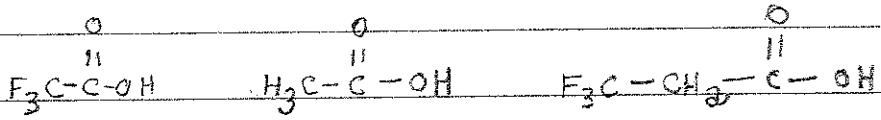
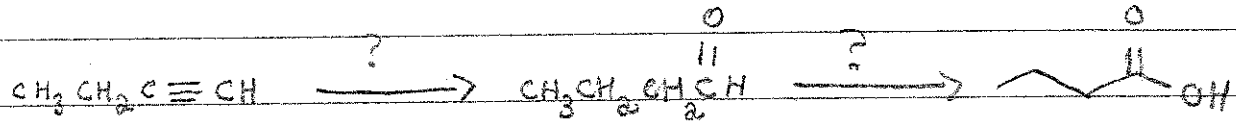
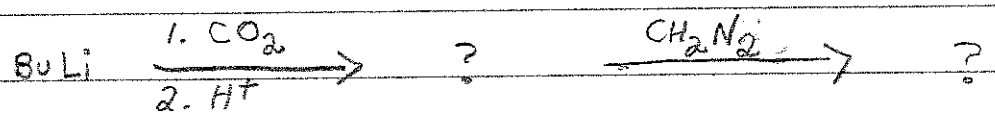
Chapter 17 Practice Problems; Introductory Level

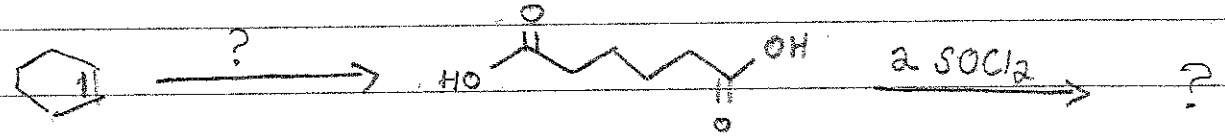
1. Which carboxylic acid is most acidic? Which has the highest pKa?



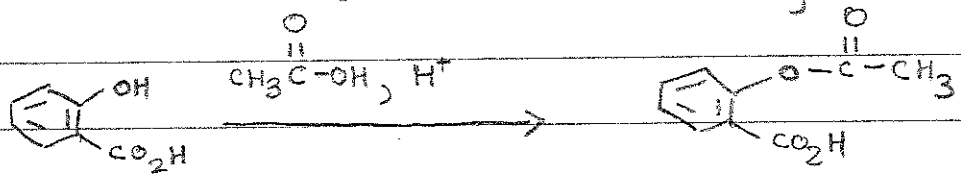
2. Fill in the missing reagents & products:

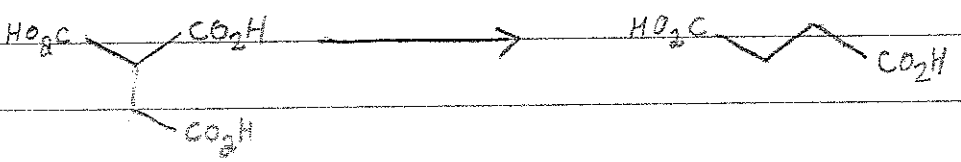
a. 

b. 

c. 

3. Show the mechanism for each of the following reactions:

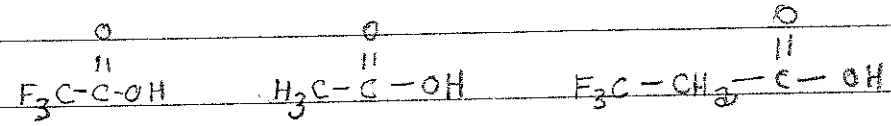
a. 

b. 

Chapter 17 Practice Problems: Introductory Level

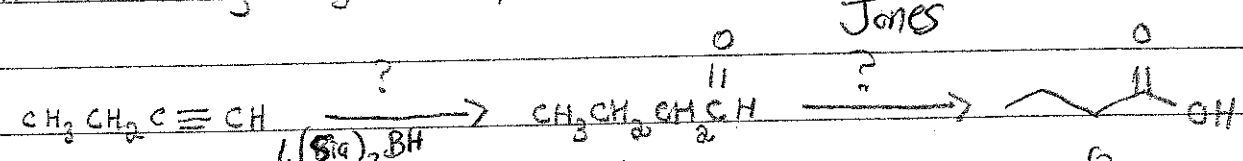
Key

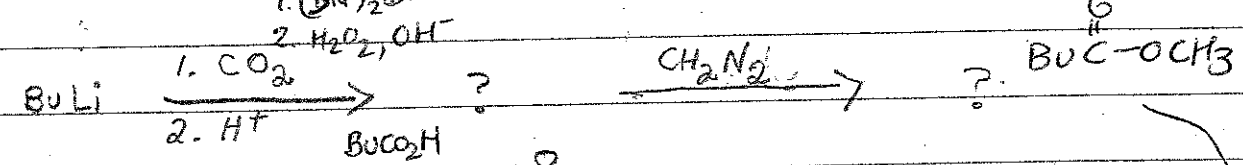
1. Which carboxylic acid is most acidic? Which has the highest pka?

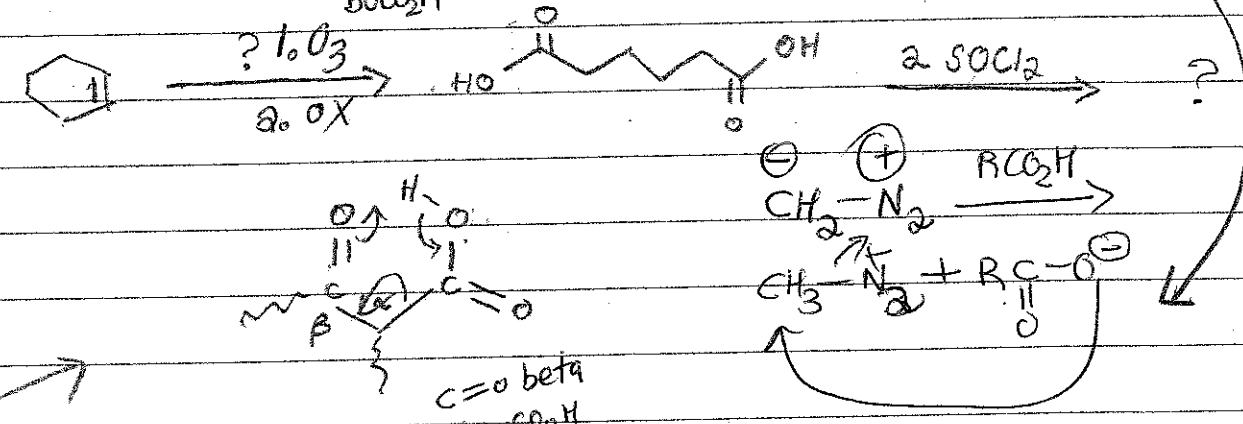


most acidic — highest pka

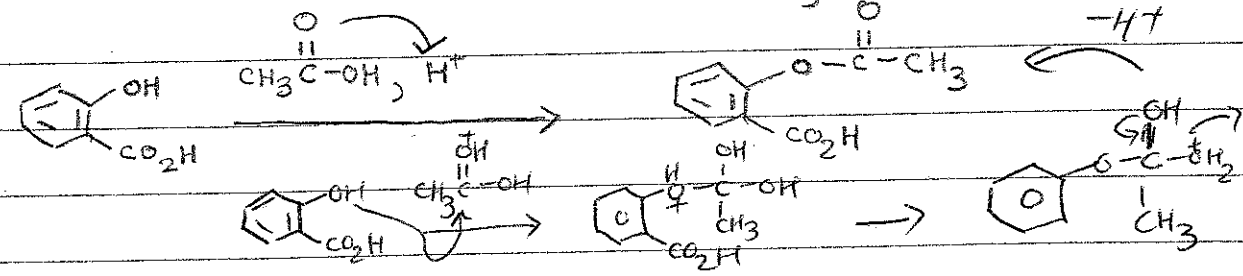
2. Fill in the missing reagents & products:

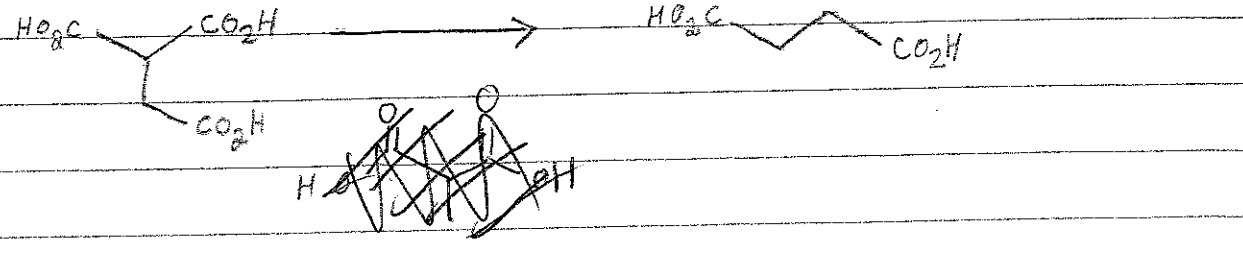
a. 

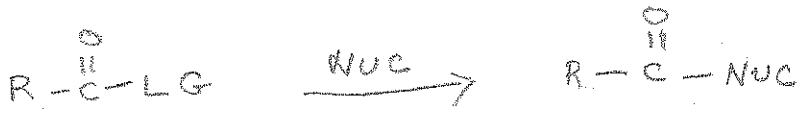
b. 

c. 

3. Show the mechanism for each of the following reactions:

a. 

b. 



