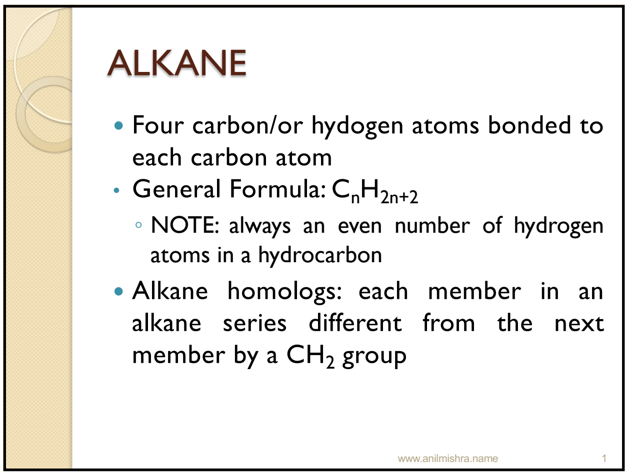
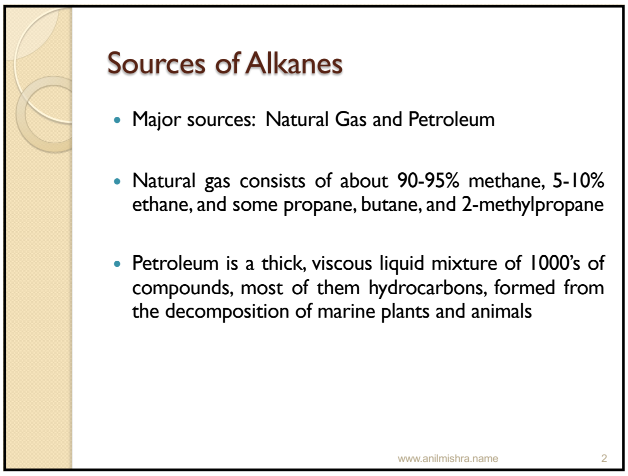


ALKANE

- Four carbon/or hydogen atoms bonded to each carbon atom
- General Formula: C_nH_{2n+2}
  - NOTE: always an even number of hydrogen atoms in a hydrocarbon
- Alkane homologs: each member in an alkane series different from the next member by a CH_2 group

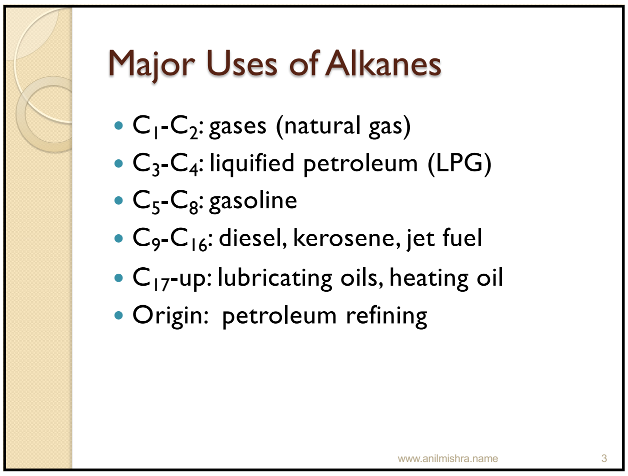
1



Sources of Alkanes

- Major sources: Natural Gas and Petroleum
- Natural gas consists of about 90-95% methane, 5-10% ethane, and some propane, butane, and 2-methylpropane
- Petroleum is a thick, viscous liquid mixture of 1000's of compounds, most of them hydrocarbons, formed from the decomposition of marine plants and animals

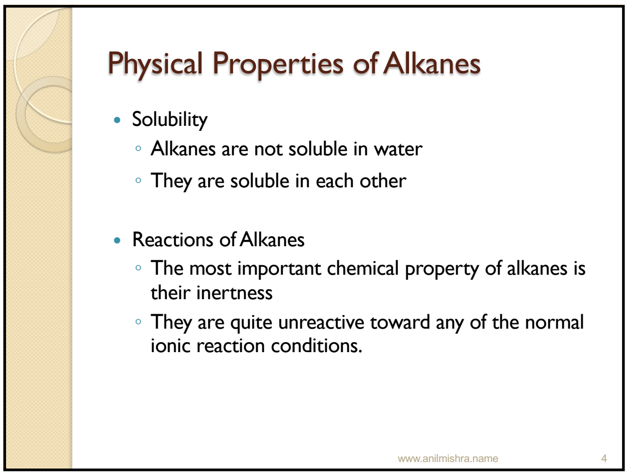
2



Major Uses of Alkanes

- C_1-C_2: gases (natural gas)
- C_3-C_4: liquified petroleum (LPG)
- C_5-C_8: gasoline
- C_9-C_{16}: diesel, kerosene, jet fuel
- C_{17}-up: lubricating oils, heating oil
- Origin: petroleum refining

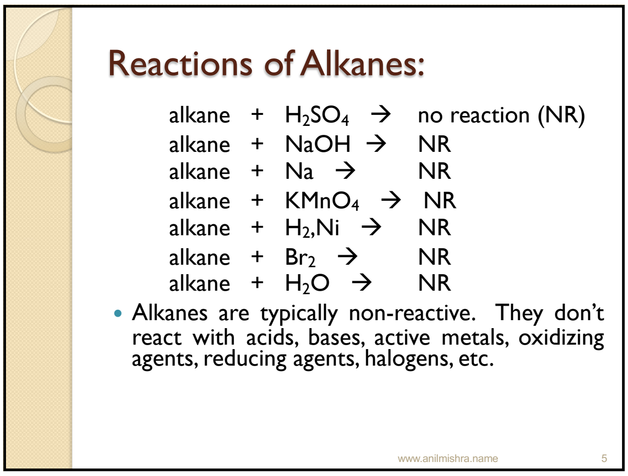
3



Physical Properties of Alkanes

- Solubility
  - Alkanes are not soluble in water
  - They are soluble in each other
- Reactions of Alkanes
  - The most important chemical property of alkanes is their inertness
  - They are quite unreactive toward any of the normal ionic reaction conditions.

4

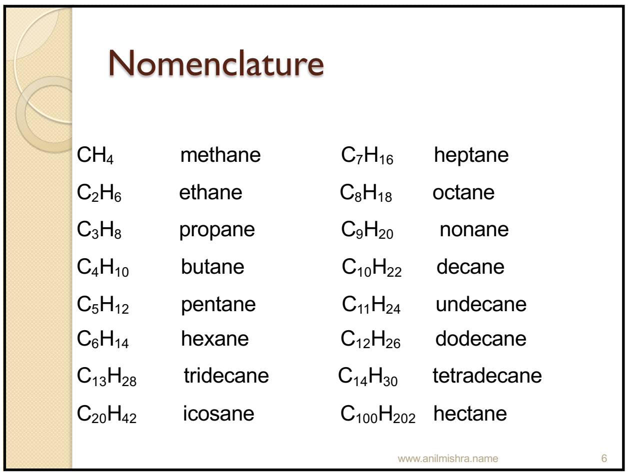


Reactions of Alkanes:

alkane + H_2SO_4 → no reaction (NR)
alkane + NaOH → NR
alkane + Na → NR
alkane + $KMnO_4$ → NR
alkane + H_2,Ni → NR
alkane + Br_2 → NR
alkane + H_2O → NR

- Alkanes are typically non-reactive. They don't react with acids, bases, active metals, oxidizing agents, reducing agents, halogens, etc.

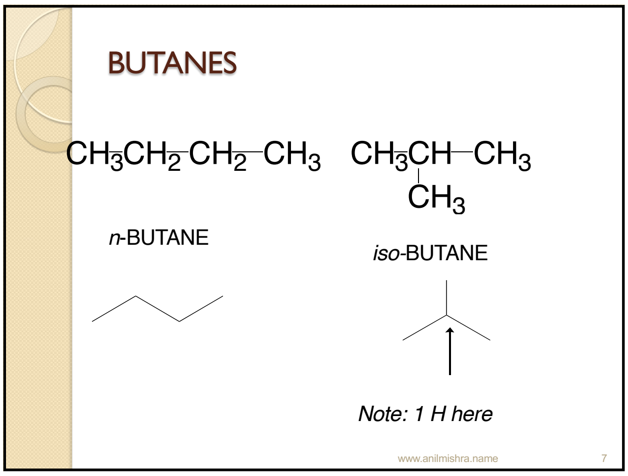
5



Nomenclature

CH_4	methane	C_7H_{16}	heptane
C_2H_6	ethane	C_8H_{18}	octane
C_3H_8	propane	C_9H_{20}	nonane
C_4H_{10}	butane	$C_{10}H_{22}$	decane
C_5H_{12}	pentane	$C_{11}H_{24}$	undecane
C_6H_{14}	hexane	$C_{12}H_{26}$	dodecane
$C_{13}H_{28}$	tridecane	$C_{14}H_{30}$	tetradecane
$C_{20}H_{42}$	icosane	$C_{100}H_{202}$	hectane

6



BUTANES

$CH_3CH_2{-}CH_2{-}CH_3$

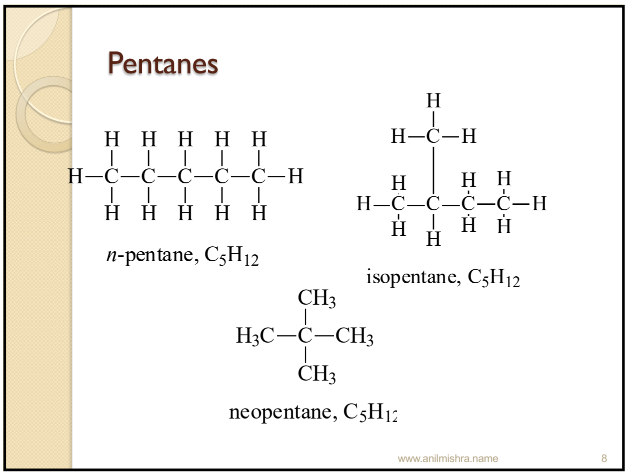
n-BUTANE

$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$

iso-BUTANE

Note: 1 H here

7



Pentanes

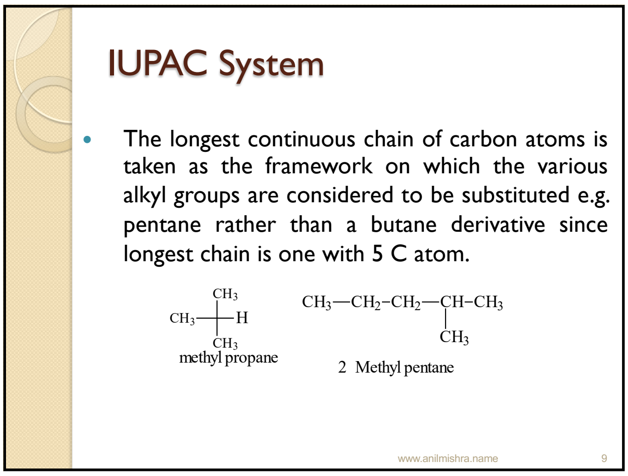
n-pentane, C_5H_{12}

isopentane, C_5H_{12}

$H_3C{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_3$

neopentane, C_5H_1

8



IUPAC System

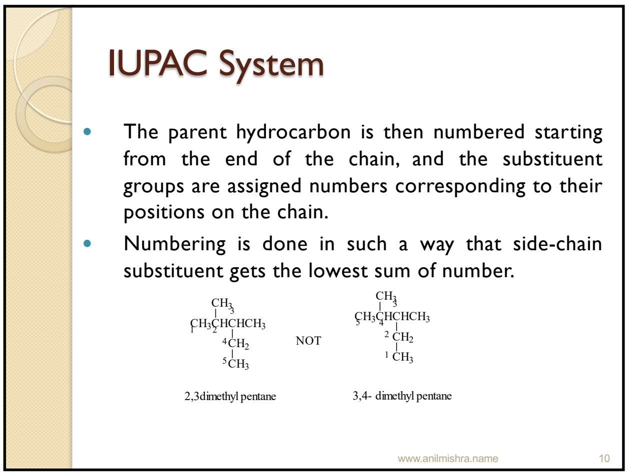
- The longest continuous chain of carbon atoms is taken as the framework on which the various alkyl groups are considered to be substituted e.g. pentane rather than a butane derivative since longest chain is one with 5 C atom.

$$\underset{CH_3}{\overset{CH_3}{CH_3\text{—}C\text{—}H}}$$

methyl propane

$$CH_3\text{—}CH_2\text{-}CH_2\text{—}\underset{CH_3}{CH}\text{-}CH_3$$

2 Methyl pentane



IUPAC System

- The parent hydrocarbon is then numbered starting from the end of the chain, and the substituent groups are assigned numbers corresponding to their positions on the chain.
- Numbering is done in such a way that side-chain substituent gets the lowest sum of number.

