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A New Type of Iminocarbonylaton of Diols, Mercaptoalkanol, and Dithiol *via* Their Dibutylstannyl Derivatives

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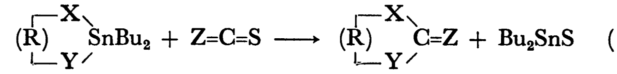
Reactions of phenyl isothiocyanate with cyclic and acyclic dibutylstannyl dialkoxides derived from several alcohols, such as 1,2- and 1,3-diols and methanol, afforded quantitatively phenyliminocarbonate derivatives with the elimination of dibutylstannyl sulfide. Cyclic organostannyl sulfides, such as 2,2-dibutyl-1,3,2-oxathiastannolane and -dithiastannolane, reacted with phenyl or alkyl isothiocyanate to give 2-imino-oxathiolane (**10**) and -dithiolane (**14**), respectively. At higher reaction temperatures, rearrengment and decomposition of products **10** and **14** occurred.

The usual method for the preparation of iminocarbonates utilizes isocyanide dichloride, $RN{=}CCl_2$, as a reactant.[1] The major disadvantage of this method is that only a limited number of the reagent is available because of their toxicities. The present study is aimed at an application of organostannyl derivatives to the iminocarbonylation of alkanol and diols, mercaptoalkanols, and dithiols with various isothiocyanates (Reaction 1).



$$(R)\langle{}^{X}_{Y}\rangle SnBu_2 + Z{=}C{=}S \longrightarrow (R)\langle{}^{X}_{Y}\rangle C{=}Z + Bu_2SnS \quad (1)$$

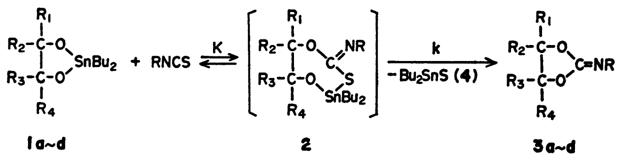
$$X, Y{=}O, S;\ Z{=}NR$$

Reactions anologously to Reaction 1 using bis(tributylstannyl) derivatives of HX(R)YH have already been reported previously which dealt with the thiocarbonylation (X, Y=NMe or O; Z=S), iminocarbonylation (X, Y=NMe or O; Z=NPh),[2] and preparation of orthocarbonates.[3] However, this method appeares to be more suit for a new type of iminocarbonylation of diols, mercaptoalkanols and dithiols, because the corresponding dibutylstannyl compounds can be easily prepared from commercially available dibutylstannyl chloride or oxide, and are less toxic than tributylstannyl compounds.

Results and Discussion

The appropriate dibutylstannyl compounds were readily prepared and these starting materials were allowed to react with isothiocyanates is in a nitrogen atmosphere to afford cyclic iminocarbonylated products (X, Y=O or S in Reaction 1).

The reaction of some 2,2-dibutyl-1,3,2-dioxastannolanes (**1a**—**c**) with phenyl isothiocyanate for 2 h in 1,2-dichloroethane at 55 °C afforded the corresponding 2-phenylimino-1,3-dioxolanes (**3a**—**c**) and dibutylstannyl sulfide (**4**)[4] in quantitative yields (Reaction 2). However, a tetra-substituted derivative, dioxastannolane **1d** in Table 1, did not react with phenyl isothiocyanate under the same coditions, *i.e.*, more severe reaction conditions were required to complete the reaction, as is seen in Table 1. This fact suggests a large steric effect in the reactions with organostannyl compounds.



(2)

The intermediate (**2**) was not detected, even by IR and NMR measurements of the reaction mixture. However, it appears probable that the reaction proceeds *via* the addition of phenyl isothiocyanate to the tin-oxygen bond, followed by the elimination of a stable organostannyl sulfide (**4**), anologously to the case of the reactions of the compounds **5** and **8** mentioned below.

