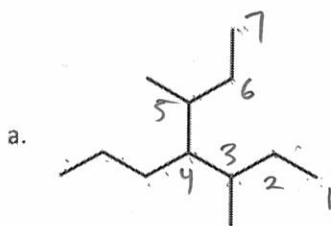


1. Name each of the following compounds using IUPAC (systematic) names. (20 points)

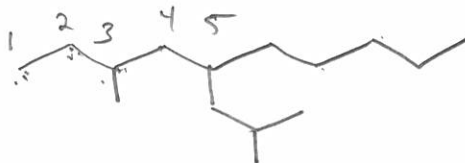


1,4-dimethyl bicyclo[2.2.2]
octane

4-propyl-3,5-dimethyl heptane

2. Draw structures for the following compounds. (20 points)

- a. 3-methyl-5-(2-methylpropyl)decane

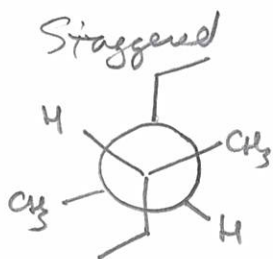
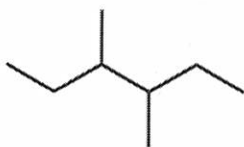


- b. *cis*-1,3-diisopropylcycloheptane



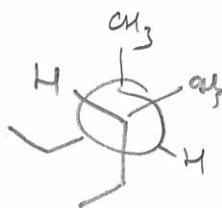
3. Consider the molecule below. Using Newman projections, draw the lowest energy and the highest energy conformations around the C3-C4 bond. In each conformation, label it as *staggered* or *eclipsed*, and indicate what type of strain is present – torsional, steric, angle, or some combination of them – be specific about this.

(50 points)



lowest

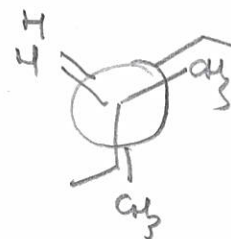
or
only
steric



torsional
+
steric



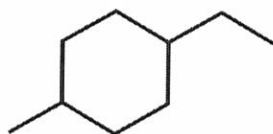
or



highest

4. Consider both the *trans* and *cis* isomers of 1-ethyl-4-methylcyclohexane.

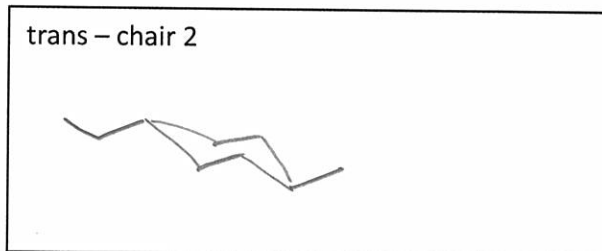
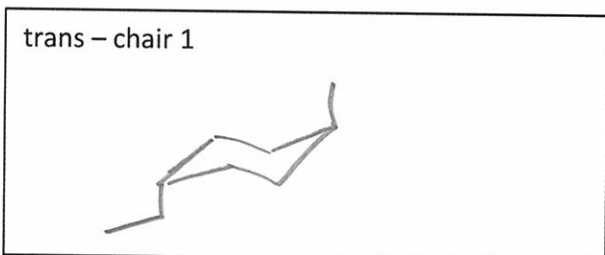
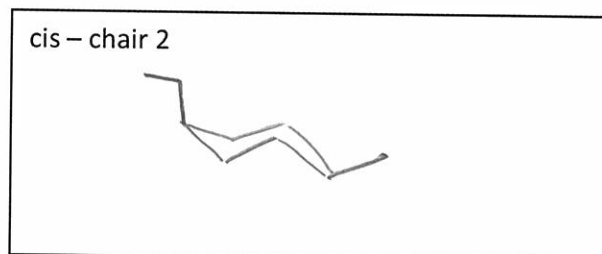
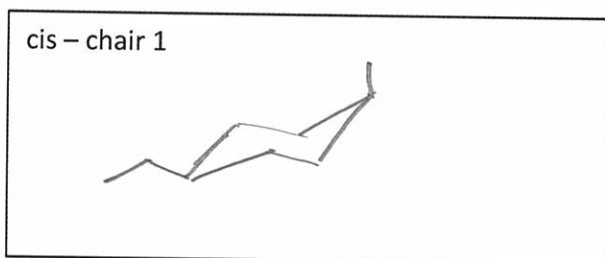
(40 points)



1,3-Diaxial Interactions

-CH ₃	7.6 kJ/mol
-CH ₂ CH ₃	8.0 kJ/mol

- a. Draw the chair conformations of both isomers.



