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Influence of Temperature and Pressure on Cyclic Carbonate Synthesis Catalyzed by Bimetallic Aluminum Complexes and Application to Overall *syn*-Bis-hydroxylation of Alkenes

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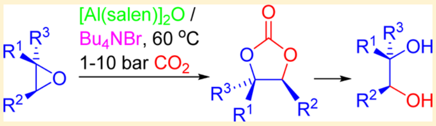
Supporting Information

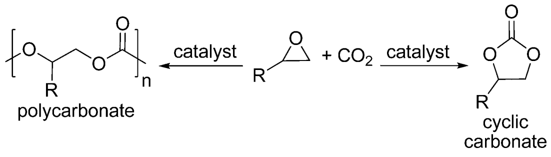
ABSTRACT: The effect of moderate temperatures (22−100 °C) and pressures (1−10 bar) on the synthesis of cyclic carbonates from epoxides and carbon dioxide catalyzed by a combination of bimetallic aluminum complexes and tetrabutylammonium bromide is investigated. The combined bimetallic complex and tetrabutylammonium bromide catalyst system is shown to be an order of magnitude more active than the use of tetrabutylammonium bromide alone at all temperatures and pressures studied. At the higher temperatures and pressures used, disubstituted epoxides become substrates for the reaction and it is shown that reactions proceed with retention of the epoxide stereochemistry. This allowed a route for the overall *syn*-bis-hydroxylation of alkenes to be developed without the use of hazardous metal based reagents. At higher pressures it is also possible to use compressed air as the carbon dioxide source.



1. INTRODUCTION

In recent years there has been a resurgence of interest in carbon dioxide chemistry,[1−4] largely based on the realization that converting waste carbon dioxide into useful chemicals (carbon capture and utilization, CCU) would be a highly desirable alternative to carbon capture and storage (CCS).[5] The relative scales of waste carbon dioxide production and chemicals production, however, mean that CCU will never make a significant contribution to reducing anthropogenic carbon dioxide emissions, though it could significantly offset the costs associated with CCS.[6] One reaction which has attracted significant attention in recent years is the reaction of carbon dioxide with epoxides which can be catalyzed to give either polycarbonates[7,8] or cyclic carbonates[9,10] (Scheme 1). Cyclic carbonates have numerous commercial applications[11,12] including as electrolytes for lithium ion batteries,[13,14] chemical intermediates,[11,12] and polar aprotic solvents.[11,12,15−19]

Scheme 1. Reaction of Epoxides with CO_2



The synthesis of cyclic carbonates from epoxides and carbon dioxide has been a commercial process since the 1950s[20] and is now carried out worldwide. However, the commercial systems still rely on the use of quaternary ammonium[21,22] or phosphonium[23−27] salts as catalysts, and this necessitates the use of elevated reaction temperatures and pressures and the use of pure carbon dioxide as feedstock. As a result, the commercial production of cyclic carbonates currently generates rather than consumes carbon dioxide. However, the synthesis of ethylene carbonate from ethylene oxide and carbon dioxide is highly exothermic ($\Delta H_r = -140$ kJ mol^{-1}),[28,29] so there is no thermodynamic reason for the harsh reaction conditions currently employed.

Over the past five years, we have shown that, in the presence of a tetraalkylammonium bromide cocatalyst, bimetallic aluminum complexes **1** and **2** (Figure 1) form highly active,[30,31] low cost,[32] and recyclable[33] catalysts for the conversion of monosubstituted epoxides into cyclic carbonates at ambient temperature and 1 bar of carbon dioxide pressure. The bimetallic structure of complexes **1** and **2** is critical for their high catalytic activity.[33] Complex **1** was shown to be compatible

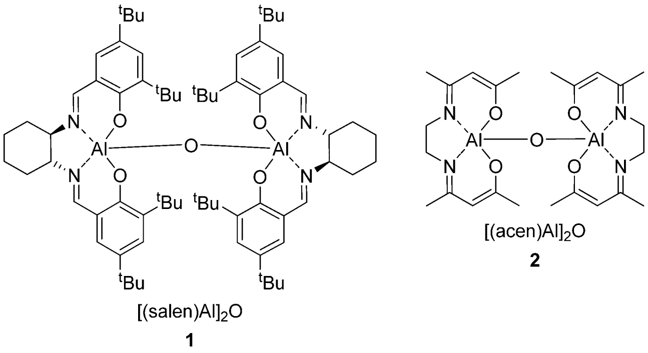


Figure 1. Structures of bimetallic aluminum based catalysts for cyclic carbonate synthesis.

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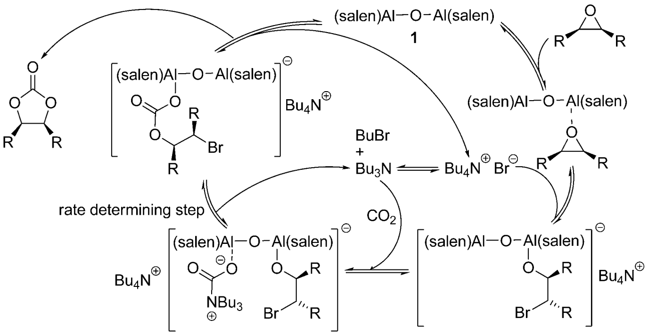
with carbon dioxide generated by oxyfuel combustion of methane.[34] Immobilized analogues of catalyst **1** have also been prepared[35] and shown to catalyze the formation of cyclic carbonates from ethylene or propylene oxide in a gas phase flow reactor.[36−38] The immobilized catalysts were shown to be compatible with both simulated[38] and real flue gas.[39] The mild reaction conditions under which complexes **1** and **2** were catalytically active facilitated a detailed kinetic study, which, combined with the detection of tributylamine formed in situ from the tetrabutylammonium bromide, allowed the catalytic cycle shown in Scheme 2 to be proposed.[33,40] The use of quaternary phosphonium salts as cocatalysts in conjunction with complex **1** was shown to result in less active catalyst systems[41] which is consistent with the important catalytic role played by the tertiary amine in Scheme 2. The main features of the catalytic cycle shown in Scheme 2 have also been shown to be applicable to other catalyst systems for the synthesis of cyclic carbonates from epoxides and carbon dioxide.[42−45]

