24

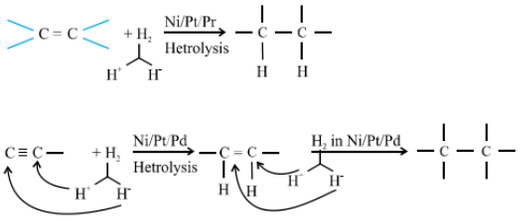
HYDROCARBONS

ALKANES (PARAFFINS)

- Alkanes are saturated hydrocarbons. They are very less reactive towards various reagents; hence, they are also referred to as paraffins (parum means little, affins means affinity).

Methods of Preparation

(1) From unsaturated hydrocarbons:



(2) Wurtz reaction:

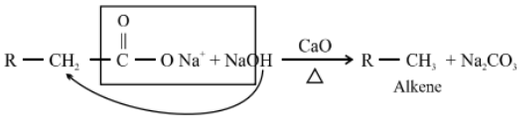
$$\text{Alkyl Halide} + \text{Na} \xrightarrow[\text{ether}]{\text{Dry}} \text{Higher alkane}$$

$$R\text{–}X + 2Na + X\text{–}R \xrightarrow{\text{Dry ether}} R\text{–}R + 2\,NaX$$

(3) Sodalime decarboxylation method:

[Sodium salt of carboxylic acid + NaOH + CaO → Alkane [n_c = 1 less]

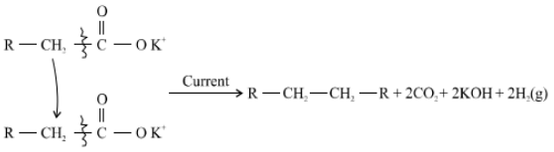
$$R\text{—}CH_2COONa^+ + NaOH \xrightarrow[\Delta]{CaO} ?$$



Koble's electrolytic method:

$$\text{Potassium salt of carboxylic acid (aq)} \xrightarrow{\text{Current}} \text{Higher alkane}$$

$$R\text{—}CH_2COO^-K^+\ (aq) \xrightarrow[\text{Electrolysis}]{} ?$$



Physical Properties of Alkanes

- Alkanes are colourless and odourless.
- They possess weak Van Der Waals forces of attraction.
- Alkanes having 1-4 carbon atoms are gases, then from 5-17 carbon atoms they are liquid and alkanes having 18 or more carbon atoms are solid at 298K.

Conformations of Ethane

- The conformational isomers can be represented in the following two ways: (i) Sawhorse representations (ii) Newman projections

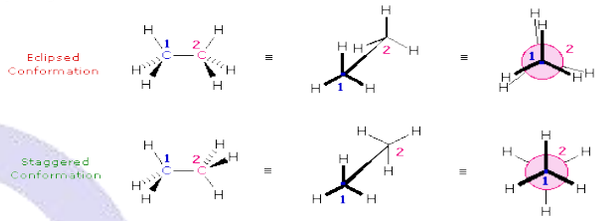


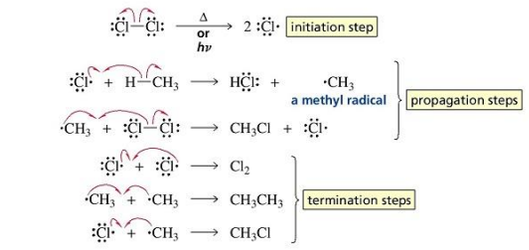
Fig: Sawhorse representations and Newman projections

Chemical Properties of Alkanes

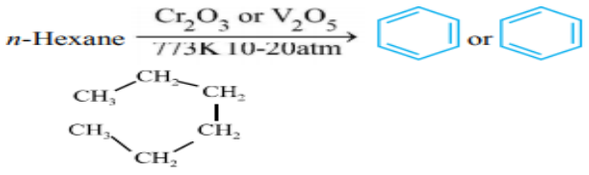
(1) Halogenation: One (H) atm is replaced by halogen at a time.

$$CH_4(g) + Cl_2(g) \xrightarrow{h\upsilon} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

mechanism for the monochlorination of methane



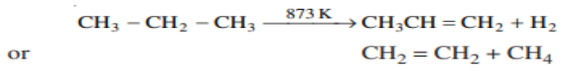
(2) Aromatisation:



(3) Oxidation: Alkanes undergo oxidation (combustion) in excess of oxygen and produce carbon dioxide and water.