Chapter Outline - Chapter 18

Very Strong Nucleophiles = $R^{\ominus}$ & $H^{\ominus}$

	$R^{\ominus}$	$H^{\ominus}$	electrophiles
strongest nuc's:	RMgBr, RLi	LAH	→ all RC(=O)–LG
	attack twice		get attacked twice
medium nuc:		DIBALH	→ RC(=O)OR' → RC(=O)–H
		attacks once	
weakest nuc:	R_2CuLi	$NaBH_4$	→ only RC(=O)–good LG
	attacks once	attacks twice	get attacked (e.g. LG = Cl)

Weaker Nucleophiles = H_2O, ROH, RNH_2

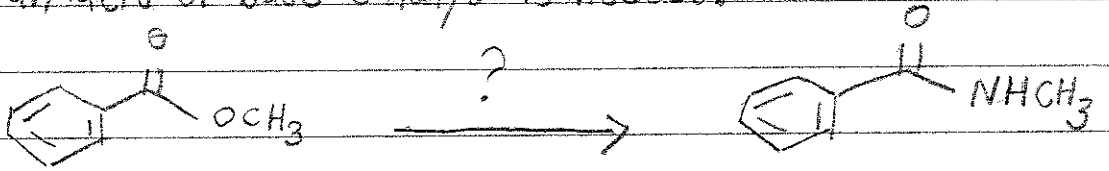
only attack once

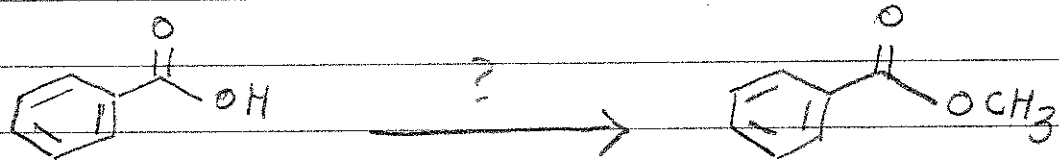
	electrophile	
no catalyst needed if electrophile is →	RC(=O)–Cl	RC(=O)–O–C(=O)R
acid or base catalyst needed if electrophile is →	RC(=O)OR	RC(=O)NH_2 → H_2O reacts; RCEN → ROH, RNH_2 no reaction
acid catalyst needed if electrophile is →	RC(=O)–OH	

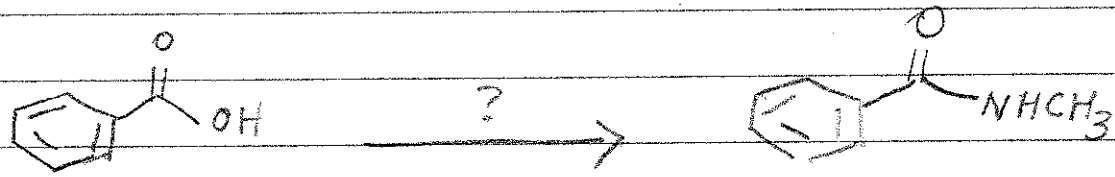
Chapter 18 Practice Problems: (Nuc = H_2O, ROH, amine, Cl^-)

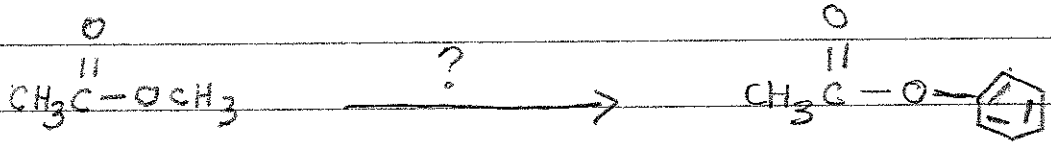
Introductory Level

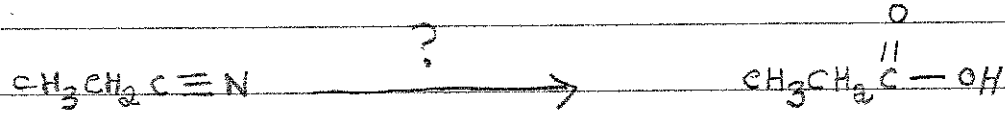
Fill in the missing reagents or products. Make sure to indicate if an acid or base catalyst is needed.

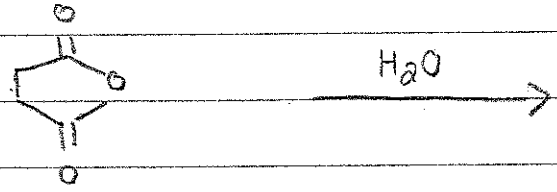
1. 

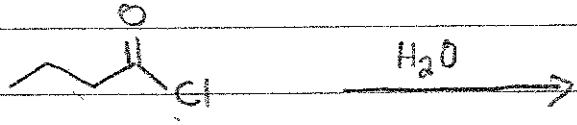
2. 

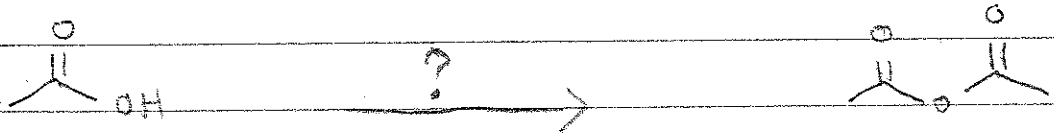
3. 

4. 

5. 

6. 

7. 

8. 

Chapter 18 Practice Problems: (Nuc = H^- or R^-)

Introductory Level

Give the products:

1. $R-\overset{O}{\overset{\|}{C}}-Cl$ → (RLi) → ; (→ (R_2CuLi) →)

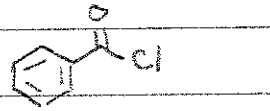
2. $R-\overset{O}{\overset{\|}{C}}-OR$ → ($RMgBr$) → ; (→ (R_2CuLi) →)

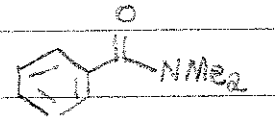
3. $R-\overset{O}{\overset{\|}{C}}-NH_2$ → (RLi) →

4a. $CH_3-\overset{O}{\overset{\|}{C}}-OH$ → ($LiAlH_4$) →

b. $CH_3CH_2C\equiv N$ → ($LiAlH_4$) →

c. $CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$ → ($NaBH_4$) →

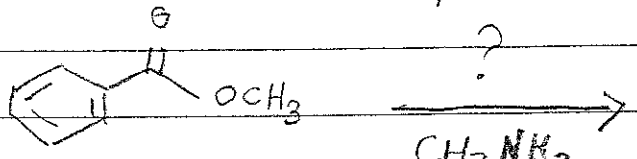
d.  → ($NaBH_4$) →

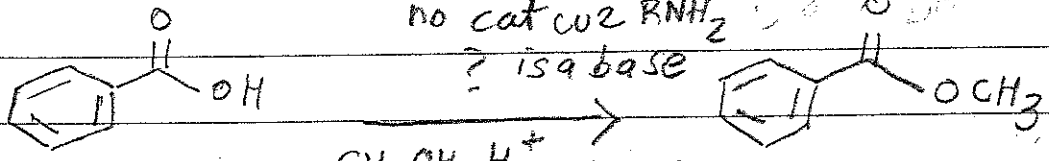
e.  → ($LiAlH_4$) →

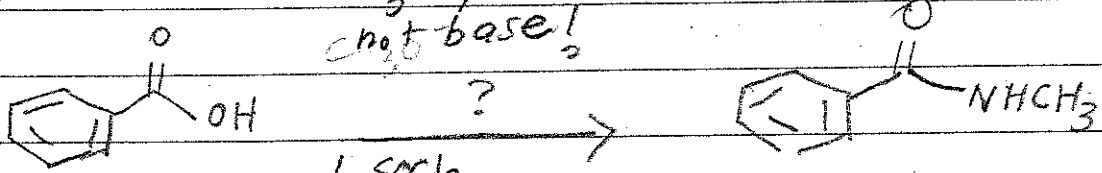
Key (Nuc = H_2O, ROH, amine, Cl^-)

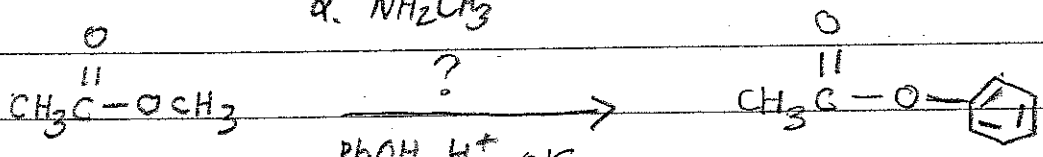
Chapter 18 Practice Problems: Introductory Level

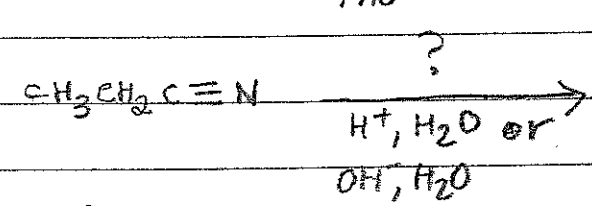
Fill in the missing reagents or products. Make sure to indicate if an acid or base catalyst is needed.

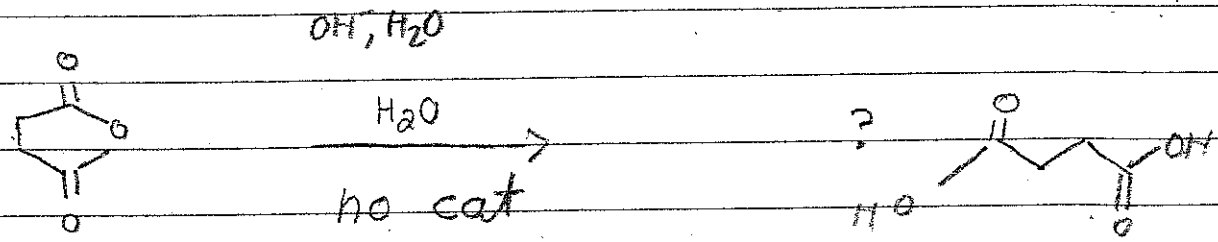
1. 

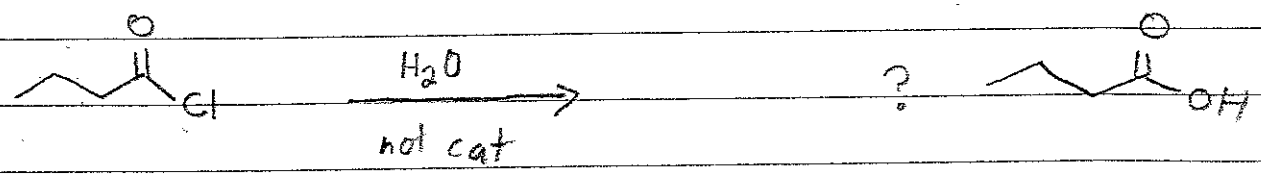
2. 

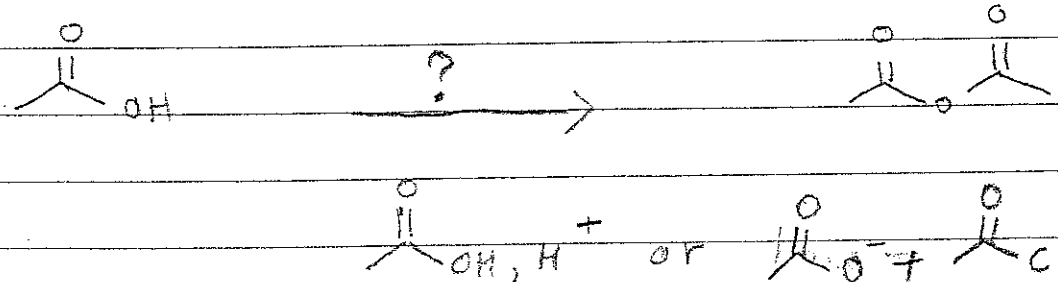
3. 

4. 

5. 

6. 

7. 

8. 

Chapter 18 Practice Problems: (Nuc = H^- or R^-)

Introductory Level

Give the products:

* goes thru imine not aldehyde

1. $RC(=O)-Cl$ —RLi→ R_3C-OH

$RC(=O)-Cl$ —R_2CuLi→ $R_2C=O$

2. $RC(=O)-OR$ —$RMgBr$→ R_3COH

aldehyde & ketone are more reactive than ester

$RC(=O)-OR$ —R_2CuLi→ NR *

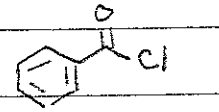
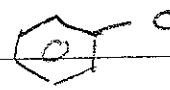
3. $RC(=O)-NH_2$ —RLi→ $RC(=O)-\overset{\ominus}{N}H + Li^{\oplus} + RH$

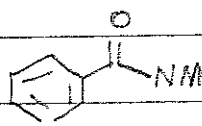
acid-base rxn!

