

University of Thi –Qar
College of science
Department of Chemistry

Organic Chemistry
Second stage
lecture 2

Dr. Athraa hameed mekky

- 1- Hydrocarbons.**
- 2- Aliphatic compounds.**
- 3- Alkanes:**
 - 1- Nomenclature of alkane**
 - 2- Molecular representation**
 - 3- Physical properties**
 - 4- Synthesis of alkanes**
 - 5- Reaction of alkanes**
 - 6- Isomers.**

Hydrocarbons

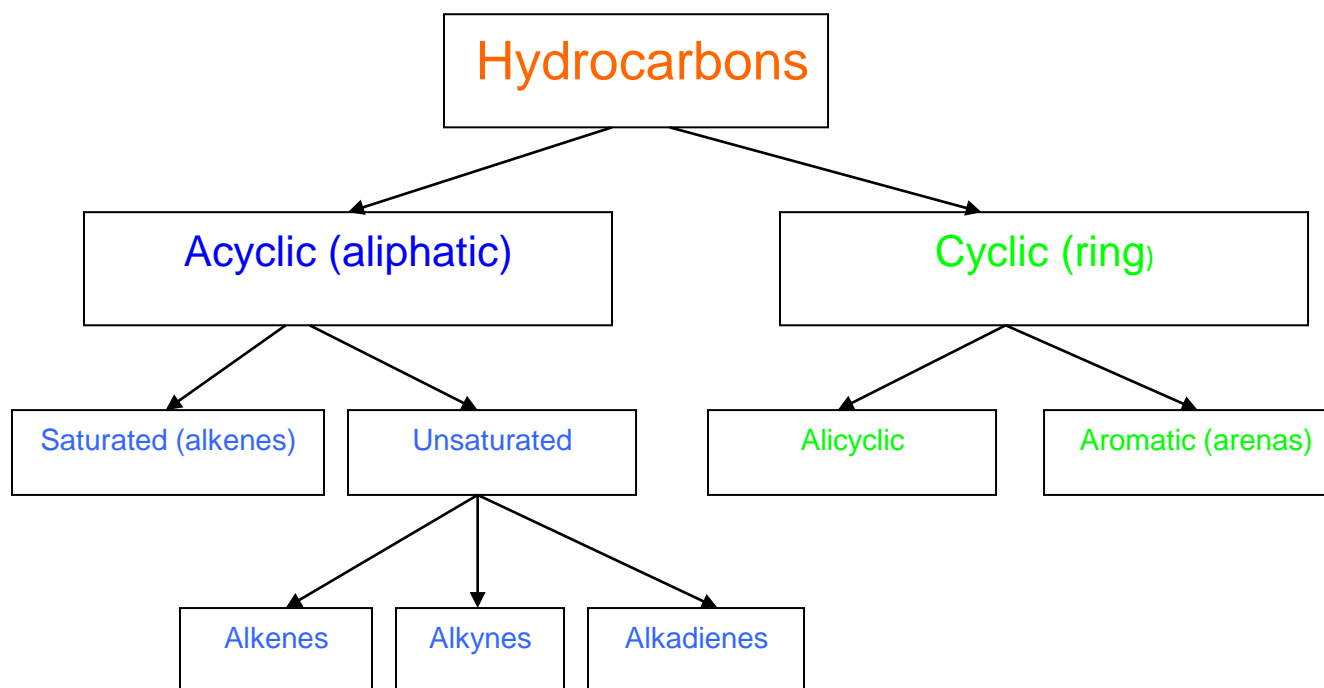
In organic chemistry, a hydrocarbon is an organic compounds consisting entirely of hydrogen and carbon.

Classifications of hydrocarbons.

•1- Aliphatic 2- Aromatic or

1. Saturated hydrocarbons : alkanes
2. Unsaturated hydrocarbons: have one or more double or triple bonds between carbon atoms. Those with double bond are called **alkenes** Those with one double bond have the formula C_nH_{2n} (assuming non-cyclic structures). Those containing triple bonds are called **alkynes** with general formula C_nH_{2n-2}
3. **Cycloalkanes** : are hydrocarbons containing one or more carbon rings to which hydrogen atoms are attached. The general formula for a saturated hydrocarbon containing one ring is C_nH_{2n} .

4- Aromatic hydrocarbons : known as arenes are hydrocarbons that have at least one aromatic ring.



1-Aliphatic compound.

Aliphatic compound is a compound containing carbon and hydrogen joined together in straight chains, branched or non-aromatic rings. Aliphatic compounds can be saturated joined by single bonds ([alkanes](#)), or unsaturated, with double bonds ([alkenes](#)) or triple bonds ([alkynes](#)). Besides hydrogen other elements can be bound to the carbon chain, the most common being oxygen nitrogen sulphur and chlorine

Alkanes

1- Alkanes are the simplest of the hydrocarbon species. The general formula for saturated hydrocarbons is C_nH_{2n+2} .

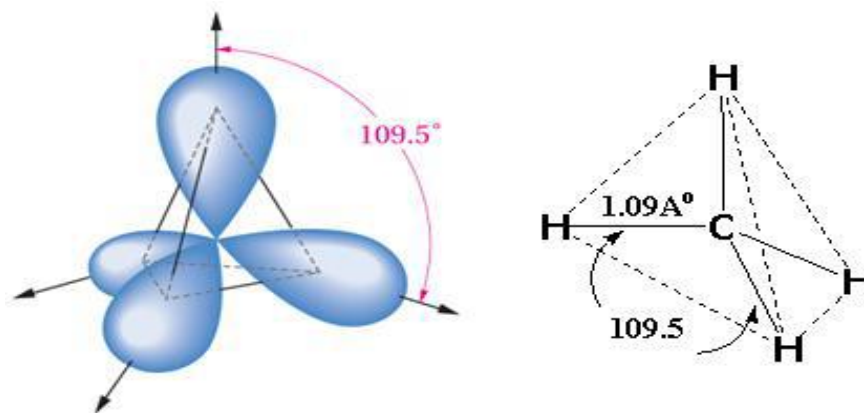
2- Alkanes are the hydrocarbons of aliphatic row.

3-Alkanes are hydrocarbons in which all the bonds are single covalent bonds (σ -bonds).

4- Alkanes are called saturated hydrocarbons.

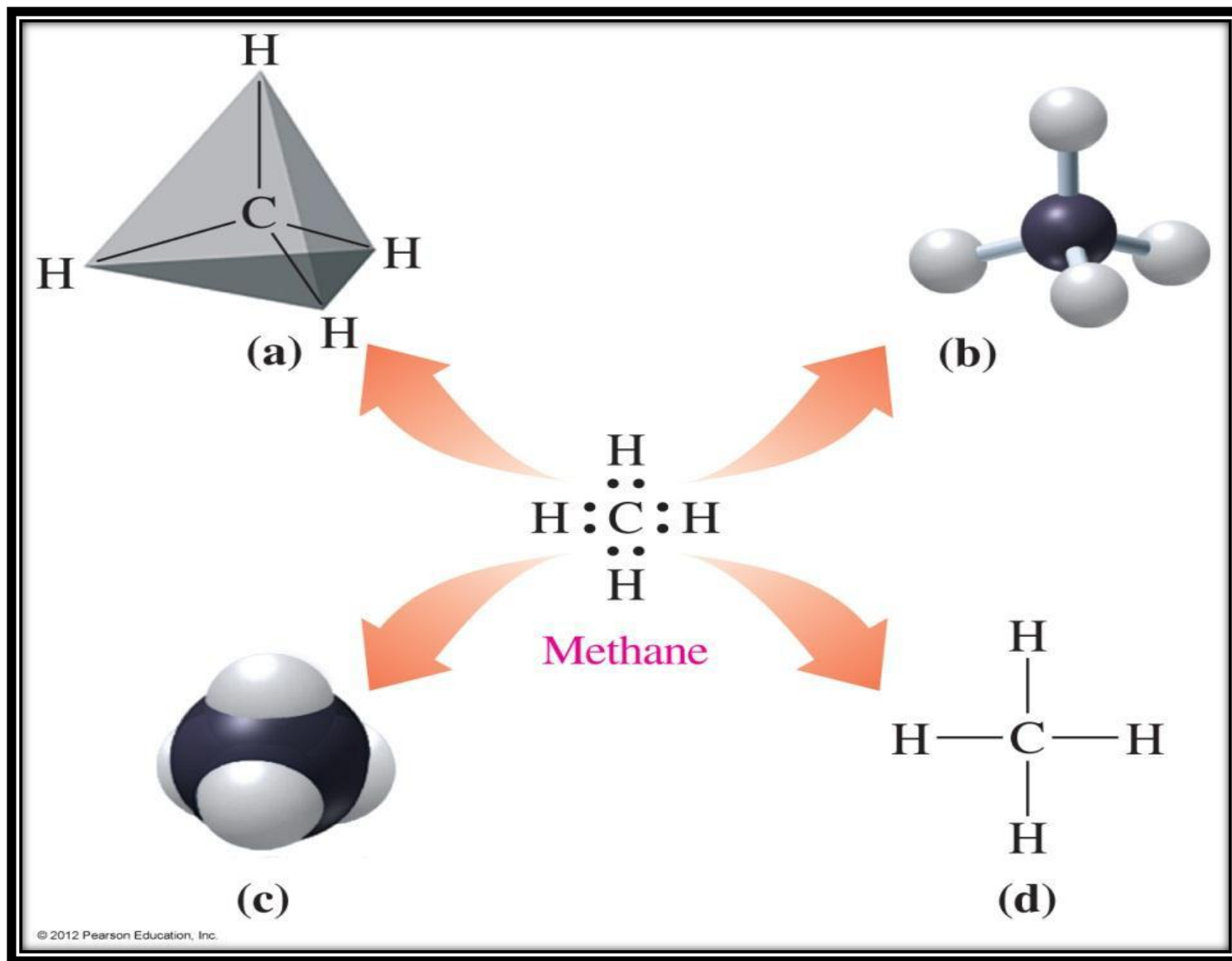
Structure of alkanes .

