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Solvent-free acetylation and tetrahydropyranylation of alcohols catalyzed by recyclable sulfonated ordered nanostructured carbon

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Rapid and practical green acetylation and tetrahydropyranylation routes of structurally diverse alcohols and phenols were applied under solvent-free reaction conditions providing excellent yields, using catalytic amounts of environmentally friendly sulfonated ordered nanoporous carbon (CMK-5-SO₃H). Non-toxic nature of the catalyst, its easy handling, recovery and reusability, and the absence of any solvent characterize the presented procedures as efficient methods. These procedures provide methods for the separation of the product by simple filtration. (\hat{c} 2013 Institute of Chemistry, Slovak Academy of Sciences

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Introduction

Acetyl and tetrahydropyranyl (THP) are the most versatile protecting groups that are often used for the protection of alcohol moieties due to their low cost, easy installation, remarkable stability, and compatibility under various reaction conditions and reagents (Greene & Wuts, 1991). Acetylation of alcohols provides an efficient route for protecting of -OH groups during oxidation, peptide coupling, and glycosidation reactions (Hanson, 1999); THP groups are also the protecting group of choice in peptides (Bodanszky & Ondetti, 1966), nucleotides (van Boom et al., 1971), carbohydrates (Augé et al., 1980), and steroids (Djerassi, 1963). Many catalysts have already been proposed for the acetylation of alcohols such as NbCl₅ (Yadav et al., 2005), $AlPW_{12}O_{40}$ (Firouzabadi et al., 2003), $Sc(OTf)_3$ (Ishihara et al., 1996), $In(OTf)_3$ (Chauhan et al., 1999), $Al(OTf)_3$ (Kamal et al., 2007), I₂ (Phukan, 2004), 12-tungstophosphoric acid (Satam & Jayaram, 2008), and $H_{14}[NaP_5W_{29}MoO_{110}]$ (Romanelli et al., 2010), and also for the tetrahydropyranylation of alcohols including *p*-toluenesulfonic acid (PTSA) (Corey et al., 1987), 2,3-dichloro-5,6-dicyano1,4-benzoquinone (DDQ) (Tanemura et al., 1992), ZnCl₂ (Ranu & Saha, 1994), I₂ (Deka & Sarma, 2001), tetrabutylammonium tribromide (Naik et al., 2001), In(OTf)₃ (Mineno, 2002), Li(OTf)₃ (Karimi & Maleki, 2002), polyaniline salts (Palaniappan et al., 2002), $Sc(OTf)_3$ (Karimi & Ma'mani, 2003), $Bi(OTf)_3 \cdot 4H_2O$ (Stephens et al., 2003), $PdCl_2$ $(CH_3CN)_2$ (Wang et al., 2004), imidazolium-based tetrachloroindate(III) (Kim & Varma, 2005), copper methanesulfonate-acetic acid (Wang et al., 2007b), $Fe(HSO_4)_3$ (Shirini et al., 2007), and $Al(OTf)_3$ (Williams et al., 2010). Although these methods are satisfactory for many molecules, some of them have serious limitations, e.g. harsh reaction conditions, elevated reaction temperatures, long reaction times, high catalyst to substrate ratio, organic solvents as media, and tedious and time-consuming work-up procedure which need be replaced by greener methods.

In recent years, solid acids catalysis has gained much attention due to the advantages of heterogeneous catalysts, like simplified product isolation, high selectivity, easy recovery of catalysts and reduced generation of harmful wastes (Corma, 1995). Therefore, to address the improvement of environ-

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Fig. 1. Schematic preparation of sulfonated ordered mesoporous carbon (CMK-5-SO₃H) (catalyst 1).

mental safety in the production of chemicals under milder reaction conditions, various solid catalysts such as $NaHSO_4 \cdot SiO_2$ (Das & Thirupathi, 2007), polymer supported $Gd(OTf)_3$ (Yoon et al., 2008), cobalt(II) salen complex (Rajabi, 2009), and sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester (Niknam & Saberi, 2009) were reported for the acetylation, and nafion-H (Olah et al., 1983), montmorillonite (Hoyer et al., 1986), clays (Campelo et al., 1994), amberlyst (Bongini et al., 1979), H-Y zeolite (Kumar et al., 1993), $Al_2(SO_4)_3$ on silica gel (Nishiguchi & Kawamine, 1990), silica chloride (Ravindranath et al., 2001), sulfuric acid on silica gel (Heravi et al., 1999), SO₃H-functionalized amorphous silica (Shimizu et al., 2004), sulfated zirconia (Reddy et al., 2005), and carbon supported sulfuric acid (Yang et al., 2008) for the tetrahydropyranylation of hydroxyl group. Despite a number of improvements, some of these procedures still suffer from long reaction time, the use of volatile and toxic organic solvents, and non-recoverable catalysts which result in the generation of large amounts of toxic waste. Thus, there is still a need for mild and efficient alternative methods, especially using recoverable heterogeneous solid acids as catalysts for the acetylation and tetrahydropyranylation of alcohols.

