

CHEMISTRY 314-01
MIDTERM # 2 – answer key
November 02, 2009

Statistics:

- Average: 61 pts (61%);
- Highest: 87 pts (87%); Lowest: 30 pts (30%)
- Number of students performing at or above average: **15 (58%)**
- Number of students performing below 55%: **9 (35%)**

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

- (T) Thiols are more acidic than water;
- (F) Ethers are hydrogen bond donors;
- (T) Ethers are Lewis bases;
- (F) Acetals are stable in acidic conditions;
- (T) Acetals are formed only in the presence of acid catalyst;
- (T) Schiff bases contain C = N bonds;
- (T) The haloform reaction requires basic conditions;
- (T) 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;

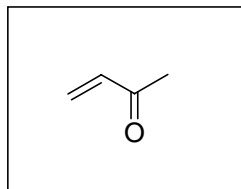
C. (3 pts) The following reactions follow an addition – elimination mechanism:

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

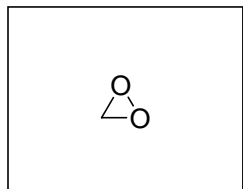
D. (3 pts) The following reactions lead to formation of carbon – carbon double bonds:

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

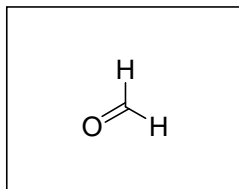
3. (5 pts) Provide the correct structure, matching each of the following names:



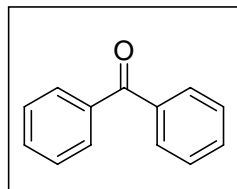
methyl vinyl ketone



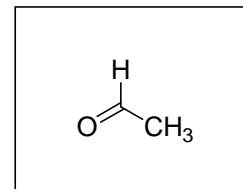
dioxirane



formaldehyde



benzophenone



acetaldehyde

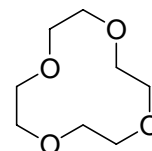
4. (3 pts) Provide suitable names for the following compounds:



**oxolane or
tetrahydrofuran**

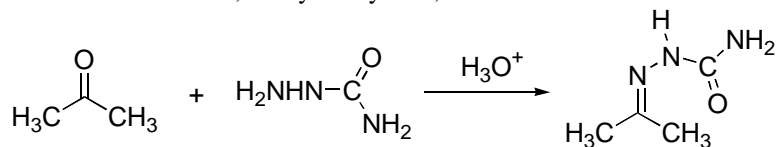


thiane

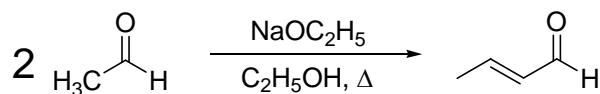


12-crown-4

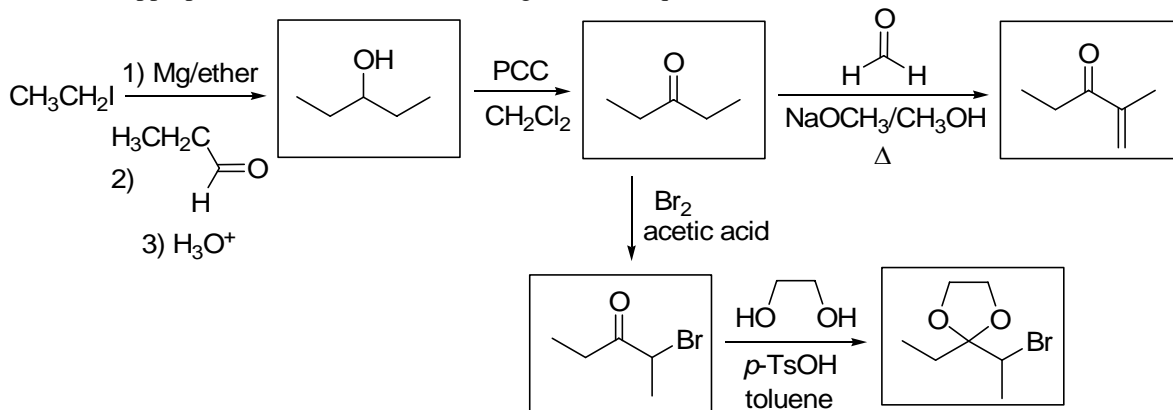
5. Write the complete equation for each of the following reactions:
 A. (2 pts) Acetone and semicarbazide, catalyzed by acid;



