Thio-Sugars. IV. Synthesis of Carbohydrate 1,3-Glycol (Six-Membered) Thionocarbonates and Their Attempted *O–S* Rearrangement[1)]

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Four six-membered cyclic thionocarbonates (two *sec–sec* and two *prim–sec*) were prepared and their radical-promoted *O–S* rearrangement reaction was examined. The results revealed that the reaction in six-membered rings is difficult compared with the simple rearrangement in five-membered rings. In the course of syntheses of the substrates, interesting acyl migration during the stannylation process occurred.

Key words six-membered cyclic thionocarbonate; thiocarbonylation; acyl migration; spiro-orthocarbonate; *O–S* rearrangement

In previous papers,[1—3)] we showed that when five-membered cyclic thionocarbonates formed from 1,2-glycols were treated with a catalytic amount of appropriate radical generators, they underwent *O–S* rearrangement to give thiolcarbonates in acceptable yields. Although the regioselectivity of the reaction is not always high, the stereochemistry of the product is exclusively *cis*. The method was successfully applied to the synthesis of thio-sugars carrying a thiol group at the secondary positions in carbohydrate molecules, while ionic reaction[4)] of the same substrate gave no reaction. The present study was undertaken to determine whether a similar rearrangement occurs in six-membered analogues formed from 1,3-glycols. During synthesis of these substrates, interesting acyl migration reactions were observed.

Results and Discussion

Synthesis of Six-membered Cyclic Thionocarbonates For the 1,3-glycols, three derivatives of 1,2-*O*-isopropylidene-α-D-glucofuranose (6-*O*-benzoate **2**,[5)] 6-*O*-tosylate **6**,[5)] and 6-deoxy compound **9**[6)]) and two derivatives of pryanosides [methyl 2,3-di-*O*-methyl-α- and -β-D-glucopyranosides (**12a**, **b**)][7)] were chosen. Thiocarbonylation of these glycols was carried out by one of the following methods: (1) stannylation with Bu_2SnO, then treatment with thiophosgene ($CSCl_2$); or (2) direct treatment with thiocarbonyldiimidazole (Im_2CS).

When the 6-*O*-benzoate **2** was thiocarbonylated using method (1), the product was not the expected 3,5-*O*-thionocabonate **5**, but 3-*O*-benzoyl-5,6-*O*-thionocarbonate **3**[3)] (67%), indicating that an acyl migration took place during the reaction. To determine which process (activation by stannylation or the reaction with thiophosgene) is responsible for this migration, **2** was treated with Bu_2SnO. The product was the 3-*O*-benzoate **4** (92%), revealing that the benzoyl migration from *O*-6 to *O*-3 occurred during the stannylation process through **D**→**E**→**F**. This compound **4** was previously reported as an intermediate in the alkaline hydrolysis of 3-*O*-benzoyl-5,6-*O*-thionocarbonate **3** to the triol **1**.[8)] Detailed comparison of the spectral data of **2** and **4** revealed that the previously reported intermediate was not the 3-*O*-benzoate **4**, but instead was the 6-*O*-benzoate **2**, indicating that acyl migration from *O*-3 to *O*-6 had taken place during alkaline hydrolysis (as **G**→**H**). Thiocarbonylation of **2** with Im_2CS (method 2) gave the expected 3,5-*O*-thionocarbonate **5** in 75% yield.

Thiocarbonylation of the 6-*O*-tosylate **6** using method (1) gave the 3,6-ether **7**,[3,8)] indicating that the activated 3-OH attacked the 6-position in an S*N*2 manner. Treatment of **6** with Im_2CS gave a solid in 75% yield, which contained one imidazole group and *m*/*z* of 312. The ^{1}H-NMR data were compatible with the structure **8** (the probable mechanism is indicated in brackets [**J**→**K**]).

