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**Department of Chemistry
SUNY/Oneonta**

**Chem 322 - Organic Chemistry II
Examination #3 - April 3, 1995**

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.

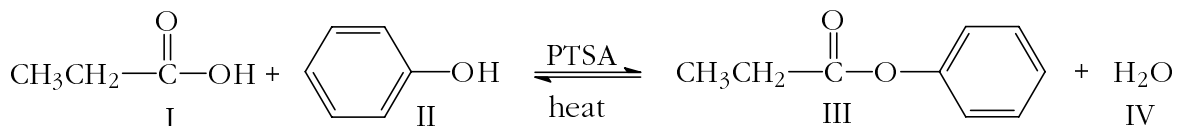
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30032201) and the test number (03); darken the appropriate bubbles under the entries, making dark black marks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

- $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-CO-NH}_2$ is
(a) 1-methylpropanamide, (b) 2-methylpropanamide, (c) butyramide,
(d) 1-methylpropanenitrile, (e) 2-methylpropanenitrile
- $\text{Ph-CO-OCH}_2\text{CH}_3$ is
(a) phenyl ethanoate, (b) phenyl acetate, (c) phenoyl ethylate,
(d) ethyl benzoate, (e) ethyl phenoate
- $\text{CH}_3\text{CH}_2\text{-CO-N}(\text{CH}_3)_2$ is
(a) ethyl propanamide, (b) α, α -dimethylpropanamide, (c) N, N-
dimethylpropanamide, (d) 1, 1-dimethylpropanamide, (e) propanamide
- $\text{CH}_3\text{-CO-CH}_2\text{-CO-OCH}_2\text{CH}_3$ is
(a) acetoacetic ester, (b) malonic ester, (c) Ester's ester
(d) acetoacetic anhydride, (e) malonic anhydride
- $\text{CH}_3\text{-CO-O-CO-CH}_3$ is
(a) acetic acetate, (b) ethyl acetate, (c) acetic anhydride, (d) formic anhydride,
(e) ethyl formate
- 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: H-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.
- A carboxylic acid is not usually converted to an amide by reacting it with an
amine, but, rather, is converted to an acid chloride which is, in turn, reacted with
an amine to give the amide. The reason for this is that

- (a) the carbonyl carbon of the acid is tetrahedral and less susceptible to nucleophilic attack by the amine than the trigonal carbonyl carbon of the acid chloride.
- (b) the basic amine deprotonates the carboxylic acid to produce the carboxylate anion which, owing to its negative charge, is not very susceptible to nucleophilic attack.
- (c) converting carboxylic acids to the chlorides is fun.
- (d) the acid chloride is more reactive because the -OH of the acid causes steric interference.
- (e) Bogus question, dude! Carboxylic acids are not converted to acid chlorides to make amides.

8.



Consider the above reaction and fill in the blanks to make the following statement correct.

If the above reaction is carried out by mixing I and II with a little *p*-toluenesulfonic acid (PTSA) catalyst in benzene and heating the mixture under reflux, ___ and ___ will predominate at completion; however, if a Dean-Stark tube is used, ___ and ___ will predominate.

- (a) I and II; III and IV, (b) III and IV; I and II, (c) I and III; II and IV, (d) II and III; I and IV
9. To prepare ethyl acetate, $\text{CH}_3\text{-CO-OC}_2\text{H}_5$, you could react
- (a) acetyl chloride with diethyl ether, (b) acetic anhydride with ethylene, (c) acetic acid with ethylene oxide, (d) acetic anhydride with ethanol, (e) acetic acid with ethane

10. To prepare $\text{CH}_3\text{-CO-N}(\text{C}_2\text{H}_5)_2$, you could react

- (a) $\text{CH}_3\text{-CO-Cl} + \text{H}_2\text{NC}_2\text{H}_5 + \text{CH}_2=\text{CH}_2$ (b) $\text{CH}_3\text{-CO-Cl} + \text{H}_2\text{NC}_2\text{H}_5 + \text{CH}_3\text{CH}_2\text{OH}$,
 (c) $\text{CH}_3\text{-CO-Cl} + 2 \text{H}_2\text{NC}_2\text{H}_5$, (d) $\text{CH}_3\text{-CO-Cl} + 2 \text{HN}(\text{C}_2\text{H}_5)_2$
 (e) $\text{CH}_3\text{-CO-Cl} + \text{H}_2\text{NC}_2\text{H}_5 + \text{H}_3\text{C-CH}_3$

Note: Ph- represents the phenyl group in some of the following questions.

