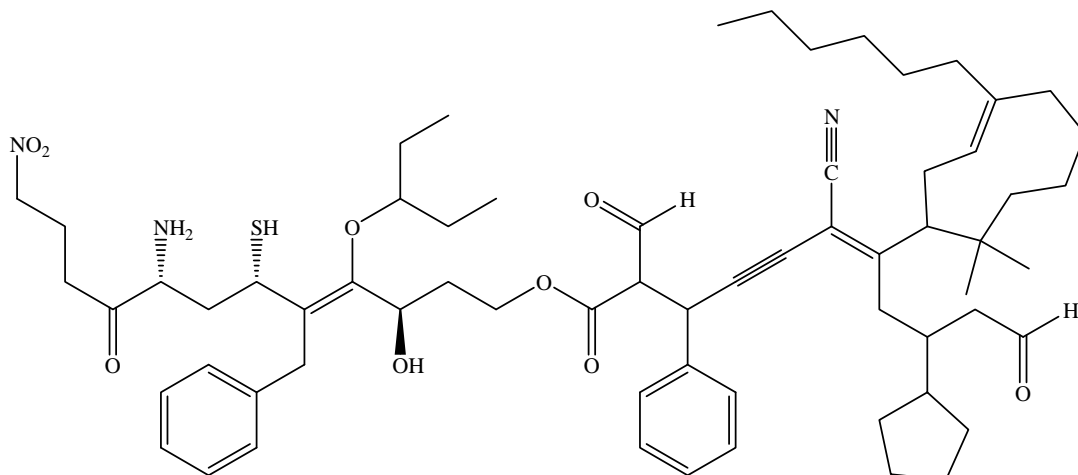


Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	X	
2. Various possibilities: Types of Isomers, Degrees of Unsaturation, common nomenclature, polarity, logic arguments of organic chemistry	X	
3. Cyclohexane Conformations, 2 substituents, Newman Projections	X	
4. Newman Projections, Conformational Energies	X	
5. Stereochemical Analysis	X	
6. 3D Structure, Hybridization, Angles, Shapes	X	
7. Forces of Interaction and Physical Properties, Inductive and Resonance Effects	X	
8. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge	X	
9. S _N /E Mechanisms, with all of the details	X	
10. Various Reactions, predict the products (20 reactions)	X	
11. Fill in all mechanistic details, curved arrows, lone pairs, formal charge, 3 examples in acid or base	X	
12. S _N /E Chemistry, Carbocations	X	
13. Free Radical Chemistry	X	
Total	X	

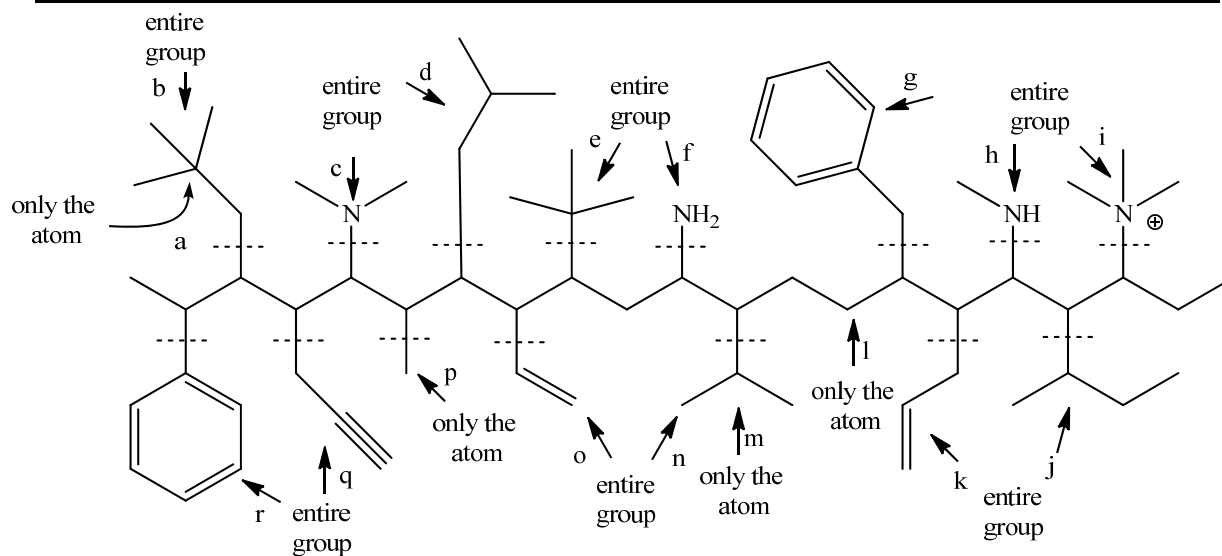
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron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

1. Provide an acceptable name for the following molecule. (X pts)



2. Match the arrows with the terms. Some arrows may be associated with more than one term. (X pts)

- | | | | |
|------------------------|----------------------|---------------------|-----------------------------------|
| 1. vinyl _____ | 7. sec-butyl _____ | 13. methyl _____ | 19. quaternary ammonium ion _____ |
| 2. allyl _____ | 8. t-butyl _____ | 14. methylene _____ | 20. tertiary amine _____ |
| 3. propargyl _____ | 9. neopentyl _____ | 15. methine _____ | 21. secondary amine _____ |
| 4. phenyl _____ | 10. quaternary _____ | 16. primary _____ | |
| 5. benzyl _____ | 11. isopropyl _____ | 17. secondary _____ | |
| 6. primary amine _____ | 12. isobutyl _____ | 18. tertiary _____ | |



