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The N-allyloxycarbonyl derivative of D-glucosamine: a potent precursor of β-glycosidation.

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Summary: The allyloxycarbonyl protective group of the amino function is a potent precursor of β-D-glucosidation of D-glucosamine and can be selectively removed or preserved in the presence of other usual carbohydrate protective groups.

The constant demand of better glycosidation procedures in the synthesis of natural oligosaccharides and our recent [1] results in the field of allyloxycarbonyl esters prompted us to report the use of O-allylcarbamates of D-glucosamine as precursors of β-glycosides.

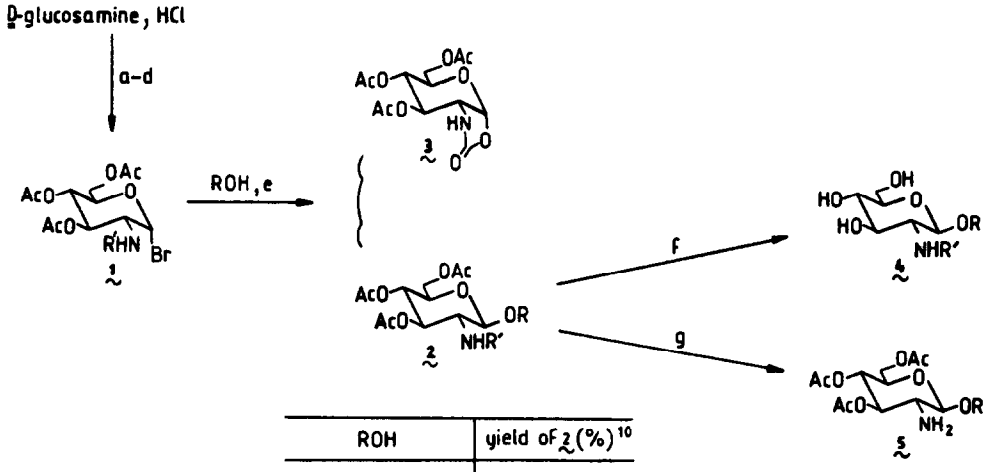
The usual procedures for the glycosidation of D-glucosamine are the so-called oxazoline method [2-4] and phtalimido method [5]. Despite their synthetic usefulness, these methods present some disadvantages, mainly the moderate yields [3,4] concerning the first one and the need of a rather drastic removal of the phtalimido group in the second one.

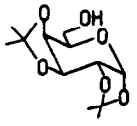
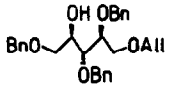
The above inconveniences were overcome, by the use of a N-allyloxycarbonyl derivative of D-glucosamine giving better results for glycosidation than those reported earlier in the literature [6,7].

The starting glycosyl bromide **1** was obtained as a white crystalline material (Mp 93-94°, $[\alpha]_D^{24}$ + 147°) from D-glucosamine by reaction with allylchloroformate (1.1 eq.) and triethylamine at 50°C during 20 min., followed by acetylation (acetic anhydride/pyridine) and treatment with 33 % hydrobromic acid in acetic acid (overall yield 74 %). The reaction of **1** with a stoichiometric amount of alcohol in dichloromethane, using either mercury (II) cyanide (room temperature) or silver trifluoromethanesulfonate / N,N,N',N'-tetramethyl urea [8] (-50°C) as promotor then afforded the corresponding β-glycosides.

In both cases the cyclic carbamate 3 [6] were obtained as a by-product, mainly with alcohols of low reactivity [9].

The formation of 1,2-trans-glycosides together with the cyclic carbamate 3 confirms the expected anchimeric assistance of the N-allyloxycarbonyl group during the glycosidation reaction.



ROH	yield of 2 (%) [10]
Methanol	91
Isopropanol	76
	86
	81

R' = N-allyloxycarbonyl; Ac = acetyl; All = allyl; Bn = benzyl

a. CH_3ONa, CH_3OH; b. ClCOOAll, Et_3N; c. Ac_2O, pyr; d. HBr, AcOH, CH_2Cl_2;
e. $Hg(CN)_2$, CH_2Cl_2; f. NH_2NH_2, EtOH; g. $Pd(PPh_3)_4$, THF, $CH_2(COOMe)_2$.

The acetyl protective groups in the series of compounds 2 could be removed, if necessary for further steps, by hydrazinolysis without affecting the N-allyloxycarbonyl function thus affording the series of compounds 4 with free C-3, C-4 and C-6 hydroxyl groups. On the other hand the N-allyloxycarbonyl protective group could be easily and quantitatively removed by catalytic treatment with tetrakistriphenylphosphine palladium (2.10^{-2} eq.) and dimethylmalonate (7 eq.) as allyl acceptor in THF at room temperature for 24 h. This later allyl acceptor was shown to be more efficient than those reported in the literature which were either acidic [11] or afforded non-volatile side-products [12]. The usual protective groups were unaffected by this treatment and, after column chromatography, the series of compounds 5 could be acetylated as in most natural glycosides of D-glucosamine or esterified with fatty acid as in glycolipids.

The synthesis of complex oligosaccharides such as artificial antigens of S.aureus is in progress [13] using this new N-allyloxycarbonyl derivative of D-glucosamine.

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Footnotes and references

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9. The reaction of **1** with 1,2:5,6-di-O-isopropylidene -α-D-glucofuranose promoted by mercury (II) cyanide at room temperature afforded compound **3** [6] as main product (56 %) together with the expected disaccharide (17 %).

10. Reactions promoted by mercury (II) cyanide in dichloromethane at room temperature. Time of reactions was dependent of the alcohols: the glycosides were crystalline except with the ribitol aglycon: Methanol (2h, Mp: 111-112°, $[\alpha]_D^{24}$ + 10.2°): Isopropanol (6h, Mp: 148-149°, $[\alpha]_D^{24}$ + 4.2°): 1,2:3,4-di-O-isopropylidene galactose (5h, Mp 135-136°, $[\alpha]_D^{24}$ -41.3°): 1-O-allyl-2,3,5-tri-O-benzyl-D-ribitol (24h, syrup, $[\alpha]_D^{24}$ -2.3°). Yields are given for separated and purified (column chromatography and/or crystallization) compounds.
The structure of all reported derivatives are in accordance with ^1H nmr (350 MHz), ^{13}C nmr (25.6 MHz) and in agreement with the elemental analysis.

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