RSC Advances

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2015, **5**, 27029

Received 23rd January 2015
Accepted 11th March 2015

DOI: 10.1039/c5ra01363a

www.rsc.org/advances

Pd-catalyzed desulfitative and denitrogenative Suzuki-type reaction of arylsulfonyl hydrazides†

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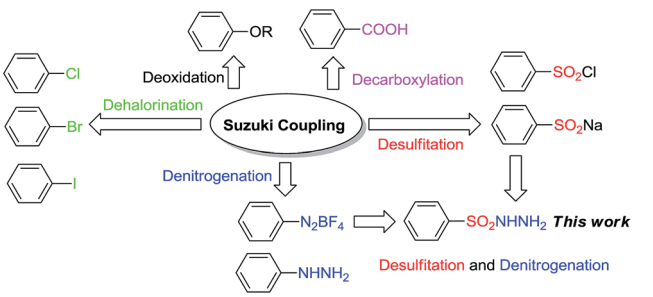
A palladium-catalyzed desulfitative–denitrogenative coupling of arylsulfonyl hydrazides and arylboronic acids with the assistance of catalytic ligands is described. The reaction showed very good selectivity and tolerated a wide range of functionalities without the aid of expensive copper- or silver-based stoichiometric co-oxidants. We have successfully applied this new cross-coupling reaction to the synthesis of terphenyls and OTBN.

Pd-catalyzed cross-coupling reactions are among the most powerful methods in organic synthesis.[1] Such procedures involving the coupling of activated electrophilic partners with nucleophilic organoboron donors are well known as Suzuki-type cross-couplings.[2] Today, the Suzuki reaction is the most widely employed of the cross-coupling reactions, finding continual application in the synthesis of drug-like molecules in the pharmaceutical industry.

Traditionally, aryl halides are most widely used electrophilic reagents in Pd-catalyzed chemistry. The Suzuki cross-coupling reactions with aryl iodines, aryl bromides, even aryl chlorides, have been well documented (Scheme 1, dehalorination).[3] Subsequently, the methods utilizing aryl tosylates/mesylates which derived from the respective phenols in Suzuki–Miyaura coupling have been developed. The transformation proceeded *via* C–O bond cleavage instead of C–X bond (Scheme 1, deoxidation).[4] Much attention has been paid to decarboxylative cross-coupling reactions. Such reactions use stable carboxylic acids as substrates and give access to various valuable product through the removal of CO_2.[5] The first decarboxylative coupling reaction of aryl carboxylic acids with arylboronic acids has been reported by Liu and co-workers (Scheme 1, decarboxylation).[6]

Nowadays, the cleavage of C–S bond has been emerged as an attractive alternative to trigger the formation of organometallic species.[7] After arylsulfonyl chlorides have been engaged in Pd-catalyzed Suzuki cross-coupling for a while, the sodium arenesulfinates have been demonstrated as good electrophilic partners in Suzuki-type coupling reactions by Qi *et al.*,[8] for its nature of a much milder arene source into the aryl syntheses than aryl carboxylic acids reagents (Scheme 1, desulfitation). In addition, Pd-catalyzed Suzuki cross-coupling through the cleavage of C–N bond providing another alternative for electrophilic partners (Scheme 1, denitrogenation). The arenediazonium salts have been applied as electrophilic reagents in Suzuki-type coupling along with the release of N_2 under mild conditions for a long time.[9] In 2014, the first example of Pd-catalyzed Suzuki cross-coupling of readily available arylhydrazines with arylboronic acids *via* C–N bond cleavage was developed under air by Gao and co-workers.[10] It provided a new procedure through the activation of C–N bond to form biaryl skeleton. Another attractive manner for Suzuki coupling reaction could be start up *via* both denitrogenation and desulfitation under mild conditions. Arylsulfonyl hydrazides are readily accessible solids and compatible with moisture, and they have been widely employed to the synthesis of hydrazones, reductants and heterocycles.[11] Arylsulfonyl hydrazides are stable in air and can be easily prepared in one step from arylsulfonyl chlorides and hydrazine hydrates. More significantly, they could both serve as ideal sulfonylating or



Scheme 1 Outline of Pd-catalyzed Suzuki-type coupling of various coupling partners with arylboronic acids.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra01363a

thiolating agents by means of denitrogenation,[12] and serve as arylating reagents by means of desulfitation.[13] Herein, we wish to report a palladium-catalyzed desulfitative and denitrogenative Suzuki-type reaction of arylsulfonyl hydrazides with arylboronic acids without additional oxidants, with the assistance of ligands and bases under aerobic conditions for 6 hours, forming a novel strategy for biaryl synthesis (Scheme 1, this work).

