

CHM 333  
Answers to Semester Exam #3  
November 19, 2008

E. B. Skibo

Print Name \_\_\_\_\_

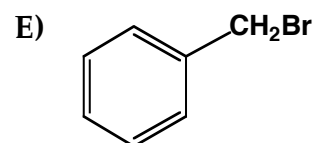
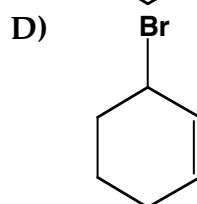
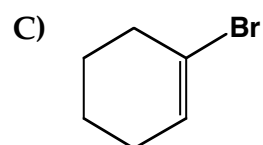
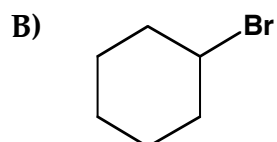
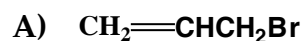
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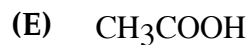
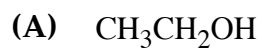
PLEASE PRINT YOUR NAME ON LAST PAGE TOO. ANSWER QUESTIONS ONLY IN THE SPACES PROVIDED. DO NOT WRITE ON THE BACK OF PAGES, I WILL NOT GRADE ANSWERS ON THE BACK OF PAGES.

1. (30 pts) Multiple choice/fill in the blanks. Put your answer in the space provided.

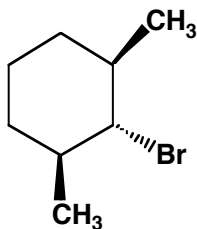
C a) Which of the following cannot undergo nucleophilic substitution reactions?



C b) Which of the following solvents is aprotic?

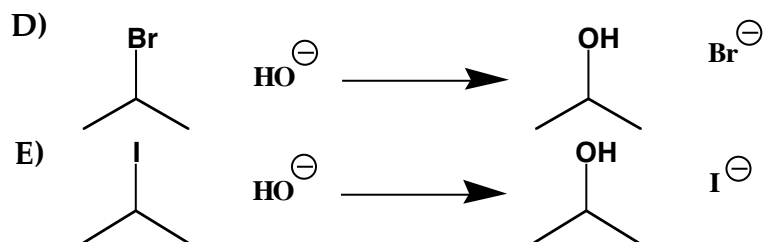
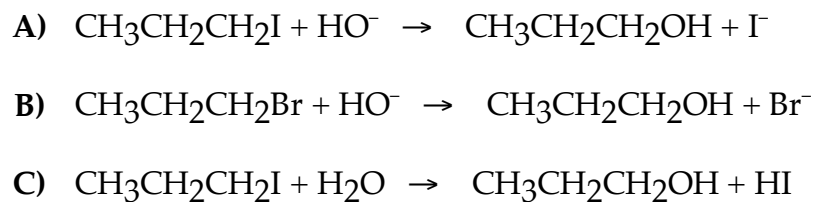


- E c) Why is the alkyl halide shown below not capable of undergoing an E2 reaction upon treatment with sodium ethoxide?



- A) Bromide is too poor a leaving group.  
B) The substrate is too hindered.  
C) Too much angle strain would be present in the alkene product.  
D) Sodium ethoxide is a poor base to use in E2 reactions.  
E) The C-H and C-Br bonds, which need to break, cannot achieve an anti-periplanar orientation.

- A d) Which of the following S<sub>N</sub>2 reactions is the fastest?



- D e) Assuming no other changes, what is the effect of doubling both the alkyl halide and the nucleophile concentrations in the above reaction?

