SYNTHESIS OF FUNCTIONALISED CYCLIC CARBONATES FROM EPOXIDES AND CARBON DIOXIDE CATALYSED BY ELECTROGENERATED NICKEL COMPLEXES

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Abstract : Functionalised cyclic carbonates are obtained in good yields and under mild conditions from epoxides and carbon dioxide by an electrochemical procedure. The cyclic carbonate formation is catalysed by Ni(cyclam)Br_2 and is carried out in single-compartment cells fitted with a magnesium anode. The presence of several functional groups such as chlorine, bromine, ether, ester or olefins are compatible with the reaction conditions.

Introduction

Cyclic organic carbonates have a wide range of applications, both in the field of industrial chemistry[1], as aprotic polar solvents[2], as linear carbonates, urethanes or carbamate sources[3], or as precursors of polycarbonates or other polymeric materials[4], and in the field of fine chemicals, for the stereochemical control in the synthesis of vicinal diols, sugars[5], antibiotics and natural products[6]

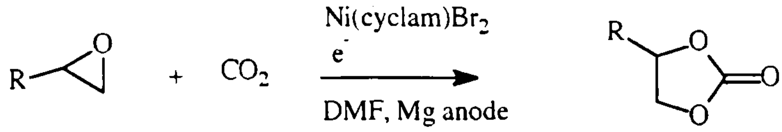
The synthesis of cyclic carbonates can be achieved by the incorporation of CO_2 into epoxides, thus avoiding the use of phosgene. The utilization of CO_2 as non-toxic, cheap and abondant C-1 buiding block is interesting from an environmental point of view[7].

Several catalytic systems for the synthesis of cyclic carbonates from epoxides and carbon dioxide have been described. Among them, ammonium, alkali salts[8] or phase transfer systems[9], have been reported, generally in reactions carried out at high temperatures and elevated CO_2 pressures. Aluminium porphyrins[10] and organoantimony compounds[11] also constitute suitable catalysts for carbonate formation. The use of transition metal catalysts offers high selectivity under milder conditions. Thus, catalysis by Ni(0)[12], Cu(I)[13] or Ti(III)[14] complexes has been reported to afford cyclic carbonates from epoxides at carbon dioxide pressures of 6-35 atm and temperatures of 100-125 °C, and mixed catalytic systems (with Mo, Co, Fe) can be operative at normal pressures[15].

We have recently described a novel catalytic system based on the use of Ni(cyclam)Br_2 in an electrochemical reaction[16]. Electrosynthesis of cyclic carbonates can be achieved at room temperature and under normal carbon dioxide pressure. We describe here the extension of this reaction to the preparation of a series of functionalized epoxides, in order to study the compatibility with several functional groups. The preparation of differently substituted cyclic carbonates widens the field of application of these compounds, particularly for the preparation of functionalized polymeric materials.

Results and discussion

Terminal epoxides bearing several functional groups have reacted with CO_2 under electrochemical conditions, in a reaction catalyzed by Ni(cyclam)Br_2 (eq. 1). □



(eq. 1)

R = functional containing group

The results are presented in Table 1. Aryl and alkyl esters of glycidol (entries 1, 2) underwent carbon dioxide incorporation selectively, without reduction or cleavage of the ester group. Aryl and alkyl glycidyl ethers (entries 3-5) were also stable under the electrochemical conditions, and the corresponding β-ether carbonates were formed in excellent yields.

The presence of a double bond in the side-chain did not interfere with the epoxide carboxylation, and thus, oct-7-ene-1,2-epoxide (entry 6) led to the corresponding unsaturated cyclic carbonate in 73% yield, without any intramolecular cyclization nor modification on the double bond This result is interesting, because the Ni^{II}(cyclam) catalyst has been reported to undergo a one-electron reduction into Ni^{I} species, able to afford radical-type intermediates in the presence of organic substrates[17]. However, in the electrochemical ring opening of epoxides by CO_2, no products formed by radical addition at the double bond were observed. The chemoselectivity of the CO_2 incorporation into the oxirane ring is also noteworthy, considering the possible competition with the electrocarboxylation of carbon-carbon double bond. Indeed, the nickel-catalyzed electrochemical CO_2 fixation into unsaturated hydrocarbons (alkenes[18], alkynes[19]) has been reported.

The presence of chlorine was also tolerated. Thus, *o*-chlorostyrene oxide (entry 7) selectively reacted with CO_2 at the oxirane ring, without reductive cleavage or carboxylation of the C-Cl bond, the cyclic *o*-chlorostyrene carbonate being obtained in 52% yield. The competitive reaction of direct electrochemical carboxylation of aryl halides to produce benzoic acid derivatives has been described[20], but this process seems to be inhibited here in the presence of the epoxide function. Moreover, the reaction selectivity is remarkable, considering the C-halogen reactivity described in electrochemical cyclizations catalyzed by Ni-cyclam or related systems, in which the activation of the carbon-halogen bond has been observed[17, 21].

