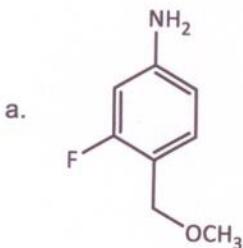
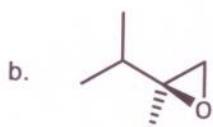


1. Provide IUPAC names for the following compounds.

(10 points)



3-fluoro-4-(methoxymethyl) aniline



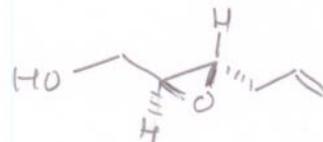
(2S)-1,2-epoxy-2,3-dimethylbutane

(2S)-2-isopropyl-2-methyl oxirane

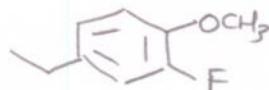
2. Provide structures for the following compounds.

(10 points)

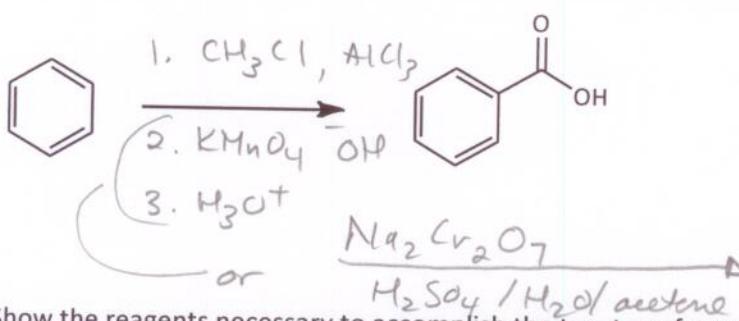
- a. (2S,3S)-2,3-epoxyhex-5-en-1-ol



- b. 4-ethyl-2-fluoroanisole

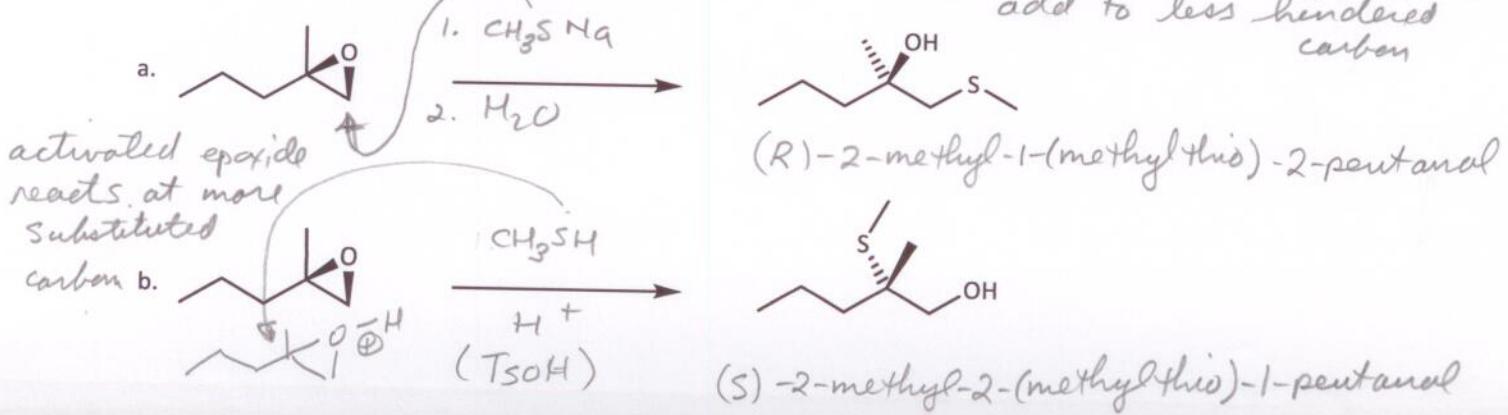


3. Show reagents to convert benzene to benzoic acid. Show all steps and any intermediate compounds. (10 points)



4. Show the reagents necessary to accomplish the two transformations. Explain your reasoning behind the choice of reagents, i.e., why they give the different products  
EXTRA CREDIT Provide IUPAC names for the products