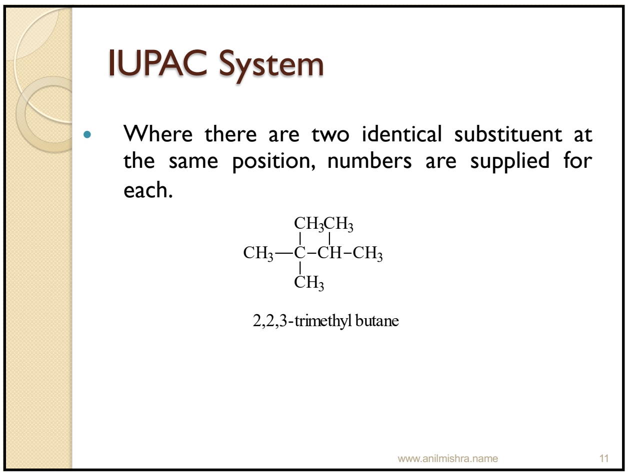
$$\underset{1}{C}H_3\overset{CH_3}{\underset{2}{C}}H\underset{\overset{|}{^4CH_2}\atop\overset{|}{^5CH_3}}{\overset{3}{C}H}CH_3$$

NOT

$$\underset{5}{C}H_3\overset{CH_3}{\underset{4}{C}}H\underset{\overset{|}{^2CH_2}\atop\overset{|}{^1CH_3}}{\overset{3}{C}H}CH_3$$

2,3dimethyl pentane

3,4- dimethyl pentane

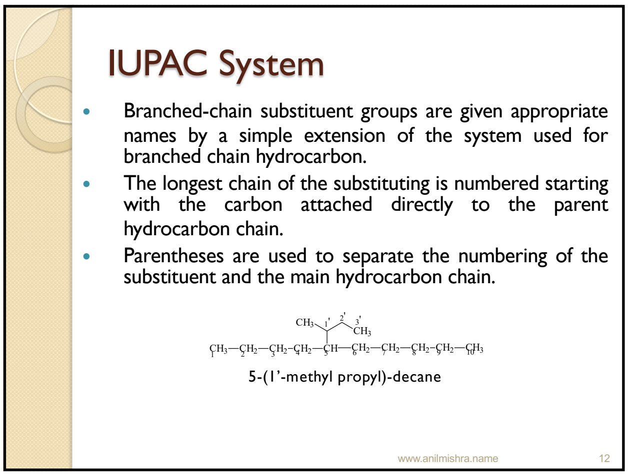


IUPAC System

- Where there are two identical substituent at the same position, numbers are supplied for each.

$$CH_3\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\overset{CH_3}{CH}\text{-}CH_3$$

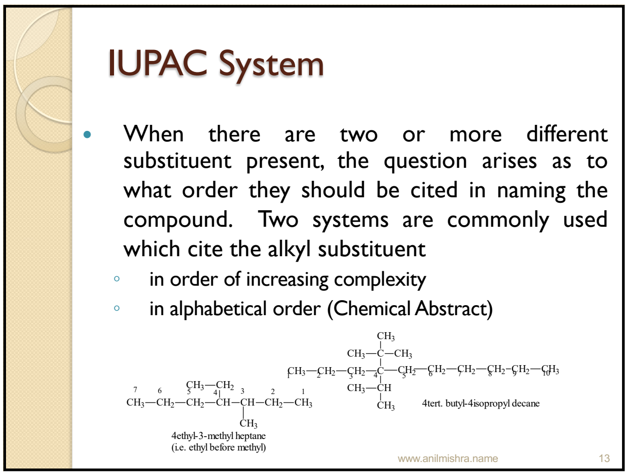
2,2,3-trimethyl butane



IUPAC System

- Branched-chain substituent groups are given appropriate names by a simple extension of the system used for branched chain hydrocarbon.
- The longest chain of the substituting is numbered starting with the carbon attached directly to the parent hydrocarbon chain.
- Parentheses are used to separate the numbering of the substituent and the main hydrocarbon chain.

5-(1'-methyl propyl)-decane



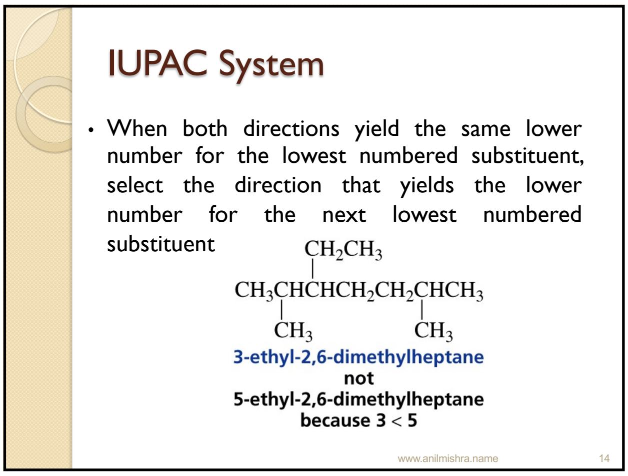
IUPAC System

- When there are two or more different substituent present, the question arises as to what order they should be cited in naming the compound. Two systems are commonly used which cite the alkyl substituent
  - in order of increasing complexity
  - in alphabetical order (Chemical Abstract)

4tert. butyl-4isopropyl decane

4ethyl-3-methyl heptane
(i.e. ethyl before methyl)

13

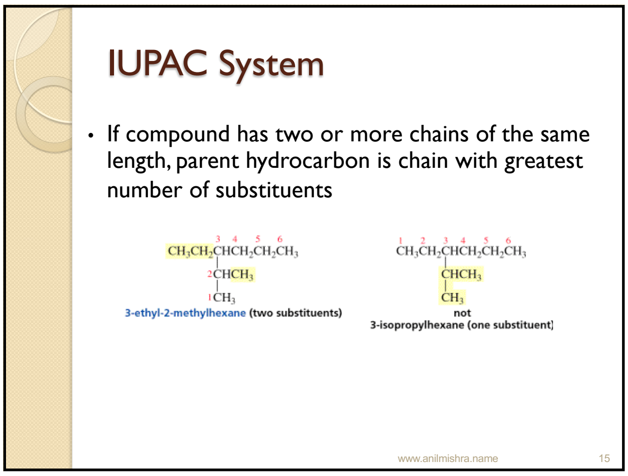


IUPAC System

- When both directions yield the same lower number for the lowest numbered substituent, select the direction that yields the lower number for the next lowest numbered substituent

3-ethyl-2,6-dimethylheptane
not
5-ethyl-2,6-dimethylheptane
because 3 < 5

14



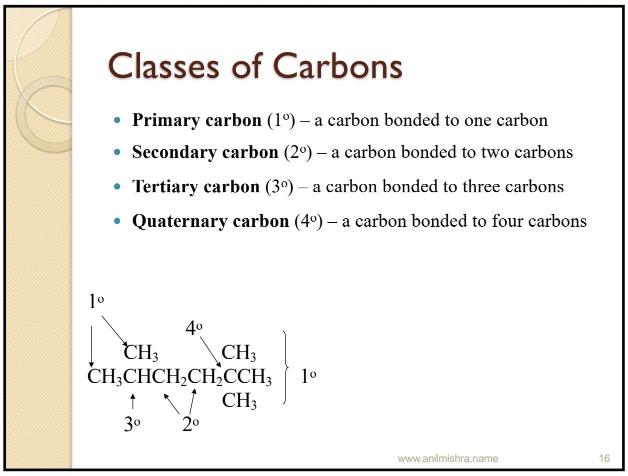
IUPAC System

- If compound has two or more chains of the same length, parent hydrocarbon is chain with greatest number of substituents

3-ethyl-2-methylhexane (two substituents)

not
3-isopropylhexane (one substituent]

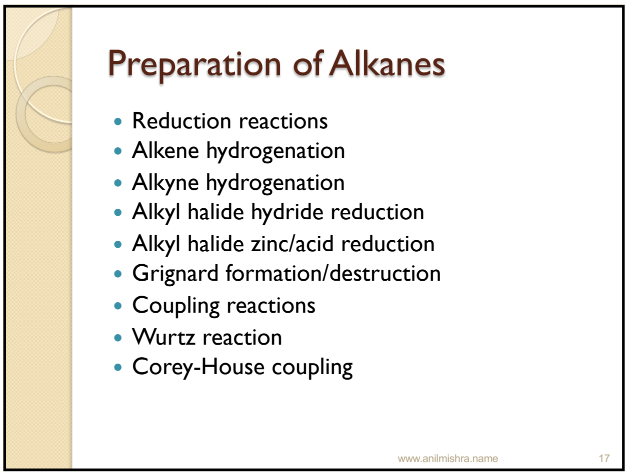
15



Classes of Carbons

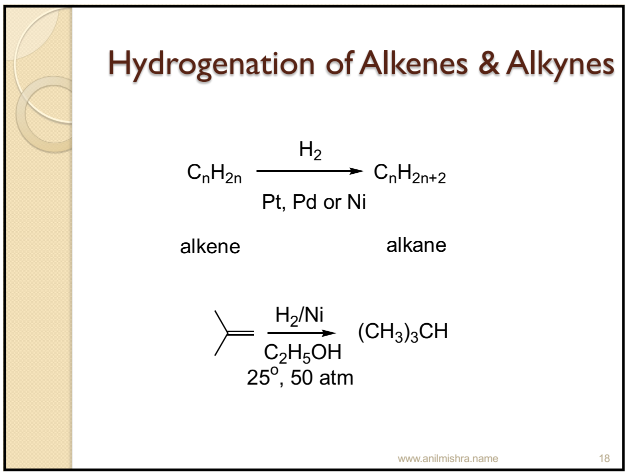
- **Primary carbon** (1°) – a carbon bonded to one carbon
- **Secondary carbon** (2°) – a carbon bonded to two carbons
- **Tertiary carbon** (3°) – a carbon bonded to three carbons
- **Quaternary carbon** (4°) – a carbon bonded to four carbons

16



Preparation of Alkanes

- Reduction reactions
- Alkene hydrogenation
- Alkyne hydrogenation
- Alkyl halide hydride reduction
- Alkyl halide zinc/acid reduction
- Grignard formation/destruction
- Coupling reactions
- Wurtz reaction
- Corey-House coupling

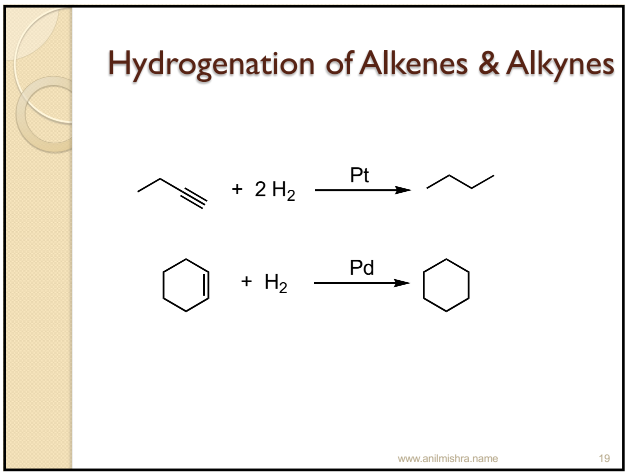


Hydrogenation of Alkenes & Alkynes

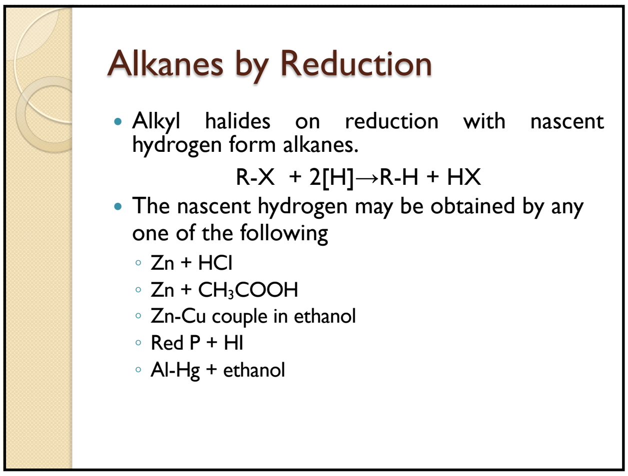
$$C_nH_{2n} \xrightarrow[\text{Pt, Pd or Ni}]{H_2} C_nH_{2n+2}$$

alkene alkane

$$\xrightarrow[\substack{C_2H_5OH \\ 25^o,\ 50\ atm}]{H_2/Ni} (CH_3)_3CH$$



Hydrogenation of Alkenes & Alkynes

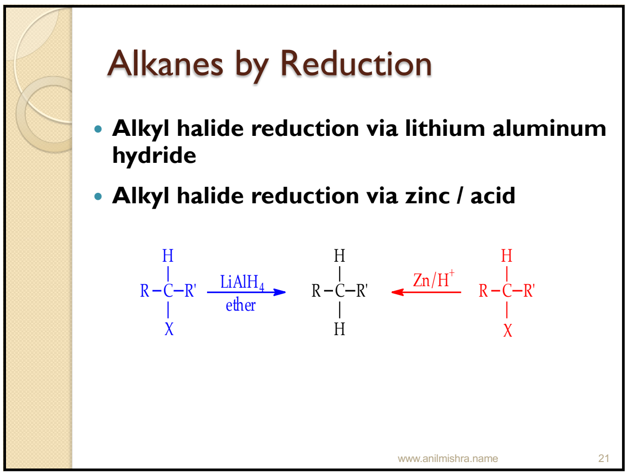


Alkanes by Reduction

- Alkyl halides on reduction with nascent hydrogen form alkanes.

