Comprehensive Organic Chemistry - Chem 225b

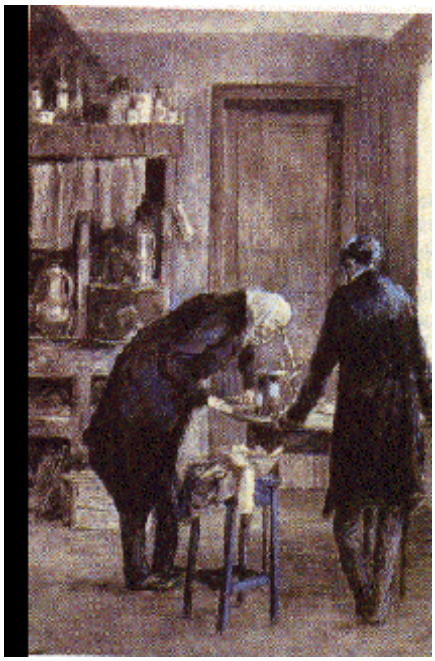
Problem Set 6

Chapter 7

Due: Monday, February 27, 2006

1. Consider the optically active diastereomer (1*S*, 2*R*)-1-bromo-1,2-dideuteriopentane (**1**).

a) What is the major product formed when **1** is exposed to CH_3ONa/CH_3OH? Provide the name and mechanism? Is it optically active?
b) Is there a significant isotope effect in a)? Explain.
c) When *t*-C_4H_9OK/*t*-C_4H_9OH is used in a) instead of CH_3ONa/CH_3OH, a different major product is formed. Name it, draw it and provide a mechanism for its formation. Is it optically active?
d) Is there a significant isotope effect in c)? Explain.
e) What is the major product formed with an optically active diastereomer of **1** having the configuration (1*S*, 2*?*) when it is exposed to the conditions of a)? Name and draw it.
f) What is the major product formed with an optically active diastereomer of **1** having the configuration (1*S*, 2*?*) when it is exposed to the conditions of c)? Name and draw it.



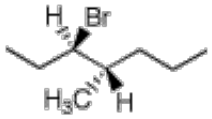
Biot examining Pasteur's tartrate crystals

2. Provide the products in each of the following questions and mechanisms for their formation. Pay attention to stereochemistry. Be explicit about enantiomers.

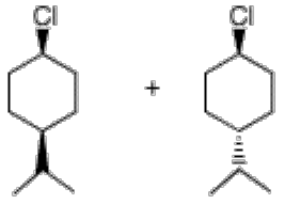
a) (*2R, 3R*)-2-bromo-3-methylpentane $\xrightarrow[KOH]{\text{aqueous}}$ **A** (major) + **B** (minor)
(each has 1 Degree of Unsaturation, D.U.)

b) (*2R, 3S*)-2-chloro-3-methylhexane $\xrightarrow[CH_3OH]{CH_3ONa}$ **A** (major) + **B** (minor)

c) (3S)-3-chloro-3-methyloctane $\xrightarrow[\text{ethanol}]{\text{excess}}$ **A**

d) (±)  $\xrightarrow{\text{EtONa, EtOH}}$ **A** (major) + **B** (minor)
C (minor minor)
(All 1 D.U.)

e) (*R*)- $CH_3CH_2CH_2CH_2CHDBr$ $\xrightarrow[\text{aq. NaOH}]{CH_3CH_2CH_2SH}$

f)  $\xrightarrow[t\text{-}C_4H_9OH]{\text{1 equiv. } t\text{-}C_4H_9OK}$ **A** + **B** (not an alkene not an ether)
1 equiv. 1 equiv.

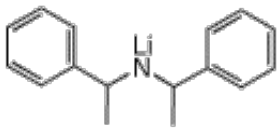
3. The monochlorination products from the free radical chlorination of 3-methylpentane are isolated.

a) Draw all constitutional isomers and diastereomers. Identify the racemates and achiral compounds. Briefly explain why.

b) Each chloride reacts with aqueous NaOH. Compounds **A** and **B** give the largest ratio of S_N2/E_2 products (S_N2 products **C** and **D**, and E_2 products **G** and **K**, respectively). Compound **E** gives **F** (ΔH_f^o = -14.8 kcal/mol) and **G** while chloride **H** gives **I** (ΔH_f^o = -15.8 kcal/mol) and **G**. The ratios **F/G** and **I/G** are greater than unity. Compounds **F**, **G** and **I** have one degree of unsaturation. Chloride **J** reacts much faster with water than do chlorides **E** and **H**. Chloride **J** gives more **I** than **F** and more **I** than **K**. What are the structures **A-K**? Explain and illustrate.

4. A student proposes to study an elimination reaction. She has access to the

hindered base **1**, both as its meso diastereomer and as its two enantiomers.
a) Draw each of these bases with their CIP designations.
b) She reacts one of the optically active bases with cis-1-bromo-4-tert-butylcyclohexane (**2**) to provide a sample of **3** rich in the dextrorotatory enantiomer. When the same experiment is conducted with the enantiomeric base **1**, a sample of **3** is isolated with the opposite rotation. When meso-**1** is employed, product **3** has no rotation. Without concern for which enantiomer of **1** provides which enantiomer of **3**, explain and illustrate what is going on here.



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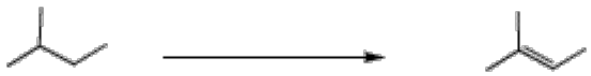
5. Provide reagents for accomplishing the following reactions. some of them may require more than one step. Show any intermediate compounds. Comment briefly on your choices---mechanisms?, etc. Answer queries in d) and e)

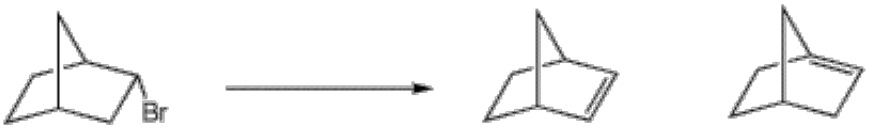
a)



b)

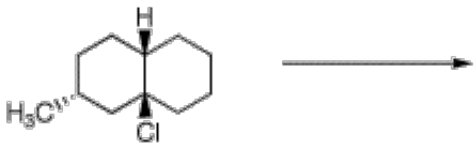
c) **A** (C_6) + **B**

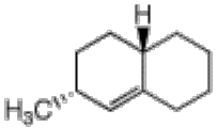
d)



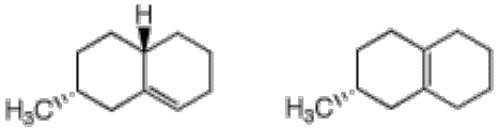
not expected!

e)





expected major product



minor products? Explain!