Name____________________________

# Department of Chemistry
# SUNY/Oneonta

# Chem 322 - Organic Chemistry II
# Examination #3 - April 2, 2001

## 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 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. $CH_3$-CH($CH_3$)-CO-$NH_2$ is

   (a) an acid chloride, (b) an ester, (c) an amine,
   (d) an amide, (e) a nitrile

2. Ph-CO-$OCH_2CH_3$ is

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

3. $CH_3CH_2$-CO-$NHCH_3$ is

   (a) methyl propanamide, (b) $\alpha$-methylpropanamide, (c) N-methylpropanamide,
   (d) 1-methylpropanamide, (e) propanamide

4. $CH_3CH_2O$-CO-$CH_2$-CO-$CH_3$ is

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

5. $CH_3$-CO-O-CO-$CH_3$ is

   (a) an ester, (b) an acid anhydride, (c) a diketone, (d) an epoxide,
   (e) None of the previous answers is correct.

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

   I: $(CH_3)_2CH$-CO-$OCH_3$, II: $CH_3$-CO-$OCH_3$, III: $(CH_3)_2CH$-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. 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 nucleophlic attack by the amine than the trigonal carbonyl carbon of the acid chloride.

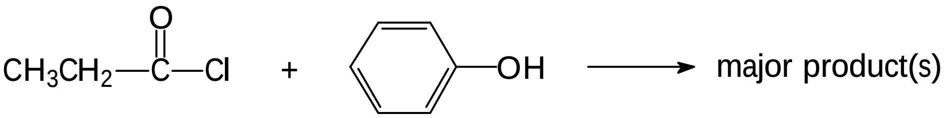
   (b) the basic amine deprotonates the carboxylic acid to the carboxylate anion which, owing to its negative charge, is not very susceptible to nucleophilic attack.

   (c) converting carboxylic acids to the chlorides is fun.

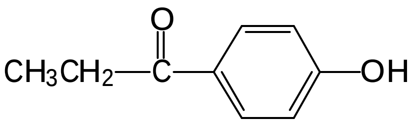
   (d) the acid chloride is more reactive because the -OH of the acid causes steric interference.

   (e) Bogus question, dude! Carboxylic acids are not converted to acid chlorides to make amides.

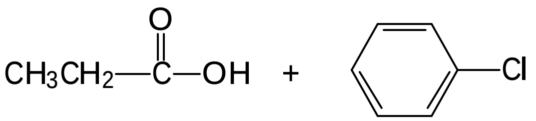
8.



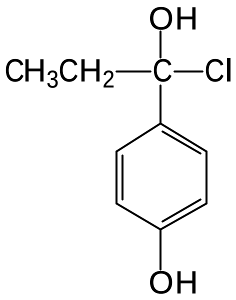
(a)



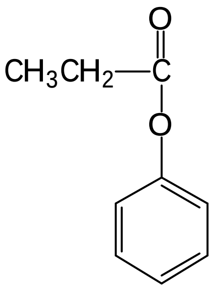
(b)



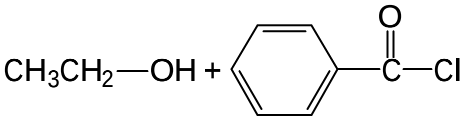
(c)



(d)



(e)



9. To prepare ethyl acetate, $CH_3$-CO-$OC_2H_5$, you could react

(a) acetyl chloride with ethanol, (b) acetic anhydride with ethylene,
(c) acetic acid with ethylene oxide, (d) acetyl chloride with diethyl ether,
(e) acetic acid with ethane

10. To prepare $CH_3$-CO-$N(C_2H_5)_2$, you could react

(a) $CH_3$-CO-Cl + $H_2NC_2H_5$ + $CH_2$=$CH_2$ (b) $CH_3$-CO-Cl + $H_2NC_2H_5$ + $CH_3CH_2OH$,
(c) $CH_3$-CO-Cl + 2 $H_2NC_2H_5$, (d) $CH_3$-CO-Cl + 2 $HN(C_2H_5)_2$
(e) $CH_3$-CO-Cl + $H_2NC_2H_5$ + $H_3C$-$CH_3$

11. Which of the following procedures give(s) benzyl alcohol, Ph-$CH_2OH$, starting with methyl benzoate, Ph-CO-$OCH_3$?

(a) $Na_2Cr_2O_7$, (b) $H_2$, Pd/$BaSO_4$, (c) 1. $LiAlH_4$, ether; 2. $H_3O^+$, (d) a & b, (e) a & c

12. The reaction in which two molecules of ethyl acetate, $CH_3COOCH_3$, react in the presence of base to produce one molecule of ethyl acetoacetate, $CH_3COCH_2COOCH_3$, is known as the ______ reaction.

