



Catalytic acetylation of alcohols, phenols, thiols and amines with zeolite H-FER under solventless conditions

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Zeolite H-FER catalyzes the acetylation of alcohols, phenols and thiols using acetic anhydride under solventless conditions in excellent yields. The catalyst can be reused without any loss of activity.

Introduction

Acetylation of alcohols and phenols, thiols and amino groups is a fundamental reaction in organic synthesis.¹ This reaction is generally carried out in the presence of bases such as triethylamine or pyridine along with 4-(dimethylamino)pyridine (DMAP) as co-catalyst.² Later, Vedejs *et al*³ reported tributylphosphine (Bu₃P) as a less basic catalyst for acetylation of alcohols. In addition to the above catalysts, protic acids such as *p*-toluenesulfonic acid⁴ and Nafion-H,⁵ Lewis acids such as ZnCl₂,⁶ CoCl₂,⁷ Sc(OTf)₃,⁸ Bi(OTf)₃,⁹ and MgBr₂¹⁰ are also known to catalyze the acetylation of alcohols and phenols. Montmorillonite K-10 and KSF clay¹¹ as heterogeneous catalysts have also been reported. Recently yttria-zirconia¹² based Lewis acid and NBS¹³ have been reported as acylating catalysts. Most of these reported acid catalysts use Ac₂O as the acetylating agent. They also suffer from certain drawbacks. The catalysts are rather expensive or moisture sensitive. Nevertheless, there is still a great demand for acid catalysts to generate esters under mild conditions.

The application of inorganic solid acids, especially zeolites, as effective heterogeneous catalysts for organic synthesis has received considerable attention in the recent decades due to their unique physical and chemical properties such as shape, selectivity, acidic and basic nature and their thermal stability.¹⁴ The advantages of these catalyst systems over homogeneous systems are well known, such as stability, ease of handling, lack of corrosion and other environmental hazards, ease of recovery and regeneration. Zeolites HSZ-360¹⁵ and H-ZSM-5¹⁶ have been reported for the acetylation of alcohols and phenols under solventless conditions.

Herein we report the acetylation of alcohols, phenols, thiols and amines using acetic anhydride in the presence of a catalytic amount of zeolite H-FER under solventless conditions in high yields, which can be reused without any loss of activity.

Results and discussions

As shown in Table 1, several alcohols, phenols and thiols underwent acetylation very smoothly in excellent yields. Under our reaction conditions chiral alcohols can be easily acetylated with complete retention of optical activity (entry 7) in high yields. The mildness of the present protocol is the key feature, which is evident in acetylation of alcohols containing acid sensitive groups such as acetal (entry 8) and tetrahydropyranyl

ether (entry 5), which survived under the reaction conditions. It was observed that primary allylic alcohol (entry 1) underwent smooth acetylation under the applied reaction conditions. An additional feature of the present reaction system is that it tolerates other acid sensitive functionalities such as C=C double and triple bonds (entries 1, 2 and 5, 6). Attempted acetylation of a tertiary alcohol (entry 9) however, gave the acetylated product in only 45% yield based on the recovery of the starting material. A minor amount (15%) of eliminated product was also obtained. This zeolite can be reused several times without any loss of activity, simply by filtering the catalyst, washing with acetone, drying and reusing immediately.

Conclusions

In conclusion, this protocol offers an efficient catalyst for acetylation of alcohols, phenols, thiols and amines with acetic anhydride under solventless conditions. All acetates were obtained in excellent yields under operationally simple experimental conditions. The catalyst can be reused without any loss of activity.

Experimental

The zeolite H-FER catalyst was synthesized according to the reported procedure.¹⁷ In a typical batch, 52.5 g of sodium

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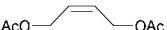
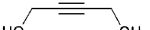
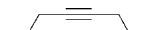



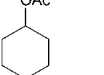


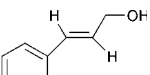
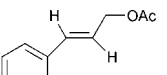
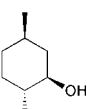
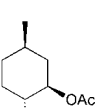
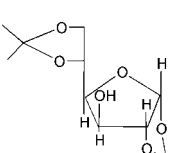
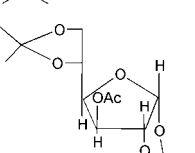

