Third Exam
CHEM 255 – Organic Chemistry I
Prof. Bastin
Summer 2015

Name Key

1. Provide *CLEAR, CONCISE* answers using unambiquous, carefully drawn structures and mechanisms for the appropriate questions. *Be sure to read each question VERY CAREFULLY.*
2. You may **ONLY** use a pen or pencil and the materials provided in this packet on this exam.
3. If you have papers and/or books with you, they are to be left on the floor **AT THE FRONT OF THE ROOM**. If you need scrap paper please ask.
4. Cell phones must be **OFF and placed on the table at the FRONT of the ROOM**.

1) ______/8 pts

2) ______/10 pts

3) ______/10 pts

4) ______/12 pts **Total: ______/100 pts**

5) ______/12 pts

6) ______/10 pts

7) ______/10 pts

8) ______/16 pts

9) ______/12 pts

1) (8 pts) Indicate whether each of the following statements are true or false. Write T or F in the blanks below.

(a) An E2 reaction obeys first-order kinetics.

(b) Primary alkyl halides react faster than secondary alkyl halides in S_N1 reactions.

(c) The mechanism of an E2 reaction usually involves only one step.

(d) Carbocations are intermediates in an S_N2 reaction.

(e) The rate of an S_N2 reaction is only proportional to the concentration of the nucleophile.

(f) The rate of an S_N1 reaction depends on the nature of the leaving group.

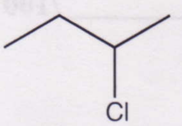
(g) An S_N1 reaction results in only inversion of configuration at the site of substitution.

(h) Resonance is the only important stabilizing factor in a carbocation intermediate.

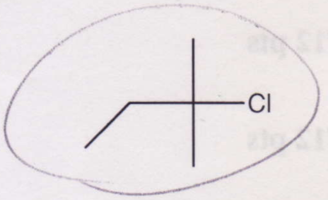
(a) F (b) F (c) T (d) F (e) F (f) T (g) F (h) F

2) (10 pts) For each of the following pairs, determine which compound would have a faster rate of S_N1. Provide an explanation for your choice.

(a)



2°

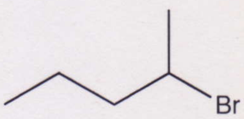


3°

3° carbocations ~~react~~ are more stable than 2°, so the RDS is faster for 3°

(b)

1°



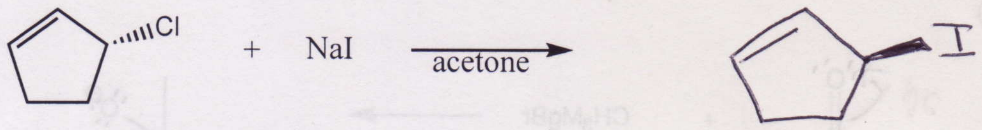
2°

2° carbocations are more stable than 1°, so the RDS is faster for 2°

3) (10 pts) Draw the product(s), if any, of the following reactions. Indicate stereochemistry where relevant.

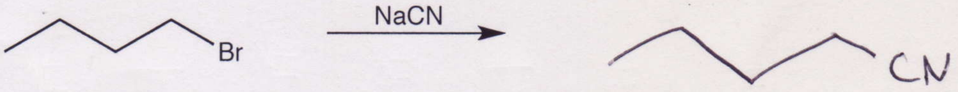
3pts

a)



