

Synthesis of 1,4-Cyclohexanedimethanol, 1,4-Cyclohexanedicarboxylic Acid and 1,2-Cyclohexanedicarboxylates from Formaldehyde, Crotonaldehyde and Acrylate/Fumarate

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Dedicated to the 70th anniversary of Dalian Institute of Chemical Physics, CAS

Abstract: Valuable polyester monomers and plasticizers—1,4-cyclohexanedimethanol (CHDM), 1,4-cyclohexanedicarboxylic acid (CHDA), and 1,2-cyclohexanedicarboxylates—have been prepared by a new strategy. The synthetic processes involve a proline-catalyzed formal [3+1+2] cycloaddition of formaldehyde, crotonaldehyde, and acrylate (or fumarate). CHDM is produced after a subsequent hydrogenation step over a commercially available Cu/Zn/Al catalyst and a one-pot hydrogenation/oxidation/hydrolysis process yields CHDA, whereas 1,2-cyclohexanedicarboxylate is obtained by a Pd/C-catalyzed tandem decarbonylation/hydrogenation step.

The catalytic conversion of renewable, cheap, and abundant lignocellulose to fuels^[1] and commodity chemicals^[2–6] has drawn tremendous attention over the past decade. 1,4-Cyclohexanedimethanol (CHDM) and 1,4-cyclohexanedicarboxylic acid (CHDA), introduced by Eastman Chemical Company, are valuable monomers for aliphatic polyesters (for example, poly(1,4-cyclohexylenedimethylene-1,4-cyclohexanedicarboxylate) (PCCD)), and copolyesters (such as poly(ethylene terephthalate-co-1,4-cyclohexylenedimethylene terephthalate) (PETG)).^[7] Compared to the traditional polyethylene terephthalate (PET), the polyesters containing the CHDM or CHDA unit have higher biodegradability, glass transition temperature, thermal stability, weather resistance, and mechanical strength.^[8] Notably, their properties can also be altered by varying the *cis/trans* ratio of the ring.^[8]

1,2-Cyclohexanedicarboxylates—another important family of cyclohexane oxygenates—have been used as environmentally benign plasticizers to replace the traditional phthalates that often leach out into the environment with time and cause health hazards.^[9] Currently, CHDM, CHDA, and 1,2-cyclohexanedicarboxylates are industrially prepared by the oxidation of petroleum-derived xylenes and subsequent hydrogenation of phthalic acids. In these processes, high pressures and temperatures are often involved (Scheme 1).^[10] Therefore, the exploration of mild approaches for the production of these cyclohexane oxygenates is in great demand.

Formaldehyde is an essential C1 bulk chemical that can be manufactured by the oxidation of methanol.^[11,12] Crotonaldehyde is the self-aldol condensation product of acetaldehyde.^[13] Ethyl acrylate can be formed by the esterification/dehydration of lactic acid.^[14] All of these compounds can be derived from biomass. Herein, we propose a two-step route for the synthesis of CHDM and CHDA with formaldehyde, crotonaldehyde, and ethyl acrylate (Scheme 1). In the first step, proline-catalyzed formal [3+1+2] cycloaddition of formaldehyde, crotonaldehyde, and ethyl acrylate affords ethyl 4-formylcyclohex-3-enecarboxylate (compound **1**) by a domino Mannich condensation and Diels–Alder (D–A) process. In the second step, hydrogenation of compound **1** over commercially available Cu/Zn/Al catalyst results in CHDM (compound **2**). As another option, CHDA (compound **3**) is synthesized by a one-pot hydrogenation/air oxidation/hydrolysis of compound **1**. Fumarate is a derivative of maleic anhydride (MA) that is obtained upon oxidation of biomass-derived furfural,^[15] 5-hydroxymethylfurfural (HMF),^[16] or levulinic acid (LA).^[17] Moreover, we developed a two-step route for the synthesis of 1,2-cyclohexanedicarboxylates by a proline-catalyzed formal [3+1+2] cycloaddition of fumarate, formaldehyde, and crotonaldehyde, followed by a Pd/C-catalyzed tandem decarbonylation/hydrogenation step (Scheme 1).

