reactions of benzoyl isocyanate with N-(trimethylmetal)dialkylamines were investigated.

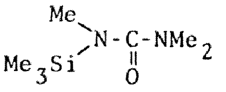
Benzoyl isocyanate (I) and N-(trimethylmetal)dialkylamines (II) gave 1:1 adducts exothermally, the products were colourless and hygroscopic and could be distilled without decomposition in the case of silylamines. This behaviour was quite similar to that in the case of phenyl isocyanate 39∿41, 43, 44). The structure of the adducts was shown by elemental analyses, i.r., and n.m.r. spectroscopies, and the formation of the corresponding demetallated ureas by hydrolyses. The properties of 1:1 adducts (III) are summarized in Table 2.1.



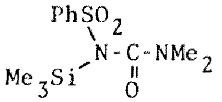
$$\mathrm{Me_3M{-}NR^1R^2} + \mathrm{Ph{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}N{=}C{=}O} \longrightarrow \mathrm{Ph{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\overset{\displaystyle MMe_3}{\overset{|}{N}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NR^1R^2} \qquad (2.3)$$

(II) (I) (III)

The n.m.r. spectra of 1:1 adducts from N-(trimethylsilyl)dialkylamines (IIIa∿g) showed a separation of a trimethylsilyl proton signal into two singlets at -43° to -52° (Table 2.1). The intensities of the two peaks were different. Since N,N,N'-trimethyl-N'-(trimethylsilyl)-urea (IVa) and N,N-dimethyl-N'-phenylsulphonyl-N'-(trimethylsilyl)urea (IVb) showed no splitting of trimethylsilyl protons at low temperatures, the separation of the trimethylsilyl proton signal for the adducts, IIIa ∿ IIIg, is characteristic of the N-benzoyl-N-(trimethylsilyl)urea structure. Furthermore, a splitting of the dimethylamino proton signal



(IVa)



(IVb)

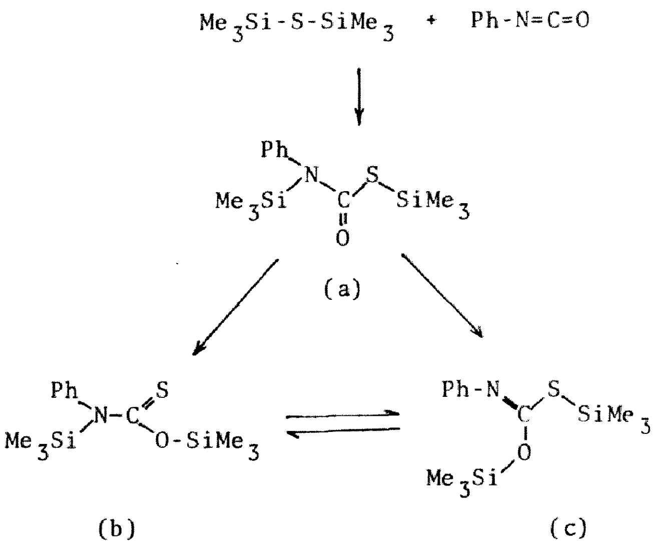
into two equal intensity singlets (τ 7.10 and 7.18) occurred at +10° for IIIa. As previously stated 56, 57), the trimethylsilyl group can be

Table 2.1. Characteristic data for the adducts (III)

	M	R^1	R^2	B.p.(°C/mmHg)	$\nu_{max.}$ (cm^{-1}) a)	Chemical shift c)			Coalescence
						$(C\underline{H}_3)_3$-M		$(C\underline{H}_3)_2$-N	temp. of
						at 20°C	at -60°C	at 20°C	$C\underline{H}_3$-M (°C)
III-a	Si	Me	Me	127-130/0.35	1665, 1645	9.66	9.71, 9.61	7.14	-45
III-b	Si	Et	Et	118-119/0.15	1660, 1643	9.65	9.70, 9.62	--	-48
III-c	Si	n-Pr	n-Pr	107-108/0.07	1661, 1642	9.65	9.72, 9.63	--	-50
III-d	Si	n-Bu	n-Bu	118-121/0.04	1659, 1639	9.65	9.71, 9.63	--	-50
III-e	Si	$-(CH_2)_4-$		114-115/0.05	1659, 1643	9.64	9.70, 9.62	--	-43
III-f	Si	$-(CH_2)_5-$		118-121/0.06	1660, 1641	9.65	9.71, 9.62	--	-52
III-g	Si	Me	C_6H_{11}	125-131/0.08	1660, 1639	9.65	9.72, 9.62	--	-48
III-h	Ge	Me	Me	----	1668	9.41	----	7.46	--
III-i	Sn	Me	Me	----	1600, 1540 b)	9.51	-----	7.14	--

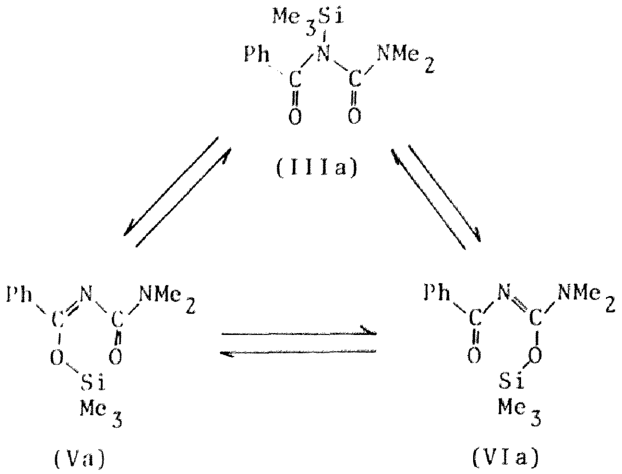
a) In CCl_4 solution. b) In C_6H_6 solution. c) In trichloroethylene 20% solution.

transferred reversibly in the adduct from bis(trimethylsilyl)sulphide and phenyl isocyanate (so-called 3-sites-2-Si 1,3-transfer) (Scheme 2.1).



SCHEME 2.1.

Since the structure of the adduct (III) is quite similar to the above structures, an analogous rearrangement may be possible. If one trimethylsilyl group of adduct III can be transferred amongst three sites (carbonyl oxygen and nitrogen atoms: 3-sites-1-Si 1,3-transfer), the three structures (IIIa, Va, and VIa) would be possible. Since the splitting of N-methyl signal was ascribed to the wellknown hindered rotation [58, 59] due to the $X\!=\!\overset{|}{C}\text{-NMe}_2$ linkage (X=O and N-R), the fact that the splitting of the N-methyl signal below 10° occurred at different temperature with that of the trimethylsilyl signal at -67° suggested the nonexistence of the structure VIa below 10°, *i.e.* "1,3-transfer" of the trimethylsilyl group occurred only between the benzoyl oxygen and the nitrogen atom (IIIa and Va). The trimethylsilyl signal at τ 9.71 might be ascribed to the structure Va, and that at τ 9.61 to the structure IIIa, since the electron density at the nitrogen atom in IIIa may



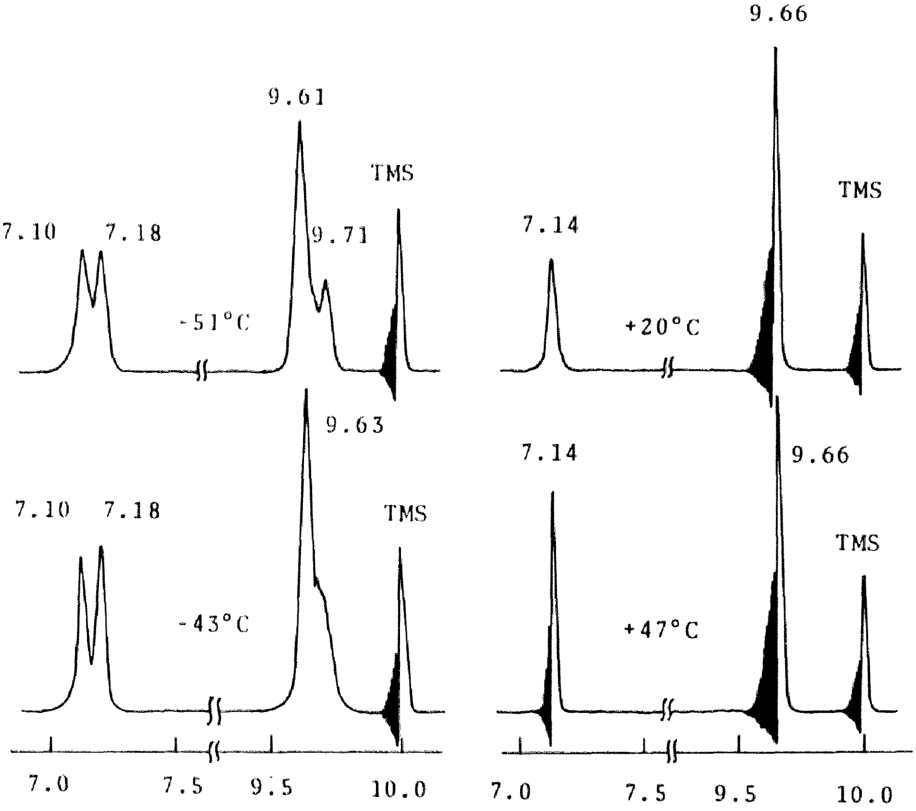
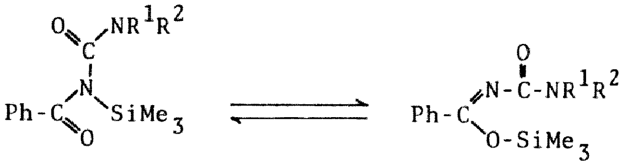
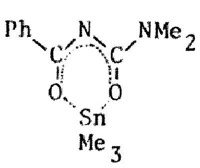


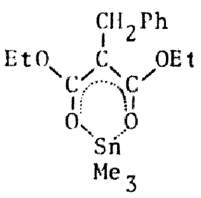
Fig. 2.1. N.m.r. spectra of adduct IIIa at 60 MHz in trichloroethylene.

be greatly depressed by the neighbouring two carbonyl groups. By the comparison of the n.m.r. peaks, the ratio of IIIa to Va was estimated to be 2.3:1 at -67°. The chemical shift (τ 9.66) of the trimethylsilyl signal at 20° {a sharp singlet; the mean value of τ 9.61 and 9.71 (IIIa and Va)} suggests that the stabilities of IIIa and Va became equal. Thus, these n.m.r. results suggested that the following equilibrium between N-silylated and O-silylated (benzoyl oxygen) structures prevailed in the 1:1 adducts (IIIa∿IIIg). As mentioned later, the formation of oxadiazinones XIV and XVIII was always accompanied by the elimination of trimethylsilyl benzoate, since the cyclic compounds are readily derived from the O-silylated structure V. This is a strong evidence of the existence of O-silylated structures. This kind of O-silylated form exists in several trimethylsilyl-urea or -amides, for example, N,O-bis-(trimethylsilyl)benzimidates [60, 61], N,N'-bis(trimethylsilyl)-N-phenyl-N'-methylurea [62].


(IIIa∿g) (Va∿g) (2.4)

An analogous adduct with $Me_3Sn-NMe_2$ (IIIi) showed a marked difference from the addition products of the corresponding silylamine. Firstly, the carbonyl stretching frequency of IIIi showed an unexpectedly low value ($\nu_{C=O}$ 1600 and 1540 cm^{-1}). Secondly, no splitting of CH_3-Sn proton signal was observed. Such a particularly low $\nu_{C=O}$ frequency is a characteristic behaviour of "chelate ligands" [63, 64]. A molecular weight

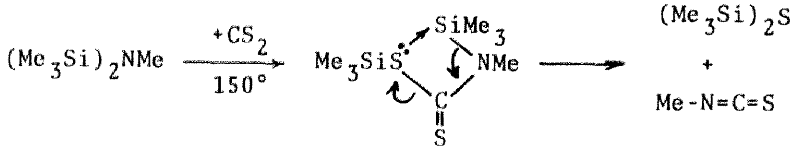

(VIIi)


(VIII)

determination showed IIIi to be monomeric, therefore, the co-ordination should be intramolecular. The five-co-ordinated structure VIIi is consistent with the above observations. A similar type of five-co-ordination in the trimethylstannyl compound VIII was recently reported 65) ($\nu_{C=O}$ 1600-1630 cm^{-1}).

2.2.2. Heptamethyldisilazane

Heptamethyldisilazane, $(Me_3Si)_2NMe$, is known to be only weakly nucleophilic because of the strong $2p_\pi$-$3d_\pi$ interaction in the Si-N-Si linkage. It is known to undergo the addition-elimination reactions with carbon disulphide or phenyl isothiocyanate 25), *e.g.*



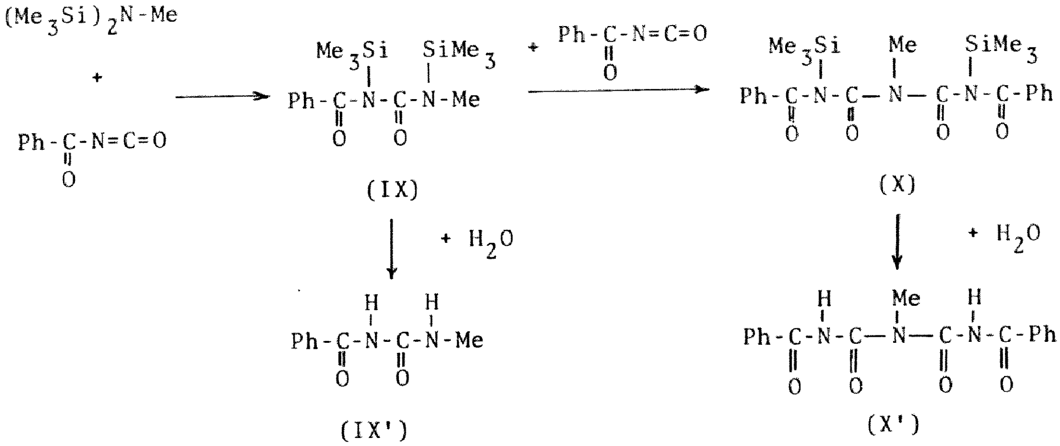
(2.5)

Benzoyl isocyanate inserts consecutively into the Si-N bonds of heptamethyldisilazane to give the 1:1 adduct IX and the symmetrical 1:2 adduct X in 73% and 85% yields, respectively. The structure of 1:2 adduct X was confirmed by means of fragmentations in the mass spectrum. This is analogous to the result with phenyl isocyanate 41, 42).

The n.m.r. spectrum of the adduct IX showed four kinds of trimethylsilyl proton at τ 9.77, 9.71, 9.67, and 9.62, and two kinds of N-methyl proton at τ 7.35 and 7.18 at -50°, so that at least two isomers are possible even at such low temperature. In this case (Y=O in scheme 2.7), all possible sites to trimethylsilyl group have "hard" character 66∿68) (two oxygen and two nitrogen atoms), consequently, the assignment of possible isomers is much more difficult than with adduct XXX.

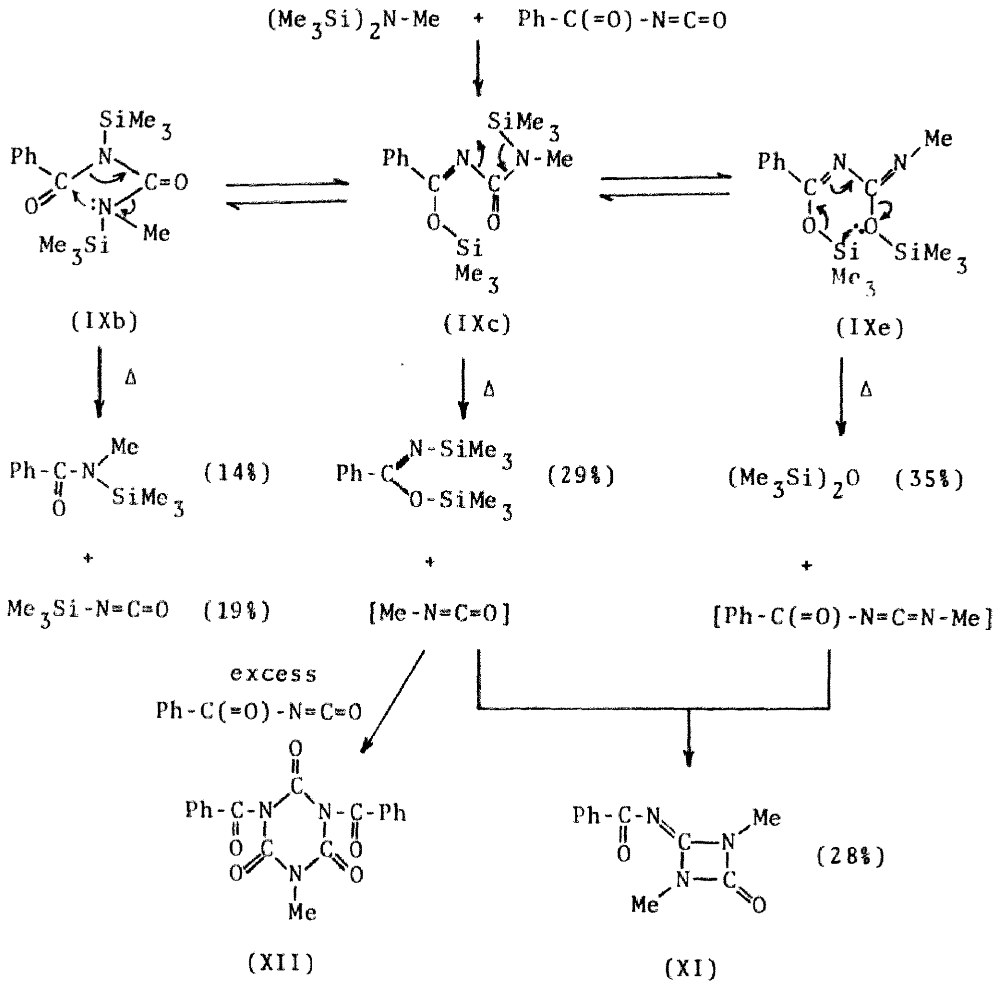
Pyrolysis of the 1:1 adduct IX above 150° gave hexamethyldisiloxane (35%), trimethylsilyl isocyanate (19%), N-methyl-N-(trimethylsilyl)-benzamide (14%), N,O-bis(trimethylsilyl)benzimidate (29%), and colourless

SCHEME 2.2



needles of 1,3-dimethyl-1,3-diazetidin-2-one-4-benzoylimide (XI) (28%). Compound XI is interpreted by a [2+2] cycloaddition between methyl isocyanate and N-benzoyl-N'-methylcarbodiimide which were initially formed by the pyrolysis of IX. Pyrolysis in the presence of benzoyl isocyanate gave 1-methyl-3,5-dibenzoyl isocyanurate (XII), the cycloadduct from one mole of methyl isocyanate and two moles of benzoyl isocyanate, and this suggests that methyl isocyanate is formed in the pyrolysis of adduct IX. The products could be rationalized by the reaction scheme 2.3, involving three possible isomers IXb, IXc, and IXe.

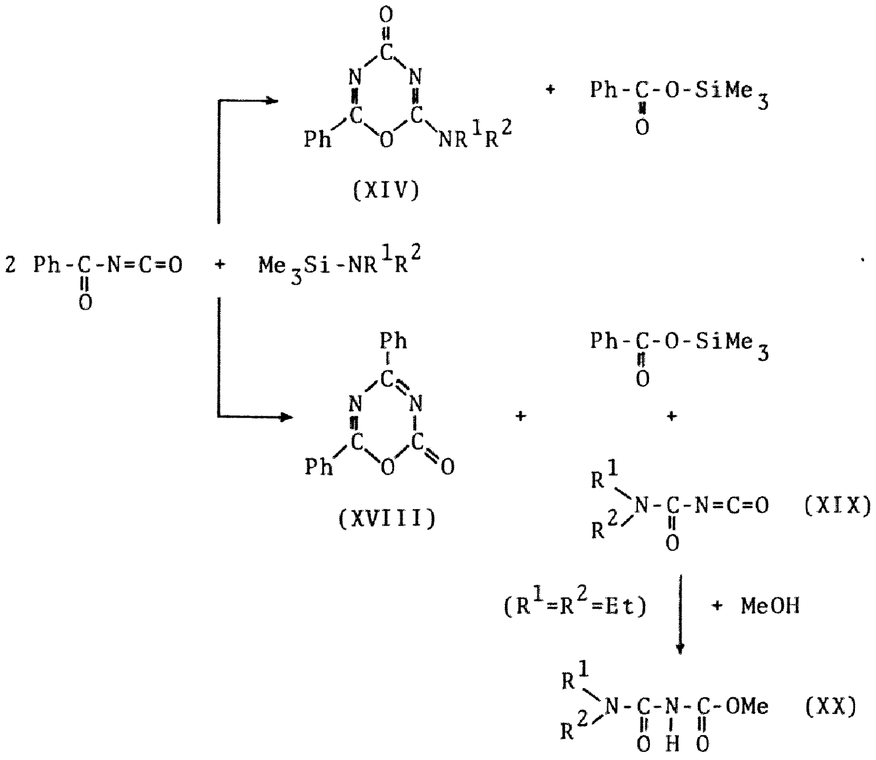
SCHEME 2.3.