11. Which of the following procedures give(s) benzyl alcohol, $\text{Ph-CH}_2\text{OH}$, starting with benzoic acid, Ph-CO-OH ?

- (a) 1. LiAlH_4 , ether; 2. H_3O^+ , (b) 1. DIBALH in toluene; 2. H_3O^+ ,
 (c) 1. $\text{LiAlH}(\text{O-}t\text{Bu})_3$, ether; 2. H_3O^+ , (d) a & b, (e) a & c

12. $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{N} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4, \text{ heat}}$ major organic product

- (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) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

13. $\text{CH}_3\text{-CH}_2\text{Br} + \text{Na}^+\text{CN}^- \longrightarrow$ major product

- (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

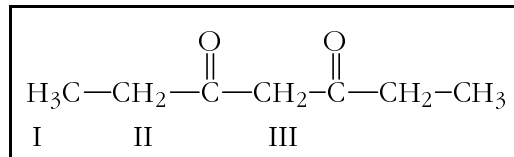
14. $(\text{Ph})_3\text{CBr} + \text{Na}^+\text{CN}^- \xrightarrow{\text{DMSO}}$ major product

- (a) $(\text{Ph})_2\text{C}=\text{CH}_2$, (b) $(\text{Ph})_2\text{C}=\text{CHCN}$, (c) $(\text{Ph})_3\text{CCN}$, (d) $(\text{Ph})_3\text{CCOOH}$

15. $\text{CH}_3\text{CH}_2\text{-CO-Cl} + (\text{Ph})_2\text{CuLi} \longrightarrow$ major product(s)

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

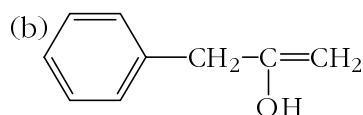
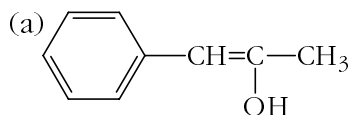
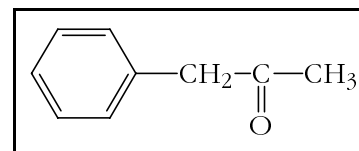
16. Rank the protons in 3,5-heptanedione in order of decreasing acidity (most acidic first).



- (a) I > II > III, (b) III > II > I,
 (c) II > III > I, (d) II > I > III
17.
$$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 \rightleftharpoons \text{H}_2\text{C}=\overset{\text{OH}}{\text{C}}-\text{CH}_3$$
- I II

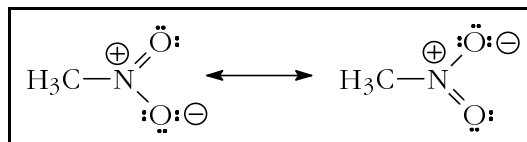
Which of the following statements is untrue in regard to the above reaction?

- (a) It is called a keto-enol tautomerization. (b) At equilibrium compound II predominates. (c) It is acid catalyzed. (d) It is base catalyzed. (e) Bogus question! All of the above statements are true.
18. Select the structure below that is the principal enol that would be in equilibrium with the phenylacetone shown to the right.



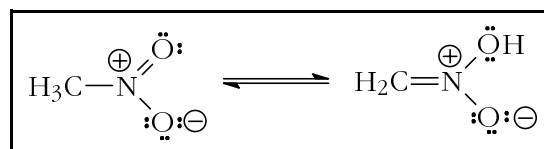
19. The structures shown to the right are

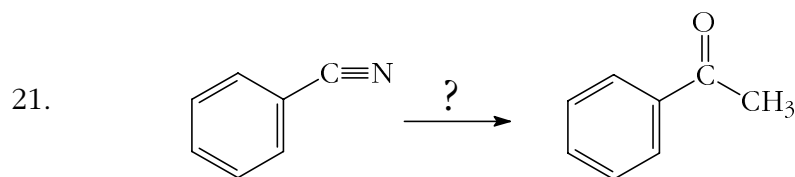
- (a) tautomers, (b) resonance structures,
 (c) enantiomers, (d) diastereomers,
 (e) none of the above.



