

ORGANIC CHEMISTRY

CHEM 12B

Exam 2 (215 points, 15 EC points)

FALL 2016, LANEY COLLEGE

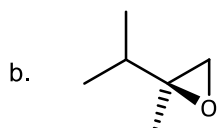
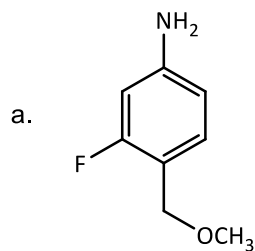
INSTRUCTOR: S. CORLETT

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Name _____

1. Provide IUPAC names for the following compounds.

(10 points)



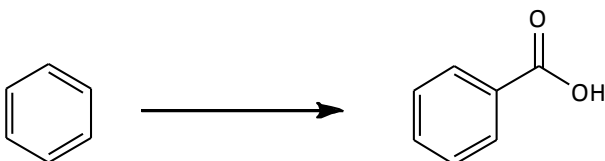
2. Provide structures for the following compounds.

(10 points)

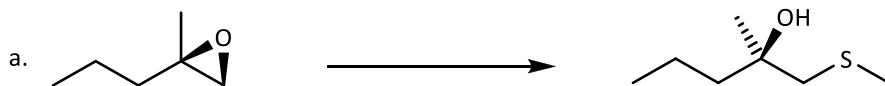
a. (2S,3S)-2,3-epoxyhex-5-en-1-ol

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 (10 points)
EXTRA CREDIT Provide IUPAC names for the products (10 EC points)

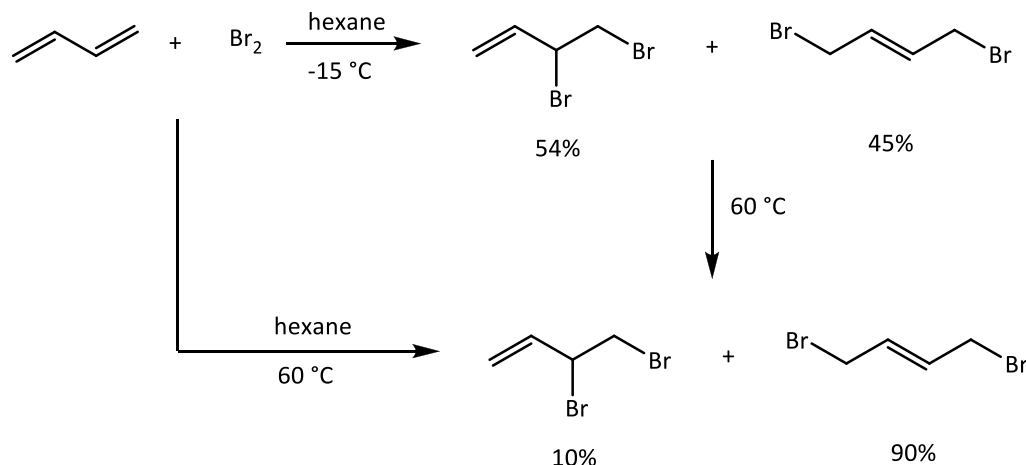


5. Consider the reaction shown below. In terms of the mechanism, clearly account for the formation of the two products and in the observed ratios at the different temperatures. Note that if the reaction is run at the colder temperature and then the mixture is warmed to 60 °C, the ratio of products is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

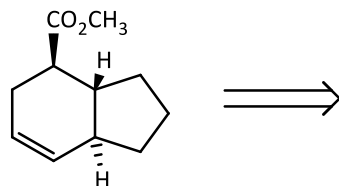
Extra Credit

(5 EC points)

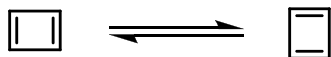
What happens to the ratio of products if the warmed mixture is then re-cooled back to -15 °C?



