النادي الطبي

Organic chemistry

Lec: 7

Done by: Yasser Yaghi

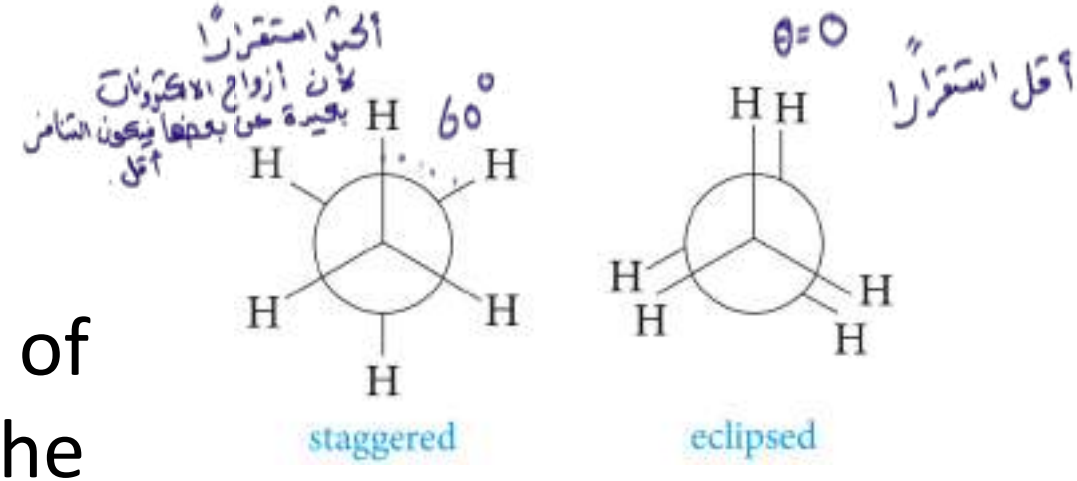
Conformational Isomers (cont'd)

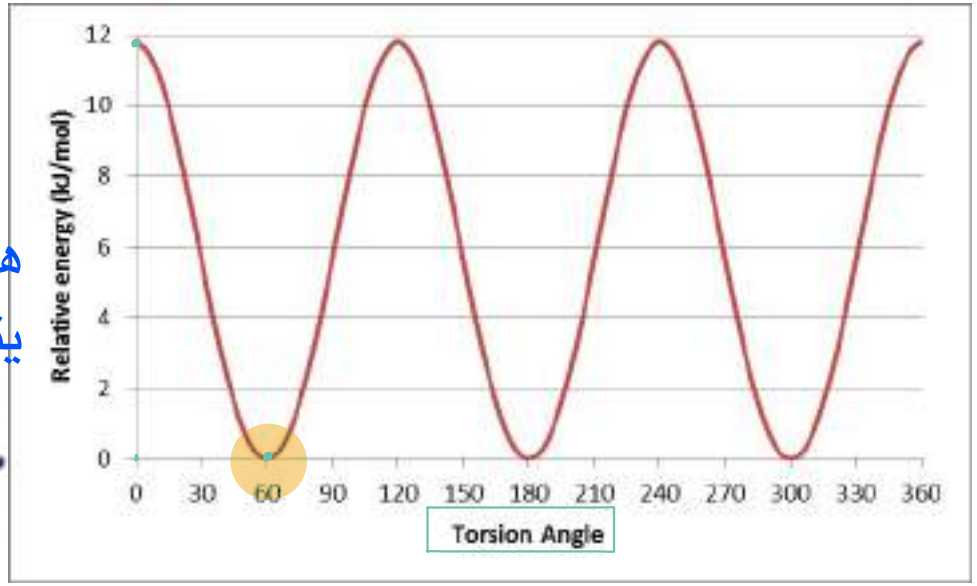
Energy $\propto \frac{1}{\text{Stability}}$

تناسب عكسي

These two extremes represent high and low energy "conformations" of ethane. The "high" E is the eclipsed and low E the staggered.

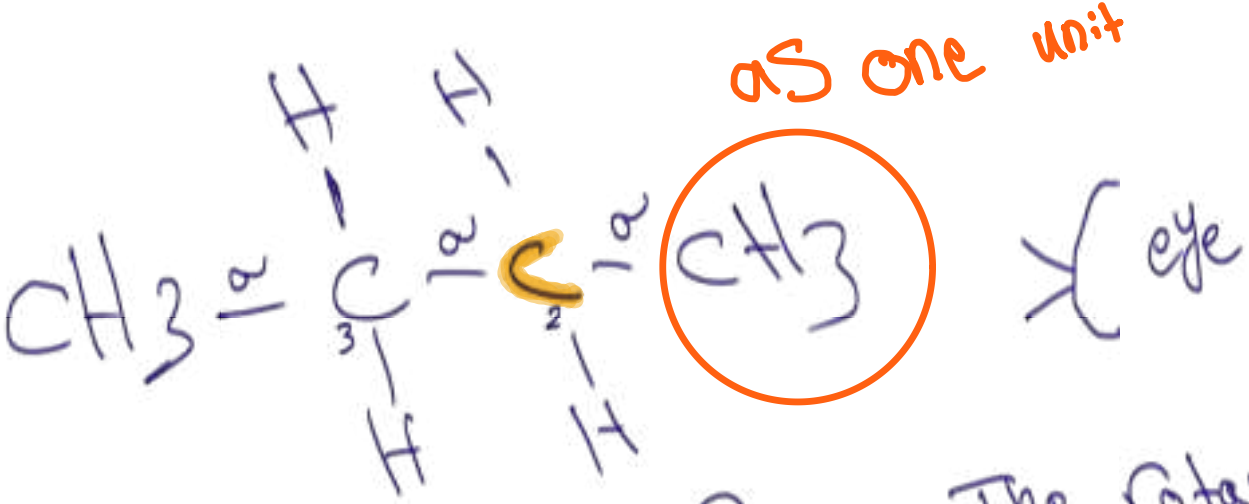
"Torsional Strain"





هل الايثان ال staggred دائما staggered أم ممكن يتحول إلى eclipsed والعكس ؟

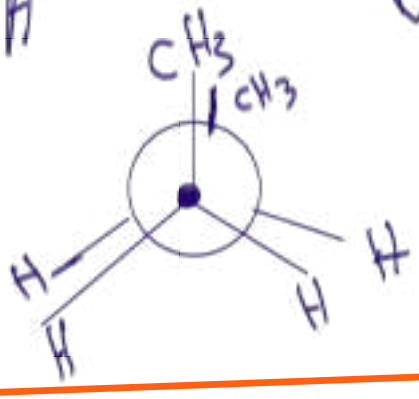
نعم يمكن خلال ٥ فرق الطاقة بين ال conformers قليلة لذلك يمكن أن يكتسب ال conformer الأكثر استقراراً (الأقل طاقة) الطاقة ويصبح أقل استقراراً (أعلى طاقة). والعكس صحيح.

