Thio-Sugars III. Radical Catalyzed Thione–Thiol Rearrangement of Cyclic Thionocarbonates on a Pyranose Ring: Formation of *cis*-Arranged Cyclic Thiolcarbonates[1,2]

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Pyranoside 3,4-*cis*-thionocarbonates, under radical-promoted reaction conditions (method A, B, or C, described in the text), gave *O–S* rearrangement products, 3,4-thiolcarbonates of *cis*-stereochemistry, in acceptable yields. 2,3-Thionocarbonates of *trans*-stereochemistry also gave the rearrangement products of *cis*-stereochemistry preferentially in method B (photolysis with hexabutyldistannane). Although regio-control of the product was not satisfactory in most cases, some of the results suggested that the regioselectivity of the reaction is markedly influenced by the stereochemistry of the anomeric position of the substrates. The products were converted to thioglycosides (peracetate forms) by conventional means.

Key words thio-sugar; thione–thiol rearrangement; cyclic thionocarbonate; tin radical; regiochemistry; stereochemistry

Thio-glycosides, in which one of the secondary hydroxyl groups is substituted by a thiol group, are of synthetic interest, because they sometimes appear as a segment of bio-active natural products.[4] Their regio- and stereo-selective synthesis, particularly in the case of those with a thiol group on a pyranose ring, from the corresponding common glycosides has been a problem, because a direct *SN*2 displacement reaction on a pyranose ring is usually difficult for stereochemical reasons. In 1987, Tsuda *et al.*[2] reported an entirely different approach *via* a radical-catalyzed *O–S* rearrangement of cyclic thionocarbonates derived from common glycosides, obtaining several thiol-pyranosides as their carbonate derivatives, all of which are otherwise hardly preparable or require multiple synthetic steps. This tin-radical-catalyzed *O–S* rearrangement is based on the discovery that deoxygenation of Me 3,4-thiocarbonyl-β-L-Ara[5] with tributyltin hydride and α,α-azobisisobutyronitrile (AIBN) was always accompanied by the formation of 3-thiol and 4-thiol-carbonates.[6] In studies to increase the yield of the thione–thiol rearrangement products, it was revealed that the use of 0.3 mol eq of tributyltin hydride and 0.3 mol eq of AIBN was enough to convert more than 60% of the substrate, clearly demonstrating that the reaction proceeded catalytically. The scheme indicated in Chart 1 was thus suggested.[2] Later, this new method was successfully applied for preparation of a thio–glycoside constituent in ene–diyne antibiotics, calicheamicins.[7]

In addition to the original method (method A: heating with tributyltin hydride and AIBN),[2] two other modifications (method B: photolysis with hexabutyldistannane, and method C: thermolysis with dimethyl phosphonate and benzoyl peroxide) were proposed.[8] The results of application of these methods to cyclic thionocarbonates derived from primary–secondary glycols were discussed in detail in a previous paper.[8] The present paper describes in detail the results for thionocarbonates prepared from secondary–secondary 1,2-glycols, and discusses the stereo- and regio-chemical outcome, *i.e.*, the formation of *cis*-arranged thiolcarbonates as the major products.

The cyclic thionocarbonates of *cis*-1,2-glycols (**1a**, **b**, **d**, **e**, **f**) are readily preparable regioselectively from the corresponding glycosides by the action of dibutyltin oxide in methanol followed by thiocarbonylation with phenoxythiocarbonyl chloride or thiophosgene.[9] In the cases of partially protected *trans*-1,2-glycols (**8**), the direct thiocarbonylation with thiophosgene in pyridine–dioxane[10] gave satisfactory results. The dibutyltin oxide method gave a mixture of the thiocarbonyl chloride (**9a**) and the thionocarbonate (**10a**). The former was convertible to the latter on treatment with 4-dimethylaminopyridine

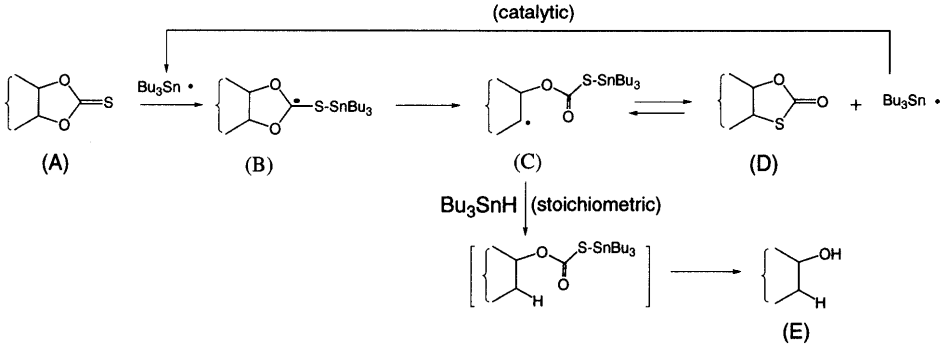

Chart 1

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(DMAP) (for details, see Experimental).

In contrast to the thionocarbonates derived from primary–secondary glycols, which afforded the primary-*S* rearrangement products in good yields when treated with KI in MeCN,[8,11] those derived from secondary–secondary glycols were inert to the ionic reaction.[12]

Results and Discussion

3,4-*cis*-*O*-Thionocarbonates of Arabinosides and Galactosides Table 1 summarizes the results for Me 2-*O*-acetyl-3,4-O-thiocarbonyl-β-L-Ara (**1b**) by method A (thermolysis with tributyltin hydride and AIBN). It indicates that

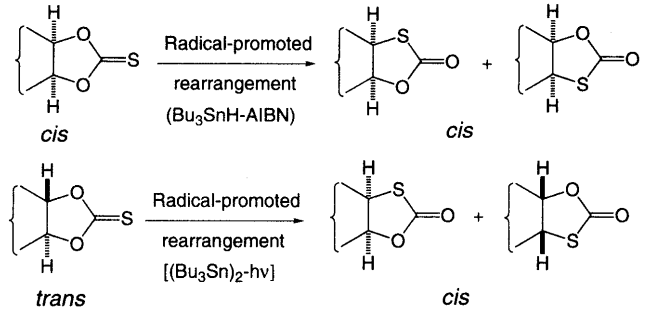
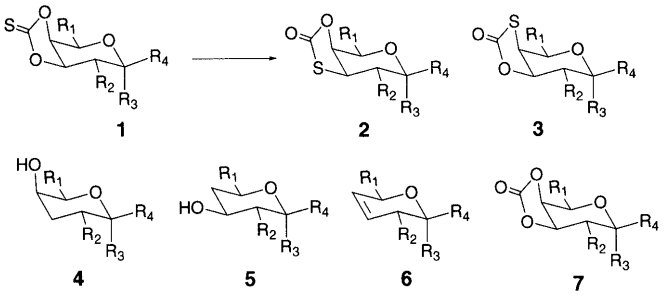


Chart 2



	R_1	R_2	R_3	R_4
a	H	OH	OMe	H
b	H	OAc	OMe	H
c	H	OTs	OMe	H
d	H	OH	H	OPh
e	CH_2OAc	OAc	OMe	H
f	CH_2OAc	OAc	H	OMe

Chart 3

the use of excess amount of AIBN over the tin hydride is effective to suppress the formation of deoxy derivatives (**4b**, **5b**). When AIBN was used catalytically, deoxygenation occurred to an appreciable extent. The formation of the oxo derivative (**7b**) is due to air contamination and/or original contamination in the substrate.[6] This compound was sometimes observed as a major product, when the reaction was slow (entry A-7) or when a stored tin hydride was used.[6] Satisfactory conversion yield (**2b**+**3b**) was obtained in the reaction in dilute toluene solution at 110 °C for 3 h with the use of 0.3 mol eq of freshly distilled Bu_3SnH and 1 mol eq of AIBN (entry A-8). The reaction at a higher concentration (entry A-9) reduced the conversion yield with increase of the recovery of the starting material.

The stereochemistry of the rearrangement products (**2**, **3**) was *cis*, as already suggested,[2] while the regioselectivity (**2b**/**3b**) was low and variable: not exceeding 2.0 except in one case (entry A-6). The other derivatives of β-arabinoside (**1a**, **1c**) gave analogous results in terms of conversion yield and selectivity (3-*S*/4-*S*) by method A (Table 2). It is noticeable that the derivative of Ph α-L-Ara (**1d**) showed relatively high selectivity, suggesting that the stereochemistry of the anomeric position may affect the selectivity in this rearrangement.

The conversion yield and selectivity were not remarkably changed in the other methods, B and C (Table 3). Method B gave comparable yield to method A. In this method, the formation of olefins (**6**) was confirmed by actual isolation. Formation of oxo derivatives (**7**) was minimized in this method. Formation of deoxy derivatives (**4**, **5**) was not avoided even in method B. It is interesting that method C (for **1b**) showed reversed regioselectivity for 3-*S* and 4-*S* products, but the selectivity was not large and the conversion yield was the lowest among the three methods (conditions were not optimized).

3,4-*O*-Thionocarbonates derived from galactosides (**1e**, **1f**) also gave *O*–*S* rearrangement products of *cis*-configuration in acceptable yields (Tables 2, 3). Although the regioselectivities for 3-*S* and 4-*S* products were not satisfactory, it is interesting that they were reversed in ratios for α- and β-galactosides. Although method C gave the highest selectivity and neither the olefin nor deoxy derivative was produced, its conversion yield was the

Table 1. *O*–*S* Rearrangement of Me 3,4-*O*-Thiocarbonyl-β-L-Ara (**1b**) by the Bu_3SnH–AIBN Method (Method A)[a]

Entry	Reagent ratio[b]	Condition		Recov. **1b**	Deoxy **4b**+**5b**	Oxo **7b**	Conv. **2b**+**3b**	Others	Selectivity (3-*S*/4-*S*) **2b**/**3b**
		°C	h						
A-1	1:1 :0.5	75	0.5	—	20	8	69	3	1.5
A-2	1:1 :0.5	110	0.5	—	55	2	42	12	1.8
A-3	1:1 :1	75	0.5	4	28	—	67	4	1.6
A-4	1:1 :5	75	0.5	8	25	8	54	4	1.7
A-5	1:0.5:0.25	110	2.5	—	30	5	62	3	1.4
A-6	1:0.8:0.8	75	0.5	11	27	8	52	10	2.1
A-7[c]	1:0.3:0.3	110	3.5	17	—	23	60	—	1.3
A-8	1:0.3:1	110	3.0	5	6	4	79	—	1.2
A-9[d]	1:0.3:1	110	6.0	42	7	26	22	3	0.9

a) The substrate **1b** (20—30 mg) in benzene (75 °C) or in toluene (110 °C) (each 3 ml) and the reagents (indicated) were heated in an Ar atmosphere and the product was analyzed by GLC (given by %). See also Experimental. *b*) The molar ratio of **1b**: Bu_3SnH: AIBN. *c*) This run was described in the communication (ref. 2). *d*) Higher concentration condition: the substrate (300 mg) in toluene (10 ml).

