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Research Article

Room Temperature N-Arylation of 1,2,4-Triazoles under Ligand-Free Condition

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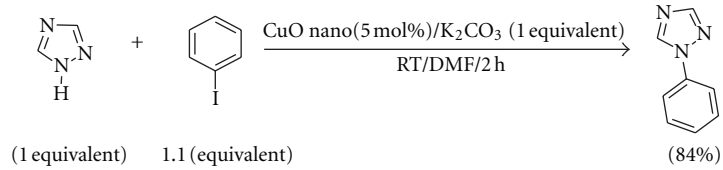
A simple and efficient method for N-arylation of 1,2,4-triazole at room temperature was described by the use of predominant (111) facet CuO nanoparticles as a catalyst in ligand-free condition. The catalyst was recyclable, and a variety of substrates give N-arylation product in high yield with short period of reaction time. The wide scope of this catalyst led us to investigate transformations involving less-reactive nitrogen nucleophiles, such as imidazole and pyrazoles. We were pleased to find that various derivatives of azoles were effectively coupled with aryl iodide to afford the desired N-arylated product in excellent yield.

1. Introduction

N-Aryl derivatives of azoles are very important organic compounds for organic synthesis because of their wide application in biology and attracted more attention as hole transport molecules for organic light-emitting diodes (LEDs) [1–3]. N-Arylation of azole was carried out by metal-mediated reactions such as the Ullmann coupling [1, 2, 4], aromatic nucleophilic substitution [3, 5], and Pd or Cu catalyzed arylation [6]. However, the employment of chelating ligand, stoichiometric amount of $Cr(CO)_3$, and harsh reaction conditions diminished the applicability of these methods, especially for large-scale production. The transition-metal-catalyzed N-arylation of azoles with aryl halides is one of the most efficient and powerful methods for the synthesis of N-aryl derivatives [7, 8]. However, current methods have some potential limitations because these transformations often use expensive transition-metal catalyst as palladium [9], rhodium [10], nickel [11], and cobalt [12] complexes. Thus, screening out inexpensive and environmentally benign metal catalysts for the N-arylation of azoles still remains a great challenge [13]. Inexpensive copper catalysts bearing various ligands provided a highly economical and efficient method for N-arylation of nitrogen-containing heterocycles with aryl halides. The ligands employed in the Cu-catalyzed reactions included beta-diketones [14], 1,2-diamines [15], phenanthrolines [16], bipyridines [17] α-amino acids [18], phosphines [19], and others [20]. The chelating ligands play an important role in controlling the concentration of active catalytic species, but they might contaminate the final products [21]. Ligand-free catalysts could be a good alternative to avoid the inconvenience of ligand removal from reaction mixtures. In the past years, CuI [22] and Cu_2O [23] have been successfully employed as catalysts for this cross-coupling reaction in the absence of organic ligands. However, these catalytic systems often required excess substrates or high catalyst loadings [24]. It was reported that simple inorganic copper (II) salts catalyzed such coupling reactions without extra ligands were of limited scope [25].

The use of CuO nanoparticle for cross-coupling reaction was first reported by Rout et al. [26]. CuO nanomaterials containing high surface area and reactive morphologies have been studied as effective catalysts for organic synthesis [27, 28]. CuO nanomaterials were of considerable interest due to role in catalysis, in metallurgy, and in high-temperature superconductors [29, 30]. These nanoparticles were found to be effective catalysts for CO and NO oxidation



Scheme 1: N-arylation of 1,2,4-triazole.

as well as oxidation of volatile organic chemicals such as methanol [31, 32]. Recently, Kantam et al. reported the asymmetric hydrosilylation of prochiral ketones, asymmetric direct aldol reaction, and N-arylation of heterocycles using nanocrystalline CuO [33, 34].

The (111) plane of CuO nanoparticles contains more active sites with higher density as compared to bulk CuO and therefore these sites actively participated in the catalysis reactions. Previously we shown an excellent catalytic activity of these predominant (111) facet nanoparticles in N-arylation of indoles [35], herein we further extended our study in case of N-arylation of azoles and reported our progress in the N-arylation of azoles with optimum conditions. It was found that, the catalytic activity of these predominant (111) facet CuO nanoparticles was very high as N-arylation of 1,2,4-triazole was carried out even at room temperature with lesser reaction time and excellent yield. The main aim of our study is to give simple and efficient method for N-arylation of azoles by the use of highly active predominant (111) faceted CuO nanoparticles as a heterogeneous catalyst in a ligand free condition.

