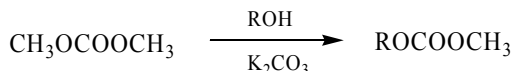


SUPPLEMENTARY INFORMATION

General procedure for the synthesis of alkyl methyl carbonates

Propyl methyl carbonate, octyl methyl carbonate, propan-2-yl methyl carbonate, *t*-butyl methyl carbonate and benzyl methyl carbonate were all synthesized by transesterification of DMC with their parent alcohols (propan-1-ol, octan-1-ol, propan-2-ol, *t*-butyl alcohol and benzyl alcohol) under refluxing conditions (90 °C), in the presence of catalytic amount of base according to Scheme 1. Pure carbonates were then isolated by distillation.



Scheme 1 Synthesis of unsymmetrical carbonates starting from DMC

Benzyl methyl carbonate, octyl methyl carbonate were prepared according to a synthetic procedure already reported in the literature (P. Tundo, F. Aricò, A. E. Rosamilia and Sofia Memoli. *Green Chem.* **10**, 1182 (2008)).

Propyl methyl carbonate

For the preparation of propyl methyl carbonate, a three-necked round bottom flask equipped with a dephlegmator was used. Propan-1-ol (73 g, 1.2 mol), DMC (330 g, 3.6 mol) and K₂CO₃ (17 g, 0.1 mol) were heated at refluxing conditions with stirring. The reaction was analyzed by GC-MS. After complete conversion of the substrate (9 hours), the mixture was filtered over Gooch n° 4 to remove the solid catalyst. The liquor was then poured in water (500 ml) and extracted with pentane (3 x 250 ml). The organic phase was recovered and dried over Na₂SO₄, filtered and distilled to obtain the pure product as a clear oil.

56 g obtained; yield: 36 %; ¹H NMR (300 MHz, CDCl₃): δ 0.95 (t, 3H); 1.65 (m, 2H); 3.78 (s, 3H); 4.10 (t, 2H). ¹³C (75 MHz, CDCl₃): δ 9.9; 21.87; 54.4; 69.4; 155.7.

Propan-2-yl methyl carbonate

For the preparation of propan-2-yl methyl carbonate, a three-necked round bottom flask equipped with a dephlegmator was used. 2-Methylpropan-1-ol (100 g, 1.7 mol), DMC (300 g, 3.3 mol) and K₂CO₃ (30 g, 0.2 mol) were heated at refluxing conditions with stirring. The reaction was analyzed by GC-MS. After complete conversion of the substrate (9 hours), the mixture was filtered over Gooch n° 4 to remove the solid catalyst. The liquor was then poured into water (500 ml) and extracted with diethyl ether (3 x 250 ml). The organic phase was recovered and dried over Na₂SO₄, filtered and distilled to obtain the pure product as a clear oil.

71 g obtained; yield: 35 %; ¹H NMR (300 MHz, CDCl₃): δ 1.31 (d, 6H); 3.8 (s, 3H); 4.91 (m, 1H). ¹³C (75 MHz, CDCl₃): δ 21.7; 54.2; 71.7; 155.2.

t-Butyl methyl carbonate

For the preparation of *t*-butyl methyl carbonate, a three-necked round bottom flask equipped with a dephlegmator was used. *t*-Butyl alcohol (97 g, 1.3 mol), DMC (354 g, 3.9 mol) and NaOMe (4 g, 0.07 mol) were heated at refluxing conditions with stirring. The reaction was analyzed by GC-MS. After complete conversion of the substrate (10 hours), the mixture was filtered over Gooch n° 4 to remove the solid catalyst. The liquor was then poured into water (500 ml) and extracted with pentane (3 x 250 ml). The organic phase was recovered and dried over

Na₂SO₄, filtered and distilled to obtain the pure product as a clear oil.

39.5 g obtained; yield: 23 %; ¹H NMR (300 MHz, CDCl₃): δ 1.52 (s, 9H); 3.72 (s, 3H). ¹³C (75 MHz, CDCl₃): δ 27.7; 53.6; 81.7; 153.9.

