

Name\_\_\_\_\_

Department of Chemistry  
SUNY/Oneonta

Chem 322 - Organic Chemistry II  
Examination #3 - April 14, 1997

INSTRUCTIONS ---

This examination has two parts. Part I is in multiple choice format and the answers should be placed on the "Test Scoring Answer Sheet" which must be turned in and will be machine graded.

Part II requires your responding to questions by writing answers into the spaces provided in this booklet. This entire Exam Booklet must be handed in and will be returned to you with a grade. Write your name in the space above NOW.

On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30032201) and the test number (03); darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

You may use a set of molecular models but no other aids during the exam.

Answer all questions. The questions on Part I are worth 2.5 points each.

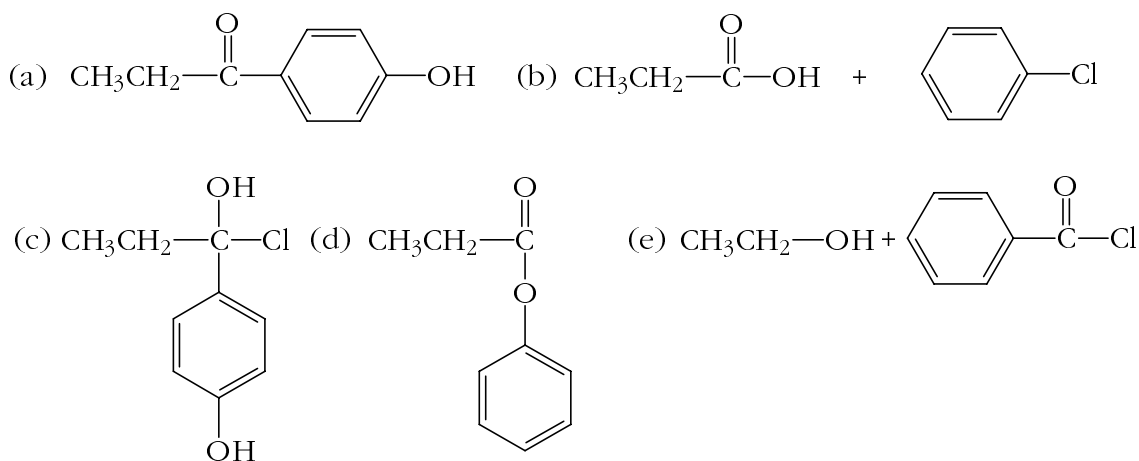
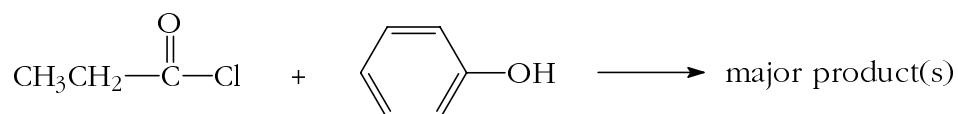
You have 90 minutes. Good luck!

1.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CO-NH}_2$  is  
(a) 1-methylpropanamide, (b) 2-methylpropanamide, (c) butyramide,  
(d) 1-methylpropanenitrile, (e) 2-methylpropanenitrile
2.  $\text{Ph-CO-OCH}_2\text{CH}_3$  is  
(a) phenyl ethanoate, (b) phenyl acetate, (c) phenoyl ethylate,  
(d) ethyl benzoate, (e) ethyl phenoate
3.  $\text{CH}_3\text{CH}_2\text{-CO-NHCH}_3$  is  
(a) methyl propanamide, (b)  $\alpha$ -methylpropanamide, (c) N-methylpropanamide,  
(d) 1-methylpropanamide, (e) propanamide
4.  $\text{CH}_3\text{CH}_2\text{O-CO-CH}_2\text{-CO-CH}_3$  is  
(a) acetoacetic ester, (b) malonic ester, (c) Ester's ester  
(d) acetoacetic anhydride, (e) malonic anhydride
5.  $\text{CH}_3\text{-CO-O-CO-CH}_3$  is  
(a) acetic acetate, (b) ethyl acetate, (c) acetic anhydride, (d) formic anhydride,  
(e) ethyl formate
6. Rank the following compounds in order from most reactive to least reactive toward nucleophilic acyl substitution:  
  
I:  $(\text{CH}_3)_2\text{CH-CO-OCH}_3$ , II:  $\text{CH}_3\text{-CO-OCH}_3$ , III:  $(\text{CH}_3)_2\text{CH-CO-NH}_2$   
  
(a) I > II > III, (b) III > II > I, (c) II > I > III, (d) III > I > II,  
(e) Bogus question! They are equally reactive.

