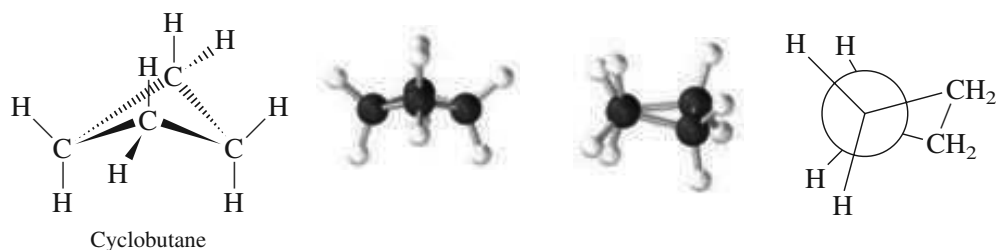


Figure 6.9

**LOWEST-ENERGY
CONFORMATION OF
CYCLOBUTANE.**



MODEL BUILDING PROBLEM 6.4

Build a model of cyclobutane. Examine the various types of strain present in the planar and nonplanar geometries.

The angles of a regular pentagon are 108° . Therefore, planar cyclopentane would have little or no angle strain. However, like planar cyclobutane, it would have considerable torsional strain because each C—C bond would be held in an eclipsed conformation. It is to be expected, then, that cyclopentane will distort from planarity to relieve this torsional strain. In one low-energy conformation, one carbon folds out of the plane so that the overall shape is somewhat like an envelope (Figure 6.10). This relieves most of the torsional strain without increasing the angle strain significantly. Overall, cyclopentane has very little strain, 6.5 kcal/mol (27 kJ/mol). It is a very common ring system and is widely distributed among naturally occurring compounds.

MODEL BUILDING PROBLEM 6.5

Build a model of cyclopentane. Examine the various types of strain present in the planar and nonplanar geometries.

6.5 CONFORMATIONS OF CYCLOHEXANE

The cyclohexane ring is very important because it is virtually strain free. This is one of the reasons why compounds containing six-membered rings are very common. If cyclohexane were planar, its C—C—C angles would be 120° —too large for the 109.5° angle of sp^3 hybrid AOs. However, the angles of the ring decrease as it becomes nonplanar. There are two nonplanar conformations, called the **chair conformation** and the **boat conformation**, that are completely free of angle strain. These conformations are shown in Figures 6.11 and 6.12, respectively. The chair conformer of cyclohexane is

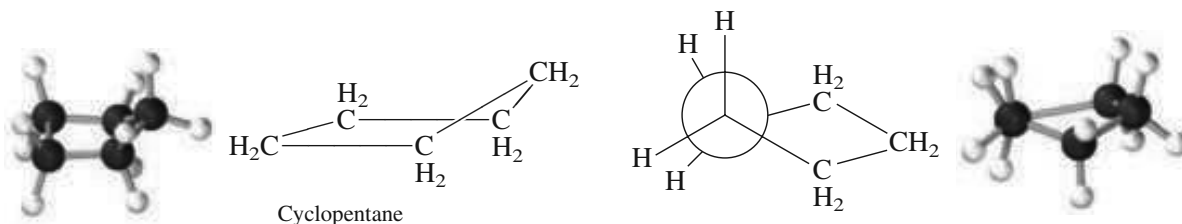
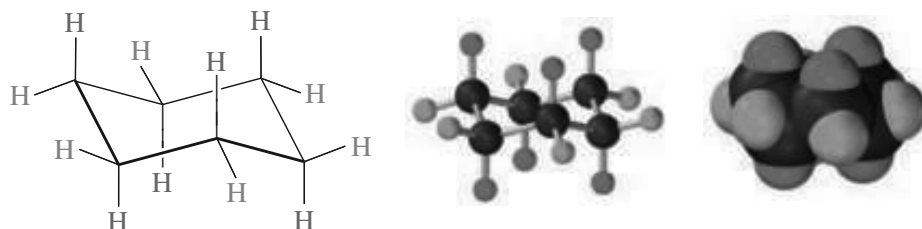
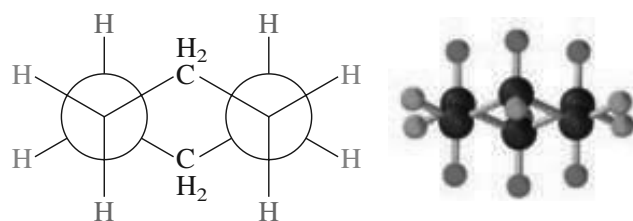


