Exam I Organic Chem II (CHEM 442) Spring 16 2/17 Dr. Hahn MWF 1pm Form A Exam# ____

Sign Name Key Print Name _____

(1 pts name above print & sign, 1 pt scantron name) (100 pts, 11 pages + 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.) Color

Circle answer on this form ~~for backup to the scantron~~. There is no ~~partial credit for showing~~ work in the multiple choice. NA = not attempted NW = no work

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

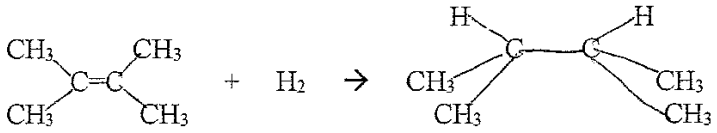
NFE = not far enough TF = too far NSE = not specific enough

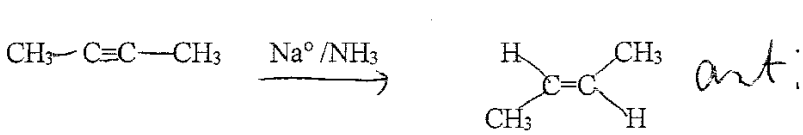
I. Multiple Choice (2 pts each, 24 pts) Choose the **one** best statement in each question.

CT = Consistent

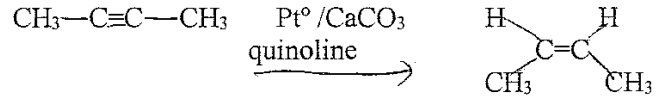
ICT = inconsistent

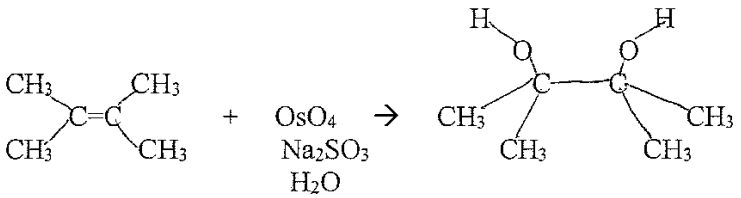
1. Which of the following reactions does **not** show a **syn** product ?

a) 

b)  anti

No partial credit mc

c) 

d) 

2. About spectra which of the following statements is incorrect ?

a) In proton NMR spectra the information that one derives is chemical shift, peak area and coupling which gives you information about the hydrocarbon structure.

b) In IR spectra 4000 cm^{-1} to 1500 cm^{-1} is the functional group region in which peaks which are representative of functional groups appear so you can use IR to find out what functional groups are in the organic molecule.

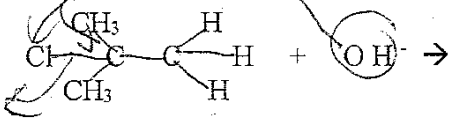
c) In IR spectra 1500 cm^{-1} to 400 cm^{-1} is the fingerprint region which can be used to match the finger prints of authentic samples of a compound with an unknown sample of an organic compound.

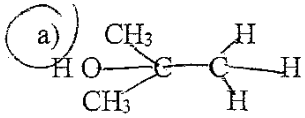
d) UV Vis spectra is observed for conjugated organic molecules. More conjugated systems have **larger** energy gaps which results in **larger** λ_{max},

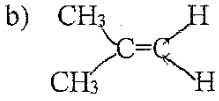
3. For the element **Sb**, circle the one incorrect statement.

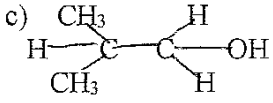
a) The atomic mass is 121.76
b) The total number of electrons for a neutral atom is 5
c) The atomic number is 51
d) The number of valence electrons is 5

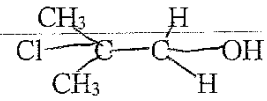
4. The product of an S_N1 reaction of the following substrate is:



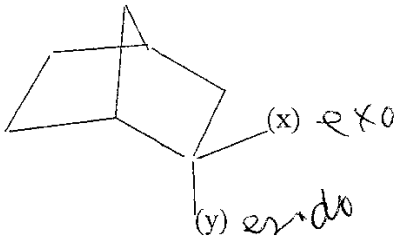
a)


b)


c)


d)


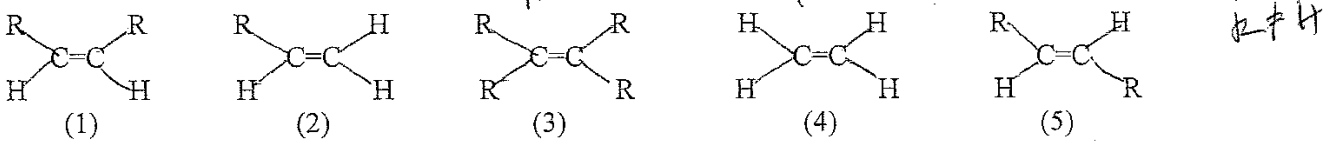
5 In the following molecule, which is endo/exo. Choose the best statement.



a) (x) is exo
b) (x) is endo
c) (y) is endo
d) There is no exo / endo in this molecule.
e) (a) and (c) are correct.

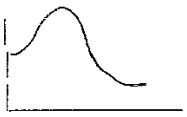
6 According to Zaitsev's (or sometimes spelled Saytzeff's) Rule, the most stable to least stable alkene is: Choose the one best statement. (R ≠ H)

most least type R ≠ H



a) Most stable (3) > (5) > (1) > (2) > (4) Least stable
b) Most stable (3) > (4) > (5) > (1) > (2) least stable
c) Most stable (4) > (2) > (1) > (5) > (3) least stable
d) You can't tell which alkene is stable by looking at the structure. All alkenes are similarly stable.

7. Which of the following does not match the E2 reaction mechanism ?

a) Energy diagram 

b) The E in E2 means elimination.
c) Rate = k [substrate][nucleophile]

d) All statements above are true about E2

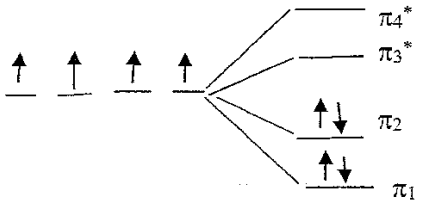
8. When you generate MO diagrams (where AO is atomic orbital and MO is molecular orbital), choose the one best statement.

a) The number of AO must equal the number of MO.
b) A node is a line through which the AO changes sign.
c) The more nodes in an AO combination, the higher the energy of the MO.
d) Bonding MO are lower in energy than the starting AO while antibonding MOs are higher in energy than the starting AO.
e) All above statements are true.

9. For a Diels Alder reaction, choose the one incorrect statement

a) The best dienophile has electron withdrawing substituents on the dienophile.
b) Cis dienophile will result in a cis product and a trans dienophile will result in a trans product.
c) Endo product is preferred because of π stacking of p orbitals of the double bonds.
d) Diels Alder cannot do reactions with s-cis dienes unless the diene can rotate into s-trans.

10. For UV – Vis spectra:

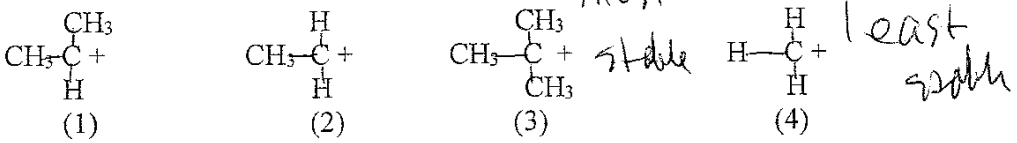


a) LUMO is π_3^*
b) HOMO is π_2
c) UV transitions measure $\pi_2 \rightarrow \pi_3^*$
d) (a) and (c) are correct
e) (b) and (c) are correct

11. Circle the one statement below which is **incorrect**.

a) In an energy diagram, a transition state is in general between either the reactant & product or between the reactant and the intermediate.
b) A heterocylic arrow looks like →
c) An "Electrophile" loves electrons while a "Nucleophile" loves nuclei
d) In an energy diagram, an intermediate is always at the top of an energy hill.