  $$R\text{-}X + 2[H] \rightarrow R\text{-}H + HX$$

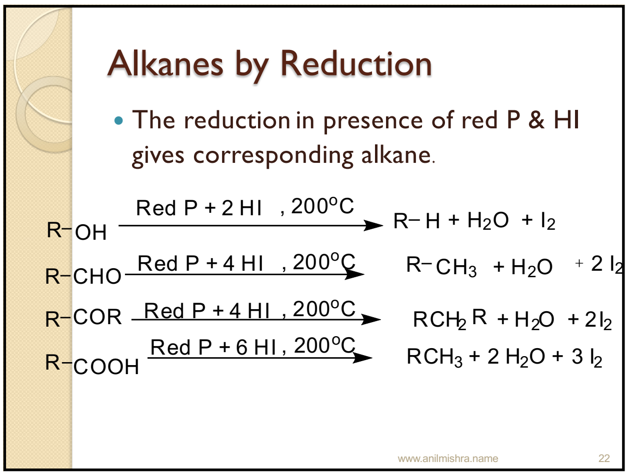
- The nascent hydrogen may be obtained by any one of the following
  - Zn + HCl
  - Zn + CH_3COOH
  - Zn-Cu couple in ethanol
  - Red P + HI
  - Al-Hg + ethanol



Alkanes by Reduction

- **Alkyl halide reduction via lithium aluminum hydride**
- **Alkyl halide reduction via zinc / acid**

$$R-\overset{H}{\underset{X}{C}}-R' \xrightarrow[\text{ether}]{LiAlH_4} R-\overset{H}{\underset{H}{C}}-R' \xleftarrow{Zn/H^+} R-\overset{H}{\underset{X}{C}}-R'$$



Alkanes by Reduction

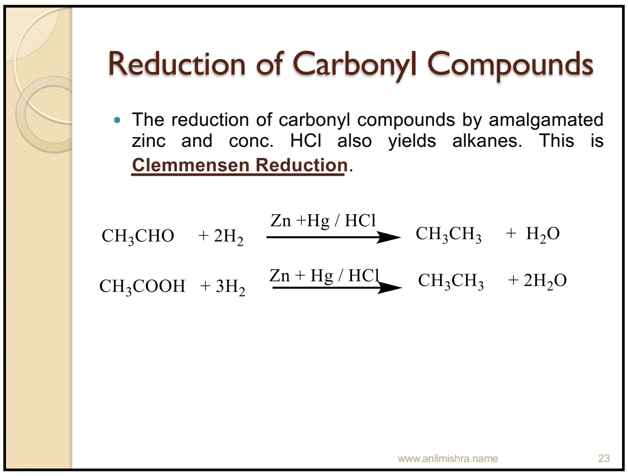
- The reduction in presence of red P & HI gives corresponding alkane.

$$R-OH \xrightarrow{\text{Red P + 2 HI , 200}^oC} R-H + H_2O + I_2$$

$$R-CHO \xrightarrow{\text{Red P + 4 HI , 200}^oC} R-CH_3 + H_2O + 2\,I_2$$

$$R-COR \xrightarrow{\text{Red P + 4 HI , 200}^oC} RCH_2R + H_2O + 2I_2$$

$$R-COOH \xrightarrow{\text{Red P + 6 HI , 200}^oC} RCH_3 + 2\,H_2O + 3\,I_2$$

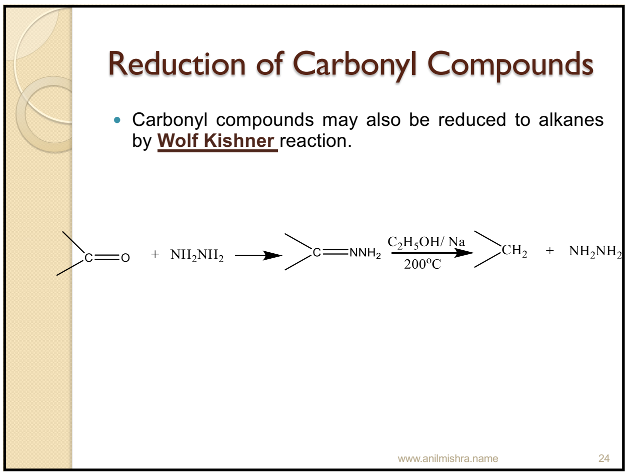


Reduction of Carbonyl Compounds

- The reduction of carbonyl compounds by amalgamated zinc and conc. HCl also yields alkanes. This is **Clemmensen Reduction**.

$$CH_3CHO + 2H_2 \xrightarrow{\text{Zn +Hg / HCl}} CH_3CH_3 + H_2O$$

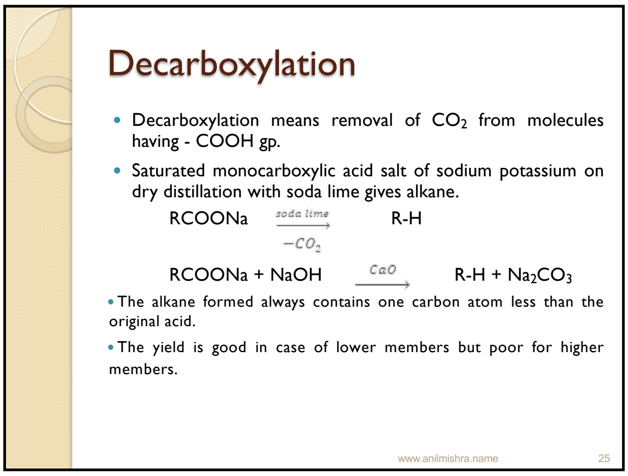
$$CH_3COOH + 3H_2 \xrightarrow{\text{Zn + Hg / HCl}} CH_3CH_3 + 2H_2O$$



Reduction of Carbonyl Compounds

- Carbonyl compounds may also be reduced to alkanes by **Wolf Kishner** reaction.

$$>C{=}O + NH_2NH_2 \longrightarrow >C{=}NNH_2 \xrightarrow[200^oC]{C_2H_5OH/\,Na} >CH_2 + NH_2NH_2$$



Decarboxylation

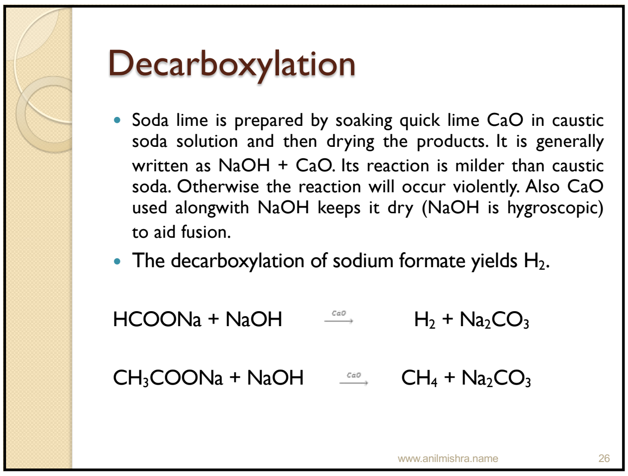
- Decarboxylation means removal of CO_2 from molecules having - COOH gp.
- Saturated monocarboxylic acid salt of sodium potassium on dry distillation with soda lime gives alkane.

$$RCOONa \xrightarrow[-CO_2]{soda\ lime} R\text{-}H$$

$$RCOONa + NaOH \xrightarrow{CaO} R\text{-}H + Na_2CO_3$$

- The alkane formed always contains one carbon atom less than the original acid.
- The yield is good in case of lower members but poor for higher members.

25



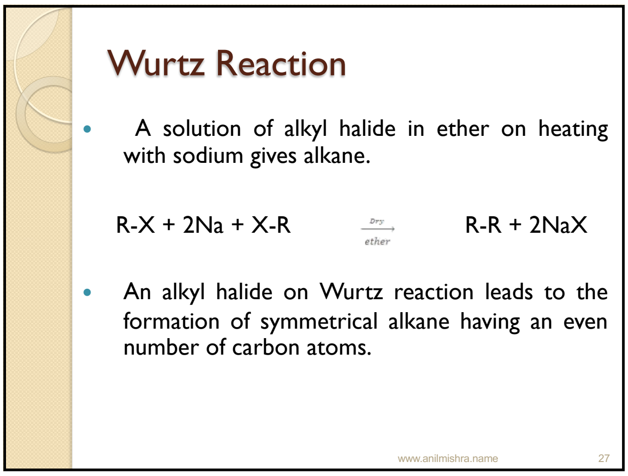
Decarboxylation

- Soda lime is prepared by soaking quick lime CaO in caustic soda solution and then drying the products. It is generally written as NaOH + CaO. Its reaction is milder than caustic soda. Otherwise the reaction will occur violently. Also CaO used alongwith NaOH keeps it dry (NaOH is hygroscopic) to aid fusion.
- The decarboxylation of sodium formate yields H_2.

$$HCOONa + NaOH \xrightarrow{CaO} H_2 + Na_2CO_3$$

$$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

26



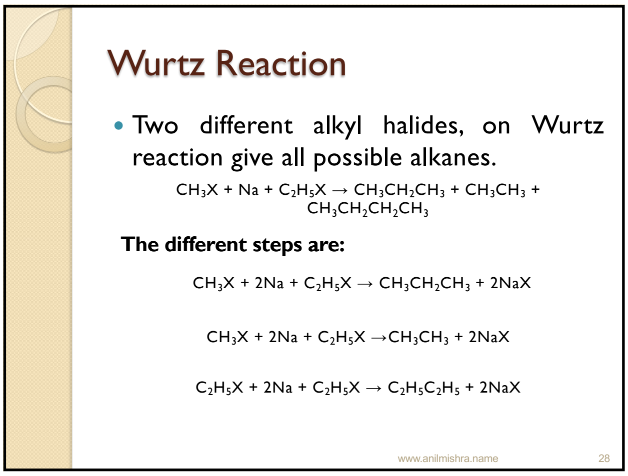
Wurtz Reaction

- A solution of alkyl halide in ether on heating with sodium gives alkane.

$$R\text{-}X + 2Na + X\text{-}R \xrightarrow[ether]{Dry} R\text{-}R + 2NaX$$

- An alkyl halide on Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms.

27



Wurtz Reaction

- Two different alkyl halides, on Wurtz reaction give all possible alkanes.

$$CH_3X + Na + C_2H_5X \rightarrow CH_3CH_2CH_3 + CH_3CH_3 + CH_3CH_2CH_2CH_3$$

The different steps are:

$$CH_3X + 2Na + C_2H_5X \rightarrow CH_3CH_2CH_3 + 2NaX$$

$$CH_3X + 2Na + C_2H_5X \rightarrow CH_3CH_3 + 2NaX$$

$$C_2H_5X + 2Na + C_2H_5X \rightarrow C_2H_5C_2H_5 + 2NaX$$

28

Mechanism of Wurtz Reaction

- The mechanism of Wurtz reaction is although not clear however two mechanisms are proposed for this reaction.

- The first proposed mechanism of Wurtz reaction involved formation of an Intermediate organometallic compound:

$$RX + 2Na \rightarrow \underset{\text{Intermediate}}{[RNa]} + NaX$$

$$RX + [RNa] \rightarrow R\text{-}R + NaX$$

Mechanism of Wurtz Reaction

- Another proposed mechanizm of Wurtz reaction involved formation of Intermediate free radicals:

$$RX + Na \rightarrow R. + Nax$$

Free radicals

$$R. + R. \rightarrow R\text{-}R$$

From Grignard Reagent

- Organic compounds in which a metal atom is directly linked to carbon atom are known as organometallic compound. e.g.
  $HC{\equiv}CNa$, $(C_2H_5)_4$ Pb, $(C_2H_5)2$ Zn

- Alkyl or aryl magnesium halide (R-MgX) are also called Grignard reagents or organometallic compounds.
  - Grignard reagent on double decomposition with water or with other compounds having active H (the hydrogen attached on O, N, F or triple bonded carbon atom are known as active hydrogen) give alkane.

