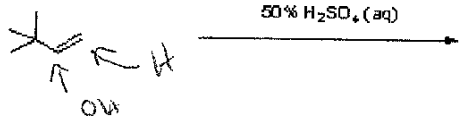
Organic Chemistry I Lecture Fall 2016 11/14/16 Exam III Monday Dr. Hahn Exam # _____

Name Key (print) Name _____ (sign)

Please show work for partial credit and full credit on the Long Answers and in some of the Short Answer Questions. Multiple choice questions have no partial credit. Please write anything you want graded legibly. If you run out of space, please continue on the empty back pages but clearly label where the remaining answer can be found. (If I can't find your answer or cannot read it, I obviously cannot grade it). Return your entire exam including the periodic table. (Please count your exam pages and make sure there are 10 real pages + periodic table)

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question. (2 pts each, 24 pts total)

1) What is the major product of the following reaction? (Markovnikov addition of water) 1) D

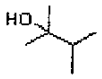


A 

B) 

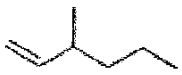
C) 

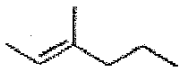
rearrange

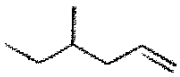
(D) 

2) Which one of these alkene would be likely to experience a carbocation rearrangement when treated with $Hg(OAc)_2$ in water, followed by reaction with sodium borohydride? 2) D

does not rearrange

A) 

B) 

C) 

(D) None of these would undergo a rearrangement.

3) Which of the following intermediates is thought to occur in the mechanism by which alkenes are hydrated in the presence of acid? 3) B

A) free radical
(B) carbocation
C) carbanion
D) alkyne
E) carbene

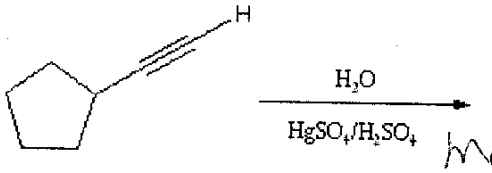
4) Treatment of cyclopentene with peroxybenzoic acid (example: MCPBA) _____. 4) C

A) yields a diol.
B) results in oxidative cleavage of the ring to produce an acyclic compound
C) yields an epoxide
D) gives the same product as treatment of cyclopentene with hot $KMnO_4$

5) Which of the following additions to alkenes occur(s) specifically in an anti fashion? 5) D

A) hydroboration-oxidation
B) addition of H_2
C) addition of H_2O in dilute acid
D) addition of Br_2

6) What is the major product of the following acid/catalyzed hydration reaction? 6) C

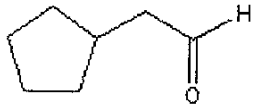


mark-to

rearrange

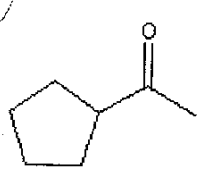
+ keto enol

A)

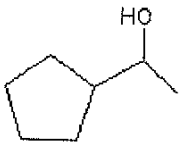


B)

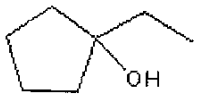
C)

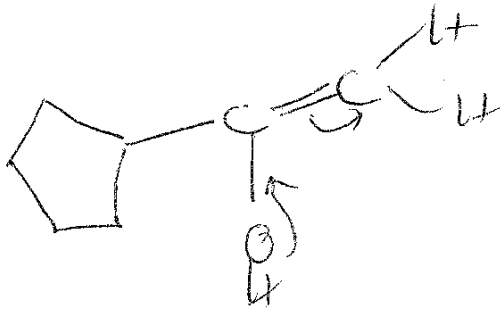


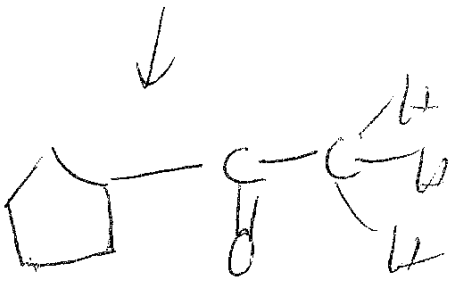
D)



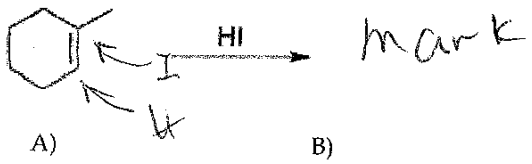
E)

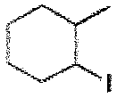


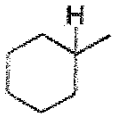


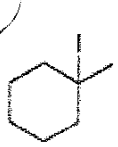


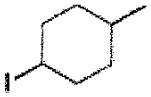
7) Predict the major product of the following reaction. 7) C



A) 

B) 

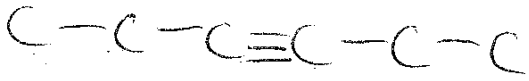
C) 

D) 

8) Which of the following improperly describes the physical properties of an alkyne? 8) B
A) relatively nonpolar
B) insoluble in most organic solvents
C) boiling point nearly the same as an alkane with similar carbon skeleton
D) nearly insoluble in water

