Replacement of Phosgene with Carbon Dioxide: Synthesis of Alkyl Carbonates

William McGhee* and Dennis Riley

Monsanto Company, 800 North Lindbergh Boulevard, St Louis, Missouri 63167

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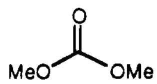
Alkyl carbonates, although not as ubiquitous as the aromatic carbonates (i.e., polymers derived from bisphenol A) do find important applications in the polymer industry. Most notably are dimethyl carbonate (**1**, DMC) and diethylene glycol diallyl dicarbonate (**2**).



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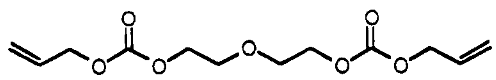
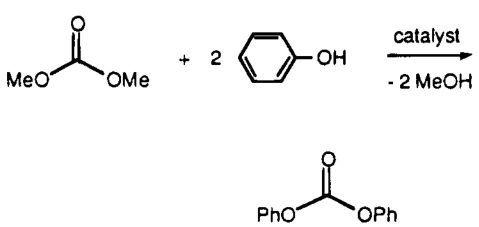


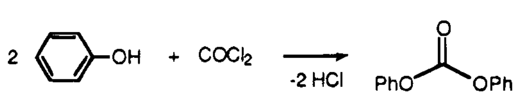
2

Dimethyl carbonate has grown in importance with numerous applications as a phosgene equivalent. One such use of DMC is as a precursor for diphenyl carbonate, eq 1.[1]



(1)

Diphenyl carbonate is traditionally generated from phenol and phosgene and is used in the synthesis of polycarbonate (eqs 2 and 3).



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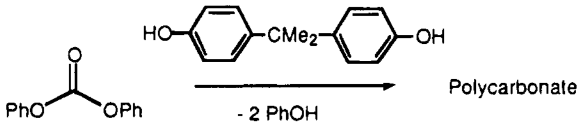
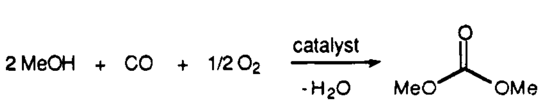


(3)

DMC has also been shown to be an octane booster in gasoline.[2] The most promising method for the generation of DMC is via oxidative carbonylation technology, eq 4.



(4)

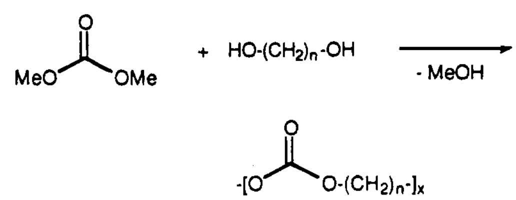
State of the art technology is hampered by low conversions (yet high selectivity) and harsh reaction conditions.

Table 1. Reaction of an Alcohol with an Alkyl Chloride in Acetonitrile under 80 psig Carbon Dioxide Pressure Using *N*-Cyclohexyl-*N′*,*N′*,*N″*,*N″*-tetramethylguanidine as Base

ROH	R′Cl	*T* (°C)	% carbonate (GC yield)	% carbonate (isolated)
BuOH	$PhCH_2Cl$	55	90–94 (**3**)	
$PhCH_2OH$	BuCl	85	53 (**3**)	
i-PrOH	$PhCH_2Cl$	55	(**4**)	85
$PhCH_2OH$	$PhCH_2Cl$	55	(**5**)	97
$O(CH_2CH_2OH)_2$	$PhCH_2Cl$	55	(**6**)	76
BuOH	BuCl	85	73 (**7**)	
$O(CH_2CH_2OH)_2$	$CH_2{=}CHCH_2Cl$	55	84 (**8**)	80

The second major commercial aliphatic carbonate material DAC (**2**) has been used in numerous applications.[3] Radical polymerization of **2** leads to hard, transparent materials useful in lens and safety shield manufacturing.

To a lesser extent, aliphatic carbonates in the molecular weight range of 1000–2000 have been used as "soft" segments in thermoplastic elastomers. These materials are most conveniently generated from the diol and phosgene or by ester exchange with DMC (eq 5).

