Pre-Ch. 17 Practice Problems

(review of chem 51 material most relevant for chapters 17, 18, 19)

Fill in the missing reagents:

1. Reduction

2. Oxidation

3. Alkylation

Which of the following 2 organometallic reagents (PhLi, PhMgBr or Ph₂CuLi) should be chosen to best accomplish each reaction shown below?

4. Enals + Enolates

Fill in the missing products:

Pre-Ch. 17
Pre Chapter 17 Practice Problems
(review of chem 51 material most relevant for chapters 17, 18, 19)

Fill in the missing reagents:

1. Reduction
   \[ \text{LiAlH}_4 \overset{\text{H}^+}{\rightarrow} \]
   \[ \text{O} \]
   \[ \text{H}_2/\text{Pt or Ni} \]

2. Oxidation
   \[ \text{Jones} \]
   \[ \text{O} \]
   \[ \text{H}_2/\text{Rh} \]
   \[ \text{O} \]

3. \[ \text{PCC} \]
   \[ \text{Jones} \]
3. **Alkylation**

Which of the following 3 organometallic reagents (PhLi, PhMgBr or Ph₂CuLi) should be chosen to best accomplish each reaction shown below?

\[ \text{Ph}₂\text{CuLi} \]

a. \[ \text{?} \quad \begin{array}{c} \text{O} \quad \text{Br} \end{array} \quad \rightarrow \quad \begin{array}{c} \text{O} \quad \text{O} \end{array} \]

\[ \text{PhLi or PhMgBr} \]

b. \[ \text{?} \quad \begin{array}{c} \overset{\text{ OH }}{\text{C}} \quad \text{H} \end{array} \quad \rightarrow \quad \begin{array}{c} \text{O} \quad \text{O} \end{array} \]

4. **Enols & Enolates**

Fill in the missing products:

9. \[ \text{CH}_3\text{CCH}_3 \quad \rightarrow \quad \text{?} \quad \rightarrow \quad \text{?} \quad \text{Br}_2 \]

\[ \text{enol} \]

b. \[ \text{?} \quad \begin{array}{c} \text{O} \quad \text{O} \quad \text{C} \quad \text{H}_3 \end{array} \quad \rightarrow \quad \text{?} \quad \rightarrow \quad \text{?} \quad \text{Cl}_2 \]

\[ \text{"iodoform"} \quad \text{enolate} \]

\[ \text{HCCl}_3 \quad \overset{\text{rxn}}{\rightarrow} \quad \begin{array}{c} \text{O} \quad \text{O} \quad \text{C} \quad \text{H}_3 \end{array} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]
Chapter 17 Practice Problems: Introductory Level

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

\[
\begin{align*}
\text{F}_3\text{C}-\text{C}-\text{OH} & & \text{H}_3\text{C}-\text{C}-\text{OH} & & \text{F}_3\text{C}-\text{CH}_3-\text{C}-\text{OH}
\end{align*}
\]

a. Fill in the missing reagents & products:

a. \(\text{CH}_3\text{CH}_2\text{C} = \text{CH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\)

b. \(\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{N}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\)

c. \(\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{Aldehyde} \rightarrow \text{Alcohol} \rightarrow \text{Acid} \rightarrow \text{Ester}\)

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

a. \(\text{CH}_3\text{C}-\text{OH} \rightarrow \text{CH}_3\text{C}-\text{CH}_3\)

b. \(\text{HO}_2\text{C} \rightarrow \text{H}_2\text{C} \rightarrow \text{CO}_2\text{H}\)
which carboxylic acid is most acidic? Which has the highest pKa?

most acidic

1. Fill in the missing reagents and products:

a. \[ \text{CH}_2\text{CH}_2\text{C} = \text{CH} \rightarrow \text{CH}_3\text{CH}_2\text{O}_2\text{C}_2 \text{H}_5 \rightarrow \text{CH}_3\text{CH}_2\text{O}_2\text{C}_2 \text{H}_5 \rightarrow \text{CH}_3\text{CH}_2\text{O}_2\text{C}_2 \text{H}_5 \]

b. \[ \text{BuLi} \rightarrow \text{CO}_2 \rightarrow \text{CH}_3\text{N}_2 \rightarrow \text{Bu}_2\text{C} = \text{OCH}_3 \]

c. \[ \text{?} \rightarrow \text{?} \rightarrow \text{?} \rightarrow \text{?} \]

