924 *Organometallics* **2004,** *23,* 924−927

Catalytic Coupling of Carbon Dioxide and 2,3-Epoxy-1,2,3,4-tetrahydronaphthalene in the Presence of a (Salen)$Cr^{III}Cl$ Derivative

Donald J. Darensbourg,* Cindy C. Fang, and Jody L. Rodgers

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received November 4, 2003

Summary: The coupling reaction of carbon dioxide and 2,3-epoxy-1,2,3,4-tetrahydronaphthalene catalyzed by (salen)$Cr^{III}Cl$, H_2salen = N,N′-bis(3,5-di-tert-butylsalicylidene)-1,2-ethylenediimine, in the presence of a cocatalyst, N-methylimidazole, affords a moderate yield of the cis cyclic carbonate product along with a trace quantity of polycarbonate. The solid-state structures of both the epoxide monomer and the cis cyclic carbonate were determined by X-ray crystallography.

Introduction

Most of the successful studies of carbon dioxide/epoxide alternating copolymerization processes catalyzed by well-defined metal complexes have utilized cyclohexene oxide as the monomer.[1] This is primarily due to the fact that, in this instance, little to no cyclic carbonate byproduct is produced. The latter pathway is inhibited as a result of ring strain imposed on the five-membered carbonate ring in order to accommodate the conformational requirements of the alicyclic cyclohexyl ring.[2] Concomitantly, the utilization of carbon dioxide as a synthetic building block coupled with oxiranes can provide an important synthetic route to cyclic carbonates. It has been amply demonstrated that poly(cyclohexylene carbonate), which has a T_g value of 115 °C, in general has inferior corresponding properties compared to the commercially widely applied polycarbonate derived from bisphenol A and phosgene.[3] Hence, a focus of our current efforts in this area has involved the investigation of the use of various monomers which when copolymerized with carbon dioxide would produce copolymers with properties more competitive with those of bisphenol-A-polycarbonate.[4] In this regard we have examined the copolymerization of 2,3-epoxy-1,2,3,4-tetrahydronaphthalene (**1**) and carbon dioxide catalyzed by (salen)$Cr^{III}Cl$ (**2**), where H_2salen = *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine.

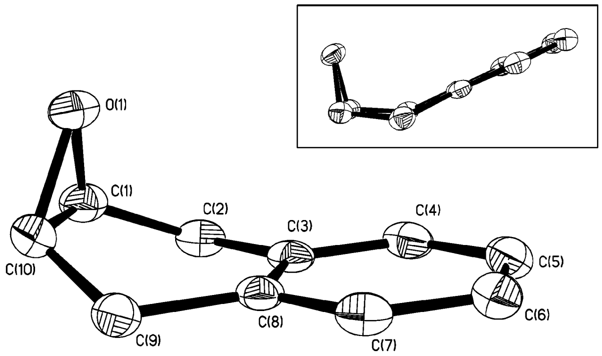
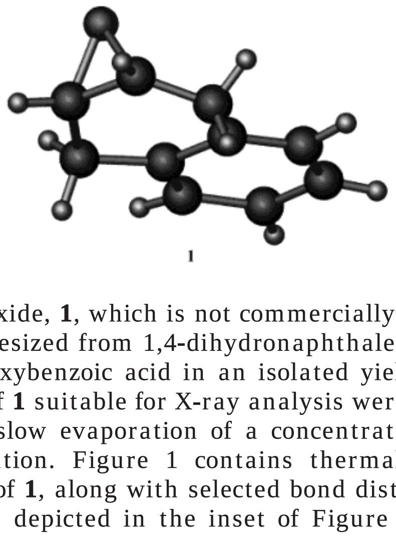


Figure 1. Thermal ellipsoid representations of compound **1**. Selected bond angles (deg) and distances (Å): C(1)−O(1)−C(10) 60.43(9), O(1)−C(1)−C(10) 59.92(10), O(1)−C(10)−C(1) 59.65(9), C(1)−C(2)−C(3) 113.47(13), O(1)−C(1)−C(2) 116.44(13), C(1)−C(10) 1.461(2), C(1)−C(2) 1.502(2), C(2)−C(3) 1.513(2), C(1)−O(1) 1.449(2), C(10)−O(1) 1.453(2), C−C bonds of aromatic ring average = 1.394(2).



