Synthesis of Thiodisaccharides using Phase-transfer Catalysis

Françoise Chrétien,* Pierre Di Cesare, and Bernard Gross
Laboratoire de Chimie Organique 3, UA CNRS 486, Université de Nancy I, BP 239, 54506 Vandoeuvre les Nancy Cedex, France.

Synthesis of thiodisaccharides or thioglycosides was performed by phase-transfer catalysis using phosphonium or ammonium salts. Starting from glycosyl halides, reaction with Na_2S gave the corresponding thiodisaccharides with inversion of configuration at the anomeric centre. With unstable glycosyl halides, a solid–liquid system was used. Unsymmetrical thiodisaccharides and 1-thioglycosides were prepared by reaction of glycosyl halides with thiolate or 1-thioglucose under p.t.c. conditions.

The synthesis of thiodisaccharides and 1-thioglycosides has recently received new interest in relation to studies of enzymatic processes.[1] Conventional synthetic methods are useful to obtain 1-thioglycosides having the 1–2 *trans* configuration.[2] In an attempt to obtain 1-thioglycosides with the 1–2 *cis* configuration, reactions was performed by using hexamethylphosphoric triamide (HMPA) as solvating agent for cations;[3] although this method allowed the synthesis of such derivatives, yields are often poor.

Our approach to the synthesis of this type of compound was dictated to us by the good results we obtained in using phase-transfer catalysis (p.t.c.) in sugar chemistry.[4] Surprisingly, this method had not received widespread application in this field. Only a few papers describe an approach to this thiodisaccharide synthesis *via* phase-transfer catalyses.[5,6] Two different routes might be used in accordance with the desired structure of the required thiosaccharides: symmetrical or unsymmetrical.

Results and Discussion

Synthesis of Symmetrical Thiodisaccharides: Case of Thiotrehalose and its Analogues in manno *and* galacto *Series.*—These compounds were obtained by a two-phase system reaction in the presence of a phosphonium or ammonium salt, the organic phase being a solution of glycosyl halide, the other phase being sodium sulphide in aqueous solution or in the solid state.

The results strongly depend upon three factors: the nature of the organic solvent, and the nature and the quantity of the catalyst.

In the case of the transformation of α-acetobromoglucose (**1**), benzene and methylene dichloride have been used (Table 1, entries 2 and 3); the best result was obtained with benzene, so we decided to perform all reactions in this solvent.

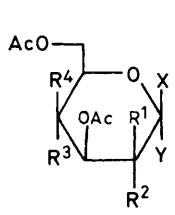
The onium salt could be used in catalytic (0.1 mol equiv.) or stoicheiometric amount without dramatic influence on the course of the reaction. The yields are nearly the same but the reaction is faster when 1 mol equiv. of the catalyst is used (Table 1, entries 1, 2, 6, and 7).

The nature of the onium salt seems to have some influence on the course of the reaction but it is difficult to relate it with the observed results. The stability of the glycosyl halide may also be involved. Several runs were performed with different salts. The results are summarized in Table 1. Whatever the reaction conditions, the configuration of the thio compound formed in the reaction is the opposite to that of the starting glycosyl halide. Nevertheless, when the α-acetobromomannose (**3**) was

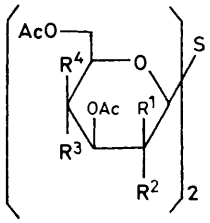
Table 1. Symmetrical thiodisaccharides prepared

