

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

'Ring-Expansion Addition' of Epoxides Using Applied Potential: An Investigation of Catalysts for Atmospheric Pressure Carbon Dioxide Utilization

Cite this: DOI: 10.1039/x0xx00000x

Benjamin R. Buckley,* Anish P. Patel, and K. G. Upul Wijayantha*

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Abstract: Interest in the use of CO₂ as a feedstock for preparation of value-added compounds has dramatically increased over the past decade. We herein investigate the insertion of atmospheric pressure carbon dioxide under electrochemical conditions into epoxides. The initial investigations involved the use of either a nickel or copper based catalyst, however, upon further optimisation and careful selection of electrode materials we found that these catalysts were not required for efficient carbon dioxide insertion to occur.

Introduction

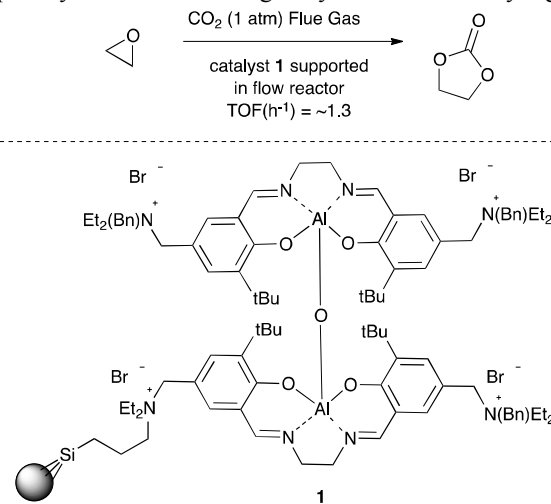
Anticipated pressures on fossil fuel resources in the coming decades mean that raw materials for the chemical industry must be found that can reduce our reliance on fossil fuel-based feedstocks.¹ Hence, the development of new production processes for chemical syntheses from renewable resources is a challenge that should be a priority for all major economies.² Research into/application of carbon dioxide utilization (CDU) technologies has recently gained increased interest.³ CDU offers an attractive alternative to the well-established carbon dioxide storage (CCS) processes, however, scale of production means that CDU is unlikely to significantly reduce anthropogenic carbon dioxide emissions, but waste carbon dioxide under CDU protocols can be converted into useful chemicals or fuels.

Carbon dioxide is abundant, cheap and non-toxic when compared to other C₁ building blocks, such as phosgene, and has been used in the manufacture of salicylic acid, urea and cyclic carbonates for 50-100 years. However, due to carbon dioxide's relative inertness these processes are significantly energy demanding with reactions taking place at high temperatures and pressures. Therefore if CDU technologies are to become viable processes with reliance on very little energy input are required, hence processes at mild temperatures (<100 °C) and atmospheric pressures should be targeted.

The chemical reduction of CO₂ has received considerable interest in the last few years, both as a method for recycling CO₂ in industrial waste streams and as well as a route to useful chemical products. For example, cyclic carbonates are widely used in the manufacture of products including solvents, paint-strippers, biodegradable packaging, as well as having applications in the chemical industry. Cyclic carbonates also

have potential for use in the manufacture of a new class of efficient anti-knocking agents in petrol.⁴

The insertion of carbon dioxide into epoxides to afford either 5-membered ring cyclic carbonates^{5,6} or the corresponding polycarbonate⁷ has attracted considerable attention due to the industrial application of the products arising from these reactions. For example, North and co-workers have employed bimetallic aluminium salen complexes incorporating an ammonium bromide co-catalyst such as **1** (Scheme 1) to prepare cyclic carbonates in good yield from not only highly



Scheme 1: One of North's catalysts for cyclic carbonate synthesis using flue gas

purified carbon dioxide but also directly from a fossil fuel power station stack by use of a supported salen catalyst and flow reactor.⁸ These reactions take place at mild temperatures and atmospheric pressures.

Other catalytic systems have also been successfully employed for example, Kleij and co-workers have recently reported the synthesis of 5-membered cyclic carbonates in excellent yield using either an iron, aluminium or vanadium based catalyst at 10-2 atm CO₂.⁹

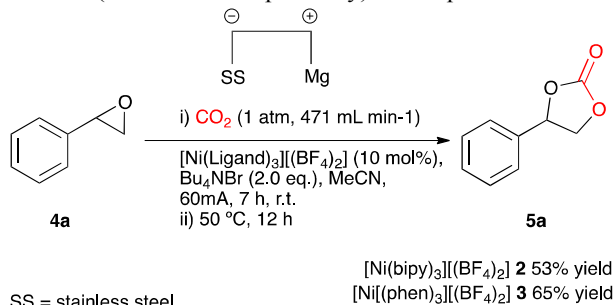
Duñach reported in the late 1990's the nickel-catalysed electrochemical carboxylation of epoxides using a nickel(II) cyclam complex (10 mol%) in DMF with a magnesium anode and KBr as electrolyte.¹⁰ This was an attractive system for fixing CO₂, when one considers that typically the reaction of epoxides with CO₂ for the preparation of cyclic carbonates is generally carried out at high temperatures (>100 °C) and elevated CO₂ pressures (>40 atm) in the presence of a transition metal as catalyst.

Results and discussion

We were interested in developing a low energy alternative in line with our current research portfolio aimed at electrosynthesis¹¹ coupled with semiconductor photoelectrodes to drive light assisted electrosynthetic reactions.¹² We were therefore attracted to the possibility of employing an electrosynthetic system as this type of process could be designed to be cost neutral in terms of energy consumption if combined with a suitable solar powered energy source and unlike many metal catalysed processes be able to run at ambient temperature and atmospheric pressure carbon dioxide.

Initial Investigations of a Nickel(I) Catalysed System

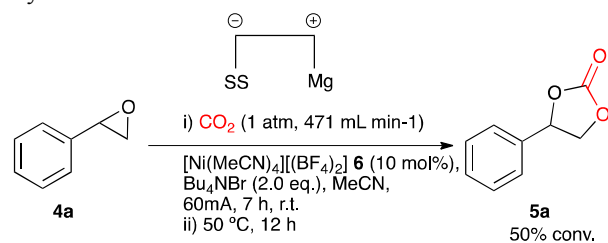
Our initial aims were to improve the Duñach system by running the reactions with cheaper and more accessible catalysts and in a more user-friendly reaction medium. Based on conditions reported in literature the catalysts required for electrochemical carboxylation: [Ni(bipy)₃][(BF₄)₂] **2** and Ni[(phen)₃][(BF₄)₂] **3** were synthesised.¹³ Reactions were screened using styrene oxide **4a** as substrate and run in acetonitrile in a single compartment cell containing a magnesium anode, a stainless steel cathode and Bu₄NBr supporting electrolyte (2 eq.), at constant current: 60 mA (7 h), with constant CO₂ flow (471 mL min⁻¹), in the presence of the nickel catalyst (10 mol%) followed by heating at 50 °C (12 h, Scheme 2). The reaction proceeded in the presence of the nickel catalysts **2** and **3**, forming the target cyclic carbonate **5a**, in moderate to good conversion (65 and 53% respectively). Attempts to increase the



Scheme 2: Initial screening conditions

conversion using catalyst **2** were successful when the heating time was increased to 18 h affording the carbonate in 81% conversion by ¹H NMR spectroscopy (replacement of Bu₄NBr with Bu₄NI resulted in only 67% conversion).

In order to improve the system and move towards cheaper more accessible catalysts, [Ni(CH₃CN)₄][(BF₄)₂] **6** was employed in the electrocarboxylation of styrene oxide **4a**. A test reaction (Scheme 3) involved electrolysis in acetonitrile in a single compartment cell containing a magnesium anode, a stainless steel cathode and Bu₄NBr supporting electrolyte (2 eq.), at constant current: 60 mA (7 h), with constant CO₂ flow (471 mL min⁻¹), in the presence of the nickel catalyst **6** (10 mol%) followed by heating at 50 °C (12 h), forming cyclic carbonate **5a** in moderate conversion (50%). A distinct colour change of the reaction solution on addition of the supporting electrolyte from blue to deep blue was observed during this reaction and it was thus believed that the active catalyst was the tetrahedral complex [Ni(Br)₄], formed from a ligand exchange reaction between bromine ions of the supporting electrolyte and the co-ordinated acetonitrile ligands. Furthermore stability issues of reported cross bromo / acetonitrile complexes,¹⁴ suggest that bromine ions have a stronger affinity towards Ni(II) in comparison to acetonitrile ligands, eliminating the possibility of a cross complex. Resulting reactions involved direct addition of the nickel reagent, [Ni(II)][(BF₄)₂] **7** to the reaction solvent containing additional supporting electrolyte, Bu₄NBr (Ni²⁺ + 4Br⁻ → Ni(Br)₄ **8**) to allow *in-situ* active catalyst formation.



