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Solvent Free Synthesis and Deprotection of 1,1-Diacetates Over a Commercially Available Zeolite Y as a Reusable Catalyst

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Abstract: Chemoselective synthesis and deprotection of 1,1-diacetates have been performed in good yields and in the absence of any solvent by zeolite HSZ-360 as a new reusable catalyst.

Selective protection and deprotection of carbonyl groups frequently represent essential steps in synthetic organic chemistry.[1] Acetals are the most common derivatives utilised to this aim. However, in many cases different strategies are desirable where selective protection of aldehydes in the presence of keto groups are requested. In this context 1,1-diacetates can be successfully utilised.[2]

A number of methods employed for the preparation of 1,1-diacetates from aldehydes includes the use of strong protic acids such as sulphuric acid, phosphoric acid and methanesulphonic acid[3] or Lewis acids such as zinc chloride, iron trichloride[4] and phosphorus trichloride.[5]

Although these methodologies can afford 1,1-diacetates in good yields, demanding reactions conditions required forebodes more widespread applications.

To this end different heterogeneous and environmentally friendly catalysts have been utilised. These include Nafion-H,[6] and tungstosilic acid,[7] β-, Y- and HZSM-5 zeolite,[8,9] sulfated zirconia[10] and expansive graphite;[11] moreover, montmorillonite clay[12] and expansive graphite[13] have been used to deprotect 1,1-diacetates. However, none of the above mentioned catalysts is claimed to give protection as well as deprotection of aldehydes (except expansive graphite[11,13]) and/or to be reusable. Moreover some of these require thermal activation (500-750°C) before use,[9,10] harmful chlorinated solvents[6,9,11] and/or demand inert atmosphere.[6,9]

In this communication we present a convenient solvent-free method for the synthesis and deprotection of 1,1-diacetates of aldehydes over the commercially available zeolite HSZ-360[14] (utilised without previous thermal or chemical treatment) as a chemoselective, reusable catalyst.

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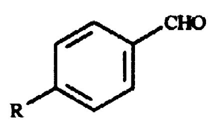
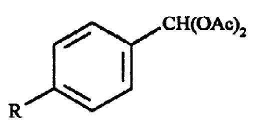
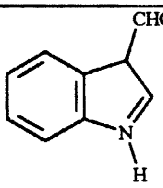
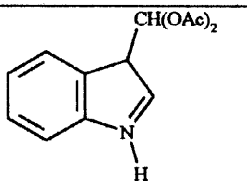
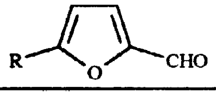
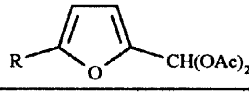
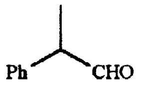
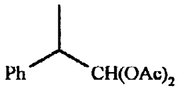
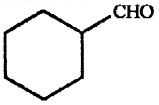
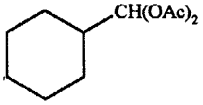
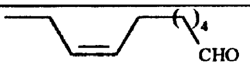
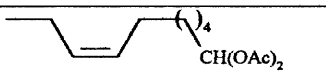
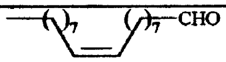
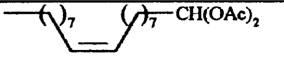
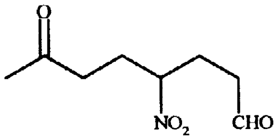
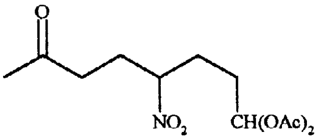
Table 1. Preparation of 1,1-diacetates from aldehydes.

Entry	Carbonyl compound 1	Product[a]	Yield (%)[b]	Reaction time (h)
1-6		 1: R = H 2: R = NO_2 3: R = Ph 4: R = Me 5: R = OMe 6: R = CN	90 94 85 97 98 93	3 7 5 3 1 7
7			92	4
8-9		 8: R = H 9: R = Me	90 85	1 6
10	CCl_3CHO	$CCl_3CH(OAc)_2$	96	3
11			90	8
12			88	7
13	$CH_3(CH_2)_{10}CHO$	$CH_3(CH_2)_{10}CH(OAc)_2$	97	4
14			85	5
15			90	7
16			80	5

[a] All 1,1-diacetates were identified by their IR and ^1H NMR spectra.
[b] Isolated yield.

