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Sn(II)-catalyzed β-citronellol esterification: a Brønsted acid-free process for synthesis of fragrances at room temperature

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Simple $SnCl_2{\cdot}2H_2O$ was demonstrated to be able to catalyze β-citronellol esterification with acetic acid at room temperature under solvent-free conditions, achieving high conversion and ester selectivity (*ca.* 88% and 99%, respectively). Tin(II) chloride is a stable and water-tolerant Lewis acid that is commercially available and less corrosive than Brønsted acid catalysts. This selective process is an attractive alternative to the mineral acid-catalyzed process because it avoids product neutralization common in those reactions. The effects of main reaction parameters such as reactant stoichiometry, temperature, solvent, and catalyst concentration were assessed. Among the tin catalysts evaluated, $SnCl_2$ was the most active and selective. Moreover, $SnCl_2$ was as active as sulfuric and *p*-toluenesulfonic acid catalysts, the Brønsted acids investigated herein, with additional advantages of being a solid and less corrosive catalyst.

Introduction

β-Citronellol is an acyclic terpenic alcohol extensively used as a valuable raw material for the perfume, beverage, food, and pharmaceutical industries.[1–3] β-Citronellyl acetate is an important flavor ingredient and fragrance being industrially produced by enzymatic processes or *via* Brønsted acid-catalyzed reactions.[4,5] Indeed, the synthesis of citronellyl acetate could be even more attractive when carried out *via* environmentally benign processes, under solvent-free conditions and where steps of product neutralization are avoided and the catalyst recovery is facilitated, minimizing the generation of salts and effluents.[6]

Among the catalysts employed in esterification reactions, Lewis acids have significant advantages compared to the liquid Brønsted acid catalysts, such as their low corrosiveness and great water tolerance.[7,8] On the other hand, enzymatic catalysts commonly used in esterification are expensive and require rigid control of the temperature and acidity of the reaction medium. Actually, enzymatic catalysts have been intensively used in the terpenic alcohol esterification; however, their high cost and the difficulty of catalyst recovery are negative aspects of these processes that compromise their application on a large scale.[9,10] In this regard, tin(II) chloride is an inexpensive and easy to handle solid catalyst that could be more potentially active in acid-catalyzed reactions.[11–15]

The development of selective processes to functionalize monoterpenes based on commercial and simple metal catalysts is a goal that has been pursued by our research group.[16,17] Recently, tin(II) halide catalysts have been successfully tested in the ketalization and esterification reactions of fatty acids and glycerol.[18,19] Earlier, tin catalysts were successfully used in transesterification reactions of vegetable oil.[20] Nevertheless, any study described its use in terpenic alcohol esterification until now. Herein, we wish to describe a simple and efficient Sn(II)-catalyzed β-citronellol esterification process with HOAc in the absence of solvent and at room temperature. We paid special attention to assessing factors driving esterification selectivity and to optimizing the reaction conditions. Remarkably, at room temperature the $SnCl_2$ catalyst that promoted esterification of β-citronellol with HOAc achieved a very high selectivity (*ca.* 99%) with *ca.* 88% conversion within a shorter reaction time than those reported in the literature.[21,22] To the best of our knowledge, this is the first report on terpenic alcohol esterification reaction catalyzed by $SnCl_2$.

Thus, the present study describes using $SnCl_2$ as a catalyst under mild reaction conditions (*ca.* room temperature and pressure) in β-citronellyl acetate synthesis in the absence of solvent. Herein, we investigated the effects of main reaction parameters in the conversion and selectivity and compared the catalytic activity of Lewis and Brønsted acids.

Experimental

Chemicals

All chemicals were commercially available and utilized without prior handling. $SnCl_2{\cdot}2H_2O$ (95 wt.%), SnF_2, $SnBr_2$

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and $Sn(CH_3COO)_2$ (99 wt.%) were purchased from Sigma Aldrich. Brønsted acid catalysts, H_2SO_4 (98 wt.%) and *p*-toluenesulfonic acid (99 wt.%), were acquired from Aldrich and Proquimios, respectively. β-Citronellol (99 wt.%) was purchased from Sigma Aldrich and used as received.

Catalytic runs

Catalytic runs were performed in a glass reactor (50 mL) equipped with a magnetic stirrer and sampling septum. Typically, β-citronellol and HOAc were dissolved in an adequate molar ratio (15 mL solution), and then the reaction was initiated by the addition of the Sn(II) catalyst (*ca.* 1 to 10 mol%).

