

Ring Expansion Reaction of 2-Alkenyl-Substituted Sulfonium Ylides

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In this study, we focused on a ring expansion reaction of cyclic sulfonium ylides formed by metal-catalyzed ylide formation of 2-alkenyl-1,3-dithiolanes **1** with diazo compounds because the generated ylide bearing an alkenyl moiety could undergo various rearrangements. Therefore, we investigated the substituent effect of the alkenyl group and diazo compounds for this ring expansion reaction to clarify the reaction mechanism.

First, we examined Rh₂(OAc)₄-catalyzed decomposition reaction of dimethyl diazomalonate (**2**) in the presence of 2-(*E*)-propenyl-1,3-dithiolane (**1a**). This reaction could proceed through dual rearrangement manners *via* the ylide **I**: [1,2] and [2,3] rearrangements (Scheme 1). In this case, [2,3] product **4a** was obtained in 48% yield as a major product along with a small amount of [1,2] product **3a**. On the other hand, when 2-(*E*)-styryl-1,3-dithiolane (**1b**) was treated, not only [2,3] product **4b** but also [1,2] product **3b** was obtained (**4b** : 47%, **3b** : 35%). Furthermore, we tried using vinyl diazo compounds **5** for this reaction because the generated ylides **II** could undergo [1,4] and/or [3,4] rearrangements in addition to [1,2] and [2,3] rearrangements (Chart 1). As a result, we revealed that a variety of rearrangements of the generated ylides **II** were controlled by varying substituents on a β -position of the alkenyl group and vinyl diazo compounds **5**. In addition, it was found that the substituent on **1** preferentially affected the reaction pathway.

