Chem 314
Final Exam   Name _____
Fall, 2014
Beauchamp

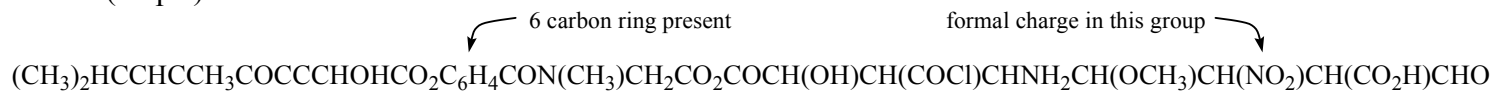| Problem	Points	Credit
1. Nomenclature (one structure)	30	
2. 2D Lewis structure (large structure with possible formal charge)	20	
3. 3D Structures, Formal Charge, Resonance, Curved Arrows, Hybridization	36	
4. Cyclohexanes, Conformations, Configurations, Stereoisomers, Newman Projection	33	
5. Stereochemisty Questions	27	
6. Open chain conformations, Newman projections energy calculations	15	
7. Acid/Base Chemistry (arrow pushing, explanation)	34	
8. Thought Problem Using Organic Logic Arguments	20	
9. S_N and E mechanisms, including stereochemical details	40	
10. SN/E Reactions, Predict Major Product(s) (12)	26	
11. Free Radicals, Predict products provide mechanism	40	
Total	321	

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 <u>show all of your work</u>. 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.

The privilege of a lifetime is being who you are.   Joseph Campbell
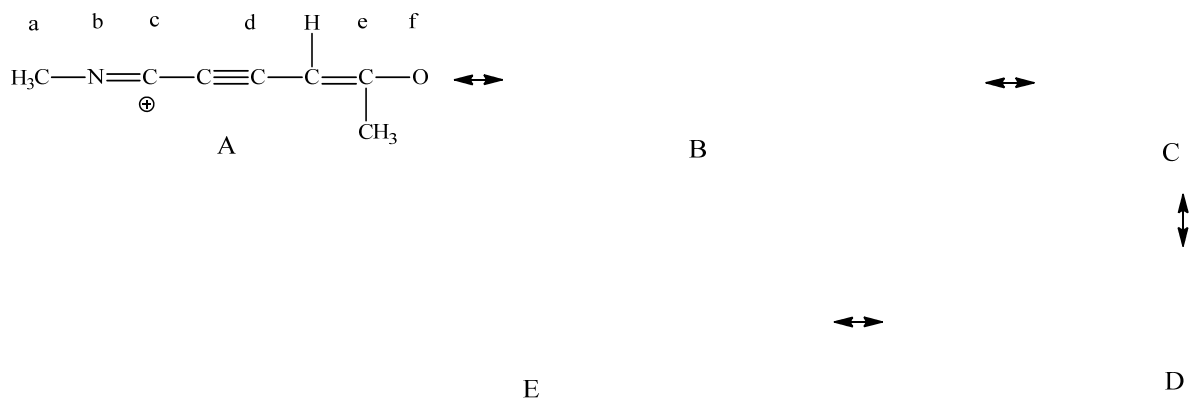
1. Provide an acceptable name for the following structure. Indicate the absolute configuration of any chiral centers shown in three dimensional form (R/S) and any E/Z stereogenic centers. (30 pts)
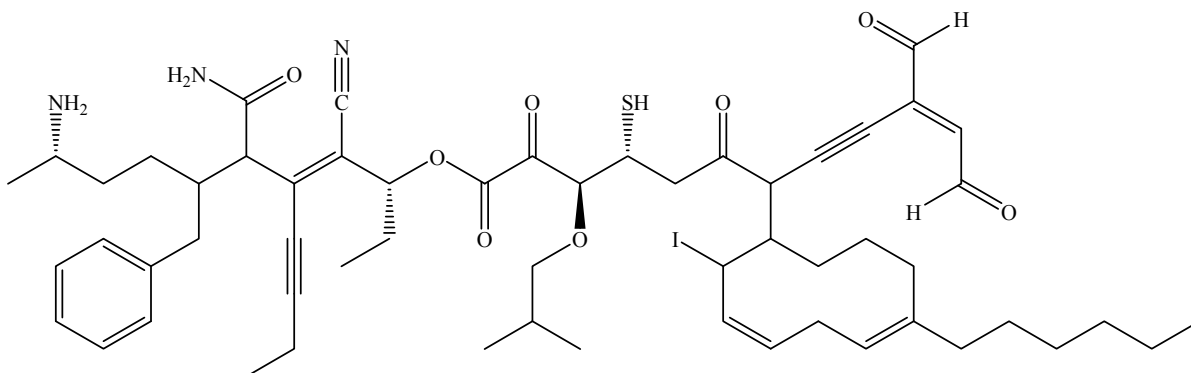
2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present. (20 pts)

