Chem 314
Final Exam
Winter, 2009
Beauchamp

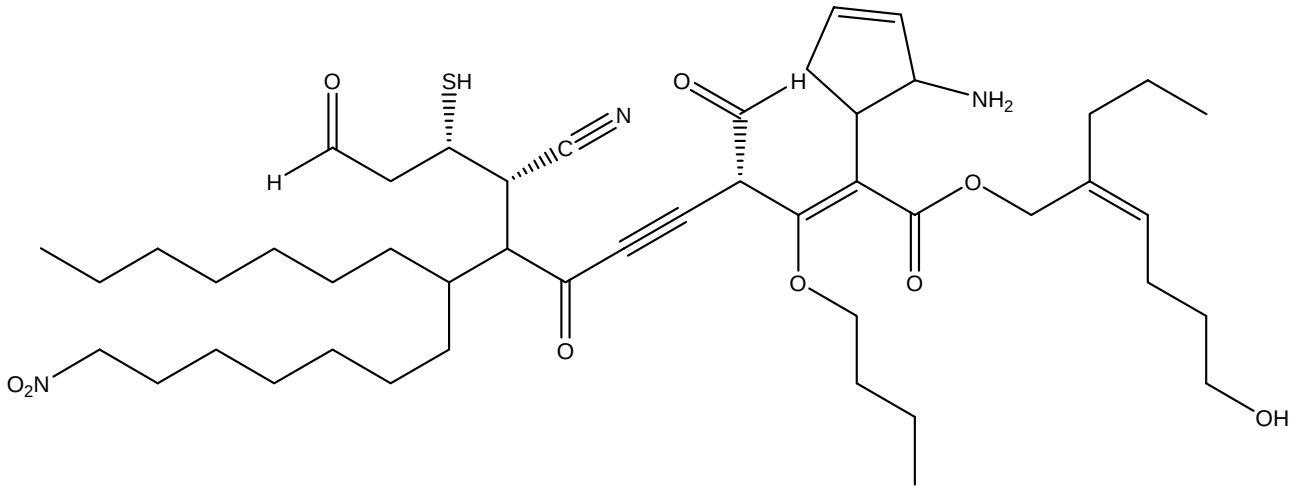
Name _____

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	30	
4. Thermodynamics, Conformations, Configurations, Stereoisomers, Energy Diagram, Newman Projections	37	
5. Stereochemisty Questions	43	
6. Acid/Base Chemistry (arrow pushing, explanation)	40	
7. S_N2 and E2 mechanisms, including stereochemical details	23	
8. RX compounds in S_N and E reactions, including stereochemistry details,	38	
9. Synthesis with acid/base, S_N2 and E2 reactions	30	
10. Free Radicals, Predict products provide mechanism	35	
Total	326	

This is a long exam. It has been designed so that no one question will make or break you. You are not expected to completely finish the exam. 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 wherever necessary. Only write on the front side of each page. Also, consider the point values in your choice of questions. Do your best to show me what you know in the available time.

The harder we work, the luckier we get. Vince Lombardi

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)



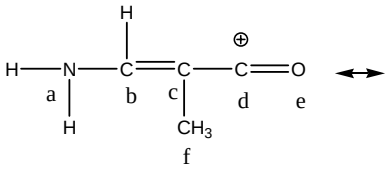
2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present. (20 pts)

6 carbon ring present

$(CH_3)_3CCCCHCHCHBrCHOHC_6H_4CHCNCH_2CONCH_3CH_2COCHCFCO_2CHNO_2CH(CHO)CH(OCH_3)CH(NO)CO_2H$

formal charge in this group

3. First, draw three 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 σ bonds as lines, wedges and dashes and the p orbitals in π 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 nonhydrogen atoms have full octets, unless a carbocation is written**. (30 pts)



