Thio-Sugars. I. Radical-Promoted Thione–Thiol Rearrangement of Cyclic Thionocarbonates: Synthesis of 5-Thioglucose[1,2]

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Received February 22, 1996; accepted April 5, 1996

The 5,6-*O*-thiocarbonyl-α-D-glucofuranose derivatives 2, when subjected to one of the following reactions, undergo a radical-promoted thione–thiol rearrangement to yield the 5-*S*-thiolcarbonates of *gluco*-configuration 8 as the major product. The reactions are, (A) thermolysis with a catalytic amount of tributyltin hydride and AIBN, (B) photolysis with hexabutyldistannane, and (C) thermolysis with dimethyl phosphonate and benzoyl peroxide. On the other hand, thermolysis of 2 with trialkylsilane (condition D) yielded olefins 13 as the major product. The 5-*S*-*gluco* product 8 was converted, in three steps, to 5-thioglucose (21) in 55% yield.

Key words cyclic thionocarbonate; thione–thiol rearrangement; 5-thioglucose; radical promoted rearrangement; hexabutyldistannane-*hν*; dimethyl phosphonate

It is well known that treatment of a cyclic thionocarbonate (**A**) derived from a 1,2-glycol with trialkyltin hydride in the presence of a radical initiator such as α,α-azobisisobutyronitrile (AIBN) results in the formation of a mono-deoxygenated product (**C**).[4] Tsuda *et al.*[2] found that, when the reaction was carried out with a catalytic amount of the reagent, the product was a thiolcarbonate (**B**), an *O–S* rearrangement product. In contrast to the stoichiometric reaction with tin hydride in the deoxygenation reaction, this *O–S* rearrangement reaction proceeds catalytically, regenerating the original radical species in the reaction.[2] Since cyclic thionocarbonates of carbohydrates are regioselectively prepared by the use of dibutyltin oxide and phenoxy-thiocarbonyl chloride[5a] or thiophosgene,[5b] the combination of these procedures (thiocarbonylation followed by rearrangement) provides a new approach to thio-glycosides from common glycosides. Stereo- and regio-chemical outcomes of the reaction, reported in a previous communication,[2] are briefly summarized as follows. 1) Thionocarbonates formed from secondary-secondary glycols always give thiolcarbonates of *cis*-configuration. However, the direction of rearrangement is not well-controlled, and the product is usually a mixture of two regio-isomers. 2) Thionocarbonates formed from primary-secondary glycols give the thiolcarbonates, in which the rearrangement occurs regioselectively toward the secondary position, but the product is usually accompanied with the other stereo-isomer. This radical-promoted rearrangement of thionocarbonates is in sharp contrast to the rearrangement of the same substrate under the ionic condition reported by Trimnell *et al.*,[6] which worked only for the primary-secondary system and yielded the primary-*S* product exclusively.

Common by-products in this rearrangement reaction are deoxy (**C**) and oxo (**D**) derivatives. Formation of the deoxy derivative (**C**) could not be avoided when a tin hydride was used as the radical source, and the amount increased with increase of the reagent. The oxo derivative (**D**) could be produced by the action of contaminating aerial oxygen on the intermediate radical (i) and was sometimes hardly avoidable. Formation of the deoxo derivative (**E**) was negligible, unless a large excess of tin hydride was used at once.[7] The olefin (**F**) was sometimes observed, depending on the reaction conditions and the nature of the substrate (see below).

The purpose of the work described here was to see whether the yiels and selectivity in the rearrangement of the 5,6-*O*-thionocarbonates (**2** and **6**), derived from 1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) and -β-L-idofuranose (**5**), respectively, could be improved by

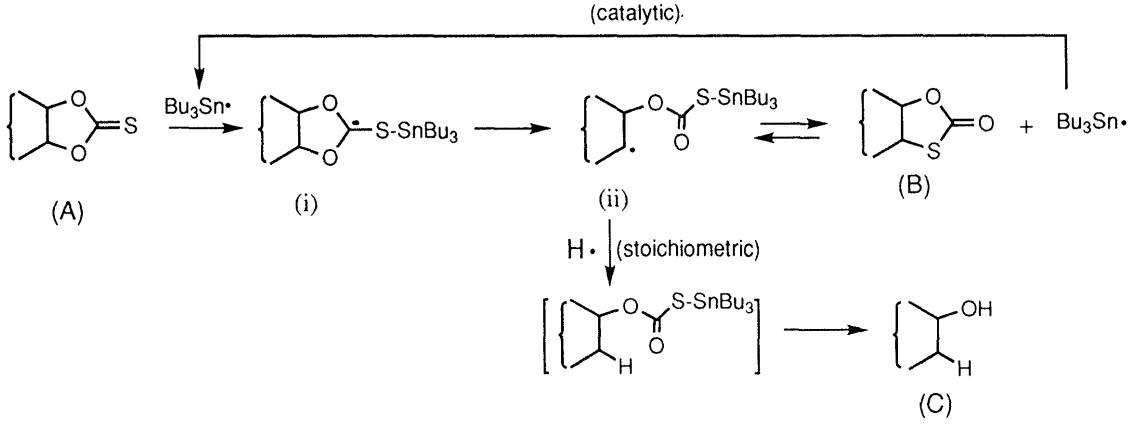

Chart 1. Radical-Catalyzed *O–S* Rearrangement of Thionocarbonates

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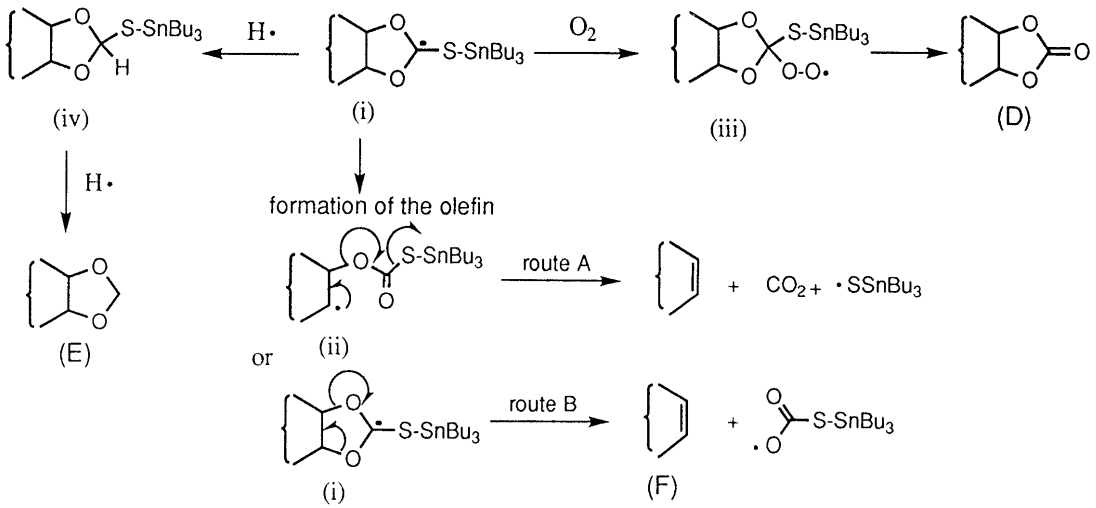

Chart 2. Side Reactions in the Radical-Catalyzed *O*–*S* Rearrangement Reaction

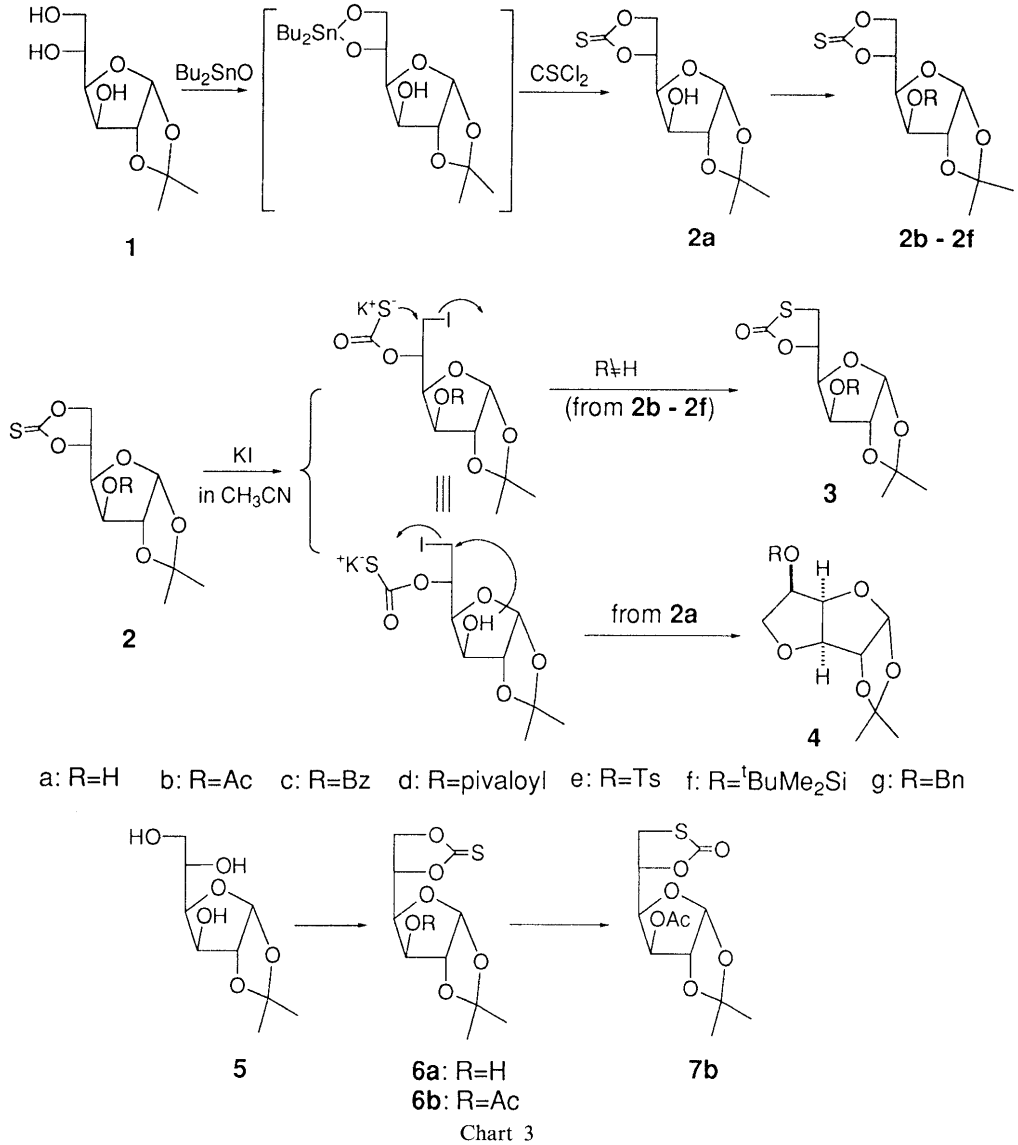

Chart 3

changing the radical source, reaction conditions, and steric features of the substrates. We also present a new, efficient route to 5-thioglucose from glucose.