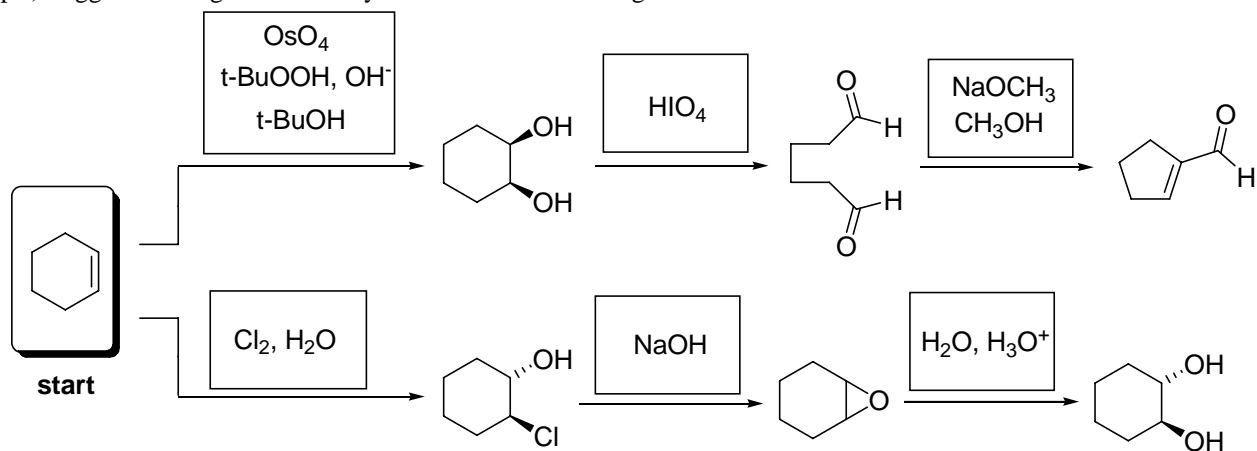
- B. (2 pts) Acetaldehyde in the presence of sodium ethoxide in ethanol, upon heating;



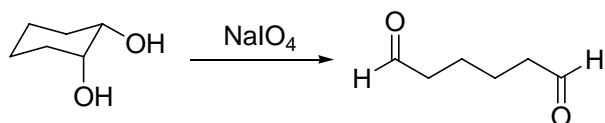
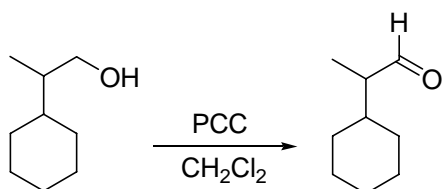
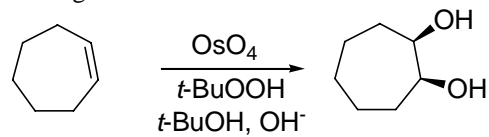
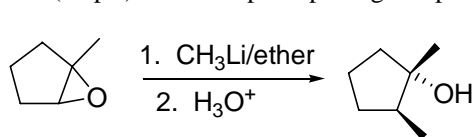
6. (5 pts) Fill in the appropriate structures in the following reaction sequence:

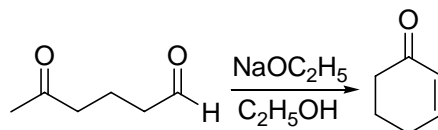
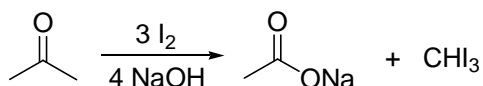
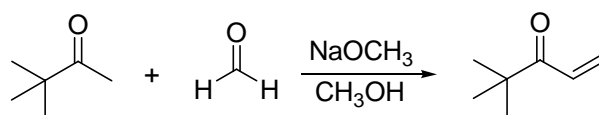
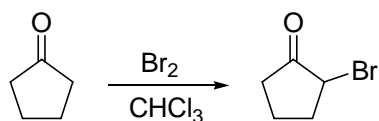
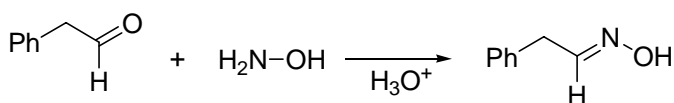
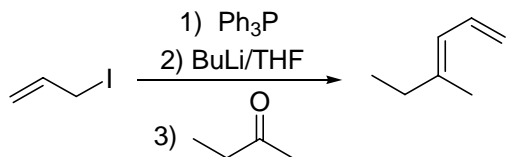
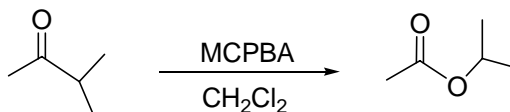
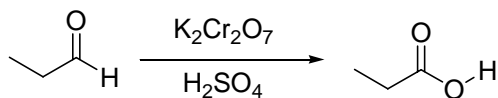
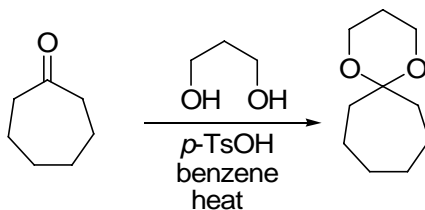
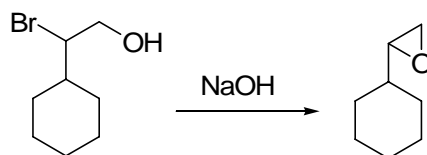
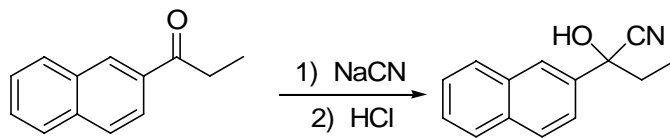
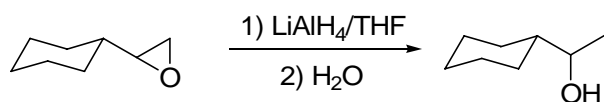
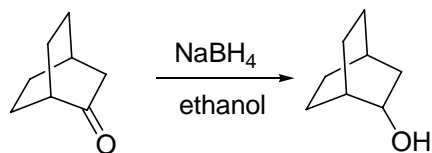
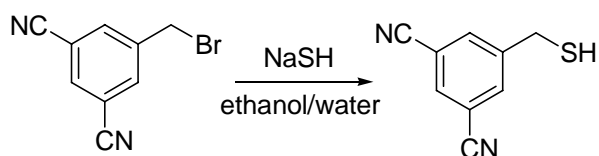


7. (6 pts) Suggest the reagents necessary to conduct the following transformations:

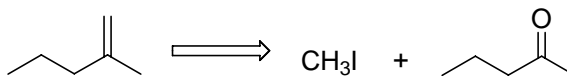
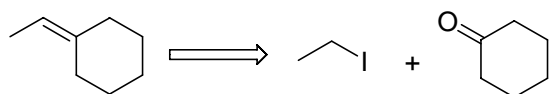


8. (20 pts) Write the principal organic product of each of the following reactions:

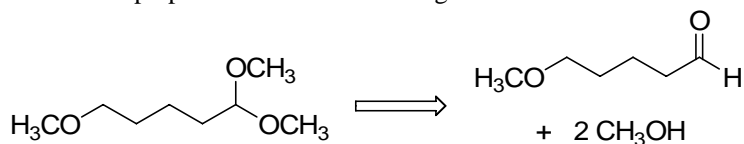
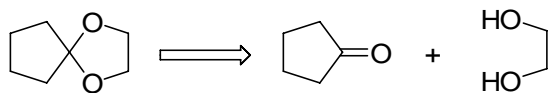




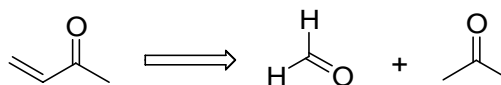
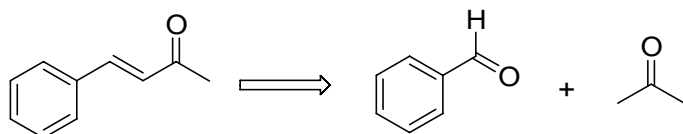
9. (4 pts) Suggest the optimal set of starting materials to prepare each of the following compounds using the Wittig reaction.