6 carbon ring present   formal charge in this group

$(CH_3)_2HCCHCCH_3COCCCHOHCO_2C_6H_4CON(CH_3)CH_2CO_2COCH(OH)CH(COCl)CHNH_2CH(OCH_3)CH(NO_2)CH(CO_2H)CHO$

3. First, draw four other 2D resonance structures to delocalize any formal charge present. Include proper curved arrow conventions, including lone pairs and formal charge. Rank your structures from best (= 1) to poorest. Draw a three-dimensional Lewis structure of "A" and the best other resonance structure. Show sigma bonds as lines, wedges and dashes and the 2p orbitals in pi bonds as well as any orbitals holding lone pairs. Draw 2 dots for lone pair and π bond electrons. Use structure A to fill in the table at the bottom. **Assume that all nonhydrogens atoms have full octets, unless a carbocation is written**. (36 pts)

a   b   c   d   H   e   f

H_3C—N$=$C—C$\equiv$C—C$=$C—O $\leftrightarrow$ $\leftrightarrow$

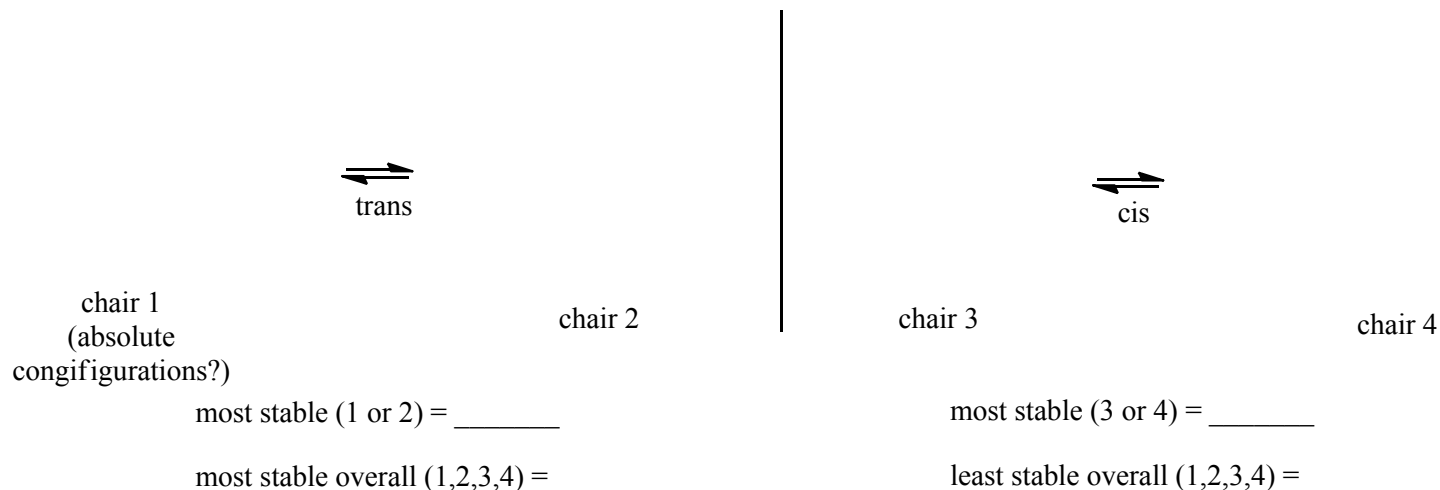A   CH$_3$ B   C

                                                                                                                        D

                                            $\leftrightarrow$

                        E

3D (A)   3D (best other)