1

The epoxide, **1**, which is not commercially available, was synthesized from 1,4-dihydronaphthalene and *m*-chloroperoxybenzoic acid in an isolated yield of 49%. Crystals of **1** suitable for X-ray analysis were obtained from the slow evaporation of a concentrated diethyl ether solution. Figure 1 contains thermal ellipsoid drawings of **1**, along with selected bond distances and angles. As depicted in the inset of Figure 1, the six carbon atoms of the aromatic ring in addition to two of

---

* Corresponding author. E-mail: djdarens@mail.chem.tamu.edu.

[1] (a) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577−7579. (b) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725−727. (c) Super, M.; Berluche, E.; Costello, C.; Beckman, E. *Macromolecules* **1997**, *30*, 368−372. (d) Super, M.; Beckman, E. *J. Macromol. Symp.* **1998**, *127*, 89−108. (e) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019. (f) Beckman, E. *Science* **1999**, *283*, 946−947. (g) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107−116. (h) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008−11009. (i) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487−12496. (j) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007−2008. (k) Inoue, S. *J. Polym. Sci.: A* **2000**, *38*, 2861−2871. (l) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303−308. (m) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, B. E.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738−8749. (n) Eberhardt, R.; Allmendinger, M.; Luinstra, G. A.; Rieger, B. *Organometallics* **2003**, *22*, 211−214. (o) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335−6342.

[2] Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C.; Fang, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 7586−7591.

[3] Koning, C.; Wildeson, J. R.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. J. *Polymer* **2001**, *42*, 3995−4004.

[4] Darensbourg, D. J.; Rodgers, J. L. Fang, C. C. *Inorg. Chem.* **2003**, *43*, 4498−4500.

10.1021/om034278m CCC: $27.50
Publication on Web 01/15/2004

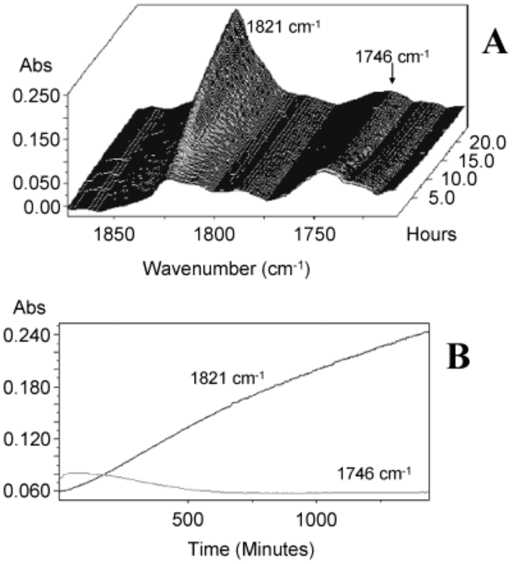


Figure 2. (A) In situ infrared monitoring in the $\nu(CO_2)$ region of reaction between **1** and CO_2. (B) Reaction profiles for the formation of copolymer and cyclic carbonate as a function of time.

the carbon atoms of the cyclohexyl ring are coplanar (rms deviation = 0.0052 Å). The dihedral angle between this plane and the plane containing C(1), C(2), C(9), and C(10) (rms = 0.0011 Å) is 151.19(1)°. The reaction of **1** dissolved in toluene under a CO_2 pressure of 55 bar at 60 °C in the presence of complex **2** (0.42 mol % relative to **1**) along with a cocatalyst (*N*-methylimidazole) was monitored by in situ infrared spectroscopy for 12 h.

During this time no products containing the CO_2 functionality were observed. Upon raising the reaction temperature to 70 °C, a slow coupling process took place as depicted in Figure 2a, which illustrates the three-dimensional stack plot of the infrared spectra in the $\nu(CO_2)$ region as a function of time. The absorbance at 1746 cm^{-1} is due to the polycarbonate, and the one at 1821 cm^{-1} corresponds to the cyclic carbonate. From Figure 2b, where the reaction profiles for the formation of polycarbonate and cyclic carbonate are described, it can be seen that after about 2 h reaction time the $\nu(CO_2)$ absorbances of copolymer and cyclic carbonate are approximately equal. However, after 24 h, the major product is the cyclic carbonate. Similarly, if the reaction is carried out at 80 °C, after 24 h the major product is the cyclic carbonate.

