CHEMISTRY
A EUROPEAN JOURNAL

COMMUNICATION

DOI: 10.1002/chem.201301818

A Highly Efficient Palladium-Catalyzed Decarboxylative *ortho*-Acylation of Azobenzenes with α-Oxocarboxylic Acids: Direct Access to Acylated Azo Compounds

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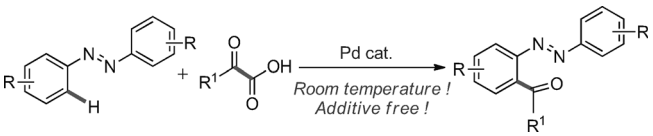
Recently, transition-metal-catalyzed decarboxylative cross-coupling reactions involving the use of readily available α, β-unsaturated and aryl carboxylic acids as potential coupling partners, in place of aryl halides or organometallic reagents, has attracted much attention and has provided a powerful tool for the construction of chemical bonds in organic synthesis.[1] Early in 2002, Myers reported a palladium-catalyzed decarboxylative Heck-type olefination of benzoic acids.[2] Since then, significant progress has been made on decarboxylative cross-coupling reactions.[3] For example, Goossen,[3a–d] Forgione,[3e] Li,[3f] Liu,[3g,h] Miura,[3i] Lee,[3j] and Tunge[3k,l] have studied decarboxylative biaryl coupling, olefination, alkynylation, aryl ketone formation and so forth. Very recently, Ge,[4] Duan,[5] Kim,[6] Tan,[7] Zhu,[8] and Saxena[9] have further demonstrated the feasiblity of decarboxylative acylation of arenes and other substrates by Pd-catalyzed group-directed C–H activation. Despite the achievements that have been made with respect to decarboxylation reactions, high reaction temperatures, and additives required for the decarboxylative process partially limit their potential applications. Therefore, it is desirable to develop a mild decarboxylative cross-coupling reaction that proceeds in the absence of any additives.

It is well known that azo compounds are important materials and have been broadly applied in many fields due to their special properties.[10] For instance, they can be used as light triggered switches in surface-modified materials,[10a] molecular machines,[10b] protein probes,[10c] and so forth.[10d–f] As a result of their importance, some typical methodologies have been established for the preparation of azobenzenes.[11] For example, the reduction of nitro compounds in the presence of an excessive amount of reducing agent,[11a] the classic coupling reaction of diazo salts with aromatic compounds at low temperature,[11b] and the aerobic oxidative dehydrogenation of aryl amines in the presence of a transition-metal catalyst.[11c–d] Although the established methodologies have been successfully applied in the synthesis of azo compounds, the restricted reaction conditions, limited substrate scope, and the formation of complex by-products are undesirable.[11a–b] It is worth noting that the synthesis of sterically hindered *ortho*-substituted azo compounds is also a big challenge, and is a reaction that has been little studied thus far. We have recently developed a Pd-catalyzed acylation of azobenzenes with aldehydes in the presence of *tert*-butylhydroperoxide (TBHP), leading to a series of acylated azobenzenes.[12] In our ongoing synthesis of *ortho*-substituted azobenzenes, we report herein a highly efficient and mild decarboxylative[13] *ortho*-acylation of azobenzenes with α-oxocarboxylic acids catalyzed by Pd at room temperature in the absence of an additive (Scheme 1).



Scheme 1. Pd-catalyzed decarboxylative acylation of azobenzenes with α-oxocarboxylic acids.

We initiated our studies with the acylation of azobenzene (**1a**) with 2-oxo-2-phenylacetic acid (**2a**) in 1,2-dichloroethane (DCE) using $Pd(OAc)_2$ as a catalyst. The results are shown in Table 1. Although no reaction occurred in the presence of $Cu(OAc)_2$, 24% of acylated product **3a** was isolated when the oxidant was switched to $(NH_4)_2S_2O_8$ at room temperature for 36 h (Table 1, entries 1 and 2). Gratifyingly, the use of $K_2S_2O_8$ could enhance the acylation of **1a** with **2a**, leading to the formation of **3a** in 76% yield (Table 1, entry 3). Unfortunately, other oxidants, such as $Mn(OAc)_3$ and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) were ineffective in the model reaction (Table 1, entries 4 and 5). When the model reaction was carried out under an oxygen atmosphere (1.0 atm) at room temperature for 48 h, **3a** was obtained in 14% yield, and most of the starting material was recovered (Table 1, entry 6). The palladium source was found to be crucial for this transformation and several commercially available Pd^{II} salts were tested in the acylation of

