Facile Oxidation of Aldehydes to Esters Using S·SnO_2/SBA-1–H_2O_2

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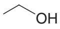
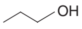
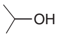
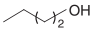
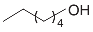
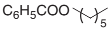
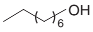
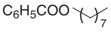
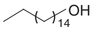
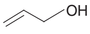
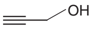
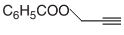
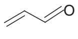
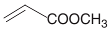
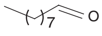
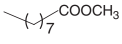
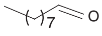
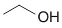
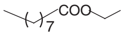
A highly efficient, mild, and simple procedure has been described for the oxidation of aldehydes to corresponding esters in alcohols with S•SnO_2/SBA-1 as catalyst and H_2O_2 as the oxidant, and the catalytic systems can be used in the preparation of a broad range of esters. Oxidation of aldehydes to corresponding esters utilizing H_2O_2 as the oxidant without any metal catalyst is also reported.

The conversion of aldehydes to esters has traditionally been accomplished by a two-step reaction sequence (oxidation followed by esterification). However, the transformation of aldehydes directly into esters is often required in organic synthesis,[1,2] especially in the synthesis of natural products.[3,4] Early research, several methods were reported for the direct preparation of aldehydes to esters, for examples, MnO_2–HCN system,[5] *N*-iodosuccinimide (NIS) system,[2] NaOMe–KI system,[6] MTO (methyltrioxorhenium)–H_2O_2 system.[7] Unfortunately, many of the methods usually require a series severe reaction conditions and poisonous or polluting reagents. Furthermore, most of these are effective to a limited range of aldehydes and alcohols. Therefore, the search for suitable green, mild, and efficient oxidation procedures, especially can be used in the preparation of a broad range of esters, is an interesting subject.

Recently, some new procedures, for example, TS-1 zeolite–air system,[8] oxone system,[9] V_2O_5–H_2O_2 system,[10] V_2O_5–SPB, or SPC (sodium peroxide or sodium percarboate) system,[11] have been developed for the oxidation of aldehydes to esters. These methods display advantages–environmentally friendly routes, mild reactions conditions, shorter reaction times–but their applications are not wide, either effective to a limited range of substrates or by the need for a large amount of peroxy salts. (1–3.5 equiv.)

As a solid superacid, sulphated SnO_2 has been used as catalyst for the transesterification of ketoesters.[12] Here, we report a novel effective procedure to directly oxidize aldehydes to the

Table 1. Oxidative esterification of aldehydes to corresponding esters with H_2O_2–S•SnO_2/SBA-1[a]

Entry	Aldehyde	Alcohol	Time/h	Product[b]	Yield[c](Purity[c])/%	
					/ [d]	S·SnO_2/SBA-1
1	C_6H_5CHO	—OH	4	$C_6H_5COOCH_3$	71(98)	98(98)
2	C_6H_5CHO		5		65(88)	98(98)
3	C_6H_5CHO		5		75(98)	95(98)
4	C_6H_5CHO		5		0(0)	75(98)
5	C_6H_5CHO		5		78(98)	95(98)
6	C_6H_5CHO		5		72(98)	95(98)
7	C_6H_5CHO		5		68(96)	98(98)
8[e]	C_6H_5CHO		18		0(0)	90(91)
9	C_6H_5CHO		5		14(99)	75(99)
10	C_6H_5CHO		5		0(0)	85(90)
11		—OH	4		24(98)	60(99)
12		—OH	6		65(98)	96(98)
13			6		55(98)	95(98)
14[f]	C_6H_5CHO	—OH	5	$C_6H_5COOCH_3$	/	98(98)

[a]Reaction conditions: aldehydes (1 mmol), S•SnO_2/SBA-1(0.1 g), 70% $HClO_4$ (0.5 mmol), H_2O_2 (4 mmol), and alcohol (4 mL), 323 K. [b]Identified by either GC-MS or GC with standard samples. [c]Determined by GC. [d]The reactions were carried out without catalyst (S•SnO_2/SBA-1). [e]*n*-hexane (5 mL, as solvent) was added into the reaction mixture. [f]Reaction results for the third run.

corresponding esters under mild reaction conditions with H_2O_2 as oxidant and sulphated SnO_2 supported on the SBA-1 zeolite as catalyst (the concentration of $S{\cdot}SnO_2$ on the zeolite is 1.5 mmol/g). Furthermore, in the above systems, it was found that several esters have been obtained in normal yield without any metal catalyst, and the reports available have not mentioned this observation.