9) What synthetic goal is achieved by subjecting an alkene to an oxymercuration–demercuration sequence? 9) A
A) Markovnikov addition of H_2O wherein skeletal rearrangement is prevented
B) anti-Markovnikov addition of H_2O wherein skeletal rearrangement is promoted
C) anti-Markovnikov addition of H_2O wherein skeletal rearrangement is prevented
D) Markovnikov addition of H_2O wherein skeletal rearrangement is promoted
E) syn-hydroxylation

10) What is the major organic product that results when 3-heptyne is subjected to excess hydrogen and a platinum catalyst? 10) E
A) 2-heptyne
B) (Z)-2-heptene
C) (Z)-3-heptene
D) (*E*)-3-heptene
E) heptane



11) In the following molecule (showing just the skeleton of the molecule) the shortest carbon–carbon bond is between carbons _____. 11) C

5 4 3 2 1
C-C≡C-C=C

A) 1 and 2 B) 2 and 3 C) 3 and 4 D) 4 and 5

12) The carbon–carbon triple bond of an alkyne is composed of _____. 12) D
A) three π bonds
B) two σ bonds and one π bond
C) three σ bonds
D) one σ bond and two π bonds

Part II: Short Answers (47 pts)

A. Nomenclature: (2 pts each, 4 pts)

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

a. name 5-bromo hex-2-yne

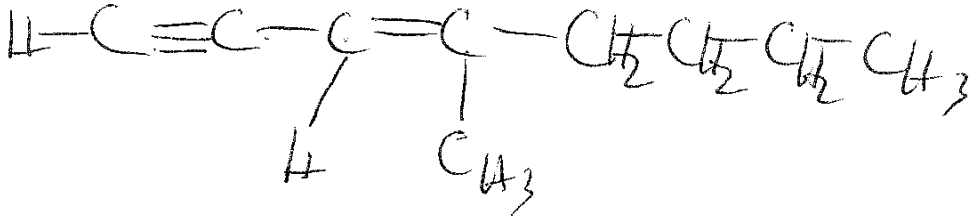
$CH_3-C\equiv C-CH_2-CH(Br)-CH_3$

1 2 3 4 5 6

hex ~~ane~~ yne

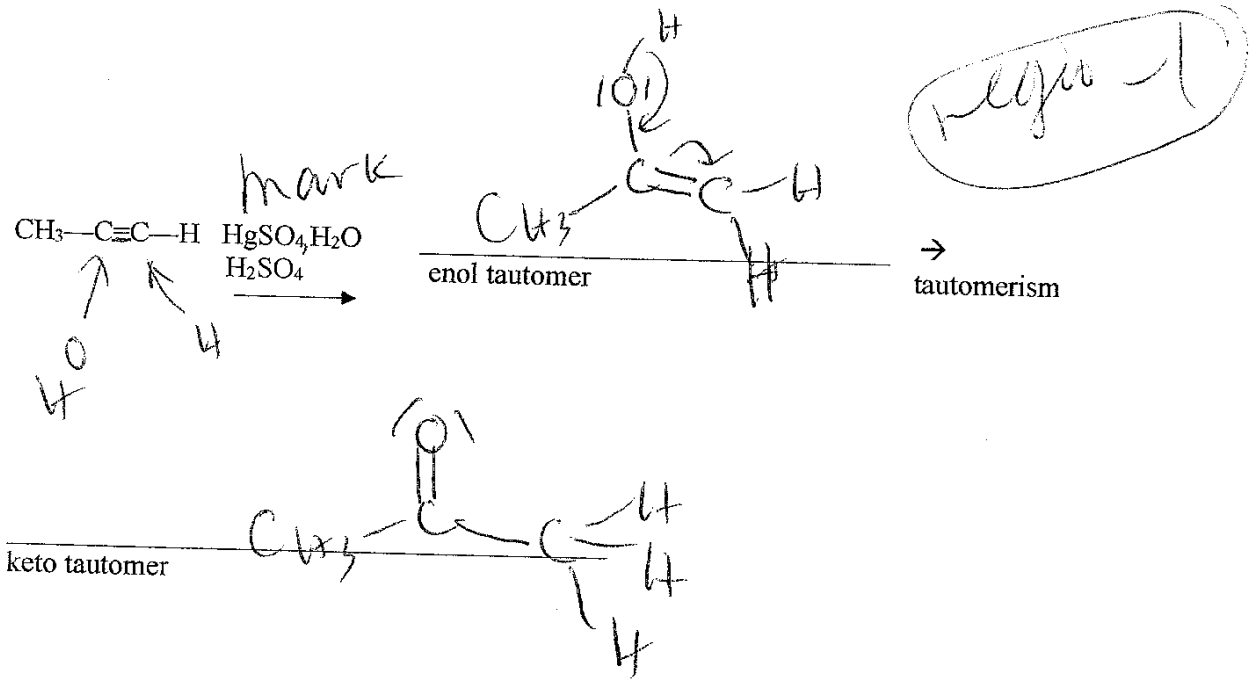
2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

