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BIS-DEOXYGENATION OF METHYL 3,6-ANHYDRO-D-PYRANOSIDES

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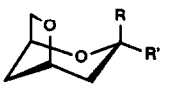
Abstract: *The synthesis and radical reduction of thiocarbonyl derivatives of methyl 3,6-anhydro pyranosides has been studied in the α-D-gluco, α-D-manno and β-D-galacto series. A cyclic intermediate is proposed to explain the fact that bis-deoxygenation only occurred in the galactose series, providing a 3 step synthesis of the desired product* **1b**.

An important goal in carbohydrate chemistry is the synthesis of biologically active deoxy sugars.[1] Amongst the known methods of synthesis, the deoxygenation of appropriately functionalised secondary alcohols has received increasing interest due to the recent development of radical deoxygenation of thiocarbonyl derivatives[2] and the direct displacement of sulphonates by highly nucleophilic hydrides.[3] Needing to prepare the new bicyclic compound **1** as either its α (**1a**) or β (**1b**) anomeric form, we decided to investigate its synthesis by reduction of the two hydroxy groups of one of the readily accessible methyl 3,6-anhydro-pyranosides.

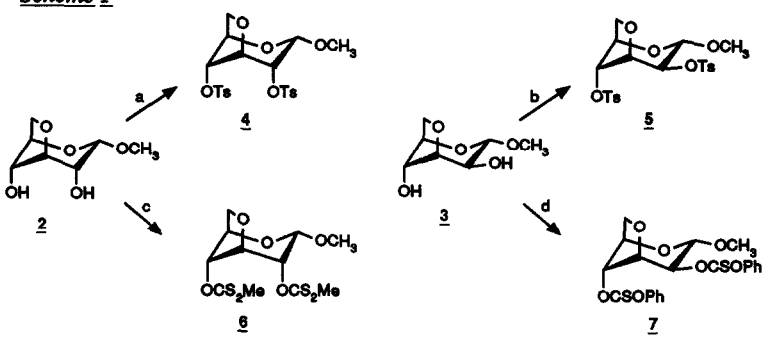


1a R = H R' = OMe
1b R = OMe R' = H

Diols **2** and **3** were prepared from methyl α-D-glucopyranoside and methyl α-D-mannopyranoside respectively using known methodologies[4,5] and subsequently tosylated to **4**[6] and **5**, or thioacylated[7,8] to **6** and **7** (scheme 1). We also developed a short and convenient method for preparing substituted 3,6-anhydro pyranosides as illustrated with the synthesis of compounds **11** and **12** from methyl α-D-glucopyranoside **8** (scheme 2). It is based on the regioselective formation of phosphonium chloride **9** described by Y. Chapleur *et al.*[9]

9 can be transformed in two more steps to the peracetylated hexafluorophosphate 10 which can be subsequently reacted with sodium methoxide to perform simultaneous deacetylation and ether formation to diol 2.[10]

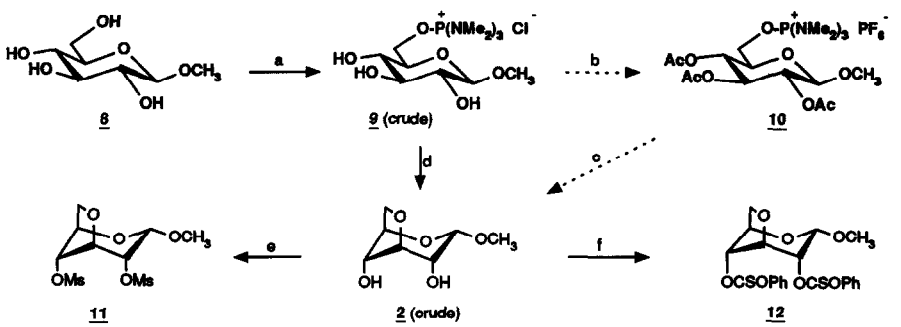
Scheme 1



a) Ref 6; b) TsCl pyridine RT, 85%; c) NaH imidazole CS_2 then MeI THF rfx., 68%; ; d) PhOCSCl pyridine CH_2Cl_2 RT, 68%.