Scheme 3: Nickel catalysed conditions

The optimum catalyst loading was also investigated, this time using 1,2-epoxyoctadecane **4b** as a test substrate. Electrocarboxylation under the test reaction conditions in the presence of nickel reagent **7** at 10, 15, 20 and 50 mol% loading, Bu₄NBr (2.4, 2.6, 2.8 and 4 equivalents) and heating for 15 hours, resulted in the corresponding cyclic carbonate **5b**, with conversion increasing with catalyst loading. Although 50 mol%, gave the highest conversion (90%) in comparison to 10 mol% (55% conversion).

In order to further increase the conversion of starting material, the flow rate of CO₂ entering the reaction system was studied. Electrocarboxylation of **4a** under the test reaction conditions in the presence of CO₂ at either 89, 287, or 471 mL min⁻¹, nickel reagent **7** (50 mol%), Bu₄NBr (4 eq.) and heating for 15 hours, produced the cyclic carbonate **5a**, with conversion generally increasing with flow rate. A flow rate of 471 mL min⁻¹ resulted in the highest conversion (88%).

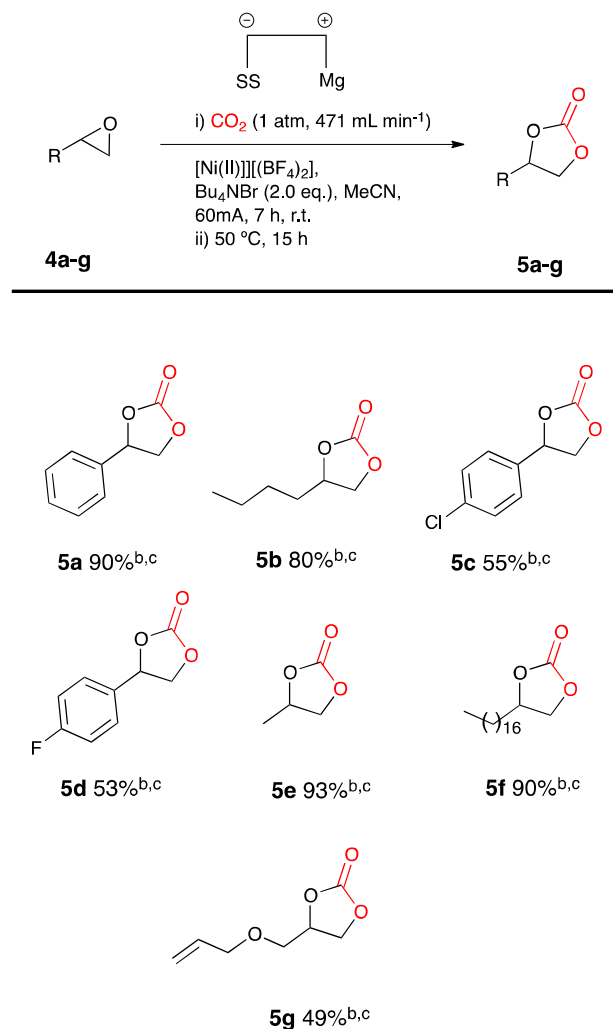
Once the optimum reaction conditions were established: 50 mol% loading of nickel reagent **7**, 15 h heating and 471 mL min⁻¹ CO₂ flow rate, and in conjunction with existing conditions: open single compartment cell, magnesium anode, stainless steel cathode, acetonitrile solvent, Bu₄NBr (4 eq.) and 7 h constant current electrolysis at 60 mA, a range of epoxide substrates were employed in order to determine the scope of the reaction conditions (Table 1). Electrocarboxylation of epoxides **4a-4g** led to the formation of the target cyclic carbonates **5a-5g** in moderate to excellent conversion (53-93%). Substrates **4c** and **4d** gave moderate conversion attributed to the electron withdrawing properties of the aromatic ring substituents, although both Cl⁻ and F⁻ substituents are mesomerically donating (+M) they are inductively withdrawing (-I), thus possibly decreasing the reactivity of both substrates to nucleophiles or Lewis acid interactions.

In order to prove the requirement of CO₂, constant CO₂ flow, Bu₄NBr addition (4 eq.) and *in-situ* formation of nickel catalyst **7**, control experiments were carried out, involving the attempted synthesis of cyclic carbonate **5b** from test substrate **4b** under optimum conditions. Electrocarboxylation with a CO₂ flush (1 h) prior to electrolysis and the absence of constant CO₂ flow during the reaction, resulted in minimal conversion (5%), whereas in the absence of CO₂ altogether no product formation could be detected by ¹H NMR spectroscopy. Electrocarboxylation using lower loadings of Bu₄NBr (1 eq.) resulted in decreased conversion (25%) in comparison to using 4 equivalents (90%), and finally electrocarboxylation using nickel catalyst **8** synthesised in CH₃CN or EtOH resulted in comparable conversion (85% and 86%) to the *in-situ* formed complex (90%).

Investigations of a Copper(I) Based System

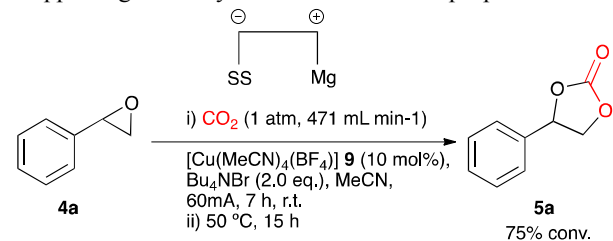
In search of more effective catalysts for the synthesis of cyclic carbonates led to the identification of [Cu(CH₃CN)₄][BF₄] **9**. This coordination complex is cheaper and less toxic in comparison to the analogous nickel species. Electrocarboxylation of the test substrate **4a** in acetonitrile in a single compartment cell containing a magnesium anode, stainless steel cathode and Bu₄NBr supporting electrolyte (2.4 eq.), at constant current: 60 mA (7 h) with constant CO₂ flow (471 mL min⁻¹) in the presence of copper catalyst **9** (10 mol%)

Table 1: Electrocarboxylation using Nickel based reagent **7**.^a



^a General reaction conditions: [Ni(II)][(BF₄)₂] (1.0 mmol), epoxide (2.0 mmol), stainless steel cathode, magnesium anode, Bu₄NBr (8 mmol), CO₂, 60mA, 25 °C, 7 h, followed by: 50 °C, 15 h; ^b Conversion evaluated from the ¹H NMR spectrum by integration of the epoxide vs. cyclic carbonate signals; ^c The cyclic carbonate was the only observed product by ¹H NMR spectroscopy

followed by heating (12 h) resulted in cyclic carbonate **5a** with good conversion (75%, Scheme 4). It appeared, however, that the above mentioned catalyst was not the active catalyst due to a distinct colour change of the reaction solution on addition of the supporting electrolyte from colourless to purple. Based on



Scheme 4: Copper(I) catalysed electrocarboxylation of styrene oxide.

previously reported systems it was thought that the active catalyst could be the tetrahedral complex $[\text{Cu}(\text{Br})_4]$ **10**.¹⁵

The reactions employing both nickel and copper based catalysts/reagents employed the use of an open reaction vessel during the electrocarboxylation process, thus an extremely high CO_2 flow rate was required in order to achieve a higher conversion of the epoxide starting material to the cyclic carbonate product. In an effort to reduce the CO_2 flow rate, the experimental set-up was altered to a pseudo-sealed reaction system, where CO_2 had a single inlet and outlet point, allowing the measurement and potential recovery of CO_2 leaving the system. Electrocarboxylation of **4a** using the conditions described above, using a pseudo-sealed reaction vessel and a decreased CO_2 flow rate of 132 mL min^{-1} , formed the corresponding cyclic carbonate **5a** in a similar conversion (76%) to the open reaction system (75%, flow rate: 471 mL min^{-1}).