A B C D

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-1,3-diphenylcyclohexane and cis-1,3-dphenylcyclohexane (you can use Ph to represent a phenyl ring, after you draw it correctly in your first structure). Indicate which conformation is more stable in each pair. Draw in all atoms at any substituted positions in the rings (hydrogen too). Which conformation, overall, is most and least stable? What is the absolute configuration of all stereogenic atoms in chair 1? (16 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) = _____

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

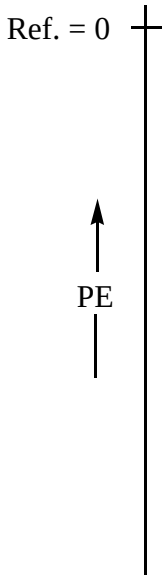
b. Write a balanced combustion equation for any isomer of 1,3-diphenylcyclohexane. (3 pts)

c. Use the second most stable conformation from part a and draw a Newman projection using bonds $C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$ for your structure (indicate which chair you are using from part a: 1,2,3 or4 and number it appropriately in part a). Point out any gauche relationships in the branches and/or the ring. (4 pts)

Newman projection of the second most stable conformation from part a

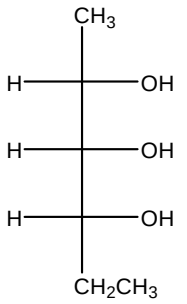
d. The heats of combustion of carbon graphite (per mole) and hydrogen (H_2) are -94.0 and -57.8 kcal/mole, respectively. Given that the heats of combustion of cis-1,3-diphenylcyclohexane and trans-1,3-diphenylcyclohexane are -2278.0 and -2280.8 , respectively, calculate the heat of formation, ΔH^{o}_{f} , for each of these isomers. Show all work and analysis clearly. Sketch a very simple diagram showing the zero reference point, heat of formation and heat of combustion for one of the isomers. (10 pts)

show work:

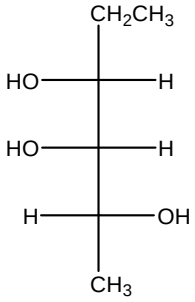


e. Use the thermodynamic data from part d, and the most stable conformation of both the cis and trans isomers to estimate the energy of an axial phenyl in a cylclohexane ring. Briefly, show your reasoning for the value indicated using sketches of these conformations. (4 pts)

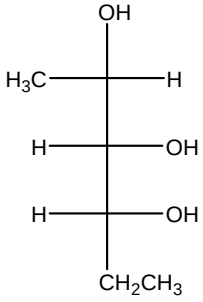
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections having the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify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



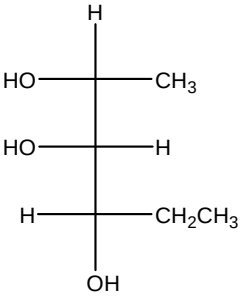
A



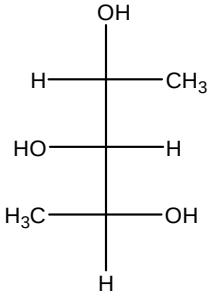
B



C



D



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

d. 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 probably rotate plane polarized light (only chiral compounds do this)?
A B C D E

g. Draw a Fischer projection of any stereoisomers of "A" which are not shown above. If there are none, indicate this. (7 pts)

h. Using isomers of methylbromocyclobutane, draw a pair of enantiomers, a pair of diastereomers where at least one of the stereoisomers is chiral, a pair of achiral diastereomers, and an achiral compound that does not have any stereoisomer. Propose a change that will allow you to draw a meso structure and draw it. (16 pts)

a pair of enantiomers

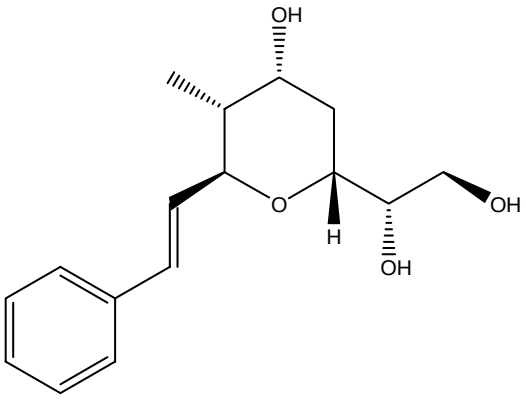
a pair of diastereomers where at least one of the stereoisomers is chiral