Strong nucleophile  
add to less hindered carbon  
(10 points)  
(10 EC points)

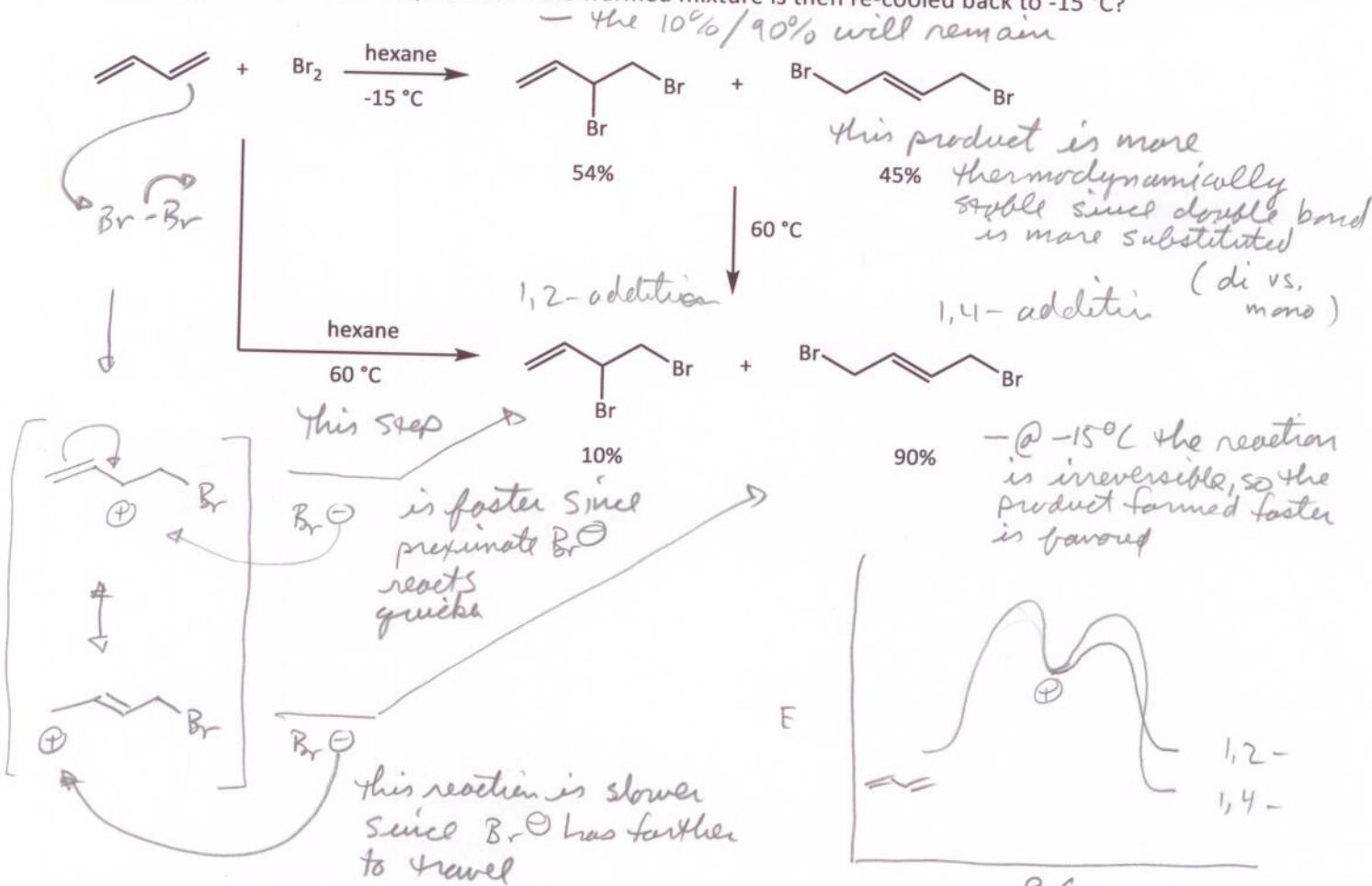


5. Consider the reaction shown below. In terms of the mechanism, clearly account for the formation of the two products and in the observed ratios at the different temperatures. Note that if the reaction is run at the colder temperature and then the mixture is warmed to 60 °C, the ratio of products is the same as if run only at the higher temperature. (20 points)