Use structure A to fill in the following table.

	hybridization	angles	shape	#σ bonds	#π bonds	# lone pairs
a						
b						
c						
d						
e						
f						

4. a. Draw both chair conformations of trans-2-ethyl-1-phenylcyclohexane and cis-2-ethyl-1-phenylcyclohexane. Make carbon #1 the left-most atom in your ring, and number towards the front. Indicate the approximate ΔH for each conformation (use the axial energy table on this page and the gauche energy table on page 6, problem 6). Show all axial and equatorial groups at substituted ring carbons. What are the absolute configurations of all stereogenic atoms in chair 1? (20 pts)

trans   cis

chair 1
(absolute
congifigurations?)   chair 2   chair 3   chair 4

most stable (1 or 2) = _____   most stable (3 or 4) = _____

most stable overall (1,2,3,4) = _____   least stable overall (1,2,3,4) = _____

Axial Energy Values (kcal/mole)	
-Br	+0.5
-Et	+1.8
-Ph	+2.9
gauche	use table

sterochemical relationship of 1 with 2? enantiomer, diastereomer, meso, identical, none

sterochemical relationship of 1 with 3? enantiomer, diastereomer, meso, identical, none

sterochemical relationship of 1 with 4? enantiomer, diastereomer, meso, identical, none

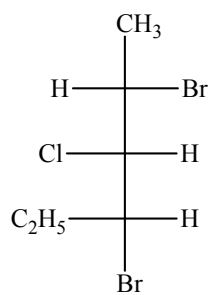sterochemical relationship of 3 with 4? enantiomer, diastereomer, meso, identical, none

b. Use the least stable conformation from part a and draw a Newman projection using bonds $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ for your structure (indicate which chair you are using from part a, (chair 1,2,3,4). Point out any gauche relationships in the branches. (5 pts)

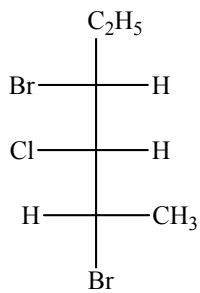Newman projection of the most stable conformation from part a

c. Using dibromocyclohexane, draw all of the chair conformations of two stereoisomers that have stereogenic centers, but do not have any chiral centers. Indicate the highest energy and the lowest energy chair conformations. What is the energy difference between them (use the above table and show your work). (8 pts)

chair 1   chair 2   chair 3   chair 4
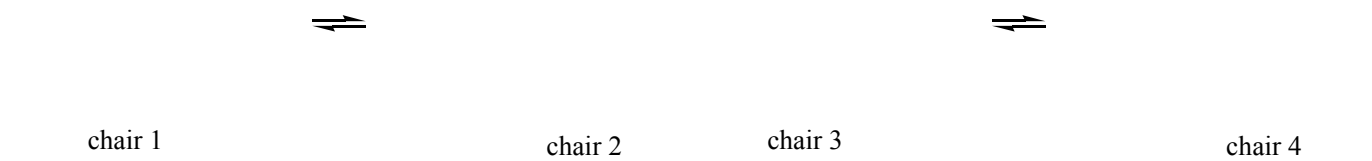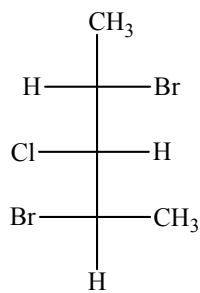
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections having the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (15 pts)
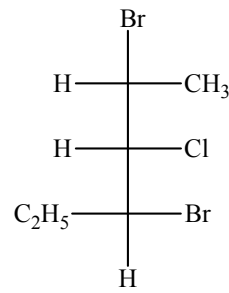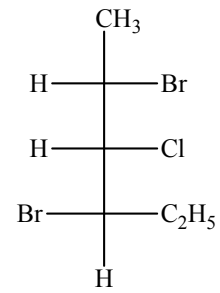

CH_3

H——Br

Cl——H

C_2H_5——H

Br

A

C_2H_5

Br——H

Cl——H

H——CH_3

Br

B

CH_3

H——Br

Cl——H

Br——CH_3

H

C

Br

H——CH_3

H——Cl

C_2H_5——Br

H

D

CH_3

H——Br

H——Cl

Br——C_2H_5

H

E

a. Which are meso?   A   B   C   D   E

b. Which is not an isomer with the others?   A   B   C   D   E

c. Which is optically active?   A   B   C   D   E

d. Which pairs are enantiomers?   AB AC AD AE BC BD BE CD CE DE

e. Which pairs are identical?   AB AC AD AE BC BD BE CD CE DE

e. Which pairs are diastereomers?   AB AC AD AE BC BD BE CD CE DE

f. Which would not rotate plane polarized light when mixed as a 50/50 racemic mixture?