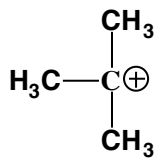
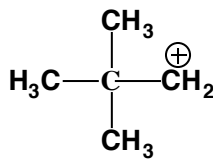
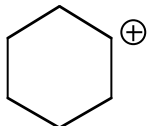


- A) No change  
B) Doubles the rate  
C) Triples the rate  
D) Quadruples the rate  
E) Rate is halved

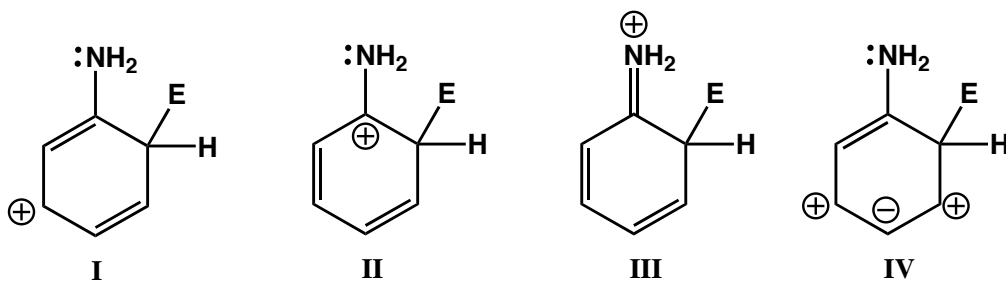
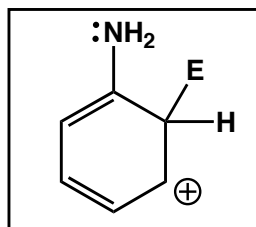
A f) Which of the following is the best nucleophile in water?

- A)  $\text{I}^-$
- B)  $\text{CH}_3\text{SCH}_3$
- C)  $\text{CH}_3\text{OCH}_3$
- D)  $\text{Cl}^-$

A g) Which of the following carbocations is the least stable?

- A)  $\text{CH}_3\text{CH}_2^+$
- B)  $\text{CH}_3\overset{\oplus}{\text{C}}\text{HCH}_3$
- C) 
- D) 
- E) 

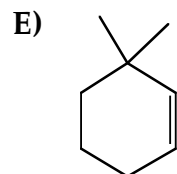
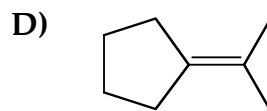
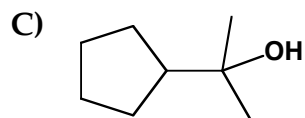
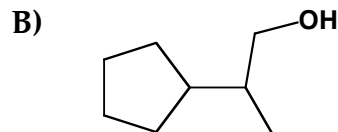
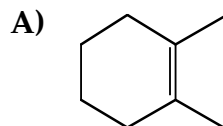
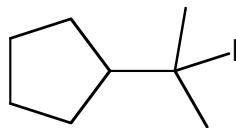
D h) Which of the following is not a resonance structure of the species shown?



- A) I
- B) II
- C) III
- D) IV

B i)

Which of the following is least likely to be found in the product mixture, which results when the alkyl iodide below is heated in water?



E j)

Which of the following statements correctly describe(s) E1 reactions of alkyl halides (RX)?

I) Rate =  $k[\text{Base}]$

II) Rate =  $k[\text{base}][\text{RX}]$

III) Rate =  $k[\text{RX}]$

IV) The reactions occur in two distinct steps

V) Rearrangements sometimes occur.

