Université d'Ottawa | University of Ottawa
Faculté des sciences | Faculty of Science
Département de chimie | Department of chemistry
Pavillon D'Iorio Hall
10 Marie Curie, Ottawa, ON, Canada

CHM 1321 A

Final Examination

April 2022 William Ogilvie

Time: 3 Hours

Name:_____

Student Number:_____

Note: The marking scheme is given for each question as a guide. It is subject to minor changes.

You have 180 minutes to complete your exam + 15 minutes to scan and upload your answers.

Points will be deducted for late submissions.

The exam will be proctored using Zoom. If you are not proctored you will have to contact the faculty of science to request a deferral.

If in the opinion of the proctors, you and your environment are not sufficiently visible to them, your exam will not be marked and you will need to contact the faculty of science to request a deferral. Please see the syllabus, the "first lecture" video, and the "tests and exams" topic for more information.

Attempt all questions. Use the back of the page or blank paper if extra space is needed.

This exam is closed book.

The use of molecular models is permitted.

The use of calculators is permitted.

No other resources besides pen, pencil and paper are permitted.

Submit your exam as a single PDF file to Brightspace, with all pages upright and in order. Points will be deducted if your file is not correctly formatted.

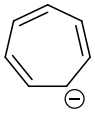
TOTAL PAGES OF EXAM: 17

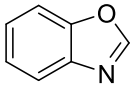
APPROXIMATE NUMBER OF POINTS 184

1) Identify whether the following molecules are aromatic, antiaromatic or non-aromatic (**4 Points**)

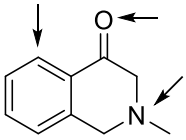
a)  anti-aromatic

b)  non-aromatic

c)  anti-aromatic

d)  aromatic

2) For the following compound:



a) What is the hybridization of the indicated atoms? (**3 points**)

C = sp^2

O = sp^2

N= sp^3

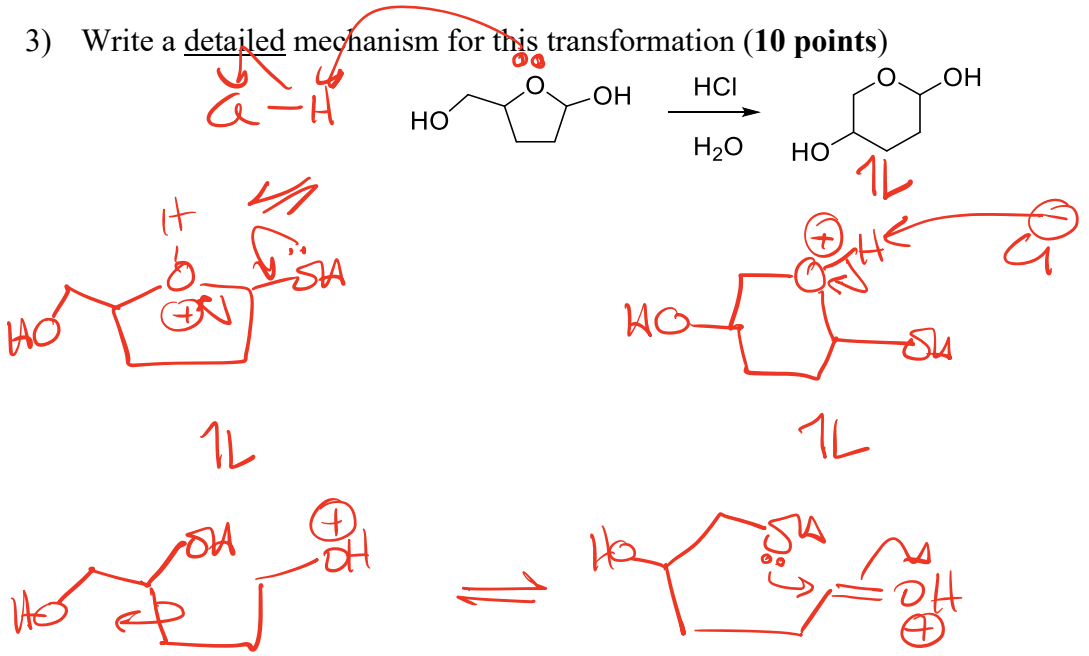
b) What type of molecular orbitals connect the following atoms to other atoms? (**5 points**)

C = σ, π

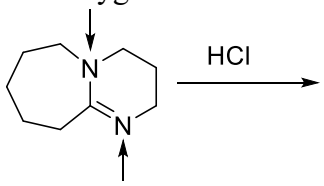
O = σ, π

N= σ

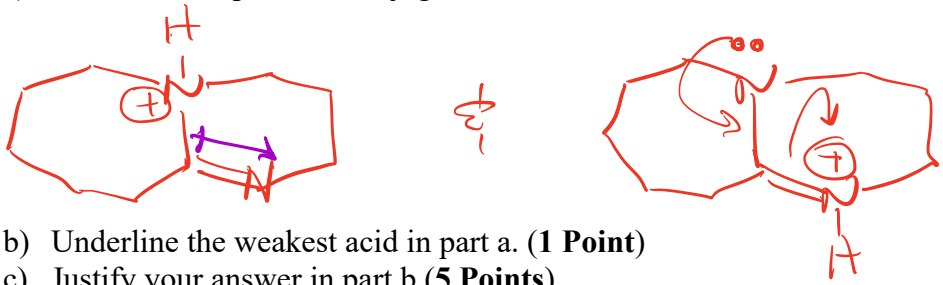
3) Write a detailed mechanism for this transformation (**10 points**)



4) On the structure below, either of the two oxygen atoms can react with HCl.



a) Draw the two possible conjugate acids that can be formed from this reaction. (**2 points**).

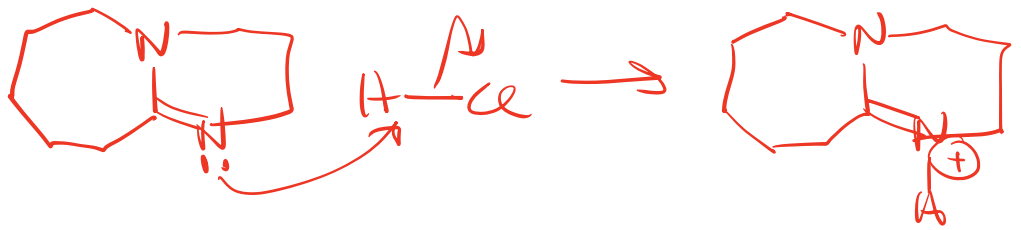


b) Underline the weakest acid in part a. (**1 Point**)

c) Justify your answer in part b (**5 Points**).

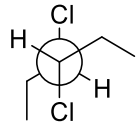
The conjugate acid on the right is stabilized by resonance (electron donation from the other nitrogen atom); the conjugate acid on the left is destabilized by polarization of the adjacent bond

d) Using your answer from part b, predict the site of protonation on the original molecule and briefly explain your choice. (**2 Points**)

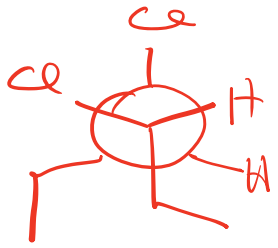


Weakest acid is thermodyn. the most favourable.

