Organic chemistry (I) 2nd midterm exam 11/23 (Tue.)

Name: _____ ; Student ID number: _____ ; Score: _____/301

I. Multiple choice (5 points each, total 145 points)

ADE 1. Which statement(s) are true according to the Hammond postulate?

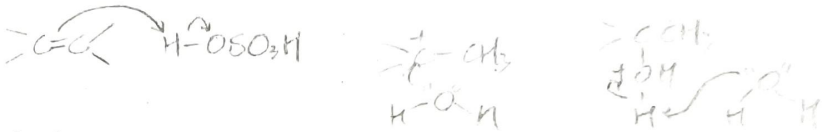
A) In an exergonic reaction, the transition state is more similar in energy to the reactant than the product.

B) In an exergonic reaction, the transition state is more similar in energy to the product than the reactant.

C) In an endergonic reaction, the transition state is more similar in energy to the reactant than the product.

D) In an endergonic reaction, the transition state is more similar in energy to the product than the reactant.

E) A and D



ABC DE 2. Identify the true statements in the mechanism in the addition of water to an alkene.

A) The addition of the electrophile is a slow step.

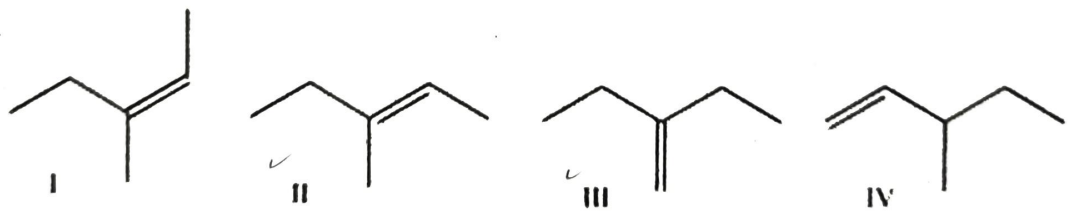
B) The addition of the nucleophile is a fast step.

C) A carbocation is formed as an intermediate.

D) Water abstracts the extra proton from the protonated alcohol.

E) all of the above

C 3. Which of the following alkenes yield(s) 3-bromo-3-methylpentane as the major product upon addition of HBr?



A) I and II only

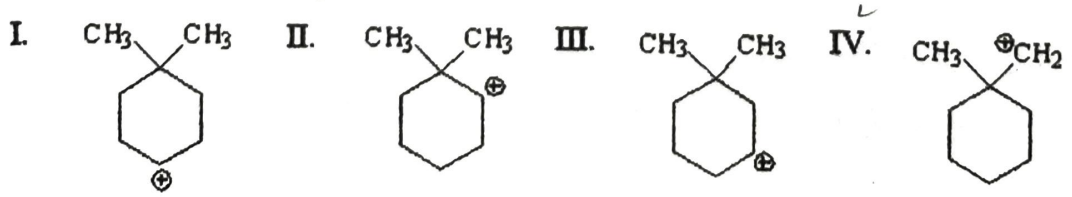
B) III only

C) I, II, and III only

D) all of them

E) none of them

BDE 4. Which of the following carbocations is likely to rearrange?



A) I

B) II

C) III

D) IV

E) II and IV

5. Which statement is true in the final product in the hydroboration-oxidation of an alkene?

A) Markovnikov orientation and syn addition occur.

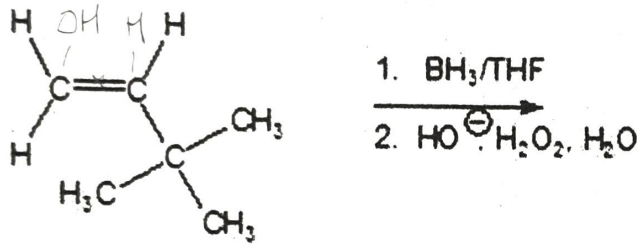
B) Markovnikov orientation and anti addition occur.

C) Anti-Markovnikov orientation and syn addition occur.

