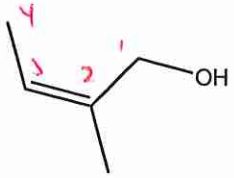
**Organic 211** Test # 3 November 5, 2019

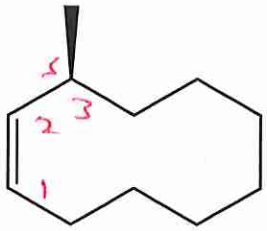
Name:_____

Directions: The test is worth 106 points but scored out of 100.

1) Give the name of the following two molecules. (2 pts. each)

a) 


Z - 2-methyl but-2-en-1-ol

b) 

~~2E,5S~~ 3-methylcyclodec-1-ene
(5,Z)

2) Draw the following two molecules. (2 pts. each)

a) (E)-pent-2-en-3ylcyclopropane 

b) (1R,2R,6S)-2-methyl-7-oxabicyclo[4.1.0]heptane
or (1R,2R,6S)-1,2-epoxy-2-methylcyclohexane 

3 3

bad question

3) Arrange the following alkenes in order of stability. (1 = most stable) (4 pts.)

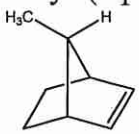
1-pentene (E)-2-pentene (Z)-2-pentene 2-methyl-2-butene

4 2 3 1

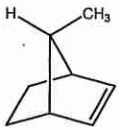
7.12

8.26

4) Compound A undergoes catalytic hydrogenation much faster than does compound B. Why? (4 pts.)



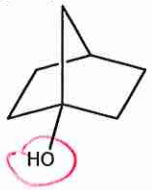
Compound A



Compound B

The methyl group in B shields one face of the double bond. Compound A's $CH_3$ does not shield the double bond.

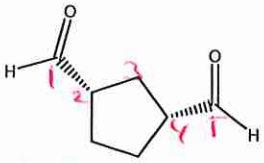
5) Alcohols in which the hydroxyl group occupies a "bridgehead" position such as bicycle[2.2.1]heptan-1-ol are relatively unreactive toward hydrogen halides. Why? (4 pts.)




→ H-O-H leaves to form stable carbocation. But carbocation from loss of $H_2O$ would not be stable due to structure.

OH would form $OH_2$ with H-X.

6) Compound A ($C_7H_{11}Br$) is converted to compound B ($C_7H_{10}$) upon treatment with sodium hydroxide. Treatment of Compound B with ozone/Zn furnishes the compound below. Give a structure for compounds A and B. (4 pts.)




$C_7H_{11}Br = C_7H_{12}$

$C_7H_{16}$
$C_7H_{12}$
$4/2 = 2$ degrees of unsaturation

$C_7H_{16}$
$C_7H_{10}$
$6/2 = 3$ degrees of unsaturation

∴ A + double bond

1 & 5 are connected

∴ 

A

B

7) a) Give a molecule that will undergo an $E_1$ reaction. (2 pts.)

lots of possibilities

must be able to form stable carbocation

∴ + Br

b) Give a molecule that will undergo an $E_2$ reaction. (2 pts.)

lots of possibilities

must have leaving group + hydrogen on adjoining carbon

+ Br

c) Give a molecule that will NOT undergo an $E_2$ reaction. (2 pts.)

bad leaving group won't undergo any elimination

So


lots of possibilities

no α hydrogen

d) Give an alkene that can undergo both Markovnikov and anti-Markovnikov addition. (2 pts.)

lots of possibilities

e) Give three reagents that will cause syn addition to a double bond. (3 pts.)

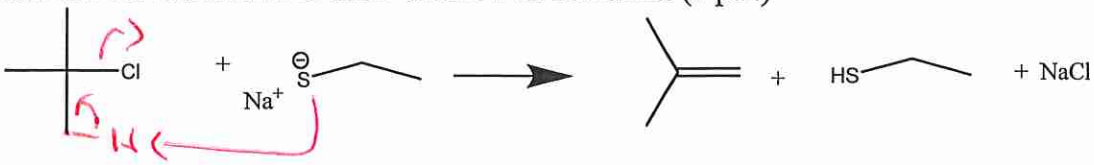
mCPBA, $OsO_4$, $H_2$/Pt, $BH_3$

f) Give one reagent that will give anti addition to a double bond. (2 pts.)