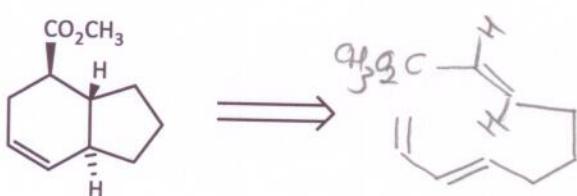
Extra Credit

(5 EC points)

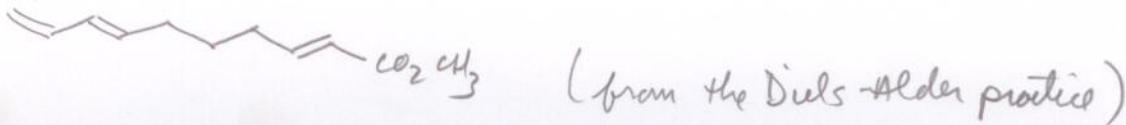
What happens to the ratio of products if the warmed mixture is then re-cooled back to -15 °C?



6. The compound below can be prepared using an *intramolecular Diels-Alder reaction*. What does the starting material look like? (5 points)

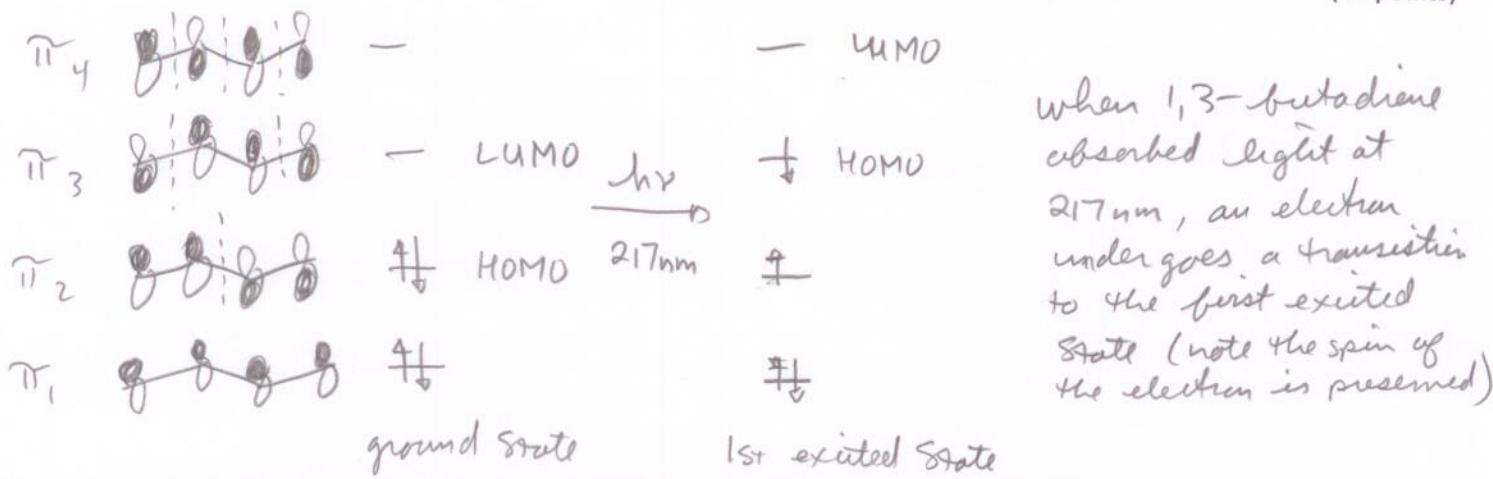


-@ 60 °C the reaction is reversible and therefore in equilibrium with the allyl cation and two products - the most stable product is the major one.