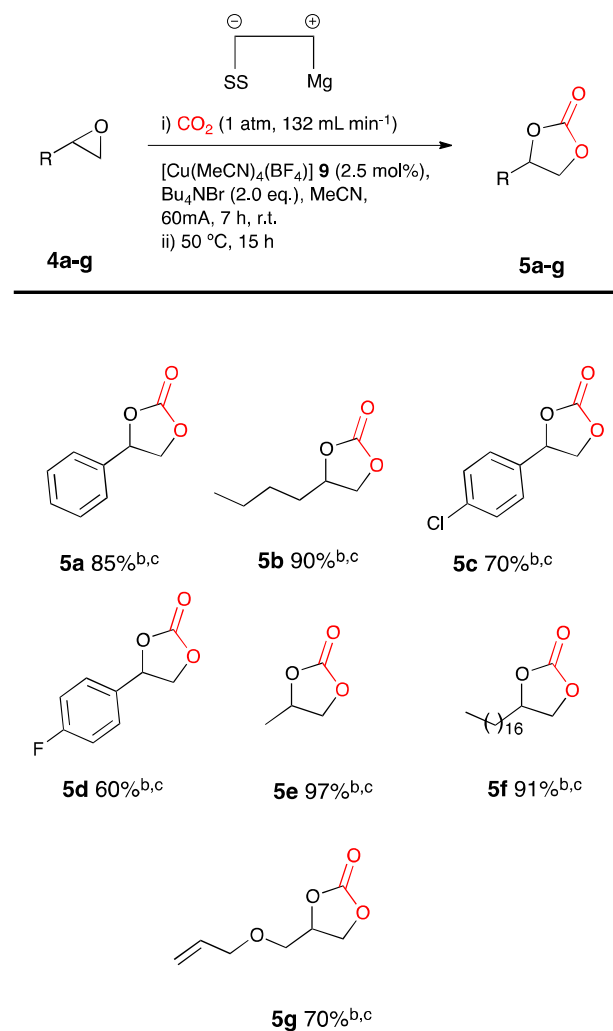
The optimum catalyst loading for this process was investigated and electrocarboxylation of **4a** under the initially employed conditions in a pseudo sealed reaction vessel, in the presence of copper catalyst **9** at 2.5, 5 and 10 mol%, Bu_4NBr (2.1, 2.2 and 2.4 eq.) and a CO_2 flow rate of 132 mL min^{-1} , resulted in the formation of the cyclic carbonate **5a**, with conversion decreasing with catalyst loading. Unusually the lowest catalyst loading of 2.5 mol% resulted in a slightly higher conversion (85%), in comparison to 5 mol% (81%) and 10 mol% (78%).

Once the optimum reaction conditions were established: pseudo-sealed single compartment cell, 2.5 mol% loading of copper catalyst **9**, 132 mL min^{-1} CO_2 flow rate, and in conjunction with the existing conditions: magnesium anode, stainless steel cathode, acetonitrile solvent, Bu_4NBr (2.1 eq.), 7 h constant current electrolysis at 60 mA and heating for 12 h, a range of epoxide substrates were employed in order to determine the scope of the reaction conditions (Table 2). Electrocarboxylation of epoxides **4a-4g** led to the formation of the target cyclic carbonates **5a-5g** in good to excellent conversion (60-97%). Substrates **4c** and **4d** gave moderate conversion for similar reasons as mentioned for the nickel based system. Furthermore post-reaction precipitation of the supporting electrolyte resulted in good recovery of Bu_4NBr (~65%).

In order to prove *in-situ* formation of copper catalyst **10**, the requirement for a catalyst and Bu_4NBr addition, control experiments were carried out, involving the attempted synthesis of cyclic carbonate **5a** from test substrate **4a** under optimum conditions. Electrocarboxylation using copper catalyst $[\text{Cu}(\text{Br})_4]$ **10** synthesised in CH_3CN or EtOH resulted in comparable conversion (81% and 83%), to the *in-situ* formed complex (90%).

Electrocarboxylation using less Bu_4NBr (0.1 eq.) and Bu_4NPF_6 (0.1 eq.), resulted in decreased conversion (15%) in comparison to Bu_4NBr (2.1 eq.) (90%). A repeat of this reaction in the absence of catalyst, also resulted in conversion of starting material (16%), although the conversion obtained was low, the result suggested the possibility of catalyst free electrocarboxylation in the presence of higher Bu_4NBr loading

Table 2: Electrocarboxylation over a range of epoxide substrates.^a



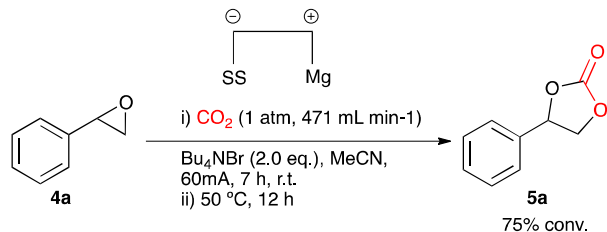
^aGeneral reaction conditions: $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ **9** (0.05 mmol) epoxide (2.0 mmol), stainless steel cathode, magnesium anode, Bu_4NBr (4.2 mmol), CO_2 , 60 mA, 25°C , 7 h, followed by: 50°C , 12 h; ^bConversion evaluated from the ^1H NMR spectrum by integration of the epoxide vs. cyclic carbonate signals. ^cThe cyclic carbonate was the only observed product by ^1H NMR spectroscopy

and CO_2 flow rates. Bu_4NPF_6 supporting electrolyte was selected in order to maintain a constant current during the reaction furthermore the PF_6^- counter-ions are labile and therefore non-coordinating. Finally electrocarboxylation in the absence of current between electrodes, resulted in no product formation.

Investigations of a catalyst free System

After conducting control experiments without the addition of a metal catalyst it was observed that some conversion to cyclic carbonate occurs (16%). This was particularly interesting as it opened up the possibility of direct CO_2 insertion without the requirement for an additional catalyst. In order to attempt to optimise the catalyst free system an initial test reaction was carried out using styrene oxide **4a** and the optimised conditions used for Cu(I) catalysis, but with an increased CO_2 flow rate

and the absence of a catalyst. Electrocarboxylation in acetonitrile in a single compartment cell containing a magnesium anode, stainless steel cathode and Bu₄NBr (2 eq.), at constant current: 60 mA (7h) with constant CO₂ flow (471 mL min⁻¹) followed by heating at 50 °C (12 h) formed the target cyclic carbonate **5a**, in good conversion (75%) (Scheme 5).



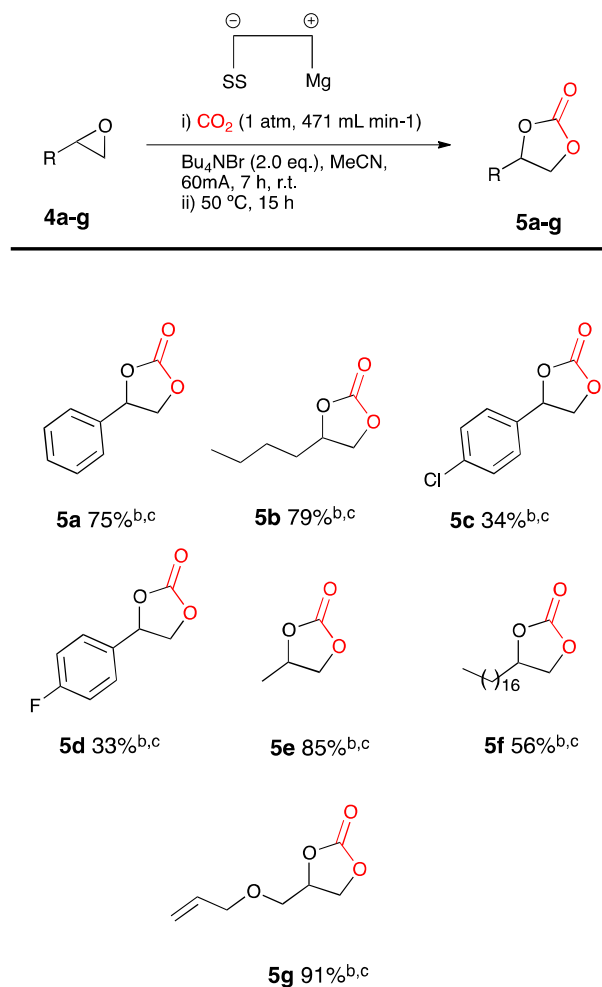
Scheme 5: Initial catalyst free conditions

In order to determine whether the result was anomalous or restricted to aryl epoxides, a range of substrates were employed using the conditions described in scheme 5 (Table 3). Electrocarboxylation of epoxides **4a-4g** led to the formation of the target cyclic carbonates **5a-5g** in poor to excellent conversion (33-91%). Again substrates **5c** and **5d** gave moderate conversion for similar reasons as the nickel and copper catalysed systems. In general all substrates produced lower conversions in comparison to the Cu(I) catalysed system, however, we observed that the copper catalyst **9** undergoes cathodic electroplating, thus suggesting that this system was actually a pseudo-catalyst free system, with electroplated copper appearing to enhance the conversion of the epoxide starting materials in comparison to the nickel catalysed systems. Furthermore as the results for the catalyst loading study for copper catalyst **9** were very similar, it is believed that once a layer of copper has been deposited on the cathode further plating has little effect on the reaction.

