Chemistry 210
"Organic Chemistry I"
Winter Semester 2004
Dr. Rainer Glaser

Examination #2
"Conformation & Configuration. Nucleophilic Substitution Reactions."

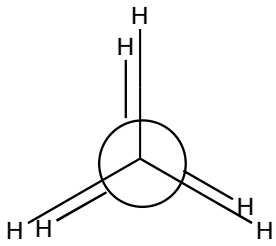
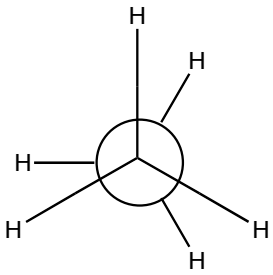
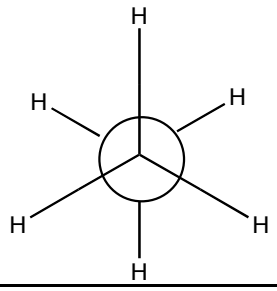
Posted: Sunday, March 14, 2004.
Collect: Wednesday, March 18, 2004, after lecture.

Name: Answer Key

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)

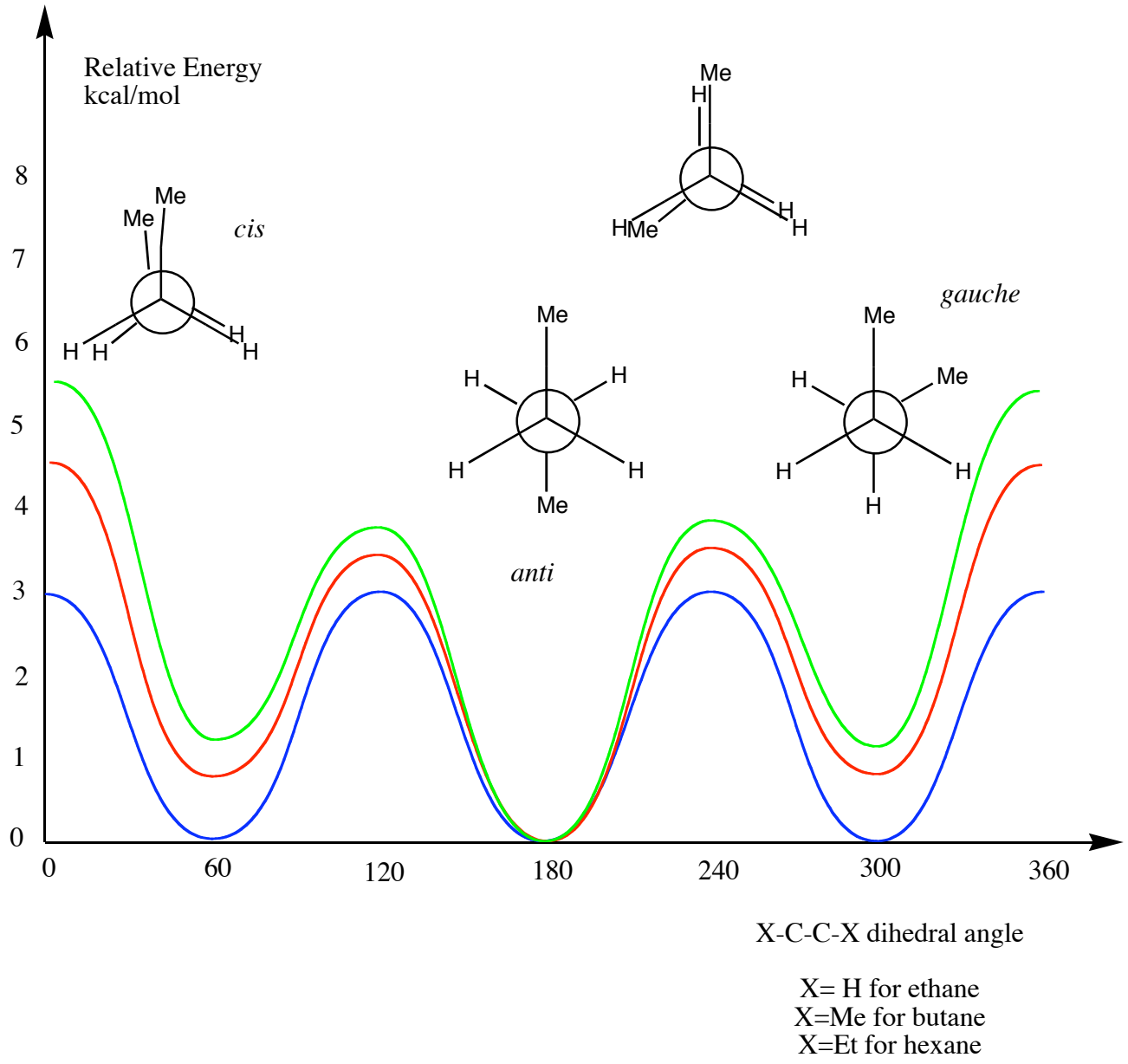
dihedral angle = 0°	dihedral angle = 30°	dihedral angle = 60°
		