Thiocarbonylation of the 6-deoxy derivative **9** using method (1) gave two products, **10** (57%) and **11** (36%), while Im_2CS gave only **10** in 83% yield, which was the expected 3,5-*O*-thionocarbonate. Compound **11** lacked a thiocarbonyl group and had the MS peak at *m*/*z* 401, which corresponded to $(M-Me)^+$ originating from the dimeric spiro-orthocarbonate structure **11** formed by the route **O**→**P**. Formation of such spiro-orthocarbonates by the reaction of thionocarbonates and tin-activated glycols has a precedent.[9)] The stereochemistry of the central carbon is uncertain.

Thionocarbonates **14a** and **14b** were best prepared by thiocarbonylation of **12a** and **12b** using method (1), followed by treatment of the resulting 6-*O*-thiocarbonyl chlorides (**13a**, **b**) with *N*,*N*-dimethylaminopyridine (DMAP) in refluxing dioxane. The other method gave poor results.

Attempted *O–S* Rearrangement The *prim–sec* thionocarbonate **14a** is known to give the primary-*S* product **15a** in ionic rearrangement (KI in MeCN).[4)] The β-anomer **14b** similarly gave **15b** in good yield.

For attempted radical-promoted *O–S* rearrangement, the following three methods, all of which gave good results for five-membered thionocarbonates,[1,3)] were tested: (A) heating with a catalytic amount of Bu_3SnH in the presence of α,α-azobis(isobutyronitrile) (AIBN); (B) photolysis with $(Bu_3Sn)_2$ in benzene; and (C) heating with dimethyl phosphonate and benzoyl peroxide.

The reaction of the *prim–sec* thionocarbonate **14b** using method A gave a mixture in which the rearrangement prod-

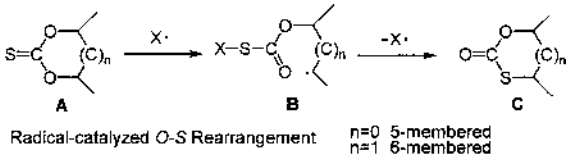

Chart 1

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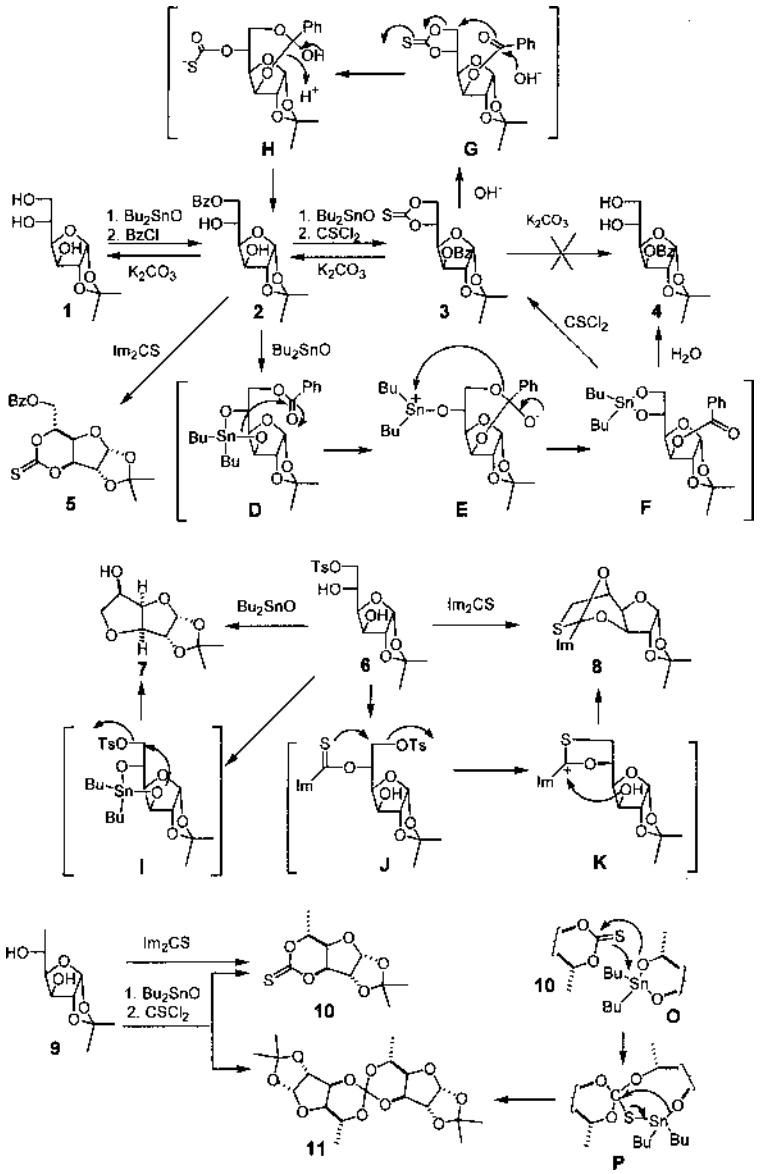

