

NAME (Print): _____

Chemistry 310M/318M

Dr. Brent Iverson

3rd Midterm

November 17, 2011

SIGNATURE: _____

Please print the
first three letters
of your last name
in the three boxes

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Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

(Your signature)

Page	Points	
1		(27)
2		(14)
3		(14)
4		(15)
5		(20)
6		(17)
7		(22)
8		(17)
9		(12)
10		(12)
11		(16)
12		(14)
13		(18)
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15		(4)
16		(12)
Total		(247)
%		
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HW		
Total Grade		

(HW score + Exam Grade) \Longrightarrow

Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	H_3O^+	-1.7
Acetic acid	$\text{CH}_3\text{C}(=\text{O})\text{OH}$	4.8
Ammonium ion	H_4N^+	9.2
β-Dicarbonyls	$\text{RC}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{R}'$	10
Ethyl ammonium ion	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	10.8
β-Ketoesters	$\text{RC}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OR}'$	11
β-Diesters	$\text{ROC}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RCH}_2\text{C}(=\text{O})\text{Cl}$	16
Aldehydes	$\text{RCH}_2\text{C}(=\text{O})\text{H}$	18-20
Ketones	$\text{RCH}_2\text{C}(=\text{O})\text{R}'$	18-20
Esters	$\text{RCH}_2\text{C}(=\text{O})\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C-H}$	25
LDA	$\text{H-N}(i\text{-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\text{CH}_2$	44
Alkanes	$\text{CH}_3\text{CH}_2\text{-H}$	51

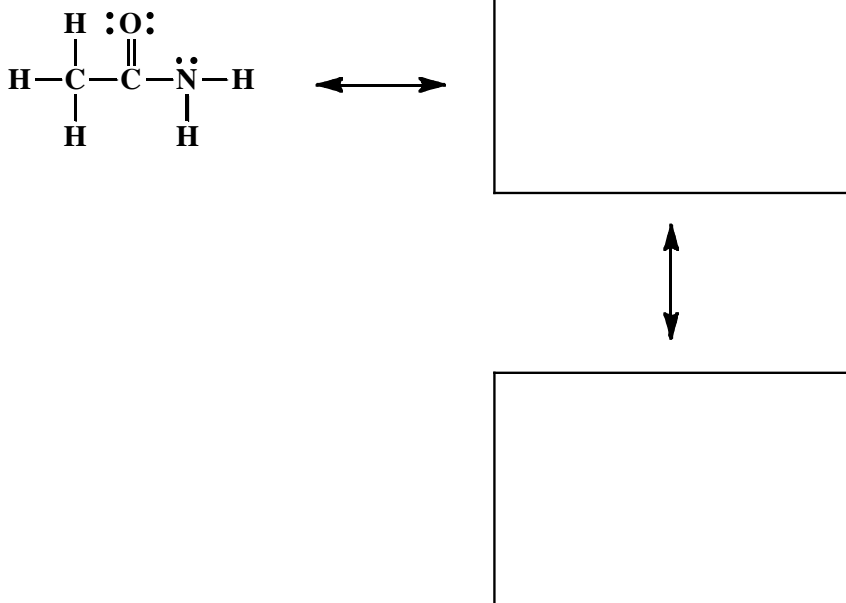
		Electron		Proton		Neutron		Positron		Neutrino		Difference in Electronegativity		18		vH	
		Symbol		P		N		P		N		N/A Dr. Pauling		18		vH	
		Atomic mass (kg)		1.672621(1) × 10 ⁻²⁷		1.674928(1) × 10 ⁻²⁷		0		0		N/A Dr. Ramsey & Smith		18		vH	
		Bohr mass (kg)		9.10938291(4) × 10 ⁻³¹		1.672621(1) × 10 ⁻²⁷		0		0				18		vH	
		Particle-electron mass ratio		1.836152673(4)		1836.152673(4)		0		0				18		vH	
		Particle-proton mass ratio		5.48579909(13) × 10 ⁻⁴		1.007276467(1) × 10 ⁻³		0		0				18		vH	
		Particle-neutron mass ratio		5.48579909(13) × 10 ⁻⁴		1.008664914(4) × 10 ⁻³		0		0				18		vH	
		Specific charge (C/kg)		1.75987436(4) × 10 ¹¹		9.57898932(9) × 10 ¹⁷		0		0				18		vH	
		Bohr (m)		5.291772085(4) × 10 ⁻¹¹		1.054571817(4) × 10 ⁻¹⁰		0		0				18		vH	
		Bohr (nm)		0.5291772085(4) × 10 ⁻¹⁰		1.054571817(4) × 10 ⁻¹⁰		0		0				18		vH	
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		Bohr (nm)		0.5291772085(4) × 10 ⁻¹⁰		1.054571817(4) × 10 ⁻¹⁰		0		0				18		vH	
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Editors: T. K. Varga, M.A.Sc. & C. Bello, M.A.Sc.
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1. (5 pts) What is the most important question in organic chemistry?

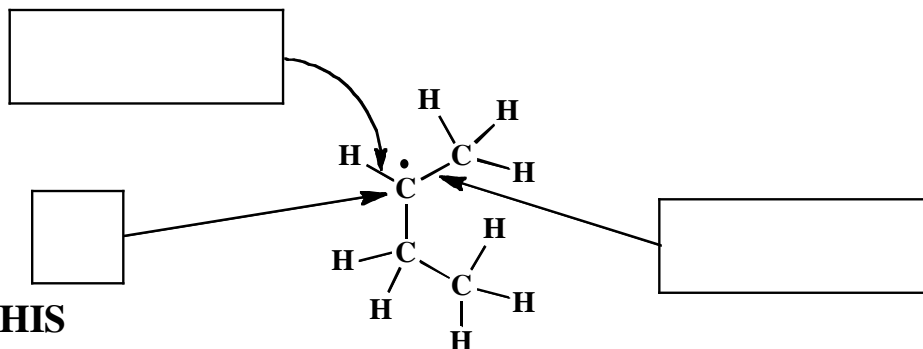
2. (10 pts) Amides are best represented as the hybrid of three contributing structures. **Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges.** For the first two structures in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing structures. You might want to read these directions again to make sure you know what we want.



