

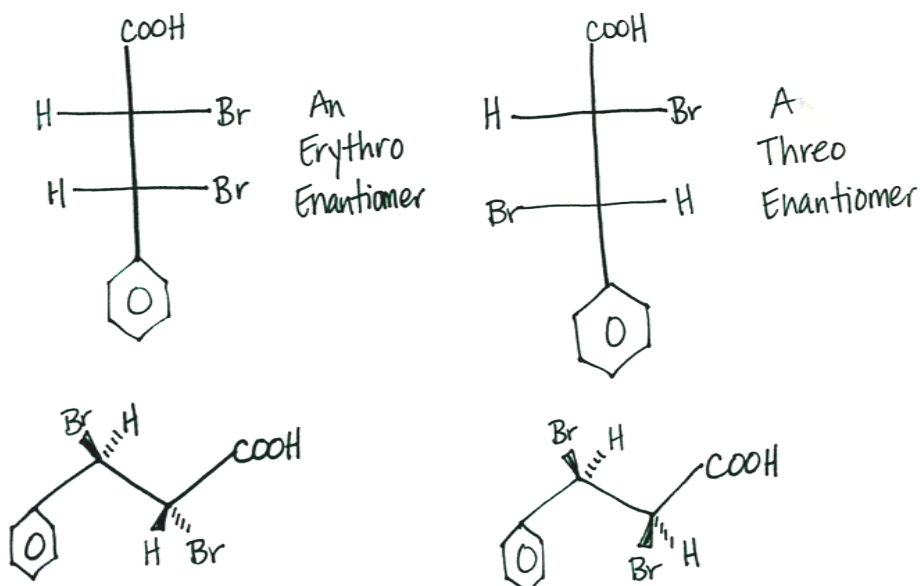
12AL Experiment 10: Chirality in Alkene Addition

Safety: Proper lab goggles/glasses must be worn (even over prescription glasses). Wear Gloves – Bromine is very toxic and glacial acetic acid can cause serious burns. Their vapors are also very damaging. As always, ask where organic waste containers are located in the lab.

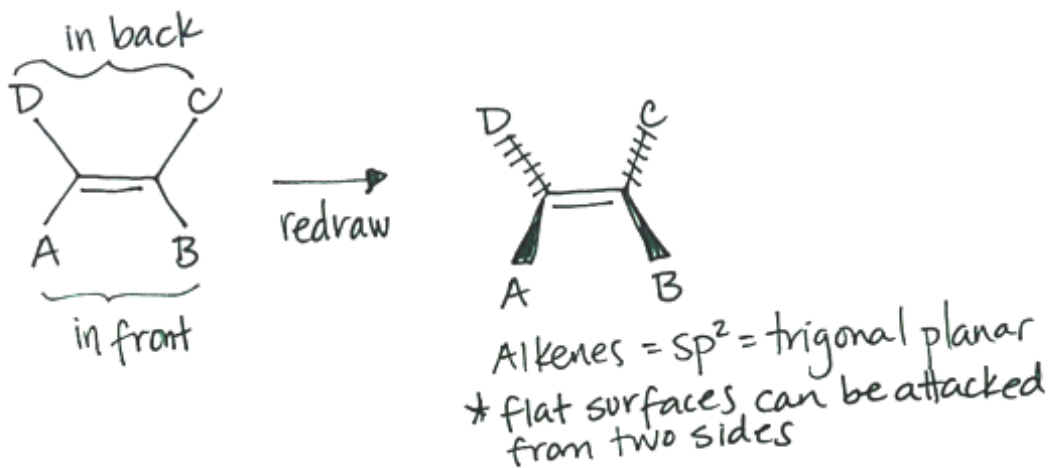
Background: Alkenes undergo two mechanism styles in addition reactions: Syn-Addition and Anti-Addition. Common reactions (to name just a few) of syn-addition seen this semester are hydrogenation with a platinum or palladium catalyst, and hydroboration-oxidation, while anti-addition has been seen in halogenation, oxymercuration-reduction, and reduction with ammonia/sodium or lithium metals. It is important to note that while most alkenes undergo the reaction mechanisms that we have studied, some alkenes may stray from the commonalities and undergo a completely different pathway.

Today you will be performing a halogenation of an alkene and proving whether or not the reaction proceeded through a Syn-Addition or an Anti-Addition mechanism. In order to do this, you will first write out both reaction mechanisms and determine the chirality of the product(s) formed. Then you will brominate *trans*-Cinnamic Acid and isolate the solid product. After purification, you will take the melting point and determine what type of enantiomers you have – the threo or erythro enantiomers. Finally, you will be able to prove what mechanism occurred.

