Organic Chemistry Peer Tutoring Department
University of California, Irvine
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Chem 51C
Professor Nowick
https://sites.uci.edu/ochemtutors/

Midterm 1 Review

Chapter 16 Concepts:

Reactions of Aromatic Compounds

-mechanisms (2-step) of electrophilic aromatic substitutions
-effects of aromatic substituents on regioselectivity
    -ortho, para, meta
    -inductive, resonance, reactivity
-types of electrophilic aromatic substitutions
    -halogenation
    -nitration
    -sulfonation
    -friedel-crafts alkylation
    -friedel-crafts acylation
-reactions of other benzene derivatives

Chapter 17 Concepts:

Introduction to Carbonyl Chemistry, Organometallic Reagents, and Oxidation and Reduction

-Types of Carbonyl Compounds and General Reactions
    -nucleophilic addition: aldehydes and ketones
    -nucleophilic substitution: carbonyl compounds with leaving groups
    -Reactivity of Aldehyde vs Ketone
-Oxidation Reactions
    -def) an increase in the number of C–Z bonds (usually C–O bonds)
        -ex. aldehydes to carboxylic acids
-Reduction Reactions
    -def) a decrease in the number of C–Z bonds
    -Hydride reduction via nucleophilic addition ($LiAlH_4$, $NaBH_4$)
        -aldehydes and ketones
    -Catalytic hydrogenation to 1° and 2° alcohols (H_2, Pd-C)
        - α,β-unsaturated aldehydes and ketones
    -Enantioselective reduction (S-CBS, R-CBS)
        -ketones
    -other reactions of acid chlorides, esters, carboxylic acids to 1° alcohols, amides to amines
-Preparation and Reactions with Organometallic Reagents
-Protecting Groups

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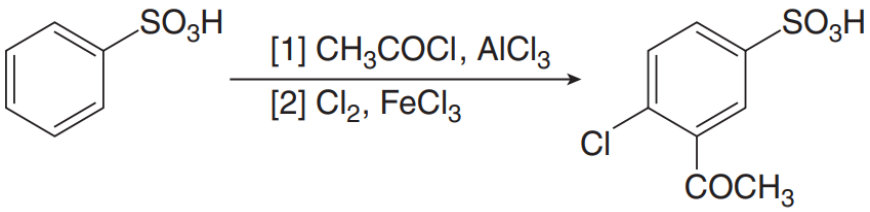
Chapter 18 Concepts:

Aldehydes and Ketones - Nucleophilic Addition

- Nucleophilic Addition Reactions
  - Addition of Hydride (H-) (18.7)
  - Addition of organometallic reagents (R-) (18.7)
  - Addition of cyanide (CN-) (18.8)
  - Wittig reaction (18.9)
  - Addition of 1° amines (18.10)
  - Addition of 2° amines (18.11)
  - Addition of H2O -Hydration (18.12)
  - Addition of alcohols (18.13)
- Other reactions
  - Synthesis of wittig reagents (18.9A)
  - Conversion of cyanohydrins to aldehydes and ketones (18.8)
  - Hydrolysis of nitriles (18.8)
  - Hydrolysis of imines and enamines (18.11)
  - Hydrolysis of acetals (18.13)

1. Explain why each of the following reactions will not form the given product and then design a correct synthesis of (a) from benzene and (b) from phenol (C6H5OH).

a.



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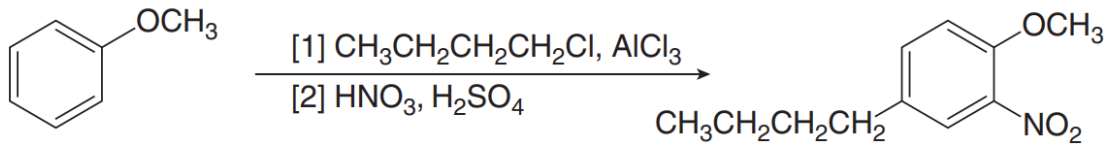
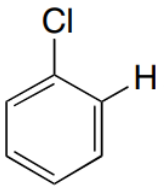
b.



