Copper-Catalyzed Hydroxylation of Aryl Halides with Tetrabutylammonium Hydroxide: Synthesis of Substituted Phenols and Alkyl Aryl Ethers

Rajesh Paul, Md Ashif Ali, Tharmalingam Punniyamurthy*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India
Fax +91(361)2690762; E-mail: tpunni@iitg.ernet.in

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Abstract: The selective hydroxylation of aryl iodides and aryl bromides with tetrabutylammonium hydroxide pentahydrate is described. For this, the combination of copper(I) iodide and 8-hydroxyquinaldine at 70–130 °C in a mixture of dimethyl sulfoxide and water (2:3) is used. The resultant phenols can be readily reacted with alkyl and allyl halides in situ to provide the corresponding alkyl or allyl aryl ethers in high yields. The reactions are simple, general, and efficient, affording substituted phenols and alkyl aryl ethers under aerobic conditions.

Key words: phenols, copper iodide, tetrabutylammonium hydroxide pentahydrate, aryl halides, hydroxylation

Phenols and their derivatives are structural constituents of numerous natural products, pharmaceuticals, and polymers.[1] The classical non-oxidative preparation routes of these class of compounds include the dienone–phenol rearrangement,[2a,b] benzannulation,[2c,d] cycloaddition,[2e] Fries rearrangement,[2f] and nucleophilic substitution of activated aryl halides.[2g] However, these protocols generally have limitations due to nonavailability of the suitable starting materials, and, in some cases, the requirement of harsh reaction conditions.[3] To overcome these drawbacks, a milder method has recently been reported, in which an iridium–phosphine complex is used for the preparation of non-*ortho*-substituted phenols by a two-step C–H activation/borylation and oxidation procedure.[4] Later, palladium–phosphine complexes,[5] polyaniline-stabilized palladium nanoparticles,[6] and copper(I) iodide or copper(I) oxide with bidentate chelating ligands such as L-proline,[7a] 1,10-phenanthroline,[7b] dibenzoylmethane,[7c,d] pyridine-2-aldoxime,[7e] 8-hydroxyquinoline,[7f] and lithium picolinate[7g] have been studied for the synthesis of substituted phenols by the hydroxylation of aryl halides in the presence of alkali metal salts, sodium hydroxide, potassium hydroxide, and cesium hydroxide. These reactions of aryl halides with hydroxide nucleophiles provide a straightforward route for the synthesis of functionalized phenols. From an industrial standpoint,[8,9] the copper-catalyzed process is attractive due to the availability of reagents, low cost, and low toxicity.

We wish to report herein results carried out in continuation of our studies on cross-coupling reactions,[10] namely the selective hydroxylation of aryl iodides and aryl bromides with tetrabutylammonium hydroxide pentahydrate[11] as nucleophile, with the reaction catalyzed by a combination of copper(I) iodide and 8-hydroxyquinalidine[12] in a mixture of dimethyl sulfoxide–water (2:3). The procedure is efficient, general, and simple, and affords substituted phenols. The phenoxides can be further reacted in situ with alkyl halides to afford alkyl aryl ethers. This method involves shorter reaction times and the use of inert reaction conditions is avoided.

Initially, the reaction conditions were optimized by using 1-iodo-4-methylbenzene as a model substrate and by using different ligands, copper sources, bases, and solvents at various temperatures (see optimization table in the Supporting Information for this article). Of the screened ligands (Figure 1), 8-hydroxyquinoline[7f,13] (**L6**) and 8-hydroxyquinalidine[12] (**L7**) were effective, and the latter gave the best result of 100% conversion, whereas ethane-1,2-diamine[14] (**L1**), 2-aminoethanol[15] (**L2**), ethane-1,2-diol[16] (**L3**), 2,2,6,6-tetramethylheptane-3,5-dione[17] (**L4**), 1,10-phenanthroline[18] (**L5**), dibenzoylmethane[19] (**L9**), 2-(2-pyridyl)pyridine[20] (**L8**), and L-proline[7a,21] (**L10**) afforded inferior result. Control experiments confirmed that only 30% yield of the desired product was obtained without the aid of the ligand. The catalytic activities of the copper sources copper(I) bromide, copper(I) iodide, copper(I) oxide, copper(II) oxide, and copper(II) acetate hydrate were compared, and copper(I) iodide was found to be superior to the others. Among the studied set of bases, potassium carbonate, potassium phosphate, potassium hydroxide, cesium carbonate, cesium hydroxide hydrate, and tetrabutylammonium hydroxide pentahydrate, the latter provided the best results. A 2:3 mixture of dimethyl