Z-4-methyloct-3-en-1-yne



B. Short Answer Part of Short Answer (25 pts)

1. Given the following, show the keto enol tautomerism (10 pts total, 5 pts each)



2. Match the following by filling the blank with a letter. Each letter will be used ONE time and each letter will be used at least one time. Each blank have an answer. (10 pts total, 2 pts each)

(A) $Hg(OAc)_2$, H_2O, $NaBH_4$ (B) BH_3:THF, H_2O_2 OH^- (C) H Br, ROOR

(D) hot $KMnO_4$ (E) Na°, NH_3

D oxidative cleavage of alkene to carboxylic acid (strong oxidation)

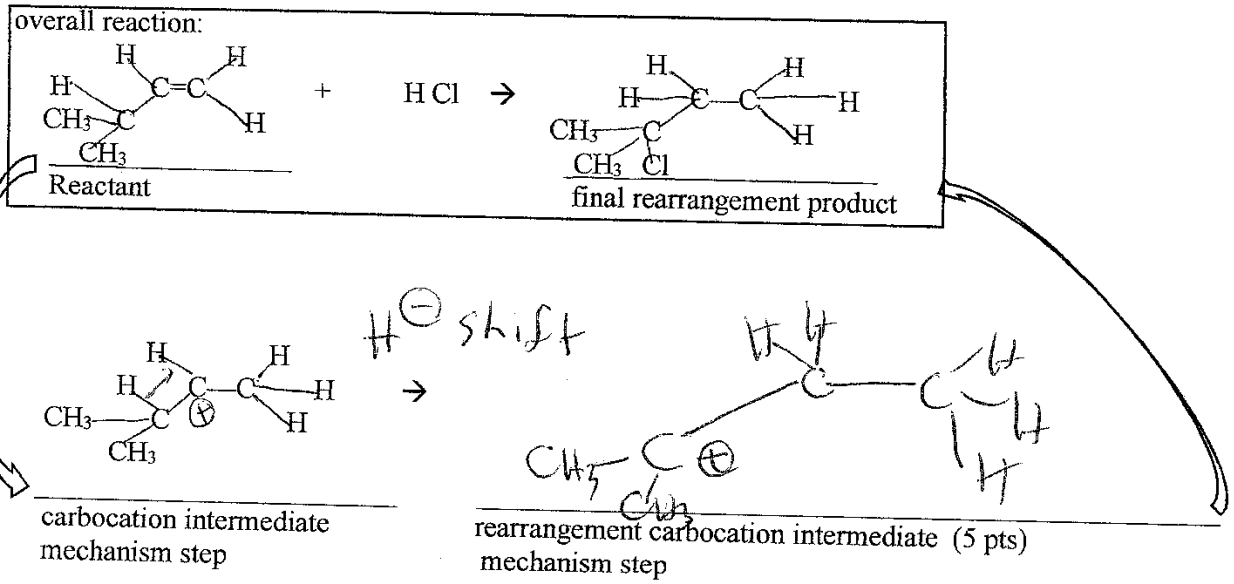
B anti-Markovnikov addition of water to double bond

C anti-Markovnikov addition of HX to double bond

E hydrogenation of alkyne (anti addition to alkene)

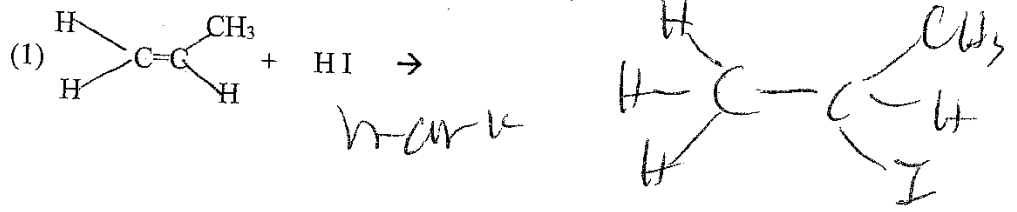
A Markovnikov addition of water to double bond

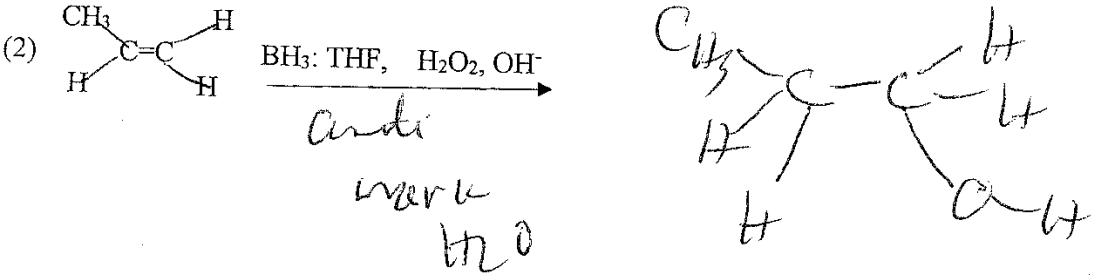
3. The following shows a rearrangement reaction for the addition of H Cl to an alkene, show the rearranged carbocation which leads to the product. (5 pts)

