Synthesis of Ethyl and Phenyl 1-Thio-1,2-*trans*-D-Glycopyranosides from the Corresponding Per-*O*-acetylated Glycopyranoses having a 1,2-*trans*-Configuration using Anhydrous Ferric Chloride as a Promoter

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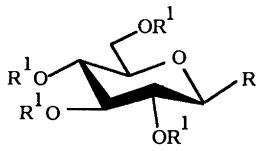
The reaction between per-*O*-acetylated hexopyranoses and suitable thiols in the presence of anhydrous ferric chloride affords the corresponding thioglycosides. Thus, ethyl 1-thio-β-D-glycopyranosides were prepared as per-*O*-acetates in gluco-, 2-acetamido-2-deoxy-gluco-, 2-deoxy-phthalimido-gluco-, and 2-chloroacetamido-2-deoxy-gluco-configurations. Ethyl 1-thio-α-D-mannopyranoside was prepared from a suitable per-*O*-acetate, as was phenyl tetra-*O*-acetyl-1-thio-β-D-glucopyranoside, using thiophenol as the glycosylating agent. Prolonged reaction time adversely affects the yield. A reaction scheme is proposed that explains this observation.

Alkyl 1-thioglycosides (alkyl = methyl, ethyl or phenyl) have been found to be useful intermediates in oligosaccharide synthesis.[1] Several methods are known for their preparation from the corresponding per-*O*-acylated 1-halo-[2] or 1-thio-[3] hexopyranoses. *trans*-Alkyl- and aryl-1-thioglycosides have been prepared by the reaction of acetylated glycosyl halides with thiols or thiophenols[4,5] or alternatively by *S*-alkylation of tetra-*O*-acetyl-1-thiosugars.[6] Conversion of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-hexopyranoses into their pseudothiourea[3] derivatives, followed by treatment with alkyl iodide (methyl or ethyl) afforded an efficient synthesis of alkyl 1-thio-β-D-glycosides.[6,7] Hanessian converted α-D-glucopyranosides into the corresponding methyl or phenyl 1-thioglucopyranoside using ZnI_2 and $RSSiMe_3$.[8] Various alkyl and aryl 1-thio-D-gluco- and D-galacto-pyranosides were synthesized from the corresponding acetobromohexopyranoses using a quaternary ammonium bromide in the so-called 'catalytic two-phase system' (CTP system).[9] Thus, whereas a large number of methods are available for the synthesis of this class of compounds, most of them are not suitable for the preparation of both alkyl as well as aryl 1-thio derivatives or they make use of toxic chemicals such as thiourea and alkyl iodides. Therefore, these are not suitable for large-scale preparations. Although the CTP method offers a practical approach, the use of non-storable 1-halo sugars makes it less attractive. Also the method was found to be unsuitable for the preparation of ethyl 1-thioglycosides owing to partial deacetylation. Thioglycosidation of the β-per-*O*-acetates of the hexopyranoses is known to take place in the presence of various Lewis acids ($ZnCl_2$, $SnCl_4$ or BF_3) or *p*-toluenesulfonic acid,[10] to afford alkyl 1-thio-β-D-glycosides. Also, $POCl_3$ has been used for the thioglycosidation of the β-per-*O*-acetates with poor selectivity and yield.[11] BF_3–diethyl ether seemed to be the best reagent, although the reaction was accompanied by a number of side products. Recently, Pozsgay and Jennings suggested[12] an alternative method in which methylthiotrimethylsilane was used in the presence of trimethylsilyl trifluoromethanesulfonate or BF_3–diethyl ether for the preparation of methyl 1-thio-D-glycopyranosides from the corresponding per-*O*-acetylated β-D-hexopyranoses. During the development of a new glycosidation technique using ethyl- or phenyl-1-thio-D-glycopyranosides[1,13] we needed the thioglycosides of D-glucose, D-mannose and D-glucosamine (**1**,**2** and **5**–**9**). It was necessary to choose one of the known methods or to develop one for large-scale preparation of these compounds. Anhydrous ferric chloride has been found to be useful for acetylation,[14] acetonation[15] and acetolysis[16,17] of carbohydrates and their derivatives. It has also been used in transesterification reactions involving lipids.[18] Its use as promoter in the *O*-glycosidation of β-per-*O*-acetates,[19–22] in the preparation of oxazolines[23] and for the direct conversion of various 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-acylamido-β-D-glucopyranoses into their *O*-glycosides[24] have been recognized. Anhydrous ferric chloride in combination with a suitable thiol seemed to be an attractive alternative method for the preparation of 1-thioalkyl(aryl) β-D-hexopyranosides from the corresponding peracetylated hexopyranoses having a 1,2-*trans*-configuration.

