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Reactions of Group IV Organometallic Compounds. XXX.[1] Stepwise Addition of Isocyanates and Isothiocyanates with *N*-Trimethylstannyl(diphenylmethylene)amine

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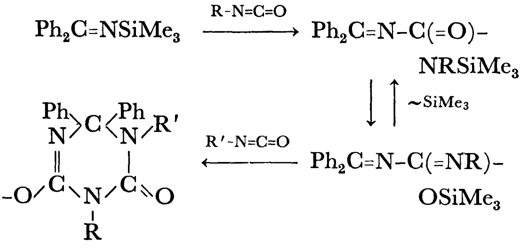
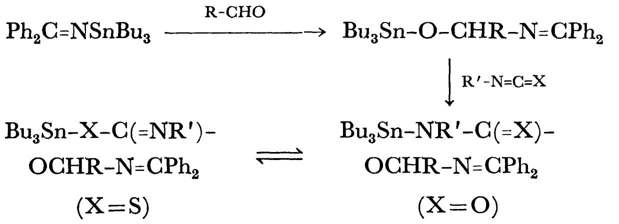
Stepwise addition of two isocyanates to *N*-trimethylstannyl(diphenylmethylene)amine, $Ph_2C=NSnMe_3$, gives 3,4-dihydro-1,3-dialkyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1*H*)-one (II) by a polar [4+2] cycloaddition of the 1/1 adduct and the second isocyanate. The isothiocyanate adducts of $Ph_2C=NSnMe_3$ react with either isocyanates or isothiocyanates to yield the corresponding consecutive insertion products (IV).

In a previous paper[2] on the insertion reaction of *N*-trimethylsilyl(diphenylmethylene)amine with isocyanates or isothiocyanates, it was reported that the amine with isocyanates in a 1/2 ratio yielded 3,4-dihydro-1,3-dialkyl-4,4-diphenyl-6-trimethylsiloxy-1,3,5-triazin-2(1*H*)-one by a polar [4+2] cycloaddition.



R=R'=Me and Ph

Several reactions of *N*-organostannyl(alkylidene)amines have been reported. Harrison[3] found many insertion reactions of $Ph_2C=NSnBu_3$ with unsaturated bonds including isocyanates and isothiocyanates. We were interested in the fact that the Sn–O bond of aldehyde adducts added to isocyanates or isothiocyanates results in consecutive insertion products.

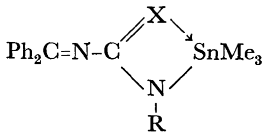


Lappert *et al.*[4] investigated various hydrogen abstraction, and insertion reactions of $R_2C=NSnMe_3$. They pointed out two aspects of the insertion reactions; (1) the N–H bond of trace $Ph_2C=NH$ showed a catalytic action, (2) the nucleophilic attack of the nitrogen atom was the primary step, resulting in a polar intermediate. This paper deals with the stepwise reactions of *N*-trimethylstannyl(diphenylmethylene)amine; $Ph_2C=N-SnMe_3$, with $R-N=C=X$ (X=O and S), in order to determine whether the stepwise reaction is a polar [4+2] cycloaddition[2] or a consecutive insertion reaction.[3]

Results and Discussion

Structure of 1/1 Insertion Products. Equimolar reaction of $Ph_2C=NSnMe_3$ with $R-N=C=X$ gave the corresponding insertion products, $Ph_2C=N-C(=X)-NR-SnMe_3$ (Ia—Ie) in line with results reported.[3,4] Spectroscopic data for 1/1 insertion products are shown in Table 1.

The appearance of satellites of the methylamino proton signals in the case of Ia and Ib (R=Me) suggests that the trimethyltin group is attached to the nitrogen atom. However, the values of $J_{Sn-N-CH}$ (Ia, 24 Hz; Ib, 12 Hz) are much lower than those of $Me_3Sn-NMe_2$ ($J^{117}=39.2$ Hz and $J^{119}=41.0$ Hz).[5] The depression of the coupling constant is consistent with the weakening of the Sn–N bond by the coordination of the lone pair to tin atom.



