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## COMMUNICATION

# AgNO<sub>3</sub> as Nitrogen Source for Rhodium(III)-Catalyzed Synthesis of 2-Aryl-2H-Benzotriazoles from Azobenzenes

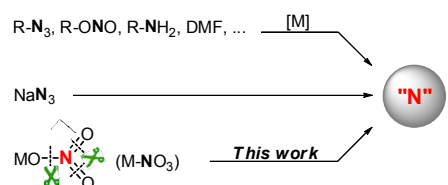
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Accepted 00th January 20xxJixing Li,<sup>ab</sup> Hui Zhou,<sup>ab</sup> Jinlong Zhang,<sup>a</sup> Huameng Yang,<sup>a</sup> and Gaoxi Jiang<sup>\*a</sup>

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A new approach has been established for Rh(III)-catalyzed direct aza oxidative cyclization of nonprefunctionalized azobenzenes to provide 2-aryl-2H-benzotriazoles in good yields, in which AgNO<sub>3</sub> instead of conventional azide reagents for the first time functions as the nitrogen source for nitrogenation reaction. Preliminary mechanistic studies suggest that Rh(III)-catalyst could be account for nitration reaction and subsequently cationic silver species itself might play a vital role for the fission of nitrogen-oxygen bond of nitro group and promote aza oxidative cyclization.

Nitrogen-containing compounds are fundamental moieties in biology, chemistry, and pharmaceutical molecules.<sup>[1]</sup> Over the past decades, noteworthy progress for direct implantation nitrogen into hydrocarbons by transition-metal catalyzed strategy with organo nitrogen donors has been achieved (Scheme 1).<sup>[2]</sup> Comprehensively, sodium azide undertakes the

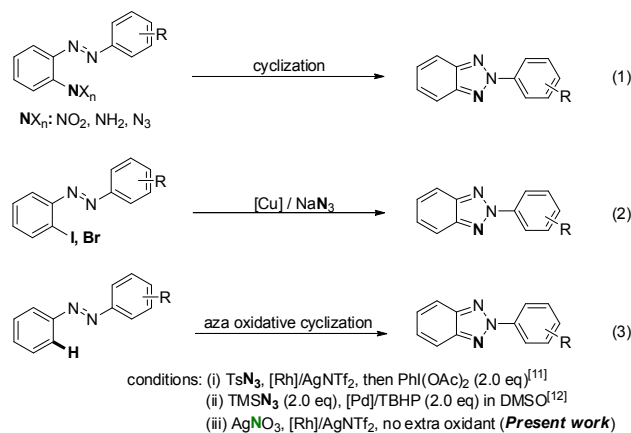


**Scheme 1.** Typical nitrogen sources in organochemistry.

most primal nitrogen donor.<sup>[3]</sup> Since it's dramatically explosive, the excavation of new safe surrogates is still in strong demand. Inorganic nitrate, thanks to its eminent merit of inexpensiveness, stability, hypotoxicity, and ease of handling, is widely used as an oxidant and nitro source in organic synthesis,<sup>[4]</sup> but unprecedented as a nitrogen source that

should be suffered from the extremely difficult cleavage of two intrinsic N=O double bonds. Herein, we report the first example with inorganic nitrate as nitrogen source for nitrogenation reaction.

Benzotriazole represents an important class of compounds bearing a unique fused five-membered ring with three vicinal nitrogen atoms.<sup>[5]</sup> In principle, such five-membered ring presents two tautomeric forms, 1H (or 3H) and thermodynamically unstable 2H isomers that make their selective synthesis more intriguing.<sup>[6]</sup> Significantly, 2-aryl-2H-benzotriazoles, i.e., 2H isomers are core motif extensively existing in pharmaceuticals and organic photoelectronic materials.<sup>[7]</sup> Therefore, considerable effort has been directed toward the regioselective synthesis of these useful units in the last few years. Typical well documented approaches are cyclization of prefunctionalized azobenzenes with an intrinsic azido, amino, or nitro group on *ortho*-position of the aryl ring (Scheme 2, eq 1).<sup>[8]</sup> Additionally, the copper catalyzed cross coupling cyclization of 2-haloaryltriazenes with NaN<sub>3</sub> has also been developed by Chen and co-workers (eq 2).<sup>[9]</sup> From the viewpoint of atom/step economy, undoubtedly, the direct



