Exam III Organic Chemistry I   CHEM 340   Spring 16 4/20 W   Dr. Hahn   MWF 8 am   Exam# _____

Sign Name _____*Key*_____ ‘ Print Name _____
(3 pt name above print,sign, 3 pts scantron name)(100 pts, 9 pages+periodic table+IR chart+ scantron sheet)

Please show work on all questions for partial credit even on questions which do not specify. Please write legibly.   If I cannot read your answer, I cannot grade your answer. (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 200 students told me what to grade on what page of the exam.)

Please READ and FOLLOW directions. This is a **TIMED EXAM**. (ex: don't give me 5 structures if I only ask for one or you will lose points on this exam by **RUNNING OUT OF TIME**)

Circle answer on this form for backup to the scantron for the multiple choice.   R=alkyl, not hydrogen on all parts of this exam.

I.   Multiple Choice (3 pts each, 24 pts) Choose the **one** best statement in each question.

1.   Choose the best statement.

   (a) In IR spectroscopy a molecule is split by an electron beam into molecular ion fragments which are then sorted by mass/charge ratio where charge is almost always +1.

   (b) In mass spectrometry the molecule vibrates after being hit by infrared waves giving information about what functional group is in the molecule.

   (c) NMR flips nuclear spins in a magnetic field by using radio waves.

   (d) All above statements are true

   (e) All above statements are false.

B A = bad attempt

N A = not attempted

2.   Choose best statement.

   (a) Wavelength (λ) is the distance between consecutive crests and troughs of a wave.

   (b) IR, NMR and UV-Vis spectroscopy all use electromagnetic spectrum

   (c)   Wavelength is inversely proportional to frequency for all electromagnetic specrum

   (d)   Lower wavelength is correlated with higher frequency and higher energy.

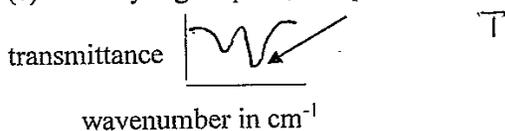   (e)   All above statements are true.

3. Choose the best statement.

[handwritten: deshielded]

(a) In proton NMR, protons closest to either an electronegative atom or π bond are ~~shielded~~ and have ~~lower~~ ppm numbers. *[handwritten: higher]*

(b) Number of peaks in a splitting pattern for proton NMR coupling equals 2nI+1 where n = number of protons with that chemical shift and ~~I=1~~ *[handwritten: I = 1/2]* *[handwritten: neighboring]*

(c) The standard used in proton NMR is the molecule $(CH_3)_3$ Si which gives ~~X~~ peaks around zero ppm. *[handwritten: one]*

(d) Hydrogens involved in hydrogen bonding such as carboxylic acid acidic hydrogen and amine hydrogens are exchanging protons which show a broad proton NMR peak and have shifting chemical shifts depending on solvent and concentration. *[circled]*

(e) All statements above are false.

4. Choose the best statement.

(a) In Mass Spectra, the base peak is the tallest peak in a given spectrum.

(b) In Mass Spectra, the molecular ion peak is the peak for the entire molecule. This peak has a m/z number which matches the molecular mass or formula mass of the entire molecule because z = +1 almost always.

(c) The molecular ion peak for the molecule $CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$ occurs at m/z of 72.

[handwritten: 12(5) + 12 = 72]

(d) α cleavage occurs at the nearest Carbon Carbon bond to most functional groups. *[handwritten: C, H]*

(e) All statements above are true. *[circled]*

5. Choose the best statement

(a) IR usually goes from around 4000 cm⁻¹ to 400 cm⁻¹ *[handwritten: T]*

(b) IR peaks are given in ~~ppm~~ *[handwritten: cm⁻¹]*

(c) A really big IR peak, are peaks that almost reach the bottom axis as shown here.

transmittance *[graph sketch]* *[handwritten: T]*

wavenumber in cm⁻¹

(d) All statements above are false.

(e) Only (b) and (d) are false. *[circled]*

5. Water addition can occur in one of 3 ways. Choose the best statement below about water addition to alkene.

6

(a) with H^+, H_2O, you get Markovnikov addition of H-OH without the possibility of rearrangement

(b) with $Hg(O\overset{O}{C}CH_3)_2$, (oxymercuration/demercuration) you get Markovnikov addition of H-OH with the possibility of rearrangement.

Out

(c) with THF:BH_3 (hydroboration/oxidation) you get anti-Markovnikov addition of H-OH T

(d) All statements above are true.

(e) All statements above are false.

