ORGANIC LETTERS

XXXX
Vol. XX, No. XX
000–000

Facile Cu(I)-Catalyzed Oxidative Coupling of Anilines to Azo Compounds and Hydrazines with Diaziridinone under Mild Conditions

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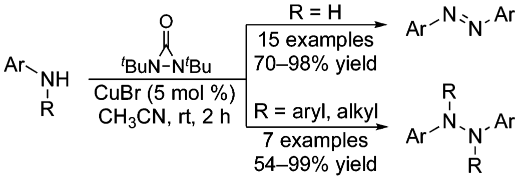
Received March 4, 2013

ABSTRACT



A mild and highly efficient Cu(I)-catalyzed oxidative coupling of anilines is described. Various primary and secondary anilines can be efficiently coupled under mild conditions to the corresponding azo compounds and hydrazines in high yields. This method provides a direct and practical access to these compounds and is also amenable to gram scale with no special precautions to exclude air or moisture.

Development of efficient methods for the synthesis of azo compounds is highly important as this class of molecules can be used as organic dyes,[1] indicators,[2] radical reaction initiators,[3] nonlinear optics,[4] chemosensors,[5] and photochemical switches.[6] Various synthetic methods[7] have been developed including oxidation of hydrazines,[8] reduction of azoxybenzenes,[9] coupling of aryl diazonium salts with nucleophiles,[10] coupling of primary anilines with

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10.1021/ol4005917

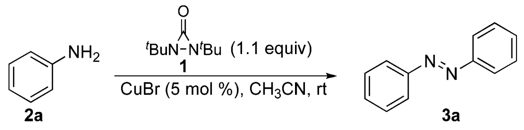
aromatic nitroso compounds,[11] and reductive coupling of nitroaromatics.[12] Azo compounds can also be obtained by oxidative coupling of anilines using stoichiometric oxidants, such as mercury(II) oxide,[13] manganese salts,[14] lead tetraacetate,[15] ferrate salts,[16] and *tert*-butyl hypoiodite.[17] Metal-catalyzed oxidative coupling of anilines using O_2 has also been reported.[18]

In our earlier studies, di-*tert*-butyldiaziridinone (**1**)[19,20] has been shown to be a highly effective nitrogen source for the diamination of olefins using Pd(0)[21] or Cu(I)[22] as catalysts. Very recently, we have shown that diaziridinone **1** can oxidize alcohols to aldehydes and ketones using CuBr as catalyst.[23] In our efforts to further explore the synthetic utility of diaziridinone, we have found that anilines can be efficiently oxidized to azo compounds and hydrazines using CuBr catalyst and diaziridinone **1**. Herein we wish to report our preliminary results on this subject.

When phenylamine (**2a**) was treated with di-*tert*-butyldiaziridinone (**1**) and 5 mol % of CuBr in CH_3CN at rt under air for 2 h, azobenzene **3a** was cleanly formed and isolated in 93% yield (Scheme 1). Similar yield (94%) was obtained when this reaction was carried out under argon. Both di-*tert*-butyldiaziridinone (**1**) and Cu(I) catalyst are required for the transformation as no oxidation was observed in the absence of **1** or CuBr under air for 24 h (Scheme 1).

As shown in Scheme 2, this oxidative coupling can be extended to a variety of primary anilines bearing either electron-donating or electron-withdrawing groups at the *para*, *meta*, and *ortho* positions on the phenyl ring, giving the corresponding azo compounds in 70−98% yield (Scheme 2, **3a**−**3n**). Halo-substituted azobenzenes can be obtained in high yields from the corresponding anilines, and no Ullmann-type C−N coupling byproducts were detected (Scheme 2, **3j**−**3l**). As illustrated in the case of 4-bromoaniline (**2l**), azo product **3l** can be obtained on gram scale in 91% yield (Scheme 2). As shown in Scheme 3, the oxidative coupling of aniline proceeded faster than the oxidation of an alcohol. Azobenzene **3o** was obtained when **2o** was treated with 1.1 equiv of diaziridinone **1** and 10 mol % of CuBr in CH_3CN at rt for 2 h. Both amine and alcohol were oxidized with 2.1 equiv of **1**, giving diketone **3o′** in 91% yield.

