

**Problem Set No. 9 (10.7.2012)**

1. a) Which stereoisomer do you expect when 2,2-dimethylhexan-3-one is deprotonated with LDA and subsequently silylated with  $\text{ClSiMe}_3$ . Explain the observed selectivity!

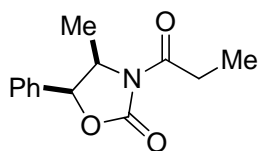
b) What will be the major product in the  $\text{BF}_3$ -promoted addition of benzaldehyde to this silyl enol ether? Draw the transition state of this reaction!

2. a) React lithium dimethylcuprate with (*S*)-4-methyl-2-cyclopenten-1-one and trap the intermediate with benzyl bromide. Which diastereomer do you expect to be formed in excess?

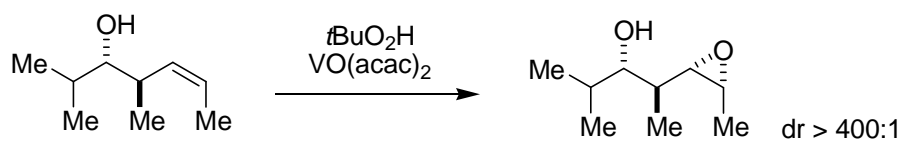
b) How is the cuprate generated?

3. The baker's yeast reduction of 3-oxobutanoic acid ethyl ester (= ethyl acetylacetoacetate) provides a secondary alcohol with good enantioselectivity. After treatment with 2 equivalents of LDA and subsequent quench with allyl bromide, the resulting product is again treated with 2 equivalents of LDA and then with methyl iodide. Which product do you expect?

4. The amide bearing an Evans auxiliary shown below can successfully be used to approach enantio-enriched  $\alpha$ -amino acid or  $\alpha$ -hydroxy carboxylic acid derivatives. Describe two sequences where the amino group is stereoselectively introduced either by electrophilic amination or by nucleophilic amination! Also suggest a sequence for an electrophilic hydroxylation of this amide!



5. Explain the observed very high selectivity in the following epoxidation reaction by providing the 3D structure of the transition state including all relevant interactions.



6. Employing L-DET as ligand the Sharpless epoxidation of 3-hydroxy-1,4-pentadiene provides an enantio-enriched product in high yield. The product undergoes a regioselective ring opening by treatment with sodium azide. Suggest a method to convert the resulting azide into an amine without reducing the remaining vinyl group (key word: Staudinger reaction!).