17 Hydrocarbons

QUICK LOOK

Compounds containing only C and H are known as hydrocarbons. The main sources of hydrocarbons are

Natural gas	→	Methane (90%), Ethane, Butanes and Hexanes in decreasing quantities.
Petroleum	→	Aliphatic hydrocarbons
Coal	→	Aromatic hydrocarbons

Petroleum, Crude oil or Mineral Oil: It is a dark coloured viscous oil (with unpleasant smell due to sulphur compounds) found deep in earth's crust. It may be of three types:

Paraffinic base type	→	It contains mainly of saturated hydrocarbons.
Asphaltic base type	→	It contains mainly cycloparaffins
Mixed base type	→	It contains both paraffinic and Asphaltic hydrocarbons.

Crude oil as such is of little importance. However, it can be separated into a number of useful fractions by fractional distillation.

Table 17.1: Temperature Range of Condensation

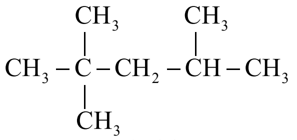
Name of the fraction	**Temperature range of condensation**	**Approximate composition**	**Uses**
Uncondensed gases	Upto 30°C	C_1-C_5	Domestic fuel, synthesis of organic chemicals, production of carbon black.
Gasoline (Petrol). On refractionation gives: (i) Petroleum ether (ii) Gasoline or petrol	$30-200°C$ $30-80°C$ $80-200°C$	C_5-C_{10} C_5-C_6 C_6-C_{10}	As a solvent for fat, oil, varnish and rubber. Fuel for the internal combustion engines of automobiles and aeroplanes, solvent and dry-cleaning.
Kerosene	$200-300°C$	$C_{10}-C_{16}$	Illuminant, fuel for stoves, for making oil gas.
Heavy oil. On re-fractionation gives: (i) Gas oil, (ii)Fuel oil, Diesel oil.	$300-350°C$	$C_{16}-C_{18}$	Fuel for diesel engines, for conversion to gasoline by cracking.
(5) Residual oil. On refractionation gives: (i) Lubricating oil (ii) Paraffin wax (iii) Petroleum jelly (Vaseline)	$350-400°C$	$C_{18}-C_{40}$ $C_{18}-C_{20}$ $C_{20}-C_{30}$ $C_{30}-C_{40}$	Lubrication Candles, boot polishes, wax paper, taprolin cloth and electrical insulation. In medicines, cosmetics, toilets and lubricants.
(6) Residue, which may be either pitch (asphalt) or petroleum coke.	$> 400°C$		Pitch is used in water proofing of roofs, road making, stabiliser for wood and metal. Petroleum coke is used as fuel.

Thus petroleum is a source of infinite number of useful compounds, it is said to be more precious than gold and hence also named as liquid gold or black gold.

Octane Number: Octane number of a gasoline is defined as the percentage of iso-octane present in a mixture of iso-octane and *n*-heptane which matches the fuel (gasoline) in knocking; higher the octane number of a gasoline better is its quality.

$$CH_3\cdot(CH_2)_5\cdot CH_3$$

n-Heptane
(Octane number = 0)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

Iso-octane (2, 2, 4-Trimethylpentane)
(Octane number = 100)

Ordinarily gasolines having an octane number of 74 are used in motor cars, scooters and motorcycles. These gasolines are known as regular gasolines. Gasolines having octane number lower than this value are called third grade gasolines, while gasolines having an octane number of 84 and above are known as premium gasolines.

Compounds having more than 100 and less than 0 octane numbers are also known. For example, triptane (2, 2, 3-trimethylbutane) has an octane number of 125, while *n*-nonane has an octane number of 45. Aviation gasoline (gasoline used as fuel in aeroplanes) has an octane number of 100 or more.

Presence of following types of organic compounds increases the octane number of gasoline.

- In case of straight chain hydrocarbons, octane number decreases with increase in the length of the chain.
- Branching of chain increases the value of octane number.
- Introduction of double or triple bond in an alkane increases the value of octane number.
- Cyclic alkanes have relatively higher value of octane number than the corresponding *n*-alkanes.
- The octane number of aromatic hydrocarbons are exceptionally high.

The Octane number of gasolines can be improved by following methods:

- By cracking,
- By alkylation,
- By isomerisation,
- By adding gasoline additives (*e.g.* TEL),
- By adding BTX (benzene, toluene and xylene)

Knocking: The objectionable metallic sound produced during the working of an internal combustion engine is known as knocking. It leads to wastage of fuel. Knocking depends upon the composition of the fuel, it falls off in the following order: Straight chain paraffins > Branched chain paraffins > Olefins > Aromatic hydrocarbons, Knocking may also be prevented or minimised by adding small amounts of certain compounds known as anti-knock compounds, *e.g.* tetraethyl lead (TEL) [$(C_2H_5)_4Pb$]. Such petrol is known as leaded petrol or ethyl petrol. Tetraethyl lead is used as a mixture of TEL (63%), ethylene bromide (26%), ethylene chloride (9%) and methylene blue (2%). About 0.5-0.6 ml of this mixture is added to 1 litre of petrol.

In the cylinder of conbustion engine, TEL decomposes to produce radicals which combine with the radicals produced due to irregular combustion. As a result, the reaction chains are broken and smooth burning of fuel occurs. This prevents knocking,

$$Pb(C_2H_5)_4 \xrightarrow{\text{heat}} Pb + 4C_2H_5$$

This lead is deposited in the cylinder which is removed by ethylene bromide to form lead bromide volatile at the ignition temperature,

$$BrCH_2 - CH_2Br \longrightarrow CH_2 = CH_2 + Br_2,$$

$$Pb + Br_2 \longrightarrow PbBr_2 \text{ (volatite)}$$

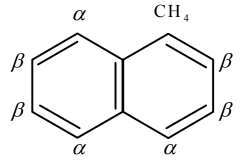
However, use of TEL in petrol is facing a serious problem of lead pollution. To avoid this, a new compound cyclopentadieny -lmanganese carbonyl (called as AK-33-X) is used, in developed countries, as anti-knocking compound.

Cetane Number

It is used for measuring the knocking character of fuel used in diesel engines. Cetane (n-hexadecane, n–$C_{16}H_{34}$) ignites very readily and is given a cetane number of 100 while α-methylnaphthalene ignites very sluggishly in a diesel engine and hence is given zero cetane number.

$CH_3 \cdot (CH_2)_{14} \cdot CH_3$

Hexadecane or Cetane
(cetane number = 100)
Spontaneous ignition



α-Methylnaphthalene
(cetane number = 0) Slow ignition

Centane number of a fuel is defined as the percentage of cetane in a mixture of cetane and α-methylnaphthalene that will have the same ignition characteristics as the fuel under examination.

Synthetic Petrol

- **Bergius process:** Finely powdered coal (coal is a mixture of high molecular complex organic compounds deficient in hydrogen) is heated with a catalyst (organic compound of tin) in presence of hydrogen.

  $$\text{Coal} + H_2 \xrightarrow[\text{250 atm}]{400°C - 500°C} \text{Hydrocarbons (l)}$$

- **Fischer-tropsch process:** Hard coke is the raw material. Steam is passed over red hot coke to give water gas (a mixture of CO and hydrogen). Carbon monoxide is removed from a part of the water gas. Hydrogen so obtained is mixed with rest of the water gas in a ratio of synthesis gas (*i.e.* H_2 and CO in a ratio of 2:1) which is heated in presence of a catalyst (cobalt-thorium oxide).

  $$n\,CO + n\,H_2 \xrightarrow[\text{Zn Oxide}]{\text{Co, Cu}} C_nH_{2n} + nH_2O\,;$$

  $$n\,CO + (2n+1)\,H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

The overall yield of Fischer – Tropsch process (66%) is higher than that obtained from obtained from Bergius process (60%) and thus, unlike Bergius process, it can be operated commercially on a small scale. Petroleum products (*e.g.* ethylene, propylene, isobutene, acetylene, *etc.*) are used in preparing thousands of organic chemicals and products like dyes, drugs, explosive, plastics, fibers, rubber, etc. Hence petroleum is literally called as liquid gold or black gold.

Petrochemicals

Organic compounds obtained directly or indirectly from natural gas or petroleum are called petrochemicals. Some petrochemicals are:

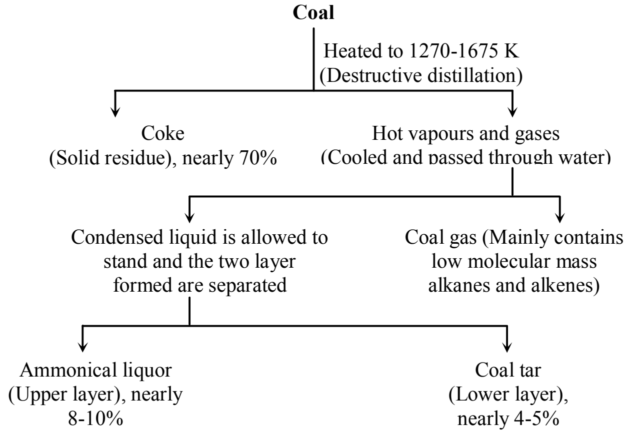
- Saturated hydrocarbons–Methane, ethane, propane, butanes, pentanes, hexanes, cyclohexanes etc.
- Unsaturated hydrocarbons – Ethylene, propylene, butylenes, acetylene etc.
- Aromatic hydrocarbons – Benzene, toluene, etc.
- Halogenderivatives–

  $CH_3Cl, CH_2Cl_2, CHCl_3, CCl_4, CH = CHCl$ (Vinyl chloride).

  Alcohols – Methyl alcohol, ethyl alcohol, allyl alcohol, butyl alcohol, glycol etc.
- Aldehydes and Ketones–Formaldehyde, acetadehyde, acetone etc.
- Alkenes and alkadienes – Styrene, 1, 3-butadiene etc.
- Acids – acetic acid.
- Nitriles – acrylonitrile.

These petrochemicals are widely used in the manufacture of iso-octane (aviation fuel), plastics (polythene, polyvinyl chloride (PVC) etc), synthetic fibers (nylone terylene, dacron etc.), synthetic rubber insecticides, pesticides, detergents, dyes, perfumes, explosives etc.

Coal: It is believed to be formed beneath earth's surface by the slow decomposition of vegetable matter over the years. Coal is mainly made up of carbon. Its carbon content, however, varies with the type of coal. For example, common varieties of coal such as anthracite contains 90% carbon, bituminous contains 70% C, lignite contains 40% C and peat contains 10-15% C. Coal also contains a number of arenes (aromatic hydrocarbons) such as benzene, toluene, xylenes, naphthalene and anthracene in addition to some organic compounds of sulphur and nitrogen. Aromatic Hydrocarbons from Coal. Aromatic hydrocarbons are obtained by destructive distillation of coal. When coal is subjected to destructive distillation, *i.e.,* heated to 1270K to 1675K in the absence of air, it decomposes to give the following main products.



