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Selective Anomeric Deacetylation of Per-Acetylated Carbohydrates Using (*i*-Pr)$_3$Sn(OEt) and Synthesis of New Derivatives

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Abstract

In this study natural carbohydrates such as glucose, galactose, xylose, fructose andlactose, are acetylated by acetic anhydride and sodium acetate catalyst. Anomeric configuration is deacetylated by (*i*-Pr)$_3$Sn(OEt)as a catalyst, an easy synthetic regioselective deacetylation of full acetylated carbohydrates using (*i*--Pr)$_3$Sn(OEt) is described. The acetylated carbohydrates reacted with HBr (solution in AcOH, 32 wt.%) for the bromination of anomeric position. The synthesis oxazaphosphorine, and bromo hexa alkyl Methylsulfonate derivatives from anomeric position of carbohydrates was reacted. FT IR, ^{1}H, ^{13}C NMR, ^{31}PNMR spectroscopy techniques were employed to examine the synthesized compounds.

Keywords: Carbohydrates, Deacetylation, Anomeric Deacetylation, (*i*Pr)$_3$Sn(OEt)

1. Introduction

Carbohydrates are a large class of organic compounds which can be found in the structure of living organisms. They are major energy source for both plants, and animals that play an important role in feeding the living organisms. Likewise, these compounds are quintessential reactions of ATP, RNA and DNA. Carbohydrates are polyhydroxy ketone or aldehydes that can be found in nature. Carbohydrates can be divided into three major classes: monosaccharides, disaccharides and polysaccharides. Monosaccharides can be classified into classes, aldose and ketose. The presence of the heteroatom in-ring has an appreciable effect on both formation and reactivity of carbohydrates. The existence of an electron-withdrawing substituent (as halogens) onto C1 in axial position is more stable due to the anomeric effect. This tendency not only is not limited to carbohydrates but also observes in annular systems like substitutability of 2-tetrahydropyrans. This phenomenon is known as the anomeric effect. (Sorg, Hull, Kliem, Mier, & Wiessler, 2005) The hydroxyl groups in carbohydrates are esterified easily. Acetylation is the most common reaction for esterification. Selective anomericde acetylation is considered as an important stage in synthesis of glycoside. Acetylated-1-hydroxy of carbohydrates contains valuable structures for diverse reactions of glycosides.

There are various procedures to release anomeric configuration of acetylated carbohydrates, such as asbutylamine, (Pawar & Edgar, 2013) ammonia, (Li, Li, Zhaivg, & Guan, 2004) bis (tributyltin) oxide, (Li, Li, Zhaivg, & Guan, 2004) HgO/HgCl, (Sambaiah, Fanwick, & Cushman, 2001) piperidine, (Zhang & Kováč, 1999) hydrazine acetate, (Excoffier, Gagnaire, & Utille, 1975) zinc chloride, (Hanessian & Kagotani, 1990) Zn–NH_4Cl–EtOH, (Zhang, Fu, Si, Wang, Wang, & Tang, 2011) $HClO_4$–SiO_2, (Tiwari & Misra, 2006) $Nd(OTf)_3$, (Tran, Deydier, Bonnaffé, & Le Narvor, 2008) $FeCl_3.6H_2O$,[12] MgO/MeOH, (Herzig & Nudelman, 2009) zinc acetate, (Kaya, Sonmez, Kucukislamoglu, & Nebioglu, 2012) $AlCl_3$, (Wang, Mo, Chiou, & Liu, 2010) enzyme, (Moriyoshi, Yamanaka, Ohmoto, Ohe, & Sakai, 2005) silica-supported boron sulfonic, (Bhat, Naikoo, Tomar, Ahmad Bhat, Malla, Kumar, & Tiwari, 2017), MgO/MeOH (Jabbari & Noroozi, 2018), Potassium carbonate, (Calvaresi & Hergenrother, 2013) Many reactions can be created by carbohydrate invertebrates that often have pharmaceutical application. Oxazophosphorin compounds are used as DNA alkylating agents in malignant chemotherapy (Park, Lee, Cho, & Park, 2007).

Carbohydrates are used in medicine usages such as heparin of anticoagulant, antibiotics, vaccines, anticancer medicines, antibacterial and antifungal (Liang, Huang, & Duan, 2007). carbohydrates hasn't been extended for cellular biology improvements in drug receiving (Mazur, Opydo-Chanek, & Stojak, 2011). Thence, carbohydrates performance hasn't been studied widespread in biology because of the complicated structures of oligosacarids, non existence of synthesis methods and analysis of structure.

In this paper, a sample of carbohydrates consisting of glucose, galactose, xylose, fructose and lactose is acetylated using Ac_2O/AcONaunder the 50-60°C and anomeric configuration of acetylated carbohydrates using $(^iPr)_3Sn(OEt)$ as a new catalyst has been released. Then, it is reacted with HBr (AcOH solution), new derivatives of oxazaphosphorine, and alkyl sulfunate from anomeric position reacted. All of these compounds are identified by FT-IR, ^1H, ^{13}C and ^{31}PNMR spectroscopy techniques.

