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

Michele Casiello[a], Francesco Iannone[a], Pietro Cotugno[a,*], Antonio Monopoli[a], Nicola Cioffi[a], Francesco Ciminale[a], Anna M. Trzeciak[c], 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
[c] University of Wrocław, Faculty of Chemistry, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

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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-

* Corresponding authors. Fax: +39 080 5442129.
E-mail addresses: pietro.cotugno@uniba.it (P. Cotugno), angelo.nacci@uniba.it (A. Nacci).

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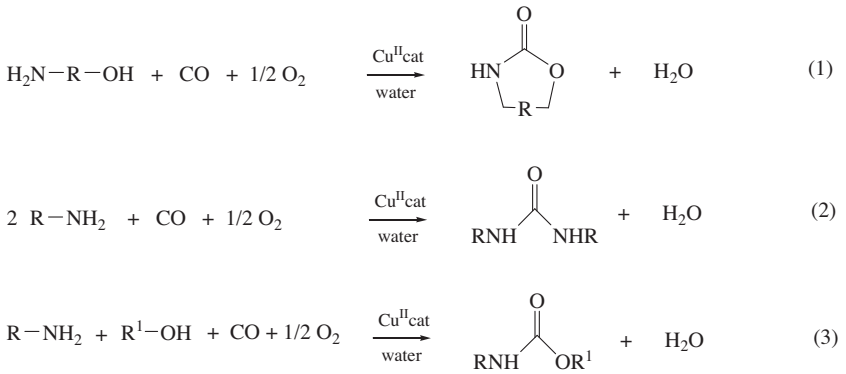
tions are carried out in common organic solvents as dioxane, THF, CH_3CN, DMA, DMF, which are toxic and therefore banned from the industrial practise [17].

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)].



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.

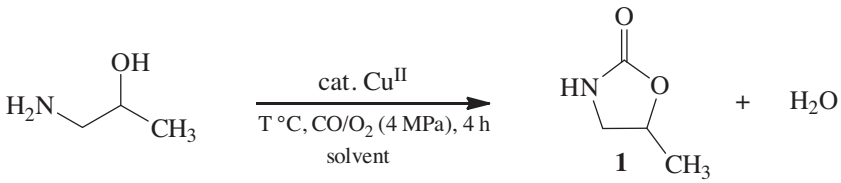
Comparative experiment carried out under the safety conditions ($CO:O_2$ = 15:1 molar ratio), was performed on a H_2O solution (5.0 mL) of aminol (2,6 mmol), catalyst ($CuCl_2$, 0.26 mmol). The vial was introduced into the autoclave which was sealed, purged and charged with O_2 (0.25 MPa) and CO up to 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

Table 1
Optimisation of reaction conditions.[a]



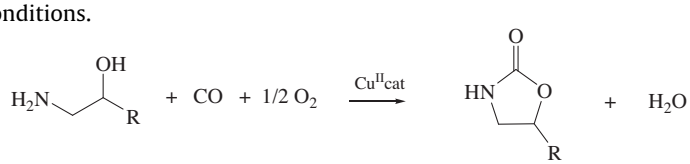
Entry	Catalyst	Solvent	Additive	T (°C)	Conv.[b] (%)	Sel.%[b] (%)
1	$CuCl_2$	CH_3CN	Py	100	22	45
2	$CuCl_2$	DMF	Py	100	20	55
3	$CuCl_2$	H_2O	Py	100	25	50
4	$CuCl_2$	CH_3CN	Na_2CO_3	100	95	55
5	$CuCl_2$	CH_3CN	–	100	90	65
6	$CuCl_2$	DMF	–	100	100	45
7	$CuCl_2$	CH_3OH	–	100	100	46
8	$CuCl_2$	THF	–	100	95	50
9	$CuCl_2$	H_2O	–	100	76	90
10	$CuCl_2$	H_2O	–	80	50	70
11	$CuCl_2$	H_2O	–	140	76	55
12	$CuBr_2$	H_2O	–	100	15	30
13	$(Ph_3PO)_2CuCl_2$ (I)	H_2O	–	100	20	10
14	(Phthalocyanine)$Cu^{(II)}$ (II)	H_2O	–	100	25	20
15	(Bipy)$CuCl_2$ (III)	H_2O	–	100	27	40
16[c]	$CuCl_2$	H_2O	–	100	70	90

