

CHEMISTRY 314-02
MIDTERM # 2 – answer key
March 08, 2005

Statistics:

- Average: 70 pts (70%);
- Highest: 98 pts (98%); Lowest: 35 pts (35%)
- Number of students performing at or above average: 24 (53%)

1. (7 pts) Mark as true (T) or false (F) the following statements. Do not explain!

- (F) Thiols are less acidic than alcohols;
- (T) Ethers are *Lewis* bases;
- (F) Ethers are hydrogen bond donors;
- (T) Acid-catalyzed ring opening of epoxides leads to attachment of the nucleophile to the more substituted carbon;
- (F) Acetals are formed only in the presence of base catalyst;
- (T) Acetals are stable in the presence of strong bases;
- (F) Ketones are more reactive than aldehydes towards nucleophiles;

2. Circle ALL that apply:

A. (3 pts) Thiols can be oxidized to:

- a. Sulfoxides;
- b. Sulfenic acids;
- c. Disulfides;
- d. Sulfones;

B. (3 pts) The following reagents are used to convert alcohol to aldehyde:

- a. PDC;
- b. MCPBA;
- c. *Simmons-Smith* reagent;
- d. THF;

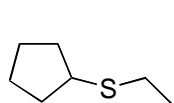
C. (3 pts) The following MS fragmentations are typical for carbonyl compounds:

- a. Elimination of water;
- b. The *McLafferty* rearrangement;
- c. α -cleavage;
- d. E2 elimination;

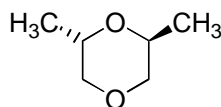
D. (3 pts) The carbonyl group IS NOT reduced to a methylene group in the following reactions:

- a. *Clemmensen* reduction;
- b. Reduction with NaBH_4 ;
- c. Catalytic hydrogenation;
- d. *Wolff-Kishner* reduction;

3. (5 pts) Provide an acceptable name for each of the following compounds. Write clearly and intelligibly.



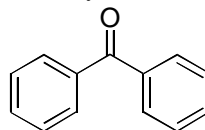
ethylthiocyclopentane or
cyclopentyl ethyl sulfide



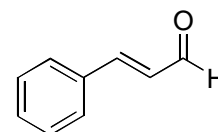
trans-2,6-dimethyl-1,4-dioxane



1,2-epoxycyclobutane

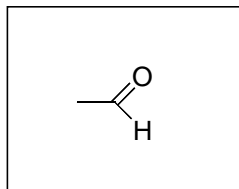


benzophenone

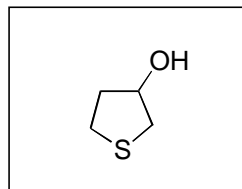


3-phenylpropenal

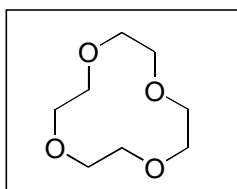
4. (5 pts) Provide the correct structure, matching each of the following names:



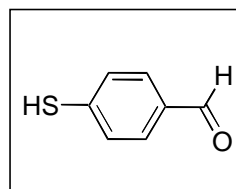
acetaldehyde



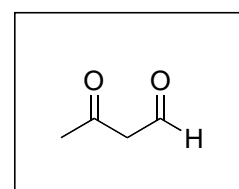
3-hydroxythiolane



12-crown-4



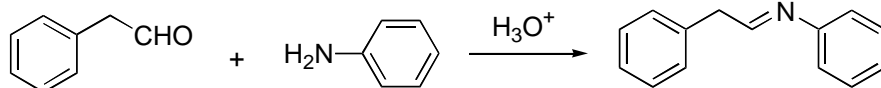
4-mercaptobenzaldehyde



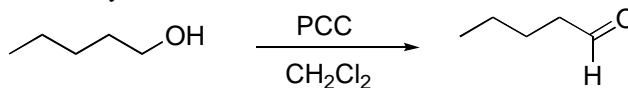
3-oxobutanal

5. Write and complete a chemical equation for each of the following reactions. Do not write mechanisms!

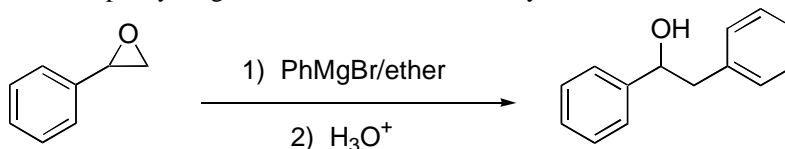
A. (3 pts) Phenylacetaldehyde + aniline, in the presence of acid;