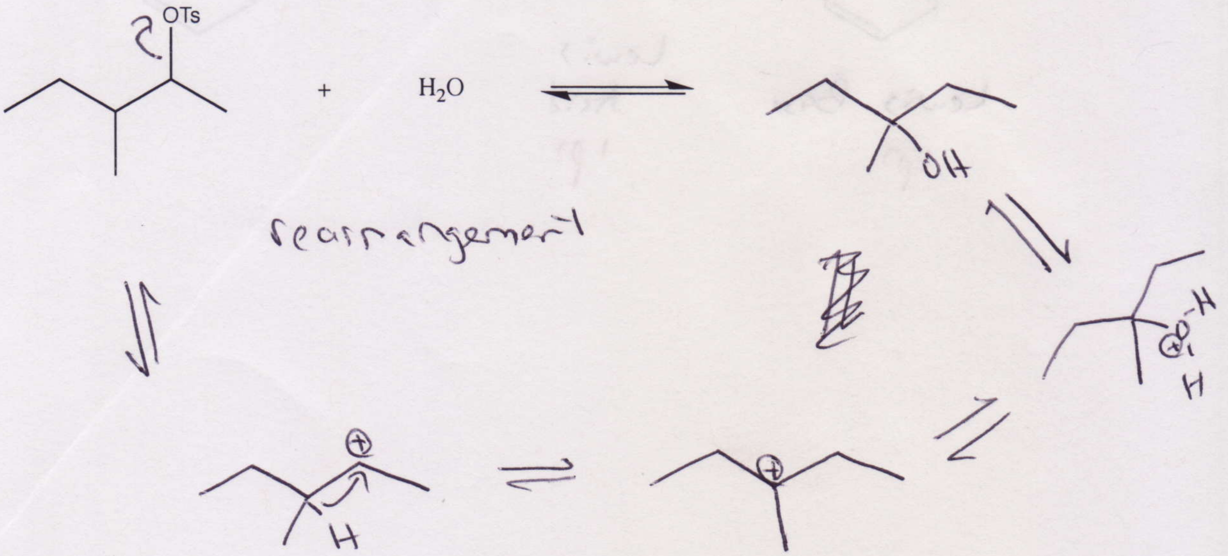
3pts

b)



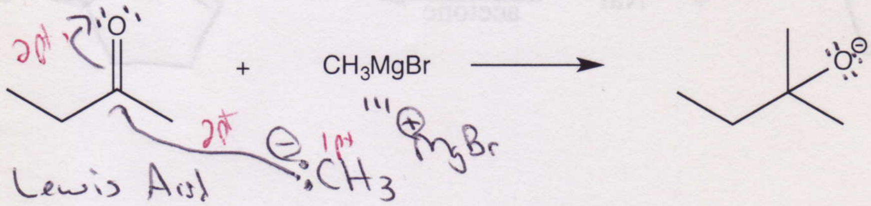
4pts

c)



4) (12 pts) Provide the curved-arrow mechanisms for each of the following reactions. Also, indicate the Lewis Acid and Lewis Base of each reaction. Be sure to add any needed lone pairs to the structures.

(a)



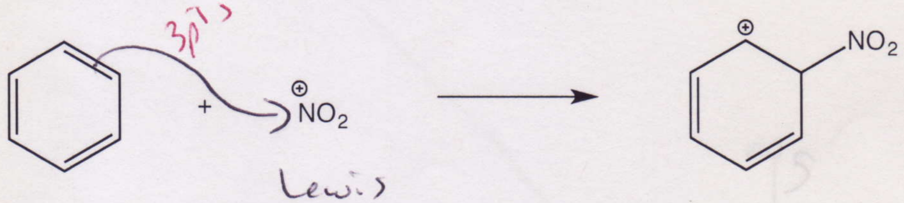
Lewis Acid

1 pt

Lewis Base

1 pt

(b)



Lewis Base

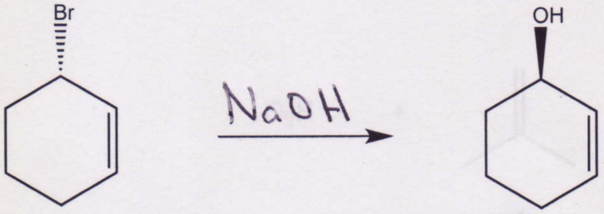
1 pt

Lewis Acid

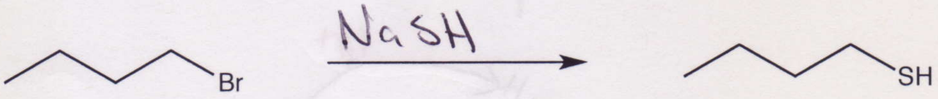
1 pt

5) (12 pts) Provide the reagents needed to bring about the following transformations.

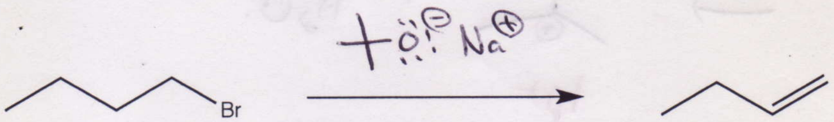
a)



(b)



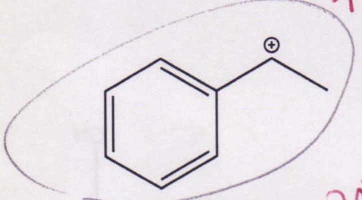
(c)

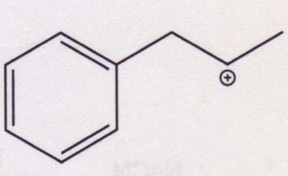


6) (10 pts) Indicate the more stable carbocation in each of the following pairs. Explain.

