[Chem. Pharm. Bull.
35(3) 1016—1029(1987)]

Selective Deoxygenation *via* Regioselective Thioacylation of Non-protected Glycopyranosides by the Dibutyltin Oxide Method¹⁾

MOHAMMED EKRAMUL HAQUE,^a TOHRU KIKUCHI,^{*,a} KIMIHIRO KANEMITSU,^b
and YOSHISUKE TSUDA^{*,b}

*Research Institute for Wakan-Yaku (Oriental Medicines), Toyama Medical and
Pharmaceutical University,^a 2630 Sugitani, Toyama 930-01, Japan and
Faculty of Pharmaceutical Sciences, Kanazawa University,^b
13-1 Takara-machi, Kanazawa 920, Japan*

(Received August 25, 1986)

Regioselective thioacylation of some non-protected glycopyranosides (Me α -D-Glc, Me β -D-Glc, Me α -D-Xyl, Me β -D-Xyl) was examined by the dibutyltin oxide method, using phenoxythiocarbonyl chloride as the thioacylating agent. This method gave the mono-thionocarbonates regioselectively in high yields. Acetylation of these thionocarbonates followed by deoxygenation with tributyltin hydride smoothly gave the corresponding deoxy derivatives, except for the primary thionocarbonates. Similar treatment of the pyranosides that have a *cis*-vicinal glycol (Me α -D-Gal, Me β -D-Gal, Me β -L-Ara, and Ph α -L-Ara) led to the formation of cyclic thionocarbonates, which on acetylation followed by olefination with trimethyl phosphite afforded the unsaturated derivatives in satisfactory yields. On deacetylation and subsequent hydrogenation over platinum oxide, they gave the corresponding dideoxy derivatives quantitatively. The compounds thus prepared were identified by analyses of their proton and carbon-13 nuclear magnetic resonance spectra.

Keywords—glycopyranoside; regioselective thioacylation; dibutyltin oxide; deoxygenation; *cis*-vicinal glycol; thionocarbonate; cyclic thionocarbonate; deoxy, dideoxy sugar; unsaturated sugar; ¹³C-NMR

Introduction

Thiocarbonyl esters of the secondary alcohols are reduced by tributyltin hydride to give the deoxygenated derivatives, usually in high yields.²⁾ In the cases of poly-hydroxy compounds (such as carbohydrates), protection of those hydroxyl groups which need not be involved in the reaction is necessary prior to the thioacylation. In our previous paper we reported the regioselective acylation³⁾ and alkylation⁴⁾ of some non-protected glycopyranosides by using tin compounds. From those results, it is evident that the method using dibutyltin oxide permits regioselective acylation and alkylation of a particular secondary hydroxyl group instead of a primary hydroxyl group, and thus thioacylation is also expected to occur in a similar manner. This reaction, in combination with deoxygenation, should allow the preparation of deoxy sugars regioselectively, providing useful intermediates for the synthesis of natural products from easily available carbohydrates. However, the utility of this approach needs to be established.

In this paper, we describe the selective deoxygenation of some non-protected glycopyranosides *via* regioselective thioacylation by the dibutyltin oxide method.

Results and Discussion

Thioacylation

Among the reagents tested for thioacylation, phenoxythiocarbonyl chloride⁵⁾ was found

to be the most suitable for the preparation of monothionocarbonates by the Bu_2SnO method. Thioacylation with other reagents, such as *p*-methoxythiobenzoyl chloride, requires prolonged reaction time (5–6 h) and elevated temperature, even in the presence of catalysts (for example, 4-dimethylaminopyridine). Under such vigorous conditions, the yields of the desired products as well as the selectivity were reduced, and in most cases, migration of the thioacyl group also occurred. Moreover, an appreciable formation of di-*p*-methoxythionobenzoate was observed.

On the other hand, when phenoxythiocarbonyl chloride was used, the regioselectivity as well as the yields of the monothionocarbonates were excellent and the dithionocarbonates were not formed. For example, the stannylene derivative of methyl β -D-xylopyranoside (**11**), when reacted with 1.1 mol eq of phenoxythiocarbonyl chloride in dioxane at room temperature, gave the 4-thionocarbonate (**12a**) quantitatively within 1 h, without any catalyst.

Identification of each product and determination of the product composition were done as described in a previous paper³⁾ by analysis of the carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectra (Table I). In most cases, the monothionocarbonates obtained by the reaction could be completely analyzed by taking account of the thioacylation shifts (estimated from the acylation shift rule) with respect to the non-acylated compounds. Moreover, the proton nuclear magnetic resonance (^1H -NMR) signals of all methine protons could be completely assigned by successive proton decoupling experiments on the acetylated derivatives (see Experimental).

Stannylation was carried out with Bu_2SnO (1.5 mol eq) in refluxing dry methanol as described in a previous paper.³⁾ In parallel with the result of acylation, methyl α -D-

TABLE I. ^{13}C -Chemical Shifts of Monothionocarbonates and Cyclic Thionocarbonates of Some Hexo- and Pentopyranosides and Their Thioacylation Shift Values (in Parentheses) in Pyridine- d_5

Thionocarbonate	C-1	C-2	C-3	C-4	C-5	C-6	OMe	C=S
Me α -D-Glc (1)	101.3	73.7	75.3	72.0	74.0	62.7	55.0	
2-Phenyl thionocarbonate (2a)	96.7 (−4.6)	84.3 (+10.6)	71.7 (−3.6)	72.0 (0)	74.1 (+0.1)	62.1 (−0.6)	54.9 (−0.1)	195.8
Me β -D-Glc (4)	105.5	74.9	78.2	71.4	78.2	62.6	56.7	
6-Phenyl thionocarbonate (5)	105.7 (+0.2)	74.9 (0)	78.2 (0)	71.2 (−0.2)	74.7 (−3.5)	74.7 (+12.1)	56.8 (+0.1)	195.6
Me α -D-Xyl (6)	101.5	73.7	75.5	71.4	63.1		55.1	
2-Phenyl thionocarbonate (7a)	97.1 (−4.4)	84.4 (+10.7)	72.3 (−3.2)	71.4 (0)	62.9 (−0.2)		55.1 (0)	195.9
4-Phenyl thionocarbonate (8a)	101.4 (−0.1)	73.6 (−0.1)	71.6 (−3.9)	83.0 (+11.6)	57.9 (−5.2)		55.4 (+0.3)	195.7
Me β -D-Xyl (11)	106.0	74.6	78.1	70.9	67.0		56.6	
4-Phenyl thionocarbonate (12a)	106.0 (0)	74.8 (+0.2)	74.3 (−3.8)	82.9 (+12.0)	62.0 (−5.0)		56.8 (+0.2)	195.6
Me α -D-Gal (15)	101.5	70.3	71.5	70.8	72.4	62.5	55.0	
3,4-Thionocarbonate (16a)	99.8 (−1.7)	67.9 (−2.4)	83.4 (+11.9)	81.2 (+10.4)	68.6 (−3.8)	60.8 (−1.7)	55.6 (+0.6)	192.6
Me β -D-Gal (13)	106.1	72.3	75.1	70.1	76.8	62.2	56.6	
3,4-Thionocarbonate (14a)	103.6 (−2.5)	71.4 (−0.9)	84.8 (+9.7)	80.8 (+10.7)	72.9 (−3.9)	61.0 (−1.2)	56.6 (0)	192.6
Me β -L-Ara (20)	102.0	70.4	70.8	70.0	63.8		55.3	
3,4-Thionocarbonate (21a)	99.7 (−2.3)	68.6 (−1.8)	82.9 (+12.1)	80.9 (+10.9)	57.6 (−6.2)		55.8 (+0.5)	192.5
Ph α -L-Ara (18)	102.7	72.0	74.4	69.3	67.2			
3,4-Thionocarbonate (19a)	99.2 (−2.5)	70.2 (−1.8)	83.7 (+9.3)	79.6 (+10.3)	61.6 (−5.6)			192.4

Chart 1

Chart 2

glucopyranoside (**1**) on stannylation followed by thioacylation with phenoxythiocarbonyl chloride at room temperature gave the 2- and 6-thionocarbonates (**2a** and **3**) in 83.0% yield, the 2-thionocarbonate (**2a**) was the major product and the 6-thionocarbonate was the minor product (Table II). On similar treatment, methyl β -D-glucopyranoside (**4**) gave the 6-thionocarbonate (**5**) as the sole product in 84.8% yield (Table II).

Reduced regioselectivity in thioacylation was observed for methyl α -D-xylopyranoside (**6**), which yielded the 2- and 4-thionocarbonates (**7a** and **8a**) in the ratio of 54:46 (Table II). This result is parallel with that of acylation³⁾ and could be ascribed to a partial contribution of the cyclic tin intermediate **10** besides the major contribution of **9**.

On the other hand, it is interesting that the thioacylation of the pyranosides that have a *cis*-vicinal glycol produced the cyclic thionocarbonates in high yields. The direct preparation of cyclic thionocarbonates from non-protected sugars by using other reagents, such as thiocarbonyldiimidazole⁶⁾ or thiophosgene⁷⁾ gave poor results, so the above method represents a facile procedure to obtain the cyclic thionocarbonates without protecting the other hydroxyl groups. The formation of cyclic thionocarbonates, however, reduces the regioselectivity of deoxygenation, but these products should be useful as intermediates for the synthesis of unsaturated and dideoxy sugars. The mechanism of cyclic thionocarbonate formation is shown in Chart 3.

