A novel and highly effective catalytic system for alkoxycarbonylation of (S)-propylene oxide

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Abstract

Methyl (*S*)-β-hydroxybutyrate, the important chiral building block for organic synthesis was produced in high yield from the methoxycarbonylation of (*S*)-propylene oxide ((*S*)-PO) using a catalytic system consisting of dicobalt octacarbonyl [$Co_2(CO)_8$] and pyrazole. The effects of different additives, temperature and CO pressure were investigated. The reaction was greatly influenced by the variation of temperature, both the conversion of (*S*)-PO and the selectivity of methyl (*S*)-β-hydroxybutyrate decreased with increasing temperature (above 80 °C). Nevertheless, the enantiomeric excess (ee) of methyl (*S*)-β-hydroxybutyrate is independent of the parameter of reaction temperature, no racemization reaction takes place even the reaction temperature reaches 150 °C. A possible process for the formation of ethers and diethers was presented. The reaction has a bright future in an industrial scale.
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1. Introduction

The synthesis of difunctional β-hydroxyesters is achieved highly attractive attention due to their versatilities in organic and polymer chemistry. β-Hydroxyesters, especially optically active β-hydroxyesters are important chiral building blocks for the synthesis of many pharmaceuticals, agrochemicals, fragrances and/or natural products [1]. For example, the (*S*)-β-hydroxyesters are used for synthesizing pheromones [2], carbapenem antibiotics [3,4], (*S*)-sulcatol (Pesticide) [5], the flavourings (*S*)-lavandulol and (*S*)-citronellol [6], L-carnitine [7], D-acosamin [8], griseoviridin precursor [9], etc. Furthermore, the β-hydroxyesters are also useful intermediates for the synthesis of 1,3-alkanediols, the important start materials for polyesters, and poly-β-hydroxyalkanoates, a class of biodegradable polyesters occurred in nature, sharing many of the physical and mechanical properties of poly(propylene) [10,11].

Several processes for the synthesis of enantiopure β-hydroxyesters have been developed including routes based on the asymmetric Reformatsky reaction [12–14], the asymmetric hydrogenation of β-keto-esters using chiral ruthenium catalysts [15–21] and the biological reduction of β-keto-esters using baker's yeast [22–24]. Nevertheless, these processes suffer from several limitations. In the asymmetric Reformatsky reaction, the reactant, α-halogen ester, is not a readily available commercial chemical, a large number of zinc powder is necessary and the yield of enantiopure β-hydroxyesters is very low; in the asymmetric hydrogenation of β-keto-esters, the metal catalysts employed are quite expensive and sensitive towards poisoning, the hydrogenation process itself usually requires high pressure reactors; the biological reduction of β-keto-esters is also of limited success, due to the low product yield and especially, high costs.

Obviously, neither asymmetric Reformatsky reaction nor reduction of β-keto-esters can be considered as an environmentally benign, atom-economy process, and a practical method for an industrial production of enantiopure β-hydroxyesters.

Now, with the increasing awareness of the environmental and the importance of synthetically useful carbonyl group,

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the development of environmentally benign and clean synthetic methodologies of organic carbonyl compounds has received a great deal of attention. Transition metal based carbonylation chemistry [25–27] using carbon monoxide as a "carbonyl source", has seen exceptional progress in both academic and industrial level during the last century. Among numerous carbonylation reactions, the direct insertion of CO into a carbon–heteroatom bond of a heterocyclic compound has attracted much more attention. By this very convenient and effective one-step procedure, lactams, lactones, etc. can be obtained with high yields [28]. Eisenmann et al. reported the carboxymethylation of propylene oxide [29] using cobalt catalysts in the presence of CO and alcohols for the formation of difunctional β-hydroxyesters under high pressures of carbon monoxide as early as 1961. Ensuing years saw little development of catalytic epoxide carbonylation until the milestone achievements reported by Drent and Kragtwijk in their European patent [30], involving the use of $Co_2(CO)_8$ and 3-hydroxypyridine to promote the carbonylation of ethylene oxide. In recent years, significant innovations have arisen successively in the area of the cobalt-catalyzed carbonylation of epoxides to synthesize β-lactones [31–40] and/or poly-β-hydroxyalkanoates [41–46] or β-hydroxyesters [47–49] since epoxides are readily available by epoxidation of olefins [50,51]. Specifically, enantiomerically pure epoxides are easily obtained by the well-established method, hydrolytic kinetic resolution of epoxides, developed by Jacobsen and co-workers [52].

