

Chem 220a

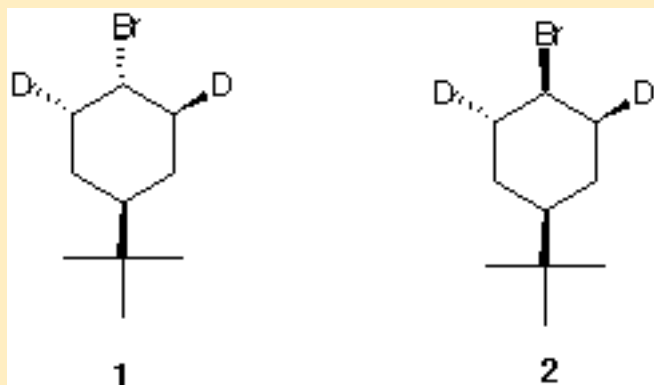
Problem Set 5

Chapter 6

Due: Monday, October 15, 2001

1. Study #2 and #3 in the Alkyl Halide module and #1 in the Ether module in [ORGO](#).

2. Consider each of the compounds **1** and **2** as a racemate.



a) What is their relationship to one another?

b) Which one undergoes elimination faster? Explain and illustrate. What is the structure of the product? Is it optically active?

c) Consider structures **1** and **2** as the enantiomers shown. They differ only in the configuration at the carbon bearing bromine, and neither one is superimposable on its own mirror image. Thus, both stereoisomers are capable of existing as enantiomers. The only "chiral carbons" in **1** (and **2** also but you need not do this one) are the ones bearing deuterium.

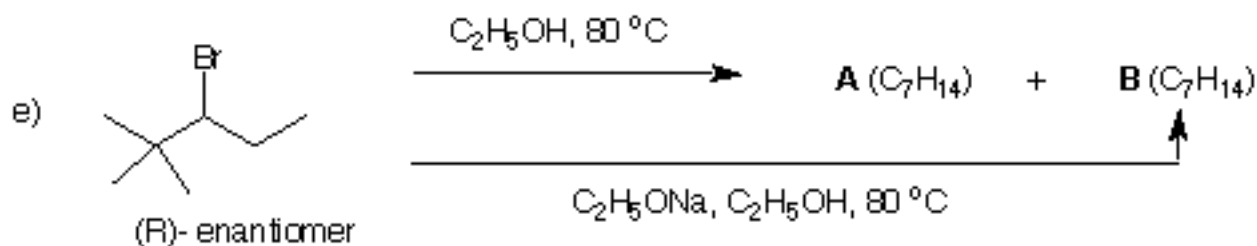
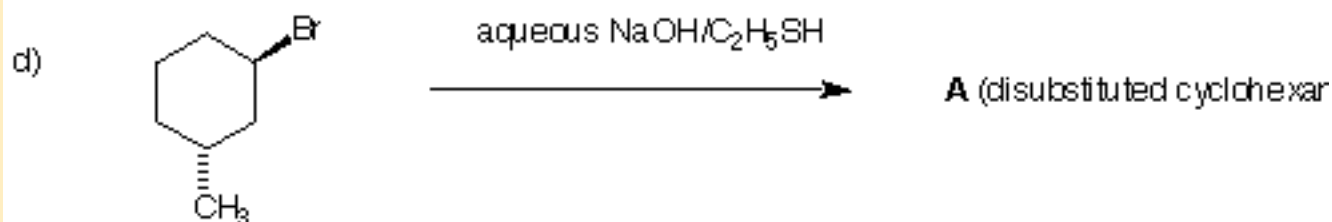
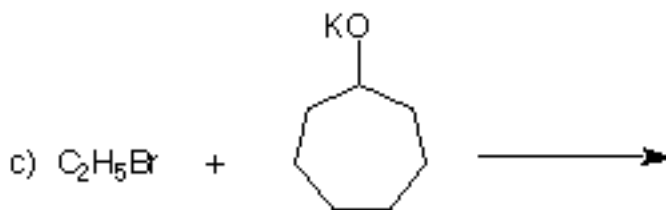
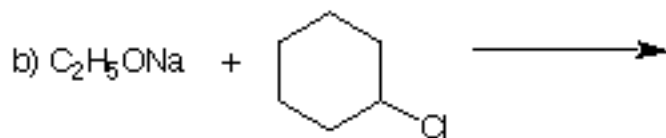
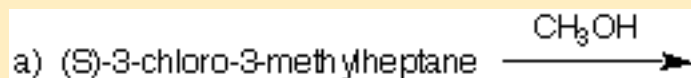


R. S. Cahn (left), C. Ingold, and V. Prelog (1966)

[One wag has suggested that "R" and "S" were chosen by Cahn for the CIP system for an obvious reason.]

