Name: _____

(Print your name, large and legibly)

Chem 2010

Spring, 2019

Midterm 2

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Spring, 2019
Beauchamp   Name _____

| Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Lewis Structures, Resonance, Formal Charge	20	
3. Cyclohexane Conformations, 2 substituents, Newman Projections, Relative Energies, K_{eq} Calculation	25	
4. Acid / Base chemistry, arrow pushing, formal charge, relative stabilities,, K_{eq} Calculation	30	
5. Free radical reactions (mechanism , ΔH and stereochemistry)	25	
6. SN /E chemistry, 3D mechanism details	40	
7. Reactions page (20)	30	
8. Synthesis (1)	30	
9. Carbocation reactions (mechanism)	20	
10. Free radical reactions	30	
Total	280	

This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Do your best to show me what you know in the time available.

The three great essentials to achieve anything worthwhile are, first, hard work, second, stick-to-itivness and third, common sense.   Thomas Edison

1. Provide an acceptable name for the following structure. Indicate the absolute configuration of any chiral centers shown in three dimensional form (R/S) and any E/Z stereogenic centers. (30 pts)
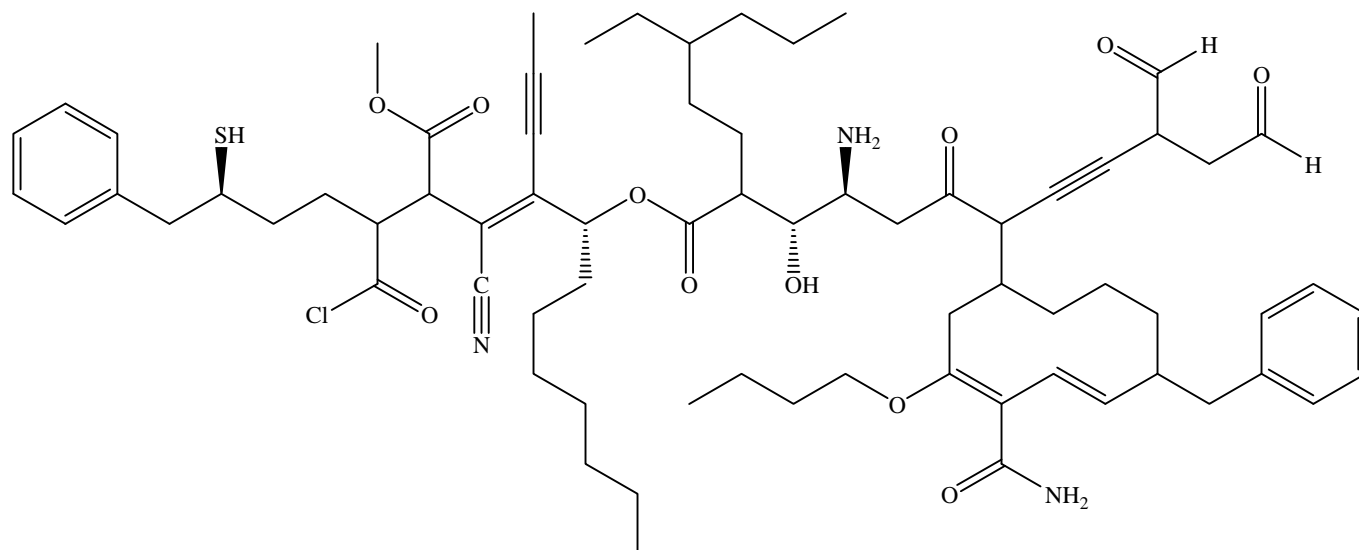
2. Assume all nonhydrogen atoms have full octets. Draw a better resonance structure for each example below. Add in any necessary lone pair electrons and use proper formal charge and arrows. Explain why the second resonance structure is better. (20 pts)

a.