            AB AC AD AE BC BD BE CD CE DE

g. Draw Fischer projections of any stereoisomers of "A" which are not shown above. If there are none, indicate this. (8 pts)

h. 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. (4 pts)

antitumor steroidal saponin OSW-1
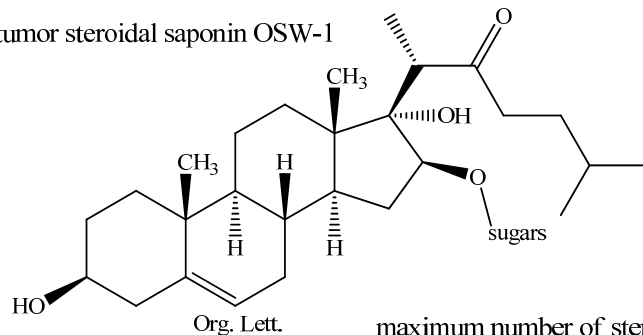
Org. Lett.   maximum number of stereoisomers = _____

6. Use Newman projections of the C2→C3 bond of 2-phenyl-3,3,4-trimethylpentane 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. (15 pts)

Approximate Eclipsing Energy Values (kcal/mole)

	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.3	1.4	1.6	3.0	1.7
Me	1.3	2.5	2.7	3.0	8.5	3.3
Et	1.4	2.7	3.3	4.5	10.0	3.8
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5
Ph	1.7	3.3	3.8	8.1	13.5	8.3

Approximate Gauche Energy Values (kcal/mole)

|	H	Me	Et	i-Pr	t-Bu	Ph
H	0	0	0.1	0.2	0.5	0.2
Me	0	0.8	0.9	1.1	2.7	1.4
Et	0.1	0.9	1.1	1.6	3.0	1.5
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9
Ph	0.2	1.4	1.5	2.1	3.9	2.3

