

CHEM 330

Exam 2

November 16, 2011

ANSWERS

Your name: _____

This document has 7 pages

This a closed-notes, closed-book exam

The use of molecular models is allowed

Time: 1.5 h

1. _____ / 10

2. _____ / 15

3. _____ / 15

4. _____ / 20

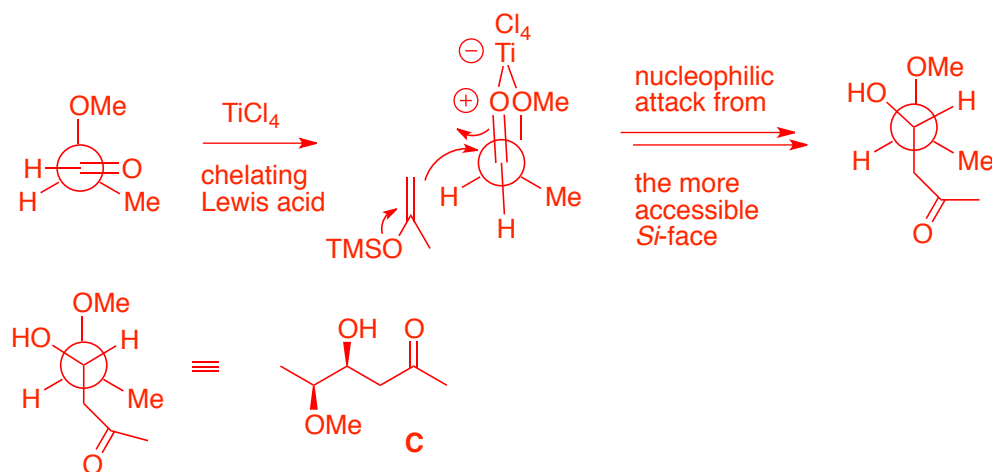
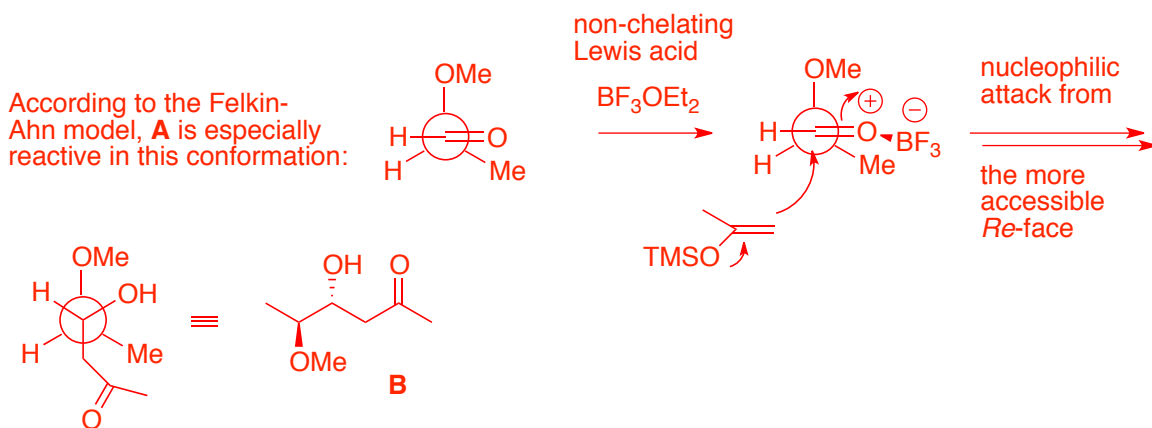
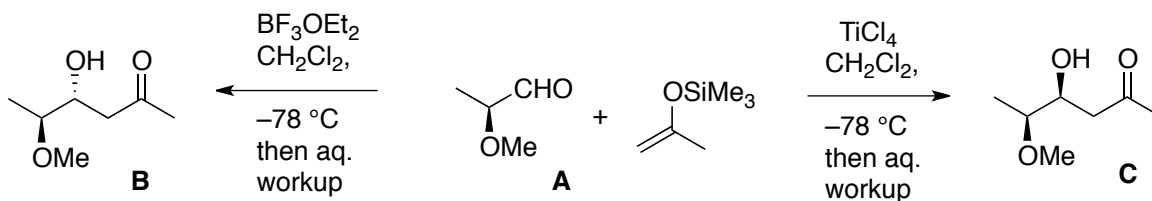
5. _____ / 20

