A study of the oxepane synthesis by a 7-endo electrophile-induced cyclization reaction of alkenylsulfides. An approach towards the synthesis of septanosides

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Dedicated to the Professor Joan Bosch at occasion of his 60th birthday

Abstract A procedure for the stereoselective synthesis of 2-deoxy-2-iodo-septanosides from pyranoses is reported. The procedure involves two reactions: Wittig-Horner olefination to give alkenyl sulfanyl derivatives, and electrophilic iodine-induced cyclization to give phenyl 2-deoxy-2-iodo-1-thio-septanosides (20) or 2-deoxy-2-iodo-septanosides (26a,b), in this case by subsequent hydrolysis of a phenylsulfanyl group under the reaction conditions. The seven membered ring of septanosides was only formed in moderate to low yields, preferably through a 7-endo cyclization, when an isopropylidene group was present as protecting group. The use of benzyl groups as protecting moieties in the pyranose does not afford the septanoside ring. However, when the reactions conditions were forced using more basic media, the furanoside derivatives 3 were obtained.

Keywords: Oxepane, septanosides, 7-endo, electrophilic cyclization, 2-deoxy-carbohydrates

Introduction

Septanosides are ring expanded analogues of pyranosides containing a seven membered ring. It has been previously demonstrated that septanoside derivatives bind concanavalin A, are glycosidase inhibitors, as well as their aza derivatives, and have been used to define new types of protein-carbohydrate interactions. Septanoses have been prepared by ring expansion of uloses, by Baeyer-Villiger oxidation of inositols and by Baeyer-Fischer reaction of sugar dialdehydes. Recently, 1,2-anhydro-septanose derivatives (glycals) have been synthesized using ring closing metathesis or by cyclization of alkynols induced by a tungsten catalyst. These 1,2-anhydro-septanose derivatives have been used to prepare new septanoside derivatives, and
disaccharides containing septanoses. Septanosides have also been prepared by acid-catalyzed cyclization of hydroxy-acetals.

Recently we reported a procedure for the synthesis of phenyl 2-deoxy-2-iodo-1-thiopyranosyl glycosides from pentoses through a two step procedure consisting of Wittig-Horner olefination to give the sulfanylalkenes, and iodonium species-induced cyclization to give the 2-deoxy-2-iodo-1-thiopyranosyl glycosides (Scheme 1).

\[ \text{pentoses} \xrightarrow{\text{Ph}_2\text{P}-\text{CH}_2-\text{SR}^2} \text{Ref 11} \]

\[ \xrightarrow{\text{I}^+} \text{Ref 11} \]

**Scheme 1**

These 1-thio-pyranosides were useful glycosyl donors for the stereocontrolled synthesis of 2-deoxy-2-iodo-disaccharides. This procedure was particularly efficient for the synthesis of 2-deoxy-β-hexo-glycosides of allo or gulo configuration. 1-Thio-glycosides were also efficiently transformed to glycals (Scheme 1).

\[ \text{RO} \xrightarrow{\text{OH}} \text{OHRO} \xrightarrow{\text{RO}} \text{RO} \xrightarrow{\text{OR}} \text{OR} \xrightarrow{\text{SR}} \text{SPh} \]

**Scheme 2**

In order to expand the scope of this strategy, we decided to explore the olefination-electrophile-induced cyclization strategy as a route to 2-deoxy-2-iodo-septanosides (Scheme 2). There are few examples for the formation of oxepane rings by electrophile-induced cyclization and these are mainly related to the formation of lactones through a 7-exo cyclization mode. To the best of our knowledge, there is only one example of formation of oxepanes by iodine-induced cyclization of hydroxyl-enolethers through a 7-endo cyclization. In this paper, we present our
results on the synthesis of heptenyl thioethers derived from protected hexo-pyranoses and pentoses and the study of electrophile induced cyclization under various conditions.

**Results and Discussion**

As shown in previous studies, the Wittig-Horner conditions for the synthesis of sulfanyl-alkenes using phosphine oxide carbanions and Li bases were the most effective in terms of chemoselectivity, diastereoselectivity and yield. The selected olefination reagent diphenyl phenylsulfanyl methyl phosphine oxide was prepared by the Arbuzov reaction in 94% yield starting from ethyl diphenyl phosphinite and chloromethyl phenyl sulfide.

When the Wittig-Horner reaction was carried out starting from 2,3,4,6-tetra-O-benzyl-D-glucopyranose and diphenyl phenylsulfanyl methyl phosphine oxide, the expected product was obtained in 63% yield as an inseparable mixture of diastereomers (Z/E=1/8), as expected for semi-stabilized carbanions.

![Scheme 3](image)

**Scheme 3**

Subsequently, the cyclization of the alkenylsulfanyl derivative was studied. Initially, the standard conditions reported by Barlett, using iodine in acetonitrile in presence of NaHCO₃, were tested. However, under these conditions only the starting material was recovered. Heating the mixture at 40 °C or using NIS as an electrophile was also ineffective.

Increasing the nucleophilicity of oxygen forming first the alkoxide was also tested. Treatment of compound 2 with KH and iodine in ether at –78 °C did not provide the oxepane ring. However, reaction with n-Buli as a base afforded 3 in 62% yield (Scheme 4).

A similar behaviour had already been observed in the cyclization reaction of tri-O-benzyl-arabino derivative in the presence of KH, which led to the formation of oxetane in 31%
yield (Scheme 5). However, in the presence of a weak base, the cyclization product 6 was preferentially formed.\textsuperscript{11a}

Scheme 5

These unexpected outcome takes place when cyclization is attempted using BuLi or KH as bases. Under strong basic conditions, the more nucleophilic alkoxide anion 7 was expected to be formed and eventually cyclize. However, and as already studied previously,\textsuperscript{11a} the preferred conformations in the arabin and gluco derivatives do not favour cyclization because the allylic alkoxide group does not occupy an inside position with respect to the \( \text{C} = \text{C} \) double bond, so that alternative reaction pathways are likely to take place. One of them could consist of a proton transfer to render an allylic anion 8 that reprotonates to give enol ether 9, which is considerable electron richer and hence more reactive towards cyclization than the starting enol thioether 7 (Scheme 6).