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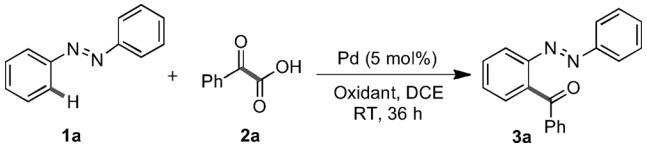
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201301818.

Table 1. Optimization of the acylation of azobenzene (**1a**) with 2-oxo-2-phenylacetic acid (**2a**).[a]



Entry	Pd source	Oxidant	Additive	Yield [%][b]
1	$Pd(OAc)_2$	$Cu(OAc)_2$	–	0
2	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	–	24
3	$Pd(OAc)_2$	$K_2S_2O_8$	–	76
4	$Pd(OAc)_2$	$Mn(OAc)_3$	–	0
5	$Pd(OAc)_2$	DDQ	–	0
6	$Pd(OAc)_2$	O_2 (1.0 atm)	–	14
7	$Pd(TFA)_2$	$K_2S_2O_8$	–	70
8	$PdCl_2$	$K_2S_2O_8$	–	42
9	$Pd(CH_3CN)_2Cl_2$	$K_2S_2O_8$	–	32
10	$Pd(PPh_3)_2Cl_2$	$K_2S_2O_8$	–	40
11	$Pd(OAc)_2$	$K_2S_2O_8$	Ag_2O (1.0 equiv)	53
12	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH (1.0 equiv)	22
13	$Pd(OAc)_2$	$K_2S_2O_8$	–	67[c]
14	$Pd(OAc)_2$	$K_2S_2O_8$	–	73[d]
15	$Pd(OAc)_2$	$K_2S_2O_8$	–	53[e]
16	$Pd(OAc)_2$	$K_2S_2O_8$	–	68[f]

[a] Reaction conditions: Azobenzene (**1a**, 0.20 mmol), 2-oxo-2-phenylacetic acid (**2a**, 0.30 mmol), Pd catalyst (5 mol%), $K_2S_2O_8$ (0.30 mmol) in DCE (1.0 mL) at room temperature under air for 36 h. [b] Isolated yields. [c] 28 h. [d] 48 h. [e] **1a**/**2a** = 1:1. [f] **1a**/**2a** = 1:2.

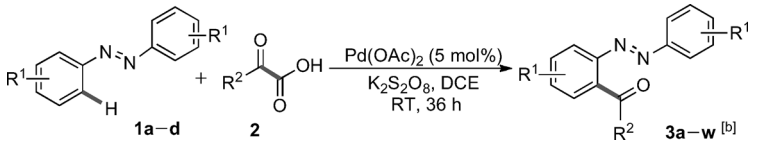
1a with **2a** at room temperature with $K_2S_2O_8$ as the oxidant and DCE as solvent. It should be noted that $Pd(OAc)_2$ exhibited high activity in the decarboxylative reaction, and was found to be more active than [$Pd(TFA)_2$] (TFA = trifluoroacetic acid) (Table 1, entry 7 vs entry 3).[4a] Several other Pd sources were screened, including $PdCl_2$, [$Pd(CH_3CN)_2Cl_2$], and [$Pd(PPh_3)_2Cl_2$], but did not enhance the yield of product **3a** (Table 1, entries 8–10). The addition of common additives, such as Ag_2O or PivOH (pivalic acid), to the reaction resulted in a reduced yield of **3a** (Table 1, entries 11 and 12). An optimization study of the reaction time and the molar ratio of **1a**/**2a** did not provide improved conditions for the synthesis of **3a** (Table 1, entries 13–16). Further investigation of the solvent effect in the model reaction showed that 1,2-dichloroethane was the most successful of the solvents tested (See TS1 in Supporting Information for details). Finally, the optimized reaction conditions were found to be: $Pd(OAc)_2$ (5 mol%), $K_2S_2O_8$ (1.5 equiv) as the oxidant and a molar ratio of (1:1.5) of azobenzene to 2-oxo-2-phenylacetic acid in DCE at room temperature under air for 36 h.