The utility of zeolites as selective adsorbents and as catalysts for petrochemical processes has been known for many years.[15] More recently the use of these catalysts for fine chemicals preparation have received increasing attention due to their characteristic properties such as shape selectivity, thermal stability, acidic and basic nature.[16]

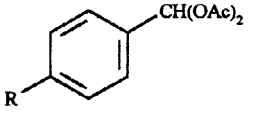
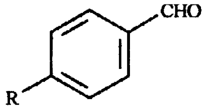
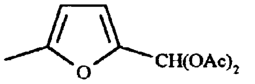
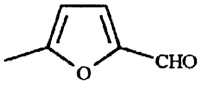
Results summarised in Table 1 show that good to high yields (85-98%) were obtained in short reaction times (1-8 h); other functionalities such as nitro, ether, cyano, furyl and *(Z)*-double bond were preserved (Table 1, entries 2, 5, 6, 8-9 and 14-15 respectively).

As underlined in the introduction of this communication, it is very important to selectively protect the aldehydic moiety in the presence of a ketonic carbonyl group. To this end we firstly reacted an equimolecular mixture of acetophenone and benzaldehyde with a three fold excess of acetic anhydride in the presence of zeolite HSZ-360. We isolated the benzaldehyde 1,1-diacetate (90% yield) and we recovered the unchanged ketonic compound. On the basis of this result we synthesised the 4-nitro-7-oxooctanal[17] and we submitted this ketoaldehyde to the model protection reaction; as expected the ketonic moiety was preserved and only the aldehydic carbonyl group was converted in the corresponding 1,1-diacetate in 80% yield (Table1, entry 16).

A typical procedure for the preparation of 1,1-diacetates is as follows: the aldehyde (10 mmol) and acetic anhydride (30 mmol) were placed in a two-necked flask with stirring at rt. After 5 min zeolite HSZ-360 (200 mg) was added and the obtained mixture was maintained at rt (only for entries 2, 9 and 11 a temperature of 70°C was needed) for the appropriate time (see Table 1). The mixture was then extracted with Et_2O and the catalyst was filtered off. After evaporation of the solvent the obtained 1,1-diacetates, if necessary, can be purified by flash chromatography (hexane-ethyl acetate 5-20%).

We next investigated the ability of the catalyst to regenerate the aldehydes from 1,1-diacetates and we found that microwave irradiation (500 W in a domestic microwave oven) of a mixture of 1,1-diacetate/zeolite HSZ-360 (1:1 w/w), for 20 min, provides the clean regeneration of the corresponding aldehydes in high yields (86-99%, see Table 2).

Table 2. Regeneration of aldehydes from 1,1-diacetates.

Entry	Substrate	Aldehyde[a]	Yield (%)[b]
1-5		 1: R = Ph 2: R = NO_2 3: R = OMe 4: R = Me 5: R = H	99 93 94 86 94
6	$CH_3(CH_2)_{10}CH(OAc)_2$	$CH_3(CH_2)_{10}CHO$	88
7			95

[a] All aldehydes were identified by comparison with authentic samples.
[b] Isolated yield.

A typical procedure for the regeneration of aldehydes from 1,1-diacetates is as follows: 0.5 g of 1,1-diacetate and 0.5 g of zeolite HSZ-360 were placed, at 500 W, in a domestic microwave oven, for 20 min. After cooling, the mixture was extracted with Et_2O and the catalyst was filtered off. Evaporation of the solvent followed by flash chromatography of the mixture produce the pure aldehyde.

Finally we turned our attention toward the possible recycling of the catalyst and as representative example we choose the conversion of dodecanal into its 1,1-diacetate (Table 1, entry 13) and the regeneration of the starting aldheyde (Table 2, entry 6). The first process has been repeated six times, through the same catalyst, with the following yields: 98%, 97%, 98%, 90%, 92% and 93%, while the regeneration of the dodecanal from the corresponding 1,1-diacetate was performed, for the first two trials, in good yields (87-88%), after which the catalyst was essentially inactive; probably the microwave irradiation promotes modification of the catalyst framework responsible for the gradual loss of activity.[18]

In conclusion in this paper we have shown a zeolite promoted protection of aldehydes as 1,1-diacetates and the regeneration of the starting aldehydes. The processes are performed under solventless conditions and the catalyst can be reused several times for the production of 1,1-diacetates.

Acknowledgements

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14) HSZ-360 is a commercial HY zeolite (Tosoh Corporation) with the following physico-chemical parameters: surface area 500±10 m^2/g (determined in our laboratory by B. E. T. method: Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60,* 309), surface acidity 0.51±0.03 meq H^+/g (determined in our laboratory by temperature programmed desorption of ammonia gas (NH_3-TPD): Berteau, P.; Delmon, B. *Catal. Today* **1989**, *5,* 121), SiO_2/Al_2O_3 ratio 14.0 and pore dimension 7.4 Å.
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18) Studies are in progress in our laboratories to regognize the change of crystallinity, surface area, surface acidity and pore dimension of the zeolite HSZ-360 upon microwave irradiation.