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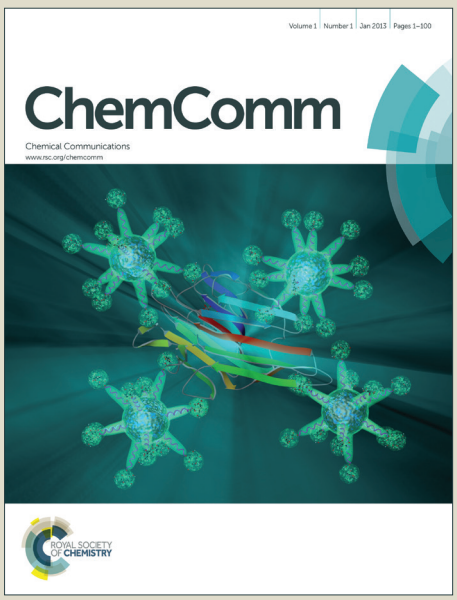

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ARTICLE TYPE

Rh-Catalyzed 1,2-Sulfur Migration/aza-Diels-Alder Cascade Initiated by aza-Vinyl Carbenoids from Sulfur-Tethered N-Sulfonyl-1,2,3-triazoles

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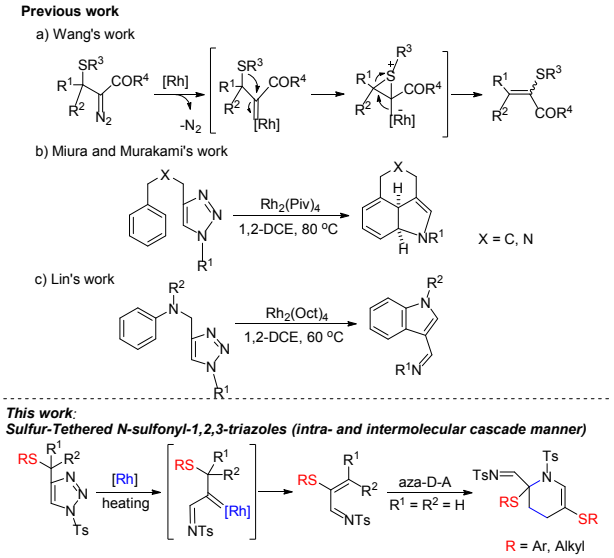
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A novel Rh(II) catalyzed intramolecular 1,2-sulfur rearrangement/intermolecular aza-Diels-Alder cascade initiated by azavinyl carbenes has been developed, efficiently affording sulfur-containing tetrahydropyridine derivatives or α,β-unsaturated imines with a broad substrate scope.

S-containing heterocycles are privileged structural motifs in many natural products and biologically active compounds[1] and the development of synthetic methods for these compounds has attracted much attention.[2] 1,2-Sulfur migration is an important chemical transformation protocol for organic chemists and this method has been developed as valuable tools for organic synthesis in the construction of S-containing compounds.[2,3] Thus far, this method has been extensively used in the synthesis of many nonaromatic or aromatic heterocycles.[4,5] The most common route of 1,2-sulfur migration usually proceeds through a thiiranium intermediate. As an important process to produce a thiiranium intermediate, 1,2-sulfur migration to a carbenoid center has been reported in recent years.[6a,6b,7] For example, in 2005, Wang and co-workers reported Rh-catalyzed 1,2-sulfur group migration through a thiiranium zwitterion, demonstrating that sulfur atom has a higher migratory aptitude over other atoms (Scheme 1a).[6a] Then, Xu's group reported the similar transformation of β-thio group substituted α-diazo carbonyl compounds to ketenes also via a thiiranium intermediate.[6b] Although metal-catalyzed 1,2-thio migration is useful and efficient, the reported examples and reaction modes for the synthesis of S-containing heterocycles are still limited.

