A New Entry to Sonochemical/Efficient Agitation Switching: Alkene Formation through Epoxide Deoxygenation

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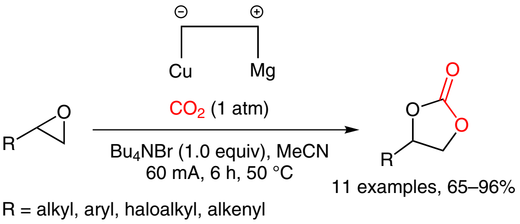
Abstract: ‘Sonochemical switching’ whereby the pathway of a reaction is changed under sonication conditions was first reported by Ando, and in fact could just be the consequence of efficient agitation. We herein report a new addition to this switching phenomenon in which epoxides are converted to cyclic carbonates by addition of CO_2 under standard heating/electrolysis conditions but are ‘switched’ to alkenes under deoxygenating sonochemical conditions.

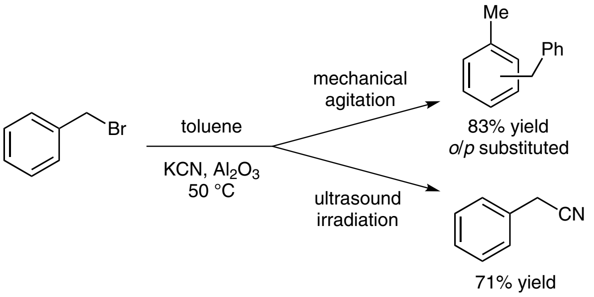
Key words: sonochemical, alkene, epoxide, cyclic carbonate, carbon dioxide

Carbon dioxide utilisation (CDU) technologies have recently gained increased interest as they offer an attractive alternative to the well-established carbon dioxide storage (CCS) processes.[1] This is due to the fact that carbon dioxide is abundant, cheap and nontoxic and waste carbon dioxide under CDU protocols can be converted into useful chemicals or fuels. Carbon dioxide 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. We have recently embarked on a programme of research directed at CDU and have recently reported our initial efforts in this area where we employed an electrosynthetic system which was easy to set up, cheap, reliable, required no expensive catalysts, ran under atmospheric CO_2 pressures and at ambient temperatures (see Scheme 1, this type of process could be designed to be cost neutral in terms of energy consumption if combined with a suitable renewable energy source e.g. solar).[2]

Sonochemistry, a technique, whereby chemistry is carried out in an acoustically cavitating field has been known for many years and has been described as a useful tool for enhancing reaction rates in certain organic reactions.[3] The phenomenon of ‘sonochemical switching’ whereby the pathway of reaction is changed under sonication conditions was first reported by Ando (Scheme 2).[4] Debate remains as to whether the ‘sonochemical effect’ actually exists and is in fact just the effect of very efficient mixing. Reisse and co-workers have reported an extensive study in this area and found that through the use of efficient stirring (using a homogeniser) the pathway of the originally proposed sonochemical switch reaction reported by Ando can be switched using this technique thus pointing towards the fact that sonochemistry has no ‘special effect’.[5]

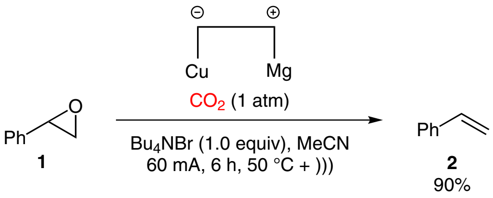


Scheme 1 Electrosynthetic CO_2 insertion to form cyclic carbonates



Scheme 2 Ando’s original sonochemical switching reactions

During the course of our optimisation studies for the electrochemical incorporation of carbon dioxide into epoxides to afford cyclic carbonates we chose to carry out the reaction using sonication with a standard cleaning bath. The reactions were run in a single compartment cell, with acetonitrile as solvent, tetrabutylammonium bromide as electrolyte, with a copper cathode, magnesium anode, and 60 mA current in a 50–60 Hz sonic bath. We were surprised to find that for our test substrate styrene oxide, on analysis of the crude reaction mixture, none of the desired cyclic carbonate was observed, instead we obtained a >99% conversion (90% isolated yield) to the parent alkene with no trace of the cyclic carbonate (Scheme 3).