Results and Discussion

The substrates, 3-*O*-protected 1,2-*O*-isopropylidene-5,6-*O*-thiocarbonyl-α-D-glucofuranoses (**2**), were readily prepared as follows. Stannylation of 1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) with dibutyltin oxide in MeOH followed by treatment with thiophosgene in dioxane gave, in good yield, the 5,6-*O*-thionocarbonate **2a**,[8] which was smoothly converted to **2b**—**f** by usual acylation or

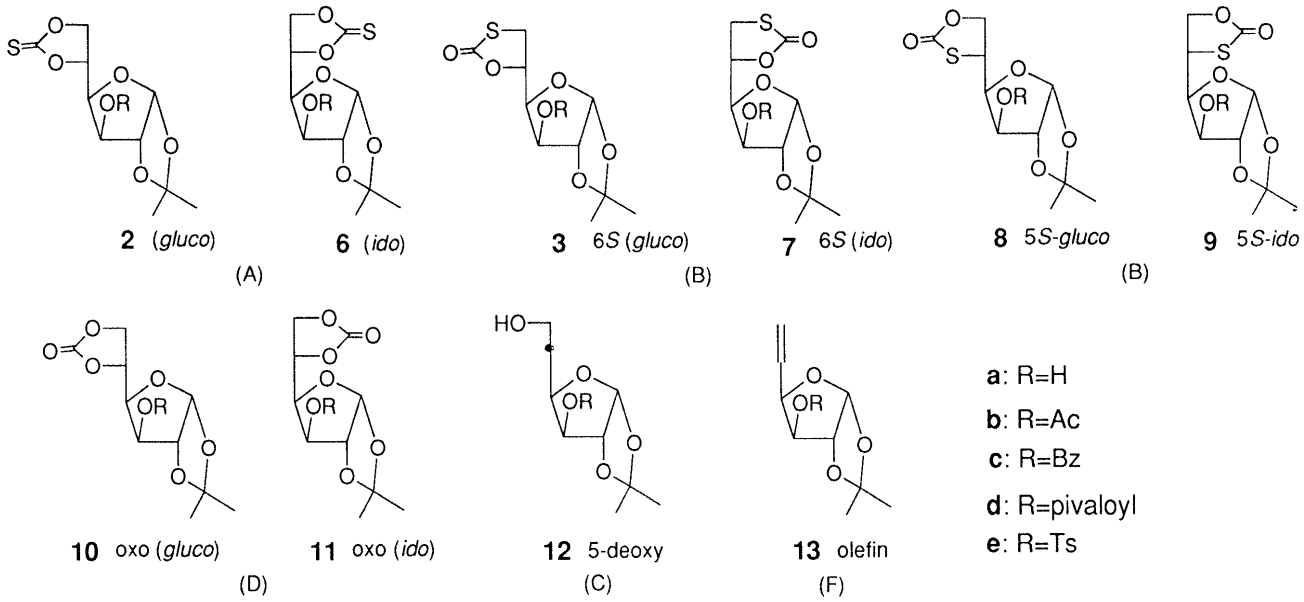

Chart 4

silylation. The 3-*O*-benzyl derivative **2g** was obtained from the known 3-*O*-benzyl-isopropylidene derivative[9] by thiocarbonylation using the above method. The stereoisomer, the *β*-L-idofuranose derivative **6b**, was prepared similarly from the corresponding idofuranose **5**.

Rearrangement of Thionocarbonates under an Ionic Condition All of the above substrates (**2**), except for **2a**, on treatment with KI in MeCN, gave 6-*S* thiolcarbonates (**3**) in good yields, as reported for **2b**.[6] The *ido* derivative **6b** also gave the 6-*S* product **7b** exclusively. However, the 3-OH derivative **2a** gave a different product, the 3,6-ether (**4a**), exclusively on the same treatment. Formation of this product was explained by attack of the 3-OH group on the intermediary 6-iodide. The structure of the product was proved by conversion to the corresponding acetate (**4b**) and benzoate (**4c**), and analysis of the ^{1}H–^{1}H and ^{13}C–^{1}H correlation spectroscopy (COSY) of the acetate **4b**.

Radical-Promoted Rearrangement of *gluco*-Type Thionocarbonates For radical-promoted rearrangement, the following four methods were examined: (A) tributyltin radical generated from tributyltin hydride and AIBN, (B) trialkyltin radical created by photolysis of hexaalkyldistannane, (C) phosphonate radical generated from dialkyl phosphonate and benzoyl peroxide, and (D) trialkylsilyl radical generated from trialkylsilane and benzoyl peroxide. In each reaction, the products (Chart 4) were analyzed by gas chromatography (GLC) (for example, Fig. 1) and their structures were determined spectroscopically after isolation. The conversion yield was calculated from the total yield (%) of the rearrangement products (**3**+**8**+**9**), the regioselectivity from the ratio of 5-*S*/6-*S*=(**8**+**9**)/**3**, and the stereoselectivity from the ratio of 5-*S*-*gluco*/5-*S*-*ido*=**8**/**9**.

(A) Tributyltin Hydride and AIBN The reaction of **2b** with Bu_3SnH (0.3 molar eq) and AIBN (0.3 molar eq) in refluxing toluene for 3 h gave rearrangement products, **3b**, **8b**, and **9b**, in the conversion yield of 61% with the regioselectivity of 2.3[10] and the stereoselectivity of 2.5,[10] with recovery of the starting material **2b** (24%). This result

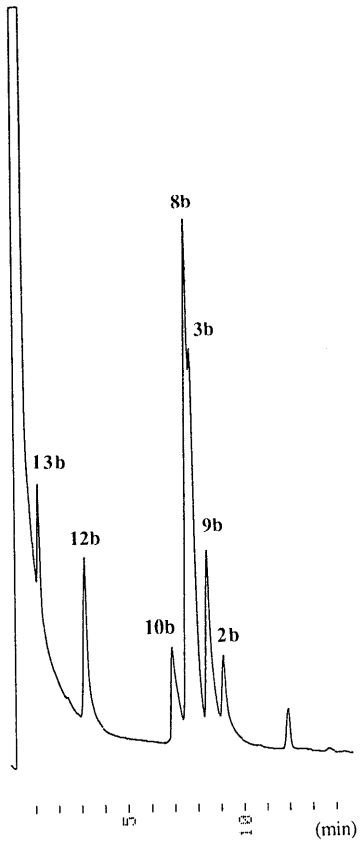

Fig. 1. Example of the GLC of Reaction Products (See Table 1, B-4)
GLC condition: N_2 flow, 45 ml/min. Injection temperature, 170 °C. Column temperature, 150 °C to 270 °C, 8 °C/min. See also Experimental.

clearly indicates that the reaction proceeded catalytically, since the conversion yield reached more than twice the amount of tin radical used for the reaction. Major by-products in this reaction were the 5-deoxy (**12b**) and oxo (**10b**) derivatives. The former was the major product when the reaction was carried with equimolar tin hydride. The yield of the oxo derivative **10b** was not constant, possibly due to the original contamination in the starting material[8] and air contamination in the reaction, as

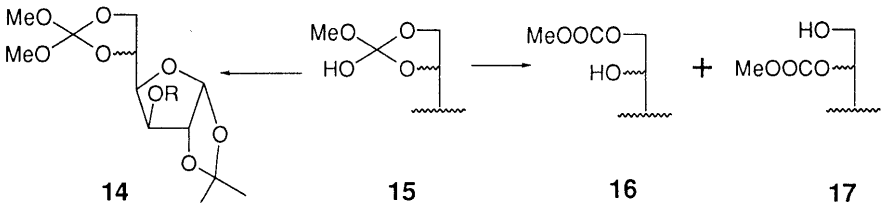

Chart 5

Table 1. Thermolysis (A)[a] and Photolysis (B)[b] of **2b** with Bu_3SnH or $(R_3Sn)_2$ Reagent (GLC Yield, %)

Method	Reagent	Recov. **2**	Olefin **13**	Deoxy **12**	Oxo **10**	5-*S*-*glc* **8**	5-*S*-*ido* **9**	6-*S* **3**	Conv. (%)	Regio s. 5-*S*/6-*S*	Stereo s. *glc*/*ido*
A-1	Bu_3SnH–AIBN, Δ	24.0	—	5.0	10.0	30.5	12.2	18.3	61.0	2.3	2.5
A-2	Combination reagent[c]	7.1	1.3	7.3	2.2	36.8	15.8	29.0	81.6	1.8	2.3
B-1	$(Bu_3Sn)_2$ (0.5 eq)–*hv*	32.3	2.9	3.5	8.5	18.3	18.3	16.1	52.7	2.3	1.0
B-2	$(Bu_3Sn)_2$ (1.8 eq)–*hv*	5.4	2.0	5.6	11.2	33.4	19.0	23.3	75.7	2.2	1.9
B-3	$(Bu_3Sn)_2$ (5.0)–*hv*	9.0	3.0	9.6	8.3	30.0	15.6	22.6	68.2	2.0	1.9
B-4	$(Me_3Sn)_2$ (1.8 eq)–*hv*	40.6	—	—	12.6	22.8	9.7	22.8	46.7	1.4	2.4
B-5	$(PhS)_2$–*hv*	76.0	—	—	24.0	—	—	—			
B-6	$(Bu_3Sn)_2+(PhSe)_2$–*hv*	32.4	2.4	13.2	11.9	17.7	6.8	13.8	38.8	1.8	2.6
B-7	$(Bu_3Sn)_2+Ph_3P$–*hv*	9.1	7.0	39.2	6.7	13.4	10.0	11.2	34.0	2.1	1.3

a) Bu_3SnH (0.3 eq), AIBN (0.3 eq) in toluene at 120 °C for 3 h (see reference 2). *b*) With a 300 W Hg lamp at 10—15 °C for 4 h. *c*) Reaction for **2c**. Reagent: Bu_3SnH (0.3 eq)–$(Bu_3Sn)_2$ (1.0 eq)–AIBN (1.0 eq). Conditions: reflux in benzene for 1 h (see Experimental).

Table 2. Solvent Effect on the Photolysis (B) of **2b** with $(Bu_3Sn)_2$ (GLC Yield, %)[a]

Entry	Solvent	Recov. **2b**	Olefin **13b**	Deoxy **12b**	Oxo **10b**	5-*S*-*glc* **8b**	5-*S*-*ido* **9b**	6-*S* **3b**	Conv. (%)	Regio s. 5-*S*/6-*S*	Stereo s. *glc*/*ido*
B-2	Benzene	5.4	2.0	5.6	11.2	33.4	19.0	23.3	75.7	2.2	1.9
B-8	Toluene	2.3	28.4	13.6	4.3	21.0	8.4	22.0	51.4	1.3	2.5
B-9	MeOH	3.3	1.2	53.5	16.1	9.3	6.1	5.8	21.2	2.7	1.5
B-10	MeCN	8.5	0.5	41.8	31.9				(17.3)[b]		
B-11	EtOAc	28.4	0.7	50.2	4.1				(16.6)		
B-12	THF	41.0	3.0	4.2	5.9				(18.4)		
B-13	Benzene+TSA	43.3	0.6	1.1	6.1	17.3	14.5	16.6	48.9	1.9	1.2
B-14	Benzene+Et_3N	90.8	—	9.2							

a) Internal irradiation with $(Bu_3Sn)_2$ (1.8 mol eq) by a 300 W Hg lamp at 10—15 °C for 4 h. *b*) Parenthetical value indicates the total yield of the rearrangement products (**3b**+**8b**+**9b**).

discussed previously.[2,7] The effects could be minimized when hexabutyldistannane was used as a co-reagent (Table 1, entry A-2). Although this reagent did not give the tin radical with AIBN (**2b** was recovered unchanged on heating with hexabutyldistannane and AIBN in toluene), the radical formed from Bu_3SnH cleaved it to a new radical, which participated in the chain reaction.

The use of MeOH entirely changed the outcome, producing more than 12 compounds, whose ratios were variable depending on the reaction conditions (amount of tin hydride, temperature, and reaction time). Although not all of them were completely analyzed, the major products were the 5-deoxy derivative (**12b**) and the ortho-ester (**14**), and sometimes the olefin (**13b**), as detected by GLC and the ^{1}H-NMR spectroscopy of the roughly separated fractions. The presence of methyl carbonates (**16b** and **17b**) and the oxo derivative (**10b**), probably produced from **15b**, was also suggested. However, it is not clear whether the reaction is radical or ionic.

(B) Photolysis with Hexaalkyldistannane In the hope of avoiding the formation of the deoxy product (**12b**) the photolysis with hexaalkyldistannane was then examined. Irradiation of a mixture of **2b** and 0.5 molar eq of $(Bu_3Sn)_2$ in benzene with >290 nm light for 4.5 h gave the expected rearrangement products with a conversion yield of 52.7%, together with the olefin **13b** (2.9%), the 5-deoxy derivative **12b** (3.5%), and the carbonate **10b** (8.5%). Increase in the amount of the reagent to 1.8 molar eq increased the conversion yield to 76%. However, the regio- and stereo-selectivities, 2.2 and 1.9, were not much improved. Further increase of the reagent improved neither the conversion yield nor the selectivities. Use of hexamethyldistannane reduced the conversion yield (47%), though the stereo-selectivity slightly increased to 2.4. Irradiation with diphenyl disulfide gave only the oxo derivative **10b** (24%) with recovery of the starting material **2b** (76%). Although the combination of $(Bu_3Sn)_2$ and $(PhSe)_2$ slightly increased the stereoselectivity to 2.4, the conversion yield was instead decreased (38.3%). The combination of $(Bu_3Sn)_2$ and Ph_3P produced the 5-deoxy derivative (**12b**) as a major product.