Herein, we present a catalyst system composed of the cobalt carbonyl complex and pyrazole that could be more effective for the formation (S)-β-hydroxyesters by alkoxycarbonylation of (S)-propylene oxide in the presence of alcohol. To the best of our knowledge, the $Co_2(CO)_8$/pyrazole catalyst system has not be reported previously.

2. Experimental

2.1. General

$Co_2(CO)_8$ was synthesized according to literature [53], pyrazole, 3-hydroxypyridine and 2-hydroxypyridine were purchased from Fluka. (S)-Propylene oxide (supplied kindly by Professor Kuiling Ding in Shanghai Institute of Organic Chemistry) and alcohols were freshly distilled from appropriate drying agents under an argon atmosphere prior to use. Carbon monoxide with a purity of 99.99% was commercially available. All other reagents were of analytical grade and were used as received. Gas chromatographic analyses of the product mixture were made on a TM (Shanghai) 7890 gas chromatograph equipped with a flame ionization detector and a PEG-20 000 capillary column (0.32 μm × 100 m) and the ee values were determined using Hewlett Packard 6890 gas chromatograph equipped with a flame ionization detector and a Supelco γ-Dex 225 capillary column (0.25 μm × 30 m). The identity of reaction products was confirmed with a Hewlett Packard 6890-5973 GC–MS.

2.2. Catalytic reactions

All carbonylation experiments were carried out in a 35 mL stainless steel autoclave equipped with magnetic stirring. In a typical experiment, alcohol (4 mL), pyrazole (0.25 mmol), $Co_2(CO)_8$ (0.125 mmol) and (S)-propylene oxide (1 mL, 14.3 mmol) were successively charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide to a pressure of 6.0 MPa. The autoclave was placed in a preheated oil bath and heated at the required temperature for 6 h. After the reaction, the autoclave was cooled, excess gas purged, and the samples were taken out of the reaction solution and passed through a small amount of silica gel, then were qualitatively and quantitatively analyzed by gas chromatograph or GC–MS.

3. Results and discussion

The synthesis of β-hydroxybutyrate was conducted under various reaction conditions and the influence of each reaction parameter was studied in detail. For the initial optimization, the reaction was carried out using (S)-PO (ee 80%), which leads to formation of methyl (S)-β-hydroxybutyrate.

3.1. Influence of auxiliary agent

N-donating compounds (e.g. pyridine, imidazole) are good ligands and have broadly used in the field of homogeneous catalysis [54]. A series of N-containing and other basic compounds had been investigated in the cobalt-catalyzed methoxycarbonylation of (S)-propylene oxide (ee 80%) (Table 1). Initially, the catalytic activity of $Co_2(CO)_8$ without any additive was examined and only 70.3% conversion of (S)-propylene oxide (ee 80%) was obtained (Table 1, entry 1). The main byproducts were diethers (2,2-dimethoxypropane, 1,2-dimethoxypropane) and ethers (1-methoxypropan-2-ol and 2-methoxypropan-1-ol), etc. This result can be reasonably explained by the equilibrium mixture of $Co_2(CO)_8$ and $[Co(MeOH)_6][Co(CO)_4]_2$ under 6.0 MPa CO pressure[55,56]. In order to further improve both the catalytic activity of $Co_2(CO)_8$ and selectivity of methyl (S)-β-hydroxybutyrate, different N-containing compounds and other organic or inorganic compounds were investigated. As shown in Table 1, 74–77 ee% of methyl (S)-β-hydroxybutyrate were achieved in all cases. Among those additives, $Co_2(CO)_8$/pyrazole had the highest catalytic activity, corresponding to a (S)-propylene oxide conversion of 96.8% and a methyl (S)-β-hydroxybutyrate selectivity of 94.1% (Table 1, entry 2). And 3-hydroxypyridine also gave better results in methoxycarbonylation of (S)-propylene oxide, with a (S)-propylene oxide conversion of 81.5% and a methyl (S)-β-hydroxybutyrate selectivity of 95.4% (Table 1, entry 4). The bulky N-containing compounds, carbazole and 8-hydroxy quinoline, had different influence on the results of the reaction, the former had very little influence but the latter gave very poor result that the selectivity of methyl (S)-β-hydroxybutyrate was reduced largely (Table 1, entries 9 and 10). 2,2-Bipyridine, 4,4-bipyridine and 1,10-phenanthroline containing expanded