We found that 9 itself can undergo the same intramolecular substitution: after having prepared it as described in reference 9, the crude reaction product was reacted with sodium methoxide providing crude 2. Mesylation and thioacylation with phenyl chlorothionoformate in pyridine gave respectively 11 and 12 in 58% and 43% overall yield from 8, after recrystallisation and without any isolation of the intermediates.

Scheme 2

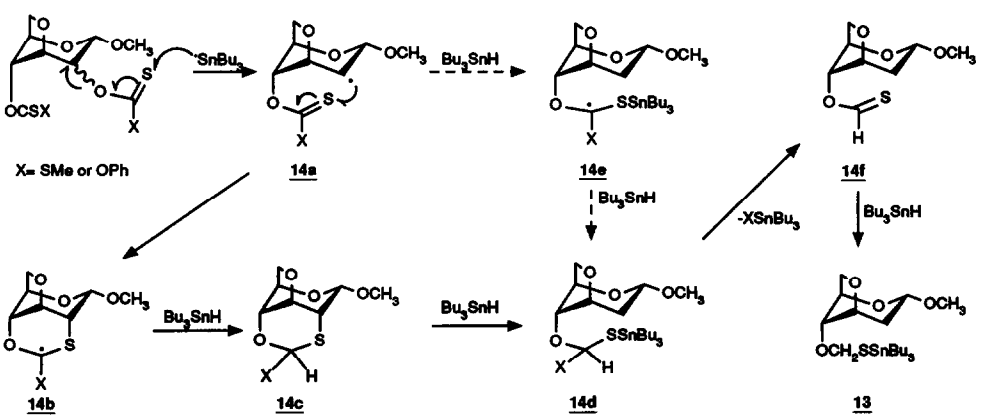


a) HMPT CCl_4 pyridine -35°C to RT; b) ref. 9; c) ref. 10, d) MeONa MeOH rfx;
e) MsCl pyridine RT, 58% from 8; f) PhOCSCl pyridine RT, 43% from 8.

We first tried the reduction of sulphonates 4, 5 and 11 by hydride substitution. However, all our attempts to reduce these products gave either the recovered starting material (sodium borohydride, DMSO 140°C[3c,d]) or the diols 2 and 3 ($LiEt_3BH$, THF reflux[3a,b]). We then tried the radical deoxygenation of the methyl xanthate 6 and the phenoxythiocarbonyl derivatives 7 and 12. In a first experiment, 12 was reacted with 3.5 equivalents of tri-n-butylstannane in refluxing toluene with a catalytic amount of AIBN (azo-bis-isobutyronitrile).[8] A rapid reaction took place giving a complex reaction mixture from which only the tin derivative 13 could be isolated (scheme 3). No trace of the expected reduced product 1a was detected. Reductions of 6 or 7 using the same conditions gave similar results. Radical reaction induced by triethylborane at ambient temperature[11] showed no advantage.

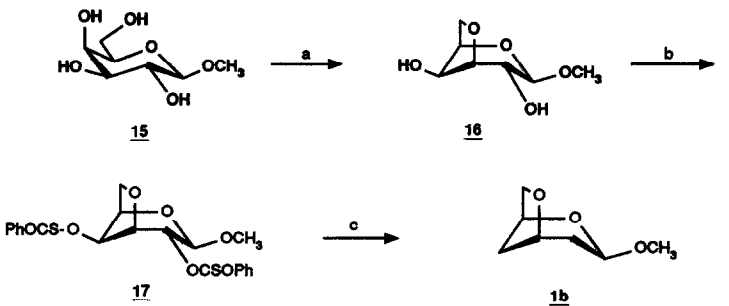
The formation of the part-reduced product 13 can be interpreted on the basis of the mechanism proposed by Barton *et al.* for this type of reaction.[12] 13 is a 2-deoxy sugar indicating that the tri-butylstannyl radical adds first to the sulphur atom of the C=S group in position 2, leading to the radical 14a. If the reactions occurring at positions 2 and 4 are considered as independent, one could imagine that after the reduction at position 2, a second mole of tri-n-butylstannyl radical adds to the C=S bond at position 4, generating 14e. Depending on the reaction conditions and substituents X, this type of intermediate is known to evolve in various ways, including the desired homolytic C-O cleavage or the reduction to 14d.[12] In the case of the reduction of a diol derivative bearing the same substituent X at both positions, the observed difference of reactivity between the two thiocarbonyl functional groups remains unexplained if we consider them as completely independent. Therefore, we believe that in an assisted mechanism, the radical in 14a is trapped by the radicophilic remaining C=S group, leading to the cyclic intermediate 14b which can then be reduced to 14d *via* 14c. The transformation of 14d into 14f and eventually to 13 is done by the accepted mechanism[12].