Chart 2

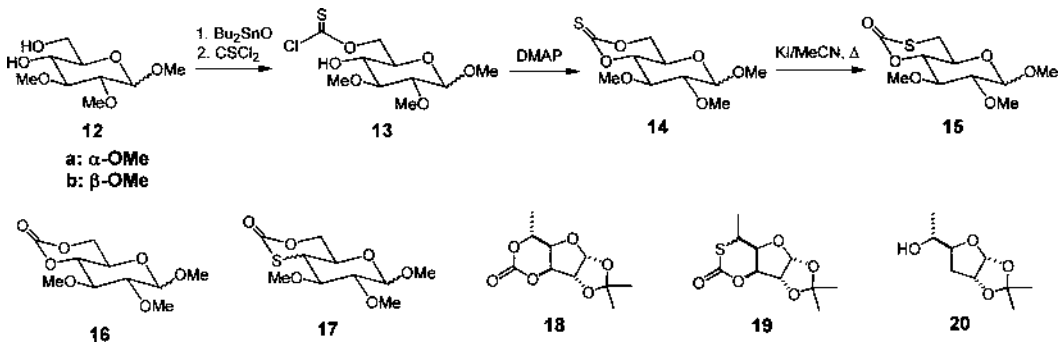

Chart 3

uct **17** was not found judging from the absence of the thiolcarbonate peak (*ca.* δ 160) in the ^{13}C-NMR. Method C gave similar results. The reaction of *sec–sec* thionocarbonate **10** was again fruitless. Using method A, the recovery of the products was low with major formation of oxo derivative **18**. The major product using method C was a dideoxy derivative **20** (24%). Although the minor presence of an *O–S* rearrangement product **19** was suggested from the ^{13}C-NMR signal at δ 171, it could not be isolated. Reactions of the 6-*O*-benzoate **5** were again fruitless: method A was of low efficacy and method C gave a complex mixture. In neither case was the formation of a rearrangement product indicated.

Table 1. ^{13}C-NMR Data for New Compounds Reported in This Paper (in $CDCl_3$)[a]

Comp.	C-1	C-2	C-3	C-4	C-5	C-6	Others[b]
2	105.0	85.2	75.8	79.4	69.8	66.7	166.7 (C=O)
4	104.9	83.0	79.6	77.2	68.2	64.2	166.5 (C=O)
8	105.5	83.3	77.6	74.2	78.5	35.3	
9	104.8	85.2	75.3	81.9	67.0	18.6	
10	104.6	82.7	80.3	73.3	76.1	18.0	187.0 (C=S)
11	106.4	83.6	83.3	71.2	76.8	19.0	
12a	97.6	81.9	82.9	70.2	70.8	62.2	
12b	104.6	83.6	85.8	69.8	75.0	62.1	
13a	97.4	81.6	82.7	69.5	68.2	75.8	186.4 (C=S)
13b	104.3	83.2	85.5	69.2	72.2	75.8	186.4 (C=S)
14a	98.6	80.8	80.3	78.4	61.1	71.5	188.1 (C=S)
14b	104.7	83.1	81.4	79.8	62.6	71.2	187.9 (C=S)
15a	97.9	80.5	82.2	79.5	61.9	30.6	163.8 (C=O)
15b	103.9	82.6	82.8	81.6	65.3	30.2	163.8 (C=O)
16b[c]	104.8	82.9	82.1	79.0	62.9	69.2	147.2 (C=O)
20	105.3	81.7	31.0	80.5	66.2	17.9	

a) Assignments were confirmed by the C–H COSY spectra. *b*) The other carbons not included here are indicated in the Experimental section. *c*) Prepared by the action of Bu_2SnO on **14b** (*cf.* Tsuda Y., Sato Y., Kakimoto K., Kanemitsu K., *Chem. Pharm. Bull.*, **40**, 1033—1036 [1992]).

