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Methionine: a green and efficient promoter for copper-catalyzed Sonogashira cross-coupling reactions

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In the presence of amino acids as environmentally friendly ligands, CuI-catalyzed Sonogashira cross-coupling of various aryl halides with phenylacetylene was conducted to afford the corresponding internal alkynes. L-Methionine was found to be useful for this palladium-free and amine-free coupling reaction. It was also found that the solvent system plays an important role in this reaction, and significantly affects the product formation and reaction rate. Sonogashira coupling of aryl iodides and aryl bromides in dimethylsulfoxide or dimethylformamide gave the coupled products in good to excellent yields. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: amino acid; copper catalysis; cross-coupling reaction; Sonogashira; internal alkyne

Introduction

Amino acids are organic compounds that form one of the most prominent tools of natural products, and they are known as the building blocks of life.[1–3]

Nowadays, a great deal of progress has been made in improving the reaction conditions and designing ligands for metal-catalyzed carbon–carbon and carbon–heteroatom bond forming reactions.[4–6] Combinations of metal salts and ligands are efficient catalytic systems for the formation of C–O, C–N and C–C bonds.[7,8] Several groups have reported that some bidentate compounds like diketones,[9] 1,2-diamines,[10,11] 1,2-diols[12] and 1,10-phenanthroline[13] could serve as ligands to facilitate metal-catalyzed carbon–carbon and carbon–heteroatom cross-coupling reactions. A number of important studies have been focused on the development of synthetic routes that minimize contamination and pollution in chemical synthesis by use of green reagents in producing materials.[14,15]

It is known that the structure of α-amino acids as ligands can accelerate metal-catalyzed reactions.[16–18] Ma *et al*. have reported the widespread applications of amino acids as promoters in Cu-assisted coupling reactions.[19,20] They reported the coupling reactions of aryl halides and α-amino acids. That group also found that *N*-methylglycine and L-proline were suitable promoters in the Cu-catalyzed coupling reactions of aryl halides with various nucleophiles.[21–27]

Transition metal-catalyzed carbon–carbon bond formation has been used in the synthesis of many pharmaceuticals and natural and industrial products.[28–30] The Sonogashira coupling reaction is a powerful synthetic method for the construction of sp^2–sp carbon–carbon bonds by the introduction of a triple bond into aromatic systems via cross-coupling of aryl/alkyl halides and terminal acetylene,[31,32] frequently employed in the synthesis of both biologically and synthetically important aryl acetylenes.[33–35] This reaction generally employs Pd catalyst and Cu(I) salt as co-catalyst simultaneously.[36,37] This reaction system results in an increased reactivity of the reagents and the ability of the reaction to be carried out at room temperature. The copper co-catalyst generates a copper acetylide intermediate that subsequently transmetallates on the palladium center. Many different palladium-based catalytic systems, regardless of whether or not a copper co-catalyst is used, have been applied for this reaction,[38–40] which is problematic for industrial use due to the cost of palladium. However, the use of effective palladium-free systems, including copper, zinc or iron, would obviously be much more interesting in view of modern organic synthesis owing to the lower cost and easy availability of these systems.[41–44] A number of important studies have focused on the development of new catalytic systems including phosphine- and palladium-free conditions.[45] Various catalytic systems based on iron,[42] cobalt,[46] nickel[47] and silver,[48] in combination with different ligands have been reported for Sonogashira coupling reactions.

Copper-based catalysts are powerful in organic reactions because they can easily access Cu(0), Cu(I), Cu(II) and Cu(III) oxidation states,[49] allowing them to act through both radical and/or powerful two-electron bond-forming pathways via organometallic intermediates similar to those of palladium catalysts. Recent attention has been focused on employing copper-only catalytic systems in Sonogashira couplings. Bolm and co-workers[50] have reported coupling reactions between various aryl iodides and terminal alkynes