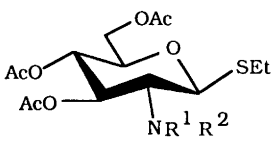


1 R = SEt, R^1 = Ac

2 R = SPh, R^1 = Ac

7 R = SEt, R^1 = Bz

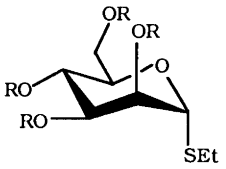
8 R = SEt, R^1 = Bn



4 R^1R^2 = H, Ac

5 R^1R^2 = Phthalimido

6 R^1R^2 = H, $COCH_2Cl$



3 R = Ac

9 R = Bn

10 = α - isomer of **2**

11 = α - isomer of **6**

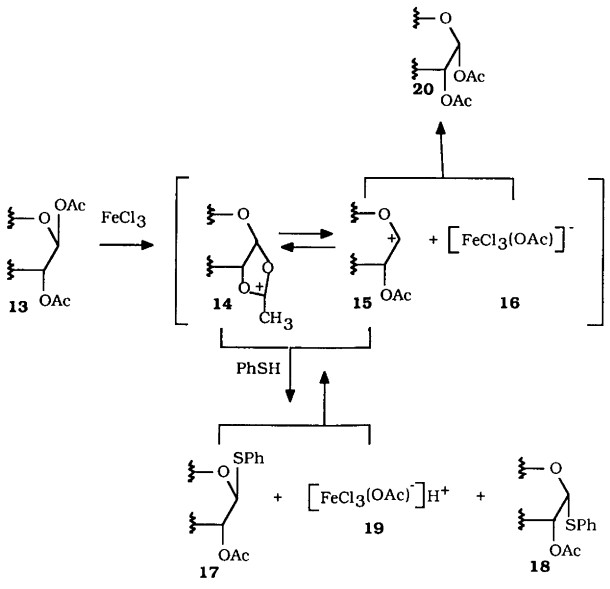
12 = β - isomer of **9**

Fig. 1.

Results and discussion

Treatment of β-D-glucopyranose pentaacetate, α-D-mannopyranose pentaacetate, 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose and 1,3,4,6-tetra-*O*-acetyl-2-chloroacetamido-2-deoxy-β-D-glucopyranose with anhydrous ferric chloride (1.0–1.1 mol equiv.) and an appropriate thiol (1.1–1.2 mol equiv.) in dichloromethane indeed afforded the β-thioglycosides as the major products within a short reaction time. In almost all reactions, minor quantities of the α-isomer were formed. The β-compound could be isolated by fractional crystallization or by carrying out chromatographic separation on a silica-gel column. The mixture of ethyl 1-thio-α- and β-D-mannopyranose tetraacetates was isolated as a syrup (α:β = >4:1, by NMR spectroscopy), which upon crystallization from ethanol afforded a solid (m.p. 104–106 °C). NMR spectroscopic investigation of this solid indicated it to be a mixture of the α- and β-isomers. Since the per-*O*-benzylated compound (**9**) was of specific interest, this mixture was deacetylated and benzylated. The α-isomer (**9**) was isolated by chromatography as a clear syrup. Among the various *N*-acylated per-*O*-acetates of β-D-glucosamines (**23**–**25**, see the Experimental), the *N*-chloroacetyl compound (**24**) reacted most efficiently to afford the corresponding β-thioglycoside (**6**). TLC examination (solvent VII) of the solutions of **23** (R_f = 0.26) and **24** (R_f = 0.49), after the addition of $FeCl_3$, indicated the formation of intermediates, possibly the corresponding oxazolines (R_f = 0.32, and R_f = 0.36, respectively), which disappeared on addition of ethanethiol to give the products **4** and **6**, respectively. Similar treatment of **25** resulted in degradation and poor yield on subsequent addition of the thiol. In this instance, ferric chloride was added to the mixture of **25** and ethanethiol in order to effect efficient thioglycosidation. Neither **23** nor **25** gave α-anomeric side products. Generally, it was observed, that the amount of β-isomer and the total yield were reduced considerably on prolonged reaction beyond the prescribed time. This phenomenon was found to be especially significant in the preparation of compound **2**, and this particular example was therefore investigated in more detail.