Scheme 2. Proposed Catalytic Cycle for Cyclic Carbonate Synthesis Catalyzed by Complex 1 and Bu_4NBr

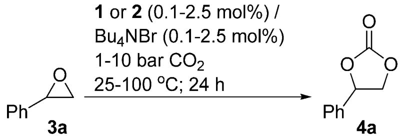


While being able to carry out cyclic carbonate synthesis at ambient temperature and pressure is attractive, waste carbon dioxide is often available at above ambient temperature (power station flue gas is typically at 60−100 °C as it enters the chimney stack) and higher gas pressures are the equivalent of higher concentrations in solution and will result in faster reaction rates and greater reactor throughput. In addition, carbon dioxide at above atmospheric pressure is likely to become readily available in the near future, as the carbon dioxide in a CCS pipeline is necessarily compressed for transport. Therefore, we initiated a study to investigate the influence of temperature and pressure on cyclic carbonate synthesis catalyzed by complex **1** or **2** with tetrabutylammonium bromide as a cocatalyst. The temperature range studied (25−100 °C) was chosen to correspond to the temperatures at which waste carbon dioxide is available, and the pressure range (1−10 bar), to correspond to the pressures which can be accommodated by standard stainless steel reactors, thus avoiding the capital costs associated with constructing specialized high pressure reactors. In this paper we report the results of this study.

2. RESULTS AND DISCUSSION

The conversion of styrene oxide **3a** into styrene carbonate **4a** (Scheme 3) was selected as the test reaction since the reaction could be easily monitored by GC or ^{1}H NMR spectroscopy. Tables 1−3 give the results obtained using catalyst **1** or **2** at 25−100 °C and at 1−10 bar of carbon dioxide pressure. Entries 1−3 of Table 1 give results obtained at 25 °C and 1 bar of CO_2 pressure and show that under these conditions catalysts **1** and **2** have no activity on their own (Table 1, entry 1) and tetrabutylammonium bromide alone displays only minimal activity (Table 1, entry 2). However, the combination of tetrabutylammonium bromide and either catalyst **1** or **2** increases the catalytic activity by a factor of 15−17 relative to the use of tetrabutylammonium bromide alone (Table 1, entry 3).

Scheme 3. Conversion of Styrene Oxide 3a into Styrene Carbonate 4a



Next, the carbon dioxide pressure was increased to 5 bar (Table 1, entries 4−11) or 10 bar (Table 1, entries 12−20). Catalysts **1** and **2** again had no catalytic activity even at these elevated pressures (Table 1, entries 4, 9, 12, and 18), and tetrabutylammonium bromide displayed only minimal activity (Table 1, entries 5, 7, 10, 13, 16, and 19). However, simultaneous use of tetrabutylammonium bromide and catalyst **1** or **2** again increased the catalytic activity relative to the use of tetrabutylammonium bromide alone. For catalyst **1**, the increase is 14−17-fold at 5 bar (Table 1, entries 6, 8, and 11) and 13−19-fold at 10 bar (Table 1, entries 14, 17, and 20). For catalyst **2**, the increases are less dramatic, 5−11-fold at 5 bar (Table 1, entries 6, 8, and 11) and 12.5-fold at 10 bar (Table 1, entry 20). At both 5 and 10 bar, the use of 2.5 mol % of catalyst **1** and tetrabutylammonium bromide gave 100% conversion of styrene oxide into styrene carbonate (Table 1, entries 11 and 20), so the rate enhancement may be higher than that recorded.

At 60 °C (Table 2), tetrabutylammonium bromide was found to show increasing catalytic activity as its concentration increased and as the reaction pressure increased (Table 2, entries 2, 4, 6, 8, 11, 16, 18, 20, and 22) with 28% conversion of **3a** into **4a** being obtained at 10 bar when 2.5 mol % of tetrabutylammonium bromide was used (Table 2, entry 22). Catalysts **1** and **2** were still catalytically inactive on their own (Table 2, entries 1, 10, and 15). To obtain sensible data for the enhancement in catalyst activity when both tetrabutylammonium bromide and catalyst **1** were used at 60 °C, it was necessary to reduce the catalyst loading to 0.1 mol % as 100% conversion was observed when 0.5 mol % or higher catalyst loadings were used (Table 2, entries 5, 7, 12, 14, 17, 21, and 23). Thus, by carrying out reactions at 60 °C, the loading of catalyst **1** and tetrabutylammonium bromide can be reduced at least 5-fold (Table 2, entries 5, 12, and 21) compared to the optimal conditions at 25 °C (Table 1, entries 3, 11, and 20), resulting in a significant reduction in the cost of the catalyst required.[32] Catalyst **2** is less reactive than catalyst **1**, and only reactions involving the use of 2.5 mol % of catalyst **2** and tetrabutylammonium bromide were found to go to 100% conversion (Table 2, entries 17 and 23).

