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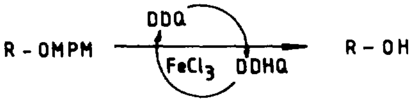
Deprotection of mono and dimethoxy phenyl methyl ethers using catalytic amounts of DDQ

S.Chandrasekhar*, G.Sumithra and J.S. Yadav

Indian Institute of Chemical Technology, Hyderabad-500 007, India

Abstract: *4-Methoxy and 3,4 dimethoxy benzyl ethers have been deprotected with catalytic amounts of DDQ by oxidative recycling of the byproduct DDHQ with $FeCl_3$ for the first time.*

Protective groups play an essential role in synthetic strategies[1] and easy removal of a particular protective group in the presence of other labile protective groups and sensitive functional groups always determines its usefulness. Oxidative methods for removing protecting groups are relatively rare and 4-methoxy and 3,4 dimethoxy benzyl (MPM and DMPM) ethers are lately added to the repertoire of standard protective groups. These undergo easy electron transfer to 2,3 dichloro-3,6-dicyano-1,4-benzoquinone (DDQ) to liberate the free alcohols under essentially neutral conditions[2]. However the DDHQ (dichloro dicyano hydroquinone) is an inevitable byproduct, removal of which is sometimes cumbersome, besides which stoichiometric DDQ is required which is expensive. To overcome these problems, herein we report an altogether novel DDQ 'regeneration technique' for the removal of said protective groups.



Thus treatment of n-decyl MPM ether (table 1, entry 1) and DMPM ether (entry 2) with 10 mole percent of DDQ and 3 equivalents of $FeCl_3$, a reagent generally used for oxidation of hydroquinones to quinones[3] in DCM:H_2O (10:1) furnished cleanly the parent alcohols in excellent yields (Table 1). To test the generality and selectivity under the reaction conditions, 1,10-decanediol was differentially protected as MPM ether and acetate(entry 3) or THP ether (entry 4) or TBDPS ether (entry 5) or benzyl ether (entry 6) or methoxy methyl ether (entry 7) and subjected to described conditions produced consistently high yields of deprotected alcohols without effecting the other protective groups. The products were isolated easily from the other byproduct using a simple column chromatography.

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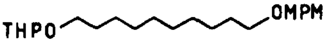
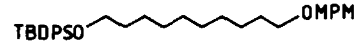
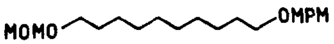
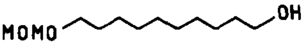
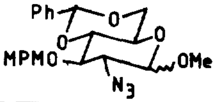
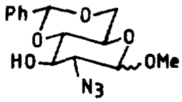
Cholesteryl-OMPM (entry 8) and sugar derivative (entry 9) also cleanly underwent the desired deprotection. However with $FeCl_3$ alone starting mateials were recovered.

Table 1

ENTRY	SUBSTRATE	PRODUCT	TIME	YIELD(%)
1			3 h	92
2			2 h	94
3			7 h	∼70
4*			3h	65
5			2 h	80
6			6 h	70
7			4 h	72
8	Cholesteryl - OMPM	Cholesterol	24 h	64
9			48 h	62

* About 10% THP ether cleavage was noticed at the end of 3h

Thus an altogether new strategy for the removal of MPM and DMPM ethers using catalytic amounts of DDQ was developed which is simple, easy, economical and selective.

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