咪唑(啉)-2-羧酸盐作为潜在的/可热活化的 有机小分子催化剂催化转酯反应

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摘要: 采用咪唑(啉)-2-羧酸盐(ImCO₂)作为催化剂前驱体, 通过温度控制脱除 ImCO₂ 的 2-位羧酸根, 再原位释放出高活性的 *N*-杂环卡宾(NHCs), 进而催化转酯反应。研究了 NHCs 在苯甲酸乙酯与一元醇、二元醇及氨基醇反应体系中的催化活性。结果表明, 在该体系中不需要选用活化酯为原料, 无需加入分子筛或加大醇酯比提高产率, 仅用少量催化剂 (0.5 mol%), 在较短时间内 (3 h), 即可使反应转化率达到 95%。

关键词: *N*-杂环卡宾; 有机小分子催化剂; 咪唑(啉)-2-羧酸盐; 转酯反应; 非活性酯

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Imidazol(in)ium-2-carboxylates as Latent, Thermally Activated Organocatalysts for Transesterification Reactions

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Abstract: 1,3-Disubstituted imidazol(in)ium-2-carboxylates (ImCO₂) were used as precatalysts for transesterification reactions of unactivated ethyl benzoate with monohydric alcohols, dihydric alcohols, and amino alcohols. Highly active *N*-heterocyclic carbenes (NHCs) are usually not used directly as catalysts because of their air and moisture sensitivity. Here they were liberated in situ by thermal decarboxylation of ImCO₂ at designated temperatures. The results showed that the yield of the reactions reached up to 95% within 3 h using only 0.5 mol% catalyst. No active enol esters, molecular sieves, or a 20-fold excess of alcohol were used to drive the reaction to completion. It was proved that unsaturated imidazolium-2-carboxylates have a better activity than saturated species in this type of reaction. Different types of substituting groups of ImCO₂ exhibited varied transesterification activity.

Key words: *N*-heterocyclic carbene; organocatalyst; imidazol(in)ium-2-carboxylate; transesterification; unactivated ethyl benzoate

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Serving both as a key intermediate and as a protecting group in organic transformations, the ester/acyl moiety is an

important functional group in polymers, drugs, and biologically relevant compounds [1]. In addition, the ester unit has

been found ubiquitous industrial applications as a building block for transformations such as polymerization (ring opening of lactones), polycondensation, or macrolactonization reactions [2].

Transesterification is one of the major means of preparation of esters. The choice of catalyst is important for an effective transesterification reaction. Although organometallic catalysts [3,4] or strongly basic catalysts such as sodium hydride and potassium *tert*-butoxide [5] have been employed, they either were limited to acid-insensitive substrates or required high catalyst loading and long reaction times.

The versatile nucleophilic organic catalysts known as *N*-heterocyclic carbenes (NHCs) [6] have been shown to effectively mediate organic transformations due to their unique electronic and steric properties [7–9]. In 2002, Grasa et al. [10] and Nyce et al. [11] simultaneously reported the use of NHCs as efficient transesterification reaction catalysts. The utilization of NHCs was complicated by their air- and moisture-sensitivity that necessitated the use of stable carbene precursors to generate free NHCs in situ. Imidazolium precursor salts were commonly used from which NHCs were generated by adding potassium *tert*-butoxide in tetrahydrofuran (Scheme 1) [10–14]. However, this method requires two reaction steps and is restricted to base-tolerant substrates.

Scheme 1. Procedure for the generation of free NHCs in situ.

A few other strategies have thus been developed to facilitate their handling and to generate NHCs in situ without the need for a strong base. For instance, the thermal activation of 2-alkoxy [15], trichloromethyl [16] or pentafluorophenyl adducts [17] of NHCs generated free carbenes more conveniently (Scheme 2). However, the chloroform, pentafluorobenzene, and alcohols released from adducts remain in the reaction system and may potentially interfere with the transesterification reaction. Therefore, obtaining a reaction environment with simple NHCs only is difficult. Moreover, these methodologies cannot be applied to generate imidazol-2-ylidenes (unsaturated NHCs).

