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Zwitterionic imidazolium salt: An efficient organocatalyst

for tetrahydropyranylation of alcohols

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Full experimental detail, Copies of ¹H and ¹³C NMR spectra. This material can be found *via* the "Supplementary Content" section of this article's webpage.

ABSTRACT

An aprotic imidazole based zwitterionic-salt, 4-(3-methylimidazolium)-butane sulfonate (MBS) has been found to be an efficient organocatalyst for tetrahydropyranylation by the reaction

of DHP and different aliphatic alcohols as well as various phenolic compounds The notable advantages of the present method are general applicability to various alcohols, clean reaction, production of no hazardous waste, open air reaction conditions and high yields. The catalyst can be reused without the loss of significant catalytic activity.

GRAPHICAL ABSTRACT



KEYWORDS: chemoselective, organocatalyst, tetrahydropyranylation, unsaturated alcohols, zwitterionic imidazolium salt

Introduction

In multistep organic synthesis common functional groups like carbonyls, hydroxyl, amine and carboxylic acid etc. need protection.^[1] Among various methods available in literature for protection of hydroxyl group tetrahydropyranyl (THP) is the most useful due to its low cost and stability under basic media, Grignard reagents, acylating agents, metal hydrides and alkyl lithiums.^[1] Glycosylation is arguably one of the most important and difficult reactions in carbohydrate chemistry^[2] which is also the formation of spiroacetal and similar to the THP ether.^[3] Several methods have been developed in literature for glycosylation reaction^[3] but we focused our target for tetrahydropyranylation of alcohols. Numerous reports are there in literature using catalytic amount of acids,^[4] Lewis acids,^[5] polyaniline salt,^[6] ferrous methanesulfonate,^[7]

 Bu_4NBr_3 .^[8] $H_{14}[NaP_5W_{30}O_{110}]$,^[9] Pyridinium Moβ.^[11] chloride.^[10] 2.4.6trichloro[1,3,5]triazine,^[12] Dowex 50WX4-100^[13] and using molecular iodine^[14] etc.. Recently, development of environmentally benign and clean synthetic techniques has become the goal of organic synthesis.^[15] Particularly, the use of nonhazardous, inexpensive catalysts is now very useful in organic synthesis and organocatalytic reactions are really meaningful to achieve this goal. Organocatalysis has become very powerful synthetic technique^[16] and is very much popular due to the simple reaction conditions, tolerant of water and air. Several reports are available in literature for tetrahydropyration using organocatlysis.^[17] During preparation of our manuscript a method has been reported under organocatalytic conditions using imidazolium based Brønsted-Lewis acidic ionic liquid as catalyst.^[18] Most of these proved to be efficient for this reaction. However, some of them have several drawbacks, such as elevated temperature, long reaction time, harmful organic solvent, expensive catalysts, and high catalyst to substrate ratio. Thus, there is still demand for the introduction of mild and efficient method for this transformation.

In continuation of our research on green synthesis, we have explored imidazole-based zwitterionic-type molten salts as a new class of organocatalyst in various chemical transformations.^[19] The requisite zwitterionic-type molten salts are obtained by the reactions of the various imidazoles with 1,4-butane sultone/1,3-butane sultone.^[20] Thus based on recent works on green synthesis, imidazole-based zwitterionic-type molten salts, which are the important precursors of room temperature ionic liquids (RTILs), have been explored as a new class of organocatalyst in various chemical transformations.^[21] Reactions of the various imidazoles with 1,4-butane sultone/1,3-propane sultone produce the requisite zwitterionic-type molten salts. The synthetic strategy is outlined in Scheme 1.^[20]

We have prepared different types of zwitterionic-type molten salts by varying imidazoles and 1,4- butane sultone/1,3-propane sultone as shown in **Figure 1**. One of the most important advantages of zwitterionic-type molten salt as catalysts is that they can easily be recovered from the reaction media and it can be reused for subsequent reactions with high catalytic activity. In addition, it is known that imidazolium motifs provide an unconventional C–H bond.^[22d,f]

Herein, we are pleased to report a convenient approach for the tetrahydropyranylation of alcohols by the reaction of 3,4-dihydro-2*H*-pyran (DHP) and various alcohols in presence of 10mol % of zwitterionic-type salt as catalyst under mild and solvent-free conditions using (Scheme 2).

