CHEM 3331 (Richardson) Midterm Exam 1 – Sep. 20, 2022

Your Name: Key

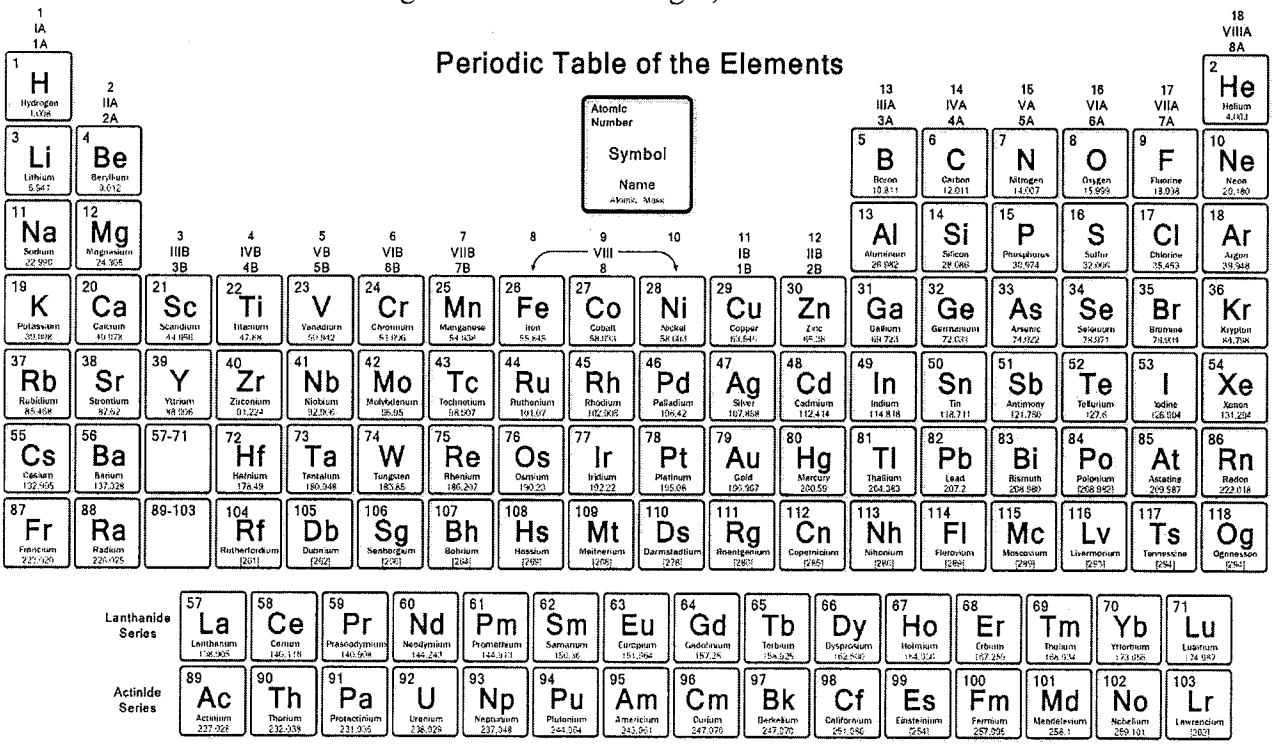
Student ID: _____

Recitation (fill in one circle):

O 134 (Wed 12:20 w/ Will)
O 135 (Wed 1:25 w/ Will)
O 136 (Wed 2:30 w/ Will)
O 137 (Wed 3:35 w/ Will)
O 142 (Thu 10:10 w/ Ethan)
O 143 (Thu 11:15 w/ Ethan)
O 144 (Thu 12:20 w/ Ethan)
O 147 (Thu 3:35 w/ Hongxuan)

Question	Score	Out of
1		15
2		10
3		30
4		15
5		10
6		20
7		10 e.c.
Total		100

This is a closed-book exam. The use of notes, calculators, or cell phones will not be allowed during the exam. You may use models sets brought in a clear bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified, you will lose points. For mechanisms, show all intermediates including correct formal charges, but do not show transition states.

