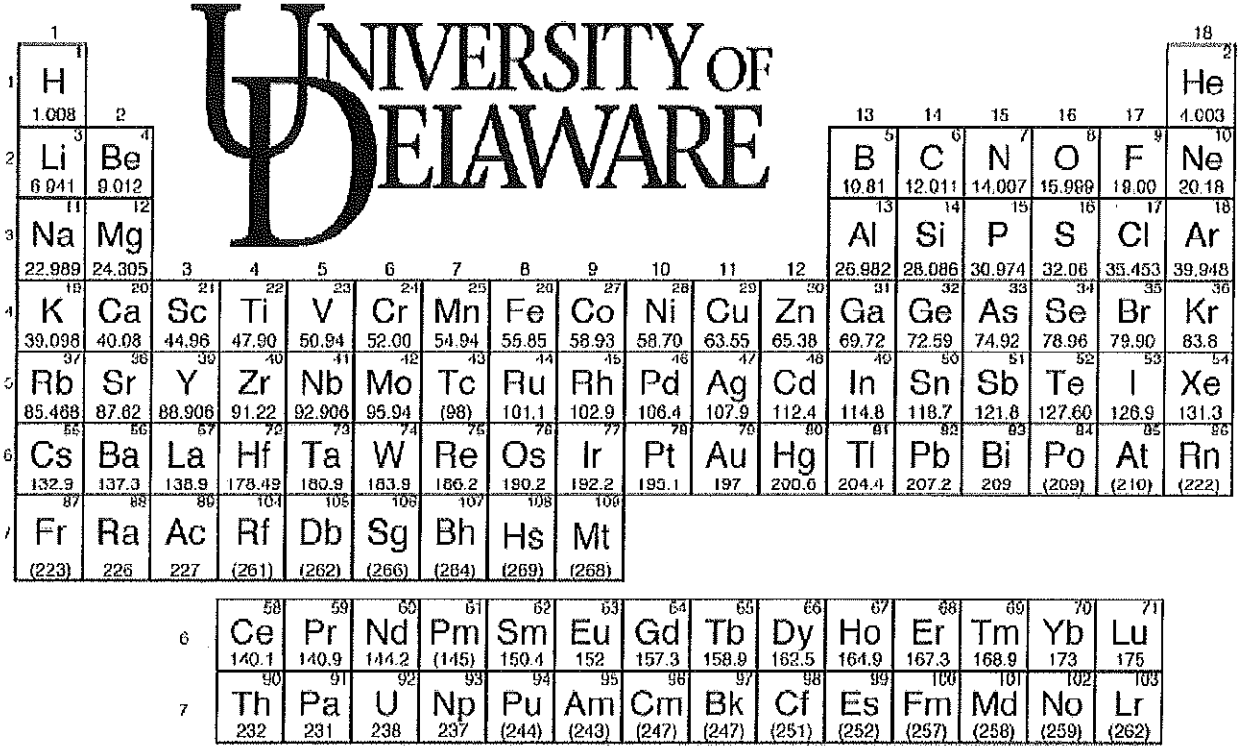
Name: Key Th

(Print your name clearly!)

Sametz: CHEM 322 Spring 2012

Organic Chemistry Exam 1

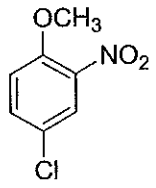
All answers should be written CLEARLY in the space provided. (If it's not clear, it's wrong).



You may raise your hand to ask a question if you are unsure what a question is asking of you.

1. Nomenclature (6 points)

a) Give a proper IUPAC name for the following compound:



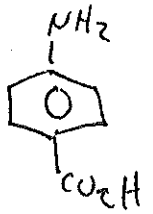
4-chloro-2-nitro anisole

1 (no o,p)

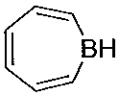
prefix 1

anisole 1

b) *para*-aminobenzoic acid (PABA) has been used in sunscreens because it absorbs ultraviolet light. Draw its structure.



