

CHEM 130: ORGANIC CHEMISTRY I

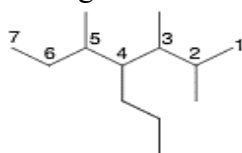
CHAPTER TWO

ALKANES

- An alkane is a hydrocarbon that contains only single bonds.
- They are the least reactive class of organic compounds because they contain only hydrogen and sp^3 hybridized carbon, and they have no reactive functional groups.
- Alkanes are saturated hydrocarbons.
A hydrocarbon with no double or triple bonds is said to be saturated because it has the maximum number of bonded hydrogens.

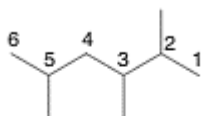
Nomenclature of Alkanes

1. Choose the longest continuous chain of carbon atoms and use the name of this chain as the base name of the compound.
2. Number the longest chain beginning with the end of the chain nearest a substituent.
3. Name the substituent groups attached to the longest chain as alkyl groups. Give the location of each alkyl group by the number of the main-chain carbon atom to which it is attached.
4. When two or more substituents are present, list them in alphabetical order. When two or more of the same alkyl substituents are present, use the prefixes di -, tri -, tetra -, (di - 2, tri - 3, tetra - 4, Penta - 5) etc., to avoid having to name the alkyl group twice. Include a position number for each substituent, even if it means repeating a number more than once.
5. When two chains of equal length compete for selection as the base chain, choose the chain with greater substituents.



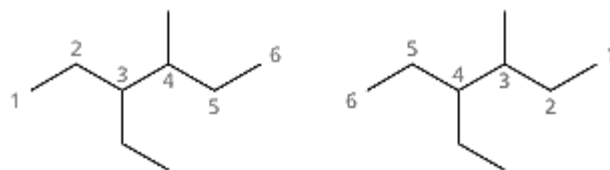
2,3,5-Trimethyl-4-propylheptane
(four substituents)

6. 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 1st point of difference.



2,3,5-Trimethylhexane
(not 2,4,5-trimethylhexane)

7. When numbering a carbon chain results in the same numbers from either end of the chain, assign the lower no alphabetically to the first substituent.



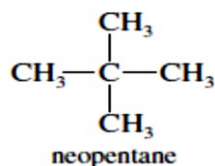
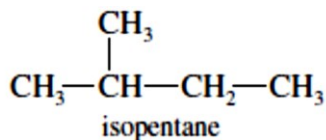
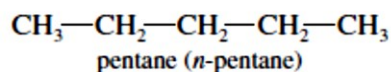
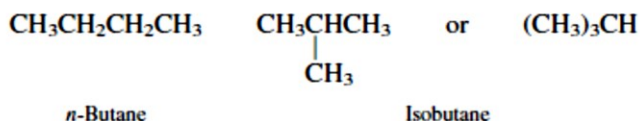
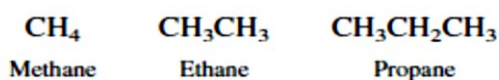
Correct

Incorrect

N/B: The prefixes di-, tri-, tetra- and so on are not included in alphabetizing. Neither are hyphenated prefixes sec- and tert-. 'Iso' as in isopropyl is included in alphabetizing.

- Separate the number from name by hyphen.
- Separate numbers from each other using commas.

Examples

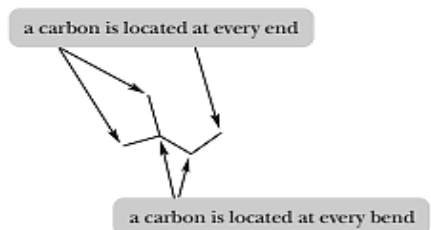


IUPAC Names of unbranched alkanes

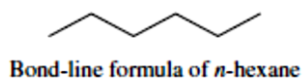
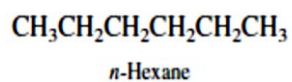
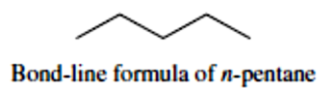
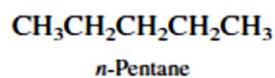
Number of carbon atoms	Name
1	Methane
2	Ethane
3	Propane
4	Butane
5	Pentane
6	Hexane
7	Heptane
8	Octane
9	Nonane
10	Decane

11	Undecane
12	Dodecane
13	Tridecane
14	Tetradecane
15	Pentadecane
16	Hexadecane
17	Heptadecane
18	Octadecane
19	Nonadecane
20	Icosane (eicosane)

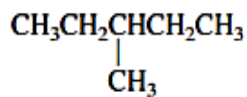
Bond – Line /Line – angle formula



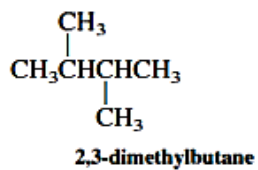
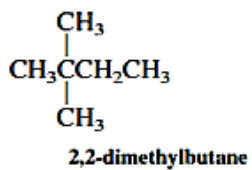
e.g