A six-membered ring compound, 2,2-dibutyl-1,3,2-dioxastannin (**1e**), was also allowed to react with phenyl isothiocyanate for 2 h at 55 °C to give 2-phenylimino-1,3-dioxane (**3e**) in a 60% yield (Reaction 3). On the other hand, the reaction of the seven-membered ring compound, 2,2-dibutyl-1,3,2-dioxoastannepane (**1f**), with phenyl isothiocyanate to form **3f** was unsuccessful, because of the instability of the product (**3f**). The instability is probably due to transfer polymerization of

Table 1. Reactions of 2-dibutylstanna-1,3-dioxolanes (**1**) with phenyl isothiocyanate

1					Conditions		Iminocarbonate	
No.	R_1	R_2	R_3	R_4	Temp/°C	Time/h	Bp/°C/mmHg	Yield/%
1a	H	H	H	H	55	2	148—150/1.5 (72.0—72.5)[a]	98 (**3a**)
1b	H	Me	H	H	55	2	131—132/1.0	95 (**3a**)
1c	H	Me	H	Me	55	5	120—122/0.4	95 (**3c**)
1d	Me	Me	Me	Me	85	40	120—125 (79—81)[a]	95 (**3d**)

a) Melting point/°C.

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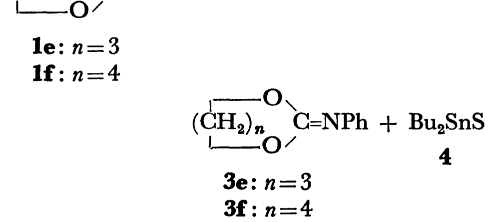
3f to give polyurethane: the C=O stretching band characteristic of urethane was observed at 1680 cm^{-1} in the IR spectrum of the reaction mixture.

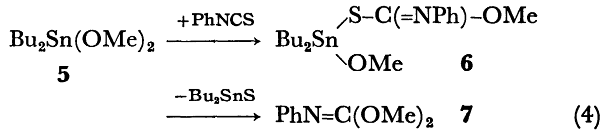


$$\mathrm{(CH_2)_n}\begin{matrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{matrix}\mathrm{SnBu_2} + \mathrm{PhNCS} \longrightarrow \mathrm{(CH_2)_n}\begin{matrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{matrix}\mathrm{C{=}NPh} + \mathrm{Bu_2SnS} \qquad (3)$$

1e: $n=3$
1f: $n=4$

3e: $n=3$
3f: $n=4$
4

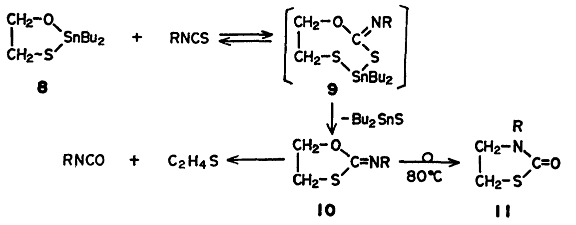
An acyclic organostannyl compound, **5**, was also submitted to the reaction with phenyl isothiocyanate in dichloroethane at 55 °C, affording only the 1:1 adduct (**6**) reported by Davies and Harrison.[5] However, under more severe conditions such as 70 °C for 16 h in 1,2-dichloroethane, the adduct (**6**) was converted to phenyl isocyanide dimethoxide (**7**) in a 96% yield (Reaction 4).



$$\underset{\mathbf{5}}{\mathrm{Bu_2Sn(OMe)_2}} \xrightarrow{+\mathrm{PhNCS}} \mathrm{Bu_2Sn}\begin{matrix}\diagup\mathrm{S{-}C({=}NPh){-}OMe}\\ \diagdown\mathrm{OMe}\end{matrix}\ \mathbf{6} \xrightarrow{-\mathrm{Bu_2SnS}} \mathrm{PhN{=}C(OMe)_2}\ \mathbf{7} \qquad (4)$$

An aliphatic isothiocyanate, MeNCS, was also allowed to react with **1a**, and 2-methylimino-1,3-dioxolane was obtained in a moderate yield (70%).

