Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 2931–2934

TETRAHEDRON
LETTERS

Cycloaddition of CO_2 to epoxides over both homogeneous and silica-supported guanidine catalysts

Alessandro Barbarini,[a] Raimondo Maggi,[a] Alessandro Mazzacani,[a] Giovanni Mori,[b]
Giovanni Sartori[a,]* and Raffaella Sartorio[a]

[a]*Clean Synthetic Methodologies Group, Dipartimento di Chimica Organica e Industriale dell'Università, Parco Area delle Scienze 17/A, I-43100 Parma, Italy*

[b]*Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Parco Area delle Scienze 17/A, I-43100 Parma, Italy*

Received 20 December 2002; revised 11 February 2003; accepted 12 February 2003

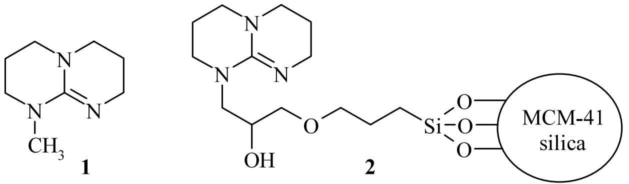
Abstract—The synthesis of cyclic carbonates by CO_2 insertion into epoxides catalysed by both homogeneous MTBD and TDB supported on MCM-41 mesoporous silica is reported. © 2003 Elsevier Science Ltd. All rights reserved.

The use of carbon dioxide in synthetic and industrial applications represents an important goal since the output of CO_2 from combustion into the atmosphere continues to raise and minimisation of its emission is desirable and can be achieved by direct fixation into the target compounds.[1] Thus, new strategies aimed at recovering and utilizing CO_2 have assumed increasing importance.

CO_2 is an inexpensive reagent, environmentally benign, non-flammable, ubiquitous and easily separable from reaction mixtures. However, due to the inert nature of CO_2, its activation and incorporation into organic substrates still remains a difficult target.

A particularly studied reaction involving CO_2 is the cycloaddition with epoxides to produce cyclic carbonates. These compounds show interesting applications as polar aprotic solvents, as precursors for polycarbonate materials and, in general, as intermediates in organic synthesis.[2] The reaction was performed by using different classes of catalysts including groups IVA, VA and VIA organometallic halides[3] and alkaline halides.[4] Aluminium and chromium porphyrinates and phthalocyaninates have also been utilised[5] as well as other transition metal complexes of nickel, palladium, chromium and copper.[6] Particular conditions to perform direct synthesis of polycarbonates by copolymerisation of CO_2 with epoxides have also been set up.[7] Less extensively studied was the use of ionic liquids as solvent catalysts[8] and heterogeneous catalysts.[9] Due to the great interest in this topic and in continuation of our studies on the preparation and use of organic catalysts supported on different polymeric materials, we present here a comparative study of the catalytic efficiency of guanidine MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene) **1** and its heterogeneous counterpart **2** (Fig. 1), obtained by covalently bonding TBD to MCM-41 silica, in the cycloaddition of CO_2 with epoxides to give cyclic carbonates.[10]

The special goals of this study were: (i) to collect information concerning the possibility of running the homogeneous reaction under catalytic conditions with maximum yield and selectivity; (ii) to compare the catalytic efficiency of the homogeneous and heterogeneous catalysts; (iii) to apply the optimised processes to the synthesis of a series of cyclic carbonates.



1
MTBD

2
MCM-41-TBD

Figure 1. Catalysts utilised in the study.

---

* Corresponding author. Tel.: +39 0521 905551; fax: +39 0521 905472; e-mail: sartori@unipr.it

0040-4039/03/$ - see front matter
doi:10.1016/S0040-4039(03)00424-6

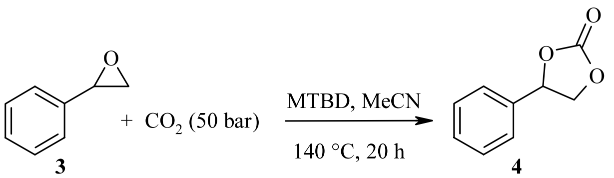
In a first series of experiments the cycloaddition of CO_2 (40 ml, 50 bar) to styrene oxide (26 mmol) in acetonitrile (5 ml) was studied as a function of the amount of catalyst MTBD under homogeneous conditions[11] in a small autoclave at 140°C (Scheme 1 and Fig. 2).

The yield of product **4** increases by increasing MTBD/**3** molar ratio and reaches a maximum value of 96% by using 4% mol of MTBD with respect to the reagent **3**.

The selectivity value is very high (>98%) at MTBD/**3** ratio values <0.04 and decreases together with yield by using larger amounts of the catalyst, due to the competitive isomerisation of styrene oxide **3** to acetophenone and phenylacetaldehyde.

The further goal was the heterogenisation of the organic catalyst by tethering TBD to the surface of a siliceous support through an easy methodology reported in the literature.[12] The mesoporous MCM-41 silica was utilised as inorganic support since the anchored active TBD molecules are expected to be more easily accessible in the mesoporous material than in an amorphous one.[13] The model reaction was successively performed by using the supported catalyst (MCM-41-TBD, loading 1.27 mmol/g) whose amount was determined on the basis of the loading value in order to have a supported-TBD/**3** ratio equal to 0.04.

