

**State University of New York at Stony Brook  
Department of Chemistry**

**CHE 322, Organic Chemistry II**

**Exam II  
Form 1**

**March 17, 2004**

Please answer all questions specifically, concisely, and readably in the spaces provided on the answer sheet, which you will turn in. Think before writing. Include stereochemistry wherever relevant. Use the fronts and backs of the question pages for scratch work. Your Student Identification Number must be **written** and **coded** on the answer sheet, and your printed name and signature must be included at the upper right. Since the answer sheets will not be returned, we suggest that you record your answers on the question pages for comparison with the posted answers. Grades will be posted on Blackboard.

The first ten questions are multiple-choice. They are worth five points each. Enter your choices (only one per question) in spaces 1-10 of the answer sheet.

Some useful reactions:

Aldol reaction: Enolate plus carbonyl  $\rightarrow$   $\beta$ -hydroxycarbonyl compound or  $\alpha,\beta$ -unsaturated carbonyl compound.

Claisen condensation: Ester enolate plus ester  $\rightarrow$   $\beta$ -ketoester.

Dieckmann condensation: intramolecular Claisen condensation

Michael addition: Conjugate addition of enolate to  $\alpha,\beta$ -unsaturated carbonyl compound.

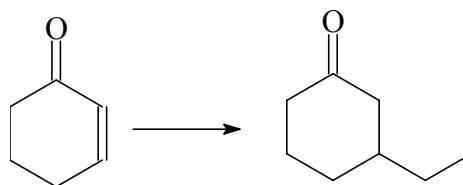
Wittig reaction: Formation of a double bond using  $\text{Ph}_3\text{P}=\text{CR}_2$  and a carbonyl compound.

Sodium borohydride reduces aldehydes, acyl chlorides, and ketones to alcohols.

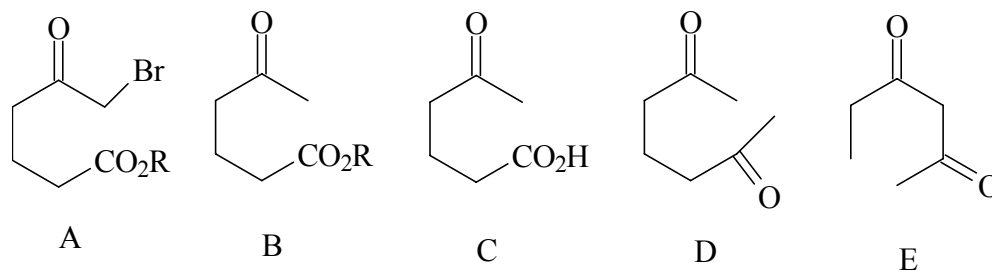
Lithium aluminum hydride reduces all carbonyl compounds to alcohols.

Note: in typescript, RCHO denotes an aldehyde. It can also be rendered as  $\text{RC}(=\text{O})\text{H}$

- Which one of the following classes of organic compound will **not** react with diisobutylaluminum hydride?
  - ketones
  - amides
  - carboxylic acids
  - esters
  - nitriles
  
- Which of the products shown below would be the principal product produced in the reaction of benzylmagnesium bromide,  $\text{PhCH}_2\text{MgBr}$ , with ethyl formate,  $\text{CH}_3\text{CH}_2\text{OCH}=\text{O}$ ?
  - $\text{PhCH}_2\text{CHO}$
  - $\text{PhCH}_2\text{COOCH}_2\text{CH}_3$
  - $\text{PhCH}_2\text{CH}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{Ph}$
  - $\text{PhCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Ph}$
  - $(\text{PhCH}_2)_3\text{COH}$
  
- Which of the following statements regarding formation of a cyclic acetal from a ketone and ethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , is **not** true?
  - The reaction can be performed using either acid or base as catalyst.
  - The reaction provides a useful method for protecting the ketone group from unwanted reactions.
  - The reaction should be carried out under anhydrous conditions.
  - The reaction can be reversed by treating the acetal with aqueous acid.
  - All of these statements are true.
  
- What combination of reagents could be used to form the product  $\text{PhC}(=\text{O})\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}_3$ , using an aldol reaction?
  - $\text{PhC}(=\text{O})\text{CH}_2\text{OH}$  and  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CHO}$
  - $\text{PhCHO}$  and  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CHO}$
  - $\text{PhC}(=\text{O})\text{CHO}$  and  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$
  - $\text{PhC}(=\text{O})\text{CH}_3$  and  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CHO}$
  - $\text{PhC}(=\text{O})\text{OCH}_3$  and  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$ .
  
- Which of the following reagents would be most effective for carrying out the conversion of 2-cyclohexenone to 3-ethylcyclohexanone?
  - Ethyl bromide
  - Ethyl-lithium
  - Ethylmagnesium bromide
  - Lithium diethylcuprate
  - Sodium ethoxide



6. Which one of the following starting materials would be most useful for synthesizing cyclohexane-1,3-dione, which is used in the Robinson annulation?

