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Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #3 - March 31, 2003 - **ANSWERS**

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 OSC student (or 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 (if you use your OSC number do not darken a bubble under the A at the beginning of the number).

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

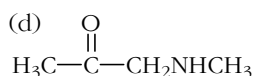
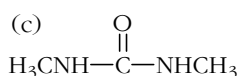
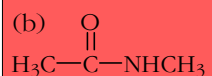
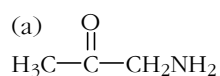
Answer all questions. The questions on Part I are worth 2 points each.

You have 90 minutes. Good luck!

Explanations are in red type.

Answers are highlighted in red.

1. The structure for N-methylacetamide is



2. Ph-CO-OCH₂CH₃ is

(a) phenyl ethanoate, (b) phenyl acetate, (c) phenoyl ethylate,
(d) ethyl benzoate, (e) ethyl phenoate

3. CH₃CH₂O-CO-CH₂-CO-OCH₂CH₃ is

(a) acetoacetic ester, (b) malonic ester, (c) Ester's ester
(d) acetoacetic anhydride, (e) malonic anhydride

4. CH₃-CO-O-CO-CH₃ is

(a) acetic acetate, (b) ethyl acetate, (c) acetic anhydride, (d) formic anhydride,
(e) ethyl formate

5. Rank the following compounds in order from most reactive to least reactive toward nucleophilic acyl substitution:

I: (CH₃)₂CH-CO-Cl, II: (CH₃)₂CH-CO-OCH₃, III: (CH₃)₂CH-CO-NH₂, IV: CH₃-CO-NH₂

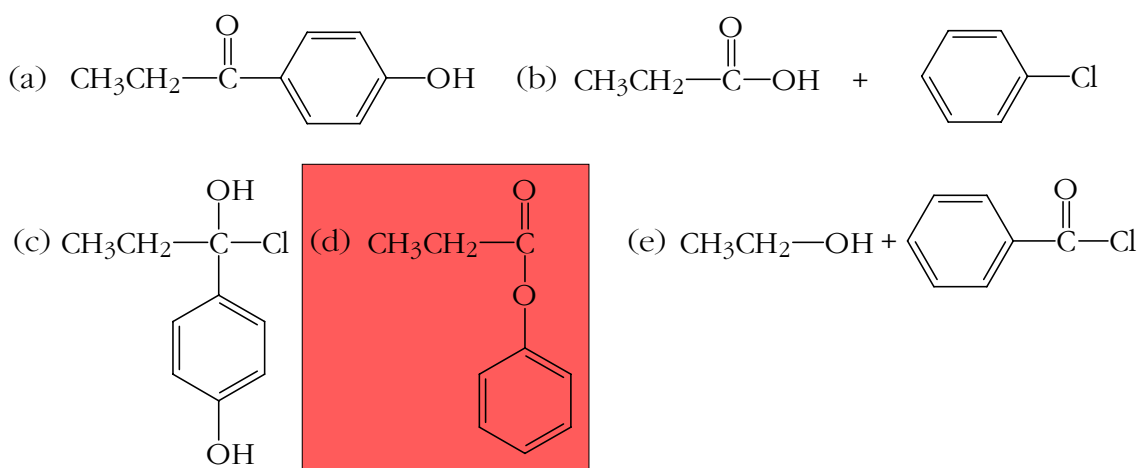
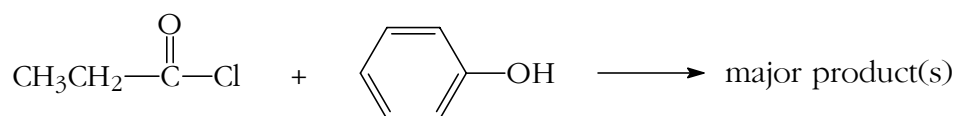
(a) I > II > III > IV, (b) IV > III > II > I, (c) II > IV > I > III, (d) IV > III > I > II,
(e) I > II > IV > III

I is an acid chloride, II is an ester, and III and IV are amides. The order of reactivity is most influenced by the functional group involved: I>II>III,IV. IV is more reactive than III because the transition state of the rate limiting step is more sterically hindered in the bulkier III than in IV.

6. The behavior of esters and ketones in a reaction with a nucleophile is different because

(a) the carbonyl carbon of the ketone is more positive.
(b) the two oxygens of the ester sterically hinder nucleophilic attack.
(c) the ester cannot form a tetrahedral intermediate.
(d) there is a reasonable leaving group in the ester.
(e) the ketone is not easily oxidized.