7. The behavior of acid chlorides and aldehydes in a reaction with a nucleophile is different because

- (a) the carbonyl carbon of the aldehyde is more positive.
- (b) the bulky chlorine sterically hinders nucleophilic attack.
- (c) the acid chloride cannot form a tetrahedral intermediate.
- (d) there is a good leaving group in the acid chloride.
- (e) the aldehyde has a readily oxidizable hydrogen.

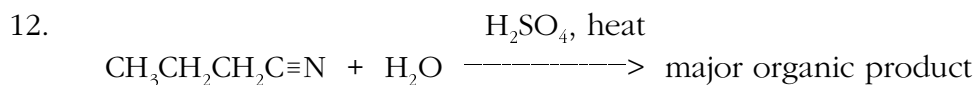
8.



The following two questions consist of a **statement** followed by the connecting word **because** followed by a **reason**. For each question choose the correct description of the statement and reason from the list below --

- (a) The statement and the reason are both factually true, and the reason is the correct explanation of the statement.
- (b) The statement and the reason are both factually true, but the reason is not the correct explanation of the statement.
- (c) The statement is true and the reason is false.
- (d) The statement is false and the reason is true.
- (e) Both statement and reason are false.

9. Carboxylic acid chlorides are more reactive than amides **because** chlorine has more lone pairs than nitrogen and therefore it can share its lone pair electrons with the carbonyl group more effectively than nitrogen.
10. The second order rate constant for saponification of  $\text{CF}_3\text{COOCH}_2\text{CH}_3$  is greater than that of  $\text{CH}_3\text{COOCH}_2\text{CH}_3$  **because** the electron withdrawing effect of the  $\text{CF}_3$  group assists nucleophilic attack on the carbonyl group of  $\text{CF}_3\text{COOCH}_2\text{CH}_3$ .
11. Which of the following procedures give(s) benzyl alcohol,  $\text{Ph-CH}_2\text{OH}$ , starting with methyl benzoate,  $\text{Ph-CO-OCH}_3$ ?
- (a) 1. DIBALH (diisobutylaluminum hydride) in toluene,  $-78^\circ\text{C}$ ; 2.  $\text{H}_3\text{O}^+$ ,  
 (b)  $\text{H}_2$ ,  $\text{Pd/BaSO}_4$ , (c) 1.  $\text{LiAlH}_4$ , ether; 2.  $\text{H}_3\text{O}^+$ ,  
 (d) a & b, (e) a & c

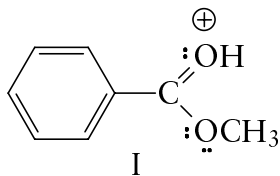


- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-NH}_2$ , (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-N=N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$   
 (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO-NH}_2$ , (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-NO}_2$ , (e)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

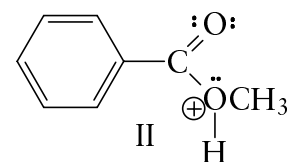


- (a)  $\text{CH}_2=\text{CH}_2$ , (b)  $\text{CH}_2=\text{CHCN}$ , (c)  $\text{CH}_3\text{CH}_2\text{CN}$ , (d)  $\text{CH}_3\text{CH}_2\text{COOH}$   
 (e) none of the above

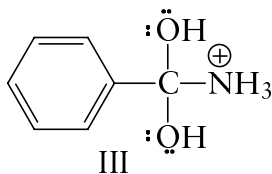
14. For each of the pairs of protonated species shown to the right, indicate which is the more stable.



