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Highly chemoselective acetalization of carbonyl compounds catalyzed by a novel recyclable ammonium triflate-functionalized silica

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Abstract

A novel ammonium triflate-functionalized silica ($NH_4^+OTf^-@SiO_2$, ATFS) has been prepared and characterized by simple operation from commercially available and relatively cheap starting materials. Various types of aldehydes as well as cyclic ketones were selectively converted to the corresponding 1,3-dioxanes in the presence of ethyl orthoformate, 1,3-propanediol and a catalytic amount of ATFS catalyst via an *in situ* acetal-exchange process. The catalyst can be recovered and reused for at least six reaction cycles without considerable loss of its reactivity.

Keywords: Solid acids; Acetalization; Protecting groups; Silica ammonium triflate; Carbonyl compounds; Interphase catalysts

1. Introduction

The protection of carbonyl compounds or diols as acetals is of paramount importance in organic synthesis, as shown by a large number of methods that have been developed for this key transformation [1–19]. Moreover, chiral acetals are particularly important precursor for the preparation of enantiomerically pure compounds [20]. The versatility of acetals requires the development of new improved and mild acetalization procedures, especially based on new selective acid catalysts [21–24]. On the other hand, many of the acid catalysts which have been explored for this transformation present limitations such as toxicity, corrosiveness, and tedious work-up procedure. However, ever-increasing environmental pressures have resulted in much attention being recently directed toward the development of environmentally friendly solid acid catalysts for clean processes in many of the fine chemical industries. Hence, various types of solid acids are receiving increased attention for various types of organic transformations due to their operational simplicity, selectivity coupled with the possibility of reusability [25–27]. A particularly interesting feature in this area is to design purely Lewis or purely Brønsted solid acids as well as those that have both characteristics and variable strength of acidity. Thus, a number of the silica-based solid acids such as HMS-supported zinc triflate [28], HMS-sulfonic acid [29], SBA-15-sulfonic acids [30], solid version of $AlCl_3$, BF_3, and SbF_3 [28], and MCM-type sulfonic acid [31] have been prepared. However, despite the importance and attractiveness of these solid acids less attention has been paid to the widespread application of these materials and also design and preparation of milder version of solid acids. Along the line of our studies in design and application of new solid catalysts in chemical transformation [32–42], we wish to introduce a new version of ammonium triflate-functionalized silica (ATFS) as a mild and recyclable Brønsted solid acid for chemoselective acetalization of carbonyl compounds.

2. Experimental

2.1. General remarks

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to isolated products unless otherwise stated. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. ^1H NMR and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ as the solvent and TMS as internal standard. Most

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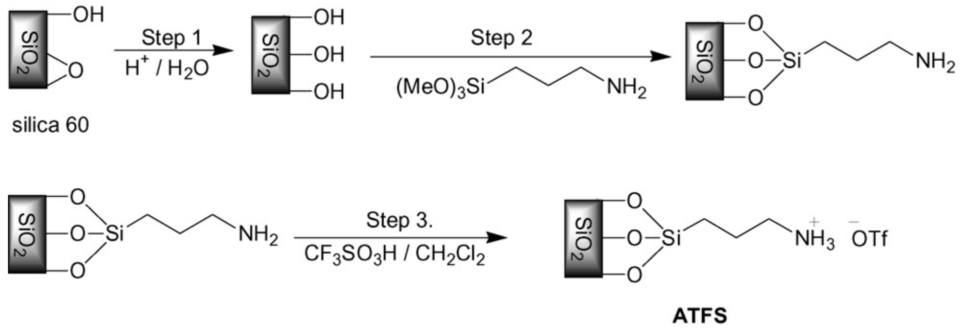


Scheme 1.

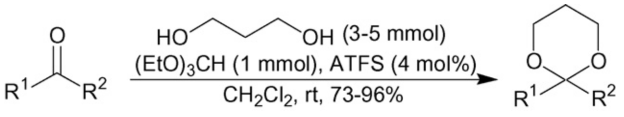
of the products are known and all of the isolated products gave satisfactory IR and NMR spectra.

2.1.1. *Preparation of ammonium triflate-functionalized silica (ATFS) catalyst*

Mesoporous silica gel (average pore diameter 60 Å) was activated by refluxing in concentrated hydrochloric acid (6 M) and then washed thoroughly with the deionized water and dried before undergoing chemical surface modification. Refluxing the activated silica gel (10 g) with 3-aminopropyltrimethoxysilane (3.3 mmol) in dry toluene for 18 h. The solid material was then filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhelet) and then dried in oven at 110 °C overnight to give the surface bound amine (AMPS) group at a loading *ca.* 0.31 mmol g^{-1} (by elemental analysis and back titration). The resulting AMPS were allowed to react with twofold excess of CF_3SO_3H in dry CH_2Cl_2 for 8 h and then filtered and washed successively with CH_2Cl_2, EtOH and Et_2O and then dried in a vacuum desiccator at 40 °C overnight to afford ATFS.

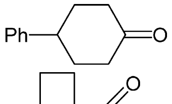
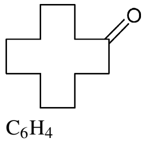
2.1.2. *General experimental procedure*

To a solution of the carbonyl compound (2 mmol), 1,3-propanediol (6–10 mmol) and $(EtO)_3CH$ (2.2 mmol), in anhydrous CH_2Cl_2 (50 mL), ATFS (0.08 mmol, 0.258 g) was added, and the resulting mixture was stirred at room temperature. After completion of the reaction (TLC or GC), the reaction mixture was filtered to a cold aqueous solution of NaOH (10%, 25 mL) and the filter cake was washed with CH_2Cl_2 and the catalyst was recovered. The organic phase was separated and washed with water (2 × 15 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave almost pure product(s). The organic solvent (CH_2Cl_2) was collected, distilled and used in the other experiments. Further purifica-



Scheme 2.

Table 1
Chemoselective acetalization of carbonyl compounds under mild conditions using ATFS in the presence of triethyl orthoformate (TEO) and 1,3-propanediol

Entry	R^1	R^2	Subst./diol/TEO/ATFS	Time (h)	Yield[a] (%)
1	Ph	H	1:3:1.1:0.04	12	89
2	4-(Cl)C_6H_4	H	1:3:1.1:0.04	16	90
3	4-(MeO)C_6H_4	H	1:3:1.1:0.04	8	90
4	4-(*i*-Pr)C_6H_4	H	1:3:1.1:0.04	5	89
5	4-(NO_2)C_6H_4	H	1:3:1.1:0.04	24	95
6	Citral (mixture)		1:5:1.1:0.04	24	90[b]
7	*n*-C_3H_7	H	1:3:1.1:0.04	15	84
8	*n*-C_6H_{13}	H	1:3:1.1:0.04	11	95
9			1:5:1.1:0.04	10	73
10			1:5:1.1:0.04	14	75
11	C_6H_4	CH_3	1:5:1.1:0.04	48	–[c]
12	$PhCH_2CH_2$	CH_3	1:5:1.1:0.04	48	–[c]
13	$CH_3CH{=}CH$	CH_3	1:5:1.1:0.04	48	–[c]
14	Cyclohexenone		1:5:1.1:0.04	48	–[d]

[a] Isolated yields.
[b] GC conversion.
[c] No reaction.
[d] Less than 25% conversion.