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REGIOSELECTIVITY IN THE FREE RADICAL DEOXYGENATION OF DIOL THIOCARBONATES INVOLVING THE TERTIARY HYDROXY GROUP OF BRANCHED CHAINED SUGARS [+]

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Abstract

The cyclic thiocarbonates 1 to 3 react with tri-(n-butyl)tin hydride under formation of the deoxygenation products 10, 11, 12, and 14. The unexpected regioselectivity of this reaction with the compounds 2 and 3 will be discussed in the following.

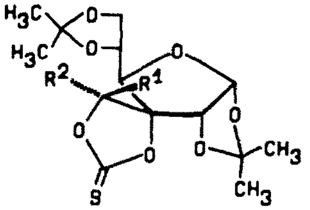
Introduction

Radical deoxygenation reactions at carbohydrates are very valuable because of the fact that the normal sequence of reactivity for the hydroxy-(or oxy-)substituents (primary > secondary > tertiary) can be reversed. In comparison with alternative methods it is therefore relatively easy to remove oxygen from the otherwise difficult accessible secondary[1] or even tertiary[2,2a] positions. In cases were oxygens of different reactivity compete, as for example in cyclic thiocarbonates, Barton and Subramanian [3] were able to show that regioselectivity of the intermediate radical formation - and hence deoxygenation - depends on various factors.

When the thiocarbonate is formed from a primary and a secondary hydroxyl-group of a sugar the deoxygenation takes place at the secondary position in accordance with the idea that in between the more stable secondary radical is formed. When the thiocarbonate is derived from secondary hydroxyl-groups a certain regioselectivity can still be observed for the radical deoxygenation with tri-(n-butyl)tin hydride. Steric or/and stereoelectronic factors must be held responsible for this observation.

[+] Taken as part 29 of the series 'Branched Carbohydrates' Part 28, H.Redlich, H-J.Neumann and H.Paulsen, J.Chem. Res (S) 1982, 36

In this work the branched chain sugars 1, 2 and 3 containing a cyclic thiocarbonate group at the branching point are reacted with tri-(n-butyl)tin hydride. In these cases the arrangements primary/tertiary and secondary/tertiary occur which have not as yet been investigated for carbohydrates. In order to avoid stereochemical complications at the branching point the 1,2;5,6-di-O-isopropylidene-D-ribo-furanose system was chosen as a model substance because it is known of this substance that hydrogen transfer to C-3 takes place from above the plane of the furane ring[4].

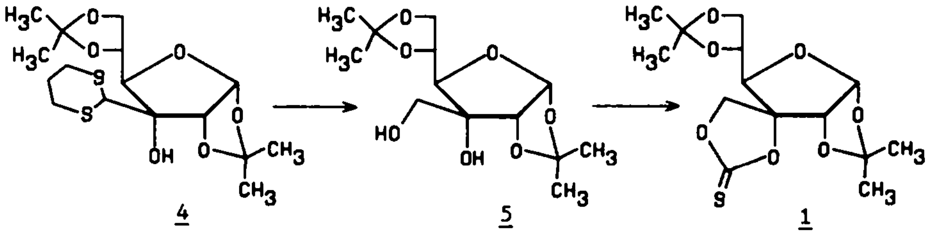


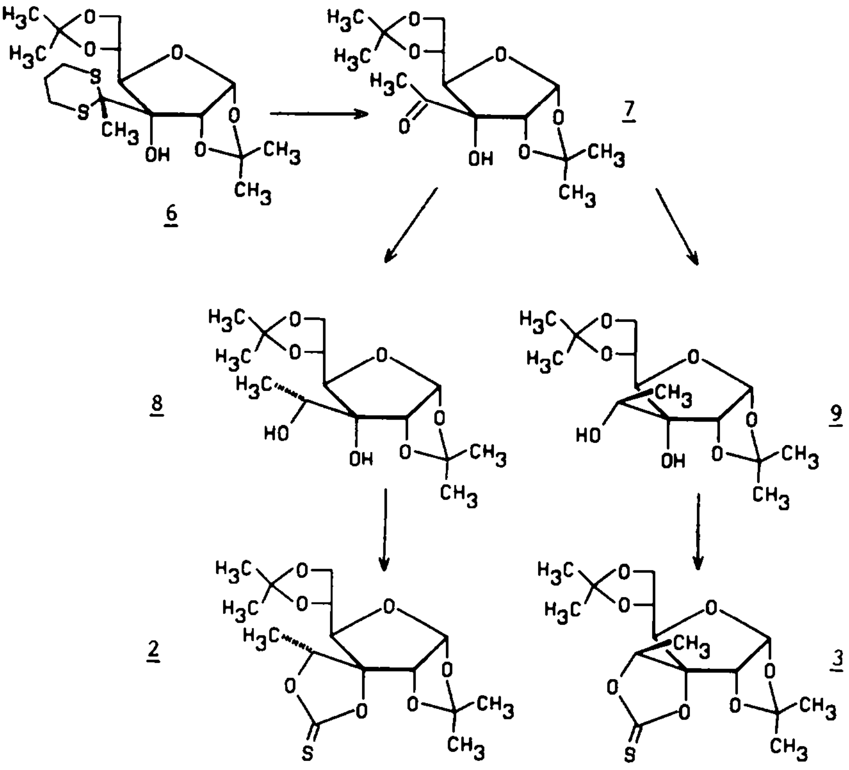
1 $R^1 = R^2 = H$
2 $R^1 = H$; $R^2 = CH_3$
3 $R^1 = CH_3$; $R^2 = H$

