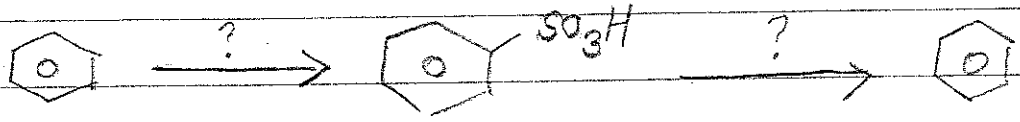
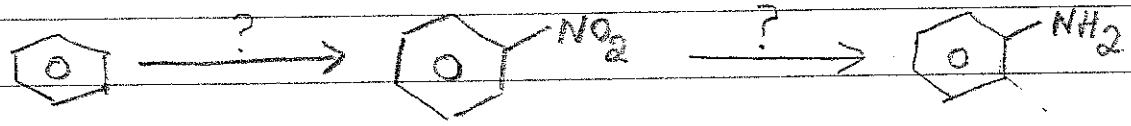
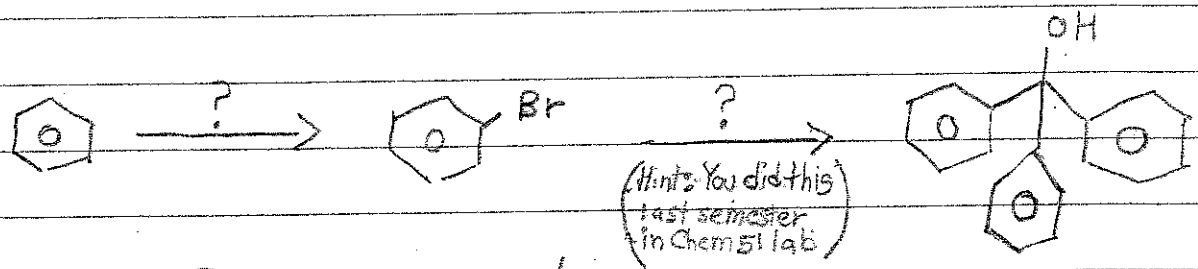
Chapter 22 Practice Problems: Introductory Level

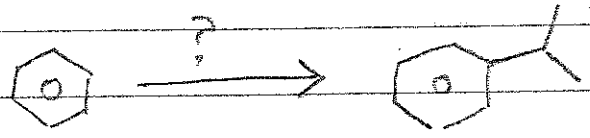
I. Electrophillic Aromatic Substitution

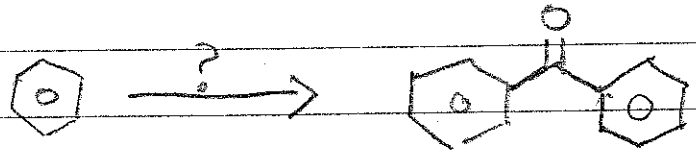
Give the reagents needed in each of the following reactions & indicate whether the product that forms is an o, p or m director & whether or not it is an activator or a deactivator.

1. 

2. 

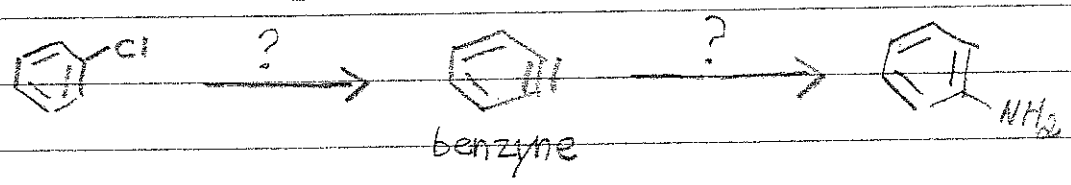
3. 

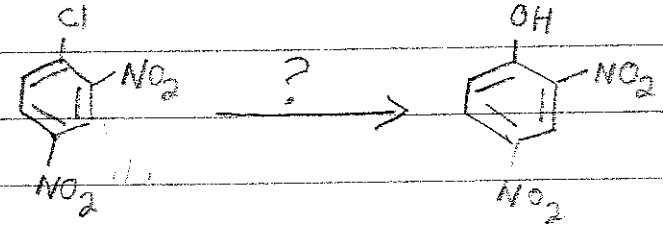
4. 

5. 

II. Nucleophillic Aromatic Substitution

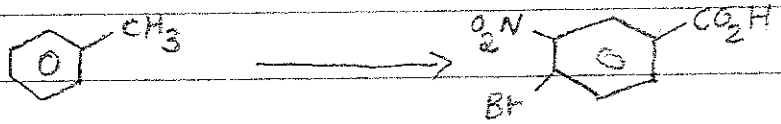
Fill in the missing reagents.

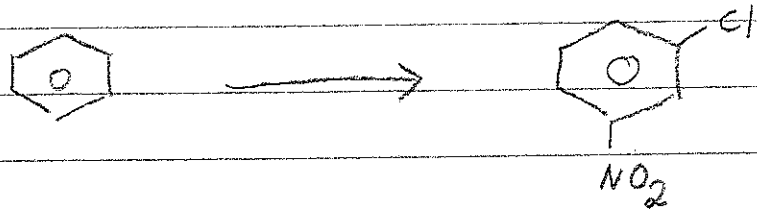
1. 

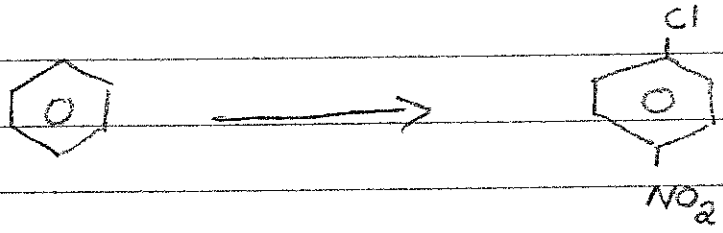
2. 

III. Synthesis

Give the reagents necessary to accomplish the following syntheses. Careful – the order in which you add things matters.

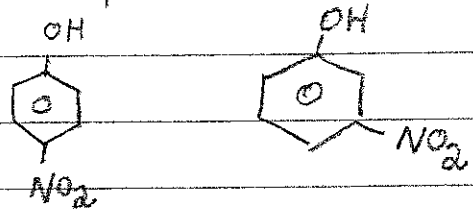
1. 

2. 

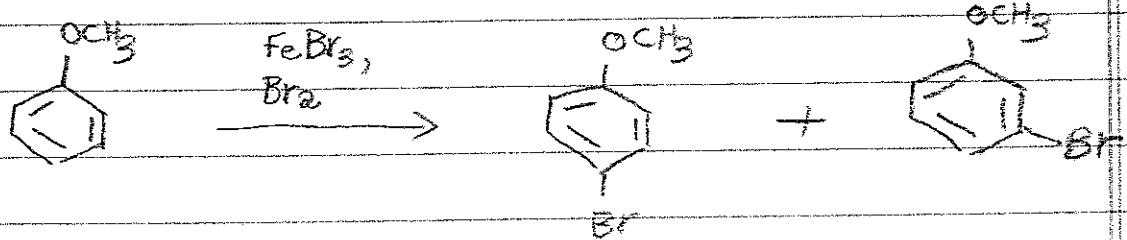
3. 

