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Pd-Catalyzed Oxidative Annulation of Hydrazides with Isocyanides: Synthesis of 2-Amino-1,3,4-oxadiazoles

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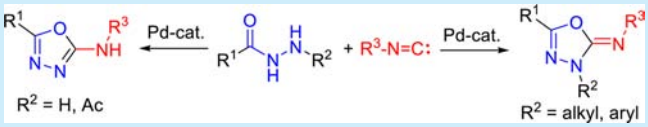
Supporting Information

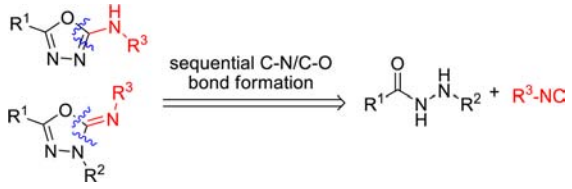
ABSTRACT: An efficient palladium-catalyzed oxidative annulation reaction was developed through sequential isocyanide insertions into N−H and O−H bonds of hydrazides, which provides an efficient access to valuable 2-amino-1,3,4-oxadiazoles and their derivatives.



The oxadiazole skeleton is one of the most attractive frameworks with a wide range of biological and pharmacological activities and has been generally recognized as a privileged structure in medicinal chemistry.[1] Due to their favorable metabolic profile and ability to engage in H-bonding, 1,3,4-oxadiazoles have exhibited a broad spectrum of biological activities such as antimicrobial,[2] antimitotic,[3] antihypertensive,[4] anticonvulsant,[5] antiinflammatory,[6] and muscle relaxant.[7] In particular, as one of the four isomers of oxadiazoles, the 1,3,4-oxadiazole nucleus is exemplified as a unique structure in many therapeutic agents, such as a potent metalloenzyme peptide deformylase (PDF) inhibitor BB-83698, a nitrofuran antibacterial Furamizole, HIV-integrase inhibitor Raltagravir, and antihypertensive agents Nesapidil and Tiodazosin. Besides, oxadiazoles are synthetically versatile substrates, which could be used as synthetic intermediates for the synthesis of natural products, for example through a [4 + 2] cycloaddition reaction to provide the pentacyclic skeleton.[8] Therefore, development of efficient methods for their preparation would be highly desirable. Generally, pharmacologically interesting 2-amino-1,3,4-oxadiazoles were prepared by cyclodehydration of acyclic semicarbazides, which requires functional group activation reagents such as the Burgess reagent,[9a] phosphonium reagents,[9b] and hypervalent iodine reagents,[9c,d] or by cyclodesulfurization of thiosemicarbazides using several desulfurating agents such as I_2/NaOH,[3] carbodiimides,[10a,d] tosyl chloride,[10b] and ethyl bromoacetate.[10c] Condensation of hydrazides and aryl isocyanide dichlorides was also reported to give 2-amino-1,3,4-oxadiazoles.[11] Recently, alternative access to 2-amino-1,3,4-oxadiazoles has been achieved through direct C(2)-amination of 1,3,4-oxadiazoles using chloroamines,[12a] *o*-benzoylhydroxylamines,[12b] or DMF[12c] as novel amination reagents, or using $TEMPO^+BF_4^-$[12d] or $PhI(OAc)_2$[12e] as an oxidant in combination with secondary amines. Although these methods are often effective, some of them suffered from substrate limitation, lack of diversity, poor functional group tolerance, and harsh conditions. Therefore, the development of novel synthetic methods for 2-aminated oxadiazoles is still in high demand in terms of synthetic efficiency and starting material availability.

Isocyanides, which function as both nucleo- and electrophiles, have proven themselves to be powerful and versatile C1 building blocks for organic synthesis due to their unique properties.[13] In addition to participating in traditional multicomponent reactions,[14] Pd-catalyzed reactions involving isocyanides insertion offer great potential for the synthesis of various N-containing heterocycles.[15,16] As a part of our continuing efforts to assemble heterocycles through a tandem strategy,[17] herein we report an efficient Pd-catalyzed aerobic oxidative annulation reaction, whereby a sequential isocyanide insertion into N−H and O−H bonds of hydrazides is described to give 2-amino-1,3,4-oxadiazoles in one pot (Scheme 1).

