

CHEM 204 2010 Ass. 1

Problem

1. The amount of energy in infrared light corresponds to:
 - a. the amount of energy needed to promote one electron from a bonding to an antibonding molecular orbital
 - b. the amount of energy needed to "flip" the spin of a ^{13}C or ^1H nucleus
 - c. the amount of energy needed to strip a molecule of one electron to generate a cation radical
 - d. the amount of energy needed to increase certain molecular motions, such as bond vibrations, in organic molecules

2. Examining the infrared spectrum of a compound allows us to:
 - a. determine the types of functional groups present in the compound
 - b. determine the carbon-hydrogen framework of the compound
 - c. determine the molecular weight of the compound
 - d. determine the nature of the conjugated pi electron system in the compound

Bond-Types

MATCH each of the following groups of bond-types to the region of the infrared spectrum in which their absorptions occur. Place the letter of the region in the blank to the left of the bond-type.

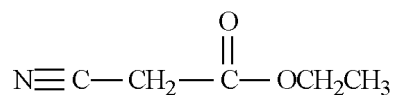
- a. 4000 to 2500 cm^{-1}
 - b. 2500 to 2000 cm^{-1}
 - c. 2000 to 1500 cm^{-1}
 - d. below 1500 cm^{-1}
3. Refer to Bond-Types. _____ C-C, C-O, C-N, and C-X single-bond vibrations.

 4. Refer to Bond-Types. _____ C=O, C=N, and C=C bond absorptions.

 5. Refer to Bond-Types. _____ N-H, C-H, and O-H stretching and bending motions.

 6. Refer to Bond-Types. _____ triple bond stretching vibrations.

7. At what approximate positions might the compound below show IR absorptions?

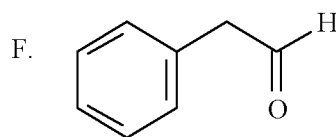
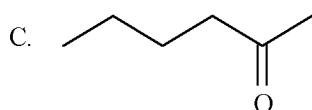
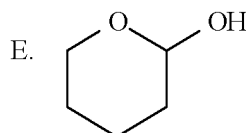
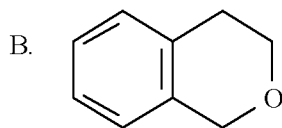
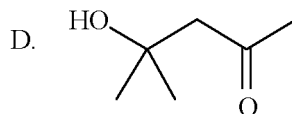
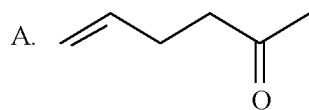


8. Assume you are carrying out the conversion of 1-bromobutane to 1-butanol. How could you use IR spectroscopy to determine when the reaction is complete?

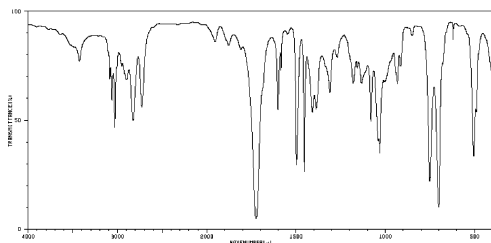


Matching 12-1

MATCH a structure from the list below to the following IR spectra. Place the letter of the structure in the blank to the left of the spectrum.

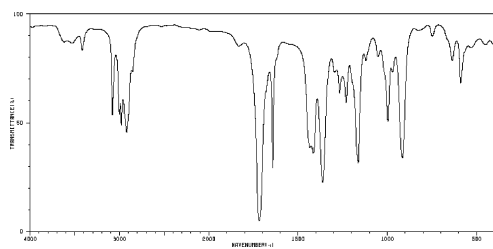


9. Refer to Matching 12-1. _____



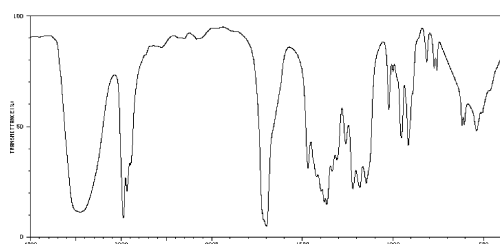
Spectrum obtained from: SDBSWeb: <http://www.aist.go.jp/RIODB/SDBS/>

