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REACTIONS OF BIS(TRIBUTYLSTANNYL) MERCAPTOETHANOLATE AND ETHANEDITHIOLATE WITH CARBON DISULFIDE, ISOTHIOCYANATES AND THIONECARBONATE DERIVATIVES

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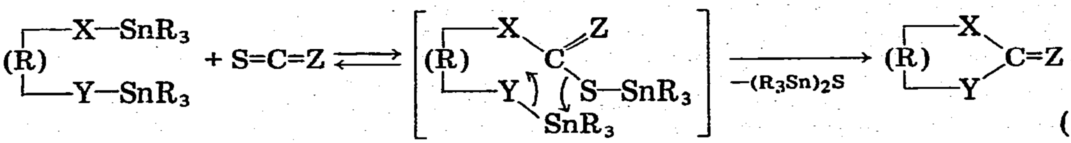
Summary

Bis(tributylstannyl) mercaptoethanolate (I) and ethanedithiolate reacted with carbon disulfide and isothiocyanates to afford mainly the corresponding cyclic thio- and imino-carbonates, respectively, with elimination of bis(tributylstannyl) sulfide. The carbonate derivatives formed decomposed partially or reacted further with I to give by-products. To clarify the course of the latter reaction compound I and related compounds were treated with thionecarbonate derivatives to afford carbonate derivatives, ethylene sulfide and bis(tributylstannyl) sulfide. These desulfurization reactions of the thione compounds are assumed to proceed via *spiro*-orthocarbonate derivatives, which then decompose.

Introduction

Organotin sulfides are stable and in general not very reactive [1—3], and their reactions have been reported in only a few examples [4,5]. In our earlier reports [7,8] we established a novel type of cyclization reaction of bis(tributylstannyl) derivatives of alkanediols, alkanolamines and alkylenediamines with carbon disulfide and phenyl isothiocyanate (eqn.1).



(1)

(X,Y = O,NR′; Z = S or NR″)

We are also interested in the same type of reactions with sulfur-containing organostannyl compounds [9]. In this paper, we discuss the reaction of bis(tributylstannyl) derivatives of β-mercaptoethanol and ethanedithiol with carbon disulfide, isothiocyanates, and thionecarbonate derivatives.

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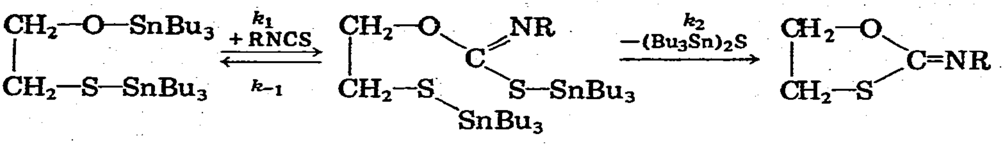
Results and discussion

Equimolar amounts of bis(tributylstannyl) mercaptoethanolate (I) and alkyl or phenyl isothiocyanate were mixed in dry nitrogen at room temperature to give the 1/1 adduct II, which showed a ν(C=N) band at 1610 cm^{-1} in the IR spectrum. Heat evolution was never observed during the reaction; on the other hand, bis(tributylstannyl) glycolate, aminoethanolate or ethylenediamide were reported to react exothermically to afford a cyclic imino- or thio-carbonyl compound and bis(tributylstannyl) sulfide [7,8].



(2)

(I) (II) (III)

To cyclize the adduct II, a mixture of I and isothiocyanate was heated to give bis(tributylstannyl) sulfide and 2-imino-1,3-oxathialane (III) which were identified by IR and NMR spectroscopic methods, by analyses and by conversion of III to the picrate. The reaction conditions and the product yields of the reaction 2 are collected in Table 1.

Fairly severe reaction conditions were required in the cyclization reactions because a stable tin—sulfur bond must be cleaved in the reaction path k_2. Except for phenyl isothiocyanate, which was reactive due to the electron-attracting and conjugative effects of the phenyl group, the steric effect of the alkyl group in the isothiocyanates on the reaction conditions is clearly seen in Table 1.

