



RAPID COMMUNICATION

CuO-Nanoparticles Catalyzed Synthesis of 1,4-Disubstituted-1,2,3-Triazoles from Bromoalkenes

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Abstract. A novel and efficient protocol involving commercially available CuO nanoparticles (CNP) as catalyst has been developed for the synthesis of 1,2,3-triazoles. A library of 1,4-disubstituted 1,2,3-triazoles has been constructed with good to excellent yields.

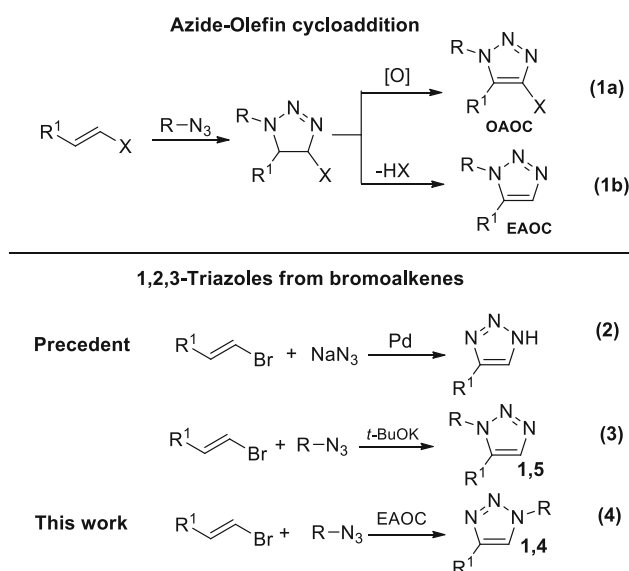
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1. Introduction

Despite the traditional Huisgen cycloaddition,^{1,2} 1,2,3-triazoles have drawn the attention of the scientific fraternity after the invention of copper-catalyzed azide-alkyne cycloaddition (CuAAC)^{3,4} owing to its amazing regio-selectivity, functional group tolerance and operational simplicity. Even though 1,2,3-triazoles have not been isolated from natural sources,⁵ they have unveiled new horizons in various areas such as drug discovery,^{6,7} materials,^{8,9} polymers¹⁰ and supramolecules.^{11,12} Besides their usage as synthetic intermediates,^{13–15} they have also enormously contributed to the industry as photo stabilizers, corrosion inhibitor, dyes, fluorescent whiteners and optical brightening agents.^{16,17} Subsequently, Ruthenium-catalyzed azide-alkyne cycloaddition (RuAAC) was developed to prepare the complementary 1,5-disubstituted 1,2,3-triazoles.^{18–20} However, alternative methods were sought out in the place of azide-alkyne cycloaddition since the synthetic and economic viability of alkynes emerged as a serious difficulty. In response to this need, olefins were envisaged in the place of alkynes since they have a better synthetic and commercial accessibility than alkynes.

This was ingeniously accomplished by oxidative azide-olefin cycloaddition (OAOC) and eliminative azide-olefin cycloaddition (EAOC). In OAOC, the triazoline formed by azide-olefin cycloaddition would concomitantly be oxidized into the corresponding triazole (Eq. 1a, Scheme 1). Whereas in EAOC, the olefin bearing a leaving group would undergo cycloaddition with the azide and the resulting triazoline would subsequently undergo elimination reaction to furnish the triazole (Eq. 1b, Scheme 1). In OAOC, electron-deficient olefins have been subjected to react with azides using various catalysts such as Cu(OTf)₂, Ce(OTf)₃, Cu(OAc)₂, CuI, CuO and Fe₂O₃-nanoparticles.^{21–26} Whereas in EAOC, olefins bearing the leaving groups such as alkoxy,^{27,28} acetate,²⁹ nitro^{30–34} and sulfone^{35,36} would be treated with azides to afford the triazoles. Another flamboyant category of EAOC is ‘organo click reactions’ in which electron-rich olefins such as enamines generated *in situ* would be treated with azides in the presence of organo catalysts such as secondary or tertiary amines.³⁷ In continuation of our previous contributions in azide-olefin cycloaddition of electron-deficient olefins and organic azides using CuO nanoparticles,^{38–41} we were prompted to examine the azide-olefin cycloaddition on

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Scheme 1. Background of EAOC of bromoalkenes and organic azides.

bromoalkenes and organic azides. Our literature perusal on this aspect revealed the palladium-catalyzed synthesis of 1*H*-1,2,3-triazoles from sodium azide and alkenyl bromides (Eq. 2, Scheme 1).⁴² Besides that, base-promoted synthesis of 1,5-disubstituted 1,2,3-triazoles from alkenyl bromides and organic azides also has been reported in the literature (Eq. 3, Scheme 1).⁴³ Kuang *et al.*, described Cu-catalyzed synthesis of 1*H*-1,2,3-triazoles from 1,1-dibromoalkenes and sodium azide.⁴⁴ Herein we report the synthesis of the complementary 1,4-disubstituted-1,2,3-triazoles from bromoalkenes and organic azides catalyzed by commercially available CuO nanoparticles (Eq. 4, Scheme 1).

