CHEMISTRY 112A FALL 2013

EXAM 1

OCTOBER 10, 2013

Answer Key

NAME- WRITE BIG ______________________________

STUDENT ID: ______________

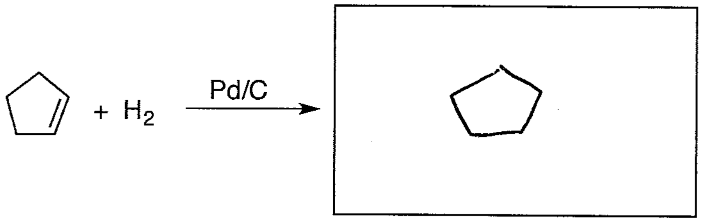
SECTION AND/OR TA IF YOU ARE IN THE LABORATORY COURSE: ________________

- **You will have 75 minutes in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **Molecular models may be used**

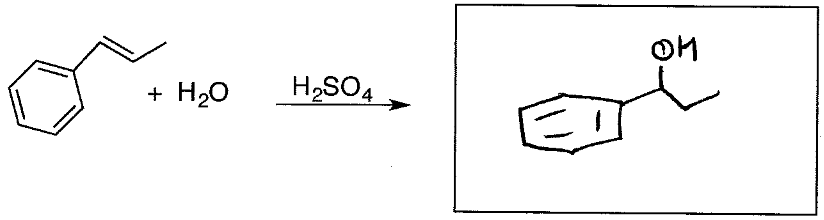
Problem	**Points (Maximum)**	**Points (Obtained)**
1	15	
2	10	
3	12	
4	10	
5	16	
6	11	
7	35	
8	16	
Total	***125***	

1. (15 points) Draw the major product of the following reactions.

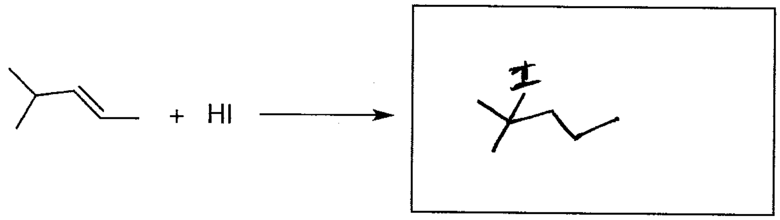
a.



b.

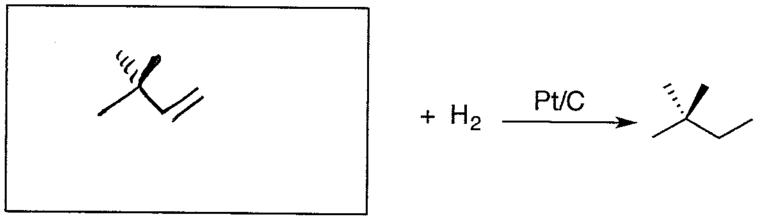


c.

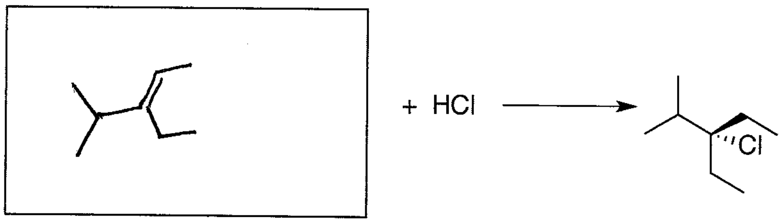


2. (10 points) Draw the structure of the alkene you should use as a reagent in the following reactions.

a.

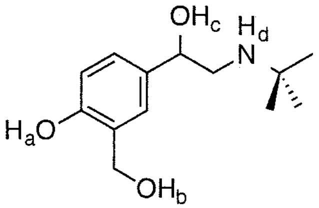


b.



3. (12 points) For the following molecules, identify the most acidic hydrogen. Explain your choice in 15 words or fewer.

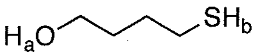
a. *Choose between hydrogens marked a-d.*



Most acidic hydrogen: Ha
Reason:

Resonance stabilized anion

b. *Choose between hydrogens marked a or b.*

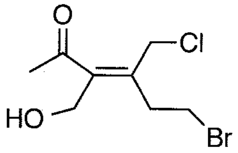


Most acidic hydrogen: Hb
Reason:

Acidity increases down periodic table because large anion is more stable. Polarizability increases down the periodic table.

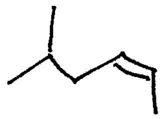
4. (10 points) Nomenclature questions:

a. Is the following molecule E or Z?

