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Synthesis of Precursor Glucosamine Building Blocks of Chitin

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Review Article

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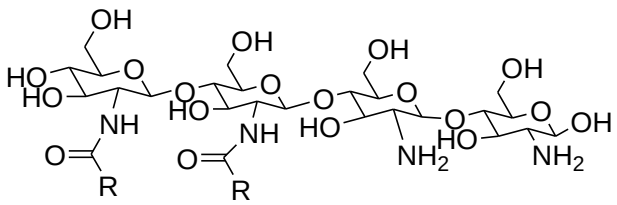
ABSTRACT

The acylation reaction is an important process for biological and chemical applications. Biologically, this reaction is used in a mechanism critical to numerous cellular processes, such as protein assembly and regulation. This article reviews the state of the art of microwave-assisted reactions and the influence of microwaves on mass and heat transfer. The heating behaviour of representative test reactions and single substances is compared for heating with microwaves and thermal energy.

INTRODUCTION

Differentially protected glucosamines are very important structural units of many bioactive products which are synthesized in human body. β–(1-4) linked N-acetyl glucosamine moiety is a frequently occurring structural unit in various naturally and biologically important oligosaccharides and their conjugates.

Chitin is a structural polysaccharide in crab shells, and chitobiose is usually found at the reducing end of *N*-glycan residues of glycoproteins. Of these biologically active chitooligosaccharides, chitotetraose has the highest affinity among chitooligosaccharides to bind to rat NKR-PL antigen, a carbohydrate-binding protein in rat natural killer (NK) cells [1-16].



Schematic view of chitin oligosaccharide

Chitosan is one of the most abundant renewable polysaccharides prepared from chitin by deacetylation. Chitosan and chitosanase are attracting a wide attention in their potential application in medicine, industry and agriculture. Also, chitooligosaccharides have received much more interest, because they are not only water-soluble

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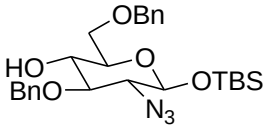
but also possess distinctive biological activity [16-24], such as antitumor, antifungal and antibacterial activities, immuno-enhancing effects [24-29], and promote host defense against infection of certain pathogens in mice.

Objective

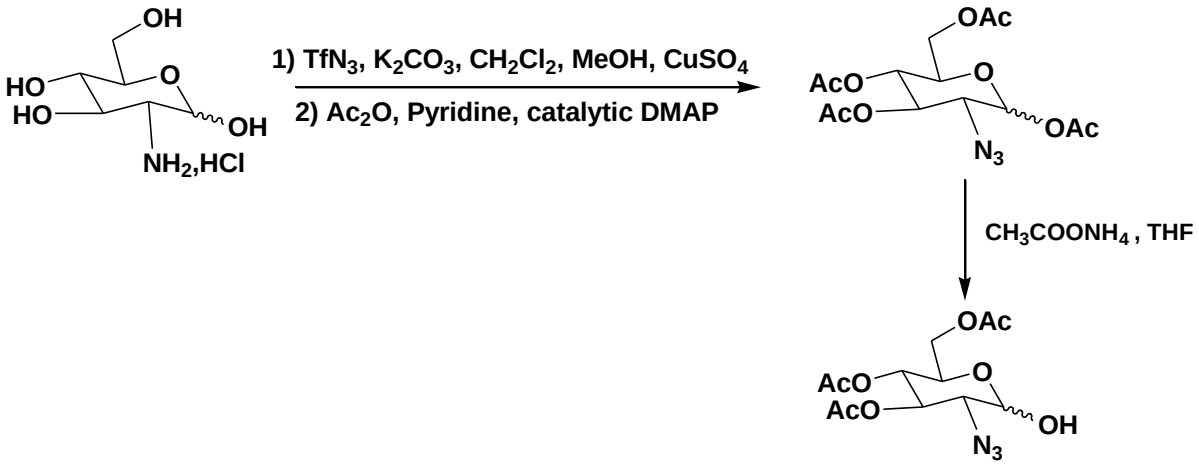
The main objective of the project is to synthesize the precursor monomer building block from glucosamine hydrochloride as starting material.



RESULTS and DISCUSSIONS

Synthesis of differentially protected glucosamines

Glucosamine derivatives are most important building blocks in carbohydrate chemistry for synthesizing oligosaccharides [29-38]. Synthesis of our monosaccharide building block starts with insitu preparation of triflic azide from triflic anhydride and sodium azide for the conversion of 2-amino group in the glucosamine to azide followed by peracetylation and anomeric deacetyation furnishes the common precursor.



EXPERIMENTAL SECTION

General methods

^{1}H NMR and ^{13}C NMR were recorded on Bruker Avance-400MHz NMR machine using solution in $CDCl_3$. ^{1}H NMR referred respectively to TMS used as an internal standard and the central line for $CDCl_3$. Chemical shifts were reported in (δ) ppm and coupling constants (J) reported in Hz. Pyridine was purchased from Merck. Triflic anhydride and other chemicals used were purchased from Aldrich. DCM was freshly distilled from CaH_2 [39-53]. Methanol was distilled from $MgSO_4$. Column Chromatography was performed over silica gel from SISCO, using hexanes and ethyl acetate mixture as eluent. Solvents were removed under reduced pressure on rotovap. Organic extracts were dried with anhydrous Na_2SO_4. The visualization of spots on TLC plates was effected by exposure to 5%MeOH in H_2SO_4.