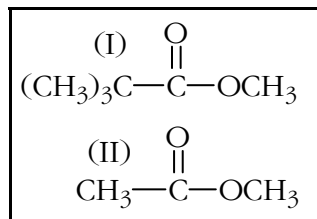
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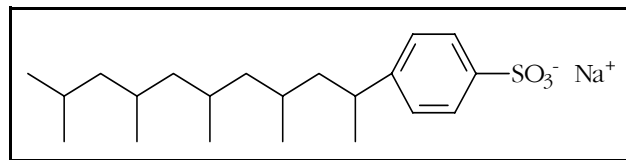
The following three questions consist of a **statement** followed by the connecting word **because** followed by a **reason**. For each question choose the correct description of the statement and reason from the list below --

- (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.
8. Under basic conditions ($\text{H}_2\text{O}/\text{NaOH}$) compound I on the right will hydrolyze more quickly than II **because** the transition state of the rate limiting step is more crowded for I than for II.

(d)



9. Branched alkylbenzenesulfonates, eg the compound to the right, are widely employed as detergents **because** they are inexpensive to make.



A Branched Alkylbenzenesulfonate.

(d)

10. A Dean-Stark apparatus is sometimes used in Fisher esterification syntheses **because** equilibrium constants in these reactions are typically about 1 and the Dean-Stark tube removes water thereby driving the reaction in the forward direction.

(a)

11. Which of the following procedures give(s) benzyl alcohol, Ph-CH₂OH, starting with methyl benzoate, Ph-CO-OCH₃?

(a) 1. DIBAH (diisobutylaluminum hydride) in toluene, -78°C; 2. H₃O⁺,

(b) H₂, Pd/BaSO₄, (c) 1. LiAlH₄, ether; 2. H₃O⁺,

(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) CH₃CH₂CH₂CH₂-NH₂, (b) CH₃CH₂CH₂CH₂-N=N-CH₂CH₂CH₂CH₃

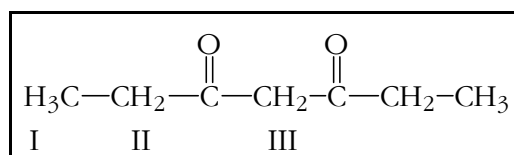
(c) CH₃CH₂CH₂CO-NH₂, (d) CH₃CH₂CH₂CH₂-NO₂, (e) CH₃CH₂CH₂COOH

13. (CH₃)₃CBr + Na⁺CN⁻ \longrightarrow major product

(a) (CH₃)₃CCN, (b) (CH₃)₂C=CHCN, (c) (CH₃)₂C=CH₂, (d) (CH₃)₃CCOOH

(e) none of the above

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

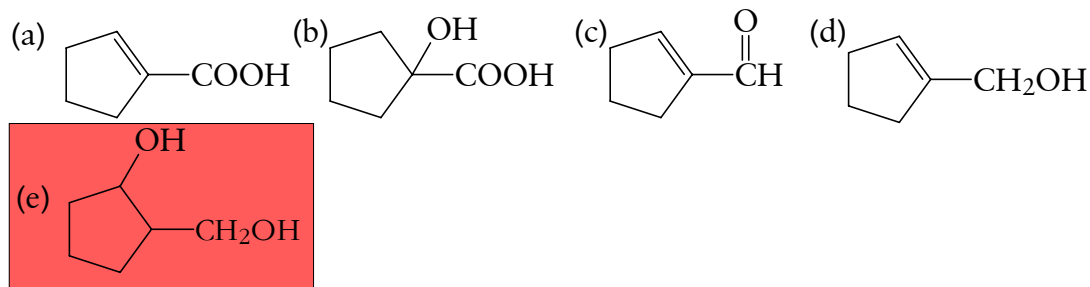
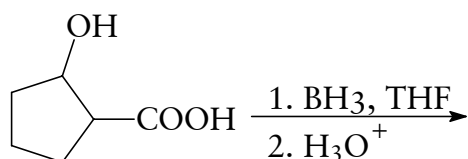


(a) I > II > III, (b) III > II > I,

(c) II > III > I, (d) II > I > III

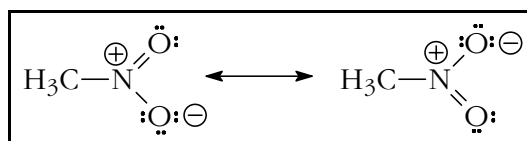
The I protons have no adjacent carbonyl group, the II protons have one, and the III protons have two. The carbonyl groups stabilize the negative charge on the anion through resonance: 2 is better than 1 and 1 is better than none.