Results and Discussion

During our initial study, readily available benzyl alcohol (**1a**) and 1.2 equiv. of DHP were taken as model substrates using 10mol % of 4-(3-methylimidazolium)butane sulfonate (MBS, **A**) as catalyst. The reaction proceeded smoothly at 60 °C and the corresponding THP ether (**3a**) was isolated in 90% yield within 10h. We have also examined few other molten salts synthesized in our laboratory as shown in the **Table 1**. It has been observed that other molten salts (**B**, **C** and **D**) are not effective like MBS (**A**) for this tetrahydropyranylation. When 4-(1-imidazolium)butane sulfonate (**IBS**, **B**) has been used (entry 2, **Table 1**) the yields are considerably lower (75%) than **A** (90%) as the catalyst. Similarly 3-(1-imidazolium)propane sulfonate (**C**, entry 3, **Table 1**) also less effective and observed the desired product with 70% yield. According to our previous observation^[15e] when we used 4-(2,3-dimethylimidazolium)butane sulfonate (**D**, entry 4, **Table 1**) a trace amount of desired product was observed. As a result aprotic zwitterion **A** was found to be an effective catalyst for this reaction. Effect of temperature has been studied as shown in the table

(entry 5–7, **Table 1**) and it has been observed that at higher temperature as well as lower temperature the yields are not satisfactory. Finally, the catalyst loading was checked under this reaction conditions using **A** as catalyst for the same reaction (entries 8 & 9, **Table 1**). We have observed that 10mol % of **A** as catalyst afforded better yield (90%) compare to that of 5mol % (74% yield). Similarly using 15mol % of the catalyst no improvement was observed. In absence of any catalyst no conversion has been detected (entry 10, **Table 1**). Finally, optimized reaction conditions were achieved using benzyl alcohol (**1a**, 1 mmol) and DHP (**2**, 1.5 mmol) in presence of 10mol % zwitterionic imidazolium salt **A** at 60 °C for 10h (entry 1, **Table 1**) under neat conditions in ambient air.

The scope and limitations of the optimized reaction conditions were examined by employing various alcohols. First, the effect of various aliphatic, saturated as well as unsaturated alcohols were tested (**Table 2**). It was observed aliphatic alcohols substituted with benzene moiety, such as benzyl alcohol, styrene alcohol and 1-(*p*-tolyl)ethanol reacted efficiently with DHP to afford the desired products with excellent yields under the present reaction conditions (**3a-3c**). Diphenylmethanol, which is sterically hindered, also underwent facile tetrahydropyranylation to afford the corresponding ether (**3d**). Acid sensitive piperonyl alcohol also afforded the desired product with excellent yield (**3e**). *Tert*-amyl alcohol also reacted smoothly to give good yield (**3f**). Alcohols present in unsaturated as well as alkyne systems were also investigated where both of these functionalities were unaffected under the present reaction conditions and reacted smoothly with DHP (**3g**-**3k**). We are pleased to inform that sterically hindered propargyl alcohol such as 1,1,3-triphenylpropargyl alcohol also afforded the desired product with good yield (**3k**). In addition, *Boc*-protected amino ethanol underwent tetrahydropyranylation with moderate yield (**3l**).

To extend the scope of the present methodology, we turned our attention to use various phenolic compounds (**Table 3**). To our delight, the desired products were obtained in good to excellent yields (**33mm -3u**). Simple phenol underwent smooth tetrahydropyranylation with good yield (33mm). Phenols bearing –Me and –OMe substituent efficiently reacted with DHP to afford the products with high yields (**3n-3p**). Electron-withdrawing halogens like –F and –Br in phenol also successfully gave the desired product without any difficulties (**3q & 3r**). This method was also applicable to phloroglucinol, which reacted with three equivalents of DHP in one pot to afford the present reaction conditions (**3t**). In addition, *Boc*-protected 2-aminophenol underwent tetrahydropyranylation with moderate yield (**3u**). All of the reported compounds have been characterized by spectral and analytical data. The reaction conditions are mild and give no decomposition of the products or polymerization of the starting materials. We have not observed any by-products for all reaction combinations which are supported with high yields.