2. Experimental

2.1 Materials and methods

All melting points were taken on Guna melting point apparatus and are uncorrected. High-resolution mass spectra were recorded on a JEOL GC Mate using electron impact ionization (EI) techniques. NMR spectra were obtained on a Bruker Ascend TM 400 NMR spectrometer; ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz respectively. The chemical shifts were reported in ppm downfield to TMS ($\delta = 0$) for ¹H NMR and relative to the middle CDCl₃ resonance ($\delta = 77.0$) for ¹³C NMR. In the ¹³C NMR spectra and the coupling constant (*J*) is given in Hz. For thin-layer chromatography (TLC), silica gel plates Merck 60 F₂₅₄ (0.25 mm thick) were used and compounds were visualized by irradiation with UV light and/or by treatment with Iodine. Column chromatography was performed either with Merck silica gel 60 (230–400 mesh) in common glass columns.

2.2 General Procedure for the Synthesis of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole

A mixture of bromostyrene (0.5 mmol), benzyl azide (1 mmol), CuO nanoparticles (50 mol%) and piperidine (1 mL) as a solvent were heated at 110 °C for 12 h. Completion of the reaction was monitored by TLC and the reaction mixture was cooled to room temperature. The resulting crude product was purified by column chromatography.

2.3 Spectral data of representative compounds

2.3a 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (3a): White solid, M.p.: 126–128 °C, ¹H NMR (400 MHz, CDCl₃): δ 7.81–7.79 (m, 2H), 7.66 (s, 1H), 7.42–7.36 (m, 5H), 7.33–7.29 (m, 3H), 5.58 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 148.3, 134.7, 130.6, 129.2, 128.8, 128.2, 128.1, 125.7, 119.5, 54.3 ppm.

3. Results and Discussion

At the outset, we embarked on our examination with β -bromostyrene (**1a**) and benzyl azide (**2a**) as the reference substrates with CuO nanoparticles in DMSO. Though we initially anticipated the 4-bromo-1,2,3-triazole by oxidative azide-olefin cycloaddition, we were surprised to see 1,4-disubstituted triazole (**3a**) in 60% yield which was accompanied by 15% of the other regioisomer **4a** (Table 1, entry 1). When *n*-octane was employed as the solvent in the place of DMSO, the yield of the triazole (**3a**) subsided to 20% (Table 1, entry 2). When other solvents such as chloroform, tetrahydrofuran, nitromethane, toluene and DMF were examined, only trace amount of the product (**3a**) was obtained (Table 1, entries 3–7). It is worth mentioning that the water has also failed to promote the reaction with a pronounceable yield of the product yield of **3a** (Table 1, entry 8). When we envisaged a basic condition for this transformation, we employed piperidine entrusted with a dual role as the base and solvent. Our expectation was vindicated with 90% yield of **3a** as the sole product (Table 1, entry 9). When the temperature of the reaction was gradually elevated from 90 °C to 110 °C, the yield of the product (**3a**) precipitously hiked to 97% (Table 1, entries 9–11). Subsequently, while other organic bases like triethylamine, morpholine and pyridine were examined in the place of piperidine, morpholine could exhibit a comparable effect with 85% yield of the product (**3a**) while the others lagged behind with a great margin (Table 1, entries 12–14). Other catalysts such as Ce(OTf)₃, Cu(OTf)₂, AlCl₃, CuCl₂, CuI and Copper nanopowder were tested in the place of CuO nanoparticles (Table 1, entries 15–20). To our surprise, only copper nanopowder has exhibited

Table 1. Optimization for the azide-olefin cycloaddition of β -bromostyrene and benzyl azide^[a].