Entry	RX	Catalyst[a]	Solvent	Time (h)[b]	Product	Yield (%)[e]
1	(**1**)	A	Benzene–water	0.25	(**9**)	60
2	(**1**)	B	Benzene–water	1.5	(**9**)	66
3	(**1**)	B	CH_2Cl_2	2.5	(**9**)	29
4	(**1**)	C	Benzene–water	1.5	(**9**)	40
5	(**1**)	D	Benzene–water	1.5	(**9**)	72
6	(**2**)	A	Benzene–water	0.25	(**10**)	52
7	(**2**)	B	Benzene–water	5	(**10**)	45
8	(**2**)	D	Benzene–water	1.15	(**10**)	62
9	(**3**)	A	Benzene–water	24	(**11**)	9[f]
10	(**3**)	C	Benzene–water	18	(**11**)	36
11	(**3**)	D	Benzene–water	20		*g*
12	(**3**)	D	Benzene	20	(**11**)	14
13	(**4**)	A	Benzene–water	4	(**12**)	16
14	(**4**)	C	Benzene–water	5	(**12**)	25
15	(**4**)	D	Benzene–water	5	(**12**)	16
16	(**4**)	A	Benzene	20	(**12**)	55
17	(**4**)	D	Benzene	20	(**12**)	36
18	(**5**)	A	Benzene–water	6[c]	(**13**)	8
19	(**6**)	A	Benzene–water	8[d]		*g*
20	(**6**)	A	Benzene	48	(**11**)	15

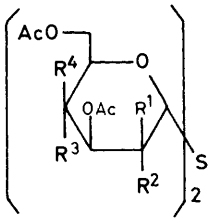
[a] A = Tributyl(hexadecyl)(phosphonium bromide, 1 mol equiv.; B = tributyl(hexadecyl)phosphonium bromide, 0.1 mol equiv.; C = tetrabutylammonium hydrogensulphate, 1 mol equiv.; D = tetrabutylammonium bromide, 1 mol equiv. [b] Reaction performed at room temperature unless otherwise stated. [c] Temperature of reaction 30 °C. [d] Temperature of reaction 45 °C. [e] Yield of pure isolated product after column chromatography. [f] 3% of αβ-derivative was observed. [g] No reaction observed.



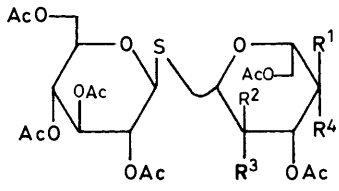
(1) X = R^1 = R^4 = H, Y = Br, R^2 = R^3 = OAc
(2) X = R^1 = R^3 = H, Y = Br, R^2 = R^4 = OAc
(3) X = R^2 = R^4 = H, Y = Br, R^1 = R^3 = OAc
(4) X = Cl, Y = R^1 = R^4 = H, R^2 = R^3 = OAc
(5) X = Cl, Y = R^2 = R^4 = H, R^1 = R^3 = OAc
(6) X = R^2 = R^4 = H, Y = Cl, R^1 = R^3 = OAc
(7) X = SH, Y = R^1 = R^4 = H, R^2 = R^3 = OAc
(8) X = $SCH_2CO_2Bu^t$, Y = R^1 = R^4 = H, R^2 = R^3 = OAc



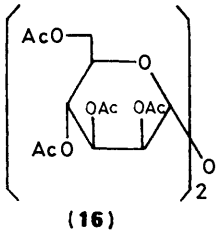
(9) R^1 = R^4 = H, R^2 = R^3 = OAc
(10) R^1 = R^3 = H, R^2 = R^4 = OAc
(11) R^1 = R^3 = OAc, R^2 = R^4 = H



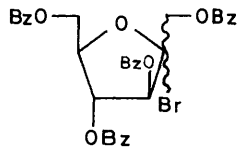
(12) R^1 = R^4 = H, R^2 = R^3 = OAc
(13) R^1 = R^3 = OAc, R^2 = R^4 = H



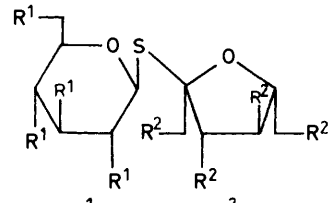
(14) R^1 = R^3 = H, R^2 = R^4 = OAc
(15) R^2 = R^4 = H, R^1 = R^3 = OAc



