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Production of Plant Phthalate and its Derivative from Bio-based Platform Chemicals

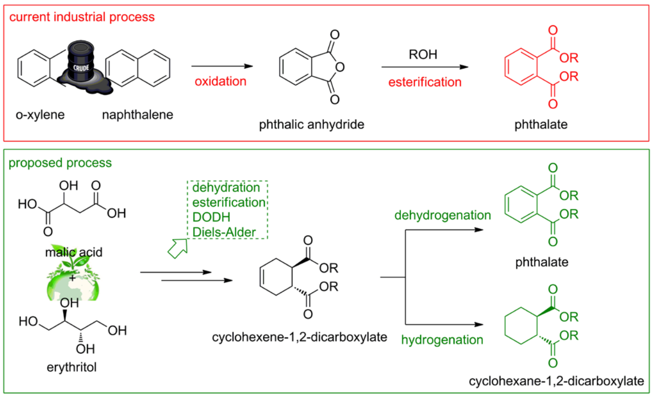
Rui Lu,[a, b] Fang Lu,*[a] Xiaoqin Si,[a, b] Huifang Jiang,[a, b] Qianqian Huang,[a, b] Weiqiang Yu,[a] Xiangtao Kong,[c] and Jie Xu*[a]

Abstract: Direct transformation of bio-based platform chemicals into aromatic dicarboxylic acids and their derivatives, which are widely used for the manufacture of polymers, is of significant importance for the sustainable development of plastic industry. However, limited successful chemical processes have been achieved. Here, we report a sustainable route for the production of phthalate and its hydrogenated derivative from bio-based malic acid and erythritol. The key Diels-Alder reaction is applied to build a substituted cyclohexene structure. The dehydration reaction of malic acid affords fumaric acid with 96.6% yield which could be used as dienophile and 1,3-butadiene generated in-situ via erythritol deoxydehydration is served as diene. Starting from erythritol and dibutyl fumarate, a 74.3% yield to dibutyl *trans*-4-cyclohexene-1,2-dicarboxylate is obtained. The palladium-catalyzed dehydrogenation reaction of cycloadduct gives a 77.8% yield of dibutyl phthalate. Near 100% yield of dibutyl *trans*-cyclohexane-1,2-dicarboxylate could be formed at mild condition via the hydrogenation of cycloadduct. Furthermore, it is demonstrated that fumaric acid and fumarate with *trans*-configuration are better candidates served as dienophiles for Diels-Alder reaction than maleic acid and maleate with *cis*-configuration based on the experimental and computational results. This new route will pave the way for the production of environmental friendly plastic materials from plant.

Synthetic plastic plays a vital role in the development of modern material science.[1] Aromatic dicarboxylic acids and their derivatives, such as phthalic anhydride, phthalate and cyclohexane-1,2-dicarboxylate, are widely used for the manufacture of plasticizers, unsaturated polyesters, and alkyd resins, with an annual consumption of multiple million tons.[2] These commodity chemicals are industrially produced via the catalytic oxidation of petroleum-derived aromatic hydrocarbon and further esterification or hydrogenation, which utilizes huge amounts of fossil oil.[3] Biomass could offer a vast and renewable resource for the sustainable production of liquid fuels and chemicals.[4] Therefore, methods for the efficient conversion of biomass resources into aromatic carboxylic acids and their derivatives are of significant importance for the sustainable development of plastic industry and energy field.

The Diels-Alder reaction of simple dienes and dienophiles without functional gourps has been presented in textbook as a representative [4+2] cycloaddition to form six-membered carbon ring. However, dienes with electron-withdrawing groups especially with carboxyl groups are difficult to perform the Diels-Alder reaction.[5] Its applications exist some challenges in which the key point lies at the structures of diene and dienophile. The production of renewable aromatics based on the controlled Diels-Alder cycloaddition of diverse dienes with suitable dienophiles has attracted much attention.[6] Our previous work developed a route to obtain diethyl terephthalate directly from biomass-derived muconic acid through tandem esterification, Diels-Alder cycloaddition, and dehydrogenation in a single reactor.[5b] Besides, the effect of diene structure on the Diels-Alder reaction has been studied and it is demonstrated that diethyl muconate, which possesses two ester groups and better solubility, is more reactive than muconic acid with ethylene in cycloaddition.

