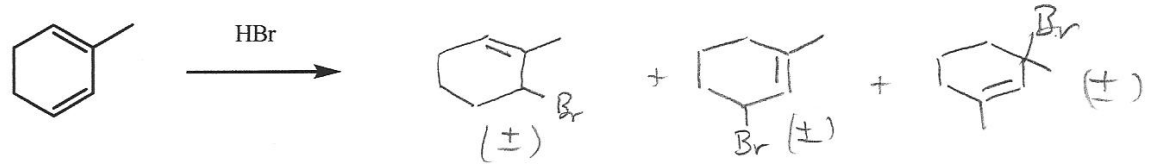
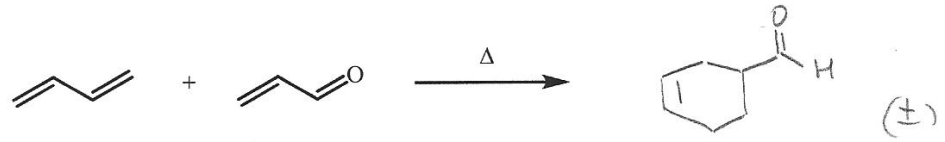
1. Show the product(s) from the following reactions. (10 points)

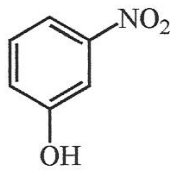
a. 


b. 

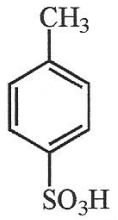

2. What are the *requirements* (conditions) for a compound to be "aromatic?" (8 points)

- cyclic
- fully conjugated – consecutive $sp^2$ carbons (guarantees planar)
- π system contains, $4n+2$ $e^-$

3. Provide IUPAC names (*not common*!) for the following compounds. (10 points)

a. 

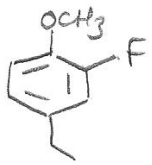

3-nitro phenol

b. 

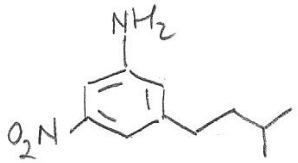

4-methyl benzene sulfonic acid

4. Draw the structure of the following compounds. (10 points)

a. 4-ethyl-2-fluoroanisole




b. 3-(3-methylbutyl)-5-nitroaniline



5. While benzene ($C_6H_6$) has only one carbon-carbon bond length (140 pm), cyclobutadiene ($C_4H_4$) has two different carbon-carbon bond lengths (135 and 156 pm). Clearly explain why. (10 points)

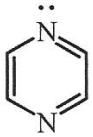
This system is anti-aromatic and to minimise the instability of this arrangement the bonds distort.

Benzene, on the hand, is aromatic and has the resonance structure shown.

6. For each of the following molecules or ions indicate whether they are *aromatic*, *anti-aromatic* or *non-aromatic*. (16 points)

a. 

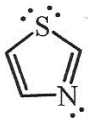
aromatic

b. 

aromatic

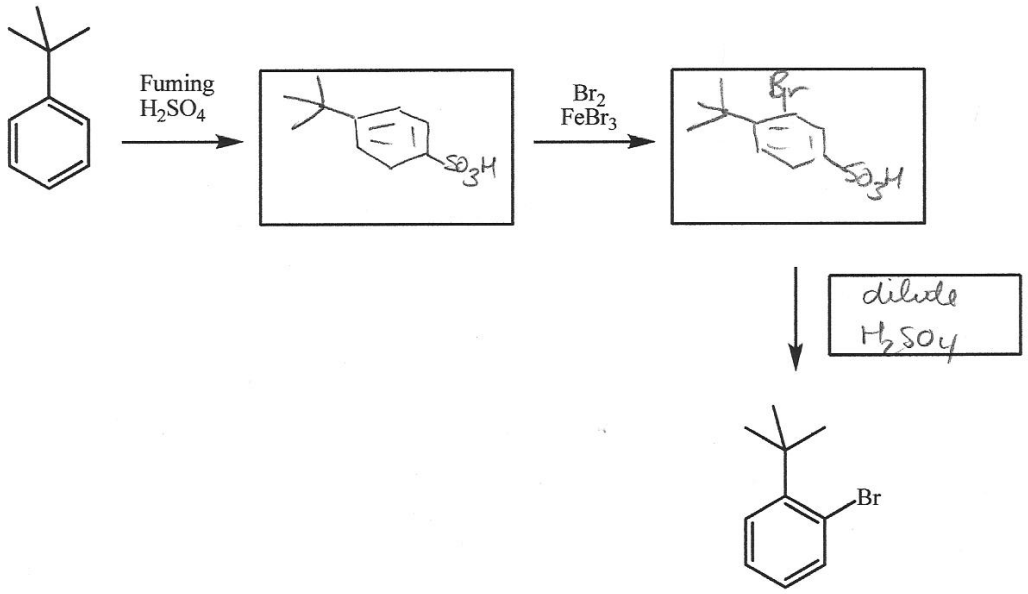
c. 