(a)

3pts





2pts

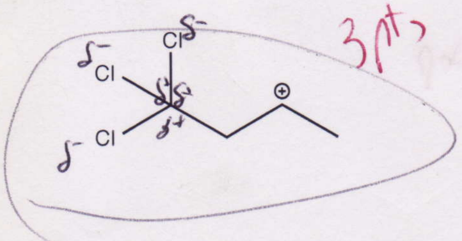
resonance stabilized

2° benzylic carbocation

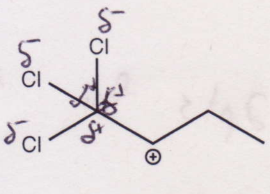
not resonance stabilized

2° carbocation

(b)



3pts

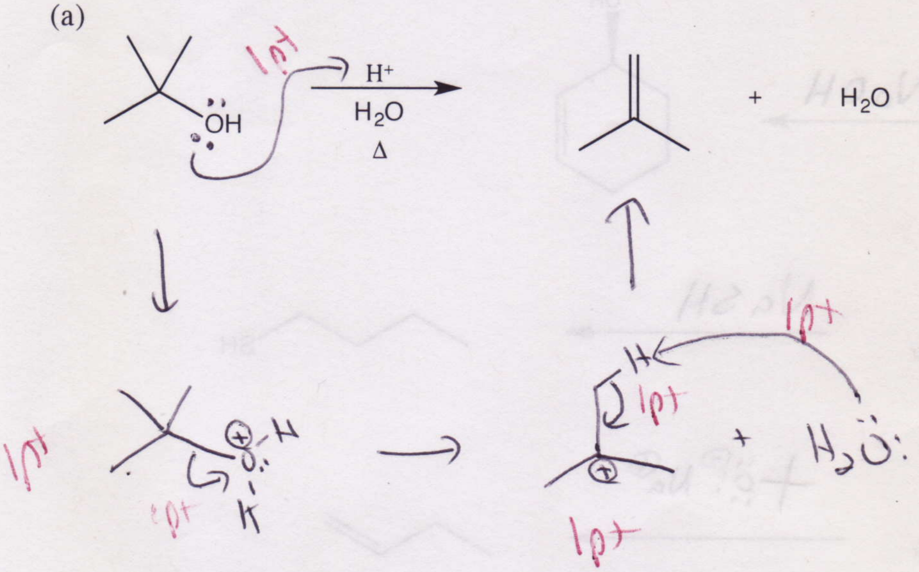


2pts

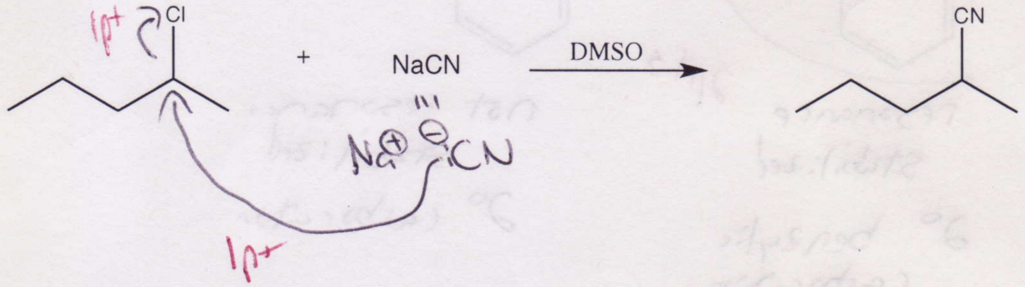
adjacent charges destabilize carbocations

7) (10 pts) Provide the curved-arrow mechanisms for the following reactions (the mechanism may involve more steps than implied by the reaction). Be sure to add any needed lone pairs to the structures.

(a)



(b)



2pts for 1 step

8) (16 pts) Which product (or products) would you expect to be the major product(s) from each of the following reactions? In each reaction give the NAME of the mechanism (S_n1, S_n2, E1, E2) by which each product is formed.