Herein, we propose a sustainable route to phthalate and its hydrogenated derivative, using bio-based malic acid and erythritol as feedstock. The process consists of the following steps: First, malic acid dehydration at solvent-free condition affords fumaric acid in high yield, and then the esterification reaction of fumaric acid is conducted to form fumarate followed by the Diels-Alder reaction with 1,3-butadiene which is in-situ generated via the deoxydehydration (DODH) of erythritol, finally the cycloadduct undergoes dehydrogenation or hydrogenation to phthalate or cyclohexane-1,2-dicarboxylate (Scheme 1). The new process using malic acid and erythritol as the source of dienophile and diene is demonstrated to be efficient and feasible to produce plant-based chemicals.



Scheme 1. Current industrial process and proposed progress for the production of phthalate and cyclohexane-1,2-dicarboxylate.

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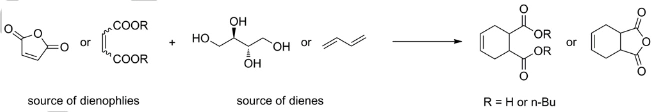
Diels-Alder cycloaddition needs suitable dienophiles. Nearly, our group reported a novel approach to obtain dimethyl malonate from malic acid through selective oxidative decarboxylation and esterification consecutively.[7] Theoretically, 2-butenedioic acid could be readily prepared from malic acid by removal of one water molecule.[8] Thus, dehydration reaction of malic acid was conducted at solvent-free condition in nitrogen atomosphere. Surprisingly, only fumaric acid could be detected in the mixture of product sample. Experimental results show that reaction temperature has a vital role on the dehydration reaction (see the Supporting Information, Figure S1). The reaction was hard to proceed under the melting point of malic acid (130 °C). As the temperature elevated, the substrate began to melt gradually. After the reaction was run at 150 °C for 2 h, 48.7% conversion to malic acid and 21.1% yield to fumaric acid were obtained. With the temperature raised to 200 °C, the yield of fumaric acid reached to 85.4%. Upon prolonging the reaction time to 4 h, a 96.6% yield to fumaric acid was obtained.

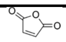
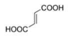
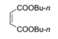
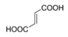
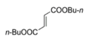
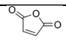
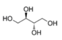
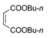
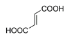
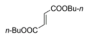
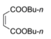
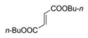
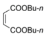
1,3-Butadiene is a good candidate for the Diels-Alder reaction with fumaric acid to perform normal electron-demand [4+2] cycloaddition. However, literatures show that high concentration of 1,3-butadiene would cause self-Diels-Alder reaction to 4-vinylcyclohexene and auto-polymerization to oligomer.[9] Therefore, in-situ generation of active 1,3-butadiene is the key for Diels-Alder reaction. DODH reaction has been effectively developed to eliminate two hydroxyl groups from vicinal diols to afford conjugated alkenes, and alcohol was served as the reductant and the solvent.[10] Thus, the tandem esterification, DODH, and Diels-Alder reaction was performed in alcohol media. Altering the type of alcohols could ultimately obtain different variety of products. Diverse alcohols were applied in the reaction and the detail results were presented in Table S1. When C4 (n-butanol and iso-butanol) and C5 (n-pentanol and 2-methyl-1-butanol) alcohols were used in the reaction, the yields of cycloadduct were from 37.8% to 48.2%, and the total yields of fumarate and cycloadduct were from 82.3% to 91.5%. As using longer carbon chain 2-ethyl hexanol (C8) and 2-propyl heptanol (C10), good yields of cycloadduct were also obtained (48.8% and 48.7%, respectively). In follow-up experiments, n-butanol was selected as the candidate of alcohol due to both excellent performance and its abundant resource from biomass.

Various metal-based catalysts were used in the tandem esterification, DODH, and Diels-Alder reaction of fumaric acid and erythritol in n-butanol (see Figure S3). Among these catalysts, Re_2O_7 possessed the best catalytic performance with the highest cycloadduct yield (48.2%) and the total yield of dibutyl fumarate and cycloadduct was up to 88.5%. Figure S4 showed that rhenium-based catalysts could obtain more amount of 1,3-butadiene left in the reaction solution than that of other catalysts. Therefore, it seems that the process combined the esterification of fumaric acid to dibutyl fumarate and DODH of erythritol to 1,3-butadiene followed by Diels-Alder reaction could be catalyzed by rhenium-based catalysts effectively.