Chart 3

Thus, methyl β -D-galactopyranoside (**13**) on stannylation followed by thioacylation gave a cyclic thionocarbonate (**14a**) as a syrup in 85.3% yield with a trace of other thionocarbonates. This compound (**14a**) exhibited no aromatic proton signals in its ^1H -NMR spectrum, but a signal at δ 192.6 due to $\text{C}=\text{S}$ was observed in the ^{13}C -NMR spectrum. On acetylation it gave the 2,6-diacetate (**14b**) quantitatively as colorless needles, mp 94–96 $^\circ\text{C}$. This compound showed two acetyl signals in its ^1H -NMR spectrum and the H-2 and H₂-6 signals appeared at low field compared with those of the parent compound (**14a**). On similar treatment, methyl α -D-galactopyranoside (**15**) produced the 3,4-cyclic thionocarbonate (**16a**) and 6-thionocarbonate (**17**) in the ratio of 71 : 29 with a combined yield of 71.5%. On acetylation, **16a** gave the 2,6-diacetate (**16b**) quantitatively as colorless needles, mp 131–132 $^\circ\text{C}$. The identity of this compound was confirmed by detailed examination of its ^1H -NMR spectrum.

Pentopyranosides, such as phenyl α -L-arabinopyranoside (**18**) and methyl β -L-arabinopyranoside (**20**) also undergo thioacylation as described above to produce the corresponding 3,4-cyclic thionocarbonates **19a** (colorless needles, mp 202—203 °C) and **21a** (syrup) in 94.9% and 83.2% yields, respectively (Table III). These products were completely analyzed by successive proton decoupling experiments on their acetylated derivatives **19b** and **21b** and from the ^{13}C -NMR spectra.

13: R ² =R ³ =R ⁴ =H, R ⁵ =CH ₂ OH, R=β-OMe	14a: R ² =H, R ⁵ =CH ₂ OH, R=β-OMe
15: R ² =R ³ =R ⁴ =H, R ⁵ =CH ₂ OH, R=α-OMe	14b: R ² =Ac, R ⁵ =CH ₂ OAc, R=β-OMe
17: R ² =R ³ =R ⁴ =H, R ⁵ =CH ₂ OCSOPh, R=α-OMe	16a: R ² =H, R ⁵ =CH ₂ OH, R=α-OMe
18: R ² =R ³ =R ⁴ =R ⁵ =H, R=α-OPh	16b: R ² =Ac, R ⁵ =CH ₂ OAc, R=α-OMe
20: R ² =R ³ =R ⁴ =R ⁵ =H, R=β-OMe	19a: R ² =R ⁵ =H, R=α-OPh
	19b: R ² =Ac, R ⁵ =H, R=α-OPh
	21a: R ² =R ⁵ =H, R=β-OMe
	21b: R ² =Ac, R ⁵ =H, R=β-OMe

Chart 4

Deoxygenation

The acetates of the above thionocarbonates undergo smooth deoxygenation when heated at 75–100 °C with 1–1.5 mol eq of Bu₃SnH in toluene with the addition of a catalytic amount of 2,2-azobisisobutyronitrile (AIBN). Under these conditions, methyl α-D-glucopyranoside 2-thionocarbonate 3,4,6-triacetate (**2b**) gave the 2-deoxy compound (**22b**) in 75.6% yield. This compound exhibited no aromatic proton signals in its ¹H-NMR spectrum, but it showed two up-field proton signals at δ 2.28 (1H, dd, *J* = 5.5 and 13.0 Hz) and at δ 1.24 (1H, ddd, *J* = 3.5, 12.0, and 13.0 Hz) due to H₂-2 protons, which were again confirmed by successive proton decoupling experiments. In the ¹³C-NMR spectrum, the C-2 carbon signal appeared at δ 39.0.

Similarly, the 2- and 4-thionocarbonate diacetates, (7b) and (8b), of methyl α -D-xylopyranoside (6) and the 4-thionocarbonate diacetate (12b) of methyl β -D-xylopyranoside (11) were deoxygenated to the corresponding deoxy derivatives in the yields given in Table II. The structures of these products were also confirmed by analyses of the ^1H - and ^{13}C -NMR spectra (Table IV).

The secondary thionocarbonates were smoothly reduced to the corresponding deoxy derivatives. However, the primary thionocarbonates produced the deoxy compounds in poor

TABLE II. Yields and Percentage Compositions of the Mono-thionocarbonates and the Deoxy Derivatives of the Glycopyranosides That Do Not Have a *cis*-Vicinal Glycol System

Starting material	Mono-thionocarbonate Composition ^{a)}			Deoxy derivatives Yield (%)	
Me α -D-Glc (1)	83.0	2-Ester (2a)	93.5	2-Deoxy (22b)	75.6
		6-Ester (3)	6.5	—	—
Me β -D-Glc (4)	84.8	6-Ester (5)	100.0	—	—
Me α -D-Xyl (6)	76.3	2-Ester (7a)	54.0	2-Deoxy (23)	91.6
		4-Ester (8a)	46.0	4-Deoxy (24)	83.2
Me β -D-Xyl (11)	97.4	4-Ester (12a)	100.0	4-Deoxy (25)	82.6

a) Composition was determined by measuring the OMe peak areas in the $^1\text{H-NMR}$ spectra.

Chart 5

Chart 6

yields [for example, the 6-thionocarbonates of α - and β -D-glucopyranoside (3 and 5) and methyl α -D-galactopyranoside (17)], clearly because of the lesser stability of the primary relative to the secondary carbon radical.⁸⁾

On the other hand, primary tosylates undergo smooth deoxygenation with an excess of lithium aluminum hydride (LAH) in refluxing tetrahydrofuran (THF). Thus, tosylation of methyl α -D-glucopyranoside (1) by using the $(\text{Bu}_3\text{Sn})_2\text{O}$ method,³⁾ gave the 6-tosylate (26) as the major product, which on reduction with an excess of LAH gave the corresponding 6-deoxy compound (27) in 71% yield. Tosylation of methyl β -D-glucopyranoside (4) by using the Bu_2SnO method produced the 6-tosylate (28) in 92.4% yield, and this was also reduced to

the corresponding 6-deoxy compound in 68% yield. These 6-deoxy compounds were characterized by analyses of their ^1H - and ^{13}C -NMR spectra.

The cyclic thionocarbonates, produced from the pyranosides with a *cis*-vicinal glycol, undergo radical deoxygenation by Bu_3SnH , but in these cases two deoxy compounds were formed, thus reducing the yield as well as the selectivity of deoxygenation. By using this method, the 3,4-cyclic thionocarbonate acetates of methyl α - and β -D-galactopyranosides were deoxygenated to the corresponding 3- and 4-deoxy derivatives in the yields shown in Table III. The products were identified and characterized by analyses of their ^1H - and ^{13}C -NMR spectra.

3,4-Cyclic thionocarbonate acetates of pentopyranosides, such as phenyl α -L-

TABLE III. Yields and Percentage Compositions of the Cyclic Thionocarbonates, Deoxy, Unsaturated, and Dideoxy Derivatives of the Pyranosides Which Possess a *cis*-Vicinal Glycol System

Starting material	3,4-Thionocarbonate	Deoxy compound		Unsaturated compound	Dideoxy compound
	Yield (%)	Yield (%)	3-Deoxy:4-Deoxy	Yield (%)	Yield (%)
Me β -D-Gal (13)	(14a) 85.3	56.0	(30) 57:(31) 43	(41b) 65.6	(42) (96)
Me α -D-Gal (15)	(16a) 62.6	56.6	(32) 67:(33) 33	(43b) 55.1	(44) 100
Ph α -L-Ara (18)	(19a) 94.9	73.6	(34) 74:(35) 26	(45b) 75.6	(46) 99
Me β -L-Ara (20)	(21a) 83.2	57.3	(36) 50:(37) 50	(47b) 64.8	(48) 99

Chart 7

arabinopyranoside (**18**) and methyl β -L-arabinopyranoside (**20**) also undergo similar deoxygenation to give the corresponding 3- and 4-deoxy derivatives in the yields given in Table III. From the $^1\text{H-NMR}$ spectra the 3-deoxy derivative (**34**) of phenyl α -L-arabinopyranoside was found to be in the 1C conformation, since its anomeric proton signal appeared at δ 5.71 as a doublet with $J=2.5$ Hz. Spectral data for the deoxy sugars are listed in Table IV.