3. Draw all possible chair conformations of trans-1-ethynyl-2-phenylcyclohexane. Draw C1 as the left-most carbon and number towards the front. Show all axial and equatorial groups. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw a Newman projections of the more stable conformation using the $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ bonds to sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of a ethynyl group is 0.5 kcal/mole and 2.9 kcal for a phenyl group and a ethynyl/phenyl gauche interaction is 1.0 kcal/mole, what is the difference in energy between the chair conformations? What is the ratio of the more stable conformation to the less stable conformation? Sketch an energy diagram that shows how the energy changes with the conformational changes. (X pts)

a.
$$K = 10^{\frac{-\Delta G}{2.3RT}}$$

$$R = 2 \text{ cal/mol-K}$$

$$T = 300 \text{ K}$$



(15 pts)

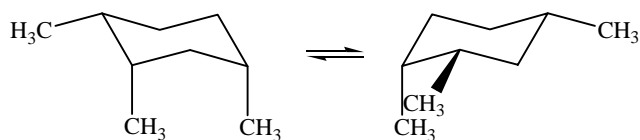
chair 1

chair 2

- b. Newman projection ($C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$) – most stable, point out any gauche interactions with the substituent(s)

- c. Energy diagram (lower to higher) and relative percents ($K_{eq} = ?$) (5 pts)

- d. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a K_{eq} . (Assume $R = 2 \text{ cal/mol-K}$ and $T = 300 \text{ K}$.) Use energy values provided in the box. Show your work. (5 pts)



One axial methyl group = +1.7 kcal/mole,
 Two axial methyl groups, on the same side (cis) = +5.5 kcal/mole,
 Three axial methyl groups, on the same side = +12.9 kcal/mole and
 1,2 gauche methyl groups = 0.8 kcal/mole.

$\Delta H \approx$

$K_{eq} \approx$

4. Use a Newman projection of the C1→C2 bond of 2-methyl-1-phenylbutane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (X pts)

2D structure

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

$$\Delta G \approx \Delta H$$

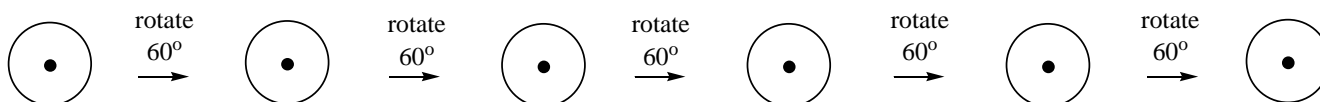
$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$$

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	1.5	1.3
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1	1.6
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9	3.3
Ph	0.2	1.4	1.5	2.1	3.9	2.3	1.9
Br	0.1	1.0	1.3	1.6	3.3	1.9	1.1

most stable
conformation



(14 pts)



$\Delta H^\circ =$

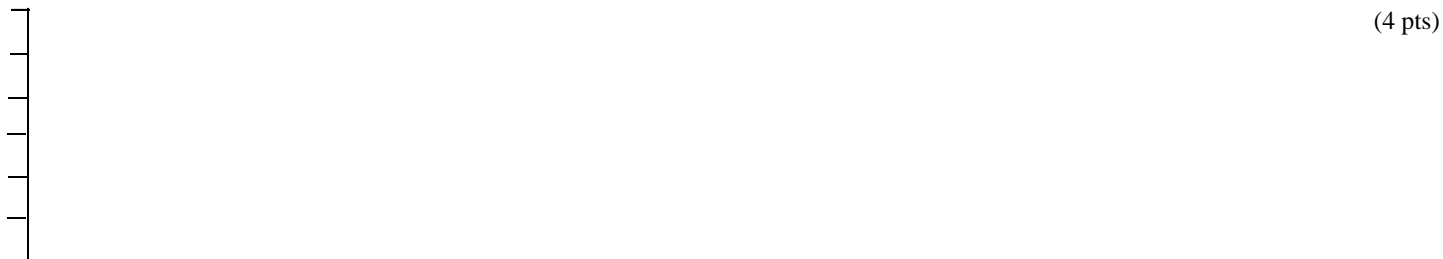
$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

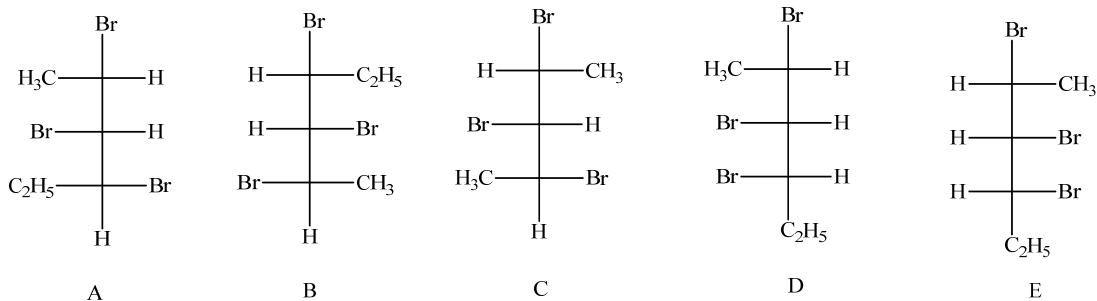
$\Delta H^\circ =$



(4 pts)