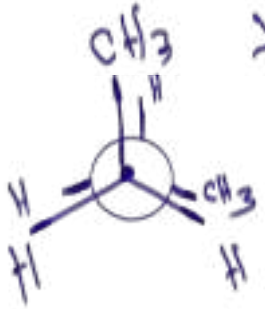


A vs. B

The rotamer A is less stable than B because the Repulsion between $CH_3 \times CH_3$ is more than between $CH_3 \times H$

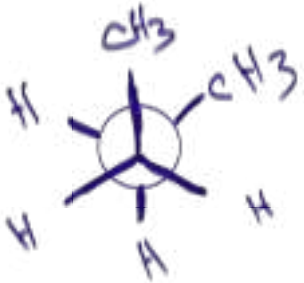
In case $\theta = 0$

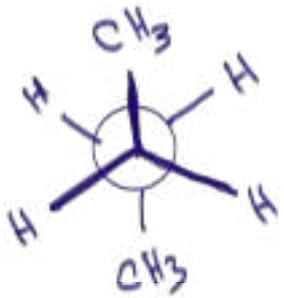




C vs. D

In case $\theta = 60^\circ$





Order of the four conformers in terms of stability

D > C > B > A

While accoriding the energy

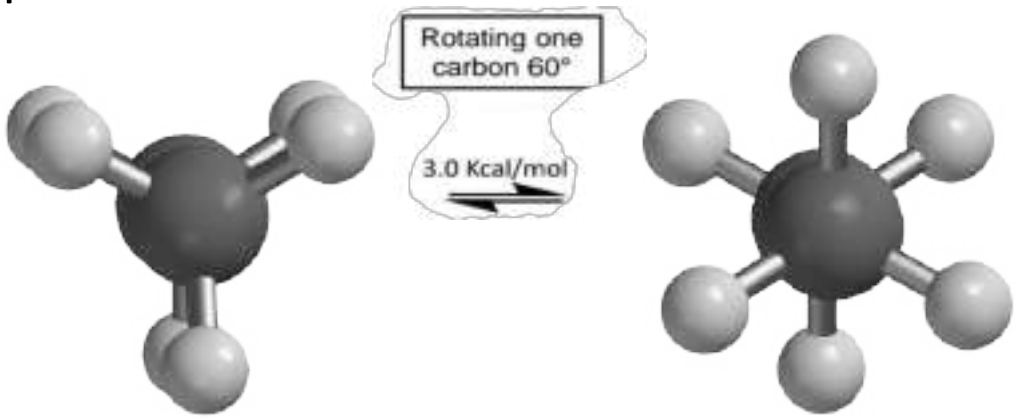
A > B > C > D

D أكثر استقراراً من C

Conformational Isomers (cont'd)

The difference in energy is caused by "**steric**" interactions between the H atoms. Steric interactions are repulsions caused when two atoms are too close together in space and their valence shell electrons repel each other.

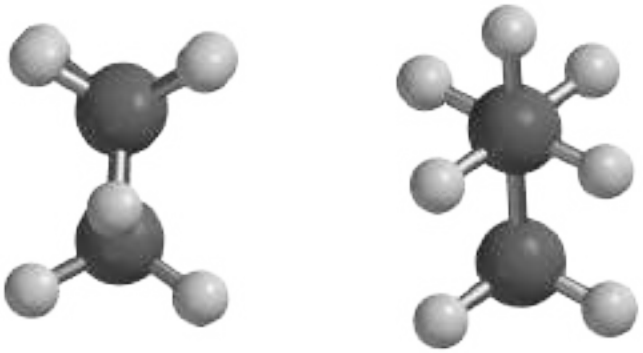
Steric effect
المعوقة الفراغية



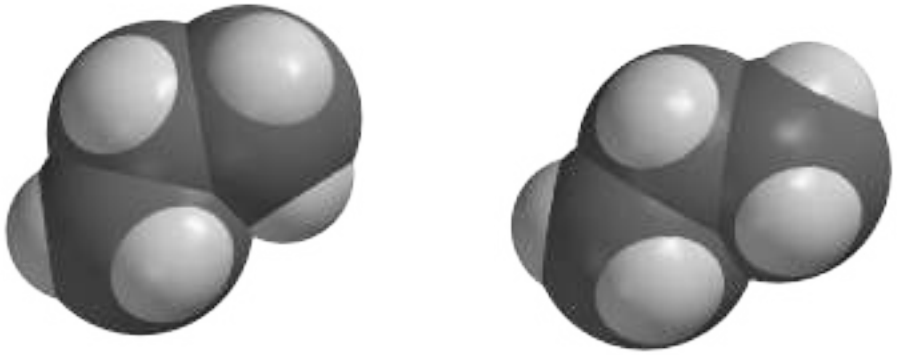
The H – H distance in the eclipsed is 2.36 Å and 2.54 Å in the staggered.

Conformational Isomers (cont'd)

The problem is worse in propane as a methyl group is larger than a H atom. The eclipsed is on the left in both sets of images.



ball & stick



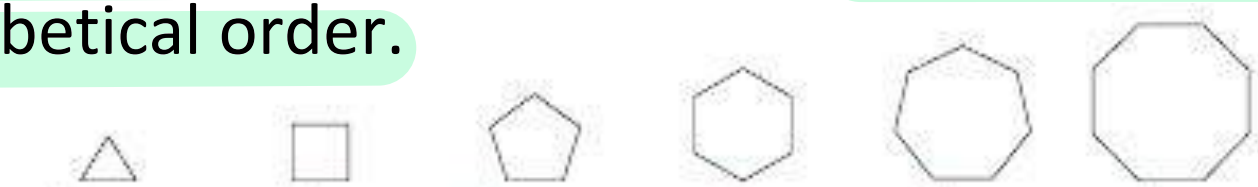
space filling

Alkanes

C_nH_{2n+2}

Cycloalkanes

- General formula C_nH_{2n}
  - Five- and six-membered rings are the most common.
- Structure and nomenclature
  - Prefix the name of the corresponding open-chain alkane with **cyclo**-, name each substituent on the ring.
  - If only one substituent, no need to give it a number.
  - If two substituents, number the ring from the substituent of lower alphabetical order.
  - If three or more substituents, number the ring to give them the lowest set of numbers, and then list them in alphabetical order.



3c

cyclopropane
bp −32.7°C

cyclobutane
bp 12°C

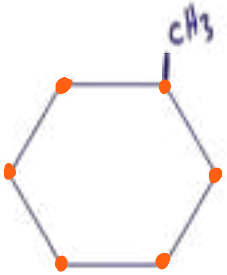
cyclopentane
bp 49.3°C

cyclohexane
bp 80.7°C

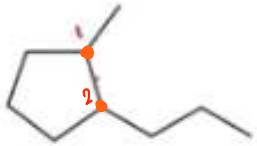
cycloheptane
bp 118.5°C

cyclooctane
bp 149°C

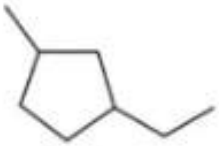
The simplest cycloalkane



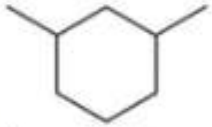
Methylcyclohexane



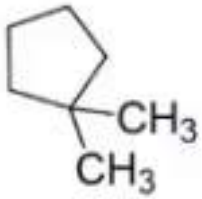
1-Methyl-2-propylcyclopentane



1-Ethyl-3-methylcyclopentane

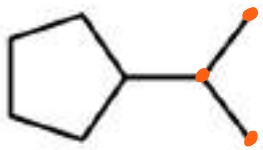


1,3-dimethylcyclohexane

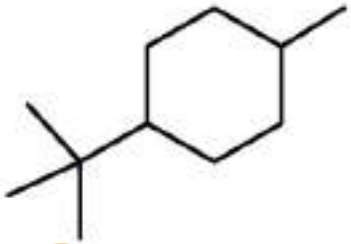


1,1-dimethylcyclopentane

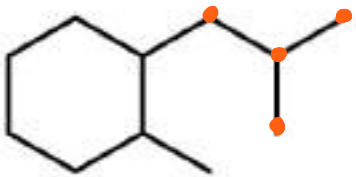
- examples:



