

1. (4 pts) Identify each of the following molecules as possessing a conjugated diene or an isolated diene.

1,2-octadiene \_\_\_\_\_

1,3-octadiene \_\_\_\_\_

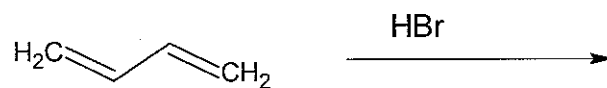
2,5-octadiene \_\_\_\_\_

1,7-octadiene \_\_\_\_\_

2. (1 pts) Circle the compound below that has the lowest heat of hydrogenation.

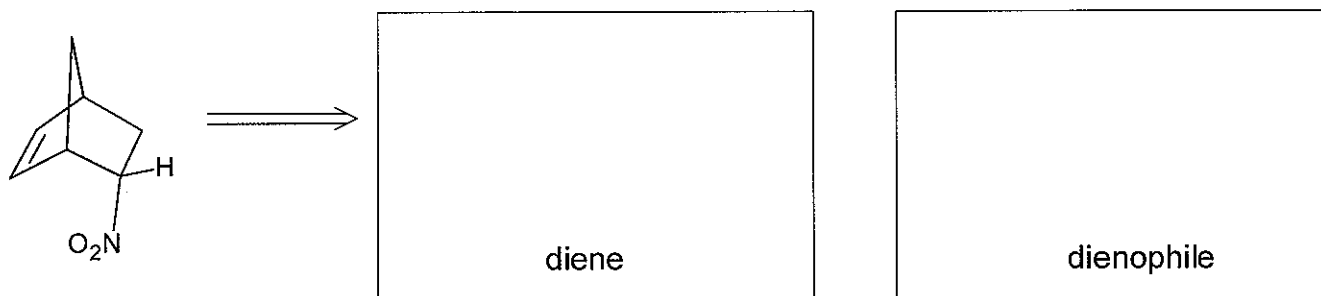
(E,E)-2,5-hexadiene    (E)-1,4-hexadiene    (Z,Z)-2,4-hexadiene    (E,E)-2,4-hexadiene

3. (4 pts) Consider the following reaction:



- a. What would the kinetically controlled product be?
- b. What would the thermodynamically controlled product be?

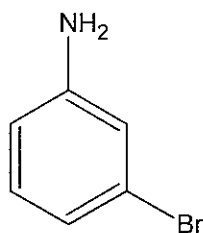
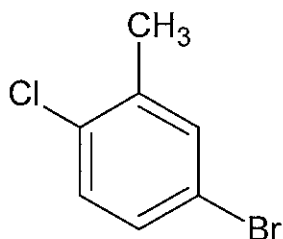
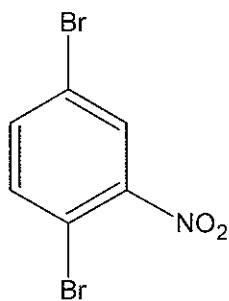
4. (4 pts) Identify the diene and dienophile that would give the following product.



5. (1 pts) A mixture of 1-heptanol and heptanoic acid in diethyl ether is shaken with an aqueous sodium hydroxide solution. Place an "X" in the blank of the entry below which correctly describes the major organic species in the two resulting immiscible solutions?

	Ether layer	NaOH layer
	heptanoic acid	1-heptanol
	1-heptanol	heptanoic acid
	sodium heptanoate	1-heptanol
	1-heptanol	sodium heptanoate

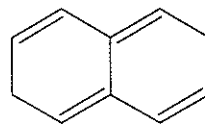
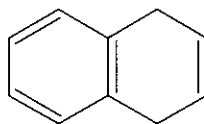
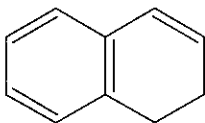
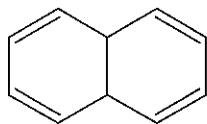
6. (6 pts) Name the following compounds. Use the o, m, p designation if appropriate.



7. (2 pts) Which of the following are consistent with the requirements of aromaticity. Place an "X" in the blank of the appropriate statements.

- \_\_\_\_\_ a system with  $\pi$  electrons in a ring delocalized over all atoms of the ring
- \_\_\_\_\_  $4n$   $\pi$  electrons in the ring
- \_\_\_\_\_ All of the ring atoms must be carbons
- \_\_\_\_\_  $(4n + 2)$   $\pi$  electrons in the ring

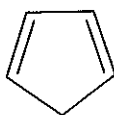
8. (1 pt) Which of the following gives off the least heat on catalytic hydrogenation with 4 moles of  $H_2$ ? Circle your answer.