a pair of achiral diastereomers

an achiral compound that is does not have any stereoisomer

your meso structure

i. The synthesis of part of a compound highly effective against gram-positive and gram-negative bacteria was recently published (Org. Lett. p.1099, 2009). Only the starting material is shown below. Circle all stereogenic features and calculate the maximum number of stereoisomers possible. (5 pts)



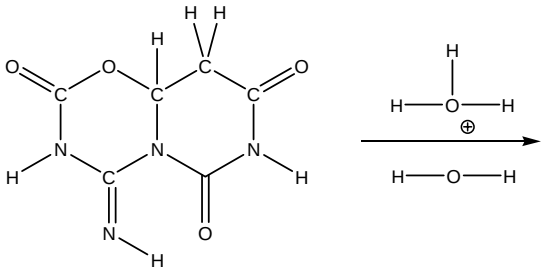
starting material for synthesis of antibiotic compound isolated from the fermentation broth of myxobacteria *Sorangium cellulosum*

Circle all chiral centers and any other stereogenic features.

Calculate the maximum number of stereoisomers possible, show your set up and answer.

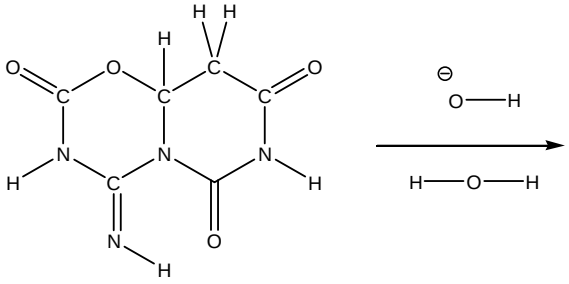
6. The following molecule can act as either an acid or a base (it's amphiprotic). Use aqueous hydronium ions, H_3O^+/H_2O, to show the molecule acting as a base at its most basic site. Continue the reaction to draw any reasonable tautomer from your protonated intermediate. In both parts, use curved arrows to show the flow of electrons and include formal charge and lone pairs. Draw all resonance structures important to the conjugate acid or base. Provide an explanation for why your answers are the "best" choices. (20 pts)

a. reaction in acid, HA



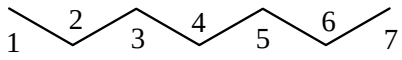
Use aqueous hydroxide to show the molecule reacting as an acid at its most acidic site. Continue the reaction to draw any reasonable "different" tautomer from your de-protonated intermediate. (20 pts)

b. reaction in base, B:



7. Use 5R-deuterio-4R-bromo-3S-methylheptane 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. (23 pts)

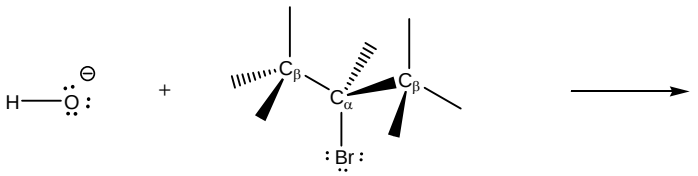
   a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (4 pts)



