Conversion of Thiocarbonyl into Carbonyl Group by *O–S* Exchange Reaction with Dibutyltin Oxide or Bistributyltin Oxide[1)]

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Cyclic thionocarbonates and thionolactones, when heated with 1.0—1.5 mol eq of dibutyltin oxide or bistributyltin oxide in dioxane, gave the corresponding carbonates and lactones in satisfactory yields, respectively.

Keywords thiocarbonyl; thionocarbonate; thionolactone; carbonyl; dibutyltin oxide; bistributyltin oxide; *O–S* exchange reaction

Various literature methods are available for the conversion of thiocarbonyl compounds into their corresponding oxo-analogs, most of them utilizing either oxidizing agents or halogens,[3)] heavy metal cations (Ag^+, Hg^{2+}, Cu^+, *etc.*),[4)] sulfoxides with strong acids or iodine,[5)] selenoxides or telluroxides,[6)] or nitrosonium ion.[7)] The major disadvantage and limitation of these methods are that they are frequently not clean and require aqueous acidic conditions with excess reagents, thus not being applicable to acid-sensitive compounds. Furthermore, none of them is chemoselective: they do not distinguish the thione group in different chemical environments.

We present here a facile method based on the *O–S* exchange reaction between thiocarbonyl group and dibutyltin oxide or bistributyltin oxide, that works under neutral conditions with roughly equimolar reagent in aprotic solvents such as dioxane. It is noteworthy that this reaction is chemoselective for cyclic thionocarbonates and thionolactones; thioamides and thioureas are affected very slowly or not at all.

This method was based on the following observations. In an attempt to prepare the cyclic thionocarbonate **1a**, we examined the reaction of carbon disulfide with methyl β-L-arabinopyranoside after activation with 3 mol eq of dibutyltin oxide and found that the product was not the expected thionocarbonate **1a** but was the cyclic carbonate **1b**. We thought that the expected thionocarbonate **1a**, once formed, would give the carbonate **1b** by the *O–S* exchange reaction in the presence of excess reagent (Chart 1).[8)] In fact, activation of methyl β-L-arabinopyranoside with 0.5 mol eq of dibutyltin oxide followed by treatment with carbon disulfide resulted in the formation of the expected thionocarbonate **1a** in 39% yield with recovery of the starting material (58%). These findings provided a new entry for converting thionocarbonates into the corresponding carbonates under mild conditions.

Results and Discussion

When thiocarbonyl compounds were heated in dioxane[9)] under reflux for 4—5 h with 1.0—1.5 mol eq of dibutyltin oxide (method A) or distributyltin oxide (method B), the corresponding carbonyl compounds were produced in acceptable yields. The products were readily separated by chromatography over silica gel or by distillation, after evaporation of the solvent from the reaction mixture. The results are summarized in Table I.

The cyclic thionocarbonates (**1a—6a**) derived from carbohydrates gave, in all cases, the corresponding carbonates (**1b—6b**) by both methods A and B. The thionocarbonates derived from alditols (**8a**, **10a**, **12a**, and **13**) gave, in some cases, low yields or unidentified products by method A. However, for such cases, method B gave the expected oxo-products in acceptable yields, though the reason for this difference is obscure at present. It must be emphasized that in both methods the acetal group (*e.g.*, **5a**, **6a**, and **13a**) and the *O*-acetate group were completely unaffected, showing the reaction condition to be neutral.

The thionolactones (**14a—16a**) were converted into the corresponding lactones (**14b—16b**) in high yields by both methods A and B. The products with low molecular weight (**14b** and **15b**) were separated by distillation from the tin compounds. For them, the conversion yields were calculated on the basis of gas chromatography (GC) results.

The tertiary thiolactam (**17a**) gave the corresponding lactam (**17b**) only by method A in low yield with considerable recovery of the starting material, suggesting that an excess of the reagent and a longer reaction time are necessary. The secondary thiolactam (**18**) and the thiourea analogs (**19—21**) were inert to both reagents.