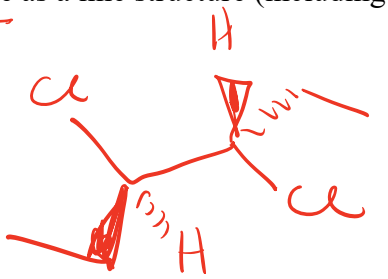
5) Consider the following molecule



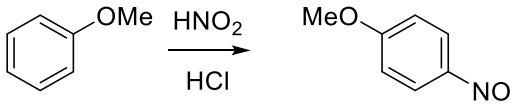
a) Draw a *different* staggered conformation of the same molecule (**2 points**).



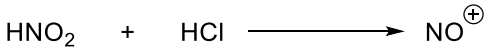
b) Draw the molecule as a line structure (including stereochemistry as necessary) (**2 points**).

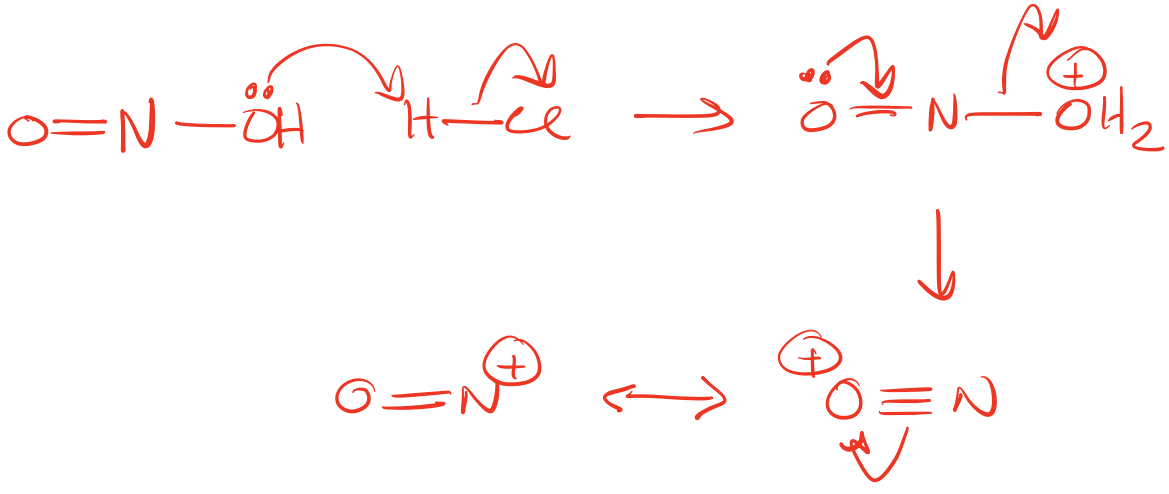


6) Consider the following reaction:

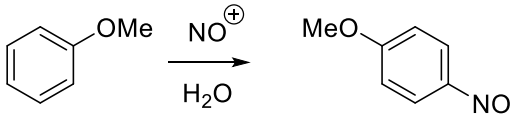


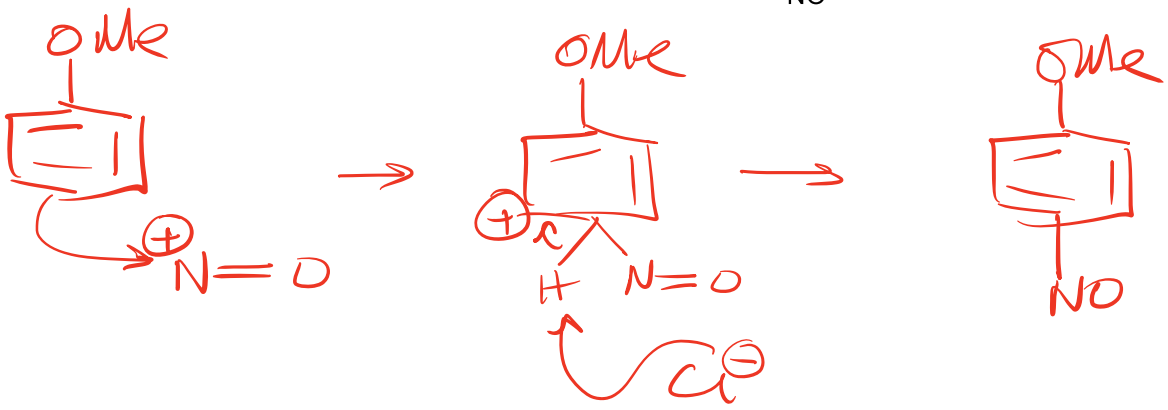
a) During the **first** part of the reaction the active electrophile is formed according to the equation below. Provide a mechanism for this transformation. Hint: draw the Lewis structure of HNO_2 first. (**5 points**).



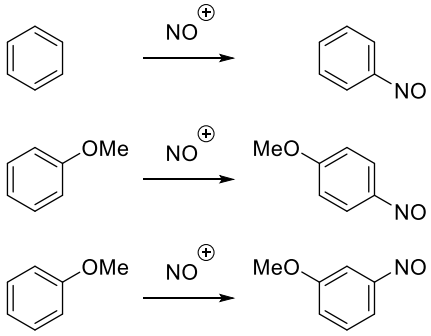


b) Provide a mechanism for the substitution. (**4 points**).





7) Consider the following reactions.