Isopropylcyclopentane



1-*tert*-Butyl-4-methyl-cyclohexane



1-Isobutyl-2-methyl-cyclohexane

1-Ethyl-1-methyl-cyclopropane

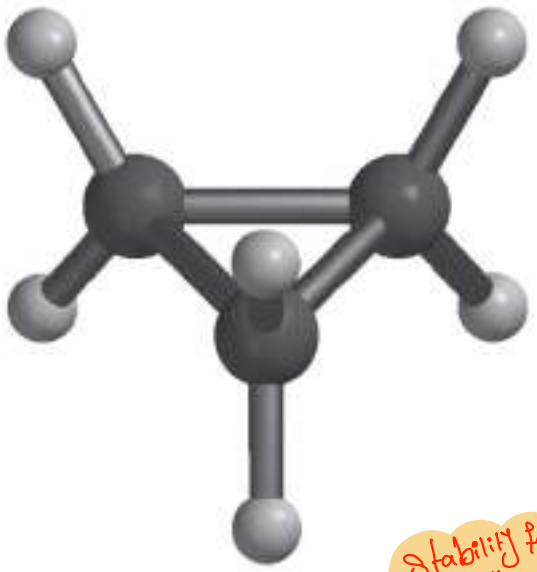
Cycloalkanes

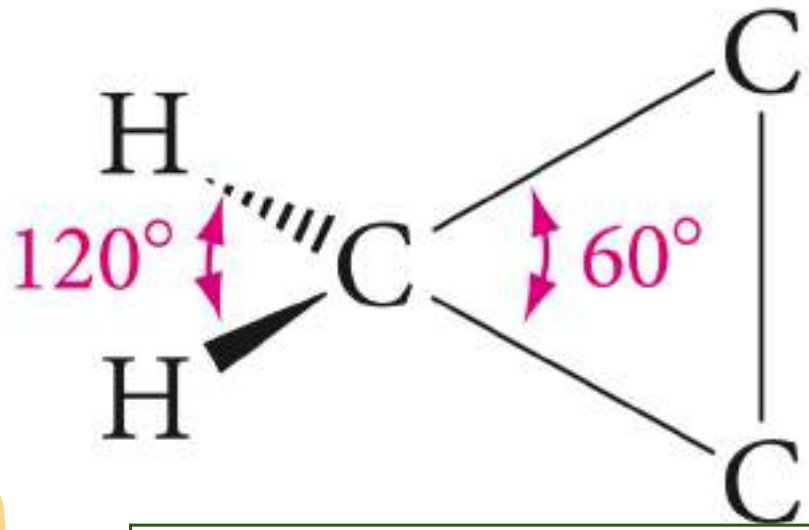
cyclopropane – is the smallest ring structure possible.

- It is rigid and very highly strained (توتر) as the bond angles (60°) are distorted from ideals (109.5°)
- It is more reactive than a linear alkane as the strained C-C bonds are easier to break (angle strain)

* cyclopropane is the most reactive cycloalkane.

↑reactive ↓stability ↑Energy





* No rotation here *

Stability for cycloalkanes is less than alkanes because the ring strain is high.

↑ Ring strain = Angle + Torsional

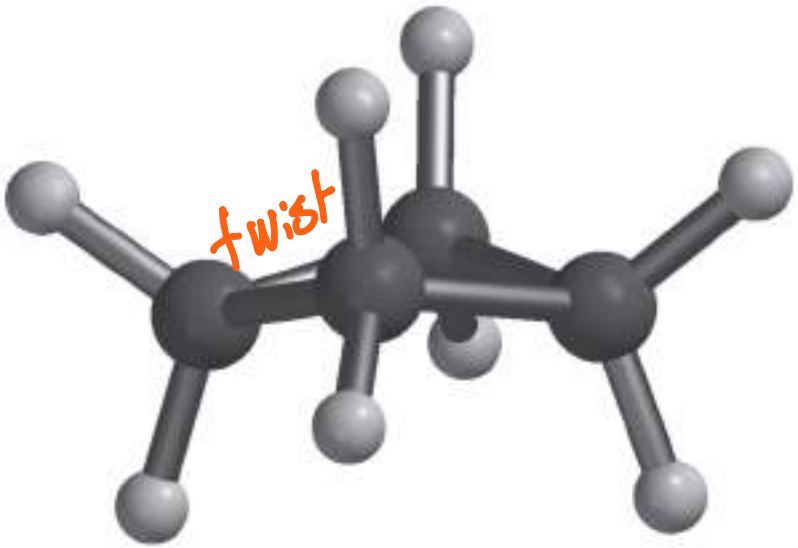
Cycloalkanes

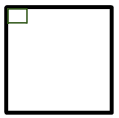
cyclopropane أكثر استقرارًا من

flexibility ∝ Stability

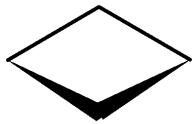
cyclobutane – “puckered” conformation

- It is more flexible than cyclopropane and is not flat although it is commonly drawn that way.
- It is more reactive than a linear alkane as the strained C-C bonds are easier to break, bond angle ~90°





common

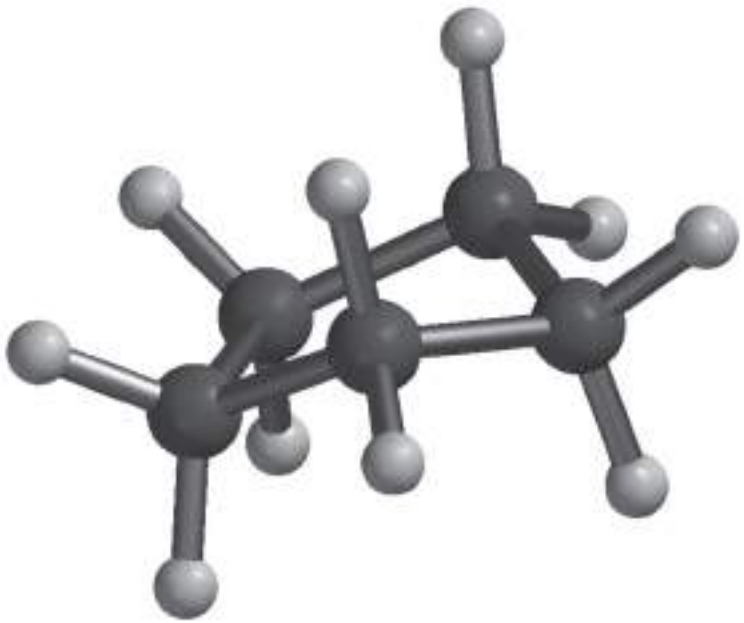


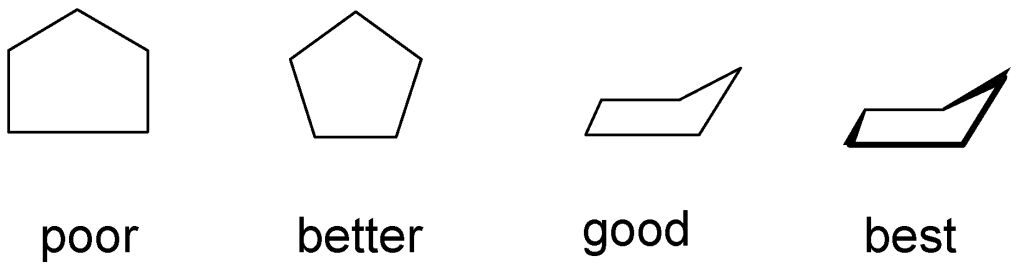
better

Cycloalkanes

cyclopentane – "envelope" conformation

- It is more flexible than cyclobutane and bond angle are ~105°, and less strained





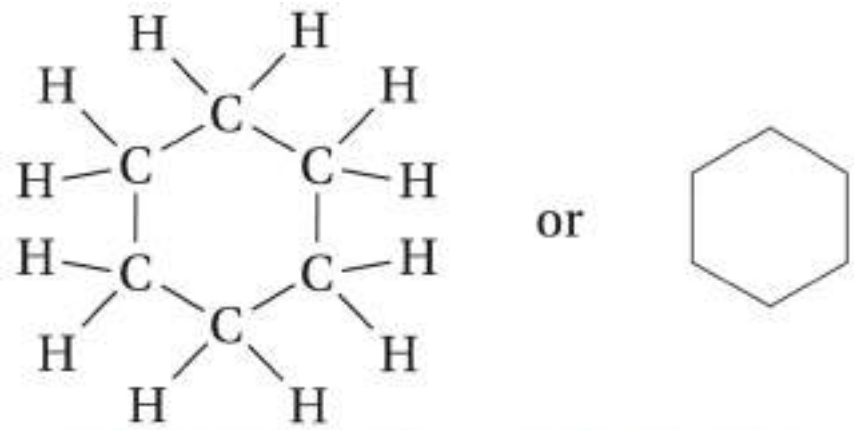
Cycloalkanes

The most stable cycloalkane.

cyclohexane – "chair"

- It is highly flexible and can adopt a strain free non-planar conformation with bond angle of 109.5°
- It is very common in nature so understanding its conformations is important.