The open chain thionocarbonate (**22**) gave, on the same reaction, the original alcohol, probably due to the instability of the intermediate phenyl carbonate. The dithiocarbonate (**23**) was recovered unchanged, and dithioacetals were not

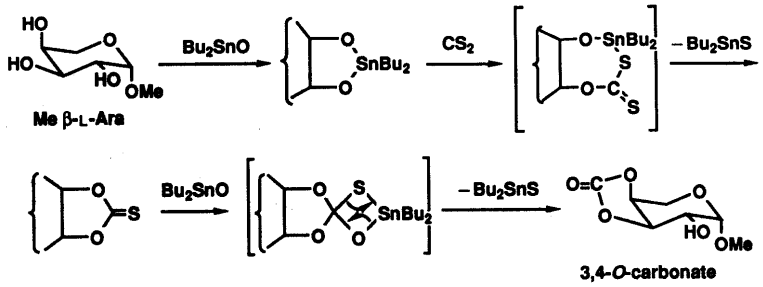

Chart 1

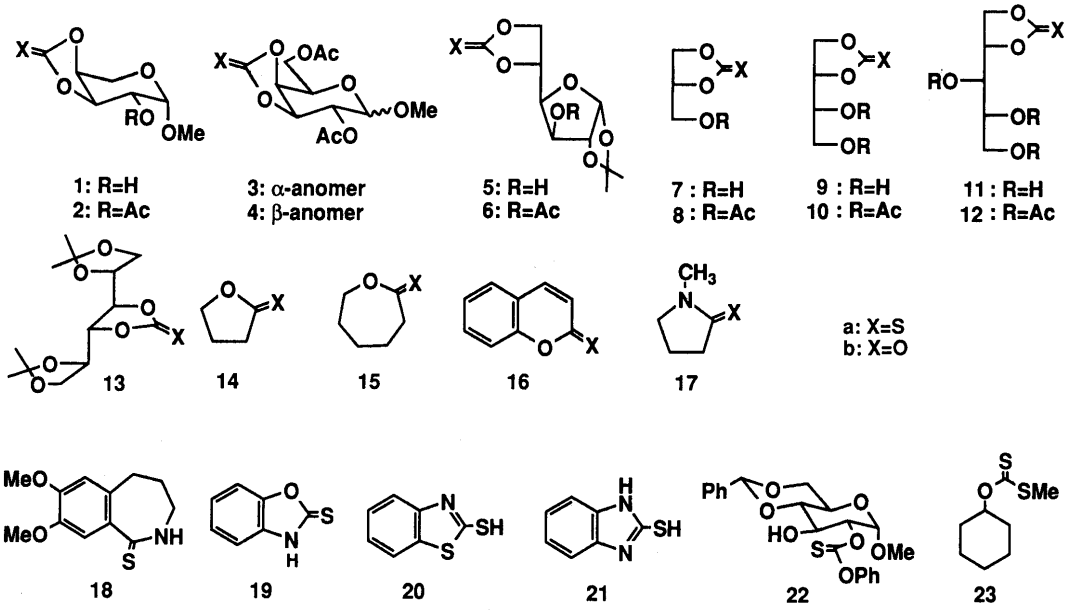

Chart 2

Table I. Conversion of Thiocarbonyl Compounds into the Oxo-Analogs by the *O–S* Exchange Reaction (Isolated Yield, %)

Thiocarbonyl	Method A[a]		Method B[b]	
	Carbonyl	s.m.[c]	Carbonyl	s.m.[c]
1a	72	—	87[d]	13[d]
2a	80	20	63	—
3a	67	—	68	—
4a	75	—	73	—
5a	85	15	80	15
6a	100	—	83	—
8a	51	—	97	—
10a	[e]	—	85	15
12a	[e]	—	86	14
13a	87	2	65	29
14a[f]	100	—	100	—
15a[f]	100	—	91	5
16a	97	3	94	5
17a	41	59	—	83

a) Bu_2SnO. *b*) $(Bu_3Sn)_2O$. *c*) Recovered starting material. *d*) Solvent, toluene. *e*) Unidentified product. *f*) Conversion yield was calculated by GC.