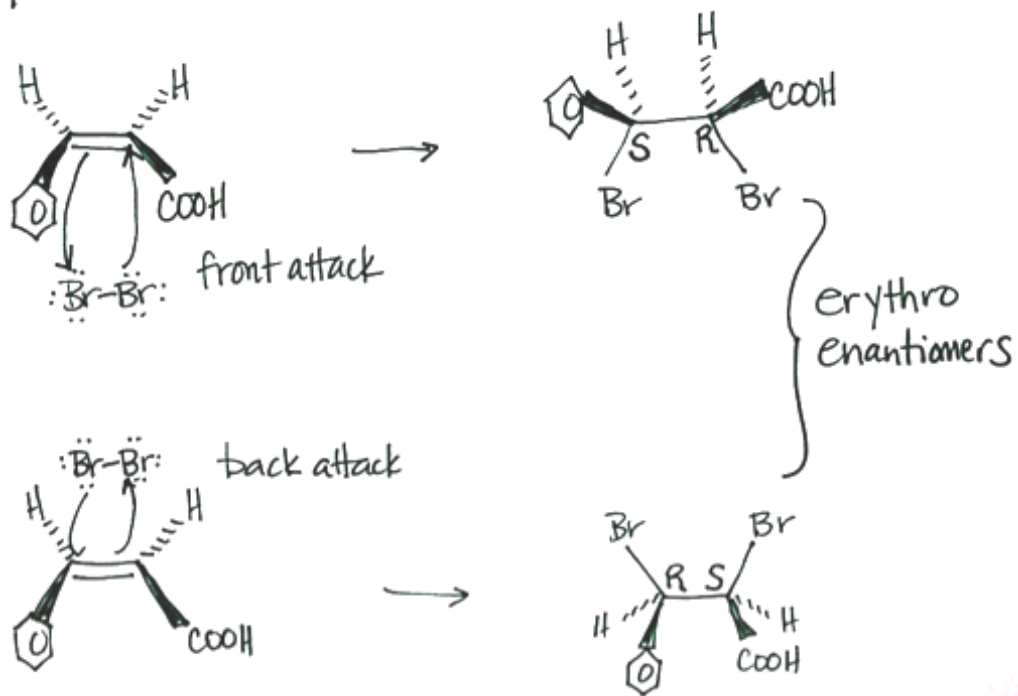
In a Fisher projection of a molecule, an erythro enantiomer has two identical substituents on the same side. A threo enantiomer has two identical substituents on opposite sides. If you rotate your Fisher projection into the classic staggered view of a molecule, an erythro enantiomer has two identical substituents in opposite planes, while the threo enantiomer now has them in the same plane. See example below:



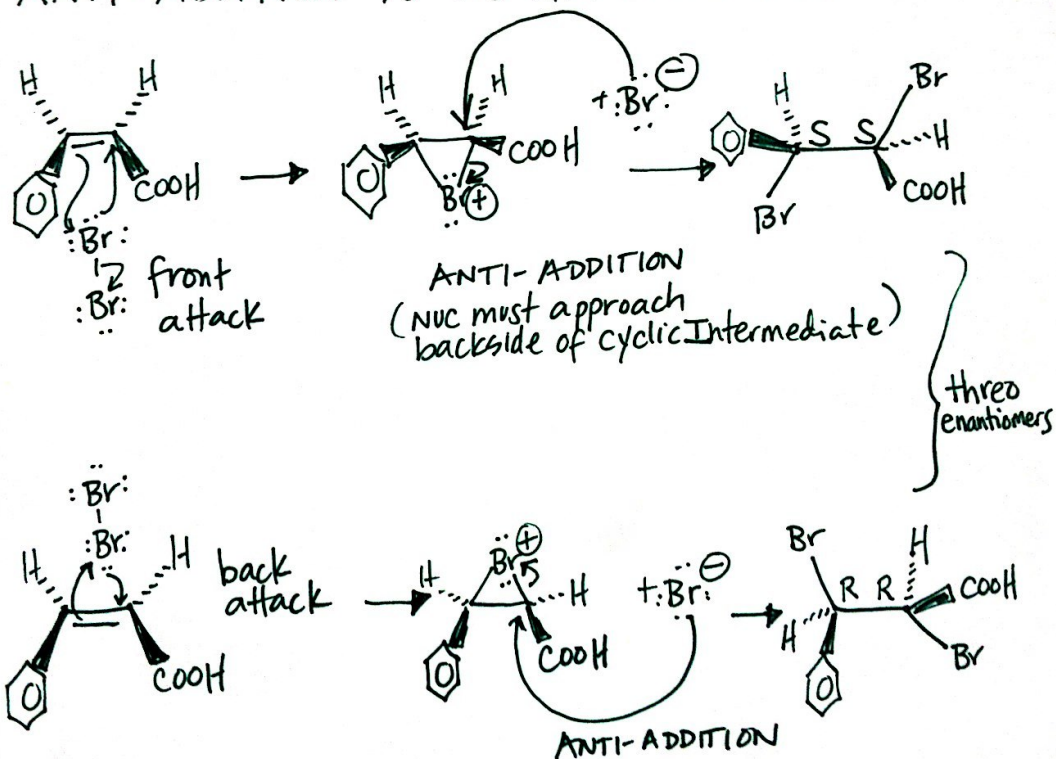
Below is an example of a syn-addition and an anti-addition halogenation on *cis*-Cinnamic Acid. Please note, this is NOT the reaction you are performing today. This example is provided to review your mechanisms learned in lecture; in addition, please review how to determine chirality.