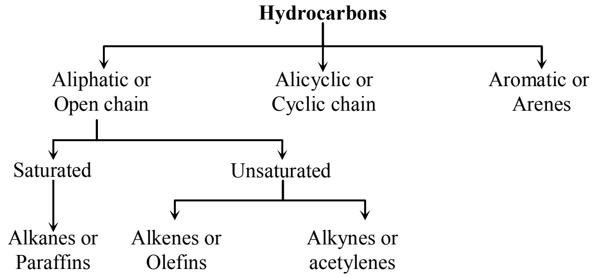
- **Coke:** It is the solid residue left after the distillation. It is mainly used as a fuel and as a reducing agent in metallurgy.
- **Coal gas:** It mainly consists of low molecular mass alkanes and alkenes. It is used as a fuel.
- **Ammonical liquor:** It is a solution of ammonium in water and is removed by absorbing in a suitable mineral acid like dil. H_2SO_4 .The ammonium sulphate thus produced is used as a fertilizer.
- **Coal tar:** It is a thick black viscous liquid with a disagreeable smell. It is a rich source of aromatic hydrocarbons (arenes) such as benzene, toluene, 1, 2-, 1, 3- and 1, 4-dimethylbenzenes (xylenes), naphthalene, anthracene and phenanthrene. These are obtained by fractional distillation of coal tar into a number of fractions.

Table: 17.2 Fractions of Coal Tar Distillation

Name of the Fraction	Temperature range (in K)	Major components
Light oil	Upto 443	Benzen, Toluene, Xylenes
Middle oil or Carbolic oil	443 – 503	Phenol, Naphthalene, Pyridine
Heavy oil or Creosote oil	503 – 543	Methyl and higher alkyl phenols, naphthalene, naphthols, etc.
Green oil or Anthracene oil	543 – 633	Anthracene, phenanthrene.
Pitch (left as residue)	Non - volatile	92 – 94% carbon (used for making black paints, varnish for wood and for water proofing).

Classification of Hydrocarbons

Hydrocarbons can be classified as follows:



Alkane or Paraffins

The functional group is an atom or group of atoms that causes a compound to behave in a particular way, i.e. it is the functional group that gives rise to homologous series. An alkyl group is the structure remaining after one H is removed from an alkane. Alkanes have general formula, C_nH_{2n+2}.

(1) Preparation

$C_nH_{2n} \xrightarrow[H_2,200-300°C]{\text{Reney Ni}} C_nH_{2n+2}$ (Sabatier Senderen's reduction)

Alloy containing equal amount of Ni and Al is digested with NaOH, the Al is dissolved away and the residual very finely divided Ni, is washed and stored under water or ethanol.

- Reduction of alkyl halide by
- metal and acid or Mg/anhyd. ether, then H_2O

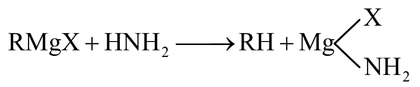
  $RX + Zn + H^{\oplus} \longrightarrow RH + Zn^{++} + X^{\ominus}$

  Mechanism: $Zn \longrightarrow Zn^{++} + 2e^-$

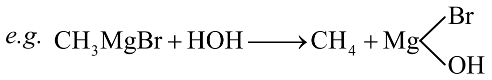
  $RX + e^- \longrightarrow R + X^- \rightarrow R^{\ominus}$

  $R^{\ominus} + C_2H_5OH \longrightarrow R - H + \overset{\ominus}{O}C_2H_5$
- Pri and sec alkyl halide $\xrightarrow{LiAlH_4}$ Alkane
- Sec and tert alkyl halide $\xrightarrow{NaBH_4}$ Alkane
- Pri, sec and tert alkyl halide $\xrightarrow{Ph_3SnH}$ Alkane

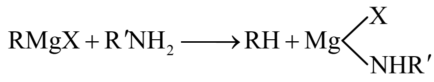
(i) From RMgX: Alkanes can be prepared by reaction of Grignard reagent with the compounds containing 'active hydrogen atom'. A compound is said to contain active hydrogen atom in which hydrogen is attached to electronegative element from which it can be easily removed. Such compounds are H_2O, ROH, NH_3, RNH_2.



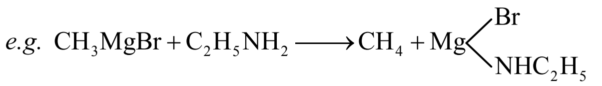
- $RMgX + HNH_2 \longrightarrow RH + Mg\left\langle\begin{matrix}X\\NH_2\end{matrix}\right.$



e.g. $CH_3MgBr + HOH \longrightarrow CH_4 + Mg\left\langle\begin{matrix}Br\\OH\end{matrix}\right.$



- $RMgX + R'NH_2 \longrightarrow RH + Mg\left\langle\begin{matrix}X\\NHR'\end{matrix}\right.$



e.g. $CH_3MgBr + C_2H_5NH_2 \longrightarrow CH_4 + Mg\left\langle\begin{matrix}Br\\NHC_2H_5\end{matrix}\right.$

(ii) Kolbe's Electrolytic Method: The reaction is only suitable for preparation of symmetrical alkane.

$RCOOK + RCOOK + 2H_2O \longrightarrow \underset{\text{at anode}}{R — R} + 2CO_2 + H_2 + 2KOH$

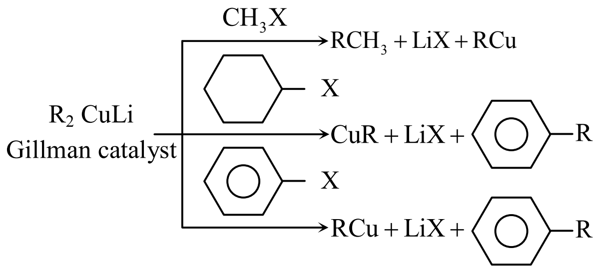
(iii) Decarboxylation of Acids

$RCOOH + NaOH \longrightarrow RH + Na_2CO_3$

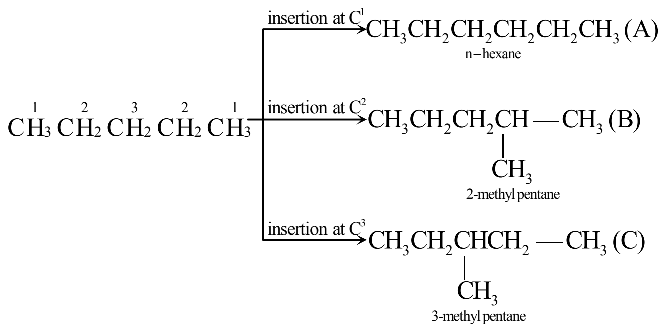
(iv) Wurtz Reaction: Alkyl bromide or iodide reacts with metallic Na to from a hydrocarbon containing twice the number of carbons that are present in alkyl halide.

$RX + 2Na + R'X \longrightarrow R-R + R'-R' + R-R' + 2NaX$

(v) Corsey-Posner Whitesides house Synthesis



- $R\ddot{N}H_2 + \overset{\ominus}{R}\overset{\oplus}{Li} \to RH + Li^+(RNH)^{\ominus}$
- By insertion of: CH_2: CH_2N_2 dissociates to from: CH_2
  The insertion of: CH_2 is random e.g.



(2) Physical Properties: $C_1 \longrightarrow C_4$ gas; $C_5 \longrightarrow C_{17}$ colourless liquid; $C_{18} \longrightarrow$ onwards: colourless solid

Density α B.P. α viscosity $\propto \frac{1}{\text{M.Pt.}} \propto \frac{1}{\text{Branching}} \propto$ No. of C atoms

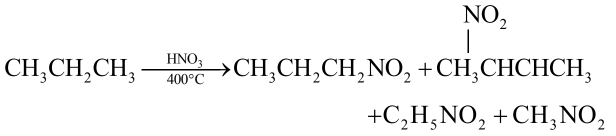
Solubility in water $\propto \frac{1}{\text{mol.wt.of alkane}}$

(3) Chemical Properties: Alkanes undergo substitution reaction.

(i) Halogenation

- Ease of substitution $\text{tert.}\,H > \text{Sec.}\,H > \text{Pri}\,H$
- $F_2 > Cl_2 > Br_2 > I_2$
- Iodination is reversible hence it may be carried out in the presence of an oxidizing agents like HIO_3, HNO_3, HgO
- Relative amt.
  Chlorination population: Pri H×1: Sec H×3.8: H×3.8:Tert H×5
  Population Bromination: Pri H×1: Sec H×82: Tert H×1600
- Kinds of monochloro derivative = Kinds of H atoms
  Ist product = Ease of substitution
  Relative population = As point IV
- The % are obtained by dividing the relative amount of each product by the sum of relative amount (3+7.6 = 10.6) and multiplying by 100.
- Chlorination in lab is carried out with sulphuryl chloride SO_2Cl_2 instead of Cl_2.

(ii) Nitration: Kinds of mononitro derivative and Ist product is same as for halogenation. But nothing for population. Kinds of mononitro derivative = Kinds of H atoms + All possible fragments



$$CH_3CH_2CH_3 \xrightarrow[400°C]{HNO_3} CH_3CH_2CH_2NO_2 + CH_3CH\overset{\overset{NO_2}{|}}{C}HCH_3 + C_2H_5NO_2 + CH_3NO_2$$

Nitration is carried out in vapour phase.

(iii) Sulphonation: Hexane or onwards $\xrightarrow{\text{Oleum}} SO_3H + H_2SO_4$

Carbonium ions are intermediate.

(iv) Oxidation: Extensive oxidation gives acids and less extensive oxidation gives mixed ketones.

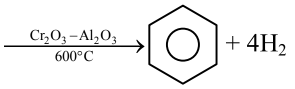
Oxidation in the presence of boric acid gives sec. alcohol.

$Me_3CH + [O] \xrightarrow{KMnO_4} Me_3C-OH$

(v) Isomerisation: n-alkane $\xrightarrow[300°C]{AlCl_3}$ Isoalkane carbonium ion is intermediate.

(vi) Cracking: Higher alkanes $\xrightarrow[\text{without catalyst}]{400-600°C\text{ with or}}$ H_2 + small alkane + alkane

(vii) Aromatisation: n-hexane



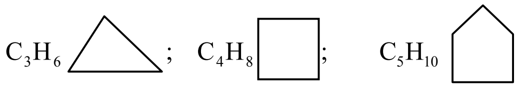
$$\text{n-hexane} \xrightarrow[600^\circ C]{Cr_2O_3-Al_2O_3} C_6H_6 + 4H_2$$

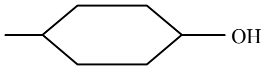
- Mechanism of $\overset{\bullet}{Br} + CH_4 \rightarrow HBr + \overset{\bullet}{C}H_3$
- Bond dissociation energy

$$\underset{58}{Cl-Cl} > \underset{46}{Br-Br} > \underset{37}{F-F} > \underset{36}{I-I}_{(\text{Kcal/mole})}$$

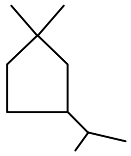
Cyclo Alkanes

General formula C_nH_{2n}, Where C–C bond forms a ring, *e.g.*

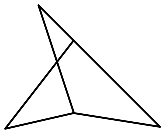




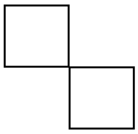
4-bromo cyclohexanol



1, 1-dime-3-isopropyl cyclopentane

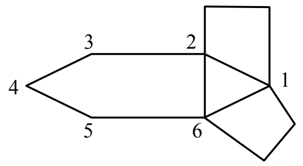


Bicyclo [2.1.1] hexane



Spiro [3.3.] heptane

Bicyclo alkane C_nH_{2n-2} with two degree unsaturation. Tricycloalkane with 3° unsaturation C_nH_{2n-4}



Tricyclo $[4.2.2.0]^{1,6}$ decane. The superscripts 1 and 6 indicates the fused C atoms.

