

Sign Name Key Print Name \_\_\_\_\_

(5 pt name above print & sign - If I can't tell who you are from NO NAME above, I have to go back to the exam taking map and hope that I can read your name on that or I may end up with an exam with no identity permanently). (5 pts scantron name - if you don't bubble in I get a grade with no name and I have to hold everyone's final grades until I figure out whose exam it is.) (100 pts, 12 pages + scantron sheet)

Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. **I will only grade what I can read (obviously).** I am not going to make up an answer for you based on writing I can't read. (use back of exam for scratch paper - If you want me to grade something not in the space for the answer, **clearly specify in writing.** Telling me during the exam where to find the answer does not qualify because I will just vaguely remember someone telling me something during the exam not which one of 250 students told me what to grade on what page.)

Circle answer on this form for backup to the scantron. There is no partial credit for showing work in the multiple choice.

In all questions on all parts of this exam, R is not equal to hydrogen but is an alkyl.

1. Multiple Choice ( 2 pts each, 24 pts) Choose the **one** best statement in each question. There is no partial credit for showing work on the multiple choice questions.

1. Choose the best statement.

- (a) Proton NMR has splitting in the coupling pattern is based on  $2nI + 1$  where  $I = \frac{1}{2}$  and  $n =$  number of neighboring protons.
- (b) There is no coupling between carbon and another carbon in carbon NMR because the natural abundance of carbon 13 is only 1.1% so there is almost never an NMR active neighboring carbon.
- (c) In IR spectroscopy the <sup>functional group</sup> region is  $1500 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  and the <sup>finger print</sup> region is between  $4000 \text{ cm}^{-1}$  and  $1500 \text{ cm}^{-1}$ . *functional*
- (d) (a) and (b) are correct.
- (e) All statements are correct.

2. For intermolecular forces the general progression from strongest to weakest intermolecular force is :

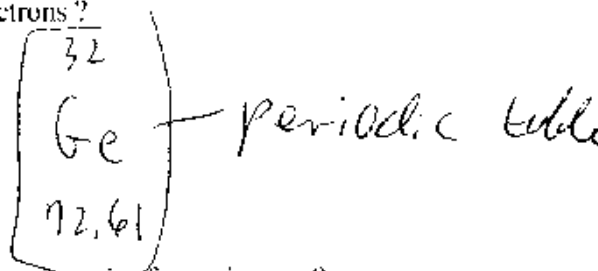
- a) Hydrogen bonding > dipolar > van der Waals
- b) Van der Waals > hydrogen bonding > dipolar
- c) Dipolar > hydrogen bonding > van der Waals
- d) None of the above is correct.

3. Which of the following bonds is a covalent bond ?

- a)  $\text{SO}_2$
- b)  $\text{BaO}$
- c)  $\text{MgCl}_2$
- d)  $\text{Li}_2\text{O}$

4. The element Ge has how many total number of electrons ?

- a) 72 electrons
- b) 32 electrons
- c) 4 electrons
- d) 14 electrons



5. Which of the following statements correctly pertains to a pair of enantiomers ?

- (a) They have different melting points. *same*
- (b) They rotate the plane of polarized light by differing amounts and in opposite directions
- (c) They have the same melting points but they have different boiling points. *same*
- (d) They rotate the plane of polarized light by exactly the same amount and in opposite directions.
- (e) They rotate the plane of polarized light by differing amounts and in the same direction.

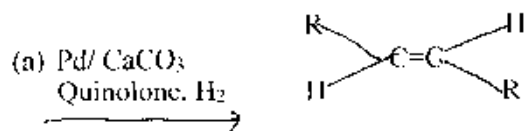
6. Given the following,

- (a)  $\text{RO}^-$  is a better nucleophile than  $\text{HO}^-$
- (b)  $\text{RO}^-$  is a better nucleophile than  $\text{ROH}$
- (c)  $\text{HO}^-$  is a better nucleophile than  $\text{H}_2\text{O}$
- (d) Nucleophilicity is interaction with carbon while Basicity is interaction with hydrogen
- (e) All above statements are true.

7. A radical reaction mechanism is:

- (a) Via hydrogenation
- (b) Done so as to produce the more stable pair of ions
- (c) Homolytic
- (d) Heterolytic
- (e) None of the above

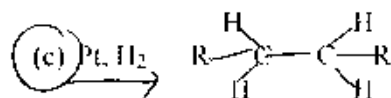
8. Choose the best statement.  $R-C=C-R$  reacts with the following to give the product shown:



*Lindlar's is syn*



*dissolving metal is anti*



(d) All reactions are correct.

9. For reaction mechanisms which of the following are true or the best statement

(a) E1 and E2 are both elimination reaction mechanisms which result in a substitution product. *elimination*

(b) S<sub>N</sub>1 and S<sub>N</sub>2 are both substitution reaction mechanism which results in an alkene product. *substitution*

(c) S<sub>N</sub>1 and E1 reaction mechanisms have a one step reaction mechanism

(d) S<sub>N</sub>2 and E2 reaction mechanisms have bimolecular kinetics.

(e) All of the above are true.

10. How many asymmetric carbon atoms are present in the following compound ?



(a) 0

(b) 1

(c) 2

(d) 3

(e) 4

11. A molecule with 4 pairs of VSEPR electron pairs around the central atom has:

- a) trigonal bipyramidal,  $120^\circ$  angle
- b) trigonal planar,  $90^\circ$  angle
- c) tetrahedral geometry,  $109.5^\circ$  angle
- d) octahedral geometry,  $120^\circ$  angle

12. For elimination reactions choose the one best statement.

- (a) Both the E1 and E2 reaction mechanism result in Zaitsev's Rule products
- (b) ~~Hofmann's~~ Hofmann's Rule products are the most stable alkene product
- (c) ~~Zaitsev's~~ Zaitsev's Rule product is the least stable alkene products
- (d) All statements above are true.

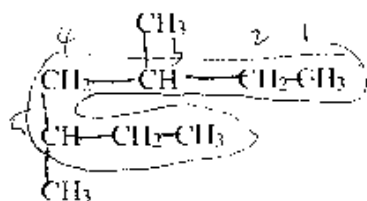
Part II. Short Answers (40 pts)

A. Nomenclature: (2 pts each, 6 pts)

1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name

3,5-dimethylheptane

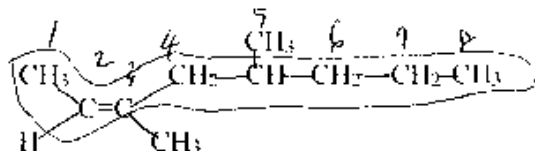


heptane

3,5-dimethyl

b. name

Z-3,5-dimethyl oct-2-ene



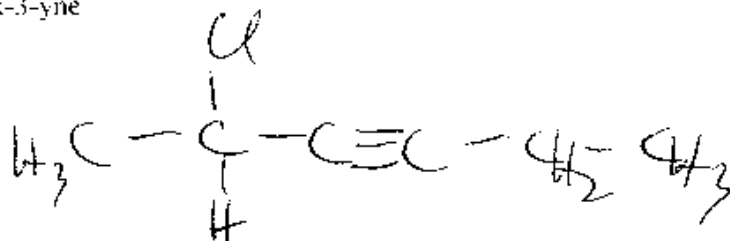
~~octane~~

2-ene

3,5-dimethyl

2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

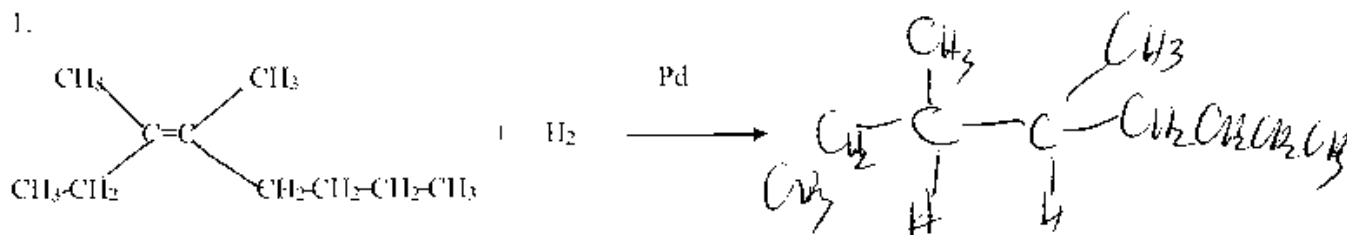
2-chlorohex-3-yne



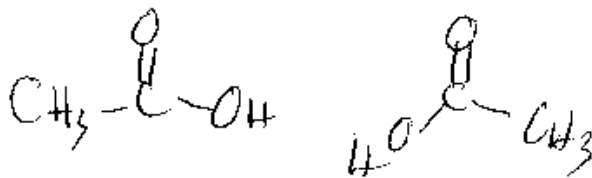
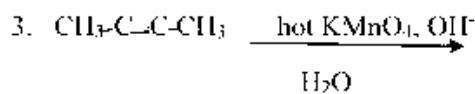
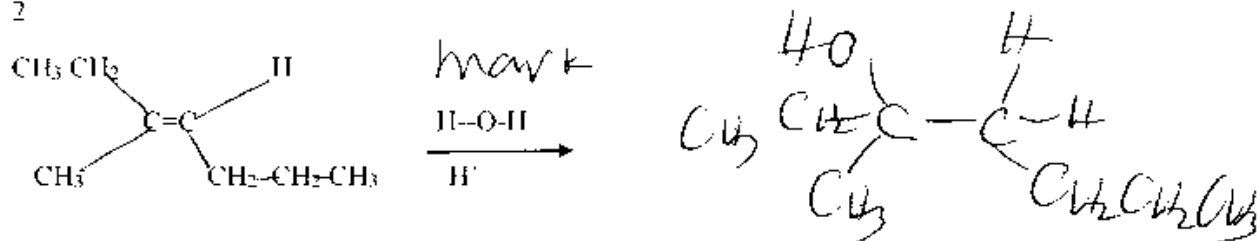
B. Reactions: Show the Organic Product for the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is not acceptable.) **DO NOT SHOW MECHANISMS.**

**Circle the number of the 5 reaction which you want counted.** If you do not choose, I will just grade the first 5 reactions. (2 pts each, 10 pts total)

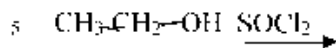
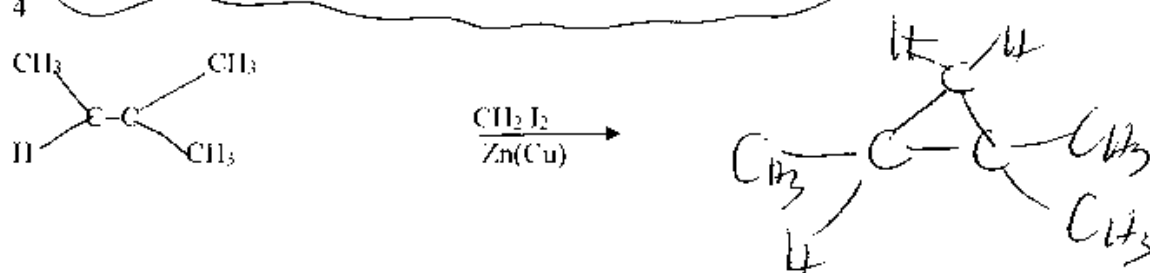
1.



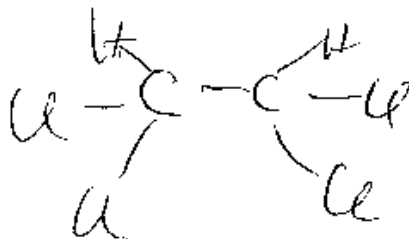
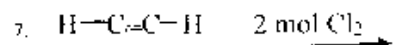
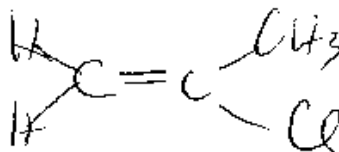
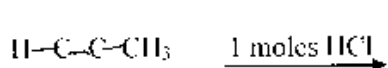
2



4



6.

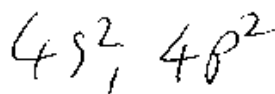


C. Short Answers part of Short Answers: (24 pts)

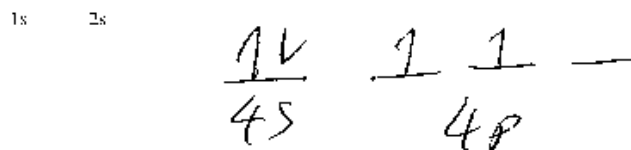
1. a. For the element **Ge** show the electron configuration for all electrons in the format  $1s^2, 2s^2, \dots$  etc (8 pts total) (2 pts this question)



- b. For the same element show the electron configuration for all **valence** electrons in the same format. (1 pt)



- c. For the same element, show the **valence** electron configuration orbital diagram in the format:  $\uparrow \downarrow \uparrow$  etc; using up and down arrows to represent electrons. (2 pts this question)

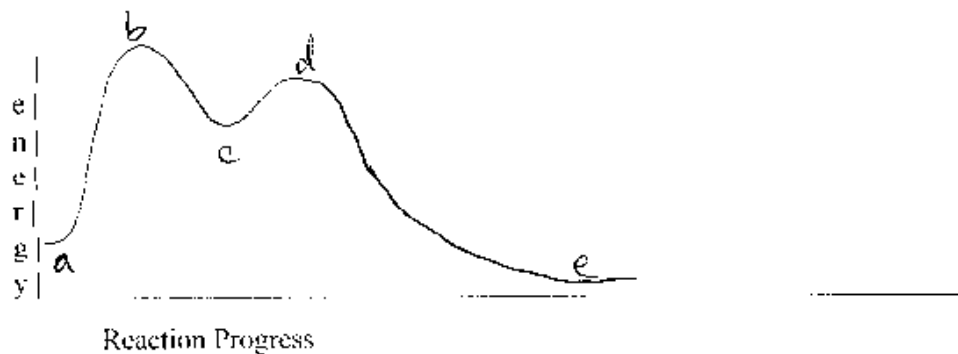


- d. For the same element, what is the **group number**? 4A (1 pt)

- e. For the same element, what is the **atomic mass**? 72.6 (1 pt)

- f. For the same element, what is the **atomic number**? 32 (1 pt)

2. Given the following energy diagram. (2 pt each, total 8 pts)



- a) How many steps is in the reaction mechanism shown [(1), (2), (3), (4)] (circle one)
- b) Which of the steps is the slowest step [(1<sup>st</sup> step), (2<sup>nd</sup> step), (3<sup>rd</sup> step), (4<sup>th</sup> step)] (circle one)

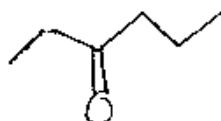
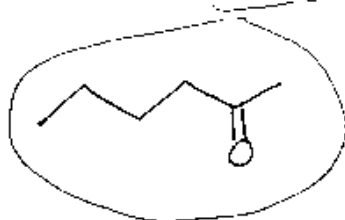
(note: just because I gave 4 potential steps does not necessarily mean that there are actually 4 steps – it could be less or more)