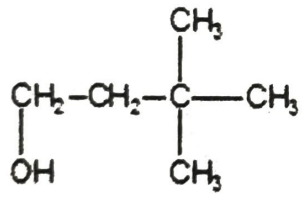
D) Anti-Markovnikov orientation and anti addition occur.

E) Markovnikov orientation and both syn and anti addition occur.

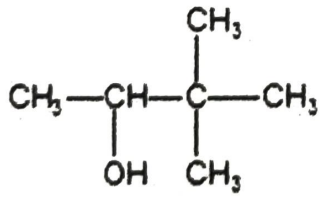
6. Provide the major organic product in the reaction below.



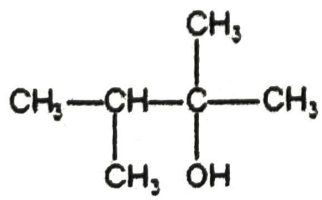
A)



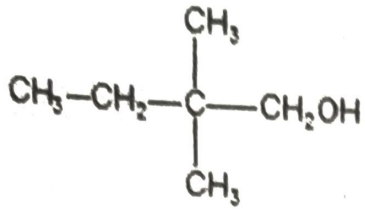
B)



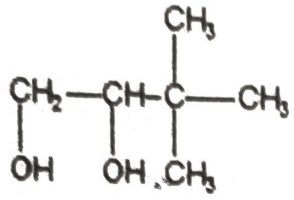
C)



D)

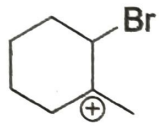


E)

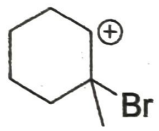


7. Which reaction intermediate is formed when Br2/CCl4 reacts with 1-methylcyclohexene?

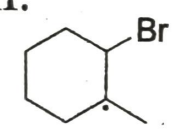
I.



II.

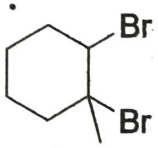


III.



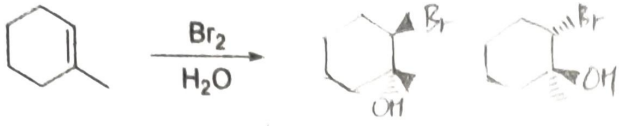
IV.

V.

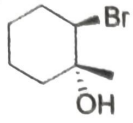


A) I
B) II
C) III
D) IV
E) V

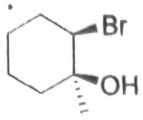
AD 8. Provide the organic product in the reaction below.



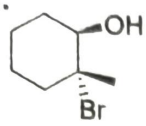
I.



IV.



II.



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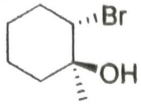

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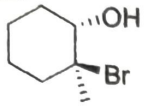
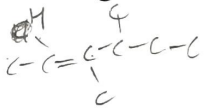


(A) I
B) II
C) IV
(D) I and V
E) II and III

D 9. Upon hydrogenation, which of the following alkenes releases the least heat per mole? fast

A) 3,4-dimethyl-1-hexene

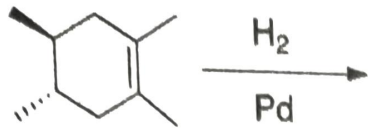


B) (*Z*)-3,4-dimethyl-2-hexene
C) (*E*)-3,4-dimethyl-2-hexene
D) (*Z*)-3,4-dimethyl-3-hexene
E) (*E*)-3,4-dimethyl-3-hexene

A 10. A reaction in which a mixture of two constitutional isomers is obtained but one is formed in higher amounts than the other is called a

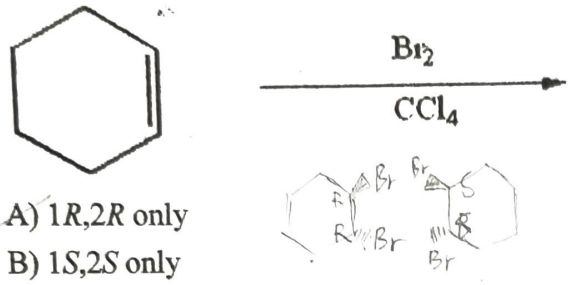
A) regioselective reaction.
B) regiospecific reaction.
C) stereospecific reaction.
D) stereoselective reaction.
E) successful reaction.

