

Full Paper

## ZrOCl<sub>2</sub>·8H<sub>2</sub>O: An Efficient, Cheap and Reusable Catalyst for the Esterification of Acrylic Acid and Other Carboxylic Acids with Equimolar Amounts of Alcohols

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Received: 20 January 2006 / Accepted: 9 April 2006 / Published: 10 April 2006

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**Abstract:** Esterifications of carboxylic acids with equimolar amount of alcohols could be efficiently catalyzed by ZrOCl<sub>2</sub>·8H<sub>2</sub>O. Acrylate esters were obtained in good yields under solvent-free conditions at ambient temperature. The esterification of other carboxylic acids with alcohols also proceeded at ambient temperature or at 50 °C to afford esters in high yields. If the esterification was performed in toluene under azeotropic reflux conditions to remove water, both the catalytic activity of ZrOCl<sub>2</sub>·8H<sub>2</sub>O and the rate of esterification could be increased greatly. Furthermore, in the present catalytic system, the esters could be easily separated from the reaction mixtures and the catalyst could be easily recovered and reused.

**Keywords:** Esterification, acrylic acid, carboxylic acid, alcohol, zirconium (IV) dichloride oxide hydrate.

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### Introduction

Esters are the important class of organic compounds, which are usually prepared by the esterification of carboxylic acids with alcohols catalyzed by H<sub>2</sub>SO<sub>4</sub>, TsOH [1, 2] and other catalysts [3-18]. Because the esterification is a reversible reaction, in order to obtain a high yield of ester, an

excess amount of one of the reactants is normally required, and/or removal of H<sub>2</sub>O by azeotropic distillation during the reaction is usually performed. However, the former is neither an atom economical nor environmentally benign process, while the latter is not suitable for the esterification of carboxylic acids which have low boiling points, and polymerization can easily occur at the higher temperatures used under the acidic reaction conditions in the cases of particularly susceptible substrates such as acrylic acid,  $\alpha$ -methylacrylic acid, etc. Consequently, development of an efficient catalytic system for esterification using 1:1 mixtures of carboxylic acids and alcohols at ambient or low temperature is still an important and interesting objective in organic synthesis.

Since some inorganic salts display Lewis acid properties and they are cheap and easily separated from the organic products, they have become interesting candidates of choice as catalysts. Very recently, a direct esterification of carboxylic acids with equimolar amounts of alcohols catalyzed by inorganic salts has been reported [19, 20].

The aim of our research described here was to develop an efficient catalytic procedure for the direct esterification of carboxylic acids with alcohols under solvent-free conditions with the following requirements: (1) esters should be obtained in high yields by the esterification of equimolar amounts of carboxylic acids and alcohols; (2) esterification should proceed at ambient or low temperature and the catalyst system should be suitable for the esterification of highly reactive carboxylic acids such as acrylic acid; (3) the esters should be easy to isolate and purify, and the catalyst should be recyclable. After screening a number of inorganic salts, we have found that ZrOCl<sub>2</sub>·8H<sub>2</sub>O worked as an efficient catalyst to catalyze esterification while possessing the necessary properties to meet the requirements as described above [21].

## Results and Discussion

### *Esterification of acrylic acid with alcohols*

Tables 1 and 2 summarize the results of the esterification of acrylic acid (**1a**) with equimolar amount of alcohols catalyzed by zirconium salts. This was carried out by simply stirring **1a**, an equimolar amount of alcohol and 5 mol% of the zirconium salt under solvent-free conditions at ambient temperature or at 50 °C for 24h.

Table 1 shows the catalytic activity of the different zirconium salts tested in the reaction of **1a** with equimolar amounts of methanol (**2a**) at ambient temperature. Among the chosen zirconium compounds, ZrOCl<sub>2</sub>·8H<sub>2</sub>O (entry 1) was very efficient in this esterification, affording methyl acrylate (**3aa**) in 71% yield (GC) without any removal of water, while ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O and Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O showed somewhat lower catalytic activities to give **3aa** in moderate yields (entries 2 and 3).