The simplest alkane is methane , **CH₄** . Methane is perfectly **tetrahedral** with the **109.5°** bond angles predicted for an **sp³** hybrid carbon . The four hydrogen atoms are covalently bonded to central carbon atom, with bond lengths of 1.09Å.



Molecular Representations

Methane is represented using different models: (a) tetrahedron, (b) ball-and-stick model, (c) space-filling model, (d) expanded structural formula



Alkanes are written with structural formulas that are .

1. **Expanded formula** to show each bond in the molecules
2. **Condensed formula** to show each carbon atom and its attached hydrogen atoms
3. **Line-angle formula:** is a form of the structural formula . A line represents a carbon-carbon bond and a vertex represents a carbon atom. A line ending in space represents a -CH_3 group.

physical properties.

1- **non-polar or only weakly polar**, cannot hydrogen bond \rightarrow relatively weak intermolecular forces . *hydrophobic* ('water hating') since they do not dissolve in water. Typically the density of alkanes is around 0.7g/ml, and so when an alkane and water are mixed, they will form two separate phases, with the alkane on top. (Oil floats on water)

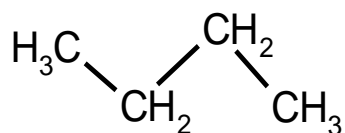
2- **lower mp / bp increase with size** ; decrease with branching The boiling points shown are for the "straight chain" isomers of which there is more than one. Cycloalkanes have boiling points that are approximately 20 K higher than the corresponding straight chain alkane .

3- **At room temperature** ($C_1 - C_4$ are gases $C_5 - C_{17}$ are liquids (*Methane to butane are gases at normal pressure Pentane to decane are liquids at normal pressures*) $> C_{17}$ are solid .

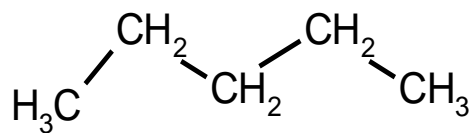
Nomenclature

Certain branched alkanes have common names that are still widely used today. These common names make use of prefixes, such as *normal*, *iso-*, *sec-*, *tert-*, and *neo* -.

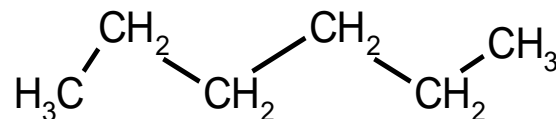
- **Noranal (n- alkane)** : which have continuous carbon chain.



n- Butane

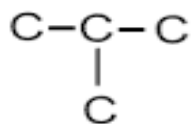


n- Pentane

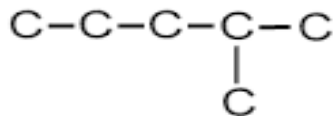


n- Hexane

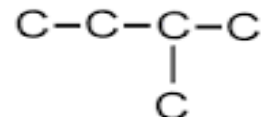
- **isoalkane** The prefix *iso-*, which stands for isomer, is commonly given to 2-methyl alkanes. In other words, if there is methyl group located on the second carbon of a carbon chain, we can use the prefix *iso-*. The prefix will be placed in front of the alkane name that indicates the *total* number of carbons. Examples isobutane which is the same as 2-methylpropane .



isobutane
2-methyl propane

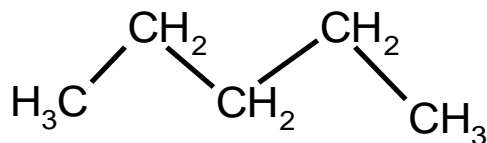


isohexane
2-methyl pentane

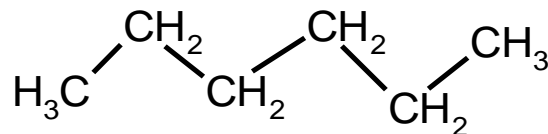


isopentane
2-methyl butane

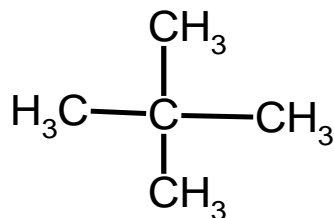
- **neoalkane** : when two methyl group bonded on the same carbon atom in the carbon chain .



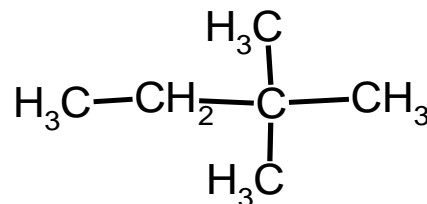
n- Pentane



n- Hexane



Neopentane
2,2- dimethyl propane



Neohexane
2,2- dimethyl butane

Systematic name .

IUPAC name (*International Union of Pure and Applied Chemistry*)

Prefix-Parent-Suffix

Parent- number of carbons in the continuous carbon chain .

Prefix- substituents on the continuous carbon chain .

Suffix- functional groups of hydrocarbons .

Naming Alkanes :

General Formula: $C_nH_{(2n+2)}$

suffix: **-ane**

Parent Names:

NO	NO of C	Parent Names	General Formula	Structure	IUPAC name
1	1	Meth	CH ₄	CH ₄	Methane
2	2	Eth	C ₂ H ₆	CH ₃ CH ₃	Ethane
3	3	Prop	C ₃ H ₈	CH ₃ CH ₂ CH ₃	Propane
4	4	But	C ₄ H ₁₀	CH ₃ (CH ₂) ₂ CH ₃	Butane
5	5	Pent	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	Pentane
6	6	hex	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	Hexane
7	7	Pent	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	Heptane
8	8	Oct	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	Octane
9	9	Non	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃	Nonane
10	10	Dec	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃	Decane

Prefix : name and position number of alkyl group which sub on the carbon chain
 (Substituents are atoms or groups of atoms attached to the carbon chain and include alkyl and halo groups. **Alkyl groups** are carbon branches attached to carbon chains named with a *y* ending)

Alkyl substituents (group): carbon chains which are a substructure of a molecule



R= Rest of the molecule (mainchain)

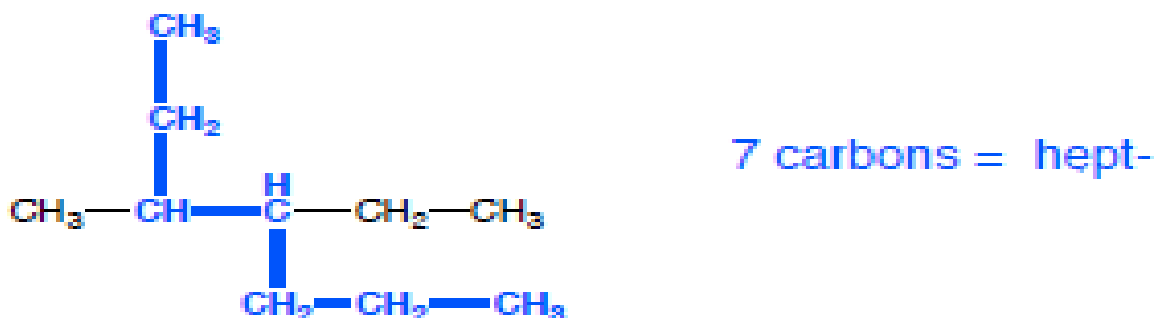
1	$\text{CH}_3\text{-R}$	Methyl
2	$\text{CH}_3\text{CH}_2\text{-R}$	Ethyl
3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{-R}$	Propyl
4	$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{-R}$	Butyl
5	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{-R}$	Pentyl
6	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{-R}$	Hexyl
7	$\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{-R}$	Heptyl
8	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{-R}$	Octyl
9	$\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{-R}$	Nonyl
10	$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{-R}$	Decyl

The prefixes are undec- (11), dodec- (12), tridec- (13), tetradec- (14), pentadec- (15), hexadec- (16), heptadec- (17), octadec- (18), nonadec- (19), and icos- (20)

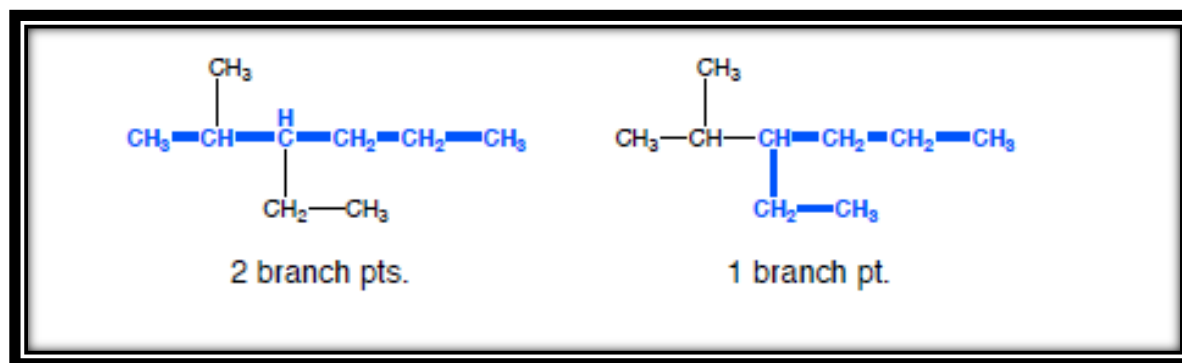
Rules for Systematic Nomenclature of Alkanes

1. Find the parent chain

a. Identify the longest continuous carbon chain as the parent chain.