2. Experiment

All materials were obtained from Merck Co.^1H, ^{13}C and ^{31}P NMR spectra of in $CDCl_3$ and/or DMSO-d6 were measured using Brucker 400 AC spectrometer as a solvent at room temperature (University of Tabriz, Tabriz, Iran and ShahidBeheshti University, Tehran, Iran).

2.1 Typical Procedure for Preparation of D-Glucose Pentaacetate (2a)

A mixture of D-glucose (15.0g), acetic anhydride (70mL), sodium acetate (15.0g) and butyl acetate (150mL) was refluxed with stirring for one-half hours. Then the reaction mixture was added to water (100mL), the mixture was stirred and produced a neutral solution with a 3% sodium hydroxide After the concentration of the organic layer it give 62.0g (yield 95%) of pentaacetyl-β-D-glucopyranose as crude crystals. The crude crystals contained 13% of pentaacetyl-α-D-glucopyranose, but recrystallization from ethanol gave 49.7g of pure pentaacetyl-β-D-glucopyranose (M. p. 132°C, yield 77%).

δ (ppm)6.6 (d, 1H, J = 3.6Hz), 5.80 (t, 1H, J = 9.8Hz), 5.33 (t, 1H, J= 9.8Hz,), 5.24 (dd, 1H, J = 10.5, 3.7Hz), 4.29 (dd, J = 12.2, 4.3Hz), 4.08-4.15 (m, 1H), 4.0 (dd, J = 12.3, 2.2Hz), 1.50-1.70 (3s, $5CH_3$).

2.2 General Procedure for Selective Anomericdeacetylation of D-Glucose Pentaacetate (3a)

$(^iPr)_3Sn(OEt)$ (1mmol) was added to solution pentaacetyl-α-D-glucopyranose (1mmol) in methanol (20mL). A drop of ammonium acetate solution was added to the reaction mixture. The reaction mixture was refluxed for 4-5 hours and controlled by TLC. then the solvent was separated, Solid matter is white. The compound was washed with hexane (3 times), and was crystallized by Ethyl acetate. and identified by NMR spectroscopy techniques.

^1H-NMR (CDCl3): δ (ppm)6.35 (d, 1H, ^4J= 3.8Hz, H-1), 5.33 (dd, 1H, ^3J = 10.1Hz, ^{3}J10.1= Hz), 4.98 (dd, 1H, ^3J = 10Hz, ^4J =10Hz), 4.98 (dd, 1H, ^3J=10.1Hz, ^4J=4.0Hz), 4.38-5.1 (m, 2H), 4.77 (d, 1H,^3J = 10.8Hz), 2.45 (s, 3H), 2.66 (s, 3H), 2.2 (s, 3H), 2.11 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ (ppm)175.19, 170.5, 166.35, 90.00, 72.51, 72.29, 69.31, 66.20, 59.01.

2.3 The Deacetylation of α-D-Lactose Octaacetate

$(^ipr)_3SnOEt$ (1mmol) was added by stirring to D-lactoseoctaacetate (1mmol) an appropriate solvent (20ml). under reflux, stirring and boiling were continued for 4-5h (hexane/EtOAc=3:1).

^1HNNR ($CDCl_3$): δ(ppm)5.97 (d,1H, ^4J= 4.1Hz), 5.52 (d, 1H,^{4}J = 3.0Hz), 5.42 (dd, 1H, ^3J= 10.7Hz, ^4J= 3.3Hz), 5.25 (dd,1H, ^3J= 10.7Hz, ^4J= 3.9Hz), 4.52 (dd, 1H, J = 5,6Hz), 4.17 (dd, 1H, ^3J= 11.4Hz, ^4J=.4Hz,), 4.11 (dd, 1H, ^3J= 11.4Hz, ^4J= 6.7Hz), 3.15 (s, 3H,), 2.11 (s, 3H,),2.06 (s, 3H,), 2.01 (s, 3H,); ^{13}C-NMR ($CDCl_3$): δ(ppm) 170.32, 170.12, 169.92, 1369.78, 91.17, 70.22, 66.77, 66.30, 68.19, 59.00.

2.4 Preparation of 2,3,4,6-Tetra-O-Acetyl-ß-D-Galactopyranozyl Bromide with HBr/AcOHAa

HBr solution in acetic acid (4.5ml) was mixed with galactosepentaacetate. The reaction mixture was stirred until it became a homogeneous mixture and was stirred for 30 min. The obtained precipitate became smooth and rinsed with water. Then it was dissolved in ether and separated by separatory funnel. Organic phase was transferred into another container and dried. Solvent, was extracted without heating in vacuum and during two steps at 5 minutes interval, insignificant amount of petroleum ether was added. After a milky precipitate was formed, it kept in freezer for 24h. After that time, 2.5ml of petroleum ether was mixed with 2.5ml of ether and added to it. Precipitate was smoothed and washed with mixture of ether and petroleum ether, a white precipitate yielded with 59% efficiency.

2.5 Preparation of 5e, 6e and 7e as New Oxazaphosphorineas a Representative

Solution of compound **3a** (0.01mol) in dry DMF (20mL), NaOH (0.01mol), pyridine (0.01mol), $POCl_3$(0.01mol) under N_2 atmosphere was reacted in 0^{oC}. The mixture could be detected (by TLC). After purification by column chromatography (petroleum ether: EtOAc, 4:1), **5a** was obtained as a yellowish-white oil.