(Me3Si)2N-Me + Ph-C(=O)-N=C=O
(IXb)
(IXc)
(IXe)
Δ
Ph-C(=O)-N(Me)SiMe3 (14%)
+
Me3Si-N=C=O (19%)
Ph-C(=N-SiMe3)O-SiMe3 (29%)
+
[Me-N=C=O]
(Me3Si)2O (35%)
+
[Ph-C(=O)-N=C=N-Me]
excess
Ph-C(=O)-N=C=O
(XII)
(28%)
(XI)

2.3. An Oxadiazinone Formation by the Reaction with Excess Benzoyl Isocyanate.

2.3.1. The Effect of the Alkyl Group in N-(Trimethylsilyl)dialkylamines

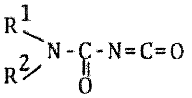
When N-(trimethylsilyl)dialkylamines were treated with two mol. equivalence of benzoyl isocyanate, 2-dialkylamino-6-phenyl-1,3,5-oxadiazin-4-one (XIV) and/or 4,6-diphenyl-1,3,5-oxadiazin-2-one (XVIII) were unexpectedly isolated. In every case, trimethylsilyl benzoate was formed at the same time (70∿80%). The relative yields of XIV and XVIII were greatly influenced by the nature of the alkyl substituents on the nitrogen atom. In all cases, when XVIII was isolated, corresponding N,N-dialkylcarbamoyl isocyanates (XIX) were identified in yields which corresponded to those of XVIII.



(2.6)

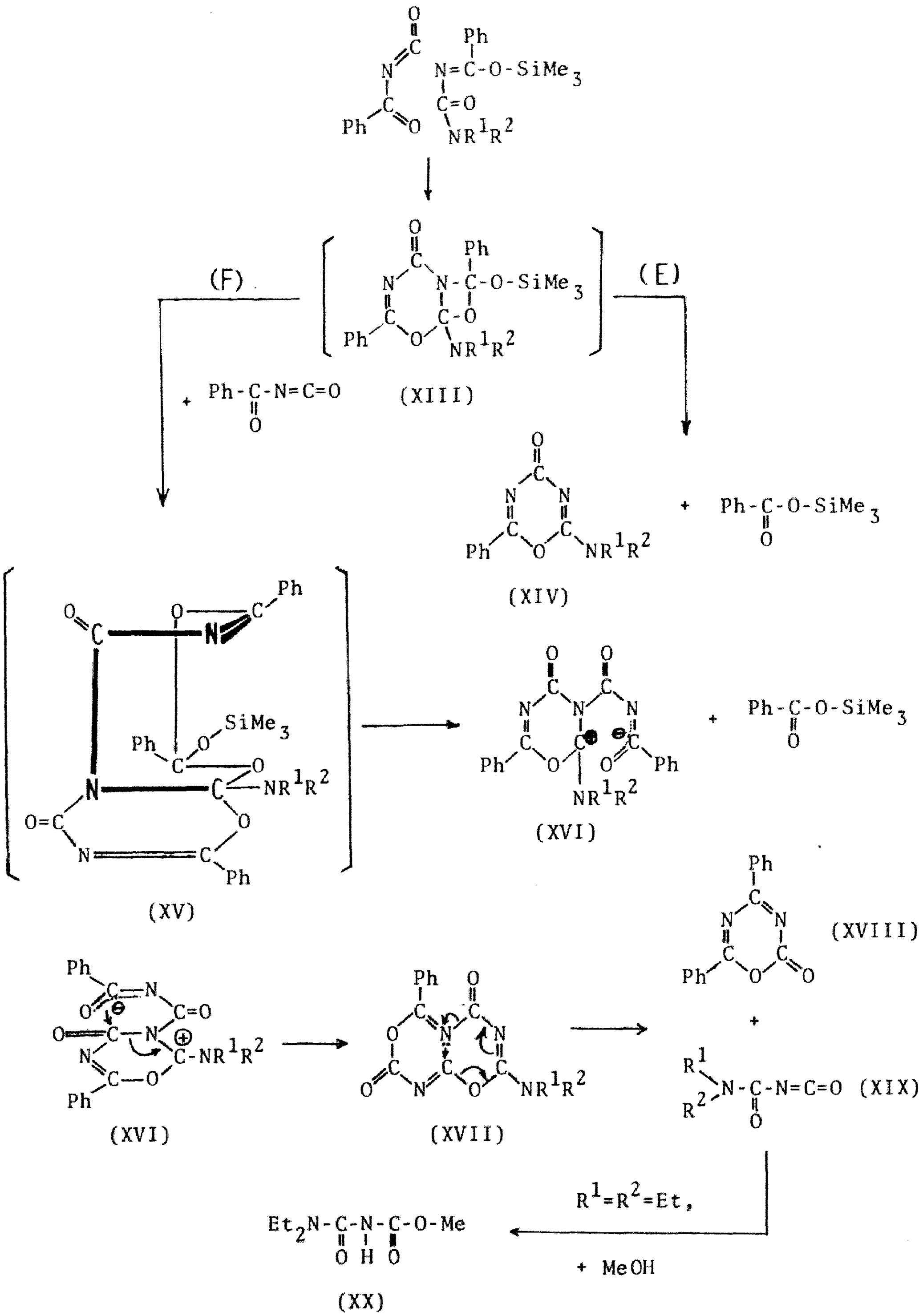
The formation of N,N-diethylcarbamoyl isocyanate was confirmed by its i.r. spectrum ($\nu_{max.}$ 2246 cm^{-1}) and by its reaction with methanol to give methyl diethylcarbamoylcarbamate (XX). All these results are summarized in Table 2.2.

Table 2.2. Yields of the products in the reaction of N-(trimethylsilyl)dialkylamines with benzoyl isocyanate.

	R^1	R^2	Trimethylsilyl benzoate (%)	Oxadiazinone XIV (%)	Oxadiazinone XVIII (%)	 $R^1R^2N-C(=O)-N=C=O$	
						(%)	$\nu_{N=C=O}$ (cm^{-1})
a	Me	Me	80	83	----	---	----
b	Et	Et	75	-----	66	70	2246
c	n-Pr	n-Pr	70	48	27	34	2245
d	n-Bu	n-Bu	71	-----	47	55	2250
e	$-(CH_2)_4-$		80	76	----	---	----
f	$-(CH_2)_5-$		73	37	32	35	2245
g	Me	C_6H_{11}	66	35	58	57	2243

The formation of both oxadiazinones can be rationalized by Scheme 2.4, which suggests that the first step of reaction is the addition of 1:1 adducts to benzoyl isocyanate (acting as a '1,4-dipole') to give the unstable intermediate XIII. A direct elimination of trimethylsilyl benzoate from XIII gives XIV (path E). Further incorporation of benzoyl isocyanate (as a '1,4-dipole' again), subsequent elimination of trimethylsilyl benzoate, and further liberation of N,N-dialkylcarbamoyl isocyanate from XVII causes formation of XVIII. There is another possible mechanism which could give oxadiazin-2-one XVIII, that is, a second molecule of benzoyl isocyanate could react with XIV to give 2,6-diphenyl-1,3,5-oxa-

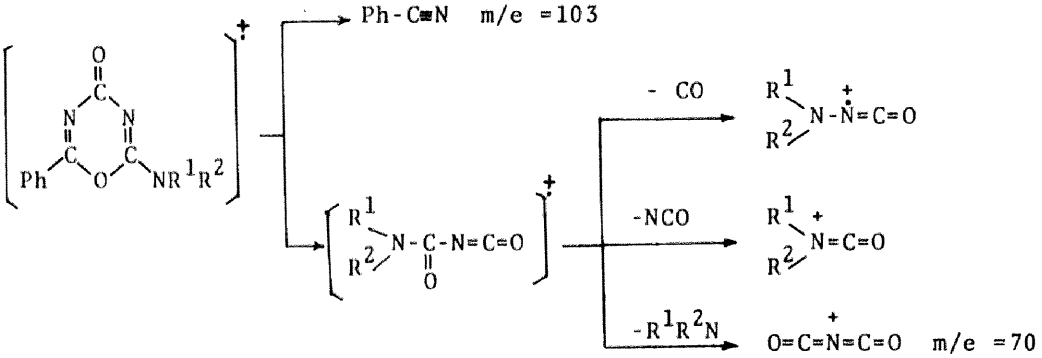
SCHEME 2.4.


(F)
(E)
(XIII)
+ Ph-C(=O)-N=C=O
(XIV)
+ Ph-C(=O)-O-SiMe3
(XV)
(XVI)
(XVII)
(XVIII)
(XIX)
R1=R2=Et,
+ MeOH
(XX)

diazin-4-one (XXII) (*vide infra*), which could isomerize to XVIII. However, the latter mechanism can be excluded by the following observations: (i) authentic XXII did not isomerize to XVIII, and (ii) the oxadiazinone XIV which was independently isolated could not be induced to react with benzoyl isocyanate. The variation of relative yield between XIV and XVIII shown in Table 2.2, cannot be rationalized by simple steric or electronic effects.

2-Dialkylamino-6-phenyl-1,3,5-oxadiazin-4-one (XIV) exhibited a characteristic fragmentation pattern as shown in Scheme 2.5 and Table 2.3.

SCHEME 2.5.

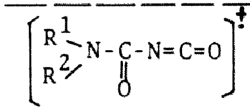
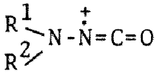
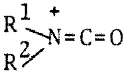


2.3.2. The Effect of the Group IVB Elements in N-(Trimethylmetal)dialkylamines.

When N-(trimethylstannyl)dimethylamine was treated with twice molar amounts of benzoyl isocyanate in benzene solution, insoluble 2,6-diphenyl-1,3,5-oxadiazin-4-one (XXII), which is the decarboxylation product of a dimeric form of benzoyl isocyanate, was isolated in 52% yield with liberation of carbon dioxide. Interestingly, the benzene solution contained IIIi, the 1:1 adduct of $Me_3Sn\text{-}NMe_2$ with benzoyl isocyanate. The mechanism of formation of XXII, for which IIIi acts as a catalyst,

Table 2.3.

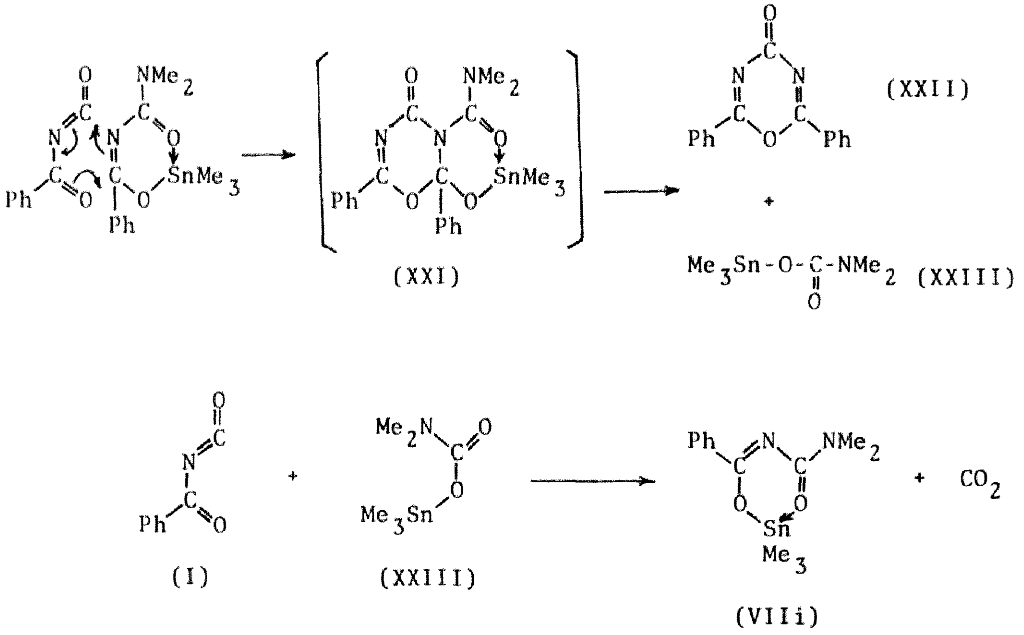
Mass spectra of oxadiazinones (XIV)*

Oxadiazinone (XIV)	Base peak (m/e)	Relative intensity (%) [m/e]					
		M^+				$O=C=\overset{+}{N}=C=O$	Ph-C≡N
a	114	8.8[217]	100 [114]	14 [86]	42 [72]	51 [70]	62 [103]
c	103	3.4[273]	16 [170]	12 [142]	3.4[128]	52	100
e	103	1.4[243]	23 [140]	15 [112]	5.6[98]	51	100
f	83	0 [257]	14 [154]	17 [126]	6.6[112]	87	56
g	139	48 [285]	18 [182]	1.3[154]	13 [140]	39	87

* Ionization potential; 75 eV., Sample temperature; ca. 100°C.

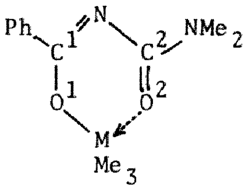
is represented in Scheme 2.6. This catalytic mechanism is strongly supported by the following observations. Firstly, treatment of Me_3Sn-NMe_2 with 10 molar amounts of benzoyl isocyanate gave XXII (39%) with evolution of carbon dioxide. Secondly, reaction of authentic trimethylstannyl N,N-dimethylcarbamate (XXIII) [44)] with benzoyl isocyanate gave VIIi and carbon dioxide (22%) by an acceptor exchange reaction [24)]. Finally, XXIII can also act as a catalyst for the decarboxylative dimerization of benzoyl isocyanate to give XXII (36%).

SCHEME 2.6.



As expected from their relative positions in the Periodic Table, the germanium compound, N-(trimethylgermyl)dimethylamine, showed behaviour intermediate between that for the corresponding silicon [formation of XIV and Ph-CO_2GeMe_3] and tin analogues [formation of XXII, CO_2, and 1:1 adduct] when it was treated with the excess molar amounts of benzoyl isocyanate. The products were (i) XIV (54%) and Ph-CO_2GeMe_3

(b.p. 52-54°/0.3mmHg; 56%) and (ii) XXII (27%) and 1:1 adduct (IIIh 19%). Accordingly, N-(trimethylgermyl)dimethylamine showed a closer resemblance to the silicon compound. The stability of five-co-ordinated structures XXIV would decrease in the order Sn > Ge > Si. The amide oxygen (O^1) will interact weakly with the metal in the case of silicon and germanium products XXIV; as a result, cyclization with benzoyl isocyanate occurs, accompanied by nucleophilic attack of O^2 to C^1 as presented in Scheme 2.4. In addition, the fact that the 1:1 adducts with the Si-N compounds exist as an equilibrium between III and V indicates little interaction between the oxygen atom (O^2) and the trimethylsilyl group (*vide supra*). On the other hand, the oxygen atom (O^2) was completely blocked by co-ordination to the metal atom in the case of the tin compound. Therefore, cycloaddition to benzoyl isocyanate across the C^1=N bond became the dominant reaction.

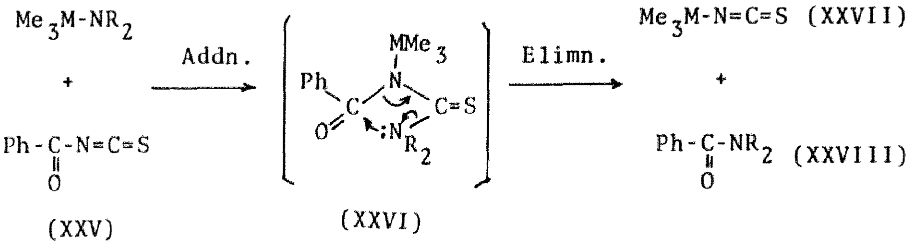


(XXIV)

2.4. The Insertion and Elimination Reactions of Benzoyl Isothiocyanate.

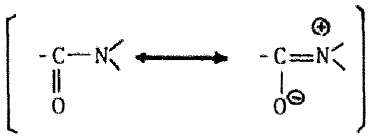
Benzoyl isothiocyanate (XXV) reacted with N-(trimethylmetal)dialkylamines (M=Si and Sn) exothermally at room temperature, however, the behaviour was quite different from that of benzoyl isocyanate. No sign of the expected insertion products (XXVI) was obtained and the sole products isolated were trimethylmetal isothiocyanate (XXVII) and N,N-dialkylbenzamide (XXVIII). They were separated by distillation or the complex formation with pyridine (trimethylstannyl isothiocyanate) and identified by the comparison with the authentic materials [69, 70].

The formation of XXVII and XXVIII can be reasonably explained by eq. 2.7, which predicts the decomposition of adduct XXVI through an β-elimination of N,N-dialkylacylamide. This β-elimination process differed from phenyl isothiocyanate 41). In the latter case, the metastable 1:1 adduct decomposed thermally back to starting materials.



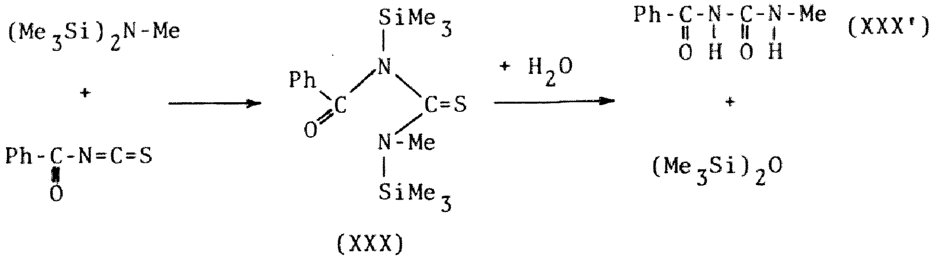
(2.7)

Above observation that the adduct XXVI was less stable than III is ascribed to the higher nucleophilicity of the dialkylthioacylamide group in XXVI. The nucleophilicity of the similar dialkylacylamide group in III is considerably depressed by the contribution of a resonance form XXIX, the involvement of which was supported by the n.m.r. splitting of the N-methyl signal in III below 10°C (Fig. 2.1). The contribution of a structure similar to XXIX must be less in the case of XXVI, because thioacylamides did not show this sort of restricted rotation.



(XXIX)

When benzoyl isothiocyanate was added to heptamethyldisilazane, viscous oily 1:1 adduct XXX was isolated. Adduct XXX was characterized by means of elementary analysis, n.m.r. and i.r. spectrometry, and quantitative formation of desilylated N-methyl-N'-phenylthiourea on hydrolysis. The formation of a stable adduct XXX at room temperature contrast with the behaviour of N-(trimethylsilyl)dimethylamine, which gives trimethylsilyl isothiocyanate and N,N-dialkylbenzamide as shown in eq. 2.7. This difference can be attributed to reduction of the nucleophilicity of nitrogen atom towards carbonyl group by $(p \rightarrow d)\pi$ overlap in the adduct XXX.



(2.8)

The proton magnetic resonance spectrum of XXX showed four kinds of trimethylsilyl and two kinds of N-methyl proton signals (Fig. 2.2), each set of which coalesced at higher temperature. This suggests the existence of two isomers which are interconvertible through the migration of trimethylsilyl groups.

Five possible isomers, (XXXa∿XXXe), interconvertible through random 1,3-transfer of trimethylsilyl groups could be formulated for the adduct XXX between heptamethyldisilazane and benzoyl isothiocyanate (see Scheme 2.7). Since the trimethylsilyl group behaves as a typical "hard" acid, structures XXXa, XXXd, and XXXe, in which silicon is linked to the "soft" sulphur atom, can be ruled out 56), leaving isomers XXXb and XXXc as possibilities.

Adduct XXX decomposed in two ways depending on the temperature. At lower temperatures it gives methyl isothiocyanate and N,O-bis(trimethylsilyl)benzimidate, and at higher temperatures it gives trimethylsilyl isothiocyanate and N-methyl-N-(trimethylsilyl)benzamide, as shown in Table 2.4.