The yield of product **4** in the model reaction was studied as a function of time (Fig. 3). As expected, production of **4** during the time with the supported catalyst MCM-41-TBD is lower than that obtained in the reaction carried out with the homogeneous counterpart, suggesting that the supported catalyst suffer from some diffusion resistance.



Scheme 1. Reaction between styrene oxide and carbon dioxide in the presence of MTBD.

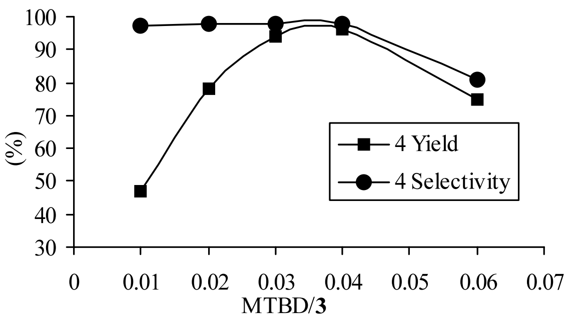


Figure 2. Yield (■) and selectivity (●) of product **4** as a function of time under MTBD catalysis.

However, the efficiency of MCM-41-TBD in the present reaction was shown by the possibility of recycling the catalyst for almost three further cycles (64, 61 and 63% yield, respectively) after filtration, washing with DMF and immediately reusing.[14]

The optimised conditions with both homogeneous (MTBD) and heterogeneous catalysts (MCM-41-TBD) were used for the preparation of some cyclic carbonates from the corresponding epoxides (Table 1).[15]

All terminal epoxides afforded the corresponding cyclic carbonates in good yield and excellent selectivity with both homogeneous and heterogeneous catalysts. As expected, being the average pore diameter of mesoporous silica 30 Å, the diffusion of reagents and products through the material is completely unrestricted and no remarkable steric limitations could be observed in the reaction of different epoxides with the supported catalyst. Lower yields have been observed with internal epoxides even if the selectivity was still good. However, it is important to stress that in both procedures the catalyst amount (4% molar ratio with respect to the epoxide) is crucial in order to avoid side reactions such as the epoxide isomerisation.

Concerning the mechanism, one can imagine that the presence on the solid catalyst of hydroxy groups such as the alcohol on the arm and the silanols on the support surface can activate the epoxide by H-bond formation. Nevertheless, no direct evidence is available to confirm this hypothesis. The sole information we can give is based on some preliminary experiments concerning the possible interaction of CO_2 with MTBD. In fact, by bubbling CO_2 at rt into an acetonitrile solution of MTBD, after a few minutes the formation of a white crystalline precipitate was observed. Whereas it has been impossible to collect comprehensible ^1H NMR or FT-IR spectra of this material as well as X-ray diffraction data due to its great instability, we succeeded in trapping intermediate **5** by reaction with CH_3I; the *O*-methylated cation derived from **5** was detected by ESI-MS (positive ion) analysis. In addition, by stirring overnight at rt this crystalline precipitate in the presence of styrene oxide in acetonitrile, compound **4** was obtained. On the basis of this simple and preliminary experiment, it is possible to hypothesise that CO_2 could

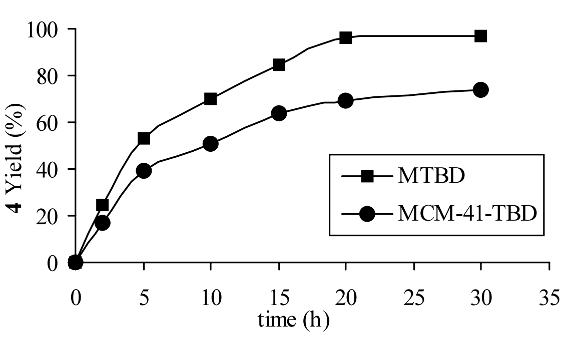
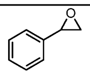
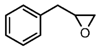
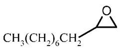
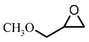
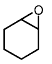
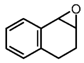
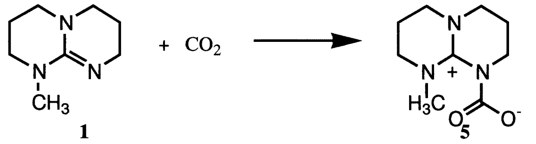


Figure 3. Comparison of the yield of product **4** as a function of time under homogeneous (■) and heterogenous (●) catalysis.