$K_{\text{calculation}}$ (4 pts)

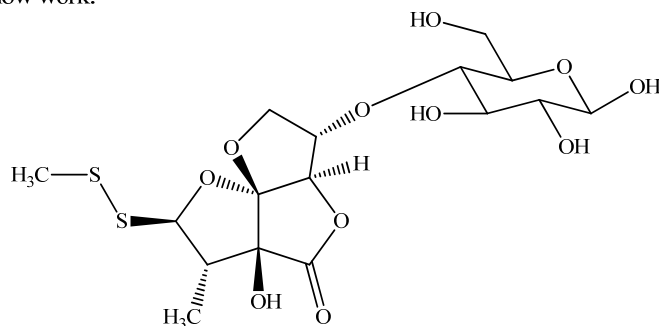
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify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



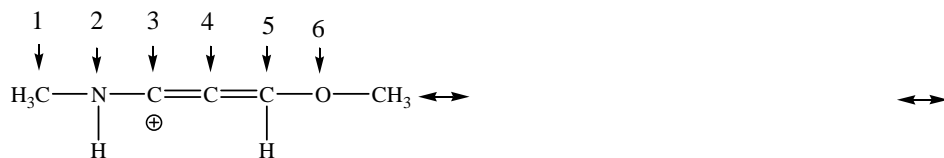
- | | |
|---|---|
| a. Which are optically active? | A B C D E |
| b. Which are meso? | A B C D E |
| c. Which is not an isomer with the others? | A B C D E |
| d. Which pairs are enantiomers? | AB AC AD AE BC BD BE CD CE DE |
| e. Which pairs are identical? | AB AC AD AE BC BD BE CD CE DE |
| f. Which pairs are diastereomers? | AB AC AD AE BC BD BE CD CE DE |
| g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? | AB AC AD AE BC BD BE CD CE DE |
| h. Draw any stereoisomers, which are not shown above, as Fischer projections. If there are none, indicate this. | |

- i. In the most recent Organic Letters, 2018, 20, 28-31, three new sulfur compounds were isolated from welsh onion plant grown in Kyoto, Japan (only Kujounin A₁ is shown). Circle all of the chiral centers. How many stereoisomers are possible? Show work.

Kujounin A₁ has anti-cancer activity.



6. Draw two additional “better” 2D resonance structures of the given structure. Which structure is best and why? Draw a 3D structure for the given resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms. (X pts)



Atom	Shape	Hybridization	Bond Angles	# σ bonds	# π bonds	# lone pairs
------	-------	---------------	-------------	------------------	---------------	--------------

1

2

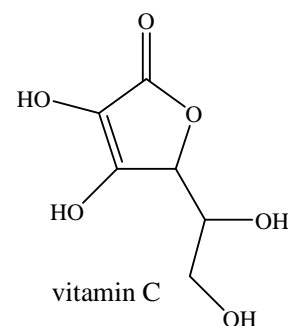
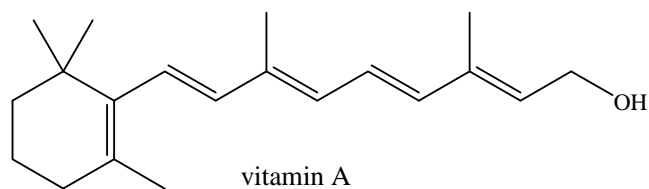
3

4

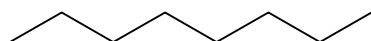
5

6

7. a. The structures of vitamin A and vitamin C are shown below. If they are taken in large daily amounts one is toxic and one is not. Explain why this observation is reasonable? (X pts)

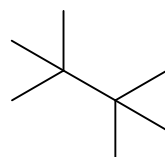


- b. The melting points and boiling points for the following two compounds are: -57°C , 101°C , 106°C and 126°C . Match those temperatures with the structures below and provide a possible explanation for the differences. (X pts)



$T_{\text{bp}} =$

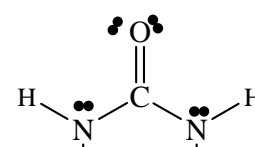
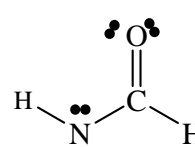
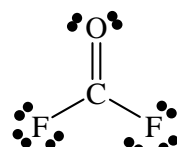
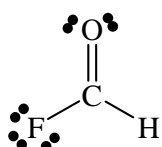
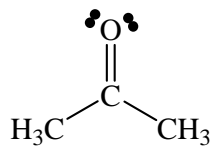
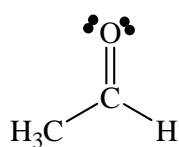
$T_{\text{mp}} =$



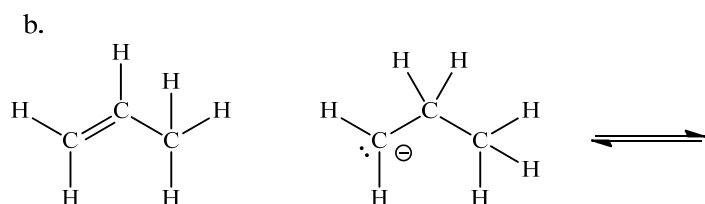
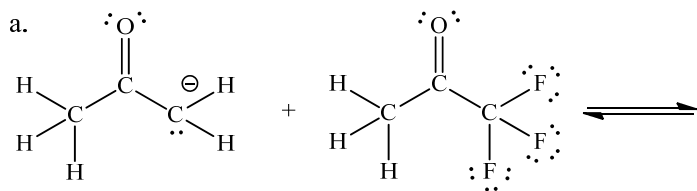
$T_{\text{bp}} =$