Table 2. *O–S* Rearrangement of Pyranoside-*cis*-3,4-*O*-Thionocarbonates by Method A (Yield, % by GLC)

Entry	Compd.	Method[a]	Condition		Recov. 1	Olefin 6	Deoxy 4+5	Oxo 7	3-*S* 2	4-*S* 3	Conv. 2+3	Selectivity 2/3
			°C	h								
1.	**1a**	A-7[b]	90	3.0	10.0	?[c]	trace	20.0	42.0	27.3	69.3 (78)[d]	1.5
2.		A-8	110	3.0	16.6	?	4.0	3.7	34.4	28.8	63.2 (76)	1.2
3.	**1b**	A-8	110	3.0	5.1	?	6.1	4.2	43.2	35.3	78.5 (83)	1.2
4.	**1c**	A-8	110	3.0	23.4	?	5.7	1.0	28.6[e]	36.7[e]	65.3 (85)	0.8[e]
5.	**1d**	A-7[b,f]	90	2.5	—	?	25.0	21.0	40.8	10.2	51.0	4.0
6.	**1e**	A-7[b]	90	3.0	trace	?	21.0	trace	34.3	44.7	79.0 (79)	0.8
7.		A-8	110	3.0	13.9	?	6.5	10.4	28.2	30.5	57.8 (67)	0.9
8.	**1f**	A-7[b]	90	3	25.0	—	10.0	8.0	29.6	27.4	57.0 (76)	1.1
9.		A-8	110	3.0	14.8	—	9.1	14.3	33.1	20.1	53.2 (62)	1.6

a) A-7 and A-8 indicate the reagent ratios as in Table 1. *b*) The results of method A-7 were reported in the communication (ref. 2). *c*) ? indicates that the olefin may be present, but was not identified, because of very low peak intensity. *d*) Parenthetical values indicate net yields. *e*) Single peak in GLC, but NMR indicated it is a mixture. The ratio was determined after separation of **2c** and **3c**. *f*) Isolation yields.

Table 3. Comparison of Radical Sources (Methods A, B, C) (Yield, % by GLC)

Entry	Compd.	Method[a]	Condition		Recov. 1	Olefin 6	Deoxy 4+5	Oxo 7	3-*S* 2	4-*S* 3	Conv. 2+3	Selectivity 2/3
			°C	h								
1.	**1b**	A	110	3.0	5.1	?[b]	6.1	4.2	43.2	35.3	78.5 (83)[c]	1.2
2.		B			—	—	18.2	3.4	38.2	38.2	76.4 (76)	1.0
3.		C			25.5	—	—	—	22.4	27.8	50.2 (67)	0.8
4.	**1e**	A	110	3.0	13.9	?	6.5	10.4	28.2	30.5	57.8 (67)	0.9
5.		B[d]			—	6.8	24.2[e]	—	24.6	26.2	50.8	0.9
6.		C			14.7	—	—	—	25.6	30.0	55.6 (65)	0.9
7.	**1f**	A	110	3.0	14.8	—	9.1	14.3	33.1	20.1	53.2 (62)	1.6
8.		B[d]			—	8.1	22.4	—	32.8	27.4	60.2	1.2
9.		C			26.6	—	—	—	25.6	11.1	36.7 (50)	2.3

a) A: Bu_3SnH–AIBN (A-8), B: $(Bu_3Sn)_2$–*hv*, C: $(MeO)_2PHO$–$(PhCOO)_2$. See Experimental. *b*) ? indicates that the compound may be present, but was not identified, because of very low intensity. *c*) Parenthetical values indicate net yields. *d*) Isolation yields. *e*) 4-Deoxy derivative (**5**) only. See Experimental.

lowest among the three methods. It is interesting that the deoxy product produced from **1e** by method B was the 4-deoxy derivative (**5e**) exclusively, though the 3-*S* and 4-*S* products (**2e**, **3e**) were produced in nearly equal amounts.

2,3-*trans*-*O*-Thionocarbonates of Glucosides Unexpectedly, the *trans*-disposed thionocarbonates (**10**) resisted the rearrangement reaction by method A (Table 4). The conversion yield (**12**+**13**) was poor even in the prolonged reaction, though the reason is unknown. Method C was again unsatisfactory. In contrast to the cases of arabinoside and galactoside, appreciable amounts of deoxy derivatives were produced. However, the compounds (**10**) smoothly rearranged by method B to afford the *cis*-products, *manno* (2-*S*) and *allo* (3-*S*) type thiolcarbonates, **12** and **13**, in satisfactory yields,[13] together with minute amounts of known by-products, **14**—**17**. The above results indicate that thiolcarbonates produced by a radical-promoted rearrangement always take *cis*-configuration regardless of the stereochemistry of the original thionocarbonates, confirming our previous suggestion[2] that radical-promoted rearrangement reaction gives the thermodynamically more stable *cis*-products in a 5–6 fused ring system. Detailed product analysis from the photolysis reaction of **10a**, however, revealed formations of other interesting by-products: the 3-*S*-*trans* derivative (**18a**) in 3% yield and the 3-phenyl derivative (**19a**) in 4% yield. These products are formed from 3-radical intermediate. A phenyl radical (possibly produced from benzene) must be involved in the formation of the latter compound. A typical gas chromatogram of the products from **10a** is shown in Fig. 1. The thioamide (**11a**) was inert to the above radical-promoted reactions.

The regioselectivity (3-*S*/2-*S*) of the products was low (0.8) in the α-isomer (**10a**), but high (3.9) in the β-isomer (**10b**). Although the result appears to suggest that the selectivity is reversed depending on the anomeric configuration, the total yield of the products from the 3-radical (**13a**+**18a**+**19a**) exceeds that from the 2-radical (**12a**) (3-radical/2-radical = 1.2), indicating that the 3-radical is preferentially generated even in the α-anomer (deoxy derivatives are omitted from the calculation because of the ambiguity of the corresponding yields).[14]

Structure Determination of the Rearrangement Products The 3-*S* and 4-*S* rearrangement products (**2**, **3**) from arabinosides and galactosides were separable from deoxy (**4**, **5**) and oxo derivatives (**7**) by column chromatography on silica gel, but were usually hardly separable from each other and from the thionocarbonates (**1**). The combination of high performance liquid chromatography (HPLC) on a Lobar silica gel column and recycling HPLC on a JAIGEL H column effected their separation. The structures of the products were readily determined by analyses of the ^1H- and ^{13}C-NMR spectra, and by ^1H–^1H and ^1H–^{13}C correlation spectroscopy (COSY), in which the proton and carbon geminal or attached to *S* always

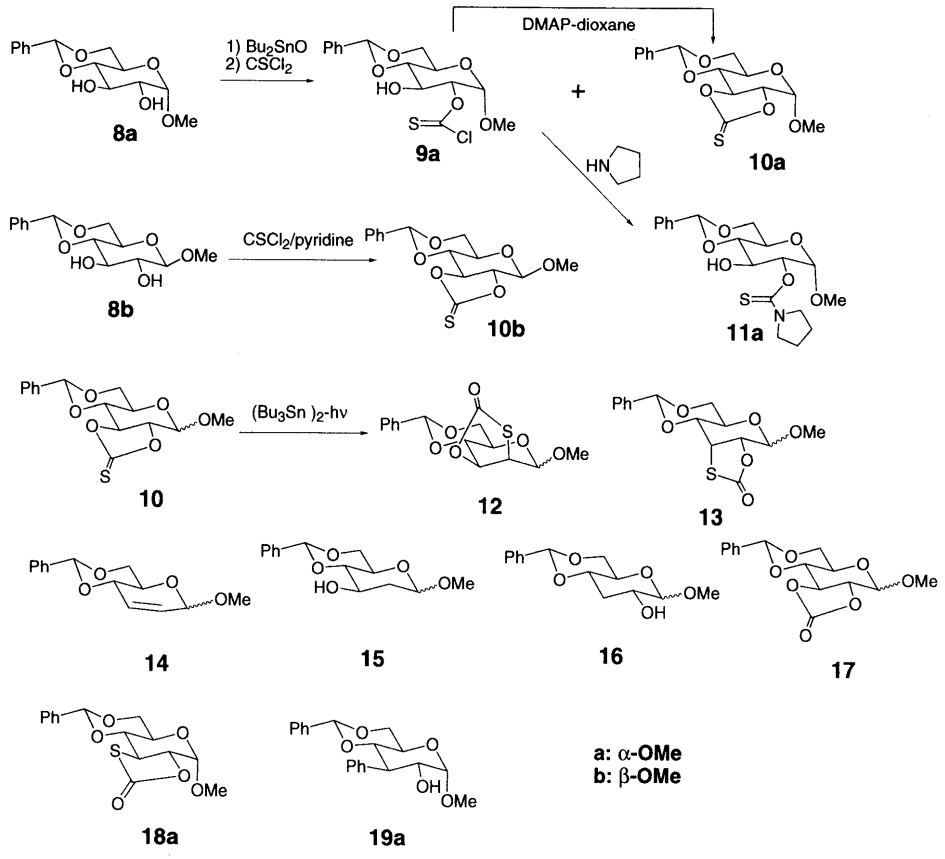


Chart 4

Table 4. *O–S* Rearrangement of 4,6-*O*-Benzylidene-2,3-*O*-thiocarbonyl-D-Glc (**10**) (Yield, % by GLC)

Entry	Compd.	Method	Condition		Recov.	Olefin	Deoxy	Oxo	2-*S*	3-*S*	Conv.	Selectivity
			°C	h	**10**	**14**	**15**+**16**	**17**	**12**	**13**	**12**+**13**	**13/12**
1.	**10a**(α)	A[a]	110	3.0	72.5	0.4	6.5	6.8	6.5	3.0	9.5 (36)[b]	0.5
2.		B		3.0	1.0	5.8	7.5	1.9	29.2	(36.2)[c]	(65.4)[c]	0.8[d]
3.		C[e]	120	1.0	10.3	—	33.1	9.4	19.9	12.8	32.7 (36)	0.6
4.	**10b**(β)	A[a]	110	6.0	57.1	0.7	9.4	10.3	4.6	16.0	20.6 (48)	3.5
5.		B		3.0	—	4.7	17.5	2.2	14.0	54.0	68.0 (68)	3.9

a) Method A-8 in Table 1. *b*) Parenthetical values indicate net yields. *c*) The peak contains **19a**, which was inseparable from **13a** in GLC. *d*) Calculated value from the isolation yields (see Experimental). *e*) In dioxane, sealed tube. Reagents were added 3 times, every 20 min.

resonated up-field than those attached to C–*O* or *O*. Structure determination of the rearrangement products of **1b** has been described already.[6] For deoxy products, a comment is necessary. The 4-deoxy products bearing a 2-OAc group were often accompanied by an acetyl migration product (*i.e.*, the 2-hydroxy-3-acetoxy derivative) in the reactions run at over 100 °C (in toluene).[6] Such easy acyl migration between equatorially disposed 1,2-glycols is particularly evident between the 2 and 3 positions of the pyranoside skeleton.[15]

The stereochemistries of the products from the *gluco*-derivatives were established similarly by detailed analysis of their two dimensional (2D)-NMR spectra after isolation of each product. The 2-*S* and 3-*S* products, **12** and **13**, had *manno* and *allo* structures, respectively, and **18a** had a *gluco*-structure. However, the ^{1}H-NMR spectrum of **13b** was rather unusual, since H-3 (geminal to *S*) appeared 0.3 ppm downfield from the signal of H-2 (geminal to *O*). Thus, X-ray analyses of **12b** and **13b** were undertaken. The results proved that the assigned structures were correct, but the reason for this spectral abnormality of **13b** is unknown.