Scheme 6

Recently, the 7-membered ring glycal 12 was synthesized by a tungsten-induced cyclization starting from alkyne 11 (Scheme 7).\textsuperscript{7} The presence of an isopropylidene protecting group was necessary in order to favor the formation of the seven-membered ring.
Scheme 7

In order to test how the presence of a dioxolane cycle in the starting material would favor the cyclization reaction, we prepared the sulfanyl alkene 14 by reaction of the ribose derivative 13 with Ph₂P(O)CH₂SPh in the presence of BuLi. Then, the reaction of 14 with benzyl bromide afforded 15, which was subsequently treated with TBAF to give 16 (Scheme 8). Compound 17 with hydroxyl groups at positions 5 and 6 was also prepared from 14 to study the competition between 6-endo and 7-endo cyclization.

Scheme 8

When 14 was treated with NIS in basic media at low temperature, compound 19 was isolated in 46% yield, as a result of 6-endo cyclization to give 18 and concomitant loss of the silyl protecting group (Scheme 9). The stereochemical outcome of the reaction was similar to that previously observed for related compounds without isopropylidene protecting groups. Compound 19 was also exclusively obtained in similar yield starting from 17, which indicates that the 6-endo cyclization is preferred over the 7-endo.

When 16 was used as starting material, the reaction evolved much slower and required heating for a long period. After 24 hours at 35°C, compound 20 was isolated in 12% yield (Scheme 9). The reaction was not complete and 40% of starting material was also recovered. The structure of 20 was determined according the following data: a) The signals of H1 and C1 which appear at chemical shifts, 5.56 ppm and 93.0 ppm respectively, characteristic of anomeric proton and carbon, and a J₆₆ value of 13Hz, indicate that cyclization has taken place. b) The
presence of iodine at position 2 was confirmed by the correlation of H2 with a $^{13}$C signal at 32 ppm (Table 1). c) From $J_{1,2}$ and $J_{2,3}$ values, an equatorial disposition for the substituents at these positions can be deduced. d) The presence of H2 on the bottom face of the molecule was confirmed by the existence of NOE with the signal at 3.81 ppm that corresponds to H6 axial.

It should be noted that the relative stereochemistry of iodine and the neighboring alkoxy group is trans, opposite to those observed for the cyclizations yielding pyranoses (Scheme 9), where the relative stereochemistry was always cis, as a result that cyclization takes place under the effect of the so-called alkoxy-inside effect. This effect establishes that in the more reactive conformer, the alkoxy chain occupies an inside conformation with respect to the double bond. The low reactivity observed can be due to the high substitution of the chain which limits the number of reactive conformations, and to the fact that cyclization in compound 16 takes place via the less reactive alkoxy-outside conformer.

\[ \text{CH}_3\text{CN, 46\%} \]

Scheme 9

In previous work, we prepared compound 22 by olefination of the lyxo derivative 21 (Scheme 10). Iodine-induced cyclization of 22 gave the 2-deoxy-2-iodo-1-thio-pyranoside 25 (Scheme 11). We had previously observed that benzyl ethers reacted in electrophile-induced cyclizations. In order to avoid this possibility, compound 22 was protected as ethyl ether to give derivative 23, which was treated with TBAF to afford 24 (Scheme 10). When 24 was treated with NIS/NaCO$_3$H, the reaction slowly evolved to give a mixture of compounds 26a and 26b in 36% yield (32% of the starting material was also recovered) as an anomeric $\alpha/\beta$ mixture, resulting from a 7-endo cyclization followed by the hydrolysis of the anomeric phenylsulfanyl group (Scheme 12). This hydrolysis was already observed in other cases when the cyclization was slow, since the activation of the 1-thiophenyl group by NIS competes. More relevant spectroscopic features allowing the structural elucidation of 26a, b are the following: a) $^{13}$C
chemical shifts at 96.9 and 98.1 ppm for C1 and at 35.4 and 32.5 for C2, for 26a and 26b respectively, together with the absence of aromatic carbons, confirms the presence of an hydroxyl group at C1 and an iodine at C2 (Table 1). b) The existence of acetalic carbons and the J_{6a,6b} value of 13Hz confirms that compounds are cyclized. c) For compound 26a, the J_{2,3} value of 10.0 Hz indicates that these protons are in a trans-diaxial position, and the NOE cross peak observed between protons H2 and H5, confirms that iodine is on the α-face. That suggests that for compound 26a the 7-endo cyclization has taken place under an alkoxy-outside control. Configuration of 26b could not be fully determined.

Scheme 10

Scheme 11

Scheme 12
Table 1. Selected $^1$H- and $^{13}$C-NMR data of compounds 20, 26a and 26b ($\delta$ en ppm, $J$ en Hz)

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nd: not determined

Conclusions

Septanosides 20 and 26 were obtained in low to moderate yields from pentoses through a two-step procedure. A Wittig-Horner olefination of pentoses 13 and 21 gave the phenylsulphanyl derivatives 14 and 22, further protection and deprotection gave compounds 16 and 24, and NIS-induced 7-endo cyclization afforded compounds 20 and 26. 7-Endo cyclization took place, preferably under alkoxy-outside control, when an isopropylidene protecting group was present in the starting alkene. This was the first example of 7-endo iodine-induced-cyclization to give highly substituted oxepanes. In the absence of an isopropylidene group the cyclization did not take place and when more basic reaction conditions were used, in order to force the cyclization, the reaction evolved in a different way to yield compound 3.

