

CHEMISTRY 314-01

MIDTERM # 2

November 02, 2009

Name

The total number of points in this midterm is 100. The total exam time is 120 min (2 h). Good luck!

1. (8 pts) Mark as true (T) or false (F) the following statements. Do not explain!

- Thiols are more acidic than water;
- Ethers are hydrogen bond donors;
- Ethers are Lewis bases;
- Acetals are stable in acidic conditions;
- Acetals are formed only in the presence of acid catalyst;
- *Schiff* bases contain C = N bonds;
- The haloform reaction requires basic conditions;
- The enol and keto forms of carbonyl compounds are structural isomers;

2. Circle ALL that apply:

A. (3 pts) The following bases are used for reversible deprotonation of carbonyl compounds:

- a. Water;
- b. Potassium hydroxide;
- c. Sodium methoxide;
- d. LDA;

B. (3 pts) The following reactions are used to prepare carbonyl compounds:

- a. Oxidation of secondary alcohols with PDC;
- b. Reaction of vicinal diols with periodic acid;
- c. Oxidation of primary alcohols with potassium permanganate;
- d. Reaction of alkenes with OsO₄ and *t*-BuOOH;

C. (3 pts) The following reactions follow an addition – elimination mechanism:

- e. Formation of *Schiff* bases;
- f. Formation of cyanohydrins;
- g. Formation of hydrates;
- h. The *Wittig* reaction;

D. (3 pts) The following reactions lead to formation of carbon – carbon double bonds:

- a. Alkene dihydroxylation;
- b. *Wittig* reaction;
- c. *Baeyer – Villiger* oxidation;
- d. *Clemmensen* reduction;

3. (5 pts) Provide the correct structure, matching each of the following names:



methyl vinyl ketone



dioxirane



formaldehyde

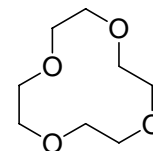


benzophenone



acetaldehyde

4. (3 pts) Provide suitable names for the following compounds:

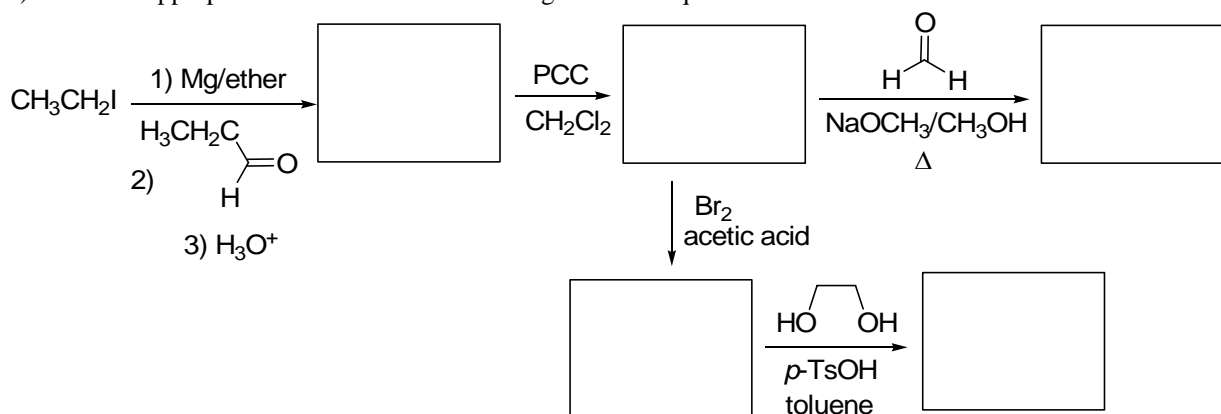


5. Write the complete equation for each of the following reactions:

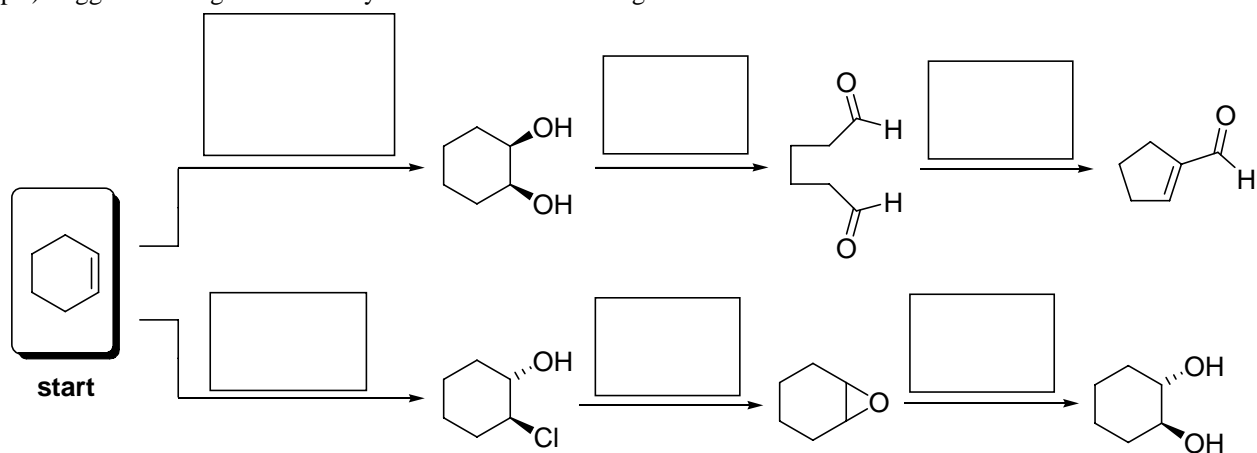
A. (2 pts) Acetone and semicarbazide, catalyzed by acid;