Scheme 3



Having proposed **14b** as a possible intermediate, it was postulated that its formation would be unlikely from the corresponding galactose derivative **17** (scheme 4), where the substituent in position 4 is equatorial and hence not in a position to intercept the incipient radical at the 2-position. We first prepared diol **16** from commercially available methyl-β-D-galactopyranoside **15** using the conditions described by G. O. Aspinall *et al.* in the α series.[13] Subsequent thioacylation afforded **17**. As expected, these methyl 3,6-anhydro-β-D-galactopyranoside derivatives were shown by ^{1}H NMR to adopt the boat conformation (for instance, the fact that H-3 appears as a singlet is consistent with the dihedral angles in this conformation), due to the strong 1,3 and 1,5 diaxial interactions which would exist in the chair conformation. Reduction with tri-n-butylstannane gave the desired reduced compound **1b**, thus satisfying our required synthetic objective and our mechanistic conclusions.

Scheme 4



a) CBr_4 PPh_3 pyridine RT, 60%, b) PhOCSCl pyridine CH_2Cl_2 RT, 70%; c) Bu_3SnH AIBN Toluene rfx , 46%

Acknowledgments:

The authors thank Dr. D. Daley and Mr. M. Vine for recording and discussing the mass and NMR spectra.

Experimental Part:

General Procedure.

Evaporations were conducted under diminished pressure at 40-50^{0}C. Flash chromatography was performed on Merk silica gel 60 (0.042-0.060 mm) eluting with the indicated solvent system. Optical rotations were measured with an Optical Activity AA-10 automatic polarimeter. NMR spectra were recorded with a Varian VXR-400s, in $CDCl_3$ with Me_4Si as internal standard. FTIR spectra were recorded on a Nicolet 205XB spectrometer. GC/MS were determined on a VG 7070E spectrometer using a OV1 column. T.l.c were performed on Polygram SIL G/UV254 fluorescent plates using the indicated eluent, and visualised by spraying with a mixture of H_2SO_4:α-naphthol:ethanol, 10:1:89 and heating with a hot air dryer. Compounds **2**, **3** and **4** were prepared as described in the references quoted in the text.

Methyl 3,6-anhydro-2,4-di-*O*-(p-tolylsulphonyl)-α-D-mannopyranoside (5).

To a cold (O^0C) stirred solution of 3[4] (1.76 g, 10 mmol) in pyridine (14 ml) was added p-toluenesulphonyl chloride (4.57 g, 24 mmol). The mixture was stirred overnight at room temperature under nitrogen and concentrated to dryness. The residue was partitioned between chloroform (50 ml) and water (50 ml) and the aqueous layer reextracted with chloroform (25 ml). The combined organic layers were washed with water (20 ml) dried over $MgSO_4$ and concentrated to dryness. Trituration with cyclohexane afforded a white solid which after recrystallisation from ethanol provided 5 (4.1 g, 85%); m.p. 154-156°C. $[\alpha]_D^{26}$ +82° (c 1, CH_2Cl_2); IR ν_{max} (KBr): 3439, 1365, 1344, 1192, 1179, 1119, 1011, 1000, 976, 953 846, 820 cmm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 and 2.48 (s each, 3H each, $ArCH_3$), 3.31 (s, 3H, OMe), 3.93 (dd, 1H, J=10.9, 2.8 Hz, H-6_{exo}), 4.04 (d, 1H, J=10.9 Hz, H-6_{endo}), 4.30 (dd, 1H, J=6.0, 1.4 Hz, 1H, H-3), 4.37 (dd, 1H, J=2.8 each, H-5), 4.50 (dd, 1H, J=6.7, 1.4 Hz, H-2), 4.69 (d, 1H, J=6.7 Hz, H-1), 4.72 (dd, 1H, J=2.8, 6.0 Hz, H-4), 7.38 7.80 (m, 4H each, Ar-H); CIMS m/z: 127, 144, 159, 176, 194, 316, 348, 502 ($M + NH_4^+$); Anal. calcd. for $C_{21}H_{24}O_9S_2$: C, 52.06; H, 4.99; S, 13.23; Found: C, 51.9; H, 4.95; S, 13.3.