From Grignard Reagent

Hydrolysis of a Grignard reagent (two steps)

i) $R{-}X + Mg \rightarrow RMgX$ (Grignard reagent)

ii) $RMgX + H_2O \rightarrow RH + Mg(OH)X$

$$\underset{n\text{-propyl bromide}}{CH_3CH_2CH_2\text{-}Br} + Mg \rightarrow \underset{n\text{-propyl magnesium bromide}}{CH_3CH_2CH_2\text{-}MgBr}$$

$$CH_3CH_2CH_2\text{-}MgBr + H_2O \rightarrow \underset{\text{propane}}{CH_3CH_2CH_3} + Mg(OH)Br$$

Corey House Synthesis

- The Corey–House synthesis
  - Also called the Corey–Posner–Whitesides–House reaction and other permutations
- It is an organic reaction that involves the reaction of a lithium dialkyl cuprate with an alkyl halide to form a new alkane, an organic Copper compound and a lithium halide.

$$R_2CuLi + R'\text{-}X \rightarrow R\text{-}R' + RCu + LiX$$

Corey House Synthesis

- This reaction occurs in two steps.
  - The alkyl halide is treated with lithium metal, and solvated in dry ether, which converts the alkyl halide into an alkyl lithium compound, R-Li.
  - The starting R-X can be primary, secondary or tertiary alkyl halide:

$$R\text{-}X + 2Li \rightarrow R\text{-}Li + Li\text{-}X$$

Corey House Synthesis

- The second step requires the alkyl lithium compound to be treated with cuprous iodide (CuI).
- This creates a lithium dialkyl cuprate compound.
  - These compounds were first synthesized by Henry Gilman of Iowa State University, and are usually called Gilman reagents in honor of his contributions:

$$2RLi + CuI \rightarrow R_2CuLi + LiI$$

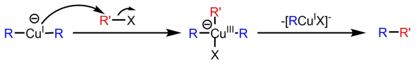
Corey House Synthesis

- The lithium dialkyl cuprate is then treated with the second alkyl halide, which couples to the compound:

$$R_2CuLi + R\text{-}X \rightarrow R\text{-}R + RCu + LiX$$

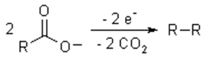
- If second alkyl halide is not the same as the first, then cross-products are formed.

$$R_2CuLi + R'\text{-}X \rightarrow R\text{-}R' + RCu + LiX$$



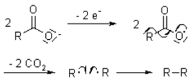
Kolbe Reaction (Electrolysis)

- The Kolbe electrolysis or Kolbe reaction is an organic reaction named after Hermann Kolbe.
- The Kolbe reaction is formally a decarboxylative dimerisation of two carboxylic acids (or carboxylate ions)



Kolbe Reaction (Electrolysis)

- The electrochemical oxidative decarboxylation of carboxylic acid salts that leads to radicals, which dimerize. It is best applied to the synthesis of symmetrical dimers, but in some cases can be used with a mixture of two carboxylic acids to furnish unsymmetrical dimers.



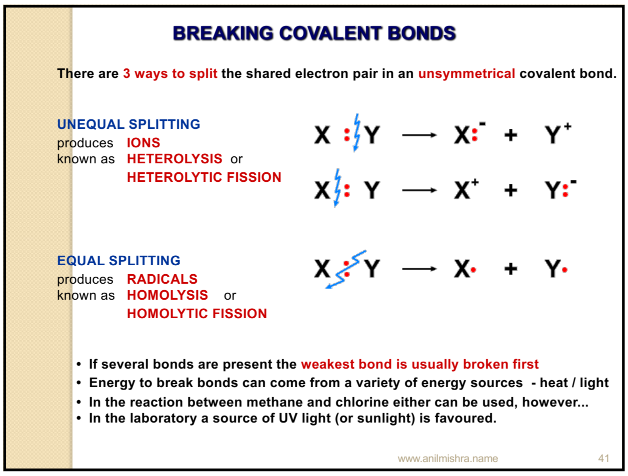
Kolbe Reaction (Electrolysis)

- If a mixture of two different carboxylates are used, all combinations of them are generally seen as the organic product structures:

$3\ R_1COO^- + 3\ R_2COO^- \rightarrow R_1{-}R_1 + R_1{-}R_2 + R_2{-}R_2 + 6CO_2 + 6\ e^-$

Reactions of Alkanes

- Halogenation
- Combustion (oxidation)
- Pyrolysis (cracking)



BREAKING COVALENT BONDS

There are 3 ways to split the shared electron pair in an unsymmetrical covalent bond.

UNEQUAL SPLITTING
produces **IONS**
known as **HETEROLYSIS** or
HETEROLYTIC FISSION

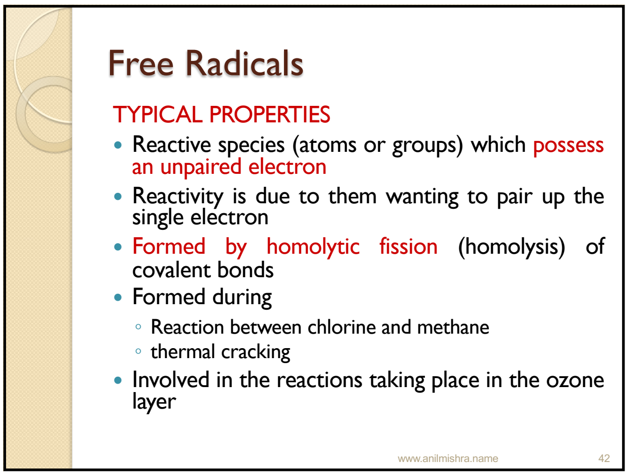
$$X\,:\!\!\wr\,Y \longrightarrow X{:}^{-} + Y^{+}$$

$$X\,\wr\!\!:\,Y \longrightarrow X^{+} + Y{:}^{-}$$

EQUAL SPLITTING
produces **RADICALS**
known as **HOMOLYSIS** or
HOMOLYTIC FISSION

$$X\,\cdot\!\wr\!\cdot\,Y \longrightarrow X\cdot + Y\cdot$$

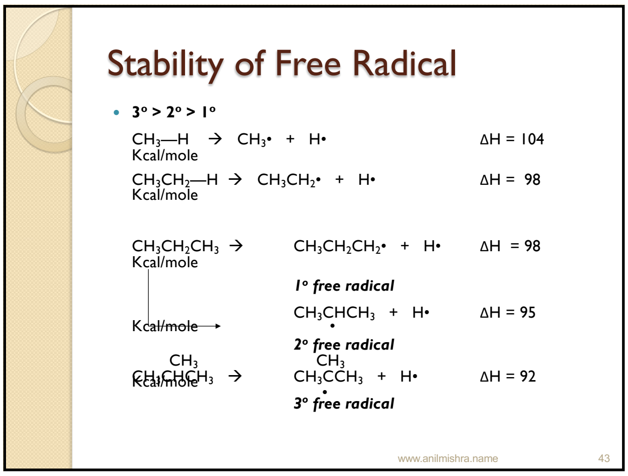
- If several bonds are present the weakest bond is usually broken first
- Energy to break bonds can come from a variety of energy sources - heat / light
- In the reaction between methane and chlorine either can be used, however...
- In the laboratory a source of UV light (or sunlight) is favoured.



Free Radicals

TYPICAL PROPERTIES

- Reactive species (atoms or groups) which possess an unpaired electron
- Reactivity is due to them wanting to pair up the single electron
- Formed by homolytic fission (homolysis) of covalent bonds
- Formed during
  - Reaction between chlorine and methane
  - thermal cracking
- Involved in the reactions taking place in the ozone layer



Stability of Free Radical

- **3° > 2° > 1°**

$CH_3—H \rightarrow CH_3\bullet + H\bullet$ ΔH = 104 Kcal/mole

$CH_3CH_2—H \rightarrow CH_3CH_2\bullet + H\bullet$ ΔH = 98 Kcal/mole

$CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2\bullet + H\bullet$ ΔH = 98 Kcal/mole

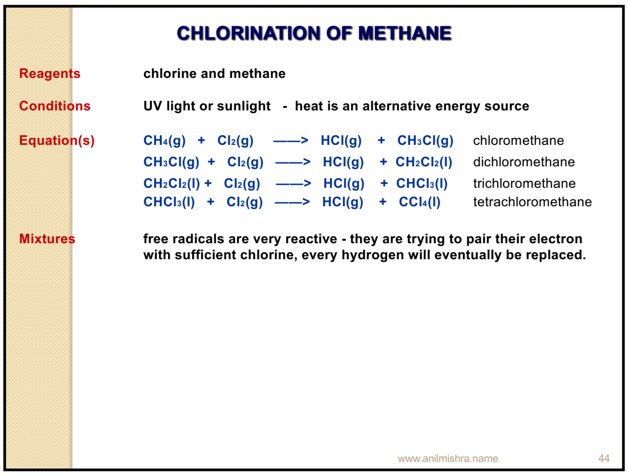
1° free radical

$\rightarrow CH_3\underset{\bullet}{C}HCH_3 + H\bullet$ ΔH = 95 Kcal/mole

2° free radical

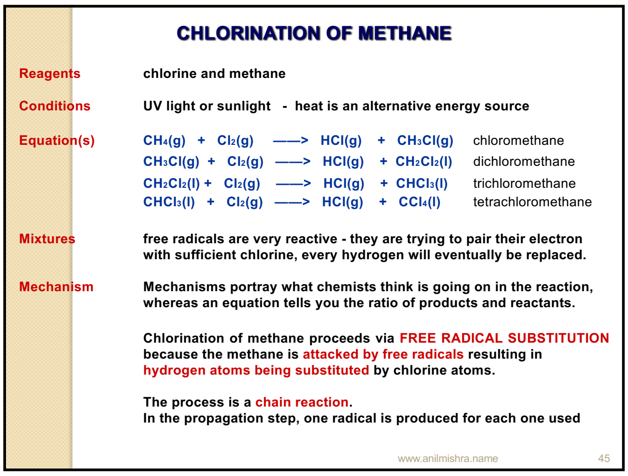
$CH_3\overset{CH_3}{C}HCH_3 \rightarrow CH_3\underset{\bullet}{\overset{CH_3}{C}}CH_3 + H\bullet$ ΔH = 92 Kcal/mole

3° free radical



CHLORINATION OF METHANE

Reagents	chlorine and methane						
Conditions	UV light or sunlight - heat is an alternative energy source						
Equation(s)	$CH_4(g)$	+ $Cl_2(g)$	——>	$HCl(g)$	+	$CH_3Cl(g)$	chloromethane
	$CH_3Cl(g)$	+ $Cl_2(g)$	——>	$HCl(g)$	+	$CH_2Cl_2(l)$	dichloromethane
	$CH_2Cl_2(l)$	+ $Cl_2(g)$	——>	$HCl(g)$	+	$CHCl_3(l)$	trichloromethane
	$CHCl_3(l)$	+ $Cl_2(g)$	——>	$HCl(g)$	+	$CCl_4(l)$	tetrachloromethane
Mixtures	free radicals are very reactive - they are trying to pair their electron with sufficient chlorine, every hydrogen will eventually be replaced.						



CHLORINATION OF METHANE

Reagents chlorine and methane

Conditions UV light or sunlight - heat is an alternative energy source

Equation(s)

$CH_4(g) + Cl_2(g) \longrightarrow HCl(g) + CH_3Cl(g)$ chloromethane

$CH_3Cl(g) + Cl_2(g) \longrightarrow HCl(g) + CH_2Cl_2(l)$ dichloromethane

$CH_2Cl_2(l) + Cl_2(g) \longrightarrow HCl(g) + CHCl_3(l)$ trichloromethane

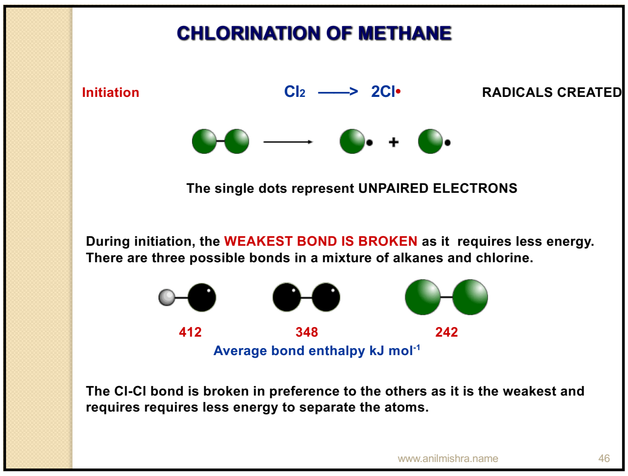
$CHCl_3(l) + Cl_2(g) \longrightarrow HCl(g) + CCl_4(l)$ tetrachloromethane

Mixtures free radicals are very reactive - they are trying to pair their electron with sufficient chlorine, every hydrogen will eventually be replaced.