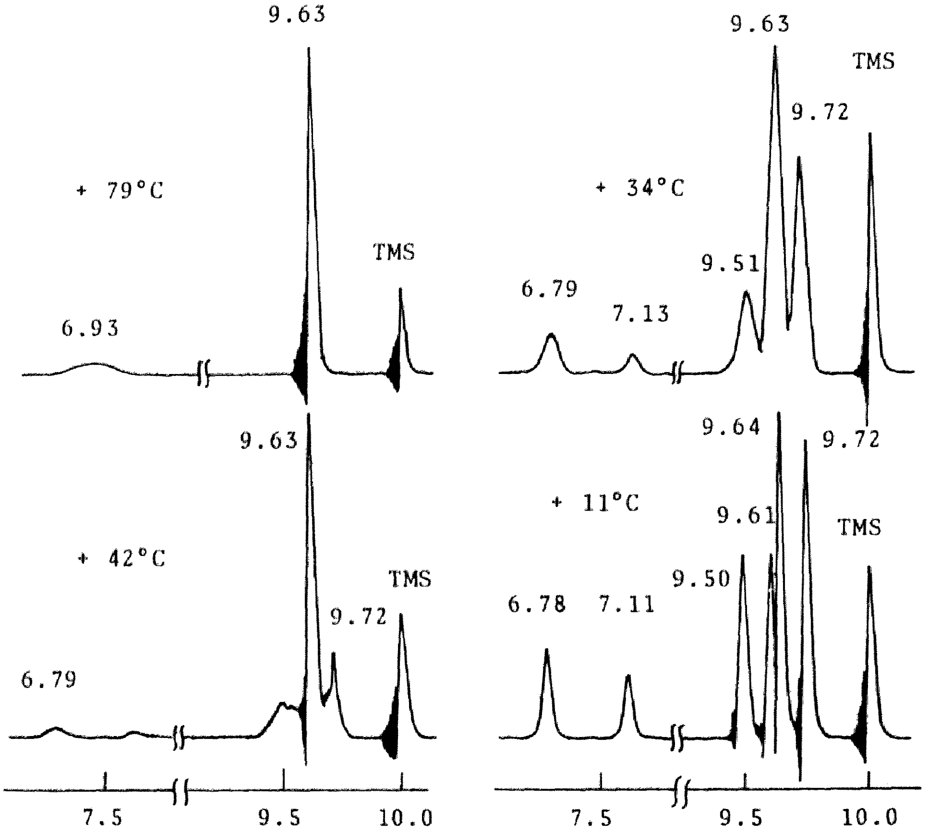
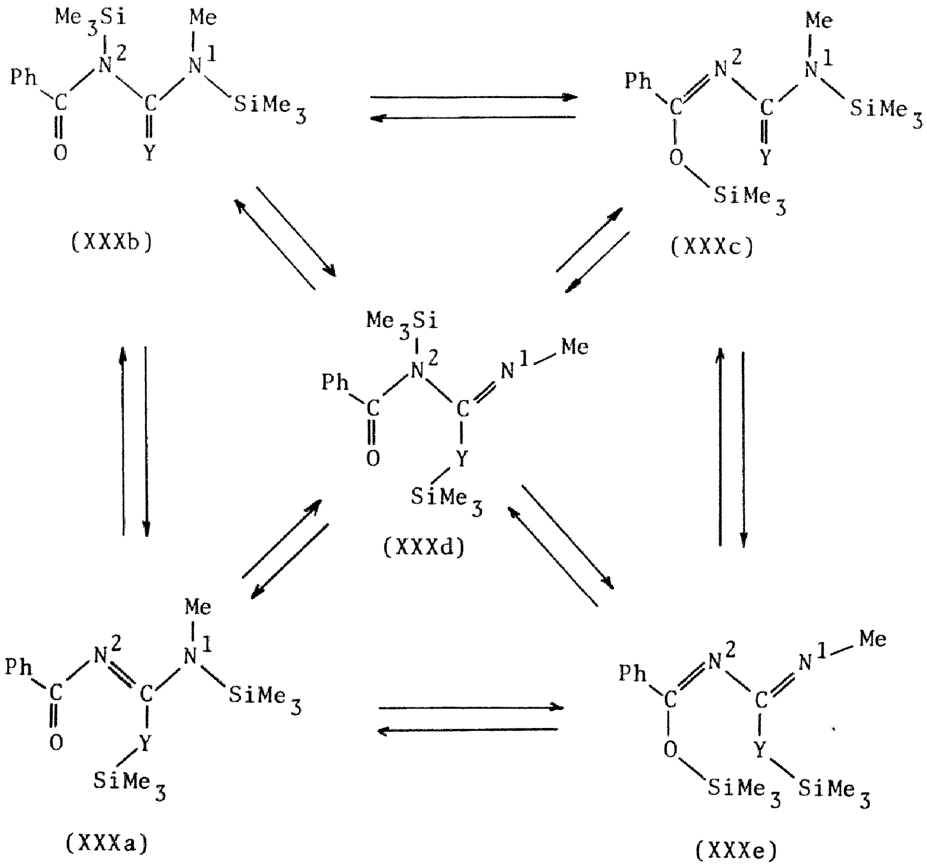


Fig. 2.2. N.m.r. spectra of adduct XXX at various temperatures (solvent; trichloroethylene)

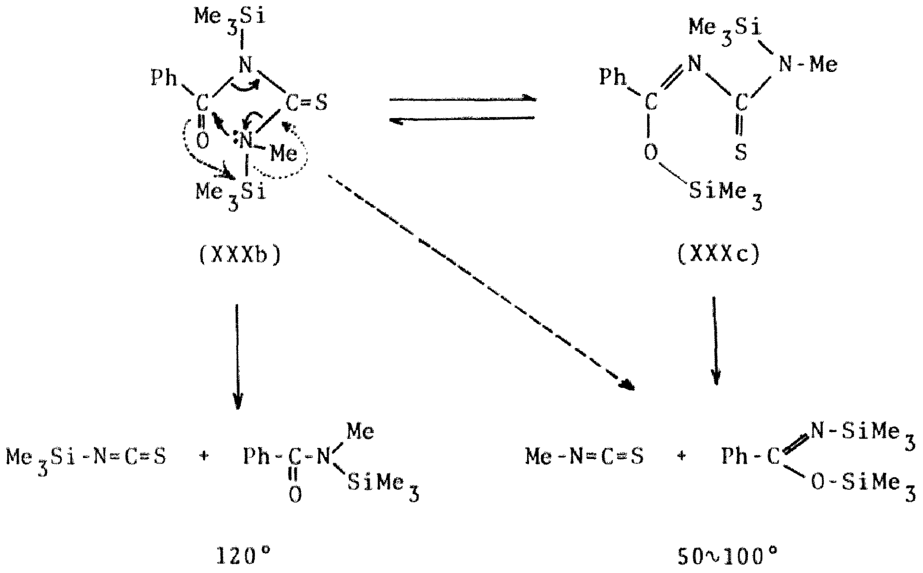
SCHEME 2.7.



Y=O and S

The results indicate the following addition-elimination reaction mechanism:

SCHEME 2.8.

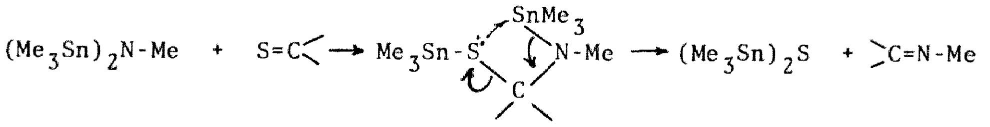


Below 100° methyl isothiocyanate is the predominant decomposition product, and thus, structure XXXc is probably preferred at these temperatures. Thus the proton signals at τ 9.72, 9.64, and 6.78 in Fig. 2.2 can be ascribed to structure XXXc, and a ratio of XXXc/XXXb of 1.5/1 at 11° can be estimated from the relative peak intensities.

Table 2.4. Thermal decomposition products from Adduct XXX at various temperature.

Temp. (°C)	Time (hr.)	$(Me\text{-}N{=}C{=}S)/(Me_3Si\text{-}N{=}C{=}S)$
50	27	only $Me\text{-}N{=}C{=}S$
100	17	4.8
120	17	1.4
150	18	0.23

Heptamethyldistannazane which was known to be an effective desulphurization agent $^{25,\ 71)}$ as eq. 2.9, could react exothermally with benzoyl isothiocyanate.



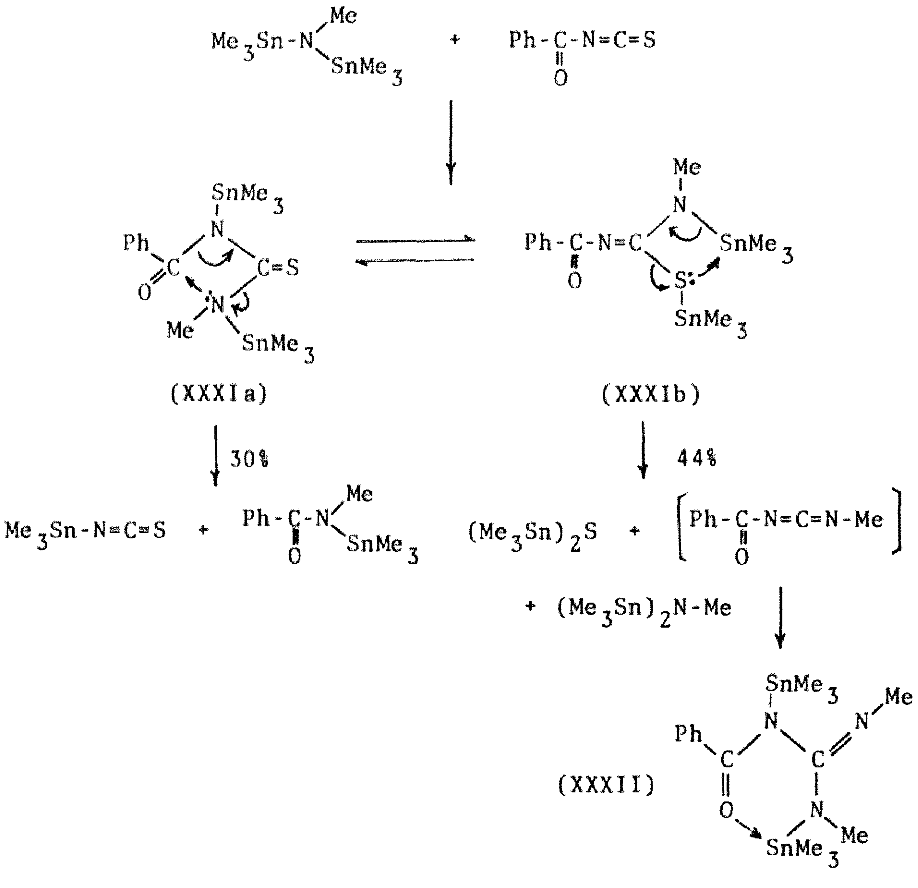
$$(Me_3Sn)_2N\text{-}Me + S{=}C\langle \longrightarrow Me_3Sn\text{-}\overset{SnMe_3}{S \cdots C \cdots N}\text{-}Me \longrightarrow (Me_3Sn)_2S + \rangle C{=}N\text{-}Me \qquad (2.9)$$

One of the reaction products, bis(trimethylstannyl)sulphide, was isolated in 44% yield by distillation. The other product would be N-benzoyl-N'-methylcarbodiimide (eq. 2.9), however, it could not be detected at all.

Since benzoyl carbodiimide behaved as an effective acceptor towards N-(trimethylstannyl)amine as it would be described later (section 2.5), unstable N-benzoyl-N'-methylcarbodiimide reacted rapidly with the remaining heptamethyldistannazane 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 trimethylstannyl isothiocyanate and N-methyl-N-(trimethylstannyl)benzamide in 30% yield, which were formed in an analogous way as eq. 2.7. These results suggested the following pathway in the case of heptamethyldistannazane.

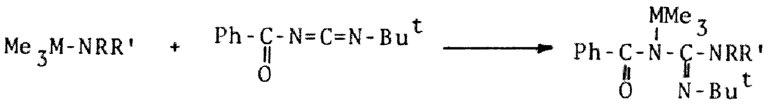
SCHEME 2.9.



2.5. The Insertion of N-Benzoyl-N'-tert-butylcarbodiimide and Pyrolyses of the Products

Since the high reactivity of benzoylcarbodiimde was predicted by the results of previous section, the view point in the present section is focussed to clarify the reaction behaviour of N-benzoyl-N'-tert-butylcarbodiimide [36)] (XXXIII) with group IVB organometallylamine.

The exothermic reactions occurred by the dropwise addition of XXXIII to four N-(trimethylmetal)amines except the particular case of heptamethyldisilazane. Generally, the addition reaction could be expressed by the following equation.



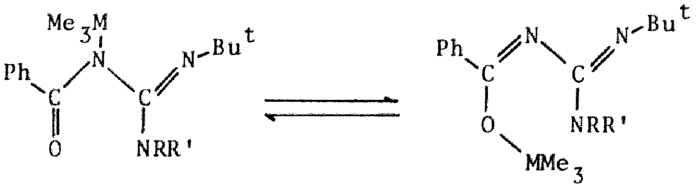
$$Me_3M\text{-}NRR' + Ph\text{-}\underset{\underset{O}{\|}}{C}\text{-}N{=}C{=}N\text{-}Bu^t \longrightarrow Ph\text{-}\underset{\underset{O}{\|}}{C}\text{-}\overset{\overset{MMe_3}{|}}{N}\text{-}\underset{\underset{N\text{-}Bu^t}{\|}}{C}\text{-}NRR' \qquad (2.10)$$

(XXXIII) (XXXIV)

The i.r. and n.m.r. data are summarized in Table 2.5. In the i.r. data, $\nu_{max.}$ bands varied remarkably. Actually no visual $\nu_{max.}$ bands around 1650 cm^{-1} were observed in the case of a, b, c, and e, however, in the case of d a very strong and broad band exists. The difference in the infrared spectroscopic behaviour is explained as follows.

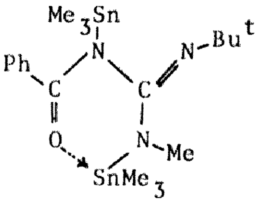
The rapid intramolecular 1,3-transfer of trimethylmetal group between the nitrogen and oxygen atom induced disappearance of the apparent carbonyl stretching frequency as cited in foregoing section (section 2.2) for a, b, and c. This view was strongly supported by the separation (τ 9.75 and 9.59) of trimethylsilyl signal of XXXIVa at low temperature. On the contrary, the migration of trimethylstannyl group is overwhelmed by the steric crowding. As the result, the appearance of $\nu_{C=O}$ band around 1630 cm^{-1} was observed in XXXIVd. Again the disappearance of $\nu_{C=O}$ in XXXIVe with two trimethylstannyl group is interpreted by the following intramolecular five-co-ordinated structure

XXXVI as VIIi. An intramolecular five-co-ordination was supported by the fact that molecular weight of XXXIVd and XXXIVe were monomeric in benzene solution (Found 385 and 545. Calcd. 410 and 558, respectively).



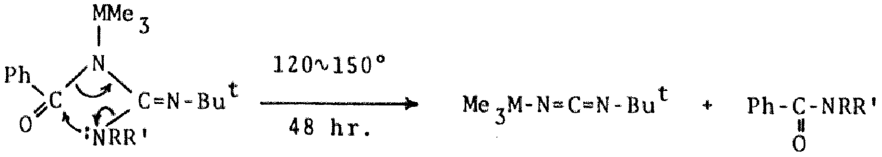
(XXXIV) (XXXV) (2.11)

M= Si and Ge



(XXXVI)

The purification by the distillation of XXXIVc induced partial pyrolysis which gave starting materials and another heterocumulene compound. Therefore, the pyrolyses of XXXIVa, b, and c were studied. The products were unknown N-(trimethylmetal)-N'-tert-butyl-carbodiimide (XXXVII) and N,N-dialkylbenzamide. The following β-elimination mechanism (eq. 2.12) analogous to eq. 2.7 seems most reasonable. The results are summarized in Table 2.6.



(XXXIV) (XXXVII) (2.12)

M= Si and Ge

Table 2.5. The i.r. and n.m.r. data of 1:1 insertion products XXXIV.

XXXIV	M	R	R'	B.p. (°C/mmHg) or M.p. (°C)	Yield (%)	I.r. (in CCl_4) $\nu_{max.}$ (cm^{-1})	N.m.r. (in CCl_4) $\tau_{M-C\underline{H}_3}$	$\tau_{C-C\underline{H}_3}$	$\tau_{N-C\underline{H}_3}$
a	Si	Me	Me	97-100/0.17	88*	1607s, 1573s, 1550s	9.64	8.91	7.34
b	Si	Me	$SiMe_3$	91-98/0.06	63*	1644w, 1605s, 1584m	9.79, 9.60	8.92	7.61
c	Ge	Me	Me	oily liquid	95	1604s, 1571s	9.37	8.96	7.22
d	Sn	Me	Me	[68-69.5]	98	1630s, 1593s, 1550m	9.53	9.02	7.18
e	Sn	Me	$SnMe_3$	[66-69]	96	1594s, 1578s, 1562s	9.74, 9.52	9.03	7.38

* Distillation yield.

Table 2.6. Pyrolysis of XXXIV

XXXIV	M	Pyrolysis products					
		$Me_3M\text{-}N=C=N\text{-}Bu^t$ (XXXVII)					$Ph\text{-}\underset{\underset{O}{\|}}{C}\text{-}NRR'$
		Yield (%)	B.p. (°C/mmHg)	$\tau_{M\text{-}\underline{CH}_3}{}^*$	$\tau_{C\text{-}CH_3}^*$	$\nu_{N=C=N}{}^*$	Yield (%)
a	Si	68	151-153/760	9.83	8.75	2144	53
b	Si	82	151-153/760	9.83	8.75	2144	65
c	Ge	75	74-77/18	9.56	8.78	2125(sh) 2099	80

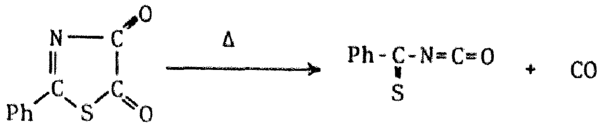
* In CCl_4 solution.

This reaction presents a preparative method of novel asymmetric trimethylmetalcarbodiimides in the moderate yields as previous papers [72, 73], which reported about bis(trimethylmetal)cabodiimide.

2.6. The Insertion Reaction of Thiobenzoyl Isocyanate

The high reactivity of thiobenzoyl isocyanate as an 1,4-dipole is of particular interest [37, 48, 49]. In this section, the reaction of N-(trimethylmetal)amines with thiobenzoyl isocyanate will be dicussed.

Because of its extreme instability, thiobenzoyl isocyanate was prepared *in situ* by the decarboxylative pyrolysis of 2-phenylthiazolin-4,5-dione in methylcyclohexane. The wine red solution of thiobenzoyl isocyanate was added immediately to N-(trimethylsilyl)-, -germyl)-,



(2.13)

or -stannyl)dimethylamine. The reaction took place instantaneously at room temperature with all four compounds with the disappearance of characteristic wine red colour of thiobenzoyl isocyanate and of the infrared absorption at 2240 cm^{-1}. The 1:1 adducts were isolated by evaporation of methylcyclohexane. Infrared and n.m.r. spectroscopic results of the 1:1 adducts XXXVIII∿XL are summarized in Table 2.7 and 2.8, respectively.

Table 2.7. N.m.r. spectra of adducts.

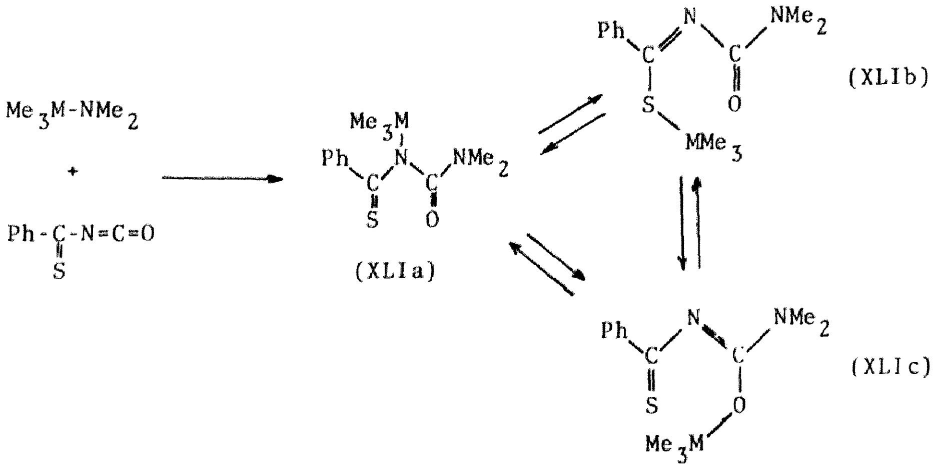
Adducts	M	Yield(%)	M.p. (°C)	$\tau_{M\text{-}C\underline{H}_3}$	$\tau_{N\text{-}C\underline{H}_3}$	Coalescence temp. (°C)
XXXVIII	Si	99	89.5-90.0	9.64*	6.99*	+ 12
XXXIX	Ge	87	47.0-49.0	9.43*	7.17*	+ 16
XL	Sn	98	124.5-125.0	9.52**	7.17, 7.10**	+ 38

* In trichloroethylene solution, ** In methylene chloride solution.

Table 2.8. I.r. spectra of adducts (in chloroform).

Adducts	ν(C=O)	ν(C=N)	ν(C=S)	$\delta_{as}(CH_3\text{-}M)$	$\delta_{sym}(CH_3\text{-}M)$	ν(C-M)
XXXVIII	1695 vs	1575 vw	1330 s	1253 vs	845 vs	685 m
XXXIX	1695 vs	1580 vw	1328 s	1238 w	823 s	605 s
XL	1645 s	1590 s 1575 s	None	1160 s	760	530 m

Three structures, XLIa∿XLIc, arise by means of the mutual interconversions through the migration of the trimethylmetal group. Such migration is important and well established in the case of the trimethylsilyl group 56, 60). The infrared spectra of XXXVIII (M=Si) and XXXIX (M=Ge) in chloroform showed two strong absorption bands ascribed to the stretching frequency of C=O and C=S bonds. A structure XLIa, in which the nitrogen atom was metallated, may thus be predominant product in the case of M=Si and Ge.

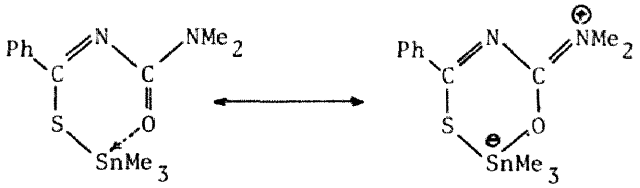


(2.14)

The adduct from the reaction between benzoyl isocyanate and N-(trimethylsilyl)dimethylamine was previously found to exist as a mixture resulting from the following equilibrium, involving 1,3-transfer of the trimethylsilyl group between a nitrogen and an oxygen atom as eq. 2.4. The difference between the adduct XLIc (M=Si) and that from benzoyl isocyanate could be ascribed to the affinity of the silicon atom (a typical "hard" acid) for an oxygen atom rather than for a sulphur atom.

On the other hand, structure XLIb was predominant in the case of the 1:1 adduct XL (M=Sn) as indicated by the absence of ν(C=S) around 1330 cm^{-1} and the appearance of a strong absorption of ν(C=N). The tin atom which is "softer" in character than silicon or germanium, is known to prefer a sulphur atom [25, 71], so the predominance of structure XLIb in XL (M=Sn) is reasonable.