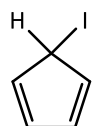
6. The compound below can be prepared using an *intramolecular* Diels-Alder reaction. What does the starting material look like? (5 points)



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)



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) (10 points)

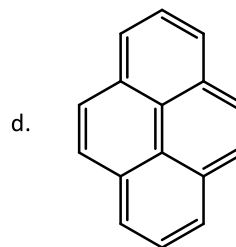
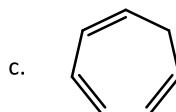
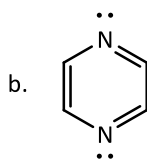
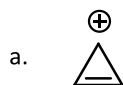


Least
reactive



Most
reactive

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

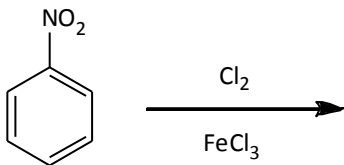


11. In the following synthesis, fill in the products or reagents. (10 points)

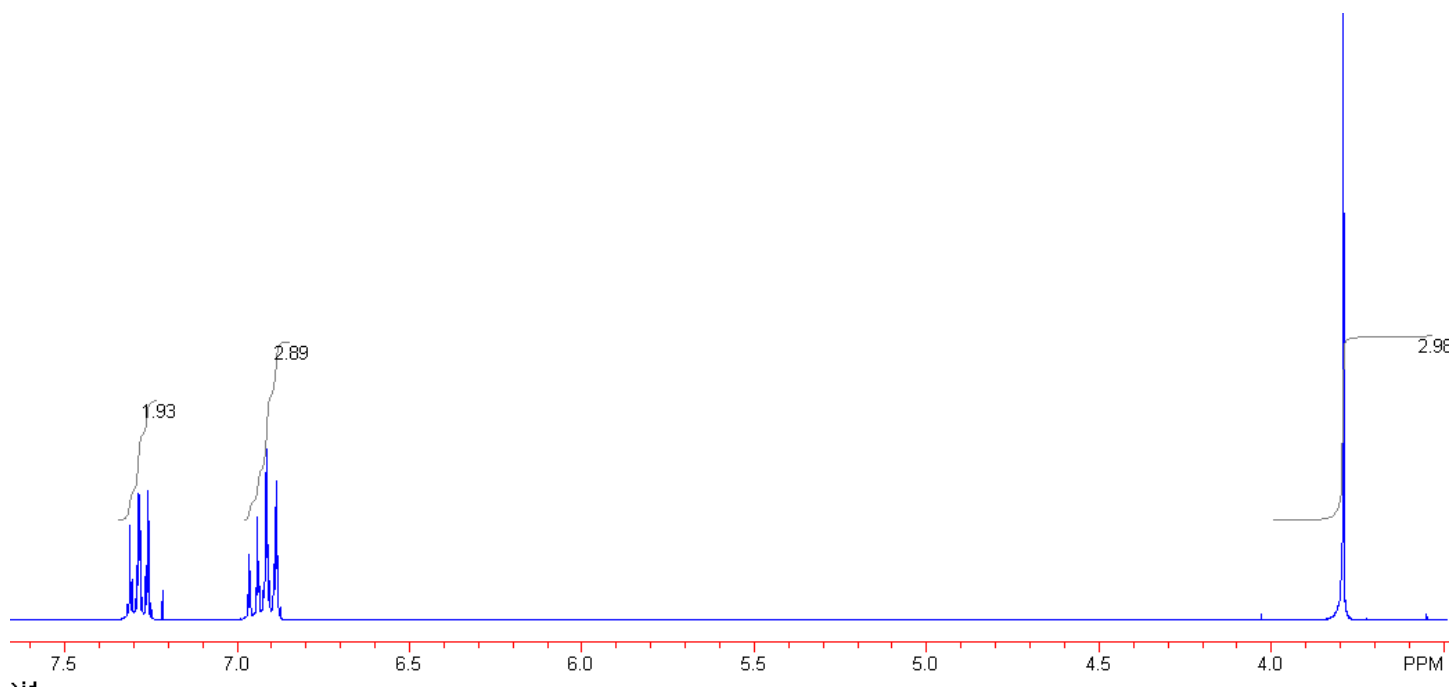


12. Show using the polygon rule (Frost circles) whether the *cycloheptatrienyl carbanion* is aromatic or anti-aromatic. (10 points)

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)



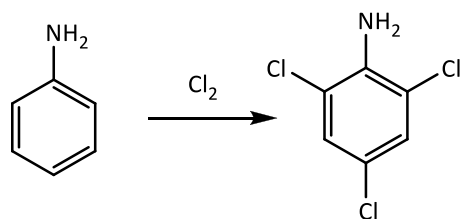
14. Calculate the ¹H chemical shifts for the aromatic hydrogens of anisole (C₇H₈O), then assign *all* of the chemical shifts in the NMR spectrum below. Be very specific about the chemical shift for the aromatic hydrogens. (use the provided data at the end of the exam). (15 points)



