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On the Diels–Alder Approach to Solely Biomass-Derived Polyethylene Terephthalate (PET): Conversion of 2,5-Dimethylfuran and Acrolein into *p*-Xylene

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Abstract: Polyethylene terephthalate (PET) is a polymeric material with high global demand. Conventionally, PET is produced from fossil-fuel-based materials. Herein, we explored the feasibility of a sustainable method for PET production by using solely bio-renewable resources. Specifically, 2,5-dimethylfuran (derived from lignocellulosic biomass through 5-(hydroxymethyl)furfural) and acrolein (produced from glycerol, a side product of biodiesel production) were converted into the key intermediate *p*-xylene (a precursor of terephthalic acid). This synthesis consists of a sequential Diels–Alder reaction, oxidation, dehydration, and decarboxylation. In particular, the pivotal first step, the Diels–Alder reaction, was studied in detail to provide useful kinetic and thermodynamic data. Although it was found that this reaction requires low temperature to proceed efficiently, which presents a limitation on economic feasibility on an industrial scale, the concept was realized and bio-derived *p*-xylene was obtained in 34% overall yield over four steps.

Keywords: biomass · Diels–Alder reactions · polyethylene terephthalate · sustainable chemistry

Introduction

In response to the increasingly urgent issue of sustainability, lignocellulosic biomass has attracted attention as a renewable and carbon-neutral energy source. However, the selective acidic hydrolysis of cellulose to glucose, the feedstock for fermentative bioethanol production, is difficult due to the recalcitrant crystalline structure of cellulose[1] and the instability of the product sugars.[2] Instead, 5-(hydroxymethyl)furfural (HMF), a dehydrated aromatic form of glucose or fructose, is typically obtained as a major byproduct under harsh conditions[3] or even as the predominant product in the presence of chromium catalysts.[4]

The utility of HMF warrants further exploration. Due to its low energy density and instability, HMF is not a promising candidate as a liquid fuel, but it is a potential intermediate for renewable chemicals. One often-proposed approach is the oxidation of HMF to 2,5-furandicarboxylic acid (FDCA).[5] FDCA has been suggested as a potential replacement for terephthalic acid (TA).[6] TA is an important raw material for the production of polyethylene terephthalate (PET), a widely used plastic with applications ranging from beverage containers to synthetic fibers (total PET consumption in the US: 5.01 million metric tons in 2007).[7] Although the direct substitution of FDCA for TA in polymer synthesis has been known since the 1970s,[8] it has not been successfully commercialized to date. This can be attributed not only to the difference in chemical properties between FDCA and TA, but also to the difficulty of introducing new chemicals into an existing market.[9]

Based on the aforementioned background, it is desirable to develop a novel route to convert HMF into an already established commodity chemical, such as TA. The envisioned transformation of HMF into TA requires the addition of a building block of at least two carbon atoms, which would ideally also come from renewable sources. The most relevant work in this context is described by two individually published patents.[10] They both claim methods to convert 2,5-dimethylfuran (DMF), the hydrogenated form of HMF, and ethylene gas into *p*-xylene through a one-pot Diels–Alder reaction and thermal dehydrative aromatization. Although this simple method gave *p*-xylene in good yields (up to 92%), the process requires a high pressure of ethylene, as well as a high reaction temperature. We thus considered other biomass-derived dienophiles and chose acrolein as the most attractive target molecule.[11]

Acrolein can be efficiently prepared from the dehydration of glycerol, which is currently overproduced as a side-product of biodiesel production.[6,12] An efficient method for the conversion of acrolein into a bulk chemical would enhance the value of bio-refinery processes while decreasing waste output. Acrolein also has the advantage of high atom economy, almost comparable to that of ethylene, as it only contains one excess carbon, which can be easily removed as CO or CO_2. It is known that ethylene glycol, the ester condensa-