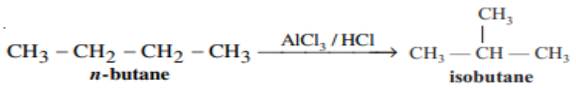
$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 890\ KJ\ mol^{-1}$$

(4) Cracking or Pyrolysis: At very high temperature and in the absence of air, the alkanes break apart into smaller fragments.



or

(5) Isomerisation: n-Alkanes, in the presence of aluminium halide and HCl, are converted to their branched isomers.



Uses of Alkanes

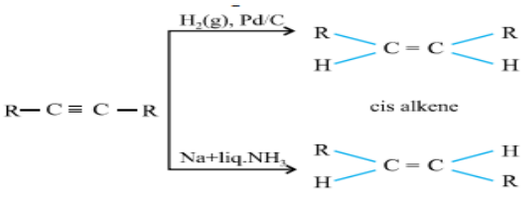
- Alkanes are important raw materials of the chemical industry and the principal constituent of gasoline and lubricating oils. Natural gas mainly contains methane and ethane and is used for heating and cooking purposes and for power utilities (gas turbines).

Alkenes

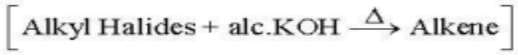
- These are unsaturated hydrocarbons containing at least one double bond between two carbon atoms. The hydrocarbons of this class are also called olefines (olefiant = oil forming)

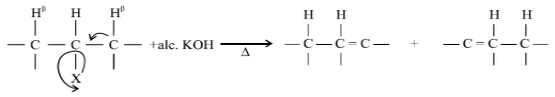
Methods of Preparation

(1) From alkynes [Alkyne + H_2O → Alkene]



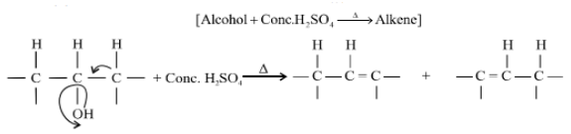
(2) From alkyl halide by (dehydrohalognation)





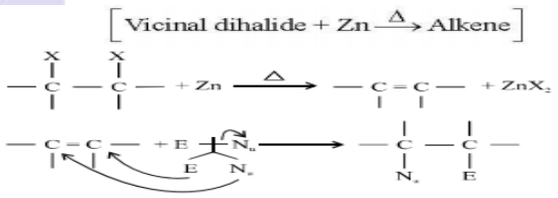
- Carbon attached with halogen is α -carbons
- Carbon attached with α -carbons is -carbonsβ
- Halogen is removed and 'H'-atom is removed from - β carbon to form (C = C) double bond.

(3) By Dehydration of alcohols (Ion of water molecule):



- Carbon attached to alcohoic group is α-carbon.
- Carbon attached to is α -carbon β- carbon

(4) From vicinal dihalides [Compounds in which halogen atom are attached with adjacent carbons]

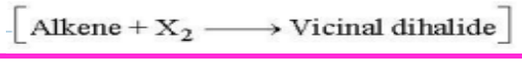


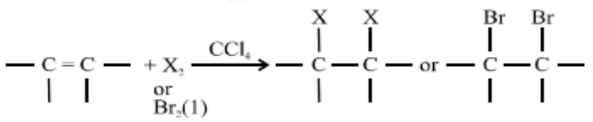
Physical Properties of Alkenes

- The boiling point of each alkene is very similar to that of the alkane with the same number of carbon atoms. Ethene, propene and the various butenes are gases at room temperature. All the rest that you are likely to come across are liquids. Boiling points of alkenes depends on more molecular mass (chain length).