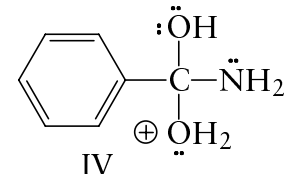
or



- (a) I&III, (b) I&IV,  
 (c) II&III, (d) II&IV

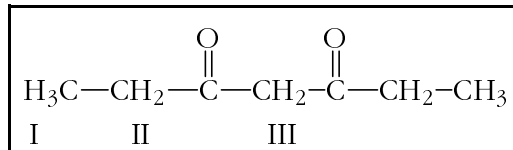
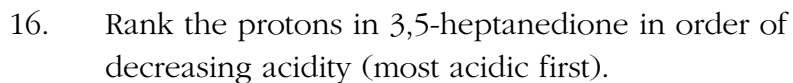


or

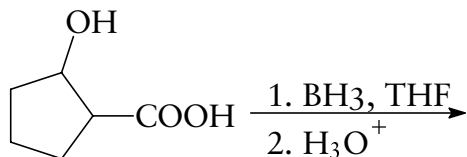
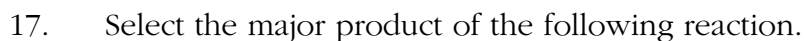


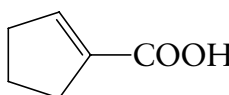
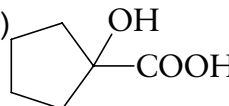
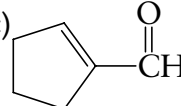
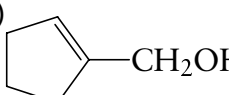
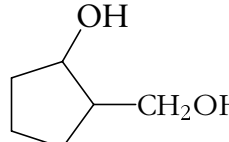


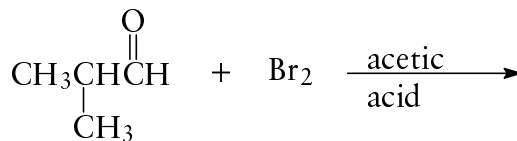
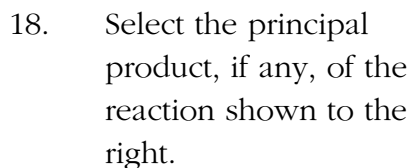
- (a)  $\text{CH}_3\text{CH}_2\text{-CO-Ph}$ , (b)  $\text{CH}_3\text{CH}_2\text{-C(OH)Ph}_2$ , (c)  $\text{CH}_3\text{CH}_2\text{-CCl(OH)Ph}$   
 (d) a & b, (e) b & c

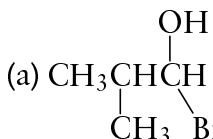
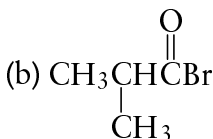
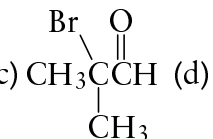
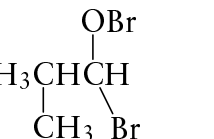


- (a)  $\text{I} > \text{II} > \text{III}$ , (b)  $\text{III} > \text{II} > \text{I}$ ,  
 (c)  $\text{II} > \text{III} > \text{I}$ , (d)  $\text{II} > \text{I} > \text{III}$



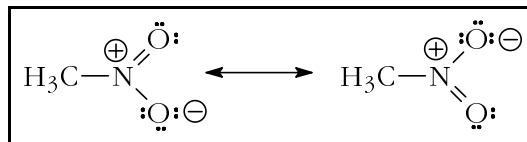
- (a)  (b)  (c)  (d)   
 (e) 



- (a)  (b)  (c)  (d)   
 (e) no reaction

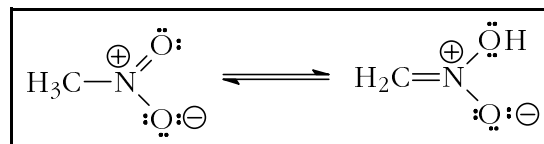
19. The structures shown to the right are

- (a) tautomers, (b) resonance structures,  
 (c) enantiomers, (d) diastereomers,  
 (e) none of the above.