General procedure for the synthesis of dialkyl carbonates

Dioct-1-yl carbonate was prepared according to a synthetic procedure already reported in the literature.¹⁷

Di propan-2-yl carbonate

For the preparation of dipropan-2-yl carbonate, a three-necked round bottom flask equipped with a dephlegmator was used. 2-Methylpropan-1-ol (500 g, 8.3 mol), DMC (450 g, 5 mol) and NaOMe (22.5 g, 0.4 mol) were heated at refluxing conditions under magnetically stirring. The reaction was analyzed by GC-MS. After 10 hours, the reaction was stopped and the mixture was distilled to obtain the pure product as a clear oil.

206 g obtained; yield: 34 %; ¹H NMR (300 MHz, CDCl₃): δ 1.22 (d, 12H); 4.95 (m, 2H). ¹³C (75 MHz, CDCl₃): δ 21.7; 71.2; 154.0.

Dibenzyl carbonate

For the preparation of dibenzyl carbonate, a three-necked round bottom flask equipped with a dephlegmator was used. Benzyl alcohol (200 g, 1.8 mol), DMC (100 g, 0.6 mol) and K₂CO₃ (15 g, 0.1 mol) were heated at refluxing conditions with stirring. The reaction was analyzed by GC-MS. After complete conversion of the substrate (10 hours), the mixture was filtered over Gooch n° 4 to remove the solid catalyst. The liquor was then poured into water (80 ml) and extracted with pentane (3 x 100 ml). The organic phase was recovered and dried over Na₂SO₄, filtered and distilled to obtain the pure product as a clear oil.

162 g obtained; yield: 67 %; ¹H NMR (300 MHz, CDCl₃): δ 5.25 (s, 4H); 7.44-7.55 (m, 10H). ¹³C (75 MHz, CDCl₃): δ 69.6; 128.2; 128.3; 128.4; 128.5, 135.1; 150.0.

Di-*t*-butyl carbonate

For the preparation of di-*t*-butyl carbonate, a three-necked round bottom flask equipped with a dephlegmator was used. *t*-Butanol (306 g, 4.1 mol), DMC (93 g, 1.0 mol) and CH₃ONa (30 g, 0.5 mol) were heated at refluxing conditions with stirring. The reaction was analyzed by GC-MS. At complete conversion of the substrate (24 hours), the mixture was filtered over Gooch n° 4 to remove the solid catalyst. The organic phase was then distilled to obtain the pure product as a low boiling solid.

8.2 g obtained; yield: 4.5 %; m.p.: 37.4 – 37.8 °C; ¹H NMR (300 MHz, CDCl₃): δ 1.35 (s, 18H). ¹³C (75 MHz, CDCl₃): δ 27.7; 80.8; 152.0.

General procedure for the reaction of carbonates with ethanol (table 1 and 2)

In a 25 ml round bottom flask the carbonate (1 g) was added to a mixture of EtOH (molar ratio carbonate/EtOH 1/50) and K₂CO₃ or Cs₂CO₃ (molar ratio carbonate/base 1/0.25). The continuously stirred mixture was heated at 60 °C. Samples were taken at time intervals and analyzed by GC and GC-MS (table 1 and table 2)

General procedure for the reaction of symmetric carbonates with ethanol (table 3)

In a 25 ml round bottom flask was prepared a mixture containing dimethyl carbonate (1 g), the selected symmetric carbonate (molar ration DMC/carbonate 1/1), ethanol (molar ratio DMC/EtOH 1/50), and K₂CO₃ (molar ratio DMC/base 1/0.25 mol). The continuously stirred mixture was

heated at 60 °C. Samples were taken at time intervals and analyzed by GC and GC-MS (table 4)

General procedure for the reaction of alcohols with dimethyl carbonate (table 4)

In a 25 ml round bottom flask was prepared a mixture containing ethanol (1 g), the selected alcohol (molar ration alcohol/EtOH 1/1) K_2CO_3 (molar ratio EtOH/base 1/0.25) and DMC (molar ratio EtOH/DMC 1/50). The continuously stirred mixture was heated at 60 °C. Samples were taken at time intervals and analyzed by GC and GC-MS (table 3)