B. (2 pts) Acetaldehyde in the presence of sodium ethoxide in ethanol, upon heating;

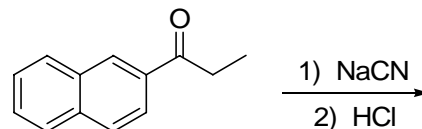
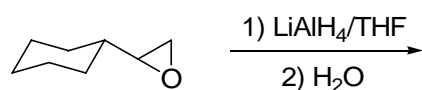
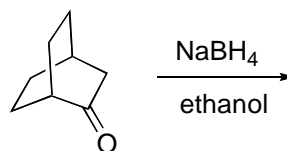
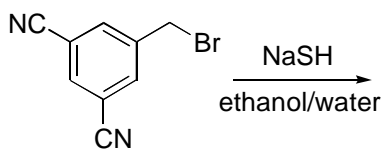
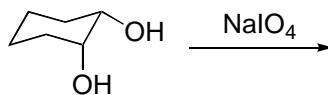
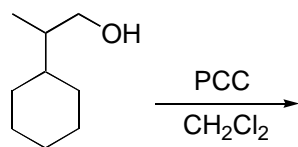
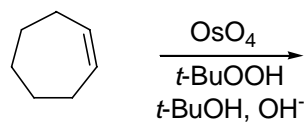
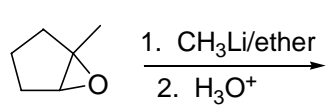
6. (5 pts) Fill in the appropriate structures in the following reaction sequence:

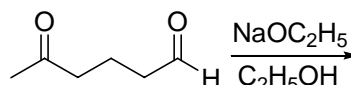
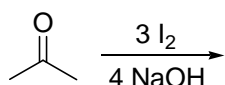
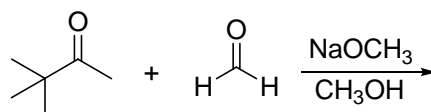
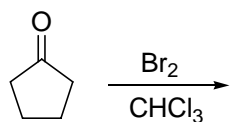
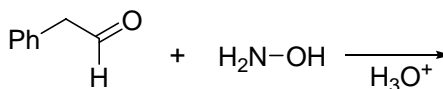
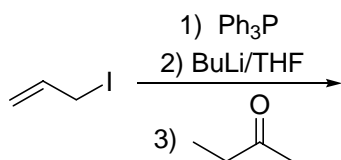
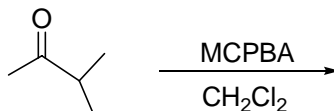
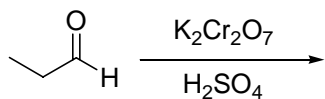
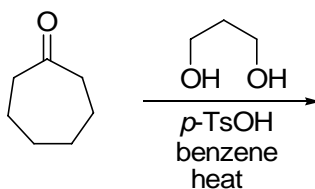
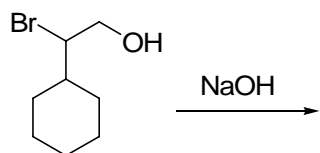


7. (6 pts) Suggest the reagents necessary to conduct the following transformations:

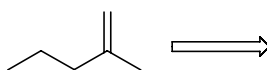
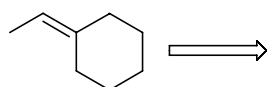


8. (20 pts) Write the principal organic product of each of the following reactions:

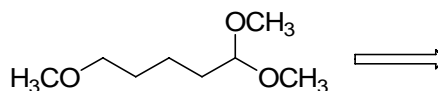
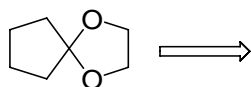




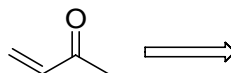
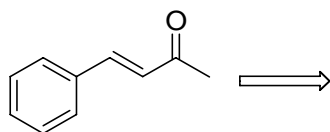
9. (4 pts) Suggest the optimal set of starting materials to prepare each of the following compounds using the *Wittig* reaction.



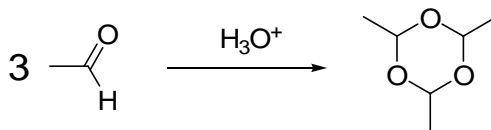
10. (4 pts) What carbonyl compound and alcohol (diol) are needed to prepare each of the following acetals:



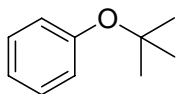
11. (4 pts) What starting materials were used to generate the following compounds using mixed aldol condensation?