most stable conformation

least stable conformation

$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}} =$$
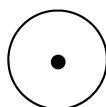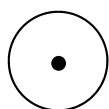
7. Each molecule below can act as either an acid or a base (they are amphiprotic). Use a general base, B:, and show molecule 1 reacting as an acid at its most acidic site. Use a general acid, HA, and show molecule 2 acting as a base at its most basic site. Use curved arrows to show the flow of electrons and include formal charge and lone pairs. Draw all resonance structures important to the conjugate acid or base. A few skeletons are provided to show your work. You may not need all of them. Provide a brief explanation for why your "acid" and "base" is the "best" choice. (12 pts each)
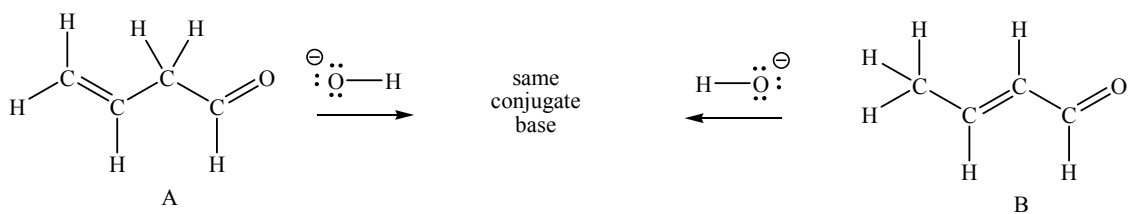
a. reaction in base, B:
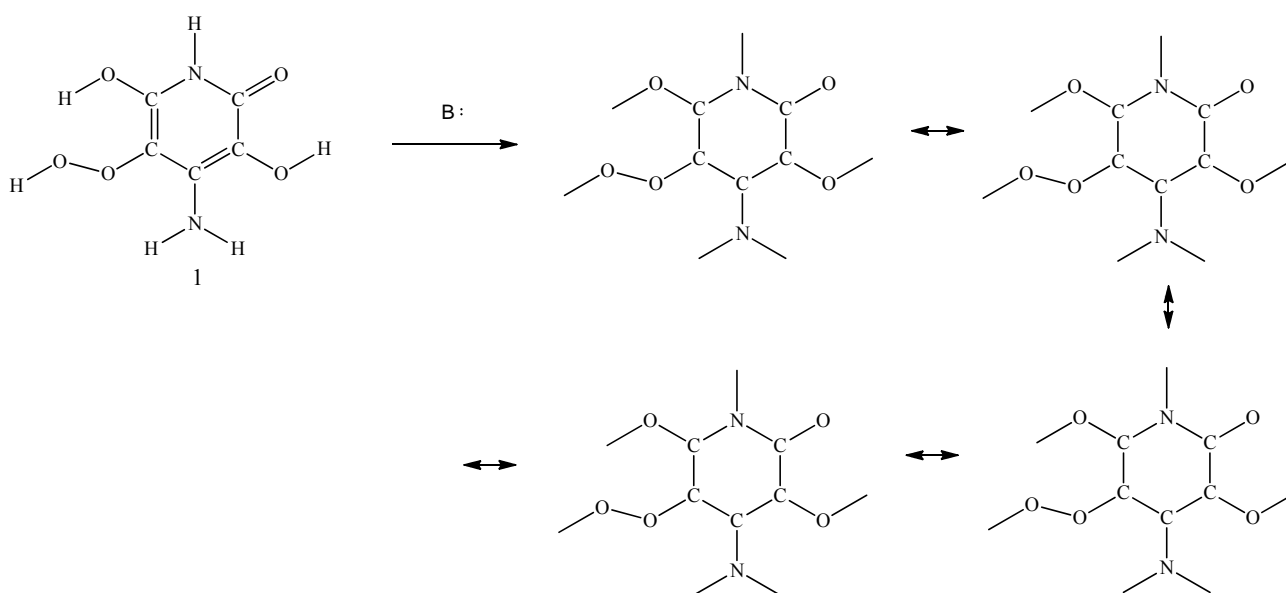

b. reaction in acid, HA
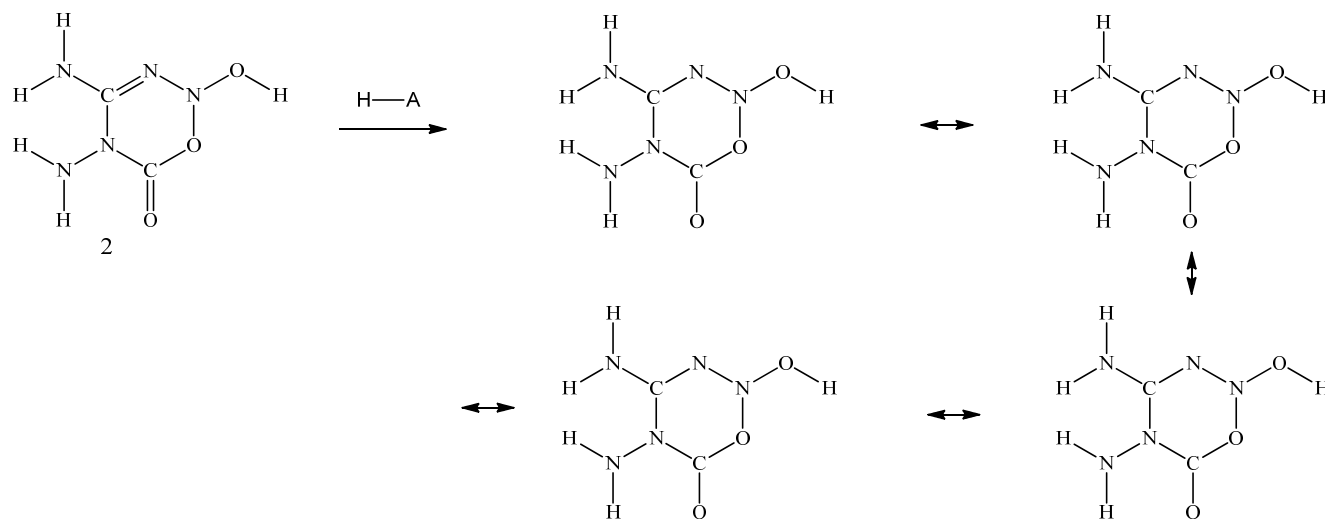
d. Acids A and B have different structures, but share a common conjugate base. Draw curved arrows to show how the proton transfer occurs in each case and explain why the conjugate base is the same for each acid. (10 pts)