Few control experiments have been carried out to prove the chemoselectivity of the present method (Scheme 3). First, when the reaction was carried out under the standard conditions by using a 1:1 mixture of phenol (**11mm**) and benzyl alcohol (**1a**), we could not find any tetrahydropyranylation of phenol (**33mm**) but 3a was formed with high yield (Scheme 3a); suggesting that benzyl alcohol is more reactive than phenol for the tetrahydropyranylation. Same results were obtained using unsaturated crotyl alcohol (**1h**) as well as propargyl alcohol (**1i**) (Scheme 3b,c). When styrene alcohol (**1b**) was used with crotyl alcohol (**1h**) and 1,1,3-triphenylpropargyl alcohol (**1k**) separately both the corresponding products were obtained with 50:50 ratios (Scheme 3d,e). Whether using a 1:1 mixture of 1,1,3-triphenylpropargyl alcohol (**1k**)

and crotyl alcohol (**1h**); 1,1,3-triphenylpropargyl alcohol did not participate in the reaction (Scheme 3f).

Reusability of the catalyst was also studied to make this protocol more effective. The catalyst, left in the reaction vessel was dried under vacuum and was reused for subsequent reactions. The catalyst was found to be effective up to fifth cycle giving a conversion of 82% in the case of **3a** (**Table 4**).

It is worthy to mention that the mechanistic path has not been studied but based on the literature^[22] and our previous works^[19] we can propose the possible pathway as shown in Scheme 4. The zwitterionic-type molten salt may act a bifunctional organocatalyst.^[22d-f] Simultaneously, it could activate dihydropyran (DHP) through hydrogen bond formation between the C2–H of the imidazolium cation and abstract the acidic hydrogen of alcohol by the sulphonate group. Nucleophilic addition of the alkoxide ion with the activated double bond gives the desired THP ether. Simple intramolecular proton transfer within the molten salt returns back to the zwitterion. The pKa value of the molten salt (**A**) has been determined by pH titrimetric method and is 6.266.

Experimental

General

¹H NMR spectra were determined on a Bruker 400 (400MHz) spectrometer as solutions in CDCl₃. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants *J* were given in Hz. ¹³C NMR spectra were recorded at 100MHz in CDCl₃ solution. Chemical shifts are expressed in parts per million (δ) and are referenced to CDCl₃ (δ = 77.16) as internal standard. TLC was done on silica gel coated glass slide (Merck, Silica gel G for TLC). Silica gel (60-120 mesh, SRL, India) was used for column chromatography. Petroleum ether refers to the fraction boiling in the range of 60-80 °C unless otherwise mentioned. All solvents were dried and distilled before use. Commercially available substrates were freshly distilled before the reaction. Solvents, reagents and chemicals were purchased from Aldrich, Merck, and Spectrochem Chemicals. All reactions involving moisture sensitive reactants were executed using oven dried glassware.

General procedure for the synthesis of 3

A mixture of corresponding alcohol (1, 1 mmol) and 3,4-dihydro-2*H*-pyran (2, 100mg, 1.2 mmol) was stirred in presence of zwitterionic-salt A (10mg, 10mol %) at 70-80 °C (oil bath) for 10-12h in a seal tube. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature and diluted with water (10mL) and extracted with ethyl acetate (20mL). Organic layer was dried over anhydrous Na₂SO₄. After evaporation of solvent the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (4% to 5%) as eluent.