$T_{\text{mp}} =$

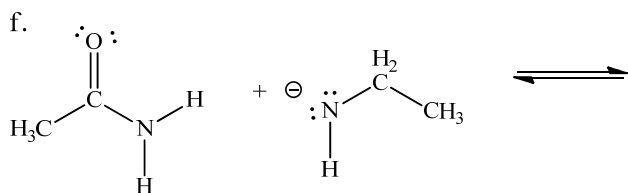
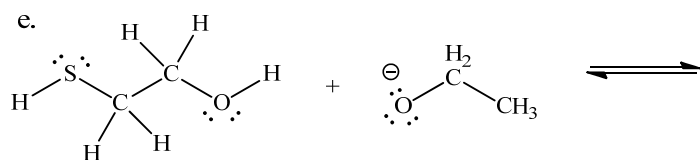
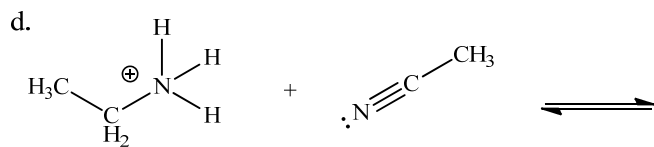
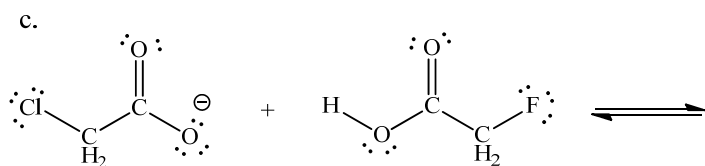
- c. Explain what the following dipole moments suggest about inductive effects and resonance effects in organic and biochemistry. You may need to draw additional structures to help your explanation. (X pts)



8. Using arrow-pushing mechanisms, write the expected products from the following reactions and indicate whether the equilibrium lies to the "right" or to the "left". Also, very briefly explain your reasoning. (X pts)



The two acids have K_a 's of 10^{-50} and 10^{-42} . Calculate an equilibrium constant for this reaction.

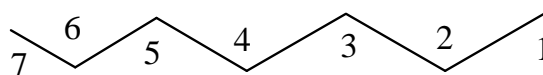


9. Use (3*S*,4*S*)-4-bromo-3-deuterioheptane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If 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. You can abbreviate (simplify) parts of the molecule that are not part of a reaction. (X 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. (X pts)

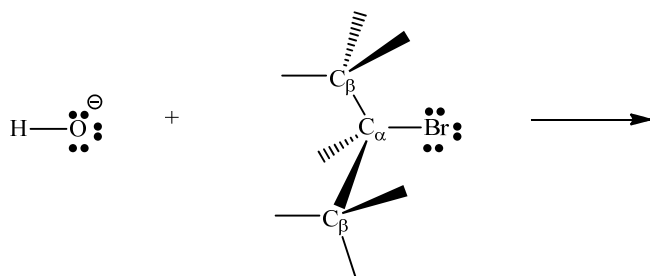
2D structure

3D structure



(3*S*,4*S*)-4-bromo-3-deuterioheptane

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

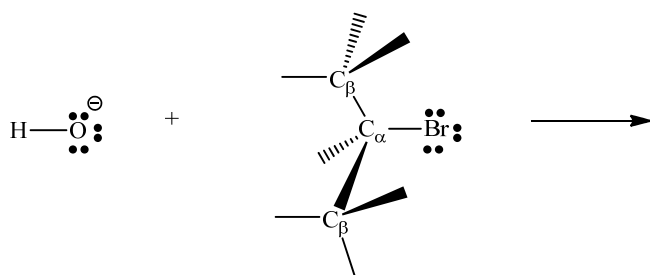


mechanism



configuration
in product

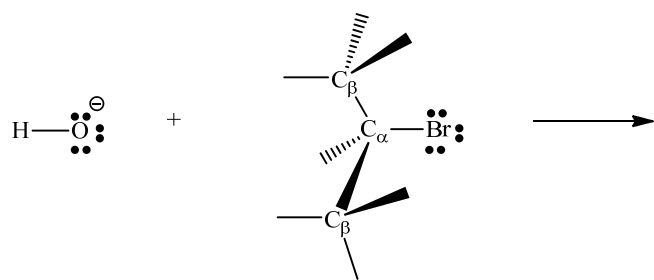
c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (X pts)