I: R=Me and Ph, X=O and S

This is strongly supported by the low frequency of the carbonyl stretching bands of the isocyanate adducts (Ia and Ic). It is reasonable to conclude that the coordination of the sulfur atom of Ib ($J_{Sn-N-CH_3}=$ 12 Hz) is stronger than that of oxygen atom of Ia

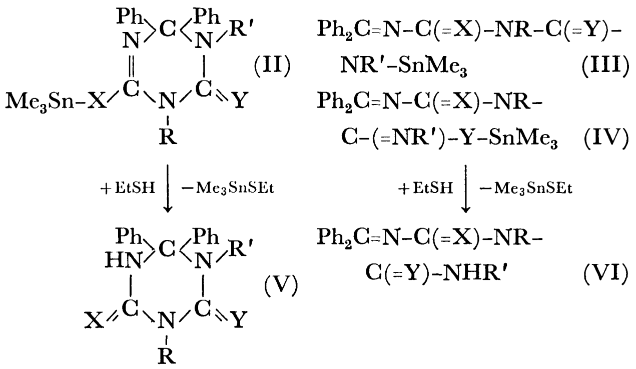
TABLE 1. 1/1 ADDUCTS: $Ph_2C=N-C(=X)-NR-SnMe_3$

Compound	R	X	Yield %	IR (cm^{-1})		NMR	
				$\nu_{C=N}$	$\nu_{C=O}$	τ_{CH_3-Sn} ($J^{117/119}$; Hz)	τ_{CH_3-N} ($J_{Sn-N-C-H}$)
Ia	Me	O	80	1627	1600	9.79 (55.5/57.0)$^{a)}$	7.47 (24.0)$^{d)}$
Ib	Me	S	80	1622		9.68 (54.8/56.5)$^{b)}$	7.38 (12.0)$^{d)}$
Ic$^{c)}$	Ph	O	97	1621	1589	9.73 (55.0/58.0)$^{a)}$	
Id	Ph	S	99	1616		9.60 (56.1/58.5)$^{b)}$	
Ie	PhCO	O	95	1626	1673$^{e)}$ 1603	9.68 (55.5/58.0)$^{b)}$	

a) Benzene solution. b) Carbon tetrachloride solution. c) Prepared by Lappert *et al.*[4] d) The splitting of J^{119}Sn and J^{117}Sn was not clear. e) Absorption due to benzoyl group.

($J_{\text{Sn-N-CH}_3}=24$ Hz). Diphenylmethylenealkyl-ureas or thioureas, $Ph_2C{=}N{-}C({=}X){-}NHR$, were obtained by the destannylation of Ia—Ie with ethanethiol. Their UV spectra showed $\pi\to\pi^*$ transition bands around 248—258 nm characteristic of the heterodiene linkage $(\rangle C{=}N{-}\overset{|}{C}{=}N)$.

Consecutive Reactions of 1/1 Adducts. The subsequent addition of the second heterocumulene to the 1/1 adducts can occur in two ways: a polar [4+2] cycloaddition yielding 3,4-dihydro-1,3-dialkyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1*H*)-one(II). The destannylation of II giving hexahydro-1,3-dialkyl-4,4-diphenyl-1,3,5-triazin-2,4-dione (V); a consecutive insertion of the second heterocumulene into the Sn–N bond of the 1/1 adduct giving either of the two possible linear insertion products, III or IV. Both linear adducts III and IV afford the same *N,N'*-dialkylmethylenebiuret (VI) by destannylation.



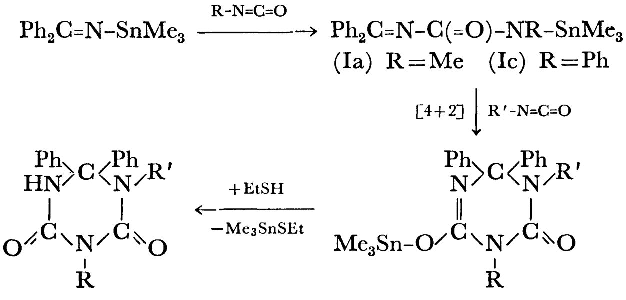
$Ph_2C{=}N{-}C({=}X){-}NR{-}C({=}Y){-}NR'{-}SnMe_3$ (III)

$Ph_2C{=}N{-}C({=}X){-}NR{-}C{-}({=}NR'){-}Y{-}SnMe_3$ (IV)

$Ph_2C{=}N{-}C({=}X){-}NR{-}C({=}Y){-}NHR'$ (VI)

Both the two pathways are actually operating, and the primary heterocumulene component of 1/1 insertion reactions plays the most important role in controlling the subsequent reactions.

