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# Multicomponent Synthesis of 1,2,3-Triazoles in Water Catalyzed by Copper Nanoparticles on Activated Carbon


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Dedicated to Professor Carmen Nájera on the occasion of her 60th birthday.

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**Abstract:** Copper nanoparticles on activated carbon have been found to effectively catalyze the multicomponent synthesis of 1,2,3-triazoles from different azide precursors, such as organic halides, diazonium salts, anilines and epoxides in water. The first one-pot transformation of an olefin into a triazole is also described. The catalyst is easy to prepare, very versatile and reusable at a low copper loading.

**Keywords:** click chemistry; copper nanoparticles; cycloaddition; heterogeneous catalysis; triazoles; water

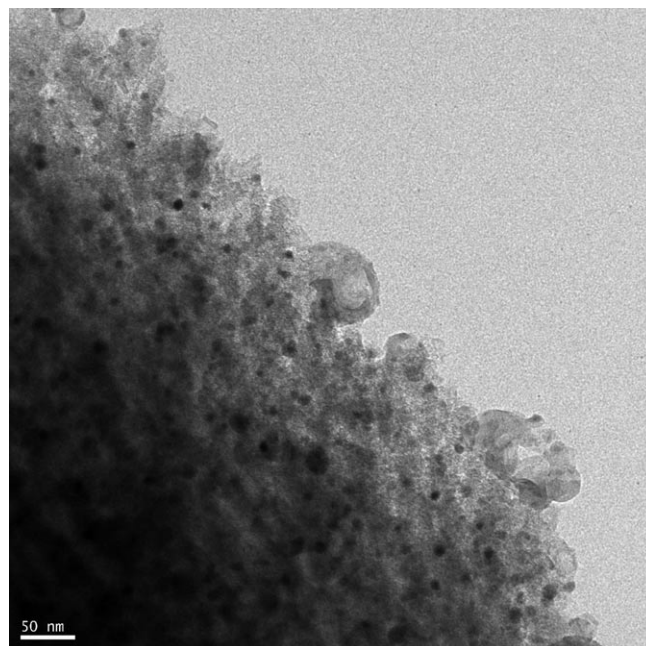
Since the paramount discovery by the groups of Meldal<sup>[1]</sup> and Sharpless<sup>[2]</sup> of the copper(I)-catalyzed Huisgen<sup>[3]</sup> 1,3-dipolar cycloaddition of organic azides and alkynes, a plethora of methods have flourished around this reaction.<sup>[4]</sup> Enormous efforts have been devoted in order to maximize the general efficiency of the process adapted to the multiple and manifold applications of the resulting 1,2,3-triazoles.<sup>[4,5]</sup> For instance, to reduce the amounts of copper in solution should be a priority, particularly for biological applications, due to its potential toxicity.<sup>[6]</sup> In this sense, heterogeneous catalysts offer several advantages over the homogeneous counterparts, such as easy recovery, easy recycling, and enhanced stability.<sup>[7]</sup> Charcoal,<sup>[8]</sup> zeolites,<sup>[9]</sup> montmorillonite,<sup>[10]</sup> NHC-modified silica,<sup>[11]</sup> polystyrene<sup>[12]</sup> or chitosan<sup>[13]</sup> are some of the supports used for copper(I) in the heterogeneous version of the title click reaction. Since the discovery that copper metal can be a source of the catalytic species,<sup>[14]</sup> copper nanoparticles have also emerged as ef-

ficient heterogeneous and potentially reusable catalysts.<sup>[15]</sup> All the aforementioned methodologies, however, involve pre-formed organic azides, for which the use of organic solvents (e.g., dioxane, toluene, DMF, dichloromethane, hexane) is, in general, mandatory. The *in-situ* generation of organic azides in the presence of the alkyne (three-component alkyne-azide cycloaddition)<sup>[16]</sup> minimizes hazards derived from their isolation and handling, at the same time this avoids the time expenditure and waste generation of an additional synthetic step. This version is especially interesting when performed under heterogeneous conditions in neat water.<sup>[17]</sup> Despite the clear advantages of heterogeneous catalysis, the long and tedious procedures usually required for the heterogenization of copper preclude the widespread utilization of this type of catalysts. Therefore, easy-to-prepare and versatile heterogeneous copper catalysts that can efficiently catalyze the multicomponent 1,3-dipolar cycloaddition of organic azides and alkynes in water are welcome.

