Chapter 2

Alkanes and Cycloalkanes

Conformational

and

Geometrical Isomerism

Hydrocarbons :

Compounds which contain only **C** and **H**

1- Saturated hydrocarbons : contain only *single* bonds

(alkanes + cycloalkanes)

2- Unsaturated hydrocarbons : contain carbon-carbon multiple bonds

(*double*, *triple*) bonds

(alkenes + alkynes)

3- Aromatic hydrocarbons : special class of cyclic compounds

related to benzene (chapter 4)

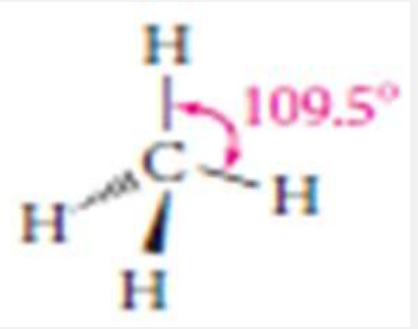
Alkanes :

Saturated Hydrocarbons containing only single bonds (C-C and C-H).

General formula: Acyclic (C_nH_{2n+2})

Cyclic (C_nH_{2n})

Simplest alkane : methane, tetrahedral structure (sp_3):



normal alkanes (***n*-alkanes**)**:** straight chains (contineous, unbranched).

Each member of this homologous series differs from next member by a (**-CH_2-**) group (**methylene group**)

PROBLEM 2.2: Which of the following is an alkane, or cycloalkane?

a- C_7H_{16} b- C_7H_{12} c- C_8H_{16} d- $C_{29}H_{60}$

Table 2.1 Names and Formulas of the First Ten Unbranched Alkanes

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

Nomenclature (Naming):

1- Common names : based on source or use of compound

Examples: limonene (lemon), *α*-pinene (pine trees) , caffeine…..

2- IUPAC names (by **I**nternational **U**nion of **P**ure and **A**pplied **C**hemistry)

IUPAC Name : **prefix** + **root name** + **suffix (ending)**

> **prefix** : substituents (branches or groups replacing H atoms)

> **root name :** name of longest carbon chain

> **suffix :** class or family (functional group)

IUPAC naming of alkanes:

1- Unbranched Alkanes : Have only **one** unbranched chain.

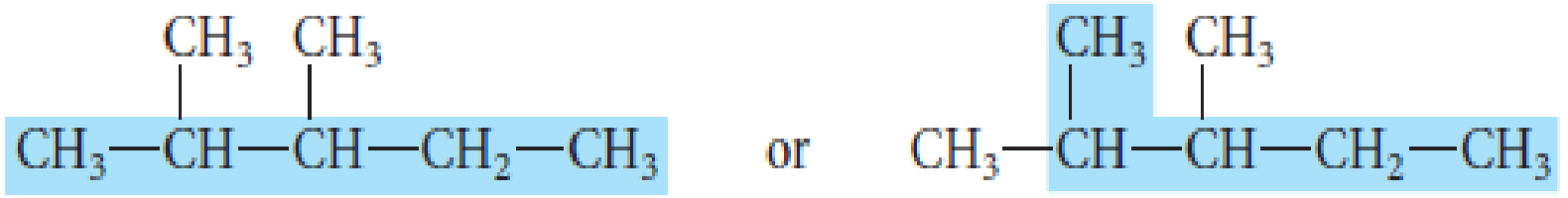
Name indicates the **number** of C atoms + **ane** (ending)

Common Names : n-alkanes (Table 2.1).

2- Branched Alkanes : **prefix** (substituents) + **root name** (longest chain) + **ane**

Only few of them have Common Names

Example:



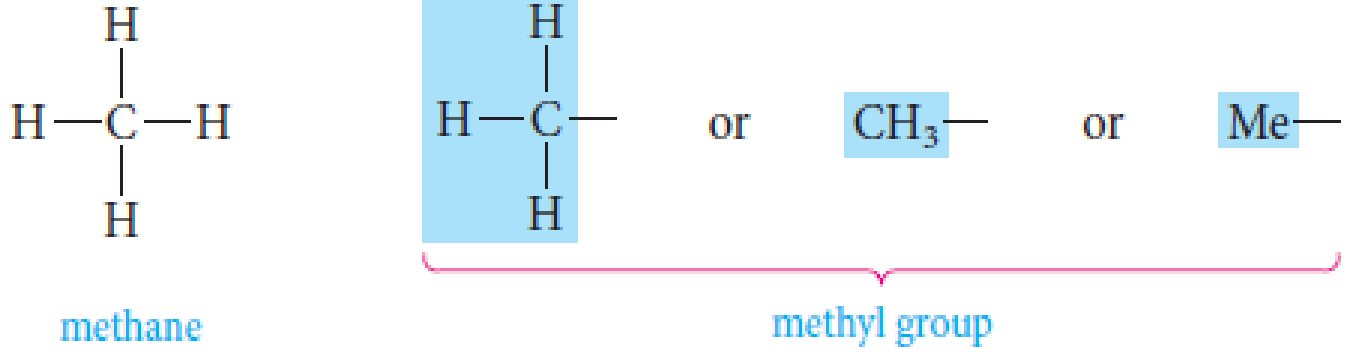
Parent Chain : Has **5 C** atoms (longest continous chain - two ends)**.**

So name is derived from ***pent*ane.**

Since it has additional groups, it is a **substituted** pentane.

Substituents : Any branch or group (other than H) on parent chain:

Alkyl groups : -CH3 (methyl); - CH2-CH3 (ethyl); ……etc.



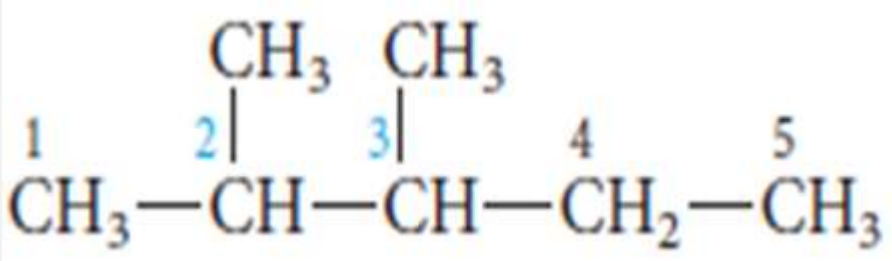
Prefix: indicates position (by number) + name of substituent.

For identical substituents : **di** (2), **tri** (3), **tetra** (4), **penta** (5), **hexa** (6), **hepta** (7), **octa** (8), **nona** (9), **deca** (10)…etc.

Punctuation : IUPAC name written as one word, without spaces.

Numbers separated by commas (**,**)

Numbers separated from letters by hyphens (**-**).

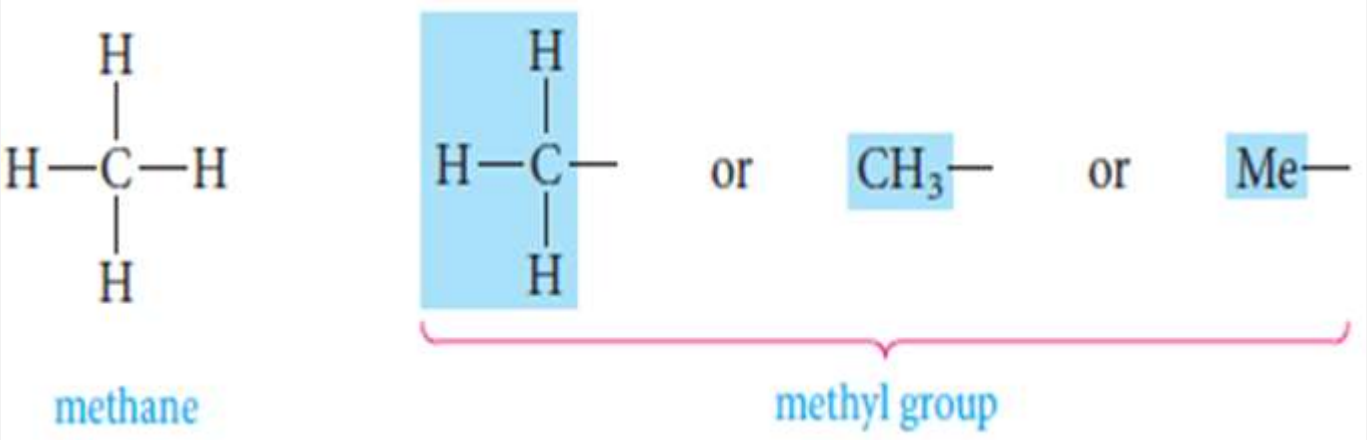


2,3-Dimethylpentane (one word)

Substituents : Groups attached to the main chain.

Saturated substituents that contain only C and H are called **alkyl groups** (methyl, ethyl. Propyl…..).

R **:** is general symbol for alkyl group.



> Main (parent) chain numbered starting from the end **nearest** to a substituent.

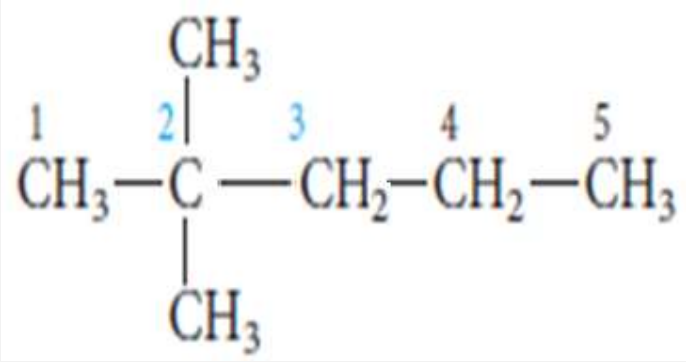
> **2**, **3**,or **4** identical groups indicated by : ***di-***, ***tri-***, or ***tetra-***

> Same number repeated twice if 2 identical substituents are at same carbon

> Substituents listed in **alphabetic order**. Prefixes (*di*-, *tri*-) not considered

> Whole name as **one word**.