2. True or False. A chlorine is a/an [o,p,m] director that activates/deactivates a benzene ring towards electrophilic attack.



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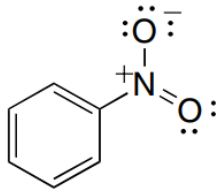
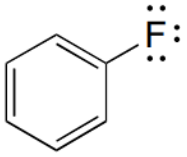
3. Draw all resonance structures for each compound, and explain why a particular substituent has an electron-donating or electron-withdrawing resonance effect: (a) C6H5NO2; (b) C6H5F

a.



b. .



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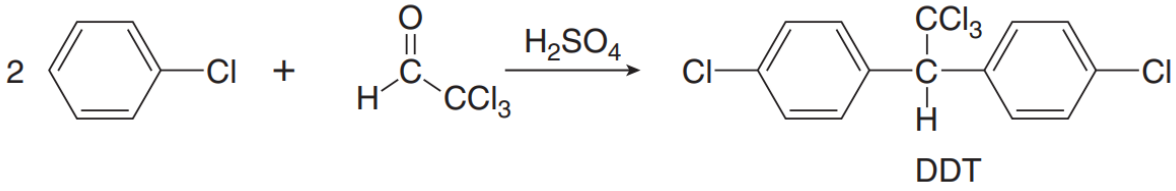
4. Draw a stepwise mechanism for the following reaction, which is used to prepare the pesticide DDT.



DDT

5. Friedel–Crafts alkylation of benzene with (2R)-2-chlorobutane and AlCl3 affords sec-butylbenzene. (a) How many stereogenic centers are present in the product? (b) Would you expect the product to exhibit optical activity? Explain, with reference to the mechanism.

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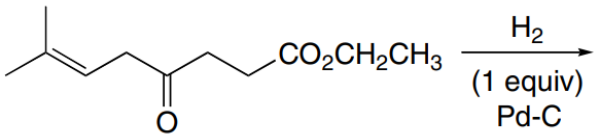
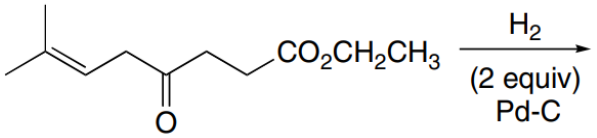
6. What product is formed when (CH3)2C — CHCH2COCH2CH2CO2CH2CH3 is treated with each reagent: (a) H2 (1 equiv), Pd-C; (b) H2 (2 equiv), Pd-C; (c) LiAlH4, followed by H2O; (d) NaBH4, CH3OH?

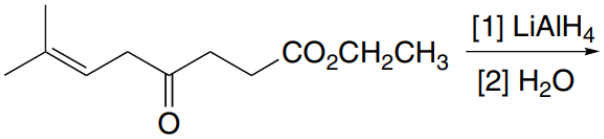
a.



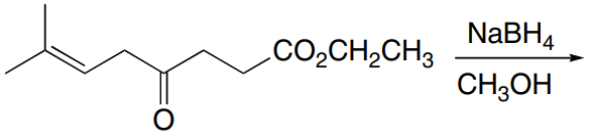
b.



c.

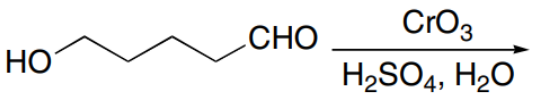


d.

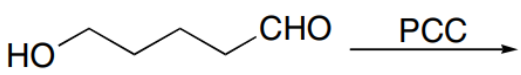


7. Draw the product formed with each reagent: (a) CrO3, H2SO4, H2O; (b) PCC; (c) Ag2O, NH4OH; (d) Na2Cr2O7, H2SO4, H2O.

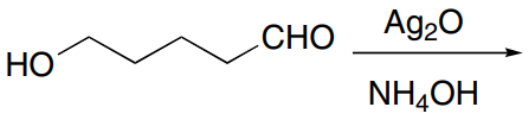
a.



