Chapter 3 Part II **Cycloalkanes** Nomenclature, Structure, **Properties, and An Introduction to Synthesis**

General molecular formulas of cycloalkanes

Cycloalkanes are alkanes that contain rings of carbon atoms. Simple cycloalkanes are named like acyclic (noncyclic) alkanes, with the prefix *cyclo*- indicating the presence of a ring.

+ The cycloalkane with four carbon atoms in a ring is called *cyclobutane*.

+ The cycloalkane with seven carbon atoms in a ring is *cycloheptane*.

> General molecular formula: $C_n H_{2n}$

+ This general formula has **two fewer hydrogen atoms** than the formula (2n + n) for an acyclic alkane because a ring has no ends, and no hydrogens are needed to cap off the ends of the chain.



Cycloalkanes are named much like acyclic alkanes.

+ Substituted cycloalkanes use the cycloalkane for the base name, with the alkyl groups named as substituents.

+ If there is just one substituent, no numbering is needed.







methylcyclopentane

tert-butylcycloheptane

(1,2-dimethylpropyl)cyclohexane

Nomenclature of cycloalkanes

 \blacktriangleright If there are two or more substituents on the ring, the ring carbons are numbered to give the lowest possible numbers for the substituted carbons.

 \blacktriangleright The numbering begins with one of the substituted ring carbons and continues in the direction that gives the lowest possible numbers to the other substituents.

 \succ The substituents are listed in alphabetical order.

 \blacktriangleright When the numbering could begin with either of two substituted ring carbons (as in a disubstituted cycloalkane), begin with the one that has more substituents, or else the one that is alphabetically first.



1,1-diethyl-4-isopropylcyclohexane

Nomenclature of cycloalkanes

> When the acyclic portion of the molecule contains more carbon atoms than the cyclic portion (or when it contains an important functional group), the cyclic portion is sometimes named as a cycloalkyl substituent.



PROBLEM 3-14

Give IUPAC names for the following compounds.



PROBLEM 3-15

Draw the structure and give the molecular formula for each of the following compounds.

- (a) 1-ethyl-3-methylcycloheptane
- (c) cyclopropylcyclopentane
- (e) 3-ethyl-2,4-dimethylhexane

- (b) isobutylcyclohexane
- (d) 3-ethyl-1,1-dimethylcyclohexane
- (f) 1,1-diethyl-4-(3,3-dimethylbutyl)cyclohexane

Cis-trans isomerism in cycloalkanes

 \triangleright Open-chain (acyclic) alkanes undergo rotations about their carbon–carbon single bonds, so they are free to assume any of an infinite number of **conformations**.

> Alkenes have rigid double bonds that prevent rotation, giving rise to cis and trans isomers with different orientations of the groups on the double bond.





trans-but-2-ene

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> Cycloalkanes are similar to alkenes in this respect.

+ A cycloalkane has **two** distinct faces.

+ If two substituents point toward the same face, they are cis.

+ If they point toward opposite faces, they are **trans**.

+ These **geometric isomers** cannot interconvert without breaking and reforming bonds.



PROBLEM 3-16

Which of the following cycloalkanes are capable of geometric (cis-trans) isomerism? Draw the cis and trans isomers.

- (a) 3-ethyl-1,1-dimethylcyclohexane
- (b) 1-ethyl-3-methylcycloheptane
- (c) 1-ethyl-3-methylcyclopentane
- (d) 1-cyclopropyl-2-methylcyclohexane

PROBLEM **3-17**

Give IUPAC names for the following cycloalkanes.



Cyclopropane

Cyclopropane bears more ring strain per methylene group than any other cycloalkane.

Two factors contribute to this large ring strain:

+ First is the **angle strain** (sometimes called **Baeyer strain**) required to compress the bond angles from the tetrahedral angle of 109.5° to the 60° angles of cyclopropane.

+ The bonding overlap of the carbon–carbon orbitals is weakened when the bond angles differ so much from the tetrahedral angle.

+ The orbitals cannot point directly toward each other, and they overlap at an angle to form weaker "bent bonds".



Cyclopropane

+ Torsional strain is the second factor in cyclopropane's ring strain: The three membered ring is planar, and all the bonds are eclipsed.
> A Newman projection of one of the carbon–carbon bonds shows that the conformation resembles the totally eclipsed conformation of butane. The torsional strain in cyclopropane is not as great as its angle strain, but it helps to account for the large total ring strain.

Cyclopropane is generally more reactive than other alkanes. Reactions that open the cyclopropane ring release 115 kJ (27.6 kcal) per mole of ring strain, which provides an additional driving force for these reactions.



Cyclobutane

- If a cycloalkane requires bond angles other than 109.5° , the orbitals of its carbon–carbon bonds cannot achieve optimum overlap, and the cycloalkane must have some **angle strain** associated with it. Figure below shows that a planar cyclobutane, with 90° bond angles, is expected to have significant angle strain.



- In addition to this angle strain, the Newman projection shows that the bonds are eclipsed, resembling the *totally eclipsed* conformation of butane. This eclipsing of bonds gives rise to torsional strain.