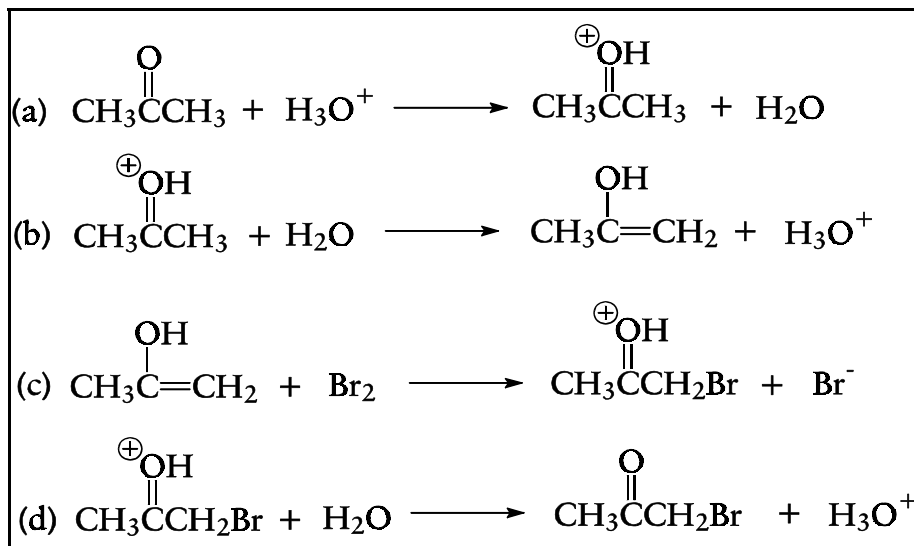


20. The structures shown to the right are

- (a) tautomers, (b) resonance structures,  
 (c) enantiomers, (d) diastereomers,  
 (e) none of the above.



For questions 21 and 22 consider the mechanism for the acid-catalyzed bromination of acetone shown to the right.



21. Which of the steps shown is incorrect?

- (a), (b), (c), (d), (e) All of the steps are essentially correct.

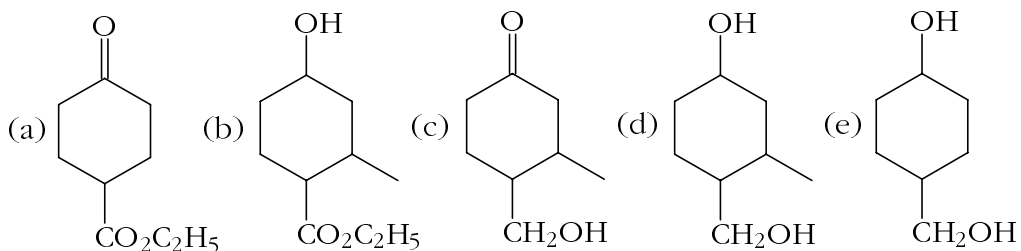
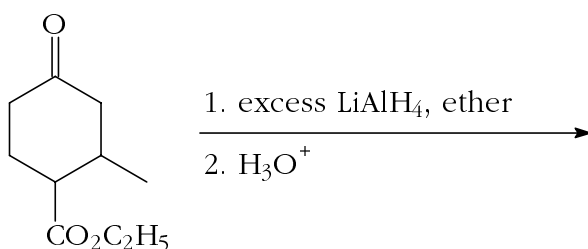
22. Which of the steps is the *slow* step in the mechanism?

- (a), (b), (c), (d), (e) There is no slow step.

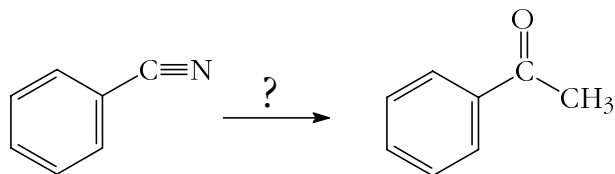
23. Which of the following compounds will react with iodine in aqueous sodium hydroxide solution to give a precipitate of iodoform,  $\text{CHI}_3$ ?

- (a)  $\text{PhCHO}$ , (b)  $\text{PhCOCH}_3$ , (c)  $\text{CH}_3\text{CH}_2\text{CHOHCH}_2\text{CH}_3$ , (d)  $\text{CH}_3\text{CHO}$

24.