The structure determination of **19a** was done as follows. It had one more phenyl group than the deoxy compounds. The H–H and C–H COSY spectra revealed the proton and carbon sequences in the skeleton and the stereochemistry as depicted.

Conversion of Thiolcarbonates to Thio-sugars Each of the above prepared thiolcarbonates (**2**, **3**) was converted to the corresponding thio-glycosides by methanolysis with 0.05 M NaOMe in the presence of $NaBH_4$ in order to minimize dimerization of the resulting thiols. They were characterized as the peracetates, **20b**—**25b**. However, formation of *S–S* dimers (designated with ') was sometimes hardly avoidable even under the above reductive condition. Similarly, **12** and **13** were converted to

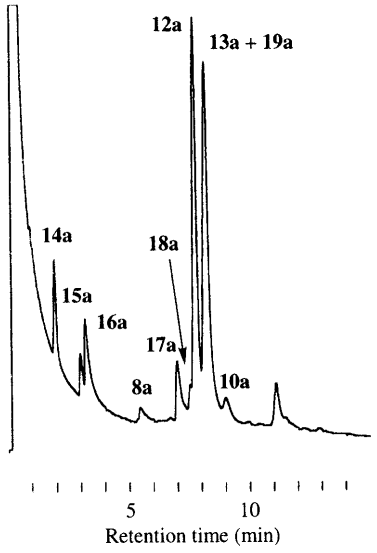


Fig. 1. Example of GLC of the Reaction Products of **10a**

See also Table 4, entry 2. GLC conditions: N_2 flow, 45 ml/min; injection temperature, 290 °C; column temperature, 150 °C to 250 °C at 8 °C/min.

26b—29b, by successive treatment with 90% AcOH, NaOMe, and Ac_2O–pyridine.

Conclusion

Thionocarbonates derived from carbohydrate 1,2-glycols, when subjected to one of the above-described radical-promoted reactions, afforded *O–S* rearrangement products in acceptable yields; these compounds were otherwise hardly preparable or required multiple synthetic steps. The stereochemistry of the product was *cis*, regardless of the stereochemistry of the original thionocarbonates. The regio-control of the product is not satisfactory, but some of the above results suggest that the regioselectivity can be improved, if the reaction is performed with a suitably designed compound under a suitably controlled condition, though further work is needed on this point.

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were determined on a Yanaco melting point apparatus and are uncorrected. IR spectra were taken in chloroform solutions and the data are given in cm^{-1}. NMR spectra were measured on a JEOL GSX-400 or GX-500 (400 MHz for ^1H and 100 MHz for ^{13}C or 500 MHz for ^1H and 125 MHz for ^{13}C) spectrometer in $CDCl_3$ solutions with tetramethylsilane as an internal standard and the chemical shifts are given in δ values. Mass spectra (MS) and high resolution MS (HR-MS) were taken with a Hitachi M-80 machine at 70 eV and M^+ and/or $M^+ - Me$ are indicated as *m/z* (%). GLC analyses were carried out with a Shimadzu GC4CM-PF gas chromatograph with a glass column (4 mm × 1 m) packed with 1.5% OV-1 on Shimalite W (80—100 mesh) and a flame ionization detector (FID), using N_2 (60 ml/min) as a carrier gas; the column temperature was increased at 5 °C/min, from 150 °C to 250 °C. Column chromatography was performed on silica gel (Wakogel C-200). HPLC was performed on a Lobar Si column (MPLC) and recycling HPLC on a JAIGEL H column with $CHCl_3$ as a mobile phase. For TLC, Merck precoated plates GF_{254} were used and spots were developed by spraying 5% H_2SO_4 and heating the plates until coloration took place. All organic extracts were washed with brine and dried over anhydrous Na_2SO_4 before concentration. Identities were confirmed by comparisons of TLC behavior and of ^1H- and/or ^{13}C-NMR spectra.

Thionocarbonates 3,4-*O*-Thionocarbonates (**1a—b**, **1d—f**) were reported in ref. 9*a* and 9*b*.

Table 5. ^{13}C-NMR Data for Thio-Glycosides and Related Compounds (in $CDCl_3$)[a,b]

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	C=X
1c	96.9	75.6	77.5	79.5	56.4	—	189.4
9a	95.7	84.3	68.5	81.1	62.1	68.7	186.7
11a	97.7	81.5	68.7	78.4	62.0	69.0	184.1
10a	96.9	79.8	79.1	80.3	64.8	68.3	190.1
10b	101.4	81.2	78.6	81.8	68.2	69.1	189.9
17a	96.6	77.7	75.9	79.7	65.0	68.0	152.9
19a	99.4	71.8	49.6	79.9	64.2	69.2	—
2b	95.7	72.8	46.1	79.5	57.0	—	171.0
	(96.3	73.5	47.0	80.6	57.5	—	171.5)[c]
2c	96.6	78.6	46.3	79.6	57.0	—	170.5
2d	(102.1	63.6	53.2	79.8	73.9	—	172.4)[c]
2e	96.0	72.6	46.6	78.9	64.8	62.8	170.5
	(97.3	73.1	47.4	79.9	65.3	64.6	170.0)[c]
2f	101.5	72.9	49.5	78.0	71.6	62.8	170.1
	(101.9	73.7	50.5	79.5	72.1	63.1	170.1)[c]
3b	97.0	68.8	77.1	47.3	57.0	—	170.9
	(97.0	69.3	78.0	48.2	57.3	—	170.1)[c]
3c	97.8	74.9	76.4	47.8	56.4	—	169.7
3d	(99.5	67.3	82.1	44.7	60.6	—	[c,d]
3e	96.9	68.9	77.1	50.4	63.4	64.4	170.5
	(96.5	69.3	78.1	51.1	63.2	64.0	170.3)[c]
3f	101.3	69.2	79.8	50.3	69.8	64.1	170.3
12a	96.7	50.7	77.6	77.1	60.8	68.5	170.0
12b	99.1	51.4	78.4	77.4	65.1	68.6	171.2
13a	97.3	74.2	48.8	75.6	57.2	68.7	173.1
13b	100.5	78.4	49.3	75.1	63.5	68.7	171.2
18a	95.8	81.0	48.4	80.2	65.9	68.7	170.6
20b	96.9	67.6	42.2	71.6	60.6	—	
20b′	96.6	69.0	52.1	70.4	60.8	—	
21b	97.6	69.3	67.3	45.0	61.8	—	
21b′	97.8	69.3	68.4	52.1	60.4	—	
22b	96.8	67.1	43.3	67.9	67.1	62.3	
23b	97.2	69.5	67.8	46.9	66.6	63.8	
23b′	97.1	68.8	69.7	57.6	66.7	63.6	
24b	103.1	67.7	47.0	68.8	73.1	61.9	
24b′	102.2	68.7	60.3	69.4	72.9	62.1	
25b	102.4	69.8	71.1	46.0	71.3	63.2	
26b	101.0	47.1	68.6	66.8	68.5	62.3	
27b	96.5	67.4	43.9	65.5	65.1	62.0	
28b	100.3	48.2	71.0	66.7	72.7	62.3	
29b	100.4	68.7	44.3	66.4	72.6	62.6	

a) Data for protecting groups are omitted. *b*) Signal assignments were confirmed by C–H COSY spectra. *c*) Parenthetical values are data in pyridine-d_5. *d*) The signal was too small to be observed.

Me 3,4-*O*-Thiocarbonyl-2-*O*-tosyl-β-L-Ara (**1c**): Tosylation of **1a** with TsCl in pyridine gave **1c** (89%) as colorless prisms from AcOEt–hexane, mp 163—164 °C. IR: 1293 (C=S). ^1H-NMR: 7.82, 7.39 (each 2H, d, J=8.2 Hz, Ar-H), 5.01 (1H, d, J=3.5 Hz, H-1), 4.92 (1H, dd, J=8.0, 7.2 Hz, H-3), 4.82 (1H, dd, J=7.2, 2.8 Hz, H-4), 4.30 (1H, dd, J=8.0, 3.5 Hz, H-2), 4.14 (1H, d, J=14.7 Hz, H-5), 3.92 (1H, dd, J=14.7, 2.8 Hz, H-5), 3.44 (3H, s, OMe), 2.47 (3H, s, Me). *Anal.* Calcd for $C_{14}H_{16}O_7S_2$: C, 46.66; H, 4.47. Found: C, 46.86; H, 4.45.

Me 4,6-*O*-Benzylidene-2,3-*O*-thiocarbonyl-β-D-Glc (10b) Thiophosgene (500 μl) and pyridine (1.5 ml) were added successively to a solution of **8b** (500 mg) in dioxane (10 ml) at 65 °C and the mixture was stirred for 10 min at the same temperature. After having been cooled to room temperature, the mixture was diluted with $CHCl_3$, washed with water 3 times, and decolorized with activated charcoal. Removal of the solvent and chromatography of the residue gave **10b** (392 mg, 68%) from the $CHCl_3$–AcOEt (39:1) eluate. It formed colorless prisms from AcOEt–hexane, mp 197—200 °C. IR: 1277 (C=S). ^1H-NMR 7.50—7.36 (5H, m, Ph-H), 5.60 (1H, s, PhC<u>H</u>O_2), 4.85 (1H, d, J=7.9 Hz, H-1), 4.52 (1H, dd, J=12.0, 10.0 Hz, H-3), 4.40 (1H, dd, J=10.5, 4.7 Hz, H-6), 4.13 (1H, dd, J=12.0, 7.9 Hz, H-2), 4.09 (1H, dd, J=10.0, 8.7 Hz, H-4), 3.93 (1H, t, J=10.5 Hz, H-6), 3.61 (3H, s, OMe), 3.49 (1H, ddd, J=10.0, 8.7, 4.7 Hz, H-5). *Anal.* Calcd for $C_{15}H_{16}O_6S$: C, 55.55; H, 4.97. Found: C, 55.57; H, 4.92.