15. Select the major product of the following reaction.



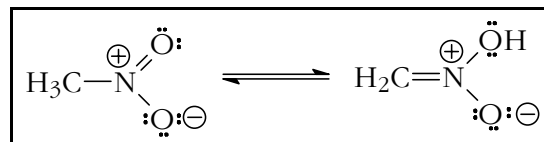
16. The structures shown to the right are

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



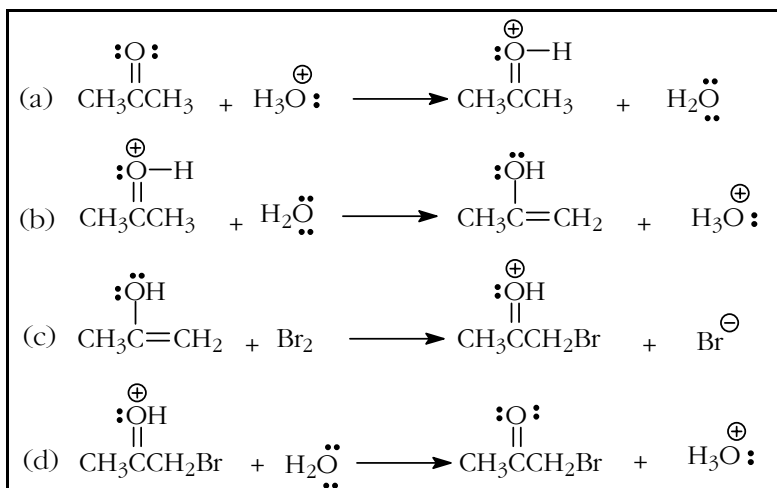
17. The structures shown to the right are

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



When drawing resonance structures we move (usually unshared and π) electrons to draw different Lewis structures of the *same* compound. Tautomers are isomers that are in (usually fairly rapid) equilibrium with each other.

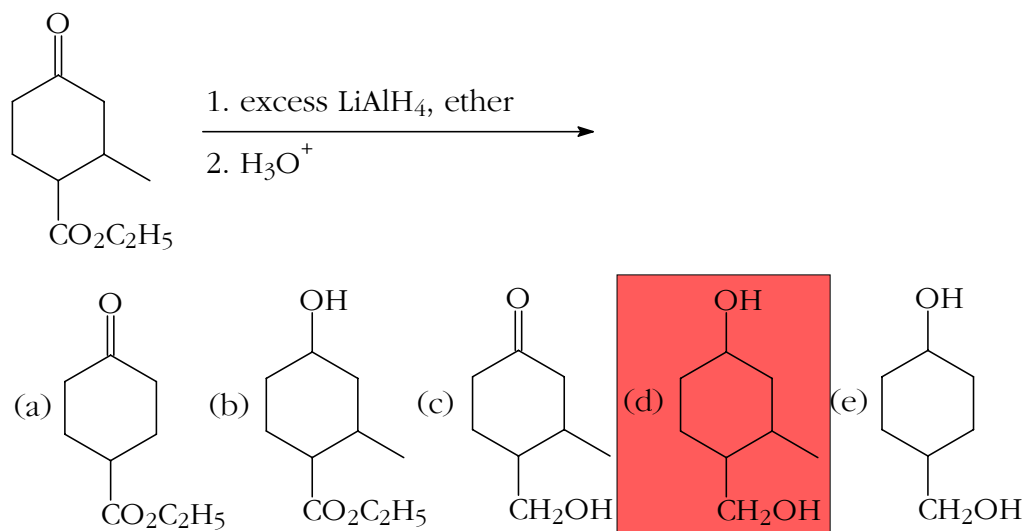
For questions 18 and 19 consider the mechanism for the acid-catalyzed bromination of acetone shown to the right. [Note: not all resonance structures are shown.]



18. Which of the steps shown is incorrect?
 (a), (b), (c), (d), **(e) All of the steps are essentially correct.**
19. Which of the steps is the *slow* step in the mechanism?
 (a), **(b)**, (c), (d), (e) There is no slow step.

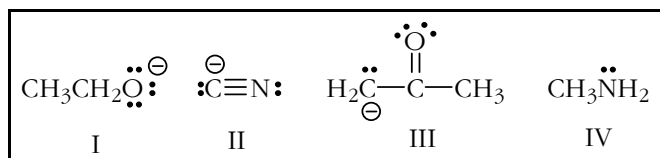
Transfer of a proton off a carbon is frequently a slow process while transfer of a proton off of oxygen or nitrogen is usually fairly fast.