20. The structures shown to the right are

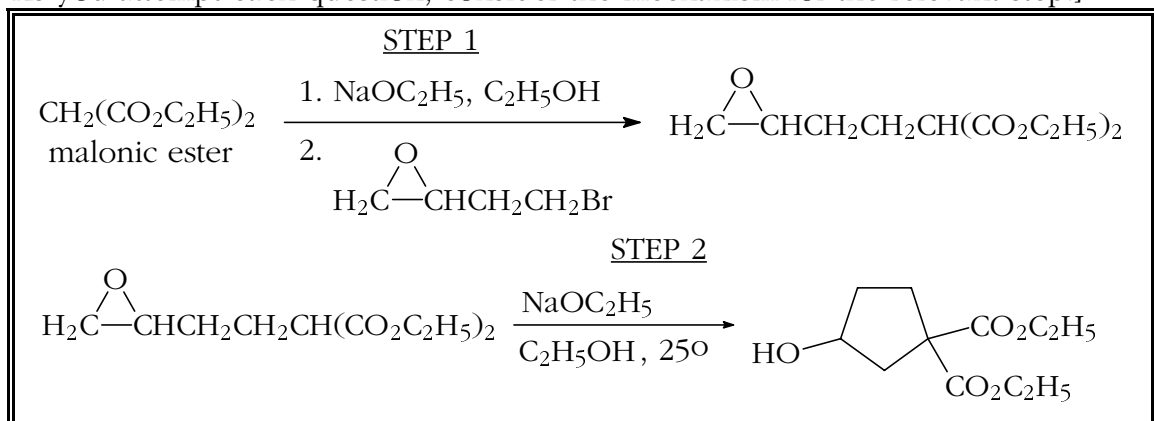
- (a) tautomers, (b) resonance structures,
 (c) enantiomers, (d) diastereomers,
 (e) none of the above.





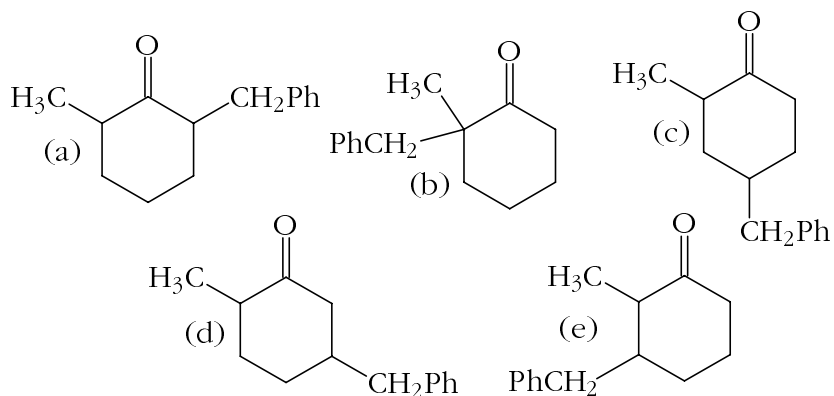
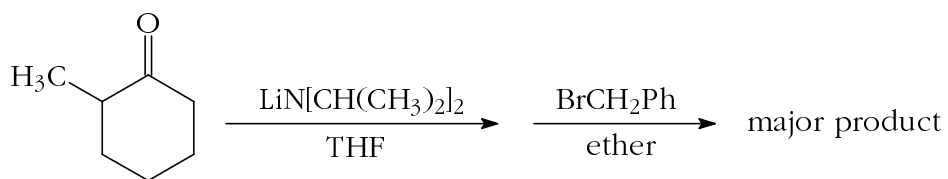
- (a) 1. CH₃MgBr, ether, 2. H₃O⁺, (b) 1. (CH₃)₂CuLi, ether, 2. H₃O⁺
 (c) CH₃OH, acid, heat, (d) acetyl chloride, then water

22-23. Consider the following two-step synthesis to answer questions 22 and 23. [Hint: As you attempt each question, consider the mechanism for the relevant step.]

