Chemistry 210
Winter Semester 1997
Examination #2

Prof. Rainer Glaser, University of Missouri—Columbia
Wednesday, March 19, 1997, in Ellis Auditorium, 8:40 - 9:30

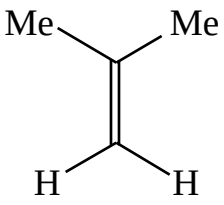
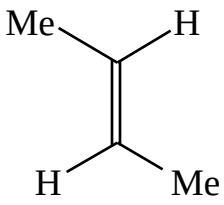
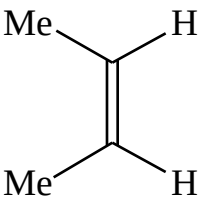
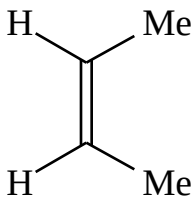
featuring
Stereochemistry & Halogenation of Alkanes

Your Name:

	Max.	Yours
Question 1	26	
Question 2	24	
Question 3	20	
Question 4	30	
Total	100	

Do not turn the page until advised to do so.

Question 1. Structure and Geometrical Isomers of Alkenes. (26 points)

A	**B**	**C**	**D**
			

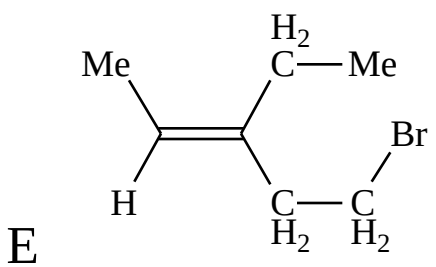
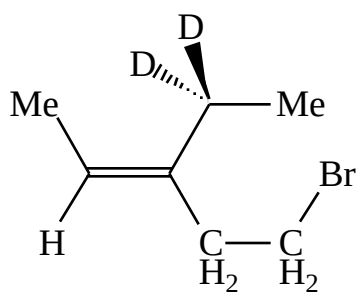
State the stereochemical relationships between the pairs of structures **A** - **D**, that is, state whether they are **geometrical isomers**, **structure isomers**, or **identical**. (6 points)

Stereochemical relation between **A** and **B**?	
Stereochemical relation between **B** and **C**?	
Stereochemical relation between **C** and **D**?	
Stereochemical relation between **A** and **C**?	
Stereochemical relation between **A** and **D**?	
Stereochemical relation between **B** and **D**?	

Among **A** - **D**, which structure(s) deserve to be called *cis*?	(2 pts)
Among **A** - **D**, which structure(s) deserve to be called *trans*?	(2 pts)

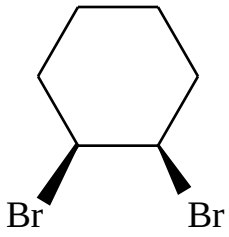
Full IUPAC name of **A**:	(4 pts)
Full IUPAC name of **B**:	(4 pts)

(b) For structures **E** and **F**, state whether they are *E* or *Z*. (8 points)

 E	 **F**

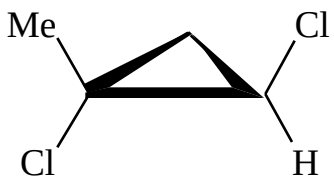
Question 2. Stereochemistry of Disubstituted Cycloalkanes. (24 points)

(a) Convert the cyclohexane shown into a perspective drawing of the **chair** form. Indicate whether this structure is ***cis*** or ***trans***. For each substituent, indicate whether it is "axial" or "equatorial". (6 points)



(b) Draw the lowest energy structure of the cyclohexane that is 1,4-disubstituted in a *cis* fashion by one methyl group and by one tert.-butyl group. Clearly indicate whether the substituents are in axial or equatorial positions. (6 points)

(c) For the cyclopropane shown, mark every asymmetric carbon by a star (*). For each of these asymmetric carbons, indicate the absolute configuration using the *R*/*S* nomenclature system. Then draw the enantiomer and a diastereoisomer and, for both, also indicate the absolute configuration of all asymmetric carbons with he *R*/*S* nomenclature system. (12 points)

