Chem 2010
Midterm #2
Fall, 2018
Beauchamp

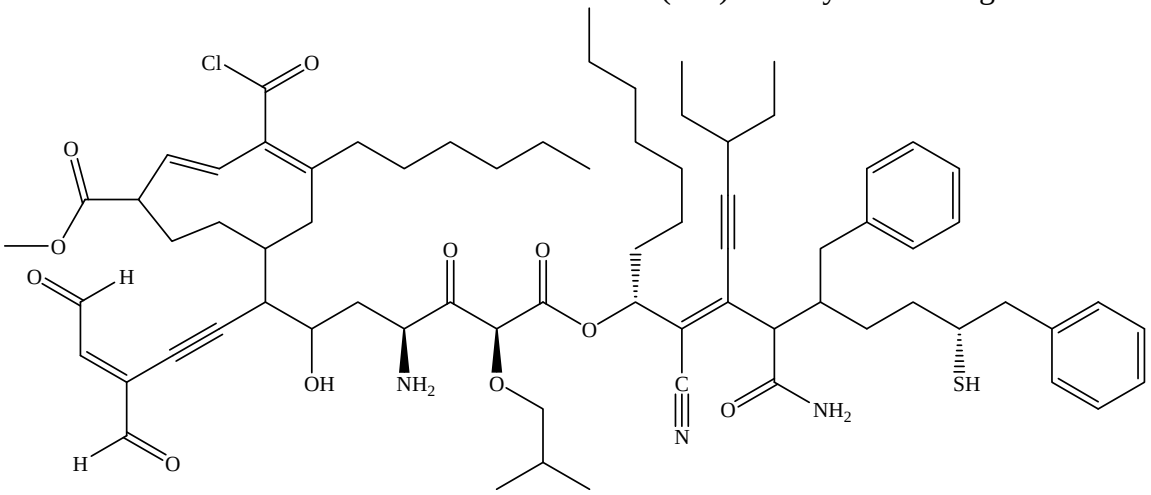
Name _____
(Print your name legibly)

Problem	Points	Credit
1. Nomenclature (one structure)	30	
2. Explain relative stabilities based on logic arguments of organic chemistry	20	
3. Chair conformations or Chain conformations or Stereochemistry or 2D/3D structures, hybridization	25	
4 Acid/base equations, draw mechanism details, estimate K_{eq}, explain answer	24	
5. S_N and E mechanisms, including stereochemical details	40	
6. Predict products (20)	30	
7.Propose short syntheses (2)	30	
8. Carbocation rearrangement	15	
9. Free Radicals, Predict products provide mechanism	30	
Total	244	

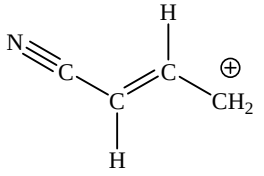
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement in mechanism and explanation problems. If resonance is part of an answer, draw the best resonance structure, plus at least one additional resonance structure to show that resonance is present. Only write answers in the space available. Do your best to show me what you know in the time available.

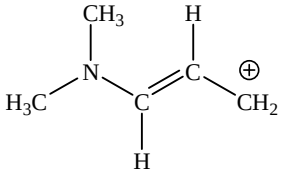
Your mission in life is not merely to survive, but to thrive; and to do so with some passion, some compassion, some humor and some style. Maya Angelou

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)

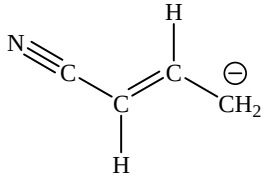


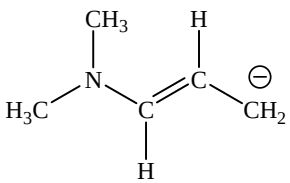
2. a. What is the most stable cation? Explain your reasoning, using structures, if necessary. Include curved arrows, formal charge and lone pairs. Hint: Consider the resonance of a C≡N group and a lone pair of electrons. (10 pts)





b. What is the most stable anion? Explain your reasoning, using structures, if necessary. Include lone pairs, formal charge and lone pairs. Hint: Consider the resonance of a C≡N group and a lone pair of electrons. (10 pts)