20. Which of the following compounds will react with iodine in aqueous sodium hydroxide solution to give a precipitate of iodoform, CHI_3 ?
 (a) PhCHO , **(b) PhCOCH_3** , (c) $\text{CH}_3\text{CH}_2\text{CHOHCH}_2\text{CH}_3$, (d) $\text{CH}_3\text{CH}_2\text{CHO}$
21. One of the principal products of the following reaction would be:



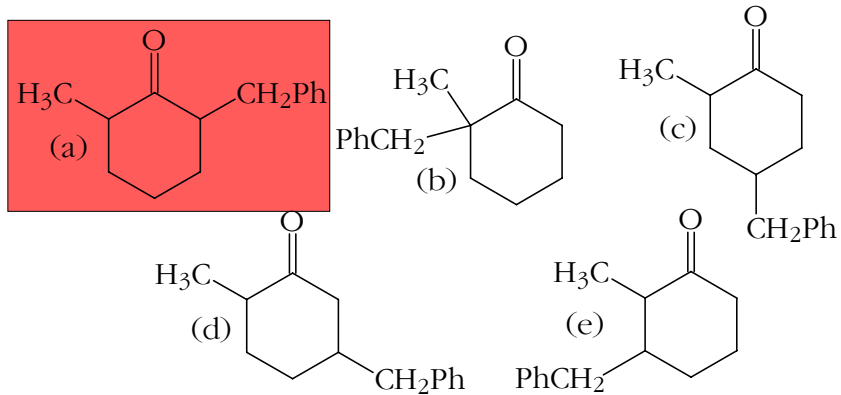
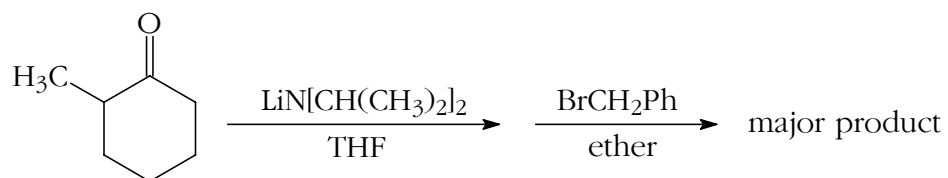
22. Some nucleophiles are said to be *ambident*. Which of the following nucleophiles are in this category?

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

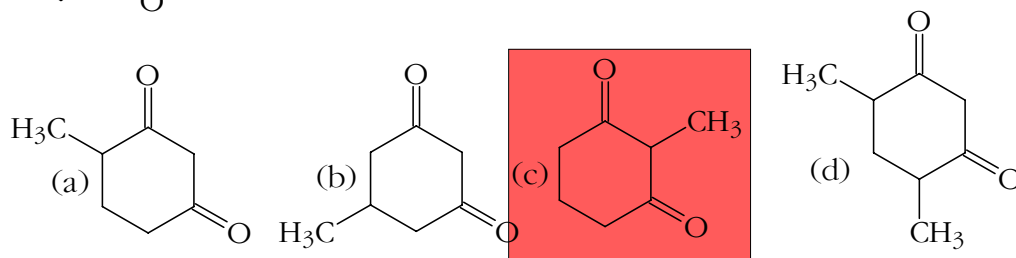
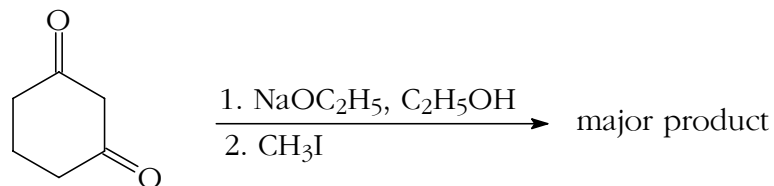


Ambident (literally, two teeth) means that there are two atoms that can use a pair of electrons to make a nucleophilic attack.

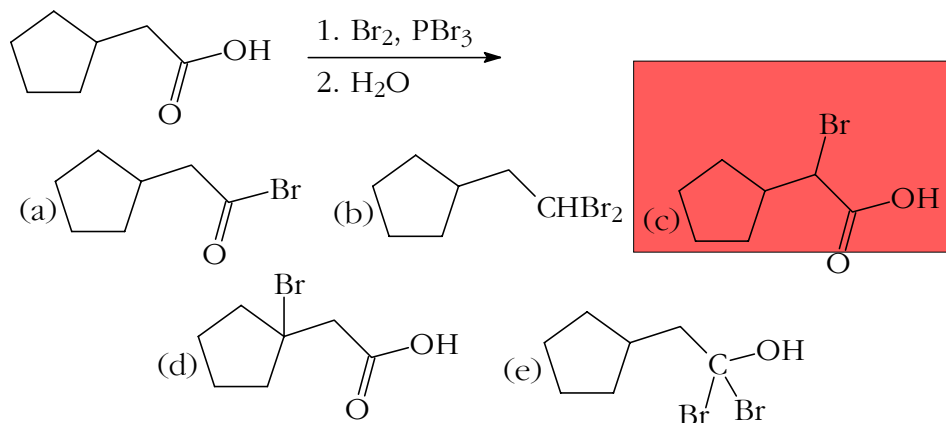
23. Select the compound that would be formed in greatest amount.