Examples



3-methylpentane

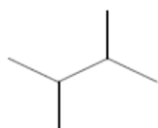




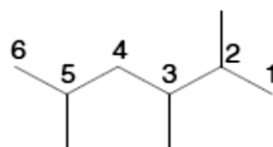
2,2,4,4-Tetramethylpentane



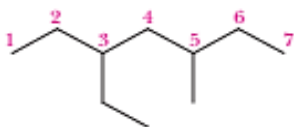
2,2,6,6,7-Pentamethyloctane



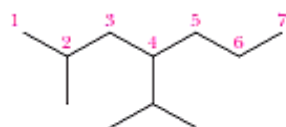
2,3-Dimethylbutane



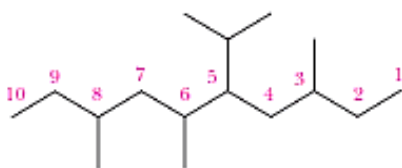
2,3,5-Trimethylhexane



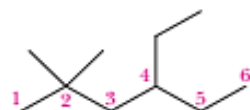
3-Ethyl-5-methylheptane



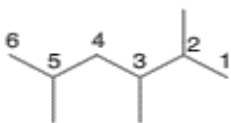
4-Isopropyl-2-methylheptane



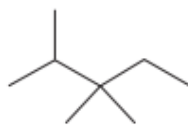
5-Isopropyl-3,6,8-trimethyldecane



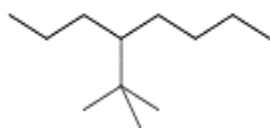
4-Ethyl-2,2-dimethylhexane



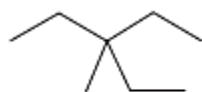
2,3,5-Trimethylhexane



2,3,3-Trimethylpentane



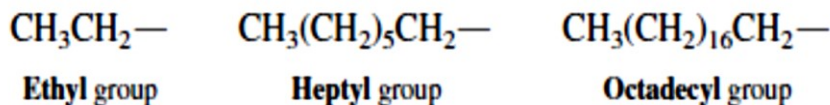
4-tert-butyl-octane



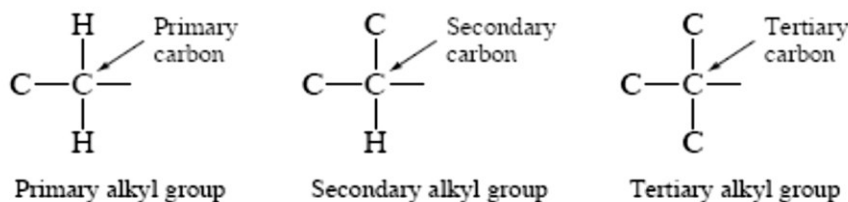
3-Ethyl-3-methylpentane

Alkyl Groups

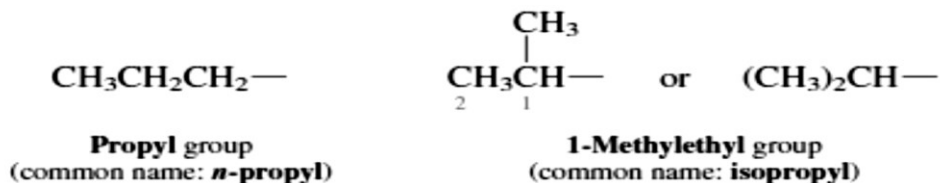
- An alkyl group lacks one of the hydrogens of an alkane.
- A methyl group ($-\text{CH}_3$) is an alkyl group derived from methane (CH_4).
- Unbranched alkyl groups in which the point of attachment is at the end of the chain are named in IUPAC nomenclature by replacing the -ane endings of the alkane by -yl.



- The dash at the end of the chain represents a potential point of attachment for some other atom or group.
- Carbon atoms are classified according to their degree of substitution by other carbons.
- A primary carbon is directly attached to one other carbon. Similarly, a secondary carbon is directly attached to two other carbons, a tertiary carbon to three, and a quaternary carbon to four.
- Alkyl groups are designated as primary, secondary, or tertiary according to the degree of substitution of the carbon at the potential point of attachment.

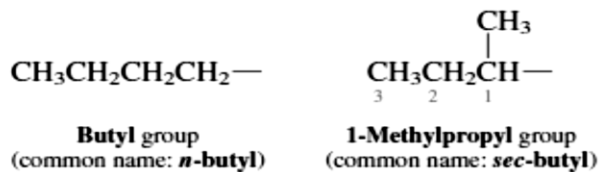


- Ethyl (CH_3CH_2-), heptyl [$\text{CH}_3(\text{CH}_2)_5\text{CH}_2-$], and octadecyl [$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2-$] are examples of primary alkyl groups.
- Branched alkyl groups are named by using the longest continuous chain that begins at the point of attachment as the parent.
- Thus, the systematic names of the two C_3H_7 alkyl groups are propyl and 1-methylethyl. Both are better known by their common names, n-propyl and isopropyl, respectively.

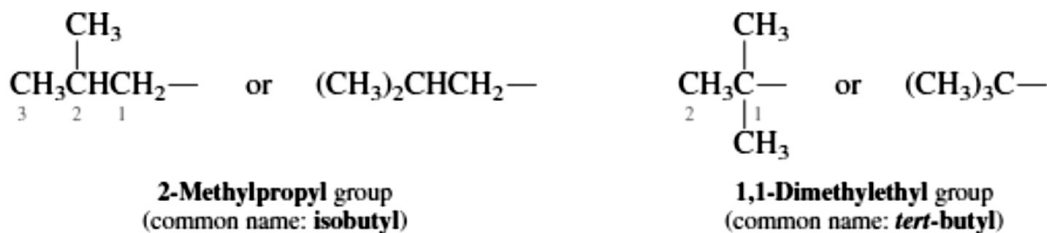


- An isopropyl group is a secondary alkyl group. Its point of attachment is to a secondary carbon atom, one that is directly bonded to two other carbons.
- The C_4H_9 alkyl groups may be derived either from the unbranched carbon skeleton of butane or from the branched carbon skeleton of isobutane.

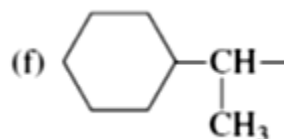
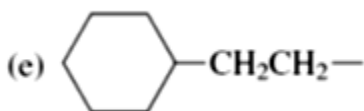
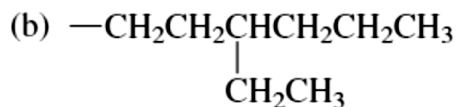
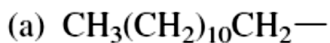
- Those derived from butane are the butyl (n-butyl) group and the 1-methylpropyl (sec-butyl) group.



- Those derived from isobutane are the 2-methylpropyl (isobutyl) group and the 1,1-dimethylethyl (tert-butyl) group.
- Isobutyl is a primary alkyl group because its potential point of attachment is to a primary carbon.
- tert-Butyl is a tertiary alkyl group because its potential point of attachment is to a tertiary carbon.