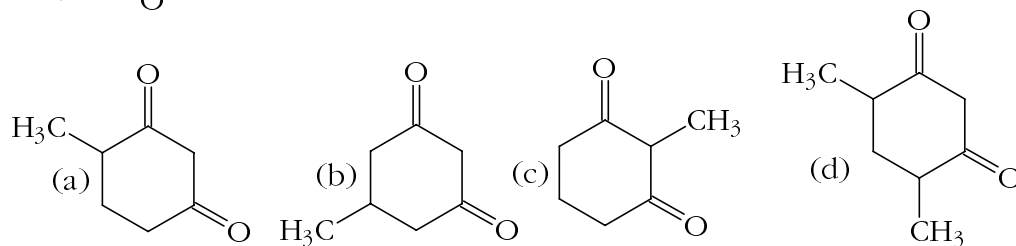
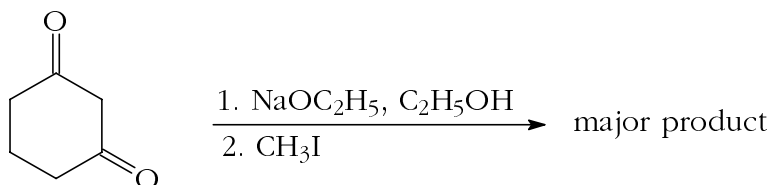


22. The carbon-carbon bond forming reaction in Step 1 is an example of
- (a) an *intramolecular* S_N2 reaction. (b) an *intermolecular* S_N2 reaction.
 (c) a carbonyl α-substitution reaction. (d) both b and c.
23. The carbon-carbon bond forming reaction in Step 2 is an example of
- (a) an *intramolecular* S_N2 reaction. (b) an *intermolecular* S_N2 reaction.
 (c) a pericyclic reaction. (d) an electrophilic addition to an epoxide.

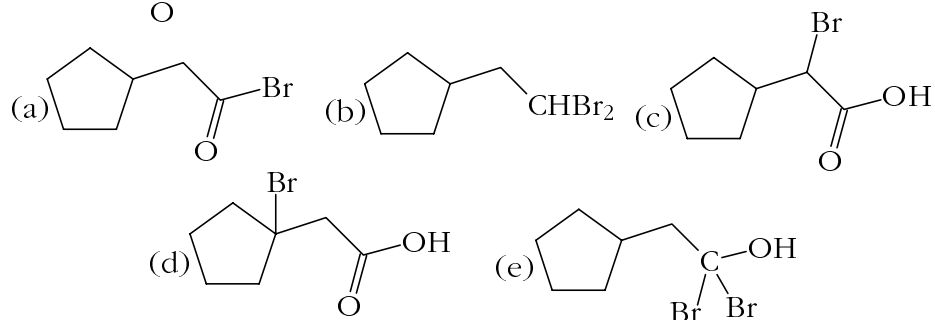
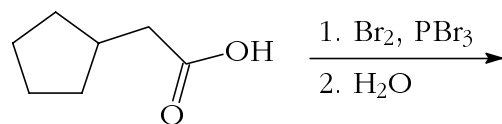
24.



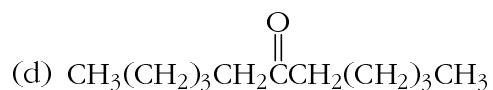
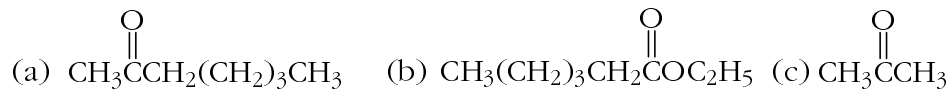
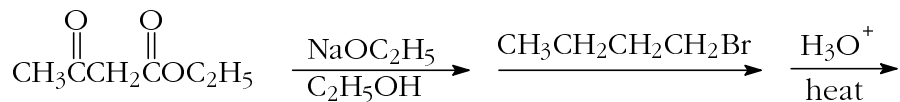
25.



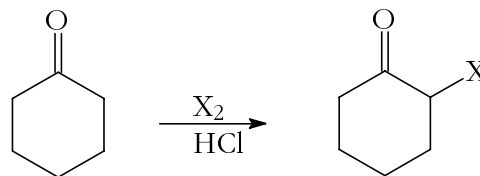
26.



27.