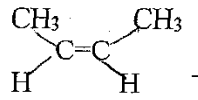
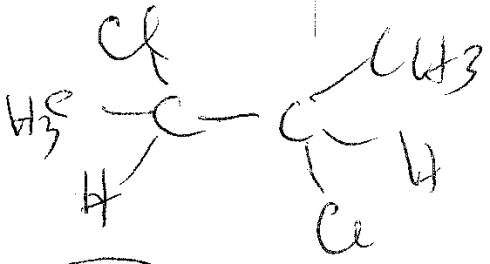


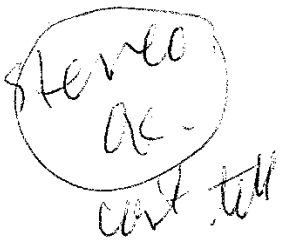
C. Reactions: (18 total, 2 pts each) give the expected organic product for the following reaction.

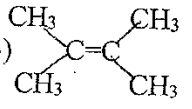
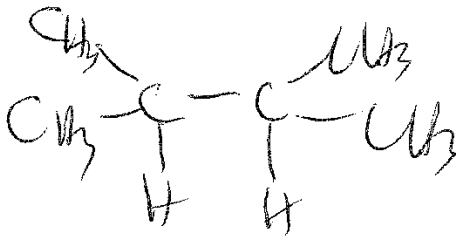
1. **Circle 9 of the following reactions you want graded**. If you do not circle, I will just grade the first 9 reactions.

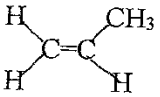
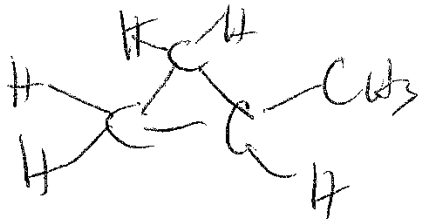
(1) 

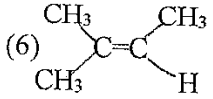
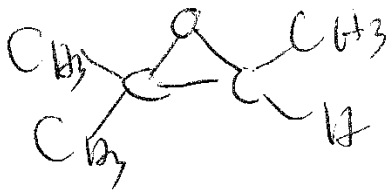
(2) 

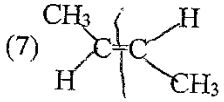
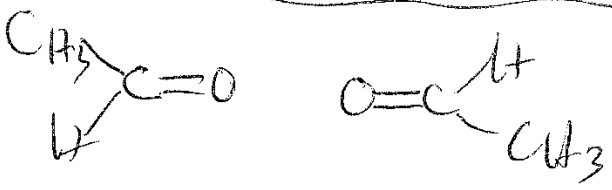
(3)  Cl_2 

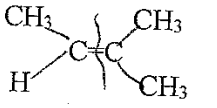
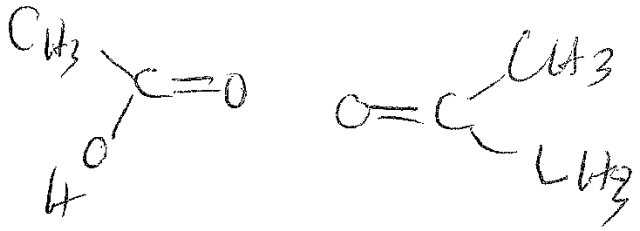


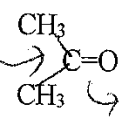
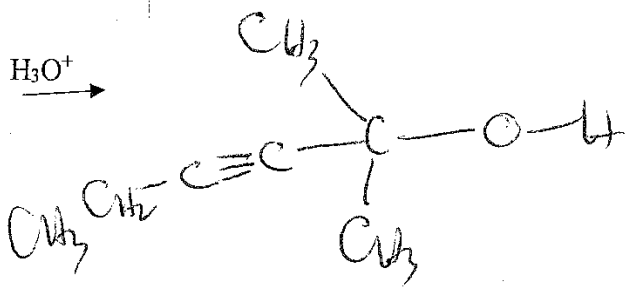
(4)  H_2, Pt 

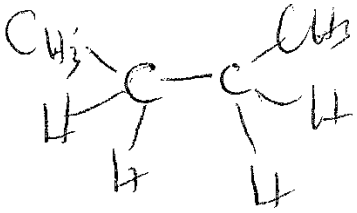
(5)  CH_2I_2 $Zn(Cu)$ 

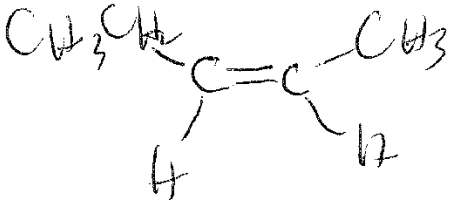
(6)  MCPBA 

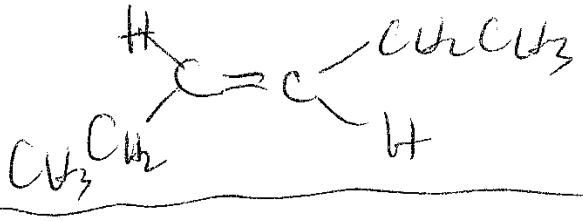
(7)  O_3 

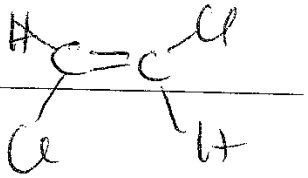
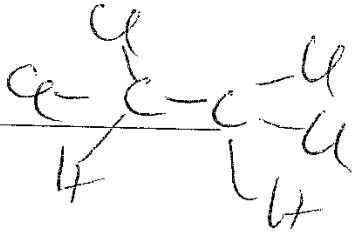
(8)  $KMnO_4$, hot 