Table II. ^{13}C-NMR Data for Thionocarbonates and Carbonates[a]

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	C=X
Thionocarbonates							
7a[b]	71.2	83.8	61.4				193.8
8a	70.4	79.0	62.5				191.2
9a[b]	71.1	83.8	70.8	63.8			193.7
10a	70.0	79.9	69.4	61.4			190.7
11a[b]	72.8	84.1	72.2	72.1	63.7		194.0
12a	70.5	79.6	69.8	69.3	61.6		190.5
13a	65.7	73.9	82.8	82.8	73.9	65.7	190.4
Carbonates							
1b[c]	99.6	69.0	76.3	78.2	58.3		155.2
2b[c]	96.6	70.8	74.7	75.9	57.7		154.4
3b	96.0	64.4	74.6	74.1	69.4	62.0	153.1
4b	98.1	67.7	72.5	72.4	67.9	62.7	153.2
5b[c]	106.3	86.4	73.9	80.9	74.7	66.6	155.3
6b	105.1	83.2	76.2	78.1	73.0	66.3	154.1
8b	66.0	73.9	63.0				154.5
10b	65.7	74.5	69.8	61.4			154.0
12b	66.1	74.4	70.1	69.2	61.1		154.0
13b	65.5	74.3	77.7	77.7	74.3	65.5	153.7

a) In $CDCl_3$. The data for OMe and other protecting groups are omitted. *b*) In CD_3OD. *c*) In pyridine-d_5.

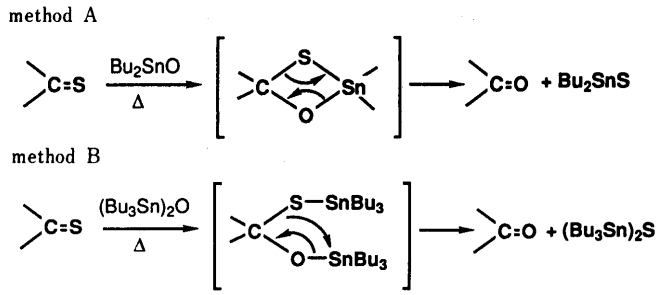

Chart 3

affected at all, as expected.

The above results show that the present methods (A and B) are chemoselective to cyclic thionocarbonates and thiolactones. In particular, the conversion of thionolactones into the corresponding lactones is important for the preparation of lactones, when coupled with the radical cyclization reaction of homoallyl xanthates into thionolactones.[10]

The reaction mechanism may be as follows: the borderline (soft) Sn species attacks the soft sulfur of the thiocarbonyl group and subsequent *O–S* exchange reaction takes place to produce the carbonyl compounds (Chart 3).

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Infrared (IR) spectra were taken in $CHCl_3$ solutions and data are given in cm^{-1}. Nuclear magnetic resonance (NMR) spectra (^{1}H, 400 MHz; ^{13}C, 100 MHz) were taken in $CDCl_3$ solutions with tetramethylsilane as an internal standard, the chemical shifts being given in δ values. For mass spectra (MS), major peaks are indicated in *m/z* (%). Identities were confirmed by mixed melting point determination (for crystalline compounds), and also comparisons of thin layer chromatographic (TLC) behavior and ^{1}H-NMR, ^{13}C-NMR, and IR spectra.

Thionocarbonates Cyclic thionocarbonates are readily preparable from polyols in a regioselective manner through activation with dibutyltin oxide followed by the action of phenoxythiocarbonyl chloride[11] or more conveniently by the action of thiophosgene as described below. The position of the resulting thiocarbonyl group was confirmed by the ^{13}C-NMR and IR spectra of the products and the corresponding carbonates obtained by the method described in this paper.

A mixture of a polyol (0.3 g) and Bu_2SnO (1.0—1.1 mol eq) in MeOH (10—30 ml) was heated under reflux for 4—5 h, and then concentrated to dryness. The dried residue was dissolved (or suspended) in dioxane (10—30 ml) and thiophosgene (1.0—1.1 mol eq) was added dropwise to this mixture under ice-cooling and stirring. After addition of the reagent, the mixture was brought to room temperature and stirring was continued for a further 1—4 h, and then the solvent was evaporated off. Chromatography of the residue gave a cyclic thionocarbonate from the chloroform and/or EtOAc eluates (yield, 67—84%).

