NEET | JEE ESSENTIALS

Class XI

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Unit 8

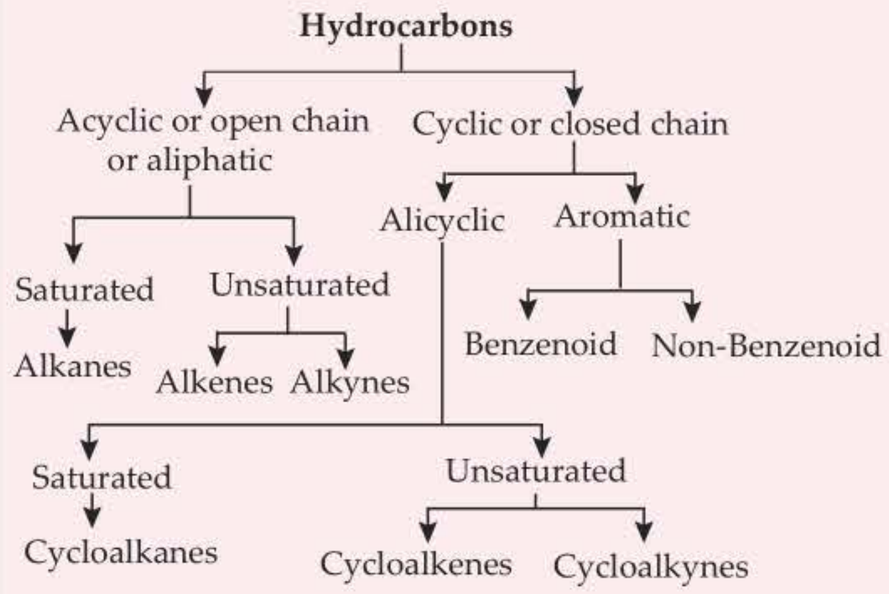
HYDROCARBONS ENVIRONMENTAL CHEMISTRY

HYDROCARBONS

Introduction

- Organic compounds composed of only carbon and hydrogen are called hydrocarbons.
- Hydrocarbons are considered to be the parent organic compounds while all other compounds are thought to have been derived from them by replacement of one or more of their hydrogen atoms by appropriate functional groups.

Classification



Alkanes

- The saturated hydrocarbons are represented by the general formula C_nH_{2n+2}.
- The normal alkanes are colourless gases (C_1 to C_4), colourless liquids (C_5 to C_{17}) and from C_{18} onwards colourless solids.
- As branching increases, melting and boiling points decrease. The boiling point increases steadily with increase in molecular mass.
- Density of alkanes also increases with size of the molecule.
- They are generally insoluble in polar solvents like water but soluble in non-polar solvents like ether, chloroform, etc.
- They are relatively unreactive towards most of the reagents such as acids, bases, oxidising and reducing agents. However under drastic conditions *i.e.*, at high temperature and pressure undergoes different types of reactions like halogenation, nitration, sulphonation, pyrolysis etc.

Methods of preparation

1. By hydrogenation of unsaturated hydrocarbons (Sabatier & Senderen's reaction) :

$$C_nH_{2n} + H_2 \xrightarrow[\Delta]{Ni} C_nH_{2n+2}$$

$$C_nH_{2n-2} + 2H_2 \xrightarrow[\Delta]{Ni} C_nH_{2n+2}$$

2. Wurtz reaction :

$$RX + 2Na + XR \xrightarrow[ether]{dry} R - R + 2NaX$$

3. Corey-House synthesis :

$$R\text{Br} + \text{Li}R'_2\text{Cu} \longrightarrow RR' + R'\text{Cu} + \text{LiBr}$$

4. Kolbe's electrolysis :

$$2R\text{COOK} + 2H_2O \xrightarrow{\text{electrolysis}} R - R + 2CO_2 + 2KOH + H_2$$

5. From Grignard's reagent :

$$RX + Mg \xrightarrow{\text{dry ether}} R - Mg - X$$

$$R - Mg - X + HOH \xrightarrow{H^+} R - H + Mg\begin{matrix}OH\\X\end{matrix}$$

6. From carbonyl compounds (Clemmensen reduction) :

$$R - \underset{\underset{O}{\|}}{C} - CH_3 \xrightarrow[\text{conc. HCl}]{Zn/Hg} RCH_2CH_3$$

ALKANES

Chemical properties

1. Halogenation :

$$CH_4 + 4Cl_2 \xrightarrow{h\upsilon} CCl_4 + 4HCl$$

2. Nitration :

$$R - H + \underset{\text{(Fuming)}}{HONO_2} \xrightarrow[\text{temp.}]{\text{high}} \underset{\text{Nitroalkane}}{R - NO_2} + H_2O$$