In order to prepare **6a**, a compound **5a** (0.01mol) and ethanol amine(0.015mol) in 30mL of dry DMF, and 0.01mol pyridine were cooled at 0°C were cooled to 0°C in N_2 atmosphere.the solvent was removed in vacuum pump. After removing solvent, **6a** was obtained as a red oil.

In order to prepare **7a** $SOCl_2$ was reacted for 1h and finally, the deprotection process of acetyl group was occurred.

2.6 Preparation 1-(2,3,4,6- Tetra –o-Acetyl –β-D- Galactopyranozile)-6-(Methyl Oxy Sulfonile) Hexane

Compound **2b** obtained from previous stage (1.4mmol). NaOH(1mmol), is dissolved in pyridine (0.4mL) and solution is cooled to 0^{0C}, and added to bromo hexa alkyl Methylsulfonate (2mmol). After 6h water (4mL) added. After gathering sediment, it dissolved in dichloromethane (12mL) and organic phase was extracted by salt water (2*6mL), then dried by using sodium solphate, and solution was filtered. Finally it was crystallized by ethanol with 53% efficiency (scheme4).

FT-IR(KBr,υcm^{-1}): 2942, 2867, 1751, 1434, 1369, 1226, 1174, 1069, 953 cm^{-1}, ^{1}H NMR(300MHz,$CDCl_3$)δ(ppm)1.23(m, 2H), 1.44(m, 2H, -O$(CH_2)_2$-$(CH_2)_2$-$(CH_2)_3$-S(=O) 1.56(m, 2H, -OCH_2-$CH_2(CH_2)_3$-CH_2-O-S(=O)-), 1.72(m, 2H, -OCH_2-$(CH_2)_3$-CH_2-CH_2-O-S(=O)-), 1.96 -1.97(2s, 3H,), 1.98-2.19(2s, 6H), 2.14- 2.17(2s, 3H), 2.14-2.17(2s, 3H,), 2.99- 3.02 (2s, 3H,), 3.32(m, 2H, -OCH_2-$(CH_2)_4$-CH_2-O-S(=O)-), 3.77(m, 2H, -OCH_2-$(CH_2)_4$-CH_2-O-S(=O)-), 4.02-4.42(m, 4H), 4.97-5.47(m, 2H), 5.68 - 6.34(2d, 1H, J=3.6Hz).

3. Results and Discussion

This paper aimed to describe the full acetylation of some carbohydrates such as D-glucose (**1a**), D-galactose (**1b**), D-xylose (**1c**), D-fructose (**1d**) and D-lactose (**1e**) in the presence of Ac_2O/AcONa as well as selective deacetylation of anomeric position using (^{i}Pr)$_3$Sn(OEt) as a new catalyst (Scheme 1, Tables 1 and 2).Anomeric configuration is deacetylated by (iPr)$_3$Sn(OEt)as a catalyst, A convenient synthetic approach to regioselectivedeacetylation of full acetylated carbohydrates using (^{i}Pr)$_3$Sn(OEt)is described. The acetylated carbohydrates are reacted with HBr (solution in AcOH, 32 wt.%) for the bromination of anomeric position. As a representative bromination of **2a** is yielded **4a** (Scheme 1, Table 3).

Representatively, the ^{1}H NMR spectrum of glucose penta acetate (**2a**) is shown in Figure 1.

Its structure was characterized by ^{1}H, ^{13}C NMR and FT-IR spectra. The ^{1}H NMR spectrum of **2a** showed doublets at δ 6.6ppm (J = 3.6Hz) for H-1, a double of doublet at δ 5.24ppm (J = 10.5Hz) for H-2, a triplet at δ 5.80ppm (J = 9.9Hz) for H-3, a triplet at δ 5.33ppm (J = 9.9Hz) for H-4, a double of doublet at δ 4.29ppm (J = 12.2Hz) for H-5, a double doublet at δ 4.0ppm (J = 12.3Hz) for H-6. Methyl groups show three singlets at δ 1.50-1.70ppm. The FT-IR spectrum showed a strong absorption at 1741cm^{-1} due to carbonyl stretching frequency (See supporting information).

