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A Novel, Mild and Facile Reductive Cleavage of Allyl ethers by $NaBH_4/I_2$ System

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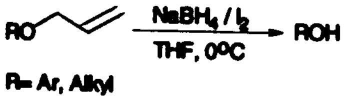
Abstract : A simple and efficient method for the deprotection of allyl ethers using $NaBH_4/I_2$ system is described. © 1997 Published by Elsevier Science Ltd.

Allyl group is commonly used protecting group in organic synthesis and more specifically in carbohydrate chemistry. Removal of this protecting group involves two step sequence by isomerization of allyl ethers to the corresponding 1-propenyl ether followed by H^+ or Hg^{2+} catalysed hydrolysis or oxidative cleavage.[1]

Recently several reagents have been employed for the deprotection of allylic ethers. These include NBS, $Pd(PPh_3)_4$-$NaBH_4$, $ZrCl_2$, $SmCl_3$, $TiCl_3$, DDQ[2-7] etc. However economic non-viability or synthetic limitations either to aromatic or aliphatic ethers makes them rather attractive.

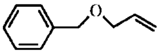
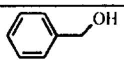
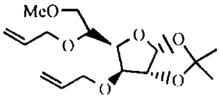
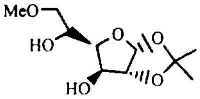
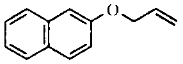
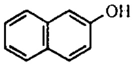
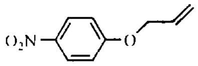
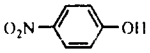
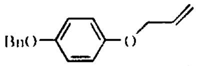
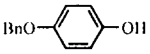
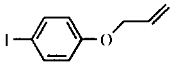
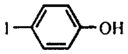
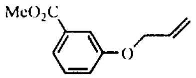
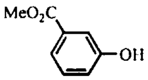
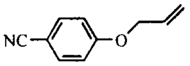
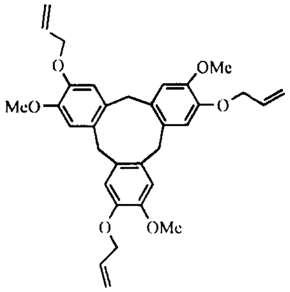
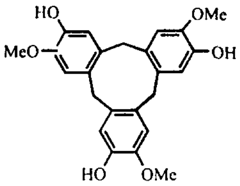
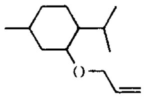
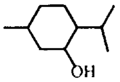
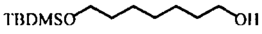
In connection with our on-going research programme on cyclotriveratrylenes, we encountered some difficulties in deallylation which led us to look for an alternate method. We found that the combination of $NaBH_4/I_2$ in THF smoothly cleaves both aromatic as well as aliphatic allylic ethers under mild reaction conditions in excellent yields (Scheme 1). The results are given in Table 1.



Scheme 1

IICT Communication No : 3815

Table 1

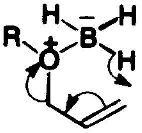
Entry	Substrate	Product	Yield (%)
1			95
2			87
3			96
4			93
5			89
6			90
7			84
8			84
9			91
10			53
11			72
12			87

* All the reactions are completed within one hour.

The reagent can be considered as a general deallylating agent useful for aliphatic as well as aromatic allyl ethers. The added advantage of this reagent is that some of the reducible functionalities[8-10] such as cyano, ester, acetonide and tetrahydropyranyl groups are unaffected under the reaction conditions. A trace amount of the hydroborated alkyl ether was found along with the desired phenol/alcohol.

The typical experimental procedure is as follows. A slurry of $NaBH_4$(0.018 mole) and allyl ether (entry 3, Table -1, 0.14 mole) in THF (20ml) was stirred at 0°C. To this, I_2 (0.007 mole) in THF (10ml) was added dropwise over a period of 10 min. under nitrogen atmosphere. After 20 min. the reaction mixture was quenched with methanol till the effervescence was ceased. Evaporation of the solvent followed by purification of the crude product over silica gel afforded pure phenol (96%).

It is known that the combination of $NaBH_4/I_2$ in THF is a source of diborane[11]. Probably the initial coordination of the borane with the etherial oxygen by subsequent hydride addition to the allyl system leads to the deprotected alcohol. This result is rationalised by assuming a six membered cyclic model as shown below.



Similar results were also found when the reactions were carried out by using commercial grade 2M borane-methylsulfide complex in THF which supports the involvement of diborane generated *in situ* in the reaction.

The easy accessibility, high chemoselectivity, shorter duration and mild reaction conditions are the special attractions of this methodology. This method should therefore find extensive application in organic synthesis where selective deprotection of allyl ethers is often a special requirement.

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