Preparation of the Thiocarbonates 1, 2 and 3

The preparation of the thiocarbonates 1, 2 and 3 proceed from the already known trimethylenedithioacetals 4[5] and 6[4]. The major problem for the synthesis of 1 is the selective cleavage of the formyl dithioacetal 4 without damage to the 5,6-isopropylidene group. By the use of s-collidine as base which is homogenous in the reaction medium small portions of the first formed 3-C-formyl compound could be isolated whose immediate reduction with $NaBH_4$ afforded the diol 5. The reaction of 5 with diimidazolethioketone provides then without problems the cyclic thiocarbonate 1. Alongside with it an O/S-isomerization product is observed (see experimental section). The thioacetal cleavage of 6 to the 3-acetyl compound 7 is considerably easier[4]. The following reduction of the carbonyl group in the side chain depends highly on the nature of the employed reduction agent. For example $NaBH_4$ in ethanol/water yields the separable compounds 8 and 9 in the ratio of 10 : 22.2 whereas $LiAlH_4$ in tetrahydrofurane leads to a ratio of 10 : 8.3. The reduction with diisobutylaluminium hydride (DIBAH) in toluene at -78 °C however is highly stereoselective and produces exclusively the L-glycero isomer 9. Similar observations for the reduction of acetyl branched sugars are described elsewhere[6].

The reaction of 8 or 9 with diimidazolethioketone provides the cyclic thiocarbonates 2 and 3 although under more drastic reaction conditions. Again alongside with them the O/S-isomerization is observed. The assignment of configuration in the side chain is done by NOE experiments[6] (see experimental section).

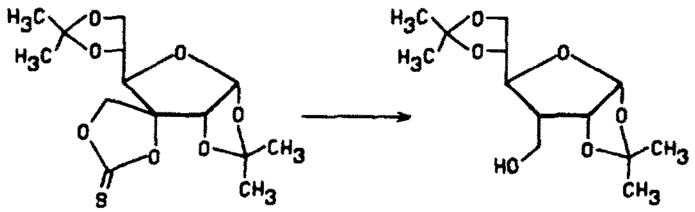




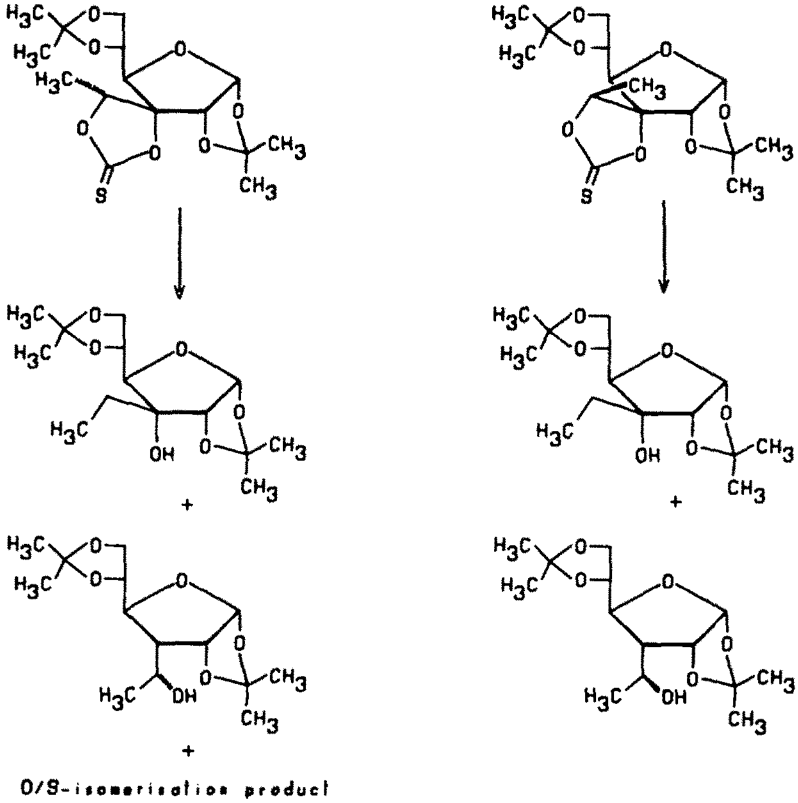
Reaction of the Thiocarbonates 1, 2 and 3 with Tri-(n-butyl)tin Hydride