Scheme 2. Chloroform, pentafluorobenzene, and alcohol adducts of carbenes.

In contrast to the aforementioned 2-adducts of NHCs, imidazol(in)ium-2-carboxylates (ImCO₂) are readily formed by reactions of virtually all types of NHCs with CO₂ [18]. The ImCO₂ readily lose their CO₂ moiety upon heating or dissolution and have been extensively used as NHCs transfer agents in organometallic chemistry for the synthesis of NHC metal complexes [19,20]. Moreover, they were used occasionally as latent organic (pre)catalysts in organic [21–23] and polymer chemistry [24–26].

In this article, we describe the transesterification between the unactivated ethyl benzoate and monohydric alcohols, dihydric alcohols, and amino alcohols utilizing ImCO₂ as precatalysts. The free and pure NHCs were liberated in situ by thermal decarboxylation of the ImCO₂ with carbon dioxide eliminating spontaneously at designated temperatures (Scheme 3).

Scheme 3. The decarboxylation of ImCO₂.

1 Experimental

All starting materials and reagents were obtained from commercial sources and used as received unless otherwise noted. All reactions were performed under an argon atmosphere using standard Schlenk techniques. All glassware was dried overnight prior to use. Ethyl benzoate and benzyl alcohol were refluxed over calcium hydride (CaH₂) overnight and then distilled from CaH₂. Flash chromatography was performed on silica gel using ethyl acetate/hexane or dichloromethane/methanol mixtures.

N,N'-disubstituted ImCO₂ (**1a–1f**, Scheme 4) were prepared according to the literatures [27–31].

Scheme 4. A series of ImCO₂ prepared in this article.

¹H NMR and ¹³C NMR spectra were recorded at 300 and 125.5 MHz, respectively, in *d*-CHCl₃ on a Bruker DRX500

spectrometer. Chemical shifts were expressed in parts per million (ppm) using TMS as internal standard for ^1H NMR and for ^{13}C NMR spectra.

1.1 Transesterification of ethyl benzoate with monohydric alcohol

Catalyst **1** (0.5 mol%) was added to a mixture of ethyl benzoate (3.0 g, 20 mmol) and benzyl alcohol (**3a**, 5.5 g, 50 mmol) under argon atmosphere and magnetic stirring. The mixture was processed continuously for 3 h at 120 °C in an oil bath. The resulting mixture was cooled and purified by column chromatography using an ethyl acetate/hexane ($V/V = 20:1$) mixture to yield benzyl benzoate (**4a**, Scheme 5). **4a**: colorless liquid. ^1H NMR: δ 5.36 (s, 2H), 7.40–7.56 (m, 8H), 8.03 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR: δ 66.7, 128.1, 128.2, 128.3, 128.6, 129.7, 130.1, 132.9, 136.1, 166.4.

Scheme 5. Reaction of ethyl benzoate with monohydric alcohol catalyzed by ImCO_2 .

1-Phenylethyl benzoate (**4b**) was prepared from ethyl benzoate and 1-phenylethanol (**3b**) using the same procedure. **4b**: colorless liquid. ^1H NMR: δ 1.62 (d, $J = 8.4$ Hz, 3H), 5.40 (m, 1H), 7.38–7.56 (m, 8H), 8.05 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR: δ 19.5, 72.1, 127.1, 127.6, 128.6, 128.9, 129.9, 130.1, 133.0, 141.8, 165.9.

Cyclohexyl benzoate (**4c**) was prepared from ethyl benzoate and cyclohexanol (**3c**) using the same procedure. **4c**: colorless liquid. ^1H NMR: δ 1.49 (m, 2H), 1.53 (m, 4H), 1.99 (m, 4H), 3.91 (m, 1H), 7.56–7.65 (m, 4H), 8.07 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR: δ 24.1, 25.7, 31.1, 70.6, 128.6, 129.9, 130.1, 133.0, 165.9.

