Catalytic Formation of Cyclic Carbonates from Epoxides and CO_2 with Chromium Metalloporphyrinates

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Introduction

Cyclic carbonates or dioxolanones are useful intermediates in the stereoselective transformation of epoxides to vicinal diols through hydrolysis.[1] The synthesis of organic carbonates by catalytic insertion of carbon dioxide into a carbon oxygen bond of an epoxide usually requires the use of high temperature and pressure.[2] A variety of catalysts including quaternary ammonium[3] and phosphonium[4] salts show greatly reduced efficiency at temperatures below 100 °C. The use of transition metal based catalysts in conjunction with phosphines or amines has been shown to be a very active combination for promoting these reactions; however, product recovery and purification is difficult using these systems.[5] Catalysts containing main group elements such as antimony and tin are effective at low temperatures, but have not been shown to catalyze the insertion of carbon dioxide into epoxides at low catalyst concentrations (<1.0 mol%).[6] Zero-valent nickel[7] phosphine and copper(I)[8] complexes represent a novel class of homogeneous catalysts of high activity. Such complexes lose practical utility due to their sensitivity to oxygen and low turnover number.

Inoue has reported the conversion of propylene oxide and carbon dioxide to propylene carbonate as catalyzed by an aluminum porphyrinate and 1-methylimidazole.[9] The copolymerizations of carbon dioxide and epoxides using such a metalloporphyrinate has been reported.[10] Under the conditions employed, the yields of polycarbonates or cyclic carbonates were modest.

Results and Discussion

In contrast to both aluminum porphyrinates and quaternary ammonium salts, we have found that chromium(III/IV) tetra-*p*-tolylporphyrinate, CrTTPX (**1**), in concert with amine cocatalysts such as *N*-methylimidazole and DMAP, more efficiently promote the formation of the dioxalanone or cyclic carbonate from carbon dioxide and epoxide.[11]

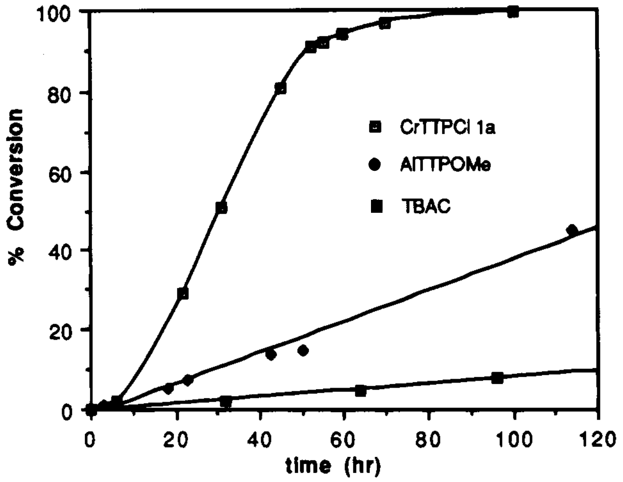
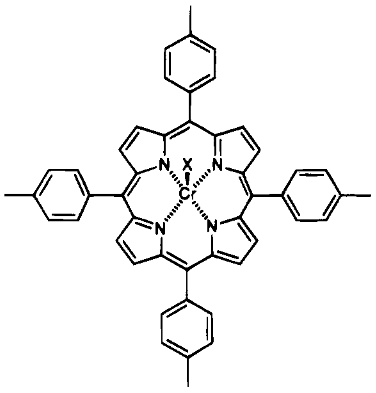


Figure 1. Conversion of butylene oxide to carbonate **2** at 780 psig carbon dioxide as a function of catalyst (50 °C).



1a: X = Cl
1b: X = O

A rate conversion profile for the transformation of *neat* butylene oxide to the corresponding cyclic carbonate **2** (Figure 1) indicates that CrTPPCl (**1a**) shows a 4–5 fold conversion rate over the analogous aluminum system and a 140-fold rate enhancement over tetra-n-butylammonium chloride.[12] Interestingly, when chromium(IV) porphyrinate **1b** was employed as catalyst, chromium(III) complex was recovered as indexed by its typical 447 nm Soret band.[13] It is likely that chromium(IV) disproportionates to Cr(III) and Cr(V) under these conditions, with Cr(V) being reduced by cocatalyst. Chromium(III) porphyrinates were also found to be most effective using the meso tetra-*p*-tolyl derivative (TTP) due to better solubility than the tetraphenyl (TPP) analogue. Although all of the transformations reported in Tables 1 and 2 were performed on neat epoxides, we found cosolvents such as methylene chloride acceptable.[14]

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(9) (a) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304–1309. (b) Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 984.