On the other hand, ordered nanoporous carbonaceous solid acids can also maintain strong acidity participating thus in many industrially important acidcatalyzed reactions. The carbon surface has been exclusively used as a support substrate, especially as electrodes with a wide potential window in electrochemistry for catalytic, analytical, and biotechnological applications (Rice et al., 1990). Recently, Joo et al. (2001) have synthesized ordered mesoporous carbon with periodic arrays of nanopores (CMK-5) using partially furfuryl alcohol-filled pores of Al-SBA-15 as a hard template. In principle, mesoporous SBA-15 with hexagonal array of nanotubes with microconnections between the mesopores was produced by the

cooperative assembly process between silica species (tetraethoxysilane, TEOS) and the amphiphilic triblock copolymer P123 in an aqueous medium (Yu et al., 2002). Al-SBA-15 was obtained by the well dispersion of calcined SBA-15 into an aqueous solution of AlCl₃. Impregnation of furfuryl alcohol into Al-SBA-15 by incipient wetness infiltration, polymerization of furfuryl alcohol by Al (surface templating), heating of the composite at 850 °C under vacuum, and removal of the silica template by HF resulted in the synthesis of ordered mesoporous carbon CMK-5. This material shows high surface area, narrow pore size distribution, and large pore volume. Covalent attachment of aryl sulfonic acid on ordered nanoporous carbon with mesoporosity both inside and between the nanopipes can be performed by homogenous reduction of 4-benzene-diazoniumsulfonate using hypophosphorous acid (Wang et al., 2007a) and it resulted in the preparation of sulfonated ordered mesoporous carbon $(CMK-5-SO_3H).$

Therefore, in view of the emerging importance of green chemistry and extending the use of recoverable heterogeneous solid acids (Karimi & Zareyee, 2008, 2009; Zareyee et al., 2011, 2012), the application of CMK-5-SO₃H (catalyst 1) as a highly effective and reusable catalyst in both acetylation and tetrahydropyranylation of alcohols and phenols under solvent-free reaction conditions at ambient temperature is introduced herein (Fig. 1) (See supporting material for experimental details).

Experimental

Acetylation procedure: CMK-5-SO₃H (13 mg, 2 mole %) was added to the mixture of alcohol (1 mmol) and acetic anhydride (Ac₂O) (1.2–1.5 mmol), and the reaction mixture was stirred in a round bottom flask at room temperature for the appropriate time (Table 1). After the completion of the reaction (TLC), the re-

Table 1. CMK-5-SO₃H (2 mole %) catalyzed acetylation of alcohols and phenols at room temperature and under solvent-free conditions

	<u> </u>	D. 1	Ac_2O	Time	\mathbf{Y} ield ^a
Entry	Substrate	Product	mmol	min	%
1	ОН	CH3	$\begin{array}{c} 1.2 \\ 1.5 \end{array}$	20 10	94 100
2	СІ	CI CH3	1.2	5	99
3	СІ	CI CH3	1.2	5	98
4	CI	CI CI CH3	1.2	5	99
5	NO2	O CH ₃	1.2	20	99
6	OH	CH ₃	1.5	10	97
7	ОН	O CH₂	1.5	10	98
8	ОН	CH ₃	1.5	10	97
9	ОН		1.5	10	99
10	OH		1.5	10	96
11	ОН	CT CH3	1.5	15	90
12	H ₃ C	H ₃ C	1.5	10	94
13			1.5	10	98
14	ОН	O O CH3	1.5	10	90
15	н₃с∽ОН	H ₃ C O CH ₃	1.5	10	94

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Tat	ole	1. ((continued)	
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Entre	Substrate	Droduct	Ac_2O	Time	\mathbf{Yield}^{a}
Entry	Substrate	Product	mmol	min	%
16	ОН	O CH ₃	1.2	10	99
17	CI	CI O CH3	$\begin{array}{c} 1.2 \\ 1.5 \end{array}$	$\frac{15}{2}$	99 96
18	CI	CI CH3	1.5	5	99
19	CI	CI CI CI CI	1.2	25	99
20	H ₃ C CH ₃	H ₃ C CH ₃ CH ₃	1.5	30	90
21	OH NO ₂	O CH ₃ NO ₂	$\begin{array}{c} 1.2\\ 1.5\end{array}$	20 10	84 99
22	No ₂ OH	No ₂ O CH ₃	1.2	15	99
23	OH	CH3 OCH3	1.2	5	99
24	OH	O CH3	$\begin{array}{c} 1.2\\ 1.5\end{array}$	10 15	45 99
25	НО	H ₃ C O CH ₃	2.5	10	97
26	HO OH	CI	3.6	15	95

a) Estimated by GC.

action mixture was filtered and diluted with water. It was extracted with ethyl acetate $(3 \times 10 \text{ mL})$ and the combined organic phases were dried (Na_2SO_4) , filtered, and evaporated under reduced pressure. Compounds with the purity below 95 % were further purified using column chromatography on silica gel to afford pure acetate. Characterization of some products was achieved by ¹H NMR and ¹³C NMR.

