Chem 314
Final Exam
Spring, 2004
Beauchamp

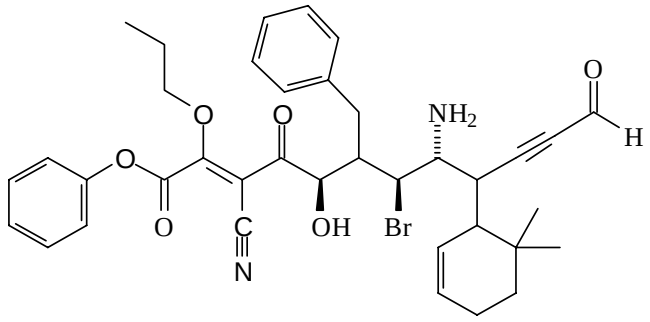
Name _____

Problem	Points	Credit
1. Nomenclature	39	
2. 2D Lewis structure (large structure with possible formal charge)	20	
3. 3D Structures, Formal Charge, Resonance, Hybridization	30	
4. Thermodynamics, Conformations, Configurations, Stereoisomers, Energy Diagram, Newman Projections	39	
5. Stereochemisty Questions	25	
6. Possible question on MO Theory or Physical Properties or Bond Energies and Reaction Energies	10	
7. Acid/Base Chemistry (arrow pushing, explanation)	26	
8. RX compounds in S_N and E reactions, including stereochemistry details	50	
9. Arrow Pushing Mechanism (curved arrows, lone pairs, formal charge)	26	
Total	265	

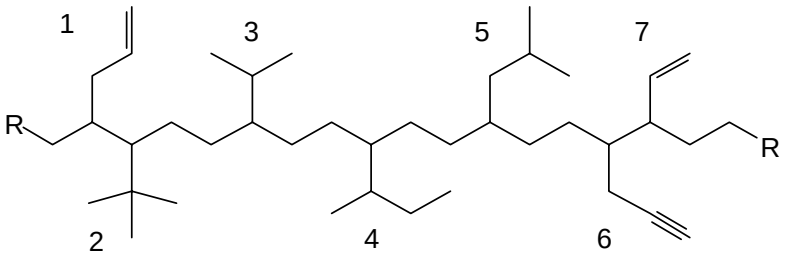
This is a long exam. It has been designed so that no one question will make or break you. You are not expected to completely finish the exam. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement. Do you best to show me what you know in the time available.

1. Provide an acceptable name for the following structure. Indicate the configuration of any stereogenic centers shown with sufficient information to make decision. (25 pts)

a.



b. Provide the common name for each substituent in the alkane chain shown below. Point out one example of a primary, secondary, tertiary and quaternary carbon. Also point out one example of a methyl, methylene and methine carbon. (14 pts)



1

2

3

4

5

6

7

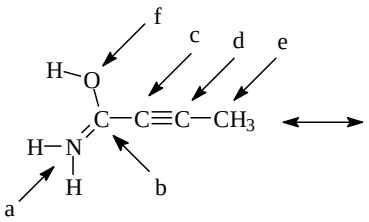
2. Draw an acceptable Lewis structure for the following formula. Indicate any formal charges present. (20 pts)

$^{\ominus}O_2CCCC(CH_3)CHCOCH(OH)CH(NO_2)CO_2CH(\overset{\oplus}{N}H_3)C(CH_3)_2CH(OCH_3)C_6H_4CON(CH_3)CH(CH_3)CHO$

6 carbon ring present

formal charge in this group

3. First, draw three other reasonable resonance structures as two-dimensional representations. Include proper curved arrow conventions. 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. Indicate any formal charge present and give the hybridization, bond angles and shape of each nonhydrogen atom. Assume that all nonhydrogens 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 cis-1-methyl-2-isopropylcyclohexane and trans-1-methyl-2-isopropylcyclohexane. Indicate which conformation is more stable in each pair and overall. Which conformation, overall, is least stable? What is the absolute configuration of all stereogenic atoms in chair 1? (17 pts)

cis

trans

chair 1 chair 2 chair 3 chair 4

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

sterochemical relationship of 1 with 2? _____ (enantiomer, diastereomer, meso, none)

sterochemical relationship of 1 with 3? _____ (enantiomer, diastereomer, meso, none)

sterochemical relationship of 1 with 4? _____ (enantiomer, diastereomer, meso, none)

b. Write a balanced combustion equation for any isomer of 1-methyl-2-isopropylcyclohexane. (2 pts)

