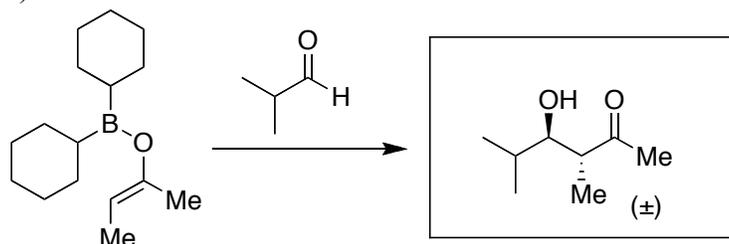


Problem set 5
Chapter 34.

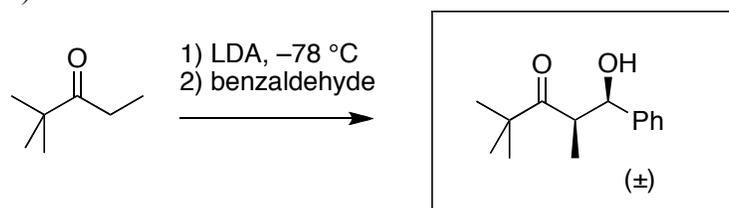
1. Fill in the boxes with the reagents required to produce the stereoisomer shown, or with the MAJOR stereoisomer produced by the reaction conditions given. For **all structures**, indicate whether the structure is achiral, a single enantiomer, or racemic.

a)



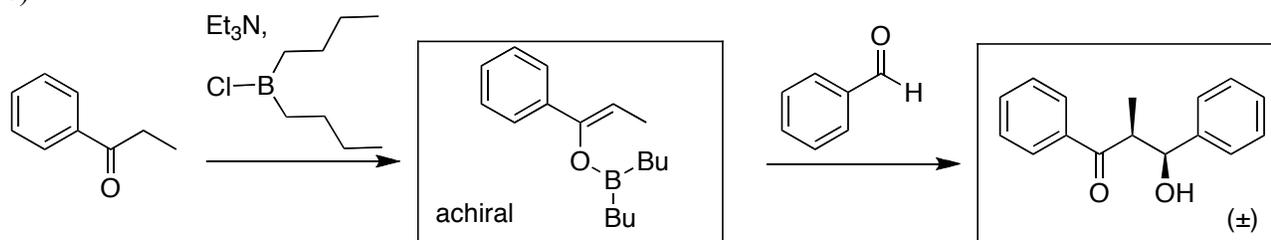
this pre-formed boron enolate has trans stereochemistry, thus the anti aldol product

b)



bulky t-butyl group favours formation of a cis-enolate, thus the syn aldol product

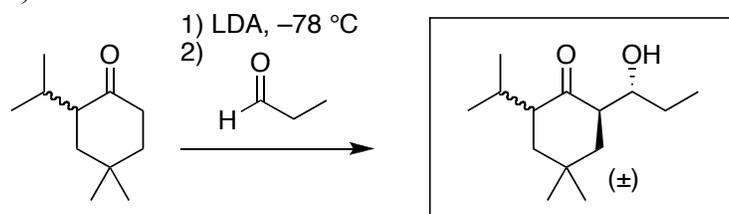
c)



boron enolate formation: cis enolate because of large phenyl group...

... gives you a syn aldol...

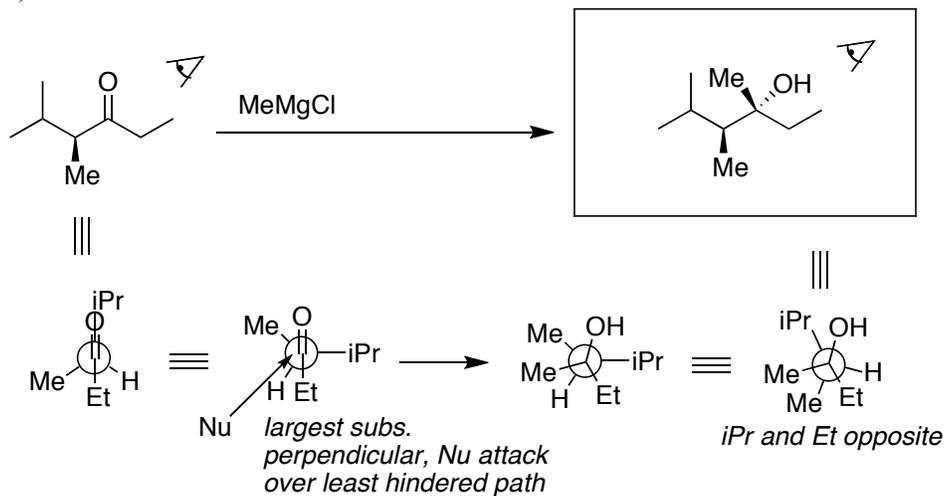
d)