6. In addition to alkene, choose the best statement.

7

(a) Addition of X_2 (where X is a halogen) occurs in an anti fashion with X attaching to opposite sides because of the halonium ion intermediate. T

(b) Addition of H_2 occurs in a syn fashion with the H-H attaching to the same side because the mechanism involves the adsorption of the alkene and H_2 to a metal surface. T
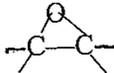
(c) Anti addition means addition from opposite sides of an alkene while syn addition means addition from the same side of an alkene. T

(d) All statement above are true.

7. In oxidation of alkene, choose the best statement.

8

(a) OsO_4 with HIO_4 gives oxidative cleavage to aldehydes and ketones.

(b) Hot $KMnO_4$ gives oxidative cleavage to carboxylic acids and ketones

(c) MCPBA leads to an epoxidation giving the following $-\overset{O}{C}-C-$

(d) All statement above are true.

II. Short Answers (39 pts)

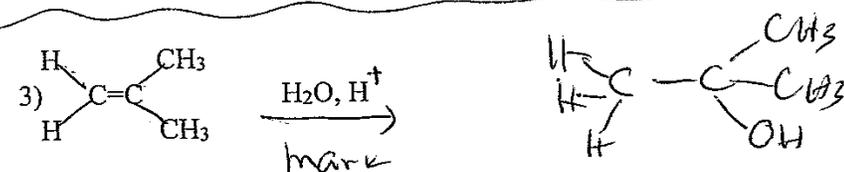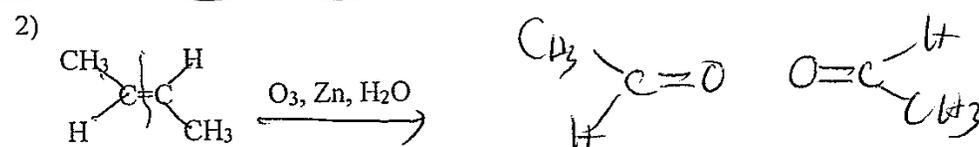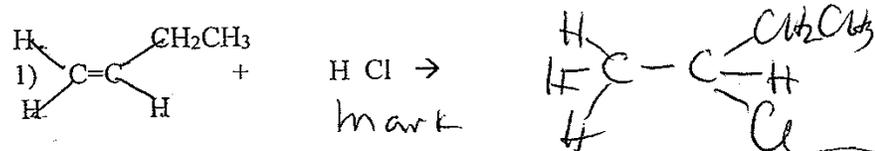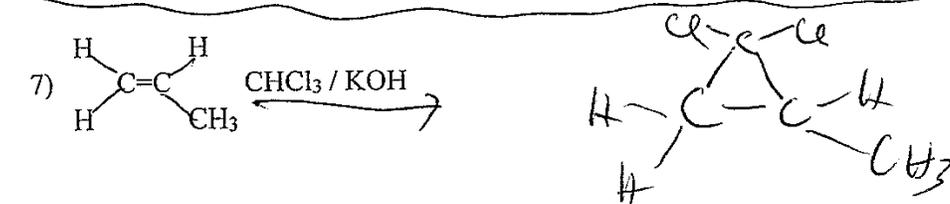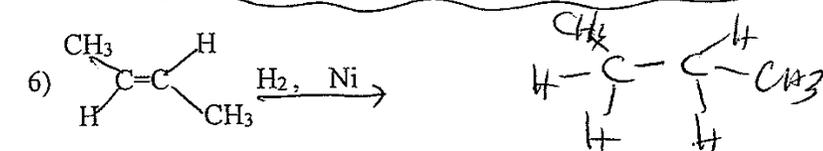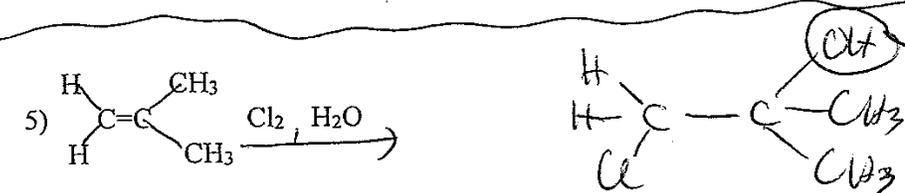A. Reactions Part of Short Answers: (2 pts per reaction, 12 pts total)

Complete the following reactions by giving the organic products. This is NOT mechanisms so you just need to give me the final product and no steps on the way to product. Reactions do NOT need to be balanced. (Circle the number of the **6 (six)** of the following reactions you want graded.)