3. For the following carbon radical:

A) State the hybridization state of the indicated atom in the square box provided. In the rectangular boxes, describe the bonds indicated by the arrows in terms of overlap between hybrid orbitals (the valence bond approach). For example, answers might be $\sigma\text{Csp}^3-\text{Csp}^3$ or $\pi\text{C}2\text{p}-\text{C}2\text{p}$.

(2 pts. each)



NOTICE THIS



B) (6 pts) This part refers to hyperconjugation. On the structure, **circle all of the sigma bonds that can take part in hyperconjugation with the carbon radical.**

4. (1 pt each) Consider the following statements that refer to S_N1 , S_N2 , E1, E2 or a radical chain reaction mechanism. To which mechanism(s), if any, does each statement apply?

Mechanisms

A. The reaction mechanism has no intermediates, only a single transition state, as it moves from reactants to products.

B. The reaction creates an alkene and follows Zaitsev's rule

C. The reaction mechanism involves a carbocation intermediate

D. The reaction mechanism involves radical intermediates

E. The reaction mechanism requires an antiperiplanar transition state geometry

F. When reaction occurs at a chiral center on a pure sample of a single enantiomer, a single enantiomer product with inversion of the chiral configuration is created.

G. The order of reactivity for this mechanism is methyl halides > 1° haloalkanes > 2° haloalkanes. There is no reaction by this mechanism with 3° haloalkanes.

H. The order of reactivity for these mechanisms is 3° haloalkanes > 2° haloalkanes. There is no reaction with these mechanisms for 1° haloalkanes or methyl haloalkanes.

I. For alkane starting materials, the order of reactivity for this mechanism is 3° hydrogens > 2° hydrogens > 1° hydrogens

J. The reaction mechanism(s) that will occur when KOtBu reacts with a haloalkane

K. The reaction mechanism(s) that will occur when Br_2 and light are used

L. The reaction mechanism(s) that will occur when HBr and peroxides with light are used

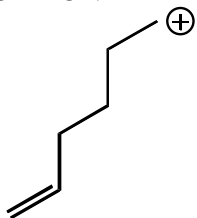
M. The reaction mechanism(s) that will occur when NBS and light are used

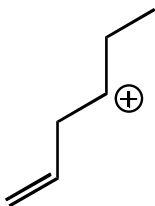
N. The reaction mechanism that occurs when the anion of a terminal alkyne reacts with a primary haloalkane.

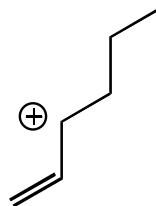
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Pg 3 _____ (14)

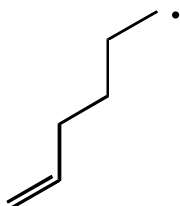
5. (3 pts) For the following carbocations, rank them from 1-3 according to overall carbocation stability, with a 1 under the LEAST STABLE CARBOCATION and a 3 under the MOST STABLE CARBOCATION.

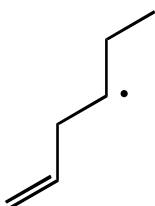


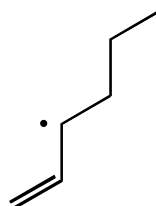




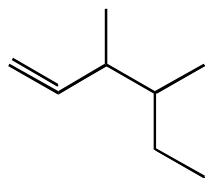
6. (3 pts) For the following radicals, rank them from 1-3 according to overall radical stability, with a 1 under the LEAST STABLE RADICAL and a 3 under the MOST STABLE RADICAL.

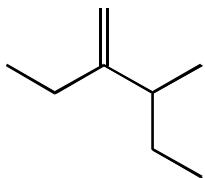


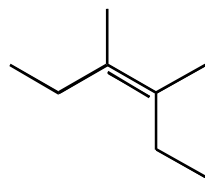


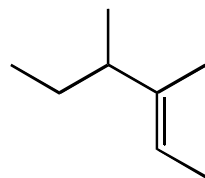


7. (4 pts) For the following constitutional isomers, rank them from 1-4 according to overall alkene stability, with a 1 under the LEAST STABLE ALKENE and a 4 under the MOST STABLE ALKENE.



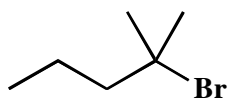


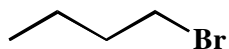


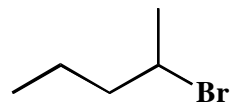


8. (4 pts) For the following haloalkanes, rank them from 1-4 with respect to reactivity in an S_N2 reaction, with a 1 under the LEAST REACTIVE HALOALKANE, and a 4 under the MOST REACTIVE HALOALKANE.