Cycloalkane have higher M.P. because they have compact shapes than n-alkane and are more closely in the solid state. Cycloalkanes are more dense because they can be closely packed also in the liquid state.

Small rings $(C_3 - C_4)$ have large ring strain, Common rings $(C_5 - C_6)$ have little or no strain.

Medium rings $(C_7 - C_{12})$ have little strain, Large rings $(> -C_{12})$ are strain free.

Order of Reactivity: Cyclopentane<Cyclobutane < Cyclopropane.

Trans cyclopropane is more stable than cis form.

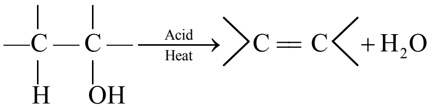
Cyclopropane has a greater acidity than propane because the $C - H$ bonds of cyclopropane have more‘s’ character than those of an alkane.

Alkenes or Olefins

General formula C_nH_{2n}, Isomeric with cycloalkanes, They contain the functional group $> C = C <$.

(1) Preparation: Following methods have been frequently used:

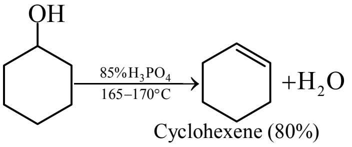
(i) Dehydration of Alcohols: General reactions is as follows:



$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow[\text{Heat}]{\text{Acid}} >C=C< + H_2O$$

Ease of dehydration of alcohols: Tertiary > Secondary > Primary,

e.g.

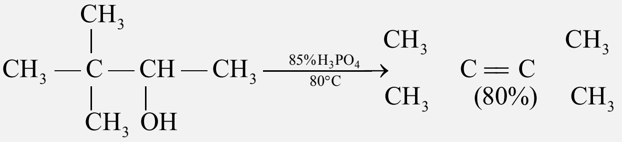


$$\xrightarrow[165-170^\circ C]{85\% H_3PO_4} \quad + H_2O$$

Cyclohexene (80%)

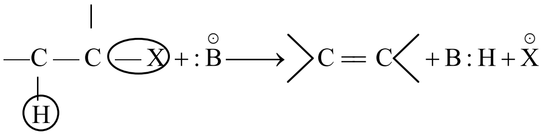
Note

Some primary and secondary alcohols also undergo rearrangments of their carbon skeleton during dehydration, *e.g.*



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[80^\circ C]{85\% H_3PO_4} (CH_3)_2C=C(CH_3)_2 \ (80\%)$$

(ii) Dehydrohalogenation of Alkyl Halides



$$-\underset{H}{C}-\overset{|}{C}-X + :\overset{\ominus}{B} \longrightarrow >C=C< + B:H + \overset{\ominus}{X}$$

$X = Cl, Br, I$, Sulphonate esters $RS(O_2)\overset{\ominus}{O}$; B.alc. KOH or $Et\overset{\ominus}{O}$

Note: It is important to note that the weaker the base, the better it is a leaving group.

(iii) By Selective Reduction of Alkynes

- When Lindlar’s catalyst $[Pd/CaCO_3/PbO$ or $Pd/CaCO_3/Pb(CH_3COO)_2]$ is used the major product is cis,

e.g. $\underset{\text{Butyne-2}}{CH_3-C\equiv C-CH_3} \xrightarrow[\text{Catalyst}]{H_2/\text{L indlar's}}$

$$\underset{\text{Cis (97\%)}}{CH_3CH=CHCH_3} + \underset{\text{Trans (3\%) Buene-2}}{CH_3CH=CH-CH_3}$$

- If Wilkinsons’s catalyst $[(Ph_3P)_3RhCl]$ is used (Tris-triphenyl chloro Rhodium II) the product is 100% cis butene-2,

$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{Wilkinson's Catalyst}]{H_2} \underset{\text{C is-Butene-2 (100\%)}}{CH_3CH=CHCH_3}$$

(iv) By Witting Reaction: When carbonyl compounds react with alkyl bromide in the presence of phenyl lithium, the alkene is formed. Ylides are reaction intermediate

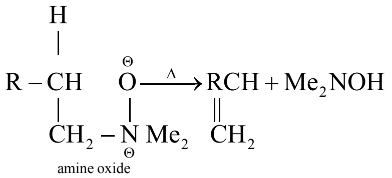
(a) $Ph_3P + RCH_2Br \xrightarrow{C_6H_5Li} \underset{\text{ylide}}{Ph_3P = CHR} + C_6H_6 + LiBr$

$\longrightarrow \underset{\text{ylide}}{Ph_3\overset{\oplus}{P}-\overset{\odot}{C}H_2-R}$

(b) $Ph_3P = CH-R + R'CH = O \longrightarrow$

$Ph_3PO + R'CH = CH-R$

(v) Cope Reaction: When amine oxides are heated, alkenes are formed, e.g.

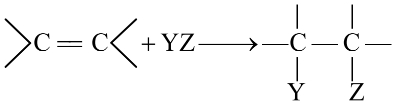


$$\underset{\text{amine oxide}}{\begin{array}{l} \quad H \\ \quad | \\ R-CH \quad \overset{\ominus}{O} \\ \quad | \qquad\; | \\ \quad CH_2-\underset{\ominus}{N}Me_2 \end{array}} \xrightarrow{\Delta} \begin{array}{c} RCH \\ \| \\ CH_2 \end{array} + Me_2NOH$$

(2) Physical Properties: Alkenes with C_2-C_4 carbon gases; C_5-C_{17} liquid and C_{18} onwards are solid.

(3) Chemical Properties

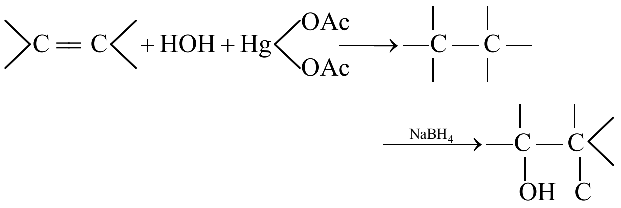
(i) Addition Reactions: Alkenes are unsaturated compounds. They undergo addition reactions in general.



$$>C=C< + YZ \longrightarrow -\underset{\underset{Y}{|}}{\overset{|}{C}}-\underset{\underset{Z}{|}}{\overset{|}{C}}-$$

Where, Y = Z = H, Pt, Pd
or Ni catalyst, Y = Z = Cl_2, Br_2,
(Y = H; Z = F, Cl, Br, I Markownikoff & Peroxide),
$Y = H; Z = HSO_4^{\ominus}$

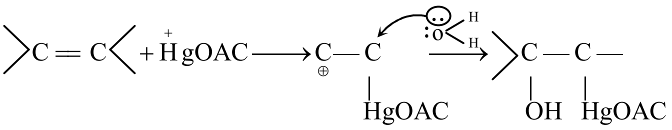
(ii) Oxymercuration or Demercuration: It is a method to convent alkenes into alcohols.



$$>C=C< + HOH + Hg\begin{matrix}OAc\\OAc\end{matrix} \longrightarrow -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}- \xrightarrow{NaBH_4} -\underset{\underset{OH}{|}}{\overset{|}{C}}-\underset{\underset{C}{|}}{\overset{|}{C}}<$$

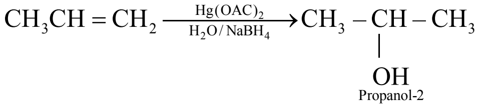
Mercuricacetate (Note: Ac Stands for CH_3CO group)

The mechanism is as follows:



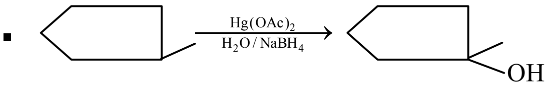
$$>C=C< + \overset{+}{H}gOAC \longrightarrow \underset{\oplus}{C}-\underset{\underset{HgOAC}{|}}{C} \xrightarrow{:\ddot{O}\begin{smallmatrix}H\\H\end{smallmatrix}} >\underset{\underset{OH}{|}}{C}-\underset{\underset{HgOAC}{|}}{C}-$$

Addition involves attachment of 'OH' to the carbon atom having less number of hydrogen atom, *e.g.*



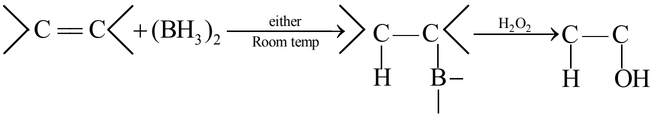
$$CH_3CH = CH_2 \xrightarrow[H_2O/NaBH_4]{Hg(OAC)_2} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Propanol-2

- 

1-methyl cyclopentanol

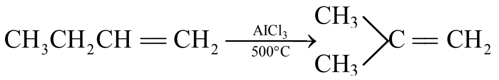
(iii) Hydroboration: When alkene reacts with diborane in ether at room temperature and then with H_2O_2, alcohol is formed.



$$>C=C< + (BH_3)_2 \xrightarrow[\text{Room temp}]{\text{either}} >\underset{\underset{H}{|}}{C}-\underset{\underset{\underset{|}{B-}}{|}}{C}< \xrightarrow{H_2O_2} \underset{\underset{H}{|}}{C}-\underset{\underset{OH}{|}}{C}$$

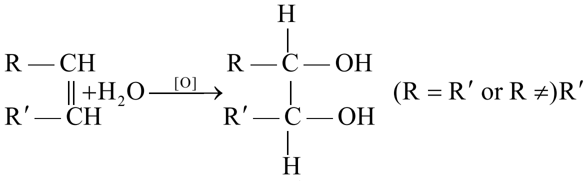
Note: The 'OH' is attached to those carbon atom having maximum number of H atoms.

