Azo Compounds

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Copper-Catalyzed Aerobic Oxidative Dehydrogenative Coupling of Anilines Leading to Aromatic Azo Compounds using Dioxygen as an Oxidant**

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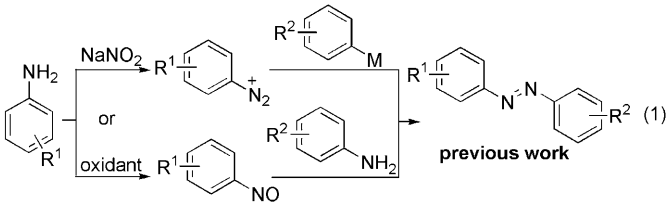
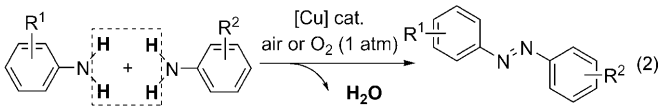
Aromatic azo compounds are ubiquitous motifs and are widely used in industry as organic dyes, indicators, pigments, food additives, radical reaction initiators, and therapeutic agents.[1] Despite numerous efforts towards the synthesis of azo derivatives, big challenges still remain because: 1) the catalytic procedures that have been reported to afford high yields have been less widely explored;[2] 2) stoichiometric and environmentally unfriendly oxidants, such as manganese salts,[3a] lead salts,[3b–c] mercury salts,[3d–e] or ferrates[3f–g] were previously employed for their preparation form aromatic amines; 3) unsymmetric aromatic azo compounds are not easy to prepare. Usually, two step syntheses are used, proceeding from anilines via diazonium salt[4] or nitrosobenzene intermediates,[5] using stoichiometric amounts of nitrite salts or other oxidants, to produce unsymmetric aromatic azo compounds, with inorganic salts as the by-products [Eq. (1)].



(1)

Recent breakthroughs were developed by Corma, García, and co-workers.[2a] They reported an oxidation of aromatic anilines to aromatic azo compounds catalyzed by gold nanoparticles using O_2 (3–5 bar) as the oxidant at 100 °C. However, the employment of a noble gold catalyst and the requirement of higher pressure and temperature may limit their applications. Herein, we demonstrate a novel approach to azo compounds from readily available anilines, under mild conditions using an inexpensive and commercial available copper catalyst and air or dioxygen as an oxidant [Eq. (2)]. To

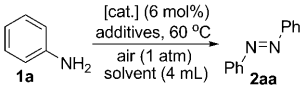


(2)

the best of our knowledge, this is the first convenient catalytic process for unsymmetric azo compounds from aromatic amines using O_2 (1 atm) as the oxidant.

The use of dioxygen as an ideal oxidant has attracted a great deal of attention.[6,7] During our investigations toward α-ketoamides synthesis using the copper-catalyzed oxidative-amidation/diketonization of terminal alkynes,[8] we observed that *trans*-1,2-diphenyldiazene (**2aa**) was easily prepared by dehydrogenative coupling[9] using a copper salt as the catalyst in air. (Table 1). Employing pyridine as a ligand was key for high efficiency in this transformation (Table 1, entries 1 and

Table 1: Copper-catalyzed oxidative coupling of **1a** under air.[a]



Entry	Catalyst	Additives (mol%)	Solvent	Yield of **2aa** [%][b]
1	CuBr	none	toluene	12
2	$CuBr_2$	pyridine (18)	toluene	60
3	CuCl	pyridine (18)	toluene	80
4	CuBr	pyridine (18)	toluene	96
5	CuI	pyridine (18)	toluene	trace
6	CuOAc	pyridine (18)	toluene	8
7	$Pd(OAc)_2$	pyridine (18)	toluene	n.r.
8	$AuBr_3$	pyridine (18)	toluene	n.r.
9	CuBr	–	pyridine	11
10	CuBr	pyridine (18)	DCE	62
11	CuBr	2,2′-bipyridine (9)	toluene	29
12	CuBr	PPh_3 (18)	toluene	n.r.
13	CuBr	1,10-phenanthroline (9)	toluene	trace
14	CuBr	pyridine (12)	toluene	65
15	CuBr	pyridine (24)	toluene	94

[a] Reaction conditions: **1a** (1 mmol), cat. (0.03 mmol), solvent (4 mL), air (1 atm), 20 h. [b] Yield of isolated product. DCE = 1,2-dichloroethane, n.r. = no reaction.

