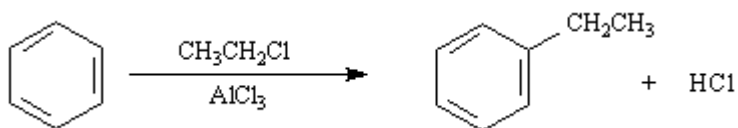


Questions 1 – 3: MATCH a structure or term from the following list with each description below. Place the letter of the structure or term in the blank to the left of the description.

- | | |
|---------------------------|--|
| a. benzyne | e. ^+NO |
| b. $^+\text{NO}_2$ | f. Meisenheimer complex |
| c. R_3C^+ | g. $\text{R}-\text{C}\equiv\text{O}^+$ |
| d. electron-donating | h. electron-withdrawing |

1. _____ The reactive electrophile in Friedel-Crafts acylation reactions.
2. _____ The electrophile in aromatic nitration.
3. _____ Intermediate in the elimination-addition mechanism of nucleophilic aromatic substitution.

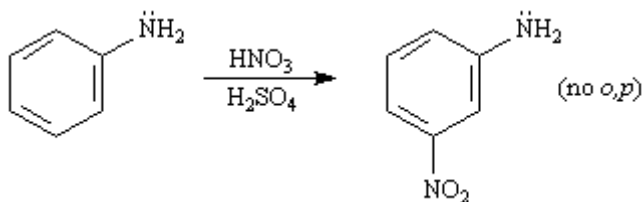
Questions 4 – 6: Consider the Friedel-Crafts alkylation reaction below to answer the following question(s):



4. Draw the structure of the electrophilic intermediate in this reaction.
5. What is the role of the AlCl_3 in the reaction?
6. Write the complete stepwise mechanism for this reaction. Show all electron flow with arrows and include all intermediate structures.

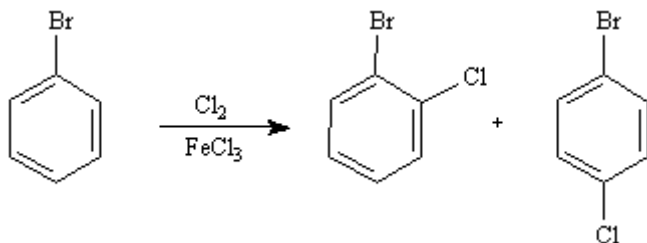
Questions 7 and 8: Consider the data below to answer the following question(s).

The -NH_2 group is listed in our textbook as the strongest *o,p*-directing activator in electrophilic aromatic substitution reactions. However, when aniline is subjected to standard nitration conditions poor yields of *m*-nitroaniline result.



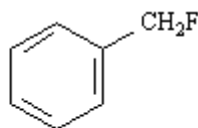
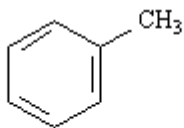
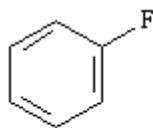
7. Draw all the resonance forms of aniline showing the electron-donating effect of the -NH_2 substituent.
8. Clearly, the reaction conditions are influencing the directing effect of the -NH_2 group. Explain why this occurs, using both words and structures.

Questions 9 and 10: Consider the reaction below to answer the following question(s).



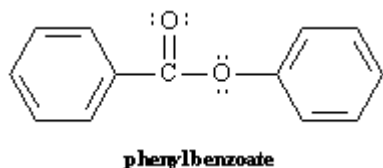
9. Write the complete stepwise mechanism for the formation of the *ortho* product. Show all intermediate structures and show all electron flow with arrows.
10. Draw resonance structures for the intermediate carbocation that explain the directing effect of the -Br .

Questions 11: 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.

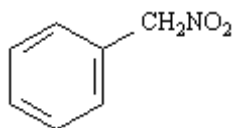


11. — — —

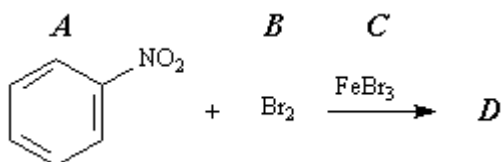
12. At what position, and on what ring, is bromination of phenyl benzoate expected to occur? Explain your answer.



13. Would you expect (nitromethyl)benzene to be more reactive or less reactive than toluene toward electrophilic substitution? Explain.



Questions 14 – 17: Consider the reaction below to answer the following question(s).



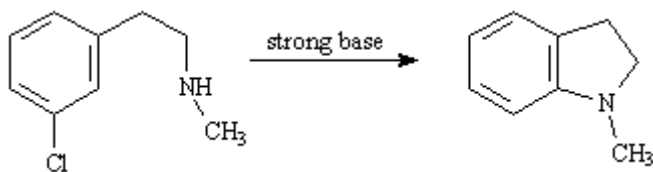
14. The nucleophile in the reaction is:

15. The Lewis acid catalyst in the reaction is:

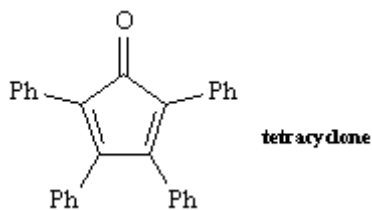
16. This reaction proceeds _____ (faster or slower) than benzene.