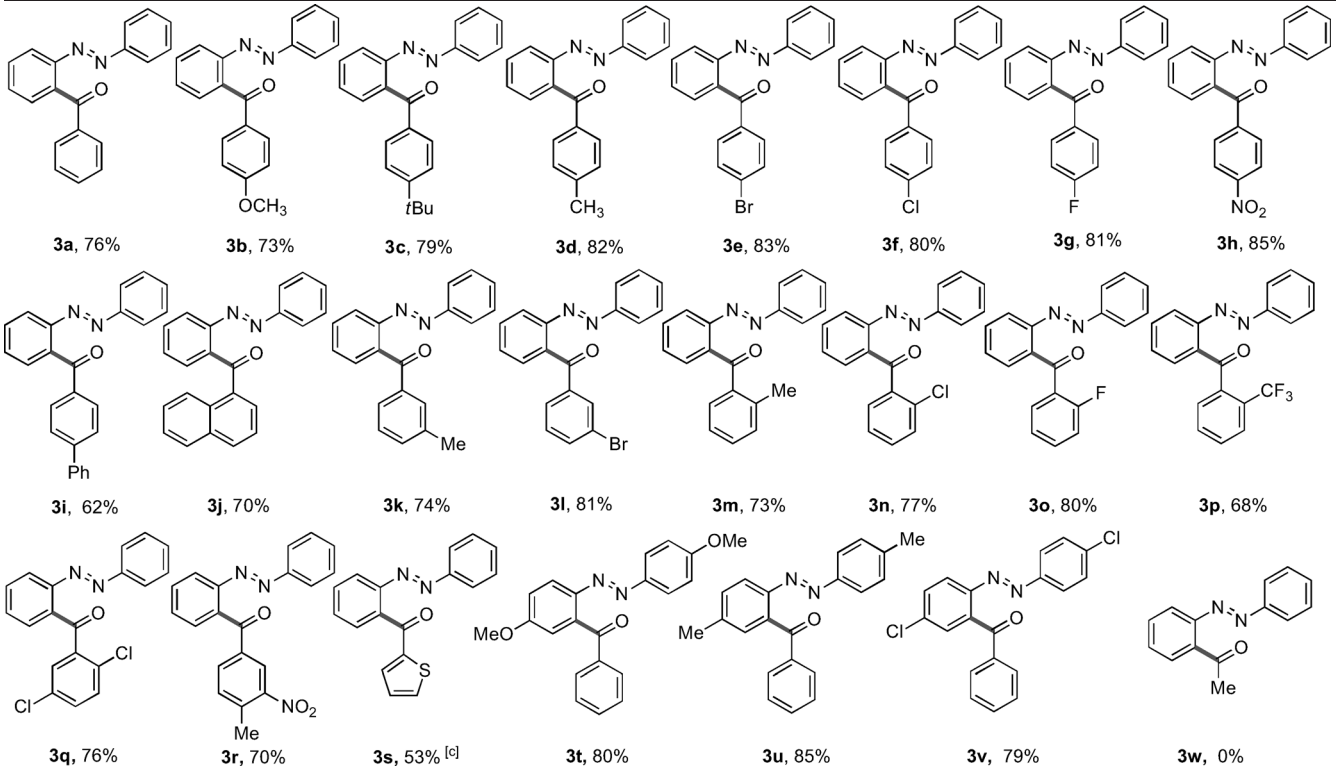
To evaluate the scope of this decarboxylative acylation reaction, various α-oxocarboxylic acids were investigated under the optimized reaction conditions, as shown in Table 2. The results indicate that azobenzene **1a** can react with various 2-oxo-2-phenylacetic acids to generate the corresponding products in good yield. Notably, electron-donating and electron-withdrawing groups (Me, MeO, *t*Bu, Br, Cl, F and NO_2) on the *para*-position of the phenyl ring of the 2-oxo-2-phenylacetic acids underwent the decarboxylative process smoothly and generated the desired products (**3b**–**h**) in 73–85% yield. It should be noted that when 2-([1,1′-biphenyl]-4-yl)-2-oxoacetic acid and 2-(naphthalen-1-yl)-2-oxoacetic acid were reacted with **1a**, the corresponding products **3i** and **3j** were obtained in 62 and 70% yield, respectively. Furthermore, it was found that the *meta*-substituted 2-oxo-2-phenylacetic acids **2k** and **2l** also reacted with **1a** and afforded **3k** and **3l** in good yields. An *ortho*-position effect was found in the reaction of **1a** with 2-oxo-2-phenylacetic acids possessing the bulky groups CF_3 or CH_3 on the phenyl ring (**3m** and **3p**). Meanwhile, no evident *ortho*-position effect was observed in the reaction of **1a** with 2-oxo-2-phenylacetic acids containing Cl or F on the phenyl ring (**3n** and **3o**). To our delight, when disubstituted 2-oxo-2-phenylacetic acids **2q** and **2r** were reacted with **1a**, the desired products **3q** and **3r** were formed in 76 and 70% yield, respectively. However, α-oxocarboxylic acid **2s** exhibited less reactivity and provided **3s** with a yield of only 53%, even after a prolonged reaction time. Next, the performance of some representative 4,4′-disubstitued azobenzenes was examined under the optimized reaction conditions. When MeO, Me, and Cl, were introduced into the phenyl rings of azobenzenes, the decarboxylative acylations of 4,4′-dimethyl azobenzene, 4,4′-dimethoxy azobenzene, and 4,4′-dichloro azobenzene with **2a** proceeded well and the corresponding products **3t**–**v** were isolated in good yields (80, 85, and 79%, respectively). However, 2-oxopropanoic acid (**2w**) failed to react with **1a** under the present reaction conditions, and none of the desired product **3w** was detected.