It should be noted that in all these cases, upon completion of the esterification, the reaction mixture became two phases at ambient temperature and the catalyst and esters were easily separated by simply decanting. GC analyses of the two phases revealed that the organic phase (the upper layer) was the product **3aa**, containing small amounts of the starting materials **1a** and **2a**. The aqueous phase (the lower layer) was a mixture of H<sub>2</sub>O, **1a**, **2a** and trace amounts of **3aa**. <sup>1</sup>H- and <sup>13</sup>C-NMR of the reaction mixture confirmed that under the present reaction conditions, polymerization of **1a** did not occur.

After removal of the organic phase, we have examined the catalytic activity of catalyst in the aqueous phase. Thus, 5.0 mmol of **1a** and 5.0 mmol of **2a** were directly added to the aqueous phase,

and the resulting mixture was then stirred. After 24h, **3aa** was formed in 64% GC yield (entry 4). If we removed the volatiles and H<sub>2</sub>O from the aqueous phase (80 °C, under vacuum), a solid residue could be obtained. The solid residue showed the almost same catalytic activity as the fresh ZrOCl<sub>2</sub>·8H<sub>2</sub>O did to afford **3aa** in 69% GC yield. These results indicated that ZrOCl<sub>2</sub>·8H<sub>2</sub>O was a reusable catalyst.

**Table 1.** Zirconium compounds-catalyzed esterification of acrylic acid **1a** with methanol **2a**<sup>a</sup>

$$\begin{array}{c}
 \text{CH}_2=\text{CH}-\text{COOH} + \text{CH}_3\text{OH} \xrightarrow[24\text{ h}]{5\text{ mol \% cat.}} \text{CH}_2=\text{CH}-\text{COOCH}_3 + \text{H}_2\text{O} \\
 \mathbf{1a} \qquad \mathbf{2a} \qquad \qquad \qquad \mathbf{3aa}
 \end{array}$$

entry	catalyst	<b>3aa</b> GC yield (%)
1	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	71
2	Zr(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	54
3	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O	44
4	b	64

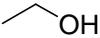
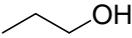
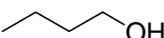
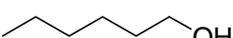
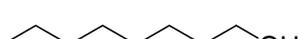
(a) The reactions were carried out using 5 mmol of **1a**, 5 mmol of **2a** and 0.025 mmol of ZrOCl<sub>2</sub>·8H<sub>2</sub>O at r.t. for 24h. (b) The reused catalyst.

Furthermore, the reactions of **1a** with other aliphatic alcohols at ambient temperature or at 50 °C without removal of water were also studied. As shown in Table 2, the yield of esterification of **1a** with ethanol (**2b**) at ambient temperature gave ethyl acrylate (**3ab**) in 69% GC yield (entry 1). The result was similar to that observed when **2a** used. It was found that there was a slight decrease in the yields with an increase of the carbon number of the alcohols (C<sub>3</sub> ~ C<sub>8</sub>), and the corresponding esters were obtained in a range of 60 ~ 63% yields (entries 2 ~ 5). These results indicated that the yields of the esterification with C<sub>3</sub> ~ C<sub>8</sub> alcohols at 50 °C without removal of water were not greatly dependent on the carbon number of alcohols.

#### Esterification of other carboxylic acids with alcohols

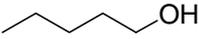
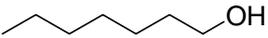
To assess the scope of ZrOCl<sub>2</sub>·8H<sub>2</sub>O-catalyzed esterification, the reactions of various other carboxylic acids with several alcohols have been investigated. Table 3 summarizes the results of the esterification of propionic acid (**1b**) with equimolar amount of alcohols at ambient temperature for 24 h. As can be seen from this data, ZrOCl<sub>2</sub>·8H<sub>2</sub>O showed highly catalytic activity for the esterification of **1b** with various alcohols. Reactions of **1b** with **2a** or **2b** afford **3ba** and **3bb** in 81% and 82% GC yields, respectively (entries 1 and 2). Similarly efficient esterifications took place using other alcohols, though the yields were slight decreased (entries 3 – 8, Table 3).