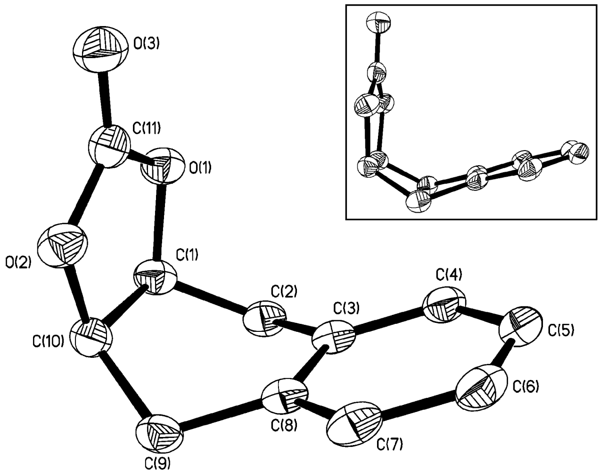


Figure 3. Thermal ellipsoid representation of compound **3**. Selected bond angles (deg) and distances (Å): O(1)−C(1)−C(2) 109.08(13), C(1)−C(2)−C(3) 111.48(13), O(2)−C(11)−O(1) 111.79(14), C(11)−O(2)−C(10) 110.66(13), C(10)−C(1)−O(1) 103.18(12), O(3)−C(11)−O(1) 124.41(16), C(11)−O(3) 1.203(2), C(11)−O(1) 1.341(2), C(10)−O(2) 1.460(2), C(1)−C(2) 1.529(2), C(1)−C(10) 1.550(2), C(2)−C(3) 1.512(2), C−C bonds of aromatic ring average = 1.396(2).

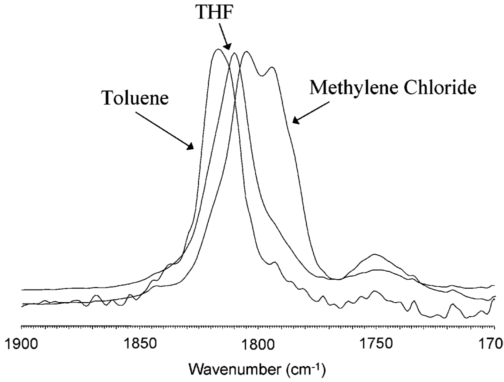


Figure 4. Overlay of cis cyclic carbonate (**3**) infrared spectra in different solvents.

The cyclic carbonate product, **3**, was purified and isolated as colorless crystals following column chromatography in about 20% yield. This represents a turnover number for the catalyst (**2**) of 37 mol of cyclic carbonate/mol of chromium. Because of the low yield of copolymer, it was not possible to obtain a pure sample of the polycarbonate. However, we were able to identify ^{13}C resonances in C_6D_6 due to the carbonate moiety in the copolymer at 155.1 and 154.2 ppm. The more intense resonance at 155.1 ppm generally corresponds to the m-centered tetrads, whereas the signals at higher field (154.2 ppm) are due to the r-centered tetrads.[5] The cyclic carbonate product has a ^{13}C signal due to the carbonate carbon center at 153.2 ppm in C_6D_6. The cis stereochemistry of **3** was established in the solid state by X-ray crystallography. Figure 3 illustrates a thermal ellipsoid drawing of **3**, along with selected bond distances and angles. As observed in compound **1**, the six carbon atoms of the aromatic ring in addition to C(2) and C(9) are nearly coplanar (rms = 0.0125 Å). However, the dihedral angle between this plane and that composed of the four carbon atoms (C(1), C(2), C(9), C(10)) at 134.09(8)° is significantly less obtuse than that seen in compound **1**.