It was interesting that the carbonyl stretching vibration of the 1:1 adduct XL (M=Sn) ν(C=O) 1645 cm^{-1}, was considerably shifted with that in the analogous adduct XXXVIII (M=Si) and XXXIX (M=Ge) ($\nu_{C=O}$ 1695 cm^{-1}). This act indicates a strong intramolecular co-ordination of carbonyl oxygen to the trimethyltin moiety as follows:

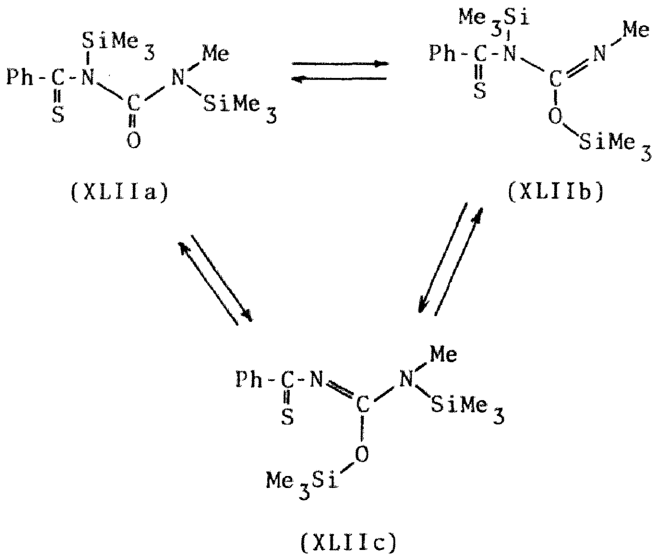


(2.15)

Much greater stability towards hydrolysis compared with their silicon or germanium adducts is also consistent with such intramolecular co-ordination to form a stable six-membered ring, with the thiobenzoyl isocyanate unit behaving as a chelate. Stronger co-ordination in the solid was indicated by infrared measurements in KBr disks; ν(C=O) absorption was found at 1605 cm^{-1}. The higher coalescence temperature for the proton signal of the dimethylamino group for XL (M=Sn) than for XXXVIII (M=Si) and XXXIX (M=Ge) (see Table 2.7) can be accounted for by intramolecular co-ordination.

For the adduct XLII, from heptamethyldisilazane, the range of structures is more complex, because four sites, NMe, N, O, and S are possibly available to the two trimethylsilyl groups. However, S-silylated structures can be reasonably ruled out because of the "hard" acid character of silicon, and thus three structures XLIIa, XLIIb, and XLIIc remain to be considered.

In carbon tetrachloride, the ν(C=O) absorption at 1710 cm^{-1} was extremely weak. Consequently, structures XLIIb and XLIIc, which are stable O-silylated forms, predominate over XLIIa, and this conclusion is supported by the appearance of a strong ν(C=N) absorption at 1615 cm^{-1}. At present, it is difficult to determine whether structure XLIIb or XLIIc predominates.



(2.16)

Experimental Section

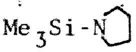
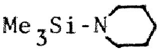
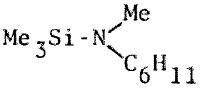
General Procedure

All reactions were carried out under argon atmosphere. N.m.r. spectra were measured (with tetramethylsilane as an internal standard) with Japan Electron Optics C-60 HL and MH-60 spectrometers. I.r. spectra were recorded with Japan Spectroscopic Co. Ltd. IR-S and DS-403G spectrometers. Mass spectra were measured with Japan Electron Optics JMS-01SG or Hitachi RMS-4 instruments.

Starting Materials

N-(Trimethylmetal)dialkylamines 74, 75), heptamethyldimetallazanes, 76, 77) benzoyl isocyanate 34), benzoyl isothiocyanate 35), N-benzoyl-N'-tert-butylcarbodiimide 36), and thiobenzoyl isocyanate 37) were prepared by the reported methods, respectively. N-(Trimethylgermyl)dimethylamine was prepared by the reaction of lithiumdimethylamide with trimethylchlorogermane. These materials are summarized in Table 2.9.

Table 2.9. Starting materials.

Compounds	B.p.(°C/mmHg)	(Lit. B.p.)	Yield(%)	References
$Me_3Si-NMe_2$	86.5/760	(86.2, 85)	68	(78, 79)
$Me_3Si-NEt_2$	125-127/760	(126.8-127.1/738)	70	(80)
$Me_3Si-N(n-Pr)_2$	64.5/22	(67/26)	75	(74)
$Me_3Si-N(n-Bu)_2$	85-86/16	(93/21)	34	(81)
	40-42/19	(141-142/760)	42	(74)
	55.5/21	(162/760)	55	(74)
 $Me_3Si-N(Me)(C_6H_{11})$	99/28		67	(75)
$Me_3Ge-NMe_2$	83-89/760		75	
$Me_3Sn-NMe_2$	119-123/760	(126/760)	70	(77)
$(Me_3Si)_2N-Me$	144-150/760	(150/760)	38	(76)
$(Me_3Sn)_2N-Me$	51-58/2	(64/3)	67	(77)
$Me_3Sn-NEt_2$	60-67/25	(43/8)	65	(77)
Ph-C(=O)-N=C=O	65-69/8	(97-98/23)	92	(34)
Ph-C(=O)-N=C=S	82-86/0.2	(58-62/0.03)	68	(35)
$Ph-C(=O)-N=C=N-Bu^t$	91-95/0.08	(78-82/0.01)	64	(36)

2.A. The Reaction of Benzoyl Isocyanate

2.A.1. Insertion Reactions

(a) N-(Trimethylsilyl)dimethylamine. Benzoyl isocyanate (1.49g, 10.2 mmol) was gradually added to equimolar amounts of N-(trimethylsilyl)-dimethylamine (1.38g, 11.9 mmol) at 0°. The reaction proceeded exothermally. After completion of the addition, the mixture was kept for 30 min. at room temperature. The adduct was distilled at 127-130°/0.35mmHg (79%).

(b∿g) The same procedures as above were carried out in all cases. Boiling points and i.r. and n.m.r. data are collected in Table 2.1.

(h) N-(Trimethylgermyl)dimethylamine. Benzoyl isocyanate (0.30g, 2.0 mmol) was added to N-(trimethylgermyl)dimethylamine (0.30g, 2.3 mmol) at -78° and the mixture was gradually warmed up to room temperature.

After removal of the excess of N-(trimethylgermyl)dimethylamine under reduced pressure, the pale yellow oily 1:1 adduct IIIh was isolated. This product was too unstable for further purification by distillation. Spectroscopic data are also included in Table 2.1.

(i) N-(Trimethylstannyl)dimethylamine. Benzoyl isocyanate (0.38g, 2.6 mmol) was added dropwise to N-(trimethylstannyl)dimethylamine (0.62g, 3.0 mmol) in benzene (2ml) at 0°. After this addition the mixture was stirred for a few minutes at room temperature. The yellow oily adduct IIIi was isolated by the removal of the excess of N-(trimethylstannyl)-dimethylamine and benzene under reduced pressure. Cryoscopic measurement of the molecular weight of IIIi gave a value of 349 (Calcd. value, 355 as monomeric unit). Attempts to distil the adduct IIIi were unsuccessful owing to the thermal decomposition which occurred readily. Results of i.r. and n.m.r. spectra are presented in Table 2.1.

(j) Heptamethyldisilazane. When benzoyl isocyanate (1.13g, 7.69 mmol) was gradually added to heptamethyldisilazane (1.41g, 8.05 mmol) at room temperature, reaction took place exothermally. The mixture was kept at 75° for 2 hr. under reduced pressure, and 1:1 adduct IX was then isolated by vacuum distillation (b.p. 105-108°/0.2 mmHg, $\nu_{max.}$ 1661 and 1630 cm^{-1}, $\tau_{Si-C\underline{H}_3}$ 9.75 and 9.66, $\tau_{N-C\underline{H}_3}$ 7.29 in trichloroethylene) in 75% yield.

Hydrolysis. Hydrolysis of IX gave white needles of N-benzoyl-N'-methylurea IX', m.p. 165-166° (from ethanol).

Pyrolysis. Pyrolysis was carried out in a sealed tube under argon, for 18 hr. at 160-170°. Distillation gave hexamethyldisiloxane (35%), trimethylsilyl isocyanate (19%), N,O-bis(trimethylsilyl)benzimidate (29%), N-methyl-N-(trimethylsilyl)benzamide (14%), and the residue which consisted of 1,3-dimethyl-1,3-diazetidin-2-one-4-benzoylimide (XI) (28%). m.p. 102.5-103.0° (from ethanol-benzene), $\nu_{max.}$ 1731, 1669, and 1593 cm^{-1} (KBr disk), τ_{N-CH_3} 6.61 (in $CDCl_3$).

(k) Reaction of Heptamethyldisilazane with Benzoyl Isocyanate in 1:2 Molar Ratio to give Adduct X and its Desilylated Biuret X'.

When benzoyl isocyanate (1.94g, 13.2 mmol) was gradually added to heptamethyldisilazane (1.15g, 6.54 mmol) at room temperature, 1:2 adduct X was obtained with evolution of heat. $\nu_{max.}$ 1705 and 1663 cm^{-1}, τ_{Si-CH_3} 9.83 and 9.66, τ_{N-CH_3} 6.89 (in trichloroethylene).

Hydrolysis. Hydrolysis of adduct X gave N,N''-dibenzoyl-N'-methylbiuret X' in 85% yield. m.p. 128-129° (from ethanol), $\nu_{C=O}$ 1742 cm^{-1}.

(1) Formation of 1-Methyl-3,5-dibenzoyl Isocyanurate from 1:3 Molar Reaction of Heptamethyldisilazane with Benzoyl Isocyanate.

Benzoyl isocyanate (1.65g, 11.2 mmol) was added to heptamethyldisilazane (0.62g, 3.5 mmol) at room temperature and the mixture was kept for one week at room temperature. The pale yellow solid obtained by evaporation of volatile materials under reduced pressure was washed with benzene to give colourless 1-methyl-3,5-dibenzoyl isocyanurate (XII) in 8% yield. m.p. 202° (from ethanol), $\nu_{max.}$ 1741 and 1705 cm^{-1}, τ_{N-CH_3} 6.60 (in $CDCl_3$).

2.A.2. Oxadiazinone Formations by the Reaction of III with Benzoyl Isocyanate.

(a) N-(Trimethylsilyl)dimethylamine. Benzoyl isocyanate (1.83g, 12.4 mmol) was added to N-(trimethylsilyl)dimethylamine (0.69g, 5.0 mmol) at -78°. After keeping the mixture for 2 hr. at room temperature, vacuum distillation of the mixture gave trimethylsilyl benzoate (0.90g, 80%). b.p. 59°/0.8 mmHg (lit.[104] 221°), τ_{Si-CH_3} 9.63 (in CCl_4), $\nu_{C=O}$ 1700 cm^{-1}. The residue (1.06g, 83%) was washed with small portions of diethyl ether and recrystallized from ethanol. Thus colourless needles of oxadiazinone XIVa were obtained. m.p. 140.0-140.5°, $\tau_{N-C\underline{H}_3}$ 6.87 (in CH_2Cl_2), $\nu_{max.}$ 1641, 1612, and 1595 cm^{-1} (KBr disk). Oxadiazinone XIVa was also prepared by the addition of benzoyl isocyanate to an equimolar amounts of IIIa.

Hydrolysis of XIVa. When XIVa (0.10g) was set aside for 2 weeks in water (2ml) at room temperature, it was quantitatively converted into 1-benzoyl-5,5-dimethylbiuret XIVa', which gave white needles. m.p. 151-152.5° (from benzene), $\tau_{N-C\underline{H}_3}$ 7.04 (in CH_2Cl_2), $\nu_{max.}$ 1764 and 1649 cm^{-1}.

(b) N-(Trimethylsilyl)diethylamine. Benzoyl isocyanate (1.68g, 11.4 mmol) was added to N-(trimethylsilyl)diethylamine (0.80g, 5.5 mmol) at -78°. The ampoule was sealed and kept for 4 days at room temperature. The crystals formed were filtered off and washed with small portions of diethyl ether. The product, 4,6-diphenyl-1,3,5-oxadiazin-2-one (XVIII) (66%), was recrystallized from benzene to give white needles, m.p. 159.5-160.0°, $\nu_{max.}$ 1767, 1757, 1612, and 1569 cm^{-1} (C=O and C=N). The i.r. spectrum of this compound was identical with that reported by Tsuge and Mizuguchi[82]. Distillation of the filtered reaction product (b.p. 33-45° at 0.2 mmHg) gave a mixture of trimethylsilyl benzoate and diethylcarbamoyl isocyanate (XIXb) ($\nu_{N=C=O}$ 2246 cm^{-1}) in yields of 75 and 70%, respectively. Diethylcarbamoyl isocyanate was characterized by conversion into methyl diethylcarbamoyl carbamate (XX) by treatment of the distillate with methanol (the product was separated from benzoic acid by chromatography on silica gel; Wako-gel C-200 chloroform), XX; $\tau_{\mathrm{CH_2C\underline{H}_3}}$ 8.84 (t), $\tau_{\mathrm{C\underline{H}_2CH_3}}$ 6.61 (q), $\tau_{\mathrm{O\text{-}C\underline{H}_3}}$ 6.36 (s), $\tau_{\mathrm{N\text{-}\underline{H}}}$ 1.40 (s), $\nu_{\mathrm{max.}}$ 1759, 1695, and 1668 cm^{-1}.

(c) N-(Trimethylsilyl)di-n-propylamine. Benzoyl isocyanate (1.70g, 11.6 mmol) was added to N-(trimethylsilyl)di-n-propylamine (1.05g, 6.1 mmol) at -78° and the mixture was kept at room temperature for a day in an ampoule. The crystals(0.95g) obtained were filtered off and washed with small portions of diethyl ether. This crude product was a mixture of 2-di-n-propylamino-6-phenyl-1,3,5-oxadiazin-4-one (XIVc) and the oxadiazinone XVIII. Pure oxadiazinone XIVc was isolated as a white powder, m.p. 117.0-118.0°, $\nu_{\mathrm{max.}}$ 1637 and 1585 cm^{-1}. The filtrate was distilled at 40-53°/0.2mm. to give a mixture of trimethylsilyl benzoate and di-n-propylcarbamoyl isocyanate XIXc ($\nu_{\mathrm{N=C=O}}$ 2245 cm^{-1}).

(d) N-(Trimethylsilyl)di-n-butylamine. See experiment 2.A.2.(b).

(e) N-(Trimethylsilyl)pyrrolidine. See experiment 2.A.2.(a). 2-Pyrrolidyl-6-phenyl-1,3,5-oxadiazin-4-one XIVe, m.p. 151.5-153.0°, $\nu_{\mathrm{max.}}$ 1662(sh), 1643, and 1603 cm^{-1}, was recrystallized from ethanol.

(f) N-(Trimethylsilyl)piperidine. See experiment 2.A.2.(c). Recrystallization of 2-piperidyl-6-phenyl-1,3,5-oxadiazin-4-one (XIVf) from ethanol gave yellow needles. 2,4,6-Triphenyl-1,3,5-triazine, m.p. 230-231° (Found; C 81.83, H 5.05, N 13.47. $C_{21}H_{15}N_3$ requires C 81.53, H 4.89, N 13.58%) was formed as an impurity which was separated by filtration of the hot ethanol solution. XIVf had m.p. 128.5-130.0°, $\nu_{\mathrm{max.}}$ 1660 (sh), 1640, 1592, and 1576 cm^{-1}.

(g) N-(Trimethylsilyl)-N-methylcyclohexylamine. See experiment 2.A.2.(c). 2-N-Methylcyclohexylamino-6-phenyl-1,3,5-oxadiazin-4-one (XIVg) was purified by recrystallization from chloroform/n-hexane (2/1) after the separation of s-triphenyltriazine which was present as an impurity, it had m.p. 139.5-141.0°, $\nu_{\mathrm{max.}}$ 1642, 1587, and 1573 cm^{-1}.

(h) N-(Trimethylgermyl)dimethylamine. Benzoyl isocyanate(1.65g, 11.2 mmol) was added to N-(trimethylgermyl)dimethylamine (0.89g, 5.5 mmol) at -78°. The ampoule was sealed and kept at room temperature for 12 hr.. Distillation of the reaction mixture gave trimethylgermyl benzoate (0.73g, 56%), b.p. 52-54°/0.3mmHg, $\tau_{\mathrm{Ge\text{-}C\underline{H}_3}}$ 9.33 (in CCl_4), $\nu_{\mathrm{max.}}$ 1682 cm^{-1}. Treatment of the residue with benzene gave crystals which were filtered off. This crystalline product was a mixture of the oxadiazinones XIVa and XXII, the yields of which were estimated as 54 and 27%, respectively from the n.m.r. spectrum of crude product. The benzene filtrate contained mainly the 1:1 adduct IIIh (19%) which was characterized by n.m.r. and i.r. spectroscopy.

(i) N-(Trimethylstannyl)dimethylamine. Benzoyl isocyanate (1.08g, 7.3 mmol) was added dropwise to N-(trimethylstannyl)dimethylamine (0.79g, 3.8 mmol) in benzene (2.4ml) at 0°. The ampoule was sealed and kept for 12 hr. at room temperature. Evolution of carbon dioxide was observed when the sealed tube was opened. 2,6-Diphenyl-1,3,5-oxadiazin-4-one (XXII) (0.18g, 52%) was filtered off and recrystallized from benzene to give white needles, m.p. 150.0-151.0°, $\nu_{max.}$ 1641, 1630, and 1562 cm^{-1}. The i.r. spectrum was identified with that described in the literature [82]. The filtrate contained mainly the 1:1 adduct IIIi.

(j) Cyclization Reaction of Benzoyl Isocyanate Catalyzed by N-(Trimethylstannyl)dimethylamine.

Benzoyl isocyanate (2.17g, 14.7 mmol) was added dropwise to N-(trimethylstannyl)dimethylamine (0.31g, 1.5 mmol) in benzene (3ml) at 0°. The ampoule was sealed and kept for 12 hr. at room temperature. Crude 2,6-diphenyl-1,3,5-oxadiazin-4-one XXII (0.65g, 39%) was filtered off. Hydrolysis of the filtrate gave a second crystalline product (0.73g, 41%) which was identified as dibenzoylurea formed by hydrolysis of benzoyl isocyanate itself, the 1:1 adduct IIIi and XXII, which had m.p. 209-210° (from ethanol).

(k) Reaction of Trimethylstannyl -N,N-dimethylcarbamate with Benzoyl Isocyanate.

Benzoyl isocyanate (0.20g, 1.8 mmol) was added to trimethylstannyl-N,N-dimethylcarbamate (XXIII) (0.45g, 1.8 mmol) in benzene (1.5ml) and the mixture was allowed to stand at room temperature. Carbon dioxide was immediately generated and was trapped with a sodium hydroxide tube in 22% yield. The 1:1 adduct IIIi was isolated from the benzene solution and was characterized by comparison of its i.r. and n.m.r. spectra with those of the authentic sample prepared from the 1:1 addition reaction.

(l) Cyclization Reaction of Benzoyl Isocyanate Catalyzed by Trimethylstannyl-N,N-dimethylcarbamate.

Benzoyl isocyanate (1.30g, 8.8 mmol) was added to trimethylstannyl-N,N-dimethylcarbamate (XXIII) (0.11g, 0.5 mmol). The mixture was heated at 80° for 8 hr. Carbon dioxide was trapped in the sodium hydroxide tube in a yield of 53% and the crude oxadiazinone XXII (0.35g, 35%) was filtered off.

2.B. The Reaction of Benzoyl Isothiocyanate.

(a) N-(Trimethylmetal)dialkylamines. Benzoyl isothiocyanate was added to the equimolar N-(trimethylmetal)dialkylamines at -78°. After warming to room temperature, the distillation of the mixture gave trimethylmetal isothiocyanate XXVII and N,N-dialkylbenzamide. The yields of each product are collected in Table 2.10.

Table 2.10. Reaction of benzoyl isothiocyanate.

Starting materials		Products	
Ph-C(=O)-N=C=S (mmol)	Me_3M-NR_2 (mmol)	$Me_3M-N=C=S$ [69, 70] Yield (%)	$Ph-C(=O)NR_2$ Yield (%)
23.3	$Me_3Si-NMe_2$ (23.5)	73	95
7.37	$Me_3Si-NEt_2$ (8.20)	88	92
7.20	$Me_3Sn-NMe_2$ (7.50)	89*	67
4.49	$Me_3Sn-NEt_2$ (4.53)	38*	83

* Isolated as trimethylstannyl isothiocyanate pyridine complex.

(b) Heptamethyldisilazane. Heptamethyldisilazane (0.73g, 4.3 mmol) was added to benzoyl isothiocyanate (0.76g, 4.3 mmol) at room temperature and the mixture was kept at 15° for 36 hr. in an ampoule. After evaporation of mixture at 10^{-5}mmHg for 3 hr., the brown 1:1 adduct XXX was isolated in 100% yield. $\nu_{max.}$ 1643 cm^{-1} (in CCl_4), $\tau_{Si-C\underline{H}_3}$ 9.64, 9.61, and 9.50, $\tau_{N-C\underline{H}_3}$ 7.13 and 6.78.

Hydrolysis. Adduct XXX was quantitatively hydrolyzed into N-benzoyl-N'-methylthiourea. m.p. 147.8-149.0° (from ethanol), $\nu_{C=O}$ 1672 cm^{-1}.