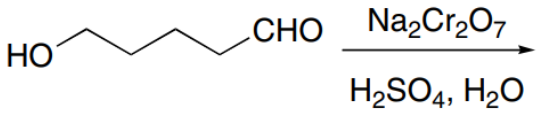
b.



c.

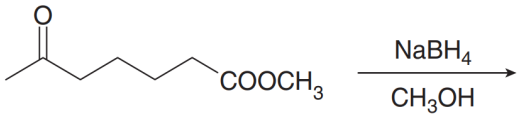


d.

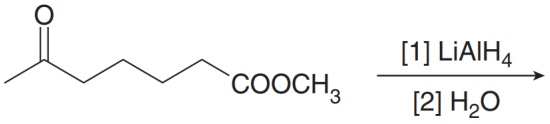


8. Draw the products of each reduction reaction.

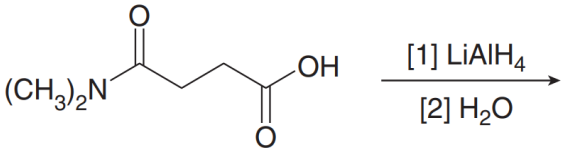
a.



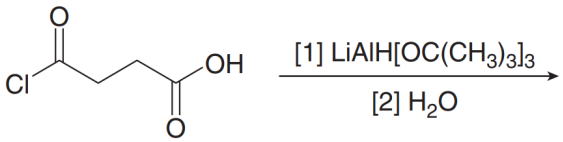
b.



c.



d.



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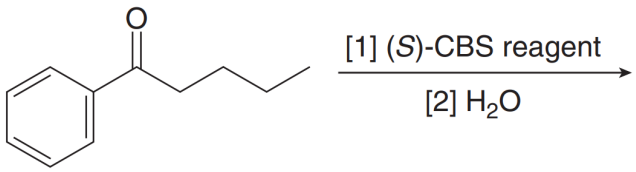
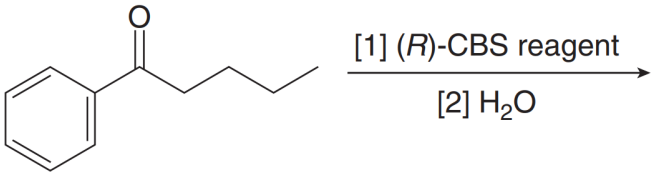
9. Draw all stereoisomers formed in each reaction.

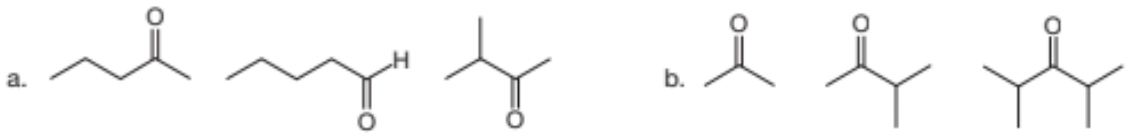
a.



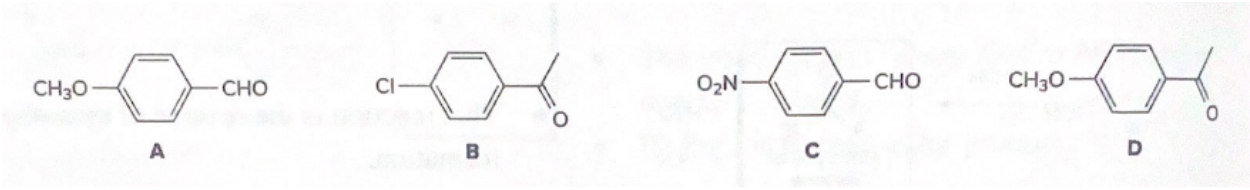
b.



