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Copper promoted Chan–Lam type O-arylation of oximes with arylboronic acids at room temperature

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ABSTRACT

to the existing protocols.

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Oximes undergo special types of C–O cross coupling reactions to vield O-aryl or O-alkyl oxime ethers that are structural components of numerous natural products, agrochemicals, and pharmaceuticals.^{1,2} Moreover O-aryl or O-alkyl oxime ethers are used for the synthesis of asymmetric primary amines,³ substituted pyrroles,⁴ trisubstituted isoxazoles,⁵ amino acids,^{6,3b} cis-1, 2-amino alcohols,^{7,3b} fluorenones,⁸ heterocyclic oximes,⁹ four-membered cyclic nitrones,¹⁰ pyrimidine,¹¹ aldehyde,¹² nitriles,¹² etc. Conventional method for the synthesis of O-aryl or O-alkyl oxime ether involves the condensation of O-arylhydroxylamines with carbonyl compounds in the presence of base,¹³ or PTC.¹⁴ Other methods involving their synthesis are the reaction of oximes with alkyl or aryl halides,¹ fluorobenzene derivatives,¹⁶ alcohols,¹⁷ aryl nitrates,¹⁸ activated ole-fins,¹⁹ allylic sp³ C–H bonds²⁰ or esters,²¹ methyl sulfate,²² alkenes²³ etc. Among these reported methods, the most interesting and conveniently used method is the copper catalyzed Chan-Lam C-O crosscoupling strategy involving aryl oxime and aryl substrates.¹⁵ In the last two decades copper (II) salts have emerged as the most versatile reagents for the C–O bond formation reactions.^{24,25} The pioneering work on copper catalyzed cross-coupling reaction of aryl oxime and aryl halide for the synthesis of oxime ether was reported by Maitra and co-workers^{15a} Arylboronic acids are the most versatile organometallic species which are frequently used in many well known cross coupling reactions²⁶ because of the greater stability, structural diversity, and lower toxicity over aryl halides. Recently Meyer and co-workers²⁷ and Huang and co-workers²⁸ have reported the use of arylboronic acid instead of aryliodide as coupling partner for the synthesis of oxime ethers. Similarly supported copper catalysts were also used for the coupling of oxime and arylboronic acid by Cai and co-workers²⁹ But most of the methods reported till today for the synthesis of oxime ether use expensive aryl or alky halides (mostly iodide), chlorinated solvents (like DCM,²⁷ DCE,²⁸ etc.), high concentration of base,^{15a,27,28} high temperature,^{15a} long reaction time,²⁷⁻²⁹ ligands,^{15a} oxidants,²⁹ moisture free atmosphere,^{27,29} and stoichiometric amount of the metal source. Moreover, most of the existing copper promoted protocols for oxime ether synthesis involving arylboronic acids require long reaction time which resulted in the formation of many side products such as biaryl, arene, phenol, diaryl ether, acetyl-aryl ether etc., and consequently lower the yield of the desired products.^{26f} Thus, the feasibility of using copper in the synthesis of O-aryloxime ether by cross coupling of aryl boronic acids and oximes deserves serious attention. In this communication we wish to report the effect of different bases, solvents, and copper loadings on the Chan-Lam C-O cross coupling methodology for the synthesis of O-aryloxime ether at room temperature using aryl oxime and aryl boronic acids as coupling partners.

An efficient copper promoted protocol for the synthesis of aryloxime ethers using aryloximes and arylbo-

ronic acids has been developed under mild reaction conditions. This method offers an efficient alternative

To investigate the effectiveness of different bases in Chan–Lam type O-arylation, the reaction of acetophenone oxime (**1a**) with phenylboronic acid (**2a**) was chosen as a model reaction using DMSO as a solvent, Cs_2CO_3 as a base, and the reactions were performed in aerobic condition at room temperature in the presence of Cu(OAc)₂.³⁰ The results are summarized in the Table 1. It has been seen from Table 1 that the reaction proceeded with 82% isolated yield within 5 hours (Table 1, entry 1). This is a significant result as most of the reported procedures of oxime ether synthesis require