2. Result and Discussion

The CuO nanoparticles with predominant (111) plane were fabricated by thermal-assisted green strategy at reflux temperature within short period of time in our laboratory as reported [35].

2.1. Reactions of 1,2,4-Triazole with Aryl Iodide. Recently, there was a report of Cu catalyzed N-arylation of azoles with aryl halide in presence of ligand but the longer reaction time and difficulty in separation of ligand limits the method [36], whereas in our method, we can easily separate CuO nanocatalyst and recycled it for at least five times without much loss in yield of the product.

Initially, the reaction of N-arylation of 1,2,4-triazole with aryl iodides was investigated (Scheme 1).

The reaction with iodobenzene occurred at room temperature to give 1-phenyl-*1H*-1,2,4-triazole in good yield (84%), whereas 4-nitro-1-iodobenzene shows greater reactivity towards 1,2,4-triazole than iodobenzene with yield around (91%). Under similar condition, electron-rich 4-iodoanisole and satirically hindered 2-iodotoluene show less reactivity towards 1,2,4-triazole (Table 1, Entry 5 and 6). We carried reactions at different temperatures in order to study the effect of temperature on yield of product but there was not much considerable increase in the yield of product with increase in temperature.

N-arylation of 1,2,4-triazole was effective under air, Iodobenzene exhibited greater reactivity compared to bromobenzene. Under these conditions, chlorobenzene show less reactivity as compared to bromobenzene and Iodobenzene. The order of reactivity was iodobenzene > bromobenzene > chlorobenzene (Table 1, entries 2, 3, and 4). There was no reaction possible in the absence of CuO nanoparticles.

To our best knowledge, this is the first report of room temperature N-Arylation of 1,2,4-triazole. The reactions were clean and no other impurity due to *C*-arylation or biaryl was obtained.

Reaction of iodobenzene with triazole was examined with various kinds of bases. N-Arylation preceded using carbonates and yield increased in order to increase basicity. However, use of Cs_2CO_3 gave no substantial amount of the product, nor did t-BuONa.

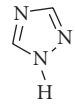
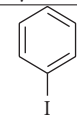
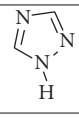
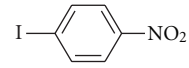
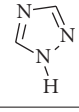
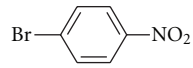
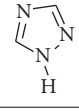
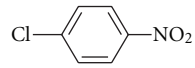
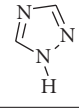
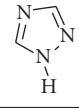
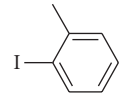
In our catalytic system, K_2CO_3 and Rb_2CO_3 worked very well. Employment of the stronger bases might deactivate the CuO nanocatalyst. Although employing 0.5 equivalent of a base gave an acceptable yield, the reaction was accelerated using 1 equivalent of the base. N-Arylation of imidazole and pyrazole proceeded similarly. As described above, K_2CO_3 and Rb_2CO_3 promoted good activity in this reaction and the use of K_2CO_3 was more preferable practically (Table 2, entry 5 and 10). Reactions of triazole with iodobenzene was carried out in toluene at room temperature for 12 h to afford the desired product in 65% yield and, with acetonitrile, methanol, and chloroform, the conversion was less as compared to toluene (Table 2). Therefore, we examined the synthesis of N-arylation of triazole in the presence of 5 mol% of CuO nanocatalyst and 1 equivalent of K_2CO_3 with DMF as a solvent.

2.2. N-Arylation of Imidazole and Pyrazole. We extended our study in case of azoles such as imidazole and pyrazole (Table 3). Initially, the reaction was carried out at room temperature but yield of product was very less. Increased in temperature increases the percentage yield and in 3 h of reflux, we get N-arylated product with excellent yield up to 97% (Scheme 2). This might because of less reactive nature of imidazole and pyrazole which makes abstraction of hydrogen from nucleophile difficult at room temperature and N-arylation reaction occurred at refluxed temperature.

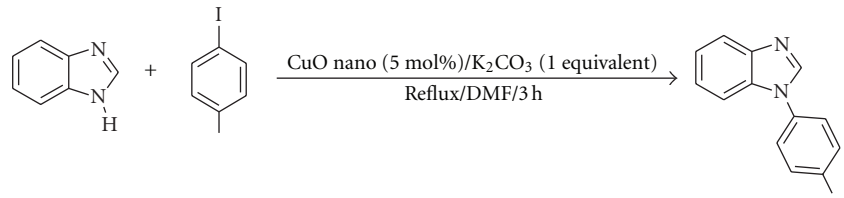
All reactions were monitored by Co-TLC and the final product characterized by LCMS, ^{1}H NMR, and ^{13}C NMR.

