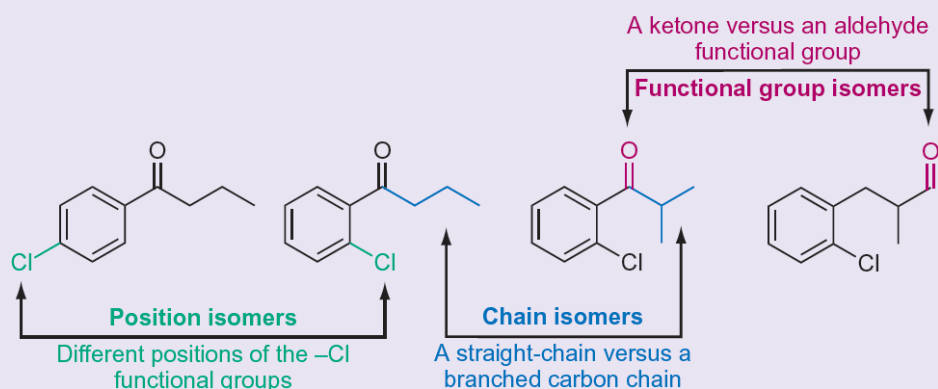


Isomerism and stereochemistry

18.1 Isomerism

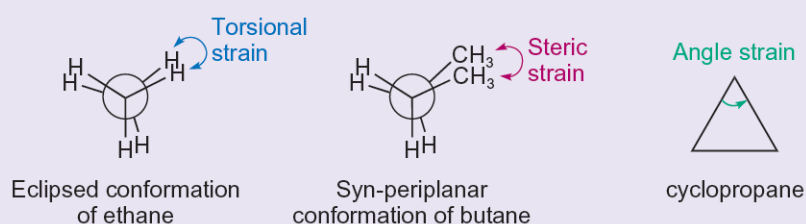
- Isomers are non-identical compounds with the same molecular formula.
- The two main classes of isomers are called structural isomers and stereoisomers.
- Structural (constitutional) isomers are compounds in which the atoms are joined together in a different order. The three types of structural isomers are chain isomers, position isomers, and functional group isomers.



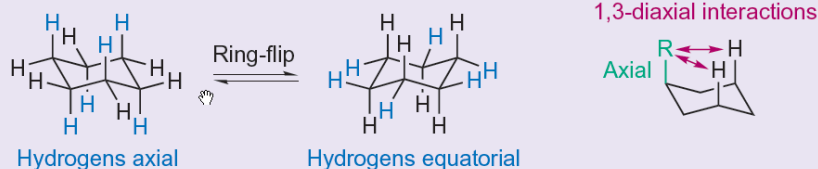
- Stereoisomers are compounds in which the atoms are joined in the same order but the positions of the atoms in space are different. The two types of stereoisomers are *E*- and *Z*-isomers and isomers with chiral centres.

18.2 Conformational isomers

- Three-dimensional arrangements of atoms that result from rotation about single bonds are called conformations (or conformers).
- Different conformations can have different amounts of strain and so have different energies.
- There are three types of strain: torsional strain; steric strain; and angle strain.
 - Torsional strain is due to electron–electron repulsions in adjacent bonds.
 - Steric strain is due to crowding of (particularly large-sized) groups in a certain conformation.
 - Angle strain (Baeyer strain) arises when the C–C–C bond angle (in non-aromatic cyclic compounds) is different from the normal tetrahedral bond angle (109.5°).



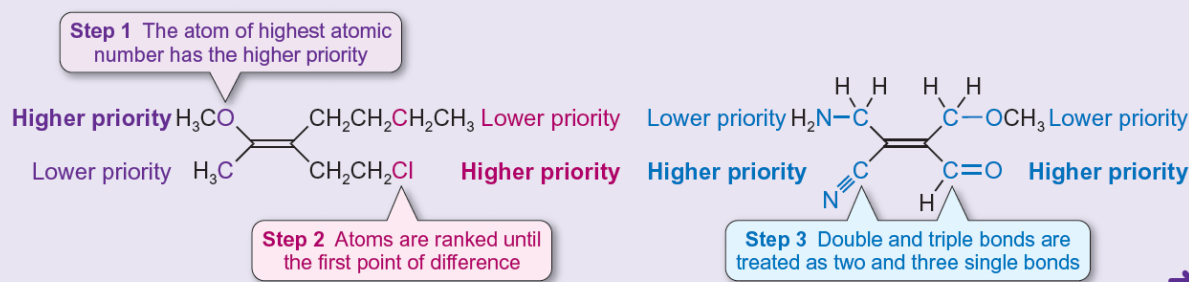
- For ethane, the staggered conformation has a lower energy than the eclipsed conformation.
- For butane, the anti-periplanar conformation has the lowest energy and the syn-periplanar conformation has the highest energy.
- Cyclopropane and cyclobutane are the least stable of the cycloalkanes because of high angle strain.
- Cyclopentane and cyclohexane are the most stable cycloalkanes (and therefore the easiest to make) because of low angle strain.
- The lowest energy conformations of cyclohexane are two chair conformations that can be interconverted by a ring-flip.
- For substituted cyclohexanes, the substituents favour equatorial positions, rather than axial positions, in order to minimize 1,3-diaxial interactions.