**Scheme 2.** Typical approaches and diverse nitrogen sources for the synthesis of 2-aryl-2H-benzotriazole.

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catalytic aza oxidative cyclization of easily accessible nonprefunctionalized azobenzenes<sup>[10]</sup> is much more attractive (eq 3). In 2014, Lee and co-workers reported an “one-pot” cascade reaction for the synthesis of 2-aryl-2H-benzotriazoles that is Rh(III)-catalyzed amidation of azobenzenes with *N*-sulfonyl azide (TsN<sub>3</sub>) followed by oxidation with PhI(OAc)<sub>2</sub> (eq 3, i).<sup>[11]</sup> Recently, Patel and co-workers realized a Pd(II)-catalysis with azidotrimethylsilane (TMSN<sub>3</sub>) as the nitrogen source and (over)stoichiometric amounts of TBHP as the oxidant (eq 3, ii).<sup>[12]</sup> Despite these important advances, further exploration of simple and easily handled methods to obviate the use of dangerous azides and excessive amounts of extra oxidant is of interest and significance yet a great challenge. In the context, we realized a new process of Rh(III)-catalysis with AgNO<sub>3</sub> as the nitrogen source (eq 3, iii). Preliminary mechanistic studies suggest that Rh(III)-catalyst could be account for nitration reaction by directing group-assisted C-H bond activation and subsequently cationic silver species itself might play a vital role for the cleavage of nitrogen-oxygen bond of nitro group and promote aza oxidative cyclization.

Initially, we treated azobenzene **1a** (0.1 mmol) with AgNO<sub>3</sub> (2.0 eq) in the presence of [Cp\**RhCl*<sub>2</sub>]<sub>2</sub> (5.0 mol %), AgNTf<sub>2</sub> (20 mol %), and H<sub>2</sub>O (0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under 150 °C for 12 hours (Table 1, entry 1). To our delight, 42% of desired

product **2a** was isolated. Encouraged by the rudimentary result, several reactions were conducted to improve the chemical yield. Screening solvents reveals that 1,2-dichloroethane (DCE) is the best choice and provided **2a** in 73% yield (entries 1-7). Changing AgNO<sub>3</sub> to other nitrate salts, such as KNO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and even organic solvent CH<sub>3</sub>NO<sub>2</sub> didn't improved the reaction (entries 8-14). Examination of counteranion additives was proved to be less effective (entries 15-20). It is noteworthy that decreasing the loading of AgNO<sub>3</sub> from 2.0 equiv to 1.0 equiv also readily led to **2a** in 67% yield (entry 21). Lowering the reaction temperature resulted in an adverse effect in the reaction (entry 22). Other transition-metal compounds such as Pd(OAc)<sub>2</sub>, Cp\**Ru*(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, and [Cp\**IrCl*<sub>2</sub>]<sub>2</sub> have no catalytic activity (see ESI).

