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Rhodium(II)-Catalyzed Intramolecular Transannulation of 4-Methoxycyclohexa-2,5-dienone Tethered 1-Sulfonyl-1,2,3-Triazoles: Synthesis of Azaspiro[5.5]undecane Derivatives

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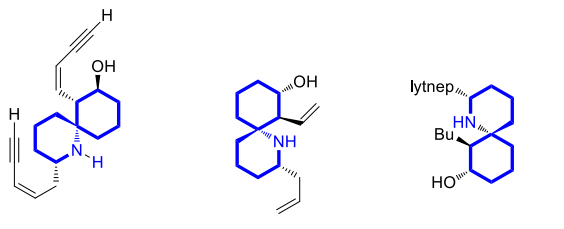
Abstract. A Rh(II)-catalyzed denitrogenative intramolecular transannulation using 4-methoxycyclohexa-2,5-dienone tethered *N*-sulfonyl-1,2,3-triazoles as substrates has been developed, affording diversified 3-methoxy-1-tosyl-1-azaspiro[5.5]undecanes in moderate to good yields under mild conditions. This new synthetic method proceeded through an oxonium ylide generated from trapping a rhodium(II)-carbene by methoxy group, a methoxy group migration, and C-N bond formation, providing an interesting synthetic strategy for the construction of spirocyclic frameworks.

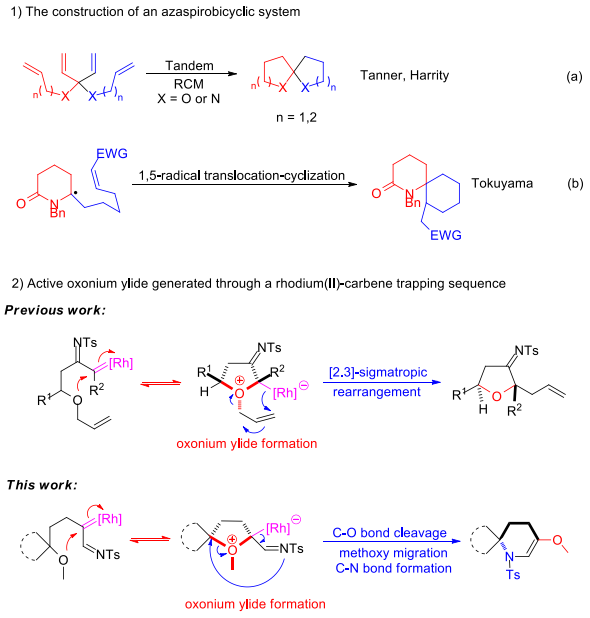
Keywords: Rh(II)-catalyzed; transannulation; *N*-sulfonyl-1,2,3-triazoles; oxonium ylide.

The 1-azaspiro[5.5]undecane skeleton is a privileged structural motif in many biologically active and medicinally valuable molecules. For example, Histrionicotoxin (HTX) analogues, a kind of alkaloids isolated from the skins of the brightly-colored "poison dart" frogs of Central America, contain an essential 1-azaspiro[5.5]undecane core and possess activity as a noncompetitive blocker of nicotinic acetylcholine receptors (Scheme 1).[1] In addition, perhydrohistrionicotoxin also has significant biological activities in medicinal chemistry.[1] Thus, the rapid construction of a novel azaspiro[5.5]bicyclic system from simple starting materials was of considerable interest in both of synthetic and medicinal chemistry.[2]



Scheme 1. Natural products containing 1-azaspiro[5.5]undecane units.

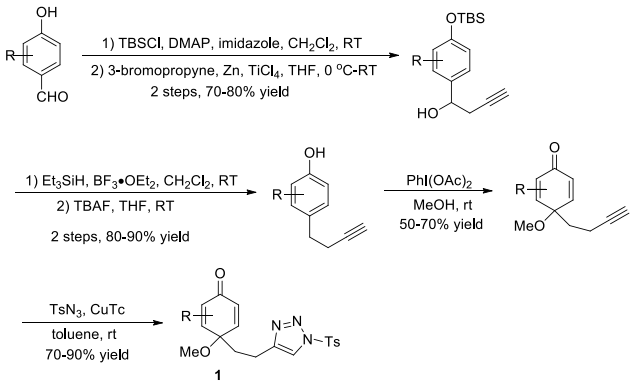
Thus far, tandem RCM reactions were frequently applied as efficient synthetic methods for the construction of spirocyclic frameworks and the elegant examples have been reported by Tanner[3a] and Harrity,[3b] respectively (Scheme 2-1, eq. a). On the other hand, radical translocation-cyclization cascade was another useful strategy reported by Tokuyama and his co-workers in the total synthesis of Histrionicotoxin[1a] (Scheme 2-1, eq. b).