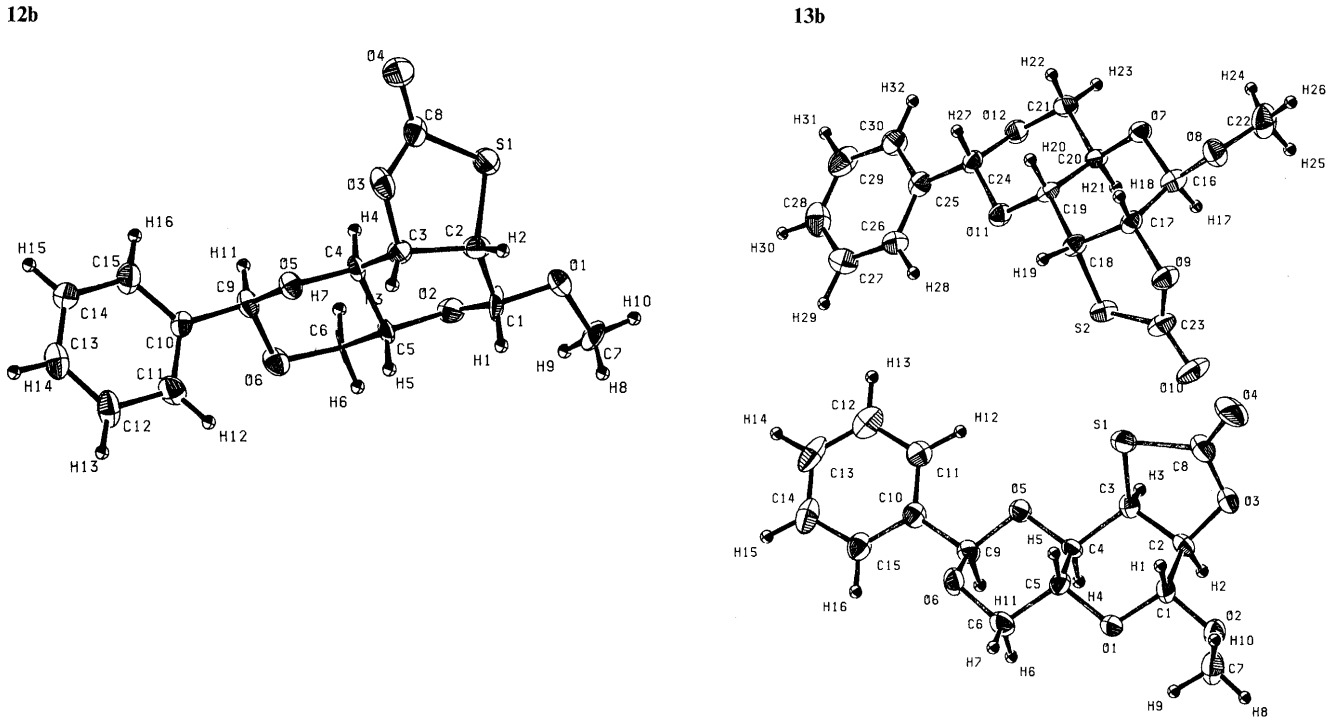


Fig. 2. ORTEP Drawing of Compounds **12b** and **13b** (The Compound Was Analyzed as a Twin Molecule)

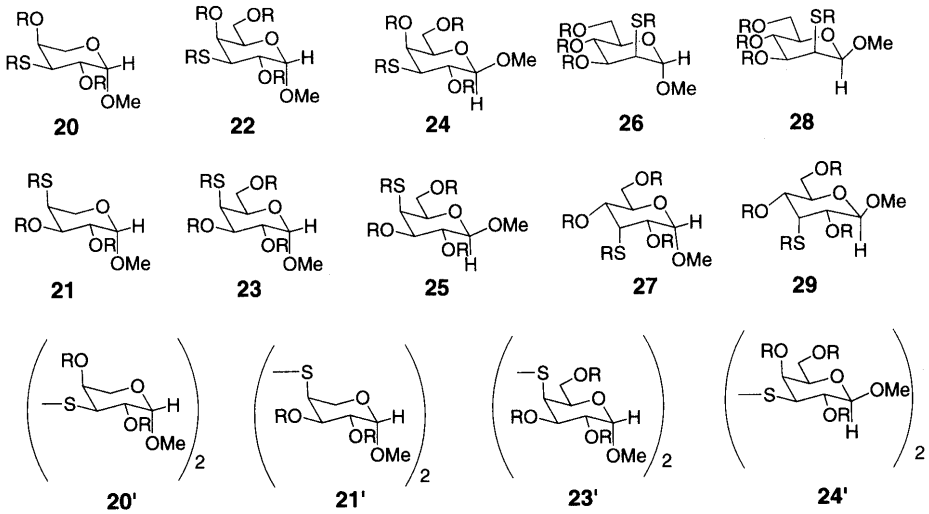


Chart 5

Me 4,6-*O*-Benzylidene-2,3-*O*-thiocarbonyl-α-D-Glc (10a) 1) The α-isomer (**8a**) was similarly treated with $CSCl_2$[10] to give **10a** (78%) as colorless needles from Et_2O, mp 134—136 °C (lit. 137—138 °C).[10]

2) A mixture of **8a** (285 mg) and Bu_2SnO (285 mg, 1.1 mol eq) in MeOH (20 ml) was heated under reflux for 3 h and concentrated to dryness. The dried residue was dissolved in dioxane (10 ml) and $CSCl_2$ (0.1 ml, 1.0 mol eq) was added at 10 °C. The mixture was stirred overnight at room temperature, poured into water, and extracted with $CHCl_3$. Chromatography of the product gave the thiocarbonyl chloride **9a** (212 mg, 58%) and the thionocarbonate **10a** (109 mg, 33%) from the $CHCl_3$–AcOEt (29:1) eluate. **9a**: Colorless needles from Et_2O, mp 175—178 °C. IR: 3430 (OH), 1295 (C=S). ^{1}H-NMR 7.50—7.37 (5H, m, Ph-H), 5.55 (1H, s, PhC$\underline{H}O_2$), 5.32 (1H, dd, J=9.8, 3.9 Hz, H-2), 5.15 (1H, d, J=3.9 Hz, H-1), 4.35 (1H, t, J=9.8 Hz, H-3), 4.31 (1H, dd, J=10.0, 4.9 Hz, H-6), 3.89 (1H, td, J=10.0, 4.9 Hz, H-5), 3.76 (1H, t, J=10.0 Hz, H-6), 3.59 (1H, t, J=9.8 Hz, H-4), 3.42 (3H, s, OMe). MS: 361 (M^+-1 for ^{37}Cl, 1.4), 359 (M^+-1 for ^{35}Cl, 3.5). *Anal.* Calcd for $C_{15}H_{17}ClO_6S$: C, 49.93; H, 4.72. Found: C, 49.88; H, 4.82.

A mixture of **9a** (70 mg) and DMAP (26 mg, 1.1 mol eq) in CH_2Cl_2 (2 ml) was stirred for 1 h at room temperature. The mixture was diluted with CH_2Cl_2 and washed with 10% HCl. Concentration of the organic layer and chromatography of the residue gave **10a** (52 mg, 83%).

The Pyrrolidino-thioamide (**11a**): Treatment of **9a** (900 mg) with pyrrolidine (0.62 ml, 3 mol eq) in CH_2Cl_2 (20 ml) at room temperature for 1 h and work-up as above gave **11a** (853 mg, 87%) as colorless prisms from AcOEt–hexane, mp 220—222 °C. ^{1}H-NMR: 7.52—7.33 (5H, m, Ph-H), 5.53 (1H, s, PhC$\underline{H}O_2$), 5.50 (1H, dd, J=10.0, 3.8 Hz, H-2), 5.07 (1H, d, J=3.8 Hz, H-1), 4.27 (1H, dd, J=10.0, 4.5 Hz, H-6), 4.21 (1H, t, J=10.0 Hz, H-3), 3.82 (1H, td, J=10.0, 4.5 Hz, H-5), 3.74 (1H, t, J=10.0 Hz, H-6), 3.56 (1H, t, J=10.0 Hz, H-4), 3.71—3.57, 1.99—1.85 (each 4H, m, pyrrolidine ring), 3.37 (3H, s, OMe). MS: 396 (M^++1, 1). *Anal.* Calcd for $C_{19}H_{25}O_6NS$: C, 57.71; H, 6.37; N, 3.54. Found: C, 57.53; H, 6.48; N, 3.49.

Analysis of the Rearrangement Products 1) Method A: The substrates (25—30 mg) and AIBN were dissolved in benzene or toluene (3—5 ml) and the vessel was filled with Ar gas. Tributyltin hydride was injected

and the mixture was heated (75—90 °C for benzene and 110 °C for toluene). For reagent ratios and reaction conditions, see Table 1. The cooled mixture was poured onto a silica gel column and the column was washed with hexane–benzene to remove tin compound(s), then eluted with AcOEt. The AcOEt eluate was concentrated and the residue was analyzed by GLC (Tables 1—4). The yield (%) was calculated from the ratio of the peak area of each product to the sum of the peak areas of all products, excluding the solvent peak.

2) Method B: A photolysis vessel containing the substrate (50 mg) in dry benzene (60 ml) was flushed and filled with Ar gas. Then, freshly distilled $(Bu_3Sn)_2$ (2 mol eq) was injected and the whole was internally irradiated by a 100 W high-pressure mercury lamp (>290 nm) for 2 h at 10—15 °C. The mixture was passed through a short silica gel column to remove tin compound(s), then the column was eluted with AcOEt and the eluate was analyzed by GLC (Tables 3, 4).

3) Method C: Each of **1b**, **1e**, and **1f** (0.05—0.5 mmol) was heated with dimethyl phosphonate (4.0 mol eq) in dioxane (5 ml) under reflux for 12 h with periodical addition of $(PhCOO)_2$ (0.4 mol eq) every 2 h. After evaporation of dioxane *in vacuo*, the residue was distributed between AcOEt and water, and the AcOEt layer was passed through a silica gel column. The eluate was analyzed by GLC (Table 3).

***O–S* Rearrangement by Method A (Preparative Reaction)** The substrates (100—300 mg) were subjected to the reaction by method A-7 or A-8. The AcOEt eluate obtained as in the analytical procedure was separated by MPLC (benzene–AcOEt, 1 : 1) and then recycling HPLC ($CHCl_3$).

1) Reaction of **1b** (300 mg) in toluene (50 ml) by Method A-8 gave the AcOEt eluate (354 mg), from which **2b** and **3b** were isolated. These were identical with the compounds previously reported.[6)]

2) Reaction of **1c** (300 mg) in toluene (50 ml) by Method A-8 gave the AcOEt eluate (354 mg), from which **2c** and **3c** were isolated.

Me 3,4-*S*, *O*-Carbonyl-2-*O*-tosyl-3-thio-β-L-Ara (**2c**): Colorless prisms from $CHCl_3$–hexane, mp 163—166 °C. IR: 1746. ^{1}H-NMR 7.81, 7.38 (each 2H, d, J=8.2 Hz, Ar-H), 4.96 (1H, d, J=3.1 Hz, H-1), 4.62 (1H, dd, J=4.7, 2.3 Hz, H-4), 4.42 (1H, dd, J=10.2, 3.1 Hz, H-2), 4.07 (1H, d, J=13.9 Hz, H-5), 3.91—3.87 (2H, m, H-3, H-5), 3.43 (3H, s, OMe), 2.47 (3H, s, Me). *Anal.* Calcd for $C_{14}H_{16}O_7S_2$: C, 46.66; H, 4.47. Found: C, 46.84; H, 4.53.

Me 3, 4-*O*, *S*-Carbonyl-2-*O*-tosyl-4-thio-β-L-Ara (**3c**): Colorless prisms from $CHCl_3$–hexane, mp 114—118 °C. IR: 1750. ^{1}H-NMR 7.81, 7.38 (each 2H, d, J=8.2 Hz, Ar-H), 4.99 (1H, d, J=3.1 Hz, H-1), 4.82 (1H, dd, J=10.5, 8.4 Hz, H-3), 4.66 (1H, dd, J=8.4, 3.1 Hz, H-2), 4.35 (1H, m, H-4), 4.01 (1H, dd, J=13.8, 3.5 Hz, H-5), 3.61 (1H, dd, J=13.8, 1.9 Hz, H-5), 3.44 (3H, s, OMe), 2.45 (3H, s, Me). *Anal.* Calcd for $C_{14}H_{16}O_7S_2$: C, 46.66; H, 4.47. Found: C, 46.65; H, 4.39.

3) Reaction of **1d** (100 mg) in benzene (25 ml) by Method A-7 gave the AcOEt eluate (103 mg) which was separated by MPLC to give the 3-*S* **2d** (42 mg), 4-*S* **3d** (9.4 mg), the oxo **7d** (22 mg) derivatives, and a 4 : 6 mixture (24 mg) of **5d** and **6d**.

