

CERIUM(IV) AS CERIC TRIETHYLAMMONIUM NITRATE: AN EFFICIENT CATALYST FOR PROTECTION AND DEPROTECTION OF ALCOHOLS WITH DIHYDROPYRAN

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ABSTRACT: *Catalytic amount of Ce(IV) as ceric triethylammonium nitrate (CTEAN) in dichloromethane or acetone can bring about an efficient tetrahydropyranylation of different types of alcohols to afford the corresponding tetrahydropyranyl ethers in high yields. Deprotection of tetrahydropyranyl ethers can also be achieved efficiently in the presence of this catalyst in methanol.*

KEY WORDS: *Ceric ammonium nitrate, Dihydropyran, Protection, Deprotection.*

INTRODUCTION

The protection of hydroxyl groups with 3,4-dihydro-2H-pyran (DHP) is a useful and outstanding method in organic synthesis. Many catalysts are available for preparation of tetrahydropyranyl derivatives [1-12], of which some have limitations such as: use in strongly acidic media, tedious and time consuming work up procedures, high temperatures and long reaction times. In addition, the reports available

on the use of most of these catalysts are only for protection of alcohols and to the best of our knowledge, there is no report on application of these catalysts for protection of hydroxy compounds carrying electron-withdrawing substituents. Different salts of Ce(IV) are well-known and versatile reagents in organic synthesis [13-17]. Ce(IV) as ceric ammonium nitrate has also been used only for protection of

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primary and secondary alcohols in acetonitrile [18].

We studied the applicability of Ce(IV) as ceric triethylammonium nitrate (CTEAN) [19] for both protection and deprotection of different classes of alcohols with dihydropyran.

EXPERIMENTAL

Products were isolated and their physical, IR, NMR and Mass spectral data were compared with those of known samples which are prepared according to literature procedures [1-12].

Tetrahydropyranylation of Alcohols; General procedure

CTEAN (2.0-3.0 mmol) was added to a solution of hydroxy compound (10 mmol) and 3,4-dihydro-2H-pyran (20 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature or under reflux condition for the specified period of time (Table 1). The progress of reaction was monitored by GLC. Solvent was evaporated, water (80 mL) was added and extracted with diethyl ether (3×50 mL). Evaporation of solvent followed by chromatography on a short column of silica-gel afforded the product in 65-93% yield.

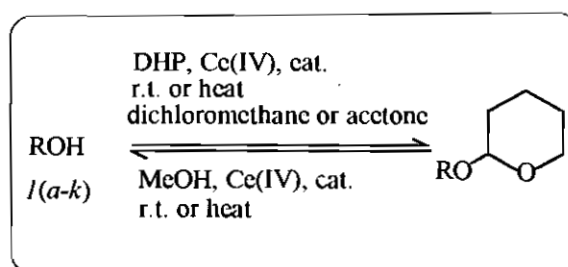
Deprotection of THP-Ether; General Procedure

A methanolic (15 mL) solution of THP-ether (10 mmol) and CTEAN (2.0-2.5 mmol) was stirred at room temperature or under reflux condition for the appropriate time (Table 1). Evaporation of the solvent in vacuum followed by chromatography on a column of silica-gel gave the corresponding alcohol in 75-93% yield.

RESULTS AND DISCUSSION

It was found that CTEAN in acetone or even in dichloromethane at room temperature or under reflux conditions can act as an efficient catalyst not only for tetrahydropyranylation of alcohols (1a-1k) but also for removal of the protecting group (Scheme 1). In addition, using

Ce(IV) as CTEAN in these solvents, tertiary butyl alcohol (1j) and deactivated alcohols (1g, 1h) can also be converted to their corresponding tetrahydropyranyl ethers in good to excellent yields. This procedure is quite general for primary, secondary, tertiary, allylic and benzylic alcohols. The corresponding THP-ethers were obtained and identified by comparison with authentic samples. The results obtained in dichloromethane are summarized in Table 1.



Scheme 1

Deprotection of tetrahydropyranyl group is also afforded by using catalytic amounts of CTEAN in a methanolic solution of tetrahydropyranyl ether at room temperature or under reflux condition. The results obtained from deprotection reactions are shown in Table 1. Under these conditions, no oxidation of alcohol to the carbonyl products was observed.

In comparison with most of the reported catalysts, CTEAN acts under neutral and milder reaction conditions. It can be used for protection of different classes of alcohols including those carrying electron-withdrawing substituents in high to excellent yields. In addition CTEAN is among the few catalysts which can also be used efficiently for deprotection of alcohols from their corresponding THP-ethers.

Considering these advantages, CTEAN can be added to the available catalysts for protection and deprotection of alcohols.

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Table 1. Protection of alcohols (1a-1k) with DHP and deprotection of RO-THP ethers catalyzed with CTEAN

Alcohol	Protection in dichloromethane			Deprotection of RO-THP ether		
	Time (h)	Mole ratio of CTEAN/Alcohol	Yield ^{I,II} (%)	Time (h)	Mole ratio of CTEAN/RO-THP	Yield ^{I,II} (%)
1a:1-Octanol	1	0.2	90	4	0.2	80
1b:2-Octanol	3 ^{III}	0.25	80	3	0.2	90
1c:Cinnamyl alcohol	1.5	0.2	87	4	0.2	75
1d:3-Phenyl-1-propanol	1.2	0.2	93	3	0.2	85
1e:Cyclohexanol	4 ^{III}	0.3	73	3	0.2	85
1f:Benzyl alcohol	0.5	0.2	87	2	0.2	73
1g:p-Nitro-benzyl alcohol	2	0.2	83	5 ^{III}	0.25	75
1h:p-Chloro-benzyl alcohol	1.5	0.2	88	4	0.2	75
1i:Phenyl ethanol	2 ^{III}	0.3	80	3	0.2	85
1j:t-Butanol	2.5 ^{III}	0.3	78	2	0.2	93
1k:Allyl alcohol	1	0.2	93	3	0.2	80

I : Yields refer to isolated products.

II : The products were identified by comparison with authentic samples.

III : The reaction was performed under reflux condition.

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