1.2 Transesterification of ethyl benzoate with dihydric alcohol

Catalyst **1a** (0.5 mol%) was added to a mixture of ethyl benzoate (7.5 g, 50 mmol) and glycol (**3d**, 1.2 g, 20 mmol) under argon atmosphere and magnetic stirring. The mixture was stirred at 120 °C for 3 h in an oil bath. The resulting mixture was cooled and purified by column chromatography

using an ethyl acetate/hexane mixture to yield 2-hydroxyethyl benzoate (**4d**, Scheme 6) and ethane-1,2-diyl dibenzoate (**4g**). **4d**: colorless liquid. ^1H NMR: δ 2.09 (s, 1H), 3.95 (t, $J = 4.7$ Hz, 2H), 4.46 (t, $J = 4.7$ Hz, 2H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 8.06 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR: δ 61.4, 66.7, 128.4, 129.7, 129.8, 133.2, 166.9. **4g**: white solid, m.p. 48–50 °C. ^1H NMR: δ 4.6 (s, 4H), 7.44 (t, $J = 7.6$ Hz, 4H), 7.56 (t, $J = 7.4$ Hz, 2H), 8.06 (d, $J = 7.1$ Hz, 4H). ^{13}C NMR: δ 62.7, 128.4, 129.7, 129.8, 133.1, 166.4.

Scheme 6. Reaction of ethyl benzoate with dihydric alcohols catalyzed by catalyst **1a**.

3-Hydroxypropyl benzoate (**4e**) and propane-1,3-diyl dibenzoate (**4h**) were prepared from ethyl benzoate and 1,3-propanediol using the same procedure. **4e**: colorless liquid. ^1H NMR: δ 1.99 (m, 2H), 2.62 (s, 1H), 3.75 (t, $J = 6.2$ Hz, 2H), 4.46 (t, $J = 6.2$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 8.02 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR: δ 31.8, 58.9, 61.8, 128.3, 129.5, 130.0, 133.9, 166.9. **4h**: white solid, m.p. 65–67 °C. ^1H NMR: δ 2.27 (m, 2H), 4.51 (t, $J = 6.2$ Hz, 4H), 7.42 (t, $J = 7.6$ Hz, 4H), 7.55 (t, $J = 7.4$ Hz, 2H), 8.05 (d, $J = 7.3$ Hz, 4H). ^{13}C NMR: δ 28.2, 61.7, 128.2, 129.5, 130.0, 132.8, 166.3.

4-Hydroxybutyl benzoate (**4f**) and butane-1,4-diyl dibenzoate (**4i**) were prepared from ethyl benzoate and 1,4-butanediol using the same procedure. **4f**: colorless liquid. ^1H NMR: δ 1.68 (m, 2H), 1.84 (m, 2H), 2.51 (s, 1H), 3.67 (t, $J = 6.5$ Hz, 2H), 4.32 (t, $J = 6.6$ Hz, 2H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 8.01 (d, $J = 7.1$ Hz, 2H). ^{13}C NMR: δ 25.1, 62.0, 64.7, 128.2, 129.4, 130.2, 132.8, 166.6. **4i**: white solid, m.p. 82–84 °C. ^1H NMR: δ 1.96 (s, 4H), 4.41 (s, 4H), 7.43 (t, $J = 7.7$ Hz, 4H), 7.56 (t, $J = 7.4$ Hz, 2H), 8.05 (d, $J = 7.3$ Hz, 4H). ^{13}C NMR: δ 25.6, 64.4, 128.3, 129.5, 130.3, 132.9, 166.6.