I. Mechanisms + Resonance

1. Which phenol is more acidic? Why?



2. Show mechanistically why product A is favored over product B:



A B

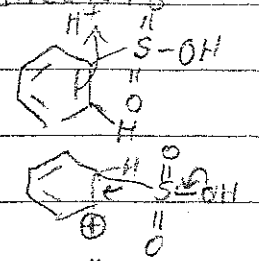
Chapter 22 Practice Problems: Introductory Level

key

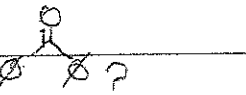
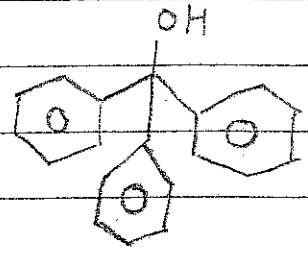
I. Electrophillic Aromatic Substitution

Give the reagents needed in each of the following reactions & indicate whether the product that forms is an o, p or m director & whether or not it is an activator or a deactivator.

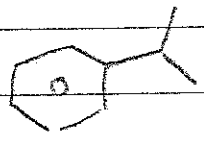
1. SO_3, H_2SO_4 → SO_3H (useful for blocking para substitution) — not in textbook: H_2O?



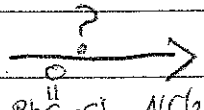
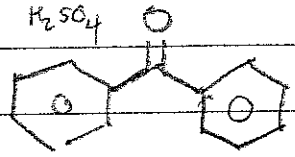
2. NO_2^+ ($H_2SO_4 + HNO_3$) → NO_2; H_2, Pd, Pt, or Ni → NH_2 (Fe, Zn or Sn with HCl)

3. $FeBr_3$ Br_2 $AlBr_3$ → Br; then  → 

(Hint: You did this last semester in Chem 51 lab)

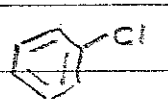
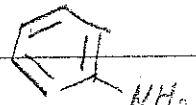
4. RCl $AlCl_3$ →  $+ H_3PO_4$ K_2SO_4

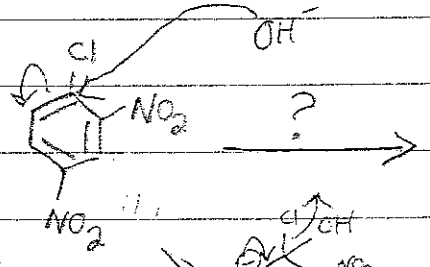
could do this with EW groups

5.  $AlCl_3$ → 

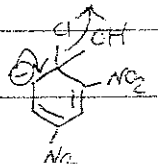
II. Nucleophillic Aromatic Substitution

Fill in the missing reagents.

1.  NH_2^- or OH^-, high P, T → benzyne → NH_3 → 

2. 

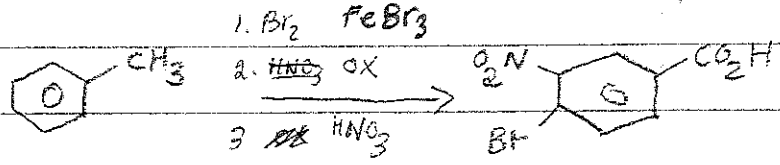
addition elimination

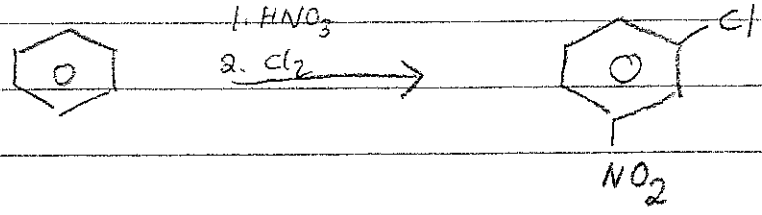


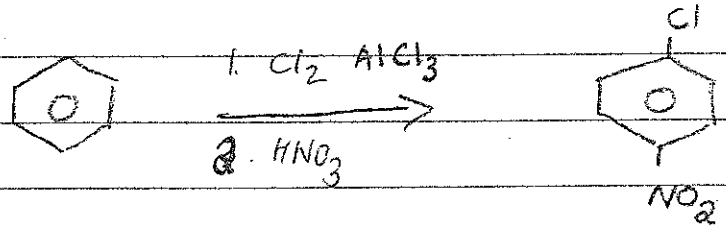
key

III. Synthesis

1. Give the reagents necessary to accomplish the following syntheses. Careful – the order in which you add things matters.

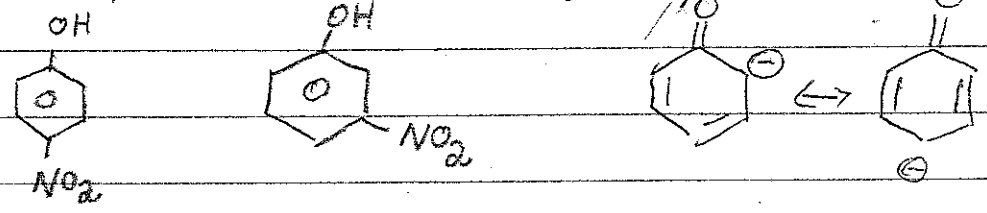
1. 

2. 

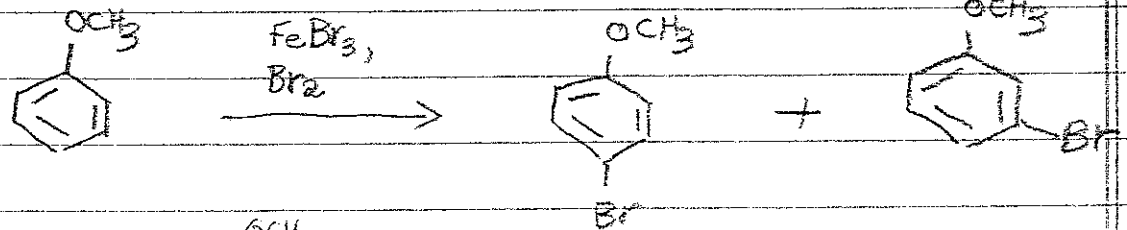
3. 

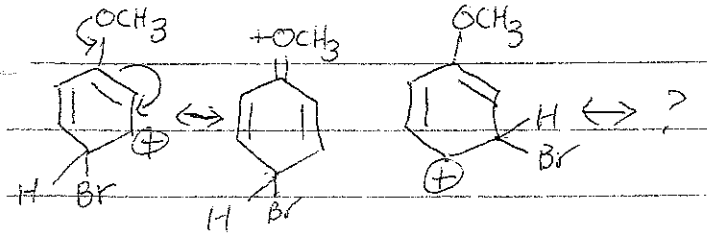
I. Mechanisms + Resonance

1. Which phenol is more acidic? Why?



2. Show mechanistically why product A is favored over product B:





Name:
Recitation Instructor:

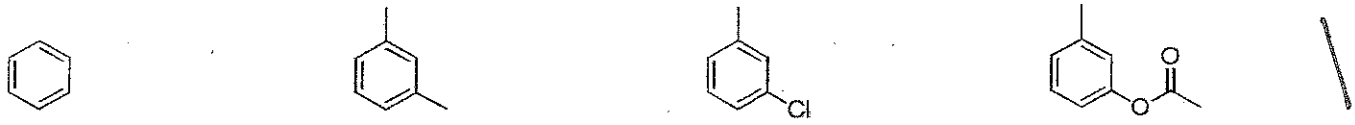
Brenner Exam II 2007 Chapter 22

6) [20 points] Propose a synthesis of **B** starting from **A**.

A **B**

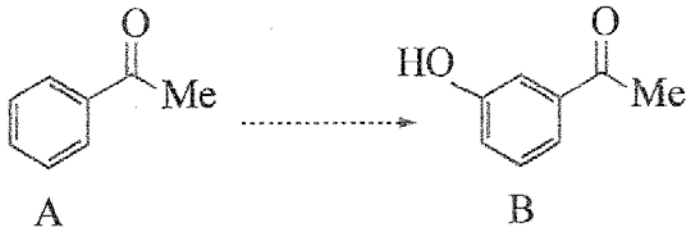
B) Circle the best nucleophile for the electrophilic aromatic substitution reaction.

chapter 22 Exam II Brenner 07



From MIT Chapter 22

6. (11 points) Provide a synthesis that will *selectively* convert **A** to **B.** Show all the key intermediates and furnish all the important reagents. This is not a one-step process.