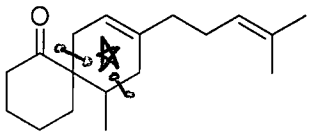


pKa Values

HI	-10	CH_3COOH	4.7	ArOH	10	HC≡CH	26
HBr	-8	HN_3	4.7	RSH	10-12	H_2	35
HCl	-6	H_2S	7.0	H_2O	15.7	NH_3	36
H_3O^+	-1.7	NH_4^+	9.3	ROH	16-18	$H_2C{=}CH_2$	45
HF	3.2	HCN	9.4	O=C-CH	9-25	CH_4	60

Avg: 59.5
Curve: 16
St. Dev: 24.8
Max: 108
Min: 10

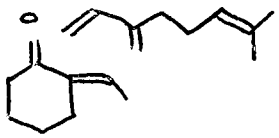
1) The molecule below was recently synthesized in one step via a Diels-Alder reaction, as a precursor to several *spiro* bicyclic compounds isolated from sea plants. (15 pts total)



a. Draw a star inside the ring which was formed during the Diels-Alder reaction. (3 pts)

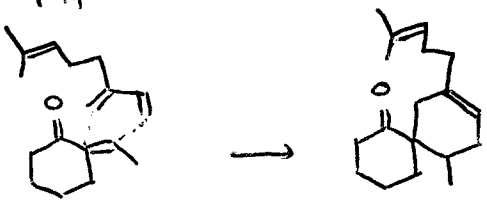
b. Draw the two disconnect lines (⟜) across the bonds that were formed during this reaction. (2 pts)

c. Draw the two molecules that reacted to form this product. (5 pts)



d. If they came together with a different orientation, these molecules could have reacted to form another product with slightly different connectivity. Draw this product. (5 pts)

Flip 1 molecule upside down:

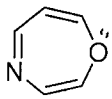


2) Describe each of the structures below as aromatic, nonaromatic, or antiaromatic. Assume each structure is planar. (10 pts)

Cyclic, planar, every atom in π, 4 e⁻ = antiaromatic

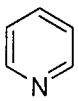
Cyclic, Planar, Every atom in π system, 6 e⁻ = aromatic

Cyclic, planar, not every atom in π = nonaromatic



* If you include 1 LP from O: Every atom in π system & 8 π e⁻ = antiaromatic

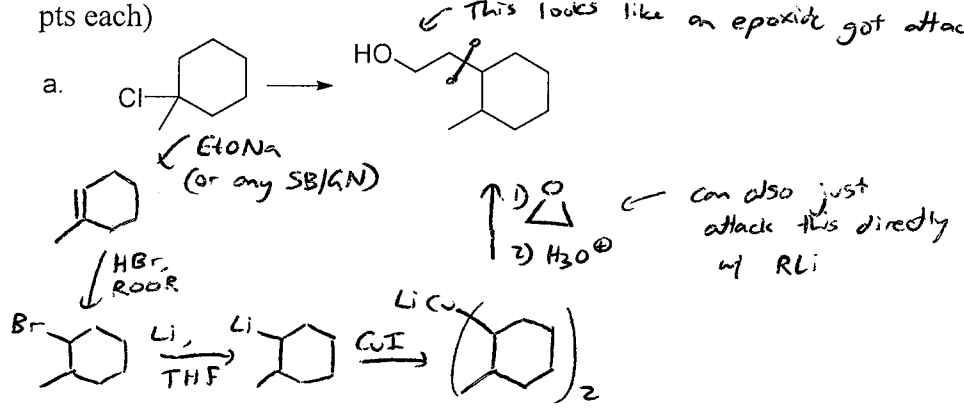
* If you don't include LP on O: not every atom in π system = nonaromatic