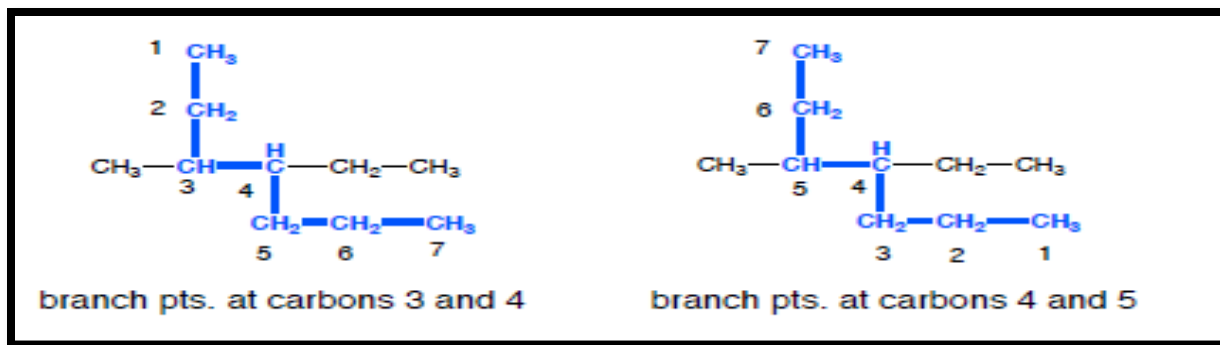


b. If more than one different chains are of equal length (number of carbons), choose the one with the greater number of branch points (substituents) as the parent.



2. Numbering the carbons of the parent chain

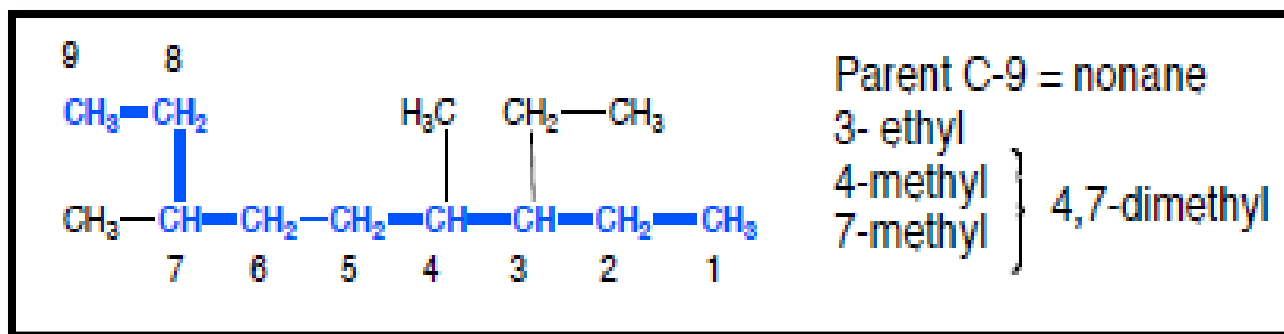
a. Number the carbon atoms of the parent chain so that any branch points have the lowest possible number



b. If there is branching equidistant from both ends of the parent chain, number so the second branch point has the lowest number

3. Substituents.

- a. Identify and number the substituents and list them in alphabetical order.
- b. If there are two substituents on the same carbon, assign them the same number.



4. Write out the name

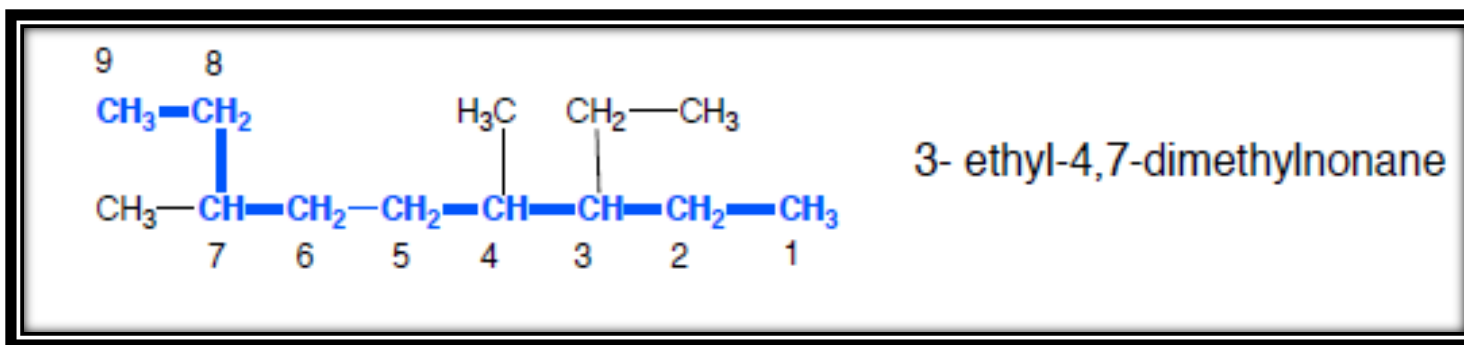
a. Write out the name as a single word.

hyphens (-) separate prefixes , commas (,) separate numbers

b. Substituents are listed in alphabetical order

4c. If two or more identical substituents are present use the prefixes: di- for two tri- for three tetra- for four

note: these prefixes (di-, tri-, tetra-, etc.) are not used for alphabetizing purposes.

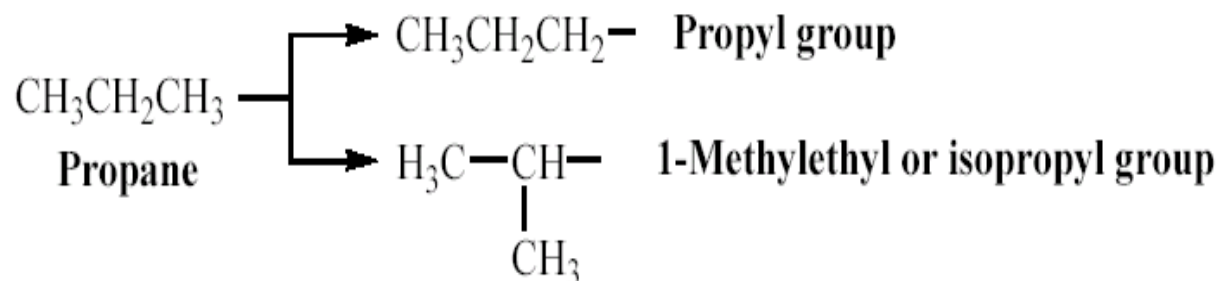


Unbranched alkyl groups

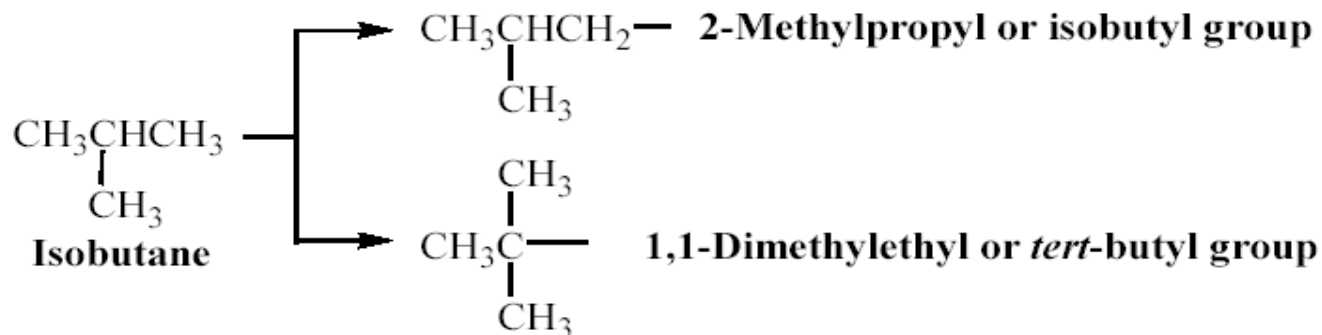
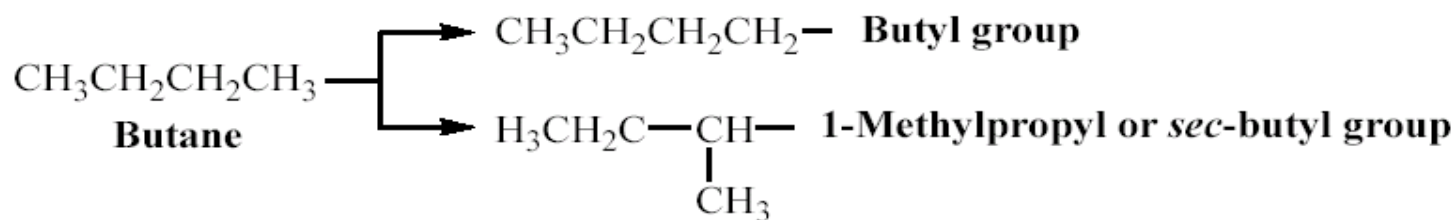
1. **Alkyl groups:** -ane \Rightarrow -yl (alkane \Rightarrow alkyl)

Alkane		Alkyl Group	Abbreviation
$\text{CH}_3\text{—H}$ Methane	becomes	$\text{CH}_3\text{—}$ Methyl	Me–
$\text{CH}_3\text{CH}_2\text{—H}$ Ethane	becomes	$\text{CH}_3\text{CH}_2\text{—}$ Ethyl	Et–
$\text{CH}_3\text{CH}_2\text{CH}_2\text{—H}$ Propane	becomes	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$ Propyl	Pr–
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—H}$ Butane	becomes	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$ Butyl	Bu–