Our ongoing interest on the reactivity of active metals<sup>[18]</sup> led us to the application of active copper [from CuCl<sub>2</sub>·2H<sub>2</sub>O, Li, and 4,4'-di-*tert*-butylbiphenyl (DTBB, cat.) in THF] in reduction reactions.<sup>[19]</sup> More recently, we discovered that unsupported copper nanoparticles, generated as above but from anhydrous CuCl<sub>2</sub>, effectively catalyze the 1,3-dipolar cycloaddition of azides and terminal alkynes in short reaction times and in the absence of any stabilizing additive or ligand.<sup>[20]</sup> Notwithstanding the superior catalytic activity when compared with other commercially available copper sources, the copper nanoparticles underwent dissolution under the reaction conditions (Et<sub>3</sub>N, THF, 65°C) and could not be reused. We wish to present herein our findings on the 1,3-dipolar cycloaddition of

alkynes and *in-situ* generated azides, from different precursors, catalyzed by copper nanoparticles supported on activated carbon in water.

A variety of copper catalysts were prepared by addition of the support to a suspension of the recently prepared copper nanoparticles, the latter readily generated from copper(II) chloride, lithium metal, and a catalytic amount of DTBB (10 mol%) in THF at room temperature. The catalysts were not subjected to any pre-treatment. Benzyl bromide (**1a**) and phenylacetylene (**2a**) were used as model substrates in order to test the activity of the different catalysts (Table 1). SiO<sub>2</sub> (entry 1), Al<sub>2</sub>O<sub>3</sub> (entry 2), Al silicate (entry 6), magnetite (entry 9), graphite (entry 14), MWCNT (entry 15), and activated carbon (entry 19) led to yields  $\geq 90\%$  in  $\leq 9$  h at 70 °C. Activated carbon, however, was shown to be more active (100% yield, 3 h) and the sole catalyst providing a quantitative yield of **3aa** when reused in a second cycle (entry 19). When the cycloaddition was performed with activated carbon, in the absence of copper, a



**Figure 1.** TEM micrograph of CuNPs on active carbon.

**Table 1.** Three-component 1,3-dipolar azide-alkyne cycloaddition catalyzed by copper on different supports.<sup>[a]</sup>

Entry	Support [mol% Cu] <sup>[b]</sup>	T [°C]	t [h]	Yield [%] <sup>[c]</sup>
1	SiO <sub>2</sub> [1]	70	4	90 (16)
2	Al <sub>2</sub> O <sub>3</sub> [1]	70	9	100 (13)
3	TiO <sub>2</sub> [1]	70	24	74
4	MgO [1]	70	24	16
5	ZnO <sub>2</sub> [1]	70	24	57
6	Al silicate [1]	70	6	100 (19)
7	Al [1]	70	24	18
8	MCM-10 [1]	70	24	17
9	magnetite [1]	70	9	100 (0)
10	graphite [5]	70	14	80
11	graphite [5] <sup>[d]</sup>	70	24	0
12	graphite [5]	25	24	33
13	graphite [1]	25	24	31
14	graphite [1]	70	7	90
15	MWCNT <sup>[e]</sup> [5]	70	6	100 (20)
16	activated carbon [5]	70	7	100
17	activated carbon [5] <sup>[d]</sup>	70	24	0
18	activated carbon [5]	25	24	30
19	activated carbon [1]	70	3	100 (100)
20	activated carbon [0]	70	24	50 <sup>[f]</sup>

<sup>[a]</sup> **1a** (1 mmol), NaN<sub>3</sub> (1.1 mmol), and **2a** (1 mmol) in H<sub>2</sub>O.

<sup>[b]</sup> Amount of copper added to the support.

<sup>[c]</sup> GLC yield; the yield after a second cycle in parenthesis.

<sup>[d]</sup> Solvent-free reaction.

<sup>[e]</sup> Multi-walled carbon nanotube.

<sup>[f]</sup> As a 1:1.3 mixture of regioisomers; alkyne 19%; azide 31%.

lower yield of the two regioisomeric triazoles was obtained (entry 20).

