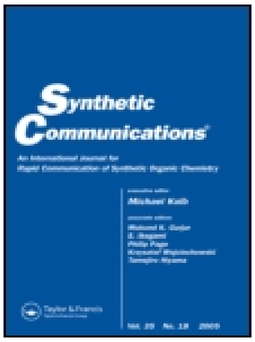

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Bis [Trinitratocerium (IV)] Chromate $[Ce(No_3)_2\ Cro_4]$ and tris-[Trinitratocerium (IV)] Paraperiodate $[(No_3)_3Ce]_3\ H_2IO_6$. Two Mild and Efficient Catalysts for Tetrahydropyranylation of Alcohols.

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Bis [trinitratocerium (IV)] Chromate $[Ce(No_3)_2 Cro_4]$ and Tris [trinitratocerium (IV)] Paraperiodate $[(No_3)_3Ce]_3 H_2IO_6$. Two Mild and Efficient Catalysts for Tetrahydropyranylation of Alcohols.

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Abstract

The tetrahydropyranyl derivatives of variety of alcohols are efficiently prepared in the presence of catalytic amounts of $[Ce(NO_3)_2Cro_4]$ and $[(NO_3)_3 Ce]_3 H_2IO_6$ in mild condition in good to excellent yields.

Tetrahydropyranylation is one of the most frequently methods to protect alcohols and phenols[1]. Because of the remarkable stability of tetrahydropyranyl ethers toward a variety of conditions such as strongly basic media reactions involving Grignard reagents and lithium alkyls, reduction with hydride, oxidation, oxidative alkylation and acylation reactions etc , tetrahydropyranylation is one of the methods of choice to protect a hydroxyl group in a multistep organic synthesis[2].

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A variety of reagents have been developed for tetrahydropyranylation of alcohlos which include mainly protic acids (hydrochloric acid, and P-toluenesulfonic acid), Lewis acids (BF_3-OEt_2),aluminum sulfate of silicagel[3], pyridinium -P-toluenesulfonate and bis (trimethyl-silyl sulfate), ion exchange resins[4,5], H-Y zeolite[6] as well as miscellaneous catalysts such as P-toluenesulfonats and charcoal and DDQ[8] etc. Although these methods are satisfactory for many molecules and purposes , some have limitations such as use in strongly acidic media, tedious and time consuming work up procedures, high temperature long reaction times, and not being reusable, consequently there is need to develop alternative reagents for this reaction .

Different salts of Ce(IV) are well known and are versatile reagents in organic synthesis. Ce (IV) as ceric ammonium nitate has been used as an effecient catalyst for protection and deprotection of alcohols with dihydropyran[9].

Bis [trinitrocerium (IV) chromate (BTNCC)[10] and tris [trinitratocerium (IV)] paraperiodate (TTNCPP) have been prpared and used as versatile oxidant[10-13] Although (TTNCPP) has been used for deprotection and direct oxidative deprotection of trimethylsilyl ethers to their corresponding alcohols and carbonyl compounds[14] to best of our knowledge, there is no report on application of these two catalysts for protection of alcohols with dihydropyran.

Now in this communication we wish to disclose that (BTNCC) and (TTNCPP) serve as two excellent catalysts for tetrahydropyranylation of alcohols.

Thus, when a variety of alcohols were treated with 3,4-dihydropyran in the presence of catalytic amounts of (BTNCC) of (TTNCPP), the corresponding THP- ethers were obtained in pretty good to excellent yields, the results are compiled in the table. The reaction conditions are particularly mild and the work up precedure is exceedingly simple and reduced to a mere filtration. The catalysts were recovered unchanged and were active for furture use.

To find a notable advantage we turned our attenton towards the possible recycling of the catalysts in the reaction with the model 1b. The catalysts were filtered on buckner funnel, washed with benzene, dried and immediately reused. Unexpectedly after allowing the reaction mixture to reflux for 1h hour in benzene the product 3b was obtained in 80% in the case of use of BTNCC

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Table. Tetrahydropyrnylation of alcohols by (BTNCC) or (TTNCPP).

	Substrate	product	Catalyst used	Reaction Time	Yield of 3
1a	cyclohexanol	3a	BTNCC	1h	82
1b	benzyalcohol	3b	BTNCC	1.5 hr	85
1c	allyl alcohol	3c	BTNCC	2 h	75
1d	2-Octanol	3d	BTNCC	2 h	86
1e	1-butanol	3e	BTNCC	1h	90
1f	tert-butyl alcohol	3f	BTNCC	2h	75
1a	tert-butyl alcohol	3a	TTNCPP	1.2 h	92
1b	benzyalcohol	3b	TTNCPP	1.2 h	95
1C	benzyl ether	3c	TTNCPP	1h	85
1d	2-octanol	3d	TTNCPP	2h	90
1e	1-butanol	3e	TTNCPP	1h	90
1f	tert-butyalcohol	3f	TTNCPP	2h	90

and 90% in the case of use of TTNCPP. Moreover we recycled the catalysts for further five experiments obtaining the product 3b with similar high yield.

In a typical reaction a mixture of alcohol, 3,4-dihydro-2H-Pyran and catalytic amounts of either (BTNCC) or (TTNCPP) was refluxed in benzene. The progress of reaction was monitored by GC. After the reaction was complete, the either catalyst was filtered off, the solvent was evaporated and product was purified by single elution by chloroform over silicagel and evaporation of solvent. A farily wide range of hydroxy compounds were converted to the corresponding THP ethers in high yield by this procedure. The results are presented in table. The reactions are reasonably fast. The reaction conditions are mild enough not to induce any isomerization of double bond during tetrahydropyranylation of allylic alcohol.

In conclusion, The present methods provides useful alternative to the preparation of tetrahydropyranyl ethers from alcohlos. The notable advantages of this methodlogy are mild conditions (reflux in benzene), fast reaction time (1 to 2h) high yield (75-95%) and reusability of catalysts. We belive this will serve as a useful addition to modern synthetic methodologies.

Experimental

Products were characterized by IR,NMR and by direct comparison with authentic samples. (BTNCC) and (TTNCPP) were prepared according to reported procedure respectively[10,11]

Tetrahydropyranyl Ethers 3a-f:Genral procedure.

To a solution of hydroxy compound (10 mmol) in benzene (15 ml) were added successively appropriate catalyst (2 mmol) and 3,4-dihydro -2H-pyran (12 mmol) and the mixture was refluxed with stirring for the specified period of time (table). The progress of reaction was monitored by TLC followed by GLC analysis. After the reaction was complete, the catalyst was filtered off. The solvent was evaporated off and purified by column chromatography over silicagel.

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