It should be noted that when this deoxygenation reaction was carried out at a higher temperature and/or a higher concentration of the reagent, undesired side reactions were observed. For example, when **21b** was treated with an excess of Bu_3SnH (5 mol eq) at 100°C , the methyldiene derivative (**38**) and a compound tentatively assigned as **39**, mp $117\text{--}119^\circ\text{C}$, were the major products. The reaction with 1.5 mol eq of the reagent at 100°C produced four products, **36**, **38**, **39**, and **40**, of which **40** is the acetyl migration product from the expected 4-deoxy derivative (**37**).⁹⁾ The best result was obtained by the reaction of **21b** with 1.5 mol eq of Bu_3SnH at 75°C , where the expected **36** and **37** were produced in a ratio of 1:1 with the combined yield of 56.7% (see Table III). Details of the above side reactions and the structure

TABLE IV. ^{13}C -Chemical Shifts of Deoxy Derivatives of Some Hexo- and Pentopyranosides in Pyridine- d_5

Deoxy sugars of	C-1	C-2	C-3	C-4	C-5	C-6	OMe	CH_3	C=O
2-Deoxy sugars of									
Me α -D-Glc (22b)	99.2	39.0	69.5	74.4 ^{a)}	73.6 ^{a)}	62.9	54.4		
Me α -D-Xyl 3,4-diAc (23)	98.5	34.9	68.8 ^{a)}	69.9 ^{a)}	59.8		54.8	20.7	160.9
								20.9	170.1
3-Deoxy sugars of									
Me α -D-Gal 2,6-diAc (32)	97.3	67.7	32.3	66.1	69.2	64.8	54.8	20.7	170.4
								20.9	170.7
Me β -D-Gal 2,6-diAc (30)	103.7	68.7	36.6	65.6	76.4	64.5	56.0	21.0	169.7
								21.7	169.9
Ph α -L-Ara 2-Ac (34)	95.1	70.2	33.6	66.2	61.6			20.9	170.1
Me β -L-Ara 2-Ac (36)	97.9	68.1	32.0	65.9	64.8		55.1	21.0	170.3
4-Deoxy sugars of									
Me α -D-Gal 2,6-diAc (33)	98.4	76.9	65.0	36.8	66.4	66.3	54.9	20.7	170.5
								20.9	170.8
Me β -D-Gal 2,6-diAc (31)	102.5	76.7	70.4 ^{a)}	36.6	69.3 ^{a)}	66.1	56.2	20.6	170.1
								21.0	170.4
Me α -D-Xyl 2,3-diAc (24)	98.3	72.8	68.2	31.3	57.3		55.0	20.7	170.1
								20.8	170.4
Me β -D-Xyl 2,3-diAc (25)	102.1	72.2	70.9	30.3	60.2		56.2	20.8	169.8
								20.8	170.2
Ph α -L-Ara 2-Ac (35)	100.2	76.3	69.3	34.0	61.7			20.9	170.1
Me β -L-Ara 2-Ac (37)	98.7	76.9	65.3	34.9	58.3		55.0	21.0	170.8
Me β -L-Ara 3-Ac (40)	101.6	71.6	71.6	31.2	57.5		55.0	20.9	170.5
6-Deoxy sugars of									
Me α -D-Glc (27)	101.4	74.0	75.1	77.4	68.5	18.6	55.0		
Me β -D-Glc (29)	105.4	75.2	78.2	72.9	76.8	18.6	56.6		

a) Assignments may be interchanged in each row.

determinations of the by-products will be presented in a separate paper.

Olefination and Hydrogenation

The acetates of the cyclic thionocarbonates synthesized in a foregoing section undergo olefination according to the Corey-Winter method,¹⁰⁾ to produce the unsaturated sugars in satisfactory yields. Thus the 3,4-cyclic thionocarbonate 2,6-diacetate (**14b**) of methyl β -D-galactopyranoside, when heated under reflux in trimethylphosphite, gave the corresponding unsaturated derivative (**41b**) (65.6%) as colorless needles, mp 78–80 °C. In the ^1H -NMR spectrum it showed low-field signals at δ 5.91 (1H, ddd, $J=1.2, 1.8,$ and 10.4 Hz) due to H-3 and at δ 5.85 (1H, ddd, $J=2.4, 3.0,$ and 10.4 Hz) due to H-4, confirming the presence of a double bond between the 3- and 4-positions. Moreover, in the ^{13}C -NMR spectrum two low-field signals due to C-3 and C-4 appeared at δ 129.2 and 124.7, respectively (Table V). Deacetylation with NaOMe in MeOH followed by hydrogenation over PtO_2 in MeOH produced the 3,4-dideoxy derivative (**42**) quantitatively. This compound showed four high-field proton signals due to H_2 -3 and H_2 -4 between δ 1.45 to 2.12 as multiplets, and in the ^{13}C -NMR spectrum the C-3 and C-4 carbon signals appeared at δ 29.0 and 26.0, respectively (Table V).

The 3,4-cyclic thionocarbonate 2,6-diacetate (**16b**) of methyl α -D-galactopyranoside also produced the unsaturated compound (**43b**) in 55.1% yield. The site of unsaturation between C-3 and C-4 was confirmed by analysis of the ^1H -NMR spectrum and from ^1H - ^{13}C shift correlation studies. This compound (**43b**) on deacetylation followed by hydrogenation gave the 3,4-dideoxy compound (**44**) quantitatively.

The 3,4-cyclic thionocarbonate acetates of pentopyranosides, such as phenyl α -L-arabinopyranoside (**19b**) and methyl β -L-arabinopyranoside (**21b**), undergo similar olefina-

Chart 9

TABLE V. ^{13}C -NMR Chemical Shifts of Some Unsaturated Glycopyranosides and Their Dideoxy Derivatives in CDCl_3

Compounds		C-1	C-2	C-3	C-4	C-5	C-6	OMe	Me	C=O
Me β -D-Gal										
3-Enoside, 2,6-diAc	(41b)	100.1	67.3	129.2	124.7	71.6	65.9	56.2	21.0	170.0
3-Enoside	(41a)	103.7	66.9	128.4	127.6	75.5	65.0	56.7	20.8	170.1
3,4-Dideoxy	(42)	106.4	69.8	29.0	26.0	76.5	65.2	56.9		
Me α -D-Gal										
3-Enoside, 2,6-diAc	(43b)	95.9	66.7	127.9	124.3	66.5	65.3	56.0	20.9	170.7
3-Enoside	(43a)	98.2	64.3	128.9	126.4	69.0	64.9	56.1	20.8	170.4
3,4-Dideoxy	(44)	99.4	68.2	27.1	26.0	68.5	65.5	55.1		
Ph α -L-Ara										
3-Enoside, 2-Ac	(45b)	95.9	65.8	131.4	120.1	59.8			21.0	170.2
3-Enoside	(45a)	98.6	64.5	129.3	124.2	60.9				
3,4-Dideoxy	(46)	100.8	68.0	27.7	22.3	63.5				
Me β -L-Ara										
3-Enoside, 2-Ac	(47b)	96.1	66.5	129.3	121.8	60.2		56.1	21.0	170.6
3-Enoside	(47a)	98.1	64.2	129.0	127.0	60.0		56.1		
3,4-Dideoxy	(48)	99.7	68.0	27.5	24.0	59.5		55.1		

tion to produce the corresponding unsaturated derivatives (**45b** and **47b**) in 75.6 and 64.8% yields, respectively. In both cases, the site of unsaturation was between the C-3 and C-4 positions. Compound **45b** was found to be in the 1H_0 conformation, since the anomeric proton signal appeared at δ 5.56 as a broad singlet in the ^1H -NMR spectrum. On deacetylation followed by hydrogenation, **45b** and **47b** gave the corresponding dideoxy derivatives **46** and **48** quantitatively, as confirmed by analyses of their ^1H - and ^{13}C -NMR spectra. From the ^1H -NMR spectrum, **46** was found to be in the $C1$ conformation, since its anomeric proton signal appeared at δ 5.03 as a doublet with $J=5.2$ Hz.

Conclusion

The glycopyranosides whose hydroxyl groups are all *trans* oriented are regioselectively mono-thioacylated by the Bu_2SnO method and are deoxygenated to the corresponding deoxy derivatives in high yields. In the cases of pyranosides which possess a *cis*-vicinal glycol system, this method produces the cyclic thionocarbonates, which are smoothly deoxygenated to the dideoxy sugars through the unsaturated derivatives. The deoxy, unsaturated, and dideoxy sugars thus obtained should be useful intermediates for syntheses of complex molecules having chiral centers.

Experimental

Melting points were determined on a Yanaco micro hot stage melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded in KBr discs on a Jasco IRA-2 spectrometer and the data are given in cm^{-1} . Unless otherwise stated, ^1H -NMR (400 MHz) spectra and ^{13}C -NMR spectra (100 MHz) were recorded with a JEOL JNM GX400 FT NMR spectrometer in pyridine- d_5 solution with tetramethylsilane as an internal standard, and the chemical shifts are given in δ values. Concentrations were about 0.1–0.3 mmol/ml. Column chromatography was performed on Wakogel C-200. For thin layer chromatography (TLC) Kieselgel 60F₂₅₄ precoated plates were used and spots were developed by spraying 1% $\text{Ce}(\text{SO}_4)_2$ in 10% H_2SO_4 and heating the plates at 100 °C until coloration took place.

Thioacylation of Pyranosides (General Procedure)—Glycopyranoside (0.3–0.9 mmol) and Bu_2SnO (1.5 mol eq) in dry MeOH (10–25 ml) were heated under reflux until the mixture became homogeneous and clear (about 1 h). The mixture was refluxed for an additional 2 h, then the solvent was evaporated off *in vacuo* to leave a glassy solid,

which was dissolved in dioxane (10–25 ml). Phenoxythiocarbonyl chloride (1.1 mol eq) was added dropwise to the stirred solution at room temperature. When the tin complex was insoluble in dioxane (in the cases of Me α -D-Gal and Me β -D-Gal), it was suspended in dioxane. The mixture became clear upon addition of phenoxythiocarbonyl chloride. Maximum conversion was checked by TLC. After 1–1.5 h, the solvent was evaporated off *in vacuo* to leave a syrupy residue, which was subjected to column chromatography for further separation.