Recently, N-sulfonyl-1,2,3-triazoles, which can be easily prepared from copper(I)-catalyzed azide-alkyne cycloadditions, have emerged as alternative precursors for the formation of α-imino metal carbenoids.[8] Thus far, it has been known that they can undergo a variety of synthetically useful transformations via typical carbene reaction manners[9-14] such as cyclopropanation,[11] C-H, O-H or N-H insertion,[12][13] and carbene induced other types of reactions.[14] Concerning about intermolecular reaction manners, due to the α-imino rhodium(II) carbene species bearing both an electrophilic carbenoid carbon and a nucleophilic nitrogen atom, they can react with many other compounds such as nitriles, isocyanates, aldehydes, heteroaromatics and so on to produce various useful N-heterocycles.[15] On the other hand, rhodium(II)-catalyzed intramolecular reactions of N-sulfonyl-1,2,3-triazoles have also aroused the interest of chemists and the novel reaction modes have been disclosed by several groups[14,16] including ours.[17] For example, in 2014, Miura and Murakami[16d] reported intramolecular dearomatizing [3+2] annulation of aza-vinyl carbenoids with aryl rings, furnishing 3,4-fused indole skeletons, in which the key steps involved the benzene ring acting as the dipolarophile to react with the α-imino Rh carbenoid (Scheme 1b). Subsequently, the group of Lin[16e] reported a reaction for converting N-propargylanilines to functionalized indoles through Rh(II)-catalyzed denitrogenative annulation of N-sulfonyl-1,2,3-triazoles (Scheme 1c). Inspired by these previous findings shown in Scheme 1, we envisaged that if a neighboring sulfur atom was introduced to the N-sulfonyl-1,2,3-triazole moiety, the aza-vinyl Rh carbene induced 1,2-sulfur migration might be able to take place due to the nucleophilicity of sulfur atom, giving a new reaction mode of aza-vinyl Rh-carbene chemistry. In fact, we indeed found that thio group-tethered N-sulfonyl-1,2,3-triazoles could be converted to tetrahydropyridine

Scheme 1. Previous work and this work.



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† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data of new compounds, and CCDC 996223, 1013188 and 1021015. See DOI: 10.1039/b000000x

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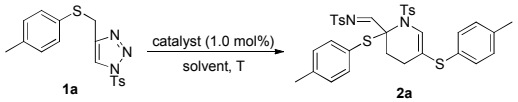
DOI: 10.1039/C4CC08829H

derivatives through intramolecular 1,2-sulfur migration/intermolecular aza-Diels-Alder cascade[18] or α,β-unsaturated imine derivatives through an intramolecular 1,2-sulfur migration process depending on the substitution pattern, respectively (Scheme 1, this work). Herein, we would like to report these interesting findings.

We initially utilized 4-(p-tolylthiomethyl)-1-tosyl-1*H*-1,2,3-triazole **1a** (R^1 = R^2 = H, Scheme 1, this work) as substrate by carrying out the reaction in 1,2-DCE (1,2-dichloroethane) in the presence of $[Rh_2(esp)_2]$ to examine the reaction outcomes. The tetrahydropyridine derivative **2a** derived from an intramolecular 1,2-sulfur migration and a subsequent intermolecular aza-Diels-Alder cascade was obtained in 88% yield based on the ^{1}H NMR spectroscopy (Table 1, entry 1). Then, we turned our attention to identify the optimized reaction conditions for the current reaction by screening various rhodium catalysts, solvents, and temperatures. The results are summarized in Table 1. Changing catalysts to $[Rh_2(OAc)_4]$ and $[Rh_2(Piv)_4]$ produced **2a** in 94% and 91% yields, respectively (entries 2 and 3). Using $[Rh_2(tfa)_4]$ as the catalyst, no reaction occurred (entry 4). $[Rh_2(OAc)_4]$ was identified as the best catalyst in this reaction, affording **2a** in 91% isolated yield. Its structure has been unambiguously determined by X-ray diffraction. Its ORTEP drawing and the CIF data are presented in the Supporting Information.[19] Moreover, the use of toluene and $CHCl_3$ as the solvents afforded **2a** in lower yields (entries 5 and 6). Carrying out the reaction temperature at 50 °C, no reaction could take place (entry 7).