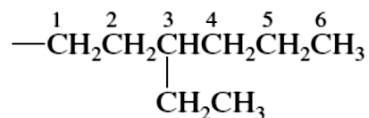


Give the IUPAC name for each of the following alkyl groups, and classify each one as primary, secondary, or tertiary:

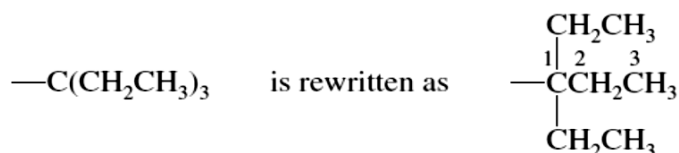


Solutions

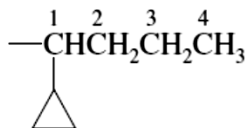
- (a) The group $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2-$ is an unbranched alkyl group with 12 carbons. It is a **dodecyl group**. The carbon at the point of attachment is directly attached to only one other carbon. It is a primary alkyl group.
- (b) The longest continuous chain from the point of attachment is six carbons; it is a hexyl group bearing an ethyl substituent at C-3. The group is a **3-ethylhexyl group**. It is a primary alkyl group.



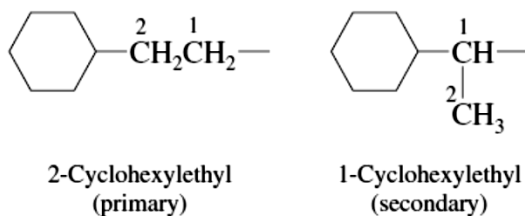
- (c) By writing the structural formula of this alkyl group in more detail, we see that the longest continuous chain from the point of attachment contains three carbons. It is a **1,1-diethylpropyl group**. Because the carbon at the point of attachment is directly bonded to three other carbons, it is a tertiary alkyl group.



- (d) This group contains four carbons in its longest continuous chain. It is named as a butyl group with a cyclopropyl substituent at C-1. It is a **1-cyclopropylbutyl group** and is a secondary alkyl group.

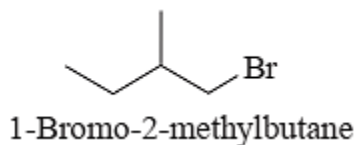
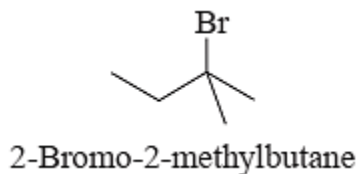
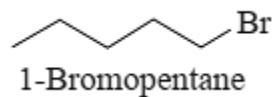
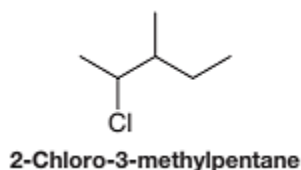
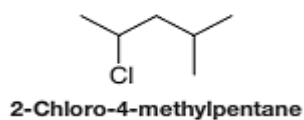
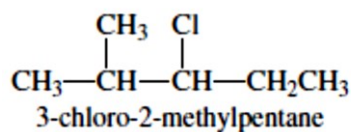
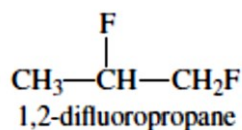
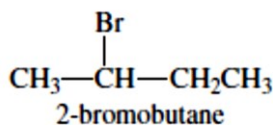


- (e, f) A two-carbon group that bears a cyclohexyl substituent is a **cyclohexylethyl group**. Number from the point of attachment when assigning a locant to the cyclohexyl group.



Haloalkanes

- Haloalkanes can be named just like alkanes, with the halogen atom treated as a substituent.
- Halogen substituents are named fluoro-, chloro-, bromo- and iodo-.

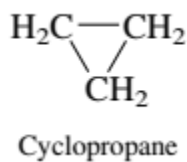


CYCLOALKANES

- A hydrocarbon that contains carbon atoms joined to form a ring is called a cyclic hydrocarbon.
- When all carbons of the ring are saturated, we call the hydrocarbon a cycloalkane.

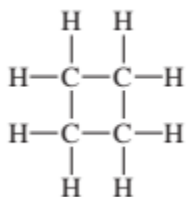
Nomenclature

1. Cycloalkanes with one ring and no substituents:
- Count the number of carbon atoms in the ring, then add “cyclo” to the beginning of the name of the alkane with that number of carbons. e.g.

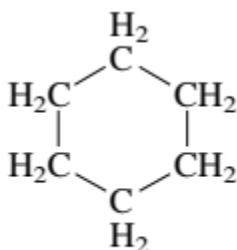


Or

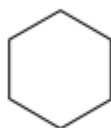




Or



Or

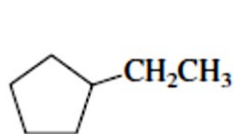


Cyclohexane

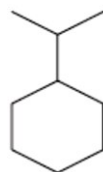
2. Cycloalkanes with one ring and one substituent:

Add the name of the substituent to the beginning of the parent's name.

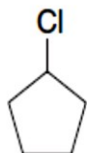
N/B: For compounds with one substituent, it is not necessary to specify a number for the carbon bearing the substituent.



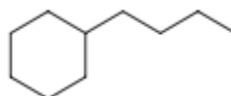
Ethylcyclopentane



Isopropylcyclohexane



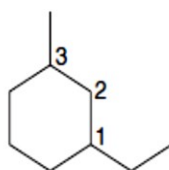
Chlorocyclopentane



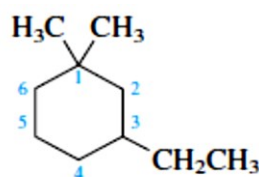
Butylcyclohexane

3. Cycloalkanes with one ring and two or more substituents:

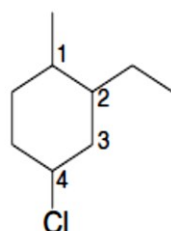
Numbering begins with one of the substituted ring carbons and continues in the direction that gives the lowest possible numbers to the other substituents. If there are substituents of different names/kinds, then they are listed in alphabetical order. When numbering could begin with either of the two substituted ring carbons the one that has more substituents or else the one that is alphabetically first is given priority. When there are three or more substituents, begin at the substituent that leads to the lowest set of numbers (locants). The substituents are listed in alphabetical order, not according to the number of their carbon atoms.