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

a. \[ \text{CH}_3\text{C} = \text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \]

b. \[ \text{H}_2\text{C} \rightarrow \text{CH}_3\text{CO}_2\text{H} \]
### Outline

#### Chapter 18

**Nucleophile**  |  **Electrophile**
--- | ---
$\text{H}^+$  |  $\text{R}^+$

**Stronger**  
$\text{Li}_4\text{AlH}_4$  
$\text{R}_2\text{MgBr}$  
$\text{Li}$

**Weaker**  
$\text{NaBH}_4$  
$\text{R}_2\text{CuLi}$

---

For $\text{Nu} = \text{H}_2\text{O}, \text{ROH}, \text{RNH}_2$

**For $\text{Nu} = \text{H}_2\text{O}, \text{ROH}, \text{RNH}_2$**

- **No catalyst is required for these electrophiles**
- **Yes catalyst is required for these electrophiles**

- **RC-Cl**
- **RC-O-C-Cl**
- **RC-O-C-R**
- **RC-OH**
- **RC-NH$_2$**

- **RC-C=O**
- **RCOR**
- **R-C=N**

- **Only acid catalyst**
- **Acid or base catalyst**
Chapter 18 Practice Problems: (Nuc = H₂O, 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. \( \text{OCH}_3 \) \( \rightarrow \) \( \text{NHCH}_3 \)

2. \( \text{OH} \) \( \rightarrow \) \( \text{OCH}_3 \)

3. \( \text{OH} \) \( \rightarrow \) \( \text{NHCH}_3 \)

4. \( \text{CH}_3\text{C} = \text{OCH}_3 \) \( \rightarrow \) \( \text{CH}_3\text{C} = \text{O} \)

5. \( \text{CH}_3\text{CH}_2\text{C} = \text{N} \) \( \rightarrow \) \( \text{CH}_3\text{CH}_2\text{C} = \text{OH} \)

6. \( \text{H}_2\text{O} \) \( \rightarrow \) \( ? \)

7. \( \text{Cl} \) \( \rightarrow \) \( ? \)

8. \( \text{OH} \) \( \rightarrow \) \( ? \)

9. \( ? \) \( \rightarrow \) \( ? \)
Chapter 18 Practice Problems:

Introductory Level

Give the products:

1. $\text{RC-Cl}$
   - $\text{RLi}$
   - $\text{B}_{2}\text{CuLi}$

2. $\text{RC-OR}$
   - $\text{RMgBr}$
   - $\text{B}_{2}\text{CuLi}$

3. $\text{RC-NH}_{2}$
   - $\text{RLi}$

4a. $\text{CH}_{3}\text{C-OLi}$
    - $\text{LiAlH}_{4}$

4b. $\text{CH}_{2}\text{CH}_{2}\text{C=NLiAlH}_{4}$

4c. $\text{CH}_{3}\text{COCH}_{2}\text{CH}_{3}$
    - $\text{NaBH}_{4}$

4d. $\text{Cl}$
    - $\text{NaBH}_{4}$

4e. $\text{NMe}_{2}$
    - $\text{LiAlH}_{4}$

($\text{Nuc} = \text{H}^- \text{or R}^-$)
Chapter 18 Practice Problems:  (Nuc = H₂O, 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. \[
\begin{align*}
\text{OCH}_3 \quad \text{?} \quad \text{NHCH}_3 \\
\text{CH}_3 \text{NH}_2 \\
\end{align*}
\]

2. \[
\begin{align*}
\text{OH} \quad \text{?} \quad \text{OCH}_3 \\
\text{CH}_3 \text{OH}, \text{H}^+ \quad \text{or} \\
\text{CH}_3^+ \text{base} \\
\end{align*}
\]

3. \[
\begin{align*}
\text{OH} \quad \text{?} \quad \text{NHCH}_3 \\
1. \text{SOCl}_2 \\
\text{aq. NH}_2\text{CH}_3 \\
\end{align*}
\]

4. \[
\begin{align*}
\text{CH}_3\text{C-OCH}_3 \quad \text{?} \quad \text{CH}_3\text{C-O-} \\
\text{PhOH}, \text{H}^+ \quad \text{or} \\
\text{PhO}^- \\
\end{align*}
\]