Isocyanates and isothiocyanates were also isolated from reaction 2. The products, 2-imino-1,3-oxathiolanes, are unstable, e.g. 2-methylimino-1,3-oxathiolane was thermally decomposed to methyl isocyanate on distillation, and 2-phenylimino-1,3-oxathiolane was polymerized by trace amounts of water to give poly(ethylenethiocarbamate) (VI) by transfer polymerization as reported

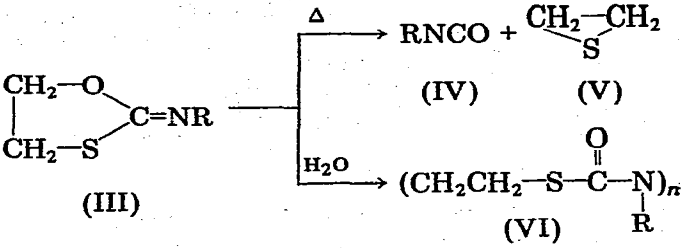
TABLE 1

THE CONDITIONS AND PRODUCT YIELDS OF EQUIMOLAR REACTIONS OF BIS(TRIBUTYLSTANNYL) MERCAPTOETHANOLATE WITH SOME ISOTHIOCYANATES

Isothiocyanate	Reaction conditions		Product yield[a]		
	Temp (°C)	Time (h)	(III)	RNCO	RNCS
Ph	60	20	49[b]	[c]	[c]
Me	60	20	64	5	5
Et	85	48	54	13	20
n-Pr	90	48	24	24	46
n-Bu	90	48	26	30	60
i-Pr	100	96	6	49	29
cyclo-C_6H_{11}	120	96	28	25	25
t-Bu	120	96	2	13	85

[a] Based on the mercaptoethanolate (I) used. [b] Accompanied by the formation of polymer (26% yield). [c] Not determined.

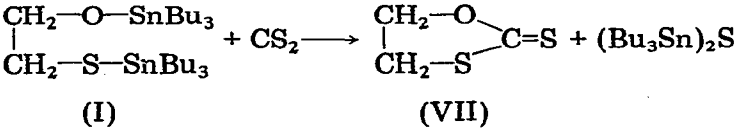
in the reaction of 2-phenylimino-1,3-dioxolane [10]. Therefore, large quantities of isocyanates and ethylene sulfide were formed under severe reaction conditions, as in the reactions of isopropyl and cyclohexyl isothiocyanates with I (eqn.3).



(3)

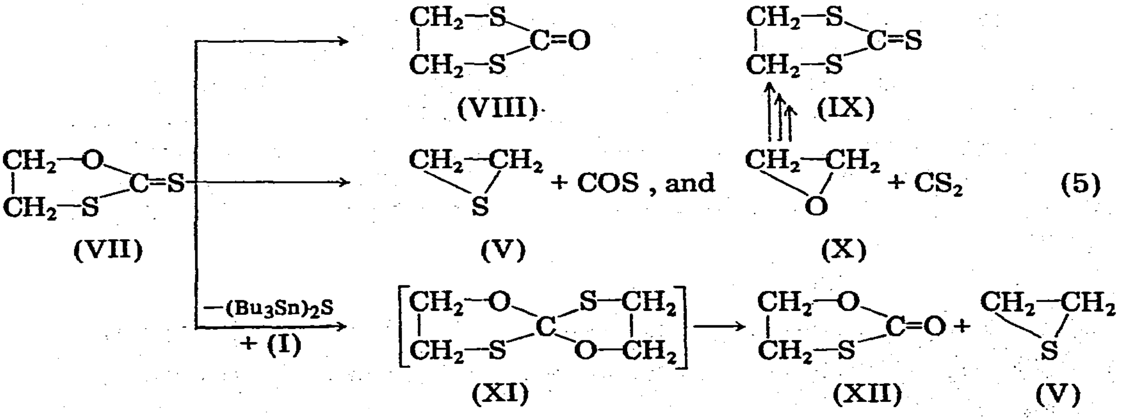
Alkyl isothiocyanates were consumed almost quantitatively by the addition reaction (k_1) of the tin—oxygen bond in I below 60° but alkyl isothiocyanates were formed on distillation of the cyclization reaction mixture. The alkyl isothiocyanate isolated could have been formed by the dissociation reaction (k_{-1}) of the adduct (II) or the decomposition reaction of the cyclic product (III) to isothiocyanate and ethylene oxide, although the latter was detected only in a trace amount.