The copper-on-activated-carbon catalyst was characterized by different means. The copper content in the catalyst, 1.6 wt%, was determined by inductively coupled plasma mass spectrometry (ICP-MS). Analysis by TEM revealed the presence of spherical nanoparticles dispersed on the active carbon with diameters of *ca.* 6 ± 2 nm (Figure 1). Energy-dispersive X-ray (EDX) analysis on various regions confirmed the presence of copper, with energy bands of 8.04, 8.90 keV (K lines) and 0.92 keV (L line). The XRD diffractogram did not show any significant peak due to the amorphous character of the sample, to the fact that the crystal domains are < 10 nm, and/or low copper loading weight. XPS analysis showed two O (1s) peaks at 532.2 and 534.2 eV, and three Cu (2p<sub>3/2</sub>) peaks at 934.1, 936.4, and 945.7 eV. From these results it can be inferred that the surface of the copper nanocatalyst is mainly oxidized. All peaks corresponding to the Cu (2p<sub>3/2</sub>) level appear at higher binding energy when compared with those obtained with unsupported copper nanoparticles,<sup>[20]</sup> with the peak at 945.7 eV being a satellite shake-up feature characteristic of Cu<sup>2+</sup> species.<sup>[21]</sup> The selected-area electron-diffraction pattern (SAED) of the copper nanoparticles is also in agreement with the presence of Cu<sub>2</sub>O and CuO. It is worthy of note that mixed Cu/Cu-oxide<sup>[15c]</sup> and, very recently, CuO nanostructures<sup>[22]</sup> have been found to catalyze the 1,3-dipolar cycloaddition of azides and terminal alkynes.

**Table 2.** Three-component 1,3-dipolar cycloaddition catalyzed by CuNPs/C using organic halides as the azide precursors.<sup>[a]</sup>

$$\text{R}^1\text{Hal} \quad \text{1} + \text{NaN}_3 + \text{C}\equiv\text{C-R}^2 \quad \text{2} \xrightarrow[\text{H}_2\text{O, 70 }^\circ\text{C}]{0.5 \text{ mol\% CuNPs/C}} \text{R}^1\text{-N=N-C=C-R}^2 \quad \text{3}$$

Entry	Organic Halide	Alkyne	t [h]	Triazole	Yield [%] <sup>[b]</sup>
1			3		98
			6		99
2			5		99
3			4		98
4			3		94
5			7		82
6			4		98
7			5 <sup>[c]</sup>		98
			8 <sup>[c,d]</sup>		94
8			8 <sup>[c]</sup>		93
9			8		89
10			7		76
11			8		84
12			8		82
13 <sup>[e]</sup>			10		87

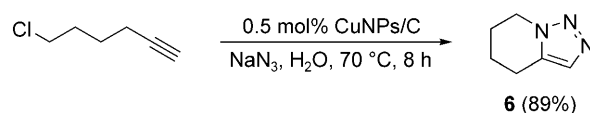
<sup>[a]</sup> Reaction conditions: **1** (1 mmol), **2** (1 mmol), NaN<sub>3</sub> (1.1 mmol), CuNPs/C (0.5 mol%) in H<sub>2</sub>O (2 mL) at 70 °C.<sup>[b]</sup> Isolated yield.<sup>[c]</sup> Reaction in H<sub>2</sub>O-EtOH 1:1.<sup>[d]</sup> Reaction at 100 °C.<sup>[e]</sup> 2 mmol of **1a**.

An array of activated organic halides (Table 2) was subjected to the three-component reaction with phenylacetylene in water at 70 °C, using 0.5 mol% CuNPs/C (Table 2, entries 1–6). Benzyl chloride reacted slower than the bromide counterpart albeit in excellent yield in both cases (entry 1). Benzyl bromides bearing either electron-withdrawing or electron-donating groups reacted nicely to furnish the corresponding triazoles in near quantitative yields (entries 2 and 3). A single product was obtained for cinnamyl bromide, with the intermediate azide not undergoing a [3,3]-sigmatropic rearrangement leading to the secondary allylic azide<sup>[23]</sup> under the reaction conditions (Table 2, entry 4). Some activated functionalized organic halides, such as  $\alpha$ -chloroacetophenone (entry 5) or ethyl  $\alpha$ -bromoacetate (entry 6), were also studied, with the former reacting more sluggishly. Interestingly, not only activated but also deactivated alkyl halides could be used as the azide precursors in the title reaction (entries 7 and 8). A solvent system composed of 1:1 H<sub>2</sub>O-EtOH is, however, recommended in order to attain optimum results. *n*-Nonyl iodide (entry 7, X=I) and cyclohexyl bromide (entry 8) reacted at 70 °C, whereas a temperature of 100 °C was required for the more reluctant to react *n*-nonyl chloride (entry 7, X=Cl). The substrate 3-(2-bromoethyl)-1*H*-indole furnished the attractive doubly heterocyclic product **3ia** (entry 9). The methodology also proved to be effective for alkynes other than phenylacetylene, such as phenyl propargyl ether (**2b**) or *N*-propargylphthalimide (**2c**) (entries 10 and 11, respectively). The successful reaction with trimethylsilylacetylene provides an indirect entry into the monosubstituted triazoles (after proper desilylation), making unnecessary the handling of acetylene (entry 12). Moreover, bistriazole **3ae** was obtained in good yield from diyne **2e** and two equivalents of benzyl bromide.

