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Preparation of L-Butyl Lactate *via* Transesterification by Using Nafion-H Catalyst

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Abstract: Optically pure L-butyl lactate was synthesized by normal transesterification using nafion-H catalyst in moderate yield. Various reaction conditions were investigated, including the reaction temperature, reaction time, ratio of the starting material and amount of the nafion catalyst.

Keywords: Nafion-H catalyst, transesterification, preparation.

L-Butyl lactate is a key intermediate in preparation of many chemicals. Such as, herbicide[1], medicine[2], food or cosmetic additive[3], *etc*. It is also a useful cosurfactant to prepare O/W microemulsions with SDS[4]. Normally, there are two traditional ways to prepare L-butyl lactate. One is esterification of lactic acid with butanol using different kinds of catalysts, for example, yttrium or lanthanum trifluoromethanesulfonate[5], solid acid $SnCl_4 \cdot 5H_2O/C$[6]. The other would be the transesterification of L-methyl lactate with butanol using a certain catalyst, for example, lipase catalyst[7-8], *p*-toluenesulfonic acis (TsOH)[9].

Here we wish to report an effective way to prepare optically pure L-butyl lactate catalyzed by solid superacid catalyst, that is, nafion-H. Nafion-H resin is perfluorinated alkyl sulfuric acid. Due to the easy separation after the reaction and highly catalytic activity, it has been widely applied in the green organic synthesis[10-12]. In order to increase the surface area of the catalyst, the nafion resin/silica composite catalyst has also been studied and it shows higher catalytic activity[13-15].

During the transesterification process catalyzed by TsOH, one more neutralization step should be involved before distillation. Moreover, trace amount of acid in the residue after distillation will definitely influence the yield and optical purity due to acid-catalyzed racemization. However, when the nafion-H resin was used instead of the TsOH in the manufacture of L-butyl lactate, these disadvantages could be avoided because nafion-H resin was easy to separate. At the meanwhile, the configuration of lactate could be absolutely remained afterwards.

A typical procedure for the reaction: L-methyl lactate, butanol and a certain amount of the catalyst were placed in a round bottom flask. The reaction mixture was refluxed and methanol was slowly distilled off in the period of the reaction. The reaction

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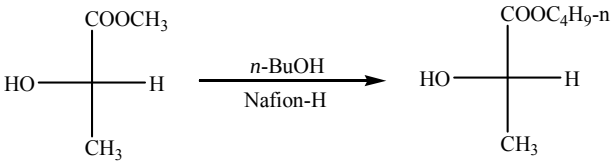
mixture was monitored by gas chromatography on SP-6800 A instrument equipped with capillary column (OV-17, 0.32 mm x 30 m) and a TCD detector. The effect of temperature, reaction time, molar ratio of starting materials and amount of the catalyst were summarized in **Table 1-5**. Not only butanol could be used in this transesterification, but hexanol, octanol could be used as the substrates too. The results were listed in **Table 6**. Moreover, the efficiency of the recycled catalyst was examined also. The catalytic activity does not change much after five or even more recycles.

A typical scaled-up procedure is as follows: In a 100 mL round bottle flask, 0.8 g nafion-H resin (4% w/w: nafion-H / L-methyl lacetate) was added to the mixture of L-methyl lactate (20.8 g, 0.2 mol) in 30 mL *n*-butanol. The reaction mixture was heated at 110 °C for 4 hours and methanol was slowly distilled off during the process. After the reaction completed, nafion-H was filtered off and the filtrate was distilled. 21.9 g L-butyl lactate (75% yield) was obtained. b.p. =146℃; $[\alpha]_D^{20}$ = -12.6 (neat). The enantiomer of L-butyl lactate was not detected by gas chromatography on chiral capillary column (β-CD, 0.25 mm x 30 m).

Scheme 1 Transesterification of L-butyl lactate



L-methyl lactate L-butyl lactate

Table 1 Effect of temperature

Reaction temperature (℃)	Conversion of L-methyl lactate (%)	Molar ratio of s:d	Yield (%)
90	77.9	48:1	77.5
100	85.3	42:1	83.3
110	89.1	36:1	86.6
120	92.5	18:1	86.7

The molar ratio of butanol to L-methyl lactate is 1.2:1.The reaction time is 4 hours. 4% (w/w) nafion-H was used. s:d ratio means the ratio of the L-butyl lactate and L-(1-methoxycarbonyl) ethyl lactate. Yield was determined by GC and calculated based on L-methyl lactate.

Table 2 Effect of the reaction time

Reaction time (min)	Conversion of L-methyl lactate (%)	Molar ratio of s:d	Yield (%)
10	20.8	/	20.8
30	46.1	143:1	46.2
60	69.2	104:1	68.5
120	79.9	61:1	78.6
180	84.9	43:1	82.6
240	89.1	36:1	86.6
300	90.1	23:1	86.3

The reaction temperature is 110℃. The molar ratio of butanol to L-methyl lactate is 1.2:1. 4% (w/w) nafion-H was used.

Table 3 Effect of ratio of butanol to L-methyl lactate

Molar ratio of butanol to L-methyl lactate	Conversion of L-methyl lactate (%)	Molar ratio of s:d	Yield (%)
1:1	86.8	21:1	82.8
1.2:1	89.1	36:1	86.6
1.5:1	89.3	41:1	87.2

The reaction temperature is 110℃. The reaction time is 4 hours. 4% (w/w) nafion-H was used.

Table 4 Effect of amount of the catalyst

Catalyst amount w/w%	Conversion of L-methyl lactate (%)	Molar ratio of s:d	Yield (%)
2	82.2	41:1	80.2
4	89.1	36:1	86.6
6	90.2	32:1	86.8

The reaction temperature is 110℃. The molar ratio of butanol to L-methyl lactate is 1.2:1. The reaction time is 4 hours.

Table 5 Effect of the recycled catalyst

Recycle times	Conversion of L-methyl lactate (%)	Molar ratio of s:d	Yield (%)
0	89.1	36:1	86.6
1	88.8	37:1	86.4
2	89.2	35:1	86.8
3	89.0	36:1	86.3
4	89.1	38:1	86.4

The reaction temperature is 110℃. The molar ratio of butanol to L-methyl lactate is 1.2:1. The reaction time is 4 hours. 4% (w/w) nafion-H was used.

Table 6 Different alcohol substrates

alcohols	Conversion of L-methyl lactate (%)	Molar ratio of s:d	Yield (%)
n-butanol	89.1	36:1	86.6
n-hexanol	90.3	42:1	87.3
n-octanol	91.1	46:1	87.8

The reaction temperature is 110℃. The molar ratio of alcohol to L-methyl lactate is 1.2:1. The reaction time is 4 hours. 4% (w/w) nafion-H was used.

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