A) II and IV

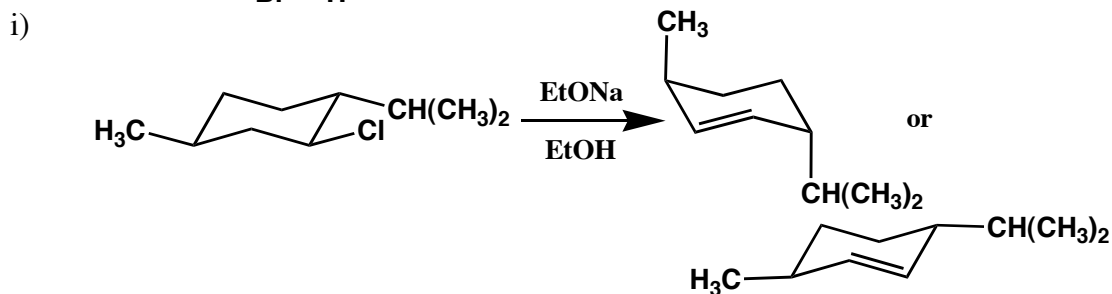
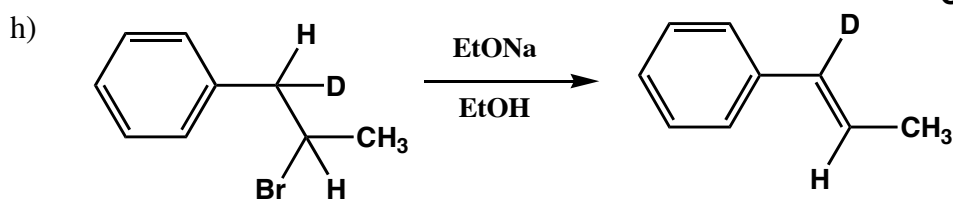
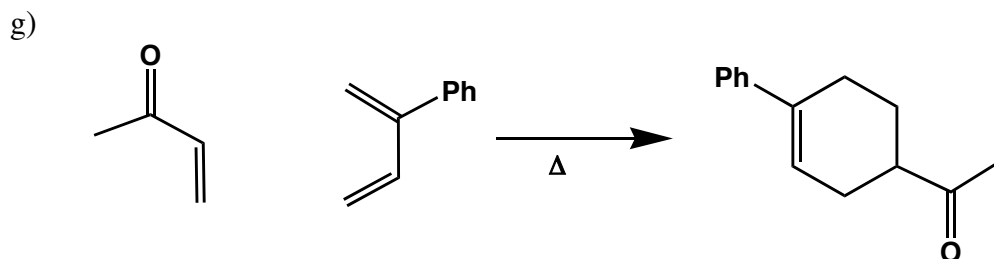
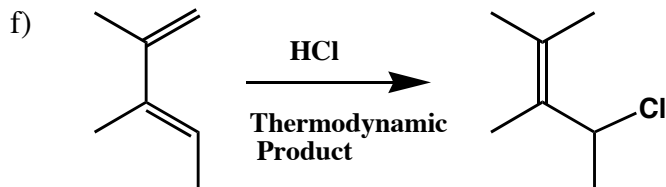
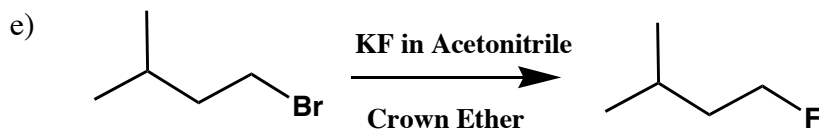
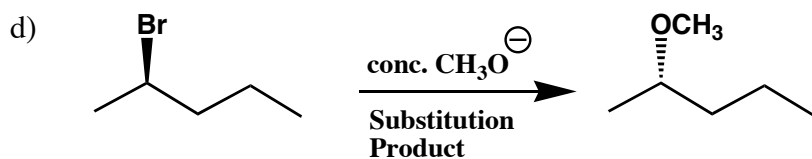
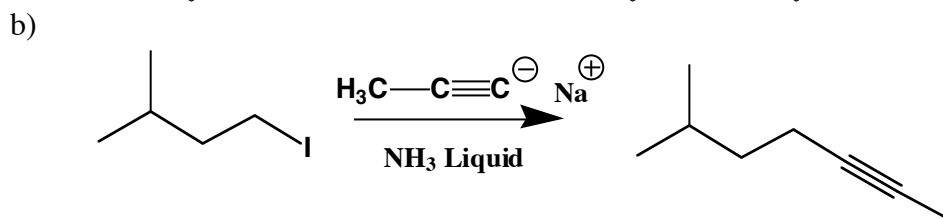
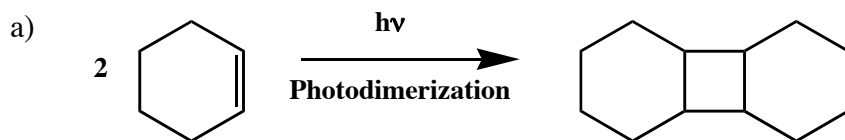
B) III and V

