CHEM 3331 (Richardson) First Hour Exam – September 20, 2016

Your Name _____

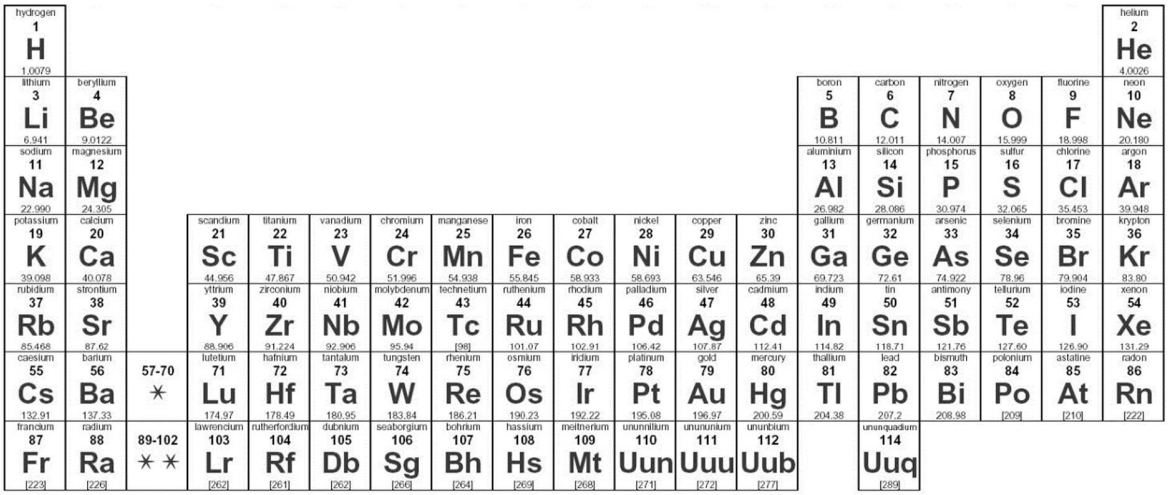
Student ID _____

Recitation (check one)

- O 1:00 Monday w/ Thomas Carey
- O 2:00 Monday w/ Thomas Carey
- O 3:00 Monday w/ Matthew Farmer
- O 9:00 Tuesday w/ Ryan McCaffrey
- O 11:00 Tuesday w/ Ryan McCaffrey
- O 1:00 Tuesday w/ Ryan McCaffrey
- O 2:00 Tuesday w/ Patrick Nordeen
- O 3:00 Tuesday w/ Matthew Farmer

Question	Score	Out of
1		20
2		30
3		30
4		10
5		10
6		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 ziplock 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.

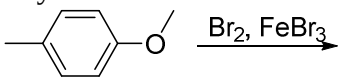


pKa Values

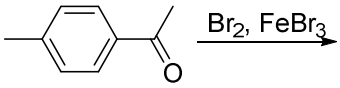
HI	-10	CH_3COOH	4.7	Phenol	10	H_2	35
HBr	-8	HN_3	4.7	RSH	10-12	NH_3	36
HCl	-6	H_2S	7.0	H_2O	15.7	$H_2C{=}CH_2$	45
H_3O^+	-1.7	NH_4^+	9.3	Alcohol (ROH)	16-18	CH_4	60
HF	3.2	HCN	9.4	HC≡CH	26		

 Name_____

1) The directing effects of groups during electrophilic aromatic substitution reactions can be explained by resonance. (20 pts; 10 pts each)
   a. The reaction below produces a single isomer as the major product. Show the mechanism for its formation, including all resonance forms for the intermediate. In thirty words or less, explain the regiochemistry of this reaction.

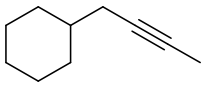


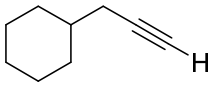
   b. The reaction below produces a single isomer as the major product. Show the mechanism for its formation, including all resonance forms for the intermediate. In thirty words or less, explain the regiochemistry of this reaction.

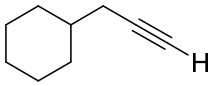


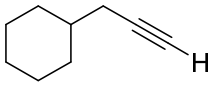
 Name_____

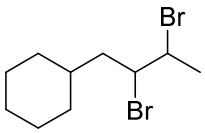
2) Predict the major product of the following reactions. If no reaction occurs, then write NR. Show stereochemistry where necessary – if a racemic mixture is formed, you can show only one product and write "racemic" or "rac". (30 pts; 3 pts each)

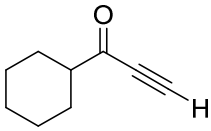
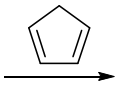
a.  $\xrightarrow{Li,\ NH_3\ (liq)}$

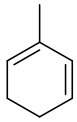
b.  $\xrightarrow{HBr\ (excess)}$

c.  $\xrightarrow[2)\ EtBr]{1)\ NaNH_2}$

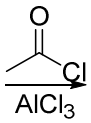
d.  $\xrightarrow[2)\ H_2O,\ H_2O_2,\ OH^-]{1)\ Disiamylborane}$

e.  $\xrightarrow{NaNH_2}$

f.  

g.  $\xrightarrow[\text{(Show both products)}]{HBr}$

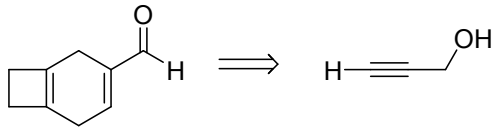
h.  $\xrightarrow[H_2SO_4]{HNO_3,}$

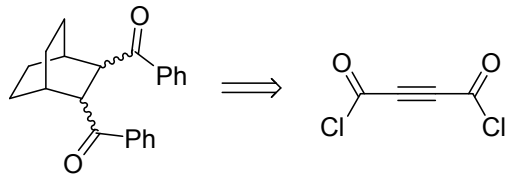
i.  

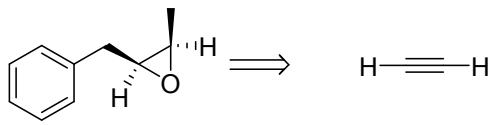
j.  $\xrightarrow[H_2SO_4]{iPrOH,}$

 Name_____

3) Find a way to synthesize the desired product from the given starting material. (Remember that the retrosynthesis arrow points from reactants to products! Also remember squiggly bonds mean that either bold or dashed bonds are okay.) If more than one step is necessary, show the product of each step. Do not show mechanisms. (30 pts; 10 pts each)

a. 

b. 

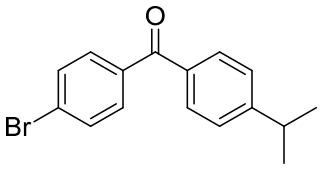
c. 

(racemic)

 Name_____

4) One of these reactions occurs much more rapidly than the other. Determine which reaction is faster and explain why in thirty words or less, plus whatever structures are necessary. (10 pts)

5) Show two ways this compound could be synthesized via a Friedel-Crafts reaction. Which of the two methods is likely to be a faster reaction? (10 pts)



6) Extra credit! Arrange each of the following groups of compounds in order of decreasing reactivity towards electrophilic aromatic substitution. Show the product(s) for each of them reacting with CH_3Cl and $AlCl_3$, or write NR if no reaction occurs. (10 pts e.c.)

1,3-dinitrobenzene, toluene, anisole, chlorobenzene, nitrobenzene