Table 1

Methoxycarbonylation in the presence of different additives[a]

Methyl (S)-β-hydroxybutyrate

(5)

2,2-dimethoxypropane (1) 1-methoxypropan-2-ol (2) 1,2-dimethoxypropane (3) 2-methoxypropan-1-ol (4)

Entry	Additive	Conversion of (S)-PO (%)[b]	Selectivity (%)[b]					Yield of 5 (%)[c]	ee (%)[d]
			1	2	3	4	5		
1	–	70.3	2.6	3.0	0.1	1.6	90.2	63.4	75
2	Pyrazole	96.8	1.4	1.0	0.3	0.7	94.1	91.1	77
3	Imidazole	68.1	0	2.3	0	1.0	94.9	64.6	77
4	3-Hydroxypyridine	81.5	0.2	1.5	0.1	0.7	95.4	77.8	75
5	2-Hydroxypyridine	76.9	1.4	2.6	0.2	1.5	92.6	71.2	77
6	2-Aminopyridine	49.2	0.2	3.8	0.2	1.6	92.9	45.7	75
7	4-Aminopyridine	61.2	0	3.6	0.2	1.1	94.2	57.7	74
8	4-Dimethylamino-pyridine	55.7	0	3.7	0	1.3	93.9	52.3	75
9	Carbazole	71.5	1.7	2.5	0	1.5	91.6	65.5	76
10	8-Hydroxy quinoline	75.0	4.7	19.6	1.7	21.4	48.1	36.1	74
11	2,2-Bipyridine	44.4	0	4.1	0.5	1.5	93.4	41.5	76
12	4,4-Bipyridine	35.6	0	6.2	0	0	93.8	33.4	75
13	1,10-Phenanthroline	37.1	0	4.3	0.5	1.4	93.5	34.7	74
14	Triphenylamine	72.2	2.3	2.9	0.3	1.7	90.4	65.3	77
15	Triphenylphosphine	10.8	5.9	23.6	0	6.2	64.4	7.0	–
16	Phenol	58.7	2.4	3.1	0	1.7	90.3	53.0	77
17	4-Aminophenol	70.8	3.5	2.6	0.3	1.5	89.9	63.6	76
18	NBu$_4$Br	54.2	0	4.0	0.1	1.5	92.9	50.4	76
19	NaOAc·3H$_2$O	51.3	0	3.9	0	1.4	93.6	48.0	76
20	K$_2$CO$_3$	38.4	0	3.1	0	1.0	94.8	36.4	75
21	Cs$_2$CO$_3$	55.3	0	3.2	0	1.0	95.8	53.0	77
22	4-Aminobenzene sulfonic acid	62.3	3.2	13.1	0.5	11.7	69.6	43.4	75
23	Aminosulfonic acid	70.9	4.1	11.8	0.4	10.0	71.8	50.9	76
24	p-Toluenesulfonic acid	77.4	2.1	22.1	0.6	21.2	52.4	40.6	74

[a] Reaction conditions: 1 mL (14.3 mmol) (S)-propylene oxide (ee 80%), 4 mL methanol, 0.87 mol% Co$_2$(CO)$_8$. 1.74 mol% additive, 6.0 MPa CO, 8 °C, 6 h.

[b] Determined by GC.

[c] Yield = conversion × selectivity.

