Chem 220 - Organic Chemistry

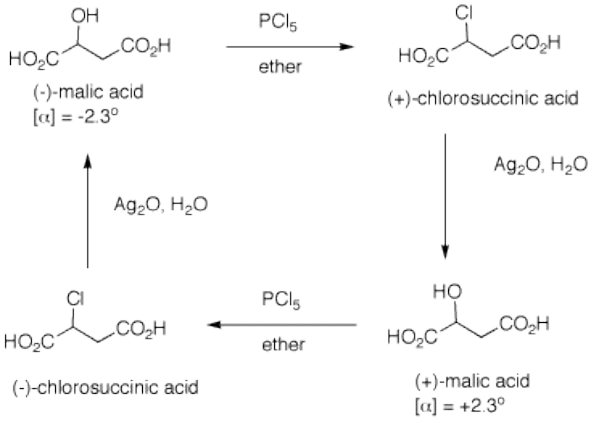
Problem Set 5

Chapter 6, Alkyl Halides: Substitution and Elimination

Due: Monday, October 11, 2010

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

xxxxxxxxxxxxxxxxx

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.

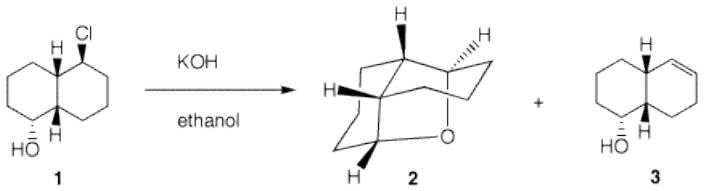
a) Show how malic acid, like any alcohol, might react with PCl_5 and then undergo inversion to form a chloride. Remember that phosphoric acid is a strong acid and its conjugate base and analogs thereof are also good leaving groups.

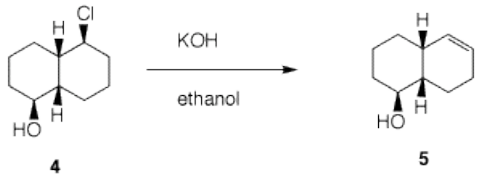
b) Silver oxide is an anhydrous form of AgOH. The carboxylic acid group closest to the hydroxyl group plays a role in the process. The reaction medium is mildly alkaline. Using these data, show how there is net retention of configuration.

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. A sample of (-)-2-iodooctane ($[\alpha]_D$ = -33.3°) reacts with radioactive iodide ($K^{131}I^-$) in methanol until 1.5% conversion (i. e.; 1.5% of the isolated 2-iodooctane contains radioactive iodide.) What is the predicted rotation of the isolated sample?

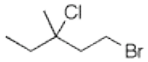
3. A student familiar with the mechanism of the S_N2 and E2 reactions predicts that the stereoisomer **1** may produce **2** and **3** while stereoisomer **4** will produce only **5** under the conditions shown. Show her reasoning. [Note: You need to know how to draw cis-decalins.]

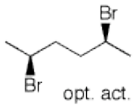


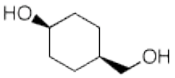


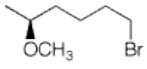
4. Provide the unknown product(s) of each reaction. In all cases, provide mechanisms and a rationale.

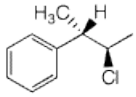
a) (S) - CHDCl —(ethyl mercaptan; ethanolic KOH)→ **A** ($C_9H_{19}DS$); configuration and structure

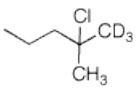
b)  —(excess CH_3OH)→ **A**

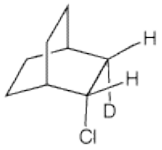
c)  opt. act. —(Na_2S; ethanol)→ A ($C_6H_{12}S$); structure, opt. act.?

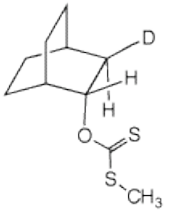
d)  —(PBr_3)→ **A**

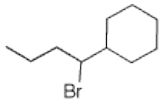
e)  opt. act. —(CH_3ONa; CH_3OH)→ **A** (major) + **B** (minor); opt. act.?

f)  opt. act. —(KOH; ethanol)→ **A** + **B** (minor); constitutional isomers

g)  —(CH_3ONa; CH_3OH)→ constitutional isomers **A** + **A'** + **B** (minor) + **C** (minor); (**A** and **A'** major; ~50:50; **B** > **C**)

h)  —(t-C_4H_9OK; t-C_4H_9OH)→ **A**

i)  —(heat; Chugaev Reaction (Google me!))→ **B** (not h-**A**) + COS + CH_3SH

j)  —(ethanol; heat)→ **A** (unrearranged) + **B** (rearranged); (constitutional isomers)