CH_3Br



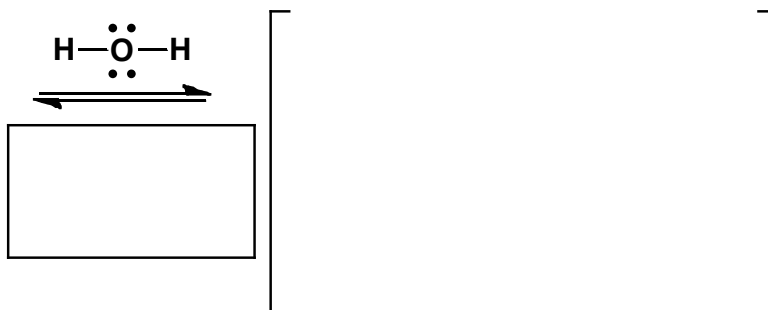
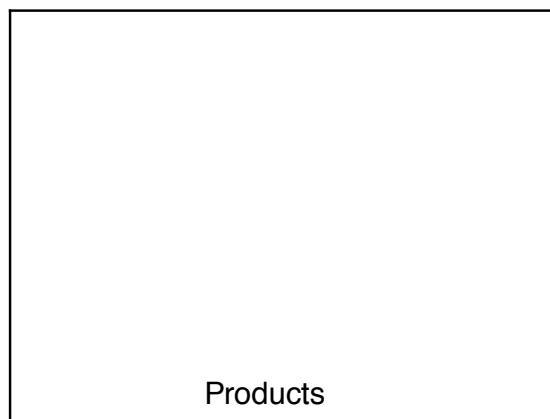
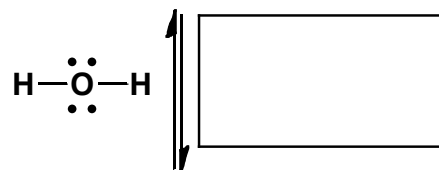
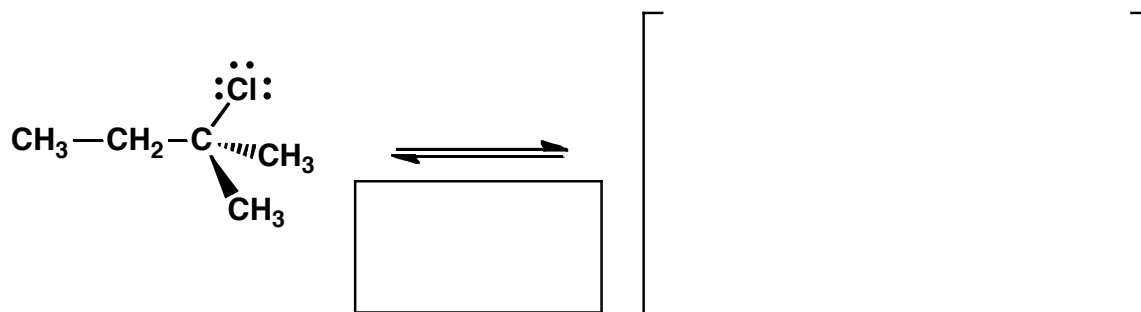




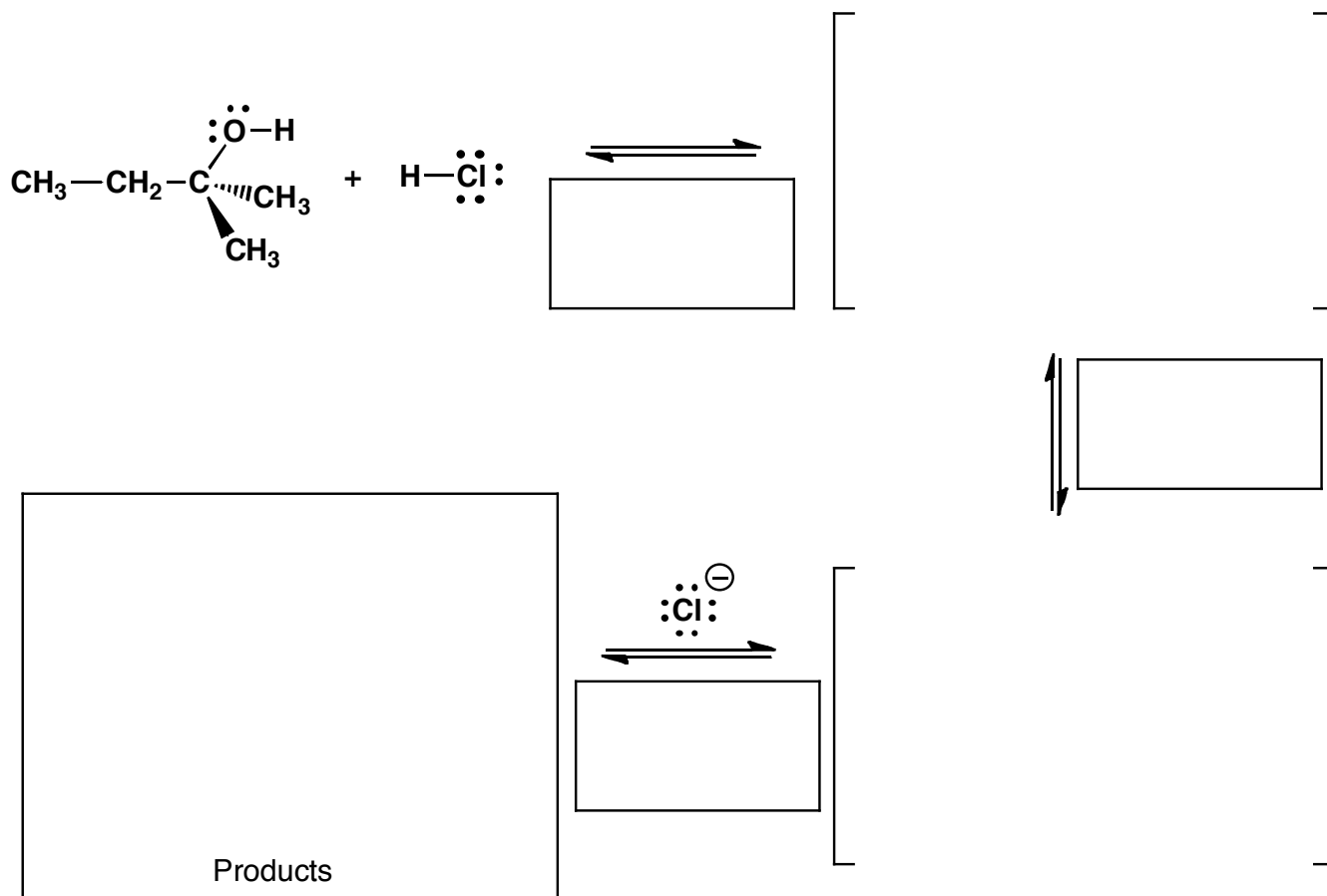
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Pg 4 _____(15)