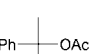

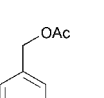

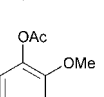

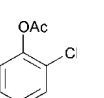

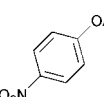

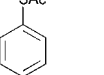

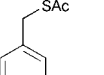

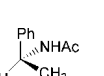

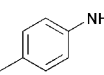
The acetylation of alcohols (and thiols) is an often used synthetic transformation, and can result in the generation of waste from the catalyst used to prepare the acetate. Aqueous washing not only precludes efficient recovery of the catalyst, but also allows the possibility of partial hydrolysis. This novel protocol relates to the use of a simple stable solid catalyst which can be easily recovered and reused, and which gives excellent conversions in a range of reactions.

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Table 1 Direct acetylation of alcohols, phenols, thiols and amines with acetic anhydride over Zeolite H-FER

$$\text{R-XH} \xrightarrow[\text{H-FER}]{\text{Ac}_2\text{O}} \text{R-XAc}$$

X = O or S or NH

Entry number	Reactant	Product	Reaction time/h	Isolated yield ^d (%)
1			2 ^a	98
2			2 ^a	98
3			2 ^a	98
4			2.5	97
5			2	91
6			2	94
7			2.5 ^b	94
8			2.5	85
9			6	45 ^e
10			1.5	99
11			2	95
12			5	94
13			5	99
14			5	91
15			5	94
16			2 ^c	99
17			2 ^c	99

^a 3 equivalents of acetic anhydride was used. ^b $[\alpha]_D -78.12^\circ$ ($c = 2$, C_6H_6). ^c Reaction carried out at room temperature. Other reactions were carried out at 75°C . ^d All products were identified by their IR, ^1H NMR, and mass spectra. ^e Based on recovery of the starting material.

silicate (in 25 ml of distilled water) was stirred with 10 ml pyrrolidine. To this solution, 2.4 g of aluminum sulfate hexadecahydrate (in 25 ml distilled water) and 1.8 g of sulfuric acid (in 10 ml distilled water) was added. Finally, 30 ml of distilled water was added and the gel (pH 11.5 ± 0.2) was stirred vigorously for 2 h and autoclaved in a 300 ml stainless steel Parr autoclave (4842, 300 ml) and heated at 160 °C for 60 h. The initial gel composition was: 20 Na₂O:Al₂O₃:37 pyrrolidine:66.5 SiO₂:6.3 H₂SO₄:1460 H₂O. The autoclave was quenched and the product filtered off, washed and dried at 100 °C for 6–8 h. The resulting material was calcined in air at 550 °C for 18–20 h and then exchanged with 1 M NH₄NO₃ solution three times, followed by calcination at 550 °C for 10 h to yield H-FER zeolite.

The catalyst was characterized by X-ray powder diffraction (Rigaku, D-Max III VC diffractometer with Cu-K α radiation, λ = 1.5404 Å) for its phase purity. The chemical composition of silica and alumina was established by a wavelength dispersive XRF (3070 Rigaku) spectrophotometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in flowing air (3 dm³ h⁻¹) at a heating rate of 10 °C min⁻¹ on an automatic TG/DTA (SETRAM 92). An Omnisorp 100 CX (COULTIER Corporation, USA) analyzer was used for the measurement of low-pressure nitrogen adsorption to determine the surface area. The Lewis and Bronsted acidity of the H-FER catalyst sample was determined by adsorbing CD₃CN on the catalyst wafer and then characterized by FTIR spectrometry (Nicolet Magne-550 FTIR).

To a mixture of acetic anhydride (15 mmol) and alcohol/thiol/amine (10 mmol), the catalyst (0.15 g) was added and the reaction mixture stirred at 75 °C for the length of time indicated in Table 1. After the completion of the reaction (monitored by TLC and GC), the reaction mixture was extracted with Et₂O and the catalyst filtered off. The filtrate was washed with water. The organic layer was then dried over anhydrous Na₂SO₄ and filtered. Evaporation of the solvent under reduced pressure followed by chromatography over silica gel using light petroleum–ethyl acetate as eluent furnished the corresponding acetate.

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