8. a. What is the most stable cation? Explain your reasoning, using structures, if necessary. Include lone pairs. (10 pts)
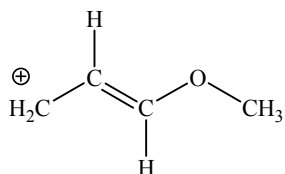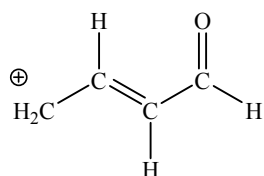

b. What is the most stable anion? Explain your reasoning, using structures, if necessary. Include lone pairs. (10 pts)
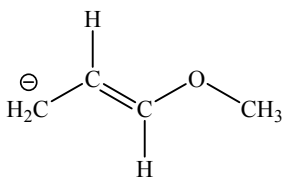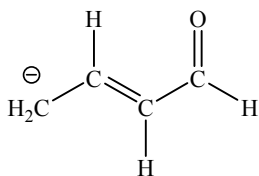
9. Use 2R-deuterio-3S-bromo-4S-methylhexane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If 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, since we did not cover them. (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)
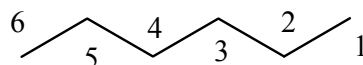

2D structure

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

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 (12 pts)
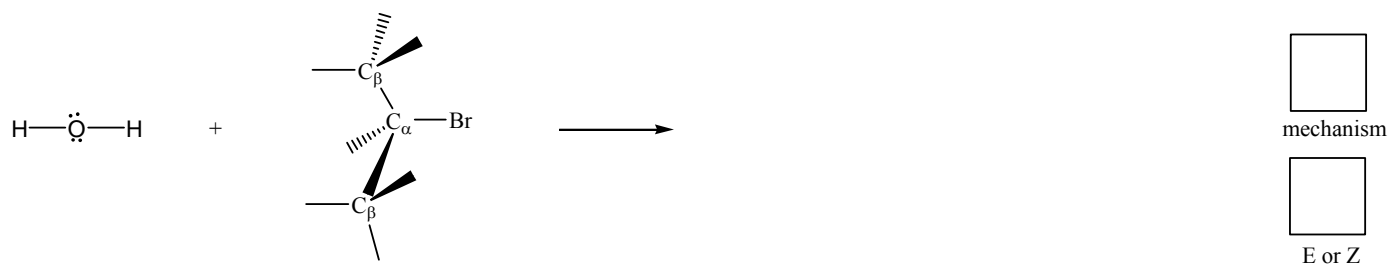

other possible E products

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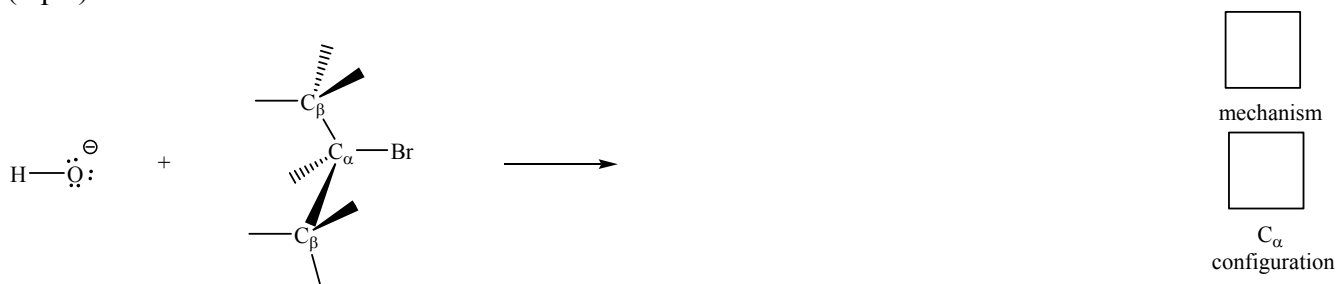
d. Show all steps of the S_N reaction (what kind?). You can use one intermediate to show all possible S_N possibilities. Indicate the absolute configuration(s) of the C_α center in the product. You can abbreviate common branch names if they are not part of your mechanism (9 pts)