7. Draw the pi molecular orbitals of 1,3-butadiene and their relative energy levels. Show how these orbitals are filled with electrons in the ground state. Indicate which orbital is the Highest Occupied MO (HOMO) and which is the Lowest Unoccupied MO (LUMO). Finally, describe what happens when 1,3-butadiene absorbs in the UV region at 217 nm.

(40 points)



8. In Klein, the discussion about cyclobutadiene indicates that the molecule undergoes rapid equilibration between two rectangular forms. In terms of the molecule's aromatic character (or lack thereof), explain why these structures are *not* resonance forms and describe why the molecule, instead has two different carbon-carbon bond lengths.

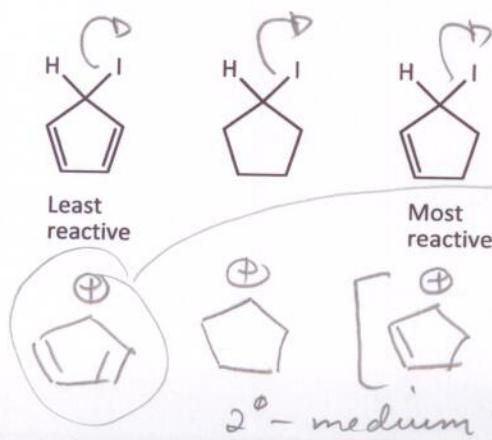
(10 points)



If cyclobutadiene were perfectly square then it would be at its high energy since it is an anti-aromatic  $\pi$  system.

To alleviate this, the molecule is distorted into a rectangle with alternating short (double bond character) and long (single bond character) C-C bond lengths. This reduces the overlap and helps lower the strain. Since the molecule changes bond lengths, say between carbons 1 & 2, then it is in equilibrium and not resonance. No bond length, angle or hybridization changes are "allowed" in resonance forms.

9. In the  $S_N1$  reaction of the compounds shown below, there is a dramatic difference in reactivity. Explain the trend. (hint: remember what makes a good substrate in the  $S_N1$ )

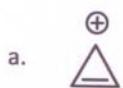


The  $S_N1$  reaction depends on the loss of a leaving group to give a carbocation

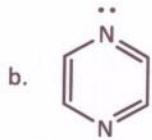
This is the cyclopentadienyl cation and is anti-aromatic, so it's the least stable and least reactive in  $S_N1$

$2^\circ$  allylic is the most stable - has resonance - so most reactive in  $S_N1$

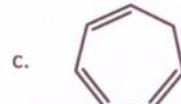
10. For each of the following molecules or ions indicate whether they are *aromatic*, *anti-aromatic* or *non-aromatic*. (20 points)