b.
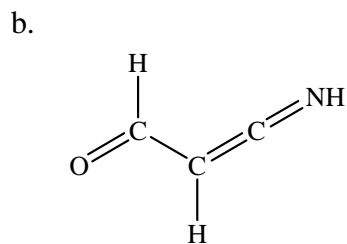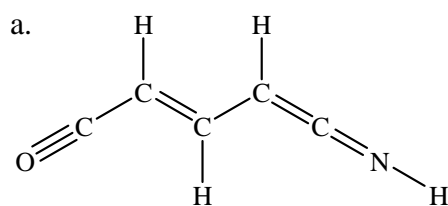
3. Draw both chair conformations of trans-1-t-butyl-3-methylcyclohexane. Include all axial and equatorial positions in both of your drawings. Axial energy for t-butyl is 5.5 and methyl is 1.8 kcal/mole. Draw the more stable conformation first. Make C_1 the left most carbon and number towards the front. Calculate a $K_{equilibrium}$ between the two conformations. Assume R = 2 cal/(mol-K) and T = 300 K.. Draw a Newman projection of the more stable conformation and point out any gauche interactions. (25 pts)
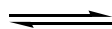
most stable conformation   less stable conformation

Newman
projection

4. The reactant acids and bases are given in acid/base equations below. Also given with each equation are two pK_a values. Complete each acid/base equation including any formal charge, lone pairs and curved arrows to show how the reactants react. Use the pK_a values to calculate a K_{eq} for each reaction. Provide a very brief explanation for which side is favored. (30 pts)

a.

pK_a values = 16 and 19

$K_{eq} =$

b.

pK_a values = 5 and 8

$K_{eq} =$

c.

pK$_a$ values = -6 and +1

K$_{eq}$ =
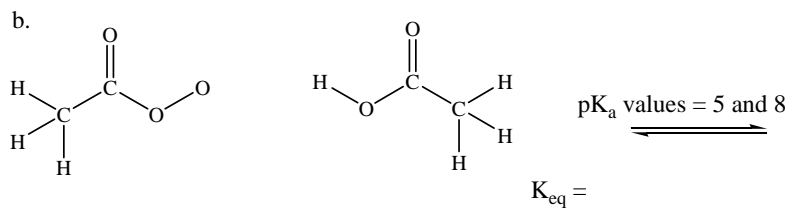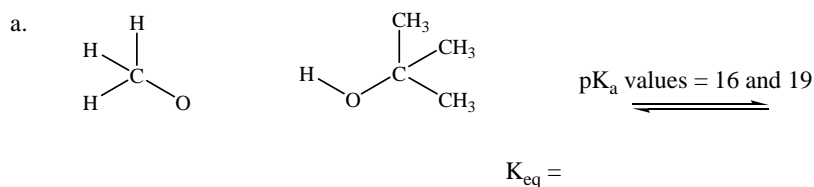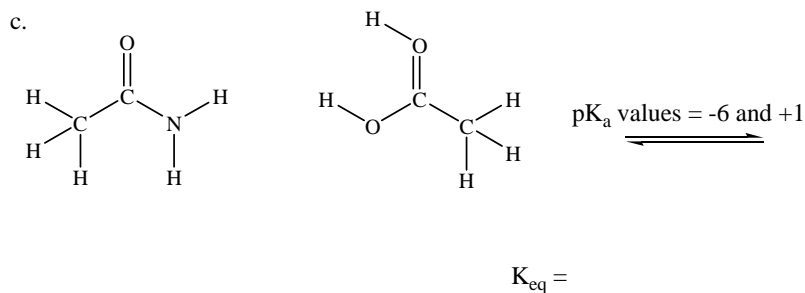
5. Write a mechanism for the given reaction. Identify each sequence of the mechanism. Use proper curved arrows. Calculate a ΔH for each step of the reaction. You only have to show your mechanism one time, but write out all possible stereoisomers and point out any relationships between them (enantiomers, diastereomers, etc.) Specify absolute configurations in your first stereoisomer. There may or may not be fewer structures than letters below. (25 pts)