10. Refer to Matching 12-1. _____



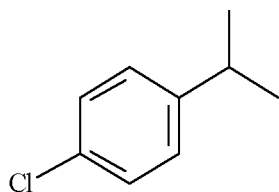
Spectrum obtained from: SDBSWeb: <http://www.aist.go.jp/RIODB/SDBS/>

11. Refer to Matching 12-1. _____

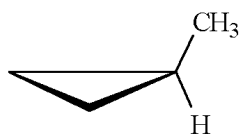


Spectrum obtained from: SDBSWeb: <http://www.aist.go.jp/RIODB/SDBS/>

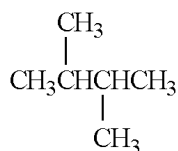
12. For the compound below tell how many types of nonequivalent protons there are.



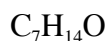
13. For the compound below tell how many types of nonequivalent protons there are.



14. Predict the splitting patterns you would expect for each proton in the molecule below:



15. Propose structures for compounds that fit the following ^1H NMR data:

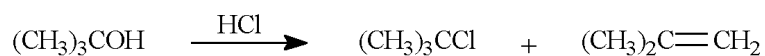


6H triplet at 0.9 d, $J = 7$ Hz

4H sextet at 1.6 d, $J = 7$ Hz

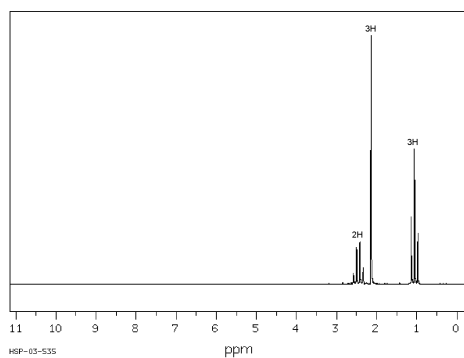
4H triplet at 2.4 d, $J = 7$ Hz

16. Treatment of *tert*-butyl alcohol with hydrogen chloride yields a mixture of *tert*-butyl chloride ($\text{S}_{\text{N}}1$ product) and 2-methylpropene (E1 product). After chromatographic separation, how would you use ^1H NMR to help you decide which was which?



Spectrum 13-2

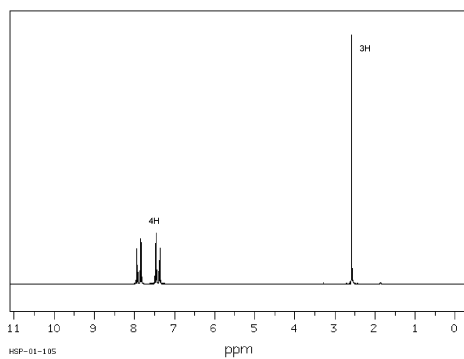
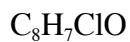
Answer the questions for each of the compounds whose ^1H NMR spectra are shown below.



Spectrum obtained from: SDBSWeb: <http://www.aist.go.jp/RIODB/SDBS/>

17. Refer to Spectrum 13-2. Propose a structure for this compound.

Spectrum 13-4

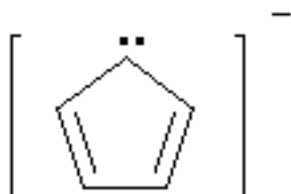


Spectrum obtained from: SDBSWeb: <http://www.aist.go.jp/RIODB/SDBS/>

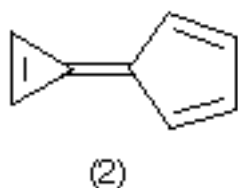
18. Refer to Spectrum 13-4. Calculate the degree of unsaturation in this compound.