Ph 3,4-*S*,*O*-Carbonyl-3-thio-α-L-Ara (**2d**): Colorless needles from AcOEt–hexane, mp 201—202 °C. IR: 1720. ^{1}H-NMR: 7.40—6.80 (5H, m, Ph-H), 5.35 (1H, d, J=7.2 Hz, H-1), 5.03—4.85 (1H, m, H-4), 4.50 (1H, dd, J=13.5, 2.8 Hz, H-5), 4.40—4.20 (2H, m, H-2, 3), 4.06 (1H, dd, J=13.5, 3.0 Hz, H-5). MS: 268 (M^+), 174 (M^+ −PhOH). HR-MS: Calcd for $C_{12}H_{12}O_5S$: 268.0405. Found: 268.0503.

Ph 3,4-*O*,*S*-Carbonyl-4-thio-α-L-Ara (**3d**): Colorless prisms from CH_2Cl_2–hexane, mp 141—143 °C. IR: 1740. ^{1}H-NMR: 7.40—6.80 (5H, m, Ph-H), 5.77 (1H, d, J=4.2 Hz, H-1), 5.18 (1H, t, J=5.5 Hz, H-3), 4.59 (1H, dd, J=5.5, 4.2 Hz, H-2), 4.68—3.80 (3H, m, H-4, 5). MS: 268 (M^+), 174 (M^+ −PhOH). HR-MS: Calcd for $C_{12}H_{12}O_5S$: 268.0405. Found: 268.0410.

Ph 3,4-*O*-Carbonyl-α-L-Ara (**7d**): Colorless needles from AcOEt–hexane, mp 188—190 °C. IR: 1800. ^{1}H-NMR: 7.25—6.80 (5H, m, Ph-H), 5.62 (1H, d, J=6.0 Hz, H-1), 5.23—5.08 (2H, m, H-3, 4), 4.60—4.37 (1H, m, H-2), 4.37—4.20 (2H, m, H-5). MS: 252 (M^+), 158 (M^+ −PhOH). *Anal.* Calcd for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80. Found: C, 57.02; H, 4.77.

4) Reaction of **1e** (200 mg) in benzene (50 ml) by Method A-7 gave the AcOEt eluate (214 mg), which afforded a mixture of **2e** and **3e** (73 mg) and a mixture of deoxy products (83 mg). See also below.

5) Reaction of **1f** (100 mg) in benzene (25 ml) by Method A-7 gave the AcOEt eluate (101 mg), which afforded a mixture of **2f** and **3f** (57 mg) and a mixture of deoxy products (16.8 mg). See also below.

***O–S* Rearrangement by Method B (Preparative Reaction)** 1) A mixture of **1e** (500 mg) in dry benzene (150 ml) and freshly distilled $(Bu_3Sn)_2$ (1.58 ml, 2 mol eq) was degassed and irradiated by a 300 W high-pressure mercury lamp for 2 h at 10—15 °C as in the analytical procedure. The reaction mixture was poured onto a silica gel column and the column was washed with benzene, then eluted with $CHCl_3$–AcOEt. The fraction with the 14 : 1 eluate gave the olefin **6e** (26 mg, 6.8%), the 3-*S* product **2e** (123 mg, 24.6%), and the 4-*S* product **3e** (131 mg, 26.2%). The 2 : 1 eluate gave the 4-deoxy derivative **5e**[9a)] (99 mg, 24.2%). The mixtures were separated by recycling HPLC.

Me 2,6-Di-*O*-acetyl-3,4-*S*,*O*-carbonyl-3-thio-α-D-Gal (**2e**): Colorless oil. IR: 1750. ^{1}H-NMR: 4.99 (1H, d, J=3.9 Hz, H-1), 4.90 (1H, dd, J=10.3, 3.9 Hz, H-2), 4.71 (1H, dd, J=4.9, 2.4 Hz, H-4), 4.35—4.33 (2H, m, H-6), 4.20—4.17 (1H, m, H-5), 3.99 (1H, dd, J=10.3, 4.9 Hz, H-3), 3.42 (3H, s, OMe), 2.13, 2.11 (each 3H, s, OAc). MS: 321 (M^++1, 1), 289 (M^+−OMe, 4). HR-MS: Calcd for $C_{11}H_{13}O_7S$ (M^+−OMe): 289.0382. Found: 289.0377.

Me 2,6-Di-*O*-acetyl-3,4-*O*,*S*-carbonyl-4-thio-α-D-Gal (**3e**): Colorless oil. IR: 1748. ^{1}H-NMR: 5.20 (1H, dd, J=9.3, 3.9 Hz, H-2), 5.02 (1H, d, J=3.9 Hz, H-1), 4.96 (1H, dd, J=9.3, 6.8 Hz, H-3), 4.51 (1H, dd, J=6.8, 2.9 Hz, H-4), 4.43 (1H, td, J=5.9, 2.9 Hz, H-5), 4.20, 4.12 (each 1H, dd, J=11.7, 5.9 Hz, H-6), 3.42 (3H, s, OMe), 2.15, 2.12 (each 3H, s, OAc). MS: 321 (M^++1, 1), 289 (M^+−OMe, 4). HR-MS: Calcd for $C_{11}H_{13}O_7S$ (M^+−OMe): 289.0382. Found: 289.0379.

2) The reaction of **1f** (500 mg) as above for 1 h gave the olefin **6f**[9a)] (31 mg, 8.1%), the 3-*S* derivative **2f** (164 mg, 32.8%), and the 4-*S* derivative **3f** (137 mg, 27.4%) from the $CHCl_3$–AcOEt (14 : 1) eluate. Further elution gave the 4-deoxy derivative **5f**[9a)] (39 mg, 9.5%) and the 3-deoxy derivative **4f** (53 mg, 12.9%).

Me 2,6-Di-*O*-acetyl-3,4-*S*,*O*-carbonyl-3-thio-β-D-Gal (**2f**): Colorless needles from AcOEt, mp 172—173 °C. IR: 1738. ^{1}H-NMR: 5.07 (1H, dd, J=9.3, 8.3 Hz, H-2), 4.68 (1H, dd, J=5.4, 1.9 Hz, H-4), 4.42 (1H, dd, J=11.2, 6.3 Hz, H-6), 4.41 (1H, d, J=8.3 Hz, H-1), 4.32 (1H, dd, J=11.2, 6.3 Hz, H-6), 4.04 (1H, td, J=6.3, 1.9 Hz, H-5), 3.79 (1H, dd, J=9.3, 5.4 Hz, H-3), 3.49 (3H, s, OMe), 2.12, 2.11 (each 3H, s, OAc). MS: 289 (M^+−OMe, 3). *Anal.* Calcd for $C_{12}H_{16}O_8S$: C, 45.00; H, 5.04. Found: C, 44.95; H, 5.01.

Me 2,6-Di-*O*-acetyl-3,4-*O*,*S*-carbonyl-4-thio-β-D-Gal (**3f**): Colorless oil. IR: 1745. ^{1}H-NMR: 5.24 (1H, t, J=8.3 Hz, H-2), 4.77 (1H, dd, J=8.3, 6.8 Hz, H-3), 4.47 (1H, dd, J=6.8, 2.4 Hz, H-4), 4.40 (1H, d, J=8.3 Hz, H-1), 4.27 (1H, dd, J=11.2, 5.4 Hz, H-6), 4.19 (1H, td, J=5.4, 2.4 Hz, H-5), 4.13 (1H, dd, J=11.2, 5.4 Hz, H-6), 3.52 (3H, s, OMe), 2.13, 2.11 (each 3H, s, OAc). MS: 289 (M^+−OMe, 1). HR-MS: Calcd for $C_{11}H_{13}O_7S$ (M^+−OMe): 289.0382. Found: 289.0386.

The 3-deoxy derivative (**4e**) was crystallized in colorless prisms from EtOH–hexane, mp 132—134 °C. It was identical with an authentic specimen (lit. syrup)[9a)] by ^{1}H-NMR comparison.

3) A mixture of **10a** (300 mg) and freshly distilled $(Bu_3Sn)_2$ (930 μl, 2 mol eq) in dry benzene (150 ml) was degassed, irradiated by a 100 W high-pressure mercury lamp for 3 h and worked up as described above. The product was chromatographed to give three fractions: i) **12a**, **14a**, and **18a** (126 mg), ii) **13a** and **19a** (85 mg), and iii) **15a** and **16a** (96 mg), from the $CHCl_3$–AcOEt (19 : 1) eluate. The AcOEt eluate gave the diol **8a** (35 mg). The above fraction i) was separated by recycling HPLC to afford 2-*S* **12a** (57.4 mg, 19.1%), the olefin **14a** (7.5 mg, 3.3%), and 3-*S*-*gluco* **18a** (9 mg, 3%). Fraction ii) gave 3-*S* **13a** (45.4 mg, 15%) and the 3-phenyl derivative **19a** (12 mg, 4%). The carbonate **17a** was isolated in some runs.

Me 4,6-*O*-Benzylidene-2,3-*S*,*O*-carbonyl-2-thio-α-D-Man (**12a**): Colorless gum. IR: 1752. ^{1}H-NMR: 7.49—7.36 (5H, m, Ph-H), 5.59 (1H, s, PhC<u>H</u>O$_2$), 4.92 (1H, dd, J=9.0, 7.0 Hz, H-3), 4.89 (1H, br s, H-1), 4.48 (1H, br d, J=7.0 Hz, H-2), 4.35 (1H, dd, J=10.0, 5.0 Hz, H-6), 4.13 (1H, dd, J=10.0, 9.0 Hz, H-4), 3.91 (1H, td, J=10.0, 5.0 Hz, H-5), 3.84 (1H, t, J=10.0 Hz, H-6), 3.41 (3H, s, OMe). HR-MS: Calcd for $C_{15}H_{17}O_6S$ (M^++1): 325.0744 . Found: 325.0709.

Me 4,6-*O*-Benzylidene-2,3-*O*,*S*-carbonyl-3-thio-α-D-All (**13a**): Colorless needles from acetone, mp 184—186 °C. IR (KBr): 1732. ^{1}H-NMR: 7.46—7.37 (5H, m, Ph-H), 5.59 (1H, s, PhC<u>H</u>O$_2$), 4.87 (1H, d, J=5.0 Hz, H-1), 4.86 (1H, dd, J=6.5, 5.0 Hz, H-2), 4.82 (1H, dd, J=6.5, 5.0 Hz, H-3), 4.38 (1H, dd, J=10.0, 5.0 Hz, H-6), 4.33 (1H, td, J=9.8, 5.2 Hz, H-5), 4.02 (1H, dd, J=9.3, 5.0 Hz, H-4), 3.79 (1H, t, J=10.0 Hz, H-6), 3.46 (3H, s, OMe). MS: 324 (M^+, 3). *Anal.* Calcd for $C_{15}H_{16}O_6S$: C, 55.55; H, 4.97. Found. 55.29; H, 5.33.