6. _____ / 20

TOTAL _____ / 100

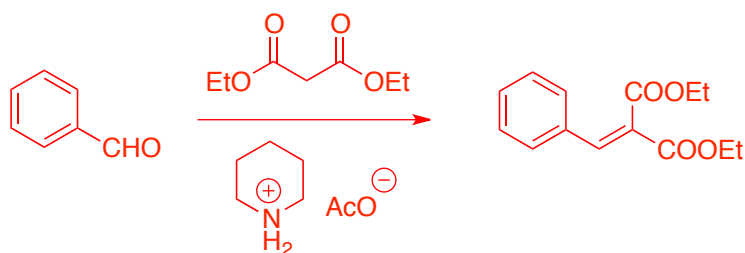
This exam counts for 25% of your CHEM 330 final grade

1. (10 pts.) Provide a rationale for the observation that the Mukaiyama aldol reaction of the silyl enol ether of acetone with aldehyde **A** selectively furnishes compound **B** when BF_3OEt_2 is used as the catalyst, but compound **C** when TiCl_4 is employed instead. Include a sketch of approximate transition state structures to account for such a diastereoselectivity.

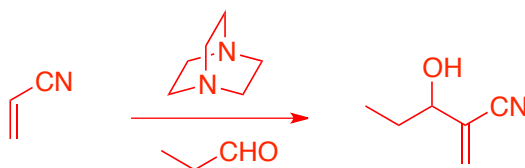


2. (15 pts.) Write a chemical equation to show an example of the following reactions (**do not** write mechanisms – just the reactions).

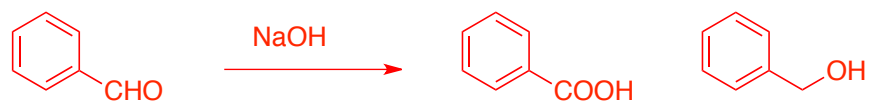
a. Knoevenagel reaction:



b. Baylis-Hillman reaction:

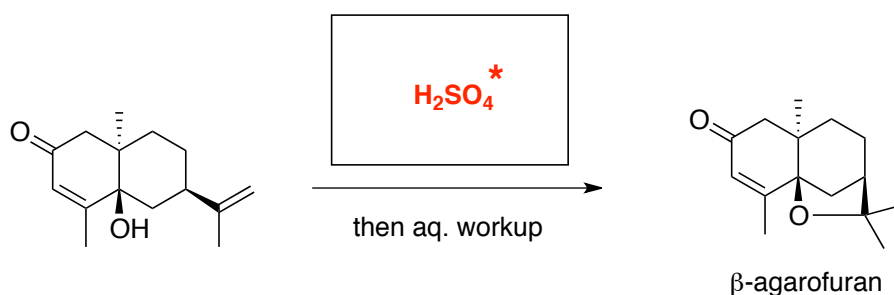
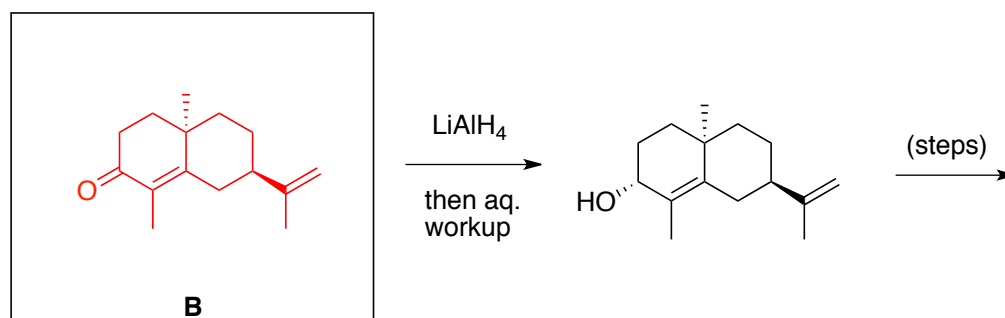
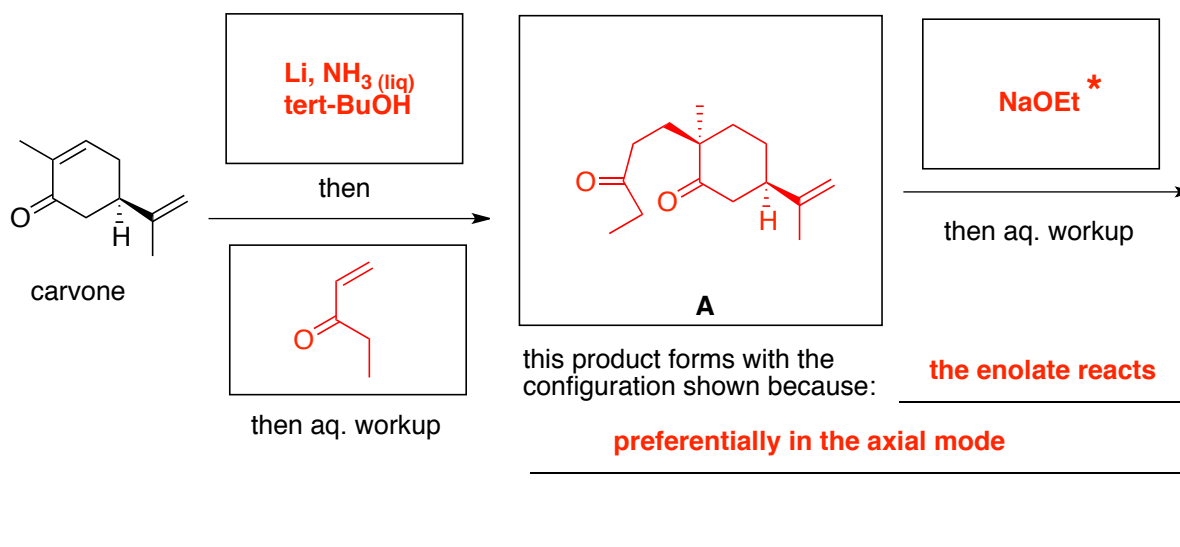