Methyl 3,6-anhydro-2,4-di-*O*-methyldithiocarbonate-α-D-glucopyranoside (6).

To a stirred solution of 2[5] (1 g, 5.68 mmol) in dry THF (14 ml) were successively added imidazole (20 mg) and sodium hydride (80% dispersion; 0.57 g, 19 mmol) and the mixture refluxed for 2 hours. Carbon disulphide (3.4 ml, 56.6 mmol) was added, and after refluxing for 1 hour, methyl iodide (3.4 ml, 56.8 mmol) was added, the reflux was continued for 1 hour. Acetic acid (3 ml) was added to the cooled reaction mixture and the clear solution evaporated to dryness. Chromatography (ethyl acetate: cyclohexane, 1:3) gave a solid which after recrystallisation from methanol: water (1:1) provided 6 (1.37 g, 68%); m.p. 93-94°C. $[\alpha]_D^{28}$ +20° (c 0.5, CH_2Cl_2); IR ν_{max} (KBr): 1219, 1198, 1097, 1060, 1020, 992, 913, 896 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.59, 2.63 (s each, 3H each, SMe), 3.57 (s, 3H, OMe), 4.08 (dd, 1H, J=3.0, 10.7 Hz, H-6_{exo}), 4.27 (d, 1H, J=10.7 Hz, H-6_{endo}), 4.75 (dd, 1H, J=3, 2.7 Hz each, H-5), 4.98 (dd, 1H, J=5 Hz each, H-3), 5.15 (d, 1H, J=3.4 Hz, H-1), 5.49 (ddd, 1H, J=5.0, 2.7. 1.0 Hz, H-4), 5.94 (dddd, 1H, J=4.5, 3.5, 0.8, 0.8 Hz, H-2); CIMS m/z: 203, 219, 236, 249, 325, 357, 374 ($M + NH_4^+$); Anal. calcd. for $C_{11}H_{16}O_5S_4$: C, 37.06; H, 4.52; S, 35.97; Found: C, 36.9; H, 4.52; S, 35.9.

Methyl 3,6-anhydro-2,4-di-*O*-phenoxythiocarbonyl-α-D-mannopyranoside (7).

To a stirred suspension of 3[4] (666mg, 4.12 mmol) in dichloromethane (10ml) and pyridine (0.82ml) was added dropwise a solution of phenyl chlorothionoformate (1.53g, 8.9mmol) in 5ml of dichloromethane at 20-25°C. Stirring was continued for 18 hours then the reaction mixture was diluted with a further 10ml dichloromethane, washed with 1N HCl (20ml), water (20ml), dried over $MgSO_4$ and evaporated to dryness. Recrystallisation of the crude oil from methanol (40ml) gave 7 (1.41g, 76%) as a white solid; m.p. 107-8°C. $[\alpha]_D^{28}$ +71° (c 1, CH_2Cl_2); IR ν_{max} (KBr): 3430, 1490, 1291, 1276, 1232, 1219, 1207, 1191, 1113 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.61 (s, 3H, OMe), 4.16 (dd, 1H, J=10.8, 2.8 Hz, H-6_{exo}), 4.29 (d, 1H, J=10.8 Hz, H-6_{endo}), 4.88 (dd, 1H, J=2.8 Hz each, H-5), 5.00 (dd, 1H, J=6.1, 1.3 Hz each, H-3), 5.14 (d, 1H, J=7.0 Hz, H-1), 5.46 (dd, 1H, J=7.0, 1.3 Hz, H-2), 5.54 (dd, 1H, J=6.2, 2.7, H-4). CIMS m/z: 113, 127, 159, 176, 203, 220, 236, 265, 281, 295, 313, 330, 401, 417, 449, 466 ($M + NH_4^+$); Anal. calcd. for $C_{21}H_{20}O_7S_2$: C, 56.24; H, 4.49; S, 14.30; Found: C, 56.0; H, 4.4, S, 14.1.

