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Sustainable synthesis of 1,2,3,4-cyclohexanetetracarboxylate from sugar-derived carboxylic acids

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Herein, we report a sustainable route for the synthesis of 1,2,3,4cyclohexanetetracarboxylate from sugar-derived muconic acid and fumaric acid. The key Diels-Alder reaction constructed a cyclohexene framework substituted by four ester groups. The isolated yield of tetramethyl 5-cyclohexene-1,2,3,4tetracarboxylate was up to 95.5% without any catalyst used. And the hydrogenation reaction of cycloadduct was catalyzed by commercial Raney Ni under room temperature and nearly 100% yield of the cyclohexyl target products was obtained.

Aromatic monomers containing benzene ring constitute main building block of the polymer materials.¹ The traditional engineering plastics and synthetic fibres are difficult to degrade and would cause serious environmental problems and threaten to human health.² And seeking for suitable alternative materials has become a research hot spot.³ In this regards, the polyesters and plasticizers synthesized by substituted cyclohexane oxygenates free of benzene ring exhibit nontoxicity and specific performance, and have been widely used in electric, electronic and optical materials, biomedical devices, plasticizers fields, etc.⁴ It is followed that the global market demand of cyclohexanecarboxylates is rising. Eastman⁵ and BASF⁶ have realized the scale production of ten thousand tons of 1,4- and 1,2-cyclohexanedicarboxylate, respectively. The current production of these chemicals, cyclohexanedicarboxylate and cyclohexanetetracarboxylate, mainly relies on catalytic hydrogenation of petroleum-based phthalate, terephthalate and pyromellitate under high temperature and pressure conditions.⁷ Compared to common aromatic products, the additional manufacturing process will inevitably result in a sharp increase in cost which impedes the further expansion of market space. Carbon neutral biomass



Scheme 1 Illustration of fossil-based route and proposed process for the production of 1,2,3,4-cyclohexanetetracarboxylate

could offer a vast and natural resource to produce liquid fuels and chemicals as a supplement to the petrochemical industry.⁸ However, methods for the efficient conversion of biomassderived feedstock into cyclohexanecarboxylate directly under mild condition are scarce and urgent to be developed.

Diels-Alder reaction is one of the powerful tools to build sixmembered carbon rings. Following the [4+2] cycloaddition, subsequent dehydro-aromatization or hydrogenation reaction can generate the final products containing aryl or cyclohexyl unit.9 The production of renewable aromatics based on the controlled Diels-Alder cycloaddition of diverse dienes with suitable dienophiles has attracted much attention.¹⁰ Our group has applied esterification, Diels-Alder and subsequent dehydrogenation reaction to produce diethyl terephthalate from trans, trans-muconic acid (ttMA), ethanol and ethylene.¹¹ If the cycloadduct undergo hydrogenation reaction instead of dehydrogenation, the final product was 1.4cyclohexanedicarboxylate. Recently, we have also realized the efficient synthesis of 1,2-cyclohexanedicarboxylate from erythritol and fumarate via successive deoxydehydration, Diels-Alder and hydrogenation reaction.¹² Li and Zhang et al. utilized the similar cyclizing strategy to synthesis 1,4cyclohexanedicarboxylic acid and 1,2cyclohexanedicarboxylates through multi-step reaction.13

Multiple functional groups including a cyclohexane ring and four carboxyl groups bring great challenge in the direct synthesis of 1,2,3,4-cyclohexanetetracarboxylate. Although Diels-Alder reaction is the effective strategy to construct

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⁺Electronic Supplementary Information (ESI) available: Experimental procedures; additional figures; and GC-MS spectra (PDF).

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cyclohexyl structure, the key point is that appropriate diene and dienophile with matched electron orbitals should be prepared and designed rationally. As an important new bioplatform molecule, ttMA could be synthesized in high yield from glucose and mucic acid through enzymatic and chemical catalysis, respectively.14 Fumaric acid and its esters, which could be used as a good candidate for dienophile, was obtained via the dehydration of malic acid under solvent free condition or the deoxydehydration of tartaric acid in our previous works.^{12,15} Here, we propose a sustainable route for the production of 1,2,3,4-cyclohexanetetracarboxylate using sugar-derived ttMA and fumaric acid as starting materials. The Diels-Alder reaction forms a substituted cyclohexene with four ester groups and the hydrogenation of cycloadduct is conducted smoothly catalyzed by commercial Raney Ni under room temperature (Scheme 1).