> Punctuation is important

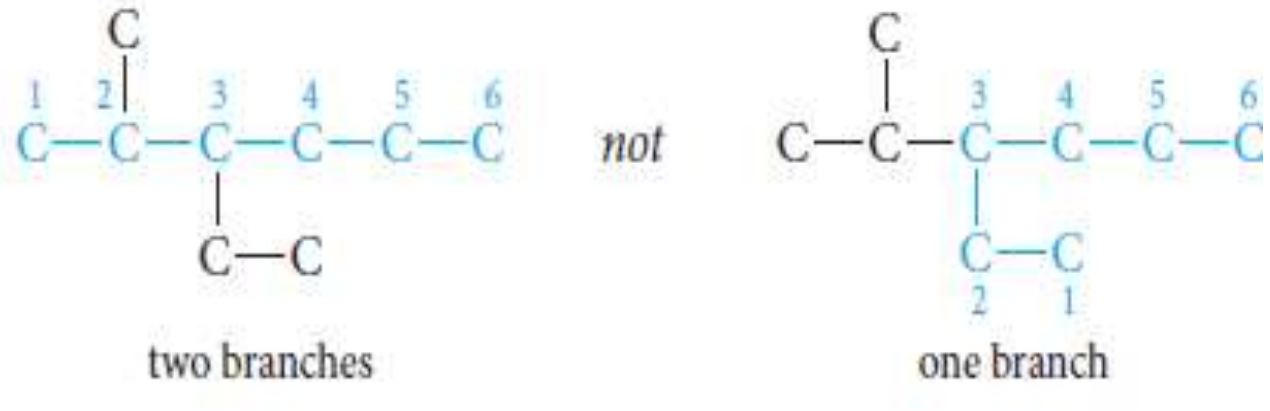


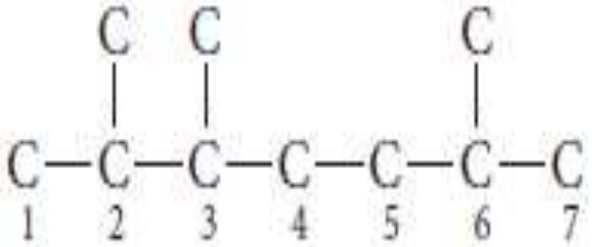
2,2-Dimethylpentane

Parent chain :
Longest chain

Numbering :
Nearest to substituent

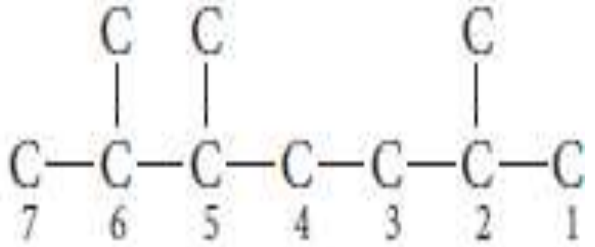
Two chains of same length:
Parent is the more branched (or more substituted) one



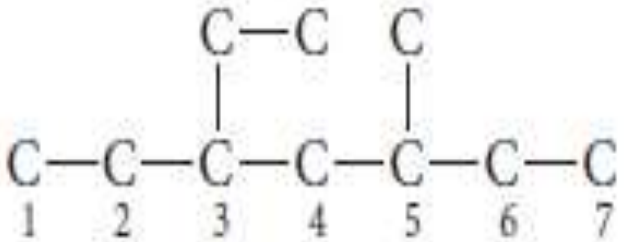


2,3,6-trimethylheptane

not

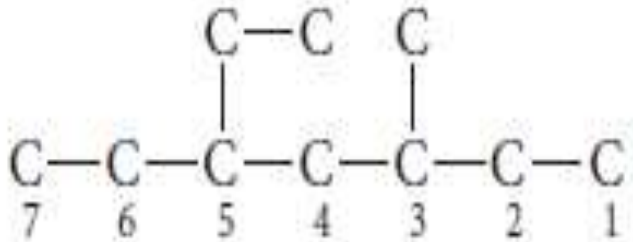


2,5,6-trimethylheptane

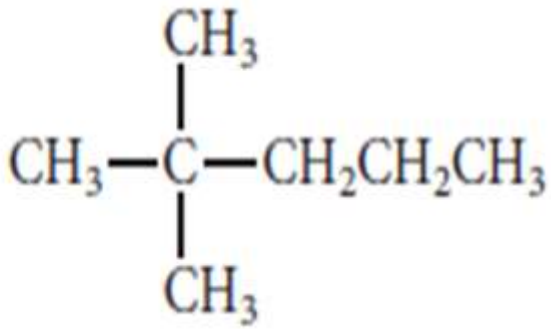


3-ethyl-5-methylheptane

not

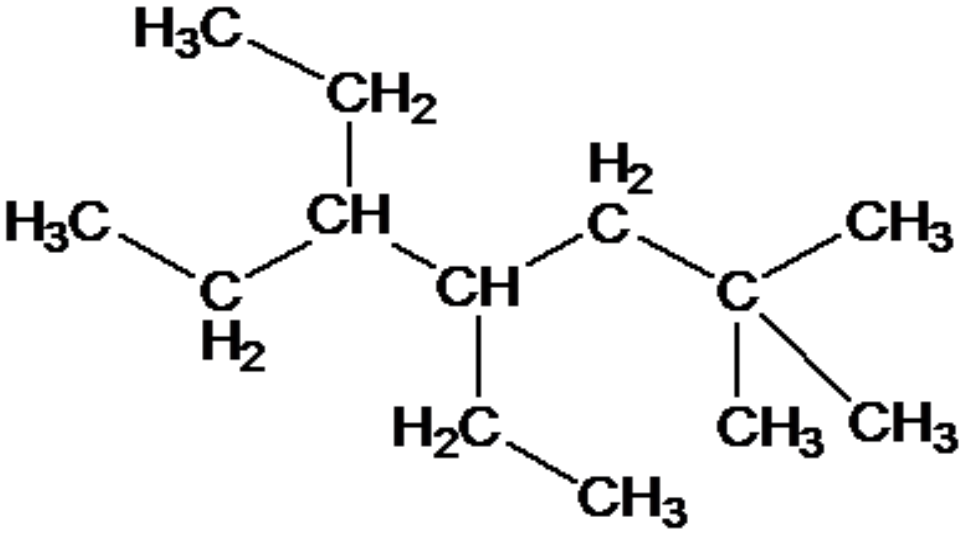


5-ethyl-3-methylheptane

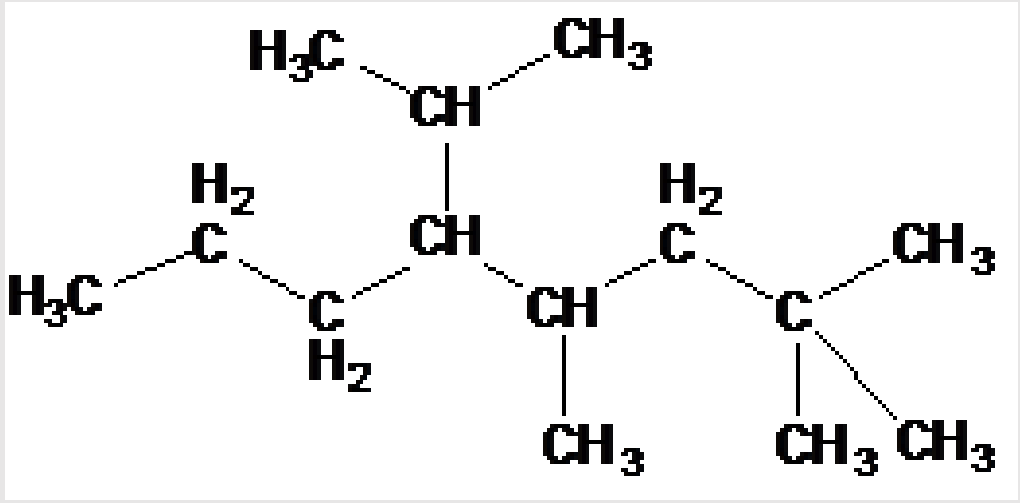
Give IUPAC name for  :

Answer : 2,2-dimethylpentane

More Examples



4,5-diethyl-2,2-dimethylheptane

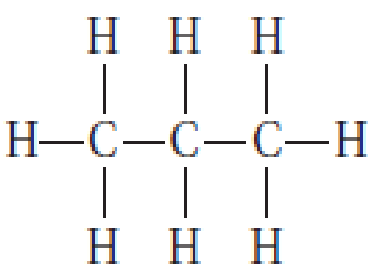


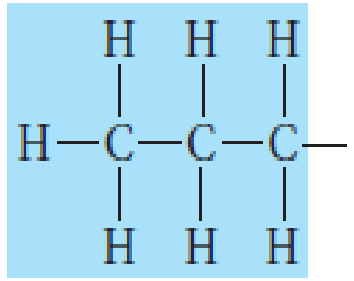
5-(1-methylethyl)-2,2,4-trimethyloctane

Alkyl and Halogen Substituents :