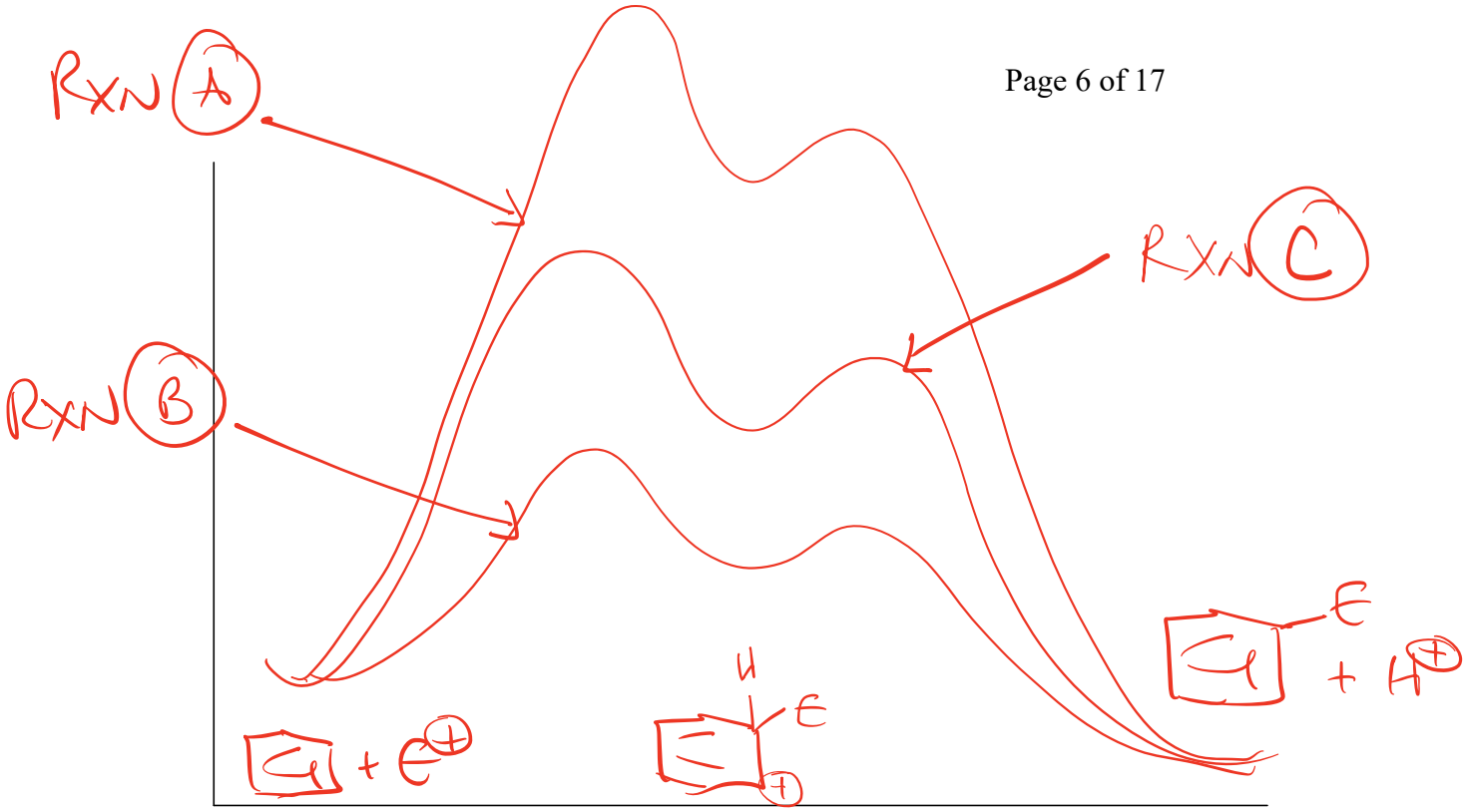


RXN A

RXN B

RXN C

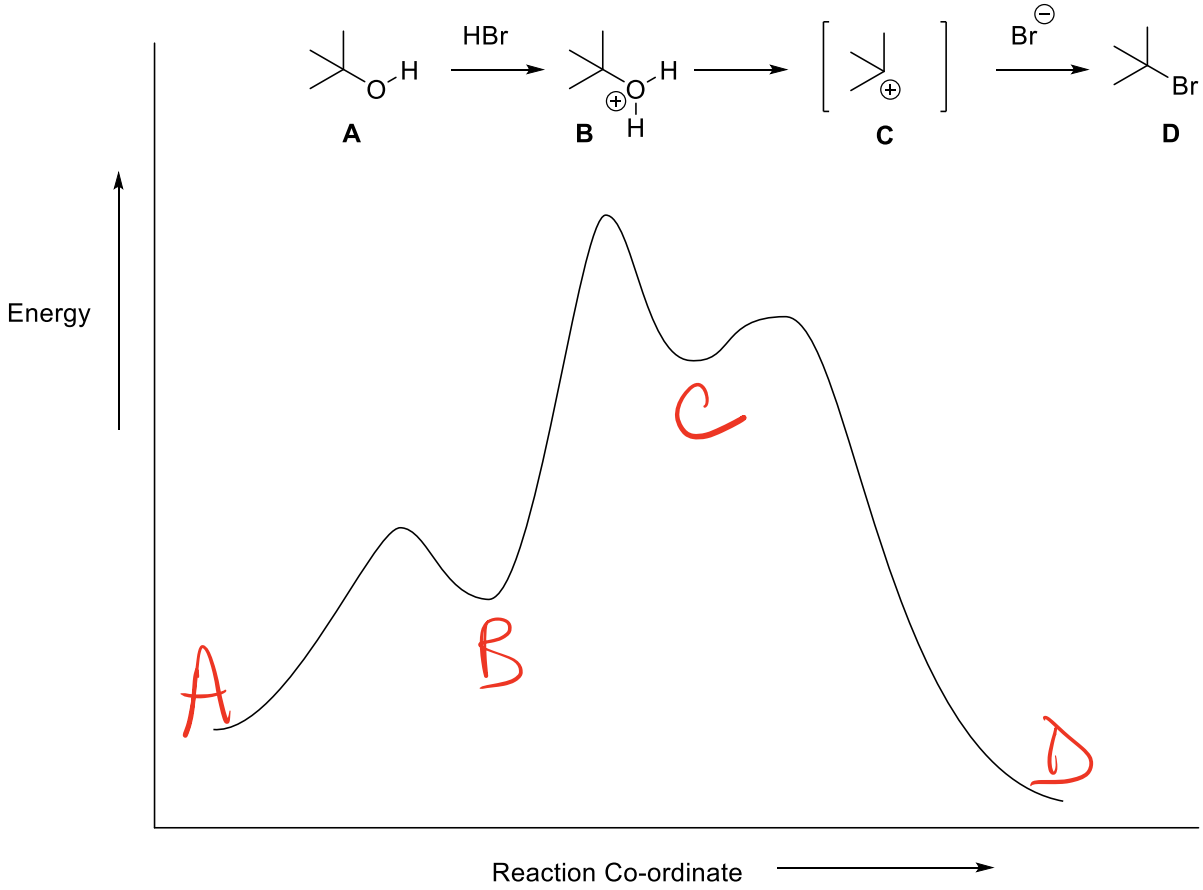
a) Draw a reaction co-ordinate diagram that shows the energy pathways for the three reactions shown above (assume the reactants and products have equal energies). (**5 Points**)



b) Which of the reactions in part (a) is the fastest and why? (**2 Points**)

Reaction (B) is the fastest because the barrier for the RDS (step 1) is the lowest. This is due to the stabilization of the forming +ve charge by the OMe group.

8) Consider the following reaction co-ordinate diagram



a) Identify the various species on the diagram by adding the letter identifying each of the structures. (**1 Point**).

b) Which species does the first transition state of the overall reaction most resemble? What kind of transition state is this? (**2 points**)

B This is a "late" TS, i.e. product-like

c) Which species does the second transition state of the overall reaction most resemble? What kind of transition state is this? (**2 points**)

C This is also a "late" TS, i.e. product-like

d) Which species does the third transition state of the overall reaction most resemble? What kind of transition state is this? (**2 points**)

C This is an "early" TS, i.e. reactant-like

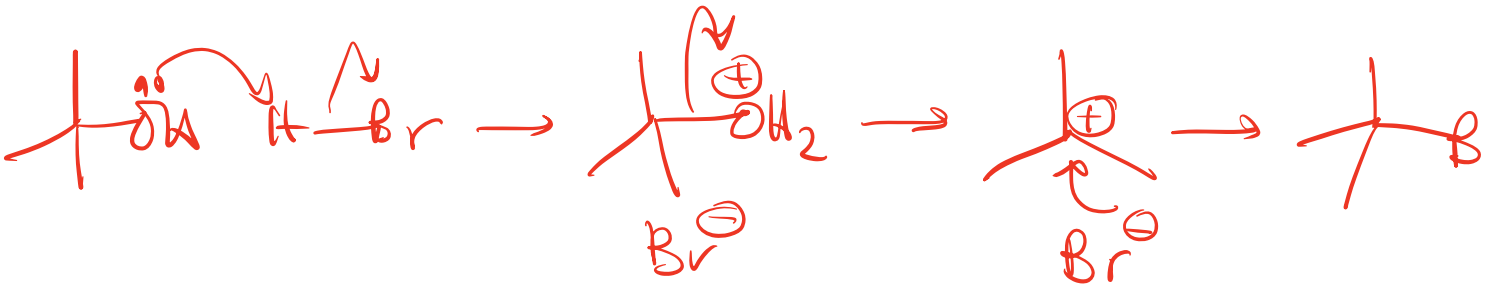
e) What is the name of the approximation used to reach the conclusions in parts (b) and (c)? (**1 Point**)