ROOR (cat.)
hv

H——Br
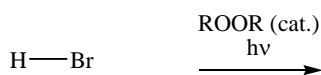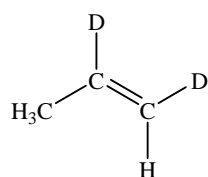
Product(s)

bond energies	
C=C	63
H-Br	88
C-Br	68
C-H	95
O-O	40
O-H	110

Possible products?
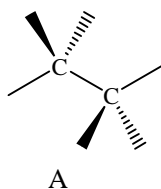
A   B   C   D   E

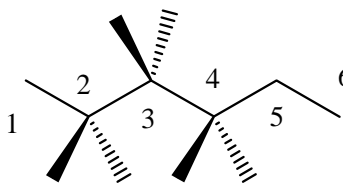6.   Use (2S,3R,4S)-2-deuterio-3-bromo-4-methylhexaneto provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. **Do not** consider carbocation rearrangement possibilities. (40 pts)
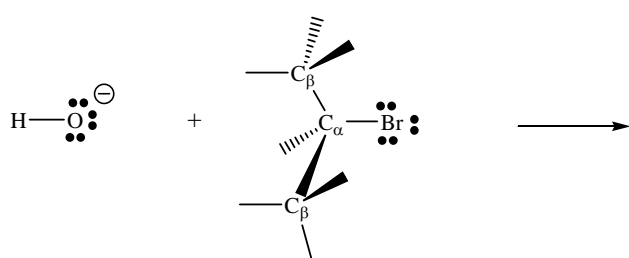
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)

2D structure   3D structure of (2S,3R,4S)-2-deuterio-3-bromo-4-methylhexane

b. Show the S$_N$ reaction (what kind?), indicate the absolute configuration(s) of the C$_\alpha$ center in the product. (6 pts)

mechanism

C$_\alpha$ configuration

c. Show a mechanism for each C$_\beta$ position and simply draw all other possible E reaction products (what kind?). Indicate if E, Z or neither. You can abbreviate common branch names if they are not part of your mechanism   There may or may not be fewer products than there are numbers. (10 pts)
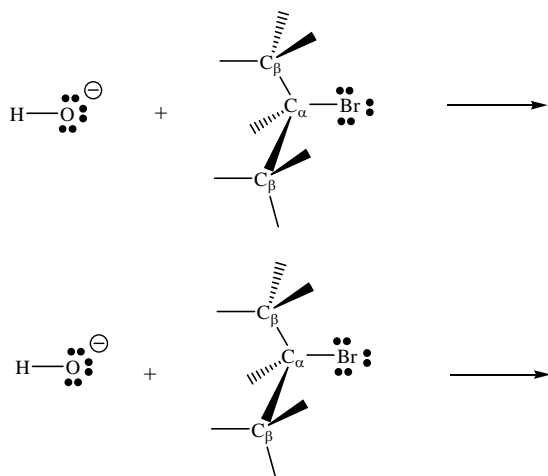
mechanism

E / Z configuration

other possible E products

E / Z configuration

1   2   3   4   5

d. Show all steps of the S_N reaction (what kind?). You can use one intermediate to show all possible S_N possibilities. Indicate the absolute configuration(s) of the C_α center in the product. You can abbreviate common branch names if they are not part of your mechanism (9 pts)

H—O—H   +   [structure: C_β, C_α—Br, C_β]   ⟶
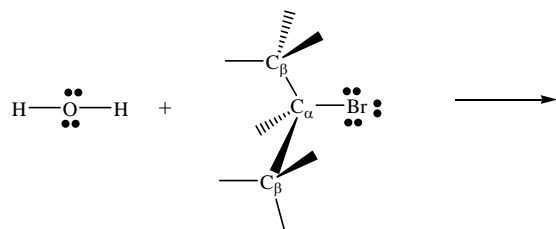
mechanism

.

e. Show a mechanism for two E products and simply draw all other possible E reaction products (you can use the same intermediate for your two mechanisms). Indicate configurations as E, Z or neither. There may or may not be fewer products than numbers. (12 pts)

H—O—H   +   [structure: C_β, C_α—Br, C_β]   ⟶
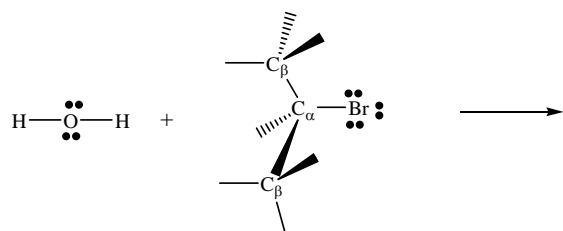
mechanism

1   2   3   4   5   .