Mechanism Mechanisms portray what chemists think is going on in the reaction, whereas an equation tells you the ratio of products and reactants.

Chlorination of methane proceeds via FREE RADICAL SUBSTITUTION because the methane is attacked by free radicals resulting in hydrogen atoms being substituted by chlorine atoms.

The process is a chain reaction.
In the propagation step, one radical is produced for each one used



CHLORINATION OF METHANE

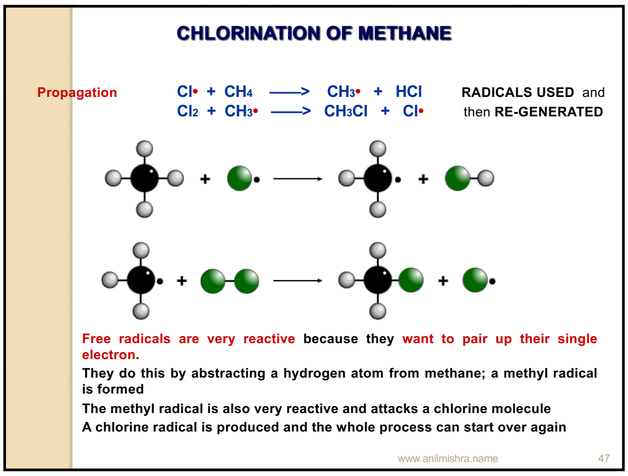
Initiation $Cl_2 \longrightarrow 2Cl\bullet$ RADICALS CREATED

The single dots represent UNPAIRED ELECTRONS

During initiation, the WEAKEST BOND IS BROKEN as it requires less energy.
There are three possible bonds in a mixture of alkanes and chlorine.

Average bond enthalpy kJ mol^{-1}

The Cl-Cl bond is broken in preference to the others as it is the weakest and requires requires less energy to separate the atoms.



CHLORINATION OF METHANE

Propagation

$Cl\bullet + CH_4 \longrightarrow CH_3\bullet + HCl$ RADICALS USED and

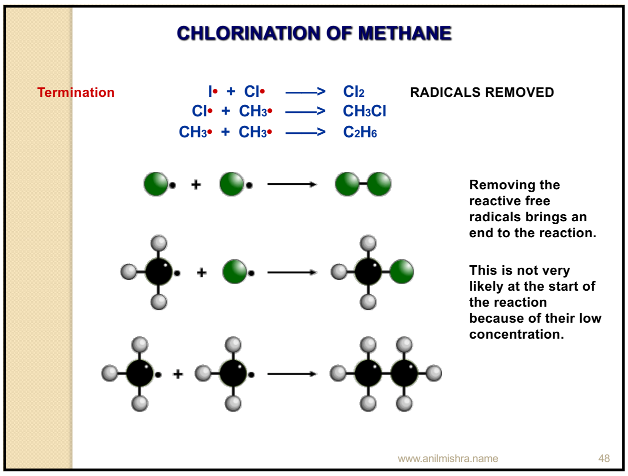
$Cl_2 + CH_3\bullet \longrightarrow CH_3Cl + Cl\bullet$ then RE-GENERATED

Free radicals are very reactive because they want to pair up their single electron.

They do this by abstracting a hydrogen atom from methane; a methyl radical is formed

The methyl radical is also very reactive and attacks a chlorine molecule

A chlorine radical is produced and the whole process can start over again



CHLORINATION OF METHANE

Termination

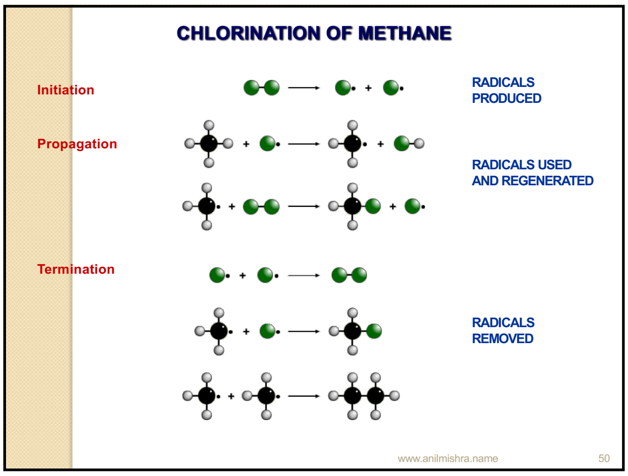
$I\bullet + Cl\bullet \longrightarrow Cl_2$ RADICALS REMOVED

$Cl\bullet + CH_3\bullet \longrightarrow CH_3Cl$

$CH_3\bullet + CH_3\bullet \longrightarrow C_2H_6$

Removing the reactive free radicals brings an end to the reaction.

This is not very likely at the start of the reaction because of their low concentration.



CHLORINATION OF METHANE

Initiation

RADICALS PRODUCED

Propagation

RADICALS USED AND REGENERATED

Termination

RADICALS REMOVED

CHLORINATION OF METHANE

Further propagation If **excess chlorine** is present, **further substitution** takes place

The equations show the propagation steps for the formation of...

dichloromethane
$Cl\bullet + CH_3Cl \longrightarrow CH_2Cl\bullet + HCl$
$Cl_2 + CH_2Cl\bullet \longrightarrow CH_2Cl_2 + Cl\bullet$

trichloromethane
$Cl\bullet + CH_2Cl_2 \longrightarrow CHCl_2\bullet + HCl$
$Cl_2 + CHCl_2\bullet \longrightarrow CHCl_3 + Cl\bullet$

tetrachloromethane
$Cl\bullet + CHCl_3 \longrightarrow CCl_3\bullet + HCl$
$Cl_2 + CCl_3\bullet \longrightarrow CCl_4 + Cl\bullet$

Mixtures Because of the **many possible reactions** there will be a **mixture of products**.
Individual haloalkanes can be **separated by fractional distillation**.

CRACKING

Involves the breaking of C-C bonds in alkanes
Converts heavy fractions into higher value products

THERMAL	proceeds via a free radical mechanism
CATALYTIC	proceeds via a carbocation (carbonium ion) mechanism

THERMAL

HIGH PRESSURE ... 7000 kPa
HIGH TEMPERATURE ... 400°C to 900°C
FREE RADICAL MECHANISM
HOMOLYTIC FISSION
PRODUCES MOSTLY ALKENES ... e.g. ETHENE for making polymers and ethanol
PRODUCES HYDROGEN ... used in the Haber Process and in margarine manufacture

Bonds can be broken anywhere in the molecule by C-C bond fission or C-H bond fission

CRACKING

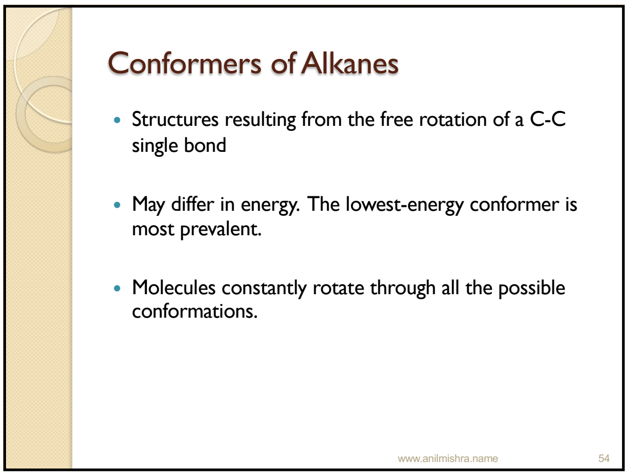
Involves the breaking of C-C bonds in alkanes
Converts heavy fractions into higher value products

THERMAL	proceeds via a free radical mechanism
CATALYTIC	proceeds via a carbocation (carbonium ion) mechanism

CATALYTIC

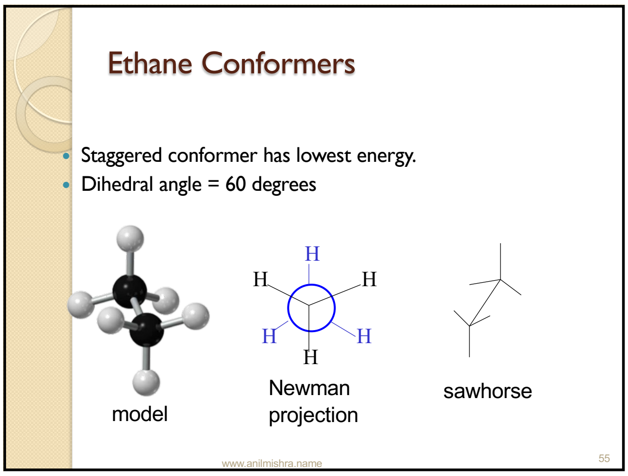
SLIGHT PRESSURE
HIGH TEMPERATURE ... 450°C
ZEOLITE CATALYST
CARBOCATION (IONIC) MECHANISM
HETEROLYTIC FISSION
PRODUCES BRANCHED AND CYCLIC ALKANES, AROMATIC HYDROCARBONS
USED FOR **MOTOR FUELS**

ZEOLITES are crystalline aluminosilicates; clay like substances



Conformers of Alkanes

- Structures resulting from the free rotation of a C-C single bond
- May differ in energy. The lowest-energy conformer is most prevalent.
- Molecules constantly rotate through all the possible conformations.



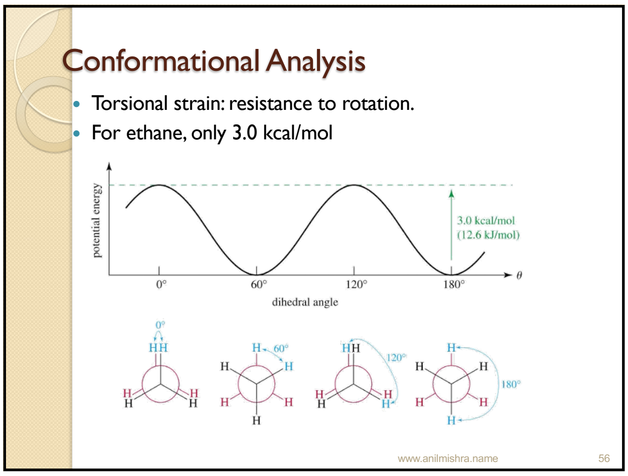
Ethane Conformers

- Staggered conformer has lowest energy.
- Dihedral angle = 60 degrees

model

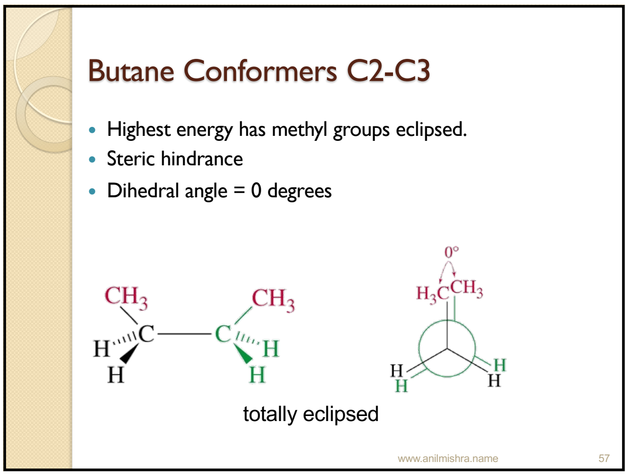
Newman projection

sawhorse



Conformational Analysis

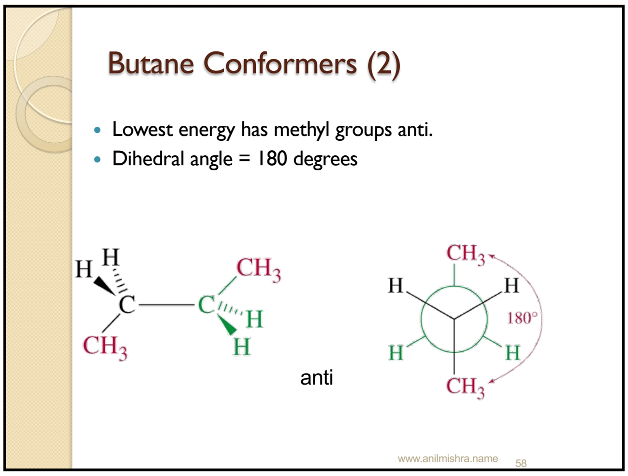
- Torsional strain: resistance to rotation.
- For ethane, only 3.0 kcal/mol