9. (15 pts total) Complete the following mechanism for an S_N1 reaction that occurs when 2-chloro-2-methylbutane is heated in water. NOTE, ALTHOUGH AN $E1$ PROCESS WILL ACCOMPANY THIS S_N1 REACTION, WE ARE ONLY INTERESTED IN THE S_N1 MECHANISM FOR THIS PROBLEM. Use appropriate arrows to show all movement of electrons, show all non-bonding electrons as dots and show any formal charges. **If any of the species are really racemic mixtures of enantiomers, you only need to draw one stereoisomer and write "racemic". In the boxes provided, write which kind of mechanistic element is being shown for that step, i.e. "make a bond", etc.**



10. (15 pts total) Complete the following mechanism for the reaction of the alcohol shown with HCl. Use appropriate arrows to show all movement of electrons, show all non-bonding electrons as dots and show any formal charges. **If any of the species are really racemic mixtures of enantiomers, you only need to draw one stereoisomer and write "racemic".** In the boxes provided, write which kind of mechanistic element is being shown for that step, i.e. "make a bond", etc.

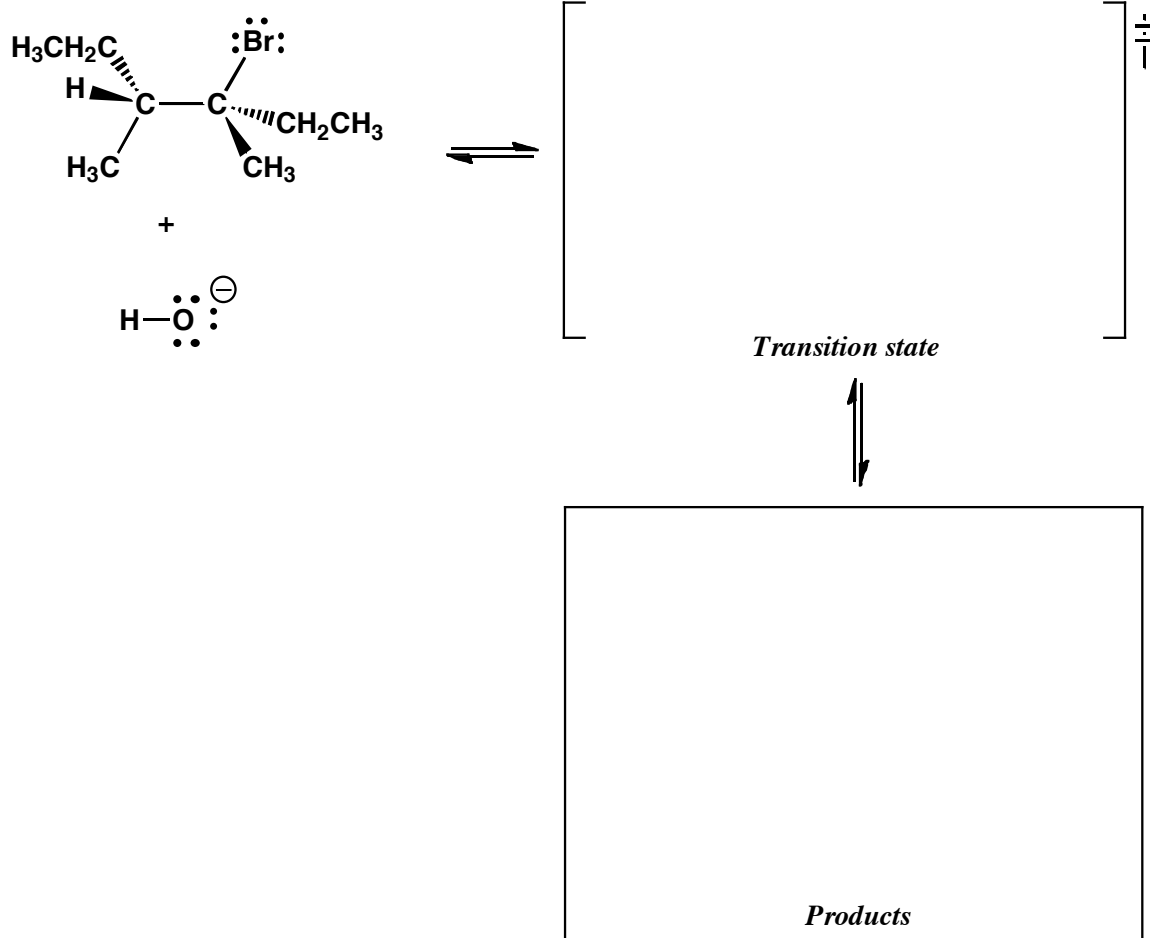


11. (5 pts) Compare the mechanisms you just wrote for problems 9 and 10. **Precisely state the relationship that exists between these two reaction mechanisms. Be specific please. The correct answer only requires one sentence and one point being made.** We are grading this as "all or nothing", so please be careful here.