Solvent Effect: As seen in Table 2, the reaction of **2b** in toluene gave the olefin **13b** as a major product. Reactions in MeOH or MeCN afforded the deoxy compound **12b** as

Table 3. Effect of 3-OR Group on the Photolysis (B) of **2** with $(Bu_3Sn)_2$ (Isolation Yield, %)[a]

Entry	3-OR group	Recov. **2**	Olefin **13**	Deoxy **12**	Oxo **10**	5-*S*-*glc* **8**	5-*S*-*ido* **9**	6-*S* **3**	Conv. (%)	Regio s. 5-*S*/6-*S*	Stereo s. *glc*/*ido*
B-15	Ac (**b**)	—	11.3	17.3	—	17.8	17.3	17.8	52.9	2.0	1.0
B-16	Bz (**c**)	—	6.1	8.6	—	38.3	16.7	19.1	74.1	2.9	2.3
B-17	Piv (**d**)	—	10.5	16.0	—	23.0	10.2	23.0	56.2	1.4	2.3
B-18	Ts (**e**)	21.3	6.7	2.5	3.6	28.0[b]	6.6	17.6[b]	52.2	2.0	4.2

a) See Experimental. *b*) Combined yield of the 3-OH (**a**) and 3-OTs (**e**) products.

Table 4. Thermolysis (C) of **2c** with $(RO)_2PHO$ (GLC Yield, %)[a]

Method	Reagent	Recov. **2c**	Oxo **10c**	5-*S*-*glc* **8c**	5-*S*-*ido* **9c**	6-*S* **3c**	Conv. (%)	Regio s. 5-*S*/6-*S*	Stereo s. *glc*/*ido*
C-1	$(MeO)_2PHO$ (0.4 eq)	69.6	7.4	9.3	6.6	5.4	21.3	3.0	1.4
C-2	$(MeO)_2PHO$ (4.0 eq)	24.5	9.3	26.2	19.7	15.2	61.1	3.0	1.3
C-3	$(EtO)_2PHO$ (4.0 eq)	47.8	8.8	17.9	12.5	9.8	40.2	3.1	1.4
C-4	$(PhO)_2PHO$ (4.0 eq)	58.2	8.6	7.8	5.3	3.9	17.0	3.4	1.5
C-5	H_3PO_2 (4.0 eq)	84.2	8.5	1.5	0.6	1.9	11.0	1.2	2.4
C-6	$(MeO)_2PHO$[b]	10.0	6.0	36.0	29.0	19.0	84.0	3.4	1.3

a) Heating with $(PhCOO)_2$ (0.4 eq) in dioxane under reflux for 2 h. *b*) In dioxane at 120 °C with $(MeO)_2PHO$ (4.0 eq) and $(PhCOO)_2$ (1.0 eq) for 20 min, then $(PhCOO)_2$ (1.0 eq) was added and the mixture was heated at 120 °C for a further 20 min.

Table 5. Effect of the 3-OR Group on Thermolysis (C) of **2** with $(MeO)_2PHO$ (GLC Yield, %)[a]

Method	3-OR group	Recov. **2**	5-*S*-*glc* **8**	5-*S*-*ido* **9**	6-*S* **3**	Conv. (%)	Regio s. 5-*S*/6-*S*	Stereo s. *glc*/*ido*
C-6	Ac (**b**)	29.4	20.0	14.4	11.1	45.5	3.1	1.4
C-1	Bz (**c**)	24.5	26.2	19.7	15.2	61.1	3.0	1.3
C-7	Piv (**d**)	24.1	34.5	20.7	20.7	75.9	2.7	1.7
C-8	Ts (**e**)	38.2	28.6	13.9	9.6	52.1	4.4	2.1
C-9	TBS (**f**)	61.9				(26.9)[b]		
C10	Bn (**g**)	51.2				(48.8)		

a) Heating with dimethyl phosphonate (4.0 molar eq) and benzoyl peroxide (0.4 eq) in dioxane under reflux for 2 h. *b*) Parenthetical values indicate the total yield of rearrangement products.

a major product, which could be produced by abstraction of hydrogen from the solvent. Tetrahydrofuran (THF) and AcOEt retarded the reaction. Addition of acid (TsOH) or base (Et_3N) also retarded the reaction.

3-*O*-Substituent: The effect of the 3-*O*-substituent was next examined (Table 3, isolation yields are indicated) by changing its bulkiness and electronegativity. The highest conversion yield (74.1%) was obtained for the benzoate **2c**. The stereoselectivity was increased for the benzoate **2c** and pivaloate **2d**, but the regioselectivity was decreased for **2d**. The tosylate **2e** gave the highest stereoselectivity (4.2), but the reaction was slower than that of **2b** (low conversion yield) and the product was accompanied by de-tosylated products **3a**, **8a**, and **9a**, thus decreasing the yield of **8e**. The above results suggest that the benzoate (**2c**) might be the preferred substrate and irradiation with hexabutyldistannane in benzene would be the practical choice for the *O*–*S* rearrangement by method B to yield the product of *gluco*-configuration.

(C) Dimethyl Phosphonate and Peroxide Method Dialkyl phosphonates (or dialkyl phosphites) produce a radical on the phosphorus atom when heated in the presence of a suitable radical initiator, and used for deoxygenation of thionocarbonates.[11] Heating of **2c** with an excess of dimethyl phosphonate (4 eq) and benzoyl peroxide (0.4 eq) in dioxane under reflux for 2 h produced the expected rearrangement products in the conversion yield of 61% with the regioselectivity of 3.0 and stereoselectivity of 1.3, together with the oxo derivative **10c** (9.3%) and recovery of the starting material **2c** (24.5%). It is noteworthy that the formation of the 5-deoxy derivative (**12c**) was negligible in this reaction.[12] When diethyl and diphenyl phosphonates were used as radical sources under similar reaction conditions, the conversion yields were decreased to 40.2% and 17%, respectively. However, the regio- and stereo-selectivities slightly increased in the latter reactions (Table 4).

THF, MeCN, and benzene were not suitable solvents in this method probably due to their low boiling point in relation to the decomposition of benzoyl peroxide. Toluene was again ineffective for the reaction, suggesting that the radical cleavage of the initiator is influenced not only by the temperature, but also by the polarity of the solvent. Addition of acid (TsOH) resulted only in decomposition of the substrate. Base (Et_3N) retarded the reaction.

As an initiator of the reaction, benzoyl peroxide was the best reagent: AIBN, Et_3B, Pr_3SiH–Et_3B, and sonication were ineffective. Practically, the best result was obtained by conducting the reaction in dioxane at 120 °C (sealed tube) with dimethyl phosphonate (4.0 molar eq)

for 40 min, with two additions of benzoyl peroxide (1.0 molar eq) at 20 min intervals, yielding 84% conversion with the regioselectivity of 3.4 and stereoselectivity of 1.3 (GLC analysis).

Effect of 3-*O*-Substituent: Table 5 indicates the effect of 3-*O*-substituents on this rearrangement using method C. Compared to the benzoate (**2c**), the reaction of the acetate (**2b**) was slower, but the regioselectivity (3.1) and stereoselectivity (1.4) were unchanged. For the pivaloate (**2d**), regioselectivity was decreased (2.7), but stereoselectivity was slightly increased (1.6). Although the tosylate (**2e**) gave the best regio- and stereo-selectivities, 4.4 and 2.1, respectively, the reaction was slow and the conversion yield was insufficient (52% after 4 h reaction).

(D) Trialkylsilane and Peroxide Method Alkyl- or aryl-silanes are sometimes used for deoxygenation of xanthates and thionocarbonates.[13] Application of these reagents with benzoyl peroxide as an initiator to the benzoate (**2c**) resulted in the formation of the olefin (**13c**) as a major product. Interestingly, **13c** was a sole product in 73.8% yield (GLC analysis), when tripropylsilane was used as the radical source.[15] When triphenylsilane was used, the olefin (**13c**) and the 5-deoxy derivative (**12c**) were produced in nearly equal amounts. In neither of these runs was the rearrangement product detected among the products, indicating that this method is not appropriate for the rearrangement reaction.

***O,S*-Rearrangement Reaction of *ido*-Type Thionocarbonates** In order to clarify the effect of C-5 stereochemistry in the substrate, the reaction of the *ido* compound (**6b**) was compared to that of the *gluco* derivative (**2b**), calculating the conversion yield from the % of (**7**+**8**+**9**), regioselectivity from (**8**+**9**)/**7**, and stereoselectivity from **8**/**9**.

In photolysis (method B), the conversion yield from **6b** was 65.4%, and the regio- and stereo-selectivities were 3.2 and 1.9, respectively, but with preferential formation of the olefin **13b** (28.9%) as compared with that from the *gluco*-derivative **2b** (2.0%). The appearance of the same stereoselectivity from the *gluco* and *ido* compounds supports the view that the 5-*S* products are produced from the same radical intermediate at C-5. The marked difference in the formation of olefin **13b** between **6b** and **2b** suggests that it was not produced from the C-5 radical, but through a different pathway (possibly route B in Chart 2), since its ratio depends on the stereochemistry at C-5 of the substrate.

Table 6. Reaction of **2c** with Trialkylsilane (GLC Yield, %)[a]

Method (D)	Reagent	Recov. **2c**	Olefin **13c**	Deoxy **12c**	Oxo **10c**
D-1	Et_3SiH (0.4 eq)	21.6	22.0	—	37.5
D-2	Et_3SiH (4.0 eq)	9.0	55.5	—	15.5
D-3	Pr_3SiH (4.0 eq)	—	100	—	—
D-4	Ph_3SiH (4.0 eq)	—	43.3	43.3	—

a) Heating under reflux in dioxane with benzoyl peroxide (0.4 molar eq) for 2 h.

The reactions with Bu_3SnH in MeOH gave analogous results for **2b** and **6b**: the major products were the deoxy (**12b**) and the ortho-ester (**14** of *ido*-configuration from **6b**).

In thermolysis with phosphonate (method C), **6b** gave the conversion yield of 78%, with regioselectivity of 2.3, and stereoselectivity of 3.2, suggesting that the radical formation is dependent on the radical source used for the reaction. The olefin **13b** was not observed in this reaction.

Structure Determination of Products Practical separation and structure determination of the products are exemplified for the acetates, as follows. The 5-deoxy derivative (**12b**) gave the lowest and the olefin (**13b**) gave the highest spots on thin layer chromatography (TLC) on silica gel, and thus could be readily separated from other components by chromatography. The starting material (**2b**), oxo derivative (**10b**), and rearrangement products **3b**, **8b**, and **9b** gave ajacent spots, from which **2b**, **9b**, and **10b** were separated by repeated chromatography on a silica-gel column. Separation of **3b** and **8b** was achieved by recycling high-performance liquid chromatography (HPLC) (see Experimental).

The olefin (**13b**) showed ^{13}C peaks at δ 130.7 and 119.5, and ^1H peaks at δ 5.79 (1H, ddd, J=6.3, 10.3, 17.0 Hz), 5.44 (1H, br d, J=17.0 Hz), and 5.28 (1H, br d, J=10.3 Hz), indicative of a $-CH=CH_2$ group.

The 6-*S* derivative (**3b**) showed ^{13}C peaks at δ 33.9 and 171.9 attributable to a CH_2–S–CO–O group, and was identical with the sample prepared by the ionic rearrangement (see above). The oxo derivative (**10b**) is known.[5b] The deoxy derivative (**12b**) characteristically showed a strong (M^+-Me) peak at m/z 231. The IR spectrum showed an OH at 3500 cm^{-1}, but no C=O and C=S absorptions. The presence of a ^{13}C signal due to the CH_2 at δ 30.9 and ^1H signals for 2H at δ 1.75—1.93 indicated that this is the 5-deoxy derivative.