As expected the cyclic thiocarbonate 1 reacts with tri-(n-butyl)tin hydride in toluene and AIBN as radical starter completely to the hydroxymethyl branched deoxy sugar 10 which is uniquely of the allo-configuration. In comparison the behaviour of the two isomeric thiocarbonates 2 and 3 clearly is more complex. In relatively high concentrated reaction mixture (c = 0.0375 moles/l) both 2 and 3 react to form solely the branched chain compound 11 with a tertiary hydroxyl-group at the branching point. The deoxygenation thus take place at the secondary oxygen. The difference in the yields is quite remarkable. Starting from 2 compound 11 is formed in 36% yield, from 3 it is formed in 66% yield, separated by column chromatography.

In a more diluted reaction mixture (c = 0.015 moles/l) besides 11 the hydroxyethyl branched deoxy sugar 12 and an O/S-isomerization product 13 is formed in



1 10

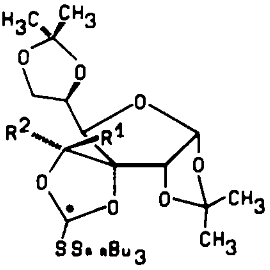


2 3 11 11 12 14 13

the reaction of 2. With an isolated overall yield of 66% the compounds 11, 12 and 13 are formed in the ratio 10 : 9.1 : 6.4. The isomeric compound of 2, compound 3, reacts in dilute reaction mixture (c = 0.015 moles/l) in an overall yield of 80% forming again 11 and the hydroxyethyl branched compound 14 in the ratio of 10 :10. No O/S-isomerization product is observed.

Discussion of the Results

The reactions of compound 1, 2 and 3 with tri-(n-butyl)tin hydride can only in parts be brought into accord with the results of previous investigations. Compound 1 does react as expected under formation of the deoxygenation product 10 corresponding to the idea that in between the more stable tertiary radical is formed. The other two compounds 2 and 3 however show a pronouncedly deviant behaviour. In both compounds the deoxygenation occurs not at the tertiary but at the secondary position in the side chain. The tertiary position is only attacked after long reaction times and with high degree of dilution. These findings let it seem doubtful that after the primary attack of a tri-(n-butyl)-tin radical on these highly substituted thiocarbonates, forming the intermediate 15 and 16 in a second step yet another C-O-bond should be cleaved. If this were the case, then, because of a higher stability of a tertiary radical as compared to a secondary one, in all cases a preferred deoxygenation at C-3 should be observed.



15 $R^1 = CH_3$; $R^2 = H$

16 $R^1 = H$; $R^2 = CH_3$

Rather, the findings given above lead to the conclusion that the hydrogen transfer takes place immediately after the formation of the intermediates 15 or 16. The positions of the thiocarbonyl carbon and the carbon atom C-3 and C-1' must be considered for such a transfer.

In the first case the initial diol would be regenerated. In the other cases because of the steric demand of the tri-(n-butyl)tin hydride the 1'-position is undoubtedly more easily accessible.

This idea could interpret the remarkable difference in the reaction behaviours of the two side chain isomers. The D-configurated intermediate 16 should react under considerably more strain because the rigid system leads to a strong sterical interaction between the methyl group R^2 and the large substituent at C-4 of the furanose. Therefore the yield of the deoxygenation product is low at high concentrations. At low concentrations and long reaction times however an O/S-isomerization product is observed together with 11 and 12. The isomeric intermediate 15 does not have such sterical interaction and therefore reacts in high yields both at high and low concentrations. The outcome for the reaction at low concentration shows that in this case both the secondary and the tertiary position are equally attacked.