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Table 1

Optimization of reaction conditions for synthesis of O-aryloxime ether^a



Entry	Catalyst (equiv)	Solvent (4 ml)	Base (1 equiv)	Time (h)	Yield of 3a ^b (%)
1	0.5	DMSO	Cs ₂ CO ₃	5	82
2	0.5	DMSO	КОН	24	Trace
3	0.5	DMSO	Na ₃ PO ₄ ·12H ₂ O	24	Trace
4	0.5	DMSO	Na ₂ CO ₃	7	64
5	0.5	DMSO	K ₂ CO ₃	7.5	71
6	0.5	DMSO	NaHCO ₃	24	40
7	0.5	DMSO	TEA	6	58
8	0.5	DMSO	Cs ₂ CO ₃	24	43 ^c
9	0.5	DMSO	Cs ₂ CO ₃	20	55 ^d
10	0.2	DMSO	Cs ₂ CO ₃	36	45
11	0.4	DMSO	Cs ₂ CO ₃	8	50
12	0.6	DMSO	Cs ₂ CO ₃	5	72
13	0.8	DMSO	Cs ₂ CO ₃	4.5	73
14	1.0	DMSO	Cs ₂ CO ₃	3	70
15	0.5	CH ₃ OH	Cs ₂ CO ₃	16	51
16	0.5	iPrOH	Cs ₂ CO ₃	6.5	61
17	0.5	DCM	Cs ₂ CO ₃	6	59
18	0.5	CH ₃ CN	Cs_2CO_3	10	30
19	0.5	Toluene	Cs ₂ CO ₃	4	53
20	0.5	H ₂ O	Cs ₂ CO ₃	48	Trace
21	1	H ₂ O	Cs ₂ CO ₃	48	41 ^e
22	1	H ₂ O/DMSO	Cs ₂ CO ₃	4	47
23	0.5	DMSO	-	48	No reaction

^a Reaction conditions: acetophenone oxime (1 mmol), phenylboronic acid (2 mmol), 28 °C, in air.

^b Isolated yield.

^c 0.5 equiv of base.

^d 2 equiv of base.

e 0.2 equiv of TBAB used.

very long reaction time. Interestingly we found a dramatic effect of bases in the progress of the reaction as the use of KOH and Na₃ PO₄·12H₂O gave only a trace amount of product (Table 1, entries 2 and 3). However Na₂CO₃ and K₂CO₃ gave good yields of product (Table 1, entries 4 and 5). The yield of the product was significantly decreased when we used NaHCO3 and we could isolate 40% yield of product (Table 1, entry 6). We examined the effect of organic base in our reaction conditions by using TEA which gave 58% isolated yield within 6 h (Table 1, entry 7). During this study Cs₂CO₃ was found to be the most effective base, with 1 equiv sufficient for optimal isolated yields of **3a** (82%) (Table 1, entries 1, 8 and 9). Several test reactions were carried out using different amounts of copper acetate and we found that the presence of $0.5 \text{ equiv of } Cu(OAc)_2$ gave better yield of products (Table 1, entries 1 and 10-14). To study the effect of solvent in our system we carried out the reaction in the presence of various solvents and the reaction was found to proceed in both protic and aprotic solvents, although significant variations in yields were noticed (Table 1, entries 15-20). The best result was obtained when DMSO was used as solvent. However no product formation was observed in water (Table 1, entry 1 and 20). Although the use of a phase transfer catalyst like TBAB improved the yield to 41% in 48 h in water (Table 1, entry 21). Use of co-solvents like water-DMSO could not increase the yield of the product and gave 47 % yield (Table 1, entry 22). However the reaction did not proceed in the absence of base (Table 1, entry 23). Usually strong bases induced side reactions thereby decreasing the yield and too weak bases were unable to activate boronic acid. Advantages of using Cs₂CO₃ over other bases are cleaner reaction, higher yields, shorter reaction time, smaller amount of reagent required, milder reaction condition and easier work-up procedure.

To demonstrate the scope and limitations of the above optimal conditions, a series of acetophenone oxime derivatives (1a-c) and electronically diverse arylboronic acids (2a-h) were used as substrates for the oxime ether synthesis (Table 2). As shown in Table 2, the reaction was compatible with a wide range of aryloximes and arylboronic acids although electronic properties of the substituents in oximes and arylboronic acids influence the yield of the product. As discussed earlier, **1a** and **2a** efficiently reacted to give **3a** in very good yield (Table 2, entry 1). Likewise, 1a reacts with 4-methoxyphenylboronic acid (**2b**) and 4-methylphenylboronic acid (**2d**) to yield **3b** and **3d** in good yields (Table 2, entries 2, 4). When 4chlorophenylboronic acid (2c) was treated with 1a the product 3c formed in higher yield (Table 2, entry 3). However when 4-acetylphenylboronic acid (2e) was used as the coupling partner, both 1a and 1b gave 65% and 55% yields respectively (Table 2, entries 5 and 11). Cross-coupling of 3-methyphenylboronic acid (3g) with **1a** gave a higher yield of product (74%) although a longer reaction time is required for this reaction (Table 2, entry 7). However 2methyphenylboronic acid (2f) did not efficiently undergo crosscoupling with 1a and resulted in lower yield of product (Table 2, entry 6), which may be due to steric hindrance. In another case 1b gave 60% and 70% isolated yields when coupled with 2a and 2d respectively (Table 2, entries 9 and 10). Moreover 4-methylacetophenone oxime (1c) was found to be a suitable substrate for oxime ether synthesis under current reaction conditions (Table 2, entry 12). However 2-thiopheneboronic acid (2h) was not compatible under these reaction conditions (Table 2, entry 8).