3. a. Use Newman projections of the C3→C4 bond of 4-phenyl-2-methylhexane to show the lowest energy and highest energy conformations and calculate the relative energies**. Show the most stable conformation first**. Calculate a $K_{equilibrium}$ between the least stable and most stable conformations. Assume R = 2 cal/(mol-K) and T = 300 K. (20 pts)

Approximate Eclipsing Energy Values (kcal/mole)
Some were estimated by me.

	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	1.0	1.4	1.5	1.6	3.0	1.7	1.6
Me	1.4	2.5	2.7	3.0	8.5	3.3	2.8
Et	1.5	2.7	3.3	4.0	10.0	3.8	3.1
i-Pr	1.6	3.0	4.0	7.8	13.0	8.1	3.6
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5	9.1
Ph	1.7	3.3	3.8	8.1	13.5	8.3	4.2
Br	1.6	2.8	3.1	3.6	9.1	4.2	3.0

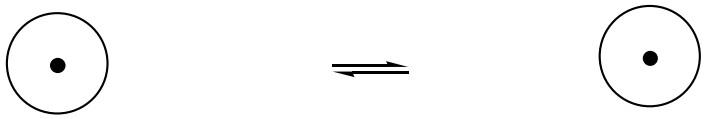
Approximate Gauche Energy Values (kcal/mole)
Some were estimated by me.

	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	0	0	0.1	0.2	0.5	0.2	0.1
Me	0	0.8	0.9	1.1	2.7	1.4	1.0
Et	0.1	0.9	1.1	1.6	3.0	1.7	1.2
i-Pr	0.2	1.1	1.6	2.4	3.5	2.1	1.6
t-Bu	0.5	2.7	3.0	3.5	7.2	3.9	3.3
Ph	0.2	1.4	1.7	2.1	3.9	2.7	1.9
Br	0.1	1.0	1.2	1.6	3.3	1.9	1.1

$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$

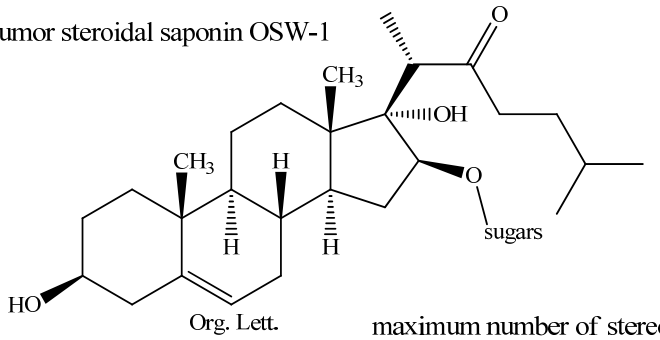
most stable Newman Conformation

least stable Newman conformation



b. Derivatives of the antitumor steroidal saponin were recently prepared. The are highly potent and selective anticancer compounds. They inhibit Na^{+}/Ca^{+2} exchange leading to higher Ca^{+2} in the cytosol and mitochrondria causing cell death (apotosis) (Org. Lett. ASAP, 2014). Circle all chiral centers and any other stereogenic features in the partial structure below, and calculate the maximum number of stereoisomers possible. (5 pts)

antitumor steroidal saponin OSW-1

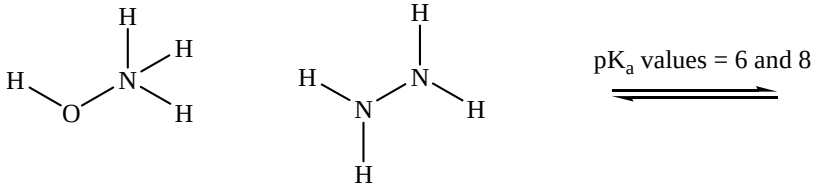


Org. Lett.