At all pressures at 60 °C, the combined use of tetrabutylammonium bromide and catalyst **1** or **2** resulted in a significant rate enhancement compared to the use of tetrabutylammonium bromide alone, though this decreased as the pressure increased, consistent with the increasing catalytic activity of tetrabutylammonium bromide. Thus, at 1 bar of carbon dioxide pressure the rate enhancement was 10−15-fold

Table 1. Synthesis of Styrene Carbonate **4a** Using Catalyst **1** or **2** at 25 °C[a]

entry	**1** or **2** (mol %)	Bu_4NBr (mol %)	CO_2 (bar)	conv. **1** (%)	TON (**1**)[b]	(**1**+Bu_4NBr)/Bu_4NBr	conv. **2** (%)	TON (**2**)[b]	(**2**+Bu_4NBr)/Bu_4NBr
1	2.5		1	0	0		0	0	
2		2.5	1	6	2		6	2	
3	2.5	2.5	1	98[c]	39	16.3	93	37	15.5
4	0.5		5	0	0		0	0	
5		0.5	5	4	8		4	8	
6	0.5	0.5	5	58	116	14.5	21	42	5.3
7		1.0	5	5	5		5	5	
8	1.0	1.0	5	79	79	15.8	49	49	9.8
9	2.5		5	0	0		0	0	
10		2.5	5	6	2		6	2	
11	2.5	2.5	5	100	40	16.7	63	25	10.5
12	0.5		10	0	0				
13		0.5	10	5	10		5	10	
14	0.5	0.5	10	69	138	13.8			
15	1.0		10	0	0				
16		1.0	10	5	5		5	5	
17	1.0	1.0	10	95	95	19.0			
18	2.5		10	0	0				
19		2.5	10	6	2		6	2	
20	2.5	2.5	10	100	40	16.7	75	30	12.5

[a] All reactions carried out for 24 h. [b] TON = turnover number = mol of **4a** produced/mol of catalyst (**1** or **2** or Bu_4NBr) used. [c] Data taken from ref 30.

Table 2. Synthesis of Styrene Carbonate **4a** Using Catalyst **1** or **2** at 60 °C[a]

entry	**1** or **2** (mol %)	Bu_4NBr (mol %)	CO_2 (bar)	conv. **1** (%)	TON (**1**)[b]	(**1**+Bu_4NBr)/Bu_4NBr	conv. **2** (%)	TON (**2**)[b]	(**2**+Bu_4NBr)/Bu_4NBr
1	0.1		1	0	0		0	0	
2		0.1	1	3	30		3	30	
3	0.1	0.1	1	32	320	10.7	23	230	7.7
4		0.5	1	7	14		7	14	
5	0.5	0.5	1	100	200	14.3	78	156	11.1
6		1.0	1	10	10		10	10	
7	1.0	1.0	1	100	100	10.0			
8		0.1	5	3	30		3	30	
9	0.1	0.1	5	36	360	12.0	33	330	11.0
10	0.5		5	0	0		0	0	
11		0.5	5	9	18		9	18	
12	0.5	0.5	5	100	200	11.1			
13		1.0	5	13	13		13	13	
14	1.0	1.0	5	100	100	7.7			
15	2.5		5	0	0		0	0	
16		2.5	5	24	10		24	10	
17	2.5	2.5	5	100	40	4.2	100	40	4.2
18		0.1	10	6	60		6	60	
19	0.1	0.1	10	58	580	9.7	47	470	7.8
20		0.5	10	13	26		13	26	
21	0.5	0.5	10	100	200	7.7			
22		2.5	10	28	11		28	11	
23	2.5	2.5	10	100	40	3.6	100	40	3.6

[a] All reactions carried out for 24 h. [b] TON = turnover number = mol of **4a** produced/mol of catalyst (**1** or **2** or Bu_4NBr) used.

using catalyst **1** (Table 2, entries 3, 5, and 7) and 7–11-fold using catalyst **2** (Table 2, entries 3 and 5). At 5 bar of carbon dioxide pressure the rate enhancement was 11–12-fold using catalyst **1** (Table 2, entries 9 and 12) and 11-fold using catalyst **2** (Table 2, entry 9), and at 10 bar of carbon dioxide pressure the rate enhancement was 7–10-fold using catalyst **1** (Table 2, entries 19 and 21) and 8-fold using catalyst **2** (Table 2, entry 19).

A similar trend was seen at 100 °C (Table 3), where the catalytic activity of tetrabutylammonium bromide increased as the pressure increased (Table 3, entries 1, 10, and 13) and as the amount of tetrabutylammonium bromide increased (Table 3, entries 1 and 7). The use of 2.5 mol % of tetrabutylammonium bromide even at 1 bar of carbon dioxide pressure gave 52% conversion of styrene oxide **3a** into styrene carbonate **4a** (Table 3, entry 7) which clearly illustrates why current commercial processes which rely on the use of

Table 3. Synthesis of Styrene Carbonate 4a Using Catalyst **1** or **2** at 100 °C[a]

entry	**1** or **2** (mol %)	Bu_4NBr (mol %)	CO_2 (bar)	conv. **1** (%)	TON (**1**)[b]	(**1**+Bu_4NBr)/Bu_4NBr	conv. **2** (%)	TON (**2**)[b]	(**2**+Bu_4NBr)/Bu_4NBr
1		0.1	1	4	40		4	40	
2	0.1	0.1	1	49	490	12.3			
3	0.5		1	0	0		0	0	
4		0.5	1	7	14		7	14	
5	0.5	0.5	1	75	150	10.7	97	194	13.9
6	2.5		1	0	0		0	0	
7		2.5	1	52	21		52	21	
8	0.5	2.5	1	85	170				
9	1.0	2.5	1	98	98				
10		0.1	5	6	60		6	60	
11	0.1	0.1	5	65	650	10.8	59	590	9.8
12	0.1		10	0	0		0	0	
13		0.1	10	8	80		8	80	
14	0.1	0.1	10	82	820	10.3	73	730	9.1

