



Zeolite HSZ-360 as a New Reusable Catalyst for the Direct Acetylation of Alcohols and Phenols Under Solventless Conditions

Roberto Ballini^{*a}, Giovanna Bosica^a, Silvia Carloni^b,
Lara Ciaralli^a, Raimondo Maggi^b, Giovanni Sartori^{*b}

^a*Dipartimento di Scienze Chimiche dell'Università, Via S. Agostino 1, I-62032 Camerino (MC), Italy*

^b*Dipartimento di Chimica Organica e Industriale dell'Università, Viale delle Scienze, I-43100 Parma, Italy*

Received 20 March 1998; accepted 15 June 1998

Abstract: Alcohols and phenols were efficiently acylated with acetic anhydride without solvent over zeolite HSZ-360. The catalyst can be reused with no activity loss. © 1998 Elsevier Science Ltd. All rights reserved.

The acetylation of alcohols and phenols is a fundamental process in organic chemistry and provides a cheap and efficient means for protecting OH groups during oxidation, peptide coupling and glycosidation reactions.¹

A variety of procedures use transesterification methodology,² routinely performed under homogeneous catalysis with acetic acid or acetyl chloride and anhydride in the presence of a convenient basic (amine,³ DMAP,⁴ tributylphosphine⁵) or acidic (toluene-*p*-sulfonic acid,⁶ zinc chloride,⁷ cobalt chloride,⁸ scandium or lanthanide derivatives⁹) catalyst.

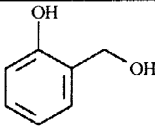
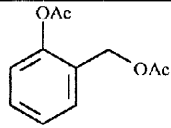
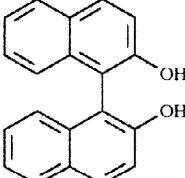
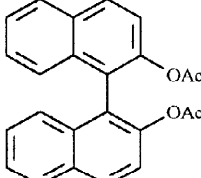
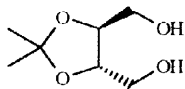
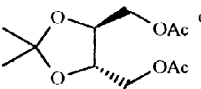
In recent years there has been a tremendous upsurge of interest in various chemical transformations performed under heterogeneous catalysis.¹⁰ Moreover, using inexpensive and non corrosive heterogeneous catalysts, chemical transformations occur with better efficiency, higher purity of the products, and easier work-up, with evident economic and ecological advantages especially for industrial processes.

Recently, montmorillonite has been reported as a remarkable acetylation catalyst.¹¹ Moreover, silica gel-supported sodium hydrogen sulfate has been used for the selective monoacetylation of unsymmetrical diols.¹² Although these methods produce good results, the use of harmful chlorinated solvents is required and the possibility of recycling the catalyst has not been reported.

In this communication we present an efficient, selective and solvent-free acetylation of alcohols and phenols over zeolite HSZ-360 as a reusable catalyst. HSZ-360 is a commercial HY zeolite (Tosoh Corp.) with the following physico-chemical parameters: surface area¹³ $500 \pm 10 \text{ m}^2/\text{g}$ and surface acidity¹⁴ $0.51 \pm 0.03 \text{ meq H}^+/\text{g}$.

The reaction was performed by heating at 60°C, for the selected time, a mixture of alcohol or phenol (10 mmol) with acetic anhydride (20 mmol) and the zeolite HSZ-360 (0.2 g) utilized without previous thermal

Table. Direct acetylation of alcohols and phenols with acetic anhydride over zeolite HSZ-360.