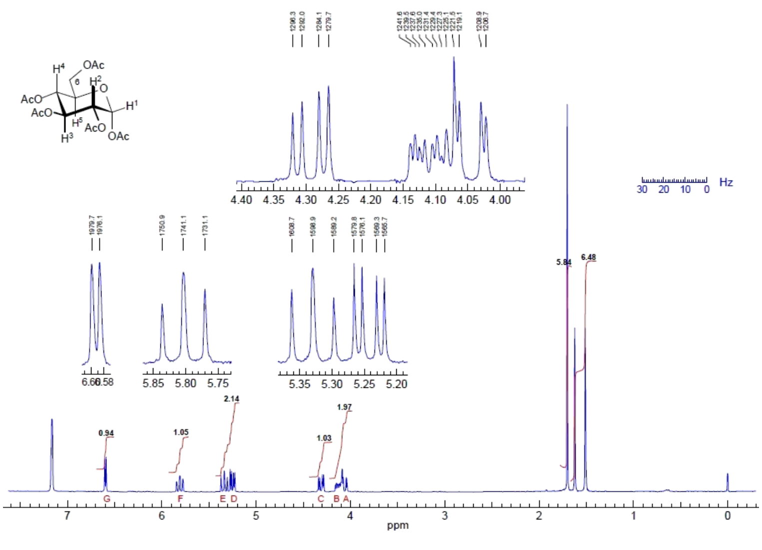
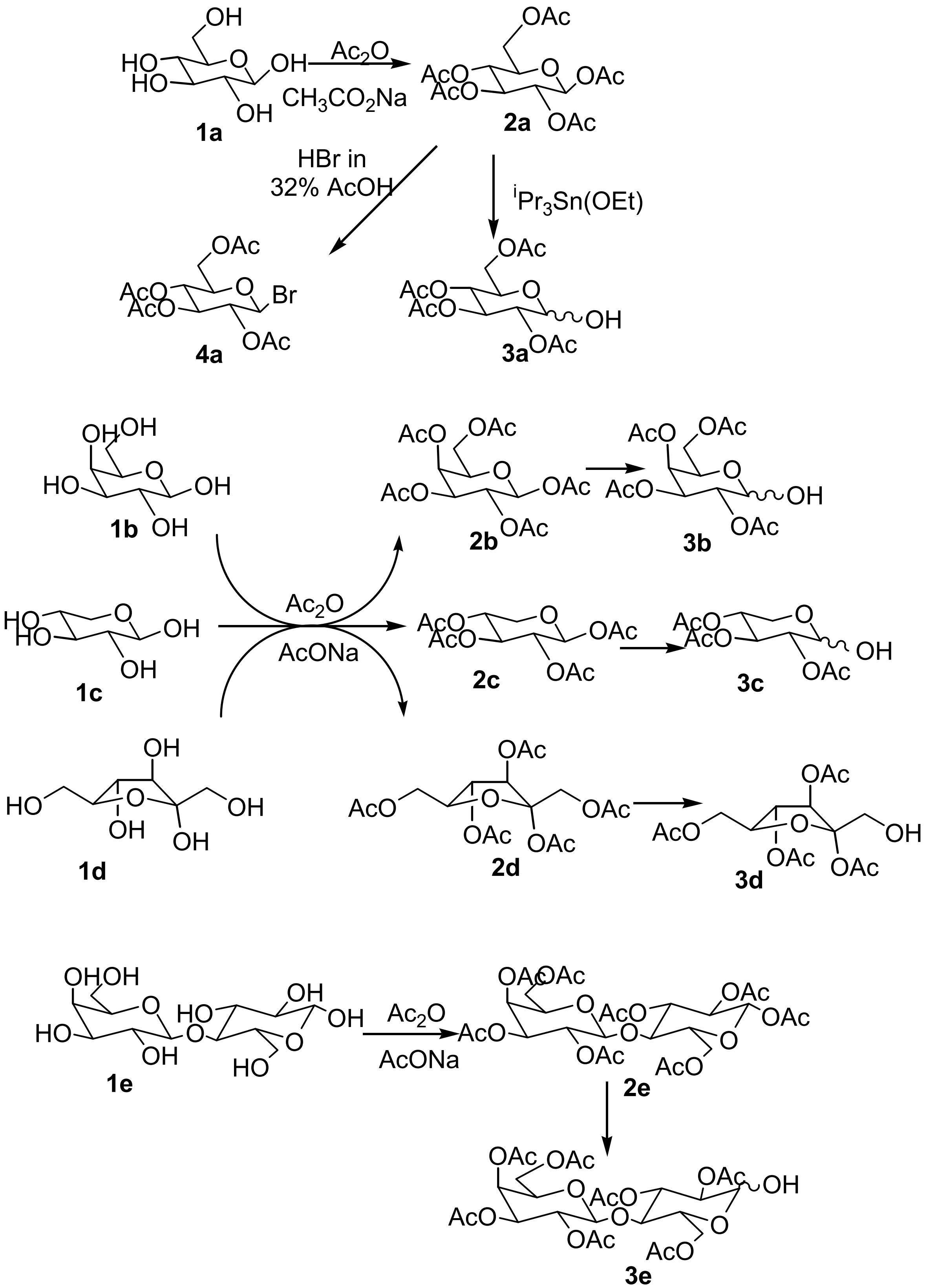
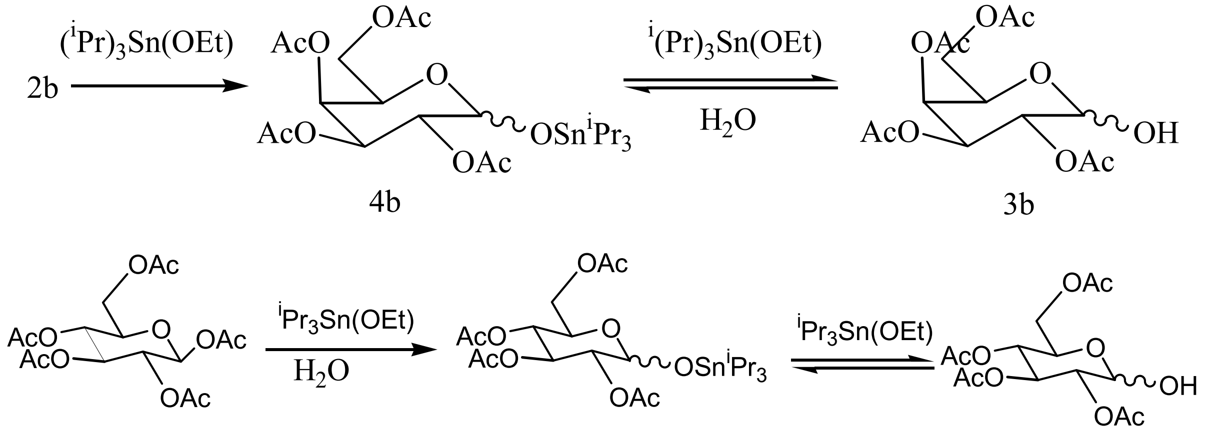