Figure 6.10

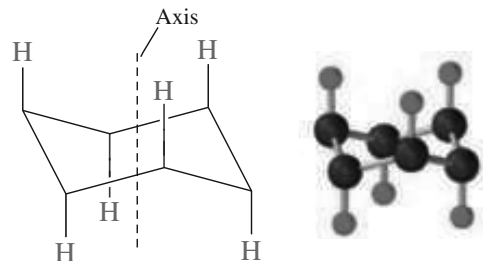
CYCLOPENTANE.

a Chair Conformation

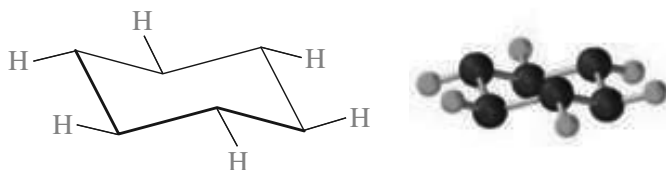
All of the C—C—C bond angles are 109.5° , so this conformation has no angle strain. In addition, it has no torsional strain because all of the C—H bonds are perfectly staggered. This can best be seen by examining a Newman projection down C—C bonds on opposite sides of the ring:

b Newman Projection

The staggered arrangement of all the bonds can be seen clearly in the Newman projection. This same picture is seen when the projection is viewed down any C—C bond. All the C—C bonds in the molecule are in conformations in which the hydrogens are perfectly staggered.

c Axial Hydrogens

In the chair conformation cyclohexane has two different types of hydrogens. The bonds to one type are parallel to the axis of the ring. These are called axial hydrogens. The axial bonds alternate up and down around the ring.

d Equatorial Hydrogens

The other hydrogens are directed outward from the ring. They are called equatorial hydrogens because they lie around the “equator” of the ring. Now go back to structure **a**, in which both types of hydrogens are shown, and identify the axial hydrogens (red) and the equatorial hydrogens (blue). Also examine the view of the axial and equatorial hydrogens provided by the Newman projection.

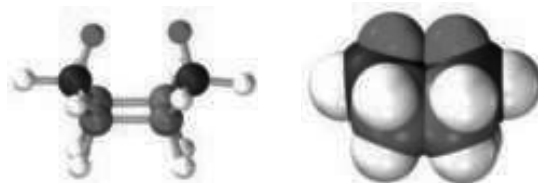
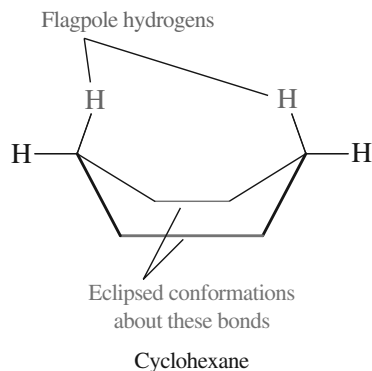
Figure 6.11

THE CHAIR CONFORMATION OF CYCLOHEXANE.

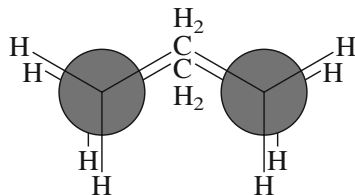
- a** CHAIR CONFORMATION,
- b** NEWMAN PROJECTION,
- c** AXIAL HYDROGENS, AND
- d** EQUATORIAL HYDROGENS.

Figure 6.12

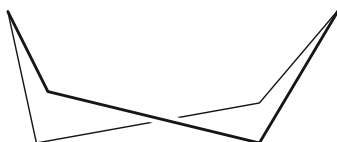
THE BOAT CONFORMATION OF CYCLOHEXANE. **(a)** BOAT CONFORMATION, **(b)** NEWMAN PROJECTION, AND **(c)** TWIST BOAT CONFORMATION.

(a) Boat conformation

Like the chair conformation, all of the C—C—C bond angles of the boat conformation are 109.5° , so it has no angle strain. However, it does have other types of strain. The two red hydrogens, called flagpole hydrogens, approach each other too closely and cause some steric strain. In addition, the conformations about the green bonds are eclipsed. This can be seen more easily in the Newman projection down these bonds:

(b) Newman Projection

The Newman projection shows that two bonds of the boat conformation are eclipsed. The torsional strain due to these eclipsing interactions and the steric strain due to the interaction of the flagpole hydrogens make the boat conformation higher in energy than the chair conformation. The boat conformation is flexible enough to twist somewhat to slightly decrease its overall strain energy.