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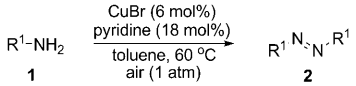
4). Attempts to use other transition-metal catalyst, such as silver, gold, iron, palladium, cobalt, or manganese were unsuccessful (see the Supporting Information). Of the copper salts tested as catalysts in the reaction, CuBr performed the best (Table 1, entries 2–6; also see the Supporting Information). We then surveyed the effect of different solvents: the reactions gave low yields in 1,2-dichloroethane, pyridine, and tetrahydrofuran, respectively (Table 1, entries 4, 9, and 10; also see the Supporting Information). Further studies indicated that the efficiency of this transformation decreased when other ligands, such as PPh_3, 2,2′-bipyridine, or 1,10-phenanthroline were used (Table 1, entries 11–13). We envisioned that the copper intermediate should have a flexible structure that could readily dissociate with the ligand and combine with a reactant. Compared with the copper/pyridine complex, the copper/bipyridine complex is harder and more inflexible; as such, the reaction with 9 mol% bipyridine gave poor yield (Table 1, entries 4 and 11). The yields decreased with higher or lower ligand loading (Table 1, entries 14 and 15). After extensive screening with the other reaction parameters (see the Supporting Information), it was discovered that 6 mol% CuBr, 18 mol% pyridine, in toluene at 60 °C under air were the optimized reaction condition (96%; Table 1, entry 4).

Under the optimized conditions, various aromatic azo compounds were produced from their corresponding simple and readily available amines. The results in Table 2 demonstrate that this reaction has a high degree of functional-group tolerance. Both electron-rich (*para*, *meta*, and *ortho* substituted) and electron-deficient substrates were well-tolerated, giving moderate to excellent yields. It is noteworthy that halo-substituted anilines survived well, leading to halo-substituted aromatic azo compounds (Table 2, entries 9–11), which could be used for further transformations.

Table 2: Copper-catalyzed oxidative coupling of aniline.[a]

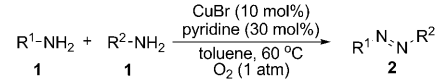


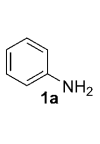
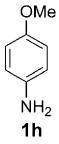
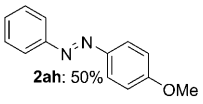
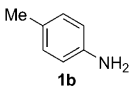
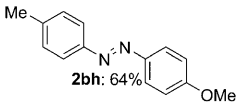
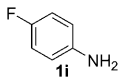
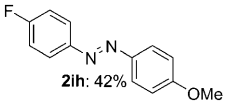
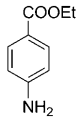
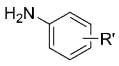
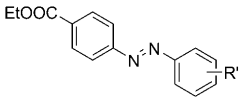
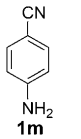
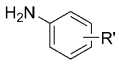
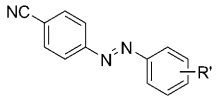
Entry	R^1	Yield of **2** [%][b]
1	Ph (**1a**)	96 (**2aa**)
2	4-Me-C_6H_4 (**1b**)	97 (**2bb**)
3	3-Me-C_6H_4 (**1c**)	96 (**2cc**)
4[c]	2-Me-C_6H_4 (**1d**)	65 (**2dd**)
5	4-Cy-C_6H_4 (**1e**)	91 (**2ee**)
6	4-CF_3O-C_6H_4 (**1f**)	91 (**2ff**)
7[c]	2,4-Me_2-C_6H_4 (**1g**)	84 (**2gg**)
8[c]	4-OMe-C_6H_4 (**1h**)	66 (**2hh**)
9	4-F-C_6H_4 (**1i**)	97 (**2ii**)
10	4-Cl-C_6H_4 (**1j**)	93 (**2jj**)
11	4-Br-C_6H_4 (**1k**)	67 (**2kk**)
12[c]	4-COOEt-C_6H_4 (**1l**)	61 (**2ll**)

[a] Standard reaction conditions: **1** (1 mmol), CuBr (0.03 mmol), pyridine (0.09 mmol), toluene (4 mL), air (1 atm), 20 h. [b] Yield of isolated product. [c] The reaction was carried out under O_2 (1 atm).