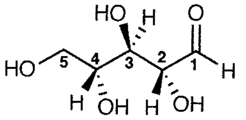


Z

b. Draw *cis*-5-methyl-2-hexene.

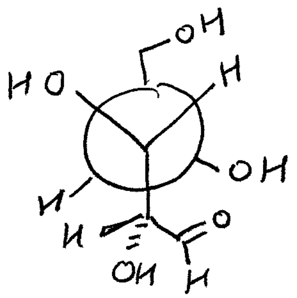


5. (16 points) The open chain form of D-ribose is shown below.

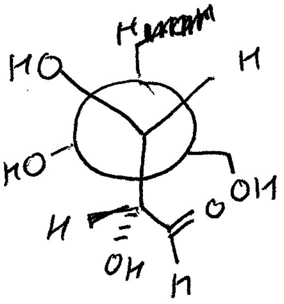


a. Draw the three staggered conformations of glucose looking down the C3-C4 bond.

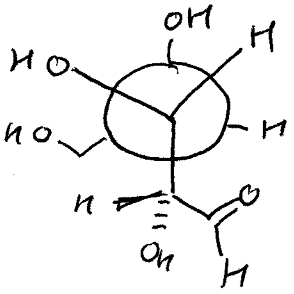
Staggered conformation 1



Staggered conformation 2



Staggered conformation 3

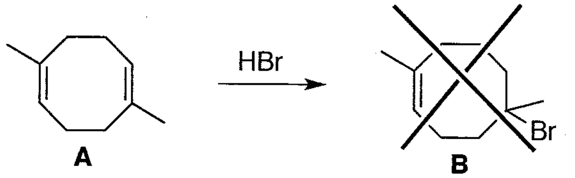


b. Which of the three structures you drew is the **most** stable? Explain your answer in 20 words or fewer.

Conformation 1:

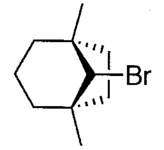
Fewest # of gauche interactions

6. (11 points) In an attempted hydrobromination of the substituted cyclooctadiene **A**, the expected addition product **B** was not isolated. Instead, **C** was obtained.



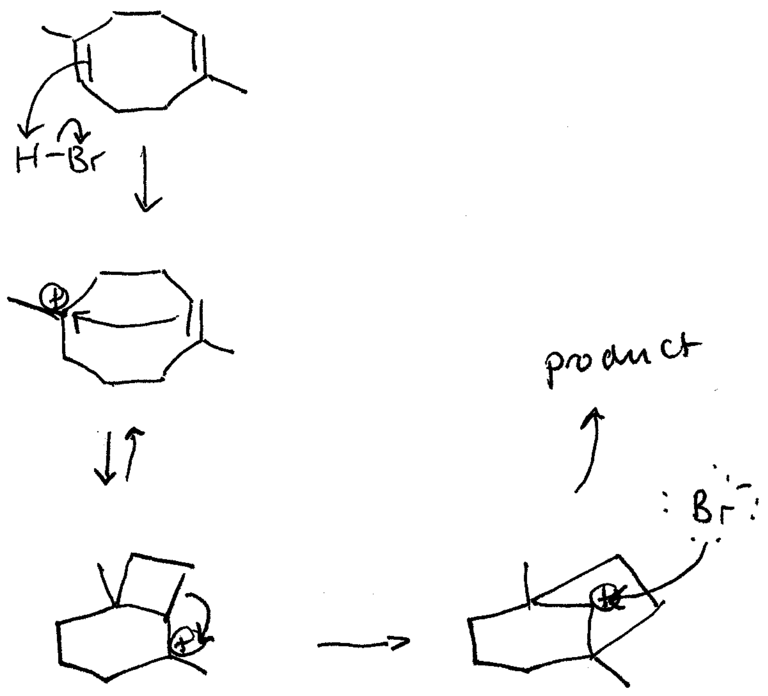
A

B
Not Observed

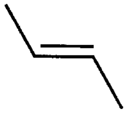
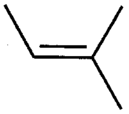


C
Observed product

Draw the mechanism for this reaction, using arrows to indicate the flow of electrons. Don't forget to draw all intermediates and indicate charge.