Scheme 2. Previous work and our working hypothesis of this work.

Recently, the *N*-sulfonyl-1,2,3-triazoles, prepared through copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC),[4] have been utilized to generate α-imino rhodium(II) carbene precursors in a series of novel carbene-induced transformations, providing an efficient protocol for the synthesis of nitrogen-containing heterocycles.[5] To date, the research groups of Fokin, Gevorgyan,[6] Davies,[7] Murakami,[8] Sarpong,[9] our group[10] and

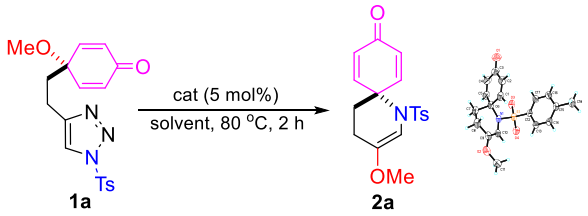
others[11] have been intensively illustrating the vast synthetic potential of these carbenoid intermediates. Notably, an active ylide would be generated if the carbene was trapped by a heteroatom, such as sulfur, nitrogen, bromine or oxygen atom,[12] which could set up a stage for the subsequent transformations. Boyer and co-workers have recently reported a rhodium(II)-catalyzed denitrogenative transformation of 1-sulfonyl-1,2,3-triazoles with pendent allyl and propargyl ether motifs to oxonium ylides that undergo [2,3]-sigmatropic rearrangement to give substituted dihydrofuran-3-imines in 2014[12c] (Scheme 2-2, previous work). Encouraged by these brilliant works, herein we wish to report a Rh(II)-catalyzed intramolecular transannulation reaction of 4-methoxycyclohexa-2,5-dienone tethered 1-sulfonyl-1,2,3-triazoles **1** through an oxonium ylide formation, C-O bond cleavage, methoxy migration and C-N bond formation process, leading to the rapid construction of 1-azaspiro[5.5]undecane derivatives (Scheme 2-2, this work).



Scheme 3. Synthesis of 4-methoxycyclohexa-2,5-dienone tethered triazoles **1**. CuTc = copper(I) thiophene-2-carboxylate.

The 4-methoxycyclohexa-2,5-dienone tethered *N*-sulfonyl-1,2,3-triazoles **1** could be easily obtained in six steps as shown in Scheme 3 (see Scheme S1 in the Supporting Information for the details). When *N*-sulfonyl-1,2,3-triazole **1a** was treated with 5 mol% $Rh_2(OAc)_4$ in dry 1,2-DCE (1,2-dichloroethane) at 80 °C, we found that the desired 3-methoxy-1-tosyl-1-azaspiro[5.5]undeca-2,7,10-trien-9-one **2a** was obtained in 70% yield after 2 hours (Table 1, entry 1). The structure of **2a** has been unequivocally assigned by X-ray diffraction. The ORTEP drawing is shown in Table 1 and the CIF data are presented in the Supporting Information. Replacing $Rh_2(OAc)_4$ with $Rh_2(Oct)_4$ gave **2a** in higher yield up to 81% (entry 2). No reaction occurred when **1a** was treated with $Rh_2(tfa)_4$ (entry 3). The use of other rhodium(II) catalysts such as $Rh_2(Piv)_4$ and $Rh_2(esp)_2$ resulted in **2a** in lower yields (entries 4 and 5). When the reaction was carried out without a catalyst, none of the desired product could be detected, and the substrate **1a** was recovered, indicating that rhodium(II) catalyst played an essential role in this reaction (entry 6). After a quick solvent screening, we found that dichloromethane led to a similar result as that of 1,2-dichloroethane (entry 7), and toluene was substantially less effective than that of 1,2-dichloroethane (entry 8). The use of tetrahydrofuran and acetonitrile as the solvents provided poor results under otherwise identical conditions (entries 9 and 10). Therefore, $Rh_2(Oct)_4$ was the most suitable catalyst for this reaction and 1,2-dichloroethane (DCE) was identified as the best solvent of choice. The use of a chiral rhodium(II) tetracarboxylate catalyst [Rh_2(S-DOSP)$_4$] afforded the corresponding product **2a** in 66% yield (entry 11), and this result provided the possibility for the exploration of asymmetric variant of this reaction.

Table 1. Optimization of the reaction conditions of Rh(II)-catalyzed intramolecular transannulation reaction of **1a**.