2.3. Comparison of Catalytic Activity. We compared the catalytic activity of these predominant (111) facet CuO

Table 1: N-arylation of 1,2,4 triazoles.

Entry	Azoles	Aryl iodide	Reaction temperature/h	(Yield)[a]
(1)			RT/2 h	84%
(2)			RT/2 h	91%
(3)			RT/4 h	72%
(4)			RT/4 h	56%
(5)			RT/2 h	78%
(6)			RT/4 h	60%

[a] Isolated yield: 1,2,4-triazoles (3 mmol), iodobenzene (3.3 mmol), CuO nanoparticles (0.15 mmol), K_2CO_3 (3 mmol), and N–N dimethyl formamide (10 mL) at room temperature.



(1 equivalent) 1.1 (equivalent) (97%)

Scheme 2: N-arylation of benzimidazole.

Table 2: Optimization of reaction condition for the N-arylation of 1,2,4-triazole with iodobenzene.

Entry	Solvent	Base	Reaction time (h)	(Isolated yield)[a]
1	Toluene	K_2CO_3	12	65%
2	CH_3CN	K_2CO_3	12	40%
3	CH_3OH	K_2CO_3	12	25%
4	$CHCl_3$	K_2CO_3	12	15%
5	DMF	K_2CO_3	2	84%
6	DMF	K_2CO_3	8	84%
7	DMF	CS_2CO_3	5	45%
8	DMF	t-BuONa	5	55%
9	DMF	NaOH	5	35%
10	DMF	Rb_2CO_3	4	75%

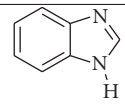
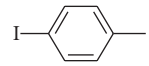
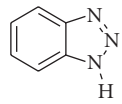
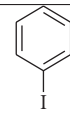
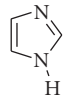
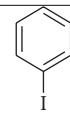
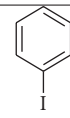
[a] Isolated yield.

nanoparticles with commercially available CuO nanoparticles and bulk CuO powder (purchased from Merck) and results are tabulated in Table 4. These results clearly show higher catalytic activity of predominant (111) facet CuO nanoparticles in N-arylation of azoles.

2.4. Effect of Catalyst Concentration. The effect of catalyst concentration on yield of product was studied. The reaction was carried out with varying amount of CuO catalyst concentration and results are tabulated in Table 5. As the concentration of catalyst was increased from 2.5 mol% to 5 mol%, the yield of the product was increased from 60% to 97% further increase in catalyst concentration did not affect overall yield of product.

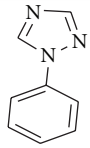
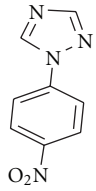
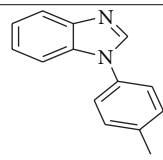
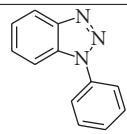
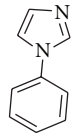
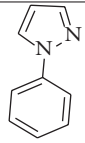
2.5. Mechanism. The greater catalytic activity of CuO nanoparticles with respect to bulk CuO powder indicated that reactions were heterogeneous and occurred on the surface of predominant (111) facet nanocatalyst. Thus, the CuO nanoparticles might undergo reaction with aryl halide to give intermediate X, where the excess positive charge generated over iodine could be shared among the CuO nanoparticles

Table 3: N-arylation of imidazole and pyrazole.

Entry	Azoles	Aryl iodide	Reaction temperature/h	(Yield)[a]
(1)			Reflux/3 h	97%
(2)			Reflux/3 h	98%
(3)			Reflux/3 h	86%
(4)			Reflux/3 h	83%

[a] Isolated yield: azole (3 mmol), iodobenzene (3.3 mmol), CuO nanoparticles (0.15 mmol), K_2CO_3 (3 mmol), and N–N dimethyl formamide (10 mL) at reflux for 3 h.

Table 4: Comparison of catalytic activity of (111) facet CuO nanoparticle.