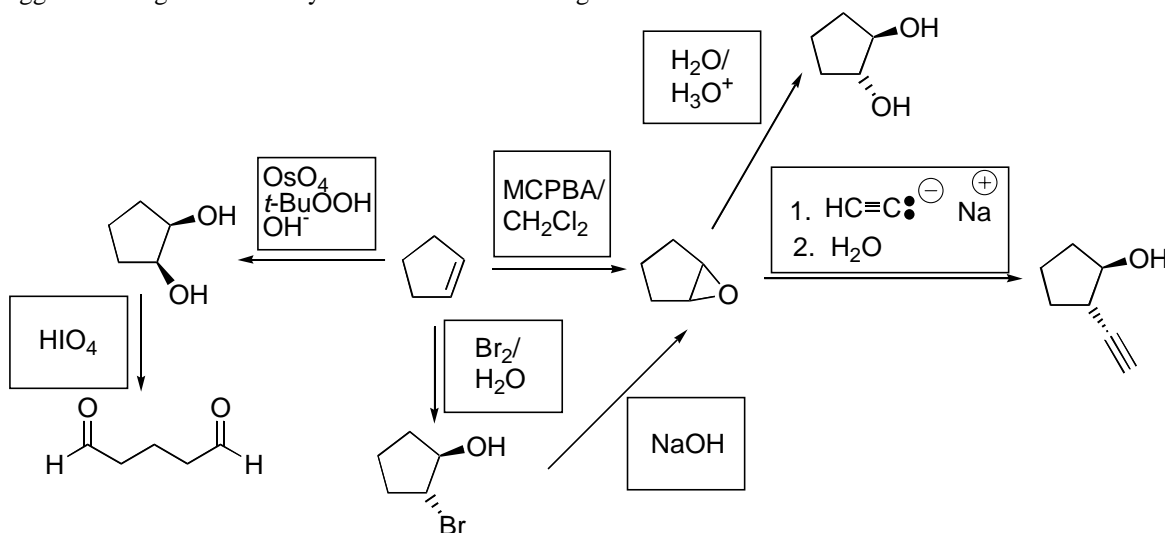
B. (3 pts) 1-Pentanol + PCC, in methylene chloride;



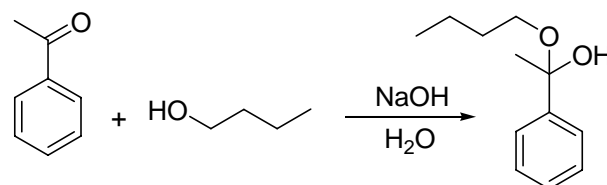
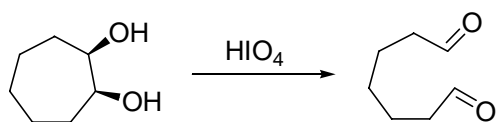
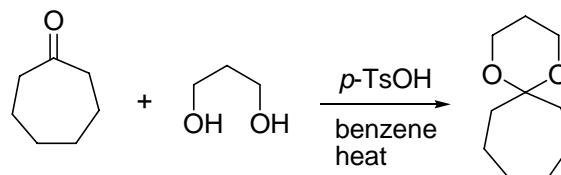
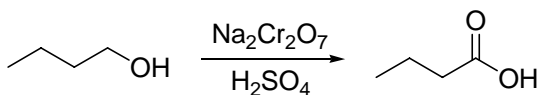
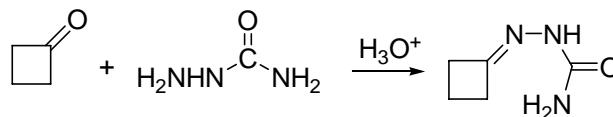
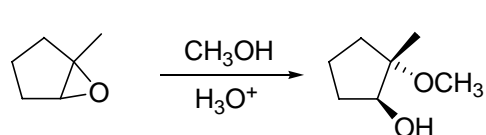
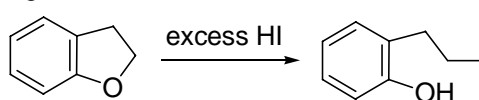
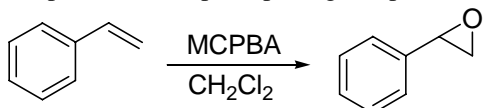
C. (3 pts) 2-Phenylloxirane + phenylmagnesium bromide, followed by acid;