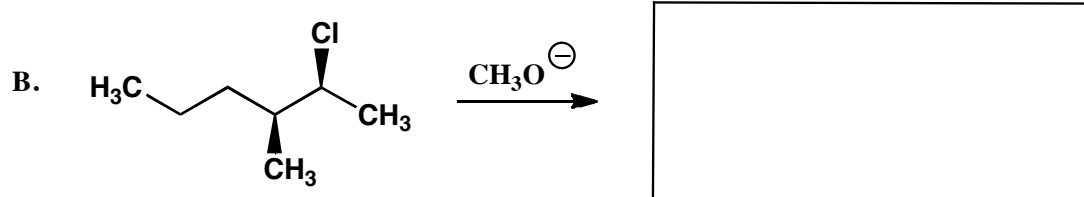
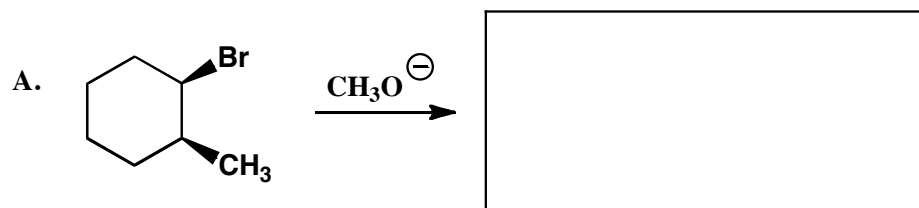
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Pg 6 _____(17)

12. (11 pts total) For the following E2 reaction, draw the transition state that leads to the predominant product(s), indicating **geometry and stereochemistry** with wedges and dashes. We will be paying particular attention to the geometry of your transition state. **No need to show any arrows for moving electrons here, we are just interested in the transition state and product structures. In your transition state structure, be sure to show bonds being made or broken as dotted lines (.....).**



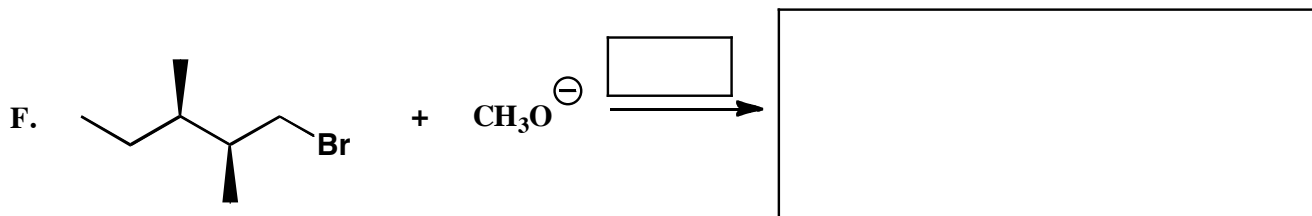
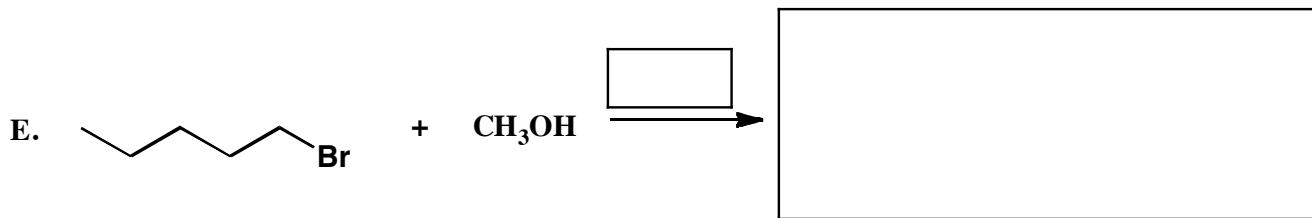
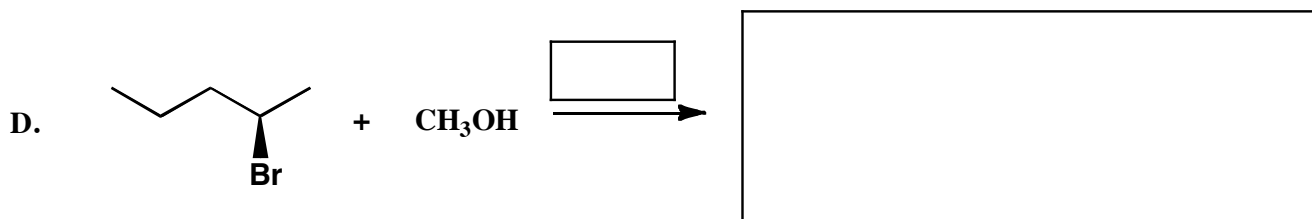
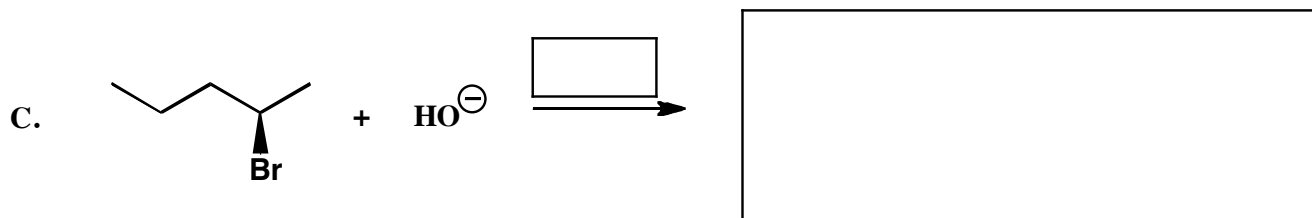
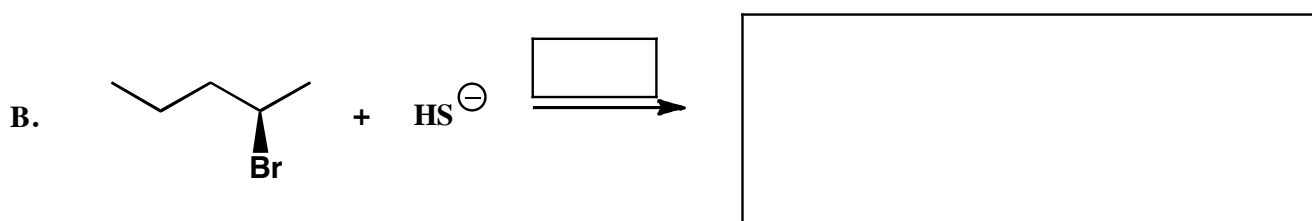
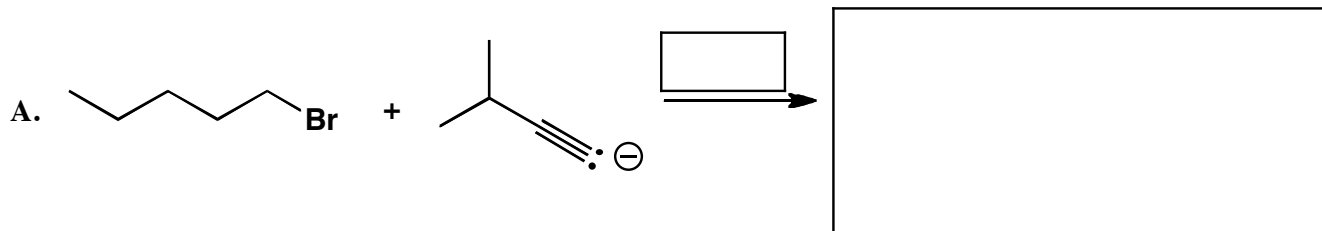
13. (6 pts) Draw the predominant product expected for each of the following E2 reactions.