Deoxygenation (General Procedure)—The mono-thionocarbonates or cyclic thionocarbonates obtained by the above procedure were acetylated with acetic anhydride and pyridine in a usual manner. The acetates (100–300 mg) thus obtained were dissolved in toluene (10–15 ml), Bu_3SnH (1.1–1.5 mol eq) was added, and the mixture was heated at 75–100 °C with the addition of catalytic amount of AIBN for 1–3.5 h. The solvent was evaporated off *in vacuo* to leave a syrup, which was chromatographed for further separation and purification.

Olefination and Hydrogenation (General Procedure)—The cyclic thionocarbonate obtained by the thioacylation of the pyranosides which possesses a *cis*-vicinal glycol was acetylated with acetic anhydride and pyridine in a usual manner. The acetate (20–200 mg) was dissolved in trimethyl phosphite (3–5 ml) and heated under reflux for 70 h. Saturated Na_2CO_3 aq. was added to the cooled mixture and the mixture was extracted with CH_2Cl_2 . The organic extract was dried and concentrated *in vacuo* to leave a residue, which was purified by silica gel column chromatography with benzene–AcOEt. The unsaturated sugar (30–60 mg) thus obtained was deacetylated with 0.2 N NaOMe (0.3–0.6 ml) in MeOH (2.5–5 ml) at room temperature for 20–30 min. The reaction mixture was then made just neutral by adding Dowex $50 \times 8 (\text{H}^+)$ and filtered. The filtrate was concentrated *in vacuo* to leave a residue, which was subjected to hydrogenation over PtO_2 in MeOH for 4–5 h without further purification. The catalyst was removed by filtration, the filtrate was carefully concentrated *in vacuo* and the residue was subjected to preparative TLC.

Methyl α -D-Glucopyranoside 2-Phenylthionocarbonate (2a)—Needles from AcOEt–light petroleum, mp 128–129 °C. $^1\text{H-NMR}$ (200 MHz): 7.06–7.36 (5H, m, ArH), 5.79 (1H, dd, $J = 3.9, 10.0$ Hz, H-2), 5.51 (1H, d, $J = 3.9$ Hz, H-1), 4.37 (1H, t, $J = 10.0$ Hz, H-3), 3.39 (3H, s, OMe). IR: 3400, 2900, 1040. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_7\text{S}$: C, 50.90; H, 5.50. Found: C, 50.96; H, 5.54.

The 3,4,6-triacetate (**2b**) was a syrup. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.03–7.44 (5H, m, ArH), 5.62 (1H, dd, $J = 10.0, 10.5$ Hz, H-3), 5.42 (1H, dd, $J = 4.0, 10.0$ Hz, H-2), 5.18 (1H, d, $J = 4.0$ Hz, H-1), 5.09 (1H, t, $J = 10.5$ Hz, H-4), 4.00–4.36 (3H, m, H-5 and H-6), 3.46 (3H, s, OMe), 2.02, 2.03, and 2.09 (3H each, s, OAc).

The 6-phenylthionocarbonate (**3**) was also formed, but was not isolated; it showed an OMe signal at δ 3.35.

Methyl β -D-Glucopyranoside 6-Phenylthionocarbonate (5)—Syrup. $^1\text{H-NMR}$: 7.17–7.41 (5H, m, ArH), 5.38 (1H, dd, $J = 0.8, 11.4$ Hz, H-6), 5.17 (1H, dd, $J = 5.5, 11.4$ Hz, H-6), 4.72 (1H, d, $J = 7.6$ Hz, H-1), 4.22 (1H, t, $J = 8.0$ Hz, H-3), 4.13 (2H, m, H-4, 5), 4.01 (1H, dd, $J = 7.6, 8.0$ Hz, H-2), 3.62 (3H, s, OMe). High resolution (HR) MS m/z Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_7\text{S}$: 318.0773. Found: 318.0772.

Methyl α -D-Xylopyranoside 2-Phenylthionocarbonate (7a)—Needles from hexane–AcOEt, mp 130–131 °C. $^1\text{H-NMR}$: 7.12–7.36 (5H, m, ArH), 5.80 (1H, dd, $J = 3.5, 9.5$ Hz, H-2), 5.49 (1H, d, $J = 3.5$ Hz, H-1), 4.71 (1H, t, $J = 9.5$ Hz, H-3), 4.27 (1H, m, H-4), 3.95–4.08 (2H, m, H-5), 3.38 (3H, s, OMe). IR: 3400, 2900, 1040. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_6\text{S}$: C, 52.00; H, 5.37. Found: C, 51.96; H, 5.39.

The 3,4-diacetate (**7b**) forms needles from hexane–ether, mp 139–140 °C. $^1\text{H-NMR}$ (CDCl_3): 7.07–7.44 (5H, m, ArH), 5.65 (1H, t, $J = 9.5$ Hz, H-3), 5.39 (1H, dd, $J = 3.7, 9.5$ Hz, H-2), 5.14 (1H, d, $J = 3.7$ Hz, H-1), 5.05 (1H, ddd, $J = 5.8, 9.5, 10.7$ Hz, H-4), 3.84 (1H, dd, $J = 5.8, 10.7$ Hz, H-5eq), 3.66 (1H, t, $J = 10.7$ Hz, H-5ax), 3.47 (3H, s, OMe), 2.05 and 2.08 (3H each, s, OAc). IR: 2950, 1740, 1040. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_8\text{S}$: C, 53.12; H, 5.25. Found: C, 53.02; H, 5.31.

Methyl α -D-Xylopyranoside 4-Phenylthionocarbonate (8a)—Needles from hexane–AcOEt, mp 115–116 °C. $^1\text{H-NMR}$: 7.17–7.36 (5H, m, ArH), 5.80 (1H, ddd, $J = 5.8, 9.2, 10.5$ Hz, H-4), 5.07 (1H, d, $J = 3.5$ Hz, H-1), 4.67 (1H, t, $J = 9.2$ Hz, H-3), 4.26 (1H, dd, $J = 5.8, 10.5$ Hz, H-5eq), 4.14 (1H, dd, $J = 3.5, 9.2$ Hz, H-2), 3.83 (1H, t, $J = 10.5$ Hz, H-5ax), 3.41 (3H, s, OMe). IR: 2900, 2400, 1040. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_6\text{S}$: C, 52.00; H, 5.31. Found: C, 51.99; H, 5.40.

The 2,3-diacetate (**8b**) forms needles from hexane–AcOEt, mp 145–147 °C. $^1\text{H-NMR}$ (CDCl_3): 7.05–7.43 (5H, m, ArH), 5.67 (1H, t, $J = 9.5$ Hz, H-3), 5.50 (1H, ddd, $J = 6.0, 9.5, 10.5$ Hz, H-4), 4.89–4.92 (2H, m, H-1 and H-2), 4.07 (1H, dd, $J = 6.0, 10.7$ Hz, H-5eq), 3.76 (1H, t, $J = 10.7$ Hz, H-5ax), 3.43 (3H, s, OMe), 2.08 and 2.10 (3H each, s, OAc). IR: 2950, 1740, 1040. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_8\text{S}$: C, 53.12; H, 5.25. Found: C, 52.85; H, 5.11.

Methyl β -D-Xylopyranoside 4-Phenylthionocarbonate (12a)—Leaflets from hexane–AcOEt, mp 136–137 °C. $^1\text{H-NMR}$ (200 MHz): 7.16–7.43 (5H, m, ArH), 5.88 (1H, dt, $J = 5.5, 9.5$ Hz, H-4), 4.67 (1H, d, $J = 7.5$ Hz, H-1), 4.61 (1H, dd, $J = 5.5, 11.5$ Hz, H-5eq), 4.48 (1H, t, $J = 9.5$ Hz, H-3), 4.08 (1H, dd, $J = 7.5, 9.5$ Hz, H-2), 3.71 (1H, dd, $J = 9.5, 11.5$ Hz, H-5ax), 3.59 (3H, s, OMe). IR: 3400, 2900, 1040. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_6\text{S}$: C, 52.00; H, 5.37. Found: C, 52.19; H, 5.49.

The 2,3-diacetate (**12b**) forms needles from hexane–ether, mp 126–127 °C. $^1\text{H-NMR}$ (CDCl_3): 7.07–7.44 (5H, m, ArH), 5.45 (1H, dt, $J = 4.5, 7.5$ Hz, H-4), 5.35 (1H, t, $J = 7.5$ Hz, H-3), 4.96 (1H, dd, $J = 6.0, 7.5$ Hz, H-2), 4.50 (1H, d, $J = 6.0$ Hz, H-1), 4.35 (1H, dd, $J = 4.5, 12.2$ Hz, H-5eq), 3.62 (1H, dd, $J = 7.5, 12.2$ Hz, H-5ax), 3.49 (3H, s, OMe), 2.09 (6H, s, OAc $\times 2$). IR: 2950, 1740, 1040. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_8\text{S}$: C, 53.12; H, 5.25. Found: C, 52.87; H, 5.30.

Methyl β -D-Galactopyranoside 3,4-Thionocarbonate (14a)—Syrup. $^1\text{H-NMR}$: 5.57 (1H, dd, $J=2.0, 7.5$ Hz, H-4), 5.48 (1H, dd, $J=6.0, 7.5$ Hz, H-3), 4.78 (1H, d, $J=7.0$ Hz, H-1), 4.51 (1H, dt, $J=2.0, 8.0$ Hz, H-5), 4.30–4.34 (2H, m, H₂-6), 4.21 (1H, dd, $J=6.0, 7.0$ Hz, H-2), 3.51 (3H, s, OMe).

