Electronic supplementary information

Carbonate, Acetate and Phenate Exchanged Phosphonium Salts as Catalysts in Transesterification Reactions for the Synthesis of Non Symmetric Dialkyl Carbonates

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### Synoptic table of major MS signals of reaction products.

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<tr>
<th>Compound</th>
<th>GC/MS (EI, 70 eV)</th>
</tr>
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<tr>
<td>Cyclohexyl methyl carbonate</td>
<td>m/z: 99 (M-CH₂CO₂⁺, 32%), 83 (M-CH₂OCHO₂⁺, 52), 82 (M-CH₂OCHO₂-H⁺, 98), 81 (21), 77 (63), 71 (42), 67 (100), 59 (27), 55 (47), 54 (31).</td>
</tr>
<tr>
<td>Cyclohexyl ethyl carbonate</td>
<td>m/z: 99 (M-CH₂CH₃CO₂⁺, 57%), 91 (100), 83 (M-CH₂CH₂OCHO₂⁺, 63), 82 (M-CH₂CH₂OCHO₂-H⁺, 67), 81 (22), 67 (74), 63 (35), 57 (51), 55 (44).</td>
</tr>
<tr>
<td>Cyclopentyl methyl carbonate</td>
<td>m/z: 91 (25%), 85 (M-CH₃CO₂⁺, 80), 69 (M-CH₃CH₂OCHO₂⁺, 53), 68 (M-CH₃OCHO₂-H⁺, 28), 67 (22), 63 (12), 58 (11), 57 (100).</td>
</tr>
<tr>
<td>Cyclopentyl ethyl carbonate</td>
<td>m/z: 91 (25%), 85 (M-CH₃CH₂CO₂⁺, 80), 69 (M-CH₃CH₂OCHO₂⁺, 53), 68 (M-CH₃OCHO₂-H⁺, 28), 67 (22), 63 (12), 58 (11), 57 (100).</td>
</tr>
<tr>
<td>Benzyl methyl carbonate</td>
<td>m/z: 166 (M⁺, 67%), 122 (M-CO₂⁺, 14), 121 ([M-CO₂-H⁺, 20], 107 ([M-CO₂ CH₃⁺, 51] 91 ([C₂H₅⁺, 100], 90 (41), 79 (30), 77 (25), 65 (15).</td>
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<tr>
<td>Menthyl methyl carbonate</td>
<td>m/z: 139 (M-CH₃OCHO₂⁺, 12%), 138 ([M-CH₃OCHO₂-H⁺, 55), 123 ([M-CH₃OCHO₂-CH₃⁺, 54] 109 ([M-CH₃OCHO₂-CH₃⁺, 11], 95 ([C₂H₅⁺, 100], 82 (23), 81 (61), 69 (12), 67 (20), 65 (15), 57 (14).</td>
</tr>
<tr>
<td>Menthyl ethyl carbonate</td>
<td>m/z: 139 (M-CH₃OCHO₂⁺, 15%), 138 ([M-CH₃OCHO₂-H⁺, 65), 123 ([M-CH₃CH₂OCHO₂-CH₃⁺, 52] 109 ([M-CH₃CH₂OCHO₂-CH₃⁺, 11], 95 ([C₂H₅⁺, 100], 82 (24), 81 (60), 71 (13), 69 (15), 67 (18), 57 (10), 55 (21).</td>
</tr>
<tr>
<td>Triphenylmethyl methyl ether⁠ †</td>
<td>m/z: 274 ([M⁺, 62%], 243 ([Ph₃C⁺, 75], 197 ([M⁺, 100], 165 (37), 105 ([PhCO⁺, 30], 77 (17). Match quality: 94.9% (ref. NIST).</td>
</tr>
<tr>
<td>1,1 diphenylethene</td>
<td>m/z: 180 ([M⁺, 100%), 179 ([M-H⁺, 74], 178 ([M-2H⁺, 62), 165 (83), 152 (12), 89 (12).</td>
</tr>
</tbody>
</table>

1. Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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NMR spectra of prepared catalysts

Figure S1 $^1$H-NMR of compound 1c in CDCl$_3$.  

Figure S2 $^{13}$C-NMR of compound 1c in CDCl$_3$.  

Figure S3 $^{31}$P-NMR of compound 1c in CDCl$_3$.

Figure S4 $^1$H-NMR of compound 1d in DMSO-$d_6$. 
Figure S5 $^{13}$C-NMR of compound 1d in DMSO-$d_6$.

Figure S6 $^{31}$P-NMR of compound 1d in DMSO-$d_6$. 
Figure S7 ESI-MS of compound 1c in acetonitrile. The spectrum shows a strong positive ion at m/z 385 corresponding to the P₈₈₈₁ cation (the anion mass was too low to be detected by ESI-MS).
**Figure S8** ESI-MS of compound 1d in acetonitrile. The spectrum shows a strong positive ion at m/z 385 corresponding to the P₈₈₈₁ cation (the anion mass was too low to be detected by ESI-MS).
NMR spectra of the isolated products

Figure S9 $^1$H-NMR of cyclohexyl methyl carbonate in CDCl$_3$.

Figure S10 $^{13}$C-NMR of cyclohexyl methyl carbonate in CDCl$_3$. 
Figure S11 $^1$H-NMR of cyclopentyl methyl carbonate in CDCl$_3$.

Figure S12 $^{13}$C-NMR of cyclopentyl methyl carbonate in CDCl$_3$. 
**Figure S13** $^1$H-NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl methyl carbonate (menthyl methyl carbonate) in CDCl$_3$.

**Figure S14** $^{13}$C-NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl methyl carbonate (menthyl methyl carbonate) in CDCl$_3$. 
Figure S15 $^1$H-NMR of benzyl methyl carbonate in CDCl$_3$.

Figure S16 $^{13}$C-NMR of benzyl methyl carbonate in CDCl$_3$. 
Figure S17 $^1$H-NMR of 1,1-diphenylethene in CDCl$_3$.

Figure S18 $^{13}$C-NMR of 1,1-diphenylethene in CDCl$_3$. 
Figure S19 $^1$H-NMR of cyclohexyl ethyl carbonate in CDCl$_3$.

Figure S20 $^{13}$C-NMR of cyclohexyl ethyl carbonate in CDCl$_3$. 
Figure S21 \(^1\text{H-NMR}\) of cyclopentyl ethyl carbonate in CDCl\(_3\).

Figure S22 \(^1\text{H-NMR}\) of cyclopentyl ethyl carbonate in CDCl\(_3\).
**Figure S23** $^1$H-NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl ethyl carbonate (menthyl ethyl carbonate) in CDCl$_3$.

**Figure S24** $^1$H-NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl ethyl carbonate (menthyl ethyl carbonate) in CDCl$_3$. 
IR spectra of new products

Figure S25 IR spectrum of cyclopentyl methyl carbonate.
Figure S26 IR spectrum of menthyl methyl carbonate.
References