12. Put in order of most stable to least stable carbocation by choosing the one best choice:



most stable ... least stable

a) Most stable carbocation to least stable carbocation is (2) > (1) > (3) > (4)
b) Most stable carbocation to least stable carbocation is (3) > (1) > (2) > (4)
c) Most stable carbocation to least stable carbocation is (4) > (2) > (1) > (3)
d) Most stable carbocation to least stable carbocation is (1) > (2) > (3) > (4)

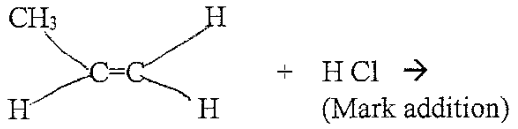
no partial credit incorrect

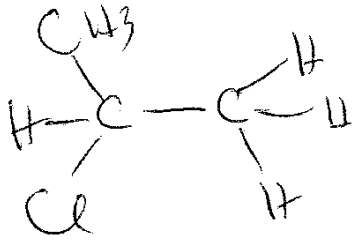
½ credit = wrong stereo, intermediate, wrong regio

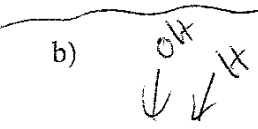
II. Short Answers (50 pts)

A. Reactions Part of Short Answers: (2 pts per reaction, 10 pts total)

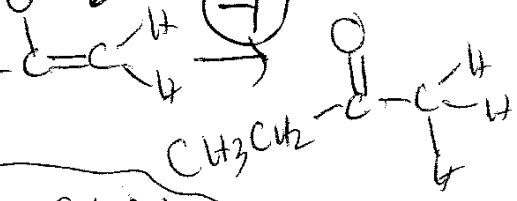
Given the following, what is the the expected organic product ? **Choose to do 5** of the following reactions you want graded by circling the letter of the reaction. If you do not choose, I will just grade the first **FIVE**.

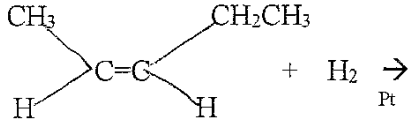
a)  + HCl → (Mark addition)

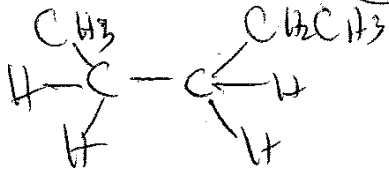


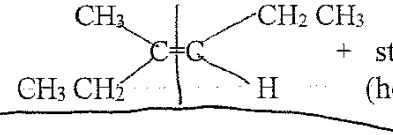
b) 

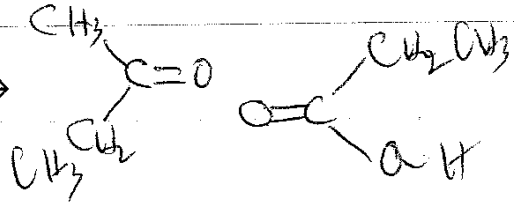
NFE – not far enough



c)  + H_2 $\xrightarrow[Pt]{}$

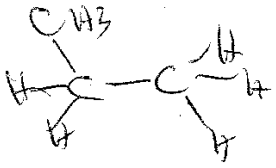


d)  + strong oxidizing agent → (hot $KMnO_4$)



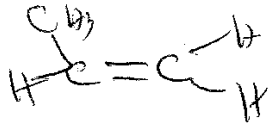
NFE – ox to diol or aldehyde –1 pt

e) CH_3-C≡C-H any reduction agent → H_2 Pt



give at least one reduction product on an alkyne
(ex: H_2/Pt, Lindlar, dissolving metal)

other



f) $CH_3\,CH_2\,CH_2$-C≡C-H + $NaNH_2/NH_3$ →

$CH_3CH_2CH_2-C\equiv C^{\ominus}\ Na^{\oplus}$

g) CH_3CH_2—O—H $\xrightarrow{SOCl_2}$ CH_3CH_2-Cl

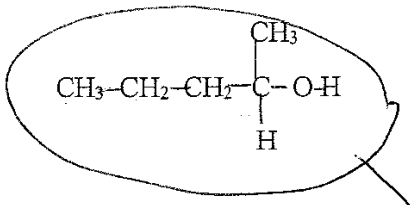
h) $CH_3CH_2\,CH_2$—Cl + Mg^0 → $CH_3CH_2CH_2MgCl$

Rmg -2 RBr mg no pt off

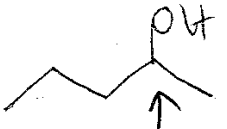
B. Short Answers part of Short Answers: (40 pts)

gave Rmg + Br OK

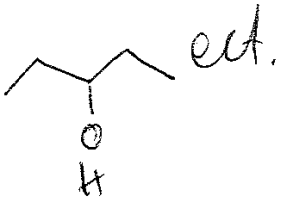
1. For the molecule below, make up one example of the following type of isomer and draw it in the space (5 pts each letter, 10 pts total)



a) structural (or constitutional) isomer of the original

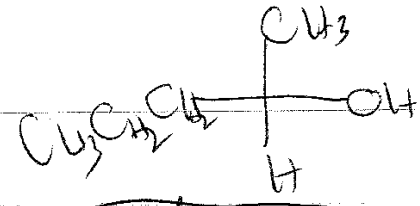


same as -5



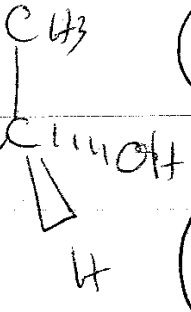
ect.

b) one enantiomer (either 3D drawing or Fisher) (chemists do not indicate a particular enantiomer without a 3D drawing or a Fisher drawing)



bad Fisher -1 to -5

drew same NO 3D info -5



bad 3D -1 to -5

attempt -2 ½

2. Spectra: For the following molecule (20 pts)

(2)
CH₃–CH₂–O–H
(1)

C–O of alcohol 1050–1150 OK

a) **Mass Spectra**: What is the molecular ion peak value for the molecule shown above (6 pts)

46 (show work) C_2H_6O

NW −3 math −1 pt

2(12) + 6(1) + 16 = 46

used atomic # −2

2(12) C 2pt ea; 6(1) H 2pt; 16 O 2pt

b) **IR Spectra**: Give one IR peak from the IR chart specifying what structure gives that peak and the peak wavenumbers. (3 pts each, 6 pts)

alkane CH ____ 2850–2960

NSE not specific enough

Functional group part is OH of alcohol giving IR peak 3400–3650 cm^{-1}

NSE −1½

c) **NMR spectra**:

NSE OH of carboxylic (−1½)

Part 1: For a proton NMR spectrum chemical shift put in order on the NMR plot by inputting the number marking the molecule in the correct place. Explain briefly. (4 pts total)

Highest ppm 1 ½ lowest ppm

Part 2: For the proton NMR spectrum of the peak (1) (bold highlighted proton) – show your coupling calculation. (4 pts total)

wrong #

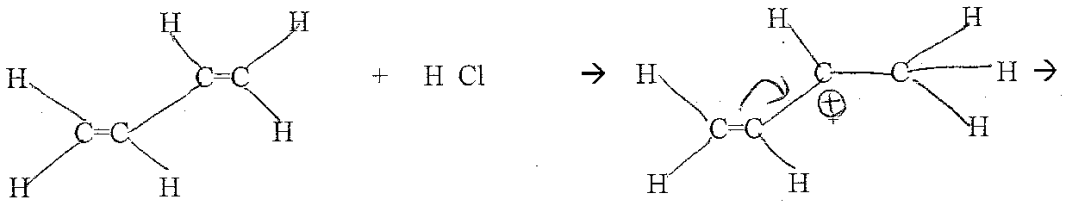
Coupling = 2 n I + 1

n [for the proton (1) is] = 2 coupling is = 3

2(2)½ + 1 = 3

NW −2

3. a) Complete the following reaction mechanism: I have provided the first intermediate. Please show the **rearrangement to 1,4 product intermediate** in the space shown. 3 D drawings not needed (10 pts)



-1 pt answer in wrong place - something else in blanic

same thing as this -6pt

not intermed gave correct product -2 pt

wrong product -3

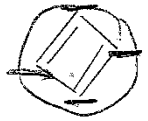
Intermediate to the 1,4 product (6 pts)

b) Is the Saytzeff's Rule product the [(kinetic) or (thermodynamic product)] (circle one) (2 pts)

c) For the 1,2 product will the energy of the final product be [(higher) or (lower)] (circle one) than the energy of the final product for the 1,4 product (2 pts)

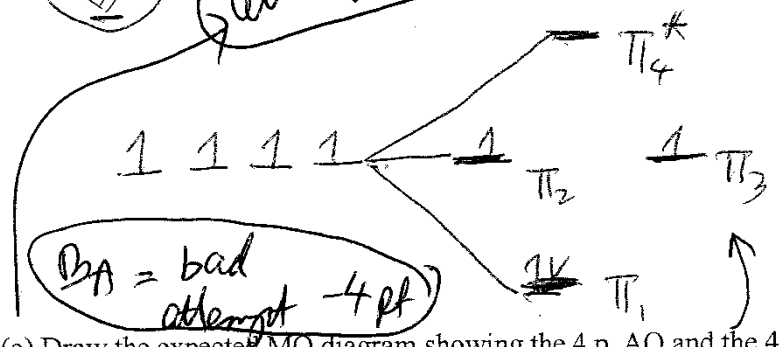
Part III. Long Answers (24 pts) Show work where applicable.