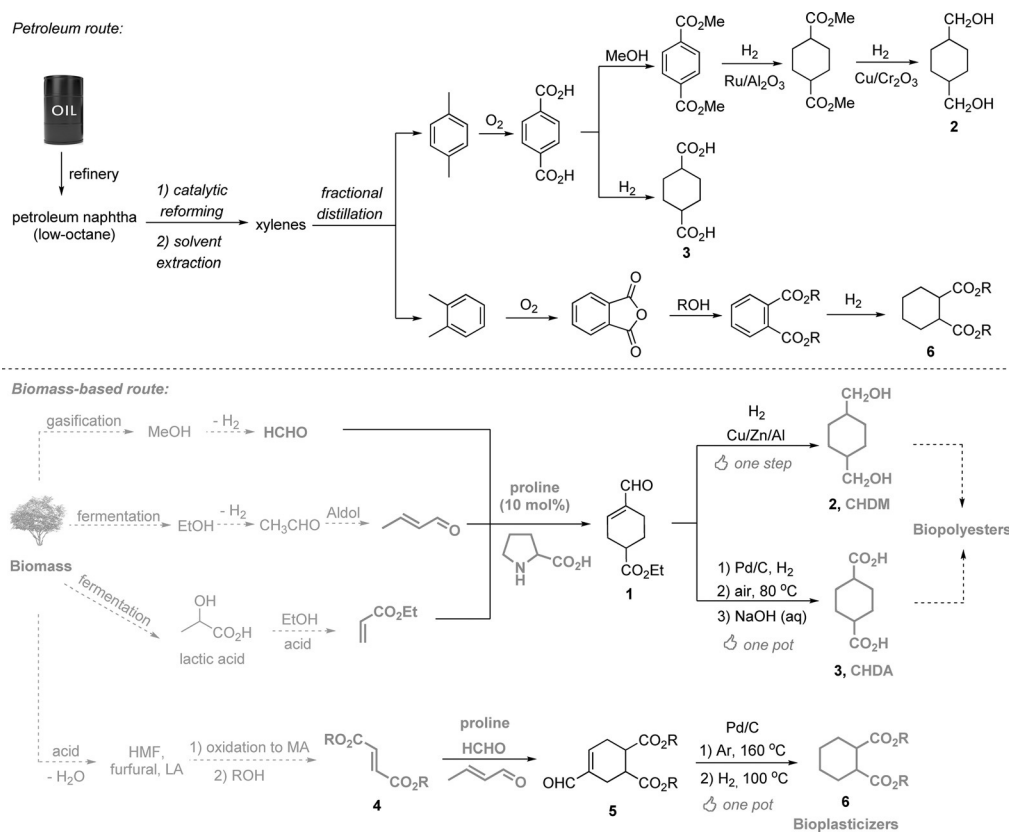
Firstly, we investigated the catalytic performances of a variety of amines for the formal [3+1+2] cycloaddition of formaldehyde, crotonaldehyde, and ethyl acrylate (Table 1, entries 1–8). The unbranched amines, such as *n*PrNH₂, ethanolamine, and *i*Pr₂NH showed low activity for this reaction, which is attributed to the instability of the iminium intermediate. Likewise, the cyclic and tertiary amines (such as pyrrolidine, Et₃N, and DABCO) also gave poor yields of compound **1**. Interestingly, a combination of acetic acid and

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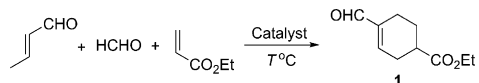
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Scheme 1. A comparison of petroleum- and biomass-based routes to cyclohexane oxygenates.

Table 1: Yield of compound **1** from the formal [3+1+2] cycloaddition of formaldehyde, crotonaldehyde, and ethyl acrylate.^[a]



Entry	Catalyst	T [°C]	Initial molar ratio ^[b]	Yield of 1 [%] ^[c]
1	<i>n</i> PrNH ₂	100	1:1:1	7
2	ethanolamine	100	1:1:1	12
3	<i>i</i> Pr ₂ NH	100	1:1:1	10
4	Et ₃ N	100	1:1:1	23
5	DABCO	100	1:1:1	10
6	pyrrolidine	100	1:1:1	17
7	pyrrolidine + HOAc	100	1:1:1	39
8	proline	100	1:1:1	47
9	proline	130	1:1:1	58
10	proline	160	1:1:1	39
11	proline	130	1.5:1.5:1	69
12	proline	130	2:2:1	91

[a] Reaction conditions: crotonaldehyde (10.0 mmol, 0.85 mL), 37% HCHO aq solution (10.0 mmol, 1.0 mL), ethyl acrylate (10.0 mmol, 1.0 mL), catalyst (10 mol%, based on the amount of acrylate), 12 h.