- **Three-Carbon Groups**



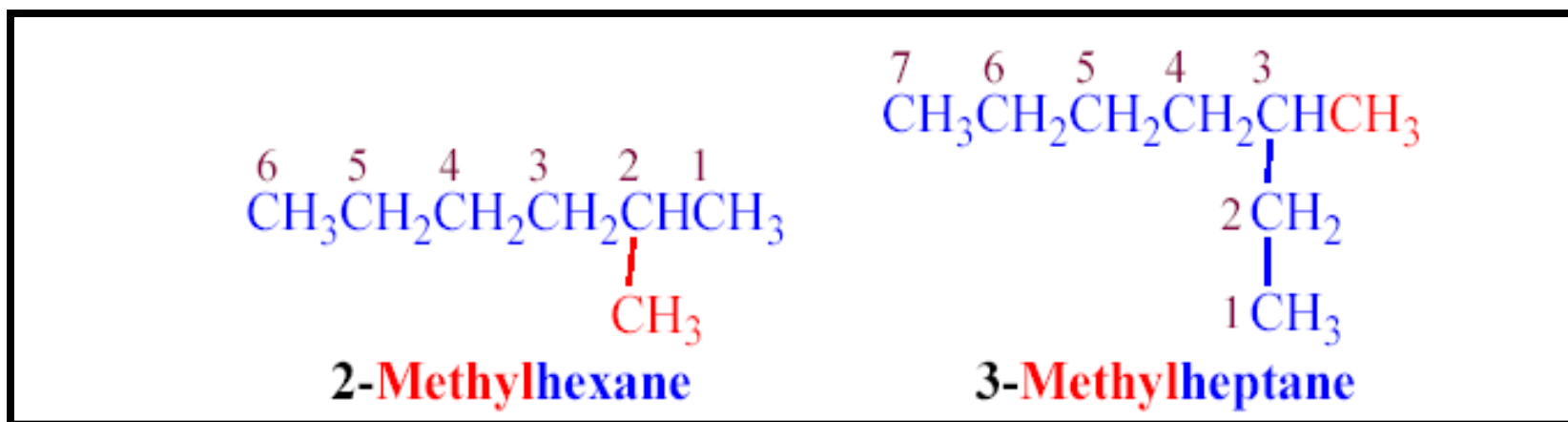
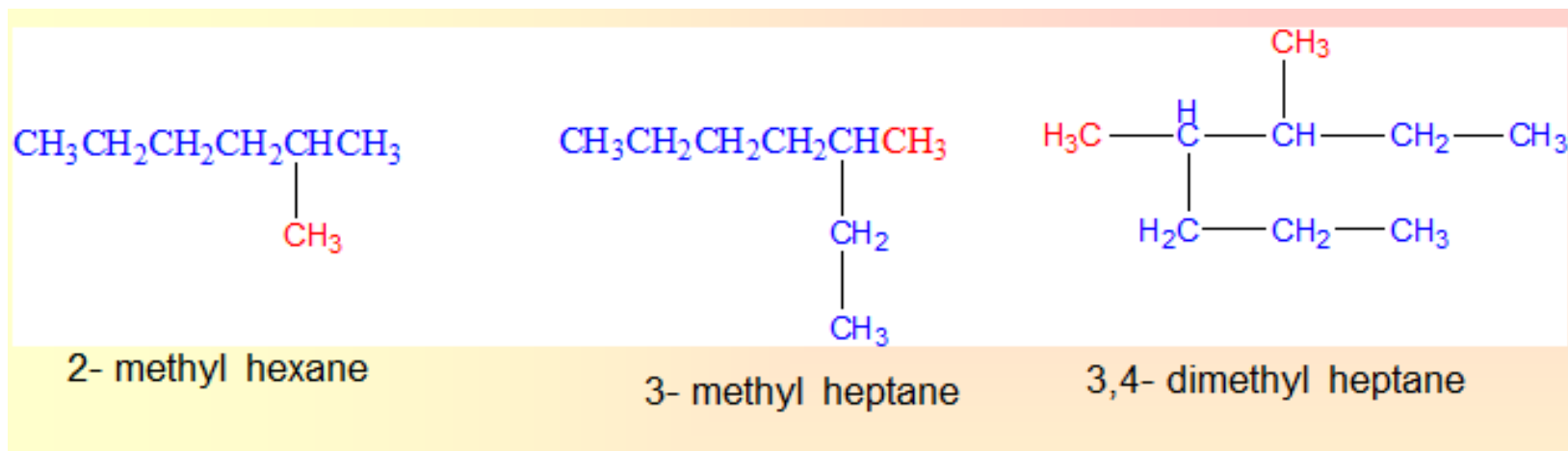
- **Four-Carbon Groups**

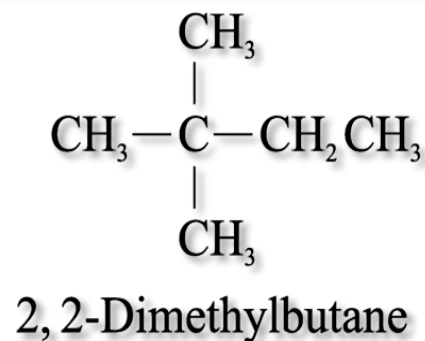
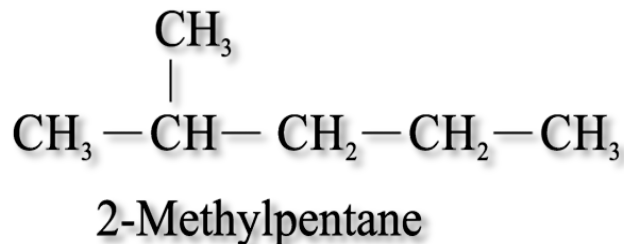
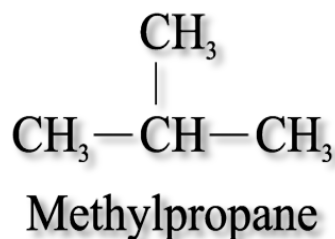
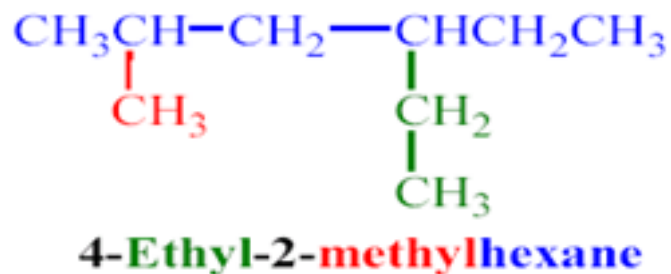


- **Halo substituents** are halogens attached to the carbon chain named as **fluoro, chloro, bromo, or iodo**

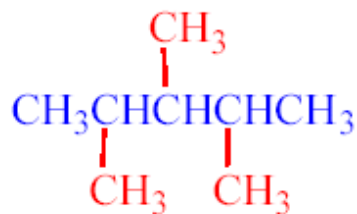
5. Complex Substituents (*substituents with branching*)

- Named by applying the four previous rules with some modification
- Number the complex substituent separately from the parent. Begin numbering at the point of attachment to the parent chain.
- Complex substituents are set off by parenthesis.

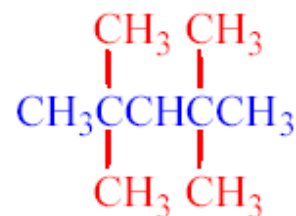




2,3-Dimethylbutane

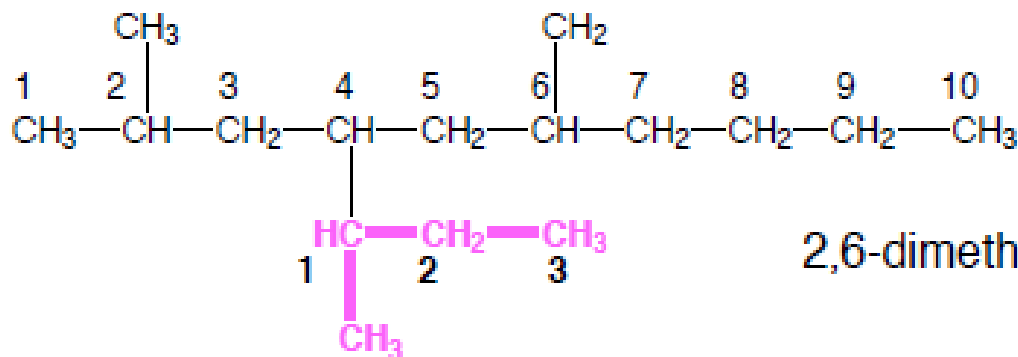


2,3,4-Trimethylpentane



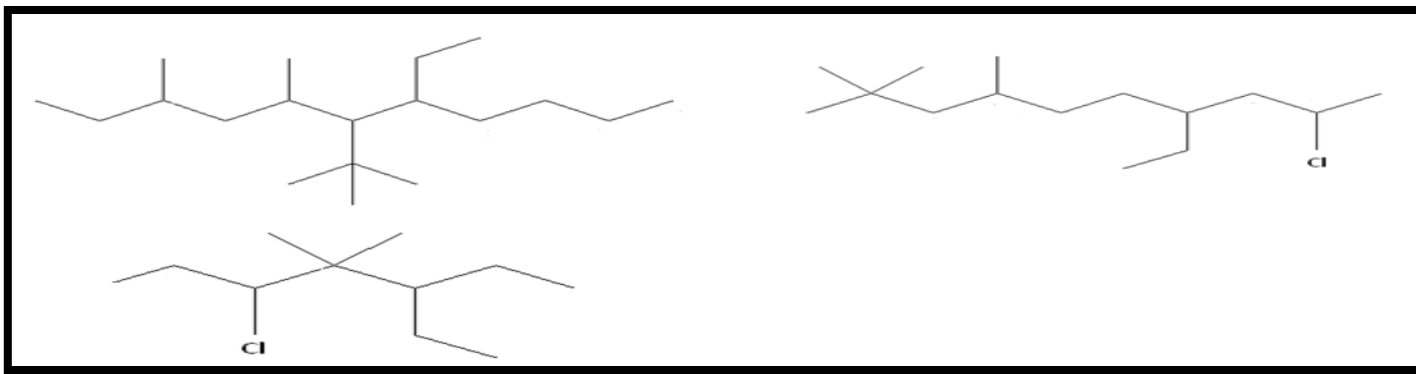
2,2,4,4-Tetramethylpentane

When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference .



2,6-dimethyl-4-(1-methylpropyl)decane

H.W: what is the systematic name of the following structures?