5. \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C=O} \quad \text{?} \quad \text{CH}_3\text{CH}_2\text{C-OH} \\
\text{H}^+, \text{H}_2\text{O} \quad \text{or} \\
\text{OH}^-, \text{H}_2\text{O} \\
\end{align*}
\]

6. \[
\begin{align*}
\text{H}_2\text{O} \quad \text{?} \quad ? \\
\text{no cat} \\
\end{align*}
\]

7. \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CHCl} \quad \text{H}_2\text{O} \quad \text{?} \quad \text{OH}^- \\
\text{no cat} \\
\end{align*}
\]

8. \[
\begin{align*}
\text{OH} \quad \text{?} \quad ? \\
\text{H}_3\text{OH}, \text{H}^+ \text{ or } \text{CH}_3\text{O}^- \quad \text{H}_3\text{O}^+ \quad \text{Cl}^- \\
\end{align*}
\]

(leave one out)
Chapter 18 Practice Problems:

Introductory Level

Give the products:

* goes thru imine not aldehyde

1. \( R_3C-\text{Cl} \)
   \[ \text{RLi} \rightarrow R_3C-\text{OH} \]
   \[ \text{RaCuLi} \rightarrow R_2C=O \]

2. \( R_3C-\text{OR} \)
   \[ \text{RMsBr} \rightarrow R_2C=O \]
   \[ \text{RaCuLi} \rightarrow \text{NR} * \]

3. \( R_3C-\text{NH}_2 \)
   \[ \text{RLi} \rightarrow R_3C-\text{NH} + \text{Li} + \text{BH} \]
   acid-base rxn!

4a. \( \text{CH}_3\text{C}-\text{OH} \)
   \[ \text{LiAlH}_4 \rightarrow \text{CH}_3\text{CH}_2\text{OH} \]

b. \( \text{CH}_3\text{CH}_2\text{C} = \text{N} \)
   \[ \text{LiAlH}_4 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 * \]

c. \( \text{CH}_3\text{COCH}_2\text{CH}_3 \)
   \[ \text{NaBH}_4 \rightarrow \text{NR} \]

d. \( \text{CH}_3\text{C}=\text{Cl} \)
   \[ \text{NaBH}_4 \rightarrow \text{CH}_2\text{OH} \]

e. \( \text{NMe}_2 \)
   \[ \text{LiAlH}_4 \rightarrow \text{CH}_2\text{NMe}_2 * \]
   not alcohol!
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

2. A

   B

III. Propose structures for compounds A, B, C, D (this question is from the Brenner Spring 2012 exam):

   Succinic Anhydride \( \overset{\text{HO}}{\rightarrow} \) A \( \overset{\text{SOCl}_2}{\rightarrow} \) B

   1. Me\(_2\)CuLi \( 2. \text{H}_2\text{O} \)

   C \( \overset{\text{MeLi (assume 1 equiv)}}{\rightarrow} \) D \((\text{C}_6\text{H}_{10}\text{O}_2)\)

IV. Propose a mechanism for the following reaction:
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.

\[ \text{NH} \quad \text{Me} \quad \text{A} \quad \text{OMe} \quad \xrightarrow{\text{HO}^-} \quad \text{O} \quad \text{Me} \quad \text{NH}_2 \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{Me} \quad \text{OMe} \quad + \quad \text{MeOH} \] (1)

Figure by MIT OCW.

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

\[ \text{NH} \quad \text{Me} \quad \text{A} \quad \text{OMe} \quad \xrightarrow{\text{excess H}^+} \quad \text{O} \quad \text{Me} \quad \text{OMe} \quad + \quad \text{NH}_4^+ \] (2)

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 19 - Outline of Rxns

I. Condensation Rxns

1. Aldol
   \[ \text{alkyl} + \text{ketone} \rightarrow \text{alcohol} + \text{aldehyde} \]

2. Claisen
   \[ \text{ester} \rightarrow \text{ester} + \text{ester} \]

II. Alkylation Rxns

1. Acetoacetic Ester
   \[ \text{ester} + \text{halogen} \rightarrow \text{ester} + \text{ester} \]

2. Malonic Ester
   \[ \text{ester} + \text{halogen} \rightarrow \text{ester} + \text{ester} \]

3a. 3b. LDA, RX, NR_2, H_3O^+
Chapter 19 - Outline of Rxns Cont

III

**Conjugate Addition**

\[
\text{alkene} + R^+ \text{Li}^+ \rightarrow \text{alkene} + R \text{OH}
\]

\[
\text{alkene} + R^- \text{MgBr} \rightarrow \text{alkene} + R \text{H}
\]