(10) (a) Aida, T.; Inoue, S. *Macromolecules* **1982**, *15*, 682. (b) Takeda, N.; Inoue, S. *Makromol. Chem.* **1978**, *179*, 1377.

(11) Kruper, W. J.; Dellar, D. U. S. Patent 4,663,467 (*Chem. Abstr.* **1987**, 107 12, 98598b).

(12) After the induction period, the turnover rate for butylenecarbonate production approaches a maximum of 2 min^{-1} with CrTTPCl/DMAP, **1**. The intial turnover numbers for AlTTPOMe/DMAP and TBAC are 0.44 min^{-1} and 0.012 min^{-1}, respectively, during a conversion that appears to be first order in epoxide concentration.

(13) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C.;. Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363.

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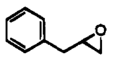
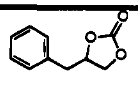
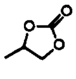
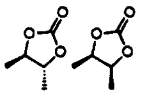
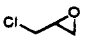
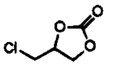
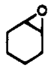
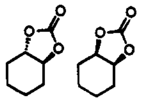
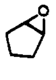
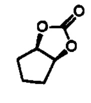
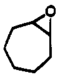
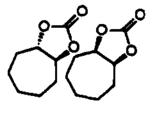
Table 1. Carbonates from Acyclic Epoxides with Metalloporphyrinate Catalysis[a]

Oxirane	Catalyst	Temp (° C)	Time	Product(s)[b]	Yield[c]
	CrTTPCl 1a[d] N-MeIm	70	16 h	 3	100%
	CrTTPCl DMAP	80	64 h	 4	95%
"	CrOTPP 1b[e] N-MeIM	80	48 h	4	95%
"	CrTTPCl DMAP	60	40 h	4	100%
	CrTTP DMAP	100	20 h	 8:8a	84% 8:8b 42:58
	CrTTPCl DMAP	60	18 h	 9	100%
"	CrTTPCl N-MeIm	70	48 h	9	100%

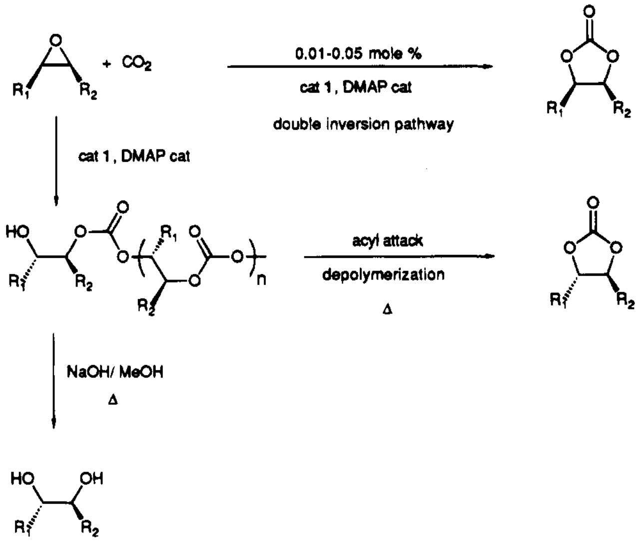
[a] Carbon dioxide at 730–780 psi continuous. [b] Products fully characterized by ^1H and ^{13}C NMR, IR, and combustion analysis. Isomer ratios based on ^1H NMR and VPC analysis. [c] Distilled based on oxirane: no other products formed. [d] 0.013 to 0.07 mol% catalyst (porphyrinate) and 4–10 mol equiv of cocatalyst. CrTTPCl (**1a**) chloro(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(III). [e] CrOTPP (**1b**) oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV).