The cyclopropane	Draw the **enantiomer**	Draw a **diastereoisomer**
		

Question 3. Hammond Postulate and Potential Energy Surfaces of Alkane Halogenation. (20 points)

(a) Give the reactions occurring in the propagation steps of the chlorination of methane. (6 points)

Propagation Step 1:
Propagation Step 2:

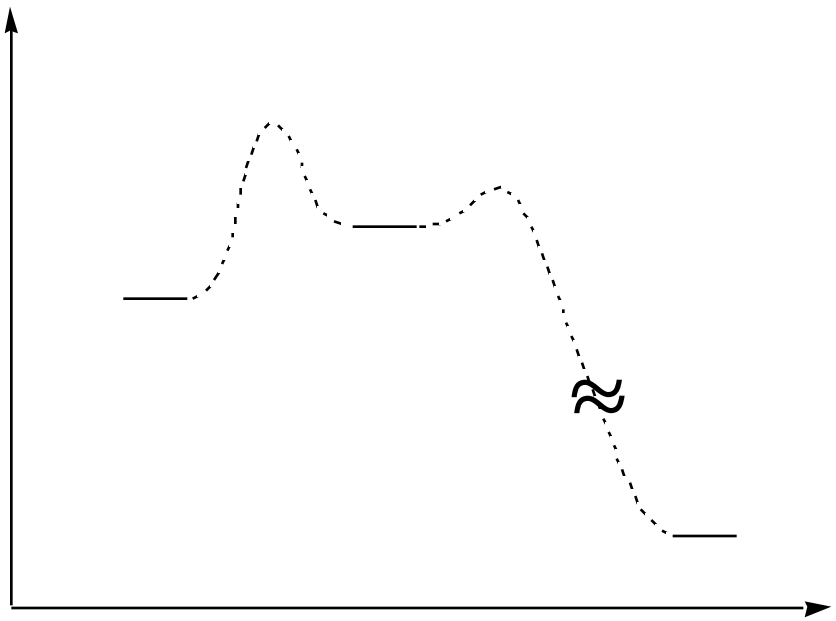
(b) A schematic potential energy surface diagram is shown using a dashed line for the two propagation steps of the chlorination of methane. First, label the axes. The products of the first propagation step are 2 kcal/mol less stable that the starting materials. The overall reaction is exothermic by 25 kcal/mol. It is your task to add the respective potential energy surface diagram for the bromination of methane using a solid line. When drawing your line, you must not be quantitative but qualitatively it must be clear as to how bromination differs from chlorination with regard to these issues:

-1- Is the first step more or less exothermic or even endothermic or about the same?

-2- Is the transition state for the first step earlier or later?

-3- Is the second step more or less exothermic or about the same?

-4- Is the transition state for the second step earlier or later?



Question 4. Halogenations of Alkanes. (30 points)

(a) Chlorination of methane may lead to mono-, di-, tri- and tetrachlorinated methane depending on the reaction conditions used. To affect dominantly monochlorination, we would choose a _____ (low, high) concentration of chlorine. To affect a high degree of polyhalogenation we would try to generate a _____ (high, low) chlorine/alkane concentration ratio. (3 points each correct answer)

(b) Write down the structural formula of the **major product** obtained by reaction of **tert. butane** …

(3 points each correct answer)

... with **chlorine**.	... with **bromine**.

(c) Write down all **four structure isomers** generated in the chlorination of 2-methylbutane (8 points). For each of the isomers, state its probability of forming based on **statistical consideration** (that is: state how many equivalent Hs exist whose replacement would yield this isomer) (4 pts). Circle the structure isomer that is produced in the **highest yield** (3 pts). Mark the isomer that originates from the **most stable intermediate** radical with the abbreviation "FMSR" (= from most stable radical) (3 pts).

statistics: ___ H	statistics: ___ H
statistics: ___ H	statistics: ___ H

The End is near. The End is near! The End is near. The End is near. **The End is here!!** Yahoo, back to the web!