CH_3CH_3 CH_3CH_2- or C_2H_5- or Et—

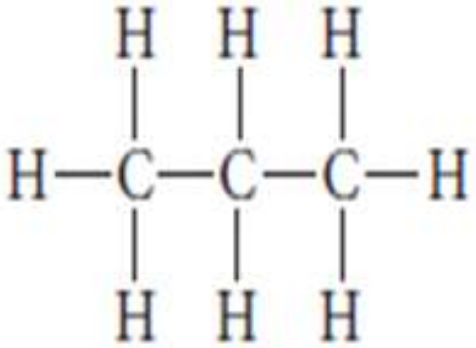
ethane ethyl group



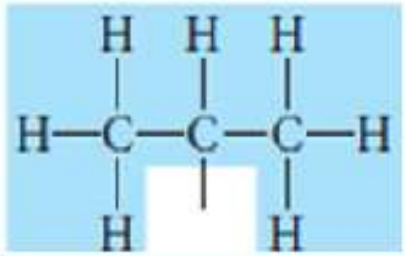


or $CH_3CH_2CH_2-$ or Pr—

propyl group

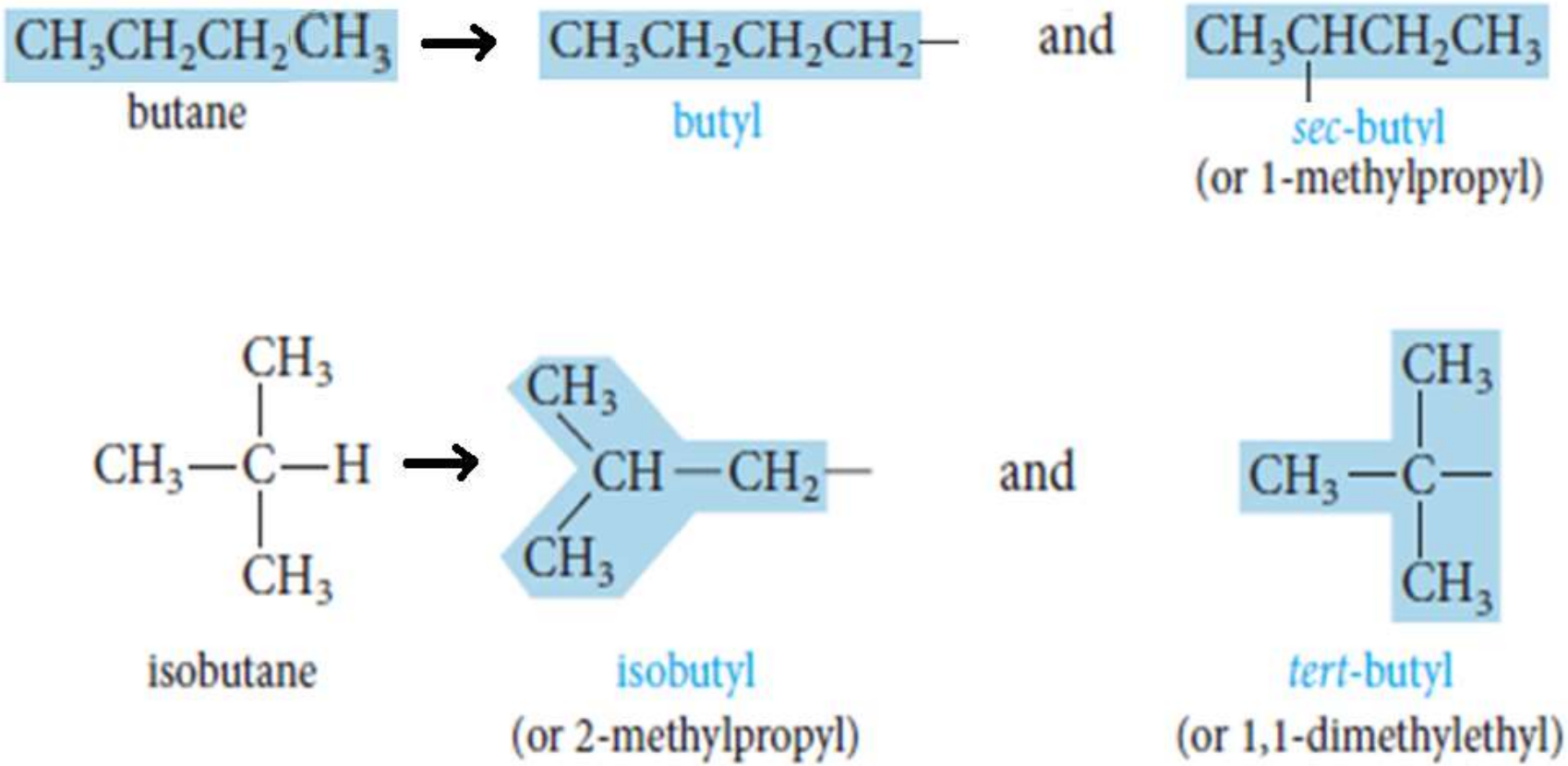


propane



or CH_3CHCH_3 or *i*-Pr—

isopropyl or 1-methylethyl

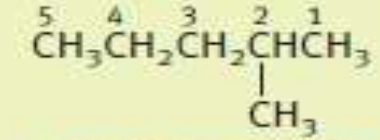
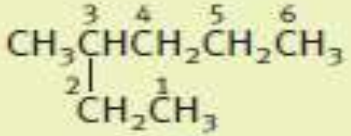
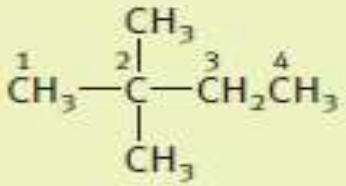
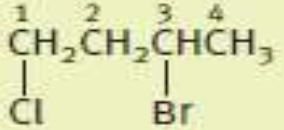


Halogen Substituents :

-F : fluoro- -Cl : chloro- -Br : bromo- -I : iodo-

2.5: Using IUPAC Rules:

Table 2.2 — Examples of Use of the IUPAC Rules

 2-methylpentane (*not* 4-methylpentane)	The ending *-ane* tells us that all the carbon–carbon bonds are single; *pent-* indicates five carbons in the longest chain. We number them from right to left, starting closest to the branch point.
 3-methylhexane (*not* 2-ethylpentane or 4-methylhexane)	This is a six-carbon saturated chain with a methyl group on the third carbon. We would usually write the structure as $CH_3CH_2CHCH_2CH_2CH_3$.
 2,2-dimethylbutane (*not* 2,2-methylbutane or 2-dimethylbutane)	There must be a number for each substituent, and the prefix *di-* says that there are two methyl substituents.
 3-bromo-1-chlorobutane (*not* 1-chloro-3-bromobutane or 2-bromo-4-chlorobutane)	First, we number the butane chain from the end closest to the first substituent. Then we name the substituents in alphabetical order, regardless of position number.

2.7: Physical properties and Intermolecular Interactions:

Alkanes are insoluble in water because water is polar, but alkanes nonpolar

Alkanes have low boiling points because they have only weak intermolecular attractive forces **(Van der Waals forces)**

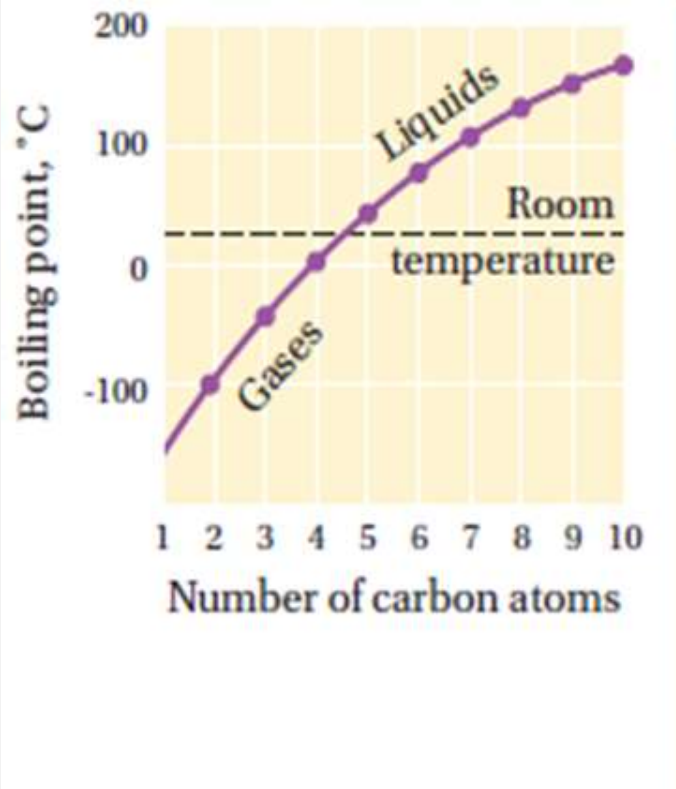
Origin of **Van der Waals forces:**

Electrons in nonpolar molecules can become temporarily unevenly distributed within the molecule, leading to partial positive and partial negative ends causing weak attractions between oppositely charged ends of nearby molecules.

They are proportional to molecular **Surface Area**.

> Boiling point increases as carbon number increases (Molecular Weight).

> Boiling point decreases with branching (molecules become spherical, less surface area, less van der Waals attractions).



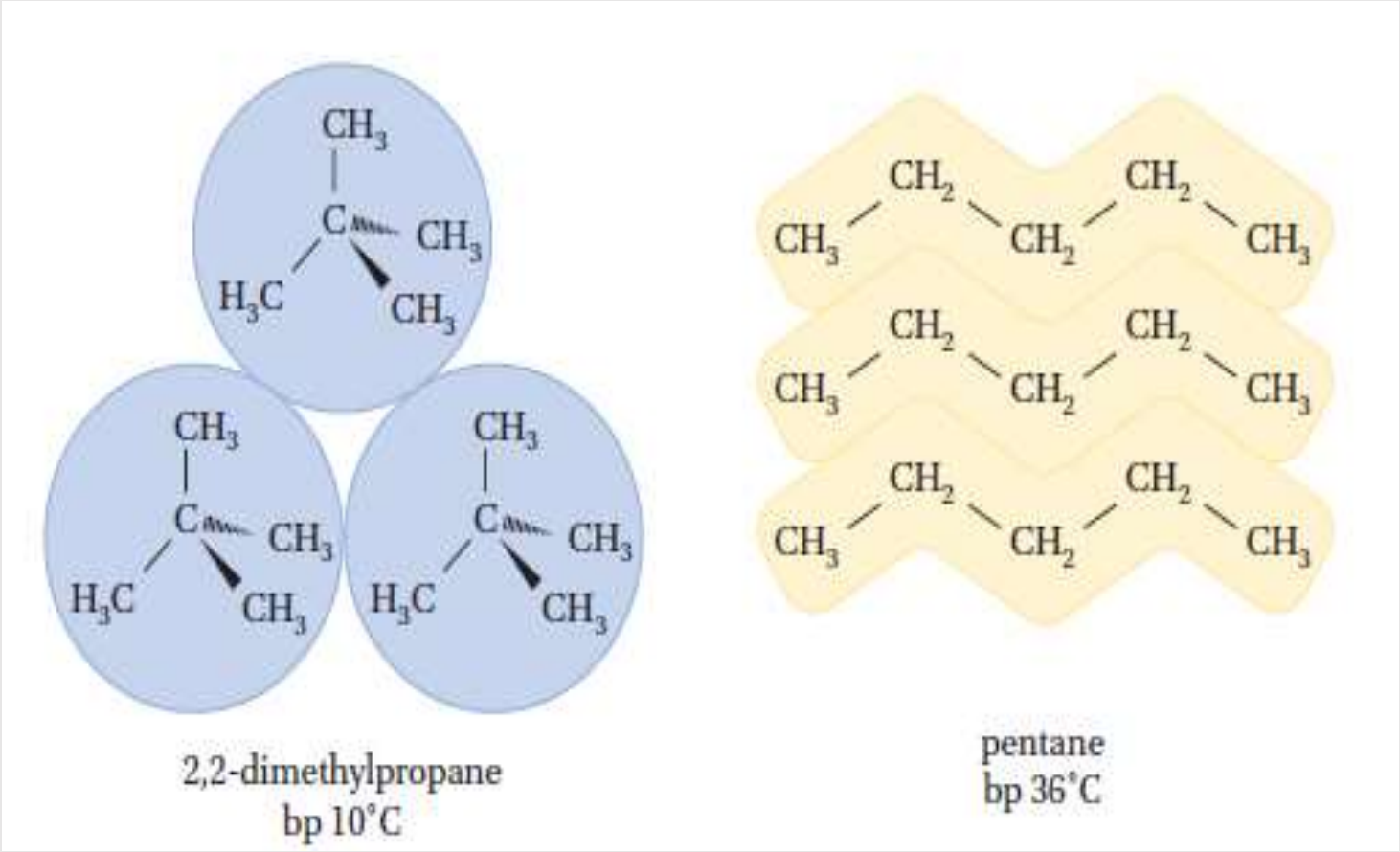
Name	Formula	Boiling point, °C
pentane	$CH_3CH_2CH_2CH_2CH_3$	36
2-methylbutane (isopentane)	$CH_3CH(CH_3)CH_2CH_3$	28
2,2-dimethyl-propane (neopentane)	$C(CH_3)_4$	10

More branching will:

1- decrease surface area,

2- decrease van der Waals forces

3- lower boiling point

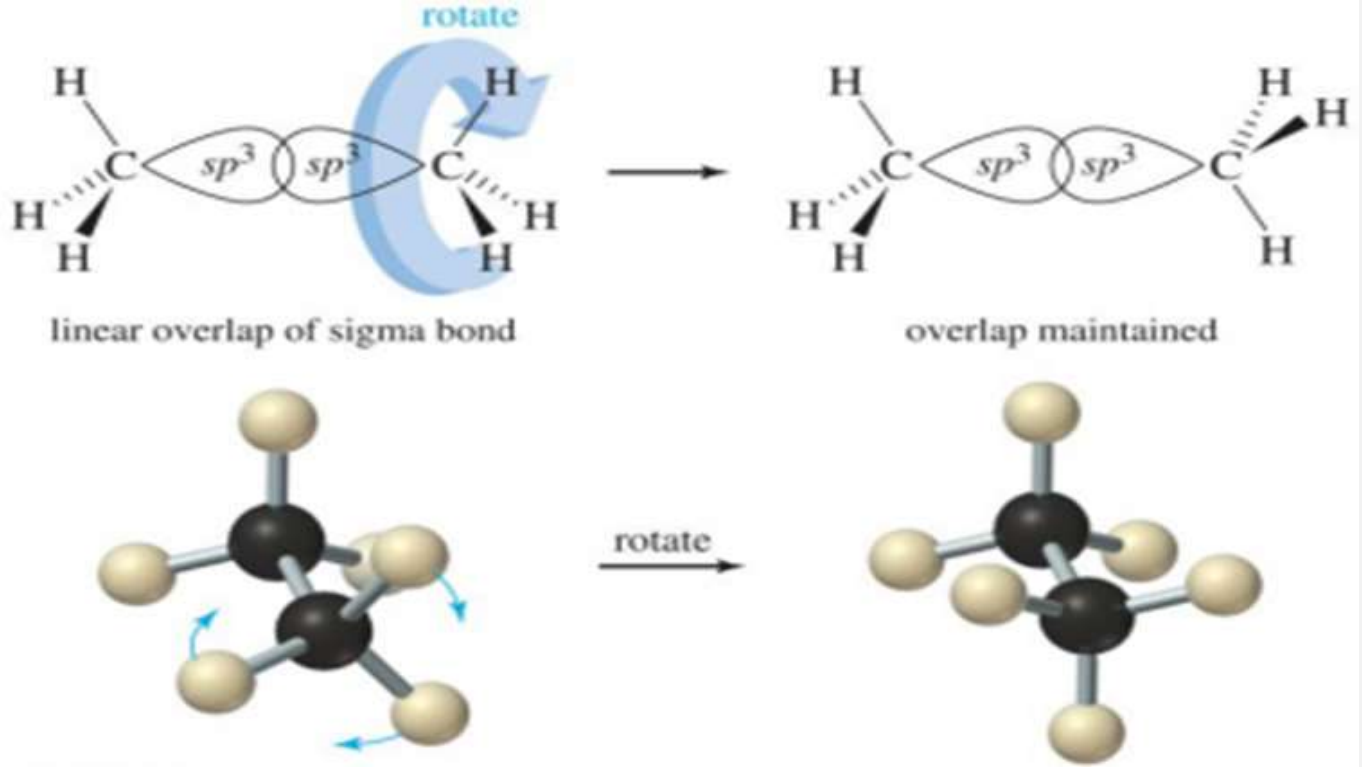


2.8: Conformations of Alkanes:

Molecules have infinite number of shapes formed by rotation about single bonds.

These shapes are called **conformations,** or **conformers,** or rotamers.

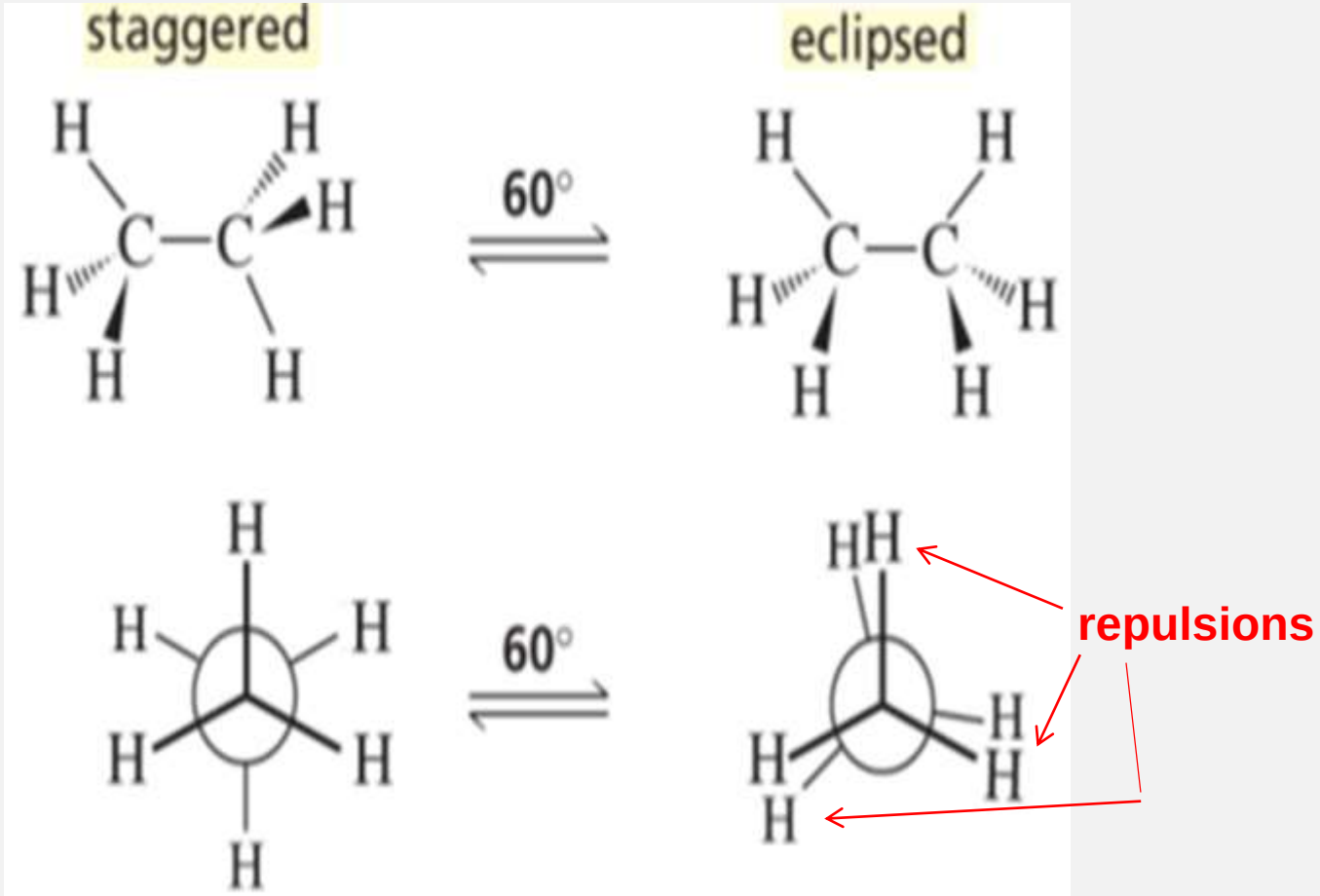
They are **stereoisomers** (conformational stereoisomers) with same atom connectivity (same order), but different arrangements of atoms in space



Conformations for ethane :

Staggered Conformation (more stable) : less repulsion

Eclipsed Conformation (less stable) : more repulsion

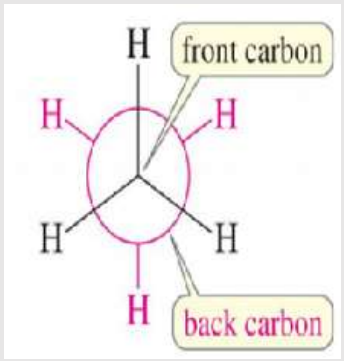


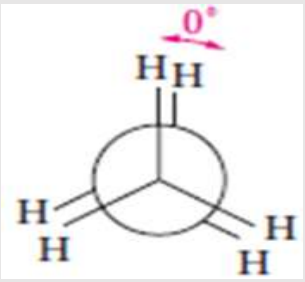
Different ways to draw conformations :

staggered

eclipsed

1- Newman projection

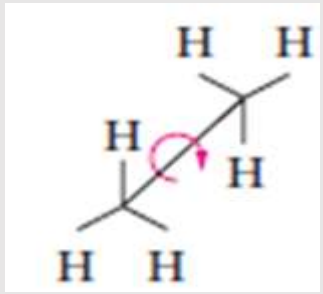


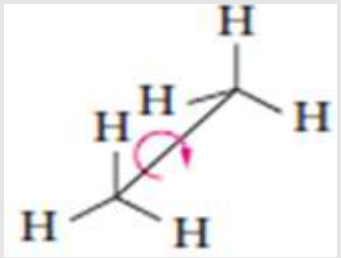


staggered

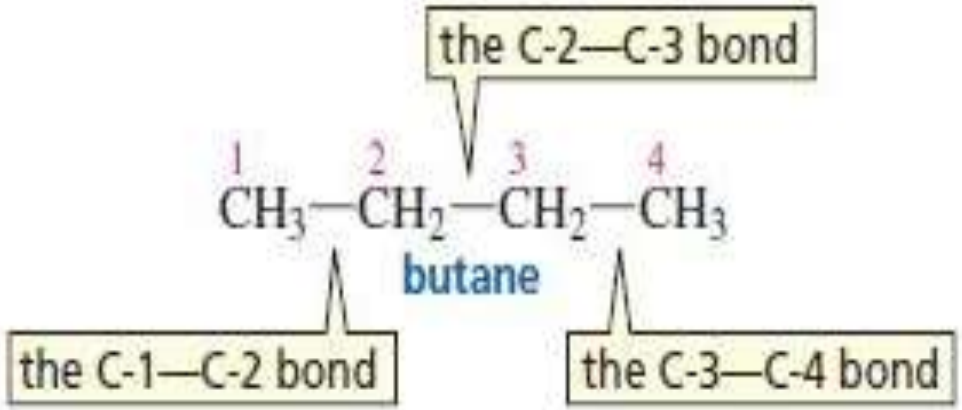
eclipsed

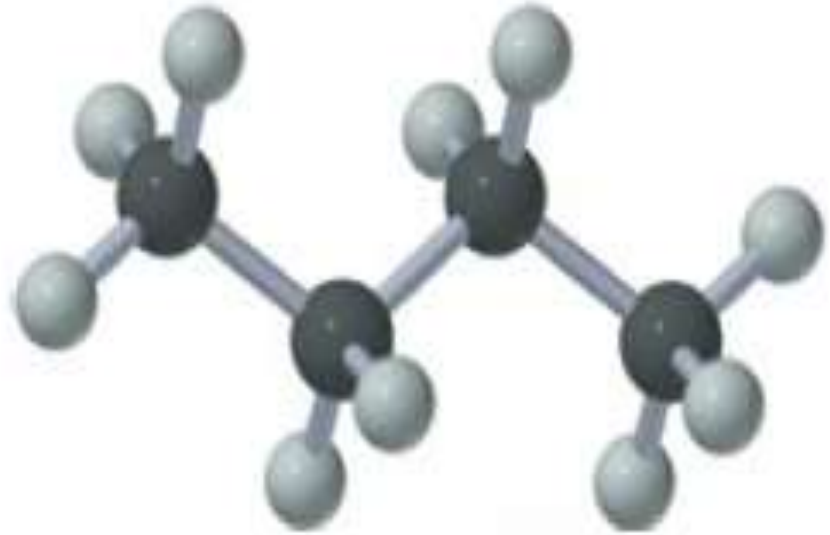
2- Sawhorse formula



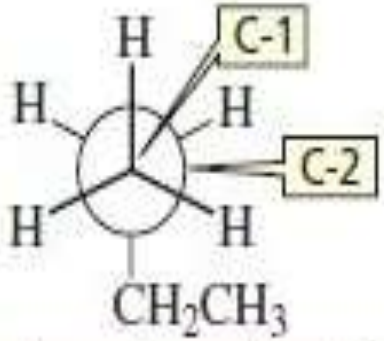


staggered

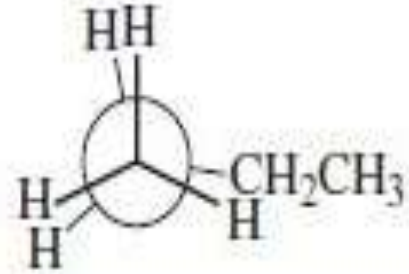




ball-and-stick model of butane

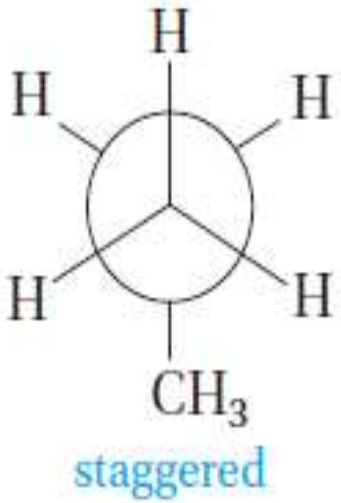


staggered conformation for rotation about the C-1—C-2 bond in butane

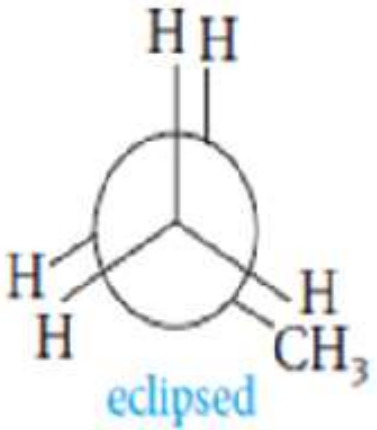


eclipsed conformation for rotation about the C-1—C-2 bond in butane

Newman projection of propane:



The projection formula is similar to that of ethane, except for the replacement of one hydrogen with methyl.