- c) Circle the label of all intermediates? [(a), (b), (c), (d), (e), (f)] (circle all that apply)
- d) Circle the label of all transition states. [(a), (b), (c), (d), (e), (f)] (circle all that apply)

3 Answer the following by circling one, to as many as all of the reactions mechanisms under each letter. (4 pts, 2 pts each letter)

- a. A tertiary substrate is best for [(S<sub>N</sub>2), (S<sub>N</sub>1), (E2), (E1)] (circle all correct mechanism)
- b. A strong bulky base but weak nucleophile favors [(S<sub>N</sub>2), (S<sub>N</sub>1), (E2), (E1)] (circle all correct mechanism)

4. Given the following molecule, draw one structural (also known as constitutional) isomers (4 pts)

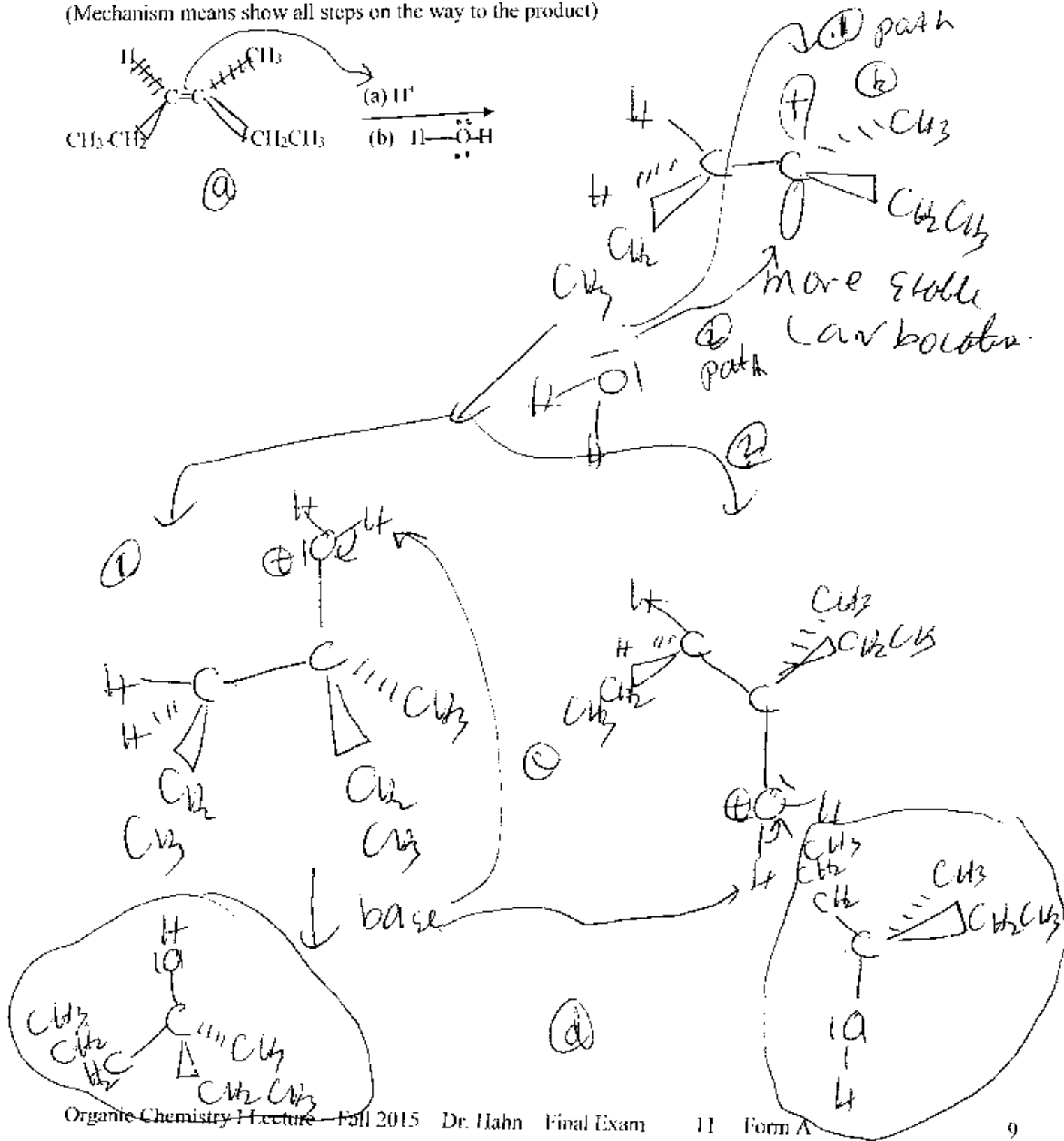


*+ many more*

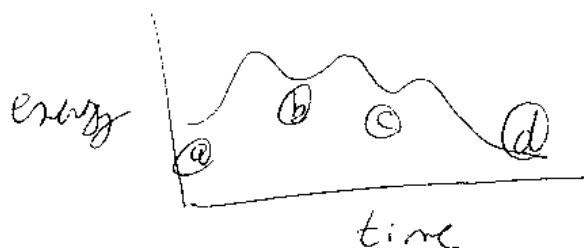


Part III. Long Answers (36 pts) Show work where applicable for partial and full credit.

1. A. Complete the following reaction mechanism. **Show all intermediates in 3D (show the empty p orbital if there is one during the reaction mechanism)** but not the transition state structures. Show electron pushing arrows and completely drawn Lewis Dot (or Kekule) structures for each step of the reaction mechanism and the correct regiochemistry and stereochemistry if required. (19 pts total, 10 pts this part) (Mechanism means show all steps on the way to the product)



B. Draw an energy diagram which matches your reaction mechanism. Label reactants, products, all intermediates **above in your mechanism with the letters (a), (b), (c), ... etc.** and then label your energy diagram below. (4 pts)



C. Does the reaction above follow Markovnikov's Rule?  (yes)  (no) (circle a parenthesis) Give any version of the definition of Markovnikov's Rule using a sentence or two. (2 pts)

"Them that has, gets" (H)  
"E" addition goes by most stable carbocation intermediate

D. There is a chiral center in the product. Is the chiral center racemic?  (yes)  (no) Explain. (3 pts)

goes by flat carbocation intermediate  
can come in with H<sub>2</sub>O from top  
or bottom in 50:50 ratio so  
racemic

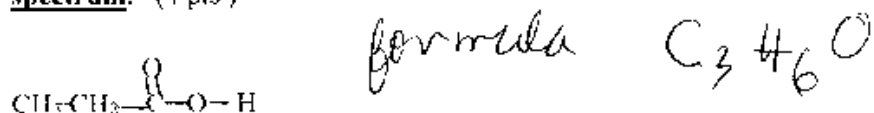
2. Let's completely structurally identify the following molecule which you expect will be produced in the reaction product that you have spent a half a year synthesizing and purifying. To figure out if you successfully made the product, we are going to do a thought experiment to show what your spectra for the molecule should look like.

If everything matches up (meaning you run the spectra and your spectra exactly match what you expect your spectra to look like), you can then dance in the street because you have completed your 10 step synthesis which will allow you to complete your doctorate after doing some arm waving to explain why your molecule is so important. (not really obviously because this molecule is not really important but I am trying to make this question as exciting as possible because I know that by now your brain has turned to mush after all the hard work of studying for and completing your exam.)

and no your grade will not be impacted by what you want to do for the rest of your life none of my business. (17 pts total)

Part I: Mass Spectra: (4 pts)

Given the molecule below, show your calculation of the number for the molecular ion peak in a mass spectrum. (4 pts)



$$3(12) + 4(1) + 2(16) = 58$$

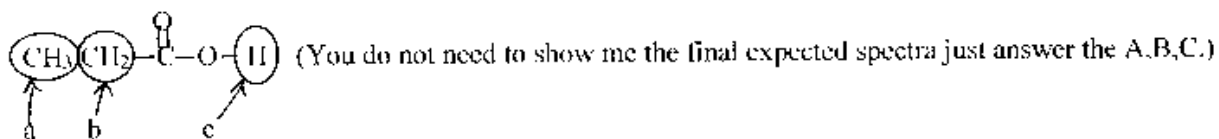
Part II: Infrared Spectra: (4 pts)

Given the molecule above, give at least 2 functional group IR peaks which you expect based on the given IR chart. Give the number of the expected peak and which part of the molecule would show that IR peaks (1 pt per blank)

1710  $\text{cm}^{-1}$  for C=O carboxylic acid stretch or bend

2500-3100  $\text{cm}^{-1}$  for OH of carboxylic acid stretch or bend

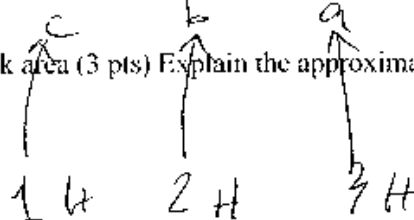
Part III: NMR Spectra (9 pts) (note: I circled the parts of the molecule for the NMR part of this question. I mean the protons inside the circles even though some of the circles also show other atoms because it is hard to just circle the protons.) Given the same molecule above from the MS and IR part of the question, explain the expected proton NMR spectrum. To do this complete all 3 parts A,B, C



(A): relative chemical shift (3 pts) Draw the approximate relative chemical shift of the protons in the molecule using the labels (a,b,c) which I have provided in the molecule above.



(B): integration peak area (3 pts) Explain the approximate integration peak area for each proton NMR peak



(C): coupling (using  $2nI+1$ ) (3 pts) Explain the coupling for each of the different proton NMR peaks by giving the number of the n and plugging it into the equation  $2nI+1$ .

peak (a) has no neighbors

peak (b)  $\rightarrow n=3, 2(3)\frac{1}{2}+1=4$

peak (c)  $\rightarrow n=2, 2(2)\frac{1}{2}+1=3$

Sign Name Key Print Name \_\_\_\_\_

(5 pt name above print & sign If I can't tell who you are from NO NAME above, I have to go back to the exam taking map and hope that I can read your name on that or I may end up with an exam with no identity permanently), (5 pts scantron name – if you don't bubble in I get a grade with no name and I have to hold everyone's final grades until I figure out whose exam it is.) (100 pts, 12 pages + scantron sheet)

Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. **I will only grade what I can read (obviously).** I am not going to make up an answer for you based on writing I can't read. (use back of exam for scratch paper - If you want me to grade something not in the space for the answer, **clearly specify in writing.** Telling me during the exam where to find the answer does not qualify because I will just vaguely remember someone telling me something during the exam not which one of 250 students told me what to grade on what page.) *color*

Circle answer on this form for backup to the scantron. There is no partial credit for showing work in the multiple choice.

In all questions on all parts of this exam, R is not equal to hydrogen but is an alkyl.

1. Multiple Choice ( 2 pts each, 24 pts) Choose the **one** best statement in each question. There is no partial credit for showing work on the multiple choice questions.

1. The element Ge has how many total number of electrons ?

- a) 4 electrons
- b) 14 electrons
- c) 72 electrons
- d) 32 electrons

2. Which of the following statements correctly pertains to a pair of enantiomers ?

- (a) They have different melting points.
- (b) They rotate the plane of polarized light by differing amounts and in opposite directions
- (c) They have the same melting points but they have different boiling points.
- (d) They rotate the plane of polarized light by exactly the same amount and in opposite directions.
- (e) They rotate the plane of polarized light by differing amounts and in the same direction.

3. A molecule with 4 pairs of VSEPR electron pairs around the central atom has:

- a) trigonal bipyramidal, 120° angle
- b) trigonal planar, 90° angle
- c) tetrahedral geometry, 109.5° angle
- d) octahedral geometry, 120° angle

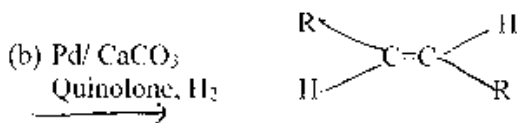
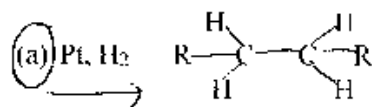
4. Which of the following bonds is a covalent bond ?

- a)  $\text{Li}_2\text{O}$
- b)  $\text{BaO}$
- c)  $\text{SO}_2$
- d)  $\text{MgCl}_2$

5. A radical reaction mechanism is:

- (a) Heterolytic
- (b) Done so as to produce the more stable pair of ions
- (c) Homolytic
- (d) Via hydrogenation
- (e) None of the above

6. Choose the best statement.  $\text{R}-\text{C}=\text{C}-\text{R}$  reacts with the following to give the product shown:

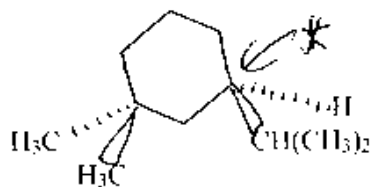


(d) All reactions are correct.

7. For reaction mechanisms which of the following are true or the best statement

- (a)  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  are both substitution reaction mechanism which results in an alkene product.
- (b)  $\text{S}_{\text{N}}1$  and  $\text{E}1$  reaction mechanisms have a ~~one~~<sup>two</sup> step reaction mechanism
- (c)  $\text{S}_{\text{N}}2$  and  $\text{E}2$  reaction mechanisms have bimolecular kinetics.
- (d)  $\text{E}1$  and  $\text{E}2$  are both elimination reaction mechanisms which result in a substitution product.
- (e) All of the above are true.

8. How many asymmetric carbon atoms are present in the following compound ?



- (a) 2
- (b) 3
- (c) 4
- (d) 0
- (e) 1

9. Given the following,

- (a) RO<sup>-</sup> is a better nucleophile than HO<sup>-</sup>
- (b) RO<sup>-</sup> is a better nucleophile than ROH
- (c) HO<sup>-</sup> is a better nucleophile than H<sub>2</sub>O
- (d) Nucleophilicity is interaction with carbon while Basicity is interaction with hydrogen
- (e) All above statements are true.

10. For elimination reactions choose the one best statement.

- (a) Both the E1 and E2 reaction mechanism result in Zaitsev's Rule products
- (b) Zaitsev's Rule product is the least stable alkene products
- (c) Hoffmann's Rule products are the most stable alkene product
- (d) All statements above are true.

11. Choose the best statement.

- (a) There is no coupling between carbon and another carbon in carbon NMR because the natural abundance of carbon 13 is only 1.1% so there is almost never an NMR active neighboring carbon.
- (b) In IR spectroscopy the ~~functional group~~ <sup>finger print</sup> region is  $1500\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  and the ~~finger print~~ <sup>functional gr.</sup> region is between  $4000\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ .
- (c) Proton NMR has splitting in the coupling pattern is based on  $2nI + 1$  where  $I = \frac{1}{2}$  and  $n =$  number of neighboring protons.
- (d) (a) and (c) are correct.
- (e) All statements are correct.

12. For intermolecular forces the general progression from strongest to weakest intermolecular force is :

- a) Dipolar > hydrogen bonding > van der Waals
- b) Hydrogen bonding > dipolar > van der Waals
- c) Van der Waals > hydrogen bonding > dipolar
- d) None of the above is correct.