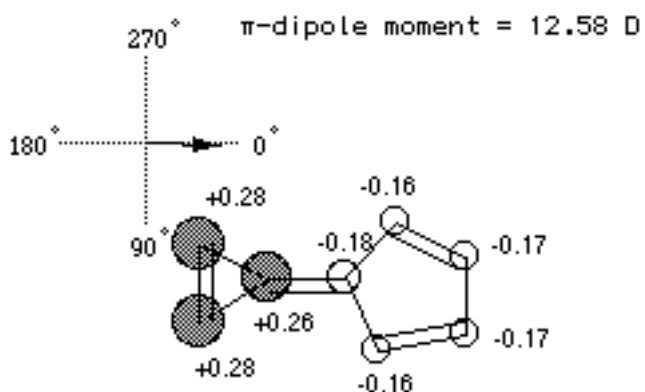
19. Refer to Spectrum 13-4. Propose a structure for this compound.

20. Use an energy diagram to illustrate why the cyclopentadienyl anion below is an aromatic ring system.



21. The C-8 system shown below has a remarkably high dipole moment of 12.6 Debye. Charge densities are shown in the diagram (circles in proportion). How do you account for this?

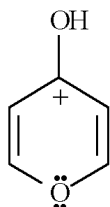




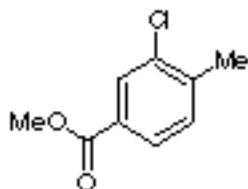
Aromatic Character

For each molecule below, predict whether the molecule would be expected to show aromatic character or not. Explain your answer in each case.

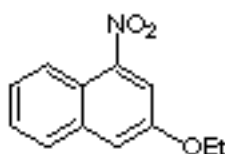
22. Refer to Aromatic Character.



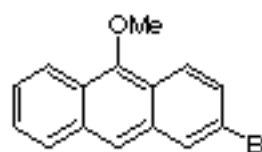
23. Give correct names for the following aromatic compounds:



(i)



(ii)



(iii)

24. Naphthalene has a resonance stabilisation energy of 251 kJ/mol. What is the heat of hydrogenation of naphthalene

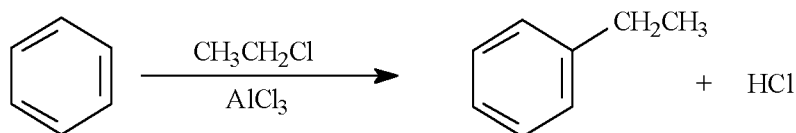
Matching 16-1

MATCH a structure or term from the following list with each description below. Place the letter of the structure or term in the blank to the left of the description.

- a. benzyne
 - b. ${}^+\text{NO}_2$
 - c. R_3C^+
 - d. electron-donating
 - e. ${}^+\text{NO}$
 - f. Meisenheimer complex
 - g. $\text{R} - \text{CO}^+$
 - h. electron-withdrawing
25. Refer to Matching 16-1. _____ The reactive electrophile in Friedel-Crafts acylation reactions.
26. Refer to Matching 16-1. _____ The electrophile in aromatic nitration.
27. Refer to Matching 16-1. _____ Intermediate in the elimination-addition mechanism of nucleophilic aromatic substitution.

Friedel-Crafts

Consider the Friedel-Crafts alkylation reaction below to answer the following questions:

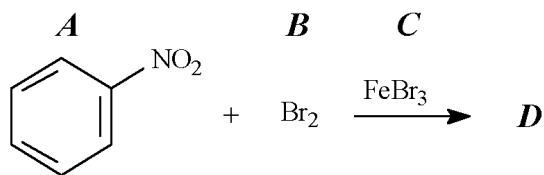


28. Refer to Friedel-Crafts. Draw the structure of the electrophile in this reaction.
29. Refer to Friedel-Crafts. What is the role of the AlCl_3 in the reaction?

30. Refer to Friedel-Crafts. Write the complete stepwise mechanism for this reaction. Show all electron flow with arrows and include all intermediate structures.
31. Draw a diagram representing the change in energy along the reaction coordinate for this reaction and insert the various structures at appropriate places on the diagram. Denote the activation energy on your diagram.