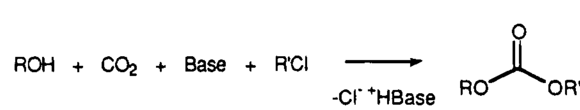


(5)

As mentioned previously, carbonylation technology has been used to generate symmetrical monomeric dialkyl carbonates. This method is not amenable toward the direct synthesis of unsymmetrical carbonates nor is it useful for oligomer synthesis (low conversion).

Research at GE has shown that symmetrical dialkyl carbonates can be generated from alkali metal carbonates and alkyl chlorides in polar aprotic solvents (i.e., *N*-methylpyrrolidinone) in moderate yields using phase transfer catalysis (PTC).[4] Yields as high as 80% were achieved using benzyl chloride to make dibenzyl carbonate with K_2CO_3/KBr and Bu_4PBr as PTC in dimethylacetamide at 150 °C. Mixed carbonates could also be generated from alkali metal carbonates, $ROCO_2^{-}{}^{+}M$ and R′Cl with PTC.

We have found that mixed or symmetrical carbonates can be generated in high yields from alcohols, carbon dioxide, and alkyl chlorides in apolar aprotic solvents using amidine/guanidine bases under surprisingly mild conditions (eq 6).



(6)

Results and Discussion

Previous studies had indicated that we could generate carbamate esters from amines/carbon dioxide and alkyl chlorides by using pentaalkylguanidines as strong, hindered, non-nucleophilic, highly polarizable bases to pro-

(1) For an example see: Mark, V. US Pat. 4,554,110 issued to GE (Nov 19, 1985); *Chem. Abstr.* **1986**, *104*, 50647c.

(2) See: US Pat. 4,600,408 (July 15, 1986); *Chem Abstr.* **1986**, *105*, 156006d. US Pat. 4,891,049 (Jan 2, 1990); *Chem. Abstr.* **1990**, *112*, 142631m. US Pat. 4,904,279 (Feb 27, 1990); *Chem. Abstr.* **1990**, *112*, 201945s.

(3) For a general discussion of DADC see: Mark, H. F.; Bikales, N. M.; Overberger, C. G. Menges, G. J.; Kroschwitz, J. I. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley and Sons: New York, 1990; p 781.

(4) Cella, J. A.; Bacon, S. W. *J. Org. Chem.* **1984**, *49*, 1122–1125.

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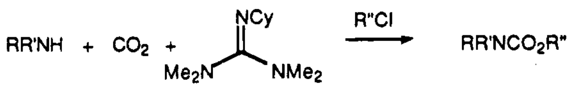
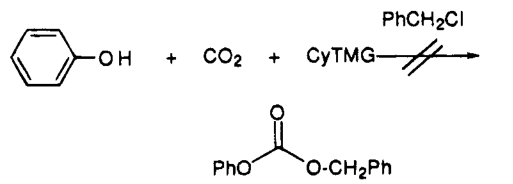
mote the nucleophilic nature of the oxygen center of the carbamate anion.[5] A logical extension to this was to generate dialkyl carbonates from alcohols, carbon dioxide and alkyl chlorides using the same pentaalkyl guanidines (eq 7). Table 1 summarizes the results of the use of



(7)

N-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine as a base in the synthesis of carbonates. The reaction is general to the use of alkyl alcohols and alkyl chlorides. In line with our previous studies, the use of polar aprotic solvents gives rise to the greatest rates of carbonate production.

This chemistry was unsuccessful in the conversion of aromatic alcohols to their corresponding carbonates (eq 8). This finding is in line with other studies.[5]



(8)

Conclusions

The logical extension to the generation of carbonates from alcohols/carbon dioxide and alkyl chlorides using the information gained in the synthesis of carbamate esters was shown to be successful. This method may prove to be a useful way to make symmetrical or unsymmetrical carbonates without the use of phosgene.