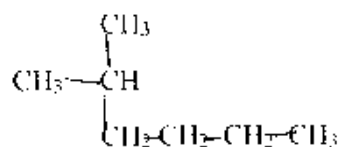


Part II. Short Answers (40 pts)

A. Nomenclature: (2 pts each, 6 pts)

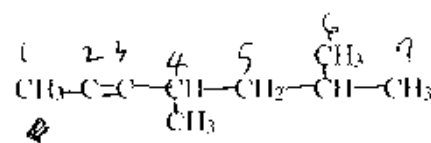
1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name \_\_\_\_\_



2-methylhexane

b. name 4,6-dimethyl-2-heptyne

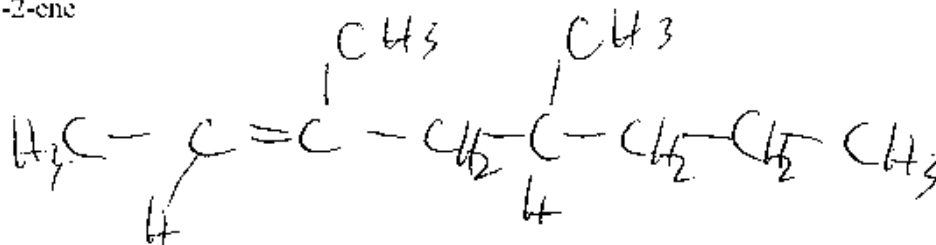


2-heptyne

4,6-dimethyl

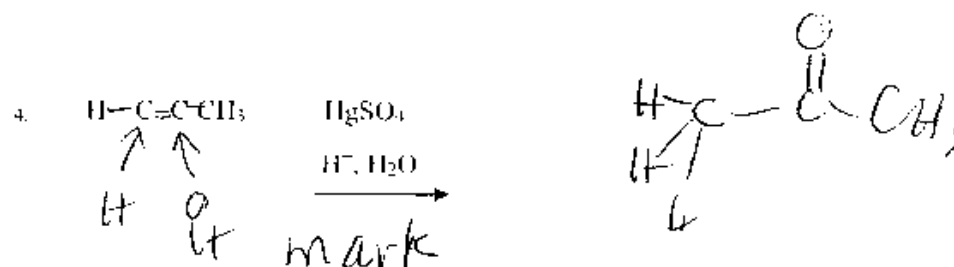
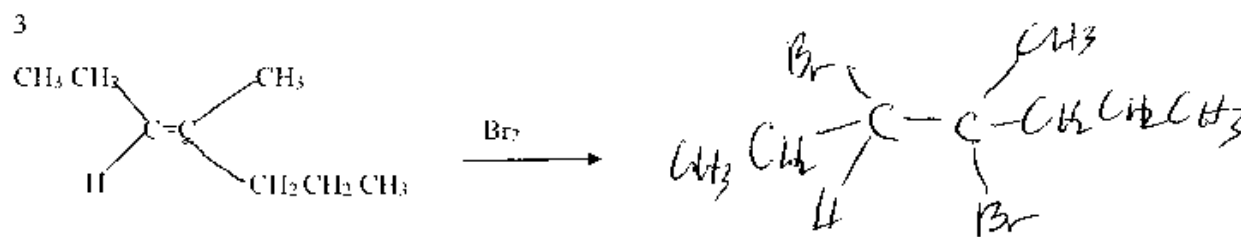
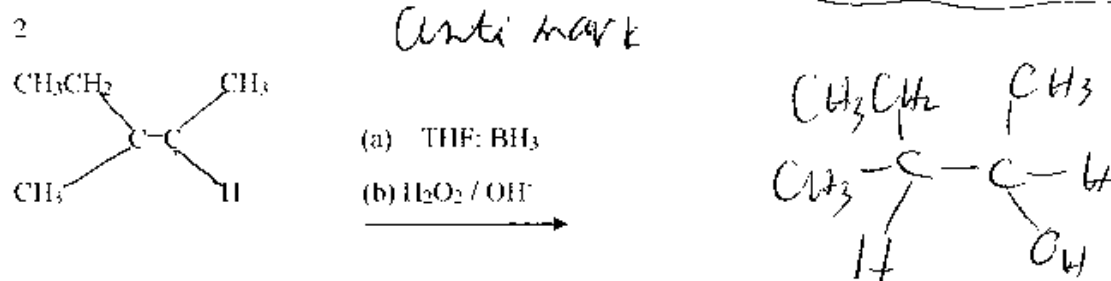
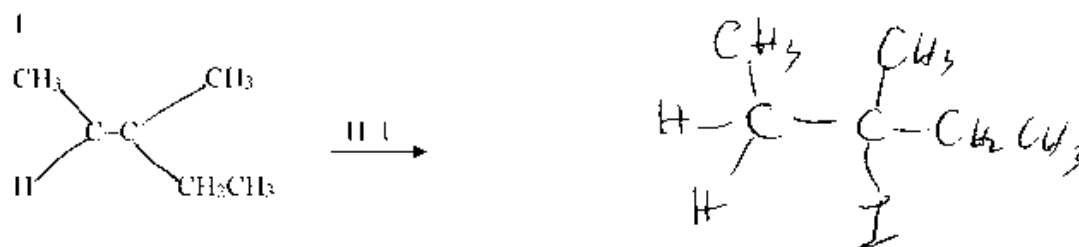
2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

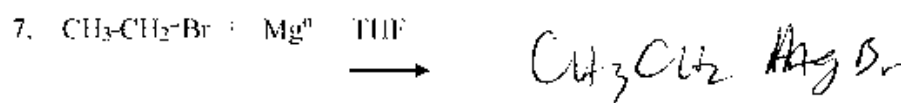
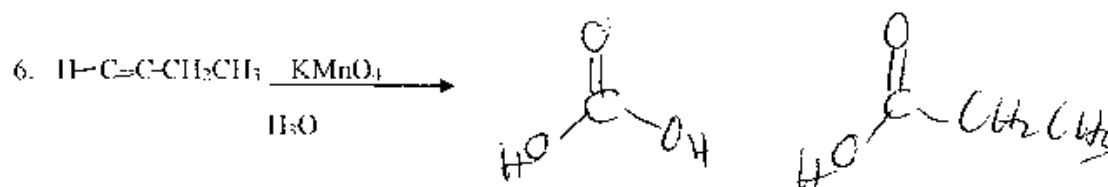
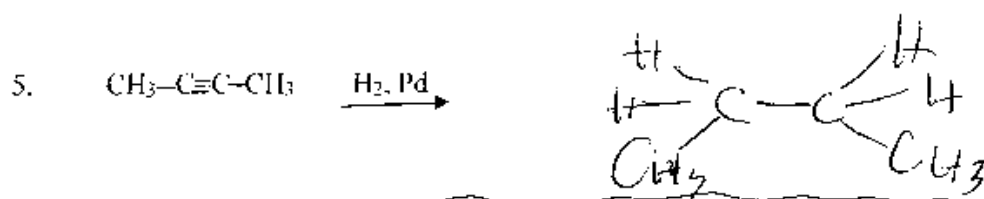
3,5-dimethyloct-2-ene



B. Reactions: Show the Organic Product for the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is **not** acceptable.) DO **NOT** SHOW MECHANISMS.

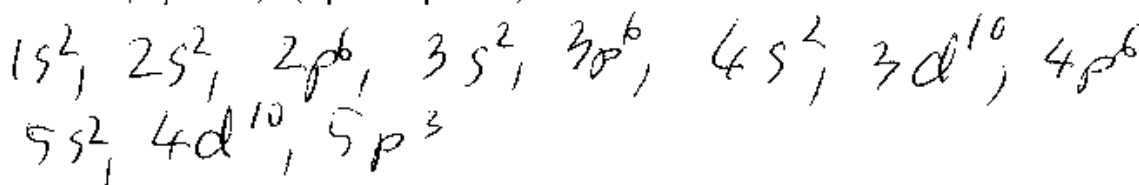
**Circle the number of the 5 reaction which you want counted.** If you do not choose, I will just grade the first 5 reactions. (2 pts each, 10 pts total)



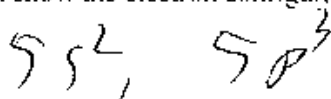


C. Short Answers part of Short Answers: (24 pts)

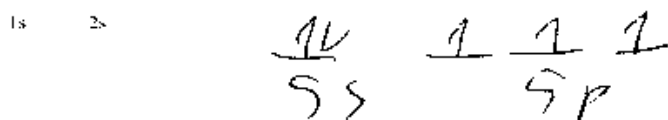
1. a. For the element Sb, show the electron configuration for all electrons in the format  $1s^2, 2s^2, \dots$  etc (8 pts total) (2 pts this question)



- b. For the same element show the electron configuration for all valence electrons in the same format. (1 pt)



- c. For the same element, show the valence electron configuration orbital diagram in the format:  $\{\uparrow\downarrow, \downarrow, \dots\}$  etc) using up and down arrows to represent electrons. (2 pts this question)

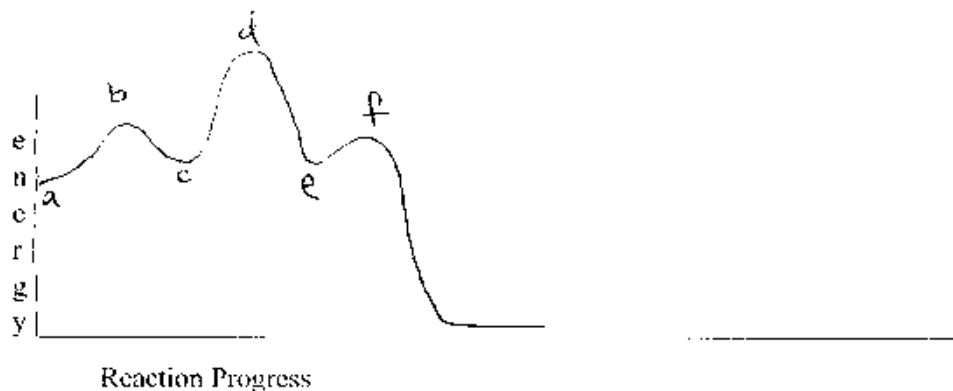


- d. For the same element, what is the group number? 5A (1 pt)

- e. For the same element, what is the atomic mass? 121.760 (1 pt)

- f. For the same element, what is the atomic number? 51 (1 pt)

2. Given the following energy diagram. (2 pt each, total 8 pts)



- a) How many steps is in the reaction mechanism shown [(1), (2), (3), (4)] (circle one)
- b) Which of the steps is the slowest step [(1<sup>st</sup> step), (2<sup>nd</sup> step), (3<sup>rd</sup> step), (4<sup>th</sup> step)] (circle one)

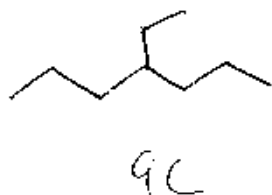
(note: just because I gave 4 potential steps does not necessarily mean that there are actually 4 steps – it could be less or more)

- c) Circle the label of all intermediates? [(a), (b), (c), (d), (e), (f)] (circle all that apply)
- d) Circle the label of all transition states. [(a), (b), (c), (d), (e), (f)] (circle all that apply)

3. Answer the following by circling one, to as many as all of the reactions mechanisms under each letter. (4 pts, 2 pts each letter)

- a. A tertiary substrate is best for [(S<sub>N</sub>2), (S<sub>N</sub>1), (E2), (E1)] (circle all correct mechanism)
- b. A strong bulky base but weak nucleophile favors [(S<sub>N</sub>2), (S<sub>N</sub>1), (E2), (E1)] (circle all correct mechanism)

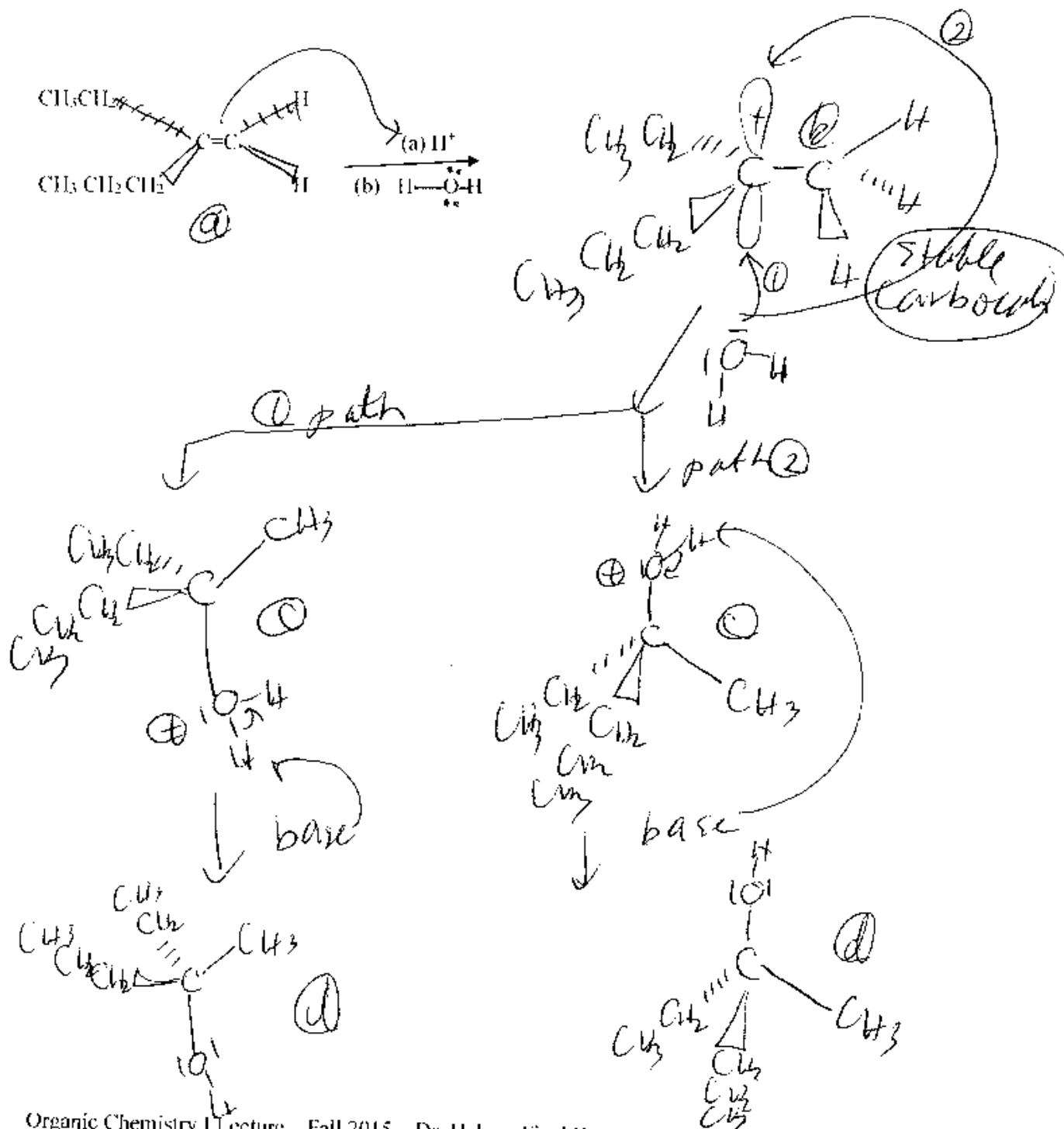
4. Given the following molecule, draw one structural (also known as constitutional) isomers (4 pts)



*I'm trying more*

Part III. Long Answers (36 pts) Show work where applicable for partial and full credit.