10. Rank the compounds in each group in order of increasing reactivity in nucleophilic addition.



11. (a) Considering compounds A-D, which compound forms the smallest amount of hydrate?
(b) Which compound forms the largest amount of hydrate?



12. Fill in the lettered reagents (A-G) in the following reaction scheme.

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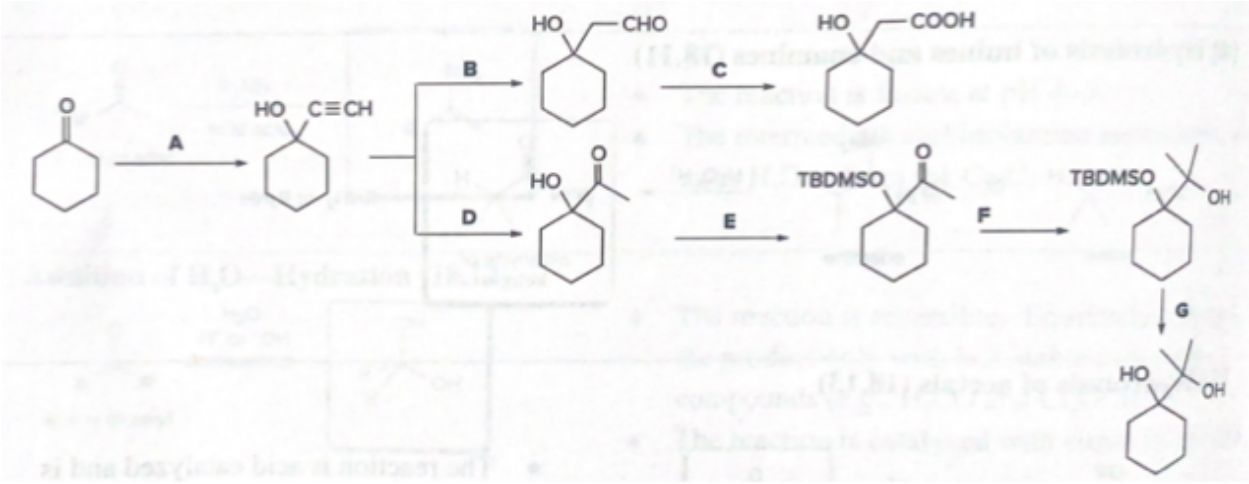
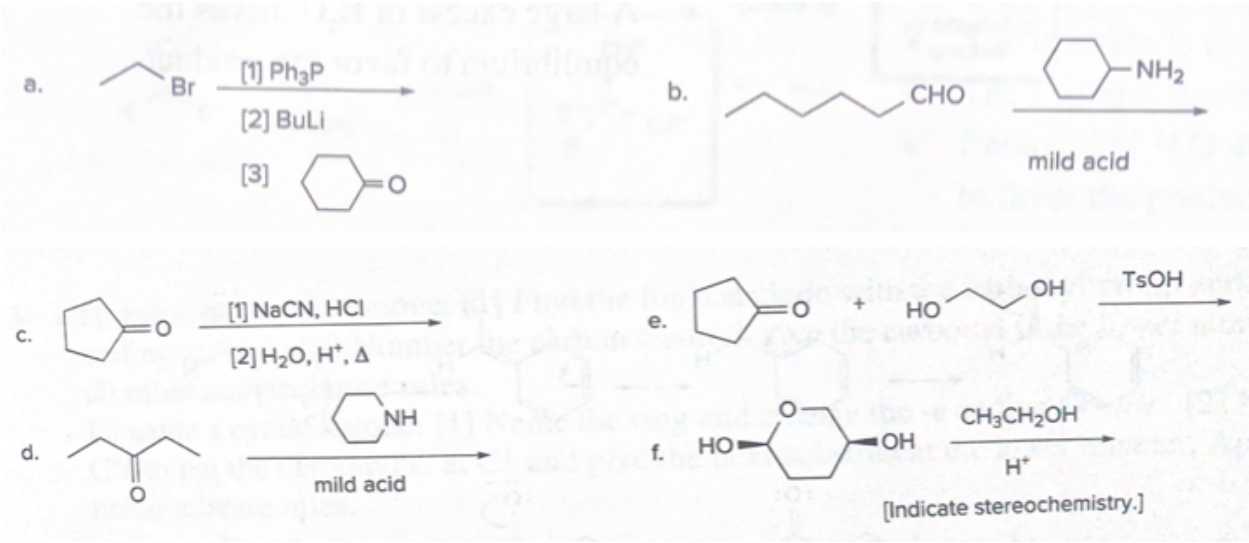
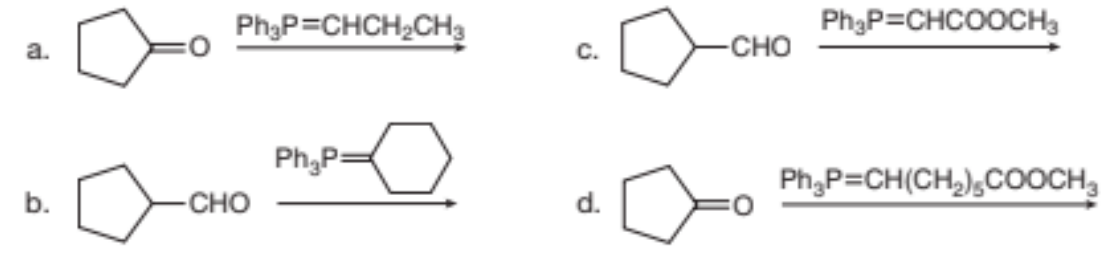