Preparation of -2-azido-2-deoxy-D-glucose

1. Preparation of TfN_3:

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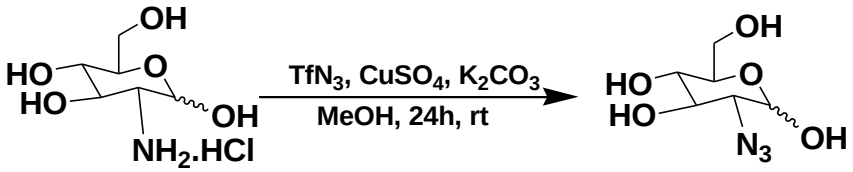
To a solution of NaN_3 (15g, 230mmol) in water (30mL) CH_2Cl_2 (40mL) was added at 0°C. The mixture is stirred vigorously and treated with Tf_2O (7.8mL, 46.36mmol). The reaction mixture was stirred at 0°C for 2.5h. The aqueous phase was extracted with CH_2Cl_2. Combined organic layers were washed with saturated Na_2CO_3, dried over Na_2SO_4 and concentrated in vacuo then immediately used for the reaction [54-69].

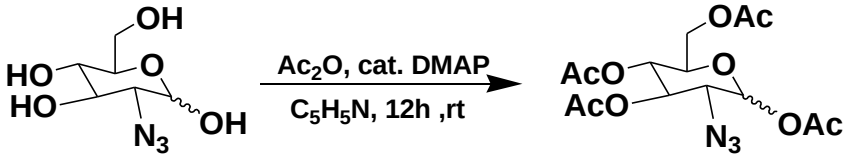
2. Conversion of 2-amino group to azide:



1` 2

To a solution of glucosamine hydrochloride (5g, 23.18mmol) in water (74mL), $CuSO_4$ $5H_2O$ (55mg, 0.22mmol) and K_2CO_3 (4.8g, 36mmol) were added. Then methanol (50mL) was added to the reaction mixture followed by addition of TfN_3 solution (prepared from triflic anhydride and sodium azide) [70-84]. Methanol was added until the solution become homogenous (~25mL). The light blue color solution was allowed to stir for 24h at room temperature. After completion of the reaction, solvents were removed to obtain compound 2 which was used directly for the next step.

Preparation of 1, 3, 4, 6-tetra-*O*-acetyl-2-azido-2-deoxy α/β-D-glucopyranose:



2 3

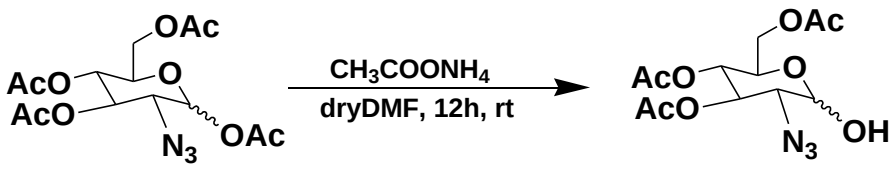
To the azido compound 2 in pyridine (25mL), Ac_2O (25mL) and catalytic DMAP were added and the reaction mixture was allowed to stir for 12h [85-89]. After completion of the reaction by TLC monitoring, it was worked up with EtOAc and dried over Na_2SO_4 followed by removal of solvent on rotovap and purified by column chromatography with Hexane and Ethyl acetate as eluents (3:1) to afford desired compound 3.

Yield = 35%

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55 (d, J = 8.6 Hz, 1H), 5.09-5.05 (m, 2H), 4.3 (dd, J=12.5, 4.4 Hz, 1H), 4.08 (dd, J=1.9, 12.5 Hz, 1H), 3.75 (m, 1H), 2.2 (s, 3H),

2.10 (s, 3H), 2.08 (s, 1H), 2.03 (s, 3H).

Preparation of 3, 4, 6-tetra-*O*-acetyl-2-azido-2-deoxy α/β-D-glucopyranose:



3 4

Peracetylated compound 3 (3g, 8.1mmol) was dissolved in dry DMF (30mL), to this ammonium acetate (1.25g, 16.2mmol) was added. The reaction mixture was stirred at room temperature overnight [90-96]. After completion of the reaction, solvent was removed and pure compound **4** (958mg, 8.04mmol) was obtained by column chromatography (Hexane/EtoAc 3:1) [97-100].

Yield: 36%

^{1}H NMR (400 MHz, CDCl3): δ 5.48 (m, 1H), 5.4 (d, J=6.4 Hz, 1H), 5.27 (m, 1H),
4.29-4.41(m, 2H), 4.12 (m, 1H), 3.17(m, 1H), 2.2-2.02(m, 9H).

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