I when treated with carbon disulfide for 20 h at 60° afforded ethylene dithiocarbonate (VII) in 65% yield, with elimination of bis(tributylstannyl) sulfide (eqn. 4). The reaction temperature must be controlled within the range



(4)

45—65° to obtain a good yield of VII. Reaction 4 is a newly established synthetic method for ethylene dithiocarbonate (VII), which was prepared for the first time from lead acetate, mercaptoethanol and thiophosgene in rather low yield by Jones and Andreades [11]. Some decomposition reaction of VII and other side-reactions occurred at 80—100° to give carbonyl sulfide, ethylene sulfide (V), dithiol carbonate (VIII), trithiocarbonate (IX), ethylene oxide (X) and thiol carbonate (XII) (eqn.5).



(5)

TABLE 2

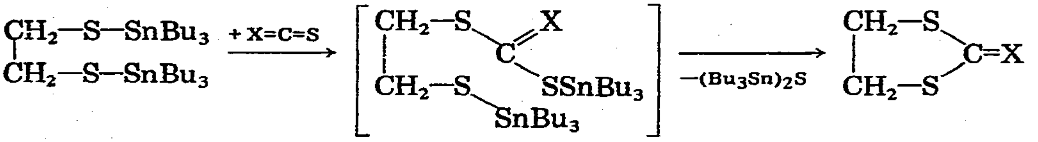
REACTION CONDITIONS AND THE PRODUCT YIELDS OF THE REACTION OF BIS(TRIBUTYLSTANNYL) ETHANEDITHIOLATE WITH HETEROCUMULENES

Heterocumulene	Reaction conditions		Product yields (%)	
	Temp (°C)	Time (h)	Dithiolane (XV)	$(Bu_3Sn)_2S$
CS_2	60	200	23 (X = S)	
PhNCS	80	120	39 (X = NPh)	≈ 100
MeNCS	80	120	57 (X = NMe)	≈ 100

The trithiocarbonate (IX) would be formed by the reaction of ethylene oxide (X) or dithiocarbonate (VII) with carbon disulfide as was proposed by Razuvaev et al. [12], and the dithiocarbonate (VII) would probably rearrange to afford the dithiol carbonate (VIII). The thiol carbonate (XII) may have arisen by decomposition of the unstable *spiro*-orthocarbonate intermediate (XI), which may have been formed from VII and I.

The reaction of bis(tributylstannyl) ethanedithiolate

Bis(tributylstannyl) ethanedithiolate (XIII) was allowed to react with carbon disulfide and methyl or phenyl isothiocyanate for several days at 40—90° to afford 2-thio- and 2-methylimino- or 2-phenylimino-1,3-dithiolanes, respectively (Table 2). This reaction is a new example of a reaction of an organostannyl sulfide.