D 11. Hydrogenation of the following compound generates



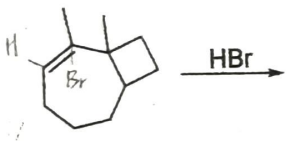
A) constitutional isomers.
B) identical compounds.
C) enantiomers.
D) diastereomers.
E) meso compounds.

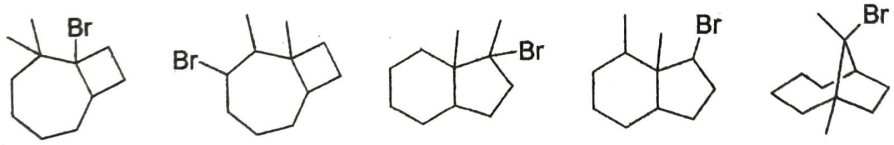
D 12. What configurations are found in the product(s) of the reaction below?



A) 1*R*,2*R* only
B) 1*S*,2*S* only
C) 1*R*,2*S* only
D) an equal mixture of 1*R*,2*R* and 1*S*,2*S*
E) an equal mixture of 1*R*,2*R* and 1*R*,2*S*

A 13. Assuming that a single carbocation rearrangement occurs, which of the following molecules is the major product of this reaction?

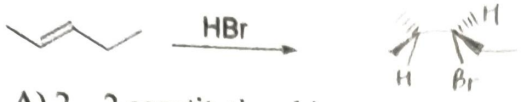




I. II. III. IV. V.

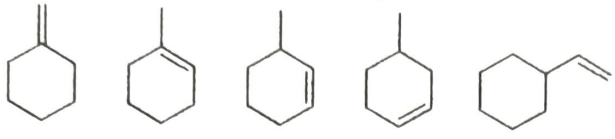
A) I
B) II
C) III
D) IV
E) V

E 14. How many and what type of isomers are formed in the following reaction:



A) 2 – 2 constitutional isomers
B) 2 – 1 pair of enantiomers
C) 3 – 1 pair of enantiomers and 1 constitutional isomer
D) 3 – 1 pair of enantiomers and 1 meso compound
E) 4 – 2 pairs of enantiomers

A 15. Which of the following compounds reacts most rapidly with HCl?

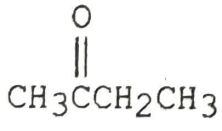


I. II. III. IV. V.

A) I
B) II
C) III
D) IV
E) V

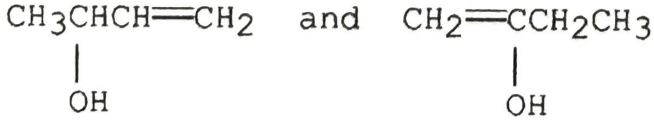
B C
AC 16. Which of the following statements correctly describes the general reactivity of alkynes?
A) An alkyne is an electron-rich molecule and therefore reacts as a nucleophile.
B) The σ bonds of alkynes are higher in energy than the π bonds and are thus more reactive.
C) Unlike alkenes, alkynes fail to undergo electrophilic addition reactions.
D) Alkynes are generally more reactive than alkenes.
E) Alkynes react as electrophiles, whereas alkenes react as nucleophiles.

E 17. Which of the following are enol forms of 2-butanone?