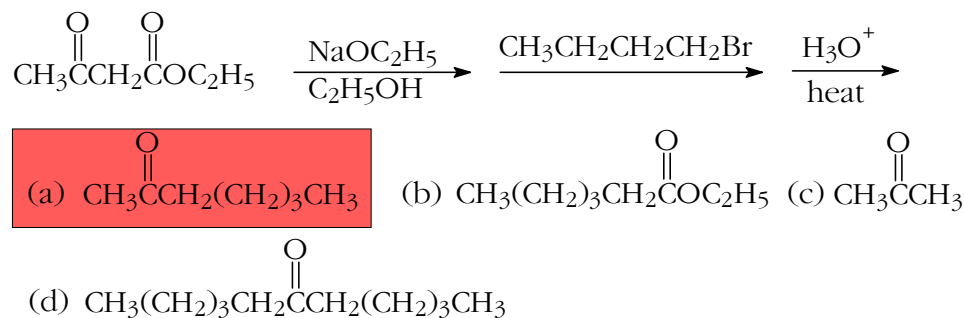
24.



25. Select the product that would be formed in greatest amount. **Hell-Volhard-Zelinskii reaction.**



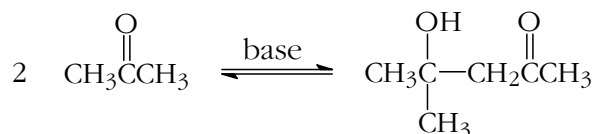
26. **Acetoacetic ester synthesis.**



27. The reaction shown to the right is an example of a(n)
- $$2 \text{ CH}_3\text{CHO} \xrightleftharpoons{\text{base}} \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$$

- (a) Claisen condensation. **(b) aldol reaction.**
 (c) demerol reaction. (d) Knoevenagel reaction. (e) Diels-Alder reaction.
In fact the common name for the product here is aldol.

28. The reaction shown to the right does not give as good a yield as the similar reaction shown in question #27. 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.

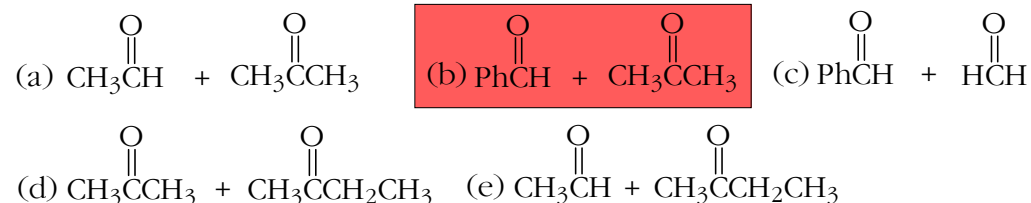
(d) the ketone has 6 acidic hydrogens while the aldehyde has only 3.

(e) Trick question, dude! Like, this reaction gives a better yield than the one in question #27.

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

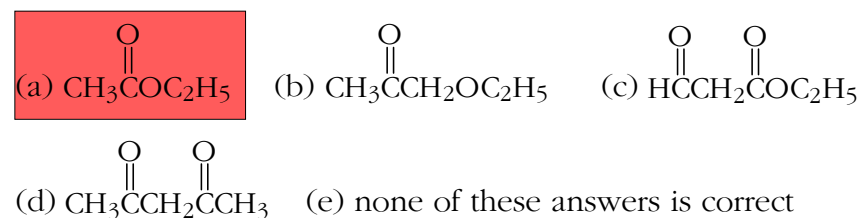
(a) Product reverts to reactant. (b) Product undergoes a spontaneous dehydration, producing a conjugated enone. (c) Product undergoes a spontaneous dehydration, producing a non-conjugated enone. (d) Product undergoes reduction, producing a diol. (e) a & b. (f) a & c. (g) b & c. (h) a, b & c.