[Handwritten annotations: "NFE – not far enough", "TF – too far", "regio", "intermediate", "½ credit"]

1)
$$H_2C=C(CH_2CH_3)(H) + HCl \rightarrow$$
mark

[Handwritten product drawing of H, H, C—C, CH₂CH₃, H, H, Cl]

2)
$$CH_3(H)C=C(H)(CH_3) \xrightarrow{O_3, Zn, H_2O}$$

[Handwritten product: CH₃(H)C=O   O=C(H)(CH₃)]

3)
$$(H)(H)C=C(CH_3)(CH_3) \xrightarrow{H_2O, H^+}$$
mark

[Handwritten product: H—C(H)(H)—C(CH₃)(CH₃)(OH)]

4)
$$(H)(CH_3)C=C(CH_3)(CH_3) \xrightarrow{Br_2}$$

[Handwritten product; annotation: "no pts off stereo because not 3 D drawing"]

5)
$$(H)(H)C=C(CH_3)(CH_3) \xrightarrow{Cl_2, H_2O}$$

[Handwritten product; annotation: "OH", "gave Cl –1"]

6)
$$(CH_3)(H)C=C(H)(CH_3) \xrightarrow{H_2, Ni}$$

[Handwritten product: H—C(CH₃)(H)—C(H)(H)—CH₃]

7)
$$(H)(H)C=C(H)(CH_3) \xrightarrow{CHCl_3 / KOH}$$

[Handwritten product: cyclopropane ring with Cl, Cl, C, H, CH₃]

8)

H $C=C$ CH_3 / CH_3 CH_3

THF: BH$_3$
H$_2$O$_2$ / OH$^-$
ant. mark

H–C(CH$_3$)(HO)... C–C(H)(CH$_3$)(CH$_3$)

---

9)

H $C=C$ H / H CH_3

Hg(OAc)$_2$ H$_2$O
NaBH$_4$
mark

H–C(H)(H)... C(CH$_3$)(OH)... H

---

10)

CH_3 $C=C$ H / H H

MCPBA →

CH$_3$–C(H)...O...C(H)(H)

---

11)

CH_3 $C=C$ H / H CH_3

OsO$_4$, NaHSO$_4$, H$_2$O →

CH$_3$(H)C=O   O=C(H)(CH$_3$)

---

12)

CH_3 $C=C$ CH_3 / H CH_3

hot KMnO$_4$ →

CH$_3$(H)C=O   O=C(CH$_3$)(CH$_3$)

H^O $\boxed{\text{Save H } \neg \text{ NFE}}$

---

13)

CH_3 $C=C$ CH_3 / H CH_3

CH$_2$I$_2$ / Zn(Cu) →

CH$_3$–C(H)(H)... C(CH$_3$)(CH$_3$)... H

B. Short Answers Part of Short Answers (27 pts)

1. (a) Given the following IR spectrum, which of the following molecule matches ? Circle the number of the molecule which matches. (11 points total, 5 pts this part)

N SE = not specific enough ex;
(C=O but did not say ester C=O)

3382 cm-1

1737 cm⁻¹

1047 cm⁻¹

5 pts choice (MC)

2210-2260 missing

(1) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-C\equiv N$

(2) $CH_3CH_2-\overset{H}{\underset{H}{N}}-H$ ← *3300-3500 + CN 1030-1230*

HO 1737

(3) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2\ CH_2-OH$

not amide
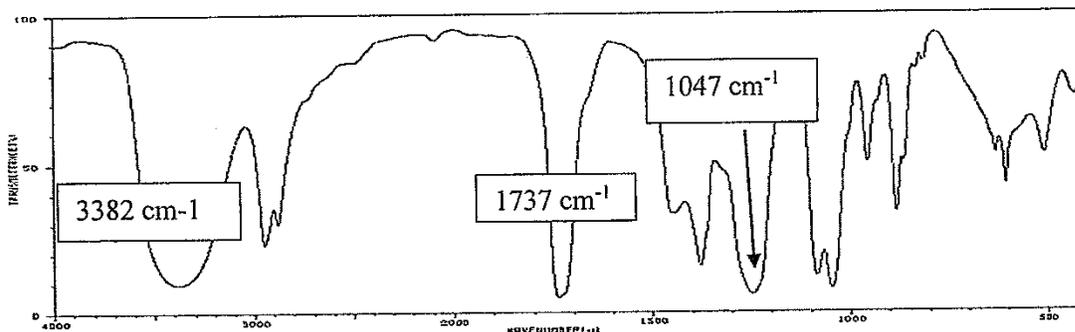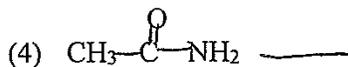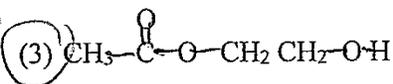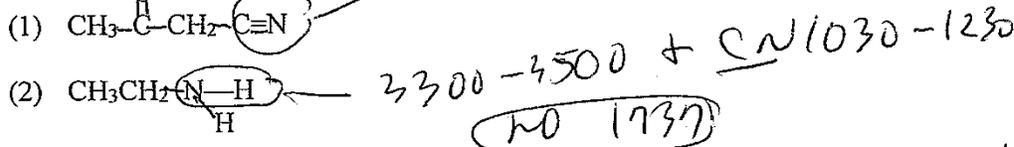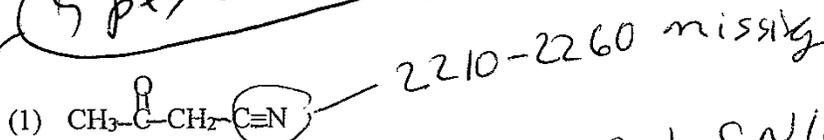
(4) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ ——— *C=O amide 1690   CN amide 1180-160*

