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Rhodium-Catalyzed Oxidative Annulation of Hydrazines with Alkynes Using a Nitrobenzene Oxidant

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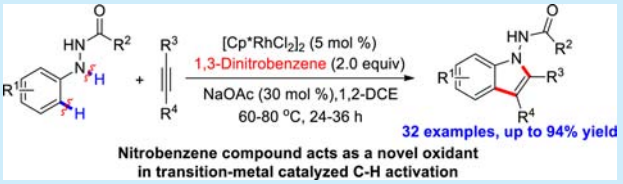
Supporting Information

ABSTRACT: Rhodium-catalyzed oxidative annulation of hydrazines with alkynes has been accomplished using 1,3-dinitrobenzene as an oxidant. A variety of hydrazines with alkynes were converted to 1-aminoindole derivatives in good to high yields. Mechanistic investigations support the idea that 1,3-dinitrobenzene serves as the oxidant during C−H activation. This is, to our knowledge, the first report of a nitrobenzene compound used as the oxidant in transition-metal-catalyzed C−H activation.



Direct and selective C−H functionalization has emerged as a powerful tool for concise, atom-economical construction of new carbon−carbon and carbon−heteroatom bonds in modern synthetic chemistry.[1] In particular, oxidative C−H activation based on transition metal catalytic systems has been widely explored because of the diverse transformations that it allows.[2] During this activation reaction, the transition metal is usually reduced to a lower oxidation state. As a result, stoichiometric or excess amounts of external oxidants must be added in order to sustain the catalytic cycle. Metal oxidants,[3] oxygen or air,[4] hypervalent iodine(III) reagents,[5] and peroxide[6] are the most common additives. Most of these oxidants require harsh conditions such as high temperature and pressure, limiting the synthetic usefulness of the overall activation reaction. Therefore, developing new external oxidants that function under relatively mild conditions remains a goal of synthetic chemists.

Nitrobenzene compounds, among the most important organic materials in modern industrial chemistry,[7] can act as mild oxidants,[8] though research into this activity has been limited primarily to dehydrogenation aromatization.[8c−g] Recently, Bouwman reported palladium-catalyzed oxidative carbonylation of methanol using nitrobenzene as an oxidant.[9a,b] More recently, Wu reported an elegant cascade reaction with nitrobenzene as an oxidant involving cross-coupling and *in situ* hydrogenation by visible light catalysis.[9c] To our knowledge, whether a nitrobenzene compound can act as the sole oxidant in transition-metal-catalyzed oxidative C−H functionalization has never been reported.

Transition-metal-catalyzed oxidative annulation, especially that involving C−H activation, is synthetically quite valuable because it can rapidly construct hetero- and carbocyclic compounds.[10] Recently, the external or internal oxidative annulation of aromatic compounds with directing groups and internal alkynes have been developed for the indole synthesis.[11] More recently, annulation of hydrazines has attracted increasing interest, leading to the preparation of indoles, 2,3-dihydro-1*H*-indazoles, and pyrazoles.[12] As an example, Glorius reported the rhodium-catalyzed hydrazine-directed C−H activation to afford the indoles in the presence of HOAc.[12a] In our continuous effort in heterocycle construction,[13] here we report an efficient rhodium-catalyzed oxidative annulation of hydrazines and alkynes using a nitrobenzene compound as the sole oxidant for C−H activation. The reaction affords a variety of 1-aminoindole derivatives, which are easily deprotected to furnish 1-aminoindoles in good yield.