7. (35 points) The rate constants for acid-catalyzed hydration at 25°C is given for each alkene below.

k = 8×10^{-8} $M^{-1}s^{-1}$ 3×10^{-8} $M^{-1}s^{-1}$ 2×10^{-4} $M^{-1}s^{-1}$

a. (5 points) The rate constant k differs by approximately a factor of 10^4 between the hydration of *trans*-2-butene and 2-methyl-2-butene. Roughly, what is the difference in free energy of activation ($\Delta G^{\ddagger}$) for these two reactions at 25°C? Show your work. ($\ln 10 = 2.3$, $RT = 0.6$ kcal/mol)

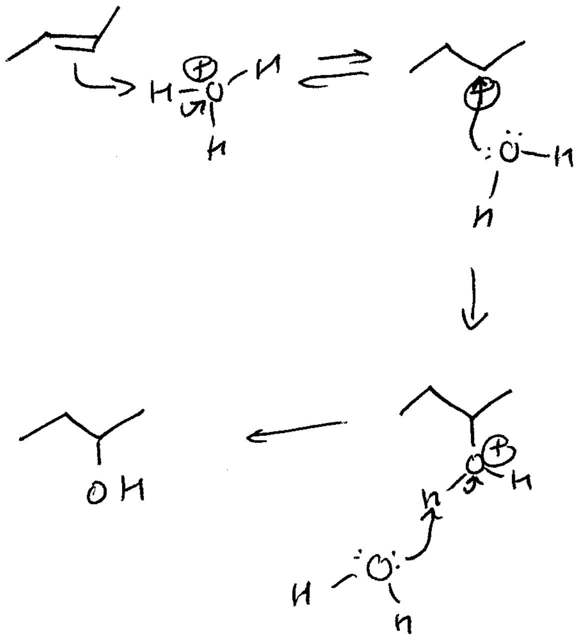
Factor of 10 in k is 1.4 kcal/mol

$10^4 \approx 5.6$ kcal/mol

or

$RT\ln 10^4 = \Delta G^{\ddagger} - \Delta G^{\ddagger}$

b. (10 points) Draw the mechanism of the aqueous acid-catalyzed hydration of *trans*-2-butene. Use arrows to show the flow of electrons. Don't forget to draw all intermediates and indicate charge.



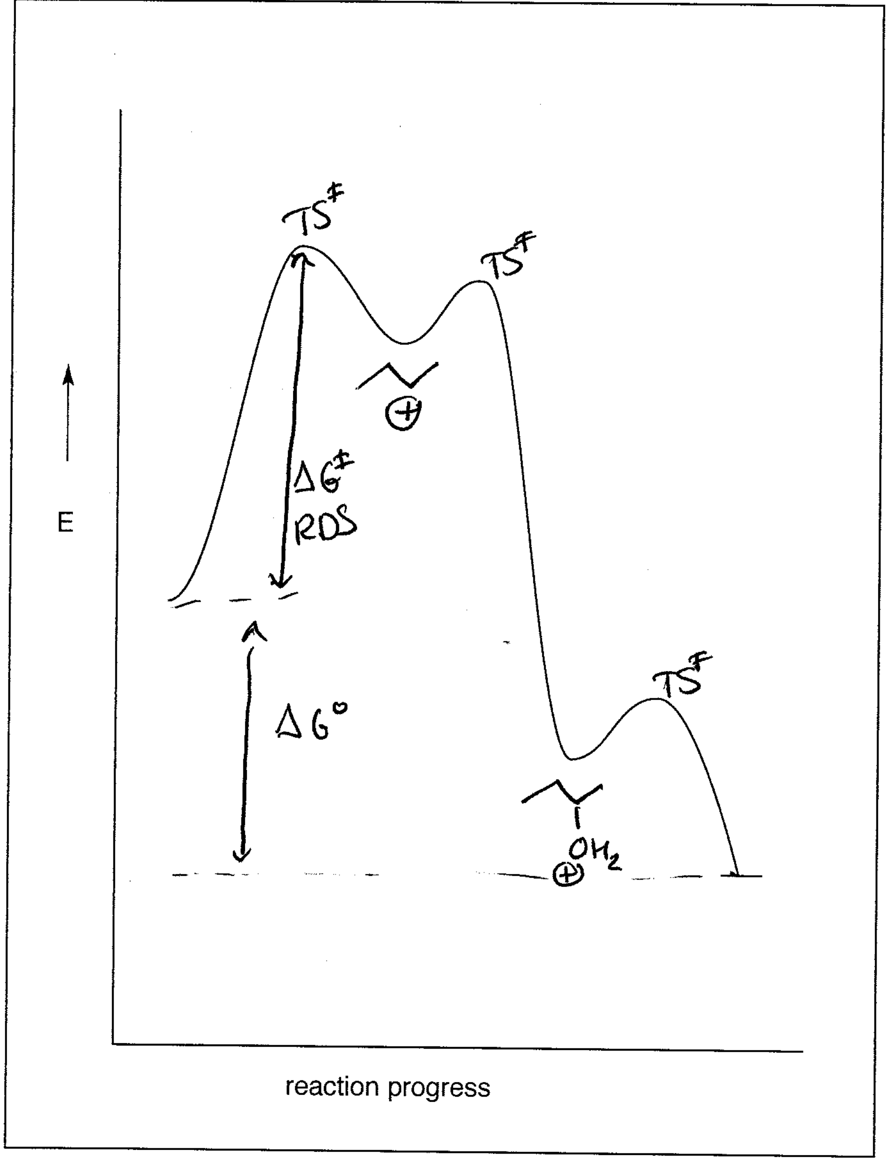
c. (5 points) Why does 2-methyl-2-butene react faster than *trans*-2-butene? (20 words or fewer)