Methyl 3,4-*O*-Thiocarbonyl-β-L-arabinopyranoside (**1a**): Yield 74%. Gum.[11] The *O*-acetate **2a**: Colorless needles from hexane–EtOAc, mp 118—120 °C (lit. 120—121 °C).[11]

Methyl 3,4-*O*-Thiocarbonyl-α-D-galactopyranoside: Yield 67%. Gum.[11] The di-*O*-acetate **3a**: Colorless needles from hexane–CH_2Cl_2, mp 132—134 °C (lit. 131—132 °C).[11]

Methyl 3,4-*O*-Thiocarbonyl-β-D-galactopyranoside: Yield 70%. Gum.[11] The di-*O*-acetate **4a**: Colorless prisms from AcOEt–benzene, mp 159—160 °C. This must be dimorphic to the reported specimen (colorless needles, mp 94—96 °C),[11] since the ^{1}H-NMR spectra of the two are superimposable. ^{1}H-NMR (500 MHz): 5.06 (1H, dd, J=8.8, 2 Hz, H-4), 5.03 (1H, t, J=3.9 Hz, H-2), 4.99 (1H, dd, J=8.8, 3.9 Hz, H-3), 4.75 (1H, d, J=3.9 Hz, H-1), 4.44, 4.31 (each 1H, dd, J=11.5, 6.4 Hz, H-6), 4.18 (1H, dt, J=6.4, 2 Hz, H-5), 3.45 (3H, s, OMe), 2.14, 2.12 (each 3H, s, OAc). The data suggest a boat conformation (probably $_2B_5$) for this compound.

1,2-*O*-Isopropylidene-5,6-*O*-thiocarbonyl-α-D-glucofuranose (**5a**): Yield 84%. Colorless needles from acetone–EtOAc, mp 215—216 °C (lit. 206—208 °C).[12] The *O*-acetate **6a**: Colorless needles from EtOH, mp 139—141 °C (lit. 144—146 °C).[12]

1,2-*O*-Thiocarbonylglycerol (**7a**): Yield 88%. Pale yellow syrup. IR: 1291 (C=S). ^{1}H-NMR (CD_3OD): 5.8—4.8 (1H, m, H-2), 4.7—4.3 (3H, m, H-1 and OH), 4.0—3.5 (2H, m, H-3). MS: 134 (M^+, 100). The *O*-acetate **8a**: Pale yellow syrup. IR: 1749 (OAc), 1294 (C=S). ^{1}H-NMR: 5.8—5.1 (1H, m, H-2), 4.8—4.2 (4H, m, H-1,3), 2.13 (3H, s, OAc). MS: 176 (M^+, 16).

1,2-*O*-Thiocarbonylerythritol (**9a**): Yield 76%. Pale yellow syrup. IR: 1288 (C=S). ^{1}H-NMR (CD_3OD): 5.1—4.9 (1H, m, H-2), 4.8—4.5 (5H, m, H-1,3 and OH), 3.60 (2H, d, J=4.6 Hz, H-4). MS: 164 (M^+, 74), 86 (100). The di-*O*-acetate **10a**: Colorless needles from ether, mp 89—92 °C. IR (KBr): 1742 (OAc), 1312 (C=S). ^{1}H-NMR: 5.4—5.3 (1H, m, H-3), 5.2—5.0 (1H, m, H-2), 4.8—4.7 (2H, m, H-1), 4.30 (2H, m, H-4), 2.13, 2.09 (each 3H, s, OAc). MS: 248 (M^+, 10). *Anal.* Calcd for $C_9H_{12}O_6S$: C, 43.55; H, 4.84. Found: C, 43.40; H, 5.00.