The observed conversion of a range epoxide starting materials in the absence of a catalyst and in the presence of a magnesium anode and stainless steel cathode, suggested that the electrochemical system had the potential to be effective under catalyst free conditions. The proficiency of the process, however, was decreased because of the high CO₂ flow rate being used, thus the need for a reduction in CO₂ waste was investigated. A test reaction involved flushing a single compartment cell containing a magnesium anode, stainless steel, Bu₄NBr supporting electrolyte (2 eq.) and test substrate **4a** in acetonitrile for 1h with CO₂, followed by electrocarboxylation at a constant current (60 mA, 7 h) under a CO₂ balloon with heating at 50 °C (12 h), resulting in cyclic carbonate **5a** formation with good conversion (75%).

In order to determine the ideal electrode couple for the reaction system, a range of cathodic electrode materials were screened. Electrocarboxylation of **4a** under the conditions described above using a copper or graphite cathode formed the corresponding cyclic carbonate **5a** in excellent conversion for copper (99%), whereas graphite produced the desired product in slightly lower conversion (85%). It appeared

Table 3: Electrocarboxylation over a range of epoxide substrates.^a



^aGeneral reaction conditions: epoxide (2.0 mmol), stainless steel cathode, magnesium anode, Bu₄NBr (4.0 mmol), CO₂, 60 mA, 25 °C, 7 h, followed by: 50 °C, 12 h; ^bConversion evaluated from the ¹H NMR spectrum by integration of the epoxide vs. cyclic carbonate signal; ^c The cyclic carbonate was the only observed product by ¹H NMR spectroscopy

that copper was a superior cathode in comparison to stainless steel (75%) and although graphite resulted in greater conversion of starting material, slight degradation of the electrode in acetonitrile solvent was observed.

A range of anodic electrode materials were also screened. Electrocarboxylation of **4a** under the test reaction conditions using either an aluminium, zinc, tin or copper anode formed the target cyclic carbonate **5a** in good conversion for aluminium (75%) and poor conversion for zinc (5%) and tin (10%), and in comparison, magnesium remained superior (99%).

Identification of a magnesium anode and a copper cathode as the optimum electrode couple, was followed by full optimisation of the catalyst free conditions. Previously it was thought that two equivalents of Bu₄NBr supporting electrolyte were required in order to form stoichiometric MgBr₂ *in-situ*, on the contrary, control reaction results obtained in the stainless steel cathode and magnesium anode catalyst free system

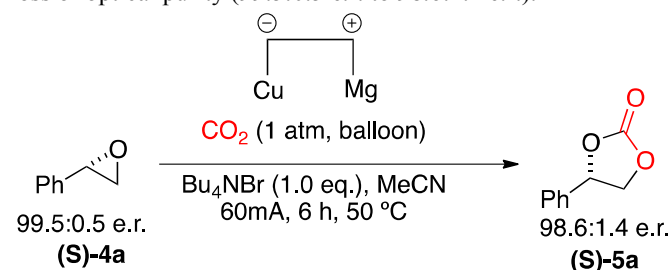
suggest otherwise, therefore the Bu₄NBr loading was investigated. Electrocarboxylation of **4a** under the test reaction conditions, conversely, in the presence of a copper cathode and supporting electrolyte Bu₄NBr at 50, 100 and 200 mol% loading, produced the cyclic carbonate **5a**, with conversion increasing with electrolyte loading. Although 200 mol% gave the highest conversion of starting material (99%), 100 mol% gave an almost equal conversion (98%), thus 100 mol% was selected as the optimum. The requirement of heating was also investigated with electrocarboxylation of **4a** under the test reaction conditions in the presence of a copper cathode, Bu₄NBr (100 mol%) and the absence of a heating step, resulting in target product **5a** formation in good conversion (72%) with an increase in the electrolysis time to 10 h again in the absence of a heating step, resulting in only moderately higher conversion (77%). In order to decrease the overall reaction time and energy requirement, electrocarboxylation of **4a** was carried out under the test reaction conditions in the presence of a copper cathode and Bu₄NBr (100 mol%) with simultaneous heating, the reaction proceeded to completion in 6h giving excellent conversion to the corresponding cyclic carbonate **5a** (98%), with a decrease in reaction time to 3 h leading to moderate conversion (76%). The final optimisation reaction involved the electrocarboxylation (6 h) of **4a** in air under the test reaction conditions in the presence of a copper cathode and Bu₄NBr (100 mol%) with simultaneous heating, however, this resulted in the return of starting material.

The optimum applied current was also investigated and electrocarboxylation of **4a** under the test reaction conditions in the presence of a copper cathode, Bu₄NBr (100 mol%), and simultaneous heating at an applied current of either 20, 40, 60, 80 or 100 mA, resulted in the formation of **5a**, with conversion increasing with applied current. The highest conversions (100%) were observed at 60, 80 and 100 mA, whereas 20 and 40 mA gave poor to moderate conversion, as there was no need for additional current, 60 mA was maintained as the optimum applied current.

Once the optimum reaction conditions were established: sealed single compartment cell, magnesium anode, copper cathode, 100 mol% Bu₄NBr loading and simultaneous heating and electrolysis at 60 mA / 50 °C for 6 h under a CO₂ balloon, a range of epoxide substrates were employed in order to determine the scope of the reaction conditions (Table 4). Electrocarboxylation of epoxides **4a-p** led to the formation of the target cyclic carbonates **4a-l** in good to excellent conversion (75-99%) and good to excellent yield (65-96%). Again substrates **4c** and **4d** initially gave moderate conversion attributed to the inductively electron withdrawing (-I) properties of the fluoro- and chloro- aromatic ring substituents, however an increase in the reaction time to 10h enhanced both conversion and yield. In line with other studies in the area,^{7,10} epoxides **4n**, **4o** and **4p** did not form the target cyclic carbonate product, and as the substrates are either di- or tri-substituted the lack of reactivity is attributed to steric hinderance, thus preventing the addition of Br⁻ to ring open the epoxide, and hence reactions resulted in the return of starting material.

Interestingly epoxide **4m** was hydrolysed and converted into cyclic carbonate **5j**. Furthermore, post-reaction precipitation of the supporting electrolyte from these reactions resulted in good recovery of Bu₄NBr (~90%).

In order to explore the mild nature of these reaction conditions we were interested in the applicability of this system to enantiopure epoxides (Scheme 6). Application of our optimized conditions to the CO₂ incorporation of (*S*)-styrene oxide (**S**)-**4a** afforded the cyclic carbonate (**S**)-**5a** in excellent yield (97%) with retention of configuration and only a slight loss of optical purity (99.5:0.5 e.r. to 98.6:1.4 e.r.).