Scheme 1. Pd-Catalyzed Tandem Isocyanide Insertion Strategy toward 2-Amino-1,3,4-oxadiazoles from Hydrazides



Initially, we started our investigation with the benchmark reaction between benzohydrazide and *tert*-butylisocyanide **2a** to afford *N*-*tert*-butyl-5-phenyl-1,3,4-oxadiazol-2-amine **3a** in 64% yield in the presence of 5 mol % of $Pd(OAc)_2$ at 80 °C in toluene (Table 1, entry 1). Intriguingly, a significant improvement of the yield was observed when *N*-acetyl substituted

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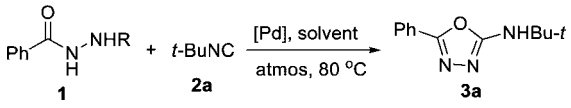
Table 1. Reaction Optimization for Oxadiazole Formation[a]



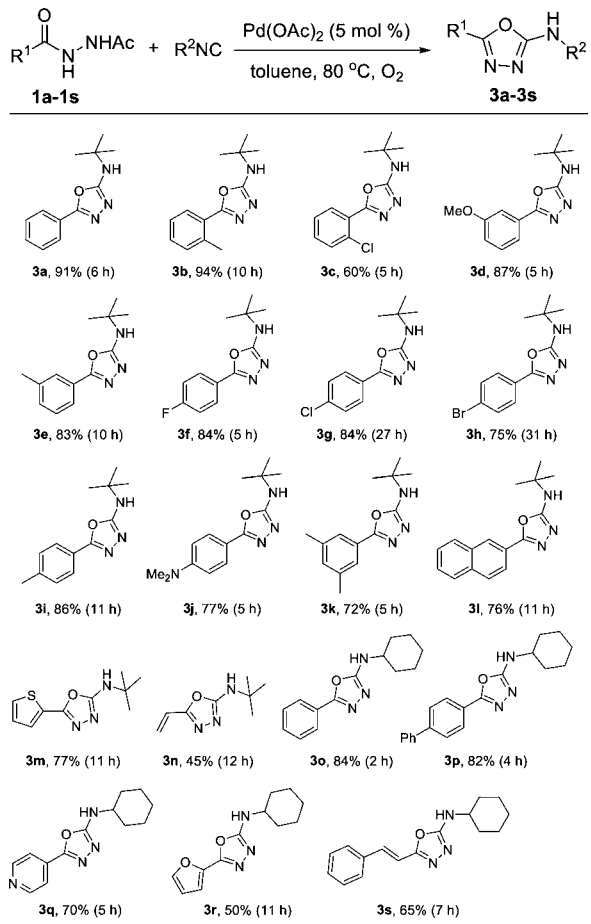
entry	R	Pd source	solvent	atmos.	time (h)	yield (%)[b]
1	H	$Pd(OAc)_2$	toluene	O_2	2	64
2	**Ac**	**$Pd(OAc)_2$**	**toluene**	O_2	**6**	**91**
3	Ac	$Pd(OAc)_2$	anisole	O_2	7	85
4	Ac	$Pd(OAc)_2$	DME	O_2	23	80
5	Ac	$Pd(OAc)_2$	*t*-AmylOH	O_2	17	41
6	Ac	$Pd(OAc)_2$	CH_3CN	O_2	23	22
7	Ac	$Pd(OAc)_2$	CH_3NO_2	O_2	48	trace
8	Ac	$Pd(OAc)_2$	DMF	O_2	23	trace
9	Ac	$Pd(OAc)_2$	DMSO	O_2	23	trace
10	Ac	$Pd(OAc)_2$	toluene	N_2	18	trace
11	Ac	$Pd(OAc)_2$	toluene	air	18	33
12	Ac	$Pd(OAc)_2$	toluene	O_2	11	82[c]
13	Ac	$Pd(OAc)_2$	toluene	O_2	28	76[d]
14	Ac	-	toluene	O_2	18	trace
15	Ts	$Pd(OAc)_2$	toluene	O_2	24	trace[e]

[a]All reactions were performed in an oxygen-purged flask on 0.3 mmol scale, using benzohydrazide **1** (1.0 equiv), *tert*-butylisonitrile (3.0 equiv), and $Pd(OAc)_2$ (5.0 mol %) in solvent (1.5 mL). *t*-AmylOH = *tert*-amyl alcohol. DME = 1,2-Dimethoxyethane. [b]Isolated yield. [c]At 70 °C. [d]$Pd(OAc)_2$ (3.0 mol %) was used as the catalyst. [e]With 51% conversion of **1**.