In conclusion, radical-promoted *O–S* rearrangement in six-membered cyclic 1,3-thionocarbonates is difficult compared with the reaction in five-membered cyclic 1,2-thionocarbonates. This difficulty must occur in the cyclization step of the intermediary radical. Although intermediary radical formation is indicated, the reaction does not proceed to rearrangement but to hydride abstraction. This is parallel with the fact that the intramolecular radical cyclization to a double bond usually preferentially produces 5-membered rings rather than 6-membered rings.

Experimental

General The same as in ref. 3.

6-*O*-Benzoyl-1,2-*O*-isopropylidene-3,5-*O*-thiocarbonyl-α-D-glucofuranose (5) A mixture of the 6-*O*-benzoate **2**[5] (200 mg) and Im_2CS (121 mg, 1.1 eq) in toluene (100 ml) was heated under reflux for 3 h. The solvent was evaporated and the residue was chromatographed. The $CHCl_3$–EtOAc eluate gave the 3,5-*O*-thionocarbonate **5** (169 mg, 75%) as colorless plates from benzene–hexane, mp 160—161 °C. IR: 1731, 1255. ^{1}H-NMR: 7.98 (2H, dd, *J*=8.4, 0.9 Hz, *o*-Ph-H), 7.61 (1H, br t, *J*=8.4 Hz, *p*-Ph-H), 7.48 (2H, br t, *J*=8.4 Hz, *m*-Ph-H), 6.04 (1H, d, *J*=3.7 Hz, H-1), 5.04 (1H, m, H-5), 4.92 (1H, d, *J*=3.0 Hz, H-3), 4.89 (1H, d, *J*=3.7 Hz, H-2), 4.71 (1H, dd, *J*=12.5, 3.9 Hz, H-6), 4.67 (1H, dd, *J*=3.0, 1.7 Hz, H-4), 4.65 (1H, dd, *J*=12.5, 2.8 Hz, H-6), 1.50, 1.34 (each 3H, s, $Me_2C<$). *Anal*. Calcd for $C_{17}H_{18}O_7S$: C, 55.73; H, 4.95. Found: C, 55.50; H, 4.90.

Acyl Migration in 2 from *O*-6 to *O*-3 A mixture of 6-*O*-benzoate **2** (100 mg) and Bu_2SnO (85 mg, 1.0 eq) in toluene (50 ml) was heated under reflux for 5 h. Chromatography and crystallization of the mixture gave the 3-*O*-benzoate **4** (92 mg, 92%) as colorless prisms from $CHCl_3$–hexane, mp 194—198 °C. It was not separable from **2** on thin-layer chromatography (TLC). ^{1}H-NMR: 8.10—7.40 (5H, m, Ph-H), 5.99 (1H, d, *J*=3.4 Hz, H-1), 5.53 (1H, d, *J*=2.0 Hz, H-3), 4.71 (1H, d, *J*=3.4 Hz, H-2), 4.30 (1H, dd, *J*=8.5, 2.0 Hz, H-4), 3.87 (1H, br d, *J*=9.5 Hz, H-6), 3.79—3.72 (2H, m, H-5, 6), 1.55, 1.34 (each 3H, s, $Me_2C<$).

Thiocarbonylation of 2 with Bu_2SnO and $CSCl_2$ Compound **2** was treated with Bu_2SnO as described above, then thioacylated with $CSCl_2$ (1.0 eq) at room temperature for 30 min to give the 3-*O*-benzoyl-5,6-*O*-thionocarbonate **3**, mp 205—206 °C, identical with the authentic specimen[3] in 67% yield.