[a] All reactions carried out for 24 h. [b] TON = turnover number = mol of **4a** produced/mol of catalyst (**1** or **2** (or Bu_4NBr when no aluminum catalyst present)) used.

tetraalkylammonium bromides as the sole catalyst employ high temperatures and pressures.[21,22] Catalysts **1** and **2** were catalytically inactive on their own even at 100 °C (Table 3, entries 3, 6, and 12). For reactions catalyzed by catalyst **1**, the enhancement relative to using tetrabutylammonium bromide alone decreased slightly from 10−13 at 1 bar of carbon dioxide pressure to 11 at 5 bar and 10 at 10 bar (Table 3, entries 2, 5, 11, and 14). For reactions catalyzed by catalyst **2**, the enhancements decreased from 14 at 1 bar of carbon dioxide pressure to 10 at 5 bar and 9 at 10 bar (Table 3, entries 5, 11, and 14).

The results presented in Tables 1−3 show that the rate enhancement seen on using tetrabutylammonium bromide and either catalyst **1** or **2** is maintained at temperatures up to 100 °C and carbon dioxide pressures up to 10 bar, and this is illustrated diagrammatically in Figure 2. Tables 1−3 also give turnover numbers (TON) for each reaction. This data show that by increasing the temperature and pressure, the TON obtained using catalyst **1** and tetrabutylammonium bromide increases from 39 at 1 bar and 25 °C (Table 1, entry 3) to 820 at 10 bar and 100 °C (Table 3, entry 14). The TON of catalyst **2** and tetrabutylammonium bromide increases similarly from 37 at 1 bar and 25 °C (Table 1, entry 3) to 730 at 10 bar and 100 °C (Table 3, entry 14). In view of this enhanced catalytic activity seen at elevated temperatures and pressures, and the higher catalytic activity associated with catalyst **1** compared to catalyst **2**, two new applications of catalyst **1** were investigated: the synthesis of cyclic carbonates from disubstituted epoxides and the synthesis of cyclic carbonates from carbon dioxide at atmospheric concentrations.

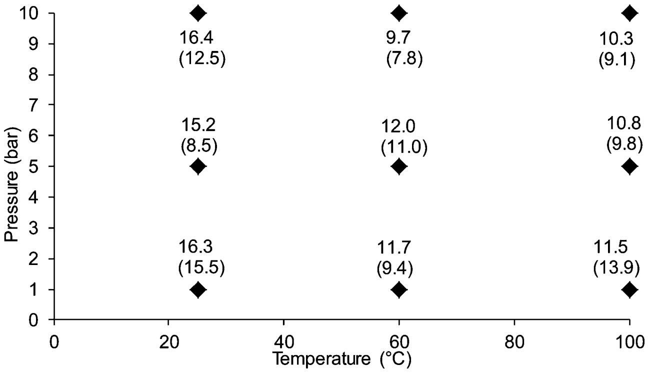
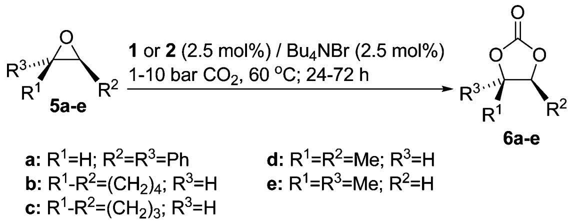


Figure 2. Enhancement in catalyst activity associated with the use of Bu_4NBr and **1** or **2** relative to Bu_4NBr alone at 25−100 °C and 1−10 bar of CO_2 pressure. Data for catalyst **2** are in brackets. The numerical values are the average of the relevant data in Tables 1−3, excluding reactions which gave low enhancements due to the reactions having gone to 100% conversion.

Previous attempts to use disubstituted epoxides as substrates for cyclic carbonate synthesis catalyzed by complex **1** and tetrabutylammonium bromide at 25 °C and 1 bar of carbon dioxide pressure were unsuccessful.[30,33] Of five disubstituted epoxides studied, only *trans*-stilbene oxide **5a** was found to react at all, and even then only 8% conversion to *trans*-1,2-diphenylethylene carbonate **6a** was observed after a reaction time of 48 h using 2.5 mol % of both catalyst **1** and tetrabutylammonium bromide. However, by raising the reaction temperature to 60 °C, disubstituted epoxides **5a−e** were found to be substrates for cyclic carbonate synthesis using catalyst **1** and tetrabutylammonium bromide, giving cyclic carbonates **6a−e** as shown in Scheme 4 with the results being presented in Table 4.