7. Write in the <u>major product</u> for each set of conditions below. Proper 3D structures are required. Arrow pushing is not required (1.5 each, 30 pts)

a

$CH_3C(=O)OH$

1. PCl_3
2. $\overset{}{\diagup}\!\!\diagdown Br$

b

$\diagup\!\!\diagdown\!\!\overset{OH}{\diagup}\!\!\diagdown$
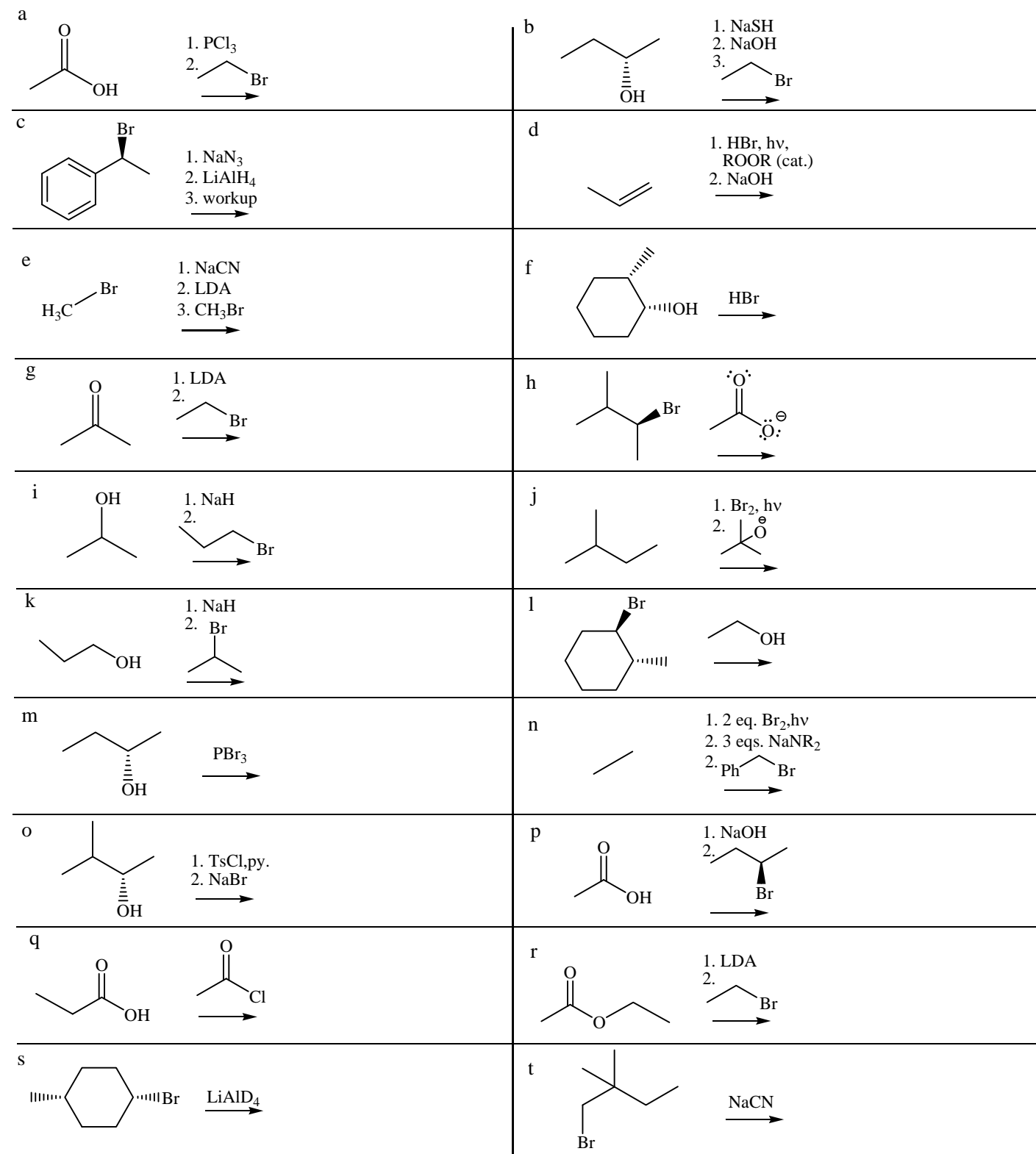
1. NaSH
2. NaOH
3. $\diagup\!\!\diagdown Br$