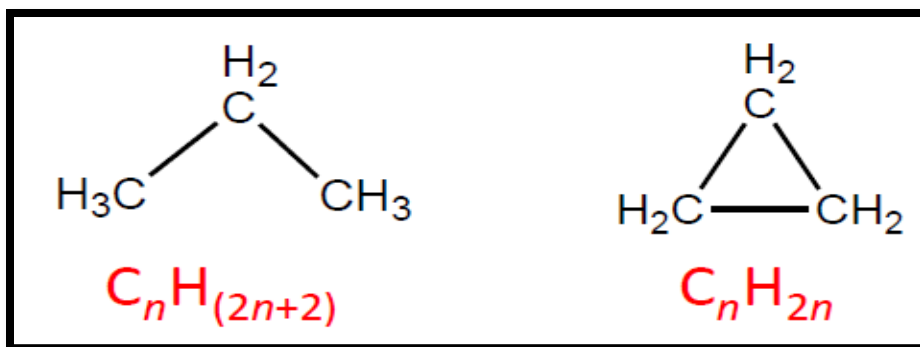


Cycloalkanes:

- Are cyclic alkanes .
- Have two less hydrogen atoms than the open chain .
- Are named by using the prefix ***cyclo*** before the name of the alkane chain with the same number of carbon atoms .

propane, C₃H₈

cyclopropane , C₃H₆

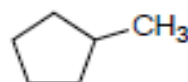


Naming Cycloalkanes

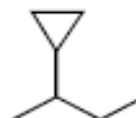
General Formula: $C_nH_{(2n)}$

1. Parent Chain

- Use the cycloalkane as the parent chain if it has a greater number of carbons than any alkyl substituent.
- If an alkyl chain off the cycloalkane has a greater number of carbons, then use the alkyl chain as the parent and the cycloalkane as a **cycloalkyl-** substituent.



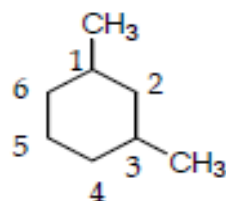
Methylcyclopentane



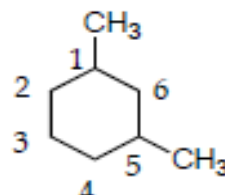
2-Cyclopropylbutane

2. Numbering the Cycloalkane

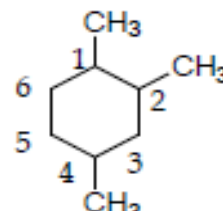
- When numbering the carbons of a cycloalkane, start with a substituted carbon so that the substituted carbons have the lowest numbers (sum).



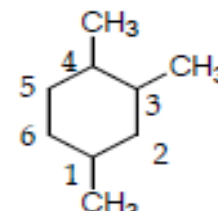
1,3-Dimethylcyclohexane



-not-
1,5-Dimethylcyclohexane



1,2,4-Trimethylcyclohexane
(1 + 2 + 4 = 7)



-not-
1,3,4-Trimethylcyclohexane
(1 + 3 + 4 = 8)

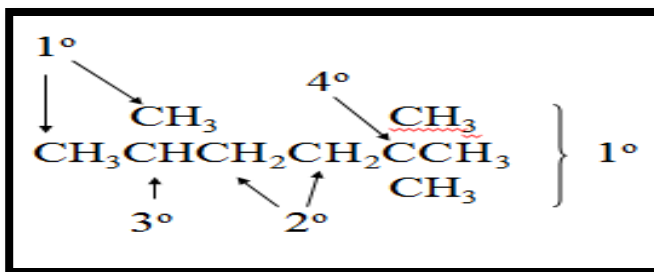
Classes of carbons

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



1° Hydrogens- hydrogens on a primary carbon. $-\text{CH}_3$ (methyl group)

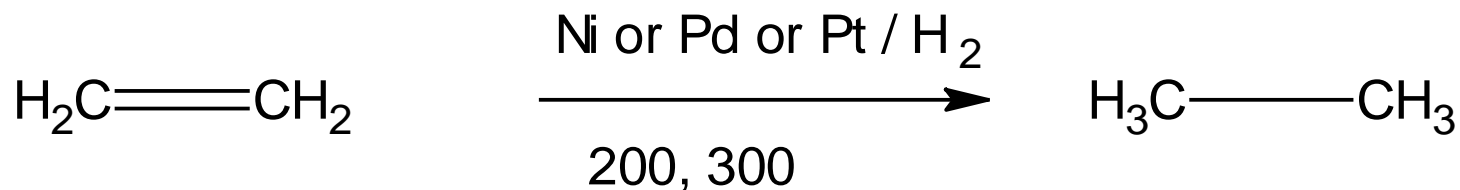
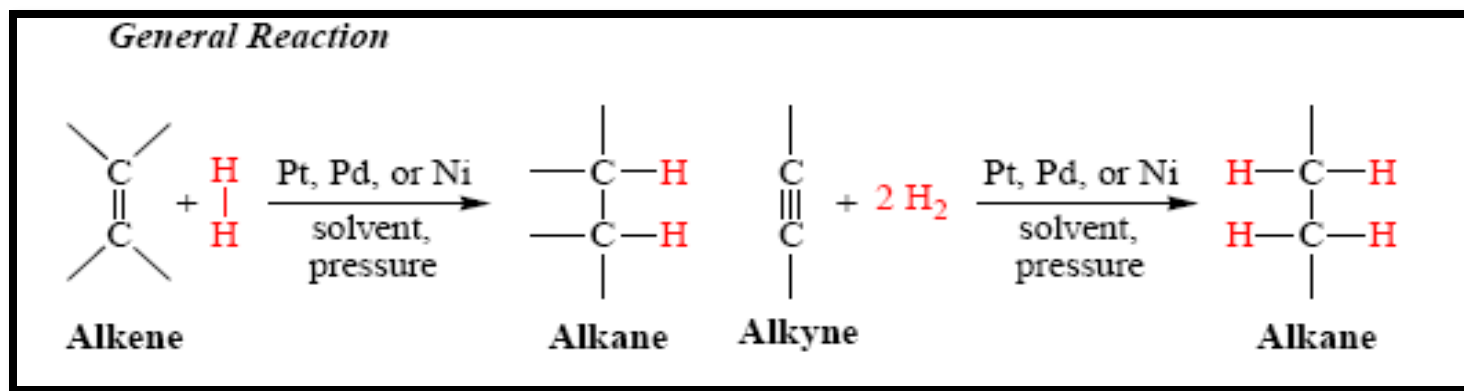
2° Hydrogens- hydrogens on a secondary carbon. $-\text{CH}_2-$ (methylene group)

3° Hydrogens- hydrogens on a tertiary carbon. CH (methane group)

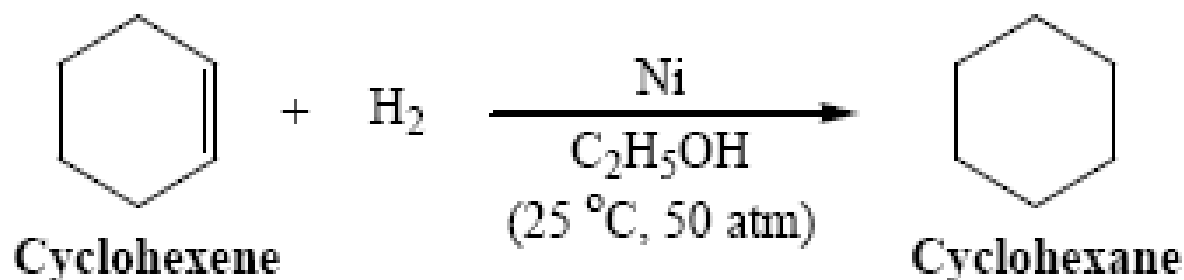
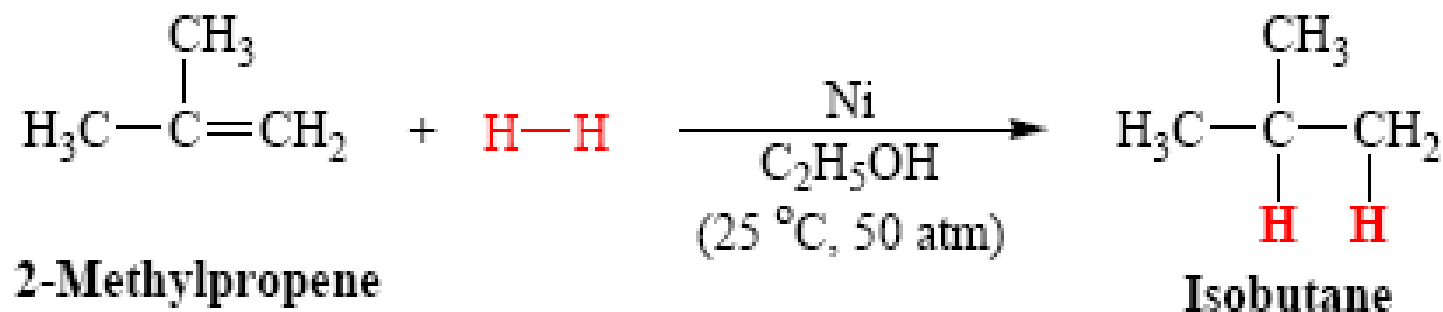
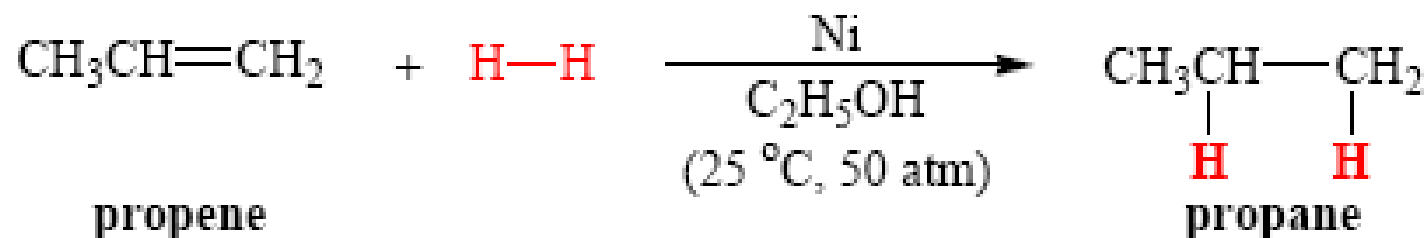
Synthesis of alkane