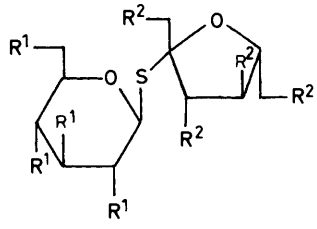
(16)



(17)



(18) R^1 = OAc, R^2 = OBz
(20) R^1 = R^2 = OH



(19) R^1 = OAc, R^2 = OBz
(21) R^1 = R^2 = OH

used as the starting material and tributyl(hexadecyl)phosphonium bromide as the catalyst (Table 1, entry 9), the reaction was sluggish, giving only 9% of the expected thiodisaccharide (**11**), a minute amount of the αβ-product (3%), and 12% of the corresponding αα-*O*-disaccharide (**16**). The reaction was very slow (24 h) as previously reported by Bogusiak and Szeja,[6] the presence of bromide ions in the solution could give rise to an anomerization of the glycosyl halide in a Lemieux-type reaction.[7] If tetrabutylammonium hydrogen sulphate was used as the catalyst, avoiding anomerization, only compound (**11**) was formed (entry 10). The β-acetochloromannose (**5**) (entry 18) did not give a thiodisaccharide at room temperature, and with heating only 8% of the coupling product was observed. Compound (**5**) is a very stable glycosyl halide as mentioned by Korytnyk[8] and Defaye.[3] The use of a heterogeneous solid–liquid system (Table 1, entries 12, 16, 17, and 20) is better when the reaction is sluggish or when the glycosyl halide is particularly prone to hydrolysis.

Synthesis of 1-*Thioglycosides*.—Synthesis of unsymmetrical thio ethers (sulphides) by p.t.c. is very efficient in aliphatic series as shown by Fochi and co-workers.[9] More recently, Hammacher[5] reported the synthesis of thiocellobiose and thiosophorose by reaction of the sodium salt of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose with methyl 2,3,6-tri-*O*-benzoyl-4-*O*-trifluoromethylsulphonyl-α-D-glucopyranoside or

Table 2. Unsymmetrical thiodisaccharides prepared.

$$RBr + R'SH \xrightarrow[\text{Benzene}]{R_4P^+, X^-} RSR'$$

(7)

Entry	RBr	Time (h)	Yield (%)	Product
1	(**1**)	2	60	(**9**)
2	(**2**)	2	70	(**14**)
3	$BrCH_2CO_2Bu^t$	0.25	75	(**8**)
4	(**3**)	6	23	(**15**)
			35	(**16**)
6	(**17**)	5	30	(**18**) + (**19**)

1,3,4,6-tetra-*O*-acetyl-2-*O*-trifluoromethylsulphonyl-β-D-mannopyranose respectively, in the presence of cryptands or crown ethers as catalyst.

Our own results show that in general the 1-thioglucose derivative (**7**) reacted with different halides in the presence of sodium hydroxide and a phosphonium salt *via* an S_N2 mechanism. The thiolate is generated by the use of a stoicheiometric amount of sodium hydroxide. Yields are generally high (see Table 2) except for the condensation of (**3**) with (**7**) where a relatively large quantity of the symmetrical disaccharide (**16**) was formed. Having in hand a good method for the synthesis of unsymmetrical thiodisaccharides we tried to prepare the 1-thioisosucrose (**18**) which may be considered as an inhibitor of invertases and related enzymes.[1]

The crude fructosyl bromide (**17**), prepared from 1,3,4,6-tetra-*O*-benzoyl-D-fructofuranose and hydrogen bromide according to the method of Helferich,[10] reacted with the 1-thioglucose (**7**) to give a mixture of 1-thiodisaccharide anomers βα (**18**) and ββ (**19**) in 30% yield. The ratio 7:3 for (**18**):(**19**) was determined by 250 MHz ^1H n.m.r. analysis, based on the 3-H signal of the fructofuranosyl moiety. The presence of an anomeric mixture may be explained by the fact that the bromide intermediate could not be isolated and fully characterized and may be a mixture of α and β anomers. The low yield of the condensation may be due to the short lifetime of the fructofuranosyl bromide as noticed by Defaye.[1] The deprotection of the hydroxy groups of compounds (**18**) and (**19**) by conventional methods afforded respectively compounds (**20**) and (**21**). Analytical data were in good agreement with those in the literature.[1]