Experimental Section

General Procedures. Optical rotations were measured at room temperature in 10 cm cells in a Perkin-Elmer 241 polarimeter. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded using a Varian Gemini 300 MHz and 400 MHz apparatus, with CDCl$_3$ as solvent, Me$_4$Si as an internal reference, and H$_3$PO$_4$ ($^{31}$P) as external standard, unless specified otherwise. Elemental analyses were performed using a Carlo-Erba Microanalyzer. Flash column chromatography was performed using silica gel 60 A CC (230-400 mesh). Radial chromatography was performed on 1, 2 or 4 mm plates of Kieselgel 60 PF$_{254}$ silica gel, depending on the amount of product. Medium-pressure chromatography (MPLC) was performed using silica gel 60 A CC (6-35 µm). Solvents were purified using standard procedures.
**Z/E-3,4,5,7-Tetra-O-benzyl-1,2-dideoxy-1-phenylsulfanyl-D-gluc-o-hept-1-enitol** (2).

Diphenyl phenylsulfanyl methylphosphine oxide (1.3 g, 4.0 mmol) was dissolved in anhydrous THF (27 ml, 0.15 M). n-BuLi (2.6 ml, 4.2 mmol, 1.6 M in hexane) was slowly added at –78 °C, stirred under an argon atmosphere until the intensive orange colour was formed. The reaction mixture was stirred for an hour at this temperature, and the THF solution of the 2,3,4,6-tetra-O-benzyl-D-glucopyranose (2.0 ml, 0.5 M) was added. The evolution of the reaction was monitored by TLC analysis with general sugar dye. The reaction did not evolve at –78 °C and the solution was warmed up to room temperature. After full conversion (24 h) and work up, the product was purified by flash chromatography (hexane:ethyl acetate = 3:1) to obtain the vinyl phenylsulfanyl compound (406 mg, 0.6278 mmol, 63%) as an inseparable mixture of Z/E = 1/8 as an oil.

NMR spectral data were extracted from the diastereoisomeric mixture. **E-2**: Rf (hexane:ethyl acetate=2:1): 0.7. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ in ppm: 7.52-7.16 (25H, m, Ar), 6.30 (1H, d, J = 15.2 Hz, H-1), 5.70 (1H, dd, J = 15.2, 8.0 Hz, H-2), 4.80 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.71 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.67 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.62 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.64 (H1, J = 11.2 Hz, CH$_3$Ph), 4.50 (2H, s, CH$_2$Ph), 4.48 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.24 (1H, dd, J = 8.0, 5.6 Hz, H-3), 4.01 (1H, m, H-5), 3.72 (2H, m, H-6), 3.60 (2H, m, H-6), 3.58 (1H, d, J = 6.4 Hz, OH). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ in ppm: 138.5, 138.3, 138.2, 138.1, 134.4 (C, Ar), 130.6-127.4 (CH, Ar), 128.6 (CH, C-1), 128.4 (CH, C-2), 81.6 (CH, C-4), 81.0 (CH, C-3), 78.6 (CH, C-6), 75.0, 73.5, 73.34 (CH$_2$Ph), 71.2 (CH$_2$Ph), 71.0 (CH$_2$Ph), 70.5 (CH, C-5).

**Z-2**: Rf (hexane:ethyl acetate=2:1): 0.6. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ in ppm: 7.35-7.18 (25H, m, Ar), 6.50 (1H, d, J = 9.2 Hz, H-1), 5.89 (1H, dd, J = 9.2, 8.8 Hz, H-2), 4.80-4.40 (8H, d, CH$_2$Ph), 4.24 (1H, m, H-3), 4.0 (1H, m, H-5), 3.82 (2H, m, H-6), 3.60 (1H, s, H-7a), 3.58 (1H, d, J = 6.4 Hz, OH). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ in ppm: 138.5, 138.3, 138.2, 138.1, 134.4 (C, Ar), 130.6-127.4 (CH, Ar), 128.6 (CH, C-1), 128.4 (CH, C-2), 81.6 (CH, C-4), 81.0 (CH, C-3), 78.6 (CH, C-6), 75.0, 73.5, 73.34 (CH$_2$Ph), 71.2 (CH$_2$Ph), 71.0 (CH$_2$Ph), 70.5 (CH, C-5).

**2,3,4-Tri-benzyl oxy-5-benzyl oxymethyl-2-(1-iodo-2-phenylsulfanyl-ethyl)-tetrahydro-furan** (3). To a solution of (55 mg, 0.085 mmol) in 1.0 ml (0.085 M) of anhydrous diethyl ether, 53 $\mu$l of n-BuLi (0.085 mmol, 1.6 M in hexane) were added at –78 °C. The mixture was stirred for one hour at this temperature under an argon atmosphere. Subsequently, a solution of I$_2$ (65 mg, 0.225 mmol) in 2.0 ml (0.43 M) of diethyl ether was added. TLC analysis showed the completion of the reaction after 5 min. The reaction was quenched with Na$_2$S$_2$O$_3$, and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with water, dried on anhydrous MgSO$_4$, and concentrated under vacuum. After purification by radial chromatography methods (hexane → hexane:ethyl acetate = 1:2), 3 (41 mg, 0.053 mmol, 62%) was obtained as an oil.

Rf (hexane:ethyl acetate=2:1): 0.67. [\alpha]$_D^{25}$ -21.5 (c 0.40, CH$_2$Cl$_2$). $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ in ppm: 7.25-7.13 (25H, m, Ar), 4.81 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.65 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.61 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.58 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.56 (1H, d, J = 6.4 Hz, H-4), 4.49 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.46 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.44 (1H, d, J = 11.2 Hz, CH$_2$Ph), 4.38 (1H, d, J = 11.6 Hz, CH$_2$Ph), 4.30 (1H, dd, J = 7.2, 6.4Hz, H-5), 4.18 (1H, d, J = 10.8, 2.8 Hz, H-2), 4.12 (1H, m, H-6), 3.86 (1H, dd, J = 14.8, 2.8 Hz, CH$_2$, H-1a),
3.69 (1H, dd, J = 10.8, 2.8 Hz, H-7a), 3.53 (1H, dd, J = 10.8, 3.6 Hz, H-7b) 3.22 (1H, dd, J = 14.8, 10.8 Hz, CH₂, H-1b). ¹³C-NMR (CDCl₃, 100.6 MHz) δ in ppm: 139.0, 138.4, 138.4, 138.1, 136.0 (C, Ar), 129.6-125.3 (CH, Ar), 105.3 (C, C-3), 87.2 (CH, C-4), 82.9 (CH, C-5), 80.6 (CH, C-6), 73.8, 73.1, 72.9 (CH₂Ph), 69.5 (CH₂, C-7), 65.8 (CH₂Ph), 41.9 (CH, C-2), 40.1 (CH₂, C-1). HRMS (TOF MS ES+): calcd for C₄₁H₄₁O₅NaSI (MNa+) 795.1617; found, 795.1600.