17. Draw the structure of product *D*.

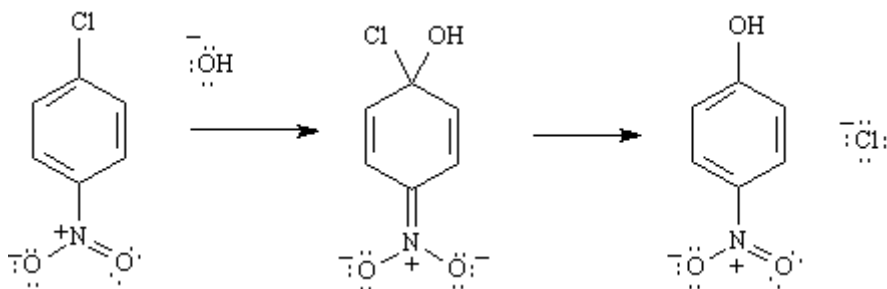
18. The following reaction proceeds by an intramolecular nucleophilic aromatic substitution mechanism. Write the complete stepwise mechanism, showing all intermediate structures and all electron flow with arrows.



19. Tetracyclone is often used to trap benzynes as Diels-Alder adducts. What is the structure of the Diels-Alder adduct that results when benzyne is trapped by tetracyclone?



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



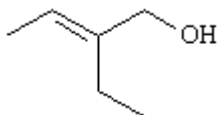
Questions 21 and 22: Draw structures corresponding to each of the given names.

21. Draw: *cis*-4-*tert*-butylcyclohexanol

22. Draw: 3-methyl-2-buten-1-ol

Questions 23 and 24: IUPAC Naming Instructions: Provide proper IUPAC names.

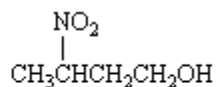
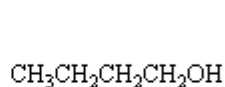
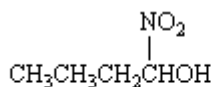
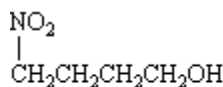
23. Name: _____



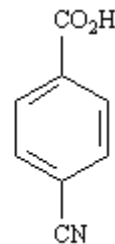
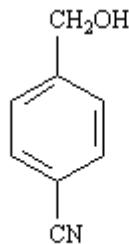
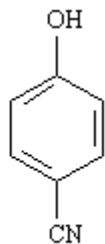
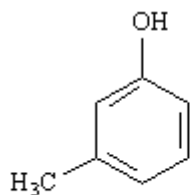
24. Name: _____



Questions 25 and 26: Rank the following groups of compounds from most acidic (1) to least acidic (4). Place the number corresponding to the compound's relative rank in the blank below the structure.



25. _____



26. _____

27. Explain why nonafluoro-2-methyl-2-propoxide is a much weaker base than *tert*-butoxide.



Questions 28 – 30: Refer to the data below to answer the following question(s).

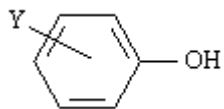
PK_a s of Some Phenols

Y

pK_a

-H

9.89



m-NO₂

8.28

p-NO₂

7.17

m-OCH₃

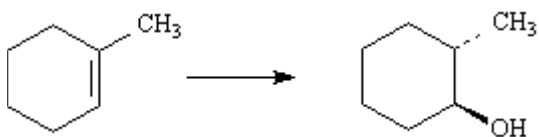
9.65

p-OCH₃

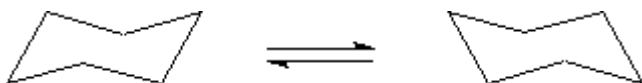
10.21

28. The *weakest* acid in the table is: _____
29. Which of the acids in the Table has the weakest conjugate base? _____
30. How do you account for the difference in acidity between *meta* and *para*-nitrophenol?

Questions 31 – 34: To answer the following question(s), consider the reaction below:

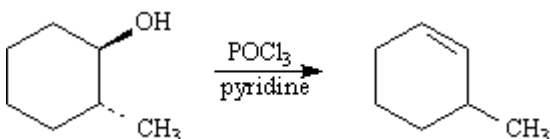


31. The best reagents for accomplishing the above transformation are:
1. OsO₄, pyridine
2. NaHSO₃, H₂O
 1. Hg(OAc)₂, H₂O
2. NaBH₄
 1. RCO₃H, CH₂Cl₂
2. H₃O⁺
 1. BH₃, THF
2. H₂O₂, ⁻OH
- Circle one: a b c d
32. The alcohol product is classified as a:
- 1° alcohol
 - 2° alcohol
 - 3° alcohol
 - 4° alcohol
- Circle one: a b c d
33. On the templates provided below, draw both conformations of the alcohol product. *Circle the least stable* conformation.



34. Provide the IUPAC name for the product alcohol. _____

Question 35: To answer the following question, consider the reaction below:

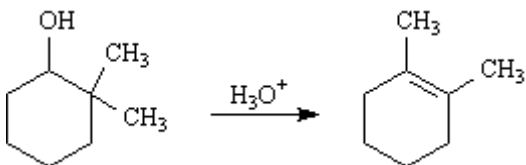


35. The dehydration of secondary and tertiary alcohols by reaction with POCl_3 in pyridine is an example of:

- a. an E1 process
- b. an S_N1 process
- c. an E2 process
- d. an S_N2 process

Circle one: a b c d

36. Acid-catalyzed dehydration of 2,2-dimethylcyclohexanol yields 1,2-dimethylcyclohexene as one of the major products. Write the complete stepwise mechanism for this reaction. Show all electron flow with arrows and show all intermediate structures.



Questins 36 and 37: To answer the following question(s), consider the reaction below:



37. Provide the complete IUPAC name for the starting material in this reaction.

38. The starting material can be classified as a:

- a. 1° alcohol
- b. 2° alcohol
- c. 3° alcohol
- d. 4° alcohol

Circle one: a b c d