To begin our studies of this reaction, we selected *N*′-phenylacetohydrazide (**1a**) and 1,2-diphenylethyne (**2a**) as the model substrates. We conducted the reaction in the presence of $[Cp^*RhCl_2]_2$ (5 mol %) and NaOAc (30 mol %) at 60 °C for 24 h under a nitrogen atmosphere. Interestingly, the solvent $MeNO_2$ led to an unexpected oxidative annulation product, *N*-(2,3-diphenyl-1*H*-indol-1-yl)acetamide (**3a**), in 51% yield (Table 1, entry 1). The identity of this product was confirmed by single-crystal X-ray crystallography (**3a**). Using the solvent $PhNO_2$ gave the product **3a** in 88% yield (entry 2), whereas other common solvents such as MeOH, MeCN, THF, 1,2-DCE, and toluene did not support the formation of **3a**. It is noteworthy that when HOAc (2 equiv) was added to the reaction with 1,2-DCE as the solvent, 2,3-diphenyl-1*H*-indole was obtained in 78% yield (see Supporting Information).[12a]

We also sought to optimize the choice of oxidant and additive. Using $PhNO_2$ (2.0 equiv) as the oxidant in the reaction of *N*′-phenylacetohydrazide (**1a**) with 1,2-diphenylethyne (**2a**) led to the product **3a** in 25% yield (entry 3). Nitrobenzenes carrying electron-donating or -withdrawing groups on the benzene ring gave the corresponding product **3a** in respective yields of 39% and 46% (entries 4 and 5). Using the dinitro-compound 1,4-dinitrobenzene improved the yield of **3a** to 50% (entry 6). To our satisfaction, using 1,3-

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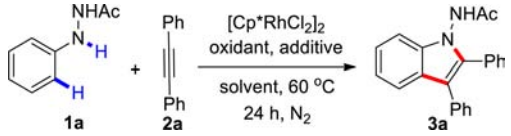
Table 1. Optimization of the Oxidative Annulation of Hydrazine (1a) and Alkyne (2a) Using a Nitrobenzene Oxidant[a]



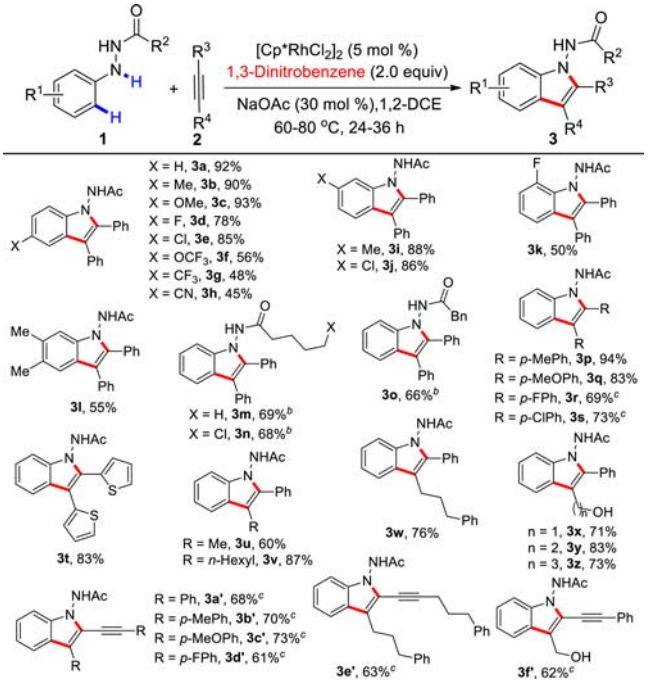
entry	solvent	oxidant	additive	yield (%)
1	$MeNO_2$	–	NaOAc	51
2	$PhNO_2$	–	NaOAc	88
3	1,2-DCE	$PhNO_2$	NaOAc	25
4	1,2-DCE	*p*-$MePhNO_2$	NaOAc	39
5	1,2-DCE	*p*-$ClPhNO_2$	NaOAc	46
6	1,2-DCE	1,4-dinitrobenzene	NaOAc	50
7	1,2-DCE	1,3-dinitrobenzene	NaOAc	92
8	MeOH	1,3-dinitrobenzene	NaOAc	85
9	MeCN	1,3-dinitrobenzene	NaOAc	71
10	toluene	1,3-dinitrobenzene	NaOAc	ND
11	1,2-DCE	1,3-dinitrobenzene	$AgSbF_6$	ND
12	1,2-DCE	1,3-dinitrobenzene	CsOAc	74
13	1,2-DCE	1,3-dinitrobenzene	AgOAc	23
14	1,2-DCE	1,3-dinitrobenzene	$Cu(OAc)_2$	26
15[b]	1,2-DCE	1,3-dinitrobenzene	NaOAc	58
16[c]	1,2-DCE	1,3-dinitrobenzene	NaOAc	75
17[d]	1,2-DCE	1,3-dinitrobenzene	NaOAc	78