(c) Twist Boat Conformation

In the twist boat conformation the “bow” and the “stern” of the boat have been twisted slightly. Although this decreases the flagpole interaction and relieves some of the torsional strain, angle strain is introduced. Overall, the twist boat conformation is a little more stable than the boat conformation but not nearly as stable as the chair conformation.

perfectly staggered about all of the C—C bonds and therefore has no torsional strain either—it is strain free. The boat conformer, on the other hand, has both steric strain, due to interactions of the flagpole hydrogens, and torsional strain. It is about 6 kcal/mol (25 kJ/mol) less stable than the chair conformer. Some of the steric and torsional strain

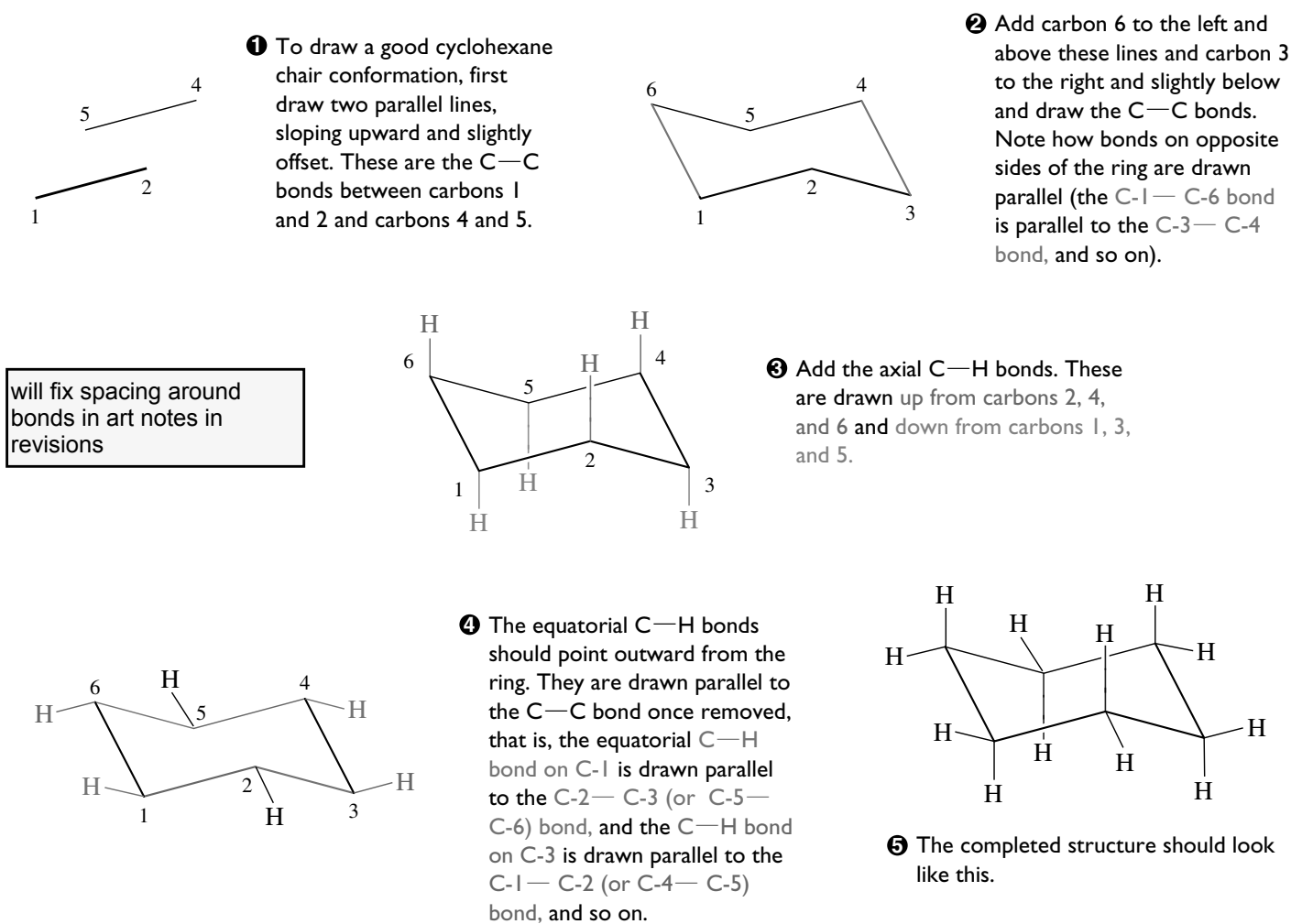


Figure 6.13

FIVE STEPS FOR DRAWING CHAIR CYCLOHEXANE.

of the boat can be relieved by twisting. The twist boat conformation is about 5 kcal/mol (21 kJ/mol) less stable than the chair conformation.

