Magnesium oxide-catalysed reaction of carbon dioxide with an epoxide with retention of stereochemistry

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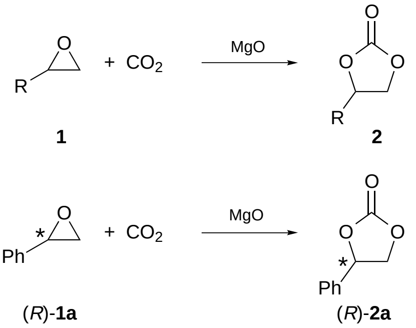
Magnesium oxide is an efficient catalyst for the cycloaddition of carbon dioxide to epoxides under mild conditions; the reaction of carbon dioxide with (*R*)-styrene oxide in the presence of magnesium oxide gives (*R*)-phenyl carbonate in 97% ee with retention of stereochemistry.

Carbon dioxide fixation has recently received much attention owing to environmental concerns and the reaction of carbon dioxide with epoxides has been of interest as a useful catalytic fixation method.[1]

The synthesis of organic compounds using metal oxides as catalysts is also of considerable current interest. For example, magnesium oxide possesses both acid and base surface sites, and many of the catalytic applications of magnesium oxide are based on the principle of acid–base catalysis. Several reports on the adsorption of carbon dioxide on the surface of magnesium oxide prompted us to develop a new method for its fixation using the metal oxide,[2] although magnesium oxide has not been used as a catalyst for the conversion of carbon dioxide. We have now found that the reaction of carbon dioxide with epoxide is promoted by the addition of magnesium oxide as a catalyst under atmospheric pressure. Here we present a novel method for the fixation of carbon dioxide by metal oxide together with the stereochemistry of the carboxylation of epoxide with carbon dioxide in the presence of magnesium oxide.

Preliminary carboxylation studies were carried out using styrene oxide **1a** as a model compound (Scheme 1). A typical experimental procedure for the carboxylation of epoxide with carbon dioxide is as follows. Magnesium oxide (0.4 g) was added to a solution of epoxide **1a** (10 mmol) in *N*,*N*-dimethylformamide (DMF, 3 ml) in a pressure bottle under a CO_2 atmosphere.† The mixture was heated at 135 °C for 12 h and then filtered. The magnesium oxide was washed with acetone and the filtrates were combined. The solvents were removed under reduced pressure and the crude product was chromatographed on silica gel to give the corresponding cyclic carbonate **2a**. The product was analysed by NMR, IR and MS spectroscopy and microanalysis and the results are shown in Table 1.



Scheme 1

The reaction of **1a** with carbon dioxide in the presence of uncalcined magnesium oxide led to the formation of phenyl carbonate **2a** in 47% yield (Table 1, entry 1). Magnesium oxide was found to be effective in the carboxylation of epoxide with carbon dioxide. An analogous result was obtained by using the calcined magnesium oxide at 300 °C (entry 2). When calcined magnesium oxide at 400 °C was used for the reaction, the yield of the carbonate **2a** was somewhat increased (entry 3). The carbon dioxide incorporation into the epoxide ring was further examined for a few epoxides (Table 1, entries 4 and 5). The aliphatic terminal epoxides afforded the corresponding cyclic carbonates in good yields. This is, to the best of our knowledge, the first example of the activation of carbon dioxide using magnesium oxide.

The yield of the carbonate **2a** in the reaction of **1a** with carbon dioxide was increased by increasing amount of magnesium oxide (Fig. 1).‡ On the other hand, the carbon dioxide pressure had no effect on the yield of the carbonate **2a**, as shown in Fig. 2, although it has been reported that the epoxide–CO_2 reaction required a high pressure of carbon dioxide.[1]

Table 1 MgO catalysed carboxylation of epoxides **1** with CO_2[a]

Entry	Epoxide **1**	R	Calcination temp./°C[b]	Yield of **2** (%)
1	**a**	Ph	—[c]	47
2	**a**	Ph	300	49
3	**a**	Ph	400	60
4	**b**	Me	400	41
5	**c**	Et	400	72

[a] Reaction conditions: MgO (0.4 g), CO_2 pressure 20 kg cm^{-2}, epoxide (10 mmol), DMF (3 ml), 135 °C, 12 h. [b] MgO was calcined for 3 h. [c] Uncalcined MgO.