A B

8. Synthesize the indicated compounds from the allowed starting materials shown below. All of the carbons of the target compounds should be derived from the allowed starting materials.

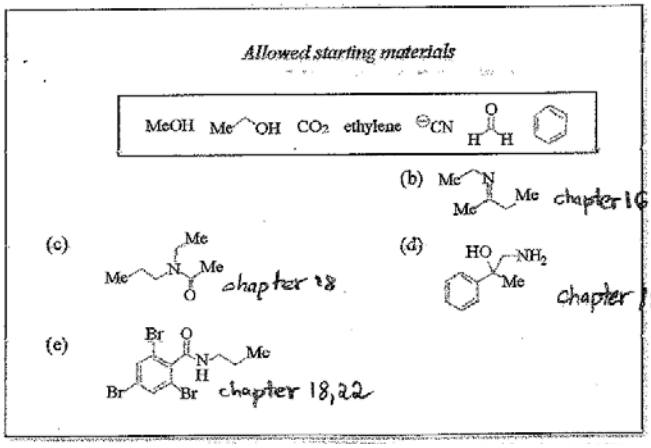
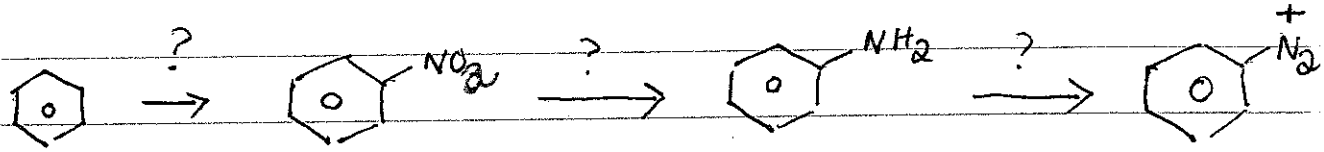


Figure by MIT OCW.

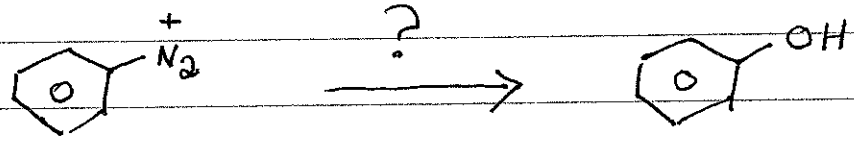
Chapter 23 Practice Problems: Introductory Level

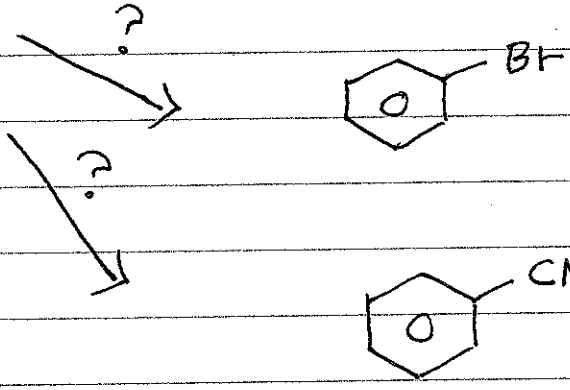
I. Fill in the missing Reagents

1.

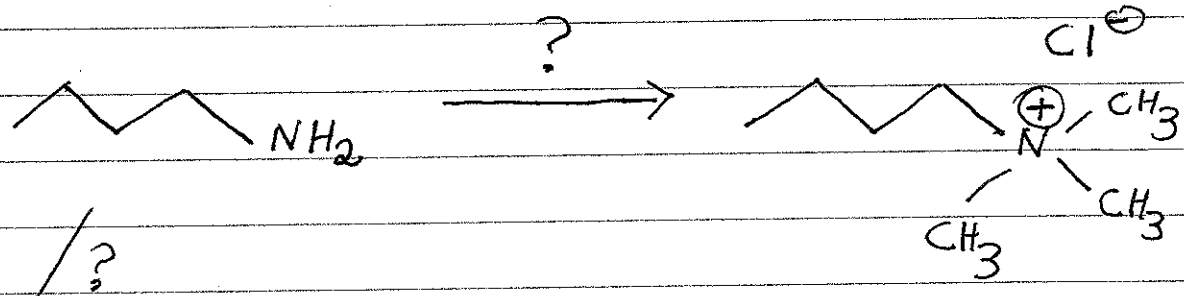


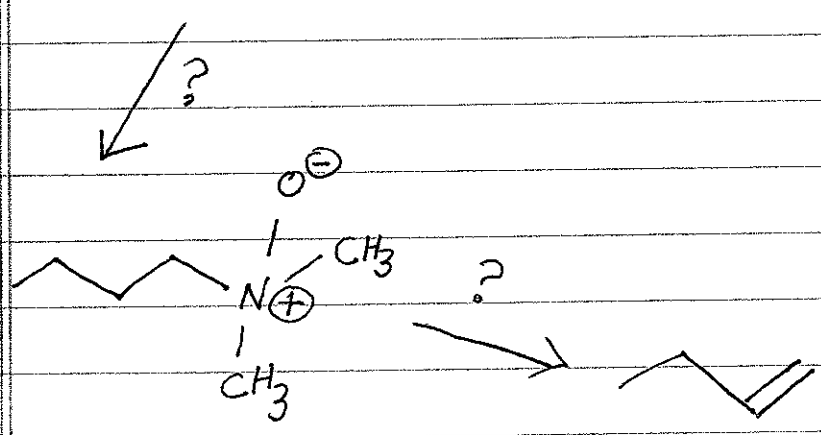
2.



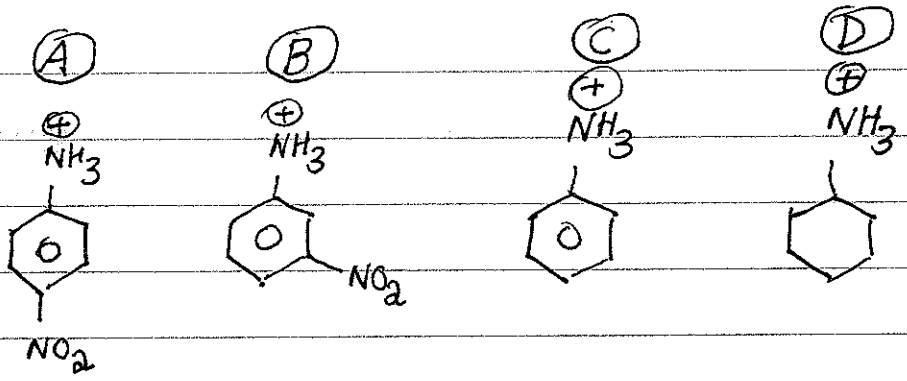


3.





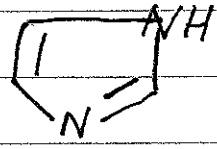
II. See questions below



pka ~ 1 pka ~ 2.5 pka ~ 5 pka ~ 11

1. Which compound is the most acidic?
2. Which conjugate base is the most basic?
3. Use resonance (+ conjugate bases) to explain the trend in pka's of compounds A thru D

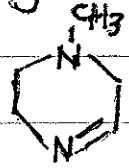
III 1a Which nitrogen is more basic? Why?



pka ~ 7 (for conjugate acid)

1b. Draw the conjugate acid & show how resonance stabilizes the acid.

