

Substituted Phthalic Anhydrides from Biobased Furanics: A New Approach to Renewable Aromatics

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A novel route for the production of renewable aromatic chemicals, particularly substituted phthalic acid anhydrides, is presented. The classical two-step approach to furanics-derived aromatics via Diels–Alder (DA) aromatization has been modified into a three-step procedure to address the general issue of the reversible nature of the intermediate DA addition step. The new sequence involves DA addition, followed by a mild hydrogenation step to obtain a stable oxanorbornane intermediate in high yield and purity. Subsequent one-pot, liquid-phase dehydration and dehydrogenation of the hydrogenated adduct using a physical mixture of acidic zeolites or resins in combination with metal on a carbon support then allows aromatization with yields as high as 84% of total aromatics under relatively mild conditions. The mechanism of the final aromatization reaction step unexpectedly involves a lactone as primary intermediate.

Aromatic di- and tricarboxylic acids such as phthalic acid (PA), isophthalic acid (IPA), terephthalic acid (TA), and trimellitic acid (TMA) are used in large amounts for the industrial production of polyester fibers and films, alkyd resins and paints, and plasticizers for PVC products.^[1] The diminishing reserves and changes in the composition of fossil resources have led to increased efforts aimed at the production of such aromatic carboxylic acids from renewable resources, biomass in particular.^[2] One particularly attractive route to such 'drop-in' renewable aromatics that is currently being actively explored makes use of a Diels–Alder (DA) addition between a biomass-derived furanic diene and an appropriate dienophile to give an oxabicyclic

adduct that can, in principle, be subsequently dehydrated to the desired aromatic compound. Efficient coupling of the DA addition and the acid-catalyzed dehydration is often critical as the intermediate adduct is unstable and prone to retro-Diels–Alder reaction. Early studies by Diels himself, as well as others, already showed that phthalic acid anhydride and its derivatives can be obtained via this DA aromatization route.^[3]

Newman et al. later reported that concentrated H₂SO₄ in sulfolane works best for the synthesis of 3-methylphthalic anhydride starting from 2-methylfuran and maleic anhydride, obtaining a yield of 66%. This reaction had to be run at –55 °C because of unfavorable competition between the retro-DA and acid-catalyzed reactions at higher, more industrially relevant temperatures.^[4] Toste et al. also performed the DA addition of 2,5-dimethylfuran (DMF) and acrolein at a temperature of –55 °C, owing to the limited stability of the adduct. To further suppress retro-DA activity, they also included an intermediate oxidation step converting the aldehyde group in the DA adduct to a carboxylic acid. Subsequent dehydration and finally decarboxylation afforded *p*-xylene, albeit in a moderate overall yield (34%).^[5] Mahmoud et al. also noted the inherent difficulties associated with the stability of DA adducts and the competition between the retro-DA and acid-catalyzed dehydration reactions. An elegant strategy was developed to address this issue, using methanesulfonic acid in combination with acetic anhydride at 80 °C to efficiently aromatize various furan-based DA adducts to (substituted) phthalic anhydrides.^[6]

Most of the efforts into furanics-based aromatization routes are actually focused on *p*-xylene production, being the drop-in precursor to TA. Heterogeneous solid acid catalysts such as zeolites (e.g., H-Y, H-ZSM-5, and H-Beta) are used to convert DMF and ethylene to *p*-xylene in high yield, with H-Beta performing best in reactions run in heptane as solvent at a reaction temperature of 250 °C and typical ethylene pressures of 62 bar.^[7] Tungstated zirconia and niobic acid also efficiently catalyze this reaction, showing higher turnover frequencies than H-Y under the applied conditions.^[8]

Pacheco et al. aimed to avoid the reductive hydrodeoxygenation of 5-hydroxymethylfurfural (HMF) to DMF and performed the DA/aromatization reaction of several oxidized derivatives of HMF with ethylene over Sn-Beta at 190 °C in dioxane, yielding the aromatic products in moderate yields and selectivities.^[9] The resulting DA-aromatization products can, in principle, be further oxidized to TA.