Experimental

All m.ps were uncorrected. IR spectra were measured as KBr discs on a Perkin Elmer Spectraphotometer 297. NMR spectra and the NOE experiment were recorded at 270 MHz or 400 MHz on WH 270 and Wh 400 (Brucker) with TMS as an internal standard. Optical rotations were measured on a Perkin Elmer Polarimeter 243. TLC analysis was carried out with Merck pre-coated plates, Kieselgel $60F_{254}$. Column chromatography was carried out under pressure (max. 6 bar) through Kieselgel 60 (230-400 mesh, Fa. Woelm).

3-C-Hydroxymethyl-1,2;5,6-di-O-isopropylidene-α-D-allo-furanose 5

To a solution of thioacetal 4 (1g, 2.21mmol) in ethanol/water 2:1 (100ml) Me-I (7.9ml, 127.2mmol) and s-Collidine (16.8ml, 127.2mmol) were added. This mixture was stirred and heated under reflux for 3 hours. After cooling down to room temperature $NaBH_4$ (150mg) was added and stirring continued over night. The mixture was concentrated in vacuo, the residue was dissolved in $CHCl_3$, washed twice with water and with cooled 2n H_2SO_4 (2*30ml) followed by washing with Na_2CO_3, brine and drying over $MgSO_4$. The organic solvent was evaporated. Column chromatography over silica gel of the residue using Tol/EtOAc 3:2 as eluent gave 121mg (20%) of compound 5 as crystals.

m.p.=68°C, $|\alpha|^{20}_{D}$=+47.5°(c=0.8,MeOH) 400MHz ^{1}H-NMR($CDCl_3$) δ=1.36(s;6H,iPr),1.46(s;3H,iPr),1.59 (s;3H,iPr),3.13(s;2H,2*OH),3.55(d,J=11.8Hz;1H,C'-H),3.86(d,J=7.8Hz;1H,4-H),3.91(d,J=11.8Hz;1H, C'-H),3.95(dd,J=8.5Hz,J=5.8Hz;1H,6-H),4.09(dd,J=8.5Hz,J=6.3Hz;1H,6-H),4.18(ddd,J=7.8Hz,J=6.3Hz J=5.8Hz;1H,5-H),4.58(d,J=4Hz;1H,2-H),5.78(d,J=4Hz;1H,1-H).
Found: C 53.9, H 7.68, Calc. for $C_{13}H_{22}O_7$:C 53.78, H 7.64.

3-C-Hydroxymethyl-1,2;5,6-di-O-isopropylidene-3,1'-thiocarbo-α-D-allo-furanose 1

Diimidazolethioketone (105mg,0.6mmol) was added to a solution of 5 (100mg,0.34mmol) in THF abs. (6ml). This mixture was heated under reflux for 5 hours. After that THF was evaporated, the residue was dissolved in a small amount of toluene and purified by column chromatography over silica gel using PE/EtOAc 5:1 as eluent. This gave 79mg (70%) of 1 as cristals and 20mg (18%) of an O/S-isomerization product, also crystals.

1 : IR(KBr)=1300cm^{-1}(C=S), m.p.=168°C, $|\alpha|^{20}_{D}$=+71.6° (c=1.2,MeOH), 400MHz ^{1}H-NMR($CDCl_3$) δ:1.32(s;3H,iPr),1.37(s;3H,iPr),1.46(s;3H,iPr),1.62(s;3H,iPr),3.95(dd,J=8.8Hz,J=3.2Hz;1H,6-H) 4.06(dd,J=8.8Hz,J=3.3Hz;1H,6-H),4.1-4.16(m;2H,4-H,5-H),4.35(d,J=9.4Hz;1H,C'-H),4.52(d,J=3.6Hz 1H,2-H),4.85(d,J=9.4Hz;1H,C'-H),5.7(d,J=3.6Hz;1H,1-H). Found: C 50.98, H 6.25, S 9.51, Calc for $C_{14}H_{20}O_7S$: C 50.59, H 6.07, S 9.64.

