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Copper(II)-catalysed oxidative carbonylation of aminols and amines in water: A direct access to oxazolidinones, ureas and carbamates

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ABSTRACT

Copper(II) chloride catalyses the oxidative carbonylation of aminols, amine and alcohols to give 2-oxazolidinones, ureas and carbamates. Reaction proceeds smoothly in water under homogeneous conditions ($P_{tot} = 4$ MPa; $P_{O2} = 0.6$ MPa, P_{CO}), at 100 °C in relatively short reaction times (4 h) and without using bases or any other additives. This methodology represents an economic and environmentally benign non-phosgene alternative for the preparation of these three important N-containing carbonyl compounds.

1. Introduction

2-Oxazolidinones, ureas, and carbamates are useful compounds that find application in many practical fields. 2-Oxazolidinone and carbamates are successfully employed as intermediates in the synthesis of agrochemical, pesticide, herbicide and pharmaceutical agents [1], but also as solvents [2] and chiral auxiliaries [3]. Acylation of 2-oxazolidinones is also a frequently used method for the synthesis of valuable compounds such as amino acids [4].

Ureas are used as dyes for cellulose fibers, antioxidants in gasoline, corrosion inhibitors, plant growth regulators, pesticides, insecticides, and as tranquilizing and anticonvulsant agents [5]. Many urea derivatives have displayed a wide spectrum of biological activity [6]; in particular, as inhibitor of HIV protease enzyme [7]. In addition, they are advantageous intermediates in the production of carbamates [8].

The classical synthesis of these compounds from the corresponding amino derivatives is based on the use of toxic and/or corrosive reagents, such as phosgene or isocyanates [9]. In recent years, however, alternative routes have been developed that utilize safer phosgene equivalents, such as triphosgene, activated carbonates (DMC and DET), carbonyl diimidazole, carbamoyl chlorides, chloroformates, CO and CO_2 as the source of the carbonyl moiety [4,10].

Particularly, for the synthesis of cyclic carbamates, reaction of aziridines, aminoalcohols, primary or acetylenic amines with CO_2 have been investigated [11]. However, most of these compounds are still usually prepared from phosgene as the carbonylating agent.

Particularly attractive from the standpoint of atom economy is the oxidative carbonylation of amino compounds, a process that has been considerably studied in the last decade. This reaction is significantly advantageous compared with the above-mentioned methods, since it avoids hazardous and/or expensive reagents and requires milder temperature conditions (373–423 K). Transition metal such as Pd [12], Ru [13], and Rh [14], have been found to promote the oxidative carbonylation of amines and aminols. However, two issues, related to the high cost of these catalysts and the toxicity of utilized solvents (DMF, DMA etc.), remained unsolved.

The use of cheaper and non-noble metals is currently explored and interesting results have been obtained with cobalt catalysts [15], which however required Schiff-base ligands and iodine or N-containing bases as promoters. Moreover, cheap metals such as copper, except for one example which involves a Cu(I)-complex bearing however an expensive N-heterocyclic carbene as ligand [16] have in fact remained unexplored. In addition, all these reac-

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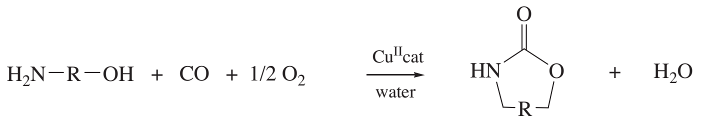
tions are carried out in common organic solvents as dioxane, THF, CH_3CN, DMA, DMF, which are toxic and therefore banned from the industrial practise [17].

As described in our previous work, we have found that oxidative carbonylation of diols [18] and glycerol [19] can be easily promoted by the inexpensive $CuCl_2$ salt as catalyst without using special ligands and/or promoters. Following our success on diols, we decided to extend such an oxidative carbonylation to amines and aminoalcohols developing a copper-based catalytic system for the synthesis of 2-oxazolidinone, ureas and carbamates in the absence of additives and using water as the solvent [Eqs. (1)–(3)].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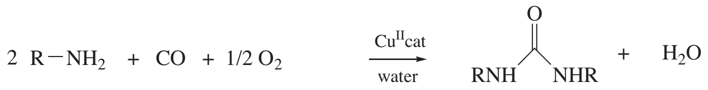
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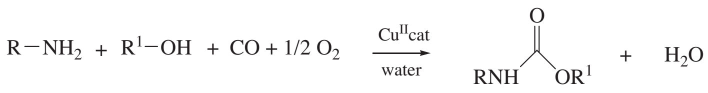
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2. Experimental