Table 1. Synthesis of cyclic carbonates **4**

Entry	Substrate		**4** yield [selectivity] (%)	
			MTBD, 20 h	MCM-41-TBD, 70 h
1		**4a**	95 [97]	90 [92][a]
2		**4b**	98 [99]	95 [97]
3		**4c**	82 [95]	77 [90]
4		**4d**	88 [90]	79 [90]
5		**4e**	70 [97]	67 [94]
6		**4f**	60 [98]	55 [92]

[a] The by-products recovered were the carbonyl compounds (mainly the ketone) produced by isomerisation of the epoxide



Scheme 2. Hypothesised MTBD-promoted CO$_2$ activation.

be activated through the formation of the zwitterionic compound **5** which can add to the epoxide via nucleophilic attack, as previously reported for solid basic catalysts (Scheme 2).[9]

In conclusion, we have demonstrated that the synthesis of cyclic carbonates by CO$_2$ insertion into epoxides can be carried out under catalytic conditions by using guanidines; the reaction performed with heterogenous MCM-41-TBD is slower than that with homogeneous MTBD, but shows the great advantage that the catalyst can easily be recovered and reused for at least three further cycles.

Acknowledgements

We acknowledge the support of the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR), Italy, and the University of Parma (National Project 'Processi puliti per la Chimica Fine'). The help rendered by Dr. C. Guzzon and Mr. P. A. Bonaldi (Lillo) is also acknowledged.

References

1. (a) Aresta, M.; Quaranta, E.; Tommasi, I.; Giannoccaro, P.; Ciccarese, A. *Gazz. Chim. Ital.* **1995**, *125*, 509–538; (b) Behles, J. A.; De Simone, J. M. *Pure Appl. Chem.* **2001**, *73*, 1281–1286; (c) Aresta, M. *Chem. Ind. (Milan)* **1998**, *80*, 1051–1056.
2. (a) Shaikh, A.-A. G.; Sivaran, S. *Chem. Rev.* **1996**, *96*, 951–976; (b) Parrish, J. P.; Salvatore, R. N.; Jung, K. W. *Tetrahedron* **2000**, *56*, 8207–8237.
3. (a) Nomura, R.; Kimura, M.; Teshima, S.; Ninagawa, A.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3200–3203; (b) Nomura, R.; Ninagawa, A.; Matsuda, H. *J. Org. Chem.* **1980**, *45*, 3735–3738; (c) Baba, A.; Nazaki, T.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1552–1554.
4. (a) Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198–6202; (b) Iwasaki, T.; Kihara, N.; Endo, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 713–719.
5. (a) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304–1309; (b) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725–727; (c) Kasuga, K.; Nagao, S.; Fukumoto, T.; Handa, M. *Polyhedron* **1996**, *15*, 69–72; (d) Kasuga, K.; Kato, T.; Kabata, N.; Handa, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2885–2888.
6. (a) Tascedda, P.; Dunãch, E. *J. Chem. Soc., Chem. Commun.* **1995**, 43–44; (b) Fujinami, T.; Suzuki, T.; Kamiya, M.; Fukuzawa, S.; Sakai, S. *Chem. Lett.* **1985**, 199–200; (c) Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498–11499; (d) Bäckvall, J.-E.; Karlsson, O.; Ljunggren, S. O. *Tetrahedron Lett.* **1980**, *21*, 4985–4988.
7. See for example: (a) Darensbourg, D. J.; White Stafford, N.; Katsurao, T. *J. Mol. Catal. A: Chem.* **1995**, *104*, L1–L4; (b) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2599–2602; (c) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749; (d) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008–11009; (e) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107–116.
8. (a) Yang, H.; Gu, Y.; Deng, Y.; Shi, F. *Chem. Commun.* **2002**, 274–275; (b) Calò, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. *Org. Lett.* **2002**, *4*, 2561–2563.
9. (a) Yano, T.; Matsui, H.; Koike, T.; Ishiguro, H.; Fujihara, H.; Yshihara, M.; Maeshima, T. *Chem. Commun.* **1997**, 1129–1130; (b) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526–4527; (c) Tu, M.; Davis, R. J. *J. Catal.* **2001**, *199*, 85–91.
10. Polymer-supported TBD is now commercially available (Aldrich).
11. The experimental parameters were selected on the basis of previous experiments made in our laboratories on similar reactions.
12. Subba Rao, Y. V.; De Vos, D. E.; Jacobs, P. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2661–2663.
13. Carloni, S.; De Vos, D. E.; Jacobs, P. A.; Maggi, R.; Sartori, G.; Sartorio, R. *J. Catal.* **2002**, *205*, 199–204.
14. A possible catalytic effect of the surface silanols of the support was excluded by carrying out a comparative experiment in the presence of unfunctionalised MCM-41 silica; product **4** was detected only in traces.
15. General procedure for the preparation of cyclic carbonates **4**: a mixture of the selected epoxide (26 mmol) and the selected catalyst (1 mmol, 0.15 g for MTBD, 0.79 g

for MCM-41-TBD) in acetonitrile (5 ml) was charged in a small autoclave; then CO_2 was introduced (50 bar) and the mixture was heated at 140°C for the selected time. The reaction mixture was then cooled to rt, methyene chloride was added (in the experiment with MCM-41-TBD, the catalyst was removed by filtration) and the products purified over silica gel column by using hexane–ethyl acetate mixtures. All products **4a**–**f** were characterised (IR, ^{1}H NMR and MS) and their mps compared with literature reported mps.