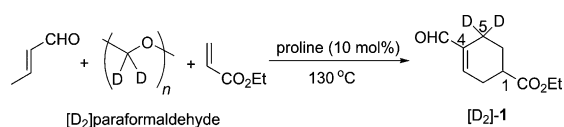
[b] The initial molar ratio of feedstocks is denoted as

$n_{(\text{crotonaldehyde})} : n_{(\text{formaldehyde})} : n_{(\text{acrylate})}$. [c] The yield of **1** was detected by gas chromatography using tridecane as the internal standard and calculated based on the initial amount of acrylate. Key: 1,4-diazabicyclo-[2.2.2]octane (DABCO).

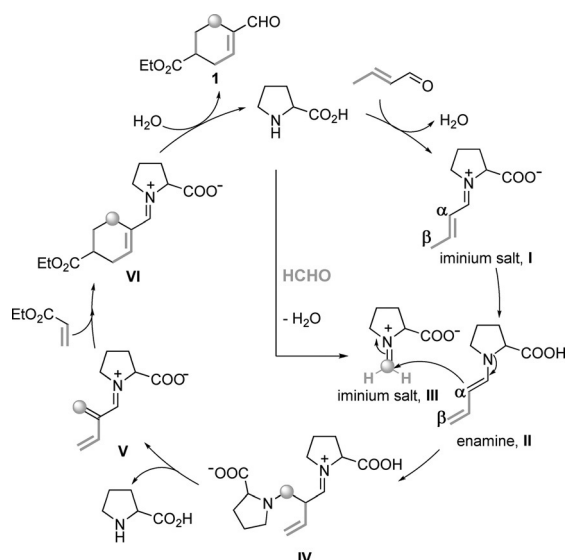
pyrrolidine gave a better result, which can be rationalized because the acid/base cocatalyst enables the formation of

a more stable iminium salt intermediate.^[18] Inspired by this result, we studied the catalytic activity of proline, which is a natural and non-toxic amino acid containing both a pyrrolidine motif and an acid functionality. As expected, proline was a good catalyst for the reaction, giving compound **1** in 47% yield. A survey of the reaction temperature indicates that the best result was obtained at 130 °C, while a higher temperature led to an inferior result (Entries 9 and 10). The initial molar ratio of the reactants also exerted an impact on the reaction (Entries 9, 11, and 12). With an increase in the initial amount of formaldehyde and crotonaldehyde, the yield of compound **1** was improved. A 91% yield of **1** was achieved when 2.0 equivalents of formaldehyde and crotonaldehyde were employed (Entry 12).

To understand the reaction pathway, an isotopic labeling experiment was performed (Scheme 2). It turned out that the deuterium atoms were distributed onto five positions of the ring (Supporting Information, Figures S1–S4), illustrating that the formyl group and C5 atom of the product originates from crotonaldehyde and formaldehyde, respectively. On the basis of this result, a plausible mechanism is proposed in Scheme 3. A nucleophilic addition of proline onto the



Scheme 2. Isotopic labeling experiment.

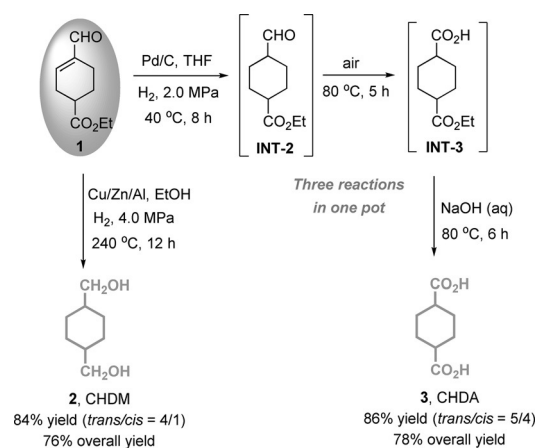


Scheme 3. Plausible mechanism for the proline-catalyzed formal [3+1+2] cycloaddition of formaldehyde, crotonaldehyde, and ethyl acrylate.

carbonyl group of crotonaldehyde, and the following dehydration step, generated the iminium salt intermediate **I**, which is prone to isomerization through the deprotonation of β -CH, resulting in the formation of enamine **II**. Likewise, formaldehyde can be activated by proline as well, providing iminium species **III**, which is further attacked by the α -carbon atom of enamine **II** to afford intermediate **IV**. A subsequent elimination of proline gives Mannich-type product **V**,^[19] which easily reacts with acrylate to deliver D–A product **VI**. A final hydrolysis of the iminium motif produces the compound **1** and regenerates the catalyst.