Experimental

^1H N.m.r. spectra were recorded at 250 MHz on a Cameca spectrometer using deuteriochloroform as solvent. Assignments were confirmed by double irradiation. Chemical shifts are reported downfield relative to internal $SiMe_4$. T.l.c. was performed on silica gel (Merck 60 F_{254}). Column chromatography used silica gel (Merck 60 70—230 mesh). Optical rotations were measured on a Perkin Elmer 141 polarimeter. M.p.s were measured in capillary tubes and were uncorrected. Elementary analyses were performed by the Service Central de Microanalyse du CNRS at Vernaison, France.

Preparation of Acetylated Symmetrical Thiodisaccharides.— To a solution of an acetohalogeno sugar (1 mmol) in benzene (2 ml) was added sodium sulphide hydrate (780 mg, 10 mmol), the catalyst (see Table 1), and water (2 ml). The mixture was stirred at room temperature and the reaction was monitored by t.l.c. with chloroform–diethyl ether (9:1) as developer. The reaction mixture was diluted with benzene, and the organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated to give the crude product.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (ββ-thiotrehalose) (**9**) was purified by recrystallization from methanol (500 mg, 72%), m.p. 174—175 °C; $[\alpha]_D$ −36° (*c* 1.18 in $CHCl_3$) (lit.,[11] 177 °C; $[\alpha]_D$ −41.7°); δ_H 2.00, 2.03, 2.05, and 2.11 (together 24 H, 4 × s, 8 × Ac), 3.71 (2 H, m, $J_{5,6a}$ 5, $J_{5,6b}$ 2.5 $J_{4,5}$ 9 Hz, 2 × 5-H), 4.15 (2 H, dd, $J_{6a,6b}$ 12 Hz, 2 × 6-H_a), 4.28 (2 H, dd, 2 × 6-H_b), 4.84 (2 H, d, $J_{1,2}$ 10 Hz, 2 × 1-H), 5.05 (2 H, dd, $J_{2,3}$ 9 Hz, 2 × 2-H), 5.10 (2 H, t, $J_{3,4}$ 9 Hz, 2 × 4-H), and 5.23 (2 H, t, 2 × 3-H).

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (**10**) was purified by recrystallization from methanol (430 mg, 62%), m.p. 202—203 °C; $[\alpha]_D$ −12.4° (*c* 0.98 in $CHCl_3$) {lit.,[12] 199—202 °C; $[\alpha]_D$ −14° (*c* 0.5 in $CHCl_3$)}; δ_H 1.98 and 2.18 (together 12 H, 2 × s, 4 × Ac), 2.06 (12-H, s, 4 × Ac), 3.93 (2 H, dt, $J_{5,6a} = J_{5,6b}$ = 6.5, $J_{4,5}$ 1 Hz, 2 × 5-H), 4.10 (2 H, dd, $J_{6a,6b}$ 11 Hz, 2 × 6-H_a), 4.19 (2 H, dd, 2 × 6-H_b), 4.82 (2 H, d, $J_{1,2}$ 10 Hz, 2 × 1-H), 5.06 (2 H, dd, $J_{3,4}$ 3.5 Hz, 2 × 3-H), 5.23 (2 H, t, 2 × 2-H), and 5.45 (2 H, dd, 2 × 4-H).