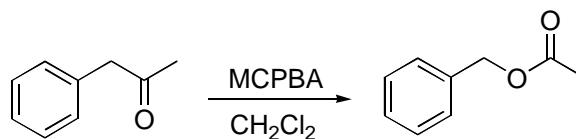
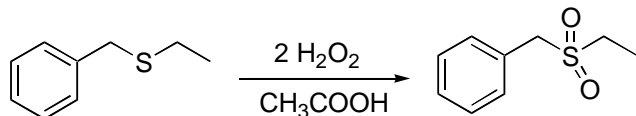
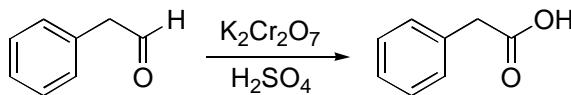
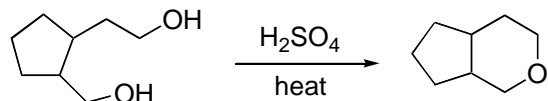
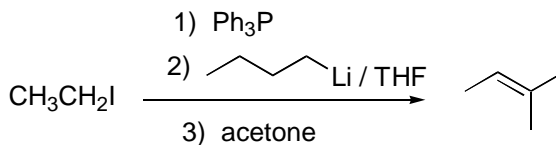
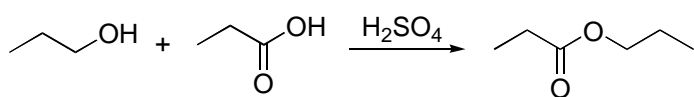
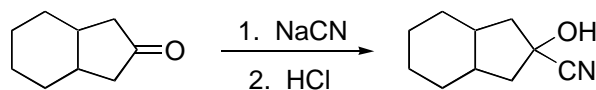
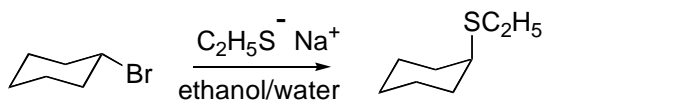


6. (8 pts) Suggest the reagents necessary to conduct the following transformations:

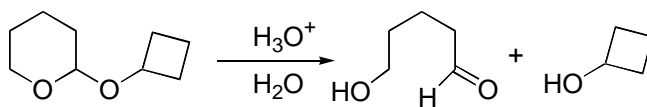
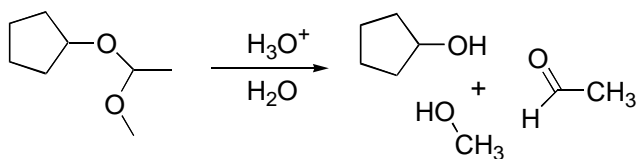


7. (20 pts) Write the principal organic product of each of the following reactions:



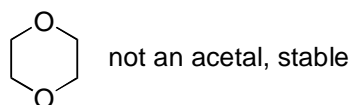
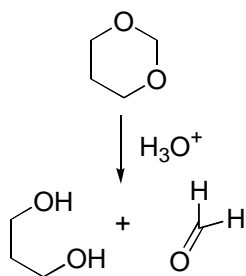


8. (5 pts) Indicate the correct products of acid hydrolysis of the following compounds:

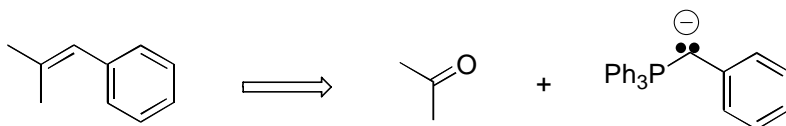


9. (5 pts) Two isomers of dioxane are given below. One of them quickly undergoes acid hydrolysis while the other is stable. Which isomer is prone to hydrolyze? Offer a brief structural rationalization (More structures, fewer words!!).