[a] General reaction conditions: 1-amino-2-propanol (4 mmol), Cu^{II} cat. (10 mol%), additive (0.5 equiv. respect to Cu) in 5 mL of solvent, heated for 4 h under stirring under a gaseous mixture of O_2 (0.6 MPa) and CO (3.4 MPa).
[b] Evaluated via GC–MS. Selectivities are referred to the moles of cyclic carbamate formed (see Section 2).
[c] Reaction carried out under safety conditions for 8 h ($CO:O_2$ = 15:1 molar ratio, see Sections 2.2 and 2.3).

of water promoted by Cu(II) which consumes CO and produces CO_2. This process became dominant at high conversion values of the starting diol, when concentration of water, by-product of the carbonylation, reaches high values into the reaction medium.

Extending these investigations to amino compounds, we found that this competition is greatly reduced, presumably because of the strong affinity of the amino group toward Cu^{2+}, and this observation encouraged us to explore the use of water as eco-friendly solvent for the carbonylation of aminols and amines.

Preliminary experiments were focused on β-aminols for the synthesis of 2-oxazolidinones. With these substrates we found that copper(II) catalysts promote the oxidative carbonylation into their cyclic carbamates according to the stoichiometry of Eq. (4) and that catalytic efficiency is affected by reaction times and temperature conditions.



(4)

The optimisation of the reaction conditions was surveyed on the model substrate 1-amino-2-propanol (Table 1), using a procedure similar to that employed in the previous protocol for diols [18]: 4 mmol of aminol, 0.4 mmol of Cu(II) catalyst (10 mol%), 0.2 mmol of pyridine as ligand dissolved in 5 mL of solvent, heated for 4 h under a CO/O_2 mixture (4 MPa, 6:1 ca. molar ratio). Preliminary blank reaction showed a total catalysis inhibition in the absence of copper, thus confirming that this metal is necessary to promote the process.

As can be seen from data in the Table 1, the beneficial effect of pyridine, which was crucial in the case of glycerol [19], totally disappeared with this aminol (Table 1, entries 1–3). This suggests that the presence of pyridine should afford the saturation of the metal center, which is chelated by the aminol substrate, leading to a remarkable inhibition of the catalytic process (see Section 3.3).

This hypothesis is supported by the good conversion values observed by replacing pyridine with Na_2CO_3 or working in the absence of bases or other additives (Table 1, entries 4–8). However, under these ligand-free conditions, the use of organic solvents such as CH_3CN, DMF, THF and CH_3OH gave poor selectivities, below 65% (Table 1 entries 5–8). Surprisingly, the use of water produced only a slight decrease of conversions but lowered significantly the formation of by-products (Table 1, entry 9).

Reaction time showed a narrow influence, with conversions that reached a plateau after 8 h, while temperature affected carbonylation in a predictable manner: at lower temperatures (80 °C) a decrease in conversions was found, while an increase of temperature at 140 °C had no effect on conversion but produced a dropping of selectivity (Table 1, entries 10–11).

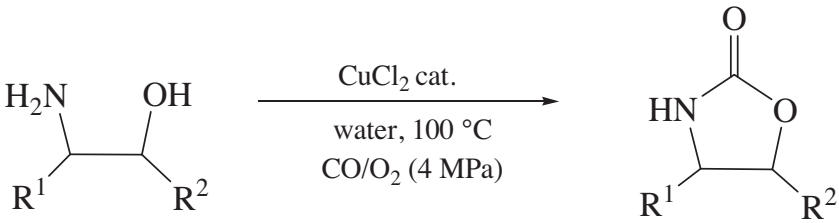
Final optimization tests were focused on searching for other copper catalyst sources. As shown in Table 1 (entries 12–15), copper salt $CuBr_2$ and Cu(II) complexes **I**-**III** furnished disappointing results, also in the case of dichlorobis(diphosphineoxide) copper(II) catalyst (**I**), that had displayed good activity with glycerol [19].