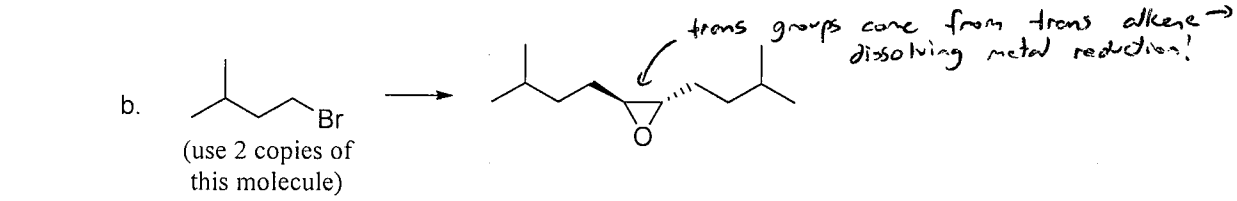
Can't include LP on N, due to it already being in a π bond. Every atom in π system & 6 π e⁻ = aromatic.

3) Find a way to synthesize the desired product from the given starting material. If more than one step is necessary, show the product of each step. Do not show mechanisms. (30 pts - 10 pts each)

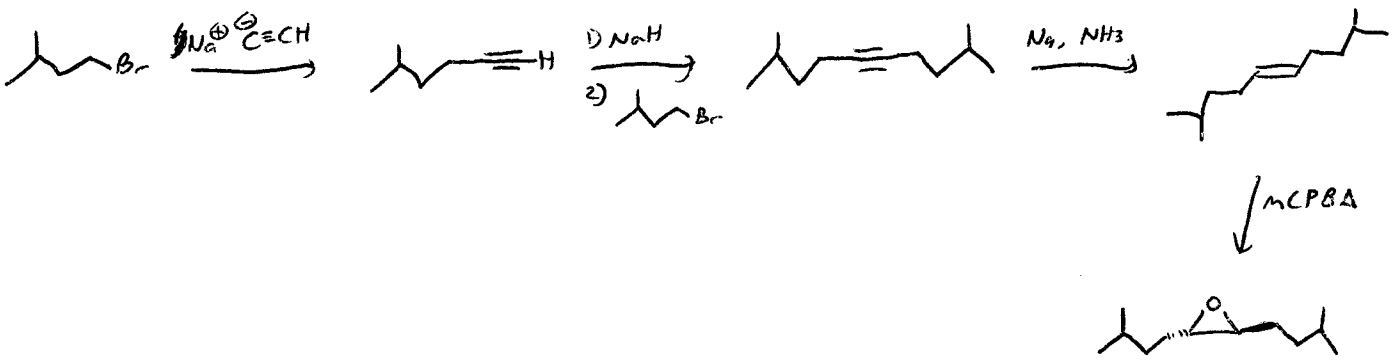
a.



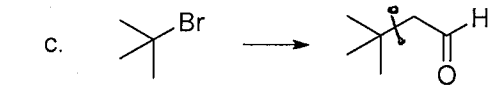
b.

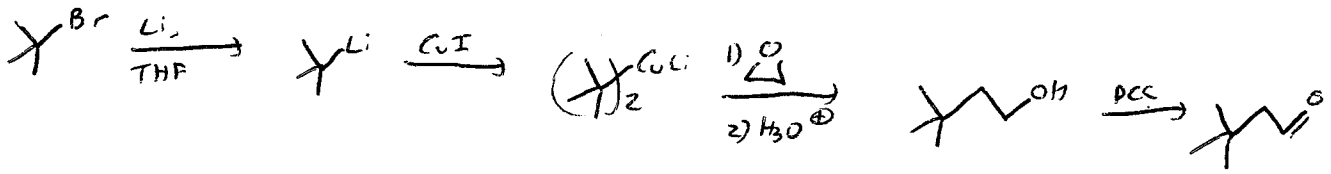


(use 2 copies of this molecule)



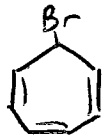
c.