The 5-*S*-*gluco* and 5-*S*-*ido* derivatives, **8b** and **9b**, had the same formula, $C_{12}H_{16}O_7S$. In the ^{13}C-NMR spectra they showed peaks at δ 171.5 and 172.4 due to the thiolcarbonate and the absorptions of CH-S at δ 45.4 and 46.7, respectively. In the ^1H-NMR spectra, the H-5 signals are shifted up-field compared to those of **2b** by 1.9 and 1.8 ppm, respectively. The stereochemistries at C-5 were determined as follows. Comparing the C-5 signal of various *gluco* and *ido* derivatives of the same planar structure revealed that C-5 of the *gluco*-derivatives always resonates at a higher field than that of the corresponding *ido*-derivatives, thus suggesting that **8b** is the *gluco* and **9b**

Table 7. Comparison of the Reactions of *gluco*- and *ido*-Thionocarbonates (GLC Yield, %)

Compd.	Method	Recov.	Olefin	Deoxy	Oxo	5-*S*-*glc*	5-*S*-*ido*	6-*S*	Conv.	5-*S*/6-*S*	*glc*/*ido*
2b (*glc*)	B (B-2)	5.4	2.0	5.6	11.2	33.4	19.0	23.3	75.7	2.2	1.9
6b (*ido*)	B	0.8	28.9	4.7	0.3	32.7	17.3	15.4	65.4	3.2	1.9
2b (*glc*)	C (C-6)	29.4	—	—		20.0	14.4	11.1	45.5	3.1	1.4
6b (*ido*)	C	22.2	—	—		41.0	13.0	24.0	78.0	2.3	3.2

is the *ido* derivative. The GLC also supported this assignment, since *gluco* derivatives always had smaller retention times than *ido* derivatives of the corresponding planar structure. Compound **8b** had a smaller retention time than **9b**.

All corresponding 3-OR derivatives were compatible with the above assignment. Finally, the assignment was confirmed by an X-ray analysis of the 3-*O*-benzoate **8c** (Fig. 2). ^{13}C-NMR data for all these compounds are listed in Table 8.

Conversion of 5-*S*-*gluco*-Thiolcarbonate (8) to 5-Thioglucose (21) Direct hydrolysis of **8b** with NaOH–H_2O followed by recyclization gave the expected 5-thioglucose (**21a**), but the yield was low. The following alternative route was found to be more practical. On treatment with 0.05 M NaOMe in MeOH at room temperature, the 5-*S*-*gluco* derivative **8c** rapidly changed

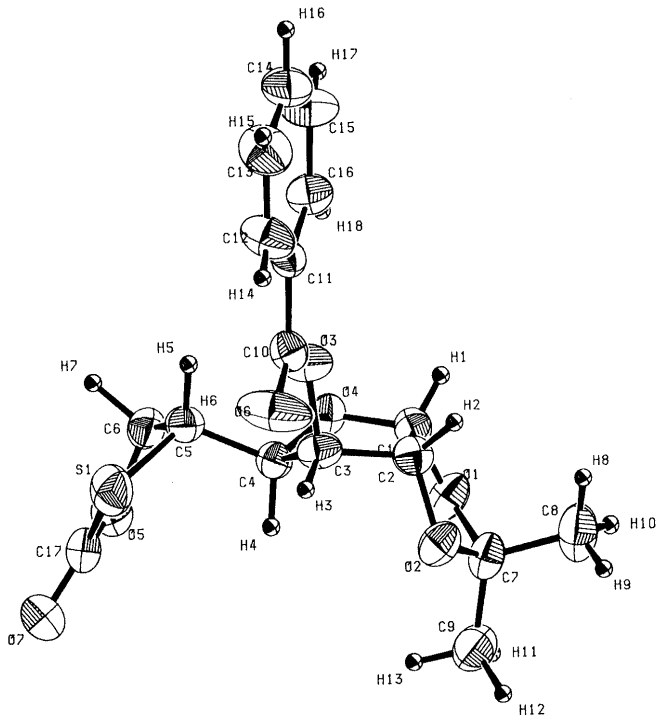

Fig. 2. ORTEP Drawing of Compound **8c**

Table 8. ^{13}C-NMR Data for Compounds in This Paper (in $CDCl_3$)

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	C=X
2a[b]	105.7	85.4	74.0	80.3	79.6	70.9	192.1
2b	105.2	83.2	76.1	77.5	78.1	70.5	190.8
2c	105.2	83.2	76.3	77.6	78.1	70.3	190.7
2d	105.1	83.3	75.9	78.0	77.7	70.7	190.8
2e	105.2	83.0	81.2	77.7	77.7	70.2	190.4
2f	105.4	85.3	75.5	78.6	79.7	70.9	191.2
2g	105.6	81.7	81.5	78.8	79.3	72.3	191.3
6b	104.8	83.4	76.1	77.9	78.8	70.8	191.1
3a	105.2	85.3	74.4	79.8	76.5	34.3	172.9
3b	104.9	83.3	75.8[a]	77.9	75.7[a]	33.9	171.9
3c	105.0	83.5	76.2[a]	78.3	76.0[a]	33.9	171.7
3d	104.9	83.4	75.9	78.1	75.5	34.0	171.7
3e	104.9	83.3	81.2	78.0	75.2	33.6	171.0
3f	105.2	85.5	76.1	79.9	75.1	34.1	172.4
7b	104.9	83.2	76.0	79.0	77.7	32.9	171.6
8a	105.4	85.4	74.6	81.3	45.5	71.0	172.5
8b	105.2	83.2	76.2	79.8	45.4	70.6	171.5
8c	105.3	83.3	76.6	80.2	45.6	70.6	171.4
8d	105.2	83.3	75.9	80.1	45.5	70.7	171.3
8e	105.1	83.0	81.4	79.6	45.0	70.2	171.4
9b	104.6	83.4	75.7	79.0	46.7	69.4	172.4
9c	104.7	83.7	76.1	79.7	46.9	69.4	172.3
9d	104.6	83.7	75.5	79.9	46.9	69.2	172.3
9e	104.5	83.3	80.5	79.9	46.6	68.7	172.2
10a[c]	106.3	86.4	73.9	80.9	74.7	66.6	155.3
10a[b]	105.6	85.4	74.1	80.1	75.0	66.7	155.6
10b	105.1	83.2	76.2	78.1	73.0	66.3	154.1
10e	105.1	83.0	81.3	78.2	72.6	65.9	153.7
12b	104.3	83.4	77.2[a]	77.4[a]	30.7	59.9	
12c	104.5	83.5	77.7[a]	77.8[a]	30.9	60.2	
12d	104.4	83.6	76.9	77.7	30.8	60.1	
12e	104.3	83.3[a]	83.2[a]	77.1	30.7	59.8	
13b	104.5	83.5	77.3	79.9	130.7	119.2	
13c	104.7	83.7	77.9	80.2	130.7	119.5	
13d	104.5	83.6	76.9	80.2	130.7	119.0	
13e	104.5	83.4[a]	83.3[a]	79.8	130.1	120.0	
4a	106.9	85.1	85.4	82.4	72.4	72.4	
4b	107.1	84.8	85.2	80.8	73.2	68.7	
4c	107.2	84.8	85.3	81.1	73.7	69.1	
18	105.5	84.9	86.0	76.4	29.6	25.1	
19	105.1	83.0	77.5	75.4	40.2	64.5	
20	96.8	75.0	78.1	76.1	40.9	64.5	
21a[d]	76.4	78.5	76.8	76.9	46.3	63.4	
21b	97.2	73.0	71.7	70.6	39.8	60.9	

a) May be interchanged in each line. *b*) In $CDCl_3$–CD_3OD. *c*) In pyridine-d_5. *d*) In D_2O. The given peaks are due to the α-anomer (see reference 21).

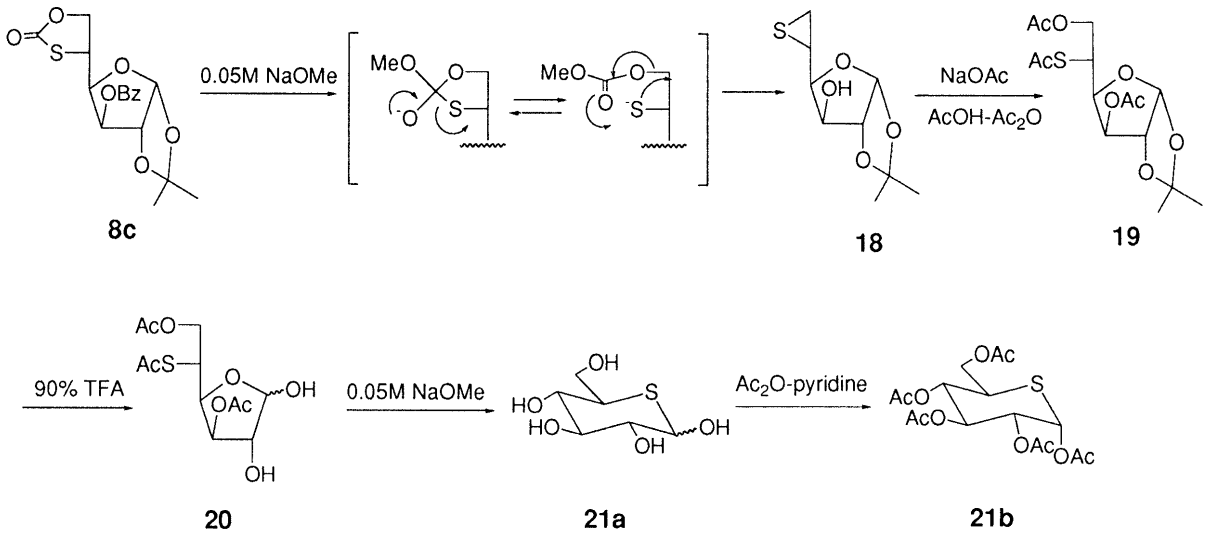

Chart 6

into the thiirane **18**[15] in 97% yield. This unique reaction is discussed in detail in the accompanying paper.[16] The thiirane **18** was converted to 5-thioglucose (**21a**) according to the method reported by Driguez and Henrissat[17]: acetolysis of **18** to **19** followed by acid hydrolysis of the isopropylidene group and then methanolysis of the resulting triacetate **20** yielded the 5-thioglucose (**21a**), which was identical with the specimen obtained above. This was finally characterized as its crystalline pentaacetate (**21b**) of α-configuration.[15,18] The overall yield of **21b** from **8c** was 55%.

The above series of reactions provides a simple and facile route to 5-thioglucose from the readily available glucofuranose derivative (**1**).

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 JEOL GX-400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometers 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 (HRMS) 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. Column chromatography was performed on a silica gel (Wako-gel C-200). Recycling HPLC was performed 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.

1,2-*O*-Isopropylidene-5,6-*O*-thiocarbonyl-α-D-glucofuranose (2a) 1,2-*O*-Isopropylidene-α-D-glucofuranose (**1**, 300 mg) and Bu_2SnO (360 mg, 1.2 molar eq) in dry MeOH (10 ml) were heated under reflux for 3 h, and the mixture was concentrated to dryness. The dried residue was dissolved in dioxane (13 ml) and treated with $CSCl_2$ (0.14 ml, 1.0 molar eq) at 5—10 °C for 1 h, and the mixture was concentrated *in vacuo*. The residue was chromatographed in benzene to remove tin compounds. Further elution of the column with $CHCl_3$–acetone (3 : 1) gave **2a** (299 mg, 84%), as colorless needles from acetone–AcOEt, mp 215—216 °C (lit. 206—208 °C).[19]

1,2-*O*-Isopropylidene-5,6-*O*-thiocarbonyl-β-L-idofuranose (6a) 1,2-*O*-Isopropylidene-β-L-idofuranose (**5**, 635 mg) and Bu_2SnO (862 mg, 1.2 molar eq) were reacted and the resulting stannylene derivative was thiocarbonylated with $CSCl_2$ (0.26 ml, 1.2 molar eq) as described above to afford **6a** (696 mg, 92%), as colorless prisms from acetone–AcOEt, mp 160—161 °C. IR (KBr): 3200—3600 (OH). ^1H-NMR (100 Mz, pyridine-d_5): 6.28 (1H, d, J=3.5 Hz, H-1), 5.60 (1H, dt, J=8.6, 7.8 Hz, H-5), 5.40—4.60 (5H, m, H-2, 3, 4, 6), 1.52, 1.35 (each 3H, s, Me). *Anal.* Calcd for $C_{10}H_{14}O_6S$: C, 45.80; H, 5.38. Found: C, 45.80; H, 5.29.