The 2,6-diacetate (14b) forms needles from benzene–AcOEt, mp 94–96 °C. $^1\text{H-NMR}$ (CDCl_3): 4.97–5.15 (3H, m, H-2, 3, 4), 4.75 (1H, br d, $J=ca. 6.0$ Hz, H-1), 4.44 (1H, dd, $J=6.4, 11.5$ Hz, H-6), 4.31 (1H, dd, $J=6.4, 11.5$ Hz, H-6), 4.18 (1H, dt, $J=2.0, 6.4$ Hz, H-5), 3.45 (3H, s, OMe), 2.12 and 2.14 (3H each, s, OAc). IR: 1810, 1740, 1040. *Anal.* Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_8\text{S}$: C, 45.00; H, 5.04. Found: C, 45.45; H, 5.10.

Methyl α -D-Galactopyranoside 3,4-Thionocarbonate (16a)—Syrup. $^1\text{H-NMR}$: 5.52–5.57 (1H, m, H-4), 5.50 (1H, t, $J=7.0$ Hz, H-3), 5.20 (1H, d, $J=4.0$ Hz, H-1), 4.56 (1H, dt, $J=2.0, 7.0$ Hz, H-5), 4.31 (1H, dd, $J=4.0, 7.0$ Hz, H-2), 4.24–4.28 (2H, m, H₂-6), 3.42 (3H, s, OMe).

The 2,6-diacetate (16b) forms needles from hexane– CH_2Cl_2 , mp 131–132 °C. $^1\text{H-NMR}$ (CDCl_3): 5.07 (1H, t, $J=7.0$ Hz, H-3), 5.02 (1H, d, $J=3.7$ Hz, H-1), 4.94–4.98 (2H, m, H-2 and H-4), 4.42 (1H, dd, $J=7.0, 11.5$ Hz, H-6), 4.37 (1H, dd, $J=6.0, 11.5$ Hz, H-6), 4.23 (1H, ddd, $J=2.5, 6.0, 7.0$ Hz, H-5), 3.42 (3H, s, OMe), 2.12 and 2.16 (3H each, s, OAc). IR: 1720, 1140, 1020. *Anal.* Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_8\text{S}$: C, 45.00; H, 5.04. Found: C, 44.82; H, 5.00.

The 6-phenylthionocarbonate (17) was also formed, but was not isolated; it showed an OMe signal at δ 3.47.

Phenyl α -L-Arabinopyranoside 3,4-Thionocarbonate (19a)—Needles from AcOEt, mp 202–203 °C. $^1\text{H-NMR}$: 6.99–7.35 (5H, m, ArH), 5.60 (1H, d, $J=6.0$ Hz, H-1), 5.52 (1H, dd, $J=6.0, 8.0$ Hz, H-3), 5.40 (1H, ddd, $J=2.5, 3.0, 8.5$ Hz, H-4), 4.55 (1H, t, $J=6.0$ Hz, H-2), 4.50 (1H, dd, $J=2.5, 14.0$ Hz, H-5eq), 4.30 (1H, dd, $J=3.0, 14.0$ Hz, H-5ax). IR: 3350, 2950, 1080. *Anal.* Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_5\text{S}$: C, 53.73; H, 4.51. Found: C, 53.97; H, 4.55.

The 2-acetate (19b) forms needles from hexane–ether– CH_2Cl_2 , mp 118–120 °C. $^1\text{H-NMR}$ (CDCl_3): 7.00–7.34 (5H, m, ArH), 5.43 (1H, d, $J=4.0$ Hz, H-1), 5.33 (1H, t, $J=4.0$ Hz, H-2), 5.11 (1H, dd, $J=4.0, 8.0$ Hz, H-4), 5.02 (1H, dd, $J=4.0, 8.0$ Hz, H-3), 4.24 (1H, dd, $J=4.0, 14.0$ Hz, H-5), 4.04 (1H, dd, $J=4.0, 14.0$ Hz, H-5). IR: 2950, 1740, 1040. *Anal.* Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_6\text{S}$: C, 54.19; H, 4.55. Found: C, 53.89; H, 4.57.

Methyl β -L-Arabinopyranoside 3,4-Thionocarbonate (21a)—Syrup. $^1\text{H-NMR}$: 5.38 (1H, t, $J=7.0$ Hz, H-3), 5.21 (1H, dd, $J=2.5, 7.0$ Hz, H-4), 4.96 (1H, d, $J=3.4$ Hz, H-1), 4.32 (1H, dd, $J=3.4, 7.0$ Hz, H-2), 4.17 (1H, d, $J=14.0$ Hz, H-5eq), 4.06 (1H, dd, $J=2.5, 14.0$ Hz, H-5ax), 3.36 (3H, s, OMe).

The 2-acetate (21b) forms needles from hexane–AcOEt, mp 120–121 °C. $^1\text{H-NMR}$ (CDCl_3): 5.05 (1H, t, $J=7.3$ Hz, H-3), 4.98 (1H, d, $J=3.7$ Hz, H-1), 4.95 (1H, dd, $J=2.7, 7.3$ Hz, H-4), 4.92 (1H, dd, $J=3.7, 7.3$ Hz, H-2), 4.20 (1H, d, $J=14.3$ Hz, H-5eq), 3.96 (1H, dd, $J=2.7, 14.3$ Hz, H-5ax), 3.42 (3H, s, OMe), 2.16 (3H, s, OAc). IR: 1740, 1050, 1000. *Anal.* Calcd for $\text{C}_9\text{H}_{12}\text{O}_6\text{S}$: C, 43.55; H, 4.87. Found: C, 43.62; H, 4.93.

Methyl 2-Deoxy- α -D-arabino-hexopyranoside 3,4,6-Triacetate (22b)—Syrup. $^1\text{H-NMR}$ (CDCl_3): 5.26–5.40 (1H, m, H-3), 5.03 (1H, t, $J=10.0$ Hz, H-4), 4.87 (1H, d, $J=3.5$ Hz, H-1), 4.33 (1H, dd, $J=5.0, 12.0$ Hz, H-6), 4.08 (1H, dd, $J=2.5, 12.0$ Hz, H-6), 3.92–4.01 (1H, m, H-5), 3.37 (3H, s, OMe), 2.28 (1H, dd, $J=5.5, 13.0$ Hz, H-2eq), 1.24 (1H, ddd, $J=3.5, 12.0, 13.0$ Hz, H-2ax), 2.03, 2.06 and 2.12 (3H each, s, OAc).

On deacetylation it gave methyl 2-deoxy- α -D-arabino-hexopyranoside (22a) as needles from AcOEt, mp 89–90 °C. $^1\text{H-NMR}$: 4.96 (1H, d, $J=3.5$ Hz, H-1), 4.34 (1H, dd, $J=5.5, 11.5$ Hz, H-3), 3.36 (3H, s, OMe), 2.46 (1H, dd, $J=5.5, 13.0$ Hz, H-2eq), 2.02 (1H, ddd, $J=3.5, 11.5, 13.0$ Hz, H-2ax). *Anal.* Calcd for $\text{C}_7\text{H}_{14}\text{O}_5$: C, 47.18; H, 7.92. Found: C, 47.04; H, 7.75.

Methyl 2-Deoxy- α -D-threo-pentopyranoside 3,4-Diacetate (23)—Syrup. $^1\text{H-NMR}$: 5.57 (1H, ddd, $J=5.0, 9.5, 10.0$ Hz, H-4), 5.17 (1H, dt, $J=5.0, 9.5$ Hz, H-3), 4.79 (1H, dd, $J=2.5, 3.5$ Hz, H-1), 3.93 (1H, dd, $J=5.0, 11.0$ Hz, H-5eq), 3.68 (1H, dd, $J=10.0, 11.0$ Hz, H-5ax), 2.29 (3H, s, OMe), 2.33 (1H, ddd, $J=2.5, 5.0, 13.0$ Hz, H-2eq), 1.82 (1H, ddd, $J=3.5, 9.5, 13.0$ Hz, H-2ax), 2.00 and 2.02 (3H each, s, OAc). HR-MS m/z Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_6$: 232.0947. Found: 232.0951.

Methyl 4-Deoxy- β -L-threo-pentopyranoside 2,3-Diacetate (24)—Syrup. $^1\text{H-NMR}$: 5.60 (1H, ddd, $J=5.5, 10.0, 12.0$ Hz, H-3), 5.16 (1H, dd, $J=3.4, 10.0$ Hz, H-2), 5.12 (1H, d, $J=3.4$ Hz, H-1), 3.70 (1H, dt, $J=2.5, 12.0$ Hz, H-5ax), 3.58 (1H, ddd, $J=1.8, 5.5, 12.0$ Hz, H-5eq), 3.30 (3H, s, OMe), 2.05–2.11 (1H, m, H-4eq), 1.78 (1H, ddd, $J=5.5, 12.0, 12.5$ Hz, H-4ax), 2.00 and 2.01 (3H each, s, OAc). HR-MS m/z Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_6$: 232.0947. Found: 232.0950.