2. (6 points) Indicate whether the following structures are aromatic, antiaromatic, or neither.

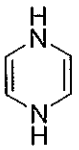


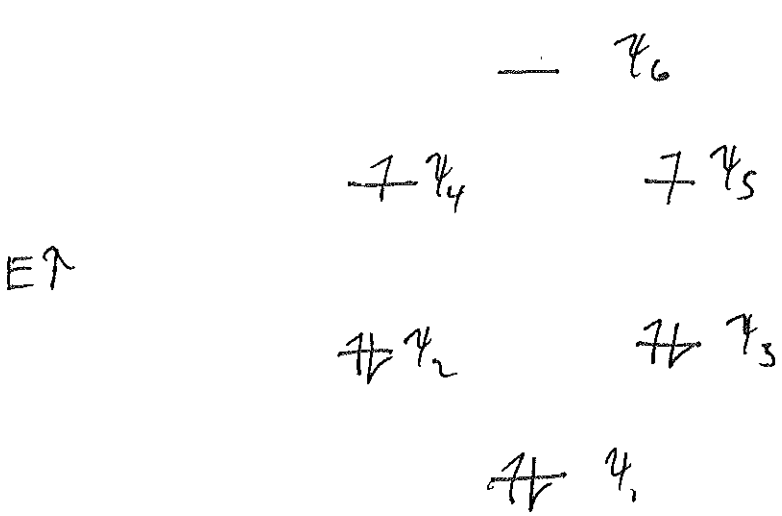
a

a

a

3. (6 points) Draw an orbital energy diagram (hint: you may use a Frost circle) to describe the molecular orbitals for dihydropyrazine (shown below). Place the π electrons into the correct orbital(s) to give the ground state electronic configuration. Use this diagram to explain whether the molecule would be aromatic or antiaromatic.





2 E levels

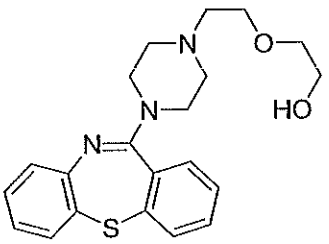
2 8 e⁻

1 E levels filled correctly

1 explain. (half-filled orbitals, "diradical" etc.)

anti-aromatic

4.Quetiapine, shown below, is an antipsychotic and antidepressive drug.

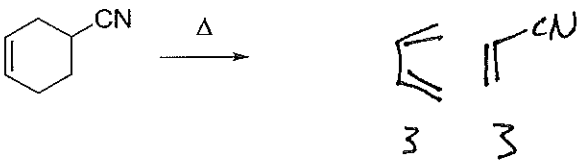


a) (4 points) Is the 7-membered ring aromatic, or antiaromatic? How many π electrons would be in this ring? 4q 8e⁻

b) (4 points) Based on your answer to a), would you expect the fused tricyclic ring system to be planar, or nonplanar? Why or why not?

nonplanar - break continuous p-orbital overlap to avoid antiaromaticity

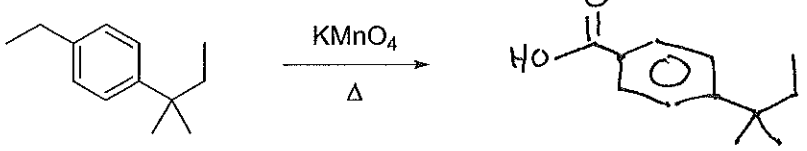
5. a) (6 points) The Diels-Alder reaction is reversible. Show the products of the following retro-Diels-Alder reaction.



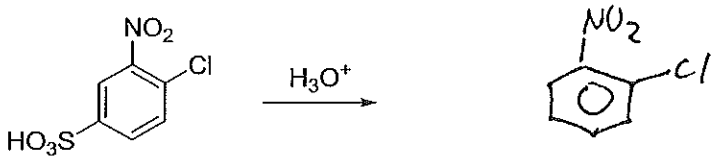
3 3

6. (30 points) Give the major organic product(s) for the following reactions.