In general, addition reactions of heterocumulenes to the tin-oxygen bond occur easily,[5] while heterocumulenes scarcely react with the tin-sulfur bond. Here, the reaction of an isothiocyanate with equimolar 2,2-dibutyl-1,2,3-oxathiastannolane (**8**), which was readily prepared from mercaptoethanol and dibutyltin oxide or chloride, was examined. For example, an equimolar mixture of phenyl isothiocyanate and **8** was heated for 2 h in dry 1,2-dichloroethane at 55 °C to afford 2-phenylimino-1,3-oxathiolane (**10**;R=Ph) and dibutylstannyl sulfide (Reaction 5). Alkyl isothiocyanates were also used in the reaction, the results of which are shown in Tables 2 and 3. The product (**10**) from the alkyl isothiocyanates were thermally unstable, and some parts decomposed to give alkyl isocyanates and thiirane.[6] Because of such thermal instability of the products, the reactions were carried out at relatively low temperatures such as 40 °C, even though alkyl isocyanates were less reactive than phenyl isothiocyanate.



(5)

TABLE 2. REACTIONS OF 2-DIBUTYLSTANNA-1,3-OXATHIOLANE (**8**) WITH ISOTHIOCYANATES (RNCS) IN DICHLOROMETHANE

R	Conditions		Product yield %		
	Temp/°C	Time/d	**10**	RNCO	Others
Me	40	3	59	2	b,e
Et	40	4	64	4	b,e
Pr	40	5	79	6	b,e
Bu	40	5	70	trace	b,e
i-Pr	40	5	39	26	b,c,e
cyclo-C_6H_{11}	40	5	36	34	b,e
t-Bu	80[a]	4	0	0	d
Ph	55[a]	2(h)	95	0	b

a) In 1,2-dichloroethane. b) Dibutylstannyl sulfide was obtained in a quantitative yield. c) Accompanied by unreacted **8** (11%). d) The unreacted **8** was recovered in a quantitative yield. e) Ethylene sulfide and isocyanate were detected.

From the results in Table 2, the apparent order of the reactivities is as follows: PhNCS>MeNCS,EtNCS,PrNCS,BuNCS≫*i*-PrNCS,*cyclo*-C_6H_{11}≫Me_3CNCS. This order suggests that the reactivity of an isothiocyanate in the insertion across the tin-oxygen bond of **8** is affected by both the electronic nature and the bulkiness of the isothiocyanate substituent.

It is reasonable to assume that the reaction course forming **10** is an addition-elimination process (**8**→**9**→**10**): the formation of the intermediate (**9**) is strongly suggested on the basis of the fact that the C=N stretching band ascribable to **9** is observed at 1500—1530 cm^{-1} in

TABLE 3. PROPERTIES OF 2-ALKYLIMINO-1,3-OXATHIOLANES (**10**) FORMED IN REACTION 5

R in **10**	Bp °C/mmHg	IR/cm^{-1}		NMR/ppm			Found (Calcd)	
		$\nu_{C=N}$	ν_{C-O}	δ_{CH_2O}	δ_{CH_2S}[b]	δ_{others}	C%	H%
Me	117—118/20	1668	1070, 1037	4.27	3.35	2.90	41.07[c] (40.94)	5.96 (6.09)
Et	68—70/0.6	1680	1047, 1037	4.25	3.35	3.00, 1.13	45.55 (45.79)	7.09 (6.91)
Pr	66.5—75.5	1680	1060, 1047	4.25	3.35	2.98, 2.5, 0.92	49.87 (49.62)	7.97 (7.64)
Bu	84—85/0.5	1676	1065, 1038	4.25	3.34	3.00, 0.92 2.1—2.7	53.09 (52.79)	8.54 (8.23)
i-Pr	63—64/0.4	1673	1100, 1033	4.24	3.42	2.95, 1.10	49.87 (49.62)	7.64 (7.64)
c-C_6H_{11}	98—99/0.3	1668	1067, 1026	4.16	3.28	2.7, 1.7—2.0	61.87 (61.80)	8.52 (8.54)

a) In carbon tetrachloride. b) Triplet, J=6.8 Hz. c) N% 11.96 (11.96).

the IR spectrum of the reaction mixture in the initial stage of the reaction at 40 °C. At elevated reaction temperatures (80 °C), **10** was partially rearranged to N-substituted thiazolidin-2-one (**11**). No such rearrangement was observed in the reaction of **8** with phenyl isothiocyanate.[7]

Finally, 2,2-dibutyl-1,3,2-dithiostannolane was allowed to react with sulfur-containing heterocumulene for several days at 40—80 °C to give a dithio-carbonate derivative (**14**) and dibutylstannyl sulfide. The results are tabulated in Table 4. Although no intermediate adduct (**13**) was detected, the reaction course may be depicted analogously to reaction scheme (5).