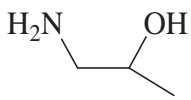
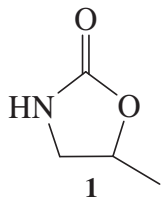
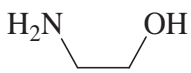
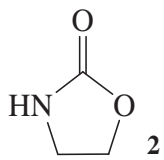
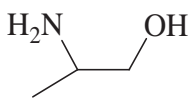
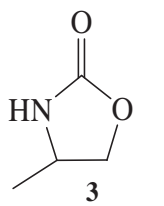
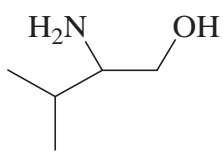
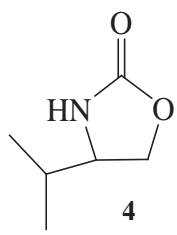
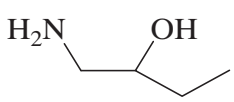
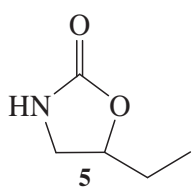
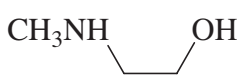
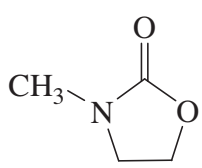
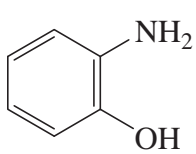
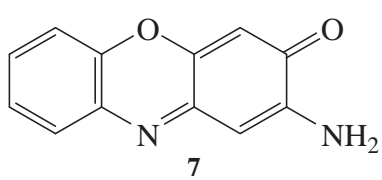
3.2. Substrate scope: synthesis of 2-oxazolidinone, carbamates and ureas

With the optimised conditions in hand, we extended oxidative carbonylation to several nucleophilic substrates such β-aminols, diamines, amines and alcohols. Data reported in Table 2 show that $CuCl_2$, under relatively mild conditions in water, exerted a good catalytic activity toward a series of β-aminols, providing the corresponding 2-oxazolidinones in moderate to good yields.

As already reported [16], aromatic aminols showed a different behavior. Indeed, in place of the carbonylation process, they experienced an oxidative condensation reaction promoted by copper.

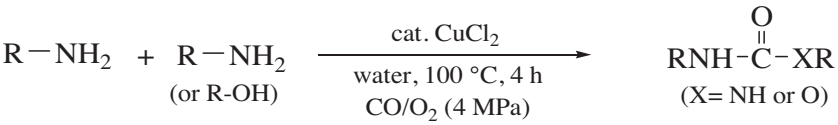
Table 2
Synthesis of 2-oxazolidinones.[a]



Run	Substrate	Product	Conv.[b] (%)	Sel.%[b] (%)
1		 **1**	76	90
2		 **2**	76	94
3		 **3**	75	91
4		 **4**	72	94
5		 **5**	75	92
6		 **6**	73	92
7		 **7**	61	60

[a] General reaction conditions: substrate (4 mmol), Cu^{II} cat. (10 mol%), 5 mL of solvent, heated under stirring under a gaseous mixture of O_2 (0.6 MPa) and CO (3.4 MPa).
[b] Evaluated via GC–MS. Selectivities are referred to the moles of 2-oxazolidinones formed (see Section 2).

Table 3
Synthesis of ureas and carbamates.[a]



Entry	Substrates		Products	Conv.[b] (%)	Sel.%[b] (%)
	R-NH_2	R-OH			
1	$PrNH_2$	–	$PrNH-C(=O)-NHPr$ **8**	90	66
2		MeOH	$PrNH-C(=O)-OMe$ **9**	97	92
3	$BuNH_2$	–	$BuNH-C(=O)-NHBu$ **10**	89	65
4		MeOH	$BuNH-C(=O)-OMe$ **11**	96	91
5		EtOH	$BuNH-C(=O)-OEt$ **12**	96	62
6	Et_2NH	–	$Et_2N-C(=O)-NEt_2$ **13**	75	51
7		MeOH	$Et_2N-C(=O)-OMe$ **14**	85	90
8	$CyNH_2$	–	$CyNH-C(=O)-NHCy$ **15**	91	49
9		MeOH	$CyNH-C(=O)-OMe$ **16**	96	95
10	n-$C_{12}H_{23}NH_2$	–	n-$C_{12}H_{25}NH-C(=O)-NHC_{12}H_{25}$-n	80	60
11		MeOH	n-$C_{12}H_{25}NH-C(=O)-OMe$ **18**	81	70
12	H_2N OH		NH O O **19**	90	51
13	H_2N OH		NH O O **20**	85	<5%[c]
14	H_2N NH_2		NH O NH **21**	<5%	–
15	H_2N NH_2		NH O NH **22**	<5%	–
16[d]				80	90