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

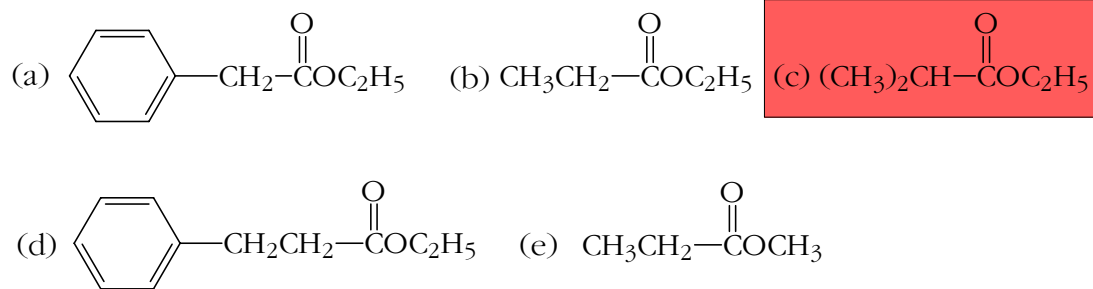


Crossed aldol reactions typically work best when *one* of the components does not have an α -hydrogen and, therefore, cannot form an enolate anion. This is true for (b), where benzaldehyde does not have an α -hydrogen, while acetone does. So, acetone forms the enolate anion which attacks benzaldehyde. The situation in (c) is that neither component has an α -hydrogen so neither can form an enolate anion. In cases (a), (d), and (e) both components have α -hydrogens.

31. To prepare acetoacetic ester (ethyl acetoacetate), which of the following compounds could you use in a Claisen condensation?

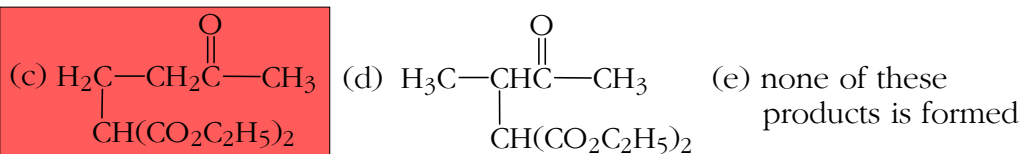
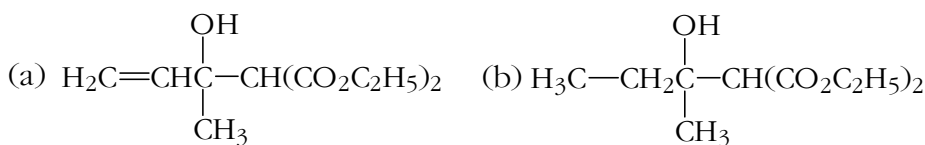
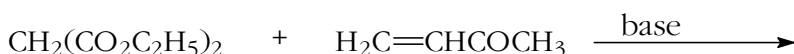


32. Which of the following compounds would not give a good yield in a Claisen condensation?



The issue here is that the ester that is used in a Claisen condensation needs two α -hydrogens because equilibrium does not favor the β -ketoester product; however, the deprotonated β -ketoester (formed by removal of the second α -hydrogen) is favored.

33. Select the product that is formed in the following Michael addition.



34. 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.

35. Which of the following bases would not convert acetone, essentially completely, to its enolate anion?

(a) butyllithium, (b) sodium hydride, (c) lithium diisopropylamide, (d) sodium hydroxide

Sodium hydroxide is the weakest base of the bunch and is a weaker base than the enolate anion formed from acetone. The others are stronger bases than the enolate anion of acetone.

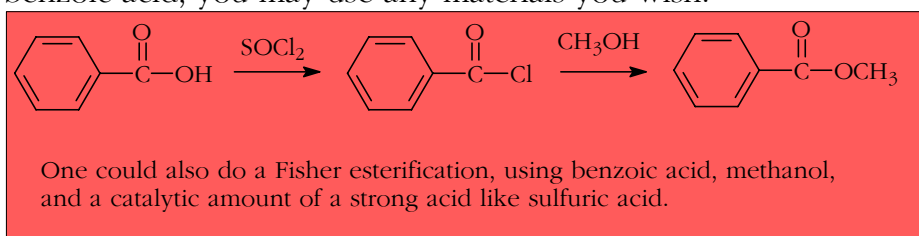
Do Not Detach The Following Sheets From The Rest Of The Exam

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.

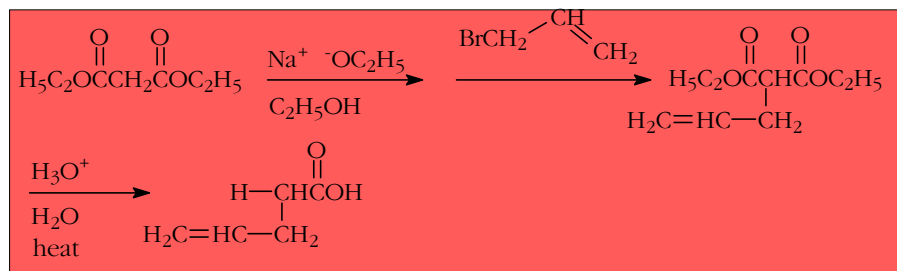
1. Synthesis. Outline the following syntheses. Show all reagents and any important conditions. Do not show mechanisms or balance equations.

