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Synthesis of methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-allopyranoside from α-D-glucose

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Abstract: Some of simple carbohydrates and their derivatives are used clinically for the treatment of various diseases. Epoxide derivatives, which can be obtained by the intramolecular elimination of water from two vicinal hydroxyl groups, are stable, but sufficiently reactive compounds very often used as intermediaries in various syntheses. Synthesis of epoxide derivative, methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-allopyranoside from α-D-glucose was achieved in high yields in the minimal number of synthetic steps. Anhydrous glucose was used as a starting material which was transformed into methyl α-D-glucopyranoside using dry, gaseous hydrogen chloride. Thus obtained derivative was treated with benzaldehyde in the presence of zinc chloride as Lewis acid giving methyl (*R*)-4,6-*O*-benzylidene-α-D-glucopyranoside. Obtained compound was treated with NBS (*N*-bromosuccinimide) in dichloromethane in the presence of barium carbonate giving methyl 4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside. In the next step obtained compound was treated with TBDMSCl (*tert*-butyldimethylsilyl chloride) in pyridine, and methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside was further mesylated, and obtained methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-3-*O*-mesyl-α-D-glucopyranoside was treated at the end with KOH to give methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-allopyranoside (yield 78 %).

Keywords: D-allose derivative; 3,4-epoxide ring; selective silylation; carbohydrates.

INTRODUCTION

When there are in the molecule two present OH groups in 1, 2 or 1, 3 positions, very often their protection can be achieved in the form of acetals, ketals and ortho

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esters. It is particularly true in the synthesis of carbohydrates.[1,2] Some of simple carbohydrates and their derivatives are used clinically for the treatment of various diseases.[3] The most often procedure for their formation is the treatment of glycol with huge access of aldehyde or ketone in the presence of acidic catalyst.[4] As acid catalysts gaseous hydrogen chloride can be used, sulfuric and *p*-toluenesulfonic acid (from protic acids), and the most frequently zinc chloride as Lewis acid. Another way is to put anhydrous copper salt which binds water.[5] The third way is to introduce into the reaction mixture instead of aldehydes themselves their acetals and ketals and then perform acid catalysed exchange of acetal groups.[4] Rarely it is possible to obtained acetals or ketals from vicinal dihalogenides and glycols under the S_N2 mechanism.[6]

Benzylidene acetals are mostly used in the carbohydrate chemistry[1,2] and they can be obtained by the treatment of carbohydrates and benzaldehydes with the acid catalysts, such as hydrogen chloride, sulfuric acid, *p*-toluenesulfonic acid and zinc chloride. Besides, it can be used dimethyl or diethyl-acetals of benzaldehyde in the acid media. The main advantage of this group is that it can be removed by catalytic hydrogenation, and the main disadvantage is that both possible diastereoisomers can be obtained during benzylidation.

The most often used agent for the selective protection of hydroxy group is *tert*-butyldimethylsilyl chloride (TBDMSCl). *tert*-Butyldimethylsilyl group[7] is appropriate for the temporary protection of hydroxyl groups because it is stable in the wide region of the reaction conditions, and it can be easily removed by the treatment with acids or fluoride ion, and tailor-made ionic liquids ([dihexaEGim][OMs]/*tert*-amyl alcohol media system).[8] This group is recommended for the selective protection of nucleosides,[9] hexapyrananosides[10] and other carbohydrate derivatives.[9]

Epoxides or oxiranes can be obtained by the intramolecular elimination of water from two vicinal hydroxyl groups. They are stable, but sufficiently reactive compounds very often used as intermediaries in various syntheses.[11] The most often way of their synthesis is the treatment of α-hydroxy-sulfonic ester with bases. The first step of the reaction is the formation of alkoxide ion, either by deprotonation of hydroxyl group, or by hydrolysis of carbonic ester using any base. In the second step it comes to the attack of alkoxide ion on C-atom to which it is attached -OSO_2R group and closure of the epoxide ring, with the inversion of configuration at the electrophilic C-atom. Leaving groups can be beside sulphonic ester, also esters of sulfuric or nitric acids, halogenides, protonated amino group, diazonium ion, *etc.*

Two epoxide derivatives in two different decades were synthesized at the Laboratory for Organic Synthesis, Faculty of Sciences and Mathematics, University of Niš and the synthesis of one of them was published at the end of 1980s.[12] Therefore, the novelty in this research is the synthesis of the second

epoxide derivative methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-allopyranoside (Fig. 1) from α-D-glucose where it was obtained in similar yields to the previously published epoxide derivative[12]. It can be an intermediary in the synthesis of biologically active compounds. To the best of our knowledge, two new compounds not previously reported were synthesised in this work: methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-3-*O*-mesyl-α-D-glucopyranoside and methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-allopyranoside.