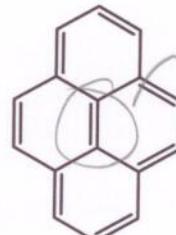
aromatic



aromatic



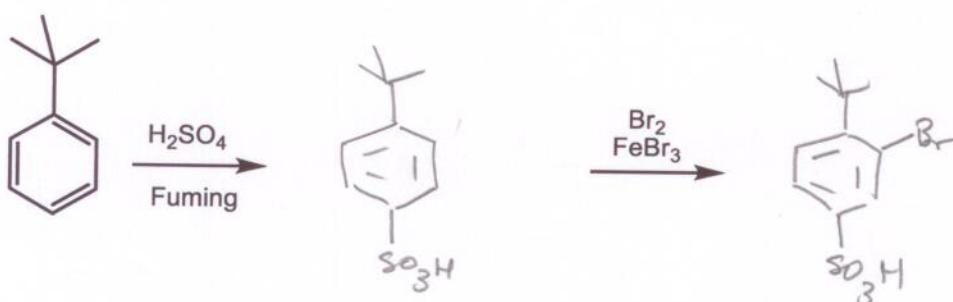
non-aromatic



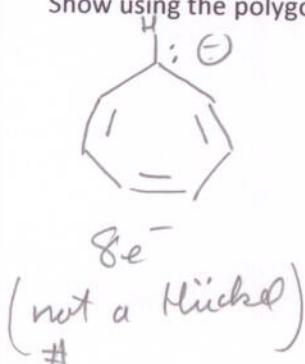
aromatic

ignore these  
for purpose of  
counting  
electrons in  
 $\pi$  system

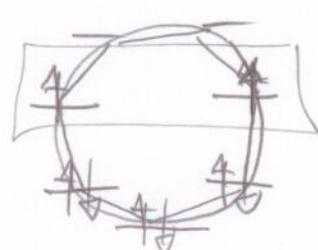
11. In the following synthesis, fill in the products or reagents. (10 points)



12. Show using the polygon rule (Frost circles) whether the *cycloheptatrienyl carbanion* is aromatic or anti-aromatic. (10 points)

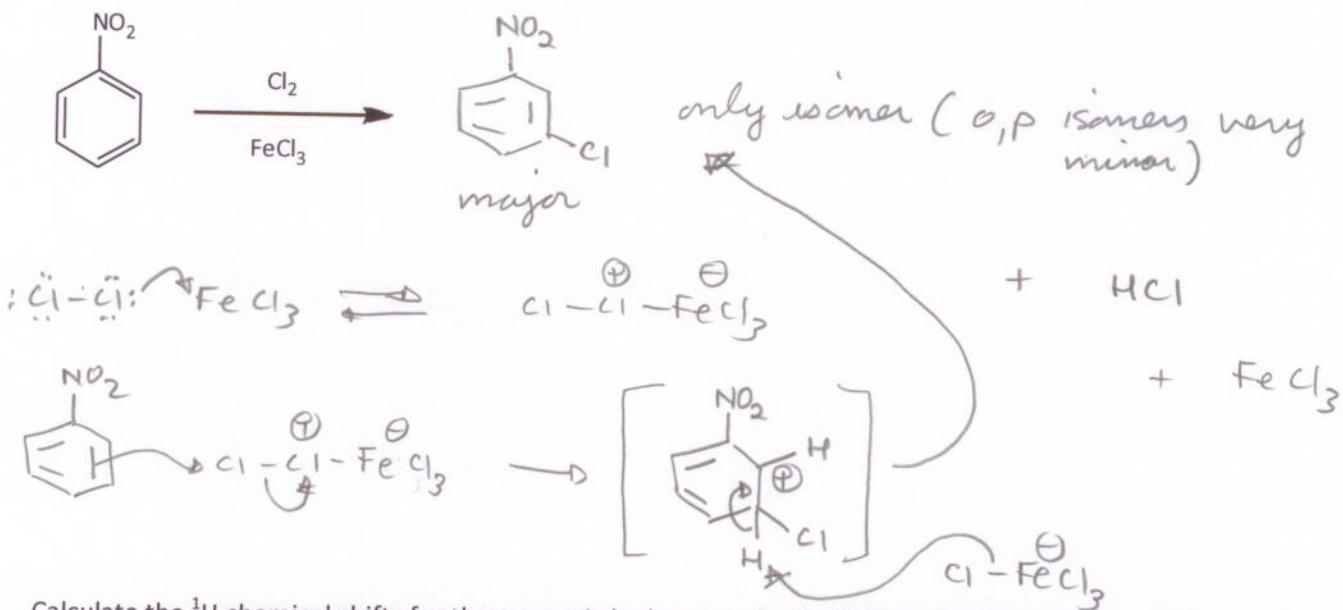


$4n$  for anti-aromatic  
(point goes down!)