1,2 addition

\[
\text{alkene} \rightarrow \text{alkane}
\]

RaCul

1,4 addition

\[
\text{alkene} + R^- \text{MgBr} \rightarrow \text{alkane}
\]

1,4 addition with enolate

\[
\text{enolate} + \text{alkene} \rightarrow \text{alkene}
\]

\[
\text{enolate} + \text{alkene} \rightarrow \text{alkene}
\]

decarboxylation

lecture IV

**Robinson Annulation** (Michael + Aldol)

\[
\text{6 membered ring} \rightarrow \text{alkene}
\]

Michael

Aldol
Chapter 19 Practice Problems: Introductory Level

I. Give the products of the following rxns:

1. \( \text{LDA} \) and \( \text{CH}_3\text{Br} \)

2. \( \text{OTs} \)

3. \( \text{acetate} \)

4. \( \text{EtO} \) and \( \text{OEt}^- \)

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

1. \( \text{EtO} \) and \( \text{OEt}^- \)

2. \( \text{EtO} \)

3. \( \text{EtO} \)

4. \( \text{CH}_3 \)

5. \( \text{OEt}^- \)
Sequential Condensation Reactions

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.

Mechanisms can be accessed at this URL

http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Questions/Synthesis/cndnprb.htm

3/9/2012
3) The retroaldo reaction is an aldol reaction in reverse; the products of a retroaldo reaction are the starting materials of an aldol reaction. Show the products of the following retroaldo reactions.

A)

B)

4) Provide structures for compounds A-F.

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

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

Question 3 (20 Points)

Provide structures for succinic anhydride and for compounds A-D. Assume you have one equivalent of every reagent listed, unless otherwise stated.

Hints: Succinic anhydride is a cyclic anhydride whose parent acid is succinic acid. Also, a molecular formula for compound D is provided.

\[
\text{succinic anhydride} \xrightarrow{\text{HO-}} A \xrightarrow{\text{SOCl}_2} B
\]

1. \((\text{CH}_3)_2\text{CuLi}, \text{ether, -78 °C}
2. \text{H}_2\text{O}

C \xrightarrow{\text{MeLi}} D

C_6\text{H}_{10}\text{O}_2

Question 4 (20 Points)

Propose a detailed mechanism for the transformation of A to B.

\[
\text{A} \xrightarrow{\text{Na}^+\text{-OEt, EtOH}} \text{B}
\]

Question 5 (20 Points)

Propose an efficient synthesis of the enol product shown below starting from methyl vinyl ketone and dimethyl malonate. More than one step is necessary, and you must illustrate the product of each step you are proposing.

\[
\text{methyl vinyl ketone} + \text{dimethyl malonate} \rightarrow \text{enol product}
\]
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)  

Problem Set #8
Due: December 4, 2006, 12:00 PM

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

\[
\begin{align*}
\text{a) } & \quad \begin{array}{c}
\text{Me} \\
\text{OCH}_3
\end{array} \\
\text{b) } & \quad \begin{array}{c}
\text{CO}_2\text{Et}
\end{array}
\end{align*}
\]

2. Write the products for the following reactions.

\[
\begin{align*}
\text{a) } & \quad \begin{array}{c}
\text{aryl ketone} \\
+ \begin{array}{c}
\text{H}_2\text{C} = \text{CH}_2
\end{array}
\end{array} \xrightarrow{\text{NaOCH}_3, \text{CH}_3\text{OH}, \Delta} \\
\text{b) } & \quad \begin{array}{c}
\text{cyclohexanone}
\end{array} \xrightarrow{1. \text{LDA}} \xrightarrow{2. \text{HC} = \text{CH}_3}
\end{align*}
\]

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

\[
\begin{align*}
\text{product} \xrightarrow{\text{NaOEt, excess EtOH}} A + \begin{array}{c}
\text{allyl alcohol}
\end{array} \xrightarrow{\text{KOH-Bu}} B \xrightarrow{\text{OH, H}_2\text{O}} \text{product}
\end{align*}
\]

