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Palladium-Catalyzed Oxidative Carbonylation of Arylazos via N═N Double Bond Cleavage

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Abstract: A new palladium-catalyzed oxidative carbonylation of arylazos has been developed via cleavage of N═N double bond with TBHP as oxidant, which provided an alternative method for synthesis of arylureas from simple arylazos. The desired products could be obtained in good to excellent yields (31% ~ 90%) catalyzed by the combination of $Pd(OAc)_2$/MeO-BIPHEP in the presence of TBHP at 110 ℃ under 3.0 MPa of CO. The primary mechanistic studies demonstrated that amines might be first formed in situ from arylazos and then the oxidative carbonylation of amines occurs to give the urea products.

Key words: arylazos; oxidative carbonylation; N═N cleavage; arylureas

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The activation and controlling transformation of the inactive chemical bonds is extremely attractive topic, and is also one of the most challenging areas in chemical research. Recently, some reactions through the inert bond activationsuch as C—H, C—N and C—O[1-4] have been developed and are becoming a powerful tool for the step-economical construction of some complex organic molecules in modern organic chemistry. However, only limited progress on the activation of inert N═N bond extensively existing in natural products and fine chemicals has been achieved. In 1956, Murahashi established a cobalt catalyzed carbonylation reaction of azobenzene to prepare the tetrahydroquinazoline ring system via the cleavage of N═N bond[5]. Muñiz discovered the first efficient homogeneous transition-metal-catalyzed activation of N═N bond[6]. Furthermore, this strategy was successfully applied to the reductive transformation of azo compounds. Inspired by these work, Jones and Stasch prepared some Mg complexes to activate the N═N bond of azobenzene[7]. Recently, Xi developed a copper-promoted tandem reaction for the synthesis of quinoline derivatives via N═N bond cleavage[8]. However, the applications of these strategies are mainly restricted by the substrates and harsh conditions. Thus, in view of the limitations of present catalytic activation methods, the development of novel and efficient protocols to activate the N═N bonds remains a challenging task.

Arylureas and their derivatives are important commodity chemicals, valuable synthetic building blocks for agrochemicals, and active pharmaceutical ingredients[9-10]. Driven by this prevalence, many methods have been developed for the synthesis of these compounds. Among many methods documented, direct amination of phosgene and its derivatives might provide the most straightforward procedure for the synthesis of aryl ureas (Scheme 1, path A)[11-12]. However, the toxicity of substrates would severely limit the applications of this method. On the other hand, transition-metal-catalyzed C—N bond formation reactions of urea

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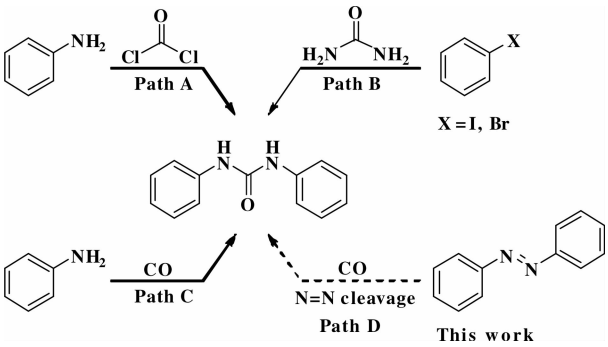
with aryl halides would be recognized as an alternative strategy towards such kind of compounds (Scheme 1, path B)[13-16].



Scheme 1 Synthetic methods of aryl ureas

Recently, transition-metal catalyzed oxidative carbonylation reaction of amines has aroused considerable attention as a powerful method for the construction of aryl ureas (Scheme 1, path C)[17-19]. However, the present catalytic systems are mainly limited to aliphatic amines and only few examples of the oxidative carbonylation of aryl amines have been developed[19]. Therefore, further development of efficient catalyst systems for obtaining arylureas via carbonylation process would be highly desired. Based on above work and in connection with our interests in the area of carbonylation[21-23], we herein described a new Pd-catalyzed oxidative carbonylation of arylazos via N═N bond activation.