(iv) Isomerisation

- $\underset{\text{Pentene-1}}{CH_3CH_2CH_2CH = CH_2} \xrightarrow[500-700°C]{AlCl_3} \underset{\text{Pentene-2}}{CH_3CH_2CH = CHCH_3}$
- 

$$CH_3CH_2CH = CH_2 \xrightarrow[500°C]{AlCl_3} \begin{matrix}CH_3\\CH_3\end{matrix}>C = CH_2$$

(v) Oxidation: The nature of product depends upon the oxidizing agent used. The general steps are as following:

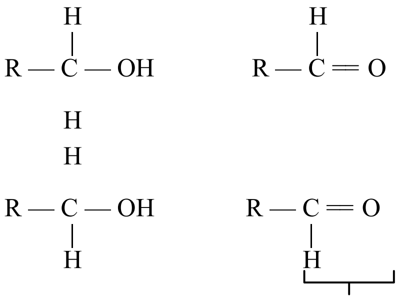
- 

$$\begin{matrix}R-CH\\ \|\\ R'-CH\end{matrix} + H_2O \xrightarrow{[O]} \begin{matrix}H\\|\\R-C-OH\\|\\R'-C-OH\\|\\H\end{matrix} \quad (R = R' \text{ or } R \neq)R'$$

Product I

Note that alkene converted into "diol"

- Add one H to each carbon of alkene and break the C — C bond. Now write oxidation product of the alcohol so obtained.



$$\begin{matrix}H\\|\\R-C-OH\\|\\H\end{matrix} \qquad \begin{matrix}H\\|\\R-C=O\end{matrix}$$

$$\begin{matrix}H\\|\\R-C-OH\\|\\H\end{matrix} \qquad \begin{matrix}R-C=O\\|\\H\end{matrix}$$

Product II

(vi) Alkadienes: Alkadiene contains two double bonds. These have further classified into three categories

(a) Conjugated alkadiene: These contain single and double bond in alternate manner,

e.g. $\underset{\text{1,3-Butadiene}}{CH_2=CH-CH=CH_2}$

(b) Isolated alkadiene: In these, the double bonds are separated by more than one single bond

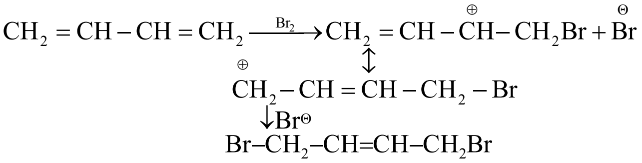
e.g. $\underset{\text{1,4-Butadiene}}{CH_2=CH-CH_2-CH=CH_2}$

(c) Cumulated alkadiene: In these, the double bonds share a carbon atom, *e.g.* $\underset{\text{Propadiene}}{H_2C=C=CH_2}$

When one equivalent of Br_2 is added to alkdaiene like 1,3-Butadiene, there is 1, 4 addition, *e.g.*

$$CH_2=CH-CH=CH_2+Br_2\longrightarrow \underset{\text{Major product}}{BrCH_2-CH=CH-CH_2Br}$$

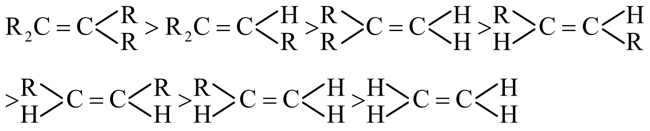
The mechanism is as following:



$$CH_2=CH-CH=CH_2\xrightarrow{Br_2}CH_2=CH-\overset{\oplus}{C}H-CH_2Br+\overset{\ominus}{Br}$$
$$\updownarrow$$
$$\overset{\oplus}{C}H_2-CH=CH-CH_2-Br$$
$$\downarrow Br^{\ominus}$$
$$Br-CH_2-CH=CH-CH_2Br$$

Stability of Alkadienes

It is based on hyperconjugation and the order is as follow:



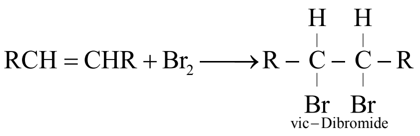
$$R_2C=C\langle^{R}_{R}>R_2C=C\langle^{H}_{R}>{}^{R}_{R}\rangle C=C\langle^{H}_{H}>{}^{R}_{H}\rangle C=C\langle^{H}_{R}$$
$$>{}^{R}_{H}\rangle C=C\langle^{R}_{H}>{}^{R}_{H}\rangle C=C\langle^{H}_{H}>{}^{H}_{H}\rangle C=C\langle^{H}_{H}$$

Alkynes

Alkynes are unsaturated hydrocarbons containing triple bond and have general formula C_nH_{2n-2}.

(1) Preparation: Alkynes can be prepared by following methods:

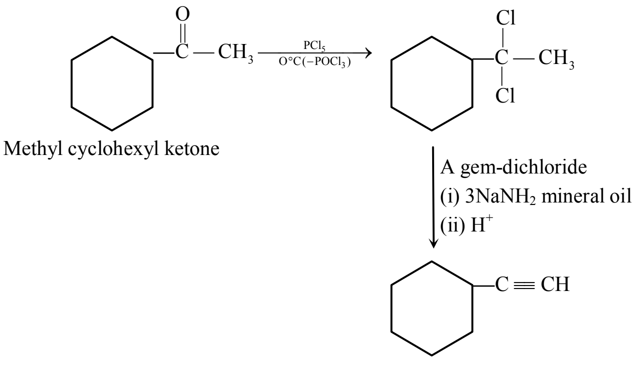
- Alkynes can be prepared from alkene by treating the latter with bromine to from a vic-dibromo compound.



$$RCH=CHR+Br_2\longrightarrow \underset{\text{vic-Dibromide}}{R-\overset{H}{\underset{Br}{C}}-\overset{H}{\underset{Br}{C}}-R}$$

  The vic-dibromide is subjected to dehydrohalogenation through it's reaction with a strong base. The dehydro-halogenation occurs is two steps.

- Ketones also yield alkyne via formation of gem-dichlorides.



Cyclohexyl acetylene

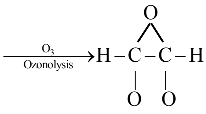
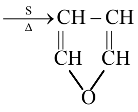
- Acetylene is synthesized industrially:

$$CaC_2+2H_2O\longrightarrow Ca(OH)_2+C_2H_2\,;$$
$$2CH_4\xrightarrow{1500°C}C_2H_2+3H_2$$

Properties

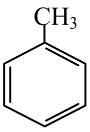
(2) Physical Properties: Alkynes have physical properties similar to those of corresponding alkanes. The lower molecular weight alkynes are gases at room temperature. Being relatively non-polar, alkynes dissolve in non-polar solvents or in solvents of low polarity. The densities of alkynes are less than that of water and are slightly or in solvents of low polarity. The densities of alkynes are less than that of water and slightly soluble in water.

(3) Chemical Properties: C_2H_2

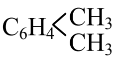
$\xrightarrow[Ni]{H_2}C_2H_4,C_2H_6$	$\xrightarrow{X_2}C_2H_2X_4$	$\xrightarrow[\text{Peroxide}]{HBr}CH_3BrCH_2Br$
$\xrightarrow[\text{No, Peroxide}]{HBr}$ CH_3CHBr	$\xrightarrow{HOCl}Cl_2CHCHO$	$\xrightarrow{HCN,Ba(CN)_2}$ $CH_2=CHCN$
$\xrightarrow{CH_3COOH,Hg^{+2}}$ $CH_3CH(OCOCH_3)_2$	$\xrightarrow[\text{(Kucherov's reaction)}]{Hg^{+2},80°C,dill.H_2SO_4}$ CH_3CHO	$\xrightarrow{Conc.H_2SO_4}$ $CH_3CH(HSO_4)_2$
$\xrightarrow[\text{Cadet \& Busen reaction}]{AsCl_3}$ $CHCl=CHAsCl_2$	$\xrightarrow[HgSO_4]{C_2H_5OH/H_2O}$ CH_3CHO	$\xrightarrow[NI(Co)_4]{CO+HOH}CH_2$ $=CH-COOH$
$\xrightarrow[NI,160°C]{CO+EtOH}$ $CH_2=CH-COOEt$	$\xrightarrow{NaNH_2}$ $Na-C\equiv C-Na$	$\xrightarrow[\text{(Toller's reagnent)}]{AgNO_3+NH_4OH}$ $Ag-C\equiv C-Ag$
$\xrightarrow{Cu_2Cl_2+NH_4O}$ $Cu-C\equiv C-Cu$	$\xrightarrow{\text{Combustion }O_2}$ CO_2+H_2O	$\xrightarrow[\text{(Red hot iron tube)}]{\text{Trimeri sation}}$ Benzene
$\xrightarrow{\text{Bayer Reagent}}\begin{matrix}CHO\\ \vert\\ CHO\end{matrix}\rightarrow HCOOH$	 $\xrightarrow[\text{Ozonolysis}]{O_3}$ $\xrightarrow{+H_2O}HCOOH$	 $\xrightarrow[\Delta]{S}$

Aromatic Hydrocarbons

Some example of aromatic hydrocarbons are follows:

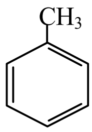


Toluene

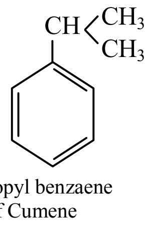


$$C_6H_4\langle^{CH_3}_{CH_3}$$

Xylene (o,m, p,)



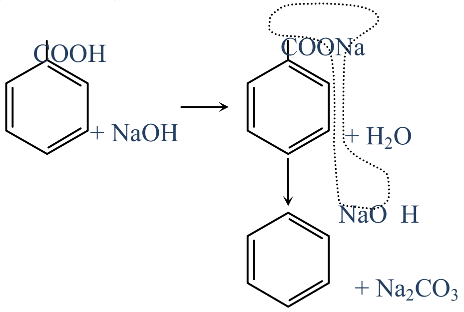
Styrene



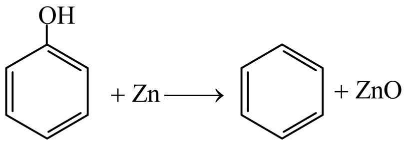
Isopropyl benzaene of Cumene

(1) Preparation

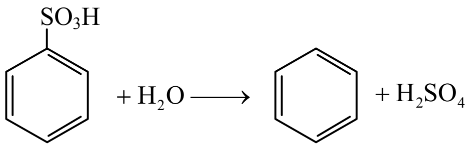
(i) By decarboxylation reaction, *eg*



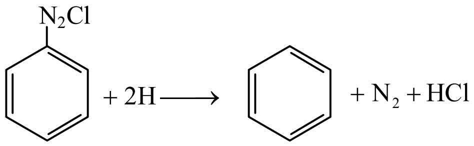
(ii) By passing vapours of phenols over heated zinc dust:



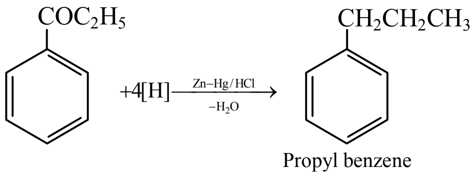
(iii) By boiling Sulphonic acids with dil. HCl under pressure and 150-200°C temperature.



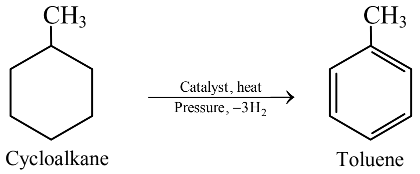
(iv) By reducing diazonium salt with alcohol or alkaline sodium stannite.

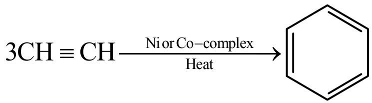


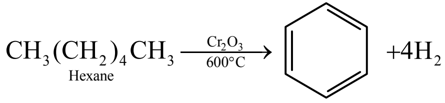
(v) By Clemmensen reduction of ketones



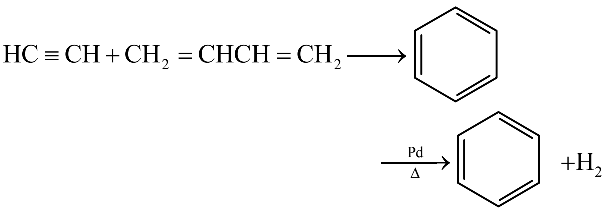
(vi) Commercially, benzene and other alkylated benzene are obtained by fractional distillation of petroleum. The catalytic dehydrogenation of cycloalkanes, a source from petroleum, also yields aromatic hydrocarbons.