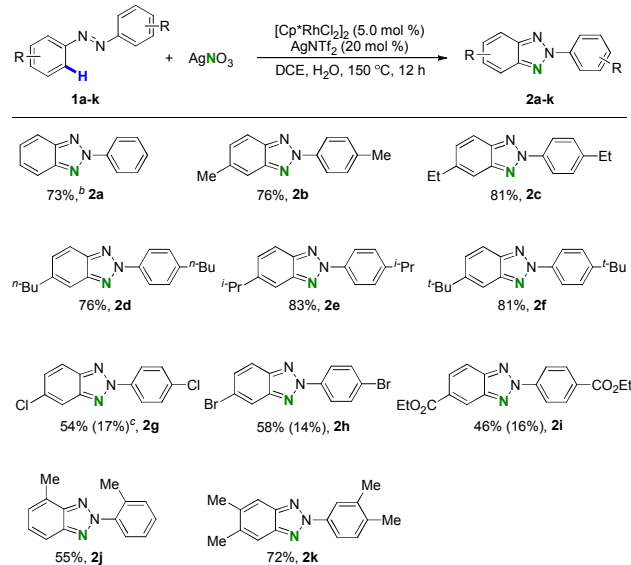
With the optimized conditions in hand, we next investigated the scope of azobenzenes to evaluate the generality of the transformation. First, besides **1a**, a series of symmetrically substituted azoarenes **1b-k** were employed and the reactions proceeded smoothly to furnish the corresponding products **2b-k** in 46–83% yields (Scheme 3). Notably, this protocol could tolerate well a range of substituents on the phenyl ring although the electronic nature

**Table 1.** Optimization of the Reaction Conditions.<sup>a</sup>

entry	"N" source	[X]	solvent	yield (%) <sup>b</sup>
1	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	52(42)
2	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	DCE	88(73)
3	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	Toluene	n.r. <sup>c</sup>
4	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	THF	n.r
5	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	DMF	n.r
6	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	PhNO <sub>2</sub>	25
7	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	CH <sub>3</sub> NO <sub>2</sub>	47
8	KNO <sub>3</sub>	AgNTf <sub>2</sub>	DCE	(39)
9	Mg(NO <sub>3</sub> ) <sub>2</sub>	AgNTf <sub>2</sub>	DCE	45
10	Zn(NO <sub>3</sub> ) <sub>2</sub>	AgNTf <sub>2</sub>	DCE	72(58)
11	Co(NO <sub>3</sub> ) <sub>2</sub>	AgNTf <sub>2</sub>	DCE	70
12	Ni(NO <sub>3</sub> ) <sub>2</sub>	AgNTf <sub>2</sub>	DCE	35
13	Cu(NO <sub>3</sub> ) <sub>2</sub>	AgNTf <sub>2</sub>	DCE	20
14	CH <sub>3</sub> NO <sub>2</sub>	AgNTf <sub>2</sub>	DCE	48
15	AgNO <sub>3</sub>	AgOTf	DCE	68
16	AgNO <sub>3</sub>	AgSbF <sub>6</sub>	DCE	35
17	AgNO <sub>3</sub>	AgBF <sub>4</sub>	DCE	50
18	AgNO <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	DCE	n.r
19	AgNO <sub>3</sub>	NaOTf	DCE	30
20	AgNO <sub>3</sub>	NaBARF	DCE	50
21 <sup>d</sup>	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	DCE	(67)
22 <sup>e</sup>	AgNO <sub>3</sub>	AgNTf <sub>2</sub>	DCE	(45)

<sup>a</sup> Unless otherwise noted, the reaction was performed with **1a** (0.1 mmol), "N" source (0.2 mmol), [Cp\**RhCl*<sub>2</sub>]<sub>2</sub> (5.0 mol %), counteranion additive [X] (20 mol %), and H<sub>2</sub>O (0.1 mmol) in 0.5 mL of solvent under 150 °C for 12 hours. <sup>b</sup> Yield was determined by GC-Mass using a standard, yield of isolated product is given in parentheses. <sup>c</sup> n.r. means no reaction upon **1a**. <sup>d</sup> 1.0 eq of AgNO<sub>3</sub> used. <sup>e</sup> Reaction carried out at 140 °C.