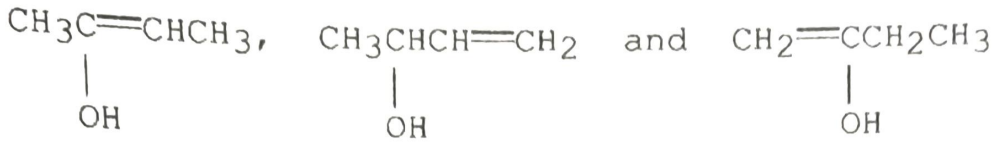


A)

B)



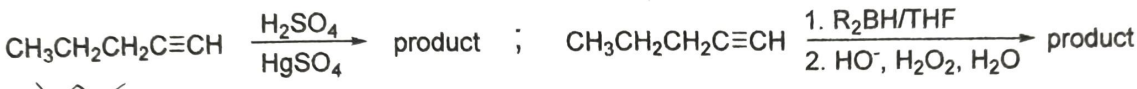
C)



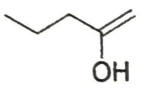
D)

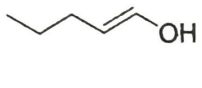
E)

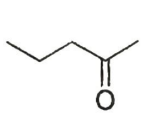
B 18. Give the major organic product for the reactions.

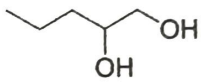


I. 

II. 

III. 

IV. 

V. 

A) I ; II

B) III ; IV

C) I ; IV

D) II ; III

E) V

BE 19. The best reagent combination needed to convert 2-butyne to *cis*-2-butene is (there may be more than one correct answer)

A) H_2/ Pd/C.

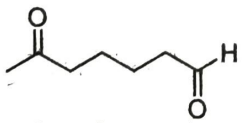
B) H_2/Pd/$CaCO_3$.

C) H_2/Raney Ni.

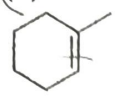
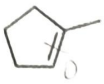
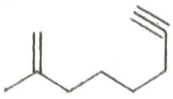
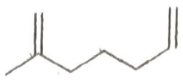
D) Na or Li /NH_3.

E) quinoline/$Pb(OAc)_2$.

A 20. Which is the correct starting material structure upon its treatment with O_3 followed by $(CH_3)_2S$ to give 6-oxo-heptanal?



6-oxoheptanal

(A)  (B)  (C)  (D)  (E) 

A 21. Which is the correct order of decreasing acidity in the following compounds?

H_2O	CH_3CH_3	NH_3	$CH_2{=}CH_2$	$HC{\equiv}CH$
A	B	C	D	E

A) A > E > C > D > B

B) A > E > D > B > C

C) E > A > C > B > D

D) A > C > E > D > B

E) E > D > B > A > C

A E C D B

B 22. What are the products of the following reaction?

$CH_3OH + CH_3C{\equiv}C\text{-}Na^+ \rightarrow ?$

A) $CH_3C{\equiv}CCH_3 + NaOH$

B) $CH_3C{\equiv}COCH_3 + NaOH$

C) $CH_3C{\equiv}CH + CH_3O\text{-}Na^+$

D) $CH_3OC{\equiv}CH + NaCH_3$

E) no reaction

CD 23. 2-butyne has higher boiling point than 2-butene because

A) 2-butyne has stronger hydrogen bonds

B) 2-butyne has stronger dipole dipole interactions

C) 2-butyne has stronger London dispersion forces

D) 2-butyne has triple bond which is harder to break

E) 2-butyne has fewer hydrogens

BDE 24. Why are mercuric ions needed during the hydration of alkynes?

A) They catalyze the reaction by reacting with the alkyne and making it more nucleophilic.

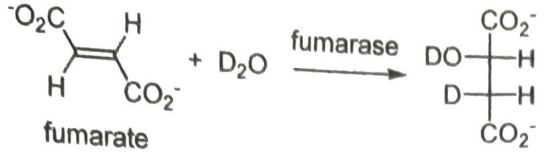
B) They catalyze the reaction by reacting with the alkyne and making it more electrophilic.

C) They make alkynes more soluble in water.

D) They increase the rate of addition reaction.