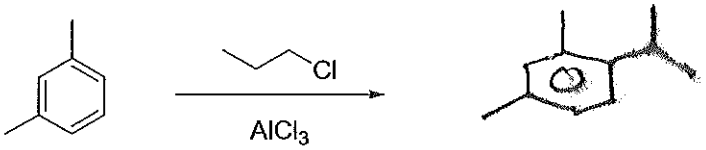
a)



b)

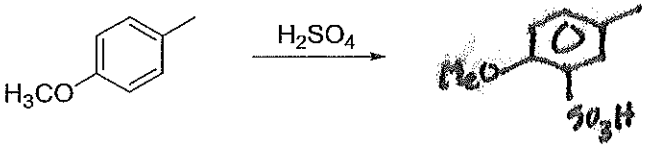


c)



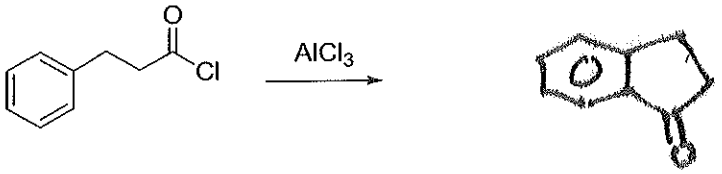
1 for n-Pr

d)



2 structure
1 regio

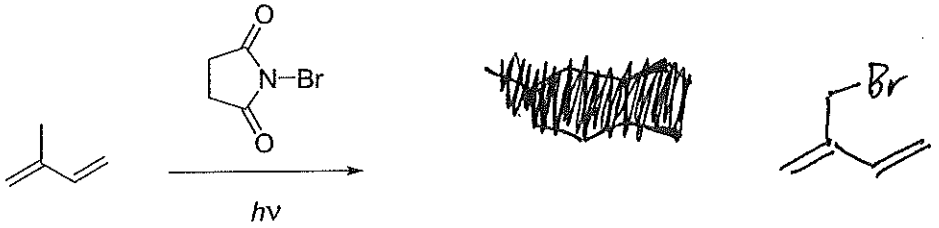
e)



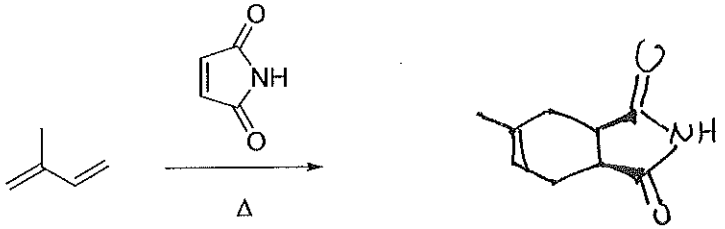
f)

Br
1

g)



h)

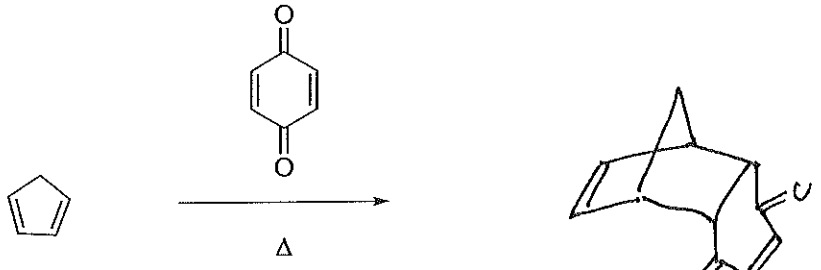


2 structure
1 stereo

i)

2 structure
1 regio

j)

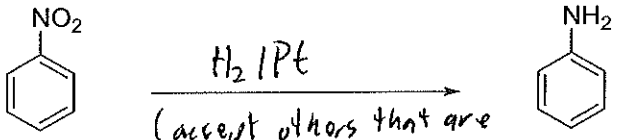


2 structure
1 clear endo

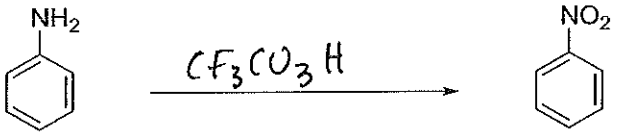
(if they react
2:1, OK as long
as one looks endo-.)