The best yield was obtained when anhydrous ferric chloride (1.0 mol equiv.) was first added to the solution of the pentaacetate (**21**) in dichloromethane followed by the addition of thiophenol (1.1 mol equiv.). The reaction was terminated within 5–7 min in order to afford the β-glycoside (**2**, R_f = 0.52, solvent VIII) as the major product along with some phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-glucopyranoside (R_f = 0.56). Prolonging the reaction resulted in the slow disappearance of the β-product and the simultaneous formation of α-D-glucopyranose pentaacetate (R_f = 0.38) and some unidentified degradation products. Eventually, the only glycosidation product that remained was the minor quantity of the α-thioglycoside. Possible routes to these transformations are shown in the generalized diagram (Scheme 1). Isomerization of acetylated alkyl 1-thio-β-D-glucopyranosides (alkyl = ethyl, isopropyl and heptyl) into the corresponding α-anomer is known to take place in the presence of inorganic as well as Lewis acids.[7] The mechanism of this transformation should be through an ionic intermediate of the type **14/15** (Scheme 1), assumed to have been formed by the initial attack of the acid on the nucleophilic sulfur, followed by the breakdown of the C–S bond which is facilitated by the anchimeric assistance offered by the *trans*-acyl group on C-2. However, in



Scheme 1.

the present reaction, there are some intriguing facts that must be noted: (a) once the thioglycosides (α- and β-) had formed, there should be no uncomplexed $FeCl_3$ left that could anomerize the β-glycoside (**17**), (b) the major side product was the α-D-glucopyranose pentaacetate (**20**), and (c) the proportion of the α-anomer (**18**) and the α-pentaacetate (**20**) remained unaffected even after a prolonged reaction period (12–18 h). On the basis of these observations, it would seem logical to suppose that the ferric chloride complex (**19**), formed as a result of glycosidation must have the ability to attack the nucleophilic sulfur in **17**, and eliminate benzenethiolate with the assistance of the *trans*-*O*-acyl group on the neighbouring carbon. Possibly, the expelled thiol is oxidized to disulfide. This should set up an equilibrium between (**17**, **19**) and (**14–16**). However, the formation of **18** and **20** act as drains on this equilibrium, eventually exhausting all of **17**. It seems that the reacetylation to give **20** is a lower-energy pathway compared with the α-anomerization step to afford **18**, so that the α-D-acetate (**20**), ends up as a major product of the reaction. The reaction terminates when **18** and **20** are formed.

We conclude that anhydrous ferric chloride can be used as promoter for the preparation of 1,2-*trans*-1-thio-D-glycopyranosides from the corresponding 1,2-*trans*-D-hexopyranose per-*O*-acetates. The method would seem suitable for large-scale syntheses of these compounds.

Experimental

General methods. Solvents were evaporated under reduced pressure. Plates precoated with silica gel 60 F_{254} (Merck) and silica gel (230–400 mesh, Merck) were used for TLC and column chromatography, respectively. All solvents were distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX270 spectrometer and optical rotations were determined in chloroform with a Perkin-Elmer 141 polarimeter. Melting points are corrected. Solvents used for chromatography were toluene–acetone (I) 170:1; (II) 100:1; (III) 80:1; (IV) 10:1; (V) 8:1; (VI) 3:1; (VII) 2:1; and toluene–EtOAc (VIII) 3:1 and (IX) 7:1.