Subsequently, we attempted to further transform the acylated azobenzenes into the corresponding indazoles, which can exhibit unique biological activity in nature. Recently we have established an efficient methodology, based on a Zn/NH_4Cl/MeOH system, for constructing the indazole backbone.[12] Ellman et al. have reported indazole synthesis through Rh^{III}-catalyzed C–H functionalization from the reaction of azobenzenes with aldehydes.[14] We have developed a more efficient transformation of acylated azobenzenes into the corresponding indazoles using a Cu_2Cl_2/$NaBH_4$/EtOH system at room temperature for 3 min. The results are listed in Table 3 and show that the presence of electron-donating and electron-withdrawing groups in acylated azobenzenes, such as MeO, *t*Bu, Me, and Br, did not affect the transformation and the corresponding products **4a**–**f** were obtained in excellent yields (97–99%).

Following this, some control experiments were carried out in order to probe the possible reaction mechanism. Firstly, a process involving free radical species could be excluded by a control experiment which showed that the addition of one equivalent of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) into the system did not affect the yield of **3a**.[15] When the reaction of azobenzene **1a** with 2-oxo-2-phenylacetic acid (**2a**) was carried out in the presence of a stoichiometric amount of $Pd(OAc)_2$ in the absence of $K_2S_2O_8$ in DCE at room temperature for 36 h, none of the desired product **3a** was isolated. This demonstrated that the reaction did not undergo the Pd^0/Pd^{II} process. Recently, Sanford