- b. Which isomer is expected to be more stable? Clearly explain your choice.

trans - has a chair conformation with essentially no strain - in each of the *cis* chairs, one of the groups must have a 1,3-diaxial interaction

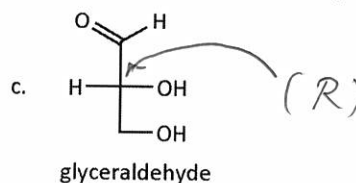
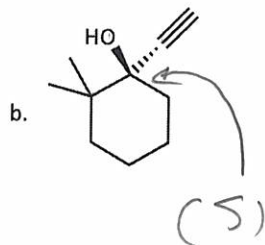
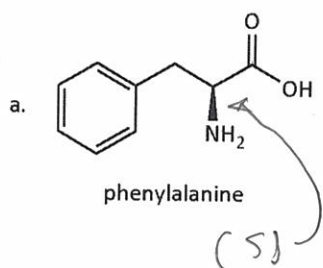
- c. The enthalpy of combustion (ΔH_c) has been measured for both isomers. The ΔH_c values for the two isomers differ by 8.0 kJ/mol. Which isomer is predicted to have a greater (i.e., more exothermic) ΔH_c value?

The least stable isomer, so the cis isomer should have the larger ΔH_c

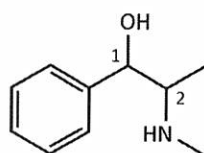
- d. Does the 8.0 kJ/mol difference in enthalpy of combustion values seem reasonable in light your analysis of the conformations of the two isomers? Clearly explain your response.

Both cis chair conformations are higher in energy than the trans-chair 2, which has 0 strain. The difference in energy is ~8.0 as predicted by 1,3-diaxial interactions. range 7.6-8.0 kJ/mol

5. Assign the *configurations* of each stereocenter in the following compounds using the appropriate notation. (15 points)

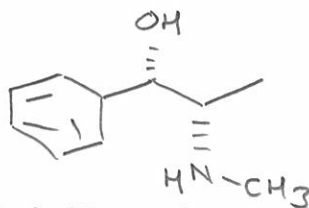


6. Ephedra alkaloids have the general structure shown below. They are found in the extract of the plant *Ephedra sinica*, which has been used to treat many medical conditions (such as asthma) and has been used in traditional Chinese Herbal Medicine for over 2000 years. The IUPAC name is provided for the structure but none of the stereochemistry is shown. (20 points)



2-(methylamino)-1-phenylpropan-1-ol

- a. How many stereoisomers are possible for the ephedra alkaloids (shown above)?
- b. The decongestant known as Sudafed[®] contains one of these alkaloids and is called **pseudoephedrine** and has the *absolute configuration* of (1*S*,2*S*). Draw this isomer using appropriate notation (line, dash, and wedge).



- c. The alkaloid called **ephedrine** is a *diastereomer* of **pseudoephedrine**. Draw a possible structure for **ephedrine** and label each stereocenter with appropriate notation.



- d. Write the complete IUPAC name for the *enantiomer* of **pseudoephedrine** using the correct notation for stereochemistry (and in the correct format).

(1*S*,2*S*)-2-(methylamino)-1-phenylpropan-1-ol

7. Indicate whether the following statements are *absolutely* true or false. (25 points)

a. All *enantiomers* are optically active.

True

b. (2*R*,3*R*)-pentane-2,3-diol is the ^a*diastereomer* of (2*S*,3*R*)-pentane-2,3-diol.

True

c. If a molecule lacks a sigma plane of symmetry (σ) then it is achiral.

False

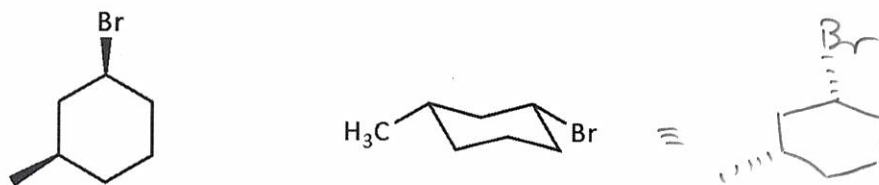
d. All *meso* compounds have $[\alpha] = 0$.

True

e. *trans*-1,3-dimethylcyclobutane is achiral.