Table 1. Optimization of the reaction conditions.

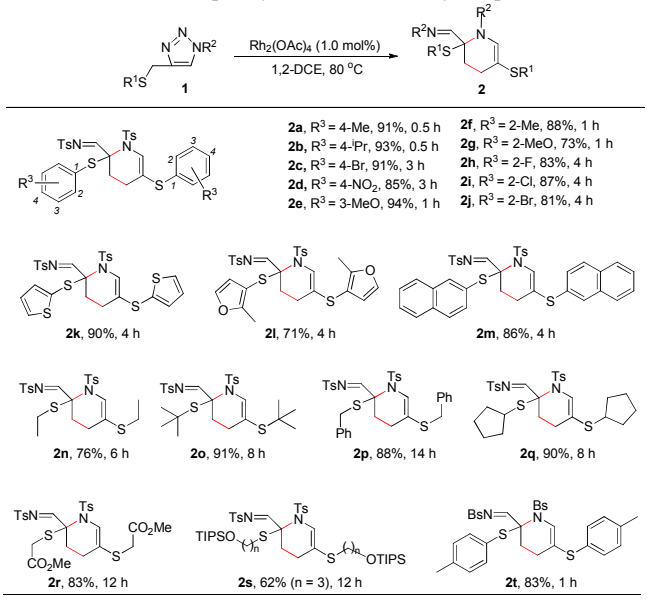


entry[a]	catalyst	solvent	time (h)	T (°C)	yield (%)[b]
1	$Rh_2(esp)_2$	1,2-DCE	0.5	80	88
2	$Rh_2(OAc)_4$	1,2-DCE	0.5	80	94 (91[c])
3	$Rh_2(Piv)_4$	1,2-DCE	0.5	80	91
4	$Rh_2(tfa)_4$	1,2-DCE	0.5	80	N.R.
5	$Rh_2(OAc)_4$	Toluene	1	80	53
6	$Rh_2(OAc)_4$	$CHCl_3$	1	80	14
7	$Rh_2(OAc)_4$	1,2-DCE	2	50	N.R.

[a] Unless otherwise specified, all reactions were performed with **1a** (0.20 mmol) and catalyst (0.002 mmol). [b] Yields are determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yields.

With this optimal reaction conditions in hand, we next surveyed the substrate scope of various triazole **1**. As shown in Table 2, as for substrates **1b-d**, the reactions proceeded smoothly to furnish the desired products **2b-d** in 85-93% yields. In addition, in the cases of substrates **1f-j**, the reactions proceeded efficiently to give the desired products **2f-j** in 73-88% yields. These results suggest that the substrates with electron-withdrawing group at the 2-position on the aromatic ring may be more conducive to the production of **2** compared to that of electron-donating ones. Introducing a electron-donating MeO group at the 3-position of benzene ring afforded the corresponding product **2e** in 94% yield under the standard conditions. The substituents on the sulfur atom could be heteroaromatic rings such as thienyl, furyl or 2-naphthyl group, providing the desired products **2k-m** in yields ranging from moderate to excellent. Furthermore, this reaction could also tolerate various aliphatic substituents or functional groups such ester group or protected OH group on the sulfur atom, indicating a broad substrate scope, giving the desired products **2n-3s** in good yields. Bs (4-bromophenylsulfonyl) substituted *N*-sulfonyl-1,2,3-triazole could be also used in this reaction, affording the corresponding product **2t** in 83% yield. As for selenium-tethered triazole **1w**, the reaction gave a complex product mixtures, perhaps due to that the corresponding product is not stable upon heating.[20]