For the molecule cyclobutadiene,



attempt -3

gave 4AO → 4mO -1pt but wrong energy



BA = bad attempt -4pt

no pts off CT Consistent

(a) Draw the expected MO diagram showing the 4 p AO and the 4 π MO and the correct energy of the MO in the space above. (6 pts)

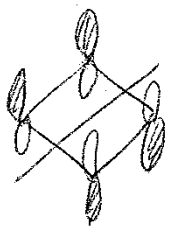
(b) Fill your MO drawing with 4 π electrons (2 pt) not 4 $\bar{e}$ -2pt

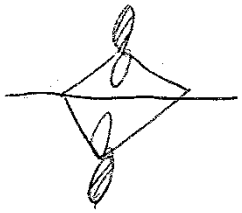
added 4 $\bar{e}$ to wrong @ mO

(c) By the MO diagram which you drew above, with the electrons filling the MO, should the molecule be stable ?. (yes, no). (2 pts) Consistent - CT no pts off

(d) Draw the p atomic orbitals involved in the MO for **one** of the MOs with **one nodes** (6 pts total) (draw just **ONE** – don't give me more, you will run out of time)

attempt -3





(e) Apply Huckel Rule equation of 4n+2 = # π electrons, to the molecule cyclobutadiene. Show work.(6 pts)

$4n+2 = 4\bar{e}$ ← wrong # $\bar{e}$ -2pt NW = -3pt

attempt -3pt

$4n = 4-2$

$4n = 2$

$n = 2/4$

-1pt math

ICT inconsistent w/e -2pt

Consistent (CT) with e OK

(f) By Huckel Rule, is your molecule [(aromatic) or (not aromatic)] (circle one) (2 pts) ?

Exam I Organic Chem II (CHEM 442) Spring 16 2/17 Dr. Hahn MWF 1pm Form B Exam# _____

Sign Name Key Print Name _____

(1 pts name above print & sign, 1 pt scantron name) (100 pts, 11 pages + scantron sheet)

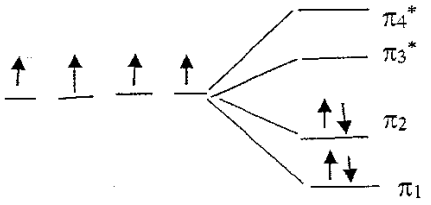
Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. If I cannot read your answer, I cannot grade your answer. (use back of exam for scratch paper – If you want me to grade something not in the space for the answer, clearly specify in writing. 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.)

Circle answer on this form for backup to the scantron. There is no partial credit for showing work in the multiple choice. NA = not attempted NW = no work

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

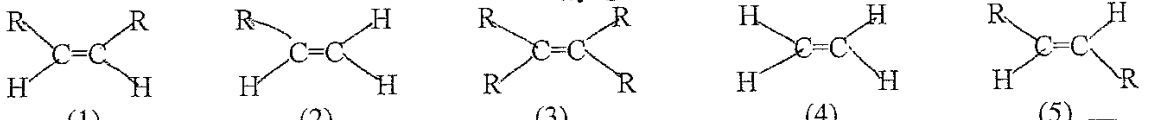
I. Multiple Choice (2 pts each, 24 pts) Choose the **one** best statement in each question.

1. For UV – Vis spectra: NFE = not far enough TF = too far NSE = not specific enough CT = consistent ICT = inconsistent



a) LUMO is π_3^*
b) HOMO is ~~π_4^*~~ π_2
c) UV transitions measure $\pi_2 \rightarrow \pi_3^*$
d) (a) and (c) are correct
e) (b) and (c) are correct

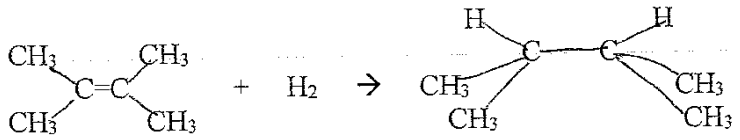
2 According to Zaitsev's (or sometimes spelled Saytzeff's) Rule, the most stable to least stable alkene is: Choose the one best statement. (R ≠ H) most stable least typo R ≠ H

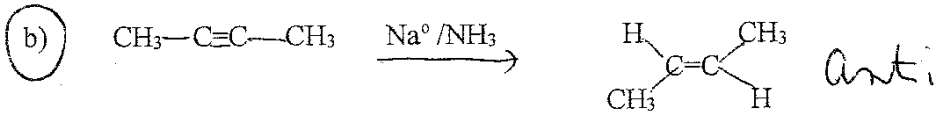


a) Most stable (3) > (5) > (1) > (2) > (4) Least stable
b) Most stable (3) > (4) > (5) > (1) > (2) least stable
c) Most stable (4) > (2) > (1) > (5) > (3) least stable
d) You can't tell which alkene is stable by looking at the structure. All alkenes are similarly stable.

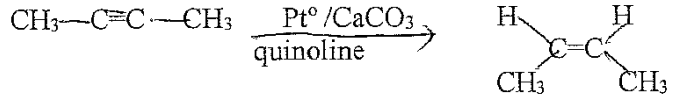
NO partial Credit MC

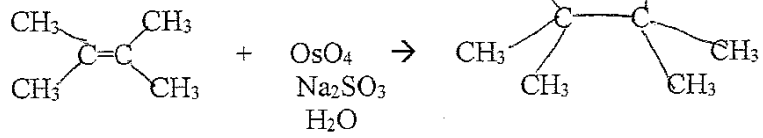
3. Which of the following reactions does **not** show a **syn** product ?

a) 

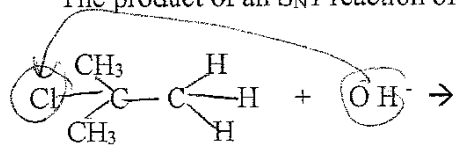
b) 

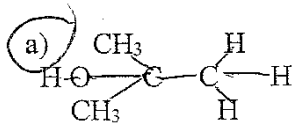
anti

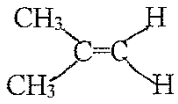
c) 

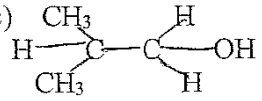
d) 

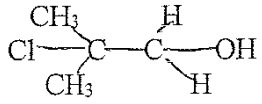
4. The product of an S_N1 reaction of the following substrate is:



a) 

b) 

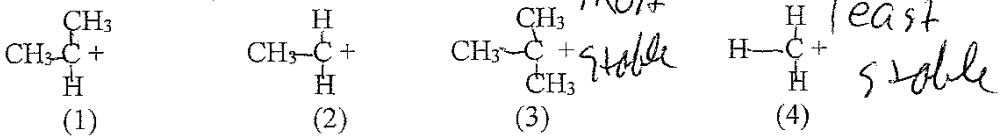
c) 

d) 

5. Circle the one statement below which is **incorrect**.

a) In an energy diagram, a transition state is in general between either the reactant & product or between the reactant and the intermediate.
b) A heterocylic arrow looks like →
c) An "Electrophile" loves electrons while a "Nucleophile" loves nuclei
d) In an energy diagram, an intermediate is always at the top of an energy hill.

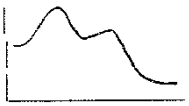
6. Put in order of most stable to least stable carbocation by choosing the one best choice:



(1) (2) (3) (4)

a) Most stable carbocation to least stable carbocation is (2) > (1) > (3) > (4)
b) Most stable carbocation to least stable carbocation is (3) > (1) > (2) > (4)
c) Most stable carbocation to least stable carbocation is (4) > (2) > (1) > (3)
d) Most stable carbocation to least stable carbocation is (1) > (2) > (3) > (4)

7. Which of the following does not match the E2 reaction mechanism ?

a. Energy diagram 

b. The E in E2 means elimination.
c. Rate = k [substrate][nucleophile]
d. All statements above are true about E2

8. When you generate MO diagrams (where AO is atomic orbital and MO is molecular orbital), choose the one best statement.

a) The number of AO must equal the number of MO.
b) A node is a line through which the AO changes sign.
c) The more nodes in an AO combination, the higher the energy of the MO.
d) Bonding MO are lower in energy than the starting AO while antibonding MOs are higher in energy than the starting AO.
e) All above statements are true.