- 

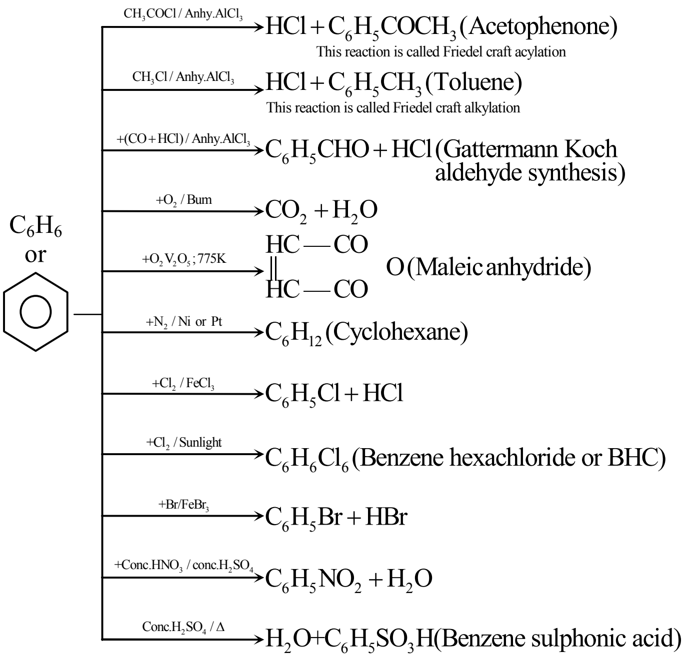
- 

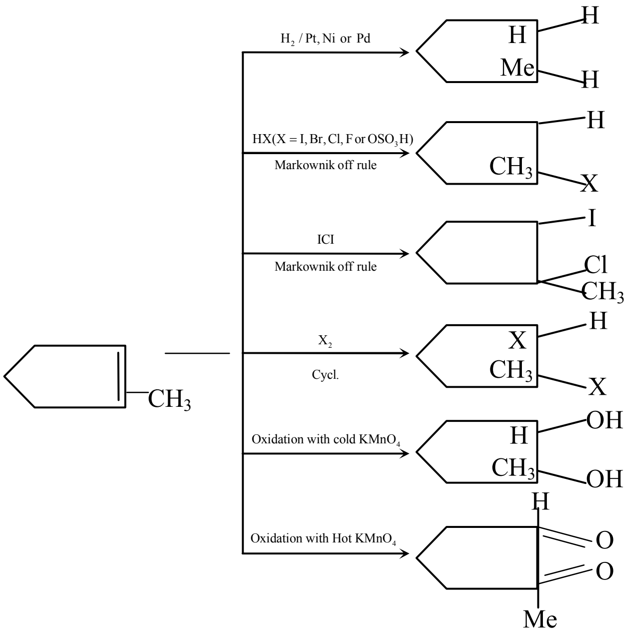
(vii) By Diel's – Alder reaction:



(2) Physical Properties: Benzene and it's homologous are colourless liquids with characteristic odour. They are miscible with organic solvent. Boiling point α Molecular weight

(3) Chemical Properties





MULTIPLE CHOICE QUESTIONS

Cyclo Alkanes

1. Methane and ethane both can be obtained in single step from:

a. CH_3I **b.** C_2H_5I

c. CH_3OH **d.** C_2H_5OH

2. The preparation of ethane by electrolysis of aqueous solution of potassium acetate is called as:

a. Wurtz reaction

b. Sabatier-Senderen's reaction

c. Kolbe's synthesis

d. Grignard reaction

3. As the number of carbon atoms in a chain increases the boiling point of alkanes:

a. Increases **b.** Decreases

c. Remains same **d.** May increase or decrease

4. The final product of complete oxidation of hydrocarbons is:

a. Acid **b.** Aldehyde

c. $H_2O + CO_2$ **d.** Dihydric alcohol

5. Which of the following represents the most oxidized form of hydrocarbon?

a. CO_2 **b.** $RCHO$

c. $RCOOH$ **d.** RCOOOH

Alkenes or Olefins

6. Which of the following hydrocarbons cannot be obtained by Sabatier and Senderen's reaction?

a. CH_4 **b.** C_2H_6 **c.** C_3H_8 **d.** All

7. In which of the following, addition of HBr does not take place against Markownikoff's rule or Anti-Markownikoff addition of HBr is not observed for?

a. Propene **b.** But-1-ene

c. But-2-ene **d.** Pent-2-ene

8. Which of the following is the most stable alkene?

a. $R_2C=CR_2$ **b.** $RCH=CHR$

c. $RCH_2=CH_2R$ **d.** $CH_2=CH_2$

9. Ethene gives with acidic $KMnO_4$ solution:

a. Ethylene glycol **b.** Ethylene oxide

c. Formaldehyde **d.** Acetaldehyde

10. When alcoholic solution of ethylene dibromide is heated with granulated zinc, the compound formed is?

a. Ethylene **b.** Ethyne

c. Cyclobutane **d.** Butane

11. Markownikoff's rule provides guidance of addition of HBr on:

a. $CH_2=CH_2$ **b.** $CH_3-CH_2-CH_3$

c. $CH_3CH=CHCH_3$ **d.** $CH_2=CHBr$

12. $CH_3CH=CHCHO$ is oxidized to $CH_3CH=CHCOOH$ using:

a. Alkaline potassium permanganate

b. Acidified potassium permanganate

c. Selenium dioxide

d. Osmium tetroxide

Aromatic Hydrocarbons

13. Poisonous gas 'Lewissite' is obtained by the reaction of:

a. $CH\equiv CH$ and $AsCl_3$ **b.** $CH_2=CH_2$ and $AsCl_3$

c. $CH\equiv CH$ and S_2Cl_2 **d.** $CH_2=CH_2$ and $NOCl$

14. $CH\equiv CH\xrightarrow[H_2SO_4]{H_2O/Hg^{2+}}X\xrightarrow{LiAlH_4}Y\xrightarrow{P_4/Br_2}Z$ Here Z is:

a. Ethylene bromide **b.** Ethanol

c. Ethyl bromide **d.** Ethylidene bromide

15. $CH\equiv CH\xrightarrow[\text{Pressure}]{Ni(CN)_2}X$. Here X in the reaction:

a. Benzene **b.** Ethane

c. Cycloctatetraene **d.** Cyclohexane

16. The ratio of σ and π bonds in benzene is

a. 2 **b.** 4 **c.** 6 **d.** 8

17. Which of the following is a hydrocarbon?

a. Urea **b.** Benzene

c. Ammonium cyanate **d.** Phenol

18. In chlorination of benzene, the reactive species is:

a. Cl^+ **b.** Cl^- **c.** Cl_2 **d.** Cl_2^-

19. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly:

a. Benzoyl chloride **b.** *m*-chlorotoluene

c. Benzyl chloride **d.** *o*- and *p*-chlorotoluenes

20. Attacking or reactive or electrophilic species in nitration of benzene is or In the nitration of benzene with concentrated HNO_3 and H_2SO_4 the attack on ring is made by:

a. NO_2^- **b.** NO_2^+ **c.** NO_3^- **d.** NO_2

21. Coaltar is main source of:

a. Aromatic compounds **b.** Aliphatic compounds

c. Cycloalkanes **d.** Heterocyclic compounds

22. Which of the following is not used in Friedel-crafts reaction?

a. Phenyl acetanilide **b.** Bromobenzene

c. Benzene **d.** Chlorobenzene

23. Pyridine is less basic than triethylamine because:
a. Pyridine has aromatic character
b. Nitrogen in pyridine is sp^2 hybridized
c. Pyridine is a cyclic system
d. In pyridine, lone pair of nitrogen is delocalized

24. Which of the following oil is obtained from benzene after fractional distillation of coal tar?
a. Light oil **b.** Heavy oil
c. Middle oil **d.** Anthracene oil

25. Order of reactivity of C_2H_6, C_2H_4 and C_2H_2 is
a. $C_2H_6 > C_2H_4 > C_2H_2$ **b.** $C_2H_2 > C_2H_6 > C_2H_4$
c. $C_2H_2 > C_2H_4 > C_2H_6$ **d.** All are equally reactive

Alkane

26. To prepare a pure sample of n-hexane using sodium metal as one reactant, the other reactant will be:
a. *n*-propyl bromide
b. Ethyl bromide and *n*-butyl bromide
c. Ethyl chloride and *n*-butyl chloride
d. Methyl bromide and *n* -pentyl chloride

27. Which of the following is oxidised by $KMnO_4$?
a. Methane **b.** Pentane
c. Isobutane **d.** Neopentane

28. In Wurtz reaction, the reagent used is:
a. Na **b.** Na/liquid NH_3
c. Na/dry ether **d.** Na/dry alcohol

29. Which of the following has highest octane number?
a. *n*-hexane **b.** *n*-heptane
c. *n*-pentane **d.** 2, 2, 4-trimethyl pentane

30. Which of the following statements is not true for ethane?
a. It can be chlorinated with chlorine
b. It can be catalytically hydrogenated
c. When oxidised produces CO_2 and H_2O
d. It is a homologue of iso-butane

31. In the commercial gasolines, the type of hydrocarbons which are more desirable is?
a. Branched hydrocarbon
b. Straight-chain hydrocarbon
c. Linear unsaturated hydrocarbon
d. Toluene

32. Petroleum ether can be used as:
a. Solvent for fat, oil, varnish and rubber
b. As a fuel
c. Both a. and b.
d. None of these

33. Which of the following are produced from coaltar?
a. Synthetic dyes **b.** Drugs
c. Perfumes **d.** All the three

34. In alkanes, the bond angle is:
a. 109.5° **b.** 109° **c.** 120° **d.** 180°

35. Cyclohexane, a hydrocarbon floats on water because:
a. It is immiscible with water
b. Its density is low as compared to water
c. It is non-polar substance
d. It is immiscible and lighter than water

36. Natural gas contains mainly:
a. Methane **b.** *n*-butane
c. *n*-octane **d.** Mixture of octane

37. Gasoline is obtained from crude petroleum oil by its:
a. Fractional distillation **b.** Vacuum distillation
c. Steam distillation **d.** Pyrolysis

38. Carbon black, which is used in making printer's ink, is obtained by decomposition of?
a. Acetylene **b.** Benzene
c. Carbon tetrachloride **d.** Methane

39. Most of the hydrocarbons from petroleum are obtained by:
a. Fractional distillation **b.** Fractional crystallization
c. Vaporization **d.** Polymerization

40. As the number of carbon atoms in a chain increases the boiling point of alkanes:
a. Increases **b.** Decreases
c. Remains same **d.** May increase or decrease

41. Which of the following will have least hindered rotation about carbon-carbon bond?
a. Ethane **b.** Ethylene
c. Acetylene **d.** Hexachloroethane

42. Which is the best antiknock compound or Which one of the following substances is used as an antiknock compound?
a. Lead tetrachloride **b.** Lead acetate
c. Zinc ethyl **d.** Tetraethyl lead (TEL)

43. B.P. of branched chain alkanes as compared to straight chain alkanes are:
a. Lower **b.** Equal
c. Higher **d.** Independent of the chain

44. In catalytic reduction of hydrocarbons which catalyst is mostly used?
a. *Pt /Ni* **b.** Pd
c. SiO_2 **d.** Misch Metal