Diverse dienophiles were tested in the tandem esterification, DODH, and Diels-Alder reaction (Table 1). Re_2O_7 was used as the catalyst and n-butanol was used as the solvent and reagent. When maleic anhydride or maleic acid was selected, the reaction was suspended at the stage of esterification and dibutyl maleate was the main product (entry 1 and 2). Using dibutyl maleate as dienophile directly, its conversion was just 17.0% (entry 3). When *trans*-form configuration fumaric acid was applied in place of *cis*-form dienophiles, the yield of cycloadduct was increased to 48.8% (entry 4). With dibutyl fumarate served as the starting dienophile, 53.2% yield to cycloadduct was obtained (entry 5). It seems to be that *trans*-configuration fumaric acid and dibutyl fumarate are more effective to obtain the cycloadduct in this reaction system. When the reaction temperature was decreased to 120 °C after running for 4 h at 170 °C, the selectivity of cycloadduct increased obviously (entry 6 and Figure S5). And the highest 74.3% yield to cycloadduct was obtained after the reaction time was prolonged to 48 h at 120 °C (entry 7). It implies that appropriate temperature contributes to realize high compatibility of the tandem esterification, DODH, and Diels-Alder reaction.

Table 1. Reaction of diverse dienophiles with erythritol or pure 1,3-butadiene.[a]



Entry	Source of dienophiles	Source of dienes	Conv. of dienophile [%]	Yield of diester [%]	Yield of cycloadduct [%]
1			>99.9	80.7	6.3
2			>99.9	82.4	5.6
3			17.0	-	5.7
4			>99.9	33.3	48.8
5			70.8	-	53.2
6[b]			58.2	-	52.5
7[c]			76.7	-	74.3
8			>99.9	-	>99.9
9[d]			23.9	-	19.8
10			0.0	-	0.0
11[d]			74.2	-	71.8
12			72.2	-	72.2
13[e]			19.8	-	19.3
14[e]			>99.9	-	>99.9
15[f]			82.8	-	82.8

[a] Reaction conditions: The reactions of diverse dienophiles with erythritol were conducted in a 15 mL glass vial, dienophiles (0.15 mmol), erythritol (0.45 mmol), Re_2O_7 (0.0225 mmol, 5 mol% to erythritol), n-butanol (5 mL), 170 °C, 12 h, N_2 atmosphere; The reactions of diverse dienophiles with 1,3-butadiene were conducted in a 50 ml Parr autoclave, dienophiles (0.6 mmol), pure 1,3-butadiene (36 mmol, 1800·mmol L^{-1}), 1,4-dioxane (20 mL), 80 °C, 4 h. The yield is calculated based on the amount of dienophiles. [b] The reaction was run at 170 °C for 4 h followed by a 8 h at 120 °C. [c] The reaction was run at

170 °C for 4 h followed by a 48 h at 120 °C. [d] Quantity analysis was conducted by ^{1}H NMR method. [e] The reactions were run at 120 °C for 4 h. [f] The reaction was run at 170 °C for 4 h.

The experimental results above-mentioned are presented that C=C configuration of dienophile plays a critical role in the combined reaction. In order to find the underlying reason, the multi-step reaction was simplified to a single Diels-Alder reaction model. Pure 1,3-butadiene in high concentration (1800 mmol L^{-1}) was directly used to react with diverse dienophiles in 1,4-dioxane (entries 8-15 in Table 1). After the reaction was run at 80 °C for 4 h, maleic anhydride had been completely consumed and nearly a 100% yield of cycloadduct tetrahydrophthalic anhydride was obtained (entry 8). Under the same condition, maleic acid had only 23.9% conversion (entry 9) and dibutyl maleate was hard to react (entry 10). Using fumaric acid as the dienophile to react with 1,3-butadiene at 80 °C, its conversion was 74.2% and the yield of cycloadduct was 71.8% (entry 11). The similar result was acquired in the case of dibutyl fumarate and a 72.2% yield of cycloadduct was obtained (entry 12). Raising the temperature to 120 °C, the conversion of dibutyl maleate had a slight increase to 19.8% and dibutyl fumarate had a full conversion. As the temperature further elevated to 170 °C, the conversion of dibutyl maleate increased to 82.8%. Obviously, maleic anhydride is the easiest to perform Diels-Alder cycloaddition with 1,3-butadiene. Fumaric acid and dibutyl fumarate are also good candidates served as dienophiles although the reactivity is slightly weaker than that of maleic anhydride. And *cis*-configuration maleic acid and dibutyl maleate are relative inert dienophiles unless the reaction is conducted at higher temperature with high concentration of 1,3-butadiene.