Pyrolysis. Adduct XXX was pyrolyzed in a sealed tube at temperatures between 50-150°. Vacuum distillation gave methyl isothiocyanate {$\nu_{N=C=S}$ 2140 cm^{-1}, $\tau_{N-C\underline{H}_3}$ 6.67 in CCl_4} and trimethylsilyl isothiocyanate {$\nu_{N=C=S}$ 2080 cm^{-1}, $\tau_{Si-C\underline{H}_3}$ 9.68 in CCl_4} in a dry ice/acetone trap , N,O-bis(trimethylsilyl)benzimidate {b.p. 77-81°/0.5 mmHg, $\nu_{max.}$ 1695 cm^{-1}, $\tau_{Si-C\underline{H}_3}$ 9.89 and 9.71 in CCl_4}, and N-methyl-N-(trimethylsilyl)benzamide {b.p. 87-89°/0.9 mmHg, $\nu_{max.}$ 1665 cm^{-1}, $\tau_{N-C\underline{H}_3}$ 7.24 and 6.98, $\tau_{Si-C\underline{H}_3}$ 9.79 in CCl_4} as distillate.

2.C. The Reaction of N-Benzoyl-N'-tert-butylcarbodiimide.

2.C.1. 1:1 Insertion Reactions.

(a) N-(Trimethylsilyl)amines. The distillation of the 1:1 mixture of N-benzoyl-N'-tert-butylcarbodiimide and N-(trimethylsilyl)amines gave adducts XXXIVa and XXXIVb.

(b) N-(Trimethylgermyl)dimethylamine. After the removal of the excess N-(trimethylgermyl)dimethylamine and solvent (CCl_4) from the mixture of N-benzoyl-N'-tert-butylcarbodiimide and N-(trimethylgermyl)amine, pale yellow oily liquid of XXXIVc was given.

(c) N-(Trimethylstannyl)amines. N-Benzoyl-N'-tert-butylcarbodiimide was added dropwise to the n-hexane solution of equimolar N-(trimethylstannyl)amines at -78°. After the reaction, white needles of XXXIVd and XXXIVe were precipitated, which were recrystallized from benzene/n-hexane.

2.C.2. Pyrolysis.

The 1:1 mixture of N-benzoyl-N'-tert-butylcarbodiimide and N-(trimethylmetal)amines (M=Si and Ge) was heated at 150° for 24 hr. in an ampoule. Produced N-(trimethylmetal)-N'-tert-butylcarbodiimide XXXVII and N,N-disubstituted benzamide were separated by the distillation of the mixture.

2.D. The Reaction of Thiobenzoyl Isocyanate.

(a) N-(Trimethylsilyl)dimethylamine. 2-Phenylthiazoline-4,5-dione (1.02g, 5.33 mmol) was suspended in 5 ml of methylcyclohexane and pyrolyzed at 90°. The solution was added to 0.9 ml (9.2 mmol) of N-(trimethylsilyl)dimethylamine, an exothermal reaction occurred and the colour changed from red to deep yellow. Evaporation of volatile materials under reduced pressure left 1.46g (98%) of the 1:1 adduct XXXVIII. Hydrolysis was readily done by atmospheric moisture, and gave N-thiobenzoyl-N',N'-dimethylurea XXXVIII' in quantitative yield. The product was recrystallized from carbon tetrachloride. m.p. 88.0-89.0°, $\nu_{C=O}$ 1670, $\nu_{C=S}$ 1330 cm^{-1} (KBr disk), $\tau_{N-C\underline{H}_3}$ 7.12 (in CCl_4).

(b) N-(Trimethylgermyl)dimethylamine. Thiobenzoyl isocyanate formed from 67.8mg (0.36 mmol) of 2-phenylthiazoline-4,5-dione, was added dropwise to N-(trimethylgermyl)dimethylamine, as described for the silicon analogue, to give the adduct XXXIX in 87% yield. Hydrolysis of the adduct XXXIX with atmospheric moisture gave N-thiobenzoyl-N',N'-dimethylurea quantitatively.

(c) N-(Trimethylstannyl)dimethylamine. The analogous procedure with 585mg (3.1 mmol) of 2-phenylthiazoline-4,5-dione and 660mg (3.2 mmol) of N-(trimethylstannyl)dimethylamine gave the adduct XL in 98% yield. It was recrystallized from benzene, and had m.p. 124.5-125.1°. It was stable to hydrolysis when exposed to the air for one week at room temperature.

(d) Heptamethyldisilazane. The adduct XLI was isolated quantitatively when 125mg (0.65 mmol) of 2-phenylthiazoline-4,5-dione was pyrolyzed and the product was added to heptamethyldisilazane (0.70 mmol) at room temperature. Evaporation of the solvent gave the adduct XLI as a viscous oil. It was readily hydrolyzed to give N-methyl-N'-thiobenzoylurea XLI' in quantitative yield. m.p. 143.5-143.9° (from ethanol), $\nu_{C=O}$ 1705, $\nu_{C=S}$ 1360 cm^{-1} (KBr disk).

Table 2.11. Elementary analyses and molecular weights.

Compounds	Formula	Molecular weight		Found (%)			Calcd. (%)		
		Found*	Calcd.	C	H	N	C	H	N
IIIa	$C_{13}H_{20}N_2O_2Si$		264	59.46	7.55	---	59.06	7.62	10.59
IIIb	$C_{15}H_{24}N_2O_2Si$		294	61.50	8.07	---	61.61	8.27	9.58
IIIc	$C_{17}H_{28}N_2O_2Si$		320	63.70	8.71	---	63.71	8.80	8.74
IIId	$C_{19}H_{32}N_2O_2Si$		348	65.32	9.05	---	65.47	9.25	8.04
IIIe	$C_{15}H_{22}N_2O_2Si$		290	62.21	7.55	---	62.07	7.64	9.64
IIIf	$C_{16}H_{24}N_2O_2Si$		304	63.24	7.88	---	63.12	7.94	9.20
IIIg	$C_{18}H_{28}N_2O_2Si$		332	65.18	8.34	---	65.02	8.49	8.42
IIIh	$C_{13}H_{20}N_2O_2Ge$		308	50.65	6.60	---	50.55	6.53	9.07
IIIi	$C_{13}H_{20}N_2O_2Sn$	349**	355	43.75	5.78	---	43.98	5.68	7.89
IX	$C_{15}H_{26}N_2O_2Si_2$		322	55.63	7.66	---	55.86	8.13	8.68
IX'	$C_9H_{10}N_2O_2$	178	178	60.27	5.83	15.95	60.66	5.66	15.72
X	$C_{23}H_{31}N_3O_4Si_2$		469	58.65	6.78	---	58.82	6.65	8.95
X'	$C_{17}H_{15}N_3O_4$	325	325	62.88	4.73	12.93	62.76	4.65	12.92
XI	$C_{11}H_{11}N_3O_2$	217	217	61.11	5.21	19.36	60.82	5.11	19.34
XII	$C_{18}H_{13}N_3O_5$	351	351	61.39	3.68	11.86	61.54	3.73	11.96
XIVa	$C_{11}H_{11}N_3O_2$	217	217	60.81	5.18	19.00	60.82	5.10	19.33
XIVa'	$C_{11}H_{13}N_3O_3$	235	235	56.40	5.59	17.51	56.17	5.57	17.16

Table 2.11. continued.

Compounds	Formula	Molecular weight		Found (%)			Calcd. (%)		
		Found*	Calcd.	C	H	N	C	H	N
XIVc	$C_{15}H_{19}N_3O_2$	273	273	66.20	7.07	15.45	65.91	7.01	15.37
XIVe	$C_{13}H_{13}N_3O_2$	243	243	64.20	5.28	17.12	64.19	5.38	17.27
XIVf	$C_{14}H_{15}N_3O_2$	257	257	65.38	5.86	16.22	65.36	5.88	16.33
XIVg	$C_{16}H_{19}N_3O_2$	285	285	67.38	6.69	14.72	67.35	6.71	14.73
XVIII	$C_{15}H_{10}N_2O_2$	250	250	72.02	4.16	11.12	71.99	4.03	11.19
XX	$C_7H_{14}N_2O_3$	174	174	48.06	7.85	16.08	48.27	8.10	16.08
XXII	$C_{15}H_{10}N_2O_2$	250	250	71.77	4.14	11.40	71.99	4.03	11.20
XXX	$C_{15}H_{26}N_2OSSi_2$		338	53.18	7.65	---	53.21	7.74	8.27
XXX'	$C_9H_{10}N_2OS$	166	166	55.43	4.83	14.15	55.65	5.19	14.42
XXXIVa	$C_{17}H_{29}N_3OSi$		319	64.07	8.98	---	63.90	9.15	8.77
XXXIVb	$C_{19}H_{35}N_3OSi_2$		377	60.60	9.45	---	60.42	9.34	11.13
XXXIVc	$C_{17}H_{29}N_3OGe$		364	55.91	7.85	---	56.09	8.03	11.54
XXXIVd	$C_{17}H_{29}N_3OSn$	385**	410	49.93	7.23	---	49.79	7.13	10.25
XXXIVe	$C_{19}H_{35}N_3OSn_2$	545**	558	40.74	6.29	---	40.83	6.31	7.52
XXXVIIa	$C_8H_{18}N_2Si$		214	44.92	8.58	---	44.73	8.44	13.04
XXXVIII	$C_{13}H_{20}N_2OSSi$		280	55.73	7.24	---	55.67	7.19	9.99
XXXVIII'	$C_{10}H_{12}N_2OS$		208	57.97	5.81	13.09	57.67	5.81	13.45
XXXIX	$C_{13}H_{20}N_2OSGe$		324	48.42	6.54	---	48.02	6.22	8.62
XL	$C_{13}H_{20}N_2OSSn$		371	42.34	5.67	---	42.02	5.43	7.55
XLI	$C_{15}H_{26}N_2OSSi_2$		338	52.81	7.46	---	53.21	7.74	8.27
XLI'	$C_9H_{10}N_2OS$		194	55.48	4.96	---	45.65	5.19	14.42

* The result of mass spectra. ** Cryoscopic data.

CHAPTER 3

Addition Reactions of Asymmetric Heptamethyldimetallazane, $Me_3M\text{-}N(Me)\text{-}M'Me_3$ with Heterocumulenes

3.1. Introduction

The chemical reactions of heptamethyldimetallazane and related compounds, especially the reactions with a number of unsaturated bonds, can be interpreted in terms of addition-elimination processes 25, 62, 72, 83, 84). The direction of the β-eliminations from the addition products are mainly determined by the affinity of the metal atom towards the nitrogen, oxygen, or sulphur atoms, and from sets of addition-elimination reactions such as those in eq. 3.1∿3.8.

$$(Me_3Si)_2N\text{-}Me \;+\; Ph\text{-}N{=}C{=}O \xrightarrow{\Delta} (Me_3Si)_2O \;+\; Ph\text{-}N{=}C{=}N\text{-}Me \;^{62)} \qquad (3.1)$$

$$\begin{array}{c} (Me_3Si)_2N\text{-}Me \\ + \\ Ph\text{-}N{=}C{=}S \end{array} \rightleftharpoons \begin{array}{c} (Me_3Si)_2N\text{-}Ph \\ + \\ Me\text{-}N{=}C{=}S \end{array} \rightleftharpoons \begin{array}{c} (Me_3Si)_2S \;\;^{25)} \\ + \\ Ph\text{-}N{=}C{=}N\text{-}Me \end{array} \qquad (3.2)$$

$$(Me_3Si)_2N\text{-}Me \;+\; S{=}C{=}S \xrightarrow{\Delta} (Me_3Si)_2S \;+\; Me\text{-}N{=}C{=}S \;^{25)} \qquad (3.3)$$

$$(Me_3Ge)_2N\text{-}Me \;+\; Ph\text{-}N{=}C{=}S \xrightarrow{\Delta} (Me_3Ge)_2S \;+\; Ph\text{-}N{=}C{=}N\text{-}Me \qquad (3.4)$$

$$(Me_2Ge)_2O \;+\; Ph\text{-}N{=}C{=}S \xrightarrow{\Delta} (Me_3Ge)_2S \;+\; Ph\text{-}N{=}C{=}O \qquad (3.5)$$

$$(Me_3Sn)_2N\text{-}Me \;+\; Ph\text{-}N{=}C{=}S \longrightarrow (Me_3Sn)_2S \;+\; Ph\text{-}N{=}C{=}N\text{-}Me \;^{25,\ 71)} \qquad (3.6)$$

$$(Bu_3Sn)_2O \;+\; Ph\text{-}N{=}C{=}S \longrightarrow (Bu_3Sn)_2S \;+\; Ph\text{-}N{=}C{=}O \;^{83)} \qquad (3.7)$$

$$(Bu_3Sn)_2N\text{-}Ar \;+\; Cl_3C\text{-}CH{=}O \longrightarrow (Bu_3Sn)_2O \;+\; Cl_3C\text{-}CH{=}N\text{-}Ar \;^{84)} \qquad (3.8)$$

the following affinity orders were established for the Me_3M groups:

Me_3Si; $O > S \geqq N$

Me_3Ge; $S > O \simeq N$

Me_3Sn; $S > O > N$

These orders would be expected to correlate with the relevant bond energies, soft-hard characters, and electronegativities, but such correlations have not been established, and the orders remain essentially empirical.

In this chapter, the addition reactions of asymmetric Group IVB dimetallazanes with isocyanates and isothiocyanates are considered; such reactions involving the asymmetric compounds have been little studied previously 31).

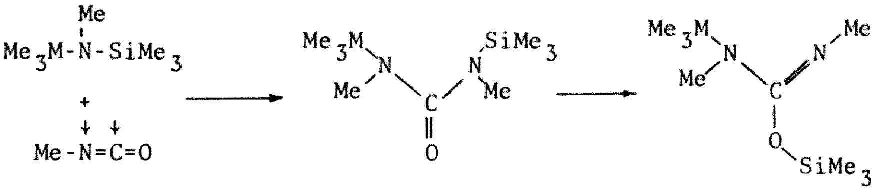
3.2. Results and Discussions

The addition products obtained from the reactions of heptamethylsilagermazane, $Me_3Si\text{-}NMe\text{-}GeMe_3$, or heptamethylsilastannazane, $Me_3Si\text{-}NMe\text{-}SnMe_3$, with methyl or phenyl isocyanate and isothiocyanate are mostly more stable than those from the symmetric dimetallazanes or from related compounds, as shown in eq. 3.1∿3.8, from which β-eliminations frequently occurred. Detailed investigation of the structures of the addition products should assist understanding the affinities of the trimethylmetallyl groups for the heteroatoms in the intermediate 1:1 adducts.

Cleavage of the metal-nitrogen bond might be expected to occur readily in the order, $Sn\text{-}N > Ge\text{-}N > Si\text{-}N$, based on Abel's basicity scales derived from $\Delta\nu_{C\text{-}D}$ (cm^{-1}, $CDCl_3$) 21), for $Me_3Sn\text{-}NEt_2$ the value of $\Delta\nu_{C\text{-}D}$ is 90, for $Me_3Ge\text{-}NEt_2$, 82, and for $Me_3Si\text{-}NEt_2$, 64 cm^{-1}.

3.2.1. Addition Reactions of $Me_3Si\text{-}NMe\text{-}MMe_3$ (M=Ge and Sn) with Isocyanates.

The addition reactions of heptamethylsilagermazane and heptamethylsilastannazane with methyl isocyanate took place exothermally, and the 1:1 adducts XLIII and XLIV, were isolated by distillation. The adduct from heptamethylsilagermazane XLIII could possibly have two isomeric structures, XLIIIa and XLIIIb, between which interconversion would be possible by a 1,3-transfer of the Me_3Si group. The fact that the n.m.r. spectra of XLIII did not change even at low temperatures suggests that only one isomer is present and a strong absorption for $\nu_{C=N}$ at 1608 cm^{-1} indicated that this was XLIIIb. Similarly, the adduct from heptamethylsilastannazane, has the structure XLIVb, as indicated by the infrared and n.m.r. spectra. The infrared spectrum had $\nu_{C=N}$ at 1613 vs and $\nu_{C=O}$ at 1645 vw, consistent with the structure XLIVb.

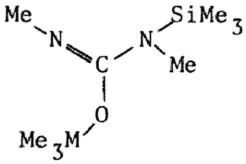


(3.9)

(XLIIIa) (M=Ge) (XLIIIb) (M=Ge)

(XLIVa) (M=Sn) (XLIVb) (M=Sn)

The possibility of the structures XLIIIc and XLIVc was excluded by the relatively high chemical shifts of CH_3-M protons, since the CH_3-M-N bonds have higher chemical shifts than those of CH_3-M-O or CH_3-M-S bonds.



(XLIIIc) (M=Ge)

(XLIVc) (M=Sn)

In addition, the appearance of satellite bands due to ^{117}Sn and ^{119}Sn in one of the two CH_3-N proton signals (τ 7.17 with J, 31 Hz) provided strong evidence in favour of structure XLIVb since XLIVc should exhibit both CH_3-N proton signals without the appearance of any satellites. Structures XLIIIb or XLIVb are in agreement with the known affinity of the trimethylsilyl group to oxygen atoms, whilst the absence of structures XLIIIc or XLIVc indicates that 1,3-transfer of Me_3M groups occur readily in the order, $Me_3Si \gg Me_3Ge$ or Me_3Sn, therefore, selective migration of the Me_3Si group yielding XLIIIb or XLIVb.

When phenyl isocyanate was used as an acceptor molecule, somewhat more complicated behaviour was observed since the introduction of a phenyl group in the adduct molecule increases the number of possible isomers in the system.

The n.m.r. spectrum of adduct XLV, purified by distillation after preparation by the instantaneous reaction between heptamethylsilagermazane with phenyl isocyanate, showed the apparent presence of two isomers in the ratio 2.5/1, with two strong assignable $\nu_{C=N}$ absorptions at 1610 cm^{-1}. This infrared evidence suggests the presence of iminoether structures, the extremely high migratory ability of the trimethylsilyl group in comparison with the trimethylgermyl group suggesting the existence of a Me_3Si-O bond in both possible isomers, similar to that in structure XLIIIb.

More interestingly, the intensity ratios among the two isomers in the reaction mixture changed from 0.5/1 to 2.5/1 with time as shown in Fig. 3.1, despite the fact that the addition reaction was apparently completed instantaneously. This variation must be ascribed to a rearrangement between the two isomers of a similar sort to that of the 1,3-transfer of either Me_3Ge or Me_3Si groups. The 1,3-transfer of the Me_3Si group occurs very rapidly 61) and therefore the rearrangement observed in this case must be due to the 1,3-transfer of the Me_3Ge group. The extrapolated value (0.5) at zero time, which corresponds to the addition reaction is consistent with the reactivity ratio Ge-N/Si-N as

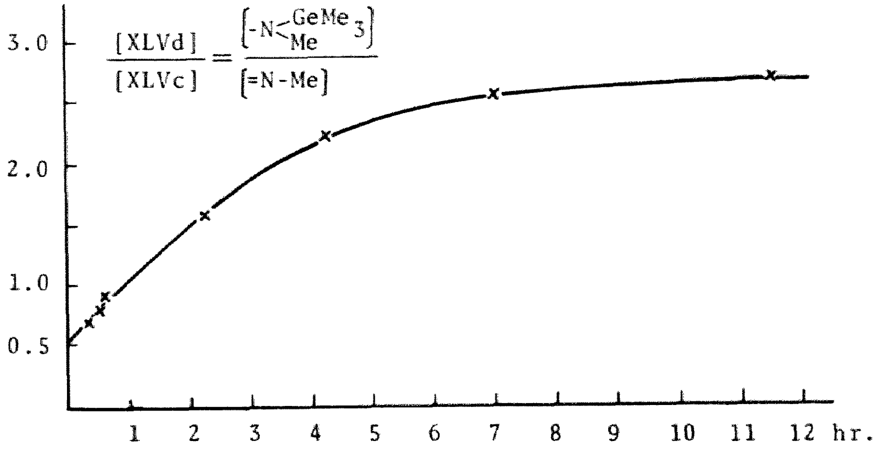


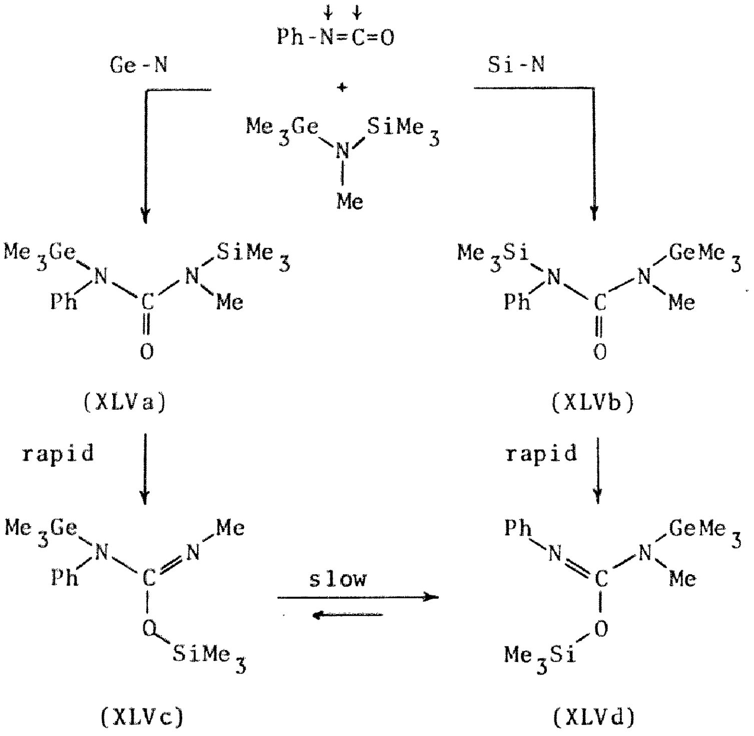
Fig. 3.1. Variation of the ratio [XLVd]/[XLVc] in the adduct of $Me_3Si-NMe-GeMe_3$ with Ph-N=C=O in CCl_4 at 25°.

estimated by the ratio of the competitive reactions of $Me_3Ge-NMe_2$ and $Me_3Si-NMe_2$ towards phenyl isocyanate (=2/1).