(Z/E)-6-O-tert-Butyldimethylsilyl-1,2-dideoxy-3,4-O-isopropylidene-1-phenylsulfanyl-D-ribo-hex-1-enitol (14). Diphenyl phenylsulfanylmethylphosphine oxide (4.26 g, 13.1 mmol) was dissolved in anhydrous THF (13 ml, 0.25 M). n-BuLi (8.6 ml, 13.8 mmol, 1.6 M in hexane) was added slowly at –78 ºC and the solution was stirred under an argon atmosphere until the intensive orange colour occurred. The reaction mixture was stirred for an hour at this temperature, then the solution of 13 (1.0 g, 3.3 mmol) in anhydrous THF (2.0 ml, 0.5 M) was added. After full conversion (24 h) and work up, the product was purified by flash chromatography (hexane:ethyl acetate = 6:1) to obtain compound 14 as an inseparable mixture of Z/E = 1/11 (920 mg, 2.24 mmol, 68%) as an oil. NMR spectral data were extracted from the diastereoisomeric mixture. E-14: Rᵣ (hexane:ethyl acetate=6:1): 0.62. ¹H-NMR (CDCl₃, 400 MHz) δ in ppm: 7.51-7.20 (5H, m, Ar), 6.50 (1H, d, J = 15.2 Hz, H-1), 6.00 (1H, dd, J = 15.2, 6.4 Hz, H-2), 4.77 (1H, dd, J = 6.4, 6.0 Hz, H-3), 4.05 (1H, dd, J = 9.2, 6.0 Hz, H-4), 3.81 (1H, dd, J = 9.6, 3.2 Hz, H-6a), 3.68 (H, dd, J = 9.6, 5.2 Hz, H-6b), 3.64 (1H, m, H-5), 2.50 (1H, d, J = 6.0 Hz, OH), 1.46 (3H, s, CH₃), 1.35 (3H, s, CH₃), 0.92 (9H, s, CH₃), 0.12 (6H, s, CH₃). ¹³C NMR (CDCl₃, 100.6 MHz) δ in ppm: 139.2, 130.0-127.0 (CH, Ar), 127.3 (CH, C-1), 126.7 (CH, C-2), 109.5 (C, Ar), 78.5 (CH, C-3), 76.9 (CH, C-4), 69.0 (CH₂, C-6), 64.6 (CH, C-5), 28.1 (CH₃), 26.1 (CH₃), 25.6 (CH₃).

(Z/E)-5-O-benzyl-6-O-tert-butyldimethylsilyl-1,2-dideoxy-3,4-O-isopropylidene-1-phenylsulfanyl-D-ribo-hex-1-enitol (15). To a suspension of sodium hydride (84 mg, 2.1 mmol) in THF, compound 14 (820 mg, 2.0 mmol) dissolved in freshly distilled THF (8.0 ml, 0.25M) was added at room temperature. The reaction mixture was further stirred for an hour and benzyl bromide (250 µl, 2.1 mmol) was slowly added. The reaction mixture was stirred overnight, and the evolution of the reaction was followed by TLC analysis. The reaction was quenched by saturated ammonium chloride solution. The aqueous layer was extracted with ethyl acetate (3x20 ml), the combined organic layers were washed with water (2x20 ml), with brine (1x20 ml) and dried on MgSO₄, filtered and concentrated under vacuum. The resulting mixture was purified by chromatography (hexane:ethyl acetate = 8:1) to obtain compound 15 as a light yellow oil (361 mg, 0.74 mmol, 37%) as an inseparable mixture of Z/E = 1/11. NMR spectral data were extracted from the diastereoisomeric mixture. E-15: Rᵣ (hexane:ethyl acetate=8:1): 0.51. ¹H-NMR (CDCl₃, 400 MHz) δ in ppm: 7.40-7.22 (10H, m, Ar), 6.52 (1H, d, J = 15.6 Hz, H-1), 5.86 (1H, dd, J = 15.6, 6.4 Hz, H-2), 4.77 (1H, d, J = 11.2 Hz CH₂Ph), 4.74 (1H, dd, J = 6.4, 5.6 Hz, H-3), 4.40 (1H, d, J = 11.2 Hz CH₂Ph), 4.26 (1H, dd, J = 8.8, 5.6 Hz, H-4), 3.86 (1H, dd, J = 10.0, 2.0 Hz, CH₂, H-6a), 3.68 (H, dd, J = 10.0, 5.2 Hz, CH₂, H-6b), 3.61 (1H, m, H-5), 1.45 (3H, s, CH₃), 1.35 (3H, s, CH₃), 0.92 (9H, s, CH₃), 0.12 (6H, s, CH₃). ¹³C
NMR (CDCl₃, 100.6 MHz) δ in ppm: 139.0, 134.5 (C, Ar), 130.0-127.0 (CH, Ar), 127.3 (CH, C-1), 126.7 (CH, C-2), 109.5 (C), 78.5 (CH, C-3), 76.9 (CH, C-4), 72.3 (CH₂, CH₂Ph), 69.8 (CH₂, C-6), 64.6 (CH, C-5), 28.1 (CH₃), 26.1 (CH₃), 25.6 (CH₃).