1. a. Complete the following reaction mechanism. **Show all intermediates in 3D (show the empty p orbital if there is one during the reaction mechanism) but not the transition state structures.** Show electron pushing arrows and completely drawn Lewis Dot (or Kekule) structures for each step of the reaction mechanism and the correct regiochemistry and stereochemistry if required. (19 pts total, 10 pts this part) (Mechanism means show all steps on the way to the product)



b Draw an energy diagram which matches your reaction mechanism. Label reactants, products, all intermediates **above in your mechanism with the letters (a), (b), (c), ... etc.** and then label your energy diagram below. (4 pts)



c. Does the reaction above follow Markovnikov's Rule?  (yes)  (no) (circle a parenthesis) Give any version of the definition of Markovnikov's Rule using a sentence of two. (2 pts)

"The one that has (H) gets (H)"

Electrophilic addition goes by most stable carbocation intermediate

d. There is a chiral center in the product. Is the chiral center racemic?  (yes)  (no) Explain. (3 pts)

Carbocation is flat OH comes in equally from both sides so 50:50 of 2 enantiomers.

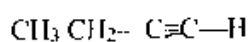
2. Let's completely structurally identify the following molecule which you expect will be produced in the reaction product that you have spent a half a year synthesizing and purifying. To figure out if you successfully made the product, we are going to do a thought experiment to show what your spectra for the molecule should look like.

If everything matches up (meaning you run the spectra and your spectra exactly match what you expect your spectra to look like), you can then dance in the street because you have completed your 10 step synthesis which will allow you to complete your doctorate after doing some arm waving to explain why your molecule is so important. (not really obviously because this molecule is not really important but I am trying to make this question as exciting as possible because I know that by now your brain has turned to mush after all the hard work of studying for and completing your exam.)

and no your grade will not be impacted by what you want to do for the rest of your life none of my business. (17 pts total)

Part I: Mass Spectra: (4 pts)

Given the molecule below, show your calculation of the number for the molecular ion peak in a mass spectrum. (4 pts)



formula  $\text{C}_4\text{H}_6$

$$4(12) + 6(1) = 54 = \text{molecular ion peak}$$

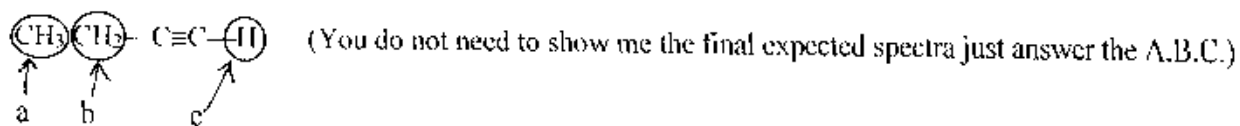
Part II: Infrared Spectra: (4 pts)

Given the molecule above, give at least 2 functional group IR peaks which you expect based on the given IR chart. Give the number of the expected peak and which part of the molecule would show that IR peak. (1 pts each blank)

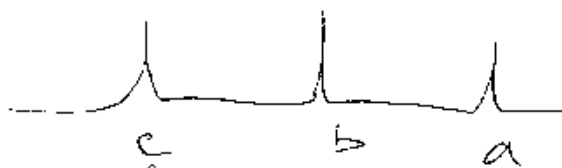
2100-2260  $\text{cm}^{-1}$  for  $\text{C}\equiv\text{C}$  stretch or bend

3300  $\text{cm}^{-1}$  for  $\text{C-H}$  stretch or bend

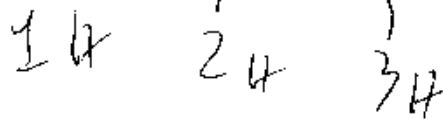
Part III: NMR Spectra (9 pts) (note: I circled the parts of the molecule for the NMR part of this question. I mean the protons inside the circles even though some of the circles also show other atoms because it is hard to just circle the protons.) Given the same molecule above from the MS and IR part of the question, explain the expected proton NMR spectrum. To do this complete all 3 parts A,B, C



(A): relative chemical shift (3 pts) Draw the approximate relative chemical shift of the protons in the molecule using the labels (a,b,c) which I have provided in the molecule above.



(B): integration peak area (3 pts) Explain the approximate integration peak area for each proton NMR peak



(C): coupling (using  $2nI + 1$ ) (3 pts) Explain the coupling for each of the different proton NMR peaks by giving the number of the n and plugging it into the equation  $2nI + 1$ .

Ⓐ  $n = \text{zero}, \text{ no coupling}$

Ⓑ  $n = 3, 2(3)\frac{1}{2} + 1 = 4$

Ⓒ  $n = 2, 2(2)\frac{1}{2} + 1 = 3$



Sign Name Key \_\_\_\_\_ Print Name \_\_\_\_\_

(5 pt name above print & sign – If I can't tell who you are from NO NAME above, I have to go back to the exam taking map and hope that I can read your name on that or I may end up with an exam with no identity permanently), (5 pts scantron name – if you don't bubble in I get a grade with no name and I have to hold everyone's final grades until I figure out whose exam it is.)(100 pts, 13 pages + scantron sheet)

Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. **I will only grade what I can read (obviously).** I am not going to make up an answer for you based on writing I can't read. (use back of exam for scratch paper – If you want me to grade something not in the space for the answer, **clearly specify in writing.** Telling me during the exam where to find the answer does not qualify because I will just vaguely remember someone telling me something during the exam not which one of 250 students told me what to grade on what page.)

Circle answer on this form for backup to the scantron. There is no partial credit for showing work in the multiple choice.

In all questions on all parts of this exam, R is not equal to hydrogen but is an alkyl.

I. Multiple Choice ( 2 pts each, 24 pts) Choose the **one** best statement in each question. There is no partial credit for showing work on the multiple choice questions.

1. Which of the following intermediates is thought to occur in the mechanism by which alkenes are hydrated in the presence of acid ?

- a) carbocation
- b) carbanion
- c) free radical
- d) carbene
- e) alkyne

2. For a given reaction, if  $\Delta G^\circ$  is greater than zero (positive), then:

- a) The reaction is going downhill in energy and will go to product.
- b) The reaction is going really fast.
- c) The reaction is going uphill in energy and will not go to product.
- d) All statements are true.
- e) All statements are false.

3. Given the following.

- (a)  $\text{RO}^-$  is a better nucleophile than  $\text{HO}^-$
- (b)  $\text{RO}^-$  is a better nucleophile than  $\text{ROH}$
- (c)  $\text{HO}^-$  is a better nucleophile than  $\text{H}_2\text{O}$
- (d) Nucleophilicity is interaction with carbon while Basicity is interaction with hydrogen

(e) All above statements are true.

4. Choose the largest dipole moment among the bonds shown.

- a)  $\text{C}-\text{Cl}$
- a)  $\text{Cl}-\text{Cl}$
- b)  $\text{N}-\text{Cl}$
- c)  $\text{C}-\text{F}$

5. Choose the tertiary alkyl halide from the list below

a)  $\text{CH}_3\text{CH}_2\text{Cl}$

b)  $\text{CH}_3\overset{\text{CH}_3}{\text{CH}}-\text{Cl}$

c)  $\text{CH}_3\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Br}$

d)  $\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Cl}$

6. For intermolecular forces the general progression from strongest to weakest intermolecular force is :

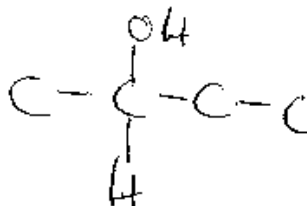
- a) Hydrogen bonding > dipolar > van der Waals
- b) Van der Waals > hydrogen bonding > dipolar
- c) Dipolar > hydrogen bonding > van der Waals
- d) None of the above is correct.

7. What synthetic goal is achieved by subjecting an alkene to an oxymercuration-demercuration sequence?

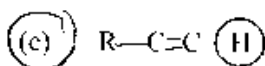
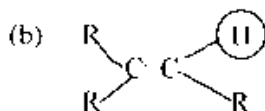
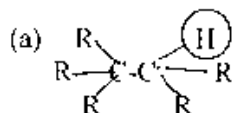
- a) Markovnikov addition of  $\text{H}_2\text{O}$  wherein skeletal rearrangement is prevented.
- b) Markovnikov addition of  $\text{H}_2\text{O}$  wherein skeletal rearrangement is promoted.
- c) Syn-hydroxylation
- d) Anti-Markovnikov addition of  $\text{H}_2\text{O}$  wherein skeletal rearrangement is prevented.
- e) Anti-Markovnikov addition of  $\text{H}_2\text{O}$  wherein skeletal rearrangement is promoted.

8. Which of the following statements is (are) true for the compound (R)-2-butanol?

- a) This compound has an enantiomer
- b) This compound is optically active.
- c) This compound is chiral.
- d) All of the above.
- e) None of the above.



9. Given the following molecules, the most acidic proton, the circled proton, in the given molecule is:



(d) All of the hydrogens are equal in acidity.

10. For the  $\text{S}_{\text{N}}2$  reaction mechanism,

- (a) If you increase the concentration of the nucleophile by 2 times, the rate will increase by 2 times.
- (b) If you decrease the concentration the substrate by  $\frac{1}{2}$  times the rate will decrease by  $\frac{1}{2}$  times.
- (c) The concentration of the nucleophile has no effect on the rate.
- d) (a) and (b) are correct
- (e) (a) (b) and (c) are all correct.

11. Choose the one best statement.

- (a) If a reaction follows Markovnikov's Rule for an alkene reaction, then the alkyne reaction will follow ~~anti~~-Markovnikov's Rule.
- (b) For an alkyne,  $HX$  ( $X = \text{halogen}$ ), can only be added one time <sup>+ 2 times</sup> to result in an alkene.
- (c) When you add water (using  $H^+$  and  $H_2O$ ) to an Alkyne, you get no reaction.
- (d) When you add water to an Alkyne using the  $Hg(OAc)_2$ , you get an ~~anti~~-Markovnikov addition which then does a tautomerism

12. Choose the best statement.

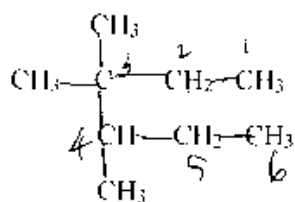
- (a) Proton NMR has splitting in the coupling pattern based on  $2nI + 1$  where  $I = \frac{1}{2}$  and  $n =$  number of neighboring protons.
- (b) Carbon NMR has splitting in the coupling pattern based on  $2nI + 1$  where  $I = \frac{1}{2}$  and  $n =$  number of neighboring carbons. ~~protons~~
- (c) In IR spectroscopy the functional group region is  $1500\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  and the finger print region is between  $4000\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ .
- (d) (a) and (b) are correct.
- (e) All statements are correct.

Part II. Short Answers ( 40 pts)

A. Nomenclature: (2 pts each, 6 pts)

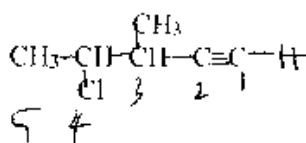
1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name 3,3,4-trimethyl hexane



hexane  
3,3,4-trimethyl

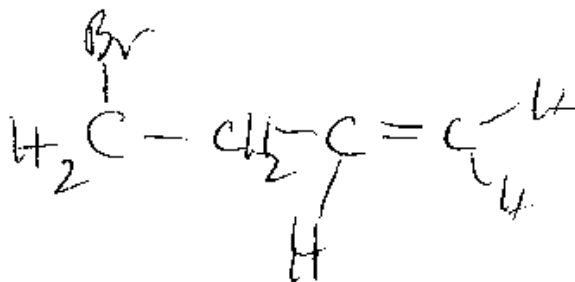
b. name 4-chloro-3-methylpent-1-yne



1-pent-yne  
3-methyl  
4-chloro

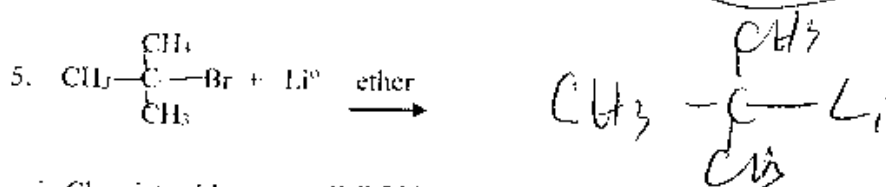
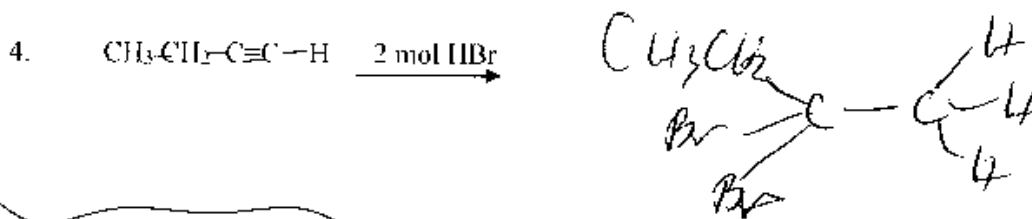
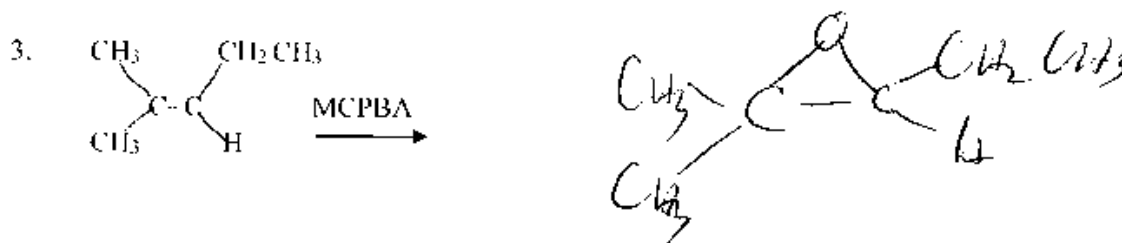
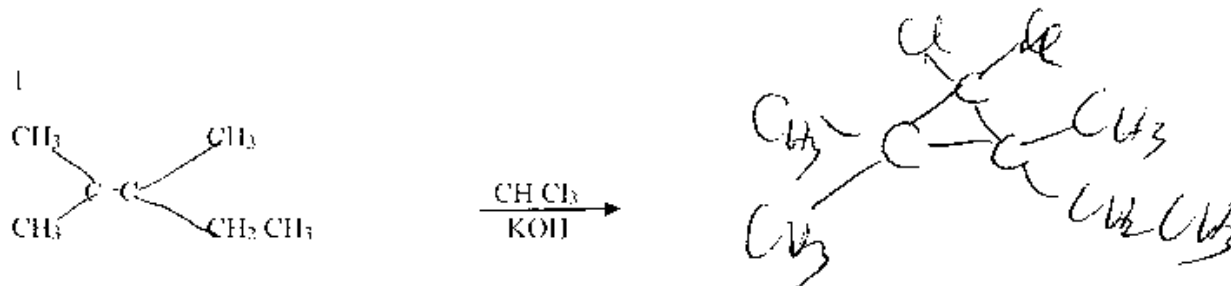
2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