Chemical Properties of Alkenes

(1) Addition of Halogens:

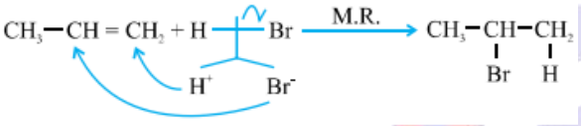




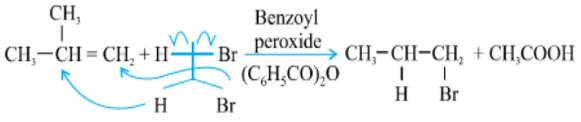
(2) Addition of H-X:

$$[\text{Alkene} + HX \longrightarrow \text{Alkyl halide}]$$

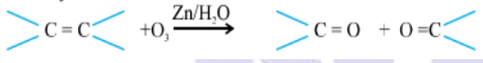
(A) Markownikoff's rule (M.R.): During electrophillic addition of hydrogen halide, the electron deficient electrophile (E^+) always attack on that doubly/triply bounded carbon atom. This already has greater number of hydrogen atoms.



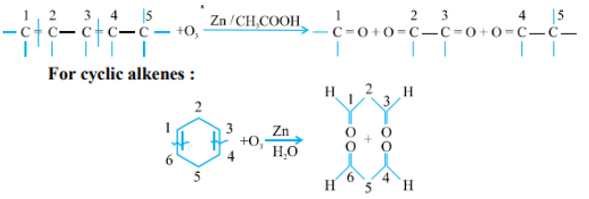
(B) Peroxide/Kharasch effect (Anti M. Rule): This effect takes place in presence of peroxides when the hydrogen free radical ($\dot{H}$) attacks on that doubly bonded carbon which has lesser number of hydrogen atoms.



(C) Ozonolysis

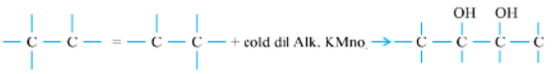


In this reaction all those carbons which form double bonds get finely converted into carbonyl carbons. If alkenes are symmetrical then both carbonyl compounds are same. If more than two double bonds are present then we get atleast one compound which has two carbonyl groups at the end. Such bifunctional compounds are formed from that part of alkene which is in between the double bonds.



For cyclic alkenes :

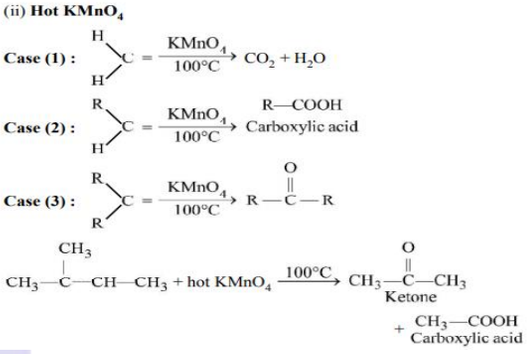
(D) With potassium paramagnate: (i) Cold dilutealkaline $KMnO_4$ = Baeyer's reagent.



$$[\text{Alkene} + \text{cold dil. } KMnO_4 \rightarrow \text{Diol}]$$

Baeyer's test for the presence of (C = C) bond
Compound + cold dil. alk. $KMnO_4$ ⟶ Purple colour decolourised
∴ Compound is alkene.

(ii) Hot $KMnO_4$



ALKYNES

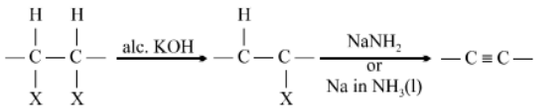
- These are also unsaturated hydrocarbons which contain atleast one triple bond between two carbon atoms. Some examples are as follows :

$$\underset{\text{Ethyne}}{CH \equiv CH}, \quad \underset{\text{Propyne}}{CH_3 - C \equiv CH}, \quad \underset{\text{But-2-yne}}{CH_3 - C \equiv C - CH_3}$$

Preparation of Ethyne (Acetylene)

(1) $CaC_2 + 2H_2O \longrightarrow \underset{\text{Calcium carbide}}{Ca(OH)_2} + \underset{\text{Acetylene}}{HC \equiv CH}$

(2) From Vicinal dihalides $\left[\text{Vicinal dihalide} + \begin{matrix}\text{(i) alc. KOH}\\ \text{(ii) } NaNH_2\end{matrix} \longrightarrow \text{Alkyne}\right]$



Physical Properties of Alkynes

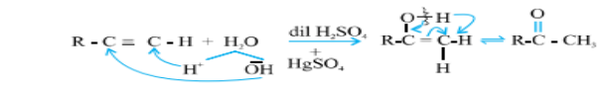
- Alkynes are nonpolar, unsaturated

hydrocarbons with physical properties similar to alkanes and alkenes. Alkynes dissolve in organic solvents, have slight solubility in polar solvents, and are insoluble in water. Compared to alkanes and alkenes, alkynes have slightly higher boiling points.