Although commonly drawn as a hexagon, implying a flat six-membered ring this is not the common conformation seen.

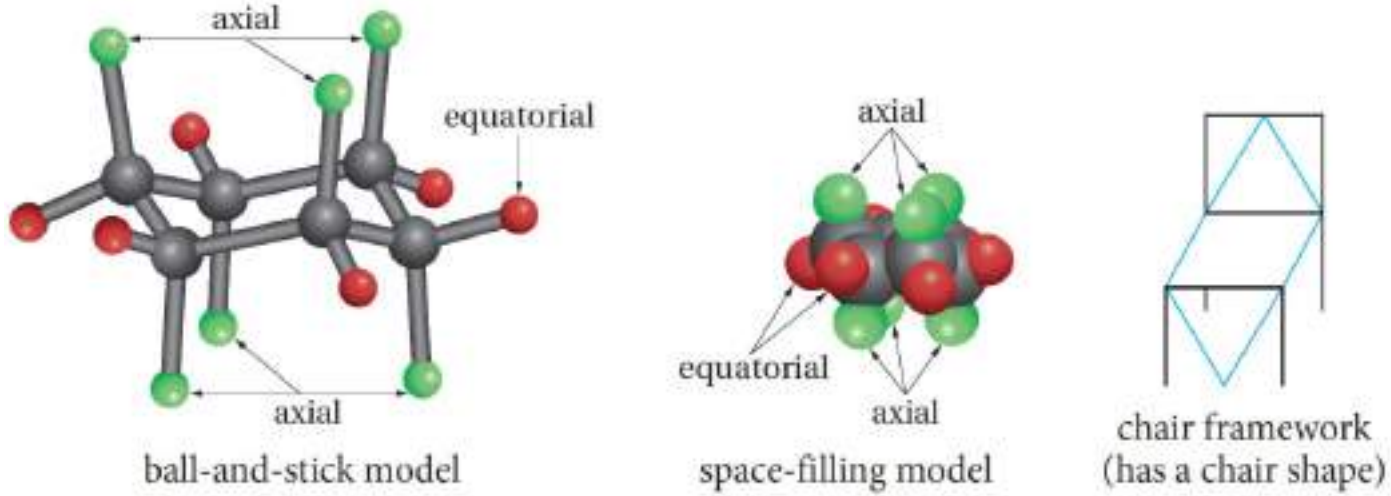


Structural and abbreviated structural formulas for cyclohexane

Ring strain free.

Cyclohexane cont'd:

The most common conformation of cyclohexane is the "chair" conformation. In this geometry the C bonds are all ~109.5° as opposed to the 120° in a planar structure.

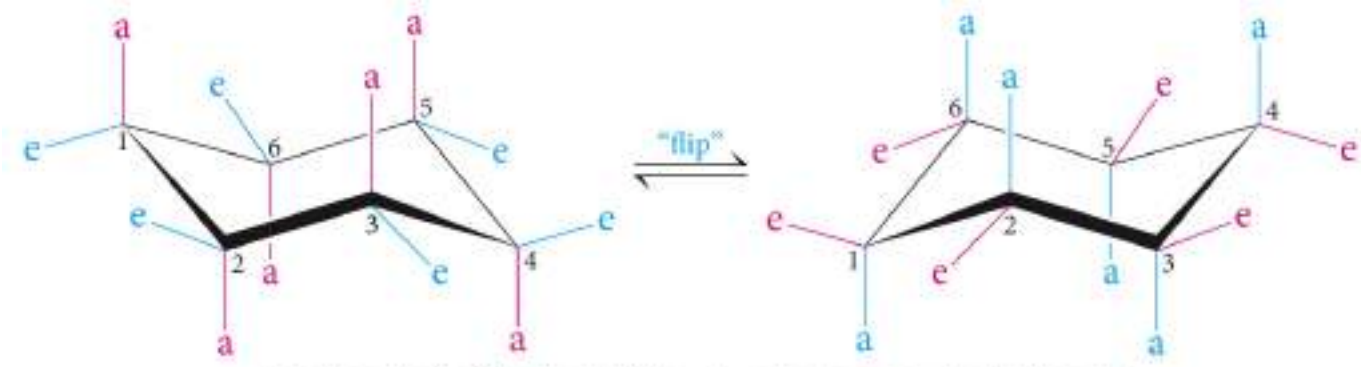


This structure creates two subsets of hydrogen atoms, those lying in the same plane as the C atoms, the equatorial H and those lying above and below that plane, the axial H atoms

Cyclohexane cont'd:

Cyclohexane cont'd:

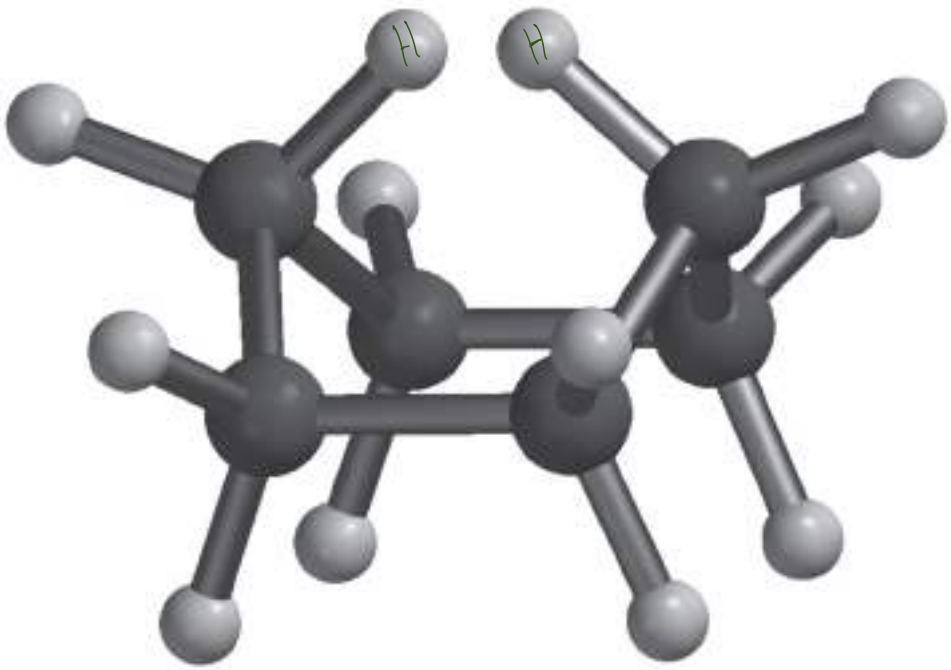
Since the C-C bonds are all single (σ) bonds, it is possible to rotate about these bonds. This process in known as a ring inversion or a "chair-chair" flip. In the process of the inversion all equatorial H become axial and axial become equatorial.