[d] The ee values (%) of methyl β-hydroxybutyrate were determined by GC on a Supelco γ-Dex 225 column. The absolute configuration is S.

conjugated ring system led to a rather low yield of methyl (S)-β-hydroxybutyrate (Table 1, entries 11–13). It is may be due to their larger steric blocking, which is unfavourable to the interruption of the Co–Co bond in Co$_2$(CO)$_8$ in forming the previous active catalyst species Co(CO)$_4^-$ anion. Triphenylamine gives moderate yield (65.3%) of the desired product (Table 1, entry 14). However, conventional ligand triphenylphosphine (TPP) inhibited the reaction and led to significantly lower conversion (10.8%) and ester formation (<10%) (Table 1, entry 15). When phenol replaces N-containing ligands in the carbonylation reaction, it also displayed poorer activity (Table 1, entry 16). Other inorganic bases also gave poor results in the conversion of (S)-propylene oxide (Table 1, entries 17–21). On the contrary, the contents of products from etherification reactions increased

rapidly when acidic compounds were added to the reaction system, that is to say, the relative distribution of byproducts changes dramatically (Table 1, entries 22–24).

3.2. Effect of the amount of Co$_2$(CO)$_8$

Following, influences of the concentrations of Co$_2$(CO)$_8$ catalyst on the carbonylation reaction were presented in Table 2. When the amount of pyrazole kept at 0.25 mmol, the conversion of (S)-propylene oxide increased from 10.1% to 96.8% when the amount of Co$_2$(CO)$_8$ increased from 0.016 mmol to 0.125 mmol and the yield of methyl (S)-β-hydroxybutyrate increased sharply from 5.9% to 91.1%, at the same time, the ee value of methyl (S)-β-hydroxybutyrate had a little change (Table 2, entries 1–4).

Table 2
Effect of the amount of $Co_2(CO)_8$ and pyrazole on the methoxycarbonylation of (S)-propylene oxide[a]

Entry	$Co_2(CO)_8$ (mmol)	Conversion of (S)-PO (%)	Selectivity (%)					Yield of 5 (%)	ee (%)
			1	2	3	4	5		
1	0.0156	10.1	0	29.4	4.1	8.5	57.9	5.9	–
2	0.0312	22.5	0	9.5	0	3.0	86.0	19.4	75
3	0.0625	72.3	0.4	2.7	0.2	1.3	93.3	67.5	74
4	0.125	96.8	1.4	1.0	0.3	0.7	94.1	91.1	77

[a] Reaction conditions: 1 mL (14.3 mmol) (S)-propylene oxide (ee 80%), 0.25 mmol pyrazole, 4 mL methanol, 6.0 MPa CO, 80 °C, 6 h. Others are the same as in Table 1.

Table 3
Effect of the amount of pyrazole on the methoxycarbonylation of (S)-propylene oxide[a]

Entry	Pyrazole (mmol)	Conversion of (S)-PO (%)	Selectivity (%)					Yield of 5 (%)	ee (%)
			1	2	3	4	5		
1	0	70.3	2.6	3.0	0.1	1.6	90.2	63.4	75
2	0.125	94.6	1.5	1.2	0.3	0.7	93.8	88.7	75
3	0.25	96.8	1.4	1.0	0.3	0.7	94.1	91.1	77
4	0.375	96.8	0.7	1.0	0.2	0.6	95.0	92.0	76
5	0.5	97.5	0.5	0.9	0.2	0.5	97.6	95.2	75

[a] Reaction conditions: 1 mL (14.3 mmol) (S)-propylene oxide (ee 80%), 0.125 mmol $Co_2(CO)_8$, 4 mL methanol, 6.0 MPa CO, 80 °C, 6 h. Others are the same as in Table 1.

3.3. Effect of the amount of pyrazole

On the other hand, an increase of the amount of pyrazole to 0.25 mmol resulted in a significant increase in the conversion of (S)-propylene oxide, at the same time, the selectivity of methyl (S)-β-hydroxybutyrate changed slightly (Table 3, entries 1–3). The consequence of a further increase in the amount of pyrazole, however, was no significant change in the conversion, the selectivity and the ee value.

3.4. Effect of CO pressure

A significant drawback associated with using CO as the reagent in organic synthesis is the potential dangers associated with operating at high reaction pressures. Next, we studied the parameter of the carbon monoxide pressure (Fig. 1). To our surprise, we found that CO pressures did not influence significantly the activity, the ee value and the production distribution. Since high pressure conditions make them expensive for industry and difficult to handle in laboratory and industry, the observation made the present carbonylation catalyst even more attractive.