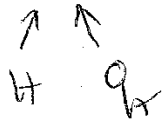
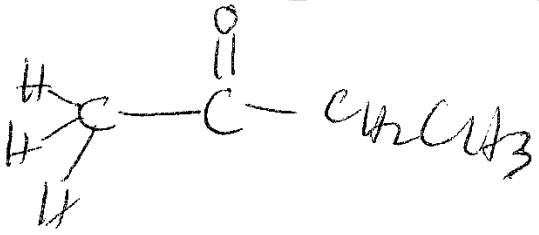
(9) $CH_3CH_2—C\equiv C\,Na$ +  H_3O^+ 

(10) $CH_3-C\equiv C-CH_3$ H_2, Pd 

(11) $CH_3-CH_2-C\equiv C-CH_3$ Lindlar's catalyst 

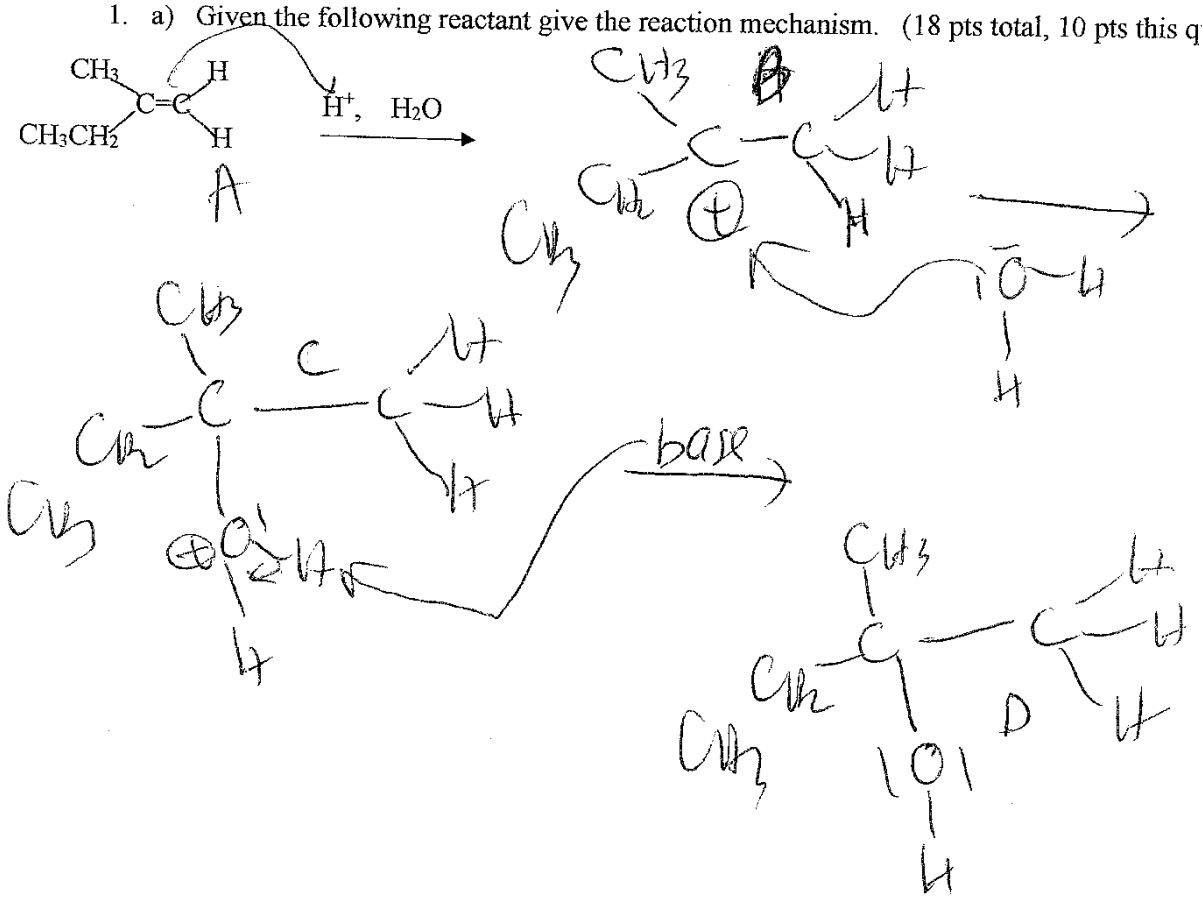
(12) $CH_3-CH_2-C\equiv C-CH_2CH_3$ Na^o, NH_3 