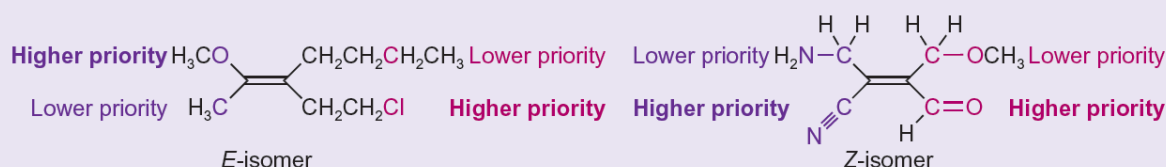
? For practice questions on these topics, see questions 1, 2, 4, and 6 at the end of this chapter (pp.858–859).

18.3 Configurational isomers: *E*- and *Z*-isomers

- The *E/Z* system of nomenclature is a general system for naming the configurational isomers of substituted alkenes.
- *trans*-Alkenes have *E*-configuration, whereas *cis*-alkenes have *Z*-configuration. The *E/Z* system for naming alkenes is preferable to using *cis*-/*trans*- because *cis*-/*trans*- is limited to naming simple alkenes (typically 1,2-disubstituted alkenes).
- The two substituents at each end of the double bond are ranked in priority using a sequence of steps.



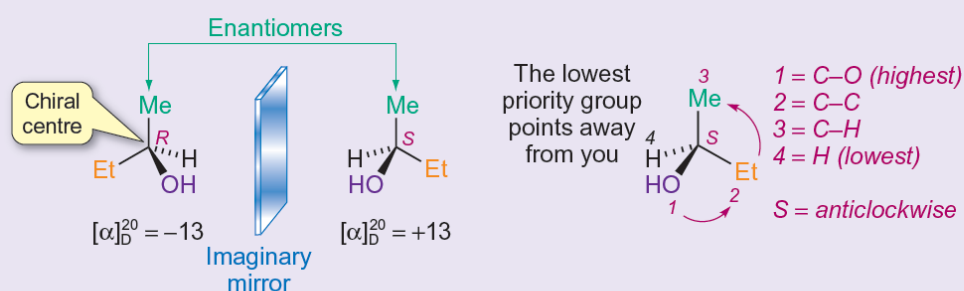
- If the substituents of higher priority are on the *opposite* sides of the double bond, the alkene has the *E*- configuration.
- If the substituents of higher priority are on the *same* side of the double bond, the alkene has the *Z*- configuration.



? For practice questions on these topics, see questions 3 and 7 at the end of this chapter (pp.858–859).

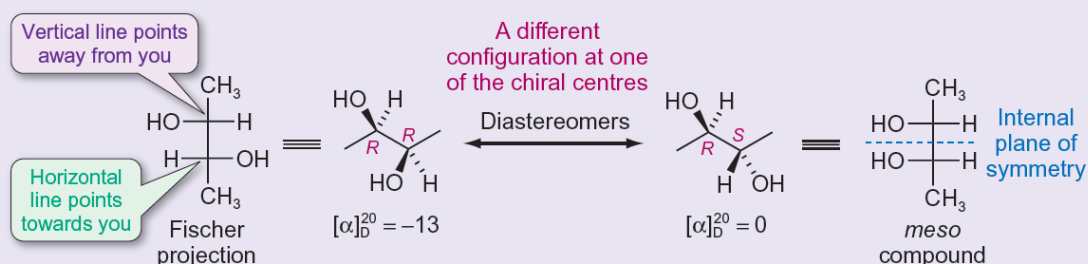
18.4 Configurational isomers: isomers with chiral centres

- The flow chart in Figure 18.30 will help you to understand how isomers with chiral centres differ from other types of isomers.
- Isomers with chiral centres are normally asymmetric molecules that do not have a plane or centre of symmetry. Achiral molecules are symmetrical molecules that have a plane or centre of symmetry.
- Enantiomers are non-identical molecules that are mirror images of one another.
- Enantiomers rotate plane-polarized light in opposite directions and often have different biological properties.
- The three-dimensional arrangement of atoms or groups attached to a chiral centre is called the configuration.
- The configuration of chiral centres is assigned as *R* or *S* using the Cahn–Ingold–Prelog (CIP) sequence rules.



The Cahn–Ingold–Prelog (CIP) sequence rules.