3.5. Effect of temperature on the methoxycarbonylation of (S)-propylene oxide

With optimal conditions, the reaction temperature was screened. Clearly, the methoxycarbonylation was greatly influenced by the variation of temperature. It should be noticed that the temperature of the reaction exerted little influence on the ee values. Decreasing the temperature below the optimal level (80 °C) (Table 4, entry 4) resulted in a dramatic decrease in catalytic activity (Table 4, entries 1–3). When the reaction temperature was too low, propylene oxide may not be activated.

However, at temperatures higher 80 °C, both the conversion of (S)-propylene oxide and the selectivity of methyl (S)-β-hydroxybutyrate decreased dramatically (Table 4, entries 5–8). At higher reaction temperature, deactivation of the catalyst became more pronounced because the reaction is an exothermic reaction.

Nevertheless, even the temperature reached as high as 150 °C, there was almost no change in the ee values (ee 75%) (Table 4, entry 8). It may be concluded that the temperature of the reaction was an important factor for the catalytic activity but presented little influence on the ee value of the ester.
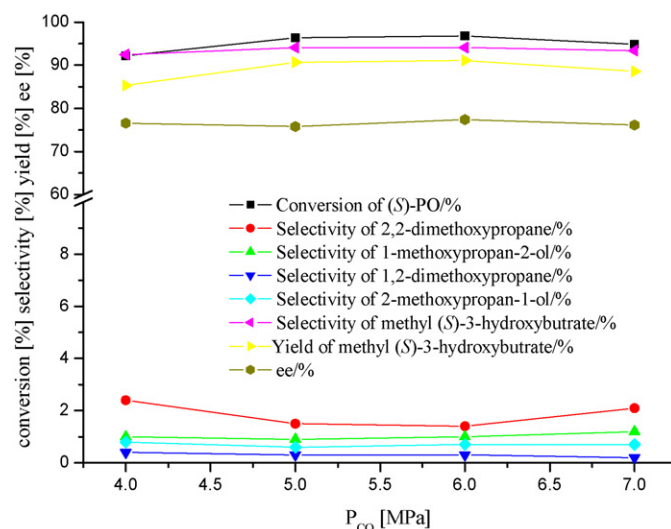

Fig. 1. Influence of the carbon monoxide pressure on conversion, selectivity, yield and ee value. Reaction conditions: 1 mL (14.3 mmol) (S)-propylene oxide (ee 80%), 4 mL methanol, 0.87 mol% $Co_2(CO)_8$, 1.74 mol% pyrazole, 80 °C, 6 h.

Table 4
Effect of temperature on the methoxycarbonylation of (S)-propylene oxide[a]

| Entry	T (°C)	Conversion of (S)-PO (%)	Selectivity (%)					Yield of 5 (%)	ee (%)
			1	2	3	4	5		
1	50	60.3	0	0.8	0	0.3	97.9	59.0	74
2	60	69.4	0	1.0	0	0.5	97.3	67.5	74
3	70	86.6	0.2	1.0	0.1	0.5	95.9	83.0	76
4	80	96.8	1.4	1.0	0.3	0.7	94.1	91.1	77
5	90	94.7	2.5	1.1	0.3	0.8	92.5	87.6	75
6	100	87.4	2.0	1.2	1.2	1.2	91.2	79.7	75
7	130	79.6	9.8	2.3	2.7	2.1	80.2	63.8	76
8	150	59.5	21.2	3.9	7.4	3.9	61.0	36.3	75

[a] Reaction conditions: 1 mL (14.3 mmol) (S)-propylene oxide (ee 80%), 4 mL methanol, 0.87 mol% $Co_2(CO)_8$, 1.74 mol% pyrazole, 6.0 MPa CO, 6 h. Others are the same as in Table 1.

3.6. Influence of reaction time

The influence of reaction time on the methoxycarbonylation of (S)-propylene oxide was also represented in Fig. 2. It was observed that the conversion of (S)-propylene oxide was increased with the increase of the reaction time. It can be seen that almost quantitative conversion (94.6%) could be achieved at 6 h. No further increase in the conversion of (S)-propylene oxide was observed above 6 h.