1-Ethyl-3-methylcyclohexane

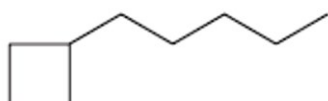


3-Ethyl-1,1-dimethylcyclohexane

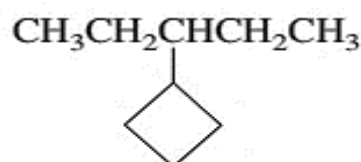


4-Chloro-2-ethyl-1-methylcyclohexane

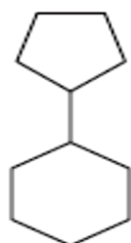
4. When the ring contains fewer carbon atoms than an alkyl group attached to it or when more than one ring system is attached to a single chain, then it is appropriate to name the compounds as cycloalkylalkanes. e.g.,



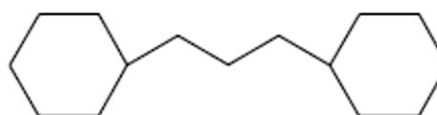
1-Cyclobutylpentane



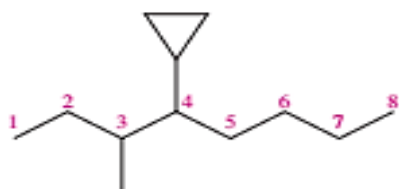
3-Cyclobutylpentane



cyclopentylcyclohexane

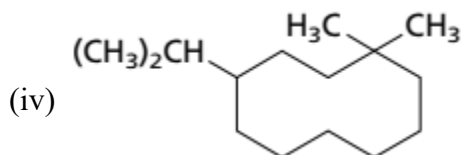
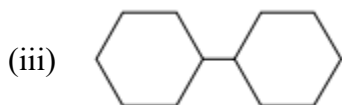
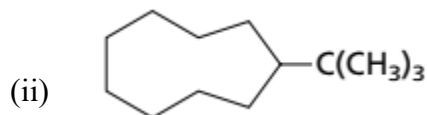
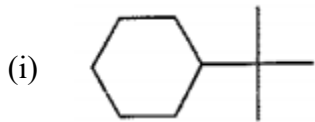


1,3-Dicyclohexylpropane



4-cyclopropyl-3-methyloctane

Give the IUPAC name of the following compounds



Solutions

- (i) tert-butylcyclohexane
- (ii) tert-butylcyclononane
- (iii) cyclohexylcyclohexane
- (iv) 4-isopropyl-1,1-dimethylcyclodecane

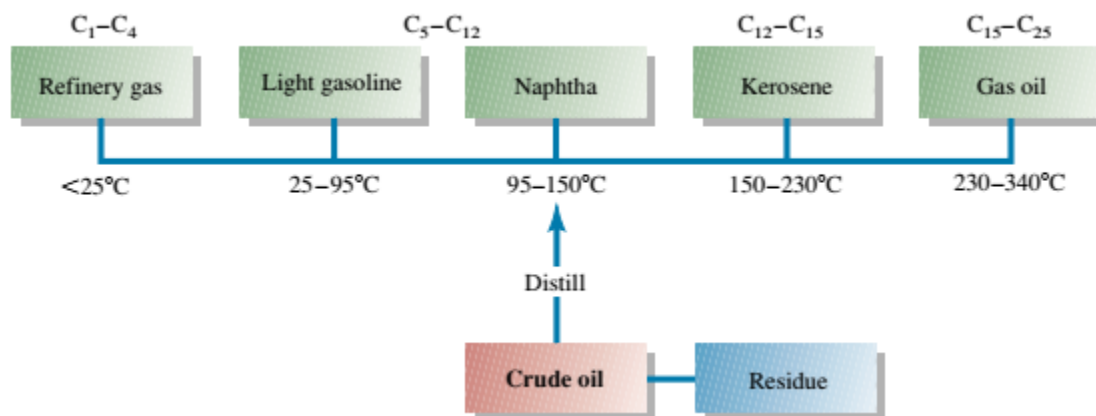
SOURCES OF ALKANES AND CYCLOALKANES

1. Natural gas

Consists of approximately 90-95% methane, 5-10% ethane and a mixture of other relatively low-boiling point alkanes chiefly propane, butane and 2-methylpropane.

2. **Petroleum** is a liquid mixture containing hundreds of substances, including approximately 150 hydrocarbons, roughly half of which are alkanes or cycloalkanes.

– Separated by fractional distillation



– Modern petroleum refining involves more than distillation, however, and includes two major additional operations:

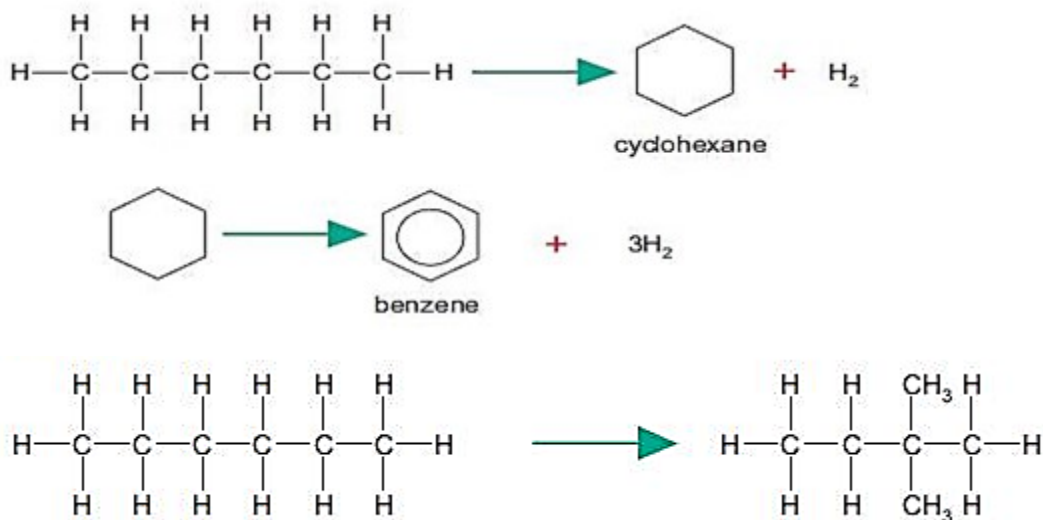
1. Cracking

- Involves breaking large hydrocarbons into small ones which are more useful as fuels.
- It is the more volatile, lower-molecular-weight hydrocarbons that are useful as automotive fuels and as a source of petrochemicals.