2. Which nitrogen is more basic? Why?

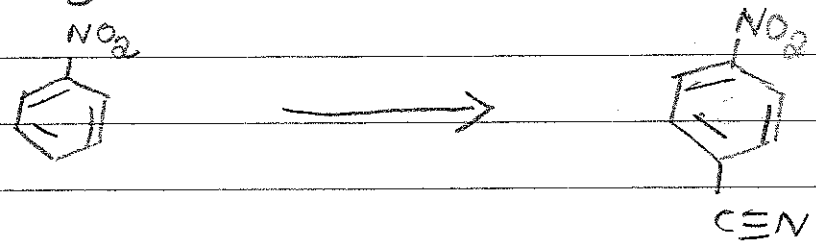


(hint compare sp^3 N to sp^2 N)

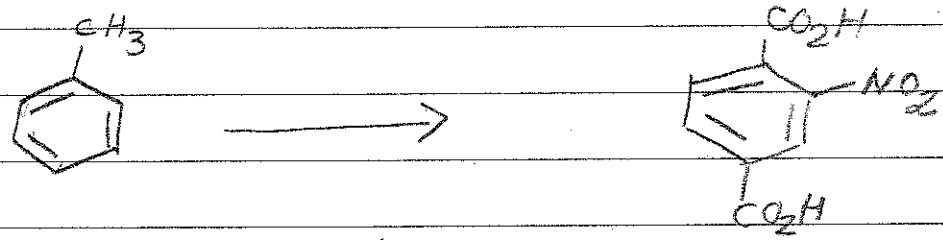
Chapter 23 Practice Problems - Synthesis

IV. Give the reagents necessary to accomplish each of the following transformations:

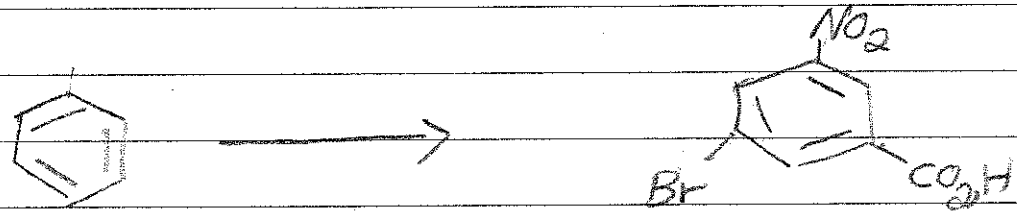
1.



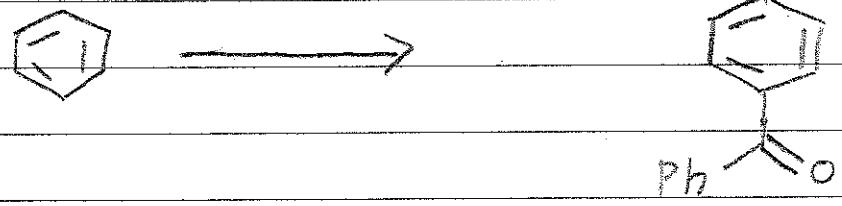
2.



3.



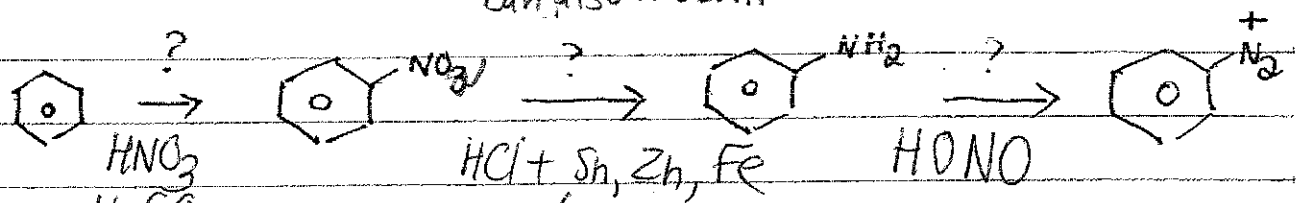
4.



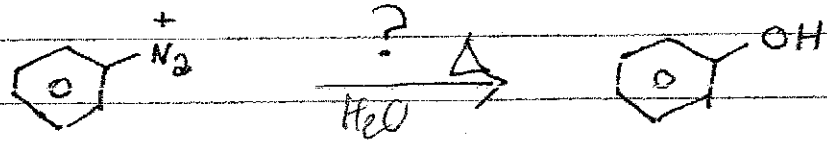
Key

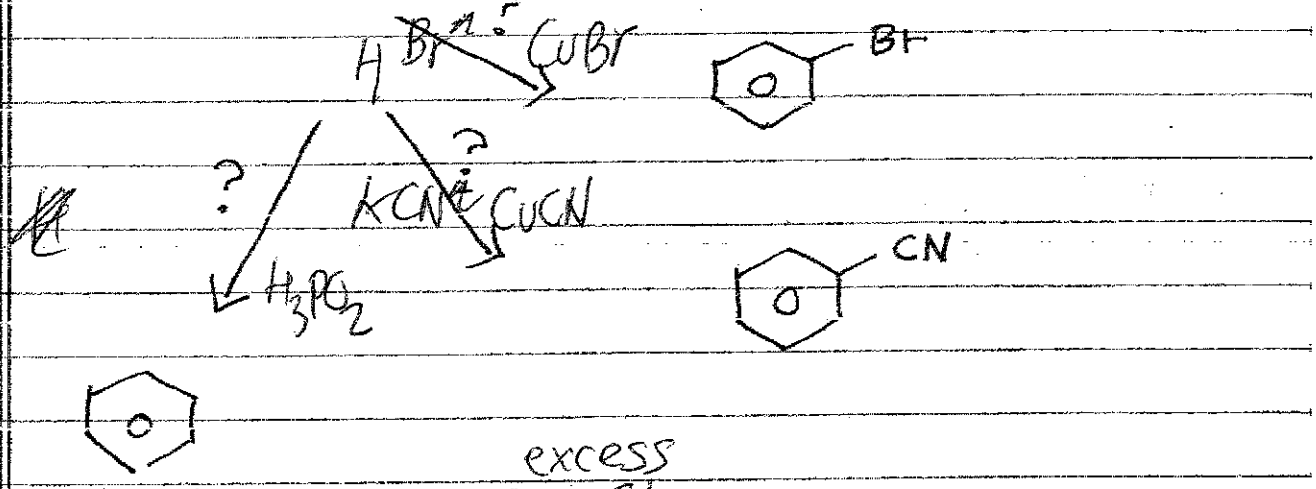
Chapter 23 Practice Problems: Introductory Level

