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Synthetic Routes to Methyl 3-Deoxy-Aldulosonic Acid Methyl Esters and their 2-Deoxy Isomers Based on the Horner-Emmons and Peterson Reaction of Sugar Lactones

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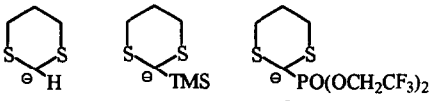
Abstract: The two reagents: 2-trimethylsilyl- and 2-[bis(2,2,2-trifluoroethoxy)phosphoryl]-1,3-dithianes were engaged in the construction of appropriate ketene thioacetals from the isomeric 2-deoxy-hexono-1,5-lactones *via* Horner-Emmons or Peterson reaction. A comparison of the results shows that the second reagent is more promising, as it forms the desired ketene thioacetals as sole products. The latter were directly transformed stereoselectively into the title α ulosonates in an oxidative hydrolysis reaction, using NBS/MeOH in CH_2Cl_2. A construction of the methyl 2-deoxy-ulosonates involved a preceding hydrogenation of the double bond by $LiBH_4$-TMSCl species, and subsequent hydrolysis with NBS in aqueous THF medium.

Keywords: Lactones; Ketene thioacetals; Homologation; Solvolysis.

Introduction

An immense biological role of 3-deoxyulosonic acids[1] has invoked great interest towards elaboration of the stereoselective methods of their synthesis.[2] Among those a sequence involving a homologation of the aldoses by different procedures has been employed.[1-3] One of these procedures reported by Horton *et al.*[4] has been based on the reaction of a 2-deoxy-1,5-lactone with 2-lithio-1,3-dithiane **A** to give an appropriate 1-*C*-(1,3-dithian-2-yl)-2-deoxy-pyranose. Subsequent transformation of 1,3-dithianyl residue to the carbonyl group afforded the desirable ulosonic acid. This result deserved a special attention as it has confirmed that the electrophilicity of the carbonyl group in the lactones is sufficient enough to react with1,3-dithian-2-yl anion.



Having this in mind we decided to explore the reaction of sugar lactones with 2-substituted 1,3-dithianyl reagents **B** and **C**. They were chosen on assumption that 2-substituted 1,3-dithianes generate the higher stabilized intermediate carboanions which might inhibit side reactions.[5,6] Therefore, compound **B**, and **C** should offer the formation of ketene dithiocetals from sugar lactones. The formation of analogous olefins from ketones *via* Peterson[7a] and Horner-Emmons[8] reactions has been well documented,[7] as well as their conversion into carboxylic acids[9] or esters.[10] However, preparation of the ketene dithioacetals from simple lactones or sugar

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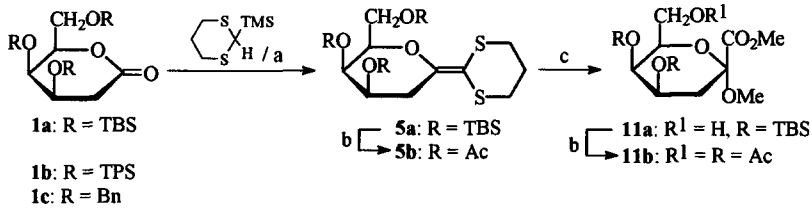
lactones, to our knowledge, has not been reported in the literature.[11] The present study supplements to some extent the ketene dithioacetal methodology, providing an alternative route to 3-deoxy-ulosonic acids.

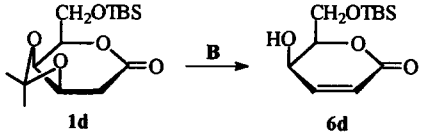
Results and discussion

The experiments were performed with all the isomeric 2-deoxy-hexono-1,5-lactones of the *lyxo* **1**, *arabino* **2**, *ribo* **3** and *xylo* **4** configuration applying the Peterson and Horner-Emmons reagents (**B** and **C**, respectively). The hydroxyl groups in the substrates were protected as *tert*-butyldimethylsilyl (TBS), *tert*-butyldiphenylsilyl (TPS), or benzyl (Bn) ethers. Anion **B** was generated by use of BuLi or *tert*-BuLi at -70 °C → -20 °C. It was observed that the sequence of introduction of both the reaction partners did not influence the course of the reaction (all experimental detail are recorded in the Experimental Section). However, this course of the reaction was strongly influenced by the configuration of the substrate, as well as by its conformation and by the kind of protection of the hydroxyl function. This was well shown in the reaction of the differently substituted 2-deoxy-D-*lyxo*-hexono-1,5-lactone **1** with the anion **B**. Thus, lactone **1a** protected by TBS ethers reacted smoothly to afford the desired ketene dithioacetal **5a** as a sole product, in high yield (Scheme 1).



Scheme 1. Reagents and conditions: a) BuLi, THF, -78 °C → -20 °C; b) TBAF, THF, then Ac_2O, Py; c) NBS, MeOH, CH_2Cl_2, rt.

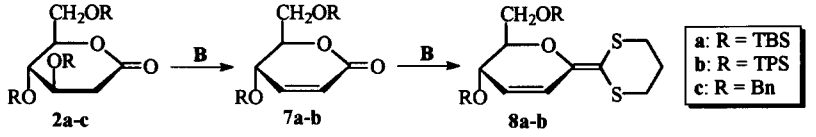
Protection of the 3,4-OH groups in **1** by the isopropylidene residue (**1d**) changed dramatically the course of the reaction, furnishing instead of ketene dithioacetal **5**, an unsaturated lactone **6d** (Scheme 2).



Scheme 2

It seems reasonable that 3,4-*O*-isopropylidene ring attenuated the reactivity of the carbonyl group, possibly through enforcing a conformation of lactone less prone to the reaction with the anion **B**. Formation of the unsaturated lactone **6d** was due to an elimination reaction caused by the basicity of the reagent.[12] The same isomer **1** protected with TPS (**1b**) or benzyl (**1c**) residue failed to react with the anion **B**.

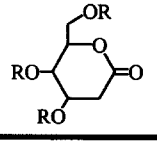
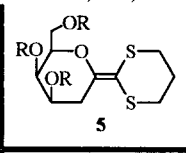
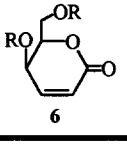
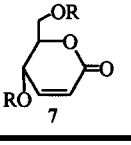
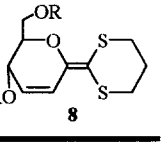
Reaction of the *arabino* isomers both with TBS (**2a**) or TPS (**2b**) protection resulted in the formation of the unsaturated ketene dithioacetals **8a** and **8b** (Scheme 3). The β-elimination process in the sugar molecule, leading to the unsaturated lactones **7** seems to be the first step of reaction. It was just confirmed by the isolation of **7**, which on treatment with an excess of the reagent **B** afforded ketene dithioacetals **8**. This suggests, that silyloxy groups causes steric crowding, making the carbonyl group unable to react with 1,3-dithianyl anion. Elimination of 3-*O*-TBS (or 3-*O*-TPS) ethers from the lactone molecule removes the steric congestion which allows the formation of ketene dithioacetals.