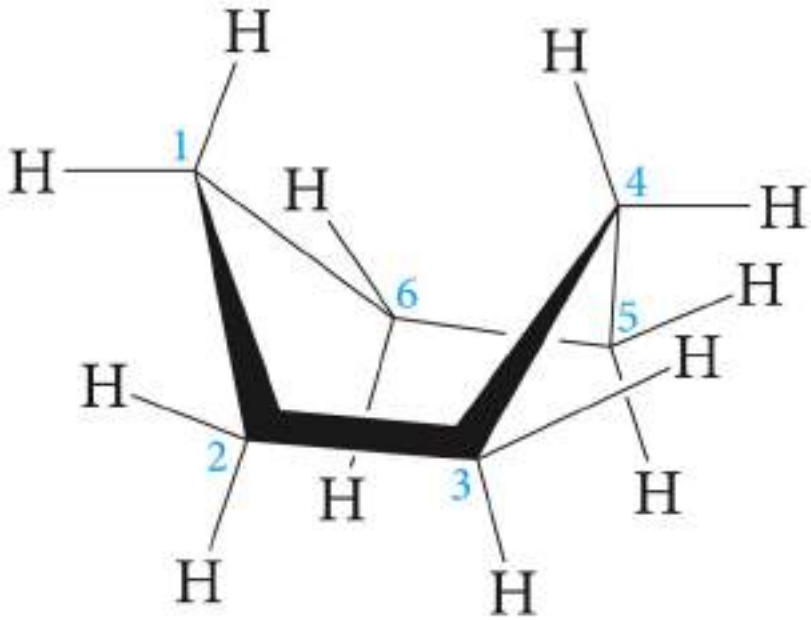


Axial bonds (red) in the left structure become equatorial bonds (red) in the right structure when the ring "flips."

Cyclohexane cont'd:

Other conformations of cyclohexane are possible but they are higher in energy and less stable, i.e. the "boat" conformation



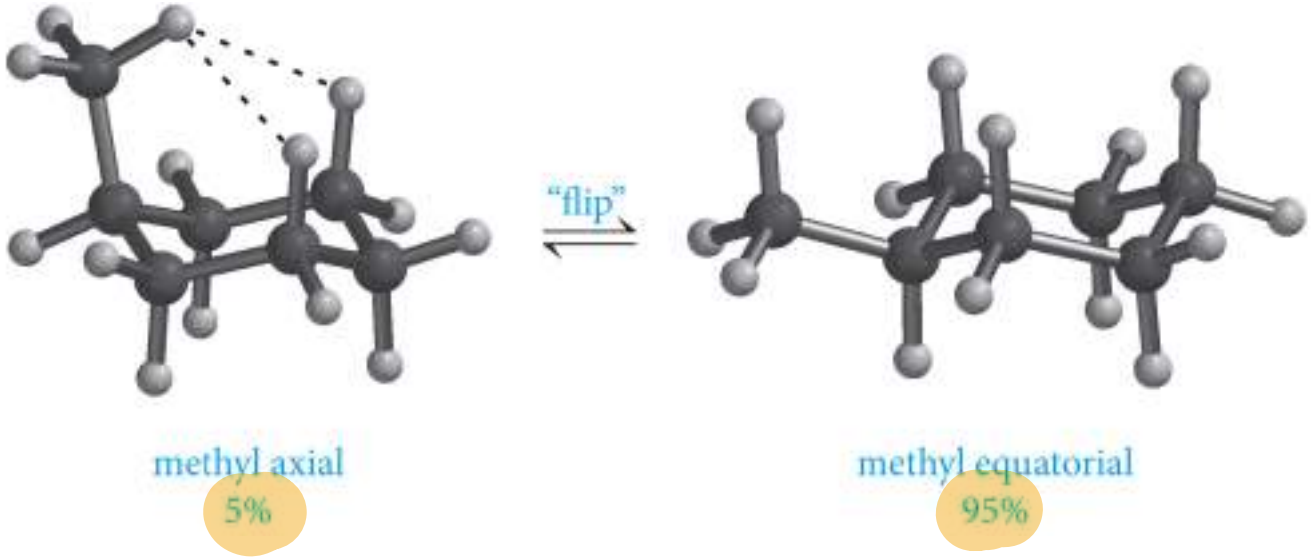


boat cyclohexane

Cyclohexane cont'd:

Substituted cyclohexane:

The addition of a methyl group on cyclohexane (methylcyclohexane) can have two conformations, the methyl can be axial or equatorial, i.e.



The equatorial is preferred as there is significantly less steric interactions than when in the axial position. This will be true for any group on a cyclohexane ring and has implications for the chemical reactivity of the compound.

Geometric Isomers

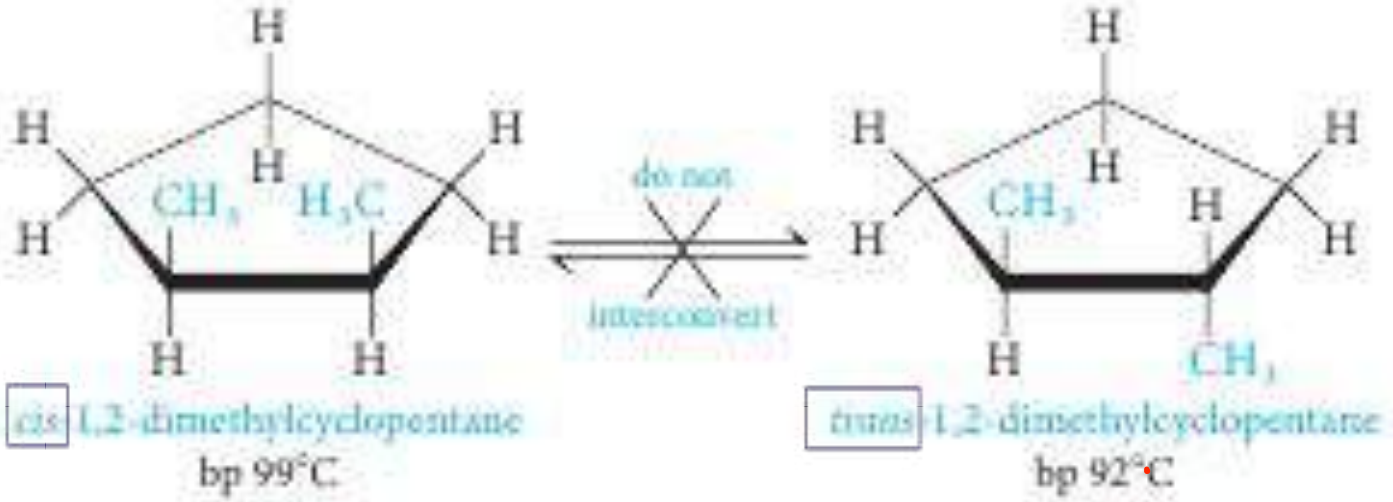
Stereoisomerism deals with molecules that have the same order of attachment of the atoms, but different arrangements of the atoms in space.

Geometric isomers (configurational isomers, or diastereomers, a subset of stereoisomers) are molecules which have the same chemical formula, the atoms are bonded in the same order, but located in different positions in space.

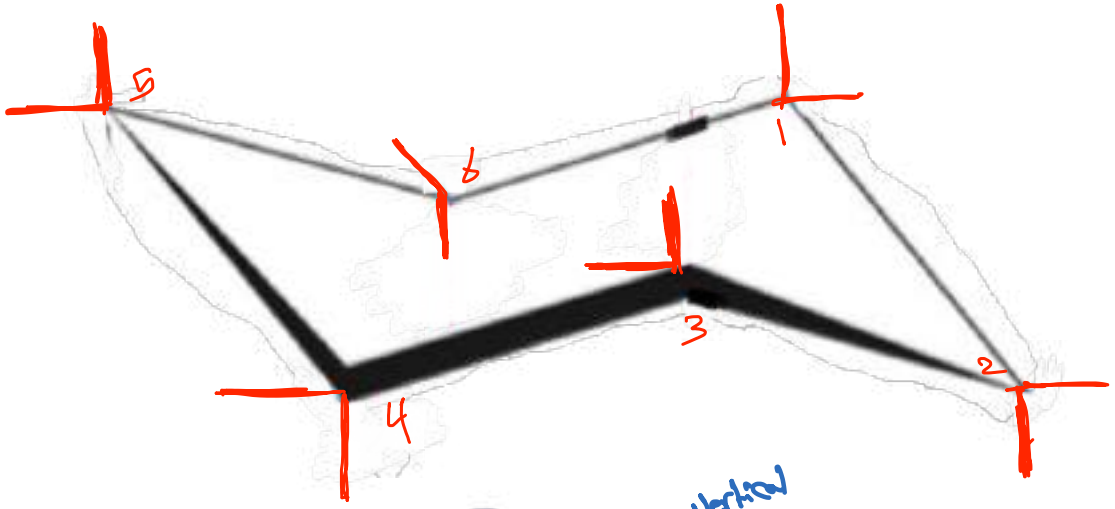
chapter لا
مستقل
لاحقًا

Cis–trans isomers = Geometric Isomers

An example of this is 1,2-dimethylcyclopentane



This structures can not interconvert without breaking a C-C bond.



