

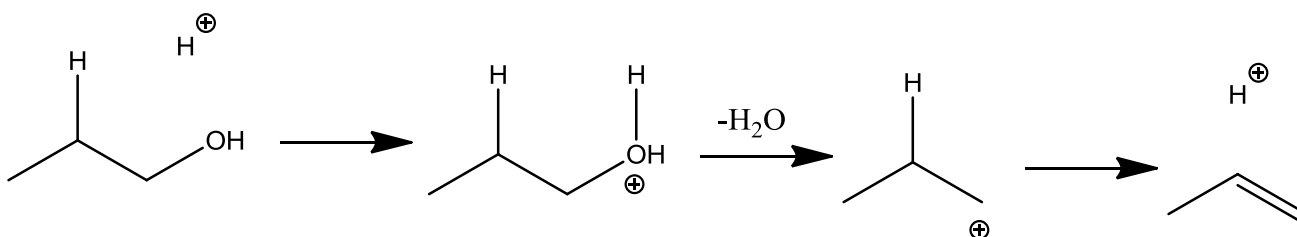
CHEM1102 Worksheet 6: Elimination Reactions and Chirality

Model 1: Elimination Reactions

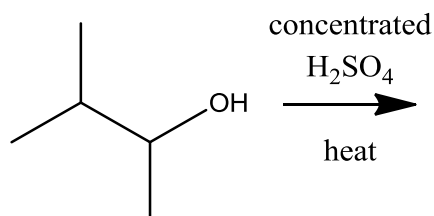
In Worksheet 3, you saw how the C=C bonds undergo electrophilic addition reactions in which a group is added to each end of the double bond and the π bond is lost. Elimination reactions are the opposite: a group is lost from each end of a C-C bond to form a C=C double bond. *Hydration* is a special example of addition: H is added to one end and OH added to the other of the C=C bond. *Dehydration* is the opposite and is a special example of elimination: H is removed from one end and OH removed from the other end of the C-C bond.

Critical thinking questions

1. Complete the mechanism for the dehydration of water from 1-propanol to form propene by adding curly arrows.



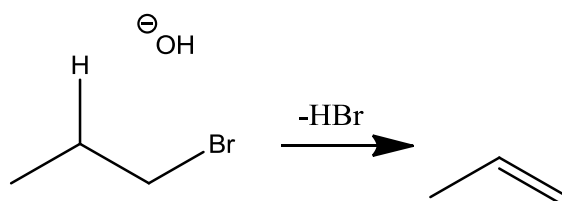
2. The first step involves protonation of the alcohol. Why is this step necessary?
3. What is the overall role of H^+ in the reaction?
4. There are two possible alkenes formed in the elimination reaction below. Draw both.



5. *More* substituted alkenes are *more* stable. Indicate the likely *major* and *minor* products in Q4.

This is an example of Zaitsev's rule: the major product of an elimination reaction will be the more substituted alkene

The acid-catalysed dehydration reaction in Model 1 is a common way to make alkenes. A second way is through base-catalysed elimination:



This is an example of an E2 reaction whereas the acid-catalysed elimination in Model 2 is an E1 reaction.

6. Complete the mechanism by adding curly arrows.

7. Explain the E1 and E2 nomenclature, using what you know about S_N1 and S_N2 reactions from Worksheet 3.

Model 2: Enantiomers and Diastereomers

You may need a molecular model set for these activities.

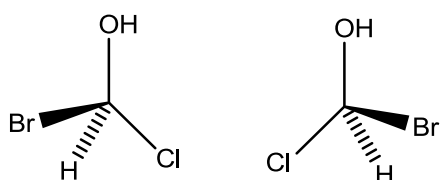
In Worksheet 2, you investigated constitutional, conformational and configuration isomers.

Critical thinking questions

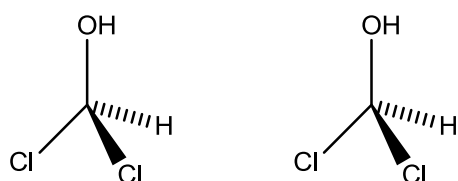
1. Draw two examples of configurational isomers, one involving a double bond and one involving a ring.

These are **diastereomers**: they are not identical and they are not mirror images. Configurational isomers that are not identical but *are* mirror images are called **enantiomers**.

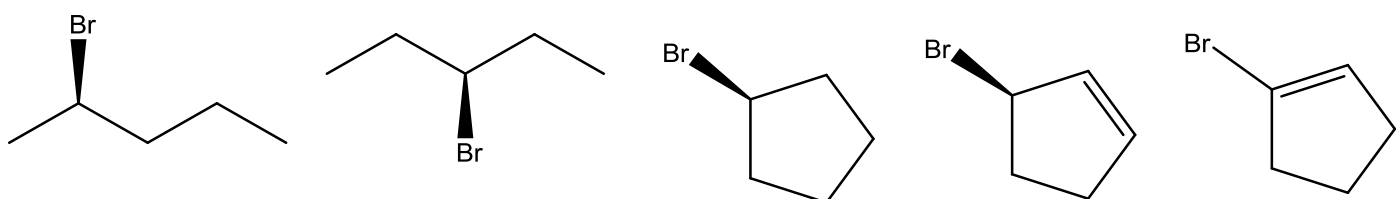
2. Using a model kits, construct the isomers below with a carbon at the centre (black) and 4 different coloured balls to represent the 4 groups bonded to it. Satisfy yourself and every member of your group that the two models are different (i.e. cannot be made the same just by being turned over).