(Z/E)-5-O-Benzyl-1,2-dideoxy-3,4-O-isopropylidene-1-phenylsulfanyl-D-ribo-hex-1-enitol (16). Compound 15 (361 mg, 0.74 mmol) was dissolved in THF (3.0 ml) and tetrabutylammonium fluoride (275 mg, 0.78 mmol) was added. The reaction mixture was stirred at room temperature and the reaction was controlled by TLC analysis. After an hour, the reaction was quenched with a saturated sodium carbonate solution. The aqueous layer was extracted with ethyl acetate (3x20 ml), and the combined organic layers were washed with water (2x20 ml), with brine (1x20 ml) dried on MgSO₄, filtered and concentrated under vacuum. The mixture was separated by chromatography (hexane → hexane:ethyl acetate = 1:1) and compound 16 was obtained as a light yellow oil (276 mg, 0.7136 mmol, 96%) as an inseparable mixture of Z/E = 1/11.

NMR spectral data were extracted from the diastereoisomeric mixture. E-16: Rₜ (hexane:ethyl acetate=4:1): 0.46. ¹H-NMR (CDCl₃, 400 MHz) δ in ppm: 7.43-7.20 (10H, m, Ar), 6.50 (1H, d, J = 15.2 Hz, H-1), 5.88 (1H, dd, J = 15.2, 6.8 Hz, H-2), 4.77 (1H, d, J = 10.8 Hz, CH₂Ph), 4.76 (1H, dd, J = 6.8, 6.0 Hz), 4.40 (2H, d, J = 10.8 Hz, CH₂Ph), 4.26 (1H, dd, J = 8.8, 6.0 Hz, H-4), 3.86 (1H, d, J = 14.8 Hz, H-6a), 3.66 (1H, dd, J = 10.4 Hz, H-6b), 3.65 (1H, d, J = 6.0 Hz), 1.45 (3H, s, CH₃), 1.35 (3H, s, CH₃). ¹³C NMR (CDCl₃, 100.6 MHz) δ in ppm: 138.4, 134.5 (C, Ar), 130.4-127.3 (CH, Ar), 128.0 (CH, C-1), 126.9 (CH, C-2), 109.2 (C), 78.4 (CH, C-3), 77.3 (CH, C-5), 76.9 (CH, C-4), 70.6 (CH₂, CH₂Ph), 29.8 (CH₃), 28.9 (CH₃).

(Z/E)-1,2-Dideoxy-3,4-O-isopropylidene-1-phenylsulfanyl-D-ribo-hex-1-enitol (17). Compound 14 (410.1 mg, 1 mmol) was dissolved in THF (4.0 ml, 0.25M) and tetrabutylammonium fluoride (331.3 mg, 1.05 mmol) was added. The reaction mixture was stirred at room temperature and the reaction was controlled by TLC analysis. After an hour, the reaction was quenched with a saturated sodium carbonate solution. The aqueous layer was extracted with ethyl acetate (3x20 ml), the combined organic layers were washed with water (2x20 ml), with brine (1x20 ml), dried on MgSO₄, filtered and concentrated under vacuum. The mixture was separated by chromatography (hexane → hexane:ethyl acetate = 1:1) and compound 17 was obtained as a light yellow oil (244 mg, 0.823 mmol, 98%) as an inseparable mixture of Z/E = 1/11.

NMR spectral data were extracted from the diastereoisomeric mixture. E-17: Rₜ (hexane:ethyl acetate=6:1): 0.62. ¹H-NMR (CDCl₃, 400 MHz) δ in ppm: 7.97-7.23 (5H, m, Ar), 6.58 (1H, d, J = 14.8 Hz, H-1), 5.90 (1H, dd, J = 14.8, 6.8 Hz, H-2), 4.78 (1H, dd, J = 6.8, 6.0 Hz, H-3), 4.90 (1H, dd, J = 8.8, 6.0 Hz, H-4), 3.86 (1H, d, J = 14.8 Hz, H-6a), 3.68 (1H, d, J = 6.0 Hz), 1.40 (3H, s, CH₃), 1.30 (3H, s, CH₃). ¹³C NMR (CDCl₃, 100.6 MHz) δ in ppm: 134.5 (C, Ar), 130.4-127.3 (CH, Ar), 128.0 (CH, C-1), 126.9 (CH, C-2), 109.2 (C), 78.2 (CH, C-3), 76.8(CH, C-4), 74.84 (CH, C-4), 70.0 (CH₂, C-6), 27.8 (CH₃), 25.4 (CH₃).
to -30 ºC. Sodium bicarbonate (59 mg, 0.70 mmol) and NIS (158.6 mg, 0.70 mmol) were then added. The reaction was controlled by TLC. After half an hour, full conversion was observed and the reaction was stopped by the addition of a saturated solution of sodium thiosulphate. The aqueous layer was extracted with ethyl acetate (3x20 ml), the combined organic layers were washed with water (2x20 ml), with brine (1x20 ml) dried on MgSO₄, filtered and concentrated under vacuum. The crude reaction mixture was purified by chromatography (hexane → hexane:ethyl acetate = 1:1) and compound 19 was obtained as a light yellow oil (101 mg, 0.239 mmol, 47%).

\[ \text{Rf (hexane:ethyl acetate=4:1): 0.62.} \]

\[ ^1\text{H-NMR}^{23} (\text{CDCl}_3, 400 \text{ MHz}) \delta \text{ in ppm 7.51-7.26 (5H, Ar), 5.60 (1H, d, J = 3.6 Hz, H-1), 4.64-4.57 (2H, m, H-2), 4.43 (1H, dd, J= 9.2, 5.6 Hz, H-3), 4.43 (1H, dd, J= 9.2, 5.6 Hz, H-4), 4.29 (1H, m, H-5), 3.93 (1H, dd, J= 12.0, 8.8 Hz, H-6a), 3.79 (1H, dd, J= 12.0, 8.8 Hz, H-6b), 1.60 (3H, s, CH₃), 1.37 (3H, s, CH₃).} \]

\[ ^{13}\text{C NMR} (\text{CDCl}_3, 100.6 \text{ MHz}) \delta \text{ in ppm: 135.2 (C, Ar), 132.1-128.1 (CH, Ar), 111.6 (C), 89.5 (CH, C-1), 78.2 (CH, C-3), 71.2 (CH, C-5), 70.4 (CH, C-4), 63.0 (CH₂, C-6), 28.4 (CH₃), 26.8 (CH₃), 25.6 (CH, C-2).} \]