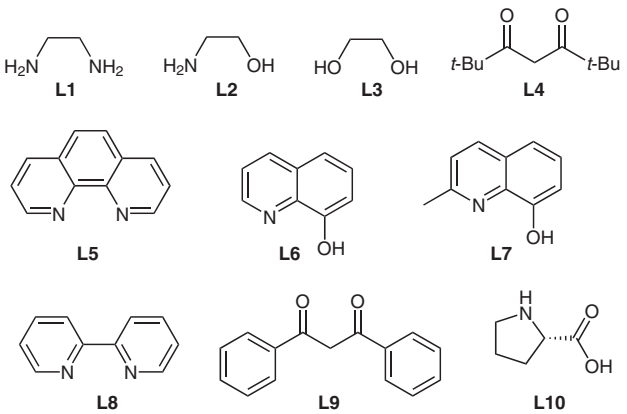

Figure 1

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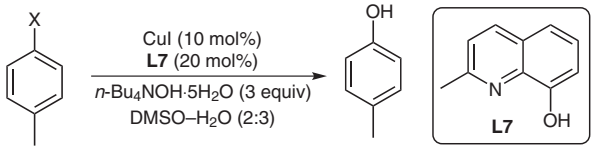
sulfoxide and water was found to be the solvent of choice for this process. Solvents such as dimethyl sulfoxide, water, *N*,*N*-dimethylformamide–water, acetonitrile–water, and tetrahydrofuran–water were found to be less effective, providing the desired product in <10% conversion. The optimum temperature was 100 °C. Lowering the catalyst amount (to 5 mol%) or the copper-to-ligand ratio (to 1:1) led to the reaction proceeding in <63% conversion.

The reaction conditions were further investigated for the hydroxylation of the less reactive aryl bromide and aryl chloride (Table 1). 1-Bromo-4-methylbenzene could be converted into the corresponding phenol at 130 °C in 93% yield (entry 2). However, 1-chloro-4-methylbenzene was less effective, affording the product at 140 °C in only 10% yield (entry 3).

With the optimized conditions in hand, the scope of the procedure was then explored for the reactions of other aryl iodides (Table 2). Iodobenzene underwent hydroxylation in seven hours, giving 98% yield (entry 1). Likewise, aryl iodides with 2-methoxy, 4-bromo, 4-chloro, 4-methoxy, 4-methyl, 2,4-dimethyl, 2,5-dimethyl, 2,6-dimethyl, 3,4-dimethyl, and 3,5-dimethyl substituents, as well as 1-iodonaphthalene could be converted into the corresponding phenols in 85–97% yield. In the case of the activated aryl iodides 1-iodo-3-nitrobenzene and 1-iodo-4-nitrobenzene (entries 3 and 8), the reactions proceeded at even lower temperature (70 °C, 5 h), providing the products in 95–98% yield.

Next, the hydroxylation of aryl bromides was examined (Table 3). Bromobenzene underwent hydroxylation to give the phenol in 14 hours in 95% yield (entry 1). Similarly, aryl bromides containing 3-methoxy, 3-methyl, 4-chloro, 4-methoxy, and 4-methyl substituents, as well as 6-methoxy-2-bromonapthalene could be transformed into the corresponding phenols in 74–93% yield. In the case of activated 1-(4-bromophenyl)ethanone (entry 5), the reaction occurred efficiently at 90 °C in 96% yield.