(a) Lord, (b) Balogun, (c) Claisen, (d) Cannizarro, (e) Dean-Stark

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

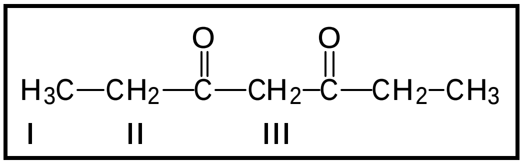
(a) the carbonyl carbon of the aldehyde is more positive.
(b) the bulky chlorine sterically hinders nucleophilic attack.
(c) the acid chloride cannot form a tetrahedral intermediate.
(d) there is a good leaving group in the acid chloride.
(e) the aldehyde has a readily oxidizable hydrogen.

14. $CH_3CH_2\text{-CO-Cl} + (Ph)_2CuLi \longrightarrow$ major product(s)

(a) $CH_3CH_2\text{-CO-Ph}$, (b) $CH_3CH_2\text{-C(OH)}Ph_2$, (c) $CH_3CH_2\text{-CCl(OH)Ph}$
(d) a & b, (e) b & c

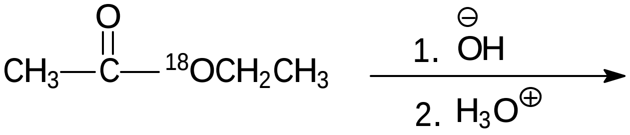
15. Rank the protons in 3,5-heptanedione in order of decreasing acidity (most acidic first).

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

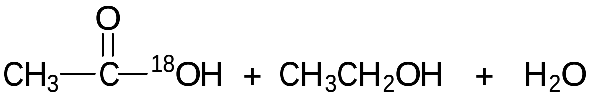


$H_3C-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_3$

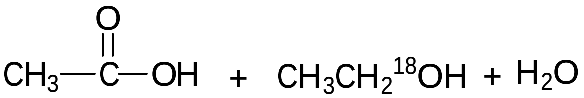
16. Hydrolysis of ethyl acetate labeled as shown with ${}^{18}O$ will yield which of the following products?



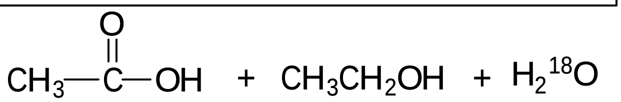
$$CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OCH_2CH_3 \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \overset{\ominus}{O}H}$$

(a) 

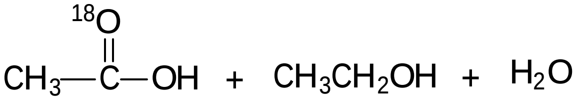
$CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}OH + CH_3CH_2OH + H_2O$

(b) 

$\boxed{CH_3-\overset{\overset{O}{\|}}{C}-OH + CH_3CH_2{}^{18}OH + H_2O}$

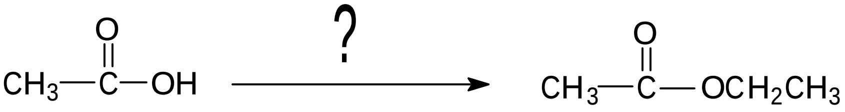
(c) 

$CH_3-\overset{\overset{O}{\|}}{C}-OH + CH_3CH_2OH + H_2{}^{18}O$

(d) 

$CH_3-\overset{\overset{{}^{18}O}{\|}}{C}-OH + CH_3CH_2OH + H_2O$

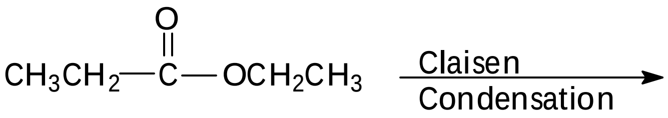
17. What conditions would you use to bring about the following conversion?



