Chem 220 - Organic Chemistry

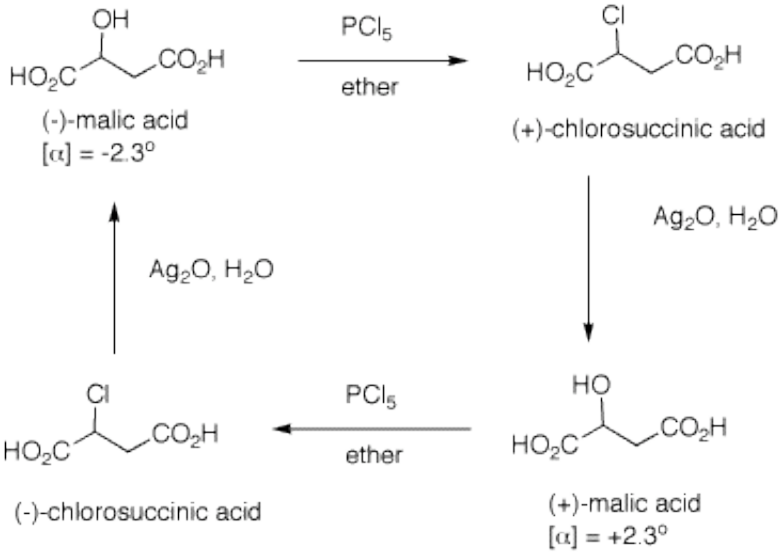
Problem Set 5

Chapter 6, Alkyl Halides: Substitution and Elimination

Due: Monday, October 12, 2009

Study #2 and #3 in the Alkyl Halide module and #1 in the Ether module in ORGO.

A Walden Cycle



Paul Walden (1863-1957)

here also

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1. The inversion of configuration in an S_N2 reaction is often called a Walden inversion, named after its discoverer, Paul Walden. In the cycle shown above, the overall conversion of one enantiomer of malic acid to the other one must require an inversion of configuration. Similarly, the same is true of the chloro acids. More generally, each interconversion of enantiomers must require an odd number of inversions. The PCl_5 reaction requires a single inversion which means that the Ag_2O reaction involves an even number of inversions of configuration, namely two in this instance. (-)-Malic acid is of the (*S*)-configuration.

a) Show how malic acid, like any alcohol, might react with PCl_5 and then undergo inversion to form a chloride. Remember that phosphoric acid is a strong acid and its conjugate base and analogs thereof are also good leaving groups.

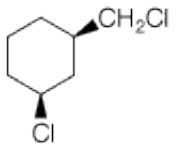
b) Silver oxide is an anhydrous form of AgOH. The carboxylic acid group closest to the hydroxyl

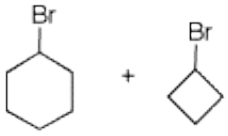
group plays a role in the process. The reaction medium is mildly alkaline. Using these data, show how there is net retention of configuration.

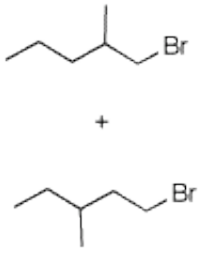
c) Draw these four enantiomers as Fischer projections with the CO_2H closest to the OH or Cl in the topmost position. (-)-Malic acid is of the (*S*)-configuration.

2. In each of the following reactions, predict the expected products. Explain.

a) (R) - $CH_3CH_2CH_2CH_2CHDBr$ $\xrightarrow[\text{1 equiv. aq. NaOH}]{C_2H_5SH}$ **A**

b)  excess LiBr acetone → **A**

c)  1 equiv of each; 1 equiv. NaCN, ethanol → **A** (major) + **B** (minor)

d)  1 equiv. of each; 1 equiv. CH_3CH_2SNa, aqueous CH_3OH → **A** (major S_N2) + **B** (minor S_N2)

3. Show how you would convert (*S*)-2-octanol into (*S*)-2-octanethiol. [Hint: how do you make a secondary hydroxyl group a good leaving group for an S_N2 reaction?]

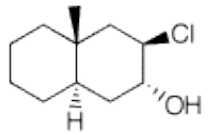
4. (*2S*,*5S*)-5-Bromo-2-hexanol (**A**) is expected to form optically inactive **B** ($C_6H_{12}O$) upon exposure

to aqueous NaOH. An optically active stereoisomer of **A**, namely, **C** also forms optically inactive **B** under the same conditions. Two other optically active stereoisomers of **A**, namely **D** and **E** as a racemic mixture, form optically inactive **F**, a diastereoisomer of **B**. What are the structures of **A-F**? The structures **D** and **E** are not distinguishable. Explain and illustrate with mechanisms. Why are **B** and **F** both optically inactive?

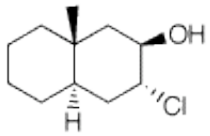
5. Provide the unknown product of each reaction. In all cases, provide mechanisms and a rationale.

a) (3*S*,6*S*)-3,6-dichlorooctane $\xrightarrow[\text{aqueous KOH}]{H_2S}$ **A** ($C_8H_{16}S$)

Is **A** opt. act? Assign R,S configurations

b) 

$\xrightarrow[CH_3OH]{NaOCH_3}$ **A** ($C_{11}H_{18}O$)

c) 

$\xrightarrow[CH_3OH]{NaOCH_3}$ **A** ($C_{11}H_{18}O$)

d) (*1R, 4S*)-$CH_3CH_2CH(CH_3)CH_2CH_2CHDCl$ $\xrightarrow[\text{methanol}]{NaN_3}$ **A**