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Two Diastereomers of d-Limonene-derived Cyclic Carbonates from d-Limonene Oxide and Carbon Dioxide with a Tetrabutylammonium Chloride Catalyst

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Two Diastereomers of d-Limonene-derivedCyclic Carbonates from d-Limonene OxideandCarbonDioxidewithaTetrabutylammoniumChloride Catalyst

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Abstract

Two diastereomers of d-limonene-derived five-membered cyclic carbonates were prepared from the corresponding isomers of d-limonene oxide with CO_2 . Their syntheses were catalyzed by commercially available tetrabutylammonium chloride with high stereoselectivity. The reaction behavior dependent on the reaction conditions such as CO_2 pressure was clarified.

Five-membered cyclic carbonates (5CCs) are versatile platform compounds for functional and reactive materials, especially for isocyanate-free synthesis of polyurethanes.¹ Therefore, synthesis of 5CCs from the epoxides with CO₂ has been widely studied.² Today, utilization of biomass as natural resource instead of fossil chemicals has been required. For this goal, fixation of CO₂ into naturally occurring chemicals has been exploited through the preparation of bio-based 5CCs.³ One group of promising naturally occurring chemicals is d-limonene as a terpene and its derivatives.⁴ It is plant waste such as citrus peels and residues of fruit juice production. Therefore, it does not compete with food production. d-Limonene oxide (LO) is a substantially bio-based chemical and is commercially available as a mixture of both cis and trans isomers (abbreviated as c-LO and t-LO, respectively). LO is reactive due to the epoxy moiety.

A LO-based 5CC obtained from LO and CO₂, d-limonene carbonate (LM5CC), which has both a 5CC moiety and a double bond, is a promising platform toward functional materials because the two functional moieties are different in their reactivity. Therefore, various kinds of synthetic processes will be possible, as is the case for LO.⁵ It is well known that an internal epoxy moiety connected to highly substituted part of the structure such as d-limonene is usually less reactive than a terminal epoxy moiety. Then, transformation of the internal epoxide into 5CC has been challenged.⁶ Recently, successful synthesis of one isomer among four kinds of LM5CCs (Scheme 1) was reported.⁷ In the article, a catalytic system comprising Al-aminotriphenolate complexes as a nucleophile was employed.



Scheme 1. Synthesis of d-limonene-derived cyclic carbonates (LM5CCs) and structures of four isomers.

However, synthesis and characterization of these types of catalysts would require specific synthetic techniques and processes as well as sufficient time.⁸ Importantly, commercially available compounds as catalysts can be instantly and directly used, and the synthetic study with as-received catalysts is also valuable both in academia and in industry. Therefore, we believe that the synthesis of LM5CC by using commercially available catalysts is of great practical importance. Additionally, there are four kinds of diastereomers for LM5CC (Scheme 1). Though one isomer 1A-LM5CC was successfully characterized at all.⁷ Stereoselective synthesis of 5CCs is one of the current research issues in this field.⁹

Here, we report on the synthesis of LM5CCs from LO, especially addressing the following points:

(1) Clarification of catalytic activities of commercially available reagents such as tetrabutylammonium chloride (TBAC) for the carbonation.

(2) By using TBAC, the carbonation of LO as a function of reaction conditions is studied.

(3) Two diastereomers, 4A-LM5CC and 1A-LM5CC (Scheme 1), obtained respectively from c-LO and t-LO, are isolated.

Among commercially available catalysts,^{1,2} TBAC was selected as a representative catalyst. It is well known that tetrabutylammonium halide (TBAX) is a catalyst for the synthesis of 5CCs.¹⁰ At first, a pure isomer¹¹ t-LO was reacted with CO₂ using 10 mol% TBAC without solvents. After 72 h at 100 °C under 3 MPa CO₂, the reaction mixture was evaluated by ¹H NMR analysis (SI). t-LO was quantitatively converted to 1A-LM5CC with high stereoselectivity. The reaction contained neither byproducts nor other isomers such as 4A-LM5CC (Scheme 1). Purification of the reaction mixture by silica gel column chromatography to remove TBAC afforded a white solid in a moderately good isolated yield (72%). It was revealed by ¹H and ¹³C NMR analyses (Figures 1S, 2S in SI) that the solid was 1A-LM5CC identical to the data reported previously.^{7b, 7c}

Similarly, another pure isomer¹¹ c-LO was reacted with



Scheme 2. Reduction of 4A-LM5CC to 4A-LMdiol having a set of (1R, 2S, 4R) configurations.