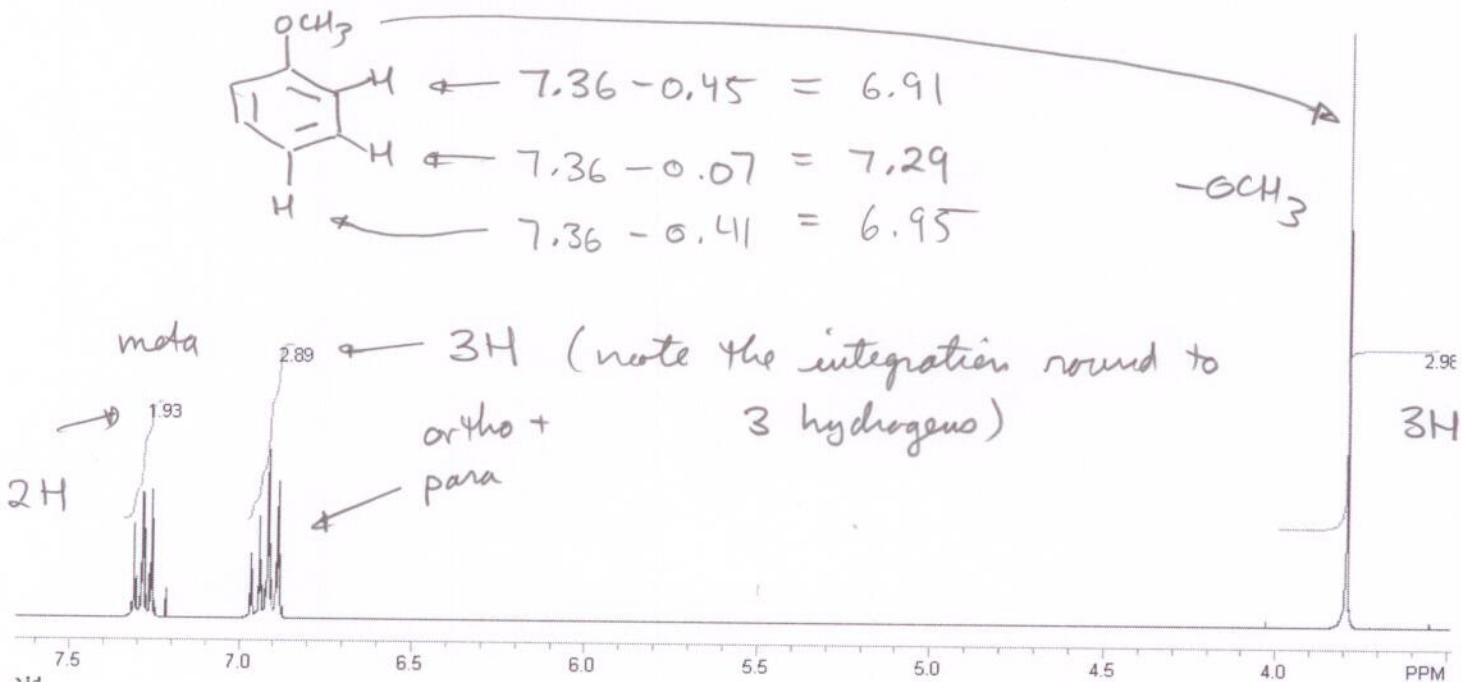


Frost circle gives relative energy levels of  $\pi$  MO's for the system.  
The last 2  $e^-$  go into degenerate orbitals, are unpaired, and form a di-radical. This arrangement explains the instability of an anti-aromatic system

13. Show the major product(s) from the following reaction. Show the *complete* mechanism for this reaction. (If more than one product is formed just show the mechanism for the formation of one of them) (15 points)



14. Calculate the  $^1\text{H}$  chemical shifts for the aromatic hydrogens of anisole ( $\text{C}_7\text{H}_8\text{O}$ ), then assign *all* of the chemical shifts in the NMR spectrum below. Be very specific about the chemical shift for the aromatic hydrogens. (use the provided data at the end of the exam). (15 points)

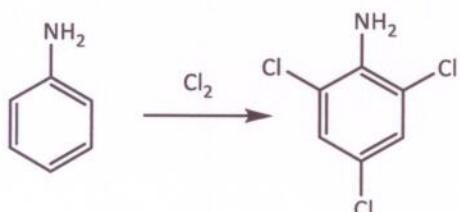


(source: Stephen Corlett)