1.3 Transesterification of ethyl benzoate with amino alcohol

Catalyst **1** (0.5 mol%) was added to a mixture of ethyl benzoate (**5a**, 3.0 g, 20 mmol) and ethanolamine (1.8 g, 30 mmol) under argon atmosphere and magnetic stirring. The mixture was stirred at 120 °C for 3 h in an oil bath. The

resulting mixture was cooled and purified by column chromatography using a dichloromethane/methanol mixture to yield *N*-(2-hydroxyethyl) benzamide (**6a**, Scheme 7) [34]. **6a**: white solid, m.p. 42–44 °C. ¹H NMR: δ 2.14 (s, 1H), 3.64 (m, 2H), 3.85 (t, *J* = 5.0 Hz, 2H), 6.60 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 2H). ¹³C NMR: δ 42.7, 61.5, 126.9, 128.4, 131.5, 134.0, 168.8.

Scheme 7. Reaction of ethyl benzoate with amino alcohols catalyzed by ImCO₂.

N-(3-hydroxypropyl) benzamide (**6b**) was prepared from ethyl benzoate and propanolamine (**5b**) using the same procedure. **6b**: white solid, m.p. 46–48 °C. ¹H NMR: δ 1.74 (m, 2H), 3.21 (s, 1H), 3.40 (s, 1H), 3.52 (q, *J* = 6.1 Hz, 2H), 3.65 (t, *J* = 5.6 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 2H). ¹³C NMR: δ 31.8, 37.3, 59.8, 126.9, 128.4, 131.4, 134.1, 168.6.

(*S*)-*N*-(1-hydroxy-3-phenyl-2-propenyl) benzamide (**6c**) was prepared from ethyl benzoate and (*S*)-2-amino-3-phenyl-1-propanol (**5c**) using the same procedure. **6c**: white solid, m.p. 167–168 °C. ¹H NMR: δ 2.63 (t, *J* = 5.2 Hz, 1H), 3.01 (d, *J* = 7.2 Hz, 2H), 3.81 (m, 2H), 4.38 (m, 1H), 6.36 (s, 1H), 7.27–7.51 (m, 8H), 7.67 (d, *J* = 7.1 Hz, 2H). ¹³C NMR: δ 37.8, 53.4, 64.4, 126.8, 128.6, 128.8, 129.3, 130.1, 131.6, 134.4, 168.0.

2 Results and discussion

2.1 Transesterification reaction of unactivated ethyl benzoate with monohydric alcohols

The synthesis of benzyl esters has been seldom reported. We studied the transesterification of benzyl alcohol **3a** with unactivated ethyl benzoate using the ImCO₂ as an effective acyl-transfer catalyst. To suppress the reversibility of the transesterification, enol esters have been always used as acylation agents [1] and molecular sieves or a 20-fold excess of alcohol [11] have been commonly added to drive the reaction to completion in earlier studies. Different molar ratios of benzyl alcohol and unactivated ethyl benzoate were

examined here in the transesterification catalyzed by 0.5 mol% of **1a** (Table 1, entries 1 to 3) at 120 °C. The results showed that yield up to 97% was obtained of the reaction between the ethyl benzoate and the benzyl alcohol when the molar excess of benzyl alcohol was 2.5 times the amount of ethyl benzoate. Thus, the amount of alcohol was greatly reduced with respect to the literature.

Table 1 Reaction of ethyl benzoate with monohydric alcohol catalyzed by ImCO₂

Entry	Catalyst	Monohydric alcohol	<i>n</i> (ethyl benzoate)/ <i>n</i> (alcohol)	Yield (%)
1	1a	3a	1:2.5	97
2	1a	3a	1:1.5	80
3	1a	3a	1:1	65
4	1b	3a	1:2.5	89
5	1c	3a	1:2.5	85
6	1d	3a	1:2.5	85
7	1e	3a	1:2.5	13
8	1f	3a	1:2.5	30
9	1a	3b	1:2.5	86
10	1a	3c	1:2.5	83

Reaction conditions: 0.5 mol% catalyst, 120 °C, 3 h.