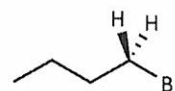
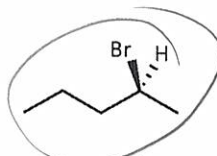
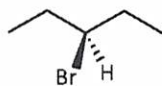
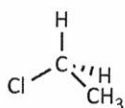
True

8. What is the relationship between the following two structures? Are they *enantiomers*, *diastereomers*, *constitutional isomers*, or *identical*? (5 points)

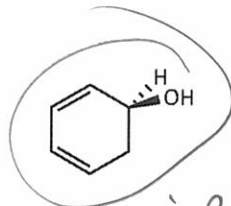


enantiomers

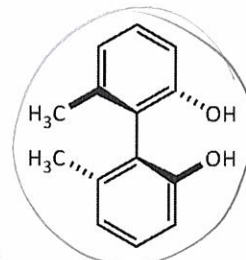
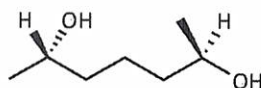
9. Indicate whether each compound below is *chiral* or *achiral*. (50 points)



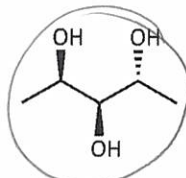
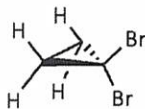
chiral



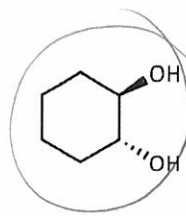
chiral



chiral



chiral



chiral

10. Consider the following reaction.

Given: $\Delta G = \Delta H - T\Delta S$ and $K_{eq} = e^{-\Delta G/RT}$

(10 points)



Bond Dissociation	
Bond	Enthalpy (BDE) - kJ/mol
C=C	632
C-C	368
C-Cl	339
C-H	410
H-Cl	431

Broken		Formed	
C=C	632	C-C	368
H-Cl	431	C-H	410
	<u>1063</u> kJ/mol	C-Cl	339
			<u>1117</u>

a. Using the BDE values in the table, calculate the estimated enthalpy (ΔH) for the above reaction. Clearly show your calculation.

ΔH

$$\Delta H = (1063 - 1117) \text{ kJ/mol} = -54 \text{ kJ/mol}$$

b. Predict the sign of the entropy (ΔS). Explain your answer.

$$\Delta S = (-)$$

high temp favors

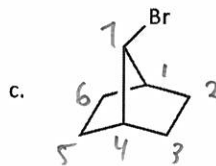
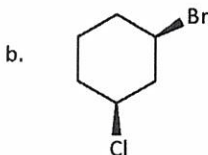
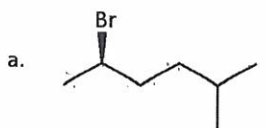
c. How is the equilibrium of this reaction dependent on temperature? Explain your answer.

Since $\Delta G = \Delta H - T\Delta S = (-) + (+)$

at low temp, favors products

11. Provide names for the following alkyl halides.

(15 points)



a. 2-bromo-5-methyl hexane

b. 1-bromo-3-chloro cyclohexane

c. 7-bromo bicyclo[2.2.1]heptane

because at high T the $-T\Delta S$ term becomes significant and dominates ΔG

12. Consider the following reaction:

(30 points)



2° halide, good nucleophile

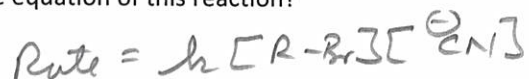
a. Indicate whether this reaction proceeds via an S_N1 or S_N2 process. Explain your answers.

the 100% inversion gives it away

b. Draw the mechanism of this reaction (with arrow pushing).



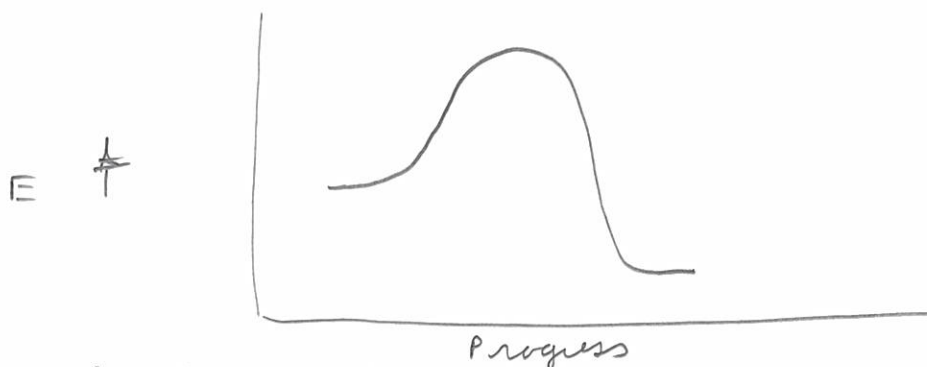
c. What is the rate equation of this reaction?



d. Would the reaction occur at a faster rate if the concentration of cyanide were doubled? Explain.

Yes, the rate would double!

e. Draw an energy diagram of the reaction above.



f. Draw a suggested transition state for this reaction – use the bracket notation $[\]^\ddagger$

