



Synthesis of 5-membered cyclic carbonates by oxidative carbonylation of 1,2-diols promoted by copper halides

Potenzo Giannoccaro^{a,*}, Michele Casiello^a, Antonella Milella^a, Antonio Monopoli^a, Pietro Cotugno^a, Angelo Nacci^{a,b}

^a Department of Chemistry, University of Bari "Aldo Moro", Via Orabona, 4, 70126 Bari, Italy

^b CNR – ICCOM, Department of Chemistry, University of Bari "Aldo Moro", Via Orabona, 4, 70126 Bari, Italy

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ABSTRACT

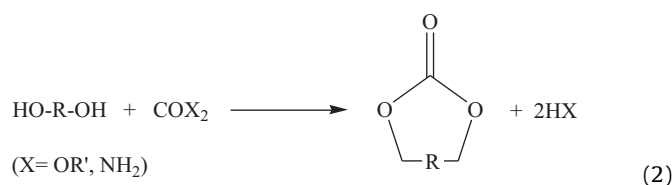
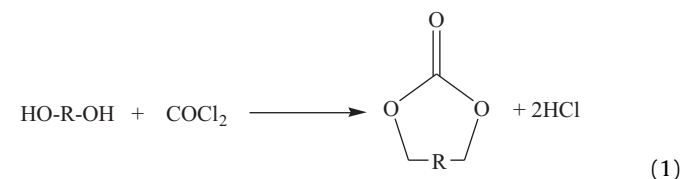
Copper halides, CuX₂ (X=Cl, Br), promote the oxidative carbonylation of vicinal diols [1,2-ethandiol (1,2-ED), 1,2-propanediol (1,2-PD), 1,2-butanediol (1,2-BD)] into the corresponding 5-membered cyclic carbonates, under CO/O₂ (P_{tot} = 3 MPa; P_(O₂) = 0.5 MPa), at 373 K, in CH₃CN and in the presence of a base as co-catalyst. Under these conditions, however, copper salts catalysts proved to be unstable (max turnover, 21.1 mol/mol), evolving into a pale green, insoluble and inactive material, by reaction with water, by-product of the carbonylation process. Contrarily, by carrying out reactions directly in diol, and using DMF as the base, catalytic systems showed to be stable and efficient. Under these conditions, when approximately 40% of the diol has been converted into carbonate, CO₂ begins to be formed, deriving from the CO oxidation promoted by H₂O that accumulates in the system. The extent of this side reaction, which lowers the yield of CO into cyclic carbonate, increases with the progress of carbonylation. After a diol conversion of 70%, the oxidation of CO to CO₂ becomes the main reaction and prevents the complete carbonylation of the diol. The most probable reaction mechanism is also reported and discussed.

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1. Introduction

Cyclic carbonates are non-toxic, easily biodegradable, high polar and high boiling liquids, that are used as raw materials for industry in a wide range of applications: solvents of degreasing, diluents of epoxy resins and polyurethanes [1,2], additives for fuels, chemical intermediates for the synthesis of polycarbonates and other polymeric substances [1,3] and for dimethyl carbonate synthesis (DMC) by a trans-esterification process with methanol [4].

The main synthetic methods of access to cyclic carbonates are based on carbonylation or carboxylation processes. The former are achieved by reacting diols with toxic phosgene (Eq. (1)) or with less toxic carbonyl derivatives, like dialkyl carbonates or urea (Eq. (2)) [5].