N H amide 3300-3500

(b) Support your answer in (a) by completing the following ABOUT the MOLECULE which you selected above. [8 pts part (b), 4 pts each blank]   *wrong here -4*   *# not in IR -4*

-2 NSE

Give one IR peak from the IR chart specifying what structure gives that peak and the peak wavenumbers. You must use one of the numbers shown above. The number may not exactly match the number from your IR chart because the number given is an experimental number.   *1735 matches*
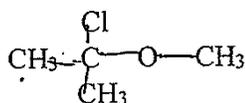
extra wrong -2

3400-3650

Functional group part is _C=O ester_ / _OH alcohol_ / _C-O alcohol_   giving IR peak at ___1050-1150___ cm⁻¹

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2. For the molecule given, show your calculation of the molecular ion peak. Show work. (6 pts)

Cl
|
CH₃—C—O—CH₃
|
CH₃

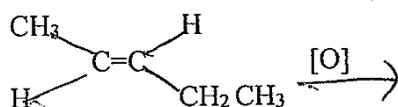$C_4H_9O\,Cl$ (1pt) (1pt) (1pt)

$4(12) + 9(1) + 16 + 35.0 = 109$ (1pt)

(1pt) (1pt) or 110 for other

Cl isotope

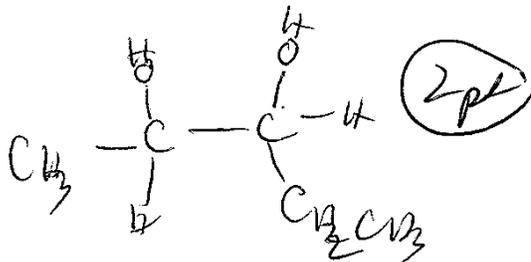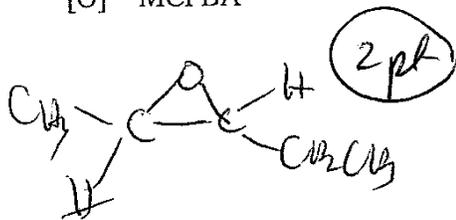(math −1) (atomic # for all −3)

3. If you do an oxidation on the following, what would be the product for the given molecule. (8 pts total, 2 pts each)   (Give the expected product by each letter for the reagent [O] oxidizing reagent.)
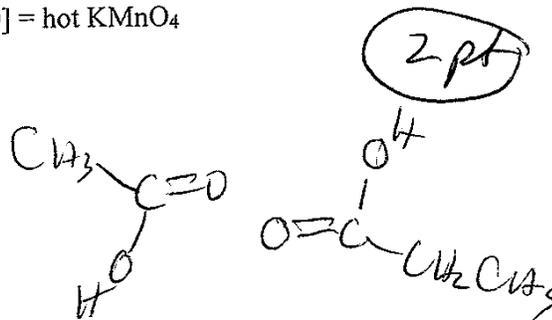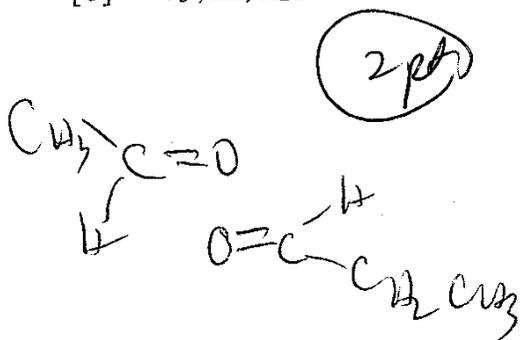
CH₃   H
  \   /
   C=C
  /   \
H   CH₂CH₃   —[O]→

gave extra
wrong −3

(a) weakest oxidation
     [O] = MCPBA

(2pt)

(b) weak oxidation
     [O] = OsO4, Na₂SO₃, H₂O
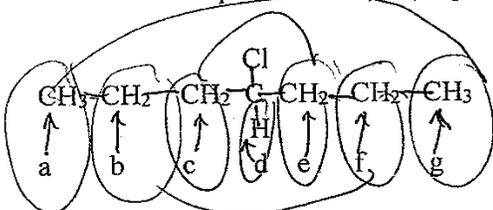
(2pt)

(c) medium oxidation
     [O] = O₃ , Zn, H₂O

(2pt)