Hammond postulate.

f) Which step in the sequence is rate determining and why? (**2 Points**)

B → C. It has the highest energy TS.

g) What is the mechanism of the reaction? (**4 Points**)



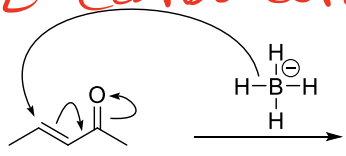
h) Which of the following reactions will be faster and why? (**2 Points**)

typo! Should be HBr

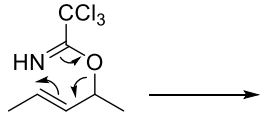
The left reaction will be faster. The RDS involves formation of a carbocation, and the 3° carbocation is more stable than the 2° carbocation, so the barrier will be lower.

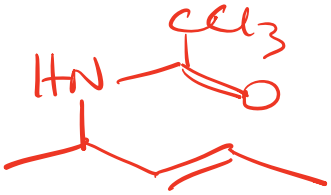
9) Draw the products of each of the following based on the mechanistic arrows used (**3 points**).

a)

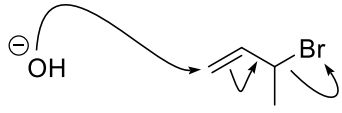


b)

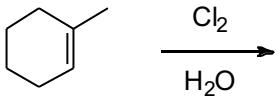




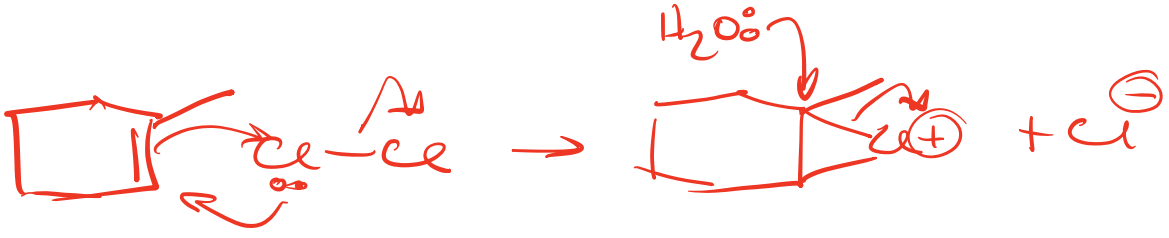
c)

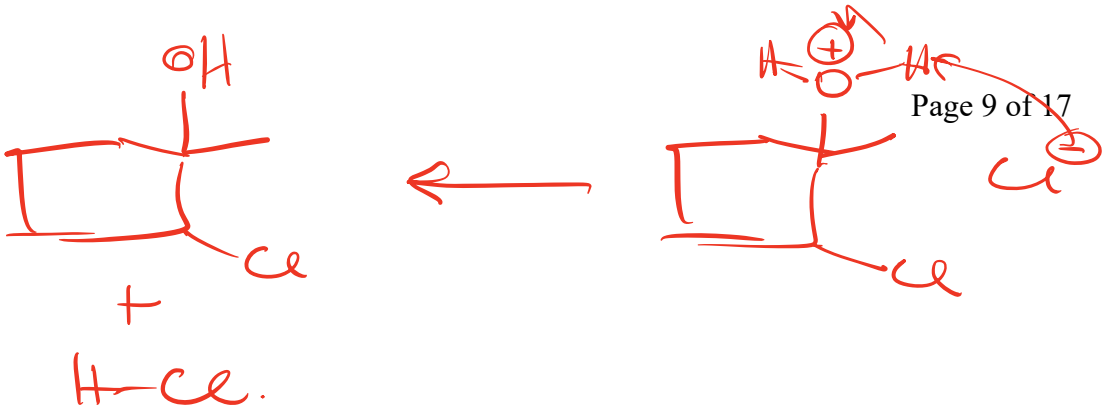


10) Consider the following reaction:



a) Write a <u>detailed</u> mechanism for this transformation (**7 points**).



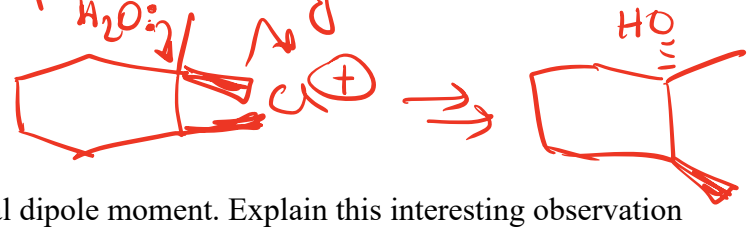


b) Provide a brief explanation for the **location** of the heteroatoms in the final product (regiochemistry). A structure may be helpful here. (**2 points**).

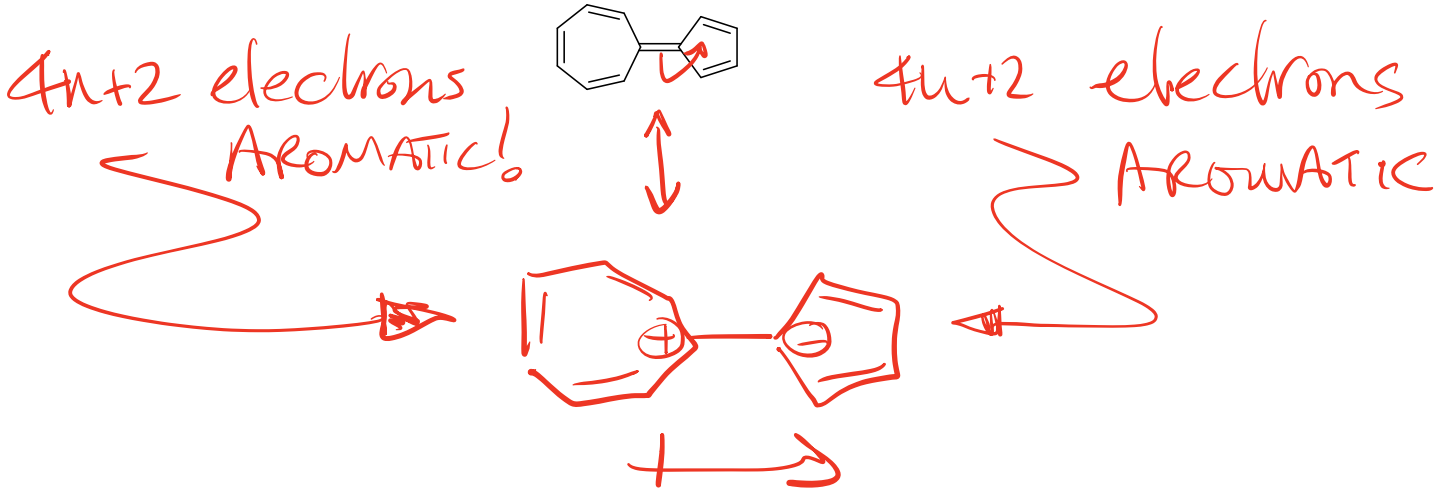
Water attacks the carbon atom best able to stabilize the δ+ in the chloronium ion:

c) Briefly account for the **stereochemistry** of the final product. A structure may be helpful here. (**2 points**).