Rotation of the "rear" carbon of the staggered conformation by 60° gives the eclipsed

https://youtu.be/ua0_UNoashU

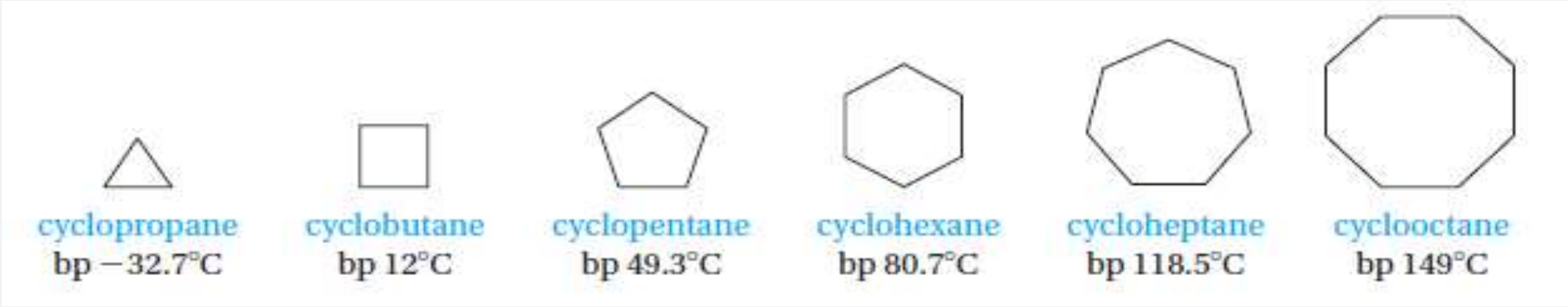
https://youtu.be/oG1aCQvkkD0

See videos on conformations on these links

2.9: Cycloalkanes Nomenclature and Conformations

Saturated hydrocarbons having at least one ring of carbon atoms

Naming : add *cyclo-* before the name

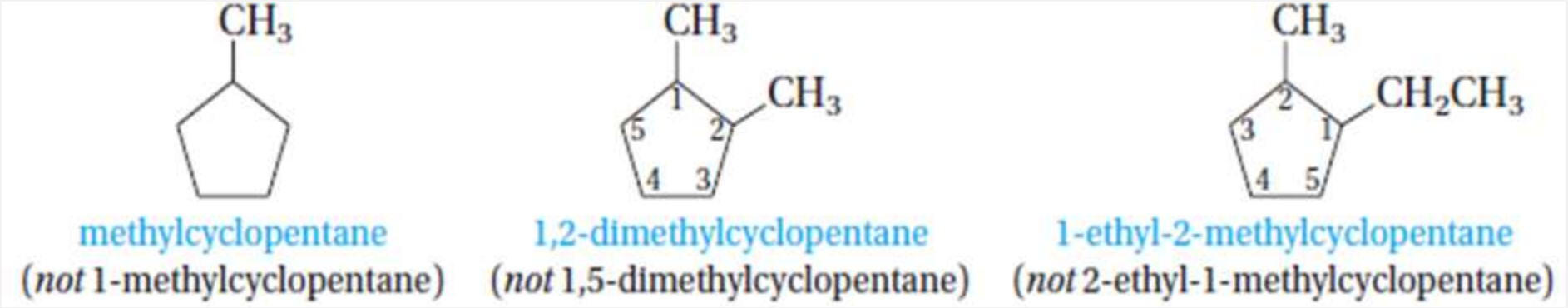


Nomenclature of substituted cycloalkanes:

Substituents attached to the rings are named in the usual way :

> One substituent : no number needed

> More than one substituent : Start at one substituent (number 1) and continue numbering in the direction of the next nearest one



methylcyclopentane (*not* 1-methylcyclopentane)

1,2-dimethylcyclopentane (*not* 1,5-dimethylcyclopentane)

1-ethyl-2-methylcyclopentane (*not* 2-ethyl-1-methylcyclopentane)

PROBLEM 2.12 Give IUPAC names for

Conformations of Cycloalkanes:

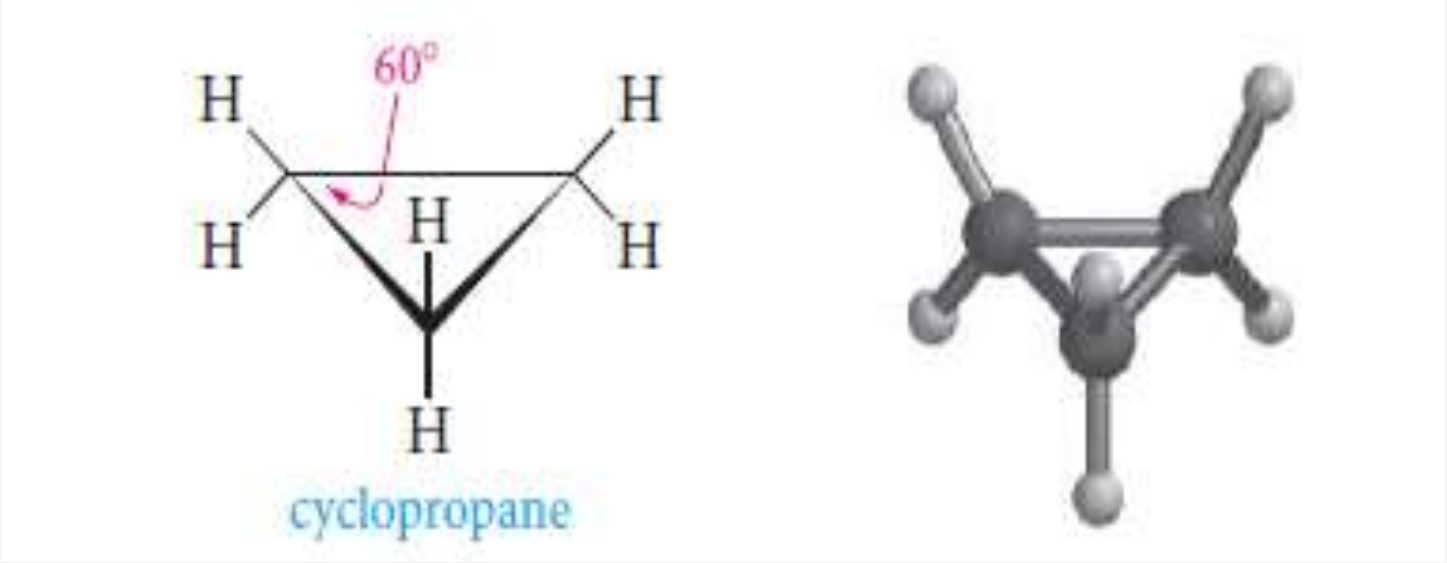
Cyclopropane :

Completely planar structure.

C-C-C bond angle = 60°, high **angle strain** (ideal sp^3 angle = 109.5°).

C-H bonds are above and below ring plane, and are all **eclipsed**.

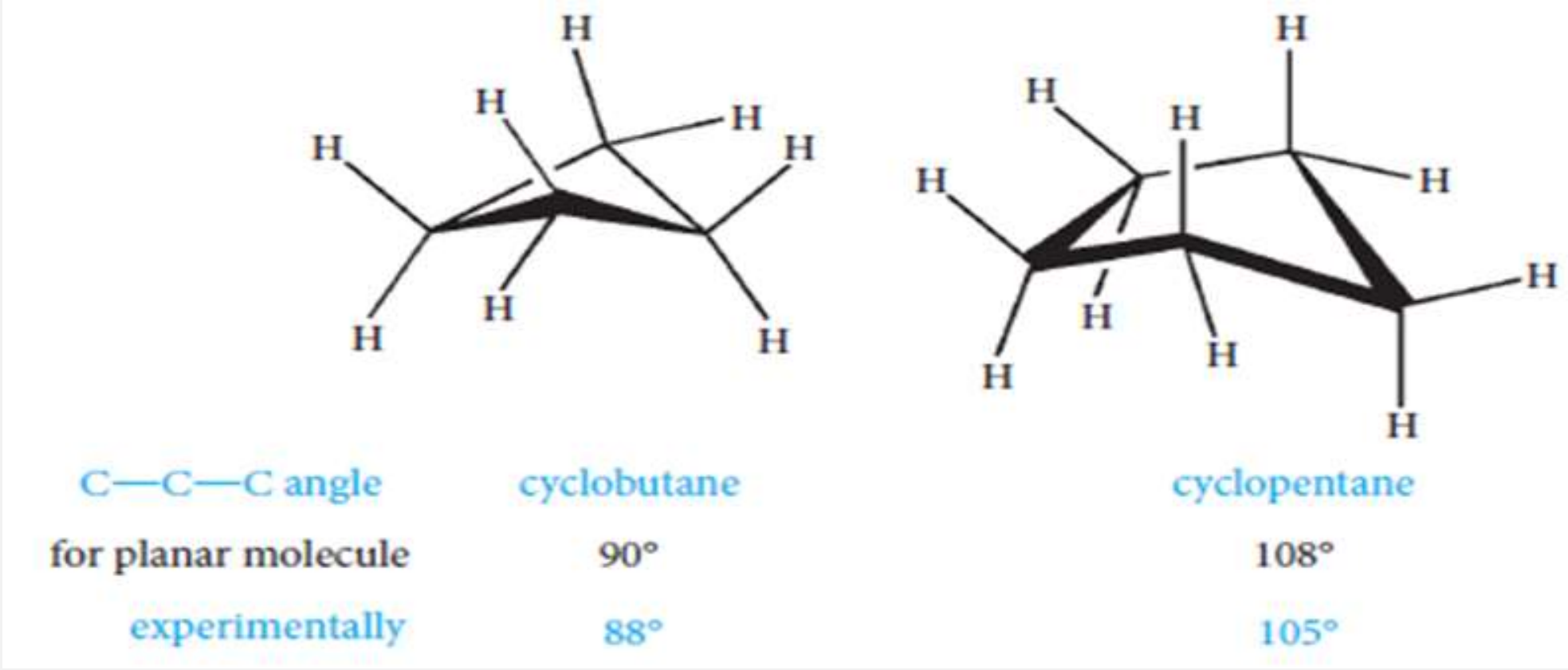
Least stable (has highest **ring strain**)



4- and 5-membered cycloalkanes :

Nonplanar, have “**puckered**” (slightly nonplanar) shape.