Butane Conformers C2-C3

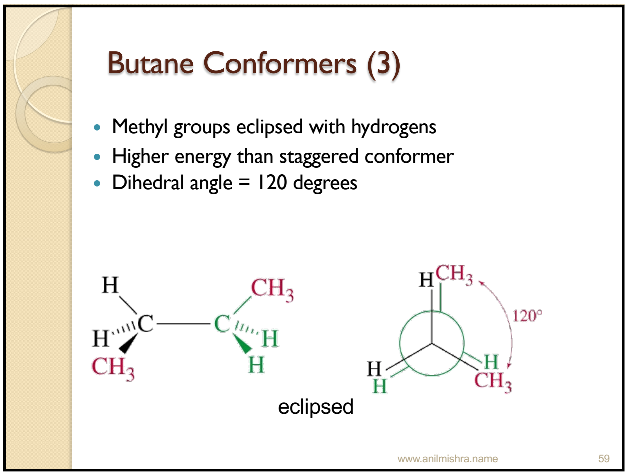
- Highest energy has methyl groups eclipsed.
- Steric hindrance
- Dihedral angle = 0 degrees

totally eclipsed



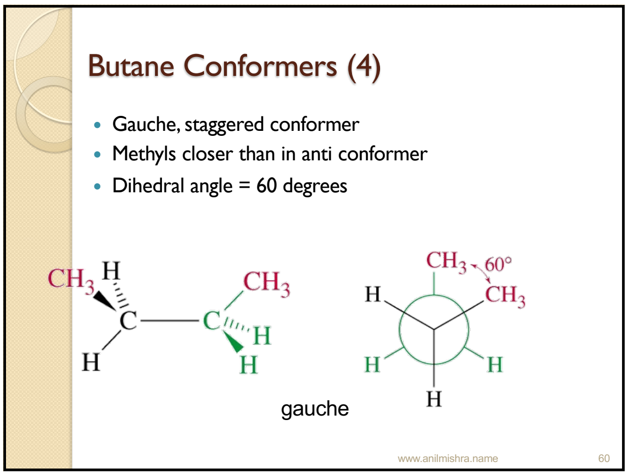
Butane Conformers (2)

- Lowest energy has methyl groups anti.
- Dihedral angle = 180 degrees



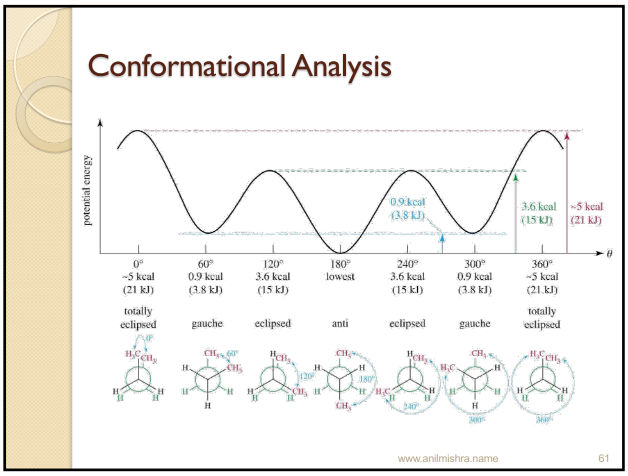
Butane Conformers (3)

- Methyl groups eclipsed with hydrogens
- Higher energy than staggered conformer
- Dihedral angle = 120 degrees



Butane Conformers (4)

- Gauche, staggered conformer
- Methyls closer than in anti conformer
- Dihedral angle = 60 degrees



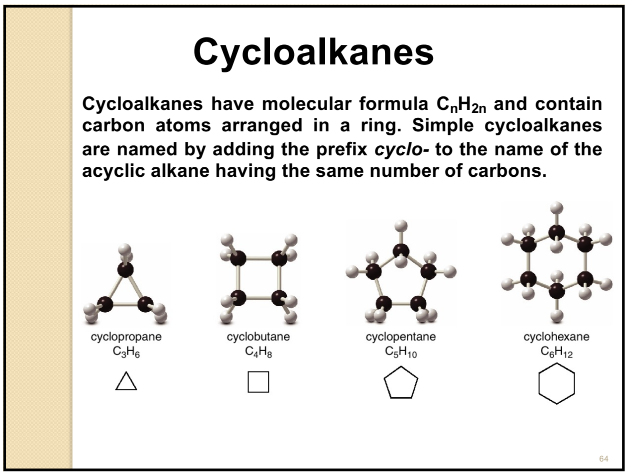
Conformational Analysis

Cycloalkanes

- If the carbon chain that forms the straight-chain hydrocarbon is long enough, the two ends coming together to form a **cycloalkane**.
- One hydrogen atom has to be removed from each end of the hydrocarbon chain to form the CC bond that closes the ring.
- Cycloalkanes therefore have two less hydrogen atoms than the parent alkane and a generic formula of **C_nH_{2n}**.

Cycloalkanes

- Rings of carbon atoms (CH$_2$ groups)
- Formula: C_nH_{2n}
- Nonpolar, insoluble in water
- Compact shape
- Melting and boiling points similar to branched alkanes with same number of carbons

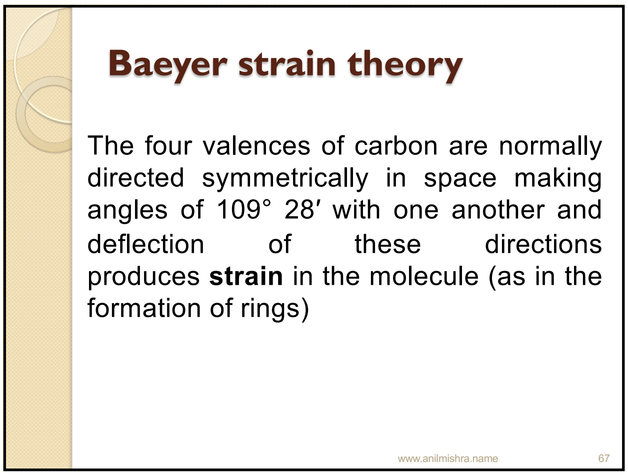


Cycloalkanes

Cycloalkanes have molecular formula C_nH_{2n} and contain carbon atoms arranged in a ring. Simple cycloalkanes are named by adding the prefix *cyclo-* to the name of the acyclic alkane having the same number of carbons.

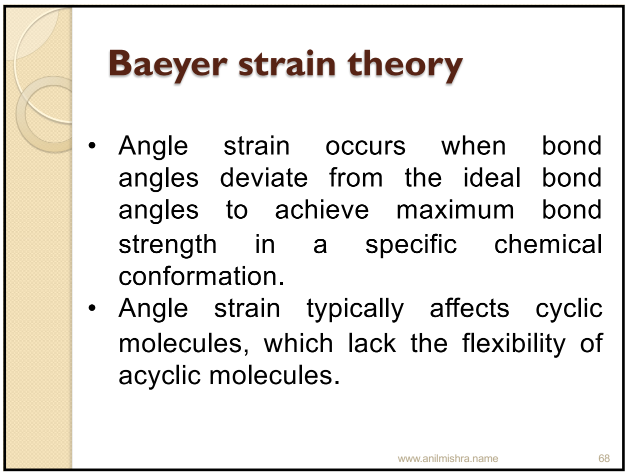
Cycloalkane Stability

- 5- and 6-membered rings most stable
- Bond angle closest to 109.5°
- Angle (Baeyer) strain
- Measured by heats of combustion per -CH$_2$ -



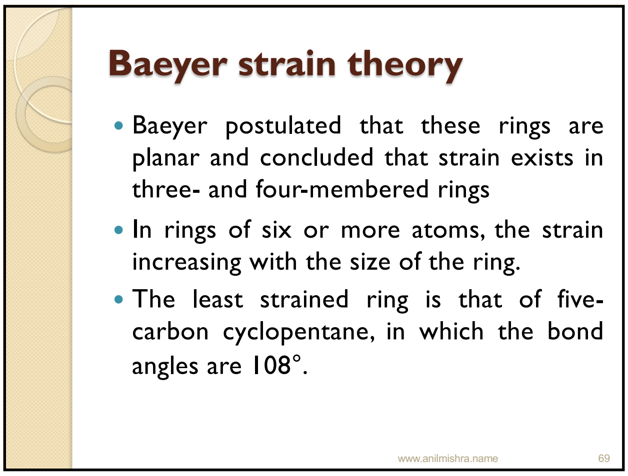
Baeyer strain theory

The four valences of carbon are normally directed symmetrically in space making angles of 109° 28′ with one another and deflection of these directions produces **strain** in the molecule (as in the formation of rings)



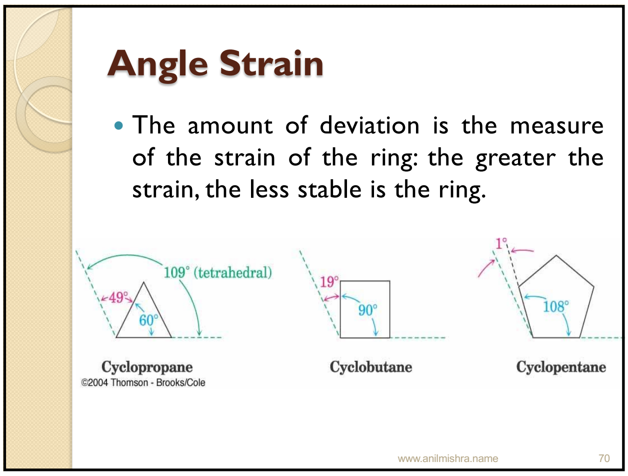
Baeyer strain theory

- Angle strain occurs when bond angles deviate from the ideal bond angles to achieve maximum bond strength in a specific chemical conformation.
- Angle strain typically affects cyclic molecules, which lack the flexibility of acyclic molecules.



Baeyer strain theory

- Baeyer postulated that these rings are planar and concluded that strain exists in three- and four-membered rings
- In rings of six or more atoms, the strain increasing with the size of the ring.
- The least strained ring is that of five-carbon cyclopentane, in which the bond angles are 108°.



Angle Strain

- The amount of deviation is the measure of the strain of the ring: the greater the strain, the less stable is the ring.

©2004 Thomson - Brooks/Cole

Nature of Ring Strain

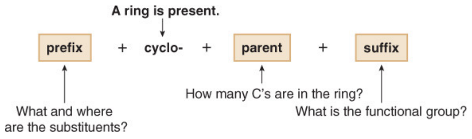
- In cycloalkanes, each carbon is bonded nonpolar covalently to two carbons and two hydrogen.
  - The carbons have sp^3 hybrization and should have ideal bond angles of 109.5°.
- Due to the limitations of cyclic structure, however, the ideal angle is only achieved in a six carbon ring —
  - cyclohexane in chair conformation.
- For other cycloalkanes, the bond angles deviate from ideal.
- In cyclopropanes (3 carbons) and cyclobutanes (4 carbons) the C-C bonds are 60° and ~90° respectively.

Cyclohexane

- Combustion data shows it's unstrained.
- Angles would be 120°, if planar.
- The chair conformer has 109.5° bond angles and all hydrogens are staggered.
- No angle strain and no torsional strain.

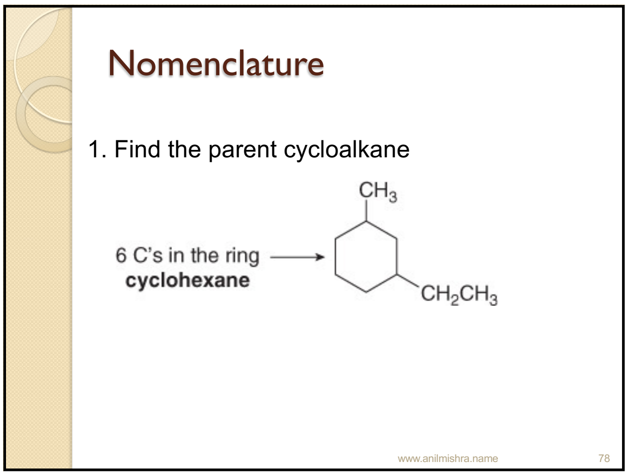
Cycloalkanes

Cycloalkanes are named by using similar rules of naming alkane, but the prefix cyclo- immediately precedes the name of the parent.