Scheme 3

As noted by others,[13] the *arabino*-1,5-lactone **2** is more prone to the *β*-elimination reaction[14] than its *lyxo* **1** counterpart. This can explain an occurrence of a competing *β*-elimination process during the formation of ketene dithioacetal. Perhaps, similar preference to the elimination reaction occurs in the case of the *xylo* (**3**) and the *ribo* (**4**) isomers (Table 1).

Table 1. Reaction of *O*-silyl derivatives of lactones **1a,b-4a,b** with anion **B** and **C**.

					
		5	**6**	**7**	**8**
R = TBS	**1a**: *lyxo*	**5a** 78%[a], 80%[b]	-	-	-
	2a: *arabino*	-	-	**7a** 78%[a], 82%[b]	**8a** 0%[a], 0%[b], 28%[c]
	3a: *xylo*	-	**6a** 56%[a], 43%[b]	-	-
	4a: *ribo*	-	-	**7a** destruction[a], 15%[b]	-
R = TPS	**1b**: *lyxo*	-	**6b** -[a], 57%[b]	-	-
	2b: *arabino*	-	-	**7b** 40%[a], 75%[b]	**8b** 18%[a], 17%[b]

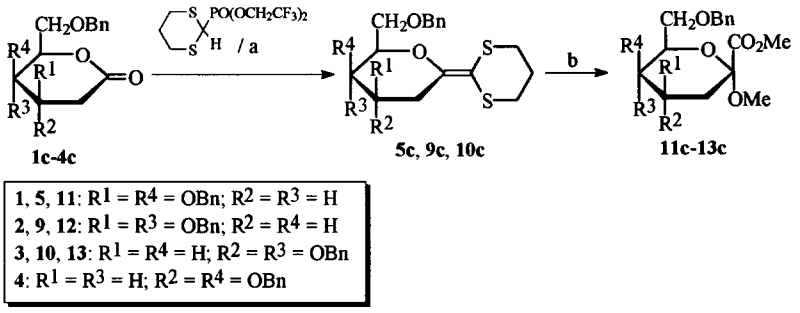
[a] reaction with 1.2 equiv. of anion **B** generated by BuLi, [b] reaction with 1.2 equiv. of anion **C** generated by BuLi, [c] reaction with 4.5 equiv. of anion **B** generated by BuLi.

A lack of the generality following from the reaction of sugar lactones **1-4** with 2-lithio-2-trimethylsilyl-1,3-dithiane (**B**) was compatible with an analogous behaviour of ketones and aldehydes with this reagent,[7a] and it has been explained by a great sensitivity of **B** to the steric hindrance. Perhaps, this was a reason for an inability of the lactone **1b** to react with **B**.

The same series of lactones (**1-4**) was submitted to the reaction with 2-[bis(2,2,2-trifluoroethoxy)phosphoryl]-1,3-dithiane **C** - a reagent, prepared recently by Mikołajczyk and co.[8] It was to be anticipated that the stronger electron withdrawing trifluoroethyl group would stabilize dithianyl anion more efficiently, which allows to avoid the *β*-elimination reaction in pyranose ring. Literature reports[15] concerned the reaction of this anion with ketones having acidic *α*-hydrogens supported such expectation.

For a generation of the anion **C** potassium bis(trimethylsilyl)amide (KHMDS) in THF at -78 °C was found to be a base of choice. To the solution of this anion were introduced separately *O*-benzyl derivatives of lactones **1c-4c**, dissolved in THF, and the reaction was allowed to proceed at 0 °C for ~3h. Then the reaction mixture was neutralised with trifluoroacetic acid and the products were isolated by flash chromatography on silica gel. In all cases but one ketene dithioacetals were formed as sole products (Scheme 4). The yield of reaction were however different, depending on the configuration of the starting lactone. Thus, the highest yields of ketene thioacetals **5c** (82%) and **9c** (62%) were obtained from the *lyxo* (**1c**) and *arabino* (**2c**) isomers, respectively. The *ribo* isomer **4c** gave ketene thioacetal **10c** in a 37% yield, whereas the *xylo* compound **3c** underwent a complete destruction under the reaction conditions. Presumably, the last two compounds having 3-*O*-Bn and 2-*H* in the *axial* position, ideally suited for the elimination reaction, are very unstable in a relation to the reagent **C**.

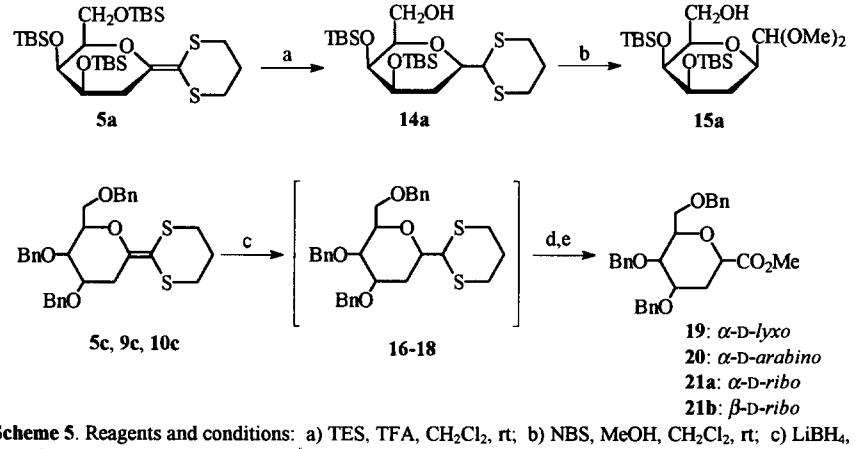
Based on the literature reports[7] we expected that ketene dithioacetals thus obtained should be easy to transform into the 3-deoxy ulosonic acids *via* an oxidative hydrolysis.[16] Unfortunately, neither of the known methods[7] were successful as a route to the hydroxy carboxylic acids. We succeeded when two equivalents of NBS in CH_2Cl_2-MeOH solution were used; ketene dithioacetals **5**, **9**, **10** were readily converted into the *α*-methyl 3-deoxy-ulosonates **11-13** with complete stereoselectivity (Scheme 4).