Although C-C-C angles become smaller, but bond eclipsing is decreased.



C—C—C angle	cyclobutane	cyclopentane
for planar molecule	90°	108°
experimentally	88°	105°

6-membered ring (cyclohexane) :

M**ost stable ring structure, nonplanar, free of strain.**.

If planar then C-C-C angles will be 120° (much larger than tetrahedral sp^3 angle 109.5°) and will have high amount of strain.

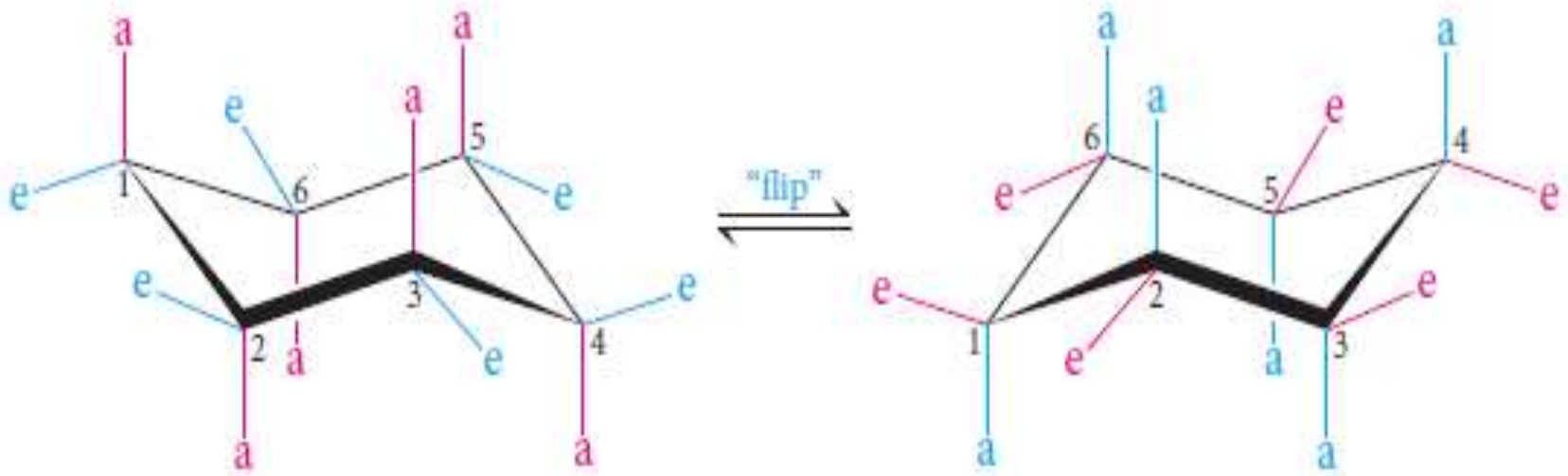
To avoid strain, it becomes nonplanar with all bond angles = **109.5°.**

It has a flexible structure and shows **conformations**:

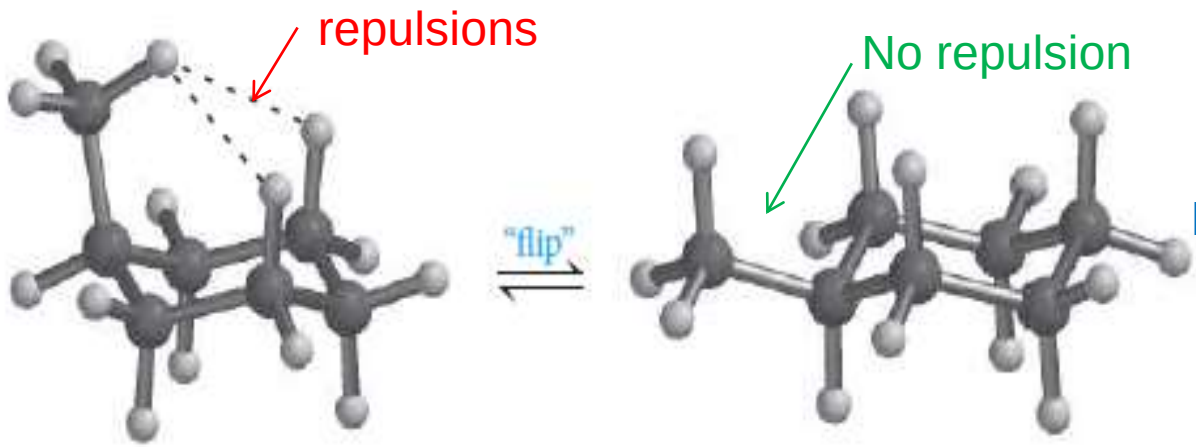
1 - Chair conformation : all bonds **staggered**.

6 bonds **axial** **:** **3** bonds straight up + **3** straight down)

6 bonds **equatorial** **:** in ring plane , **3** slightly up + **3** slightly down.



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

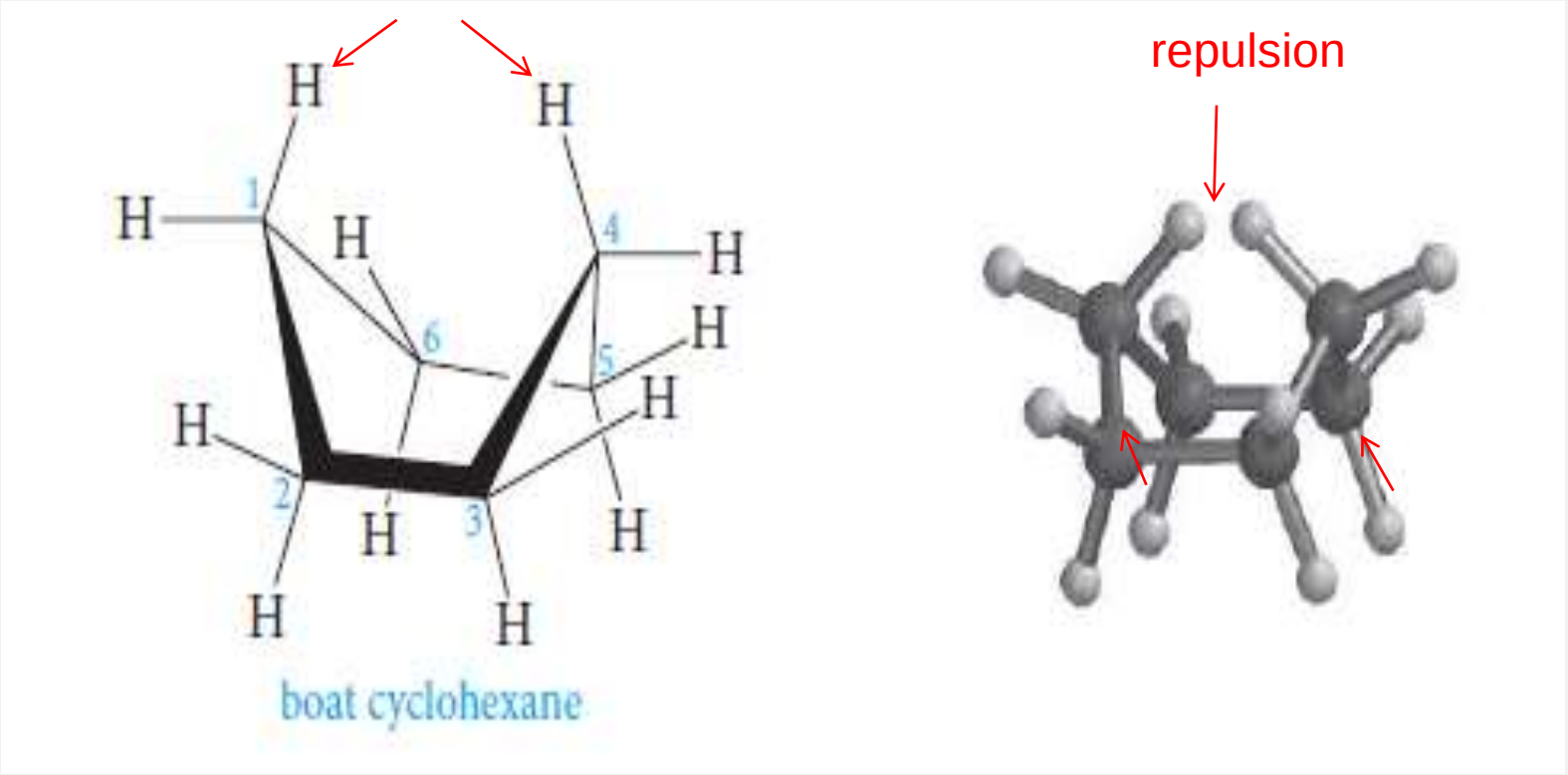


methyl axial
5%

methyl equatorial
95%

Large group equatorial (more stable)

2- Boat conformation : has some eclipsed bonds (some strain)