Figure 1. ^{1}H NMR spectrum of D-glucose pentaacetate 2a of a representative



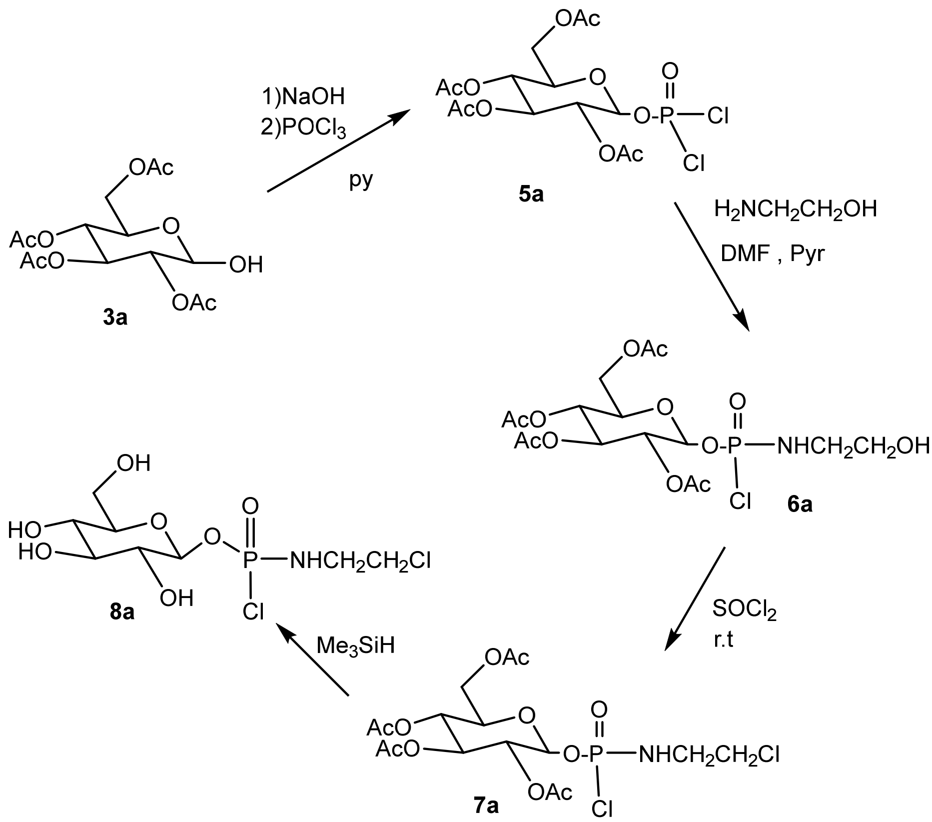
Scheme 1. Full acetylation and anomeric deacetylation of carbohydrates

The acetyl ester plays an important role for protection of the hydroxyl group in organic synthesis. Methodologies that are widely used have been put forth for the esterification. The deprotection of the acetyl esters is much less studied despite its practical significance in synthetic processes. A convenient methodology has been developed for the selective removal of the anomeric acyl group of carbohydrate derivatives using $(^{i}Pr)_3SnOEt$ conditions. Representatively, the proposed mechanism of the formation of **3b** is shown in Scheme 2.



2a **2a/** **3a**

Scheme 2. Representatively, proposed mechanism of the formation of 3b



Scheme 3. Synthesis of 8a from 3a as representative

In IR spectrums the existence of $1730cm^{-1}$ peaks shows a Carbonyl group and peaks $1000cm^{-1}$ are related to aliphatic group. absorption vibrate of esters are appeared in $1000\text{-}1300cm^{-1}$ acetylation of galactos while organizing Carbonyle in position 2 which shows the effect of neighbor group so the existing quitter group easily take apart from number one carbon and organize stable Carbocation. In this mode there is a possibility of attacking carbon anomeric by nucleofilic agent. Absorption band in $1379cm^{-1}$ location is related to symmetrical curvature of methyl CO-CH_3 and seen absorption in 1221cm^{-1} is related to neighbor C-O vibration of ester Carbonyl group and absorption band in 1100cm^{-1} is related to ester tension of alcoholic section of ester.