1- From Alkenes & Alkynes

Hydrogenation of unsaturated hydrocarbon produce alkane with the same carbon chain



Specific Examples

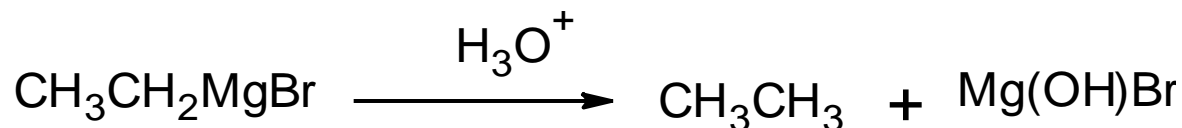
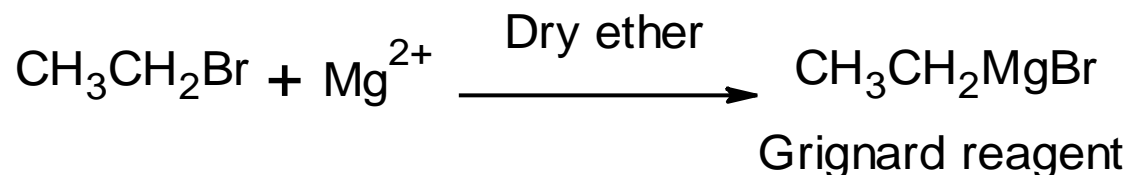
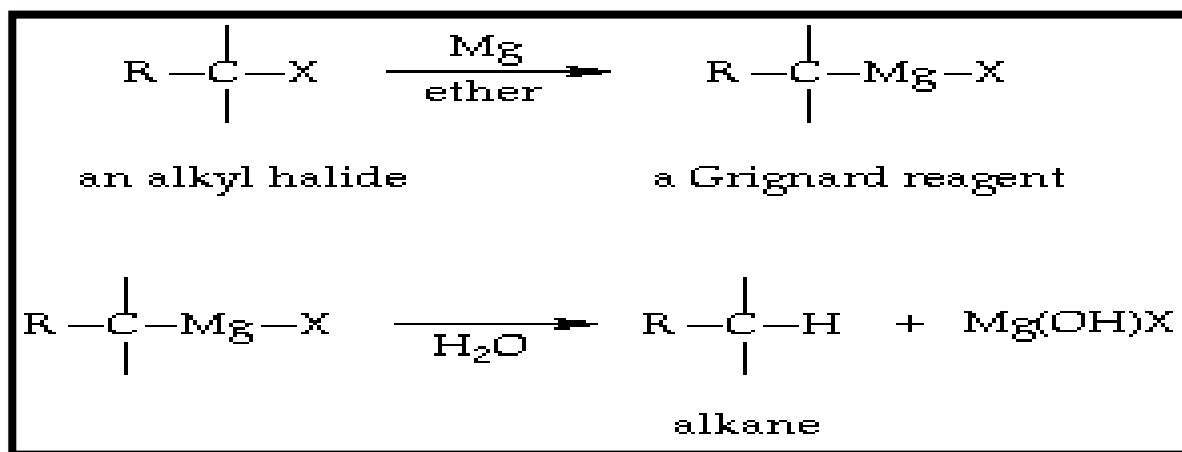


2) Hydrolysis of Grignard Reagent

Grignard reagent is an alkyl magnesium halide compound, R-Mg-X

The Grignard reagent is formed when a solution of an Alkyl Halide (R-X) is allowed to stand over a metallic magnesium in the presence of dry ether

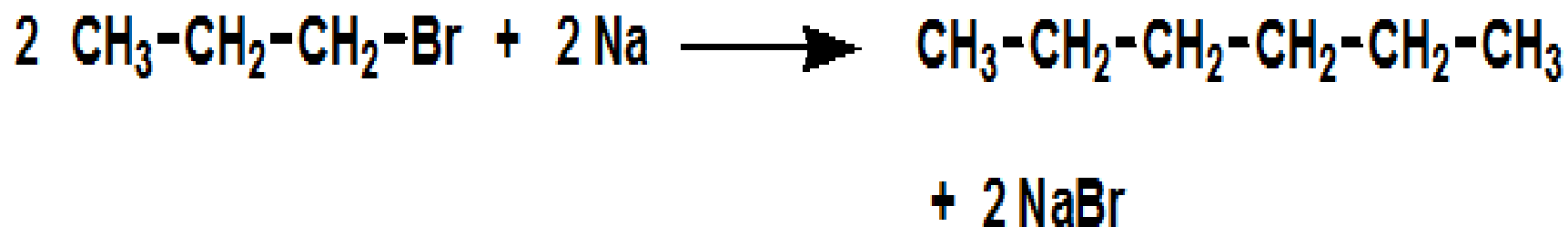
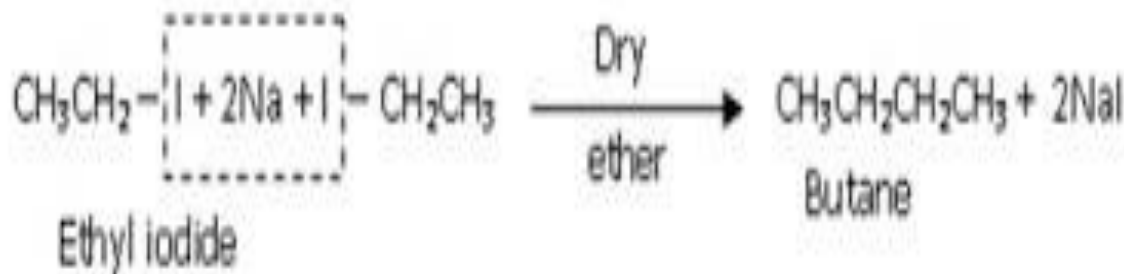
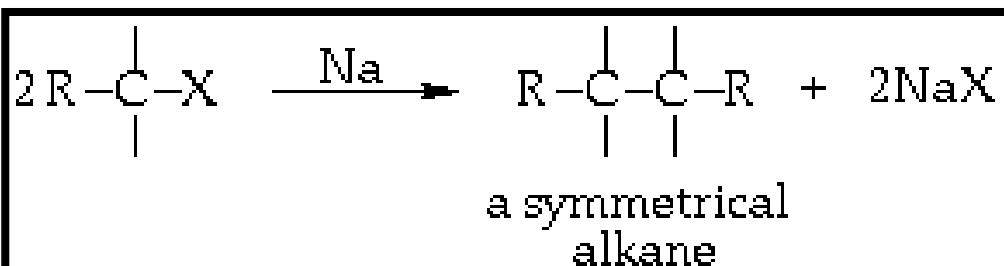
Then Grignard reagent react with water or alcohol to form alkane



- 3- Wurtz Reaction

This is the reaction of two alkyl halides (R-X) with metallic sodium to give symmetrical alkanes.

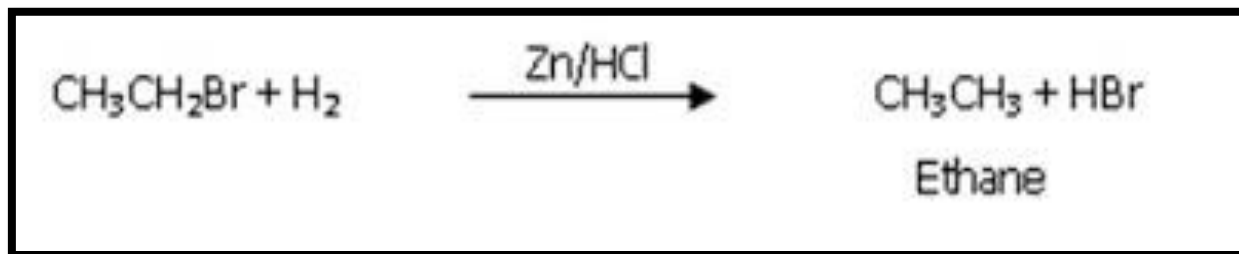
The wurtz reaction is a poor method for the preparation of unsymmetrical alkanes.



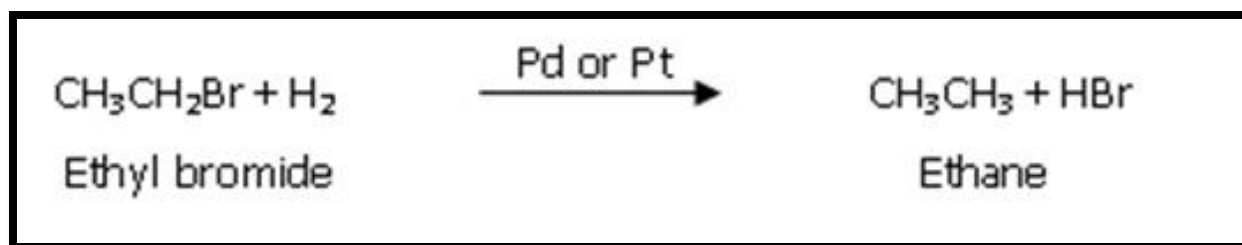
4. Reduction of alkyl halides.