3-*O*-Acyl-1,2-*O*-isopropylidene-5,6-*O*-thiocarbonyl-α-D-glucofuranoses (2b—e) 1) Acetylation of **2a** with Ac_2O and pyridine as usual gave the acetate **2b** in 96% yield. Colorless needles from MeOH, mp 141—144 °C (lit. 144—146 °C).[19]

2) Benzoylation of **2a** with benzoyl chloride and pyridine gave the benzoate **2c** in 89% yield. Colorless prisms from EtOAc–hexane, mp 205—206 °C. IR (KBr): 1720 (OBz), 1297 (C=S). ^1H-NMR: 7.96 (2H, d, J=7.8 Hz, Ph-H), 7.63 (1H, t, J=7.8 Hz, Ph-H), 7.48 (2H, t, J=7.8 Hz, Ph-H), 6.02 (1H, d, J=3.4 Hz, H-1), 5.57 (1H, d, J=3.0 Hz, H-3), 5.19 (1H, ddd, J=8.8, 7.3, 5.1 Hz, H-5), 4.84 (1H, dd, J=8.8, 7.3 Hz, H-6), 4.70 (1H, dd, J=5.1, 3.0 Hz, H-4), 4.68 (1H, d, J=3.4 Hz, H-2), 4.65 (1H, t, J=8.8 Hz, H-6), 1.56, 1.33 (each 3H, s, Me). MS: 366 (M^+, 7), 351 ($M^+ - Me$, 6). *Anal.* Calcd for $C_{17}H_{18}O_7S$: C, 55.74; H, 4.95. Found: C, 55.68; H, 4.98.

3) Pivaloylation of **2a** with pivaloyl chloride and pyridine gave the pivaloate **2d** in 93% yield. Colorless needles from Et_2O, mp 111—112 °C. IR (KBr): 1744 (OCO), 1304 (C=S). ^1H-NMR: 5.91 (1H, d, J=3.7 Hz, H-1), 5.25 (1H, d, J=3.1 Hz, H-3), 5.10 (1H, dt, J=7.6, 6.0 Hz, H-5), 4.78 (1H, dd, J=8.5, 7.6 Hz, H-6), 4.71 (1H, dd, J=8.5, 7.6 Hz, H-6), 4.58 (1H, dd, J=6.0, 3.1 Hz, H-4), 4.45 (1H, d, J=3.7 Hz, H-2), 1.53, 1.32 (each 3H, s, Me). 1.22 (9H, s, *tert*-Bu). MS: 346 (M^+, 14), 331 ($M^+ - Me$, 14). *Anal.* Calcd for $C_{15}H_{22}O_7S$: C, 52.02; H, 6.40. Found: C, 51.85; H, 6.66.

4) Tosylation of **2a** with *p*-toluenesulfonyl chloride and pyridine gave the tosylate **2e** in 73% yield. Colorless needles from EtOH, mp 159—161 °C (lit. 154—156 °C).[19] ^1H-NMR: 7.81, 7.42 (each 2H, d, J=8.3 Hz, Ar-H), 5.95 (1H, d, J=3.6 Hz, H-1),4.92—4.86 (1H, m, H-5), 4.87 (1H, d, J=3.2 Hz, H-3), 4.67 (1H, d, J=3.6 Hz, H-2), 4.67—4.59 (2H, m, H-6), 4.48 (1H, dd, J=5.0, 3.2 Hz, H-4), 2.49 (3H, s, Me), 1.47, 1.29 (each 3H, s, Me).

3-*O*-*tert*-Butyldimethylsilyl-1,2-*O*-isopropylidene-5,6-*O*-thiocarbonyl-α-D-glucofuranose (2f) Silylation of **2a** with *tert*-butyldimethylsilyl chloride and imidazole in dimethyl formamide (DMF) at 70 °C for 15 h gave **2f** in 51% yield. Colorless oil. ^1H-NMR: 5.91 (1H, d, J=3.4 Hz, H-1), 5.01 (1H, ddd, J=8.8, 6.8, 5.4 Hz, H-5), 4.75 (1H, dd, J=8.8, 6.8 Hz, H-6), 4.64 (1H, t, J=8.8 Hz, H-6), 4.43 (1H, dd, J=5.4, 2.9 Hz, H-4), 4.36 (1H, d, J=3.4 Hz, H-2), 4.31 (1H, d, J=2.9 Hz, H-3), 1.48, 1.31 (each 3H, s, Me). 0.90 (9H, s, *tert*-Bu), 0.17, 0.14 (each 3H, s, SiMe). MS: 361 ($M^+ - Me$, 5).

3-*O*-Benzyl-1,2-*O*-isopropylidene-5,6-*O*-thiocarbonyl-α-D-glucofuranose (2g) 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[9] (1.7 g) was stannylated with Bu_2SnO (1.8 g, 1.3 eq) in MeOH (100 ml) and treated with $CSCl_2$ (0.55 ml, 1.3 eq) as described for **2a** to give **2g** (1.7 g, 88%) as a colorless oil. IR: 1310 (C=S). ^1H-NMR: 7.26—7.37 (5H, m, Ph-H), 5.96 (1H, d, J=3.9 Hz, H-1), 5.04 (1H, m, H-5), 4.75 (1H, dd, J=9.3, 7.3 Hz, H-6), 4.67, 4.49 (each 1H, d, J=11.7 Hz, CH_2), 4.63 (1H, d, J=3.9 Hz, H-2), 4.59 (1H, t, J=9.3 Hz, H-6), 4.57 (1H, m, H-4), 4.09 (1H, d, J=3.9 Hz, H-3), 1.50, 1.33 (each 3H, s, Me). MS: 352 (M^+, 2).

3-*O*-Acetyl-1,2-*O*-isopropylidene-5,6-*O*-thiocarbonyl-β-L-idofuranose (6b) Acetylation of **6a** with Ac_2O-pyridine gave the *O*-acetate **6b** in 77% yield, as colorless needles from EtOH–H_2O, mp 171—173 °C. IR (KBr): 1743. ^1H-NMR: 5.99 (1H, d, J=3.6 Hz, H-1), 5.28 (1H, d, J=3.2 Hz, H-3), 5.10 (1H, td, J=8.0, 4.3 Hz, H-5), 4.79—4.30 (4H, m, H-2, 4, 6), 2.20 (3H, s, OAc), 1.54, 1.36 (each 3H, s, Me). *Anal.* Calcd for $C_{12}H_{16}O_7S$: C, 47.37; H, 5.30. Found: C, 47.40; H, 5.37.

***O,S*-Rearrangement of Thionocarbonates (2) with KI** A mixture of **2b**, **2c**, or **2f** (0.3 mmol) and KI (4.0 molar eq) in MeCN (3 ml) was heated in a sealed tube at 140 °C for 6 h. The cooled mixture was taken into $CHCl_3$, washed with 1% $NaHSO_3$, and concentrated to give 3-*O*-acyl-5,6-*O*,*S*-carbonyl-1,2-*O*-isopropylidene-6-thio-α-D-glucofuranose (**3b**, **3c**, or **3f**), which was purified by chromatography.

3b: Yield 99%. Colorless needles from MeOH, mp 107—109 °C (lit. 108—110 °C).[6,20] ^1H-NMR: 5.89 (1H, d, J=3.9 Hz, H-1), 5.26 (1H, d, J=2.9 Hz, H-3), 4.85 (1H, td, J=8.3, 6.8 Hz, H-5), 4.57 (1H, d, J=3.9 Hz, H-2), 4.44 (1H, dd, J=8.3, 2.9 Hz, H-4), 3.66 (2H, d, J=6.8 Hz, H-6), 2.12 (3H, s, OAc), 1.53, 1.32 (each 3H, s, Me).

3c: Yield 99%. Colorless needles from Et_2O, mp 138—141 °C. IR (KBr): 1715. ^1H-NMR: 8.00 (2H, d, J=7.8 Hz, Ph-H), 7.61 (1H, t, J=7.8 Hz, Ph-H), 7.47 (2H, t, J=7.8 Hz, Ph-H), 5.98 (1H, d, J=3.9 Hz, H-1), 5.54 (1H, d, J=2.9 Hz, H-3), 4.97 (1H, dt, J=8.3, 6.8 Hz, H-5), 4.70 (1H, d, J=3.9 Hz, H-2), 4.56 (1H, dd, J=8.3, 2.9 Hz, H-4), 3.72, 3.70 (each 1H, dd, J=11.7, 6.8 Hz, H-6), 1.57, 1.34 (each 3H, s, Me). MS: 366 (M^+, 0.1), 351 ($M^+ - Me$, 17). *Anal.* Calcd for $C_{17}H_{18}O_7S$: C, 55.74; H, 4.95. Found: C, 55.71; H, 4.96.

3f: The reaction required 30 h. Yield 51%. Colorless oil. IR: 1744. ^1H-NMR: 5.89 (1H, d, J=3.4 Hz, H-1), 4.83 (1H, dt, J=8.3, 6.8 Hz, H-5), 4.39 (1H, d, J=3.4 Hz, H-2), 4.29 (1H, d, J=2.9 Hz, H-3), 4.27 (1H, dd, J=8.8, 2.9 Hz, H-4), 3.66, 3.63 (each 1H, dd, J=11.7, 6.8 Hz, H-6), 1.50, 1.32 (each 3H, s, Me). 0.90 (9H, s, *tert*-Bu), 0.16, 0.15 (each 3H, s, Me). MS: 361 ($M^+ - Me$, 5).

Formation of the 3,6-Ether (4a) from 2a A mixture of **2a** (131 mg) and KI (250 mg, 3 eq) in MeCN (3 ml) was reacted for 12 h and worked up as described above. Chromatography of the product gave **4a** (77 mg, 59%) from the AcOEt eluate as a colorless oil (lit. mp 53—55 °C).[21] IR: 3560 (OH). ^1H-NMR: 5.94 (1H, d, J=3.4 Hz, H-1), 4.78 (1H, m, H-4), 4.63 (1H, d, J=3.4 Hz, H-2), 4.51 (1H, d, J=3.9 Hz, H-3), 4.28 (1H, m, H-5), 3.94 (1H, dd, J=8.8, 6.4 Hz, H-6), 3.50 (1H, dd, J=8.8, 7.3 Hz, H-6), 2.61 (1H, br s, OH), 1.51, 1.35 (each 3H, s, Me). MS: 187 ($M^+ - Me$, 12).

Acetylation of **4a** gave the *O*-acetate **4b** as an oil (95%). IR: 1741

(OAc). ^{1}H-NMR: 5.96 (1H, d, J=3.9 Hz, H-1), 5.11 (1H, ddd, J=8.3, 6.8, 3.9 Hz, H-5), 4.95 (1H, dd, J=4.5, 3.4 Hz, H-4), 4.61 (1H, d, J=3.9 Hz, H-2), 4.53 (1H, d, J=3.4 Hz, H-3), 4.06 (1H, dd, J=8.5, 7.3 Hz, H-6), 3.73 (1H, t, J=8.5 Hz, H-6), 2.12 (3H, s, OAc), 1.61, 1.49 (each 3H, s, Me). MS: 229 (M^+ −Me, 15).

Benzoylation of **4a** gave the *O*-benzoate **4c** as a colorless solid (92%). IR: 1722 (OBz). ^{1}H-NMR: 7.42—8.13 (5H, m, Ph-H), 5.98 (1H, d, J=3.9 Hz, H-1), 5.33 (1H, ddd, J=8.3, 6.8, 4.4 Hz, H-5), 5.09 (1H, dd, J=4.4, 3.4 Hz, H-4), 4.66 (1H, d, J=3.4 Hz, H-3), 4.60 (1H, d, J=3.9 Hz, H-2), 4.18 (1H, dd, J=8.3, 6.8 Hz, H-6), 3.89 (1H, t, J=8.3 Hz, H-6), 1.50, 1.34 (each 3H, s, Me). MS: 291 (M^+ −Me, 100).