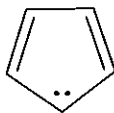
9. (8 pts) Draw the  $\pi$  molecular orbital diagrams for the following species and determine if the following species are anti-aromatic, aromatic or not aromatic.

Molecular Orbital Diagram

Aromatic ( yes or no)?



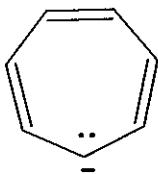
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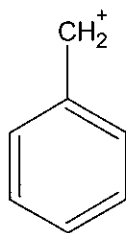
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10. (4 pts) Rank the following compounds in order of decreasing reactivity to aromatic electrophilic bromination (#1 is the most reactive compound).

benzene (B)      toluene(T)      benzoic acid(BA)      phenol(P)

\_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_

11. (3 pts) The benzyl carbocation is shown below. Besides the benzylic carbon, determine any other carbon atoms which carry a partial positive charge based on resonance theory. Place an "X" in the appropriate blank or blanks.

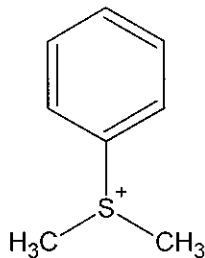


\_\_\_\_\_ ortho

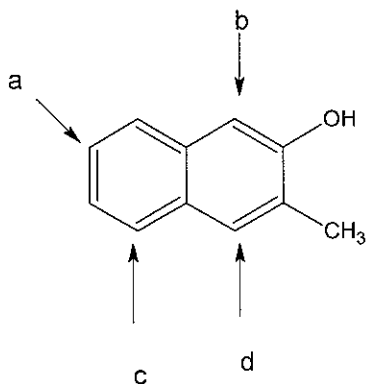
\_\_\_\_\_ meta

\_\_\_\_\_ para

12. (6 pts) Predict the effect the substituent attached to the benzene ring below would have on nitration. Determine if it is a ring activator or deactivator and whether it is an ortho, para or a meta director? Although you have not seen this substituent before, you have the background to determine how it will affect the ring. Use drawings of resonance structures comparing o,p-attack with m-attack to justify your choice.

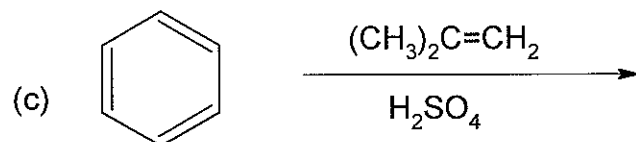
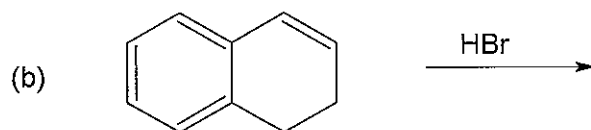
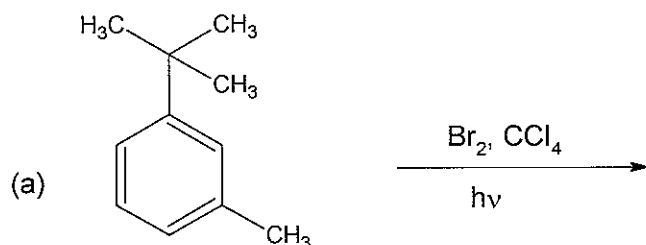