Scheme 4. Reagents and conditions: a) KHMDS, THF, -78 °C → 0 °C; b) NBS, MeOH, CH_2Cl_2, rt.

It is worth to notice that during hydrolysis of ketene **5a** under these conditions the 7-*O*-TBS residue was lost to give **11a**, which after a complete desilylation (TBAF/THF) and acetylation afforded **11b** (Scheme 1).

Continuing the studies we considered ketene dithioacetals as suitable precursors of 2,3-dideoxy-ulosonic acids. With this aim, the double bond in the ketene dithioacetals has to be reduced. Using TES/TFA,[7] **5a** was readily converted into **14a** (Scheme 5). This procedure, however, was not applicable to the hydrogenation of the benzyl derivatives. Therefore, several methods of a reduction of the double bond were explored.[17] The most satisfactory procedure involved a reaction of **5c**, **9c**, **10c** with $LiBH_4$/TMSCl species in THF[18] which afforded the hydrogenated dithianyl compounds **16-18**. These, without isolation, were subjected to hydrolysis employing the above described procedure for transformation of the dithianyl group into an ester. Unfortunately, hydrolysis led to the acetal **15a** (Scheme 5). To avoid this, the reaction was conducted in THF-H_2O (10:1) solution with 10 fold excess of NBS, followed by treatment of the product with diazomethane. These conditions resulted in the formation of methyl 2,3-dideoxy-ulosonates **19-21** (Scheme 5).



Scheme 5. Reagents and conditions: a) TES, TFA, CH_2Cl_2, rt; b) NBS, MeOH, CH_2Cl_2, rt; c) $LiBH_4$, TMSCl, THF, 50 - 60 °C; d) NBS, THF-H_2O (10:1), rt; e) CH_2N_2, Et_2O.

The hydrogenation was fully stereoselective in the case of the *lyxo* **5c**, and the *arabino* **9c** isomers, affording the α anomers. Hydrogenation-hydrolysis of the *ribo* **10c** isomer led to a mixture of α (**21a**) and β (**21b**) anomers in a (3:2) ratio. The configuration of compound **20** was confirmed by comparison of their NMR spectra with those of compound earlier reported.[3b]

In summary, the above results illustrate that the choice of a proper protecting groups and a fitting anion is the key to construction ketene dithioacetals from sugar lactones.

Further studies on utilising of compounds **5**, **9**, **10** for the synthesis of new sugar derivatives are in progress.

Experimental

General methods

Optical rotations were measured with a JASCO Dip-360 Digital Polarimeter at room temperature. ^{1}H NMR spectra were recorded on Varian AC-200 (200 MHz) and Bruker AM-500 (500 MHz) spectrometers with Me_4Si as internal standard. Mass spectra were taken on a AMD-604 mass spectrometer. IR spectra were taken with a Perkin Elmer FT-IR-1600 spectrophotometer. Reactions were controlled using TLC on silica [Merck alu-plates (0.2 mm)]. All reagents and solvents were purified and dried according to common methods. All organic solutions were dried over $MgSO_4$. Reaction products were purified by flash chromatography using Merck's Kieselgel 60 (240-400 mesh or 70-230 mesh). All acetylation reactions were performed using acetic anhydride-pyridine (1:1) at room temperature (with catalytic amount of DMAP if necessary).

2,6-Anhydro-4,5,7-tri-*O*-(*tert*-butyldimethylsilyl)-1-(propane-1,3-diyl-dithioacetal)-1,3-dideoxy-D-*lyxo*-hept-1-enitol (5a)

2-Trimethylsilyl-1,3-dithiane (79 μL, 0.42 mmol) dissolved in dry THF (3 mL) was treated with a solution of BuLi in hexanes (0.26 mL, 0.42 mmol) at -78 °C under Ar. The mixture was stirred for 30 min and, then added dropwise to a solution of 3,4,6-tri-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*lyxo*-hexono-1,5-lactone (**1a**)[13] (200 mg, 0.40 mmol) in THF (5 mL) at -78 °C. After 30 min the reaction was quenched by addition of TFA (38 μL, 0.5 mmol) and the solvents were evaporated under reduced pressure. Purification by column chromatography on silica gel (hexane/ether, 45:1) afforded **5a** (187 mg, 78%) as an oil: $[\alpha]_D$ +40.0 (c 0.78, $CHCl_3$); ν_{max}(liquid film) 2929.2, 2857.1, 1684.2, 1596.4, 1471.6, 1253.3, 1102.2 cm^{-1}; δ_H (500 MHz, $CDCl_3$): 0.06, 0.07, 0.09, 0.10, 0.11, 0.12 (6×3 H, 6 s, 3×Me_2Si), 0.89, 0.90, 0.92 (3×9 H, 3 s, 3×^{t}BuSi), 2.06-2.17 (2 H, m, H-2'ax, H-2'eq), 2.58 (1 H, dd, *J* 10.8, 14.1 Hz, H-3ax), 2.75-2.82 (4 H, m, H-1'ax, H-1'eq, H-3'ax, H-3'eq), 2.90 (1 H, dd, *J* 4.7, 14.1 Hz, H-3eq), 3.62 (1 H, m, *J* 1.6, 5.6 Hz, H-6), 3.73 (1 H, ddd, *J* 2.1, 4.7, 10.7 Hz, H-4), 3.74-3.82 (2 H, m, H-7a, H-7b), 3.94 (1 H, br s, H-5); δ_C ($CDCl_3$): -4.8, -4.7, -4.4, -4.1, -4.0, -3.5 (3×Si($\underline{Me}$)$_2$CMe_3), 18.2, 18.3, 18.5 (3×Si(Me)$_2\underline{C}Me_3$), 26.5, 26.6, 26.7 (3×Si(Me)$_2$C$\underline{Me}_3$), 26.3, 30.2, 30.9, 31.7, 62.0, 69.9, 71.7, 81.8, 101.2 (C-1), 151.9 (C-2); HRMS (EI): $[M]^+$, found 606.3111. $C_{28}H_{58}O_4S_2Si_3$ requires 606.3084.