(a) Annelation Reactions of Isocyanate 1/1 Adducts: When the isocyanate 1/1 adduct (Ia or Ib) was treated with methyl or phenyl isocyanate, crystalline products were isolated in good yields. They were concluded to be 1/2 adducts by analyses, NMR and IR spectra. The destannylation of isolated 1/2 adducts proceeded quantitatively by means of ethanethiol. None of the destannylation products showed a $\pi\to\pi^*$ transition due to a heterodiene linkage, $\rangle C{=}N{-}\overset{|}{C}{=}O$. This supports the cyclic structure (V: X=Y=O) and is not consistent with the linear structure (VI: X=Y=O). Much stronger evidence of the cyclic structure (V) was obtained from the mass spectra of the destannylation products. Two destannylation products (runs a and c) showed peaks due to $[Ph_2C{=}N{-}CH_3]^+$ ($m/e=195$) and $[Ph_2C{=}N{=}CH_2]^+$ ($m/e=194$). The appearance of these peaks suggests the direct bonding of diphenylmethylene with the alkylamino group (R'–N) introduced by the second isocyanate, and are explained by the cyclic structure (V). The destannylation product of run b (order of addition: methyl then phenyl isocyanate) showed M^+–MeNCO peak ($m/e=300$). The presence of M^+–MeNCO is fully consistent with structure (V), because fragmentation of the linear structure (VI) should occur from the terminal position (only M^+—PhNCO would appear; direct elimination of the central component M^+—MeNCO, not being detectable). The IR spectrum of run d is also consistent with the cyclic structure (V: R=R'=Ph, X=Y=O); the carbonyl stretching frequencies at 1730 and 1657 cm^{-1} were similar to those of 1,3,5-triazindiones (1720 and 1680 cm^{-1}).[6] Mixed mp analyses, IR, and NMR spectra were the same as those of authentic hexahydro-1,3-dialkyl-6,6-diphenyl-1,3,5-triazin-2,4-dione (V).[2] Thus, the consecutive insertion process, giving III or IV then VI, is excluded, and the annelation products of isocyanate 1/1 adducts with the second isocyanate are concluded to be 3,4-dihydro-1,3-dialkyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1*H*)-one (IIa—IIe) by a polar [4+2] cycloaddition.



$Ph_2C{=}N{-}SnMe_3 \xrightarrow{R{-}N{=}C{=}O} Ph_2C{=}N{-}C({=}O){-}NR{-}SnMe_3$ (Ia) R=Me (Ic) R=Ph

(Va) R=R'=Me	(IIa) R=R'=Me
(Vb) R=Me, R'=Ph	(IIb) R=Me, R'=Ph
(Vc) R=Ph, R'=Me	(IIc) R=Ph, R'=Me
(Vd) R=R'=Ph	(IId) R=R'=Ph

The treatment of IIa and IId with ethanethiol afforded the corresponding hexahydro-1,3-dialkyl-6,6-diphenyl-1,3,5-triazin-2,4-dione (Va—Vd) quantitatively. This method provides a synthetic route for the preparation of triazindiones with three different

Table 2. The [4+2] cycloaddition of isocyanate adducts; 3,4-dihydro-1,3-dialkyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1*H*)-one (II) and their demetallation products; hexahydro-1,3-dialkyl-6,6-diphenyl-1,3,5-triazin-2,4-dione (V)

Run	R	R'	II					V[a]		
			Yield (%)	Mp (°C)	ν_{max} (cm^{-1})	$\tau_{CH_3-Sn}(J^{117/119})$	τ_{CH_3-N}	Mp (°C)	$\nu_{C=O}$ (cm^{-1})	τ_{CH_3-N}
a	Me	Me	77	149.0—152.0	1688, 1621	9.89(56.0/58.0)	7.41 6.75	238.0—239.0[b]	1723, 1648[b]	7.29 7.03
b	Me	Ph	76	169.0—172.0	1686, 1624	9.83(54.5/57.0)	6.73	240.0—241.0	1720, 1674	6.93
c	Ph	Me	46	179.0—181.0	1692, 1630	9.90(55.5/57.5)	7.38	264.0—265.0	1729, 1663	7.22
d	Ph	Ph	96	166.0—167.0	1731, 1697	9.88(53.0/55.3)	—	215.0—216.0[b]	1730, 1657[b]	—

a) Formation of V by the destannylation of II was quantitative. b) Identical with values in Ref. 2.

substituents on the nitrogen atoms such as Vb and Vc. The yields and properties of these [4+2] cycloaddition products (IIa—IId) and their destannylation products (Va—Vd) are summarized in Table 2.