1 Experimental

1.1 General experiment

All non-aqueous reactions and manipulations were performed in a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and degassed by standard methods and stored under nitrogen. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avance Ⅲ (400 MHz) spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker Micro TOF-QII mass(ESI). Arylazos used here were known compounds and synthesized according to the reported methods[24].

1.2 General procedure for the reaction

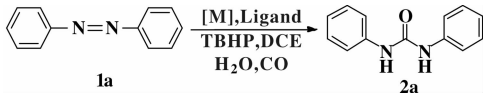
A mixture of $Pd(OAc)_2$(2.3 mg, 0.01 mmol), MeO-BIPHEP (5.8 mg, 0.01 mmol), azo derivative (0.2 mmol), TBHP (80 μL, 0.4 mmol), H_2O (3.6 mg, 0.2 mmol) and DCE (1 mL) was added into an autoclave. Then the autoclave was purged and charged with CO at 3.0 MPa. The reaction mixture was stirred at 110 ℃ for 12 hours. After cooling to room temperature, CO was carefully released. The corresponding reaction mixture was purified by flash column chromatography on a silica gel to give the desired product.

2 Results and discussion

2.1 Optimization of reaction conditions

Our initial investigation focused on the carbonylation of azobenzene (**1a**). With TBHP as the oxidant, H_2O as the hydrogen source and DCE as the solvent, we first examined the effect of catalyst precursors (Table 1). To our delight, the carbonylation reaction of **1a** could proceed smoothly in the presence of Pd complex, and the result revealed that $Pd(OAc)_2$ was the most effective palladium source. To achieve better results, various commercially available phosphine ligands were screened, and the results proved that MeO-BIPHEP was the best choice. Subsequently, different oxidants and solvents were examined. The results showed that TBHP and DCE were proved to be the best for the formation of **2a**. After these optimized conditions were developed, the effects of pressure of CO and temperature were studied as well. Investigation of temperature revealed that yield was temperature-dependent. Running the reaction at 80 ℃ instead of 110 ℃, only trace amount of desired product was afforded. Besides, with either an increase or decrease of the pressure of CO, inferior results were observed. Finally, control reactions revealed that the desired product was not detected at all in the absence of palladium catalyst (Table 1, entry 22).

Table 1 Optimization of the reaction conditions[a]



1a　　2a

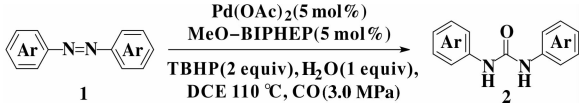
Entry	Cat.	Ligand	Oxidant	Solvent	Yield[%][b]
1	$Co_2(CO)_8$	None	TBHP	DCE	NR
2	$Rh_2(OAc)_4$	None	TBHP	DCE	NR
3	Pd/C	None	TBHP	DCE	25
4	$Pd(OAc)_2$	None	TBHP	DCE	78
5	$PdCl_2$	None	TBHP	DCE	72
6	$Pd(CF_3COO)_2$	None	TBHP	DCE	31
7	$Pd_2(dba)_3$	None	TBHP	DCE	30
8[c]	$Pd(OAc)_2$	$(o\text{-tol})_3P$	TBHP	DCE	83
9	$Pd(OAc)_2$	DPPP	TBHP	DCE	67
10	$Pd(OAc)_2$	MeO-BIPHEP	TBHP	DCE	90
11	$Pd(OAc)_2$	MeO-BIPHEP	TBP	DCE	trace
12	$Pd(OAc)_2$	MeO-BIPHEP	DDQ	DCE	NR
13	$Pd(OAc)_2$	MeO-BIPHEP	$K_2S_2O_8$	DCE	NR
14	$Pd(OAc)_2$	MeO-BIPHEP	Oxone	DCE	NR
15	$Pd(OAc)_2$	MeO-BIPHEP	TBHP	DMF	17
16	$Pd(OAc)_2$	MeO-BIPHEP	TBHP	CH_3CN	trace
17	$Pd(OAc)_2$	MeO-BIPHEP	TBHP	*i*-PrOH	NR
18[d]	$Pd(OAc)_2$	MeO-BIPHEP	TBHP	DCE	59
19[e]	$Pd(OAc)_2$	MeO-BIPHEP	TBHP	DCE	81
20[f]	$Pd(OAc)_2$	MeO-BIPHEP	TBHP	DCE	53
21[g]	$Pd(OAc)_2$	MeO-BIPHEP	TBHP	DCE	80
22	None	MeO-BIPHEP	TBHP	DCE	NR