benzoylhydrazide **1a** was used instead of benzohydrazide (entry 2). By switching the solvent from toluene to anisole or DME, the yield was slightly decreased (entries 3−4); other solvents provided a limited reaction and gave diminished yields (entries 5−6) or trace amounts of product (entries 7−9). A largely dropped yield was afforded when the reaction was conducted under a nitrogen or air atmosphere (entries 10−11), indicating that oxygen was crucial to this oxidative cyclization reaction. Further investigation of other parameters revealed that lowering the temperature or reducing the loading of $Pd(OAc)_2$ resulted in decreased yields with elongated reaction times (entries 12−13). No reaction could be observed in the absence of the Pd catalyst (entry 14). Changing the acetyl substitution of benzohydrazide to tosyl led to a negative impact on this reaction (entry 15), which indicates that the leaving group reactivity (i.e., Ac vs Ts) has an important effect on this transformation.

With the optimized reaction conditions in hand, we next investigated the scope of this reaction, as illustrated in Scheme 2. *N*-Acetyl benzohydrazides bearing various substituents in the aryl rings, regardless of their electronic properties and substitution positions, all gave the desired products in good to excellent yields (**3a**−**3j**). It is worth noting that this reaction was compatible with various functional groups such as halogens (F, Cl, and Br), which could be subjected to further synthetic transformations. Hydrazide substrates with disubstitution in the aryl ring (**3k**) or containing the substructure of naphthalene (**3l**) could also afford the corresponding oxadiazoles in good yields. To our delight, hydrazides with heterocyclic or alkenyl subsituents both gave the targeted products (**3m**, **3n**), which would significantly expand the scope of this reaction. In addition to *tert*-butylisocyanide, secondary isocyanide such as cyclohexyl isocyanide also worked well and gave similar results (**3o**−**3s**). However, no product was observed when phenyl isocyanide was used, which is presumably due to the quick

Scheme 2. Hydrazide Scope in the Synthesis of 2-Amino-1,3,4-oxadiazoles[a]



[a]All reactions were performed in an oxygen-purged flask on 0.3 mmol scale, using hydrazide (1.0 equiv), isonitrile (3.0 equiv), and $Pd(OAc)_2$ (5.0 mol %) in toluene (1.5 mL). [b] Isolated yield.

polymerization of phenyl isocyanide under the reaction conditions.[18]

Encouraged by the success of this Pd-catalyzed isocyanide insertion reaction of hydrazides, to explore the generality and scope of this practical approach further, the *N*-acetyl group of hydrazides was replaced by a variety of *N*-aryl or alkyl substitutions (Scheme 3). To our delight, this reaction predominantly resulted in the formation of novel (imino)-oxadiazoles (**5a**−**5i**), which have shown potent biological activities[19] and are difficult to prepare from easily available substrates.[19,20] The identity of **5a** was determined by spectral analysis and further confirmed by X-ray crystallographic analysis, and the *exo* C═N bond adopts the *Z*-configuration in solid state.[21]

Benzohydrazides bearing *N*-aryl or naphthyl substitutions underwent clean conversion to the desired (imino)oxadiazoles (**5a**−**5g**) in good to excellent yields. Aza analogues with pyridine substituents could afford the corresponding product **5h** smoothly in moderate yield. It is worth noting that oxadiazole **5i** bearing an *N*-alkyl substituent could be prepared in moderate yield from *N*-*tert*-butyl-benzohydrazide, albeit a longer reaction time was required, which will further illustrate the broad substrate scope.