EXPERIMENTAL

Apparatus

The NMR analyses were performed on a Bruker AC–250 instrument with standard Bruker software. All analyses were carried out using regular 5 mm NMR tubes.

Reagents

All chemicals used for syntheses were of the analytical reagent grade. Solutions were prepared for NMR analyses in $CDCl_3$ (Merck, Germany), purity 99.8 %. The chemical shifts are referred to tetramethylsilane (TMS, δ_H= 0.00 ppm) in $CDCl_3$.

Synthetic procedures

Methyl α-D-glucopyranoside (**1**). Methyl α-D-glucopyranoside (**1**) was synthesized from α-D-glucose using Fisher glycosidation method with methanolic HCl, where the formation of the thermodynamically favored pyranoside was achieved with a prolonged reaction time and refluxing.[13] In total, it was obtained 25.1 g methyl α-D-glucopyranoside (**1**) starting from 50 g (0.2775 mol) α-D-glucose. The yield was 46.58 %. m.p. 164-165 °C. The melting point was in accordance with the previously reported data.[14]

Methyl (R)-4,6-O-benzylidene-α-D-glucopyranoside (**2**). Methyl (*R*)-4,6-*O*-benzylidene-α-D-glucopyranoside (**2**) was synthesised using the procedure reported by Hall[15], starting from 16.5 g (0.121 mol) anhydrous $ZnCl_2$, 25 mL (0.2462 mol) benzaldehyde (ρ=1.045 g/mL) and 16.5 g (0.0851 mol) powdered methyl α-D-glucopyranoside (**1**). The crude product was recrystallized with optimal quantity of hot ethanol. It was obtained 14.15 g methyl (*R*)-4,6-*O*-benzylidene-α-D-glucopyranoside (**2**) (yield 59 %), m.p. 165 °C. The reported melting point was in accordance with the previously published. [15-17]

Methyl 4-O-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside (**3**). Methyl 4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside (**3**) was prepared according to modified procedure published by Hanessian[18] where we started from 0.910 g (3.22 mmol) methyl (*R*)-4,6-*O*-benzylidene-α-D-glucopyranoside (**2**), 0.364 g (1.84 mmol) $BaCO_3$ and 0.6825 g (3.83 mmol) NBS and used dichloromethane as a solvent instead of 1,1,2,2-tetrachloroethane. Obtained crystals have m.p.=121-122 °C, which is in accordance with the previously published value.[18] Obtained substance was chromatographed on silica-gel column using the eluent chloroform: methanol=15:1, and pure methyl 4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside (**3**) was obtained with the mass 0.73 g, yield 65.68 %.

Methyl 4-O-benzoyl-6-bromo-2-O-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (**4**) and methyl 4-O-benzoyl-6-bromo-3-O-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (**5**). 0.73 g (2.02 mmol) methyl 4-O-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside (**3**) and pyridine was put in round bottomed flask and stirred by hand until the complete dissolution of the carbohydrate derivative. Flask with the solution was left to cool down at 0 °C, and then

0.448 g (2.97 mmol) TBDMSCl was added into previously dissolved substance and cooled at 0 °C. The reaction mixture was left at room temperature for 8 days and followed using TLC with the mobile phase chloroform : methanol = 15 : 1. The reaction was terminated by the evaporation of pyridine on vacuum evaporator using ethanol. Thus obtained oil was eluted on silica gel column with the mixture chloroform : methanol = 40 : 1. In this way three reaction products were separated: methyl 4-O-benzoyl-6-bromo-2-O-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (**4**) (150 mg, 15.42 %) (^{1}H NMR spectrum together with the assignment is available in the Supplementary Material (Figure S1)), methyl 4-O-benzoyl-6-bromo-3-O-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (**5**) (180 mg, 18.51 %) and methyl 4-O-benzoyl-6-bromo-6-deoxy-2,3-di-O-*tert*-butyldimethylsilyl-α-D-glucopyranoside (50 mg, 4.1 %).