[a] General reaction conditions: substrate (4 mmol), Cu^{II} cat. (10 mol%), of doubled distilled water (5 mL), T = 100 °C for 4 h under O_2 (0.6 MPa) and CO (3.4 MPa).
[b] Evaluated by GC–MS.
[c] Linear δ-hydroxylated ureas are the major reaction products.
[d] Reaction carried out with Pd(PNPy)Cl_2 catalyst (IV) (1 mol%, see Fig. 3).

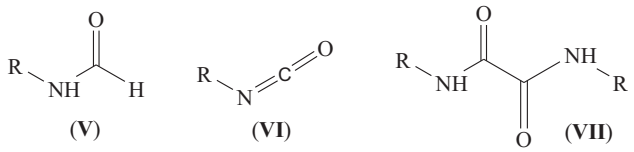


Fig. 1. Major carbonylation by-products of amines and aminols (R = alkyl or -CH_2CH_2OH).

As an example, 2-aminophenol afforded 2-amino-3*H*-phenoxazin-3-one (**7**) as main product (Table 2, run 7). Under these conditions, 1,2-disubstituted aminols proved to be less reactive.

Further investigations showed that this copper catalyst system in water could also be successfully applied to the oxidative carbonylation of simple amines to produce ureas and carbamates (in the latter case an alcohol must be present into the reaction mixture, Table 3).

Excellent conversions (75% ÷ 96%) were observed with aliphatic monoamines like n-propylamine, n-butylamine, diethylamine, cyclohexylamine and n-dodecylamine (Table 3, entries 1,3,6,8,10, respectively).

However, reactions in water on these substrates occurred with lower selectivity (up to 65%) respect to aminols, due to the formation of by-products arising from partial carbonylation (predominantly formamides **V** and isocyanates **VI**), or from oxidative coupling reactions, that afforded oxalamides **VII** (see Fig. 1). These by-products were also observed in the case of β-aminols although in much smaller percentages (see Section 2).

The nature of alkyl chain (R) somehow affected reactivity of these alkylamines in water. Indeed, substrates bearing longer chain afforded slightly lower conversions, because of their lower solubility in water (Table 3, entries 1,3,10). At the same time, cyclohexylamine and diethylamine, probably due to steric reasons, gave also a decrease of selectivity (Table 3 entries 6, 8).

In contrast, oxidative carbonylation of the same aliphatic amines carried out in the presence of short-chain alcohols resulted highly efficient, affording the corresponding linear carbamates in high yields and moderate to good selectivities (Table 3, entries 2,3,5,7,9,11).

Notably, γ- and δ-aminols promptly reacted with CO and O_2 giving good conversions but poor selectivities due to the greater distance between the two functional groups OH- and -NH_2 that would favour the competitive intermolecular carbonylation process and produce great amounts of linear γ- and δ-hydroxylated ureas (Table 3, entries 12,13).

3.3. Mechanistic insights

Based on our previous works [18,19] and the analogous reactions promoted by palladium [24], we propose the mechanism shown in Fig. 2 for the oxidative carbonylation of a generic β-aminol.