Figure 6.11 also shows that there are two different types of hydrogens, called **axial** hydrogens and **equatorial** hydrogens, in the chair conformer of cyclohexane. The axial C—H bonds are parallel to the axis of the ring; the equatorial C—H bonds project outward from the ring around its “equator.” Steps to help you learn to draw the chair conformation of cyclohexane, including the axial and equatorial hydrogens, are provided in Figure 6.13.

The chair conformation of cyclohexane is not rigid. It can convert to a twist boat conformation and then to a new chair conformation in a process termed ring-flipping, as shown Figure 6.14 (not all the hydrogens are shown for clarity).

In the ring-flipping process, C-1 flips up to give a twist boat. Then C-4 can flip down to produce another chair conformation. When opposite carbons flip like this, all axial and equatorial bonds interconvert; that is, all hydrogens that were axial are converted to equatorial

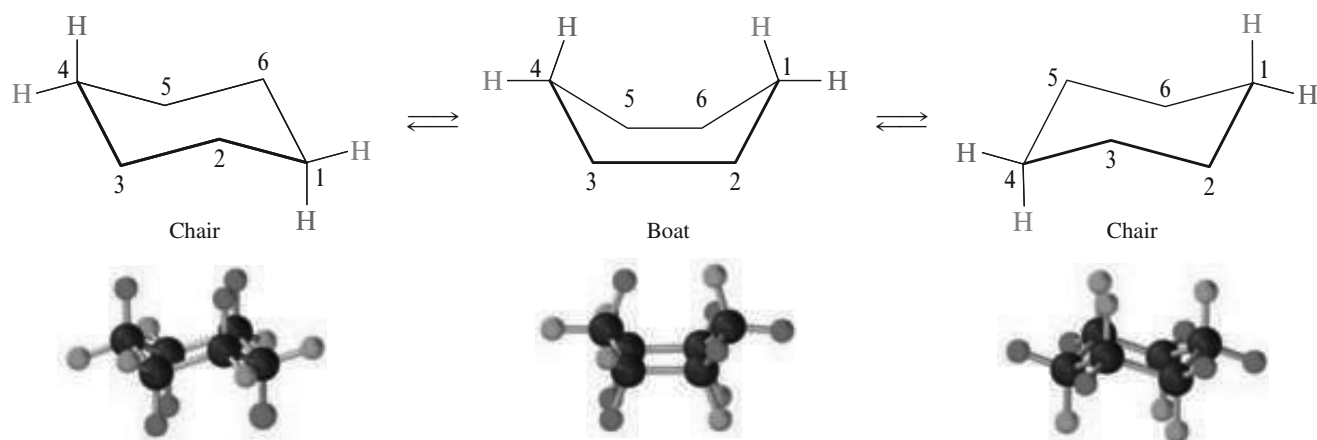


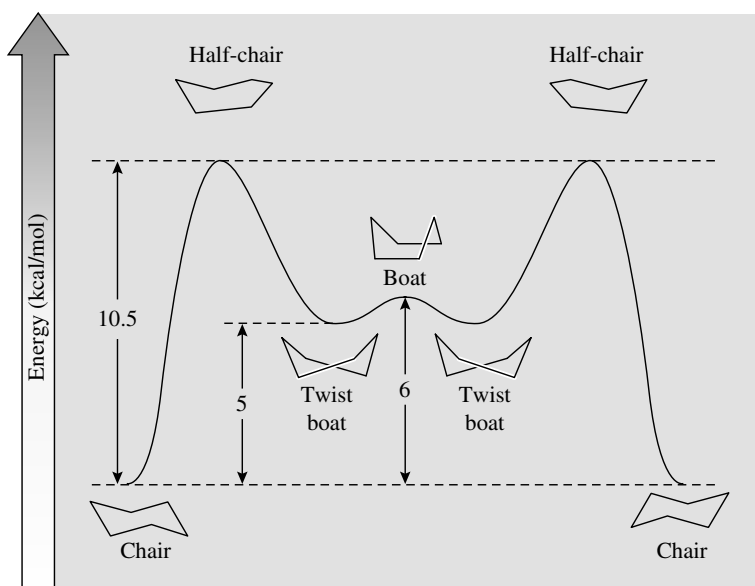
Figure 6.14

RING-FLIPPING. Converting chair cyclohexane to boat and then to a new chair.