Subsequently, we studied the synthesis of CHDM and CHDA from compound **1**. Cu-based catalysts have been widely used for the hydrogenation of esters to alcohols.^[20] We found that compound **1** can be hydrogenated to CHDM over commercially available Cu/Zn/Al catalyst. Under the optimized reaction conditions (240 °C, 4.0 MPa of H₂, 12 h), a high yield (84 %) of CHDM was achieved (Figure S5). After taking the optimized yield of compound **1** (91 %) into account in the first step, the overall yield of CHDM starting from formaldehyde, crotonaldehyde, and ethyl acrylate, reached 76 % (Scheme 4).

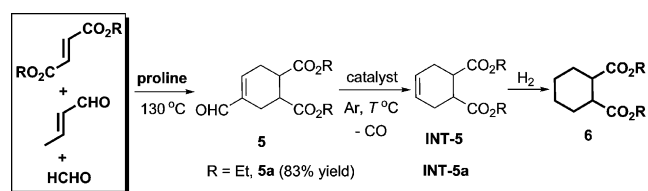
As another option, the C=C bond of compound **1** could be hydrogenated over Pd/C in H₂ (2.0 MPa) at 40 °C, giving ethyl 4-formylcyclohexanecarboxylate (**INT-2**) as the sole product. In the absence of any catalyst, **INT-2** was easily oxidized into carboxylic acid (**INT-3**) by air at 80 °C. A final hydrolysis yielded CHDA (Scheme 4). Notably, the three distinct reactions can be combined into a one-pot sequence. To do this, a mixture of compound **1**, Pd/C, and tetrahydrofuran (THF) was first stirred at 40 °C in H₂ (2.0 MPa) for 8 h. Subsequently, H₂ was released and the mixture stirred at 80 °C in air for 5 h. Eventually, an aqueous solution of NaOH was introduced, and the system stirred further at 80 °C for 6 h. This sequential operation yielded CHDA in 86 % yield (Scheme 4). As a result, CHDA was produced in two steps



Scheme 4. Reaction pathways for the production of CHDM and CHDA using compound **1** as the feedstock.

with an overall yield of 78 % using formaldehyde, crotonaldehyde, and ethyl acrylate as the feedstocks.

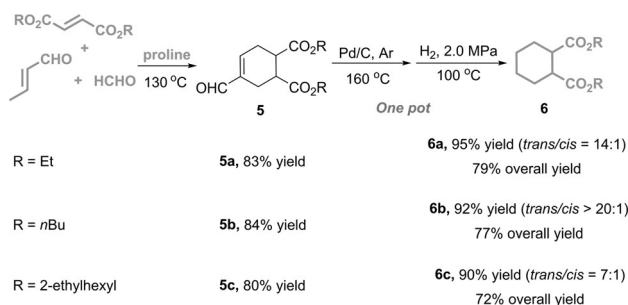
Fumarates can participate in the proline-catalyzed formal [3+1+2] cycloaddition as well, affording 4-formylcyclohex-4-ene-1,2-dicarboxylates (compound **5**) as the products (Scheme 5). For example, the utilization of diethyl fumarate



Scheme 5. Proposed pathway for the production of 1,2-cyclohexanedicarboxylate from formaldehyde, crotonaldehyde, and fumarate.

as the reactant gave diethyl 4-formylcyclohex-4-ene-1,2-dicarboxylate (compound **5a**) in 83 % yield. A subsequent decarbonylation and hydrogenation step would produce 1,2-cyclohexanedicarboxylates (compound **6**) (Scheme 5), which are used as safe plasticizers for those polyvinyl chloride (PVC) products that come into close contact with human beings, such as toys, childcare articles, plastic wrap, cosmetics, intravenous bags, and medical tubing. An investigation of different metal catalysts reveals that Pd/C exhibits the highest activity for the decarbonylation of **5a** (Supporting Information, Table S2). At the optimized reaction temperature (160 °C), 100 % conversion of **5a** and 96 % yield of **INT-5a** were achieved over Pd/C catalyst (Figure S6).