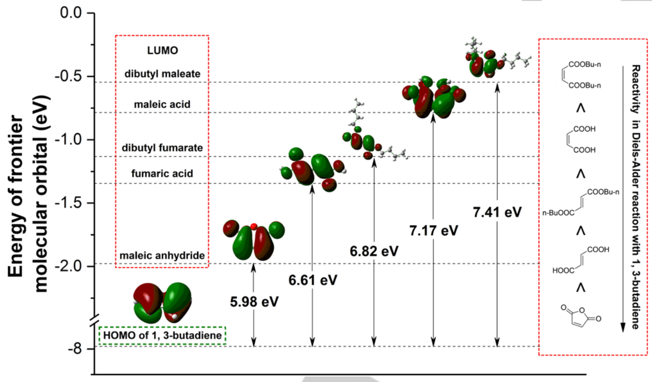


Figure 1. HOMO-LUMO orbital analysis and associated energy gaps of the Diels-Alder cycloaddition reaction of different dienophiles with 1,3-butadiene. Quantum chemical calculations were performed using Gaussian 09 program suite. All structures are optimized at the M06-2X level of density functional theory using the def2-SVP basis set on all atoms (C, H, O), incorporating solvent effects via the SMD continuum solvation model.[11]

To confirm the reactivity order of diverse dienophiles used in the Diels-Alder reaction with 1,3-butadiene, we carried out theoretical calculations at the DFT level to analyzing the electronic structures of reacting molecules (see Figure 1 and Table S5). A comparative computational study showed that 1,3-butadiene and maleic anhydride has the shortest HOMO-LUMO gap (5.98 eV), hence, maleic anhydride is the greatest candidate among these dienophiles used in the study. The energy gaps of fumaric acid and dibutyl fumarate with 1,3-butadiene are 6.61 eV and 6.82 eV, respectively. And the two *trans*-configuration dienophiles have slightly weaker reactivity than maleic anhydride. The HOMO-LUMO gaps of 1,3-butadiene and maleic acid or dibutyl maleate are the larger, and the values are 7.17 eV and 7.41 eV, respectively. Thus, the calculations further confirm that the reactivity sequence of dienophiles in Diels-Alder cycloaddition with 1,3-butadiene is depicted as follows: maleic anhydride > fumaric acid > dibutyl fumarate > maleic acid > dibutyl maleate. Although not complete coverage the dienophiles in our study, Sarotti reported similar calculated result in which maleic anhydride reacts more easily with 1,3-butadiene than maleic acid and fumaronitrile with *trans*-configuration is a better dienophile than maleonitrile.[12]

Although maleic anhydride is the best candidate to react with 1,3-butadiene in Diels-Alder cycloaddition, it showed poor performance in the tandem esterification, DODH, and Diels-Alder reaction (see entry 1 in Table 1). Because maleic anhydride was firstly converted to dibutyl maleate in n-butanol and the latter was hard to undergo Diels-Alder reaction in the current reaction system. Besides, the byproduct 4-ethenylcyclohexene derived from self-Diels-Alder reaction of 1,3-butadiene in high concentration was detected by the GC-MS measurement under high temperature (see Figure S29-S31), and the oligmer obtained from the auto-polymerization of 1,3-butadiene was presented in Figure S32. Therefore, it's necessary to avoid the self-Diels-Alder reaction and auto-polymerization of 1,3-butadiene in cycloaddition reaction. It turns out to be that the Diels-Alder reaction of fumarate derived from malic acid with erythritol which could in-situ generate 1,3-butadiene via DODH was run in high efficiency.