2,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-mannopyranoside (**11**) was purified by column chromatography, with diethyl ether as eluant (250 mg, 36%), m.p. 225—227 °C; $[\alpha]_D$ −105° (*c* 1.19 in $CHCl_3$) {lit.,[3] 226—230 °C; $[\alpha]_D$ −107° (*c* 0.81 in $CHCl_3$)}; δ_H 1.98, 2.05, 2.09, and 2.17 (together 24 H, 4 × s, 8 × Ac), 3.69 (2 H, m, $J_{4,5}$ 10, $J_{5,6a}$ 2.5, $J_{5,6b}$ 5.5 Hz, 2 × 5-H), 4.18 (2 H, dd, $J_{6a,6b}$ 12 Hz, 2 × 6-H_a), 5.06 (2 H, br s, 2 × 1-H), 4.28 (1 H, dd, 2 × 6_b-H) 5.07 (2 H, dd, $J_{2,3}$ 3.5, $J_{3,4}$ 10 Hz, 2 × 3-H), 5.27 (2 H, t, $J_{4,5}$ 10 Hz, 2 × 4-H), and 5.49 (2 H, dd, 2 × 2-H).

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-glucopyranoside (**12**) was purified by column chromatography with diethyl ether as eluant (174 mg, 25%), m.p. 189—190 °C (from MeOH); $[\alpha]_D$ +205° (*c* 2.3 in $CHCl_3$) {lit.,[3] 191—193 °C (from MeOH); $[\alpha]_D$ +200° (*c* 1.1 in $CHCl_3$)}; δ_H 2.02, 2.04, 2.09, and 2.10 (together 24 H, 4 s, 8 × Ac), 4.08 (2 H, dd, $J_{5,6b}$ 4, $J_{6a,6b}$ 14 Hz, 2 × 6-H_b), 4.23 (2 H, m, 2 × 5-H), 4.25 (2 H, m, 2 × 6-H_a), 5.02 (2 H, t, $J_{4,5}$ 10, $J_{3,4}$ 10 Hz, 2 × 4-H), 5.06 (2 H, dd, $J_{2,3}$ 10, $J_{1,2}$ 6 Hz, 2 × 2-H), 5.36 (2 H, t, 2 × 3-H), and 5.84 (2 H, d, 2 × 1-H).

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (**13**) was purified by column chromatography with diethyl ether as eluant (55 mg, 8%), m.p. 179—180 °C; $[\alpha]_D$ +135° (*c* 1.08 in $CHCl_3$) {lit.,[3] 167—173 °C; $[\alpha]_D$ +148° (*c* 0.27 in $CHCl_3$)}; δ_H 2.02, 2.07, 2.10, and 2.17 (together 24-H, 4 × s, 8 × Ac), 4.09 (2 H, dd, $J_{6a,6b}$ 14, $J_{5,6a}$ 5 Hz, 2 × 6-H_a), 4.32 (4 H, m, 2 × 5-H and 2 × 6-H_b), 5.20 (2 H, dd, $J_{2,3}$ 3.5, $J_{3,4}$ 10 Hz, 2 × 3-H), 5.33 (2 H, dd, $J_{1,2}$ 15 Hz, 2 × 2-H), 5.36 (2 H, t, $J_{4,5}$ 10 Hz, 2 × 4-H), and 5.40 (2 H, d, 2 × 1-H).

Preparation of Acetylated Unsymmetrical Thioglycosides.— To a solution of 1-thio-β-D-glucose tetra-acetate (**7**) (364 mg, 1 mmol) and tributyl(hexadecyl)phosphonium bromide (507 mg, 1 mmol) in benzene (4 ml) was added 1M-NaOH (1 ml). After the mixture had been stirred for 5 min, the bromide derivative was added (1 mmol). The reaction was monitored by t.l.c. with hexane–ethyl acetate (3:2), or chloroform–diethyl ether (9:1) as solvent. The reaction mixture was diluted with methylene dichloride, and the organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated to give the crude product.