4a. $CH_3C(=O)-OH$ —$LiAlH_4$→ CH_3CH_2OH

b. $CH_3CH_2C\equiv N$ —$LiAlH_4$→ $CH_3CH_2CH_2NH_2$ *

c. $CH_3C(=O)OCH_2CH_3$ —$NaBH_4$→ NR

d.  —$NaBH_4$→ 

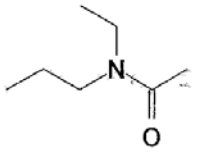
e.  —$LiAlH_4$→ 

not alcohol!

Chapter 18

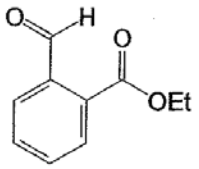
more advanced

I Synthesize the following compound using only CN^-, MeOH, EtOH as your sources of carbon:

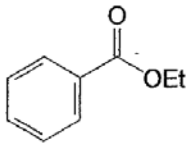


II. In each of the following hydrolysis reactions, compound A reacts much faster than compound B. Propose a reason for this in each case:

1.



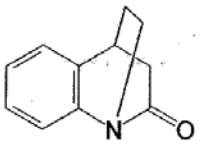
A



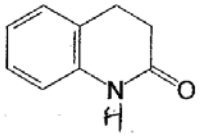
B

OH^- →

2.



A



B

From MIT Chapter 18 more advanced

7. Methyl acetimidate (**A**) is hydrolyzed in aqueous sodium hydroxide to give mainly acetamide and methanol (eq 1). In aqueous acid, **A** hydrolyzes to give primarily methyl acetate and ammonium ion (eq 2).

a) Provide a detailed mechanism for the illustrated process. Please show all arrow pushing.

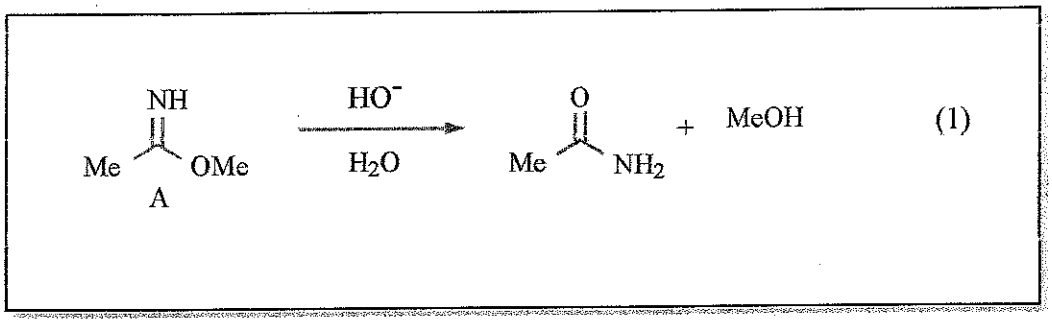


Figure by MIT OCW.

b) Provide a detailed mechanism for the illustrated process. Please show all arrow pushing.

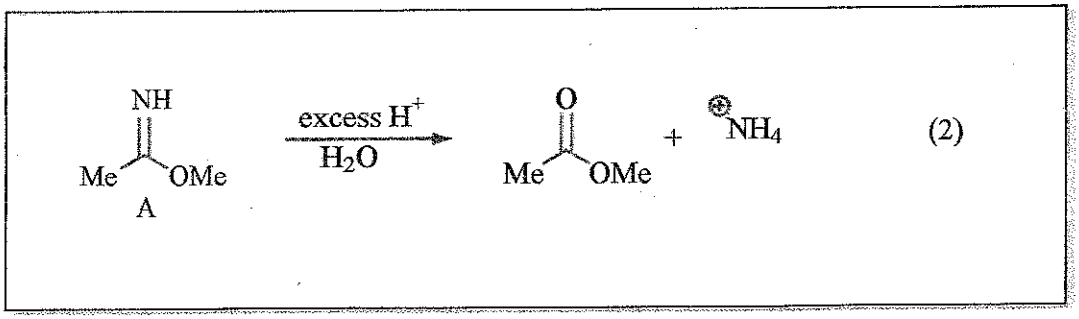


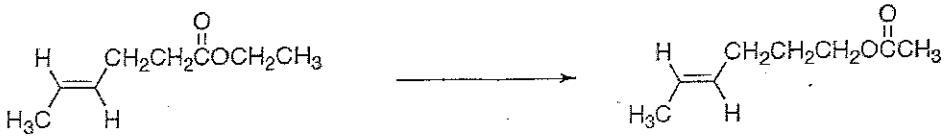
Figure by MIT OCW.

c) Briefly explain why the two reactions provide different products.

---

2) Provide conditions for the following transformations. More than one step may be necessary. chapter 18 Synthesis Brenner Exam I 07

A)



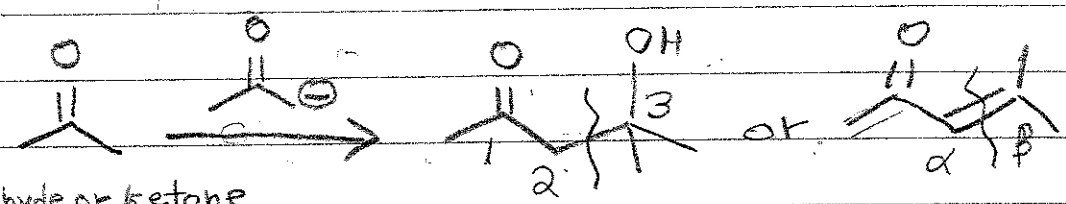
B)

