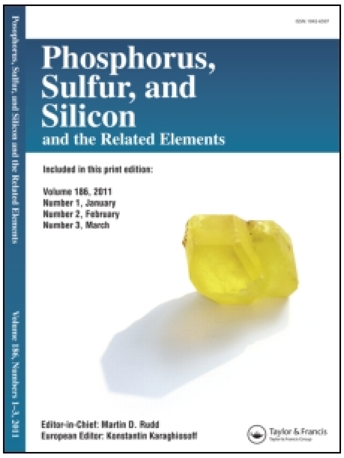

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PHOSPHORUS PENTOXIDE AS AN EFFICIENT CATALYST FOR THE TETRAHYDROPYRANYLATION OF ALCOHOLS UNDER SOLVENT-FREE CONDITIONS

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A facile and efficient method for the preparation of tetrahydropyranyl ethers from alcohols is improved in solvent-free media. These reactions are catalyzed by P_2O_5 and afford various tetrahydropyranyl ethers in shorter reaction time, with good to excellent yields (75–95%) at room temperature. This method is also compatible with substrates containing acid-sensitive functional groups.

Keywords: Alcohols; phosphorus pentoxide; protection; tetrahydropyranyl ethers

INTRODUCTION

Tetrahydropyranyl (THP) ethers have been the most useful and representative protecting groups of alcohols in synthetic organic chemistry.[1] Among various procedures available for the protection of hydroxy groups, tetrahydropyranylation is the most frequently used process because of the remarkable stability of tetrahydropyranyl ethers under a variety of conditions such as strong basic media, reactions involving Grignard reagents, oxidation, reduction, acylation reactions etc., and also the ease with which they can be removed. A variety of catalysts have been developed for tetrahydropyranylation, such as protic acids,[2] Lewis acid and pyridinium p-toluene sulfonate,[3] ion exchange resins,[4] clay materials,[5] $ZnCl_2$,[6] $SnCl_2, 2H_2O$,[7] $AlCl_3, 6H_2O$,[8] $In(OTf)_3$,[9] $Sc(OTf)_3$,[10] LiBr,[11] $CuCl_4$,[12] SiO_2/H_2SO_4,[13] Ph_3P/Me_3SiI,[14] tetra-n-buthylammonium peroxydisulfate,[15] etc. Although many of these methods and procedures are useful, there is still need for a simple, efficient,

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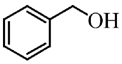
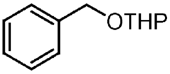
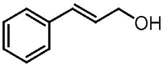
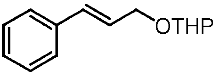
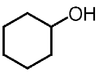
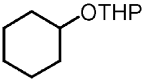
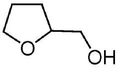
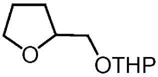
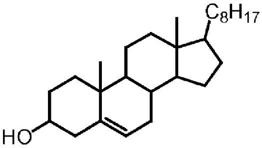
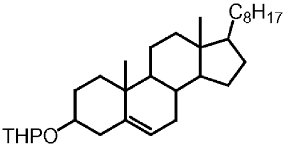
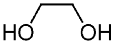
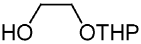
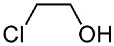
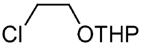
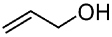
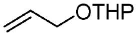
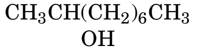
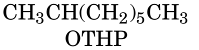
TABLE I Conversion of Alcohols into THP-Ethers Catalyzed by P_2O_5

Entry	Alcohols	Product	Yield %[a,b]
1			95
2			86
3			95
4			85
5			75
6			90
7			85
8			89
9	$(CH_3)_3C\text{-}OH$	$(CH_3)_3C\text{-}OTHP$	90
10	$(CH_3)_2CHCH_2\text{-}OH$	$(CH_3)_2CHCH_2CH_2\text{-}OTHP$	85
11	$CH_3(CH_2)_6CH_2\text{-}OH$	$CH_3(CH_2)_6CH_2\text{-}OTHP$	95
12	 $CH_3\underset{OH}{CH}(CH_2)_6CH_3$	 $CH_3\underset{OTHP}{CH}(CH_2)_5CH_3$	95

[a] Isolated yield.

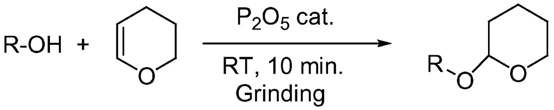
[b] All the compounds gave satisfactory spectral data (IR and ^{1}H NMR).

and high-yielding alternate catalyst that works at ambient temperature, mild reaction conditions, and shorter reaction times. Phosphorus pentoxide is a catalyst that meets all of these requirements.

In this article we wish to report a very simple and efficient method for the tetrahydropyranylation of alcohols utilizing a catalytic amount of P_2O_5 in solvent-free condition.