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), additive (0.06 mmol), and oxidant (0.4 mmol) in solvent (1.0 mL) at 60 °C for 24 h under a nitrogen atmosphere. Isolated yields are shown. [b]$[Cp^*RhCl_2]_2$ (0.005 mmol). [c]NaOAc (0.03 mmol) was used. [d]**1a** (7.5 mmol), **2a** (5 mmol), $[Cp^*RhCl_2]_2$ (0.25 mmol), NaOAc (1.5 mmol), 1,3-dinitrobenzene (10 mmol), and 1,2-DCE (25 mL) were used.

dinitrobenzene dramatically increased the yield of **3a** to 92% (entry 7). This may be because nitrobenzenes with electron-withdrawing groups are reduced more easily than those with electron-donating groups. The other common oxidants that we tested, including $PhI(OAc)_2$, $(t\text{-}BuO)_2$, $Cu(OAc)_2$, and $Na_2S_2O_8$ did not improve the yield of **3a** (see Supporting Information). When the reaction was carried out under an O_2 (1 atm) atmosphere, only a small amount of product **3a** was observed. Screening solvents showed that 1,2-DCE provided a higher yield of **3a** than MeOH, MeCN, and toluene (entries 8–10). When $AgSbF_6$ was used as the additive, product **3a** was not detected, demonstrating the essential role of the acetate anion (entry 11). NaOAc proved to be the most effective additive, affording **3a** in 92% yield (entries 12–14). Decreasing the loading of the catalyst or additive substantially reduced the product yield (entries 15 and 16). The reaction proceeded smoothly even on the gram scale, producing **3a** (1.2 g) in 78% yield (entry 17).

After defining the optimal reaction conditions for oxidative annulation promoted by 1,3-dinitrobenzene, we investigated the substrate scope (Scheme 1). First, we examined various substituted hydrazines for their ability to react with 1,2-diphenylethyne **2a** and form 1-aminoindole derivatives. *N*′-Phenylacetohydrazides with electron-donating groups such as Me or MeO at the *para* position of the benzene ring gave the corresponding product **3b** or **3c** in a respective yield of 90% or 93%. *N*′-Phenylacetohydrazides carrying halogens such as F or Cl also gave good yields of product **3d** or **3e**. However, *N*′-phenylacetohydrazides bearing electron-withdrawing groups

Scheme 1. Substrate Scope for Oxidative Annulation Promoted by 1,3-Dinitrobenzene[a]



[a]Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), NaOAc (0.06 mmol), and 1,3-dinitrobenzene (0.4 mmol) in 1,2-DCE (1.0 mL) at 60 °C for 24–36 h under a nitrogen atmosphere. Isolated yields are shown. [b]Reaction time was extended to 48 h. [c]Reaction temperature was increased to 80 °C.

such as CF_3O, CF_3, or CN gave substantially lower yields of products **3f–h**. These results suggest that the catalytic reaction prefers electron-donating and halogen substituents over electron-withdrawing ones on the benzene ring of *N*′-phenylacetohydrazide. Moreover, *N*′-phenylacetohydrazide substituted with Me or Cl at the *meta* position reacted well with **2a**, producing the corresponding product **3i** or **3j** in a respective yield of 88% or 86%.

The *ortho*-F substituted *N*′-phenylacetohydrazide also gave the desired product **3k** in a slightly lower yield of 50%. This indicates that steric hindrance at the benzene ring can inhibit annulation, which was confirmed when *N*′-phenylacetohydrazide substituted with *ortho*-Me failed to react. Nevertheless, the reaction tolerated simultaneous Me substitutions at both *meta* and *para* positions, affording product **3l** in 55% yield. Note that heteroaryl hydrazides such as *N*′-(pyridin-2-yl)acetohydrazide could not react with **2a** to give the desired product under current reaction conditions.