3,6-Ether (7) A mixture of the 6-*O*-tosylate **6** (150 mg) and Bu_2SnO (120 mg, 1.2 eq) in toluene (40 ml) was heated under reflux for 4 h. Removal of the solvent and chromatography of the residue gave the 3,6-ether **7** (83 mg, 100%) from the benzene–hexane eluate as a colorless oil (lit.[3] mp 53—55 °C). The NMR and IR spectra were identical with those of the authentic specimen.[3,8]

Imidazole Derivative (8) A mixture of **6** (561 mg) and Im_2CS (1.1 eq) in toluene (100 ml) was heated under reflux for 2 h. The solvent was removed under reduced pressure and the residue was chromatographed to give, from the benzene–AcOEt (1 : 1) eluate, compound **8** (350 mg, 75%) as colorless plates from AcOEt–hexane, mp 128—130 °C. IR (KBr): 1377, 1296, 1237, 1040. ^{1}H-NMR: 6.04 (1H, d, *J*=3.6 Hz, H-1), 5.21 (1H, br d, *J*=6.8 Hz, H-5), 4.38 (1H, d, *J*=2.8 Hz, H-3), 4.76 (1H, d, *J*=3.6 Hz, H-2), 4.08 (1H, t, *J*=2.0 Hz, H-4), 3.72 (1H, dd, *J*=10.3, 6.8 Hz, H-6), 3.27 (1H, d, *J*=10.3 Hz, H-6), 1.52, 1.35 (each 3H, s, $Me_2C<$). ^{13}C-NMR: 135.0, 129.4, 116.8 (imidazole), 116.3 (C-7), 112.3, 28.8, 26.1 ($Me_2C<$). MS: 312 (M^+, 47), 297 (M^+-Me, 55), 279 (100), 95 (90). *Anal*. Calcd for $C_{13}H_{18}O_5N_2S$: C, 49.99; H, 5.16; N, 8.97. Found: C, 49.91; H, 5.13; N, 8.88.

6-Deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (9) This was prepared from the 6-*O*-tosylate **6** by $LiAlH_4$ reduction in 85% yield. mp 90—92 °C (lit.[6] 90—91 °C).

Thiocarbonylation of 9 (1) With Bu_2SnO–$CSCl_2$: A mixture of **9** (200 mg) and Bu_2SnO (274 mg, 1.1 mol eq) in dry toluene (80 ml) was heated under reflux for 2 h. After cooling the mixture to room temperature, $CSCl_2$ (84 μl, 1.1 mol eq) was added drop by drop, and the mixture was stirred for 2.5 h at room temperature. The mixture was poured onto a silica gel column, and the column was washed thoroughly with benzene to remove excess reagents. Elution of the column with benzene–AcOEt (5 : 1) gave the 3,5-*O*-thionocarbonate **10** (137 mg, 57%) and the spiro-orthocarbonate **11** (81 mg 36%).

(2) With Im_2CS: A mixture of **9** (600 mg) and Im_2CS (1.1 eq) in toluene (40 ml) was heated under reflux for 3 h. The cooled reaction mixture was poured onto a silica gel column and the column was washed with benzene. Elution of the column with benzene–AcOEt (5 : 1) gave 6-deoxy-1,2-*O*-isopropylidene-3,5-*O*-thiocarbonyl-α-D-glucofuranose (**10**) (613 mg, 83%) as colorless prisms from $CHCl_3$–hexane, mp 171 °C. IR (KBr): 1296, 1274, 1249, 1199. ^{1}H-NMR: 6.02 (1H, d, *J*=3.7 Hz, H-1), 4.89 (1H, d, *J*=3.1 Hz, H-3), 4.85 (1H, d, *J*=3.7 Hz, H-2), 4.82 (1H, qd, *J*=7.0, 1.7 Hz, H-5), 4.08 (1H, dd, *J*=3.0, 1.7 Hz, H-4), 1.56 (3H, d, *J*=7.0 Hz, H-6), 1.52, 1.35 (each 3H, s, $Me_2C<$). MS: 246 (M^+, 100), 231 (M^+-Me, 28). *Anal*. Calcd for $C_{10}H_{14}O_5S$: C, 48.77; H, 5.73. Found: C, 48.73; H, 5.70.