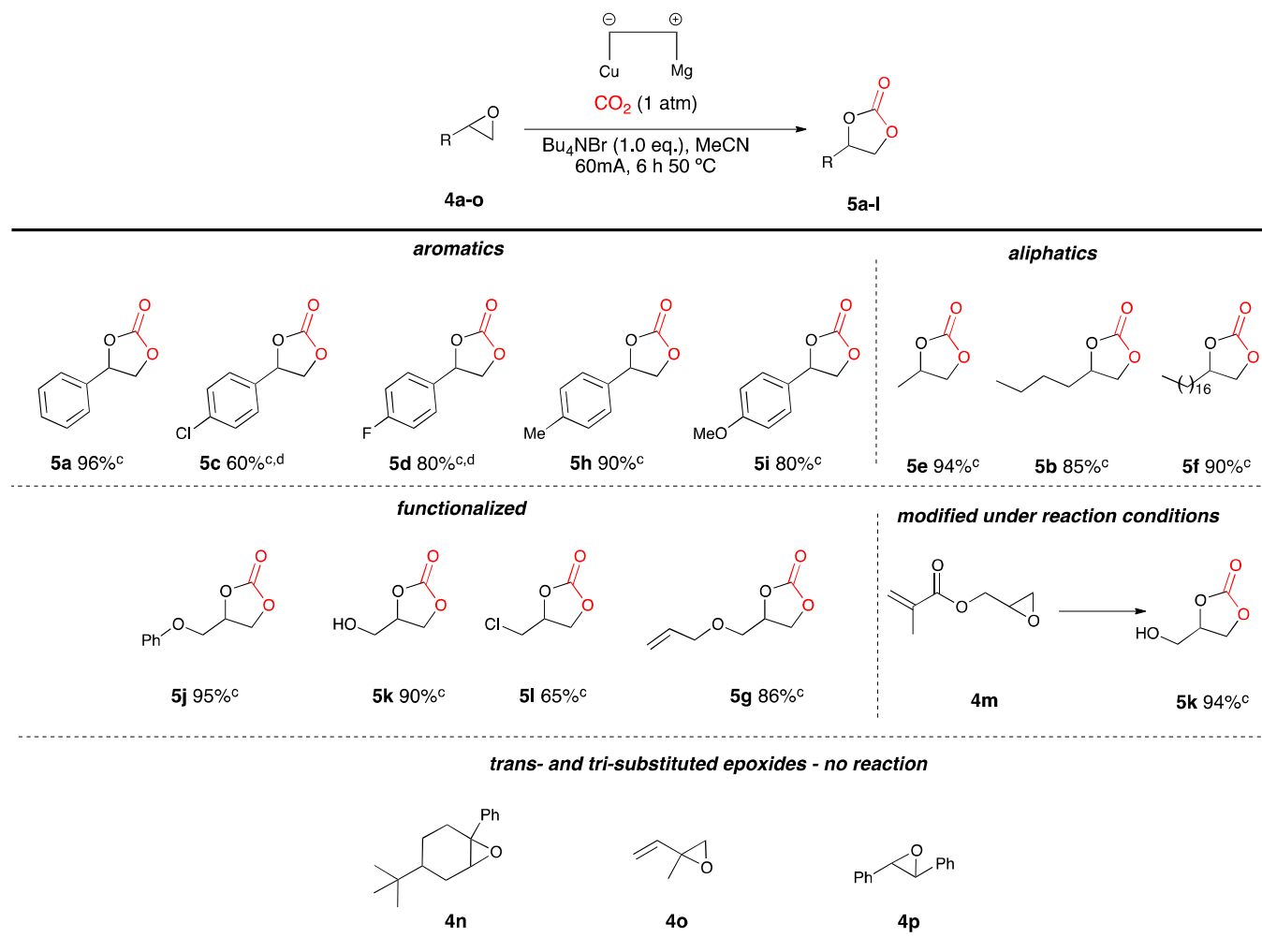
Scheme 6. Electrocarboxylation of (*S*)-styrene oxide (**S**)-**4a** to afford the enantiomerically pure cyclic carbonate (**S**)-**5a** with retention of configuration.

The scalability of the reaction for large scale synthesis was explored using propylene oxide **4g** as the test substrate (Table 4), primarily due to the carboxylated product: 4-methyl-1,3-dioxolan-2-one (propylene carbonate) **5g** being currently synthesised in industry for use as a polar aprotic solvent.²⁴ Electrocarboxylation of **4g** (170 mmol) under optimised conditions resulted in the formation of the target product **5g** in excellent conversion (100%, 91% yield).

A proposed mechanism of our process is highlighted in scheme 7. Under standard heating and stirring conditions we believe the pathway shown is in operation due to the recent reports by North and coworkers^{7e} and the retention of stereochemical information in the final cyclic carbonate product.

Conclusions

In conclusion we have studied the effect of several transition metal catalysts and electrode materials on the ring-expansion addition of epoxides with carbon dioxide. This process is one of a handful of emerging approaches that allow this reaction to proceed at atmospheric pressure and at ambient-mild temperatures. The yields obtained are comparable or better than those already reported in the area and our approach benefits from not employing an additional catalyst into the reaction, which in some cases can be toxic or expensive. The equipment required to perform this CO₂ incorporation reaction is cheap and should be readily available in any undergraduate teaching facility i.e. copper wire, magnesium ribbon and a power supply.

Table 4 Application to a range of epoxides^{a,b}

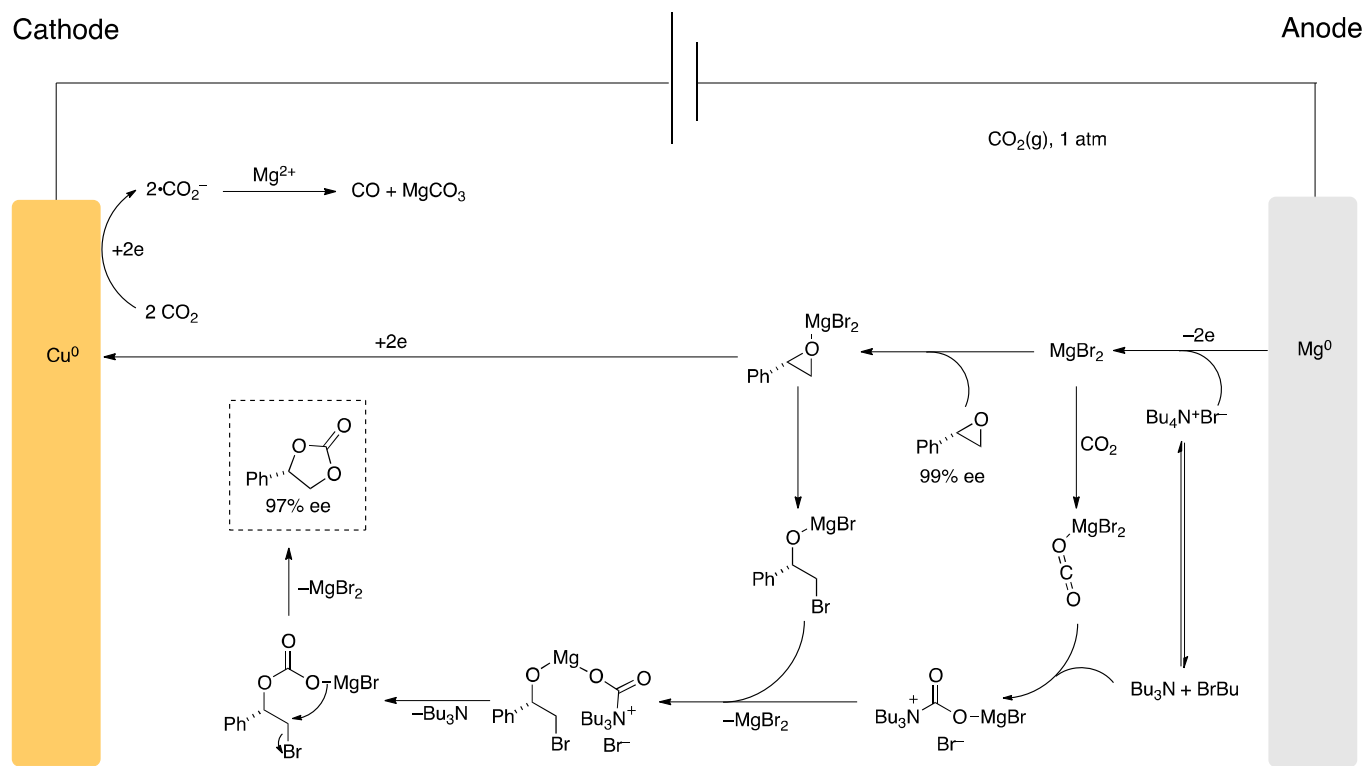
^a General conditions: CO_2 , Cu cathode, Mg anode, Bu_4NBr (2.0 equiv.), MeCN, single compartment cell, 60mA, 6 h 50 °C; ^b On average 90-95% of the Bu_4NBr is recovered after each reaction by precipitation with EtOAc and the cyclic carbonate was the only observed product by ^1H NMR spectroscopy; ^c isolated yield after column chromatography; ^d Reaction ran for 8 h.