 CO_2 under the same conditions (100 °C, 72 h, and 3 MPa CO_2). The reaction contained no other isomers such as 1A-LM5CC. Here, the conversion and NMR yield are defined as the consumption of LO and the yield of LM5CC in the reaction mixture estimated by ¹H NMR, respectively. Compared with t-LO, the conversion of c-LO and NMR yield of 4A-LM5CC were as low as 42% and 30%, respectively, even after 72 h. Hence, the isolated yield was relatively low at 22% (Figures 3S, 4S in SI). It was already reported that, when reacted with nucleophiles such as primary and secondary amines, c-LO is less reactive than t-LO because c-LO has a higher energy transition state involving the formation of a boat-like structure.¹¹ The report is in good agreement with the low conversion and the isolated yield of the reactions of c-LO with CO_2 in our study.

Though the isolated yield was low, 4A-LM5CC was obtained for the first time. We also determined the configuration of the C1 and C2 positions (Scheme 1) of the 5CC moiety by means of reducing 4A-LM5CC with lithium aluminium hydride (LAH) to the corresponding 4A-LMdiol¹²⁻¹⁴ having (1*R*, 2*S*, 4*R*) configurations in Scheme 2. Reduction of 5CC with LAH gives a corresponding diol with the same configuration around the carbon atoms as that of the original 5CC.¹⁵ Our X-ray analysis indicates the structure is consistent with 4A-LMdiol of *cis* configuration in Figure 1 (SI for details). Therefore, the synthesis of 4A-LM5CC was successfully achieved, which was supported by the identification of the diol, 4A-LMdiol.

It is elucidated that, among the four diastereomers of LM5CCs, we achieved syntheses of 1A-LM5CC from t-LO and 4A-LM5CC from c-LO with CO_2 , stereoselectively. Other carbonates such as 2A-LM5CC and 3A-LM5CC were not detected. In this reaction, TBAC met the catalytic reaction requirements. The carbonation maintained the configuration at the C1 and C2 positions of the cyclohexane ring. A double inversion reactions mechanism has been suggested to account for the maintenance.⁷

In order to clarify the reaction behavior of LO with CO_2 in detail, we measured the conversion of LO and the NMR yield of LM5CC as a function of the reaction conditions. Here, not pure isomers but a mixture of as-received c-LO and t-LO (abbreviated as ct-LO, *cis/trans* = 43/57) was used as the substrate.

First, we changed the catalysts, and commercially available TBAX and lithium halide were selected. The reaction

Table 1. Reactions of ct-LO with CO₂^a

	run	catalyst ^b	conversion (%) ^c			NMR yield (%) ^c
			ct-LO ^d	c-LO ^e	t-LO ^e	4A1A- LM5CC ^f
	1	TBAC	51	19	76	50
Ĩ	2	TBAB	36	22	52	32
	3	TBAI	14	8	18	7

^a100 °C, 20 h, 3 MPa CO₂. ^b10 mol% based on ct-LO. ^cdetermined by ¹H NMR. ^dsum of c-LO and t-LO. ^eanalyzed from the reaction mixture of ct-LO with CO₂. ^fsum of 4A-LM5CC and 1A-LM5CC

Figure 1. Solid state structure of 4A-LMdiol·H₂O

conditions were fixed to 10 mol% catalyst based on ct-LO at 100 °C for 20 h under 3 MPa CO₂ without solvents. After the reaction, the reaction mixture contained 4A-LM5CC and 1A-LM5CC, as confirmed by comparison of ¹H NMR spectra of the two LM5CCs. The conversion of ct-LO (sum of c-LO and t-LO), as well as each of c-LO or t-LO, was measured from equations in SI (Figure 7S). Similarly, the NMR yield of 4A1A-LM5CC (sum of 4A-LM5CC and 1A-LM5CC) was also measured.