$Br_2$

8) The rate of the reaction below is first order in tert-butyl chloride and first order in Sodium ethyl thiolate. Give the symbol (E1 or E2) for the most reasonable mechanism and use curved arrows to show the flow of electrons. (6 pts.)

7.4P

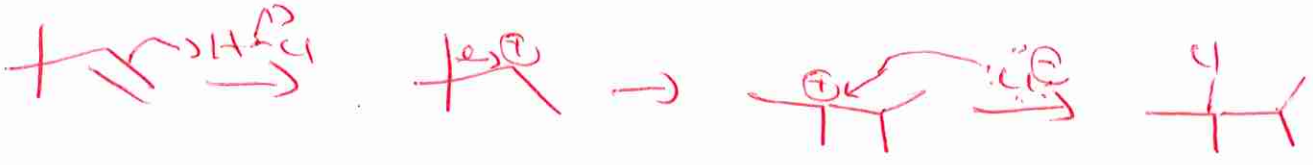



E2

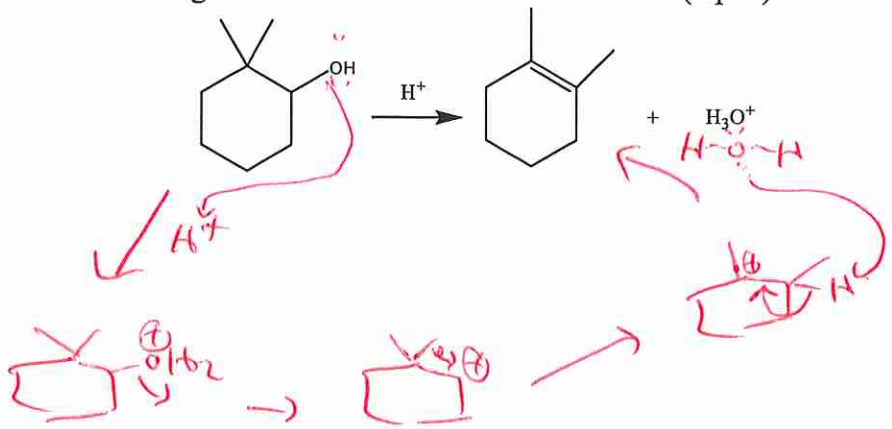
9) Addition of hydrogen chloride to 3,3-dimethyl-1-butene gives a mixture of two isomeric chlorides in approximately equal amounts. Suggest reasonable structures for these two compounds and offer a mechanistic explanation for their formation. (6 pts.)

8.7

or

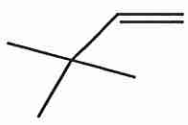


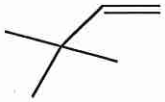
10) Work the following mechanism. SHOW EVERY STEP! (6 pts.)




7.20

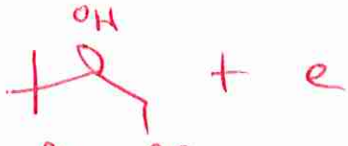
11) Give the missing products for the following reactions. Show stereochemistry if important. You may draw +E for enantiomer or +D for diasteromer. Indicate if no reaction is possible. For an $SN_1/E_1$ reaction, it is not necessary to draw the $E_1$ products. (3 pts. each)

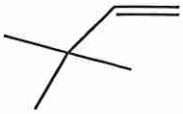
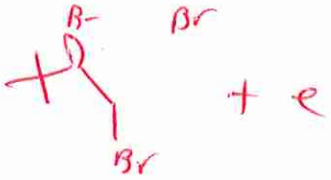
a)  HBr → NO Peroxides → 

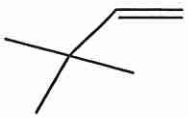
b)  HBr → Peroxides → 

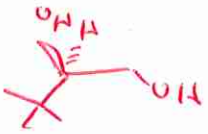
c)  1) $BH_3/H_2O$ 2) $H_2O_2/OH^-$ → 

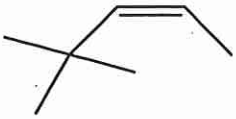
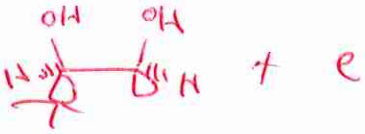
d) Product of C → 1) $^-NH_2$ 2) Ethyl bromide → 