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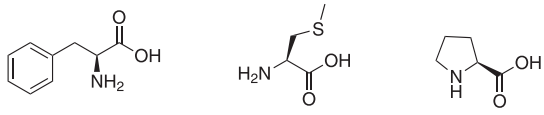
using [Cu(*N*,*N*′-dimethylethylenediamine)$_2$]Cl$_2$·H$_2$O as a catalyst precursor in dioxane at 135°C in a reaction time of 22 h. Li *et al.*[51] investigated the CuI/1,4-diazabicyclo[2.2.2]octane (DABCO) catalytic system in Sonogashira cross-couplings of aryl halides and vinyl halides. Here, the coupling reactions were carried out using 10 mol % of CuI catalyst, 20 mol% of DABCO ligand and Cs_2CO_3 as the base in dimethylformamide (DMF) at 135–140°C in 4–25 h. Sonogashira coupling of a variety of aryl halides using 10 mol% of CuI, 30 mol % of β-diketone ligand and K_2CO_3 base in DMF at 90–120°C in 24–40 h was reported by Monnier *et al.*[52] Ma and Liu[53] introduced a Cu(I)/amino acid catalytic system for Sonogashira coupling reactions. They obtained coupled products using CuI (10 mol%) as catalyst and *N*,*N*-dimethylglycine hydrochloride salt (30 mol%) as promoter in the presence of K_2CO_3 and DMF at 100°C in 24–36 h. Xu *et al*. have recently reported catalytic systems featuring low copper loading (0.5 mol% $<$ Cu $<$ 5 mol%) for copper-catalyzed Sonogashira-type reactions accelerated by a catalytic amount of additives such as polycyclic aromatic hydrocarbon or organophosphate as the ligand.[54,55] They found Cu(OTf)$_2$ as an effective copper source in this reaction system. Based on these reports, it can be concluded that most of the palladium-free copper-catalyzed Sonogashira coupling reactions usually require high temperatures and/or long reaction times.

In continuation of our recent studies on the design of catalytic systems containing amino acids,[56,57] and as a part of our goal to develop copper-based catalysts for Sonogashira coupling reactions,[58,59] in the work reported herein we evaluated the actions of several combinations of CuI/amino acids in Sonogashira coupling reactions (Scheme 1). Between the different tested amino acids (phenylalanine, methionine and proline), methionine showed the best results. The solvent system was found to have an important role in this reaction system. A variety of aryl halides with phenylacetylene were coupled to afford the corresponding internal alkynes in good to excellent yields. A catalytic amount of methionine (8 mol%) as a green promoter was used for aryl iodides in this transformation.

Results and discussion

Here, the efficiency of CuI/amino acid has been examined as a catalytic system for the reaction of aryl halides with phenylacetylene. Initially, we chose the reaction of 4-iodonitrobenzene with phenylacetylene as a model to begin this investigation (Table 1). It is found that, in the absence of supporting ligand, the reaction gives 1,4-diphenylbuta-1,3-diyne as the main product from homocoupling of phenylacetylene through a Glaser-type reaction.[60] Many research groups have reported the use of amino acids as promoter ligands in metal-catalyzed coupling reactions,[16,19] especially for copper-based catalytic systems. Accordingly, we examined the efficiency of using CuI catalyst in combination with amino acid ligands for this reaction system.



Scheme 1. Structure of amino acids examined in this study.

It is found that by employing CuI (10 mol%), K_3PO_4 (2 equiv.) and L-proline (30 mol%) in the mixed solvent DMF–H$_2$O (80:20) at 130°C, the corresponding alkyne product is obtained in 67% yield after 3 h (Table 1, entry 1). This result clearly indicates that the α-amino acid has an accelerating effect on the coupling of 4-iodonitrobenzene with phenylacetylene. Encouraged by this result, we also investigated the efficiency of two amino acids, phenylalanine and methionine, as the ligands in this reaction. Using phenylalanine as the promoter, a decreased yield of the desirable product **2a** is obtained from the reaction of substrate 4-iodonitrobenzene with phenylacetylene (46% yield; Table 1, entry 3). However, the yield of **2a** is increased to 83% when using methionine (Table 1, entry 2). These results show that under these reaction conditions, methionine is more effective than phenylalanine and proline.

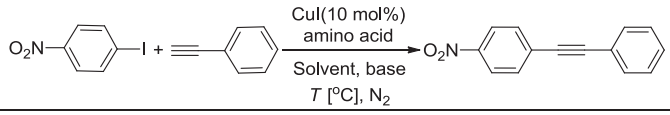
To further investigate and compare the performance of proline and methionine as the promoter in this transformation, we also examined the efficiency of both promoters using 4-iodoanisole as the substrate. It is found that the treatment of 4-iodoanisole with phenylacetylene, CuI (10 mol%), proline (8 mol%) and K_3PO_4 (2 equiv.) in dimethylsulfoxide (DMSO) at 135–140°C affords the coupled product in 75% GC yield after 7 h. However, methionine shows a better result under the same reaction conditions, affording 93% GC yield of the desired product. We also investigated the efficiency of methionine (8 mol%) as the ligand in this transformation using 4-iodoanisole substrate and employing CuI (10 mol%) and K_2CO_3 (3 equiv.) in DMF at 100°C. The corresponding Sonogashira product is obtained in 10% yield after 7 h and in 65% yield after 15 h.