Scheme 4. Conversion of Disubstituted Epoxides 5a−e into Cyclic Carbonates 6a−e



At 1 bar of carbon dioxide pressure, cyclohexene oxide **5b** was converted into cyclohexene carbonate **6b** in 35% yield after 24 h (Table 4, entry 1). By increasing the carbon dioxide pressure to 10 bar, the yield of **6b** increased to 65%, so these conditions were taken as standard and applied to each of the epoxides **5a−e**, resulting in the formation of cyclic carbonates **6a−e** in 26−71% yield (Table 4, entries 2, 3, 5−7). The yields of cyclic carbonates **6a,e** were rather low under these conditions (Table 4, entries 3, 7); however, by increasing the

Table 4. Synthesis of Disubstituted Cyclic Carbonates 6a−e Using Catalyst 1 at 60 °C

entry	epoxide	CO_2 (bar)	time (h)	yield[a] (%)
1	**5b**	1	24	35
2	**5b**	10	24	65
3	**5a**	10	24	32
4	**5a**	10	72	100
5	**5c**	10	24	71 (47)
6	**5d**	10	24	49 (30)
7	**5e**	10	24	26
8	**5e**	10	72	100

[a] Yields in brackets were obtained using catalyst **2**.

reaction time to 72 h, the yields of these cyclic carbonates increased to 100% (Table 4, entries 4, 8). Acen based catalyst **2** could also be used to form disubstituted cyclic carbonates under these conditions, though the yields were lower than those obtained using catalyst **1**. Thus, cyclic carbonate **6c** was obtained in 47% yield and cyclic carbonate **6d** in 30% yield using catalyst **2** (Table 4, entries 5,6).

The reactions employing epoxides **5a−d** also provided an opportunity to study the stereochemistry of cyclic carbonate synthesis catalyzed by catalyst **1** or **2** and tetrabutylammonium bromide, as previously reported for cyclic carbonate synthesis catalyzed by organotin iodides with HMPA or tetrabutylphosphonium iodide as a cocatalyst.[46] The catalytic cycle in Scheme 2 predicts that the epoxide stereochemistry should be retained as the mechanism involves double inversion at the carbon−oxygen bond which is broken during the reaction. This was found to be the case for each of the substrates **5a−d** as the cyclic carbonate had the same stereochemistry as the epoxide from which it was formed. The results with epoxides **5a,b,d** were particularly characteristic as both diastereomers of cyclic carbonates **6a,b,d** are known. In the case of compound **6a**, the spectra of the product obtained using catalyst **1** matched the literature data for the *trans*-isomer and were clearly different from those of the *cis*-isomer,[47] the stereochemistry of the *trans*-isomer having been previously confirmed by X-ray crystallography.[48] The data for **6b** prepared using catalyst **1** matched the literature data for the *cis*-isomer and were different from the literature data for the *trans*-isomer, the stereochemistry of which had been unambiguously determined by X-ray crystallography.[49] The spectra of cyclic carbonate **6d** prepared using catalyst **1** also matched the literature data for the *cis*-isomer and were different from the literature data for the *trans*-isomer.[47] In the case of cyclic carbonate **6c**, only the *cis*-isomer is known and the spectra matched the literature data for the *cis*-isomer.[50,51]

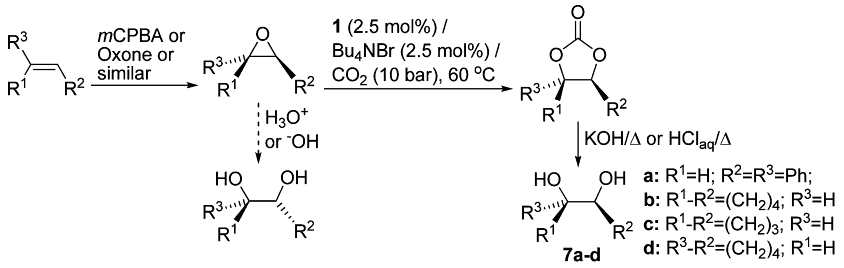
Cyclohexene carbonate is commonly formed as a byproduct in the copolymerization of cyclohexene oxide and carbon dioxide using various catalyst systems due to backbiting of the growing polymer chain.[49,52,53] However, in these cases *trans*-cyclohexene carbonate is formed, so the exclusive formation of *cis*-cyclohexene carbonate using catalyst **1** and tetrabutylammonium bromide is indicative of its formation by a different mechanism which does not involve polycarbonate formation.

Since the conversion of epoxides **5a−d** into cyclic carbonates **6a−d** had been shown to occur with retention of stereochemistry, it opened the way to develop methodology for the synthesis of 1,2-diols by overall *syn*-bis-hydroxylation of alkenes avoiding the use of hazardous transition metal based oxidants such as osmium tetroxide or potassium permanganate. The route is shown in Scheme 5 and is stereocomplementary to the direct hydrolysis of epoxides which results in overall *anti*-addition to the alkene. Thus, cyclic carbonates **6a,c** were treated with aqueous potassium hydroxide to give diols **7a,c** in 45−90% yield. The melting point and spectroscopic data for diol **7a** matched the literature data[54−56] for the *trans*-isomer of the diol, while for **7c** the corresponding data matched the literature data for the *cis*-isomer of the diol.[55,57] Interestingly, attempts to extend this chemistry to cyclohexane carbonate **6b** resulted in the formation of a 1:3 mixture of diols **7b** and **7d** from which the major *trans*-diol **7d** could be isolated by crystallization. This unexpected stereochemical outcome is probably due to the axial C−O bond in cyclic carbonate **6b** favoring hydrolysis by a $B_{AL}2$ mechanism rather than a $B_{AC}2$ mechanism and thus resulting in hydrolysis with inversion of diol configuration. However, by carrying out the hydrolysis of cyclic carbonate **6b** under acidic conditions, exclusive formation of *cis*-diol **7b** in 86% yield was observed. The melting points and spectroscopic data for diols **7b,d** matched the literature data.[55,57]

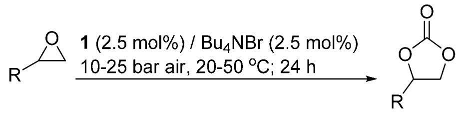
In previous work, we have used catalyst **1** to achieve cyclic carbonate synthesis with pure carbon dioxide[30,33] or with 5% carbon dioxide in helium.[34] Mechanistic studies[33,40] have also shown that the reaction is first order in carbon dioxide concentration, so no reaction occurs when a mixture of catalyst **1**, tetrabutylammonium bromide, and epoxide is left exposed to air as the carbon dioxide concentration is only 385 ppm. However, in view of the enhanced catalytic activity seen with catalyst **1** at elevated temperatures and pressures (Tables 1−3), we decided to investigate the synthesis of cyclic carbonates from epoxides and compressed air.