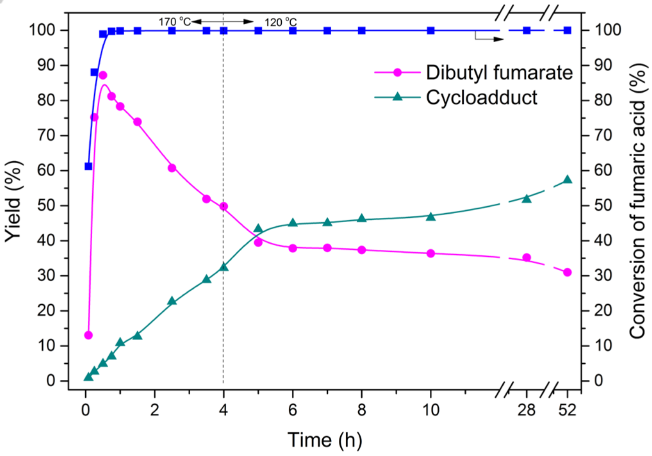


Figure 2. Time course of the tandem esterification, DODH, and Diels-Alder reaction of fumaric acid and erythritol in n-butanol. Reaction conditions: 15 mL glass vial, fumaric acid (0.15 mmol), erythritol (0.45 mmol), Re_2O_7 (0.0225 mmol, 5 mol% to erythritol), n-butanol (5 mL), N_2 atmosphere. Cycloadduct is dibutyl *trans*-4-cyclohexene-1,2-dicarboxylate.

To further investigate the tandem esterification, DODH, and Diels-Alder reaction of fumaric acid and erythritol in n-butanol, the reaction was run for different periods of time (Figure 2). In the initial thirty minutes, fumaric acid reacted rapidly with n-butanol to dibutyl fumarate and erythritol underwent DODH reaction to 1,3-butadiene catalyzed by Re_2O_7. Meanwhile, the cycloadduct was formed gradually through Diels-Alder reaction of dibutyl fumarate and 1,3-butadiene. At this point, the yield of dibutyl fumarate reached a maximum of 87.2% and only 4.9% yield to cycloaddcut was obtained, and the concentration of 1,3-butadiene left in the solution also achieved the peak value of 15.4 mmol L^{-1} (see Figure S8). As the reaction time was prolonged further, the amounts of dibutyl fumarate and 1,3-butadiene decreased gradually. The reaction time course indicates that esterification and DODH reaction are carried through first to dibutyl fumarate and 1,3-butadiene, and then the two intermediates are combined to cycloadduct via the Diels-Alder reaction gradually.

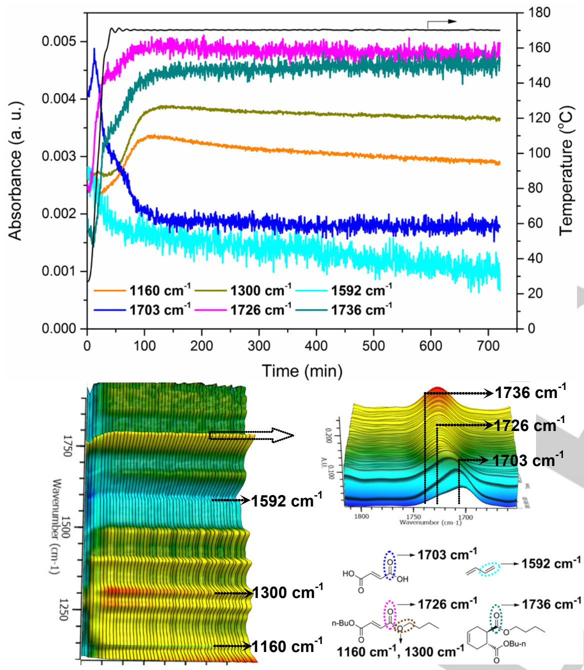
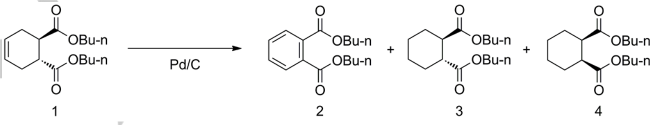


Figure 3. Real-time in situ FT-IR spectroscopic analysis of the esterification, DODH, and Diels-Alder reaction of fumaric acid and erythritol in n-butanol. Reaction conditions: Fumaric acid (2 mmol), erythritol (6 mmol), n-butanol (10 mL), NH_4ReO_4 (0.3 mmol), 170 °C, 12 h, N_2.