Chapter 19 - Outline of Rxns

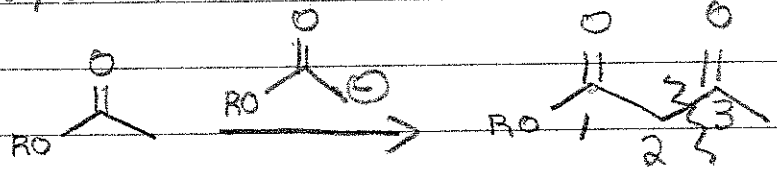
lecture 1

I. Condensation Rxns

1. Aldol



2. Claisen

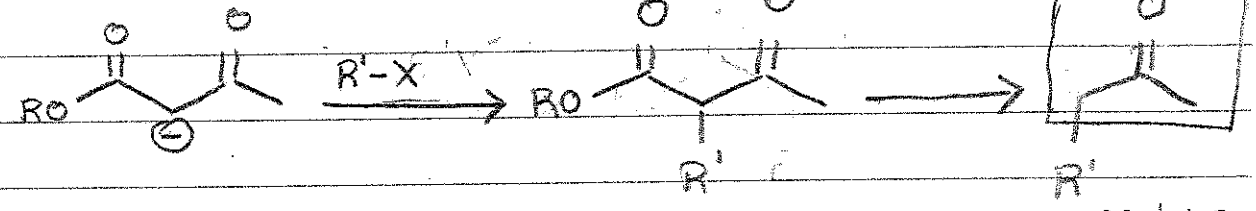


~~ester~~

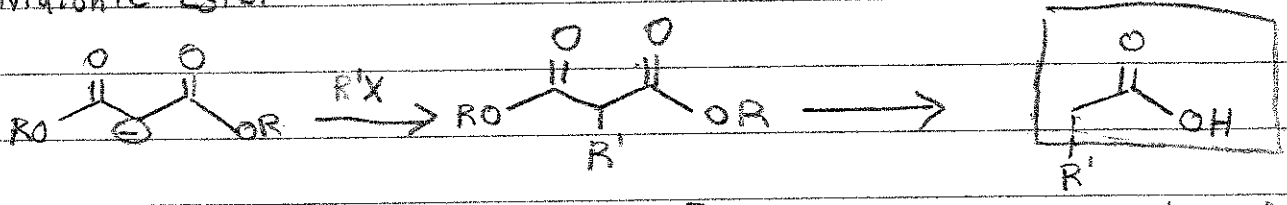
lecture 2

II. Alkylation Rxns

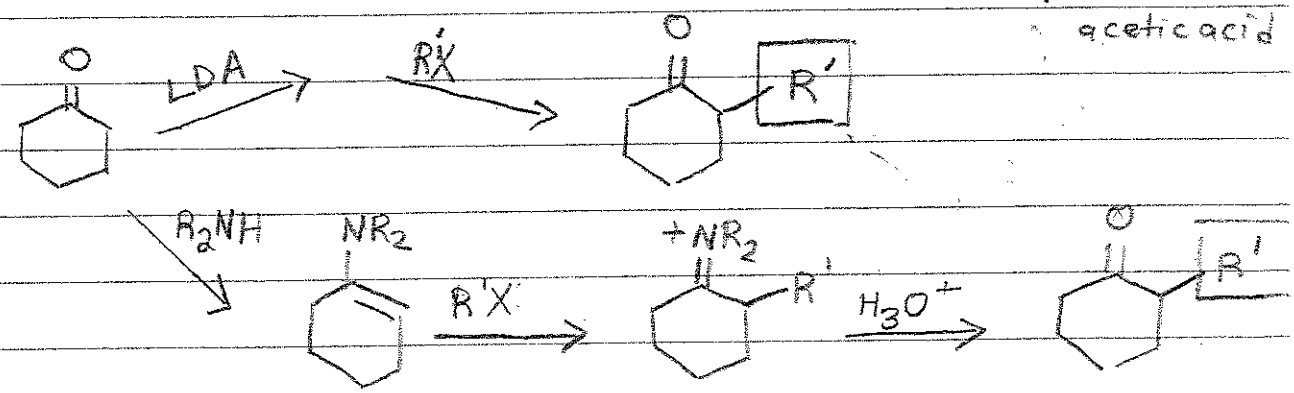
1. Acetoacetic Ester



2. Malonic Ester



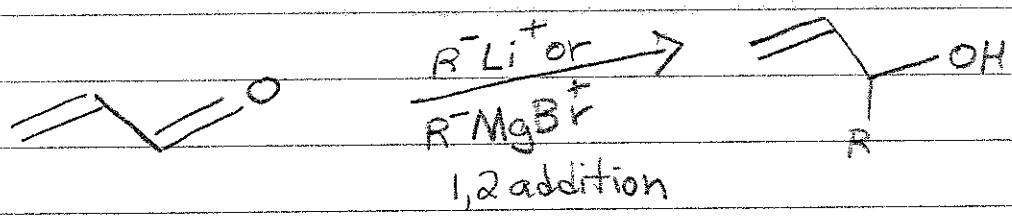
3a & 3b



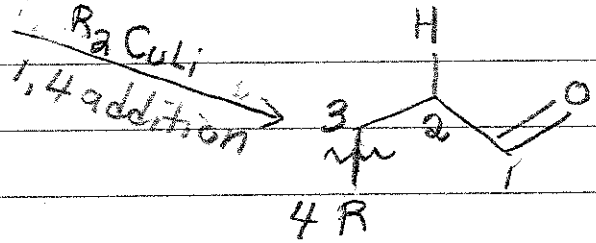
Chapter 19- Outline of Rxns Cont

III. Conjugate Addition

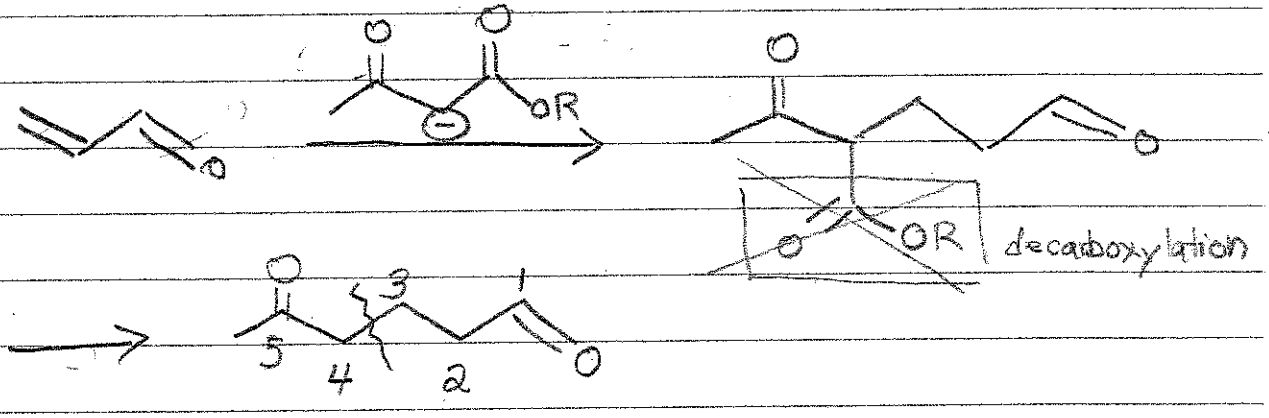
lecture 3



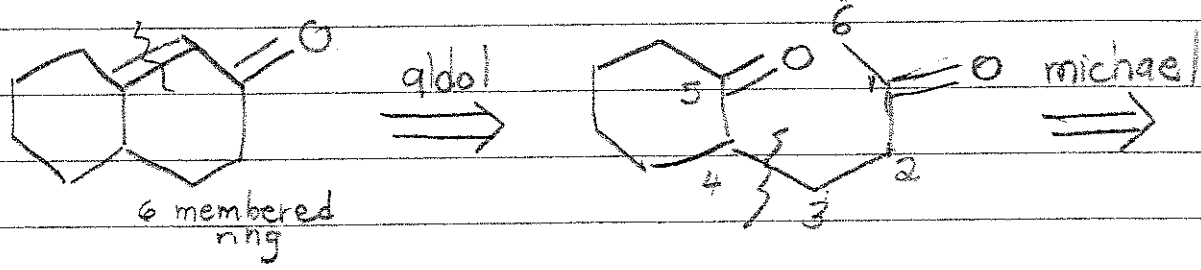
1,2 addition

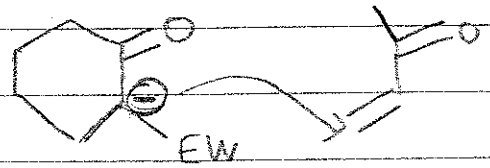


1,4 addition with enolate



lecture 3 IV. Robinson Annulation (michael + aldol)

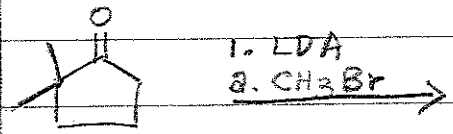




Chapter 19 Practice Problems: Introductory Level

I. Give the products of the following rxns:

Lecture # ↓

1. 

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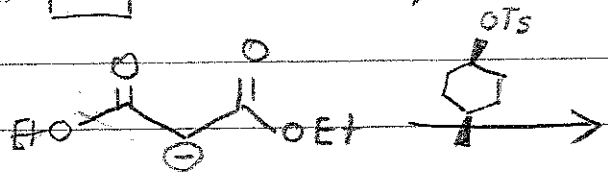
2. 

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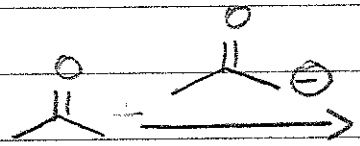
3. 

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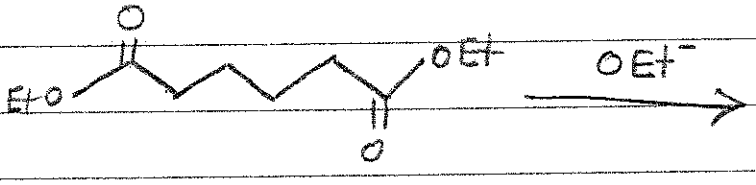
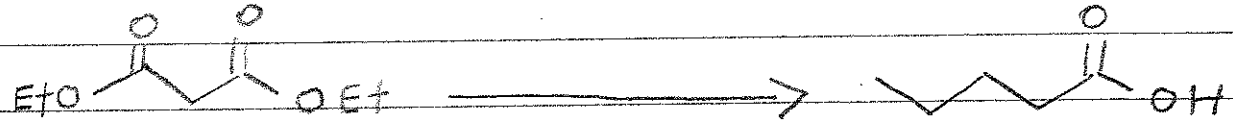
4. 

1

II. Give the reagents necessary to accomplish the following syntheses:

1. 

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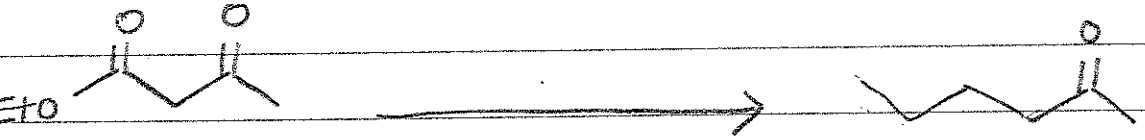
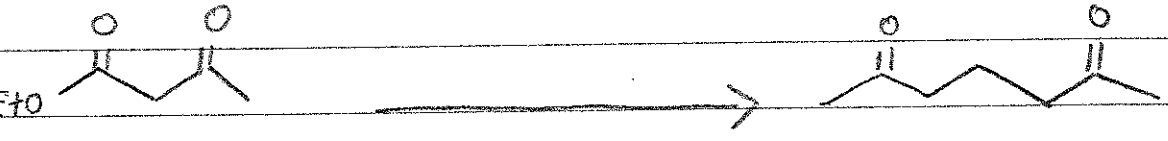
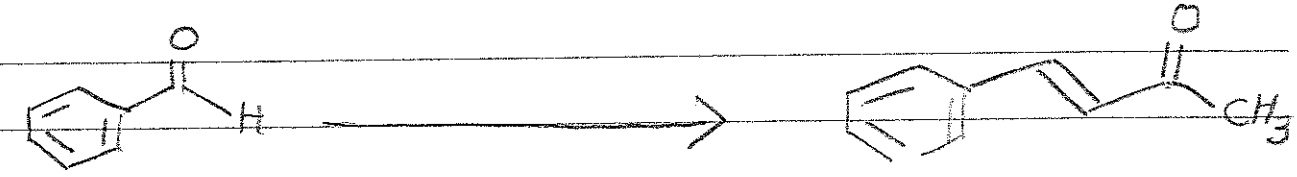
2. 

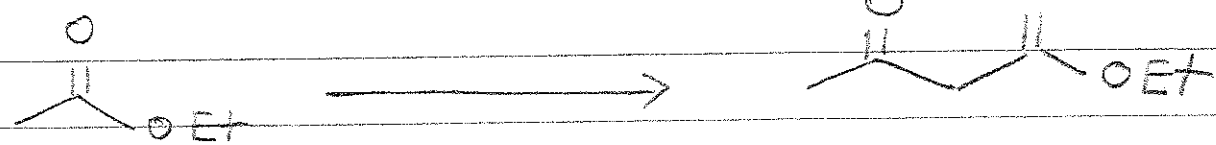
2

3. 

3

4. 

2

1 5. 

chapter 14 mech practice

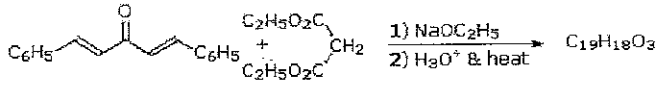
Sequential Condensation Reactions

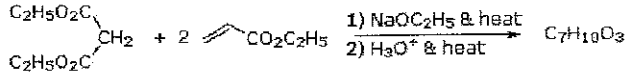
Advanced

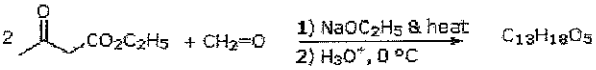
Part 1

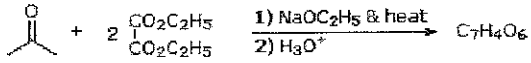
Many useful synthetic procedures involve sequences of aldol, Claisen, Michael and Mannich reactions. The following equations describe a few examples. Consider each reaction in turn and try to write a mechanism for the transformation.

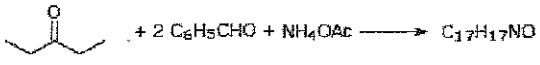
By clicking on an equation a plausible mechanism for it will be drawn in the space on the right. Electron pair shifts are designated by magenta arrows.

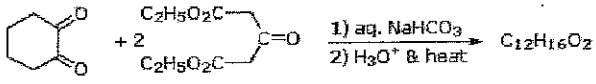
1 

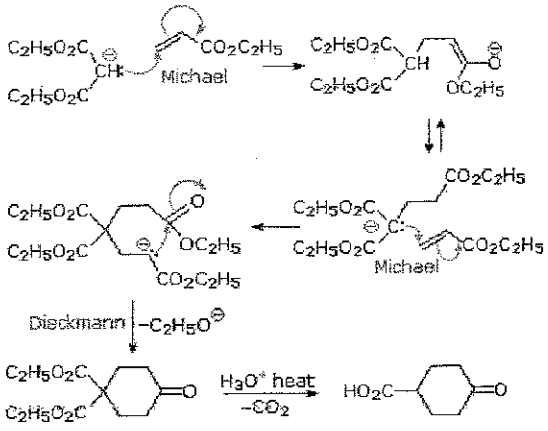
2 

3 

4 

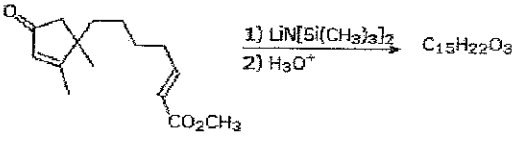
5 

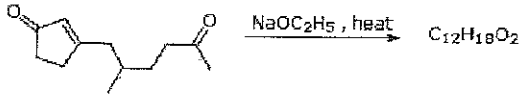
6 

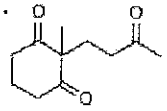
2. 

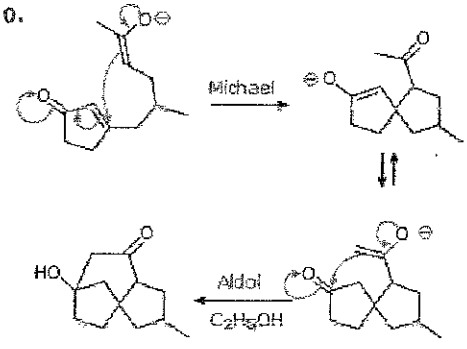
7 

8 

9 

10 

11. 

10. 