9. For a Diels Alder reaction, choose the one incorrect statement

a) The best dienophile has electron withdrawing substituents on the dienophile.
b) Cis dienophile will result in a cis product and a trans dienophile will result in a trans product.
c) Endo product is preferred because of π stacking of p orbitals of the double bonds.
d) Diels Alder cannot do reactions with s-cis dienes unless the diene can rotate into s-trans.

10. About spectra which of the following statements is incorrect ?

a) In proton NMR spectra the information that one derives is chemical shift, peak area and coupling which gives you information about the hydrocarbon structure.

b) In IR spectra 4000 cm^{-1} to 1500 cm^{-1} is the functional group region in which peaks which are representative of functional groups appear so you can use IR to find out what functional groups are in the organic molecule.

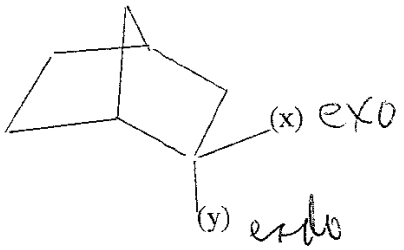
c) In IR spectra 1500 cm^{-1} to 400 cm^{-1} is the fingerprint region which can be used to match the finger prints of authentic samples of a compound with an unknown sample of an organic compound.

d) UV Vis spectra is observed for conjugated organic molecules. More conjugated systems have **larger** energy gaps which results in **larger** λ_{max}, smaller

11. For the element **Sb**, circle the one incorrect statement.

a) The atomic mass is 121.76
b) The total number of electrons for a neutral atom is 5
c) The atomic number is 51
d) The number of valence electrons is 5

12 In the following molecule, which is endo/exo. Choose the best statement.



a) (x) is exo
b) (x) is endo
c) (y) is endo
d) There is no exo / endo in this molecule.
e) (a) and (c) are correct.

II. Short Answers (50 pts)

no partial credit if incorrect

A. Reactions Part of Short Answers: (2 pts per reaction, 10 pts total)

Given the following, what is the the expected organic product ? **Choose to do 5** of the following reactions you want graded by circling the letter of the reaction. If you do not choose, I will just grade the first **FIVE**.

½ credit - wrong stereo, regio intermediate

a) CH_3, H, C=C, CH_3, H + HCl → (Mark addition)

b) $CH_3—C\equiv C-H$ $Hg(SO_4)_2$ → Mark "addition of water"

NR = not far enough

c) CH_3, CH_3, C=C, H, H + H_2 → (Pt)

d) CH_3, CH_2CH_3, C=C, H, CH_3 + strong oxidizing agent → (hot $KMnO_4$)

NR = ox to diol, aldehyde -1 pt

e) CH_3-C≡C- CH_3 any reduction agent →

give at least one reduction product on an alkyne
(ex: H_2/Pt, Lindlar, dissolving metal)

H_2 Pt

Lindlar

Na° / NH_3

f) CH_3 -C≡C-H + $NaNH_2/NH_3$ →

$CH_3—C\equiv C^{\ominus}\ Na^{\oplus}$

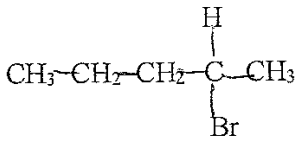
g) $CH_3CH_2CH_2-O-H \xrightarrow{SOCl_2}$ $CH_3CH_2CH_2-Cl$

h) $CH_3CH_2-Br + Mg^{\circ} \rightarrow$ CH_3CH_2MgBr

RMg -2 pt RBrMg - no pts off Gave RMg + Br no pts off

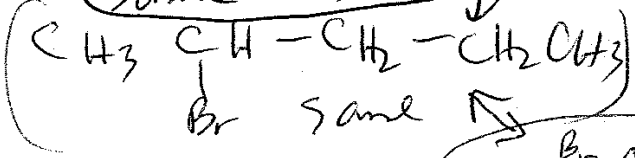
B. Short Answers part of Short Answers: (40 pts)

1. For the molecule below, make up one example of the following type of isomer and draw it in the space (5 pts each letter, 10 pts total)

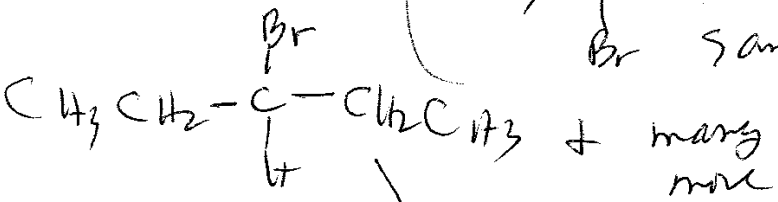


a) structural (or constitutional) isomer of the original

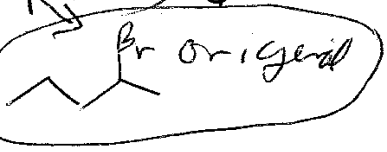
same - 5pt



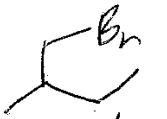
same



+ many more

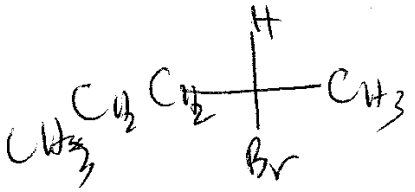


Br original



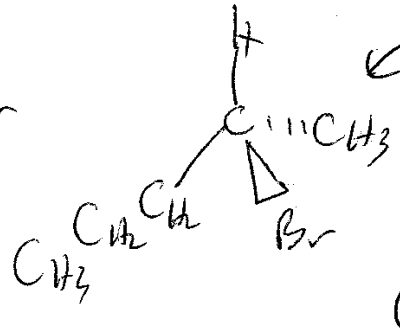
etc.

b) one enantiomer (either 3D drawing or Fisher)(chemists do not indicate a particular enantiomer without a 3D drawing or a Fisher drawing)



bad Fisher -1 to -5 pt

or



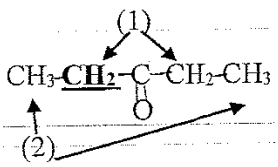
bad 3D -1 to -5

attempt -2½

drew same thing no 3D info -5 pt

2. Spectra: For the following molecule (20 total pts)

math $-\frac{1}{2}$ pt



NW = -3 no work

a) **Mass Spectra**: What is the molecular ion peak value for the molecule shown above (6 pts)

_____ (show work) $C_5H_{10}O$

$5(12) + 10(1) + 1(16) = 86$

C 2pt H 2pt O 2pt

used atomic # -2pt

b) **IR Spectra**: Give one IR peak from the IR chart specifying what structure gives that peak and the peak wavenumbers. (3 pts each, 6 pts) Alkane 2850-2960 OK

Functional group part is C=O ketone giving IR peak 1715 cm^{-1}

c) **NMR spectra**: (8 pts total) C=O — 1670-1780 -1 $\frac{1}{2}$ NDE not specific enough

Part 1: For a proton NMR spectrum chemical shift put in order on the NMR plot by inputting the number marking the molecule in the correct place. Explain briefly. (4 pts)

Highest ppm 1 2 lowest ppm

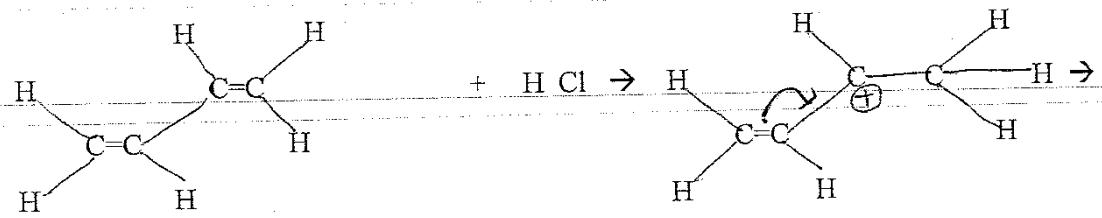
Part 2: For the proton NMR spectrum of the peak (1) (bold highlighted proton) – show your coupling calculation. (4 pts total)

Coupling = 2 n I + 1

n [for the proton (1) is] = 3 wrong # + each coupling is = 4

$2(3)\frac{1}{2} + 1 = 4$ NW -2pt

3. a) Complete the following reaction mechanism: I have provided the first intermediate. Please show the **rearrangement to 1,4 product intermediate** in the space shown. 3 D drawings not needed (10 pts)



reactant (a) intermediate (b)

answer in wrong place - something else in +1 pt blank

something as this +6 pt

not intermediate gave correct product -2 pt

wrong product -3

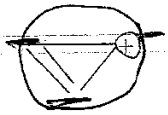
Intermediate to the 1,4 product (6 pts)

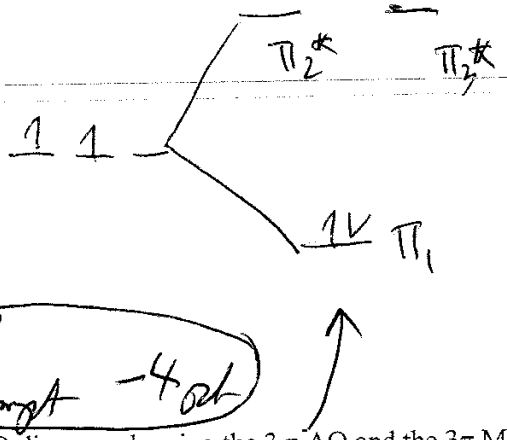
b) Is the Saytzeff's Rule product the [(kinetic) or (thermodynamic product)] (circle one) (2 pts)

c) For the 1,2 product will the energy of the final product be [(higher) or (lower)] (circle one) than the energy of the final product for the 1,4 product (2 pts)

Part III. Long Answers (24 pts) Show work where applicable.