Methyl 4-Deoxy- α -L-threo-pentopyranoside 2,3-Diacetate (25)—Syrup. $^1\text{H-NMR}$: 5.22–5.25 (2H, m, H-2 and H-3), 4.49 (1H, d, $J=6.7$ Hz, H-1), 3.94 (1H, dt, $J=3.8, 12.0$ Hz, H-5ax), 3.84 (1H, ddd, $J=1.0, 2.8, 12.0$ Hz, H-5eq), 3.43 (3H, s, OMe), 2.05–2.11 (1H, m, H-4), 1.68–1.78 (1H, m, H-4), 1.99 and 2.01 (3H each, s, OAc). HR-MS m/z Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_6$: 232.0947. Found: 232.0954.

Methyl 6-O-Tosyl- α -D-glucopyranoside (26)—Needles from AcOEt, mp 118–120 °C. $^1\text{H-NMR}$: 8.00 (2H, d, $J=7.6$ Hz, ArH), 7.20 (2H, d, $J=7.6$ Hz, ArH), 5.04 (1H, d, $J=3.7$ Hz, H-1), 4.92 (1H, d, $J=10.5$ Hz, H-6), 4.77 (1H, dd, $J=5.8, 10.5$ Hz, H-6), 4.44 (1H, t, $J=8.9$ Hz, H-3), 4.50 (1H, dd, $J=5.8, 8.9$ Hz, H-5), 3.97–4.05 (2H, m, H-2 and H-4), 3.36 (3H, s, OMe), 2.17 (3H, s, Me). IR: 3400, 2920, 1351, 1340, 1195, 1160. *Anal.* Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_8\text{S}$: C, 48.27; H, 5.79. Found: C, 48.23; H, 7.81.

Methyl 6-Deoxy- α -D-glucopyranoside (27)—Methyl α -D-glucopyranoside 6-tosylate (1.4 g) and LiAlH_4 (0.73 g, 4.4 mol eq) in THF (100 ml) were refluxed for 16 h. After decomposition of the excess reagent by sat. Na_2SO_4 aq., the mixture was filtered and the residue was extracted several times with hot AcOEt. The residue was decomposed by adding 1 N HCl and neutralized with NaHCO_3 , then concentrated to dryness, and the residue was extracted

thoroughly with hot EtOH–AcOEt. All organic extracts were combined and concentrated to dryness and the residue was chromatographed in AcOEt. The AcOEt and AcOEt–EtOH (99:1) eluates gave **27** in 71% yield (550 mg) as needles from AcOEt, mp 96–98 °C (lit. mp 99 °C).¹¹ ¹H-NMR: 5.05 (1H, d, *J* = 3.7 Hz, H-1), 4.42 (1H, t, *J* = 9.2 Hz, H-3), 4.09–4.14 (1H, m, H-5), 4.08 (1H, dd, *J* = 3.7, 9.2 Hz, H-2), 3.67 (1H, t, *J* = 9.2 Hz, H-4), 3.41 (3H, s, OMe), 1.58 (3H, d, *J* = 6.4 Hz, 6-Me).

Methyl 6-*O*-Tosyl-β-D-glucopyranoside (28)—Syrup. ¹H-NMR: 7.99 (2H, d, *J* = 8.0 Hz, ArH), 4.93 (1H, d, *J* = 10.0 Hz, H-6), 4.74 (1H, dd, *J* = 4.5, 10.0 Hz, H-6), 4.61 (1H, d, *J* = 8.0 Hz, H-1), 4.11 (1H, t, *J* = 8.0 Hz, H-3), 3.94–4.07 (2H, m, H-4 and H-5), 3.89 (1H, t, *J* = 8.0 Hz, H-2), 3.52 (3H, s, OMe), 2.18 (3H, s, Me).

On acetylation it gave a triacetate as colorless needles from hexane–CH₂Cl₂, mp 173–175 °C. ¹H-NMR (CDCl₃): 7.78 (2H, d, *J* = 8.0 Hz, ArH), 7.35 (2H, d, *J* = 8.0 Hz, ArH), 5.17 (1H, t, *J* = 9.5 Hz, H-3), 4.91 (1H, t, *J* = 9.5 Hz, H-4), 4.89 (1H, dd, *J* = 8.0, 9.5 Hz, H-2), 4.38 (1H, d, *J* = 8.0 Hz, H-1), 4.13 (1H, dd, *J* = 3.0, 11.0 Hz, H-6), 4.08 (1H, dd, *J* = 5.5, 11.0 Hz, H-6), 3.75 (1H, ddd, *J* = 3.0, 5.5, 9.5 Hz, H-5), 3.44 (3H, s, OMe), 2.46 (3H, s, Me), 1.98, 2.00, and 2.03 (3H each, s, OAc). IR: 2900, 1740, 1350, 1175. *Anal.* Calcd for C₂₀H₂₆O₁₁S: C, 50.63; H, 5.53. Found: C, 50.35; H, 5.54.

Methyl 6-Deoxy-β-D-glucopyranoside (29)—Reduction of **28** with LAH was carried out as described for **27**, in 68% yield. After isolation, the product was crystallized from AcOEt as needles, mp 132–133 °C (lit. mp 130–131 °C).¹¹ ¹H-NMR: 4.61 (1H, d, *J* = 7.6 Hz, H-1), 4.10 (1H, t, *J* = 7.6 Hz, H-3), 3.97 (1H, t, *J* = 7.6 Hz, H-2), 3.65–3.80 (2H, m, H-4, 5), 3.61 (3H, s, OMe), 1.61 (3H, d, *J* = 5.5 Hz, 6-Me). IR: 3400, 2900. *Anal.* Calcd for C₇H₁₄O₅: C, 47.18; H, 7.92. Found: C, 46.94; H, 7.92.

Methyl 3-Deoxy-β-D-xylo-hexopyranoside 2,6-Diacetate (30)—Syrup. ¹H-NMR: 4.93–5.06 (1H, m, H-2), 4.38 (1H, d, *J* = 6.5 Hz, H-1), 4.34 (1H, dd, *J* = 6.5, 12.0 Hz, H-6), 4.22 (1H, dd, *J* = 6.5, 12.0 Hz, H-6), 3.91 (1H, br s, H-4), 3.76 (1H, dt, *J* = 1.0, 6.5 Hz, H-5), 3.52 (3H, s, OMe), 2.34–2.45 (1H, m, H-3), 1.58–1.72 (1H, m, H-3), 2.06–2.16 (3H each, s, OAc). HR-MS *m/z* Calcd for C₁₁H₁₈O₇: 262.1052. Found: 262.1059.

Methyl 4-Deoxy-β-D-xylo-hexopyranoside 2,6-Diacetate (31)—Syrup. ¹H-NMR: 5.27 (1H, dd, *J* = 8.0, 9.0 Hz, H-2), 4.54 (1H, d, *J* = 8.0 Hz, H-1), 4.22–4.38 (2H, m, H₂-6), 3.82–3.94 (2H, m, H-3 and H-5), 3.48 (3H, s, OMe), 2.22 (1H, ddd, *J* = 2.0, 5.5, 12.5 Hz, H-4eq), 1.86 (1H, t, *J* = 12.5 Hz, H-4ax), 1.98 and 1.99 (3H each, s, OAc). HR-MS *m/z* Calcd for C₁₁H₁₈O₇: 262.1052. Found: 262.1057.

Methyl 3-Deoxy-α-D-xylo-hexopyranoside 2,6-Diacetate (32)—Syrup. ¹H-NMR: 5.75 (1H, ddd, *J* = 3.7, 5.2, 12.0 Hz, H-2), 5.17 (1H, d, *J* = 3.7 Hz, H-1), 4.70 (1H, dd, *J* = 7.6, 11.3 Hz, H-6), 4.60 (1H, dd, *J* = 4.6, 11.3 Hz, H-6), 4.25 (1H, br s, H-4), 4.18 (1H, dd, *J* = 4.6, 7.6 Hz, H-5), 3.44 (3H, s, OMe), 2.37 (1H, dt, *J* = 5.2, 12.0 Hz, H-3ax), 2.13 (1H, ddd, *J* = 3.2, 5.2, 12.0 Hz, H-3eq), 1.99 and 2.03 (3H each, s, OAc). HR-MS *m/z* Calcd for C₁₁H₁₈O₇: 262.1052. Found: 262.1047.

Methyl 4-Deoxy-α-D-xylo-hexopyranoside 2,6-Diacetate (33)—Syrup. ¹H-NMR: 5.21 (1H, d, *J* = 3.7 Hz, H-1), 5.15 (1H, dd, *J* = 3.7, 10.0 Hz, H-2), 4.56 (1H, ddd, *J* = 2.0, 5.0, 10.0 Hz, H-3), 4.25–4.33 (2H, m, H₂-6), 4.12–4.18 (1H, m, H-5), 3.36 (3H, s, OMe), 2.27 (1H, ddd, *J* = 2.0, 5.0, 12.5 Hz, H-4eq), 1.88 (1H, ABq, *J* = 12.5 Hz, H-4ax), 1.97 and 2.03 (3H each, s, OAc). HR-MS *m/z* Calcd for C₁₁H₁₈O₇: 262.1052. Found: 262.1049.

Phenyl 3-Deoxy-β-L-threo-pentopyranoside 2-Acetate (34)—Syrup. ¹H-NMR: 7.04–7.40 (5H, m, ArH), 5.71 (1H, d, *J* = 2.5 Hz, H-1), 5.46 (1H, dt, *J* = 2.5, 3.5 Hz, H-2), 4.39–4.54 (1H, m, H-4), 4.01 (1H, br s, H-5), 3.98 (1H, d, *J* = 3.0 Hz, H-5), 2.26 (2H, dd, *J* = 3.5, 7.5 Hz, H₂-3), 2.08 (3H, s, OAc). HR-MS *m/z* Calcd for C₁₂H₁₆O₅: 240.0998. Found: 240.1001.