Me 4,6-*O*-Benzylidene-2,3-*O*,*S*-carbonyl-3-thio-α-D-Glc (**18a**): Colorless gum. IR: 1747. ^{1}H-NMR: 7.48—7.36 (5H, m, Ph-H), 5.56 (1H, s, PhC<u>H</u>O$_2$), 5.11 (1H, d, J=3.1 Hz, H-1), 4.50 (1H, dd, J=11.9, 10.6 Hz,

H-3), 4.31 (1H, dd, $J=10.6$, 4.5 Hz, H-6), 4.27 (1H, dd, $J=11.9$, 3.1 Hz, H-2), 3.93 (1H, ddd, $J=10.3$, 8.9, 4.5 Hz, H-5), 3.84 (1H, dd, $J=10.6$, 8.9 Hz, H-4), 3.83 (1H, t, $J=10.5$ Hz, H-6), 3.55 (3H, s, OMe). MS: 324 (M^+, 9), 281 (48), 175 (21), 149 (31), 136 (100). HR-MS: Calcd for $C_{15}H_{16}O_6S$: 324.0668 (M^+). Found: 324.0676.

The olefin (**14a**): Colorless needles, mp 119—121 °C (lit. 119—120 °C).[16]

Me 4,6-*O*-Benzylidene-2,3-*O*-carbonyl-α-D-Glc (**17a**): Gum. IR: 1800. ^{1}H-NMR: 7.71—7.36 (5H, m, Ph-H), 5.60 (1H, s, PhC$\underline{H}$O$_2$), 5.18 (1H, d, $J=3.0$ Hz, H-1), 4.88 (1H, dd, $J=11.3$, 10.0 Hz, H-3), 4.31 (1H, dd, $J=9.7$, 3.9 Hz, H-6), 4.24 (1H, dd, $J=11.3$, 3.0 Hz, H-2), 4.07 (1H, dd, $J=10.0$, 8.5 Hz, H-4), 3.90 (1H, dd, $J=10.7$, 9.7 Hz, H-6), 3.85 (1H, ddd, $J=9.7$, 8.5, 3.9 Hz, H-5), 3.55 (3H, s, OMe). HR-MS: Calcd for $C_{15}H_{16}O_7$: 308.0896 (M^+). Found: 308. 0882.

Me 4,6-*O*-Benzylidene-3-deoxy-3-phenyl-α-D-Glc (**19a**): Colorless needles, mp 254—255 °C. ^{1}H-NMR: 7.38—7.24 (10H, m, Ph-H), 5.42 (1H, s, PhC$\underline{H}$O$_2$), 4.86 (1H, d, $J=3.7$ Hz, H-1), 4.33 (1H, dd, $J=10.2$, 4.9 Hz, H-6), 3.98—3.91 (2H, m, H-2, 5), 3.77 (1H, t, $J=10.2$ Hz, H-6), 3.68 (1H, dd, $J=10.7$, 9.2 Hz, H-4), 3.53 (3H, s, OMe), 3.18 (1H, t, $J=10.7$ Hz, H-3), 1.92 (1H, d, $J=9.5$ Hz, OH, disappeared on addition of D_2O). ^{1}H-NMR (C_6D_6): 3.92 (1H, ddd, $J=10.2$, 9.2, 4.9 Hz, H-5), 3.76 (1H, td, $J=10.8$, 3.7 Hz, H-2). MS: 342 (M^+, 25), 193 (44), 120 (100). *Anal.* Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found. 69.74; H, 6.50.

4) A mixture of **10b** (300 mg) and $(Bu_3Sn)_2$ (930 μl, 2 mol eq) in dry benzene (150 ml) was degassed and irradiated for 3 h by a 100 W mercury lamp and worked up as described above to give a mixture of 2-*S* and 3-*S* products (245 mg) from $CHCl_3$–EtOAc (19 : 1) eluate; they were separated into **12b** (63.7 mg, 21.2%) and **13b** (115.4 mg, 38.5%) by recycling HPLC. The olefin **14b** (3 mg, 1.3%) and a mixture (61 mg) of **15b**, **16b**, and the diol **8b** were also obtained.

Me 4, 6-*O*-Benzylidene-2,3-*S*,*O*-carbonyl-2-thio-β-D-Man (**12b**): Colorless needles from AcOEt–hexane, mp 211—213 °C. IR (KBr): 1733. ^{1}H-NMR 7.51—7.35 (5H, m, Ph-H), 5.58 (1H, s, PhC$\underline{H}$O$_2$), 4.82 (1H, dd, $J=8.2$, 7.2 Hz, H-3), 4.80 (1H, d, $J=2.8$ Hz, H-1), 4.53 (1H, dd, $J=7.2$, 2.8 Hz, H-2), 4.40 (1H, dd, $J=10.9$, 5.1 Hz, H-6), 4.20 (1H, dd, $J=10.0$, 8.2 Hz, H-4), 3.84 (1H, t, $J=10.4$ Hz, H-6), 3.53 (3H, s, OMe), 3.48 (1H, td, $J=10.1$, 5.1 Hz, H-5). MS: 324 (M^+, 10), 323 (M^+-1, 13), 105 (100). *Anal.* Calcd for $C_{15}H_{16}O_6S$: C, 55.55; H, 4.97. Found. 55.49; H, 4.94.

Me 4,6-*O*-Benzylidene-2,3-*O*,*S*-carbonyl-3-thio-β-D-All (**13b**): Colorless prisms from AcOEt–hexane, mp 135—138 °C. IR (KBr): 1751. ^{1}H-NMR 7.46—7.36 (5H, m, Ph-H), 5.57 (1H, s, PhC$\underline{H}$O$_2$), 4.83 (1H, dd, $J=7.1$, 5.0 Hz, H-3), 4.77 (1H, d, $J=6.4$ Hz, H-1), 4.57 (1H, t, $J=6.7$ Hz, H-2), 4.43 (1H, dd, $J=10.5$, 5.0 Hz, H-6), 4.13 (1H, dd, $J=9.7$, 5.0 Hz, H-4), 4.06 (1H, dt, $J=9.7$, 5.0 Hz, H-5), 3.80 (1H, t, $J=10.3$ Hz, H-6), 3.56 (3H, s, OMe). MS: 324 (M^+, 51), 323 (M^+-1, 10), 292 (6), 105 (100). *Anal.* Calcd for $C_{15}H_{16}O_6S$: C, 55.55; H, 4.97. Found. 55.49; H, 4.94.

X-Ray Crystallographic Analyses of 12b and 13b The reflection data were collected on a Rigaku AFC-5 four-circle diffractometer using graphite monochromated MoK_α radiation at the ω-2θ scan speed of 6°/min for $3° < 2\theta < 55°$. Of the reflections collected, those above the $3\sigma(I)$ level (731 for **12b**, 1407 for **13b**) were used for the calculation. The structures were solved by the direct method using MITHRIL (for **12b**) or SIR (for **13b**) and refined by the full-matrix least-squares procedure with anisotropic temperature factors for the non-hydrogen atoms. All hydrogen atoms were located at calculated positions. Positional parameters and the ORTEP drawings of the molecules are given in Table 6 and Fig. 2, respectively. Crystal data: **12b**: $C_{15}H_{16}O_6S$, orthorhombic, $a=11.277(5)$ Å, $b=15.727(7)$ Å, $c=8.488(3)$ Å, $V=1505(1)$ Å^3, $Dc=1.431$ g/cm^3, $Z=4$. Space group, $P2_12_12_1$, $R=0.041$. **13b**: $C_{15}H_{16}O_6S$, orthorhombic, $a=9.731(6)$ Å, $b=32.49(2)$ Å, $c=9.519(5)$ Å, $V=3009(3)$ Å^3, $Dc=1.432$ g/cm^3, $Z=8$. Space group, $P2_12_12_1$, $R=0.039$.

Conversion of Thiolcarbonates to Thio-Glycosides (General Procedure). From 2 and 3 A mixture of the thiolcarbonate (10—30 mg) and $NaBH_4$ (5—10 mg) in 0.05 M NaOMe (1—2 ml) was stirred overnight at room temperature. The reaction was quenched with NH_4Cl and the mixture was concentrated to dryness. The residue was acetylated with Ac_2O (1—2 ml) and pyridine (2—4 ml) at room temperature overnight, and the product obtained by usual work-up was purified by chromatography to yield the monomeric and dimeric compounds.

1) Compound **2b** (10 mg) gave **20b** (6 mg, 48.6%) and **20b′** (2 mg, 18.9%) from the $CHCl_3$–AcOEt (4 : 1) eluate.

Me 3-Thio-β-L Ara Triacetate (**20b**): Colorless gum. IR: 1743, 1698. ^{1}H-NMR: 5.12 (1H, dd, $J=12.1$, 3.5 Hz, H-2), 5.09 (1H, br d, $J=3.0$ Hz, H-4), 4.86 (1H, d, $J=3.5$ Hz, H-1), 4.34 (1H, dd, $J=12.1$, 3.0 Hz, H-3), 3.96 (1H, dd, $J=13.1$, 1.4 Hz, H-5), 3.69 (1H, dd, $J=13.1$, 1.8 Hz, H-5), 3.44 (3H, s, OMe), 2.32 (3H, s, SAc), 2.14, 2.08 (each 3H, s, OAc). MS: 291 (M^+-Me, 2), 275 (M^+-OMe, 1), 247 (M^+-OAc, 18), 187 (48), 69 (100). HR-MS: Calcd for $C_{11}H_{15}O_6S$ (M^+-OMe): 275.0589. Found: 275.0585.

Table 6-1. Positional Parameters and B_{eq} for **12b**

Atom	x	y	z	B_{eq}
S(1)	0.7107 (2)	0.1367 (1)	0.1132 (3)	4.5 (1)
O(1)	0.8635 (5)	0.2820 (3)	0.1519 (8)	4.5 (3)
O(2)	0.9815 (4)	0.1922 (3)	0.0112 (7)	3.6 (3)
O(3)	0.8011 (6)	−0.0095 (3)	0.1899 (7)	4.1 (3)
O(4)	0.6174 (5)	−0.0159 (4)	0.091 (1)	5.9 (4)
O(5)	1.0339 (4)	−0.0354 (3)	0.0353 (6)	3.4 (3)
O(6)	1.1757 (4)	0.0253 (3)	−0.1329 (8)	4.0 (3)
C(1)	0.9326 (7)	0.2086 (5)	0.160 (1)	3.7 (5)
C(2)	0.8505 (7)	0.1370 (6)	0.218 (1)	3.9 (4)
C(3)	0.8994 (8)	0.0467 (6)	0.190 (1)	3.7 (5)
C(4)	0.9664 (7)	0.0418 (5)	0.036 (1)	2.9 (4)
C(5)	1.0504 (6)	0.1163 (5)	0.015 (1)	3.3 (4)
C(6)	1.1141 (7)	0.1055 (5)	−0.138 (1)	4.3 (5)
C(7)	0.9305 (7)	0.3578 (6)	0.128 (1)	6.0 (5)
C(8)	0.703 (1)	0.0255 (5)	0.127 (1)	4.3 (5)
C(9)	1.0975 (7)	−0.0429 (5)	−0.110 (1)	3.3 (4)
C(10)	1.1688 (6)	−0.1242 (5)	−0.102 (1)	3.1 (4)
C(11)	1.2725 (7)	−0.1270 (5)	−0.016 (1)	4.3 (5)
C(12)	1.3365 (7)	−0.2032 (6)	−0.008 (1)	5.0 (5)
C(13)	1.2963 (9)	−0.2729 (5)	−0.087 (1)	4.4 (5)
C(14)	1.1952 (8)	−0.2693 (5)	−0.175 (1)	4.8 (5)
C(15)	1.1311 (8)	−0.1940 (6)	−0.181 (1)	4.4 (5)
H(1)	0.9968	0.2150	0.2422	5.4
H(2)	0.8352	0.1464	0.3299	4.5
H(3)	0.9577	0.0339	0.2756	4.4
H(4)	0.9099	0.0427	−0.0518	3.4
H(5)	1.1077	0.1173	0.1032	4.0
H(6)	1.1700	0.1530	−0.1600	4.8
H(7)	1.0585	0.1081	−0.2275	4.8
H(8)	0.9843	0.3672	0.2177	6.8
H(9)	0.9809	0.3539	0.0367	6.8
H(10)	0.8823	0.4065	0.1190	6.8
H(11)	1.0414	−0.0468	−0.2007	3.9
H(12)	1.3029	−0.0763	0.0374	5.3
H(13)	1.4131	−0.2051	0.0540	5.9
H(14)	1.3412	−0.3260	−0.0764	5.3
H(15)	1.1661	−0.3194	−0.2320	5.2
H(16)	1.0582	−0.1916	−0.2496	5.3