7. (18 points) Give reagents that will effect the following transformations.

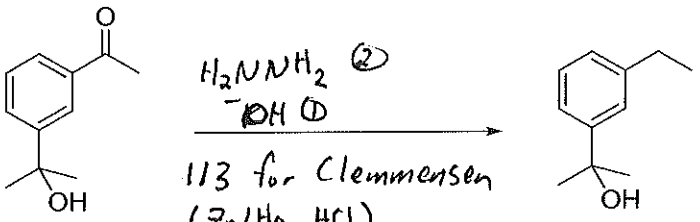
a)



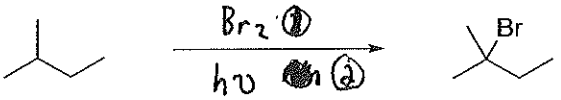
b)



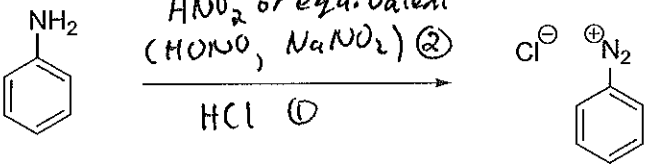
c)



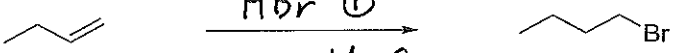
d)



e)



f)