**Scheme 3.** Substrate Scope for Symmetrical Azoarenes to 2-Aryl-2H-Benzotriazoles.<sup>a</sup>



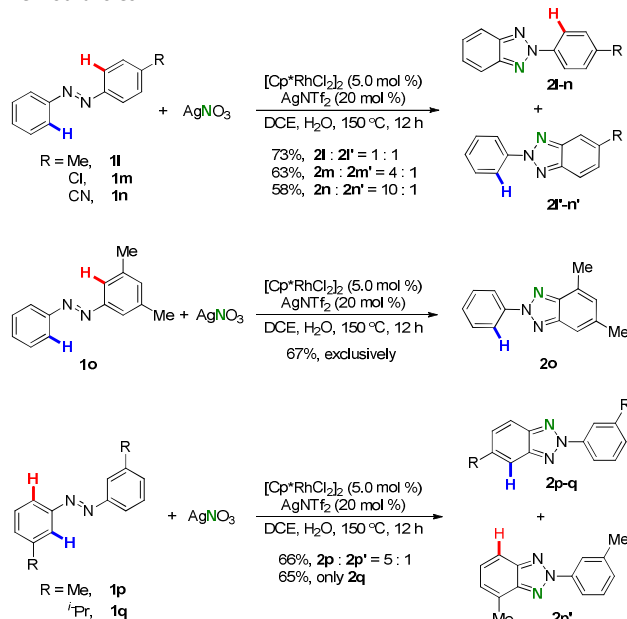
<sup>a</sup> Reaction conditions: **1a-k** (0.1 mmol), AgNO<sub>3</sub> (0.2 mmol), [Cp\**RhCl*<sub>2</sub>]<sub>2</sub> (5.0 mol %), AgNTf<sub>2</sub> (20 mol %), and H<sub>2</sub>O (0.1 mmol) in DCE (0.5 mL) under 150 °C for 12 hours. <sup>b</sup> Yield of isolated product. <sup>c</sup> Recovered azoarene in parentheses.

and steric hindrance of substrates had influence on the reaction result. Basically, the relatively electron-rich azoarenes always exhibited better reactivity than relatively electron-deficient ones. For instance, azobenzenes **1b-f** bearing alkyl group converted readily into the desired 2-aryl-2H-Benzotriazoles **2b-f** in more than 76% yields while ones **1g-i** having chloro-, bromo-, and ester substituent afforded products **2g-i** in mere yield of 46-58%. Gratifyingly, *ortho*-methyl and 3,4-dimethyl substituted azoarenes **1j-k** were also

amenable to the reaction condition, providing **2j** and **2k** in 55% and 72% yields, respectively.

Compared to symmetrical azoarenes, unsymmetrically substituted ones are much more challenging due to the difficult control of regioselectivity. To excavate the influence of electronic and steric effect and realize high regioselectivity, a series of substrates were treated to the standard reaction conditions (Scheme 4). Phenyldiazenes containing a Me (**1l**), Cl (**1m**), and CN (**1n**) group at 4-position on another aromatic ring

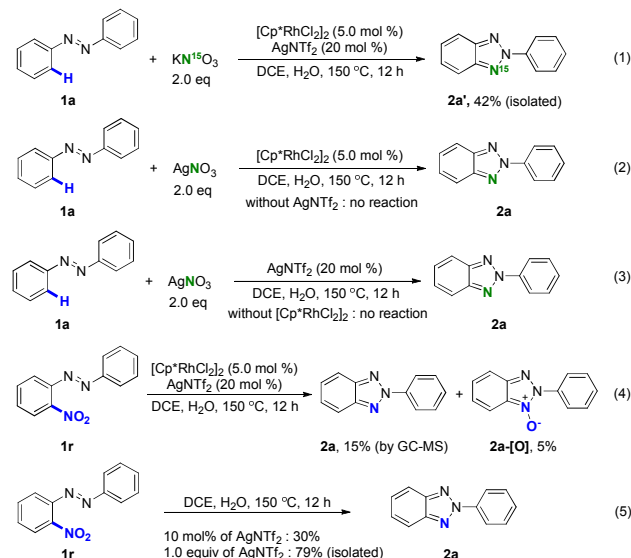
**Scheme 4.** Regioselectivity for Unsymmetrical Azoarenes to 2-Aryl-2H-Benzotriazoles.