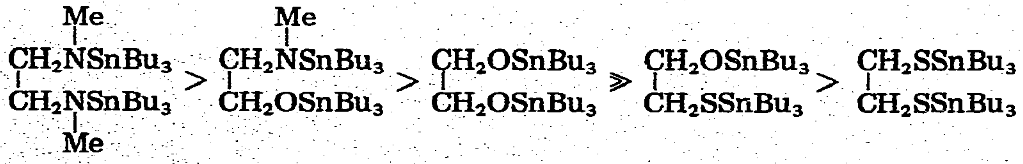
(6)

(XIII) (XIV) (XV)

(X = S,NMe or NPh)

Although XIV, the insertion product of a heterocumulene across a tin—sulfur bond, has not been detected, the reaction probably proceeds via an addition—elimination process as in the case of the reaction of bis(tributylstannyl) mercaptoethanolate. Bis(tributylstannyl) sulfide was isolated in almost quantitative yield from the reaction mixture by column chromatography. The difference between the yields of dithiolane (XV) and the sulfide suggests that XV decomposes to isothiocyanate and ethylene sulfide, because the latter two compounds were detected in the reaction mixture by IR and NMR spectroscopy.

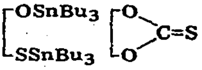
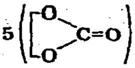
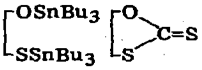
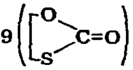
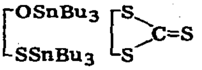
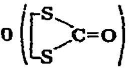
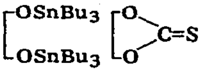
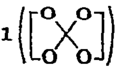
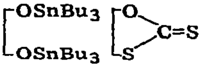
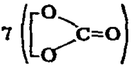
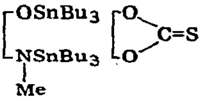
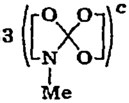
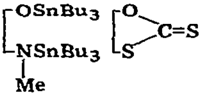
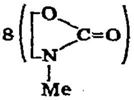
From a comparison of the reaction conditions, bis(tributylstannyl) ethanedithiolate has the lowest reactivity among the bis(tributylstannyl) derivatives studied [7,8], and the reactivity order of the bis(tributylstannyl) compound is as follows:



$$\begin{array}{c}CH_2N(Me)SnBu_3\\|\\CH_2N(Me)SnBu_3\end{array} > \begin{array}{c}CH_2N(Me)SnBu_3\\|\\CH_2OSnBu_3\end{array} > \begin{array}{c}CH_2OSnBu_3\\|\\CH_2OSnBu_3\end{array} \gg \begin{array}{c}CH_2OSnBu_3\\|\\CH_2SSnBu_3\end{array} > \begin{array}{c}CH_2SSnBu_3\\|\\CH_2SSnBu_3\end{array}$$

TABLE 3

THE EQUIMOLAR REACTION OF BIS(TRIBUTYLSTANNYL) COMPOUNDS WITH THIONECARBONATE DERIVATIVES

Reactants	Reaction condition		Products (%)[a]	
	Temp (°C)	Time (h)	(XVIII)	C_2H_4S
	60	20	75 	93
	60	20	29 	35[b]
	150	20	20 	
	R.t.	1	61  [c]	
	60	20	37 	25
	R.t.	0.5	83  [c]	
	60	20	98 	84

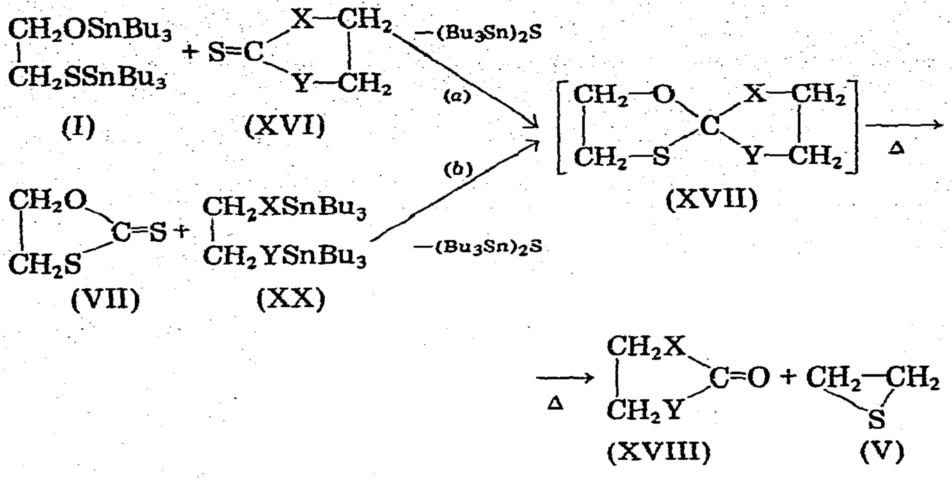
[a] $(Bu_3Sn)_2S$ was also formed. [b] Carbonyl sulfide was detected in the IR spectrum [ν(COS) 2040 cm^{-1}). [c] Cited from literature [8].