**Table 2.** ZrOCl<sub>2</sub>·8H<sub>2</sub>O-catalyzed esterification of acrylic acid (**1a**) with aliphatic alcohols<sup>a</sup>

entry	alcohol	GC yield (%)
1 <sup>b</sup>	<b>2b</b> 	<b>3ab</b> 69
2	<b>2c</b> 	<b>3ac</b> 61
3	<b>2d</b> 	<b>3ad</b> 63
4	<b>2e</b> 	<b>3ae</b> 61
5	<b>2f</b> 	<b>3af</b> 60

<sup>a</sup> The reactions were carried out using 5 mmol of **1a**, 5 mmol of alcohol and 0.025 mmol of ZrOCl<sub>2</sub>·8H<sub>2</sub>O at 50 °C for 24h. (b) At r.t. for 24h.

**Table 3.** ZrOCl<sub>2</sub>·8H<sub>2</sub>O-catalyzed esterification of propionic acid (**1b**) with alcohols<sup>a</sup>

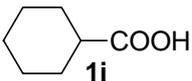
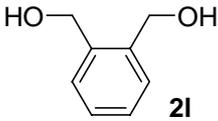
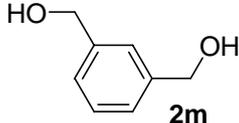
entry	alcohol	GC yield (%)
1	<b>2a</b>	<b>3ba</b> 81
2	<b>2b</b>	<b>3bb</b> 82
3	<b>2c</b>	<b>3bc</b> 76
4	<b>2d</b>	<b>3bd</b> 75
5	<b>2g</b> 	<b>3bg</b> 75
6	<b>2e</b>	<b>3be</b> 65 (62) <sup>b</sup>
7	<b>2h</b> 	<b>3bh</b> 71
8	<b>2f</b>	<b>3bf</b> 68

<sup>a</sup> The reactions were carried out using 5 mmol of acid, 5 mmol of alcohol and 0.025 mmol of ZrOCl<sub>2</sub>·8H<sub>2</sub>O at r.t. for 24h; <sup>b</sup> The yield in parenthesis was obtained by using the reused catalyst.

Table 4 shows the ZrOCl<sub>2</sub>·8H<sub>2</sub>O-catalyzed esterification of several different acids with equimolar amounts of a variety of alcohols at ambient temperature without removal of water or under azeotropic reflux conditions. As **1a** and **1b** did, the reactions of chloroacetic acid (**1c**), isobutyric acid (**1d**), pentanoic acid (**1e**) and hexanoic acid (**1f**) with **2a** at ambient temperature gave the corresponding esters in good yields (entries 1 ~ 4). If we carried out the esterification in toluene under azeotropic reflux conditions to remove water, the rate of reaction could be greatly increased. For example, in the presence of 0.5 mol% of ZrOCl<sub>2</sub>·8H<sub>2</sub>O, the reaction of octanoic acid (**1g**) with 1-C<sub>8</sub>H<sub>17</sub>OH (**2i**) in toluene under azeotropic reflux for 5 h afforded the corresponding ester **3gi** in 99% GC yield (entry 5).

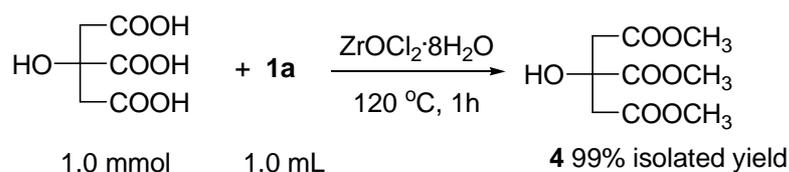
Although the rate of esterification of phenol (**2j**) was slower than with aliphatic alcohols, the esterification of **1g** with **2j** also proceeded with the azeotropic removal of water technique to give the expected ester **3gj** in 35% GC yield after 36 h (entry 6). Under the same conditions, the  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ -catalyzed the esterification of benzoic acid (**1h**) with benzyl alcohol (**2k**) gave **3hk** in 82% yield (entry 7). In addition, the esterification of cyclohexanecarboxylic acid (**1i**) with **2k** produced **3ik** in high isolated yield (entry 8), and the dehydration of **1i** with 0.5 equivalent of a diol, such as 1,2-benzenedimethanol (**2l**) or 1,3-benzenedimethanol (**2m**) proceeded completely to afford the expected esters in good isolated yields (entries 9 and 10). Furthermore, we examined the esterification of citric acid with an excess of **1a** at 120 °C for 1h. As shown Scheme 1, ester **4** was isolated in almost quantitative yield.