The catalytic activity of a series of ImCO₂ catalysts was studied, including IPrCO₂ (**1a**), IMesCO₂ (**1b**), EMimCO₂ (**1c**), BBimCO₂ (**1d**), SIPrCO₂ (**1e**), and SIMesCO₂ (**1f**). As can be seen in Table 1, the unsaturated imidazolium-2-carboxylates (**1a–1d**) were more active than the saturated species (**1e** and **1f**). They exhibited excellent catalytic activity and yields (85%–97%) in the presence of 2.5 mol% alcohol and 0.5 mol% of **1a–1d**. However, poor transesterification yields were obtained under the same conditions when the catalysts were changed to the saturated ImCO₂ (**1e** and **1f**, yield = 13% and 30%, respectively). It was reported by Wanzlick and Kleiner [32] that the imidazolidin-2-ylidene was prone to dimerization and the dimeric electron-rich olefins were gained. In addition to the possibility of dimer formation, the different nucleophilicity of the saturated and unsaturated carbenes may also influence the reaction. Saturated NHCs are stronger nucleophiles [33] and can easily attract the carbonyl carbon atom of esters and form acyl-imidazolin intermediates (Scheme 8). The C–C bond between the saturated carbene and the carbonyl carbon was stable. This made the release of free carbene difficult in

Scheme 8. NHCs in the transesterification reaction.

the next reversible step and the carbene was prevented from participating in the catalytic cycle of transesterification.

Unsaturated ImCO₂ with different substituting groups also influenced the efficiency of the transesterification. The corresponding aryl-substituted ImCO₂, **1a** and **1b**, gave higher product yields (Table 1, entries 1 and 4) than the alkyl-substituted **1c** and **1d** (Table 1, entries 5 and 6). All previous reports have shown that the alkyl-substituted NHCs have relatively strong activity due to their higher nucleophilicity and smaller steric hindrance [34,35]. The opposite results obtained here were probably due to that the alkyl-substituted ImCO₂ with high activity promoted the reverse reaction simultaneously, which lead to the decline of the yield.

We investigated the transesterification of different monohydric alcohols, such as 1-phenylethanol (**3b**) and cyclohexanol (**3c**), with ethyl benzoate in the presence of 0.5 mol% catalyst **1a**, which gave high product yield (Table 1, entries 9 and 10). It proved that the unsaturated ImCO₂ were efficient organic catalysts for transesterification of unactivated ethyl benzoate with both primary alcohols and secondary alcohols.

2.2 Transesterification of ethyl benzoate with dihydric alcohols

The catalytic activity of the ImCO₂, which was excellent in the transesterification of unactivated ethyl benzoate with monohydric alcohols, was investigated by replacing the monohydric alcohols with dihydric ones in order to test the range and the generality of the reaction. Three dihydric alcohols, i.e. glycol (**3d**), 1,3-propanediol (**3e**), and 1,4-butanediol (**3f**), were examined at 120 °C with IPrCO₂ as the catalyst and a 2.5-fold molar excess of ethyl benzoate. Two kinds of products, monosubstituted and disubstituted, were obtained because of the two hydroxyl groups of dihydric alcohols.

Under the same reaction conditions as before, the yields improved with increasing carbon chain length in dihydric alcohols (Table 2). The reason for the yield increase may be due to the extensibility and flexibility of the carbon chain in dihydric alcohols, which leads to facile contact with ethyl

Table 2 Reaction of ethyl benzoate with dihydric alcohols catalyzed by catalyst **1a**

Entry	Dihydric alcohol	Yield (%)	Selectivity (%)	
			Monosubstituted	Disubstituted
1	3d	41	42 (4d)	58 (4g)
2	3e	79	54 (4e)	46 (4h)
3	3f	95	57 (4f)	43 (4i)

Reaction conditions: 0.5 mol% catalyst, ethyl benzoate/dihydric alcohol molar ratio = 2.5/1, 120 °C, 3 h.