Table 2. Carbonates from Cyclic Epoxides with Metalloporphyrinate Catalysis[a]

Oxirane	Catalyst	Temp (°C)	Time	Product(s)[b]	Yield[c]
	CrTTPCl[d] 1a DMAP	95	18 h	 5:5a	97%[f] 95 : 5 5:5a
"	N-MeIm	130	44 h	"	0%
"	CrTTPCl or CrOTTP[e] 1b	130	44 h	"	0%
"	CrTTPCl N-MeIm	100	24 h	"	90%
	CrTTP N-MeIm	90	60 h	 6	90%
	CrTTP N-MeIm (DMAP)	85	22 h	 7a:7b	97% 7a:7b 90:10 (73:23)

[a] Carbon dioxide at 730–780 psi continuous. [b] Products fully characterized by ^1H and ^{13}C NMR, IR, and combustion analysis. Isomer ratios based on ^1H NMR and VPC analysis. [c] Distilled based on oxirane: no other products formed. [d] 0.013–0.07 mol% catalyst (porphyrinate) and 4–10 mol equiv of cocatalyst. CrTTPCl (**1a**) chloro(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(III). [e] CrOTPP (**1b**) oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV). [f] Distilled yield of *trans*-carbonate **5** upon pyrolysis (130 °C/1 mm) of alternating *trans*-copolymer **5b**.

Scheme 1



Moreover, catalyst **1a** is highly active (turnover numbers approach 10,000 per metal center with terminal oxiranes), regardless of (III)/(IV) oxidation state, and appears to be recyclable without any remediation due to its thermodynamic stability. In this respect, the carbonate of phenylglycidyl epoxide **3** was distilled quantitatively from the catalyst which was recovered and subjected to three more cycles without loss of activity. A detailed study of how carbon dioxide pressure effected conversion rate was not conducted, yet complete conversion of several epoxides to their corresponding carbonates was observed at lower pressures (50–80 psig) which were conducted in Fisher–Porter vessels. The reaction appeared to be temperature dependent, but not overly sensitive to air and water. The use of higher temperature (95–130 °C) was found to be advantageous for effecting more rapid conversion and for promoting depolymerization of lower weight oligomeric carbonates which were observed in the carbonation of propylene oxide and the exceptional case of cyclohexene oxide. Control experiments (Table 2) indicated that both porphyrin and cocatalyst are required for the transformation.

The conversion of starting material to product was found to proceed through either of two mechanisms (Scheme 1), the nature of which had an effect on stereochemistry of the resulting carbonate. For example, when cyclohexene oxide was subjected to the carbonation conditions, a quantitative yield of a low molecular weight polycarbonate **5b**[15] was obtained, which if saponified, cleanly afforded *trans*-1,2-cyclohexanediol.[16] When this polycarbonate was subjected to vacuum pyrolysis, stereochemically pure *trans*-carbonate **5** was obtained as the distillate. Thermal unzipping or depolymerization of **5b**

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[14] Reactions were conducted under identical conditions (see Experimental Section) with 10 wt % epoxide versus solvent. No exotherms or polyol formation was experienced in reactions conducted above 50 psig of CO_2.

through acyl attack must therefore proceed without a second inversion of the carbonate stereocenter. There is also evidence for the buildup of low molecular weight aliphatic polycarbonates from propylene oxide/CO_2 and other epoxides using the chromium catalyst at lower temperatures. Preservation of *cis*-stereochemistry was observed for the tranformation of cyclopentene oxide to its carbonate **6**, and there was no evidence for the formation of any polymeric intermediate. We feel the variability of stereochemistry for representative examples noted in Table 1 is suggestive of either the direct insertion pathway (double inversion with retention of sterochemistry) or the polymerization/depolymerization pathway (inversion of stereochemistry) and for certain epoxides both mechanisms may be operative. For an internal, linear epoxide, such as *trans*-2-butylene oxide, the loss of stereospecificity by a third mechanism cannot be ruled out. In this case a ring opened chlorohydrin intermediate formed by oxirane insertion into the chromium−chlorine bond can undergo rotational isomerization followed by carbonate activation and closure to give carbonates **8**/**8a**.