H—Ö—H   + C_β — C_α —Br   ⟶

☐
mechanism

☐
C_α
configuration(s)
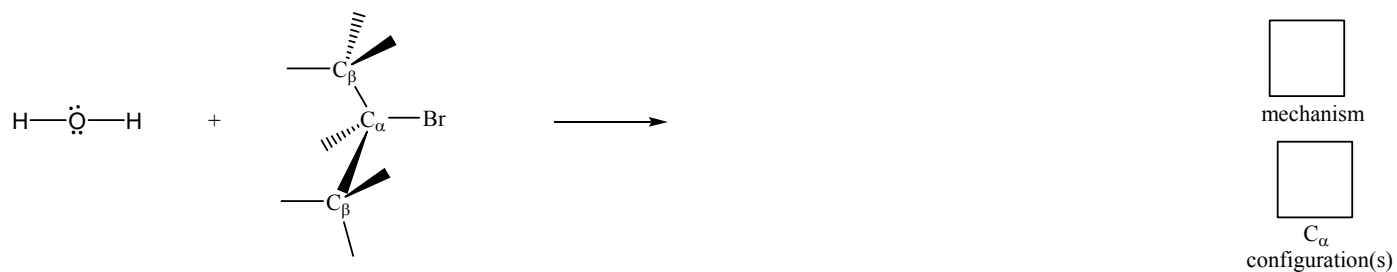
e. Show a mechanism for two E products and simply draw all other possible E reaction products (you can use the same intermediate for your two mechanisms). Indicate if E, Z or neither. (10 pts)