An atempt to react phenyl isothiocyanate with isocyanate 1/1 adducts (Ia and Ic) was unsuccessful, resulting in the recovery of starting materials. The less reactive phenyl isothiocyanate cannot add to 1/1 isocyanate adducts (Ia and Ic), since the nucleophilicity of the nitrogen atom in Ia or Ic is depressed by the electron-withdrawing group.

(b) Insertion Reactions of Isothiocyanate 1/1 Adducts: Further reactions of Ib or Id (isothiocyanate 1/1 adducts) with other isocyanates or isothiocyanates were found to proceed by a consecutive insertion reaction in a similar manner to those reported by Harrison.[3] The demetallation products of 1/2 adducts were concluded to be *N*-diphenylmethylene-*N'*,*N''*-dialkylthio- or dithiobiuret, which showed apparent $\pi\rightarrow\pi^*$ transitions due to the heterodiene linkage, $\rangle C{=}N{-}\overset{|}{C}{=}S$, around 269~292 nm ($\log \varepsilon \simeq 4$). The fragmentation pattern of the destannylation products from the reaction of Ib with methyl isocyanate is consistent with the linear structure (VI), $[Ph_2C{=}N{-}C{=}S]^+$ (*m*/*e*=224), $[Ph_2C{=}N]^+$ (*m*/*e*=180), $[Ph_2C{=}N{-}C({=}S){-}NMe]^+$ (*m*/*e*=253). Thus a further reaction of isothiocyanate adducts (Ib or Id) with either isocyanate or isothiocyanate should give the corresponding linear products(III or IV). No ^{117}Sn, or ^{119}Sn satellite band corresponding to the CH_3-N proton signal were observed in the NMR spectra of the products obtained in the case of runs e and f. Only linear structure (IV) is consistent with these spectroscopic properties.

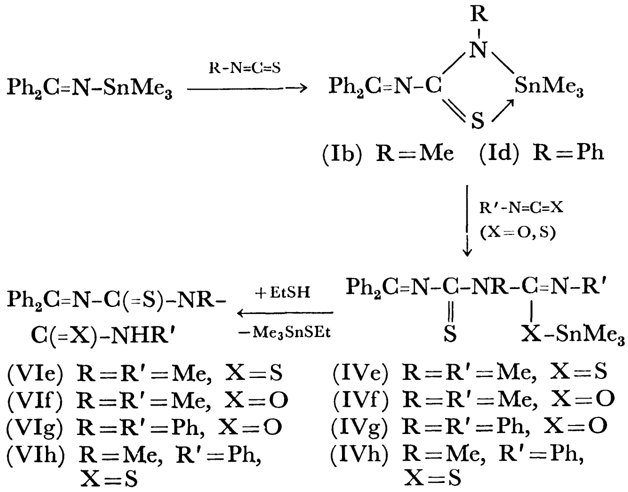


Table 3. Consecutive insertion of isocyanates and isothiocyanates to isothiocyanate 1/1 adducts

Run	R	R'	X	IV					VI[e]			
				Yield (%)	Mp (°C)	ν_{max}[a] (cm^{-1})	$\tau_{CH_3-Sn}(J^{117/119})$[a]	τ_{CH_3-N}[a]	Mp (°C)	$\nu_{C=O,\ C=N,\ C=S}$[b] (cm^{-1})	λ_{max}[c] (nm)	τ_{CH_3-N}[d]
e	Me	Me	S	84	158.0—160.0	1597, 1371	9.72(57.0/59.0)	6.93 6.31	242.0—244.0	1531, 1290	278	6.79 6.36
f	Me	Me	O	67	163.0—166.0	1683, 1603	9.76(55.0/57.0)	7.39 6.66	241.0—242.0	1692, 1533, 1296	269	7.20 6.65
g	Ph	Ph	O	100	165.0—166.0	1698, 1355	9.72(55.5/58.5)	—	252.0—254.0	1703, 1513, 1240	279	—
h	Me	Ph	S	80[f]	not isolated				213.0—215.0	1521, 1287	292	6.36
i	Ph	Me	S		no reaction							

a) Benzene solution. b) KBr disk. c) Ethanol solution. d) Deuterochloroform solution. e) The formation of VI was quantitative. f) Yield of VIh was 80% based on Ib.