Eclipsed or staggered? Chiral or **achiral**? 3 planes (HCCH) 1 plane through C-C center 3 C_2-axes 1 C_3-axis	Eclipsed or staggered? Chiral or **achiral**? No planes 3 C_2-axes 1 C_3-axis	Eclipsed or **staggered**? Chiral or **achiral**? 3 planes (HCCH) 3 C_2-axes 1 C_3-axis

(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)

In contrast to ethane, butane does <u>not</u> have the C_3-axis!
Now there are chiral structures.
But each chiral structure comes with its equally likely enantiomer.
Overall: No chirality.

(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.



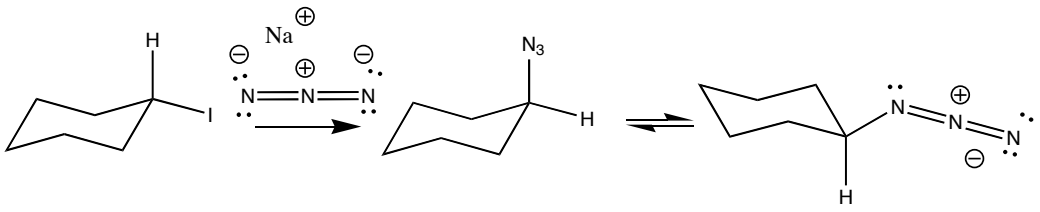
(d) Draw the rotational energy diagram for butane about the C2-C3 bond in the above graph in RED color. Draw Newman projections of the minima and maxima and provide their names. (8 points).

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

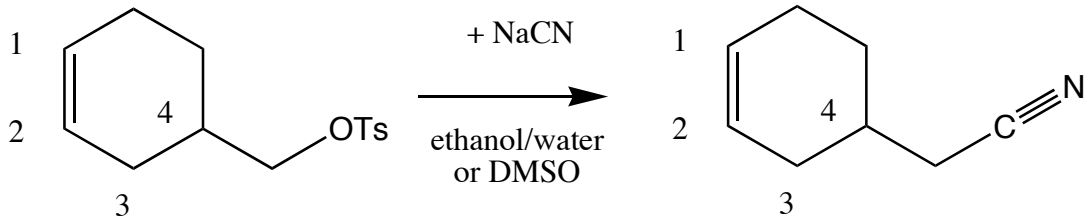
Question 2. Nucleophilic Substitution in Synthesis. (30 points)

