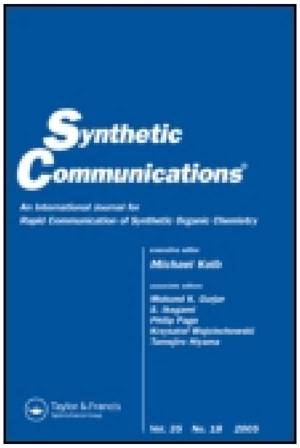

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Solvent-Free Tetrahydropyranylation of Alcohols with Sulfamic Acid as Reusable Catalyst

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Solvent-Free Tetrahydropyranylation of Alcohols with Sulfamic Acid as Reusable Catalyst

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ABSTRACT

An efficient H_2NSO_3H-catalyzed solvent-free tetrahydropyranylation of various alcohols at room temperature was investigated. The features of mild conditions, cost-efficient catalyst, simple work-up, and the recyclability of the catalyst were displayed in this article.

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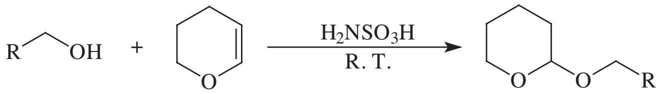
INTRODUCTION

Protection of hydroxy groups by their conversion to the corresponding tetrahydropyranyl ethers (THP ethers) is a common and widely used transformation in organic synthesis.[1,2] The THP ethers are attractive because they are undoubtedly low expensive, stable enough to a wide range of reaction conditions, and easy to be deprotected.

In addition to the well known protic and Lewis acid, a variety of catalysts have been developed for tetrahydropyranylation of hydroxy functions, such as *bis*[trimethylsilyl]sulfate,[3] trimethyliodosilane,[4] $Ru(CH_3)_3$-(triphos)]$(OTf)_2$,[5] zirconium sulfophenyl phosphonate,[6] lithium perchlorate–diethylether,[7] polyaniline salts,[8] vanadyl(IV) acetate,[9] tributylammonium bromide,[10] and lithium triflate[11]; very recently, iodinemicrowave irradiation[12,13] and ionic liquids[14] as catalysts have been used to promote the tetrahydropyranylation of alcohols. Besides, tetrahydropyranylation have been carried out using some heterogeneous catalysts, e.g., montmorillonite (an acid clay),[15] zeolites,[16–18] heteropolyacids,[19] etc. Although these methods are suitable for many synthetic conditions, most of them have drawbacks such as harsh and strong acidic conditions, expensive reagents, high temperature, and nonreusability of catalysts, and also volatile organic solvents or large amounts of solid supports are usually used, which would eventually result in the generation of a large amount of toxic waste. Thus, it is interesting for a solvent-free and catalytically efficient alternative for the protection of hydroxyl functionality as THP ether.

In our development of new methods for functional group transformations, we are especially interested in developing the potential uses of various types of low-cost, mild, and efficient catalysts. Sulfamic acid (H_2NSO_3H), which is a common organic acid with mild acidity, involatility, and incorrosivity, has been studied as an acid catalyst in acetalization and ketalization reactions.[20] Particularly, H_2NSO_3H is insoluble in common organic solvents, and so, its separation and recycling is very easy in catalytic reaction. Herein, we report an efficient H_2NSO_3H-catalyzed solvent-free tetrahydropyranylation of alcohols at room temperature.



EXPERIMENTAL

Typical Procedure of Tetrahydropyranylation

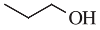
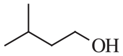
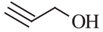
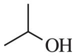
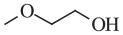
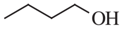
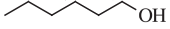
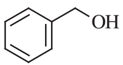
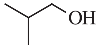
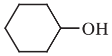
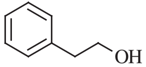
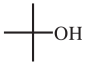
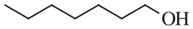
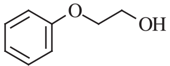
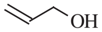
To a stirred mixture of an alcohol (10 mmol) and 3,4-dihydro-2*H*-pyran (13 mmol) in a reaction flask, H_2NSO_3H (0.19 g) was added. The mixture was stirring at room temperature (15°C), and the progress of the reaction was monitored by Hewlett-Packard 6890/5793 GC/MS. After completion of the reaction, diethyl ether (100 mL) was added to the mixture, and a white solid, sulfamic acid, was precipitated. The catalyst was recovered from the mixture by filtration. The filtrate was dried over anhydrous Na_2SO_4 and then evaporated to give almost pure product. Further purification was achieved through a short column of silica gel (2 cm in length, 0.5 cm in diameter) with petroleum ether to obtain the pure THP ether.

RESULTS AND DISCUSSIONS

In the present method, alcohol, 3,4-dihydro-2*H*-pyran (DHP) and H_2NSO_3H catalyst were mixed together to yield the corresponding THP ether at room temperature. It was very interesting that at initial stage of the reaction, H_2NSO_3H catalyst was soluble in the mixture when short chain alcohols, such as *n*-propanol, *i*-propanol, and *n*-butanol, were used. H_2NSO_3H could be crystallized from this homogenous solution as these alcohols were converted gradually. This dissolution at beginning of reaction should be attributed to the high polarity of the reaction mixture dissolving short chain alcohols. With the decrease in concentration of the alcohols with the reaction, the polarity of the mixture accordingly decreased, and thus the progressively precipitating of H_2NSO_3H was reasonable. After the reaction, the catalyst was conveniently recovered from reaction mixture by filtration and the product was obtained by simple distillation. A wide variety of alcohols were converted to the corresponding THP ethers in high yield via this procedure (see Table 1).

Primary, secondary, tertiary, benzylic, allylic, as well as propiolic alcohols can be conveniently protected to be tetrahydropyranyl ethers under mild conditions. It is important to note that the acid sensitive alcohols, such as *t*-amyl alcohol and *t*-butanol, undergo protection as tetrahydropyranyl ethers in 4.5 h without the formation of dehydration products, indicating the usefulness of this method. The recovered sulfamic acid could be used directly in next run without any treatment. Even if sulfamic acid has been reused four times, no considerable activity loss was observed in the tetrahydropyranylation of butanol.

Table 1. Tetrahydropyranylation of alcohols catalyzed by NH_2SO_3H.

Alcohols	Time (h)	Yield (%)	Alcohols	Time (h)	Yield (%)	Alcohols	Time (h)	Yield (%)
	2	100[a]		4.5	94		2	100[a]
	2	100[a]		4.5	82		2.5	84
	3	98		4.5	96		3	95
	3	97		4.5	78		6	87
	4.5	93		4.5	86		6	93
	4.5	95		2	100[a]		4.5	92[b]

[a] GC yields.
[b] Reused for the fourth time.

CONCLUSION

Sulfamic acid is effective for tetrahydropyranylation of alcohols with the features of mild and solvent-free conditions, cost-efficient catalyst, simple work-up, and the recyclability of the catalyst. Therefore the present catalytic method is useful in synthetic organic chemistry.

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