(13) $H-C\equiv C-H$ Cl_2 (1st mole)  Cl_2 (2nd mole) 

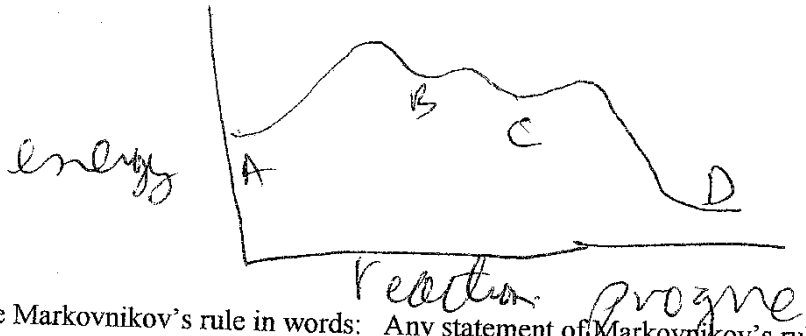
(14) $H-C\equiv C-CH_2-CH_3$  H_2O, $HgSO_4$, H_2SO_4 

Part III: Long Answers (30 pts)

1. a) Given the following reactant give the reaction mechanism. (18 pts total, 10 pts this question)



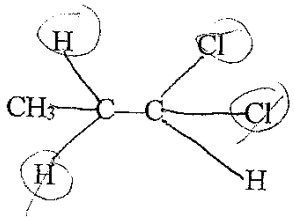
b) give the energy diagram for the reaction mechanism above. (4 pts)



c) Give Markovnikov's rule in words: Any statement of Markovnikov's rule will suffice – there are about 3 different ways to give this rule. (4 pts)

① Then that has (H) gets
② mechanism goes by most stable carbocation intermediate

2. Complete the following synthesis: (12 pts, 3 pts each)



----->
Remove
2 H Cl
strong base

$CH_3-C\equiv C-H$

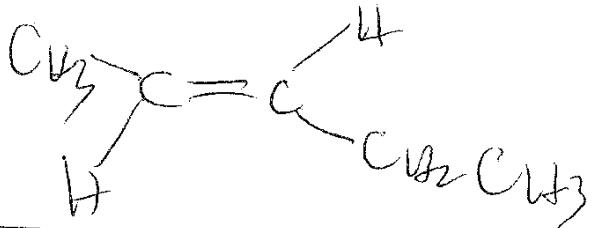
A C_3H_4 → $NaNH_2$
(acid base rxn with terminal alkyne)

$CH_3C\equiv C^{\ominus}\ :Na^{\oplus}$

B C_3H_3Na → CH_3CH_2Cl

$CH_3-C\equiv C-CH_2CH_3$

C C_5H_8 → Na°, NH_3
(one of hydrogenation method)



D C_5H_{10}

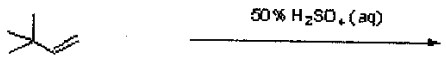
Organic Chemistry I Lecture Fall 2016 11/14/16 Exam III Monday Dr. Hahn Exam # 8

Name_____ (print) Name _____(sign)

Please show work for partial credit and full credit on the Long Answers and in some of the Short Answer Questions. Multiple choice questions have no partial credit. Please write anything you want graded legibly. If you run out of space, please continue on the empty back pages but clearly label where the remaining answer can be found. (If I can't find your answer or cannot read it, I obviously cannot grade it). Return your entire exam including the periodic table. (Please count your exam pages and make sure there are 10 real pages + periodic table)

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question. (2 pts each, 24 pts total)

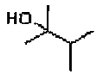
1) What is the major product of the following reaction? (Markovnikov addition of water) 1) _____



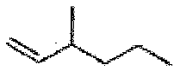
A) 

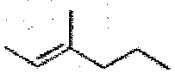
B) 

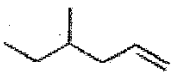
C) 

D) 

2) Which one of these alkene would be likely to experience a carbocation rearrangement when treated with $Hg(OAc)_2$ in water, followed by reaction with sodium borohydride? 2) _____

A) 

B) 

C) 

D) None of these would undergo a rearrangement.

3) Which of the following intermediates is thought to occur in the mechanism by which alkenes are hydrated in the presence of acid? 3) _____

A) free radical
B) carbocation
C) carbanion
D) alkyne
E) carbene

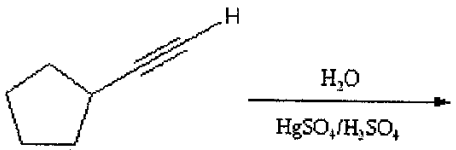
4) Treatment of cyclopentene with peroxybenzoic acid (example: MCPBA) _____. 4) _____

A) yields a diol.
B) results in oxidative cleavage of the ring to produce an acyclic compound
C) yields an epoxide
D) gives the same product as treatment of cyclopentene with hot $KMnO_4$

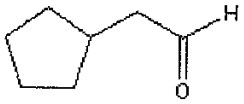
5) Which of the following additions to alkenes occur(s) specifically in an anti fashion? 5) _____