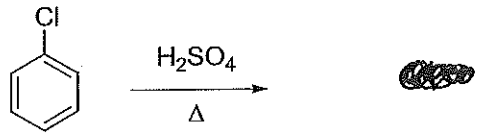


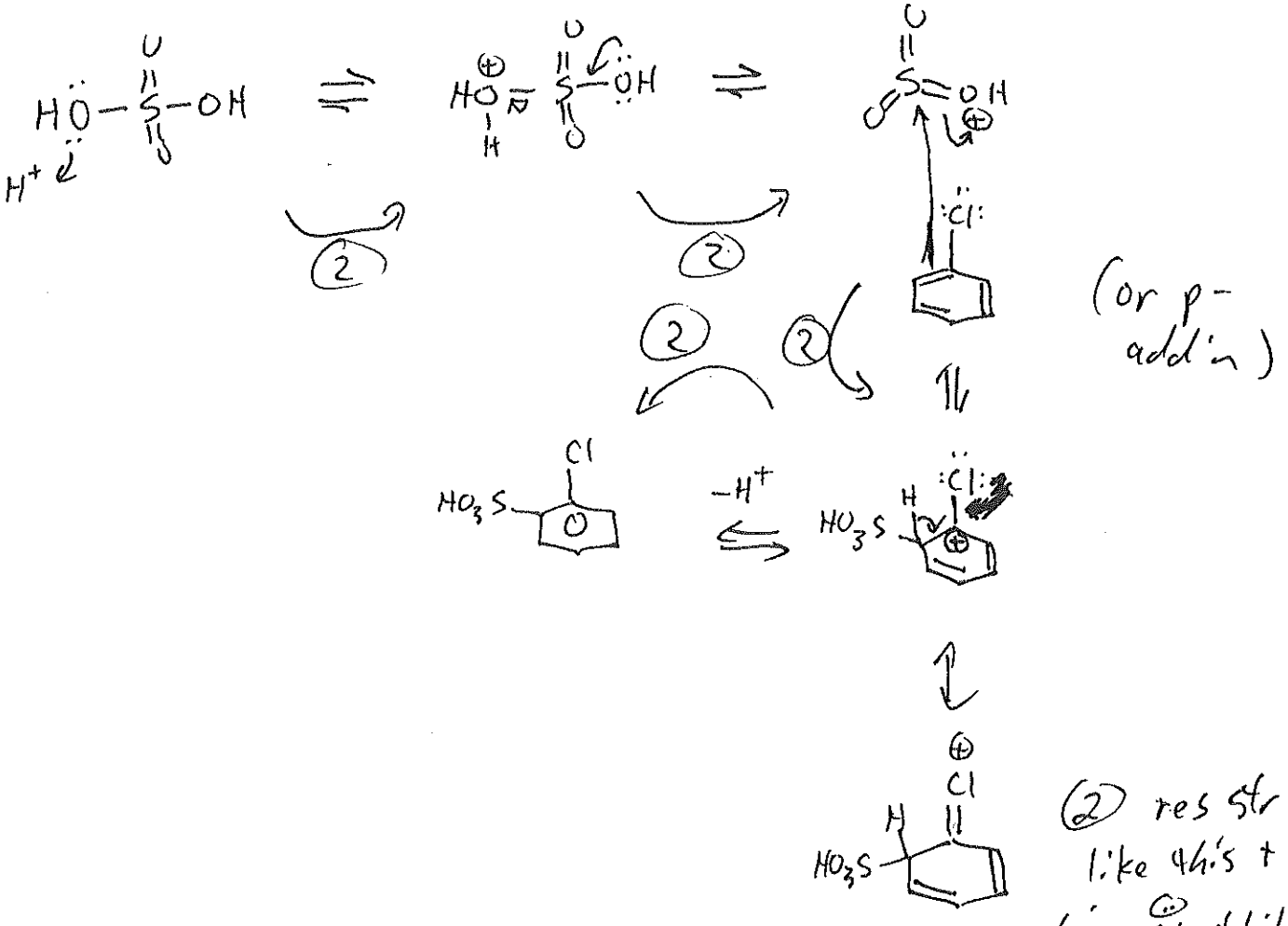
8. (13 points) a) Is chlorobenzene more reactive, or less reactive, than benzene to electrophilic aromatic substitution? Explain why. (2)

3 (1) less: (halogen EWG by induction)

b) Give the major product(s) for sulfonation of chlorobenzene, and show a complete reaction mechanism that accounts for formation of a major product (i.e. if there is only one major product, give the mechanism for its formation; if there is more than one, choose one to work with). Your mechanism must show formation of the electrophile as well as addition of the electrophile to the ring. Use the mechanism to explain the observed regioselectivity for the reaction.

10



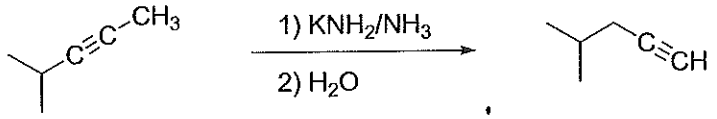


(2) res str like 4h's + explain Cl stabilizes adjacent ⊕ when o or p substitution

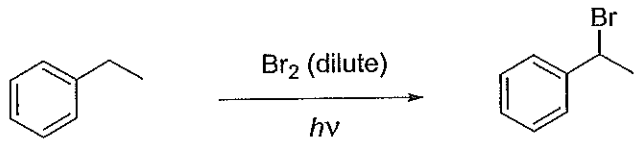
9. (8 points) Choose **ONE** of the following two reactions and give a complete reaction mechanism. It is best if you only show work on one. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

If you choose b), you must also show all resonance structures for the intermediate formed, and explain why, despite having an intermediate with multiple resonance structures, only one product is formed.