Reaction progress was followed by GC analyses of aliquots taken at regular time intervals using a Shimadzu GC 2010 instrument, FID, fitted with a Carbowax 20M capillary column. Toluene was the internal standard. To calculate the reaction conversions, we compared the corresponding product chromatographic peak areas with the calibration curves. To adjust the concentration to the calibration curve we diluted all the aliquots with acetonitrile.

Product identification

The reaction products were analyzed on a Shimadzu MS-QP 2010 ultra mass spectrometer operating at 70 eV coupled to a Shimadzu 2010 GC. We isolated the major product by column chromatography using silica gel (60G). The ^1H and ^{13}C NMR spectra were recorded on a Mercury-300 Varian spectrometer at 300 and 75 MHz, respectively, in $CDCl_3$ solution using TMS as the internal standard. FT-IR spectroscopy analyses were carried out using a Varian 660 FT-IR spectrometer. The spectroscopic data for β-citronellyl acetate (Fig. 1) are summarized as follows:

^1H NMR (300 MHz, $CDCl_3$-*d*1): δ (integration, multiplicity, coupling constant, attribution); 0.90 (d, 3H, 9 –CH_3); 1.13–1.53 (m, 5H, 2 –CH_2, 3 –C*H* and 4 –CH_2); 1.60 (s, 3H, 10 –CH_3); 1.68 (s, 3H, 8 –CH_3); 1.92–2.04 (m, 2H, 5 –CH_2); 2.04 (s, 3H, 2′ –$OCCH_3$); 4.06–4.12 (m, 2H, 1 –OCH_2); 5.05–5.10 (m, 1H, 6 –CH).

^{13}C NMR (75 MHz, $CDCl_3$-*d*1): δ (integration, multiplicity, coupling constant, attribution); 17.63 (C10); 19.38 (C2′); 21.05 (C9); 25.35 (C5); 25.71 (C8); 29.42 (C3); 32.37 (C2); 36.94 (C4); 63.02 (C1); 124.52 (C6); 131.34 (C7); 171.26 (C1′).

FT-IR (ν (cm^{-1})): 2962; 2922; 1743; 1455; 1367; 1239; 1055.

GC-MS (*m*/*z*/relative intensity): 198/0.05; 138/23; 123/31; 109/17; 95/57; 81/77; 69/69; 55/42; 41/100.

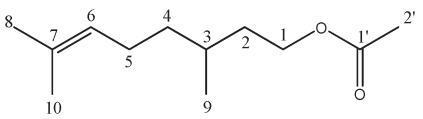


Fig. 1 β-Citronellyl acetate.

Results and discussion

General aspects

Recently, we have described the use of tin halides as catalysts in the esterification reactions of glycerol as well as free fatty acids.[17,18] In those studies, among the tin catalysts assessed, $SnCl_2$ was always the most effective catalyst. Thus, inspired by these findings, we investigated the catalytic activity of $SnCl_2{\cdot}2H_2O$ in terpenic alcohol esterification reactions. β-Citronellol was selected as the model molecule and initially the reactions were carried out in CH_3CN solutions.

Effect of temperature on the $SnCl_2$-catalyzed β-citronellol esterification with HOAc

The $SnCl_2$-catalyzed β-citronellol esterification with HOAc was accomplished at different temperatures (*ca.* 298 to 333 K) in the presence or absence of the catalyst; by simplification, only the main results are displayed in Table 1.

Despite the acidity of HOAc and even using a slight excess in relation to β-citronellol (*i.e.* molar ratio of 2 : 1), ester formation was detected in the absence of the catalyst, regardless of the reaction temperature studied (*i.e.* 298 or 333 K, Table 1).

On the other hand, in the presence of $SnCl_2$ the β-citronellol esterification reactions became catalytic at room temperature or when the reaction was heated to 333 K (runs 3 and 4, Table 1).

We verified that an increase in temperature affected the conversion and reaction selectivity. Noticeably, the undesirable formation of oligomers (*ca.* 58% selectivity, Table 1) in the reactions performed at 333 K compromised the ester selectivity. Conversely, oligomers were not formed when the reaction was carried out at 298 K. Oligomers are not detectable by GC analysis because of the high molar weight. However, a checking of mass balance proved that oligomers were formed upon comparing the GC peak area of formed products against the GC peak area of β-citronellol consumed. In addition, after cooling of the reaction solution the oligomers were precipitated as a white solid and analyzed by FT-IR spectroscopy, allowing its identification.