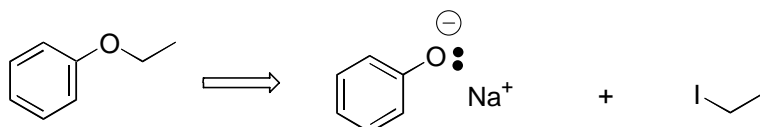
acetal, quickly hydrolyzes in acid



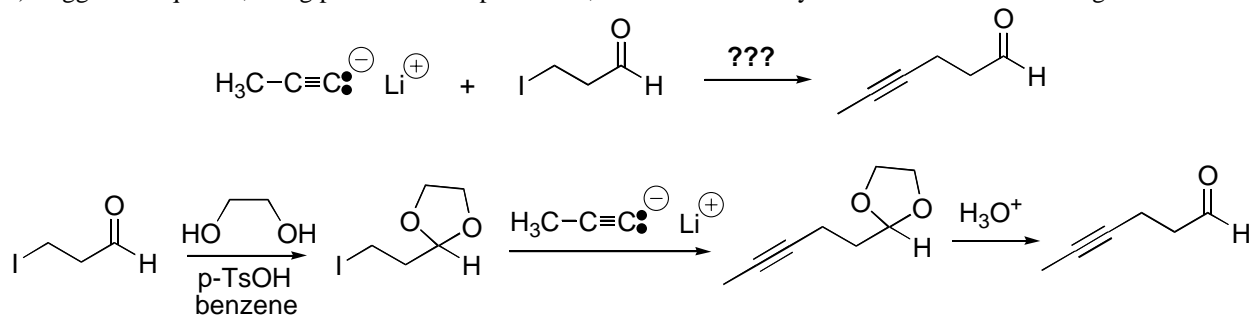
10. (2 pts) Suggest the most appropriate set of starting materials for the preparation of the following compound *via* the Wittig reaction.



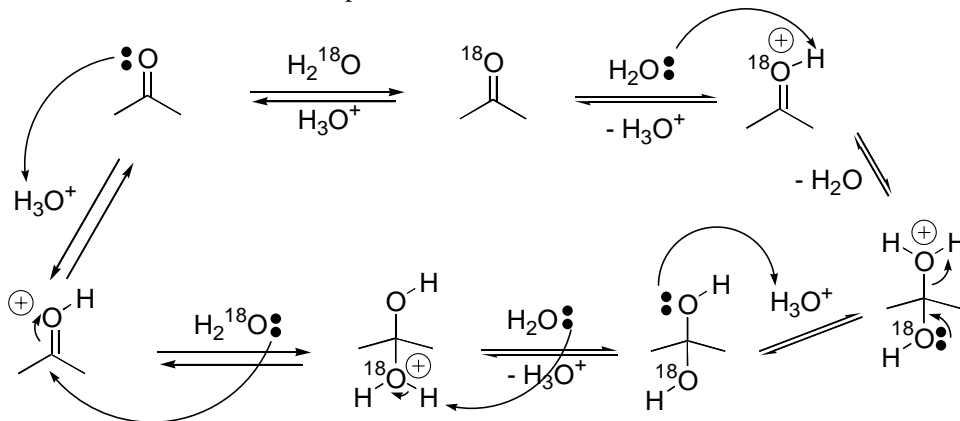
11. (2 pts) Suggest the most appropriate set of starting materials for the preparation of the following compound *via* the Williamson ether synthesis.



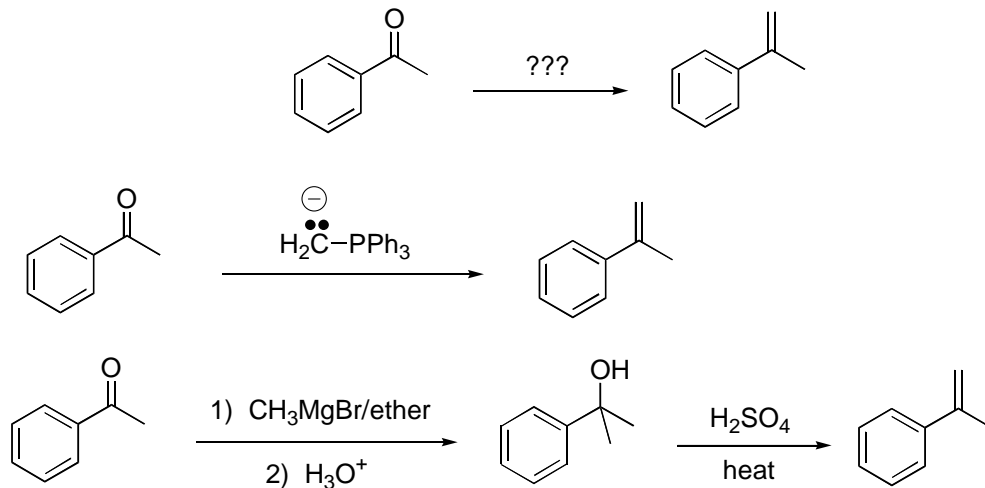
12. (5 pts) Suggest a sequence, using protection – deprotection, that would enable you to conduct the following transformation:



13. (5 pts) The following experiment was performed: Acetone was dissolved in water that contained a different isotope of oxygen (^{18}O), in the presence of small amount of acid. As a result, incorporation of the ^{18}O was observed in the carbonyl group. Suggest a detailed mechanism that would account for this phenomenon.