The reaction of cyclic thionecarbonate derivatives

The reaction of bis(tributylstannyl) ethylene glycolate or aminoethanolate with ethylene thionecarbonate to afford a cyclic orthocarbonate derivative, such as 1,4,6,9-tetraoxa- or 1-aza-4,6,9-trioxa-*spiro*[4,4]nonane, has already been disclosed in our previous paper [8]. In order to clarify the reaction path 5, we intend to discuss reaction 7 via sulfur-containing *spiro*-orthocarbonate derivatives (XVII).

Both in reaction *a* of the thionecarbonate (XVI, X = Y = O) with bis(tributylstannyl) mercaptoethanolate (I) and in the reaction *b* of the dithiocarbonate (VII) with bis(tributylstannyl) glycolate (XX, X = Y = O) for 20 h at 60°, the same products, i.e. bis(tributylstannyl) sulfide, ethylene carbonate, and ethylene sulfide, were isolated, which suggests that 1,4,6-trioxa-9-thia-*spiro*-[4,4]nonane (XVII, X = Y = O) is a common intermediate. Some efforts to isolate the intermediate (XVII) failed, although *spiro*-orthocarbonate derivatives containing sulfur and nitrogen atoms are known [8,13].

Reaction 7 was widely studied (Table 3) and afforded a new type of desulfurization reaction by organostannyl compounds.



(7

(X, Y = O,S or NMe)

Experimental

All boiling and melting points were uncorrected. Analyses were performed by Toa-gosei Chemical Co., Ltd. IR spectra were recorded on Nippon Bunko Model 403-G and IR-S spectrometers. NMR spectra were run with TMS as an internal standard on Japan Electron Optics C-60HL and JNM-HM60 spectrometers. All reactions and measurements were performed in dry nitrogen.

Solvents, ethylene carbonate, and trithiocarbonate were dried and distilled before use. Bis(tri-n-butylstannyl) glycolate [7], *N*-methyl aminoethanolate [8] tri-n-butylstannyl alkoxide and amide [14], ethylene thionecarbonate [7], and isothiocyanate [15] were prepared by reported methods.

Preparation of bis(tri-n-butylstannyl) mercaptoethanolate (I)

(A). Metallic sodium (0.31 mol) was added to a solution of 2-mercaptoethanol (0.15 mol) in dry toluene (200 ml), and refluxed with stirring for 3 h. Then, a solution of tri-n-butyltin chloride (0.30 mol) in toluene (100 ml) was added dropwise to the mixture, and the mixture was refluxed for 3 h. The sodium chloride which formed was separated by centrifugation. Distillation of the liquid mixture gave bis(tributylstannyl) mercaptoethanolate (I) in 63% yield; b.p. 200—210° (0.3 mmHg). IR ($CHCl_3$): 1070, 1000 and 960 cm^{-1}; NMR (CCl_4): τ 6.40 (t, CH_2O, 2H, J 6.3 Hz), 7.52 (t, CH_2S, 2H, J 6.3 Hz), and 8.15—9.3 ppm (br, SnBu, 54H). (Found: C, 47.32; H, 8.52. $C_{26}H_{58}OSSn$ calcd.: C, 47.74; H, 8.63%.)