The present method also enabled the preparation of cyclic carbonates from epichlohydrine and epibromhydrine (entries 8, 9), interesting synthons for further transformations.

The reactions were carried out in a single-compartment cell[22], with a sacrificial magnesium anode and a stainless steel cathode, in anhydrous DMF as solvent, at room temperature and atmospheric carbon dioxide pressure. The catalyst, Ni(cyclam)Br_2 was added in 10 molar % with respect to the epoxide substrate, and KBr was used as supporting electrolyte in a 10^{-2} M concentration. No cyclic carbonate formation took place in the absence of electricity or in the absence of the nickel catalyst.

In the preparative-scale epoxide carboxylations, the reactions at the electrodes are, at the anode, the oxidation of the magnesium metal rod into magnesium ions in solution, and at the cathode, the Ni^{II} complex is reduced to Ni^{I}. The electrochemical reduction of Ni(cyclam)Br_2 takes place as a one-electron process, to generate a Ni(cyclam)$^+$ species, according to the results reported in the literature[17]. Cyclic voltammetry experiments show that this reduction is a quasi-reversible process at -1.3 V vs SCE, in the DMF / KBr system. The electrogenerated Ni^{I} species are the active catalytic species, responsible for the catalytic reaction. Electrogenerated Ni(cyclam)$^+$ complexes have already been reported to activate CO_2 and to act as good catalysts for the efficient conversion of CO_2 into CO in water[23]. In the present reaction, although we observed some CO_2 side-reduction into a mixture of oxalate (by reductive dimerization) and CO and carbonate (by reductive disproportionation), the main reaction pathway remained the carbon dioxide incorporation into the epoxide to form the cyclic carbonate.

Conclusion

In conclusion, the nickel-catalyzed electrochemical method constitutes a very mild alternative to the synthesis of cyclic carbonates from epoxides and CO_2. It allows the selective preparation of differently functionalized cyclic carbonates, with no interference of the reduction of functional groups such as chlorine, esters, ethers or olefins.

Experimental part

General electrochemical procedure : The single-compartment electrolysis cell was similar than that described in ref. 22, fitted with a magnesium rod anode (diameter 1 cm) and a stainless steel cathode grid (apparent surface of 2 cm^{-2}). A freshly distilled DMF (40mL) solution of Ni(cyclam)Br_2 (0.3 mmol)[24] containing KBr (0.4 mmol) and the functionalised epoxide (3 mmol) was electrolysed under bubbling of carbon dioxide (1 atm) at room temperature with continuous stirring. A current of 60 mA was initially applied between the electrodes connected to a DC power supply (apparent cathodic current density of 3 A.dm^{-2}) during 7 h. The current was limited by a maximum applied voltage of 15 V. The reaction mixture was then heated at 50 °C in DMF for 12 h. The solution was hydrolyzed with 50 mL of 0.1 N HCl solution and extracted with Et_2O, and the organic layer was washed with H_2O, dried over $MgSO_4$ and evaporated. The cyclic carbonates were isolated by flash chromatography on silica gel with pentane/Et_2O mixtures as the eluent. The products were analyzed by NMR and IR spectrometry, mass spectroscopy and GLC and compared to authentic samples.

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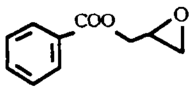
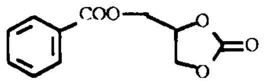
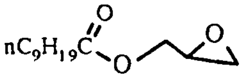
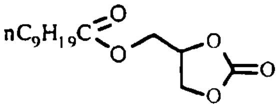
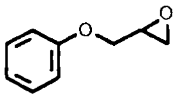
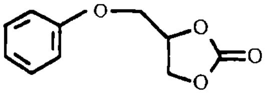
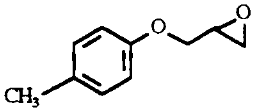
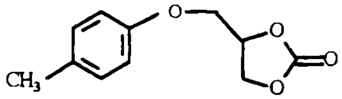
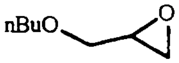
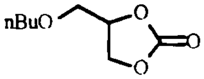
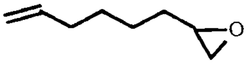
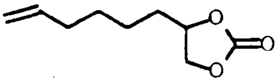
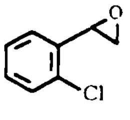
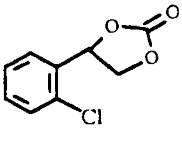
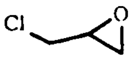
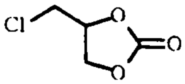
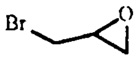
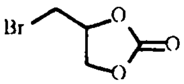
Table 1 : Cyclic carbonate formation from functionalised epoxides and carbon dioxide, in an electrochemical reaction catalysed by Ni(cyclam)Br_2, at room temperature and atmospheric CO_2 pressure.

Entry	Starting epoxide	Cyclic carbonates	Isolated yield
1			92%
2			77%
3			98%
4			98%
5			84%
6			73%
7			52%
8			50%
9			50%