The tandem esterification, DODH, and Diels-Alder reaction of fumaric acid and erythritol in n-butanol was also monitored by real-time in situ FT-IR spectroscopy (Figure 3). After background correction (see Figure S38), fumaric acid (reactant), 1,3-butadiene (DODH product) and dibutyl *trans*-4-cyclohexene-1,2-dicarbocylate (cycloadduct) gave rise to characteristic absorptions at 1703 cm^{-1}, 1592 cm^{-1} and 1736 cm^{-1}, respectively. And the characteristic peaks of dibutyl fumarate (esterification product) were appeared at 1726 cm^{-1}, 1300 cm^{-1} and 1160 cm^{-1}.

All above peaks could be used to measure changes in the reaction process. The intensity of the peak at 1703 cm^{-1} had a trend of rise first then fall. It's because that fumaric acid only partially dissolved in n-butanol at room temperature. With temperature increased, the substrate dissolved gradually, and the amount of fumaric acid consumption was slower than that of dissolution at the beginning. With the temperature elevated further, fumaric acid dissolved completely and the peak at 1703 cm^{-1} declined rapidly. The peaks at 1726 cm^{-1}, 1300 cm^{-1} and 1160 cm^{-1}, which were assigned to the characteristic absorptions of dibutyl fumarate, climbed quickly at first and then drop slowly in general. The peak at 1592 cm^{-1} corresponding to the C=C stretching vibration of 1,3-butadiene also had a slow downward trend after the reaction temperature was reached. The intensity of the peak at 1736 cm^{-1} was ultra low at the initial stage and increased gradually as the reaction progress. The result of real time in situ FT-IR spectroscopy further confirms that the esterification and DODH reactions are conducted first, and the two intermediates of 1,3-butadiene and dibutyl fumarate transform to cycloadduct via Diels-Alder reaction gradually.

Table 2. Dehydrogenation of dibutyl *trans*-4-cyclohexene-1,2-dicarboxylate catalyzed by Pd/C.[a]



1 2 3 4

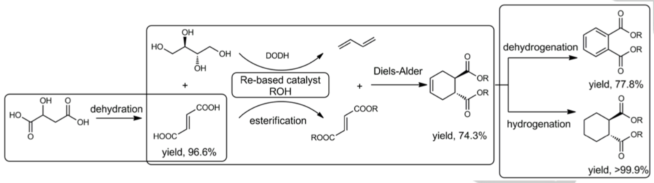
Entry	Solvent	Conv. [%]	Select. [%]			
			2	3	4	Others
1	n-butanol	>99.9	38.4	61.6	0.0	0.0
2	1,4-dioxane	99.5	44.2	55.8	0.0	0.0
3	DMF	>99.9	59.8	38.9	1.3	0.0
4	tetraglyme	95.7	68.1	24.2	7.6	0.1
5[b]	tetraglyme	>99.9	77.8	20.9	1.2	0.1

[a] Reaction conditions: 50 mL flask with two necks, dibutyl *trans*-4-cyclohexene-1,2-dicarboxylate (1.0 mmol), 5% Pd/C (5 mol% to substrate, 0.05 mmol Pd), solvent (8 mL), 200 °C (the temperature of oil bath), 11 h, the flow rate N_2 of (20 mL min^{-1}). The actual reaction temperatures of entries 1-3 were the boiling points. DMF: *N*,*N*-dimethylformamide. Others include the products of partial dehydrogenation. [b] K_3PO_4 (0.1 mmol).

The excellent performance of palladium-based catalyst in dehydro-aromatization reaction has been reported in our previous work.[5b] Therefore, Pd/C was used in the dehydrogenation of cycloadduct in this study. First, tetrahydrophthalic anhydride, which was the cycloadduct of 1,3-butadiene and maleic anhydride, was served as substrate in the dehydrogenation in n-butanol. Some decarboxylation products such as butyl benzoate have been detected by GC-MS except for the target products of phthalic anhydride and dibutyl phthalate (Figure S9). We turned to the derivative of tetrahydrophthalic anhydride or the cycloadduct of 1,3-butadiene and dibutyl maleate, dibutyl *cis*-cyclohexane-1,2-dicarboxylate. A 68.2% yield of dibutyl phthalate was obtained after the dehydrogenation was run 6 h at 220 ^{o}C in nitrogen. When the reaction was conducted in air atomosphere in which O_2 was acted as an additional hydrogen acceptor, the yield of dibutyl phthalate improved to 86.7% (Figure S10).