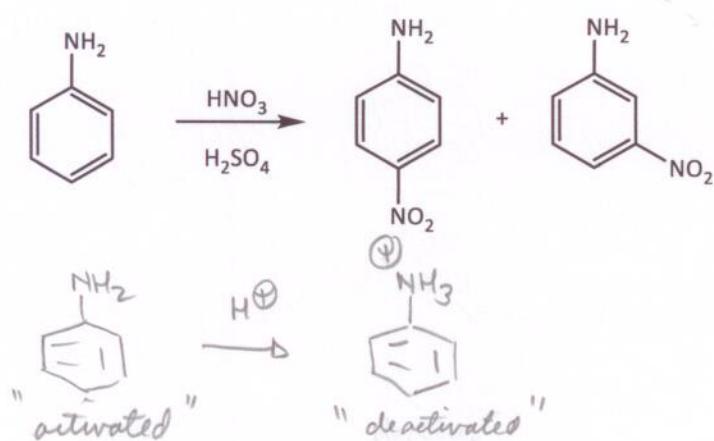
15. Using the same NMR data to explain why anisole reacts faster in the nitration reaction than benzene and why the methoxy group is an *ortho*-*para* directing group. (10 points)

The *ortho* & *para* positions are more shielded in the  $^1\text{H}$  NMR so the carbons they are attached to are (presumably) more electron-rich and therefore more nucleophilic than benzene (this is activating). The *meta* position is relatively unaffected so the methoxy group is an *ortho*/ *para* directing group.

16. Challenge problem. Aniline is one of the most reactive aromatic compounds in the electrophilic aromatic substitution reaction with  $\text{Cl}_2$  and gives a single product, 2,4,6-trichloroaniline – note no catalyst is used, the reaction is way faster than benzene and substitution occurs at all possible activated sites.



However, nitration ( $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ) of aniline, also an electrophilic substitution reaction, is *slower* than benzene and leads to a mixture of 3-nitroaniline (50%) and 4-nitroaniline (50%)(and lots of other by-products). Explain the difference in the outcomes for these two reactions. The NMR data provided below may be useful. (Hint: what does the nitrogen of aniline look like under acidic conditions? For comparison, see the data for the substituent  $-\text{NMe}_3^+ \text{I}^-$ )



(10 points)  
Under strongly acidic conditions the aniline nitrogen is protonated. The ammonium (anilinium) ion is a deactivating group due to its inductive electron-withdrawing effect.

The  $^1\text{H}$  NMR prediction for the similar compound show the following chemical shifts!

The *meta* and *para* positions have nearly the same shift and are most shielded of the aromatic positions – so nitration occurs there

$$7.36 + 0.31 = 7.67$$

$$7.36 + 0.36 = 7.72$$

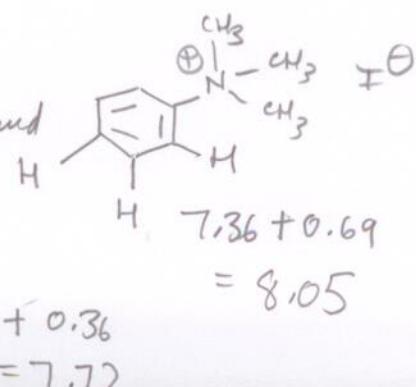
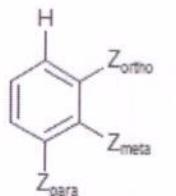


