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β-Cyclodextrin promoted allylation of aldehydes with allyltributyltin under supramolecular catalysis in water ☆

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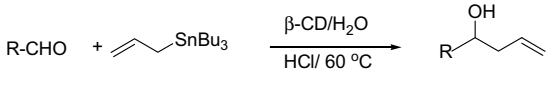
Abstract—A novel and highly efficient allylation of aldehydes using allyltributyltin has been developed in aqueous medium catalyzed by β-cyclodextrin in the presence of HCl without any metal catalysts to afford the corresponding homoallylic alcohols in good yields. The β-cyclodextrin can be recovered and reused for a number of runs without significant loss of activity.

Allylation of carbonyl compounds is an important carbon–carbon bond forming reaction in organic chemistry for the preparation of homoallylic alcohols,[1] which are useful tools for the construction of complex molecules and which can be easily converted to many important building blocks for the synthesis of natural products.[2] Though various kinds of Lewis, Bronsted acid and organometallic reagent catalyzed allylation reactions have been reported with allyltin reagents in organic[3] as well as in a mixture of organic and aqueous media,[4] no allylation reaction exclusively in an aqueous medium using allyltributyltin has been reported.[4a] Lewis acids containing boron, aluminium, titanium and tin are extremely moisture sensitive and so some of these reactions must be carried under strictly anhydrous conditions. In some cases, Lewis acid promoters have also to be used.[4b] In the case of some Lewis acids, even a small amount of water inhibits these reactions because the reagents react immediately with the water rather than with the substrate.[3b]

Although Lewis or Bronsted acid catalyzed allylation reactions in mixtures of organic and aqueous media have been reported with allyltributyltin, more active and efficient catalytic systems may be beneficial. Recently there was a report of carrying out these reactions in ionic liquids[5] and polyethylene glycol (PEG).[6] These ionic liquids, especially the imidazolium ones with PF_6 and BF_4 counter ions, have been shown to have serious drawbacks.[7] The high cost[8] and disposability of these solvents also limit their usefulness.

Cyclodextrins (CDs) are cyclic oligosaccharides possessing hydrophobic cavities, which bind substrates selectively and which catalyze chemical reactions with high selectivity. They catalyze reactions by supramolecular catalysis involving reversible formation of host–guest complexes by non-covalent bonding as seen in enzymes.[9] Complexation depends on the size, shape and hydrophobicity of the guest molecule, thus mimicking biochemical selectivity, which is due to the orientation of the substrate by complex formation. This positions only certain regions for attack and can be superior to chemical selectivity, which involves random attack dependent on the intrinsic reactivity of the substrate at different positions. Our earlier expertise in the field of biomimetic modelling of organic chemical reactions involving cyclodextrins[10] prompted us to attempt the allylation



Scheme 1.

Keywords: Aldehydes; Allylation; Allyltributyltin; β-Cyclodextrin; HCl; Water.
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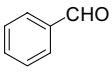
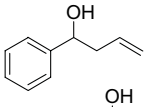
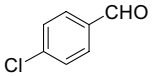
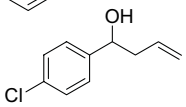
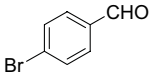
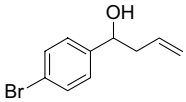
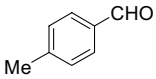
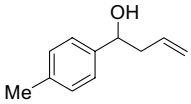
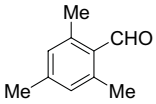
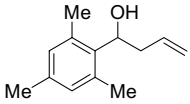
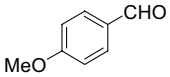
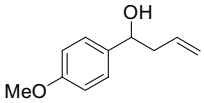
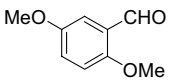
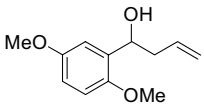
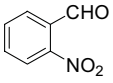
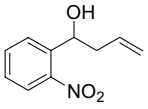
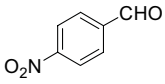
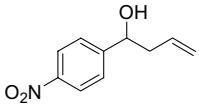
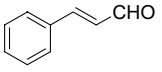
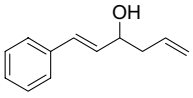
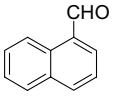
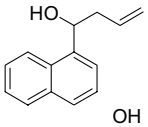
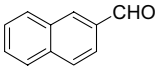
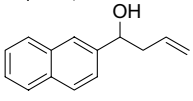
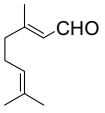
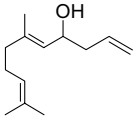
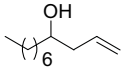
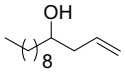
Table 1. β-Cyclodextrin catalyzed allylation of aldehyde using an acidic aqueous medium