The examples discussed above illustrate the problems that result from the adducts' tendency for retro-DA, thus requiring

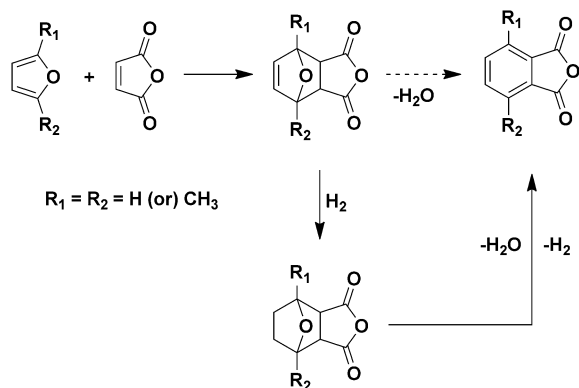
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reactions to be run either at very low temperatures or at high ethylene gas pressures. The aim of this study is to develop a novel approach to the synthesis of furanics-derived, renewable aromatics, especially towards (substituted) phthalic acid anhydrides. The new route specifically addresses the challenges resulting from the chemical instability of the DA adduct intermediate. In particular, a three-step procedure consisting of DA addition, hydrogenation, and finally aromatization of the hydrogenated DA adduct has been developed (Scheme 1). The



Scheme 1. New route to renewable (substituted) phthalic anhydrides via Diels–Alder addition, hydrogenation, and aromatization of furan derivatives with maleic anhydride.

strategy of hydrogenating the double bond in the DA adduct eliminates the possibility of retro-DA reaction at the elevated temperatures required for aromatization. Using a catalyst system capable of both dehydration and dehydrogenation, the desired aromatic compound can then be obtained in good overall yields and selectivities.

The new route is first demonstrated for the combination of 2-methylfuran (2-MF) and maleic anhydride (MA), both of which can be readily obtained from renewable resources.^[10] The *exo*-isomer of the DA adduct **1** was obtained in near quantitative yield by reacting MA with 1.2 equiv of 2-MF (see Supporting Information). Attempts to aromatize **1** in the presence of an acid catalyst failed to produce any aromatic compounds; in fact, the reaction over H-Y ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 5.2) in toluene at 150 °C gave a tarlike material. The adduct is almost fully lost to retro-DA to again produce MA and 2-MF, of which the latter is known to undergo acid-catalyzed self-polymerization resulting in the formation dimers and oligomers.^[7b] This prompted us to study the stability of **1** in detail as a function of time, temperature, and solvent. Rapid retro-DA was observed in all solvents tested, with decomposition already being observed at temperatures as low as 20 °C. The loss of the adduct **1** to retro-DA as function of temperature studied by thermogravimetric analysis (TGA) and ¹H NMR is depicted in Figure 1, showing different onset temperatures for retro-DA in solution and the solid state. Details regarding the stability of the adduct and kinetics of retro-DA can be found in the Supporting Information.

1 can be very easily and efficiently hydrogenated over Pd/C in THF at room temperature using 5–80 bar H₂ depending on