In summary, chromium metalloporphyrinates which are now commercially available represent a recyclable and very active catalyst for the conversion of oxiranes to carbonates. The intervention of three possible mechanisms for carbon dioxide incorporation explains the variability of stereospecificity in carbonate formation.

Experimental Section

4-Methyl-1,3-dioxolan-2-one (4) from Propylene Oxide Using CrOTPP (1b),[12] CrTTPCl (1a),[17] and AlTTPOMe.[8] Propylene oxide (16.4 g, 0.282 mole), CrOTPP (25 mg), and 1-methylimidazole (25 mg) were heated and magnetically stirred at 80 °C for 48 h in a stainless steel autoclave under 750 psig of carbon dioxide. This procedure afforded 4-methyl-1,3-dioxolan-2-one (**4**) (26 0 g, 91%, 99.5 area % GC purity) after distillation (bp 65 °C/0.1−0.2 mm).

Conversional Profile of 1-Butylene Oxide to 4-Ethyl-1,3-dioxolan-2-one (2) as a Function of Catalyst CrTTPCl (17 mg) or AlTTPOMe (17 mg) and DMAP (17 mg) were placed in a 40 mL stainless steel autoclave with 1-butylene oxide (11.5 g, 159 mmol). The reactors were sealed and heated to 50 °C under a pressure of 780 psig of carbon dioxide with efficient stirring. Aliquots were periodically sampled and assayed by VPC (110 °C for 2 min then to 200 °C at 16 °C/min using 6 ft x $^1/_8$ in. nickel column with 5% OV 225 on 80−100 mesh Anachrom Q) to establish conversion. Alternatively, tetra-*n*-butylammonium chloride (TBAC) (50 mg, 0.11 mol%) was used as a catalyst under identical conditions. The conversion versus time plot is shown in Figure 1. In the case of the CrTTPCl-catalyzed reaction, the product, 4-ethyl-1,3-dioxolan-2-one, was distilled (59 °C/0.3 mm, 99.6 area% GC purity) as a clear liquid. This compound has been reported[18] but was incompletely characterized: ^1H NMR ($CDCl_3$) δ 4.6 (m, 2H), 4.1 (m, 1H), 1.8 (m, 2H) 1.0 (t, 3H, J = 5.6 Hz); ^{13}CNMR ($CDCl_3$) δ 155.1, 75.6, 67.0, 26.9, 8.4; IR (neat) 2990, 2890, 1800(s), 1182, 1070, 785.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (3). 2,3-Epoxypropyl phenyl ether (10.0 g, 66.6 mmol), CrTTPCl (25 mg), and 1-methylimidazole (25 mg) were heated (70 °C/16 h) under 780 psig of carbon dioxide to afford dioxolanone **3**[19] in quantitative yield (13.0 g). Kugelrohr distillation (270 °C/0.2 mm) provided an analytical sample (mp 96−98 °C): ^1H NMR ($CDCl_3$) δ 6.7−7.4 (m, 5H), 4.7−5.2 (m, 1H), 4.4−5.2 (m, 2H), 4.05−4.2 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 157.8, 154.7, 129.6, 121.9, 114.6, 74.3, 67.0, 66.1. Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.97; H, 5.24.

Poly(*trans*-7,9-dioxabicyclo[4.3.0]nonan-8-one) (5) from *cis*-Cyclohexene Oxide. Cyclohexene oxide (5.0 g, 50.9 mmol), CrTTPCl (20 mg), and DMAP (30 mg) were heated (95 °C/18 h) under 780 psig of carbon dioxide with stirring in a 40 mL autoclave. The title polycarbonate **5b**[20] with *trans*-stereochemistry was obtained (7.0 g, 96%) as a brittle solid (mp 75−85 °C): ^1H NMR ($CDCl_3$) δ 4.55 (m, 2H), 1.1−2.4 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 153.7, 76.8, 29.5 (br), 22.9 (br); IR (neat) 2950, 1740(s), 1285. N_{INH} = 0.17 in CH_2Cl_2 (25 °C/0.5 wt %). This compound was pyrolyzed (190 °C pot) and short-path distilled (bp134 °C/3 mm) to afford *trans*-7,9-dioxabicyclo[4.3.0]nonan-8-one (**5**) in nearly quantitative yield (mp 53−54 °C/ mp$_{lit}$ 53−54 °C):[21] ^1H NMR ($CDCl_3$) δ 3.90 (m, 2H), 1.0−2.4 (m, 8H); IR (neat) 2960, 1790(s), 1205, 1158, 1110, 1050, 940. Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.04. Found: C, 59.30; H, 7.19. AlTTPOMe (25 mg) and 1-methylimidazole (25 mg) converted cyclohexene oxide (9.7 g, 99 mmole) to the *trans*-copolymer **5b** (13.1g, 93%) using carbon dioxide (700 psig, 110 °C/18 h).