Next we investigated hydrazines with various substitutions at the R^2 position. Placing a long alkyl chain there led to 1-aminoindole derivatives **3m** and **3n** in 69% and 68% yield, whereas a benzyl substituent at that position gave product **3o** in only 66% yield. In contrast, adding a substituted aryl to the R^2 position led to no observable product. Adding a *t*-Bu substitution to the R^2 position similarly failed to give the desired product. This indicates that steric hindrance at the R^2 position of hydrazines can inhibit annulation.

Subsequently, we explored the scope of substituted alkynes **2** that can react with *N*′-phenylacetohydrazide **1a**. Reaction of **1a** with diaryl alkynes bearing electron-donating groups such as Me or MeO at the *para* position of the benzene ring gave the

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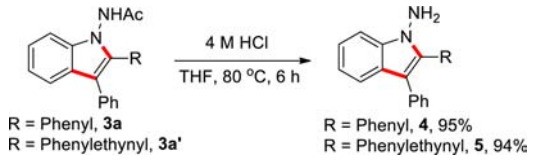
corresponding product **3p** or **3q** in a respective yield of 94% or 83%. Diaryl alkynes with halogens such as F or Cl also gave the desired product **3r** or **3s** in a good yield. Similarly, 1,2-di(thiophen-2-yl)ethyne reacted well with **1a**, giving the product **3t** in 83% yield. In addition to symmetric alkynes, some unsymmetrical alkynes also underwent the transformation to give the desired products **3u**−**z** in 60−87% yields. For phenyl acetylenes substituted with various alkyl species, including alkyl species with OH groups, only one regioisomer was isolated in their reactions with **1a**.

To further explore the flexibility of oxidative annulation promoted by 1,3-dinitrobenzene, we tried to react *N*′-phenylacetohydrazide **1a** with various substituted 1,3-diynes. Diaryl- or dialkyl-substituted 1,3-diynes reacted well to give the corresponding products **3a**′−**e**′ in good yields. Asymmetrical 1,3-diynes such as 5-phenylpenta-2,4-diyn-1-ol also gave the desired product **3f**′ in 62% yield. Single-crystal X-ray diffraction analysis of **3c**′ confirmed the regioselectivity of the oxidative annulation of 1,3-diynes.[14]

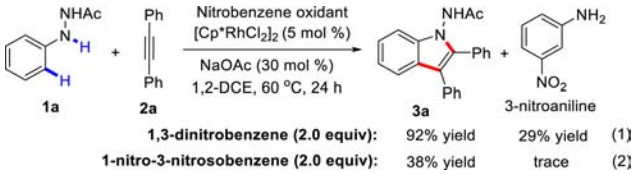
1-Aminoindoles are an important subfamily of indoles, displaying a broad spectrum of biological activities, and their synthesis has attracted increasing attention in recent years.[15] Using simple deprotection of the acetyl group under acidic conditions, we easily converted the oxidative annulation products **3a** and **3a**′ to 1-aminoindoles **4** and **5** in respective yields of 95% and 94%. This demonstrates the usefulness of our approach for synthesizing 1-aminoindoles (Scheme 2, eq 1).[12c]

Scheme 2. Deprotection of Oxidative Annulation Products To Afford 1-Aminoindoles



To clarify the role of 1,3-dinitrobenzene in this annulation, we tried to capture byproducts formed from 1,3-dinitrobenzene. When hydrazine **1a** and alkyne **2a** reacted under optimal reaction conditions, the product of 1,3-dinitrobenzene reduction, 3-nitroaniline, was isolated in 29% yield (Scheme 3, 1). When the same reaction was performed in the absence of

