

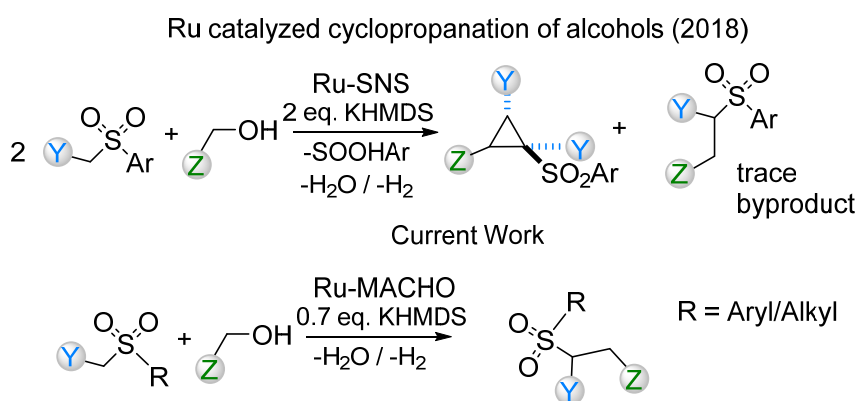
CYCLOPROPANATION OF ALIPHATIC ESTERS AND ALCOHOLS EXTENDED TO ONE-STEP CATALYTIC LINEAR SULFONE

Tomas Vojkovsky, Eugene Khaskin

Okinawa Institute of Science and Technology Graduate University, Onna, Japan

We recently reported a novel cyclopropanation reaction catalyzed by Ru(II) complexes where aliphatic alcohols and esters could be transformed to cyclopropanes upon a 1:2 reaction with sulfones [1]. The products were formed in high diastereoselectivity and yields, containing three new stereocenters and a quaternary carbon.

A side product formed during the reaction was a linear sulfone made from a 1:1 coupling of the alcohol and sulfone. We have determined the conditions to form the linear sulfone products exclusively in high yields, leading to easy access to a large library of diverse linear sulfones from cheap starting materials. A number of primary and secondary alpha carbon sulfones were found to participate in the reaction. Linear alkyl sulfones that can be synthesized from readily available phenyl methyl sulfone and dimethyl sulfone are useful value-added products. The reaction proceeds with a sub-stoichiometric amount of base, with the only byproducts being hydrogen gas and water. Preliminary mechanistic studies indicate that the catalyst is involved not only in the dehydrogenation of the alcohol, but also the dehydration of the intermediate, which occurs under milder conditions with the appropriate Ru(II) catalyst to preempt cyclopropane formation.



Scheme 1. Previously reported cyclopropanation and current results

[1] Jankins, T.C.; Fayzullin, R.R.; Khaskin, E. Three-Component [1+1+1] Cyclopropanation with Ruthenium(II), *Organometallics*, 2018, 37, 2609-2617.