2,6-Anhydro-4,5,7-tri-*O*-acetyl-1-(propane-1,3-diyl-dithioacetal)-1,3-dideoxy-D-*lyxo*-hept-1-enitol (5b)

TBAF (252 mg, 0.80 mmol) was added to a solution of **5a** (120 mg, 0.20 mmol) in THF (3 mL). The reaction mixture was stirred at rt. Evaporation of the solvent and acetylation *in situ* gave compound **5b** which was purified by column chromatography (hexane/ether, 1:1) (60 mg, 78%): colourless oil: $[\alpha]_D$ +94.3 (c 1.00, $CHCl_3$); δ_H (200 MHz, $CDCl_3$): 2.02, 2.08, 2.14 (3×3 H, 3 s, 3×Ac), 2.00-2.15 (2 H, m, H-2'ax, H-2'eq), 2.47 (1 H, dd, *J* 11.9, 19.9 Hz, H-3ax), 2.70-2.90 (4 H, m, H-1'ax, H-1'eq, H-3'ax, H-3'eq), 3.20 (1 H, dd, *J* 5.3, 13.9 Hz, H-3eq), 3.98 (3 H, m, H-6, H-7a, H-7b), 5.00 (1 H, ddd, *J* 2.9, 5.3, 11.9 Hz, H-4), 5.38 (1 H, m, H-5); δ_C ($CDCl_3$): 21.2, 21.3, 21.4 (3×Ac), 25.6, 27.7, 29.5, 30.4, 62.3, 66.6, 68.8, 75.9, 110.9 (C-1), 147.2 (C-2), 170.5, 170.7, 171.1 (3×Ac).

6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-D-*threo*-hex-2-eno-1,5-lactone (6d)

Based on the above described procedure, the reaction of **1d**[20] (100 mg, 0.32 mmol) with the anion **B**, after work up in the usual way followed by filtration through a silica column afforded **6d** (51 mg, 62%) as a colourless oil: $[\alpha]_D$ -88.5 (c 0.83, $CHCl_3$); ν_{max}(liquid film) 2954.0, 2930.5, 2857.5, 1713.9, 1471.4, 1256.9, 1097.9 cm^{-1}; δ_H ($CDCl_3$): 0.13 (6 H, s, Me_2Si), 0.90 (9 H, s, ^{t}BuSi), 3.09 (1 H, d, *J* 5.5 Hz, OH,), 4.02 (1 H, dd, *J* 4.8, 10.8 Hz, H-6a), 4.10 (1 H, dd, *J* 6.2, 10.8 Hz, H-6b), 4.34-4.46 (2 H, m, H-4, H-5), 6.14 (1 H, d, *J* 9.7 Hz, H-2), 7.00 (1 H, dd, *J* 5.5, 9.7 Hz, H-3); HRMS (LSIMS): $[M+H]^+$, found 259.1337. $C_{12}H_{22}O_4Si$ requires 259.1366.

4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-D-*erythro*-hex-2-eno-1,5-lactone (7a) and 2,6-anhydro-5,7-di-*O*-(*tert*-butyldimethylsilyl)-3,4-dideoxy-1-(propane-1,3-diyl-dithioacetal)-D-*erythro*-hept-3-en-1-enitol (8a)

Based on the procedure described for preparation of **5a** lactone **2a**[13] (100 mg, 0.20 mmol) was treated with the anion **B** (1.5 eqiuiv.) at -78 °C. Then the reaction was allowed to warm slowly at -20 °C for 2 h. Neutralisation

with TFA and column chromatography gave **7a** as a white solid (57 mg, 78%); m.p. 45 °C $[\alpha]_D$ +44.5 (c, 0.87 in $CHCl_3$); (lit. m.p. 36-38 °C; $[\alpha]_D$ +29.0 (c, 1.0 in $CHCl_3$) [13]); ν_{max}(KBr) 2955.6, 2928.4, 2857.0, 1749.0, 1472.4, 1256.9, 1143.7 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 0.09, 0.09, 0.13, 0.13 (4×3 H, 4 s, 2×Me_2Si), 0.90, 0.91 (2×9 H, 2 s, 2×^{t}BuSi), 3.79-3.94 (2 H, m, H-6a, H-6b), 4.18 (1 H, m, *J* 2.8, 6.1 Hz, H-5), 4.70 (1 H, m, *J* 2.0, 8.8 Hz, H-4), 4.91 (1 H, dd, *J* 10.0, 1.9 Hz, H-2,), 5.72 (1 H, dd, *J* 10.0, 2.2 Hz H-3); HRMS (LSIMS): $[M+H]^+$, found 373.2235. $C_{18}H_{36}O_4Si_2$ requires 373.2230.

When **2a** was treated with 4.5 equiv. of anion at -40 °C (~2 h) **8a** was isolated from the reaction mixture (26 mg, 28%): white yellow oil; $[\alpha]_D$ +56.6 (c 1.43, $CHCl_3$); δ_H (200 MHz, $CDCl_3$): 0.09, 0.10, 0.10, 0.12 (4×3 H, 4 s, 2×Me_2Si), 0.98, 0.99 (2×9 H, 2 s, 2×^{t}BuSi), 2.05-2.20 (2 H, m, H-2'ax, H-2'eq), 2.75-2.92 (4 H, m, H-1'ax, H-1'eq, H-3'ax, H-3'eq), 3.64 (1 H, m, H-6), 3.86 (2 H, m, H-7a, H-7b), 4.47 (1 H, m, H-5), 5.75 (1 H, dd, *J* 10.2, 2.5 Hz, H-3), 6.67 (1 H, dd, *J* 1.9, 10.2 Hz, H-4); HRMS (LSIMS): $[M]^+$, found 474.2112. $C_{22}H_{42}O_3S_2Si_2$ requires 474.2114.

Analogous sample **8a** was isolated in 36% yield from a reaction of **7a** with anion **B**.

4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-D-*threo*-hex-2-eno-1,5-lactone (6a)

Based on the previously described procedure, reaction of **3a**[20] (100 mg, 0.20 mmol) with **B** gave after usual isolation the product **6a** (41 mg, 56%) as a white solid: m.p. 58-60 °C; $[\alpha]_D$ -148.2 (c 1.12, $CHCl_3$); ν_{max}(KBr) 2953.0, 2931.6, 2857.8, 1714.9, 1257.2, 1089.5 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 0.08, 0.10, 0.10, 0.11 (4×3 H, 4 s, 2×Me_2Si), 0.88, 0.89 (2×9 H, 2 s, 2×^{t}BuSi), 3.82 (1 H, dd, *J* 5.3, 10.0 Hz, H-6a), 3.96 (1 H, dd, *J* 7.6, 10.0 Hz, H-6b), 4.22-4.34 (2 H, m, H-4, H-5), 6.08 (1 H, dd, *J* 9.7, 0.8 Hz, H-2), 6.88 (1 H, dd, *J* 9.7, 5.5 Hz, H-3); HRMS (EI): $[M-^tBu]^+$, found 315.1439. $C_{18}H_{36}O_4Si_2$ requires 315.1448.

A - General procedure for reaction of lactones with potassium (or lithium)-2-[bis(2,2,2-trifluoroethoxy)phosphoryl]-1,3-dithiane.