Although the phosgene method is simple to be realized and requires mild temperature conditions, it has the disadvantage of using a highly toxic and hazardous reagent. In addition, this suffers from two other drawbacks: the low selectivity in the reaction products and the cost of disposing of HCl, that is formed in stoichiometric amounts. The other two procedures, while being more eco-friendly routes, show the problems of requiring stoichiometric amounts of organic carbonates or urea, which have a cost, the need for high temperatures ($T > 130^\circ\text{C}$) and for expensive catalysts based on metal oxides [6]. Moreover, since the synthetic reactions are reversible, the conversion is never complete, and tedious separation steps are necessary. In the case of reactions with urea, the recycling of ammonia, that is formed in stoichiometric amounts, is mandatory [7]. With regard to the carboxylation method, it is mostly accomplished by reacting CO₂ with olefins and oxygen, or directly CO₂ with epoxides or diols. Although these procedures are preferable to the phosgene route, as they have the advantage of using a greenhouse gas, they suffer from other problems, which still

* Corresponding author. Tel.: +39 060 5442093; fax: +39 080 5442129.
E-mail address: giannoccaro@chimica.uniba.it (P. Giannoccaro).

remain unsolved. In particular, procedures employing olefin and oxygen [8], have the disadvantage of requiring drastic reaction temperatures and efficient control systems, being the olefin/oxygen mixtures potentially explosive. Protocols with epoxides are interesting [9], because they occur under milder conditions, but require expensive starting materials. Finally, procedures based on CO₂ and diols are to be preferred from the economical point of view, but usually occur at high temperatures and proceed with lower conversions [10].

It is noteworthy that many valuable organic compounds, like linear organic carbonates [11], ureas and carbamates [12], and oxalates [11a], can be prepared conveniently by oxidative carbonylation processes, using dioxygen as an oxidant (Eq. (3)). These processes should be preferred to the methods described above, since they do not give by-products.



(Y = OR, -NH₂, -NHR; -NR₂)

Recently, these procedures have been successfully applied to the carbonylation of bi-functional substrates, such as amino-alcohols and diamines, which have been converted into cyclic carbamates [13], N,N-bis(hydroxyalkyl)ureas [14], and cyclic ureas [15].

Little attention has been devoted to the oxidative carbonylation of diols, which could be conveniently converted into cyclic carbonates (Eq. (4)). In the middle of '80. Tam [16] reported that Pd(II) can promote this reaction, but the method appeared of little synthetic importance, due to both the requirement of stoichiometric amounts of copper, as an oxidant, and the very poor catalyst stability. The formation of ethylene carbonate by oxidative carbonylation of ethylene glycol, promoted by Co(OAc)₂, using O₂ as an oxidant, has also been reported in a patent [17]. The catalytic system, in this case, seems to be not efficient due to the very low values of both yields (2%) and turnover.

Only recently two different research groups have reported their preliminary results on some palladium-based catalytic systems, that are able of promoting efficiently the oxidative carbonylation of diols into cyclic carbonates under both homogeneous [18] and heterogeneous [19] conditions.

The oxidative carbonylation method has been also extended to glycerol, a triol, that has been converted into glycerol carbonate as described in a patent [20] and in a recent study [21,22a].

In this paper we describe the first copper-based catalytic systems, able to convert diols into the corresponding cyclic carbonates, using O₂ as an oxidant.

2. Experimental

Unless otherwise stated, all manipulations were carried out in air. Solvents, copper halides (CuCl₂, CuBr₂), diols [1,2-ethandiol (1,2-ED), 1,2-propanediol (1,2-PD), 1,2-butanediol (1,2-BD)], bases (Na₂CO₃, C₆H₅COONa, CH₃COONa, NEt₃, pyridine, N,N-dimethylformamide (DMF), ligands [triphenylphosphine (PPh₃), triphenylphosphine oxide (OPPh₃), 1,2-bis(diphenylphosphino)ethane (dppe) and 2,2'-bipyridine (bipy)] were Aldrich or Fluka products and were used as received. Products were identified by IR, GLC and GLC-MS and by comparison with the literature data. IR spectra were recorded on a Shimadzu IR-Prestige-21 spectrophotometer. GLC quantitative analyses and separations were performed by using a Varian Cromopack CP3800 GLC equipped with a CP Sil 8 CB capillary column (50 m, 0.53 mm ID), connected to a FID detector. GLC-MS analyses were carried out with a Shimadzu GLC 17-A linked to a Shimadzu GLC/MS QP5050A selective mass detector (capillary column: HP-5 MS, 30 m). Analyses of gas mixture: at the end of reaction, the residual

gas mixture was collected at atmospheric pressure in a graduated cylinder connected to a gas burette and analyzed for CO₂. Analyses were carried out on a Poropak Q (3.5 m) column, using a Varian Cromopack CP3800 GLC equipped with a thermal conductivity detector.