- Cracking increases the proportion of these hydrocarbons at the expense of higher molecular-weight ones by processes that involve the cleavage of carbon–carbon bonds induced by heat (*thermal cracking*) or with the aid of certain catalysts (*catalytic cracking*).

2. Reforming.

- Reforming converts the hydrocarbons in petroleum to aromatic hydrocarbons and highly branched alkanes, both of which show less tendency for knocking than unbranched alkanes and cycloalkanes.
e.g



- **Knocking** – Preignition in high compression automobile engines.

Engine knocking occurs when a portion of the air-fuel mixture explodes prematurely (usually as a result of heat developed during compression) and independently of ignition by the spark plug.

SYNTHESIS OF ALKANES AND CYCLOALKANES

1. Hydrogenation of alkenes and alkynes

Alkenes and alkynes react with hydrogen in presence of metal catalysts such as nickel, palladium and platinum to produce alkanes.



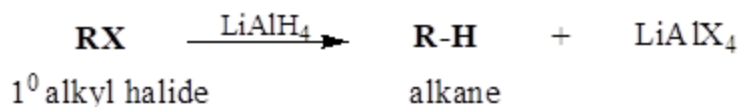
The reaction is usually carried out by dissolving the alkene or alkyne in a solvent such as ethanol, adding the metal catalyst, and then exposing the mixture to hydrogen gas under pressure.

e.g

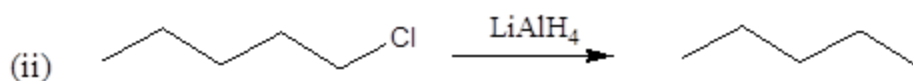
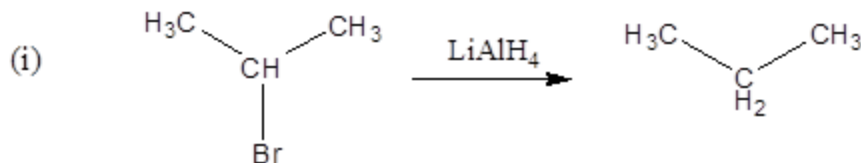


(ii) Reduction by use of variety of reducing agents like Lithium aluminium hydride (LiAlH_4) and Sodium borohydride (NaBH_4)

Primary (1^0) and secondary (2^0) alkyl halides are readily reduced by LiAlH_4 (Lithium Aluminium Hydride)

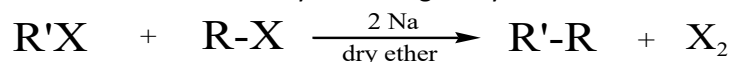


e.g.

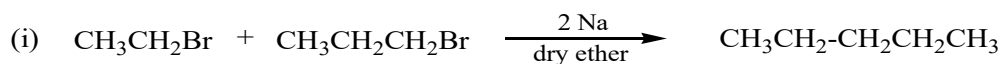


3. Wurtz reaction

- Coupling of alkyl halides with sodium in dry ether to give hydrocarbons.



e.g.

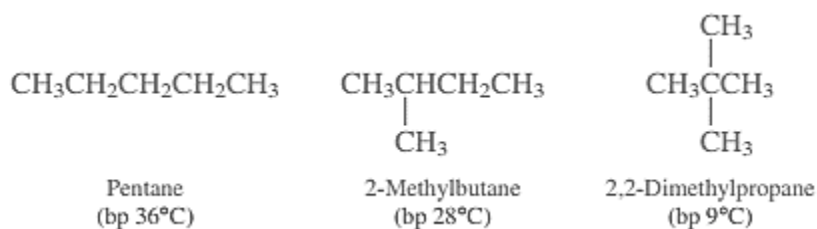


Physical properties of alkanes and cycloalkanes

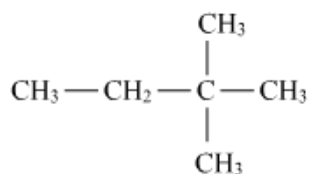
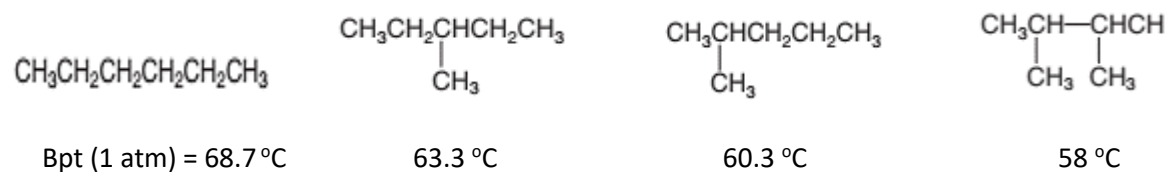
(i) Boiling points

- At room temperature (25°C) and 1 atm pressure the first four members of the homologous series of unbranched alkanes are gases, the $\text{C}_5\text{-C}_{17}$ unbranched alkanes (pentane to heptadecane) are liquids, and the unbranched alkanes with 18 and more carbon atoms are solids.
- The boiling points increase smoothly with increasing numbers of carbon atoms and increasing molecular weights.
- With unbranched alkanes, as molecular weight increases, so too do molecular size and even more importantly molecular surface area.
- With increasing surface area, the dispersion (van der Waals) forces between molecules increase therefore, more energy is required.
- Extended shape of an unbranched alkane permits for more points of contacts for intermolecular associations.
- Branching reduces the surface area of alkanes which lowers the boiling point. e.g