2.1. Materials and general procedure

Copper salts [$CuCl_2$, $CuBr_2$] were dried under vacuum overnight before their use. $PdCl_2$, aminols, amines, alcohols, diphenylphosphine, 2-vinylpyridine, solvents (CH_3CN, N,N-dimethylformamide DMF, N,N-dimethylacetamide DMA, CH_3OH), ligands (pyridine, triphenylphosphineoxide 2,2′-bipyridyl), external standard (butanone), and Na_2CO_3 were Aldrich or Fluka products and were used as received.

Copper complex (29H, 31H-phthalocyaninato(2-)-N29,N30,N31,N32) copper(II) (**II**) (INTATRADE GmbH) was commercially available, dichloro(2,2′-bipyridyl) copper(II) (**III**) [20], dichlorobis(triphenylphosphineoxide) copper(II) (**I**) [21], and dichloro[2-(β-diphenylphosphinoethyl) pyridine]palladium(II) (**IV**) [22] were prepared according to the literature.

Reactions products were detected by GC–MS and identified by comparison of their IR and MS spectra with literature data (see supplementary material). FT-IR spectra were recorded on a Perkin–Elmer Spectrum BX spectrophotometer. GC–MS analyses were carried out with an Agilent GC 6850 (equipped with a capillary column: HP-5 MS, 30 m) linked to an Agilent 5975C selective mass detector.

Special care was devoted to the cleaning of the equipment (glass vials, magnetic stirrer, etc.) carried out with aqua-regia to prevent metal contaminations.

2.2. Safety advices

It is well known that the high-pressure experiments with CO/O_2 mixtures are potentially explosive in the range 16.7–93.5% [23] and may represent a significant risk. Consequently, experiments with compressed gases should only be carried out in conjunction with the use of suitable equipments and special care. In this work, autoclaves equipped with appropriate rupture discs (strength 10 MPa) and mixtures of $CO/O_2 = 6:1$ ca. molar ratio (~85%) very close to the upper limit of the above-mentioned range were used. In any case, a comparative carbonylation experiment has been performed at a $CO:O_2 = 15:1$ molar ratio (93.7%), demonstrating that the catalyst works also under the safety conditions even if with longer reaction times. This result has been added in Table 1 (entry 16) and the procedure described in Section 2.3.

2.3. Catalytic tests

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, additives, solvent and reagents were introduced in a glass vial (~20 mL) and 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 35 ÷ 40 mL.

In a typical experiment the glass vial was charged with a doubled distilled water solution (5.0 mL) of substrate (amine or aminol) (4 mmol), catalyst ($CuCl_2$, 0.40 mmol), which appeared transparent and deep blue colored. The vial was introduced into the autoclave which was sealed, purged and charged with O_2 (0.6 MPa) and CO up to a total pressure of 4 MPa. Under these conditions, the substrate should be deemed the limiting reagent, also taking into account the head space of the autoclave and the stoichiometry of the carbonylation process [Eq. (1)].

The mixture was heated at 100 °C and allowed to react for 4 h. After this time, the autoclave was cooled at room temperature and then the residual gas was evacuated.

Identification of reaction products was performed via GC–MS by comparison of their MS spectra with those reported in the literature (and with the help of NIST database). A complete list of mass spectral data of the major reaction products, including by-products, was reported into the supplementary material section. Quantitative analysis of reaction mixture was accomplished by GC–MS using butanone as an external standard. Conversions and yields were reported in Tables 1–3.

Comparative experiment carried out under the safety conditions ($CO:O_2 = 15:1$ molar ratio), was performed on a H_2O solution (5.0 mL) of aminol (2,6 mmol), catalyst ($CuCl_2$, 0.26 mmol). The vial was introduced into the autoclave which was sealed, purged and charged with O_2 (0.25 MPa) and CO up to a total pressure of 4 MPa. Under these conditions, the mixture was heated at 100 °C and allowed to react for 8 h. After this time, the reaction mixture was analysed by GC–MS for assessing conversions and selectivities as reported in Table 1, entry 18.

3. Results and discussion

3.1. Optimization of catalysis conditions

In our previous works [18,19] we had shown that the presence of water, even in small quantities, negatively influenced the catalytic activity of copper(II) in the oxidative carbonylation of polyols. This damaging effect was ascribed to a competitive carbonylation