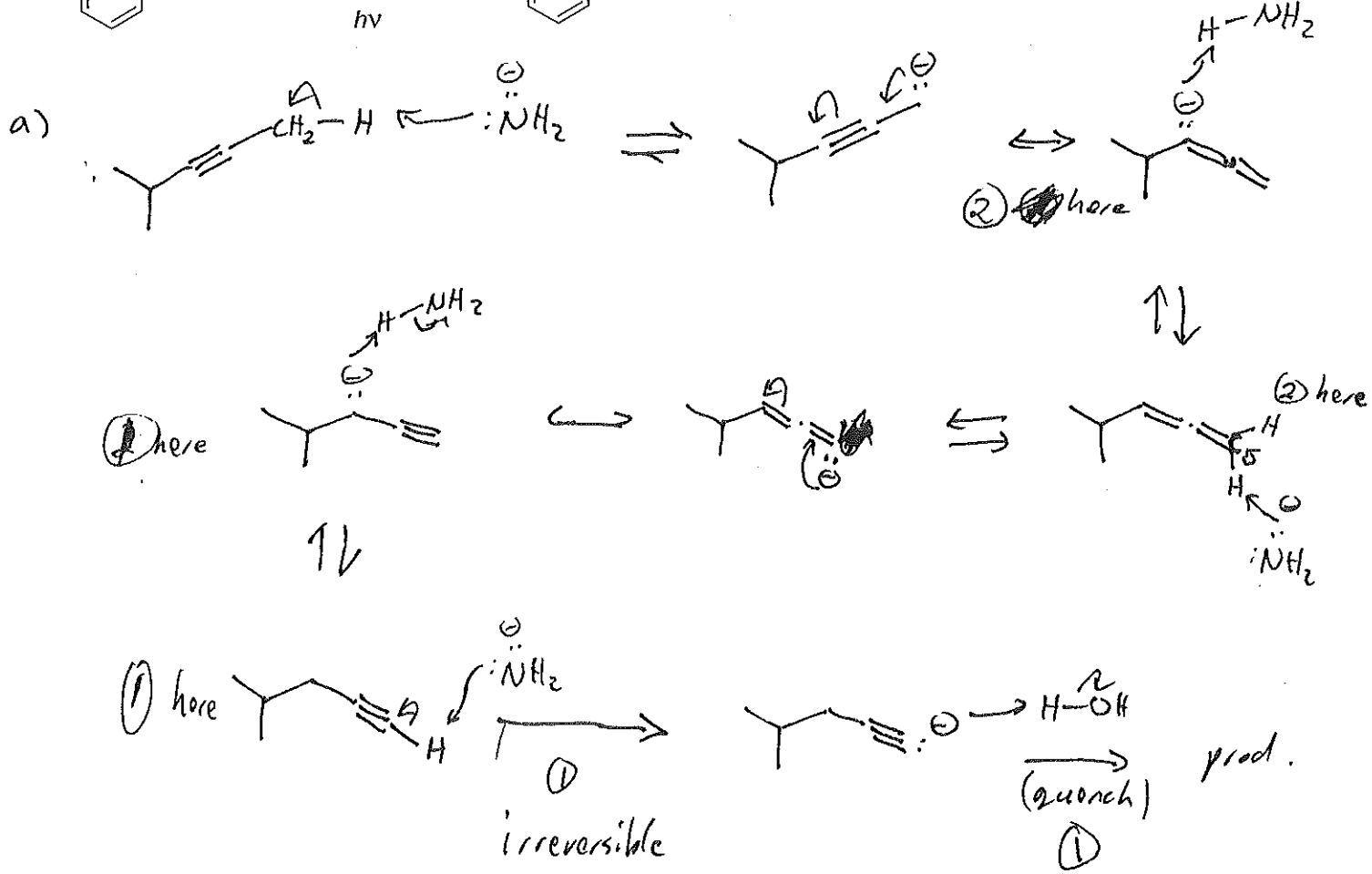
a)



b)