torial, and all hydrogens that were equatorial are converted to axial. This can be seen in Figure 6.14, in which the red hydrogens, which are axial in the left chair, are converted to equatorial hydrogens in the right chair. The energy required for this ring-flipping process is shown in Figure 6.15. The highest barrier, called the half-chair conformation, is about 10.5 kcal/mol (44 kJ/mol) higher in energy than the chair conformation. Again, the 20 kcal/mol (83.7 kJ/mol) of energy that is available at room temperature provides plenty of energy to surmount this barrier; therefore, this ring-flipping is fast. It occurs about 100,000 times per second at room temperature.

Figure 6.15

ENERGY DIAGRAM FOR THE CYCLOHEXANE RING-FLIPPING PROCESS.



MODEL BUILDING PROBLEM 6.6

Build a model of cyclohexane.

- Examine the strain present when the geometry is planar.
- Examine the strain present in the boat conformation.
- What strain is introduced in the twist boat conformation? What strain is relieved?
- Examine the strain present in the chair conformation. Examine the conformations about one of the C=C bonds. Identify the axial and equatorial hydrogens.
- Try a ring flip with your model. Label an axial hydrogen and determine what happens to it when the ring flips.

MODEL BUILDING PROBLEM 6.7

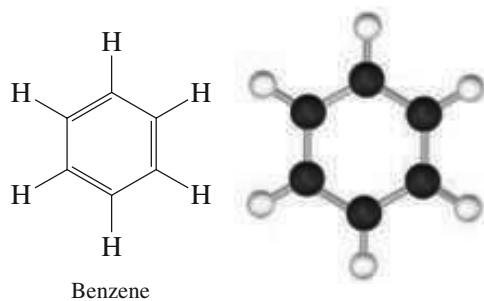
Draw a chair cyclohexane. Show the axial and equatorial hydrogens.

6.6 CONFORMATIONS OF OTHER RINGS

Conformational analysis of rings larger than cyclohexane is more complicated. These rings are also less common than cyclohexane, so we discuss their conformations only briefly. As can be seen from Table 6.1, the seven-membered ring compound cycloheptane has only a small amount of strain. Obviously, it is nonplanar to avoid angle strain. It does have some torsional strain, but the overall strain is comparable to that of cyclopentane. It is a fairly common ring system.

Larger rings, having from 8 to 11 carbons, have somewhat more strain than cycloheptane. They are nonplanar, but even so, they seem to have some strain due to bond angles that are too large for the tetrahedral bond angle of 109.5° . They also have some torsional strain. In addition, these rings have a new type of strain, called **transannular** or **cross-ring strain**. This occurs because some C—H bonds are forced to point toward the center of the ring. The hydrogens of these bonds experience steric crowding from their interactions with atoms on the other side of the ring. Rings of 12 or more carbons no longer have transannular strain and are essentially strain-free.

Compounds that contain a benzene ring are also quite common and important. The carbons of benzene are sp^2 hybridized, with bond angles of 120° , which match exactly the angles of a regular hexagon. Thus, benzene is a planar molecule with no angle strain. It is rigid because any deviation from planarity would increase angle strain and decrease the overlap of the p orbitals of the conjugated pi system.