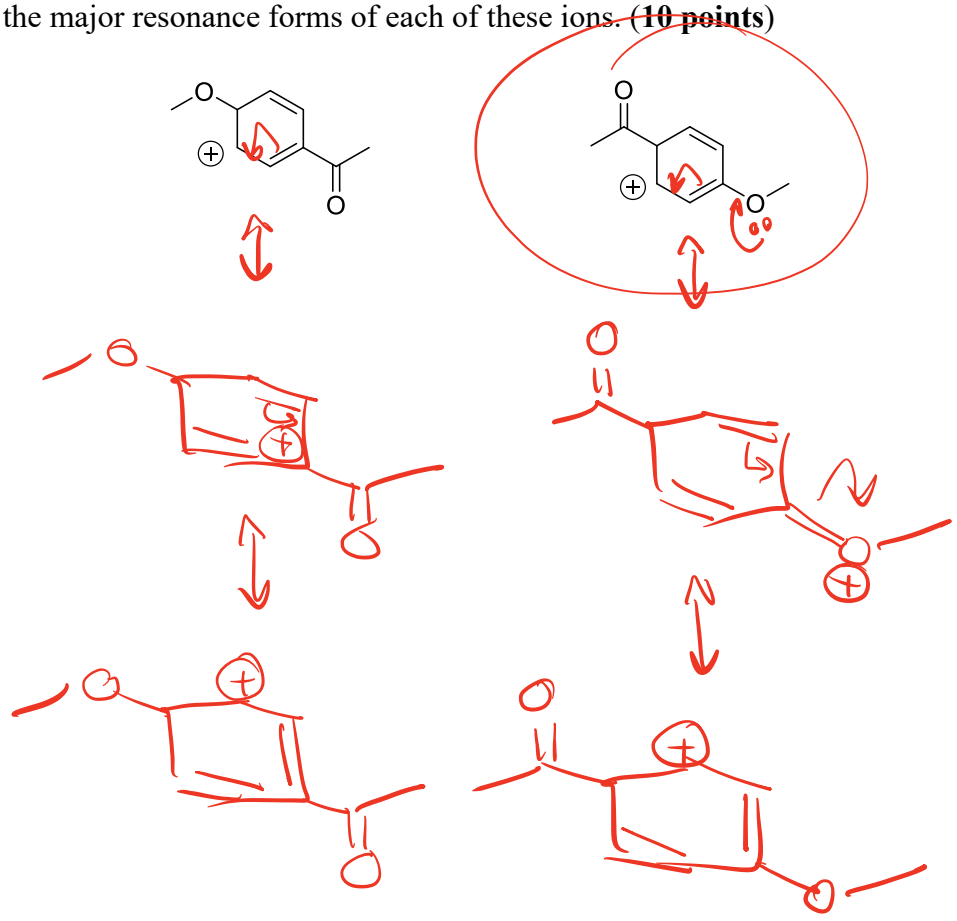
The Cl and OH groups will be anti because water approaches from the opposite side of the ring from the chloronium ion, e.g.



11) The following hydrocarbon has an unusual dipole moment. Explain this interesting observation using chemical structures and/or a mechanism (**4 Points**).



12) (a) Draw the major resonance forms of each of these ions. (~~**10 points**~~)

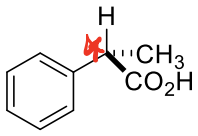


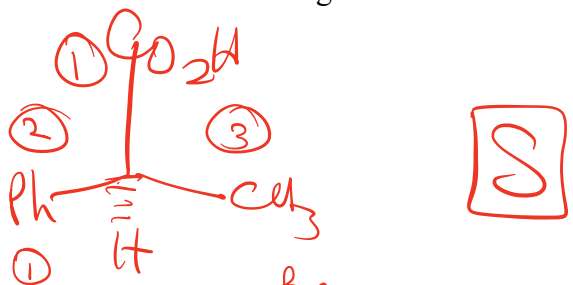
(b) Circle the most stable of the two ions in part a. (**1 Point**)

13) For the following compounds

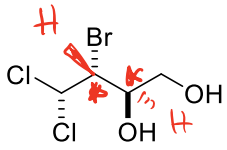
a) show the stereogenic centre(s) by labeling them with a star (*)(**3 points**)
b) determine the priorities of the substituents on each stereogenic centre. For compounds with more than one centre, make sure you clearly indicate which priorities refer to which centre. (re-drawing the structure helps) (**6 points**)
c) determine the configuration of each stereocentre (**3 points**)

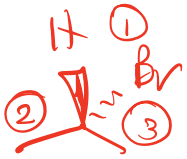
(i)



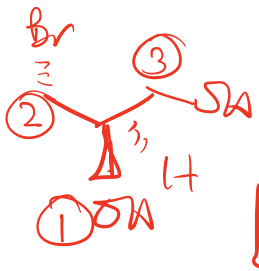


(ii)





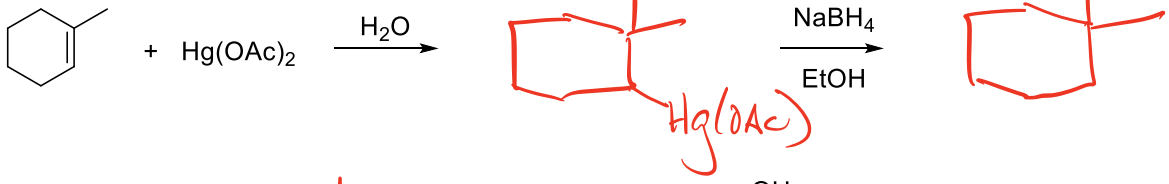
S as shown, but inverted, so R



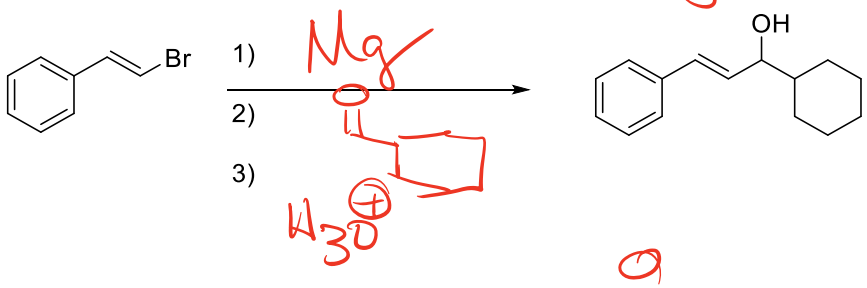
R

14) For each of the following, provide the product or reagent as necessary (**24 Points**)

