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Tunable and Chemoselective Syntheses of Dihydroisobenzofurans and Indanones via Rhodium-Catalyzed Tandem Reactions of 2-Triazole-benzaldehydes and 2-Triazole-alkylaryl Ketones

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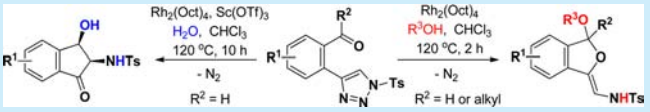
Supporting Information

ABSTRACT: Two novel rhodium(II)-catalyzed tandem reactions were developed for the synthesis of dihydroisobenzofuran and indanone derivatives from 2-triazole-benzaldehydes and 2-triazole-alkylaryl ketones. Dihydroisobenzofuran derivatives were obtained in good yields with high regioselectivities when alcohols were used as nuclophiles in these reactions, whereas the replacement of the alcohol with water resulted in the diastereoselective formation of highly functionalized indanone derivatives.



Annulation reactions involving the addition of heteroatoms to multiple C−C bonds represent an important method for the synthesis of heterocyclic compounds,[1] and reactions of these types tend to proceed with high levels of atom economy, operational simplicity, and variability. 1,3-Dihydroisobenzofurans and indanones are privileged scaffolds[2] which can be found in a broad range of natural products and biologically active compounds,[3] and various methods have been developed to synthesize these compounds.[4] In this context, the cyclization of 2-alkynylbenzyl alcohols to give 1,3-dihydroisobenzofurans is particularly attractive[5] because 2-alkynylbenzyl alcohol can be readily prepared from the corresponding 2-alkynyl-benzaldehydes. Cyclization reactions of this type, however, can be challenging because 2-alkynylbenzyl alcohols can undergo both 6-*endo*-*dig* and 5-*exo*-*dig* cyclization reactions which compete with each other,[6] and the regioselectivities of these reactions must therefore be strictly controlled to avoid the formation of intractable mixtures of five- and six-membered rings. In the case of the 5-*exo*-*dig* process, it is also necessary to control the nature of the addition to the triple bond (i.e. *anti*- versus *syn*-addition) to avoid the formation of a mixture of *Z*- and *E*-isomeric isobenzofurans.[5]

Recently, Fokin, Gevorgyan and co-workers[7] disclosed that *N*-sulfonyl 1,2,3-triazoles **A** existed in equilibrium with diazoimine tautomer **B**,[8] which can be efficiently intercepted by transition-metal catalysts to give rise to highly reactive rhodium(II) azavinyl carbenes **C**[9] (eq 1, Figure 1). This reactive intermediate has been applied to a range of intriguing transformations, including cyclopropanation,[10] transannulation,[11] C−H bond insertion,[12] and dehydrogenative rearrangement,[13] as well as other novel rhodium carbene based

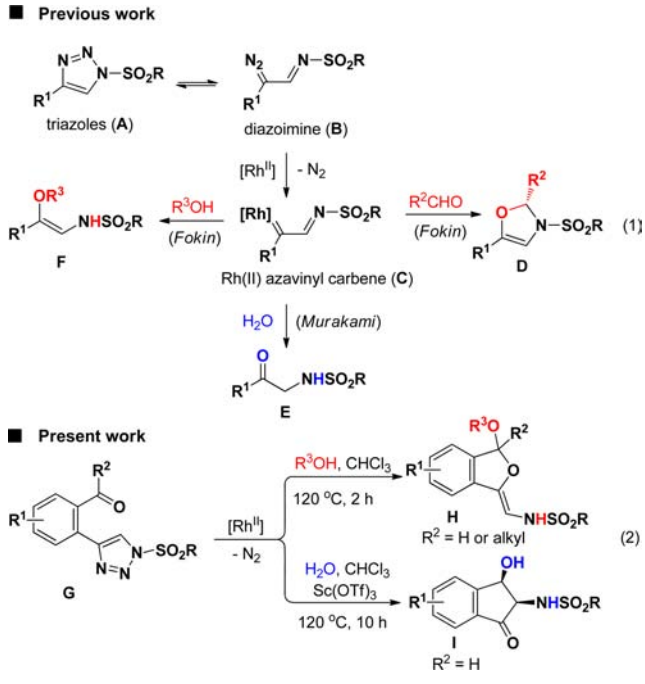


Figure 1. Synthetic analysis.