O/S-isomerization product : IR(KBr):1800cm^{-1}(C=O), 400MHz ^{1}H-NMR(C_6H_6) δ=1.07(s;3H,iPr)1.13 ps,3H,iPr),1.39(s;3H,iPr),1.44(s;3H,iPr),3.22(d,J=8.8Hz;1H,4-H),3.55(d,J=3.6Hz;1H,2-H),3.75 (ddd,J=8.8Hz,J=5.8Hz,J=3.4Hz;1H,5-H),3.78(dd,J=8.8Hz,J=5.8Hz;1H,6-H),3.84(dd,J=8.8Hz,J=3.4Hz 1H,6-H),4.05(d,J=9.2Hz;1H,C'-H),4.22(d,J=9.2Hz;1H,C'-H),5.05(d,J=3.6Hz;1H,1-H).

3-C-Acetyl-1,2;5,6-di-O-isopropylidene-α-D-allo-furanose 7

s-Collidine hydrochloride (6.3g,40mmol) and HgO (4.33g,20mmol) in methanol (500ml) were heated under reflux until nearly all HgO was dissolved. Then water (240ml) and thioacetale 6 (3.13g,8mmol) were added and refluxing was continiued for 1-1.5 hours. During that time a white precipitate is observed. The solution was concentrated in vacuo, the residue dissolved in $CHCl_3$, twice washed with aq. 1m KI solution, once with water and dried over $MgSO_4$. Evaporation of the solvent and separation by column chromatography over silica gel (eluent Tol/Eth 6:1) yielded 1.6g (60%) of 7 as crystals.

m.p.=86°C, $|\alpha|^{20}_{D}$=+46.7° (c=1.27,MeOH), 270MHz ^{1}H-NMR(C_6H_6) δ=0.99(s;3H,iPr),1.25(s;3H,iPr) 1.4(s;3H,iPr),2.36(s;3H,C'-CH_3),3.14(s;1H,3-OH),3.81(dd,J=8.8Hz,J=5.8Hz;1H,6-H),3.9(dd,J=8.8Hz J=4.4Hz;1H,6-H),3.96-4.07(m;2H,4-H,5-H),4.12(d,J=4Hz;1H,2-H),5.84(d;J=4Hz;1H,1-H).
Found: C 55.01, H 7.34, Calc for $C_{14}H_{22}O_7$: C 55.62, H 7.33.

3-C-(D-glycero-hydroxyethyl)-1,2;5,6-di-O-isopropylidene-α-D-allo-furanose 8 and 3-C-(L-glycero-hydroxyethyl)-1,2;5,6-di-O-isopropylidene-α-D-allo-furanose 9

Reduction with $NaBH_4$: $NaBH_4$ (210mg) was added to a stirred solution of 7 in ethanol/water 1:1 (100ml). After 2 hours the reaction mixture was quenched with $NaHCO_3$ and stirring continued for an additional hour. Then the mixture was concentrated in vacuo and extracted with $CHCl_3$ (250ml). The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was separated by column chromatography over silica gel with PE/EtOAc 2:3 as eluent.This yielded the 2 isomeres 8 (186mg,26.4%) and 9 (411mg,58.4%), both crystals.

Reduction with $LiAlH_4$: $LiAlH_4$ (48mg) was added to 7 (200mg,0.66mmol) in $THF_{abs.}$ (15ml) and stirred for 30 min. The exess of $LiAlH_4$ was quenched with water, and the precipitates were removed by filtration. After evaporation of THF, dissolving of the residue in $CHCl_3$, the organic layer could be separated and dried over $MgSO_4$. Column chromatography, as previous discribed, gave 89mg (44%) of 8 and 72mg (36.4%) of 9.

Reduction with DIBAH : A solution of DIBAH in n-hexane (1m,5.2ml) was added dropwise to a stirred and cooled (-78°C) solution of 7 (400mg,1.3mmol) in $Tol_{abs.}$ (15ml) under N_2 atmosphere. The reaction was completed after 3 hours. Subsequently MeOH (1ml) was added dropwise at -78°C. The vessel was filled up with EtOAc and sat. aq. solution of Na·K· tatrates (10ml). The temperature was allowed to rise to room temperature. The mixture was partioned between EtOAc (150ml) and Na·K·tatrate solution (500ml). The organic solvent was dried ($MgSO_4$) and concentrated in vacuo to give 395mg (98%) of 9.