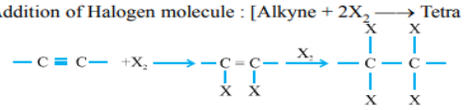
Chemical Properties of Alkynes

(1) Hydration [Addition of water]

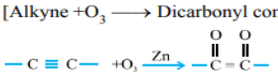
$$\text{Alkyne} + H_2O \xrightarrow[Hg^{2+}]{H^+} \text{Carbonyl compound}$$



(2) Addition of Halogen molecule : [Alkyne + $2X_2$ ⟶ Tetra halides]



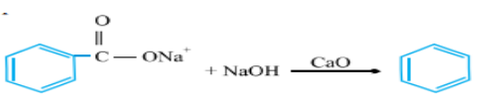
(3) Ozonolysis : [Alkyne + O_3 ⟶ Dicarbonyl compound]



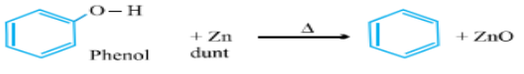
(4) $3HC \equiv CH \xrightarrow[\text{tube/873K}]{\text{Fe red hot}}$ 

AROMATIC HYDROCARBONS

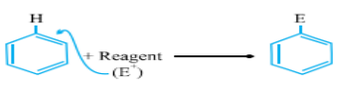
Preparation:

(1) 

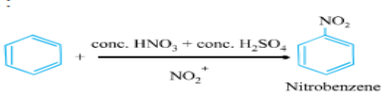
(2) $3HC \equiv CH \xrightarrow[873K]{\text{Fe red hot tube}}$ 

(3) 

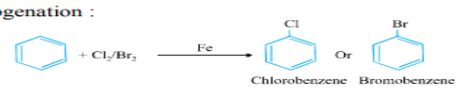
Chemical Properties



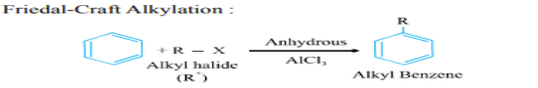
(1) Nitration :



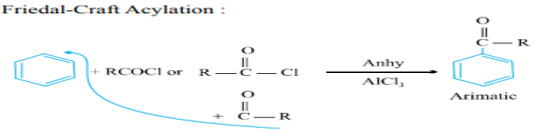
(2) Halogenation :



(3) Friedal-Craft Alkylation :

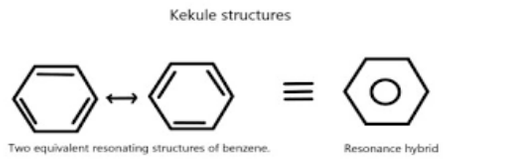


(4) Friedal-Craft Acylation :



Huckel's Rule:

Conditions : (i) Compound most be planar.
(ii) Complete delocalisation of πe^-
(iii) Presence of $(4n + 2)\ \pi e^-$.$(n = 1, 2, 3, ...)$



Preparation of Aromatic Compounds

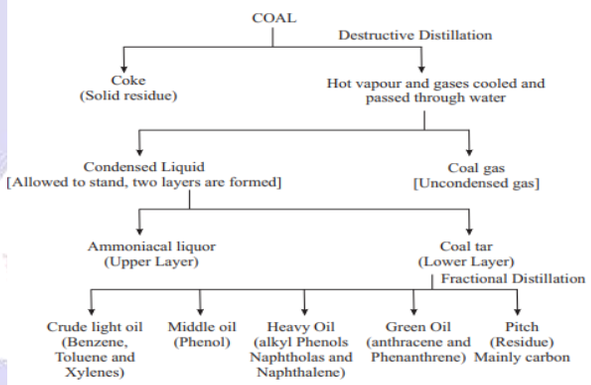
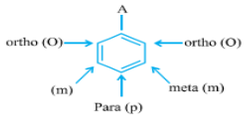


Fig. 24.1: Destructive Distillation of coal

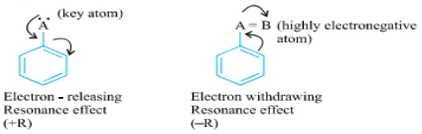
- **Resonance:** The phenomenon by virtue of which a single molecule can be Compounds represented in two or more structures is called resonance.