Isomers of pentane

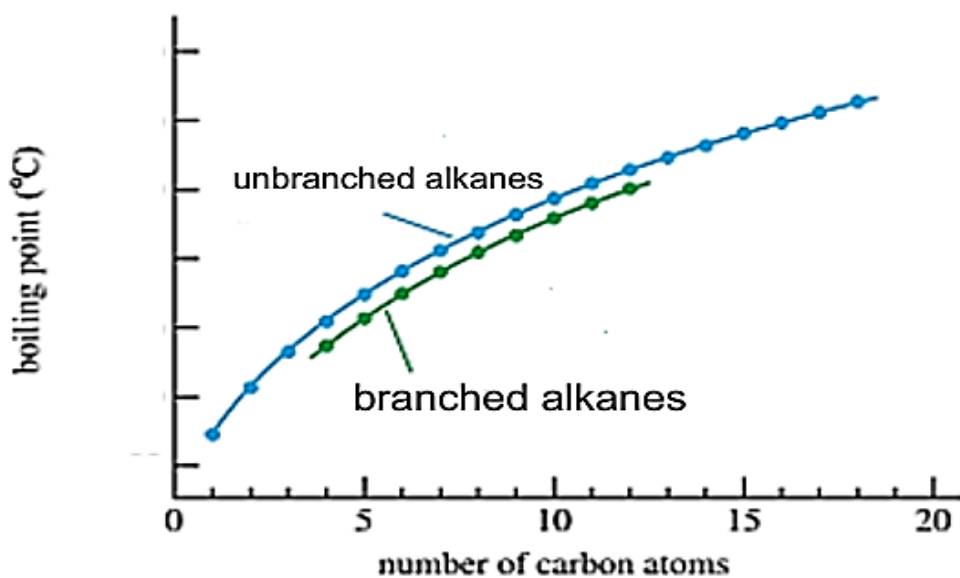


Isomers of hexane



49.7 °C

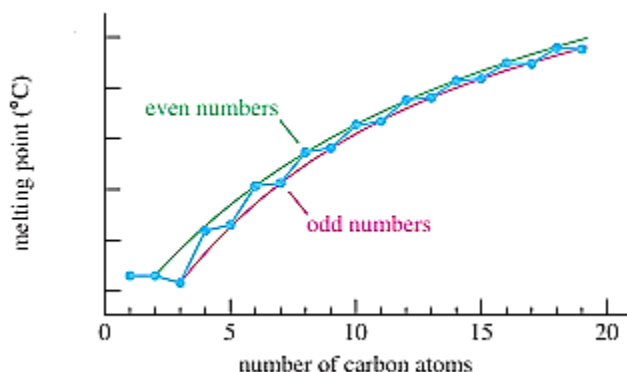
- Chain branching makes a molecule more compact, reducing its surface area, which reduces the van der waal forces and hence lowering the boiling points.



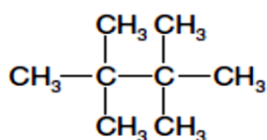
(ii) Melting point

- Like their boiling points, the melting points increase with increasing molecular weight.

- Unbranched alkanes do not show the same smooth increase in melting points with increasing molecular weight that they show in their boiling points.
- Alkanes with even numbers of carbon atoms pack better into a solid structure, so that higher temperatures are needed to melt them.
- Alkanes with odd numbers of carbon atoms do not pack as well, and they melt at lower temperatures.



- The melting points curve for n-alkane with even number of carbon atoms is slightly higher than the curve for alkane with odd number of carbon atoms.
- Cycloalkanes have much higher melting points than their open-chain counterparts
- Branching produces highly symmetrical structures that results in abnormally high melting points. e.g.



2,2,3,3-Tetramethylbutane mpts = 100.7°C

- Branching increases the packing of alkanes in the solid phase leading to higher intermolecular forces hence higher melting points.

(iii) Density

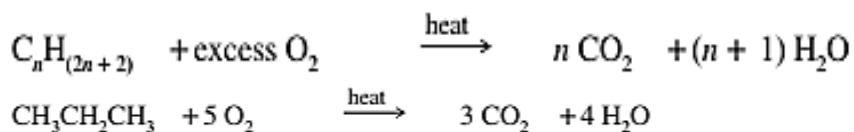
- Alkanes and cycloalkanes are the least dense of all groups of organic compounds. All alkanes and cycloalkanes are less dense than water (1.00 g mL⁻¹).
- As a result, petroleum floats on water.

(iv) Solubility

- Alkanes and cycloalkanes are almost totally insoluble in water due to their very low polarity and their inability to form hydrogen bonds. Liquid alkanes and cycloalkanes are soluble in one another, and they generally dissolve in solvents of low polarity such as benzene, CCl₄, chloroform and other hydrocarbons.

CHEMICAL REACTIONS OF ALKANES

- Alkanes and cycloalkanes are considered to be unreactive.
 - They are quite unreactive towards most reagents, a behavior consistent with the fact that they are nonpolar compounds containing only sigma bonds.
 - However, under suitable conditions, they do react.
1. Combustion- It is a rapid oxidation that takes place at high temperatures converting alkanes to carbon dioxide and water.

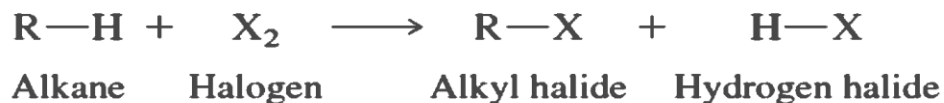


2. Halogenation- (Substitution reaction)

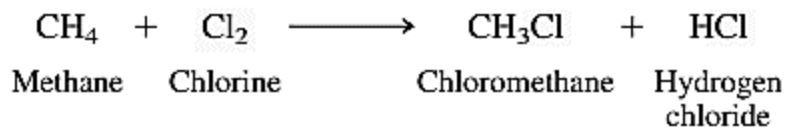
- Alkanes react with the first three members of the halogen family (F_2 , Cl_2 , Br_2).
- Alkanes react very slowly or not at all with iodine.
- Heat or light is usually needed to initiate this halogenation.