The oxidative esterification results are shown in Table 1. In most cases, the desired esters were obtained in poor to normal yields without any metal catalyst. It is a surprising observation because H_2O_2 and metal catalyst are usually used together in the oxidative esterification systems in the report available.[7,10,11] Using $S{\cdot}SnO_2/SBA$-1 as catalyst, most substrates give good to excellent yields of corresponding esters. For examples, benzaldehyde and straight chain alcohol (including long-chain alcohol) were oxidized to corresponding esters efficiently (Entries 1–3, 5–8). However, the oxidative esterification result of benzaldehyde and 2-propanol was not satisfactory (Entry 4), and no ester was detected from GC analysis after 6 h. at 323 K when benzaldehyde and *tert*-butanol were used as substrates. This trend indicates that steric effect is an important factor in the reaction systems. In comparison with benzaldehyde and saturated straight chain alcohols, benzaldehyde and unsaturated alcohols are less reactive to oxidative esterification (Entries 9, 10). Besides benzaldehyde, this catalytic system is also suitable for unsaturated and straight chain aldehydes (Entries 11–13). For instance, excellent results were obtained with pelargonaldehyde as substrate (Entries 12, 13).

In above catalytic systems, the reaction can be carried out even in the absence of any external acid, but the reactions are rather sluggish. For example, only 45% benzaldehyde was selectively oxidized to methyl benzoate with methanol as solvent in 4 h.

Furthermore, $S{\cdot}SnO_2/SBA$-1 is stable and can be reused after oxidative esterification. After reaction, $S{\cdot}SnO_2/SBA$-1 was separated from the reaction mixture by filtrating, thoroughly washed with acetone, and then reused as catalyst for the next run under the same conditions. The reaction results indicate that there is no difference in either activity or selectivity between the first and third runs (Entries 1 and 14).

In summary, it was found that several esters can be obtained in normal yields without any metal catalyst, and a new system for oxidative esterification of aldehydes, wherein $S{\cdot}SnO_2/$ SBA-1 was used as catalyst and H_2O_2 was used as oxidant, has been demonstrated. The reaction results indicate that the procedure is facile, effective and easy to work up and can be used in the preparation of a broad range of esters. Moreover, $S{\cdot}SnO_2/$ SBA-1 catalyst can be easily separated from reaction mixture and reused at least three times.

References

1 D. R. Williams, F. D. Klingler, E. E. Allen, and F. W. Lichtenthaler, *Tetrahedron Lett.*, **29**, 5087 (1988).

2 C. Mcdonald, H. Holcomb, K. Kennedy, and E. Kirkpatrick, *J. Org. Chem.*, **54**, 1213 (1989).

3 S. R. Wilson, S. Tofigh, and R. N. Misra, *J. Org. Chem.*, **47**, 1360 (1982).

4 P. J. Garegg, L. Olsson, and S. Oscarson, *J. Org. Chem.*, **60**, 2200 (1995).

5 E. J. Corey, N. W. Gilman, and E. E. Ganem, *J. Am. Chem. Soc.*, **90**, 5616 (1968).

6 M. Okimoto and T. Chiba, *J. Org. Chem.*, **53**, 218 (1988).

7 J. H. Espenson, Z. Zhu, and T. H. Zauche, *J. Org. Chem.*, **64**, 1191 (1999).

8 R. Zhao, Y. Ding, and Z. Peng, *Catal. Lett.*, **87**, 81 (2003).

9 B. R. Travis, M. Sivakumar, G. O. Hollist, and B. Borhan, *Org. Lett.*, **5**, 1031 (2003).

10 R. Gopinath and B. K. Patel, *Org. Lett.*, **2**, 577 (2000).

11 R. Gopinath, B. Barkakaty, B. Talukdar, and B. K. Patel, *J. Org. Chem.*, **68**, 2944 (2003).

12 S. P. Chavan, P. K. zubaidha, and S. W. Dantale, *Tetrahedron Lett.*, **37**, 233 (1996).

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