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Montmorellonite Clays Catalysis Ix¹: A Mild and Efficient Method for Removal of Tetrahydropyranyl Ethers

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MONTMORILLONITE CLAYS CATALYSIS IX¹: A MILD AND EFFICIENT METHOD FOR REMOVAL OF TETRAHYDROPYRANYL ETHERS

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Abstract: A variety of tetrahydropyranyl ethers of alcohols and phenols are easily removed in the presence of catalytic amount of montmorillonite clays in methanol at 40-50 °C in excellent yield.

Selective introduction and removal of protective groups is of great significance in organic synthesis.² Tetrahydropyranlation of hydroxyl groups has been recognised as a useful and representative method for protection of alcohols and phenols due to its easy installation and remarkable stability towards basic media, Grignard reagents and reactions involving oxidation and reduction by inorganic hydrides.³

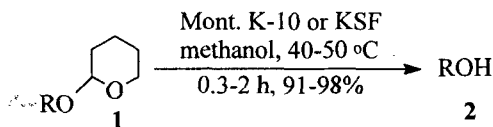
2-Tetrahydropyranyl ethers (THPEs) are usually transformed into their parent alcohols or phenols under acid-catalysed conditions.⁴ A wide variety of catalysts have been already applied for this conversion, including the use of

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protic acids⁵ (acetic acid, *p*-toluenesulfonic acid, boric acid), Lewis acids⁶ (magnesium bromide in ether, dimethylaluminium chloride), Lewis acids (copper sulphate and iron(III) chloride) supported on silica gel,⁷ electrogenerated acid,⁸ pyridinium *p*-toluenesulfonate,⁹ ion-exchange resins¹⁰ (amberlyst H-15, Dowex 50W-X8, Nafion-H), bentonitic earth,¹¹ organotin phosphate condensates,¹² triphenylphosphine dibromide (PPh₃Br₂)¹³ and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).¹⁴ More recently, heteropoly acid,¹⁵ lithium chloride,¹⁶ expansive graphite¹⁷ and reductive cleavage using sodium cyanoborohydride and BF₃·OEt₂¹⁸ have been developed to this reaction. However, some of these procedures suffer from using expensive reagents, strongly acidic condition, formation of considerable amounts of side products and/or the necessitate aqueous work-up. Consequently, there is still a demand to develop a mild and efficient alternative procedure for the deprotection of THPEs.

Montmorillonite clays has been extensively used as efficient catalyst for a variety of organic reactions.¹⁹ Previously we have developed efficient and convenient methods for preparation of 5(6)/5'(6')-unsaturated 3β,3'β-disteryl ethers,²⁰ preparation²¹ and cleavage²² of acetals, protection and deprotection of aldehydes by formation²³ and cleavage²⁴ of 1,1-diacetates, synthesis of triarymethenes²⁵ and coumarins²⁶ and acylation of alcohols, thiols, phenols and amines²⁷ under catalysis of montmorillonite clays. Hoyer and Laszlo have developed an efficient procedure for tetrahydropyranlation of alcohols and phenols catalysed by montmorillonite K 10.²⁸ However, the deprotection of THPEs with montmorillonite clays remains unreported. As a part of our work on



Scheme 1

montmorillonite clays catalysis, herein we wish to report an efficient cleavage of THPEs catalysed by montmorillonite K-10 and KSF under mild conditions.

As summarised in **Table 1**, in the presence of montmorillonite K-10 or KSF, the deprotection of THPEs could be carried out rapidly in methanol to afford the corresponding parent hydroxy compounds (**2**) at 40-50 °C in high yields. The present procedure for deprotection of THPEs is quite general as a wide range of THPEs of primary (**1a-1c** and **1h**), secondary (**1d-1i**) and benzylic alcohols (**1c**, **1g** and **1i**) as well as phenols and naphthols (**1j-1q**) were cleaved in excellent yield. K-10 and KSF gave similar results in term of reaction time and yield. The acid-sensitive functionalities such as methoxy (**1l**) is tolerated, double bond in steroid compound (**1e** and **1f**) remained unaffected in this procedure as well as the formation of THPE of cholesterol.²⁸ Betulin diTHPE (**1h**) was not converted into allobetulin under these conditions. The reaction proceeds cleanly and the work-up is simple, involving only the filtration of the catalyst and the removal of solvent to obtain the product in high purity.

The reaction was studied in a variety of solvents and the results are shown in **Table 2**. The deprotection of the THPEs in non alcoholic solvents has been reported, for example, in chloroform,^{7a} in hexane-methylene chloride,^{6b} in acetone,¹¹ in DMSO,¹⁶ in acetonitrile,¹⁴ and in dry medium^{7b} *etc.* However, there are no reports about the mechanism of the reaction. As dihydro-4*H*-pyran was detected by GC in our non alcoholic deprotection of the THPEs. We presume that the deprotection of THPEs in non alcoholic solvents undergoes a pyrolysis to furnish the corresponding hydroxy compounds and dihydro-4*H*-pyran. From **Table 2**, it is clear that methanol is the best solvent system in this procedure in which methanol performs a trans-etherification reaction.