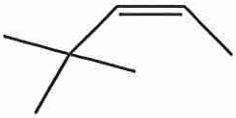
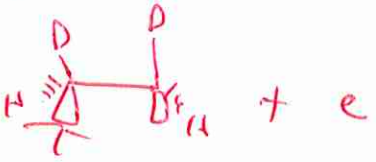
e)  $Br_2/H_2O$ → 

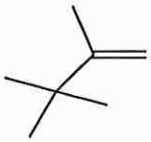
f)  $Br_2/CCl_4$ → 

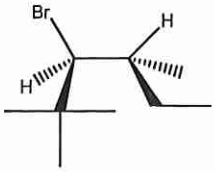
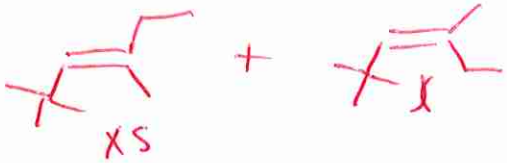
g)  MCPBA → 

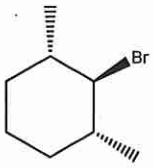
h) Product of G $\xrightarrow{^-OH/H_2O}$ 

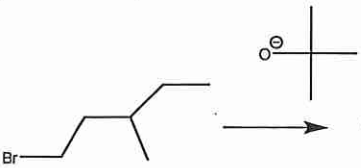
i)  $\xrightarrow[2)\ KHSO_3]{1)\ OsO_4}$ 

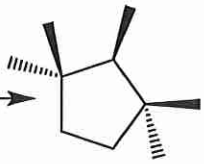
j)  $\xrightarrow{D_2/Pt}$ 

k)  $\xrightarrow[2)\ NaBH_4]{1)\ Hg(OAc)_2}$ 

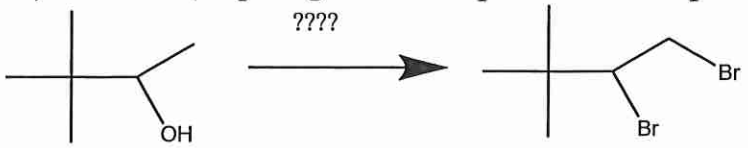
l)  $\xrightarrow{\text{Potassium Ethoxide}}$ ??? 

m)  $\xrightarrow{^-NH_2}$ no reaction possible

n) 

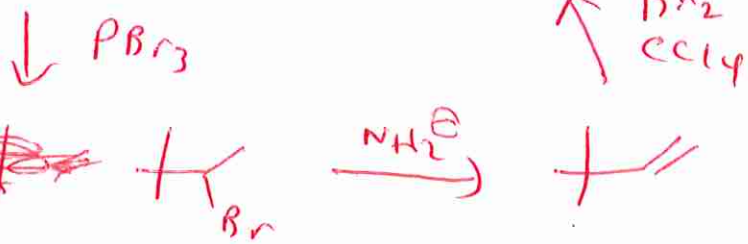
o) ??? $\xrightarrow{H_2/Pd}$  

12) Outline the steps to go from Compound A to Compound B.(5 pts.)



Compound A Compound B

8.24



13) Free Question: Give something you studied that was not asked on this test. (4 pts.)

**Substitution/Elimination Determination Table**

Reference: Dr. Mark Arant (Northeast Oklahoma University) uses a table very similar to this one for determining whether a reaction goes $SN_2$, $E_2$ or $SN_1/E_1$.

| **pKa of conjugate acid of nucleophile** | **Primary Halides** | **Secondary Halides** | **Tertiary Halides** |
|---|---|---|---|
| <10 | $SN_2$ | $SN_2$ – polar aprotic solvent<br>$SN_1/E_1$ – polar protic solvent | $SN_1/E_1$ |
| 10-25 | $SN_2$ | $E_2$ | $E_2$ |
| >25 | $E_2$ | $E_2$ | $E_2$ |

How to read the chart: 1) Determine whether the carbon that has the leaving group is primary, secondary, or tertiary. 2) Next, draw the conjugate acid of the nucleophile and determine its pKa.

Exceptions: a) This table determines the reaction most likely to take place. $SN_1$ and $SN_2$ are limiting reactions with most reactions taking place by a combination of mechanisms instead of by just one mechanism. b) If the base is bulky like tert-butoxide, elimination will dominate via $E_2$ even though the pKa of tert-butyl alcohol is less than 25. c) If the primary carbocation is stabilized (i.e. allyl or benzyl) the $SN_1$ reaction may dominate.