45. Which one of the following has the minimum boiling point?
a. 1-Butene **b.** 1-Butyne **c.** n-Butane **d.** Isobutane

Alkene

46. In paraffins, with the increasing molecular weight, it is found that?

a. Freezing point decreases

b. Boiling point decreases

c. Boiling point increases

d. Vapour pressure decreases

47. A gas decolourised $KMnO_4$ solution but gives no precipitate with ammoniacal cuprous chloride is or Which of the following gases does not give a precipitate with ammoniacal solution of silver nitrate but decolourizes $KMnO_4$ (neutral or slightly alkaline)

a. Ethane **b.** Methane

c. Ethene **d.** Acetylene

48. Which of the following occurs easily in ethylene?

a. Addition **b.** Substitution

c. Elimination **d.** Rearrangement

49. Conjugate double bond is present in

a. Propylene **b.** Butadiene

c. Isobutylene **d.** Butylene

50. Which of the following is the most stable?

a. 1-butene **b.** 2-butene

c. 1-pentene **d.** 2-pentene

51. A reagent used to test for unsaturation of allkene is:

a. conc. H_2SO_4 **b.** Ammonical Cu_2Cl_2

c. Ammonical $AgNO_3$ **d.** Solution of Br_2 in CCl_4

52. Which of these does not follow Anti-Markownikoff's rule?

a. 2-butene **b.** 1-butene

c. 2-pentene **d.** 2-hexene

Alkyne

53. The homologue of ethyne is:

a. C_2H_4 **b.** C_2H_6

c. C_3H_8 **d.** C_3H_4

54. The distinguishing test for triple bond containing acidic hydrogen is:

a. $Ag(NH_3)_2^+$ **b.** Br_2 in CCl_4

c. Alkaline $KMnO_4$ **d.** $AlCl_3$

55. A mixture of ethane, ethene and ethyne is passed through ammoniacal $AgNO_3$ solution. The gases which remain unreacted are:

a. Ethane and ethene **b.** Ethane and ethyne

c. Ethene and ethyne **d.** Ethane only

56. Shortest C–C bond length is present in

a. $CH_3-CH_2-CH_3$ **b.** $CH_3CH_2CH_2CH_3$

c. $CH_2=CH-CH=CH_2$ **d.** $CH\equiv C-C\equiv CH$

57. What happens when a mixture of acetylene an hydrogen is passed over heated Lindlar's catalyst?

a. Ethane and water are formed

b. Ethylene is formed

c. Acetylene and ethane are formed

d. None of these

58. What is the product when 2-butyne is treated with liquid NH_3 in presence of lithium?

a. *n*-butane **b.** *cis*-2-butene

c. *trans*-2-butene **d.** 1-butene

59. Which of the following shows linear structure?

a. Ethane **b.** Ethene **c.** Acetylene **d.** CCl_4

60. Which of the following used for the conversion of 2-hexyne into trans-2-hexane?

a. $H_2/Pd/BaSO_4$ **b.** H_2, PtO_2

c. $NaBH_4$ **d.** $Li-NH_3/C_2H_5OH$

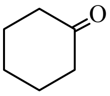
NCERT EXEMPLAR PROBLEMS

More than One Answer

61. Which of the following compounds exhibit geometrical isomerism?

a. $CH_3=CH=CH-COOH$ **b.** $Br-CH=CH-Br$

c. $C_6H_5CH=NOH$ **d.**



62. Which of the following has dipole moment?

a. cis-2-butene **b.** trans-2-butene

c. cis-1,2-dibromoethene **d.** trans-1,2-dibromoethene

63. Amongst the following the most basic compound is:

a. Benzylamine **b.** Aniline

c. Acetanilide **d.** *p*-nitroaniline

64. Among the following compound which one is planar in shape?

a. Methane **b.** Acetylene

c. Benzene **d.** Isobutane

65. The cis hydroxylation of alkenes can be effected by:

a. the addition of a 1% $KMnO_4$ solution

b. reaction with osmium tetraoxide followed by treatment with water

c. the addition of ozone to the alkene, followed by treatment of the ozonide with H_2O_2

d. none of these

66. Which of the following reactions can be used to prepare methane?
a. Clemmensen reduction
b. Wurtz reaction
c. Catalytic hydrogenation of methyl iodide
d. Reduction of methyl iodide by using a zinc-copper couple

67. A mixture of ethyl iodide and methyl iodide is subjected to the Wurtz reaction. The products formed are:
a. ethane **b.** butane
c. propane **d.**2-methylpropane

68. Which represents an alkane**?**
a. C_5H_8 **b.** C_8H_6
c. C_9H_{10} **d.** C_7H_{16}

69. Sodium acetate can be converted to ethane by**:**
a. Heating with $LiAlH_4$
b. Electrolysing its aqueous solution
c. Heating with sodalime
d. Heating with calcium acetate

70. Alkenes usually show which type of reaction?
a. Addition **b.** Substitution
c. Elimination **d.** Superposition

71. Which of the following has highest knocking property?
a. Aromatic hydrocarbons
b. Olefins
c. Branched chain paraffins
d. Straight chain paraffins

72. Oils are converted into fats by:
a. Hydration
b. Decarboxylation
c. Hydrogentation
d. Dehydrogenation

73. Cyclic hydrocarbon molecule A has all the carbon and hydrogens in a single plane. All the carbon-carbon bonds are of same length and less that 1.54 Å but more than 1.34 Å. $C-C-C$ bond angles will be:
a. 120° **b.** 180°
c. 100° **d.** $109^{\circ}\ 28'$

74. Which of the following gases is used for welding?
a. Methane **b.** Ethane
c. Acetylene **d.** Ethene

75. Which of the *C–C* bond is strongest?
a. Formed by sp^3–sp^3 hybridised carbon atoms (as in alkanes)
b. Formed by sp^2–sp^2 hybridised carbon atoms (as in alkenes)
c. Formed by sp–sp hybridised carbon atoms (as in alkynes)
d. All are equal

76. Benzene molecule is:
a. Tetrahedral **b.** Planar
c. Pyramidal **d.** Trigonal

77. Hydrocarbon C_6H_6 decolourise Br_2 water and gives ppt. with ammonical $AgNO_3$ Hydrocarbon can be
a. 1, 3, 5 Cyclohexatriene
b. 1, 5 Hexadiyne
c. 2, 4 Hexadiyne
d. None

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

a. If both assertion and reason are true and the reason is the correct explanation of the assertion.
b. If both assertion and reason are true but reason is not the correct explanation of the assertion.
c. If assertion is true but reason is false.
d. If the assertion and reason both are false.
e. If assertion is false but reason is true.

78. **Assertion:** 1-Butene on reaction with HBr in the presence of peroxide produces 1-bromo-butane.
Reason: It involves the free radical mechanism.

79. **Assertion:** Addition of Br_2 to 1-butene gives two optical isomers.
Reason: The product contains one asymmetric carbon.

80. **Assertion:** Pyrrole is an aromatic heterocyclic compound.
Reason: It has a cyclic, delocalised 6π electrons.

81. **Assertion:** CH_4 does not react with Cl_2 in dark.
Reason: Chlorination of CH_4 takes place in sunlight.

82. **Assertion:** Alkyl benzene is not prepared by Friedel-Crafts alkylation of benzene.
Reason: Alkyl halides are less reactive than acyl halides.

83. **Assertion:** Styrene on reaction with HBr gives 2-bromo-2-phenyl-ethane.
Reason: Benzyl radical is more stable than alkyl radical.

84. **Assertion:** Iodination of alkanes is reversible.
Reason: Iodination is carried out in presence of iodic acid.

85. **Assertion:** Isobutane on oxidation with $KMnO_4$ gives tert-butyl alcohol.
Reason: Oxidising agents have no effect on alkanes.

86. **Assertion:** Neopentane forms only one monosubstituted compound.
Reason: Neopentane has high bond energy.

87. **Assertion:** 2-Butanol on heating with H_2SO_4 gives 1-butene and 2-butene.
Reason: Dehydration of 2-butanol follows saytzeff rule.

88. **Assertion:** All the hydrogen atoms in $CH_2 = C = CH_2$ lie in one plane.
Reason: All the carbon atoms in it are sp^2 hybridized.

89. **Assertion:** Nitration of toluene is easier than benzene.
Reason: The methyl group in toluene is electron-releasing.

Comprehension Based

Paragraph –I

The term arene is used to benzene and its homologues. The term aromatic refers for the organic compounds which obey Huckel rule, *i.e.,* all aromatic compounds must possess π electrons equal to (4n+2) where n is any positive integer. Due to aromatic nature benzene and it homologues show electrophilic substitution reactions producing o-and p-substituted derivatives or m-substituted derivatives. The orientation (new incoming group's substitution) in benzene nucleus is explained in terms of directive influence of the groups.

90. Side chain of a nucleus can be oxidized to —COOH group only when it has atleast one:

a. vinylic H
b. benzylic H
c. allylic H
d. olefinic H

91. The general formula for arenes having monocylic nature where y represents number of 6-membered rings is?

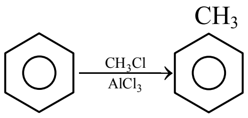
a. C_nH_{2n-6y}
b. C_nH_{2n-8y}
c. C_nH_{2n-4y}
d. C_nH_{2n-5y}

92. Which of the following are m-directing groups?

(I) $—NH_3^+$
(II) $—NH_2$in acid
(III)$—CCl_3$
(IV) $—COO^-$
(V) —NC
(VI) —CN

a. I, II, III, VI
b. IV, V, VI
c. III, IV, V
d. III, IV, VI

93. Which of the following statements regarding Sg reaction in C_5H_5 is wrong?



a. $AlCl_3$acts as Lewis acid
b. $AlCl_3$acts to produce free radical
c. $AlCl_3$acts to produce electrophile
d. $AlCl_3$acts as halogen carrier

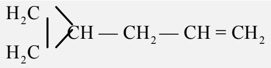
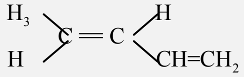
Match the Column

94. Match the statement of Column I with those in Column II:

Column I	Column II
(A) Chiral	**1.** Polynuclear hydrocarbons
(B) Asymmetric synthesis	**2.** Dissymmetirc
(C) Napthalene	**3.** Preferential formation of one enantiomer
(D) Cyclic con-jugated polyenes with (4n+2) πelectrons	**4.** Aromatic compounds
(E) o-dichloro benzene does not exist as two isomers	**5.** delocalization of π-electrons

a.A→1; B→2; C→3; D→4; E→5
b. A→2, B→3, C→1, D→5; E→4
c. A→3, B→2, C→1, D→4; E→5
d. A→2, B→1, C→4, D→3; E→5

95. Match the statement of Column I with those in Column II:

Column I	Column II
(A) $CH_3CH(CH_3)CH_2CH(CH_3)_2$	**1.** 2,4-Dimethyl pentane,
(B) $(CH_3)_3C—(CH_2)_5—C(CH_3)_3$	**2.** 2,2,8,8, - Tetra-methylnonane
(C) 	**3.** 3-Cyclopropyl-1-propene
(D) 	**4.** 1,3-Pentadiene (trans)

a.A→4; B→3; C→2; D→1
b. A→1; B→2; C→3; D→4
c. A→3; B→2; C→1; D→4
d. A→2; B→1; C→4; D→3

Integer

96. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_6H_4 is:

97. The maximum number of isomers (including stereoisomerism) that are possible on mono-chlorination of the following compound is $CH_3CH_2CH(CH_3)CH_2CH_2$.