Importantly, unsymmetrically substituted azobenzenes, which are typically synthesized through reaction of the diazonium salt with electron-rich aromatic compounds, can be constructed using this oxidative dehydrogenative method with H_2O as the by-product (Table 3). Notably, even when 4-bromo- or 4-chloro-aniline were employed as substrates, which reacted with **1l** to afford unsymmetric azo compounds **2lj** and **2lk**, respectively (73% yield; Table 3, entries 9 and 10). The copper-catalyzed Ullmann-amination reaction,[10] which results in the formation of a new C–N bond, was not observed in these cases, nor in Table 2, entries 10 and 11. The homocoupling of anilines with electron-donating aryl substituents react faster than those of anilines with electron-withdrawing aryl substituents. The kinetic experiments of **1b** and **1l** clearly illustrated the different reaction rates (see the Supporting Information). Therefore, a larger excess of electron-poor anilines was employed to enhance the yield of the cross-coupled diazo compounds.

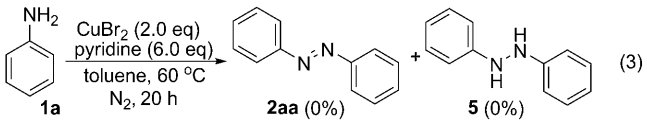
Table 3: Copper-catalyzed oxidative coupling of anilines for unsymmetric azo compounds.[a]



Entry	R^1	R^2	Yield of **2** [%][b]
1	 **1a**	 **1h**	 **2ah**: 50%
2	 **1b**	**1h**	 **2bh**: 64%
3	 **1i**	**1h**	 **2ih**: 42%
	 **1l**		
4	**1l**	R′ = H (**1a**)	**2la**: 69%
5	**1l**	R′ = *p*-Me (**1b**)	**2lb**: 43%
6	**1l**	R′ = *m*-Me (**1c**)	**2lc**: 54%
7	**1l**	R′ = *o*-Me (**1d**)	**2ld**: 60%
8	**1l**	R′ = *p*-OCF_3 (**1f**)	**2lf**: 64%
9	**1l**	R′ = *p*-F (**1i**)	**2li**: 53%
10	**1l**	R′ = *p*-Cl (**1j**)	**2lj**: 73%
11	**1l**	R′ = *p*-Br (**1k**)	**2lk**: 73%
	 **1m**		
12	**1m**	R′ = H (**1a**)	**2ma**: 42%
13	**1m**	R′ = *p*-OCF_3 (**1f**)	**2mf**: 50%

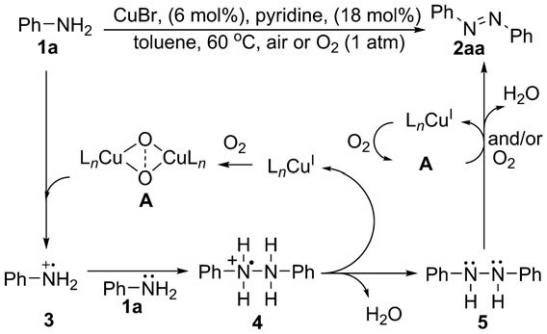
[a] Standard reaction conditions: R^1–NH_2 (1 mmol), R^2–NH_2 (0.2 mmol), CuBr (0.02 mmol), pyridine (0.06 mmol), toluene (4 mL), O_2 (1 atm), 24 h. [b] Yield of isolated product.

To probe the mechanism of this transformation, the reaction of **1a** in the presence of 2.0 equivalents of a copper(I) or copper(II) catalyst under N_2 was investigated respectively [Eq. (3); see Eq. S1 in the Supporting Information]. How-



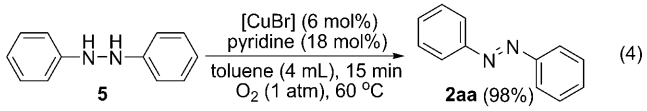
(3)

ever, no product, such as 1,2-diphenylhydrazine, nitrosobenzene, or the expected aromatic azo **2aa** was detected in both of these reactions. We therefore postulated that the dioxygen acted not only as the oxidant, but also as an initiator to trigger this catalytic process. Enlightened by the growing amount of information about copper(I)–dioxygen reactivity,[11] we hypothesized that a (μ–η^2:η^2–peroxo)dicopper(II) complex[11] **A** (Scheme 1) might be the active catalytic species, produced