2D structure

3D structure of 5R-deuterio-4R-bromo-3S-methylheptane

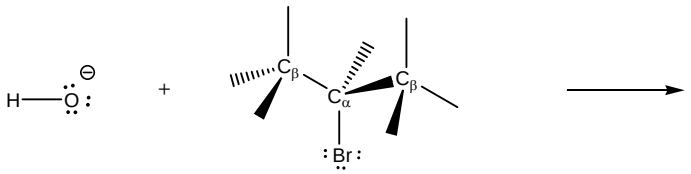
   b. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the *product*. (6 pts)



mechanism

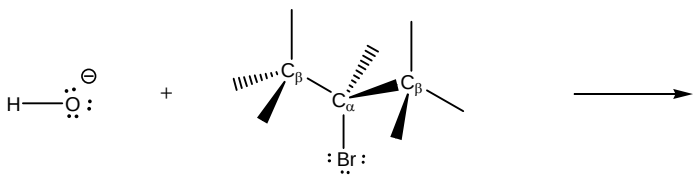
C_α configuration in the product

   c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (13 pts)

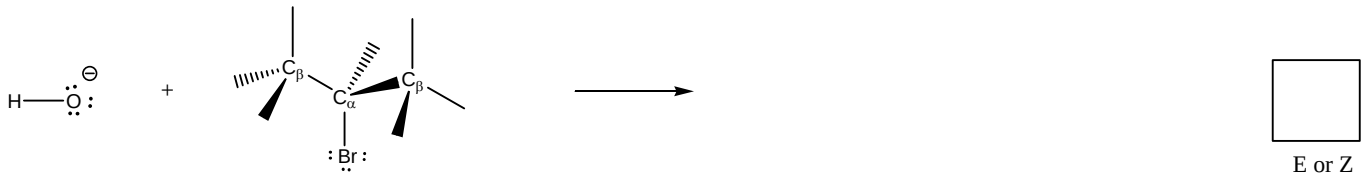


mechanism

E or Z

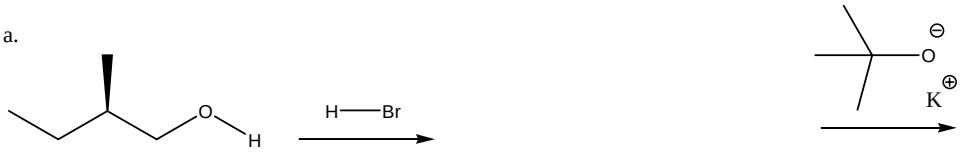


E or Z



8. Predict all possible S_N2 product(s); if none are expected, indicate so. Only predict the major E2 product. State whether S_N2 or E2 is major, minor or they are about the same. Finally, state by what mechanism each product was formed (S_N2, E2, acid/base, etc.). DO NOT DRAW MECHANISMS. (38 pts)

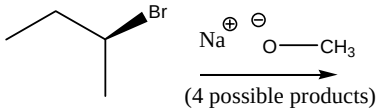
a.



b.

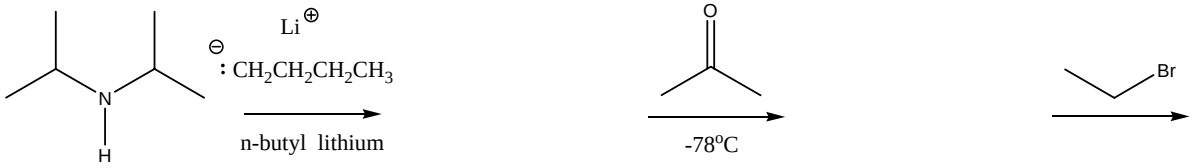
c.

d.

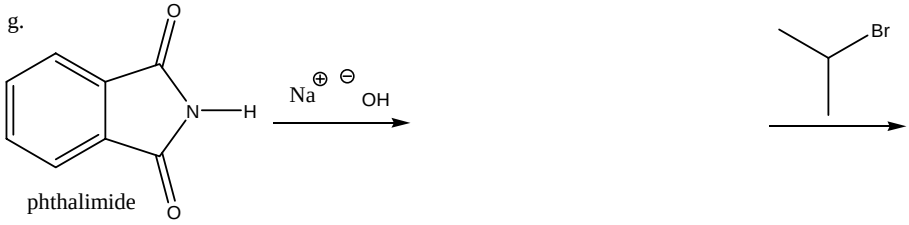


e.

f.



g.



h.

