SHORT PAPER

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Zn mediated transesterification of β-ketoesters†

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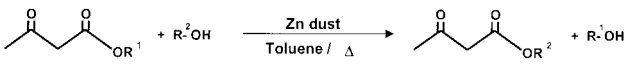
Methyl/ethyl β-ketoesters when treated with various alcohols along with catalytic amount of Zn dust in refluxing toluene undergo smooth transesterification.

Keywords: Zn mediated transesterification, β-ketoesters

Transesterification, one of the most effective methods for ester synthesis is usually conducted under acidic or basic conditions. Although quite a few methods have been reported for transesterification, they are not general as far as β-ketoesters are concerned. Normal reactions of transesterification are equilibrium driven reactions where the use of excess of one of the reactents is mandatory to obtain good yields. The reported methods include use of reagents as DMAP,[1a,b] t-butyl acetoacetate[2], tetrabutyl distannoxanes,[3,4] solid super acids like sulfated SnO_2[5] to effect transesterification. Some of these methods[1a,b] use toxic and expensive reagents and in relatively large amounts. The *t*-butyl acetoacetate method is restricted to *t*-butyl esters, thus lacking generality. It was therefore felt necessary to develop a suitable methodology for interconversion of readily available esters by transesterification. We wish to report Zn dust as a novel and efficient catalyst for transesterification of β-ketoesters (Scheme 1).



Scheme 1

Various β-ketoesters were prepared by treating methyl/ethyl β-ketoester with equivalent amount of alcohol (primary, secondary, tertiary, benzylic, allylic) in the presence of catalytic amount of Zn dust in refluxing toluene with a distillation condenser to remove methanol/ethanol. The effectiveness of protocol is self explained by its selectivity towards β-ketoesters whereas normal esters found to be unreactive. Another important point to note is that *t*-butanol, which is also rather unreactive, gave a good result yielding *t*-butyl ester in moderate yield. The protocol also allows the use of the allylic alcohols for transesterification which is in contrast to the reported method[1b] where the presence of molecular sieves in large excess in addition to stoichiometric amounts of DMAP is required for effective exchange.

In conclusion we have demonstrated that Zn dust is an efficient, inexpensive and a general catalyst to effect transesterification. The superiority and flexibility of the methodology lies in the ease of operation coupled with simplicity in the workup which involves mere filtration of Zn dust followed by evaporation of the solvent.

Typical procedure: β-Ketoester (5 mmol), alcohol (5 mmol), Zn dust (100 mg) in toluene (20 ml) was heated to 110°C in a round bottom flask with distillation condenser to remove methanol /ethanol.After completion (TLC) the reaction mixture was cooled, filtered and filtrate was concentrated and chromatographed on SiO_2 (hexane-ethyl acetate, 9:1) to afford ester, a colourless viscous liquid in excellent yield.

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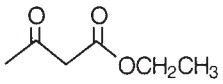
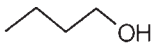
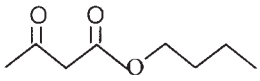
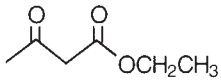
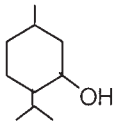
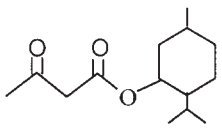
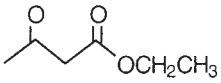
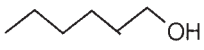
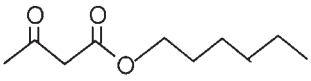
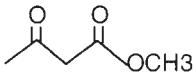
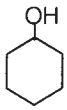
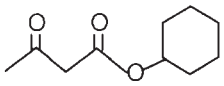
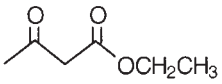
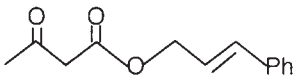
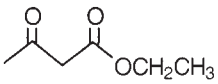
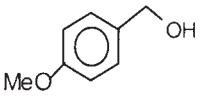
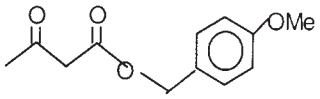
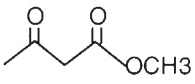
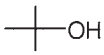
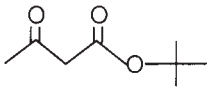
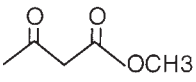
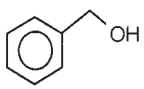
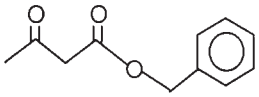
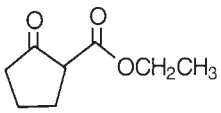
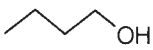
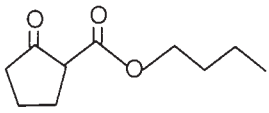
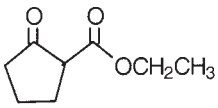
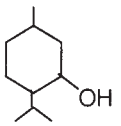
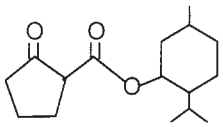
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Zn mediated transesterification of β-ketoesters

Entry	β-ketoester	Alcohol	Time/h	Product	Yield/%[a,b]
1			2		98
2			2.5		88
3			2		94
4			3		88
5			2		63
6			2		82
7			8		52
8			2		85
9			2.5		76
10			3.5		83

[a]Yields are of isolated pure products. [b]Products are characterised by their IR, ^{1}H NMR and comparison with authentic samples.