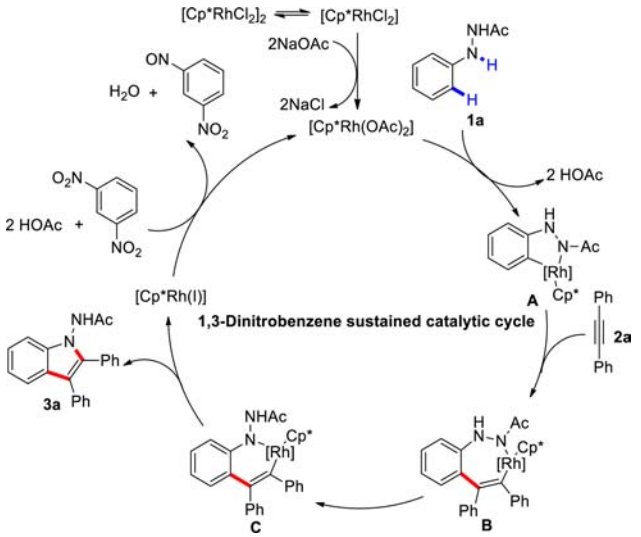
Scheme 3. Mechanistic Investigation of Oxidative Annulation Promoted by 1,3-Dinitrobenzene



2a, 1,3-dinitrobenzene was recovered intact and no 3-nitroaniline was detected, excluding the possibility that hydrazine **1a** reduces 1,3-dinitrobenzene and further confirming that the 1,3-dinitrobenzene was the oxidant for the annulation to produce **3a**. Consistent with this interpretation, reacting **1a** and **2a** under optimal reaction conditions using 1-nitro-3-nitrosobenzene as the oxidant gave a lower 38% yield of **3a** (Scheme 3, 2). Reacting **1a** with 1-nitro-3-nitrosobenzene without **2a** led to the conversion of 1-nitro-3-nitrosobenzene into traceable 3-nitroaniline and other complicated products. Moreover, when PhNO (3 equiv) was used instead of 1,3-dinitrobenzene, the annulaiton product **3a** was almost undetectable even after 48 h. These results suggest that nitrosobenzene is not a suitable oxidant for this annulation. They also suggest that 1,3-dinitrobenzene might be reduced to 1-nitro-3-nitrosobenzene during the reaction, which is in turn converted into complicated products such as 3-nitroaniline.

On the basis of the above experiments and previous studies of hydrazines with alkynes that undergo reactions catalyzed by $[Cp^*RhCl_2]_2$,[12] we propose a tentative mechanism for oxidative annulation promoted by 1,3-dinitrobenzene (Scheme 4). First, the active catalyst $[Cp^*Rh(OAc)_2]$ forms from the

Scheme 4. Proposed Mechanism of Oxidative Annulation Promoted by 1,3-Dinitrobenzene



$[Cp^*RhCl_2]_2$/NaOAc catalytic system, and it directly promotes C−H activation of hydrazine **1a**. The resulting arene rhodation intermediate **A** undergoes alkyne coordination and insertion with alkyne **2a**, giving the seven-membered rhodacycle **B**. The metallacycle rearranges to a more stable six-membered rhodium complex **C**, which subsequently undergoes reductive elimination to release the annulation product **3a** and [Cp*Rh(I)]. In contrast, rhodium complex **C** could also undergo the internal oxidation to release the 2,3-diphenyl-1*H*-indole by N−N bond cleavage in the presence of a stoichiometric amount of HOA.[12a] Finally, external oxidant 1,3-dinitrobenzene reoxidizes [Cp*Rh(I)] to regenerate the active catalyst $[Cp^*Rh(OAc)_2]$.

In summary, we have achieved an efficient rhodium-catalyzed oxidative annulation of hydrazines with alkynes under mild conditions, using 1,3-dinitrobenzene as a new oxidant in C−H activation. The catalytic reactions afforded 1-aminoindole derivatives in good to excellent yields, and these products could be further deprotected to generate 1-aminoindoles. Mechanistic investigation demonstrated that 1,3-dinitrobenzene served as the oxidant during the reaction, consuming the leaving hydrogen atoms. This protocol may open the door for using nitrobenzene oxidants in transition-metal-catalyzed C−H functionalization.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, ^{1}H and ^{13}C NMR spectra for all compounds, and X-ray crystallographic data for **3a** and **3c′**. 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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