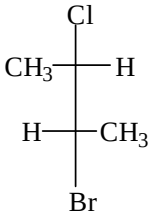
c. The heats of combustion of carbon graphite (per mole) and hydrogen (H_2) are -94.0 and -57.8 kcal/mole, respectively. Given that the heats of combustion of cis-1-methyl-2-isopropylcyclohexane and trans-1-methyl-3-isopropylcyclohexane are -1464.9 and -1463.0 , respectively, calculate the heat of formation, ΔH^{o}_{f} , for each of these isomers. Show all work and analysis clearly, so that I can understand your logic in solving this problem. (10 pts)

d. Use the thermodynamic data from part c to estimate the energy of an axial methyl in a cylclohexane ring. Briefly, state your reasoning for the value provided. (4 pts)

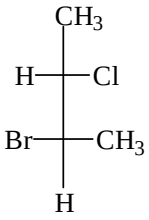
e. Use the second most stable conformation from part a and draw a Newman projection using bonds $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ for your structure. Point out any gauche relationships in the branches of the ring (6 pts)

second most stable conformation from part a

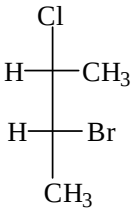
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections having the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (17 pts)



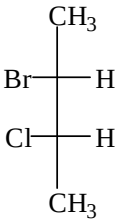
A



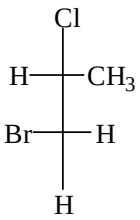
B



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

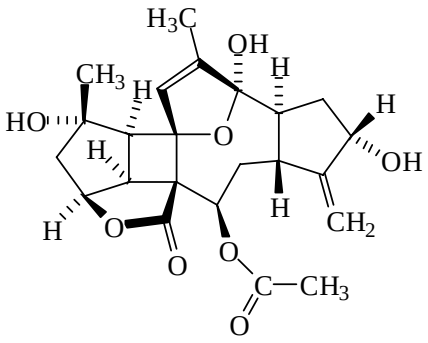
f. Which would rotate plane polarized light when mixed in a 50/50 ratio?

AB AC AD AE BC BD BE CD CE DE

g. Draw any stereoisomers of 2-bromo-3-chlorobutane, as Fischer projections, which are not shown above. If there are none, indicate this. (2 pts)

h. Would any answers above change if the Cl was switched with a Br? (2 pts)

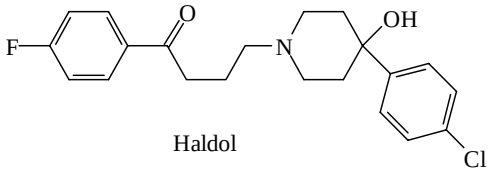
i. A never before seen carbon skeleton was discovered in a natural product from coral in the Caribbean (Org. Lett. p.1661, 2004). It has shown anti-malarial and anti-cancer activity against two cell lines. Circle all chiral centers and calculate the maximum number of stereoisomers possible. (4 pts)



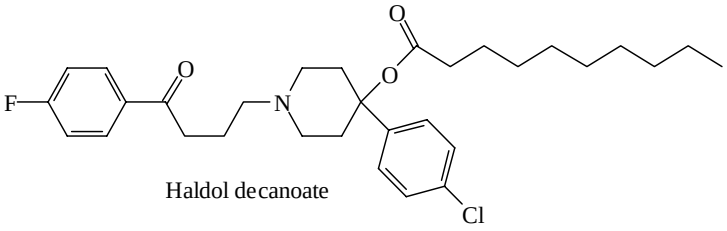
bielschowskysin - naturally occuring diterpene

maximum number of stereoisomers possible? _____

6. Haldol is a potent orally active central nervous system tranquilizer used in the treatment of psychoses. Peak plasma levels when taken orally are 2-6 hours (in the aqueous blood). Cell membranes, on the other hand, are composed largely of alkane-like fatty acid chains. A decanoate ester prodrug was prepared to increase is lifetime in the body. When injected intramuscularly its anti-psychotic activity lasted about 1 month. Provide an explanation for its longer lifetime. (10 pts)



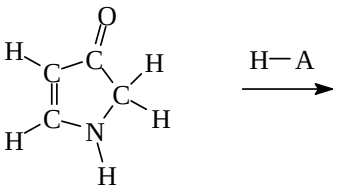
Haldol



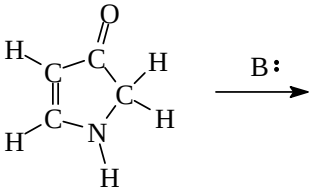
Haldol decanoate

7. The following molecule can act as either an acid or a base (it's amphiprotic). Use a general acid, HA, and show the molecule acting as a base at its most basic site. Use a general base, B:, and show the molecule reacting as an acid at its most acidic 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. Provide an explanation for your answers. (26 pts)

a. reaction in acid, HA

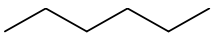


b. reaction in base, B:



8. Use 2R-deuterio-3S-bromo-4S-methylhexane to provide a simple, arrow-pushing mechanism for the following reaction conditions. 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 convenient form. (32 pts)

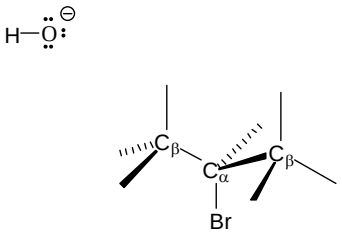
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (4 pts)



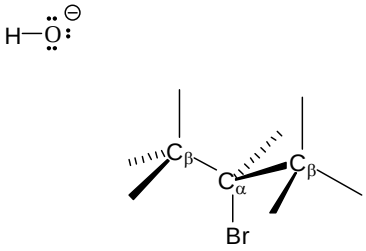
2D structure

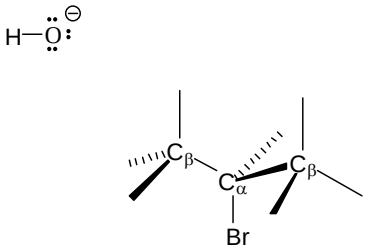
3D structure of 2R-deuterio-3S-bromo-3S-methylhexane

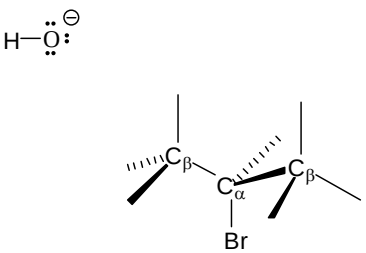
b. Show the S_N reaction (what kind?), indicate absolute configuration of all chiral centers. (7 pts)



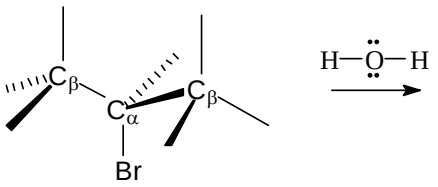
c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (21 pts)





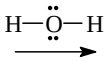


d. Show the S_N reaction (what kind?), indicate absolute configuration of all chiral centers. (7 pts)

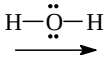


e. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show a single mechanism and just draw the additional possible products. (21 pts)

redraw intermediate from 8d (above)

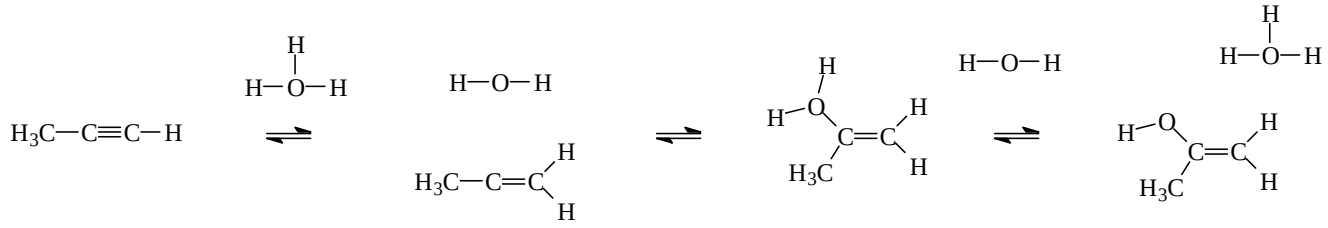


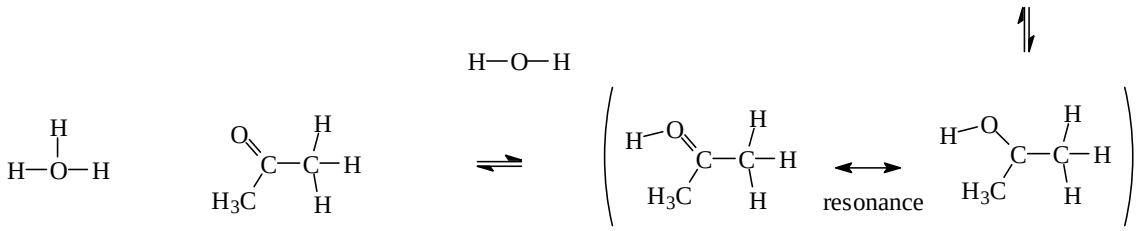
redraw intermediate from 8d (above)



9. Supply any formal charge present, lone pairs and curved arrows to show how the electrons move in each step. In the second step of each sequence, identify the Lewis acid and Lewis base. (26 pts)

a. reaction in acid





b. reaction in base