non-aromatic

d. 

aromatic

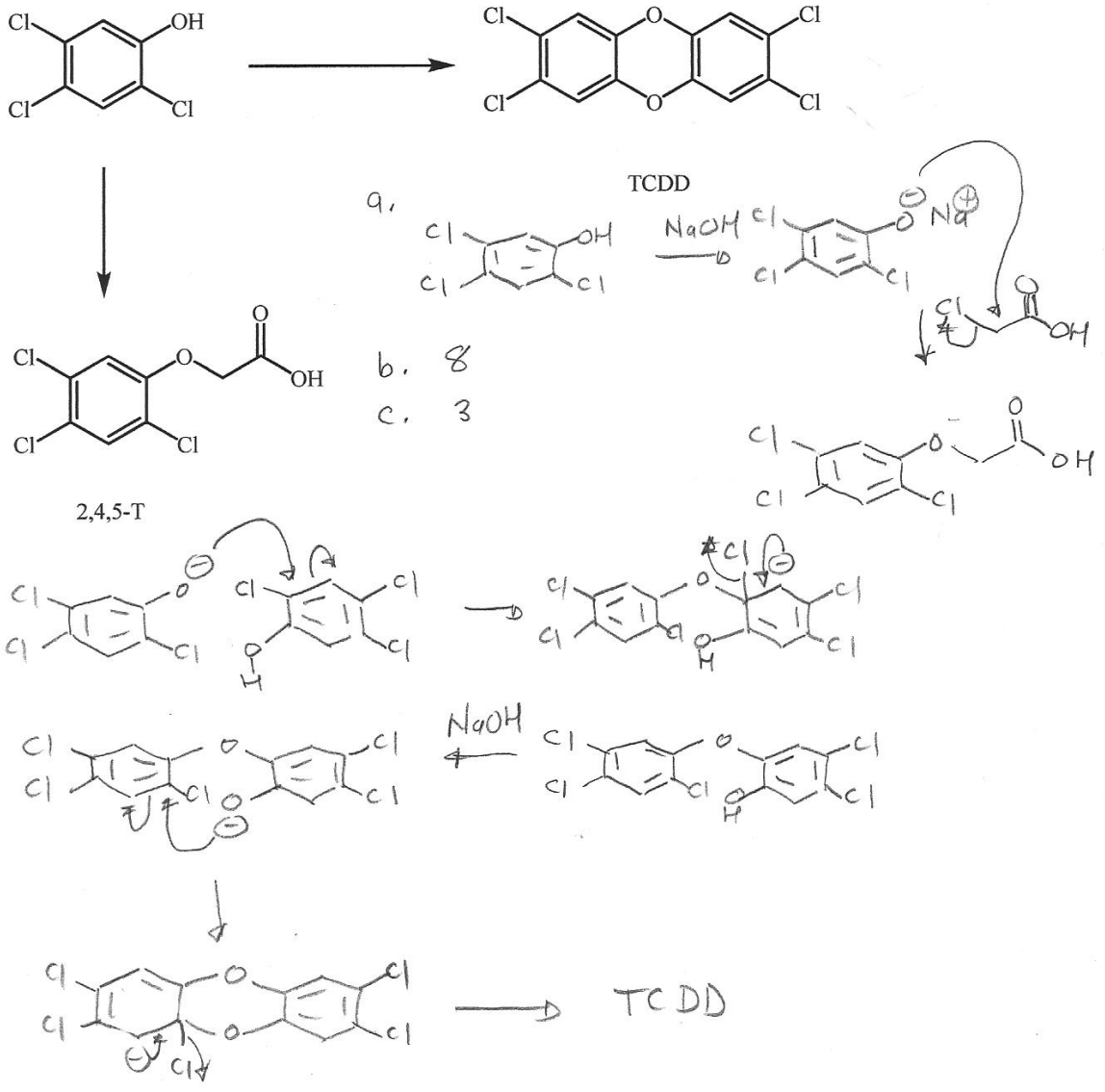
7. In the following synthesis, fill in the products or reagents. (15 points)