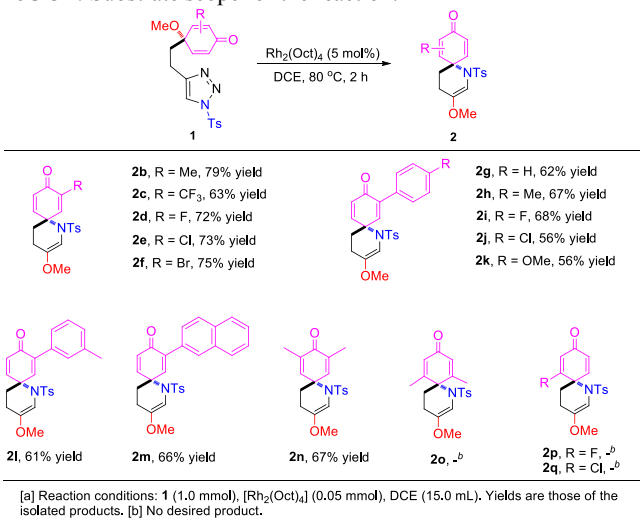
entry[a]	cat	solvent	yield (%)[b]
1	$Rh_2(OAc)_4$	DCE	70
2	**$Rh_2(Oct)_4$**	**DCE**	**81**
3	$Rh_2(tfa)_4$	DCE	–
4	$Rh_2(Piv)_4$	DCE	54
5	$Rh_2(esp)_2$	DCE	63
6	–	DCE	–
7	$Rh_2(Oct)_4$	DCM	78[c]
8	$Rh_2(Oct)_4$	toluene	53
9	$Rh_2(Oct)_4$	THF	27
10	$Rh_2(Oct)_4$	CH_3CN	14
11	Rh_2(S-DOSP)$_4$	DCE	66

[a] Reaction conditions: **1a** (0.2 mmol), cat (0.01 mmol), solvent (3 mL). [b] Yields of isolated product. [c] The reaction was carried out in a sealed tube.

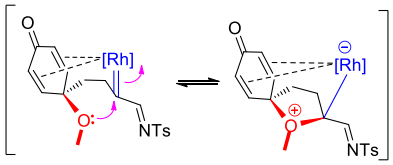
With the optimal reaction conditions in hand, we next investigated the substrate scope and generality of this new spirocyclization reaction, and the results are shown in Table 2. As illustrated, introducing methyl group, trifluoromethyl group or halogen atom as the substituent at the α-position of the carbonyl group (substrates **1b-1f**), the reactions proceeded smoothly, affording the desired products **2b-2f** in moderate to good yields ranging from 63% to 79%. We also attempted to introduce more functional groups at the α-position of the carbonyl group. However, when a methoxy group was introduced at the α-position of the carbonyl group, the corresponding *N*-sulfonyl-1,2,3-triazole product could not be obtained, but some unidentified oily by-products were isolated. In addition, when an ester group or a heteroaromatic group was introduced at the α-position of the carbonyl group, the corresponding dehydroxylation product could not be obtained due to that these intermediates were not stable under reduction with Et_3SiH and $BF_3{\cdot}OEt_2$ (see Scheme S3 in the Supporting Information). A variety of aryl groups could be introduced at the α-position of the carbonyl group by a Suzuki-Miyaura cross coupling reaction of 3-bromo-4-hydroxybenzaldehyde and arylboronic acids (see Supporting Information). As shown in Table 2, these α-aryl group substituted triazoles **1g-1l** could produce the corresponding products **2g-2k** in 56-68% yields under the standard conditions regardless of whether electron-neutral or electron-rich or electron-deficient substituent was introduced on the benzene ring, suggesting that the electronic property of aromatic ring did not have significant impact on the reaction outcome. The methyl group could be introduced on the *meta*-position of phenyl ring, giving the desired product **2l** in 61% yield. Naphthyl group was also tolerated, furnishing the desired product **2m** in 66% yield. When the two α-

positions of the carbonyl group were occupied by two methyl groups, the reaction also took place smoothly to give the corresponding product **2n** in 67% yield. Unfortunately, substrates **1o-1q** having substituents at the β-position of the carbonyl group were not tolerated in this transformation. In these cases, none of the desired products **2o-2q** could be obtained and the starting materials were hydrolyzed during the reaction since the corresponding by-product $TsNH_2$ could be detected. We assumed that the dienone skeleton played an essential role in this reaction through the coordination with rhodium metal center, and the coordination probably shortened the distance between the rhodium carbene and the nucleophilic oxygen atom, allowing the intramolecular reaction to take place smoothly. Nevertheless, the steric bulkiness due to the substituent at the β-position would impair this coordination and block out the nucleophilic attack of oxygen atom to the rhodium carbene (Scheme 4). For substrate **1p** having a fluorine atom, the electronic effect may also dramatically affect the reaction proceeding.