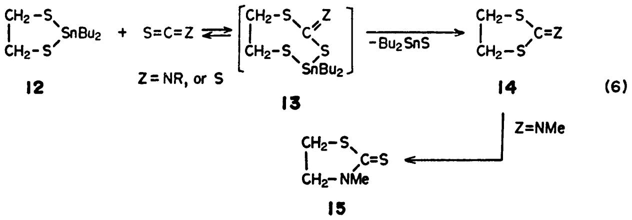


Table 4. Equimolar reactions of 2-dibutylstanna-1,3-dithiolane with heterocumulenes in dichloromethane

Hetrocumulene used	Conditions		Product yield/%[a)]	
	Temp/ °C	Time/ d	**14**	Bu_2SnS
MeNCS	40	5	76(X=NMe)	91
MeNCS	80	4	64[b)]	86
PhNCS	80[c)]	5	65(X=NPh)	90
CS_2	40	9	39(X=S)	35

a) A trace amount of ethylene sulfide was detected by NMR measurements. b) Yield (%) of *N*-methylthiazolidin-2-thione. c) In 1,2-dichloroethane.

At elevated temperatures, 1-methylthiazolidine-2-thione (**15**) was obtained. Thus it is suggested that thermal rearrangement of **14** to **15** occured, as has been reported by Ueno *et al.*[6]

Organostannyl sulfides are known to be stable in ordinary reactions.[8] However, it is interesting to note that dibutylstannyl sulfide (**12**) is moderately reactive in reaction with methyl isothiocyanate. From a comparison of the result in Table 2 with that in Table 3, it is seen that methyl isothiocyanate is less reactive in reaction with **8** than is phenyl isothiocyanate, although the former is more reactive in reaction with **12** than is the latter. Moreover, carbon disulfide reacts with **12** to afford ethylene trithiocarbonate, but did not react with **8**, even in a mixture of **8** and carbon disulfide that was heated for nine days at 40 °C. These results cannot be explained by the usual rate order observed in reaction of simple organostannyl compounds, *i.e.*, Sn–N>Sn–O>Sn–S.[8,9] Therefore, the difference in the degree of association between **1a**—**d** or **8** (dimer) and **12** (monomer) and in the co-ordinating power of heterocumulene molecules to tin atom in these organostannyl compounds may affect their reactivities. A detailed discussion of the reaction rate and mechanism will be published elsewhere.[11]

Experimental

All melting and boiling points are uncorrected. The IR spectra were obtained on a Nippon-Binko DS-403G and IR-S spectrometers. The NMR spectra were recorded on a Japan Electron Optics Model C-60HL spectrometer with TMS as the internal standard. A Japan Electron Optics Model JMS-OISG mass spectrometer and a Yanagimoto Model GCG-220 gas chromatograph (Silicone DC-200, 25%) were also used. Analyses were performed in the laboratories of Professor Sasaki and of the Toa-gosei Co. All reactions and measurements were carried out using dry solvents.

All isothiocyanates (RNCS) were prepared using a reported method;[12] bp 117—119 (R=Me), 132—135 (Et), 153—154 (Pr), 170—175 (Bu), 137—142 (*i*-Pr), 120 (*cyclo*-C_6H_{11}) °C and 131—133 °C/10 mmHg (Me_3C). All solvents were dried over P_2O_5 and distilled before use. Mercaptoethanol and ethane-1,2-dithiol were obtained commercially and distilled in nitrogen; bp 55—58 °C/15 mmHg and 70—73 °C/50 mmHg, respectively. The dioxastannolanes (**1a**—**f**) were prepared from diol,Bu_2SnCl_2 and Na_2CO_3, or from diol and Bu_2SnO,[13] and stored in a dessicator containing blue silica gel.