$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{?} CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_3$$

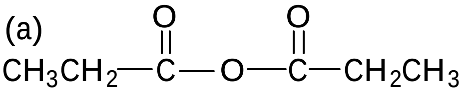
(a) $CH_3CH_3$ + NaOH + $H_2O$, heat, (b) $CH_3CH_2O^-$ $Na^+$ + ethanol,
(c) ethanol + $H_3O^+$, heat, (d) ethanol + NaOH + $H_2O$,
(e) None of the previous methods would be successful.

18. The Claisen condensation of ethyl propanoate should produce which of the following compounds?



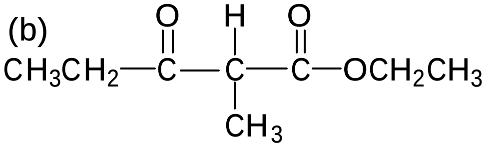
$CH_3CH_2C(=O)OCH_2CH_3 \xrightarrow[\text{Condensation}]{\text{Claisen}}$

(a)



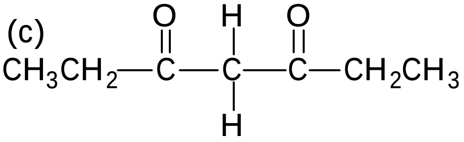
$CH_3CH_2C(=O)OC(=O)CH_2CH_3$

(b)



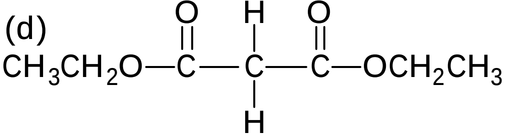
$CH_3CH_2C(=O)CH(CH_3)C(=O)OCH_2CH_3$

(c)



$CH_3CH_2C(=O)CH_2C(=O)CH_2CH_3$

(d)



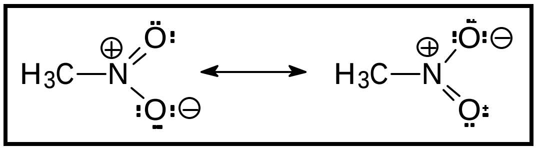
$CH_3CH_2OC(=O)CH_2C(=O)OCH_2CH_3$

19. β-keto esters, like ethyl acetoacetate (acetoacetic ester), are able to donate a proton to ethoxide ion because

(a) the enolate anion which forms is stabilized by two resonance structures in which the negative charge is delocalized onto two carbonyl oxygens.
(b) ethyl alcohol is more acidic than β-keto esters.
(c) β-dicarbonyl compounds are strong bases.
(d) The above statement is not true; β-keto esters will not donate a proton to ethoxide.

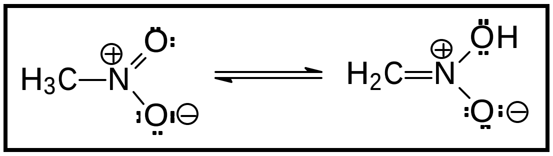
20. The structures shown to the right are

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

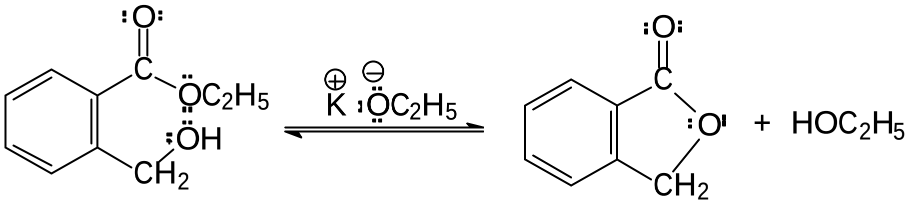


21. The structures shown to the right are

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



22-24. Consider the following reaction:



22. This reaction is an example of

(a) an *intermolecular* nucleophilic acyl substitution.
(b) an *intramolecular* nucleophilic acyl substitution.
(c) an *intermolecular* $S_N$2 substitution.
(d) an *intramolecular* $S_N$2 substitution.
(e) none of the above.