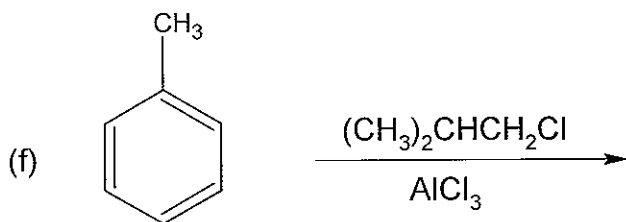
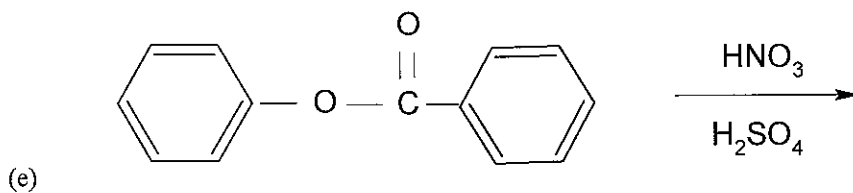
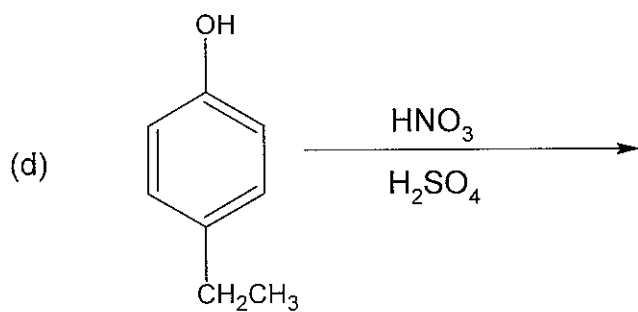
13. (2 pts) Using what you have learned about the electrophilic aromatic substitution of benzene, predict which position of the naphthalene compound below is most reactive with electrophiles in electrophilic aromatic substitution. Circle your answer.



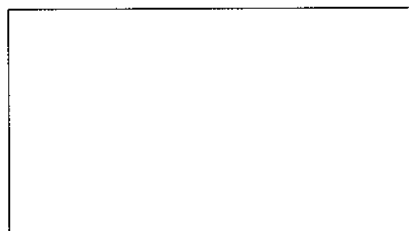
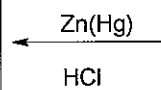
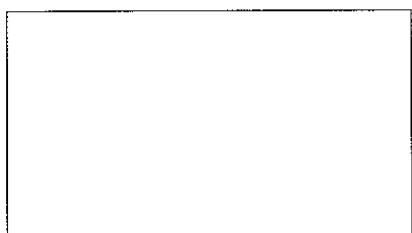
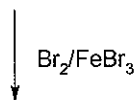
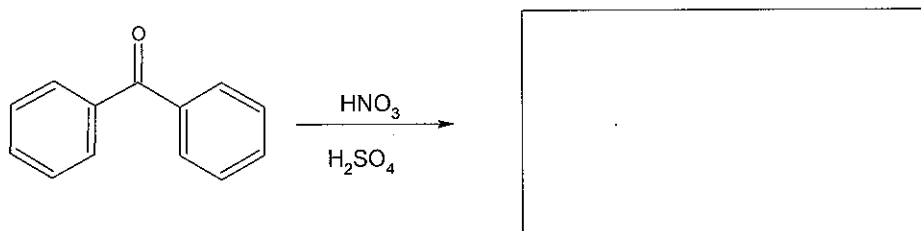
14. (1 pt) In the Friedel-Crafts alkylation of benzene, dialkylation is often a significant byproduct. In the Friedel-Crafts acylation of benzene, diacylation is not a significant byproduct. What is the primary reason for this difference?