Signature _____

Pg 7 _____ (22)

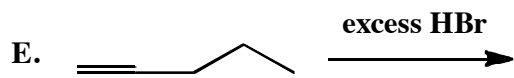
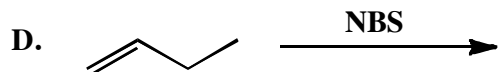
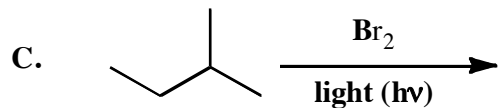
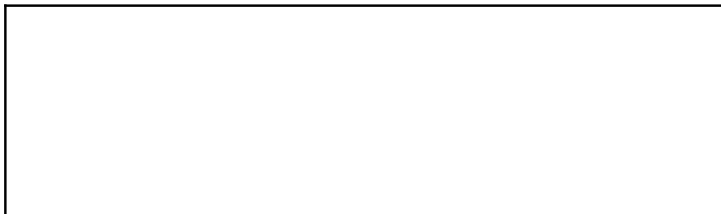
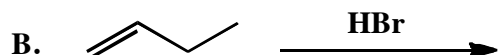
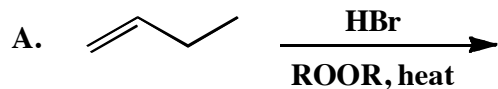
14. (3 or 7 pts each) For the following reactions, write the predominant product(s) in the space provided, then in the **box above the arrow** write the **predominant mechanism of the reaction**. **Make sure to indicate stereochemistry with wedges and dashes as appropriate.**



Signature _____

Pg 8 _____(17)

15. (3 or 5 pts each) Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry**. When a racemic mixture is formed, **you must write "racemic"** under both structures **EVEN THOUGH YOU DREW BOTH STRUCTURES**.

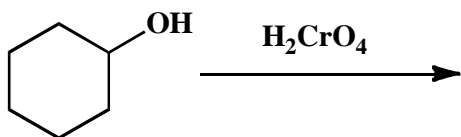


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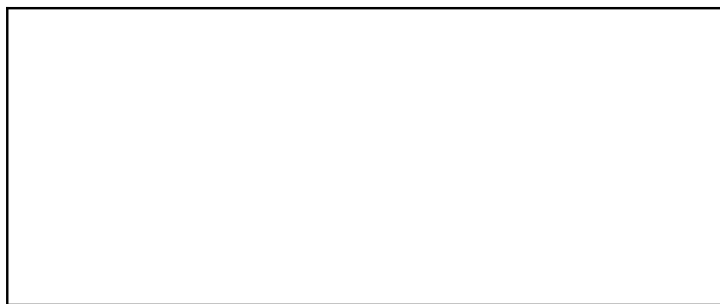
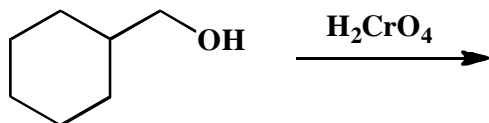
Pg 9 _____(12)

15 (cont.) (3 or 5 pts each) Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry**. When a racemic mixture is formed, **you must write "racemic"** under both structures **EVEN THOUGH YOU DREW BOTH STRUCTURES**.