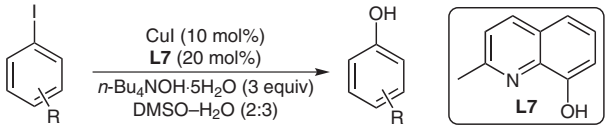
Table 1 Copper(I)-Catalyzed Hydroxylation of Different Aryl Halides[a]

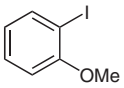
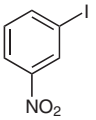
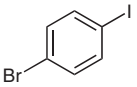
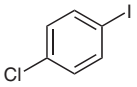
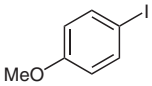
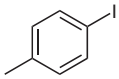
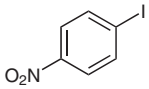
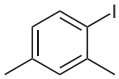
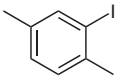
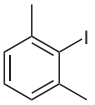
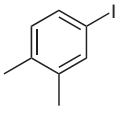
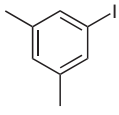
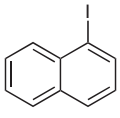


Entry	X	Time (h)	Temp (°C)	Yield (%)[b]
1	I	7	100	97
2	Br	14	130	93
3	Cl	14	140	10

[a] Reaction conditions: Aryl halide (1 mmol), CuI (10 mol%), 8-hydroxyquinaldine (**L7**; 20 mol%), *n*-$Bu_4NOH·5H_2O$ (3 mmol), DMSO–H_2O (2:3; 1 mL).
[b] Isolated yield.

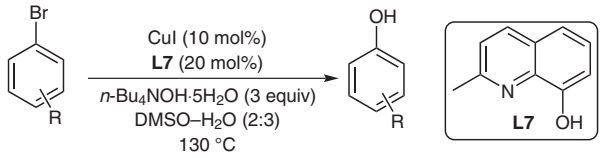
Table 2 Copper(I)-Catalyzed Hydroxylation of Aryl Iodides[a]

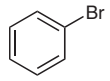
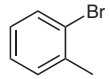
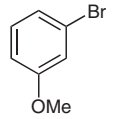
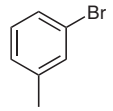
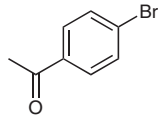
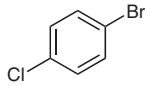
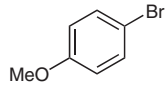
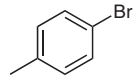
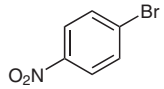
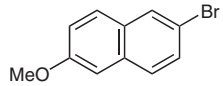


Entry	Aryl Iodide	Time (h)	Yield (%)[b]
1		7	98
2		10	94
3		5	98[c]
4		7	85
5		7	89
6		7	96
7		7	97
8		5	95[c]
9		10	91
10		10	93
11		10	88
12		10	96
13		10	95
14		10	85

[a] Reaction conditions: Aryl iodide (1 mmol), CuI (10 mol%), 8-hydroxyquinaldine (**L7**; 20 mol%), *n*-$Bu_4NOH·5H_2O$ (3 mmol), DMSO–H_2O (2:3; 1 mL), 100 °C.
[b] Isolated yield.
[c] Reaction temperature = 70 °C.

Table 3 Copper(I)-Catalyzed Hydroxylation of Aryl Bromides[a]



Entry	Aryl Bromide	Time (h)	Yield (%)[b]
1		14	95
2		21	84
3		21	74
4		14	91
5		21	96[c]
6		14	81
7		21	75
8		14	93
9		8	97[c]
10		21	81

[a] Reaction conditions: Aryl bromide (1 mmol), CuI (10 mol%), 8-hydroxyquinaldine (**L7**; 20 mol%), *n*-$Bu_4NOH·5H_2O$ (3 mmol), DMSO–H_2O (2:3; 1 mL), 130 °C.
[b] Isolated yield.
[c] Reaction temperature = 90 °C.