*tt*MA possessing two electron-withdrawing carboxyl groups is not a great candidate as diene in the normal-electron-demand Diels-Alder reaction. An efficient way is that *tt*MA undergoes esterification to form muconate. Compared to the acid, muconate is more reactive with ethylene in cycloaddition due to its altered electronic property and better solubility.¹¹ To build a substituted cyclohexene with four carboxyl groups, it needs a dienophile such as fumaric acid to react with muconate. To simplify the quantitative analysis process, dimethyl fumarate was selected as dienophile to react with



Fig. 1 Time course of the Diels-Alder reaction of dimethyl *trans,trans*-muconate (*tt*DMM) and dimethyl fumarate in air (**a**) and argon (**b**) atomosphere. Reaction conditions: *tt*DMM (0.05 mmol), dimethyl fumarate (0.15 mmol), 1,4-dioxane (0.5 mL), 150 °C, 4 h. The selectivity of cycloadduct was calculated based on the molar amount of *tt*DMM input.

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dimethyl *trans,trans*-muconate (*tt*DMM) instead_{ie} of *t*funaric acid. And the major product of cycloadd Rod Was⁹ (Etramethyl 5-cyclohexene-1,2,3,4-tetracarboxylate and a small amount of cycloadduct isomers was also detected by GC-MS (Fig. S1).

The Diels-Alder reactions of ttDMM with dimethyl fumarate were conducted in air atomosphere at first (Fig. 1a). It was found that the conversion of ttDMM was up to 63.8% after reacting for 0.5 h at 150 °C. When the reaction time was extended to 4 h, ttDMM was almost consumed completely and the yield of cycloadduct was only 12.8%. As depicted in Fig. 1b, argon was used to purge the vial instead of air. The conversion of ttDMM had a decrease to 67.8% and the selectivity of cycloadduct was improved to 97.4% significantly after reacting for 4 h. Argon was chosen as the reaction atomosphere in the following experiment due to the excellent performance. The above-mentioned results showed that the performance of cycloaddition between ttDMM and dimethyl fuamrate could greatly be affected by reaction atomosphere: it was much better in argon than that in air. A visual reaction phenomenon was that the color of solution changed from colorless to brown after reacting in air while kept almost unchanged in argon (Fig. S5, a and b). It was speculated that some side reactions such as oligomerization reaction of the substrates might exist in air atomosphere which resulted in the poor selectivity of cycloadduct. This was proved by LC-QTOF-MS analysis in which some oligomers with higher molecular weight were detected except unreacted substrates and cycloadduct (Fig. S6).

The stability tests of each substrate were also conducted to further clarify the effect of reaction conditions (Fig. 2). *tt*DMM and dimethyl fumarate were put into the reactor and heated under air and argon, respectively. The stability was measured by the recovery of the substrate. After heated in air for 4 h with 1,4-dioxane as solvent, the recovery of dimethyl fumarate was only 8.4% and *tt*DMM could almost not be detected. When the operation was conducted in argon, the recoveries of dimethyl fumarate and *tt*DMM had a sharp increase to 82.6% and 96.8%, respectively. Therefore, it might be proposed that the Diels-Alder reaction was competed with oligomerization of the substrates; and the oligomerization was mainly occurred in air while the Diels-Alder reaction could run smoothly in argon



Fig. 2 Stability tests of dimethyl fumarate and dimethyl *trans,trans*-muconate (*tt*DMM) under different conditions. Reaction conditions: *tt*DMM (0.05 mmol) or dimethyl fumarate (0.15 mmol), solvent (0.5 mL), 150 °C, 4 h.

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to form cycloadduct. Besides, *n*-octane was also used as solvent instead of 1,4-dioxane in the tests and the recovery of dimethyl fumarate further increased to 97.3% and 98.2% recovery of *tt*DMM was achieved. The cause of this association was not known warranting further investigation.

Result optimization experiments were also studied. The feed ratio of substrates had an important influence on the reaction results (Table 1, entries 1-4). With the input of dimethyl fumarate increased, the conversion of ttDMM was improved as well as the yield of cycloadduct. And the molar ratio of dimethyl fumarate to ttDMM was enhanced from 3/1 to 4/1, the conversion of *tt*DMM and the yield of cycloadduct had no remarkable increase (Table 1, entries 3 and 4). Therefore, the feed ratio of 3/1 was chosen in the following test. ttDMM almost converted completely as the temperature was elevated to 180 °C and the yield of cycloadduct was risen to 96.9% (entry 5). And using *n*-octane as solvent resulted a slight increase of yield to 97.4% (Table 1, entry 6). To amplify the cycloaddition reaction, 1.0 mmol of ttDMM and 3.0 mmol of dimethyl fumarate were charged and the reaction was conducted at 180 °C for 4 h in n-octane under argon atomosphere. The products were isolated by column chromatography and a 95.5% yield of tetramethyl 5cyclohexene-1,2,3,4-tetracarboxylate (about 300 milligrams) was obtained. The unreacted dimethyl fumarate could be recycled for next batch of experiment.