In order to synthesize the new oxazaphosphorine derivatives, the anomeric hydroxyl group should be deprotected. For this purpose, we used $(^{i}Pr)_3SnOEt$ for the selectively deacetylation of the anomeric position. Therefore, as a representative, **2a** was selectively converted to **3a** in good yield (Scheme 1). The reaction of compound **3a** with $POCl_3$ yielded **5a**. The reaction of this compound with 2-eyhanolamine gave **6a,** then in the presence of thionyl chloride yielded **7a**. The deprotection of acethyl groups of later compound (**7a**) in the presence of trimethylsilane yielded **8a.**

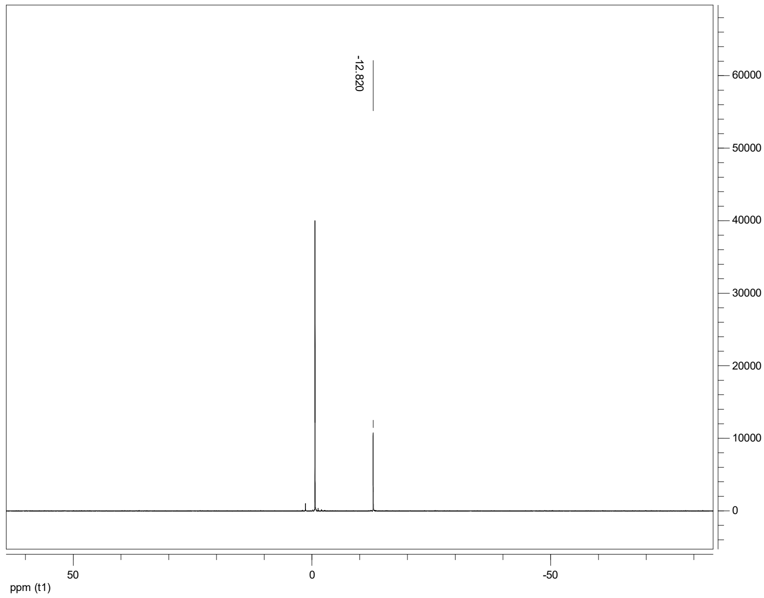


Figure 2. Representatively, ^{31}P NMR spectrum of 7a

The ^{31}P NMR spectrum of **7a** is shown in Figure 2. A singlet peak at δ -12.82 ppm corresponded to a unique phosphorous atom connected to oxygen, nitrogen and halogen atoms.

Table 1. Reaction conditions and conversions of carbohydrate to per acetate with Ac_2O/AcONa

Entry	Sugar	Product	Reaction Temperature(°C)	Reaction time (min)	Conversion (%)
1	**1a**	**2a**	30-40	180	77
2	**1b**	**2b**	50-60	180	79
3	**1c**	**2c**	60	240	72
4	**1d**	**2d**	60-70	240	75
5	**1e**	**2e**	70-80	300	65

Table 2. Selective anomericdeacetylation of carbohydrates

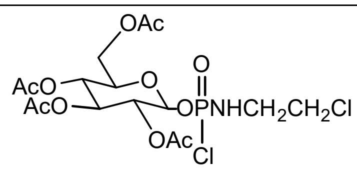
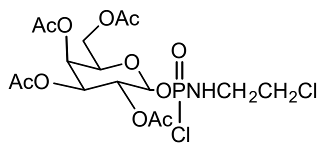
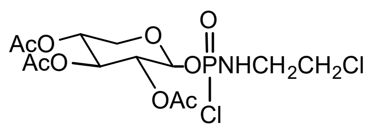
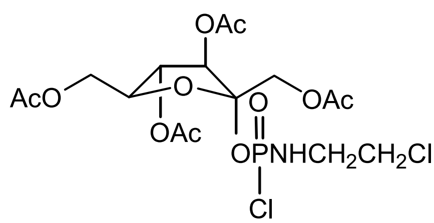
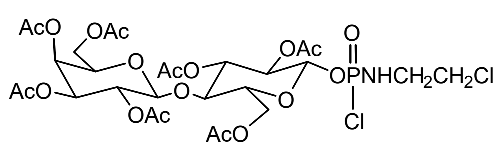
Entry	Sugar	Product	Reaction Temperature(°C)	Reaction time (min)	Conversion (%)
1	**2a**	**3a**	70	240	79
2	**2b**	**3b**	80	240	77
3	**2c**	**3c**	80	240	70
4	**2d**	**3d**	80	260	70
5	**2e**	**3e**	90	300	61

Table 3. Bromination of some carbohydrates in anomeric position, reaction times and yields

Entry	Sugar	Reaction Temperature(°C)	Reaction time (h)	Conversion (%)
1	**2a**	70	12	65
2	**2b**	80	12	61
3	**2c**	80	18	60
4	**2d**	80	18	62
5	**2e**	90	30	59

As a representative, FTIR spectrum of **2b** showed vibration bands of carbonyl (C=O), C-O groups are appeared in 1746 and 1224cm^{-1}, respectively, and vibration band at 1371cm^{-1} is related to bending vibration of methyl group. No hydroxyl group stretching frequency was observed at 3500-3600cm^{-1}. These observations demonstrated the full acetylation of **1b** the acetylation of D-galactose within formation of acethoxy group in position 2 demonstrates neighboring group participation (NGP). In this manner, charging of nucleophilic agent to anomeric carbon is only possible from one side. The selective deacetylation of **2b** was carried out in the presence of (^{i}Pr)$_3$Sn(OEt) and yielded **3b**.