Phenyl 4-Deoxy-α-L-threo-pentopyranoside 2-Acetate (35)—Syrup. ¹H-NMR: 7.02–7.37 (5H, m, ArH), 5.54 (1H, t, *J* = 8.0 Hz, H-2), 5.30 (1H, d, *J* = 8.0 Hz, H-1), 4.16–4.28 (1H, m, H-3), 4.02–4.12 (1H, m, H-5), 3.65 (1H, dt, *J* = 2.5, 11.0 Hz, H-5), 1.88–2.21 (2H, m, H-4), 2.01 (3H, s, OAc). HR-MS *m/z* Calcd for C₁₂H₁₆O₅: 240.0998. Found: 240.1000.

Treatment of 21b with Tributyltin Hydride—i) With excess Bu₃SnH: A toluene solution (12 ml) of **21b** (80 mg), Bu₃SnH (470 mg, 5 mol eq), and AIBN (4 mg) was heated at 100 °C for 1 h in an argon atmosphere with stirring. Chromatography of the product in benzene–ethyl acetate gave **38** (syrup, 44 mg), **39** (mp 117–119 °C, 20 mg), and trace amounts of **40** and **36**.

ii) With 1.5 mol eq of Bu₃SnH at 100 °C: **21b** (100 mg) in toluene (15 ml) was deoxygenated with Bu₃SnH (175 mg) as described above. Four compounds were obtained after chromatography: **38** (30 mg), **39** (25 mg), **40** (syrup, 22 mg), and **36** (syrup, 10 mg) slightly contaminated with **37**.

iii) With 1.5 mol eq of Bu₃SnH at 75 °C: **21b** (150 mg) in toluene (23 ml) was deoxygenated with Bu₃SnH (261 mg) and AIBN (6 mg) at 75 °C for 1 h. Chromatography of the product gave **38** (35 mg) (contaminated with the other compounds), **39** (27 mg), and an inseparable mixture of **37** and **36** (51 mg). The ¹H- and ¹³C-NMR spectra of **37** were obtained by subtraction of the spectra of **36** from those of the mixture, and confirmed by comparisons of the COSY and C–H COSY spectra of the mixture and those of the pure **36**. The ratio (1:1) was determined from the intensity ratio of the OMe peaks.

Methyl 3,4-*O*-Methylidene-β-L-arabinopyranoside 2-Acetate (38)—Syrup. ¹H-NMR (CDCl₃): 5.21 and 5.00 (1H each, s, –OCH₂O–), 4.85 (1H, d, *J* = 3.5 Hz, H-1), 4.83 (1H, dd, *J* = 3.5, 7.5 Hz, H-2), 4.37 (1H, dd, *J* = 5.5, 7.5 Hz, H-3), 4.07 (1H, d, *J* = 13.5 Hz, H-5ax), 4.04 (1H, dd, *J* = 3, 5.5 Hz, H-4), 3.92 (1H, dd, *J* = 3.0, 13.5 Hz, H-5eq), 3.40

(3H, s, OMe), 2.15 (3H, s, OAc). ^{13}C -NMR (CDCl_3): 170.5 (C=O), 97.1 (C-1), 94.6 ($-\text{OCH}_2\text{O}-$), 74.5, 72.3, 70.2 (C-2, 3, 4), 58.2 (C-5), 55.6 (OMe), 21.0 (OAc). HR-MS m/z Calcd for $\text{C}_9\text{H}_{14}\text{O}_6$: 218.0786. Found: 218.0790.

Methyl β -L-Arabinopyranoside 3,4-Carbonate 2-Acetate (39)—Colorless needles from hexane- CH_2Cl_2 , mp 117–119°C. ^1H -NMR: 5.43 (1H, dd, $J=3.7, 7.3$ Hz, H-2), 5.27 (1H, t, $J=7.3$ Hz, H-3), 5.17 (1H, dd, $J=2.7, 7.3$ Hz, H-4), 5.16 (1H, d, $J=3.7$ Hz, H-1), 4.17 (1H, d, $J=14.3$ Hz, H-5eq), 3.98 (1H, dd, $J=2.7, 14.3$ Hz, H-5ax), 3.29 (3H, s, OMe), 1.99 (3H, s, OAc). ^{13}C -NMR: 169.9 ($\text{CH}_3\text{C}=\text{O}$), 154.4 ($\text{O}=\text{C}$), 96.6 (C-1), 75.9 (C-4), 74.7 (C-3), 70.8 (C-2), 57.7 (C-5), 55.8 (OCH_3), 20.5 ($\text{CH}_3\text{C}=\text{O}$). IR: 1814, 1724. Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}_7$: C, 46.55; H, 5.21. Found: C, 46.73; H, 5.29.

Methyl 4-Deoxy- β -L-threo-pentopyranoside 3-Acetate (40)—Syrup. ^1H -NMR: 5.56 (1H, dt, $J=5.0, 10.5$ Hz, H-3), 5.06 (1H, d, $J=4$ Hz, H-1), 4.00 (1H, dd, $J=4.0, 10.0$ Hz, H-2), 3.74 (1H, dt, $J=12.0, 2.0$ Hz, H-5ax), 3.60 (1H, ddd, $J=2.0, 5.0, 12.0$ Hz, H-5eq), 3.37 (3H, s, OMe), 2.09 (1H, ddt, $J=12.5, 5.0, 2.0$ Hz, H-4eq), 2.01 (3H, s, OAc), 1.76 (1H, ddt, $J=12.5, 5.0, 10.5$ Hz, H-4ax). HR-MS m/z Calcd for $\text{C}_8\text{H}_{14}\text{O}_5$: 190.0841. Found: 190.0845.

Methyl 4-Deoxy- β -L-threo-pentopyranoside 2-Acetate (37)— ^1H -NMR: 5.14 (1H, br d, $J=3.5$ Hz, H-1), 5.12 (1H, dd, $J=3.5, 9$ Hz, H-2), 4.46 (1H, ddd, $J=5, 9, 11$ Hz, H-3), 3.79 (1H, dt, $J=12.0, 2.5$ Hz, H-5ax), 3.65 (1H, ddd, $J=2.0, 5.5, 12.0$ Hz, H-5eq), 3.33 (3H, s, OMe), 2.12 (1H, ddt, $J=12.5, 5.0, 2.5$ Hz, H-4eq), 1.97 (3H, s, OAc), 1.95 (1H, ddt, $J=5.0, 11.0, 12.5$ Hz, H-4ax).

Methyl 3-Deoxy- α -L-threo-pentopyranoside 2-Acetate (36)—Syrup. ^1H -NMR: 5.74 (1H, ddd, $J=3, 5, 11.5$ Hz, H-2), 5.06 (1H, br d, $J=3$ Hz, H-1), 4.20–4.24 (1H, m, H-4), 3.92 (1H, dd, $J=2, 12$ Hz, H-5ax), 3.77 (1H, dd, $J=2, 12.0$ Hz, H-5eq), 3.41 (3H, s, OMe), 2.33 (1H, ddd, $J=3, 11.5, 12.5$ Hz, H-3ax), 2.23 (1H, ddd, $J=4, 5, 12.5$ Hz, H-3eq), 1.99 (3H, s, OAc). HR-MS m/z Calcd for $\text{C}_8\text{H}_{14}\text{O}_5$: 190.0841. Found: 190.0848.

Methyl 3,4-Dideoxy- β -D-erythro-hex-3-enopyranoside 2,6-Diacetate (41b)—Needles from isopropyl ether, mp 78–80°C. ^1H -NMR (CDCl_3): 5.91 (1H, ddd, $J=1.2, 1.8, 10.4$ Hz, H-3), 5.85 (1H, ddd, $J=2.4, 3.0, 10.4$ Hz, H-4), 5.14–5.17 (1H, m, H-2), 4.62 (1H, d, $J=4.9$ Hz, H-1), 4.48–4.54 (1H, m, H-5), 4.19 (1H, dd, $J=6.4, 11.3$ Hz, H-6), 4.15 (1H, dd, $J=5.2, 11.3$ Hz, H-6), 3.50 (3H, s, OMe), 2.09 and 2.10 (3H each, s, OAc). IR: 1800, 1720. Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_6$: C, 54.09; H, 6.60. Found: C, 54.02; H, 6.63.

Methyl 3,4-Dideoxy- β -D-erythro-hex-3-enopyranoside (41a)—Syrup. ^1H -NMR (CDCl_3): 5.86 (1H, dt, $J=10.2, 2.4$ Hz, H-3), 5.74 (1H, dt, $J=10.2, 1.8$ Hz, H-4), 4.42 (1H, d, $J=5.8$ Hz, H-1), 4.36–4.41 (1H, m, H-5), 4.08 (1H, dt, $J=5.8, 2.4$ Hz, H-2), 3.76 (1H, dd, $J=3.2, 12.0$ Hz, H-6), 3.62 (1H, dd, $J=6.0, 12.0$ Hz, H-6), 3.57 (3H, s, OMe).