Entry	Substrate	Product ^a	Yield ^b (%)	Reaction time (h)
1-3	CH ₃ (CH ₂) _n CH ₂ OH	1: n=5	89	2.0
		2: n=9	88	2.0
		3: n=10	98	1.0
4	Benzyl alcohol	Benzyl acetate	84	1.0
5,6	R(CH ₂) ₂ CH ₂ OH	5: R=(CH ₃) ₂ CH	89	3.0
		6: R= <i>p</i> -O ₂ NC ₆ H ₄ CH ₂	100	2.0
7	9-Decen-1-ol	9-Decen-1-yl acetate	97	1.0
8	<i>cis</i> -9-Octadecenol	<i>cis</i> -9-Octadecenyl acetate	84	8.0
9	α -Naphthol	α -Naphthyl acetate	100	1.5
10	β -Naphthol	β -Naphthyl acetate	100	1.5
11	2,6-Dimethyl-4-heptanol	2,6-Dimethyl-4-heptyl acetate	100	2.0
12-14	RCH(OH)CHNO ₂ R'	12: R=H, R'=H	100	2.0
		13: R=Et, R'=Me	100	3.0
		14: R=Pr ^d , R'=CH ₃ (CH ₂) ₄	98	2.0
15	(-)-Menthol	(-)-Menthyl acetate ^c	100	1.0
16	Cinnamyl alcohol	Cinnamyl acetate	100	1.0
17			100	1.5
18			100	12
19			89	2.0
20	2-Methyl-3-butyn-2-ol	2-Methyl-3-butyn-2-yl acetate	98	1.0
21	Propargyl alcohol	Propargyl acetate	100	1.0

^a All products were identified by their IR and ¹H NMR spectra. ^b Isolated yield. ^c [α]_D -80°(c=2, C₆H₆)¹⁵. ^d [α]_D -25°(c=2, CHCl₃)

or chemical treatment. Good to high yields (80-100%) were observed in all cases. The present reaction tolerates other functionalities such as C-C double and triple bonds, nitro groups and ketals. In addition, allylic alcohols can be acetylated in high yield and selectivity (entry 16).

Of particular interest is the efficient acetylation of β -nitroalcohols (entries 12-14) which very often produce nitroolefins on treatment with acid.¹⁶

Under the present conditions chiral alcohols can be easily acetylated in high yields with complete retention of optical activity (entries 15 and 19). In addition, we found that zeolite HSZ-360 can be reused several times without loss of activity, simply by filtering the catalyst, washing with acetone, drying and immediately reusing. In fact, the acetylation of 2,6-dimethylheptan-4-ol (entry 11) has been repeated seven times, using the same catalyst with **respectably** high yields: 92-100%.

Zeolite HSZ-360 (with SiO₂/Al₂O₃ ratio 14.0 corresponding to moderately hydrophilic cages) shows good catalytic activity which is independent of the different polarities of the reactants (compare, for example, entries 1-3 and 19). Thus, it seems likely that almost all reagents utilised in the present study can reach the active sites of the catalyst surface (pore dimension 7.4 Å). As expected the bulkiness of the reagents represents a crucial factor in the present process: for example complete conversion of α - and β -naphthol to the corresponding acetate needs 1.5 hours (entries 9 and 10) whereas binaphthol takes 12 hours (entry 18). In this particular case the bulkiness of the reagent limits or completely inhibits its diffusion through the pores of the catalyst and the reaction probably occurs only on the external surface or on the external acidic sites. However binol acetate was obtained in 98% yield by carrying out the reaction at 100°C for 3 hours.

In a typical procedure the alcohol or phenol (10 mmol) and acetic anhydride (20 mmol) were placed in a two-necked flask with stirring. After 5 min zeolite HSZ-360 (0.2 g) was added and the mixture heated at 60 °C for the appropriate time (see Table 1). After cooling, the mixture was extracted with Et₂O and the catalyst filtered off. After evaporation of the solvent, the acetate could be purified by distillation or flash chromatography.

In conclusion, we have shown that an efficient acetylation of alcohols and phenols with acetic anhydride is promoted by zeolite HSZ-360. All acetates are obtained in high yields under simple experimental conditions. The catalyst can be reused without any loss of activity.

Acknowledgements

Financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Rome), the University of Camerino and the University of Parma (National Project "Stereoselezione in Sintesi Organica. Metodologie ed Applicazioni) is gratefully acknowledged.