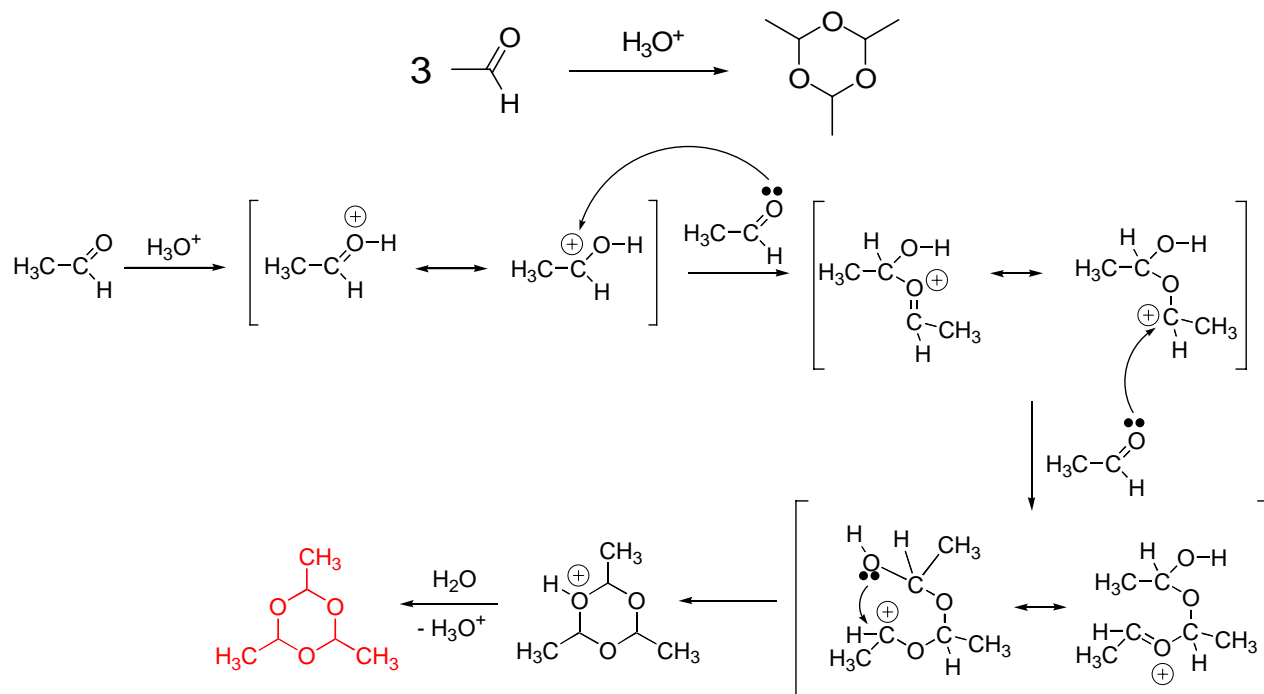
10. (4 pts) What carbonyl compound and alcohol (diol) are needed to prepare each of the following acetals:



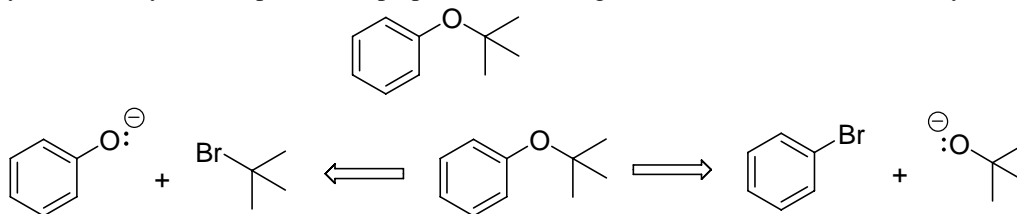
11. (4 pts) What starting materials were used to generate the following compounds using mixed aldol condensation?