The intermediate carbocation is more stable because it is more substituted.

Hammond postulate -
TS will be similar to carbocation

d. (8 points) Fill in the reaction energy diagram for the mechanism of the aqueous acid-catalyzed hydration of *trans*-2-butene that you drew in part b of this question. Label:

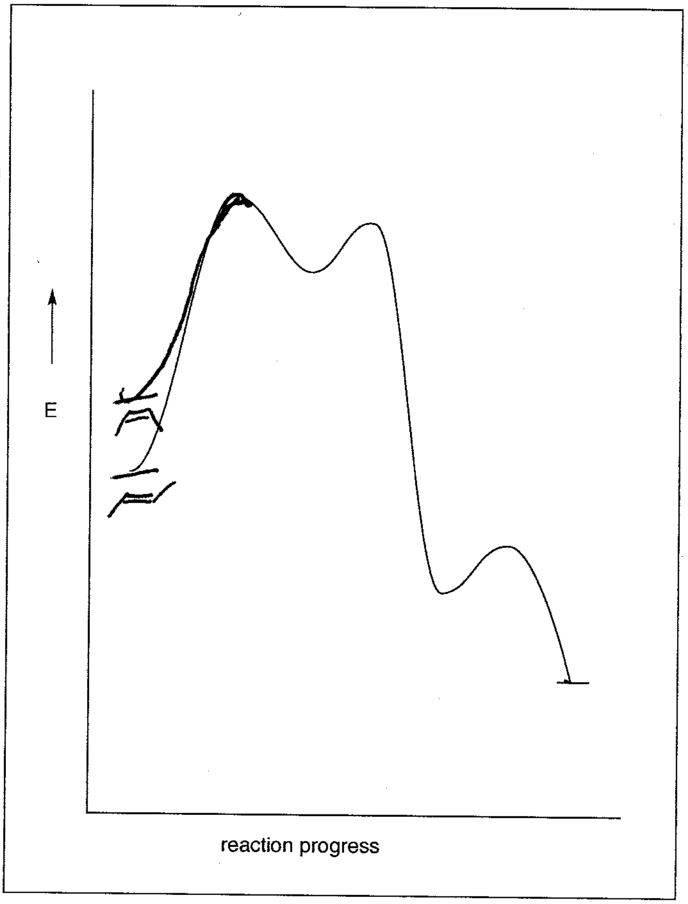
i. all intermediates with the structures from your mechanism in part b
ii. all transition states with TS‡
iii. the rate-determining step with RDS
iv. ΔG°
v. ΔG‡ of the rate-determining step



e. (7 points) Why does *cis*-2-butene react faster than *trans*-2-butene? In addition to your answer in words, **add** *cis*-2-butene to the reaction energy diagram for *trans*-2-butene on the right. This is an identical diagram as that drawn in part d.

Reason:

 is less stable than . Both form same carbocation. Therefore, ΔG‡ is smaller for  & rate is faster



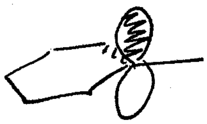
8. (16 points) Carbocations can react with a variety of different nucleophiles. For example, see the reaction below:

Circle:
[✓ Electrophile]
Nucleophile

Circle:
Electrophile
[✓ Nucleophile]

a. Circle the appropriate electrophile and nucleophile label for the two reagents in the above reaction.

b. Identify the orbital that is acting as the Lewis acid in this reaction. Label, identify, and draw a picture of this orbital that shows where the orbital is located in the molecule.



empty
p orbital
on C

c. Identify the orbital that is acting as the Lewis base in this reaction. Label, identify, and draw a picture of this orbital that shows where the orbital is located in the molecule.

lone pair on N
sp hybridized