Dehydro-aromatization of cyclohexene or substituted cyclohexene has been studied extensively as a kind of foundational model reactions.¹⁶ The hydrogen generated from dehydrogenation reaction could be added to C=C bond of the substrate again. Theoretically, it need remove four hydrogen atoms of cyclohexene to form benzene ring. If the reaction reaches equilibrium, the final molar ratio of hydrogenation products and aromatization product was 2/1 without additive hydrogen acceptor or operation for hydrogen removal. Thus, to take full advantage of the active hydrogen, a strategy for simultaneous synthesis of tetramethyl 1.2.3.4 cyclohexanetetracarboxylate and tetramethyl 1,2,3,4prehnitate was proposed (Fig. S9 and S10). The two products

Table 1 The optimization for Diels-Alder reaction of dimethyl trans, trans-muconate (ttDMM) and dimethyl fumarate^a

| Entry | Dienophile/Diene (mol/mol) | Conversion of <i>tt</i> DMM (%) | Selectivity of cycloadduct ^b (%) | Yield of cycloadduct ^b (%) |
|------------------|-------------------------------|---------------------------------------|---|---|
| 1 | 1/1 | 28.0 | 96.1 | 26.9 |
| 2 | 2/1 | 45.3 | 97.3 | 44.1 |
| 3 | 3/1 | 67.8 | 97.4 | 66.1 |
| 4 | 4/1 | 71.8 | 98.0 | 70.4 |
| 5 ^c | 3/1 | >99.9 | 96.9 | 96.9 |
| 6 ^{c,d} | 3/1 | >99.9 | 97.4 | 97.4 |

^{*a*} Reaction condition: *tt*DMM (0.05 mmol), 1,4-dioxane (0.5 mL), 150 °C, 4 h, argon atomosphere. ^bThe selectivity of cycloadduct was calculated according to the input amount of *tt*DMM and *the* yield of cycloadduct was based on the molar ratio of the detected amount to the theoretical value. ^{*c*} *tt*DMM (0.1 mmol), 180 °C. ^{*d*} *n*-Octane (0.5 mL).

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Scheme 2 Complete synthetic process of tetramethyl 1,2,3,4cyclohexanetetracarboxylate from dimethyl *trans,trans*muconate and dimethyl fumarate

were all high value-added chemicals and could be widely used in polymer field. With Pd/C as catalyst, 39.6% and 10.6% yield of hydrogenated and aromatic products were obtained under inert atomosphere, respectively. Besides, 8.5% yield of trimethyl trimellitate was formed through the dealkoxycarbonylation process. To acquire the substituted cyclohexane products, the hydrogenation reaction of cycloadduct was conducted with commercial Raney Ni as catalyst under mild condition. The main product was 1 which could be identified by GC and NMR method (Fig. S11 and S12-S17). Although they could not be distinguished by routine chromatographic column, it was predicted that a small amount of stereoisomers 2 and 3 might be also formed via the serial isomerization and hydrogenation reaction of cycloadduct. All of the three products could be used as cyclohexyl monomers and nearly 100% total yield was obtained after reaction for 24 h at room temperature (Scheme 2).

Conclusions

In summary, a sustainable route for the production of cyclohexanetetracarboxylate using sugar-derived carboxylic acid as starting materials was developed. The Diels-Alder reaction of dimethyl *trans,trans*-muconate and dimethyl fumarate could be efficiently conducted under optimized reaction condition without any catalyst used and the maximum isolated yield of cycloadduct was up to 95.5%. A strategy for simultaneous synthesis of benzene and cyclohexane with four ester groups was also proposed to make the best of the formed hydrogen. With extra hydrogen resource introduced, nearly 100% yield of tetramethyl 1,2,3,4-cyclohexanetetracarboxylates was obtained. This work expands the way of employing Diels-Alder reaction to synthesize green monomer and also provides a novel strategy for utilizing the by-product hydrogen.

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Conflicts of interest

There are no conflicts to declare

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A sustainable route for the production of 1,2,3,4-cyclohexanetetracarboxylate from sugar-derived carboxylic acids is presented.