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

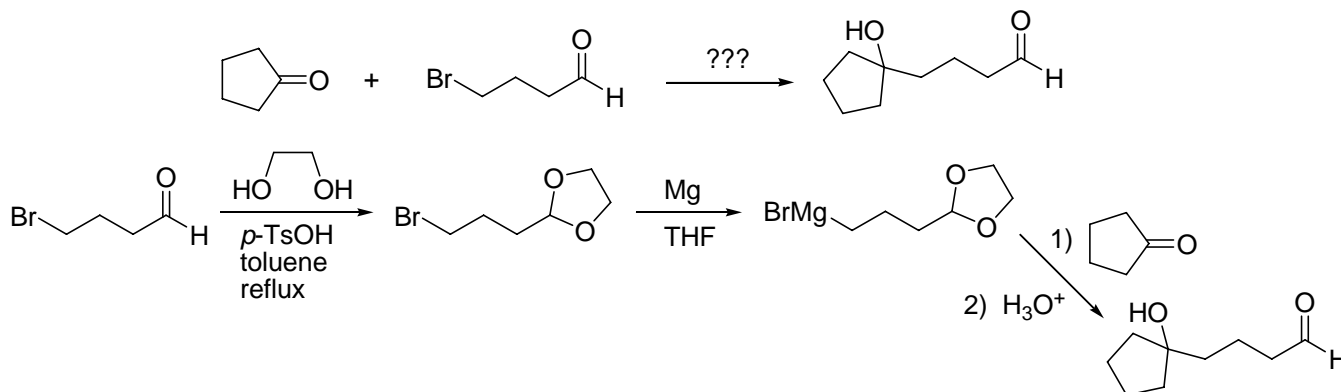


13. (2 pts) Briefly account why it is not possible to prepare the following ether *via* the *Williamson* ether synthesis:



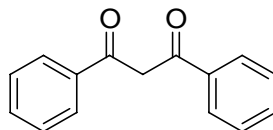
The *Williamson* ether synthesis is based on an $\text{S}_{\text{N}}2$ reaction between an alkoxide and an alkyl halide. For the compound above, retrosynthetic analysis leads to two options, neither of which would lead to the desired product because they involve either a tertiary alkyl halide or an aryl halide. Tertiary alkyl halides undergo $\text{E}2$ (but not $\text{S}_{\text{N}}2$) while aryl halides are completely inert in these conditions.

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

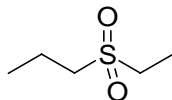


15. (3 pts) Suggest one particular structure of each of the following:

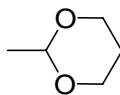
A. A β -dicarbonyl compound;



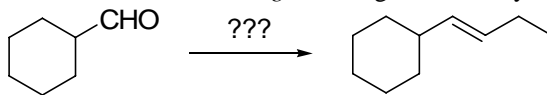
B. A sulfone;



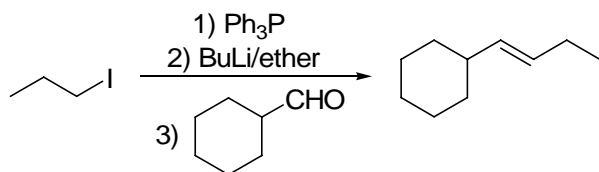
C. A cyclic acetal;



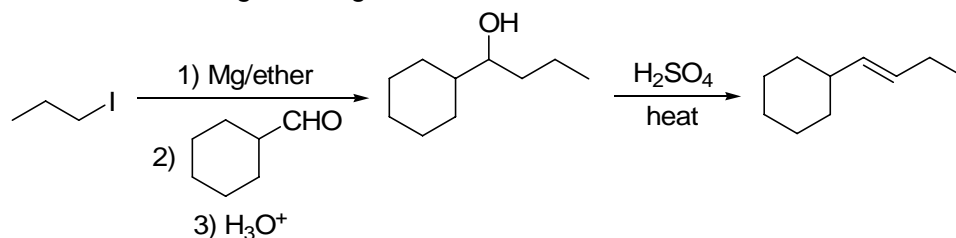
16. (4 pts) Show two different sequences to carry out the following transformation: (1) A sequence based on the use of the *Wittig* reaction, and (2) a sequence based on the use of a *Grignard* reagent. Use any necessary organic or inorganic reagents.