References and notes

1. a) Rana, S.S.; Barlow, J.J.; Matta, K.L. *Tetrahedron Lett.*, **1981**, 22, 5007; b) Li, T.-S.; Li, Y.-L.; Liang, X.-T. *Steroids*, **1990**, 55, 263; c) Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*, Wiley, New York, 2nd ed., 1991; d) Kocienski, P.J. *Protecting Groups*, Thieme, Stuttgart, 1994.
2. a) Otega, J. *Chem. Rev.*, **1993**, 93, 1449; b) Loupy, A.; Petit, A.; Ramdani, M.; Yvanaeff, C.; Majdoub, M.; Labiad, B.; Villemin, D. *Can. J. Chem.*, **1993**, 71, 90; c) Ishii, Y.; Takena, M.; Kawasaki, Y.; Muromachi, A.; Nishiyama, Y.; Sakaguchi, S. *J. Org. Chem.*, **1996**, 61, 3088; d) Balaji, B.S.; Sasidharan, M.; Kumar, R.; Chanda, B. *Chem. Commun.*, **1996**, 707.

3. a) Zhdanov, R.I.; Zhenodarova, S.M. *Synthesis*, **1975**, 222; b) Horton, D. *Org. Synth.*, **1973**, 5, 1.
4. a) Hofle, G.; Steglich, V.; Vorbruggen, H. *Angew. Chem., Int. Ed. Engl.*, **1978**, 17, 569; b) Scriven, E.F.V. *Chem. Soc. Rev.*, **1983**, 12, 129.
5. Vedejs, E.; Diver, S.T. *J. Am. Chem. Soc.*, **1993**, 115, 3358.
6. Cope, A.C.; Herrick, E.C. *Org. Synth.*, **1963**, 4, 304.
7. Baker, R.H.; Bordwell, F.G. *Org. Synth.*, **1955**, 3, 141.
8. Iqbal, J.; Scrivastava, R.R. *J. Org. Chem.*, **1992**, 57, 2001.
9. a) Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.*, **1996**, 61, 4560; b) Barret, A.G.M.; Braddock, D.C. *J. Chem. Soc., Chem. Commun*, **1997**, 351.
10. a) Posner, G.H. *Angew. Chem., Int. Ed. Engl.*, **1978**, 17, 487; b) Bailey, D.C.; Langer, S.H. *Chem. Rev.*, **1981**, 81, 109; c) Laszlo, P. *Acc. Chem. Res.*, **1986**, 19, 121; d) Arienti, A.; Bigi, F.; Maggi, R.; Marzi, E.; Moggi, P.; Rastelli, M.; Sartori, G.; Tarantola, F. *Tetrahedron*, **1997**, 53, 3795; e) Arienti, A.; Bigi, F.; Maggi, R.; Moggi, P.; Rastelli, M.; Sartori, G.; Trerè, A. *J. Chem. Soc., Perkin Trans. 1*, **1997**, 1391; f) Bigi, F.; Carloni, S.; Maggi, R.; Muchetti, C.; Sartori, G. *J. Org. Chem*, **1997**, 62, 7024; g) Ballini, R.; Bosica, G. in *Recent Research Developments In Organic Chemistry*, Transworld Research Network, Trivandrum (India), 1997, vol.1, pag. 11.
11. Breton, G.W. *J. Org. Chem.*, **1997**, 62, 8952.
12. Li, A.-X.; Li, T.S.; Ding, T.-H. *Chem. Commun.*, **1997**, 1389.
13. Determined in our laboratory by B.E.T. method: Brunauer, S.; Emmett, P.H.; Teller, E. *J. Am. Chem. Soc.*, **1938**, 60, 309.
14. Determined in our laboratory by temperature programmed desorption of ammonia gas (NH₃-TPD): Berteau, P.; Delmon, B. *Catal. Today*, **1989**, 5, 121.
15. Aldrich catalogue, **1996-97**, pag. 953: $[\alpha]_D -81^\circ$ (c=8, C₆H₆).
16. a) Barret, A.G.W.; Grasboski, G.G. *Chem. Rev.*, **1986**, 86, 751; b) Kabalka, G.B.W.; Varma, R.S. *Org. Prep. Proc. Int.*, **1987**, 19, 283; c) Ballini, R.; Palestini, C. *Tetrahedron Lett.*, **1994**, 35, 5731; d) Ballini, R.; Bosica, G.; Schaafstra, R. *Liebigs Ann.*, **1994**, 1235; e) Perekalin, V.V.; Lipina, E.S.; Berestovitskaya, V.M.; Efremov, D.A. *Nitroalkenes, Conjugated Nitro Compounds*, Wiley, Chichester, 1994.