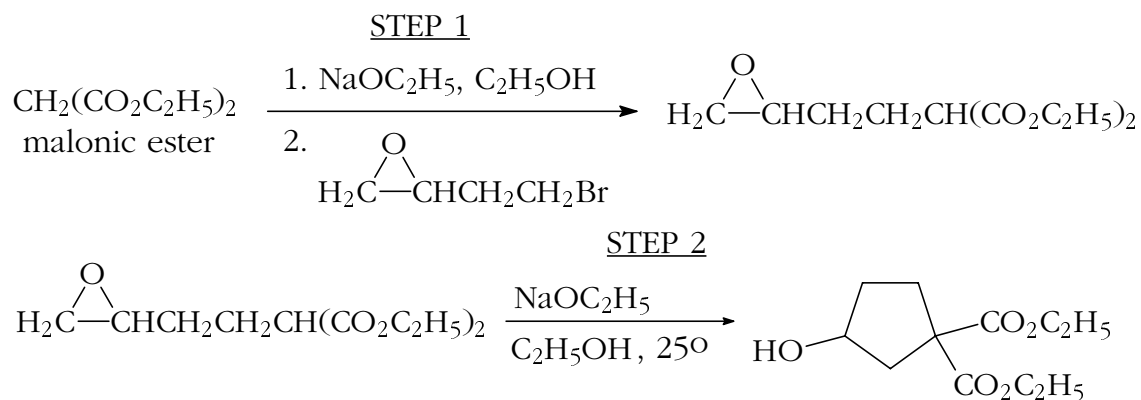


25.



- (a) 1.  $\text{CH}_3\text{MgBr}$ , ether, 2.  $\text{H}_3\text{O}^+$ , (b) 1.  $\text{CH}_3\text{I}$ , ether, 2.  $\text{H}_3\text{O}^+$   
 (c)  $\text{CH}_3\text{OH}$ , acid, heat, (d) acetyl chloride, then water

Consider the following two-step synthesis to answer questions 26 and 27. [Hint: As you attempt each question, consider the mechanism for the relevant step.]



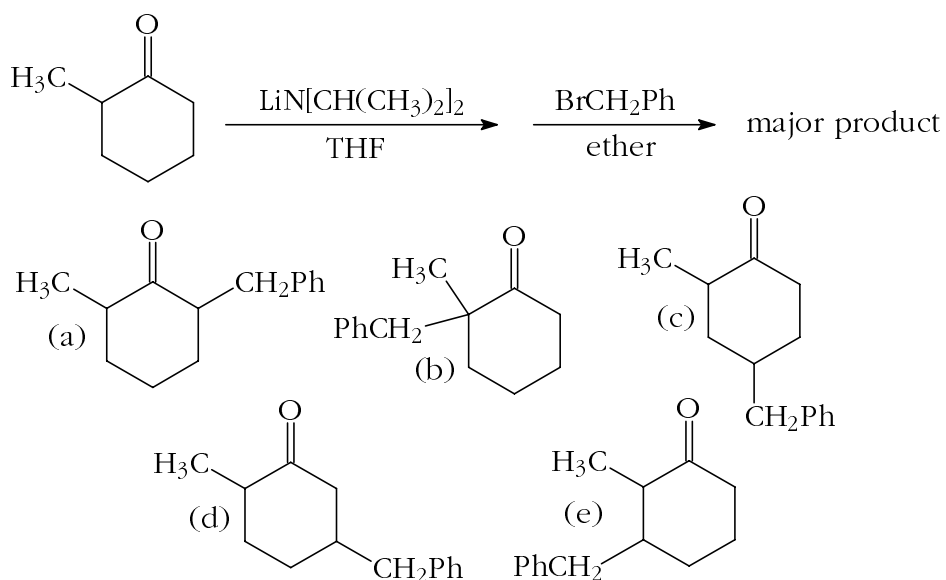
26. The carbon-carbon bond forming reaction in the second reaction of Step 1 is an example of

- (a) an *intramolecular*  $S_N2$  reaction. (b) an *intermolecular*  $S_N2$  reaction.  
 (c) a carbonyl  $\alpha$ -substitution reaction. (d) both b and c.

27. The carbon-carbon bond forming reaction in Step 2 is an example of

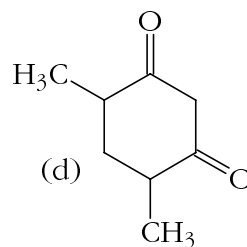
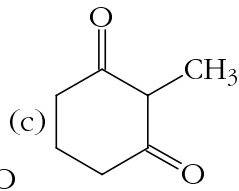
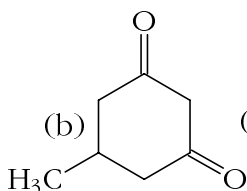
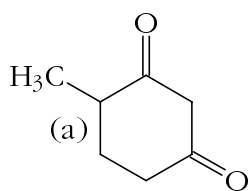
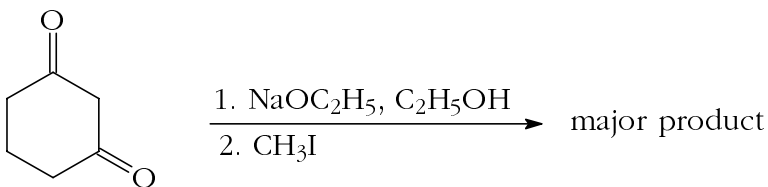
- (a) an *intramolecular*  $S_N2$  reaction. (b) an *intermolecular*  $S_N2$  reaction.  
 (c) a pericyclic reaction. (d) an electrophilic addition to an epoxide.