ذرة الكربون رقم 1 ⌊ vertical / horizontal نفس رقم 3 ، 5

ذرة الكربون رقم 2 ⌈ نفس رقم 4 ، 6 .

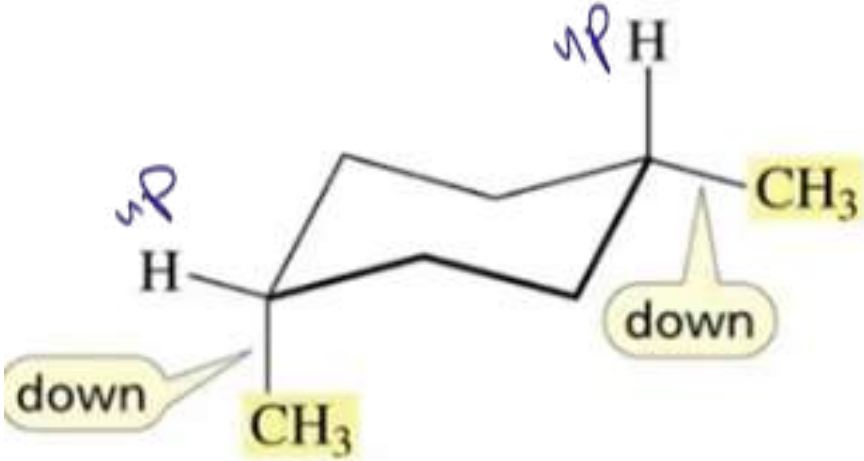
بحيث يكون مجموع التفرعات 12 .

$\boxed{6}$ للأسفل والأعلى (بالتساوي 3 لأعلى و 3 لأسفل) "Axial"

$\boxed{6}$ لليمين واليسار "Equatorial"

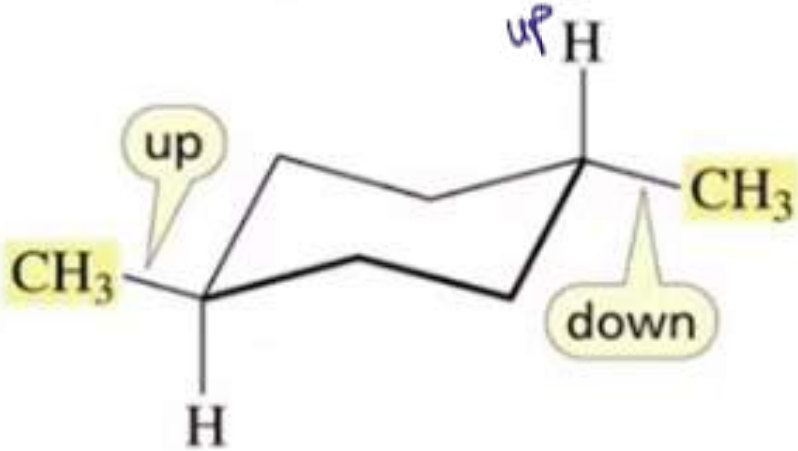
Cis and Trans Isomers

two methyl groups are on the same side of the ring

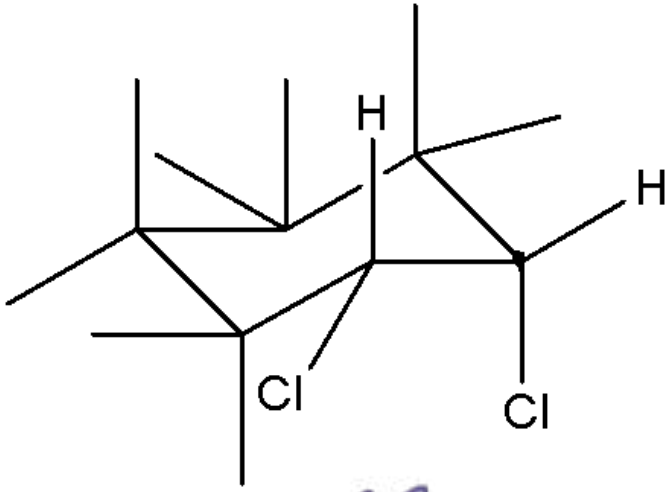


cis-1,4-dimethylcyclohexane

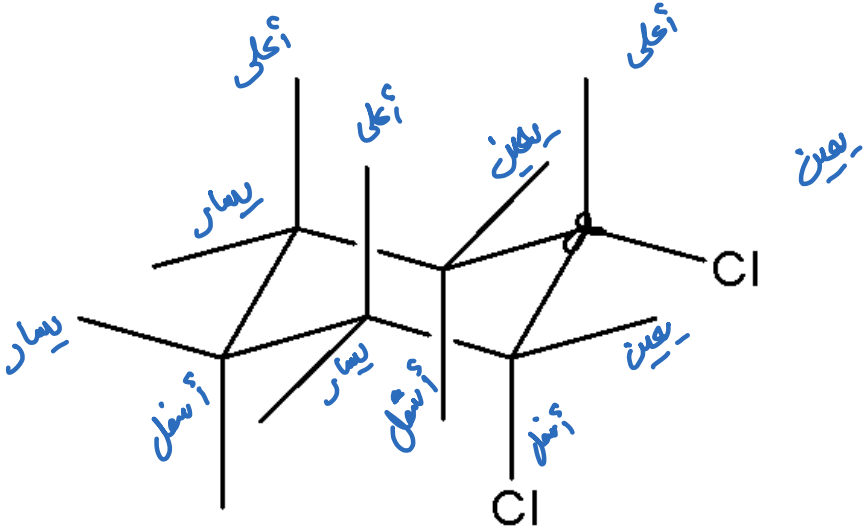
two methyl groups are on opposite sides of the ring