The accelerating effect of amino acid ligands in the coupling of aryl bromides with phenylacetylene was also investigated using the coupling of 4-bromonitrobenzene and phenylacetylene as a model reaction. As evident from Table 2, all amino acids that we chose can prompt the coupling reaction by employing CuI (10 mol%) and K_3PO_4 (2 equiv) in DMSO at 140°C. Here, similar to the case of aryl iodides, methionine and proline give better conversions than phenylalanine. Based on these results, we applied methionine as the promoter for the CuI-catalyzed Sonogashira coupling of various aryl halides.

In order to optimize the reaction conditions, we then examined the effect of different reaction parameters such as solvent, temperature and amino acid concentration on yields of the coupling products as summarized in Tables 1 and 2. The data show that the best results are obtained using K_3PO_4 as the base at 135–140°C. It is noteworthy that the solvent system plays an important role in this reaction. Among the various solvents tested, such as DMF, DMSO, poly(ethylene glycol) (PEG), *N*-methyl-2-pyrrolidone (NMP) and DMF–H$_2$O (8:2), DMSO gives the best result. However, for some aryl halide substrates in this reaction system, DMF gives better results (Table 3, entries 6 and 14). The concentration of methionine was also examined in this reaction system. Amounts of 8 mol% for aryl iodide substrates and 15 mol% for aryl bromides are obtained as the optimum amounts.

After optimizing the reaction conditions, we then explored the scope and limitations of this transformation (Table 3), and the CuI/amino acid catalytic system was applied in the Sonogashira coupling of various aryl halides with phenylacetylene. The corresponding internal alkynes are produced in moderate to excellent yields. In this reaction system, the effect of solvent on the resulting yields and conversion times of the reactions is important to note. In most cases, DMSO is an effective medium for the coupling reactions (Table 3, entries 1, 2, 4, 10, 12). However, for some substrates (Table 3, entries 6, 14, 15), DMF gives better results. For example,

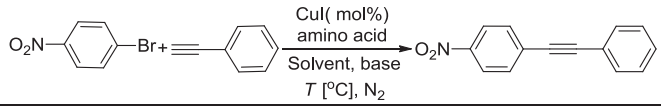
Table 1. Optimization of reaction conditions for Sonogashira coupling[a]



Entry	Solvent	Base (2 equiv.)	Ligand	T (°C)	Yield (%)[b]
1	DMF–H_2O (80:20)	K_3PO_4	L-Proline (30 mol%)	130	67
2	DMF–H_2O (80:20)	K_3PO_4	L-Methionine (30 mol%)	130	83
3	DMF–H_2O (80:20)	K_3PO_4	L-Phenylalanine (30 mol%)	130	46
4	DMF–H_2O (80:20)	K_2CO_3	L-Methionine (30 mol%)	130	82
5	DMF–H_2O (80:20)	KOH	L-Methionine (30 mol%)	130	55
6	DMF–H_2O (80:20)	K_2CO_3	L-Methionine (15 mol%)	130	78
7	DMSO	K_3PO_4	L-Methionine (8 mol%)	140	95
8	DMF	K_3PO_4	L-Methionine (8 mol%)	140	50
9	DMF–DMSO (50:50)	K_3PO_4	L-Methionine (8 mol%)	140	43
10	DMF	K_2CO_3 (3 equiv.)	L-Methionine (8 mol%)	100	12

[a]Reaction conditions: 4-nitroiodobenzene (0.1 mmol), phenylacetylene (0.12 mmol), reaction time: 3 h.
[b]GC yield.