28.

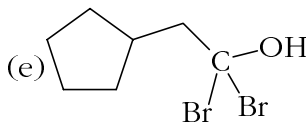
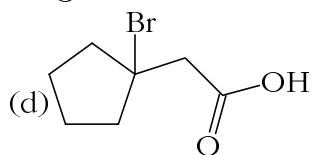
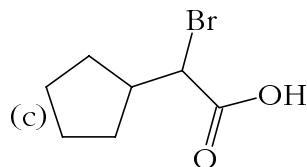
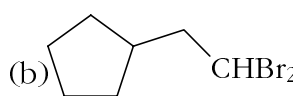
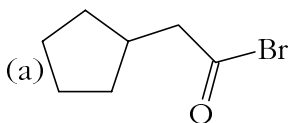
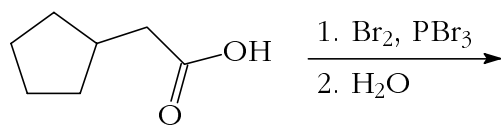




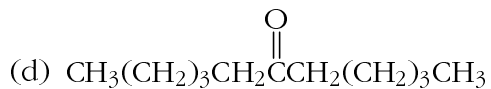
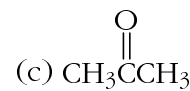
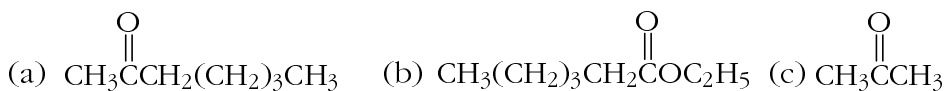
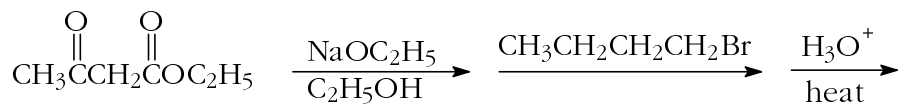
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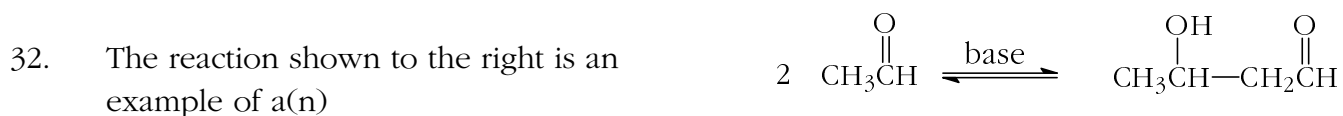


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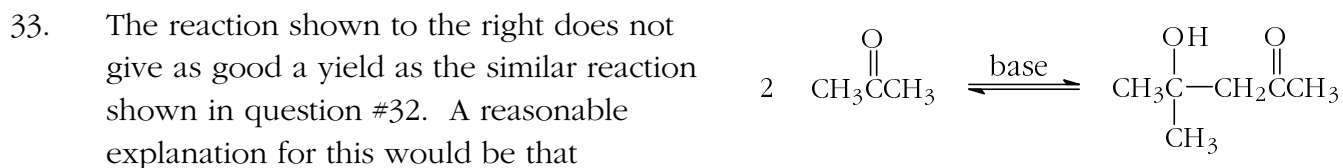


31.





- (a) Claisen condensation. (b) aldol reaction. (c) demerol reaction.  
 (d) Knoevenagel reaction. (e) Diels-Alder reaction.

