

An efficient and selective deprotection of allyl ethers by a $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI system

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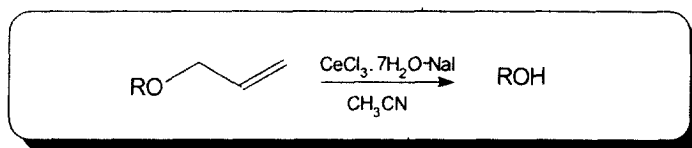
Abstract

A mild, novel and chemoselective method for the deprotection of allyl ethers by a $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI system is described. © 1999 Elsevier Science Ltd. All rights reserved.

Key words: Alcohols, cerium and compounds, ethers phenols

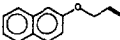

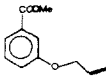

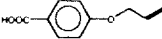

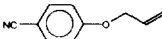

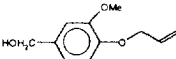
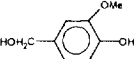
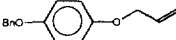


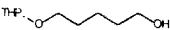
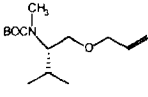
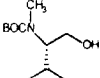
The importance of protecting hydroxyl groups in synthetic organic chemistry is reflected in the appearance in the literature of biologically active molecules possessing hydroxyl groups. The allyl group has been frequently used in organic synthesis as a protecting group for alcohols and phenols due to its stability under basic and acidic conditions.¹ Numerous methods are available for the deprotection of the allyl group which have been recently reviewed.² However many of these deprotection procedures suffer from drawbacks; lack of selectivity, unsatisfactory yields, cost or toxicity of the reagents or the necessity for anhydrous conditions. These limitations prompted us to investigate further new convenient methodology for the selective cleavage of allyl ethers over a wide range of functional groups. During the development of new methods for deprotection of allyl ethers,³ we found that the combination of cerium(III) chloride and sodium iodide⁴ in refluxing acetonitrile can smoothly cleave allyl ethers within 4 to 6h with high chemoselectivity. (Scheme)

Scheme



This opened the possibility for this procedure to be developed as a deprotecting system for allyl ethers which has several advantages in the use of this reagent: no strongly basic or acidic conditions are required nor expensive reagent, no precautions need to be taken to exclude the moisture or oxygen from the reaction system. The results are summarized in the table; in all the cases the yields were excellent.

Table

Entry	Substrate	Product	Time (hrs)	Yield (%)
1			6	90
2			4.5	69
3			4	93
4			6	98
5			6	94
6			6	92
7			5.5	95
8			5	86

Typical experimental procedure: A solution of allyl ether (entry 1, Table 0.5g, 2.7mmol), and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (1.2g, 3.2mmol) in acetonitrile (8ml) was treated with NaI (0.48g, 3.2mmol) and was refluxed until the TLC indicate that no starting materials remained. The reaction was quenched with 1N HCl and the solvent stripped off *in vacuo*. The crude material was dissolved in dichloromethane washed with water and dried over Na_2SO_4 . Upon solvent removal the crude was purified by column chromatography. The structures of the phenol thus obtained were confirmed from the ^1H NMR, I.R. and mass spectral analysis by comparing with authentic samples.

In conclusion our present methodology offers very attractive features such as compatibility with functional groups, easy handling, mild reaction conditions and economic viability of the reagent which will have wide scope in organic synthesis.

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