A solution of potassium bis(trimethylsilyl)amide in toluene (2.0 equiv.) was added dropwise to 2-[bis(2,2,2-trifluoroethoxy)phosphoryl]-1,3-dithiane (**C**, 2.0 equiv.) dissolved in anhydrous THF (5 mL/mmol of lactone) at -78 °C under Ar. The temperature was maintained at -78 °C for 1h and then a solution of an appropriate hexono-1,5-lactone in THF (1.5-2 mL/mmol) was added dropwise. The reaction was stirred for ~3 h while the temperature was allowed to rise to 0 °C. The reaction was neutralised with TFA, and the crude product was purified by flash chromatography.

2,6-Anhydro-4,5,7-tri-*O*-benzyl-1-(propane-1,3-diyl-dithioacetal)-1,3-dideoxy-D-*lyxo*-hept-1-enitol (5c)

Based on the procedure **A** **1c**[13] (1.29 g, 3 mmol) was reacted with anion **C** to give after usual work-up and chromatography the product **5c**[11] as a white solid: yield 82%, m.p. 69-70 °C, $[\alpha]_D$ +51.9 (c 1.19, $CHCl_3$); ν_{max}(KBr) 3061.1, 3027.8, 2896.5, 1868.3, 1807.7, 1586.3, 1227.4, 1103.3 cm^{-1}; δ_H (500 MHz, $CDCl_3$): 2.08-2.14 (2 H, m, H-2'ax, H-2'eq), 2.63 (1 H, dd, *J* 11.8, 14.2 Hz, H-3ax), 2.71-2.85 (4 H, m, H-1'ax, H-1'eq, H-3'ax, H-3'eq), 3.30 (1 H, ddd, *J* 0.9, 5.1, 14.2 Hz, H-3eq), 3.64 (1 H, ddd, *J* 2.2, 4.9, 11.6 Hz, H-4), 3.73 (2 H, m, H-7a, H-7b), 3.83 (1 H, td, *J* 1.3, 6.2 Hz, H-6), 3.93 (1 H, br s, H-5), 4.46-4.94 (3×2 H, 3×ABq, C$\underline{H_2}$Ph), 7.22-7.40 (15 H, m, Ar); δ_C ($CDCl_3$): 25.5 (C-2'), 28.0 (C-3), 29.6 (C-3'), 30.3 (C-1'), 68.8 (C-7), 70.4 (Bn), 72.5 (C-5), 73.5 (Bn), 74.1 (Bn), 76.7 (C-4), 78.7 (C-6), 105.6 (C-1), 127.3-128.4 and 138.1-138.6 (Ar), 150.3 (C-2); HRMS (LSIMS): $[M+Na]^+$, found 557.1823. $C_{31}H_{34}O_4S_2$ requires 557.1796.

2,6-Anhydro-4,5,7-tri-*O*-benzyl-1-(propane-1,3-diyl-dithioacetal)-1,3-dideoxy-D-*arabino*-hept-1-enitol (9c)

Based on the procedure **A** **2c**[13] (864 mg, 2 mmol) was reacted with anion **C** to give after usual work-up and chromatography the product **9c**[11] as a white solid: yield 62%, m.p. 40-42 °C, $[\alpha]_D$ +44.9 (c 1.08, $CHCl_3$); δ_H (500 MHz, $CDCl_3$): 2.09-2.14 (2 H, m, H-2'ax, H-2'eq), 2.47 (1 H, dd, *J* 8.8, 14.5 Hz, H-3ax), 2.73-2.84 (4 H, m, H-1'ax, H-1'eq, H-3'ax, H-3'eq), 3.32 (1 H, ddd, *J* 4.8, 14.7 Hz, H-3eq), 3.67-3.76 (3 H, m, H-4, H-5, H-6), 3.77 (1 H, dd, *J* 3.5, 11.3 Hz, H-7a), 3.81 (1 H, dd, *J* 2.4, 11.3 Hz, H-7b), 4.54-4.82 (3×2 H, 3×ABq, C$\underline{H_2}$Ph), 7.15-7.40 (15 H, m, Ar); δ_C ($CDCl_3$): 25.5 (C-2'), 29.7 (C-3), 30.4 (C-3'), 30.5 (C-1'), 68.9 (C-7), 71.2 (Bn), 73.5 (C-5), 74.1 (Bn), 77.4 (Bn), 78.2 (C-4), 79.3 (C-6), 105.6 (C-1), 127.5-128.4 and 138.1-138.3 (Ar), 150.2 (C-2); HRMS (LSIMS): $[M]^+$, found 534.1889. $C_{31}H_{34}O_4S_2$ requires 534.1899.

2,6-Anhydro-4,5,7-tri-*O*-benzyl-1-(propane-1,3-diyl-dithioacetal)-1,3-dideoxy-D-*ribo*-hept-1-enitol (10c)
Based on the procedure **A** **3c**[20] (150 mg, 0.35 mmol) was reacted with anion **C** to give after usual work-up and chromatography the product **10c** as an oil (69 mg, 37%): $[\alpha]_D$ +96.0 (c 1.02, $CHCl_3$); ν_{max}(liquid film) 3029.6, 2918.8, 1878.0, 1811.3, 1683.4, 1495.9, 1453.2, 1094.8 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 2.06 (2 H, m, H-2'ax, H-2'eq), 2.18 (1 H, dd, *J* 2.75, 15.0 Hz, H-3ax), 2.65 (4 H, m, H-1'ax, H-1'eq, H-3'ax, H-3'eq), 3.48 (1 H, dd, *J* 4.8, 15.2 Hz, H-3eq), 3.75-3.88 (3 H, m, H-5, H-7a, H-7b), 3.92 (1 H, m, H-4), 4.29 (1 H, dt, *J* 3.0, 8.9 Hz, H-6), 4.44-4.25 (3×2 H, 3×ABq, $C\underline{H}_2Ph$), 7.20-7.40 (15 H, m, Ar); HRMS (LSIMS): $[M]^+$, found 534.1907. $C_{31}H_{34}O_4S_2$ requires 534.1899.