(d) strongest oxidation
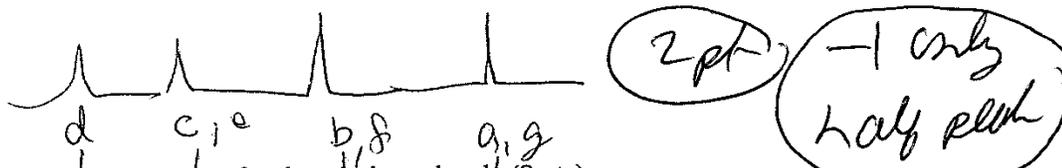   [O] = hot KMnO₄

(2pt)

(For NFE −1) (not far enough
(too far oxidized)   oxidized)

Part III.   Long Answers (36 pts)   Show work.   Note that you earn partial credit for "attempt".
"Attempt" is defined as not just rewriting the question but doing something towards getting the final answer.

1.   Given the following molecule   draw the expected NMR spectrum by completing the following
      information.   You must show all work for full credit.   (# peaks in coupling pattern = 2nI + 1 where I
      = ½ for proton NMR).   (16 pts)

$$CH_3-CH_2-CH_2-C-CH_2-CH_2-CH_3$$

with Cl and H on central C; labels a, b, c, d, e, f, g below

1) Show approximate relative chemical shift (note: my letters do not
   necessarily mean that the peaks show up separately at the position of the letter, it may or may not)(2 pts)

d   c | e   b, f   a, g

(2 pt)   (-1 only half peak)

2)   Explain integration peak area for the whole molecule (2 pts)
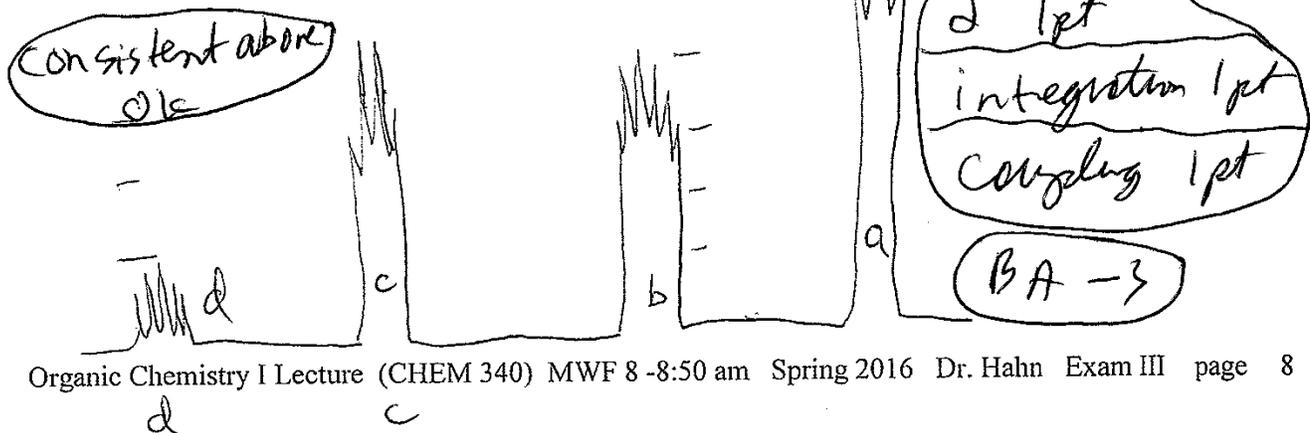
1 H   4 H   4 H   6 H   (2 pt)

3) Explain coupling for whole molecule (8 pts)

$$d \rightarrow n = 4 \quad 2(4)\tfrac{1}{2} + 1 = 5 \quad (NW-5)$$

$$c \rightarrow n = 3 \quad 2(3)\tfrac{1}{2} + 1 = 4$$

$$b \rightarrow n = 5 \quad 2(5)\tfrac{1}{2} + 1 = 6$$

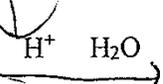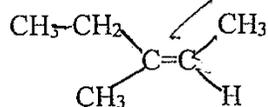$$a \rightarrow n = 2 \quad 2(2)\tfrac{1}{2} + 1 = 3$$

(BA = -6 bad attempt)

(8 pt)   (2 pts each)

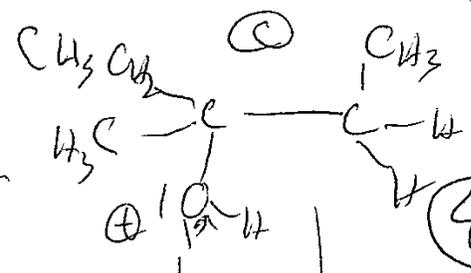4) Show the approximate completed final NMR spectrum (4 pts)