***cis*-2,4-Dioxabicyclo[3.3.0]octan-3-one (6):** (bp 90 °C/0.3 mm)/mp 34−36 °C);^1H NMR ($CDCl_3$) δ 5.11 (m, 2H), 1.8−2.2 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 155.3, 81.7, 32.9, 21.3; IR (CCl_4) 2979, 1800(s), 1375, 1170, 1055. Anal. Calcd for $C_7H_{10}O_3$: C, 56.24; H, 6.29. Found: C, 56.23; H, 6.38.

***cis*- and *trans*-8,10-Dioxabicyclo[5.3.0]decan-9-one (7b and 7a).** Cycloheptene oxide (500 mg, 4.45 mmol), CrTTPCl (3.0 mg), and 4-chloropyridine (3.0 mg) were placed in a 3 dram glass vial with a small stir bar. This assembly was placed in the 40 mL autoclave and pressurized (800 psig 85 °C/88 h) with carbon dioxide. A 90:10 ratio of *trans*- to *cis*-dioxolane (690 mg, 100%) was obtained. The isomer ratio was determined by ^1H NMR and authentic samples of *cis*- and *trans*-compounds were prepared through carboxylation of the *cis*-epoxide (quatenary ammonium salt catalyst) and reaction of phosgene with the *trans*-diol (methylene chloride and pyridine), respectively. Similarly, the AlTTPOMe/DMAP catalyst system resulted in a 92:8 ratio of *trans*-/*cis* -isomers whereas CrTTPCl/2−methylimidazole gave 77:23, both in quantitative yield.

***cis*-8,10-Dioxabicyclo[5.3.0]decan-9-one (7b):** bp 110 °C/0.2 mm; mp 69−72.5 °C; ^1H NMR ($CDCl_3$) δ 4.82 (m, 2H), 0.9−2.1 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 154.5, 79.6, 30.0, 29.7, 23.2; IR (neat) 2940, 2860, 1780(s), 1373, 1180, 1050.

***trans*-8,10-Dioxabicyclo[5.3.0]decan-9-one (7a):** bp 115 °C/0.3 mm; mp 76−78 °C; ^1H NMR ($CDCl_3$) δ 4.35 (m, 2H), 1.1−2.4 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 154.7, 82.6, 28.4, 24.1, 23.9; IR (neat) 2940, 2860, 1790(s), 1453, 1225, 1070, 1060. Anal. Calcd for $C_8H_{12}O_3$: C, 61.53; H, 7.74. Found: C, 61.66; H, 7.71.

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[15] Zinc resorcinolate has been used as a catalyst to make polycarbonate **5b** with the same sterochemistry: S. Inoue in *Organic and Bio-inorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamzaki, Y., Eds., Halstaed Press: New York, 1981; p 174. Also see ref 17.

[16] Control experiments (using same experimental conditions as with catalyst **1a**) using quatenary ammonium salts such as TBAC convert cyclohexene and cycloheptene oxides to the corresponding *cis*-carbonates. This observation is consistent with an initial ring opening of the oxirane to form a vicinal chlorocarbonate anion which ring closes to give carbonate by halide displacement. Thus a double inversion at the stereocenter results in the sterospecific process.

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[19] Nishikubo, T.; Shinna, A.; Isobe, N. *Chem. Lett.* **1988**, 1605.

[20] Inoue, S.; Koinuma, H.; Yokoo,Y.; Tsuruta, T. *Makromol. Chem.* **1971**, *143*, 97.

[21] Kardouche, N. G.; Owen, L. N. *J. Chem. Soc., Perkins Trans.* **1975**, 754.