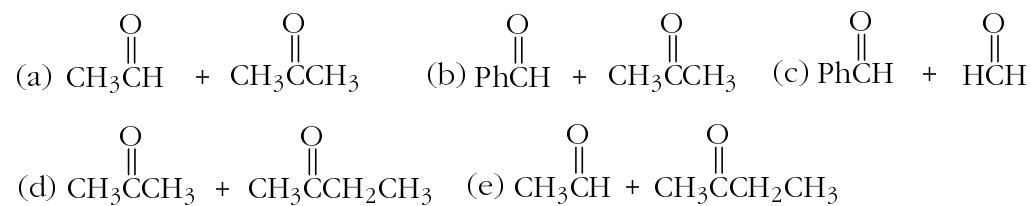


- (a) the aldehydic proton is more acidic than the methyl protons.  
 (b) the product formed from acetone undergoes a subsequent reaction, thus reducing the yield.  
 (c) a steric factor is involved as a result of the intermediate (and product) being more crowded in these reactions and the ketone case is worse than the aldehyde in this respect.  
 (d) the ketone has 6 acidic hydrogens while the aldehyde has only 3.  
 (e) Trick question, dude! Like, this reaction gives a better yield than the one in question 32.

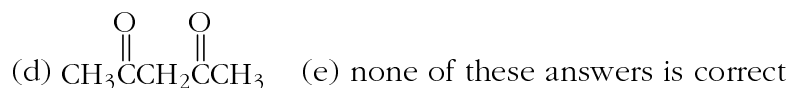
34. Which of the following describe common situations encountered with aldol reactions?

- (a) Product reverts to reactant. (b) Product undergoes a spontaneous dehydration, producing a conjugated enone. (c) Product undergoes a spontaneous dehydration, producing a non-conjugated enone. (d) Product undergoes reduction, producing a diol.  
 (e) a & b, (f) a & c, (g) b & c, (h) a, b & c.

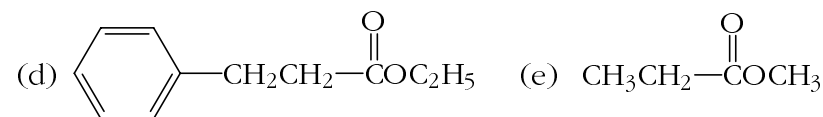
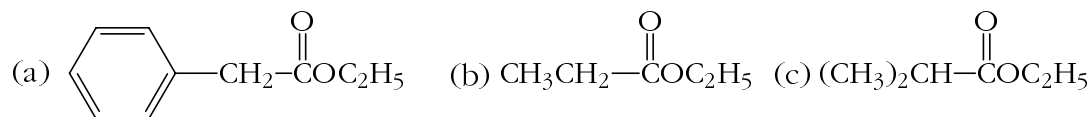
35. Which of the following pairs of compounds would be the most reasonable choice for an attempt at a "mixed" or "crossed" aldol condensation?



36. To prepare acetoacetic ester, which of the following compounds could you use in a Claisen condensation?



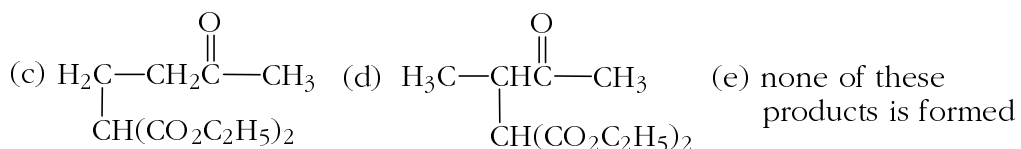
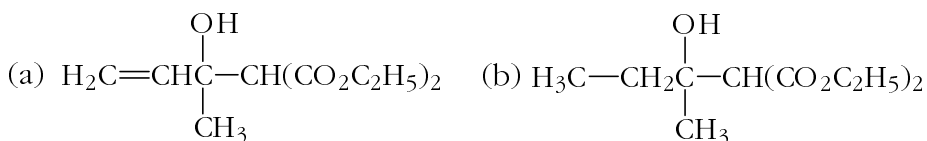
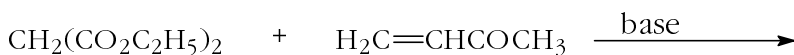
37. Which of the following compounds would not give a good yield in a Claisen condensation?



38. An intramolecular Claisen condensation is known as a

(a) Perkin reaction.    (b) Wright reaction.    (c) Michael reaction.  
(d) Dieckmann reaction.    (e) Krom reaction.

39. Select the product which is formed in the following Michael addition.



40. A frequent aim of synthesis is to make larger molecules from smaller ones. Which of the following syntheses does *not* accomplish this?
- (a) aldol reaction, (b) Claisen condensation, (c) Grignard synthesis,  
(d) Diels-Alder reaction, (e) saponification reaction.