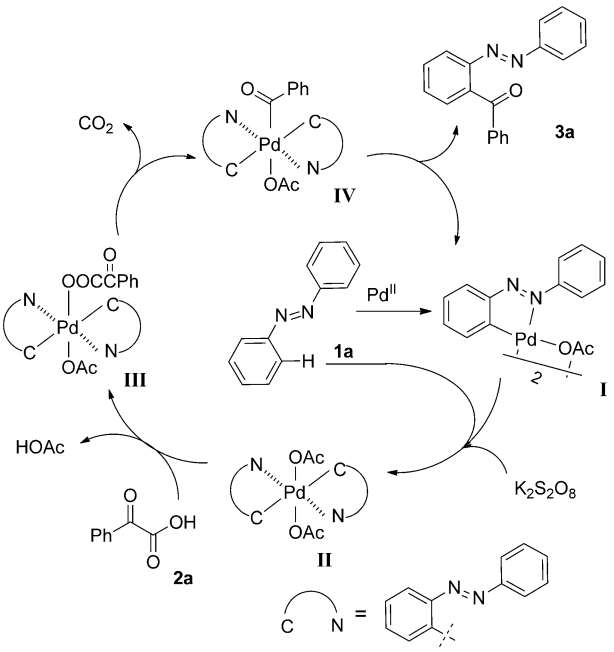
Table 2. The scope of the acylation of azobenzene **1a** with α-oxocarboxylic acids.[a]





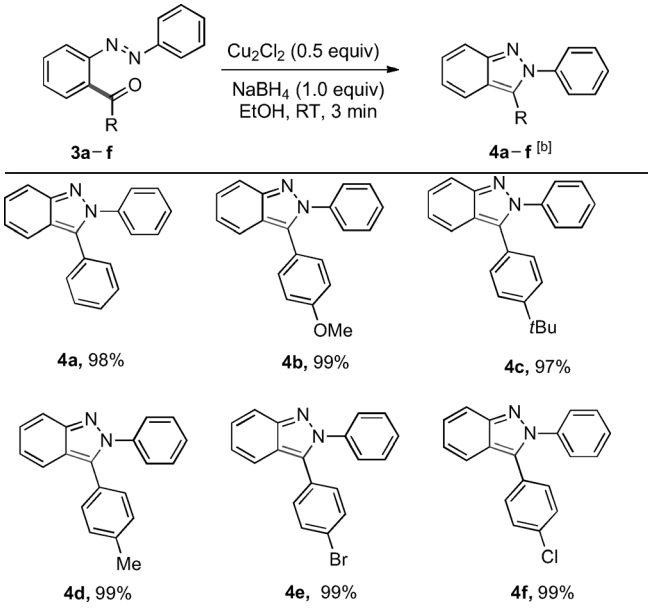
[a] Reaction conditions: Azobenzene (**1**, 0.20 mmol), α-oxocarboxylic acid (**2**, 0.30 mmol), $Pd(OAc)_2$ (5 mol%), $K_2S_2O_8$ (0.30 mmol) in DCE (1.0 mL) at room temperature under air for 36 h. [b] Isolated yields. [c] At room temperature for 48 h.

et al. have carried out detailed research on Pd-catalyzed C–H activation and a reaction mechanism involving a Pd^{II}/Pd^{IV} process was proposed and confirmed.[16] Inspired by Sanford's excellent work, a complex of Pd^{IV} with azobenzene was prepared in situ[16,17] and was then reacted with 2-oxo-2-phenylacetic acid (**2a**) in DCE at room temperature for 36 h, after which time **3a** was isolated with a yield of 47% (see the control experiments in Supporting Information for details). Based on the above results, a reaction mechanism involving a Pd^{II}/Pd^{IV} process for this system was proposed and is shown in Scheme 2. Although we failed to isolate the possible intermediate from the reaction of $Pd(OAc)_2$ with azobenzene **1a** through C–H insertion, the complex **I** is still considered as the key active species for the next functionalization, because similar five-membered intermediates have previously been reported.[18] Subsequently, cyclopalladated complex **I** is oxidized in the presence of $K_2S_2O_8$ to provide the Pd^{IV} intermediate **II**. The anion exchange between complex **II** and α-keto acid **2a** can then lead to the formation of complex **III** and the release of HOAc. Decarboxylation of complex **III** will generate complex **IV** along with extrusion of CO_2.[19] Finally, reductive elimination of **IV** can afford the product **3a**, and Pd^{II} intermediate **I** for the next cycle.