Table 2. Substrate scope for the reaction.[a]

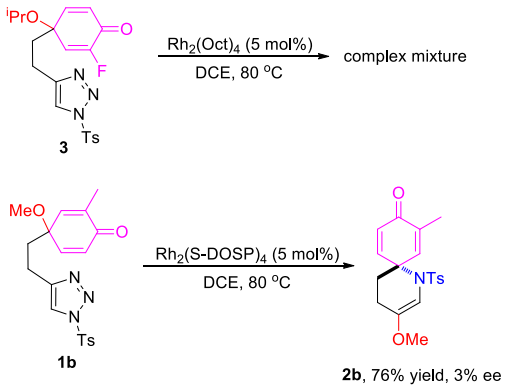


[a] Reaction conditions: **1** (1.0 mmol), $[Rh_2(Oct)_4]$ (0.05 mmol), DCE (15.0 mL). Yields are those of the isolated products. [b] No desired product.



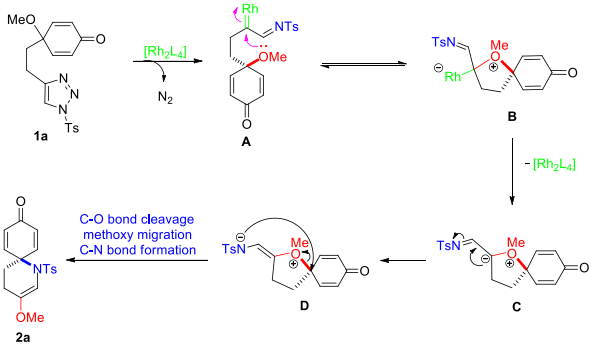
Scheme 4. A plausible transition state to form oxonium ylide.

To further clarify the substrate scope of this reaction, we utilized *N*-sulfonyl triazole **3** bearing an ^{i}PrO group as a substrate to carry out the reaction, but found that the desired spirocyclic product could not be obtained under the standard conditions and complex product mixtures were formed, presumably due to steric bulkiness of isopropoxy group (Scheme 5). Moreover, the examination of its asymmetric variant was conducted by using $[Rh_2(S\text{-}DOSP)_4]$ as the catalyst for the transformation of substrate **1b**, giving the corresponding product **2b** in 76% yield along with low *ee* value (Scheme 5).



Scheme 5. Further examination of the substrate scope and the preliminary asymmetric trial.

On the basis of the above results, a plausible reaction mechanism is illustrated in Scheme 6 by using **1a** as a model substrate. Upon treatment with rhodium(II) catalyst, *N*-sulfonyl triazole **1a** underwent a denitrogenation process to generate the corresponding α-imino rhodium carbene **A**, which could be further trapped by the methoxy group to produce an oxonium ylide **B**.[13] After release of the rhodium catalyst, an intermediate **C** was formed. The intermediate **C** underwent an intramolecular isomerization to give an intermediate **D**, which subsequently underwent an intramolecular nucleophilic attack to cleave the C-O bond, affording the corresponding 1-azaspiro[5.5]undecane **2a**.



Scheme 6. A plausible mechanism for the formation of **2a**.

In summary, we have developed a step-economical and practically useful synthetic method for the preparation of 1-azaspiro[5.5]undecane derivatives based on a novel rhodium(II)-catalyzed intramolecular transannulation reaction of 4-methoxycyclohexa-2,5-dienone tethered *N*-sulfonyl triazoles for the first time. A variety of functional groups can be tolerated although the substituent at the β-position of the carbonyl group can block out this transannulation reaction. This new cascade reaction in the rhodium(II)-catalyzed cyclization of *N*-sulfonyl triazoles goes through the formation of an oxonium ylide intermediate, a methoxy group migration, and C-N bond formation to give the spiroheterocycles **2** in moderate to good yields. Further application of this methodology to the synthesis of biologically active alkaloid natural products are currently underway.

Experimental Section

General Procedures for the Synthesis of 2

Under argon atmosphere, $Rh_2(Oct)_4$ (0.05 mmol, 0.05 equiv.) was added to a solution of 1-sulfonyl-1,2,3-triazole **1** (1.0 mmol, 1.0 equiv.) in dry 1,2-dichloroethane (15.0 mL) in a Schlenk tube. The reaction mixture was stirred for about 2 h at 80 °C until **1** was completely consumed by TLC monitoring. Then, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 8/1~4/1) to give the desired product **2**.

Supporting Information Available

Detailed descriptions of experimental procedures and their spectroscopic data as well as the crystal structures are presented in the Supporting Information. CCDC 1822731 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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