S. no.	Substrate	Product[a]	Time (h)	Yield[b] (%)
1			3.0	90
2			2.5	95[c]
3			2.5	95
4			2.5	94
5			3.5	90
6			3.0	92
7			3.5	90
8			3.5	90
9			2.5	96
10			3.5	90
11			3.0	90
12			2.5	93
13			3.5	89
14			3.5	88
15			3.5	88

[a] All the products were characterized by MS, ^{1}H NMR and IR spectroscopy.
[b] Isolated yields.
[c] Catalyst was recovered and reused for five consecutive runs in this reaction without any change in the yield and purity.

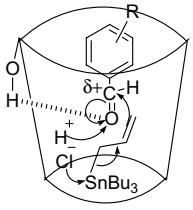


Figure 1.

of aldehydes using allyltributyltin under biomimetic conditions using cyclodextrins with water as the solvent in an acidic media at 60 °C (Scheme 1 and Table 1).[11]

This is the first feasible allylation reaction of aldehydes with allyltributyltin in an acidic aqueous medium. The reaction proceeds efficiently at 60 °C without the need of any Lewis acid or transition metal catalyst. The reaction goes to completion in a short time (2.0–3.5 h). This methodology is compatible with other functionalities such as bromo, chloro, methyl, methoxy and nitro groups, double bonds, napthaldehydes and aliphatic aldehydes under mild reaction conditions. No by-product formation was observed. These reactions are clean with nearly quantitative yields with short reaction times, high selectivities and a recyclable catalyst. These reactions do take place with α-CD, however, β-CD was chosen as the preferred catalyst since it is inexpensive and easily accessible.

Although inclusion complexation takes place in situ during the reaction, the complexes have been isolated and characterized by powder X-ray[12] and ^{1}H NMR studies.[13] All the products were characterized by MS, ^{1}H NMR, IR and by comparison with the known compounds.[3,4] It was observed that although these reactions take place with a catalytic amount of CD (0.1 mmol), the reaction takes longer (10–12 h). The fact that these reactions do not take place in the absence of cyclodextrin indicates the essential role of the CD. In water and HCl alone, without the presence of β-CD, the reaction did not proceed with allyltributyltin.[4a] The aldehyde is complexed in the cyclodextrin cavity with the CD hydroxyl groups forming hydrogen bonding with the carbonyl oxygen of the aldehyde. Present catalytic allylation with cyclodextrin exhibited a high chemoselectivity towards aldehydes (Fig. 1).

β-Cyclodextrin, apart from being non-toxic, is also considered as metabolically safe.[14] In contrast to existing methodologies using Lewis acid and transition metal catalysts, this method is simple and high yielding.

Acknowledgements

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11. The reaction was carried out as follows: β-CD (1 mmol) was dissolved in water (15 ml) by warming up to 60 °C until a clear solution was formed and then the aldehyde (1 mmol) dissolved in acetone (1 ml) was added slowly with stirring. After 15 min at this temperature 2 N HCl (1 mmol) and allyltributyltin were added and the mixture stirred at that temperature until the reaction was complete (Table 1). The organic material was extracted with ethyl acetate, dried and concentrated under reduced pressure and the resulting product, as though seen as single compound by TLC, was further purified by passing over a column of silica gel. The CD was recovered by filtration and reused.
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