1,2-*O*-Thiocarbonylxylitol (**11a**): Yield 89%. Colorless needles from acetone, mp 119—120°C. IR (KBr): 1282 (C=S). ^{1}H-NMR (CD_3OD): 5.2—5.1 (1H, m, H-2), 4.9—4.5 (5H, m, H-1, 3, 4 and OH), 3.8—3.7 (4H, m, H-5 and OH). MS: 194 (M^+, 73), 57 (100). *Anal.* Calcd for $C_6H_{10}O_5S$: C, 37.11; H, 5.16. Found: C, 36.97; H, 5.26. The tri-*O*-acetate **12a**: Colorless prisms from AcOEt–hexane, mp 99—103 °C. IR: 1746 (OAc), 1296 (C=S). ^{1}H-NMR: 5.4—5.1 (3H, m, H-2, 3, 4), 4.8—4.1 (4H, m, H-1, 5), 2.19 2.14, 2.08 (each 3H, s, OAc). MS: 320 (M^+, 9). *Anal.* Calcd for $C_{12}H_{16}O_8S$: C, 45.00; H, 5.00. Found: C, 45.03; H, 5.26.

1,2;5,6-Di-*O*-isopropylidene-3,4-*O*-thiocarbonylmannitol (**13a**): Yield 58%. Colorless needles from ether, mp 165—167 °C (lit. 160—161 °C).[13] IR (KBr): 1324, 1301 (C=S). ^{1}H-NMR: 4.71—4.68 (2H, m, H-3,4), 4.3—4.2 (2H, m, H-2,5), 4.2—4.1, 4.0—3.9 (each 2H, m, H-1,6), 1.47, 1.35 (each 6H, s, Me). MS: 304 (M^+, 52), 101 (100). *Anal.* Calcd for $C_{13}H_{20}O_6S$: C, 51.31; H, 6.58. Found: C, 51.53; H, 6.62.

Thionolactones and Other Thiocarbonyl Compounds Compounds **14a**—**17a** and **18** were prepared from the corresponding lactones and lactams by the action of Lawesson's reagent and purified by chromatography. Compounds **19**—**21** are commercially available. The other thiocarbonyl compounds were prepared by conventional methods.

Reaction of Thiocarbonyl Compounds with Dibutyltin Oxide (Method A) A mixture of a thiocarbonyl compound (100—500 mg) and Bu_2SnO (1—1.1 mol eq) in dioxane (5—30 ml) was heated under reflux for 1—3 h. Progress of the reaction was monitored by TLC. The cooled mixture was concentrated to dryness and chromatographed. Elution of the column with benzene removes tin compound(s). Further elutions with AcOEt and AcOEt–acetone gave the carbonyl compound and the unchanged thiocabonyl compound (if present).

Reaction of Thiocarbonyl Compounds with Bistributyltin Oxide (Method B) A mixture of a thiocarbonyl compound (100—500 mg) and bistributyltin oxide (1—1.1 mol eq) in dioxane or toluene was heated under reflux for 2—4 h with stirring. The progress of the reaction was monitored by TLC. Evaporation of the solvent and chromatography of the residue as described above gave the corresponding carbonyl compounds.

Methyl 3,4-*O*-Carbonyl-β-L-arabinopyranoside (**1b**): Colorless needles from AcOEt–hexane, mp 115—119 °C. IR: 3400 (OH), 1780 (C=O). ^{1}H-NMR (pyridine-d_5): 5.19 (1H, t, J=7.0 Hz, H-3), 5.25—5.08 (1H, m, H-4), 4.99 (1H, d, J=3.6 Hz, H-1), 4.30 (1H, dd, J=7.0, 3.6 Hz, H-2), 4.10 (2H, d, J=1.5 Hz, H-5), 3.37 (3H, s, OMe). *Anal.* Calcd for $C_7H_{10}O_6$: C, 44.21; H, 5.30. Found: C, 43.92; H, 5.37.

Methyl 2-*O*-Acetyl-3,4-*O*-carbonyl-β-L-arabinopyranoside (**2b**): Colorless prisms from AcOEt–hexane, mp 118 °C. IR: 1813 (C=O), 1742 (OAc). ^{1}H-NMR (pyridine-d_5): 5.43 (1H, dd, J=7.3, 3.7 Hz, H-2), 5.17 (1H, dd, J=7.3, 2.7 Hz, H-4), 5.16 (1H, d, J=3.7 Hz, H-1), 4.17 (1H, d, J=14.3 Hz, H-5), 3.98 (1H, dd, J=14.3, 2.7 Hz, H-5), 3.29 (3H, s, OMe), 1.99 (3H, s, OAc). *Anal.* Calcd for $C_9H_{12}O_7$: C, 46.55; H, 5.21. Found: C, 46.39; H, 5.33.