Preparation of 2,2-Dibutyl-1,3,2-oxathiastannolane (8). (A) Mercaptoethanol (15.6 g, 200 mmol), dibutyltin dichloride (60.4 g, 200 mmol), and sodium carbonate (60 g) were heated under reflux in toluene (150 cm³) in an atmosphere of nitrogen for 10 h in a flask equipped with a Dean-Stark water-separater, a condensor, and a stirrer. The hot reaction mixture was filtered, and evaporated to recover the toluene used. The residue was distilled in a vacuum to give crude **8** in a 90% yield (52.8 g). Redistillation afforded white solid **8**; bp 173—176 °C/0.4 mmHg; mp 92—93.5 °C (Ref.[10,14] 89—90 °C). The IR and NMR spectra coincided well with those previously reported.[1,14]

(B) Mercaptoethanol (15.6 g, 200 mmol) and Bu_2SnO (48 g, 200 mmol) were allowed to react under reflux in toluene and were treated as mentioned above, to afford **8** in a 92% (54 g) yield.

Preparation of 2,2-Dibutyl-1,3,2-dithiastannolane (12). A mixture of ethane-1,2-dithiol (18.2 g, 200 mmol), Bu_2SnCl_2 (60.4 g, 200 mmol), and Na_2CO_3 (65 g) was heated for 10 h in refluxing toluene (200 cm⁻¹) in an atmosphere of nitrogen, and treated as mentioned above to give **12** in a 77% yield; bp 127—129 °C/0.1 mmHg; mp 57—58 °C (Ref.[15] 59—60 °C); NMR (CCl_4) δ 2.93 (s, 4H, CH_2S) and 0.7—1.7 ppm (br., 18H, SnBu); IR (CCl_4) 1285, 1245, 925, and 845 cm⁻¹. The dithiastannolanes **12** was also prepared in a 86% yield (53 g) from Bu_2SnO instead of Bu_2SnCl_2 and Na_2CO_3.

The Reaction of 2,2-Dibutyl-1,2,3-dioxastannolane (1a) with PhNCS. To a solution of **1a** (5.8 g, 20 mmol) in dry 1,2-dichloroethane (40 cm³) in a flask equipped with a condenser and a drying tube, PhNCS (2.8 g, 21 mmol) was added and the mixture was heated with stirring for 2 h at 55 °C. Then, the solvent was evaporated, and the residue was distilled in a vacuum to give 2-phenylimino-1,3-dioxolane (**3a**) in a 98% yield (3.2 g, 19.6 mmol); bp 148—150 °C/15mmHg; mp (recrystallized from toluene) 72—72.5 °C (Ref.[16] 74—75 °C); NMR δ 4.43 (s, 4H, CH_2O) and 6.8—7.3 ppm (m, 5H, Ph); IR ($CHCl_3$) 1721 ($\nu_{C=N}$) and 1056 cm⁻¹. The spectral data were the same as those of an authentic sample. The pot residue showed the same IR spectrum that of the authentic Bu_2SnS (ν_{SnSSn} at 360 cm⁻¹); yield 91% (4.9 g).

The Reaction of 2,2-Dibutyl-4-methyl-1,3,2-dioxastannolane (1b) with PhNCS. The stannolane **1b** was allowed to react with PhNCS for 2 h at 55 °C, and was treated as mentioned above; yield 95%; bp 131—132 °C/1 mmHg; NMR (CCl_4)

δ 1.23 (d, J=5.1 Hz, 3H, CH_3), 3.5—4.8 ($ABCX_3$·pattern, 3H,CH_2CH), and 6.8—7.3 ppm (m, 5H, Ph); IR ($CHCl_3$) 1708 ($\nu_{C=N}$) and 1040 (ν_{C-O}) cm^{-1}; Found C, 67.55; H, 6.37; N, 7.88%. Calcd for $C_{10}H_{11}ON$: C, 67.78; H, 6.29; N, 7.90%.

Dibutylstannyl sulfide was obtained as a pot residue in a 95% yield.