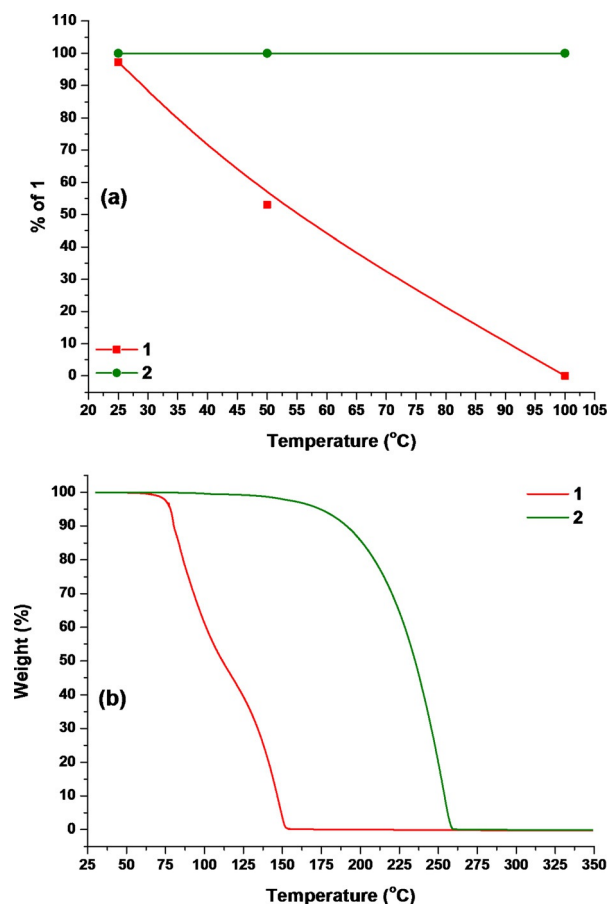
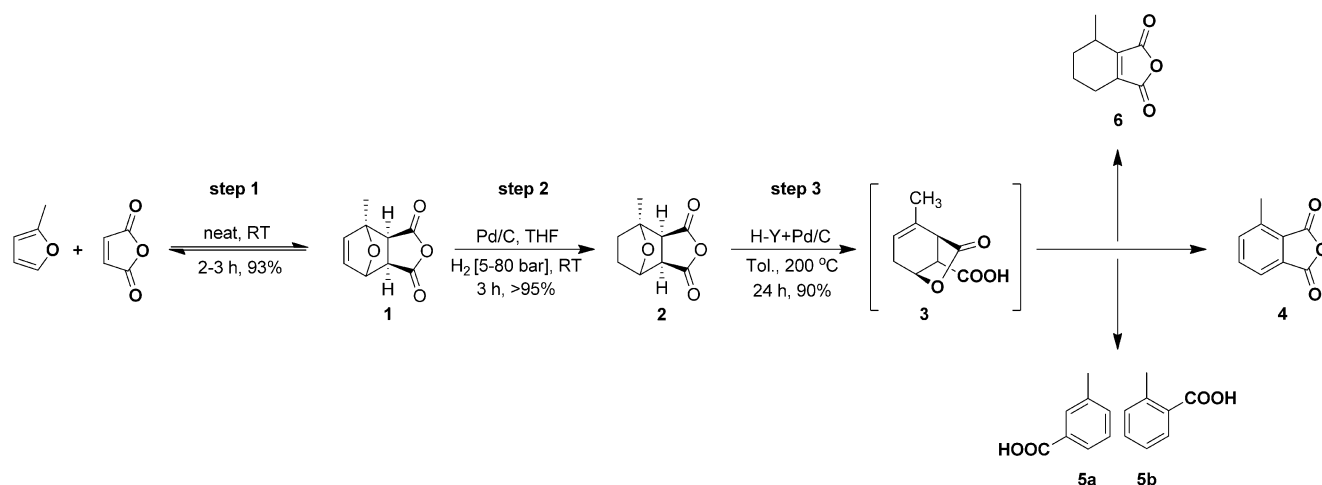


Figure 1. Stability comparisons of the Diels–Alder (DA) adduct of methylfuran and maleic anhydride (**1**) and the corresponding hydrogenated DA adduct (**2**): (a) loss of **1** by retro-DA in d-toluene as function of temperature as determined by ¹H NMR; (b) Weight loss determined by TGA analysis under N₂ atmosphere.

the scale of the reaction, yielding **2** as a colorless, crystalline solid in near-quantitative yield (Scheme 2). Variable temperature NMR and TGA analyses of **2** (Figure 1) showed this new intermediate to be more thermally stable. The first indication of the desired aromatization of **2** was obtained from a reaction using a physical mixture of a solid acid (H-Y, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 5.2, 10 wt% w.r.t. the substrate) and a dehydrogenation catalyst (10 wt% Pd/C, 3 wt% w.r.t. the substrate) in toluene at 150 °C. A low 4% yield of the desired aromatic product 3-methylphthalic anhydride **4** was detected together with three other products, that is, *m*-toluic acid **5a** (2%), 3-methylcyclohexenedicarboxylic acid anhydride (transfer hydrogenation product) **6** (3%), and, unexpectedly, the γ -lactone **3** (23%) at 50% conversion (see Supporting Information Table S1, entry 1). The influence of temperature, time, and catalyst loading on aromatization efficiency was subsequently assessed. Experiments with the individual catalysts (either zeolite or Pd/C catalyst) provided insights into the reaction network. While the use of only the 10 wt% Pd/C catalyst did not give any conversion of **2** at 200 °C (Table S1, entry 5), the use of zeolite H-Y alone resulted in 50% conversion after 24 h at 150 °C in toluene. In the latter reaction, γ -lactone **3** is predominantly obtained (45% selectivity), as well as minor amounts of **4** and the byproducts



Scheme 2. Three-step Diels–Alder addition, hydrogenation and aromatization strategy to produce 2-methylfuran-derived 3-methylphthalic anhydride and *ortho/meta*-toluic acids; the tandem-catalyzed final step requires H-Y and Pd/C and involves lactone **3** as primary intermediate.