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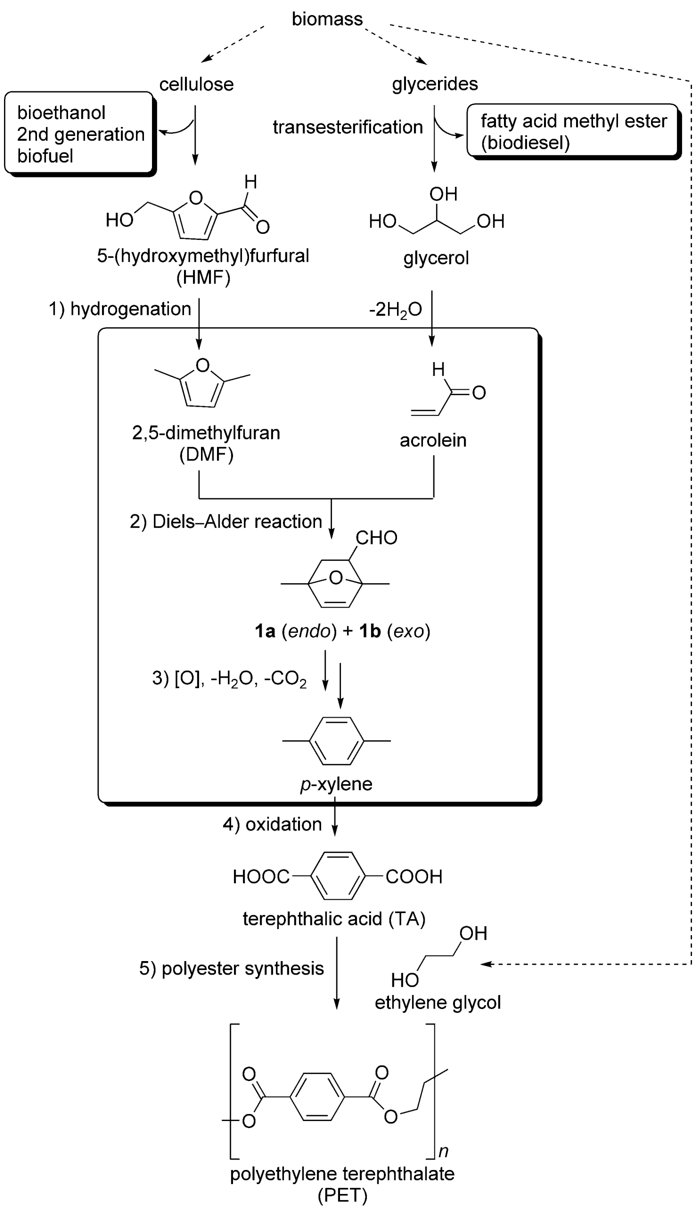
tion partner in the final polyester synthesis step, can be produced from sugar-based feedstocks[13] or from cellulose by using a nickel–tungsten carbide catalyst.[14] Therefore, this approach could provide fully renewable, solely biomass-derived PET.

To realize this concept, our strategy consists of the following five steps (Scheme 1): 1) hydrogenation of HMF to give DMF; 2) Diels–Alder reaction with acrolein to construct 7-oxabicyclo[2,2,1]hept-2-ene core structure **1**; 3) oxidation of the aldehyde, aromatization, and decarboxylation to obtain *p*-xylene, 4) oxidation of *p*-xylene to TA; and finally 5) condensation of TA and ethylene glycol to form PET. Currently, PET is mass-produced by steps four and five by using *p*-xylene obtained from crude oil. Therefore, its replacement with bio-derived *p*-xylene would be easily implemented because few changes would be required in the downstream infrastructure and operational methods. As step one is precedented,[15] this work focuses on the conversion of DMF and acrolein to *p*-xylene (steps 2 and 3).

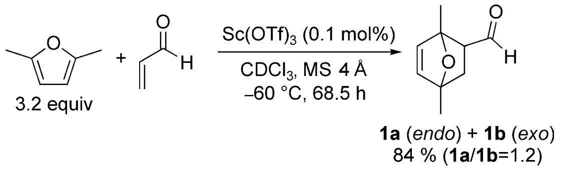


Scheme 1. The proposed PET synthesis by using biomass-derived carbon feedstocks.