(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)

16. *Challenge problem.* Aniline is one of the most reactive aromatic compounds in the electrophilic aromatic substitution reaction with 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 (HNO_3 , H_2SO_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)

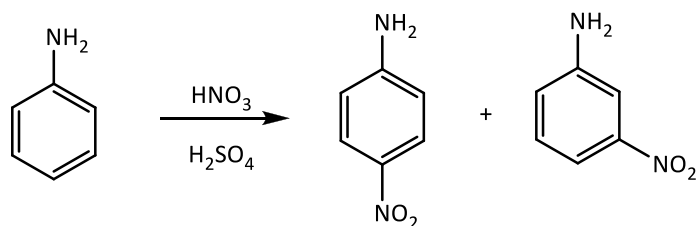
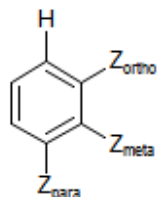


Table from: <http://www.chem.wisc.edu/areas/reich/chem605/index.htm>

Benzene Substituent Effects



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

Substituent R	Z _{ortho}	Z _{meta}	Z _{para}		Substituent R	Z _{ortho}	Z _{meta}	Z _{para}
H	0.0	0.0	0.0		OH ^a	-0.53	-0.14	-0.43
CH ₃ ^a	-0.18	-0.11	-0.21		OCH ₃ ^a	-0.45	-0.07	-0.41
C(CH ₃) ₃	0.02	-0.08	-0.21		OPh ^a	-0.36	-0.04	-0.28
o-Propyl	-0.33	-0.15	-0.26	SDBS	O-C(O)CH ₃ ^a	-0.27	-0.02	-0.13
CH ₂ Cl	0.02	-0.01	-0.04		O-C(O)Ph ^a	-0.14	0.07	-0.09
CH ₂ OH	-0.07	-0.07	-0.07		O-SO ₂ Me	-0.05	0.07	-0.01
CF ₃	0.32	0.14	0.20		SH	-0.08	-0.16	-0.22
CCl ₃	0.64	0.13	0.10		SMe	-0.08	-0.10	-0.24
CH=CH ₂	0.04	-0.04	-0.12		SPh	0.06	-0.09	-0.15
CH=CHCOOH ^a	0.19	0.04	0.05		SO ₂ Cl	0.76	0.35	0.45
C≡C-H	0.15	-0.02	-0.01		NH ₂ ^a	-0.71	-0.22	-0.62
C≡C-Ph ^a	0.17	-0.02	-0.03		NMe ₂	-0.66	-0.18	-0.67
Ph ^a	0.23	0.07	-0.02		NEt ₂ ^a	-0.68	-0.15	-0.73
COOH ^a	0.77	0.11	-0.25		NMe ₃ +I-	0.69	0.36	0.31
C(O)OCH ₃ ^a	0.68	0.08	0.19		NHC(O)CH ₃ ^a	0.14	-0.07	-0.27
C(O)OPh ^a	0.85	0.14	0.27		NH-NH ₂	-0.60	-0.08	-0.55
C(O)NH ₂ ^a	0.46	0.09	0.17		N=N-Ph	0.67	0.20	0.20
C(O)Cl ^a	0.76	0.16	0.33		N=O	0.58	0.31	0.37
C(O)CH ₃ ^a	0.60	0.10	0.20		NO ₂ ^a	0.87	0.20	0.35
C(O)C(CH ₃) ₃	0.44	0.05	0.05		P(O)(OMe) ₂	0.48	0.16	0.24
C(O)H ^a	0.53	0.18	0.28		SiMe ₃	0.22	-0.02	-0.02
C(NPh)H	0.6	0.2	0.2					
C(O)Ph ^a	0.45	0.12	0.23					
C(O)C(O)Ph ^a	0.62	0.15	0.30					
C≡O ^a	1.54	0.96	1.40	JA-69-5320				
CN ^a	0.29	0.12	0.25					
F	-0.29	-0.02	-0.23					
Cl ^a	-0.02	-0.07	-0.13					
Br ^a	0.13	-0.13	-0.08					
I	0.39	-0.21	0.00					
I-Ph ^a Cl ⁻	0.63	-0.01	0.15					

^a Data in dilute CDCl₃ 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.