Catalytic tests were carried out in a 55,6 mL stainless steel autoclave mounted in an electrical oven having a magnetic stirrer on its base. Catalyst, co-catalyst, solvent and reagents were introduced in a glass vial (~12 mL) placed into the autoclave, in order to avoid any contact with metal walls. Under these conditions, the free volume for gaseous mixture is in the range 30–35 mL. Activity and selectivity were obtained by GLC, detecting the reacted diol and the formed carbonate using toluene or xylene as an external standard.

XPS analyses were carried out using a Thermo Fisher Theta Probe spectrometer equipped with a monochromatic Al K α X-ray source (1486.6 eV) with a spot size of 400 μ m, corresponding to a power of 100 W and at a take-off angle of 53°. Survey spectra (0–1300 eV) were acquired at a pass energy of 200 eV with a resolution of 1 eV. High resolution spectra for C1s, O1s, Cl2p and Cu2p were recorded at a pass energy of 100 eV with a resolution of 0.05 eV. Charge correction of the spectra was performed by taking the alkyl type carbon (C–C, C–H) component of the C1s spectrum as internal reference (binding energy, BE = 284.5 eV).

Atomic percentages were calculated from the high resolution spectra using the Scofield sensitivity factors set in the Thermo Avantage software (Thermo Fisher Corporation) and a non-linear Shirley background subtraction algorithm. XPS analysis was repeated on three different spot of the sample.

2.1. CO/O₂ ratio

Although the CO/O₂ compressed mixtures are potentially explosive in a wide range (flammability range for CO in O₂ at room temperature is 16.7–93.5%) [23], many studies on oxidative carbonylation have been conducted and are still carried out with a 2:1 ratio (CO:O₂), without the occurrence of incidents [22]. As an example, DMC synthesis on industrial scale (the EniChem process) is carried out with this ratio [24]. However, when using mixtures in the flammability range, it is always advisable using suitable equipment and special care. In this work, we used autoclaves equipped with appropriate rupture discs (strength 10 MPa). Due to their small size (see above) and in the absence of a device able to carry the reactions at a constant pressure, we used 5:1 mixtures of CO/O₂. In any way, we found that the reactions take place even using mixture with 15:1 ratios. In these cases reactions are slower.

2.2. Catalytic tests

2.2.1. Synthesis of 4-methyl-1,3-dioxolan-2-one

In a typical experiment the glass vial was charged with solvent (CH₃CN, 9.0 mL), catalyst (CuCl₂, 0.60 mmol), co-catalyst (Na₂CO₃, 0.60 mmol) and 1,2-PD (10 mmol). The vial was introduced into the autoclave which was sealed and charged with O₂ (0.5 MPa) and CO up to a total pressure of 3 MPa. Under these conditions, also taking into account the free volume of the autoclave and the stoichiometry of the carbonylation process (Eq. (4)), the diol is the limiting reagent. The autoclave was heated at 100 °C and allowed to react for 3 h. After this time, it was cooled to room temperature and the residual gas mixture was analyzed for CO₂. The reaction mixture was analyzed by IR, GLC and GLC-MS for reactants and products. GLC analyses were performed by adding to the reaction mixture a weighed amount of toluene as external standard. The IR spectrum showed the presence of a strong absorptions around 1800 cm⁻¹ assigned to cyclic carbonates 4-methyl-1,3-dioxolan-2-one [25], whose presence was confirmed by means of GLC-MS analysis [*m/z* (in parenthesis, relative intensity): 102 (M⁺, 2), 87

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