

Chemistry 210
“Organic Chemistry I”
Winter Semester 2004
Dr. Rainer Glaser

Examination #2
“Conformation & Configuration.
Nucleophilic Substitution Reactions.”

Posted: Sunday, March 14, 2004.

Collect: Wednesday, March 18, 2004, after lecture.

Name:

Question 1. Rotational Energy Profiles. Ethane, Butane, Hexane.	35	
Question 2. Nucleophilic Substitution in Synthesis.	30	
Question 3. Symmetry Elements.	10	
Question 4. Optical Activity & Chirality. Substituted Cyclohexanes.	10	
Question 5. Resolution.	15	
Total	100	

Question 1. Rotational Energy Profiles. Ethane, Butane, Hexane. (35 points)

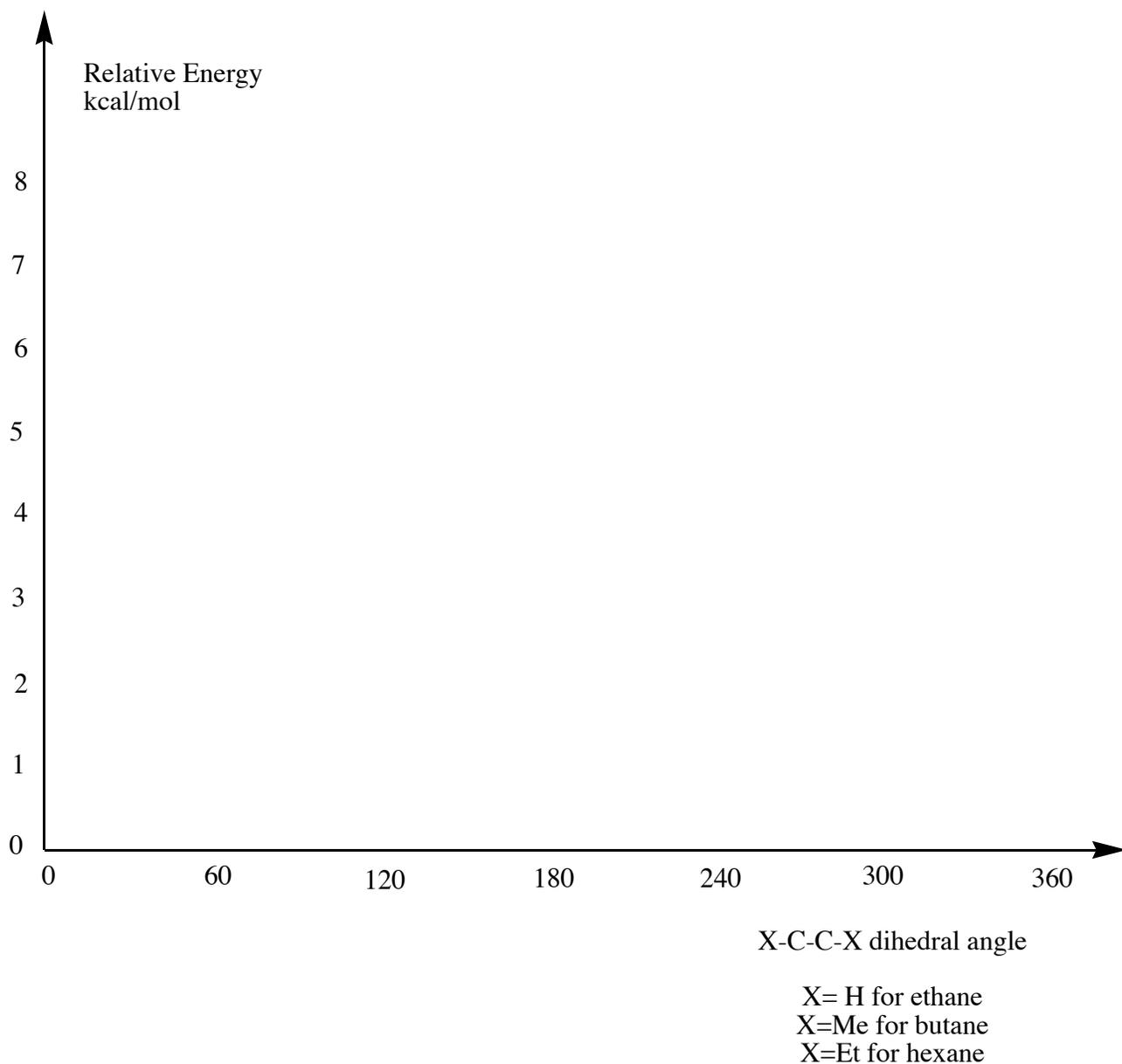
(a) Draw the Newman Projections for ethane with dihedral angles 0° , 30° , and 60° . Indicate which one is eclipsed and which one is staggered. For each structure, indicate whether it is chiral or not chiral. If it is not chiral, give one reason as to why it is not chiral (e.g. show the presence of one symmetry element that makes the structure achiral). (15 points)

