Electrophilic Addition: Bromination of trans-Cinnamic Acid

Safety

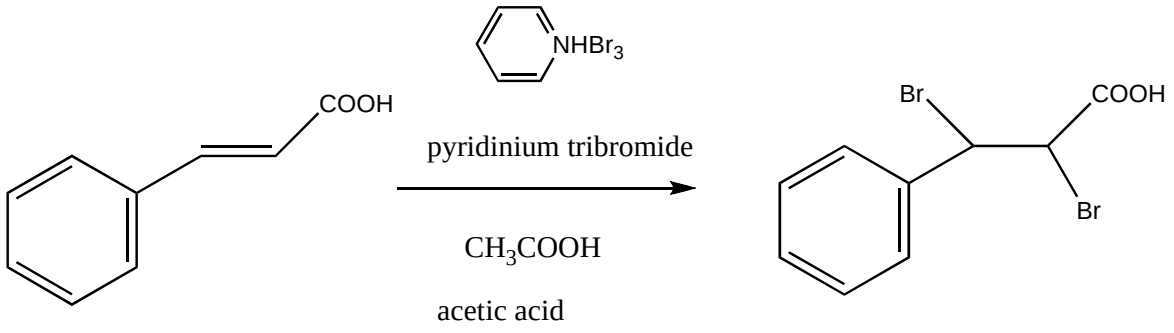
1. Bromine (red liquid) which is generated from pyridinium tribomide is extremely dangerous. It causes extreme burns to the mucous membranes and to the skin which must be treated specially. Being a solid (red solid), pyridinium perbromide is a much safer substance to work with, but under no circumstances should you handle it without gloves on and if it comes in contact with any of your person, it should be rinsed for 15 minutes with cold water. You should report such an accident to your instructor.

2. Trans-cinnamic acid is an irritant and any exposure should be treated as usual with fifteen minutes of flushing with water.

3. Glacial acetic acid is a corrosive material. It can cause very bad burns to the skin and mucous membranes. It is very irritating to breath in. Please rinse for fifteen minutes with cold water.

4. Dichloromethane is an irritant and it is extrmely irritating when trapped under a glove or ring. If you notice your skin burning, even with gloves on, take the gloves off and rinse the area for fifteen minutes with cold water. Replace the gloves.

5. Ethanol is not so worrisome, but it is toxic and obviously it crosses the brain barrier. Some of the ethanol we use contains a small amount of a substance to denature the alcohol rendering it undrinkable. With this in mind, please wear gloves and rinse any exposed area for fifteen minutes for five minutes.



trans-cinnamic acid

trans-cinnamic acid dibromide

No stereochemistry implied in drawing

Electrophilic addition reactions are fundamental reactions in organic chemistry. The following experiment will give you the opportunity to perform an electrophilic addition reaction, bromination on an alkene, trans-cinnamic acid (as shown above). You should review bromination of alkenes in your text book. You need especially to understand the mechanism and stereochemistry of the reaction. As you have learned in lecture, this reaction is stereospecific. A stereospecific reaction is a reaction where one stereoisomer (as in trans in this case – there is no cis) gives rise to one stereoisomer or at most a pair of enataniomers. In addition to reviewing an important reaction studied in lecture, you will thoroughly explore the stereochemistry of the reaction. Today's investigation will allow you to explore the stereochemistry of the reaction.

In terms of safety, please note the following.

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Be mindful that most organic materials are flammable, you have to be espscially careful with ethanol which is extremely flammable. Do not heat up ethanol on your hot plate the way you would water. Do not put the heater on high. Gently heat the ethanol at a low setting below the halfway point on the dial of the heater.

Working individually, carry out the reaction shown above as described below and then complete the following worksheet. Try to complete your worksheet while in lab. It is important that you calculate the grams and in the case of liquids the milliliters needed for the experiment. Very often in labs involving reactions, you will have to carry out these calculations yourself. Think about how you convert mmoles to moles and moles to grams and grams to mL. What information do you need. This goes back to general chemistry. So far we have been isolating compounds. This is your first synthesis where the isolated product has a different molecular mass than the reactant.

1. Place 4 mmole of trans-cinnamic acid, 4 mmole of pyridinium bromide perbromide (a source of bromine) and 4 mL of glacial acetic acid in a 50 mL roundbottom.

2. Equip this flask for reflux by attaching a water cooled condenser and heat gently to reflux with a heating mantle. The reflux apparatus is similar to the one you set up for the free radical halogenation in the last lab, except you need no trap.

If this is not clear, please see the youtube on setting up a standard reflux with and without trap. The link is on the website schedule.

3. After 30 minutes of reflux (note: this is thirty minutes of reflux, not thirty minutes of heating – don't start timing until you see drips coming back into the flask), a slight orange color should persist. The reaction fades, but it never consumes all the bromine, so the color should be their at the end. If not, consult your instructor. Remove the heating mantle and allow the solution to cool to room temperature. Induce precipitation of your product by adding 15 mL of distilled water. Why does the compound "crash out" with the addition of water?

4. Maximize the yield by cooling your round bottom in an ice bath. You can bring the ice bath up to the sample as it sits attached to the monkey bars. Allow it to sit for five minutes and then collect the crystals by vacuum filtration. Use your smallest set up. Wash the

crystals several times with small portions of cold water and then cold methylene chloride (dichloromethane).

5. Purify the product by re-crystallization. Dissolve the product in the minimum quantity of hot ethanol (keep track of the volume as you add the ethanol in increments). Add a volume of water equal to that of the ethanol. Isolate the resulting crystals by vacuum filtration. Please se the Youtube that covers this technique – which is recrystallizing a small amount of material from two solvent systems. Specifically, the Youtube covers how to do the micro-recrystallization and it is called "how to make an omlette" Please see it on the schedule for the lab course.

Small scale recrystallization is very difficult. You need to heat gently and add the minimum amount of ethanol needed to get the compound into solution. This could just be a couple mL. Then when you dissolve the compound, you can take it off the hotplate and add a quantity of water equal to the quantity of ethanol you used to dissolve. The idea is that you don't have a single solvent suitable for the recrystallization, i.e., a solvent that the compound dissolves in when it is hot and is insoluble when it is cold. So in place of a single solvent we are using a solvent that the compound is too soluble in and a solvent it is not very soluble in (which is which?) . The combination results in the intermediate solubility needed to recrystallize.

6. Place the crystals in a tared glass container. Measure the mass and melting point of the crystals after a suitable drying period.

Electrophilic Addition: Bromination of trans-Cinnamic Acid Worksheet.

1. Data

mass of product: _____

melting point range of product:

(12 points)

2. Calculate the percent yield of product . Note you need to work in moles. How many moles of reactants do you have? Which reagent is the limiting reagent? How many moles of product should you get. Your percent yield (one way to calculate it is the moles of product obtained divided by the moles of product expected based on the limiting reagent .

(16 points)

3. If all bromination approaches are considered, four stereoisomeric products are possible from this reaction. Draw the structures and look up the melting point of each. Often one set of enantiomers is called the erythro-trans-cinamic acid dibromide and the other is called the erythro. You might also find it under erythro- or threo-2,3-dibromo-3-phenylpropanoic acid. (12 points)

4. Which product (s) did you isolate? Is the material that you isolated chiral? Would it give an optical rotation? Explain briefly.(12 points)

5. Write a complete mechanism that explains the formation of your product. Use arrow formalism, show intermediates and write all products. You only need to do this for the formation of one stereoisomer. (20 points)

6. What products would be expected if cis-cinnamic acid was subjected to the same reaction conditions? (12 points)