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

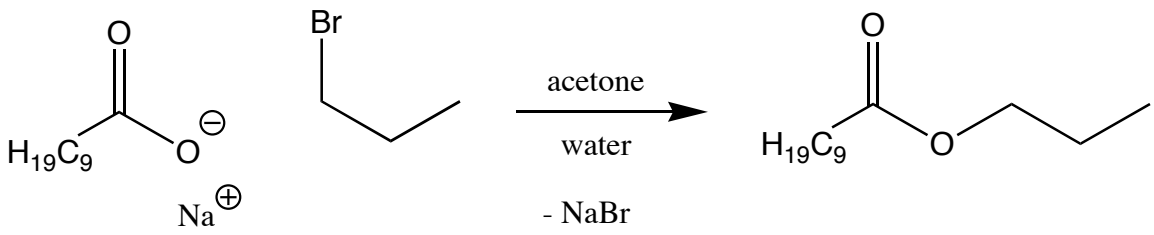
Cyclohexyl iodide reacts with sodium azide by way of an S_N2 reaction. Draw structures for substrate, reagent, and product.



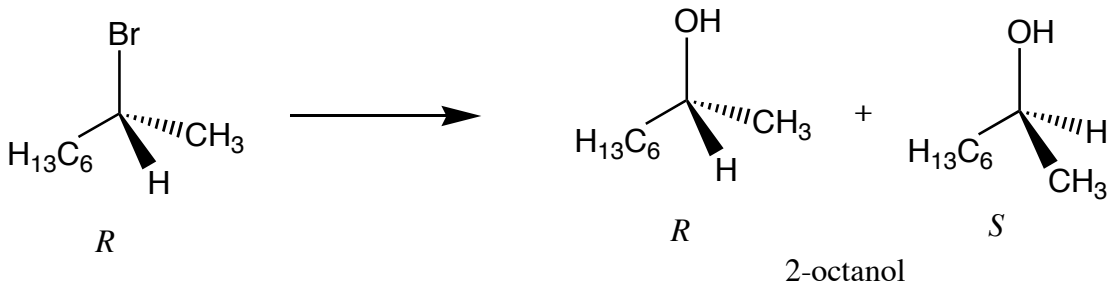
Suggest a synthesis of 4-(cyanomethyl)cyclohexene by way of a nucleophilic substitution of a tosylate by cyanide. Draw structures for substrate, reagent, and product. Suggest a solvent for the reaction.



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.

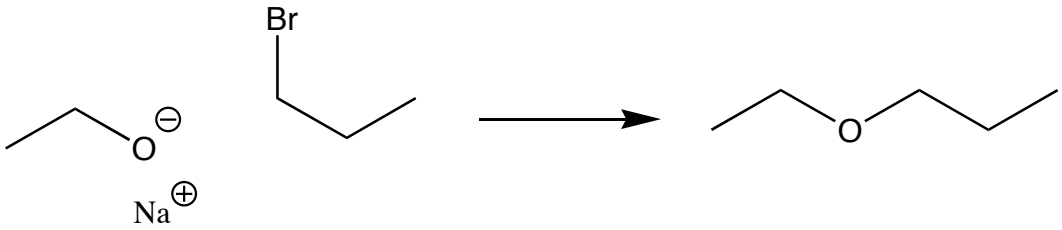


Draw perspective drawings of the structures of the substrate and of the products of the hydrolysis of (*R*)-(-)-2-bromooctane assuming that the reaction is completely S_N1 and provide complete names of the products.



2-octanol

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?

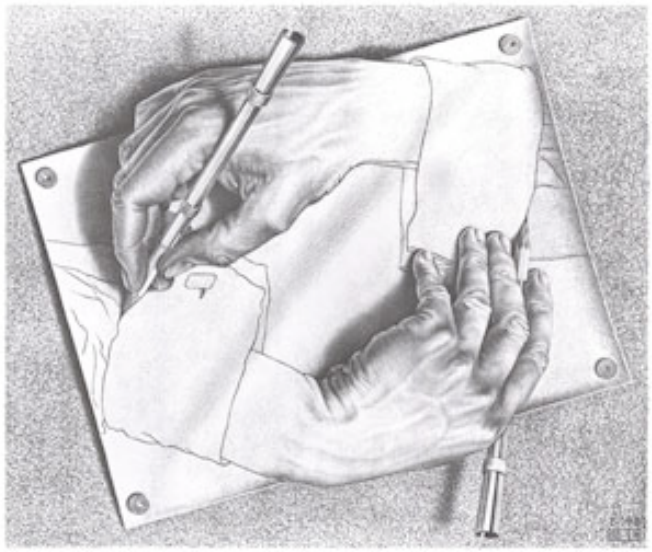


Clean S_N2 at primary alkyl bromide.