Results and Discussion

To the best of our knowledge, there are only two reports on the Diels–Alder reaction between DMF and acrolein.[16,17] Burrell et al. used very high pressure (15 kbar) whereas Laszlo et al. used an Fe^{III}-doped K-10 bentonite clay catalyst. Due to the rather moderate yields (≈40 %) in both methods, we decided to seek a more efficient simple Lewis acid catalyst capable of mediating this transformation. The difficulty soon became apparent; our initial screening of common Lewis acids, such as $AlCl_3$, Et_2AlCl, $TiCl_4$, $SnCl_2$, $BF_3{\cdot}Et_2O$, $ZnCl_2$, and ZnI_2 (room temperature, 0 °C or −78 °C, DMF (1–3 equiv)) showed no promise, mainly due to the instability of acrolein. In most cases, we observed either no reaction or immediate and complete decomposition of acrolein. However, when we specifically focused on group three and four metal species (Sc, Y, Zr, and Hf), inspired by a reported $HfCl_4$-catalyzed Diels–Alder reaction of DMF and benzyl acrylate,[18] we observed a trace amount of **1** in the ^{1}H NMR spectrum by using $Sc(OTf)_3$ (8 mol %; −40 °C, DMF (2 equiv), $CDCl_3$; TfO = trifluoro methanesulfonate).[19]

Considering the negative reaction entropy ($\Delta S°$) of the Diels–Alder reaction, we thought that decreasing the temperature and increasing the concentration would be beneficial to the reactivity. Indeed, both parameters had dramatic effects. In general, lowering the temperature gave better yields and reduced starting-material decomposition. Higher concentrations were also favorable; however, the neat reaction mixture froze at about −60 °C (DMF m.p. −62 °C). We found that a ≈1:1 (v/v) mixture of DMF and chloroform (m.p. −64 °C) does not freeze even at −78 °C due to cryoscopy, and thus this mixture was employed as the standard conditions to investigate the lower temperature reactions. To further suppress acrolein decomposition and improve the selectivity for **1**, we also decreased the catalyst loading while prolonging the reaction time. We concluded that 0.1 mol % was the optimal amount of the catalyst (–60 °C, $CDCl_3$; see Table S1 in the Supporting Information). When more than 0.5 mol % of $Sc(OTf)_3$ was employed, the decomposition of acrolein was significant. When the catalyst loading was decreased to 0.05 mol %, the selectivity for **1** was good but the reaction proceeded much more slowly. The addition of molecular sieves (MS; 4 Å) or other drying agents was also found to be essential for the progression of the reaction at a reasonable rate. This is likely due to the deactivation of $Sc(OTf)_3$ by water. By using the optimized conditions, we were finally able to obtain the desired adduct **1** in good yield as a mixture of the *endo* and *exo* diastereomers (Scheme 2). Envisioning the formation of the same product from both ste-



Scheme 2. Optimized conditions for the Diels–Alder reaction of DMF and acrolein.

reoisomers after the aromatization step (Scheme 1), we were not concerned by the low diastereoselectivity.

The significant temperature dependence of the yield observed in the optimization process implied that this Diels–Alder reaction was under thermodynamic rather than kinetic control. We thought that a more thorough understanding of the reaction mechanism and thermodynamics could offer insights that might lead to further improvements in the yield and efficiency of the reaction. To investigate this point, the reaction profiles were compared at different temperatures by using the conditions in Scheme 2 (Figure 1). At higher temperatures, the reaction proceeded faster but the yield reached a plateau at a lower level (e.g., 84 % in 3 days at −60 °C vs. 75 % in less than 24 h at −55 °C). When the equilibrium constant $K_{eq}=[\mathbf{1}]/([\mathrm{DMF}][\mathrm{acrolein}])$ was calculated by using the converged values at each temperature (−60 °C to RT) and $\ln(K_{eq})$ was plotted against $1/T$ (T in K), a clear linear relationship was discovered (Figure 2). Thus, it was found that this reaction is indeed under thermodynamic control, and the standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were experimentally determined to be $\Delta H° = -6.41$ kcal mol^{-1} and $\Delta S° = -0.0304$ kcal K^{-1} mol^{-1} for **1a**, and $\Delta H° = -6.39$ kcal mol^{-1} and $\Delta S° = -0.0307$ kcal K^{-1} mol^{-1} for **1b**.