Scheme 1



a) under air, 2 h	93% yield
b) under Ar, 2 h	94% yield
c) no diaziridinone **1**, under air, 24 h	no reaction
d) no CuBr, under air, 24 h	no reaction

When diphenylamine (**4a**) was subjected to the reaction conditions, tetraphenylhydrazine (**5a**) was obtained in

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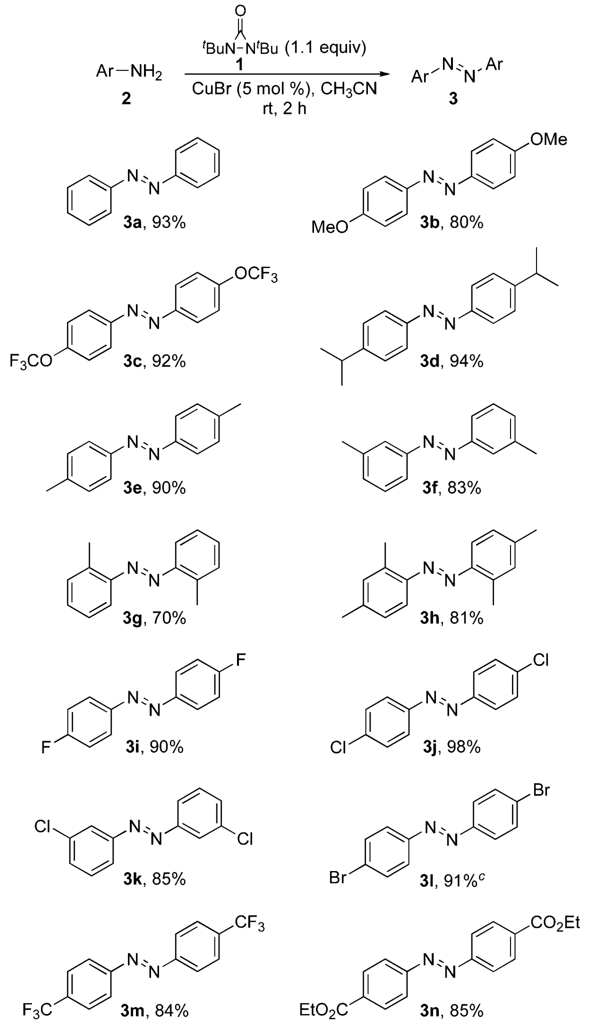
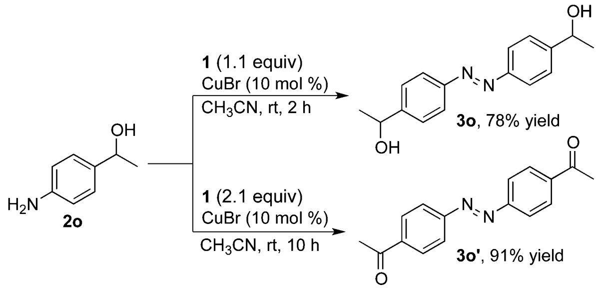
Scheme 2. Oxidative Coupling of Primary Anilines[a,b]



[a] All reactions were carried out with primary aniline **2** (0.80 mmol), **1** (0.88 mmol), and CuBr (0.040 mmol) in CH$_3$CN (1.6 mL) at rt for 2 h unless otherwise stated. [b] Isolated yield based on primary aniline **2**. [c] The reaction was carried out on 8.0 mmol scale.

60% yield (Scheme 4). This coupling process is also applicable to various other secondary anilines, giving the corresponding tetrasubstituted hydrazines in 54−99% yield (Scheme 4, **5b**−**5g**). As illustrated in the case of bis(4-bromophenyl)amine (**4f**), hydrazine **5f** can be obtained on gram scale in 99% yield (Scheme 4). Hydrazines are a class of very important compounds.[24] Substituted hydrazines are usually prepared by derivatization of simple hydrazine precursors.[24,25] There are few methods reported in the literature for the direct synthesis of substituted hydrazines from readily available secondary anilines.[26] The current method provides a viable process for the synthesis of tetrasubstituted hydrazines.

Scheme 3



In order to better understand the mode of reactivity, 1,2-diphenylhydrazine (**6a**) was subjected to the reaction conditions. Azobenzene **3a** was obtained in 96% yield in only 5 min (Scheme 5), suggesting that **6a** is a possible intermediate for the oxidative coupling of aniline. Attempts to isolate intermediate **6a** in the coupling of aniline **2a** using 0.55 equiv of **1** proved unsuccessful, yielding azobenzene **3a** in 47% yield along with unreacted starting material (Scheme 5).