8 : m.p.=145°C, $|\alpha|^{20}_{D}$=+16.1°(c=0.75,MeOH), 270MHz ^1H-NMR($CDCl_3$) δ=1.23(d,J=6.4Hz;3H,C'-CH_3) 1.38(s;3H,iPr),1.4(s;3H,iPr),1.51(s;3H,iPr),1.58(s;3H,iPr),3.8(s;2H,2*OH),3.93(d,J=5.8 Hz;1H,4-H),4.1(dd,J=8.4Hz,J=7.4Hz;1H,6-H),4.14(dd,J=8.4Hz,J=7Hz;1H,6-H),4.55(d,J=4Hz;1H,2-H), 4.6(ddd,J=7.4Hz,J=7Hz,J=5.8Hz;1H,5-H),5.82(d,J=4Hz;1H,1-H). Found: C 55.51, H 8.03, Calc. for $C_{14}H_{24}O_7$= C 55.25, H 7.95.

9 : m.p.=91°C, $|\alpha|^{20}_{D}$=+21° (c=0.67,MeOH), 270MHz ^1H-NMR(C_6H_6) δ=1.03(s;3H,iPr),1.05(d, J=6.6Hz;3H,C'-CH_3),1.25(s;3H,iPr),1.3(s;3H,iPr),1.43(s;3H,iPr),2.79(s;1H,OH),2.98(s;1H,OH) 3.91-3.96(m;2H,2*6-H),4.00(d,J=8.8Hz;1H,4-H),4.14(ddd,J=8.8Hz,J=5.8Hz,J=5Hz;1H,5-H),4.24(qd J=6.6Hz,J=1,4Hz;1H,C'-H),4.33(d=J=4Hz;1H,2-H),5.63(d,J=4Hz;1H,1-H). Found: C 55.3, H 8.17 Calc. for $C_{14}H_{24}O_7$: C 55.25, H 7.95.

NOE experiments on 8 were carried out in acetone D_6 at 270 MHz. Irradiation on 1'-H shows an enhencement of the 2-H signal (8%). Irradiation on 1'-CH_3 shows an enhencement of the 5-H signal (9%).

3-C-(D-glycero-hydroxyethyl)-1,2;5,6-di-O-isopropylidene-3,1'-thiocarbo-α-D-allo-furanose 2

Under exclusion of light,230mg (0.7mmol) of 8 in $dioxane_{abs.}$ (15ml) and 245mg (1.4mmol) of diimidazolethioketone were heated under reflux for 5 days. The solvent was evaporated, the residue was dissolved in $CHCl_3$, twice washed with brine and dried over $MgSO_4$. Purification with column chromatography over silica gel (eluent PE/EtOAc 3:1) yielded 204mg (83%) of 2 as colourless crystals.

m.p.=158°C, $|\alpha|^{20}_{D}$=+67.6°(c=1.2,MeOH), IR(KBr)=1290cm^{-1}(C=S), 270MHz ^1H-NMR($CDCl_3$) δ=1.34(s;3H, iPr),1.49(s;3H,iPr),1.62(s;3H,iPr),1.73(d,J=6.8Hz;3H,C'-CH_3),3.87(dd,J=8.8Hz,J=4Hz;1H,6-H),4.17 (d,J=9.8Hz;1H,4-H),4.2(dd,J=8.8Hz,J=5.8Hz;1H,6-H),4.41(ddd,J=9.8Hz,J=5.8Hz,4Hz;1H,5-H),4.63(d J=3.6Hz;1H,2-H),4.9(q,J=6.8Hz;1H,C'-H),5.77(d,J=3.6Hz;1H,5-H). Found: C 52.32, H 6.5, S 9.16 Calc.for $C_{15}H_{22}O_7S$: C 52.01, H 6.4, S 9.26.

3-C-(L-glycero-hydroxyethyl)-1,2;5,6-di-O-isopropylidene-3-1'-thiocarbo-α-D-allo-furanose 3

Under exclusion of light, 200mg (0.57mmol) of 9 in $DMF_{abs.}$ (10ml) and 200mg (1.14mmol) of diimidazolethioketone were heated at 100°C for 7 days. Now two compounds are formed. After work up as previous discribed, the crude oil was separated with column chromatography over silica gel (eluent PE/EtOAc 3:1) and gave 156mg (79%) of 3 as main product, besides 20mg (10%) of an O/S-isomerization product (colourless coystals) could be isolated.