reactions.[14] As illustrated in Figure 1, 3-sulfonyl-4-oxazolines (**D**), α-amino ketones (**E**), and alkoxy enamines (**F**) could be made by the reactions of *N*-sulfonyl 1,2,3-triazoles with

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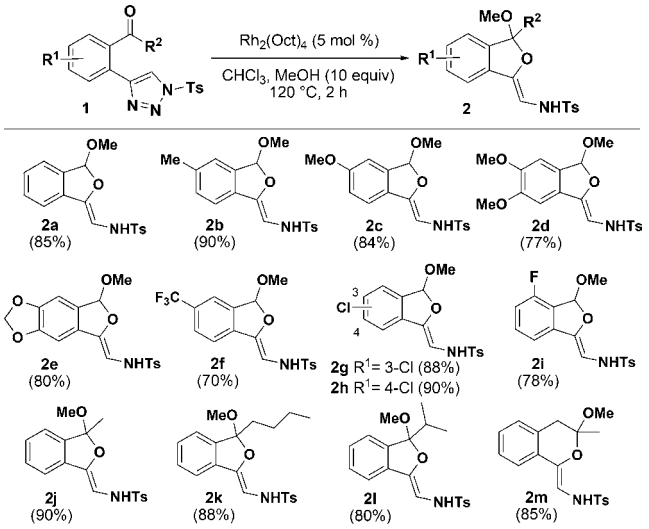
aldehydes,[11b] water,[14a] and alcohols,[14g] respectively. In this aspect, we have reported the synthesis of oxaspirocycles via a Rh(II)-catalyzed annulation of 1-tosyl-1,2,3-triazole-based allyl ethers.[15]

As part of our ongoing work toward the development of novel carbenoid transformations, we herein reported two new reactions for the synthesis of dihydroisobenzofurans and indanones dihydroisobenzofurans (**H**) and indanones (**I**) via the Rh(II)-catalyzed tandem reaction of *N*-sulfonyl 1,2,3-triazoles (**G**) with alcohols and water, respectively (eq 2, Figure 1).

In our previous investigation, we identified that $Rh_2(Oct)_4$ was an efficient catalyst[15] to mediate the equilibrium between **A** and **B** (Figure 1). We envisaged that when substrate **G** (Figure 1) had an *ortho*-carbonyl group, the formed electrophilic carbene **C** might be trapped by this carbonyl group, and the resultant intermediate might lead to a novel type of reaction. To explore this feasibility, we first made triazole **1a** according to the published protocol[16] and then treated it with $Rh_2(Oct)_4$ (5 mol %) in the presence of MeOH in $CHCl_3$ at 120 °C in a sealed tube (Table 1); to our delight, benzofuran **2a** was

Table 1. Substitutional Effects on the Rh(II)-Catalyzed Tandem Reactions of 2-Triazole-benzaldehydes and 2-Triazole-alkylaryl Ketones[a]



[a]Isolated yield.