5a and **6** (Table S1, entry 1). Increasing the amount of H-Y from 10 wt% to 50 wt% further increased the selectivity towards the γ -lactone **3** to 57% (Table S1, entry 2). The methyl ester of **3**, a highly interesting multifunctional building block in its own right, has been reported previously using a five-step route starting from 2-MF.^[11] Increasing the temperature from 150 °C to 200 °C using 10 wt% H-Y resulted in a further shift to the aromatic product **4**, now obtained with 33% selectivity at 200 °C, accompanied by a concomitant decrease in selectivity to the γ -lactone (**3**) (Table 1, entry 1).

The use of a Pd/C + H-Y physical mixture at 200 °C resulted in full conversion of the starting material after 24 h, yielding 56% of the desired 3-methylphthalic anhydride **4** with a 75% cumulative selectivity towards aromatics (Table 1, entry 2). Under these conditions, γ -lactone **3** is not observed anymore, while *m*-toluic acid **5a** has become the most prominent byproduct at 17% yield. Molecular hydrogen was (qualitatively) detected by GC analysis of the headspace of the reaction. Monitoring the conversion as function of time (Figure 2) showed the γ -lactone **3** to be a primary intermediate, gradually being further aromatized (see Table S1, entries 6–9). Increasing the weight loading of H-Y to 30 wt% or 50 wt% (Table 1, entries 3 and 4) did not result in any significant changes; the transfer hydrogenation product **6** was no longer detected at higher loadings of H-Y, however.

Variation of the zeolite showed that H-VUSY (SiO₂/Al₂O₃ mole ratio: 11.5) gave a higher yield (84%) in aromatics than H-Y at full conversion (mole balance of 90%), while H-Beta (SiO₂/Al₂O₃ mole ratio: 25) showed a significantly lower conversion (55%) and a high selectivity towards the γ -lactone **3** under the standard conditions (Table 1, entries 5 and 6). The 3-methylphthalic anhydride yield of 59% can be compared to earlier reports showing yields of 48% or 66% from **1** and methanesulfonic acid^[6] or conc. H₂SO₄^[4] respectively. The total aromatics yield of 84% is similar to the 87% yield of PA and phthalic anhydride that was recently reported by Mahmoud et al.^[6]

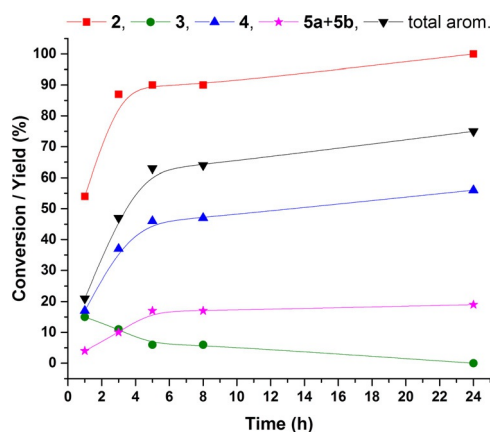








Figure 2. Conversion of hydrogenated DA adduct **2**, yields of γ -lactone **3**, 3-methylphthalic anhydride **4**, *o*- and *m*-toluic acid **5a** + **5b**, and total aromatics yield as a function of time.

Two organic solid acids were also tested at 175 °C (Table 1, entries 8 and 9). The highly acidic Nafion resin (NR50) shows higher conversion and selectivities to the desired aromatics than H-Y at this particular temperature (Table 1, entries 7–9), while the performance of the acidic ion exchange resin Amberlyst 70 is more comparable to H-Y (Table 1, entry 7). The lactone is detected in 10–15% with both types of acid catalysts. Notably, the organic solid acids produce markedly lower amounts of the decarboxylated by-products **5a** and **5b**. A series of commercial (5 wt%) metal on carbon catalysts, including Pd/C (benchmark), Pt/C, Ru/C, Rh/C, were tested as dehydrogenation catalyst (Table 1, entries 10–13). The results show that Pt/C performs best, giving the highest selectivity towards aromatics.