Experimental Section

Materials. Alcohols used in this work were obtained from either Aldrich Chemical Co. or Kodak Chemical Co. and were used as received. Anhydrous solvents under nitrogen were purchased from Aldrich Chemical Co.; CyTMG (*N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine) was synthesized according to literature procedure.[6] Carbon dioxide was supplied from Acetylene Gas Co. (welding grade) and used without any further purification.

Carbonic Acid, Butyl Phenylmethyl Diester (3). A Fischer-Porter bottle was charged with 1.48 g (0.02 mol) of butanol, 5.3 g (0.027 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*- tetramethylguanidine, and 20 mL of 1-methyl-2-pyrrolidinone (NMP). The Fischer-Porter bottle was attached to a pressure head, and at room temperature with stirring was added 80 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction, and cooling with ice was required. Into a second Fischer-Porter bottle was added 10.12 g (0.08 mol) of benzyl chloride in 10 mL of NMP. This mixture was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the benzyl chloride solution was added all at once under 80 psig CO_2 to the pre-formed carbonate anion solution generated in the first Fischer-Porter bottle. After addition, the reaction mixture was warmed to 55 °C for 18 h. After this time the reaction mixture was allowed to cool to room temperature and then the pressure was released. An aliquot was taken and diluted with diethyl ether, $CyTMGH^+Cl^-$ was filtered off, and by GC analysis a 90% yield of benzyl butyl carbonate was calculated vs biphenyl (internal standard): oil; ^1H NMR ($CDCl_3$) δ 7.44–7.38 (overlapping, m 5H), 5.20 (s, 2H), 4.20 (t, J = 6.7 Hz, 2H), 1.70 (m, 2H), 1.44 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.8, 136.0, 129.0, 128.8, 69.9, 68.5, 31.2, 19.4, 14.2; IR (film) 1746, 1262. Anal. Calcd for $C_{12}H_{15}O_3$: C, 69.53; H 7.30. Found: C, 69.29; H, 7.75.

Carbonic Acid, 1-Methylethyl Phenylmethyl Diester (4). Procedures as described in the synthesis of **3**. The carbonate was isolated by pouring the crude reaction mixture into diethyl ether, extracting with 2 × 100 mL of 0.5 M aqueous HCl and 1 × 100 mL brine, drying over Na_2CO_3, filtering, concentrating, and chromatography on silica gel (85%, a small amount of dibenzyl carbonate was detected and was separable from the product): oil; ^1H NMR ($CDCl_3$) δ 7.44–7.35 (overlapping m, 5H), 5.19 (s, 2H), 4.95 (7 line pattern, J = 6.3 Hz, 1H), 1.34 (d, J = 6.2 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.2, 136.0, 129.1, 128.9, 128.8, 72.6, 69.7, 22.3; IR (film) 1740, 1260; MS (FAB) m/z = 195 (MH^+). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.01; H, 7.27. Found: C, 68.31; H, 6.95.

Carbonic Acid, Bis(phenylmethyl) Diester (5). Procedures as described in synthesis of **3**. The carbonate was isolated by pouring the crude reaction mixture into diethyl ether, extracting with 2 × 100 mL of 0.5 M aqueous HCl and 1 × 100 mL of brine, drying over Na_2CO_3, filtering, concentrating, and chromatography on silica gel (97%): oil; ^1H NMR ($CDCl_3$) δ 7.45–7.35 (overlapping m, 10H), 5.25 (s, 4H); IR (film) 1746, 1262. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.35; H, 5.83. Found: C, 74.08; H, 6.06.

2,5,8-Trioxanonanedioic Acid, Bis(phenylmethyl) Diester (6). Procedures as described in synthesis of **3**. The carbonate was isolated by pouring the crude reaction mixture into diethyl ether, extracting with 2 × 100 mL of 0.5 M aqueous HCl and 1 × 100 mL of brine, drying over Na_2CO_3, filtering, concentrating, and chromatography on silica gel (76%): oil; ^1H NMR ($CDCl_3$) δ 7.43–7.34 (overlapping m, 10H), 5.20 (s, 4H), 4.33 (m, 4H), 3.74 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.6, 135.7, 129.1, 129.0, 128.9, 70.2, 69.4, 67.5; IR (film) 1742, 1260; MS (FAB) m/z = 375 (MH^+). Anal. Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.49; H, 6.19.