dihedral angle = 0°	dihedral angle = 30°	dihedral angle = 60°
Eclipsed or staggered? Chiral or achiral?	Eclipsed or staggered? Chiral or achiral?	Eclipsed or staggered? Chiral or achiral?

(b) Explain in simple terms why butane is not chiral even though it can assume many, many chiral conformations in the neighborhoods of its staggered and symmetric structures. (4 points)

(c) Draw the rotational energy diagram for ethane on the following page in **BLUE** color. (4 points).

Figure. Rotational energy profiles of ethane, butane and hexane.



(d) Draw the rotational energy diagram for butane about the C2-C3 bond in the above graph in **RED** color. Draw Newman projections of the minima and maxima and provide their names. (8 points).

(e) **QUALITATIVELY**, draw the rotational energy diagram for hexane about the C3-C4 bond in the above graph in **GREEN** color. (4 points)

Question 2. Nucleophilic Substitution in Synthesis. (30 points)

Show complete Lewis-Kekule structures, do not use abbreviations. 6 points each question.

Cyclohexyl iodide reacts with sodium azide by way of an S_N2 reaction. Draw structures for substrate, reagent, and product.

Suggest a **synthesis of 4-(cyanomethyl)cyclohexene** by way of a nucleophilic substitution of a tosylate by cyanide. Draw structures for substrate, reagent, and product. Suggest a solvent for the reaction.

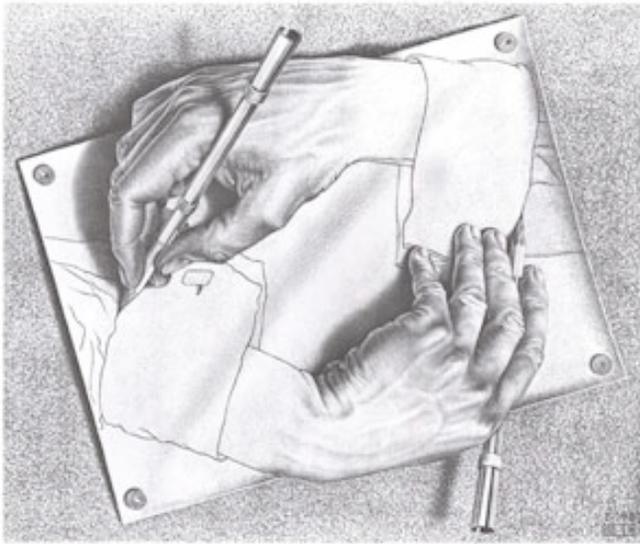
Suggest a **synthesis of propyldecanoate** by way of a nucleophilic substitution with a carboxylate as the nucleophile. Draw structures for substrate, reagent, and product. Suggest a solvent for the reaction.

Draw perspective drawings of the structures of the substrate and of the products of the **hydrolysis of (R)-(-)-2-bromooctane** assuming that the reaction is completely S_N1 and provide complete names of the products.

Consider **ethyl isopropyl ether** and **ethyl propyl ether**. Only one of these ethers can be made by the reaction of sodium ethoxide with an alkyl bromide. Which one? Draw structures for substrate, reagent, and product of this case. Why does it work in this case but not the other?

Question 3. Symmetry Elements. (10 points)

For each of the M. C. Escher paintings, write to its right what symmetry elements are present (inversion center, symmetry plane(s), rotational axes), indicate all of the symmetry elements in the paintings, and make a conclusions as to whether the painting is symmetric, asymmetric, or dissymmetric and as to whether the painting is chiral.



M. C. Escher, *Drawing Hands*



M.C. Escher, *Angels & Devils*

Question 4. Optical Activity & Chirality. Substituted Cyclohexane. (10 points)

The specific rotation $[\alpha]$ is given by $[\alpha] = 100 \alpha / (c l)$, where α is the measured optical rotation, c is the concentration in grams per 100 mL and l is the length of the polarimeter tube in decimeter.