The increase in the conversion rate with decreasing temperature suggests an exothermal character for this process (Fig. 2). Although this aspect was not further described in the literature, it was described as another kind of reaction

Table 1 Temperature effects on the $SnCl_2$-catalyzed β-citronellol esterification with HOAc[a]

Run	T (K)	$SnCl_2$ (mol%)	Conversion (%)	Selectivity[b] (%)		
				1	Ni	Olig.
1	298		0	0	0	0
2	333	0	0	0	0	0
3	298	10	42	90	2	8
4	333	10	21	40	2	58

[a] Reaction conditions: β-citronellol (7.8 mmol), HOAc (15.6 mmol), CH_3CN solution (15 mL), 6 h. [b] (1) = β-citronellyl acetate; ni = complex mixture of non-identified products.

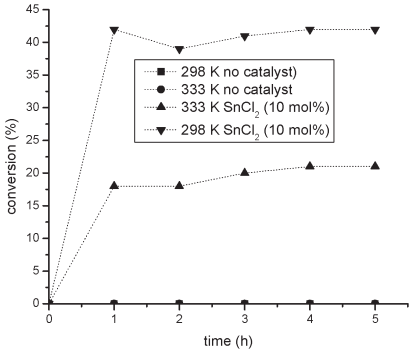


Fig. 2 Effects of temperature on $SnCl_2$-catalyzed β-citronellol esterification. Reaction conditions: β-citronellol (7.8 mmol), HOAc (15.6 mmol), CH_3CN solution (15 mL), 6 h.

involving alcohols and carbonylic reactant (*i.e.* glycerol and ketone), and the same observation was found.[23]

Thermodynamic studies

To calculate the equilibrium constant (K_{eq}) for the β-citronellol esterification reaction with HOAc some considerations deserve to be highlighted. Firstly, it should be considered that it is independent of HOAc concentration (due to its being in excess). In addition, we must take into account that the reaction products (*i.e.* water and β-citronellyl acetate) are formed with the same concentration. Thus, after these simplifications, we can write the equation for the equilibrium constant as follows:

$$K_{eq} = [\beta\text{-citronellyl acetate}]^2/[\beta\text{-citronellol}] \quad (1)$$

The initial concentration of β-citronellol was equal to 0.873 mol L^{-1}. Table 2 shows the equilibrium constant for each reaction at the different temperatures studied. Eqn (2) is true when the enthalpy variation is constant with temperature.

$$\ln K_{eq} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

From data shown in Table 2, we could build the linear plot of $\ln K_{eq}$ *versus* $1/T$ (Fig. 3) and by using eqn (2) the respective values of ΔS and ΔH were calculated.

Table 2 Values of enthalpy and entropy variation for the $SnCl_2$-catalyzed β-citronellol esterification reactions with HOAc[a]

Temperature (K)	Equilibrium constant (K_{eq})	$-R \ln K_{eq}$	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})
298	0.161	0.150	−0.312	0.0012
308	0.113	0.178		
318	0.073	0.215		
328	0.046	0.252		

[a] Reaction conditions: β-citronellol (7.8 mmol), HOAc (15.6 mmol), CH_3CN solution (15 mL), 6 h.

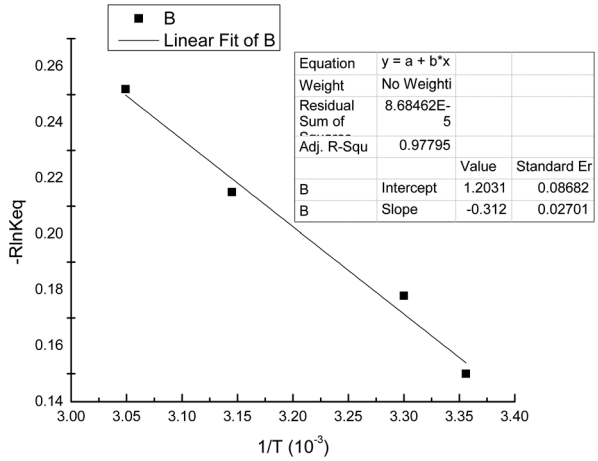


Fig. 3 Linear plot of $-R \ln K_{eq}$ *versus* $1/T$.

