

BASE-CATALYZED ISOMERIZATION OF DIENYL ALKYL ETHERS AND DIENOLS: DFT STUDIES

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Recently, our group has developed a protocol for the metal-free isomerization of allylic alcohols and ethers using a simple bicyclic guanidine base as catalyst [1]. The group has extended this protocol to dienyl alkyl ethers and dienols (Figure 1). These unsaturated enols and ethers are prevalent moieties in numerous natural products and pharmaceuticals [2].

For a better understanding of the reaction mechanism, we have investigated the reaction pathways with DFT calculations. Our calculations revealed that the reaction proceeds via stepwise mechanism with an ion pair as common intermediate. Kinetic simulations were also performed to predict the product ratio, which is nearly identical to experimental ratio [3].

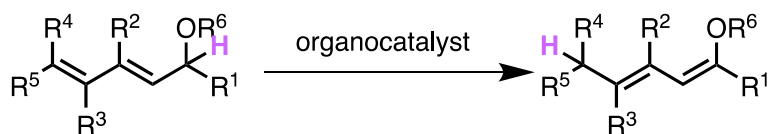


Figure 1. Base-catalyzed isomerization of dienyl alkyl ether and dienols.

[1] Martinez-Erro, S.; Sanz-Marco, A.; Gómez A. B.; Vázquez-Romero, A.; Ahlquist, M. S. G.; Martín-Matute, B. *J. Am. Chem. Soc.* **2016**, 138, 13408.

[2] Brandt, D.; Bellosta, V.; Cossy, J.; *Org. Lett.* **2012**, 14, 5594-5597

[3] Manuscript in preparation.