Furan and 2,5-dimethylfuran were also investigated as diene in the aromatization reaction (Table 1, entries 14 and 15). For both substrates, the hydrogenated adduct can again be readily obtained in excellent yields (see experimental section in the Supporting Information). The hydrogenated DA adduct of furan and maleic anhydride is much less reactive than **2**, giving

Table 1. Tandem-catalytic aromatization of hydrogenated Diels–Alder adducts.^[a]

Entry	Solid acid catalyst [wt%] ^[b]	Metal on carbon (3 wt%) ^[b]	T [°C]		Conversion [mol%] ^[c]	Molar yield [%] (Selectivity [%]) ^[c]				Mole balance [%] ^[d]	
											
1	H-Y (10%)	– ^[e]	200	X = Me; Y = H	64	15 (23)	22 (33)	4 (6)	– ^[f]	3 (4)	80
2	H-Y (10%)	Pd/C ^[g]	200	X = Me; Y = H	100	– ^[f]	56 (56)	17 (17)	2 (2)	10 (10)	85
3	H-Y (30%)	Pd/C ^[g]	200	X = Me; Y = H	100	– ^[f]	59 (59)	19 (19)	2 (2)	– ^[f]	80
4	H-Y (50%)	Pd/C ^[g]	200	X = Me; Y = H	100	– ^[f]	56 (56)	18 (18)	2 (2)	– ^[f]	76
5	H-VUSY (10%)	Pd/C ^[g]	200	X = Me; Y = H	100	– ^[f]	59 (59)	19 (19)	6 (6)	6 (6)	90
6	H-Beta (10%)	Pd/C ^[g]	200	X = Me; Y = H	55	21 (40)	22 (42)	6 (13)	4 (9)	– ^[f]	98
7	H-Y (10%)	Pd/C ^[g]	175	X = Me; Y = H	66	10 (15)	29 (44)	10 (15)	2 (3)	2 (3)	87
8	Amb-70 (10%)	Pd/C ^[g]	175	X = Me; Y = H	74	15 (19)	31 (42)	2 (2)	4 (5)	4 (5)	82
9	Nafion (10%)	Pd/C ^[g]	175	X = Me; Y = H	92	11 (12)	48 (52)	5 (5)	3 (4)	4 (5)	79
10	H-Y (10%)	Pd/C ^[h]	200	X = Me; Y = H	88	6 (6)	48 (54)	18 (20)	2 (2)	2 (2)	88
11	H-Y (10%)	Pt/C ^[h]	200	X = Me; Y = H	87	– ^[f]	52 (60)	23 (26)	– ^[f]	2 (2)	90
12	H-Y (10%)	Ru/C ^[h]	200	X = Me; Y = H	56	18 (32)	29 (53)	5 (10)	– ^[f]	2 (4)	98
13	H-Y (10%)	Rh/C ^[h]	200	X = Me; Y = H	56	17 (31)	28 (50)	8 (16)	– ^[f]	2 (5)	99
14	H-Y (10%)	Pd/C ^[g]	200	X = Y = H	24	– ^[f]	10 (41)	4 (17) ^[i]	– ^[f]	– ^[f]	90
15	H-Y (10%)	Pd/C ^[g]	200	X = Y = Me	100	– ^[f]	67 (67)	12 (12) ^[j]	– ^[f]	– ^[f]	79

[a] Conditions: 1.5 g scale, 24 h in toluene, catalyst(s) and temperature are indicated in the table. [b] wt% relative to substrate. [c] Calculated by q-NMR using 1,4-dinitrobenzene as internal standard. [d] Mole balance is determined from the total number of moles calculated from the crude mixture after the reaction by NMR analysis. [e] No catalyst was added. [f] Not observed. [g] 10 wt% metal on carbon. [h] 5 wt% metal on carbon. [i] Benzoic acid. [j] *p*-Xylene.






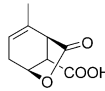
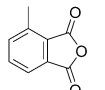
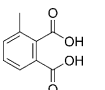
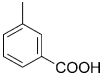
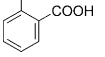
only 24% conversion after 24 h under the standard reaction conditions (200 °C, 10 wt% H-Y and 3 wt% Pd/C), but the selectivity to the aromatic products is nonetheless similar. In contrast, the hydrogenated adduct obtained of 2,5-dimethylfuran and maleic anhydride was readily converted in 24 h under standard conditions, giving only the desired dimethyl phthalic anhydride and *p*-xylene as the only products (i.e., no 2,5-dimethylbenzoic acid is detected). The difference in activity between the three different hydrogenated DA adducts is not unexpected, given that the ease of the acid-catalyzed ring opening of the oxanorbornane ring will depend on the furan substitution pattern, with ipso electron-releasing substituents (i.e., the methyl group) able to stabilize the positive charge developing on the carbon in the transition state.