SYN-ADDITION TO CIS-CINNAMIC ACID



ANTI-ADDITION TO CIS-CINNAMIC ACID



Objective: To perform an alkene addition reaction with bromine and determine whether the mechanism was classic anti-addition or syn-addition through chirality of products.

Procedure:

1. Set up a hot-stir-plate in the HOOD. Two students can share a hot plate (two reflux set-ups per hot plate). Make a 50°C water bath using your 150 mL beaker.
2. Into your micro-kit erlenmeyer flask, put 0.1482 grams of *trans*-Cinnamic Acid.
3. Using your micro syringe, measure out 0.80 mL of glacial acetic acid, and slowly add to the flask as well.
4. Check out a micro stir bar from your instructor and add to the flask too.
5. Clamp your flask in the 50°C water bath and begin to stir.
6. Measure out 1.0 mL of a 1.0M bromine in acetic acid solution, and using a plastic pipette, add very SLOWLY, DROP BY DROP, to the flask.

7. Heat in the 50°C water bath until the red-brown color from the bromine fades to light orange / pale yellow (meaning it is reacting with the pi bond). THEN HEAT FOR AN ADDITIONAL 15 minutes. If the mixture becomes colorless, add more bromine solution until you have a light orange / pale yellow color – add slowly!
 8. If at the end of the 15 minutes your solution in the flask is still very medium-dark orange, add a few drops of cyclohexene – this alkene will react with the excess bromine; the resulting 1,2-dibromocyclohexane will eventually be filtered out in the liquid waste.
 9. Cool the flask in an ice-water bath (clamp it!) for 10 OR MORE minutes; scratch the sides of the flask to induce crystallization (note: some students have crystals immediately). This is a LONG PROCESS for many students. If necessary, leave in ice-water bath for another 10-20 minutes.
- *Please make your own ice-water bath! Students always spill over their flasks and even knock over other students' flasks in a big bucket. Clamp your flask to prevent spilling and having to start over!!!
10. Once you have a sufficient amount of crystals, use your micro vacuum filtration set-up to filter the mixture. Wash your solid crystals with several portions of ice-cold water and continue the suction.
 11. Dry your crystals on a watch glass in the oven (or over-night drying in lab drawer).
 12. Grind your crystals into a powder in order to take a melting point range.
 13. Record your melting point range.

12AL Prelab Experiment 10: Chirality in Alkene Addition

1. What is the melting point of.....

threo 2,3-dibromo-3-phenylpropanoic acid?

erythro 2,3-dibromo-3-phenylpropanoic acid?

2. Draw the entire mechanism for the *syn*- addition of bromine + *trans*-cinnamic acid. All stereochemistry must be shown. All chirality (R, S) must be labeled for chiral centers.

3. Draw the entire mechanism for the *anti*- addition of bromine + *trans*-cinnamic acid. All stereochemistry must be shown. All chirality (R, S) must be labeled for chiral centers.

*Use backside of paper.

12AL Postlab Experiment 10: Chirality in Alkene Addition

1. Which enantiomers (threo or erythro) did you synthesize today based on your experimental melting point?

2. Which mechanism did the *trans*-cinnamic acid undergo, Anti or Syn – Addition?

3. Give the major product(s) of the following reactions – all stereochemistry of any cis/trans or chiral products must be shown properly AND any chiral centers labeled as R or S. Circle your product(s). (Do not repeat products so always doublecheck to make sure you did not draw identical structures!)

*As in lecture, any halogenation X_2 of alkenes should be considered to undergo classic Anti-Addition.

a. Cyclohexene + Cl_2

b. 1-methyl-1-cyclohexene + Br_2

c. *trans*-2-pentene + Cl_2

d. *cis*-2-pentene + Cl_2

e. 1-pentene + Br_2