Experiment 7: Cis to Trans Isomerization

Purpose:

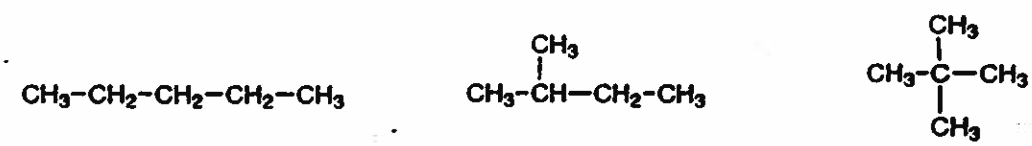
Isomerize the cis double bond in maleic acid to fumaric acid and study the difference in properties of the two isomers.

Background:

Many organic compounds have similar molecular formulas but different physical and chemical properties. These differences are primarily due to the structure of the molecule. When two or more compounds have exactly the same molecular formula, but different properties, they are called isomers. Isomers have different properties because the arrangement, or precise placement of specific atoms within the molecule, differs. Understanding the placement of atoms within a molecule will sometimes lead to a better understanding of its properties and reactivity.

There are two main classes of isomers, structural isomers and stereoisomers. Structural isomers contain the same number and types of atoms but one or more bonds differ. Many structural isomers cannot be converted into one another because bonds have to be broken and reformed which requires a great deal of energy. For example, there are three structural isomers for the molecular formula C_5H_{12}: *n*-pentane, isopentane, and neopentane (Figure 1). These structural isomers are not easily interconverted to one another because a carbon–carbon bond would have to be broken and then reformed.

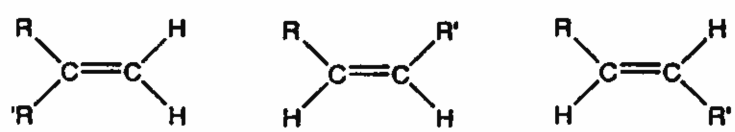
Figure 1



n-Pentane | Isopentane | Neopentane

Stereoisomers have the same number and types of atoms, the same bonding arrangement, but the spatial arrangement of the individual atoms differ. One type of stereoisomers is called geometric isomers because the atoms or groups of atoms assume different geometric positions around a rigid bond or ring of atoms. Carbon–carbon double bonds are very rigid bonds and are common in organic compounds. There are three different arrangements that two different atoms or groups of atoms can take around a carbon–carbon double bond (Figure 2). [In many organic structural drawings, R and R′ represent an atom or a group of atoms (e.g., OH, CH_3, or C_6H_5).]

Figure 2



cis-isomer | trans-isomer

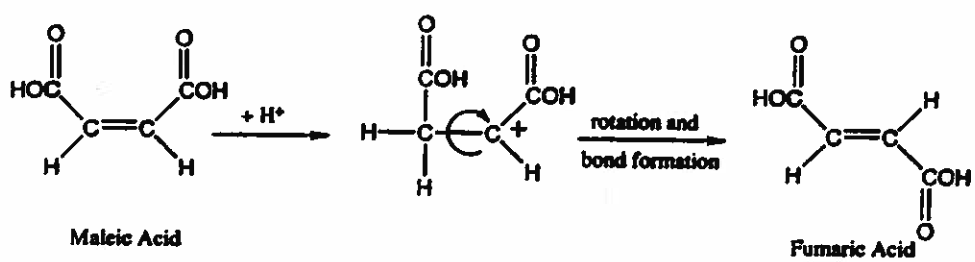
The isomer with the R and R′ bonded to the same carbon is a structural isomer of the cis and trans isomers because a carbon–carbon bond would have to be broken to convert it into one of the other two isomers. The cis and trans isomers are stereoisomers because the atoms are identical, are bonded to the same atoms, but their geometry is different. Cis and trans isomers always have a hydrogen and a non-hydrogen atom bonded to each carbon of the double bond. The cis isomer is the isomer where both hydrogens are on one side of the double bond and the trans isomer has the hydrogen atoms on opposite sides.