Experimental

Representative procedure for the ring expansion addition reaction using nickel based catalysts (Scheme 2): Styrene oxide **4a** (0.24 g, 2.0 mmol) in acetonitrile (50 mL) was electrolysed at constant current: 60 mA for 7 h in a single compartment cell containing a stainless steel cathode and magnesium anode, in the presence of catalyst (10 mol%), supporting electrolyte: Bu_4NBr (0.128 g, 4 mmol) and CO_2 , followed by heating at 50 °C for 12 h or 18 h. On completion

the reaction mixture was filtered and the filtrate washed with HCl (50 mL / 0.1 M) followed by extraction using Et_2O (3 x 35 mL). The combined organic extracts were washed with H_2O (50 mL), dried over MgSO_4 and evaporated to dryness affording 4-phenyl-1,3-dioxolan-2-one **5b** as a crude amber oil. $[\text{Ni}(\text{bipy})_3][(\text{BF}_4)_2]$ **2** (0.10 g, 10 mol%) (conv.: 65%); $\text{Ni}[(\text{phen})_3][(\text{BF}_4)_2]$ **3** (0.12 g, 10 mol%) (conv.: 53%).

Catalyst loading study using 7 and 4b: 1,2-epoxyoctadecane **4b** (0.54 g, 2.0 mmol) in acetonitrile (50 mL) was electrolysed at constant current: 60 mA with constant stirring for 7 h in a



Scheme 7. Proposed mechanism for carbon dioxide 'Ring-Expansion Addition' of epoxides using applied potential

single compartment cell containing a stainless steel cathode and magnesium anode, in the presence of $[\text{Ni}(\text{II})][(\text{BF}_4)_2]$ **7**, supporting electrolyte: Bu_4NBr and CO_2 , followed by heating at 50°C for 15 h. On completion the reaction mixture was filtered and the filtrate washed with HCl (50 mL / 0.1 M) followed by extraction using Et_2O (3 x 35 mL). The combined organic extracts were washed with H_2O (50 mL), dried over MgSO_4 and evaporated to dryness affording 4-hexadecyl-1,3-dioxolan-2-one **5b** as a brown solid. $[\text{Ni}(\text{II})][(\text{BF}_4)_2]$ (0.068 g, 10 mol%) and Bu_4NBr (1.55 g, 4.8 mmol) (conv: 53%). $[\text{Ni}(\text{II})][(\text{BF}_4)_2]$ (0.10 g, 15 mol%) and Bu_4NBr (1.68 g, 5.2.0 mmol) (conv: 66%). $[\text{Ni}(\text{II})][(\text{BF}_4)_2]$ (0.14 g, 20 mol%) and Bu_4NBr (1.81 g, 5.6 mmol) (conv: 73%). $[\text{Ni}(\text{II})][(\text{BF}_4)_2]$ (0.34 g, 50 mol %) and Bu_4NBr (2.56 g, 8 mmol) (conv: 90 %).

Representative procedure for the ring expansion addition reaction using $[\text{Ni}(\text{II})][(\text{BF}_4)_2]$ **7 (Table 1):** Styrene oxide **4a** (2.0 mmol, 0.24 g) in acetonitrile (50 mL) was electrolysed at constant current: 60mA with constant stirring for 7 h in a single compartment cell containing a stainless steel cathode and magnesium anode, in the presence of $[\text{Ni}(\text{II})][(\text{BF}_4)_2]$ **7** (0.34 g, 50 mol%), supporting electrolyte: Bu_4NBr (2.56 g, 8 mmol) and CO_2 (flow rate: 471 mL min^{-1}), followed by heating at 50°C for 15 h. On completion the reaction mixture was filtered and the filtrate washed with HCl (50 mL / 0.1 M) followed by extraction using Et_2O (3 x 35 mL). The combined organic extracts were washed with H_2O (50 mL), dried over MgSO_4 and evaporated to dryness, followed by purification by column chromatography on silica affording affording 4-phenyl-1,3-dioxolan-2-one **5a** as a colourless solid (90% conv.).

Representative procedure for the ring expansion addition reaction using $[\text{Cu}(\text{MeCN})_4(\text{BF}_4)]$ **9 (Table 2):** Styrene oxide **4a** (0.24 g, 2.0 mmol) in acetonitrile (150 mL) was electrolysed at constant current: 60 mA with constant stirring for 7 h in a single compartment cell containing a stainless steel cathode and magnesium anode, in the presence of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ **9** (0.018 g, 2.5 mol%), supporting electrolyte: Bu_4NBr (1.35 g, 4.2.0 mmol) and CO_2 (flow rate: 132 mL min^{-1}), followed by heating at 50°C for 12 h. On completion the reaction mixture was filtered and filtrate was evaporated to dryness followed by addition of EtOAc (50 mL). After 1 h precipitated Bu_4NBr (0.48 g, 65% recovered) was removed by filtration and the solvent evaporated, followed by purification by column chromatography on silica affording 4-phenyl-1,3-dioxolan-2-one **5a**, as a colourless solid (conv: 85 % conv.).

Representative procedure for the ring expansion addition reaction using a stainless steel anode and magnesium cathode under catalyst free conditions (Table 3): Styrene oxide **4a** (0.24 g, 2.0 mmol) in acetonitrile (150 mL) was electrolysed at constant current: 60 mA with constant stirring for 7 h in a single compartment cell containing a stainless steel cathode and magnesium anode, in the presence of supporting electrolyte: Bu_4NBr (1.28 g, 4 mmol) and CO_2 (flow rate: 471 mL min^{-1}), followed by heating at 50°C for 12 h. On completion the reaction mixture was filtered and filtrate was evaporated to dryness followed by addition of EtOAc (50 mL). After 1h precipitated Bu_4NBr (~70% recovered) was removed by filtration and the solvent evaporated, affording 4-phenyl-1,3-dioxolan-2-one **5a**, as a crude amber oil (conv: 75%).

General Procedure for the ring expansion addition reaction using a copper anode and magnesium cathode under catalyst free conditions (Table 4): Representative procedure

for the synthesis of phenyl ethylene carbonate **5a**: Styrene oxide **4a** (0.12 g, 1.0 mmol) and CO₂ (balloon) in acetonitrile (150 mL) were electrolysed (constant current: 60mA) for 6h in a single compartment cell (Mg anode and Copper(0) cathode) containing Bu₄NBr (0.32 g, 1.0 mmol) as supporting electrolyte at 50°C. On completion the reaction mixture was washed with aqueous 0.1 M HCl (50 mL) followed by extraction with Et₂O (3 x 35 mL). The combined organic extracts were then dried over MgSO₄ and evaporated under reduced pressure to afford a amber oil, which was suspended in EtOAc (100 mL). After 1 h the precipitated Bu₄NBr (0.30 g, 95%) was removed by filtration and the solvent evaporated under reduced pressure to afford an amber oil. This crude material was purified by column chromatography on silica gel eluting with ethyl acetate:light petroleum. Colourless solid (0.157 g, 96%).

Data for the cyclic carbonates **5a-5l**

4-Phenyl-1,3-dioxolan-2-one (styrene carbonate) 5a: Colourless solid; mp 49-51 °C; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1160 (C-O), 1756 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 3.45 (1H, dd, *J* = 7.93, *J* = 7.93), 4.80 (1H, dd, *J* = 8.49, *J* = 8.33), 5.68 (1H, dd, *J* = 7.99, *J* = 7.99), 7.35 – 7.45 (5H, m); ¹³C NMR (400MHz, CDCl₃) δ : 71.2, 78.00, 125.9, 129.3, 129.8, 135.8, 154.8.

4-Butyl-1,3-dioxolan-2-one (1-hexene carbonate) 5b: Colourless oil; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1171 (C-O), 1770 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 0.93 (3H, t, *J* = 7.36, *J* = 7.38), 1.34 – 1.49 (2H, m), 1.65 – 1.74 (2H, m), 1.78 – 1.87 (2H, m), 4.07 (1H, dd, *J* = 7.2, *J* = 7.2), 4.53 (1H, dd, *J* = 7.98, *J* = 8.26), 4.69-4.72(1H, m); ¹³C NMR (400MHz, CDCl₃) δ : 13.8, 22.8, 26.5, 29.7, 33.6, 69.4, 155.1.

4-(4-Chlorophenyl)-1,3-dioxolan-2-one (4-chlorostyrene carbonate) 5c: Colourless solid; mp 67-69 °C; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1165 (C-O), 1761 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 4.31 (1H, dd, *J* = 7.85, *J* = 7.89), 4.80 (1H, dd, *J* = 8.43, *J* = 8.43), 5.66 (1H, dd, *J* = 7.96, *J* = 7.96), 7.27 – 7.32 (2H, m), 7.42 – 7.44 (2H, m); ¹³C NMR (400MHz, CDCl₃) δ : 71.0, 77.2, 127.3, 129.5, 134.3, 135.8, 154.5.

