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1,3-Dioxolanes from Carbonyl Compounds over Zeolite HSZ-360 as a Reusable, Heterogeneous Catalyst

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Abstract: Carbonyl compounds are converted, in good yields, into their 1,3-dioxolanes over zeolite HSZ-360, as a new reusable catalyst. Good chemoselectivity is also observed. © 1998 Elsevier Science Ltd. All rights reserved.

The carbonyl group is one of the most versatile functional groups in organic chemistry and a great deal of synthetic work has been done on the protection and masking of the carbonyl compounds. 1,3-Dioxolanes are the most frequently used protecting groups for this purpose.¹ The most convenient and practical methods for their syntheses are to react carbonyl compounds with ethylene glycol, in the presence of an appropriate catalyst, with removal of water formed. *p*-Toluenesulfonic acid² and pyridinium salts,³ are usually utilized as acidic catalyst.

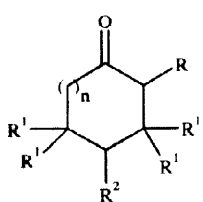
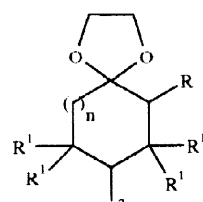
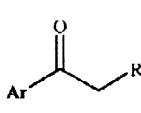
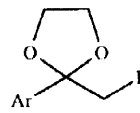
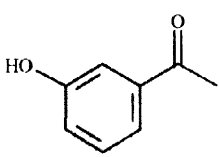
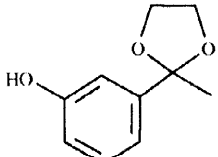
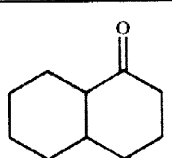
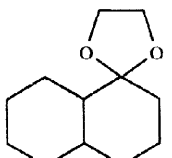
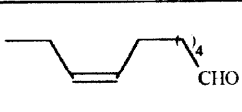
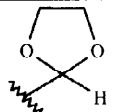
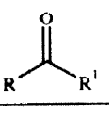
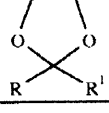
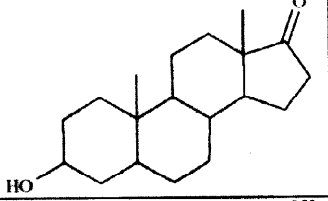
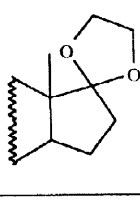
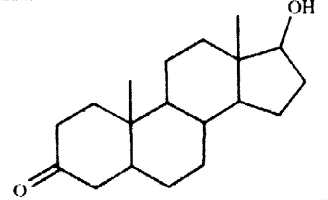
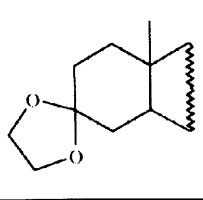
Environmental and economical considerations prompt an urgent need to redesign commercially important processes. In this context, heterogeneous catalysts play a dramatic role;⁴ in fact, the advantages of these catalysts are (i) the easy work-up (separation of the catalyst simply by filtration), (ii) the high purity of the products, (iii) and the possibility of recycling catalysts, as well as avoiding the use of noxious substances.

Different heterogeneous catalysts such as molecular sieves,^{5a} montmorillonite,^{5d,e} sulfated zirconia,^{5g} and envirocat EPZG,^{5h} have been employed for the acetalization of carbonyl compounds and, in particular, alumina/KSF,^{5h} natural kaolinitic clay,^{5f} and Y zeolite,^{5c} have been proposed for the preparation of 1,3-dioxolanes. However, just one of these^{5h} is reported as a reusable catalyst.

In this communication we present the preparation of 1,3-dioxolanes **2** over zeolite HSZ 360 as a very efficient, chemoselective reusable catalyst. HSZ-360 is a commercial HY zeolite (Tosoh Corp.) with the following physico-chemical parameters: surface area⁶ 500±10 m²/g, surface acidity⁷ 0.51±0.03 meq H⁺/g, SiO₂/Al₂O₃ ratio 14.0 and pore dimension 7.4Å. Our procedure is performed by refluxing the mixture of the carbonyl compound (10 mmol), the selected diol (11 mmol) and toluene (30 ml) in the presence of 0.2 g of zeolite HSZ-360 (utilized without previous thermal or chemical treatment) for the selected reaction time, with azeotropic removal of

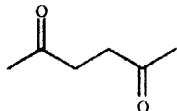
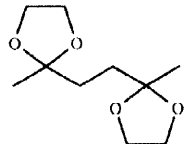
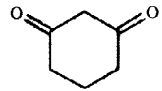
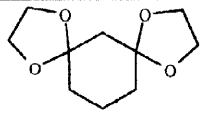
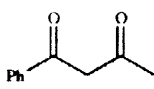
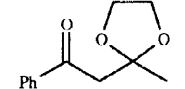
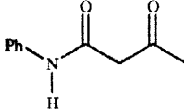
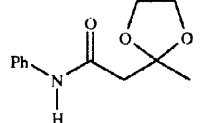
water. The 1,3-dioxolanes were purified by distillation or by flash chromatography over silica gel (0.040-0.063 mm) and fully characterized.