For the molecule cyclopropenyl cation,





Gave 3AO → 3MO wrong energy -1 pt

attempt -3

BA = bad attempt -4 pt

(a) Draw the expected MO diagram showing the 3 p AO and the 3π MO and the correct energy of the MO in the space above. (6 pts)

(b) Fill your MO drawing with 2 π electrons (2 pts)

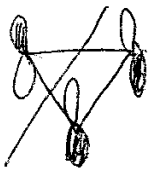
not 2 $\bar{e}$ -2pt

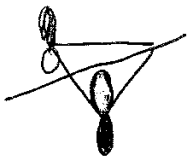
CT consistent added 2 $\bar{e}$ to your wrong no pts off

(c) By the MO diagram which you drew above, with the electrons filling the MO, should the molecule be stable ? (yes, no). (2 pts)

CT consistent w ⓑ no pts off

(d) Draw the p atomic orbitals involved in the MO for one of the MOs with **one nodes** (6 pts total)
(draw just **ONE** – don't give me more, you will run out of time)





attempt -3 pt

(e) Apply Huckel Rule equation of 4n+2 = # π electrons, to the molecule cyclopropenyl cation. Show work. (6 pts)

$4n+2 = 2\bar{e}$

$4n = 2-2$

$n = zero$

wrong # $\bar{e}$ -2 pt

NW -4 pt

attempt -3 pt

-2 pt math

ICT inconsistent w your ⓔ -2 pt

CT no pts off

(f) By Huckel Rule, is your molecule [(aromatic) or (not aromatic)] (circle one) (2 pts) ?

Exam I Organic Chem II (CHEM 442) Spring 16 2/17 Dr. Hahn MWF 1pm Form A Exam# _____

Sign Name _____ Print Name _____

(1 pts name above print & sign, 1 pt scantron name) (100 pts, 11 pages + scantron sheet)

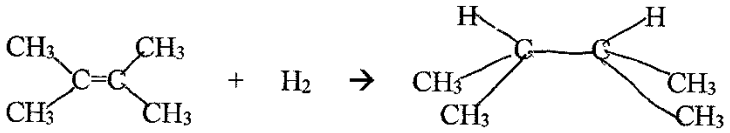
Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. If I cannot read your answer, I cannot grade your answer. (use back of exam for scratch paper – If you want me to grade something not in the space for the answer, clearly specify in writing. 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.) Color

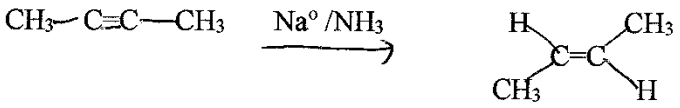
Circle answer on this form for backup to the scantron. There is no partial credit for showing work in the multiple choice.

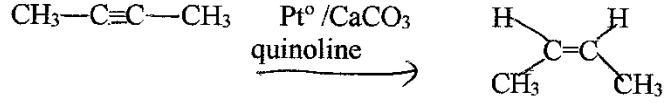
In all questions on all parts of this exam, R is not equal to hydrogen but is an alkyl.

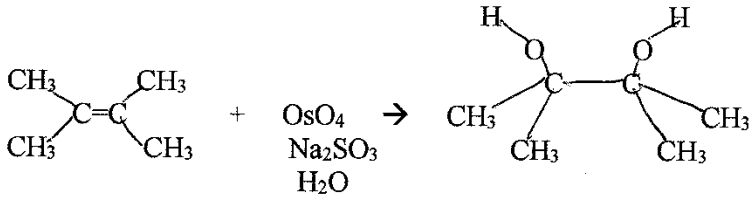
I. Multiple Choice (2 pts each, 24 pts) Choose the **one** best statement in each question.

1. Which of the following reactions does **not** show a **syn** product ?

a) 

b) 

c) 

d) 

2. About spectra which of the following statements is incorrect ?

a) In proton NMR spectra the information that one derives is chemical shift, peak area and coupling which gives you information about the hydrocarbon structure.

b) In IR spectra 4000 cm^{-1} to 1500 cm^{-1} is the functional group region in which peaks which are representative of functional groups appear so you can use IR to find out what functional groups are in the organic molecule.

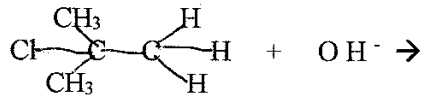
c) In IR spectra 1500 cm^{-1} to 400 cm^{-1} is the fingerprint region which can be used to match the finger prints of authentic samples of a compound with an unknown sample of an organic compound.

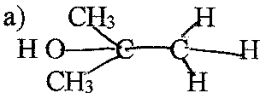
d) UV Vis spectra is observed for conjugated organic molecules. More conjugated systems have **larger** energy gaps which results in **larger** λ_{max},

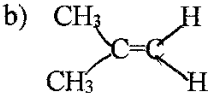
3. For the element **Sb**, circle the one incorrect statement.

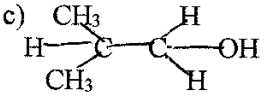
a) The atomic mass is 121.76
b) The total number of electrons for a neutral atom is 5
c) The atomic number is 51
d) The number of valence electrons is 5

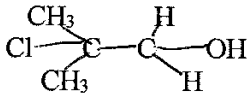
4. The product of an S_N1 reaction of the following substrate is:



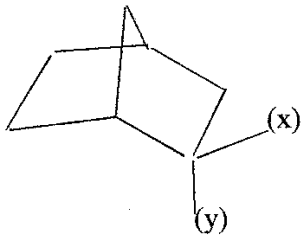
a)


b)


c)


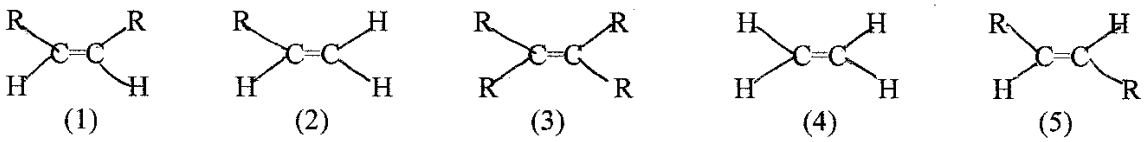
d)


5 In the following molecule, which is endo/exo. Choose the best statement.



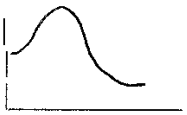
a) (x) is exo
b) (x) is endo
c) (y) is endo
d) There is no exo / endo in this molecule.
e) (a) and (c) are correct.

6 According to Zaitsev's (or sometimes spelled Saytzeff's) Rule, the most stable to least stable alkene is: Choose the one best statement. (R ≠ H)



a) Most stable (3) > (5) > (1) > (2) > (4) Least stable
b) Most stable (3) > (4) > (5) > (1) > (2) least stable
c) Most stable (4) > (2) > (1) > (5) > (3) least stable
d) You can't tell which alkene is stable by looking at the structure. All alkenes are similarly stable.

7. Which of the following does not match the E2 reaction mechanism ?

a) Energy diagram 

b) The E in E2 means elimination.
c) Rate = k [substrate][nucleophile]

d) All statements above are true about E2

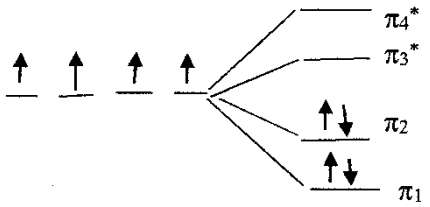
8. When you generate MO diagrams (where AO is atomic orbital and MO is molecular orbital), choose the one best statement.

a) The number of AO must equal the number of MO.
b) A node is a line through which the AO changes sign.
c) The more nodes in an AO combination, the higher the energy of the MO.
d) Bonding MO are lower in energy than the starting AO while antibonding MOs are higher in energy than the starting AO.
e) All above statements are true.