4,6-Di-*O*-(*tert*-butyldiphenylsilyl)-2,3-dideoxy-D-*threo*-hex-2-eno-1,5-lactone (6b)
Based on the procedure **A** a reaction of **3b**[20] (175 mg, 0.20 mmol) with **C** (BuLi) after usual isolation of the product afforded **6b** as a colourless oil: yield 57%; $[\alpha]_D$ -81.4 (c 1.15, $CHCl_3$); ν_{max}(liquid film) 3071.3, 2957.4, 2931.4, 2853.6, 1893.0, 1823.6, 1716.0, 1471.9, 1427.9, 1113.0 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 0.97, 1.07 (2×9 H, 2 s, 2×^{t}BuSi), 3.98-4.16 (2 H, m, H-6a, H-6b), 4.26 (1 H, ddd, *J* 2.7, 6.0 Hz, H-5), 4.38 (1 H, dd, *J* 2.8, 5.4 Hz, H-4), 5.88 (1 H, d, *J* 9.7 Hz, H-2), 6.36 (1 H, dd, *J* 5.3, 9.7 Hz, H-3), 7.25-7.75 (20 H, m, Ar).

4,6-Di-*O*-(*tert*-butyldiphenylsilyl)-2,3-dideoxy-D-*erythro*-hex-2-eno-1,5-lactone (7b) and 2,6-anhydro-3,4-dideoxy-5,7-di-*O*-(*tert*-butyldiphenylsilyl)-1-(propane-1,3-diyl-dithioacetal)-D-*erythro*-hept-3-en-1-enitol (8b)
2b[20] (175 mg, 0.20 mmol) was combined with anion **C** (BuLi) (2.0 equiv., procedure **A**), at -78 °C. The reaction was warmed to rt for 2 h, then quenched by addition of solid NH_4Cl. Evaporation of the solvents left a syrup which was subjected to chromatography on a silica gel column. Elution with hexane/ether (4:1) afforded **8b** (30 mg, 18%) in the first fraction: yellow oil; $[\alpha]_D$ +38.6 (c 1.33, $CHCl_3$); δ_H (200 MHz, $CDCl_3$): 0.99, 1.00 (2×9 H, 2 s, 2×^{t}BuSi), 2.05-2.21 (2 H, m, H-2'ax, H-2'eq), 2.75-2.94 (4 H, m, H-1'ax, H-1'eq, H-3'ax, H-3'eq), 3.52-3.85 (2 H, 2× dd, *J* 3.2, 5.0, 11.0 Hz, H-7a, H-7b), 4.06 (1 H, m, H-6), 4.51 (1 H, m, H-5), 5.55 (1 H, dd, *J* 2.9, 10.3 Hz, H-3), 6.58 (1 H, dd, *J* 1.7, 10.3 Hz, H-4), 7.25-7.72 (20 H, m, Ar).
The second fraction contained the lactone **7b** as a clear syrup: (92 mg, 75%): $[\alpha]_D$ +55.0 (c 1.08, $CHCl_3$); ν_{max}(liquid film) 3071.1, 2957.7, 3931.5, 2857.8, 1893.8, 1825.4, 1738.7, 1427.7, 1111.8 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 0.96, 1.03 (2×9 H, 2 s, 2×^{t}BuSi), 3.72 (1 H, dd, *J* 4.4, 11.1 Hz, H-6a), 3.82 (1 H, dd, *J* 3.9, 11.2 Hz, H-6a), 4.52 (1 H, m, H-5), 4.62 (1 H, ddd, *J* 1.2, 4.0, 6.1 Hz, H-4), 5.80 (1 H, dd, *J* 1.2, 9.9 Hz, H-2), 6.40 (1 H, dd, *J* 3.3, 10.2 Hz, H-3), 7.25-7.72 (20 H, m, Ar).
When KHMDS was used as a base **7b** was isolated as a sole product (63%). The use of 4 equivalents of anion **C** gave **8b** in 72% yield.

Methyl [methyl 4,5-di-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-α-D-*lyxo*-hept-2-ulopyranosid]onate (11a)
A solution of **5a** (60 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) was treated with methanol (0.5 mL) and NBS (45 mg, 0.25 mmol). The mixture was stirred at rt until the reaction was complete (~0.5 h), and then was filtered through a short column of silica gel and evaporated. The residue was purified by chromatography on silica to give the ester **11a** as crystals (41 mg, 73%): m.p. 115-117 °C; $[\alpha]_D$ +40.9 (c 1.16, $CHCl_3$); δ_H (200 MHz, $CDCl_3$): 0.07, 0.09, 0.10, 0.10 (4×3 H, 4 s, 2×Me_2Si), 0.89, 0.90 (2×9 H, 2 s, 2×^{t}BuSi), 1.62 (1 H, br s, OH), 1.86 (1 H, dd, *J* 0.9, 4.6, 12.5 Hz, H-3eq), 2.09 (1 H, dd, *J* 11.4, 12.4 Hz, H-3ax), 3.23 (3 H, s, OMe), 3.62-3.78 (2 H, m), 3.80 (3 H, s, CO_2Me), 3.90-4.00 (2 H, m), 4.06 (1 H, ddd, *J* 2.4, 4.6, 11.3 Hz, H-4); HRMS (LSIMS): $[M+Na]^+$, found 487.2523. $C_{21}H_{44}O_7Si_2$ requires 487.2523.

Methyl [methyl 4,5,7-tri-*O*-acetyl-3-deoxy-α-D-*lyxo*-hept-2-ulopyranosid]onate (11b)
This compounds was obtained from **11a** (100 mg, 0.26 mmol) by a procedure above described, for **5b**, to give 64 mg (69%) of **11b** which was identical by the NMR data with those previously described in the literature.[19]

B - General procedure for transformation of ketene dithioacetals into α-methyl glycosides of ulosonic acid methyl esters.

A solution of ketene dithioacetal (**5**, **9**, **10**) (100 mg, 0.19 mmol) in CH_2Cl_2 (3 mL) was treated with methanol (1mL) and NBS (68 mg, 0.38 mmol). The mixture was stirred at rt until the reaction was complete (~0.5 h), and then was filtered through a short column of silica gel and evaporated. The residue was purified by chromatography on silica to give the desired esters. All compounds after hydrogenolysis (H_2-Pd/C, EtOH) and acetylation were transformed into per-*O*-acetyl-α-methoxy esters identical by the NMR data with those synthesized by a previously elaborated methodology.[19]

Methyl (methyl 4,5,7-tri-*O*-benzyl-3-deoxy-α-D-*lyxo*-hept-2-ulopyranosid)onate (11c)

This compounds was obtained from **5c** by a procedure **B**: colourless oil; yield 87%; $[\alpha]_D$ +23.0 (c, 0.92 in $CHCl_3$); ν_{max}(liquid film) 3491.5, 3030.6, 2915.0, 1747.6, 1453.9, 1064.8 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 2.20-2.30 (2 H, m, H-3ax, H-3eq), 3.22 (3 H, s, OMe), 3.64-3.77 (3 H, m, H-6, H-7a, H-7b), 3.79 (3 H, s, CO_2Me), 3.90 (1 H, br s, H-5), 3.93 (1 H, m, H-4), 4.41-4.95 (3×2 H, 3×ABq, $C\underline{H}_2Ph$), 7.22-7.35 (15 H, m, Ar); HRMS (LSIMS): $[M+Na]^+$, found 529.2200. $C_{30}H_{34}O_7$ requires 529.2202.