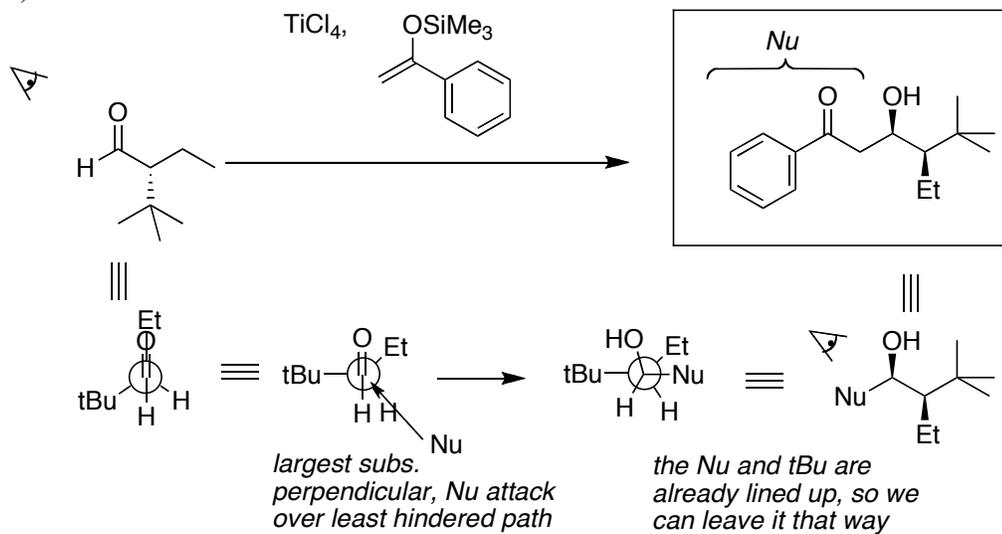
kinetic deprotonation and trans enolate formation... must make an anti aldol product

2. Give the product of the following reactions. Explain the origin of the observed stereoselectivity in one short phrase, and draw 3D stereochemical diagrams of **starting materials and products** to illustrate your point.

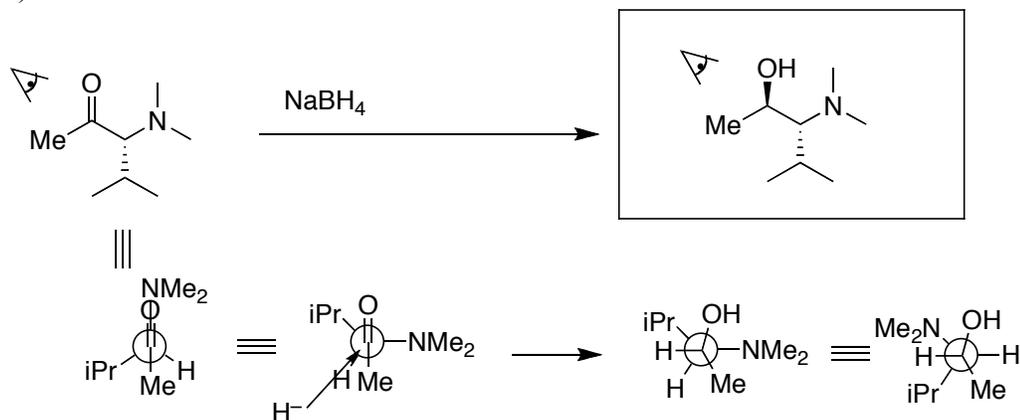
a)



b)