In summary, small (3- and 4-membered) rings have a large amount of strain, due primarily to angle strain with some contribution from torsional strain. Rings that have

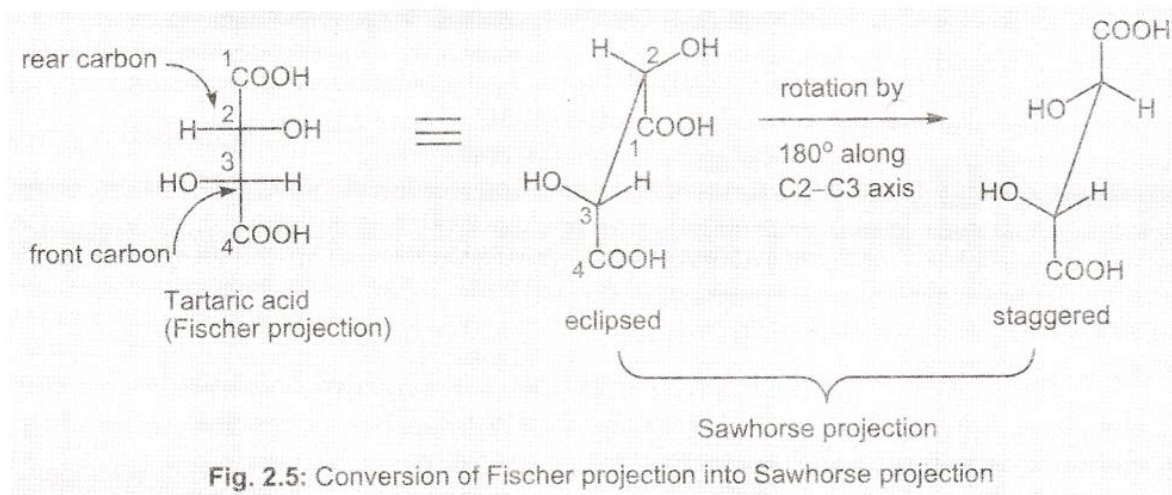
1 Interconversion of Fischer Projection Formula into Sawhorse Projection and vice-versa:

In this topic, we will be discussing the Interconversions of Fischer Projection Formula into Sawhorse Projection form. Then we will be talking the conversion of Sawhorse Projection into Fischer form.

1.1 Fischer Projection to Sawhorse Projection:

Fischer projection of a compound can be converted into Sawhorse projection; first in the eclipsed form (in Fischer projection the groups on neighbouring carbons are considered to be eclipsing each other), by holding the model in horizontal plane in such a way that the groups on the vertical line point above, and the last numbered chiral carbon faces the viewer. Then, one of the two carbons is rotated by an angle of 180° to get the staggered form (more stable or relaxed form).

For example, Fischer projection of an optically active tartaric acid is converted into staggered Sawhorse projection as shown.



1.2 Sawhorse Projection to Fischer Projection:

First, the staggered Sawhorse projection is converted to an eclipsed projection. It is then held in the vertical plane in such a manner that the two groups pointing upwards are away from the viewer, i.e. both these groups are shown on the vertical line. Such a conversion for 2,3-dibromobutane is shown.