The model reaction for this study was again the synthesis of styrene carbonate **4a** from styrene oxide **3a** with the reaction conditions being shown in Scheme 6 and the results in Table 5. Table 5, entry 1 shows that at, 50 °C and 10 bar of pressure, styrene oxide was converted into styrene carbonate, the reaction having gone to 61% conversion after 24 h. Extending the reaction time to 3 days (Table 5, entry 2) resulted in a

Scheme 5. Synthesis of Diols from Alkenes via Cyclic Carbonates



Scheme 6. Synthesis of Cyclic Carbonates 4a−h Using Compressed Air



3a-h **4a-h**

a: R=Ph; **b**: R=Bu; **c**: R=$^nC_8H_{17}$; **d**: R=$^nC_{10}H_{21}$; **e**: R=CH_2Cl; **f**: R=CH_2OPh; **g**: R=4-ClC_6H_4; **h**: R=4-BrC_6H_4

Table 5. Synthesis of Cyclic Carbonates 4a−h Using Compressed Air

entry	epoxide	air (bar)	*T* (°C)	*t* (h)	conversion (%)
1	**3a**	10	50	24	61
2	**3a**	10	50	72	78
3	**3a**	25	50	24	79
4	**3a**	25	20	24	19
5	**3a**	25	20	8 + 16	25
6	**3a**	10	50	8 + 16	54
7	**3b**	25	50	24	57
8	**3c**	25	50	24	73
9	**3d**	25	50	24	39
10	**3e**	25	50	24	31
11	**3f**	25	50	24	53
12	**3g**	25	50	24	54
13	**3h**	25	50	24	28

slight increase in conversion, and the same effect was obtained by increasing the pressure to 25 bar (Table 5, entry 3). Table 5, entry 4 shows that the elevated temperature was important to obtain a reasonable conversion as only 19% conversion was observed in a reaction carried out at 20 °C. Finally, Table 5, entries 5 and 6 show the effect of venting and then repressurizing the autoclave with fresh compressed air part way through the reaction to see if the reactions were being retarded by the decrease in carbon dioxide concentration during the reaction. However, comparison of Table 5, entries 4 and 5 or of Table 5, entries 1 and 6 shows no significant change in the observed conversions.

The conditions of Table 5, entry 3 were therefore taken as optimal and applied to seven other epoxides (**3b**−**h**) to form cyclic carbonates **4b**−**h** with 28−73% conversion (Table 5, entries 7−13). One limitation of this chemistry is that the 330 mL autoclave to which we had access only contained 0.13 mmol of carbon dioxide even when pressurized to 25 bar (assuming a carbon dioxide concentration in compressed air of 385 ppm and that 1 mol of air occupies 24 000 mL at room temperature and pressure). Thus, it was necessary to work with very small amounts of epoxides (0.1 mmol) to ensure that even a slight excess of carbon dioxide was present. Therefore, the reaction with epoxide **3c** was carried out a total of eight times to give sufficient cyclic carbonate **4c** to allow it to be purified by chromatography with an isolated yield of 67%, which compares favorably with the 73% conversion (Table 5, entry 8).

3. CONCLUSIONS

It has been shown that the use of bimetallic aluminum based catalyst **1** or **2** along with tetrabutylammonium bromide results in an order of magnitude improvement in activity compared to the use of tetrabutylammonium bromide alone over a temperature range of 25−100 °C and a pressure range of 1−10 bar. Over this temperature and pressure range, the intrinsic catalytic activity of the **1** or **2** plus tetrabutylammonium bromide catalyst system increases 20-fold as measured by turnover numbers. The higher catalytic activities seen at elevated temperatures and pressures have been exploited to allow cyclic carbonates to be prepared from disubstituted epoxides and pure carbon dioxide or from monosubstituted epoxides and carbon dioxide at atmospheric concentrations. The use of disubstituted epoxides allowed the stereochemistry of the reaction to be studied, and it was found that the reaction always occurred with retention of the epoxide stereochemistry. This allowed the development of a facile approach to the *syn*-bis-hydroxylation of alkenes avoiding the use of toxic, corrosive, and expensive transition metal based oxidants.

4. EXPERIMENTAL SECTION

4.1. General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz for ^{1}H and 75 MHz for ^{13}C. All spectra were recorded at ambient temperature and were referenced to the residual solvent peak. For ^{1}H NMR spectra, multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), or a combination of these. GCMS were recorded on a FactorFour (VF-5 ms) capillary column (30 m × 0.25 mm) with helium as the carrier gas. The conditions used were as follows: initial temperature 60 °C, hold at initial temperature for 3 min and then ramp rate 15 °C/min to 270 °C; hold at final temperature for 5 min. For the first 3.50 min, the eluent was routed away from the mass detector. Subsequently, the detector was operated in full EI or CI scan mode.