These observations may be reasonably explained in terms of the following scheme in which both XLVc and XLVd contribute towards the final structure of the 1:1 adduct XLV. Initially, the conversion XLVa →XLVc, involving Ge-N bond cleavage, occurs at nearly twice the rate of the conversion XLVb → XLVd, which involves Si-N bond cleavage, and leads to an isomer ratio [XLVd]/[XLVc] = 0.5/1. Subsequently, due to the gradual migration of the Me_3Ge group from N-Ph to N-Me this isomer ratio is modified to 2.5/1, a value in complete agreement with that observed for the distilled adduct.

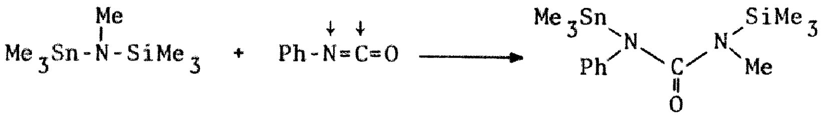
The reaction of phenyl isocyanate with heptamethylsilastannazane occurs instantaneously to yield the 1:1 adduct XLVI. The n.m.r. spectrum of XLVI shows the presence of only one isomer and the CH_3-N proton signal (τ 7.72) gave no indication of any satellite bands due to ^{117}Sn and ^{119}Sn. The chemical shifts of both CH_3-Si and CH_3-Sn, observed at τ 9.80 and 9.75, respectively, suggest that the attachment of both group IVB organometallyl groups is to nitrogen. These results may be explained

SCHEME 3.1.



$[XLVc]/[XLVd] = 1/2.5$

on the basis of the amide structure XLVIa which is produced by the selective cleavage of the Sn-N bond in heptamethylsilastannazane because the nucleophilicity of Sn-N bonds is considerably higher than that of Si-N bonds, a conclusion in agreement with Abel's basicity scale 21).



(XLVIa)

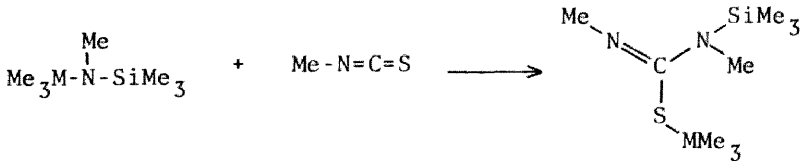
(3.10)

Structure XLVIa is also consistent with the observed infrared measurements in which a strong absorption ascribed to $\nu_{C=O}$ was observed at 1665 cm^{-1}. The absence of 1,3-transfer of the Me_3Si group in XLVI is somewhat difficult to explain, although either a weak co-ordination of the carbonyl oxygen atom to the trimethyltin moiety or the existence of steric hindrance in the iminoether structure would tend to inhibit the transfer of the silicon atom from the nitrogen to the oxygen atom.

3.2.2. Addition Reactions of Me_3Si-NMe-MMe_3 (M=Ge and Sn) with Isothiocyanates.

The addition reactions of methyl or phenyl isothiocyanates with heptamethylsilagermazane or -stannazane proceeded more slowly than the reactions with the corresponding isocyanates, and for this reason the rate differences between Si-N and M-N (M=Ge and Sn) bond cleavage are higher in the case of isothiocyanates.

Both heptamethylsilagermazane and heptamethylsilastannazane gave the stable 1:1 adducts XLVII and XLVIII, respectively, with methyl isothiocyanate. The n.m.r. spectra of either XLVII or XLVIII exhibit quite low chemical shifts for the CH_3-M proton signals, viz., τ 9.48 for M=Ge and τ 9.54 for M=Sn, which strongly suggests that XLVII and XLVIII possess Me_3M-S linkages. The strong affinities of both Me_3Ge and Me_3Sn groups for sulphur atoms, as discussed earlier, support the preferential formation of germanium- or tin-sulphur bonded structures as depicted below.

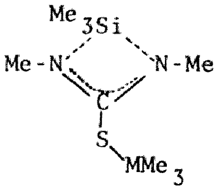


(3.11)

(XLVII) (M=Ge)

(XLVIII) (M=Sn)

However, the observation that the CH_3-N proton signals appeared as singlets in both cases (τ 7.05 for M=Ge and τ 7.02 for M=Sn) indicates that transfer of the Me_3Si group between the two chemically equivalent N-Me groups takes place over the n.m.r. time scale. For this reason, the structures of these compounds are best represented as XLVIIa or XLVIIIa, the appearance of $\nu_{C=N}$ at 1608 and 1603 cm^{-1}, for M=Ge and M=Sn, respectively, in the infrared spectra providing further for the proposed structure*.



(XLVIIa) (M=Ge)
(XLVIIIa) (M=Sn)

Reactions of phenyl isothiocyanate with these heptamethylsilametallazane result in the adducts XLIX and L with considerably different structures from those of XLVIIa and XLVIIIa discussed above. In addition, the stability of the 1:1 adduct L obtained from the reaction between heptamethylsilastannazane and phenyl isothiocyanate was extremely low, the adduct decomposing readily during distillation to give methylphenylcarbodiimide and a mixture of bis(organometallic)sulphides.

The chemical shifts of the respective CH_3-M proton signals were τ 9.73 for XLIX (M=Ge) and τ 9.80 for L (M=Sn), both being quite high field values indicating that bonding between the Me_3M groups and the nitrogen atoms should occur. The absence of any satellites due to ^{117}Sn and ^{119}Sn in the spectrum of adduct L suggests the existence of a Me_3Sn-N(Ph) linkage. The chemical shifts of CH_3-Si proton signals in both adducts occurred at low field value, *viz.*, around τ 9.70,

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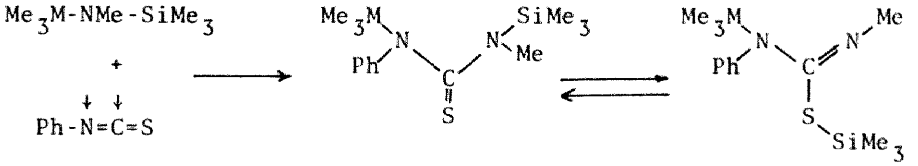
* The time scale of measurements by infrared spectroscopy is much shorter than that of measurements by n.m.r. spectroscopy.

being lower than the correponding CH_3-M proton signals associated with the N-Ph groups.

The n.m.r. and the infrared results mentioned above, in which both $\nu_{C=N}$ and $\nu_{C=S}$ occurred with considerable intensity, may be explained by the existence of two interconvertible structures, *i.e.*,



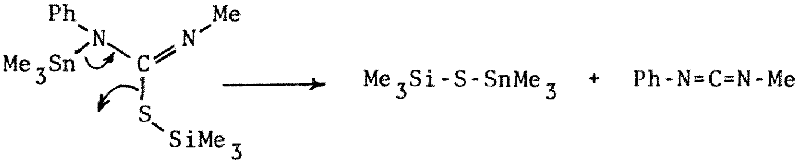
(3.12)

(XLIXa) (M=Ge) (XLIXb) (M=Ge)

(La) (M=Sn) (Lb) (M=Sn)

Interconversion involving 1,3-transfer of Me_3Si groups occurs over the n.m.r. time scale, since affinity of Me_3Si groups for nitrogen and sulphur atoms is similar. The low chemical shifts observed for the CH_3-Si proton signals may be ascribed to the partial contributions of the two structures XLIXb and Lb to the overall system.

The thermal instability of the 1:1 adduct L may be reasonably explained in terms of the proposed structure Lb. The pyrolysis products were methylphenylcarbodiimide, trimethylsilyltrimethylstannyl sulphide, bis(trimethylstannyl)sulphide, and bis(trimethylsilyl)sulphide, the latter three group IVB organometallic sulphides being obtained by thermal disproportionation. From this it follows that the decomposition of adduct L proceeds *via* the β-elimination of Me_3Si-S-$SnMe_3$ from the structure Lb to give methylphenylcarbodiimide, the soft S-$SiMe_3$ group readily attacking the soft Me_3Sn moiety.



(3.13)

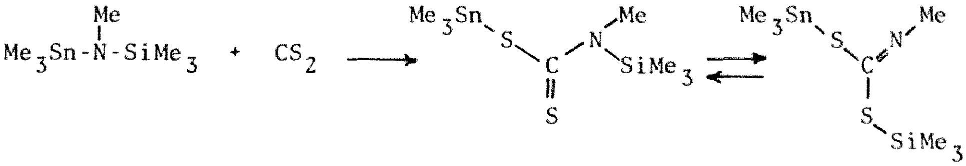
Table 3.1. N.m.r. spectra of adducts and predominant structures.

Adducts	Components		Chemical shifts (τ ppm)[a]				Coupling constants (Hz)		Predominant structures
	Acceptors	Addenda	$C\underline{H}_3$-Si	$C\underline{H}_3$-M	$C\underline{H}_3$-N	$C\underline{H}_3$-N=C	$J(^{119}Sn-H)$	$J(^{117}Sn-H)$	
XLIII	Me-N=C=O	Me_3Si-NMe-$GeMe_3$	9.82[b]	9.61[b]	7.28	7.25			(XLIIIb)
XLIV	Me-N=C=O	Me_3Si-NMe-$SnMe_3$	9.84	9.73	7.17[c]	7.22	57.5	54.8	(XLIVb)
XLV	Ph-N=C=O	Me_3Si-NMe-$GeMe_3$	9.82	9.63	7.87				(XLVd)
			9.85	9.59		7.73			(XLVc)
XLVI	Ph-N=C=O	Me_3Si-NMe-$SnMe_3$	9.80	9.75	7.72[d]		58.5	55.7	(XLVIa)
XLVII	Me-N=C=S	Me_3Si-NMe-$GeMe_3$	9.84[b]	9.48[b]	7.05				(XLVIIa)
XLVIII	Me-N=C=S	Me_3Si-NMe-$SnMe_3$	9.88	9.54	7.02[d]		57.5	54.8	(XLVIIIa)
XLIX	Ph-N=C=S	Me_3Si-NMe-$GeMe_3$	9.70[b]	9.73[b]	7.02				(XLIXa) (XLIXb)
L	Ph-N=C=S	Me_3Si-NMe-$SnMe_3$	9.71	9.80	7.05[d]		56.9	54.3	(La) (Lb)
LI	CS_2	Me_3Si-NMe-$SnMe_3$	9.58	9.45	6.85[d]				(LIa) (LIb)

a) Measured in CCl_4 relative to internal TMS as τ 10.00. b) Peak assignments between CH_3-Si and CH_3-Ge were made on the basis of differences in the ^{13}C satellites; $J(H-^{13}C)$ 115∿124 Hz for Me_3Si and $J(H-^{13}C)$ 125∿130 Hz for Me_3Ge. c) $J(H-C-^{117,119}Sn)$ 30.6 Hz. d) No satellite due to $^{117,\ 119}Sn$ was observed.

This kind of β-elimination has already been extensively studied as illustrated by eq. 3.1, 3.2, 3.3, 3.4, and 3.6.

Adduct LI formed by the addition reaction of heptamethylsilastannazane and carbon disulphide, was stable. Its structure may also be represented in solution as an isomeric mixture of LIIa and LIIb since the chemical shifts of CH_3-Si and N-CH_3 (τ 9.58 and τ 6.85, respectively) 84∿86) are close to those of L.


(3.14)

(LIa) (LIb)

3.3. Conclusions.

The affinity orders of group IVB organometallyl groups, from the basis of their addition-elimination reactions, are closely correlated with the type of bonds between the organometallyl moieties and to the particular heteroatoms in the addition products formed. For this reason, β-elimination during addition-elimination reactions is controlled by the nature of the isomers preferentially formed amongst the 1:1 adducts. Bond formation for the group IVB organometallyl groups studied were found to occur in the following order: R_3Si; $O > S \simeq N$, R_3Ge; $S > O \simeq N$, R_3Sn; $S > O > N$

It has been found that the 1,3-transfer of trimethylmetallyl groups is an important factor in determining the structure of the predominant species formed during the reaction. In general, as has been shown previously, these transfers were found to be extremely rapid in terms of the n.m.r. time scale at room temperature. During the conversion XLVc⇌XLVd, however, the migration of the Me_3Ge group was found to be quite slow and no clear evidence for the transfer of the Me_3Sn group has been obtained from the reactions studied in the present investigation. It appears, therefore, that the ease of 1,3-transfer amongst Me_3M group occurs in the series Si ≫ Ge > Sn.

Experimental Section

Heptamethylsilagermazane and heptamethylsilastannazane were prepared by the method proposed by Scherer $^{85, 86)}$ in 75% yield (b.p. 39-40°/12 mmHg) and 55% yield (b.p. 69-70°/30 mmHg), respectively.

3.A. The Reaction with Isocyanates.

3.A.1. The Equimolar Reactions. Isocyanate (4.0 mmol) was gradually added to a solution of equimolar heptamethylsilagermazane or heptamethylsilastannazane in carbon tetrachloride at room temperature. An exothermic reaction occurred and the 1:1 adducts were isolated by vacuum distillation. The yields and boiling points are summarized in Table 3.2.

The interconversion between XLVd and XLVc was studied by mixing equimolar amounts of both components in carbon tetrachloride in a n.m.r. tube which was sealed under atmosphere of argon. The ratio of XLVc to XLVd was measured in terms of the two CH_3-N proton signals at τ7.87 and 7.83, respectively at appropriate time intervals at 25°.

3.A.2. Competitive Reactions of Me_3Si-NMe_2 and Me_3Ge-NMe_2 with Phenyl Isocyanate.

To a mixture of Me_3Si-NMe_2 (0.54g, 4.63 mmol) and Me_3Ge-NMe_2 (0.74g, 4.58 mmol) in 0.8 ml of carbon tetrachloride at 0°, 0.51g (4.30 mmol) of phenyl isocyanate was added. After disappearance of the characteristic infrared maxima of phenyl isocyanate, the molar ratio of the two 1:1 adducts, Me_3Si-NPhCO-NMe_2 and Me_3Ge-NPhCO-NMe_2, were measured in terms of the two CH_3-M proton signals.

3.B. The Reaction with Isothiocyanates.

Isothiocyanates (4∿5 mmol) were gradually added to a solution of equimolar heptamethylsilagermazane or heptamethylsilastannazane in carbon tetrachloride at room temperature. After the reaction the mixture gave pure 1:1 adduct by the distillation under reduced pressure.

Table 3.2. 1:1 Adducts with heterocumulenes.

Adducts	Acceptors	Addenda	B.p. (°C/mmHg)	Yield (%)	$\nu_{max.}$ (cm^{-1})
XLIII	Me-N=C=O	Me_3Si-NMe-$GeMe_3$	48-49/0.08	70	1640vw (C=O), 1608vs (C=N)
XLIV	Me-N=C=O	Me_3Si-NMe-$SnMe_3$	54-55/0.08	69	1645vw (C=O), 1613vs (C=N)
XLV	Ph-N=C=O	Me_3Si-NMe-$GeMe_3$	70-73/0.06	78	1655w(C=O), 1610vs, 1590vs(C=N)
XLVI	Ph-N=C=O	Me_3Si-NMe-$SnMe_3$	93/0.08	69	1663vs (C=O), 1595m (C=N)
XLVII	Me-N=C=S	Me_3Si-NMe-$GeMe_3$	59-61/0.04	63	1608 s (C=N)
XLVIII	Me-N=C=S	Me_3Si-NMe-$SnMe_3$	70/0.12	79	1608 s (C=N)
XLIX	Ph-N=C=S	Me_3Si-NMe-$GeMe_3$	87-88/0.05	60	1580s (C=N), 1335m (C=S)
L	Ph-N=C=S	Me_3Si-NMe-$SnMe_3$	---	99	1590m (C=N), 1285s (C=S)
LI	CS_2	Me_3Si-NMe-$SnMe_3$	m.p. 67-69	43	1325 vs (C=S)

However, in the case of 1:1 adduct L, an attempt to purify the crude adduct by vacuum distillation caused complete decomposition of L. The yields and boiling points are summarized in Table 3.2.

Pyrolysis of Adduct L. Adduct L completely decomposed at 100° within 1 hr.. Distillation of the mixture gave methylphenylcarbodiimide (30%), hexamethylsilastannathiane (20%), hexamethyldisilthiane (10%) and hexamethyldistannathiane (55%), as well as polymeric residues. All of the above materials were identified by the comparison of their n.m.r. and infrared spectra with those of authentic samples.

3.C. The Reaction with Carbon Disulphide.

Carbon disulphide (0.37g, 4.94 mmol) reacted exothermally with heptamethylsilastannazane (1.22g, 4.60 mmol) at room temperature. After the evolution of heat had ceased, the reaction mixture was converted into a light yellow solid. After 30 min. the 1:1 adduct LI was recrystallized from dry n-hexane to give the pure colourless compound in 43% yield. m.p. 67-69°.

Table 3.3. Elementary analyses.

Compounds	Formula	Found (%)		Calcd. (%)	
		C	H	C	H
XLIII	$C_9H_{24}N_2OSiGe$	39.10	8.88	39.03	8.73
XLIV	$C_9H_{24}N_2OSiSn$	33.59	7.39	33.46	7.49
XLV	$C_{14}H_{26}N_2OSiGe$	49.75	7.58	49.60	7.73
XLVI	$C_{14}H_{26}N_2OSiSn$	44.77	6.63	43.66	6.80
XLVII	$C_9H_{24}N_2SSiGe$	36,73	8.25	36.89	8.26
XLVIII	$C_9H_{24}N_2SSiSn$	32.01	7.28	31.87	7.13
XLIX	$C_{14}H_{26}N_2SSiGe$	47.50	7.31	47.35	7.38
LI	$C_8H_{21}NS_2SiSn$	27.61	6.60	28.09	6.19

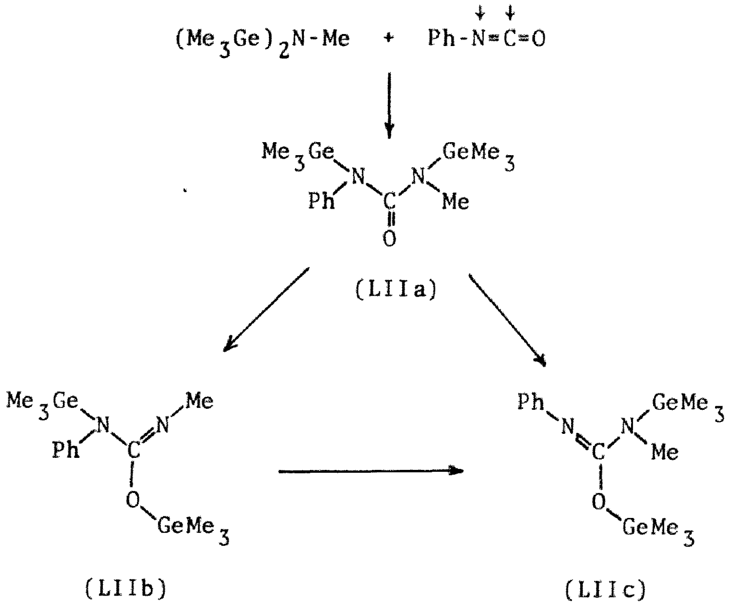
CHAPTER 4.

Insertion and Subsequent Elimination Reactions of Bis(trimethylgermyl)methylamide, -oxide, and -sulphide.

4.1. Reactions of Heptamethyldigermazane; $(Me_3Ge)_2NMe$

The addition of phenyl isocyanate with heptamethyldigermazane occurred instantaneously and a 1:1 addition product LII was isolated by distillation. Three possible isomers, LIIa ∿ LIIc, exist for the structure of LII. N.m.r. spectroscopic studies of LII show the presence of only one of these three possible isomeric structures. Thus, the two kinds of CH_3-Ge proton signals at τ 9.65 and 9.62 as well as one CH_3-N signals at τ 7.84 observed in the spectrum have values very similar to those observed for adduct XLV.

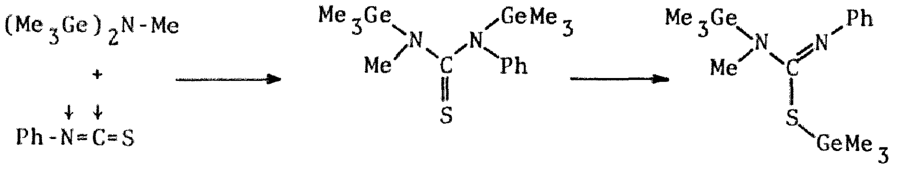
SCHEME 4.1.



In addition, the infrared spectrum of LII showed a strong $\nu_{C=N}$ absorption at 1588 cm^{-1}, which when taken together with above n.m.r. spectroscopic evidence strongly suggests that the predominant structure of LII is LIIc which is presumably derived by the one step Me$_3$Ge transfer LIIa→LIIc or by two step transfers involving two Me$_3$Ge groups *i.e.* LIIa→LIIb→LIIc.

