



## Tetrahedron report 1141

## Transition metal-catalyzed [2,3]-sigmatropic rearrangements of ylides: An update of the most recent advances

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## ABSTRACT

[2,3]-sigmatropic rearrangements of ylides are useful methods for synthesizing functional molecules, especially for these containing heteroatoms. This short report focuses on the most recent advances in transition-metal-catalyzed [2,3]-sigmatropic rearrangements of sulfonium, oxonium, and ammonium ylides.

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## 1. Introduction

[2,3]-Sigmatropic rearrangements of ylides represent one of the fascinating chemical bond reorganizations in organic chemistry,

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and they have been demonstrated wide applications in organic synthesis.<sup>1,2</sup> These reactions typically occur with neutral or charged substrates *via* 6 $\pi$ -electrocyclic transition state and the process includes  $\sigma$ -bond rupture and a new bond formation between two adjacent  $\pi$ -bond (Scheme 1).

The ylides for the [2,3]-sigmatropic rearrangement reactions can be accessed mainly by two methods: 1) the traditional one is the deprotonation of the corresponding salts with base; 2) an alternative method is the reaction of electrophilic metal carbene with nucleophile. The latter has been the focus of research in the past two decades because it is possible to develop catalytic reaction with this strategy. The interaction of the electron-deficient carbenic carbon of the metal carbene intermediate with a pair of non-bonding electrons contributed from a Lewis base (B:) generates a metal complex-associated ylide **1** or a free ylide **2**. In these transformations, the common Lewis bases that are used to form ylides involve ethers, sulfides, amines, etc (Scheme 2). The generated active ylide intermediates further undergo various transformations, typically including [2,3]-sigmatropic rearrangements and 1,2-shifts.

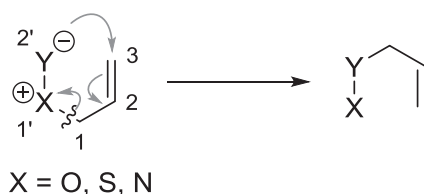
The formation of ylides from metal carbene and Lewis base may occur in either inter- or intramolecular manner, and the subsequent [2,3]-sigmatropic rearrangements make it possible to rapidly access the products with considerable complexity. Besides, [2,3]-sigmatropic rearrangements generally show excellent chemo-, regio-, and stereoselectivities. In the past decades, great efforts have been devoted to this area and significant progresses have been made, which have been summarized in a number of review articles.<sup>3</sup> In this short report we will concisely cover the most recent advances made in the past five years in transition-metal-catalyzed [2,3]-sigmatropic rearrangements of sulfonium, oxonium, and ammonium ylides.

## 2. Transition metal-catalyzed [2,3]-sigmatropic rearrangements of sulfonium ylides

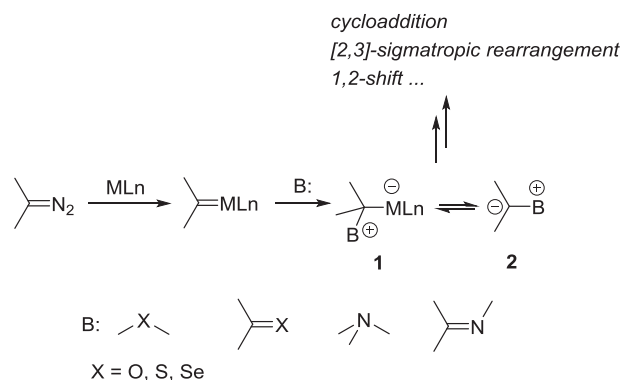
[2,3]-Sigmatropic rearrangement of sulfonium ylides generated from carbene species, known as Doyle-Kirmse reaction, represents one of the unique methods for the construction of C–S bonds. The sulfur ethers applied in this type of reaction include allylic, propargylic and allenic sulfides. This type of rearrangement reactions have been studied in detail, including asymmetric catalysis.<sup>4</sup> The following is the summary of some progresses that have been made in the past few years in this area.