Methyl (methyl 4,5,7-tri-*O*-benzyl-3-deoxy-α-D-*arabino*-hept-2-ulopyranosid)onate (12c)

This compounds was obtained from **9c** by a procedure **B**: colourless oil; yield 92%; $[\alpha]_D$ +41.3 (c, 1.16 in $CHCl_3$); (lit. $[\alpha]_D$ +36.5 (c, 2.0 in $CHCl_3$) [3b]); δ_H (200 MHz, $CDCl_3$): 1.76 (1 H, dd, *J* 11.2, 13.0 Hz, H-3ax), 2.52 (1 H, dd, *J* 5.1, 13.0 Hz, H-3eq), 3.24 (3 H, s, OMe), 3.54-3.80 (4 H, m, H-5, H-6, H-7a, H-7b), 3.81 (3 H, s, CO_2Me), 4.02 (1 H, ddd, *J* 5.1, 8.4, 11.2 Hz, H-4), 4.50-4.90 (3×2 H, 3×ABq, $C\underline{H}_2Ph$), 7.15-7.40 (15 H, m, Ar); HRMS (LSIMS): $[M+Na]^+$, found 529.2189. $C_{30}H_{34}O_7$ reqiures 529.2202.

Methyl (methyl 4,5,7-tri-*O*-benzyl-3-deoxy-α-D-*ribo*-hept-2-ulopyranosid)onate (13c)

Based on the procedure **B** the ketene dithioacetal **10c** was transformed into the ester **13c** (75 mg, 79%): colourless oil; $[\alpha]_D$ +61.7 (c, 1.50 in $CHCl_3$); δ_H (200 MHz, $CDCl_3$): 2.72 (1 H, dd, *J* 3.4, 15.0 Hz, H-3ax), 2.53 (1 H, dd, *J* 3.5, 15.0 Hz, H-3eq), 3.30 (3 H, s, OMe), 3.65 (1 H, dd, *J* 3.0, 9.5 Hz, H-5), 3.79 (3 H, s, CO_2Me), 3.94 (2 H, m, H-7a, H-7b), 3.94 (1 H, m, H-4), 4.30 (1 H, dt, *J* 3.1, 6.6, 9.7 Hz, H-6), 4.37-4.83 (3×2 H, 3×ABq, $C\underline{H}_2Ph$), 7.20-7.40 (15 H, m, Ar); HRMS (LSIMS): $[M+Na]^+$, found 529.2189. requires $C_{30}H_{34}O_7$ 529.2202.

2,6-Anhydro-4,5-di-O-(tert-butyldimethylsilyl)-1-(propane-1,3-diyl-dithioacetal)-1,3-dideoxy-D-*lyxo*-heptose (14a)

Trifluoroacetic acid (55 μL, 0.72 mmol) was added dropwise to a stirred solution of ketene dithioacetal **5a** (110 mg, 0.18 mmol) and triethylsilane (114 μL, 0.72 mmol) in anhydrous CH_2Cl_2 (2 mL) at -20 °C under Ar. The solution was stirred overnight at rt, then neutralised with triethylamine. After evaporation the residue was chromatographed on silica gel (hexane/ether, 3:2) to give crystalline **14a** (65 mg, 73%): m.p. 124 °C; $[\alpha]_D$ -7.7 (c 0.93, $CHCl_3$); ν_{max}(KBr) 3556.4, 2954.0, 2856.9, 1471.2, 1103.0 cm^{-1}; δ_H (500 MHz, $CDCl_3$): 0.04, 0.08, 0.09, 0.11 (4×3 H, 4 s, 2×Me_2Si), 0.89, 0.91 (2×9 H, 2 s, 2×^{t}BuSi), 1.63 (1 H, m, *J* 2.11, 3.6, 13.6 Hz, H-3eq), 1.86-1.96 (2 H, m, H-2'ax, H-2'eq), 2.12 (1 H, m, *J* 11.5 Hz, H-3ax), 2.80-2.94 (4 H, m, H-1'ax, H-1'eq, H-3'ax, H-3'eq), 3.40 (1 H, dd, *J* 4.0, 8.1 Hz), 3.53 (1 H, m), 3.63 (1 H, ddd, *J* 2.2, 5.3, 11.5 Hz, H-2), 3.68-3.71 (2 H, m, H-7a, H-7b), 3.87 (1 H, m), 4.14 (1 H, d, *J* 5.3 Hz, H-1); δ_C (500 MHz, $CDCl_3$): -4.7, -4.6, -4.3, -3.7 (2×Si($\underline{Me}$)$_2$CMe_3), 18.4, 18.5 (2×Si(Me)$_2\underline{C}$Me$_3$), 26.0, 26.2 (2×Si(Me)$_2$C$\underline{Me}_3$), 26.1, 30.1, 30.2, 32.5, 51.5, 63.6, 70.2, 72.7, 78.4, 80.3; HRMS (EI): $[M]^+$, found 494.2381. $C_{22}H_{46}O_4S_2Si_2$ requires 494.2376.

Carbonylo [4,5-di-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-α-D-*lyxo*-hept-2-ulopyranosid] dimethylacetal (15a)

A solution of **14a** (100 mg, 0.20 mmol) in CH_2Cl_2 (4 mL) was treated with methanol (1 mL) and NBS (80 mg, 0.45 mmol). The mixture was stirred at rt until the reaction was complete (~0.5 h), and then was filtered through a short column of silica gel and evaporated. The residue was purified by chromatography on silica to give the dimethyl acetal **15a** (59 mg, 65%) as an oil: $[\alpha]_D$ +23.5 (c 1.74, $CHCl_3$); ν_{max}(liquid film) 3468.3,

2954.8, 2857.4, 1471.4, 1255.2, 1107.2 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 0.05, 0.08, 0.10, 0.12 (4×3 H, 4 s, 2×Me_2Si), 0.90, 0.91 (2×9 H, 2 s, 2×^{t}BuSi), 1.57 (1 H, m, *J* 2.2, 4.0, 12.4 Hz, H-3eq), 1.88 (1 H, q, H-3ax), 2.06 (1 H, dd, *J* 2.9, 9.2 Hz, OH), 2.24-3.60 (2 H, m), 3.39, 3.42 (2×3 H, 2 s, 2×OMe), 3.58-3.80 (2 H, m), 3.88 (1 H, m), 4.27 (1 H, d, *J* 5.6 Hz, H-1); HRMS (LSIMS): $[M+Na]^+$, found 473.2719. $C_{21}H_{46}O_6Si_2$ requires 473.2731.