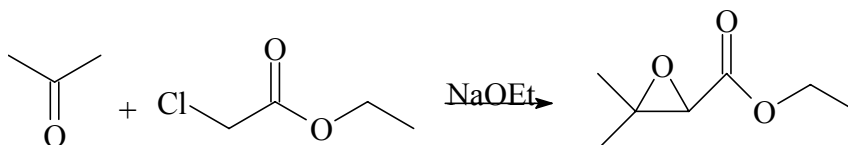


7. Which combination of reagents would give a successful mixed aldol reaction (one principal product) on treatment with sodium ethoxide in ethanol? (Ph = phenyl, C<sub>6</sub>H<sub>5</sub>)

- (A) CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub> and PhCHO  
 (B) CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub> and PhCOCH<sub>3</sub>  
 (C) CH<sub>3</sub>COCH<sub>3</sub> and PhCHO  
 (D) CH<sub>3</sub>COCH<sub>3</sub> and PhCOCH<sub>3</sub>  
 (E) CH<sub>3</sub>COCH<sub>3</sub> and PhCOOCH<sub>3</sub>

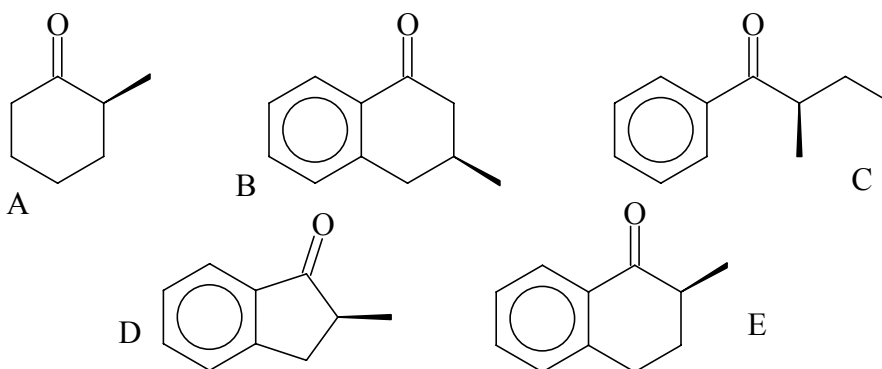
8. The following reaction is an example of a Darzens condensation:

Which of the following is **not** an intermediate in the Darzens condensation?

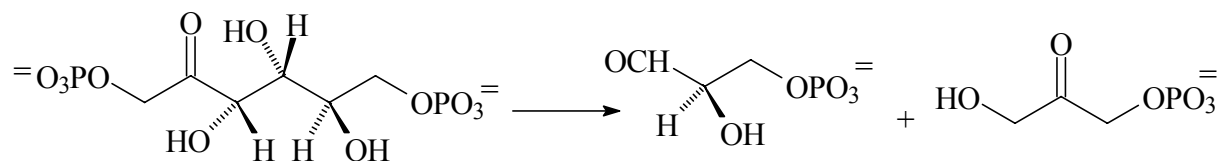


- (A) CH<sub>3</sub>COCH<sub>2</sub>-  
 (B) ClCH=C(O<sup>-</sup>)OEt  
 (C) EtOCOCHCl  
 (D)   
 (E) All of the above are intermediates

9. Which of the following ketones would **not** racemize if treated with a drop of sulfuric acid?

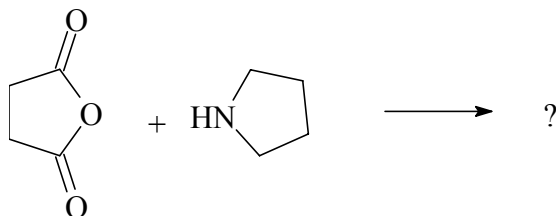


10. In the biochemical process of glycolysis, sugars are broken down to provide energy to cells in the body. A key step is the following:

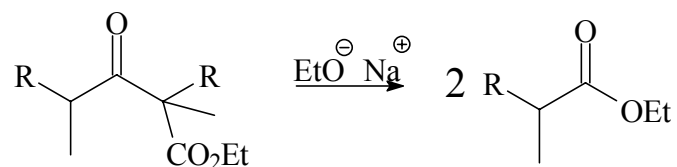


What type of reaction is this?

- (A) A reverse aldol reaction  
 (B) A reverse Claisen condensation  
 (C) A reverse Wittig reaction  
 (D) A reverse Michael addition  
 (E) A reverse Dieckmann condensation
11. (10 points) Draw the structures of the products of reaction of succinic anhydride with excess pyrrolidine:



12. (10 points) Benzoic acid reacts with dicyclohexyl carbodiimide,  $\text{RN}=\text{C}=\text{NR}$ , to form an intermediate, A, which yields N-ethylbenzamide on treatment with ethylamine. Write the structure of A.
13. (10 points) Write a mechanism which shows why mild heating of acetoacetic acid,  $\text{CH}_3\text{COCH}_2\text{COOH}$ , in the presence of bromine results in formation of 1-bromo-2-propanone.
14. (10 points) Write the structure of the cyclic hemiacetal formed by butan-1-al-3,4-diol,  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{CHO}$ , on standing in the presence of acid or base.
15. (10 points) Explain why the following reaction occurs as written when  $\text{R} = \text{methyl}$ , but not when  $\text{R} = \text{H}$ .



16. (10 point Bonus) How would you synthesize fenchone, a terpene from fennel oil, shown below, from the following diester?