### 2.1. Catalytic sulfur ylide [2,3]-sigmatropic rearrangement with non-diazo precursors

Diazo compounds are the typical precursors for generating metal carbene species in transition-metal-catalyzed reactions. However, the potentially toxic and explosive nature of those compounds limits their wide applications. Usually the stabilized diazo compounds which bear electron-withdrawing substituents, typically  $\alpha$ -diazocarbonyl compounds, are used in catalytic carbene transfer



Scheme 1. [2,3]-Sigmatropic rearrangement of ylide.



Scheme 2. Ylides generated from metal carbene.

reactions. On the contrary, diazo compounds without electron-withdrawing substituents are generally not stable and therefore are not so easy to handle. Their applications in catalytic carbene transfer are thus rather limited. In recent years, the exploration of non-diazo precursors for the generation of metal carbene has been actively pursued,<sup>5</sup> and such strategy has also been applied in the reaction of sulfur ylide [2,3]-sigmatropic rearrangement.

#### 2.1.1. Reactions with *N*-tosylhydrazones and *N*-sulfonyl-1,2,3-triazoles as the carbene precursors

One of the useful surrogate of diazo compounds is the application of *N*-tosylhydrazones, from which non-stabilized diazo compounds can be generated *in situ* by the treatment of base, known as Bamford-Stevens reaction.<sup>6</sup> The *in situ* generated diazo compounds can serve as the metal carbene precursor in transition-metal-catalyzed reactions. Since *N*-tosylhydrazones are easily derived from ketones and aldehydes and they are usually stable crystalline compounds, this strategy has attracted significant attention in recent years.<sup>7</sup> However, its application in sulfonium ylide [2,3]-sigmatropic rearrangement has not been explored previously. Wang and coworkers realized the first application of *N*-tosylhydrazones in Doyle-Kirmse reaction (Scheme 3).<sup>8</sup> In this transformation the diazo substrate is generated *in situ* from *N*-tosylhydrazone **3** in the presence of Cs<sub>2</sub>CO<sub>3</sub>. With this strategy, under the catalysis by Rh<sub>2</sub>(OAc)<sub>4</sub> the *N*-tosylhydrazone reacts with both allyl sulfides **4** and propargyl sulfides **5** to afford the rearrangement products **6** in moderate to good yields through a process involving sulfonium ylide formation/[2,3]-sigmatropic rearrangement.

In addition to *N*-tosylhydrazones, *N*-sulfonyl-1,2,3-triazoles have been recently extensively explored as  $\alpha$ -imino metal carbene precursors in various transition-metal-catalyzed carbene transfer reactions.<sup>9</sup> In 2013, Murakami and co-workers reported a step-economical method for the synthesis of  $\alpha$ -allyl- $\alpha$ -sulfanylimines from terminal alkynes, azides, and allyl sulfides. The one-pot reaction of terminal alkyne, tosyl azide and allyl sulfide with Cu(I) and Rh(II) as catalysts, followed by reduction with LiAlH<sub>4</sub>, provides  $\alpha$ -allyl- $\alpha$ -phenylsulfanylimine in moderate to good yields (Scheme 4).<sup>10</sup> The reaction is initiated Cu(I)-catalyzed by click reaction to generate *N*-sulfonyl-1,2,3-triazole **7**, which is in equilibrium with  $\alpha$ -imino diazo compound **8** upon heating. The diazo compound **8** is decomposed by Rh(II) catalyst to generate  $\alpha$ -imino Rh(II) carbene **9**, which reacts with allyl sulfide to give sulfonium ylide species **10**. Subsequent [2,3]-sigmatropic rearrangement of the sulfur ylide gives the  $\alpha$ -allyl- $\alpha$ -phenylsulfanylimine **11**. Interestingly, when  $\gamma$ -dimethyl allyl sulfide **12** was used, direct S<sub>N</sub>2 reaction occurred in preference to [2,3]-sigmatropic rearrangement to give **13** as the product, presumably because of the steric hindrance.

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