A Mild and Rapid Regeneration of Alcohols from Allyl Ethers by $ZrCl_4/NaBH_4$

K. Purushothama Chary, G. Hari Mohan, and D. S. Iyengar*

Discovery Laboratory, Organic Division II, Indian Institute of Chemical Technology, Hyderabad 500 007, India

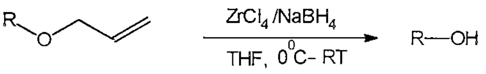
(Received July 19, 1999; CL-990636)

A new extremely facile, spontaneous and efficient cleavage of allyl protection is developed employing $ZrCl_4/NaBH_4$.

The protection of alcohol functionality by the allyl 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 under different conditions. These include $AlCl_3$-N, N dimethyl aniline,[2] hydrogen activated cationic iridium complex,[3] $SmCl_3$ catalyzed electrolysis,[4] $TiCl_3$-Mg-THF,[5] Cp_2Zr,[6] $PdCl_2/CuCl/DMF\text{-}H_2O/O_2$,[7] Pd $(Ph_3)_4/NaBH_4$,[8] NBS,[9] $BCl_3\text{-}Me_2S$,[10] DDQ,[11] $NaBH_4/I_2$,[12] $Ti(O^iPr)_4$/nBuMgCl,[13] and TMSCl/NaI.[14]

In continuation of our ongoing research in exploring the potential utility of $ZrCl_4/NaBH_4$ reagent system,[15,16] we observed that this reagent system in THF, cleaves both aromatic as well as aliphatic allyl ethers smoothly and rapidly under mild reaction conditions in excellent yields (Table 1).

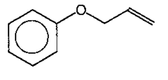
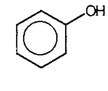
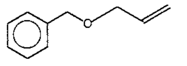
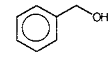
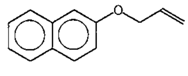
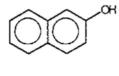
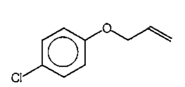
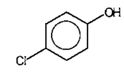
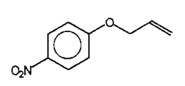
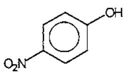
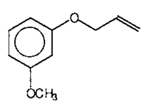
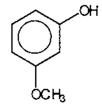
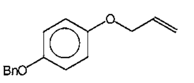
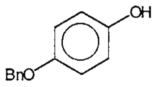
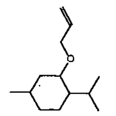
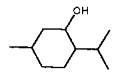
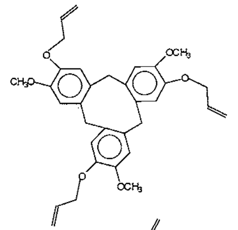
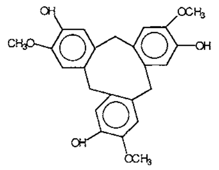
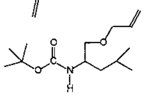
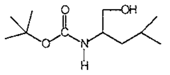
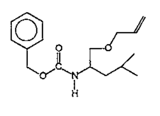
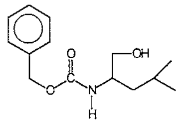
Scheme 1.



The reagent system can be considered as a general deallylating agent useful for aliphatic as well as aromatic allylic ethers. The added advantage of this reagent lies in its tolerance towards some of the reducible functionalities such as nitro, alkoxy, halo, benzyloxy, Boc, and Cbz.