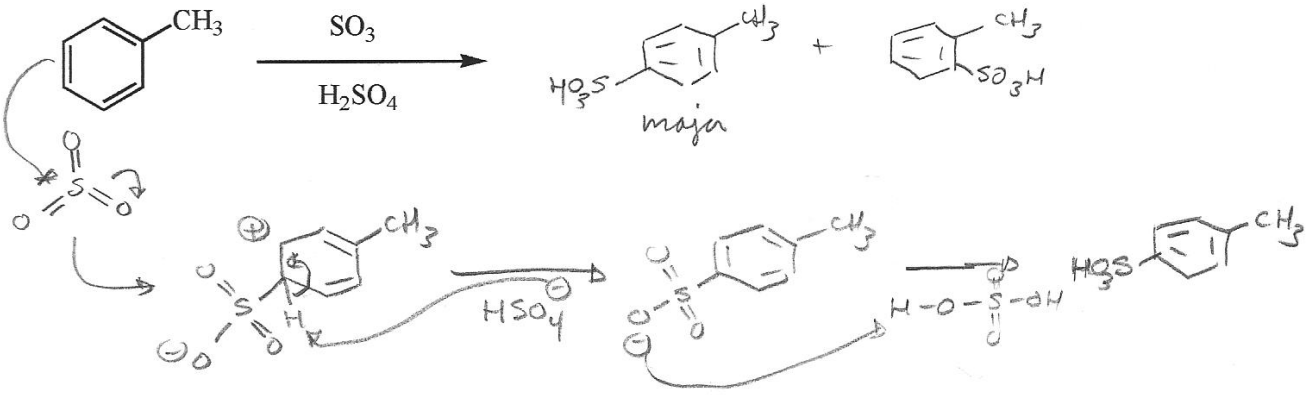
8. The broad-leaf defoliant, known as 2,4,5-T is one of the key ingredients in the mixture known as Agent Orange, which was widely used during the Vietnam war in the 1970's. Since then it's use has been banned world-wide for health reasons, primarily since during the manufacturing process of 2,4,5-T an impurity is formed known as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which turns out to be one of the most toxic dioxins known.

a. Show how to prepare 2,4,5-T from 2,4,5-trichlorophenol using a Williamson ether synthesis (hint: using $ClCH_2CO_2H$ – chloroacetic acid).
b. How many peaks would you expect in the $^{13}C$ NMR spectrum of 2,4,5-T?
c. How many peaks would you expect in the $^{13}C$ NMR spectrum of TCDD?
d. Suggest a mechanism for the formation of the impurity TCDD under basic conditions

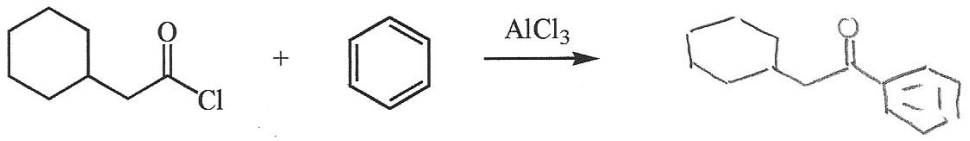
(20 points)