3 : IR(KBr)=1290cm^{-1}(C=S), m.p.=130°C, $|\alpha|^{20}_{D}$=+63.4°(c=1.1,MeOH), 270MHz ^1H-NMR($CDCl_3$) δ=1.32 (s;3H,iPr),1.38(s;3H,iPr),1.46(s,3H,iPr),1.54(d,J=6.7Hz;3H,C'-CH_3),1.63(s;3H, iPr),3.99(dd, J=8.4Hz,J=3.4Hz;1H,6-H),4.08(ddd,J=9Hz,J=5.6Hz,J=3.4Hz;1H,5-H),4.17(dd,8.4Hz,J=5.6Hz;1H,6-H) 4.23(d,J=9Hz;1H,4-H),4.77(d,J=3.6Hz;1H,2-H),5.7(d,J=3.6Hz;1H,1-H).

Found: C 52.19, H 6.41, S 9.48, Calc.for $C_{15}H_{22}O_7S$: C 52.01, H 6.4, S 9.26.

O/S-isomerization product : IR(KBr)=1800cm^{-1}(C=O), m.p.=143°C, $|\alpha|^{20}_D$=+19.8°(c=0.95,MeOH), 400MHz ^{1}H-NMR(CDCl$_3$) δ=1.33(s;3H,iPr),1.38(s;3H,iPr),1.48(d,J=6.6Hz;3H,C'-CH$_3$),1.63(s;3H,iPr) 4.00(dd,J=8.8Hz,J=3.2Hz;1H,6-H),4.09-4.19(m;3H,6-H,5-H,4-H),4.73(d,J=3.6Hz;1H,2-H),5.03(q,J=6.6Hz;1H,C'-H),5.68(d,J=3.6Hz;1H,1-H). Found: C 52.11, H 6.41, S 9.17, Calc.for $C_{15}H_{22}O_7S$: C 52.01, H 6.4, S 9.26.

Deoxygenation of 1

3-C-Deoxy-3-C-hydroxymethyl-1,2;5,6-di-O-isopropylidene-α-D-allo-furanose 10

Compound 1 (50mg,0.15mmol), nBu$_3$SnH (87mg,0.3mmol) and AIBN (2mg) in Tol$_{abs.}$ (1ml) were added dropwise to refluxing Tol$_{abs.}$ (3ml) under N_2 atmosphere. The reaction was complete in 30 min.. The solution was treated with aq. NaOH (2.5m,0.5ml) over night. The organic layer was separated and the aq. layer re-extracted with ether. The combined organic extract was washed with water until free of base and dried (MgSO$_4$). Concentration to a syrup, followed by column chromatography over silica gel (eluent PE/EtOAc 6:1) gave 22mg (53%) of 10 as an oil.

Characterization as acetate (crystals): m.p.=68°C, $|\alpha|^{20}_D$=+47.5°(c=0.8,MeOH), 400MHz ^{1}H-NMR δ=1.33(s;6H,iPr),1.4(s;3H,iPr),1.51(s;3H,iPr),2.08(s;3H,OAc),2.27(dddd,J=10.2Hz,J=9.8Hz,J=4.8Hz J=4.6Hz;1H,3-H),3.78(dd,J=7.4Hz,J=9.8Hz;1H,4-H),3.92(dd,J=8.3Hz,J=5.2Hz;1H,6-H),4.02(ddd,J=7.4 Hz,J=6.4Hz,J=5.2Hz;1H,5-H),4.1(dd,J=8.3Hz,J=6.4Hz;1H,6-H),4.21(dd,J=10.8Hz,J=10.2Hz;1H,C'-H) 4.5(dd,J=10.8Hz,J=4.8Hz;1H,C'-H),4.72(dd,J=4.6Hz,J=3.6Hz;1H,2-H),5.79(d,J=3.6Hz;1H,1-H) Found: C 57.2, H 7.65, Calc.for $C_{15}H_{24}O_7$: C 56.95, H 7.65.

Deoxygenation of 2 and 3

3-C-Ethyl-1,2;5,6-di-O-isopropylidene-α-D-allo-furanose 11

3-Deoxy-3-C-(D-glycero-hydroxyethyl)-1,2;5,6-di-O-isopropylidene-α-D-allo-furanose 12

O/S-isomerization product 13

3-Deoxy-3-C-(L-glycero-hydroxyethyl)-1,2;5,6-di-O-iospropylidene-α-D-allo-furanose 14

Compound 2 or 3 (100mg,0.3mmol), nBu$_3$SnH (0.16ml,0.6mmol) and AIBN (2mg) in Tol$_{abs.}$ (5ml) were added dropwise to refluxing Tol$_{abs.}$ under N_2-atmosphere during 30 min. Subsequent addition of nBu$_3$SnH (0.05ml) and AIBN after 2 hours was necessary. In the case of 2 the reaction was complete in 2 hours and 3 products are formed, for compound 3 the reaction time was 2.5 hours and only 2 products are formed. Work up and chromatographic separation as previous discribed gave in the reaction with 2 : 11 (29mg,33%,crystals), 12 (26mg,30%,oil), 13 (22mg,21% crystals). In the reaction with 3 the yields are : 11 (35mg,40%,crystals), 14 (35mg 40%,oil).