- **Derivatives of Benzenes :**



Ortho/Para directors : Group which direct the incoming electrophile to attach at ortho/para positions.

Meta directors : Groups which direct the incoming electrophile to attack at meta position.



Check Yourself

1. The position of double bond in alkenes can be located by:

(A) Hydrogenation of oil (B) Ozonolysis

(C) Photolysis (D) Hydration

2. Some meta-directing substituent's in aromatic substitution are given. Which one is most deactivating?

(A) –C≡N (B) $-SO_3H$

(C) –COOH (D) $-NO_2$

3. Which of the following compounds will exhibit geometrical isomerism?

(A) 1 – Phenyl – 2 – butene

(B) 3 – Phenyl – 1 – butene

(C) 2 – Phenyl – 1 butene

(D) 1, 1 – Diphenyl – propene.

4. Pure methane can be prepared by

(A) Soda lime decarboxylation

(B) Kolbes electrolytic method

(C) Wurtz reaction

(D) Reduction with H_2

5. Hydrocarbon containing following bond is most reactive

(A) C ≡ C (B) C = C

(C) C-C (D) All of these

Test Yourself

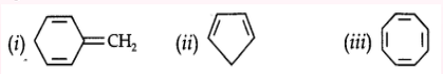
Question: What effect does branching of an alkane chain has on its boiling point?

Answer: Branching of carbon atom chain decreases the boiling point of alkane.

Stretch Yourself

1. How will you convert benzene into (i)p-nitrobromobenzene (ii) m-nitrochlorobenzene (iii) p-nitrotoluene (iv) acetophenone?

2. Explain why the following systems are not aromatic?



3. What are the necessary conditions for any system to be aromatic? Draw the cis- and trans-structures for hex-2-ene. Which iosmer will have higher b.p. and why?

4. Draw the cis- and trans-structures for hex-2-ene. Which iosmer will have higher b.p. and why?

5. Write chemical equations for the combustion reaction of the following hydrocarbons,

(i) Butane (ii) Pentene

(iii) Hexyne (iv) Toluene

Answers

Check Yourself

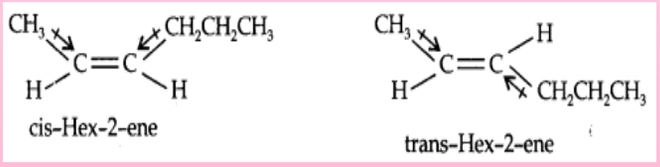
Answer: 1(B); 2(D); 3(A); 4(A); 5(A)

Stretch Yourself

1. Do it by yourself.
2. Do it by yourself.
3. The necessary conditions for a molecule to be aromatic are:

   I. It should have a single cyclic cloud of delocalised n-electrons above and below the plane of molecule.
   II. It should be planar. This is because complete delocalization of n-electrons is possible only if the ring is planar to allow cyclic overlap of p-orbitals.
   III. It should contain Huckel number of electrons, i.e., (4n + 2) n-electrons where n = 0, 1, 2, 3 e
   IV. A molecule which does not satisfy any one or more of the above conditions is said to be non aromatic.

4. The structures of cis- and trans-isomer of hex-2-ene are:



   The boiling point of a molecule depends upon dipole-dipole interactions. Since cis-isomer has higher dipole moment, therefore, it has higher boiling point.

5. (i) $C_4H_{10}(g) + 13/2\ (g) \xrightarrow{\Delta} 4CO_2(g) + 5H_2O(g)$ (Butane)

   (ii) $C_5H_{10}(g) + 15/2O_2(g) \xrightarrow{\Delta} 5CO_2(g) + 5H_2O(g)$ (Pentene)

   (iii) $C_6H_{10}(g) + 17/2O_2(g) \xrightarrow{\Delta} 6CO_2(g) + 5H_2O(g)$ (Hexyne)

   (iv)  (g) or $C_7H_8(g) + 9O_2(g) \xrightarrow{\Delta} 7CO_2(g) + 4H_2O(g)$ (Toluene)