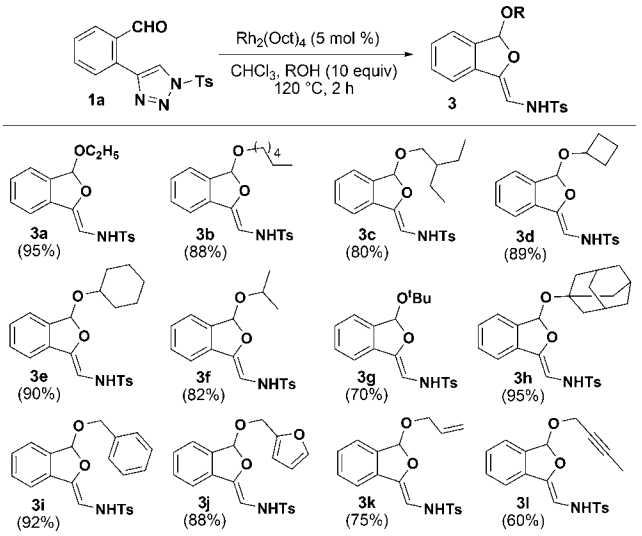
obtained in 85% yield under optimal reaction conditions (see Supporting Information). The structure of **2a** was unambiguously established by X-ray crystallographic analysis of its derivative.[17]

The scope of *N*-sulfonyl 1,2,3-triazoles bearing electron-donating or -withdrawing groups on their aryl rings was investigated as shown in Table 1.

Pleasingly, all of the substrates reacted smoothly under the optimized conditions to give the corresponding products in satisfactory yields. According to the results, we can make the following observations: (1) both electron-rich (**2b**−**2e**) and electron-deficient (**2f**−**2i**) 2-triazole-benzaldehydes are good substrates; (2) 2-triazole-benzoketones can form benzofurans bearing quaternary carbon centers (**2j**−**2l**) in a regioselective manner; (3) when triazole based phenylpropan-2-one is selected as a substrate, the six-membered carbocycle **2m** can be obtained in good yield.

To further evaluate the effect of the nucleophilic alcohol on the outcome of this reaction, twelve different alcohols were selected. As expected, all the reactions proceeded smoothly to give the corresponding products in good yields (Table 2).

Table 2. Rh(II)-Catalyzed Tandem Reactions of 2-Triazole-benzaldehyde 1a with Diverse Alcohols[a]

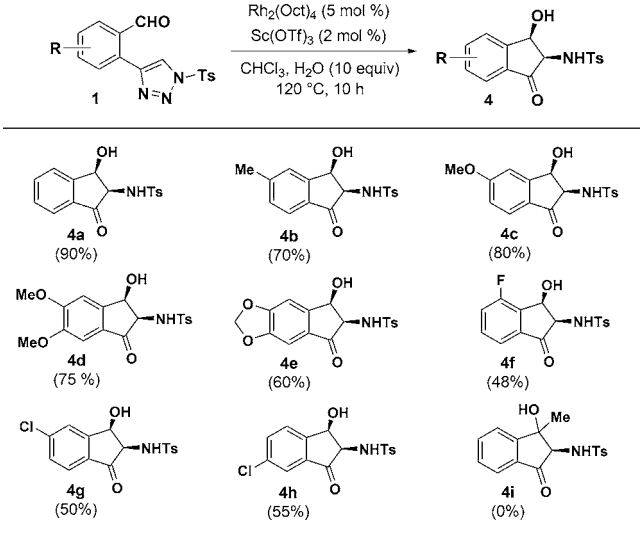


[a]Isolated yield.

To expand the application of this reaction, we investigated the replacement of alcohol with water as the nucleophile. For model substrate **1a**, the use of water did not result in the expected product **2′** and, instead, led to the formation of highly functionalized 2-amino-3-hydroxyl-indanone **4a**, which was isolated as a single isomer in 90% yield when $Sc(OTf)_3$ (2 mol %) was added (Table 3). The relative configuration of **4a** was established by NOESY experiments (see Supporting Information for details).

2-Amino-3-hydroxyl-indanone is the core structure of nature product spirobenzylisoquinolines,[18] as well as many other

Table 3. Rh(II)-Catalyzed Tandem Reactions of 2-Triazole-benzaldehyde with Water[a]



[a]Isolated yield.