mechanism

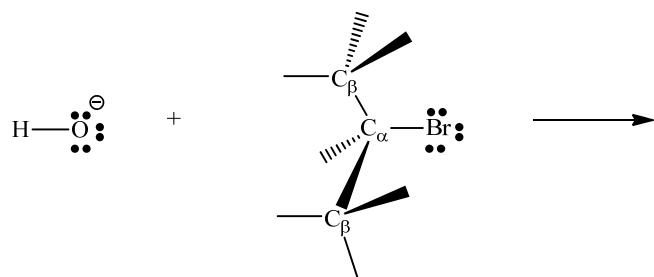


configuration
in product



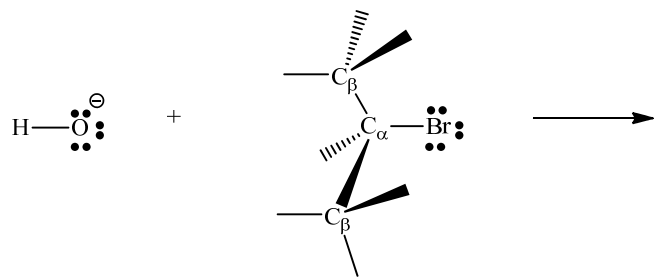
mechanism

configuration
in product



mechanism

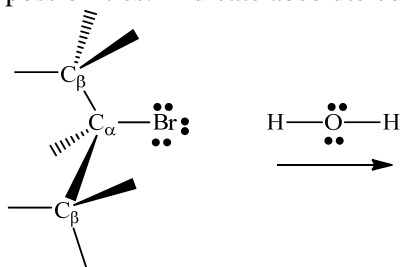
configuration
in product



mechanism

configuration
in product

d. Show the S_N reaction (what kind?). You can use one intermediate to show all possible mechanistic S_N possibilities. Indicate absolute configuration(s) of the C_α center in your product(s). (X pts)



mechanism



configuration
in product

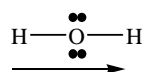
e. Redraw the intermediate used in 8d above to show all possible E reaction products. Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show the possibilities for a single hydrogen atom and just draw the additional possible "E" products. (10 pts)