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

\[
\begin{align*}
\text{a) } & \quad \begin{array}{c}
\text{Me}
\end{array} \xrightarrow{\text{O}} \text{H} \xrightarrow{\text{Ph}} \\
\text{b) } & \quad \begin{array}{c}
\text{Me}
\end{array} \\
\text{c) } & \quad \begin{array}{c}
\text{Me}
\text{O}
\text{N}
\text{Me}
\end{array} \\
\text{d) } & \quad \begin{array}{c}
\text{Ph}
\text{Me}
\end{array}
\end{align*}
\]

5. Only sources of carbon

\[
\begin{array}{c|c|c}
\text{MeOH} & \text{EtOH} & \text{PrOH} \\
\hline
\text{Ph} - \text{OH} & \text{OH} & \text{starting materials}
\end{array}
\]
11. Provide a reasonable mechanism for each of the following transformations.

a) \[ \text{K}_2\text{CO}_3 \rightarrow \text{HO} \]

b) \[ 2 \text{H}_2\text{O}, \text{H}_2\text{O}^+ \rightarrow \text{heat} \]

c) \[ \text{NaOEt} \rightarrow \text{heat} \]

d) \[ \text{KOH} \rightarrow \text{heat} \]

e) \[ \text{NaOEt} \rightarrow \text{NaOH} \rightarrow \text{heat} \]

*fDon't need to show mechanism for this step.*

g) \[ \text{Hg}^{2+}, \text{H}_2\text{SO}_4 \rightarrow \text{heat} \]

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

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

a) \[ \rightarrow \text{HO} \]

c) \[ \text{acetoacetic ester or malonic ester} \]

b) \[ \rightarrow \text{Ph} \]

d) \[ \text{acetoacetic ester or malonic ester} \]
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. \[ \text{carbocation} + \overset{\text{H}^+}{\text{Br}}^{-} \]
   \[ \text{1,2 addition} \quad \text{1,4 addition} \quad \text{1,2 addition} \]

2. \[ \overset{\text{1,4 addition}}{\text{carbocation}} + \overset{\text{1,2 addition}}{\text{carbocation}} + \overset{\text{1,2 addition}}{\text{carbocation}} \]

   * why doesn't this one form? 
   \[ \overset{\text{Br}^{-}}{} \]

   \[ \text{carbocation} + \overset{\text{Br}^{-}}{} \]

   \[ \text{carbocation} + \overset{\text{Br}^{-}}{} \]

   \[ \text{carbocation} + \overset{\text{Br}^{-}}{} \]

   \[ ? \quad ? \quad ? \quad ? \]
Chapter 26 cont

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

1. 

\[ \text{1 equiv } \text{Br}_2 \]

2. 

\[ \text{1 equiv } \text{Br}_2 \]

3. 

\[ \text{1 equiv } \text{DCl} \]

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

1. on bonding \( \pi \), 5 nodes

2. on antibonding \( \pi \), 4 nodes

3. on antibonding \( \pi \), 3 nodes

4. on bonding \( \pi \), 2 nodes

5. on bonding \( \pi \), 1 node

6. on bonding \( \pi \), 0 nodes
Chapter 20 Practice Problems: Introductory Level

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

\[ \text{Ph} \xrightarrow{\text{Br}^-} \text{carbocation} + \text{Ph} \xrightarrow{\text{Br}^-} \text{carbocation} \]

thermo kinetic
\[ \text{Br} \xrightarrow{1,2 \text{ addition}} \text{Br} \xrightarrow{1,4 \text{ addition}} \text{Br} \]

\[ \text{H} \xrightarrow{1,2 \text{ addition}} \text{H} \xrightarrow{1,4 \text{ addition}} \text{H} \]

why doesn't this one form?

\[ \text{Br} \xrightarrow{1,2 \text{ addition}} \text{Br} \xrightarrow{1,4 \text{ addition}} \text{Br} \]

thermo kinetic kinetic
II. Draw all possible products and label the thermodynamic and kinetic products.