c

Br, phenyl-CH(Br)-CH_3

1. NaN_3
2. $LiAlH_4$
3. workup

d

$\diagup\!\!\diagdown\!\!=$

1. HBr, hv,
   ROOR (cat.)
2. NaOH

e

$H_3C\diagup\!\!\diagdown Br$

1. NaCN
2. LDA
3. CH_3Br

f

cyclohexane with CH_3 and OH

HBr

g

$(CH_3)_2C=O$ (acetone)

1. LDA
2. $\diagup\!\!\diagdown Br$

h

$(CH_3)_2CH-CH(CH_3)-Br$; $CH_3C(=O)O^-$

$\longrightarrow$

i

$(CH_3)_2CHOH$

1. NaH
2. $\diagup\!\!\diagdown\!\!\diagup Br$

j

$(CH_3)_2CHCH_2CH_3$

1. Br_2, hv
2. $(CH_3)_3C-O^-$

k

$\diagup\!\!\diagdown\!\!\overset{}{\diagdown}OH$

1. NaH
2. $\diagup\!\!\diagdown Br$

l

cyclohexane with Br

$\diagup\!\!\diagdown OH$

m

$\diagup\!\!\diagdown\!\!\overset{OH}{\diagdown}$

PBr_3

n

$\diagup\!\!\diagdown$

1. 2 eq. Br_2,hv
2. 3 eqs. $NaNR_2$
3. $Ph\diagup\!\!\diagdown Br$

o

$(CH_3)_2CH-CH(OH)-CH_3$

1. TsCl,py.
2. NaBr

p

$CH_3C(=O)OH$

1. NaOH
2. $\diagup\!\!\diagdown\!\!\overset{}{\diagdown}Br$

q

$\diagup\!\!\diagdown C(=O)OH$; $CH_3C(=O)Cl$

$\longrightarrow$

r

$CH_3C(=O)O-CH_2CH_3$

1. LDA
2. $\diagup\!\!\diagdown Br$

s

cyclohexane with Br

$LiAlD_4$

t

neopentyl-type structure with Br

NaCN

8. Propose a reasonable synthetic sequence to make the given target molecules using the given starting materials. Show each step with an arrow and the necessary reagents to accomplish the indicated transformation. If you make a molecule in one part you can use it in any other part. (30 pts)