**Phenyl 5-O-benzyl-2-deoxy-2-iodo-3,4-O-isopropylidene-1-thio-α-D-altro-septanoside (20).**

Compound 16 (276 mg, 0.7136 mmol) was dissolved in acetonitrile (14.3 ml, 0.05M) and cooled to -30 ºC and sodium bicarbonate was added (89.9 mg, 1.0704 mmol) followed by NIS (240.8 mg, 1.0704 mmol). The reaction was controlled by TLC analysis. The reaction was stirred for 24 hours at –10 ºC, then at room temperature for 30 hours and was finally heated at 35 ºC for 24h. Full conversion was not reached but the reaction was quenched with a solution of sodium thiosulfate. The aqueous layer was extracted with ethyl acetate (3x20 ml), the combined organic layers were washed with water (2x20 ml), with brine (1x20 ml) dried on MgSO₄, filtered and concentrated under vacuum. The reaction mixture was separated by chromatography (hexane → hexane:ethyl acetate = 1:1) and compound 20 was obtained as a light yellow oil (45 mg, 0.0878 mmol, 12%). Starting material (109 mg, 0.281 mmol, 40 %) were also recovered.

\[ \text{Rf (hexane:ethyl acetate=8:1): 0.38.} \]

\[ [\alpha]D^{25}_{25} 156º (c 0.16, CH₂Cl₂). \]

\[ ^1\text{H-NMR}^{23} (\text{CDCl}_3, 400 \text{ MHz}) \delta \text{ in ppm: 7.50-7.26 (10H, m, Ar), 5.56 (1H, d, J = 8.8 Hz, H-1), 5.13 (1H, t, J = 8.8, Hz, H-2), 4.73 (1H, d, J = 11.2 Hz, CH₂Ph), 4.70 (1H, d, J = 11.2 Hz, CH₂Ph), 4.65 (1H, dd, J = 7.6, 7.6 Hz, H-3), 4.58 (1H, dd, J = 13.6, 1.0 Hz, H-6a), 4.49 (1H, dd, J = 7.6, 2.0 Hz, H-4), 4.13 (1H, m, H-5), 3.81 (2H, dd, J = 13.6, 5.2 Hz, H-6b), 1.60 (3H, s, CH₃), 1.40 (3H, s, CH₃).} \]

\[ ^{13}\text{C NMR} (\text{CDCl}_3, 100.6 \text{ MHz}) \delta \text{ in ppm: 138.3 (C, Ar), 131.5-127.6 (CH, Ar), 108.3 (C), 93.0 (CH, C-1), 80.1 (CH, C-3), 77.8 (CH, C-5), 76.9 (CH, C-4), 73.5 (CH₂, CH₂Ph), 63.5 (CH₂, C-6), 32.0 (CH, C-2), 26.4 (CH₃), 23.9 (CH₃).} \]


**(Z/E)-6-O-tert-Butyldimethylsilyl-1,2-dideoxy-3,4-O-isopropylidene-1-phenylsulfanyl-D-lyxo-hex-1-enitol (22).**

Diphenyl phenylsulfanyl methylphosphine oxide (6.488 g, 20.0 mmol) was dissolved in anhydrous THF (20 ml, 0.25 M) and n-BuLi (13.1 ml, 21.0 mmol, 1.6 M in hexane) was added slowly to the solution at –30 ºC and the mixture was stirred under an argon atmosphere until the occurrence of a intensive orange colour. The reaction mixture was further...
stirred for one hour at this temperature. Then a solution of \(21\) (1.522 g, 5.0 mmol) in anhydrous THF (10.0 ml, 0.5 M) was added. The reaction was allowed to warm up to room temperature. After full conversion (24 h) and work up, the resulting product was purified by flash chromatography (hexane:ethyl acetate = 6:1) to yield compound \(22\) (1.14 g, 2.779 mmol, 56%) as a yellow oil that revealed to be an inseparable mixture of \(Z/E=1/4\).

NMR spectral data were extracted from the diastereoisomeric mixture. \(E-22\): \(R_f\) (hexane:ethyl acetate=6:1): 0.67. \(^1\)H-NMR \(^{23}\) (CDCl\(_3\), 400 MHz) \(\delta\) in ppm: 7.50-7.20 (5H, m, Ar), 6.52 (1H, d, J = 14.8 Hz, H-1), 5.95 (1H, dd, J = 14.8, 7.2 Hz, H-2), 4.05 (1H, dd, J = 6.4, 4.0 Hz, H-4), 4.68 (1H, dd, J = 7.2, 6.4 Hz, H-3), 4.13 (1H, m, H-5), 3.93 (1H, dd, J = 11.2, 5.2 Hz, H-6a), 3.81 (1H, dd, J = 11.2, 6.8 Hz, H-6b), 2.35 (1H, d, J = 5.6 Hz, OH), 1.46 (3H, s, CH\(_3\)), 1.35 (3H, s, CH\(_3\)), 0.92 (9H, s, CH\(_3\)), 0.12 (6H, s, CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\), 100.6 MHz) \(\delta\) in ppm: 134.2 (C, Ar), 130.8-126.9 (CH, Ar), 127.5 (CH, C-1), 126.9 (CH, C-2), 108.8 (C), 80.9 (CH, C-5), 80.0 (CH, C-4), 78.5 (CH, C-3), 61.6 (CH\(_2\), C-6), 27.4 (CH\(_3\)), 26.0 (CH\(_3\)), 25.2 (CH\(_3\)).