**Table 4.**  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ -catalyzed esterification of carboxylic acids with alcohols <sup>a</sup>

entry	acid	alcohol	solvent	temp (°C)	time (h)	GC yield (%)
1	chloroacetic acid <b>1c</b>	<b>2a</b>		r. t.	24	<b>3ca</b> 76
2	isobutyric acid <b>1d</b>	<b>2a</b>		r. t.	24	<b>3da</b> 61
3	pentanoic acid <b>1e</b>	<b>2a</b>		r. t.	24	<b>3ea</b> 72
4	hexanoic acid <b>1f</b>	<b>2a</b>		r. t.	24	<b>3fa</b> 62
5 <sup>b</sup>	octanoic acid <b>1g</b>	1-C <sub>8</sub> H <sub>17</sub> OH <b>2i</b>	toluene	reflux	5	<b>3gi</b> 99
6 <sup>b</sup>	<b>1g</b>	Phenol <b>2j</b>	toluene	reflux	36	<b>3gj</b> 35
7 <sup>b</sup>	benzoic acid <b>1h</b>	PhCH <sub>2</sub> OH <b>2k</b>	toluene	reflux	8	<b>3hk</b> 82
8 <sup>b</sup>	 <b>1i</b>	<b>2k</b>	toluene	reflux	16	<b>3ik</b> (91) <sup>c</sup>
9 <sup>d</sup>	<b>1i</b>	 <b>2l</b>	toluene	reflux	16	<b>3il</b> (84) <sup>c</sup>
10 <sup>d</sup>	<b>1i</b>	 <b>2m</b>	toluene	reflux	16	<b>3im</b> (89) <sup>c</sup>

<sup>a</sup> The reactions were carried out using 5 mmol of acid, 5 mmol of alcohol and 0.025 mmol of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ; <sup>b</sup> 3.0 mL of toluene was used; <sup>c</sup> Isolated yield; <sup>d</sup> **1i**:diol = 2:1.

Scheme 1.



## Conclusions

In summary, we have investigated the  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ -catalyzed esterification of carboxylic acids with equimolar amount of alcohols at ambient temperature, at 50 °C or under azeotropic reflux conditions. It has been found that  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  showed high catalytic activities in the esterification of acrylic acid and other aliphatic acids with alcohols at ambient temperature or at 50 °C without removal of water, although both the catalytic activity of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and the rate of esterification could be increased greatly under azeotropic reflux conditions in toluene. In addition, in the present catalytic system, the esters could be easily separated from the reaction mixture, and catalyst could be easily recovered and reused. The present procedures offer some merits from the viewpoint of green chemistry.

## Acknowledgements

This project (20573061) was supported by National Natural Science Foundation of China.

## Experimental Section

### General

All the organic reagents and zirconium salts are commercially available and were used without further purification. GC analyses of organic compounds were performed on an Agilent Technologies 1790 GC instrument with a TC-WAX 25 m capillary column. GC-MS was performed on a Hewlett Packard 5890 Series II GC/MS spectrometer with a PEG-25M column.  $^1\text{H-NMR}$  (300 MHz) and  $^{13}\text{C-NMR}$  (75 MHz) spectra were recorded on a Bruker DPX-300 spectrometer.