Table 1. Acetalization of carbonyl compounds **1** with ethylene glycol.

Entry	Carbonyl compound 1	Product 2	Yield (%)	Reaction time (h)	
a-h			n=1 a: R,R ¹ ,R ² =H	100	3
			b: R=Me, R ¹ ,R ² =H	94	4
			c: R,R ¹ =H,R ² =Me	82	6
			d: R,R ¹ =H,R ² =Ph	90	1.5
			e: R,R ¹ =H,R ² =Bu ^t	92	4
			f: R,R ² =H,R ¹ =Me	91	3
		n=2 g: R,R ¹ ,R ² =H	75	7	
		n=3 h: R=SO ₂ Ph,R ¹ ,R ² =H	88	9	
i-m			i: Ar=Ph,R=H	97	4
			j: Ar=Ph,R=Br	60	4
			k: Ar= <i>p</i> -MeOC ₆ H ₄ ,R=H	89	1.5
			l: Ar= <i>p</i> -NO ₂ C ₆ H ₄ ,R=H	100	1
			m: Ar= <i>p</i> -CNC ₆ H ₄ ,R=H	100	5
n			88	11	
o			86	10	
p			100	4	
q,r			q: R,R ¹ =PhCH ₂	95	5
			r: R=Me,R ¹ =(CH ₂) ₂ CH=CH	100	8
s			97	10	
t			80	12	

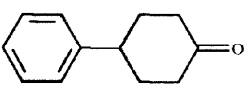
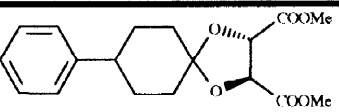
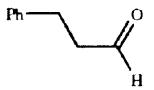
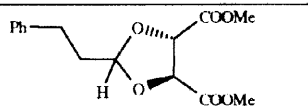
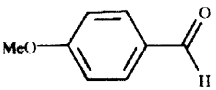
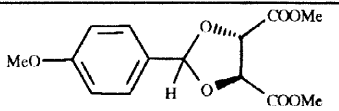
Good to high yields were obtained in all cases and, as summarized in Table 1, other functionalities such as phenolic and alcoholic hydroxy groups, (*Z*)-double bond, cyano, nitro, ether, bromide, and sulphone were preserved under these conditions. When 1,4- and 1,3-diketones **3u,v** were used as starting materials, double 1,3-dioxolanes **4u,v** were obtained, while with high enolizable starting compounds (**3w,x**) the mono 1,3-dioxolane **4w,x** were obtained in moderate yield (Table 2).

Table 2. Acetalization of dicarbonyl compound **3** with ethylene glycol.

Entry	Dicarbonyl compound 3	Product 4	Yield (%)	Reaction time (h)
u			100	8
v			100	8
w			15	8
x			20	8

In order to amplify the utility of the present procedure we sought to synthesize chiral derivatives **5** by reaction of carbonyl compounds **1d,y,z** (10 mmol) with *R,R*-dimethyltartrate (50 mmol). The resultant acetalization proceeded in good yield to give products **5d,y,z** with complete retention of optical activity (Table 3).

Table 3. Acetalization of carbonyl compound **1** with *R,R*-dimethyltartrate.

Entry	Carbonyl compound 1	Product 5	$[\alpha]_D^{25}$ (<i>c</i> =3, MeOH)	Yield (%)	Reaction time (h)
d			-5.7°	95	5
y			-32.1°	92	3
z			-33.5° ^a	85	4

In addition, we found that zeolite HSZ 360 could be reused different times without loss of the activity, simple by filtering the catalyst, washing with acetone, drying at rt and immediately reusing. In fact, the conversion of acetophenone into its 1,3-dioxolane (**1i** to **2i**) has been repeated five times, through the same catalyst, with the following yields: 97%, 94%, 95%, 93% and 94%.

Finally, we tried the regeneration of the carbonyl group, directly from the reaction mixture obtained after the acetalization, by addition of water (15 ml) and heating at 100 °C for 15 h the resulting mixture. As representative examples we chose the acetals **2a,j** which were quantitatively converted into the starting cyclohexanone **1a** and α -bromo acetophenone **1j**.

Concerning the role of the catalyst, it is well stated that reactions on zeolites generally involve previous adsorption and diffusion of reactants through the pores and channels. However in the present liquid phase reaction the acid sites on the external surface of the catalyst could play a crucial role in the activation of reactant molecules particularly with large and bulky compounds such as **1s** and **1t**. In fact under these conditions the pores (7.4Å) are completely filled with solvent as well as reactant and product molecules and the curvature effects on the external surface of the zeolite catalyst are likely to promote reagents activation and process selectivity.⁹

In conclusion, we have shown the synthesis of 1,3-dioxolanes in a new and efficient way using an economical and reusable catalyst which can be used without activation. Moreover, our procedure if compared with the previously reported methods for the preparation of title compounds,^{5b,c,f} generally, affords better yields.

Acknowledgements

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