Methyl 4-O-benzoyl-6-bromo-2-O-tert-butyldimethylsilyl-6-deoxy-3-O-mesyl-α-D-glucopyranoside (**6**). 150 mg (0.32 mmol) methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (**4**) was placed in round bottomed flask (100 mL) and dissolved in pyridine, and then cooled in ice bath to 0 ºC, and then added 0.06 mL (0.7752 mmol) methanesulfonyl chloride (ρ=1.48 g/mL). The obtained mixture was left at 0 °C for 24 h. The reaction was monitored using TLC and terminated by the addition of small quantity of water. Pyridine from the reaction mixture was removed by the co-evaporation with ethanol, and obtained oil was put on the silica gel column and eluted using chloroform. Mass of the obtained substance (**6**) was 60 mg (34.36 %). ^{1}H NMR spectrum and the assignments are available in the Supplementary Material (Figure S2).

Methyl 4-O-benzoyl-6-bromo-3-O-tert-butyldimethylsilyl-6-deoxy-2-O-mesyl-α-D-glucopyranoside (**7**). 180 mg (0.38 mmol) methyl 4-*O*-benzoyl-6-bromo-3-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (**5**) was put in the round bottom flask (100 mL) and dissolved in pyridine, then cooled in ice bath to 0 °C and added methanesulfonyl chloride (0.06 mL, 0.7752 mmol). Obtained mixture was left to stand at 0 °C for 24 h. The reaction was monitored using TLC and interrupted by the addition of small quantity of water. Pyridine was removed from the reaction mixture by co-evaporation with ethanol, and the obtained oil was put on silica gel column and eluted using chloroform. Mass of the obtained substance (**5**) was 80 mg (38.18 %).

Methyl 3,4-anhydro-6-bromo-2-O-tert-butyldimethylsilyl-6-deoxy-α-D-allopyranoside (**8**). Methyl 4-*O*-benzoyl-6-bromo-3-*O*-*tert*-butyldimethylsilyl-6-deoxy-2-*O*-mesyl-α-D-glucopyranoside (**7**) was put in the round bottomed flask (100 mL), and the same operation was performed for methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-3-*O*-mesyl-α-D-glucopyranoside (**6**). To both flasks, ethanol was added in the quantity to dissolve the substance, and into thus obtained solutions 0.06 g (1.0693 mmol) KOH was added. The reaction was heated for 15 min at 70 °C which is enough time for the reaction to proceed quantitatively; it was monitored using TLC and chloroform as the mobile phase. Only one of those two makes epoxide, and it is compound methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-3-*O*-mesyl-α-D-glucopyranoside (**6**) because it possesses good leaving group in the position 3, and the proof for it is TLC and recorded ^{1}H NMR spectrum (Supplementary Material Figure S3). Mass of the obtained epoxide (methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-allopyranoside) (**8**) is 30 mg (yield 78 %).

RESULTS AND DISCUSSION

Anhydrous glucose was used as a starting material which was transformed into methyl α-D-glucopyranoside (**1**) using dry, gaseous HCl. Reaction was

performed in a such a way that 50 g anhydrous glucose was refluxed for 72 h giving after cooling pure crystalline methyl α-D-glucopyranoside (**1**) (m.p. 164 °C) (Fig. 1). Yield of the first harvest was 16.5 g. The filtrate was after filtering of crystals evaporated to half volume and left to stay in the fridge overnight. Obtained crystals were filtered and dried; 8.6 g methyl α-D-glucopyranoside (**1**) was obtained in the second harvest. Total yield of this reaction was 46.58 %.