The reaction rate is markedly dependent on temperature. We found that at room temperature the reaction proceeds much more slowly, for example, complete conversion of α -naphthyl THPE (**1n**) to α -naphthol (**2n**) needed 8 h, cholesteryl THPE (**1e**) only was cleaved 74% in methanol under catalysis of

Table 1. Deprotection of THPES of alcohols and phenols catalysed by montmorillonite clays

Entry	Substrate	Catalyst	Time(h)	Yield (%) ^a
a	<i>n</i> -C ₈ H ₁₇ -OTHP	K-10	0.8	94
		KSF	1.0	91
b	<i>n</i> -C ₁₀ H ₂₁ -OTHP	K-10	0.8	92
c	C ₆ H ₅ CH ₂ -OTHP	K-10	0.5	95
		KSF	0.6	94
d	<i>n</i> -C ₆ H ₁₃ CH(OTHP)CH ₃	K-10	1.2	94
		KSF	1.2	96
e	Cholesteryl-OTHP	K-10	1.2	96
		KSF	1.5	92
f	β-Sitosteryl-OTHP	K-10	0.5	96
		KSF	0.5	94
g	(C ₆ H ₅) ₂ CH-OTHP	K-10	0.8	94
		KSF	0.8	93
h	Lup-20(29)-en-3β,28-diyl-diOTHP	K-10	2.0	95
i	C ₆ H ₅ CH(OTHP)COC ₆ H ₅	K-10	0.8	92
		KSF	1.0	93
j	C ₆ H ₅ OTHP	K-10	0.4	98
		KSF	0.4	97
k	<i>p</i> -CH ₃ C ₆ H ₄ OTHP	K-10	0.3	96
		KSF	0.4	97
l	<i>p</i> -CH ₃ OC ₆ H ₄ OTHP	K-10	0.5	94
		KSF	0.7	92
m	Resorcyyl-(OTHP) ₂	K-10	0.6	94
		KSF	0.7	92
n	α-Naphthyl-OTHP	K-10	0.6	96
		KSF	0.7	94
o	β-Naphthyl-OTHP	K-10	1.0	94
p	<i>m</i> -O ₂ NC ₆ H ₄ OTHP	K-10	0.4	96
		KSF	0.5	94
q	<i>p</i> -O ₂ NC ₆ H ₄ OTHP	K-10	0.4	98
		KSF	0.4	96

^a Isolated yield.

Table 2. Deprotection of cholesteryl-OTHP in various solvents catalysed by montmorillonite K-10^a

Entry	Solvent	Temperature(°C)	Time(h)	Conversion rate	Net yield(%)
1	MeCN	50	8	42	88
2	MeNO ₂	50	8	80	82
3	Et ₂ O	reflux	8	84	94
4	CH ₂ Cl ₂	reflux	8	48	90
5	DMF	50	8	6	80-85
6	DMSO	50	8	5	90-95
7	<i>n</i> -Hexane	50	8	24	95
8	EtOAc	50	8	46	98
9	Acetone	50	8	12	82
10	MeOH	50	1.2	100	96
11	MeOH	25	24	74	95

^a Reaction was carried out using 20 mg K-10, 5 ml solvent and 50 mg cholesteryl-OTHP.

montmorillonite K-10. The catalyst was easily regenerated by washing with ethanol followed by drying at 120 °C for 1 h. The catalyst could be reused four times for the deprotection of cholesteryl THPE (1e) without any loss in catalytic activity.

In conclusion, the present procedure provides a general methodology for the deprotection of THPEs from a variety of primary, secondary and benzylic alcohols and phenols. The operational simplicity, use of inexpensive, non-corrosive and reusable catalyst, high yields and short reaction time can make this procedure a useful and attractive alternative to the currently available methods.

Experimental

Montmorillonite K-10 and KSF were purchased from Aldrich and all solvent were analytical grade and employed directly for this reaction. THPEs were synthesised from the corresponding hydroxyl compounds (2) according to our

recent report.²⁹ The products were characterised by IR and ¹H NMR spectra and by comparison of their TLC and mps or bps with authentic samples.

General procedure for deprotection of THPEs:

A mixture of THPE (2 mmol), methanol (5 ml) and montmorillonite K-10 or KSF (100 mg) was stirred at 40-50 °C for the length of time indicated in **Table 1**. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by filtration and washed with CH₂Cl₂ (5 ml). Evaporation of the solvent gave the corresponding essentially pure parent hydroxyl compound (**2**). Further purification was performed by flash column chromatography on silica gel with light petroleum-diethyl ether as eluent wherever necessary.

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