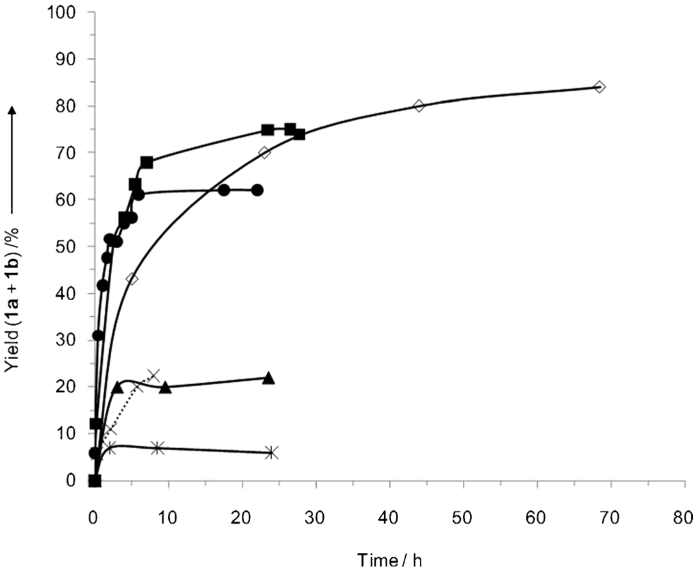


Figure 1. The temperature dependence of the DMF–acrolein Diels–Alder reaction (×: −78 °C; ◇: −60 °C; ■: −55 °C; ●: −40 °C; ▲: 0 °C; *: 25 °C (RT)).

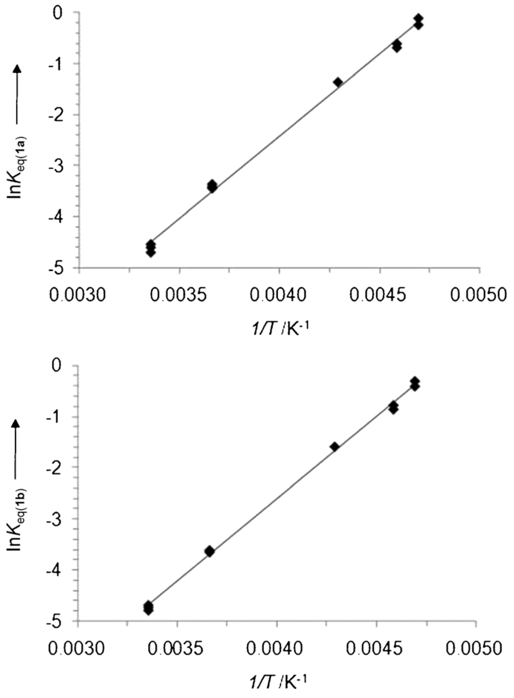


Figure 2. The linear relationship between K_{eq} and $1/T$ for **1a** (top; $y = 3225.4x - 15.33$; $R^2 = 0.996$) and **1b** (bottom; $y = 3217.5x - 15.47$; $R^2 = 0.998$).

Since cooling is a cost- and energy-intensive operation, it is desirable that this Diels–Alder reaction be performed at ambient temperature. Unfortunately, the thermodynamic values show that the low temperature is an inherent requirement regardless of the catalytic conditions. The only other method to increase the equilibrium yield is to increase the concentration of the starting materials. From the $\Delta H°$ and $\Delta S°$ values, we estimated how many equivalents of DMF are theoretically required to reach a particular yield at a given temperature. For example, at −55 °C, 6 equivalents of DMF would give ≈84 % of **1a**+**1b** on a reasonable time scale. However, more than 40 equivalents of DMF would be necessary to obtain a 90 % yield (see Table S2 in the Supporting Information). Due to the smaller K_{eq} at room temperature, even more DMF is needed to reach similar yields. Because this is impractical, improving the yield by increasing the amount of DMF was not pursued further.