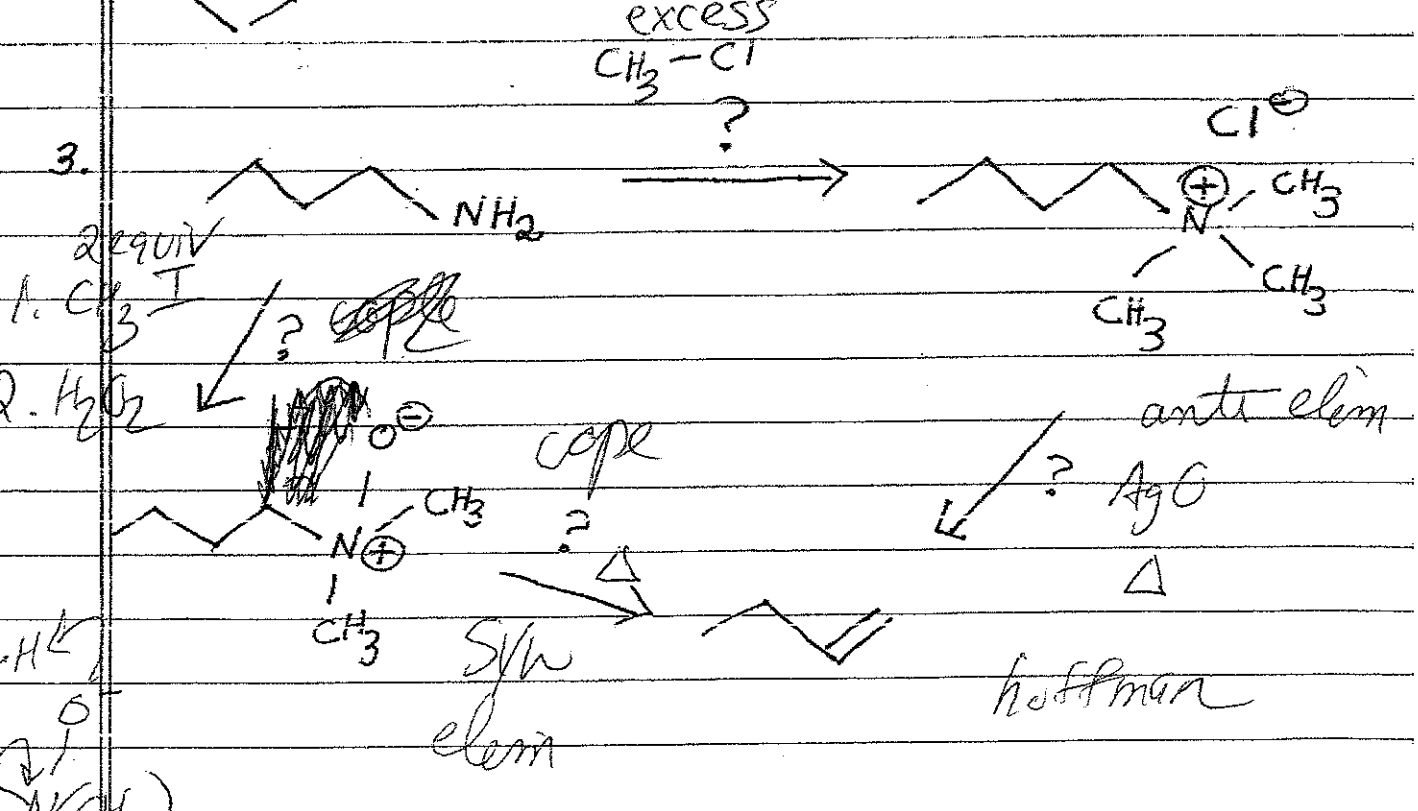
I. Fill in the missing Reagents

1. 

Can also use LAH

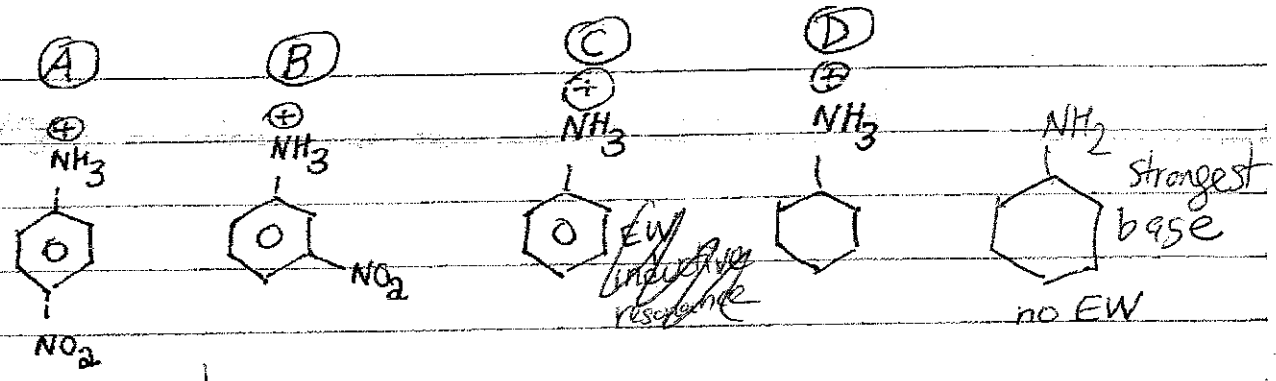
2. 



3. 

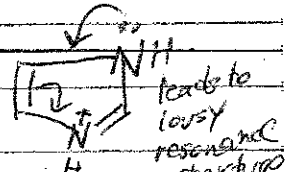
Key

II See questions below

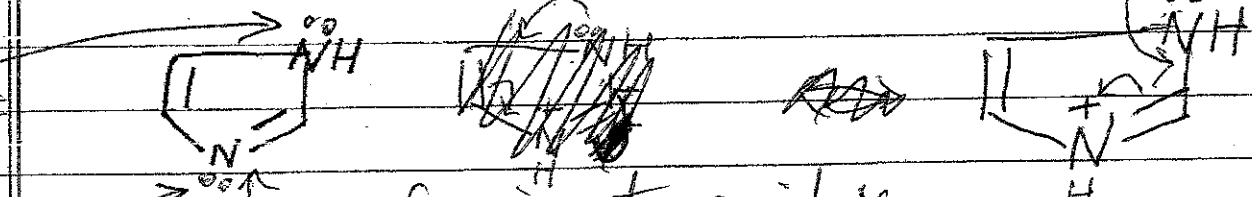


pka ~ 1 (most acidic; EW ind/resonance; weakest base) | pka ~ 2.5 | pka ~ 5 (base; EW inductive resonance) | pka ~ 11 (least acidic)

1. Which compound is the most acidic?
2. Which conjugate base is the most basic?
3. Use resonance + conjugate base to explain the trend in pka's of compounds A thru D (using conjugate base)

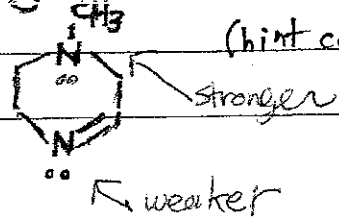


III 1a Which nitrogen is more basic? Why?



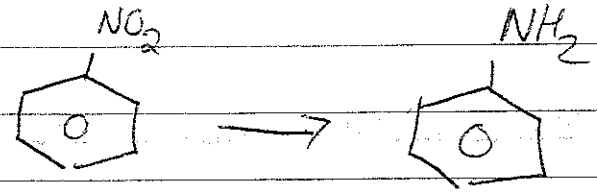
1b. Draw the conjugate acid & show how resonance stabilizes the acid

2a. Which nitrogen is more basic? Why?

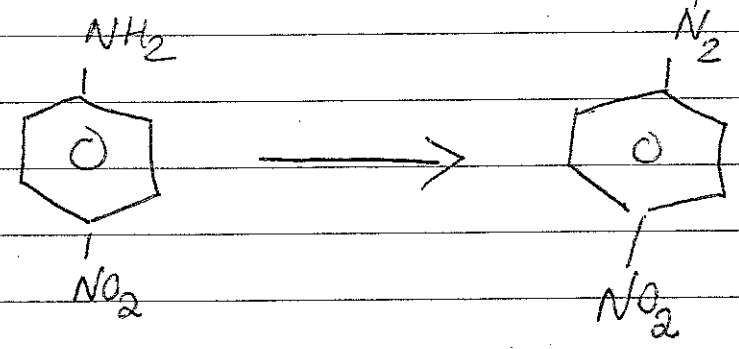


chapter 23 key

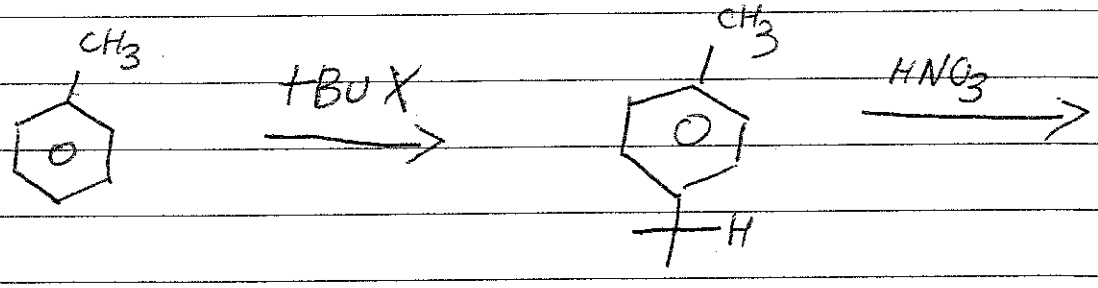
IV.