c. Cannizzaro reaction:



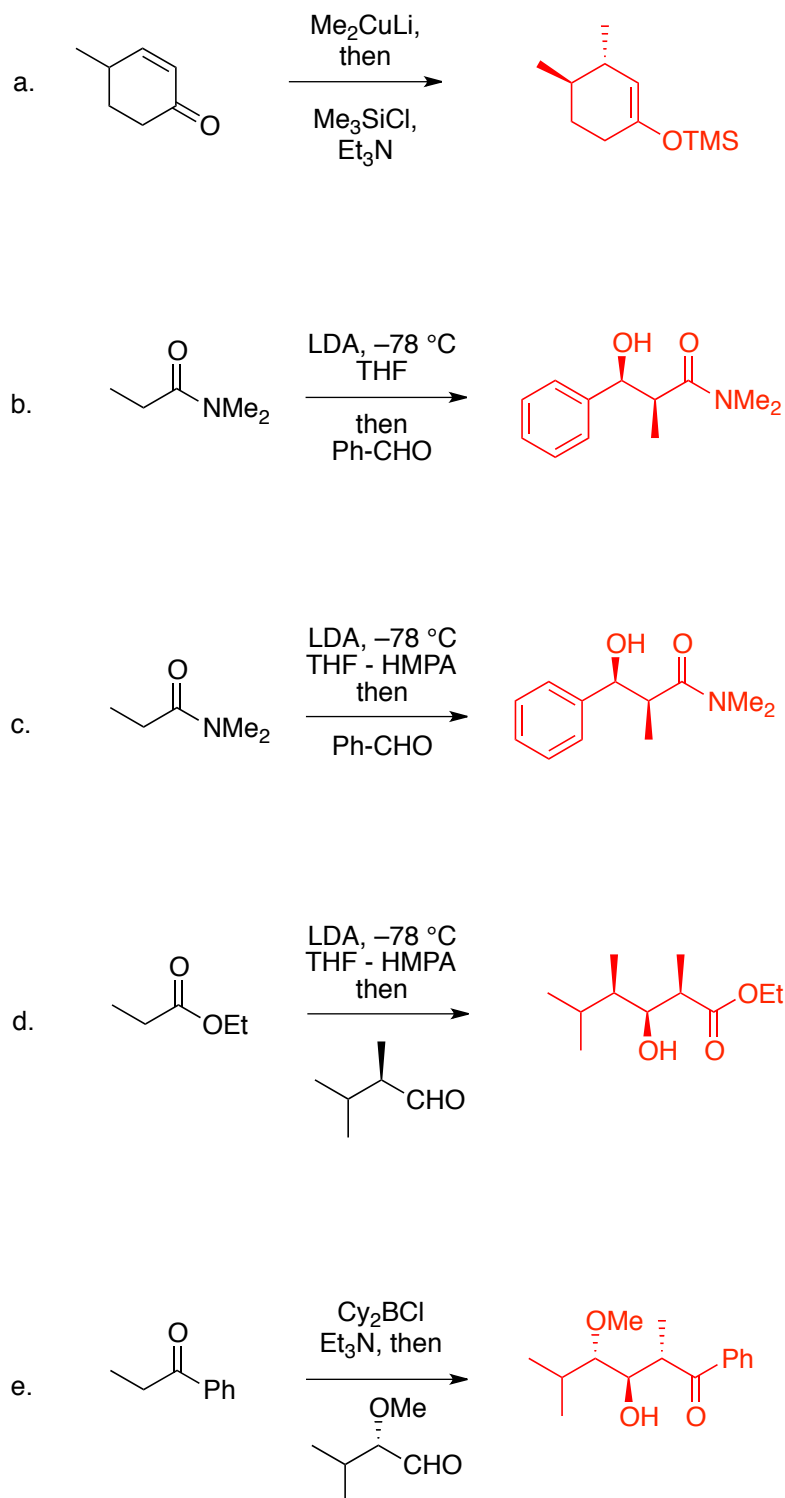
(alternative substrates / reagents may be acceptable)