Methyl 3,6-anhydro-2,4-di-*O*-mesyl-α-D-glucopyranoside (11).

Crude phosphonium chloride 9.

A solution of carbon tetrachloride (15.4g, 0.1mol) in pyridine (50ml) was added to a solution of methyl-α-D-glucopyranoside 8 (9,7g, 50mmol) in pyridine (400ml) and the mixture cooled to -35°C. A solution of hexamethylphosphorous triamide (13.25g, 81mmol) in pyridine (50ml) was added dropwise over a period of 15 minutes and the mixture stirred for a further 15 minutes. Tlc (ethyl acetate: methanol, 70:30) showed no starting material. The mixture was warmed to room temperature and evaporated to dryness, providing crude phosphonium chloride 9.

Crude methyl 3,6-anhydro-α-D-glucopyranoside 2.

The previous crude material 9 was taken up in dry methanol (250ml) and 27.5% w/w sodium methoxide solution in methanol (23g, 117mmol) added. The mixture was refluxed for 2 hours then cooled to room temperature. Triethylamine hydrochloride (15g) was added to neutralise excess sodium methoxide and the mixture evaporated to dryness giving 26g of a brown syrup whose tlc (chloroform: methanol, 10:1) showed diol 2 as being the main product.

Dimesylate 11.

Methane sulphonyl chloride (45.8g, 0.4mol) was added dropwise over 30 minutes to a solution of the previously prepared crude 2 in pyridine (400ml) and the mixture stirred at room temperature for one hour. The mixture was evaporated to dryness and the residue chased out with toluene (2 X 200ml). Distilled water (300ml) was added to the thick brown residue and the mixture stirred at room temperature. A solid came out which was filtered, washed with water and dried giving 9.17g of a light brown solid; m.p.: 157-158.5°C. The filtrates were extracted with dichloromethane (2 X 100ml) and the combined organic layers washed with water (100ml), dried over $MgSO_4$ and evaporated to dryness giving an oil which after trituration with methanol provided a further 1.6g of solid. Recrystallisation of the combined two batches in refluxing ethanol:methanol (95:5, v:v, 900ml) gave 9.55g (57.5%) of 11; m.p.: 158-9°C. $[\alpha]_D^{28}$ +70° (c 0.8, chloroform); (Litt.[6] m.p.:160-1°C; $[\alpha]_D^{22}$ + 66° (c 1, chloroform)); IR ν_{max} (KBr): 3435, 1359, 1173, 1049, 972, 895, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.63 (s, 3H, OMe), 4.04 (dd, 1H, J=11.0, 2.9 Hz, H-6_{exo}), 4.23 (d, 1H, J=11.0 Hz, H-6_{endo}), 4.62 (dd, 1H, J=2.9 Hz each, H-5), 4.65 (dd, 1H, J=5.1 Hz each, H-3), 4.73 (m, 1H, H-2), 4.89 (ddd, 1H, J=5.2, 2.9, 0.8, H-4), 5.06 (d, 1H, J=3.0 Hz, H-1). CIMS m/z: 113, 127, 175, 240, 253, 272, 318, 350 (M + NH_4^+); Anal. calcd. for $C_9H_{16}O_9S_2$: C, 32.53; H, 4.85; Found: C, 32.3; H, 4.97.

Methyl 3,6-anhydro-2,4-di-*O*-phenoxythiocarbonyl-α-D-glucopyranoside (12).