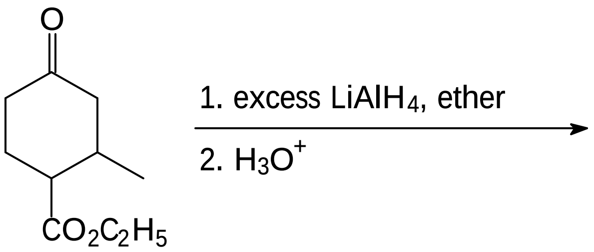
23. The purpose of the potassium ethoxide catalyst in this reaction is

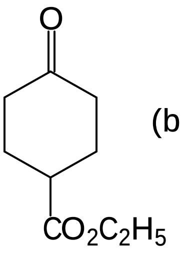
(a) to polarize the carbonyl group to make it more electrophilic.
(b) to convert the ester to an intermediate carboxylic acid.
(c) to convert the alcohol group to an alkoxide anion, which is a better nucleophile.
(d) All of the above.
(e) none of the above.

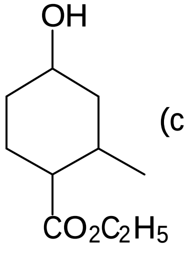
24. The product of this reaction is

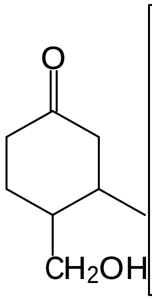
(a) a lactone. (b) an anhydride. (c) a lactam. (d) an ether. (e) an acetal.

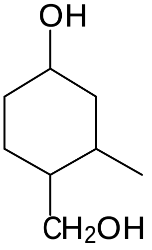
25.

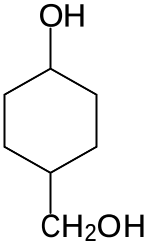


(a)


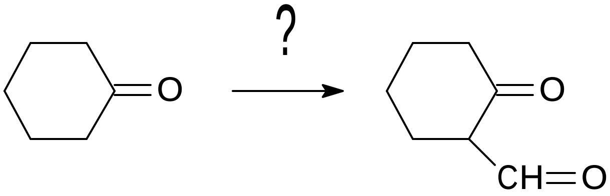
(b)


(c)


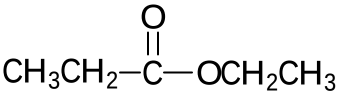
(d)


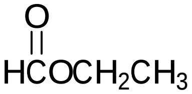
(e)


26. Select the materials that will effect the following conversion.

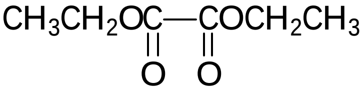


(a) $H_2$ and $CH_2{=}O$

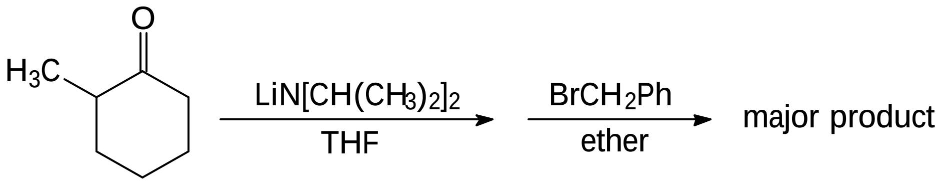
(b) $Na^+ \ {}^-OC_2H_5$ followed by

$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

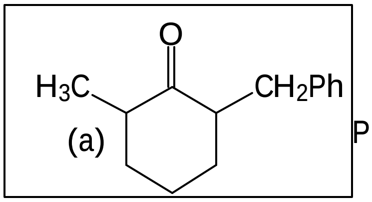
(c) $Na^+ \ {}^-OC_2H_5$ followed by

$H\overset{O}{\overset{\|}{C}}OCH_2CH_3$

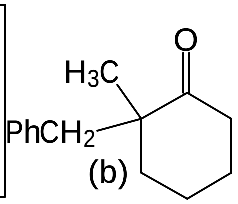
(d) $Na^+ \ {}^-OC_2H_5$ followed by $CH_3CH_2OCH_3$