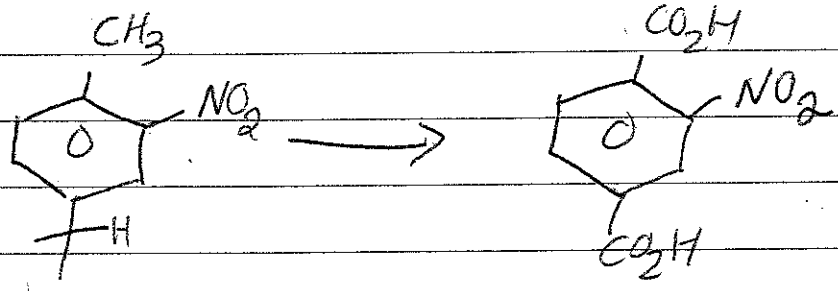


make sure to tell students - cannot do friedel crafts alkylation in the presence of an EW group (acylation is ok)



2.





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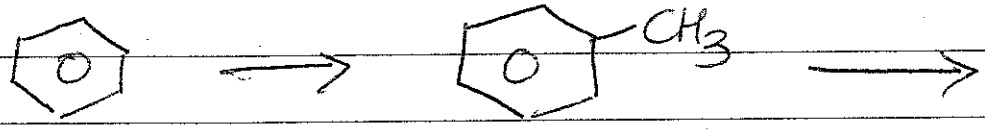

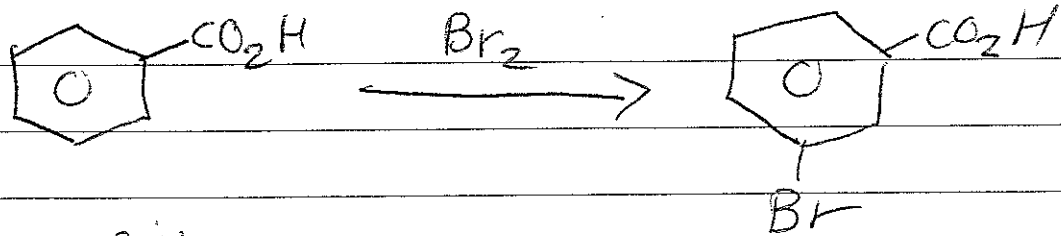

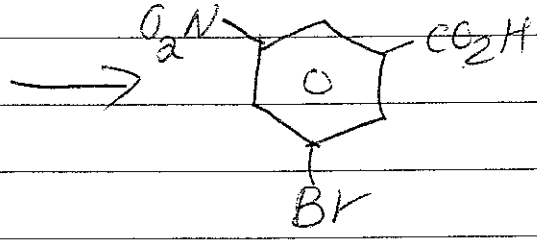

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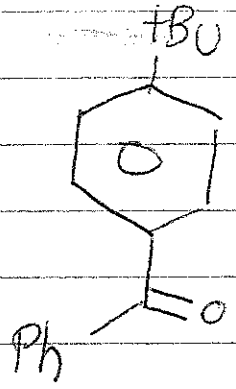
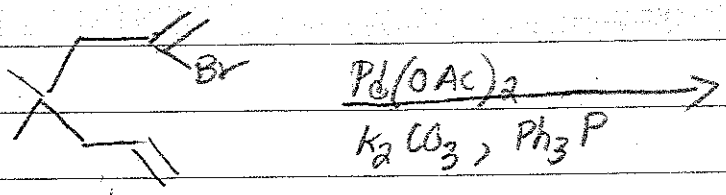
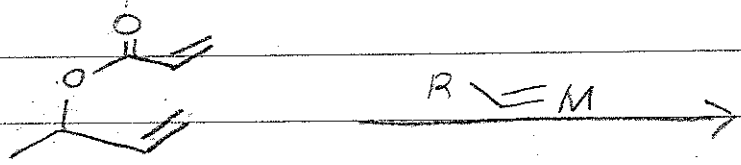
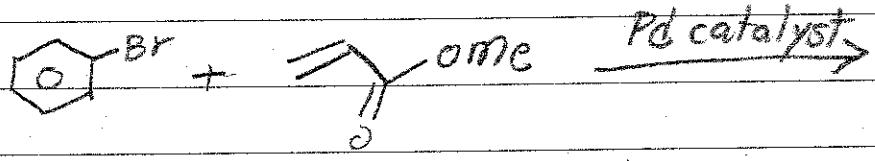


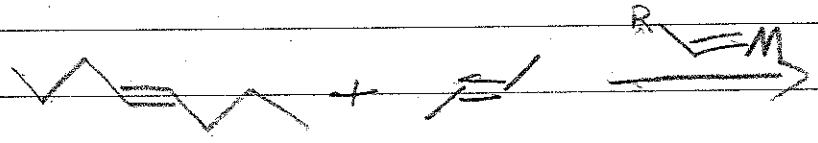
Chapter 24 Practice Problems: Introductory Level

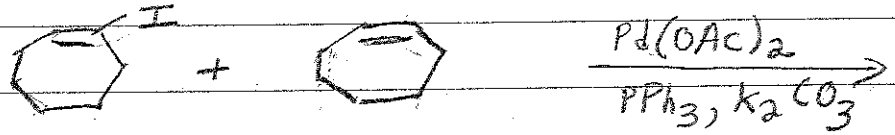
I. Give the products:

1. 

2. 

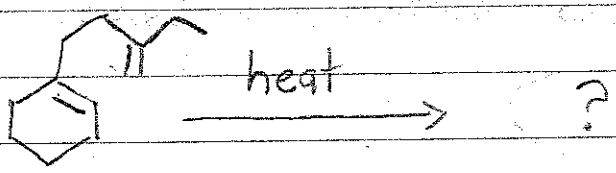
3. 

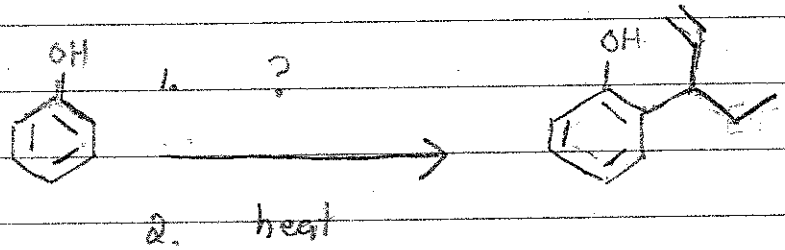
4. 

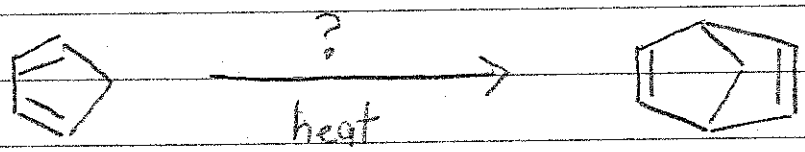
5. 