(a) The observed rotation α of a 0.3 g sample of cholesterol in 15 mL chloroform contained in a 10 cm polarimeter tube is -0.78° . Determine the specific rotation of cholesterol. Show work. (3 points)

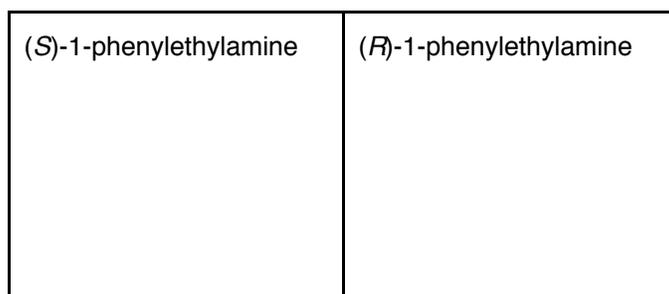
(b) The optical rotation is usually specified by the $[\alpha]_D$ value. What is the significance of the subscript “D”? (3 points)

(c) Draw a perspective drawing of the best conformation (most stable) of (*R,R*)-*trans*-1,2-dichlorocyclohexane. This molecule is _____ (symmetric, asymmetric, dissymmetric). (4 points)

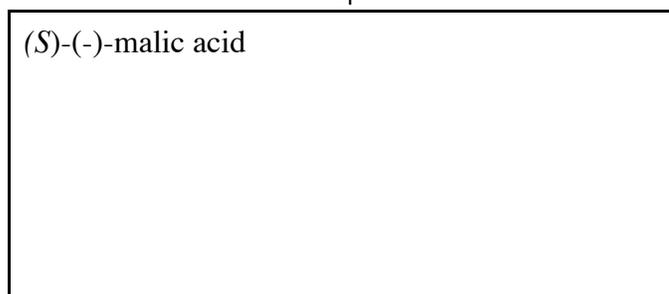
Question 5. Resolution of racemic 1-phenylethylamine with pure (*S*)-(-)-malic acid. (15 points)

Answer the following questions at the appropriate place in the flow diagram.

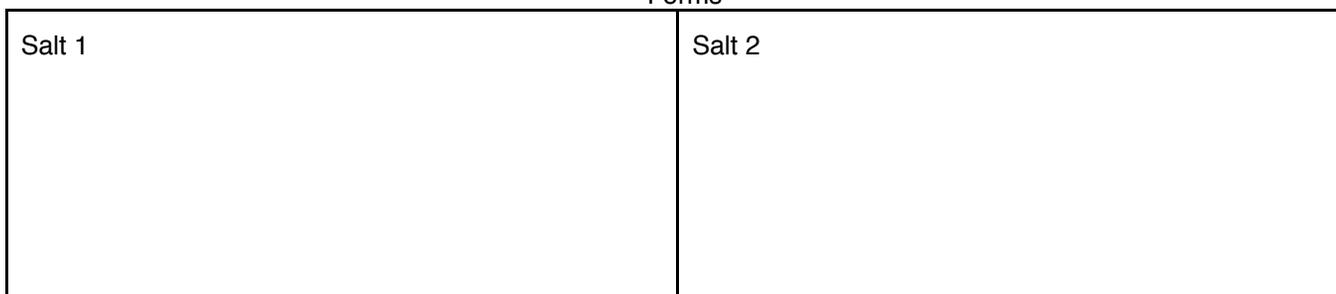
- (a) Draw perspective drawings of the *S*- and *R*-enantiomer of 1-phenylethylamine.
- (b) Draw a perspective drawing of (*S*)-(-)-malic acid.
- (c) Draw perspective drawings of the diastereoisomeric salts formed.
- (d) Indicate how the diastereoisomeric salts are separated.
- (e) Specify the reagent needed to liberate the free base after separation.



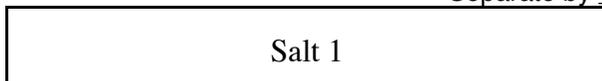
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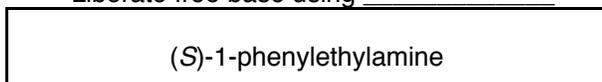
Forms



Separate by _____



Liberate free base using _____



Liberate free base using _____