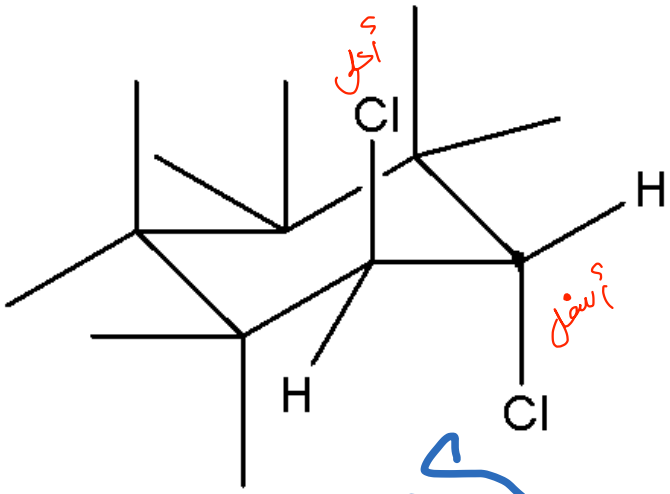
trans-1,4-dimethylcyclohexane



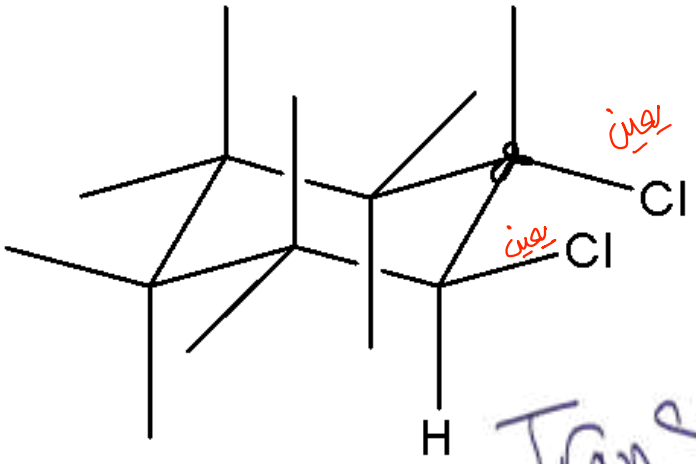
cis



cis

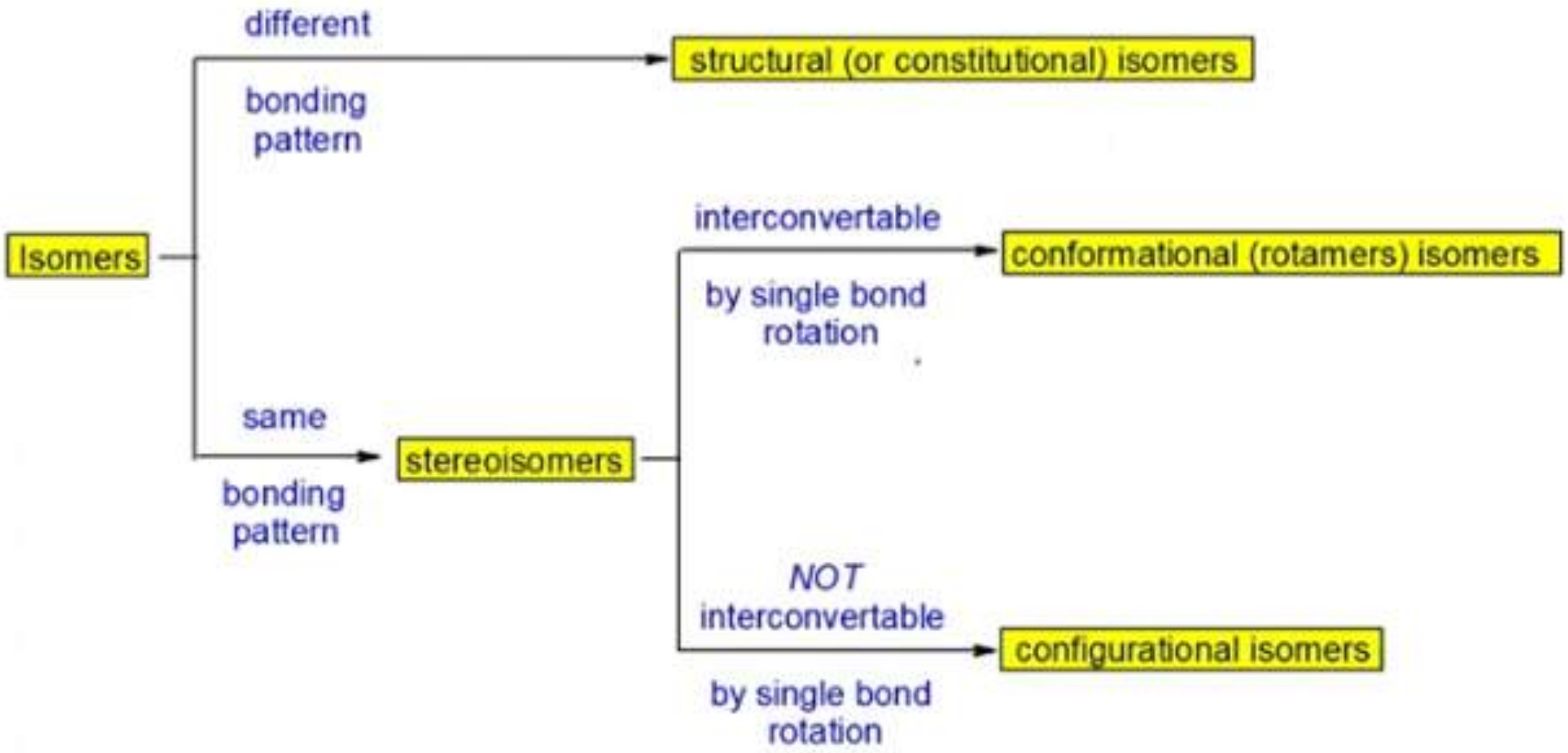


trans



Trans

Summary of Isomers (to date)



Chemical Reactions of Alkanes

In general, because of their strong non-polar covalent bonds alkanes are fairly inert. They do not react with most common acids, bases, oxidizing or reducing reagents. They means they do make good solvents for extraction, recrystallization or as a reaction solvent. They do however have two substances they react with; molecular oxygen and halogens.

Oxidation Reactions

All chemical processes are redox (oxidation / reduction) reactions. Formally oxidation is the loss of electrons (increase in oxidation sate) and reduction the gain of electrons (decrease in oxidation sate). The two processes are coupled since whatever gains the electrons must gain them from somewhere and whatever loses the electrons must lose them to somewhere.

Oxidation Reactions (cont'd)

For the C atom, oxidation involves increasing the number of C-O (or other atoms more EN than C) bonds and/or decreasing the number of C-H bonds.

Reduction will be the opposite, a decrease in the number of C-O bonds or increase in the number of C-H bonds.

Oxidation and combustion

The most import use of alkanes is as a fuel. The light weight ones are gases and intermediate weight liquids which makes them handy for storage and transportation. Natural gas is composed primarily of methane with varying amounts of ethane, propane and butanes. It is commonly used to heat homes. The liquid hydrocarbons are used as gasoline, kerosene and jet fuels.

التأكسد : زيادة في المحتوى الأكسجيني أو نقصان في المحتوى الهيدروجيني

Oxidation Reactions (cont'd)

The energy of the hydrocarbon is released when combusted or burned. This is an oxidation process and requires atmospheric oxygen. The final oxidation product (assuming sufficient oxygen) is carbon dioxide.

+ heat

gives us heat

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \Delta H^\circ = \boxed{-}886\ \text{kJ/mol}(-212\ \text{kcal/mol})$$

Methane

$$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O \qquad \Delta H^\circ = -2{,}220\ \text{kJ/mol}(-530\ \text{kcal/mol})$$

Propane

$$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4\,CO_2 + H_2O + \text{Heat}$$

الألكانات هلجنة

Halogenation of Alkanes

Besides combustion, the only other useful chemical reaction that alkanes undergo is halogenation.

This is a free radical process in which heat or light is used to break a halide-halide bond forming two halide free radicals.

Halogenation of Alkanes (cont'd)

This type of reaction is a *substitution reaction* where a halide atom is substituted for a H atom in the alkane.

Br_2 و Cl_2 يمثل X_2

$$R{-}H + X_2 \xrightarrow[\text{or light}]{\text{heat}} R{-}X + H{-}X \quad (X = Cl, Br)$$

The two common halides used are chlorine and bromine.

$$CH_4 + Cl_2 \xrightarrow[\text{light}]{\Delta} CH_3Cl + HCl$$

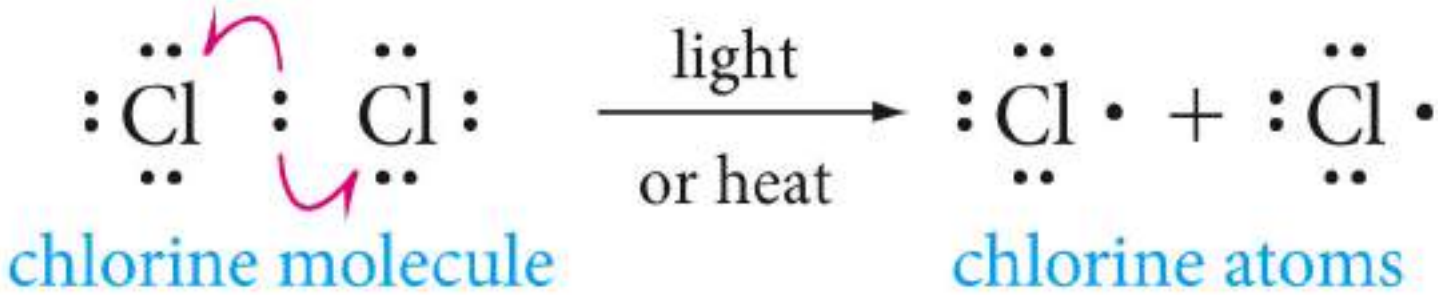
محذوف

Halogenation of Alkanes (cont'd)