The Reaction of 2,2-Dibutyl-4,5-dimethyl-1,3,2-dioxastannolane (1c) with PhNCS. This compound (**1c**) was allowed to react with PhNCS for 5 h in 1,2-dichloroethane at 55 °C and was treated as described above to give **3c** (95% yield; bp 120—122 °C/0.4 mmHg). The IR and NMR spectra coincided well with those of an authentic sample.[16]

Reaction of Dimethoxydibutylstannane (5) with PhNCS. To a solution of **5** (5.9 g, 20 mmol) in 1,2-dichloroethane, PhNCS (2.7 g, 20 mmol) was added dropwise and the reaction mixture showed δ_{CH_3-O} at 3.93 and 3.51 ppm in the NMR spectrum and $\nu_{C=N}$ band at 1630 cm^{-1} in the IR spectrum, which are the same as those reported for the 1: 1 adduct (**6**).[5] This adduct (**6**) was heated for 16 h at 70 °C, and distilled to give phenyl isocyanide dimethoxide **7** in a 96% yield; bp 60—62 °C/0.3 mmHg; NMR ($CDCl_3$) δ 3.17 (s, 6H, CH_3) and 6.7—7.3 ppm (m, 5H, Ph); IR ($CHCl_3$) 1677 ($\nu_{C=N}$) cm^{-1}. Those spectral data coincided well with those of a commercial sample.

The Reaction of 2,2-Dibutyl-1,3,2-dioxastannoxane (1e) with PhNCS. Compound **1e** was allowed to react with PhNCS in 1,2-dichloroethane as in the case of **1a**. The reaction mixture was fractionally distilled to afford 2-phenylimino-1,3-dioxacyclohexane **3e** in a 60% yield; bp 136—139 °C/0.2 mmHg; NMR ($CDCl_3$) δ 4.25 (t, J=5.5 Hz, 4H, CH_2O), ≈1.9 (m, 2H, CCH_2C), and 6.8—7.3 ppm (m, 5H, Ph); IR ($CHCl_3$) 1690 and 1100 cm^{-1}. Found: C, 67.48; H, 5.98; N, 7.75%. Calcd for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.90%.

The Reaction of 2,2-Dibutyl-1,3,2-dioxastannaepane (1f) with PhNCS. Compound **1f** was allowed to react with an equimolar amount of PhNCS for 20 h in 1,2-dichloroethane at 70 °C, to give a mixture which showed the characteristic $\nu_{C=N}$ band ascribable to 2-phenylimino-1,3-dioxepane (**3f**) at 1690 cm^{-1}, but distillation gave a resinous product having an IR band at 1680 cm^{-1}.

The Reaction of 1a with MeNCS. This compound (**1a**) was allowed to react with MeNCS for 16 h in dry 1,2-dichloroethane at 70 °C, to give 2-methylimino-1,3-dioxolane in a 70% yield; bp 98—100 °C/25 mmHg, NMR ($CDCl_3$) δ 2.99 (s, 3H, CH_3) and 4.38 ppm (s, 4H, CH_2); IR ($CHCl_3$) 1740 cm^{-1}. Found: C, 47.83; H, 7.12; N, 13.59%. Calcd for $C_4H_4O_2N$; C, 47.52; H, 6.98; N, 13.86%.

Reaction of 2,2-Dibutyl-1,3,2-oxathiostannolane (8) with PhNCS. An equimolar mixture of **8** and PhNCS was heated for 2 h in dry 1,2-dichloroethane at 55 °C. The reaction mixture was concentrated in vacuum and cooled to precipitate crude crystal of 2-phenylimino-1,3-oxathiolane (**10**, R=Ph) in a 95% yield; mp (recrystallized from a toluene-hexane (1: 1) mixture) 65.0—65.5 °C; NMR ($CDCl_3$) δ 3.35 (t, J=6.3 Hz, 2H, CH_2S), 4.66 (t, J=6.3 Hz, 2H, CH_2O), and 6.8—7.3 ppm (m, 5H, Ph); IR ($CHCl_3$) 1658 ($\nu_{C=N}$) 1113, and 1038 (ν_{C-O}) cm^{-1}. Found: C, 60.10; H, 5.11; N, 7.80%. Calcd for C_9H_9ONS: C, 60.31; H, 5.06; N, 7.81%. The parent solution contained Bu_2SnS (97% yield).