Tetraacetate of the Dimer (**20b′**): This was the only product when a limited amount of $NaBH_4$ (5 mg for 30 mg of **2b**) was used. Colorless oil. IR: 1740. ^{1}H-NMR: 5.31 (1H × 2, m, H-4), 5.03 (1H × 2, dd, $J=12.0$, 3.4 Hz, H-2), 4.86 (1H × 2, d, $J=3.4$ Hz, H-1), 3.83 (1H × 2, dd, $J=12.8$, 1.1 Hz, H-5), 3.74 (1H × 2, dd, $J=12.8$, 1.7 Hz, H-5), 3.41 (3H × 2, s, OMe), 3.39 (1H × 2, dd, $J=12.0$, 3.2 Hz, H-3), 2.16, 2.14 (each 3H × 2, s, OAc). MS: 526 (M^+, 51). HR-MS: Calcd for $C_{20}H_{30}O_{12}S_2$ (M^+): 526.1179. Found: 526.1183.

2) Compound **3b** gave **21b** (72.4%) and **21b′** (6.7%) from the $CHCl_3$–AcOEt (9 : 1) eluate.

Me 4-Thio-β-L-Ara Triacetate (**21b**): Colorless gum. IR: 1747, 1697. ^{1}H-NMR: 5.46 (1H, dd, $J=10.3$, 4.5 Hz, H-3), 4.95 (1H, dd, $J=10.3$, 3.6 Hz, H-2), 4.89 (1H, d, $J=3.6$ Hz, H-1), 4.23 (1H, m, H-4), 4.18 (1H, dd, $J=12.2$, 2.4 Hz, H-5), 3.62 (1H, dd, $J=12.2$, 2.3 Hz, H-5), 3.38 (3H, s, OMe), 2.35 (3H, s, SAc), 2.07, 1.96 (each 3H, s, OAc). MS: 275 (M^+-OMe, 3), 243 (47), 171 (100). HR-MS: Calcd for $C_{11}H_{15}O_6S$ (M^+-OMe): 275.0589. Found: 275.0587.

Tetraacetate of the Dimer (**21b′**): Colorless gum. IR: 1741. ^{1}H-NMR: 5.38 (1H × 2, dd, $J=10.3$, 4.4 Hz, H-3), 5.22 (1H × 2, dd, $J=10.3$, 3.5 Hz, H-2), 4.90 (1H × 2, d, $J=3.5$ Hz, H-1), 4.10 (1H × 2, dd, $J=12.8$, 2.5 Hz, H-5), 3.88 (1H × 2, dd, $J=12.8$, 2.4 Hz, H-5), 3.60 (1H × 2, m, H-4), 3.38 (3H × 2, s, OMe), 2.22, 2.09 (each 3H × 2, s, OAc). MS: 526 (M^+, 77). HR-MS: Calcd for $C_{20}H_{30}O_{12}S_2$ (M^+): 526.1179. Found: 526.1176.

Table 6-2. Positional Parameters and B_{eq} for **13b**

Atom	x	y	z	B_{eq}
S(1)	0.3490 (2)	0.80603 (7)	0.4973 (3)	4.0 (1)
S(2)	0.2408 (2)	0.94318 (7)	0.1309 (3)	4.0 (1)
O(1)	0.6481 (6)	0.8215 (2)	0.7627 (5)	3.6 (3)
O(2)	0.8032 (6)	0.8002 (2)	0.5989 (6)	4.0 (3)
O(3)	0.5783 (6)	0.7708 (2)	0.4274 (6)	4.3 (3)
O(4)	0.4646 (8)	0.7983 (3)	0.2486 (7)	7.7 (5)
O(5)	0.2891 (5)	0.7968 (2)	0.8199 (6)	3.3 (3)
O(6)	0.3516 (6)	0.8491 (2)	0.9738 (6)	4.1 (3)
O(7)	−0.0103 (5)	0.9316 (2)	−0.1856 (6)	3.4 (3)
O(8)	0.1624 (6)	0.9495 (2)	−0.3345 (6)	4.4 (3)
O(9)	0.3202 (6)	0.9792 (2)	−0.0987 (7)	4.3 (3)
O(10)	0.4905 (6)	0.9517 (2)	0.0250 (8)	6.3 (4)
O(11)	−0.0742 (5)	0.9537 (2)	0.1822 (6)	3.4 (3)
O(12)	−0.2345 (5)	0.9049 (2)	0.1047 (6)	3.7 (3)
C(1)	0.666 (1)	0.8108 (3)	0.6192 (9)	3.4 (4)
C(2)	0.5817 (9)	0.7727 (2)	0.5787 (8)	3.1 (4)
C(3)	0.4328 (8)	0.7744 (2)	0.6286 (9)	3.0 (4)
C(4)	0.4280 (9)	0.7910 (2)	0.7794 (8)	2.9 (4)
C(5)	0.5062 (8)	0.8308 (2)	0.791 (1)	3.3 (4)
C(6)	0.495 (1)	0.8460 (3)	0.941 (1)	4.4 (5)
C(7)	0.893 (1)	0.8343 (3)	0.599 (1)	5.4 (6)
C(8)	0.473 (1)	0.7915 (3)	0.371 (1)	5.1 (6)
C(9)	0.2871 (8)	0.8103 (3)	0.9629 (9)	3.7 (5)
C(10)	0.142 (1)	0.8120 (2)	1.017 (1)	3.7 (4)
C(11)	0.034 (1)	0.7973 (3)	0.941 (1)	4.0 (5)
C(12)	−0.098 (1)	0.7986 (3)	0.997 (1)	5.8 (6)
C(13)	−0.118 (1)	0.8153 (3)	1.128 (1)	5.8 (7)
C(14)	−0.008 (1)	0.8302 (3)	1.204 (1)	5.7 (6)
C(15)	0.122 (1)	0.8280 (3)	1.148 (1)	4.2 (5)
C(16)	0.1326 (9)	0.9402 (3)	−0.195 (1)	3.9 (5)
C'17)	0.1716 (8)	0.9774 (2)	−0.109 (1)	3.2 (4)
C(18)	0.1184 (8)	0.9759 (2)	0.0414 (9)	3.2 (4)
C(19)	−0.0283 (8)	0.9604 (2)	0.0409 (9)	3.0 (4)
C(20)	−0.0459 (8)	0.9219 (2)	−0.0433 (8)	2.8 (4)
C(21)	−0.1944 (8)	0.9093 (3)	−0.039 (1)	3.8 (5)
C(22)	0.155 (1)	0.9162 (3)	−0.428 (1)	6.1 (6)
C(23)	0.371 (1)	0.9583 (3)	0.010 (1)	4.3 (5)
C(24)	−0.2174 (8)	0.9425 (3)	0.178 (1)	3.1 (4)
C(25)	−0.2699 (9)	0.9369 (2)	0.327 (1)	3.5 (4)
C(26)	−0.1974 (8)	0.9516 (3)	0.439 (1)	3.9 (5)
C(27)	−0.252 (1)	0.9486 (3)	0.574 (1)	4.6 (5)
C(28)	−0.380 (1)	0.9312 (3)	0.592 (1)	5.4 (6)
C(29)	−0.451 (1)	0.9163 (3)	0.480 (1)	5.3 (6)
C(30)	−0.3971 (8)	0.9191 (3)	0.346 (1)	4.1 (5)
H(1)	0.6414	0.8344	0.5579	4.8
H(2)	0.6295	0.7483	0.6170	3.8
H(3)	0.3937	0.7462	0.6291	4.5
H(4)	0.4716	0.7709	0.8450	3.3
H(5)	0.4685	0.8517	0.7266	4.7
H(6)	0.5431	0.8259	1.0018	5.3
H(7)	0.5454	0.8715	0.9536	5.3
H(8)	0.9868	0.8276	0.5881	6.5
H(9)	0.8859	0.8509	0.6861	6.5
H(10)	0.8699	0.8542	0.5244	6.5
H(11)	0.3390	0.7896	1.0200	4.8
H(12)	0.0502	0.7848	0.8455	5.0
H(13)	−0.1774	0.7882	0.9394	6.9
H(14)	−0.2084	0.8159	1.1699	7.4
H(15)	−0.0263	0.8432	1.2957	6.4
H(16)	0.2008	0.8388	1.2020	5.6
H(17)	0.1853	0.9151	−0.1638	5.2
H(18)	0.1338	1.0012	−0.1595	4.0
H(19)	0.1190	1.0041	0.0813	3.8
H(20)	−0.0883	0.9815	−0.0031	3.8
H(21)	0.0101	0.8994	−0.0047	3.9
H(22)	−0.2491	0.9294	−0.0885	4.9
H(23)	−0.2079	0.8832	−0.0910	4.9
H(24)	0.0665	0.9031	−0.4289	6.4
H(25)	0.2218	0.8950	−0.4049	6.4
H(26)	0.1748	0.9245	−0.5236	6.4
H(27)	−0.2701	0.9645	0.1301	3.6
H(28)	−0.1056	0.9639	0.4264	4.8
H(29)	−0.2018	0.9599	0.6571	6.2
H(30)	−0.4165	0.9282	0.6884	7.4
H(31)	−0.5395	0.9029	0.4959	6.2
H(32)	−0.4485	0.9090	0.2635	5.2

3) Compound **2e** gave **22b** (64.9%) from the $CHCl_3$–MeOH (39 : 1) eluate.

Me 3-Thio-α-D-Gal Tetraacetate (**22b**): Colorless oil. IR: 1748, 1699. ^{1}H-NMR: 5.35 (1H, dd, J=3.0, 1.2 Hz, H-4), 5.09 (1H, dd, J=12.4, 3.5 Hz, H-2), 4.92 (1H, d, J=3.5 Hz, H-1), 4.33 (1H, dd, J=12.4, 3.0 Hz, H-3), 4.27 (1H, td, J=6.0, 1.2 Hz, H-5), 4.09 (1H, dd, J=11.3, 5.7 Hz, H-6), 4.01 (1H, dd, J=11.3, 7.0 Hz, H-3), 3.45 (3H, s, OMe), 2.32 (3H, s, SAc), 2.14, 2.09, 2.06 (each 3H, s, OAc). MS: 347 (M^+−OMe, 5), 303 (M^+−SAc, 37), 243 (83), 141 (74), 81 (100). HR-MS: Calcd for $C_{14}H_{19}O_8S$ (M^+−OMe): 347.0801. Found: 347.0800 (7.5%).