3. On *one* model, swap two of the balls. What is the relationship between the two models now?
4. On *one* model, swap a second pair of balls. What is the relationship now?
5. Make the models below and repeat these exercises. What do you notice?



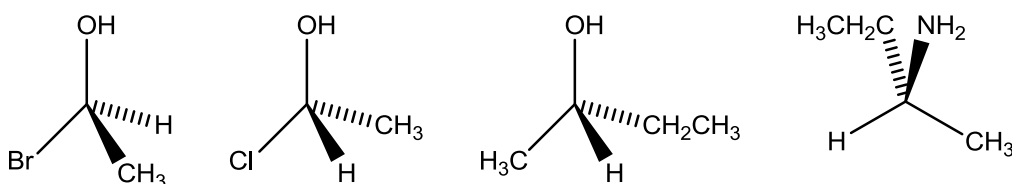
6. When a molecule can exist in 2 enantiomeric forms, it is said to be **chiral**. From your experiments above, can you suggest a key requirement for molecules to be chiral?
7. Identify the molecules below as chiral or achiral (= non-chiral).



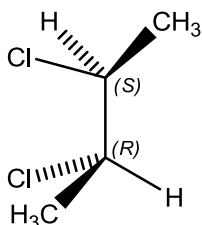
Just as (*E*) & (*Z*) and *cis* & *trans* are used to distinguish between diastereomers, (*S*) & (*R*) are used to denote the stereochemistry for the two enantiomers of a chiral molecule.

To assign the *absolute stereochemistry*,

- (i) Number the four substituents on the chiral centre in terms of priority (the same rules apply as for double bond isomers here)
 - (ii) Draw the molecule with the *lowest priority group pointing into the page*
 - (iii) Count around the remaining groups from highest priority to lowest:
 - (iv) Assign the stereochemistry as (*R*) if these numbers are ordered clockwise and (*S*) if these numbers are ordered anti-clockwise.
8. Assign the absolute stereochemistry of the following molecules (some may need to be redrawn, use the model kit if you need to). Name them, including (*R*) or (*S*) at the beginning.



Things become more complex when the molecule contains a second (or third or fourth. ...) chiral centre. One isomer of 2,3-dichlorobutane is shown below. It has two chiral centres with the absolute configurations shown.



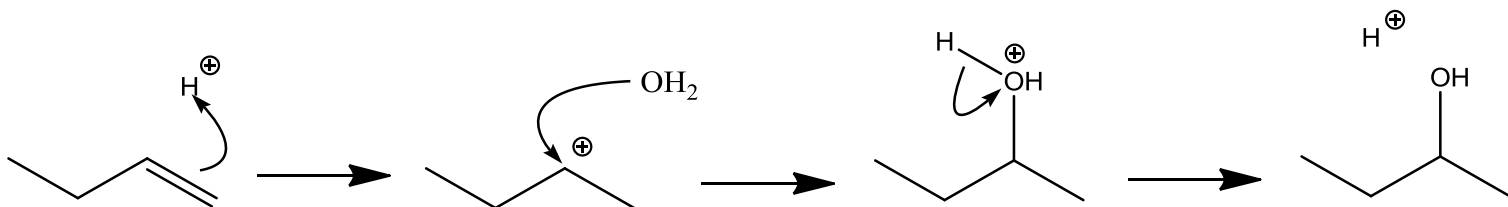
9. Draw the other forms of 2,3-dichlorobutane in the space above.
10. Identify the relationships between *each pair*. *Hint*: they will either be enantiomers, diastereomers or the same. The pair that are the same as each other are not isomers – this is the ***meso form***.
11. **Extension**: If you replace one of the chlorine groups with bromine and repeat the exercise, will you still get a pair of meso compounds? (Try to do this as a thought experiment first, then draw out the structures if you need to.)

Model 3: Stereochemistry and Reactions

Now that you are familiar with the different types of isomers, you can start looking at the stereochemical outcomes of the reactions that you have studied.

Critical thinking questions

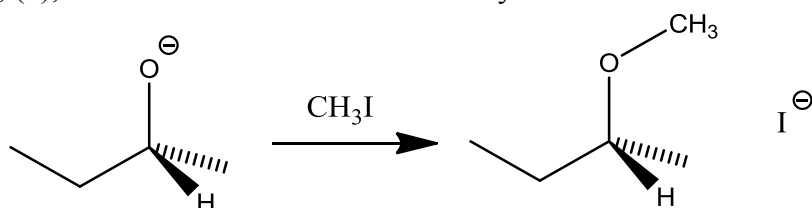
1. Label the starting material, the carbocation intermediate and the product in the reaction below as chiral or achiral.



2. Imagine that water attacks the carbocation intermediate from above the plane of the page, draw the product and assign the stereochemistry. Repeat, this time imagining that water has attacked from below.
3. Which of these enantiomers do you think will actually be the product of this reaction?

Creating a chiral molecule from an achiral molecule generally leads to a 50:50 mixture of both enantiomers. **This is called a racemic mixture.**

4. The reaction below is an $\text{S}_{\text{N}}2$ reaction and leads to the formation of an ether. Do you expect the product to be (*R*), (*S*), a racemic mixture or achiral? Why?



5. **Extension:** The substitution reaction below goes *via* an $\text{S}_{\text{N}}2$ mechanism. Draw the product in 3D and assign the stereochemistry of both reactant and product.