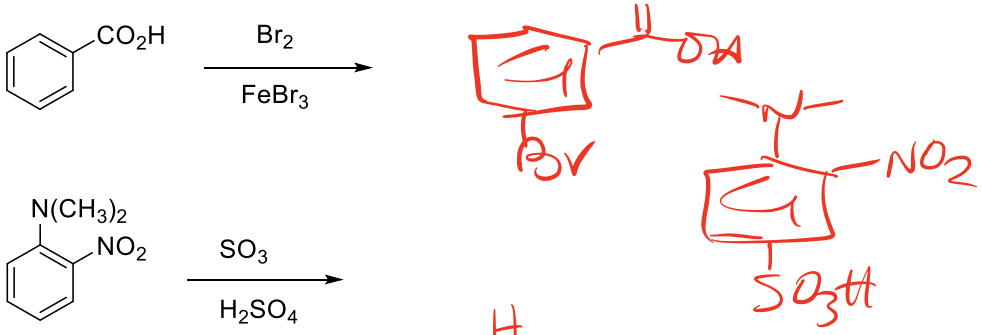
a)



b)

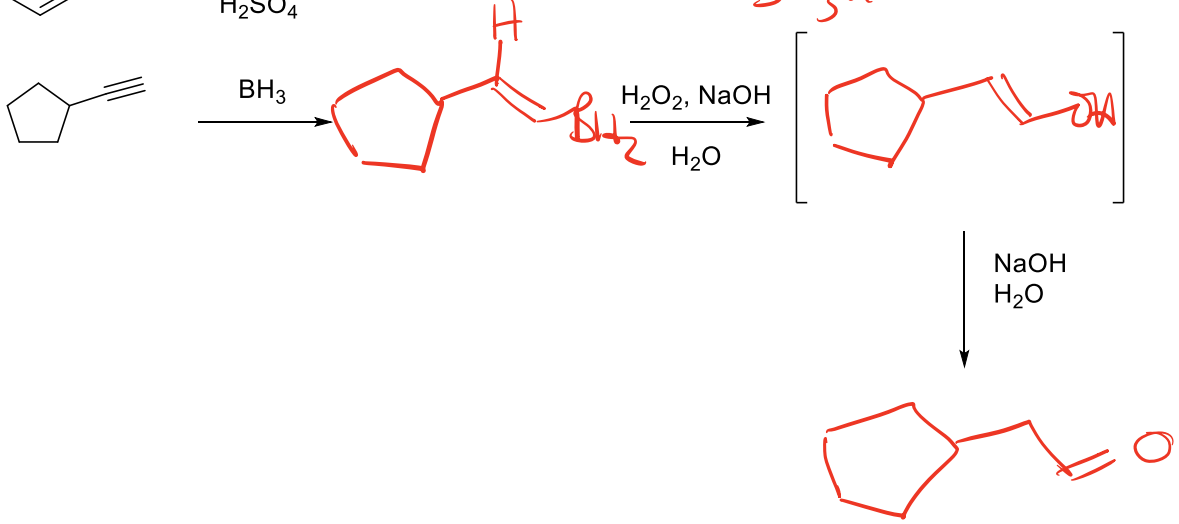


c)

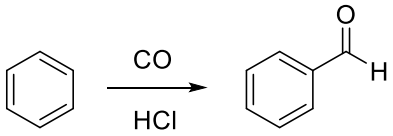


d)

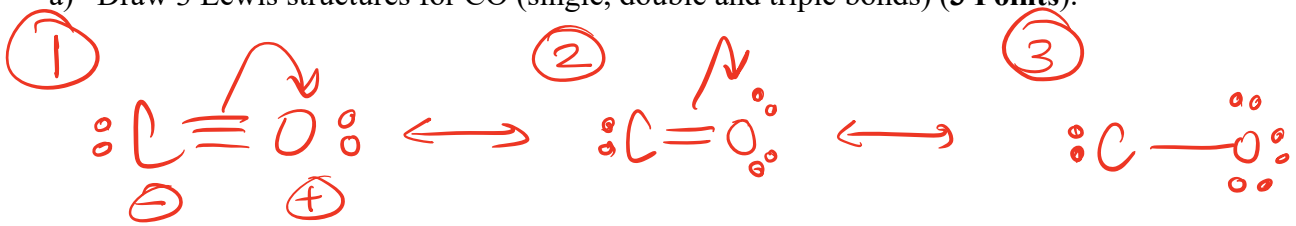
e)



15) The Gatterman-Koch reaction can be used to make aromatic aldehydes.



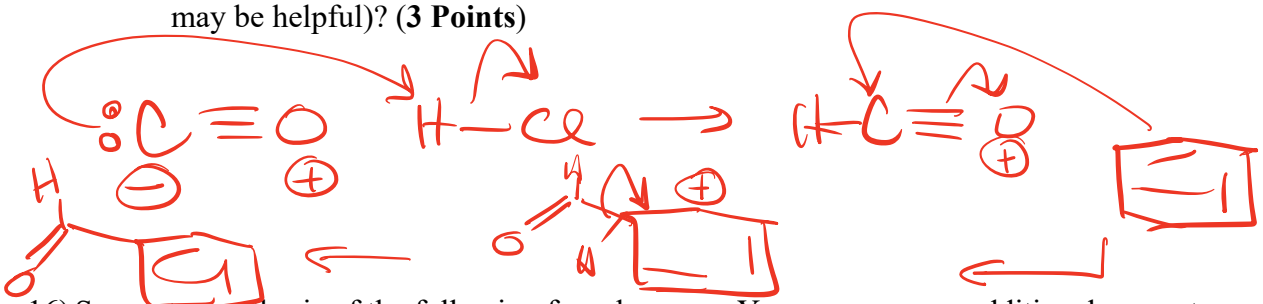
a) Draw 3 Lewis structures for CO (single, double and triple bonds) (**3 Points**).



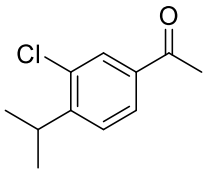
b) Rank the structures in part a in order of increasing "quality" and briefly justify your choice. (**3 Points**)

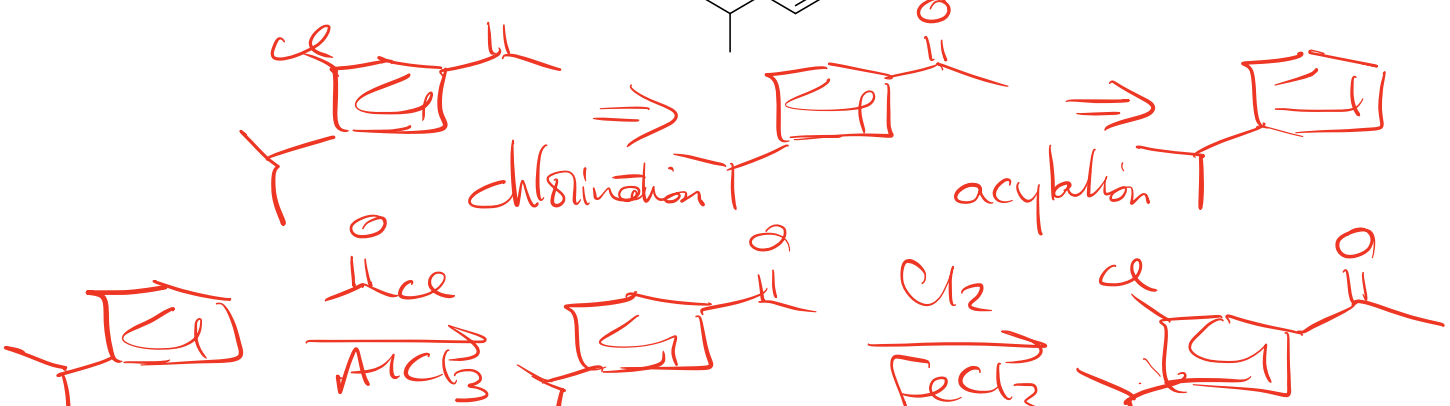
① — full octets on both atoms.
② — octet only on O; C miss 2e.
③ — octet only on O; C miss 4e.