- Together, the **angle strain** and the **torsional strain** add to give what we call the **ring strain** of the cyclic compound. The amount of ring strain depends primarily on the size of the ring.

Cyclobutane

 \succ The total ring strain in cyclobutane is almost as great as that in cyclopropane, but is distributed over four carbon atoms.

> If cyclobutane were perfectly planar and square, it would have 90° bond angles. A planar geometry requires eclipsing of all the bonds, however, as in cyclopropane.

➤ To reduce this torsional strain, cyclobutane actually assumes a slightly **folded** form, with bond angles of 88°. These smaller bond angles require slightly more angle strain than 90° angles, but the relief of some of the torsional strain appears to compensate for a small increase in angle strain.



Cyclopentane

> If cyclopentane had the shape of a planar, regular pentagon, its bond angles would be 108° , close to the tetrahedral angle of 109.5° . A planar structure would require all the bonds to be eclipsed, however.

➢ Cyclopentane actually assumes a slightly puckered "envelope" conformation that reduces the eclipsing and lowers the torsional strain.

> This puckered shape is not fixed, but undulates by the thermal up-and down motion of the five methylene groups. The "flap" of the envelope seems to move around the ring as the molecule undulates.



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Cyclohexane conformation: Chair and Boat conformations

 \succ Cyclohexane has bond angles that are near the tetrahedral angle (no angle strain) and also have no eclipsing of bonds (no torsional strain).

+ A planar, regular hexagon would have bond angles of 120° rather than 109.5°, implying some angle strain. A planar ring would also have torsional strain because the bonds on adjacent groups would be eclipsed. Therefore, the cyclohexane ring cannot be planar.



chair conformation



viewed along the "seat" bonds





Newman projection

Viewed from the side, the chair conformation of cyclohexane appears to have one methylene group puckered upward and another puckered downward. Viewed from the Newman projection, the chair has no eclipsing of the carbon–carbon bonds. The bond angles are 109.5°.

> Cyclohexane achieves tetrahedral bond angles and staggered conformations by assuming a puckered conformation. The **most stable conformation** is₁the **chair conformation**.

Cyclohexane conformation: Chair and Boat conformations

> The **boat conformation** of cyclohexane also has bond angles of 109.5° and avoids angle strain.

 \succ The boat conformation resembles the chair conformation except that the "footrest" methylene group is folded upward.

> The boat conformation suffers from torsional strain, however, because there is eclipsing of bonds. This eclipsing forces two of the hydrogens on the ends of the "boat" to interfere with each other. These hydrogens are called **flagpole hydrogens** because they point upward from the ends of the boat like two flagpoles.

➤ The Newman projection shows this eclipsing of the carbon-carbon bonds along the sides of the boat.



Axial and equatorial positions

> There are two different kinds of carbon–hydrogen bonds:

+ Six of the bonds (one on each carbon atom) are directed up and down, parallel to the axis of the ring. These are called **axial bonds**.
+ The other six bonds point out from the ring, along the "equator" of the ring. These are called **equatorial bonds**.



 \succ Each carbon atom in cyclohexane is bonded to two hydrogen atoms, one directed upward and one downward.

> C1 has an axial bond upward and an equatorial bond downward. C2 has an equatorial bond upward and an axial bond downward. The pattern alternates. The odd-numbered carbon atoms have axial bonds up and equatorial bonds down, like C1. The even-numbered carbons have equatorial bonds up and axial bonds down, like C2.

Drawing chair conformation

Step 1

 \succ To draw the carbon–carbon bond framework, first draw two parallel lines, slightly slanted and slightly offset. The atoms at the ends of these bonds lie in a plane.

Step 2

 \succ Draw the headrest and footrest carbons, and draw the lines connecting them to the armrests. The two lines connecting the headrest carbon should be parallel to the two lines connecting the footrest.



Step 3

➤ Fill in the axial and equatorial bonds. The axial bonds are drawn vertically, either up or down. When a vertex of the chair points upward, its axial bond also points upward. If the vertex points downward, its axial bond points downward. C1 is a downward-pointing vertex, and its axial bond also points downward. C2 points upward, and its axial bond points upward. axis

Chair-chair interconversion

> A substituent on a cyclohexane ring (in the chair conformation) can occupy either an axial or an equatorial position. In many cases, the reactivity of the substituent depends on whether its position is axial or equatorial.

 \succ The two possible chair conformations for methylcyclohexane are shown in Figure below. These conformations are in equilibrium because they interconvert at room temperature.



Chair–chair interconversion of methylcyclohexane. The methyl group is axial in one conformation, and equatorial in the other.

Chair-chair interconversion



Chair–chair interconversion of methylcyclohexane. The methyl group is axial in one conformation, and equatorial in the other.

➤ The boat serves as an intermediate in this chair-chair interconversion, sometimes called a "ring-flip."

 \succ The two chair conformations of methylcyclohexane interconvert at room temperature, so the one that is lower in energy predominates.

> The chair with the methyl group in an equatorial position is the most stable conformation. It is about 7.6 kJ mol (1.8 kcal mol) lower in energy than the conformation with the methyl group in an axial position.