Whilst the slope of the curve gives the value of ΔH, the Y axis intercept provides ΔS. The values for enthalpy and entropy variations were found to be −0.312 kJ mol^{-1} and 0.0012 kJ mol^{-1}, respectively (Fig. 3).

The negative value of ΔH confirms the exothermic character of the reaction, which explains the observed increase in conversion when the temperature was decreased from 333 to 298 K (Fig. 2).

Effect of reactant molar ratio on the $SnCl_2$-catalyzed β-citronellol esterification

When performed at room temperature, the only product obtained in the β-citronellol esterification with HOAc was β-citronellyl acetate (Fig. 4), always with selectivity equal to or higher than 95%, determined *via* GC-MS analyses.

The reactant stoichiometry is a key aspect in this reaction and its effect was investigated in the range of 1 : 1 to 1 : 10 (Table 3). Although the β-citronellol : HOAc molar ratio has been increased to 1 : 10, only a poor conversion (*ca.* lower than 5%) was reached in the absence of the catalyst. Conversely, in the $SnCl_2$-catalyzed reactions the conversion drops to almost 90% when the proportion of reactants was equal to or higher than 1 : 6. A decrease in ester selectivity was observed in all these reactions at room temperature. Selectivity for β-citronellyl acetate remained equal to or higher than 95% independent of the reactant molar ratio employed.

The kinetic curves displayed in Fig. 5 show that both initial rate and final conversion were almost the same in the reactions with a molar ratio between 1 : 6 and 1 : 10. Thus, this was the proportion selected to perform the reactions in the absence of solvent. We verified that without solvent and

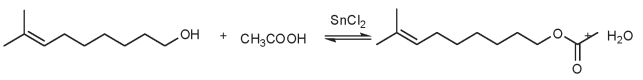


Fig. 4 $SnCl_2$-catalyzed β-citronellol esterification with HOAc. Reaction conditions: β-citronelol : HOAc ratio 1 : 2; $SnCl_2$ (10 mol%); 298 K; 6 h.

Table 3 Effect of reactant stoichiometry in the $SnCl_2$-catalyzed β-citronellol esterification with HOAc[a,b]

Run	HOAc : β-citronellol molar ratios	Conversion (%)	
		$SnCl_2$-catalyzed reactions	Blank reactions
1	2 : 1	43	0
2	4 : 1	69	0
3	6 : 1	88	0
4	8 : 1	89	<5
5	10 : 1	89	5

[a] Reaction conditions: β-citronellol (7.8 mmol), CH_3CN solution (15 mL), $SnCl_2$ (10 mol%), 298 K, 3 h. [b] β-Citronellyl acetate selectivity determined *via* GC was equal to or higher than 95% in all catalytic runs.

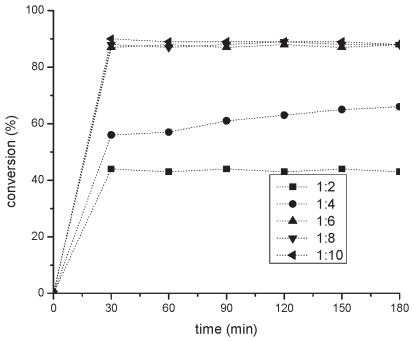


Fig. 5 Kinetic curves of $SnCl_2$-catalyzed β-citronellol esterification with HOAc using different molar ratios of reactants. Reaction conditions: β-citronellol (7.8 mmol), $SnCl_2$ (10 mol%), 3 h.

with a molar ratio equal to 1 : 6, the reaction behavior was the same in terms of conversion and selectivity (not shown in Fig. 4 by simplification).

In addition to the recovery problems and toxicity, some enzymatic catalysts are sensitive to the presence of acetic acid, so that the choice of the adequate solvent becomes a crucial aspect for those reactions.[24,25]

However, in the $SnCl_2$-catalyzed reaction described herein, the reactants themselves were used as a liquid phase and thus this problem was easily circumvented.

The reason for the fast deactivation of the catalyst was investigated. We performed experiments using different initial concentrations of water (*ca.* 0.1 to 10 mol% in relation to the catalyst). We verified that beginning reactions with water concentrations higher than 10 mol% resulted in a noticeable decrease in the initial rate. Starting a reaction with a 1 : 6 molar ratio of β-citronellol : HOAc and an initial amount of water equal to 10 mol% resulted in the lowering of the conversion rate to 40% after 30 minutes. In contrast, in the reactions in the absence of water, conversions near to 90% were obtained (Fig. 5). Besides the shift in equilibrium toward reactants, water may coordinate to the tin(II) cations, compromising its activity.