Mechanisms can be accessed at this URL

↓

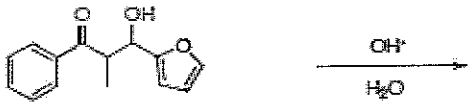
http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Questions/Synthsis/cndnprb.htm 3/9/2012

Chapter 19 Advanced Brenner Spring 07

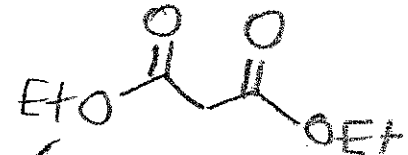
3) The retroaldol reaction is an aldol reaction in reverse; the products of a retroaldol reaction are the starting materials of an aldol reaction. Show the products of the following retroaldol reactions.

chapter 19

A)

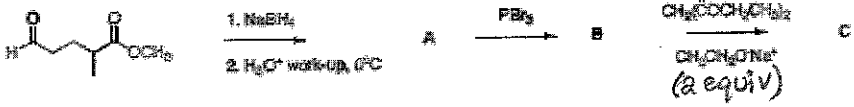


B)



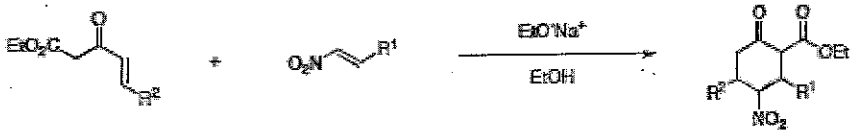
chapters 18-19 Road Map

4) Provide structures for compounds A-F.

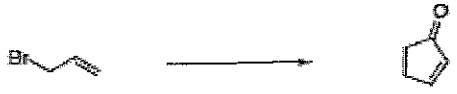


$C_9H_{10}O_5K_2$ $C_9H_{14}O_3$

5) Propose a detailed mechanism for the following transformation. When appropriate, include resonance structures: chapter 19

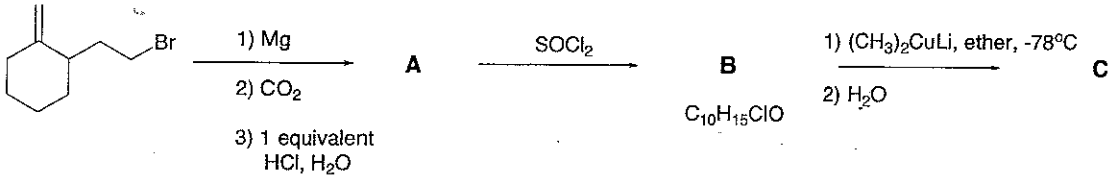


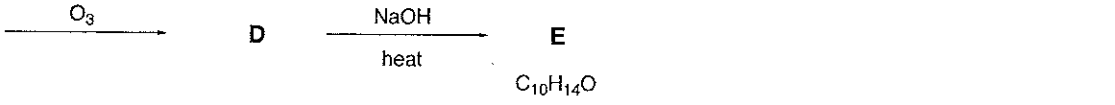
6) Propose a synthesis of compound **B** using the acetoacetic ester synthesis and starting from compound **A**. chapter 19



A B

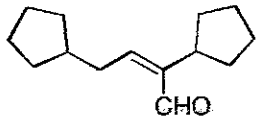
Provide structures for compounds **A**-**E**. Hint: molecular formulas for compounds **C** and **E** are provided. Chapters 17, 18, 19 Road Map

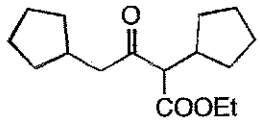


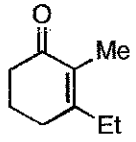


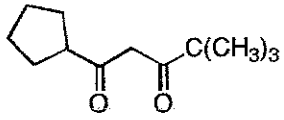
Chapter 19 Advanced

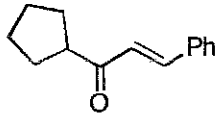
9. Provide a retrosynthetic analysis of how the following compounds could be made via an aldol, Claisen, or other type of condensation. Clearly indicate the starting materials that you would use.

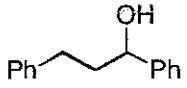
a) 

b) 

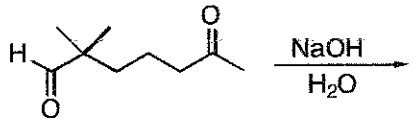
c) 

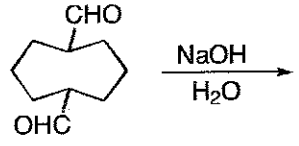
d) 

e) 

f) 

10. Provide products for the following reactions.

a) 

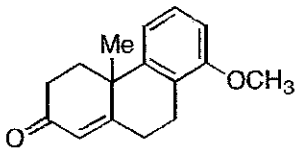
b) 

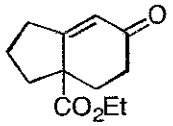
chapter 19
advanced

Problem Set #8

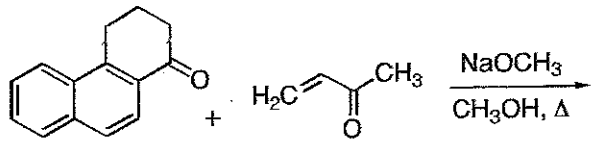
Due: December 4, 2006, 12:00 PM

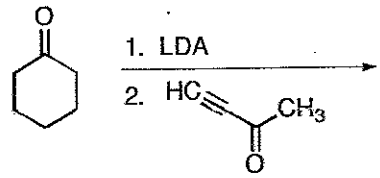
1. Propose a one-step synthesis for the following compounds using the Robinson annulation.

a) 

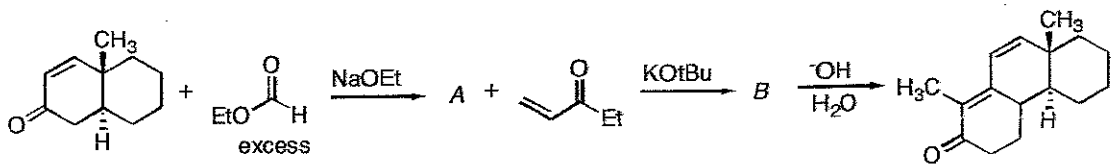
b) 

2. Write the products for the following reactions.

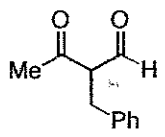
a) 

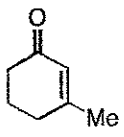
b) 

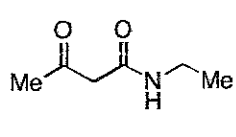
3. Identify the intermediates *A* and *B* in the transformation below and show how they are formed (mechanism).

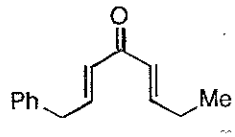


6. Provide a synthesis for each of the following products.

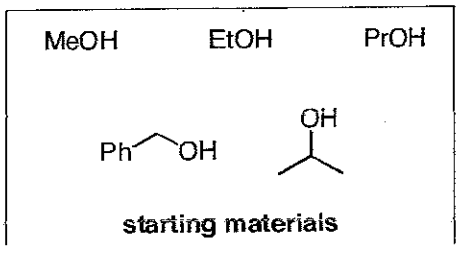
a) 

b) 

c) 

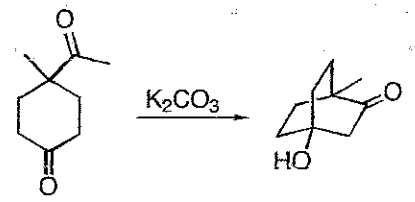
d) 

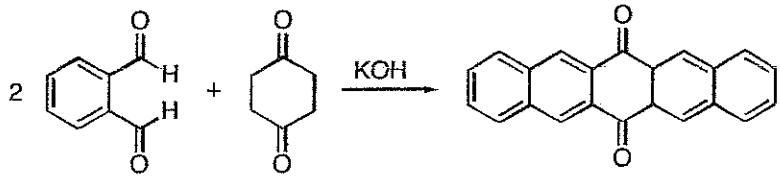
only sources of carbon →

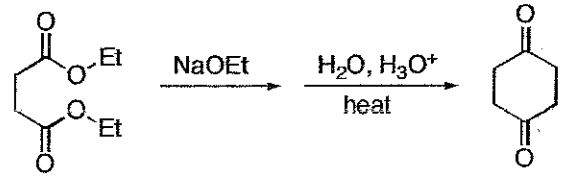


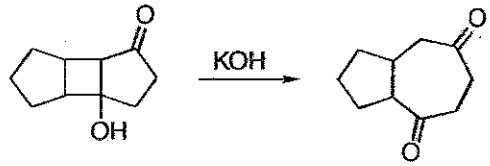
Chapter 19
Advanced

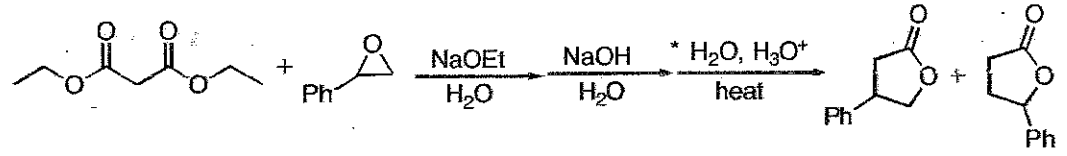
11. Provide a reasonable mechanism for each of the following transformations.

a) 

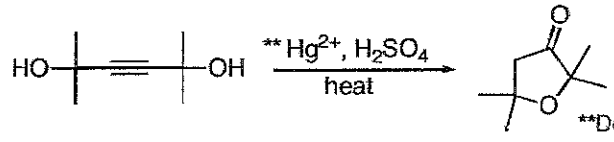
b) 

c) 

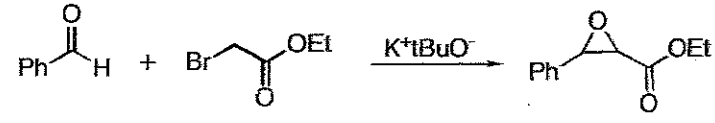
d) 

e) 

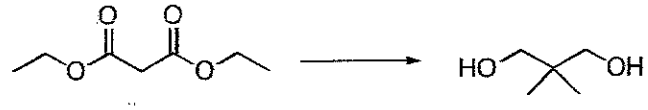
*Don't need to show mechansim for this step.

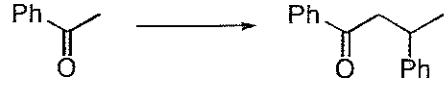
f) 

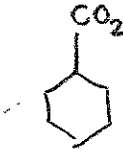
**Don't need to show mechansim for alkyne hydration.