In our preliminary optimization of the reaction conditions, 4-methylbenzenesulfonohydrazide and phenylboronic acid were chosen as the model substrates with $Pd(OAc)_2$ in the presence of K_2CO_3 in MTBE (methyl *tert*-butyl ether), the desired products were detected in the yield of 45% (Table 1, entry 1). To our delight, the introduction of ligand was helpful to improve the efficiency of this transformation. We began to screen ligands for the assistance of the Pd-catalyzed system. Many ligands have been tested and showed obvious influence on the reaction. Table 1 presents the effects of various ligands for the Pd-catalyzed Suzuki-type coupling reaction. Examination of entries 2 and 3 of Table 1 shows that the cross-coupling yields were increased to 63% and 61% respectively, by the addition of 10 mol% of dppe (1,2-bis(-diphenylphosphino)ethane) and dppp (1,3-bis(diphenylphosphino)propane) as the ligand. Much higher yields for the desired product were obtained by the addition of phosphine ligands such as BINAP ((±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene), JohnPhos (2-(di-*t*-butylphosphino)biphenyl) SPhos (2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl) and XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) (Table 1, entries 4–7). Interestingly, even higher cross-coupling yields were isolated by the addition of dppb (1,2-bis(diphenylphosphino)butene), dppf (1,1′-bis(dicyclohexylphosphino)ferrocene) and Xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene), leading to the formation of 1,4-diphenylbuta-1,3-diyne at yields of 88%, 91% and 95%, respectively (Table 1, entries 8–10). *N*-contained ligands such as TMEDA (*N*,*N*,*N*,*N*-tetramethylethylenediamine), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), DBN (1,5-diazabicyclo[4.3.0]non-5-ene) and DABCO (1,4-diazabicyclo[2.2.2]octane), were inefficient (Table 1, entries 11–14).

Afterwards, we optimized catalysts using in this desulfinative–denitrogenative reaction with Xantphos and K_2CO_3 at 60 °C in MTBE for 6 h under air. 95% yield of the desired product was isolated with $Pd(OAc)_2$ (Table 2, entry 1). Applications of $PdCl_2$ afforded 77% yield of 4-methyl biphenyl (Table 2, entry 2). Other Pd(II) catalyst such as $PdBr_2$ and PdI_2 did not favor the formation of the product (Table 2, entries 3 and 4). $Pd(TFA)_2$ is efficiently and selectively catalyst which afforded the desired product in the yield of 92% (Table 2, entry 5). Pd(0) catalysts such as $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ inhibit the formation of biaryls (Table 2, entries 6 and 7). During the screening of solvents, we found that ether solvents had a dramatic effect on the reaction compared to many regular solvents, such as toluene, CH_3CN, DMSO, DMF and NMP (*N*-methyl-pyrrolidone) (Table 2, entries 8–12). The yields of the products are obtained with THF, 1,4-dioxane, DME (1,2-dimethoxyethane) and DIPE (diisopropyl ether) in 71–84% (Table 2, entries 13–16), and MTBE was shown the best.

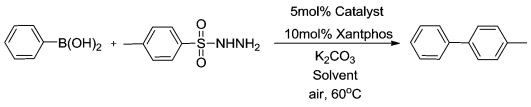
With the optimized reaction conditions in hand, we investigated the effect of electronic and structural variations of the desulfinative–denitrogenative coupling. The scope of the reaction is presented in Table 3. Generally, the reaction efficiency was not sensitive to the electronic property of the groups on the phenyl ring of boronic acids. Electron-donating groups (methoxy substituent) gave a slight lower yield than electron-withdrawing groups (nitro substituent) (Table 3, entries **3a** and **3b**). The hindrance of the phenyl ring of boronic acids had slight effect on the efficiency (Table 3, entries **3b–3d**). Halogen substituents such as fluoro, chloro, and bromo were tolerated under the optimal reaction conditions, and the desired products were obtained in good yields (Table 3, entries **3e–3g**).

Table 1 Suzuki-type-coupling reaction in the presence of various ligands[a]

Entry	Ligand	Yield[b] (%)	Entry	Ligand	Yield[b] (%)
1	—	45	8	dppb	88
2	dppe	63	9	dppf	91
3	dppp	61	10	Xantphos	95
4	BINAP	75	11	DABCO	44
5	JohnPhos	82	12	TMEDA	51
6	SPhos	79	13	DBU	49
7	XPhos	80	14	DBN	41

[a] Reaction conditions: 4-methylbenzenesulfonohydrazide (0.5 mmol), phenylboronic acid (0.5 mmol), $Pd(OAc)_2$ (5.0 mol%), ligand (10 mol%), K_2CO_3 (0.5 mmol), MTBE (1.0 ml) at 60 °C for 6 hours under air. [b] Isolated cross-coupling yield.

