CHEMISTRY 3A SPRING 2013

EXAM 2

Answer Key.

APRIL 4, 2013

NAME _____

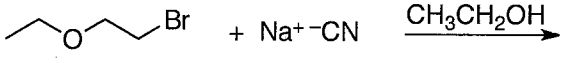
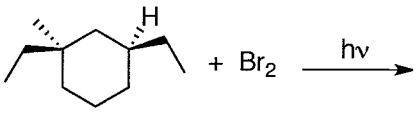
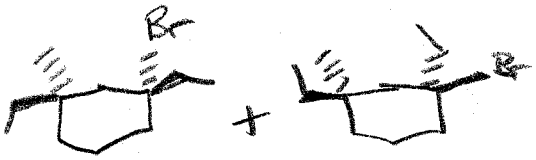
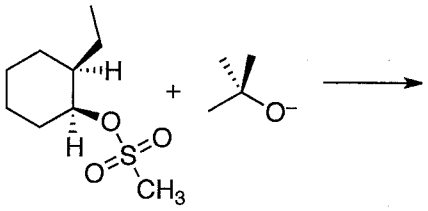
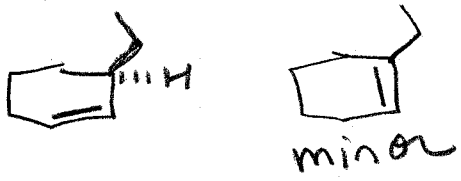
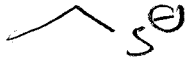
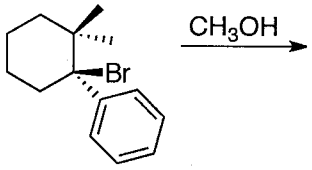
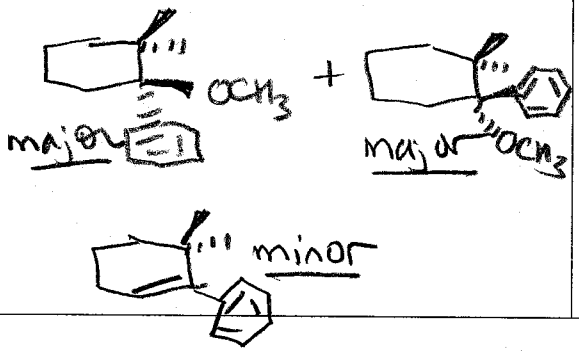
SECTION AND/OR TA IF YOU ARE IN THE LABORATORY COURSE: _____

STUDENT ID: _____

- **You will have 2 hours in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **Molecular models may be used**

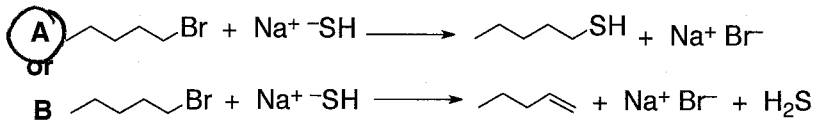
Page	Points (Maximum)	Points (Obtained)
2	30	
3	28	
4	44	
5	20	
6	25	
7	18	
8	22	
9	13	
Total	*200*	

1. (30 points) For each reaction:
   (i) Draw the major and minor organic products. Write NR if you think there will be no reaction.
   (ii) Label each product you draw as major or minor.
   (iii) Indicate the stereochemistry of the products.
   (iv) Identify the type of mechanism(s): S_N2, S_N1, E1, E2, radical halogenation, or Brønsted acid/base.

	Product(s)	Mechanism Type
a. 		SN2
b. 		radical halogenation
c. 		E2
d.		Acid/ Base
e. 		SN1 E1

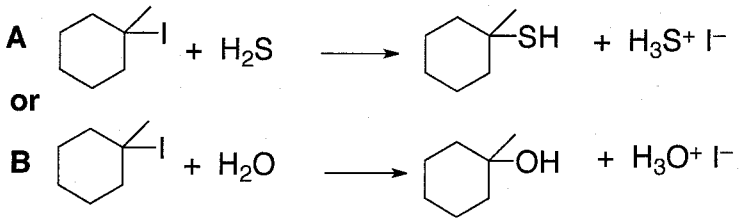
2. (28 points) Which reaction in the following pairs of reactions would you expect to go faster? It is possible that both reactions have the same rate. Give brief explanations in the boxes provided.

a.