t-Butyl(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosylthio*)-*acetate* (**8**) was purified by column chromatography with hexane–ethyl acetate (3:2) as eluant (358 mg, 75%), m.p. 105—106 °C; $[\alpha]_D$ −65.7° (*c* 1.06 in $CHCl_3$) (Found: C, 50.2; H, 6.3; S, 6.6. $C_{20}H_{30}SO_{11}$ requires C, 50.20; H, 6.32; S, 6.67%); δ_H 1.05 (9 H, s, OBu^t), 2.01, 2.03, 2.06, and 2.09 (together 12-H, 4 × s, 4 × Ac), 3.20 (1 H, d, $J_{7a,7b}$ 15 Hz, C*H*HS), 3.42 (1 H, d, CH*H*S),

3.72 (1 H, m, $J_{4,5}$ 9, $J_{5,6a}$ 2.5, $J_{5,6b}$ 4.5 Hz, 5-H), 4.12 (1 H, dd, $J_{6a,6b}$ 12 Hz, 6-H_a), 4.27 (1 H, dd, 6-H_b), 4.74 (1 H, d, $J_{1,2}$ 10 Hz, 1-H), 5.02 (1 H, dd, $J_{2,3}$ 9 Hz, 2-H), 5.10 (1 H, t, $J_{3,4}$ 9 Hz, 4-H), and 5.24 (1 H, t, 3-H).

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**14**) was purified by column chromatography with hexane–ethyl acetate (3:2) as eluant (486 mg, 70%), m.p. 158 °C; $[\alpha]_D$ −12° (*c* 0.66 in $CHCl_3$) {lit.,[12] 169—171 °C; $[\alpha]_D$ −38.3° (*c* 0.50 in $CHCl_3$)}; δ_H 1.98, 2.00, and 2.04 (together 9 H, 3 × s, 3 × Ac), 2.06 (6 H, s, 2 × Ac), 2.07, 2.10, and 2.17 (together 9 H, 3 × s, 3 × Ac), 3.70 (1 H, m, $J_{5,6b}$ 2.5, $J_{5,6a}$ 5, $J_{4,5}$ 9 Hz, 5-H), 3.92 (1 H, dt, $J_{5',6'a} = J_{5',6'b}$ = 6.5, $J_{4',5'}$ 0.5 Hz, 5'-H), 4.15 (3 H, m, 6'-H_a, 6'-H_b and 6-H_b), 4.28 (1 H, dd, $J_{6a,6b}$ 12 Hz, 6-H_a), 4.82 (1 H, d, $J_{1,2}$ 10 Hz, 1-H), 4.84 (1 H, d, $J_{1',2'}$ 10 Hz, 1'-H), 5.03 (1 H, t, $J_{2,3}$ 10 Hz, 2-H), 5.05 (1 H, dd, $J_{2',3'}$ 10, $J_{3',4'}$ 3.5 Hz, 3'-H), 5.09 (1 H, t, 4-H), 5.22 (1 H, t, 2'-H), 5.23 (1 H, t, 3-H), and 5.44 (1 H, dd, 4'-H).*

2,3,4,6-*Tetra*-O-*acetyl*-β-D-*glucopyranosyl* 2,3,4,6-*tetra*-O-*acetyl*-1-*thio*-β-D-*mannopyranoside* (**15**) was purified by column chromatography with hexane–ethyl acetate (3:2) as eluant (160 mg, 23%), m.p. 191—193 °C; $[\alpha]_D$ −56° (*c* 1.2 in $CHCl_3$) (Found: C, 48.85; H, 5.5; S, 4.5. $C_{28}H_{38}O_{18}S$ requires C, 48.42; H, 5.51; S, 4.61%); δ_H 1.97, 2.00 and 2.03 (together 9 H, 3 × s, 3 × Ac), 2.05 and 2.11 (together 12 H, 2 × s, 4 × Ac), 2.17 (3 H, s, Ac), 3.72 (2 H, m, 5- and 5'-H), 4.16 (1 H, dd, $J_{5',6'a}$ 2.5, $J_{6'a,6'b}$ 12.5 Hz, 6'-H_a), 4.18 (1 H, dd, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 12.5 Hz, 6-H_a), 4.27 (1 H, dd, $J_{5',6'b}$ 5 Hz, 6'-H_b), 4.32 (1 H, dd, $J_{5,6b}$ 5 Hz, 6-H_b), 4.84 (1 H, d, $J_{1,2}$ 10 Hz, 1-H), 5.03 (1 H, dd, $J_{2,3}$ 9 Hz, 2-H), 5.10 (1 H, br s, 1'-H), 5.10 (1 H, dd, $J_{2',3'}$ 3.5 $J_{3',4'}$ 10 Hz, 3'-H), 5.11 (1 H, t, $J_{3,4}$ 9 Hz, 4-H), 5.23 (1 H, t, 3-H), 5.27 (1 H, t, $J_{4',5'}$ 10 Hz, 4'-H), and 5.50 (1 H, dd, $J_{1',2'}$ 0.5 Hz, 2'-H).†