The process involves three steps:

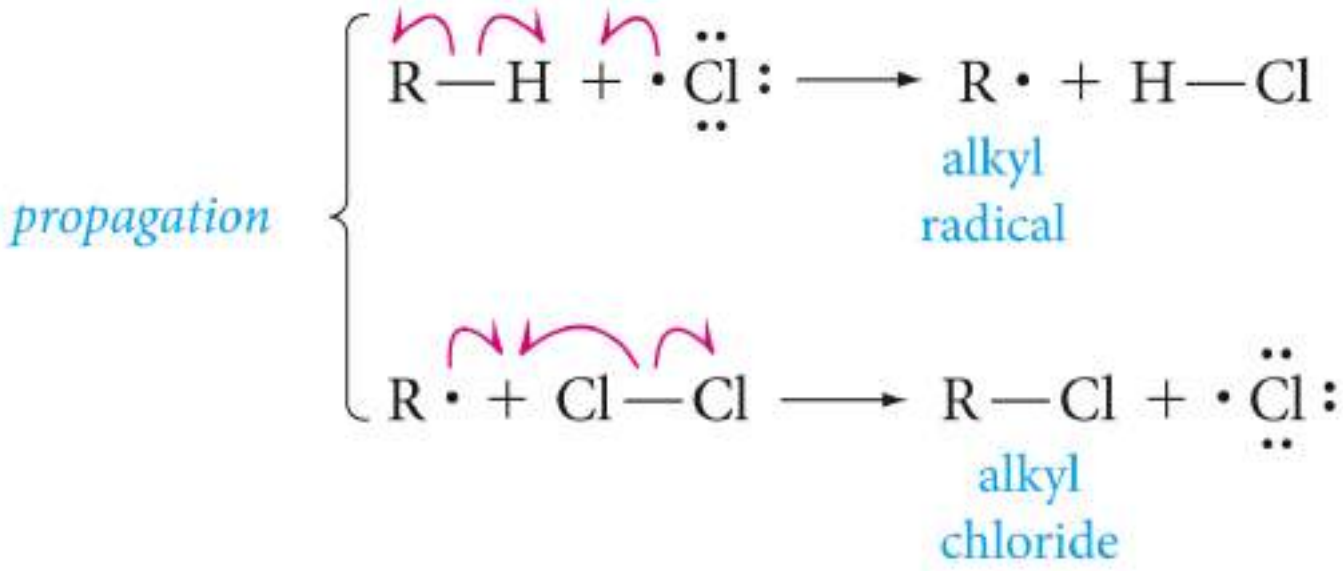
1. initiation: this is where the free radical is formed: note we generate 2 free radical atoms in this process.

initiation



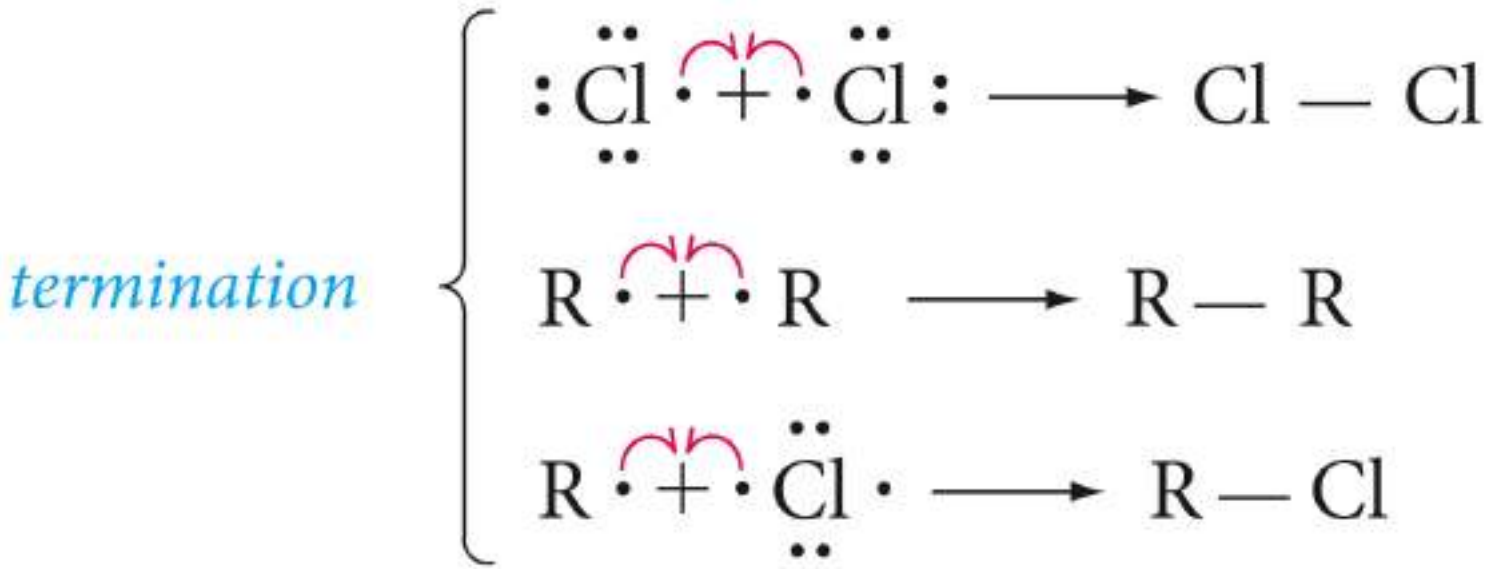
Halogenation of Alkanes (cont'd)

2. Propagation: this is where the halide free radical reacts with the hydrocarbon, extracting a H atom, generating an intermediate C radical, and then adding a halide atom. This process can repeat many times depending on the amount of halide radical available.



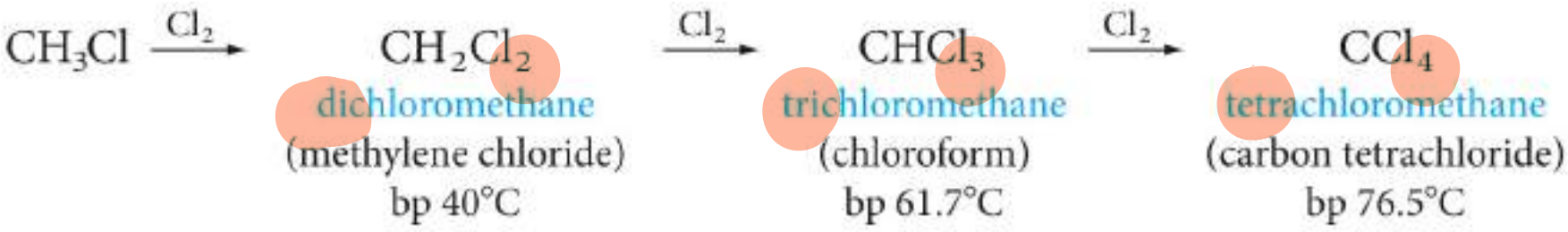
Halogenation of Alkanes (cont'd)

3. Termination: this is the final step where the remaining free radicals are consumed. It can involve the halide radical reacting with another halide radical, a carbon radical or two carbon radicals combining.



Halogenation of Alkanes (cont'd)

A single alkane molecule can undergo several substitution steps depending on the concentration of the halide radical, i.e.



As a matter of fact, unless the concentration of chlorine is kept quite low there will be a mixture of these produces.