c) What is the mechanism of the Gatterman-Koch reaction (your answers to parts a and b may be helpful)? (**3 Points**)

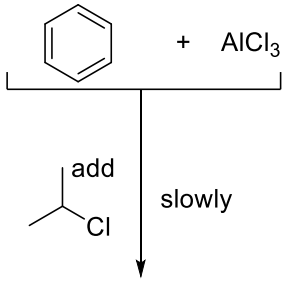


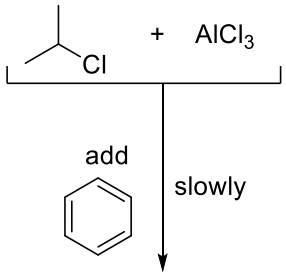
16) Suggest a synthesis of the following from benzene. You may use any additional reagents as necessary. Be sure to include a retrosynthesis. (**6 points retrosynthesis, 8 points synthesis**)





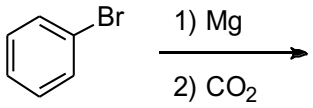
17) During a Friedel-Crafts alkylation, the order in which the reagents are mixed is important. Generally, these reactions are done by slowly adding the alkylating agent to the aromatic component. What is the advantage of mixing the ingredients in this order rather than slowly adding the aromatic component to the alkylating agent? (**4 Points**)





Adding the aromatic component to the alkylating agent is likely to result in multiply-alkylated products. Since an alkyl group is electron-donating, the aromatic ring becomes increasingly reactive upon alkylation. Therefore it is desirable to keep the concentration of the starting aromatic high from the beginning of the reaction.

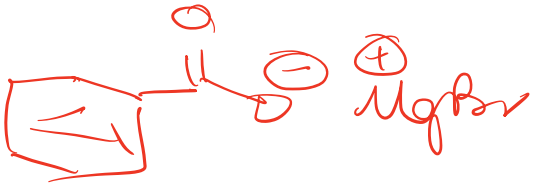
18) In one of your experiments, you used a Grignard reaction to make a carboxylic acid.



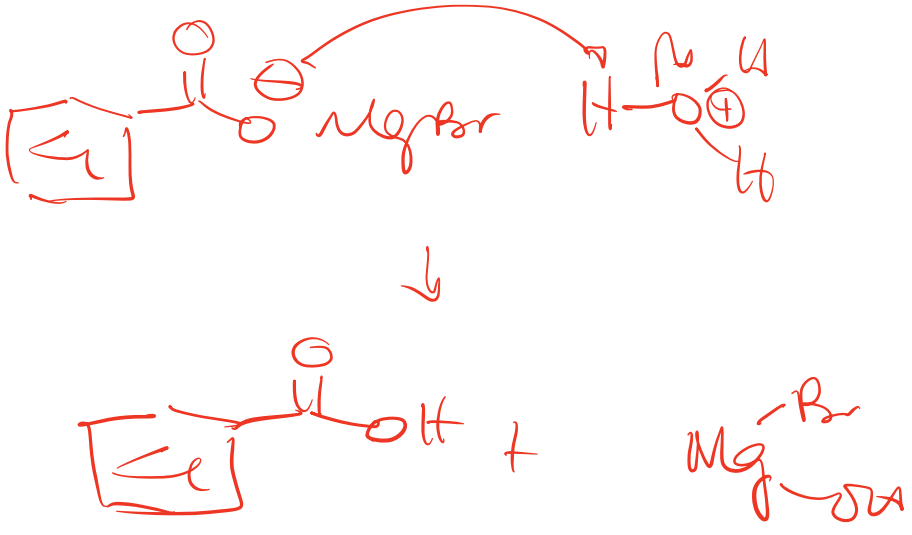
As part of this experiment, the following procedures were given:

1. When the Grignard reaction begins to slow down, place 10 g of crushed dry ice in a 150 mL beaker. Do not take time to weigh the dry ice. Use approximately the amount in the beaker indicated by your instructor. The CO_2 is in large excess and will not affect your calculation of percent yield of benzoic acid product. Cover the beaker with a watch glass.
2. When most of the magnesium has reacted and the ether boiling subsides, quickly pour the contents of the tube into the beaker containing dry ice.
3. Add a few milliliters of ether to the test tube and swirl to rinse. Add the rinse liquid to the beaker.
4. Cover the beaker with the watch glass and allow it to stand until the next lab period. During the interim, the excess dry ice will have sublimed.
5. Hydrolyze the Grignard addition product by slowing adding 30 mL of 6M HCl to the beaker with the sublimed dry ice and reaction mixture. Stir the mixture with a glass stirring rod. If there is excess magnesium present, it will react with the HCl to evolve hydrogen gas.
6. Add 30 mL of tert-butyl methyl ether (TBME) to the beaker. Stir the mixture. There should now be two distinct liquid layers.

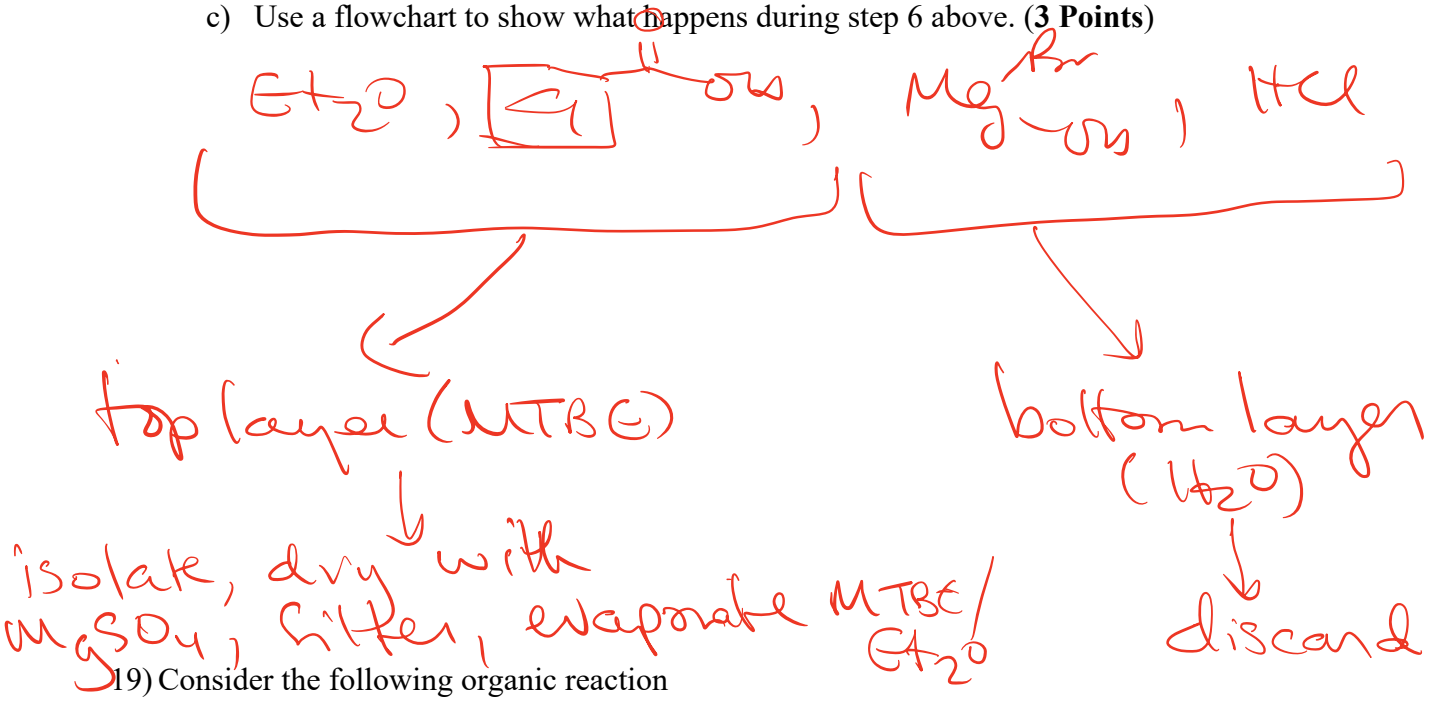
a) What is the structure of the organic compound present in the beaker at the end of step 4? (**2 Points**)