(a) Make methyl benzoate, Ph-CO-OCH₃, starting from benzoic acid. In addition to benzoic acid, you may use any materials you wish.



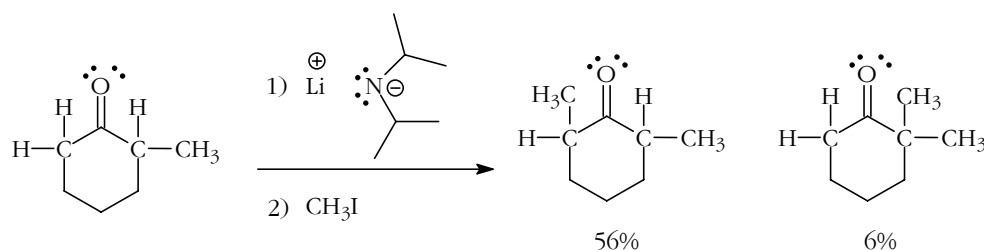
The Fisher esterification method was the one you used in lab last semester.

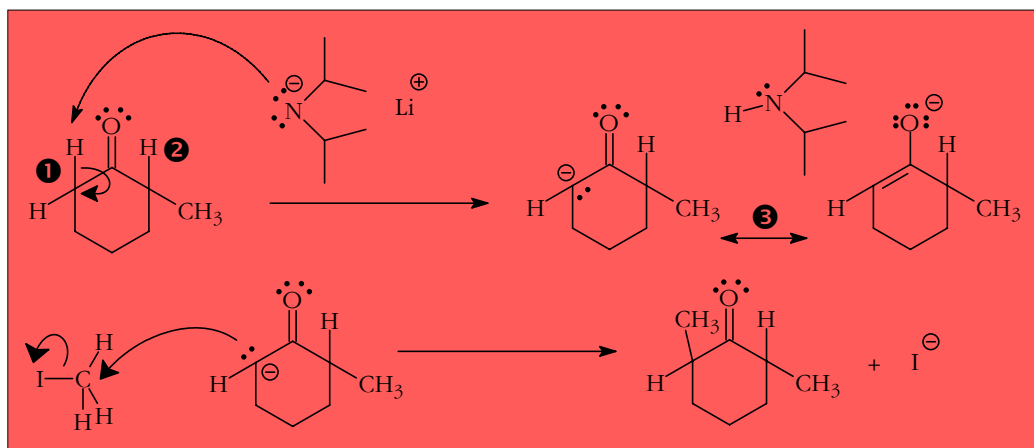
(d) Outline a synthesis of 4-pentenoic acid, CH₂=CHCH₂CH₂COOH, starting from malonic ester (diethyl malonate), CH₃CH₂O-CO-CH₂-CO-OCH₂CH₃. In addition to malonic ester you may use any materials you wish.



2. Mechanism.

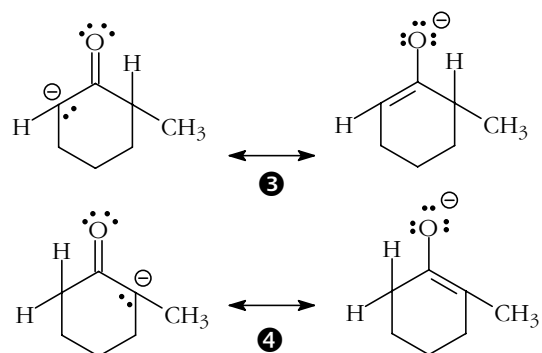
(a) Show all steps in the mechanism of the following enolate methylation reaction sequence leading to the major product (2,6-dimethylcyclohexanone). Be sure to show relevant resonance structures of intermediates.





(b) Based on the mechanisms for the formation of the major (56%) and minor (6%) products above (which are the same except for the hydrogen replaced), explain why the amount of 2,6-dimethylcyclohexanone produced is about 10 times greater than that of 2,2-dimethylcyclohexanone.