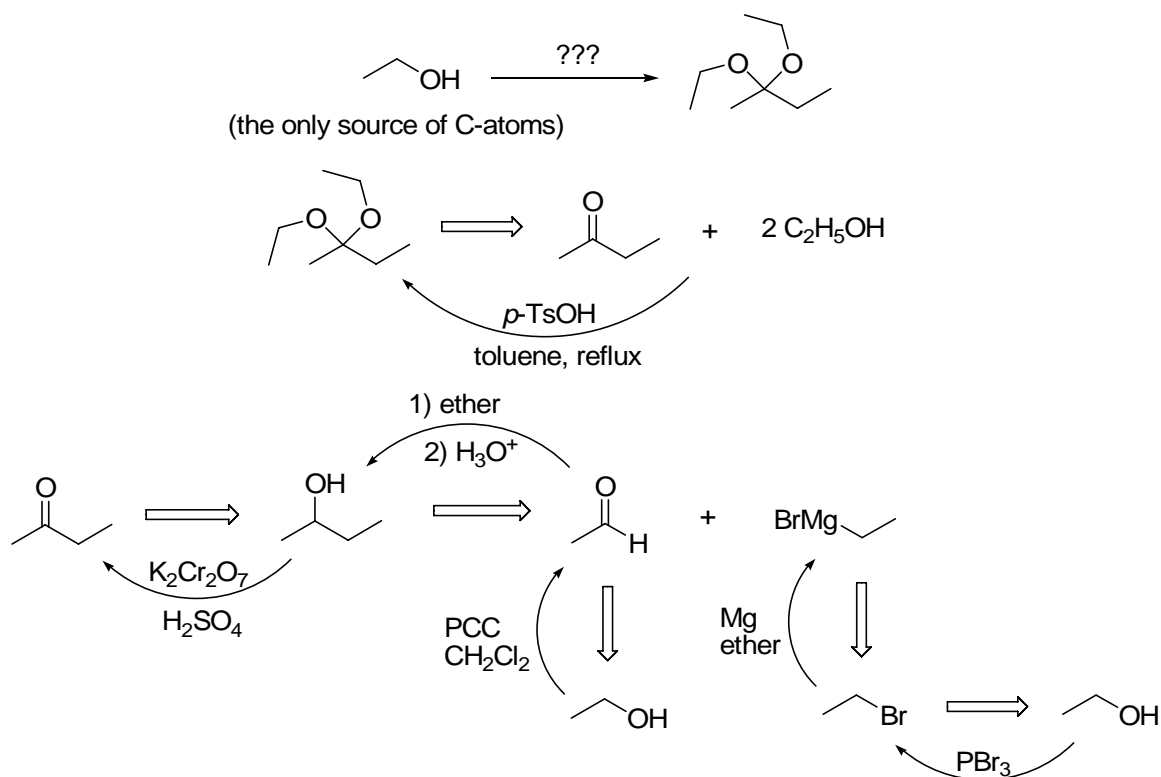
Sequence based on the *Wittig* reaction:



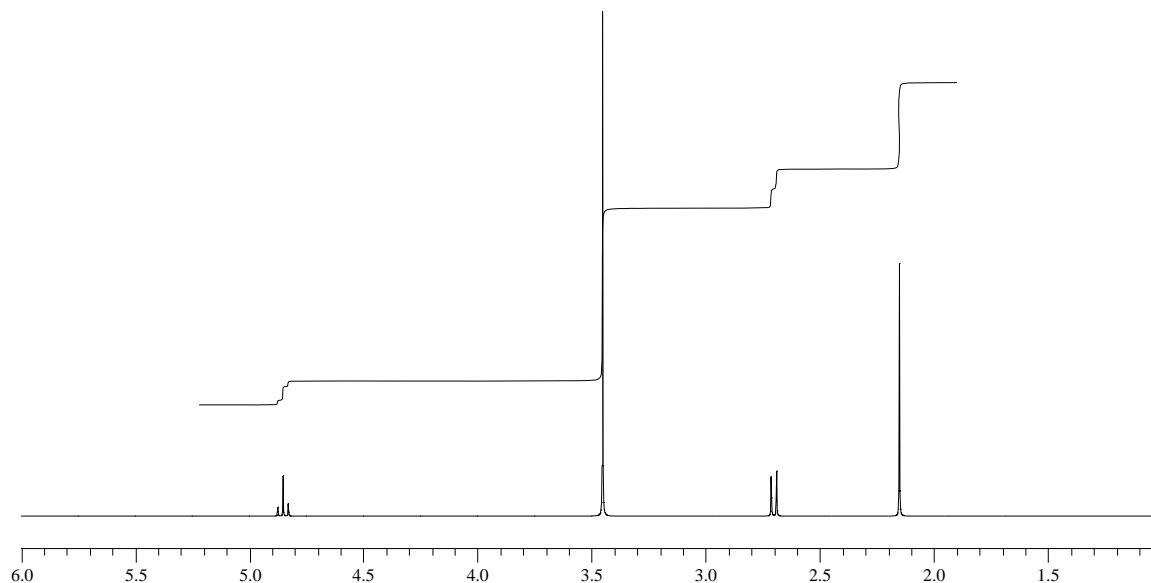
Sequence based on a *Grignard* reagent:



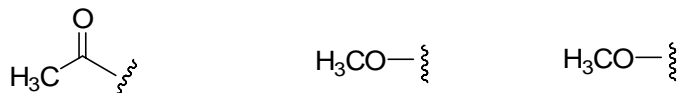
17. (4 pts) Suggest a plausible synthetic sequence for the preparation of the following compound, using **ethanol as the exclusive source** of carbon atoms. You may use any other necessary organic or inorganic reagents.



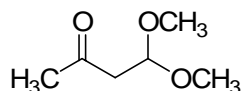
18. (4 pts) The ^1H NMR spectrum of a compound **A**, with molecular formula $\text{C}_6\text{H}_{12}\text{O}_3$, is shown below. The ^{13}C NMR spectrum of **A** shows signals at 211.0, 98.2, 67.5, 42.8 and 39.8. On contact with dilute mineral acid compound **A** rapidly decomposes to give compound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



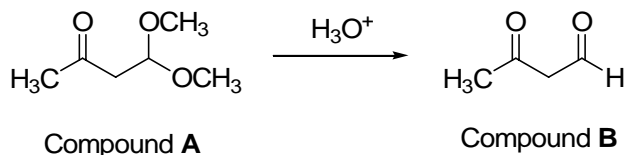
Solution: Compound **A** has e.u. = 1. Its ^{13}C NMR has a signal at 211.0 ppm, which is very likely a ketone carbonyl group. The ^1H NMR of **A** shows a singlet for 3H at ~ 2.2 ppm, doublet for 2H at ~ 2.7 ppm, singlet for 6H at ~ 3.5 ppm and triplet for 1H at ~ 4.8 ppm. A singlet for 3H is most likely an isolated methyl group, which, judging by the shift, is attached to the carbonyl group. The singlet for 6H is very likely two equivalent, isolated CH_3 – groups. With a shift of ~ 3.5 ppm, they are probably attached to oxygen. In other words, we can guess the following substructures:



Since the CH_3O – groups are equivalent, they are very likely attached to the same carbon atom. We have a total of two remaining carbon centers. If the two methoxy groups are attached to one of them, and the other is attached to the carbonyl group, then we get for the structure of **A**:



The triplet for 1H is shifted considerably downfield, which is consistent with two oxygen centers attached to that carbon. The proposed structure of **A** is an acetal. If mixed with acid, it would instantly react and give the corresponding carbonyl compound **B**, which has a new, aldehyde group, consistent with the fact that its carbon spectrum does show a signal at 199.7 ppm:



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).