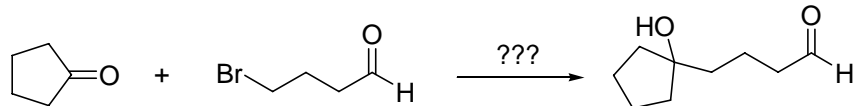
12. (4 pts) Paraldehyde, a sedative and hypnotic agent, is prepared by treatment of acetaldehyde with acid catalyst. Propose a mechanism for the reaction.



13. (2 pts) Briefly account why it is not possible to prepare the following ether *via* the *Williamson* ether synthesis:



14. (4 pts) Suggest a sequence, using protection – deprotection, that would enable you to conduct the following transformation:



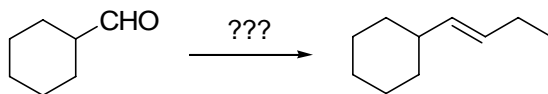
15. (3 pts) Suggest one particular structure of each of the following:

A. A β -dicarbonyl compound;

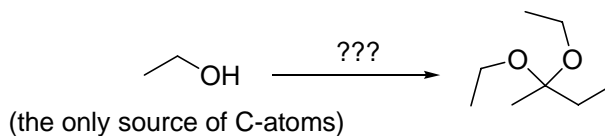
C. A cyclic acetal;

B. A sulfone;

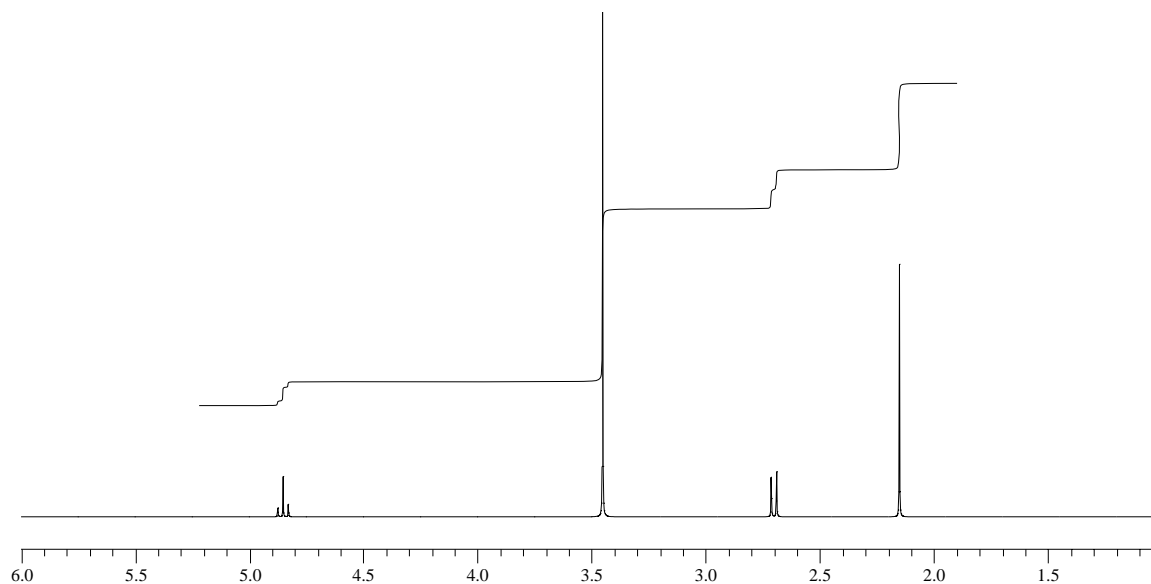
16. (4 pts) Show two different sequences to carry out the following transformation: (1) A sequence based on the use of the *Wittig* reaction, and (2) a sequence based on the use of a *Grignard* reagent. Use any necessary organic or inorganic reagents.



17. (4 pts) Suggest a plausible synthetic sequence for the preparation of the following compound, using ethanol as the exclusive source of carbon atoms. You may use any other necessary organic or inorganic reagents.



18. (4 pts) The ^1H NMR spectrum of a compound **A**, with molecular formula $\text{C}_6\text{H}_{12}\text{O}_3$, is shown below. The ^{13}C NMR spectrum of **A** shows signals at 211.0, 98.2, 67.5, 42.8 and 39.8. On contact with dilute mineral acid compound **A** rapidly decomposes to give compound **B**, whose molecular formula is $\text{C}_4\text{H}_6\text{O}_2$. The ^{13}C NMR spectrum of **B** shows signals at 211.4, 199.7, 55.5 and 39.3. Deduce the structures of **A** and **B**.



19. (2 pts) **BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!)**. Sulfur ylides are also used in organic synthesis. They are generated from sulfonium salts and are used in reactions with carbonyl compounds, to generate epoxides. Suggest a detailed mechanism for the epoxide formation shown below (i.e. the second reaction).