A) hydroboration–oxidation
B) addition of H_2
C) addition of H_2O in dilute acid
D) addition of Br_2

6) What is the major product of the following acid/catalyzed hydration reaction? 6) _____

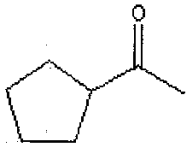


A)

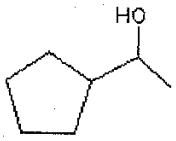


B)

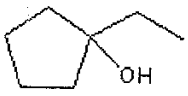
C)



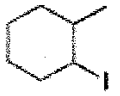
D)

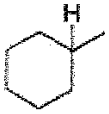


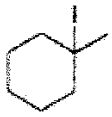
E)

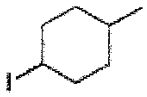


7) Predict the major product of the following reaction. 7) _____

A) 

B) 

C) 

D) 

8) Which of the following improperly describes the physical properties of an alkyne? 8) _____
A) relatively nonpolar
B) insoluble in most organic solvents
C) boiling point nearly the same as an alkane with similar carbon skeleton
D) nearly insoluble in water

9) What synthetic goal is achieved by subjecting an alkene to an oxymercuration–demercuration sequence? 9) _____
A) Markovnikov addition of H_2O wherein skeletal rearrangement is prevented
B) anti-Markovnikov addition of H_2O wherein skeletal rearrangement is promoted
C) anti-Markovnikov addition of H_2O wherein skeletal rearrangement is prevented
D) Markovnikov addition of H_2O wherein skeletal rearrangement is promoted
E) syn-hydroxylation

10) What is the major organic product that results when 3-heptyne is subjected to excess hydrogen and a platinum catalyst? 10) _____
A) 2-heptyne
B) (Z)-2-heptene
C) (Z)-3-heptene
D) (*E*)-3-heptene
E) heptane

11) In the following molecule (showing just the skeleton of the molecule) the shortest carbon–carbon bond is between carbons _____. 11) _____

5 4 3 2 1
C-C≡C-C=C

A) 1 and 2 B) 2 and 3 C) 3 and 4 D) 4 and 5

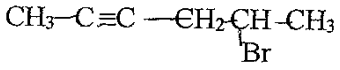
12) The carbon–carbon triple bond of an alkyne is composed of _____. 12) _____
A) three π bonds
B) two σ bonds and one π bond
C) three σ bonds
D) one σ bond and two π bonds

Part II: Short Answers (47 pts)

A. Nomenclature: (2 pts each, 4 pts)

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

a. name _____

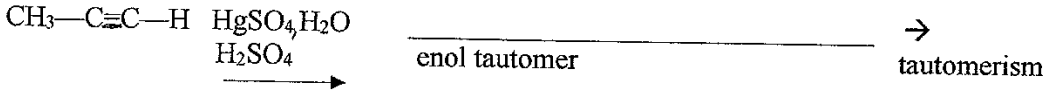


2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

Z-4-methyloct-3-en-1-yne

B. Short Answer Part of Short Answer (25 pts)

1. Given the following, show the keto enol tautomerism (10 pts total, 5 pts each)



keto tautomer

2. Match the following by filling the blank with a letter. Each letter will be used ONE time and each letter will be used at least one time. Each blank have an answer. (10 pts total, 2 pts each)

(A) $Hg(OAc)_2$, H_2O, $NaBH_4$ (B) BH_3:THF, H_2O_2 OH^- (C) H Br, ROOR

(D) hot $KMnO_4$ (E) Na°, NH_3

_____ oxidative cleavage of alkene to carboxylic acid (strong oxidation)

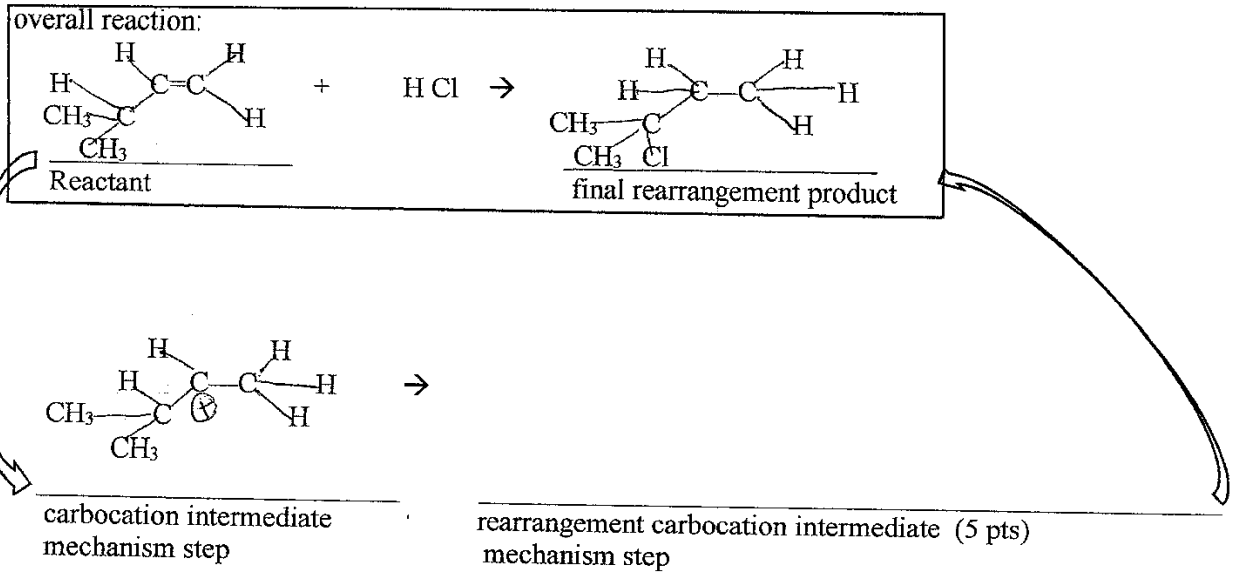
_____ anti-Markovnikov addition of water to double bond