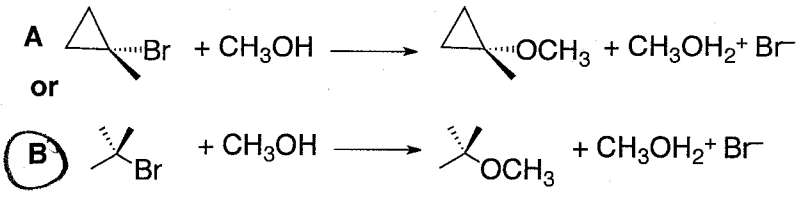
Explanation:
A is faster because −SH is a great nucleophile & a weak base. Unhindered 1° substrate. Therefore, SN2 faster

b.



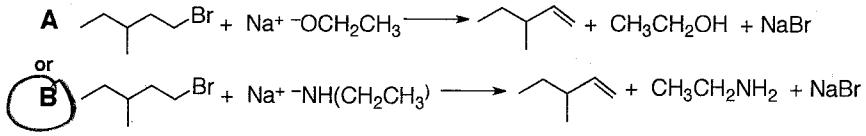
Explanation:
Same rate
These are SN1 rxns
The rate of the rxn only depends on alkyliodide, Rate does not depend on nucleophile.

c.



Explanation:
B is faster. In A the transition state & carbocation intermediate are destabilized by bond angle strain. It is difficult for the 3-membered ring w/ 60° angles to become sp^2 hybridized.

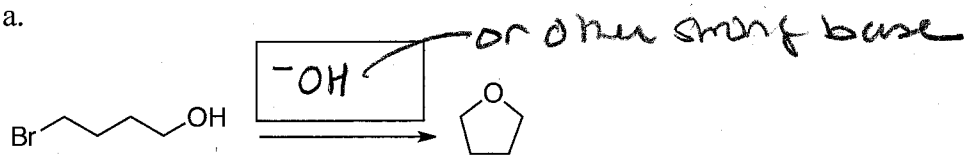
d.



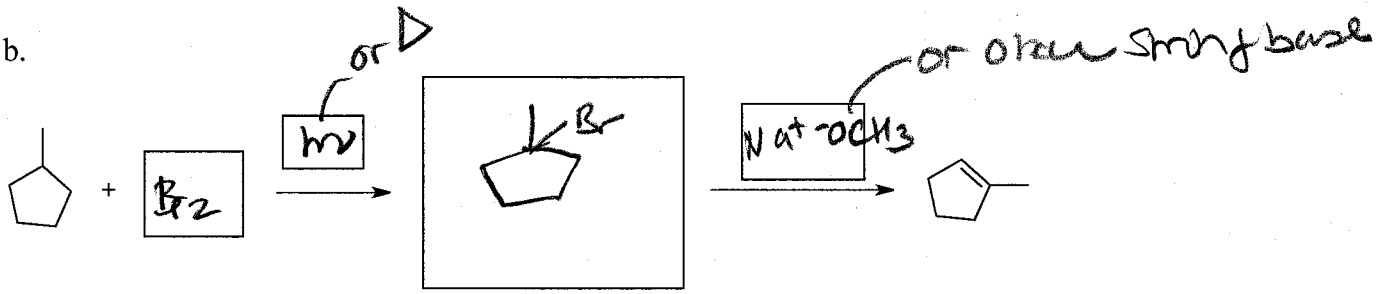
Explanation
B is faster. This is an E2 rxn & −NHCH2CH3 is a stronger base than −OCH2CH3

3. (28 points) Fill in the boxes in the following reactions to yield the indicated products in the highest yield with the fewest number of steps. Note that only the organic products have been drawn.

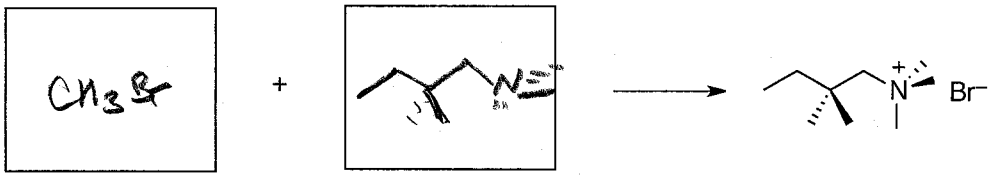
a.



b.



c.



an alkyl halide

4. (16 points) Give the mechanism(s) that are true for the following statements. Choose from S_N2, S_N1, E1, E2, and/or radical halogenation.