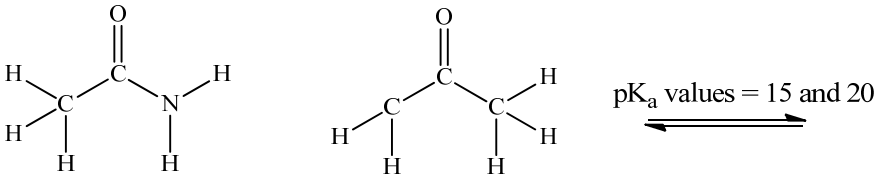
maximum number of stereoisomers = _____

4. The reactant acids and bases are given in two 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. Assume all nonhydrogen atoms have full octets. (24 pts)

a.

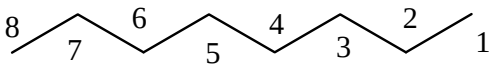


b.



5. Use 4S-bromo-5R-deuteriooctane to 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)

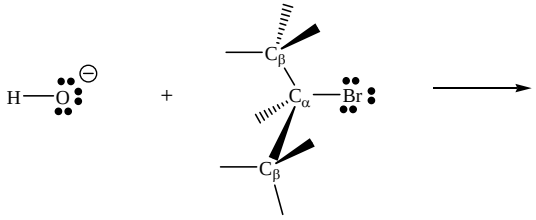
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)



2D structure

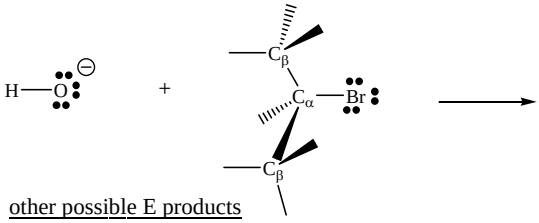
3D structure of (4S,5R)-5-deuterio-4-bromooctane

b. Show a mechanism for each C_β 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

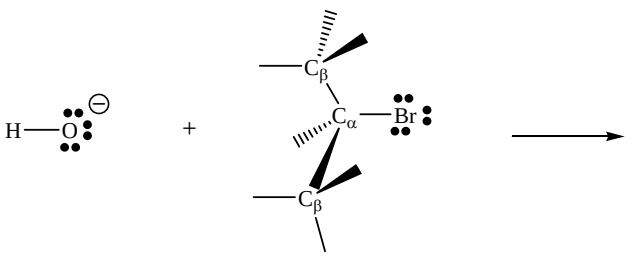


other possible E products

E / Z configuration

1 2 3 4 5

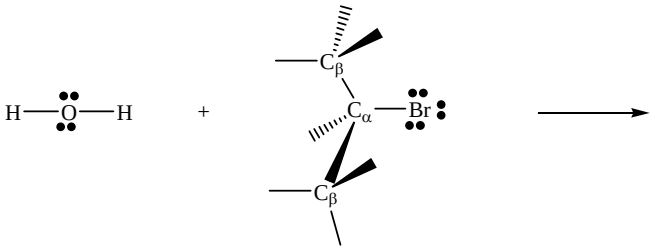
c. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the product. (6 pts)



mechanism

C_α configuration

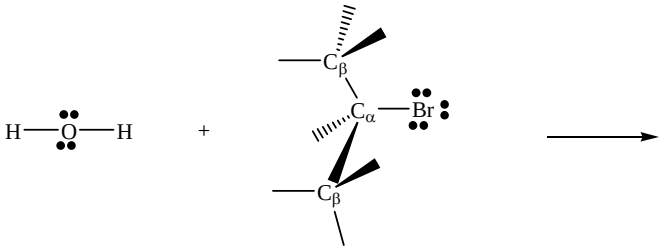
d. Show all steps of the S_N reaction (what kind?). You can use one intermediate to show all possible S_N possibilities. Indicate the absolute configuration(s) of the C_α center in the product. You can abbreviate common branch names if they are not part of your mechanism (9 pts)



mechanism

C_α configuration(s)