4.2. Synthesis of Styrene Carbonate[38] 4a Using Catalyst 1 or 2 at Atmospheric Pressure. Catalyst **1** or **2** (0.1−2.5 mol %) and/or Bu_4NBr (0.1−2.5 mol %) were weighed into a glass tube fitted with a magnetic stirrer bar. Styrene oxide **3a** (106 mg, 0.88 mmol) was added, and the tube was sealed with a rubber stopper. A balloon was filled with CO_2 from a cylinder, attached to a needle, and fitted to the reaction tube through the stopper. The reaction was stirred at 25−100 °C for 24 h after which time the contents were analyzed by ^{1}H NMR spectroscopy and/or GCMS to determine the conversion to styrene carbonate **4a**. The reaction mixture was dissolved in dichloromethane (3 mL) and passed through a glass Pasteur pipet half filled with silica to remove the catalyst and Bu_4NBr which are retained on the surface of the silica. The eluent was evaporated, and the residue was triturated with petroleum ether to crystallize cyclic carbonate **4a** as a white solid. Mp 49−52 °C (lit.[58] 50−51 °C); ν_{max}(ATR) 3047, 3020, 2968, 2899, 1812, and 1592 cm^{-1}; δ_H($CDCl_3$) 4.36 (1H, t *J* 8.4 Hz), 4.82 (1H, t *J* 8.5 Hz), 5.69 (1H, t *J* 8.0 Hz), 7.2−7.5 (5H, m); δ_C($CDCl_3$) 71.1, 78.0, 125.8, 129.2, 129.7, 135.8, 154.7; GCMS t_R 11.96 min; *m*/*z*(EI) 164 (M$^+$, 55), 120 (30), 91 (100).

4.3. Synthesis of Styrene Carbonate[38] 4a Using Catalyst 1 or 2 at 5−10 bar of Pressure. Catalyst **1** or **2** (0.1−2.5 mol %) and/or Bu_4NBr (0.1−2.5 mol %) were weighed into a glass tube fitted with a magnetic stirrer bar. Styrene oxide **3a** (106 mg, 0.88 mmol) was added, and the tube was placed within a 330 mL stainless steel autoclave which was sealed and pressurized to 5 or 10 bar with CO_2. The reaction was stirred at 25−100 °C for 24 h after which time the pressure was released, the autoclave was opened, and the contents were analyzed by ^{1}H NMR spectroscopy and/or GCMS to determine the conversion to styrene carbonate **4a**. The reaction mixture was dissolved in dichloromethane (3 mL) and passed through a glass Pasteur pipet half filled with silica to remove the catalyst and Bu_4NBr which are retained on the surface of the silica. The eluent was evaporated, and the residue was triturated with petroleum ether to crystallize cyclic carbonate **4a** as a white solid with analytical data identical to those reported in section 4.2.

4.4. General Procedure for the Synthesis of Disubstituted Cyclic Carbonates 6a−e. Catalyst **1** (25.5 mg, 0.022 mmol) and Bu_4NBr (7.1 mg, 0.022 mmol) were added to a glass tube containing a magnetic stirrer bar. Epoxide **5a**−**e** (0.88 mmol) was added, and the tube was placed within a 330 mL stainless steel autoclave which was sealed and pressurized to 10 bar with CO_2. The reaction was stirred at

60 °C for 24 or 72 h after which time the pressure was released and the autoclave was opened. The reaction mixture was dissolved in dichloromethane (3 mL) and passed through a glass Pasteur pipet half filled with silica to remove the catalyst and Bu_4NBr which are retained on the surface of the silica. The eluent was evaporated, and the residue was triturated with petroleum ether to crystallize cyclic carbonate **6a**−**e** as a white solid or to leave the product as an oil.

*trans-1,2-Diphenylethylene Carbonate **6a**.*[47] Mp 112−118 °C (lit.[47] 110−111 °C); ν_{max}(ATR) 3030, 2964, 1815, and 1458 cm^{-1}; $\delta_H(CDCl_3)$ 5.45 (2H, s), 7.3−7.4 (4H, m), 7.4−7.5 (6H, m); $\delta_C(CDCl_3)$ 85.3, 126.1, 129.3, 129.8, 135.3, 153.9; GCMS t_R 14.86 min; m/z(CI) 241 (MH$^+$, 12), 196 (100), 178 (25), 167 (60), 105 (55), 89 (75).

*cis-1,2-Cyclohexene Carbonate **6b**.*[49] Mp 35−37 °C (lit.[51] 34−35 °C); ν_{max}(ATR) 2946, 2869, and 1788 cm^{-1}; $\delta_H(CDCl_3)$ 1.4−1.5 (2H, m), 1.6−1.7 (2H, m), 1.9−2.0 (4H, m), 4.6−4.7 (2H, m); $\delta_C(CDCl_3)$ 19.0, 26.7, 75.6, 155.1.

*cis-1,2-Cyclopentene Carbonate **6c**.*[50,51] Mp 30−33 °C (lit.[50] 29−30 °C); ν_{max}(ATR) 2956, 2885, and 1792 cm^{-1}; $\delta_H(CDCl_3)$ 1.5−1.9 (4H, m), 2.1−2.3 (2H, m), 5.0−5.2 (2H, m); $\delta_C(CDCl_3)$ 21.5, 33.1, 81.7, 155.2; GCMS t_R 8.38 min; m/z(CI) 129 (MH$^+$, 17), 83 (17), 55 (100), 41 (25).

*cis-2,3-Butene Carbonate **6d**.*[47] Obtained as a pale yellow oil; ν_{max}(ATR) 2939, 2881, and 1791 cm^{-1}; $\delta_H(CDCl_3)$ 1.32 (6H, d *J* 6.1 Hz), 4.7−4.9 (2H, m); $\delta_C(CDCl_3)$ 14.3, 76.0, 154.5; GCMS t_R 6.52 min; m/z(CI) 117 (MH$^+$, 25), 43 (100).