Reaction of 8 with Some Alkyl Isothiocyanates. A typical example is as follows: the oxathiostannolane **8** and MeNCS (each 25 mmol) were heated for three days at 40 °C in dry dichloromethane in a flask equipped with a condensor and a drying tube. During the course of the reaction, the mixture showed the $\nu_{C=N}$ band of the 1: 1 adduct at 1610 cm^{-1} in the IR spectrum. After the reaction, the solvent and the low boiling by-product were recovered in a cold trap by distillation at atmospheric pressure, and the residue was distilled in a vacuum, to afford 2-methylimino-1,3-oxathiolane (**10**;R=Me) in a 59% yield; bp 117—118 °C/20 mmHg. The identification of **10** was performed using IR and NMR spectroscopies and elemental analysis. It was confirmed by VPC and NMR measurements that the trapped mixture comprised the solvent, thiirane (3%), MeNCO (2%), and MeNCS (1%).

Bu_2SnS was obtained as a residue in an almost quantitative yield.

The results of the reactions of **8** with other alkyl isothiocyanates are summerized in Tables 2 and 3.

Picrate Formation of 10. Compound **10** (R=Me and Et) was added to a solution of picric acid in EtOH at room temperature, and cooled at 0 °C to precipitate the picrate crystals. The picrate of **10** (R=Me): mp (EtOH) 143—144 °C; IR (KBr) 1628, 1609, 1551, 1367, and 1268 cm^{1-}; Found: C, 34.69; H, 2.91; N, 16.18%. Calcd for $C_{10}H_{10}O_8S$: C, 34.57; H, 3.14; N, 16.26%. The picrate of **10** (R=Et): mp (EtOH) 80—82 °C; IR (KBr) 1660, 1615 (br.), 1368, and 1275 cm^{-1}; Found: C, 36.34; H, 3.64; N, 15.15%. Calcd for $C_{11}H_{12}O_8N_4S$: C, 36.67; H, 3.36; N, 15.15%.

The Rearrangement of 10 to 11 (R=Me). Compound **10** prepared *in situ* from **8** and MeNCS (25 mmol each) was heated under reflux for four days in 1,2-dichloroethane, and the reaction mixture was distilled to afford **11** (R=Me) in a 46% yield; bp 73—75 °C/0.2 mmHg (Ref.[6] 84—86 °C/0.2 mmHg); IR ($CHCl_3$) 1689 cm^{-1} (Ref.[6] 1685 cm^{-1}). Under the same reaction conditions, **10** (R=Ph) was not rearranged and recovered by distillation in an almost quantitative yield.

The Reactions of 2,2-Dibutyl-1,3,2-dithiostannolane (12) with MeNCS and PhNCS. This compound (**12**) was allowed to react with an equimolar amount of MeNCS for five days in dry dichloromethane under reflux, and was distilled to give 2-methylimino-1,3-dithiolane (**14**; Z=NMe) in a 76% yield; bp 64—68 °C/0.3 mmHg (Ref.[6] 79—81 °C/0.45 mmHg); the IR and NMR spectra coincided well with those prepared by a published method.[16] The trapped distillate contained only a trace amount of thiirane.

The reaction of **8** with MeNCS was carried out for one day in refluxing 1,2-dichloroethane, and the reaction mixture showed the characteristic C=N stretching band of **14** (Z=NMe) at 1614 cm^{-1}. The reaction was further continued for three days at 80 °C. Then, the solvent was evaporated, and the residual solid was recrystallized from CCl_4 to give 1-methylthiazolidine-2-thione (**15**) in a 64% yield; mp 68—69 °C (Ref.[6] 68—69 °C); NMR (CCl_4) δ 2.37 (t, J=7.3 Hz, 2H, CH_2N) and 4.08 (t, J=7.3 Hz, 2H, CH_2S); IR (CCl_4) 1308 cm^{-1}. These spectral data are the same as those prepared by a published method.[16]

The Reaction of the Dithiostannolane (12) with CS_2. An equimolar mixture of **12** and CS_2 was allowed to react for nine days in 1,2-dichloroethane at 40 °C, and the reaction mixture was submitted to column chromatography on silica gel (Wakogel C-100; CCl_4-$CHCl_3$) to give ethylene trithiocarbonate **14** (Z=S, 39% yield), dibutylstannyl sulfide (35%), and the unreacted **12** (65%). The IR ($\nu_{C=S}$ 1080 cm^{-1}) and NMR (δ_{CH_2} 3.92 ppm) spectra coincided well with those of a commercial sample.

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