β-D-Glucopyranose pentaacetate (**21**),[25] α-D-mannopyranose pentaacetate (**22**),[14] 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (**23**),[24] 1,3,4,6-tetra-*O*-acetyl-2-chloroacetamido-2-deoxy-β-D-glucopyranose (**24**)[24] and 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose (**25**)[26] were prepared by known methods.

General method of preparation of Alkyl, aryl 1, 2-trans-1-*thio*-D-*hexopyranosides.* All thioglycosides, except **5**, were prepared as follows. A solution of the per-*O*-acetate in CH_2Cl_2 (1 g/5 ml) was stirred (1 h) with freshly dried molecular sieves 4 Å (0.5–1.0 g/g of per-*O*-acetate). The solution was cooled (5 °C), anhydrous $FeCl_3$ (1.0–1.1 mol equiv.) was added and the stirring was continued until all the crystals of $FeCl_3$ had disappeared to give a dark yellow solution. The appropriate thiol (1.1–1.2 mol equiv.) was quickly added to the flask, which was then transferred to a bath maintained at room temperature (20–23 °C) and the reaction was allowed to continue for the appropriate duration. The mixture was filtered through Celite into a stirred, cold (5 °C), aqueous solution of $NaHCO_3$ (saturated). The flask and the residue were further washed with CH_2Cl_2. Stirring was continued until the organic layer became almost colourless. The CH_2Cl_2 solution was separated, washed a second time with $NaHCO_3$ solution and then with water, dried ($MgSO_4$), filtered and evaporated to dryness. The crude products were purified in the manner noted below for each individual compound.

*Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-*D*-glucopyranoside* (**1**). Reaction was carried out (8–10 min) using **21** (1.25 g, 3.2 mmol), $FeCl_3$ (0.62 g, 3.8 mmol) and EtSH (0.26 ml, 3.5 mmol). Usual work-up afforded a syrup which contained a major proportion of **1** ($R_f = 0.36$, solvent IV). Crystallization (EtOH) gave pure **1** (0.85 g, 68 %), m.p. 84–85 °C, $[\alpha]_D^{22}$ −27.9° (*c* 1.9); lit.[27] m.p. 82–82 °C, $[\alpha]_D$ −24.4° (*c* 1.16).

*Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-*D*-glucopyranoside* (**2**). Compound **21** (10 g, 25.6 mmol) and thiophenol (2.8 ml, 27.2 mmol) were allowed to react (5–7 min) in the usual manner in the presence of $FeCl_3$ (4.5 g, 27.7 mmol). Crystallization of the crude solid (Et_2O–hexane) afforded **2** (8.4 g, 75 %), m.p. 121–122 °C, $[\alpha]_D^{22}$ −18.1° (*c* 2.3); lit.[28] m.p. 115–117 °C, $[\alpha]_D$ −17.5° (*c* 3.0).

Reaction of **21** (8.5 g) for a longer period (15 h) gave a mixture of products which was purified by silica-gel (350 g) column chromatography using, successively, solvent VIII (300 ml) and solvent IX. The first eluate was compound **10** (0.5 g) which was crystallized (Et_2O–hexane) to give the pure α-thioglycoside, m.p. 90–91 °C, $[\alpha]_D^{22}$ +153.8° (*c* 1.8). ^1H NMR ($CDCl_3$): δ 2.0–2.1 (12 H, Ac), 4.0–4.3 (2 dd, 2 H, H-6,6′), 4.65 (m, 1 H, H-5), 5.08–5.14 (m, 2 H, H-2,4), 5.4 (t, 1 H, *J* 9.3 Hz, H-3), 5.92 (d, 1 H, *J* 5.5 Hz, H-1), 7.3–7.5 (5 H, arom). Further elution afforded α-D-glucopyranose pentaacetate (>2.5 g), which was crystallized (ethanol), m.p. 111–112 °C, $[\alpha]_D^{22}$ +101° (*c* 2); lit.[2] m.p. 112–113 °C, $[\alpha]_D^{20}$ +102°.

*Ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-*D*-glucopyranoside* (**4**). Thioglycosidation of **23** (3 g, 7.7 mmol) was carried out using ethanethiol (0.69 ml, 9.2 mmol) and $FeCl_3$ (1.4 g, 8.6 mmol) in the usual manner (4 h). However, addition of a further two portions of $FeCl_3$ (0.6 g and 0.3 g) after 1 h and 2 h, respectively, was necessary (total $FeCl_3$ used, 2.4 g, 14.2 mmol) for satisfactory conversion into the product. Column chromatography (silica-gel, 200 g), using first solvent VII (230 ml) and then solvent VI, afforded the pure product. Crystallization from EtOH gave **4** (1.7–1.95 g, 54–62 %, $R_f = 0.36$, solvent VII), m.p. 196–197 °C, $[\alpha]_D^{22}$ −55.6° (*c* 1.5); lit.[29] m.p. 181 °C, $[\alpha]_D$ −38° (*c* 1, MeOH). Anal. $C_{16}H_{25}NO_9S$: C, H, N, S. ^1H NMR ($CDCl_3$): δ 1.2 (t, 3 H, SCH_2CH_3), 1.9–2.1 (m, 12 H, Ac), 2.7 (m, 2 H, SCH_2CH_3), 3.7 (m, 1 H, H-5), 4.0–4.3 (m,

3 H, H-2,6,6'), 4.6 (d, 1 H, *J* 10.3 Hz, H-1), 5.1–5.2 (2 t, 2 H, H-3,4), 5.9 (d, 1 H, NH).

*Ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-*D*-glucopyranoside* (**5**). Compound **25** (3.8 g, 7.9 mmol) was dissolved in CH_2Cl_2 (30 ml) containing molecular sieves 4 Å (2 g) and ethanethiol (0.9 ml, 11.5 mmol) was added. After the reaction mixture had been stirred for some time (20 min), $FeCl_3$ (1.3 g, 8.0 mmol) was transferred into the reaction flask. At the end of the reaction (75–90 min) TLC (solvent IV) of the supernatant showed only one product ($R_f = 0.35$). The reaction mixture was worked up as usual and the crude product was purified by chromatography from a silica-gel column (200 g) using solvent IV as the eluant to afford **5** (3.2 g, 85 %), m.p. 119–121 °C (EtOH), $[\alpha]_D^{22}$ +70.5° (*c* 1.3); lit.[30] m.p. 118–119 °C, $[\alpha]_{578}^{22}$ +44° (*c* 0.8, CH_2Cl_2).

*Ethyl 3,4,6-tri-*O*-acetyl-2-chloroacetamido-2-deoxy-1-thio-β-*D*-glucopyranoside* (**6**). Compound **24**[23] (3 g, 7.6 mmol), ethanethiol (0.6 ml, 7.9 mmol) and $FeCl_3$ (1.25 g, 7.7 mmol) were allowed to react in the usual manner. After work-up, the crude product was charged onto a dry silica-gel column (200 g) and eluted successively with solvent V (250 ml) and solvent IV. The α-product, **11** (0.2–0.3 g, $R_f = 0.27$, solvent V) eluted first, m.p. 112–113 °C (ethanol), $[\alpha]_D^{22}$ +127° (*c* 2). ^{1}H NMR ($CDCl_3$): δ 1.3 (t, 3 H, SCH_2CH_3), 2.0–2.1 (3 s, 9 H, Ac), 2.6 (m, 2 H, SCH_2CH_3), 4.0 (d, 2 H, *J* 3 Hz, $COCH_2Cl$), 4.1–4.3 (2 dd, 2 H, H-6,6'), 4.4 (m, 1 H, H-5), 4.5 (m, 1 H, H-2), 5.2 (m, 2 H, H-3,4), 5.45 (d, 1 H, *J* 5.5 Hz, H-1), 6.8 (d, 1 H, *J* 8.4 Hz, NH).