Although the low temperature required for the Diels–Alder reaction step presents a severe economic challenge for scaling up the reaction, it is still valuable to achieve the synthesis of *p*-xylene solely from biomass waste products. Given the good yield and product selectivity achieved, we decided to isolate **1** and investigate its downstream conversion into *p*-xylene. To obtain a good yield of **1**, it was essential to quench the catalyst at low temperature after completion of the reaction. As expected from the measured equilibrium constants, **1** readily undergoes a retro-Diels–Alder reaction if allowed to warm in the presence of $Sc(OTf)_3$. In fact, equilibration was extremely rapid above 0 °C; if the −60 °C reaction mixture containing catalyst and an 83 %

yield of **1** was brought to 0 °C or RT, the same equilibrium states as those obtained from the forward reaction (Figure 1, 20 % yield at 0 °C and 8 % yield at RT) were reached in less than 10 min.

Moreover, at room temperature, the retro-Diels–Alder reaction of **1** was fast even after removal of the catalyst.[20] This raised a fundamental technical problem because the common isolation/purification techniques could not be applied to **1** at room temperature. Although we clearly could not relieve the inherent thermodynamic driving force, we anticipated that a reduction in workup temperature would render the reverse reaction slow enough to allow the preservation of **1**. To address this issue and determine which temperature is sufficient for this purpose, we sought more information regarding the kinetics of the thermal retro-Diels–Alder reaction.

Thus, the first-order decay of **1** in the absence of the catalyst was monitored by ^{1}H NMR spectroscopy at room temperature (Figure 3), and the rate constant (k), Gibbs free energy of activation (ΔG^{+}) and half-life ($T_{1/2}$) at this temperature were determined in several different solvents (Table 1). Because the transition state represents a state between two molecules and one molecule, ΔS^{+} is likely to be positive. Therefore, ΔG^{+} at lower temperatures should be larger than $\Delta G^{\ddagger}_{RT}$ for this retro-Diels-Alder reaction. If the $\Delta G^{\ddagger}_{RT}$ values in Table 1 are used, the half-lives ($T_{1/2}$) for **1a** and **1b** at 0 °C, in chloroform are calculated to be 85 and 95 h, respectively, suggesting that **1** is stable towards a retro-Diels–Alder reaction at ≤0 °C. Indeed, when NMR samples of **1** were kept at 0 °C instead of RT, essentially no reaction was observed over a period of 10 h in $CDCl_3$, CD_2Cl_2, CD_3CN, or [D$_8$]toluene.

Based on the knowledge garnered from this mechanistic investigation, the best approach to isolate the Diels–Alder product appeared to be a three-step sequence consisting of a Diels–Alder reaction at −60 to −55 °C, quenching the catalyst at the same low temperature, and derivatization of **1** to a more stable compound at ≤0 °C. Regarding the choice of derivatization method, we considered that the oxidation of aldehyde **1** to more stable carboxylic acid **2** could solve the problem of the retro-Diels–Alder reaction while also advancing towards the desired end product, *p*-xylene (Scheme 1).[21] In particular, we chose the Pinnick oxidation by using H_2O_2 as a mild, green, and economical method[22] and successfully devised an operationally straightforward, one-pot Diels–Alder/Pinnick oxidation protocol (Scheme 3). After confirming ≈75 % conversion of acrolein into **1** by ^{1}H NMR spectroscopy, the catalyst was quenched by adding an aqueous NaH_2PO_4/CH_3CN mixture at −55 °C. The reaction mixture was allowed to warm to 0 °C, and H_2O_2 and $NaClO_2$ were added. The oxidation was complete in 5 h, giving **2** in good yield (>99 % for oxidation step, 77 % from DMF and acrolein). Notably, the excess reagents and byproducts can all be removed by simple aqueous workup and evaporation under reduced pressure, leaving **2** in nearly pure form without further purification. Carboxylic acid **2** was much less prone to the retro-Diels–Alder reaction than **1** and could be stored for a few hours at room temperature or for several months at −20 °C.[23]