The substrates with electron-withdrawing groups (EWGs) exhibited enhanced reactivity in comparison to those bearing electron-donating groups (EDGs). The *ortho*-substituted substrates required slightly longer reaction times. This may be due to the steric hindrance between the *ortho* substituents of the substrates and the catalyst during the transition state of the reaction.

This methodology can be combined with Williamson ether synthesis leading to the formation of alkyl aryl ethers in a one-pot procedure from aryl halides (Table 4). Aryl halides were first converted into phenoxides, which on subsequent treatment with alkyl halides gave the corresponding alkyl aryl ethers. For examples, aryl iodides with 2-methoxy, 2,6-dimethyl, and 3,4-dimethyl substituents could be transformed into the corresponding phenoxides, which in situ readily underwent reaction with 1-bromooctane to give the corresponding ethers in 85–89% yields (entries 1, 9, and 10). Similarly, aryl bromides with 2-methyl, 4-chloro, 4-methoxy, and 4-methyl substituents underwent reaction with 3-bromoprop-1-ene, 1-bromoethane, 1-(chloromethyl)benzene, or 1-bromooctane to provide the corresponding ethers in 70–90% yield (entries 2–8).

In conclusion, the selective hydroxylation of aryl halides with tetrabutylammonium hydroxide pentahydrate as described here occurs in shorter times by the combined use of copper(I) iodide and 8-hydroxyquinaldine at moderate temperature. The process is efficient, general, and simple, and can be used to synthesize substituted phenols without the need for the use of inert conditions. The resultant phenoxides can be reacted in situ with alkyl halides to afford alkyl aryl ethers in high yield.

CuI (98%), Cu_2O (97%), *n*-$Bu_4NOH·5H_2O$ (>97%), K_3PO_4 (98%), Cs_2CO_3 (99%), and $CsOH·H_2O$ (99.5%) were purchased from Aldrich, and $Cu(OAc)_2·H_2O$ (>98%) was purchased from Merck; these reagents were used without further purification. Aryl iodides were prepared according to literature procedures.[22] Chromatography was carried out on silica gel (230–400 mesh) and EtOAc and hexane were used as eluents. Analytical TLC was performed with Rankem silica gel G & GF254 plates. NMR spectra (400 MHz for ^1H and 100 MHz for ^{13}C) were recorded on a DRX-400 Varian spectrometer; $CDCl_3$ and DMSO-d_6 were used as solvents and TMS as an internal standard. Melting points were determined on a Buchi B-540 melting point apparatus and are uncorrected. Elemental analysis was carried out on a Perkin Elmer-2400 CHNS analyzer. The Supporting Information for this article contains an optimization table as well as the characterization data and NMR spectra (^1H and ^{13}C) of the phenols and ethers, and is available online at http://www.thieme-connect.de/ejournals/toc/synthesis.