_____ anti-Markovnikov addition of HX to double bond

_____ hydrogenation of alkyne (anti addition to alkene)

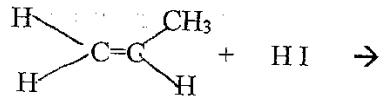
_____ Markovnikov addition of water to double bond

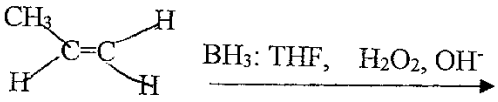
3. The following shows a rearrangement reaction for the addition of H Cl to an alkene, show the rearranged carbocation which leads to the product. (5 pts)

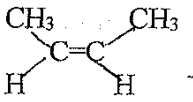


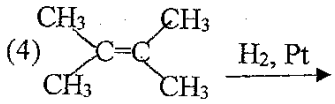
C. Reactions: (18 total, 2 pts each) give the expected organic product for the following reaction.

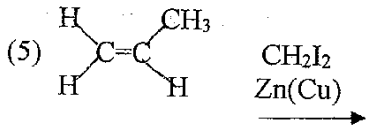
1. **Circle 9 of the following reactions you want graded**. If you do not circle, I will just grade the first 9 reactions.

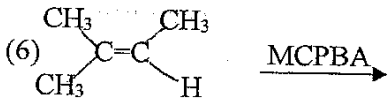
(1) 

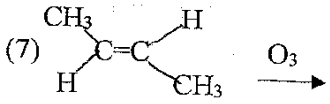
(2) 

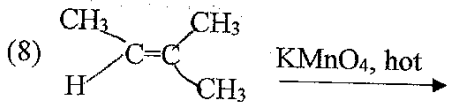
(3) 
CH3
CH3
C=C
H
H
Cl2

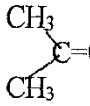
(4) 
CH3
CH3
C=C
CH3
CH3
H2, Pt

(5) 
H
CH3
C=C
H
H
CH2I2
Zn(Cu)

(6) 
CH3
CH3
C=C
CH3
H
MCPBA

(7) 
CH3
H
C=C
H
CH3
O3

(8) 
CH3
CH3
C=C
H
CH3
KMnO4, hot

(9) $CH_3CH_2{-}C{\equiv}C\,Na$ +  $\xrightarrow{H_3O^+}$

(10) $CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow{H_2,\ Pd}$

(11) $CH_3{-}CH_2{-}C{\equiv}C{-}CH_3 \xrightarrow{\text{Lindlar's catalyst}}$

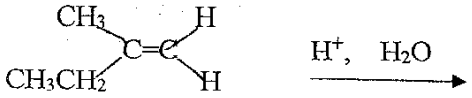
(12) $CH_3{-}CH_2{-}C{\equiv}C{-}CH_2CH_3 \xrightarrow{Na^\circ,\ NH_3}$

(13) $H{-}C{\equiv}C{-}H \xrightarrow{Cl_2\ (1^{st}\ \text{mole})} \xrightarrow{Cl_2\ (2^{nd}\ \text{mole})}$

(14) $H{-}C{\equiv}C{-}CH_2{-}CH_3 \xrightarrow[H_2SO_4]{H_2O,\ HgSO_4,}$

Part III: Long Answers (30 pts)

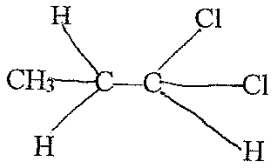
1. a) Given the following reactant give the reaction mechanism. (18 pts total, 10 pts this question)



b) give the energy diagram for the reaction mechanism above. (4 pts)

c) Give Markovnikov's rule in words: Any statement of Markovnikov's rule will suffice – there are about 3 different ways to give this rule. (4 pts)

2. Complete the following synthesis: (12 pts, 3 pts each)



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Remove
2 H Cl
strong base

A C_3H_4 → $NaNH_2$ (acid base rxn with terminal alkyne)

B C_3H_3Na → CH_3CH_2 Cl

C C_5H_8 → Na^o, NH_3 (one of hydrogenation method)

D C_5H_{10}