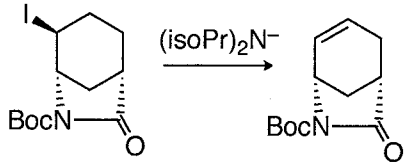
a. These reaction mechanisms involve carbocation intermediates SN1, E1

b. These reactions follow a second order rate equation SN2, E2

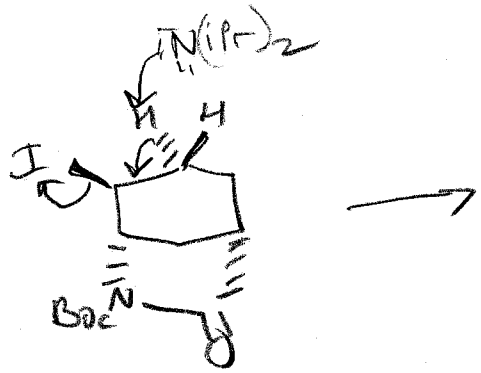
c. Alkyl iodides react faster than alkyl bromides in reactions that proceed by these mechanisms. SN1, E1, E2, SN2

d. These reactions proceed through propagation steps. radical halogenation

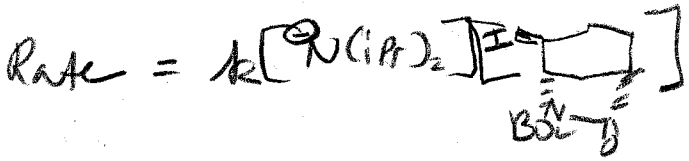
5. (20 points) Tamiflu is a medication used to prevent and treat flu. A step in the synthesis of Tamiflu is shown below.



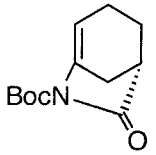
a. Draw the mechanism of this reaction using arrows to represent electron flow.



b. Write the rate equation for this reaction.



c. Why is the alkene shown below not a product of this reaction?



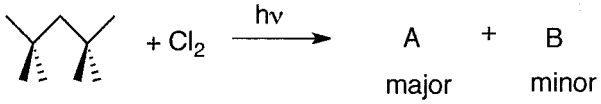
Three reasons

(1) No anti planar H's

(2) large base favors Hoffman elimination

(3) Ring strain from double bond at bridgehead position

6. (37 points) Radical chlorination of $(CH_3)_3CCH_2C(CH_3)_3$ gives a mixture of monochlorinated alkanes in a 2:1 ratio. Remember that the relative reactivity of 3°:2°:1° C-H bonds is 5:4:1.



a. Is the observed product ratio consistent with the relative reactivity of 3°, 2°, and 1° C-H bonds? Show a calculation that justifies your answer.

10 H = 18 Hs x 1 = 18

20 H = 2 Hs x 2 = 8

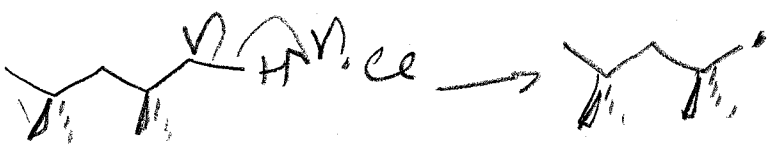
approximate 2:1 ratio

b. What is the major product of chlorination?

c. Draw the mechanism of the formation of the major product of chlorination using arrows to show electron flow.

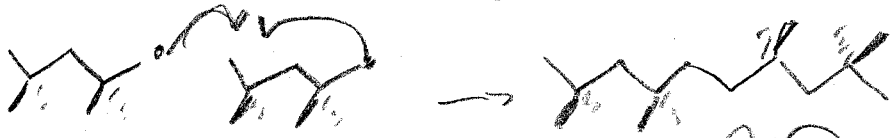
Initiation:

Propagation:



Termination: Any reaction that does not form a radical

ie.