Entry	Product	Temperature/time (h)	Synthesized CuO nano (yield %)[a]	Commercial CuO nano (yield %)[b]	CuO bulk powder (yield %)[c]
1		RT/2 h	84%	45%	No reaction
2		RT/2 h	91%	52%	No reaction
3		Refluxed temperature/3 h	97%	40%	12%
4		Refluxed temperature/3 h	98%	48%	15%
5		Refluxed temperature/3 h	86%	40%	10%
6		Refluxed temperature/3 h	83%	40%	12%

[a,b,c] Isolated yield.

Table 5: Effect of catalyst concentration on the N-arylation of benzimidazole.

Entry	Catalyst conc. (mol%)	Reaction time (h)	Yield (%)[a]
1	2.5	3	60
2	5	3	97
3	10	3	97
4	15	3	96

[a]Isolated yield.

Table 6: Recyclability of CuO nanoparticles as a catalyst.

Entry	Cycle	(Yield %)[a]
1	1st	97
2	2nd	93
3	3rd	90
4	4th	80
5	5th	78

[a]Isolated yield, reaction conditions: azole (3 mmol), iodobenzene (3.3 mmol), CuO nanoparticles (0.15 mmol), K_2CO_3 (3 mmol), and N–N dimethyl formamide (10 mL) at reflux for 3 h.

present on the surface of the cluster (Scheme 3). Later, X might undergo reaction with triazole to give intermediate Y that can complete the catalytic cycle by the formation of the N-arylated product. The CuO nanoparticles become free at the end of reaction.

2.6. Recyclability of Catalyst. Finally, the stability and activity of the catalyst was tested in the recycle-use experiments. The CuO nanoparticles recycled for five times without loss of its catalytic activity (Table 6). The used catalyst was then separated by centrifugation and washed with hot water two-three times before being recycled in next reaction. It was found that during recycle experiments, there was not much loss in yield of the product which shows the recyclability and reusability of catalyst without significant loss of its catalytic activity.

3. Experimental Section

3.1. General Procedure for the N-Arylation of 1,2,4-Triazole. 1,2,4-Triazole (3 mmol), iodobenzene (3.3 mmol), CuO nanoparticles (0.15 mmol), K_2CO_3 (3 mmol), and N–N dimethyl formamide (10 mL) were taken in a glass reactor. Stirred the reaction mixture at room temperature and monitored by Co-TLC till completion of reaction. After completion of reaction, dilute the reaction mixture with 20 mL water. The entire reaction mixture was washed with ethyl acetate (2 × 10 mL). Aqueous layer was centrifuged to recover CuO nanocatalyst. The combined organic extracts were washed with brine and dried by sodium sulphate. Solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography on silica gel with ethyl acetate: petroleum ether (1 : 9) as eluent to yield analytically pure product.

1-Phenyl-1H-1,2,4-Triazole (1a). Nature: light yellow oil. ^{1}H NMR 400 MHz ($CDCl_3$): δ 7.26 (s, 2H), 7.34 (s, 3H), 8.32 (d, J = 8.4 Hz, 1H), 8.64 (s, 1H). ^{13}C NMR 100 MHz ($CDCl_3$): δ 119.20, 123.25, 123.39, 129.34, 129.65, 135.18, 146.34. LCMS: (M + 1) = 145.

1-(4-Nitrophenyl)-1H-1,2,4-Triazole (2a). Nature: yellow solid, M.P. = 170–173°C.^{1}H NMR 400 MHz ($CDCl_3$): δ 7.89–7.94 (m, 4H), 8.46 (s, 1H), 8.78 (s, 1H). ^{13}C NMR 100 MHz ($CDCl_3$): δ 124.85, 130.35, 130.45, 138.65, 147.73, 154.71. LCMS: (M + 1) = 191.

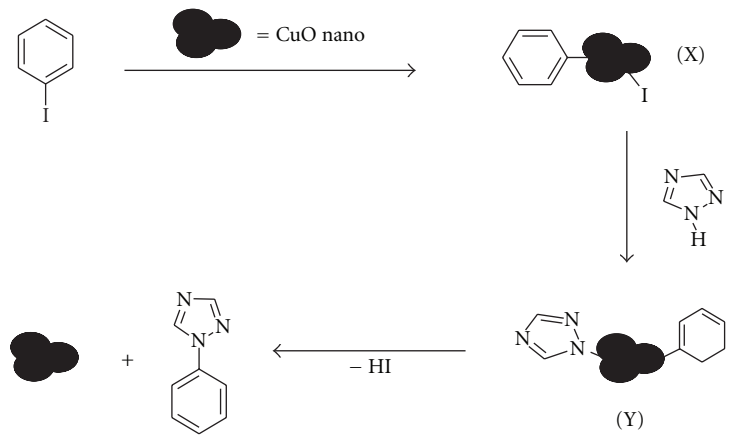
3.2. General Procedure for N-Arylation of Imidazole and Pyrazole. Azole (3 mmol), iodobenzene (3.3 mmol), CuO nanoparticles (0.15 mmol), K_2CO_3 (3 mmol), and N–N dimethyl formamide (10 mL) were taken in a glass reactor fitted with a condenser. Refluxed the mixture and monitored by Co-TLC, till completion of reaction. Workup procedure and purification of products were performed as described for the 1,2,4-triozole reactions.