9. For a Diels Alder reaction, choose the one incorrect statement

a) The best dienophile has electron withdrawing substituents on the dienophile.
b) Cis dienophile will result in a cis product and a trans dienophile will result in a trans product.
c) Endo product is preferred because of π stacking of p orbitals of the double bonds.
d) Diels Alder cannot do reactions with s-cis dienes unless the diene can rotate into s-trans.

10. For UV – Vis spectra:

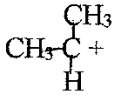


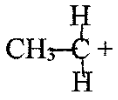
a) LUMO is π_3^*
b) HOMO is π_4^*
c) UV transitions measure $\pi_2 \rightarrow \pi_3^*$
d) (a) and (c) are correct
e) (b) and (c) are correct

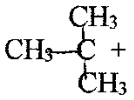
11. Circle the one statement below which is **incorrect**.

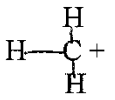
a) In an energy diagram, a transition state is in general between either the reactant & product or between the reactant and the intermediate.
b) A heterocylic arrow looks like →
c) An "Electrophile" loves electrons while a "Nucleophile" loves nuclei
d) In an energy diagram, an intermediate is always at the top of an energy hill.

12. Put in order of most stable to least stable carbocation by choosing the one best choice:


(1)


(2)


(3)

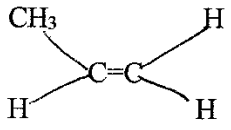

(4)

a) Most stable carbocation to least stable carbocation is (2) > (1) > (3) > (4)
b) Most stable carbocation to least stable carbocation is (3) > (1) > (2) > (4)
c) Most stable carbocation to least stable carbocation is (4) > (2) > (1) > (3)
d) Most stable carbocation to least stable carbocation is (1) > (2) > (3) > (4)

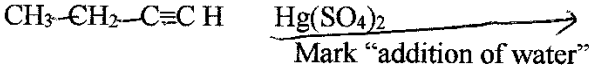
II. Short Answers (50 pts)

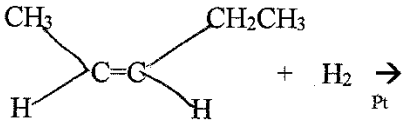
A. Reactions Part of Short Answers: (2 pts per reaction, 10 pts total)

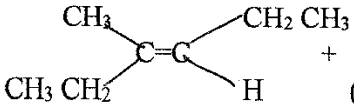
Given the following, what is the the expected organic product ? **Choose to do 5** of the following reactions you want graded by circling the letter of the reaction. If you do not choose, I will just grade the first **FIVE**.

a)  + H Cl → (Mark addition)

b)



c)  + H_2 → (Pt)

d)  + strong oxidizing agent → (hot $KMnO_4$)

e) CH_3-C≡C-H any reduction agent →

give at least one reduction product on an alkyne
(ex: H_2/Pt, Lindlar, dissolving metal)

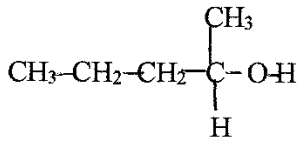
f) $CH_3\ CH_2\ CH_2$-C≡C-H + $NaNH_2/NH_3$ →

g) CH_3CH_2—O—H $\xrightarrow{SOCl_2}$

h) $CH_3CH_2\ CH_2$—Cl + Mg^o →

B. Short Answers part of Short Answers: (40 pts)

1. For the molecule below, make up one example of the following type of isomer and draw it in the space (5 pts each letter, 10 pts total)



a) structural (or constitutional) isomer of the original

b) one enantiomer (either 3D drawing or Fisher) (chemists do not indicate a particular enantiomer without a 3D drawing or a Fisher drawing)

2. Spectra: For the following molecule (20 pts)

(2)

CH_3-CH_2-O–H

(1)

a) **Mass Spectra**: What is the molecular ion peak value for the molecule shown above (6 pts)

_____ (show work)

b) **IR Spectra**: Give one IR peak from the IR chart specifying what structure gives that peak and the peak wavenumbers. (3 pts each, 6 pts)

Functional group part is _____ giving IR peak _____ cm^{-1}

c) **NMR spectra**:

Part 1: For a proton NMR spectrum chemical shift put in order on the NMR plot by inputting the number marking the molecule in the correct place. Explain briefly. (4 pts total)

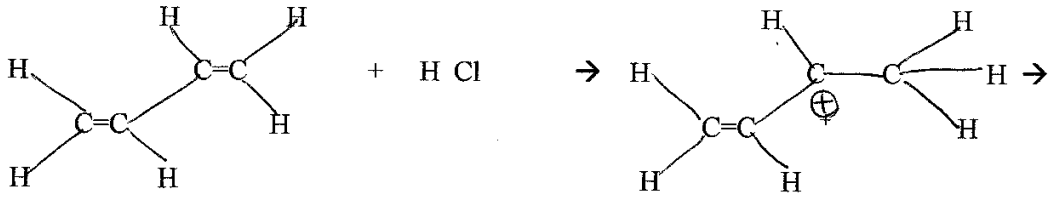
Highest ppm _____ _____ lowest ppm

Part 2: For the proton NMR spectrum of the peak (1) (bold highlighted proton) – show your coupling calculation. (4 pts total)

Coupling = 2 n I + 1

n [for the proton (1) is] = _____ coupling is = _____

3. a) Complete the following reaction mechanism: I have provided the first intermediate. Please show the **rearrangement to 1,4 product intermediate** in the space shown. 3 D drawings not needed (10 pts)



reactant (a)

intermediate (b)

Intermediate to the 1,4 product (6 pts)

b) Is the Saytzeff's Rule product the [(kinetic) or (thermodynamic product)] (circle one) (2 pts)

c) For the 1,2 product will the energy of the final product be [(higher) or (lower)] (circle one) than the energy of the final product for the 1,4 product (2 pts)

Part III. Long Answers (24 pts) Show work where applicable.

For the molecule cyclobutadiene,

(a) Draw the expected MO diagram showing the 4 p AO and the 4 π MO and the correct energy of the MO in the space above. (6 pts)

(b) Fill your MO drawing with 4 π electrons (2 pt)

(c) By the MO diagram which you drew above, with the electrons filling the MO, should the molecule be stable ?. (yes, no). (2 pts)

(d) Draw the p atomic orbitals involved in the MO for **one** of the MOs with **one nodes** (6 pts total) (draw just **ONE** – don't give me more, you will run out of time)

(e) Apply Huckel Rule equation of 4n+2 = # π electrons, to the molecule cyclobutadiene. Show work.(6 pts)

(f) By Huckel Rule, is your molecule [(aromatic) or (not aromatic)] (circle one) (2 pts) ?

Table 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional Group	Absorption (cm^{-1})	Intensity
Alkane		
C–H	2850–2960	Medium
Alkene		
=C–H	3020–3100	Medium
C=C	1640–1680	Medium
Alkyne		
≡C–H	3300	Strong
C≡C	2100–2260	Medium
Alkyl halide		
C–Cl	600–800	Strong
C–Br	500–600	Strong
Alcohol		
O–H	3400–3650	Strong, broad
C–O	1050–1150	Strong
Arene		
C–H	3030	Weak
Aromatic ring	1660–2000	Weak
	1450–1600	Medium
Amine		
N–H	3300–3500	Medium
C–N	1030–1230	Medium
Carbonyl compound		
C=O	1670–1780	Strong
Aldehyde	1730	Strong
Ketone	1715	Strong
Ester	1735	Strong
Amide	1690	Strong
Carboxylic acid	1710	Strong
Carboxylic acid		
O–H	2500–3100	Strong, broad
Nitrile		
C≡N	2210–2260	Medium
Nitro		
NO_2	1540	Strong

Periodic Table of the Elements

	1A												3A	4A	5A	6A	7A	8A
1	1 H 1.00794	2A							8B								1 H 1.00794	2 He 4.002602
2	3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
3	11 Na 22.989770	12 Mg 24.3050	3B	4B	5B	6B	7B				1B	2B	13 Al 26.981538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
6	55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.96655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98038	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

58 Ce 140.116	59 Pr 140.90765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.03588	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Exam I Organic Chem II (CHEM 442) Spring 16 2/17 Dr. Hahn MWF 1pm Form B Exam# _____

Sign Name _____ Print Name _____

(1 pts name above print & sign, 1 pt scantron name) (100 pts, 11 pages + scantron sheet)

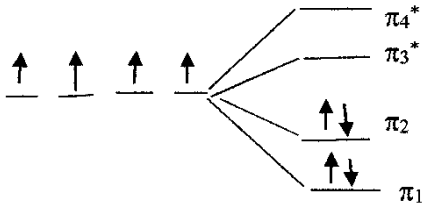
Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. If I cannot read your answer, I cannot grade your answer. (use back of exam for scratch paper – If you want me to grade something not in the space for the answer, clearly specify in writing. 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.)