While a precise understanding of the reaction mechanism awaits further study, a plausible catalytic pathway for the oxidative coupling of anilines is proposed in Scheme 6. The N−N bond of di-*tert*-butyldiaziridinone (**1**) is reductively cleaved by CuBr to form Cu(II) nitrogen radical **A**[27,28] and/or Cu(III) species **B**,[22e,f] which reacts with

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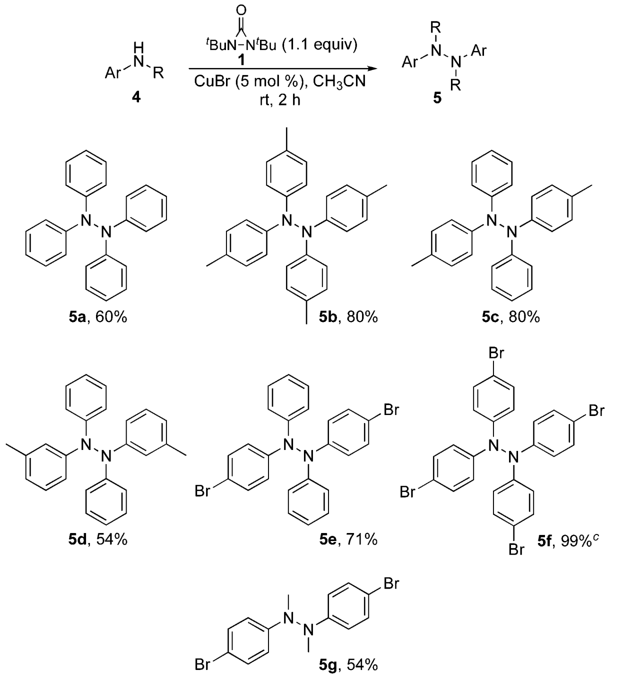
Scheme 4. Oxidative Coupling of Secondary Anilines[a,b]

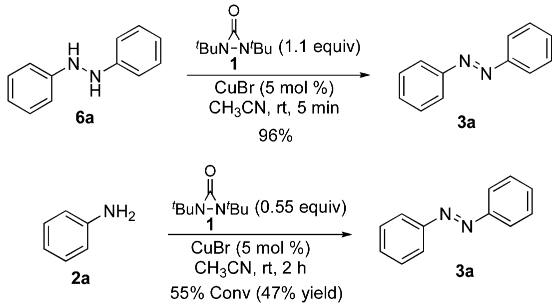


[a] All reactions were carried out with secondary aniline **4** (0.80 mmol), **1** (0.88 mmol), and CuBr (0.040 mmol) in CH_3CN (1.6 mL) at rt for 2 h unless otherwise stated. [b] Isolated yield based on secondary aniline **4**. [c] The reaction was carried out on 8.0 mmol scale.

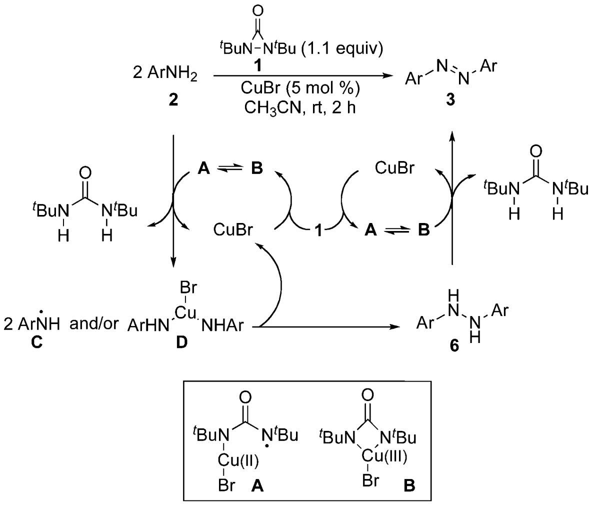
aniline **2** to generate the corresponding nitrogen radical **C**[28] and/or Cu(III) species **D**. Hydrazine **6** is subsequently formed via the dimerization of radical **C** or reductive elimination of species **D**. The dehydrogenation of **6** by Cu species **A** and/or **B** forms product **3**.

In summary, we have developed a novel oxidative coupling of anilines using CuBr as catalyst and di-*tert*-butyldiaziridinone (**1**) as oxidant. Various primary and secondary anilines can be efficiently coupled under mild conditions to give the corresponding azo compounds and hydrazines in high yields. This reaction is operationally simple and is amenable to gram scale. The results further illustrate the synthetic potential of diaziridinone as a versatile oxidation reagent. Development of other reaction processes with this class of compounds is currently underway.

Scheme 5



Scheme 6. Proposed Catalytic Cycle for the Oxidative Coupling



Acknowledgment. We are grateful for the generous financial support from the General Medical Sciences of the National Institutes of Health (GM083944-05).

Supporting Information Available. Experimental procedures, characterization data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.