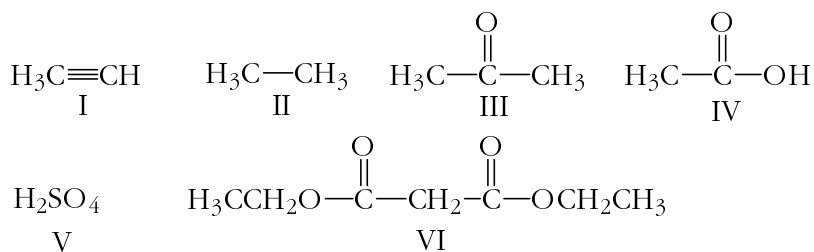


28. In the reaction shown to the right, which halogen would react fastest?



(a) Cl_2 , (b) Br_2 , (c) I_2 , (d) Chlorine, bromine, and iodine would react at about the same rate.

29. Rank the following compounds in order of decreasing acidity (most acidic first).

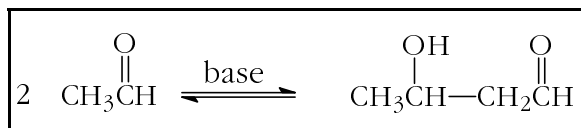


(a) $\text{I} > \text{II} > \text{III} > \text{IV} > \text{V} > \text{VI}$, (b) $\text{VI} > \text{V} > \text{IV} > \text{III} > \text{II} > \text{I}$,
 (c) $\text{V} > \text{I} > \text{IV} > \text{VI} > \text{III} > \text{II}$, (d) $\text{IV} > \text{V} > \text{I} > \text{VI} > \text{III} > \text{II}$,
 (e) None of the above answers is correct.

30. Carbonyl condensation reactions take place between two carbonyl components and involve a combination of [1] nucleophilic [2] addition and [3] beta-[4] substitution steps.

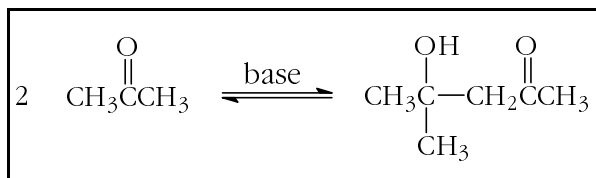
- (a) The above statement is true as written.
 (b) The above statement would be true if [1] were changed from nucleophilic to electrophilic.
 (c) The above statement would be true if [2] were changed from addition to substitution.
 (d) The above statement would be true if [3] were changed from beta to alpha.
 (e) The above statement would be true if [4] were changed from substitution to addition.

31. The reaction shown to the right is an example of a(n)



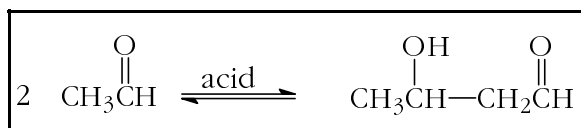
- (a) Claisen condensation. (b) aldol reaction. (c) Chan reaction. (d) Garcia-Galan reaction. (e) Kotkin-Reingold reaction. (f) Blessin reaction. (g) Wade-Young reaction.

32. The reaction shown to the right does not give as good a yield as the similar reaction shown in question #31. A reasonable explanation for this would be that



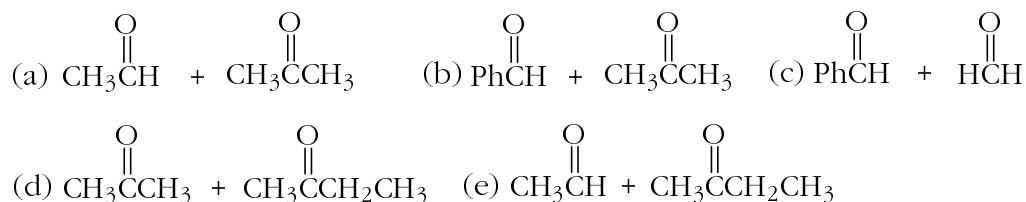
- (a) the aldehydic proton is more acidic than the methyl protons.
 (b) the product formed from acetone undergoes a subsequent reaction, thus reducing the yield.
 (c) a steric factor is involved as a result of the intermediate (and product) being more crowded in these reactions and the ketone case is 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 2.