Naming the cycloalkanes:

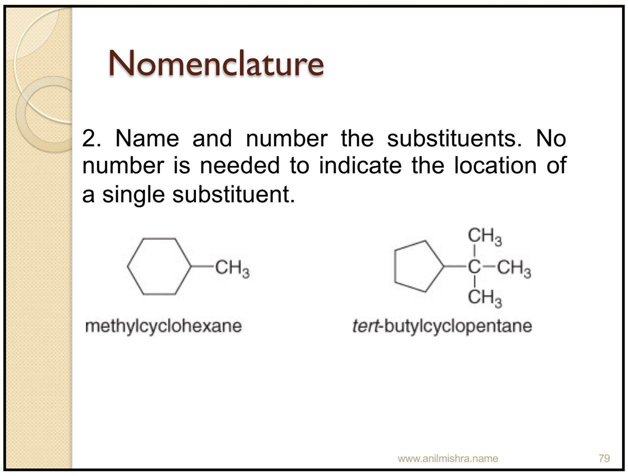
- Find the longest continuous loop of carbon atoms in the skeleton structure.
- Name the compound as a derivative of the cycloalkane with this number of carbon atoms:3-C = cyclo***prop***ane
  4-C = cyclo***but***ane
  5-C = cyclo***pent***ane



Nomenclature

1. Find the parent cycloalkane

6 C's in the ring →
cyclohexane

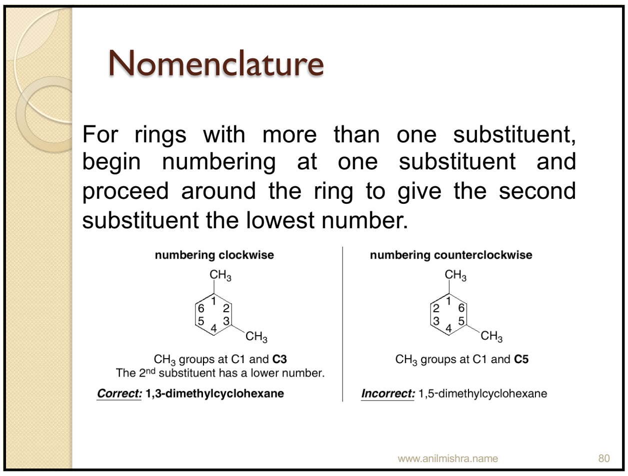


Nomenclature

2. Name and number the substituents. No number is needed to indicate the location of a single substituent.

methylcyclohexane

tert-butylcyclopentane



Nomenclature

For rings with more than one substituent, begin numbering at one substituent and proceed around the ring to give the second substituent the lowest number.

numbering clockwise

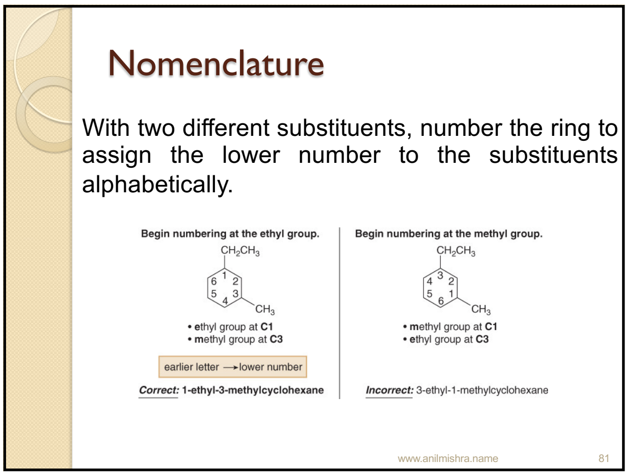
CH_3 groups at C1 and **C3**
The 2nd substituent has a lower number.

Correct: **1,3-dimethylcyclohexane**

numbering counterclockwise

CH_3 groups at C1 and **C5**

Incorrect: 1,5-dimethylcyclohexane



Nomenclature

With two different substituents, number the ring to assign the lower number to the substituents alphabetically.

Begin numbering at the ethyl group.

- **e**thyl group at **C1**
- **m**ethyl group at **C3**

earlier letter → lower number

Correct: **1-ethyl-3-methylcyclohexane**

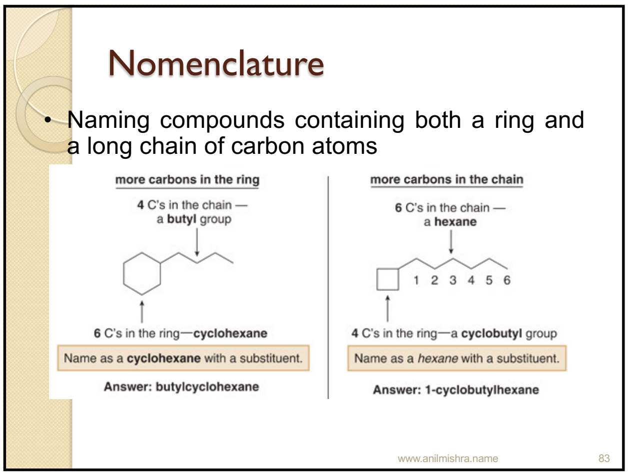
Begin numbering at the methyl group.

- **m**ethyl group at **C1**
- **e**thyl group at **C3**

Incorrect: 3-ethyl-1-methylcyclohexane

Nomenclature

- An alkane composed of both a ring and a long chain.
- If the number of carbons in the ring is greater than or equal to the number of carbons in the longest chain, the compound is named as a cycloalkane.



Nomenclature

- Naming compounds containing both a ring and a long chain of carbon atoms

more carbons in the ring

4 C's in the chain — a **butyl** group

6 C's in the ring—**cyclohexane**

Name as a **cyclohexane** with a substituent.

Answer: butylcyclohexane

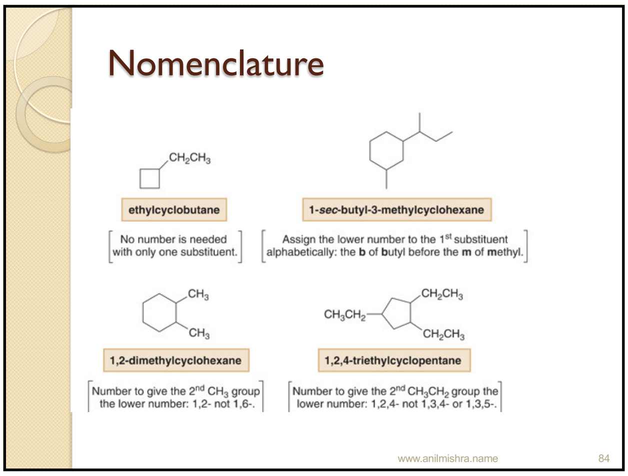
more carbons in the chain

6 C's in the chain — a **hexane**

4 C's in the ring—a **cyclobutyl** group

Name as a *hexane* with a substituent.

Answer: 1-cyclobutylhexane



Nomenclature

ethylcyclobutane

[No number is needed with only one substituent.]

1-*sec*-butyl-3-methylcyclohexane

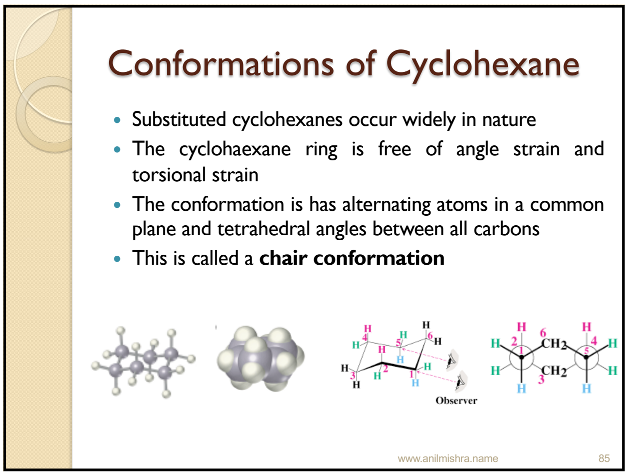
[Assign the lower number to the 1st substituent alphabetically: the **b** of **b**utyl before the **m** of **m**ethyl.]

1,2-dimethylcyclohexane

[Number to give the 2nd CH_3 group the lower number: 1,2- not 1,6-.]

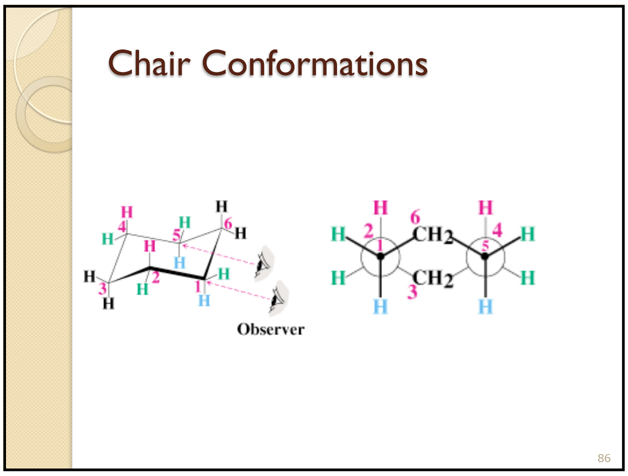
1,2,4-triethylcyclopentane

[Number to give the 2nd CH_3CH_2 group the lower number: 1,2,4- not 1,3,4- or 1,3,5-.]



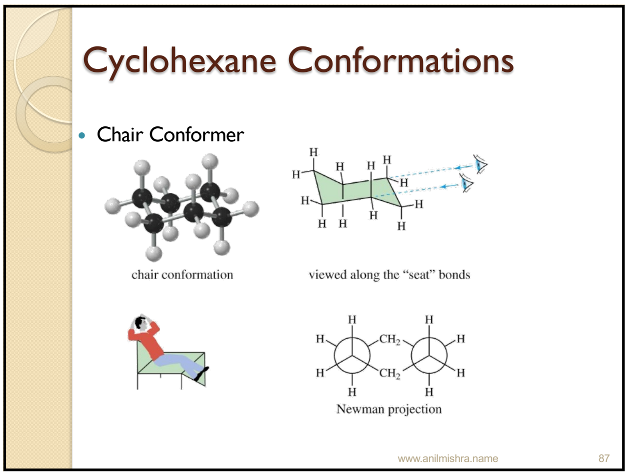
Conformations of Cyclohexane

- Substituted cyclohexanes occur widely in nature
- The cyclohaexane ring is free of angle strain and torsional strain
- The conformation is has alternating atoms in a common plane and tetrahedral angles between all carbons
- This is called a **chair conformation**