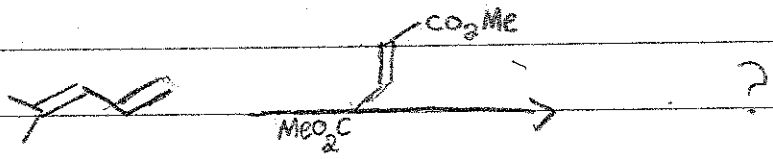
Chapter 24 Practice Problems Cont

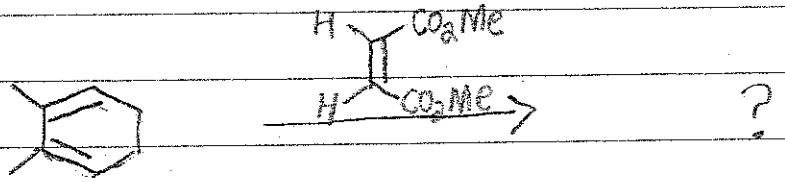
II. Fill in the missing reagents or products & show mechanistic arrows:

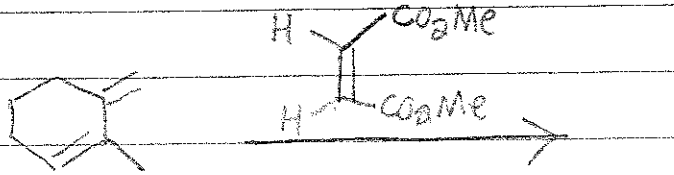
1. 

2. 

3. 

4. 

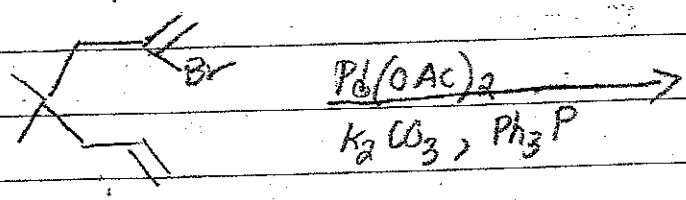
5. 

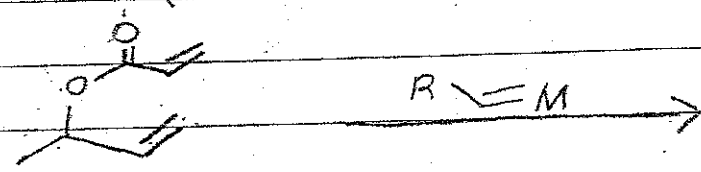
6. 

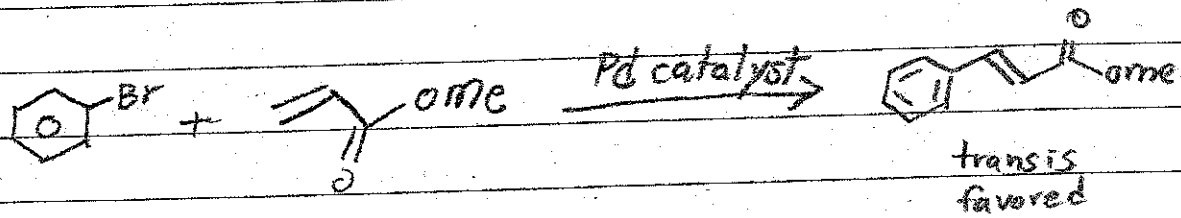
Chapter 24 Practice Problems: Introductory Level

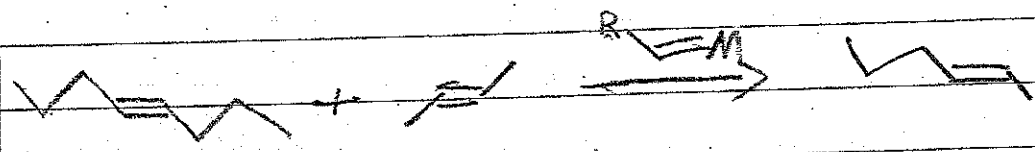
Key

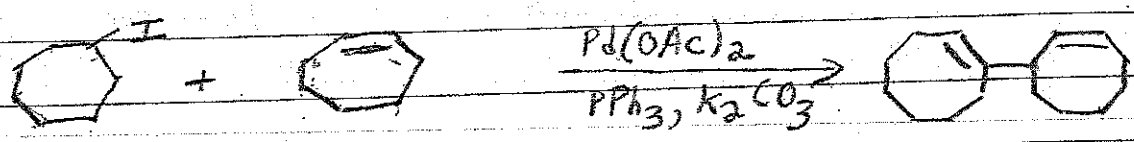
I. Give the products:

1. 

2. 

3. 

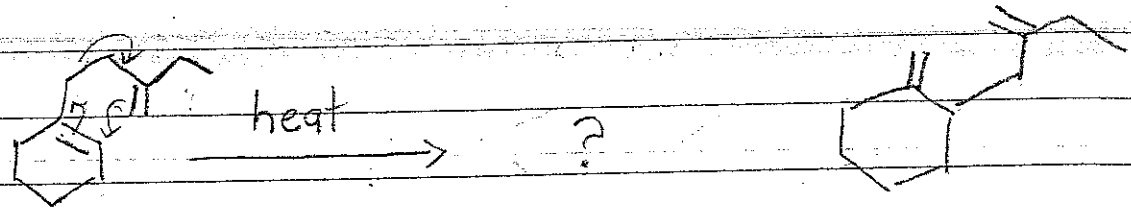
4. 

5. 

Chapter 24 Practice Problems Cont'd Key

II. Fill in the missing reagents or products & show mechanistic arrows:

1.



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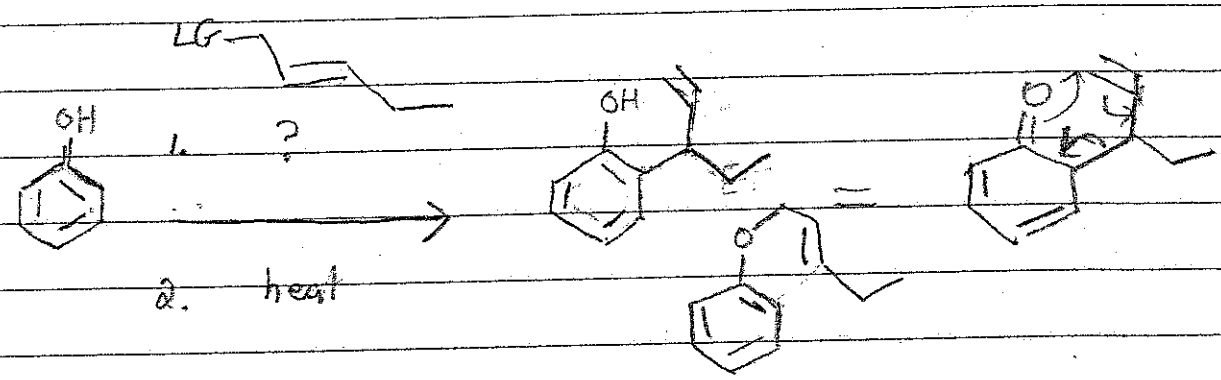

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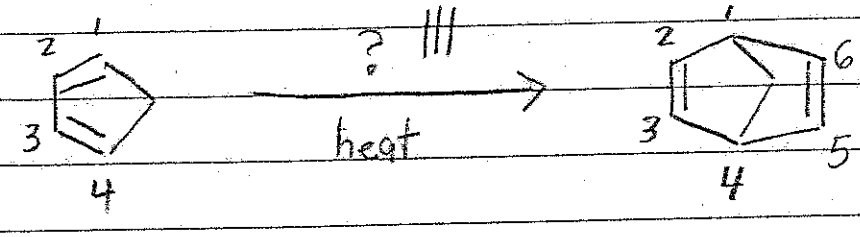