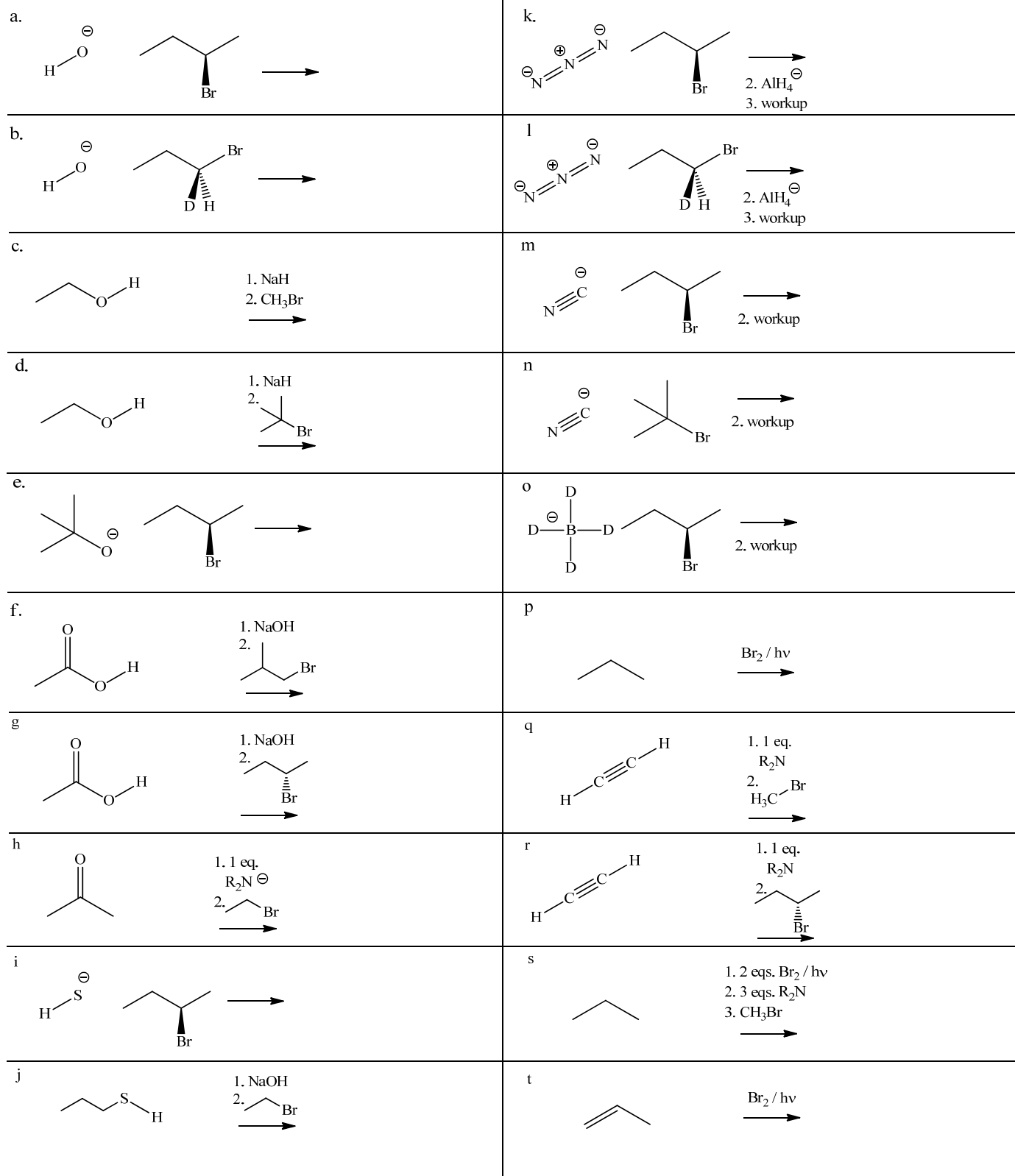
mechanism



E or Z

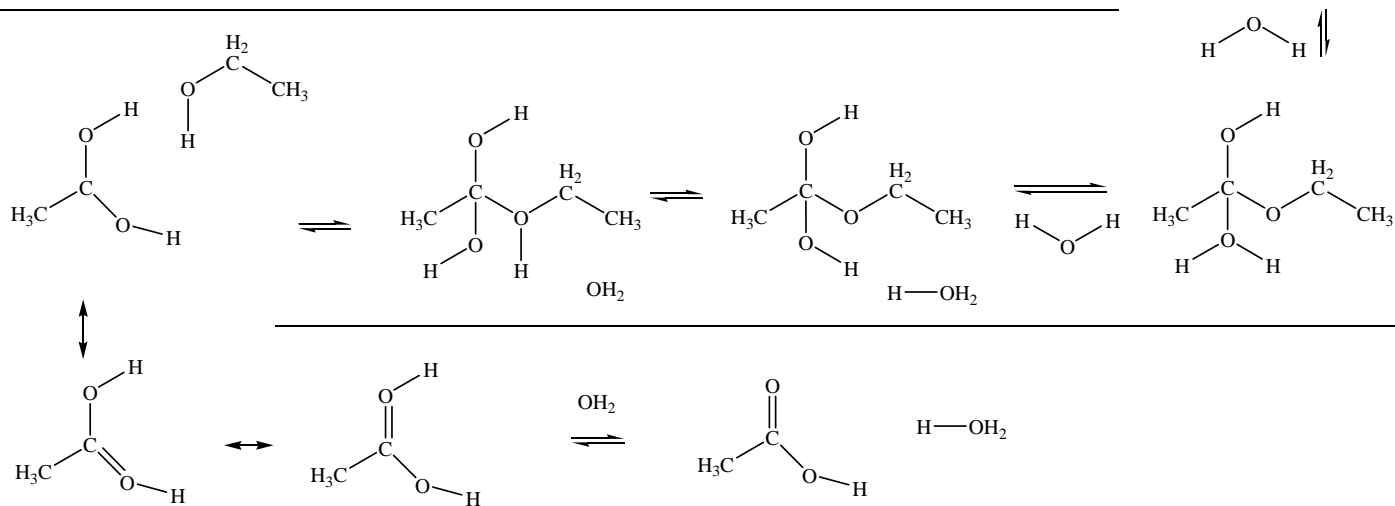
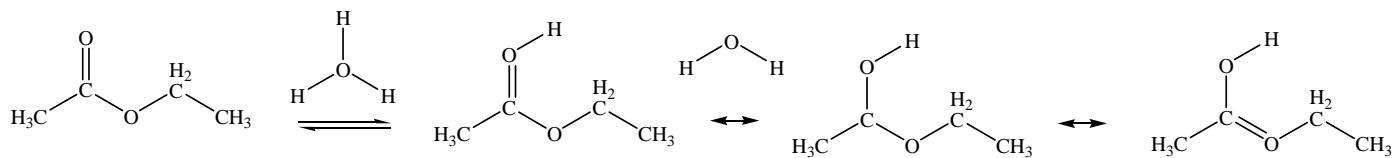


10. Indicate the **major** product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralize conditions) (X pts)

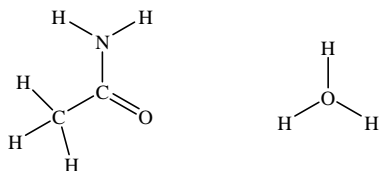
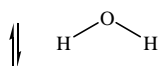
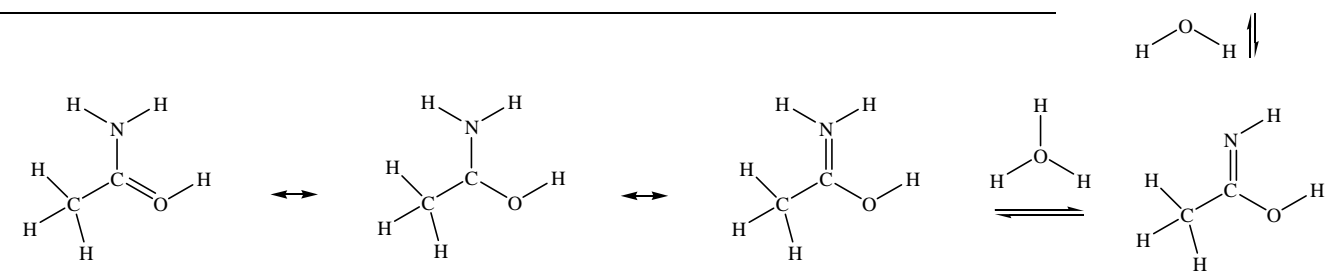
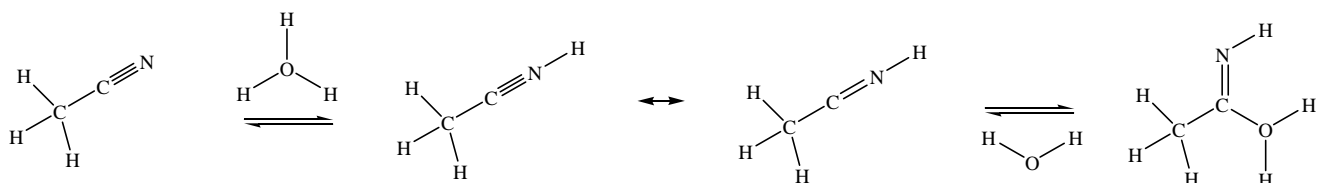


11. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformations, one in acid and one in base. Assume all nonhydrogen atoms have full octets unless a positive charge is written by the atom. (Xpts)

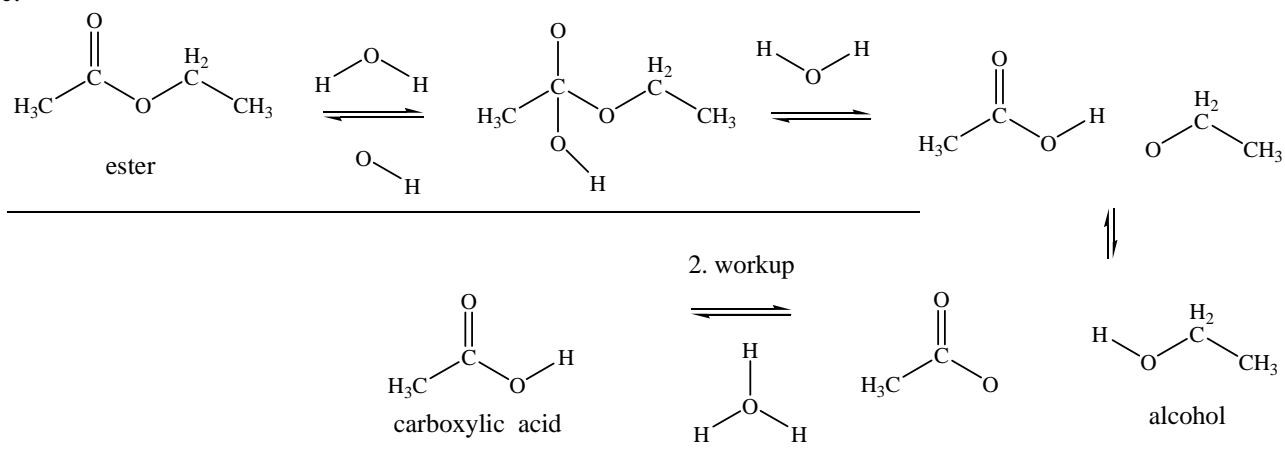
a.



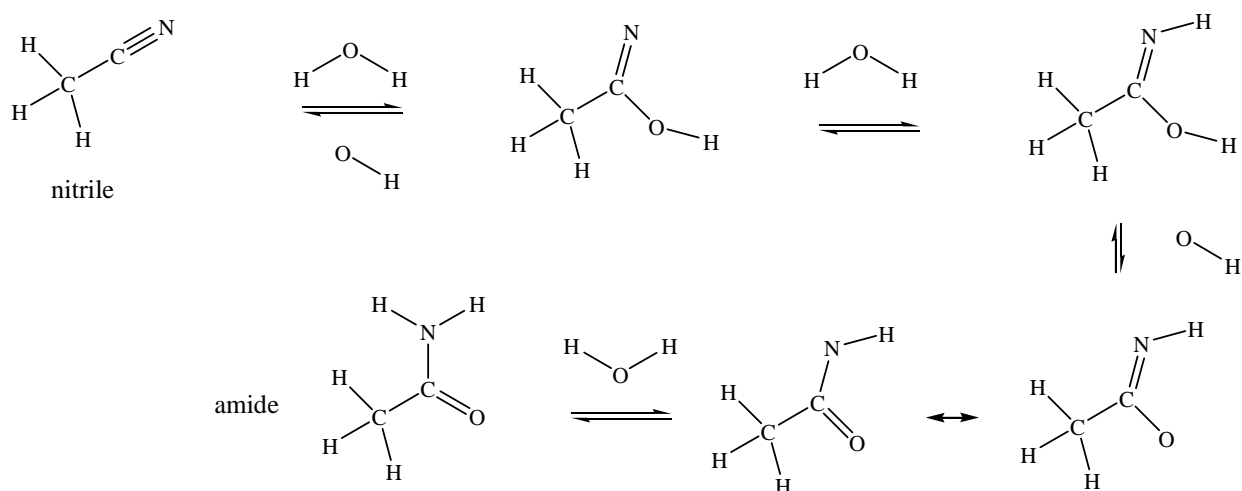
b.



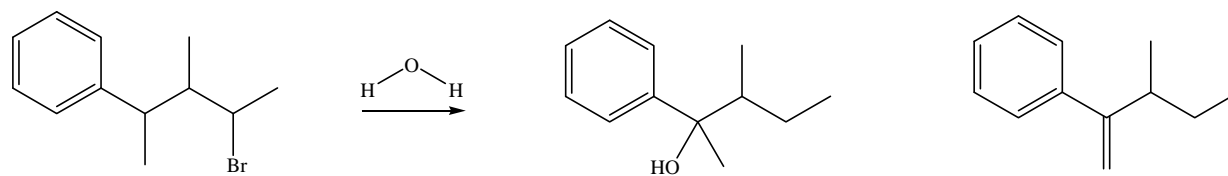
c.



d.