3.7. Alkoxycarbonylation of (S)-propylene oxide in different alcohols

Next, the general scope of our catalyst system for the alkoxycarbonylation of (S)-propylene oxide in different alcohols were investigated (Table 5). Methoxycarbonylation using the enantiomerically pure (S)-propylene oxide (ee 100%) gave exclusively methyl (S)-β-hydroxybutyrate (Table 5, entry 1). Middle conversion and excellent selectivity

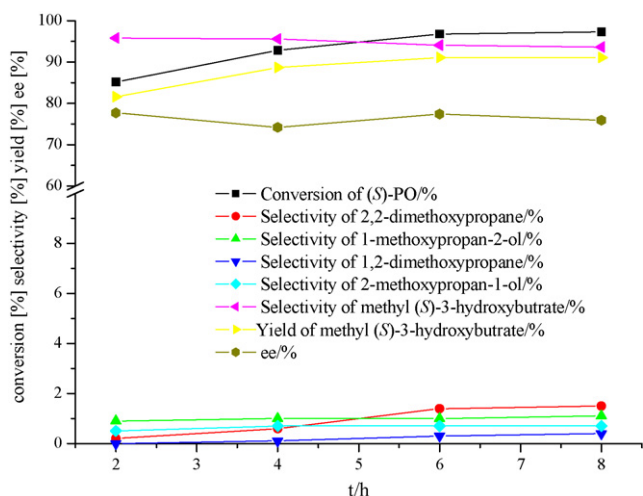Scheme 1. A plausible process for the formation of ethers and diethers.
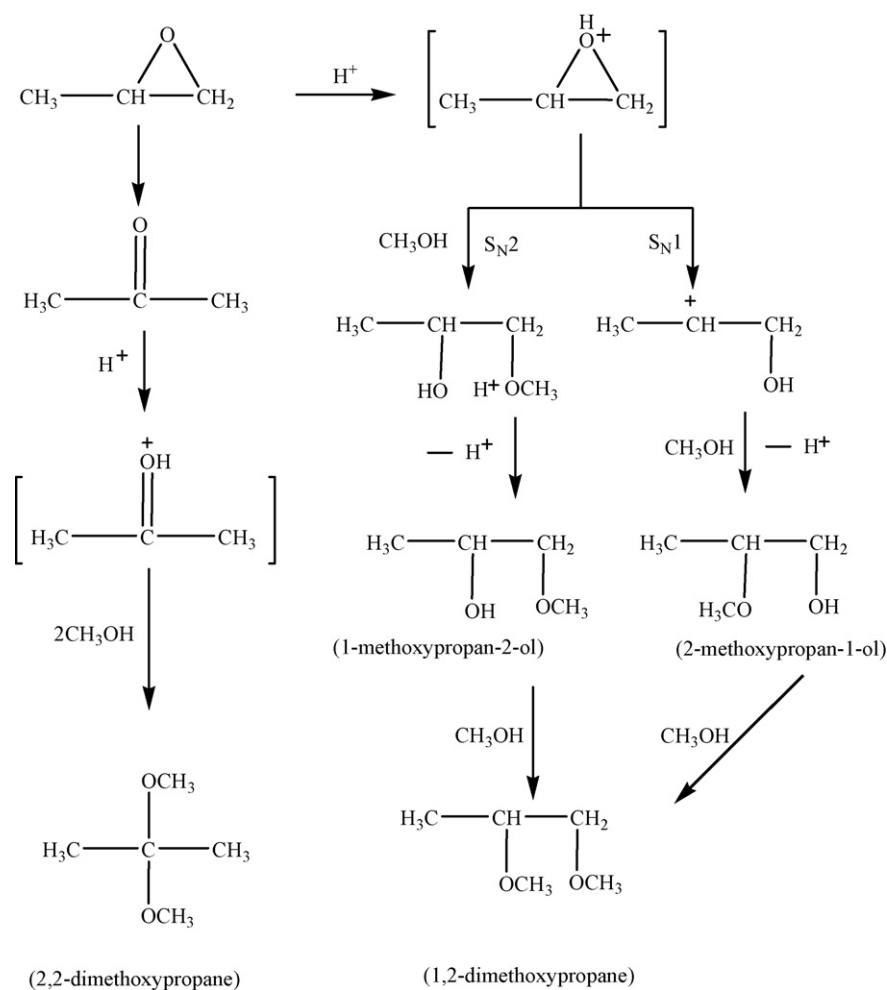
Fig. 2. Influence of the reaction time on conversion, selectivity, yield and ee value. Reaction conditions: 1 mL (14.3 mmol) (S)-propylene oxide (ee 80%), 4 mL methanol, 0.87 mol% $Co_2(CO)_8$, 1.74 mol% pyrazole, 6.0 MPa CO, 80 °C.