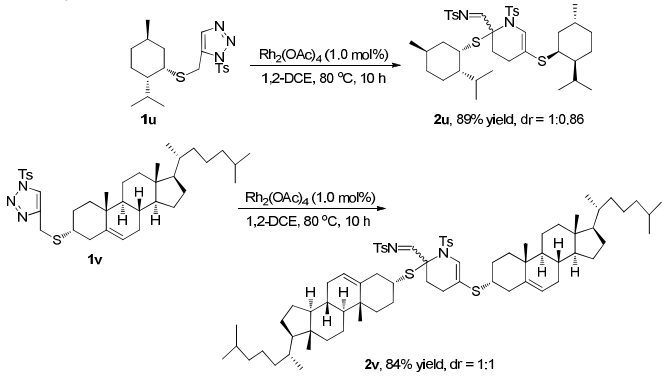
Table 2. Reaction Scope: Synthesis of heterocyclic products **2**.[a]



[a] Conditions: **1** (0.20 mmol) and $Rh_2(OAc)_4$ (0.002 mol) were heated in DCE (2 mL) at 80 °C for appropriate time.

Furthermore, *L*-menthol and cholesterol derived *N*-sulfonyl-1,2,3-triazoles **1u** and **1v** were also employed in this reaction, delivering the desired products **2u** and **2v** in 89% and 84% yields respectively as a pair of diastereomers (Scheme 2). These results suggest the potential application of this methodology in the linkage with naturally occurring bioactive substances.

Scheme 2. Reaction of L-Menthol and Cholesterol derived N-sulfonyl-1,2,3-triazole.



Next, the further examinations were performed to extend the substrate scope in which R^1 or R^2 is not a H atom under the standard conditions (Scheme 1, this work). We found that α,β-unsaturated imine derivatives **4** were given instead of the tetrahydropyridine derivatives due to that the following aza-Diels-Alder reaction was shut down, perhaps because of the steric hindrance. As shown in Table 3, the substrate **3a** or **3d** bearing a Me or Bu group at the methylene position (R = Me or Bu) gave the corresponding imine product **4a** or **4d** in 81% yield or 75% yield, respectively. The substituent on the sulfur atom could be bromobenzene as well, giving the desired product **4b** in 85% yield. Meanwhile, substrate **3c** bearing two Me groups at the methylene position also afforded the corresponding product **4c** in

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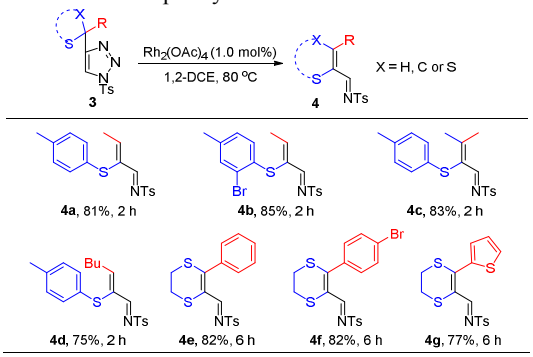
83% yield. In addition, as for the dithioacetal substrates **3e**, **3f** and **3g**, the reactions proceeded smoothly to afford the desired products containing a six-membered S-heterocycle **4e**, **4f** and **4g** in good yields. The Z-configuration of **4a**, **4b** and **4d** was determined based on the X-ray crystal structure of **4a**.[21]

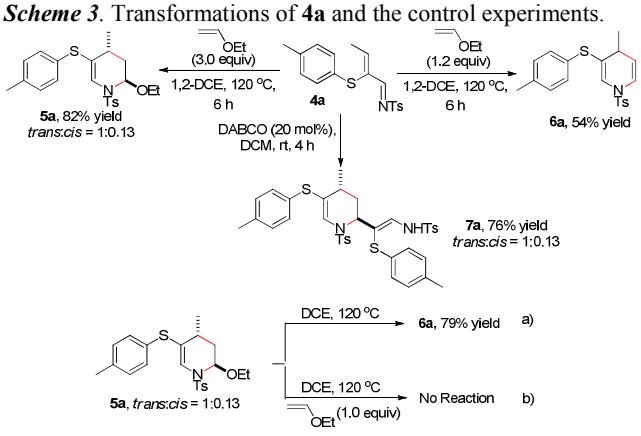
Table 3. Reaction Scope: Synthesis of Product **4**.[a]



[a] Conditions: **3** (0.20 mmol) and $Rh_2(OAc)_4$ (0.002 mol) were heated in DCE (2 mL) at 80 °C for appropriate time.