To obtain more insight into the reaction mechanism, the observed aromatic products and possible intermediates were also subjected to the typical reaction conditions (Table 2). First, the γ -lactone **3** was purposely synthesized according to the reaction conditions described in Table S1, entry 2 and purified by distillation. Using the γ -lactone **3** as substrate resulted in complete conversion, giving the anhydride **4** in 52% and the decarboxylated products, *m*-toluic acid **5a** and *o*-toluic acid **5b** in 28% and 4%, respectively (Table 2, entry 1). This again emphasises the key role the lactone plays as primary intermediate and furthermore shows that all aromatic products obtained are in fact derived from this intermediate. The desired product **4** itself is highly stable in the presence of H-Y and Pd/C at 200 °C for 24 h, and was quantitatively recovered after the reaction (Table 2, entry 2). We also tested the reactivity of 3-methylphthalic acid, as this compound could be considered a precursor to the toluic acids and can potentially be formed by iso-

merization/dehydrogenation of the lactone or hydrolysis of **4** by any of the water formed during reaction. Complete conversion was observed for this compound, with 88% of the substrate being simply converted to the anhydride **4** (Table 2, entry 3); no decarboxylation to **5a** or **5b** was observed, though. Finally, the toluic acids were found to give conversions of 9% and 11%, respectively (Table 2, entry 4 and 5), but no compounds other than the starting compounds could be detected by ¹H NMR. Toluene could be formed by decarboxylation of the toluic acids, but this product cannot be detected as the reactions were performed in toluene as the solvent. Taken together, these results do suggest that decarboxylation occurs prior to the aromatization step.

Based on the results shown in Tables 1 and 2 and Table S1, it is clear that the first step of the tandem-catalyzed conversion consists of the isomerization of the hydrogenated adduct to give the lactone, a reaction that requires only the acid catalyst. Aromatization, decarboxylation, and transfer hydrogenation do occur with only the zeolite present, but to a limited extent. Indeed, a dehydrogenation catalyst is required to efficiently convert the lactone and to give high yields of aromatic products. It should be noted in this sense that the addition of the dehydrogenation catalyst enhanced both the aromatization and the decarboxylation reaction. So far this new method was found to be applicable to dienes such as furan, 2-methyl furan and 2,5-dimethylfuran in combination with maleic anhydride. Possible extension of the substrate scope to other dienophiles such as methyl acrylate, fumaronitrile, as well as maleimides is the subject of a mechanistic study that focuses on the role and importance of the lactone intermediate in the new route and will be reported separately.

Table 2. Reactivity of possible intermediates, including lactone **3** and the aromatic products **4**, **5a**, and **5b** under typical aromatization conditions.^[a]

Entry	Starting material	Conversion [mol%] ^[b]	Molar yield [%] ^[b] (Selectivity [%]) ^[c]					Mole balance [%] ^[d]
								
1		100	52 (52)	28 (28)	4 (4)	— ^[e]	— ^[e]	84
2		0	100 (100)	— ^[e]	— ^[e]	— ^[e]	— ^[e]	100
3		100	88 (88)	— ^[e]	— ^[e]	— ^[e]	— ^[e]	88
4		11	— ^[e]	89	— ^[e]	— ^[e]	— ^[e]	89
5		9	— ^[e]	— ^[e]	91	— ^[e]	— ^[e]	91

[a] Conditions: 1.5 g scale, H-Y (10 wt%), Pd/C (3 wt%) at 200 °C for 24 h in toluene. [b and c] Calculated by q-NMR using 1,4-dinitrobenzene as internal standard. [d] Mole balance is determined from the total number of moles calculated from the crude mixture after the reaction by NMR analysis. [e] Not observed.

In conclusion, it is successfully demonstrated that renewable substituted phthalic anhydrides can be prepared in good yield starting from furan-derived DA adducts. A hydrogenation step is included to stabilize the DA adducts and to prevent any retro-DA reactivity during aromatization. By doing so, the overall aromatics yield can be dramatically enhanced for the diene/dienophile combinations studied. The novel route makes use of a physical mixture of two types of solid catalysts, zeolites (H-Y or H-VUSY) and Pd/C. A lactone is identified as the primary intermediate of the reaction and found to be an important precursor to all aromatic products formed in the process. The new route and tandem catalytic final step is thought to be more generally applicable and can also serve as a solution for other DA-aromatization reactions limited by the thermal stability of the intermediate adduct.

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Keywords: aromatics · aromatization · Diels-Alder reaction · furans · hydrogenation

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