Scheme 2. Proposed reaction mechanism.

Table 3. Transformation of the acylated azobenzenes into the corresponding indazoles.[a]



[a] Reaction conditions: Acylated azobenzene (**3**, 0.20 mmol), Cu_2Cl_2 (0.10 mmol), $NaBH_4$ (0.20 mmol), EtOH (0.50 mL), room temperature, 3 min. [b] Isolated yields.

In summary, we have developed a novel Pd-catalyzed *ortho*-acylation of azobenzenes with α-oxocarboxylic acids in the presence of $K_2S_2O_8$ at ambient temperature without the presence of an additive. The reactions of azo compounds with a variety of α-oxo-2-arylacetic acids proceeded smoothly to generate the corresponding products in good yields. The reaction is highly efficient and has a broad substrate scope. In addition, several indazole derivatives were efficiently prepared from the acylated azobenzenes using a $Cu_2Cl_2/NaBH_4$/EtOH system with excellent yields. A more detailed mechanistic study is currently ongoing in our laboratory.

Experimental Section

Typical procedure for the palladium-catalyzed *ortho*-acylation of azobenzenes with α-keto acid 2a: Under an atmosphere of air, a 5.0 mL sealed tube was charged with azobenzene (**1a**, 36.4 mg, 0.20 mmol), 2-oxo-2-phenylacetic acid (**2a**, 45.0 mg, 0.30 mmol), $Pd(OAc)_2$ (4.6 mg, 0.02 mmol), $K_2S_2O_8$ (81.1 mg, 0.30 mmol), and 1,2-dichloroethane (1.0 mL) at room temperature for 36 h. H_2O (20.0 mL) was added to the resulting solution and extracted with dichloromethane (2×5.0 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:20–1:50, v/v), affording the desired product **3a** as a red solid (43.0 mg, 76%).

Typical procedure for the synthesis of indazole derivatives: Under an atmosphere of air, a 5.0 mL reaction tube was charged with Cu_2Cl_2 (0.10 mmol), EtOH (0.50 mL), **3a** (57.2 mg, 0.20 mmol), and $NaBH_4$ (0.20 mmol). The reaction mixture was stirred at room temperature for 3 min. After the red color had completely disappeared, the resulting slurry was quenched with saturated NH_4Cl solution. The filter liquor was then extracted with EtOAc (3×5.0 mL) and dried over $MgSO_4$. Then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:3–1:5, v/v), affording the desired product **4a** as a white solid (53.0 mg, 98%).

Acknowledgements

We are grateful to the National Natural Science Foundation of China (21372095 and 21172092) for financial support.

Keywords: azobenzenes · decarboxylation · *ortho*-acylation · palladium catalysis · oxocarboxylic acids

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Received: May 12, 2013
Published online: ■■ ▮▮, 0000

Palladium Catalysis

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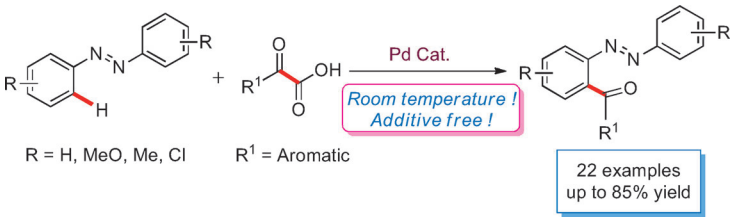
A Highly Efficient Palladium-Catalyzed Decarboxylative *ortho*-Acylation of Azobenzenes with α-Oxocarboxylic Acids: Direct Access to Acylated Azo Compounds



Avoiding additives: A highly efficient and mild Pd-catalyzed decarboxylative *ortho*-acylation of azobenzenes with α-oxocarboxylic acids was developed that provides an alternative route to acylated azo compounds. This decarboxylative acylation process was completed in the absence of any additives at ambient temperature, to afford the acylated azobenzenes in moderate to good yields (see scheme).