4) Most alkyl bromides are water-insoluble liquids. But when 7-bromo-1,3,5-cycloheptatriene was first isolated, its high melting point of 203 °C and its water solubility led its discoverers to comment that it behaves more like a salt. (15 pts total)

a. Draw this structure, based on its name. (2 pts)



b. Draw the mechanism for bromine detaching from the molecule to create two ions. (3 pts)

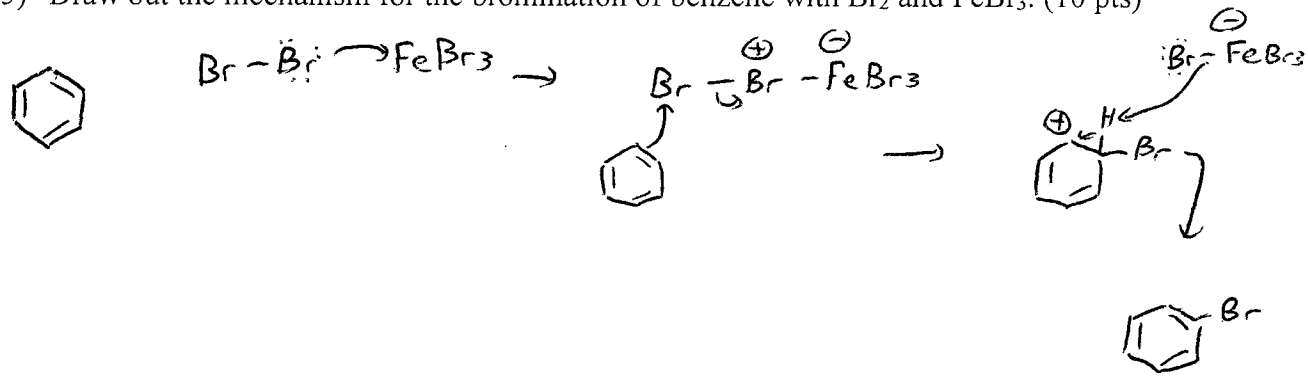
c. One of these ions is unusually stable. Explain why in under thirty words. (5 pts)

The ring is aromatic! Cyclic, assume planar, every atom in π system, and 6π electrons.

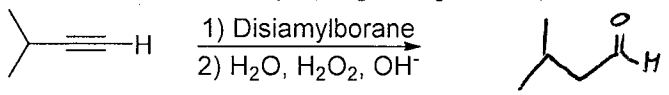
d. Explain why this molecule behaves like a salt, in under thirty words. (5 pts)

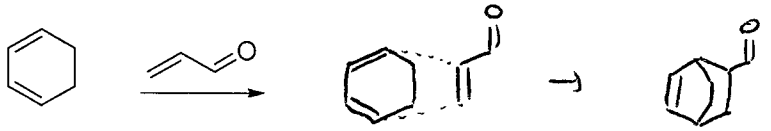
There is a large increase in stability when the ring becomes aromatic, so the compound favors splitting into two ions.

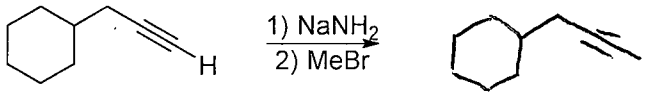
5) Draw out the mechanism for the bromination of benzene with Br_2 and $FeBr_3$. (10 pts)

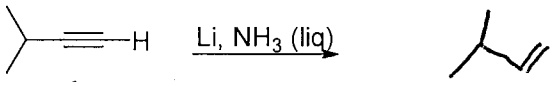


6) Predict the major product of the following reactions. If no reaction occurs, then write NR. Do not show stereochemistry. (20 pts; 4 pts each)

a. 

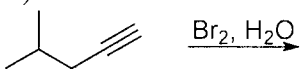
b. 

c. 

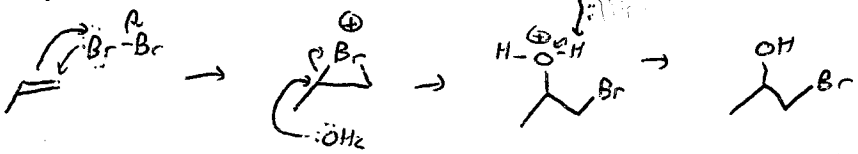
d. 

e. 

7) Extra credit! This reaction forms a molecule with a carbonyl in it. Based on what you know of alkyne and alkene reactions, draw the product of this reaction and the mechanism for how it forms. (10 pts extra credit)



Alkenes do halohydrin rxn:



Alkynes do the same thing...