12. Provide a complete arrow-pushing mechanism for the following transformations. (X pts)



13. a. Show all possible products when 2-methylpentane is brominated with $\text{Br}_2/h\nu$? 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 and tertiary = 1600. (X pts)

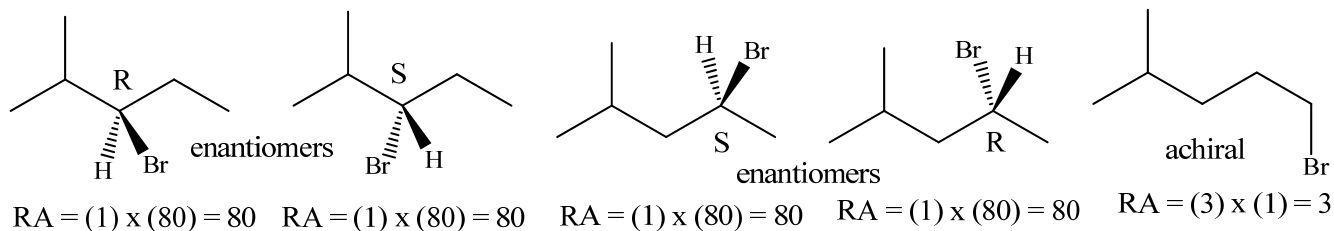
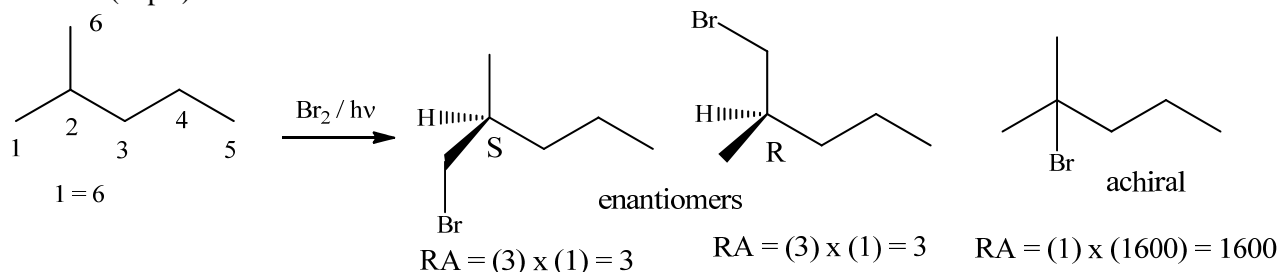
b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. To make a bond is positive energy and to make a bond is negative bond energy. (X pts)

Br—Br	46
H—Br	87

Me C-H	105
1° C-H	98
2° C-H	95
3° C-H	92

Me C-Br	70
1° C-Br	68
2° C-Br	68
3° C-Br	67

13. (possible answer) a. Show all possible products when 2-methylpentane is brominated with $\text{Br}_2/h\nu$? 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 and tertiary = 1600. Specify the absolute configuration of any chiral centers. (X pts)

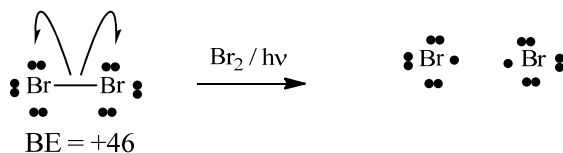


- b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. To make a bond is positive energy and to make a bond is negative bond energy. (X pts)

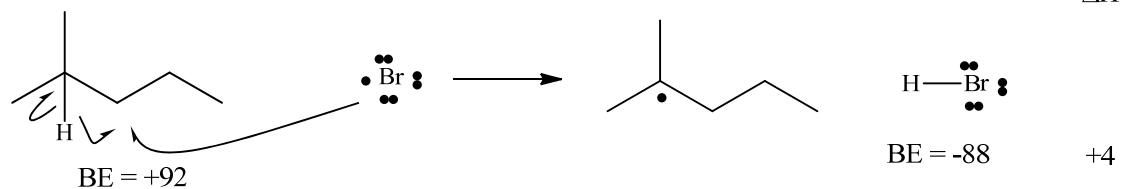
Br—Br	46
H—Br	87

Me C-H	105
1° C-H	98
2° C-H	95
3° C-H	92
Me C-Br	70
1° C-Br	68
2° C-Br	68
3° C-Br	67

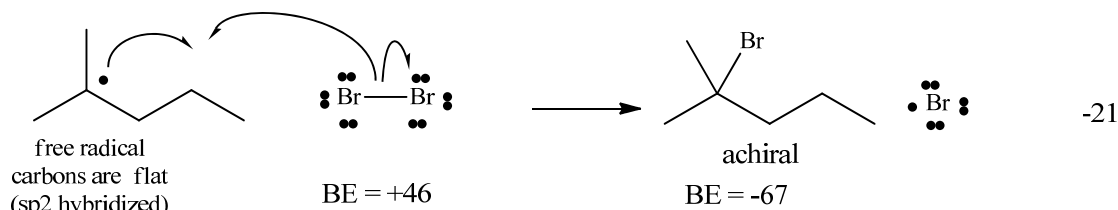
1. initiation



2a. propagation - The weakest C-H bond reacts the fastest.



2b. propagation



$\Delta H_{\text{overall}} = -19$

3. termination = combination of 2 radicals to shut down chain reaction

