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A Mild and Rapid Regeneration of Alcohols from their Allylic Ethers by Chlorotrimethylsilane/Sodium Iodide

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Abstract: A new extremely facile and efficient cleavage of allyl ethers is developed employing chlorotrimethylsilane/sodium iodide. © 1998 Elsevier Science Ltd. All rights reserved.

The protection of alcohols by allyl protecting groups is an important step in the preparation of many organic compounds.[1] Several new methods have been developed for the removal of the allyl group under different condition; these include; $SmCl_3/e^-$,[2] Ti(O),[3] $PdCl_2/CuCl/O_2$,[4] Cp_2Zr,[5] NBS/hυ,[6] $Ti(O\text{-}i\text{-}Pr)_4/n$-BuMgCl,[7] DDQ,[8] $NaBH_4/I_2$,[9] $TolSO_2H/Pd(PPh_3)_4$,[10] and $I(CF_2)_6F/Zn$.[11] In comparison to classical procedures which involve a two-step sequence using strongly basic as well as acidic conditions,[12] the recently introduced procedures are better. Nevertheless, there is scope for milder and improved methods for the cleavage of allyl ethers.

In this communication, we wish to report a new practical regeneration of alcohols from their allylic ethers employing chlorotrimethylsilane and sodium iodide (*in situ* generation of iodotrimethylsilane). In recent years, the use of organosilicon reagents has gained much importance in organic synthesis. Furthermore, the use of the chlorotrimethylsilane and sodium iodide reagent system has been found to be a convenient and inexpensive alternative to iodotrimethylsilane.[13] Recently, we found a new use of the above reagent system for the reduction of azido functionality.[14] In continuation of this effort, particularly for the total synthesis of natural products, the present investigation describes a facile cleavage of allyl ethers. Although, cleavage of esters and lactones has been reported employing the chlorotrimethylsilane-sodium iodide system under reflux conditions,[15] the cleavage of allyl ethers by this reagent system remained unexplored.

This led us to utilise this reagent system for the cleavage of allyl ethers following this procedure: To a solution of allyl ether (1 mmol) in acetonitrile (10 ml), NaI (1.5 mmol) was added and the mixture stirred for 2 min. To this stirred suspension, a solution of chlorotrimethylsilane (1.5 mmol) was added and the stirring continued for another 2 min (for entry 7, 4.5 equivalent of the reagents were used). On completion of the reaction, as indicated by TLC, the reaction mixture was quenched using sodium thiosulphate and extracted

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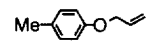
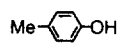
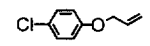
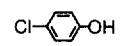
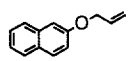
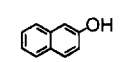
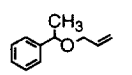
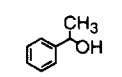
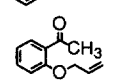
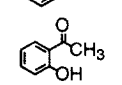
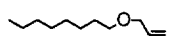
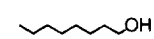
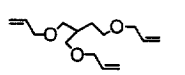
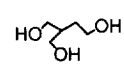
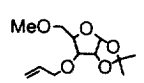
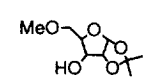
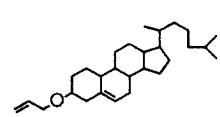
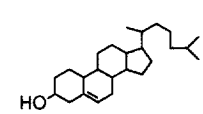
with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the product which was purified by column chromatography (EtOAc-hexane, 2 : 3) to give the final product.

The generality of this method is illustrated in the following Table:

Entry	Substrate	Time(min)	Product	Yield(%)
1		2		98
2		2		98
3		2		98
4		3		96
5		5		90
6		3		95
7		3		95[16]
8		2		93
9		3		93

In summary, the method described in this communication is rapid and efficient and proceed under mild conditions. Therefore, it will find applications in organic synthesis which require deprotection of allyl ethers.

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16. Conversion monitored by HPLC.

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