4-bromobut-1-ene

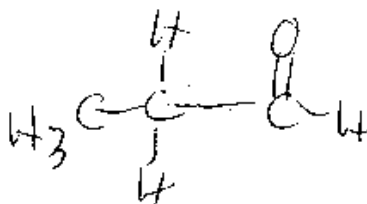
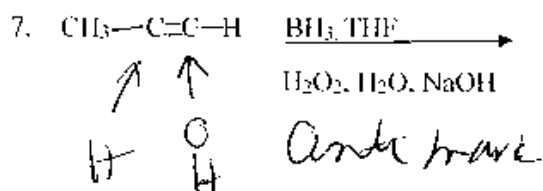


B. Reactions: Show the Organic Product for the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is not acceptable.) **DO NOT SHOW MECHANISMS.**

**Circle the number of the 5 reaction which you want counted.** If you do not choose, I will just grade the first 5 reactions. (2 pts each, 10 pts total)

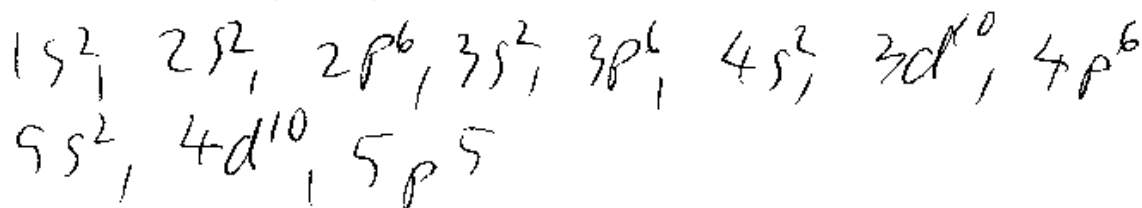


6.

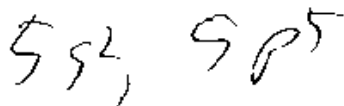


C. Short Answers part of Short Answers: (24 pts)

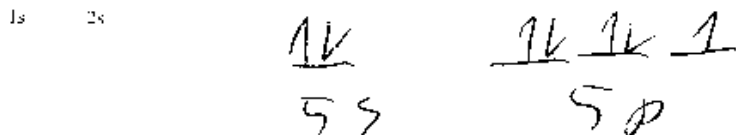
1. a. For the element **(I)** show the electron configuration for all electrons in the format  $1s^2, 2s^2, \dots$  etc (8 pts total) (2 pts this question)



- b. For the same element show the electron configuration for all **valence** electrons in the same format. (1 pt)



- c. For the same element, show the **valence** electron configuration orbital diagram in the format:  $\{\uparrow\downarrow, \downarrow, \dots\}$  etc using up and down arrows to represent electrons. (2 pts this question)

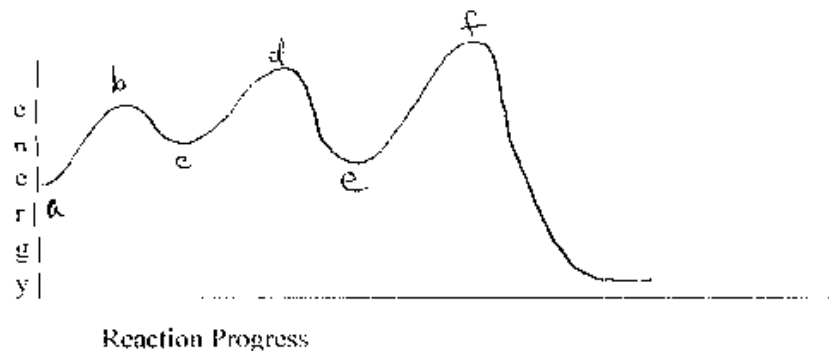


- d. For the same element, what is the **group number**? 7A (1 pt)

- e. For the same element, what is the **atomic mass**? 126.9 (1 pt)

- f. For the same element, what is the **atomic number**? 53 (1 pt)

2 Given the following energy diagram, (2 pt each, total 8 pts)



- a) How many steps is in the reaction mechanism shown [(1), (2), (3), (4)] (circle one)
- b) Which of the steps is the slowest step [(1<sup>st</sup> step) (2<sup>nd</sup> step) (3<sup>rd</sup> step) (4<sup>th</sup> step)] (circle one)

(note: just because I gave 4 potential steps does not necessarily mean that there are actually 4 steps – it could be less or more)

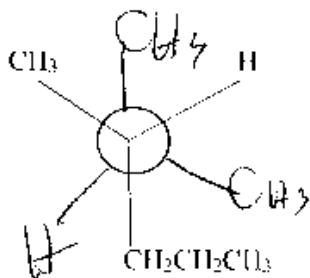
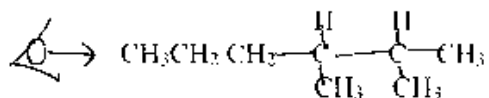
- c) Circle the label of all intermediates? [(a), (b), (c), (d), (e), (f)] (circle all that apply)
- d) Circle the label of all transition states. [(a), (b), (c), (d), (e), (f)] (circle all that apply)

3 Answer the following by circling one, to as many as all of the reactions mechanisms under each letter. (4 pts, 2 pts each letter)

- a. A strong nucleophile or higher concentration nucleophile favors [(S<sub>N</sub>2), (S<sub>N</sub>1), (E2), (E1)] (circle all correct mechanism)
- b. A polar aprotic solvent favors [(S<sub>N</sub>2), (S<sub>N</sub>1), (E2), (E1)] (circle all correct mechanism)



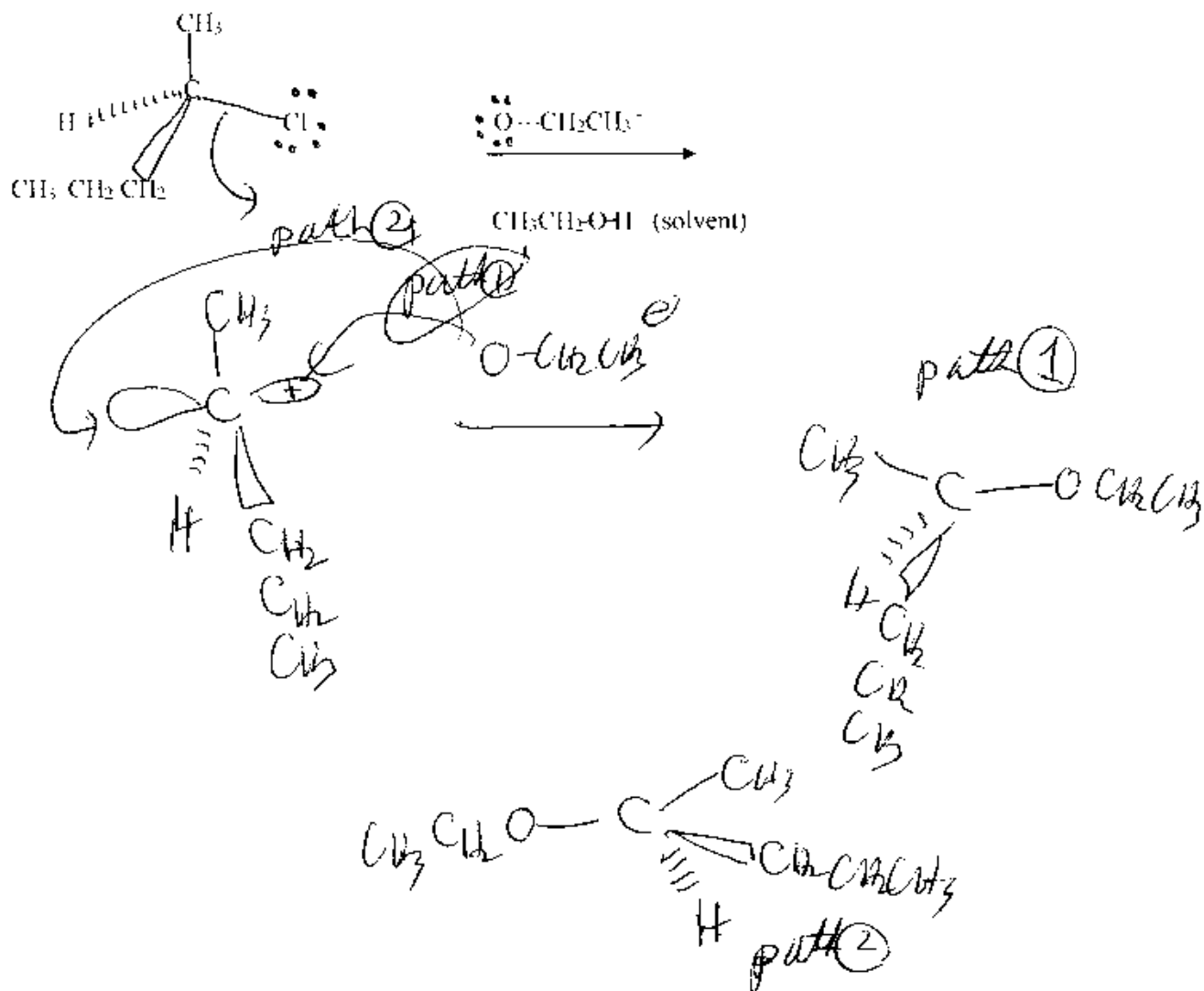
4 For the following molecule, complete the correct Newman projection for: (4 pts) (point of view eye is shown) for the 2,3-dimethylhexane molecule using the 2 and 3 carbons as the 2 Newman projection central atoms. I have shown the front carbon attachment bonds. You have to draw in the correct attachment to the back bonds and show what is attached to the bonds.



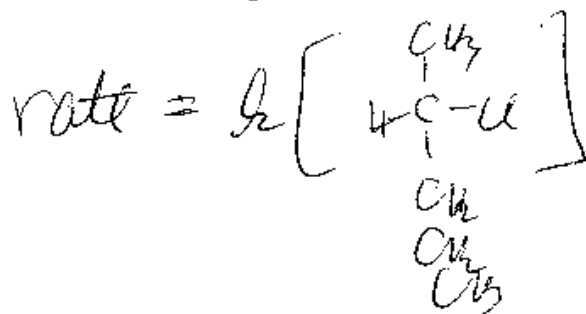
lowest energy Newman Projection formula

Part III. Long Answers (36 pts) Show work where applicable for partial and full credit.

A. Given the following reactant: Assume that the reaction undergoes an  $S_N1$  reaction mechanism. Please show the entire reaction mechanism including electron pushing arrows. Please show either the transition state or intermediate (depending on which is the correct one to show for the mechanism that you have) and the Organic Major Product. Show the reaction mechanism using a 3 D structure including the empty p orbital if appropriate. Show the derivation of the racemic or inverted product as appropriate using your 3 D structure. (10 pts this part, 19 pts total)



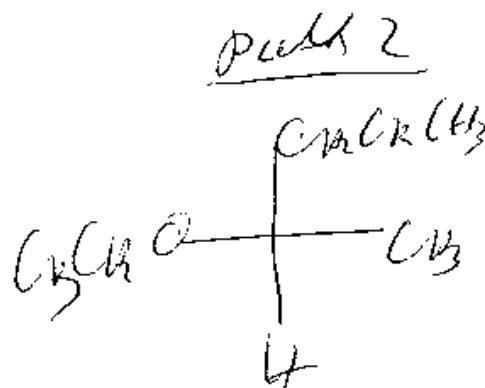
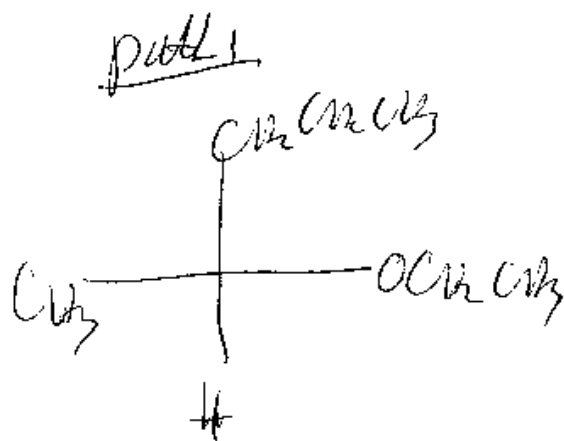
B. Write the rate law for the reaction mechanism using the actual molecule in your reaction above. If you write the rate law using the words substrate or nucleophile, I will count off. (4 pts)



C. If you start the reaction with chiral center (R or S) as shown, is your substitution product (R) or (S) or (racemic) (circle one) (2 pts)

Carbocation is flat so it can come in either by path 1 + path 2

D. Give the Fisher projection formula of the expected product or products. (3 pts)



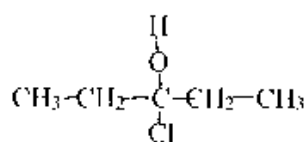
2. Let's completely structurally identify the following molecule which you expect will be produced in the reaction product that you have spent a half a year synthesizing and purifying. To figure out if you successfully made the product, we are going to do a thought experiment to show what your spectra for the molecule should look like.

If everything matches up (meaning you run the spectra and your spectra exactly match what you expect your spectra to look like), you can then dance in the street because you have completed your 10 step synthesis which will allow you to complete your doctorate after doing some arm waving to explain why your molecule is so important. (not really obviously because this molecule is not really important but I am trying to make this question as exciting as possible because I know that by now your brain has turned to mush after all the hard work of studying for and completing your exam.)