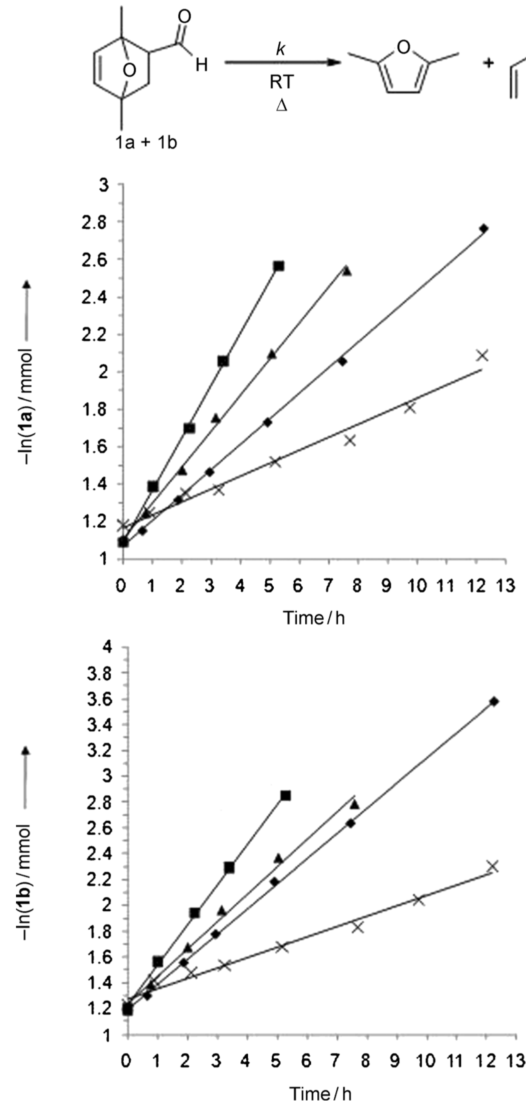
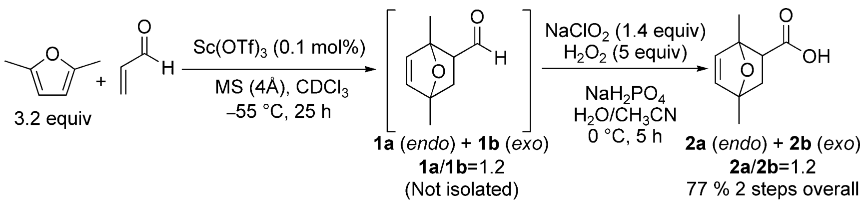


Figure 3. The kinetics of the thermal retro-Diels–Alder reaction at room temperature for **1a** (top) and **1b** (bottom). Top: ■: $CDCl_3$, $y=0.2795x+1.0905$, $R^2=0.9994$; ▲: CD_2Cl_2, $y=0.1919x+1.1088$, $R^2=0.9976$; ◆: CD_3CN, $y=0.1364x+1.0701$, $R^2=0.9987$; ×: [D$_8$]toluene, $y=0.0694x+1.1676$, $R^2=0.9792$. Bottom: ■: $CDCl_3$, $y=0.3103x+1.2256$, $R^2=0.9989$; ▲: CD_2Cl_2, $y=0.2129x+1.2329$, $R^2=0.992$; ◆: CD_3CN, $y=0.1946x+1.1948$, $R^2=0.9995$; ×: [D$_8$]toluene, $y=0.0801x+1.2764$, $R^2=0.9827$.

Table 1. The thermal retro-Diels–Alder reaction at room temperature.

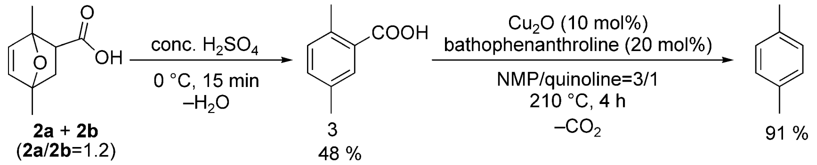
	1a			**1b**		
Solvent	k_{RT} [×10^{-5}]	$\Delta G^{\ddagger}_{RT}$ [kcal mol^{-1}]	$T_{1/2,RT}$ [h]	k_{RT} [×10^{-5}]	$\Delta G^{\ddagger}_{RT}$ [kcal mol^{-1}]	$T_{1/2,RT}$ [h]
$CDCl_3$	7.76	23.04	2.48	8.62	22.98	2.23
CD_2Cl_2	5.33	23.27	3.61	5.91	23.21	3.26
CD_3CN	3.79	23.47	5.08	5.41	23.26	3.56
[D$_8$]toluene	1.93	23.87	9.99	2.22	23.78	8.65