Table 2. Optimization of reaction conditions for Sonogashira coupling[a]



Entry	Solvent	Base (2 equiv.)	Ligand	CuI (mol%)	T (°C)	Yield (%)[b]
1	DMSO	K_3PO_4	L-Proline	10	140	90
2	DMSO	K_3PO_4	L-Methionine	10	140	90
3	DMSO	K_3PO_4	L-Phenylalanine	10	140	78
4	DMF	K_3PO_4	L-Proline	10	140	45
5	NMP	K_3PO_4	L-Proline	10	140	15
6	PEG	K_3PO_4	L-Proline	10	140	-
7	DMSO	K_2CO_3	L-Methionine	10	140	50
8	DMSO	K_3PO_4	L-Methionine	10	130	25
9	DMF–H_2O (80:20)	K_3PO_4	L-Proline	10	130	Trace
10	DMF–H_2O (80:20)	K_3PO_4	L-Methionine	10	130	Trace
11	DMSO	K_3PO_4	L-Methionine	5	140	85

[a]Reaction conditions: 4-nitrobromobenzene (0.1 mmol), phenylacetylene (0.12 mmol), ligand (15 mol%), reaction time: 1 h.
[b]GC yield.

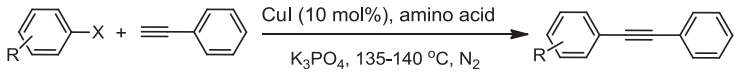
with 4′-iodoacetophenone as the substrate in DMSO solvent only a trace amount of the corresponding Sonogashira product is afforded (Table 3, entry 5); however, the use of DMF as the solvent system, under the same reaction conditions, increases the yield of the coupled product strongly (up to 91%).

We examined the electronic and steric effects on the yields and reaction times of the couplings. This catalytic system is compatible with a wide range of functional groups such as nitro, cyano, methoxy and carbonyl on the aryl halides. Electron-poor aryl halides transform to the corresponding coupled products rather than electron-rich aryl halides with better conversion and shorter reaction times. The effects of steric hindrance of the procedure were examined using 2-iodonitrobenzene (Table 3, entry 8). An increasing hindrance in the vicinity of the leaving group results in a decrease in the conversion. As evident from Table 3, most aryl iodides are successfully converted to the corresponding Sonogashira products in excellent yields. Aryl bromides also react with phenylacetylene to afford the corresponding alkyne products (Table 3, entries 12–15). However, the reactivity of aryl bromides is lower than that of aryl iodides and they require longer times giving lower yields. Aryl chlorides are inactive in this reaction system.

For the Cu(I)/α-amino acid catalytic system, an accelerating effect is induced by the structure of the α-amino acid in Cu-catalyzed coupling reactions. It is well known that copper ions can form chelates with amino acids through carboxyl and amino groups.[19] The ability of amino acids to promote coupling reactions might be dependent on their coordination ability as bidentate additives.

To date, several mechanisms for copper-assisted Sonogashira coupling reactions have been described in the literature.

Table 3. Sonogashira coupling reactions of aryl halides with phenylacetylene[a]



Entry	Ar–X	Solvent	Time (h)	Yield (%)[b]
1	*p*-O_2N–Ph–I	DMSO	2	92
2	*p*-MeO–Ph–I	DMSO	7	90
3	*p*-MeO–Ph–I	DMF	15	75
4	*p*-NC–Ph–I	DMSO	2	98
5	*p*-MeOC–Ph–I	DMSO	10	Trace
6	*p*-MeOC–Ph–I	DMF	6	91
7	*m*-O_2N–Ph–I	DMSO	1.5	98
8	*o*-O_2N–Ph–I	DMSO	2	20
9	*p*-Me–Ph–I	DMSO	20	65
10[c]	*p*-I–Ph–I	DMSO	4	99
11	Ph–I	DMSO	7	80
12	*m*-Me–Ph–I	DMSO	15	70
13[d]	*m*-Br–Ph–I	DMSO	7	81
14	*p*-O_2N–Ph–Br	DMSO	1	80
15	*p*-MeOC–Ph–Br	DMSO	15	Trace
16	*p*-MeOC–Ph–Br	DMF	15	50
17[e]	*p*-NC–Ph–Br	DMF	5	80
18	*p*-O_2N–Ph–Cl	DMSO	10	Trace

[a]Reaction conditions: aryl halide (0.5 mmol), phenylacetylene (0.52 mmol), K_3PO_4 (1 mmol), methionine (8 mol% for Ar–I and 15 mol% for Ar–Br), solvent, CuI (10 mol%), nitrogen atmosphere.

[b]Isolated yield.

[c]1.2 mmol phenylacetylene was used for 0.5 mmol aryl halide. Final product was 1,4-bis(phenylethynyl)benzene.

[d]1.2 mmol pPhenylacetylene was used for 0.5 mmol aryl halide. Selected product was 1,3-bis(phenylethynyl)benzene.