11 : m.p.=90°C, $|\alpha|^{20}_D$=+26.8°(c=1.4,MeOH), 400MHz ^{1}H-NMR(CDCl$_3$) δ=1.06(t;J=7.4Hz;3H,C'-CH$_3$), 1,31-1.47(m;1H,C'-H),1.37(s;3H,iPr),1.44(s;3H,iPr),1.59(s;3H,iPr),1.85(qd,J=7.4Hz,J=14.8Hz;1H C'-H),2.55(s;1H,3-OH),3.81(d,J=8Hz;1H,4-H),3.91(dd,J=12Hz,J=5.6Hz;1H,6-H),4.1(dd,J=12Hz,J=6Hz 1H,6-H),4.13(ddd,J=8Hz,J=6Hz,J=5.6Hz;1H,5-H),4.36(d,J=3.6Hz;1H,2-H),5.69(d,J=3.6Hz;1H,1-H) Found: C 58.28, H 8.55, Calc.for $C_{14}H_{24}O_6$: 58.32, H 8.63.

12 : Characterization as acetate, $|\alpha|^{20}_D$=+26°(c=1,MeOH), 270MHz ^{1}H-NMR(CDCl$_3$) δ=1.31(s;3H,iPr 1.34(s;3H,iPr),1.39(d,J=6.2Hz;3H,C'-CH$_3$),1.4(s;3H,iPr),1.52(s;3H,iPr),1.98(ddd,J=9.2Hz,J=9Hz J=4.7Hz;1H,3-H),2.04(s;3H,OAc),3.9(dd,J=7.8Hz,J=6.4Hz;1H,6-H),4.02-4.16(m;3H,4-H,5-H,6-H),4.65 (dd,J=4.7Hz,J=3.6Hz;1H,2-H),5.21(qd,J=9.2Hz,J=6.2Hz;1H,C'-H),5.75(d,J=3.6Hz;1H,1-H) Found: C 59.03, H 7.9, Calc.for $C_{16}H_{26}O_7$: C 58.67, H 7.84.

O/S-isomerization product 13: IR(KBr)=1730cm^{-1}(C=O), m.p.=168°C, $|\alpha|^{20}_D$=+51.3°(c=0.8,MeOH), 270MHz ^{1}H-NMR(CDCl$_3$) δ=1.35(s,3H,iPr),1.38(s;3H,iPr),1.43(s;3H,iPr),1.46(d,J=7Hz;3H,C'-CH$_3$), 1.61(s;3H,iPr),3.97-4.05(m;1H,6-H),4.09-4.17(m;2H,5-H,6-H),4.28(d,J=9Hz;1H,4-H),4.66(q,J=7Hz 1H,C'H),4.89(d,J=3.7Hz;1H,2-H),5.72(d,J=3.7Hz;1H,1-H). Found: C 52.01, H 6.52, S 9.15, Calc. for $C_{15}H_{22}O_7S$: C 52.01, H 6.4, S 9.26.

14 : Characterization as acetate, $|\alpha|^{20}_D$=+53.6°(c=0.67,MeOH), 270MHz ^{1}H-NMR(CDCl$_3$) δ=1.31(s 3H,iPr),1.39(s;3H,iPr),1.41(d,J=6.4Hz;3H,C'-CH$_3$),1.52(s;3H,iPr),1.99(ddd,J=9.4Hz,J=5.8Hz J=4.8Hz;1H,3-H),2.05(s;3H,OAc),3.92(dd,J=10.8Hz,J=8.8Hz;1H,6-H),4.02-4.11(m;2H,5-H,6-H),4.12 (dd,J=9.4Hz,J=5.6Hz;1H,4-H),4.74(dd,J=4.8Hz,J=3.6Hz;1H,2-H),5.27(qd,J=6.4Hz,J=5.8Hz;1H,C'-H), 5.75(d,J=3.6Hz;1H,1-H). Found: C 58.9, H 8.01, Calc.for $C_{16}H_{26}O_7$: C 58.67, H 7.84.

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