The synthetic utility of α,β-unsaturated imine products was exemplified by further transformations. As shown in Scheme 3, tetrahydropyridine derivative **5a** could be obtained in 82% yield as a stereoisomeric mixture upon treating **4a** with 3.0 equiv of ethoxyethene in 1,2-DCE at 120 °C in a sealed tube. Its structure has been fully characterized by spectroscopic data (see Supporting Information). When 1.2 equiv of ethoxyethene was used, 1,4-dihydropyidine derivative **6a** could be obtained in 54% yield presumably derived from the elimination of ethanol from **5a**. The control experiments indicated that in the presence of extra ethoxyethene, **5a** is stable under the standard conditions (Scheme 3, eq a and b). The reason of this phenomenon may be due to the partial decomposition of ethoxyethene by ambient water at high temperature during the reaction proceeding to generate ethanol, which may inhibit the release of ethanol from **5a** under otherwise identical conditions (see Supporting Information for details).

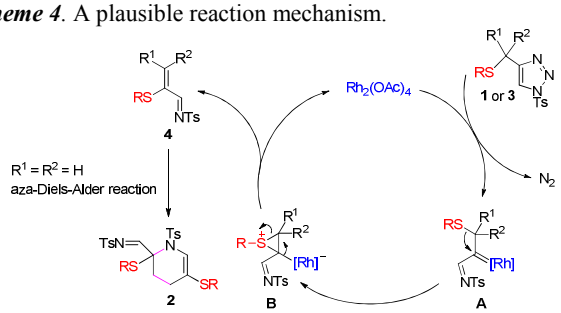
Scheme 3. Transformations of **4a** and the control experiments.



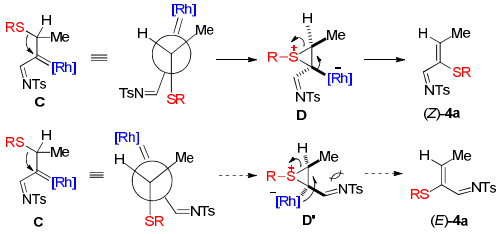
Moreover, in the presence of 1,4-diaza[2.2.2]bicyclooctane (DABCO) (20 mol%), **4a** could be transformed to the dimeric cyclic product **7a** in 76% yield as 10:1 diastereomeric ratio through a sequential isomerization and formal aza-Diels-Alder process (see Supporting Information for the detailed mechanism). The structure of **7a** was further determined by the X-ray diffraction. Its ORTEP drawing and the CIF data are presented in the Supporting Information.[22]

Based on the above results and the previously reported literature, a plausible mechanism for this reaction is outlined in Scheme 4. This reaction begins with a rapid formation of α-imino rhodium(II) carbenoid **A** upon heating **1** or **3** with Rh catalyst. Subsequent sulfur 1,2-migration through intermediate **B** generates the corresponding α,β-unsaturated imine product **4**. When R^1 and R^2 groups are H atom, an intermolecular aza-Diels-Alder reaction can be induced to give the corresponding *N*-heterocycle **2** presumably due to that this product is very reactive to undergo the bimolecular cycloaddition. In the case of **3a**, upon nucleophilic addition to the rhodium carbene, both intermediates **D** and **D'** would be formed (Scheme 5). However, intermediate **D** is more stable than **D'** probably due to the less steric repulsion between the *trans*-configured NTs and methyl group. Therefore, after ring-opening process, (*Z*)-**4a** was formed exclusively from intermediate **D**.