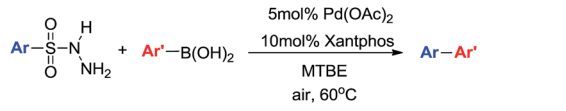
Table 2 Catalyst and solvent selection for Pd-catalyzed desulfitative–denitrogenative Suzuki-type coupling[a]

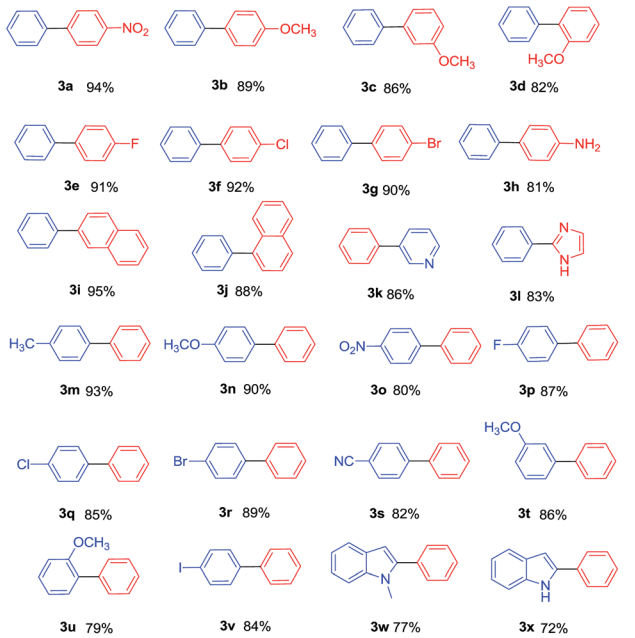


Entry	Catalyst	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$	MTBE	95
2	$PdCl_2$	MTBE	77
3	$PdBr_2$	MTBE	82
4	PdI_2	MTBE	76
5	$Pd(TFA)_2$	MTBE	92
6	$Pd_2(dba)_3$	MTBE	12
7	$Pd(PPh_3)_4$	MTBE	16
8	$Pd(OAc)_2$	Toluene	—
9	$Pd(OAc)_2$	CH_3CN	—
10	$Pd(OAc)_2$	DMSO	20
11	$Pd(OAc)_2$	DMF	17
12	$Pd(OAc)_2$	NMP	28
13	$Pd(OAc)_2$	THF	71
14	$Pd(OAc)_2$	1,4-Dioxane	77
15	$Pd(OAc)_2$	DME	80
16	$Pd(OAc)_2$	DIPE	84

[a] Reaction conditions: 4-methylbenzenesulfonohydrazide (0.5 mmol), phenylboronic acid (0.5 mmol), catalyst (5.0 mol%), Xantphos (10 mol%), K_2CO_3 (0.5 mmol), solvent (1.0 ml) at 60 °C for 6 hours under air. [b] Isolated cross-coupling yield.

Table 3 Pd-catalyzed desulfitative–denitrogenative Suzuki-type coupling of arylsulfonyl hydrazides with arylboronic acids[ab]





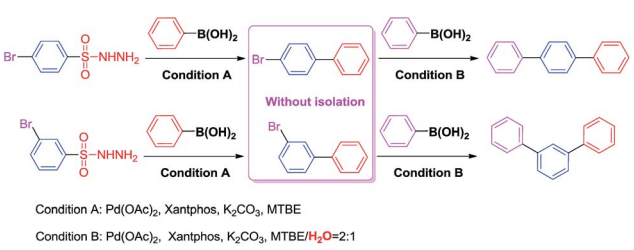
[a] Reaction conditions: arylsulfonohydrazide (0.5 mmol), arylboronic acid (0.5 mmol), $Pd(OAc)_2$ (5.0 mol%), Xantphos (10 mol%), K_2CO_3 (0.5 mmol), MTBE (1.0 ml) at 60 °C for 6 hours under air. [b] Isolated cross-coupling yield.

Notably, amino group on the phenyl ring of boronic acids survived in the procedure (Table 3, **3h**). Importantly, the desired product was formed in good yield when naphthalene was subjected to this procedure (Table 3, entries **3i** and **3j**). Good coupling yield (95% and 88%) was still able to obtain when coupled with heterocyclics, such as pyridinyl and imidazoyl (Table 3, **3k** and **3l**). As expected, a series of functional groups on the phenyl ring of sulfonyl hydrazides, such as alkyl, alkoxy, nitro, fluoro, chloro, bromo and cyano, were compatible under this procedure, and the products were isolated in good to excellent yields (80–93%) (Table 3, **3m**–**3s**). The *m*-, *o*-substitution didn't affect the reaction obviously and showed good reactivity (Table 3, **3t** and **3u**). Notably, the iodo group is extremely reactive in the Suzuki reaction, and its tolerance is seldom reported in Pd-catalyzed cross-coupling reactions (Table 3, **3v**). Indolylsulfonyl hydrazides were efficiently coupled with phenylboronic acid, no matter with methyl group on 1-position or not (Table 3, **3x**).