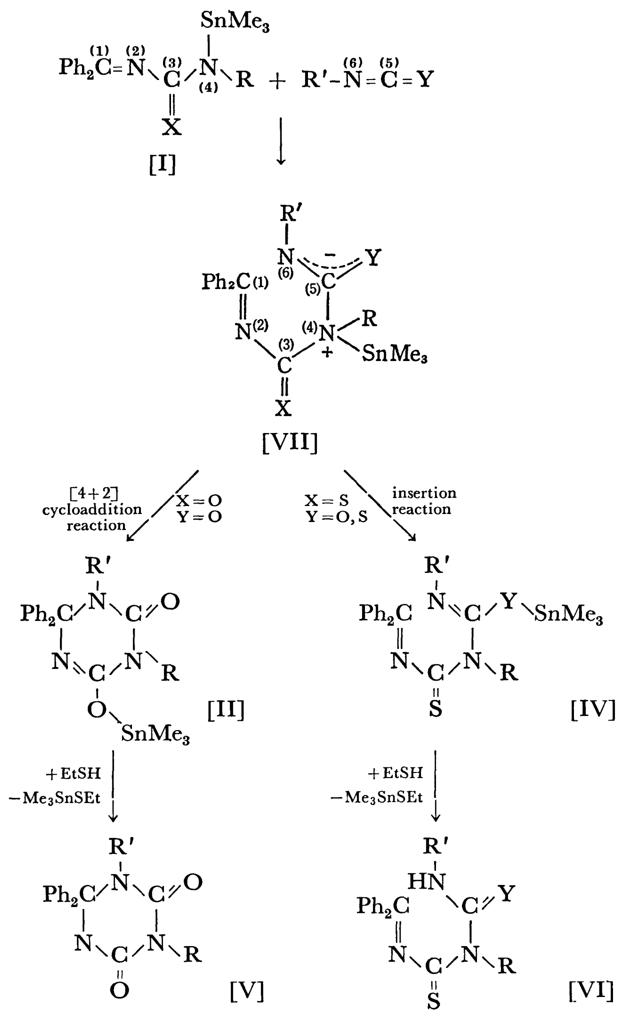
Table 4. Analytical data[a, b]

Compd.	C (%)	H (%)	N (%)	Calcd for
Ia	54.08 (53.90)	5.63 (5.53)		$C_{18}H_{22}N_2OSn$
Ic	59.85 (59.65)	5.27 (5.22)		$C_{23}H_{24}N_2OSn$
Ie	58.78 (58.69)	5.05 (4.92)		$C_{24}H_{24}N_2O_2Sn$
IIa	58.63 (58.24)	5.80 (5.83)		$C_{20}H_{25}N_3O_2Sn+C_6H_6$
IVe	51.38 (51.18)	5.26 (5.27)		$C_{20}H_{25}N_3S_2Sn+(1/3)C_6H_6$
IVf	53.97 (53.82)	5.45 (5.50)		$C_{20}H_{25}N_3OSSn+(1/2)C_6H_6$
IVg	60.05 (60.22)	4.91 (4.89)		$C_{30}H_{29}N_3OSSn$
Vb	73.40 (73.93)	5.47 (5.36)	11.60 (11.76)	$C_{22}H_{19}N_3O_2$
Vc	74.09 (73.93)	5.50 (5.36)	11.60 (11.76)	$C_{22}H_{19}N_3O_2$
VIe	65.34 (65.54)	5.59 (5.50)	11.34 (11.46)	$C_{17}H_{17}N_3S_2+C_6H_6$
VIf	68.58 (68.54)	5.83 (5.75)	12.25 (11.99)	$C_{17}H_{17}N_3OS+(1/2)C_6H_6$
VIg	76.74 (77.16)	5.59 (5.30)	7.78 (8.18)	$C_{27}H_{21}N_3OS+C_6H_6$
VIh	67.07 (67.83)	5.00 (4.92)	10.56 (10.79)	$C_{22}H_{19}N_{19}N_3S_2$

a) Calculated values in parentheses. b) The demetallated products, Va and Vd, were identified with the authentic samples.

The consecutive insertion products of isothiocyanate 1/1 adducts [IVe—IVh] are summarized in Table 3.