In a first instance, it can be postulated the formation of the chelated species **VIII** [path a)], as evidenced by the deep blue color assumed by the starting reaction mixture (see Section 2.3). Then,

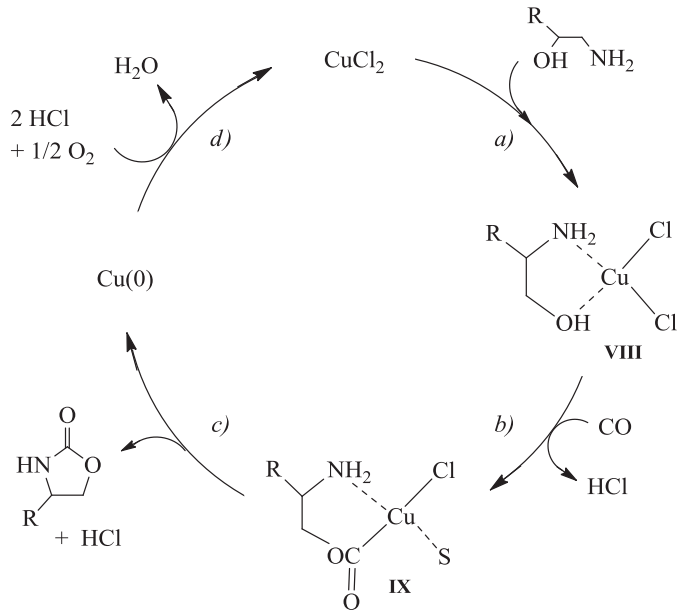


Fig. 2. The plausible carbonylation mechanism of β-aminols (S = solvent).

the process should proceed with the formation of the alkoxycarbonyl copper species **IX** [path b)], passing most probably through a preliminary ligand exchange between CO and hydroxyl group. The reductive elimination should afford 2-oxazolidinone product and Cu(0) [path c)], and the latter should be re-oxidized by molecular oxygen to the active species Cu(II) [path d)].

It should be noted that the distinctive feature of this protocol on β-aminols is the high stability of copper catalyst toward the detrimental effect of water, which has been the main trouble of reactions with diols and glycerol [18,19], This could be explained with the chelating effect of these substrates that would give very stable square planar complexes **X** as depicted in Fig. 3 [25].

This coordination is crucial for reactivity these substrates bearing two functionalities with different ligand power. Indeed, the amino group can act as a "hook" onto the metal center, preventing the damaging effect of water, while the hydroxyl group, being a weaker ligand, could be more promptly replaced, at the appropriate time, by coordination of CO allowing the catalyst to work.

It can also be assumed that in the case of diamines the strong chelating action could impedes the coordination of carbon monoxide CO totally inhibiting the catalysis (see Fig. 3, complex **XI**). This detrimental effect is clearly observed in the case of 1,2- and 1,3-diamines (Table 3, entries 14,15) and is similar to that observed with glycerol in reactions carried out in the presence of strong chelating ligands like *o*-phenantroline and bipyridyl [19].

To verify this assumption we carried out the oxidative carbonylation of ethylendiamine in the presence of a different metal center such as palladium, for which amino groups show a lower affinity. Specifically, reaction was performed in H_2O in the presence of the complex $Pd(PNPy)Cl_2$ (**IV**) (see Fig. 3) and NaI as cocatalyst [26]. As

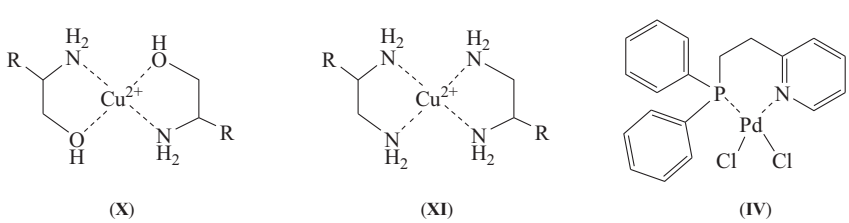


Fig. 3. Square planar complexes of copper and palladium.

expected, catalyst did work without inhibition (Table 3, entry 16), thus confirming our hypothesis.

4. Conclusions

In summary, we have successfully developed an efficient and simple $CuCl_2$ based catalyst system without any additive for the oxidative carbonylation of β-aminoalcohols, amines and alcohols, to produce 2-oxazolidinones, disubstituted ureas and carbamates. This is the second example in the literature [16] on the use of copper catalyst in the oxidative carbonylation of amino alcohols and amines, but this protocol presents the advantage of using water as an eco-friendly solvent that improves sustainability of the process. This methodology represents an economic and environmentally benign non-phosgene alternative for the preparation of these three important N-containing carbonyl compounds.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2015.06.007

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