

**CHEM 330**

**Exam 2**

November 16, 2011

**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

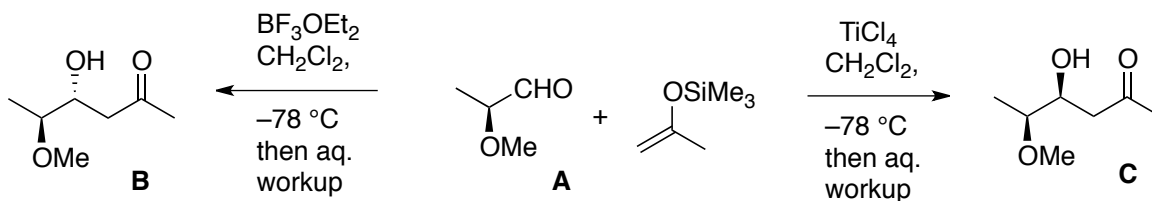
5. \_\_\_\_\_ / 20

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  $\text{BF}_3\text{OEt}_2$  is used as the catalyst, but compound **C** when  $\text{TiCl}_4$  is employed instead. Include a sketch of approximate transition state structures to account for such a diastereoselectivity.



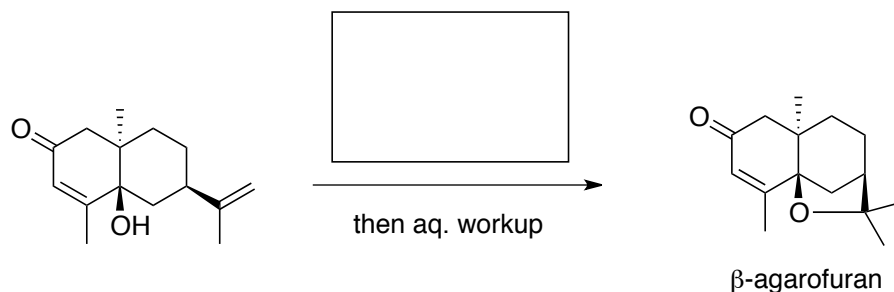
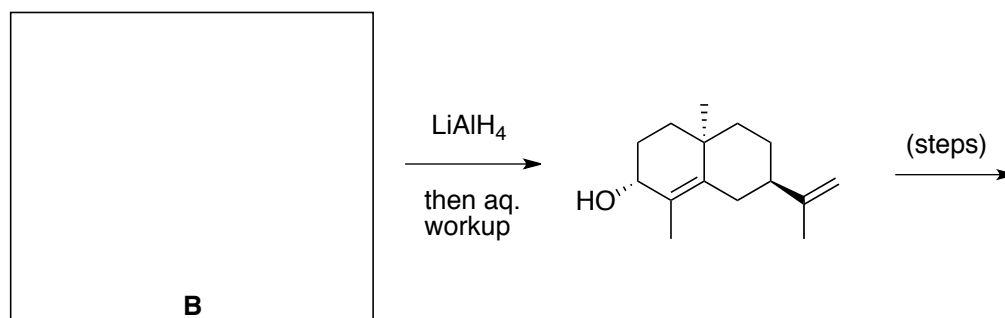
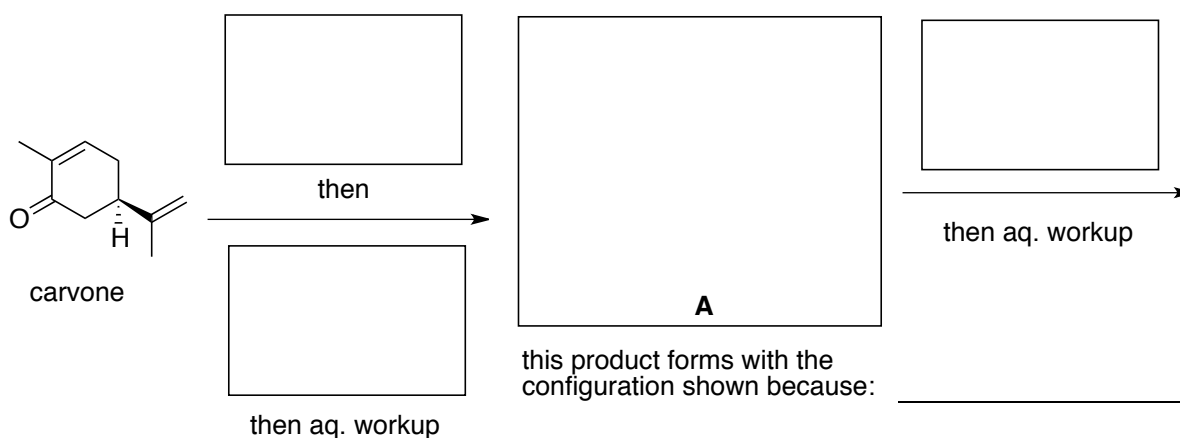
2. (15 pts.) Write a chemical equation to show an example of the following reactions (**do not** write mechanisms – just the reactions).

a. Knoevenagel reaction:

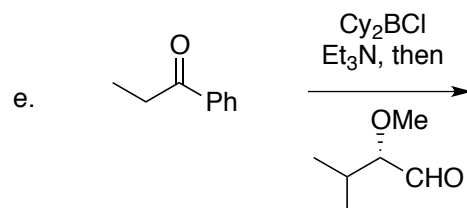
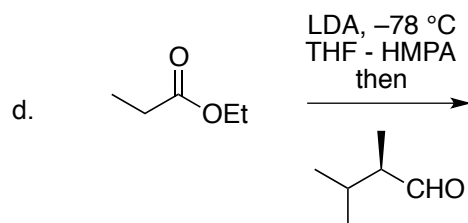
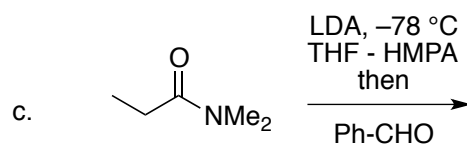
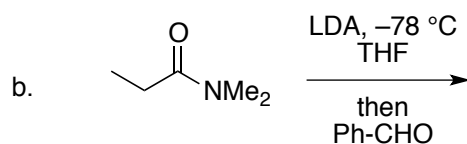
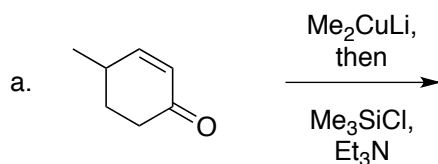
b. Baylis-Hillman reaction:

c. Cannizzaro reaction:

3. (15 pts.) A synthesis of the natural product,  $\beta$ -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.**



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.



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.**