33. In the reaction shown to the right, the nucleophile is

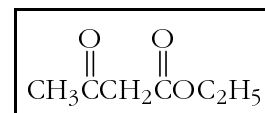


- (a) $\text{CH}_3\overset{\text{O}}{\parallel}\text{CH}$ (b) $\text{CH}_3\overset{\oplus}{\text{C}}\text{H}\text{OH}$ (c) $\text{CH}_3\overset{\ominus}{\text{C}}\text{H}\text{OH}$ (d) $\text{CH}_2\overset{\ominus}{\text{C}}\text{H}\text{O}$ (e) $\text{CH}_2=\overset{\text{OH}}{\text{C}}\text{H}$
34. Which of the following describe common situations encountered with aldol reactions?

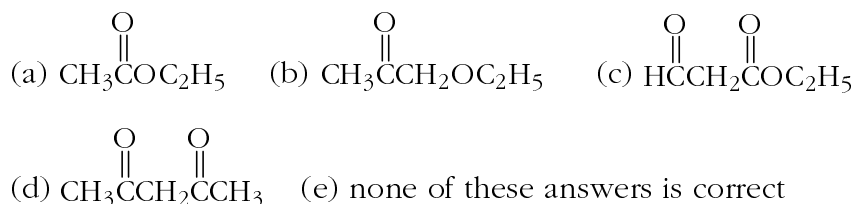
- (a) Product reverts to reactant. (b) Product undergoes a spontaneous dehydration, producing a conjugated enone. (c) Product undergoes a spontaneous dehydration, producing a non-conjugated enone. (d) Product undergoes reduction, producing a diol. (e) a & b, (f) a & c, (g) b & c, (h) a, b & c.
35. Which of the following pairs of compounds might be a reasonable choice for an attempt at a "mixed" or "crossed" aldol condensation?



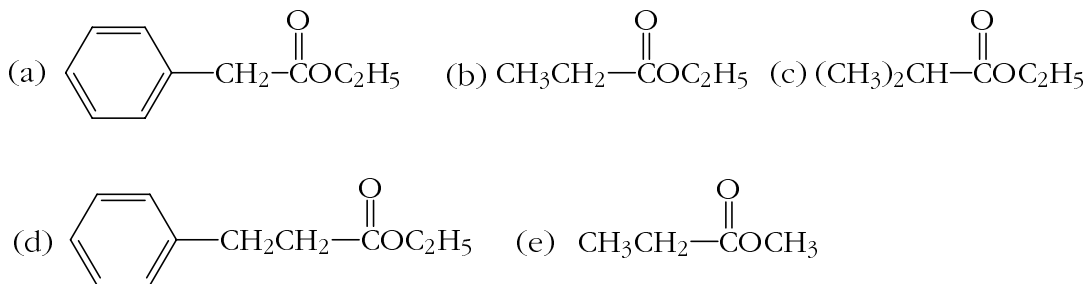
36. To prepare acetoacetic ester, which of the following compounds could you use in a Claisen condensation?



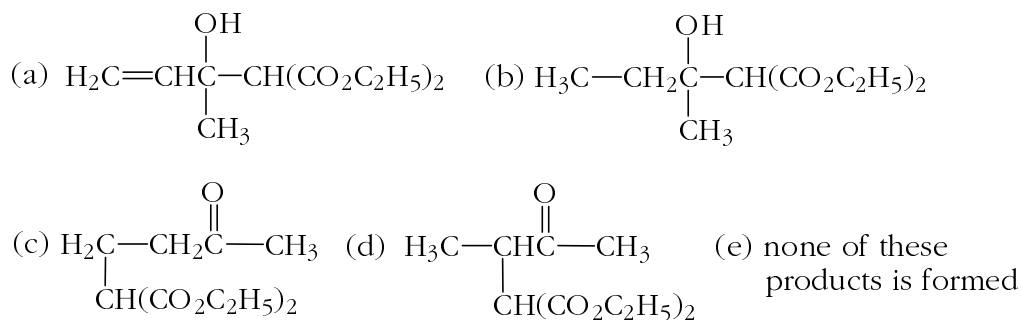
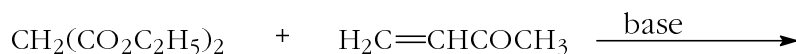
Acetoacetic Ester



37. An intramolecular Claisen condensation is known as a
- (a) Perkin reaction. (b) Knoevenagel reaction. (c) Michael reaction.
 (d) Dieckmann reaction. (e) Lagier reaction. (f) Muto reaction. (g) Obermeyer reaction. (h) Osterhoudt reaction.
38. Which of the following compounds would not give a good yield in a Claisen condensation?