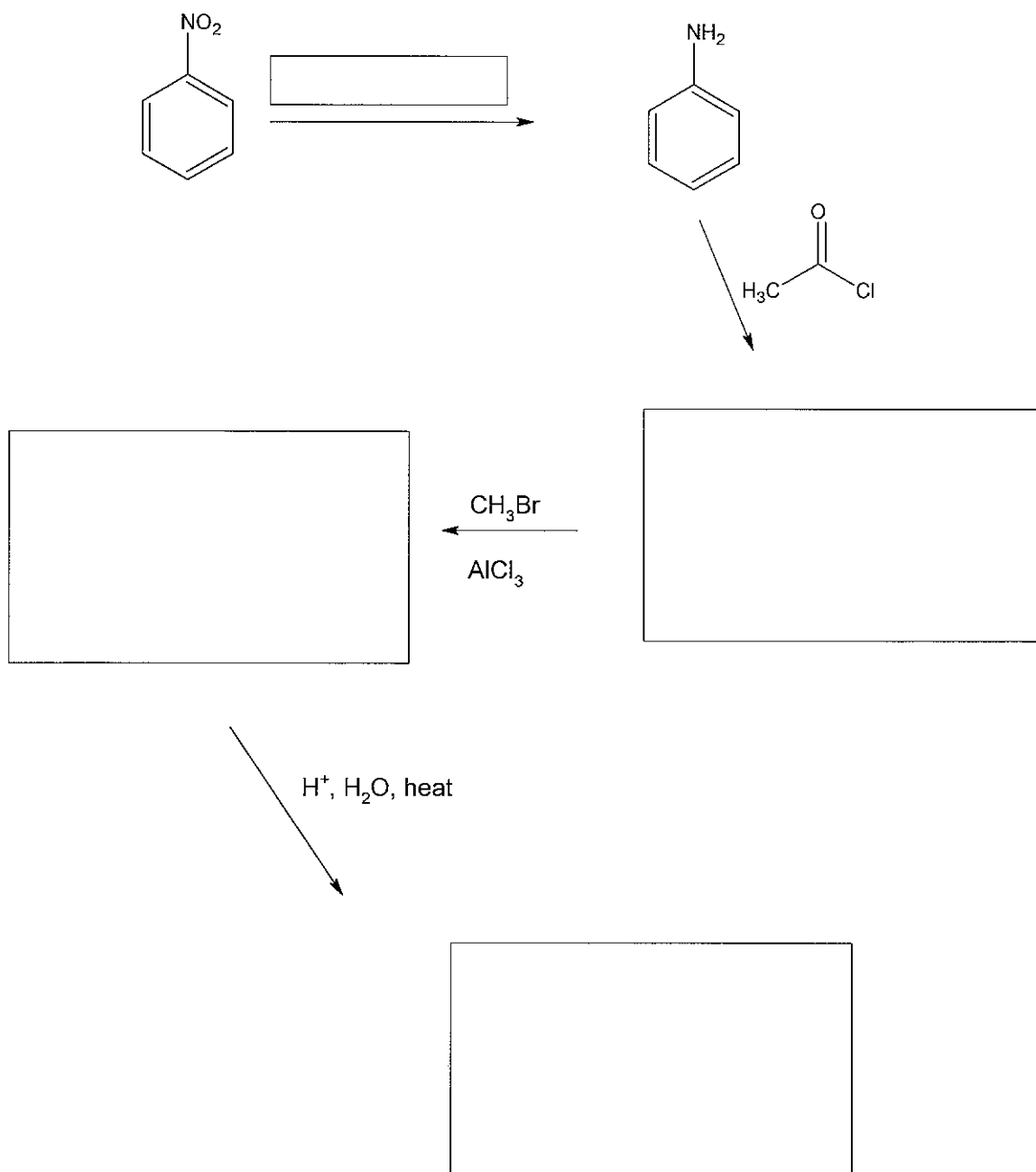
15. (12 pts) Give the major product for each of the following reactions.





16. (7 pts) Complete the following syntheses.



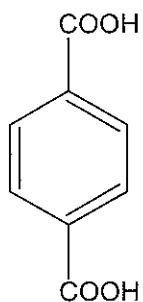


17. (13 total points) Write syntheses for the following compounds. Assume that any ortho, para directed reaction will give primarily para substitution in these syntheses.
- (a) (3 pts) *m*-bromopropylbenzene from benzene and any other compounds that you need.

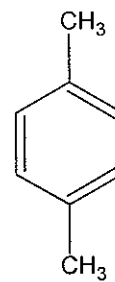
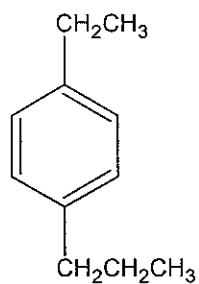
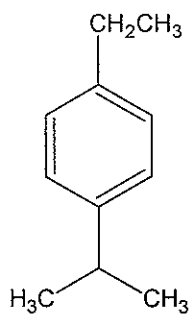
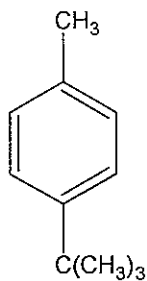
(b) (2 pts) *m*-bromobenzoic acid from toluene and any other compounds that you need.

(c) (4 pts) *o*-Nitrophenol starting from any monosubstituted benzene compound that you wish to use. Your synthesis must give *o*-nitrophenol as the major product.