With isolated **2** in hand, we studied its conversion into *p*-xylene. The reported aromatization reactions of the simi-



Scheme 3. The one-pot Diels–Alder/Pinnick sequence.

lar 7-oxabicyclo[2,2,1]hept-2-ene structure mainly use strongly acidic conditions for dehydration.[24] When we treated the crude **2a**/**2b** mixture with concentrated H_2SO_4, compound **3** was obtained in 48 % yield (Scheme 4). Base-catalyzed dehydration by using potassium hexamethyldisilazide (KHMDS) or other reagents[25] was unsuccessful, presumably due to the presence of an unprotected COOH group. Direct pyrolysis[26] was also inapplicable because **2** undergoes a retro-Diels–Alder reaction and decomposes if heated. We are currently seeking more efficient aromatization methods in our laboratory. The Cu_2O-catalyzed protodecarboxylation of aromatic carboxylic acids was recently reported by Gooβen et al.[27] When **3** was subjected to this system, *p*-xylene was obtained in 91 % yield without optimization. Combined with the two steps described in Scheme 3, this route from DMF and acrolein to *p*-xylene gives a 34 % overall yield over four steps, thereby realizing the concept of biomass-derived PET synthesis (Scheme 1).



Scheme 4. Conversion of **2** into *p*-xylene.

Conclusion

We have developed a route to convert DMF and acrolein into *p*-xylene for bio-renewable PET production, with the aim to expand the range of major commodity chemicals that can be synthesized from biomass. Both raw materials are derived from waste products (HMF and glycerol) of biofuel production. Our method consisting of a Diels–Alder reaction, oxidation, dehydrative aromatization, and decarboxylation is designed to maximize atom economy and avoid toxic byproducts. Unfortunately, the process revealed in this study would certainly not be immediately practical due to the low-temperature conditions required in the Diels–Alder reaction step and the moderate yield of the aromatization step. Nonetheless, this solely bio-renewable PET synthesis serves as a valuable demonstration of sustainable chemistry in the field of biomass utilization.

Experimental Section

Diels–Alder reaction of DMF and acrolein: A vial (20 mL) fitted with a PTFE septum screw cap was charged with a magnetic stirring bar, $Sc(OTf)_3$ (3.0 mg, 0.006 mmol), and activated molecular sieves (4 Å powder, 300 mg) and then purged with nitrogen by using a vacuum/N_2 cycle (×4). Tetraethylsilane (115 μL, 90.9 mg, 0.63 mmol) and $CDCl_3$ (1.8 mL) were added and the mixture was cooled to −55 °C. DMF (1.93 mL, 19 mmol) and acrolein (400 μL, 5.9 mmol) were subsequently added over a few minutes. The reaction progress was monitored by ^{1}H NMR spectroscopy as follows: A small aliquot (≈10 μL) of the reaction mixture was removed by use of a syringe and diluted in pre-cooled (−55 °C) $CDCl_3$. The sample was immediately filtered through a Pasteur pipette filled with Na_2SO_4 into a NMR tube and the ^{1}H NMR spectrum was collected at RT. The sample was kept frozen at −78 °C (acetone/dry ice bath) if immediate ^{1}H NMR analysis was not possible. The yield and conversion were determined by using the peak of tetraethylsilane as an internal standard. After stirring at −55 °C for 24 h, a 75 % ^{1}H NMR yield of **1** (**1a** = 2.4 mmol, **1b** = 2.0 mmol, **1a**/**1b** = 1.2) was obtained (remaining DMF = 13 mmol, acrolein = 1.4 mmol). The signals used for the yield/conversion calculation: tetraethylsilane $\delta = 0.51$ ppm (q, $J = 8.0$ Hz, 8 H); DMF $\delta = 5.86$ ppm (s, 2 H); acrolein $\delta = 6.52$ ppm (dd, $J = 9.5$, 1.0 Hz, 1 H); **1a** $\delta = 6.12$ ppm (d, $J = 5.6$ Hz, 2 H); **1b** $\delta = 6.16$ ppm (d, $J = 5.6$ Hz, 2 H). The relative stereochemistry of **1a** and **1b** was determined by using $\delta = 2.84$–2.88 (m, 1 H) and 2.39–2.34 ppm (m, 1 H). In analogy to the *exo* hydrogen in **2a**, which has a more downfield resonance than the *endo* hydrogen in **2b** (see the Supporting Information), the former was assigned to be **1a** (*endo*, major) and the latter was assigned to be **1b** (*exo*, minor).