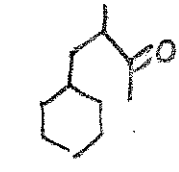
g) 

13. Propose a synthesis for each of the following compounds from the given starting materials.

a) 

b) 

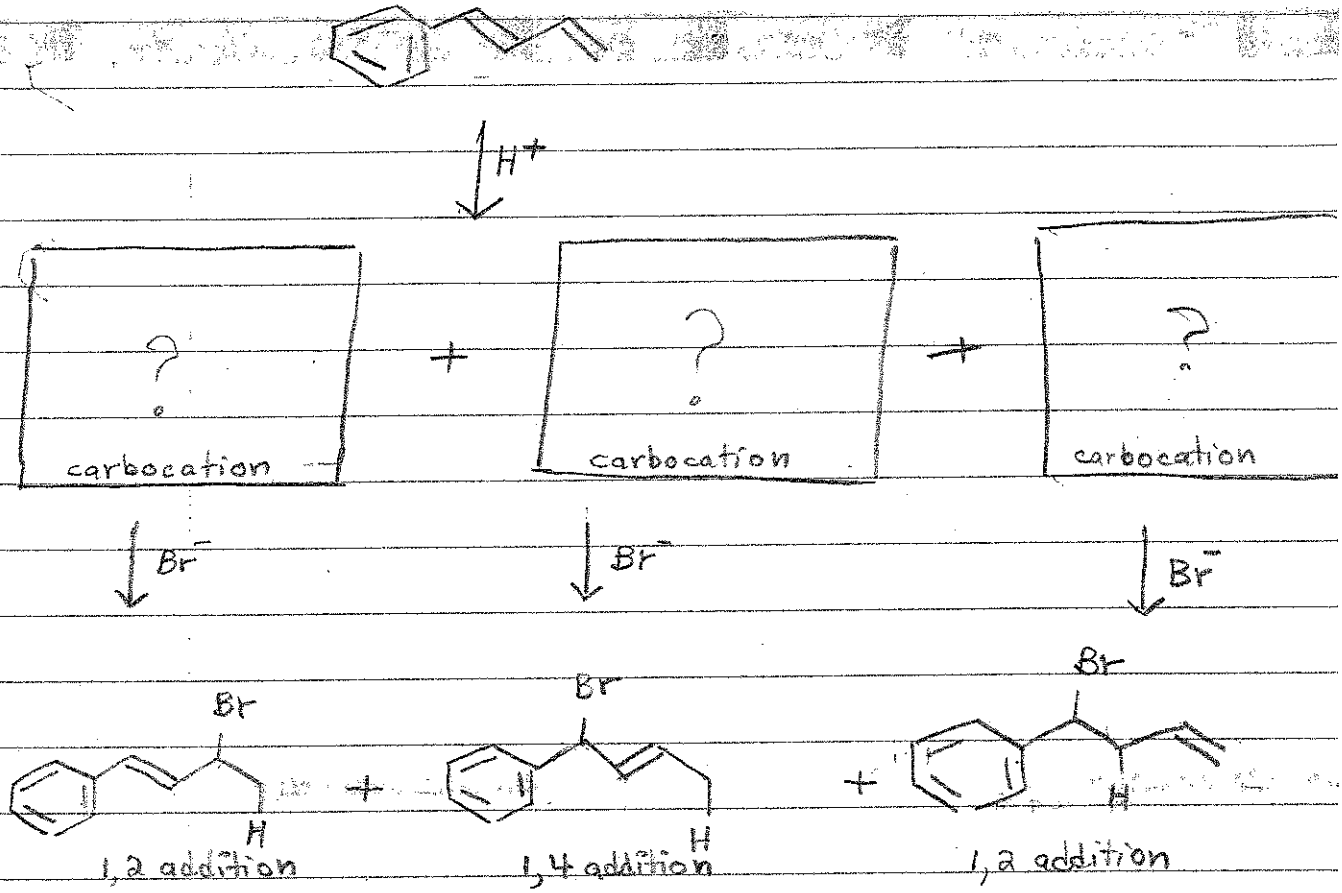
c) acetoacetic ester or malonic ester → 

d) acetoacetic ester or malonic ester → 

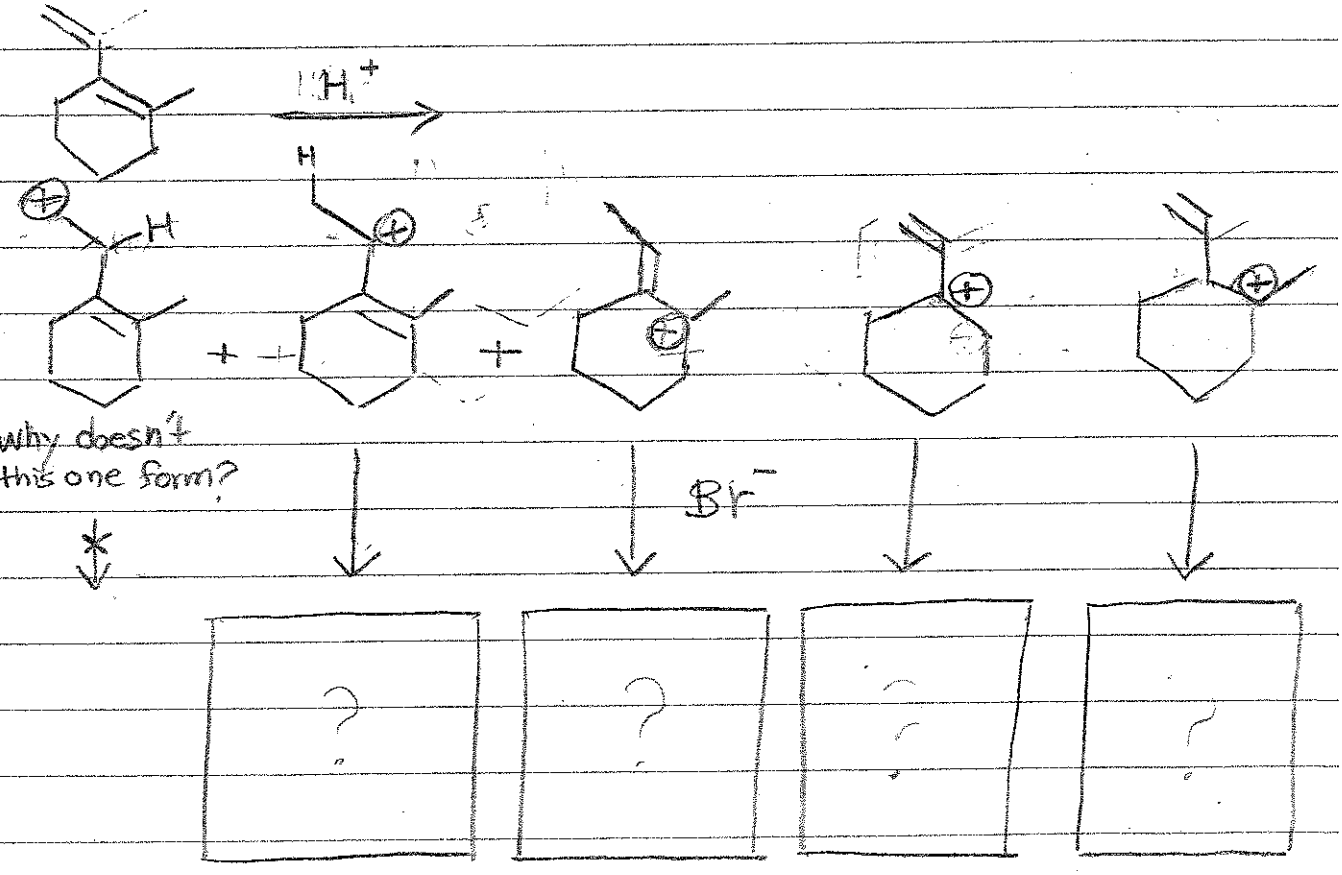
Chapter 20 Practice Problems: Introductory Level

I. Fill in the missing species in the following reactions (intermediates or products). Label the thermodynamic & kinetic products.

1.

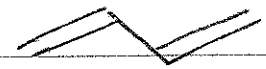


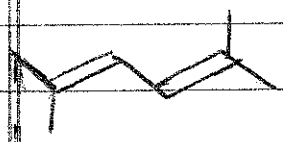
2.

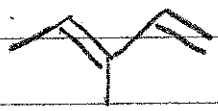


Chapter 20 cont

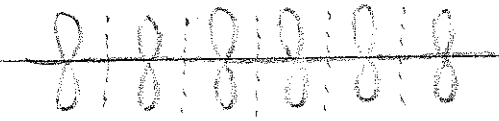
II. Draw all possible products. Label the thermodynamic & kinetic products.

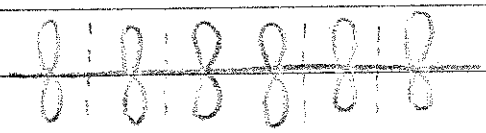
1.  1 equiv Br_2 →

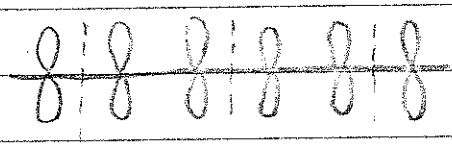
2.  1 equiv Br_2 →

3.  1 equiv DCl →

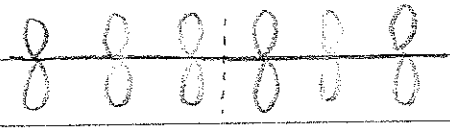
III. Shade in the molecular orbitals of 1,3,5-hexatriene (π_1 is done for you.)
(Nodes are drawn for you too.)

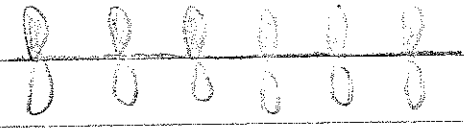
 antibonding π_6 5 nodes

 antibonding π_5 4 nodes

 antibonding π_4 3 nodes

 bonding π_3 2 nodes

 bonding π_2 1 node

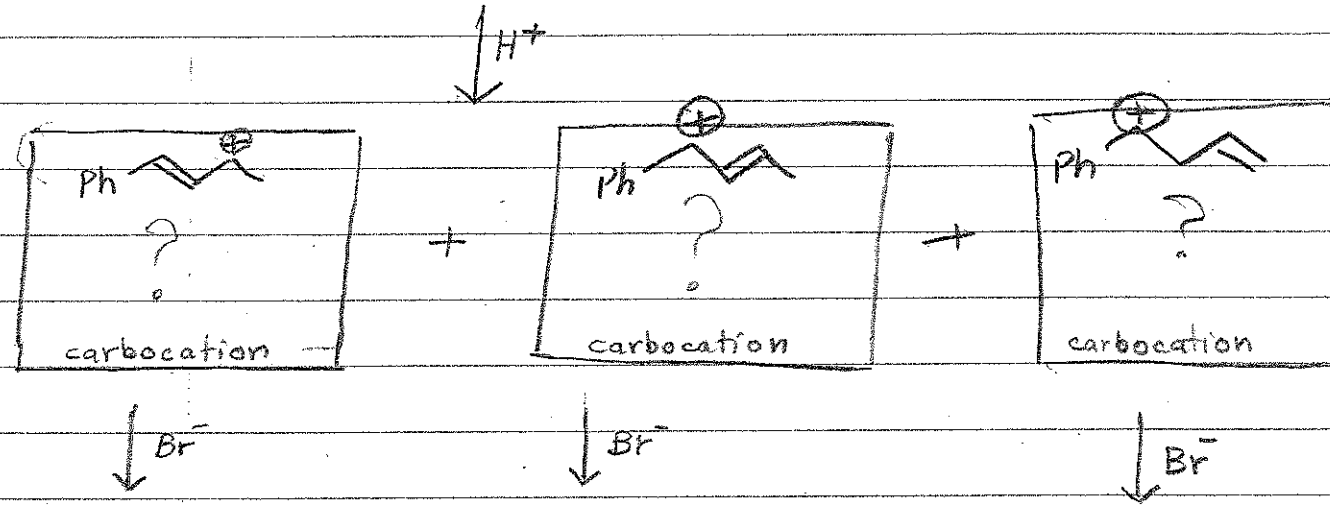
 bonding π_1 0 nodes

Chapter 20 Practice Problems! Introductory Level

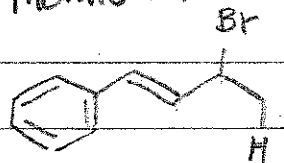
Key

I. Fill in the missing species in the following reactions (intermediates or products). Label the thermodynamic & kinetic products.