Table 4. Conjugated $POCl_3$ and ethanol amine in anomeric position, reaction times and yields

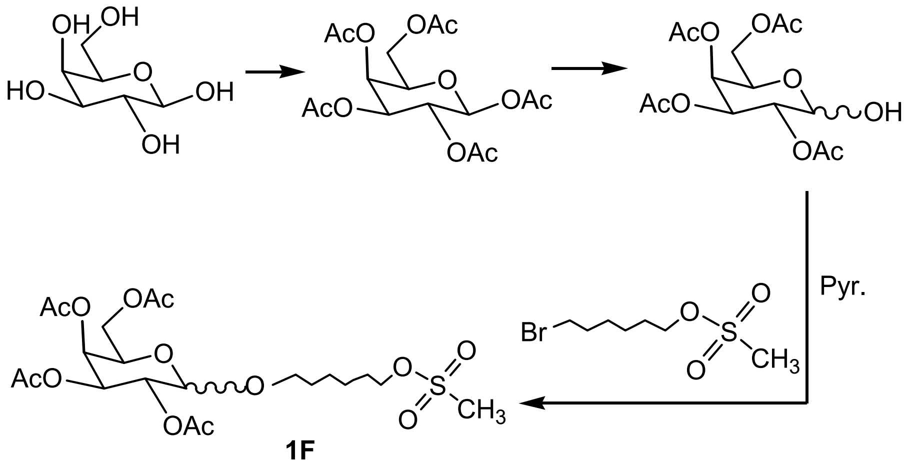
Entry	Reactant	Products (**7**)	Yield%	Ref (Jabbari & Noroozi, 2018)
1	**3a**		77	
2	**3b**		72	
3	**3c**		67	
4	**3d**		62	
5	**3e**		52	

Carbohydrate is one of the natural materials with the biggest organic compounds classification which exist in a high level biomolecule such as lipids or glycoproteins. Carbohydrates play an important role in different kinds of biological processes. Mutual and specific performances of protein-carbohydrate in processes such as cell breakdown, cell adhesion, safety reaction, congestion and tumor cell.

Metamorphosis, glycolipid, glycoprotein and Polysaccharide creation in lektins and proteins, are the biological responsibilities of carbohydrates.

The FT-IR spectrum in combination with it, showed that there was no penetration with the OH absorption range. All compounds synthesized in Table 4 are confirmed by ^{31}PNMR spectroscopy.

In order to prepare (**1F**), compound **3b** obtained from previous stage (1.4mmol) was dissolved in pyridine (0.4mL) and deprotonated by NaOH. A mixture is cooled at 0'^{C} in an ice water bath, then bromohexaalkylsulfunat is added (2mmol, 0.2mL), and then the reaction mixture is stirred for 6 h at room temperature. After gathering sediment, it is dissolved in dichloromethane (12mL) and organic phase is extracted by salt water (2*6mL) and then dried by using sodiumsolphate, the solution is filtered and removed by rotary, and crystallized by ethanol with 53% efficiency (scheme 4).



Scheme 4. Reaction process and synthesis of 1F

Under base conditions, Compound **1F** is reacted in bromo hexaalkyl Methylsulfonate reaction in presence of pyridine. In FT-IR spectrum (Figure 4), peak 1226, and 1751cm^{-1} is related to ester carbonyl strength groups and peak locd ated at 2942, and 2867cm^{-1} is related to CH aliphatic group. Also, 1173cm^{-1} peak is related to (S=O) group and 1374cm^{-1} peak is related to methyl absorption group, 1069cm^{-1} peak is related to (-CH_2-O-CH_2-) absorption group. Removal of OH peak showed product formation.