(Consistent above) OK

d   c   b   a

(δ 1pt, integration 1pt, coupling 1pt)

(BA -3)

d   c

2. a) Complete the following reaction mechanism. (total pts 21, 15 pts part a)

CH_3-CH_2
CH_3
$C=C$
CH_3 H

H^+ H_2O

(a)

e) electron push arrow -1 (e)

CH_3CH_2 (+) (b) CH_3
C — C — H
CH_3 H

(4pt)   no charge -1

$\bar{|O}-H$
H   (e) -1

CH_3CH_2 (c) CH_3
H_3C — C — C — H
(+) $|\bar{O}-H$ H
H
base   (4pt)
(e) -1

CH_3CH_2 (d) CH_3
H_3C — C — C — H
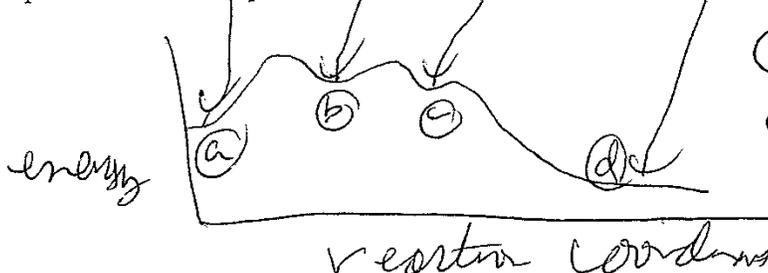$|\bar{O}|$ H
H   (4pt)

regio -2

BBA bad bad attempt no product -10
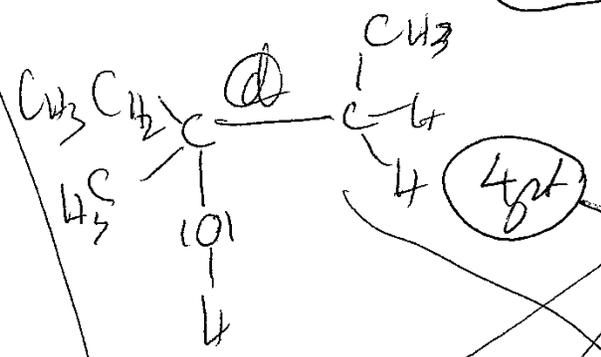
BBA with product -8

b) Draw an energy vs. reaction coordinate diagram to match your mechanism and label your energy diagram with molecules in your reaction mechanism. Your energy diagram MUST be for the mechanism above and your labeling may NOT be a general label such as "reactant", "intermediate", "transition state" but must be a specific label for a specific molecule in your reaction mechanism pathway which you showed above. (6 pts)

energy   (a) (b) (c)   (d)

BA -4 (bad attempt)
missing one hill -1
label 3 pt

reaction coordinate

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Sign Name _____ ˙ Print Name _____
(3 pt name above print,sign, 3 pts scantron name)(100 pts, 9 pages+periodic table+IR chart+ scantron sheet)

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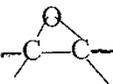(e) All statements above are false.

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(c) The molecular ion peak for the molecule CH_3-$\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}$-$CH_3$ occurs at m/z of 72.

(d) α cleavage occurs at the nearest Carbon Carbon bond to most functional groups.

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5.   Choose the best statement

(a) IR usually goes from around 4000 cm^{-1} to 400 cm^{-1}

(b) IR peaks are given in ppm

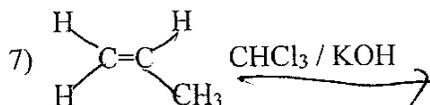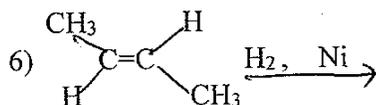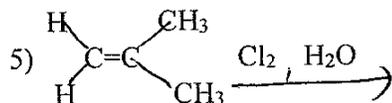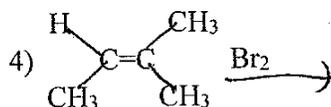(c) A really big IR peak, are peaks that almost reach the bottom axis as shown here.

transmittance

wavenumber in cm^{-1}
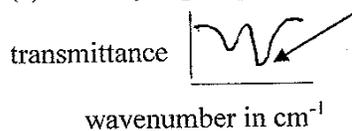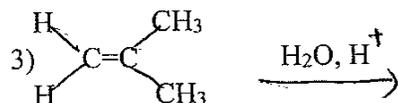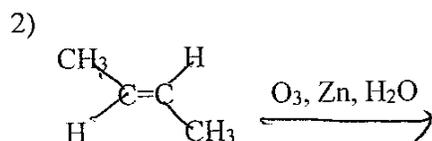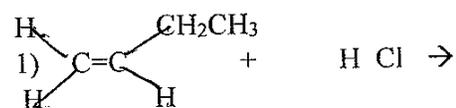
(d) All statements above are false.