1.



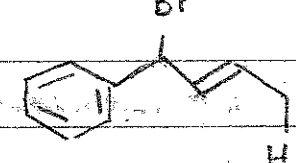
thermo + kinetic



1,2 addition

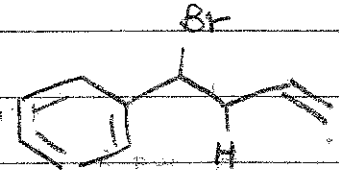
+

kinetic



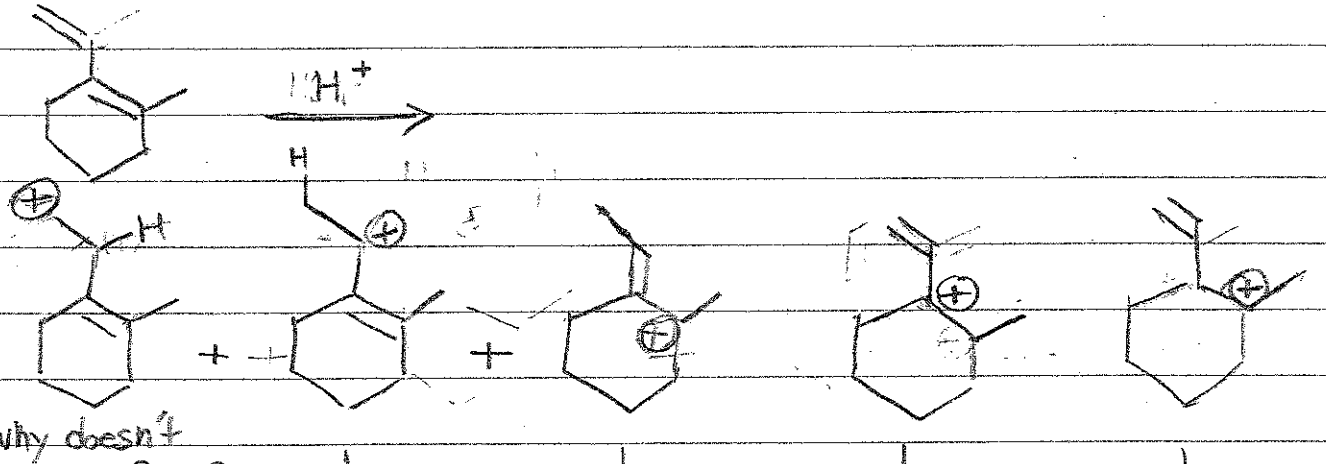
1,4 addition

+



1,2 addition

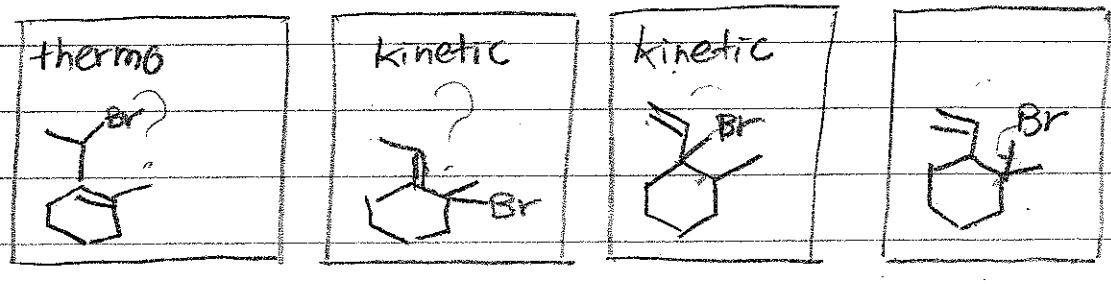
2.



why doesn't this one form?

*

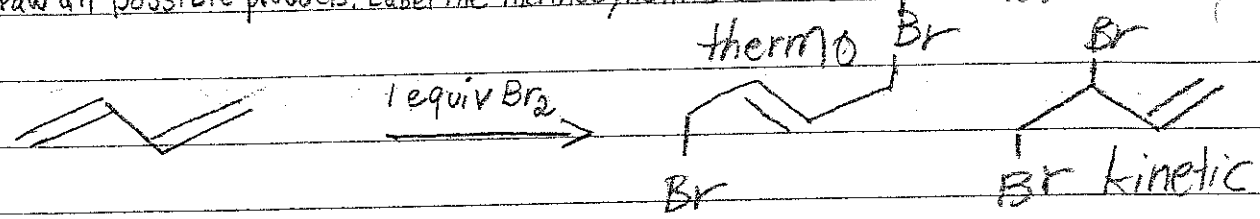
Br−

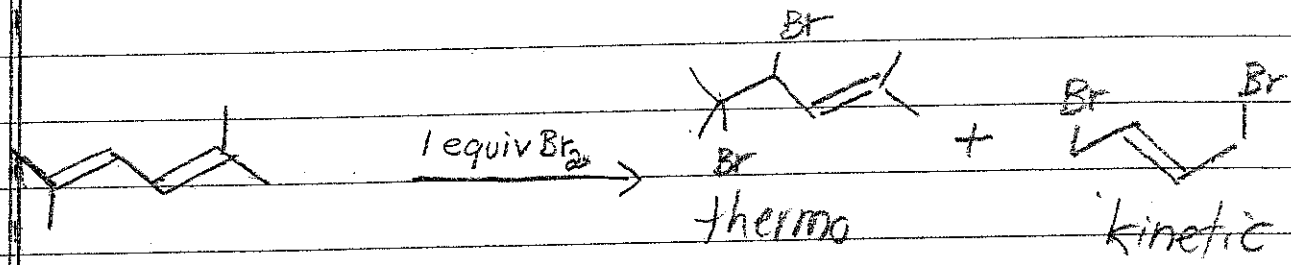


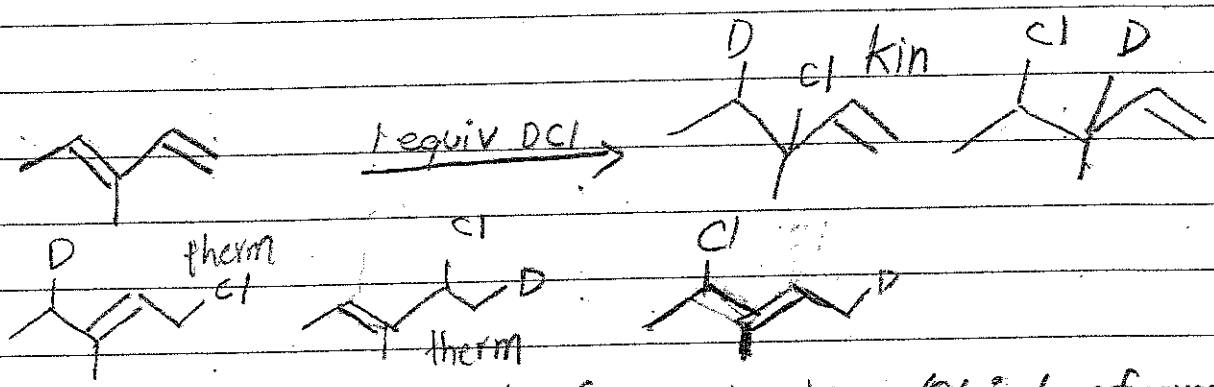
Chapter 20 cont

key

II. Draw all possible products. Label the thermodynamic & kinetic products.

1. 

2. 

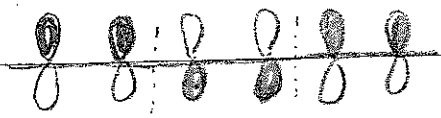
3. 

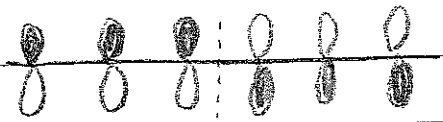
III. Shade in the molecular orbitals of 1,3,5-hexatriene (Π_1 is done for you.)
(Nodes are drawn for you too.)

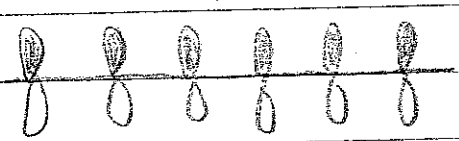

antibonding Π_6 5 nodes


antibonding Π_5 4 nodes


antibonding Π_4 3 nodes

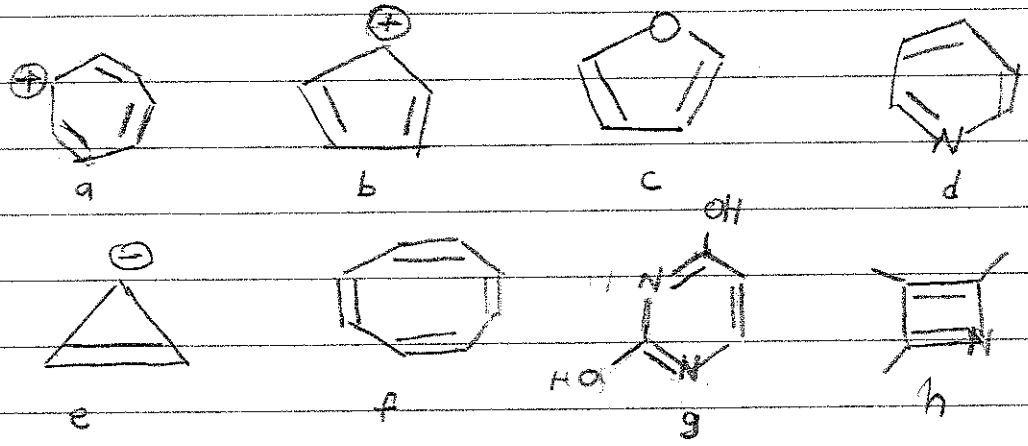

bonding Π_3 2 nodes


bonding Π_2 1 node


bonding Π_1 0 nodes

Chapter 21 Practice Problems: Introductory Level

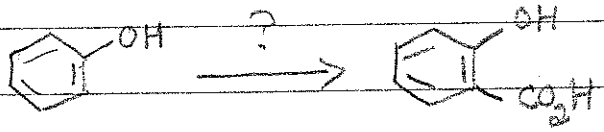
1. Determine whether each of the following compounds is non-aromatic, aromatic or antiaromatic:

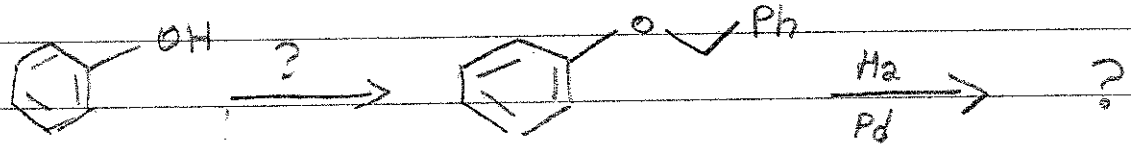


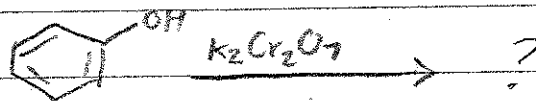
2. Draw a frost circle for compound f above. Fill in the π electrons & label the energy levels as bonding, nonbonding or antibonding.