Phenyl chlorothionoformate (12g, 69mmol) was added dropwise over 15 minutes to a solution of crude diol 2 (prepared as above on half the scale from 4.85g of methyl-α-D-glucopyranoside 8) in 100ml pyridine and the solution stirred at room temperature for 2 hours. The mixture was evaporated to dryness and the residue chased out with toluene (2 X 100ml). The residue was partitioned between water (100ml) and dichloromethane (100ml). The aqueous layer was reextracted with dichloromethane (100ml) and the combined organic layers were washed with 0.5N HCl (100ml), water (100ml), dried over $MgSO_4$ and evaporated to dryness. Trituration of the residue with 100ml of diethyl ether gave 5.5g of a brownish solid; m.p.: 150-65°C. Recrystallisation from ethylacetate (40ml) in the presence of charcoal gave 4.85g of 12 (43%) as a white crystalline solid; m.p.: 168-70°C; $[\alpha]_D^{20}$ +88° (c 1, CH_2Cl_2); IR ν_{max} (KBr): 3437, 1311, 1281, 1268, 1232, 1193 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.66 (s, 3H, OMe), 4.12 (dd, 1H, J=3.0, 10.7 Hz, H-6_{exo}), 4.27 (dd, 1H, J=4.9 Hz each, H-3), 4.31 (d, 1H, J=10.7 Hz, H-6_{endo}), 4.79 (dd, 1H, J=2.7 Hz each, H-5), 5.20 (ddd, 1H, J=5.2, 2.7, 1.0 Hz, H-4), 5.23 (d, 1H, J=3.3 Hz, H-1), 5.68 (dddd, 1H, J=4.6, 3.3, 0.8, 0.8 Hz, H-2), 7.05 to 7.5 (m, 10H, Ar-H). CIMS m/z: 113, 160, 176, 203, 219, 236, 265, 295, 417, 449, 466 (M + NH_4^+); Anal. calcd. for $C_{21}H_{20}O_7S_2$: C, 56.24; H, 4.49; S, 14.30; Found: C, 56.4; H, 4.49; S,14.3.

Methyl 3,6-anhydro-2-deoxy-4-*O*-(tri-n-butylstannylthiomethyl)-α-D-*arabino*-hexopy ranoside (13).

To a degassed (argon bubbling) solution of 12 (0.7 g, 1.56 mmol) and AIBN (60 mg, 0.36 mmol) in toluene was added tri-n-butylstannane (1.5 ml, 5.4 mmol) and the mixtured stirred at reflux for 30 minutes. The solution was then concentrated to dryness and the residue purified by chromatography (ethyl acetate: cyclohexane, 1:3) to give 13 as a clear oil (370 mg, 48%), $[\alpha]_D^{23}$ -39° (c 0.36, CH_2Cl_2); IR ν_{max} (KBr): 2957, 2929, 2871, 2832, 1147, 1114, 1075, 1027, 910, cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 to 1.65 (m, 27H, n-Bu), 1.93 (m, 2H, H-2), 3.50 (s, 3H, OMe), 3.97 (dd, 1H, J=10.4, 3.1 Hz, H-6_{exo}), 4.17 (d, 1H, J=10.4 Hz, H-6_{endo}), 4.26 (dd, 1H, J=5.6, 2.7 Hz, H-4), 4.30 (ddd, 1H, J=5.6, 3.6, 2.0 Hz, H-3), 4.40 (dd, 1H, J=3.0 Hz each, H-5), 4.96 (dd, 1H, J=7.6, 5.5 Hz, H-1), 4.99 (dd, 2H, J=42.0, 10.5 Hz, OCH_2S), assignment confirmed by 2D NMR (COSY). EIMS m/z: 121, 151, 177, 219, 235, 265, 291, 333, 361, 393, 439 (M - ($C_4H_9^+$)); Anal. calcd. for $C_{20}H_{40}O_4SSn$: C, 48.50; H, 8.14; Found: C, 49.0; H, 8.0.

Note: the same reaction from 6 and 7 gave mixtures from which only 13 could be isolated.

Methyl 3,6-anhydro-β-D-galactopyranoside (16).

