

# Green Trimellitic Anhydride and Hemimellitic Anhydride from Malic Acid

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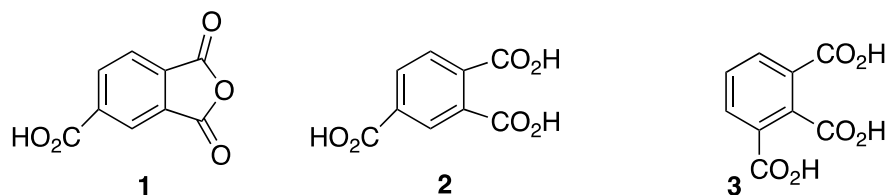
Keywords: trimellitic anhydride, hemimellitic anhydride, malic acid, acetoxy succinic anhydride, maleic anhydride

Abstract: A direct synthesis of trimellitic anhydride (TMA) and hemimellitic anhydride (HMA) has been reported in which all the carbons of TMA and HMA are derived from malic acid. Acetoxy succinic anhydride represents a convenient in situ equivalent of maleic anhydride.

## 1. Introduction

Trimellitic anhydride (TMA) (**1**) and trimellitic acid (**2**) are valuable industrial materials.<sup>1</sup> Both compounds are derived from petroleum sources. The most commonly used precursor to TMA is 1, 2, 4-trimethylbenzene which is oxidized to the triacid by a vigorous procedure involving a continuous liquid-phase air oxidation at high temperature using a Br-Co-Mn catalyst.<sup>2</sup> Compounds **1** and **2** are utilized industrially to make plasticizers for poly (vinyl chloride).<sup>3</sup> TMA is also used to produce polyimides and polyesters which can be applied to coatings for electrical insulation and as a useful curing agent for epoxy resins.<sup>4</sup> There are few renewable pathways to **1** and **2**. Zhang recently reported an innovative synthesis of aromatic tri- and tetra-acids in several steps starting from diethyl maleate and pinacol, a precursor to 2,3-dimethylbutadiene.<sup>5</sup> Hemimellitic acid **3** has been used in metal organic frameworks and is made commercially from 1, 2, 3-trimethylbenzene.<sup>6</sup> As part of a program to convert inexpensive organic acids into

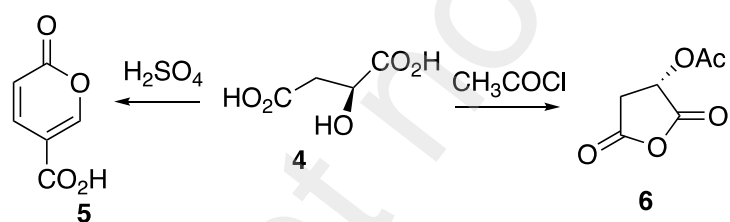
renewable materials, we report herein a direct synthesis of trimellitic anhydride and hemimellitic anhydride in which all of the carbons of TMA and HMA are derived from malic acid.



**Figure 1.** Industrially valuable benzene-based acids and anhydride.

## 2. Our previous work

We have previously described improvements in the conversion of malic acid (**4**) to coumalic acid (**5**).<sup>7</sup> Our improved procedure avoids the use of  $\text{SO}_3$  and proceeds in 85% yield on multigram scales. Eskici reported the synthesis of acetoxy succinic anhydride (**6**) from malic acid in 96% yield (Scheme 1).<sup>8</sup> Anhydride **6** has been employed for the regioselective construction of amide acids<sup>9</sup> and tetronic acids<sup>10</sup>.