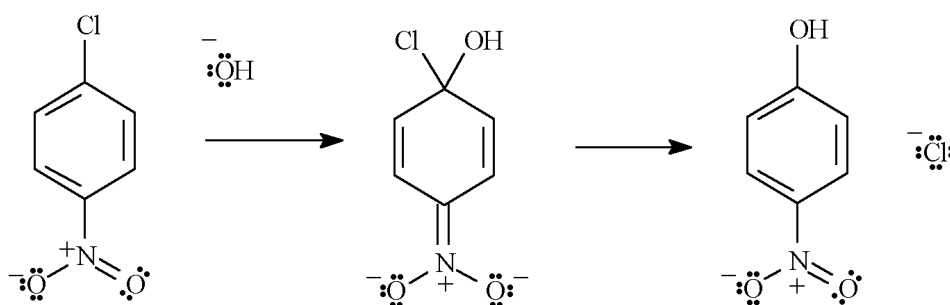
Reaction 16-2

Consider the reaction below to answer the following questions.

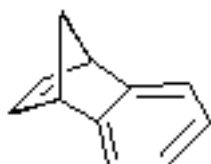


32. Refer to Reaction 16-2. The nucleophile in the reaction is:
33. Refer to Reaction 16-2. The Lewis acid catalyst in the reaction is:
34. Refer to Reaction 16-2. This reaction proceeds _____ (faster or slower) than benzene.
35. Refer to Reaction 16-2. Draw the structure of product **D**.

36. On the structural intermediates below, show all electron flow with arrows for the nucleophilic aromatic substitution reaction of *p*-nitrochlorobenzene with KOH.

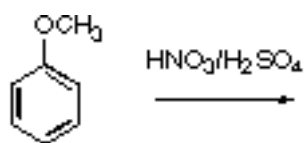


37. When bromobenzene is treated with NaNH_2 in liq. ammonia and in the presence of cyclopentadiene, the product is:



- (a) What reaction is involved?
(b) Give the mechanism of the reaction;
(c) Draw the structure of the intermediate which is formed showing the reactive orbitals.

ANISOLE



38. Refer to ANISOLE

This reaction proceeds faster or slower than the same reaction on benzene?

39. Refer to ANISOLE

What is(are) the final product(s)?

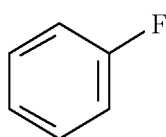
40. Refer to ANISOLE

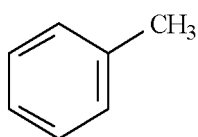
Draw the sigma complex intermediate for ortho, meta and para nitration and explain why this gives rise to the observed product(s)

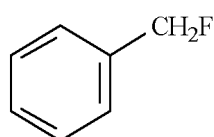
Relative Reactivity

Rank the compounds in each group below according to their reactivity toward electrophilic aromatic substitution (most reactive=1 ; least reactive=3). Place the number corresponding to the compounds' relative reactivity in the blank below the compound.

41. Refer to Relative Reactivity.



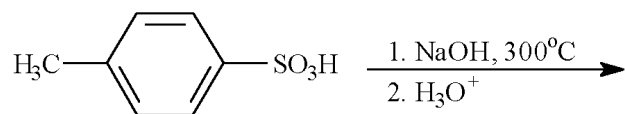




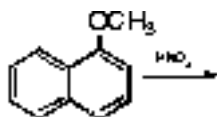
Major Organic Products

Given the major organic product(s) of each of the following reactions. If no is predicted, write "N.R."

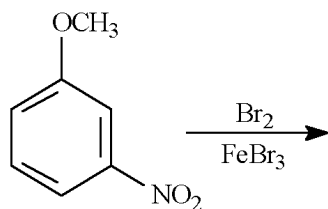
42. Refer to Major Organic Products.