Alkyl halides are reduced to alkanes by suitable reducing agents. For example,

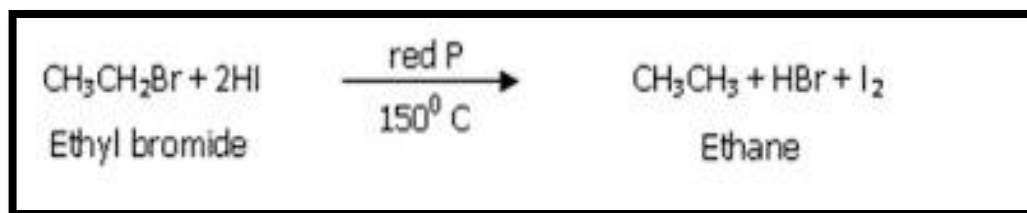
i. With zinc and HCl



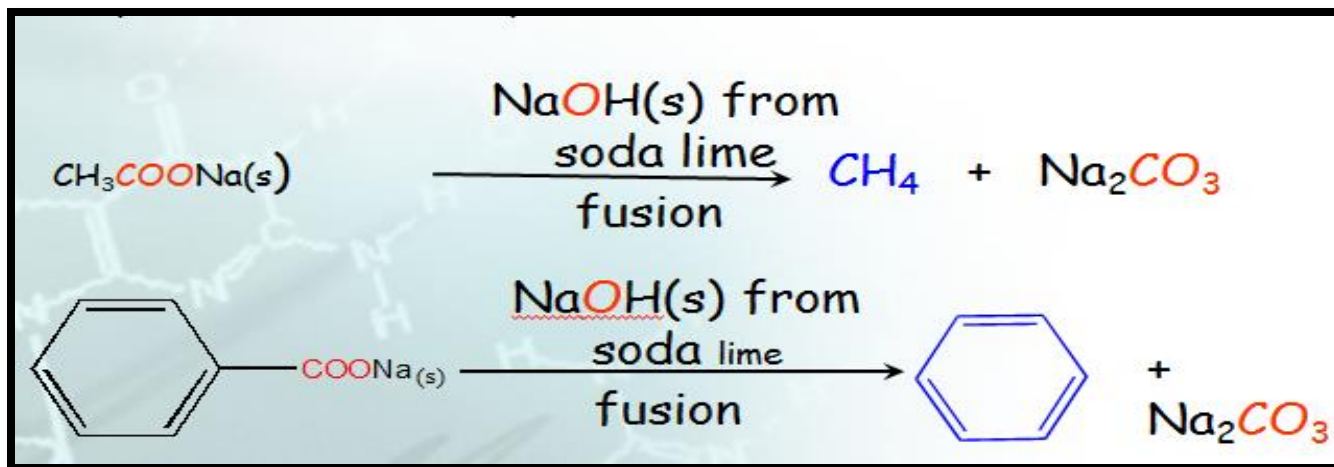
ii. With hydrogen in the presence of platinum or palladium (catalytic hydrogenation)



iii. With hydrogen iodide in the presence of red phosphorus.



4- Decarboxylation of sodium alkanoate such as sodium ethanoate or sodium benzoate by heating with soda lime ($\text{NaOH} + \text{CaO}$)

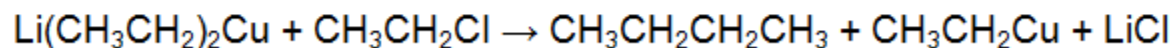
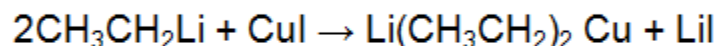


Not easy to separate mixture into individual alkanes.

Not suitable for preparing alkanes other than methane.

6-By Corey – House Synthesis

Alkyl chloride chloroethane reacts with lithium in presence of ether to give lithium alkyl then reacts with CuI to give lithium dialkyl cuprate. This lithium dialkyl cuprate now again reacts with alkyl chloride to give alkane.



Reactions of alkanes:

Alkanes are the least reactive class of organic compounds. Their low reactivity is reflected in another term for alkanes: paraffins. The name paraffin comes from two latin terms, para, meaning "opposed to," and affinas, meaning "affinity". Chemists found that alkanes do not react with strong acids or bases , nor with most other reagents. They attributed this low reactivity to a lack of affinity for other reagents, and they coined the name "paraffins"

Reactions of alkanes:

alkane + $\text{H}_2\text{SO}_4 \rightarrow$ no reaction (NR)

alkane + $\text{NaOH} \rightarrow$ NR

alkane + $\text{Na} \rightarrow$ NR

alkane + $\text{KMnO}_4 \rightarrow$ NR

alkane + $\text{H}_2, \text{Ni} \rightarrow$ NR

alkane + $\text{Br}_2 \rightarrow$ NR

alkane + $\text{H}_2\text{O} \rightarrow$ NR

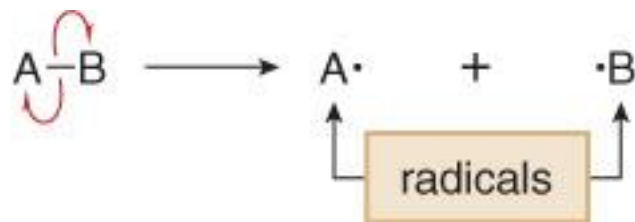
(Alkanes are typically non-reactive. They don't react with acids, bases, active metals, oxidizing agents, reducing agents, halogens, etc.)

Alkane, reactions:

1. Halogenation
2. Combustion (oxidation)
3. Pyrolysis (cracking)

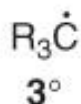
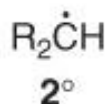
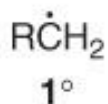
Radical Reactions

- A **radical** is a reactive intermediate with a single unpaired electron, formed by homolysis of a covalent bond.
- A radical contains an atom that does not have an octet of electrons.
- Half-headed arrows are used to show the movement of electrons in radical processes.

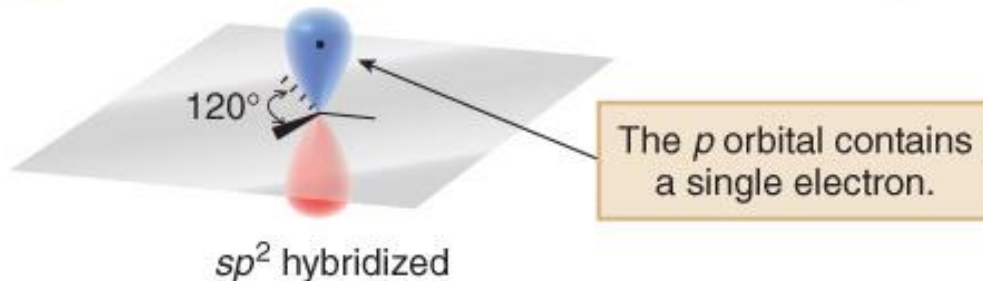


- Carbon radicals are classified as 1° , 2° or 3° .
- A carbon radical is sp^2 hybridized and trigonal planar, like sp^2 hybridized carbocations.
- The unhybridized p orbital contains the unpaired electron and extends above and below the trigonal planar carbon.

Classification of carbon radicals



The trigonal planar geometry of a carbon radical



- ◆ The stability of a radical increases as the number of alkyl groups bonded to the radical carbon increases.

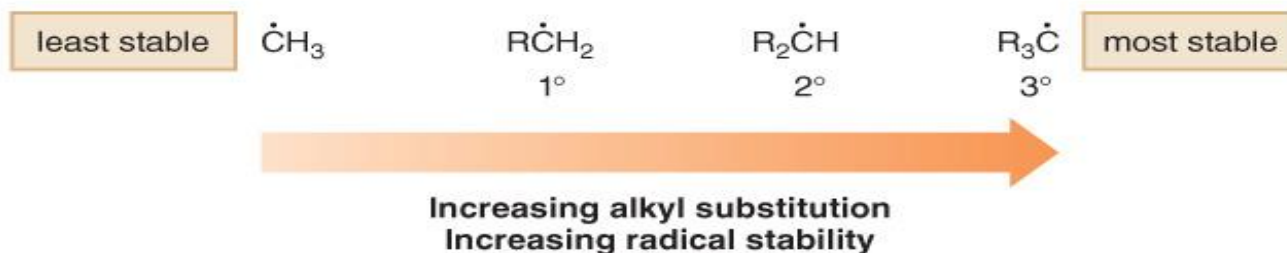
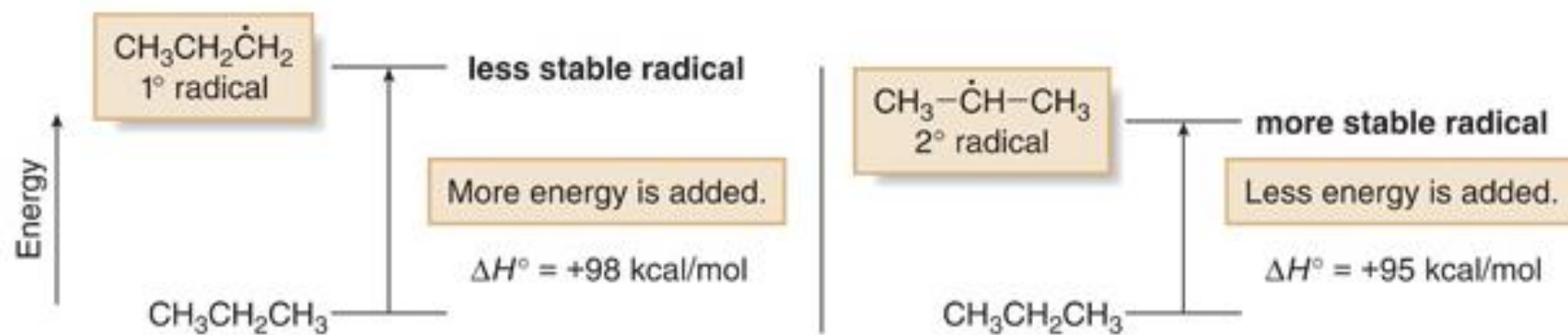
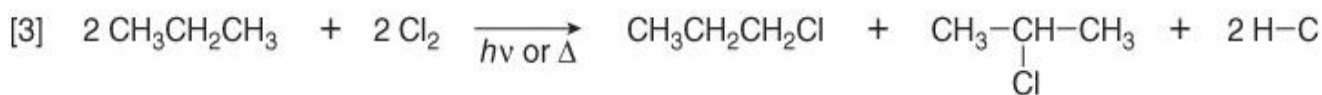
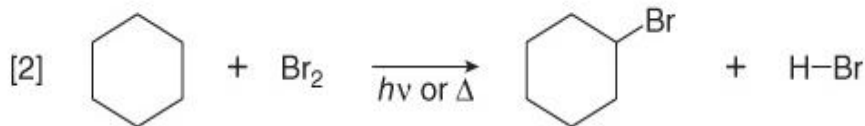
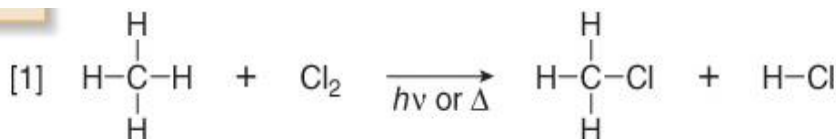
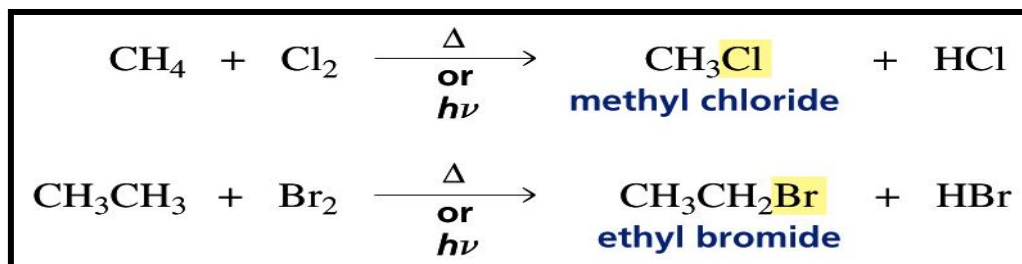