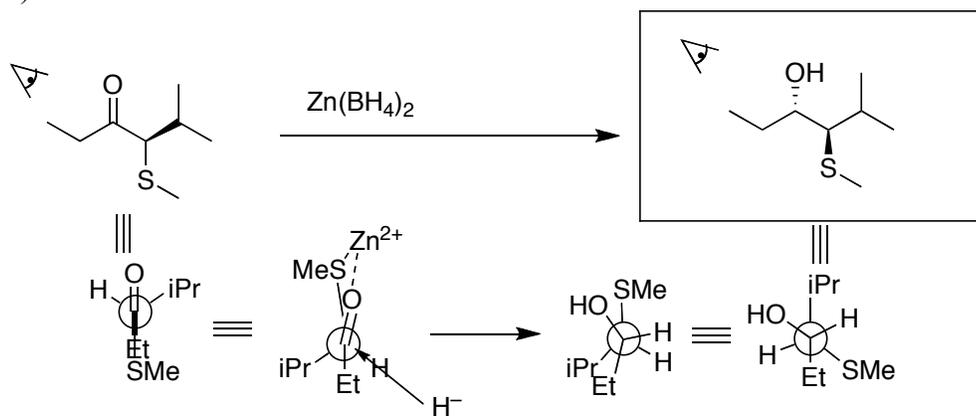
c)



electron-withdrawing NMe₂ group perpendicular, Nu attack over least hindered path

I chose to put the NMe₂ back in the plane of the paper... there are lots of ways to draw the right product, but it's often easiest to put the starting material back in the orientation it started in.

d)

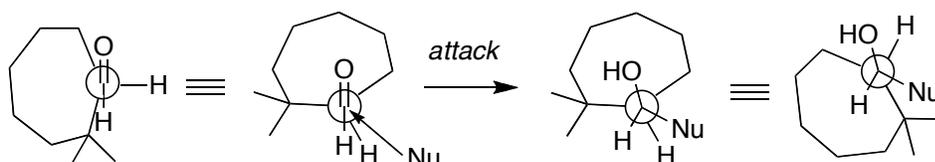
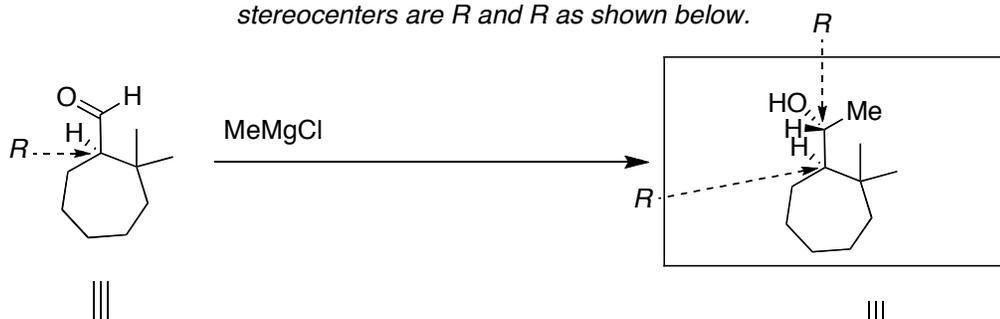


C=O and SMe chelate Zn²⁺

rearrange to help the re-draw

e)

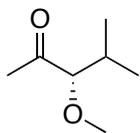
There are many ways to draw this product. To compare your answer to the correct answer below, make sure that the stereocenters are R and R as shown below.



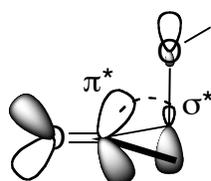
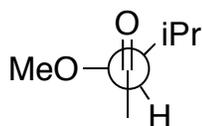
rotate so largest subs. is perpendicular — that's the quaternary carbon centre on the ring

rotate to make re-drawing easier

3. In what conformation is the compound below attacked by a nucleophile? Use orbital diagrams and text to clearly indicate WHY this is the most reactive conformation.



This compound will adopt a conformation with its electron-withdrawing OMe group perpendicular to the plane of the carbonyl, as shown below left. In this conformation, the low-energy σ^* orbital of the α -carbon—O bond is aligned with the π^* orbital of the carbonyl (see below, right). The conjugation between these two orbitals lowers the energy of the π^* orbital and makes it easier for a nucleophile to attack.



$s^* - p^*$ conjugation when C—OMe is perpendicular to C=O