α-D-*Fructofuranosyl*-1-*Thio*-β-D-*glucopyranoside* (**20**) *and* β-D-*Fructofuranosyl* 1-*Thio*-β-D-*glucopyranoside* (**21**).—To a solution of 1-thio-β-D-glucose tetra-acetate (**7**) (364 mg, 1 mmol) and tributyl(hexadecyl)phosphonium bromide (507 mg, 1 mmol) in benzene (4 ml) was added 1M-NaOH (1 ml). After the mixture had been stirred for 5 min, the crude fructosyl bromide (**17**) (1 mmol), prepared from 1,3,4,6-tetra-*O*-benzoyl-D-fructofuranose and hydrogen bromide according to the method of Helferich,[10] was added. The reaction was monitored by t.l.c. with hexane–ethyl acetate (3:2) as developer. The reaction mixture was diluted with methylene dichloride, and the organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated. Protected glycosides (**18**) and (**19**) were obtained in 30% yield as a mixture after column chromatography. The deprotection of the hydroxy groups with sodium methoxide in methanol afforded glycosides (**20**) and (**21**). Analytical data were in good agreement with literature values.[1]

* The galacto residue is primed.
† The manno residue is primed.

References

1 J. Defaye, H. Driguez, S. Poncet, R. Chambert, and M. F. Petit-Glatron, *Carbohydr. Res.*, 1984, **130**, 299.
2 D. Horton and D. H. Hutson, *Adv. Carbohydr. Chem. Biochem.*, 1963, **18**, 123.
3 M. Blanc-Muesser, J. Defaye, and H. Driguez, *Carbohydr. Res.*, 1978, **67**, 305.
4 P. Di Cesare and B. Gross, *Carbohydr. Res.*, 1976, **48**, 271; 1977, **58**, C-1; P. Duchaussoy, P. Di Cesare, and B. Gross, *Synthesis*, 1979, 198.
5 K. Hamacher, *Carbohydr. Res.*, 1984, **128**, 291.
6 J. Bogusiak and W. Szeja, *Carbohydr. Res.*, 1985, **141**, 165.
7 R. U. Lemieux, K. B. Hendriks, R. V. Stick, and K. James, *J. Am. Chem. Soc.*, 1975, **97**, 4056.
8 W. Korytnyk and J. A. Mills, *J. Chem. Soc.*, 1959, 636.
9 I. Degani, R. Fochi, and V. Regondi, *Synthesis*, 1979, 178.
10 B. Helferich and L. Bottenbruch, *Chem. Ber.*, 1953, **86**, 651.
11 M. Cerny and J. Pacak, *Collect. Czech. Chem. Commun.*, 1959, **24**, 2566.
12 J. Stanek, M. Sindlerova, O. Hanova, M. Cerny, and J. Pacak, *Collect. Czech. Chem. Commun.*, 1965, **30**, 2494.

Received 11*th January* 1988; *Paper* 8/00088C