4-(4-Fluorophenyl)-1,3-dioxolan-2-one (4-fluorostyrene carbonate) 5d: Colourless solid; mp 62-64 °C; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1167 (C-O), 1763 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 4.33 (1H, dd, *J* = 7.93, *J* = 8.75), 4.80 (1H, dd, *J* = 8.21, *J* = 8.59), 5.66 (1H, dd, *J* = 8.02, *J* = 8.02), 7.11 – 7.17 (2H, m), 7.34 – 7.39 (2H, m); ¹³C NMR (400MHz, CDCl₃) δ : 71.1, 76.7, 77.4, 116.0, 127.4, 131.5, 154.6, 162.2, 164.6.

4-Methyl-1,3-dioxolan-2-one (propylene carbonate) 5e: Colourless oil; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1204 (C-O), 1779 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 1.49 (3H, d, *J* = 6.27), 4.04 (1H, dd, *J* = 7.27, *J* = 7.27), 4.57 (1H, dd, *J* = 7.71, *J* = 7.81), 4.83 – 4.90 (1H, m); ¹³C NMR (400MHz, CDCl₃) δ : 19.4, 70.7, 73.6, 155.1.

4-Hexadecyl-1,3-dioxolan-2-one (1-octadecene carbonate) 5f: Colourless solid; mp 45-47 °C; ν_{\max} (film)/cm⁻¹ 1170 (C-O), 1774 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 0.88 (3H, t, *J* = 7.06, *J* = 6.97), 1.21-1.48 (26H, m), 1.63 - 1.72 (2H, m), 1.77 - 1.86 (2H, m), 1.63 - 1.72 (2H, m), 4.07 (1H, dd, *J* = 7.43, *J* = 7.37), 4.52 (1H, dd, *J* = 8.07, *J* = 8.15), 4.69 (1H, m); ¹³C NMR (400MHz, CDCl₃) δ : 14.1, 22.7, 24.4, 29.2, 29.4, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 31.9, 33.9, 69.4, 155.1.

4-(Allyloxymethyl)-1,3-dioxolan-2-one 5g: Colourless oil; ν_{\max} (film)/cm⁻¹ 1179 (C-O), 1646 (C=C), 1792 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 3.60 – 3.73 (2H, m), 4.00 – 4.08 (2H, m), 4.39 – 4.44 (1H, m), 4.50 – 4.57 (1H, m), 4.81 – 4.87

(1H, m), 5.21 – 5.31 (2H, m) 5.83 – 5.94 (1H, m); ¹³C NMR (400MHz, CDCl₃) δ : 66.3, 68.9, 72.5, 75.1, 117.9, 133.7, 155.1.

4-(4-Methylphenyl)-1,3-dioxolan-2-one (4-methylstyrene carbonate) 5h: Colourless solid; mp 40-41 °C; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1165 (C-O), 1460 (C=C), 1737 (C=O); ¹H NMR (400 MHz, CDCl₃, Me₄Si) 2.35 (3H, s), 4.34 (1H, dd, *J* 8.18), 4.77 (1H, dd, *J* 8.56), 5.64 (1H, dd, *J* 8.06), 7.23-7.28 (4H, m); ¹³C (100 MHz, CDCl₃, Me₄Si) 21.3, 71.2, 76.9, 78.1, 126.0, 129.9, 132.7, 139.9.

4-(4-Methoxyphenyl)-1,3-dioxolan-2-one (4-methoxystyrene carbonate) 5i: Colourless solid; mp 42-44 °C; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1072 (C-O), 1812 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 3.83 (3H, s), 4.35 (1H, dd, *J* = 8.14, *J* = 8.17), 4.75 (1H, dd, *J* = 8.17, *J* = 8.17), 5.62 (1H, dd, *J* = 8.05, *J* = 8.11), 6.94 – 6.97 (2H, dd, m), 7.26-7.32 (2H, m). ¹³C NMR (400MHz, CDCl₃) δ : 55.4, 71.1, 78.1, 114.6, 127.6, 154.9, 160.8.

4-Phenoxymethyl-[1,3]-dioxolan-2-one 5j: Colourless solid; mp 103-105 °C; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1166 (C-O), 1783 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 4.14 – 4.26 (2H, m), 4.52 – 4.64 (2H, m), 5.00 – 5.06 (1H, m), 6.90 – 6.92 (2H, m), 7.00 – 7.04 (1H, m), 7.26 – 7.33 (2H, m); ¹³C NMR (400MHz, CDCl₃) δ : 66.3, 66.9, 74.1, 114.6, 122.0, 129.7, 154.6, 157.7

4-(Hydroxymethyl)-1,3-dioxolan-2-one 5k: Colourless oil; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1180 (C-O), 1782 (C=O), 3411 (O-H); ¹H NMR (400MHz, CDCl₃) δ : 2.89 (1H, s), 3.71 (1H, dd, *J* = 3.49, *J* = 3.41), 3.99 (1H, dd, *J* = 2.97, *J* = 2.97), 4.50-4.56 (2H, m), 4.97-4.84 (1H, m); ¹³C NMR (400MHz, CDCl₃) δ : 61.7, 65.8, 76.7, 155.5.

4-(Chloromethyl)-1,3-dioxolan-2-one 5l: Colourless oil; ν_{\max} (CH₂Cl₂)/cm⁻¹ 1078 (C-Cl), 1193 (C-O), 1643 (C=O); ¹H NMR (400MHz, CDCl₃) δ : 3.72 – 3.81 (2H, m), 4.42 (1H, dd, *J* = 5.77, *J* = 5.68), 4.60 (1H, dd, *J* = 8.30, *J* = 8.79), 4.94 – 5.00 (1H, m); ¹³C NMR (400MHz, CDCl₃) δ : 43.6, 66.0, 74.2, 154.1.

Large Scale Synthesis of 4-Methyl-1,3-dioxolan-2-one (propylene carbonate) 5g: Propylene oxide **5g** (10 g, 170 mmol) in acetonitrile (100 mL) was added to a solution of supporting electrolyte: Bu₄NBr (54.8g, 170 mmol) in acetonitrile (500 mL), the resulting solution was flushed with CO₂ (flow rate: 1000 mL min⁻¹) for 1 h, followed by heated electrolysis at 50 °C and constant current: 60 mA with constant stirring for 10 h under CO₂ balloon, in a single compartment cell containing a magnesium anode and copper cathode. On completion the reaction mixture was evaporated to dryness affording 4-methyl-1,3-dioxolan-2-one **5g** as a crude amber solid (conv: 100%). The solid was partitioned between aqueous 0.1 M HCl (50 mL) and Et₂O and extracted. The combined organic extracts were then dried over MgSO₄ and evaporated under reduced pressure to afford a amber oil, which was suspended in EtOAc (100 mL). After 1 h the precipitated Bu₄NBr was removed by filtration and the solvent evaporated under reduced pressure to afford an amber oil. This crude material was purified by column chromatography on silica gel eluting with ethyl acetate:light petroleum. To afford the product as a colourless oil.

Acknowledgements

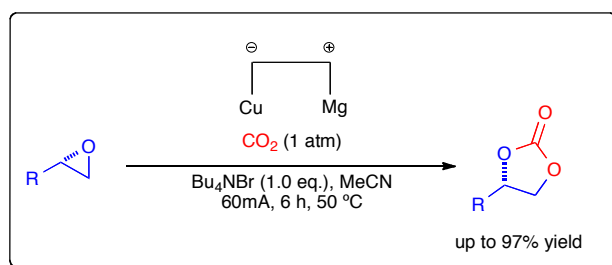
B.R.B. and K.G.U.W. would like to thank Research Councils UK for RCUK fellowships and Loughborough University for funding a PhD studentship (to A.P.P.).

