



## Facile Deprotection of Allyl Esters Mediated by Solid Superacid (Sulphated $\text{SnO}_2$ )<sup>+</sup> #

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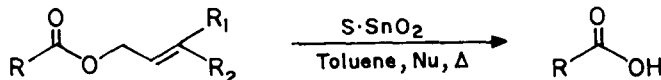


*Abstract : Facile deprotection of allyl esters in the presence of sulphated  $\text{SnO}_2$  is described.*

Selective protection and deprotection of functional groups is of prime importance in synthetic organic chemistry. We have been engaged in working towards development of new methodologies towards this.<sup>1</sup> Esters are no exception to this. This is evident by recent publications devoted towards development of this methodology.<sup>2,3,4</sup> Allyl esters serve as important protecting groups of esters by virtue of their stability and ease with which they can be obtained by the reaction of the corresponding alcohols with acid chloride or alkylation of the acid with the corresponding allyl halide under base catalysed conditions.

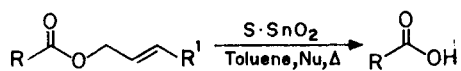
In fact, recent publications describing the methodologies developed for deprotection of allyl esters include treatment with formic acid at elevated temperatures<sup>2</sup>, palladium catalysed deprotection<sup>3</sup>, treatment with excess iodine.<sup>4</sup> Earlier, a two step protocol for deprotection of cinnamyl esters has been described by Corey.<sup>5</sup>


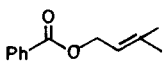
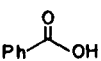
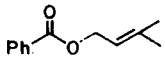
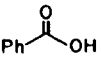
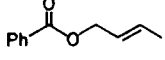
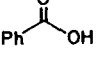
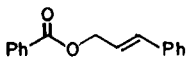
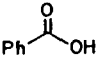
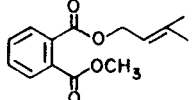
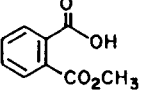
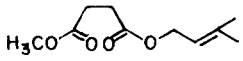
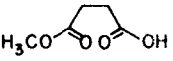
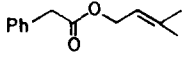
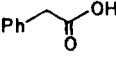
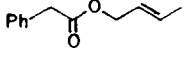
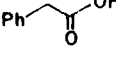
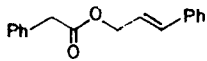
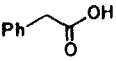
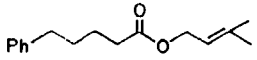
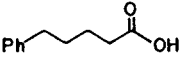
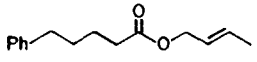
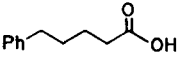
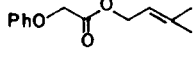
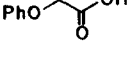
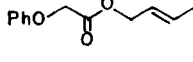
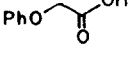
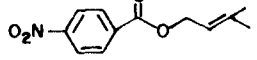
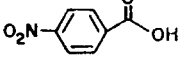
Recent publications describing the deprotection of allyl esters prompt us to disclose our findings in this area.



Although solid superacids have been widely employed in the petroleum industry, their usage in effecting organic transformations has been almost non-existent. In continuation of our search for non-polluting and environmentally friendly technologies and our programme on solid superacids and zeolites mediated organic transformations, we have shown that solid superacids (sulphated  $\text{SnO}_2$ ) can serve as efficient catalysts for transesterification of ketoesters.<sup>6</sup> (accompanying paper).

Table-1



Entry	Allyl ester	Nu  (eq.)	Time (hr)	Product	% Yield
1 a)		—	7		82
b)		2	5		92
c)		2	8		50
d)		2	6		81
2		—	2		72
3		—	5		60
4 a)		—	5		68
b)		2	5		70
c)		2	12		80
5 a)		2	10		85
b)		2	10		78
6 a)		2	10		89
b)		2	4		85
7		2	2		80

This communication describes the utility of solid superacid (sulphated  $\text{SnO}_2$ ) in effective deprotection of allyl esters. Sulphated  $\text{SnO}_2$  was conveniently prepared from stannous chloride.<sup>6</sup>

When allyl esters were refluxed in toluene in the presence of sulphated  $\text{SnO}_2$  (10 mol %), corresponding acids were obtained in excellent yields (Table ). It is noteworthy that the above reaction is performed under anhydrous conditions and the formation of allyl cations by solid superacid is followed by the alkylation by aromatic nucleus, toluene or anisole. This in effect constitutes "hydrolysis" under anhydrous conditions. It is evident from the table that prenyl esters are easily deprotected whereas the cinnamyl and crotyl esters require presence of more nucleophilic aromatic species viz. anisole. It is pertinent to note that normal esters remain unaffected under the reaction conditions (entries 2 and 3 ). Allyl esters could be easily and selectively deprotected in the presence of ethyl and methyl esters offering selective manipulation of esters in a synthetic sequence, as shown by entries of Table 1 where only the prenyl ester is selectively hydrolysed. Anhydrous conditions employed in our methodology may be contrasted with the earlier reported methodology involving formic acid<sup>2</sup> as the solvent and presence of water for hydrolysis.

Solid superacids offer advantages over conventional homogeneous acid/superacids, as their heterogeneous nature allows easy workup and retrieval of the products (acids) by mere filtration of the catalyst. Additionally the catalyst can be reused and recycled.

We are currently engaged in the study of other materials like resins, clays and zeolites to effect similar transformations.

**General Procedure:** A mixture of allyl ester (1 eq), anisole (2 eq) and the catalyst (100 mg, 10% by weight) in toluene (20 mL) was heated with stirring at 110°C. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered and aq. NaOH was added to the filtrate and the aqueous solution was extracted once with ethyl acetate. The aqueous layer was neutralised with dilute HCl, saturated with NaCl and extracted with ethyl acetate (3 x 20 ml). The organic layer was dried (anhydrous  $\text{Na}_2\text{SO}_4$ ) and concentrated to give the corresponding acid in high yields.

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#### References & Notes

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