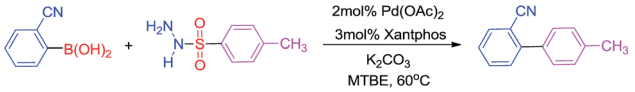
Another application of the presented desulfitative–denitrogenative coupling is its potential for combination with Pd-catalyzed Suzuki–Miyaura cross-coupling to synthesize terphenyl derivatives under "One-pot" process. The Pd-catalyzed coupling of 4-bromo-phenylsulfonohydrazide (4-bromo-phenylsulfonohydrazide) under condition A, followed by consecutive Suzuki cross-coupling by the simply addition of phenylboronic acid and H_2O (0.5 ml, condition B), provides the *p*-terphenyl (*m*-terphenyl) in the yield of 82% (84%). This approach has great potential in combination of this transformation to traditional Suzuki cross-coupling by the sequential addition of water, without the demand for isolation of 4-bromobiphenyl(3-bromo-biphenyl) (Scheme 2).

The practicality of this Pd-catalyzed desulfitative–denitrogenative coupling reaction was further demonstrated by the synthesis of 2-cyano-4-methylbiphenyl (OTBN, Scheme 3). This biaryl compound is the key intermediate for the synthesis of angiotensin receptor blocker (ARB) type antihypertensive drug, such as candesartan cilexetil, valsartan and telmisartan.[14] The synthesis of AT2 antagonists represent one of the most important industrial applications of Pd-catalyzed Suzuki reaction. Our method provided a novel and effective route for synthesis of OTBN intermediate. After further careful optimization of our initial process, the coupling reaction of (2-cyanophenyl) boronic acid and a slight excess of 4-methylbenzenesulfonohydrazide (1.05 equiv.) could be carried out very smoothly in 1 gramscale with 2.0 mol% of Pd catalyst and a lowered equivalent of ligand. The yield of the crude product was almost quantitative. The ^{1}H-NMR analysis of the crude products revealed that the purity of the desired product was about 95% containing only a small amount of the homocoupled product of boronic acid as an impurity. The crude product can be used for the following transformation without further purification.

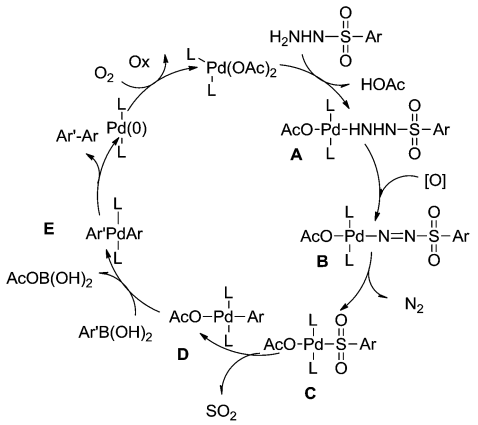
A plausible catalytic cycle, as adapted from the mechanistic studies performed on the Pd(II)-catalyzed desulfitative–denitrogenative coupling reactions of arylsulfonyl hydrazides,[13] is depicted in Scheme 4. Starting with the ligand coordinated Pd(II)-complex, it is converted to Pd(II) species A and HOAc by deprotonation with arylsulfonyl hydrazide. Next, (sulfonyldiazenyl)PdOAc intermediate B is furnish by oxidation with molecular oxygen. Liberation of N_2 with intermediate B generates the acetoxy(arylsulfonyl)palladium C, that form arylpalladium complex D by successive extrusion of sulfur dioxide. Transmetallation occurs with an arylboronic acid to affords the diarylpalladium(II) species E. The reductive elimination provides the cross-coupling product and the active palladium(0) species. Finally, Pd(II) species are then regenerated by the oxidation of the Pd(0) species with oxygen to close the cycle.



Scheme 2 "One-pot" synthesis of terphenyl.



Scheme 3 Gram-scale synthesis of OTBN with this method.



Scheme 4 Possible mechanism.

Conclusions

In summary, the Pd-catalyzed cross-coupling of the arylsulfonyl hydrazides with arylboronic acids provides a versatile mean for the construction of biaryl motifs. The methodology complements the more established methods for Suzuki cross-coupling. Considering the attractive features of arylsulfonyl hydrazide substrates, the coupling reaction's broad scope, and the applications of "One-pot" processes of terphenyl and gram-scale synthesis of OTBN, we expect this methodology will prove useful in synthesis and will further encourage the development of biaryl synthetic transformations.

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