Notes and references

Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

1. R. J. Pearson et al., Proceedings of the IEEE, 2012, 100, 440.
2. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 2007, B. Metz, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer (eds), Cambridge University Press, United Kingdom and New York, NY, USA.
3. P. Styring, D. Jansen, H. de Coninck, K. Armstrong, Carbon Capture and Utilisation in the green economy, Report No. 501, July 2011, The Centre For Low Carbon Futures, ISBN 978-0-9572588-0-8.
4. M. North, R. Pasquale, C. Young, *Green Chem.*, 2010, **12**, 1514.
5. For some recent reviews and articles on high pressure and/or temperature approaches to cyclic carbonates see: (a) C. Maeda, Y. Miyazaki and T. Ema, *Catal. Sci. Technol.*, 2014, **4**, 1482; (b) N. Kielland, C. J. Whiteoak and A. W. Kleij, *Adv. Synth. Catal.*, 2013, **355**, 2115; (c) I. Omae, *Coord. Chem. Rev.*, 2012, **256**, 1384; (d) D. J. Darensbourg and S. J. Wilson, *Green Chem.*, 2012, **14**, 2665–2671; (e) S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460; (f) T. Sakakura, K. Kohno, *Chem. Commun.* 2009, 1312; (g) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388.
6. (a) T. Ema, Y. Miyazaki, T. Taniguchi and J. Takada, *Green Chem.*, 2013, **15**, 2485; (b) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, *Chem. Commun.*, 2012, **48**, 4489; (c) Z.-Z. Yang, Y.-N. Zhao, L.-N. He, J. Gao and Z.-S. Yin, *Green Chem.*, 2012, **14**, 519; (d) D. Bai, Q. Wang, Y. Song, B. Li and H. Jing, *Catal. Commun.*, 2011, **12**, 684; (e) F. Ahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork and A. R. Khosropour, *Inorg. Chem. Commun.*, 2011, **14**, 1489; (f) S. Liang, H. Liu, T. Jiang, J. Song, G. Yang and B. Han, *Chem. Commun.*, 2011, **47**, 2131; (g) L. Han, H.-J. Choi, S.-J. Choi, B. Liu and D.-W. Park, *Green Chem.*, 2011, **13**, 1023; (h) H. Zhou, Y.-M. Wang, W.-Z. Zhang, J.-P. Qu and X.-B. Lu, *Green Chem.*, 2011, **13**, 644; (i) Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema and T. Sakai, *Org. Lett.*, 2010, **12**, 5728; (j) M. Ulusoy, E. Çetinkaya and B. Çetinkaya, *Appl. Organomet. Chem.*, 2009, **23**, 68; (k) J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang and B. Han, *Green Chem.*, 2009, **11**, 1031.
7. (a) M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676; (b) A. Buchard, F. Jutz, M. R. Kember, A. J. White, H. S. Rzepa, and C. K. Williams, *Macromolecules*, 2012, **45**, 6781; (c) M. R. Kember, F. Jutz, A. Buchard, A. J. P. White, and C. K. Williams, *Chem. Sci.*, 2012, **3**, 1245; (d) J. G. Kim, C. D. Cowman, A. M. LaPointe, U. Wiesner and G. W. Coates, *Macromolecules*, 2011, **44**, 1110; (e) F. Jutz, A. Buchard, M. R. Kember, S. B. Fredriksen, and C. K. Williams, *J. Am. Chem. Soc.*, 2011, **133**, 17395; (f) G.-P. Wu, S.-H. Wei, W.-M. Ren, X.-B. Lu, T.-Q. Xu and D. J. Darensbourg, *J. Am. Chem. Soc.*, 2011, **133**, 15191; (g) H. Li and Y. Niu, *Appl. Organomet. Chem.*, 2011, **25**, 424; (h) K. Nakano, K. Kobayashi and K. Nozaki, *J. Am. Chem. Soc.*, 2011, **133**, 10720; (i) A. Buchard, M. R. Kember, K. G. Sandeman, and C. K. Williams, *Chem. Commun.* 2010, **47**, 212; (j) M. R. Kember, A. Buchard, and C. K. Williams, *Chem. Commun.* 2010, **47**, 141; (k) K. Nakano, S. Hashimoto and K. Nozaki, *Chem. Sci.*, 2010, **1**, 369; (l) D. J. Darensbourg, *Inorg. Chem.*, 2010, **49**, 10765; (m) J. Yoo, S. J. Na, H. C. Park, A. Cyriac, B. Y. Lee, *Dalton Trans.* 2010, **39**, 2622; (n) S. I. Vagin, R. Reichardt, S. Klaus and B. Rieger, *J. Am. Chem. Soc.*, 2010, **132**, 14367; (o) M. R. Kember, A. J. P. White, and C. K. Williams, *Inorg. Chem.*, 2009, **48**, 9535; (p) M. R. Kember, P. D. Knight, P. T. R. Reung, and C. K. Williams, *Angew. Chem. Int. Ed.*, 2009, **48**, 931; (q) K. Nakano, M. Nakamura and K. Nozaki, *Macromolecules*, 2009, **42**, 6972.
8. (a) M. North, B. Wang, and C. Young, *Energy Environ. Sci.*, 2011, **4**, 4163; (b) M. North and C. Young, *Catal. Sci. Technol.*, 2011, **1**, 93; (c) W. Clegg, R. W. Harrington, M. North, and P. Villuendas, *J. Org. Chem.*, 2010, **75**, 6201; (d) W. Clegg, R. W. Harrington, M. North, F. Pizzato, and P. Villuendas, *Tetrahedron: Asymmetry*, 2010, **21**, 1262; (e) W. Clegg, R. W. Harrington, M. North, and R. Pasquale, *Chem. Eur. J.*, 2010, **16**, 6828; (f) I. S. Metcalfe, M. North, R. Pasquale, and A. Thursfield, *Energy Environ. Sci.*, 2010, **3**, 212; (g) M. North, P. Villuendas, and C. Young, *Chem. Eur. J.*, 2009, **15**, 11454; (h) M. North, *Angew. Chem. Int. Ed.*, 2009, **48**, 4104; (i) M. North and R. Pasquale, *Angew. Chem. Int. Ed.*, 2009, **48**, 2946; (j) J. Meléndez, M. North, and P. Villuendas, *Chem. Commun.*, 2009, 2577; (k) J. Meléndez, M. North, and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, **2007**, 3323.
9. (a) F. Castro-Gómez, G. Salassa, A. W. Kleij, and C. Bo, *Chem. Euro. J.*, 2013, **19**, 6289; (b) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1288; (c) C. J. Whiteoak and A. W. Kleij, *Synlett*, 2013, 1748; (d) C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz, and A. W. Kleij, *Adv. Synth. Catal.*, 2012, **354**, 469; (e) A. Coletti, C. J. Whiteoak, V. Conte, and A. W. Kleij, *ChemCatChem*, 2012, **4**, 1190.
10. (a) P. Tascetta, E. Duñach, *J. Chem. Soc., Chem. Commun.*, 1995, 43-44; (b) E. Duñach, P. Tascetta, M. Weidmann, E. Dinjus, *Appl. Organometal. Chem.*, 2001, **15**, 141.
11. (a) B. R. Buckley, A. P. Patel, K. G. U. Wijayantha *Chem. Commun.* **2011**, 47, 11888; (b) B. R. Buckley, Y. Chan, N. Dreyfus, C. Elliott, F. Marken, P. C. B. Page, *Green Chem.* **2012**, **14**, 2221; (c) P. C. B. Page, F. Marken, C. Williamson, Y. Chan, B. R. Buckley, D. Bethell, *Adv. Synth. Catal.*, **2008**, 350, 1149.
12. (a) A. A. Tahir, K. G. U. Wijayantha, *J. Photochem. Photobiol. A*, 2010, **216**, 119; (b) A. A. Tahir, K. G. U. Wijayantha, S. Saremi-Yarahmadi, M. Mazhar, V. McKee, *Chem. Mate.* 2009, **21**, 3763; (c) K. Tennakone, G. R. R. A. Kumara, K. G. U. Wijayantha, I. R. M. Kottegoda, V. P. S.Perera, M. L. P. Aponsu, *J. Photochem. Photobiol. A*, 1997, **108**, 175.
13. E. Dunach and J. Perichon, *J. Organomet. Chem.*, 1988, **352**, 239.
14. (a) Getsis, A. V. Mudring, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2130; (b) Getsis, A. V. Mudring, *Z. Anorg. Allg. Chem.*, 2008, **634**, 619.
15. E. Styczen, W. K. Jozwiak, M. Gazda, D. Wyrzykowski, *J. Therm. Anal. Cal.*, 2008, **91**, 979.

Graphical Abstract



Abstract: Interest in the use of CO_2 as a feedstock for preparation of value-added compounds has dramatically increased over the past decade. We herein investigate the insertion of atmospheric pressure carbon dioxide under electrocatalytic conditions into epoxides. The initial investigations involved the use of either a nickel or copper based catalyst, however, upon further optimisation and careful selection of electrode materials we found that these catalysts were not required for efficient carbon dioxide insertion to occur.