(>93%) were obtained for the alkoxycarbonylation in various alcohols.

3.8. Possible reaction scheme

Until now, it is unclear, how the by-products are formed. A plausible process for the formation of ethers and diethers is presented in Scheme 1. Ethers (1-methoxypropan-2-ol and 2-methoxypropan-1-ol) may be obtained according to a very traditional mechanism of acid-catalyzed reactions between propylene oxide and methanol [57,58]. This is in accordance with the fact that the products from etherification reactions, especially, ethers increase rapidly when acidic compounds were added to the reaction system (Table 1, entries 22–24). 1,2-Dimethoxypropane may be obtained through the reactions between ethers and methanol, the condensation reactions between acetone and methanol may give 2,2-dimethoxypropane [59].

It is well established that [Lewis acid]$^+$ [Co(CO)$_4$]$^-$ is the active species for epoxide carbonylation [31–45,60]. The [Lewis

Table 5
Alkoxycarbonylation of (S)-propylene oxide in different alcohols[a]

Entry	Nucleophile	Product	Conversion of (S)-PO (%)	Selectivity of ester (%)	Yield of ester (%)	ee (%)
1[b]	MeOH		97.1	94.2	91.5	100
2[c]	EtOH		69.5	93.5	65	78
3[c]	n-PrOH		58.8	94.7	55.7	79
4[c]	i-PrOH		ND[d]	ND[d]	ND[d]	77
5[c]	n-BuOH		59.0	94.6	55.8	80
6[c]	PhCH$_2$OH		72.3	93.5	67.6	ND[e]

[a] Reaction conditions: 1 mL (14.3 mmol) (S)-propylene oxide, 4 mL alcohol, 0.87 mol% $Co_2(CO)_8$, 1.74 mol% pyrazole, 6.0 MPa CO, 80 °C, 6 h. Others are the same as in Table 1.

[b] 1 mL (S)-propylene oxide (ee 100%) was used.

[c] 1 mL (S)-propylene oxide (ee 80%) was used.

[d] Not determined by GC because (S)-propylene oxide and i-PrOH are difficult to be separated in capillary column.

[e] Not determined by GC with a Supelco γ-Dex 225 capillary column.

acid]$^+$ is thought to be responsible for the initial activation (polarization) of epoxide and the anionic species, [Co(CO)$_4$]$^-$ is accountable for nucleophilic attack on the less hindered carbon atom of coordinated epoxide. According to the methoxy-carbonylation of (S)-propylene oxide in methanol, HCo(CO)$_4$ which results probably through consecutive steps of dispro-portionation of Co$_2$(CO)$_8$ under the presence of Lewis Base, then reaction with MeOH. In succession, HCo(CO)$_4$ reaction with propylene oxide and CO insertion give acylcobalt complexes –CH$_3$CH$_2$(OH)CH$_2$C(O)Co(CO)$_4$. Finally, methyl-β-hydroxybutyrate can be obtained through the reaction between methanol and acylcobalt complexes [56,61–63].

4. Conclusions

In conclusion, we have presented a general carbonylation procedure for the synthesis of enantiopure β-hydroxyesters from the corresponding epoxides. Excellent results were obtained under comparatively mild conditions (6.0 MPa, 80 °C, 6 h) when using Co$_2$(CO)$_8$/pyrazole as catalyst. Possible process for the formation of ethers and diethers had been proposed. Due to the efficiency and easy handling of the catalyst, we believe that this novel carbonylation protocol allows one to perform such reactions on an industrial scale.

Acknowledgements

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