1. \( \text{1 equiv Br}_2 \)

   - Thermodynamic: \( \text{Br} \)
   - Kinetic: \( \text{Br} \)

2. \( \text{1 equiv Br}_2 \)

   - Thermodynamic: \( \text{Br} \)
   - Kinetic: \( \text{Br} \)

3. \( \text{1 equiv DCl} \)

   - Thermodynamic: \( \text{D} \)
   - Kinetic: \( \text{Cl} \)

III. Shade in the molecular orbitals of 1,3,5-hexatriene (one is done for you.)

   - antibonding \( \Psi_0 \) - 5 nodes
   - antibonding \( \Psi_3 \) - 4 nodes
   - antibonding \( \Psi_4 \) - 3 nodes
   - bonding \( \Psi_3 \) - 2 nodes
   - bonding \( \Psi_2 \) - 1 node
   - bonding \( \Psi_1 \) - 0 nodes
Question 2 (28 Points; Parts A, B and C)

Answer Parts A, B and C about hexatriene.

\[
\text{hexatriene}
\]

A) How many molecular orbitals will hexatriene have?

B) Draw the 3 lowest energy molecular orbitals of hexatriene. For the 3 molecular orbitals that you drew, indicate clearly which is lowest in energy and which is highest in energy.

C) Would you expect that more or less energy is required to excite an electron from the highest energy filled orbital to the lowest energy unfilled orbital in hexatriene vs. in butadiene?
1. Determine whether each of the following compounds is non-aromatic, aromatic, or antiaromatic:

- [Diagrams of compounds a through h are shown here.]

2. Draw a Frost circle for compound f above. Fill in the π electrons and label the energy levels as bonding, non-bonding, or antibonding.
3. Fill in the missing reagents or products:

9. \[
\text{OH} \quad ? \quad \text{OH} \quad \text{CO}_2\text{H}
\]

b. \[
\text{OH} \quad ? \quad \text{Ph} \quad \text{H}_2 \quad \text{Pd} \quad ?
\]

c. \[
\text{OH} \quad \text{K}_2\text{Cr}_2\text{O}_7 \quad ?
\]

d. \[
\text{K}_2\text{Cr}_2\text{O}_7 \quad ?
\]

e. \[
\text{NBS} \quad ?
\]

4. Which phenol is most acidic? Which has the highest pK_a?
Chapter 21 Practice Problems: Introductory Level

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

   [Chemical structures of compounds a to d are shown]

   a. 
   b. 
   c. 
   d. 

2. Draw a first circle for compound f above. Fill in the 1\textsuperscript{st} planar electrons and label the energy levels as bonding, non-bonding, or antibonding.

   [Chemical structure of compound f is shown]

question 1. 4\textsuperscript{th} aromatic

question 2. 4\textsuperscript{th} antiaromatic

For heteroatom, count for lone pairs or double bond, NOT both.

[Chemical structures are shown with circles and labels for bonding and non-bonding electrons]
3. Fill in the missing reagents or products:

i. \( \text{NaOH} \)  \( \xrightarrow{\text{CO}_2} \)  \( \text{CO}_2 \)

b. \( \text{PhCH}_2 \text{X} \)
   1. \( \text{Na} \)
   2. \( \text{PhCH}_2 \text{X} \)  \( \xrightarrow{\text{Pd}} \)  \( \text{H}_2 \)  \( \text{PhCH}_3 \)  \( \xrightarrow{\text{PhCH}_3} \)  \( \text{toluene} \)

e. \( \text{NBS} \)  \( \xrightarrow{\text{Br}} \)  \( \text{Ph}_2 \text{C} \text{Br} \)

4. Which phenol is most acidic?
Which has the highest \( \text{pK}_a \)?

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{OH} )  ( \text{OMe} )</td>
<td>( \text{OH} )  ( \text{Me} )</td>
<td>( \text{OH} )  ( \text{CH}_3 )</td>
<td>( \text{OH} )  ( \text{CO}_2 \text{H} )</td>
</tr>
<tr>
<td>ED resonance</td>
<td>ED resonance</td>
<td>EW resonance</td>
<td>EW resonance</td>
</tr>
<tr>
<td>EW inductive</td>
<td>EW inductive</td>
<td>EW inductive</td>
<td>Conjugate base is stabilized</td>
</tr>
<tr>
<td>highest ( \text{pK}_a )</td>
<td>most acidic</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 your 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:

   ![Chemical Structures]

B) Circle the compound that is aromatic:

   ![Chemical Structures]

C) Draw the Frost circle for the aromatic compound from part B.
Question 2 (Parts A and B): 15 points

A) Circle the lone pair(s) that can participate in π 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.

[C] C_{20}H_{28}O_2 → D

E C_{13}H_{16}O_2