4) Compound **3e** gave **23b** (51%) and **23b'** (38%) from the benzene–AcOEt (2 : 1) eluate.

Me 4-Thio-α-D-Gal Tetraacetate (**23b**): Colorless oil (lit.[17] syrup). IR: 1740, 1700. ^{1}H-NMR: 5.52 (1H, m, H-3), 4.96 (1H, d, J=4.0 Hz, H-1), 4.94 (1H, dd, J=9.7, 4.0 Hz, H-2), 4.43 (1H, ddd, J=7.3, 5.1, 1.6 Hz, H-5), 4.35 (1H, dd, J=6.0, 1.7 Hz, H-4), 4.21 (1H, dd, J=11.7, 7.3 Hz, H-6), 4.09 (1H, dd, J=11.7, 5.0 Hz, H-6), 3.39 (3H, s, OMe), 2.39 (3H, s, SAc), 2.08, 2.06, 1.96 (each 3H, s, OAc). The multiplet of H-3 in $CDCl_3$ changed into a clean doublet of doublets at δ 5.61 (J=10.6, 4.3 Hz) in C_6D_6. MS: 378 (M^+, 0.5), 347 (M^+−OMe, 5), 243 (100). HR-MS: Calcd for $C_{15}H_{22}O_9S$ (M^+): 378.0944. Found: 378.0975.

Hexaacetate of the Dimer (**23b'**): Colorless gum. IR: 1746. ^{1}H-NMR: 5.32 (1H × 2, dd, J=10.6, 4.1 Hz, H-3), 5.16 (1H × 2, dd, J=10.7, 3.6 Hz, H-2), 4.93 (1H × 2, d, J=3.9 Hz, H-1), 4.36 (1H × 2, dd, J=10.9, 6.9 Hz, H-6), 4.24 (1H × 2, td, J=5.3, 2.0 Hz, H-5), 4.13 (1H × 2, dd, J=10.9, 5.0 Hz, H-6), 3.62 (1H × 2, dd, J=4.1, 1.8 Hz, H-4), 3.34 (3H × 2, s, OMe), 2.14, 2.11, 2.10 (each 3H × 2, s, Ac). MS: 670 (M^+, 100). HR-MS: Calcd for $C_{26}H_{38}O_{16}S_2$ (M^+): 670.1601. Found: 670.1597.

5) Compound **2f** gave **24b** (44%) and **24b'** (32%) in the reaction without $NaBH_4$ followed by chromatography of the product in hexane–AcOEt (1 : 1).

Me 3-Thio-β-D-Gal Tetraacetate (**24b**): Colorless oil. IR: 1748, 1700. ^{1}H-NMR: 5.29 (1H, d, J=3.4 Hz, H-4), 5.03 (1H, dd, J=11.7, 7.8 Hz, H-2), 4.45 (1H, d, J=7.8 Hz, H-1), 4.10 (1H, dd, J=13.2, 3.4 Hz, H-6), 4.09 (1H, dd, J=13.2, 7.6 Hz, H-6), 4.01 (1H, m, H-5), 3.93 (1H, dd, J=11.7, 3.4 Hz, H-3), 3.50 (3H, s, OMe), 2.31 (3H, s, SAc), 2.13, 2.05, 2.05 (each 3H, s, OAc). MS: 303 (M^+−SAc, 8), 243 (27), 141 (34).

Hexaacetate of the Dimer (**24b'**): Colorless gum. IR: 1746. ^{1}H-NMR: 5.63 (1H × 2, br d, J=2.9 Hz, H-4), 4.86 (1H × 2, dd, J=11.7, 7.8 Hz, H-2), 4.38 (1H × 2, d, J=7.8 Hz, H-1), 4.12 (1H × 2, dd, J=11.0, 6.2 Hz, H-6), 4.11 (1H × 2, dd, J=11.0, 3.0 Hz, H-6), 3.98 (1H × 2, m, H-5), 3.05 (1H × 2, dd, J=11.7, 2.9 Hz, H-3), 3.49 (3H × 2, s, OMe), 2.17, 2.10, 2.06 (each 3H × 2, s, Ac). MS: 670 (M^+, 2).

6) Compound **3f** gave **25b** (64.9%) from the benzene–AcOEt (2 : 1) eluate.

Me 4-Thio-β-D-Gal Tetraacetate (**25b**): Colorless gum. IR: 1750, 1699. ^{1}H-NMR: 5.19 (1H, dd, J=10.3, 4.5 Hz, H-3), 5.00 (1H, dd, J=10.3, 7.8 Hz, H-2), 4.38 (1H, d, J=7.8 Hz, H-1), 4.30 (1H, dd, J=4.2, 1.5 Hz, H-4), 4.28 (1H, dd, J=11.3, 6.7 Hz, H-6), 4.15 (1H, dd, J=11.3, 6.0 Hz, H-6), 4.64 (1H, td, J=6.1, 1.5 Hz, H-5), 3.48 (3H, s, OMe), 2.39 (3H, s, SAc), 2.06, 2.06, 1.96 (each 3H, s, OAc). MS: 347 (M^+−OMe, 0.5), 318 (M^+−AcOH, 9), 303 (M^+−SAc, 1), 243 (100).

From 12 and 13 A mixture of the thiolcarbonate **12** or **13** (20—30 mg) and 90% AcOH (2 ml) was heated for 1 h at 100 °C and concentrated to dryness. The residue and $NaBH_4$ (10 mg) in 0.05 M NaOMe (3 ml) was stirred overnight at room temperature. The reaction was quenched with NH_4Cl and the mixture was concentrated to dryness. The residue was acetylated with Ac_2O (2 ml) and pyridine (4 ml) at room temperature overnight, and the product obtained by usual work-up was purified by chromatography with hexane–AcOEt (1 : 1) to yield the peracetates **26b**—**29b**.

7) Compound **12a** gave **26b** (62%).

Me 2-Thio-α-D-Man Tetraacetate (**26b**): Colorless gum. IR: 1746, 1694. ^{1}H-NMR: 5.57 (1H, dd, J=10.0, 4.8 Hz, H-3), 5.08 (1H, t, J=10.0 Hz, H-4), 4.77 (1H, d, J=1.5 Hz, H-1), 4.27 (1H, dd, J=4.8, 1.5 Hz, H-2), 4.22 (1H, dd, J=12.3, 5.0 Hz, H-6), 4.11 (1H, dd, J=12.3, 2.3 Hz, H-6), 3.97 (1H, ddd, J=10.0, 5.0. 2.3 Hz, H-5), 3.40 (3H, s, OMe), 2.38 (3H, s, SAc), 2.12, 2.04, 1.97 (each 3H, s, OAc). MS: 347 (M^+−OMe, 2), 318 (M^+−AcOH, 4), 155 (100). HR-MS: Calcd for $C_{14}H_{19}O_8S$ (M^+−OMe): 347.0801. Found: 347.0813.

8) Compound **13a** gave **27b** (21%).

Me 3-Thio-α-D-All Tetraacetate (**27b**): Colorless gum. IR: 1747, 1685. ^{1}H-NMR: 5.25 (1H, dd, J=5.3, 3.4 Hz, H-3), 5.16 (1H, dd, J=10.2, 4.3 Hz, H-4), 4.82 (1H, d, J=3.4 Hz, H-1), 4.58 (1H, t, J=4.7 Hz, H-3), 4.29 (1H, dd, J=12.2, 4.7 Hz, H-6), 4.16 (1H, dd, J=12.2, 2.1 Hz, H-6), 4.00 (1H, ddd, J=10.2, 4.3, 2.1 Hz, H-5), 3.44 (3H, s, OMe), 2.36 (3H, s, SAc), 2.10, 2.09, 1.95 (each 3H, s, OAc). MS: 347 (M^+−OMe, 1), 303 (9), 243 (58), 81 (100). HR-MS: Calcd for $C_{14}H_{19}O_8S$ (M^+−OMe): 347.0801. Found: 347.0798.

9) Compound **12b** gave **28b** (54%).

Me 2-Thio-β-D-Man Tetraacetate (**28b**): Colorless solid, mp 140—150 °C (lit. 151—153 °C).[18] IR: 1748, 1692. ^{1}H-NMR: 5.23 (1H, dd, J=9.8, 4.3 Hz, H-3), 5.12 (1H, t, J=9.7 Hz, H-4), 4.71 (1H, d, J=1.6 Hz, H-1), 4.42 (1H, dd, J=4.3, 1.6 Hz, H-2), 4.43 (1H, dd, J=12.0, 5.0 Hz, H-6), 4.16 (1H, dd, J=12.0, 2.9 Hz, H-6), 3.67 (1H, ddd, J=9.4, 5.0. 2.9 Hz, H-5), 3.53 (3H, s, OMe), 2.39 (3H, s, SAc), 2.10, 2.05, 1.97 (each 3H, s, OAc). MS: 318 (M^+−AcOH, 4), 155 (100). HR-MS: Calcd for $C_{13}H_{18}O_7S$ (M^+−AcOH): 318.0773. Found: 318.0763.

10) Compound **13b** gave **29b** (54%).

Me 3-Thio-β-D-All Tetraacetate (**29b**): Colorless gum. IR: 1748, 1696. ^{1}H-NMR: 5.13 (1H, dd, J=8.0, 4.2 Hz, H-4), 5.03 (1H, dd, J=6.8, 4.3 Hz, H-2), 4.60 (1H, t, J=4.3 Hz, H-3), 4.48 (1H, d, J=6.8 Hz, H-1), 4.29 (1H, dd, J=12.0, 4.8 Hz, H-6), 4.23 (1H, dd, J=12.0, 3.8 Hz, H-6), 3.89 (1H, ddd, J=8.0, 4.8, 3.8 Hz, H-5), 3.49 (3H, s, OMe), 2.38 (3H, s, SAc), 2.09, 2.06, 2.01 (each 3H, s, OAc). MS: 303 (M^+−SAc, 6), 243 (56), 141 (72), 81 (100). HR-MS: Calcd for $C_{13}H_{19}O_8$ (M^+−SAc): 303.1080. Found: 303.1075.

References and Notes

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5) Abbreviations: Me=methyl, Ph=phenyl, Ac=acetyl, Ts=*p*-toluenesulfonyl, Ara=arabinoside, Gal=galactoside, Glc=glucoside, Man=mannoside, All=alloside.

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12) Recently, *O–S* rearrangement of thionocarbonates by Bu_4NBr was reported [Ko S. Y., *J. Org. Chem.*, **60**, 6250—6251 (1995)]. This method is mechanistically identical with Trimnell's ionic method and was proved to be ineffective with our substrates (**1**).

13) It is necessary to use a dilute solution ($<6\times10^{-3}$ M). Higher concentrations retarded the rearragement reaction with increase of recovery of the starting material.

14) Tin hydride-deoxygenation of **10a** produces **15a** and **16a** in a ratio of 1:2 [Barton D. H. R., Subramanian R., *J. Chem. Soc.*, **1977**, 1718—1723]. Disagreement of this ratio with the selectivity in rearrangement suggests that the deoxygenation is the final result of many reversible reactions as suggested in ref. 6. Total yield of the products from the 3-radical roughly agreed with the result of deoxygenation.

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