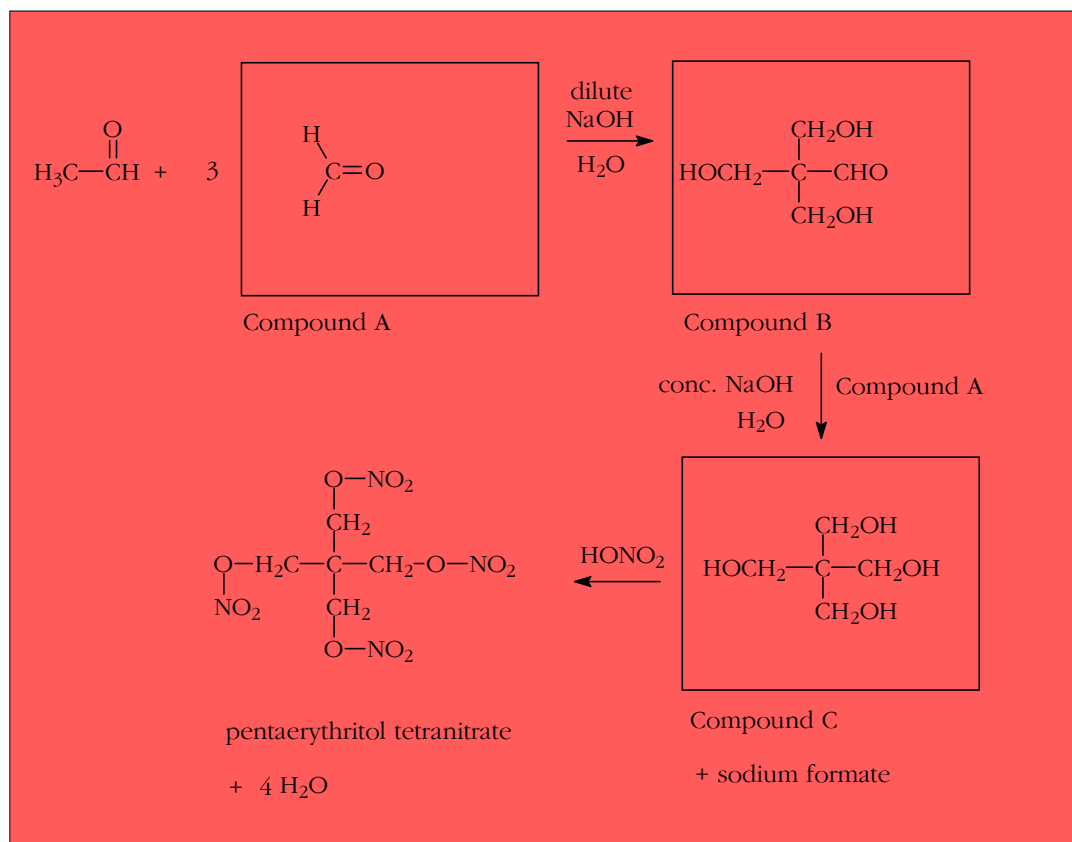
The first step in this mechanism is the rate limiting step. In this step enolate anion **3** is formed by removal of a proton **1** from the ketone reactant to form the major product. For the minor product to form, proton **2** would be removed to form enolate anion **4**. Since the ratio of major product to minor product is about 9 to 1, the rate of formation of **3** to **4** is also about 9 to 1. Why is this? Because the transition state leading to the formation of **3** is lower in energy than that of **4**. By the Hammond Postulate, the transition state energies should be reflected in the energies of the enolate anions themselves. Thus, **3** is more stable than **4**. This is reasonable in that **4** has some negative charge on C-2, while **3** has some negative charge on C-6. The negative charge on C-2 is intensified by the attached methyl group, raising the energy of **4**. There is no similar alkyl group attached to C-6 in **3**. In other words, proton **1** is more acidic than protons **2** owing to the electron donating methyl group.



3.

Roadmap.

One mole of acetaldehyde reacts with 3 moles of Compound A. This constitutes a sequence of three crossed aldol reactions that produce one mole of compound B. Concentrated aqueous sodium hydroxide and one mole of Compound A are added to Compound B and the mixture is heated, giving Compound C and sodium formate. A mole of compound C reacts with 4 moles of nitric acid to produce a nitrate tetraester, pentaerythritol tetranitrate, which is used in medicine as a vasodilator and to make Primacord fuse. Compounds A and B each give a positive Tollen's test; C does not. Draw the structures of A, B, and C.



The chemically astute among you might have used the clue, "A mole of compound C reacts with 4 moles of nitric acid to produce a nitrate tetraester, pentaerythritol tetranitrate," to get at the structure of compound C. You would need to recall that when esters form from alcohols and acids, the acid loses an OH, the alcohol loses an H, and the ester bond forms. If you were less astute, the structure of the final product should have told you that compound C has five carbons and the 2,2-dimethylpropyl skeleton structure.

Since the final product has 5 carbons and the starting material, acetaldehyde, has two, three carbons need to be added. The 3 molecules of compound A will likely do this – one carbon per molecule. Since this reaction is a crossed aldol, compound A must be an aldehyde or ketone. Since it has one carbon, it must be formaldehyde. Another clue is the sodium formate formed in the reaction that converts B to C, a Cannizzaro reaction.

Part I (70)	_____
Part II	_____
1. (10)	_____
2. (10)	_____
3. (10)	_____
Total(100)	_____