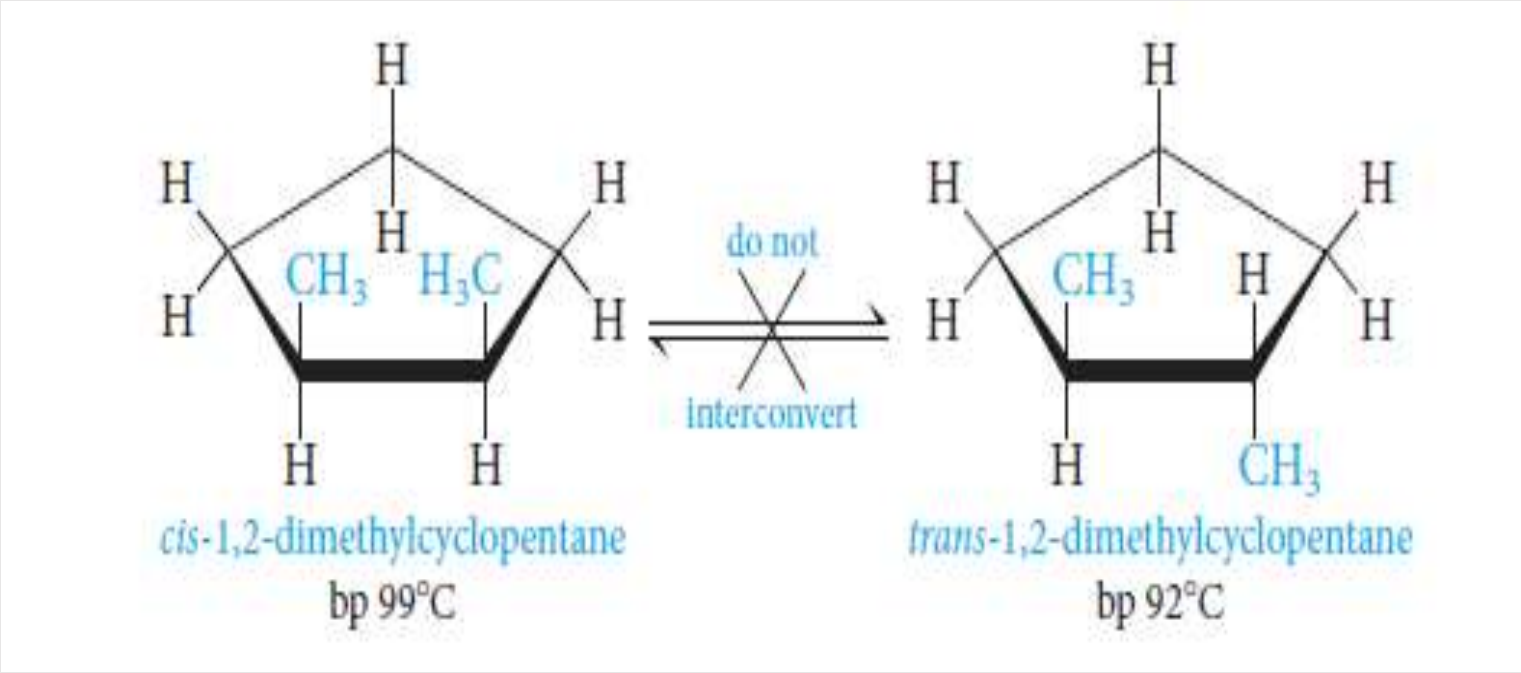
Chair conformation is **more stable** than boat

2.10 Cis-Trans Isomerism in Cycloalkanes:

Stereoisomers : molecules having same attachment of atoms,

but different arrangements of atoms in space.

Example : ***Cis–trans*** **isomers** (**geometrical isomers**) :



Two conditions for *cis-trans* isomerism:

1- Restricted rotation : (ring or C=C bond)

2- Two carbons each having different atoms or groups

Cis : like groups on same side - (on ring or C=C)

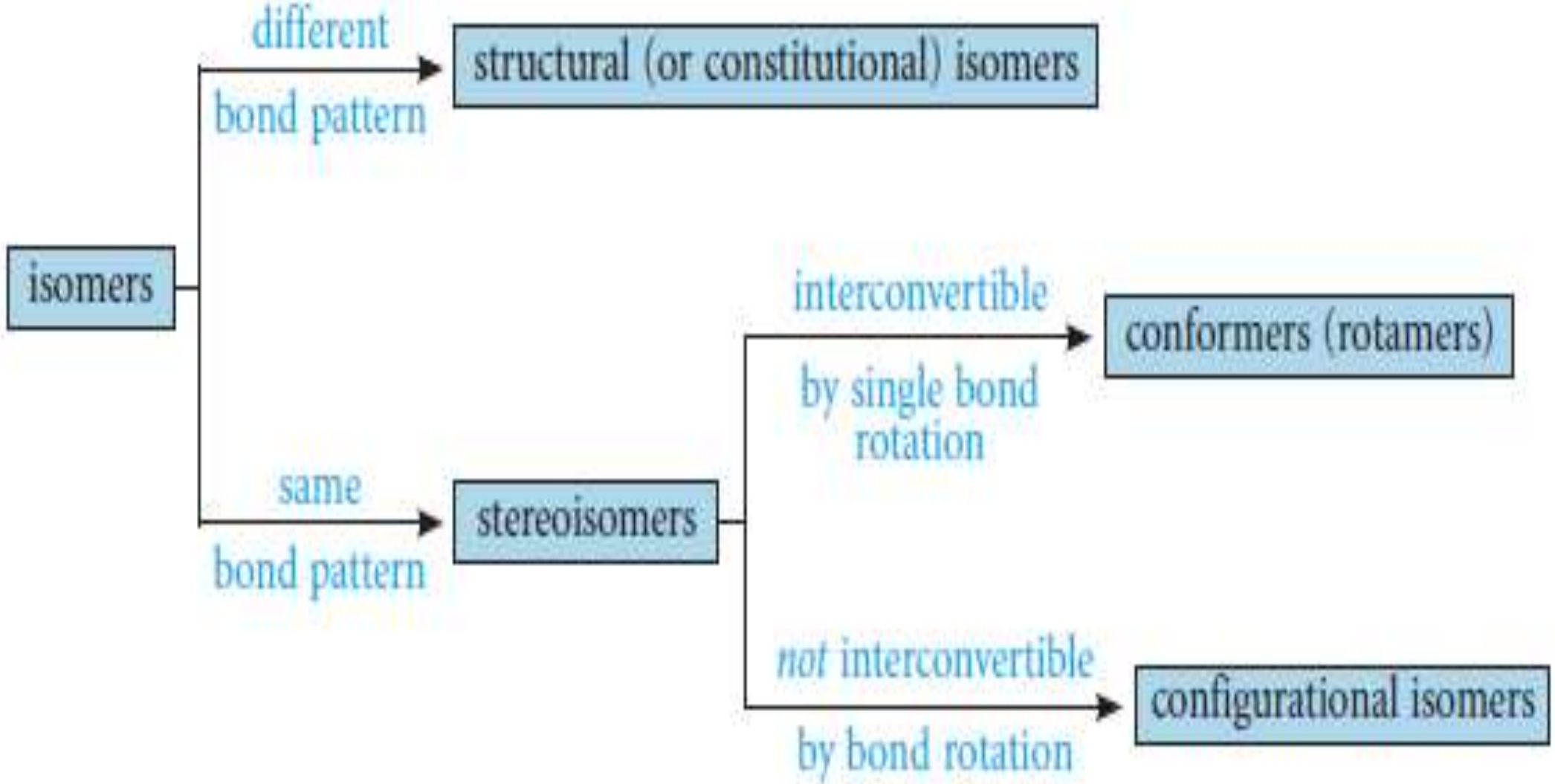
Trans : like groups on opposite sides

PROBLEM 2.17 Classify the following pairs:

a. *cis*- and *trans*-1,2-dimethylcyclohexane
b. chair and boat forms of cyclohexane
c. 1-fluoropropane and 2-fluoropropane

PROBLEM 2.16 Draw the structure for the *cis* and *trans* isomers of

a. 1,3-dibromocyclopentane
b. 1-chloro-2-methylcyclopropane


isomers
different
bond pattern
structural (or constitutional) isomers
same
bond pattern
stereoisomers
interconvertible
by single bond
rotation
conformers (rotamers)
not interconvertible
by bond rotation
configurational isomers

2.12 Reactions of Alkanes:

All bonds are **Nonpolar** :

- relatively Inert,
- low reactivity
- only few reactions
- used as solvents for :
  - extraction
  - crystallization
  - chemical reactions

1- (a) - Combustion Reactions (as fuel) :

$$\underset{\text{methane}}{CH_4} + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + \text{heat}\ (212.8\ \text{kcal/mol})$$

$$\underset{\text{butane}}{C_4H_{10}} + \tfrac{13}{2}\,O_2 \longrightarrow 4\,CO_2 + 5\,H_2O + \text{heat}\ (688.0\ \text{kcal/mol})$$

(b) - Partial (incomplete) oxidation reactions :

$$2\,CH_4 + 3\,O_2 \longrightarrow \underset{\text{carbon monoxide}}{2\,CO} + 4\,H_2O$$

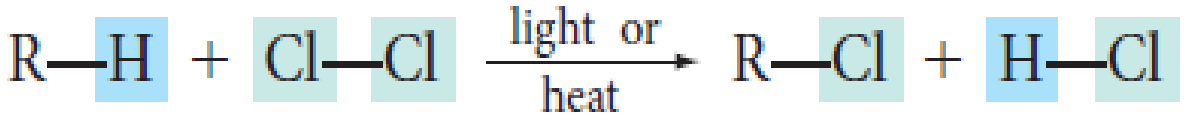
$$CH_4 + O_2 \longrightarrow \underset{\text{carbon}}{C} + 2\,H_2O$$

$$CH_4 + O_2 \longrightarrow \underset{\text{formaldehyde}}{CH_2O} + H_2O$$

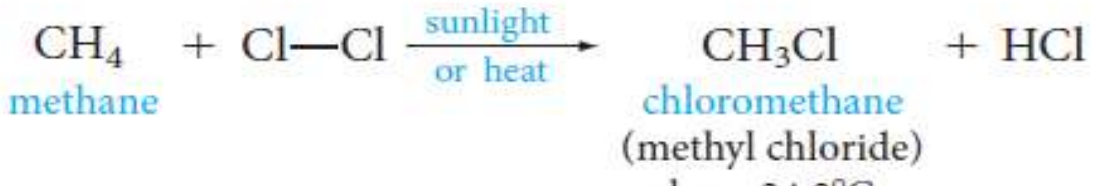
$$2\,C_2H_6 + 3\,O_2 \longrightarrow \underset{\text{acetic acid}}{2\,CH_3CO_2H} + 2\,H_2O$$

2- Halogenation Reaction (free radical substitution):

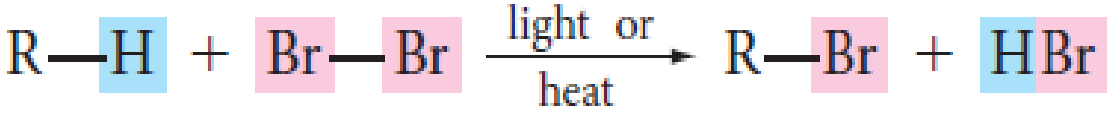
- General equation :



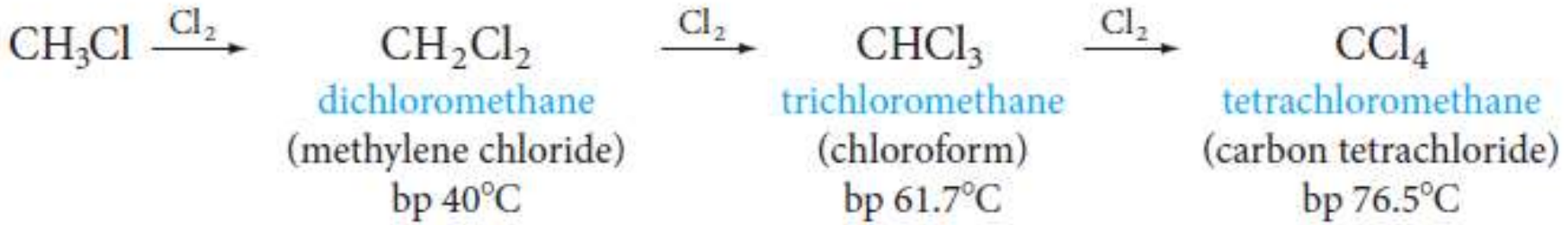
Example: **Chlorination** (of methane) :