Reactivity of X_2 $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 (> \text{I}_2)$

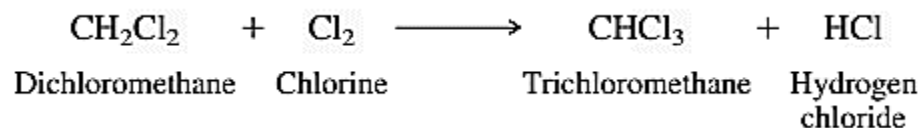
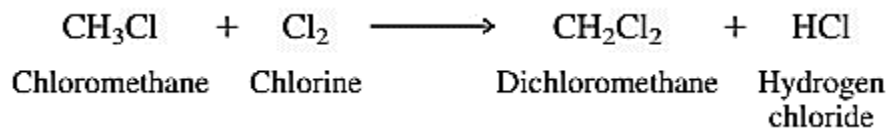
Unreactive

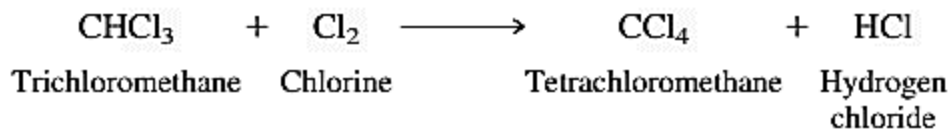


e.g

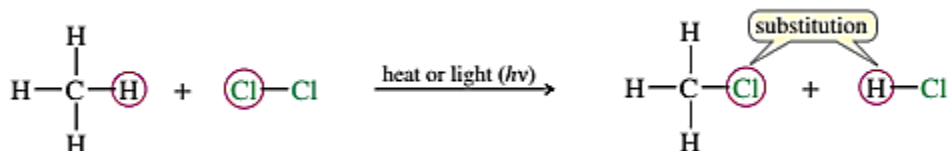


If an excess chlorine is present, the reaction can proceed further.



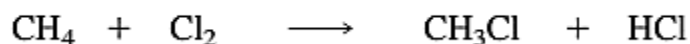


Reaction with methane.

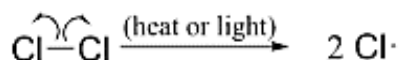


Mechanism of halogenation

- Halogenation reaction of alkenes takes place by a radical mechanism e.g.



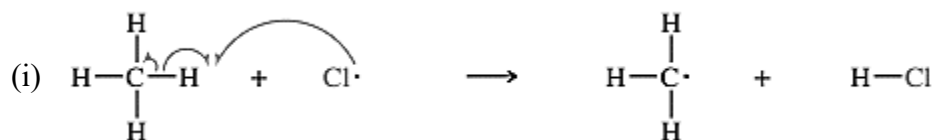
Step 1: Chain initiation



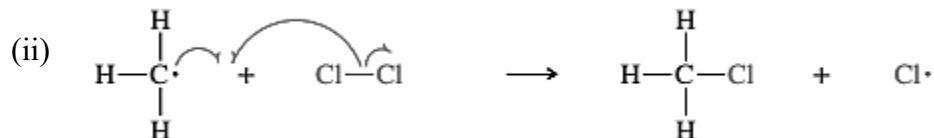
- Chlorine molecule dissociating homolytically (each atom carries its unpaired electron) under the influence of heat or light to form two highly reactive chlorine atom radicals.

(An atom or group of atoms possessing an odd (unpaired) electron is called free radical).

Step 2: Chain propagation



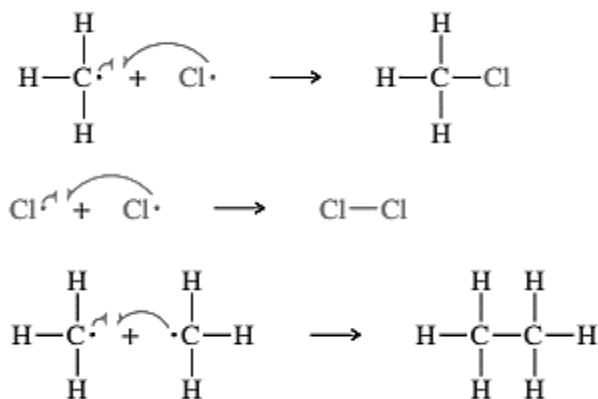
- Chlorine radical abstracts a hydrogen atom from methane to produce HCl and methyl radical.



- Methyl radical abstracts chlorine atom from a chlorine molecule. The chlorine radical ($\text{Cl}\cdot$) produced now causes a repetition of step 2 (i)

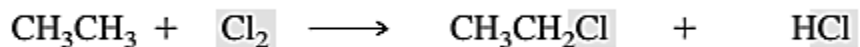
Step 3: Chain termination

- Involves combination of radicals produced in step 1 and 2 to form a molecule.

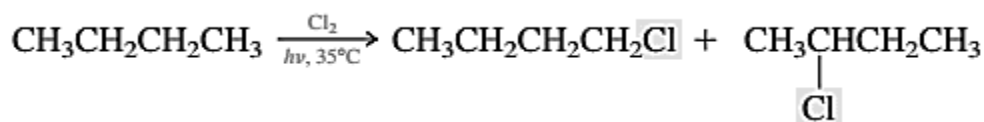


Chlorination of Higher Alkanes

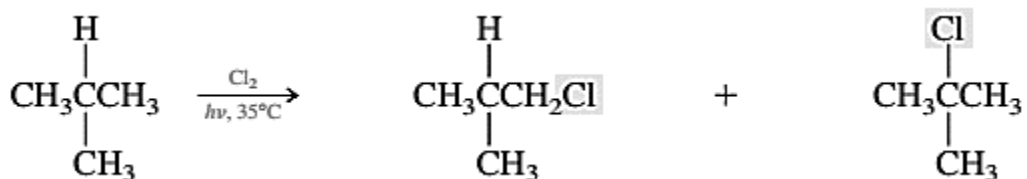
- Like the chlorination of methane, chlorination of ethane is carried out on an industrial scale as a high-temperature gas-phase reaction.



- Methane and ethane share the common feature that each one can give only a single monochloro derivative.
- Chlorination of alkanes in which all the hydrogens are not equivalent give mixtures of isomeric monochloro products as well as highly halogenated compounds.



- Chlorine is relatively unselective and does not discriminate greatly among the different types of hydrogen atoms (1°, 2°, 3°) in an alkane e.g.