(a)

1°

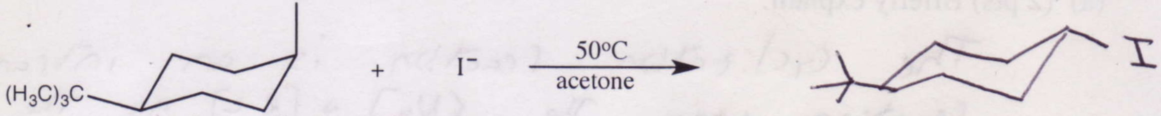
$CH_3CH_2CH_2CH_2Br + (CH_3)_3CO^- \xrightarrow[(CH_3)_3COH]{50^oC}$

	Sn1	Sn2	E1	E2	Notes
Nu				1	very strong base very weak Nu
[Nu]		1		1	
L	~~1~~	1	~~1~~	1	
Solvent	~~1~~		~~1~~		polar, protic

3

E2

(b)

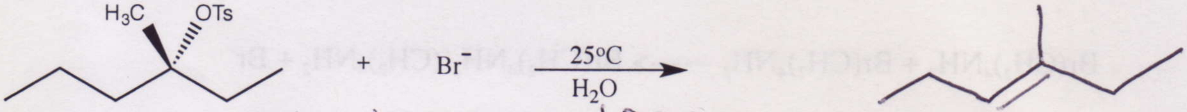


2°

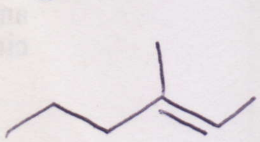
	Sn1	Sn2	E1	E2	Notes
Nu		1			strong Nu weak base
[Nu]		1		1	
L	1	1	1	1	
Solvent		1		1	polar, aprotic

Sn2

(c)



+

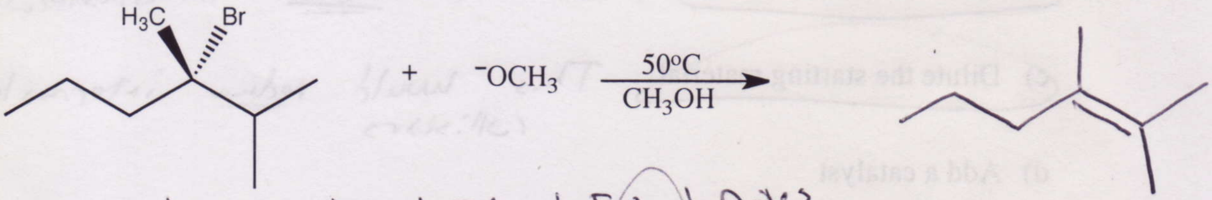


3°

	Sn1	Sn2	E1	E2	Notes
Nu			1		weak base strong Nu
[Nu]				1	
L	1		1	1	
Solvent	1		1	3	

E1

(d)



3°

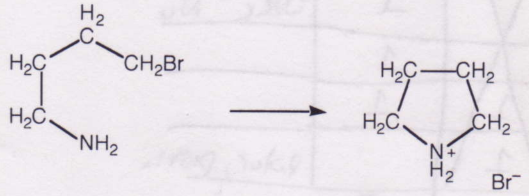
	Sn1	Sn2	E1	E2	Notes
Nu				1	strong
[Nu]				1	
L	1		1	1	
Solvent	1		1		

E2

9) (12 pts) The following reaction of methyl bromide with methylamine to give dimethylammonium bromide is a typical S_N2 reaction that is described by second-order kinetics.

$$CH_3Br + CH_3NH_2 \longrightarrow (CH_3)_2NH_2^+Br^-$$

However, the analogous cyclization of 4-bromobutylamine shows first order kinetics.



(a) (2 pts) Briefly explain.

The cyclization reaction is an intramolecular reaction where the [Nu] + [R-L] are the same molecule, so the rate-law is reduced to a 1st-order reaction.

The forgoing intramolecular displacement reaction is a useful method for making cyclic amines (nitrogen containing compounds). However, a competing side reaction is the intermolecular displacement:

$$Br(CH_2)_4NH_2 + Br(CH_2)_4NH_2 \longrightarrow Br(CH_2)_4NH_2^+(CH_2)_4NH_2 + Br^-$$

(b) (10 pts) Circle the experimental conditions that would best minimize this side reaction and maximize the production of the cyclic amine. Briefly explain your choice to circle or not circle.

a) Raise the temperature This would cause more intermolecular collisions

[✓ b) Lower the temperature] This would reduce intermolecular collis

[✓ c) Dilute the starting material] This would reduce intermolecular collisions

d) Add a catalyst

e) Use a more polar solvent