

Exploitation of the Chemistry of Magnesium Carbenoids and Related Reactive Species

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Synthetic organic chemistry is a base of medicinal chemistry and the exploitation of new methods for carbon-carbon bond formation is of most importance in synthetic organic chemistry. Carbenes **1** and carbenoids **2** have long been known to be highly reactive carbon species that show a variety of unique reactivity. However, those reactive species are not fully used in organic synthesis. The reasons are as follows: one is the precursors for the generation of carbenes and carbenoids are quite limited and the other is that the reactivity of the species is too high to control.

In order to solve the problem mentioned above, we used α -haloalkyl (or alkenyl) aryl sulfoxides **3** as the precursors and used sulfoxide-magnesium exchange reaction for generation of much mild magnesium carbenoids. α -Haloalkyl (or alkenyl) aryl sulfoxides **3** are quite easily synthesized in high overall yields. Magnesium carbenoid **4**, cyclopropylmagnesium carbenoid **5**, cyclobutylmagnesium carbenoid **6**, magnesium β -oxido carbenoid **7**, and magnesium alkyldiene carbenoid **8** are generated at low temperature from the corresponding sulfoxides with Grignard reagent in quantitative yields. They were found to be stable usually at below $-60\text{ }^\circ\text{C}$ for at least 30 min. The each magnesium carbenoids have their own unique reactivity and we could found many unprecedented reactions from these reactive species. For example, the reaction of magnesium alkyldiene carbenoid **8** with *N*-lithio arylamines resulted in the formation of *o*-alkenylated arylamines **11**. The reaction of **8** with 2-lithiofurans and 2-lithiothiophenes gave alkenylmagnesium intermediates **12**, which were trapped with electrophiles to afford fully substituted olefins **13** in good yields. The chemistry of oxiranyl anions **9** and aziridinyl anions **10** is developed by using the sulfoxide-metal exchange reaction.