(c) Mechanism of the Subsequent Reaction of the 1/1 Adducts: The drastic variation of the addition depending on the first component of the 1/1 adducts is illustrated by the following scheme.



	X	Y	R	R'		X	Y	R	R'
a	O	O	Me	Me	e	S	S	Me	Me
b	O	O	Me	Ph	f	S	O	Me	Me
c	O	O	Ph	Me	g	S	O	Ph	Ph
d	O	O	Ph	Ph	h	S	S	Me	Ph

Scheme

The primary step of addition of the Sn–N bond to the heterocumulene was assumed to occur by the nucleophilic attack of the nitrogen atom[4] giving a zwitterionic intermediate(VII). When X=O (run a∼d) the positive charge on C(1) is enhanced largely by the conjugated carbonyl group and is stabilized by resonance with the two phenyl rings. Thus the nucleophilic ring closure occurs between N(6) and C(1). The following migration of the trimethylstannyl group from the ammonium nitrogen to the oxygen atom yields the 1,3,5-triazin-2(1*H*)-one derivatives [IIa∼IId]. The positive charge on C(1) is small when X=S (run e∼h), since the thiocarbonyl group is weakly electron-withdrawing as compared with the carbonyl group. Consequently, the anionic center(Y) captures the electrophilic trimethylstannyl group giving the corresponding consecutive insertion products [IVe∼IVh]. In Harrison's case,[3] the aldehyde adducts did not have an electron-withdrawing group at C(3), and the formal charge on C(1) is consequently zero. The [4+2] cycloaddition reaction would therefore be impossible.

Experimental

Mps were determined in sealed capillaries filled with argon. Analyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. IR spectra were recorded with a Japan Spectroscopic Co., Ltd. IR-S instrument. ^{1}H NMR spectra were measured with a Japan Electron Optics Lab. Co., Ltd. C-60HL instrument. *N*-Trimethylstannyl(diphenylmethylene)amine was prepared according to Chan and Rochow.[7] Isocyanates and isothiocyanates were distilled before use.

Reaction of N-*Trimethylstannyl(diphenylmethylene)amine with one Molar Equivalent of Benzoyl Isocyanate.* A colorless solution was obtained by addition of benzoyl isocyanate (0.692 g, 4.71 mmol) to a solution of *N*-trimethylstannyl(diphenylmethylene)amine (1.77 g, 5.15 mmol) in *ca.* 6 ml of benzene at 0 °C. The reaction was completed instantaneously. The 1/1 adduct (Ie) precipitated as white needles by the addition of *ca.* 4 ml of *n*-hexane was washed with *n*-hexane and dried *in vacuo* (2.19 g, 95%). Mp 52.0—54.0 °C. Found: C, 58.78; H, 5.05%. Calcd for $C_{24}H_{24}N_2O_2Sn$: C, 58.69; H, 4.92%. IR (in C_6H_6): 1673 and 1626 cm^{-1}. ^{1}H NMR (in $CDCl_3$): τ 9.68 (Me_3Sn, $J^{117/119}$ Sn–C–H=55.0/58.0 Hz). Equimolar reactions of *N*-trimethylstannyl(diphenylmethylene)amine with other isocyanates or isothiocyanates were carried out under similar reaction conditions (at 0 °C under an atmosphere of nitrogen). The yields and results of elemental analyses of the 1/1 adducts are summarized in Tables 1 and 4, respectively.

*Reaction of 1/1 Adduct (Ia) with Methyl Isocyanate. Formation of 3,4-Dihydro-1,3-dimethyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1*H*)-one (IIa)*: To a solution of 0.81 g (2.02 mmol) of the 1/1 adduct of methyl isocyanate in 2 ml of *n*-hexane was added 0.129 g (2.26 mmol) of methyl isocyanate at 0 °C under nitrogen. White needles which separated out in a few minutes were washed with *n*-hexane and recrystallized from a mixed solvent of *n*-hexane and benzene (1/1). This was identified as 1/2 adduct (IIa) (0.835 g, 77%). Elemental analysis and ^{1}H NMR spectrum identified the crystal as 3,4-dihydro-1,3-dimethyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1*H*)-one (IIa) containing 1 equivalent of benzene of crystallization. Mp 149.0—152.0 °C. Found: C, 58.63; H, 5.80%. Calcd for $C_{20}H_{25}N_3O_2Sn+C_6H_6$: C, 58.24; H, 5.83%. IR (in C_6H_6) 1688 and 1621 cm^{-1}. ^{1}H NMR (in $CDCl_3$): τ 9.88(Me_3Sn, $J^{117/119}$ Sn–C–H=54.0/56.0 Hz), 7.43 (Me–N), 6.96 (Me–N). Preparation of other 3,4-dihydro-4,4-diphenyl-1,3,5-triazin-2(1*H*)-ones; IIb (1-methyl-3-phenyl), IIc (1-phenyl-3-methyl), and IId (1,3-diphenyl) was achieved similarly. Yields and spectroscopic results are summarized in Table 2, and analytical data in Table 4.