Further elution provided pure **6** (3.0 g, 92 %, $R_f = 0.2$, solvent V), m.p. 197–198 °C (EtOH), $[\alpha]_D^{22}$ −24.4° (*c* 1.7). Anal. $C_{16}H_{24}ClNO_8S$: C, H, N, S. ^{1}H NMR ($CDCl_3$): δ 1.27 (t, 3 H, SCH_2CH_3), 2.0–2.1 (9 H, Ac), 2.7 (m, 2 H, SCH_2CH_3), 3.7 (m, 1 H, H-5), 4.02 (d, 2 H, $COCH_2Cl$). 3.96–4.3 (m, 3 H, H-2,6,6'), 4.73 (d, 1 H, *J* 10 Hz, H-1), 5.1 (t, 1 H, H-4), 5.3 (t, 1 H, H-3), 6.7 (d, 1 H, *J* 8.8 Hz, NH). ^{13}C NMR ($CDCl_3$): δ 14.9 (SCH_2CH_3), 20.6, 20.7 ($COCH_3$), 24.3 (SCH_2CH_3), 42.5 ($COCH_2Cl$), 53.7, 62.4, 68.7, 73.3, 75.9 (C2–C6), 83.9 (C1), 166.5–170.8 (4 CO).

*Ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-*D*-glucopyranoside* (**7**). Compound **1** (2 g) was deacetylated with NaOMe (catalytic) in methanol (20 ml), the solution was neutralized (IR 120 H^+), filtered and evaporated. The crude product was dispersed in CH_2Cl_2 (20 ml) containing pyridine (8 ml) and allowed to react (6 h) with benzoyl chloride (6 ml). The organic layer was successively washed with cold water, cold aqueous H_2SO_4 (0.5 M), water, aqueous $NaHCO_3$ (satd.) and water, dried ($MgSO_4$), filtered and evaporated to give crude **7** (3 g, 92 %), m.p. 106–107 °C (Et_2O–hexane), $[\alpha]_D^{22}$ +22° (*c* 2.3); lit.[31] m.p. 108 °C, $[\alpha]_D^{25}$ +27° (*c* 1.8).

*Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-*D*-glucopyranoside* (**8**). Compound **1** (4.5 g) was deacetylated and the product was benzylated with benzyl bromide and NaH in DMF.[32] The crude product was purified by column chromatography (silica-gel 350 g) using solvent I to give **8** (6 g, 89 %), m.p. 94–95 °C (Et_2O–hexane), $[\alpha]_D^{22}$ +2.7° (*c* 1.6); lit.[31] m.p. 94 °C, $[\alpha]_D^{24}$ +4.7° (*c* 2).

*Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-α- and β-*D*-mannopyranoside* (**9**, **12**). D-Mannose (10 g, 55.5 mmol) was acetylated,[14] the crude product (syrup) was dissolved in CH_2Cl_2 (70 ml) and thioglycosidation was carried out in the usual manner with ethanethiol (4 ml, 54 mmol) and $FeCl_3$ (8 g, 49.3 mmol) to afford a mixture (14.5 g, 69 %) containing the α-thioglycoside (**3**, major) and its β-anomer. A portion (3 g) of the mixture obtained above was deacetylated and then benzylated according to the known procedure[32] to afford a mixture of products (R_f, major = 0.25, R_f, minor = 0.19, solvent II). The crude product was charged onto a dry silica-gel column (300 g) and eluted with solvent II (400 ml) followed by solvent I. Compound **9** eluted first as a syrup (1.3 g), $[\alpha]_D^{22}$ +65° (*c* 2.1). Anal. $C_{36}H_{40}O_5S$: C, H, S. ^{13}C NMR ($CDCl_3$): δ 14.9 (SCH_2CH_3), 25.3 (SCH_2CH_3), 69.3, 72.0, 72.1, 73.3, 75.0, 75.1, 76.5, 80.4, 81.9 (C-1, J_{C1-H1} 163.2 Hz), 138.2, 138.3, 138.45, 138.6 (4 C-1 of phenyl).

Further elution afforded a mixture of **9** and **12** (1.9 g), followed by pure **12** as a syrup (0.2 g), $[\alpha]_D^{22}$ −7.9° (*c* 1). ^{13}C NMR ($CDCl_3$): δ 14.1 (SCH_2CH_3), 25.9 (SCH_2CH_3), 84.5 (C-1, J_{C1-H1} 141.1 Hz). Repeated column chromatography of the isolated mixture completely separated **9** and **12**.

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