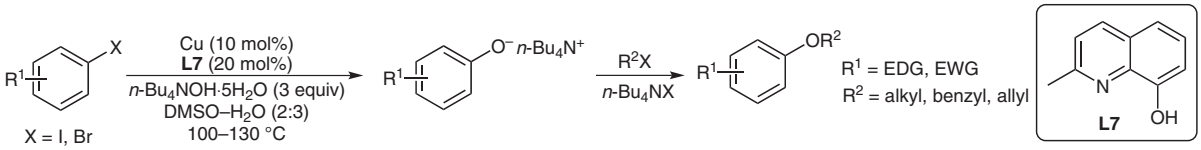
Phenols; General Procedure

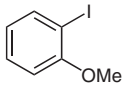
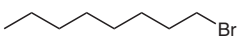
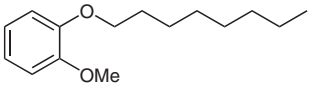
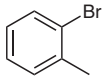
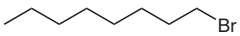
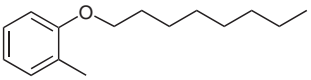
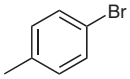
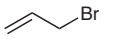
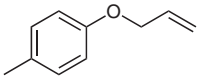
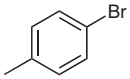
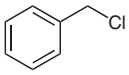
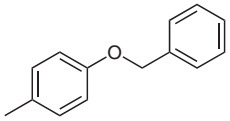
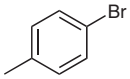
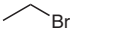
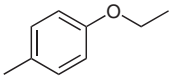
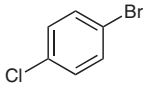
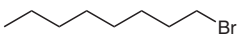
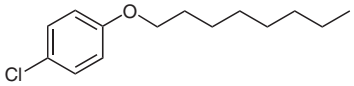
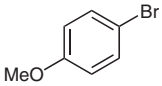
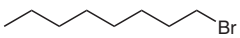
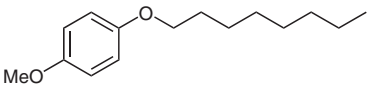
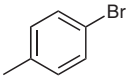
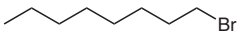
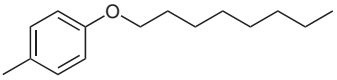
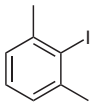
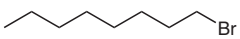
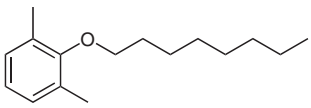
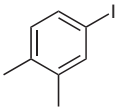
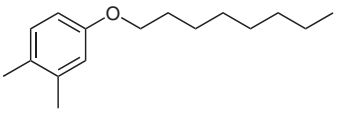
The appropriate aryl halide (1 mmol), *n*-$Bu_4NOH·5H_2O$ (544 mg, 3 mmol), and H_2O (0.6 mL) were added over 0.1 h to a stirred solution of CuI (19.0 mg, 10 mol%) and 8-hydroxyquinaldine (**L7**; 31.8 mg, 20 mol%) in DMSO (0.4 mL), and the reaction mixture was stirred at 70–100 °C (aryl iodides) or 90–130 °C (aryl bromides). The progress of the reaction was monitored by TLC (EtOAc–hexane). The reaction mixture was then cooled to r.t. and acidified with 0.5 M HCl (0.5 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL) and dried (Na_2SO_4). Evaporation of the solvent gave a residue that was purified by column chromatography (short pad of silica gel, EtOAc–hexane).

Alkyl Aryl Ethers; General Procedure

The appropriate aryl halide (1 mmol), *n*-$Bu_4NOH·5H_2O$ (544 mg, 3 mmol), and H_2O (0.6 mL) were added over 0.1 h to a stirred solution of CuI (19.0 mg, 10 mol%) and 8-hydroxyquinaldine (**L7**; 31.8 mg, 20 mol%) in DMSO (0.4 mL), and the resultant reaction mixture was stirred at 100 °C (aryl iodide) or 130 °C (aryl bromide). The progress of the reaction was monitored by TLC (EtOAc–hexane). The reaction mixture was then cooled to r.t. and treated with the appropriate alkyl or allyl halide (2 mmol). The resultant mixture was

Table 4 One-Pot Synthesis of Alkyl Aryl Ethers from Aryl Halides[a]



Entry	Aryl halide	R^2X	Product	Yield (%)[b]
1				86
2				81
3				84
4				90
5				90
6				75
7				70
8				89
9				85
10				89

[a] Reaction conditions: (a) Aryl halide (1 mmol), CuI (10 mol%), 8-hydroxyquinaldine (**L7**; 20 mol%), *n*-$Bu_4NOH·5H_2O$ (3 mmol), DMSO–H_2O (2:3; 1 mL), 100 °C (aryl iodide) or 130 °C (aryl bromide), 10–21 h; (b) alkyl/allyl halide (2 mmol), 100 °C, 4–21 h.
[b] Isolated yield.

further stirred at 100 °C for 4–21 h. The reaction mixture was then cooled to r.t. and extracted with EtOAc (3 × 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by column chromatography (short pad of silica gel, EtOAc–hexane).

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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