gave a mixture of two inseparable constitutional isomers in 73–58% yield but with a regularly increased ratio from 1:1 to 10:1. The observation declares that the nitrogenation of  $C_{sp^2}$ -H bond is preferred at the electron-rich aromatic rings. In the light of the understanding, 1-(3,5-dimethylphenyl)-2-phenyldiazene **1o** was employed and as expected provided **2o** exclusively in good yield. Additionally, two azoarenes having two unsymmetrical *ortho*-C-H reaction sites were used to investigate the steric hindrance effect. For **1p**, a ratio of 5:1 with total 66% yield of **2p** and **2p'** was obtained that disclosed the capacious C-H position is favourable. Thus increasing the steric hindrance from methyl to isopropyl (**1q**) furnished **2q** alone in acceptable yield.

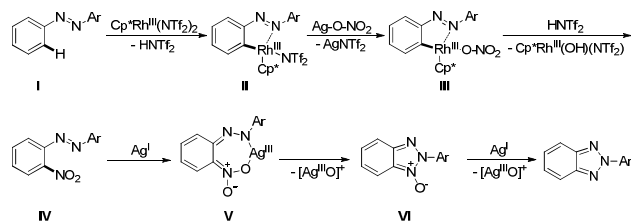
To explore the mechanism of this transformation, several controlled reactions were performed (Scheme 5). First, isotopic tracer experiments were executed. Treatment of **1a** with commercially available  $KN^{15}O_3$  instead of  $AgNO_3$  to the standard reaction conditions delivered the corresponding isotope labeled product **2a'** in 42% yield (eq 1). The result confirms undoubtedly that the inorganic nitrate functions as the real nitrogen source. No reaction occurred in the absence of  $AgNTf_2$  reveals the strong effect of counter anion (eq 2). And

**Scheme 5.** Preliminary Mechanistic Study



$[Cp^*RhCl_2]_2$  is also necessary for the catalytic transformation (eq 3). 1-(2-nitrophenyl)-2-phenyldiazene **1r** partly converted into **2a** in the presence of catalytic amount of Rh(III) and  $AgNTf_2$  with the formation of unstable triazole 1-oxide **2a-[O]** simultaneously (eq 4). Furthermore, **1r** could turn into **2a** completely by increasing the amount of  $AgNTf_2$  from 10 mol % to 1.0 eq (eq 5). Although the mechanism of this catalytic transformation is not completely clear yet, on the basis of previous reports<sup>[13]</sup> and the above-mentioned observations, a possible reaction process is postulated in Scheme 6. The counter anion exchange between  $[Cp^*RhCl_2]_2$  and  $AgNTf_2$  gives

**Scheme 6.** The Postulated Reaction Process.



a cationic Rh(III) species, which facilitates the directing group-assisted C–H activation of azoarene **I** to provide a five-membered rhodacycles **II** with release of  $HNTf_2$ . Then **II** reacts with  $AgNO_3$  to afford the nitrate ion-containing Rh(III) complex **III**. Elimination of **III** in the presence of  $HNTf_2$  liberates 2-nitroazoarene **IV** and another Rh(III) compound, the latter might regenerate the catalytic Rh(III) complex by reaction with  $AgNTf_2$ . Oxidative addition of **IV** and cationic Ag(I) species might assemble the seven-membered Ag(III) intermediate **V**, followed by aza cyclization to form triazole 1-oxide **VI** and a cationic  $[Ag(III)O]^+$  species<sup>[14]</sup>. Subsequently, the second oxidation of **VI** with cationic Ag(I) species produces the desired adduct.

In conclusion, that inorganic AgNO<sub>3</sub> instead of conventional azide reagents for the first time functions as the nitrogen source for nitrogenation reaction was realized. The Rh(III)-catalyzed process without addition of extra oxidant streamlines the synthesis of 2-aryl-2H-benzotriazoles from nonprefunctionalized azobenzenes. Preliminary mechanistic studies suggest that Rh(III)-catalyst could be account for directing group-assisted nitration reaction and cationic Ag(I) species itself might play a vital role for the fission of nitrogen-oxygen bond of nitro group to promote subsequent aza oxidative cyclization.

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