Scheme 3 Sonochemical deoxygenation using electrosynthesis

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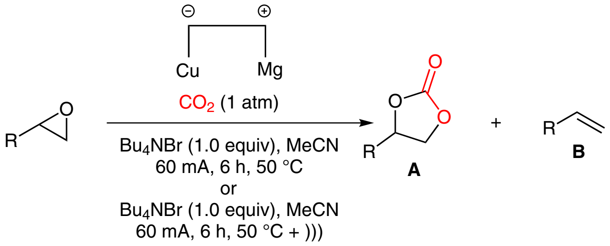
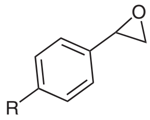
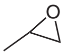
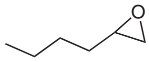
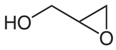
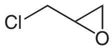
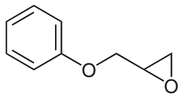
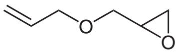
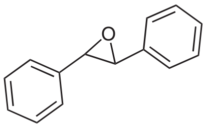
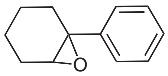
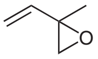
Table 1 A Comparison of Conventional versus Ultrasonic Reaction Conditions[11,12]



Entry	Epoxide	Ratio of products under standard heating conditions (**A**:**B**)[a,b,]2	Ratio of products under sonochemical reaction conditions (**A**:**B**)[b,c]	Conversion (%)[d]
1	 R = H	>99:1	1:>99	>99 (90)
2	R = Br	>99:1	62:38	67
3	R = Cl	>99:1	10:90	72
4	R = F	>99:1	93:7	95
5	R = Me	>99:1	>99:1	>99
6	R = OMe	>99:1	42:58	>99
7		>99:1	>99:1	>99
8		>99:1	>99:1	>99
9		>99:1	>99:1	>99
10		>99:1	>99:1	>99
11		>99:1	>99:1	>99
12		>99:1	>99:1	>99
13		–	–	<5
14		–	–	<5
15		–	–	<5

[a] General conditions for the standard reaction: CO_2 (1 atm), Cu cathode, Mg anode, Bu_4NBr (1.0 equiv), MeCN, single compartment cell, 60 mA, 6 h, 50 °C.

[b] Ratio evaluated from the ^1H NMR spectrum by integration of alkene vs. cyclic carbonate peaks.

[c] General conditions for the sonochemical reaction: CO_2 (1 atm), Cu cathode, Mg anode, Bu_4NBr (1.0 equiv), MeCN, single compartment cell, 60 mA, 50–60 Hz sonication, 6 h, 50 °C.

[d] Conversion evaluated from the ^1H NMR spectrum by integration of epoxide vs. cyclic carbonate and alkene peaks, numbers in parenthesis refer to isolated yield after chromatography.

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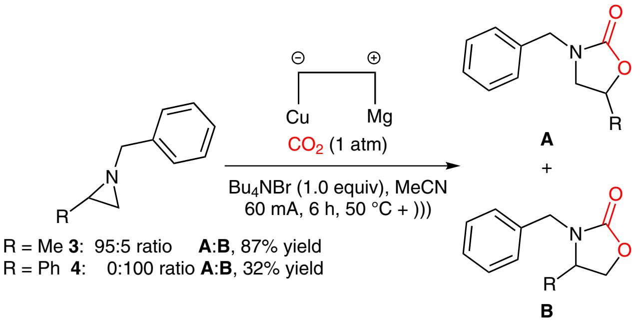
The deoxygenation of epoxides is a challenging area of research, since the successful reduction presents the epoxide unit as a viable protecting group for alkenes.[6,7] Several research groups have developed processes for epoxide deoxygenation, often requiring harsh reaction conditions or expensive gold catalysts.[8,9] Recently Huang and co-workers have reported the electrochemically supported deoxygenation of epoxides into alkenes in aqueous solution and this prompted us to investigate our system further.[10]

Intrigued by our initial findings we performed a series of control reactions in which we found that it was essential to have a carbon dioxide atmosphere (under argon no reaction was observed), in the absence of current no reaction occurred and without heating we still observed alkene formation (67% conversion by ^{1}H NMR).