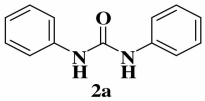
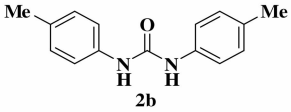
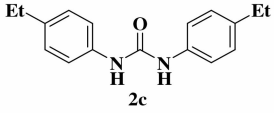
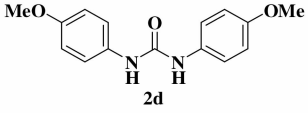
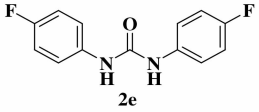
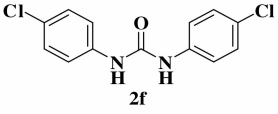
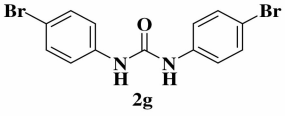
a. Reaction conditions: **1a** (0.2 mmol), [M] (5%), ligand (5 mol%), oxidant (0.4 mmol), H_2O (0.2 mmol), CO (3.0 MPa), solvent (1 mL), 110 ℃, 12 h; b. Isolated yield; c. Ligand: 10%; d. 100 ℃ instead of 110 ℃; e. 120 ℃ instead of 110 ℃; f. CO (2.0 MPa); g. CO (4.0 MPa)

2.2 Substrate scope of arylazos

With the optimized reaction conditions in hand, we subsequently examined the scope of thearylazos in the oxidative carbonylation reaction (Table 2). The results showed that the reactions of azo compounds bearing an electron-donating or electron-neutral group at the *para* position of the phenyl ring proceeded smoothly to provide corresponding adducts **2a-2d** in moderate to good yield (Table 2, entries 1-4). The reaction of bis(4-fluorophenyl) diazene also proceeded smoothly and gave the urea product in good yield (Table 2, entry 5). However, lower yields were obtained when substrates containing an electron-withdrawing group were employed (Table 2, entries 6 and 7). In contrast to the azos with electron-donating substituents, the desired ureas were obtained in less than 40% yield under the same conditions, when chlorine or bromide was attached on the phenyl ring of the arylazo. It was worth noting that the tolerance of halogens on the aromatic ring in this transformation offered an opportunity for further transformations with transition-metal catalysis, which facilitated expedient synthesis of complex ureas. Unlike these *para*-substituted arylazos, the compounds containing substituents at the *ortho*- and *meta*-positions were not suitable substrates and no desired products were observed.

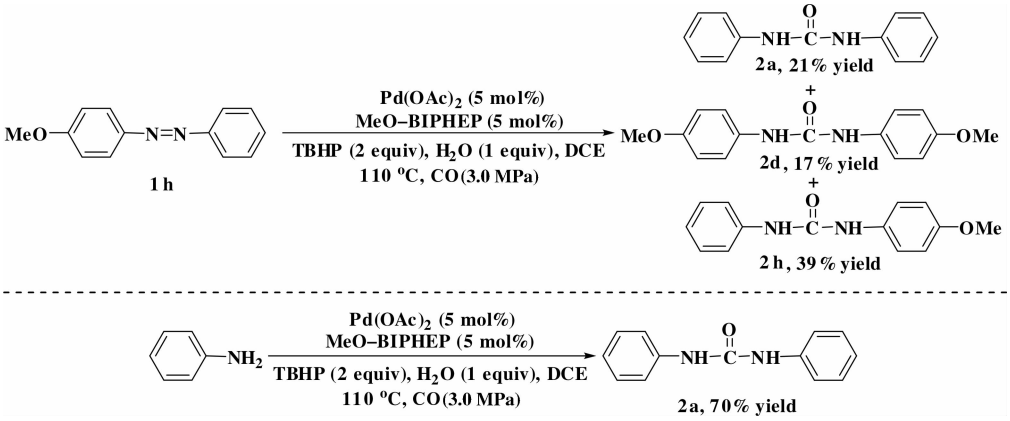
Table 2 Substrate scope of arylazos [a]