We also attempted the direct synthesis of diethyl 1,2-cyclohexanedicarboxylate (compound **6a**) with **5a** by a Pd/C-catalyzed tandem decarbonylation/hydrogenation process. A mixture of **5a**, Pd/C, and ethyl acetate was first stirred in a batch reactor at 160 °C in argon atmosphere for 10 h. Subsequently, 2.0 MPa of H₂ was charged into the reactor, and the mixture was stirred at 100 °C for 4 h. As anticipated, **6a** was obtained in a high isolated yield (95 %) without the separation of **INT-5a** (Scheme 6). Consequently, the synthesis of **6a** from formaldehyde, crotonaldehyde, and diethyl



Scheme 6. Yields of different products from the two-step route toward 1,2-cyclohexanedicarboxylates. Reaction conditions for the first step: proline (10 mol%, 115 mg), crotonaldehyde (20.0 mmol, 1.7 mL), 37% HCHO aq solution (20.0 mmol, 2.0 mL), fumarate (10.0 mmol), 130 °C for 18 h. Reaction conditions for the second step: compound 5 (10 mmol), Pd/C (10 wt%), ethyl acetate (20 mL), Ar (1.0 atm), 160 °C for 10 h; subsequently, H₂ (2.0 MPa) was charged, 100 °C for 4 h.

fumarate was accomplished in two steps with an overall yield of 79%.

Other biomass-derived fumarates bearing a longer alkyl group were also examined. When dibutyl fumarate (an ester of biomass-derived butanol with MA) was used as the feedstock, 77% overall yield of dibutyl 1,2-cyclohexanedicarboxylate (compound **6b**) was achieved (Scheme 6). 2-Ethylhexanol is produced by sequential aldol condensation and hydrogenation of biomass-derived *n*-butyraldehyde.^[21] Its esterification product di(2-ethylhexyl) fumarate was smoothly transformed into di(2-ethylhexyl) 1,2-cyclohexanedicarboxylate (DEHCH, compound **6c**) in 72% overall yield (Scheme 6), which could replace the widespread plasticizer bis(2-ethylhexyl) phthalate (DEHP).^[22]

To evaluate the environmental footprint of our approaches, *E*-factor analysis^[23] was conducted and the details are provided in Tables S3–S8. Based on our calculations, the *E*-factors for CHDM, CHDA, and diethyl 1,2-cyclohexanedicarboxylate were determined as 4.474, 4.823, and 2.325 kg kg⁻¹, respectively, which is in accordance with Sheldon's analysis of bulk chemicals that have an *E*-factor of 1–5 (Table S9).^[23] Moreover, life-cycle assessments^[24] of biomass- and fossil-based routes toward the aforementioned three compounds were also performed (Tables S10–S12 and Figures S7–S10). As shown in Figure S9, greenhouse gas (GHG) emissions released during CHDM (compound **2**) synthesis by the biomass-based pathway are 13.14% less than that generated by the fossil fuel pathway. In contrast, the biomass-based route toward CHDA (compound **3**) releases more GHGs than the fossil pathway. For diethyl 1,2-cyclohexanedicarboxylate (compound **6a**), the GHGs from the fossil- and biomass-based routes are comparable. Based on the contributions of GHGs to the life cycles of the three biomass-based routes (Figure S10), we think that further optimization of feedstock productions and reducing the dosage of NaOH and HCl are the two most effective ways to decrease GHGs (Table S13 and Figures S11).

In conclusion, we have developed a two-step route for the production of CHDM and CHDA and 1,2-cyclohexanedicarboxylates with formaldehyde, crotonaldehyde, and acrylate/fumarate, which can be derived from biomass. Our approach

provides a potential alternative to conventional fossil-based routes for the manufacture of renewable polyesters and plasticizers.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: 1,2-cyclohexanedicarboxylate · crotonaldehyde · formaldehyde · plasticizers · polyester monomers

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