To a cold (O°C) solution of 15 (3.88 g, 20 mmol) in pyridine (160 ml) were successively added carbon tetrabromide (6.66 g, 20 mmol) and triphenylphosphine (10.54 g, 40 mmol). The reaction mixture was stirred 4 hours at room temperature and 1 hour at 60°C. After addition of methanol (100 ml), the solution was evaporated to dryness and the residue purified by chromatography (chloroform: methanol, 10:1) to give a solid which, after recrystallisation from dichloromethane gave 16 (2.11 g, 60%); m.p. 114-17°C. $[\alpha]_D^{19}$ -108° (c 1, water), $[\alpha]_D^{29}$ -48° (c 1, MeOH), (Lit.[14] $[\alpha]_D^{18}$ -115 (c 1, water)); IR ν_{max} (KBr): 3403, 1124, 1082, 1065, 1049, 976, 938 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.49 (s, 3H, OMe), 3.66 (dd, 1 H, J=4.8, 0.8 Hz, OH), 4.25 (d, 1H, J=4.6 Hz, OH), 3.97 (dd, 1H, J=9.5, 3.2 Hz, H-6_{exo}), 4.01 (dd, 1H, J=4.6 Hz each, H-2), 4.15 (d, 1H, J=9.4 Hz, H-6_{endo}), 4.22 (d, 1H, J=4.8 Hz, H-1), 4.26 (m, 1H, H-5), 4.44 (dd, 1H, J=4.8, 2.0 Hz, H-4), 5.49 (s, 1H, H-3). CIMS m/z: 162, 1076, 180, 194 ($M + NH_4^+$); Anal. calcd. for $C_7H_{12}O_5$: C, 47.73; H, 6.87; Found: C, 47.4; H, 6.90.

Methyl 3,6-anhydro-2,4-di-*O*-phenoxythiocarbonyl-β-D-galactopyranoside (17).

Following the same procedure as for 7, starting from 12.48 g (71 mmol) of 16, gave 17 (22.23 g, 70%); m.p. 142-4°C. $[\alpha]_D^{27}$ -112° (c 1, CH_2Cl_2); IR ν_{max} (KBr): 1311, 1271, 1202, 1188, 1071 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.50 (s, 3H, OMe), 4.10 (dd, 1H, J=10.0, 3.3 Hz, H-6_{exo}), 4.44 (d, 1H, J=10.0 Hz, H-6_{endo}), 4.71 (m, 1H, H-5), 4.83 (s, 1H, H-3), 5.05 (d, 1H, J=5.0 Hz, H-1), 5.54 (d, 1H, J=5.0 Hz, H-2), 5.76 (d, 1H, J=1.7 Hz, H-4). CIMS m/z: 113, 128, 146, 160, 176, 220, 233, 263, 280, 295, 312, 330, 417, 449, 466 ($M + NH_4^+$); Anal. calcd. for $C_{21}H_{20}O_7S_2$: C, 56.24; H, 4.49; S, 14.30: Found: C, 56.2; H, 4.47; S, 14.2.

Methyl 3,6-anhydro-2,4-dideoxy-β-D-*threo*-hexopyranoside (1b).

To a degassed (argon bubbling) refluxing solution of 17 (2.24 g, 5 mmol) and AIBN (200 mg, 1.2 mmol) in 40 ml of toluene was added dropwise tri-n-butylstannane (3.3 ml, 12 mmol) over a period of 30 minutes. The mixture was stirred at reflux for a further 30 minutes and the solution was concentrated under atmospheric pressure to a residual volume of 6 ml. The residue was purified by chromatography (ethyl acetate: cyclohexane, 1:2) to give 1b (330 mg, 46%) as an oil; $[\alpha]_D^{20}$ -151° (c 1.18, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.78 to 2.06 (m, 4H, H-2 and H-4), 3.40 (s, 3H, OMe), 3.75 (dd, 1H, J=9.4, 3.2 Hz, H-6_{exo}), 4.29 (dd, 1H, J=9.4, 1.1 Hz, H-6_{endo}), 4.47 (m, 1H, H-5), 4.56 (ddd, 1H, J=6.0, 4.0, 1.7 Hz, H-3), 4.74 (d, 1H, J=6.0 Hz, H-1), assignment confirmed by 2D NMR (COSY). ^{13}C NMR δ 36.4, 37.9, 55.7, 72.8, 73.05, 74.1, 98.5. EIMS m/z: 58, 69, 75, 84, 101, 113, 127, 144 (M^+).Anal. calcd. for $C_7H_{12}O_3$: C, 58.32; H, 8.39; Found: C, 57.9; H, 8.5.

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