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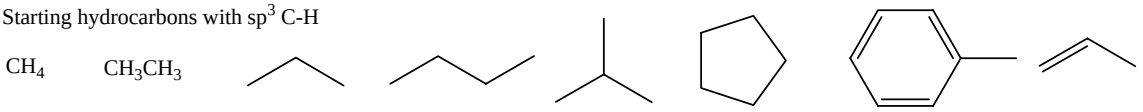
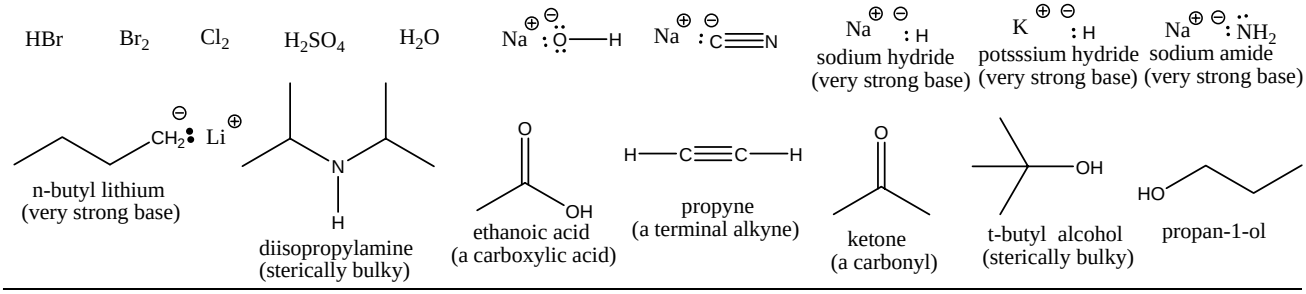
9. Propose a reasonable synthetic approach for the following six molecules (a-f) starting from a given hydrocarbon. You may use any of the reagents available below. Five points for each synthesis. (30 pts)

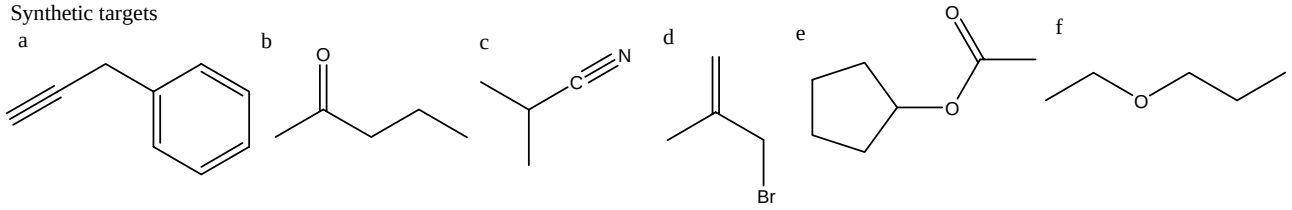
Starting hydrocarbons with sp^3 C-H



Miscellaneous Reagents



Synthetic targets



10. a. How many different types of sp^3 hydrogen atoms are present in 2R-bromopentane? Show all possible products when 2R-bromopentane is monobrominated with $Br_2/h\nu$ (you can use Fischer projections)? Put an asterisk by all chiral centers. Use any product structure that has at least 2 chiral centers to draw a 3D representation which identifies each absolute configuration as R or S. If any stereoisomers form, specify what type of isomerism is present (enantiomers, diastereomers, meso compounds, achiral, etc.). Under each structure Indicate the approximate relative amount of 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 bromo substituted carbon = 200. (20 pts)

b. Provide a complete arrow pushing mechanism to explain formation of one of the products 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	87
Me C-H	105
1° C-H	98
2° C-H	95
3° C-H	92
α-bromo C-H	93
Me C-Br	70
1° C-Br	68
2° C-Br	68
3° C-Br	67
α-bromo C-Br	67