(e) Only (b) and (d) are false.

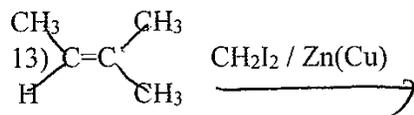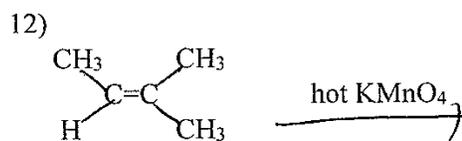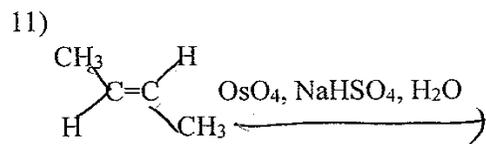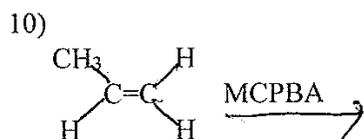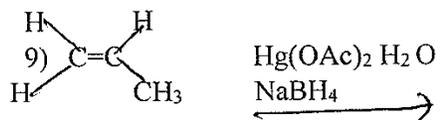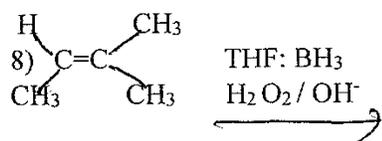7. Water addition can occur in one of 3 ways. Choose the best statement below about water addition to alkene.

   (a) with H^+, H_2O, you get Markovnikov addition of H-OH without the possibility of rearrangement

   (b) with $Hg(O\text{-}C\text{-}CH_3)_2$, (oxymercuration/demercuration) you get Markovnikov addition of H-OH with the possibility of rearrangement.

   (c) with THF:BH$_3$ (hydroboration/oxidation) you get anti-Markovnikov addition of H-OH

   (d) All statements above are true.

   (e) All statements above are false.

6. In addition to alkene, choose the best statement.

   (a) Addition of X$_2$ (where X is a halogen) occurs in an anti fashion with X attaching to opposite sides because of the halonium ion intermediate.

   (b) Addition of H$_2$ occurs in a syn fashion with the H-H attaching to the same side because the mechanism involves the adsorption of the alkene and H$_2$ to a metal surface.

   (c) Anti addition means addition from opposite sides of an alkene while syn addition means addition from the same side of an alkene.

   (d) All statement above are true.

7. In oxidation of alkene, choose the best statement.

   (a) OsO$_4$ with HIO$_4$ gives oxidative cleavage to aldehydes and ketones.

   (b) Hot KMnO$_4$ gives oxidative cleavage to carboxylic acids and ketones

   (c) MCPBA leads to an epoxidation giving the following $-\overset{O}{\underset{}{C}}-C-$

   (d) All statement above are true.

II. Short Answers (39   pts)

A.   Reactions Part of Short Answers: (2 pts per reaction, 12 pts total)

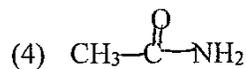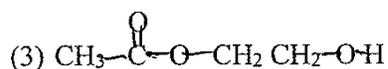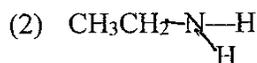Complete the following reactions by giving the organic products. This is NOT mechanisms so you just need to give me the final product and no steps on the way to product.   Reactions do NOT need to be balanced.
(Circle the number of the **6 (six)** of the following reactions you want graded.)

1)
$$\underset{\text{H}}{\overset{\text{H}}{>}}C=C\underset{\text{H}}{\overset{\text{CH}_2\text{CH}_3}{<}} \quad + \quad \text{H Cl} \rightarrow$$

2)
$$\underset{\text{H}}{\overset{\text{CH}_3}{>}}C=C\underset{\text{CH}_3}{\overset{\text{H}}{<}} \quad \xrightarrow{\text{O}_3,\ \text{Zn},\ \text{H}_2\text{O}}$$

3)
$$\underset{\text{H}}{\overset{\text{H}}{>}}C=C\underset{\text{CH}_3}{\overset{\text{CH}_3}{<}} \quad \xrightarrow{\text{H}_2\text{O},\ \text{H}^{+}}$$

4)
$$\underset{\text{CH}_3}{\overset{\text{H}}{>}}C=C\underset{\text{CH}_3}{\overset{\text{CH}_3}{<}} \quad \xrightarrow{\text{Br}_2}$$

5)
$$\underset{\text{H}}{\overset{\text{H}}{>}}C=C\underset{\text{CH}_3}{\overset{\text{CH}_3}{<}} \quad \xrightarrow{\text{Cl}_2,\ \text{H}_2\text{O}}$$