RESULTS AND DISCUSSION

The general reaction is illustrated in Scheme 1 and the results are reported in Table I. All reactions were carried out by simply



SCHEME 1

grinding the reagents at room temperature under solvent-free medium for 10 min. Like primary alcohols, secondary alcohols and tertiary alcohols were readily transformed into the corresponding THP ethers in good-to-excellent yields. Additionally, alcohols having other functional groups underwent chemoselective reaction to give the THP ethers in excellent yields with no undesired reactions. Especially, acid-sensitive functional groups such as an allylic alcohols (entries 2 and 8), benzylic alcohol (entry 1), and tetrahydrofuryl alcohol (entry 4) were significantly unaffected under these reaction conditions. Ethylene glycol (entry 6) undergoes selective monoprotection in high yield in solvent-free media.

The purity of the products was determined by ^{1}H NMR, IR spectra, and melting point. In all IR spectra the characteristic peaks of the OH group of alcohols and the double bond of dihydropyrane disappeared, and in the ^{1}H NMR spectra the acetalic CH groups were observed at around 4.3–4.8 as a triplet.

In conclusion, the reported procedure is an easy and novel method for the preparation of tetrahydropyranyl ethers from alcohols in solvent-free conditions. These reactions catalyzed by P_2O_5 afford various tetrahydropyranyl ethers in shorter reaction time (10 min) with good-to-excellent yields (75–95%) at room temperature. This method is also compatible with substrates containing acid-sensitive functional groups. We believe that this will be a useful addition to modern synthetic methodologies.

EXPERIMENTAL

All melting points recorded are uncorrected open-capillary measurements. IR spectra were recorded on a Shimadzu-IR 470 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker-80 MHz instrument using tetramethylsilane (TMS) as an internal standard. Column chromatography was carried out on short columns of silica gel 60 (230–400 mesh) in glass columns (2–3 cm diameter) using 15–30 g of silica gel per 1 g of crude mixture.

Preparation of the Tetrahydropyranyl Ethers: General Procedure

In a typical reaction, a mixture of alcohol (2 mmol), 3,4-dihydro(2H)-pyrane (2 mmol), and phosphorus pentoxide (0.1 mmol) were ground thoroughly in a mortar for 10 min. The completion of the reaction was monitored by IR and TLC examination. After the completion of the reaction, water (30 ml) was added to the mixture and extracted with CH2Cl2 (2 × 20 ml). The extracts were combined and washed with 5% sodium hydroxide solution (30 ml) and water (30 ml) and dried over CaCl2. Evaporation of the solvent under vacuum gave tetrahydropyranyl ethers with high purity (based on TLC, ^{1}H NMR, IR, and melting point).

REFERENCES

[1] T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd ed. (John Wiley & Sons, Inc., New York, 1991).

[2] K. F. Bernady and M. J. Weiss, *J. Org. Chem.*, **44,** 1438 (1979).

[3] M. Miyashita, A. Yosikoshi, and P. A. Grieco, *J. Org. Chem.*, **42,** 3772 (1977).

[4] a) A. Bongini, G. Cardillo, M. Orena, and S. Sandri, *Synthesis*, 681 (1979); b) G. A. Olah, A. Hussain, and B. P. Singh, *Synthesis*, 892 (1983).

[5] a) S. Hoyer and P. Laszlo, *Synthesis*, 655 (1986); b) P. Kumar, C. U. Dinesh, R. S. Reddy, and B. Pandey, *Synthesis*, 1069 (1993).

[6] B. C. Ranu and M. Saha, *J. Org. Chem.*, **59,** 8269 (1994).

[7] K. J. Davis, U. T. Bhalerao, and B. V. Rao, *Synth. Commun.*, **29,** 1679 (1999).

[8] V. V. Namboodiri and R. S. Varma, *Tetrahedron Lett.*, **43,** 1143 (2002).

[9] T. Mineno, *Tetrahedron Lett.*, **43,** 7975 (2002).

[10] T. Watahiki, H. Kikumoto, M. Matsyzaki, T. Suzuki, and T. Oriyama, *Bull. Chem. Soc. Jpn.*, **75,** 367 (2002).

[11] M. A. Reddy, L. R. Reddy, N. Bhanumathi, and K. R. Rao, *Synth. Commun.*, **30,** 4323 (2000).

[12] U. T. Bhalerao, K. J. Davis, and B. V. Rao, *Synth. Commun.*, **26,** 3081 (1996).

[13] M. M. Heravi, D. Ajami, and M. Ghassemzadeh, *Synth. Commun.*, **29,** 1013 (1999).

[14] K. H. Cha, T. W. Kang, H. W. Lee, E. N. Kim, N. H. Choi, J. W. Kim, and C. I. Hong, *Synth. Commun.*, **28,** 2131 (1998).

[15] H. C. Choi, K. II, Cho, and Y. H. Kim, *Synlett.*, 207 (1995).