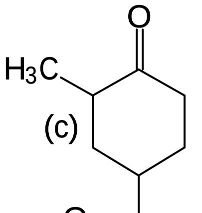
(e) $Na^+ \ {}^-OC_2H_5$ followed by

$CH_3CH_2O\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}OCH_2CH_3$

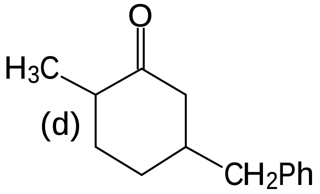
27.

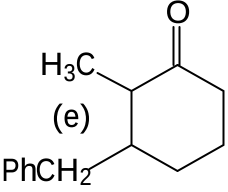

O
H3C
LiN[CH(CH3)2]2
THF
BrCH2Ph
ether
major product


O
H3C
CH2Ph
(a)

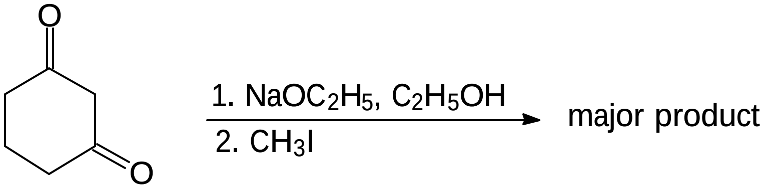

H3C
O
PhCH2
(b)

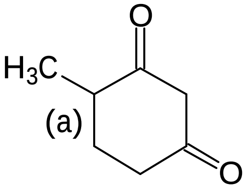

O
H3C
(c)
CH2Ph

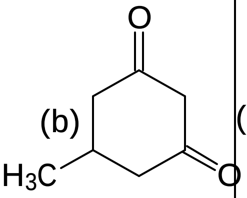

O
H3C
(d)
CH2Ph

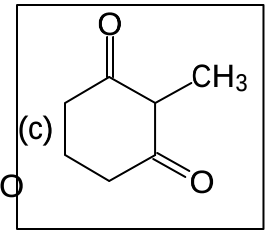

O
H3C
(e)
PhCH2

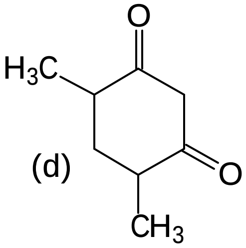
28.


O
O
1. NaOC2H5, C2H5OH
2. CH3I
major product

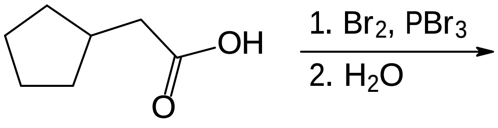

O
H3C
(a)
O

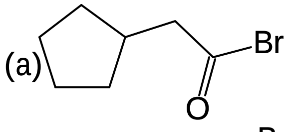

O
(b)
H3C
O

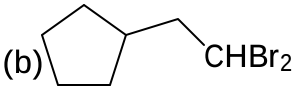

O
CH3
(c)
O

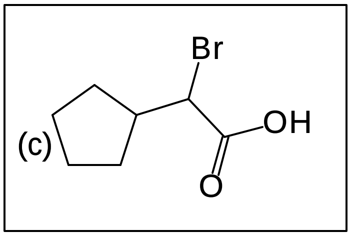

O
H3C
(d)
O
CH3

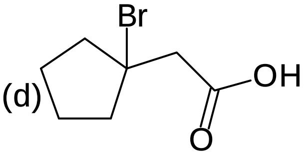
29.

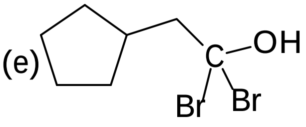

OH
O
1. Br2, PBr3
2. H2O


(a)
Br
O

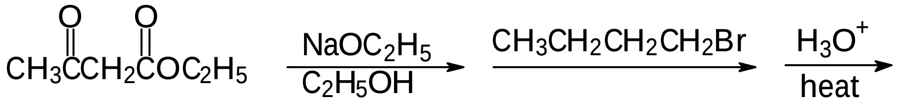

(b)
CHBr2


Br
(c)
OH
O

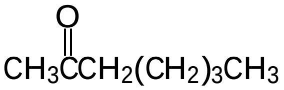

Br
(d)
OH
O


(e)
C
OH
Br
Br

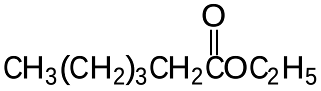
30.