**Do Not Detach The Following Sheets From The Rest Of The Exam**

**Part II. Enter your answers in the space provided. If there is inadequate room, continue on the back of the page and clearly indicate on the front of the page that you have done this.**

**Hand in this entire exam booklet when you are finished; it will be returned to you with your grade. Make sure your name is on the front sheet.**

1. Synthesis. Outline the following syntheses. Show all reagents and any important conditions. Do not show mechanisms or balance equations.

(a) Make acetophenone (phenyl methyl ketone), Ph-CO-CH<sub>3</sub>, starting from benzonitrile, Ph-CN. In addition to benzonitrile, you may use any materials you wish.

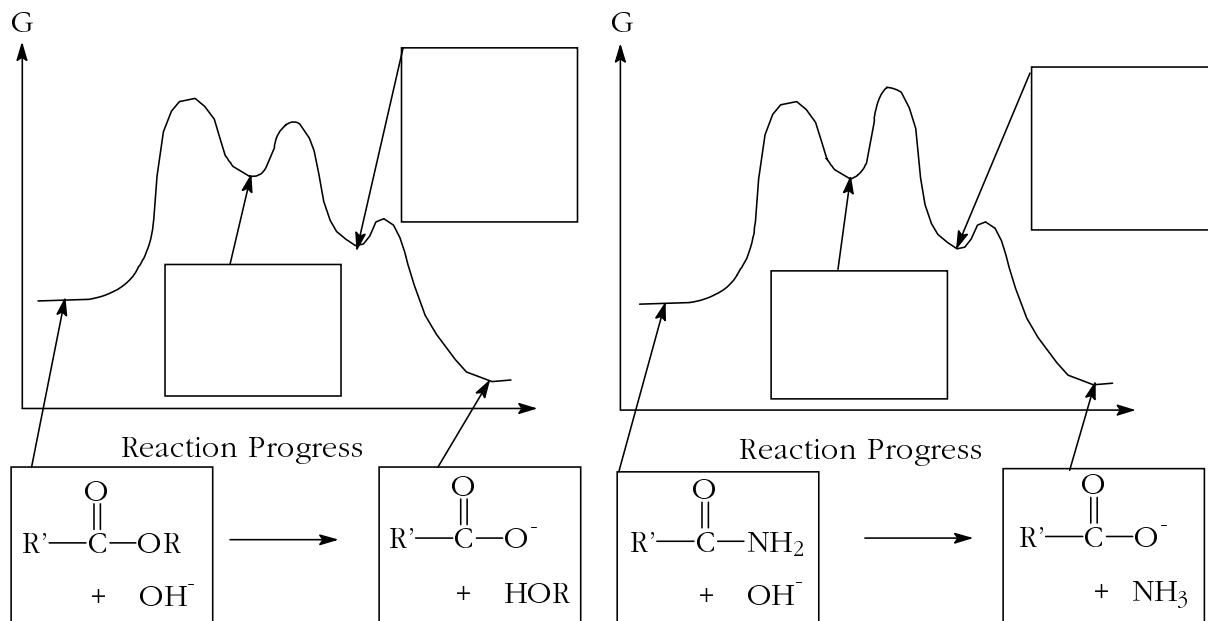
(d) Make 3-phenylpropanoic acid, Ph-CH<sub>2</sub>CH<sub>2</sub>COOH, starting from malonic ester (diethyl malonate), CH<sub>3</sub>CH<sub>2</sub>O-CO-CH<sub>2</sub>-CO-OCH<sub>2</sub>CH<sub>3</sub>. In addition to malonic ester you may use any materials you wish.

2. Mechanism.

(a) Show all steps in the mechanism of the following Fisher esterification:



- (b) (i) On the reaction coordinate diagrams below for the basic hydrolysis of esters and amides draw the structures of the intermediates in the boxes which are provided. [Note that the structures of reactants and products are already drawn on the diagrams.]



- (ii) Explain why the second transition state for the amide hydrolysis is higher in energy than the second transition state for the ester hydrolysis.

 Please return the pencil. 

Part I (100)\_\_\_\_\_

Part II

1. (10)\_\_\_\_\_

2. (15)\_\_\_\_\_

Total (125)\_\_\_\_\_