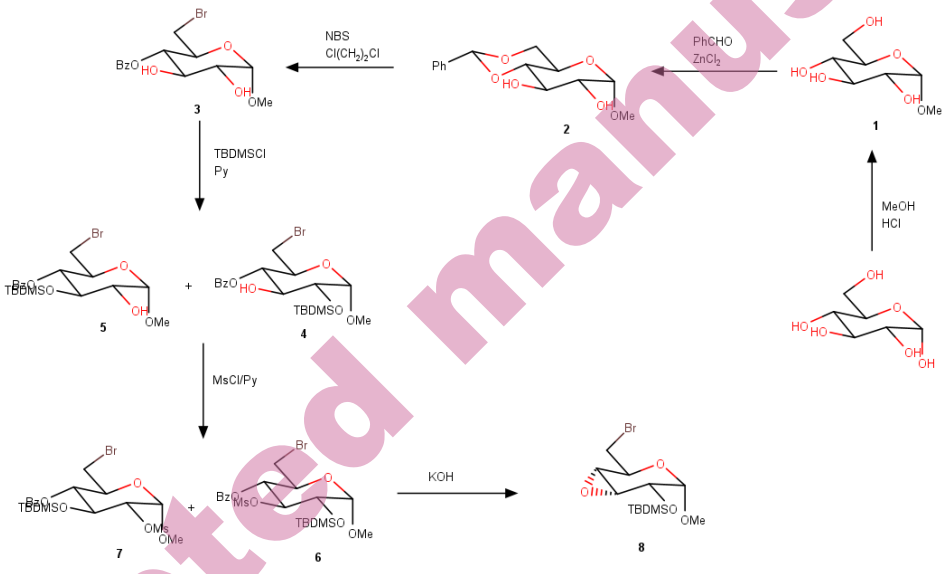

Fig. 1. Synthesis of methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-allopyranoside (**8**) from α-D-glucose

Thus obtained methyl α-D-glucopyranoside (**1**) was treated with benzaldehyde in the presence of $ZnCl_2$ as Lewis acid giving methyl (*R*)-4,6-*O*-benzylidene-α-D-glucopyranoside (**2**) (Fig. 1). The procedure was performed according to instructions from D. M. Hall's method,[15] according to which it was firstly formed the complex between anhydrous $ZnCl_2$ and benzaldehyde, and then added methyl α-D-glucopyranoside. The yields were different in this reaction and depended obviously on the purity of benzaldehyde, the presence of moisture in obtained methyl α-D-glucopyranoside, warming, the presence of moisture in $ZnCl_2$. Therefore, to get yields around 65 % it is necessary each component to be maximally clean and dry.

Obtained methyl (*R*)-4,6-*O*-benzylidene-α-D-glucopyranoside (**2**) was treated with NBS (*N*-bromosuccinimide) in dichloromethane in the presence of $BaCO_3$.[19] This reaction is very useful and important because in one step from inactive benzylidene acetal in the position 6 Br group was introduced which is easily reduced in necessary CH_3 group, and in the position 4 alkaline labile benzoyl group

was left. Using alkaline hydrolysis of benzoyl group obtained alkoxide ion easily closes epoxide of *allo*-configuration taking out *trans*-3-*O*-mesyl group. The reaction was performed in such a way that 0.91 g (3.22 mmol) methyl (*R*)-4,6-*O*-benzylidene-α-D-glucopyranoside (**2**) was treated with 0.6825 g freshly prepared NBS in 35 mL dichloromethane previously dried through Al_2O_3 column. $BaCO_3$ was also added into the reaction (0.364 g, 1.84 mmol). The mixture was refluxed with stirring for 2.5 h and followed the changes using TLC. After completion of the reaction, we filtered off and separated insoluble $BaCO_3$ and after the evaporation of the solvent we got the oil. After silica-gel chromatography methyl 4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside (**3**) was obtained as a solid (yield 65.68 %) (Fig. 1). Its malting point was in good agreement with the reported values.[18]

In the next step obtained compound was treated with TBDMSCl in pyridine, in a way that the compound was dissolved in pyridine, cooled at 0 °C in ice bath, and then added TBDMSCl in a ratio 1.4 mol TBDMSCl on 1 mol of the compound. We got three products: methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (**4**), methyl 4-*O*-benzoyl-6-bromo-3-*O*-*tert*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (**5**), and methyl 4-*O*-benzoyl-6-bromo-6-deoxy-2,3-di-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranoside (Fig. 1). This mixture of products was separated on silica-gel column using the eluent chloroform : methanol = 40:1.