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 if E, Z or neither. There may or may not be fewer products than numbers. (12 pts)

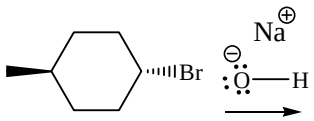


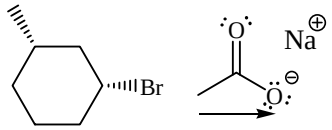
mechanism

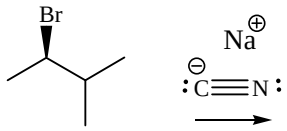
E or Z

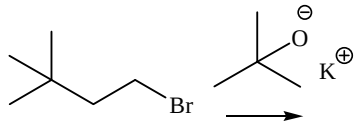
other possible E products

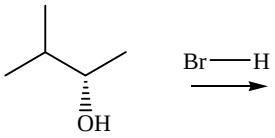
6. Write in the major product and type of reaction for each set of conditions below. Arrow pushing is not required (1.5 each, 30 pts)

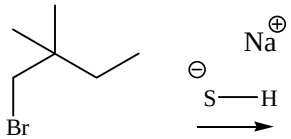
a 

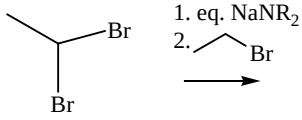
b 

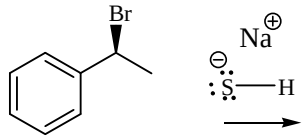
c 

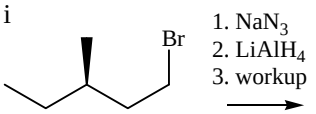
d 

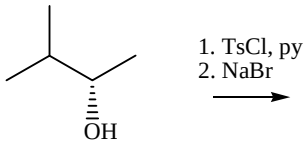
e 

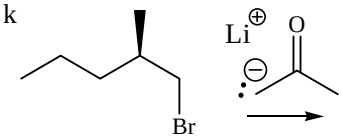
f 

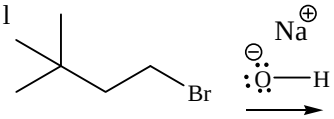
g 

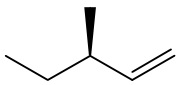