Treatment of IIa with Ethanethiol. Formation of Hexahydro-1,3-dimethyl-6,6-diphenyl-1,3,5-triazin-2,4-dione (Va): Addition of ethanethiol to a benzene solution of the 1/2 adduct (IIa) afforded the destannylated product (Va) as white prisms. Mp 238.0—239.0 °C. IR (in KBr) 1723 and 1648 cm^{-1}. This compound was identified as the triazindione [Va] which could be prepared independently by the hydrolysis of the 1/2 adduct of *N*-trimethylsilyl(diphenylmethylene)amine with methyl isocyanate. Preparation of other *s*-triazindiones Vb, Vc, and Vd was achieved similarly. Yields, mp, and IR data are given in Table 2 and elemental analysis data in Table 4.

Reaction of 1/1 Adduct (Id) with One Equivalent of Phenyl Isocyanate. To a solution of 0.910 g (2.65 mmol) of *N*-trimethylstannyl(diphenylmethylene)amine in *ca.* 2 ml of benzene was added 0.350 g (2.59 mmol) of phenyl isothiocyanate at 0 °C under the atmosphere of nitrogen. On addition of phenyl isothiocyanate the color of the reaction mixture turned yellowish brown. The reaction mixture was left overnight at room temperature. Its IR spectrum showed the formation of 1/1 adduct [Id]. A solution of 0.314 g (2.64 mmol) of phenyl isocyanate in *ca.* 4 ml of benzene was then added at 0 °C. The mixture was warmed up to room temperature and allowed to stand for 15 hr. White prisms of the 1/2 adduct (IVg) separated out quantitatively were washed with benzene and recrystallized from a mixed solvent of *n*-hexane and benzene (4/6). Mp 164.5—166.0 °C. Found: C, 60.05; H, 4.91%. Calcd for $C_{30}H_{29}N_3OSSn$: C, 60.22; H, 4.89%. IR (in C_6H_6) 1698 and 1355 cm^{-1}. ^{1}H NMR (in $CDCl_3$) τ 9.72 (Me_3Sn, $J^{117/119}$ Sn–C–H= 56.0/58.0 Hz).

Destannylation of IV. Addition of ethanethiol to the benzene solution of 1/2 adduct (IVg) gave the destannylated product (VIg) as white prisms. Mp 252.0—254.0 °C. IR (in KBr) 1703 cm^{-1}. $\lambda_{\max}^{\mathrm{EtOH}}$ 279 nm (log ε=4.50). Consecutive insertion reactions of the isothiocyanate 1/1 adducts (Ib or Id) with another isocyanate or isothiocyanate were performed under similar reaction conditions. The yields and the results of the elemental analyses are summarized in Tables 3 and 4, respectively.

References

1) (a) Part XXIX, K. Itoh, H. Hayashi, M. Fukui, and Y. Ishii, *J. Organometal. Chem.*, **78**, 339 (1974).
(b) A part of this paper was reported by one of the authors (Y. Ishii) at the VIth Internat. Conf. Organometal. Chem., Amherst, U. S. A., August 1973.

2) I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc. Perkin I*, **1972**, 1678.

3) P. G. Harrison, *ibid.*, **1972**, 130.

4) M. F. Lappert, J. McMeeking, and D. E. Palmer, *J. Chem. Soc. Dalton*, **1973**, 151.

5) J. Lorberth, *J. Organometal. Chem.*, **16**, 235 (1969).

6) R. Richter and W. P. Trautwein, *Chem. Ber.*, **102**, 931, 938 (1969).

7) L. H. Chan and E. G. Rochow, *J. Organometal. Chem.*, **9**, 231 (1967).