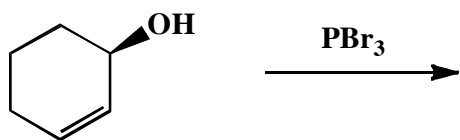
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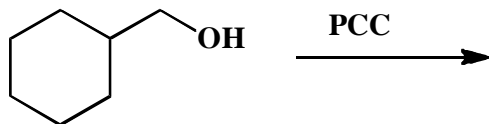
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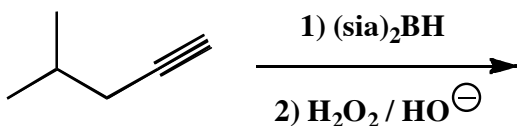


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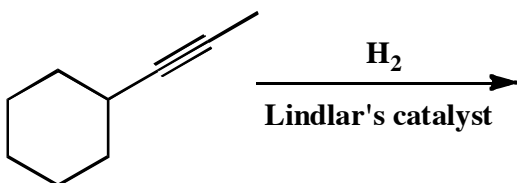
Pg 10 _____(12)

13 (cont.) (3 or 5 pts each) Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry**. When a racemic mixture is formed, **you must write "racemic"** under both structures **EVEN THOUGH YOU DREW BOTH STRUCTURES**.

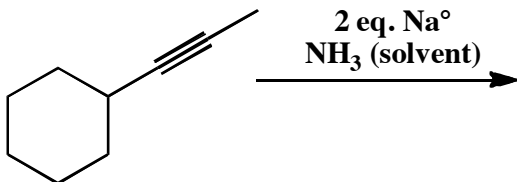
J.



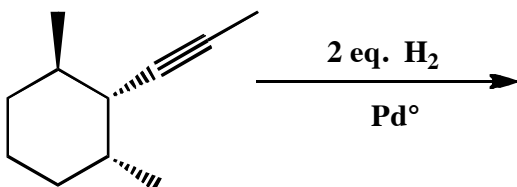
K.



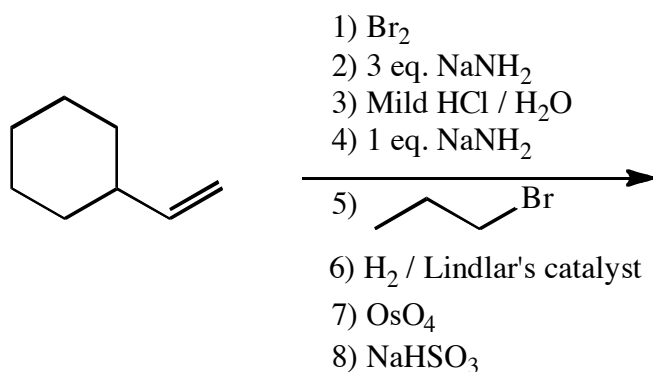
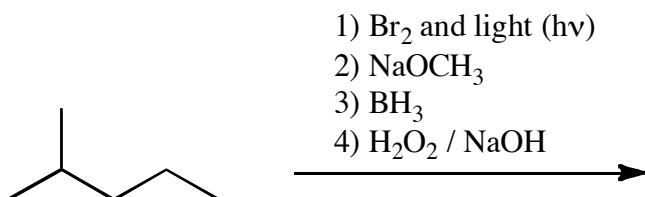
L.



M.



16. (7 and 9 pts) For the following sequences of reactions, work through all the different reactions and then write the final product(s). Assume only the predominant product is formed at each step. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place. **You do not need to draw any of the molecules synthesized along the way, just the final product(s).**

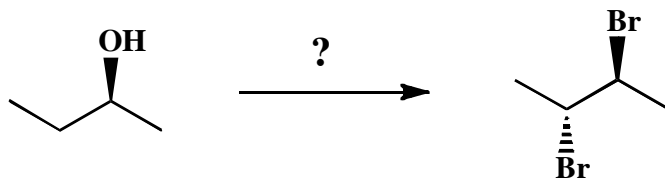


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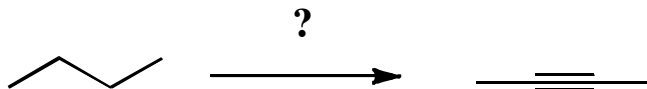
Pg 12 _____(14)

17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). **Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction.** You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate.

A) (4 pts)



B) (10 pts)

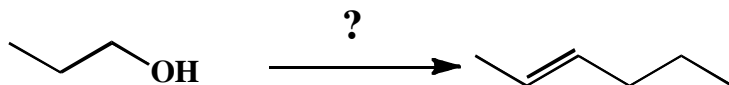


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Pg 13 _____(18)

17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). **Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction.** You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate.

C) (18 pts) For this one, all of the carbon atoms of the product must come from the 1-propanol starting material.

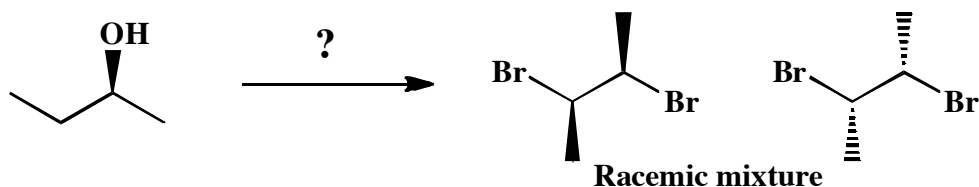


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Pg 14 _____(13)

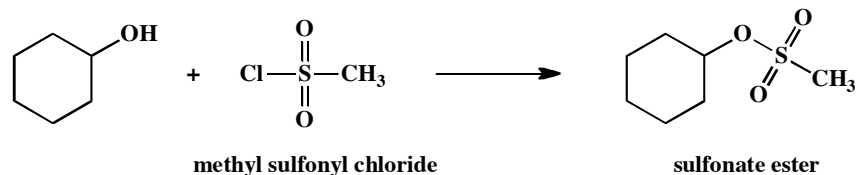
17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). **Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction.** You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate.