C) I, IV, and V

D) I only

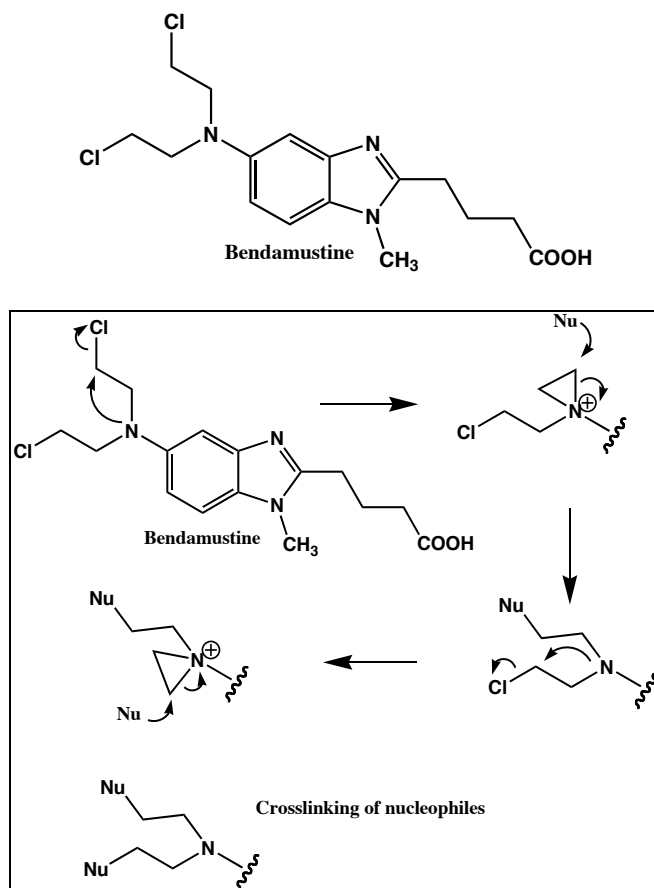
E) III, IV, and V

2. (45 pts) Predict the major product of the following reactions. If there is no reaction, write NR. Show the stereochemical consequence of the reaction if any.



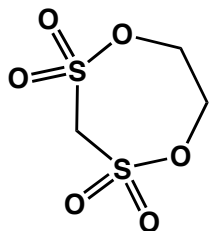
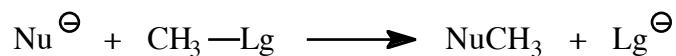
3. (20 pts) Answer the following questions regarding alkylating agents.

a) Bendamustine is a cancer drug used to treat leukemia. Provide a mechanism for its alkylation reactions.

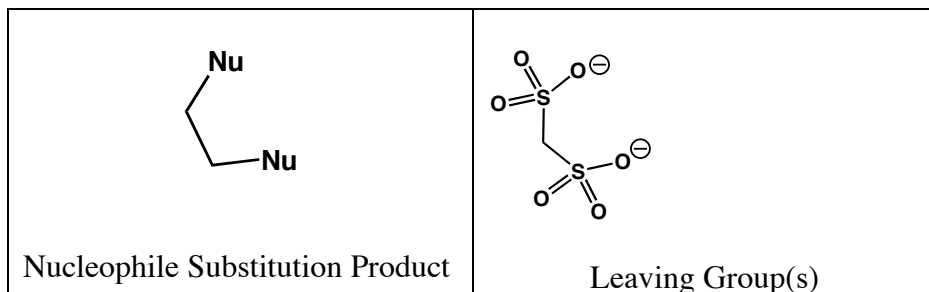


b) The following antitumor agent is under investigation at the National Cancer Institute. Show the structure of the nucleophile substitution product using "Nu-" as your generic nucleophile. Also show the structure of the leaving group(s) resulting from this reaction.

example

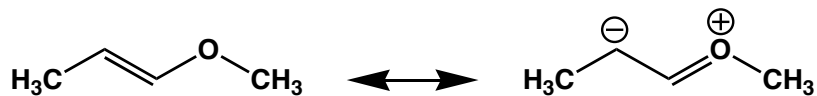


Cyclodisone

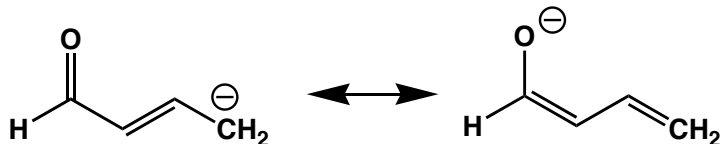


4. (15 pts) Resonance problems. Answer the following questions.