[e]Proline (20 mol%) was used as the ligand.

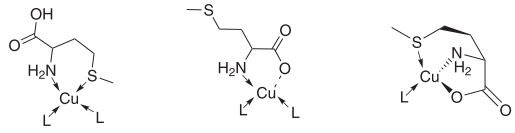
Taillefer and co-workers[52] have reported a mechanism of Cu-catalyzed Sonogashira coupling in the presence of β-diketone ligand. They proposed that the resting state Cu(I)–diketone complex reacts with alkyne in the presence of base to generate a Cu(I)–acetylide intermediate. This then would react by oxidative addition with the aryl halide to form a four-coordinated Cu (III) complex which undergoes reductive elimination to expel the coupled product. Miura and co-workers also suggested a Cu(I)/Cu(III) mechanistic pathway for copper-catalyzed coupling reactions.[61]

Bolm and co-workers[50] investigated the coupling reaction between aryl iodides and terminal arylalkynes using a copper catalyst being accelerated by diamine ligands at 135°C. They proposed a mechanism for this coupling reaction based on kinetic measurements and density functional theory calculations. That group suggested that the reaction proceeds by concerted C–I bond dissociation and new C–C bond formation, and that this is the rate-limiting step. They believed that in this pathway for the coupled-product formation, there is no stable Cu(III) intermediate. A similar mechanism was suggested by Sagadevan and Hwang[62] for the Sonogashira C–C coupling reaction using copper(I) chloride catalyst under blue light-emitting diode light irradiation at room temperature. Based on these reports, two mechanisms can be put forward for our Cu(I)-catalyzed amino acid-promoted Sonogashira coupling reactions. In the oxidative addition/ reductive elimination pathway, involving a four-coordinate Cu(III) intermediate, the complex formation of Cu(I) with an amino acid makes Cu(I) species more reactive toward the oxidative addition to form a copper(III) complex or stabilizes this intermediate, promoting the coupling reaction.

According to the mechanism of Bolm and co-workers,[50] this reaction may also proceed by a concerted breaking of the aryl halide bond and formation of a new C–C bond, giving the coupled product.

There is less experimental evidence for mechanisms of aryl halide activation in Cu(I)-catalyzed coupling reactions. Whether a Cu(III) complex is ever formed, or the product is formed directly, is under investigation in mechanistic studies.[63]

As previously mentioned, among the tested amino acids as promoters in this reaction system (L-phenylalanine, L-proline and L-methionine), methionine gives the best results. Methionine is a sulfur-containing amino acid. The greater ability of this amino acid to promote coupling reactions might be dependent on the presence of thioether sulfur donors in its structure. Methionine addition to the N and O donor groups[64] using sulfur groups can also be chelated, which may lead to more active and stable Cu(I) species in the reaction medium (Scheme 2).



Scheme 2. Possible complexations of methionine and copper.

Conclusions

We have demonstrated that amino acid ligands are able to promote copper-catalyzed Sonogashira C–C bond formation reactions. The key was the choice of a suitable amino acid as the ligand. Using the palladium-free catalytic system CuI/amino acid, a variety of substituted aromatic alkynes were prepared in good to excellent yields. In most cases, a catalytic amount of L-methionine was effective as the promoter for the coupling reactions. The contamination of product with ligands is always one of the most important problems of homogeneous catalysis. It is worth mentioning that this promoter is inexpensive and readily available. In addition, it is soluble in water and can be removed from the crude products by simply washing with water.

Experimental

General procedure for sonogashira cross-coupling

Aryl halide (0.5 mmol), K_3PO_4 (1 mmol), methionine (8 mol%, 0.006 g for Ar–I; 15 mol%, 0.011 g for Ar–Br), CuI (10 mol%, 0.01 g) and phenylacetylene (0.52 mmol) in DMSO or DMF were introduced into a round-bottom flask equipped with a stirring bar and a reflux condenser under a nitrogen atmosphere. The mixture was stirred at 135–140°C and the reaction progress was monitored using TLC and GC. After the reaction was complete, or when the progress of the reaction had stopped, the cooled resulting mixture was diluted by adding EtOAc–H_2O. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous $CaCl_2$, filtered and concentrated to give the corresponding product, which could be purified using column chromatography (hexane–EtOAc). The arylalkyne products were known compounds[52,65,66] and were characterized using Fourier transform infrared, ^{1}H NMR and ^{13}C NMR spectroscopies.

Acknowledgments

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