Pergamon

Tetrahedron Letters, Vol. 37, No. 2, pp. 233-236, 1996
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0040-4039/96 $15.00 + 0.00

0040-4039(95)02136-1

Use of Solid Superacid (Sulphated SnO_2) as Efficient Catalyst in Facile Transesterification of Ketoesters+

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Abstract : *Facile one to one transesterification of ketoesters catalysed by solid superacid (sulphated* SnO_2*) is described.*

Pioneering contributions by Prof. Olah[1] in the area of superacids have opened up new vistas for physical organic as well as synthetic chemists alike. Although enough information on liquid superacids is available in literature, solid superacids remain relatively unexplored and unexploited.

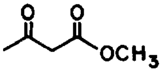
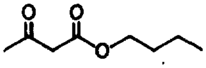
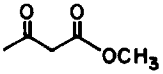
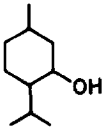
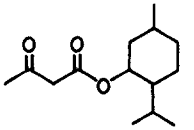
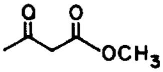
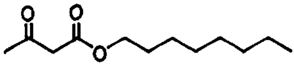
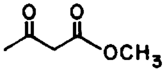
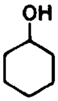
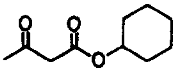
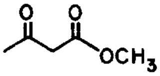
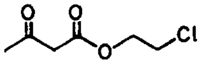
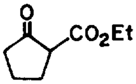
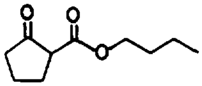
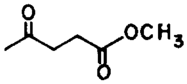
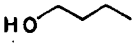
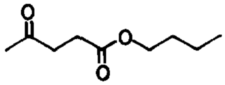
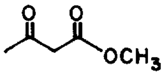
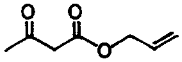
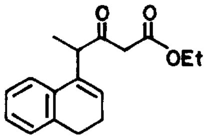
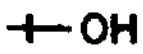
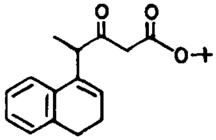
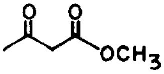
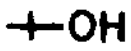
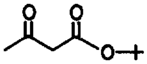
Ketoesters serve as important synthons by virtue of the ease with which they can be transformed to chiral building blocks by chemical and enzymatic transformations as well as a tool for chain extension reactions. As a consequence of their importance their interconversion to different esters has received considerable attention.[2a,b.]

In connection with our programme on the synthesis of biologically active compounds viz. podophyllotoxin, we wanted to effect transesterification of ß-ketoester 1 to 2 (Scheme 1).

Scheme 1

Although quite a few methods are reported for transesterification, they are not general as far as ß-ketoesters are concerned. Normal methods of transesterification of ß-ketoesters are equilibrium driven reactions where usage of excess of one of the reactants is mandatory to obtain good yields. Recently, DMAP catalysed transesterification of ß-ketoesters with good to excellent yields has been reported[3a]. However, this method makes use of toxic and expensive DMAP in relatively large amounts (30 mol %) in addition to excess usage of ß-ketoester and the reaction is performed at elevated temperatures for extended period of time. Another recent publication[4] describes an efficient method of transesterification employing commercially available tertiary butyl acetoacetate. Although efficient, this method is restricted to tertiary butyl esters thus lacking generality. Otera et al[5,6.] have shown that ketoesters can be smoothly transesterified by tetrabutlydis-

Table-1

Entry	β Keto ester	Alcohol	Rx Time, hr	Product	% Yield
1			6		97
2			6		91
3			7		89
4			7		84
5			6		92
6			7		63
7			10		45
8			8		65
9			8		50
10			12		50

tannoxanes as the catalyst under mild conditions.

It was, therefore, felt necessary to develop a suitable methodology for interconversion of readily available esters by transesterification.