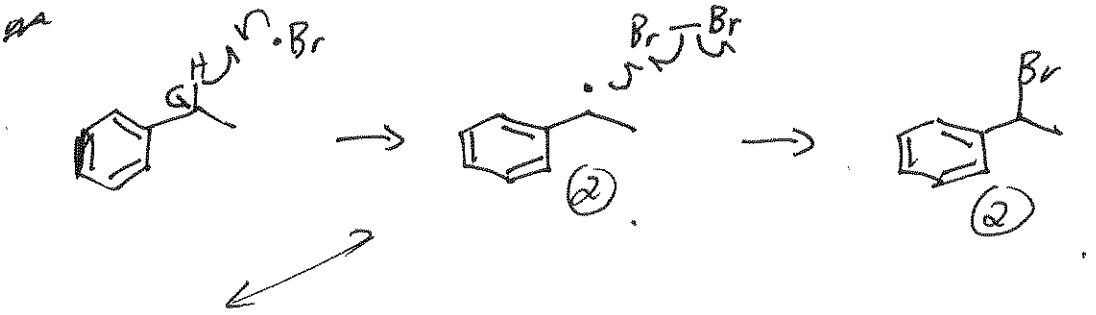


a)



(over for b))

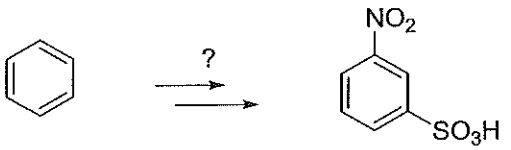
b) $Br_2 \xrightarrow{h\nu} 2\,Br\cdot$ (2)



if  or  , product isn't aromatic ∴ less stable. (2)

10. (8 points) Multistep synthesis Propose syntheses for the compounds on the right from the starting material on its left.

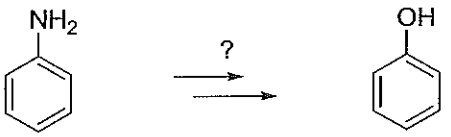
a)



HNO_3, H_2SO_4 → H_2SO_4, Δ or opposite order

(2) (2)

b)

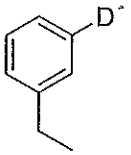


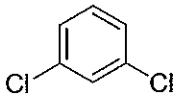
-1 if HNO_3 (3)

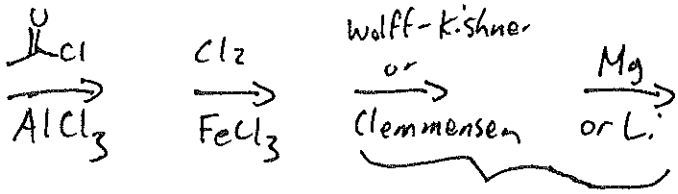
HNO_2 (2), HCl (or equivalent) (2)

CuO, H_2O (2)

11. (10 points) Multistep synthesis: choose **ONE** of the following two molecules, and show how it could be synthesized from benzene. Retrosynthetic analysis can be worth partial credit, but for full credit write the sequence of reactions in the forward direction. Again, if you work on more than one, **CLEARLY** indicate which you want graded for credit, or the grader chooses for you.





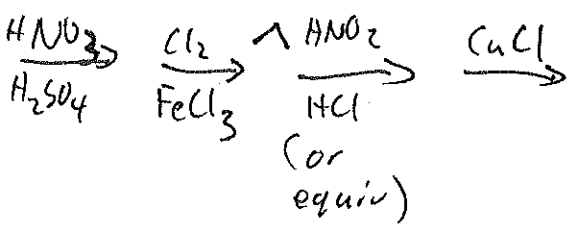


2 eq.

note: some students have not seen Grignard add'n to ketone yet. If they reduce after Grignard give credit but point out ↻

(-4) if their sequence would give wrong regio

oops, insert this in sequence!



2 eq.