In a typical experimental procedure into a two necked round bottom flask equipped with magnetic bead and nitrogen balloon adapter was placed $ZrCl_4$ (0.636 g, 2.72 mmol, 1 eq), dry THF (25 ml) was syringed into the flask. Immediate formation of red brown solution was observed. The contents were cooled to 0 °C, $NaBH_4$ (0.413 g, 10.9 mmol, 4 eq) was added in portion to the above solution. Red brown solution slowly turned to pale pink. To this reagent system at 0 °C was added allylated alcohol (entry 3) (0.5 g, 2.73 mmol, 1 eq) in dry THF (10 ml). After complete addition of allylated alcohol ice cooling was removed and contents were brought to room temperature (35 °C). The progress of the reaction monitored by TLC clearly indicated the disappearance of the allylated alcohol in 15-20 minutes. Contents were cooled to 0 °C and quenched by the dropwise addition of 5% aq. HCl solution. From the reaction mixture THF was evaporated under vacuum and the remaining aqueous layer was extracted with ethyl acetate. The organic fractions were combined washed successively with brine, water and dried over anhydrous Na_2SO_4. Evaporation of solvent followed by purification of the crude product by silica gel column chromatography gave pure β-Napthol (0.354 g, 90% yield).

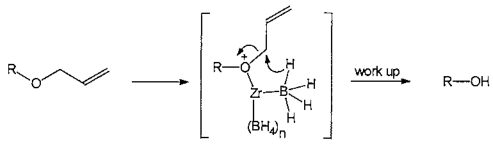
Table 1.

Entry	Substrate	Product [a]	Yield/%
1			95
2			90
3			90
4			85
5			80
6			94
7			87
8			80
9			92
10			85
11			92

[a] All the reactions were completed in 15 – 20 min duration.

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

Scheme 2.



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

The authors wish to thank Dr. K. V. Raghavan, the Director, IICT for encouragement, KPC is thankful to UGC, New Delhi and GHM acknowledge CSIR, New Delhi for the award of research fellowship.

References

1 a) T. W. Greene and P. G. M. Wuts, "Protective Groups in Organic Synthesis," 2nd ed, John Wiley, New York (1991). b) P. J. Kochienski, "Protecting Groups," Thieme, Stuttgart (1994).

2 T. Akiyama, H. Hirofuji, and S. Ozaki, *Tetrahedron Lett.*, **32**, 1321 (1991).

3 a) D. Baudry, M. Ephriti Khine, and H. Felkin, *Chem. Commun.*, **1978**, 694. b) J. J. Oltvoort, C. A. A. van Boeckel, J. H. D. Koning, and J. H. Van Boom, *Synthesis*, **1981**, 305.

4 B. Espanet, E. Dunach, and J. Perichon, *Tetrahedron Lett.*, **33**, 2485 (1992).

5 S. M. Kadam, S. K. Nayak, and A. Banerji, *Tetrahedron Lett.*, **33**, 5129 (1992).

6 H. Ito, T. Taguchi, and Y. Hanzawa, *J. Org. Chem.*, **58**, 774 (1993).

7 H. B. Mereyala and S. Guntha, *Tetrahedron Lett.*, **34**, 6929 (1993).

8 R. Beugelmans, S. Bourdet, A. Bigot, and J. Zhu, *Tetrahedron Lett.*, **35**, 4349 (1994).

9 R. R. Diaz, C. R. Melgarejo, M. T. P. L-Espinosa, and I. I. Cubero, *J. Org. Chem.*, **59**, 7928 (1994).

10 M. S. Congreve, E. C. Davison, M. A. M. Fuhey, A. B. Holmes, A. N. Payne, R. A. Robinson, and S. E. Ward, *Syn. Lett.*, **1992**, 663.

11 J. S. Yadav, S. Chandrasekhar, G. Sumitra, and R. Kache, *Tetrahedron Lett.*, **37**, 6603 (1996).

12 R. Mathew Thomas, G. Hari Mohan, and D. S. Iyengar, *Tetrahedron Lett.*, **38**, 4721 (1997).

13 J. Lee and J. K. Cha, *Tetrahedron Lett.*, **37**, 3663 (1996).

14 A. Kamal, E. Laxman, and N. Venugopal Rao, *Tetrahedron Lett.*, **40**, 371 (1999).

15 Y. R. Santosh Laxmi and D. S. Iyengar, *Synth. Commun.*, **27**, 1731 (1997).

16 K. Purushothama Chary, Y. R. Santosh Laxmi, and D. S. Iyengar, *Synth. Commun.*, **29**(**8**), 1257 (1999).

IICT Communication No: 4367.