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.

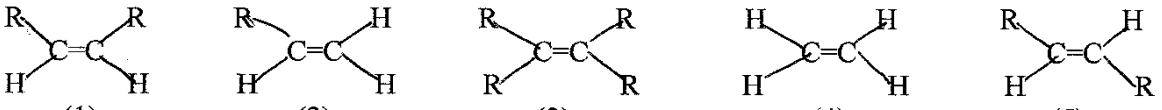
I. Multiple Choice (2 pts each, 24 pts) Choose the **one** best statement in each question.

1. For UV – Vis spectra:



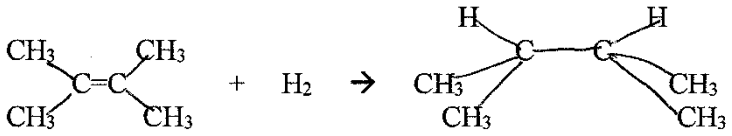
a) LUMO is π_3^*
b) HOMO is π_4^*
c) UV transitions measure $\pi_2 \rightarrow \pi_3^*$
d) (a) and (c) are correct
e) (b) and (c) are correct

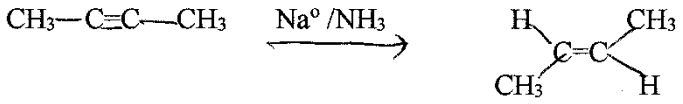
2 According to Zaitsev's (or sometimes spelled Saytzeff's) Rule, the most stable to least stable alkene is: Choose the one best statement. (R ≠ H)

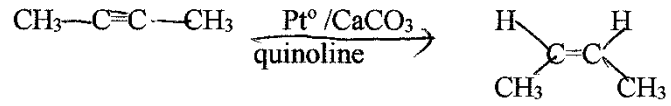


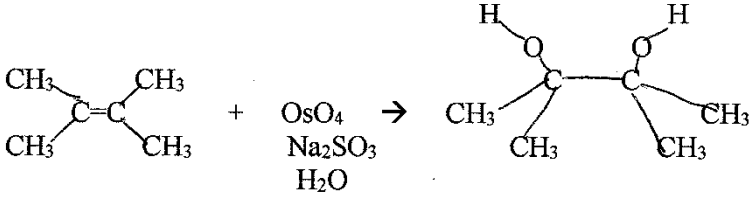
a) Most stable (3) > (5) > (1) > (2) > (4) Least stable
b) Most stable (3) > (4) > (5) > (1) > (2) least stable
c) Most stable (4) > (2) > (1) > (5) > (3) least stable
d) You can't tell which alkene is stable by looking at the structure. All alkenes are similarly stable.

3. Which of the following reactions does **not** show a **syn** product ?

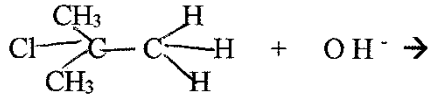
a) 

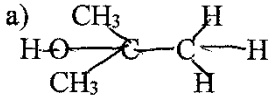
b) 

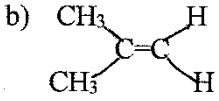
c) 

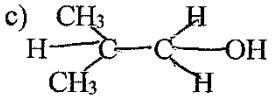
d) 

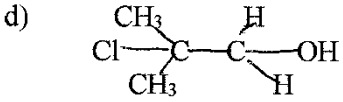
4. The product of an S_N1 reaction of the following substrate is:



a) 

b) 

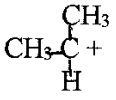
c) 

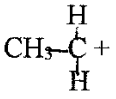
d) 

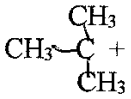
5. Circle the one statement below which is **incorrect**.

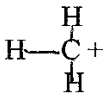
a) In an energy diagram, a transition state is in general between either the reactant & product or between the reactant and the intermediate.
b) A heterocylic arrow looks like →
c) An "Electrophile" loves electrons while a "Nucleophile" loves nuclei
d) In an energy diagram, an intermediate is always at the top of an energy hill.

6. Put in order of most stable to least stable carbocation by choosing the one best choice:


(1)

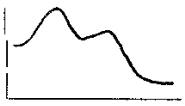

(2)


(3)


(4)

a) Most stable carbocation to least stable carbocation is (2) > (1) > (3) > (4)
b) Most stable carbocation to least stable carbocation is (3) > (1) > (2) > (4)
c) Most stable carbocation to least stable carbocation is (4) > (2) > (1) > (3)
d) Most stable carbocation to least stable carbocation is (1) > (2) > (3) > (4)

7. Which of the following does not match the E2 reaction mechanism ?

a. Energy diagram 

b. The E in E2 means elimination.
c. Rate = k [substrate][nucleophile]
d. All statements above are true about E2

8. When you generate MO diagrams (where AO is atomic orbital and MO is molecular orbital), choose the one best statement.

a) The number of AO must equal the number of MO.
b) A node is a line through which the AO changes sign.
c) The more nodes in an AO combination, the higher the energy of the MO.
d) Bonding MO are lower in energy than the starting AO while antibonding MOs are higher in energy than the starting AO.
e) All above statements are true.

9. For a Diels Alder reaction, choose the one incorrect statement

a) The best dienophile has electron withdrawing substituents on the dienophile.
b) Cis dienophile will result in a cis product and a trans dienophile will result in a trans product.
c) Endo product is preferred because of π stacking of p orbitals of the double bonds.
d) Diels Alder cannot do reactions with s-cis dienes unless the diene can rotate into s-trans.

10. About spectra which of the following statements is incorrect ?

a) In proton NMR spectra the information that one derives is chemical shift, peak area and coupling which gives you information about the hydrocarbon structure.

b) In IR spectra 4000 cm^{-1} to 1500 cm^{-1} is the functional group region in which peaks which are representative of functional groups appear so you can use IR to find out what functional groups are in the organic molecule.

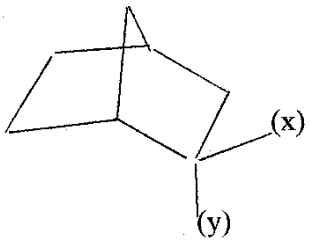
c) In IR spectra 1500 cm^{-1} to 400 cm^{-1} is the fingerprint region which can be used to match the finger prints of authentic samples of a compound with an unknown sample of an organic compound.

d) UV Vis spectra is observed for conjugated organic molecules. More conjugated systems have **larger** energy gaps which results in **larger** λ_{max},

11. For the element **Sb**, circle the one incorrect statement.

a) The atomic mass is 121.76
b) The total number of electrons for a neutral atom is 5
c) The atomic number is 51
d) The number of valence electrons is 5

12 In the following molecule, which is endo/exo. Choose the best statement.

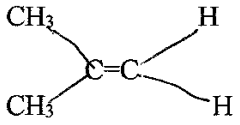


a) (x) is exo
b) (x) is endo
c) (y) is endo
d) There is no exo / endo in this molecule.
e) (a) and (c) are correct.

II. Short Answers (50 pts)

A. Reactions Part of Short Answers: (2 pts per reaction, 10 pts total)

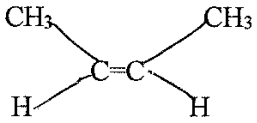
Given the following, what is the the expected organic product ? **Choose to do 5** of the following reactions you want graded by circling the letter of the reaction. If you do not choose, I will just grade the first **FIVE**.