Entry	Ar	Product 2	Yield[%] [b]
1	C_6H_5	 2a	90
2	4-MeC_6H_5	 2b	85
3	4-EtC_6H_4	 2c	43
4	4-$MeOC_6H_5$	 2d	80
5	4-FC_6H_5	 2e	77
6	4-ClC_6H_5	 2f	34
7	4-BrC_6H_5	 2g	31

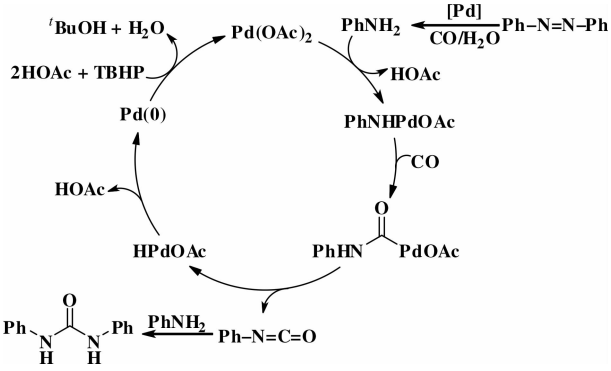
a. Reaction conditions: **1** (0.2 mmol), $Pd(OAc)_2$(5%), MeO-BIPHEP (5%), TBHP (0.4 mmol), H_2O (0.2 mmol), CO (3.0 MPa), DCE (1 mL), 110 ℃, 12 h; b. Isolated yield

To gain some preliminary understanding of the mechanism, several experiments were carried out under the optimized conditions. Radical scavengers, such as BHT and 1,1-diphenylethylene, were employed in the standard reaction. The desired product was obtained in 62% and 76% yields, respectively, which suggested that a free radical process was not involved in the oxidative carbonylation process. Subsequently, when 1-(4-methoxyphenyl)-2-phenyldiazene was served as a substrate, three kinds of products **2a**, **2d** and **2h** were obtained and the ratio of these compounds is 1∶1∶2, indicating that N═N bond cleavage would be involved in the reaction (Scheme 2). In addition, when the carbonylation of arylazos was proceed for 1.5 h, aniline was determined by GC-MS. Furthermore, the carbonylation of arylazos did not proceed at all without TBHP under optimized conditions, and aniline was not observed. Finally, we found aniline could be transformed to the corresponding urea in good yield under the standard conditions, which revealed that aniline might be involved in the present carbonylation reaction.



Scheme 2 Preliminary mechanistic studies

Although the mechanistic details of this transformation are not clear at the moment, on the basis of the results we obtained here, a plausible mechanism for the present process can be proposed (Scheme 3). Initially, the reduction of azo by CO and H_2O can furnish



Scheme 3 Proposed reaction mechanism

the corresponding amine via the cleavage of N═N bond[8,25]. Subsequently, aniline reacts with $Pd(OAc)_2$ and CO to give carbamoylpalladium complex, which would undergo β-hydride elimination to deliver palladium hydride species as well as isocyanate. The phenylurea product is then produced from nucleophilic attack of a primary on the isocyanate. Pd(0) is generated from reductive elimination of palladium hydride species and then oxidized by TBHP in the presence of HOAc to form the $Pd(OAc)_2$ for the next catalytic cycle.

2.3 Experimental characterization data for products

1,3-diphenylurea (**2a**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (s, 2H), 7.46 (d, J = 7.6 Hz, 4H), 7.29 (t, J =8.4 Hz, 4H), 6.97 (t, J =7.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.5, 139.7, 128.8, 121.8, 118.2; HRMS (ESI) calcd. for $C_{13}H_{13}N_2O$ [M + H]: 213.1022, found: 213.1018.

1,3-di-*p*-tolylurea (**2b**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 2H), 7.31 (d, J = 8.4 Hz, 4H), 7.07 (d, J = 8.0 Hz, 4H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.6, 137.2, 130.5, 129.1, 118.2, 20.3; HRMS (ESI) calcd. for $C_{15}H_{17}N_2O$ [M + H]: 241.1335, found: 241.1331.