With our optimised conditions in hand we then chose to screen a range of substrates to see what effect substituents would make to the deoxygenation reaction, with mixed results (Table 1). As a general rule under our conditions aliphatic epoxides produced the cyclic carbonate in excellent conversion but di-, and trisubstituted epoxides remained untouched. Styrene oxide remains the only substrate to fully convert to the alkene with no trace of the corresponding cyclic carbonate and disappointingly there appears to be no correlation with the electron-withdrawing or electron-donating ability of the substituents present on the aromatic substrates. However, this work does represent the first report of sonochemical switching for this type of process. We also found that aziridine substrates were compatible with our carbon dioxide incorporation process but they too did not undergo formation of the parent alkene under sonochemical conditions (Scheme 4).[13]



Scheme 4 Formation of cyclic carbamates; no denitrogenation is observed under sonochemical conditions

In conclusion we have identified a new entry into the sonochemical switching process that works well for styrene oxide but further investigations are required in order to develop this into a practical approach to alkene group protection as epoxides. We are currently investigating the proposed mechanism, under standard heating and stirring conditions. We believe that an ionic mechanism similar to that reported by North and co-workers[14] is in operation as retention of stereochemical information in the final cyclic carbonate product is observed when employing enantiomerically enriched epoxides. We believe that the reaction utilising ultrasonic irradiation promotes a single-electron-transfer (SET) process that could be similar to that reported by Huang and co-workers, presumably aromatic systems tend to undergo the SET process due to stabilisation of the benzyl radical, which cannot be achieved when employing aliphatic epoxides. However, under our conditions we do not observe alkene formation in the absence of carbon dioxide, and we also do not observe conversion of cyclic carbonate to alkenes under the reaction conditions.[15]

We are also investigating the factors that influence the ratio of products in our laboratory and full results will be published in due course.

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(10) **Representative Procedure for the Standard Synthesis of Phenyl Ethylene Carbonate (Ref. 2)**: Styrene oxide (**1**; 0.12 g, 1.0 mmol) and CO_2 (balloon) in MeCN (150 mL) were electrolysed (constant current: 60 mA) for 6 h in a

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single compartment cell [Mg anode and copper(0) cathode] containing Bu_4NBr (0.32 g, 1.0 mmol) as supporting electrolyte at 50 °C. On completion the reaction mixture was washed with aq 0.1 M HCl (50 mL) followed by extraction with Et_2O (3 × 35 mL). The combined organic extracts were then dried over $MgSO_4$ and evaporated under reduced pressure to afford an amber oil, which was suspended in EtOAc (100 mL). After 1 h the precipitated Bu_4NBr (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 EtOAc–light petroleum to yield a colourless solid (conversion: 99%; yield: 0.12 g, 96%); mp 49–51 °C. IR (CH_2Cl_2): 1167 (C–O), 1789 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3/Me_4Si$): $\delta = 4.35$ (dd, $J = 7.9, 8.4$ Hz, 1 H), 4.80 (dd, $J = 8.5$ Hz, 1 H), 5.68 (dd, $J = 7.99$ Hz, 1 H), 7.35–7.45 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3/Me_4Si$): $\delta = 71.2$, 78.0, 125.9, 129.3, 129.8, 135.8, 154.8.