In general, rotation about a carbon–carbon single bond occurs readily at room temperature, while rotation about carbon–carbon double bonds does not occur. Cis and trans isomers can be interconverted or isomerized under a variety of conditions depending on the molecule. Carbon–carbon double bonds are isomerized using heat, photolysis, or a catalyst. Common catalysts include enzymes, transition metal catalysts, and simple protic acids. Most carbon–carbon double bond isomerization processes involve a carbon–carbon single bond intermediate that can undergo a bond rotation to give either the cis or trans isomer. (Figure 3.)

Trans isomers are generally more stable than the corresponding cis isomer because the large "R" groups are farther apart and steric hinderance is minimized. Steric hinderance is due to the atoms in the "R" groups being too close to one another. Since the trans isomer is usually more stable, it is often the preferred product in an isomerization reaction. However, intramolecular interactions such as hydrogen bonding can sometimes favor the cis isomer. Most isomerization processes give some mixture of cis and trans isomers.

A simple example of a cis-to-trans isomerization is the conversion of maleic acid to fumaric acid. Maleic acid is *cis*-butendioic acid and fumaric acid is *trans*-butendioic acid. A proposed mechanism for the cis-to-trans isomerization reaction is an electrophilic addition of a hydrogen ion to form the carbonium cation followed by rotation about the carbon–carbon single bond to move the two acid groups as far away from each other as possible. Elimination of a hydrogen ion gives the trans isomer (Figure 3).

Figure 3

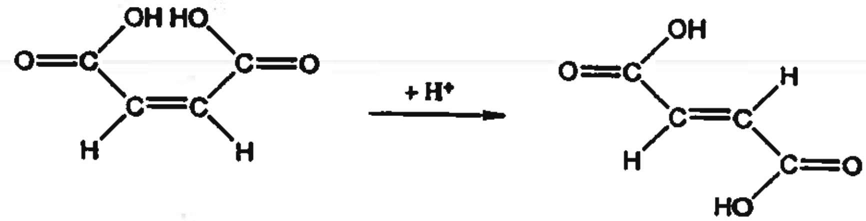


Cis and trans isomers usually differ in properties. Trans isomers generally have more symmetry, a smaller dipole moment, a higher melting point and lower solubility. Cis isomers are not as stable and normally have higher heats of formation (about 1–2 kcal/mol higher). For this reason, cis isomers can often be transformed into the trans isomer by heating. At higher temperatures, enough energy is available to break the carbon–carbon double bond. Rotation about the carbon–carbon single bond can occur and the molecule will prefer to be in a lower energy conformation so when the double bond reforms, the trans isomer is the predominate product.

Maleic Acid Isomerization

Reaction and Physical Properties

Figure 4



Maleic Acid

Fumaric Acid

	Maleic Acid	Hydrochloric Acid	Fumaric Acid
Amount	0.4 g	3 mL	—
M.W.	116.07	36.46	116.07
Concentration	—	6 M	—
mmol	3	1.8	—

Safety and Chemical Hazards:

Hydrochloric acid is highly toxic by ingestion or inhalation and is severely corrosive to skin and eyes. Avoid all body tissue contact. Maleic acid is moderately toxic by ingestion and a body tissue irritant. Fumaric acid is an eye irritant. Always place the immersion heater in the water before plugging it in. Always wear chemical splash goggles, chemical-resistant gloves and a chemical-resistant apron.

