An Efficient One-Pot Conversion of THP- and TMS Ethers to Sulfonate Esters Using $FeCl_3$-Montmorillonite K-10 Clay

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Various tetrahydropyranyl and trimethylsilyl ethers are efficiently transformed into the corresponding sulfonate esters with sulfonyl chlorides in the presence of $FeCl_3$-Montmorillonite K-10 clay.

Key words: Sulfonate Esters, $FeCl_3$-Montmorillonite K-10, Trimethylsilyl Ethers, Tetrahydropyranyl Ethers, Clay Catalyst

Sulfonate esters are especially useful substrates in nucleophilic substitution reactions used in synthesis. Their preparation from alcohols is an effective way of installing a reactive leaving group, *e.g.* on an alkyl chain. *p*-Toluenesulfonate- and methanesulfonate esters are the most frequently used groups for preparative work. The usual method for preparation of sulfonates relies on the use of the corresponding sulfonyl chloride or anhydride in the presence of triethylamine [1], pyridine [2], 1,4-diazabicyclo[2.2.2]octane (DABCO) [3] or aqueous base in a Schotten-Baumann type reaction. An alternative for preparing tosylates and mesylates is to convert the alcohol into its lithium salt, which is then allowed to react with the sulfonyl chloride [4]. Sulfonic acids are also used for the synthesis of sulfonate esters but expensive alkylating agents such as trialkyl orthoformate, alkyl ethers, esters or 2-alkoxybenzothiazolium salts are employed instead of alcohol [5]. To the best of our knowledge, direct conversion of tetrahydropyranyl (THP) and trimethylsilyl (TMS) ethers into the corresponding sulfonate esters have not been reported in the literature.

Results and Discussion

Heterogeneous reactions that are facilitated by supported reagents on various solid surfaces have received attention in recent years [6]. The advantage of these methods over conventional homogeneous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products, and simplicity of handling. Previously, we have developed several direct conversions of THP and TMS ethers into the corresponding carboxylic esters in the presence of Montmorillonite K-10 clay [7, 8]. In continuation of our ongoing program to develop environmentally benign methods using supported reagents, this article describes a new, simple, and efficient one-pot protocol for the deprotection-sulfonylation of THP and TMS ethers with sulfonyl chlorides in refluxing acetonitrile using $FeCl_3$ impregnated Montmorillonite K-10 as a mild and non-corrosive solid catalyst (Scheme 1). The focal point of this report is on the transformations of O-C and O-Si bonds into O-SO_2 bonds.

$$\begin{matrix}\text{RO-THP}\\ \text{RO-TMS}\end{matrix} + \text{R'}SO_2Cl \xrightarrow[CH_3CN,\ \text{reflux}]{FeCl_3-\text{Mont. K 10}} ROSO_2\text{R'}$$

Scheme 1.

The catalyst used here can easily be prepared [9] from readily available and inexpensive $FeCl_3$ and Montmorillonite K-10 clay in dry acetonitrile. In order to have a background knowledge of the activity of the extensively used Montmorillonite clays, *n*-butylOTHP was treated with TsCl using different clays (Table 1). It was found that $FeCl_3$ supported Montmorillonite K-10 is most effective among the clays for the deprotection-sulfonylation of THP ethers. The iron content of the clay determined by the atomic absorption technique was 0.15 mmol/g of solid catalyst. Using *n*-butylOTHP, the amount of catalyst was optimized and an ether to clay ratio of 1 : 0.038 was taken. The catalyst can be recovered and reused after activation at 280 °C. In this study, different aliphatic THP

Table 1. Deprotection-sulfonylation of *n*-butylOTHP using various clay catalysts.

Clay catalyst	Time (h)	Yield[a] (%)
Montmorillonite K-10	24	25
Montmorillonite KSF	24	20
Fe^{3+}-Montmorillonite K-10	24	57
$FeCl_3$-Montmorillonite K-10	7	81

[a] Isolated yields.

Table 2. Preparation of sulfonate esters from THP ethers using $FeCl_3$-Mont. K-10.

Entry	THP ether	Sulfonyl chloride	Time (h)	Yield[a] (%)	Ref.[b]
1	CH_3CH_2OTHP	*p*-$CH_3C_6H_4SO_2Cl$	6	75	[10]
2	$CH_3(CH_2)_2CH_2OTHP$	*p*-$CH_3C_6H_4SO_2Cl$	7	81	[11]
3	$CH_3(CH_2)_3CH_2OTHP$	*p*-$CH_3C_6H_4SO_2Cl$	7	79	[10]
4	$CH_3(CH_2)_6CH_2OTHP$	*p*-$CH_3C_6H_4SO_2Cl$	7	80	[1]
5	$PhCH_2OTHP$	*p*-$CH_3C_6H_4SO_2Cl$	8	70	[12]
6	CH_2=$CHCH_2OTHP$	*p*-$CH_3C_6H_4SO_2Cl$	8	72	[10]
7	CyclohexylOTHP	*p*-$CH_3C_6H_4SO_2Cl$	11	78	[10]
8	$(CH_3)_2CHOTHP$	*p*-$CH_3C_6H_4SO_2Cl$	10	70	[10]
9	D,L-$CH_3(CH_2)_5$-$CH(CH_3)OTHP$	*p*-$CH_3C_6H_4SO_2Cl$	11	68	[10]
10	CyclohexylOTHP	$C_6H_5SO_2Cl$	8	77	[10]
11	CyclohexylOTHP	CH_3SO_2Cl	3	88	[10]
12	$CH_3(CH_2)_2CH_2OTHP$	CH_3SO_2Cl	2	86	[11]
13	$CH_3CH_2CH_2OTHP$	CH_3SO_2Cl	2	83	[13]