Both monosilyl derivatives were mesylated. To the cooled pyridine solution of silyl derivatives, mesyl chloride was added in a ratio 2.4 mol mesyl chloride: 1 mol silyl substrate. Reaction mixture was left at 0 °C for 24 h, and then upon the completion of the reaction, which flow was monitored using TLC, obtained products (**6**, **7**) were isolated and separated on silica gel column using chloroform as an eluent.

We did not bother about the structure of these two compounds because in the next step by the treatment with the base, the compound having TBDMS in position 3, cannot close the epoxide upon the attack of the alkoxide ion in position 4, and only hydrolysis of benzoyl group takes place. Another compound having OMs group in the position 3 after hydrolysis closes 3,4-epoxide ring with *allo*-configuration (**8**) (Fig. 1). This compound was characterized using ^{1}H NMR which spectrum is available in the Supplementary information (Figure S3). The simulated ^{1}H NMR spectrum of the same compound using NMRium[20] is also available in the Supplementary information (Figure S4), which was useful during the assignment process.

Earlier, based on *in vivo* studies, epoxides were considered to possess toxicity and poor pharmacokinetics.[21] However, recent studies on compounds, such as fosfomycin (an antibiotic for the treatment especially of lower urinary tract infections), carfilzomib (an anti-cancer medication), fumagillin (an antimicrobial

agent), TNP-470 (an anti-cancer candidate), clearly showed the role of epoxide moiety in drug potency.[22] The obtained epoxide derivative can be used, therefore, as an intermediary in the syntheses of biologically active molecules.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/12572, or from the corresponding author on request.

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И З В О Д

СИНТЕЗА МЕТИЛ 3,4-АНХИДРО-6-БРОМО-2-*О*-*ТЕРЦ*-БУТИЛДИМЕТИЛСИЛИЛ-6-ДЕОКСИ-α-D-АЛОПИРАНОЗИДА ИЗ α-D-ГЛУКОЗЕ

ЂОРЂЕ ГЛИШИН, ОЛГА ЈОВАНОВИЋ, ГОРДАНА СТОЈАНОВИЋ, АЛЕКСАНДРА ЖИВКОВИЋ, ДРАГАН СТОЈАНОВИЋ, МАРИНА ПАВЛОВИЋ И БИЉАНА АРСИЋ*

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Неки једноставни угљени хидрати и њихови деривати се користе клинички у третману различитих болести. Епоксидни деривати, који се могу добити интрамолекулском елиминацијом воде из две вицинале хидроксилне групе, су стабилни, али довољно реактивна једињења која се често користе као интермедијери у различитим синтезама. Синтеза епоксидног деривата, метил 3,4-анхидро-6-бромо-2-*О*-*терц*-бутилдиметилсилил-6-деокси-α-D-алопиранозида из α-D-глукозе је остварена у високом приносу у минималном броју синтетичких корака. Анхидрована глукоза је коришћена као полазни материјал који је трансформисан у метил α-D-глукопиранозид коришћењем сувог, гасовитог хлороводоника. Тако добијени дериват је третиран са бензалдехидом у присуству цинк хлорида као Луисове киселине дајући метил (*R*)-4,6-*О*-бензилиден-α-D-глукопиранозид. Добијено једињење је третирано са НБС (*N*-бромсукцинимидом) у дихлорметану у присуству баријум-карбоната дајући метил-4-*О*-бензоил-6-бромо-6-деокси-α-D-глукопиранозид. У следећој фази добијено једињење је третирано са TBDMSCl (*терц*-бутилдиметилсилил-хлоридом) у пиридину, и метил 4-*О*-бензоил-6-бромо-2-*О*-*терц*-бутилдиметилсилил-6-деокси-α-D-глукопиранозид је даље мезилован, и добијени метил 4-*О*-бензоил-6-бромо-2-*О*-*терц*-бутилдиметилсилил-6-деокси-3-*О*-мезил-α-D-глукопиранозид је третиран на крају са KOH дајући метил 3,4-анхидро-6-бромо-2-*О*-*терц*-бутилдиметилсилил-6-деокси-α-D-алопиранозид (принос 78 %).

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