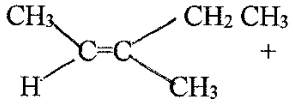
a)  + H Cl → (Mark addition)

b)

$CH_3—C\equiv C-H$ $Hg(SO_4)_2$

Mark "addition of water"

c)  + H_2 $\xrightarrow[Pt]{}$

d)  + strong oxidizing agent → (hot $KMnO_4$)

e) CH_3-C≡C- CH_3 any reduction agent →

give at least one reduction product on an alkyne
(ex: H_2/Pt, Lindlar, dissolving metal)

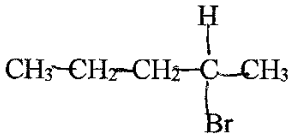
f) CH_3 -C≡C-H + $NaNH_2/NH_3$ →

g) $CH_3CH_2\,CH_2\text{-}O\text{-}H \xrightarrow{SOCl_2}$

h) $CH_3CH_2\text{-}Br + Mg^{o} \rightarrow$

B. Short Answers part of Short Answers: (40 pts)

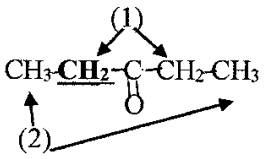
1. For the molecule below, make up one example of the following type of isomer and draw it in the space (5 pts each letter, 10 pts total)



a) structural (or constitutional) isomer of the original

b) one enantiomer (either 3D drawing or Fisher)(chemists do not indicate a particular enantiomer without a 3D drawing or a Fisher drawing)

2. Spectra: For the following molecule (20 total pts)



a) **Mass Spectra**: What is the molecular ion peak value for the molecule shown above (6 pts)

_____ (show work)

b) **IR Spectra**: Give one IR peak from the IR chart specifying what structure gives that peak and the peak wavenumbers. (3 pts each, 6 pts)

Functional group part is _____ giving IR peak _____ cm^{-1}

c) **NMR spectra**: (8 pts total)

Part 1: For a proton NMR spectrum chemical shift put in order on the NMR plot by inputting the number marking the molecule in the correct place. Explain briefly. (4 pts)

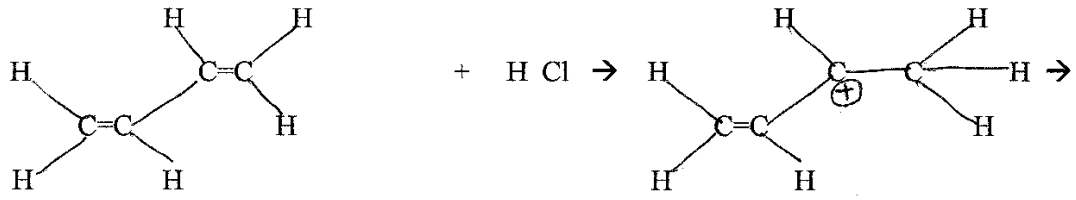
Highest ppm _____ _____ lowest ppm

Part 2: For the proton NMR spectrum of the peak (1) (bold highlighted proton) – show your coupling calculation. (4 pts total)

Coupling = 2 n I + 1

n [for the proton (1) is] = _____ coupling is = _____

3. a) Complete the following reaction mechanism: I have provided the first intermediate. Please show the **rearrangement to 1,4 product intermediate** in the space shown. 3 D drawings not needed (10 pts)



reactant (a) intermediate (b)

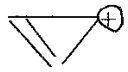
Intermediate to the 1,4 product (6 pts)

b) Is the Saytzeff's Rule product the [(kinetic) or (thermodynamic product)] (circle one) (2 pts)

c) For the 1,2 product will the energy of the final product be [(higher) or (lower)] (circle one) than the energy of the final product for the 1,4 product (2 pts)

Part III. Long Answers (24 pts) Show work where applicable.

For the molecule cyclopropenyl cation,



(a) Draw the expected MO diagram showing the 3 p AO and the 3π MO and the correct energy of the MO in the space above. (6 pts)

(b) Fill your MO drawing with 2 π electrons (2 pts)

(c) By the MO diagram which you drew above, with the electrons filling the MO, should the molecule be stable ?. (yes, no). (2 pts)

(d) Draw the p atomic orbitals involved in the MO for **one** of the MOs with **one nodes** (6 pts total) (draw just **ONE** – don't give me more, you will run out of time)

(e) Apply Huckel Rule equation of $4n+2 = \#\ \pi$ electrons, to the molecule cyclopropenyl cation. Show work. (6 pts)

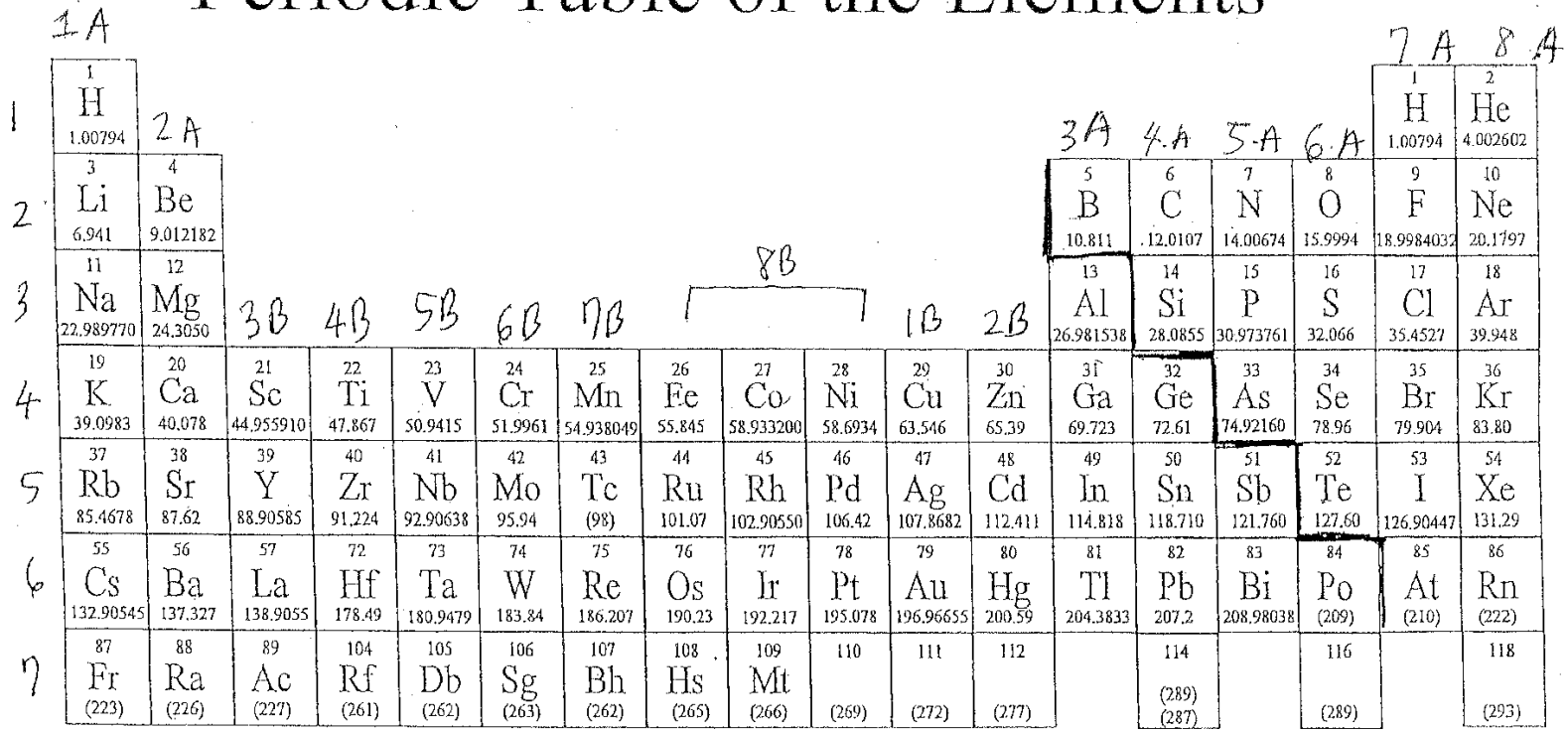
(f) By Huckel Rule, is your molecule [(aromatic) or (not aromatic)] (circle one) (2 pts) ?

Table 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional Group	Absorption (cm^{-1})	Intensity
Alkane		
C–H	2850–2960	Medium
Alkene		
=C–H	3020–3100	Medium
C=C	1640–1680	Medium
Alkyne		
≡C–H	3300	Strong
C≡C	2100–2260	Medium
Alkyl halide		
C–Cl	600–800	Strong
C–Br	500–600	Strong
Alcohol		
O–H	3400–3650	Strong, broad
C–O	1050–1150	Strong
Arene		
C–H	3030	Weak
Aromatic ring	1660–2000	Weak
	1450–1600	Medium
Amine		
N–H	3300–3500	Medium
C–N	1030–1230	Medium
Carbonyl compound		
C=O	1670–1780	Strong
Aldehyde	1730	Strong
Ketone	1715	Strong
Ester	1735	Strong
Amide	1690	Strong
Carboxylic acid	1710	Strong
Carboxylic acid		
O–H	2500–3100	Strong, broad
Nitrile		
C≡N	2210–2260	Medium
Nitro		
NO_2	1540	Strong

Table 12-1, p. 439

Periodic Table of the Elements



58 Ce 140.116	59 Pr 140.90765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.03588	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)