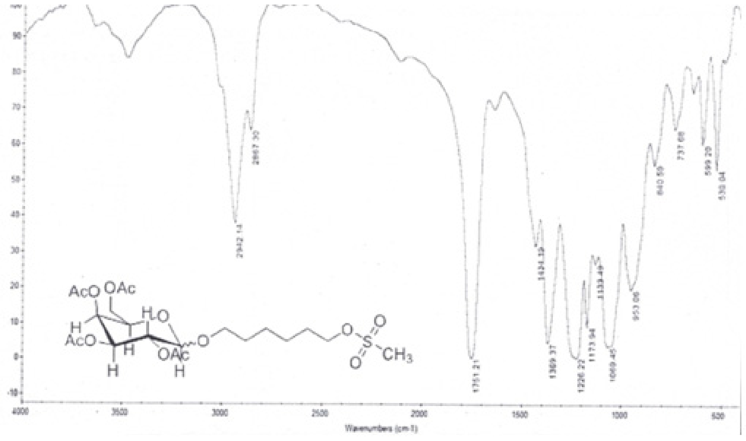


Figure 4. FT IR spectrum of compound of 1F

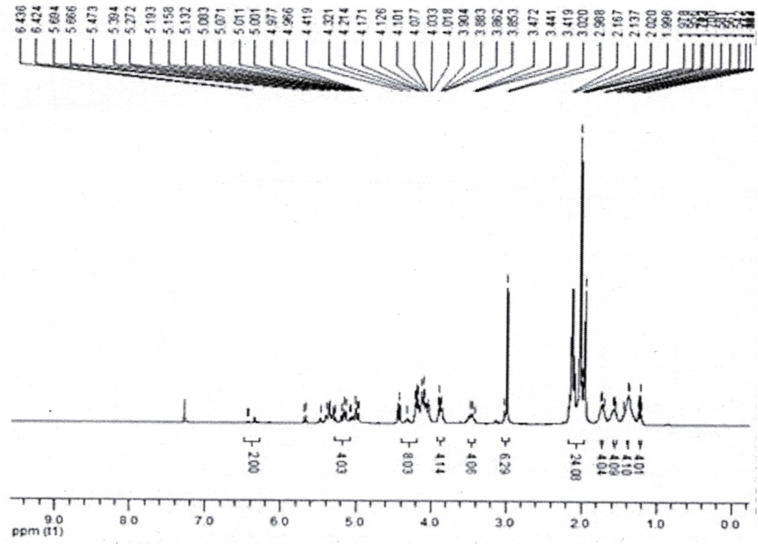


Figure 5. [1]H NMR spectrum of 1F

In [1]H NMR spectrum of **1f**, (-O$(CH_2)_2$-$(CH_2)_2$-$(CH_2)_2$-S(=O)-) is a quintet peak at δ = 1.23 and δ = 1.38ppm is for 4 protons and δ = 1.56ppm is for two protons. One peak at δ = 1.72ppm is for two protons (Figure 5). All of peaks corresponded to the equilibrium mixture of α and β isomers. A peak at δ = 1.96, 1.97, 2.02, 2.09, 2.14, 2.17ppm is related to 12 methyl's protons. Two singlet peaks are related to (S$(=O)_2$-CH_3) in chemical shift with δ = 2.99 and δ = 3.02ppm and they equal with 3 protons of α and β isomers. Two doublet of doublets peaks relate to (-O-CH_2-$(CH_2)_4$-CH_2-O-S(=O)-) at δ = 3.42-4.02ppm. Multiplet peaks at δ=4.02-4.42ppm corresponded to (C4, C5 and C6-H). A doublet of doublet peak for (C2 and C3-H) at δ = 4.97 -5.47 ppm has 4 protons relate to α and β isomers.

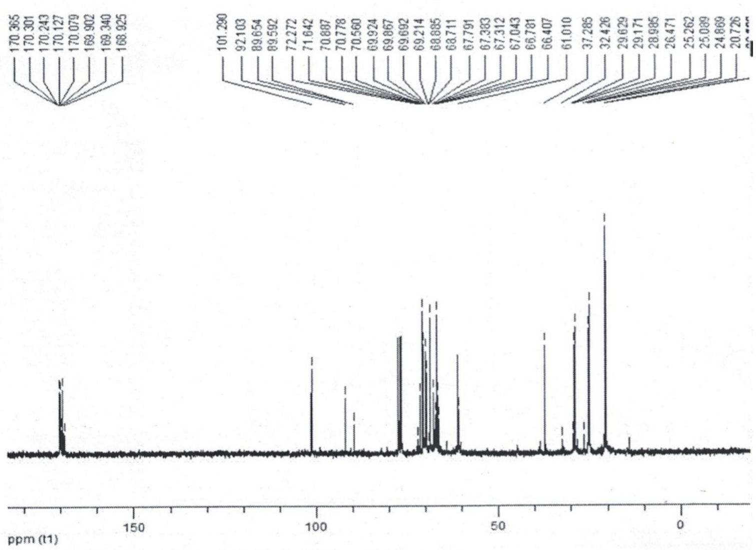


Figure 6. [13]C NMR spectrum of 1F

In [13]C NMR spectrum of **1f**, four peaks observed at δ = 20.9, 20.7, 20.63, 20.56ppm are related to four methyls of OAc groups. Four peaks observed at δ = 29.6, 29.2, 29.0, 26.5, 25.3, 25.1 and 24.9ppm are related to six carbons (-$(CH_2)_6$-) of α and β isomers. Two peaks observed at δ 37.3 and 32.4ppm related to (S$(=O)_2$-CH_3) are equal with two carbons in α and β isomers. Observed peak at δ 61ppm is related to methylene carbon (C6). Also, Observed peak at δ 101.3ppm corresponded to anomeric carbon atom. Eight peaks in carbonyl region at δ 169.9, 170.07, 170.13, 170.3, 170.3, 168.9, 169.3 and 170.4ppm corresponded to α and β isomers (Figure 6).

4. Conclusion

The present study investigated a productive manner for deacetylation of anomeric position. This method has several advantages such as the good-natured reaction conditions, experimental simplicity, good yield .then the basic reagents are unfavorable for anomeric deacetylation this approach can be very effective. In all cases, The yields were good to excellent. However, in this paper carbohydrates such as glucoss, xylose, fructose, galactose, lactose by acetic anhydride in the presence of sodium acetate were acetylated. Then the deacetylation of anomeric position by($(^iPr)_3Sn(OEt)$) was reacted. In order to prepare derivatives such as oxazaphosphorine and bromoheptyl methanesulfonate, deporptonation of the hydroxyl group was reacted with carbohydrates to supply new compounds.

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Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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