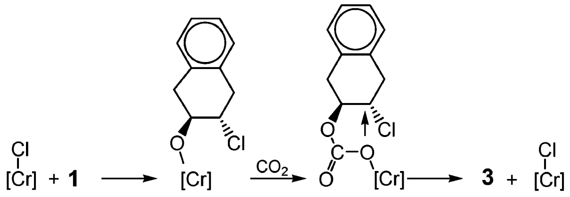
The infrared spectrum of the cyclic carbonate observed while monitoring the coupling reaction of **1** and CO_2 and that obtained on the isolated purified sample **3** were shown to be identical. Therefore, the major cyclic carbonate product produced for this reaction is the cis isomer (compound **3**). It is noteworthy to mention that the infrared spectrum in the $\nu(CO_2)$ region of the isolated crystalline **3** is solvent dependent (see Figure 4), similar to what was observed for the cyclic carbonate produced from CO_2 and cyclohexene oxide.[6] The cis

---

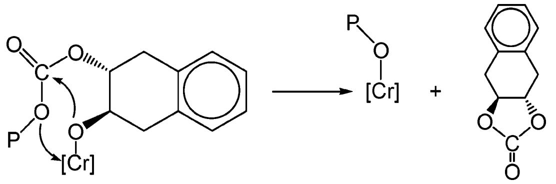
(5) Nakano, K.; Nozaki, K.; Hiyana, T. *Macromolecules* **2001**, *34*, 6325−6332.

(6) Darensbourg, D. J.; Lewis, S. J.; Rodgers, J. L.; Yarbrough, J. C. *Inorg. Chem.* **2003**, *42*, 581−589.

Scheme 1



Scheme 2



stereochemistry of the cyclic carbonate is indicative of a double inversion pathway for its production (Scheme 1),[7] as opposed to a backbiting mechanism for polymer degradation which provides the trans isomer (Scheme 2).[8] This is consistent with the product profiles shown in Figure 2b, where there is very little buildup of copolymer. Nevertheless, a small quantity of the trans isomer afforded by the copolymer degradation process could have gone undetected.

Conclusions

The present study demonstrates that the (salen)CrCl derivative is capable of catalyzing the coupling reaction of CO_2 and 2,3-epoxy-1,2,3,4-tetrahydronaphthalene. It is noteworthy that the previously examined zinc catalysts, which were quite active at coupling CO_2 and cyclohexene oxide, were unreactive toward 2,3-epoxy-1,2,3,4-tetrahydronaphthalene. The major product from the reaction of CO_2 and **1** is the cis cyclic carbonate. This is to be contrasted with what is observed in the case of the analogously catalyzed reaction between cyclohexene oxide and CO_2, where the copolymer is the primary product.[2] We assume this difference in selectivity for cyclic carbonate versus polycarbonate is due to electronic factors. Nevertheless, the synthesis of cyclic carbonates from the coupling reaction of oxiranes and carbon dioxide represents an important route to organic carbonates. Indeed, five-membered cyclic carbonates are involved in a variety of significant applications.[9] Particularly relevant to this report, cis cyclic carbonates provide a synthetic route to cis diols, which can readily be converted into other derivatives, such as cyclic sulfites and sulfates. Furthermore, we have ongoing efforts in this area that suggest that by modifying the initiator and cocatalyst it might be possible to alter the selectivity of this coupling process catalyzed by (salen)CrX derivatives in favor of polycarbonate formation. For example, we and others have found the selectivity for product distribution as a function of cyclohexene oxide versus propylene oxide to be highly dependent both on the nature of the salen ligand and the cocatalyst.[10]

Table 1. X-ray Crystallographic Data for Compounds 1 and 3

	1	3
empirical formula	$C_{10}H_{10}O$	$C_{11}H_{10}O_3$
fw (g mol^{-1})	146.18	190.19
temperature (K)	110(2)	110(2)
wavelength (Å)	0.71073	0.71073
space group	$P\bar{1}$	$P2(1)/n$
a (Å)	8.227(7)	8.943(3)
b (Å)	8.769(8)	9.950(3)
c (Å)	8.920(8)	10.833(4)
α (deg)	112.535(13)	
β (deg)	93.380(15)	112.996(5)
γ (deg)	103.536(13)	
volume (Å)^3	569.9(9)	887.4(5)
Z	3	4
D_{calc} (g cm^{-1})	1.278	1.424
absolute coeff (mm^{-1})	0.081	0.104
R^a	0.0437	0.0485
$R_w{}^b$	0.1186	0.1264
goodness-of-fit on F^2	1.079	1.150