Spectral data of 2-(1,1,3-Triphenylprop-2-ynyloxy)-tetrahydro-2H-pyran (3k)

Yield: 76%, white solid, M.P. (53-55 °C); ¹H NMR (CDCl₃, 400MHz): δ 7.57 (d, *J* = 7.6Hz, 4H), 7.43-7.41 (m, 2H), 7.26-7.12 (m, 9H), 5.06 (t, *J* = 7.2Hz, 1H), 3.92-3.87 (m, 1H), 3.34 (d, *J* = 11.6Hz, 1H), 1.90 (t, *J* = 14.4Hz, 1H), 1.65 (d, *J* = 2.8Hz, 2H), 1.46 (t, *J* = 10.4Hz, 3H); ¹³C NMR (CDCl₃, 100MHz): δ 144.7, 144.0, 131.7, 128.5, 128.3, 128.1, 127.9, 127.6, 127.4, 127.1, 126.9, 122.8, 95.6, 89.7, 89.1, 79.7, 62.5, 31.6, 25.5, 19.6. Anal. Calcd for C₂₆H₂₄O₂: C, 84.75; H, 6.57%; Found: C, 84.68; H, 6.51%.

Conclusions

In conclusion we have reported, imidazole-based zwitterionic type molten salt to be an efficient catalyst for the tetrahydropyranylation of alcohols. High yields, chemoselectivity, reusability of the catalyst, general applicability, clean reaction, production of no hazardous waste and open air reaction conditions are the advantages of our methodology.

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Table 1. Optimization of the reaction conditions^a



Entry	Catalyst (mol%)	Temp (°C)	Time (h)	Yields ^b (%)
1	A (10)	60	10	90
2	B (10)	60	10	75
3	C (10)	60	10	70
4	D (10)	60	10	Trace
5	A (10)	80	10	84
6	A (10)	40	12	60
7	A (10)	rt	10	25
8	A (5)	60	10	74
9	A (15)	60	10	90
10	E	60	12	ND ^c

^aCarried out with 0.5 mmol of **1a** and 0.5 mmol of **2**in the presence of 10mol % catalyst in neat conditions.

^bIsolated yields.

^cND = Not detected on TLC.

Table 2. Studies on the scope of aliphatic alcohols^a





^aReaction Conditions: Alcohols 1 (1 mmol), DHP 2 (1.2 mmol), zwitterionic salt A (10mol %) at 60 °C for 10h.

^bAll are isolated yields.

^c0.5mL THP was used as solvent.

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Zwitterionic salt A (10 mol%) R-OH + C 60 °C, 10 h O 3 2 1 Yields^b (%) References Entry Phenols Products OH 82 [5d] 1 ںٰ 3m 1m OH [5a] 82 2 Me Me 1n 3n [5f] 3° OH 80 MeO MeO 30 10 OH [26a] 4 75 OMe 3p оМе 1p [5a] 5^c OH 84 Ó F 3q 1q OH [5a] 6 71 Ò Br Br 3r 1r 7^{c,d} ŌН 74 -HO OH 1s 3s 8^c OH 78 [5a] 3t 1t

Table 3. Studies on the scope of aryl alcohols^a



^aReaction Conditions: Alcohols 1 (1 mmol), DHP 2 (1.2 mmol), zwitterionic salt A (10mol %) at 60 °C for 10h.

^bAll are isolated yields.

^c0.5mL THP was used as solvent.

^d3 equiv. DHP was used.

Table 4. Recycling of the catalyst A for synthesizing 3a^a



No of cycles	Yields ^b (%)	Time (h)
1	90	10
2	90	10
3	88	10
4	85	12
5	82	12

^aCarried out with 1 mmol of **1a** and 1.2 mmol of **2**in the presence of 10mol % zwitterionic salt **A** at 60 °C.

^bIsolated yields.

Seek .

Figure 1. Different types of zwitterionic-type molten salts.



Scheme 1. Synthetic strategy for zwitterionic-type molten salts.



Scheme 2. Zwitterionic salt-catalyzed tetrahydropyranylation of alcohols.





Scheme 3. Control experiments for chemoselectivity test.

Scheme 4. Probable mechanistic pathway.