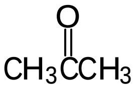
$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[C_2H_5OH]{NaOC_2H_5} \xrightarrow{CH_3CH_2CH_2CH_2Br} \xrightarrow[heat]{H_3O^+}$



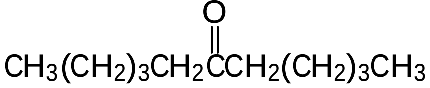
(a) $\boxed{CH_3\overset{O}{\overset{\|}{C}}CH_2(CH_2)_3CH_3}$



(b) $CH_3(CH_2)_3CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$

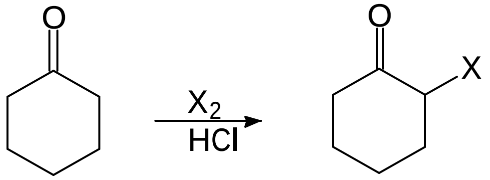


(c) $CH_3\overset{O}{\overset{\|}{C}}CH_3$



(d) $CH_3(CH_2)_3CH_2\overset{O}{\overset{\|}{C}}CH_2(CH_2)_3CH_3$

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

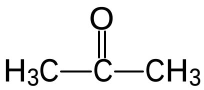


(a) $Cl_2$, (b) $Br_2$, (c) $I_2$,
(d) Chlorine, bromine, and iodine would react at about the same rate.

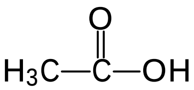
32. Rank the following compounds in order of decreasing acidity (most acidic first).

$H_3C{\equiv}CH$
I

$H_3C{-}CH_3$
II

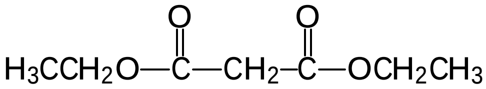


$H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_3$
III



$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH$
IV

$H_2SO_4$
V



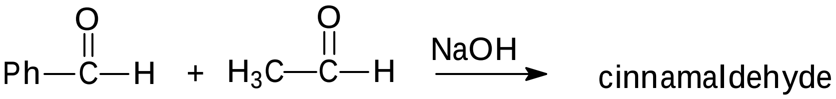
$H_3CCH_2O{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OCH_2CH_3$
VI

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

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.

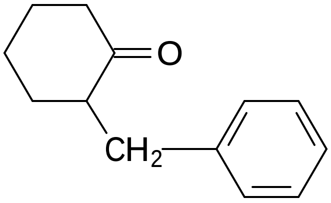
1. Synthesis. Outline the following syntheses. Show all reagents and any important conditions. Do not show mechanisms or balance equations.

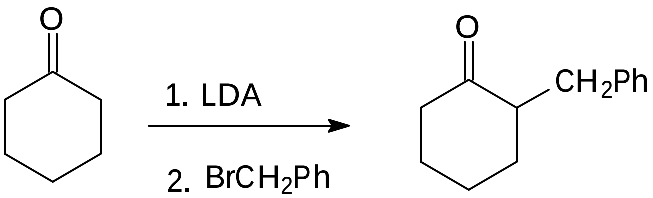
(a) Starting with benzaldehyde, Ph-CH=O, outline a synthesis of cinnamaldehyde, Ph-CH=CH-CH=O, using a mixed aldol condensation reaction. Show all reagents employed.