13. Draw the organic products formed in the following reactions



14. Draw the products formed in each Wittig reaction. Draw all stereoisomers formed when a mixture of products results.



15. Draw the products of each reaction.

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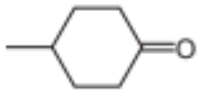
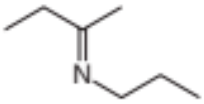
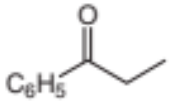
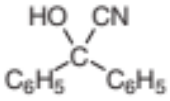
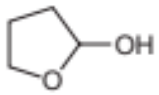
a. CH_3CH_2CHO + H_2N– ⟶ (mild / acid)

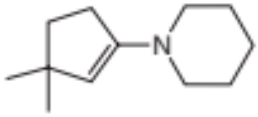
b.  ⟶ $HOCH_2CH_2OH$, H^+

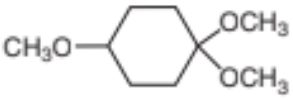
c.  ⟶ H_3O^+

d.  +  ⟶ (mild / acid)

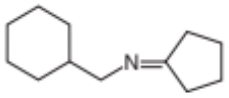
e.  ⟶ H_3O^+, Δ

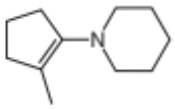
f.  ⟶ CH_3CH_2OH, H^+

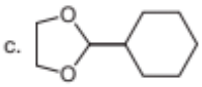
g.  ⟶ H_3O^+

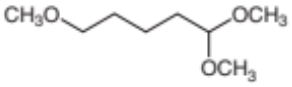
h.  ⟶ H_3O^+

16. What carbonyl compound and amine or alcohol are needed to prepare each product?

a. 

b. 

c. 

d. 

17. Draw the products formed in each reaction sequence.

a. CH_3CH_2Cl ⟶ [1] Ph_3P; [2] BuLi; [3] $(CH_3)_2C{=}O$

b. $C_6H_5CH_2Br$ ⟶ [1] Ph_3P; [2] BuLi; [3] $C_6H_5CH_2CH_2CHO$

c.  ⟶ [1] Ph_3P; [2] BuLi; [3] $CH_3CH_2CH_2CHO$