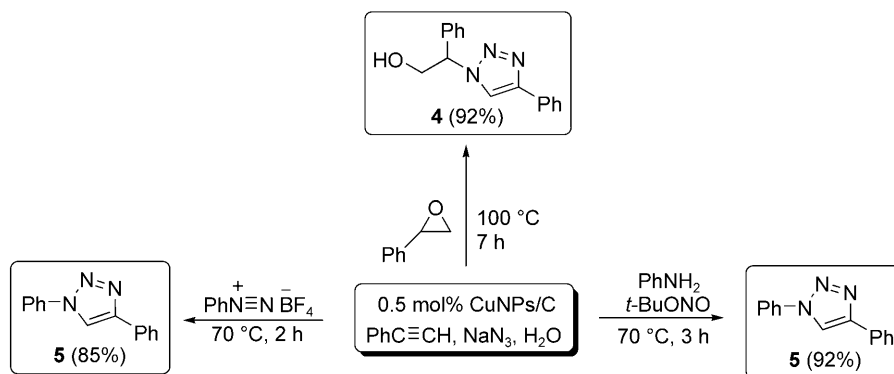
We next explored the possibility of using alternative substrates to the organic halides as azide precursors which, being compatible with the standard reaction conditions, could expand the versatility of the

catalyst (Scheme 1). We were delighted to discover that epoxides reacted in water at 100 °C in a three-component mode,<sup>[24]</sup> while other protocols require the sequential addition of reagents.<sup>[24a]</sup> As an example, styrene oxide was regioselectively transformed into the corresponding 2-substituted triazol-1-yl alcohol in high yield (Scheme 1). Diazonium salts, such as commercially available phenyldiazonium tetrafluoroborate, were utilized for the first time as potential substitutes of the less reactive aromatic halides (Scheme 1). Even more attractive was the four-component strategy involving an aromatic amine and *tert*-butyl nitrite at 70 °C (Scheme 1). This result is remarkable if we take into account that, in the only published method for this transformation, *t*-BuONO was used together with TMSN<sub>3</sub> (NaN<sub>3</sub> in our case) and applied sequentially in organic media.<sup>[25]</sup> It is noteworthy that the reactivity of both the diazonium salt and aniline were comparable to that of benzyl bromide (2–3 h).

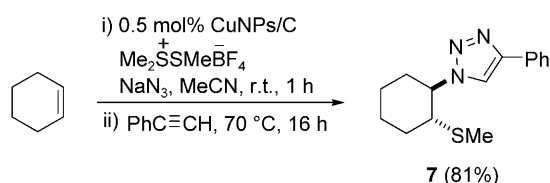
We were intrigued by the possibility of using haloalkynes, the derived azides of which might react either in an intramolecular or intermolecular fashion. Our expectations came to reality by subjecting 6-chlorohex-1-yne to the standard reaction conditions (Scheme 2). The bicyclic triazole **6** was synthesized for the first time in a straight-forward manner using click chemistry, while other reported procedures involved several synthetic steps.<sup>[26]</sup> Furthermore, the transformation of alkenes into triazoles was also devised by taking advantage of the azasulfenylation of alkenes developed by Trost et al.<sup>[27]</sup> In this methodolo-



**Scheme 2.** Intramolecular three-component click reaction catalyzed by CuNPs/C in water.



**Scheme 1.** Reaction of phenylacetylene with different azide precursors catalyzed by CuNPs/C in water.



**Scheme 3.** One-pot multicomponent synthesis of a 1,2,3-triazole from cyclohexene catalyzed by CuNPs/C.

gy, an alkene was treated with dimethyl(methylthio)sulfonium tetrafluoroborate (DMTSF) at 0°C to room temperature, followed by the addition of a nitrogen nucleophile at room temperature and stirring for 1–4 days. We applied a variation of this method in which the alkene was directly mixed with the CuNPs/C, DMTSF, and NaN<sub>3</sub> in MeCN to produce the corresponding methylsulfanyl azide in only 1 h at room temperature. The subsequent reaction with the alkyne represents, to the best of our knowledge, the first example of triazole synthesis from an alkene in one pot (Scheme 3). The conditions and yield were not optimized yet but it seems a promising route to directly transform carbon-carbon double bonds into triazoles bearing a versatile methylsulfanyl group.