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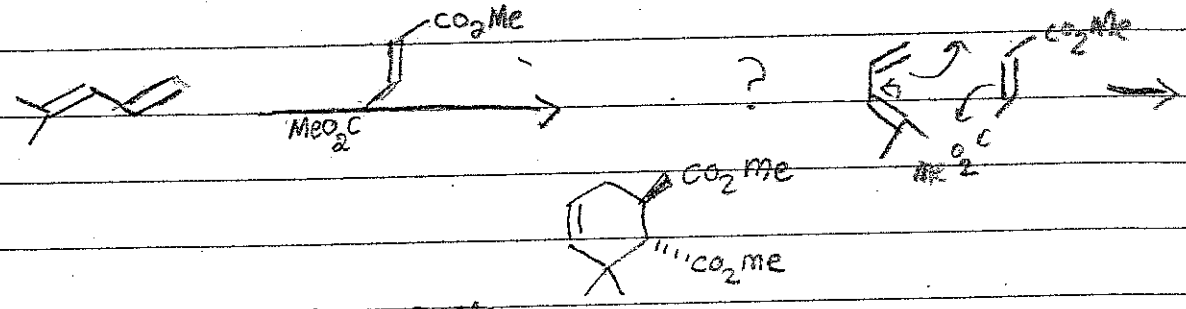

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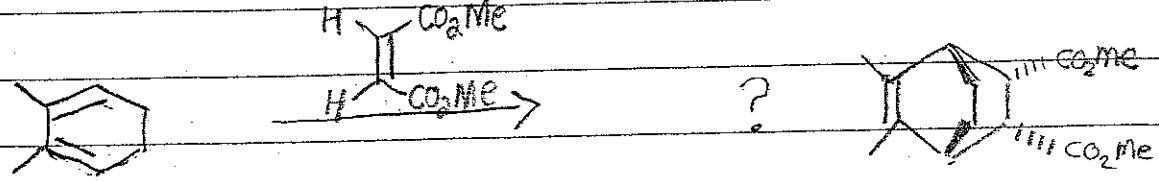

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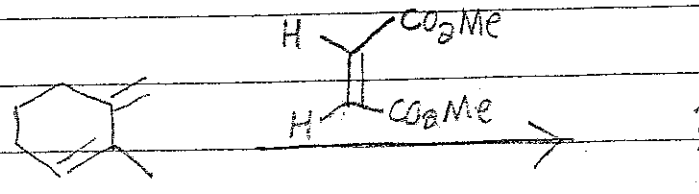
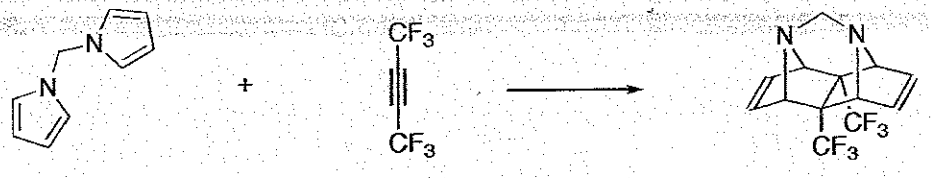


Chapter 24

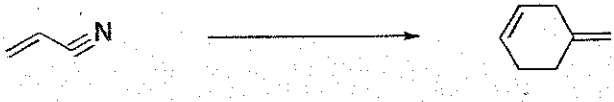
Brenner Exam II 2007

Name:
Recitation Instructor:

1. [20 points] Propose a detailed mechanism for the following transformation.

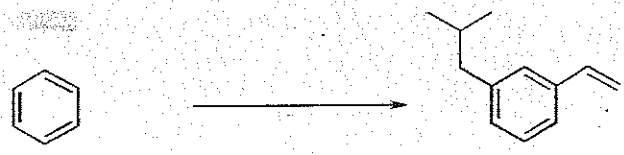


2. Propose a synthesis of **B** starting from **A**.



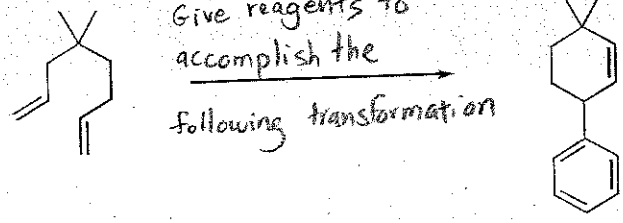
A **B**

3. Propose a synthesis of **B** starting from **A**. You must use the **Heck reaction** somewhere in your synthesis.

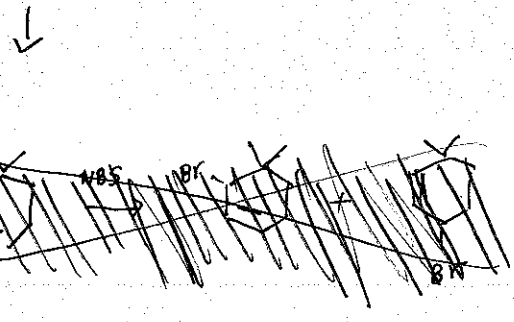


A **B**

4.



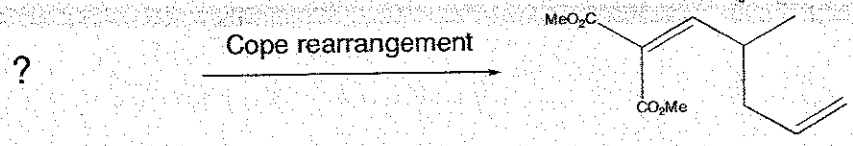
Give reagents to accomplish the following transformation



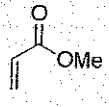
Name:

Brenner's Exam I 2007 Chapter 24 Recitation Instructor:

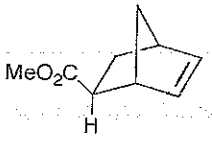
5. [14 points] The following compound was formed by a Cope rearrangement. Show the substrate for the Cope rearrangement.

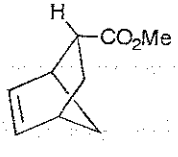


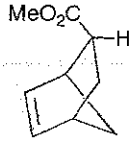
6. The following compound was formed by a Diels-Alder cycloaddition. Show the substrate for the Diels-Alder cycloaddition.

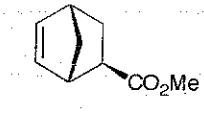
7. Circle the product that will form in the Diels-Alder reaction between and 

Brenner 07 chapter 24 Exam II



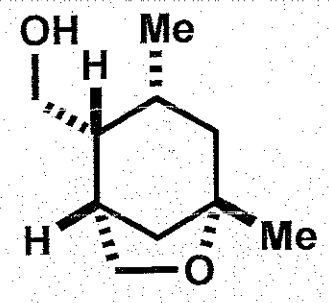






From MIT Chapter 24

8. (22 points total) Using retrosynthetic analysis, propose a synthesis of the molecule to the right (**A**). You may use any reagents you wish, as long as your **starting materials** and any other reagent that is used to install a **carbon** that is found in the final product (target molecule **A**) have **no more than 6 carbon atoms**. For example, 1,3-butadiene and benzene would be acceptable, but benzyl bromide ($PhCH_2Br$) would not be.



target molecule (**A**)

Write your synthesis in the "forward" direction, showing all steps and reagents necessary. (You may include solvents, but you are not required to do so.) **Draw a box around or circle your final synthesis.**

Hint: Use a Diels-Alder reaction.