One-pot Pinnick oxidation of 1 to form 2: Following the procedure described above, a Diels–Alder reaction of DMF and acrolein was conducted in a septum-capped flask (100 mL) on a 14.3 mmol scale (−55 °C, 25 h). A pre-cooled (0 °C) mixture of CH_3CN (14 mL), $NaH_2PO_4{\cdot}H_2O$ (1.11 g, 8.0 mmol), and H_2O (6 mL) was slowly added to this mixture at −55 °C. The mixture was kept at −55 °C for 10 min and then aqueous H_2O_2 (34 %, 7 mL, 70 mmol, 0 °C) was added. The mixture was allowed to warm to 0 °C and $NaClO_2$ (80 %, 1.77 g, 20 mmol) in H_2O (20 mL, 0 °C) was added in small portions over 3 h. The reaction progress was monitored by ^{1}H NMR spectroscopy (by using the sampling procedure described above) and TLC. Upon complete consumption of **1** in an additional 5 h, the molecular sieves were filtered off and the organic solvents were removed in vacuo without heating. The mixture was extracted with CH_2Cl_2 (3×40 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude 1. The aqueous layer was then acidified to pH 3 with aqueous HCl (0.1 N), extracted with CH_2Cl_2 (3×40 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude 2. Both crude products gave a sufficiently pure **2a**/**2b** mixture. The diastereoselectivity (*endo*/*exo* ratio) was determined by ^{1}H NMR analysis: $\delta = 3.00$ ppm (dd, $J = 9.0$, 3.5 Hz, 1 H; **2a**, *endo* major), $\delta = 2.62$ ppm (dd, $J = 8.0$, 3.5 Hz; 1 H, **2b**, *exo* minor). Crude 1: thick pale-yellow oil, 1.62 g (9.7 mmol, **2a**/**2b** = 1.2); crude 2: thick colorless oil, 0.238 g (1.4 mmol, **2a**/**2b** = 1.5), Overall: 1.86 g (11.1 mmol, **2a**/**2*b*** = 1.2), 77 % yield over the two steps from DMF and acrolein. LCMS found two peaks corresponding to diastereomers **2a** and **2b**: both *m/z* calcd for $[C_9H_{11}O_3]^-$: 167.1; found: 167.1. Retention times matched those obtained from a Diels–Alder reaction of DMF and 2,2,2-trifluoroethyl acrylate followed by hydrolysis (see the Supporting Information).

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[11] In the course of our investigation, we also studied maleic anhydride and 2,2,2-trifluoroethyl acetate as alternative raw materials. *p*-Xylene was obtained in both cases in moderate overall yields. Acrylic acid is an oxidized form of acrolein and thus can be obtained from glycerol. Maleic acid can also be produced from bio-derived fumaric acid. See the Supporting Information for details.

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[20] At room temperature, the equilibrium yield (7–8%) was also reached in the forward direction with no catalyst; see Table S1, entry 7 in the Supporting Information.

[21] Hydrogenation of the double bond on Pd/C and reduction of the aldehyde to the alcohol by $NaBH_4$ or $LiAlH_4$ were also attempted in one pot at −55°C and the desired compounds were obtained. Rh-catalyzed decarbonylation and base- or acid-catalyzed aromatization were not successful on **1**.

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