C - General procedure for the reduction of the double bond in the ketene dithioacetals and subsequent hydrolysis of the dithiane function.

To a mixture of $LiBH_4$ (11 mg, 0.5 mmol) in dry THF (2 mL) was added TMSCl (160 μL, 1.25 mmol) at rt under Ar, and the reaction was stirred for 1 h at rt. Then the solution of ketene dithioacetal (55 mg, 0.1 mmol) in THF was added dropwise. The mixture was slowly warmed to 40-50 °C and stirring was continued until disappearance of the substrate (TLC, hexane-ether, 1:1). Then methanol was cautiously added, followed by neutralisation with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ether. After concentration, the crude product was redissolved in a mixture THF-water (9:1, 3 mL) and NBS (178 mg, 1 mmol) was added in one portion at rt. The mixture was stirred until TLC showed disappearance of the substrate. The reaction was washed with saturated aqueous Na_2SO_3 and extracted with AcOEt. The organic layers were washed with brine, dried and concentrated. The resulting crystals were redissolved in ether and treated with a solution of CH_2N_2 in ether. After evaporation the residue was chromatographed on silica gel to give the desired 2-deoxy esters.

Methyl (4,5,7-tri-*O*-benzyl-2,3-dideoxy-α-D-*lyxo*-hept-2-ulopyranosid)onate (19)

According to the procedure **C**, ketene dithioacetal **5c** was transformed into 2-deoxy ester **19** (52%): colourless oil; $[\alpha]_D$ -6.4 (c 1.34, $CHCl_3$); ν_{max}(liquid film) 3386.4, 3030.8, 2866.4, 1755.6, 1602.8, 1113.5 cm^{-1}; δ_H (200 MHz, C_6D_6): 2.20 (1 H, m, *J* 12.3 Hz, H-3eq), 2.50 (1 H, q, *J* 12.1 Hz, H-3ax), 3.27 (1 H, ddd, *J* 2.2, 4.2, 11.4 Hz, H-4), 3.41 (3 H, s, CO_2Me), 3.46 (1 H, m, H-6), 3.75-3.92 (4 H, m, H-2, H-5, H-7a, H-7b), 4.20-5.20 (3×2 H, 3×ABq, $C\underline{H}_2Ph$), 7.15-7.50 (15 H, m, Ar); HRMS (LSIMS) $[M+Na]^+$ found 499.2039. $C_{29}H_{32}O_6$ requires 499.2097; hydrogenolysis and acetylation this compound gave **methyl (4,5,7-tri-*O*-acetyl-2,3-dideoxy-α-D-*lyxo*-hept-2-ulopyranosid)onate**: δ_H (200 MHz, C_6D_6): 1.71, 1.72, 1.79 (3×3 H, 3 s, 3×Ac), 1.97 (1 H, dddd, *J* 1.0, 2.5, 5.0, 12.6 Hz, H-3eq), 2.22 (1 H, q, *J* 12.3 Hz, H-3ax), 3.34 (3 H, s, CO_2Me), 3.42 (1 H, td, *J* 1.1, 6.6 Hz, H-6), 3.70 (1 H, dd, *J* 2.6, 12.1 Hz, H-2), 4.28 (2 H, m, H-7a, H-7b), 4.90 (1 H, ddd, *J* 3.2, 5.0, 12.1 Hz, H-4), 5.46 (1 H, m, H-5).

Methyl (4,5,7-tri-*O*-benzyl-2,3-dideoxy-α-D-*arabino*-hept-2-ulopyranosid)onate (20)

Based on the procedure **C**, ketene dithioacetal **9c** was converted into the ester **20** (58%) identically by the NMR data with this previously described in the literature[3b]: ν_{max}(KBr) 3029.0, 2920.8, 2870.7, 1752.8, 1453.0, 1112.5 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 1.72 (1 H, q, *J* 12.3 Hz, H-3ax), 2.50 (1 H, ddd, *J* 2.1, 4.8, 12.9 Hz, H-3eq), 3.46-3.80 (5 H, m), 3.77 (3 H, s, CO_2Me), 4.02 (1 H, dd, *J* 2.2, 12.1 Hz, H-2), 4.50-4.92 (3×2 H, 3×ABq, $C\underline{H}_2Ph$), 7.12-7.40 (15 H, m, Ar).

Methyl (4,5,7-tri-*O*-benzyl-2,3-dideoxy-α (21a) and β-D-*ribo*-hept-2-ulopyranosid)onate (21b)

Processing was similar to that described for the preparation of **19**, to give after column chromatography (toluene/ether, 95:5) pure two anomers in a ratio α:β (3:2) (overal yield 55%). Eluted first was the α-isomer **21a** as a colourless oil (33%): $[\alpha]_D$ +27.0 (c 0.90, $CHCl_3$); δ_H (200 MHz, C_6D_6): 1.69 (1 H, m, *J* 2.1, 12.1, 14.0 Hz, H-3ax), 2.26 (1 H, ddd, *J* 2.2, 3.7, 13.9 Hz, H-3eq), 3.43 (3 H, s, CO_2Me), 3.65 (1 H, dd, *J* 2.6, 9.7 Hz, H-5), 3.75 (1 H, m, H-4), 3.28-4.00 (2 H, m, H-7a, H-7b), 4.20-4.52 (8 H, m, H-2, H-6, 3×$C\underline{H}_2Ph$), 7.10-7.50 (15 H, m, Ar); HRMS (LSIMS) $[M+Na]^+$ found 499.2057. $C_{29}H_{32}O_6$ requires 499.2097; eluted second was β-isomer **21b**: colourless oil (22%): $[\alpha]_D$ +68.1 (c 0.36, $CHCl_3$); δ_H (200 MHz, C_6D_6): 1.52 (1 H, ddd, *J* 14.2, 6.9, 1.9 Hz, H-3ax), 2.55 (1 H, ddd, *J* 14.1, 3.8, 1.3 Hz, H-3eq), 3.37 (3 H, s, CO_2Me), 3.55-4.05 (4 H, m, H-4, H-5, H-7a, H-7b), 4.30-4.52 (7 H, m, H-2, 3×$C\underline{H}_2Ph$), 4.95 (1 H, m, H-6), 7.10-7.50 (15 H, m, Ar); HRMS (LSIMS): $[M+Na]^+$, found 499.2044. $C_{29}H_{32}O_6$ requires 499.2097.

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