[a] Yields refer to pure isolated products characterized by IR and ^{1}H NMR spectroscopy; [b] references for known compounds.

Table 3. Preparation of sulfonate esters from TMS ethers using $FeCl_3$-Mont. K-10.

Entry	TMS ether	Sulfonyl chloride	Time (h)	Yield[a] (%)
1	$CH_3(CH_2)_2CH_2OTMS$	*p*-$CH_3C_6H_4SO_2Cl$	5	78
2	$CH_3(CH_2)_3CH_2OTMS$	*p*-$CH_3C_6H_4SO_2Cl$	6	75
3	$CH_3(CH_2)_6CH_2OTMS$	*p*-$CH_3C_6H_4SO_2Cl$	6	80
4	$PhCH_2OTMS$	*p*-$CH_3C_6H_4SO_2Cl$	7	72
5	CH_2=$CHCH_2OTMS$	*p*-$CH_3C_6H_4SO_2Cl$	6	75
6	CyclohexylOTMS	*p*-$CH_3C_6H_4SO_2Cl$	10	80
7	$(CH_3)_2CHOTMS$	*p*-$CH_3C_6H_4SO_2Cl$	9	77
8	$CH_3(CH_2)_5CH(CH_3)OTMS$	*p*-$CH_3C_6H_4SO_2Cl$	11	71
9	CyclohexylOTMS	$C_6H_5SO_2Cl$	7	82
10	CyclohexylOTMS	CH_3SO_2Cl	3	87
11	$CH_3(CH_2)_2CH_2OTMS$	CH_3SO_2Cl	3	85
12	$CH_3CH_2CH_2OTMS$	CH_3SO_2Cl	3	85

[a] Isolated yields.

ethers were treated with *p*-toluenesulfonyl, benzenesulfonyl, and methanesulfonyl chloride in the presence of the catalyst in refluxing acetonitrile to obtain the corresponding sulfonate esters in good to high yields (Table 2). The catalyst, $FeCl_3$-Mont. K-10 clay, is also efficient for the preparation of sulfonate esters from TMS ethers (Table 3). It is worth noting that in both reactions carbon-carbon double bonds remains unaffected (entry 6, Table 2, and entry 5, Table 3). Sulfonate esters prepared from methanesulfonyl chloride (entries 11 – 13, Table 2, and entries 10 – 12, Table 3) need shorter reaction times and generally give higher yields than those produced from arylsulfonyl chlorides.

Conclusion

A simple, and efficient method has been developed for one-step deprotection-sulfonylation of a wide range of THP and TMS ethers by using an inexpensive, nonhazardous, and easily available catalyst. The present protocol has the additional advantages of easy workup and high yield.

Experimental Section

$FeCl_3$-Montmorillonite K-10 catalyst was prepared according to the method reported by Laszlo *et al.* [9]. All products were characterized by comparison of their spectroscopic data with those of known samples. IR spectra were obtained using a Shimadzu 470 instrument. ^{1}H NMR spectra were determined by a Bruker AQS Avance 300 MHz spectrometer.

General procedure for the conversion of THP ethers into their corresponding sulfonate esters

To a stirred suspension of the THP ether (1.0 mmol), dry acetonitrile (6 ml), and $FeCl_3$-Montmorillonite K-10 (250 mg, containing 0.038 mmol of $FeCl_3$), the sulfonyl chloride (1.0 mmol) was added. The reaction mixture was heated at reflux for the time specified in Table 2. Progress of the reaction was monitored by TLC; on completion, after cooling, the catalyst was removed by filtration and the filtrate was evaporated. The resulting crude product was purified and isolated by preparative TLC (silica gel, eluent petroleum ether : ethyl acetate = 50 : 1) to afford the desired ester.

General procedure for the conversion of TMS ethers into their corresponding sulfonate esters

To a solution of the TMS ether (1.0 mmol) in dry acetonitrile (6 ml) was added $FeCl_3$-Montmorillonite K-10 clay (250 mg, containing 0.038 mmol of $FeCl_3$). The mixture was refluxed for the appropriate time (Table 3) and cooled. After filtration, the filtrate was concentrated and the product purified and isolated by preparative TLC (silica gel, eluent petroleum ether : EtOAc = 50 : 1).

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