Organic Chemistry I

Mohammad Jafarzadeh Faculty of Chemistry, Razi University

1

Organic Chemistry, (9th edition)

By John McMurry, Cengage Learning, 2016

3. Organic Compounds: Cyclolkanes

Naming Cycloalkanes

Saturated cyclic hydrocarbons are called **cycloalkanes**, or **alicyclic** compounds (**ali**phatic **cyclic**).

Because cycloalkanes consist of rings of $-CH_2$ - units, they have the general formula $(CH_2)_n$, or C_nH_{2n} , and can be represented by polygons in skeletal drawings.



STEP 1 Find the parent

Count the number of carbon atoms in the ring and the number in the largest substituent.

If the **number of carbon atoms** in the ring is **equal to or greater than** the **number in the substituent**, the compound is named as an **alkyl-substituted cycloalkane**.

If the number of carbon atoms in the largest substituent is greater than the number in the ring, the compound is named as a **cycloalkyl-substituted alkane**.



CH₂CH₂CH₂CH₃

3 carbons 4 carbons

Methylcyclopentane

1-Cyclopropylbutane

STEP 2 Number the substituents, and write the name

For an alkyl- or halo-substituted cycloalkane, choose a point of attachment as carbon 1 and number the substituents on the ring so that the *second* substituent has as low a number as possible.



(a) When two or more different alkyl groups are present that could potentially take the same numbers, number them by alphabetical priority.



1-Ethyl-2-methylcyclopentane

2-Ethyl-1-methylcyclopentane

CH₂CH₃

(b) If halogens are present, treat them just like alkyl groups.

Cis–Trans isomerism in Cycloalkanes

The chemistry of cycloalkanes is like that of open-chain alkanes: both are nonpolar and fairly inert.

There are, however, some important differences. One difference is that cycloalkanes are less flexible than open-chain alkanes.

In contrast with the relatively free rotation around single bonds in open-chain alkanes, there is much less freedom in cycloalkanes.

Cyclopropane must be a rigid, planar molecule because three points (the carbon atoms) define a plane. No bond rotation can take place around a cyclopropane carbon–carbon bond without breaking open the ring.

The common ring sizes $(C_3 - C_7)$ are severely restricted in their molecular motions.

Cycloalkanes have two faces when viewed edge-on, a "top" face and a "bottom" face, therefore, isomerism is possible in substituted cycloalkanes.

For example, there are two different 1,2-dimethylcyclopropane isomers, one with the two methyl groups on the same face of the ring and one with the methyl groups on opposite faces.

Both isomers are stable compounds, and neither can be converted into the other without breaking and reforming chemical bonds.

Unlike the constitutional isomers butane and isobutane, which have their atoms connected in a different order, the two 1,2-dimethylcyclopropanes have the same order of connections but differ in the **spatial orientation** of the atoms.

Such compounds, with atoms connected in the same order but differing in threedimensional orientation, are called **stereochemical isomers** or **stereoisomers**.

More generally, the term **stereochemistry** is used to refer to the three-dimensional aspects of chemical structure and reactivity.

The 1,2-dimethylcyclopropanes are members of a subclass of stereoisomers called **cis**-**trans isomers**.

The prefixes *cis*- (Latin "on the same side") and *trans*- (Latin "across") are used to distinguish between them.

cis-1,3-Dimethylcyclobutane

trans-1-Bromo-3-ethylcyclopentane

Stability of Cycloalkanes: Ring strain

A theoretical interpretation was proposed in 1885 by Adolf von Baeyer, who suggested that small and large rings might be unstable due to **angle strain**—the strain induced in a molecule when bond angles are forced to deviate from the ideal 109° tetrahedral value.

Baeyer based his suggestion on the simple geometric notion that a three-membered ring (cyclopropane) should be an equilateral triangle with bond angles of 60° rather than 109°, a four-membered ring (cyclobutane) should be a square with bond angles of 90°, a five-membered ring should be a regular pentagon with bond angles of 108°, and so on.

To measure the amount of strain in a compound, the total energy of the compound measure and then subtract the energy of a strain-free reference compound. The difference between the two values should represent the amount of extra energy in the molecule due to strain. The simplest experimental way to do this for a cycloalkane is to measure its *heat of combustion,* the amount of heat released when the compound burns completely with oxygen. The more energy (strain) the compound contains, the more energy (heat) is released by combustion.

```
(CH_2)_n + 3n/2 O_2 \longrightarrow n CO_2 + n H_2O + Heat
```

Because the heat of combustion of a cycloalkane depends on size, we need to look at heats of combustion per CH_2 unit. Subtracting a reference value derived from a strain-free acyclic alkane and then multiplying by the number of CH_2 units in the ring gives the overall strain energy.

The Baeyer's theory is only partially correct. Cyclopropane and cyclobutane are indeed strained, but cyclopentane is more strained than predicted, and cyclohexane is strain-free.

Baeyer's theory is wrong for the simple reason that he assumed all cycloalkanes to be flat, while most cycloalkanes **are not flat**; they adopt puckered three-dimensional conformations that allow bond angles to be nearly tetrahedral.

As a result, angle strain occurs only in three- and four-membered rings, which have little flexibility.

For most ring sizes, particularly the medium-ring (C_7-C_{11}) cycloalkanes, **torsional strain** caused by $H \leftarrow \rightarrow H$ eclipsing interactions at adjacent carbons and steric strain caused by the **repulsion between nonbonded atoms** that approach too closely are the most important factors.

Three kinds of strain contribute to the overall energy of a cycloalkane.

- Angle strain—the strain due to expansion or compression of bond angles
- Torsional strain—the strain due to eclipsing of bonds between neighboring atoms

• Steric strain—the strain due to repulsive interactions when atoms approach each other too closely