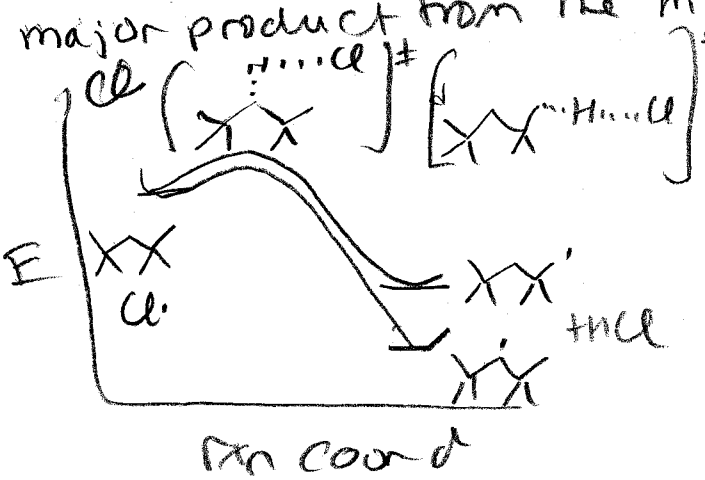


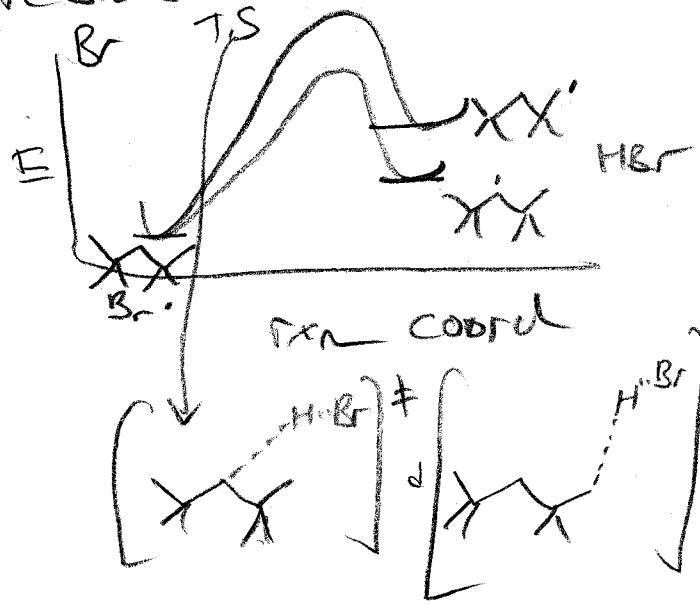
or

d. If this reaction is performed with Br_2 instead of Cl_2, then the major product is structure **B** with Br substituted for Cl. Explain why a different major product is observed with Br_2. Include in your answer a discussion of the Hammond postulate and the transition state structures involved in these reactions. The table lists some BDE's (bond dissociation energies) for your reference.

Bond	BDE (kcal/mol)
HCl	103
HBr	87
Br_2	46
Cl_2	58
1° C-H	101
2° C-H	98

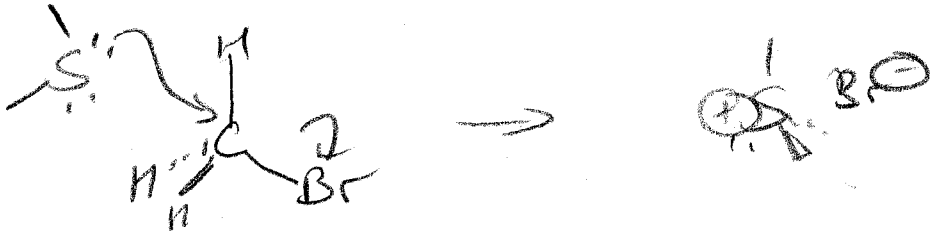
The first step of propagation determines which C-H bond is halogenated. This step is endothermic for Br_2 & exothermic for Cl_2. the Hammond postulate states that the TS for exothermic will look more like S.M. & T.S. for endothermic will look more like products. Therefore, T.S. for Cl_2 will look more like alkane & T.S. for Br_2 will look more like radicals. Therefore, there will be a larger energy difference between 1° C-H & 2° C-H rxns for Br_2 than Cl_2 & Br_2 will therefore yield the major product from the more stable radical (B)