Figure 13.1 The relative stability of 1° and 2° carbon radicals

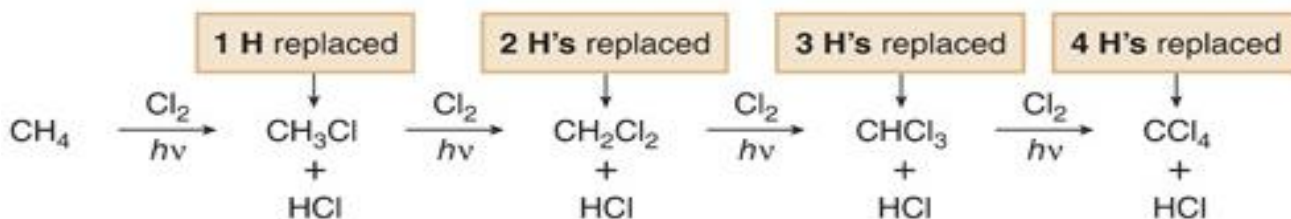


Halogenation of Alkanes

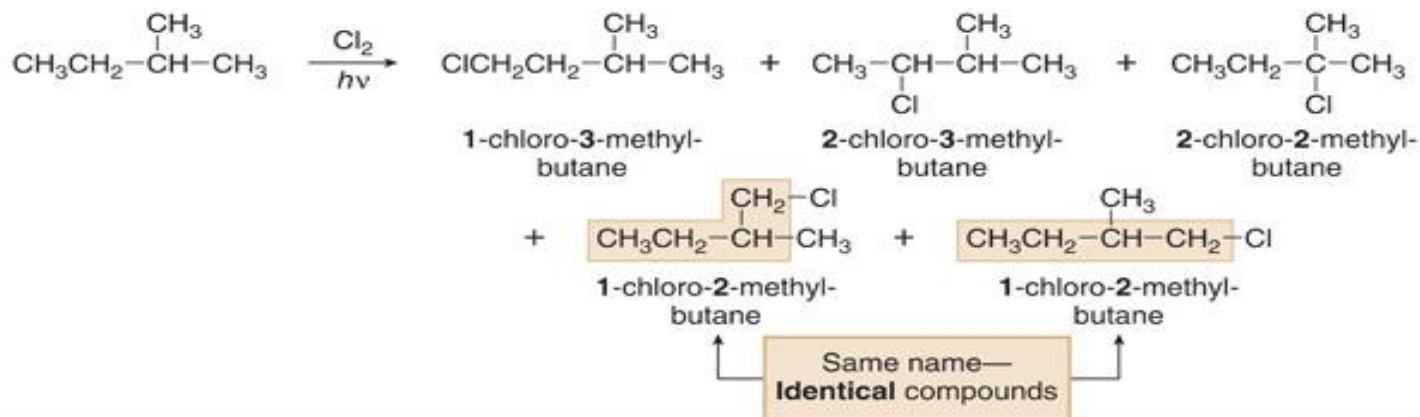
- In the presence of heat or light, alkanes react with halogens to form alkyl halides.
- Halogenation of alkanes is a radical substitution reaction.
- Halogenation of alkanes is only useful with Cl_2 or Br_2 . Reaction with F_2 is too violent, and reaction with I_2 is too slow to be useful.
- With an alkane that has more than one type of hydrogen atom, a mixture of alkyl halides may result.



An example is the chlorination of methane. Methane reacts with chlorine under diffuse sunlight or heating but not in dark. A mixture of products (CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4) is formed with the replacement of hydrogen by one or more chlorine atoms.

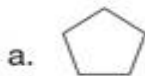


If methane is in excess CH_3Cl is major product, if chlorine is excess CCl_4 is major product



PROBLEM 13.4

Draw all constitutional isomers formed by monochlorination of each alkane.



PROBLEM 13.5

What alkane of molecular formula C_5H_{12} gives a single product of monohalogenation when heated with Cl_2 ?

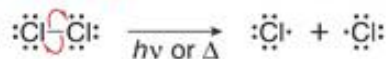
General mechanism

The chain mechanism is as follows, using the chlorination of methane as a typical

Radical Halogenation of Alkanes

Initiation

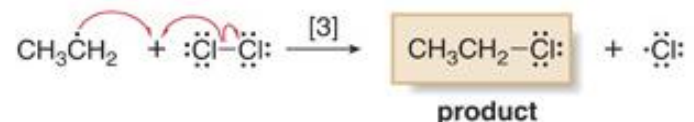
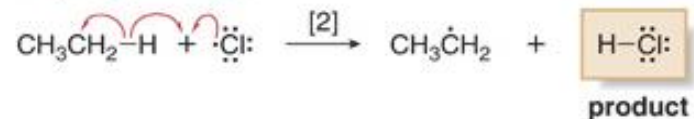
Step [1] Bond cleavage forms two radicals.



- ◆ The reaction begins with homolysis of the weakest bond in the starting materials using energy from light or heat.
- ◆ Thus, the Cl–Cl bond ($\Delta H^\circ = 58 \text{ kcal/mol}$), which is weaker than either the C–C or C–H bond in ethane ($\Delta H^\circ = 88$ and 98 kcal/mol , respectively), is broken to form two chlorine radicals.

Propagation

Steps [2] and [3] One radical reacts and a new radical is formed.

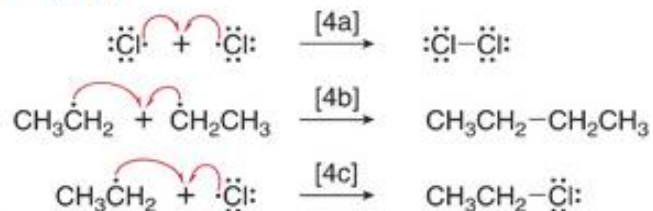


Repeat Steps [2], [3], [2], [3], again and again.

- ◆ The $\text{Cl}\cdot$ radicals are highly reactive (they lack an octet of electrons), so they abstract a hydrogen atom from ethane (Step [2]). This forms H–Cl and leaves one unpaired electron on carbon, generating the ethyl radical ($\text{CH}_3\text{CH}_2\cdot$).
- ◆ $\text{CH}_3\text{CH}_2\cdot$ is highly reactive, so it can abstract a chlorine atom from Cl_2 (Step [3]), forming $\text{CH}_3\text{CH}_2\text{Cl}$ and a new chlorine radical ($\text{Cl}\cdot$).
- ◆ The $\text{Cl}\cdot$ radical formed in Step [3] is a reactant in Step [2], so Steps [2] and [3] can occur repeatedly without an additional initiation reaction (Step [1]).
- ◆ In each propagation step, one radical is consumed and one radical is formed. The two products— $\text{CH}_3\text{CH}_2\text{Cl}$ and HCl—are formed during propagation.

Termination

Step [4] Two radicals react to form a σ bond.

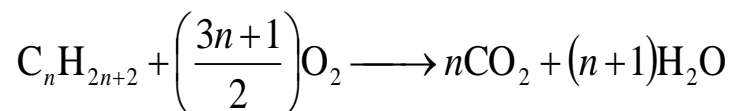


- ◆ To terminate the chain, two radicals react with each other in one of three ways (Steps [4a, b, and c]). Because these reactions remove reactive radicals and form stable bonds, they prevent further propagation via Steps [2] and [3].

2- Combustion

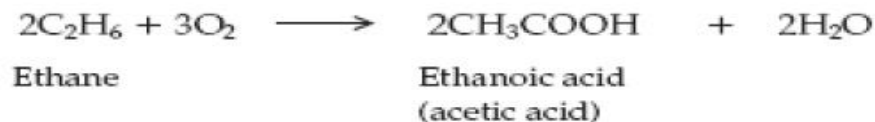
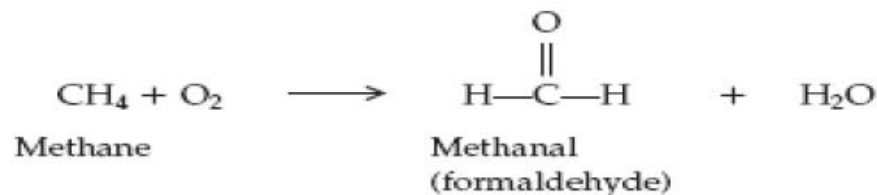
Complete combustion : Alkanes react with sufficient oxygen to give carbon dioxide and water through a series of reaction with the release of a large amount of energy.

General formula



Methane

incomplete combustion



3- Pyrolysis (cracking)

alkane, 400-600°C \rightarrow smaller alkanes + alkenes + H₂

Used to increase the yield of gasoline from petroleum. Higher boiling fractions are “cracked” into lower boiling fractions that are added to the raw gasoline. The alkenes can be separated and used in to make plastics.