3-*O*-Acetyl-5,6-*O*,*S*-carbonyl-1,2-*O*-isopropylidene-6-thio-β-L-idofuranose (7b) A mixture of **6b** (50 mg) and KI (50 mg) in MeCN (3 ml) was heated at 125 °C for 15 h and worked up as described above to give **7b** (46 mg, 92%) as colorless needles from EtOH, mp 161—162 °C. IR (KBr): 1741. ^{1}H-NMR: 6.00 (1H, d, J=3.5 Hz, H-1), 5.32 (1H, d, J=3.3 Hz, H-3), 4.83 (1H, ddd, J=9.0, 7.0, 5.0 Hz, H-5), 4.59 (1H, d, J=3.5 Hz, H-2), 4.41 (1H, dd, J=5.0, 3.3 Hz, H-4), 3.56 (1H, dd, J=11.0, 9.0 Hz, H-6), 3.44 (1H, dd, J=11.0, 7.0 Hz, H-6), 2.14 (3H, s, OAc), 1.52, 1.33 (each 3H, s, Me). MS: 304 (M^+, 0.6), 289 (M^+ −Me, 86). *Anal.* Calcd for $C_{12}H_{16}O_7S$: C, 47.37; H, 5.30. Found: C, 47.15; H, 5.42.

Radical-Promoted Reactions (Analytical Procedure) Method A: A mixture of the acetate **2b** (50 mg), Bu_3SnH (0.1—1.0 molar eq), and AIBN (0.3 molar eq) in toluene (5 ml) was heated at 120 °C for 3—7 h in a sealed tube filled with an Ar atmosphere. The cooled mixture was passed through a short silica gel column to remove tin compound(s). The products obtained from the AcOEt eluate was analyzed by GLC. The best result was obtained with 0.3 and 0.3 molar eq combination of the reagents, as shown in Table 1.[2,10]

Method B: A mixture of the acetate **2b** (50 mg) and $(R_3Sn)_2$ (1.8 molar eq) in a solvent (50—120 ml) was internally irradiated with a high-pressure Hg lamp through a Pyrex filter (>290 nm) for 4 h at 10—15 °C under an Ar atmosphere. After evaporation of the solvent, the residue was chromatographed in benzene to remove tin compound(s). The product obtained from the AcOEt eluate was analyzed by GLC (see Tables 1, 2, and 3).

Method C: A mixture of **2b—g** (0.3 mmol), $(RO)_2PHO$ (4.0 or 0.4 eq), and $(PhCOO)_2$ (0.4 eq) in an appropriate solvent (10 ml) was heated under reflux for 2 h under an N_2 atmosphere. The mixture was passed through a silica gel column and the AcOEt eluate was analyzed by GLC (see Tables 4 and 5). The best result for **2c** was obtained in the reaction at 120 °C with two additions of the initiator (Table 4, C-6).

Method D: A mixture of **2c** (110 mg), R_3SiH (4.0 or 0.4 eq) and $(PhCOO)_2$ (0.1 eq) in dioxane (10 ml) was heated under reflux for 2 h under an N_2 atmosphere. The mixture was concentrated to dryness and the residue in AcOEt was passed through a short silica gel column. The product thus obtained was analyzed by GLC (see Table 6).

Reaction of the *ido*-Derivative (7b) The *ido*-derivative **7b** (15 mg) was treated by the above methods and the product was analyzed in the same way as described above (see Table 7).

Reaction of the Thionocarbonate (2c) with Bu_3SnH-$(Bu_3Sn)_2$-AIBN Bu_3SnH (66 μl, 0.3 molar eq) was injected into a boiling solution of a mixture of the thionocarbonate **2c** (300 mg), $(Bu_3Sn)_2$ (416 μl, 1 molar eq), and AIBN (135 mg, 1 molar eq) in benzene (70 ml) and heating was continued for 1 h under an Ar atmosphere. The cooled mixture was passed though a silica gel column to remove tin compounds. The AcOEt eluate (GLC data are shown in Table 1, entry 2) was re-chromatographed to yield a mixture of **2c**, **8c**, **9c**, and **3c** from the benzene–AcOEt (10 : 1) eluate and 5-deoxy derivative **12c** (19 mg, 8%) from the AcOEt eluate. The mixture was subjected to recycling HPLC to separate **8c** (100 mg, 33%) and a mixture of **2c**, **9c**, and **3c**. The latter mixture was separated by HPLC ($CHCl_3$–AcOEt, 40 : 1) on a Lobar column to afford **9c** (45 mg, 15%), **3c** (70 mg, 23%), and **2c** (24 mg).

Preparative Reactions and Isolation of Products (Example for Method B) 1) From the Acetate **2b**: The acetate **2b** (400 mg) and $(Bu_3Sn)_2$ (1.3 ml, 2.0 molar eq) in dry benzene (150 ml) were irradiated with a high-pressure Hg lamp (>290 nm) for 4 h with ice-water cooling under an Ar atmosphere. The solvent was removed under reduced pressure and the residue was chromatographed in benzene to remove tin compounds. Elution of the column with $CHCl_3$–EtOAc (29 : 1) gave the olefin **13b** (34 mg, 11.3%), a mixture of **3b** and **8b** (153 mg), and **9b** (69 mg, 17.3%). Further elution with $CHCl_3$–EtOAc (4 : 1) gave the 5-deoxy derivative **12b** (56 mg, 17.3%). The mixture of **3b** and **8b** was subjected to recycling HPLC to yield **3b** (71 mg, 18%) and **8b** (72 mg, 18%).

Olefin **13b**: Colorless oil. IR: 1731 (OAc). ^{1}H-NMR: 5.95 (1H, d, J=3.9 Hz, H-1), 5.79 (1H, ddd, J=17.0, 10.3, 6.3 Hz, H-5), 5.44 (1H, br d, J=17.0 Hz. H-6), 5.28 (1H, br d, J=10.3 Hz, H-6), 5.21 (1H, d, J=2.9 Hz, H-3), 4.75 (1H, m, H-4), 4.55 (1H, d, J=3.9 Hz, H-2), 2.06 (3H, s, OAc), 1.53, 1.32 (each 3H, s, Me). MS: 213 (M^+ −Me, 4).

3-*O*-Acetyl-5,6-*S*,*O*-carbonyl-1,2-*O*-isopropylidene-5-thio-α-D-glucofuranose (5-*S*-*gluco*, **8b**): Colorless needles from EtOH, mp 112—113 °C. IR (KBr): 1736. ^{1}H-NMR: 5.91 (1H, d, J=3.9 Hz, H-1), 5.20 (1H, d, J=2.9 Hz, H-3), 4.69 (1H, dd, J=10.3, 2.9 Hz, H-4), 4.55 (1H, d, J=3.9 Hz, H-2), 4.50 (1H, dd, J=10.3, 6.3 Hz, H-6), 4.44 (1H, dd, J=10.3, 2.9 Hz, H-6), 3.98 (1H, ddd, J=10.3, 6.3, 2.9 Hz, H-5), 2.11 (3H, s, OAc), 1.53, 1.31 (each 3H, s, Me). MS: 289 (M^+ −Me, 9). *Anal.* Calcd for $C_{12}H_{16}O_7S$: C, 47.37; H, 5.30. Found: C, 47.29; H, 5.21.

3-*O*-Acetyl-5,6-*S*,*O*-carbonyl-1,2-*O*-isopropylidene-5-thio-β-L-idofuranose (5-*S*-*ido*, **9b**): Colorless needles from EtOH, mp 157—158 °C. IR (KBr): 1750. ^{1}H-NMR: 5.94 (1H, d, J=3.7 Hz, H-1), 5.24 (1H, d, J=3.0 Hz, H-3), 4.56 (1H, d, J=3.7 Hz, H-2), 4.48 (1H, dd, J=10.0, 7.3 Hz, H-6), 4.43 (1H, dd, J=6.8, 3.0 Hz, H-4), 4.37 (1H, dd, J=10.0, 6.4 Hz, H-6), 4.15 (1H, ddd, J=7.3, 6.8. 6.4 Hz, H-5), 2.14 (3H, s, OAc), 1.52, 1.32 (each 3H, s, Me). MS: 304 (M^+, 0.1), 289 (M^+ −Me, 21). *Anal.* Calcd for $C_{12}H_{16}O_7S$: C, 47.37; H, 5.30. Found: C, 47.59; H, 5.27.

5-Deoxy Derivative **12b**: Colorless oil. IR: 3500 (OH), 1740 (OAc). ^{1}H-NMR: 5.90 (1H, d, J=3.4 Hz, H-1), 5.17 (1H, d, J=2.9 Hz, H-3), 4.51 (1H, d, J=3.4 Hz, H-2), 4.44 (1H, m, H-4), 3.78 (2H, m, H-6), 2.42 (1H, br s, OH), 1.88, 1.79 (each 1H, m, H-5), 2.10 (3H, s, OAc), 1.52, 1.31 (each 3H, s, Me). MS: 231 (M^+ −Me, 13).

2) From the Benzoate **2c**: Irradiation of **2c** (360 mg) and $(Bu_3Sn)_2$ (1.0 ml, 2.0 molar eq) and work-up of the product as described above gave **13c** (17.4 mg, 6.1%), **12c** (26 mg, 8.6%), **9c** (60 mg, 16.7%), **8c** (138 mg, 38.3%), and **3c** (68.8 mg, 19.1%).

Olefin **13c**: Pale yellow oil. IR: 1718 (OBz). ^{1}H-NMR: 8.01 (2H, d, J=7.8 Hz, Ph-H), 7.58 (1H, t, J=7.8 Hz, Ph-H), 7.44 (2H, t, J=7.8 Hz, Ph-H), 6.03 (1H, d, J=3.9 Hz, H-1), 5.89 (1H, ddd, J=17.1, 10.7, 6.4 Hz, H-5), 5.48 (1H, br d, J=17.1 Hz. H-6), 5.45 (1H, d, J=2.9 Hz, H-3), 5.27 (1H, d, J=10.7 Hz, H-6), 4.87 (1H, m, H-4), 4.69 (1H, d, J=3.9 Hz, H-2), 1.57, 1.34 (each 3H, s, Me). MS: 290 (M^+, 0.1), 275 (M^+ −Me, 10).

5-*S*-*gluco* Derivative **8c**: Colorless needles from Et_2O and colorless prisms from EtOH, mp 116—118 °C. IR (KBr): 1736. ^{1}H-NMR: 7.99 (2H, d, J=7.8 Hz, Ph-H), 7.62 (1H, t, J=7.8 Hz, Ph-H), 7.47 (2H, d, J=7.8 Hz, Ph-H), 5.99 (1H, d, J=3.9 Hz, H-1), 5.47 (1H, d, J=2.9 Hz, H-3), 4.74 (1H, dd, J=9.8, 2.9 Hz, H-4), 4.68 (1H, d, J=3.9 Hz, H-2), 4.55 (1H, dd, J=10.3, 3.4 Hz, H-6), 4.51 (1H, dd, J=10.3, 6.4 Hz, H-6), 4.08 (1H, ddd, J=9.8, 6.4, 3.4 Hz, H-5), 1.57, 1.33 (each 3H, s, Me). MS: 366 (M^+, 0.1), 351 (M^+ −Me, 37). *Anal.* Calcd for $C_{17}H_{18}O_7S$: C, 55.74; H, 4.95. Found: C, 55.69; H, 4.91.

5-*S*-*ido* Derivative **9c**: Colorless oil. IR: 1723. ^{1}H-NMR: 8.02 (2H, d, J=7.8 Hz, Ph-H), 7.63 (1H, t, J=7.8 Hz, Ph-H), 7.48 (2H, t, J=7.8 Hz, Ph-H), 6.03 (1H, d, J=3.9 Hz, H-1), 5.51 (1H, d, J=2.9 Hz, H-3), 4.69 (1H, d, J=3.9 Hz, H-2), 4.54 (1H, dd, J=7.3, 2.9 Hz, H-4), 4.47 (1H, dd, J=10.0, 7.3 Hz, H-6), 4.37 (1H, dd, J=10.0, 6.4 Hz, H-6), 4.20 (1H, td, J=7.3, 6.4 Hz, H-5), 1.56, 1.34 (each 3H, s, Me). MS: 351 (M^+ −Me, 8).