*Typical procedure for esterification of propionic acid (1b) with 1-butanol (2d) at ambient temperature (Table 3, entry 4):*

A mixture of propionic acid (**1b**, 5 mmol), 1-butanol (**2d**, 5 mmol) and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (0.025 mmol) was stirred at ambient temperature in a 5-mL round-bottomed glass tube under an air atmosphere for 24 h. Upon completion the reaction, diethyl ether (15 mL) was added to the reaction mixture, and the mixture was washed with water and dried with anhydrous magnesium sulfate. After removal of drying agent, the filtrate was concentrated to ca. 3.0 mL and analyzed by gas chromatography after addition of an appropriate amount of mesitylene as internal standard. **3bd** was formed in 75% GC yield.

Typical procedure for esterification of octanoic acid (**1g**) with 1-octanol (**2i**) in toluene under azeotropic reflux conditions (Table 4, entry 5):

A mixture of octanoic acid (**1g**, 5.0 mmol), 1-octanol (**2i**, 5.0 mmol) and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (0.025 mmol) in toluene (3.0 mL) was heated to reflux in a 25-mL round bottom flask equipped with distillation condenser and a water knockout vessel containing a quartz cotton plug and anhydrous magnesium sulfate to remove water. The consumption of reactants was monitored by GC. The reaction mixture was cooled after heating for 8 h, and diluted by addition of diethyl ether (15 mL). The ether solution was subjected to gas chromatographic analysis after addition of an appropriate amount of mesitylene as internal standard. **3gi** was isolated in 92% yield (purity: 97%) by distillation under reduced pressure, the GC yield was found in 99%.

Esters **3il** and **3im** are new compounds, and they were characterized by  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR, elemental analysis and GC-MS. **3ik** and **4** are known compounds and their structures were confirmed by  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR and GC-MS. The other esters are all known compounds and their identities were confirmed by GC and GC-MS comparison with the authentic samples. GC yields of esters were determined by addition of the appropriate internal standards.

#### Selected spectral data

**3ik**:  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  7.31~7.35 (m, 5H), 5.10 (s, 2H), 2.34 (m, 1H), 1.22~1.95 (m, 10H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  175.9, 136.3, 128.5, 128.1, 128.0, 65.9, 43.2, 29.0, 25.7, 25.4; GCMS  $m/z$  (% rel. inten.): 218 ( $\text{M}^+$ , 16), 111 (24), 91 (100), 83 (59), 55 (34).

**3il**:  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  7.33~7.42 (m, 4H), 5.18 (s, 4H), 2.37 (m, 1H), 1.22~1.94 (m, 10H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  175.7, 134.7, 129.5, 128.5, 63.6, 43.2, 29.0, 25.7, 25.4; GCMS  $m/z$  (% rel. inten.): 230 (10), 148 (9), 111 (82), 83 (100), 55 (21); Anal Calcd for  $\text{C}_{22}\text{H}_{30}\text{O}_4$ : C, 73.71; H, 8.44. Found C, 73.82; H, 8.41.

**3im**:  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  7.26~7.38 (m, 4H), 5.11 (s, 4H), 2.36 (m, 1H), 1.18~1.95 (m, 10H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  175.8, 136.7, 128.7, 127.6, 127.3, 65.6, 43.2, 29.0, 25.7, 25.4; GCMS  $m/z$  (% rel. inten.) 230 (7), 111 (99), 83 (100), 44 (20); Anal Calcd for  $\text{C}_{22}\text{H}_{30}\text{O}_4$ : C, 73.71; H, 8.44. Found C, 73.81; H, 8.44.

**4**:  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  4.14 (sb, 1H), 3.84 (s, 3H), 3.70 (s, 6H), 2.91 (d, 2H, AB,  $J = 15\text{Hz}$ ), 2.82 (d, 2H, AB,  $J = 15\text{Hz}$ );  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  173.9, 170.3, 73.3, 53.3, 52.1, 43.1;  $m/z$  (% rel. inten.): 175 (15), 143 (100), 111 (4), 101 (57), 59 (13), 43 (7).

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*Sample availability:* Available from the authors.

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