benzoate. A monosubstituted product and a disubstituted product were obtained, because with dihydric alcohols two hydroxide radicals could participate in the transesterification reaction, respectively. The ratios of monosubstituted and disubstituted products were similar when ethyl benzoate reacted with any of the three kinds of dihydric alcohols. The disubstituted product of glycol **4g** was gained in 58% yield (percentage of the total products) while **4d** was obtained at 42% yield. The yield of the monosubstituted products of both 1,3-propanediol and 1,4-butanediol were higher than the disubstituted ones, 54% **4e** and 57% **4f**, respectively. It can be assumed from the above results that the yield of monosubstituted products may increase and the ones the disubstituted products may decrease when dihydric alcohols with longer carbon chain were chosen.

2.3 Synthesis of amides

The synthesis of amides is important in many areas of chemistry, including peptide, polymer, and complex molecule synthesis. Herein, we report the amidation of unactivated esters with amino alcohols catalyzed by ImCO₂. Movassaghi and Schmidt [36] suggested that the reaction mechanism involves a carbon-centered Brønsted base nucleophile activation, which initiates a transesterification. This activation is then followed by a rapid N→O acyl-transfer reaction.

The completion of the catalytic amidation reaction does not require the use of excess coupling components, molecular sieves, or activated esters. The catalysts with different structure listed in Scheme 8 were tested in the amidation reaction of ethyl benzoate with ethanolamine **5a**. This procedure was carried out at 120 °C for 3 h in the presence of 0.5 mol% catalyst with ethanolamine in a 1.5-fold excess of ethyl benzoate. The transesterification equilibria were influenced by the nature of the nucleophile [2]. The stronger nucleophilic alkyl-substituted **1c** and **1d** performed better (yield = 99% and 90%, respectively, Table 3, entries 3 and 4) than the aryl-substituted **1a** and **1b** (yield = 85% and

Table 3 Reaction of ethyl benzoate with amino alcohols catalyzed by ImCO₂

Entry	Catalyst	Amino alcohol	Amide	Yield (%)
1	1a	5a	6a	85
2	1b	5a	6a	83
3	1c	5a	6a	99
4	1d	5a	6a	90
5	1e	5a	6a	41
6	1f	5a	6a	30
7	1a	5b	6b	89
8	1a	5c	6c	77

Reaction conditions: 0.5 mol% catalyst, ethyl benzoate/amino alcohol molar ratio = 1/1.5, 120 °C, 3 h.

83%, respectively) in the model reaction. It was demonstrated that the unsaturated imidazolium-2-carboxylates (**1a–1d**) exhibited better activity than the saturated species (**1e** and **1f**) as analogous to the results of the reaction of benzyl alcohol **3a** with unactivated ethyl benzoate. Various substrates were investigated. Propanolamine **5b** gave the product at 89% yield, while (*S*)-2-amino-3-phenyl-1-propanol **5c** led to a lower conversion (possibly due to its steric bulk, Table 3, entries 7 and 8).

3 Conclusions

The ImCO₂ could catalyze efficiently both transesterification and amidation reactions. The application range of this method was shown to include reactions of unactivated ethyl benzoate with monohydric alcohols, dihydric alcohols, and amino alcohols. The conversions of the reactions were satisfactory without need to use activated esters, molecular sieves, or a 20-fold excess of alcohol. The ImCO₂ precatalysts decarboxylated at a designated temperature to liberate NHCs in situ for catalysis of the transesterification. Carbon dioxide is eliminated in this process which spontaneously escapes from the leaving a controlled reaction environment with simple NHCs behind. The unsaturated imidazolium-2-carboxylates (**1a–1d**) displayed a better catalytic activity than the saturated species (**1e** and **1f**) both in the reactions of benzyl alcohol and ethanolamine with ethyl benzoate. The alkyl-substituted ImCO₂ (**1c** and **1d**) have a relatively high activity due to their higher nucleophilicity and smaller steric hindrance.

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