Supporting Information

Facile and Efficient Synthesis of Cyclic Anhydrides from Dicarboxylic Acids

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1. General Considerations

Solvents (THF, MeTHF) were freshly distilled from Na/K amalgam. NMR spectra were recorded on Bruker Avance-300, and Avance-400 spectrometers. $^1$H and $^{13}$C chemical shifts are reported in ppm versus SiMe$_4$ and were determined by reference to the residual solvent peaks. Assignment of signals was made from multinuclear 1D ($^1$H, $^{13}$C{$^1$H}) and 2D (COSY, HMQC, HMBC) NMR experiments. IR analyses were carried out using a FT/IR-4100 Jasco instrument, with an ATR PRO450-S, a TGR detector, 2mm/sec scanning speed and a resolution of 16 cm$^{-1}$.

2. Materials

$(1R,3S)$-$(+)$-camphoric acid, glutaric acid, pimelic acid, adipic acid, methylsuccinic, diphenic acid, maleic acid were purchased from Sigma-Aldrich. Succinic acid, itaconic acid, phenylsuccinic acid and phtalic acid were ordered from Alfa Aesar. All the diacids were recrystallized three times with THF/pentane or methylene chloride/diethyl ether and dried overnight under vacuum. Dimethyl dicarbonate and di-tert-butyl dicarbonate (purchased from Aldrich) were carefully stored in the freezer and used as received.

3. Representative Procedure for 50 eq. of succinic acid converted

MgCl$_2$ (2 mg, 0.02 mmol, 1 eq.), succinic acid (118 mg, 1mmol, 50 eq.), di-tert-butyl dicarbonate (220 mg, 1 mmol, 50 eq.) in 1ml of THF are stirred in a round-bottom flask at 40°C in air. After the allocated reaction time, the conversion was checked by $^1$H NMR spectroscopy, which indicated complete and selective conversion of the starting dicarboxylic acid. When the conversion is complete, volatiles were removed under vacuum overnight. The cyclic anhydride was quantitatively separated from MgCl$_2$ by sublimation.
4. Characterization of cyclic anhydrides

**Succinic anhydride**:  
\[ \text{H NMR (300 MHz, CDCl}_3, \delta \text{ ppm)} : 3.01 (s, 4H, CH}_2\text{CO) } \]
\[ \text{C}^{13}\text{H NMR (75 MHz, CDCl}_3, \delta \text{ ppm)} : 170.6 (CO), 28.3 (CH}_2\text{CO) } \]

**Glutaric anhydride**:  
\[ \text{H NMR (300 MHz, CDCl}_3, \delta \text{ ppm)} : 2.74 (t, 4H, CH}_2\text{CO), 2.03 (m, 2H, CH}_2) \]
\[ \text{C}^{13}\text{H NMR (75 MHz, CDCl}_3, \delta \text{ ppm)} : 166.8 (CO), 30.3 (CH}_2\text{CO), 16.7 (CH}_2) \]

**Adipic anhydride**:  
\[ \text{H NMR (300 MHz, CDCl}_3, \delta \text{ ppm)} : 2.51 (m, 4H, CH}_2\text{CO), 1.72 (m, 2H, CH}_2) \]
\[ \text{C}^{13}\text{H NMR (75 MHz, CDCl}_3, \delta \text{ ppm)} : 168.8 (CO), 34.7 (CH}_2\text{CO), 23.2 (CH}_2) \]

**Pimelic anhydride**:  
\[ \text{H NMR (300 MHz, CDCl}_3, \delta \text{ ppm)} : 2.46 (t, 4H, CH}_2\text{CO), 1.66 (m, 4H, CH}_2), 1.41 (m, 2H, CH}_2) \]
\[ \text{C}^{13}\text{H NMR (75 MHz, CDCl}_3, \delta \text{ ppm)} : 169.2 (CO), 35.0 (CH}_2\text{CO), 28.0 (CH}_2), 23.8(CH}_2) \]

**Phtalic anhydride**:  
\[ \text{H NMR (300 MHz, CDCl}_3, \delta \text{ ppm)} : 7.97 (m, 2H, CH), 7.86 (m, 2H, CH) \]
\[ \text{C}^{13}\text{H NMR (75 MHz, CDCl}_3, \delta \text{ ppm)} : 162.7 (CO), 136.0 (CH), 131.3 (Cq), 125.7 (CH) \]

**Diphenic anhydride**:  
\[ \text{H NMR (300 MHz, CDCl}_3, \delta \text{ ppm)} : 7.80 (m, 2H, CH), 7.63 (m, 4H, CH), 7.46 (m, 2H, CH) \]
\[ \text{C}^{13}\text{H NMR (75 MHz, CDCl}_3, \delta \text{ ppm)} : 162.9 (CO), 135.5 (Cq), 133.4 (CH), 130.9 (CH), 130.4 (Cq), 129.1 (CH), 128.9 (CH) \]
Maleic anhydride:

$^1$H NMR (300 MHz, CDCl$_3$, $\delta$ ppm): 6.43 (s, 2H, CH)
$^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, $\delta$ ppm): 164.5 (CO), 136.5 (CHCO)

Itaconic anhydride:

$^1$H NMR (300 MHz, CDCl$_3$, $\delta$ ppm): 6.55 (m, 1H, CH), 5.90 (m, 1H, CH), 3.60 (m, 2H, CH$_2$)
$^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, $\delta$ ppm): 167.6 ; 164.4 (CO), 130.0 (C$_q$), 126.6 (CH$_2$=), 33.6 (CH$_2$)

Methylsuccinic anhydride:

$^1$H NMR (300 MHz, CDCl$_3$, $\delta$ ppm): 3.19 (m, 1H, CH), 2.64 (d, 2H, CH$_2$), 1.45 (d, 3H, CH$_3$)
$^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, $\delta$ ppm): 174.3; 169.0 (CO), 36.0 (CH), 35.5 (CH$_2$), 16.1 (CH$_3$)

Camphoric anhydride:

<table>
<thead>
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<th>Group</th>
<th>$^1$H NMR ($\delta$ ppm)</th>
<th>$^{13}$C{$^1$H} NMR ($\delta$ ppm)</th>
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<td>A</td>
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</tr>
<tr>
<td>B</td>
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</tr>
<tr>
<td>C</td>
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</tr>
<tr>
<td>D</td>
<td>-</td>
<td>43.7</td>
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<tr>
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<td>33.4</td>
</tr>
<tr>
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<td>2.24 ; 2.13 ; 1.98</td>
<td>24.4</td>
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<tr>
<td>G, H, I</td>
<td>1.27 ; 1.10 ; 1.00</td>
<td>20.7 ; 20.2 ; 14.13</td>
</tr>
</tbody>
</table>
Figure S1: $^1$H NMR Spectrum of Camphoric Anhydride (300 MHz, CDCl$_3$)

Figure S2: $^{13}$C{$^1$H} NMR Spectrum of Camphoric Anhydride (75 MHz, CDCl$_3$)
Figure S3: IR Spectrum of Camphoric Anhydride

\[ \tilde{\nu} (CO) = 1755 \text{cm}^{-1} \]