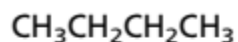


- Alkanes chlorination usually yields a complex mixture of products and are therefore generally not useful for synthesis of pure alkyl halides.

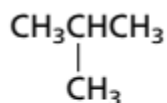
STRUCTURAL ISOMERISM

- Isomers- different compounds with the same molecular formula.
- Constitutional isomers- are compounds that have the same molecular formula, but different structural formula.
- Constitutional isomers have different physical properties.
e.g.

1. C_4H_{10} Butane



IUPAC name: **butane**
(common name: *n*-butane)

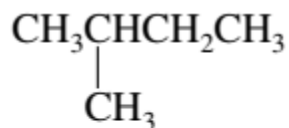


IUPAC name: **2-methylpropane**
(common name: isobutane)

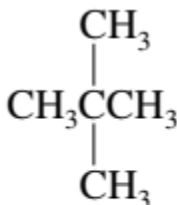
2. Pentene (C_5H_{12})



IUPAC name: **pentane**
Common name: *n*-pentane

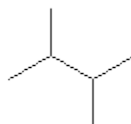
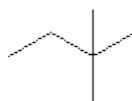
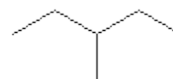


IUPAC name: **2-methylbutane**
Common name: isopentane



IUPAC name: **2,2-dimethylpropane**
Common name: neopentane

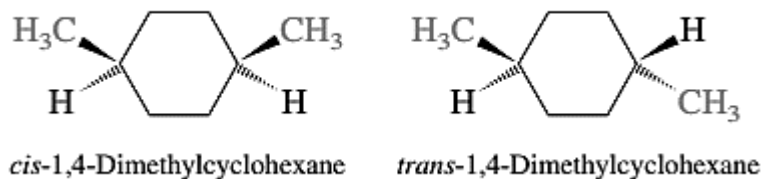
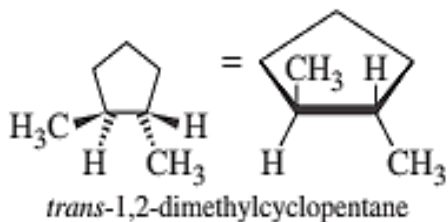
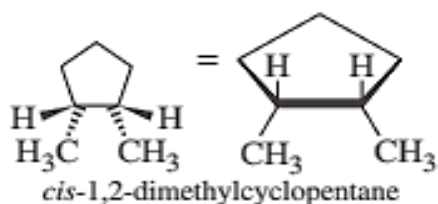
3. Hexane (C_6H_{14})



Geometric Isomerism in Cycloalkanes

- Open – chain (acyclic) alkanes undergo rotations about their carbon – carbon single bonds, so they are free to assume any of an infinite no of conformations.
- Alkenes have rigid double bonds that prevent rotation which gives rise to Cis and trans isomers with different orientations of the groups on the double bond.
- Cycloalkenes are similar to alkenes in this respect.
- Cycloalkanes with substituents on two or more carbons of the ring show a type of isomerism called Cis – trans isomerism.
- Cis – trans isomers have;
 - (i) The same molecular formula.
 - (ii) The same order of attachment of atoms.
 - (iii) An arrangement of atoms that cannot be interchanged by rotation about sigma bonds under ordinary conditions.
- If two substituents point towards the same face, they are cis. If they point toward opposite faces, they are trans.

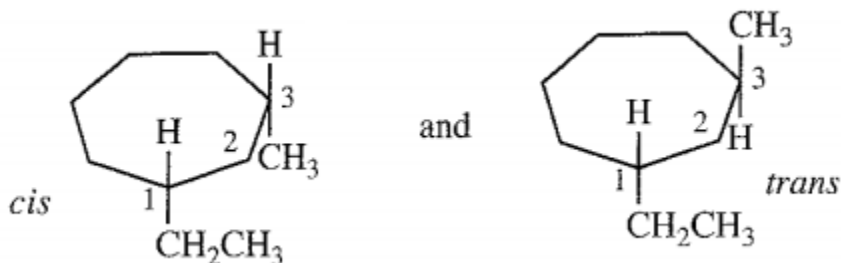
e.g.



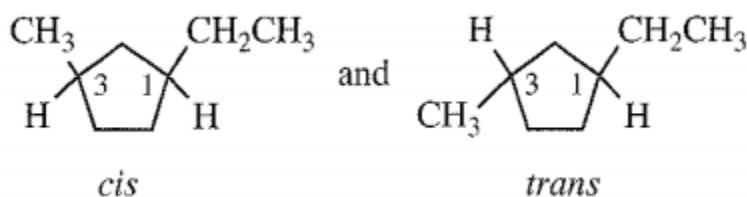
Examples

Draw cis and trans isomers of

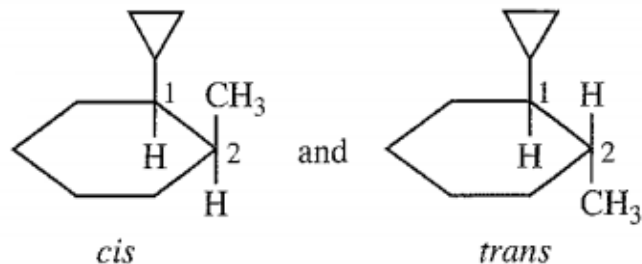
a) 1-ethyl-3-methylcycloheptane



b) 1-ethyl-3-methylcyclopentane



c) 1-cyclopropyl-2-methylcyclohexane



MAJOR USES OF ALKANES

- 1) $C_1 - C_2$ (Methane and ethane) are gases at room temperature. The mixture is natural gas. They burn hence used as cooking gas.
- 2) Liquefied petroleum gas (LPG) $\rightarrow C_3 - C_4$ (propane and butane) used as fuels for heating and for internal combustion engines.
- 3) Gasoline ($C_5 - C_8$) \rightarrow petrol engines
- 4) $C_9 - C_{16}$ - $\begin{cases} \text{Diesel} \\ \text{Kerosine} \\ \text{Jet fuel} \end{cases}$
- 5) Non-volatile residues \rightarrow produced to give lubricating oils, greases, petroleum jelly. Paraffin wax etc.