Dibutyl *trans*-cyclohexane-1,2-dicarboxylate is the cycloadduct prepared from the multi-step reaction. And the final aromatization step should be performed on the *trans*-isomer. However, dibutyl phthalate from the dehydrogenation of *trans*-isomer presented a quite low yield (17.1 %) in autoclave (entry 6 in Table S3). During the dehydrogenation process, the hydrogenation and dehydrogenation are competing reaction. And removing the formed hydrogen is the key to improve the selectivity of dehydrogenated product. Therefore, the dehydrogenation was conducted in a glass flask with flow of nitrogen instead of a sealed autoclave (Table 2). Using tetraglyme as the solvent, a 65.2% yield of dibutyl phthalate was obtained. As introduced K_3PO_4 to the reaction system, the yield could further increase to 77.8%. This could be explained by that the additive weakened the hydrogenated performance of Pd/C catalyst so as to enhance the selectivity of dehydrogenated product. And the selectivity of dibutyl phthalate increased from 68.1% to 77.8%.

Cyclohexane-1,2-dicarboxylate could be easily formed by hydrogenating 4-cyclohexene-1,2-dicarboxylate at mild condition (Table S4). The catalyst of Pd/C gave an excellent performance of near 100% yield of *trans*-cyclohexane-1,2-dicarboxylate. At lower temperature, Ni/C catalyst presented the weaker activity, and raising the reaction temperature to 120 ^{o}C could also obtain 100% yield of hydrogenated product.



Scheme 2. Process for the production of *trans*-4-cyclohexene-1,2-dicarboxylate followed by dehydrogenation or hydrogenation to phthalate or *trans*-cyclohexane-1,2-dicarboxylate from malic acid and erythritol.

In summary, a sustainable route to directly obtain phthalate and its hydrogenated derivative from bio-based malic acid and erythritol has been developed. The optimum results of each step in the entire route were presented in Scheme 2. The highest yield of fumaric acid could reach to 96.6% from malic acid. Starting from erythritol and dibutyl fumarate, a 74.3% yield to dibutyl *trans*-4-cyclohexene-1,2-dicarboxylate was obtained. The palladium-catalyzed dehydrogenation reaction of cycloadduct gives the maximum yield of dibutyl phthalate up to 77.8%. Also near 100% yield of dibutyl *trans*-cyclohexane-1,2-dicarboxylate could be formed at mild condition via the hydrogenation of cycloadduct. The results demonstrate that in-situ generation of 1,3-butadiene could effectively reduce self-Diels-Alder reaction and auto-polymerization of reactants. In addition, experimental and computational results reveal that fumaric acid and fumarate with *trans*-configuration are better candidates served as dienophiles than maleic acid and maleate with *cis*-configuration. Thus, the Diels-Alder reaction of fumarate derived from malic acid with erythritol which could in-situ generate 1,3-butadiene via DODH was run in high efficiency. This work provides the guidance in the design of new route based on Diels-Alder reaction, and opens up the opportunities for the production of new environmental friendly plastic materials from plant.

Acknowledgements

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Keywords: aromatic • biomass • catalysis • Diels-Alder • plastics

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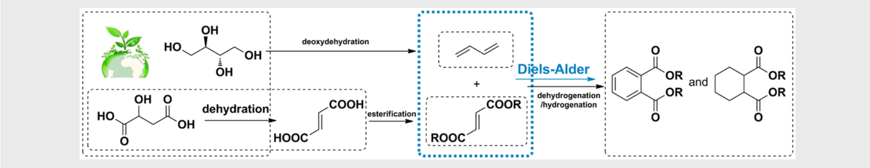

A sustainable route to directly obtain phthalate and cyclohexane-1,2-dicarboxylate from biomass-derived malic acid and erythritol is presented. The key Diels-Alder reaction is used to build a substituted cyclohexene structure. And fumaric acid and fumarate with *trans*-configuration are better candidates served as dienophiles than maleic acid and maleate with *cis*-configuration.

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