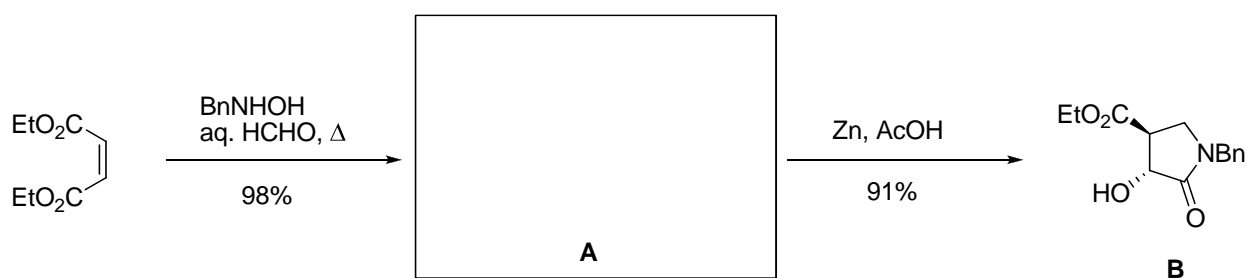


Problem Set No. 13/14 (11.2.2013)

1. Write the reaction mechanisms of the formation of benzonitrileoxide starting from benzaldehyde (Huisgen method) and react the 1,3-dipole with styrene! How many isomers (regioisomers and stereoisomers) are possible? Why can the resulting isoxazole derivatives be regarded as equivalents of an aldol addition product?

2. In the following sequence the first step involves a 1,3-dipolar cycloaddition forming the intermediate heterocycle **A**. Describe the formation of the intermediate 1,3-dipole in detail! What is the name of this type of 1,3-dipole? Also provide a mechanistic explanation for the formation of the final product **B** (only relative configuration given)!



3. The 1,3-dipolar cycloaddition of dimethyl diazomalonate with 1-(diethylamino)propyne provides a cycloadduct with excellent regioselectivity. Draw the equation and try to explain the regioselectivity with the frontier orbital model (orbital coefficient of the diazomalonate are qualitatively the same as those for diazoacetate). Why is the reaction faster than the reaction of this alkyne with methyl diazoacetate?

4. The thermal $\text{Rh}(\text{OAc})_4$ -catalyzed reaction of diallyl diazomalonate with benzophenone can afford a product via intramolecular 1,3-dipolar cycloaddition. Write down this reaction sequence. What are the names for the crucial intermediates? How many stereoisomers are possible?

5. Suggest an example for a [2+2] cycloaddition involving a 1,4-zwitterion leading to a cyclobutane.

6. Propose a mechanism for the copper(I)-catalyzed cycloaddition of benzylazide with methylpropargylether!

7. Propose a mechanism for the conversion of benzaldehyde into phenylacetylene with $\text{CH}_3\text{CO-CN}_2\text{-PO(OMe)}_2$ in the presence of K_2CO_3 /methanol (Bestmann-Ohira reaction).

8. Prepare the corresponding alkyl azide either starting from (*S*)-2-bromopentane or (*S*)-2-aminopentane! Give the required reagents and consider the stereochemistry of these transformations!