Tetrahydropyranylation procedure: to a stirred mixture of alcohol (1 mmol) and 3,4-dihydropyran (DHP) (0.129 g, 1.5 mmol), catalyst 1 (13 mg, 2 mole

%) was added and stirring continued at ambient temperature for the period of time indicated in Table 2. Progress of the reaction was monitored by GC and TLC (eluent, hexane : ethyl acetate volume ratio, $\varphi_{\rm r}$ = 4 : 1). When the reaction was completed, 15 mL of ethyl acetate were added and the mixture was filtered. The solid was washed with ethyl acetate. The organic phase was evaporated under reduced pressure to give the products in good to excellent yields (Table 2). If needed, further purification was performed by passing through a short column of silica gel.

Table 2. CMK-5-SO₃H (2 mole %) catalyzed tetrahydropyranylation of alcohols and phenols at room temperature and under solvent-free conditions

Es trus	Caladarata	Dry hast	Time	\mathbf{Yield}^{a}	
Entry	Substrate	Product	min	%	
1	ОН	ОТНР	30	100	
2	CI	OTHP	70	82	
3	СІ	CI	40	85	
4	CI OH	CI CI	80	75	
5	Н3С ОН	H ₃ C OTHP	50	95	
6	O ₂ N OH	O ₂ N OTHP	60	88	
7	ОН	OTHP	90	100	
8	OH	OTHP	100	94	
9	ОН	ООТНР	75	100	
10	ОН	OTHP	45	100	
11	OH	OTHP	60	100	
12	OH	OTHP	50	100	
13	ОН	OTHP	75	h 95	
14	ОН		80	91	
15	ОН	OTHP	100	98	
16	t-Bu	OTHP t-Bu	95	94	
17	OH	OTHP	60	96	

Table 2. (continued)

Entry	Substrate	Product	$\frac{\text{Time}}{\text{min}}$	$\frac{\text{Yield}^a}{\%}$	
18	OH	OTHP	80	100	
19	CI	CI	70	85	
20	OH NO ₂	OTHP NO2	160	70	
21	H ₃ C OH CH ₃	H ₃ C OTHP CH ₃	70	99	
22	OH OH	OTHP H O	100	92	

a) Estimated by GC.



Fig. 2. Acetylation and tetrahydropyranylation of benzyl alcohol using 2 mole % of CMK-5-SO₃H at room temperature under solvent-free conditions.

Results and discussion

Our initial investigations were focused on finding appropriate conditions for the acetylation and tetrahydropyranylation of benzyl alcohol. According to our findings, 1.2–1.5 mmol of Ac₂O and 1.5 mmol of DHP in the presence of 2 mole % of CMK-5-SO₃H under solvent-free reaction conditions at ambient temperature gave the best results and produced acetate and THP ethers of benzyl alcohol in a short reaction time and quantitative yields (Fig. 2). Lowering the catalyst 1 loading resulted in lower yields. Furthermore, there is no considerable reaction when benzyl alcohol was allowed to react with Ac₂O or DHP in the absence of a catalyst.

Having established the optimal reaction conditions, a study to explore the scope of this catalytic system was initiated. First, acetylation of a variety of primary aromatic and aliphatic alcohols with Ac₂O was examined (Table 1, entries 1-8). It is noteworthy that the reactions proceeded efficiently in good to excellent yields for all studied alcohols. This method is also efficient for the acetylation of secondary aliphatic alcohols (Table 1, entries 9-15), and for phenol (Table 1, entry 16) and its derivatives (Table 1, entries 17–22). 1-Naphthol and 2-naphthol also underwent the reaction producing the corresponding esters in excellent yields (Table 1, entries 23 and 24). It has also been found that CMK-5-SO₃H effectively catalyzed the acetylation of diols and triols (Table 1, entries 25) and 26).