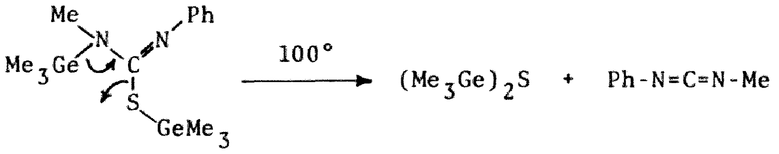
In a similar fashion addition reaction of heptamethyldigermazane and phenyl isothiocyanate also occurs instantaneously at room temperature. In this case, however, the adduct LIII could only be successfully isolated by distillation in high vacuum because of its ready decomposition.

The existence of a low field chemical shift at τ 9.53 for one of the CH$_3$-Ge protons suggests the formation of a Ge-S bond in the predominant structure of this compound. The infrared spectrum of LIII possesses $\nu_{C=N}$ at 1560 cm^{-1} and the similarities between the n.m.r. and infrared spectra of this adduct with those of the adduct obtained from the reaction of phenyl isothiocyanate with Me$_3$Ge-NMe-SiMe$_3$ [XLIX in the preceding chapter] support LIIIb as the predominant structure in this system.


(LIIIa) (LIIIb)

(4.1)

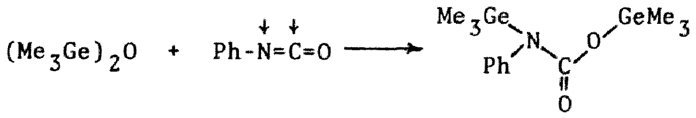
Adduct LIII decomposes completely around 100° to give methylphenylcarbodiimide and bis(trimethylgermyl)sulphide as the main products, thus providing further evidence in favour of structure LIIIb since methylphenylcarbodiimide may be formed from this structure through a selective β-elimination reaction involving (Me$_3$Ge)$_2$S. The selective formation of methylphenylcarbodiimide and bis(trimethylgermyl)sulphide from the metastable 1:1 adduct LIIIb indicates that the showed Me_3Ge group is much more closely related to the corresponding Me_3Sn group in its behaviour than the Me_3Si group [25)].



(4.2)

4.2. Reactions of Hexamethyldigermoxane; $(Me_3Ge)_2O$

The simple insertion reactions of isocyanate, chloral, and β-propio lactone into Bu_3Ge-OMe have been reported previously [87)]. A similar addition reaction of phenyl isocyanate into one of the Ge-O bonds in hexamethyldigermoxane took place at room temperature over a period of 1.5 hr., indicating that the reactivity of hexamethyldigermoxane is considerably less than that of heptamethyldigermazane and suggesting that the reactivity order should be Ge-N > Ge-O. Adduct LIV, isolated as colourless crystals, showed two independent CH_3-Ge proton signals with equal intensities at τ 9.65 and 9.49 respectively, and with $\nu_{C=O}$ absorptions at 1637 and 1662 cm^{-1} in the i.r. spectrum. This spectroscopic evidence supports structure LIVa rather than LIVb since the latter would be eliminated on the basis of the above n.m.r. results, since it should only exhibit one CH_3-Ge signal.

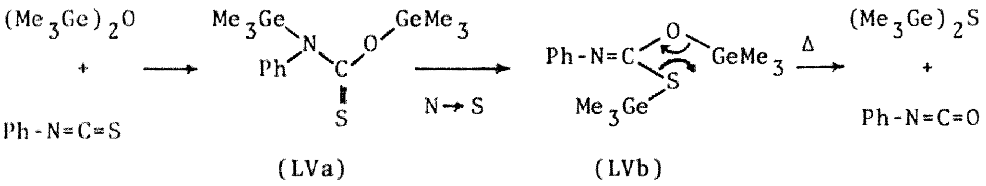


(4.3) $Ph\text{-}N{=}C(OGeMe_3)_2$

(LIVb)

(LIVa)

As mentioned previously, isothiocyanates are weaker acceptors than the corresponding isocyanates, because the polarity of C=S bonds is much lower than that of C=O bonds making isothiocyanates less electrophilic. Phenyl isothiocyanate does not react at all with hexamethyldigermoxane at room temperature, and even under much more drastic conditions, *i.e.*, 150° for 200 hr., the expected simple insertion product LV was not isolated. The sole reaction which occurred was an elimination reaction which yielded bis(trimethylgermyl)sulphide and phenyl isocyanate as the products. This suggests that the following addition-elimination mechanism occurs in which Me_3Ge prefers the soft sulphur to the hard oxygen atom, the similarity of the Me_3Ge group to the R_3Sn group again being demonstrated 83, 88).



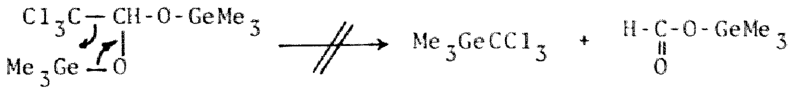
(LVa) (LVb) (4.4)

Hexamethyldigermoxane does, however, react instantaneously with chloral, even at room temperature, to give the insertion product LVI.

$$(Me_3Ge)_2O \; + \; Cl_3C\text{-}CH{=}O \longrightarrow Cl_3C\text{-}CH(OGeMe_3)_2 \qquad (4.5)$$

(LVI)

The structure of adduct LVI was identified through the presence of the characteristic C-H proton signal at τ 4.93 [*cf.* $Cl_3C\text{-}CH(SEt)(OSiMe_3)$ at τ 5.00 61), and the equivalent CH_3-Ge proton signal at τ 9.50 as a singlet]. Elimination of Me_3GeCCl_3 from LVI was not observed in the present investigation, although such elimination was well established for organotin and organolead oxides 89, 90, 91).



4.3. Attempted Reactions Involving Bis(trimethylgermyl)sulphide; $(Me_3Ge)_2S$.

Attempts to react bis(trimethylgermyl)sulphide with chloral or phenyl isothiocyanate were unsuccessful the starting materials being recovered unchanged. When bis(trimethylgermyl)sulphide was treated with phenyl isocyanate under drastic conditions, *i.e.*, 150° for 264 hr., trace amounts of triphenyl isocyanurate, the cyclic trimer of phenyl isocyanate, were identified as the sole product. The formation of triphenyl isocyanurate in excellent yield at room temperature has already been reported as a result of the reaction of bis(trimethylstannyl)sulphide with phenyl isocyanate 61). On the basis of Abel's basicity order 21), the basicity of group IVB organometallyl sulphides should lie in the series $Sn\text{-}S > Ge\text{-}S > Si\text{-}S$; our results, however, indicate the somewhat unexpected sequence, $Sn\text{-}S > Si\text{-}S \gg Ge\text{-}S$. The decreased nucleophilicity of Ge-S bonds to unsaturated polar double bonds may possibly be explained in terms of the electronegativity difference between group IVB metals and the sulphur atom on the basis of the Allred-Rochow scale 12); Si 1.74, Ge 2.02, Sn 1.72 and S 2.44.

4.4. Conclusions.

The basicity of $(Me_3Ge)_2X$ (X=NMe, O, and S) towards unsaturated compounds follows the order $(Me_3Ge)_2NMe > (Me_3Ge)_2O \gg (Me_3Ge)_2S$, which was quite consistent with Abel's basicities 21); $\Delta\nu_{C-D}$ (cm^{-1}) for $Me_3Ge\text{-}NEt_2$ 82, $(Me_3Ge)_2O$ 55, $(Me_3Ge)_2S$ 38.

The addition-elimination reactions of heptamethyldigermazane or hexamethyldigermoxane with phenyl isothiocyanate led to the selective formation of bis(trimethylgermyl)sulphide, a behaviour quite similar to that of the corresponding organotin analogues. Thus, on the basis of addition-elimination reactions the bond strength of Ge-X lies in the order Ge-S > Ge-O ≈ Ge-N, which differs from that of both the organosilicon and organotin compounds, *viz.*, Si-O > Si-S ≫ Si-N and Sn-S > Sn-O > Sn-N.

Experimental Section

Heptamethyldigermazane [85], hexamethyldigermoxane[92], and bis(trimethylgermyl)sulphide[93] were prepared as described in the literature.

(a) Reaction of Heptamethyldigermazane with Phenyl Isocyanate.

Phenyl isocyanate (0.35g, 2.88 mmol) was added to heptamethyldigermazane (0.84g, 3.18 mmol) at room temperature. The addition reaction was completed instantaneously and the 1:1 adduct LII was isolated by distillation under reduced pressure in 63% yield. b.p. 76-78°/0.05 mmHg, (Found, C 43.87, H 6.73. $C_{14}H_{26}N_2OGe_2$, Calcd. C 43.84, H 6.83%), $\nu_{C=N}$ 1588 cm^{-1}(vs), $\nu_{C=O}$ 1651 cm^{-1}(vw), $\tau_{Ge-C\underline{H}_3}$ 9.65 and 9.62 with $J(^{13}C\text{-}H)$ 125 Hz, $\tau_{N-C\underline{H}_3}$ 7.84.

(b) Reaction of Heptamethyldigermazane with Phenyl Isothiocyanate.

Phenyl isothiocyanate (0.49g, 3.61 mmol) was added to heptamethyldigermazane (0.92g, 3.50 mmol) at room temperature. Instantaneous reaction occurred and the 1:1 adduct LIII was obtained in 60% yield by the following vacuum distillation. b.p. 92-94°/5×10^{-5} mmHg, (Found, C 42.22, H 6.49. $C_{14}H_{26}N_2SGe_2$ Calcd., C 42.08, H 6.56%), $\nu_{C=N}$ 1560 cm^{-1} (vs) and $\nu_{C=S}$ 1330 cm^{-1}(vw), $\tau_{Ge-C\underline{H}_3}$ 9.76 with $J(^{13}C\text{-}H)$ 126 Hz, and 9.53 with $J(^{13}C\text{-}H)$ 127 Hz, $\tau_{N-C\underline{H}_3}$ 7.04.

Pyrolysis of adduct LIII. Heating the adduct LIII (3 mmol) under an atmosphere of argon at 150° for 150 hr., led to the formation of bis(trimethylgermyl)sulphide (75% yield) and the polymer of methylphenylcarbodiimide (80% yield). Both products were identified by the comparison of their n.m.r. and i.r. spectra with those of authentic samples.

(c) Reaction of Hexamethyldigermoxane with Phenyl Isocyanate.

A mixture of phenyl isocyanate (0.39g, 3.28 mmol) and hexamethyldigermoxane (0.91g, 3.63 mmol) was allowed to stand for 1.5 hr. at room temperature. The whole reaction mixture became solidified and evaporation of the low boiling materials *in vacuo* led to the crude 1:1 adduct LIV in 97% yield. Recrystallization from n-hexane gave pure LIV in 73% yield. m.p. 61-62° (Found, C 41.94, H 6.38, $C_{13}H_{23}NO_2Ge_2$ Calcd., C 42.14, H 6.26%), $\nu_{C=O}$ 1637 and 1662 cm^{-1} (in CCl_4), $\tau_{Ge-C\underline{H}_3}$ 9.65 with $J(^{13}C-H)$ 126 Hz, and 9.49 with $J(^{13}C-H)$ 124 Hz (in CCl_4).

(d) Reaction of Hexamethyldigermoxane with Phenyl Isothiocyanate.

Phenyl isothiocyanate (0.50g, 3.73 mmol) and hexamethyldigermoxane (1.0g, 3.97 mmol) were placed in a sealed tube under an atmosphere of argon. The mixture was kept at 150° for 200 hr., when distillation gave bis(trimethylgermyl)sulphide (33%) and phenyl isocyanate (40%), both were characterized by comparison of their spectra with those of authentic samples.

(e) Reaction of Hexamethyldigermoxane with Chloral.

Chloral(0.65g, 4.39 mmol) was gradually added to hexamethyldigermoxane (0.84g, 3.35 mmol) at room temperature. The addition reaction was completed in a few minutes and the 1:1 adduct LVI was isolated by distillation in 63% yield. b.p. 72°/0.2 mmHg, (Found , C 24.12, H 4.88, $C_8H_{19}Cl_3Ge_2O_2$ Calcd., C 24.10, H 4.88%), $\tau_{Ge-C\underline{H}_3}$ 9.50 with $J(^{13}C-H)$ 127 Hz, $\tau_{-C\underline{H}-}$ 4.93 (in CCl_4)

(f) Reaction of Bis(trimethylgermyl)sulphide with Phenyl Isocyanate.

A mixture of phenyl isocyanate (10 mmol) and bis(trimethylgermyl)-sulphide (10 mmol) was heated at 150° for 48 hr. in a sealed tube filled with argon. Distillation of the reaction mixture gave the initial starting materials. Recrystallization of the residue of the distillation process from an acetone/petroleum ether mixture (2/1 v/v) gave triphenyl isocyanurate in 3% yield. m.p. 290-292°.

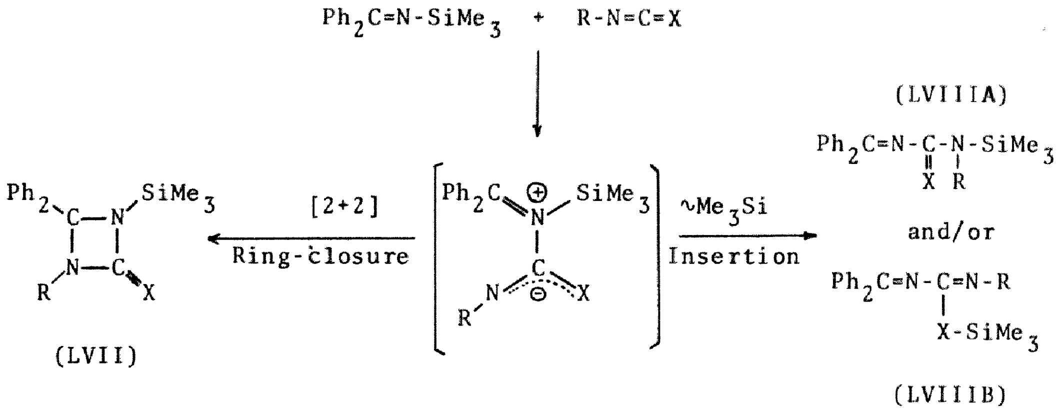
CHAPTER 5.

Insertion Reactions and Subsequent [4+2] Cycloadditions of N-(Trimethylsilyl)benzophenoneimine with Iso(thio)cyanates.

5.1. Introduction.

N-(Trimethylsilyl)benzophenoneimine 94); $Ph_2C{=}N\text{-}SiMe_3$, has two possible pathways for the addition reactions with unsaturated bonds. (1) An insertion reaction into the Si-N bond as usual organosilylamides 39∿42), (2) [2+2] cycloaddition across C=N bond of this imine to give a four-membered ring 95∿97). These two possibilities by the reaction with isocyanates are summarized by the following scheme.

SCHEME 5.1.



In this chapter, it became clear that the insertion reaction prevailes against the [2+2] cycloaddition. Furthermore, a new [4+2] cycloaddition of 1:1 adducts is also described.

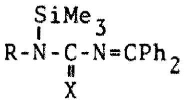
5.2. Results and Discussions

5.2.1. Insertion Reactions of N-(Trimethylsilyl)benzophenoneimine with Iso(thio)cyanates

Treatment of N-(trimethylsilyl)benzophenoneimine with equimolar isocyanates or isothiocyanates gave 1:1 adducts LVIIIb, LVIIId, and LVIIIe. These adducts were identified by means of analyses, as well as infrared, n.m.r., and mass spectroscopies. Isolation of the adduct with methyl isocyanate LVIIIa was unsuccessful, since it was readily induced to the subsequent reactions and the product became a mixture of 1:1 and 1:2 adducts. Several properties of 1:1 adducts LVIII and their desilylated derivatives LIX by hydrolysis were summarized in Table 5.1.

Infrared spectra of LVIII showed the strong absorptions around 1650 cm^{-1} which values were reasonable for linear ureas. Mass spectra of LVIIIb and LVIIIe as well as desilylated products LIXa$\sim$LIXf suggested the presence of the fragment ion; $Ph_2C=\overset{\oplus}{N}=C=X$ and $Ph_2C=\overset{\oplus}{N}$. These ions also supported the linear structure depicted in scheme 5.1. The latter ion is induced by an elimination of $:C\equiv X$ from the former, because the relative intensities of $Ph_2C=\overset{\oplus}{N}$ increased at higher ionization potentials. The presence of $\pi\rightarrow\pi^*$ transitions around 250 nm. ($\log \varepsilon = 4$), which were ascribed to a conjugated $X=\overset{|}{C}-N=CPh_2$ linkage, supported the linear structure. All these spectroscopic evidences excluded the possibility of a [2+2] cycloaddition to give four-membered ring LVII. Consequently, the 1:1 adducts have linear structures LVIII and the insertion reactions of iso(thio)cyanates across Si-N bond of $Ph_2C=N-SiMe_3$ were predominant path. Thus, the migration of Me_3Si moiety from immonium nitrogen to either amino- or oxy-anions took place far more rapidly than the nucleophilic attack of the amide anion to the carbonium ion did.

Table 5.1. 1:1 Adducts

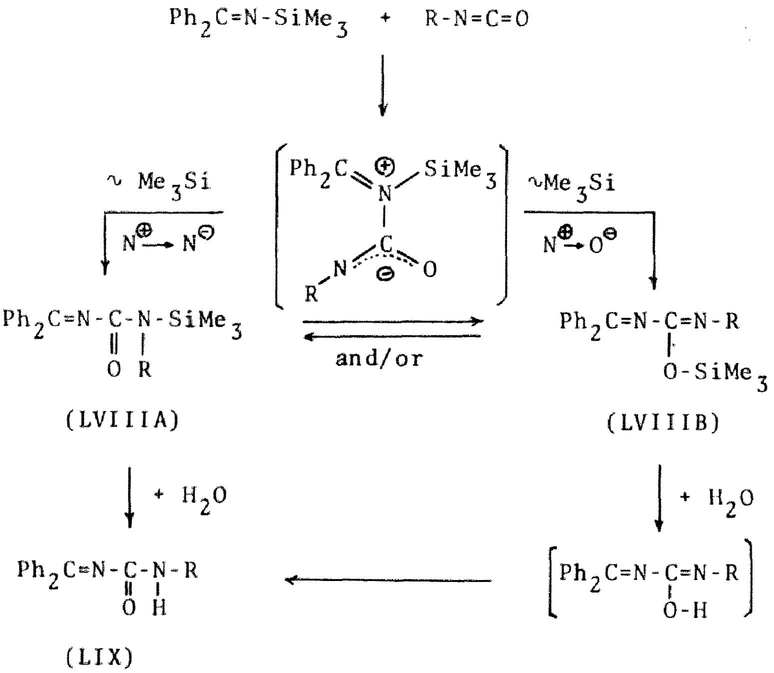


$R-N-\underset{\overset{\|}{X}}{\overset{\overset{SiMe_3}{|}}{C}}-N=CPh_2$ (LVIII)

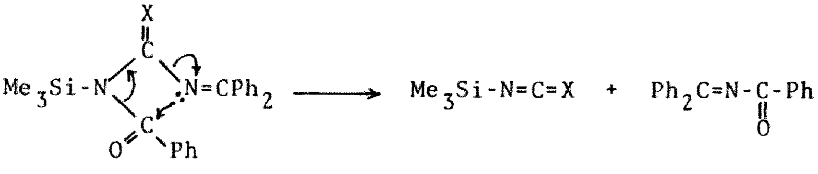
	R	X	1:1 Adducts (LVIII)			Desilylated products (LIX)		
			M.p. (°C)	$\nu_{max.}$ (cm^{-1})*	$\tau_{Si-C\underline{H}_3}$*	M.p. (°C)	$\nu_{max.}$ (cm^{-1})***	$\lambda_{max.}^{EtOH}$ (nm.)
a	Me	O	oily liquid	1648, 1627	9.86	187.5-189.5	1645	252
b	Ph	O	118.0-119.0	1647	9.87**	159.0-160.5	1650, 1543	250
c	$Ph-\underset{\overset{\|}{O}}{C}$	O	oily liquid	1672, 1631. 1581	9.80	151.0-153.0	1711, 1659, 1631	243
d	Me	S	oily liquid	1623, 1334	9.67	170.0-171.0	1612, 1362	248
e	Ph	S	125.5-127.0	1631.1317	9.72**	132.0-133.0	1643, 1362	258
f	$Ph-\underset{\overset{\|}{O}}{C}$	S	oily liquid	1643, 1626, 1325	9.74	137.0-138.0	1705, 1255	260, 243

* In CCl_4 solution, ** In $CDCl_3$ solution, *** KBr disk.

SCHEME 5.2.



The 1:1 adducts by benzoyl isocyanate LVIIIc or isothiocyanate LVIIIf decomposed to N-benzoylbenzophenoneimine and trimethylsilyl isocyanate, during distillation. This decomposition could be explained by the following mechanism.



