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## Facile Acylation of Alcohols Using Esters and Silica Gel-supported Metallic Sulphates and Hydrogen Sulphates

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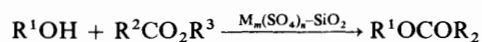
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Alcohols are acylated in a quite simple operation in high yields by being heated in esters in the presence of silica gel-supported metallic sulphates and hydrogen sulphates, such as  $\text{Ce}(\text{SO}_4)_2$ ,  $\text{Ti}(\text{SO}_4)_2$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{NaHSO}_4$ .

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Reactions using reagents or reactants on insoluble inorganic supports are often much easier to perform than their homogeneous counterparts.<sup>1,2</sup> In the course of studying dehydration of alcohols catalyzed by metallic sulphates or hydrogen sulphates supported on silica gel [abbreviation;  $\text{M}_m(\text{SO}_4)_n$ -

$\text{SiO}_2$ ],<sup>3</sup> we found alcohols were acylated when esters were used as solvents.



**Table.** Acylation of various alcohols by an ester and  $M_m(\text{SO}_4)_n\text{-SiO}_2$ .<sup>a</sup>

Alcohol	Ester	$M_m(\text{SO}_4)_n$	Time (h)	Yield (%)
Dodecan-1-ol	Ethyl formate	$\text{Ce}(\text{SO}_4)_2$	1	100
Octan-2-ol	Ethyl formate	$\text{Ce}(\text{SO}_4)_2$	0.5	91
Octan-2-ol <sup>b</sup>	Ethyl formate	$\text{Ce}(\text{SO}_4)_2$	24	90
Dodecan-1-ol	Ethyl acetate	$\text{Ce}(\text{SO}_4)_2$	0.25	97
Dodecan-1-ol <sup>c,d</sup>	Ethyl acetate	$\text{Ce}(\text{SO}_4)_2$	1	91
2-Methylbutan-1-ol	Ethyl acetate	$\text{NaHSO}_4$	1	99
Butane-1,4-diol <sup>e</sup>	Ethyl acetate	$\text{Fe}_2(\text{SO}_4)_3$	8	98
Dodecan-1-ol	Methyl propionate	$\text{Ce}(\text{SO}_4)_2$	1	98
Dodecan-1-ol	Methyl isobutyrate	$\text{Ce}(\text{SO}_4)_2$	1	99
Dodecan-1-ol <sup>d,f</sup>	Phenyl acetate	$\text{Ce}(\text{SO}_4)_2$	2	98
<i>p</i> -Methoxyphenol <sup>c,d</sup>	Methyl benzoate	$\text{Fe}_2(\text{SO}_4)_3$	3	97

<sup>a</sup>An alcohol (1 mmol) and a sulphate or a hydrogen sulphate (1 mmol) supported on silica gel (0.33 g) were heated in a refluxing ester (10 ml). Yields are isolated yields. <sup>b</sup>This reaction was carried out at room temperature. <sup>c</sup>The alcohol (1 mmol), the catalyst (0.5 mmol), and the ester (10 mmol) were heated in  $\text{CCl}_4$  (10 ml). <sup>d</sup>Yields were determined by g.l.c. using an internal standard. <sup>e</sup>The diol (1 mmol) and the catalyst (0.5 mmol) were heated in the refluxing solvent (15 ml). The product was diacetate. <sup>f</sup>Reaction temperature was 120 °C.

The catalysts were easily prepared by the previously reported method.<sup>3</sup> The procedure of the transesterification reaction was quite straightforward. Heating a primary alcohol and a catalyst in a refluxing ester (serving as both reagent and solvent), filtering the solution to remove the catalyst, and evaporating the solvent gave a product which was pure by g.l.c., <sup>1</sup>H NMR and IR analysis when the boiling point of the solvent was not high. Fractional distillation or column chromatography was needed to remove the solvent completely when methyl benzoate or phenyl acetate was used as the solvent. The product yields suggest that equilibrium was established in the reaction

mixtures when  $\text{CCl}_4$  was used as a solvent. The results are summarized in the Table. A small amount of alcohol was sometimes recovered by washing the separated catalysts with ethanol even when no alcohols were detected in the reaction solution. This suggests that small amounts of polar by-products, if formed, would remain on the catalysts. The catalytic activity of many metallic sulphates and hydrogen sulphates was examined in the acetylation of dodecan-1-ol by ethyl acetate and  $\text{Ce}(\text{SO}_4)_2$ ,  $\text{Ti}(\text{SO}_4)_2$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{NaHSO}_4\text{-SiO}_2$  were found to be most active. The activity of  $\text{Fe}_2(\text{SO}_4)_3$  was reduced considerably when it was not supported. Primary alcohols, including diols, were acylated by various esters in high yields. Secondary alcohols underwent formylation effectively in the reaction with ethyl formate, but also yielded olefins on acetylation by ethyl acetate. The formylation of octan-2-ol by ethyl formate proceeded even at room temperature. As the anhydride and the acid chloride of formic acid are unstable, this method may be especially useful for formylation. Phenols having an electron donating substituent were acetylated by phenyl acetate in high yields in  $\text{CCl}_4$ , although they were not acetylated by ethyl acetate.

## References

- 1 'Preparative Chemistry Using Supported Reagents,' ed. P. Laszlo, Academic Press, New York, 1987.
- 2 Although alumina is not a supported reagent, see the following references describing transesterification catalysed by alumina and citing references concerning transesterification catalysed by acids and bases: (a) G. H. Posner, S. S. Okada, K. A. Babiak, K. Miura, and K. Rose, *Synthesis*, 1981, 789; (b) G. H. Posner and M. Okada, *Tetrahedron Lett.*, 1981, 22, 5003.
- 3 T. Nishiguchi and C. Kamio, *J. Chem. Soc., Perkin Trans. 1*, 1989, 707.

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