Methyl 2,6-Di-*O*-acetyl-3,4-*O*-carbonyl-α-D-galactopyranoside (**3b**): Colorless prisms from ether–hexane, mp 134—135 °C. IR (KBr): 1808 (C=O), 1742 (OAc). ^{1}H-NMR (500 MHz): 5.00 (1H, dd, J=6.8, 3.9 Hz, H-2), 4.99 (1H, d, J=3.9 Hz, H-1), 4.86 (1H, t, J=6.8 Hz, H-3), 4.82 (1H, dd, J=6.8, 2.4 Hz, H-4), 4.34 (2H, m, H-6), 4.19 (1H, dt, J=10.3, 2.4 Hz, H-5), 3.41 (3H, s, OMe), 2.15, 2.11 (each 3H, s, OAc). MS: 305 (M^++1), 273 (M^+−OMe, 4). *Anal.* Calcd for $C_{12}H_{16}O_9$: C, 47.37; H, 5.26. Found: C, 47.31; H, 5.43.

Methyl 2,6-Di-*O*-acetyl-3,4-*O*-carbonyl-β-D-galactopyranoside (**4b**): Colorless prisms from AcOEt–hexane, mp 149—150°C. IR (KBr): 1809 (C=O), 1745 (OAc). ^{1}H-NMR: 5.03 (1H, t, J=3.4 Hz, H-2), 4.89 (1H, dd, J=8.3, 2 Hz, H-4), 4.79 (1H, d, J=3.4 Hz, H-1), 4.77 (1H, dd, J=8.3, 3.4 Hz, H-3), 4.39, 4.28 (each 1H, dd, J=11.2, 6.3 Hz, H-6), 4.15 (1H, dt, J=6.3, 2 Hz, H-5), 3.44 (3H, s, OMe), 2.14, 2.12 (each 3H, s, OAc). The data suggest a boat conformation (probably $_2B_5$) for this compound. *Anal.* Calcd for $C_{12}H_{16}O_9$: C, 47.37; H, 5.26. Found: C, 47.08; H, 5.37.

5,6-*O*-Carbonyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**5b**): Colorless needles from AcOEt, mp 233—235 °C. IR (KBr): 1791 (C=O). ^{1}H-NMR (pyridine-d_5): 6.25 (1H, d, J=3.7 Hz, H-1), 5.20 (1H, m, H-5), 4.92, 4.56 (each 1H, d, J=8.2 Hz, H-6), 4.9—4.0 (3H, m, H-2, 3, 4), 1.51, 1.31 (each 3H, s, Me). *Anal.* Calcd for $C_{10}H_{14}O_7$: C, 48.78; H, 5.73. Found: C, 48.88; H, 5.65.

3-*O*-Acetyl-3,4-*O*-carbonyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**6b**): Colorless needles from AcOEt–hexane, mp 133 °C. IR: 1802 (C=O), 1743 (OAc). ^{1}H-NMR (pyridine-d_5): 5.94 (1H, d, J=3.8 Hz, H-1), 5.27 (1H, d, J=3.5 Hz, H-3), 4.88 (1H, dt, J=8.5, 6.0 Hz, H-5), 4.58 (1H, dd, J=8.5, 6.5 Hz, H-6), 4.51 (1H, dd, J=6.0, 3.5 Hz, H-4), 4.51 (1H, t, J=8.5 Hz, H-6), 2.11 (3H, s, OMe), 1.53, 1.32 (each 3H, s, Me). *Anal.* Calcd for $C_{12}H_{16}O_8$: C, 50.00; H, 5.60. Found: C, 49.96; H, 5.67.

3-*O*-Acetyl-1,2-*O*-carbonylglycerol (**8b**): Pale yellow oil. IR: 1811 (C=O), 1747 (OAc). ^{1}H-NMR: 5.1—4.8 (1H, m, H-2), 4.7—4.1 (4H, m, H-1, 3), 2.12 (3H, s, OAc). MS: 161 (M^++1, 10), 130 (100).