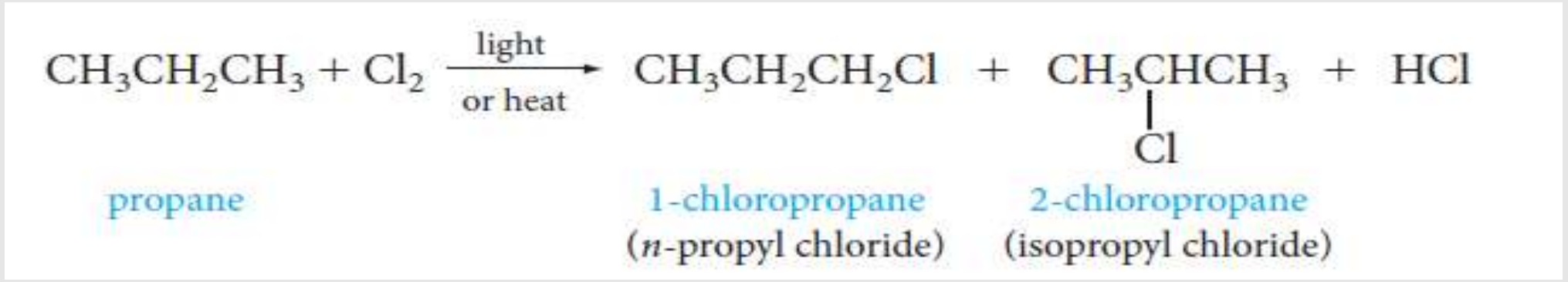
Bromination :

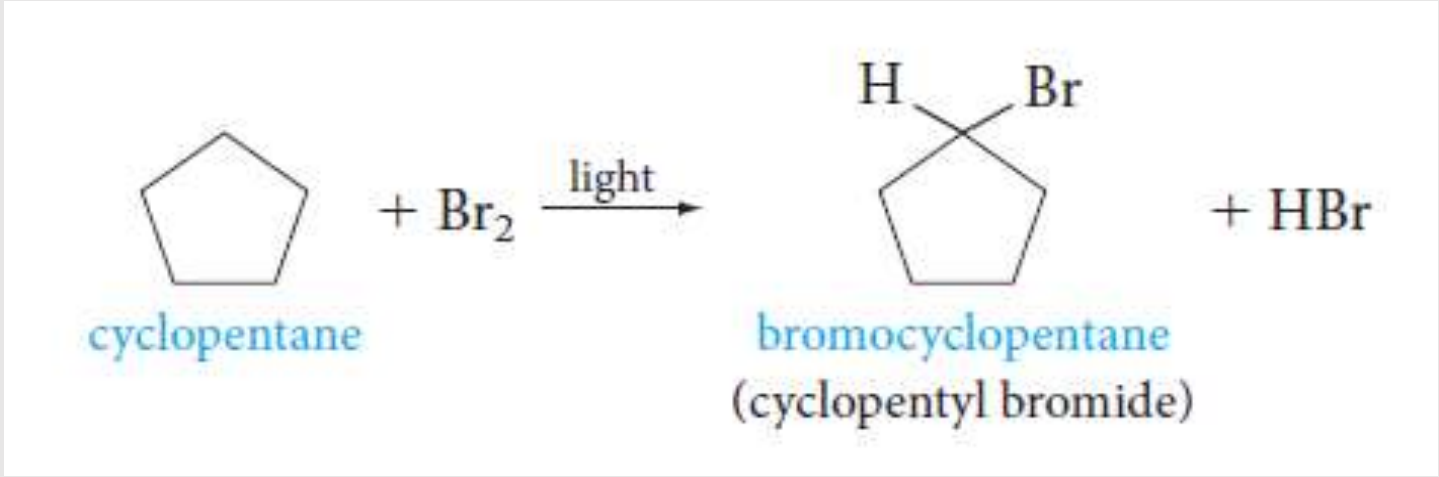


Excess halogen:



Reactions of Other alkanes and cycloalkanes :





2.13 : Mechanism of Free Radical Halogenation:

Reaction Mechanism : Step-by-step description of bond-breaking and bond-making

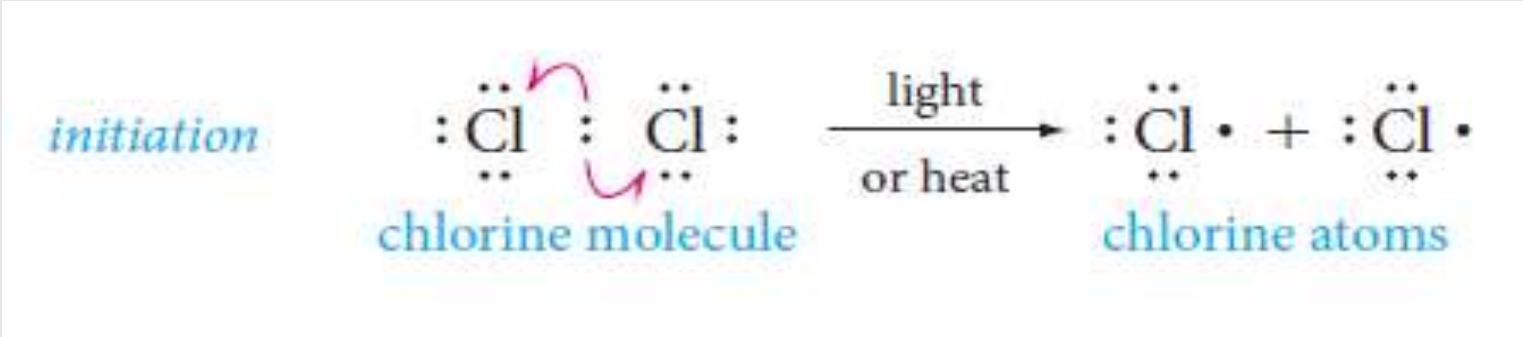
Halogenation is a **(free radical chain)** reaction:

Steps: **1-** chain-initiating step

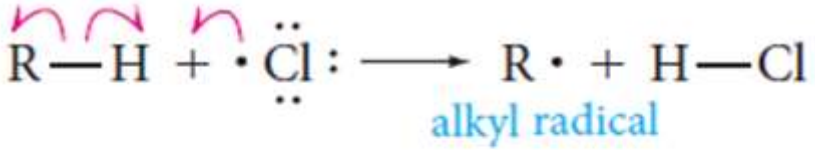
2- chain-propagating steps

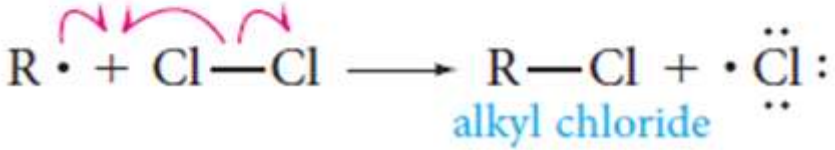
3- chain-termination steps

1- Chain initiation: Breaking of weak (X-X) bond into (X) atoms (Cl or Br atoms).

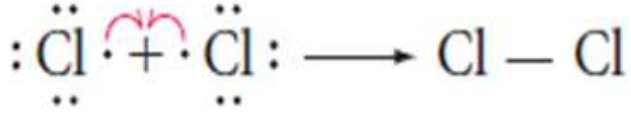


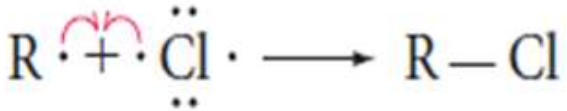
2- Chain-propagating steps:



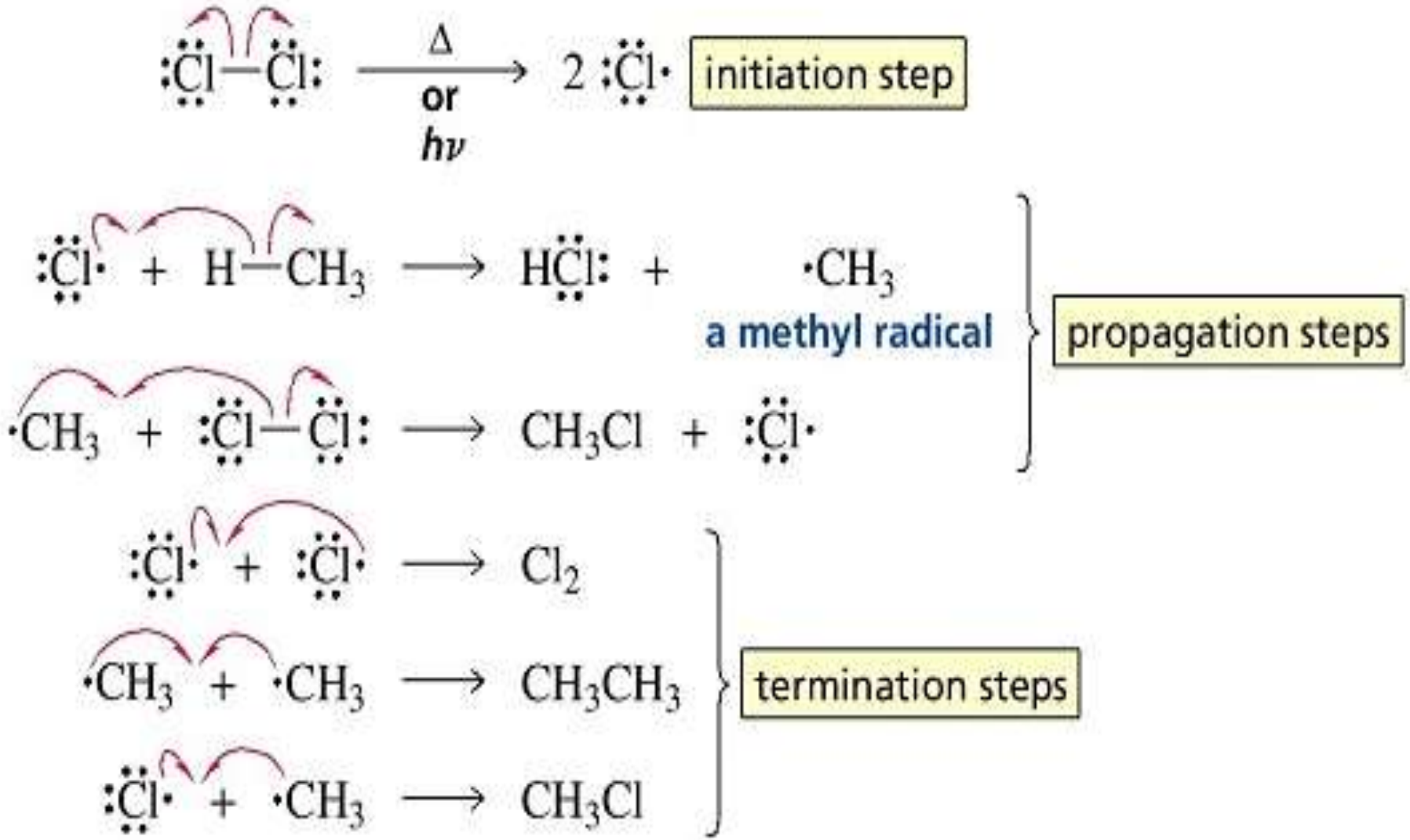


3- chain-terminating steps:





mechanism for the monochlorination of methane



Exercise questions

15	17	19
20	22	26
31	36	38
42	44	49