Experimental Section

Synthesis of 2,3-Epoxy-1,2,3,4-tetrahydronaphthalene (1).[11] In a Schlenk flask fitted with a medium-porosity frit, 4.01 g (90% purity, 27.7 mmol) of 1,4-dihydronaphthalene (purchased from TCI America and shown to be 90% pure by ^{1}H NMR) was dissolved in 20 mL of dichloromethane and cooled to 0 °C. An excess of *m*-chloroperoxybenzoic acid (8.42 g, 57−86% purity) was dissolved in 45 mL of dichloromethane and dried over Na_2SO_4. The MCPBA solution was cannulated into the reaction mixture through the frit to remove any solid material. After stirring for 2 h at 0 °C, the cloudy solution was filtered to separate out the precipitated *m*-chlorobenzoic acid. The organic phase was washed with saturated Na_2CO_3, saturated $NaHCO_3$, distilled water, and brine (1 × 50 mL each). Thick layer chromatography (silica gel, dichloromethane as eluent) followed by removal of solvent in vacuo gave a pale yellow solid (2.00 g, 49% yield). Crystals suitable for X-ray analysis were grown from slow evaporation of diethyl ether. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.00−7.05 (m, 2H, Ph-H), 6.80−6.85 (m, 2H, Ph-H), 2.95 (s, 2H, epoxide-CH), 2.59−2.93 (m, 4H, Ph-CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 50 MHz): δ 132.6, 129.8, 126.9, 51.5, 30.3.

Reaction of 1 with Carbon Dioxide. The coupling reaction of **1** and carbon dioxide was carried out in a 300 mL stainless steel Parr reactor modified to accommodate an ASI ReactIR SiCOMP in situ probe. In a typical experiment, 10 mL of toluene was added to the reactor that was heated to 80 °C, and a background spectrum was recorded. The catalyst, 50 mg (0.086 mmol) of (salen)Cr^{III}Cl (H_2salen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene-1,2-ethylenediimine), along with 15.5 μL (0.19 mmol; 2.25 equiv) of *N*-methylimidazole and 3.0 g (20.5 mmol) of epoxide (**1**), was dissolved in 5 mL of toluene and added to the reactor via the injection port. The reaction vessel was pressurized with bone dry carbon dioxide to 55 bar and maintained at the desired temperature for 12 h. After that time, the autoclave was cooled and the CO_2 vented into a fume hood. The reactor was opened, and the reaction solution was evacuated under vacuum, leaving behind a viscous liquid. Compound **3** was obtained as colorless crystals from the reaction mixture by column chromatography (4:1, hexanes/ethyl acetate). The isolated yield of purified **3** was 0.60 g or 20%. This corresponds to a TON of 37 mol of **3**/mol of Cr. It should be noted that there was only a small quantity of unreacted epoxide at the end of the reaction, as revealed by

---

[7] Dümler, W.; Kisch, H. *Ber.* **1990**, *123*, 277−283.

[8] Kuran, W.; Listos, T. *Macromol. Chem. Phys.* **1994**, *195*, 977−984.

[9] Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951−976.

[10] (a) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24*, 194−196. (b) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem.*, submitted for publication.

[11] Becker, A. R.; Janusz, J. M.; Bruice, T. C. *J. Am. Chem. Soc.* **1979**, *101*, 5679−5687.

^{1}H NMR. This observation, along with the low yield of copolymer, suggests that the low isolated yield of compound **3** is the result of its method of isolation. Hence, the TON is probably significantly higher than 37, but less than the theoretical maximum value of 184. $^{13}C\{^1H\}$ NMR (C_6D_6, 50 MHz): δ 153.2 ppm (s, CO_3). IR (toluene): ν_{CO_2} 1817 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.20; H, 5.36.

X-ray Crystallography. The X-ray data for compounds **1** and **3** were obtained on a Bruker CCD diffractometer and covered more than a hemisphere of reciprocal space by a combination of three sets of exposures. Crystal data and details of data collection are provided in Table 1. The structures were solved by direct methods [SHELXS, SHELTXL-PLUS program package, Sheldrick (1997)].[12]

Acknowledgment. Financial support from the National Science Foundation (CHE 99-10342 and CHE 02-34860) and CHE 98-07975 for the purchase of X-ray equipment and the Robert A. Welch Foundation is greatly appreciated.

Supporting Information Available: Complete details of the X-ray diffraction study of complexes **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034278M

---

(12) Sheldrick, G. *SHELXL-97*: *Program for Crystal Structure Refinement*; Institut fur Anorganische Chemie der Universitat: Gottingen, Germany, 1998.