3. (15 pts.) A synthesis of the natural product, β -agarofuran, started with another readily available natural substance, carvone, and proceeded according to the diagram outlined below (cf. Büchi, G., *et al.*, *J. Am. Chem. Soc.* **1967**, 89, 5665). Complete this scheme by writing the structures of products **A** and **B** (**with the correct relative configuration**) and all missing reagents and the in the corresponding boxes, and by briefly accounting for the stereochemical outcome of the first sequence of reactions. **It is not necessary to write mechanisms.**



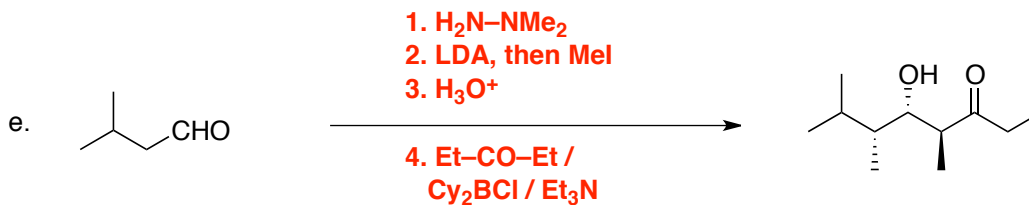
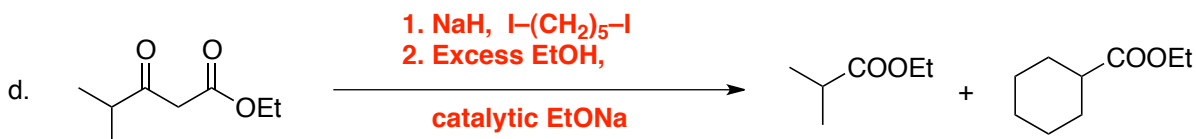
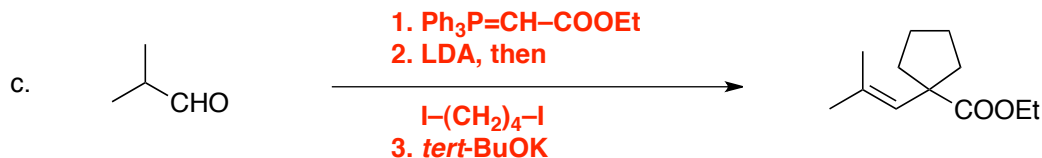
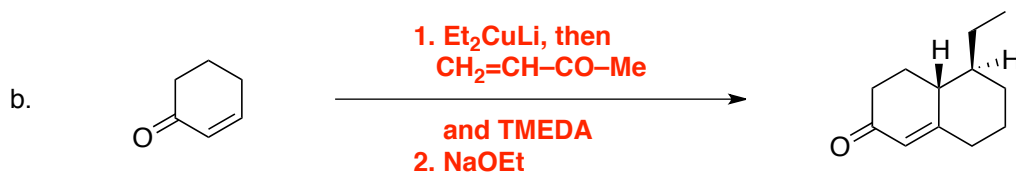
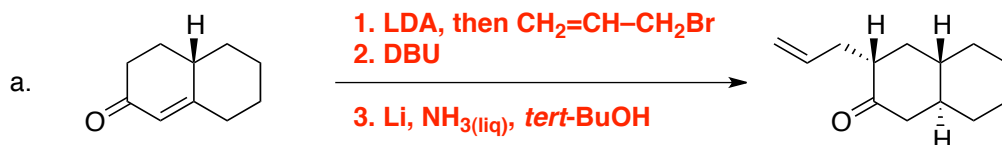
* alternative reagents may be acceptable

4. (20 pts.) Predict the structure of the major product expected from the following reactions. Configurations must be clearly shown for products incorporating multiple stereogenic centers. **It is not necessary to draw mechanisms.** Also, aqueous workups are understood



5. (20 pts.) Complete the following equations by indicating all the reagents that are necessary to effect the transformations shown. Provide your answers as a numbered list of reagents, in the correct order, written over/under the reaction arrows.

Note: aqueous workups are understood and are not to be included in your answers.



(alternative answers may be acceptable)

6. (20 pts.) Propose a method to accomplish the transformations shown below. In each case, a multistep sequence (= not just one reaction, but several) may be necessary. Assume the availability of all required reagents (e.g., bases, alkyl halides, etc.). Present your answer as a flowchart that clearly shows all intermediate products.

Note: **It is not necessary to draw mechanisms.**