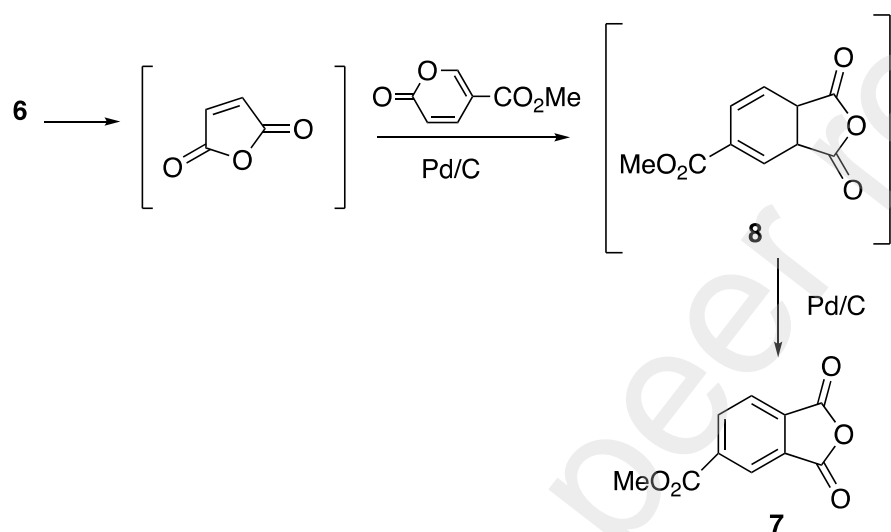


**Scheme 1.** Preparation of coumalic acid and acetoxy succinic anhydride.

## 3. Results and discussion

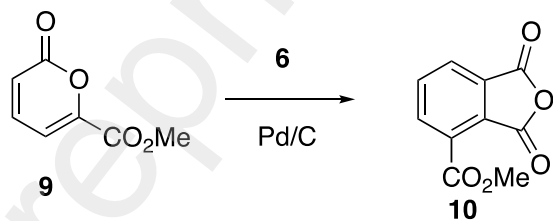
Interestingly, the thermochemistry of **6** had not been reported. Anhydride **6** might be transformed into maleic anhydride by heating in an anhydrous solvent. To test this question, anhydride **6** was reacted with methyl coumalate at temperatures ranging from 110 ° to 200 °C.

Adduct **7**<sup>11</sup> was isolated in 43% yield as shown in Scheme 2. The reaction of anhydride **6** with methyl coumalate at 200 °C generated a tricyclic intermediate which rapidly lost carbon dioxide to produce the anhydride **8**. Subsequent in situ dehydrogenation with palladium on carbon catalyst afforded TMA in 32% yield.<sup>12</sup> The trimellitic anhydride produced by this procedure<sup>13</sup> was identical to the commercial material by proton NMR and melting point.



**Scheme 2.** Preparation of trimellitic anhydride methyl ester using thermochemistry.

Hemimellitic anhydride was directly prepared from pyrone **9**<sup>14</sup> and **6** by the same protocol in 49% yield as shown in Scheme 3. Its NMR and melting point matched the literature values.<sup>15</sup>



**Scheme 3.** Preparation of hemimellitic anhydride using thermochemistry.

#### 4. Conclusion

The direct synthesis of TMA and HMA from renewable precursors has been achieved. A key feature is the use of acetoxysuccinic anhydride as a maleic anhydride equivalent. This pathway avoids the harsh benzylic oxidation conditions used by other approaches.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Acknowledgment:** We thank Iowa State University for partial support of this research.

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13. **Preparation of adduct 7.** Combined 5 mmol of Acetoxysuccinic anhydride, 2 mmol of methyl coumalate, 0.2 mmol of Pd/C and 5 ml of mesitylene in a bomb flask. Sparged the mixture with argon and heated to 200°C with stirring for 23 hours. Cooled to an ambient temperature. Filtered off the catalyst on a celite

plug and washed it with acetonitrile, 80 ml. Collected the organic mixture and washed it 4 times with 30 ml of hexanes. Acetonitrile phase concentrated on a rotary evaporator. Column chromatographed using gradient 1:4 to 1:3 ethyl acetate:hexanes. Product's Rf on TLC (1:4 ethyl acetate:hexanes) is 0.24 and the spot sits on top of methyl coumalate spot. <sup>1</sup>H NMR( 400 MHz, CDCl<sub>3</sub>): 8.63(s,1H), 8.56(d, J=5.2 Hz,1H), 8.1(d, J= 5.2 Hz,1H),4.02(s,3H).