(B). Equivalent amounts of diethylamino- or ethoxy-tri-n-butyltin and mercaptoethanol were heated for 2 h at 80°, and distilled to give the mercaptoethanolate (I) in 72 and 83% yields, respectively.

Preparation of bis(tri-n-butylstannyl) ethanedithiolate (XIII)

In the same manner as in (A) above, disodium ethanedithiolate prepared in situ from ethanedithiol (0.10 mol), and metallic sodium (0.20 mol) in toluene

(200 ml) were treated with tri-n-butyltin chloride, and the reaction mixture was distilled to afford bis(tri-n-butylstannyl) ethanedithiolate (XIII) in 58% yield; b.p. 210—220° (0.5 mmHg). IR (CCl_4): 1190, 1073, 961, 875 and 868 cm^{-1}; NMR (CCl_4): τ 7.48 (s, CH_2S, 4H) and 8.2—9.3 ppm (br, SnBu, 54H). (Found: C, 46.90; H, 8.59. $C_{26}H_{58}S_2Sn_2$ calcd.: C, 46.59; H, 8.40%.)

Reaction of bis(tri-n-butylstannyl) mercaptoethanolate (I) with isothiocyanates

As a typical example, the reaction with methyl isothiocyanate is described. Methyl isothiocyanate (21.4 mmol) was added to the mercaptoethanolate (I, 22.0 mmol) at room temperature, which showed the ν(C=N) band of the 1/1 adduct (II) at 1610 cm^{-1} in its IR spectrum. The mixture was heated for 20 h at 60°, and distilled to give 2-methylimino-1,3-oxathiolane (III, R = Me) in 64% yield; b.p. 117—118° (20 mmHg). IR (CCl_4): 1665 [ν(C=N)], 1070 and 1037 cm^{-1}; NMR (CCl_4): τ 7.10 (s, CH_3, 3H) and 6.65 ppm (t, *J* 6.7 Hz, CH_2O, 2H). (Found: C, 41.07; H, 5.94; N, 11.96. C_4H_7NOS calcd.: C, 40.96; H, 6.02; N, 11.96%.) Picrate: m.p. 143—144° (EtOH). IR (KBr): 1628, 1609, 1551, 1367 and 1330 (br) cm^{-1}. (Found: C, 34.54; H, 3.14; N, 16.26. $C_{10}H_{10}N_4O_8S$ calcd.: C, 34.69; H, 2.91; N, 16.18%.)

The volatiles trapped in a glass tube cooled by liquid nitrogen were analyzed by gas chromatography (Silicone DC-200, 25% column), which showed that they contained methyl isocyanate (5%). The distillation residue showed the characteristic band of ν(SnSSn) of bis(tri-n-butyltin) sulfide at 360 cm^{-1} in the IR spectrum, which agreed well with the spectrum of the authentic sulfide.

The reaction of I with ethyl, n- and iso-propyl, n- and tert-butyl, and cyclohexyl isothiocyanate were performed in the same manner, to afford the corresponding *N*-substituted 2-imino-1,3-oxathialanes (III), isocyanates and isothiocyanate, as shown in Table 1. The various 2-iminooxathiolanes (III) were identified by comparison of their m.p. or b.p., IR and NMR spectra with those of authentic samples [16.]

Phenyl isothiocyanate was treated with an equimolar amount of I in a sealed glass tube for 20 h at 60°, and n-hexane was added to precipitate 2-phenylimino-1,3-oxathialone; m.p. 65.5—66.5°(lit. [17] 65.0—65.5°), IR ν(C=N) (KBr): 1645 cm^{-1}; NMR (CCl_4): τ 5.60 (t, CH_2O, *J* 6.2 Hz, 2H), 6.69 (t, CH_2S, *J* 6.2 Hz, 2H), and 2.6—3.4 ppm (br, Ph, 5H). Distillation of the mother liquid gave bis(tributylstannyl) sulfide in 96% yield and the polymer (VI) [ν(CO) 1653 cm^{-1}] in 26% yield. The polymer was also obtained from the oxathiolane (III, R = Ph) by addition of a trace amount of water.