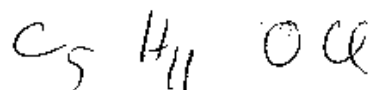
and no your grade will not be impacted by what you want to do for the rest of your life - none of my business. (17 pts total)

Part I: Mass Spectra: (4 pts)

Given the molecule below, show your calculation of the number for the molecular ion peak in a mass spectrum. (4 pts)



formula



$$\begin{array}{ccccccc} 5 & (12) & + & 11 & (1) & + & 16 & + & 35 & = & 122 \\ \text{C} & & & \text{H} & & & \text{O} & & \text{Cl} & & \end{array}$$

molecular ion peak at 122

Part II: Infrared Spectra: (4 pts)

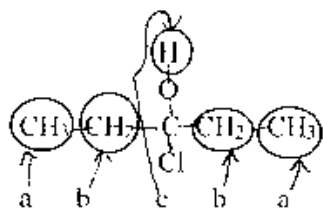
Given the same molecule above, give at least 2 functional group IR peaks which you expect based on the given IR chart. Give the number of the expected peak and which part of the molecule would show that IR peak. (1 pts each blank)

1050-1150  $\longrightarrow$  C-O

3400-3650  $\text{cm}^{-1}$  for O-H alcohol stretch or bend

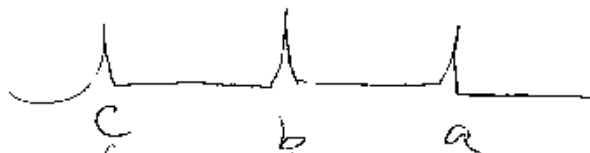
600-800  $\text{cm}^{-1}$  for C-Cl stretch or bend

Part III: NMR Spectra (9 pts) (note: I circled the parts of the molecule for the NMR part of this question. I mean the protons inside the circles even though some of the circles also show other atoms because it is hard to just circle the protons.) Given the same molecule above from the MS and IR part of the question, explain the expected proton NMR spectrum. To do this complete all 3 parts A,B, C



(You do not need to show me the final expected spectra just answer the A,B,C)

(A): relative chemical shift (3 pts) Draw the approximate relative chemical shift of the protons in the molecule using the labels (a,b,c) which I have provided in the molecule above.



(B): integration peak area (3 pts) Explain the approximate integration peak area for each proton NMR peak

1H      4H      6H

(C): coupling (using  $2n+1$ ) (3 pts) Explain the coupling for each of the different proton NMR peaks by giving the number of the n and plugging it into the equation  $2n+1$ .

Ⓒ  $n = \text{zero, no coupling}$

Ⓑ  $n = 3, 2(3) + 1 = 7$

Ⓐ  $n = 2, 2(2) + 1 = 5$

Sign Name \_\_\_\_\_ Print Name \_\_\_\_\_

(5 pt name above print & sign – If I can't tell who you are from NO NAME above, I have to go back to the exam taking map and hope that I can read your name on that or I may end up with an exam with no identity permanently). (5 pts scantron name – if you don't bubble in I get a grade with no name and I have to hold everyone's final grades until I figure out whose exam it is.)(100 pts,12 pages + scantron sheet)

Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. **I will only grade what I can read (obviously)**. I am not going to make up an answer for you based on writing I can't read. (use back of exam for scratch paper – If you want me to grade something not in the space for the answer, **clearly specify in writing**. Telling me during the exam where to find the answer does not qualify because I will just vaguely remember someone telling me something during the exam not which one of 250 students told me what to grade on what page.)

Circle answer on this form for backup to the scantron. There is no partial credit for showing work in the multiple choice.

In all questions on all parts of this exam. R is not equal to hydrogen but is an alkyl.

I. Multiple Choice ( 2 pts each, 24 pts) Choose the **one** best statement in each question. There is no partial credit for showing work on the multiple choice questions.

1. Choose the best statement.

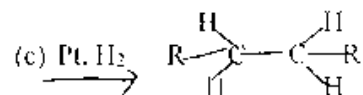
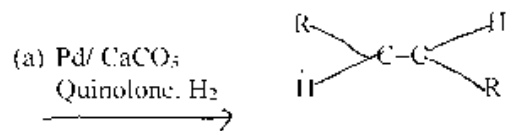
- (a) Proton NMR has splitting in the coupling pattern is based on  $2nI + 1$  where  $I = \frac{1}{2}$  and  $n$  = number of neighboring protons.
- (b) There is no coupling between carbon and another carbon in carbon NMR because the natural abundance of carbon 13 is only 1.1% so there is almost never an NMR active neighboring carbon.
- (c) In IR spectroscopy the functional group region is  $1500\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  and the finger print region is between  $4000\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ .
- (d) (a) and (b) are correct.
- (e) All statements are correct.

2. For intermolecular forces the general progression from strongest to weakest intermolecular force is :

- a) Hydrogen bonding > dipolar > van der Waals
- b) Van der Waals > hydrogen bonding > dipolar
- c) Dipolar > hydrogen bonding > van der Waals
- d) None of the above is correct.

3. Which of the following bonds is a covalent bond ?
- SO<sub>2</sub>
  - BaO
  - MgCl<sub>2</sub>
  - Li<sub>2</sub>O
4. The element Ge has how many total number of electrons ?
- 72 electrons
  - 32 electrons
  - 4 electrons
  - 14 electrons
5. Which of the following statements correctly pertains to a pair of enantiomers ?
- They have different melting points.
  - They rotate the plane of polarized light by differing amounts and in opposite directions
  - They have the same melting points but they have different boiling points.
  - They rotate the plane of polarized light by exactly the same amount and in opposite directions.
  - They rotate the plane of polarized light by differing amounts and in the same direction.
6. Given the following,
- RO<sup>-</sup> is a better nucleophile than HO<sup>-</sup>
  - RO<sup>-</sup> is a better nucleophile than ROH
  - HO<sup>-</sup> is a better nucleophile than H<sub>2</sub>O
  - Nucleophilicity is interaction with carbon while Basicity is interaction with hydrogen
  - All above statements are true.
7. A radical reaction mechanism is:
- Via hydrogenation
  - Done so as to produce the more stable pair of ions
  - Homolytic
  - Heterolytic
  - None of the above

8. Choose the best statement.  $R-C=C-R$  reacts with the following to give the product shown:



(d) All reactions are correct.

9. For reaction mechanisms which of the following are **true or the best statement**

(a) E1 and E2 are both elimination reaction mechanisms which result in a substitution product.

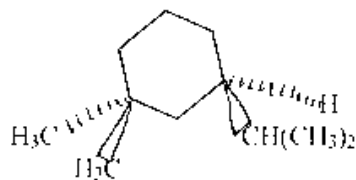
(b) S<sub>N</sub>1 and S<sub>N</sub>2 are both substitution reaction mechanism which results in an alkene product.

(c) S<sub>N</sub>1 and E1 reaction mechanisms have a one step reaction mechanism

(d) S<sub>N</sub>2 and E2 reaction mechanisms have bimolecular kinetics.

(e) All of the above are true.

10. How many asymmetric carbon atoms are present in the following compound ?



(a) 0

(b) 1

(c) 2

(d) 3

(e) 4



11. A molecule with 4 pairs of VSEPR electron pairs around the central atom has:

- a) trigonal bipyramidal,  $120^\circ$  angle
- b) trigonal planar,  $90^\circ$  angle
- c) tetrahedral geometry,  $109.5^\circ$  angle
- d) octahedral geometry,  $120^\circ$  angle

12. For elimination reactions choose the one best statement.

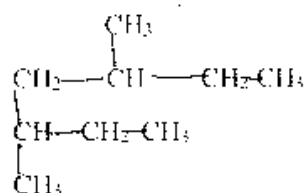
- (a) Both the E1 and E2 reaction mechanism result in Zaitsev's Rule products
- (b) Hoffmann's Rule products are the most stable alkene product
- (c) Zaitsev's Rule product is the least stable alkene products
- (d) All statements above are true.

Part II. Short Answers (40 pts)

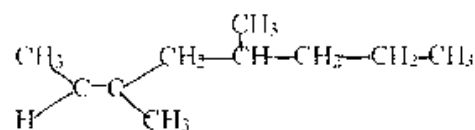
A. Nomenclature: (2 pts each, 6 pts)

1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name \_\_\_\_\_



b. name \_\_\_\_\_



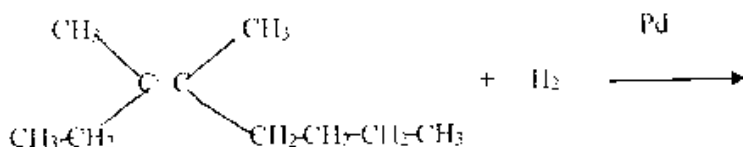
2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

2-chlorohex-3-yne

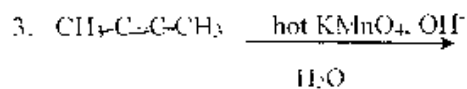
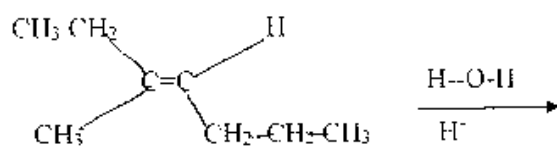
B. Reactions: Show the Organic Product for the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is not acceptable.) DO NOT SHOW MECHANISMS.

Circle the number of the 5 reaction which you want counted. If you do not choose, I will just grade the first 5 reactions. (2 pts each, 10 pts total)

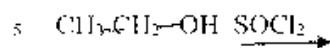
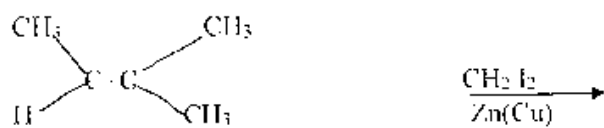
1.



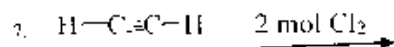
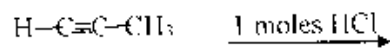
2.



4.



6.



C. Short Answers part of Short Answers: (24 pts)

1. a. For the element **Ge** show the electron configuration for all electrons in the format  $1s^2, 2s^2, \dots$  etc ( 8 pts total) (2 pts this question)

- b. For the same element show the electron configuration for all **valence** electrons in the same format. (1 pt)

- c. For the same element, show the **valence** electron configuration orbital diagram in the format:  $\uparrow\downarrow, \downarrow, \dots$  etc; using up and down arrows to represent electrons. (2 pts this question)

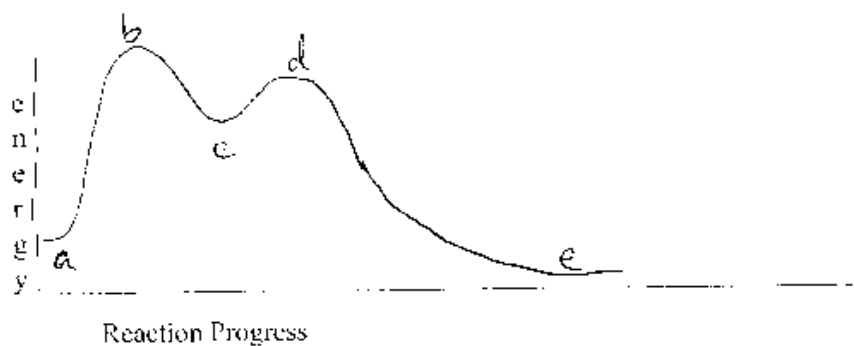
$1s$       $2s$

- d. For the same element, what is the **group number**? \_\_\_\_\_ (1 pt)

- e. For the same element, what is the **atomic mass**? \_\_\_\_\_ (1 pt)

- f. For the same element, what is the **atomic number**? \_\_\_\_\_ (1 pt)

2. Given the following energy diagram, (2 pt each, total 8 pts)



- a) How many steps is in the reaction mechanism shown [(1).(2).(3)(4)] (circle one)
- b) Which of the steps is the slowest step [(1<sup>st</sup> step) (2<sup>nd</sup> step) (3<sup>rd</sup> step)(4<sup>th</sup> step)] (circle one)

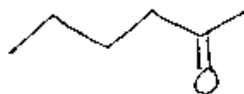
(note: just because I gave 4 potential steps does not necessarily mean that there are actually 4 steps - it could be less or more)

- c) Circle the label of all intermediates ? [(a).(b).(c)(d)(e)(f)] (circle all that apply)
- d) Circle the label of all transition states. [(a)(b)(c)(d)(e)(f)] (circle all that apply)

3 Answer the following by circling one, to as many as all of the reactions mechanisms under each letter. (4 pts, 2 pts each letter)

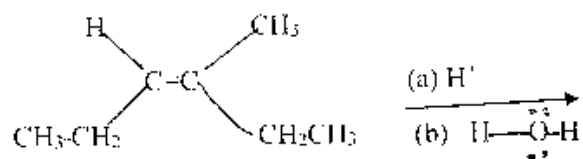
- a. A tertiary substrate is best for [(S<sub>N</sub>2). (S<sub>N</sub>1). (E2). (E1)] (circle all correct mechanism)
- b. A strong bulky base but weak nucleophile favors [(S<sub>N</sub>2). (S<sub>N</sub>1). (E2). (E1)] (circle all correct mechanism)

4. Given the following molecule, draw one structural (also known as constitutional) isomers (4 pts)



Part III. Long Answers (36 pts) Show work where applicable for partial and full credit.

1. A. Complete the following reaction mechanism. Show all intermediates in 3D (show the empty p orbital if there is one during the reaction mechanism) but not the transition state structures. Show electron pushing arrows and completely drawn Lewis Dot (or Kekule) structures for each step of the reaction mechanism and the correct regiochemistry and stereochemistry if required. (19 pts total, 10 pts this part) (Mechanism means show all steps on the way to the product)



B. Draw an energy diagram which matches your reaction mechanism. Label reactants, products, all intermediates **above in your mechanism with the letters (a), (b), (c), ... etc.** and then label your energy diagram below. (4 pts)

C. Does the reaction above follow Markovnikov's Rule?  (yes)  (no) (circle a parenthesis) Give any version of the definition of Markovnikov's Rule using a sentence or two. (2 pts)

D. There is a chiral center in the product. Is the chiral center racemic? (yes, no) Explain. (3 pts)

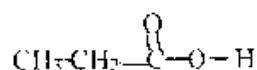
2. Let's completely structurally identify the following molecule which you expect will be produced in the reaction product that you have spent a half a year synthesizing and purifying. To figure out if you successfully made the product, we are going to do a thought experiment to show what your spectra for the molecule should look like.

If everything matches up (meaning you run the spectra and your spectra exactly match what you expect your spectra to look like), you can then dance in the street because you have completed your 10 step synthesis which will allow you to complete your doctorate after doing some arm waving to explain why your molecule is so important. (not really obviously because this molecule is not really important but I am trying to make this question as exciting as possible because I know that by now your brain has turned to mush after all the hard work of studying for and completing your exam.)

and no your grade will not be impacted by what you want to do for the rest of your life - none of my business. (17 pts total)

Part I: Mass Spectra: (4 pts)

Given the molecule below, show your calculation of the number for the molecular ion peak in a mass spectrum. (4 pts)



Part II: Infrared Spectra: (4 pts)

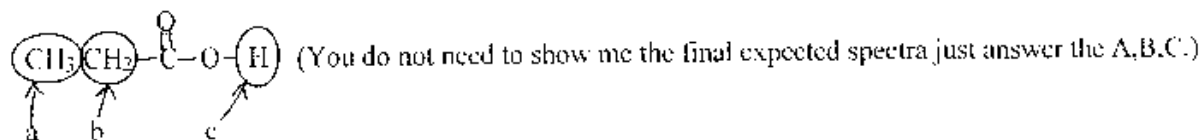
Given the molecule above, give at least 2 functional group IR peaks which you expect based on the given IR chart. Give the number of the expected peak and which part of the molecule would show that IR peaks (1 pt per blank)

\_\_\_\_\_  $\text{cm}^{-1}$  for \_\_\_\_\_ stretch or bend

\_\_\_\_\_  $\text{cm}^{-1}$  for \_\_\_\_\_ stretch or bend



Part III: NMR Spectra (9 pts) (note: I circled the parts of the molecule for the NMR part of this question. I mean the protons inside the circles even though some of the circles also show other atoms because it is hard to just circle the protons.) Given the same molecule above from the MS and IR part of the question, explain the expected proton NMR spectrum. To do this complete all 3 parts A,B, C



(A): relative chemical shift (3 pts) Draw the approximate relative chemical shift of the protons in the molecule using the **labels (a,b,c)** which I have provided in the molecule above.