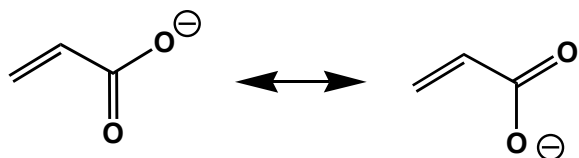
a) Draw the lowest-energy alternative resonance structure for this compound.



b) Draw the lowest-energy alternative resonance structure for this compound. There are two resonance structures for this molecule. Draw the better one.



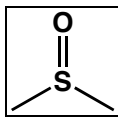
c) Show all charge delocalization structures for the following charged species. Include all degenerate structures



5. (20 pts) Provide the structures of the following common laboratory solvents.

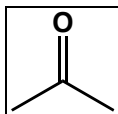
a)

**DMSO**



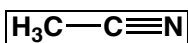
b)

**Acetone**



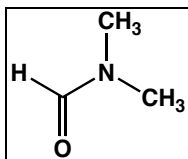
c)

**Acetonitrile**



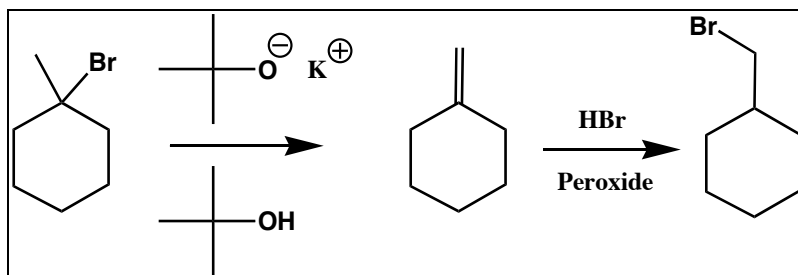
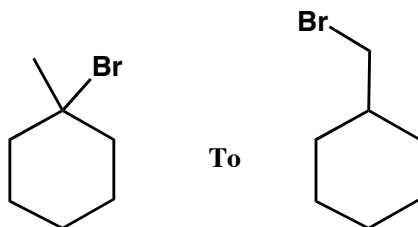
d)

**Dimethylformamide (DMF)**

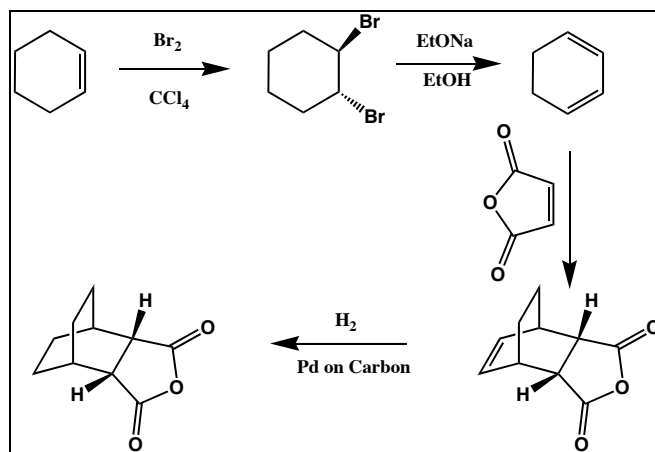
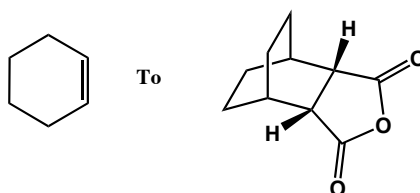


6. (30 pts.) Multistep Synthesis. Starting with the starting material shown below show how the synthesis of the product can be carried out. Use any necessary carbon sources and reagents in your synthesis.

