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$CuSO_4$ as a Mild, Green, and Efficient Catalyst for the One-pot Conversion of *THP* Ethers to Acetates

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Summary. An efficient direct conversion of *THP* ethers into the corresponding acetates was achieved with acetic anhydride in the presence of $CuSO_4 \cdot 5H_2O$ as an available and green catalyst in high yields.

Keywords. *THP* ethers; Acetates; Acetylation; $CuSO_4$; One-pot.

Introduction

The interconversion of one protecting group into another is highly important and useful in multistep organic and total synthesis. Thus, in recent years a vast variety of methods has been developed to uncover a number of new reagents and catalysts for such interconversion [1]. Tetrahydropyranyl (*THP*) ethers constitute one of the most useful and common protecting group of alcohols [2].

The acetylation of alcohols is a useful transformation in day-to-day synthetic organic chemistry. There are several methods for conversion of alcohols into acetates under acidic and basic conditions [3]. *THP* ethers are not suitable for use under acidic conditions. On the other hand, acetates are stable to acids. Thus, the interconversion of *THP* ethers to the corresponding acetates is a useful and important transformation. Nowadays, this kind of interconversions is rather limited. The methods available have their own merits but several of them suffer from serious drawbacks, such as high temperature, long reaction times, unsatisfactory yields, and applicability for *THP* ethers of only primary alcohols [4].

Results and Discussion

We have recently observed that *THP* ethers can be readily converted into the corresponding acetate by reacting with *Ac*OH in the presence of ferric perchlorate [5]. Armed with this experience and while working with copper(II) sulfate as a green and available catalyst [6], we observed that benzyl *THP* ether can be directly converted into the corresponding acetate with Ac_2O in the presence of a catalytic amount of $CuSO_4 \cdot 5H_2O$ in CH_2Cl_2. The reaction could also be extended to conversion of several *THP* ethers. The details are described in this paper.

At the outset, alcohols were protected as the *THP* ethers by a known method [7]. We decided to study the direct conversion of these *THP* ethers to their corresponding acetate using acetic anhydride in the presence of *Lewis* acids. This conversion has been already reported in the presence of $Cu(OTf)_2$ [8]. Due to its rather high price we decided to introduce a milder, less expensive, green, and easily available reagent. Our first choice was $CuSO_4 \cdot 5H_2O$ as a green and available *Lewis* acid. We found that in the presence of a catalytic amount (5 mol%) of $CuSO_4 \cdot 5H_2O$, *THP* ethers can be efficiently converted to their corresponding acetates with acetic anhydride in CH_2Cl_2 under reflux condition in 3 h

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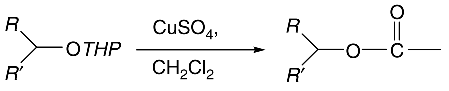


Scheme 1

(Scheme 1). *THP* ethers of secondary alcohols, such as cyclohexanol, undergo this conversion smoothly (entry 5). The triple bond remained unaffected and isomerization was not observed (entry 7). It is noteworthy to mention that the conversion of *THP* ethers of primary alcohols, such as amyl alcohol and *n*-octanol, was not satisfactory. With this protocol a mixture of *THP* ethers, unmasked alcohols, and acetylated products was obtained.

It should be stressed that $CuSO_4 \cdot 5H_2O$ works under heterogeneous conditions. Thus, our protocol has all advantages devoted to a superior kind of catalysis [9]. Although the catalyst is inexpensive and harmless it is worthwhile to mention that it can be recovered and reused. As a test it was used in three consecutive reactions after recovery with only insignificant variation in the yields. We also tried the conversion in different solvents, such as *THF*, CH_3CN, Et_2O, and CH_2Cl_2 and found that CH_2Cl_2 is the solvent of choice.

In conclusion, we developed an efficient and green method for the one-pot conversion of *THP* ethers to the corresponding acetate in the presence of a catalytic amount of $CuSO_4 \cdot 5H_2O$ as an available inexpensive and eco-friendly catalyst. We believe this work is attractive and a useful contribution to present methodologies.

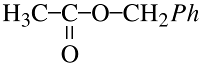
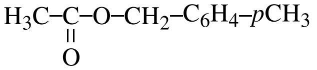
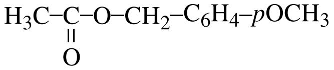
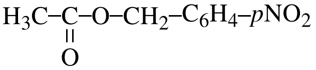
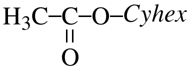
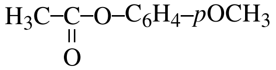
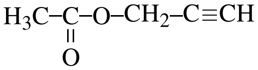
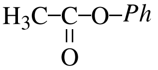
Experimental

The structures of all acetates obtained were established from their physical and spectral data by comparison with those reported already. *THP* ethers were prepared according to the reported method [7].

Direct Conversion of THP Ethers to Acetates. General Procedure

To a stirred solution of 1 mmol *THP* ether in 2 cm^3 CH_2Cl_2 and 1.5 cm^3 acetic anhydride (1 mmol), 8 mg $CuSO_4 \cdot 5H_2O$ (5 mol%) were added for 3 h. The reaction mixture was refluxed for 3 h. The progress of reaction was monitored by TLC using pet ether:ethylacetate = 8:2. Upon completion of the reaction the mixture was filtered. The catalyst can be recovered. The filtrate was washed with an aqueous solution of $NaHCO_3$ (5%). The organic layer was dried (Na_2SO_4) and separated. The solvent was evaporated to dryness under reduced pressure to give the pure product (Table 1).

Table 1. Conversion of *THP* ethers to the corresponding acetates with acetic anhydride in the presence of $CuSO_4 \cdot 5H_2O$ in CH_2Cl_2

Entry	Substrate	Time/h	Product[a]	Yield/%[b]
1	*THP*–O–CH_2*Ph*	3	 $H_3C-\underset{\underset{O}{\Vert}}{C}-O-CH_2Ph$	73
2	*THP*–O–CH_2–C_6H_4–*p*CH_3	3	 $H_3C-\underset{\underset{O}{\Vert}}{C}-O-CH_2-C_6H_4-pCH_3$	61
3	*THP*–O–CH_2–C_6H_4–*p*OCH_3	3	 $H_3C-\underset{\underset{O}{\Vert}}{C}-O-CH_2-C_6H_4-pOCH_3$	57
4	*THP*–O–CH_2–C_6H_4–*p*NO_2	3	 $H_3C-\underset{\underset{O}{\Vert}}{C}-O-CH_2-C_6H_4-pNO_2$	51
5	*THP*–O–*Cyhex*	3	 $H_3C-\underset{\underset{O}{\Vert}}{C}-O-Cyhex$	51
6	*THP*–O–C_6H_4–*p*OCH_3	3	 $H_3C-\underset{\underset{O}{\Vert}}{C}-O-C_6H_4-pOCH_3$	76
7	*THP*–O–$CH_2C{\equiv}CH$	3	 $H_3C-\underset{\underset{O}{\Vert}}{C}-O-CH_2-C{\equiv}CH$	63
8	*THP*–O–*Ph*	2.5	 $H_3C-\underset{\underset{O}{\Vert}}{C}-O-Ph$	89

[a] The structures of products were determined by comparison of their physical and spectroscopic data with those of authentic samples [10]

[b] Yields refer to GC/MS analysis

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