D) (13 pts)

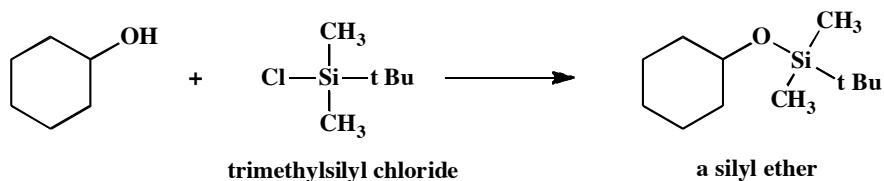


18. Here is an "apply what you know" problem in the format of an MCAT style passage. Circle the correct answers.

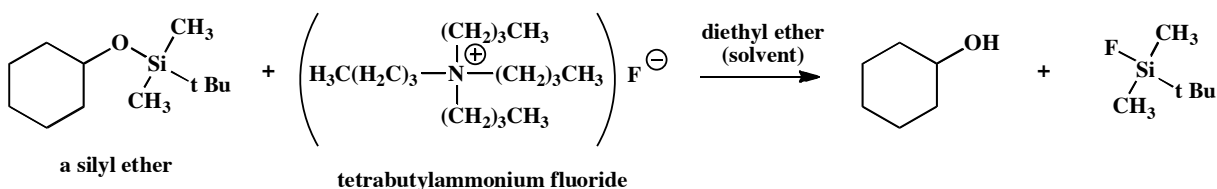
Alcohols react with a variety of Z-Cl bonds to make new bonds between O of the alcohol and the Z atom. For example, we have seen that Z can be sulfur in the form of sulfonyl chlorides that react to give sulfonate esters.



In an analogous way, silyl chlorides react with alcohols at silicon to give a functional group referred to as a silyl ether.



Recall that silicon is directly below carbon in the periodic table. The compounds of silicon have many similarities to carbon, most importantly the preference for making 4 bonds. Molecules with Si-C bonds are not only common, they are useful. Reaction of a silyl ether with tetrabutylammonium fluoride in an organic solvent such as diethyl ether breaks the Si-O bond and regenerates the alcohol.

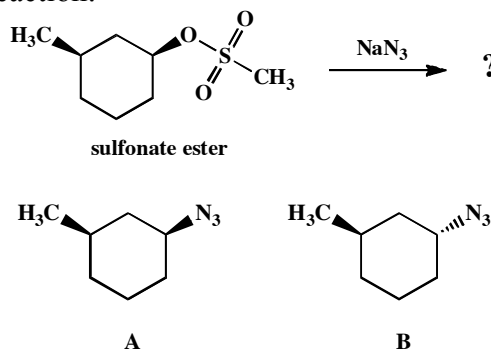


The big picture here is that the silyl ether formation can be used to temporarily block the reactions of an OH group, then it can be removed when desired using the fluoride reagent. This kind of group, capable of temporarily and reversibly blocking the reactions of a functional group, is referred to as a protecting group. Silyl ethers are widely used protecting groups for the -OH group.

1. The fluoride ion reacts with silyl ether groups to regenerate the OH function by breaking the Si-O bond. State which of the following best explain the **motive (thermodynamic driving force)** for this process.
 - A. Si-F bonds are significantly stronger than Si-O bonds
 - B. Despite the steroids, one of the best home run hitters of all time is Bobby Bonds.
 - C. The reaction of fluoride anion is fast because it has a high activation barrier.
 - D. Both A. and C.

18 (cont.).

2. (4 pts) The tetrabutylammonium cation is used to make a salt with the fluoride anion in these reactions as opposed to NH_4^+ because:
- A. The butyl groups take part in the reaction mechanism.
 - B. There really is no scientific reason for this, it is just an arbitrary choice here.
 - C. The four butyl groups increase solubility in organic solvents such as diethyl ether, so using this cation is used to increase the solubility of the fluoride anion salt in organic solvent.
 - D. NH_4^+ would react with the fluoride anion to make HF, a dangerous acid that dissolves skin and leaves permanent scars.
3. (4 pts) The fluoride anion reacts as a nucleophile with the backside of the Si-O bond despite there being three alkyl groups (two methyl groups, one *tert*-butyl group) attached to Si. Tertiary haloalkanes do not react directly with any nucleophiles. Which of the following might explain why the reaction between the fluoride anion and the Si atom can take place when a similar reaction could not take place at carbon with similar alkyl groups attached.
- A. The fluoride anion is relatively small
 - B. The Si atom is a lot larger than a C atom so there is much more room to attack the Si atom directly in spite of the two methyl and one *tert*-butyl groups.
 - C. The fluoride anion and Si atom are the same size.
 - D. Both A. and B.
4. (4 pts) Sulfonate esters react with nucleophiles in a characteristic manner. Predict the predominant product(s) of the following reaction:



- A. The product labeled as "A"
- B. The product labeled at "B"
- C. Both "A" and "B" as a racemic mixture
- D. Both "A" and "B" but not as a racemic mixture