Spectral data is extracted from the diastereoisomeric mixture. \(Z-22\): \(R_f\) (hexane:ethyl acetate=6:1): 0.67. \(^1\)H-NMR \(^{23}\) (CDCl\(_3\), 400 MHz) \(\delta\) in ppm: 7.50-7.20 (5H, m, Ar), 6.48 (1H, d, J = 7.8 Hz, H-1), 5.90 (1H, dd, J = 7.8, 7.2 Hz, H-2), 5.17 (1H, dd, J = 7.2, 7.2 Hz, H-3), 4.32 (1H, dd, J = 7.2, 4.0 Hz, H-4), 4.28 (1H, dd, J = 7.2, 2.4 Hz, H-5), 3.93 (1H, m, H-5), 3.81 (1H, m, H-6a), 3.26 (1H, m, H-5), 1.46 (3H, s, CH\(_3\)), 1.35 (3H, s, CH\(_3\)), 0.92 (9H, s, CH\(_3\)), 0.12 (6H, s, CH\(_3\)).

(Z/E)-6-O-tert-Butyldimethylsilyl-5-O-benzyl-1,2-dideoxy-3,4-O-isopropylidene-1-phenylsulfanyl-D-lyxo-hex-1-enitol (23). To a suspension of sodium hydride (16 mg, 0.66 mmol) in THF, compound \(22\) (244 mg, 0.60 mmol) dissolved in freshly distilled THF (2.4 ml, 0.25M) was added at room temperature. The reaction mixture was further stirred for an hour at room temperature and subsequently freshly distilled ethyl bromide (67 \(\mu\)l, 0.9 mmol) was slowly added. The reaction mixture was stirred overnight, and the evolution of the reaction was followed by TLC. The reaction was then quenched with a saturated ammonium chloride solution. The aqueous layer was extracted with ethyl acetate (3x20 ml), the combined organic layers were washed with water (2x20 ml), with brine (1x20 ml), dried on MgSO\(_4\), filtered and concentrated under vacuum. The mixture was purified by chromatography (hexane \(\rightarrow\) hexane:ethyl acetate = 1:1) and compound \(23\) was obtained as a light yellow oil (361 mg, 0.74 mmol, 37%), as an inseparable mixture of \(Z/E=1/4\).

NMR spectral data were extracted from the diastereoisomeric mixture. \(E-23\): \(R_f\) (hexane:ethyl acetate=8:1): 0.56. \(^1\)H-NMR \(^{23}\) (CDCl\(_3\), 400 MHz) \(\delta\) in ppm: 7.50-7.20 (5H, m, Ar), 6.45 (1H, d, J = 15.2 Hz, H-1), 5.90 (1H, dd, J = 15.2, 7.8 Hz, H-2), 4.63 (1H, dd, J = 7.8, 6.8 Hz, H-3), 4.28 (1H, dd, J = 6.8, 4.0 Hz, H-4), 3.74-3.64 (3H, m, H-6a, CH\(_2\) (Et)), 3.43 (1H, dd, J = 9.2, 7.2 Hz, H-6b), 3.26 (1H, m, H-5), 1.46 (3H, s, CH\(_3\)), 1.35 (3H, s, CH\(_3\)), 1.21-1.14 (3H, m, CH\(_3\)), 0.92 (9H, s, CH\(_3\)), 0.12 (6H, s, CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\), 100.6 MHz) \(\delta\) in ppm: 134.5 (C, Ar), 130.2-127.0 (CH, Ar), 126.9 (CH, C-1), 126.6 (CH, C-2), 109.1 (C), 78.4 (CH, C-5), 77.6 (CH, C-3), 76.8 (CH, C-4), 66.7 (CH\(_2\)), 62.6 (CH\(_2\), C-6), 29.8 (CH\(_3\)), 27.4 (CH\(_3\)), 26.0 (CH\(_3\)), 25.2 (CH\(_3\)).

\(Z-23\): \(R_f\) (hexane/AcOEt=8/1): 0.55. \(^1\)H-NMR \(^{23}\) (CDCl\(_3\), 400 MHz) \(\delta\) in ppm: 7.50-7.20 (5H, m, Ar), 6.48 (1H, d, J = 7.8 Hz, H-1), 6.04 (1H, dd, J = 7.8, 7.2 Hz, H-2), 5.17 (1H, dd, J = 7.2, 7.2
Hz, H-3), 4.32 (1H, dd, J = 7.2, 2.4 Hz, H-4), 3.74-3.26 (5H, m, H-5, H-6a, H-6b, CH$_2$ (Et)), 1.46 (3H, s, CH$_3$), 1.35 (3H, s, CH$_3$), 1.21-1.14 (3H, m, CH$_3$), 0.92 (9H, s, CH$_3$), 0.12 (6H, s, CH$_3$).

(Z/E)-1,2-Dideoxy-5-0-ethyl-3,4-O-isopropylidene-1-phenylsulfonyl-D-lyxo-hex-1-enitol (24). Compound 23 (150 mg, 0.34 mmol) was dissolved in THF (3.0 ml) and tetrabutylammonium fluoride (118.3 mg, 0.38 mmol) was added to the solution. The reaction mixture was stirred at room temperature and the reaction was monitored by TLC. After one hour the reaction was quenched with a saturated sodium carbonate solution. The aqueous layer was extracted with ethyl acetate (3x20 ml), the combined organic layers were washed with water (2x20 ml), with brine (1x20 ml) dried on MgSO$_4$, filtered and concentrated under vacuum. The mixture was separated by chromatography (hexane $\rightarrow$ hexane:ethyl acetate = 1:1) and compound 24 was obtained as a light yellow oil (89 mg, 0.277 mmol, 81% as an inseparable mixture of Z/E = 1/4.