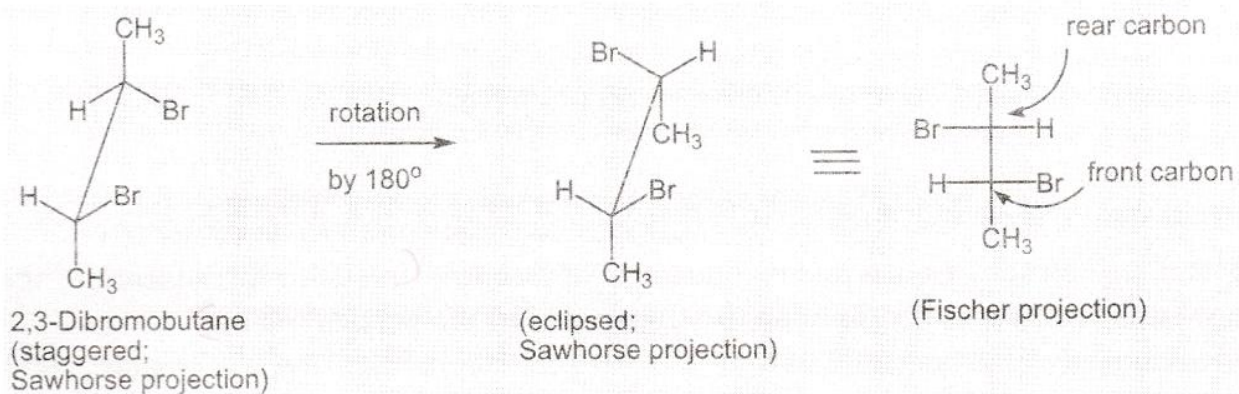


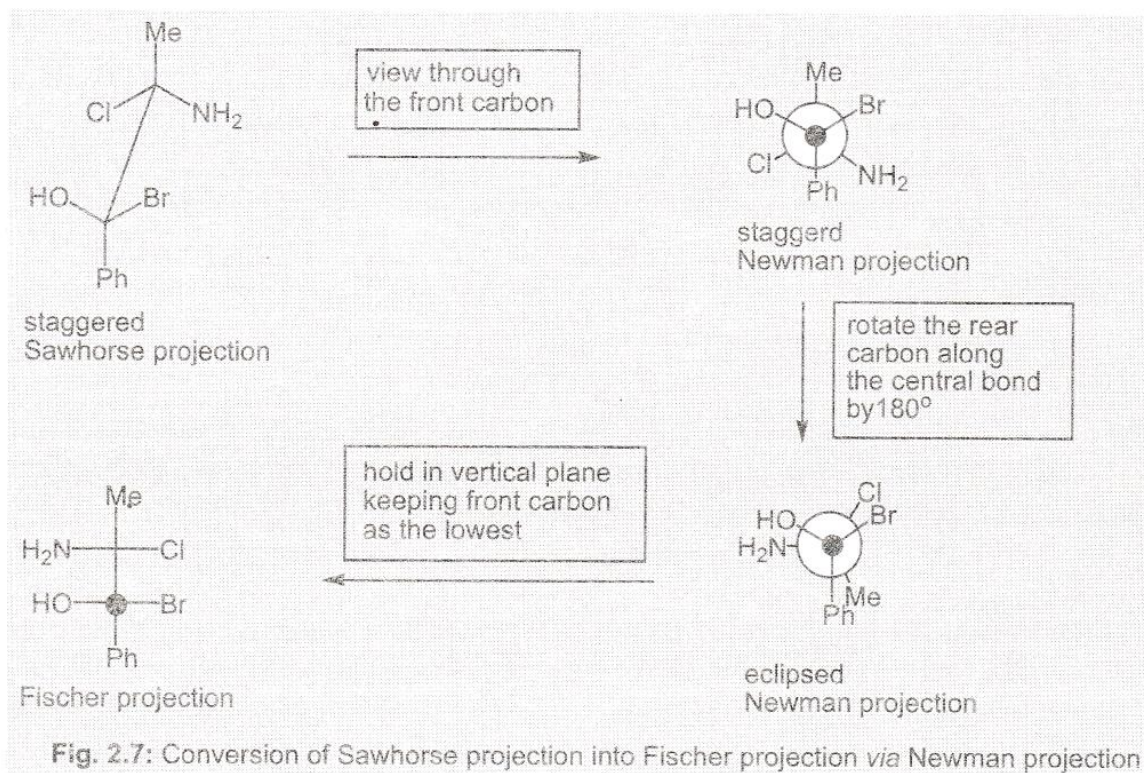
Fig. 2.6: Conversion of Sawhorse projection into Fischer projection

2 Interconversion of Sawhorse Projection Formula to Fischer Projection via Newman Projection and vice-versa:

In this topic, we will be discussing the Interconversions of Sawhorse Projection Formula into Newman Projection form followed by Fischer form. Then we will be talking the conversion of Fischer Projection into Newman form followed by Sawhorse Projection.

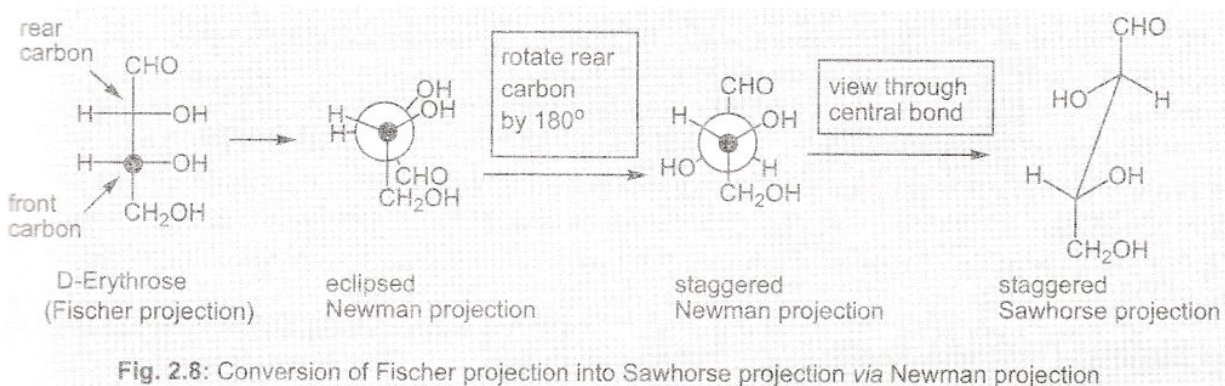
2.1 Sawhorse Projection to Newman Projection And then Fischer Projection:

Conversion of Sawhorse projection to Newman projection is quite easy. The molecule is viewed from front carbon (the central C-C bond being invisible) to get the staggered Newman projection. The rear carbon is rotated by 180° to get eclipsed Newman projection. Then, the molecule is held in the vertical plane, i.e. central bond is visible in the vertical plane in such a manner that front carbon is the lowest carbon.



2.2 Fischer Projection to Newman Projection and then Sawhorse Projection:

The molecule is viewed through the lowest chiral carbon, which becomes the front carbon, and thus eclipsed Newman projection is drawn. It is then converted into staggered conformation. Finally, the molecule is viewed through the bond connecting the front carbon with rear carbon. Such a conversion of D-erythrose is illustrated in the following scheme.



3. Interconversion of Fischer Projection Formula into Flying Wedge Projection and vice-versa:

In this topic, we will be discussing the Interconversions of Fischer Projection Formula into Flying Wedge Projection form. Then we will be talking the conversion of Flying Wedge Projection into Fischer form.

3.1 Fischer Projection to Flying Wedge Projection:

The vertical bonds in the Fischer projection are drawn in the plane of the paper using simple lines(—). Consequently, horizontal bonds will project above and below the plane ('a' and 'b' in the fig.). Conversion of Fischer projection of one of the enantiomers of α -bromopropanoic acid into five flying wedge formulae (without changing the configuration) is illustrated in the fig.

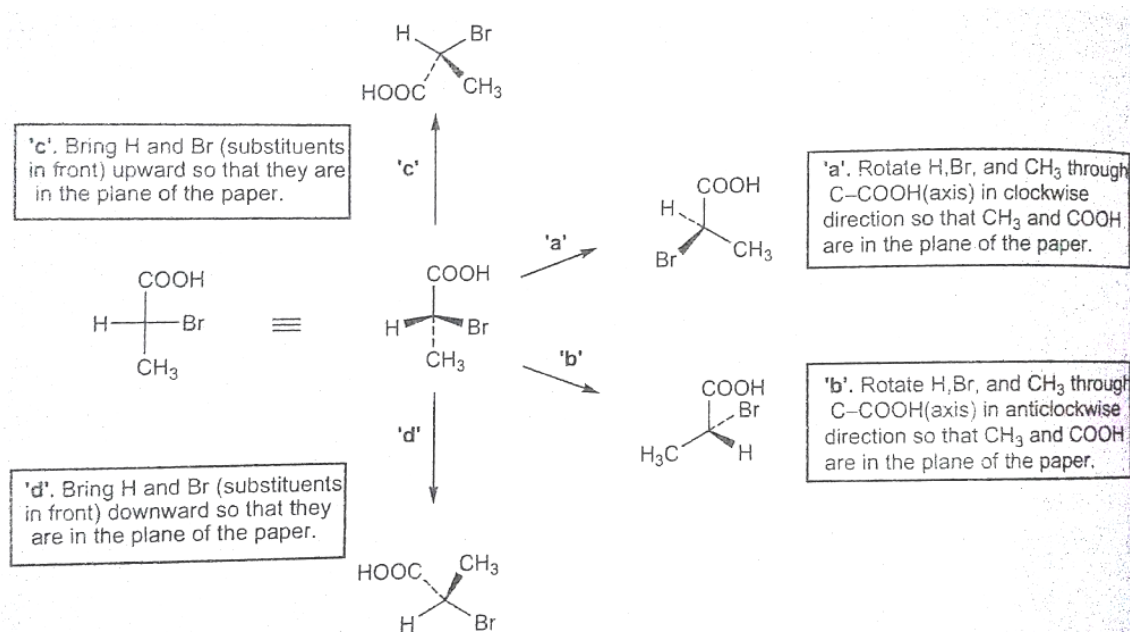


Fig. 2.9: Conversion of Fischer projection into flying wedge projections

3.2 Flying Wedge Projection to Fischer Projection:

The molecule is rotated (in the vertical plane) in such a way that the bonds shown in the plane of the paper go away from the viewer, and are vertical.