43. Refer to Major Organic Products



44. Refer to Major Organic Products.

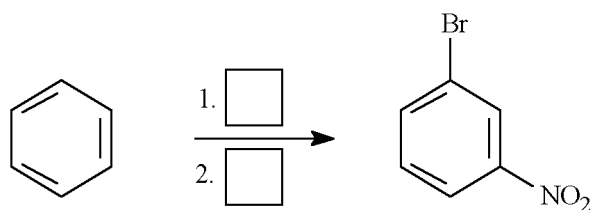


Matching 16-2

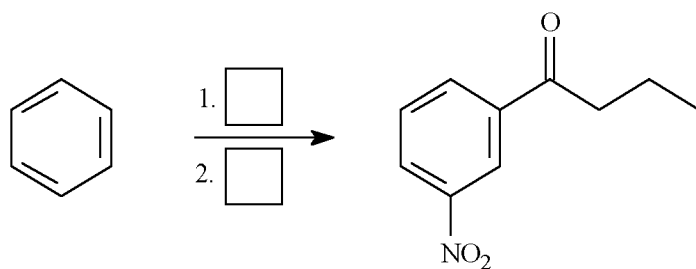
Choose the *best* reagent(s) from the list provided below for carrying out the following conversions. Place the letter of the reagent in the box beside the reaction number over the arrow. There is only one answer for each reaction.

- $\text{KMnO}_4, \text{H}_3\text{O}^+$
- $\text{Br}_2, \text{FeBr}_3$
- $\text{Cl}_2, \text{FeCl}_3$
- $\text{CH}_3\text{Cl}, \text{AlCl}_3$
- $\text{HNO}_3, \text{H}_2\text{SO}_4$
- $\text{ClCO}(\text{CH}_2)_2\text{CH}_3, \text{AlCl}_3$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}, \text{AlCl}_3$
- H_2/Pd
- NBS, peroxides

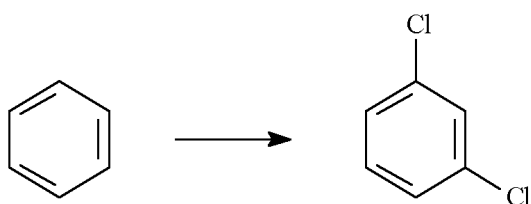
45. Refer to Matching 16-2.



46. Refer to Matching 16-2.



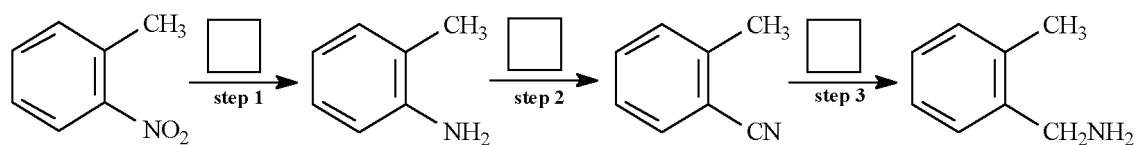
47. Show how the following transformation might be best accomplished. More than one step may be required. Show all reagents and all intermediate structures.



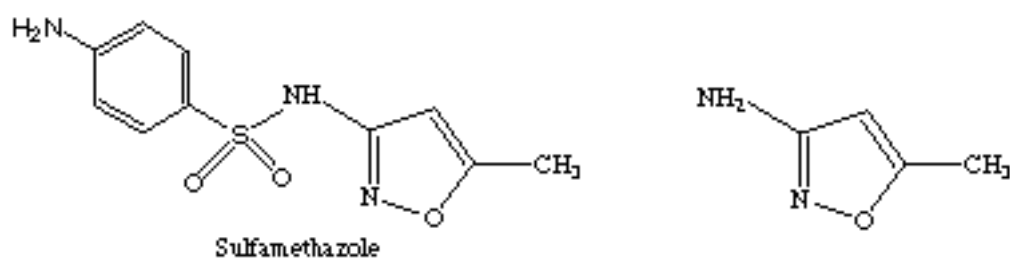
48. From the list provided below, choose the best reagent(s) for each step in the following synthesis. There is only one answer for each reaction.

- NaBH_4 , ethanol
- KCN , acetone
1. LiAlH_4 , THF
2. H_2O
1. HNO_2 , H_2SO_4
2. CuCN
1. SnCl_2 , H_3O^+

2. NaOH, H₂O
f. HNO₃, H₂SO₄



49. Sulfamethoxazole is a widely prescribed antibacterial for the treatment of acute otitis media (middle ear infection) in children. Propose a synthesis of sulfamethoxazole from benzene and the amine, 3-amino-5-methyloxazole shown below.



50. Give the major organic product(s) of the following reaction or sequence of reactions. Show all relevant stereochemistry.