5-Deoxy Derivative **12c**: Colorless oil. IR: 1722. ^{1}H-NMR: 8.03 (2H, d, J=7.8 Hz, Ph-H), 7.59 (1H, t, J=7.8 Hz, Ph-H), 7.46 (2H, t, J=7.8 Hz, Ph-H), 5.99 (1H, d, J=3.7 Hz, H-1), 5.42 (1H, d, J=2.9 Hz, H-3), 4.65 (1H, d, J=3.7 Hz, H-2), 4.56 (1H, m, H-4), 3.85—3.75 (2H, m, H-6), 2.07 (1H, br s, OH), 2.05—1.85 (2H, m, H-5), 1.56, 1.34 (each 3H, s, Me). MS: 293 (M^+ −Me, 20).

3) From the Pivaloate **2d**: Irradiation of a mixture of **2d** (400 mg) and $(Bu_3Sn)_2$ (1.2 ml, 2.0 molar eq) and work-up of the product as described above gave **13d** (32.8 mg, 10.5%), **12d** (53.3 mg, 16.0%), **9d** (41 mg, 10.2%), **8d** (90 mg, 17.8%), and **3d** (91 mg, 17.8%).

Olefin **13d**: Colorless oil. IR: 1729. ^{1}H-NMR: 5.95 (1H, d, J=3.9 Hz, H-1), 5.77 (1H, ddd, J=17.0, 10.7, 6.3 Hz, H-5), 5.43 (1H, dt, J=17.0, 1.4 Hz. H-6), 5.26 (1H, dt, J=10.7. 1.4 Hz, H-6), 5.19 (1H, d, J=3.0 Hz, H-3), 4.78 (1H, m, H-4), 4.49 (1H, d, J=3.9 Hz, H-2), 1.54, 1.33 (each 3H, s, Me), 1.18 (9H, s, *tert*-Bu). MS: 213 (M^+ −Bu^{tert}, 8), (M^+ −$COBu^{tert}$, 16).

5-*S*-*gluco* Derivative **8d**: Colorless needles from Et_2O, mp 116—118 °C. IR (KBr): 1738. ^{1}H-NMR: 5.90 (1H, d, J=3.4 Hz, H-1), 5.18 (1H, d, J=2.9 Hz, H-3), 4.69 (1H, dd, J=10.3, 2.9 Hz, H-4), 4.52 (1H, dd, J=10.3, 6.3 Hz, H-6), 4.47 (1H, d, J=3.4 Hz, H-2) 4.46 (1H, dd, J=10.3, 2.9 Hz, H-6), 3.96 (1H, ddd, J=10.3, 6.3, 2.9 Hz, H-5), 1.54, 1.32 (each

3H, s, Me), 1.22 (9H, s, *tert*-Bu). MS: 346 (M^+, 0.1), 331 (M^+-Me, 100). *Anal.* Calcd for $C_{15}H_{22}O_7S$: C, 52.02; H, 6.40. Found: C, 51.85; H, 6.33.

5-*S*-*ido* Derivative **9d**: Colorless oil. IR: 1737. ^{1}H-NMR: 5.92 (1H, d, J=3.4 Hz, H-1), 5.21 (1H, d, J=3.0 Hz, H-3), 4.49 (1H, d, J=3.4 Hz, H-2), 4.45 (1H, dd, J=8.1, 2.9 Hz, H-4), 4.42 (1H, dd, J=10.0, 7.3 Hz, H-6), 4.30 (1H, dd, J=10.0, 6.0 Hz, H-6), 4.08 (1H, ddd, J=8.1, 7.3, 6.0 Hz, H-5), 1.53, 1.32 (each 3H, s, Me), 1.24 (9H, s, *tert*-Bu). MS: 331 (M^+-Me, 16).

6-*S*-*gluco* Derivative **3d**: Colorless needles from Et_2O, mp 138—141 °C. IR (KBr): 1729. ^{1}H-NMR: 5.88 (1H, d, J=3.9 Hz, H-1), 5.24 (1H, d, J=2.9 Hz, H-3), 4.82 (1H, dt, J=8.3, 6.8 Hz, H-5), 4.48 (1H, d, J=3.9 Hz, H-2), 4.47 (1H, dd, J=8.3, 2.9 Hz, H-4), 3.71, 3.65 (each 1H, dd, J=11.2, 6.8 Hz, H-6), 1.53, 1.32 (each 3H, s, Me), 1.23 (9H, s, *tert*-Bu). MS: 346 (M^+, 0.5), 331 (M^+-Me, 41). *Anal.* Calcd for $C_{15}H_{22}O_7S$: C, 52.02; H, 6.40. Found: C, 51.84; H, 6.31.

5-Deoxy Derivative **12d**: Colorless oil. IR: 1723. ^{1}H-NMR: 5.89 (1H, d, J=3.9 Hz, H-1), 5.14 (1H, d, J=2.4 Hz, H-3), 4.47 (1H, m, H-4), 4.44 (1H, d, J=3.9 Hz, H-2), 3.81-3.73 (2H, m, H-6), 2.30 (1H, br s, OH), 1.94—1.75 (2H, m, H-5), 1.52, 1.31 (each 3H, s, Me), 1.22 (9H, s, *tert*-Bu). MS: 273 (M^+-Me, 17).

4) From the Tosylate **2e**: Irradiation of a mixture of **2e** (450 mg) and $(Bu_3Sn)_2$ (1.1 ml, 2.0 molar eq) in benzene (100 ml) and work-up of the product as described above gave **13e** (24.6 mg, 6.7%), a mixture of **2e**, **3e**, and **8e** (257 mg), a mixture of **9e** and **10e** (50 mg) from the $CHCl_3$–AcOEt (29 : 1) eluate, and a mixture of **12e**, **3a**, and **8a** (38.5 mg) from the $CHCl_3$–AcOEt (4 : 1) eluate. Recycling HPLC of the first mixture gave **8e** (95.6 mg, 21.3%), **3e** (64.0 mg, 14.2%), and **2e** (95.6 mg, 6.6%), and that of the third mixture gave **12e** (9.6 mg, 2.5%), **8a** (19 mg, 6.7%), and **3a** (9.6 mg, 3.4%). Preparative TLC of the second mixture gave **10e** (15.5 mg, 3.6%) and **9e** (29.5 mg, 6.6%).

Olefin **13e**: Colorless oil. IR: 1371, 1173. ^{1}H-NMR: 7.77, 7.34 (each 2H, d, J=8.3 Hz, Ar-H), 5.93 (1H, d, J=3.9 Hz, H-1), 5.63 (1H, ddd, J=17.1, 10.3, 6.8 Hz, H-5), 5.32 (1H, dt, J=17.1, 1.5 Hz. H-6), 5.18 (1H, dt, J=10.3, 1.5 Hz, H-6), 4.74 (1H, d, J=2.9 Hz, H-3), 4.69 (1H, d, J=3.9 Hz, H-2), 4.64 (1H, m, H-4), 2.46, 1.49, 1.30 (each 3H, s, Me). MS: 340 (M^+, 0.1), 325 (M^+-Me, 8).

5,6-*S*,*O*-Carbonyl-1,2-*O*-isopropylidene-5-thio-α-D-glucofuranose (**8a**): Colorless prisms from Et_2O–hexane, mp 151—153 °C. IR (KBr): 3480 (OH), 1748 (OCO). ^{1}H-NMR: 5.94 (1H, d, J=3.9 Hz, H-1), 4.71 (1H, dd, J=9.8, 2.4 Hz, H-6), 4.52 (1H, d, J=3.9 Hz, H-2), 4.51 (1H, dd, J=9.8, 6.4 Hz, H-6), 4.34 (1H, dd, J=10.3, 2.9 Hz, H-4), 4.29 (1H, d, J=2.9 Hz, H-3), 4.10 (1H, ddd, J=10.3, 6.4, 2.4 Hz, H-5), 1.52, 1.32 (each 3H, s, Me). MS: 247 (M^+-Me, 49). *Anal.* Calcd for $C_{10}H_{14}O_6S$: C, 45.80; H, 5.38. Found: C, 45.73; H, 5.35.

3-*O*-Tosylate **8e**: Colorless needles from Et_2O-hexane, mp 80—83 °C. IR (KBr): 1751, 1378, 1189. ^{1}H-NMR: 7.81, 7.42 (each 2H, d, J=8.3 Hz, Ar-H), 5.93 (1H, d, J=3.7 Hz, H-1), 4.80 (1H, d, J=3.7 Hz, H-2), 4.78 (1H, d, J=2.8 Hz, H-3), 4.66 (1H, dd, J=10.0, 1.8 Hz, H-6), 4.39 (1H, dd, J=10.0, 6.0 Hz, H-6), 4.30 (1H, dd, J=10.0, 2.8 Hz, H-4), 3.87 (1H, ddd, J=10.0, 6.0, 1.8 Hz, H-5), 2.49, 1.49, 1.30 (each 3H, s, Me). MS: 416 (M^+, 2), 401 (M^++Me, 24). *Anal.* Calcd for $C_{17}H_{20}O_8S_2$: C, 49.04; H, 4.84. Found: C, 48.98; H, 4.87.

5,6-*S*,*O*-Carbonyl-1,2-*O*-isopropylidene-5-thio-3-*O*-tosyl-β-L-idofuranose (**9e**): Pale yellow oil. IR: 1747, 1371, 1173. ^{1}H-NMR: 7.82, 7.42 (each 2H, d, J=8.3 Hz, Ar-H), 5.88 (1H, d, J=3.9 Hz, H-1), 4.90 (1H, d, J=2.9 Hz, H-3), 4.55 (1H, d, J=3.9 Hz, H-2), 4.36 (1H, dd, J=8.3, 2.9 Hz, H-4), 4.33 (1H, m, H-6), 4.17—4.09 (2H, m, H-5,6), 2.50, 1.49, 1.27 (each 3H, s, Me). MS: 401 (M^+-Me, 5).

5,6-*O*-Carbonyl-1,2-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose (**10e**): Colorless oil. IR: 1814, 1380, 1172. ^{1}H-NMR: 7.80, 7.41 (each 2H, d, J=8.3 Hz, Ar-H), 5.95 (1H, d, J=3.4 Hz, H-1), 4.88 (1H, d, J=2.9 Hz, H-3), 4.70 (1H, m, H-5), 4.69 (1H, d, J=3.4 Hz, H-2), 4.5-4.4 (3H, m, H-4, 6), 2.49, 1.48, 1.30 (each 3H, s, Me). MS: 400 (M^+, 0.6), 385 (M^+-Me, 46).

5-Deoxy Derivative **12e**: Colorless oil. IR: 1372, 1175. ^{1}H-NMR: 7.81, 7.37 (each 2H, d, J=8.3 Hz, Ar-H), 5.88 (1H, d, J=3.9 Hz, H-1), 4.76 (1H, d, J=2.9 Hz, H-3), 4.63 (1H, d, J=3.9 Hz, H-2), 4.40—4.36 (1H, m, H-4), 3.70 (2H, t, J=5.9 Hz, H-6), 1.92—1.84, 1.67—1.60 (each 1H, m, H-5), 1.73 (1H, br s, OH), 2.47, 1.48, 1.28 (each 3H, s, Me). MS: 343 (M^+-Me, 38).

5,6-*O*,*S*-Carbonyl-1,2-*O*-isopropylidene-6-thio-α-D-glucofuranose (**3a**): Colorless needles from Et_2O–hexane, mp 160—162 °C. IR (KBr): 3375, 1729, 1704. ^{1}H-NMR: 5.94 (1H, d, J=3.4 Hz, H-1), 4.92 (1H, dt, J=8.3, 6.8 Hz, H-5), 4.56 (1H, d, J=3.4 Hz, H-2), 4.38 (1H, d, J=2.9 Hz, H-3), 4.31 (1H, dd, J=8.3, 2.9 Hz, H-4), 3.71, 3.65 (each 1H, dd, J=11.8, 6.8 Hz, H-6), 1.51, 1.33 (each 3H, s, Me). MS: 262 (M^+, 3), 247 (M^+-Me, 43). *Anal.* Calcd for $C_{10}H_{14}O_6S$: C, 45.80; H, 5.38. Found: C, 45.96; H, 5.26.