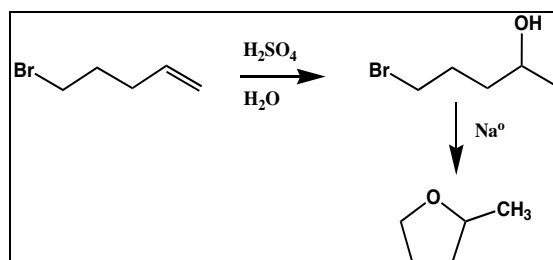
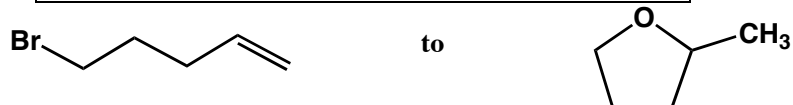
a)



b)

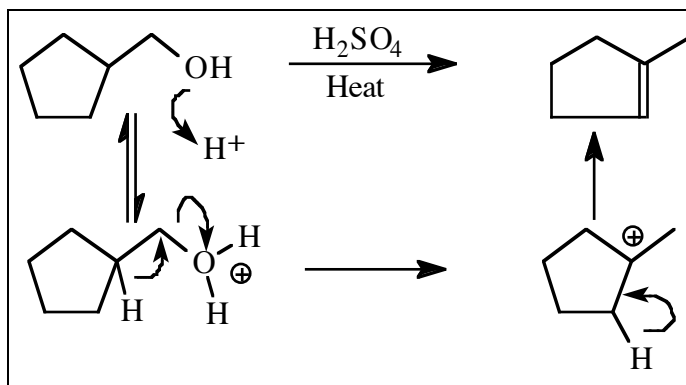
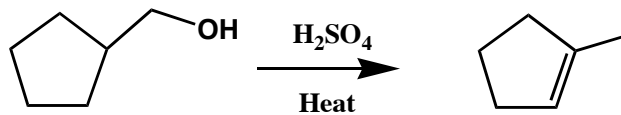


c)

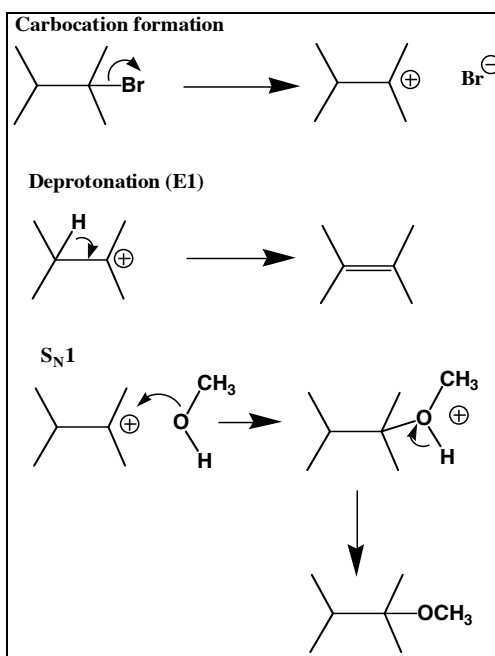
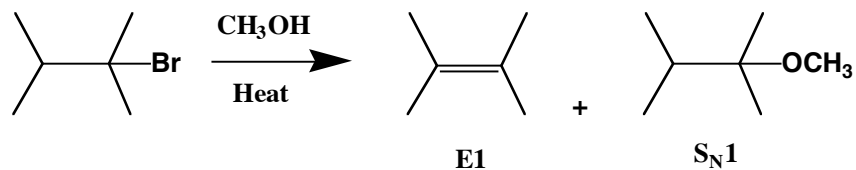


7. (20pts) Mechanisms. Provide a mechanism for the following reactions. Show intermediates present in the reaction along with curved arrows and proton transfers.