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



40. With the possible exception of Chem 221, is Chem 322 the greatest course you ever took?
- (a) yes (I want the 2.5 point gift). (b) no (I don't want the 2.5 point gift).

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.

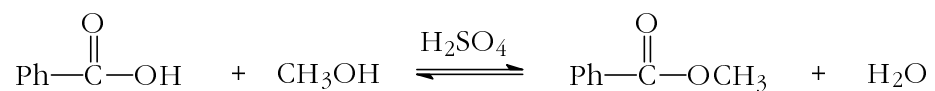
(a) Make butyl butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, using 1-butanol as your only source of carbon. You may use any inorganic reagents and solvents you need.

(b) Make acetophenone (phenyl methyl ketone), $\text{Ph}-\text{CO}-\text{CH}_3$, starting from benzonitrile, $\text{Ph}-\text{CN}$. In addition to benzonitrile, you may use any materials you wish.

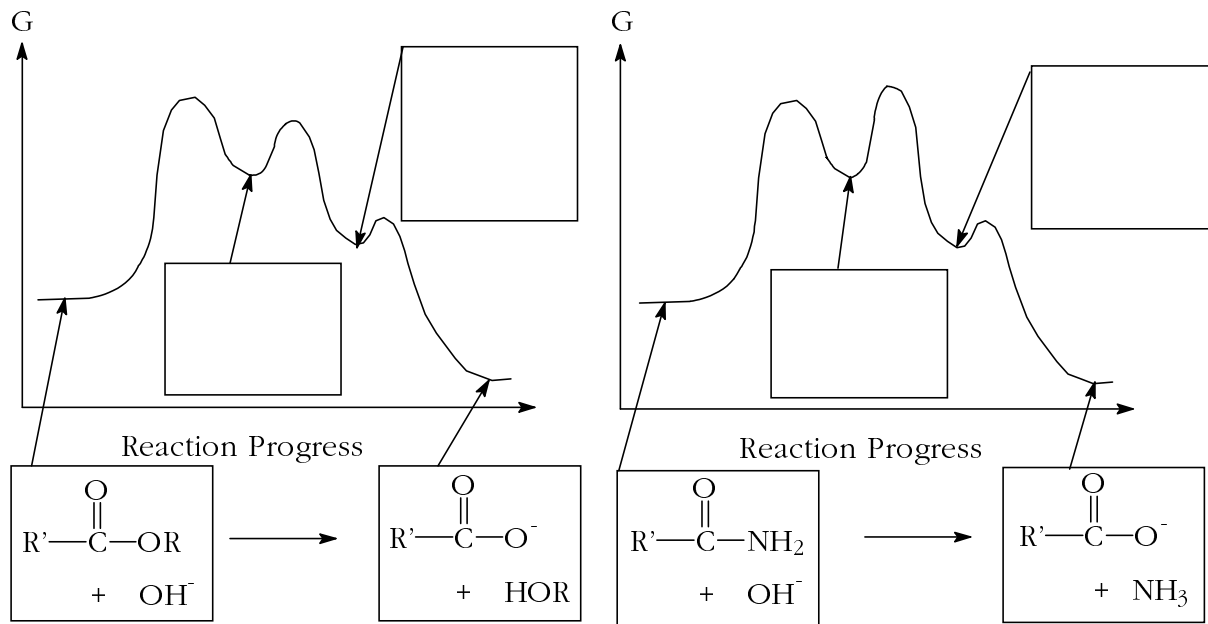
(c) Make 3-phenylpropanoic acid, $\text{Ph-CH}_2\text{CH}_2\text{COOH}$, starting from malonic ester (diethyl malonate), $\text{CH}_3\text{CH}_2\text{O-CO-CH}_2\text{-CO-OCH}_2\text{CH}_3$. In addition to malonic ester you may use any materials you wish.

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 

Part I (100)_____

Part II

1. (15)_____

2. (10)_____

Total (125)_____