E) B and D

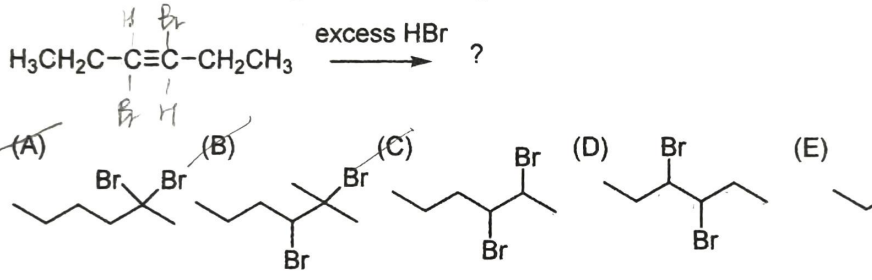
B 25. When a fumarate reacts with D2O in the presence of enzyme fumarase, only one isomer of the product is formed, as shown below. Is the enzyme catalyzing a syn, anti, radical, or π-complex type addition of D_2O?



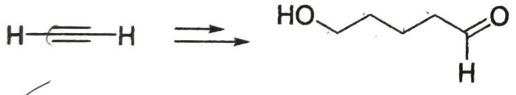
A) syn addition
B) anti addition
C) π-complex addition
D) radical addition
E) both B and C

26. Is the enzymatic reaction specified above (Q.25) a regioselective, stereoselective, stereospecific, regioisomeric, or non-stereoselective?
A) regioselective.
B) stereoselective.
C) stereospecific.
D) regioisomeric.
E) on-stereoselective.

27. Which of the following is the correct product structure?



28. Which of the following methods would give the product in reasonable yield?



A) 1. $NaNH_2$ 2. CH_2=$CHCH_2Br$ 3. H_2O, H_2SO_4
B) 1. $NaNH_2$ 2. CH_2=$CHCH_2Br$ 3. HCl
C) 1. $NaNH_2$ 2. CH_2=$CHCH_2Br$ 3. R_2BH/THF 4. HO^-, H_2O_2, H_2O
D) 1. $NaNH_2$ 2. $HOCH_2CHCH_2Br$ 3. R_2BH/THF 4. HO^-, H_2O_2, H_2O
E) Both C and D

29. Which of the following sets of reactions accomplishes the synthesis shown below?

A) 1. $NaNH_2$ 2. CH_2=$CHCH_2Br$ 3. H_2, Lindlar 4. BH_3/THF 5. HO^-,H_2O_2, H_2O
B) 1. $NaNH_2$ 2. CH_2=$CHCH_2Br$ 3. MCPBA

C) 1. $NaNH_2$ 2. $CH_3CH_2CH_2Br$ 3. BH_3/THF 4. HO^-,H_2O_2, H_2O

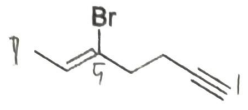
D) 1. $NaNH_2$ 2. CH_2=$CHCH_2Br$ 3. $Na/NH_{3(liq)}$ 4. MCPBA

E) 1. $NaNH_2$ 2. $CH_3CH_2CH_2Br$ 4. 9-BBN-THF 5. HO^-,H_2O_2, H_2O

II. Provide suitable names, structure(s), reagent(s), or explanation(s) for the following questions. (total 156 points)

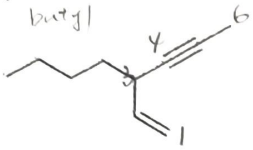
1. Provide an acceptable name or structure for the following questions. (4 pts each, total 24pts)

(a)

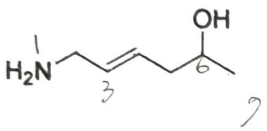


hepten-

(b)



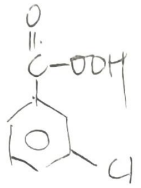
(c)