NMR spectral data were extracted from the diastereoisomeric mixture. E-24: R$_f$ (hexane:ethyl acetate=4:1): 0.51. $^1$H-NMR$^{23}$ (CDCl$_3$, 400 MHz) $\delta$ in ppm: 7.40-7.24 (5H, m, Ar), 6.54 (1H, d, J = 15.2 Hz, H-1), 5.96 (1H, dd, J = 15.2, 6.4 Hz, H-2), 4.78 (1H, dd, J = 6.4, 5.6 Hz, H-3), 4.06 (1H, dd, J = 8.8, 5.6 Hz, H-4), 3.86-3.41 (5H, m, H-5, H-6a, H-6b, CH$_2$ (Et)), 2.46 (1H, d, J = 5.2 Hz, OH), 1.45 (3H, s, CH$_3$), 1.35 (3H, s, CH$_3$), 1.22-1.04 (3H, m, CH$_3$). 13C NMR (CDCl$_3$, 100.6 MHz) $\delta$ in ppm: 134.5 (C, Ar), 130.2-127.0 (CH, Ar), 126.9 (CH, C-1), 126.6 (CH, C-2), 109.1 (C), 78.4 (CH, C-5), 77.6 (CH, C-4), 76.8 (CH, C-3), 69.7 (CH$_2$), 61.6 (CH$_2$, C-6), 27.4 (CH$_3$), 26.0 (CH$_3$), 25.2 (CH$_3$). Z-24: R$_f$ (hexane:ethyl acetate=4:1): 0.51. $^1$H-NMR$^{23}$ (CDCl$_3$, 400 MHz) $\delta$ in ppm: 7.50-7.20 (5H, m, Ar), 6.48 (1H, d, J = 7.8 Hz, H-1), 6.04 (1H, dd, J = 7.8, 7.2 Hz, H-2), 5.17 (1H, dd, J = 7.2, 7.2 Hz, H-3), 4.32 (1H, dd, J = 7.2, 2.4 Hz, H-4), 3.74-3.26 (5H, m, H-5, H-6a, H-6b, CH$_2$ (Et)), 2.51 (1H, d, J = 5.2 Hz, OH), 1.46 (3H, s, CH$_3$), 1.35 (3H, s, CH$_3$), 1.21-1.14 (3H, m, CH$_3$).

2-Deoxy-5-0-ethyl-3,4-O-isopropylidene-2-iodo-β-D-galacto-septanose (26a) and 2-deoxy-5-0-ethyl-3,4-O-isopropylidene-2-iodo-α-D-galacto-septanose (26b). Compound 24 (89 mg, 0.277 mmol) was dissolved in acetonitrile (5.5 ml, 0.05M) and cooled to -30 ºC, and then sodium bicarbonate (35 mg, 0.415 mmol) and NIS (93.3 mg, 0.415 mmol) were added. The reaction was stirred overnight at –10 ºC, then at room temperature for 30 hours and finally heated at 35 ºC for 24 hours. The reaction was then quenched with the addition of a saturated solution of sodium thiosulphate. The aqueous layer was extracted with ethyl acetate (3x20 ml), the combined organic layers were washed with water (2x20 ml), with brine (1x20 ml) dried on MgSO$_4$, filtered and concentrated under vacuum. The mixture was separated by chromatography (hexane $\rightarrow$ hexane:ethyl acetate = 1:1) and compounds 26a,b were obtained as an inseparable mixture as a light yellow oil (23 mg, 0.099 mmol, 36%). Starting material Z-24 (29 mg, 0.088 mmol, 32 %) was also recovered.

R$_f$ (hexane:ethyl acetate=4:1): 0.37. NMR spectral data were extracted from the isomeric mixture. 26a: $^1$H-NMR$^{23}$ (CDCl$_3$, 400 MHz) $\delta$ in ppm: 5.48 (1H, d, J = 1.2 Hz, H-1, 4.72 (1H, dd, J = 10.0, 8.0 Hz, H-3), 4.25 (1H, dd, J = 8.0, 7.2 Hz, H-4), 4.18 (1H, dd, J = 10.0, 1.2 Hz, H-2), 3.95 1H, dd, J = 13.2, 9.6 Hz, H-6a), 3.57 (1H, dd, J = 13.2, 2.0 Hz, H-6b), 3.47 (1H, m, H-5),
1.51 (3H, s, CH₃), 1.39 (3H, s, CH₃), 1.33-1.18 (3H, m, CH₃). ¹³C NMR (CDCl₃, 100.6 MHz) δ in ppm: 108.2 (C), 96.9 (CH, C-1), 80.4 (CH, C-4), 78.8 (CH, C-5), 76.5 (CH, C-3), 66.1 (CH₂, CH₂Me), 60.7 (CH₂, C-6), 35.4 (CH, C-2), 27.7 (CH₃), 24.9 (CH₁), 15.6 (CH₃, Et).

26b: ¹H NMR (CDCl₃, 400 MHz) δ in ppm: 5.41 (1H, d, J = 8.0 Hz, H-1), 4.41 (1H, dd, J = 11.6, 7.2 Hz, H-3), 4.33 (1H, m, H-6a), 4.32 (1H, m, H-4), 4.10 (1H, dd, J = 11.6, 8.0 Hz, H-2), 3.78-3.74 (2H, m, H-5, CH₂(Et)), 3.48-3.45 (1H, m, H-6b), 1.51 (3H, s, CH₃), 1.39 (3H, s, CH₃), 1.33-1.18 (3H, m, CH₃). ¹³C NMR (CDCl₃, 100.6 MHz) δ in ppm: 109.1 (C), 98.1 (CH, C-1), 78.5 (CH, C-4), 78.1 (CH, C-5), 77.0 (CH, C-3), 67.0 (CH₂, CH₂Me), 62.0 (CH₂, C-6), 32.5 (CH, C-2), 27.5 (CH₃), 24.5 (CH₁), 15.8 (CH₃, Et). HRMS (TOF MS ES⁺): calcd for C₁₁H₁₉O₅NaI (MNa⁺) 381.0175; found, 381.0180. Elemental Analysis: Calculated: C, 36.89%; H, 5.35%. Found: C: 37.55%, H: 5.47%.

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References and Footnotes


23. For clarity, hydrogen and carbon atoms have been numbered according to the respective alkene starting material.