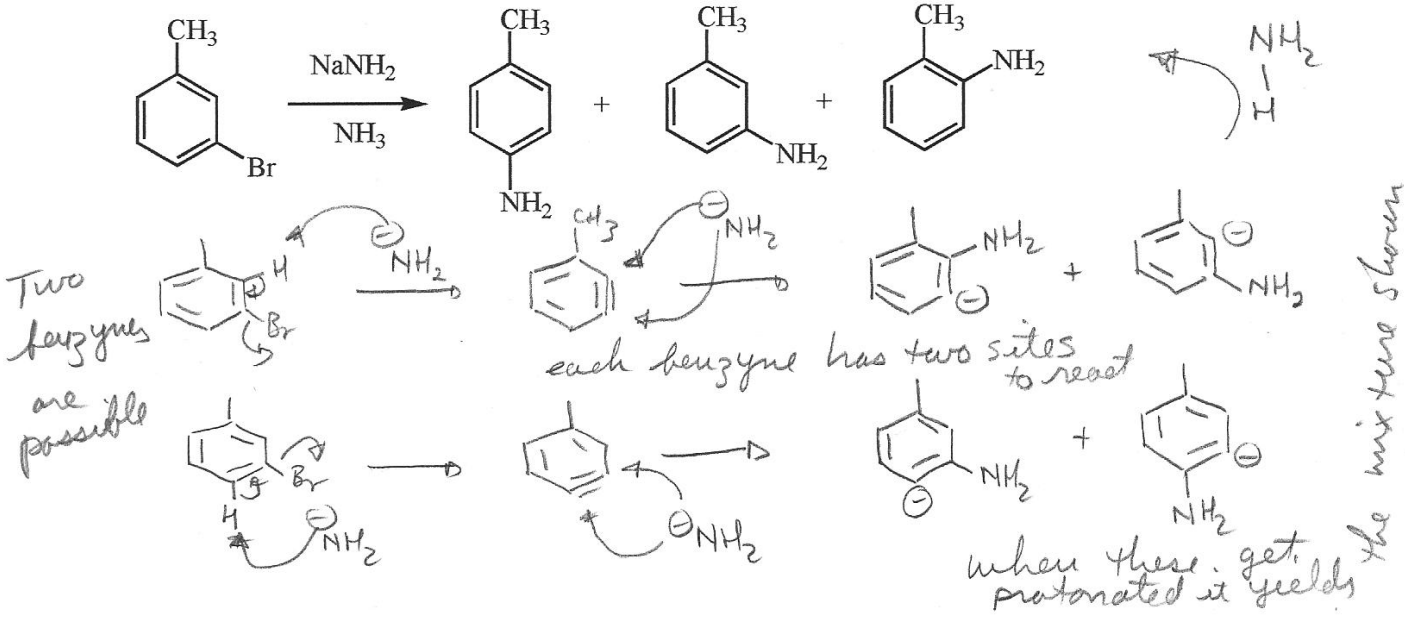
9. Show the product (s) and the complete mechanism (with electron-pushing) for the following reaction. (if more than one isomer is formed show the mechanism for only one of them, but be sure show all expected products) (15 points)



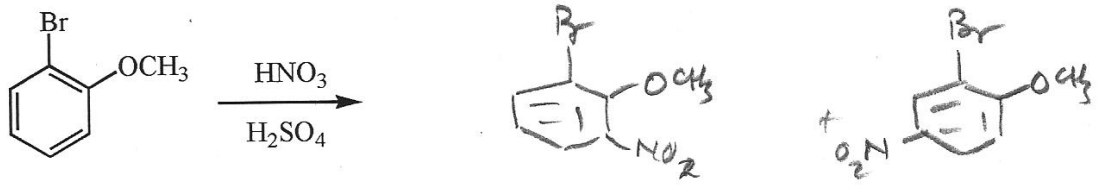

10. Show the product(s) from the following Friedel-Crafts acylation. (5 points)

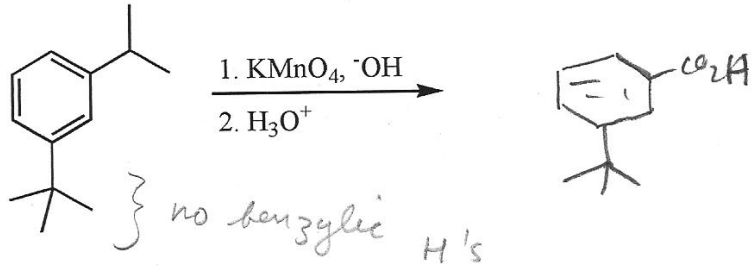



11. Explain in terms of the mechanism of the reaction why the reaction below produces the three products shown in roughly equal amounts. (10 points)