Reaction of bis(tri-n-butylstannyl) mercaptoethanolate (I) with carbon disulfide

An equimolar mixture (15 mmol of each) of I and carbon disulfide was heated in a sealed glass tube for 20 h at 60°, and the reaction mixture was submitted to column chromatography (Wako-gell C-100; n-hexane/$CHCl_3$) to afford ethylene dithiocarbonate (VII) in 65% yield; b.p. 65—69°(0.2 mmHg). IR ($CHCl_3$): ν(C=S) 1180 cm^{-1}; NMR ($CHCl_3$): τ 5.02 (t, CH_2O, *J* 7.2 Hz, 2H), and 6.28 (t, CH_2S, *J* 7.2 Hz, 2H); mass spectrum *m/e* 120. (Found: C, 29.96; H, 3.50. $C_3H_4O_2S$ calcd.: C, 29.98; H, 3.35%.) These results agreed well with those recently reported by Jones and Andreades [11].

At higher reaction temperatures (80—100°), the reaction mixture showed the ν(COS) band at 2030 cm^{-1} in the IR spectrum, and τ(CH_2—S) of ethylene sulfide at τ 7.63 ppm and τ(CH_2O) of ethylene oxide at 7.45 ppm in the NMR spectrum. By the column chromatographic separation, ethylene sulfide (V), thiol carbonate (XII) [ν(CO) 1743 cm^{-1}; τ(CH_2O) 5.54, τ(CH_2S) 6.41 ppm], dithiol carbonate (VIII) [ν(CO) 1743 cm^{-1}], and trithiocarbonate (IX) were isolated in small amounts. Minor products were identified by the comparison of their IR and NMR data with those of authentic samples.

Reaction of bis(tri-n-butylstannyl) ethanedithiolate (XIII) with phenyl isothiocyanate and methyl isothiocyanate

The mixture of the ethanedithiolate (XIII; 5.7 mmol) and phenyl isothiocyanate (2.5 mmol) was heated in a sealed glass tube for 5 days at 80°. The reaction mixture showed the ν(NCS) band of phenyl isothiocyanate at 2080 cm^{-1} in the IR spectrum and τ(CH_2S) of ethylene sulfide at τ 7.63 ppm in the NMR spectrum, and was submitted to column chromatography (Wakogell C-100; n-hexane/$CHCl_3$) to afford 2-phenylimino-1, 3-dithiolane, m.p. 44.5—45.5° (lit. [13] 47—48°), in 39% yield and bis(tributylstannyl) sulfide in almost quantitative yield.

Methyl isothiocyanate was treated with XIII for 5 days at 80° in the same manner as described above, and *N*-methylimino-1,3-dithiolane was obtained in 57% yield; b.p. 62—65° (0.1 mmHg). IR: ν(C=N) 1614 cm^{-1}; NMR: τ 6.90 (s, CH_3, 3H) and 6.3—6.8 ppm (m, OCH_2CH_2S, 4H). These spectra were the same of those of the authentic sample prepared by another method [13].

Reaction of bis(tri-n-butylstannyl) ethanedithiolate (XIII) with carbon disulfide

Carbon disulfide was allowed to react for 4 days at 60° with XIII and trithiocarbonate was obtained in 23% yield by column chromatography (Wakogell C-100; CCl_4/$CHCl_3$); m.p. 34—35°. Its IR and NMR spectra coincided well with those of the commercial sample.

The reaction of bis(tri-n-butylstannyl) compounds with thionecarbonate derivatives

An equimolar mixture of the title compounds (15 mmol of each) was heated under a dry nitrogen atmosphere, and the reaction mixture was separated by column chromatography to afford ethylene carbonate derivatives, ethylene sulfide, and bis(tri-n-butylstannyl) sulfide. Identification was performed by the comparison of IR and NMR spectra with those of authentic samples. The results are summarized in Table 3.

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