

Problem Set No. 10 (28.1.2013)

1. Olefin metathesis:

a) Treat cinnamaldehyde with an excess of allyl alcohol (cat. amount acid) and treat the resulting acetal with Grubbs-II catalyst. What are the possible products formed by RCM?

b) Treat 4-methyl-4-pentenal with vinyl magnesium bromide and work up with water. What is the product after treatment with Grubbs-I catalyst? Why are Schrock type catalysts not suitable for this transformation?

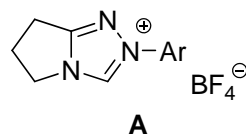
c) What are the possible products of CM of allyl(trimethyl)silane with allyl acetate employing Grubbs-I catalyst? If you treat the product derived from two different olefins with trifluoroacetic acid you will obtain a desilylated compound. Propose a mechanism for this step!

2. a) Give an example for an intermolecular ene-yne metathesis process and treat the resulting 1,3-diene thermally with maleinic acid anhydride to give the Diels-Alder product !

b) What is the product if 3-methyloct-1-en-7-yne is treated with Grubbs-I catalyst?

3. a) Give examples of N-heterocyclic carbenes with imidazoline, imidazol, thiazol, 1,2,4-triazol moieties as heterocyclic core. Draw the structure of a carbene dimer for a less stabized system!

b) Supplement the following equation involving a NHC-catalyst!



(Y. Takemoto et al. Beilstein J. Org. Chem. 2012, 8, 1499)

Suggest a mechanism for the transformation! What is the Breslow intermediate for this process?