Although a detailed reaction mechanism remains to be clarified, a plausible mechanism for the formation of 1,3,4-

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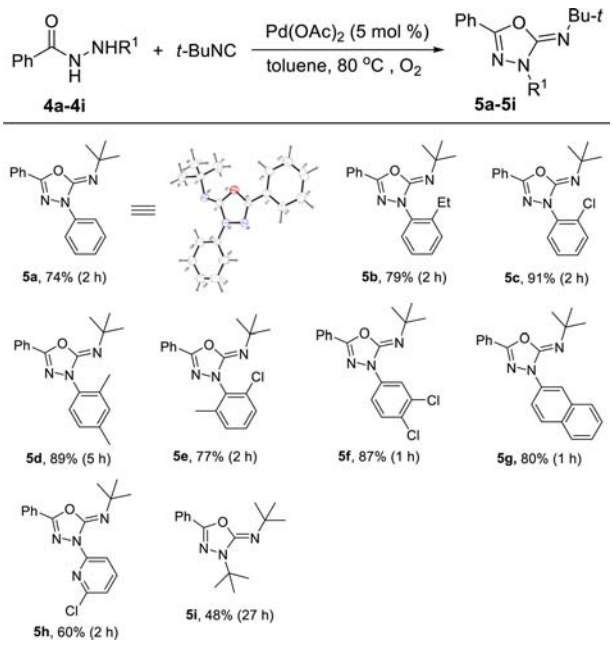
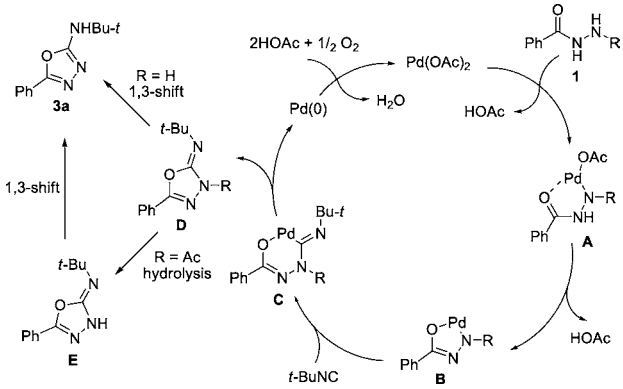
Scheme 3. Hydrazide Scope in the Synthesis of 2-Imino-1,3,4-oxadiazolines[a]



[a]All reactions were performed in an oxygen-purged flask on 0.3 mmol scale, using hydrazide (1.0 equiv), isonitrile (3.0 equiv) and $Pd(OAc)_2$ (5.0 mol %) in toluene (1.5 mL). [b] Isolated yield.

Scheme 4. Plausible Mechanism for Synthesis of 3 and 5



oxadiazoles is proposed as shown in Scheme 4. The catalytic cycle is likely initiated by N−H activation of **1** with the aid of its carbonyl group to give a Pd complex **A**. The formed intermediate **A** continues to coordinate to the O-atom of carbonyl and form a five-membered palladacycle **B**.[22] Subsequent insertion of isocyanide into the Pd−N bond[16a,d] results in the formation of a cyclic imidoyl palladium intermediate **C**. Reductive elimination of **C** affords compound **D** (if R = alkyl or aryl, **5a**−**5i**) and Pd(0), which is reoxidized by oxygen and regenerates Pd(II). When R is H, oxadiazole **3a** is provided through a spontaneous 1,3-shift from **D**. However, if R is Ac, hydrolysis followed by a 1,3-shift through intermediate **E** could also afford compound **3a**.[23]

In conclusion, we have developed an efficient Pd-catalyzed aerobic oxidative annulation reaction through sequential isocyanide insertions into N−H and O−H bonds of hydrazides. This approach provides one of the easiest pathways for straightforward synthesis of valuable 2-amino-1,3,4-oxadiazoles from easily available hydrazides and isocyanides with operational simplicity. The characteristics of a broad substrate scope, good functional group tolerance, and synthesis modularity will provide the described reaction broad utility in organic synthesis. Further insight into the mechanism, reaction scope, and the synthetic applications for bioactive compounds are now under investigation in our group.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data for all compounds, X-ray structure of **5a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(21) Crystallographic data for compound **5a**: $C_{18}H_{21}N_3O$, M = 295.38, monoclinic, $P21/n$ (No. 14), a = 7.713(5) Å, b = 14.167 (5) Å, c = 11.379 (5) Å, β = 103.102 (5)°, V = 1211.0 (10) Å^3, Z = 4. Crystal size: 0.28 × 0.21 × 0.18 mm^3, T = 295 K, ρ_{calcd} = 1.367 g·cm^{-3}, R_1 = 0.0360 ($I > 4\sigma(I)$), wR_2 = 0.1016 (all data), GOF = 1.033, reflections collected/ unique: 7377/2752 (R_{int} = 0.0182), Data: 2752, restraints: 0, parameters: 173.

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