Entry	Solvent	Temp (°C)	Catalyst	Yield of 3a (%) ^[b]	Yield of 4a (%) ^[b]
1	DMSO	90	CNP	60	15
2	<i>n</i> -Octane	90	CNP	20	3
3	CHCl ₃	90	CNP	trace	-
4	THF	90	CNP	trace	-
5	CH ₃ NO ₂	90	CNP	trace	-
6	Toluene	90	CNP	trace	-
7	DMF	90	CNP	trace	-
8	Water	90	CNP	10	-
9	Piperidine	90	CNP	90	-
10	Piperidine	100	CNP	95	-
11^[c,d]	Piperidine	110	CNP	97	-
12	Et ₃ N	110	CNP	45	7
13	Morpholine	110	CNP	85	-
14	Pyridine	110	CNP	30	10
15	Piperidine	110	Ce(OTf) ₃	50	15
16	Piperidine	110	Cu(OTf) ₂	70	-
17	Piperidine	110	AlCl ₃	40	8
18	Piperidine	110	CuCl ₂	69	-
19	Piperidine	110	CuI	65	-
20	Piperidine	110	Cu nanopowder	90	-
21	Piperidine	110	CuO	70	-
22	-	110	CNP	45	12
23	Piperidine	110	-	40	15

[a] Reaction conditions: β -Bromostyrene (0.5 mmol), Benzyl azide (1.0 mmol), catalyst (50 mol%) and solvent (1.0 mL) were heated for 12 h. [b] Isolated yields. [c] Reaction with 0.5 mmol of azide led to 68% yield of **3a** and 0.75 mmol of azide furnished 84% yield of **3a** after 12 h. [d] Upon performing the reaction with 10, 20, 40 and 60 mol% of CNP, the yields of **3a** were 57, 83, 90 and 97%, respectively.

comparable efficiency as that of CuO nanoparticles which is evident from the yield (Table 1, entry 20). However, it is worth mentioning that copper nanopowder is costlier than the CuO nanoparticles. Most importantly, bulk CuO also failed to exhibit the efficiency as its nano brother as testified from the poor yield of the product (Table 1, entry 21). The decline of yields of the products observed under solvent-free and catalyst-free conditions, ascertain the crucial role played by the solvent and the catalyst in this protocol (Table 1, entries 22–23).

Having fixed the optimized condition (Table 1, entry 11) for CuO nanoparticles catalyzed synthesis of 1,4-disubstituted 1,2,3-triazoles *via* azide-olefin cycloaddition of bromoalkenes and organic azides, a variety of olefins and azides were studied and the results were summarized in Table 2. Initially, benzyl azide (**2a**) was subjected to this reaction condition with various

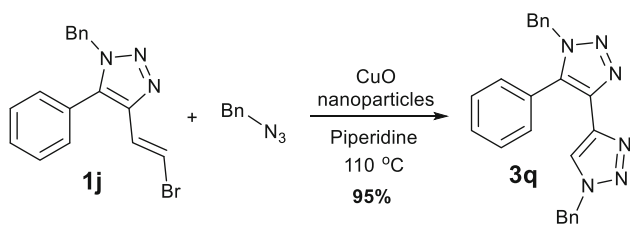
bromoalkenes (Table 2, entries 1–9). As discussed in the optimization part, β -bromostyrene (**1a**) furnished 97% yield of the required 1,2,3-triazole (**3a**) with benzyl azide (Table 2, entry 1). Methoxy substituent which is a mesomeric electron donor has dramatically boosted up the reaction to an excellent yield (Table 2, entry 2). On the other hand, methyl substituent which is an inductive electron donor has shown a slight lessening in the efficacy of this transformation (Table 2, entry 3).

In case of halogen substitutions, chloro substitution has revealed a remarkable improvement of yield than fluoro and bromo substitutions (Table 2, entries 4–6). On the other hand, strongly electron withdrawing nitro group has significantly suppressed the efficiency of this protocol which is evident from the slump of yield to 65% (Table 2, entry 7). When other aromatic substitutions such as naphthyl and thiophenyl were investigated, thiophenyl sored up to a great

Table 2. CuO nanoparticles catalyzed synthesis of 1,4-disubstituted 1,2,3-triazoles from bromoalkenes and azides^[a].