(11) **Representative Procedure for the Sonochemical Synthesis of Styrene (2)**: Styrene oxide (**1**; 0.12 g, 1.0 mmol) and CO_2 (balloon) in MeCN (150 mL) were electrolysed (constant current: 60mA) for 6 h in a single compartment cell [Mg anode and copper(0) cathode] containing Bu_4NBr (0.32 g, 1.0 mmol) as supporting electrolyte. The reaction vessel was submerged in a sonication bath at 50–60 Hz. On completion the reaction mixture was washed with aq 0.1 M HCl (50 mL) followed by extraction with Et_2O (3 × 35 mL). The combined organic extracts were then dried over $MgSO_4$ and evaporated under reduced pressure to afford an amber oil, which was suspended in EtOAc (100 mL). After 1 h the precipitated Bu_4NBr (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 EtOAc–light petroleum to yield a colourless liquid (0.094 g, 90%). IR (CH_2Cl_2): 1442 (C=C), 1610 (C=C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3/Me_4Si$): $\delta = 5.25$ (dd, $J = 0.8, 11.0$ Hz, 1 H), 5.75 (dd, $J = 1.2, 17.5$ Hz, 1 H), 6.72 (dd, $J = 11.0, 17.5$ Hz, 1 H), 7.24–7.41 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3/Me_4Si$): $\delta = 113.7$, 126.2, 127.8, 128.5, 137.0, 137.7.

(12) **General Procedure for Cyclic Carbamate Formation**: The aziridine (2.0 mmol) in MeCN (20 mL) was added to a solution of supporting electrolyte Bu_4NBr (0.64 g, 2.0 mmol) in MeCN (130 mL), and the resulting solution was flushed with CO_2 for 1 h, followed by heated electrolysis at 50 ºC with constant stirring at a constant current of 60 mA for 6 h under a CO_2 balloon, in a single compartment cell containing a magnesium anode and copper cathode. On completion the reaction mixture was filtered to remove the precipitated $MgCO_3$ and evaporated to dryness followed by addition of EtOAc (50 mL). After 1 h the precipitated Bu_4NBr (ca. 70% recovered) was removed by filtration and the solvent evaporated under reduced pressure. The crude carbamate was then analysed by ^1H NMR spectroscopy to determine the regioselectivity and then purified by column chromatography on silica gel eluting with EtOAc–light petroleum.

(13) **3-Benzyl-4-methyloxazolidin-2-one (3)**: colourless oil, mixture of regioisomers observed in a 95:5 ratio in favour of the title compound (conversion: 98%; yield: 0.34 g, 87%). IR (CH_2Cl_2): 1181 (C–N), 1255 (C–O), 1416 (C=C), 1721 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3/Me_4Si$): $\delta = 1.21$ (d, $J = 6.0$ Hz, 3 H), 2.97 (dd, $J = 6.8, 8.6$ Hz, 1 H), 3.50 (dd, $J = 8.4$ Hz, 1 H), 4.37–4.46 (m, 2 H), 4.57–4.67 (m, 1 H), 7.26–7.33 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3/Me_4Si$): $\delta = 18.3$, 46.7, 50.8, 64.7, 127.8, 127.9, 128.3, 128.8, 158.3.
3-Benzyl-5-phenyloxazolidin-2-one (4): colourless solid, single regioisomer observed (conversion: 51%; yield: 0.162 g, 32%); mp 61–63 °C. IR (CH_2Cl_2): 1157 (C–N), 1250 (C–O), 1454 (C=C), 1752 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3/Me_4Si$): $\delta = 3.30$ (dd, $J = 7.5, 8.8$ Hz, 1 H), 3.75 (dd, $J = 8.8$ Hz, 1 H), 4.41–4.56 (m, 2 H), 5.45 (dd, $J = 8.3$ Hz, 1 H), 7.21–7.40 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3/Me_4Si$): $\delta = 45.9$, 48.5, 74.6, 125.5, 126.3, 128.1, 128.2, 128.8, 128.9, 135.7, 138.6, 158.0.

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(15) This was confirmed by subjecting phenyl ethylene carbonate instead of styrene oxide to the reaction conditions reported in reference 11. Only phenyl ethylene carbonate and supporting electrolyte was observed in the crude reaction ^1H NMR spectrum.

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