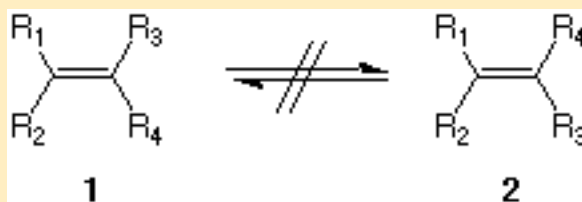
What is the common configuration (R,S) at these carbons? The carbons bearing the Br- and t-butyl groups are not chiral (why?) but they are stereogenic. Explain. [Hint: Try to use R and S on the carbons bearing the Br- and t-butyl groups. Any luck? Try inverting the configuration at the carbons bearing the Br- and t-butyl groups. What happens?]

3. Predict and explain the formation of each of the products of the following reactions. Be sure to address issues of stereochemistry and optical activity.



4. An optically active compound (R)-**A**, $\text{C}_5\text{H}_{11}\text{Cl}$, undergoes free radical chlorination to give 5 constitutional (structural) isomers ($\text{C}_5\text{H}_{10}\text{Cl}_2$), one of which is a pair of diastereomers. Dichlorides **B** and **C** are optically inactive while the remaining four, **D**, **E**, **F**, and **H** are optically active. The pair of diastereomers is **D** and **E**. The carbon bearing the new chlorine atom in **E** is of the (S)-configuration. Compound **C** reacts more rapidly with water than any of the dichlorides and forms compound **G**, $\text{C}_5\text{H}_{11}\text{ClO}$. Dichloride **H** is geminally substituted. What are the structures of **A-H**? Provide R/S configurations for **D**, **E**, **F**, and **H**. Include explanations for the following: a) Why are **B** and **C** optically inactive?, b) Why does **C** react rapidly with water?, c) Is **G** optically active? Explain.

5. Rotation about the double bond of an alkene does not occur readily. Thus, **1** and **2** are geometrical stereoisomers that have different properties. When (3S, 4R)-4-bromo-3-methylheptane (**A**) reacts with C_2H_5ONa in ethanol, a trisubstituted alkene (olefin) **B** is formed as well as a trans disubstituted alkene **C**.



- What are the structures of **B** and **C** and how are they formed? Show the mechanism.
- Are **B** and/or **C** optically active? Explain.

A diastereomer of **A** (**A'**) reacts with C_2H_5ONa in ethanol to provide a stereoisomer of **B** (**B'**) and the enantiomer of **C** (**C'**).

- What is a structure for **A'**? Assign R/S configurations. Does it matter which enantiomer of **A'** you use? Explain.
- What are the structures of **B'** and **C'** and how are they formed? Show the mechanism.

6. Let us revisit [PS3 #3](#).

- Which monochlorinated constitutional isomers are achiral?
- Which ones can form diastereomers? Draw the diastereomers.
- Which structures from a) and b) have enantiomers? Draw them.
- Why are the diastereomers of a given constitutional isomer not necessarily formed in equal amounts?
- Are any of the diastereomers optically active? Explain.

7. In section 6-19, pg. 268 of your text, the reaction of hydroxide with (\pm)-2-bromobutane to form 1-butene (19%) and 2-butene (81%) is illustrated.

- How much of each alkene is derived from each of the enantiomers of the alkyl bromide?

The 2-butene is comprised of cis-2-butene and trans-2-butene (see pg. 273)?

- These geometrical stereoisomers do not interconvert. Why?

The heat of formation of the cis isomer is -1.9 kcal/mol while the trans isomer is -3.0 kcal/mol.

- Which isomer is more stable?