Allowed starting materials

CH_4
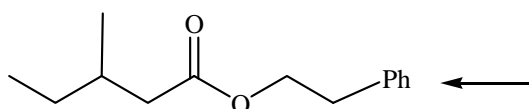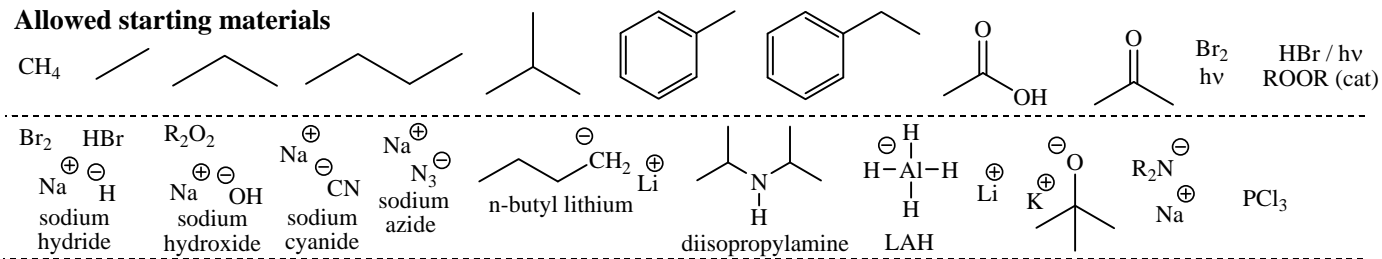
9. Propose a complete arrow-pushing mechanism for the following transformation. Use proper arrows, formal charge, and lone pairs. If resonance is important, show it. (20 pts)
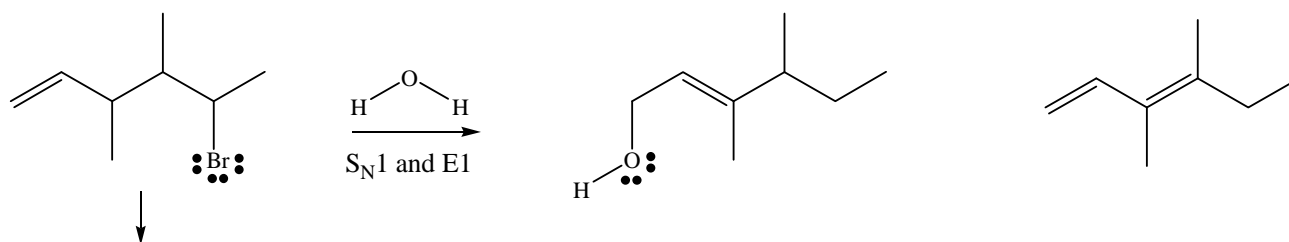
10. a. How many different types of sp^3 hydrogen atoms are present in 2S-bromopentane? Show all possible products when 2S-bromopentane is brominated with $Br_2/h\nu$? Use Fischer projections. Put R or S by any chiral centers. If stereoisomers form, specify what type of isomerism is present (enantiomers, diastereomers, meso compounds, achiral, etc.). Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp^3 C-H bond are: primary = 1, secondary = 80, tertiary = 1600 and bromine substituted carbon = 2000. (15 pts)

| starting structure | A | B | C | D | E | F | G |
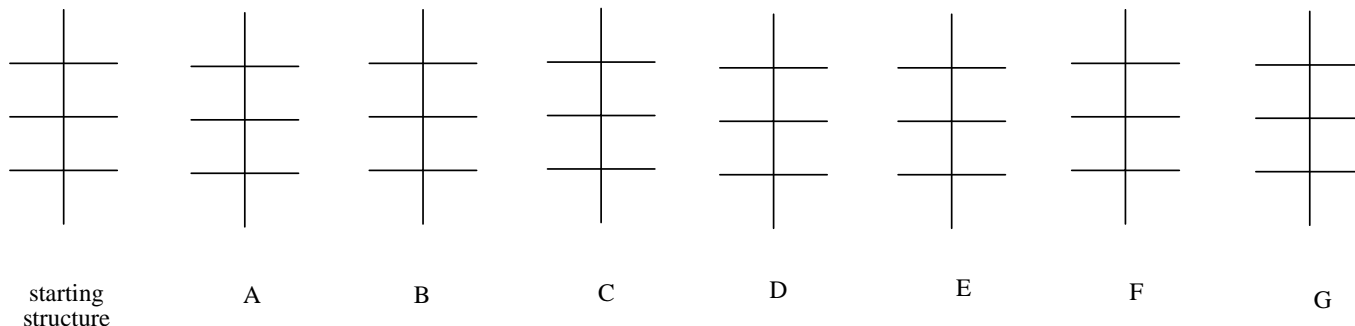
b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrow conventions, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. (15 pts)

Bond	Energy
Br-Br	46
H-Br	88
O-O	40
O-H	110
CH₃-H	105
1° C-H	98
2° C-H	95
3° C-H	92
C$_\alpha$Br-H	88
CH₃-Br	70
1° C-Br	68
2° C-Br	67
3° C-Br	66
C$_\alpha$Br-Br	64

Overall reaction for main product

We can't solve problems by using the same kind of thinking we used when we created them. Albert Einstein