Entry	R ¹	1	R ²	2	3	Yield (%) ^[b]
1	Ph	1a	Bn	2a	3a	97
2	4-(MeO)Ph	1b	Bn	2a	3b	99
3	4-(Me)Ph	1c	Bn	2a	3c	78
4	4-(F)Ph	1d	Bn	2a	3d	79
5	4-(Br)Ph	1e	Bn	2a	3e	83
6	4-(Cl)Ph	1f	Bn	2a	3f	96
7	3-(NO ₂)Ph	1g	Bn	2a	3g	65
8	2-Naphthyl	1h	Bn	2a	3h	74
9	2-Thiophenyl	1i	Bn	2a	3i	97
10	Ph	1a	4-(Me)Bn	2b	3j	95
11	Ph	1a	4-(MeO)Bn	2c	3k	99
12	Ph	1a	Phenethyl	2d	3l	98
13	Ph	1a	<i>n</i> -Hexyl	2e	3m	83
14	Ph	1a	CH ₂ CO ₂ Et	2f	3n ^[c]	70
15	Ph	1a	Ph	2g	3o	68
16	4-(MeO)Ph	1b	Phenethyl	2d	3p	76

[a] Reaction conditions: Bromoalkenes (0.5 mmol), organic azide (1.0 mmol), CuO Nanoparticles (50 mol%) and piperidine (1.0 mL) were heated for 12 h. [b] Isolated yields. [c] 2-(4-phenyl-1H-1,2,3-triazol-1-yl)-1-(piperidin-1-yl)ethanone forms as the solvent reacts with the ester group of the triazole.

**Scheme 2.** Synthesis of *bis*-triazole by azide-olefin cycloaddition of (2-bromovinyl)triazole with benzyl azide.

margin while naphthyl slipped to poor yield (Table 2, entries 8–9). On the other part of this study, fixing the olefin (**1a**), various azides were subjected to this condition and examined the outcome (Table 2, entries 10–15). Excellent yields of triazoles were registered with methyl and methoxy benzyl azides (Table 2, entries 10–11). In case of aliphatic azides, phenethyl azide (**2d**) was found to be benign while *n*-hexylazide (**2e**) was hostile to this reaction condition as reflected in the difference of yields of the products (Table 2, entries 12–13). Being aliphatic and electron deficient, ethyl-2-azidoacetate seemingly suppressed the yield (Table 2, entry 14). Phenyl azide, being aromatic as well as electron deficient, has also markedly retarded

Table 3. Recycling of CuO nanoparticles.

Entry	Catalyst recovery (%)	Catalytic Cycle	Yield (%)
1 ^[a]	97	1	97
2 ^[b]	92	2	94
3 ^[b]	86	3	90
4 ^[b]	82	4	88

[a] Reaction conditions: Bromoalkenes (2.5 mmol), organic azide (5.0 mmol), CuO Nanoparticles (250 mol%) and piperidine (5.0 mL) were heated for 12 h. [b] The recovered catalyst was under identical reaction conditions to those for the first run.

the efficacy of the protocol since the yield decreased to 68% (Table 2, entry 15). Unlike its reaction with β -bromostyrene (**1a**), phenethyl azide (**2d**) has furnished a diminished yield of the product when it confronts 4-methoxy- β -bromostyrene (**1b**) as stated in Table 2, entry 16.

Even the (2-bromovinyl)triazole (**1j**) was submissive to this reaction condition and furnished excellent yield of *bis*-triazole (**3q**) by using this protocol (Scheme 2).

Finally, recyclability of the heterogeneous CuO nanoparticles was also examined. The catalyst was recovered from the reaction mixture after each cycle as follows. The reaction mixture was concentrated *in vacuo* and diluted with water (10 mL). The resulting heterogeneous mixture was filtered and the solid residue was washed with ethylacetate and dried in the hot air oven at 110 °C for 2 h. It was observed that the catalyst remains active even for four cycles (Table 3).

4. Conclusions

In conclusion, a method commercially available CuO nanoparticles-catalyzed synthesis of 1,2,3-triazoles *via* azide-olefin cycloaddition of bromoalkenes and organic azides has been developed and a diverse array of 1,4-disubstituted 1,2,3-triazoles is built up. This method is distinct from the existing Cu-catalyzed azide-alkyne cycloaddition due to the accessibility of the starting material and less cytotoxicity of the CuO nanoparticles than the conventional copper(I) reagents.⁴⁵ This method is different from the existing Pd-catalyzed synthesis of 1,2,3-triazoles from bromoalkenes by the economic viability of the CuO nanoparticles over the Pd catalysts. This method is also unique from the *t*-BuOK-promoted azide-alkene cycloaddition of bromoalkenes because of its complementary regioselectivity and versatility of azides employed (benzyl, alkyl and aryl). These salient attributes make this method as a highly desirable one among the other existing methods.

Supplementary Information (SI)

Additional experimental data and spectroscopic characterization data are given. Supplementary Information is available at www.ias.ac.in/chemsci.

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