Effect of catalyst concentration on the $SnCl_2$-catalyzed β-citronellol esterification

In all runs catalyzed by Sn(II), the high initial rate of β-citronellol esterification allows reaching a maximum conversion within the first 30 minutes of reaction, staying almost constant from this point forward regardless of catalyst concentration (Fig. 5).

From the rate constant measured within the first 30 minutes of reaction (*i.e.* mmol β-citronellol converted/1800 s) for each run with a specific catalyst concentration (*ca.* 0.10 to 10 mol%) it was possible to build a linear plot (Fig. 6) and determine the reaction order in relation to the $SnCl_2$ concentration.

A high linear coefficient (R^2 = 99.9%) clearly shows that a first-order dependence in relation to $SnCl_2$ concentration determined by the slope of the curve (*ca.* 1.2) may be suggested for these reactions (Fig. 7).

A first-order dependence has also been verified in the $SnCl_2$-catalyzed reaction in which the substrates were glycerol and HOAc.[26] Thus, it suggests that in the rate determining step of the reaction only one tin atom should be involved (Scheme 1).

Although there are different approaches in the literature as regards carbonyl group activation that could be performed by tin coordinated to the anionic ligands or partially dissociated, it is reasonable to suppose that the carbonyl polarization becomes more favorable when attacked by the hydroxyl group as described in Scheme 1.[27]

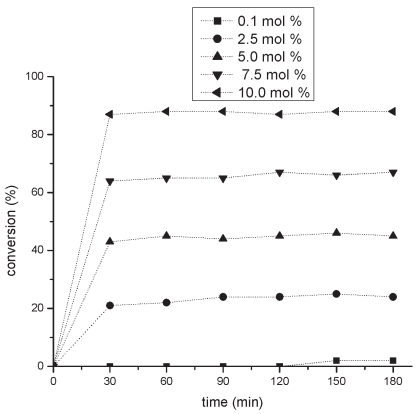


Fig. 6 Effect of $SnCl_2{\cdot}2H_2O$ concentration in the β-citronellol esterification with HOAc. Reaction conditions: β-citronellol (13.1 mmol), HOAc (78.6 mmol), 298 K, 3 h.

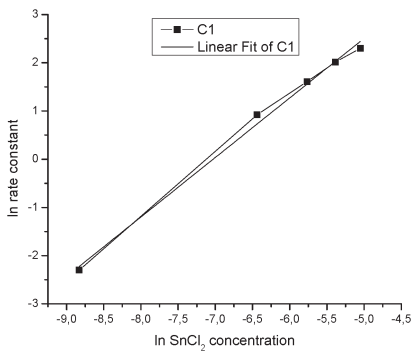
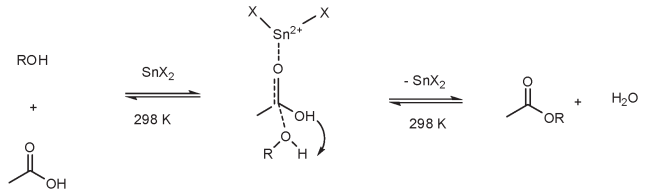


Fig. 7 Determination of order in relation to the $SnCl_2$ catalyst concentration.



Scheme 1 Proposed mechanism for tin-catalyzed esterification of alcohols with HOAc.

It can be noted that decreasing the catalyst concentration does not result in any significant change in the reaction selectivity. Regardless of $SnCl_2$ concentration, the β-citronellyl acetate selectivity (1) remained higher than 96% and with no oligomer formation (Table 4). A highly selective conversion of β-citronellol to β-citronellyl acetate was achieved using $SnCl_2$ at 10 mol% within a reaction time shorter than those reported in the literature about enzymatic processes.[28] Those authors suggested that HOAc had an inhibitory effect on the catalytic action of the lipase assessed.[29]

Lewis or Brønsted acid-catalyzed β-citronellol esterification with HOAc

The effect of catalyst nature (*i.e.* Brønsted or Lewis acids) was assessed in the kinetic curves obtained and are displayed in Fig. 8. In most of the cases, the acid strength determined the activity of Brønsted acid catalysts. Considering that sulfuric acid and *p*-toluenesulfonic acid were used at the same hydrogen ion concentration, the fact that reactions catalyzed by them have achieved almost equal conversions (*ca.* 90%) could be attributed to the probable levelling effect caused by the composition of the reaction medium.