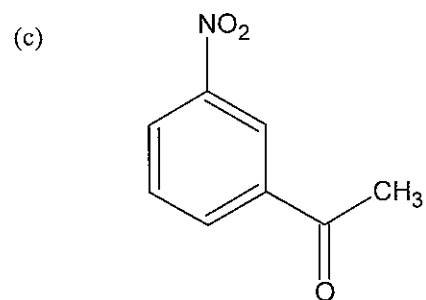
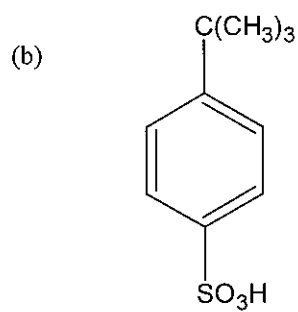
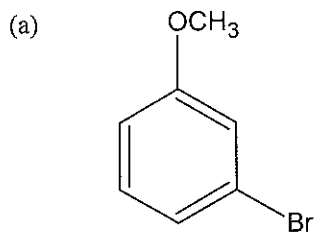
18. (4 pts) An unknown compound has a formula of  $C_{11}H_{16}$ . When treated with chromic acid the following product is obtained:



Circle any compounds below that could be the unknown compound.

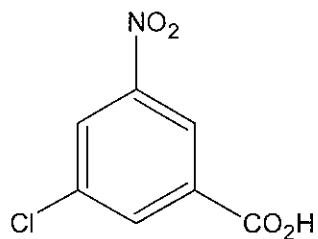


19. (6 pts) Determine if the following compounds can be obtained from BENZENE by using two consecutive electrophilic aromatic substitution reactions. If it is not possible, explain why not. If it is possible, write out the reaction sequence.

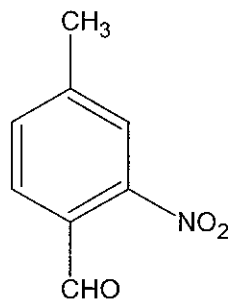


20. (4 pts) Determine if the following compounds can be obtained from electrophilic aromatic substitution on a disubstituted benzene (already has two groups on the ring). If it is not possible, explain why not. If it is possible, write out the reaction sequence.

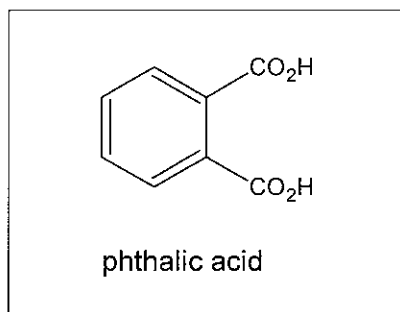
(a)



(b)



21. (2 pts) The compound indene, C<sub>9</sub>H<sub>8</sub>, found in coal tar, rapidly decolorizes Br<sub>2</sub>/CCl<sub>4</sub> and gives a brown precipitate with cold dilute KMnO<sub>4</sub>. Only one mole of H<sub>2</sub> is consumed readily to form indane, C<sub>9</sub>H<sub>10</sub>. Oxidation of indene with hot KMnO<sub>4</sub> yields phthalic acid. What are the structures of indane and indene?

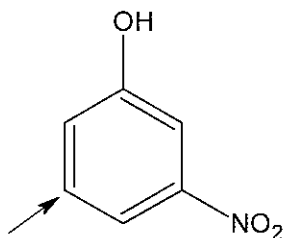


Indane:

Indene:

22. (3 pts) Indicate if the following statements are true or false. Circle the correct response.

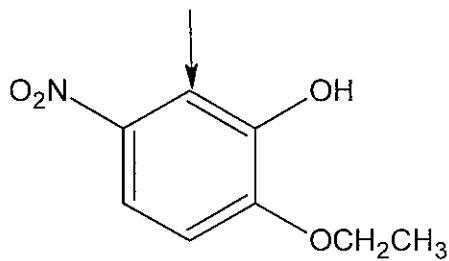
(a) When m-nitrophenol undergoes electrophilic aromatic substitution, the  $-\text{NO}_2$  group will activate the indicated position more than the  $-\text{OH}$  group will activate this same position.



True

False

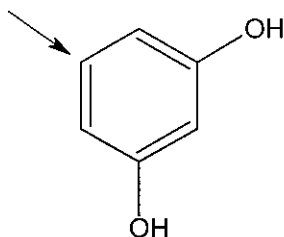
(b) When 2-ethoxy-5-nitrophenol reacts with nitric acid, the new nitro group will be added to the position indicated.



True

False

(c) When resorcinol undergoes electrophilic aromatic substitution, the indicated position is the least active position.



True

False

23. (2 pts) For the following three carboxylic acids, write the number corresponding to the appropriate answer on the blank provided.

(1) 2-methoxyacetic acid ( $\text{CH}_3\text{OCH}_2\text{COOH}$ )

(2) acetic acid

(3) benzoic acid.

The strongest acid is \_\_\_\_\_.

The weakest acid is \_\_\_\_\_.