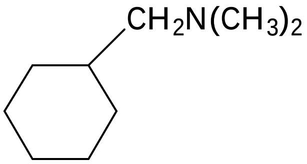
$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}H} + \mathrm{H_3C{-}\overset{\overset{O}{\|}}{C}{-}H} \xrightarrow{\mathrm{NaOH}} \text{cinnamaldehyde}$$

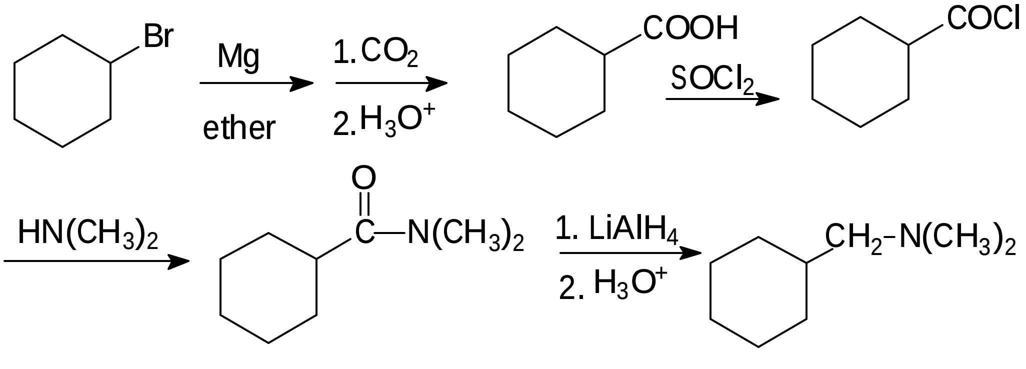
(b) Make 2-benzylcyclohexanone from cyclohexanone. You may use any other materials you need.





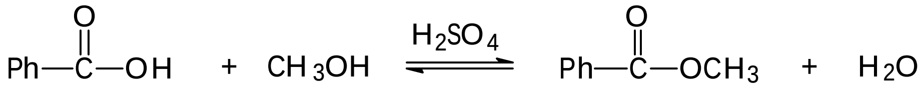
(c) How would you use the reaction of an amide with LiAlH$_4$ as the key step in going from bromocyclohexane to (N,N-dimethylaminomethyl)cyclohexane? Show all steps in the reaction sequence, using any materials you need.