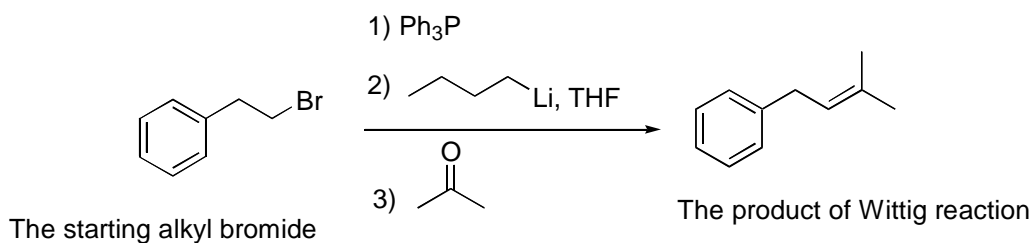


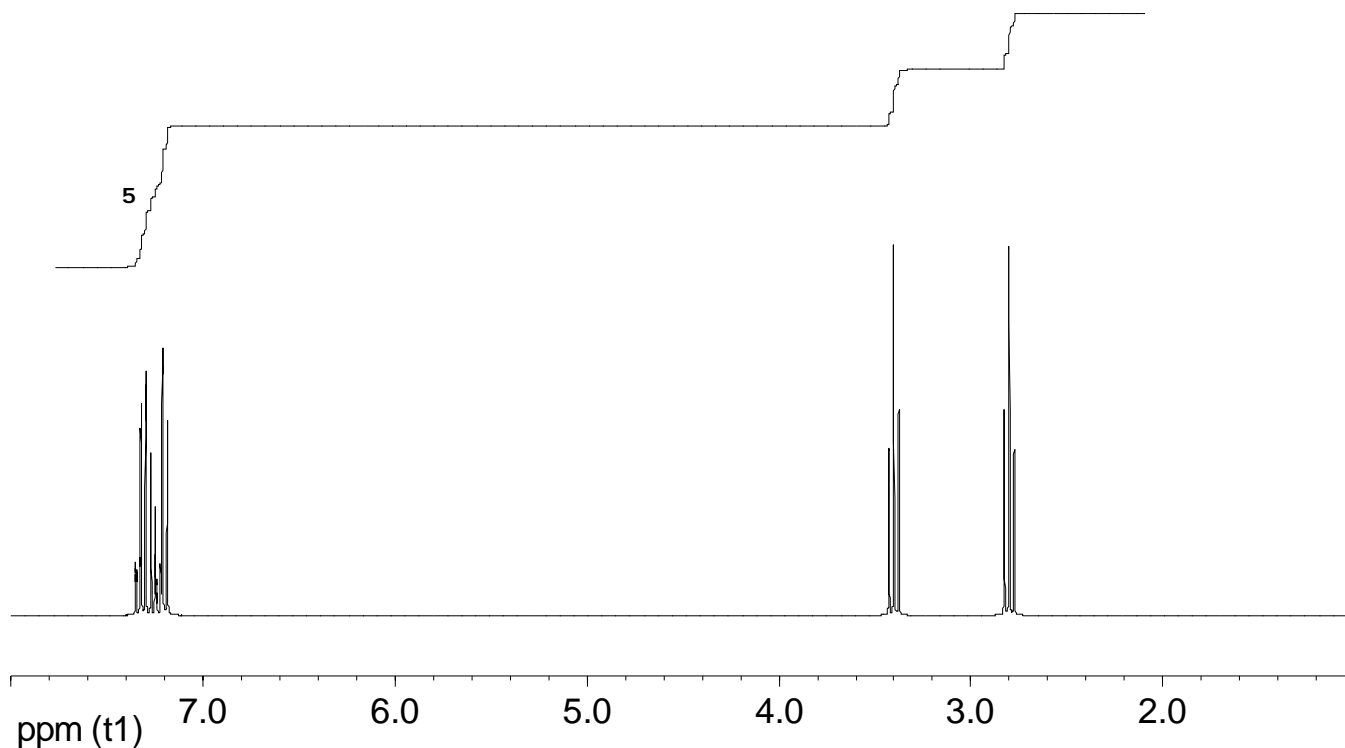
14. (5 pts) Suggest two different synthetic sequences to carry out the following conversion. Use any necessary organic or inorganic reagents.



15. (5 pts) The ^1H NMR spectrum below belongs to an alkyl bromide, which was used to prepare an ylide to be used for a *Wittig* reaction. The product of the *Wittig* reaction has molecular formula $\text{C}_{11}\text{H}_{14}$.

- What is the structure of the alkyl bromide?
- Suggest a structure for the product of the *Wittig* reaction.





16. (3 pts) **BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!).** Another way to prepare alkenes is to react epoxides with triphenylphosphine, as shown below. Suggest a detailed mechanism for this reaction. Your mechanism should account for the observed stereochemistry!