1-P-Tolyl-1H-benzo[d]imidazole (1b). Nature: oil, ^{1}H NMR 400 MHz ($CDCl_3$): δ 2.43 (s, 3H), 7.26–7.36 (m, 6H), 7.48 (d, J = 8 Hz, 1H), 7.87 (d, J = 8 Hz, 1H), 8.09 (s, 1H). ^{13}C NMR 100 MHz ($CDCl_3$): δ 21.14, 110.53, 120.40, 122.79, 123.67, 124.00, 130.59, 133.67, 133.79, 138.21, 142.30, 143.58. LCMS: (M + 1) = 209.10. IR (cm^{-1}) = 3054, 3036, 1610, 1515, 1486, 1453, 1375, 1320, 1287, 1227, 1203, 1140, 1109, 1009, 976, 887, 818, 780, 764, 737, 708, 620, 586, 565.

1-Phenyl-1H-benzol[d][1,2,3]Triazole (2b). Nature: white crystalline solid. M.P. = 86–88°C. ^{1}H NMR 400 MHz ($CDCl_3$): δ (t, J = 7.12 Hz, 1H), 7.49–7.57 (m, 2H), 7.61 (t, J = 8.16 Hz, 2H), 7.75–7.80 (m, 3H), 8.15 (d, J = 8.36 Hz, 1H). ^{13}C NMR 100 MHz ($CDCl_3$): 110.39, 120.36, 122.91, 124.42, 128.26, 128.70, 129.89, 132.33, 137.02, 146.53. LCMS: (M + 1) = 195. IR (KBr cm-1) = 3098, 3040, 2918, 1655, 1595, 1560, 1500, 1458, 1290, 1275, 1244, 1188, 1143, 1126, 1089, 1059, 1010, 924, 785, 762, 708, 694, 659, 572, 517, 434.

1-Phenyl-1H-Imidazole (3b). Nature: oil. ^{1}H NMR 400 MHz ($CDCl_3$): δ 7.26 (d, J = 3.76 Hz, 1H), 7.30 (s, 1H), 7.41 (d, J = 6.96 Hz, 3H), 7.51 (t, J = 8.64 Hz, 2H), 8.05 (s, 1H). ^{13}C NMR 100 MHz ($CDCl_3$): δ 118.53, 121.67, 127.97, 128.93, 130.01, 135.44, 136.99. LCMS (M + 1) = 145.

1-Phenyl-1H-Pyrazole (4b). Nature: oil. ^{1}H NMR 400 MHz ($CDCl_3$): δ 6.47 (s, 1H), 7.25–7.30 (m, 1H), 7.45 (t, J = 8.28 Hz, 2H), 7.70 (t, J = 7.68 Hz, 3H), 7.94 (s, 1H). ^{13}C NMR 100 MHz ($CDCl_3$): δ 107.69, 115.41, 119.27, 120.30, 126.52, 126.91, 129.47, 129.59, 140.16, 141.10. LCMS (M + 1) = 145.



Scheme 3: Proposed mechanism for N-arylation of triazole catalysed by CuO.

4. Conclusion

A simple, general, and efficient procedure was described for N-arylation of 1,2,4-triazoles at room temperature with aryl iodides under ligand-free condition by the use of predominant (111) facet CuO nanoparticles as a catalyst. The catalyst was recyclable, and a variety of substrates undergo reaction in high yield. The wide scope of this catalyst led us to investigate transformations involving less-reactive azoles such as imidazole and pyrazole. We were pleased to found that various azole derivative effectively coupled with aryl iodide to afford the desired N-arylated products in excellent yields. See supplementary material available online at doi:10.1155/2012/515092.

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