Spiro-orthocarbonate (11) Pale yellow oil. IR: 1164, 1097, 1073, 1030. ^{1}H-NMR: 6.02 (1H×2, d, *J*=4.0 Hz, H-1), 4.68 (1H×2, d, *J*=4.0 Hz, H-2), 4.40 (1H×2, d, *J*=4.0 Hz, H-3), 4.26 (1H×2, m, H-4), 3.89 (1H×2, m, H-5), 1.4 (3H×2, d, *J*=7.0 Hz, H-6), 1.52, 1.35 (each 3H×2, s, $Me_2C<$). ^{13}C-NMR: 119.0 (central C), 112.4, 27.3, 26.7 ($Me_2C<$). MS: 401 (M^+-Me, 19), 231 (100), 113 (92).

Methyl 3-*O*-methyl-4,6-*O*-thiocarbonyl-α-D-glucopyranoside 14a (1) Thiocarbonylation of **12a** with Bu_2SnO and $CSCl_2$: A mixture of **12a** (1.0 g) and Bu_2SnO (1.12 g, 1.0 mol eq) in toluene (20 ml) was heated under reflux for 2 h, then cooled to 0 °C. $CSCl_2$ (0.38 ml, 1.1 eq) was added drop by drop, and the mixture stirred for 30 min at room temperature, then poured onto a silica gel column. After washing the column with benzene, elution with AcOEt–hexane (1 : 1) gave methyl 6-*O*-chlorothiocarbonyl-2,3-di-*O*-methyl-α-D-glucopyranoside (**13a**) (1.3 g, 98%) as a syrup. ^{1}H-NMR: 4.87 (1H, d, *J*=3.7 Hz, H-1), 4.79 (1H, dd, *J*=11.7, 2.0 Hz, H-6), 4.71 (1H, dd, *J*=11.7, 5.6 Hz, H-6), 3.93 (1H, ddd, *J*=8.2, 5.6, 2.0 Hz, H-5), 3.65, 3.51, 3.46 (each 3H, s, OMe), 3.49—3.47 (2H, m, H-3, 4), 3.27 (1H, dd, *J*=9.3, 3.7 Hz, H-2), 2.48 (1H, d, *J*=2.0 Hz, 4-OH).

A mixture of **13a** (1.25 g) and DMAP (508 mg, 1.0 mol eq) in toluene (5 ml) was stirred for 10 min at room temperature. Chromatography of the reaction mixture gave the 4,6-*O*-thionocarbonate **14a** (1.3 g) as a syrup. ^{1}H-NMR: 4.90 (1H, d, *J*=3.7 Hz, H-1), 4.59 (1H, dd, *J*=10.0, 6.0 Hz, H-6), 4.27 (1H, t, *J*=10.2 Hz, H-6), 4.14 (1H, td, *J*=10.3, 6.0 Hz, H-5), 4.02 (1H, t, *J*=9.8 Hz, H-4), 3.70 (1H, t, *J*=9.3 Hz, H-3), 3.67, 3.56, 3.48 (each 3H, s, OMe), 3.29 (1H, dd, *J*=9.4, 3.7 Hz, H-2).

(2) The Colidine-$CSCl_2$ method[10] gave **14a** in <5% yield.

(3) The Im_2CS method gave **14a** in 15% yield.

Methyl 3-*O*-methyl-4,6-*O*-thiocarbonyl-β-D-glucopyranoside 14b (1) Thiocarbonylation of **12b** with Bu_2SnO and $CSCl_2$: Compound **12b** (1.43 g) was stannylated with Bu_2SnO (1.6 g, 1.0 mol eq) and treated with $CSCl_2$ (0.54 ml, 1.1 mol eq), then worked up as described for the α-anomer to give the 6-*O*-chlorothiocarbonyl derivative **13b** (1.9 g, 100%), as a syrup. ^{1}H-NMR: 4.83 (1H, dd, *J*=11.9, 2.0 Hz, H-6), 4.68 (1H, dd, *J*=11.9, 6.0 Hz, H-6), 4.25 (1H, d, *J*=7.6 Hz, H-1), 3.64, 3.57, 3.55 (each 3H, s, OMe), 3.63 (1H, m, H-5), 3.46 (1H, t, *J*=9.2 Hz, H-4), 3.14 (1H, t, *J*=8.8 Hz, H-3), 3.04 (1H, dd, *J*=9.1, 7.6 Hz, H-2).