Carbonic Acid, Dibutyl Diester (7). A 160 mL Parr autoclave was charged with 2.22 g (0.03 mol) of butanol, 6.9 g (0.035 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine, and 30 mL of CH_3CN. The autoclave was attached to a pressure head, and at room temperature with stirring was added 160 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a Fischer-Porter bottle was added 8.33 g (0.09 mol) of butyl chloride in 10 mL of CH_3CN. This mixture was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the butyl chloride solution was added all at once under 80 psig CO_2 to the pre-formed carbonate anion solution generated in the autoclave. After addition, the pressure was raised to 160 psig with carbon dioxide, and the reaction mixture was warmed to 85 °C for 16 h. After this time the reaction mixture was allowed to cool to room temperature, and then the pressure was released. An aliquot was taken and diluted with diethyl ether, $CyTMGH^+Cl^-$ was filtered off, and by GC analysis a 73% yield of dibutyl carbonate was calculated vs biphenyl (internal standard): oil; ^1H NMR ($CDCl_3$) δ 4.14 (t, J = 6.6 Hz, 4H), 1.66 (m, 4H), 1.41 (m, 4H), 0.94 (t, J = 7.3 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.9, 68.2, 31.2, 19.4, 14.1; IR (film) 1746, 1260; MS (FAB) m/z = 175 (MH^+). Anal. Calcd for $C_9H_{18}O_3$: C, 62.02; H, 10.42. Found: C, 62.23; H, 10.40.

2,5,8-Trioxanonanedioic Acid, Di-2-propenyl Ester (8). A Fischer-Porter bottle was charged with 1.06 g (0.01 mol) of diethylene glycol, 5.3 g (0.027 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine, 154 mg (0.001 mol) of biphenyl as GC internal standard, and 20 mL of CH_3CN. The Fischer-Porter bottle was attached to a pressure head, and at room temperature with stirring was added 80 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a second Fischer-Porter bottle was added 4.6 g (0.06 mol) of allyl chloride in 10 mL of CH_3CN. This was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the allyl chloride solution was added all at once under 80 psig CO_2 to the pre-formed carbonate anion solution generated in the first Fischer-Porter bottle. After addition the reaction mixture was warmed to 55 °C for 14 h. After this time the reaction mixture was allowed to cool to room temperature and then the pressure was released.

(5) McGhee, W. D.; Pan, Y.; Riley, D. P. *J. Chem. Soc., Chem. Commun.* **1994**, 699–700. McGhee, W. D.; Parnas, B. L.; Riley, D. P.; Talley, J. J. US Pat. 5,223,638 (June 29, 1993); *Chem. Abstr.* **1993**, *118*, 213762.

(6) Bredereck, H.; Bredereck, K. *Chem. Ber.* **1961**, *94*, 2278–2295.

An aliquot was taken and diluted with diethyl ether, $CyTMGH^+Cl^-$ was filtered off, and by GC analysis a yield of 84% was calculated. The crude material was poured into 100 mL of diethyl ether and was then extracted with 2 × 100 mL of 0.5 M aqueous HCl and 100 mL of brine. The ethereal layer was dried over Na_2CO_3, filtered, and concentrated. The residue was chromatographed on silica gel using 100% hexane to remove internal standard and then CH_2Cl_2 giving 2.2 g (80%) of the dicarbonate **8**: oil; ^1H NMR ($CDCl_3$) δ 5.91 (m, 2H), 5.35 (dq, J = 17.2, 1.4 Hz, 2H), 5.25 (dq, J = 10.4, 1.4 Hz, 2H), 4.62 (dt, J = 5.8, 1.4 Hz, 4H), 4.28 (m, 4H), 3.72 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.4, 132.0, 119.3, 69.4, 69.0, 67.3; IR (film) 1746, 1649, 1258. Anal. Calcd for $C_{12}H_{18}O_7$: C, 52.53; H, 6.62. Found: C, 52.94; H, 6.75.

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