Scheme 4. A plausible reaction mechanism.

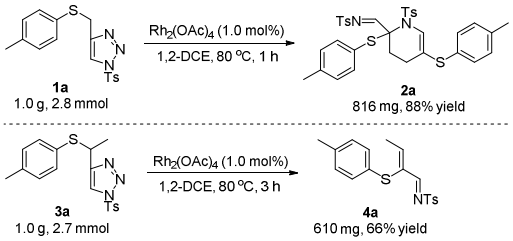


Scheme 5. A plausible explanation for the exclusive formation of (*Z*)-**4a**.



For the potential utility of this protocol, the reaction has been also carried out on a 1.0 g scale. As shown in Scheme 6, as for triazole substrate **1a**, the reaction proceeded smoothly to give the desired product **2a** in 88% yield. Carrying out the reaction of **3a** on a 1.0 g scale under the standard conditions produced **4a** in 66% yield presumably due to the partial decomposition of this imine product in silica gel column chromatography during the purification.

Scheme 6. Gram scale reaction of **1a** and **3a**.



In summary, we have developed a novel and efficient synthetic protocol to easily access S-containing tetrahydropyridine derivatives from the rhodium-catalyzed cascade of sulfur-tethered

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N-sulfonyl-1,2,3-triazole derivatives. The reaction involves an intramolecular 1,2-sulfur migration/intermolecular aza-Diels-Alder cascade initiated by aza-vinyl Rh carbenoid. Further investigation indicated that α,β-unsaturated imine derivatives can be readily produced when R^1 or R^2 is not H atom, and a series of novel S-containing heterocycles could be also synthesized upon further transformation. This chemistry can be used to the naturally occurring bioactive substances as well. These new findings subsequently enrich the aza-vinyl Rh carbene chemistry at the present stage. The potential application and extension of the substrate scope of this novel synthetic methodology are currently underway in our laboratory.

We are grateful for the financial support from the National Basic Research Program of China (973)-2015CB856603, and the National Natural Science Foundation of China (20472096, 21372241, 21361140350, 20672127, 21102166, 21121062, 21302203 and 20732008).

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[19] The crystal data of **2a** have been deposited in CCDC with number 996223.

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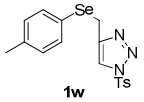

1w

[21] The crystal data of **4a** have been deposited in CCDC with number 1021015.

[22] The crystal data of **7a** have been deposited in CCDC with number 1013188.

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DOI: 10.1039/C4CC08829H

S-containing heterocycles

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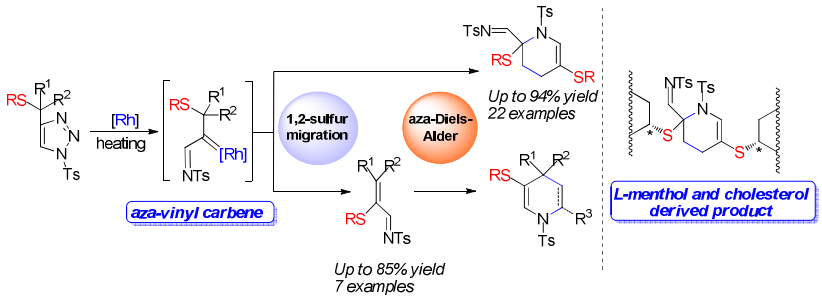

Rh-Catalyzed 1,2-Sulfur Migration/aza-Diels-Alder Cascade Initiated by aza-Vinyl Carbenoids from Sulfur-Tethered N-Sulfonyl-1,2,3-triazoles

A novel Rh(II) catalyzed intramolecular 1,2-sulfur migration/intermolecular aza-Diels-Alder cascade of sulfur-tethered N-sulfonyl-1,2,3-triazoles has been developed, efficiently affording sulfur-containing tetrahydropyridine derivatives.