6)
$$\underset{\text{H}}{\overset{\text{CH}_3}{>}}C=C\underset{\text{CH}_3}{\overset{\text{H}}{<}} \quad \xrightarrow{\text{H}_2,\ \text{Ni}}$$

7)
$$\underset{\text{H}}{\overset{\text{H}}{>}}C=C\underset{\text{CH}_3}{\overset{\text{H}}{<}} \quad \xrightarrow{\text{CHCl}_3\ /\ \text{KOH}}$$

8)

H, CH₃
 C=C
CH₃ CH₃

THF: BH₃
H₂O₂ / OH⁻
———————→

9)

H, H
 C=C
H CH₃

Hg(OAc)₂ H₂O
NaBH₄
———————→

10)

CH₃ H
  C=C
H H

MCPBA
———————→

11)

CH₃ H
  C=C
H CH₃

OsO₄, NaHSO₄, H₂O
———————————————→

12)

CH₃ CH₃
  C=C
H CH₃

hot KMnO₄
———————→

13)

CH₃ CH₃
  C=C
H CH₃

CH₂I₂ / Zn(Cu)
———————————→

1.   (a) Given the following IR spectrum, which of the following molecule matches ?   Circle the
       number of the molecule which matches. (11 points total, 5 pts this part)

(1) CH₃–C(=O)–CH₂–C≡N

(2) CH₃CH₂–N(–H)–H

(3) CH₃–C(=O)–O–CH₂ CH₂–OH

(4) CH₃–C(=O)–NH₂

   (b) Support your answer in (a) by completing the following ABOUT the MOLECULE which you
   selected above.   [8 pts part (b), 4 pts each blank]

Give one IR peak from the IR chart specifying what structure gives that peak and the peak wavenumbers.
You must use one of the numbers shown above.   The number may not exactly match the number from your
IR chart because the number given is an experimental number.

   Functional group part is _____   giving IR peak at _____ cm⁻¹

2.   For the molecule given, show your calculation of the molecular ion peak. Show work.   (6 pts)
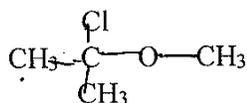
$$CH_3-\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{C}}-O-CH_3$$

3.   If you do an oxidation on the following, what would be the product for the given molecule. (8 pts total, 2 pts each)   (Give the expected product by each letter for the reagent [O] oxidizing reagent.)

$$\underset{H}{\overset{CH_3}{\diagdown}}C=C\underset{CH_2CH_3}{\overset{H}{\diagup}} \quad \xrightarrow{\text{[O]}}$$
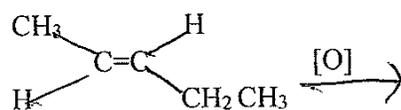
(a)   weakest oxidation
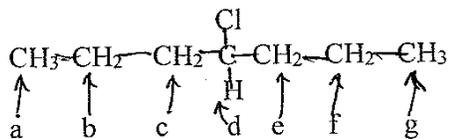   [O] = MCPBA

(b)   weak oxidation
      [O] = OsO4, Na2SO3, H2O

(c)   medium oxidation
       [O] = O3 , Zn, H2O

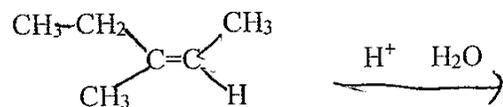(d)   strongest oxidation
      [O] = hot KMnO4

Part III.   Long Answers (36 pts)   Show work. Note that you earn partial credit for "attempt".
"Attempt" is defined as not just rewriting the question but doing something towards getting the final answer.

1.   Given the following molecule   draw the expected NMR spectrum by completing the following
information. You must show all work for full credit. (# peaks in coupling pattern = 2nI + 1 where I
= ½ for proton NMR). (16 pts)

$$CH_3-CH_2-CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-CH_2-CH_3$$

a   b   c   d   e   f   g

1) Show approximate relative chemical shift (note: my letters do not
   necessarily mean that the peaks show up separately at the position of the letter, it may or may not)(2 pts)

2)   Explain integration peak area for the whole molecule (2 pts)

3) Explain coupling for whole molecule (8 pts)

4) Show the approximate completed final NMR spectrum (4 pts)

2. a) Complete the following reaction mechanism. (total pts 21, 15 pts part a)

CH₃-CH₂   CH₃
        \   /
         C=C
        /   \
     CH₃   H

H⁺   H₂O
——————————⟶

b) Draw an energy vs. reaction coordinate diagram to match your mechanism and label your energy diagram with molecules in your reaction mechanism.   Your energy diagram MUST be for the mechanism above and your labeling may NOT be a general label such as "reactant", "intermediate", "transition state" but must be a specific label for a specific molecule in your reaction mechanism pathway which you showed above. (6 pts)