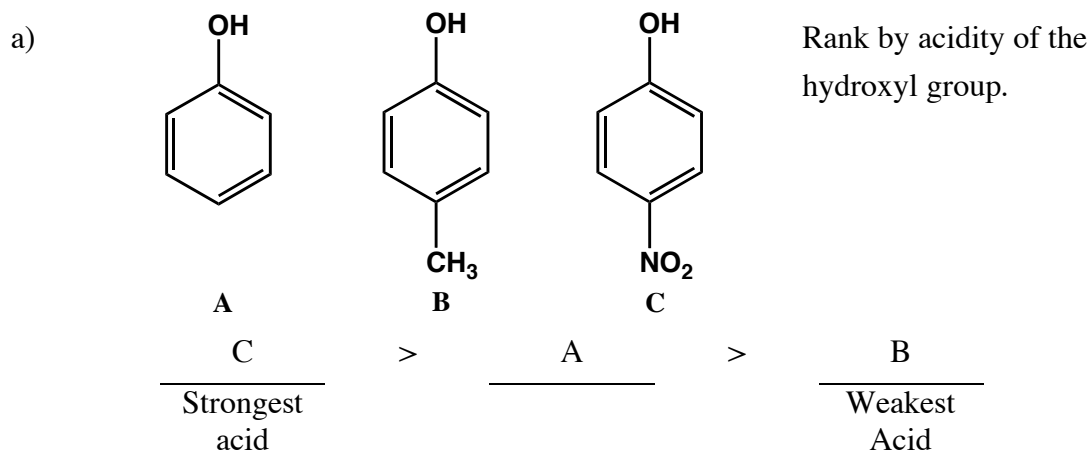
a)



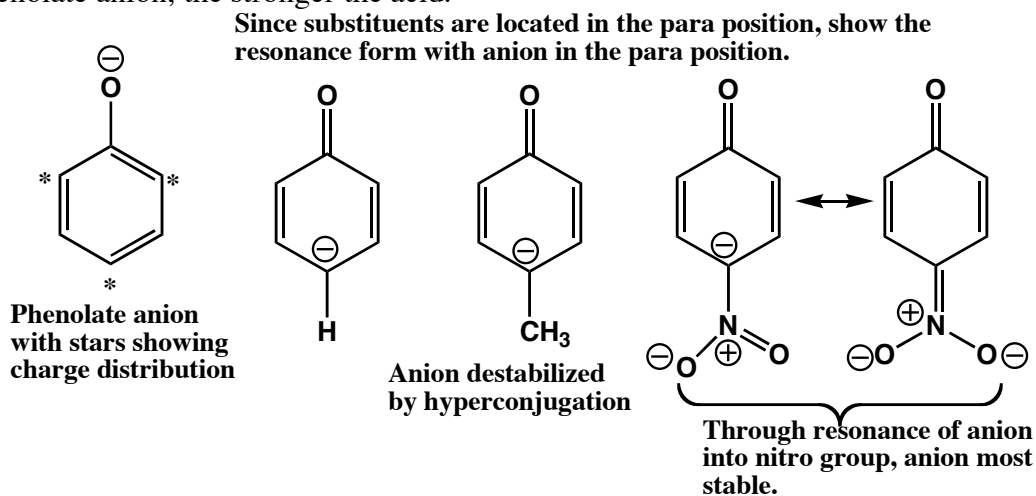
b) Show mechanisms for both the E1 and  $\text{S}_{\text{N}}1$  products of the reaction shown below.



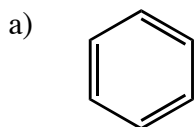
8. (10pts) Rank the following groups of compounds as instructed. Provide an explanation for your ranking along with supporting resonance structures.



To answer this problem show the distribution of the phenolate anion using stars. The influence of the substituent on the anion can then be assessed. The more stable the phenolate anion, the stronger the acid.



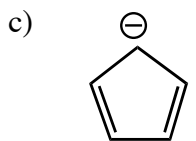
9. (10pts) Classify each of the following compounds as aromatic or antiaromatic using the Hückel rule. Assume all compounds are flat.



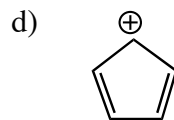
Aromatic



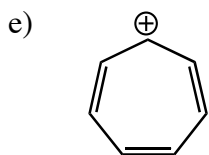
Antiaromatic



Aromatic



Antiaromatic



Aromatic