> The steric interference between substituents in axial positions is particularly severe when there are large groups on two carbon atoms that bear a 1,3-diaxial relationship (*cis* on C1 and C3, or C1 and C5).

> The less stable conformation has both methyl groups in axial positions. The more stable conformation has both methyl groups in equatorial positions. Note the strongly unfavorable 1,3-diaxial interaction between the two methyl groups in the **diaxial** conformation. The molecule can relieve this 1,3-diaxial interference by flipping to the diequatorial conformation.



> The most stable conformation of the cis isomer has both methyl groups in equatorial positions. 20

1,3-Dimethylcyclohexane

trans-1,3-Dimethylcyclohexane does not have a conformation with a 1,3-diaxial interaction between two methyl groups.
 Either of its chair conformations places one methyl group in an axial position and one in an equatorial position. These conformations have equal energies, and they are present in equal amounts.

Chair conformations of trans-1,3-dimethylcyclohexane



SOLVED PROBLEM 3-3

- (a) Draw both chair conformations of *cis*-1,2-dimethylcyclohexane, and determine which conformer is more stable.
- (b) Repeat for the trans isomer.
- (c) Predict which isomer (cis or trans) is more stable.



Extremely bulky groups

 \triangleright Some groups, such as *tertiary*-butyl groups, are so bulky that they are extremely strained in axial positions.

> Regardless of the other groups present, cyclohexanes with *tert*butyl substituents are most stable when the *tert*-butyl group is in an equatorial position. The following figure shows the **severe steric interactions** in a chair conformation with a *tert* butyl group axial.



Physical properties of cycloalkanes

 \blacktriangleright Most cycloalkanes resemble the **acyclic** (noncyclic), open-chain alkanes in their physical properties and in their chemistry.

 \succ They are nonpolar, relatively inert compounds with boiling points and melting points that depend on their molecular weights.

 \succ The cycloalkanes are held in a more compact cyclic shape, so their physical properties are similar to those of the compact, branched alkanes.

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Cycloalkane	Formula	Boiling Point (°C)	Melting Point (°C)	Density
cyclopropane	C_3H_6	-33	-128	0.72
cyclobutane	C_4H_8	-12	-50	0.75
cyclopentane	C_5H_{10}	49	-94	0.75
cyclohexane	$\mathrm{C_6H_{12}}$	81	7	0.78
cycloheptane	C_7H_{14}	118	-12	0.81
cyclooctane	C_8H_{16}	148	14	0.83

TABLE 3-4 Physical Properties of Some Simple Cycloalkanes

1. Initiation step

- Draw a step involving cleavage of the weak bond in the initiator.
- ➤ The use of light with bromine suggests a free-radical reaction, with light providing the energy for dissociation of this homolytic cleavage initiates the chain reaction by generating two radicals.

Initiation step
$$Br \longrightarrow Br \cdot + \cdot Br$$

Free-radical substitution with halogen

2. Propagation step

 \triangleright Draw a reaction of the initiator with one of the starting materials.

First propagation step



> Draw a reaction of the free-radical version of the starting material with another starting-material molecule to form a bond needed in the product and to generate a new radical intermediate.

Second propagation step



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3. Termination step

Ring opening of cyclopropane and cyclobutane

Ring opening of cyclopropane by hydrogenation and other reagents



Ring opening of cyclobutane by hydrogenation

$H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_3$

Synthesis of cycloalkanes: Addition of carbenes to alkenes

 \succ Methylene is the simplest of the **carbenes**: uncharged, reactive intermediates that have a carbon atom with two bonds and two nonbonding electrons.

 \succ Methylene is a potent electrophile because it has an unfilled octet. It adds to the electronrich pi bond of an alkene to form a cyclopropane.



$$\begin{bmatrix} \ddot{}: \ddot{N} = \dot{N} = CH_2 \iff N \equiv \dot{N} = \ddot{CH_2} \\ \text{diazomethane} & N \equiv \ddot{N} = \ddot{CH_2} \end{bmatrix} \xrightarrow{\text{heat or ultraviolet light}} N_2 + C H$$

- The methylene generated from diazomethane reacts with alkenes to form cyclopropanes, but diazomethane is very toxic and explosive, and the methylene generated is so reactive that it forms many side products.
- A safer and more reliable way to make cyclopropanes is with 2the Simmons–Smith reagent.

Synthesis of cycloalkanes: Simmons-Smith reaction

> The **Simmons–Smith reagent**, named for the two DuPont chemists who discovered it, is made by adding methylene iodide to the "zinc–copper couple" (zinc dust that has been activated with an impurity of copper).

> The reagent probably resembles iodomethyl zinc iodide, This kind of reagent is called a *carbenoid* because it reacts much like a carbene, but it does not actually contain a divalent carbon atom.



PROBLEM 8-26

Predict the carbenoid addition products of the following reactions. (a) trans-hex-3-ene + CH₂I₂, Zn(Cu) (b) cis-hept-2-ene + CH₂I₂, Zn(Cu)