*2-Methylpropene Carbonate **6e**.*[59] Obtained as a pale yellow oil; ν_{max}(ATR) 2960, 2812, and 1784 cm^{-1}; $\delta_H(CDCl_3)$ 1.51 (6H, s), 4.14 (2H, s); $\delta_C(CDCl_3)$ 26.2, 75.5, 81.8, 154.7; GCMS t_R 7.17 min; m/z(CI) 117 (MH$^+$, 100), 86 (26), 55 (28), 43 (68).

4.5. General Procedure for the Synthesis of Cyclic Carbonates 4a−h Using Compressed Air. Epoxide **3a**−**h** (0.1 mmol), catalyst **1** (2.8 mg, 2.5 × 10^{-3} mmol), and Bu_4NBr (0.75 mg, 2.5 × 10^{-3} mmol) were added to a glass vial fitted with a stirrer bar. The vial was placed in an autoclave, pressurized to 25 bar with compressed air, and heated to 50 °C. The reaction was stirred under these conditions for 24 h, then the reactor was cooled using an acetone/dry ice bath, and the pressure was released. The reaction mixture was analyzed by ^{1}H NMR spectroscopy to determine the conversion of epoxide **3a**−**h** into cyclic carbonate **4a**−**h**. In the case of epoxide **3c**, this procedure was carried out a total of 8 times and the reaction mixtures combined to give sufficient material to purify by flash chromatography (eluting with hexane/EtOAc, 8:1 to 1:1) to give cyclic carbonate **4c** (107.0 mg, 67%) as a colorless oil. ν_{max}(ATR) 2926, 2856, and 1834 cm^{-1}; $\delta_H(CDCl_3)$ 0.89 (3H, t *J* 6.9 Hz), 1.2−1.6 (12H, m), 1.6−1.75 (1H, m), 1.75−1.9 (1H, m), 4.07 (1H, dd *J* 8.3, 7.4 Hz), 4.53 (1H, t *J* 8.1 Hz), 4.71 (1H, ddd *J* 13.0, 7.7, 5.5 Hz); $\delta_C(CDCl_3)$ 14.0, 22.6, 24.4, 29.0, 29.1, 29.3, 31.8, 33.9, 69.4, 155.0; GCMS t_R 13.48 min; m/z(CI) 201 (MH$^+$, 50), 95 (55), 81 (100).

4.6. General Procedure for the Synthesis of Diols 7a,c,d. To cyclic carbonate **6a**−**c** (0.3 mmol) in a round bottomed flask were added 5 M aqueous KOH (20 mL) and THF (10 mL). The resulting solution was refluxed for 3 h, then cooled to room temperature, and extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined and washed with 1 M aq. HCl (60 mL). The organic layer was dried (Na_2SO_4) and evaporated to dryness to leave diols **7a,c,d**.

*trans-1,2-Diphenylethan-1,2-diol **7a**.*[54−56] Obtained as a white solid in 90% yield. Mp 145−149 °C (lit.[56] 150 °C), ν_{max}(ATR) 3270 and 1454 cm^{-1}; $\delta_H(CDCl_3)$ 4.70 (2H, s), 7.0−7.1 (4H, m), 7.1−7.2 (6H, m); $\delta_C(CDCl_3)$ 78.8, 127.2, 127.7, 128.0, 140.8.

*cis-Cyclopentane-1,2-diol **7c**:.*[55,57] Obtained as a white solid in 45% yield. Mp 28−31 °C (lit.[57] 28−29 °C), ν_{max}(ATR) 3361, 1338, and 1035 cm^{-1}; $\delta_H(CDCl_3)$ 1.0−2.2 (8H, m), 3.9−4.2 (2H, br); $\delta_C(CDCl_3)$ 19.9, 31.5, 74.0.

*trans-Cyclohexane-1,2-diol **7d**.*[55,57] The initially formed 1:3 mixture of diols **7b** and **7d** was recrystallized from petroleum ether to give diol **7d** as a white solid in 46% yield. Mp 105−108 °C (lit.[60] 105−107 °C), ν_{max}(ATR) 3276, 2932, 2859, 1444, and 1065 cm^{-1}; $\delta_H(CDCl_3)$ 1.2−1.4 (4H, m), 1.6−1.8 (2H, m), 1.9−2.1 (2H, m), 2.20 (2H, s), 3.3−3.4 (2H, m); $\delta_C(CDCl_3)$ 24.4, 33.0, 76.0.

4.7. Synthesis of *cis*-Cyclohexane-1,2-diol[55,57] 7b. To cyclic carbonate **6b** (42.6 mg, 0.3 mmol) were added methanol (20 mL) and conc. hydrochloric acid (5 mL). The resulting solution was heated at reflux for 24 h, cooled, and then evaporated to dryness using ethanol to form an azeotrope with the water. The residue was washed with cold petroleum ether and then dried under vacuum to give diol **7b** as a white solid in 86% yield. Mp 90−94 °C (lit.[57] 93−95 °C), ν_{max}(ATR) 3256, 2930, 2865, 1440, 1364, and 1073 cm^{-1}; $\delta_H(CDCl_3)$ 1.3−1.4 (4H, br), 1.6−1.7 (2H, br), 1.8−1.9 (2H, br), 1.98 (2H, s); 3.7−4.0 (2H, br); $\delta_C(CDCl_3)$ 21.5, 30.2, 70.7.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR and GCMS spectra for cyclic carbonates; ^{1}H and ^{13}C NMR spectra for epoxides **5a**−**e** and diols **7a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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