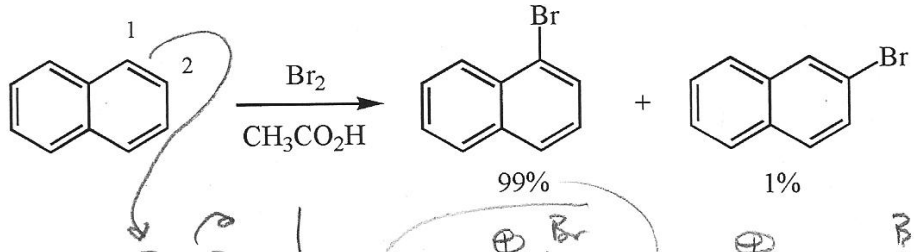
12. Show the expected product (or products) from the following reactions. (10 points)

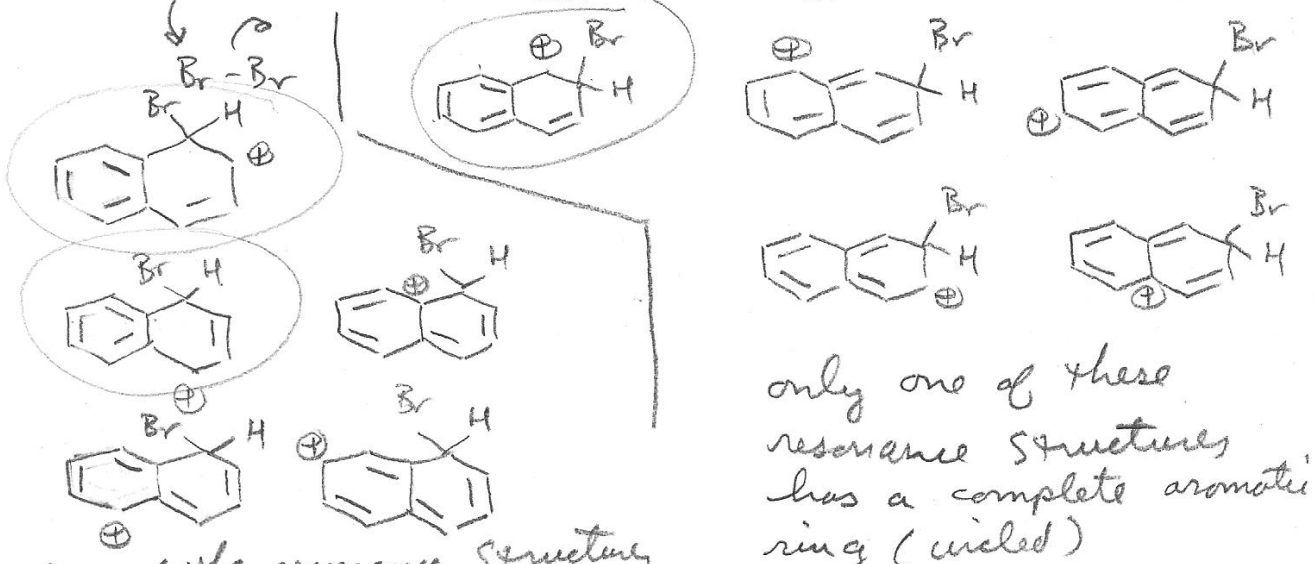
a. 


b. 

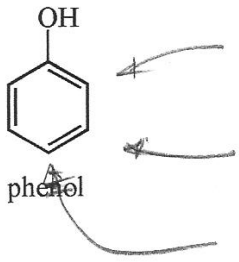

13. Naphthalene is considerably more reactive than benzene toward bromine, although it still undergoes electrophilic aromatic substitution instead of reactions like alkenes, a strong Lewis acid catalyst is not required. Suggest an explanation for the observed *selectivity* for the bromination reaction. (Hint: consider the mechanism of the reaction)

(10 points)



14. Use the included NMR data sheet to estimate the chemical shifts for phenol (o, m, and p). Explain how the chemical shift data indicate whether the aromatic substituent is an ortho/para director or a meta director in an Electrophilic Aromatic Substitution reaction. (15 points)




7.36 − 0.53 = 6.83 ppm

7.36 − 0.14 = 7.22 ppm

7.36 − 0.43 = 6.93 ppm

all three protons are shifted upfield relative to benzene, so the -OH group is an activating group. proton

The ortho and para chemical shifts are the furthest upfield and thus more shielded. More shielded means greater electron density; so the carbons next to these proton should be more nucleophilic the the meta carbon.

Thus the -OH is an o/p director.