The Bronsted and Lewis acidity of the metal oxides can be modified by treatment with acids thereby making them solid superacids.[7] We have recently prepared and characterised sulphated tin oxide as solid superacid and have shown its potential as gas sensors (3-60) at ppm level for hydrocarbons, NH_3 and ethanol.[8]

Although solid superacids have been widely employed in petrochemical industries, their potential by synthetic organic chemists remains unexplored. This communication describes the facile interconversion of ß-ketoesters catalysis by a solid superacids *viz.* Sulphated SnO_2.Sulphated SnO_2 can be conveniently prepared from stannous chloride. When methyl ß-ketoesters were treated with an equivalent amount of alcohol (primary, secondary as well as chiral) in the presence of sulphated SnO_2 (10 mol%), under reflux of toluene, with distillation to remove methanol, the corresponding esters were obtained in good to excellent yields (Table 1). This method offers obvious advantages over the existing methods, especially when ß-ketoesters and alcohols are expensive. At this temperature a very small amount of toluene is collected alongwith liberated methanol/ethanol and there is no need to add additional toluene.

Our protocol allows the use of allyl alcohols for transesterification. This may be contrasted with the earlier reported procedure[3b] where presence of molecular sieves in large excess in addition to stoichiometric amounts of DMAP is mandatory for effective exchange. Another most important point that demonstrates the generality and superiority of our method is that even tertiary butyl esters can be prepared employing solid superacid. This may be compared with earlier reported procedures where tertiary butyl esters are not accessible.

The effectiveness of our protocol is manifested in its selectivity towards ß&γ-ketoesters whereas normal esters are found to be unreactive.Transesterification of ketoesters (entry 7,table-1) in addition to efficient transformation of ketoester suggests that the role of a carbonyl group in enhancing the reactivity of the ester by chelation with the metal oxide is crucial for the success of the reaction.

In conclusion, we have demonstrated that solid superacids such as sulphated SnO_2 serve as an efficient, convenient and a general catalyst to effect transesterification. The superiority and flexibility of our method over the existing methods, coupled with the ease of operation and the simplicity in the workup which involves mere filtration of the catalyst which can be recycled and reused, should find widespread application in transesterification of many ketoesters.

We are currently engaged in exploring the reactivity of other materials which include clays, resins and zeolites to effect similar transformations.

Procedure for the preparation of catalyst: 22.56 g of stannous chloride was dissolved in 200 ml deionised water to get a clear solution. 25 ml of aqueous ammonium hydroxide was added to this solution with stirring until pH 8. The yellowish precipitate thus obtained was washed well with deionised water, dried at 110^0 for 12 hours to get stannous hydroxide (18 gms). 5 g of the dry hydroxide powder was then equilibrated with 25 ml of 2N H_2SO_4 for 2 hour and then it was evaporated to dryness, calcinated at 500^0 for 4 hour to get the catalyst.

General Procedure for transesterification: A mixture of ketoester (1 eq), alcohol (1 eq), and catalyst (100 mg, 10% by weight) in toluene (20 ml) was heated to 110°C in a two-necked round bottomed flask provided with a distillation condenser to remove methanol. The reaction was monitored by T.L.C. After completion of the reaction (ca. 6 h), the catalyst was filtered and the filtrate was concentrated and chromatographed on SiO_2. (95:5 pet-ether : ethyl acetate) to afford the ester as a viscous colourless liquid in excellent yields.

Acknowledgement: Financial assistance to SWD and AK by CSIR, India is gratefully acknowledged. We thank Prof. B.D. Tilak for his constant support and encouragement.

References & Notes

+NCL Communication No.6310

#Presented at the International Conference on Organic Synthesis (IUPAC), Bangalore, India.; Dec. 11-16, 1994

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(*Received in UK* 20 *September* 1995; *revised* 7 *November* 1995; *accepted* 10 *November* 1995)