Scheme 1. The proposed mechanism for the direct transformation.

in situ through the reaction of the L_n/Cu^I complex with O_2. Furthermore, nitrosobenzene was employed as the substrate in the coupling reaction with ethyl 4-aminobenzoate **1l** (see Eq. S3 in the Supporting Information); however, no hetero-coupling product was detected, which indicated that nitrosobenzene is not an intermediate of this oxidative process. Interestingly, 1,2-diphenylhydrazine can easily be converted into aromatic azo product **2aa** (98% yield) under the standard conditions [Eq. (4)]. We also investigated the effect of copper and pyridine in this progress (see Table S6



(4)

in the Supporting Information). It is noteworthy that pyridine play an important role in this oxidation step. The fast oxidation of 1,2-diphenylhydrazine into aromatic azo under the standard conditions [15 min; Eq. (4)] indicates that this step is not the rate-determining step in this transformation.

On the basis of the above results, a plausible mechanism for the oxidative dehydrogenative coupling is illustrated in Scheme 1. The copper(I) salt was initially chelated by a pyridine ligand[6h,8] and oxidized by dioxygen to form the more-active (μ-η^2:η^2-peroxo)dicopper(II) complex **A**. Then, a single-electron oxidation of aniline, mediated by the copper(II) complex, into corresponding radical cation **3**, followed by subsequent coupling of **3** with **1a** forms a three-electron sigma bond **4**,[2a,12] which consecutively donates two protons and one electron leading to hydrazine **5**. Hydrazine **5** is further oxidized by the (μ-η^2:η^2-peroxo)dicopper(II) complex **A** or dioxygen to generate the corresponding aromatic azo product.[2a,12]

In conclusion, we have developed a novel copper-catalyzed approach to aromatic azo compounds, which are highly valued chemicals and widely used in industry. Both symmetric and unsymmetric substituted azobenzenes can be conveniently prepared by this method. Notably, air (or dioxygen), the most environment friendly oxidant, was employed under mild reaction conditions. Studies are ongoing in our laboratory to understand the reaction mechanism and investigate further synthetic applications.

Experimental Section

(*E*)-1,2-Diphenyldiazene (**2aa**).[13] Typical procedure: CuBr (4.2 mg, 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), and aniline **1a** (93 mg, 1 mmol) were mixed in toluene (4 mL) under air (1 atm). The reaction mixture was stirred vigorously at 60 °C for 20 h. After cooling down to room temperature and concentrating under vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether) to afford 87.6 mg (96%) of **2aa**; yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.93$–7.91 (m, 4H), 7.52–7.44 ppm (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 152.7$, 131.0, 129.1, 122.8 ppm; Ms (70 ev): m/z (%): 182.1 (32) [M^+], 77.1 (100); IR (neat): $\nu = 3418$, 1581, 1481, 1452, 775, 688 cm^{-1}.

(*E*)-1-(4-Methoxyphenyl)-2-phenyldiazene (**2ah**). Typical procedure: CuBr (2.9 mg, 0.02 mmol), pyridine (4.8 mg, 0.06 mmol), aniline **1a** (93 mg, 1 mmol), and 4-methoxybenzenamine **1h** (25 mg, 0.2 mmol) were mixed in toluene (4 mL) under an O_2 atmosphere (1 atm). The reaction mixture was vigorously stirred at 60 °C for 24 h. After cooling down to room temperature and concentrating under vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 200:1) to afford 21.2 mg (50%) of **2ah**; yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta =$ 7.93 (d, $J = 8.8$ Hz, 2H), 7.88 (d, $J = 7.2$ Hz, 2H), 7.52–7.41 (m, 3H), 7.02 (d, $J = 8.8$ Hz, 2H), 3.89 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 162.0$, 152.8, 147.1, 130.3, 129.0, 124.7, 122.6, 114.2, 55.6 ppm; Ms (70 ev): m/z (%): 212.1 (64) [M^+], 107.0 (100); IR (neat) $\nu = 2923$, 2852, 1601, 1251, 1029, 840 cm^{-1}; HRMS m/z (ESI) calcd for $C_{13}H_{13}N_2O$ [M+H]$^+$ 213.1022 found 213.1020.

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Keywords: azo compounds · copper · cross-coupling · ligand effects · oxidation

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