(B): integration peak area (3 pts) Explain the approximate integration peak area for each proton NMR peak

(C): coupling (using  $2nI+1$ ) (3 pts) Explain the coupling for each of the different proton NMR peaks by giving the number of the **n** and plugging it into the equation  $2nI+1$ .

Sign Name \_\_\_\_\_ Print Name \_\_\_\_\_

(5 pt name above print & sign – If I can't tell who you are from NO NAME above, I have to go back to the exam taking map and hope that I can read your name on that or I may end up with an exam with no identity permanently). (5 pts scantron name – if you don't bubble in I get a grade with no name and I have to hold everyone's final grades until I figure out whose exam it is.) (100 pts, 12 pages + scantron sheet)

Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. **I will only grade what I can read (obviously).** I am not going to make up an answer for you based on writing I can't read. (use back of exam for scratch paper If you want me to grade something not in the space for the answer, **clearly specify in writing.** Telling me during the exam where to find the answer does not qualify because I will just vaguely remember someone telling me something during the exam not which one of 250 students told me what to grade on what page.) *color*

Circle answer on this form for backup to the scantron. There is no partial credit for showing work in the multiple choice.

In all questions on all parts of this exam, R is not equal to hydrogen but is an alkyl.

1. Multiple Choice ( 2 pts each, 24 pts) Choose the one best statement in each question. There is no partial credit for showing work on the multiple choice questions.

1. The element Ge has how many total number of electrons ?

- a) 4 electrons
- b) 14 electrons
- c) 72 electrons
- d) 32 electrons

2. Which of the following statements correctly pertains to a pair of enantiomers ?

- (a) They have different melting points.
- (b) They rotate the plane of polarized light by differing amounts and in opposite directions
- (c) They have the same melting points but they have different boiling points.
- (d) They rotate the plane of polarized light by exactly the same amount and in opposite directions.
- (e) They rotate the plane of polarized light by differing amounts and in the same direction.

3. A molecule with 4 pairs of VSEPR electron pairs around the central atom has:

- a) trigonal bipyramidal, 120° angle
- b) trigonal planar, 90° angle
- c) tetrahedral geometry, 109.5° angle
- d) octahedral geometry, 120° angle

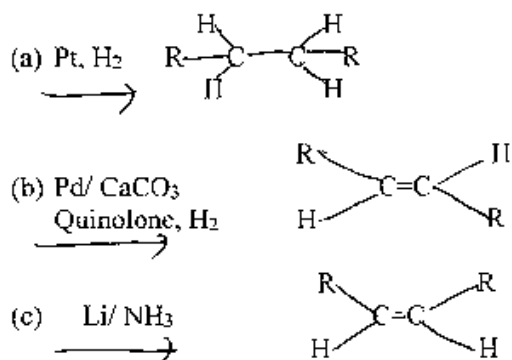
4. Which of the following bonds is a covalent bond ?

- a)  $\text{Li}_2\text{O}$
- b)  $\text{BaO}$
- c)  $\text{SO}_2$
- d)  $\text{MgCl}_2$

5. A radical reaction mechanism is:

- (a) Heterolytic
- (b) Done so as to produce the more stable pair of ions
- (c) Homolytic
- (d) Via hydrogenation
- (e) None of the above

6. Choose the best statement.  $\text{R}-\text{C}\equiv\text{C}-\text{R}$  reacts with the following to give the product shown:

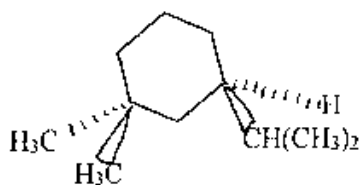


(d) All reactions are correct.

7. For reaction mechanisms which of the following are true or the best statement

- (a)  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  are both substitution reaction mechanism which results in an alkene product.
- (b)  $\text{S}_{\text{N}}1$  and  $\text{E}1$  reaction mechanisms have a one step reaction mechanism
- (c)  $\text{S}_{\text{N}}2$  and  $\text{E}2$  reaction mechanisms have bimolecular kinetics.
- (d)  $\text{E}1$  and  $\text{E}2$  are both elimination reaction mechanisms which result in a substitution product.
- (e) All of the above are true.

8. How many asymmetric carbon atoms are present in the following compound ?



- (a) 2
- (b) 3
- (c) 4
- (d) 0
- (e) 1

9. Given the following.

- (a)  $\text{RO}^-$  is a better nucleophile than  $\text{HO}^-$
- (b)  $\text{RO}^-$  is a better nucleophile than  $\text{ROH}$
- (c)  $\text{HO}^-$  is a better nucleophile than  $\text{H}_2\text{O}$
- (d) Nucleophilicity is interaction with carbon while Basicity is interaction with hydrogen
- (e) All above statements are true.

10. For elimination reactions choose the one best statement.

- (a) Both the E1 and E2 reaction mechanism result in Zaitsev's Rule products
- (b) Zaitsev's Rule product is the least stable alkene products
- (c) Hoffmann's Rule products are the most stable alkene product
- (d) All statements above are true.

11. Choose the best statement.

- (a) There is no coupling between carbon and another carbon in carbon NMR because the natural abundance of carbon 13 is only 1.1% so there is almost never an NMR active neighboring carbon.
- (b) In IR spectroscopy the functional group region is  $1500\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  and the finger print region is between  $4000\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ .
- (c) Proton NMR has splitting in the coupling pattern is based on  $2nI + 1$  where  $I = \frac{1}{2}$  and  $n$  = number of neighboring protons.
- (d) (a) and (c) are correct.
- (e) All statements are correct.

12. For intermolecular forces the general progression from strongest to weakest intermolecular force is :

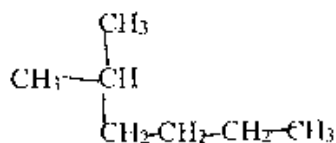
- a) Dipolar > hydrogen bonding > van der Waals
- b) Hydrogen bonding > dipolar > van der Waals
- c) Van der Waals > hydrogen bonding > dipolar
- d) None of the above is correct.

Part II. Short Answers ( 40 pts)

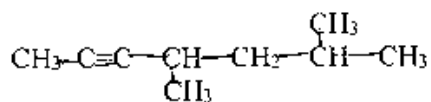
A. Nomenclature: (2 pts each. 6 pts)

1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name \_\_\_\_\_



b. name \_\_\_\_\_



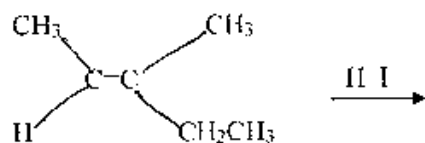
2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

3,5-dimethyloct-2-ene

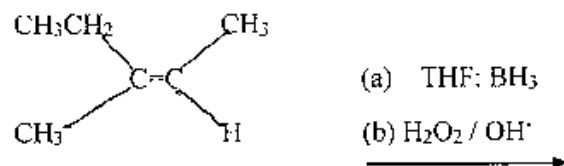
B. Reactions: Show the Organic Product for the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is not acceptable.) **DO NOT SHOW MECHANISMS.**

**Circle the number of the 5 reaction which you want counted.** If you do not choose, I will just grade the first 5 reactions. (2 pts each, 10 pts total)

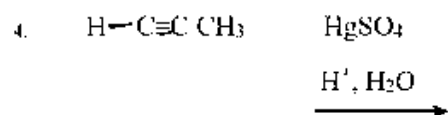
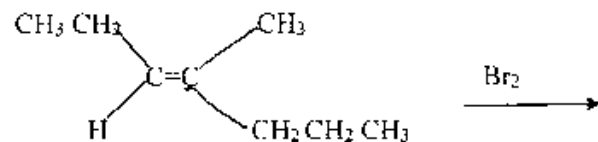
1

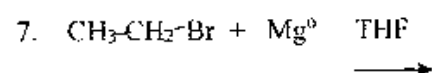
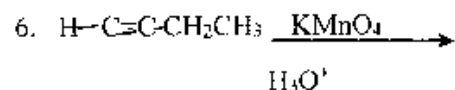
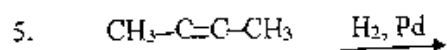


2



3





C. Short Answers part of Short Answers: (24 pts)

1. a. For the element Sb show the electron configuration for all electrons in the format  $1s^2, 2s^2, \dots$  etc (8 pts total) (2 pts this question)

- b. For the same element show the electron configuration for all valence electrons in the same format. (1 pt)

- c. For the same element, show the valence electron configuration orbital diagram in the format:  $\{ \underset{1s}{\downarrow\uparrow} \underset{2s}{\downarrow} \dots \}$  etc} using up and down arrows to represent electrons. (2 pts this question)

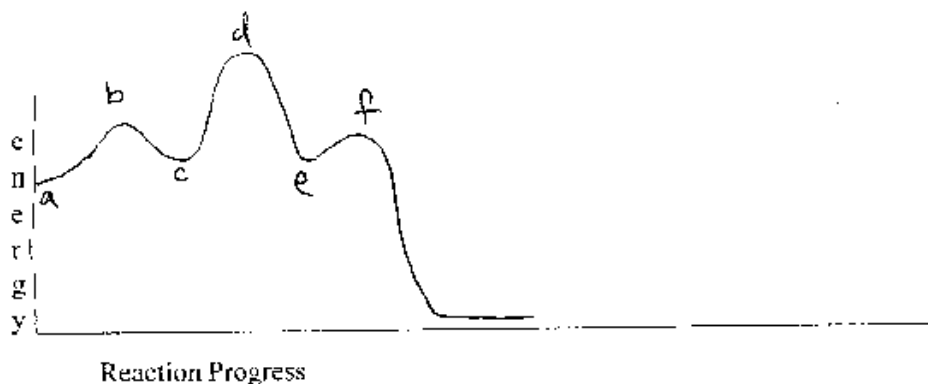
- d. For the same element, what is the group number? \_\_\_\_\_ (1 pt)

- e. For the same element, what is the atomic mass? \_\_\_\_\_ (1 pt)

- f. For the same element, what is the atomic number? \_\_\_\_\_ (1 pt)



2. Given the following energy diagram. (2 pt each, total 8 pts)



- a) How many steps is in the reaction mechanism shown [(1), (2),(3)(4)] (circle one)
- b) Which of the steps is the slowest step [(1<sup>st</sup> step) (2<sup>nd</sup> step) (3<sup>rd</sup> step)(4<sup>th</sup> step)] (circle one)

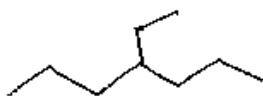
(note: just because I gave 4 potential steps does not necessarily mean that there are actually 4 steps – it could be less or more)

- c) Circle the label of all intermediates ? [(a),(b),(c) (d) (e) (f)] (circle all that apply)
- d) Circle the label of all transition states. [(a) (b) (c) (d) (e) (f) ] (circle all that apply)

3. Answer the following by circling one, to as many as all of the reactions mechanisms under each letter. (4 pts, 2 pts each letter)

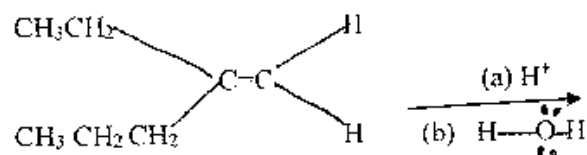
- a. A tertiary substrate is best for [(S<sub>N</sub>2), (S<sub>N</sub>1), (E2), (E1)] (circle all correct mechanism)
- b. A strong bulky base but weak nucleophile favors [(S<sub>N</sub>2), (S<sub>N</sub>1), (E2), (E1)] (circle all correct mechanism)

4. Given the following molecule, draw one structural (also known as constitutional) isomers (4 pts)



Part III. Long Answers (36 pts) Show work where applicable for partial and full credit.

1. a. Complete the following reaction mechanism. **Show all intermediates in 3D (show the empty p orbital if there is one during the reaction mechanism)** but not the transition state structures. Show electron pushing arrows and completely drawn Lewis Dot (or Kekule) structures for each step of the reaction mechanism and the correct regiochemistry and stereochemistry if required. (19 pts total, 10 pts this part) (Mechanism means show all steps on the way to the product)



b Draw an energy diagram which matches your reaction mechanism. Label reactants, products, all intermediates **above in your mechanism with the letters (a), (b), (c), ... etc.** and then label your energy diagram below. (4 pts)

c. Does the reaction above follow Markovnikov's Rule? [(yes)(no)](circle a parenthesis) Give any version of the definition of Markovnikov's Rule using a sentence or two. (2 pts)

d. There is a chiral center in the product. Is the chiral center racemic? (yes,no) Explain. (3 pts)

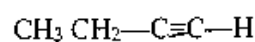
2. Let's completely structurally identify the following molecule which you expect will be produced in the reaction product that you have spent a half a year synthesizing and purifying. To figure out if you successfully made the product, we are going to do a thought experiment to show what your spectra for the molecule should look like.

If everything matches up (meaning you run the spectra and your spectra exactly match what you expect your spectra to look like), you can then dance in the street because you have completed your 10 step synthesis which will allow you to complete your doctorate after doing some arm waving to explain why your molecule is so important. (not really obviously because this molecule is not really important but I am trying to make this question as exciting as possible because I know that by now your brain has turned to mush after all the hard work of studying for and completing your exam.)

and no your grade will not be impacted by what you want to do for the rest of your life – none of my business. (17 pts total)

Part I: Mass Spectra: (4 pts)

Given the molecule below, show your calculation of the number for the molecular ion peak in a mass spectrum. (4 pts)



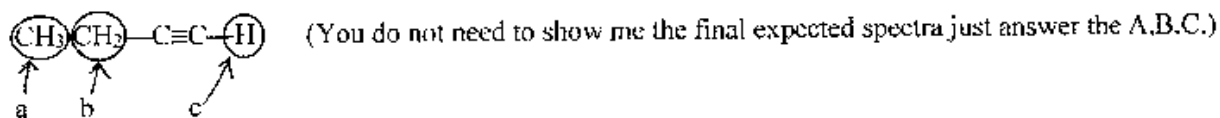
Part II: Infrared Spectra: (4 pts)

Given the molecule above, give at least 2 functional group IR peaks which you expect based on the given IR chart. Give the number of the expected peak and which part of the molecule would show that IR peak. (1 pts each blank)

\_\_\_\_\_  $\text{cm}^{-1}$  for \_\_\_\_\_ stretch or bend

\_\_\_\_\_  $\text{cm}^{-1}$  for \_\_\_\_\_ stretch or bend

Part III: NMR Spectra (9 pts) (note: I circled the parts of the molecule for the NMR part of this question. I mean the protons inside the circles even though some of the circles also show other atoms because it is hard to just circle the protons.) Given the same molecule above from the MS and IR part of the question, explain the expected proton NMR spectrum. To do this complete all 3 parts A,B, C



(A): relative chemical shift (3 pts) Draw the approximate relative chemical shift of the protons in the molecule using the labels (a,b,c) which I have provided in the molecule above.