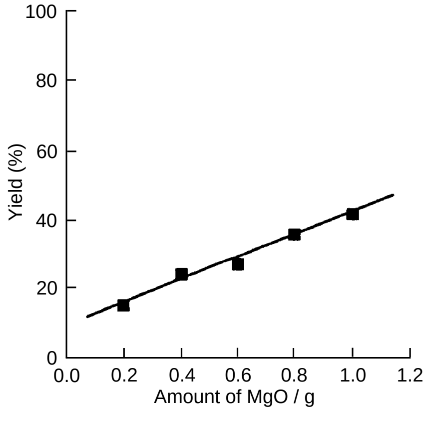


Fig. 1 Relationship between the yield of phenyl carbonate **2a** and the amount of MgO. The reaction was carried out with epoxide **1a** (5 mmol) in the presence of MgO in DMF (2 ml) under CO_2 (20 kg cm^{-2}) at 135 °C for 4 h.

Interestingly, magnesium oxide controlled the stereochemistry of the epoxide, *i.e.* treatment of a chiral epoxide, (*R*)-**1a**, with carbon dioxide in the presence of magnesium oxide gave (*R*)-(②)-phenyl carbonate, (*R*)-**2a**, in 63% chemical yield with 99% ee (Scheme 1).§ The absolute configuration of this compound was *R*, as deduced from (*R*)-(②)-1-phenylethane-1,2-diol which was obtained from the hydrolysis of (*R*)-**2a** with 1 M NaOH.¶ Thus the carboxylation proceeded with retention of the epoxide configuration. We thus propose the following mechanism (Scheme 2). Carbon dioxide and the epoxide are adsorbed on MgO to form the complex **3** and then the carboxylate anion of **3** attacks the β-carbon atom of the epoxide to generate the oxy anion of **4**, which subsequently attacks the carbonyl group of **4** to afford the cyclic carbonate **2**.

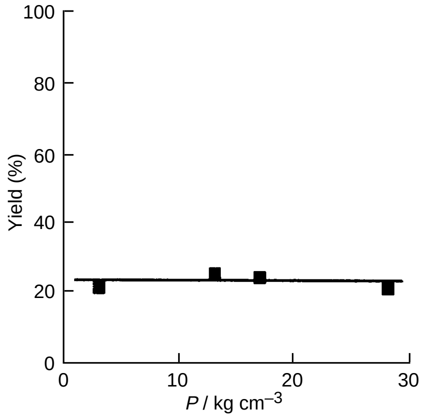
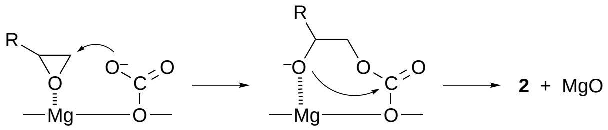


Fig. 2 Relationship between the yield of phenyl carbonate **2a** and the pressure of CO_2. The reaction was carried out with epoxide **1a** (5 mmol) in the presence of MgO (0.4 g) in DMF (2 ml) under CO_2 at 135 °C for 4 h.



Scheme 2

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Footnotes

† MgO was obtained from Wako Pure Chemical Industries Ltd. The surface area of MgO was 47.2 m^2 $g^{②1}$.

‡ The yield of carbonate **2a** in the absence of MgO was 8%.

§ The enantiomeric excess of (*R*)-(②)-phenyl carbonate was determined by HPLC using Daicel Chiralcel (eluent, hexane–propan-2-ol, 9 : 1) at 40 °C.

¶ Hydrolysis of (*R*)-**2a**, led to (*R*)-(②)-1-phenyl ethane-1,2-diol, $[\alpha]_D^{25}$ ②38.6 (*c* 2.4, EtOH) [lit.,[3] $[\alpha]_D^{25}$ ②39.7 (*c* 4.33, EtOH].

References

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