h 

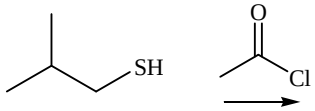
i 

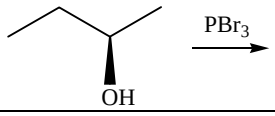
j 

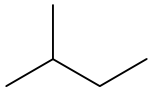
k 

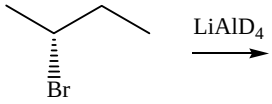
l 

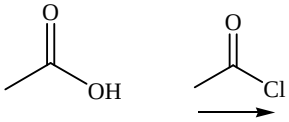
m 

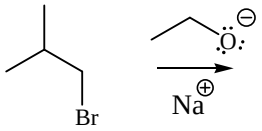
n 

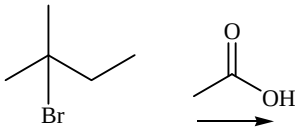
o 

p 

q 

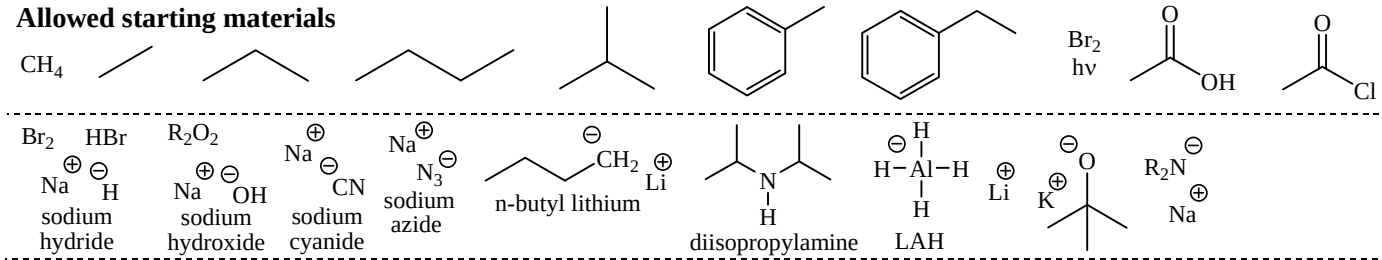
r 

s 

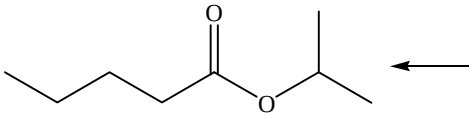
t 

7. 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)

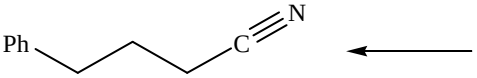
Allowed starting materials



a.

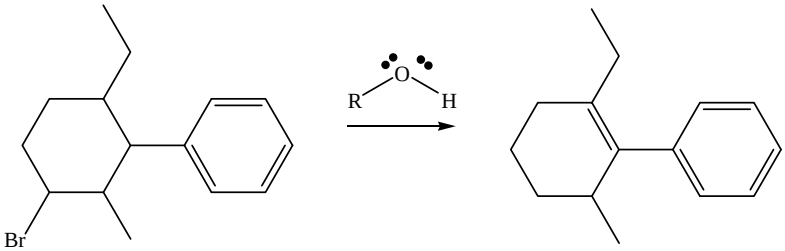


b.

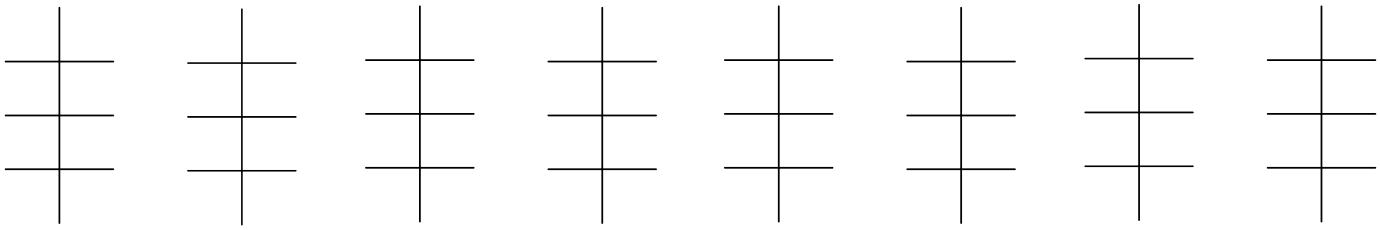


8. Propose a complete arrow-pushing mechanism for the following transformation. (15 pts)

c.



9. 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 a dot 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. (21 pts)