Materials

- Small reaction vial
- Hot water setup
- Ice water setup
- Microtip pipet, 2
- Watch glass or weighing dish
- Small test tube with cork stopper, 2
- Test tube tongs
- Spatula
- Graduated cylinder, 10 mL
- Filter paper
- Copper wire
- Filter setup
- Melting point capillary tubes

Chemicals

- Maleic acid
- Hydrochloric acid, 6M
- Distilled or deionized water
- Cresol red indicator solution, 0.02%

Experimental Procedure

Procedure—Setup

1. Add approximately 300 mL of water to a 400- or 600-mL beaker. Place an immersion heater in the water, plug it in, and allow the water to come to a boil. Do not plug in the immersion heater until after it is placed in the water.
2. Place 0.4 g of maleic acid in a small reaction vial.
3. Add 3 mL of 6 M hydrochloric acid to the reaction vial.
4. Seal the reaction vial and shake vigorously for 1–2 minutes to dissolve the solid. If the solid does not completely dissolve, wait 1–2 minutes and shake again. Any remaining solid will dissolve when the solution is heated. Wrap a piece of copper wire under the cap to form a handle.
5. Using the copper wire handle or tongs, place the reaction vial in the beaker containing boiling water and the immersion heater. If at any time during the reaction a small stream of bubbles begins to flow out of the reaction vial cap, remove the vial from the boiling water, allow it to cool and tighten the cap.
6. After heating for about 10 minutes, a white solid will begin to appear. Observe how the crystals grow and then slowly fall to the bottom of the vial.
7. After a total of 25 minutes, remove the vial from the hot water using tongs or the copper wire handle and place it on the table top. Allow the vial to cool for a minute and then place it in an ice water bath for 2–3 minutes.

   Isolate the product using a pipet, vacuum filtration or gravity filtration.

Isolation of Product—Filtration Procedure

8. Remove the copper wire handle. Shake the reaction vial to create a suspension. Quickly pour the suspension into a gravity filtration or vacuum filtration setup.
9. Add 2 mL of cold deionized or distilled water to the reaction vial. Place the cap back on the vial and shake the vial to dislodge any solid product. Pour the water and any solids into the filtration setup.
10. Rinse the solid twice more with 1–2 mL of cold water.
11. If using a vacuum filtration setup, allow the product to dry for a few minutes before transferring it to a watch glass or weighing dish to dry overnight.
12. If using a gravity filtration setup, remove the filter paper when all the filtrate has flowed through the filter paper. Open up the filter paper and place it on a paper towel or larger filter paper to help wick away as much water as possible from the product.
13. Allow the product to dry overnight. Drying can be hastened by placing the product under an incandescent lamp.

Purification and Analysis

14. After the product has dried, determine the mass of the product and calculate percent yield. Record in the data sheet.

15. pH test: Place a small sample (a few particles) of maleic acid and your product in two small test tubes (or vials). Add 2 mL of distilled water. Cap the test tubes with cork or rubber stoppers and shake vigorously. Add 2–3 drops of 0.02% cresol red indicator to each tube. Shake again to mix the indicator in the solution. Record your observations in Table 1. Discard the mixtures down the drain. Rinse the test tubes.

16. Solubility test: Place approximately equal amounts (about 0.1 g) of maleic and your product in two small test tubes (or vials). Add 2 mL of distilled water. Cap the test tubes with cork or rubber stoppers and shake vigorously. Record your observations in Table 1 below. Discard the mixtures down the drain. Rinse out the vials.

17. Melting point: Place approximately equal amounts of maleic acid and the acid you isolated in two capillary tubes. Place the capillary tubes in the Mel-Temp and find the melting point of the maleic acid. Under the experimental melting point for fumaric acid, record your observations of what happens to your acid when the maleic acid melted.

Student Data Sheet

Data:

Percent yield: Mass of starting material: ____________

Mass of dry product: ____________

Percent yield: ____________

	Maleic acid		Fumaric acid	
	Literature*	**Experimental**	**Literature***	**Experimental**
Acid Dissociation Constant k_1		—		—
Acid Dissociation Constant k_2		—		—
pH test				
Solubility in H_2O				
Melting point				

*Obtain from reference manual.

Questions:

1. Would the isomerization of maleic acid occur if the reaction were performed in neutral water?

2. What is the function of the hydrochloric acid in the isomerization of maleic acid?

3. Explain how the results from the analysis show that the product is indeed fumaric acid and not maleic acid.