The secondary bromide would lead to some elimination as well.

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 conclusion as to whether the painting is symmetric, asymmetric, or dissymmetric and as to whether the painting is chiral.



No inversion center.
No plane.
No rotational axis (note the pens).

ASYMMETRIC!

CHIRAL!

M. C. Escher, *Drawing Hands*

C_3 axis (trough center, perpendicular to paper plane).

3 symmetry planes (perpendicular to paper plane, 6-to-12, 4-to10, 8-to-2)

SYMMETRIC.

NOT CHIRAL.

M.C. Escher, *Angels & Devils*

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

The specific rotation [α] 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)

$$[\alpha] = 100 \bullet (-0.78°) / ([100 \bullet \{0.3\ g/\ 15\ mL\}] \bullet 1\ dm)$$

gram in 100 mL 1 dm = 10 cm

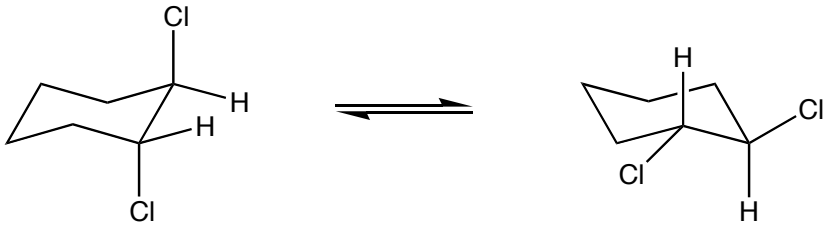
$$[\alpha] = 39°$$

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

The D-line of the sodium lamp is used, yellow at 589 nm.

The optical rotation varies with the wave length of the light that is being rotated. (Dispersion.)

(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)



minor major

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.

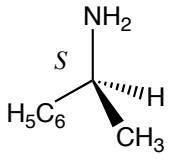
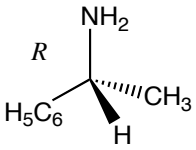
(a) Draw perspective drawings of the *S*- and *R*-enantiomer of 1-phenylethylamine.

(b) Draw a perspective drawing of (*S*)-(-)-malic acid.

(c) Draw perspective drawings of the diastereoisomeric salts formed.

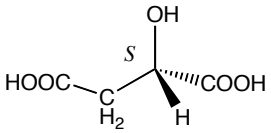
(d) Indicate how the diastereoisomeric salts are separated.

(e) Specify the reagent needed to liberate the free base after separation.

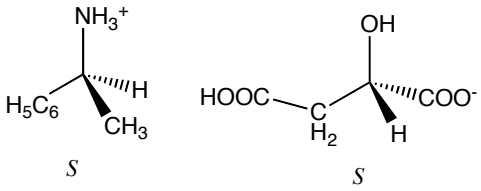
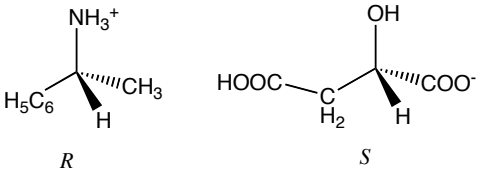
(*S*)-1-phenylethylamine	(*R*)-1-phenylethylamine
	

+

(*S*)-(-)-malic acid



Forms

Salt 1	Salt 2
	

Separate by Crystallization

Salt 1	Salt 2
Liberate free base using NaOH	Liberate free base using NaOH
(*S*)-1-phenylethylamine	(*R*)-1-phenylethylamine