Treatment of **13b** (1.9 g) in dioxane (5 ml) with DMAP (100 mg) for 30 min as described for the α-anomer gave the cyclic 4,6-*O*-thionocarbonate **14b** (800 mg, 48%), as colorless prisms from $CHCl_3$–hexane, mp 173—

175 °C. IR (KBr): 1298, 1278, 1119. ^{1}H-NMR: 4.64 (1H, dd, J=10.3, 6.0 Hz, H-6), 4.38 (1H, d, J=7.8 Hz, H-1), 4.29 (1H, t, J=10.4 Hz, H-6), 4.06 (1H, t, J=9.7 Hz, H-4), 3.78 (1H, td, J=10.1, 6.0 Hz, H-5), 3.67, 3.59, 3.55 (each 3H, s, OMe), 3.42 (1H, t, J=8.2 Hz, H-3), 3.09 (1H, t, J=8.2 Hz, H-2). MS: 264 (M^+, 24), 232 (5), 203 (10), 145 (33), 88 (100). *Anal*. Calcd for $C_{10}H_{16}O_5S$: C, 45.45; H, 6.10. Found: C, 45.29; H, 5.70.

(2) The Im_2CS method gave **14b** in only 7% yield.

Rearrangement of 14b under Ionic Conditions A mixture of **14b** (100 mg) and KI (600 mg) in MeCN (4 ml) was heated in a sealed tube at 70 °C for 24 h. The cooled mixture was filtered and the filtrate was chromatographed on a short silica gel column to give the methyl 4,6-*O*,*S*-carbonyl-3-*O*-methyl-6-thio-β-D-glucopyranoside **15b** as a syrup (slightly contaminated with **14b**). ^{1}H-NMR: 4.30 (1H, d, J=7.8 Hz, H-1), 4.13 (1H, t, J=9.2 Hz, H-4), 3.77 (1H, td, J=10.0, 5.7 Hz, H-5), 3.37 (1H, t, J=9.0 Hz, H-3), 3.23 (1H, t, J=10.3 Hz, H-6), 3.17 (1H, dd, J=11.2, 5.7 Hz, H-6), 3.05 (1H, dd, J=9.0, 7.8 Hz, H-2), 3.64, 3.59, 3.55 (each 3H, s, OMe).

Attempted Radical Rearrangement Each 50 mg was treated using methods A, B, and C (see text), respectively. The result was judged from the peak at δ 160—170 (thiolcarbonate), *ca*. 140 (carbonate) in the ^{13}C-NMR of the product.

Reaction of 10 by Method C Benzoyl peroxide (101 mg, 1.0 eq) was added every 30 min to a heated mixture of the deoxy derivative **10** (100 mg) and dimethyl phosphonate (153 μl, 4.0 eq) in dioxane (5 ml) in a sealed tube at 120 °C, and heating was continued for 1 h. The mixture was diluted with $CHCl_3$, washed with $NaHCO_3$, dried, and concentrated. Chromatography of the residue with benzene–AcOEt (10 : 1 to 0 : 1) gave 3,6-dideoxy-α-D-glucofuranose (**20**) (18 mg, 24%). ^{1}H-NMR: 5.82 (1H, d, J=3.7 Hz, H-1), 4.75 (1H, t, J=4.0 Hz, H-2), 4.17 (1H, ddd, J=10.5, 4.9, 3.4 Hz, H-4), 4.11 (1H, ddd, J=9.8, 6.6, 3.4 Hz, H-5), 1.96 (1H, dd, J=13.5, 3.9 Hz, H-3), 1.89 (1H, ddd, J=13.5, 10.4, 4.5 Hz, H-3), 1.52, 1.33 (each 3H, s, $Me_2C<$), 1.14 (3H, d, J=6.6 Hz, H-6).

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