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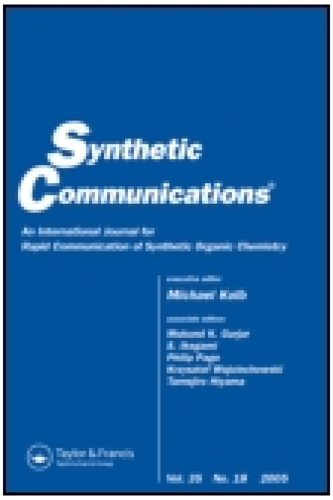

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A MILD CHEMOSELECTIVE AND RAPID REGENERATION OF ALCOHOLS FROM O-ALLYL ETHERS BY LiCl/NaBH$_4$*

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A MILD CHEMOSELECTIVE AND RAPID REGENERATION OF ALCOHOLS FROM *O*-ALLYL ETHERS BY LiCl/$NaBH_4$*

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ABSTRACT

An efficient chemoselective cleavage of *O*-allyl protected is developed employing LiCl/$NaBH_4$.

The protection of alcohol functionality by the group is an important synthetic step in the preparation of various compounds, more specifically in carbohydrate chemistry.[1] Recently various methods have been developed for the cleavage of allyl group, some of the methods reported include $AlCl_3$-N,N dimethyl aniline,[2] $TiCl_3$-Mg-THF,[3] $PdCl_2$/CuCl/DMF-H_2O/O_2,[4] NBS,[5]

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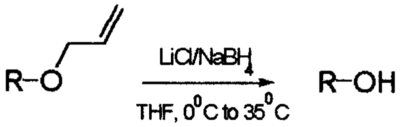
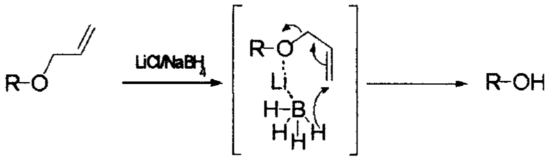
BCl_3-Me_2S,[6] DDQ,[7] $NaBH_4/I_2$,[8a] $ZrCl_4/NaBH_4$[8b] and TMSCl/NaI.[9] In continuation of our research in exploring the novel methods for the production of alcohols from respective *O*-ally ethers,[8] we observed that $LiCl/NaBH_4$ (1 eq.) reagent system in THF, cleaves both aromatic as well as aliphatic allyl ethers smoothly, and chemoselectively under mild reaction conditions in excellent yields furnishing the corresponding alcohols (Scheme 1).



Scheme 1.

The reagent system can be considered as a general deallylating agent useful for aliphatic as well as aromatic allyl ethers. The regeneration of alcohols from *O*-allyl ethers is visualized on the basis of insitu formation of $LiBH_4$.[10] The added advantage of this reagent lies in its chemoselective production of alcohols from respective *O*-allyl ethers in presence of some of the reducible functionalities such as nitro (entry 5), benzyloxy (entry 7), Boc (entry 10), and Cbz (entry 11). The obvious advantage of this reagent system is its low volume requirement of the reagent compared to any other modified borohydride reagent.

The deallylation can be rationalized by assuming the following cyclic transition state. Probably the initial coordination of the lithium with the ethereal oxygen followed by subsequent hydride delivery lead to the deallylated alcohol (Scheme 2).

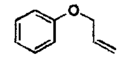
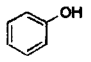
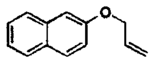
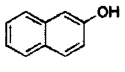
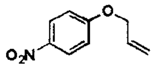
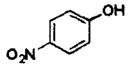
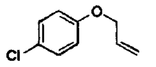
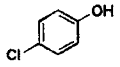
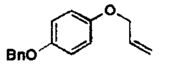
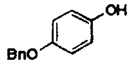
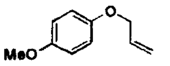
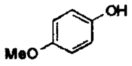
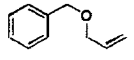
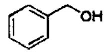
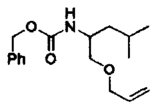
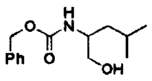
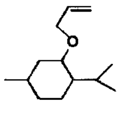
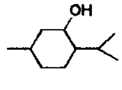
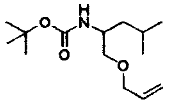
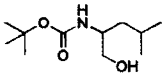


Scheme 2.

This method should find extensive application in organic synthesis where selective deprotection of allyl ethers is often a special requirement.

Generality of the reaction is shown in the table.

Table. Regeneration of Alcohols from *O*-allyl-Ethers Using LiCl/NaBH$_4$

Entry	Substrate	Product[a]	Yield[b]
1			92
2			85
3			80
4			87
5			85
6			90
7			89
8			70
9			75
10			78

[a] All reactions were completed in 30 to 45 min period, at 35°C stirring.

[b] Yields (%) refer to unoptimised, isolated and chromatographically pure products.

TYPICAL EXPERIMENTAL PROCEDURE

Into a two necked round bottom flask equipped with magnetic bead and nitrogen balloon adapter was placed LiCl (1 eq), dry THF (25 ml) was syringed into the flask. The contents were cooled to 0°C, and $NaBH_4$ (1 eq) was added in portion to the above solution. To the reagent system at 0°C was added a solution of allylated ether (1 eq) in THF. After complete addition, ice cooling was removed and contents were brought to room temperature (35°C). The progress of the reaction was monitored by TLC, which indicated the disappearance of the allylated ether in 30–45 min period. Contents were cooled to 0°C and quenched by dropwise addition of 5% aq. HCl solution, the solvent was evaporated under vaccum and the remaining aqueous layer was extracted with ethyl acetate.

The organic fractions were combined, and washed successively with brine, water and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification of the crude product by column chromatography using silicagel gave alcohol (isolated yields 70–92%). All the products thus obtained were characterized by IR, ^{1}H NMR, and Mass spectral data analysis and comparing with authentic samples.

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