1,3-bis(4-ethylphenyl)urea (**2c**). ^{1}H NMR(400 MHz, DMSO-d_6) δ 8.51(s, 2H), 7.34 (d, J = 8.4 Hz, 4H), 7.10(d, J = 8.4 Hz, 4H), 2.53(q, J = 8.0 Hz, 4H), 1.16 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.6, 137.4, 137.0 127.9, 118.3, 27.5, 15.8; HRMS (ESI) calcd. for $C_{17}H_{20}N_2ONa$ [M + Na]: 291.1468, found: 291.1470.

1,3-bis(4-methoxyphenyl)urea (**2d**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 (s, 2H), 7.33-7.36 (m, 4H), 6.85-6.88 (m, 4H), 3.71 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6)δ154.3, 152.9, 132.9, 119.9, 113.9, 55.1; HRMS (ESI) calcd. for $C_{15}H_{17}N_2O_3$[M+H]: 273.1234, found: 273.1237.

1,3-bis(4-fluorophenyl)urea (**2e**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.69 (s, 2H), 7.43-7.48 (m, 4H), 7.09-7.35 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.5, 156.1, 152.7, 136.0,

135.9, 120.0, 120.0, 115.3, 115.1; HRMS (ESI) calcd. for $C_{13}H_{10}F_2N_2ONa$ [M + Na]: 271.0653, found: 271.0651.

1,3-bis (4-chlorophenyl) urea (**2f**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85 (s, 2H), 7.48-7.50 (m, 4H), 7.32-7.34 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.3, 138.5, 128.6, 125.5, 119.8; HRMS (ESI) calcd. for $C_{13}H_{11}Cl_2N_2O$ [M+H]: 281.0243, found: 281.0248.

1,3-bis (4-bromophenyl) urea (**2g**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.86 (s, 2H), 7.42-7.47 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.2, 138.9, 131.5, 120.2, 113.4; HRMS (ESI) calcd. for $C_{13}H_{11}Br_2N_2O$ [M+H]: 368.9233, found: 368.9240.

1-(4-methoxyphenyl)-3-phenylurea (**2h**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 1H), 8.47 (s, 1H), 7.44-7.46 (m, 2H), 7.35-7.38 (m, 2H), 7.25-7.29 (m, 2H), 6.94-6.97 (m, 1H), 6.85-6.89 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.4, 152.7, 139.8, 132.7, 128.7, 121.6, 120.0, 118.1, 113.9, 55.1; HRMS (ESI) calcd. for $C_{14}H_{14}N_2O_2Na$ [M + Na]: 265.0947, found: 265.0944.

3 Conclusions

In summary, we have developed a new catalyst system for the carbonylation of azos. With $Pd(OAc)_2$ as the catalyst, MeO-BIPHEP as the ligand, TBHP as the oxidant, and H_2O as the hydrogen source, the reaction can proceed smoothly to afford the desired ureas with up to 90% yield. This new catalyst system gives a supplement to the prior reported catalytic system for the oxidative carbonylation of amines. Further studies on the carbonylation of unsymmetrical azos are on going in our group.

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钯催化芳基偶氮的氧化羰基化反应

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摘要: 采用 TBHP 作为氧化剂, 发展了钯催化芳基偶氮化合物 N═N 双键断裂的氧化羰基化反应. 芳基偶氮的羰基化反应在 $Pd(OAc)_2$(5%), MeO-BIPHEP (5%), 芳基偶氮 (0.2 mmol), TBHP (2 equiv), H_2O (1 equiv), DCE (1 mL), CO (3.0 MPa)的条件下 110 ℃反应 12 h 后, 经柱层析纯化分离得到 31%-91% 的芳基脲. 初步的机理研究表明, 芳基偶氮化合物的 N═N 双键断裂原位产生芳基胺, 再进一步氧化羰基化生成芳基脲.

关键词: 芳基偶氮; 氧化羰基化; N═N 键断裂; 芳基脲