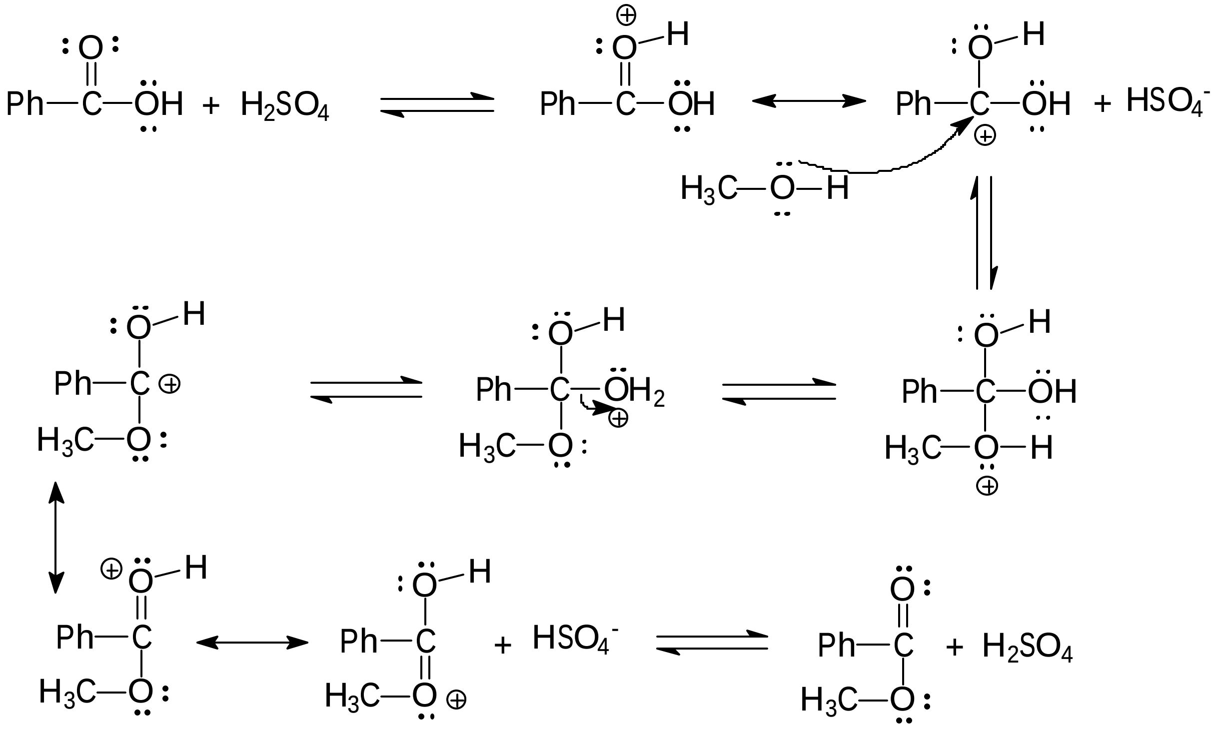


2. Mechanism.

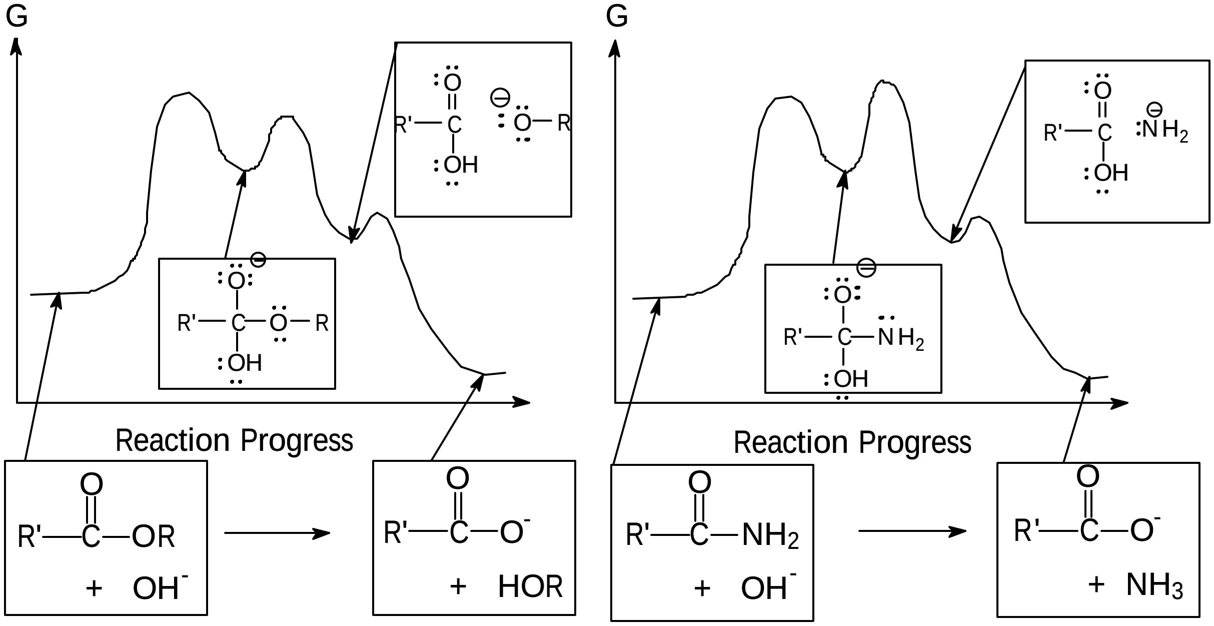
(a) Show all steps in the mechanism of the following Fisher esterification:



$$\mathrm{Ph{-}C({=}O){-}OH} + \mathrm{CH_3OH} \xrightleftharpoons{H_2SO_4} \mathrm{Ph{-}C({=}O){-}OCH_3} + \mathrm{H_2O}$$



(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.

In the second case a carbon-nitrogen bond is being broken; in the first case a carbon-oxygen bond is being broken. It is easier to break the carbon-oxygen bond because oxygen is more electronegative than nitrogen and more readily accepts the incipient negative charge. [The other thing that happens in the transition state is that an oxygen-carbon $\pi$ bond is forming – but this is the same in both cases so it doesn't make a difference.]

Part I (80)________
Part II
1. (10)________

2. (10)________

Total (100)________