Chair Conformations

86



Cyclohexane Conformations

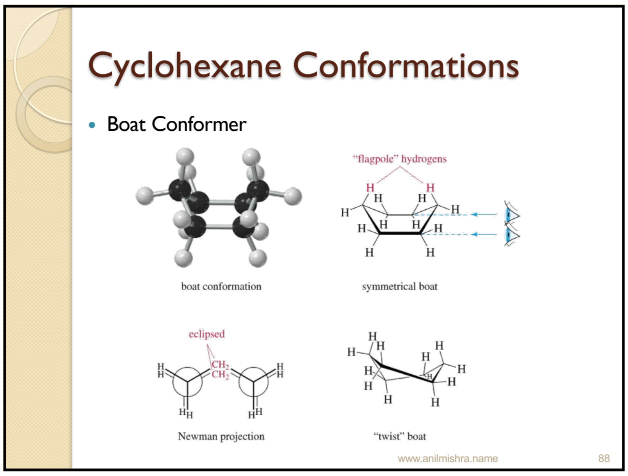
- Chair Conformer

chair conformation

viewed along the "seat" bonds

Newman projection

87



Cyclohexane Conformations

- Boat Conformer

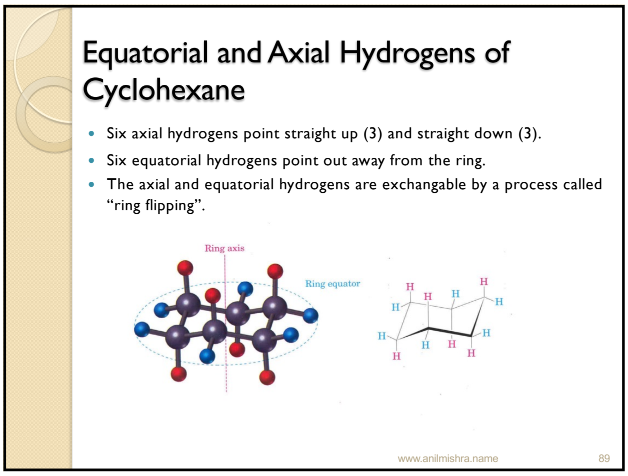
boat conformation

symmetrical boat

Newman projection

"twist" boat

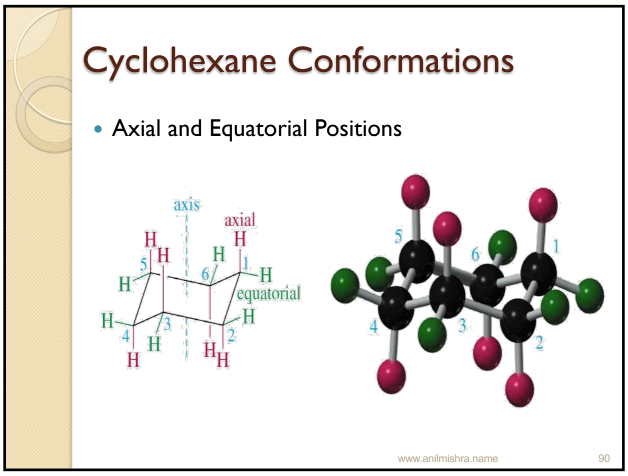
88



Equatorial and Axial Hydrogens of Cyclohexane

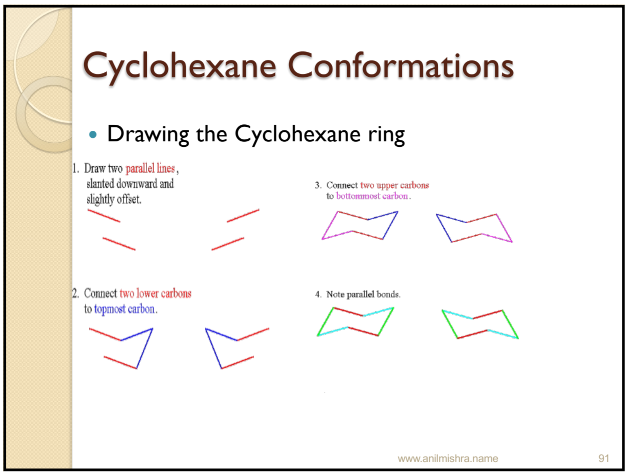
- Six axial hydrogens point straight up (3) and straight down (3).
- Six equatorial hydrogens point out away from the ring.
- The axial and equatorial hydrogens are exchangable by a process called "ring flipping".

89



Cyclohexane Conformations

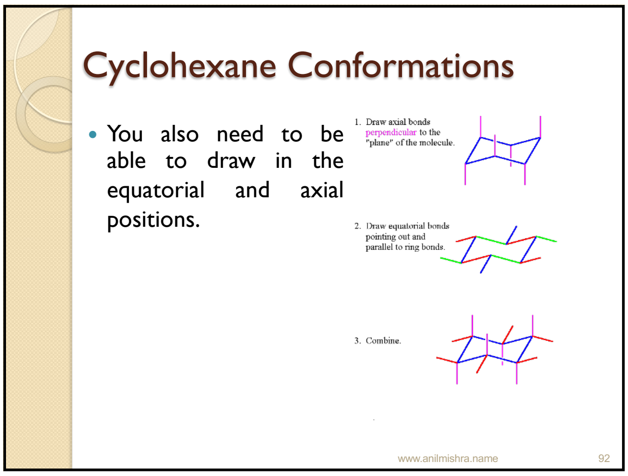
- Axial and Equatorial Positions



Cyclohexane Conformations

- Drawing the Cyclohexane ring

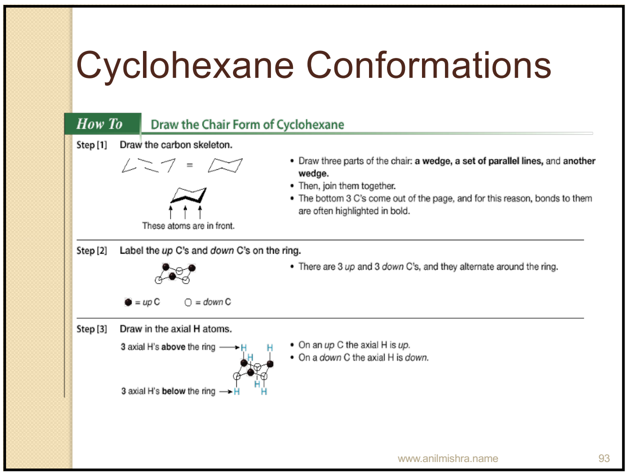
1. Draw two parallel lines, slanted downward and slightly offset.
2. Connect two lower carbons to topmost carbon.
3. Connect two upper carbons to bottommost carbon.
4. Note parallel bonds.



Cyclohexane Conformations

- You also need to be able to draw in the equatorial and axial positions.

1. Draw axial bonds perpendicular to the "plane" of the molecule.
2. Draw equatorial bonds pointing out and parallel to ring bonds.
3. Combine.



Cyclohexane Conformations

How To Draw the Chair Form of Cyclohexane

Step [1] Draw the carbon skeleton.

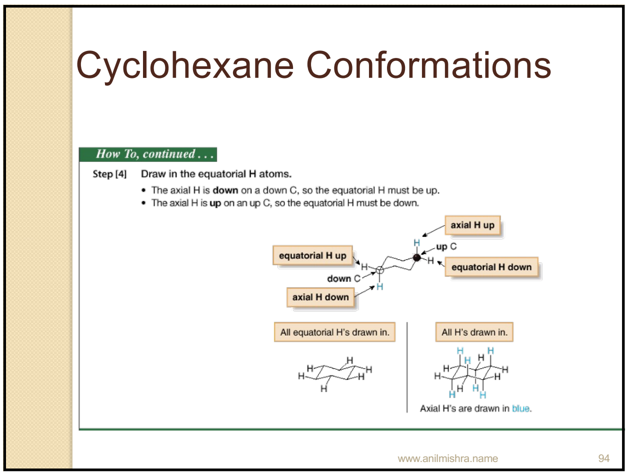
- Draw three parts of the chair: **a wedge, a set of parallel lines,** and **another wedge.**
- Then, join them together.
- The bottom 3 C's come out of the page, and for this reason, bonds to them are often highlighted in bold.

Step [2] Label the *up* C's and *down* C's on the ring.

- There are 3 *up* and 3 *down* C's, and they alternate around the ring.

Step [3] Draw in the axial H atoms.

- On an *up* C the axial H is *up.*
- On a *down* C the axial H is *down.*



Cyclohexane Conformations

How To, continued . . .

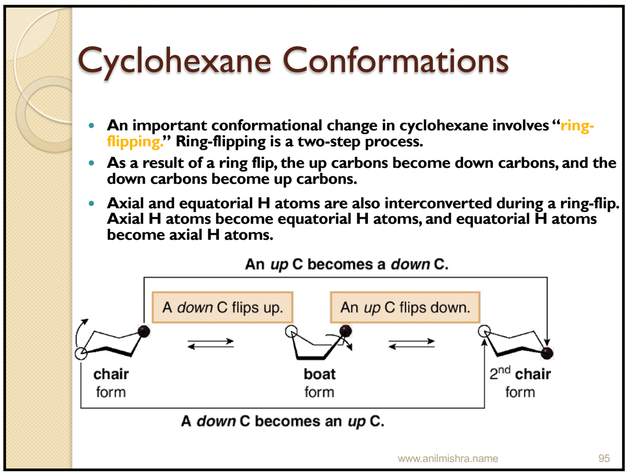
Step [4] Draw in the equatorial H atoms.

- The axial H is **down** on a down C, so the equatorial H must be up.
- The axial H is **up** on an up C, so the equatorial H must be down.

Axial H's are drawn in blue.

www.anilmishra.name 94

94

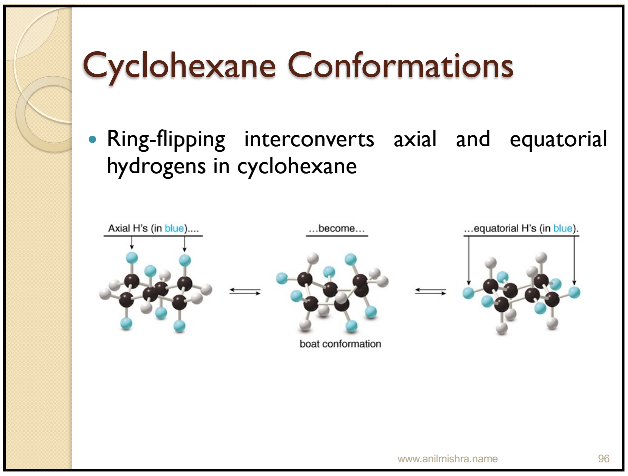


Cyclohexane Conformations

- **An important conformational change in cyclohexane involves "ring-flipping." Ring-flipping is a two-step process.**
- **As a result of a ring flip, the up carbons become down carbons, and the down carbons become up carbons.**
- **Axial and equatorial H atoms are also interconverted during a ring-flip. Axial H atoms become equatorial H atoms, and equatorial H atoms become axial H atoms.**

www.anilmishra.name 95

95

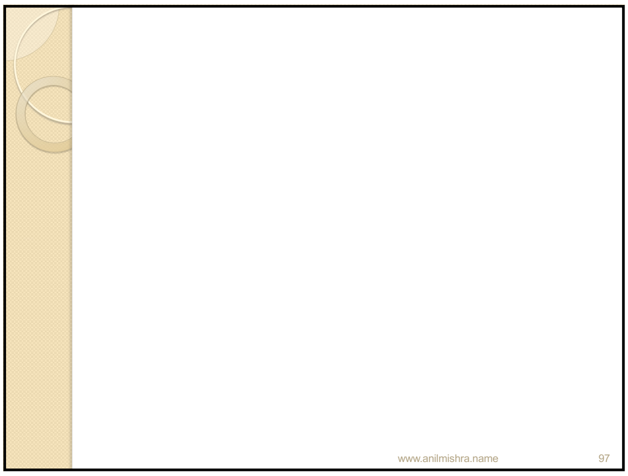


Cyclohexane Conformations

- Ring-flipping interconverts axial and equatorial hydrogens in cyclohexane

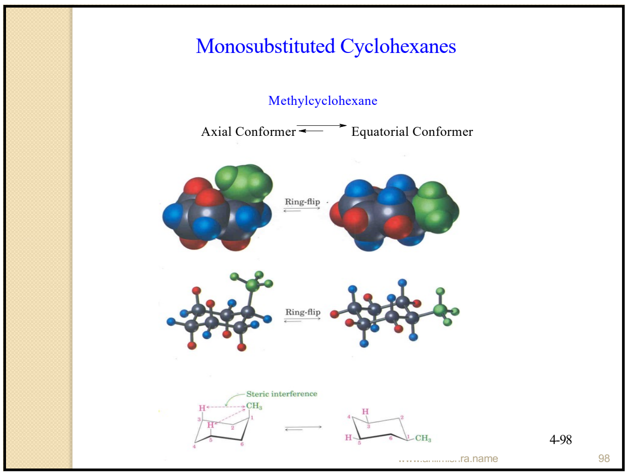
www.anilmishra.name 96

96



www.anilmishra.name 97

97



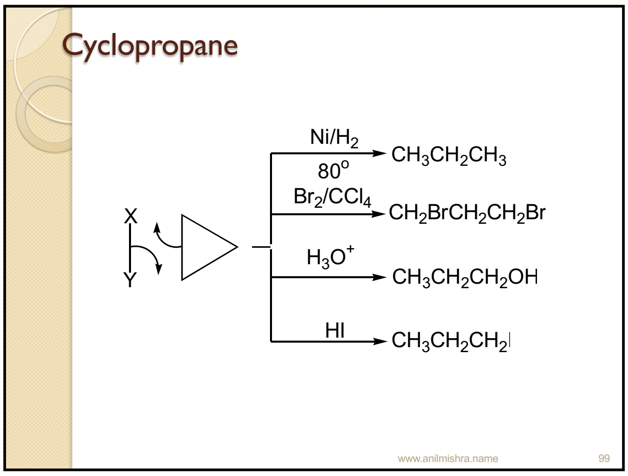
Monosubstituted Cyclohexanes

Methylcyclohexane

Axial Conformer ⇌ Equatorial Conformer

4-98

98



Cyclopropane

$\xrightarrow[80^o]{Ni/H_2}$ $CH_3CH_2CH_3$

$\xrightarrow{Br_2/CCl_4}$ $CH_2BrCH_2CH_2Br$

$\xrightarrow{H_3O^+}$ $CH_3CH_2CH_2OH$

$\xrightarrow{HI}$ $CH_3CH_2CH_2I$

99