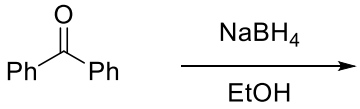
b) What happens when the 6M HCl is added in step 5? (give a mechanism) (**4 Points**)



c) Use a flowchart to show what happens during step 6 above. (**3 Points**)

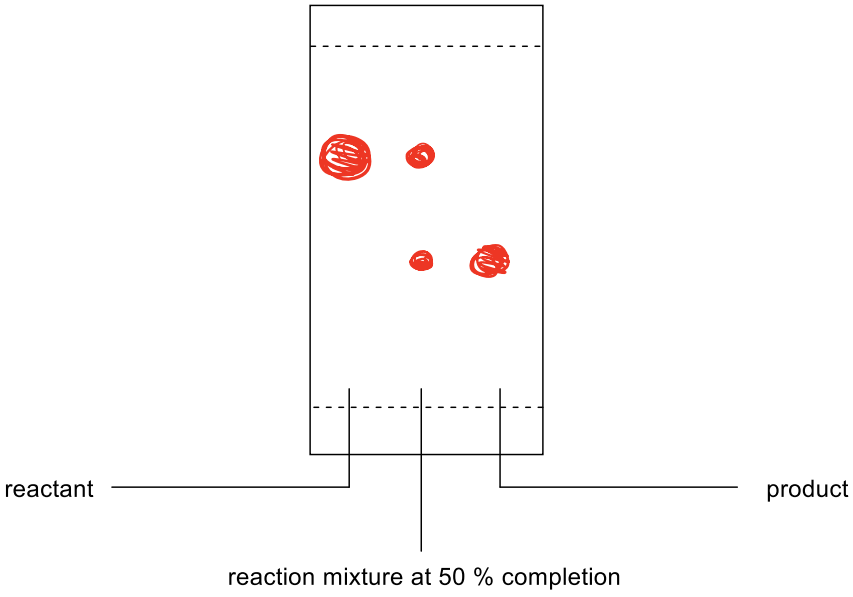


19) Consider the following organic reaction

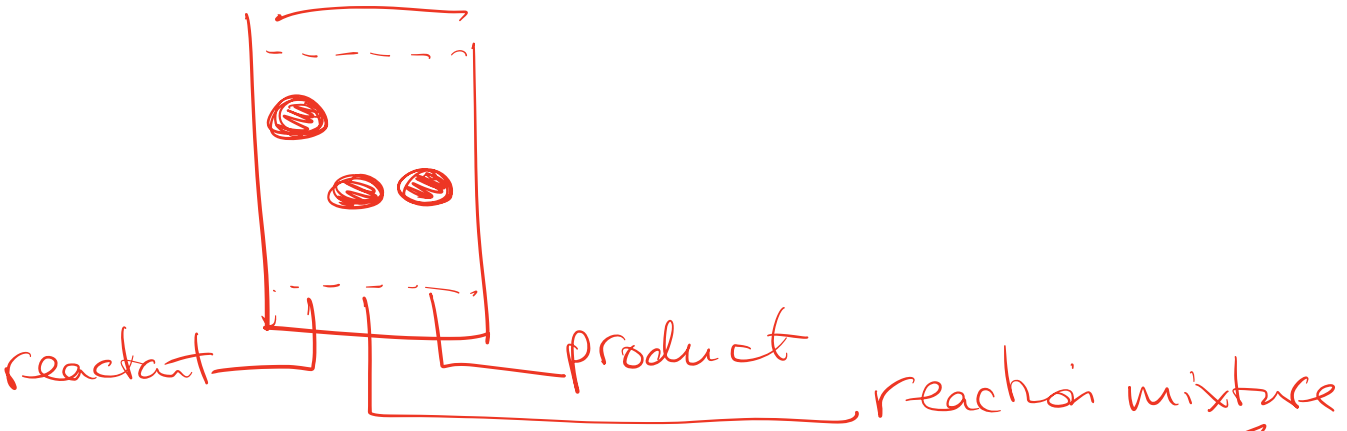


a) Draw the product of the reaction (**2 points**)

b) Draw the TLC plate that you would expect to see when the reaction is 50 % complete (**3 Points**).

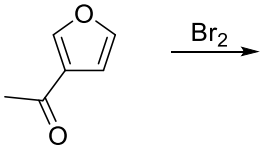


c) Draw the TLC when the reaction is 100 % complete (**1 point**)

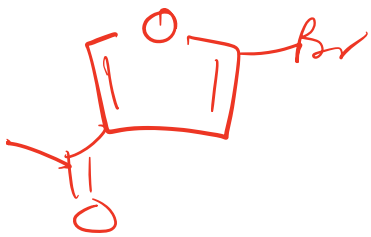


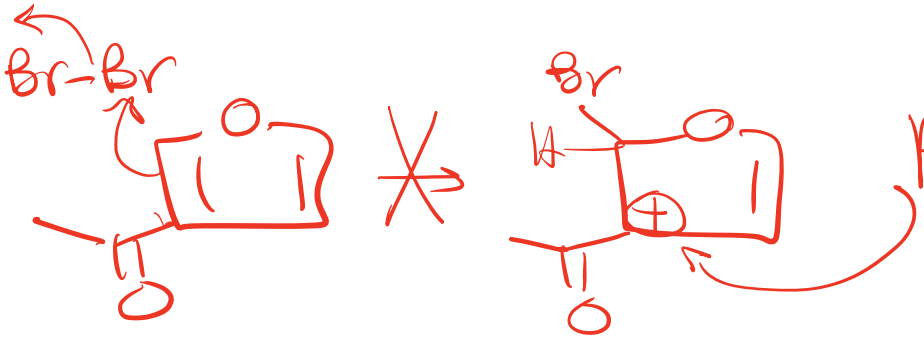
20) Draw an apparatus for a fractional distillation and label the parts (**9 Points**)

21) Bonus! Predict the product of the following reaction and justify your choice (**3 Points**)



Substitution is preferred on C adjacent to O, but not on same side as EWG!





positive charge on C that has EWG!