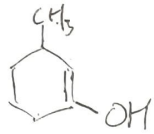
(d)

epoxy

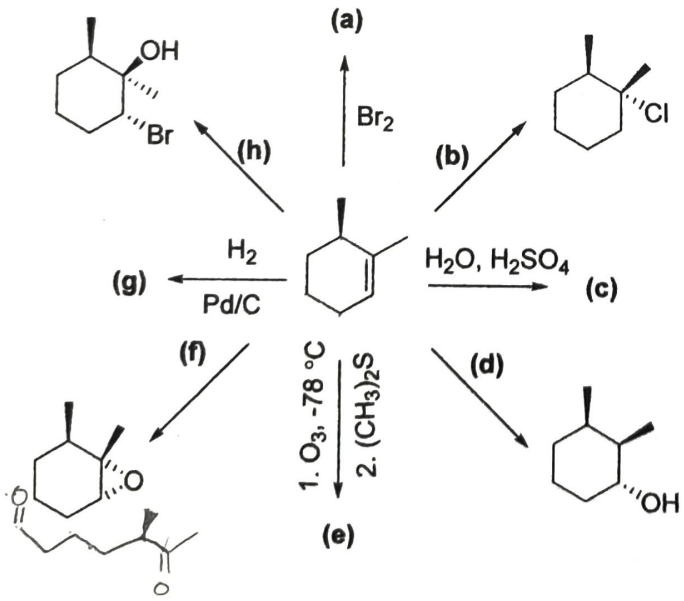
(e) 3-chloroperoxybenzoic acid



(f) 6-methyl-2-cycloxenol

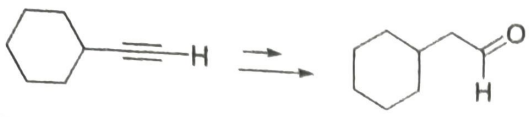


2. Complete the following tree of reactions by giving the major products. (4 pts each, total 32pts)



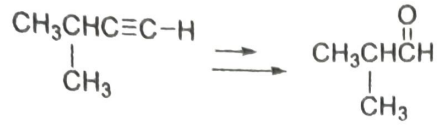
3. Suggest a plausible scheme for the following multiple step synthesis. (total 35pts)

a)



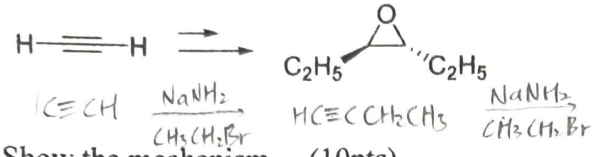
(5pts)

b)

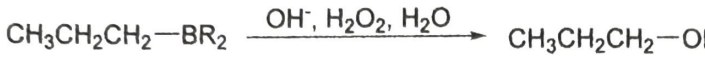


(10pts)

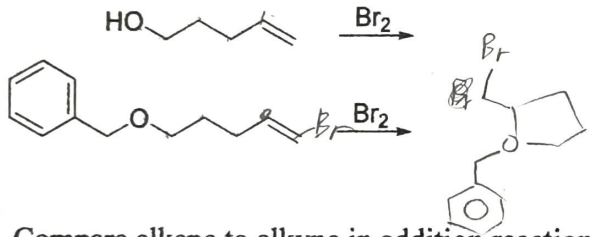
c) Show <u>also the mechanism</u> in the epoxide formation step. (10pts)



d) Show the mechanism. (10pts)



4. a) Provide the major <u>product structure</u> and a detailed, <u>step-by-step mechanism</u> for each reaction shown below. b) Base on the mechanisms, explain why two reactions undergo different kind of chemistry. (20pts and 5 pts, respectively. total 25 pts)



5. Compare alkene to alkyne in addition reaction. a) Which is more reactive? b) Which is more stable? c) Explain the reasons with reaction coordinate diagram, and draw the transition state structures and intermediates. (3pts, 3pts and 12pts, respectively. total 18pts)

6. As the reaction shown below. a) Provide the product structure with absolute structure. b) Provide the mechanism in first step c) Explain the reason that results in preferential cis or trans selectivity. (6pts, 10pts and 6pts, respectively. total 22pts)