Entry	Protection	Catalyst (content in mole %)	Solvent	<i>Т</i> °С	Time min	Yi	ield %	Reference
1	Acetylation	CMK-5-SO ₃ H (2)	Solvent-free	\mathbf{rt}	10	ę	97^a	Present work ^{b}
2	Acetylation	polymer supported $Gd(OTf)_3$ (0.5)	DMSO	\mathbf{rt}	90	> 9	99	Yoon et al. $(2008)^{b,c}$
3	Acetylation	cobalt(II) salen complex (1)	Solvent-free	50	45	ę	99	Rajabi $(2009)^d$
4	Acetylation	sulfuric acid ([3-(3-silicapropyl) sul- fanyl]propyl)ester (0.002 g)	Solvent-free	rt	6	ę	96	Niknam and Saberi $(2009)^e$
5	Tetrahydropyranylation	$CMK-5-SO_3H(2)$	Solvent free	\mathbf{rt}	30	ę	96^a	Present work
6	Tetrahydropyranylation	SO_3H -functionalized amorphous silica (0.5)	$\mathrm{CH}_2\mathrm{Cl}_2$	\mathbf{rt}	30	ę	92	Shimizu et al. $(2004)^f$

Table 3. Comparison of the catalytic efficiency of CMK-5-SO₃H against other catalysts used for the protection of benzyl alcohol

a) Isolated yield; b) 1.5 mmol Ac₂O was used; c) long reaction time; d) 5 mmol Ac₂O was used at 50 °C; e) 1 mL Ac₂O was used; f) p-methoxybenzyl alcohol was used as a substrate in toxic solvent (CH₂Cl₂); g) toxic solvent (CH₂Cl₂) and only recovered twice.

Tetrahydropyranylation carbon supported sulfuric acid (cata- CH₂Cl₂

lyst : alcohol mass ratio of 0.6:1)

The application of catalyst 1 was also extended to the tetrahydropyranylation of alcohols and phenols. For this purpose, several primary alcohols were protected with DHP in the presence of catalytic amounts of CMK-5-SO₃H (2 mole %) at ambient temperature and under solvent-free reaction conditions in good to excellent yields (Table 2, entries 1–11). Aromatic alcohols possessing both electron-donating as well as electron-withdrawing groups underwent tetrahydropyranylation to afford the corresponding THP ethers. Secondary aliphatic (Table 2, entries 12–16) and aromatic (Table 2, entry 17) alcohols, and phenol (Table 2, entry 18) and its derivatives (Table 2, entries 19–22) were also converted to the related compounds under similar reaction conditions.

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The results of acetylation and tetrahydropyranylation of alcohols with polymer supported $Gd(OTf)_3$ (Yoon et al., 2008), cobalt(II) salen complex (Rajabi, 2009), sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl) ester (Niknam & Saberi, 2009), SO₃H-functionalized amorphous silica (Shimizu et al., 2004), and activated carbon supported sulfuric acid (Yang et al., 2008) were compared with those of the presented method (Table 3). The results show that $CMK-5-SO_3H$ is a powerful catalyst for the protection of alcohols. This may be attributed to the high surface area of the ordered nanostructure of CMK-5 and beneficial hydrophobicity of the catalyst 1 in the catalysis of the acetylation and tetrahydropyranylation reactions, especially under solvent-free condition.

In view of green chemistry, efficient recovery and reuse of catalysts are highly preferable. Overall, this methodology offers the advantages of the catalyst's recyclability enabling its use without further purification. Based on this concept, the reaction of benzyl alcohol with Ac₂O or DHP in the presence of catalyst 1 was studied. After the completion of the first run, ethyl acetate was added and the catalyst 1 was isolated from the reaction mixture by filtration. The recovered CMK-5-SO₃H was directly reused in ten successive runs with no significant decreases in its efficiency, providing high yields of the respective products in both reactions. Compared with the traditional methods using volatile solvents and non-recoverable catalysts which are energy consuming and environmentally malign, the easy recycling is an attractive property of catalyst 1.

98

40 150

Yang et al. $(2008)^g$

Conclusions

In conclusion, new efficient methods for the acetylation and tetrahydropyranylation of alcohols by highly recoverable CMK-5-SO₃H at ambient temperature and under solvent-free reaction conditions have been introduced. The present methods are quite general as a wide range of structurally varied alcohols and phenols underwent protection catalyzed by catalyst 1 to afford the corresponding esters and THP ethers in excellent yields. It is apparent that excellent catalytic capacity and outstanding stability of the catalyst, the exceedingly simple work-up, and ready reutilization of CMK-5-SO₃H ensure an efficient synthesis route. Thus, this method provides an efficient and environmentally benign alternative to the reported methods in terms of yield, reaction time, and work-up procedure. Efforts are currently underway in our research group to apply this hydrophobic ordered solid acid in the construction of potentially valuable organic molecules in H_2O as a green solvent.

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Supplementary data

Experimental procedures, TGA, BJH, and N_2 adsorption-desorption experiment results for CMK-5 and CMK-5-SO₃H, the spectra of some products, and general procedures for acetylation and tetrahydropyranylation of alcohols are available. Supplementary data associated with this article can be found in the online version of this paper (DOI: 10.2478/s11696-013-0369-x).

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