As listed in Table 1, by using TBAC (run 1), the individual conversions of c-LO and t-LO were 19% and 76%, respectively, and 51% of ct-LO was converted in total. Moreover, the NMR yield of 4A1A-LM5CC was 50%. The trend for the lower reactivity of c-LO than t-LO was the same as the aforementioned results. When the catalyst was changed to tetrabutylammonium bromide and iodide (TBAB, TBAI), both the conversion and NMR yield decreased. Among three kinds of TBAX, the catalytic activity decreased in the order of TBAC > TBAB > TBAI. This order is consistent with the nucleophilic activity of the anionic halide ion in aprotic solvents and is the same as that reported previously.^{10,16} Both LiCl and LiBr (Table 9S in SI) were ineffective, presumably because of their low solubility in ct-LO. Binary catalysts using a mixture of LiX (X = Br or Cl, 10 mol%) and TBAC or TBAB (10 mol%) were also applied to the carbonation reaction (Table 9S). However, the binary catalysts caused the decrease in the NMR yield of 4A1A-LM5CC with the production of unknown byproducts while the conversion increased.

Next, we focused on TBAC as the catalyst and studied the effects of the reaction conditions. Starting from the typical conditions (10 mol% TBAC based on ct-LO, 100 °C, 20 h, and 3 MPa CO₂), one parameter such as CO₂ pressure was varied. Regarding the reaction time, the conversion of ct-LO for a reaction time of 20 h was 51% (Table 1). Prolongation of the time to 48 or 72 h did not sufficiently improve the conversion of ct-LO, which was 65% or 69%, respectively. This is due to the low conversion of ct-LO within ct-LO.



Figure 2. Conversion of ct-LO (\circ), t-LO (Δ), and c-LO (\Box), and NMR yield of 4A1A-LM5CC (\bullet) as a function of CO₂ pressure. Reaction conditions: 10 mol% TBAC, 100 °C, and 20 h.



Figure 3. Conversion of ct-LO (\circ), t-LO (Δ), and c-LO (\Box), and NMR yield of 4A1A-LM5CC (\bullet) as a function of TBAC amount (mol%). Reaction conditions: 100 °C, 20 h, and 3 MPa CO₂.

Figure 2 shows a set of conversions of LO and the NMR yield of 4A1A-LM5CC as a function of CO₂ pressure. Under ambient CO₂ pressure, the carbonation of ct-LO barely proceeded. Once CO₂ was pressurized, the reaction of ct-LO smoothly proceeded. In the region examined, values of the conversion of ct-LO were similar to those of the NMR yield. Before the CO₂ pressure reached 5 MPa, the conversions of both c-LO and t-LO increased with increasing pressure. They reached 27% and 85% under 5 MPa CO₂, and the NMR yield of 4A1A-LM5CC reached 56%. However, when the pressure was further increased beyond 5 MPa, the conversion decreased slightly with increasing pressure. Next, the effect of TBAC amount on the conversion of ct-LO and NMR yield of 4A1A-LM5CC was also evaluated. As shown in Figure 3, with 1 mol% TBAC, the conversion was very low. The conversion and NMR yield increased gradually with increasing TBAC amount. The conversion of t-LO was about four times higher than that of c-LO. With 40 mol% TBAC, t-LO reached quantitative consumption, whereas the conversion of c-LO was still as low as 48%.

The conversion and NMR yield depended on the reaction temperature (Figure 10S in SI). At 60 °C and 80 °C, the conversion of ct-LO was 15% and 24%, respectively. It is obvious that the increase of temperature enhanced the conversion and NMR yield. When the temperature was raised to 100 °C or 120 °C, the conversion increased to 51% or 71%, respectively. It increased to 75% at 140 °C; however, unknown by-products in a NMR yield of $\sim ca$. 5% were detected. From these results in Figures 2, 3, and 10S, it became clear that LM5CCs can be obtained with only TBAC by choosing the reaction conditions.

In conclusion, LO with CO_2 was reacted to give d-limonene-derived 5CCs (LM5CCs). Among the four kinds of diastereomers of LM5CCs, we achieved the individual synthesis of 4A-LM5CC from *cis*-LO and 1A-LM5CC from *trans*-LO. The syntheses can be made highly stereoselective simply by commercially available TBAC. Moreover, we studied the relationship between the reaction conditions and the conversion of LO and NMR yield of LM5CCs. We believe that this synthetic study will help to develop a bio-based polyurethane industrial process starting from LM5CC, as well as the synthesis of limonene-derived bioactive compounds.

Supporting Information

Supplemental data, experimental procedures, characterization data.

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Graphical Abstract

<Title>

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<Summary>

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<Diagram>