3-*O*-Tosylate **3e**: Colorless oil. IR: 1751, 1377, 1196. ^{1}H-NMR: 7.81, 7.38 (each 2H, d, J=8.3 Hz, Ar-H), 5.95 (1H, d, J=3.9 Hz, H-1), 4.87 (1H, d, J=3.9 Hz, H-2), 4.80 (1H, d, J=2.9 Hz, H-3), 4.60 (1H, dt, J=8.3, 6.8 Hz, H-5), 4.29 (1H, dd, J=8.3, 2.9 Hz, H-4), 3.55, 3.53 (each 1H, dd, J=11.7, 6.8 Hz, H-6), 2.46, 1.48, 1.32 (each 3H, s, Me). MS: 416 (M^+, 2), 401 (M^+-Me, 11).

Tosylation of 3a The above obtained 6-*S*-*gluco* derivative **3a** (2 mg) was tosylated with *p*-toluenesulfonyl chloride (7 mg) in pyridine (1 ml) overnight at room temperature to give **3e** (TLC identification).

Photolysis of 6b with Hexabutyldistannane A mixture of **6b** (100 mg) and $(Bu_3Sn)_2$ (0.3 ml, 1.8 molar eq) in benzene (60 ml) was irradiated and worked up as described for **2b** to yield **8b** (56 mg, 28%), **9b** (29.6 mg, 14.8%), and **7b** (26.4 mg, 13.2%).

Reactions with Bu_3SnH in Methanol 1) A mixture of **2b** (20 mg), AIBN (0.3 molar eq), and Bu_3SnH (1.3 molar eq) in dry MeOH (2 ml) was heated under reflux or at 100 °C (in a sealed tube) for 7 h, and the product was analyzed by GLC and GC-MS, which showed two major peaks corresponding to **12b** and **14** together with more than 10 minor peaks. Compound **14** separated by chromatography was of 65% purity and gave the following data. ^{1}H-NMR: 5.89 (1H, d, J=3.6 Hz, H-1), 5.30 (1H, d, J=2.6 Hz, H-3), 4.52 (1H, d, J=3.6 Hz, H-2), 4.28—4.00 (4H, m, H-4, 5, 6), 3.44, 3.41 (each 3H, s, OMe), 2.15 (3H, s, OAc), 1.56, 1.35 (each 3H, s, Me). MS: 319 (M^+-Me, 25).

2) A mixture of **7b** (20—50 mg), AIBN (0.3 molar eq), and Bu_3SnH (1.1 molar eq) in MeOH (2 ml) was treated as above to give two major products corresponding to **12b** and **14** (*ido*-isomer) together with more than 10 minor peaks in GLC.

Conversion of 8b to 5-Thioglucose (21a) *via* Hydrolysis with NaOH–H_2O Compound **8b** (60 mg) was hydrolyzed with 10% NaOH at 80 °C for 1 h. The mixture was de-ionized with Ambelite IR-120-H^+ and concentrated. The residue was stirred with water (10 ml) containing 6 drops of H_2SO_4 for 5 d, again de-ionized with Ambelite IR-45-OH^-, and concentrated to give **21a** (10 mg, 27%), whose ^{1}H- and ^{13}C-NMR data were identical with reported values.[22]

Thiirane (18) The 5-*S*-*gluco* derivative **8c** (50 mg, 0.14 mmol) was stirred with 0.05 M NaOMe in MeOH (3 ml) for 10 min at room temperature. The reaction was quenched with NH_4Cl and the mixture was concentrated. The residue was extracted with AcOEt. Chromatography of the product gave **18** (29 mg, 97.4%) from the AcOEt–hexane (1 : 1) eluate, as colorless needles, mp 153—154 °C (lit. 140—141 °C).[15] See also the accompanying paper.[16]

Conversion of the Thiirane (18) to 5-Thioglucose (21) 1) Triacetate **19**: The thiirane **18** (30 mg, 0.14 mmol) and NaOAc (22 mg, 1.6 eq) in AcOH–Ac_2O (10 : 1, v/v, 5 ml) were heated under reflux for 5 h. The mixture was poured into ice-water, and extracted with AcOEt. The extract was washed with saturated $NaHCO_3$ solution and brine, then dried and concentrated. Chromatography of the residue in hexane–AcOEt (1 : 1) gave the triacetate **19** (49 mg, 98%) as colorless needles from MeOH, mp 148—150 °C (lit. 149—150 °C).[15] ^{1}H-NMR: 5.91 (1H, d, J=3.9 Hz, H-1), 5.29 (1H, d, J=2.9 Hz, H-3), 4.45 (1H, d, J=3.9 Hz, H-2), 4.42 (1H, dd, J=11.2, 5.4 Hz, H-6), 4.41 (1H, dd, J=6.8, 2.9 Hz, H-4), 4.34 (1H, dd, J=11.2, 4.9 Hz, H-6), 4.12 (1H, ddd, J=6.8, 5.4. 4.9 Hz, H-5), 2.31, 2.06, 2.05 (each 3H, s, Ac), 1.51, 1.30 (each 3H, s, Me). MS: 362 (M^+, 0.3), 347 (M^+-Me, 20).

2) Diol **20**: The triacetate **19** (44 mg, 0.12 mmol) in 90% trifluoroacetic acid (3 ml) was stirred for 4 h at room temperature. The mixture was extracted with AcOEt and the extract was washed with saturated $NaHCO_3$ solution and brine, then dried and concentrated. Chromatography of the residue gave the diol **20** (34 mg, 87%) from the hexane–AcOEt (1 : 1) eluate, as colorless leaflets from hexane–AcOEt, mp 108—109 °C (lit. 106—109 °C).[17] ^{1}H-NMR: 5.52(1H, d, J=3.9 Hz, H-1), 5.18 (1H, d, J=3.4 Hz, H-3), 4.50 (1H, dd, J=10.3, 3.4 Hz, H-4), 4.40 (1H, dd, J=11.2, 3.4 Hz, H-6), 4.34 (1H, dd, J=11.2, 4.9 Hz, H-6), 4.12—4.04 (2H, m, H-2, 5), 2.31, 2.07, 2.06 (each 3H, s, Ac).

3) 5-Thioglucose (**21**): The diol **20** (32 mg) was stirred with 0.05 M NaOMe in MeOH (5 ml) at room temperature overnight. The mixture was quenched with NH_4Cl and concentrated. Acetylation of the residue with Ac_2O–pyridine (1 : 2, 2 ml) and chromatography of the product gave the pentaacetate **21b** (27 mg, 66.5% from **20**) from the AcOEt–hexane

Table 9. Positional Parameters and B (eq) for Compound **8c**

Atom	x	y	z	B_{eq}
S(1)	0.4764 (1)	0.7492 (1)	0.8067 (2)	7.6 (1)
O(1)	0.8743 (4)	0.9361 (2)	0.7374 (4)	6.2 (2)
O(2)	0.7746 (3)	0.9152 (2)	0.5126 (4)	5.7 (2)
O(3)	0.7645 (3)	0.7259 (2)	0.5864 (4)	5.9 (2)
O(4)	0.8096 (3)	0.8270 (2)	0.8324 (4)	4.8 (2)
O(5)	0.5194 (4)	0.8195 (2)	1.0596 (6)	7.0 (2)
O(6)	0.6424 (4)	0.7002 (2)	0.3941 (7)	10.3 (3)
O(7)	0.3340 (4)	0.8332 (3)	0.9724 (8)	10.5 (3)
C(1)	0.8787 (5)	0.8616 (3)	0.7181 (7)	5.1 (3)
C(2)	0.8199 (5)	0.8479 (3)	0.5601 (7)	5.2 (3)
C(3)	0.7166 (6)	0.7981 (3)	0.5988 (7)	5.2 (3)
C(4)	0.6927 (5)	0.8147 (3)	0.7685 (6)	4.6 (3)
C(5)	0.6318 (5)	0.7575 (3)	0.8646 (7)	5.1 (3)
C(6)	0.6211 (6)	0.7743 (3)	1.0352 (8)	6.0 (3)
C(7)	0.8431 (5)	0.9681 (3)	0.5911 (7)	5.5 (3)
C(8)	0.9538 (7)	0.9863 (5)	0.502 (1)	8.1 (5)
C(9)	0.7650 (9)	1.0318 (4)	0.621 (1)	7.4 (4)
C(10)	0.7247 (4)	0.6838 (3)	0.4747 (6)	4.8 (3)
C(11)	0.7909 (4)	0.6162 (3)	0.4623 (7)	4.7 (2)
C(12)	0.7562 (6)	0.5659 (4)	0.3556 (9)	7.2 (4)
C(13)	0.8176 (8)	0.5018 (4)	0.345 (1)	8.4 (5)
C(14)	0.9131 (7)	0.4887 (4)	0.435 (1)	7.9 (4)
C(15)	0.9503 (8)	0.5390 (5)	0.539 (1)	8.3 (5)
C(16)	0.8890 (6)	0.6028 (3)	0.5549 (8)	6.2 (3)
C(17)	0.4337 (6)	0.8082 (3)	0.963 (1)	7.1 (4)
H(1)	0.954 (4)	0.842 (3)	0.721 (6)	6 (1)
H(2)	0.877 (4)	0.830 (2)	0.475 (6)	5 (1)
H(3)	0.652 (4)	0.802 (2)	0.526 (6)	4 (1)
H(4)	0.637 (4)	0.859 (2)	0.764 (5)	5 (1)
H(5)	0.676 (4)	0.712 (2)	0.839 (6)	6 (1)
H(6)	0.689 (5)	0.799 (2)	1.063 (6)	5 (1)
H(7)	0.608 (4)	0.727 (3)	1.111 (6)	6 (1)
H(8)	0.989 (6)	0.940 (3)	0.450 (9)	9 (2)
H(9)	0.936 (5)	1.005 (3)	0.403 (7)	7 (2)
H(10)	1.015 (5)	1.014 (3)	0.565 (7)	8 (2)
H(11)	0.800 (5)	1.062 (3)	0.697 (8)	8 (2)
H(12)	0.739 (6)	1.057 (3)	0.508 (8)	10 (2)
H(13)	0.693 (5)	1.019 (3)	0.684 (8)	8 (2)
H(14)	0.702 (5)	0.577 (3)	0.286 (7)	6 (1)
H(15)	0.803 (7)	0.471 (5)	0.25 (1)	13 (3)
H(16)	0.954 (4)	0.446 (3)	0.426 (6)	6 (1)
H(17)	1.003 (5)	0.531 (3)	0.600 (7)	7 (2)
H(18)	0.908 (5)	0.637 (3)	0.627 (7)	8 (2)

(1 : 1) eluate, as colorless needles from EtOH, mp 101—103 °C (lit. 103 °C).[15] ^{1}H-NMR: 6.15 (1H, d, J=2.9 Hz, H-1), 5.43 (1H, t, J=9.8 Hz, H-3), 5.33 (1H, dd, J=10.8, 9.8 Hz, H-4), 5.24 (1H, dd, J=9.8, 2.9 Hz, H-2), 4.37 (1H, dd, J=12.2, 4.9 Hz, H-6), 4.07 (1H, dd, J=12.2, 2.9 Hz, H-6), 3.59 (1H, ddd, J=10.8, 4.9, 2.9 Hz, H-5), 2.18, 2.08, 2.05, 2.02, 1.99 (each 3H, s, OAc). MS: 347 (M^+ −OAc, 7)

X-Ray Analysis of 3-*O*-Benzoyl-5,6-*S*,*O*-carbonyl-1,2-isopropylidene-5-thio-α-D-glucofuranose (8c) Reflection data were collected on a Rigaku AFC-5R four-circle diffractometer controlled by the MSC/AFC program package, using Mo K_α radiation monochromated by a graphite monochromator, in the 2θ-ω scan mode. Of the total of 2435 reflections, 1107 with intensity above the $3\sigma(I)$ level were used for the structure determination. The structure was solved with SIR and refined by a full-matrix least-squares method using anisotropic temperature factors for non-hydrogen atoms. All hydrogen atoms were located from the Fourier map and refined with isotropic temperature factors. Positional parameters and the ORTEP drawing of the molecule are given in Table 9 and Fig. 2, respectively. Crystal data: $C_{17}H_{18}O_7S$, orthorhombic, a=11.197(2) Å, b=18.724(4) Å, c=8.537(2) Å, V=1789.8(6) A^3, D_c=1.36 g/cm^3, Z=4. Space group, $P2_12_12_1$. R=0.036.

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