Table from: <http://www.chem.wisc.edu/areas/reich/chem605/index.htm>

### Benzene Substituent Effects



$$\delta_{Ar-H} = 7.36 + Z_{ortho} + Z_{meta} + Z_{para}$$

Substituent R	Z <sub>ortho</sub>	Z <sub>meta</sub>	Z <sub>para</sub>	Substituent R	Z <sub>ortho</sub>	Z <sub>meta</sub>	Z <sub>para</sub>
H	0.0	0.0	0.0	OH <sup>a</sup>	-0.53	-0.14	-0.43
CH <sub>3</sub> <sup>b</sup>	-0.18	-0.11	-0.21	OCH <sub>3</sub> <sup>b</sup>	-0.45	-0.07	-0.41
C(CH <sub>3</sub> ) <sub>3</sub>	0.02	-0.08	-0.21	OPh <sup>b</sup>	-0.36	-0.04	-0.28
o-Propyl	-0.33	-0.15	-0.26	O-C(O)CH <sub>3</sub> <sup>b</sup>	-0.27	-0.02	-0.13
CH <sub>2</sub> Cl	0.02	-0.01	-0.04	O-C(O)Ph <sup>b</sup>	-0.14	0.07	-0.09
CH <sub>2</sub> OH	-0.07	-0.07	-0.07	O-SO <sub>2</sub> Me	-0.05	0.07	-0.01
CF <sub>3</sub>	0.32	0.14	0.20	SH	-0.08	-0.16	-0.22
CCl <sub>3</sub>	0.64	0.13	0.10	SMe	-0.08	-0.10	-0.24
CH=CH <sub>2</sub>	0.04	-0.04	-0.12	SPh	0.06	-0.09	-0.15
CH=CHCOOH <sup>a</sup>	0.19	0.04	0.05	SO <sub>2</sub> Cl	0.76	0.35	0.45
C≡C-H	0.15	-0.02	-0.01	NH <sub>2</sub> <sup>b</sup>	-0.71	-0.22	-0.62
C≡C-Ph <sup>b</sup>	0.17	-0.02	-0.03	NMe <sub>2</sub>	-0.66	-0.18	-0.67
Ph <sup>b</sup>	0.23	0.07	-0.02	NEt <sub>2</sub> <sup>b</sup>	-0.68	-0.15	-0.73
COOH <sup>a</sup>	0.77	0.11	-0.25	NMe <sub>3</sub> +I-	0.69	0.36	0.31
C(O)OCH <sub>3</sub> <sup>b</sup>	0.68	0.08	0.19	NHC(O)CH <sub>3</sub> <sup>b</sup>	0.14	-0.07	-0.27
C(O)OPh <sup>b</sup>	0.85	0.14	0.27	NH-NH <sub>2</sub>	-0.60	-0.08	-0.55
C(O)NH <sub>2</sub> <sup>b</sup>	0.46	0.09	0.17	N=N-Ph	0.87	0.20	0.20
C(O)Cl <sup>b</sup>	0.76	0.16	0.33	N=O	0.58	0.31	0.37
C(O)CH <sub>3</sub> <sup>b</sup>	0.60	0.10	0.20	NO <sub>2</sub> <sup>b</sup>	0.87	0.20	0.35
C(O)C(CH <sub>3</sub> ) <sub>3</sub>	0.44	0.05	0.05	P(O)(OMe) <sub>2</sub>	0.48	0.18	0.24
C(O)H <sup>b</sup>	0.53	0.18	0.28	SiMe <sub>3</sub>	0.22	-0.02	-0.02
C(NPh)H	0.6	0.2	0.2				
C(O)Ph <sup>b</sup>	0.45	0.12	0.23				
C(O)C(O)Ph <sup>b</sup>	0.62	0.15	0.30				
C≡O <sup>c</sup>	1.54	0.96	1.40	JA-89-5320			
CN <sup>b</sup>	0.29	0.12	0.25				
F	-0.29	-0.02	-0.23				
Cl <sup>b</sup>	-0.02	-0.07	-0.13				
Br <sup>b</sup>	0.13	-0.13	-0.08				
I	0.39	-0.21	0.00				
I-Ph <sup>c</sup> Cl <sup>c</sup>	0.63	-0.01	0.15				

<sup>a</sup> Data in dilute CDCl<sub>3</sub> by Paul Schatz, University of Wisconsin, Madison. Original data from J. Am. Chem. Soc. 1956, 78, 3043 at 30 MHz with 50% solutions in cyclohexane.