98. Number of acidic hydrogen atoms in butyne-1 are:

99. The A sample of gasoline contains 81% *iso*-octane and 19% *n*-heptane. Its octane number will be:

100. A fuel contains 25 % *n*-heptane and 75 % iso-octane. Its octane number is:

ANSWER

1.	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**10.**
a	c	a	c	a	a	c	a	c	a
11.	**12.**	**13.**	**14.**	**15.**	**16.**	**17.**	**18.**	**19.**	**20.**
d	b	a	c	c	b	b	a	d	b
21.	**22.**	**23.**	**24.**	**25.**	**26.**	**27.**	**28.**	**29.**	**30.**
a	a	d	a	c	a	c	c	d	b
31.	**32.**	**33.**	**34.**	**35.**	**36.**	**37.**	**38.**	**39.**	**40.**
a	a	d	a	d	a	a	d	a	a
41.	**42.**	**43.**	**44.**	**45.**	**46.**	**47.**	**48.**	**49.**	**50.**
a	d	a	a	d	c	c	a	b	d
51.	**52.**	**53.**	**54.**	**55.**	**56.**	**57.**	**58.**	**59.**	**60.**
d	a	d	a	a	d	b	c	c	d
61.	**62.**	**63.**	**64.**	**65.**	**66.**	**67.**	**68.**	**69.**	**70.**
a,b,c	a,c	a	c	a,b	c,d	a,b,c	d	b	a
71.	**72.**	**73.**	**74.**	**75.**	**76.**	**77.**	**78.**	**79.**	**80.**
d	c	a	c	c	b	d	a	a	a
81.	**82.**	**83.**	**84.**	**85.**	**86.**	**87.**	**88.**	**89.**	**90.**
b	b	b	b	b	c	a	c	a	b
91.	**92.**	**93.**	**94.**	**95.**	**96.**	**97.**	**98.**	**99.**	**100.**
a	a	b	b	b	5	6	3	81	75

SOLUTION

Multiple Choice Questions

1. **(a)** $CH_3I + 2H \xrightarrow{Zn/HCl} CH_4 + HI$

   $CH_3I + 2Na + ICH_3 \xrightarrow[Ether]{Dry} CH_3 - CH_3 + 2NaI$

2. **(c)** $2CH_3COOK + 2H_2O \xrightarrow{Electrolysis}$

   $2CO_2 + \underbrace{CH_3 - CH_3 + 2KOH}_{Anode} + \underbrace{H_2}_{Cathode}$

3. **(a)** Boiling point of alkanes increases with the number of carbon atoms because surface area increases which increases the Vander Waal forces.

4. **(c)** $\underset{Methane}{CH_4} + 2O_2 \longrightarrow CO_2 + 2H_2O$

   $\underset{Ethene}{C_2H_4} + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

   All hydrocarbons saturated or unsaturated on complete combustion always produce CO_2 and H_2O.

5. **(a)** Hydrocarbons on complete oxidation produce CO_2 and water

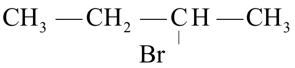
   $$CH_3 - CH_3 + 3\frac{1}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

6. **(a)** Methane cannot be obtained by Sabatier and Sendern's reaction because in this the product obtained contain minimum two carbon atoms.

   $CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$

   $CH \equiv CH + 2H_2 \xrightarrow{Ni} CH_3 - CH_3$

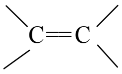
7. **(c)** $CH_3 - CH = CH - CH_3 + HBr \xrightarrow{Peroxide}$

   
   $CH_3 - CH_2 - \underset{\underset{Br}{|}}{C}H - CH_3$

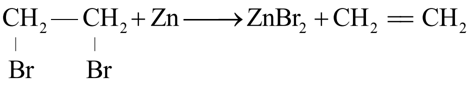
   2–Bromobutane

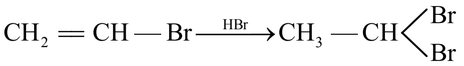
   Anti-markownikoff's rule is not applicable to symmetrical alkenes.

8. **(a)** We know that greater the number of alkyl groups attached to double bonded carbon atoms, more stable is the alkene. Therefore most stable is $R_2C = CR_2$

9. **(c)** $CH_2 = CH_2 + 2[O] \xrightarrow{KMnO_4} HCHO + \underset{Formaldehyde}{HCHO}$

10. **(a)** 
    $\underset{\underset{Br}{|}}{CH_2} - \underset{\underset{Br}{|}}{CH_2} + Zn \longrightarrow ZnBr_2 + CH_2 = CH_2$

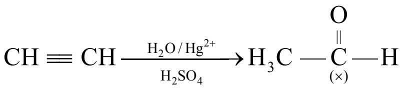
11. **(d)** 
    $CH_2 = CH - Br \xrightarrow{HBr} CH_3 - CH \begin{smallmatrix} \diagup Br \\ \diagdown Br \end{smallmatrix}$

    According to Markownikoff's rule *H* atom or positive part goes to that carbon atom which is more hydrogenated.

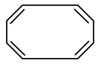
12. **(b)** $CH_3 - CH = CH - CHO \xrightarrow[KMnO_4]{Acidic}$

    $CH_3 - CH = CH - COOH$

13. **(a)** $HC \equiv CH + AsCl_3 \longrightarrow \underset{\text{2-chlorovinyl dichloroarsine (Lewsite)}}{ClHC = CHAsCl_2}$

14. **(c)** 
    $CH \equiv CH \xrightarrow[H_2SO_4]{H_2O/Hg^{2+}} H_3C - \underset{(x)}{\overset{\overset{O}{\|}}{C}} - H$

    $\underset{(y)}{CH_3 - CH_2 - OH} \xrightarrow{P_4/Br_2} \underset{(z)}{C_2H_5Br}$

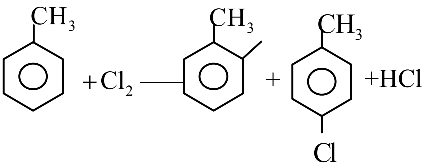
15. **(c)** $4CH \equiv CH \xrightarrow[Pressure]{Ni(CN)_2}$ 

    Cyclo octatatraene

16. **(b)** $\text{Ratio} = \frac{\sigma \text{ bonds}}{\pi \text{ bonds}} = \frac{12}{3} = 4$

17. **(b)** Benzene C_6H_6 is made up of hydrogen and carbon only.

18. **(a)** Halogenation is initiated by free redical.

19. **(d)** 

    o- and *p*-chlorotoluene

20. **(b)** $HO-NO_2 + H^+HSO_4^- \longrightarrow H_2O + \underset{\substack{\text{Nitronium ion}\\\text{(attacking species)}}}{NO_2^+} + HSO_4^-$

21. **(a)** Coal tar is a main source of aromatic hydrocarbons like benzene, naphthalene, anthracene, phenol etc

22. **(a)** Friedel-Craft's reaction involves the introduction of an alkyl or acyl group into benzene ring in the presence of a catalyst. The presence of an electron withdrawing group in the ring hinders the reaction. Therefore phenyl acetanilide is not used.

23. **(d)** Basicity of amines is due to availability of an unshared pair (lone pair) of electrons on nitrogen. This lone pair of electrons is available for the formation of a new bond with a proton or Lewis acid.
Pyridine is less basic than triethylamine because lone pair of nitrogen in pyridine is delocalised.

24. **(a)** Benzene on fractional distillation gives light oil [It is lighter than water and hence called as light oil]

25. **(c)** Unsaturated hydrocarbons are more reactive than saturated hydrocarbons. Among ethyne (C_2H_2) and ethene (C_2H_4) the later is more reactive as $C\equiv C$ triple bond is quite strong bond and therefore ethyne generally require catalysts (like Hg^{2+} etc.) in its reactions.

26. **(a)** According to wurtz reaction.

$$2CH_3CH_2CH_2Br + 2Na \xrightarrow{\text{ether}} CH_3(CH_2)_4CH_3 + 2NaBr$$

27. **(c)** $(CH_3)_3CH \xrightarrow{KMnO_4} \underset{\text{tertiary butyl alcohol}}{(CH_3)_3C-OH}$

28. **(c)** $RCl + 2Na + RCl \xrightarrow[\text{Ether}]{\text{Dry}} 2NaCl + \underset{\text{Alkane}}{R-R}$

29. **(d)** *iso*-octane *i.e.* 2,2,4-trimethyl pentane has highest octane number.

30. **(b)** Ethane is a saturated compound it cannot be catalytically hydrogenated.

31. **(a)** Branched hydrocarbons are more desirable because they are more volatile.

32. **(a)** Solvent for fat, oil, varnish and rubber

33. **(d)** Synthetic dyes, drugs, perfumes all are made from coal tar.

34. **(a)** In alkanes, hybridization is sp^3. Hence bond angle is $109^o.5'$.

35. **(d)** Cyclohexane, is immiscible and lighter than water. Hence, floats on the surface of water.

36. **(a)** Methane is the main component of natural gas.

37. **(a)** Fractional distillation is used because the difference between the boiling point of different component is less.

38. **(d)** $CH_4 + O_2 \xrightarrow[\substack{\text{Limited}\\\text{supply}\\\text{of air}}]{\Delta} C + 2H_2O$

It contains 98-99% carbon. It is used in making black ink, paints and shoe polishes.

39. **(a)** Fractional distillation is based on the difference in the boiling point of different components.

40. **(a)** Boiling point of alkanes increases with the number of carbon atoms because surface area increases which increases the Vander Waal forces.

41. **(a)** Free rotation around carbon–carbon bond takes place easily in alkanes. Now ethane and hexachloroethane both are alkanes. But in hexachloroethane bulky chlorine atom hinders the rotation. Therefore least hindered rotation takes place in ethane.

42. **(d)** Tetraethyl lead (TEL) is an anti-knocking compounds when mixed with petrol tend to improve the octane no. and therefore, decreases the knocking in the cylinder of the combustion engine.

43. **(a)** As the number of branches increases, surface area decreases, due to which Vander Waal forces of attraction decreases. Hence, boiling point also decreases.

44. **(a)** *Pt./Ni* is used in catalytic reduction of hydrocarbon.

45. **(d)** Among the isomeric alkanes, the normal isomer has a higher boiling point than the branched chain isomer. The greater the branching of the chain, the lower is the boiling point. The *n*-alkane have larger surface area in comparison to branched chain isomer (as the shape approaches that of a sphere in the branched chain isomers). Thus, intermolecular forces are weaker in branched chain isomers; therefore they have lower point in comparision to straight chain isomers.

46. **(c)** Paraffins are non-polar compounds. The intermolecular forces are weak Vander Waal's forces. As the molecular mass increases Vander Waal's forces increases. Hence boiling point increases.

47. **(c)** Ethane and Methane does not decolourise $KMnO_4$ and does not react with ammonical cuprous chloride. Acetylene decolourise $KMnO_4$ solution and also gives red ppt. with ammonical cuprous chloride. On the other hand ethene decolourize $KMnO_4$ solution but does not react with ammonical cuprous chloride.