- The D/L nomenclature is a system for assigning the configurations of chiral amino acids and sugars, using glyceraldehyde as the standard.
- Fischer projections show the spatial arrangement of groups attached to a chiral centre—horizontal lines represent bonds that point toward you and vertical lines represent bonds that point away from you.
- Diastereomers are stereoisomers with more than one chiral centre that are not mirror images.
- Unlike enantiomers, diastereomers have different chemical and physical properties.



- A compound that contains more than one chiral centre but is achiral because it has an internal plane of symmetry is called a *meso* compound. →

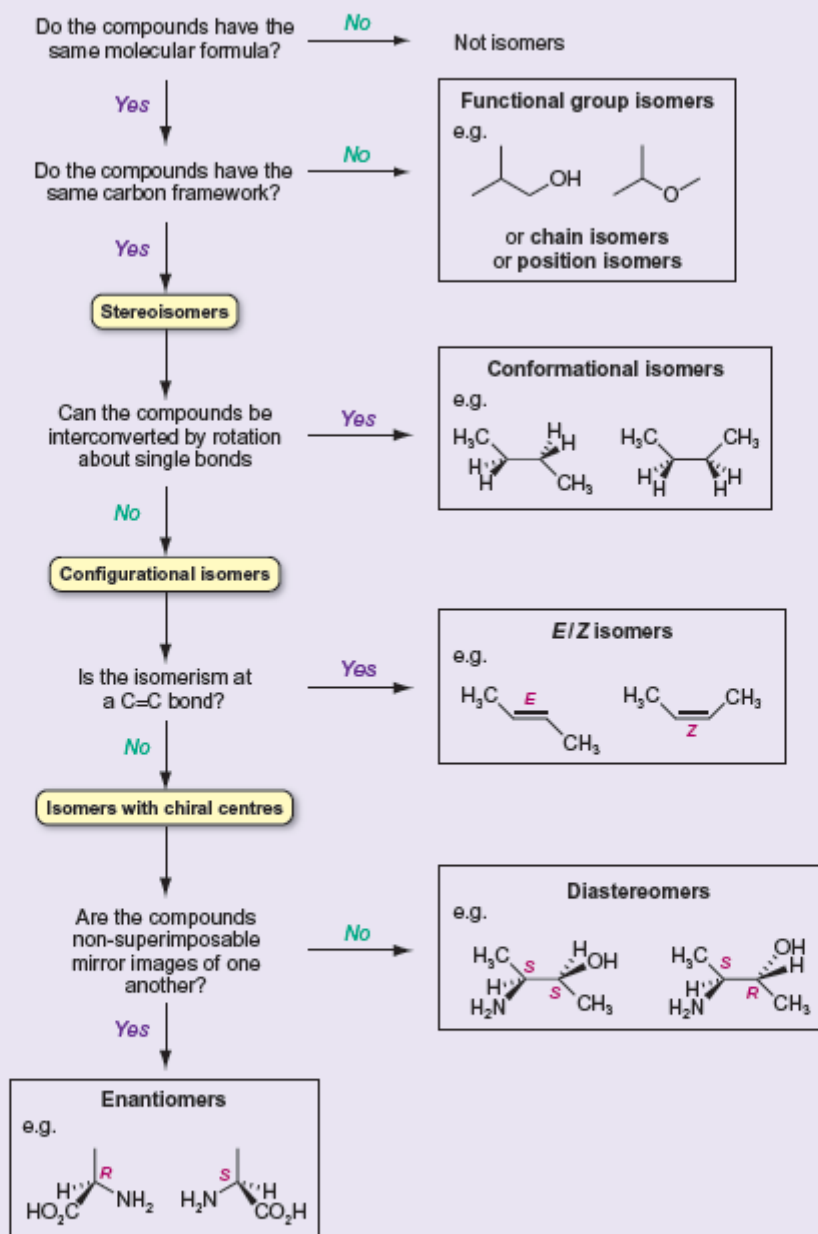


Figure 18.30 Recognizing different isomers.

 For practice questions on these topics, see questions 2, 3, and 5–7 at the end of this chapter (pp.858–859).



Concept review

By the end of this chapter, you should be able to do the following.

- Recognize the three types of structural isomers—chain isomers, position isomers, and functional group isomers.
- Understand the difference between structural isomers and stereoisomers.
- Recognize conformational isomers and understand the factors (torsional strain, steric strain, and angle strain) that influence the conformation of organic molecules, such as ethane, butane, cyclohexane, and substituted cyclohexanes.
- Recognize both types of configurational isomers—*E/Z* isomers and isomers with chiral centres (see Figure 18.30).
- Name substituted alkenes using the *E/Z* system of nomenclature.
- Recognize enantiomers and assign the configuration of chiral centres as *R* or *S* using the Cahn–Ingold–Prelog sequence rules.
- Understand the *D/L* system of nomenclature.
- Convert a hashed–wedged line structure into a Fischer projection (and vice versa).
- Recognize diastereomers and the difference between diastereomers and enantiomers.