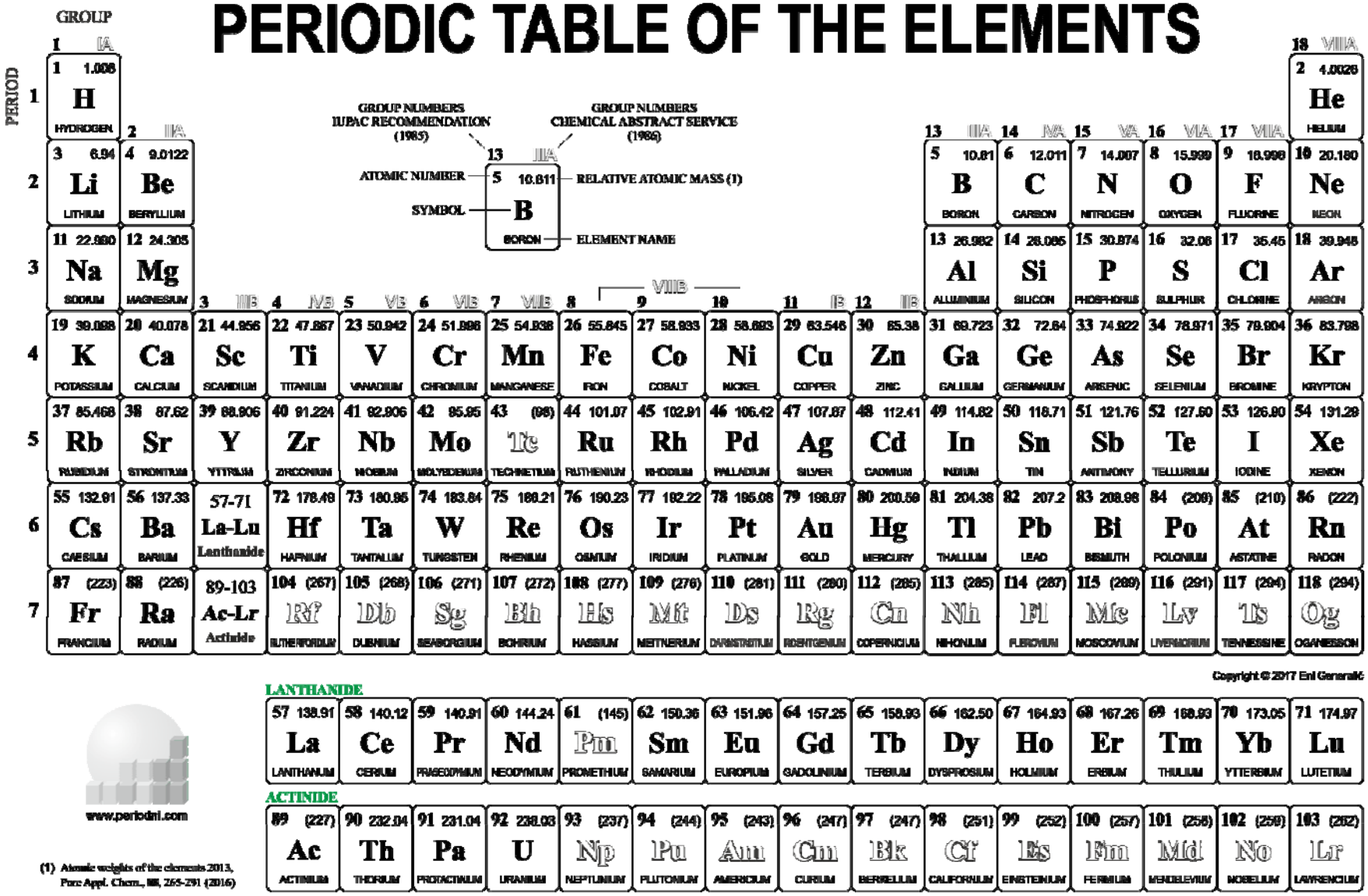
starting structure | A | B | C | D | E | F | G

enantiomers =
diastereomers =
meso =

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)

Br—Br	46
H—Br	88
CH_3-H	105
1^o C-H	98
2^o C-H	95
3^o C-H	92
C_αBr-H	88
CH_3-Br	70
1^o C-Br	68
2^o C-Br	67
3^o C-Br	66
C_αBr-Br	64

It is in your moments of decision that your destiny is shaped. Tony Robbins


PERIODIC TABLE OF THE ELEMENTS
GROUP
PERIOD
GROUP NUMBERS IUPAC RECOMMENDATION (1985)
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)
ATOMIC NUMBER
SYMBOL
RELATIVE ATOMIC MASS (1)
ELEMENT NAME
VIIB
LANTHANIDE
ACTINIDE
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www.periodni.com
(1) Atomic weights of the elements 2013, Pure Appl. Chem., 88, 265-291 (2016)