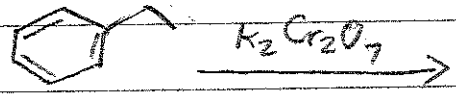
Chapter 21 cont

3. Fill in the missing reagents or products:

a. 

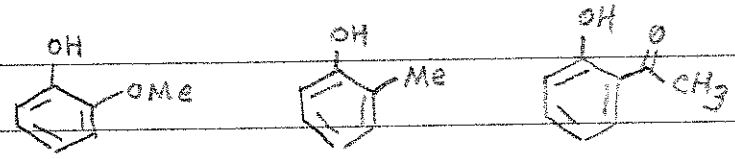
b. 

c. 

d. 

e. 

4. Which phenol is most acidic?
Which has the highest pka?

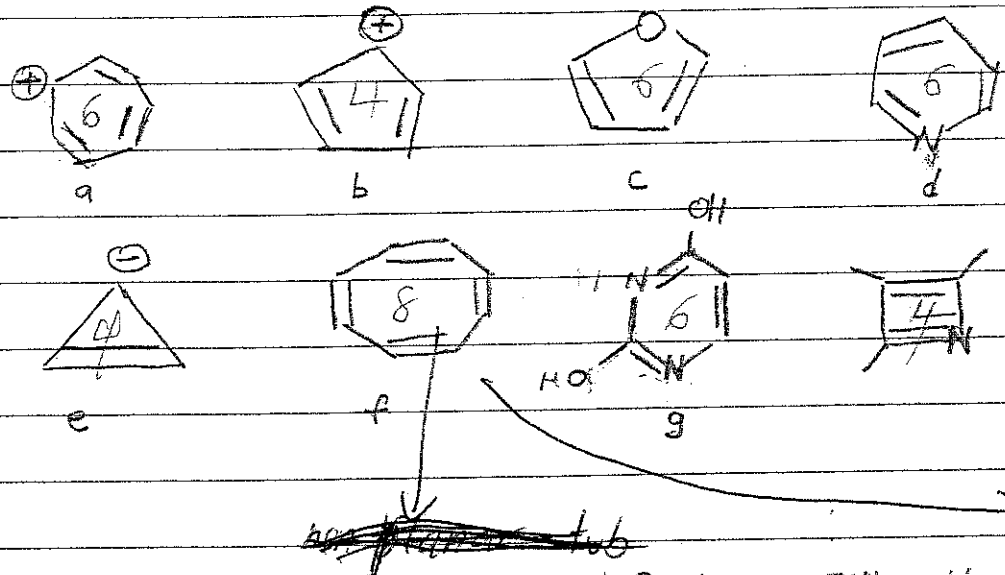


a b c

Chapter 21 Practice Problems: Introductory Level

Key

1. Determine whether each of the following compounds is non-aromatic, aromatic or antiaromatic: (assume all are planar)



actually exists as a tub; not planar

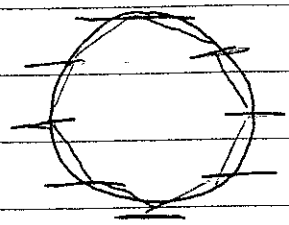
2. Draw a frost circle for compound f above. Fill in the π electrons & label the energy levels as bonding, nonbonding or antibonding.

question 1, 4n+2 aromatic

4n antiaromatic

for heteroatom, count lone pairs Or double bond, NOT both

question 2



1 — 1 — non bond

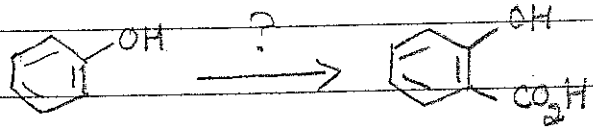
1↓ 1↓ bonding

1↓ bonding

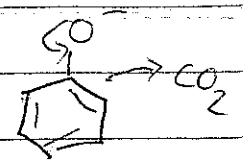
Chapter 21 cont

key

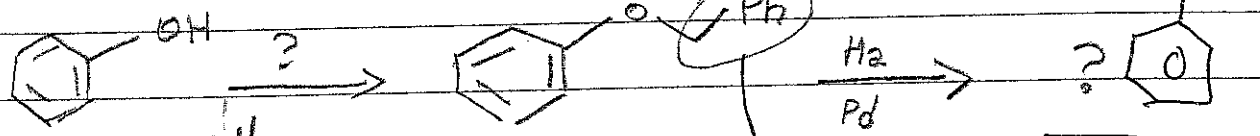
3. Fill in the missing reagents or products:

a. 

1. NaOH
2. CO_2



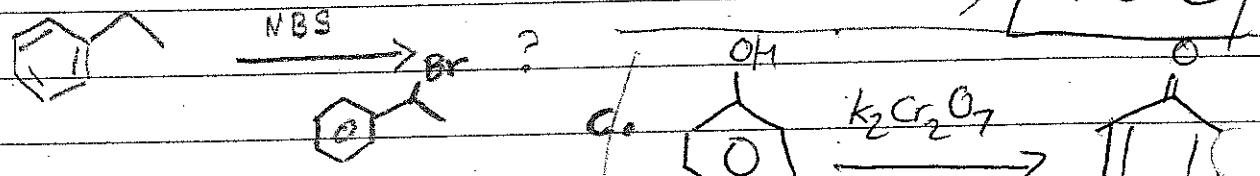
(think enolate)

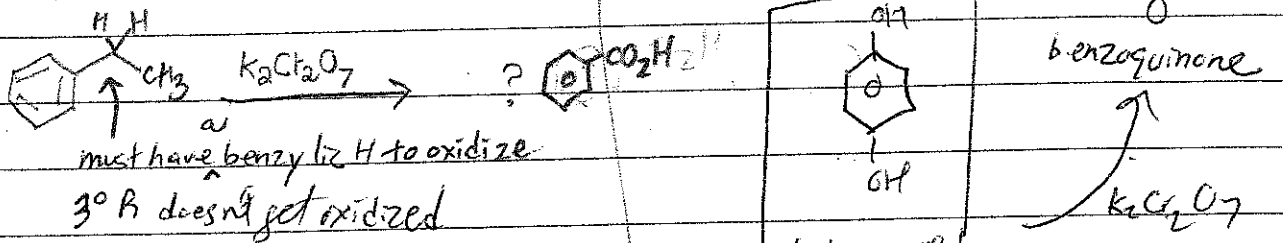
b. 

1. Na
2. $PhCH_2X$

H_2, Pd

+ $PhCH_3$ ✱ toluene

c. 

d. 

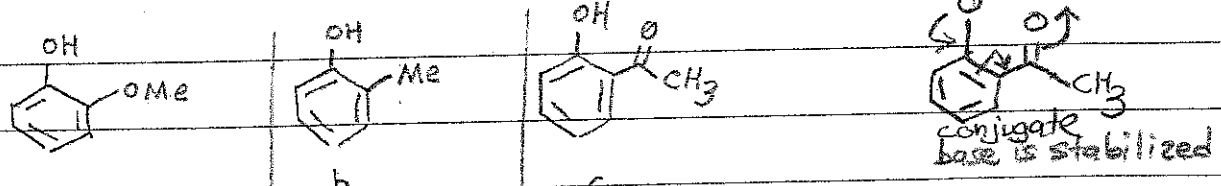
must have benzylic H to oxidize

3° R doesn't get oxidized

hydroquinone

benzoquinone

4. Which phenol is most acidic?
Which has the highest pka?



a: ED resonance, EW inductive — highest pka

b: ED inductive

c: EW resonance, EW inductive — most acidic

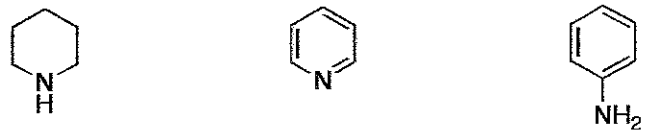
conjugate base is stabilized

Exam II Brenner 07
Chapter 21

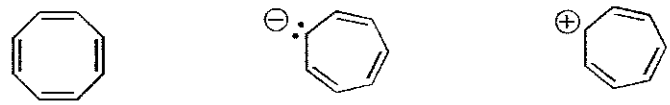
Name:
Recitation Instructor:

INSTRUCTIONS: Write your name and the name of your recitation instructor on each page of this exam. Write your answers on this exam; do not write your answers on the backs of the pages. Write you answers in pen, or you will not be eligible for a regrade, in the event that you request one. There are 6 questions. Good luck!

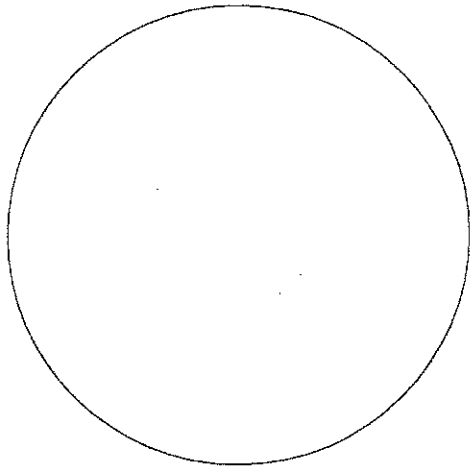
1. [10 points] A) Circle the best base:



B) Circle the compound that is aromatic:



C) Draw the Frost circle for the aromatic compound from part B.

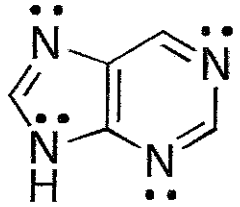


Chapter 21 Brenner Exam II '2007

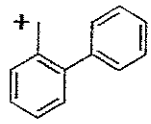
Name:
Recitation Instructor:

Question 2 (Parts A and B): 15 points

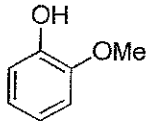
A) Circle the lone pair(s) that can participate in pi bonding in the rings?

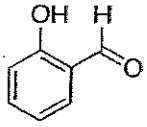


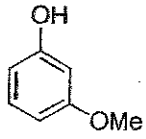
B) Draw all possible resonance structures of the benzylic cation:

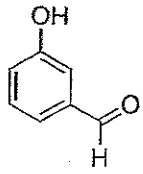


A) Circle the phenol with the highest pKa.

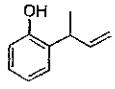


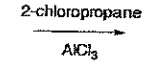




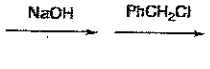


4) [18 points] Provide structures for compounds A-F.

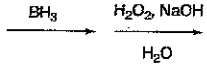




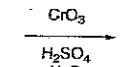
A



B

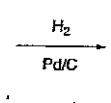


C
$C_{20}H_{26}O_2$



mild conditions

D



E
$C_{13}H_{16}O_2$