48. **(a)** In case of ethene double bond is present. Hence, addition reactions occur easily.

49. **(b)** Butadiene $CH_2 = CH - CH = CH_2$
A single bond separated by two double bonds is known as conjugated double bond.

50. **(d)** $CH_3 - CH = CH - CH_2 - CH_3$ will be the most stable because greater the number of alkyl groups attached to double bonded carbon atoms, more stable is the alkene.

51. **(d)** Solution of bromine in carbon tetrachloride is used to test for unsaturation of alkene. Red colour of bromine disappears due to the formation of colourless dibromo ethane $(C_2H_4Br_2)$.

52. **(a)** Markownikoff as well as anti-Markownikoff's rule is valid only for unsymmetrical alkenes.

53. **(d)** C_2H_2 and C_3H_4 are homologue because they differ by $-CH_2$ group. Both have triple bond in their molecule.

54. **(a)** $Ag(NH_3)_2^+$ gives white *ppt* with terminal alkynes.

55. **(a)** Ethyne reacts with ammonical $AgNO_3$ to give white ppt of silver acetylide while ethane and ethene do not react because acidic hydrogen is absent.

56. **(d)** Bond length decrease with increase in Bond order. Hence triple bonded carbon has minimum bond length.
C – C bond length = 1.54 Å
C = C bond length = 1.33 Å
C ≡ C bond length = 1.22 Å

57. **(b)** $\underset{\text{Acetylene}}{CH \equiv CH} + H_2 \xrightarrow[\text{Catalyst pd. BaSO}_4]{\text{Lindlar}} \underset{\text{Ethylene}}{CH_2 = CH_2}$

58. **(c)** Reduction of alkynes with liquid NH_3 / Li gives trans alkenes.

59. **(c)** In acetylene both carbons are *sp*-hybridised so it has linear structure.

60. **(d)** The partial reduction of alkynes by active metal in liquid ammonia takes place through trans vinylic anion which ultimately produces trans alkene.

NCERT Exemplar Problems

More than One Answer

61. **(a,b,c)** Alkenes with the formula ba C = C ab or ba C = C ed exhibit geometrical isomerism. The oximes of aldehydes also exhibit geometrical isomerism because hindered rotation is possible with a carbon-nitrogen double bond.

62. **(a,c)** Trans isomers, in general have zero dipole moment.

63. **(a)** $-NH_3$ group is not linked with benzene ring.

64. **(c)** All 6 carbons of Benzene are sp^2-hybridised so it is planar.

65. **(a, b)** The addition of a 1% $KMnO_4$ solution and reaction with osmium tetraoxide followed by treatment with water.

66. **(c, d)** Catalytic hydrogenation of methyl iodide and Reduction of methyl iodide by using a zinc-copper couple

67. **(a, b,c)** ethane, butane and propane.

68. **(d)** C_7H_{16} (C_nH_{2n+2})

69. **(b)** $\underset{\text{Sodium acetate}}{2CH_3COONa} + 2H_2O \xrightarrow{\text{Electolysis}}$

$CH_3 - CH_3 + 2CO_2 + 2NaOH + H_2$

70. **(a)** Alkenes are unsaturated hydrocarbon having double bond so generally gives addition reaction.

71. **(d)** Octane number increases in the order
Straight chain alkanes < Branched chain alkanes < lefins < Cyclo alkanes < Aromatic compounds
Since, straight chain alkane has minimum octane number. Hence, it produces maximum knocking.

72. **(c)** Oil are unsaturated esters which are converted into fats by saturating it by catalytic hydrogenation.

73. **(a)** Cyclic hydrocarbon in which all the carbon atoms are present in the same plane is benzene. In this C–C bond length is 1.39Å which is more than 1.34A^o but less than 1.54Å. Hence bond angle is 120° with sp^2 hybridization.

74. **(c)** $2CH \equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O \quad \Delta H = -1300 \text{ KJ}$
The combustion of acetylene is highly exothermic and the heat produced during the combustion can be used for welding purposes in the form of oxy acetylene flame.

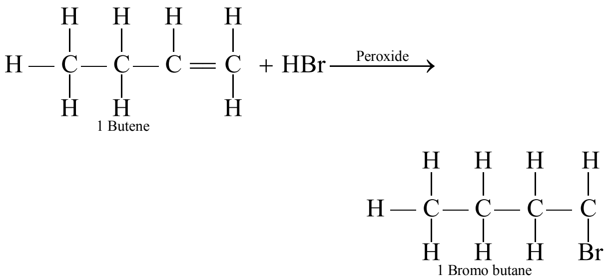
75. **(c)** $sp - sp > sp^2 - sp^2 > sp^3 - sp^3$
Order of bond strength

76. **(b)** In benzene all the six carbon atoms are present in the same plane. All the carbon atoms are sp^2 hybridized. Hence, it is a planar molecule.

77. **(d)** Because Ammonical $AgNO_3$ reduce $C \equiv CH$ bond of yne.

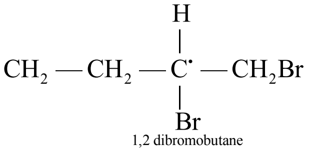
Assertion and Reason

78. **(a)** This reaction is followed by against of Markownikoff rule



In this reaction anti Markownikoff's addition is explained on the basis of the fact that in the presence of peroxide the addition takes place Via a free radical mechanism rather than the ionic mechanism.

79. **(a)** $\underset{\text{1 Butene}}{CH_3 — CH_2 — CH = CH_2} + Br_2 \longrightarrow$



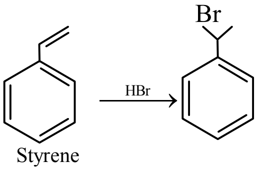
$$\underset{\text{1,2 dibromobutane}}{CH_2 — CH_2 — \overset{H}{\underset{Br}{C^{\bullet}}} — CH_2Br}$$

80. **(a)** Pyrrole is a heterocyclic compound having five membered ring. It has 6π electrons. As 4π electrons in the ring and 2π electrons donated by nitrogen atom present in the ring.

81. **(b)** The assertion that chlorination of CH_4 does not take place in dark is correct because it is a free radical reaction and free radicals are obtained in presence of sun light.

82. **(b)** The alkyl benzene is not prepared by Friedel Craft's alkylation of benzene because the monoalkyl product formed undergo alkylation to produce polyalkylated benzene. The reason that alkyl halides are less reactive than acyl halides is also correct but this is not the correct explanation of assertion.

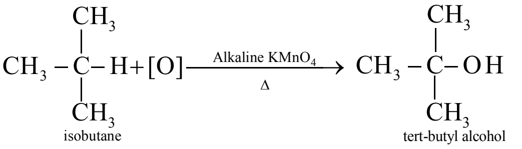
83. **(b)** HBr adds to the double bond of the styrene forming 1-bromo-1-phenylethane.



This is an example of elimination-addition reaction.
Note: Here given assertion is wrong.

84. **(b)** Iodination is reversible since formed HI is a strong reducing agent and reduces the alkyl iodide back to alkane. $CH_4 + I_2 \rightleftharpoons CH_3I + HI$

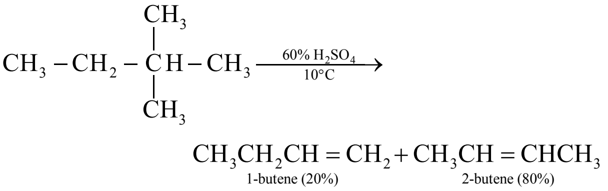
85. **(b)** Normally oxidising agents have no effect on alkanes. However, alkanes containing a tertiary hydrogen atom can be oxidised by oxidising agents such as $KMnO_4$ to the corresponding alcohols. For example,



$$\underset{\text{isobutane}}{CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - H} + [O] \xrightarrow[\Delta]{\text{Alkaline } KMnO_4} \underset{\text{tert-butyl alcohol}}{CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - OH}$$

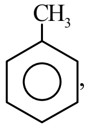
86. **(c)** Neopentane has four identical methyl groups attached on 4° carbon atom and thus only one product is possible during monosubstitution.

87. **(a)** In the dehydration of secondary and tertiary alcohols. When there is a possibility of formation of two isomers. The hydrogen atom is preferentially eliminated from the adjacent carbon atom with the fewer number of hydrogen atoms. This is Saytzeff's rule.



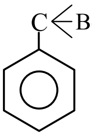
$$CH_3 - CH_2 - \overset{CH_3}{\underset{CH_3}{C}}H - CH_3 \xrightarrow[10°C]{60\%\ H_2SO_4} \underset{\text{1-butene (20\%)}}{CH_3CH_2CH = CH_2} + \underset{\text{2-butene (80\%)}}{CH_3CH = CHCH_3}$$

88. **(c)** The two hydrogen atoms on first carbon and the two H-atoms on the third carbon atom lie in perpendicular planes. The central carbon atom is sp-hybridized while terminal carbon atoms are sp^2-hybridized.

89. **(a)** In toluene , the $–CH_3$ group is electron Pushing.

It is an activating group. By its +I effect, $–CH_3$ group activates the benzene ring at ortho and para position relative to it. Due to increased activity towards electrophilitic substitution toluene can be more easily nitrated than benzene.

Comprehension Based

90. **(b)**  Benzylic carbon; H-atom attached on carbon joined directly to an aromatic ring

Side chain must have at least one H or C (benzylic carbon)

91. **(a)** y = 1 for monocyclic, thus C_nH_{2n-6}.

92. **(a)** A positive charge makes the last pg*m*-directing whereas a –ve charge makes a gp o-and p-directing. In CCl$_3$ follow HammickIlling worth rule.

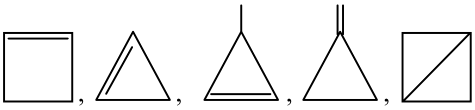
93. **(b)** $\underset{\text{Acid}}{AlCl_3} + CH_3Cl \longrightarrow [AlCl_4]^- + CH_3^+$

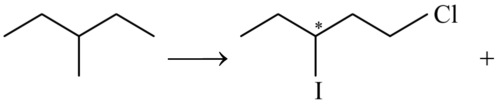
Match the Column

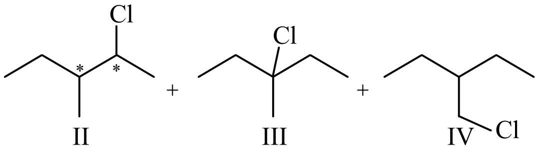
94. **(b)** A→2, B→3, C→1, D→5; E→4

95. **(b)** A→1; B→2; C→3; D→4

Integer

96. **(5)** 

97. **(6)** 



I has one chiral carbon = two isomers
II has two chiral carbons and no symmetry = four isomers,
III and IV have no chiral carbon, no stereoisomers.

98. **(3)** The hydrogen atom which is attached to triple bond is acidic.

99. **(81)** Octane number is related to the percentage of *iso*-octane since *iso*-octane is 81% hence octane number is 81%.

100. **(75)** Octane number is the percentage by volume of iso-octane in the mixture of iso-octane and *n*-heptane which has the same antiknocking properties as the fuel under examination.
Given fuel (25% *n*-heptane +75% iso-octane) Hence, octane number = 75 (because iso octane is 75%).

∗ ∗ ∗