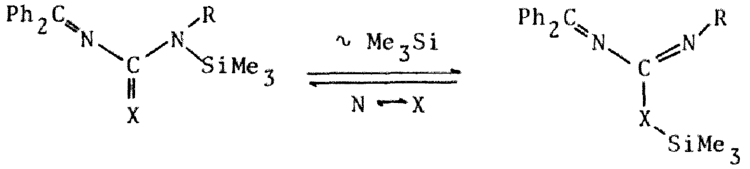
(5.1)

LVIIIc X=O

LVIIIf X=S

5.2.2 Spectroscopic Evidences on the 1,3-Transfer of Trimethylsilyl Group.

Although the structure of 1:1 adducts LVIII were decided as linear form, there are still two possibilities, silylamide form LVIIIA or silylimidate form LVIIIB. These two possible structures, LVIIIA and LVIIIB can be interconvertible each other by the 1,3-transfer of the trimethylsilyl group. Such reversible isomerizations were established for heterocumulene adducts with organosilylamines 62), phosphines 98), or sulphides 56). Variable temperature n.m.r. technique seems to be the most convenient to study these dynamic phenomena. The insertion products LVIIIc, LVIIId, and LVIIIe showed two separated trimethylsilyl proton signals at low temperature as shown in Fig. 5.1. All results on the variable temperature n.m.r. experiments were summarized in the Table 5.2. The intensities of two separated signals were variable with temperature. This non-equivalency of two separated signals is ascribed to the 1,3-transfer of trimethylsilyl group. The non-equivalency due to fixed-rotation around carbon-nitrogen bonds were excluded. If the above separation involves fixed-rotation, both of the separated signals should have equal intensities. Adducts LVIIId and LVIIIe are the first examples of the complete splitting of trimethylsilyl proton signals in silylthioamide⇄silthianylimidate equilibria.



(LVIIIA) (LVIIIB) (5.2)

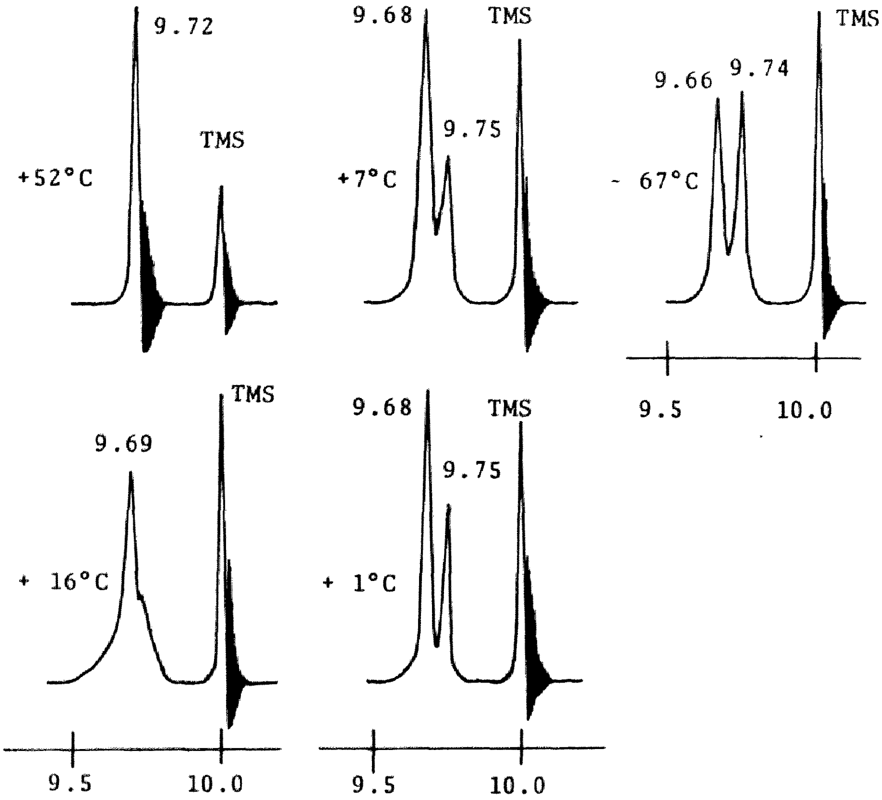


Fig. 5.1. N.m.r. spectra of LVIIIe at various temperature in (CDCl$_3$)

Table 5.2. Variable temperature n.m.r. study of adducts LVIII.

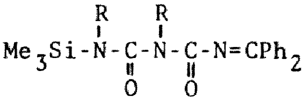
Compounds	Coalescence temp. (°C)	Chem. shifts $(C\underline{H}_3)_3$-Si τ (ppm)		Relative intensity ratio $\frac{[LVIIIA]}{[LVIIIB]}$	
		low temp.	high temp.	0°C	-50°C
LVIIIc	24	9.79, 9.86(-66°)*	9.79(30°)*	4.8/1	3.4/1
LVIIId	30	9.61, 9.68(-67°)*	9.67(79°)*	2/1	2/1
LVIIIe	17	9.66, 9.74(-67°)**	9.72(52°)**	1/1.6	1/1

* In trichloroethylene, ** In CDCl$_3$ solution.

Additional evidence of trimethylsilyl group transfer in 1:1 adducts was obtained by mass spectroscopy. The mass spectrum of LVIIIe showed two independent series of fragmentation patterns from isomeric parent ions, (1) $M^{+}-NPh(SiMe_3)$ ($Ph_2C=\overset{\oplus}{N}=C=S$; relative intensity 31%) (2) $M^{+}-S\text{-}SiMe_3$ ($PhN=C=\overset{\oplus}{N}=CPh_2$; relative intensity 51%). Appearance of these ions was considered to be the primary steps in fragmentations.

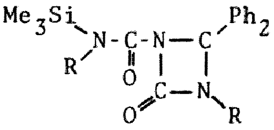
5.2.3. Cyclization Reactions under Excess Isocyanates.

When N-(trimethylsilyl)benzophenoneimine was treated with twice molar amounts of isocyanates, white crystalline products were obtained. Analytical, infrared, n.m.r., and mass spectroscopic results suggested that the products were 1:2 adducts. Same products were also obtained quantitatively when the 1:1 adduct LVIIIb was treated with second molar isocyanate. Therefore, the 1:2 adducts were given definitely by the further addition of the isocyanate with 1:1 adducts. The following four structures arose as possibilities, (1) the stepwise insertion of isocyanates into Si-N bond of LVIII to give linear 1:2 adducts LX, (2) [2+2] cycloaddition between C=N bond of LVIII with isocyanate to give LXI, (3) [4+2] cycloaddition by LVIIIA to give LXII, and (4) [4+2] cycloaddition by LVIIIB to give LXIII.

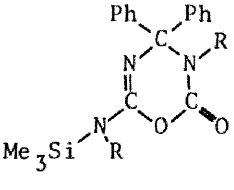


$$Me_3Si-\overset{R}{\underset{}{N}}-\underset{\underset{\displaystyle O}{\|}}{C}-\overset{R}{\underset{}{N}}-\underset{\underset{\displaystyle O}{\|}}{C}-N=CPh_2$$

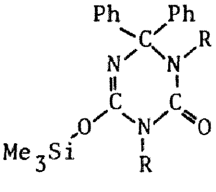
(LX)



(LXI)



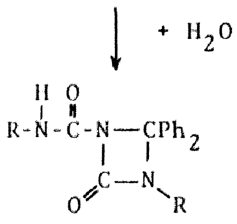
(LXII)



(LXIII)

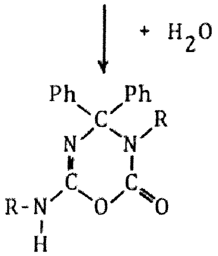
The structure LX was excluded since the conjugated $\pi \rightarrow \pi^*$ transitions of $O=\overset{|}{C}-N=CPh_2$ linkage disappeared completely. Another spectroscopic data were not complete to decide which of the remaining three structures was correct. Acidic hydrolysis of the desilylated 1:2 adduct (R=Ph) gave conclusive evidence. Hydrolysis of the desilylated 1:2 adducts with phenyl isocyanate in the presence of hydrochloric acid N,N'-diphenylurea (70%), benzophenone (35%) and ammonium chloride (41%).

LXI



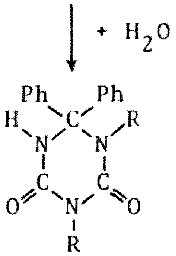
(LXIV)

LXII



(LXV)

LXIII

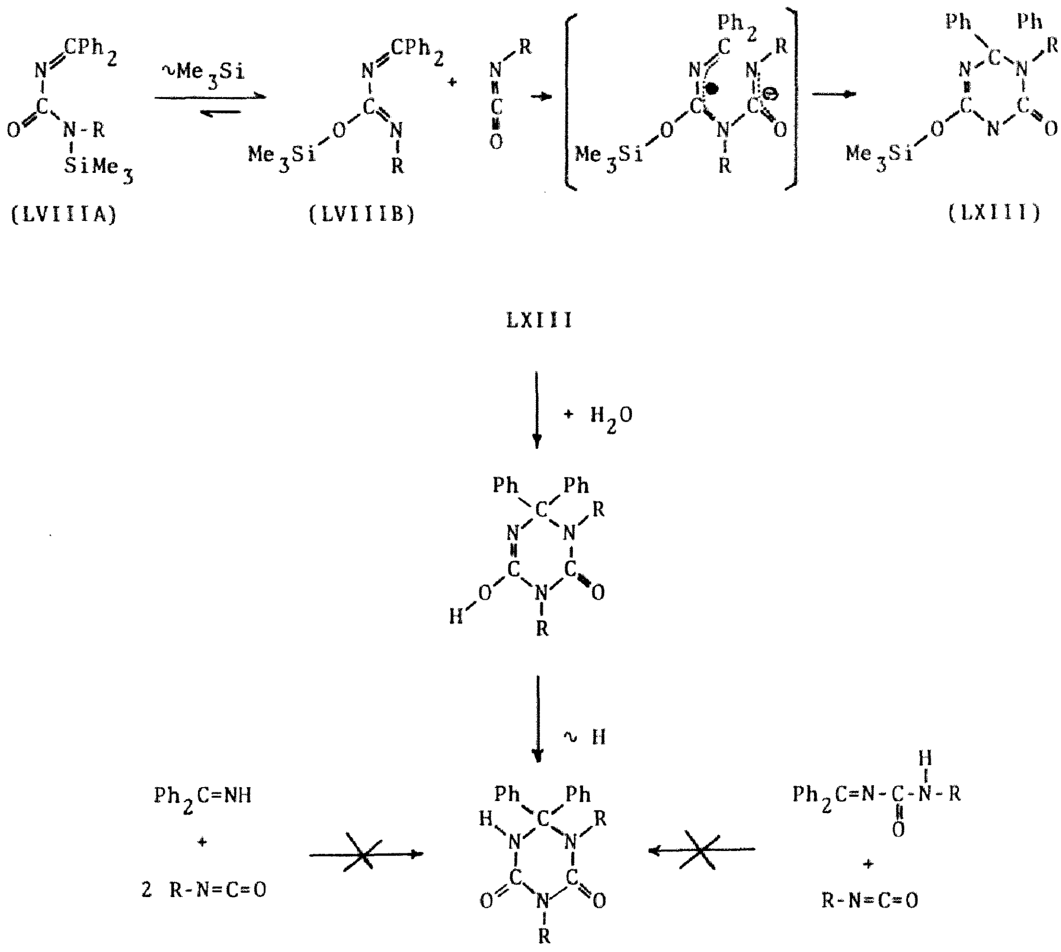


(LXVI)

The formation of N,N'-diphenylurea can only be explained by LXVI (R=Ph). Both LXIV and LXV should give N-phenylurea by this degradation reaction. This conclusion is consistent with the fact that LXVI did not react with hydroxide ion, aniline, acetic anhydride, or picric acid. Infrared spectrum of LXVI (R=Ph) is well explained by the proposed structure, because the carbonyl stretching frequencies at 1730 and 1660 cm^{-1} were similar to those of reported 1,3,5-triazinones 96) (1720 and 1680 cm^{-1}). Consequently, the structure of 1:2 adducts was concluded as LXIII. Formation of LXIII is explained by a [4+2] cycloaddition between O-silylimidate form (LVIIIB) of 1:1 adducts and the second isocyanate. This conclusion is also compatible with the above spectroscopic evidences of the existence of O-silylimidate LVIIIB.

It is important that LXVI could not be prepared either by the direct reaction of benzophenoneimine with twice molar isocyanates, or by the interaction of desilylated products LIX with isocyanates. An introduction of trimethylsilyl group would increase the proportion of the reactive iminoether form LVIIIB because of the strong Si-O bond. Thus, [4+2] cycloaddition to give LXIII [99] occurred readily. Modifications of keto⇌enol [100∿103] or amide⇌imidate [103] tautomerism by the introduction of trimethylsilyl groups are useful methods for organic synthesis. These new [4+2] cycloadditions may be included in such synthetic utilities.

SCHEME 5.3.



(LVIIIA) (LVIIIB) (LXIII)

LXIII

(LXVI) (R=Me and Ph)

Experimental Section

N-(Trimethylsilyl)benzophenoneimine was prepared by modified Rochow's method 94), *i.e.*, the interaction of N-(bromomagnesium)benzophenoneimine with trimethylchlorosilane.

5.A. 1:1 Insertion Reactions.

All reactions were carried out in accord with the method in the case of phenyl isocyanate. The reaction are summarized in Table 5.2.

Phenyl isocyanate 0.92g (7.70 mmol) was added to the benzene solution of N-(trimethylsilyl)benzophenoneimine 2.00g (7.90 mmol) and then slightly exothermic reaction occurred. About half an hour later, the removal of the solvent gave white powder of LVIIIb in nearly quantitative yield. The reprecipitation of the product from the mixture of benzene and n-hexane (1/1) gave white needles which are very hygroscopic. m.p. 118-119°.

Hydrolysis of LVIIIb gave white needles of LIXb which was recrystallized from the mixture of chloroform and n-hexane (1/1). m.p. 159-160.5°.

Table 5.2. Reaction conditions of 1:1 insertion.

	$Me_3SiN=CPh_2$ (mmol)	R-N=C=X (mmol)	Solvent	Reaction time (hr)	Temperature (°C)	1:1 Adduct Yield (%)
a	7.85	Me-N=C=O (8.60)	None	12	20	****
b	7.90	Ph-N=C=O (7.70)	C_6H_6	0.5	5	98
c	6.62	$\mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}N{=}C{=}O}$(7.15)	CCl_4	0.1	5	97
d	8.02	Me-N=C=S (11.5)	None	24	90	100
e	4.07	Ph-N=C=S (8.80)	C_6H_6	12	90	98
f	4.66	$\mathrm{Ph{-}\underset{\overset{\|}{O}}{C}{-}N{=}C{=}S}$(5.37)	None	0.1	5	100

**** The mixture of 1:1 and 1:2 adducts.

5.B. Ring Formation Reactions.

(a) 2-Trimethylsiloxy-4-oxo-3,5-dimethyl-6,6-diphenyl-tetrahydro-1,3,5-triazine (LXIIIa).

The mixture of N-(trimethylsilyl)benzophenoneimine 1,55g (6.12 mmol) and methyl isocyanate 0.75g(13.35 mmol) was kept for 1 day at room temperature and then it was solidified. After removal of excess methyl isocyanate (crude yield; quantitatively), the reprecipitation from the mixture of benzene and n-hexane (1/1) gave colourless prisms of LXIIIa in the yield of 90%. m.p. 153.5-155.0°, $\tau_{Si-\underline{CH}_3}$ 9.73, $\tau_{N-\underline{CH}_3}$ 7.33 and 6.91 (in $CDCl_3$), $\nu_{max.}$ 1693 and 1668 cm^{-1} (in CCl_4).

Hydrolysis of LXIIIa in the air moisture gave white solid which was recrystallized from ethanol to afford colourless prisms of 2,4-dioxo-3,5-dimethyl-6,6-diphenyl-hexahydro-1,3,5-triazine (LXIVa) in the yield of 92%. m.p. 238.0-239.0°, $\tau_{N-\underline{CH}_3}$ 7.28 and 7.03 (in $CDCl_3$), $\nu_{max.}$ 1723 and 1648 cm^{-1} (KBr disk).

(b) 2-Trimethylsiloxy-4-oxo-3,5,6,6-tetraphenyl-tertahydro-1,3,5-triazine (LXIIIb).

(b-i) Phenyl isocyanate 1.75g (14.6 mmol) was added dropwisely to N-(trimethylsilyl)benzophenoneimine 1.56g (6.15 mmol) in benzene 2ml with slightly exothermic reaction. After addition, n-hexane was added to the mixture and kept for 30 min. at room temperature. White needles were precipitated and the mixture was dried after removal of the supernatant. It was crude LXIIIb which gave white needles by the reprecipitation from the mixture of benzene and n-hexane (1/1) in the yield of about 80%. m.p. 142.0-145.0°, $\tau_{Si-\underline{CH}_3}$ 9.88 (in $CDCl_3$), $\nu_{max.}$ 1702 and 1664 cm^{-1}.

(b-ii) Phenyl isocyanate 0.76g (6.35 mmol) was added to the benzene solution 5ml of 1:1 adduct LVIIIb 2.43g (6.55 mmol). After keeping the mixture for 6 hr at room temperature, the infrared absorption of $\nu_{N=C=O}$ disappeared. Solvent was removed from the mixture and the white solid LXIIIb 3.02g (6.15 mmol) was isolated in the yield of 97%. The reprecipitation of crude LXIIIb from the mixture of benzene and n-hexane (1/1) gave white needles 2.35g (4.78 mmol), 75% of theoretical yield.

Hydrolysis of LXIIIb in the air moisture gave solid which was recrystallized from the mixture of ethanol and benzene to give white needles of 2,4-dioxo-3,5,6,6-tetraphenyl-hexahydro-1,3,5-triazine (LXVIb) in the yield of 90%. m.p. 215.0-216.0°, $\nu_{max.}$ 1730 and 1657 cm^{-1} (KBr disk).

Hydrolysis of LXVIb by Hydrochloric Acid.

Compound LXVIb 0.63g (1.51 mmol) was dissolved in ethanol 30 ml and conc. hydrochloric acid 21 ml was added to the solution. The solution was refluxed for 4 days. The mixture was extracted several times by chloroform. The removal of solvent from chloroform layer gave residue which was separated to benzophenone 0.10g (35%) and N,N'-diphenylurea 0.23g (70%) by the difference of solubility in diethyl ether. Ammonium chloride 0.03g (41%) was obtained by the drying of the water layer.

Table 5.3. Elementary analyses and molecular weights.

Compounds	Formula	Molecular weight		Found (%)			Calcd. (%)		
		Found*	Calcd.	C	H	N	C	H	N
LVIIIb	$C_{23}H_{24}N_2OSi$	372	372	74.02	6.37	--	74.15	6.49	7.52
LVIIId	$C_{18}H_{22}N_2SSi$	---	342	62.85	6.39	--	63.12	6.48	8.18
LVIIIe	$C_{23}H_{24}N_2SSi$	388	388	70.94	6.24	--	71.09	6.22	7.21
LIXa	$C_{15}H_{14}N_2O$	238	238	75.60	5.96	11.82	75.61	5.92	11.75
LIXb	$C_{20}H_{16}N_2O$	300	300	79.91	5.47	9.32	79.98	5.37	9.33
LIXc	$C_{21}H_{16}N_2O_2$	328	328	76.80	5.00	8.45	76.81	4.91	8.53
LIXd	$C_{15}H_{14}N_2S$	254	254	71.00	5.57	10.86	70.84	5.55	11.01
LIXe	$C_{20}H_{16}N_2S$	316	316	75.89	5.22	8.96	75.92	5.10	8.85
LIXf	$C_{21}H_{16}N_2OS$	344	344	73.47	4.88	8.01	73.23	4.68	8.13
LXIIIa	$C_{20}H_{25}N_3O_2Si$	367	367	65.48	6.99	--	65.36	6.86	11.43
LXIIIb	$C_{30}H_{29}N_3O_2Si$	491	491	73.23	6.15	--	73.29	5.95	8.55
LXVIa	$C_{17}H_{17}N_3O_2$	295	295	69.11	5.84	14.37	69.13	5.80	14.23
LXVIb	$C_{27}H_{21}N_3O_2$	412	412	73.21	4.60	8.80	73.25	4.45	8.84

* Mass spectral data.

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List of Publications

1. Benzoyl Isocyanate and Isothiocyanate as Acceptors for N-(Trimethylsilyl)dialkylamines.
   I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc. (C)*, 701 (1969).

2. Reactions of Benzoyl Heterocumulenes with Trimethylstannylalkylamines.
   K. Itoh, I. Matsuda, and Y. Ishii, *Tetrahedron Letters*, 2675 (1969).

3. Addition Reactions of Heptamethyldisilazane with Benzoyl Iso(thio)cyanate and Subsequent Eliminations.
   I. Matsuda, K. Itoh, and Y. Ishii, *J. Organometal. Chem.*, 19, 339 (1969).

4. The Addition Reaction of Thiobenzoyl Isocyanate with Group IV (Organometallyl)amines.
   K. Itoh, I. Matsuda, T. Katsuura, and Y. Ishii, *J. Organometal. Chem.*, 19, 351 (1969).

5. An Extensive Study on Preparation of Some Oxadiazinones by the Reaction of N-Trimethylmetal(IV)dialkylamines with Benzoyl Isocyanate.
   I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc. (C)*, 1870 (1971).

6. Some Addition Reactions of Asymmetric Heptamethyldimetallazanes, $Me_3M\text{-}NMe\text{-}M'Me_3$, with Heterocumulenes.
   K. Itoh, T. Katsuura, I. Matsuda, and Y. Ishii, *J. Organometal. Chem.*, in the press.

7. Addition and Subsequent Elimination Reactions of Bis(trimethylgermyl)methylamide, -oxide, and -sulphide.
   K. Itoh, I. Matsuda, T. Katsuura, S. Kato, and Y. Ishii, *J. Organometal. Chem.*, in the press.

8. Insertion Reactions and Subsequent [4+2] Cycloadditions of N-(Trimethylsilyl)benzophenoneimine with Iso(thio)cyanates.
   I. Matsuda, K. Itoh, and Y. Ishii, submitted to *J. Chem. Soc. (C)*.