Methyl 3,4-Dideoxy- β -D-erythro-hexopyranoside (42)—Volatile liquid. ^1H -NMR (CDCl_3): 4.14 (1H, d, $J=7.6$ Hz, H-1), 3.59–3.63 (3H, m, H-5 and H-6), 3.56 (3H, s, OMe), 3.39 (1H, ddd, $J=5.5, 7.6, 10.5$ Hz, H-2), 2.12 (1H, ddd, $J=2.5, 5.5, 10.5$ Hz, H-3), 1.59–1.67 (1H, m, H-3), 1.45–1.58 (2H, m, H-4). HR-MS m/z Calcd for $\text{C}_7\text{H}_{14}\text{O}_4$: 162.0892. Found: 162.0895.

Methyl 3,4-Dideoxy- α -D-erythro-hex-3-enopyranoside 2,6-Diacetate (43b)—Colorless liquid. ^1H -NMR (CDCl_3): 5.84 (1H, dt, $J=10.7, 2.1$ Hz, H-3), 5.75 (1H, dt, $J=10.7, 2.1$ Hz, H-4), 5.30–5.34 (1H, m, H-2), 5.11 (1H, d, $J=4.2$ Hz, H-1), 4.36–4.42 (1H, m, H-5), 4.18 (2H, d, $J=4.9$ Hz, H-6), 3.50 (3H, s, OMe), 2.10 and 2.12 (3H each, s, OAc).

Methyl 3,4-Dideoxy- α -D-erythro-hex-3-enopyranoside (43a)—Volatile liquid. ^1H -NMR (CDCl_3): 5.81 (1H, dt, $J=10.4, 2.1$ Hz, H-3), 5.69 (1H, dt, $J=10.4, 2.1$ Hz, H-4), 4.92 (1H, d, $J=4.6$ Hz, H-1), 4.19–4.26 (2H, m, H-2, 5), 3.74 (1H, dd, $J=3.0, 11.3$ Hz, H-6), 3.60 (1H, dd, $J=6.1, 11.3$ Hz, H-6), 3.53 (3H, s, OMe).

Methyl 3,4-Dideoxy- α -D-erythro-hexopyranoside (44)—Volatile liquid. ^1H -NMR (CDCl_3): 4.70 (1H, d, $J=3.7$ Hz, H-1), 3.72–3.79 (1H, m, H-5), 3.62 (1H, dd, $J=3.4, 11.6$ Hz, H-6), 3.59–3.63 (1H, m, H-2), 3.51 (1H, dd, $J=6.7, 11.6$ Hz, H-6), 3.45 (3H, s, OMe), 1.90 (1H, ddd, $J=4.0, 5.5, 11.5$ Hz, H-3eq), 1.71 (1H, dddd, $J=4.0, 8.0, 11.5, 11.9$ Hz, H-3ax), 1.61 (1H, ddd, $J=3.4, 4.0, 11.9$ Hz, H-4eq), 1.48 (1H, dddd, $J=4.0, 8.0, 11.9, 11.9$ Hz, H-4ax). HR-MS m/z Calcd for $\text{C}_7\text{H}_{14}\text{O}_4$: 162.0892. Found: 162.0898.

Phenyl 3,4-Dideoxy- β -D-glycero-pent-3-enopyranoside 2-Acetate (45b)—Syrup. ^1H -NMR (CDCl_3): 7.27–7.32 (2H, m, ArH), 7.01–7.09 (3H, m, ArH), 6.17 (1H, dt, $J=2.5, 10.0$ Hz, H-4), 4.94–4.98 (1H, m, H-3), 5.56 (1H, br s, H-1), 5.18 (1H, br d, $J=4.0$ Hz, H-2), 4.28 (1H, dd, $J=2.5, 17.0$ Hz, H-5), 4.02 (1H, dd, $J=2.5, 17.0$ Hz, H-5).

Phenyl 3,4-Dideoxy- β -D-glycero-pent-3-enopyranoside (45a)—Syrup. ^1H -NMR (CDCl_3): 7.00–7.32 (5H, m, ArH), 6.00 (2H, s, H-3 and H-4), 5.47 (1H, d, $J=2.1$ Hz, H-1), 4.24 (1H, dd, $J=2.0, 17.5$ Hz, H-5ax), 4.15 (1H, dd, $J=1.2, 17.5$ Hz, H-5eq), 4.08 (1H, br s, H-2).

Phenyl 3,4-Dideoxy- β -D-glycero-pentopyranoside (46)—Volatile oil. ^1H -NMR (CDCl_3): 7.00–7.31 (5H, m, ArH), 5.03 (1H, d, $J=5.2$ Hz, H-1), 3.96 (1H, ddd, $J=3.5, 6.3, 11.5$ Hz, H-5), 3.76 (1H, ddd, $J=4.0, 5.2, 7.8$ Hz, H-2), 3.58 (1H, ddd, $J=3.0, 7.6, 11.5$ Hz, H-5), 2.20 (1H, m, H-3), 1.84 (1H, m, H-4), 1.69 (1H, ddd, $J=4.3, 7.8, 12.5$ Hz, H-3), 1.58–1.66 (1H, m, H-4). HR-MS m/z Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$: 194.0943. Found: 194.0949.

Methyl 3,4-Dideoxy- α -D-glycero-pent-3-enopyranoside 2-Acetate (47b)—Highly volatile liquid. ^1H -NMR (CDCl_3): 5.95 (1H, dt, $J=10.4, 2.4$ Hz, H-4), 4.66 (1H, dd, $J=2.4, 10.4$ Hz, H-3), 5.30 (1H, m, H-2), 4.93 (1H, d, $J=4.0$ Hz, H-1), 4.23 (1H, dd, $J=2.4, 16.8$ Hz, H-5), 4.08 (1H, dd, $J=2.4, 16.8$ Hz, H-5), 3.50 (3H, s, OMe), 2.12 (3H, s, OAc).

Methyl 3,4-Dideoxy- α -D-glycero-pent-3-enopyranoside (47a)—Highly volatile liquid. ^1H -NMR (CDCl_3): 5.82

(1H, dt, $J=10.5$, 2.4 Hz, H-4), 5.73 (1H, dd, $J=2.1$, 10.5 Hz, H-3), 4.77 (1H, d, $J=4.0$ Hz, H-1), 4.17—4.21 (1H, m, H-2), 4.14 (1H, dd, $J=2.4$, 16.8 Hz, H-5), 4.02 (1H, dd, $J=2.4$, 16.8 Hz, H-5), 3.53 (3H, s, OMe).

Methyl 3,4-Dideoxy- α -D-glycero-pentopyranoside (48)—Highly volatile liquid. $^1\text{H-NMR}$ (CDCl_3): 4.58 (1H, d, $J=3.1$ Hz, H-1), 3.61—3.69 (1H, m, H-2), 3.42—3.53 (2H, m, H₂-5), 3.45 (3H, s, OMe), 1.79—1.85 (1H, m, H-3), 1.62—1.75 (3H, m, H-3 and H₂-4). HR-MS m/z Calcd for $\text{C}_6\text{H}_{12}\text{O}_5$: 132.0787. Found: 132.0792.

Acknowledgement One of the author (M. E. H.) is grateful to the Ministry of Education, Science and Culture of Japan for a scholarship. We also thank Miss Y. Ito for technical assistance for some experiments. This work was supported in part by a Grant-in-Aid for Developmental Research (No. 58870102, 1983 and 1984) to Y. T. and K. K. from Ministry of Education, Science and Culture of Japan.

References and Notes

- 1) Utilization of Sugars in Organic Syntheses. XVII. Part XVI: M. E. Haque, T. Kikuchi, K. Kanemitsu, and Y. Tsuda, *Chem. Pharm. Bull.*, **34**, 430 (1986).
- 2) a) D. H. R. Barton and S. W. McCombie, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1574; b) D. H. R. Barton and R. Subramanian, *ibid.*, **1977**, 1718; c) T. S. Fuller and R. V. Stick, *Aust. J. Chem.*, **33**, 2509 (1980); d) D. H. R. Barton and R. Subramanian, *J. Chem. Soc., Chem. Commun.*, **1977**, 867; e) D. H. R. Barton and R. V. Stick, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1773.
- 3) Y. Tsuda, M. E. Haque, and K. Yoshimoto, *Chem. Pharm. Bull.*, **31**, 1612 (1983).
- 4) M. E. Haque, T. Kikuchi, K. Yoshimoto, and Y. Tsuda, *Chem. Pharm. Bull.*, **33**, 2243 (1985).
- 5) a) M. Miyazaki and K. Nakahashi, *Jpn. Tokkyo Koho*, 1322 (1957) [*Chem. Abstr.*, **52**, 4684g (1958)]; b) M. J. Robins, J. S. Wilson, and F. Hansske, *J. Am. Chem. Soc.*, **105**, 4059 (1983).
- 6) H. A. Staab and G. Walther, *Justus Liebigs Ann. Chem.*, **657**, 98 (1962).
- 7) B. Classon, P. J. Gregg, and T. Norberg, *Acta Chem. Scand.*, **B38**, 195 (1984).
- 8) a) C. Walling, "Free Radicals in Solution," Wiley, New York, 1959; b) Ingold and B. P. Roberts, "Free Radical Substitution Reaction," Wiley-Interscience, New York, 1971.
- 9) Occurrence of a facile *trans*-acyl migration between O-2 and O-3 in pyranosides has been proved [K. Yoshimoto and Y. Tsuda, *Chem. Pharm. Bull.*, **31**, 4324 (1983)].
- 10) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).
- 11) M. E. Evans, L. Long, Jr., and F. W. Parrish, *J. Org. Chem.*, **33**, 1074 (1968).