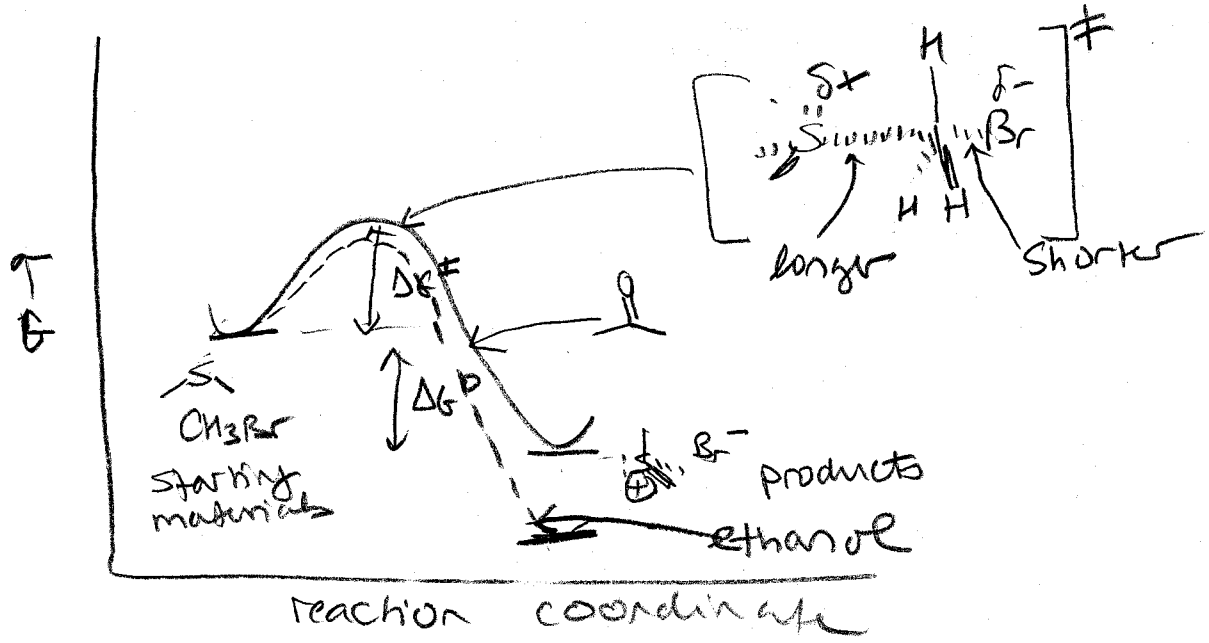


7. (28 points) Consider the equilibrium shown below.

a)Draw the mechanism for this reaction.



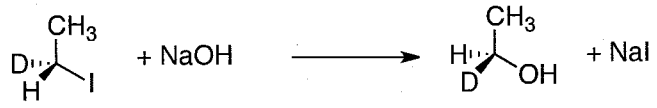
b) Draw a reaction coordinate diagram for this reaction. Label the axes, starting materials, products, $\Delta G°$, $\Delta G^{\ddagger}$, intermediates, and transition states. Include a drawing of the transition state structure.

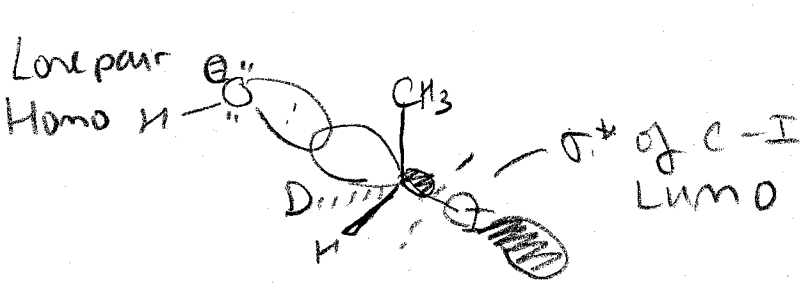


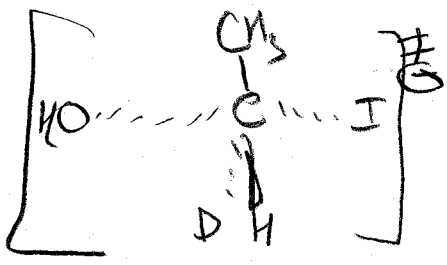
c) The *equilibrium* of this reaction lies farther to the right in ethanol than in acetone. Explain this observation. As part of your explanation, annotate the diagram you drew in part b to include reactions in both solvents.

The products of this reaction are charged. The starting materials are neutral. The T.S. is partially charged. Therefore, the more polar EtOH will stabilize the products through solvation. The neutral starting materials will not be very affected by solvation. Therefore, the equilibrium will lie further to the right in the more polar solvent EtOH. (The T.S. will also be stabilized by increased solvation in EtOH, but by less than products)

8. (13 points) The S_N2 mechanism is stereospecific and proceeds with inversion of configuration. An example of a reaction that proceeds by an S_N2 mechanism is shown below. Explain why the S_N2 mechanism proceeds with inversion of configuration. Include in your explanation a discussion of and labeled drawings of the orbitals involved in this reaction.







The lone pair of the $HO^{\ominus}$ initiates the reaction by donating e^- into σ^* of C-I bond. σ^* orbital is larger away from the C-I bond (the back of the bond). The back of the C-I bond is also less sterically hindered than the front of the C-I bond. Approach from the front of the bond would yield equal interactions w/ both signs of σ^* orbital & these would cancel out leading to no interaction. The C-I bond breaks at the same time as the C-O bond forms. The T.S. is a trigonal bipyramidal structure & the molecule undergoes an umbrella flip during this reaction. Together these reasons cause inversion of configuration

ChemGlobe - Periodic table of elements