

A Convenient and Efficient Deallylation Procedure

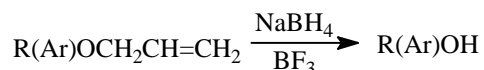
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Abstract: In the presence of NaBH₄/BF₃, allyl ethers underwent deallylation to the corresponding alcohols or phenols in good yield and high reaction rate.

Keywords: Ether, deallylation.

Allyl group has been often used in protection of alcohols or phenols in an ether form¹. Deprotection of the allyl group can be effected with t-BuOH² or metal catalysts, such as Pd/C³, Ph₃PRhCl⁴ and followed by acidic or oxidative cleavage. Recently several new deprotection methods including PdCl₂/CuCl/O₂⁵, CP₂Zr⁶, NBS/hν⁷, Ti(O-i-Pr)₄/BuMgCl⁸, TsOH/Pd(PPh₃)₄⁹, NaCNBH₃/TMSCl¹⁰ were developed. However, most of these reagents are not easy to prepare or hazardous. We wish to report now a simple and efficient method for the conversion of allyl ethers to the corresponding alcohols.



The allyl ethers were prepared by reaction between allyl bromide and the alcohols or phenols in DMSO in the presence of KOH¹¹. Treatment of the allyl ethers with NaBH₄/BF₃ at room temperature smoothly afforded the alcohols or phenols in the yields ranging from 75-95% (**Table 1**). The reaction rate was high (0.25-6.0 h) and the operation simple.

Typical procedure: To a stirred mixture of allyl benzyl ether (200 mg, 1.35 mmol), NaBH₄ (43 mg, 1.62 mmol) and anhydrous THF (20 mL) was treated with BF₃/ether (0.5 mL) under N₂ atmosphere. The resulting reaction mixture was stirred at rt until the reaction completed (monitored by TLC, 2.5 h). MeOH (2 mL) was added. The reaction mixture was poured into 30 mL brine and extracted with ether (40 mL) for 3 times. The combined ether was dried over Na₂SO₄. Evaporation of the ether followed by bulb to bulb distillation yielded 140 mg of benzyl alcohol in 95% yield.

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Table 1 Reaction time and yield of deallylation

Substrate	Product ^{a)}	Time (h)	Yield (%) ^{b)}
Allyl benzyl ether	Benzyl alcohol	2.5	95
Allyl 1-phenylethyl ether	1-Phenylethanol	4.0	87
Allyl 2-phenylethyl ether	2-Phenylethanol	5.5	79
Allyl n-pentyl ether	n-Pentanol	4.0	75
Allyl n-octadecyl ether	n-Octadecanol	6.0	77
Allyl phenyl ether	Phenol	0.25	93
Allyl 2-naphthyl ether	2-Naphthol	0.4	91
Diallyl binaphthyl ether	Binaphthol	0.67	83

^{a)} All the products were identified by spectroscopic methods.

^{b)} Yield refers to the isolated yield.

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