3,4-Di-*O*-acetyl-1,2-*O*-carbonylerythritol (**10b**): Colorless oil. IR: 1813 (C=O), 1746 (OAc). ^{1}H-NMR: 5.4—5.1 (1H, m, H-3), 5.0—4.8 (1H, m, H-2), 4.6—4.5 (2H, m, H-1), 4.30 (2H, m, H-4), 2.13, 2.09 (each 3H, s, OAc). MS: 233 (M^++1, 1).

3,4,5-Tri-*O*-acetyl-1,2-*O*-carbonylxylitol (**12b**): Colorless prisms from AcOEt–hexane, mp 99—101 °C. IR: 1812 (C=O), 1738 (OAc). ^{1}H-NMR: 5.4—5.3 (2H, m, H-3, 4), 5.0—4.9 (1H, m, H-2), 4.6—4.4 (2H, m, H-1), 4.20 (2H, m, H-5), 2.18, 2.12, 2.07 (each 3H, s, OAc). MS: 305 (M^++1, 5). *Anal.* Calcd for $C_{12}H_{16}O_9$: C, 47.37; H, 5.26. Found: C, 47.16; H, 5.49.

3,4-*O*-Carbonyl-1,2;5,6-di-*O*-isopropylidenemannitol (**13b**): Colorless needles from ether, mp 150—151 °C (lit. 147 °C).[13] IR (KBr): 1815 (C=O). ^{1}H-NMR: 4.5—4.45 (2H, m, H-3, 4), 4.3—4.22 (2H, m, H-2, 5), 4.2—4.1, 4.0—3.95 (each 2H, m, H-1, 6), 1.46, 1.35 (each 6H, s, Me). MS: 289 (M^++1, 2), 273 (M^+−Me, 100). *Anal.* Calcd for $C_{13}H_{20}O_7$: C, 54.17; H, 6.94. Found: C, 54.01; H, 7.09.

Reaction of Methyl β-L-Arabinopyranoside with Carbon Disulfide through Activation by Bu_2SnO (1) Methyl β-L-arabinopyranoside (0.2 g) and Bu_2SnO (0.91 g, 3 mol eq) in MeOH (20 ml) were heated under reflux for 3 h, and then the solvent was evaporated off *in vacuo*. The dried residue was suspended in dichloroethane (10 ml) and CS_2 (2 ml) and the suspension was stirred at 100 °C for 25 h. The mixture was concentrated and the residue was chromatographed to give the 3,4-*O*-carbonyl derivative **1b**

(75 mg, 30%), mp 115—119 °C, from the benzene–AcOEt (1 : 1) eluate.

(2) Methyl β-L-arabinopyranoside (0.2 g) was stannylated with Bu_2SnO (0.18 g, 0.5 mol eq) and treated with CS_2 (2 ml) in dichloroethane (10 ml) as described above. Chromatography of the product gave the 3,4-*O*-thiocarbonyl derivative **1a** (97 mg, 39%) as a gum, from the benzene–AcOEt (1 : 1) eluate. The AcOEt eluate gave recovered starting material (116 mg, 58%).

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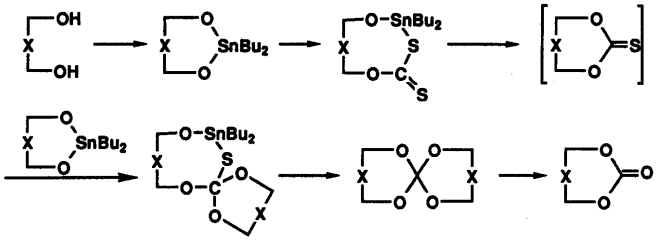

Chart 4

9) When the reaction of **1a** with dibutyltin oxide was carried out in MeOH, the product was a mixture of the methyl 3-*O*-carbonate and the methyl 4-*O*-carbonate in a ratio of 10 : 3. The same reaction with the *O*-mesylate (**1a**, R = Ms) instead resulted in the dimethyl orthoester. These results indicate that addition of the solvent to the thione group followed by hydrolytic cleavage takes place in hydroxylic solvents, supporting the *O–S* exchange reaction proposed in this paper.
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