(B): integration peak area (3 pts) Explain the approximate integration peak area for each proton NMR peak

(C): coupling (using  $2nI+1$ ) (3 pts) Explain the coupling for each of the different proton NMR peaks by giving the number of the n and plugging it into the equation  $2nI+1$ .

Sign Name \_\_\_\_\_ Print Name \_\_\_\_\_

(5 pt name above print & sign – If I can't tell who you are from NO NAME above, I have to go back to the exam taking map and hope that I can read your name on that or I may end up with an exam with no identity permanently). (5 pts scantron name – if you don't bubble in I get a grade with no name and I have to hold everyone's final grades until I figure out whose exam it is.)(100 pts, 13 pages + scantron sheet)

Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. **I will only grade what I can read (obviously).** I am not going to make up an answer for you based on writing I can't read. (use back of exam for scratch paper – If you want me to grade something not in the space for the answer, **clearly specify in writing.** Telling me during the exam where to find the answer does not qualify because I will just vaguely remember someone telling me something during the exam not which one of 250 students told me what to grade on what page.)

Circle answer on this form for backup to the scantron. There is no partial credit for showing work in the multiple choice.

In all questions on all parts of this exam, R is not equal to hydrogen but is an alkyl.

1. Multiple Choice ( 2 pts each, 24 pts) Choose the **one** best statement in each question. There is no partial credit for showing work on the multiple choice questions.

1. Which of the following intermediates is thought to occur in the mechanism by which alkenes are hydrated in the presence of acid ?

- a) carbocation
- b) carbanion
- c) free radical
- d) carbene
- e) alkyne

2. For a given reaction, if  $\Delta G^\circ$  is greater than zero (positive), then:

- a) The reaction is going downhill in energy and will go to product.
- b) The reaction is going really fast.
- c) The reaction is going uphill in energy and will not go to product.
- d) All statements are true.
- e) All statements are false.

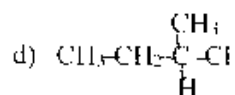
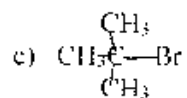
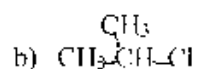
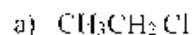
3. Given the following.

- (a)  $\text{RO}^-$  is a better nucleophile than  $\text{HO}^-$
- (b)  $\text{RO}^-$  is a better nucleophile than  $\text{ROH}$
- (c)  $\text{HO}^-$  is a better nucleophile than  $\text{H}_2\text{O}$
- (d) Nucleophilicity is interaction with carbon while Basicity is interaction with hydrogen
- (e) All above statements are true.

4. Choose the largest dipole moment among the bonds shown.

- a)  $\text{C}-\text{Cl}$
- a)  $\text{Cl}-\text{Cl}$
- b)  $\text{N}-\text{Cl}$
- c)  $\text{C}-\text{F}$

5. Choose the **tertiary** alkyl halide from the list below



6. For intermolecular forces the general progression from strongest to weakest intermolecular force is :

- a) Hydrogen bonding > dipolar > van der Waals
- b) Van der Waals > hydrogen bonding > dipolar
- c) Dipolar > hydrogen bonding > van der Waals
- d) None of the above is correct.

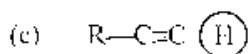
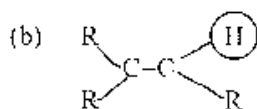
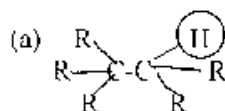
7. What synthetic goal is achieved by subjecting an alkene to an oxymercuration-demercuration sequence ?

- a) Markovnikov addition of  $H_2O$  wherein skeletal rearrangement is prevented.
- b) Markovnikov addition of  $H_2O$  wherein skeletal rearrangement is promoted.
- c) Syn-hydroxylation
- d) Anti-Markovnikov addition of  $H_2O$  wherein skeletal rearrangement is prevented.
- e) Anti-Markovnikov addition of  $H_2O$  wherein skeletal rearrangement is promoted.

8. Which of the following statements is (are) true for the compound (R)-2-butanol ?

- a) This compound has an enantiomer
- b) This compound is optically active.
- c) This compound is chiral.
- d) All of the above.
- e) None of the above.

9. Given the following molecules, the most acidic proton, the circled proton, in the given molecule is:



(d) All of the hydrogens are equal in acidity.

10. For the  $S_N2$  reaction mechanism,

- (a) If you increase the concentration of the nucleophile by 2 times, the rate will increase by 2 times.
- (b) If you decrease the concentration the substrate by  $\frac{1}{2}$  times the rate will decrease by  $\frac{1}{2}$  times.
- (c) The concentration of the nucleophile has no effect on the rate.
- (d) (a) and (b) are correct
- (e) (a) (b) and (c) are all correct.



11. Choose the one best statement.

- (a) If a reaction follows Markovnikov's Rule for an alkene reaction, then the alkyne reaction will follow anti-Markovnikov's Rule.
- (b) For an alkyne,  $\text{H X}$  ( $\text{X} = \text{halogen}$ ), can only be added one time to result in an alkene.
- (c) When you add water (using  $\text{H}^+$  and  $\text{H}_2\text{O}$ ) to an Alkyne, you get no reaction.
- (d) When you add water to an Alkyne using the  $\text{Hg}(\text{OAc})_2$ , you get an anti-Markovnikov addition which then does a tautomerism

12. Choose the best statement.

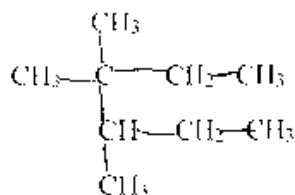
- (a) Proton NMR has splitting in the coupling pattern based on  $2nI + 1$  where  $I = \frac{1}{2}$  and  $n = \text{number of neighboring protons}$ .
- (b) Carbon NMR has splitting in the coupling pattern based on  $2nI + 1$  where  $I = \frac{1}{2}$  and  $n = \text{number of neighboring carbons}$ .
- (c) In IR spectroscopy the functional group region is  $1500 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  and the finger print region is between  $4000 \text{ cm}^{-1}$  and  $1500 \text{ cm}^{-1}$ .
- (d) (a) and (b) are correct.
- (e) All statements are correct.

Part II. Short Answers (40 pts)

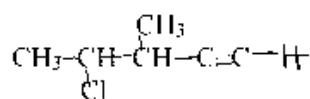
A. Nomenclature: (2 pts each, 6 pts)

1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name \_\_\_\_\_



b. name \_\_\_\_\_



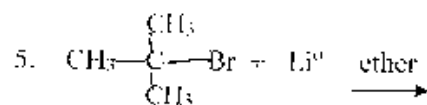
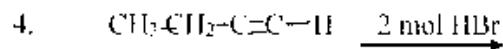
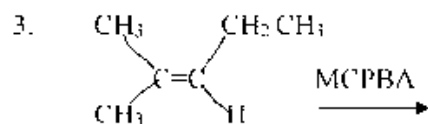
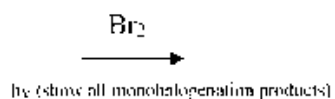
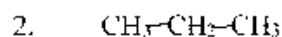
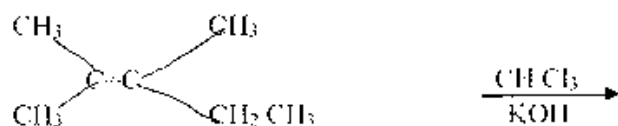
2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

4-bromobut-1-ene

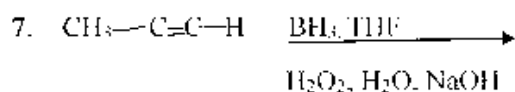
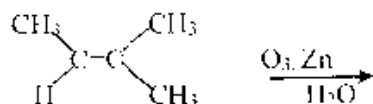
15. Reactions. Show the Organic Product for the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is **not** acceptable.) DO **NOT** SHOW MECHANISMS.

**Circle the number of the 5 reaction which you want counted.** If you do not choose, I will just grade the first 5 reactions. (2 pts each, 10 pts total)

1



6.



C. Short Answers part of Short Answers: (24 pts)

1. a. For the element **(1)** show the electron configuration for all electrons in the format  $1s^2, 2s^2, \dots$  etc ( 8 pts total) (2 pts this question)

b. For the same element show the electron configuration for all **valence** electrons in the same format. (1 pt)

c. For the same element, show the **valence** electron configuration orbital diagram in the format:  $\{ \uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \dots \}$  etc} using up and down arrows to represent electrons. (2 pts this question)

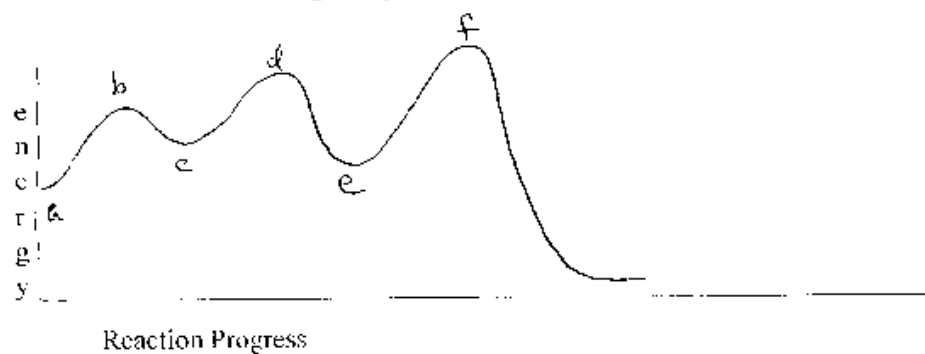
1s      2s

d. For the same element, what is the **group number**? \_\_\_\_\_ (1 pt)

e. For the same element, what is the **atomic mass**? \_\_\_\_\_ (1 pt)

f. For the same element, what is the **atomic number**? \_\_\_\_\_ (1 pt)

2 Given the following energy diagram. (2 pt each, total 8 pts)



- a) How many steps is in the reaction mechanism shown [(1).(2).(3)(4)] (circle one)
- b) Which of the steps is the slowest step [(1<sup>st</sup> step) (2<sup>nd</sup> step) (3<sup>rd</sup> step)(4<sup>th</sup> step)] (circle one)

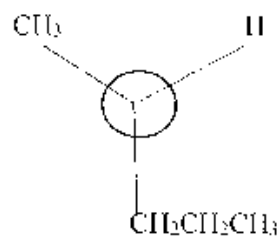
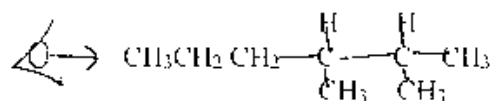
(note: just because I gave 4 potential steps does not necessarily mean that there are actually 4 steps – it could be less or more)

- c) Circle the label of all intermediates ? [(a),(b),(c)(d)(e)(f)] (circle all that apply)
- d) Circle the label of all transition states. [(a)(b)(c)(d)(e)(f)] (circle all that apply)

3 Answer the following by circling one, to as many as all of the reactions mechanisms under each letter. (4 pts, 2 pts each letter)

- a. A strong nucleophile or higher concentration nucleophile favors [(S<sub>N</sub>2). (S<sub>N</sub>1). (E2). (E1)] (circle all correct mechanism)
- b. A polar aprotic solvent favors [(S<sub>N</sub>2). (S<sub>N</sub>1). (E2). (E1)] (circle all correct mechanism)

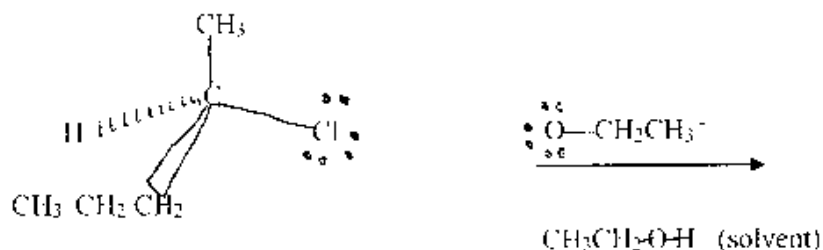
4 For the following molecule, complete the correct Newman projection for: (4 pts) (point of view eye is shown) for the 2,3-dimethylhexane molecule using the 2 and 3 carbons as the 2 Newman projection central atoms. I have shown the front carbon attachment bonds. You have to draw in the correct attachment to the back bonds and show what is attached to the bonds.



lowest energy Newman Projection formula

Part III. Long Answers (36 pts) Show work where applicable for partial and full credit.

A. Given the following reactant: Assume that the reaction undergoes an  $S_N1$  reaction mechanism. Please show the entire reaction mechanism including electron pushing arrows. Please show either the transition state or intermediate (depending on which is the correct one to show for the mechanism that you have) and the Organic Major Product. Show the reaction mechanism using a 3 D structure including the empty p orbital if appropriate. Show the derivation of the racemic or inverted product as appropriate using your 3 D structure. (10 pts this part, 19 pts total)



B. Write the rate law for the reaction mechanism using the actual molecule in your reaction above. If you write the rate law using the words substrate or nucleophile, I will count off. (4 pts)

C. If you start the reaction with chiral center (R or S) as shown, is your substitution product [ (R) or (S) or (racemic)] (circle one) (2 pts)

D. Give the **Fisher projection formula** of the expected product or products. (3 pts)



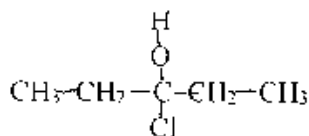
2. Let's completely structurally identify the following molecule which you expect will be produced in the reaction product that you have spent a half a year synthesizing and purifying. To figure out if you successfully made the product, we are going to do a thought experiment to show what your spectra for the molecule should look like.

If everything matches up (meaning you run the spectra and your spectra exactly match what you expect your spectra to look like), you can then dance in the street because you have completed your 10 step synthesis which will allow you to complete your doctorate after doing some arm waving to explain why your molecule is so important. (not really obviously because this molecule is not really important but I am trying to make this question as exciting as possible because I know that by now your brain has turned to mush after all the hard work of studying for and completing your exam.)

and no your grade will not be impacted by what you want to do for the rest of your life – none of my business. (17 pts total)

Part I: Mass Spectra: (4 pts)

Given the molecule below, show your calculation of the number for the molecular ion peak in a mass spectrum. (4 pts)



Part II: Infrared Spectra: (4 pts)

Given the same molecule above, give at least 2 functional group IR peaks which you expect based on the given IR chart. Give the number of the expected peak and which part of the molecule would show that IR peak. (1 pts each blank)

\_\_\_\_\_ cm<sup>-1</sup> for \_\_\_\_\_ stretch or bend

\_\_\_\_\_ cm<sup>-1</sup> for \_\_\_\_\_ stretch or bend