H—Ö—H   + C_β — C_α —Br   ⟶

☐
mechanism

☐
E or Z

other possible E products

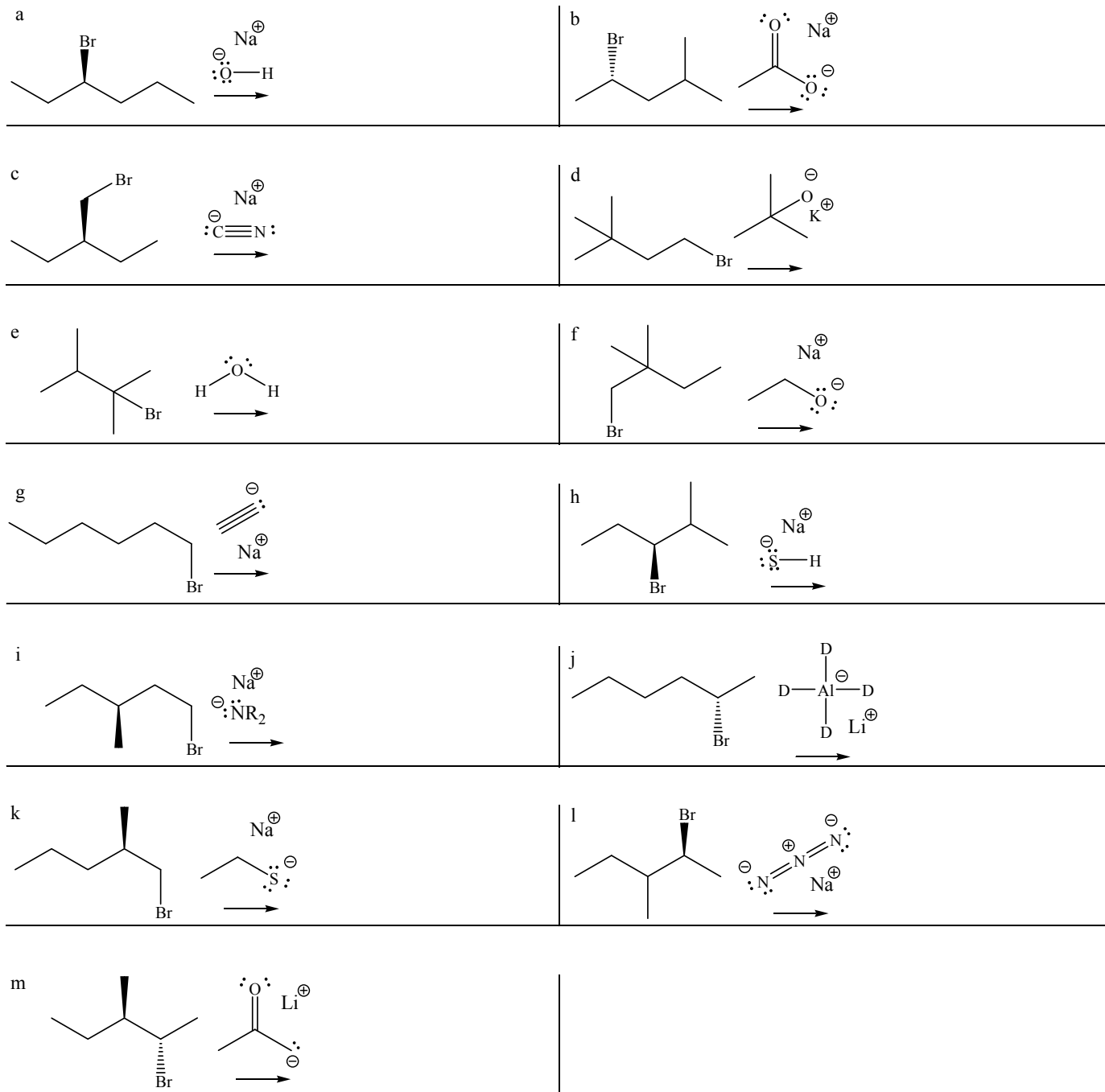1   2   3   4   5

10. Write in the major product (s) and type of reaction for each set of conditions below. Arrow pushing is not required (26 pts)

a

b

c

d

e

f

g

h

i

j

k

l

m

11. a. How many different types of sp^3 hydrogen atoms are present in 2R-chloro-3S-phenylpentane? Show all possible products when 2R-chloro-3S-phenylpentane is chlorinated with $Cl_2/h\nu$? 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 chlorine atom with an sp^3 C-H bond are: primary = 1, secondary = 4, chlorine substituted carbon = 6 and phenyl substituted carbon = 20. (25 pts)
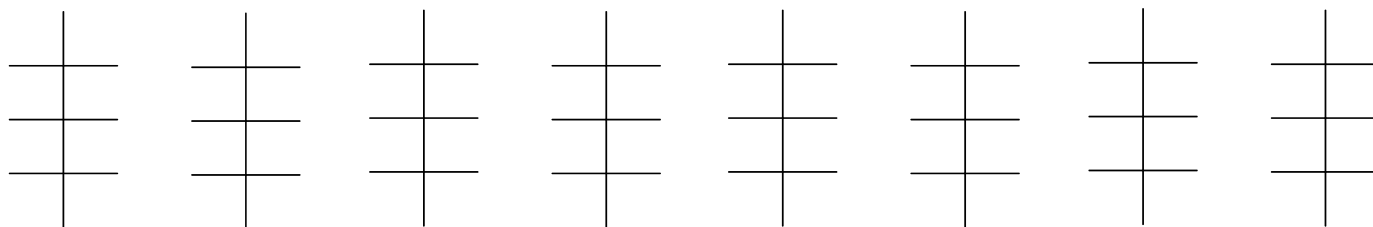
starting structure   A   B   C   D   E   F   G

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)

Cl——Cl	58
H——Cl	103
CH$_3$-H	105
1° C-H	98
2° C-H	95
3° C-H	92
benzylic C-H	85
C$_\alpha$Cl-H	88
CH$_3$-Cl	85
1° C-Cl	82
2° C-Cl	81
3° C-Cl	80
benzylic C-Cl	65
C$_\alpha$Cl-Cl	76

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