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biologically active molecules.[19] Therefore, the development of a stereoselective method[20] for their synthesis remains highly desirable. With this in mind, we conducted an investigation of our newly discovered reaction, with the aim of developing a robust and stereoselective process for the synthesis of 2,3-disubstituted indanones. The scope of this annulation reaction was evaluated using a broad range of 2-triazole-benzaldehydes bearing electron-donating or -withdrawing groups on their phenyl rings (Table 3). The results of these scoping reactions revealed that substrates bearing electron-donating groups gave the corresponding indanones (**4b**−**4e**) in good yield, whereas substrates bearing electron-withdrawing groups (F^- or Cl^-) gave lower yields (**4f**−**4h**). Furthermore, the application of the optimized reaction conditions to 2-triazole-alkylaryl ketone failed to provide any of the desired product **4i**, with the substrate undergoing decomposition.

Based on the results described above, we proposed a mechanism for these catalytic reactions (Figure 2). The initial

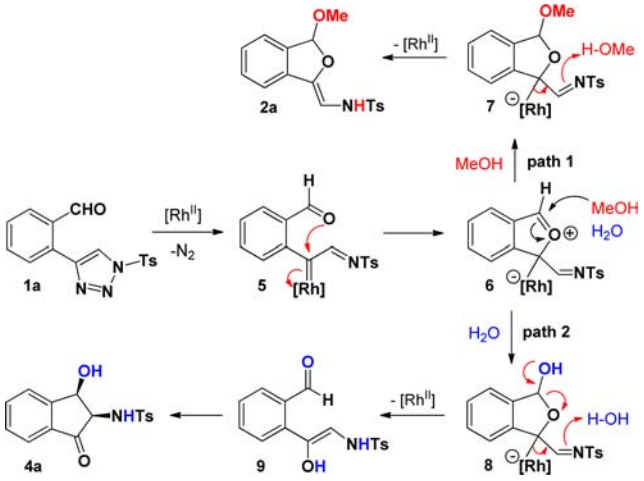

Figure 2. Proposed reaction mechanisms for the formation of dihydroisobenzofurans and 2-amino-3-hydroxyl indanones.

Rh(II)-catalyzed denitrogenation of the *N*-sulfonyl 1,2,3-triazole **1a** would give the rhodium(II) azavinyl carbene **5**, which was then subjected to a nucleophilic addition of the oxygen atom of the carbonyl group[21] to form the key oxonium intermediate **6**. The nucleophilic addition of MeOH or water[6e] to the intermediate **6** would result in the formation of intermediate **7** by path 1 or intermediate **8** by path 2, respectively. Finally, decoordination of rhodium from **7** and **8** would liberate the corresponding products and regenerate the catalyst.

To support the existence of the oxonium intermediate **6** as a key intermediate in these reactions, we conducted a single reaction where compound **1a** was initially treated with a catalytic amount[22] of $Rh_2(Oct)_4$ in $CHCl_3$ at 120 °C. After 2 h, the substrate **1a** was consumed, and methanol, water, and a catalytic amount of $Sc(OTf)_3$ were then added, respectively, followed by reaction for an additional 2 and 10 h. As a result, products **2a** and **4a** were obtained in 80% and 82% yield, respectively. These results suggested that the oxonium intermediate **6** was initially formed via a nucleophilic addition of its carbonyl group, which trigged the downstream reactions.

In summary, a regio- and stereoselective synthesis of structurally diverse dihydroisobenzofurans and 2-amino-3-hydroxyl indanones has been achieved via a novel type of rhodium(II)-catalyzed tandem reaction of 2-triazole-benzaldehydes and 2-triazole-alkylaryl ketones by using alcohols and water as nucleophiles, respectively. Mechanistic studies suggest that a Rh-associated oxonium intermediate is involved in the stereoselective reaction. Despite the prevalence of rhodium(II) azavinyl carbene (**C** in Figure 1) in the rhodium-catalyzed reactions of *N*-sulfonyl 1,2,3-triazoles, these reactions demonstrate the potential of this organometallic species in the construction of scaffolds which are important in biomedical research and drug discovery.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral and other characterization data. 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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