It is worthwhile mentioning that all the reactions were carried out without air exclusion. Furthermore, reactions at a higher dilution, such as 0.1 M or even 0.01 M, also afforded the expected triazoles in high yields, albeit longer reaction times were required (i.e., 8 and 24 h, respectively, for benzyl bromide and phenylacetylene). In addition, the catalyst could be easily recovered by filtration and reused, leading to triazole **3aa** in quantitative yield along five consecutive cycles. No leaching of copper was detected after the fifth cycle (ICP-MS). Nonetheless, in order to test the robustness of the catalyst and unveil the nature of the catalysis, the reaction of benzyl bromide and phenylacetylene was run up to a 100% conversion (<3 h), and the resulting mixture containing the triazole was subjected to additional heating until a total time of 24 h. Then, the catalyst and the triazole were filtered off, the aqueous phase was extracted with ethyl acetate and fresh starting materials were again added to the resulting aqueous phase, which were allowed to react at 70°C for 24 h. A *ca.* 1:1 mixture of the corresponding regioisomeric triazoles was obtained with 17% conversion, thereby indicating that, in this case, the cycloaddition proceeded uncatalyzed under thermal conditions. ICP-MS analyses of the resulting aqueous phase gave <50 ppb of copper. These results point to a process of heterogeneous nature.

Finally, we compared the CuNPs/C catalyst with commercially available Cu, Cu<sub>2</sub>O, and CuO in the reaction of benzyl bromide and phenylacetylene under the standard conditions at 10 and 1 mol% catalyst

loading. Interestingly, 10 mol% Cu<sub>2</sub>O reached a maximum 90% conversion, albeit side products (10%) were also obtained and its reutilization furnished the corresponding triazole in 20% conversion after 24 h as a *ca.* 4:1 mixture of regioisomers. Therefore, the nanosized character of our catalyst makes all the difference.

In conclusion, we have presented a new heterogeneous catalyst for the multicomponent Huisgen 1,3-dipolar cycloaddition in water. The catalyst consists of oxidized copper nanoparticles on activated carbon and it is readily prepared from commercially available chemicals under mild conditions. The CuNPs/C, at a low catalyst loading (0.5 mol%), manifested a high versatility as not only organic halides, but other azide precursors, including epoxides, diazonium salts, anilines, or alkenes, could be successfully transformed into the corresponding 1,2,3-triazoles. The catalyst is reusable and seemingly operates under heterogeneous conditions. Further research to extend the substrate scope and better understand the catalysis is under way.

## Experimental Section

### Typical Procedure for the Preparation of CuNPs/C

Anhydrous copper(II) chloride (135 mg, 1 mmol) was added to a suspension of lithium (14 mg, 2 mmol) and 4,4'-*di-tert*-butylbiphenyl (DTBB, 27 mg, 0.1 mmol) in THF (2 mL) at room temperature under an argon atmosphere. The reaction mixture, which was initially dark blue, rapidly changed to black, indicating that the suspension of copper nanoparticles was formed. This suspension was diluted with THF (18 mL) followed by the addition of the activated carbon (1.28 g). The resulting mixture was stirred for 1 h at room temperature, filtered, and the solid successively washed with water (20 mL), THF (20 mL) and dried under vacuum.

### General Procedure for Three-Component 1,3-Dipolar Cycloaddition Catalyzed by CuNPs/C in Water

NaN<sub>3</sub> (72 mg, 1.1 mmol), the azide precursor (organic halide, diazonium salt, or epoxide, 1 mmol) and the alkyne (1 mmol) were added to a suspension of CuNPs/C (20 mg, 0.5 mol% Cu) in H<sub>2</sub>O (2 mL). The reaction mixture was warmed to 70°C and monitored by TLC until total conversion of the starting materials. Water (30 mL) was added to the resulting mixture followed by extraction with EtOAc (3 × 10 mL). The collected organic phases were dried with MgSO<sub>4</sub> and the solvent was removed under vacuum to give the corresponding triazole, which did not require any further purification (except compounds **3ia** and **7**).

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