On the other hand, steric or electronic factors of anionic ligands may change the catalytic activity of Lewis acids such as Sn(II) salts. However, it was also important to take into account the solubility of catalysts. $Sn(OAc)_2$ and $SnBr_2$ were partially soluble, whereas $SnCl_2$ and SnF_2 were completely solubilized. For this reason, tin acetate or bromide were less active catalysts than the soluble salts. In addition, the low activity of $Sn(OAc)_2$ may be attributed to low lability of the acetate ligand. This bidentate ligand probably hinders the activation of the carbonyl group of HOAc by the few molecules of the $Sn(OAc)_2$ soluble catalyst. In this sense, it is reasonable to accept that the activation of the carbonyl group of HOAc depends on the Sn(II) cation concentration available in the solution.

Table 4 Effect of $SnCl_2{\cdot}2H_2O$ concentration in the β-citronellol esterification with HOAc[a]

Run	$SnCl_2$ (mol%)	Conversion (%)	Product selectivity[b] (%)		
			1	Ni	Olig
1	0.1	2	99	1	0
2	2.5	21	96	4	0
3	5.0	44	99	1	0
4	7.5	64	97	3	0
5	10.0	87	99	1	0

[a] Reaction conditions: β-citronellol (13.1 mmol), HOAc (78.6 mmol), 298 K, 3 h. [b] (1) = β-citronellyl acetate; ni = complex mixture of non-identified products.

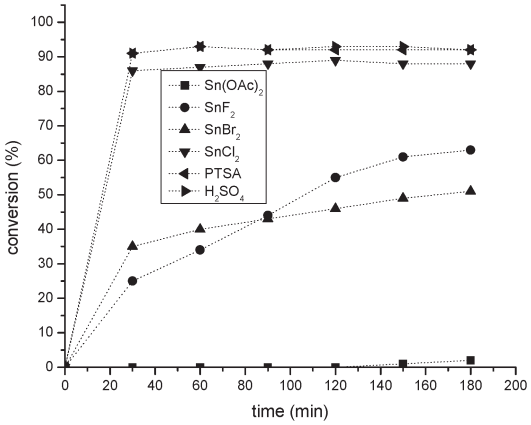


Fig. 8 Effect of catalyst nature in β-citronellol esterification with HOAc. Reaction conditions: β-citronellol (13.1 mmol), HOAc (78.6 mmol), Lewis acid catalyst (10 mol% Sn^{2+} in relation to β-citronellol); Brønsted acid catalyst (10 mol% H^+ in relation to β-citronellol), 3 h, 25 °C. Selectivity for β-citronellyl acetate was higher than 98% in all runs except in the $Sn(OAc)_2$-catalyzed reaction where it was not obtained.

Conversely, the high activity of $SnCl_2$ may be attributed not only to its high solubility but also to the higher stability of chloride anion, which is recognized as a leaving group better than the fluoride anion present in SnF_2. This result is in agreement with the literature.[25]

Finally, the most auspicious result is the high activity of $SnCl_2$; although it has been slightly lower than those of the Brønsted acids studied, the use of tin catalyst has significant advantages such as avoiding neutralization steps, generating less corrosion and being easily handled because it is a solid compound.

Conclusions

An efficient process to synthesize terpenic esters (*i.e.* β-citronellyl acetate) was developed. Tin(II) chloride dihydrate, an inexpensive and commercially available catalyst, was used under environmentally benign reaction conditions (*i.e.* in the absence of solvent and at room temperature). The tin(II) chloride catalyst efficiently promoted the β-citronellol esterification reaching the same conversion and selectivity (*ca.* 90% and 98%, respectively) that the corrosive Brønsted acid catalyst (*i.e.* H_2SO_4) achieved. In addition, among the other tin catalysts assessed herein, we found out that $SnCl_2$ was the most active and selective. The comparison with other tin catalysts provides the following order of activity: $SnCl_2 > SnF_2 > SnBr_2 > Sn(OAc)_2$. Tin-catalyzed esterification processes are less corrosive than those catalyzed by Brønsted acids and faster and cheaper than enzymatic processes reported in the literature.

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