To the best of our knowledge, the mechanism involving inorganic bases for the formation of O-aryloxime ether from oximes in the presence of $Cu(OAc)_2$ has never been reported. Lam et al.

Table 2

Cross-coupling of acetophenone oxime derivative with arylboronic acids^a



^a Reaction conditions: Aryl Oximes (1 mmol), Arylboronic acid (2 mmol), Cu(OAc)₂ (0.5 mmol), Cs₂CO₃ (1 mmol), DMSO (4 ml).
 ^b Isolated yield: All compounds were characterized by ¹H NMR, ¹³C NMR, FT-IR and Mass spectroscopy.

reported that when amine based substrates are added to insoluble mixture of Cu(OAc)₂ in methylene chloride, Cu(OAc)₂ gets instantaneously dissolved and gives a deep blue copper-complex responsible for the formation of the cross coupling product.³¹ However $Cu(OAc)_2$ is soluble in DMSO and we found very good yield of products in DMSO (Table 1, entry 1).

It is believed that during the course of reaction, oximes gets coordinated to $Cu(OAc)_2$ to generate in situ Cu(II) complex **A**. The complex A upon transmetallation with arylboronic acid formed copper (II) complex **B**. Reductive elimination of complex **B** yields the corresponding oxime ether. The plausible steps are shown in Scheme 1. To prove the involvement of the Cu (II) complex A, we carried out a reaction between 1a and Cu(OAc)₂. The IR spectroscopic studies of the product of the above reaction showed the presence of a band in the region of 3271–3477 cm⁻¹, which could be assigned to OH group. The presence of OH group in the metal complex implies that the coordination of metal occurs through



the nitrogen atom of the oxime group. This assumption was supported by the observation that v (C=N) of the free oxime ligand at 1639 cm⁻¹ is considerably shifted to lower frequency³² at 1610 cm⁻¹ after complexation. Formation of **A** was further supported by the observation of a new band in the region of 451 cm⁻¹, assigned to v (Cu–N) stretching vibration.³³ Moreover antisymmetric and symmetric COO stretching bands at 1582 and 1425 cm⁻¹ are found to be shifted to lower and higher frequencies 1562 and 1444 cm⁻¹ respectively upon coordination indicating the presence of COO group in the complex.^{32a} Additionally mass spectroscopic studies also support the formation of A. The same Cu (II) complex **A** was formed in the presence or absence of the base indicating that the base did not play any role in the complex formation. It is important to mention here that when we stir the mixture of 1a, 1b, and Cs₂CO₃ in the presence of Cu(OAc)₂, a deep blue colored solution was formed. This may be due to the formation of a copper oxime complex.³¹ Interestingly we found that 0.5 equiv of Cu(OAc)₂ is enough for the formation of the O-aryloxime ether, which indirectly supports the involvement of copper complex **A** in the reaction. Moreover the reaction of preformed Cu(II) complex A and **2a** gave the same product in good yield which supports the involvement of in situ formed Cu(II) complex A in the reaction.

In summary we have developed an efficient protocol for the synthesis of oxime ethers under mild reaction conditions. The reaction was promoted by $Cu(OAc)_2$ in the presence of Cs_2CO_3 as base. The reaction was carried out in DMSO which is a usable solvent.³⁴ This method offers a mild and efficient alternative to the existing protocols since the reaction proceeded at room temperature within shorter reaction time in the presence of inorganic base.

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- 30. General procedure: To a mixture of acetophenone oxime (**1a**, 135 mg, 1 mmol), $Cu(OAc)_2$ (100 mg, 0.5 mmol), Cs_2CO_3 (325 mg, 1 mmol), aryl boronic acid (**2a**, 242 mg, 2 mmol) and 4 ml of DMSO was added in open atmosphere in a 50 ml round bottom flask. The mixture was stirred at room temperature and the progress was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with dil. NH₄Cl-H₂O solution and extracted with ethyl acetate (3×20 ml). Then the extract was washed with brine (2×20 ml) and dried over Na₂SO₄ and evaporated on reduced pressure. Residue was purified by silica gel chromatography (ethyl acetate–hexane: 1:9) to obtained the desired products. Thin-layer chromatography was carried out with Merck silica gel 60F₂₅₄ plates. Products were characterized by ¹H NMR, ¹³C NMR, FTIR spectroscopy and Mass spectroscopy.
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