3. Sulphonation:

$$R - H + HOSO_3H \xrightarrow[\text{Prolonged heating}]{SO_3} RSO_3H + H_2O$$

4. Complete combustion :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

5. Incomplete combustion :

$$CH_4 + \underset{\text{(Limited)}}{O_2} \xrightarrow{\text{Burn}} \underset{\text{Carbon black}}{C} + 2H_2O$$

6. Catalytic oxidation :

$$\underset{9}{2CH_4} + \underset{1}{O_2} \xrightarrow[100\text{ atm}/200^\circ C]{\text{Cu tube}} 2CH_3OH$$

7. Aromatisation :

$$\underset{n\text{-Hexane}}{C_6H_{14}} \xrightarrow[600^\circ C/15\text{ atm}]{Cr_2O_3/Al_2O_3} \underset{\text{Benzene}}{C_6H_6} + 4H_2$$

8. Pyrolysis :

$$CH_4 \xrightarrow{1000^\circ C} C + 2H_2$$

$$C_2H_6 \xrightarrow[Cr_2O_3 + Al_2O_3]{500^\circ C} CH_2 = CH_2 + H_2$$

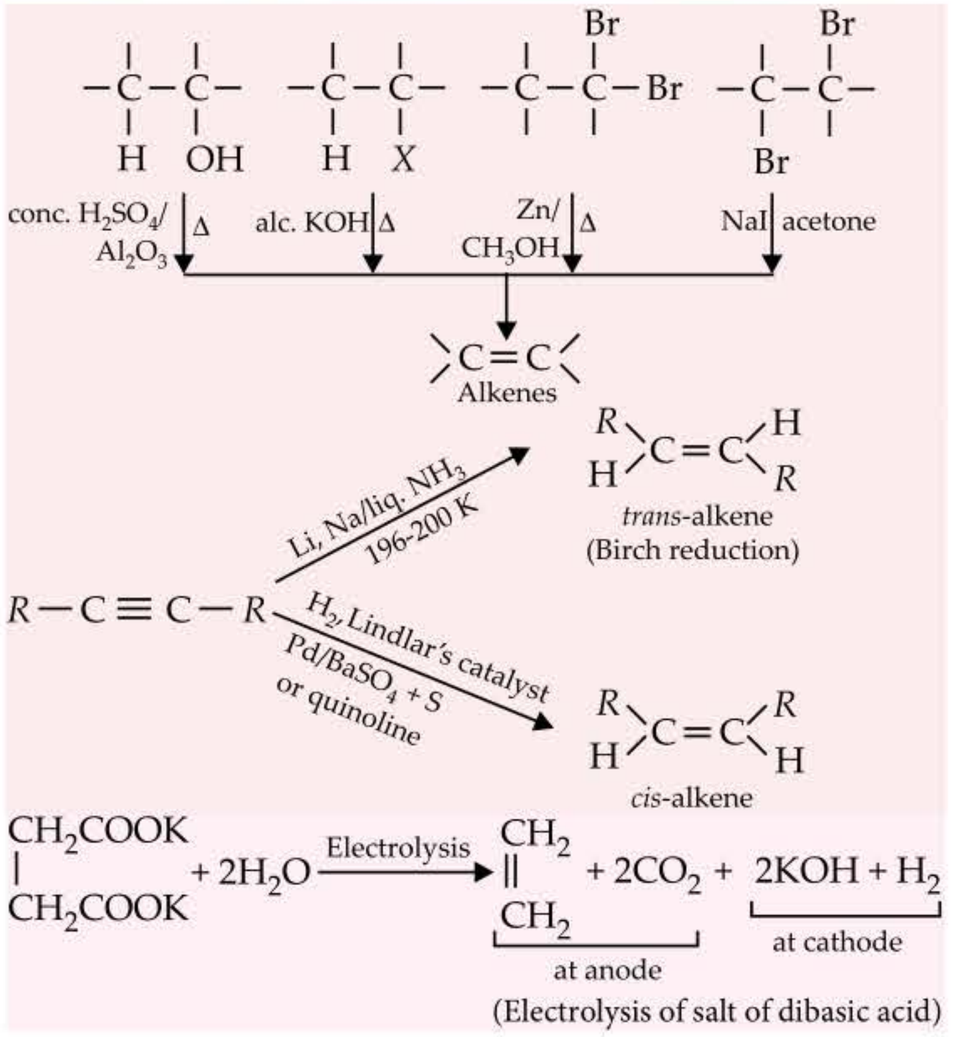
Alkenes (Olefins)

- The open chain hydrocarbons which contain lesser number of hydrogen atoms than the corresponding alkanes containing same number of carbon atoms are called *unsaturated hydrocarbons*.
- The member which contain two hydrogen atoms less than the corresponding saturated hydrocarbons are known as alkenes (olefins). These are represented by general formula C_nH_{2n}.
- Organic compounds containing C = C are known as *alkenes*. Alkenes with two double bonds are known as *dienes*.

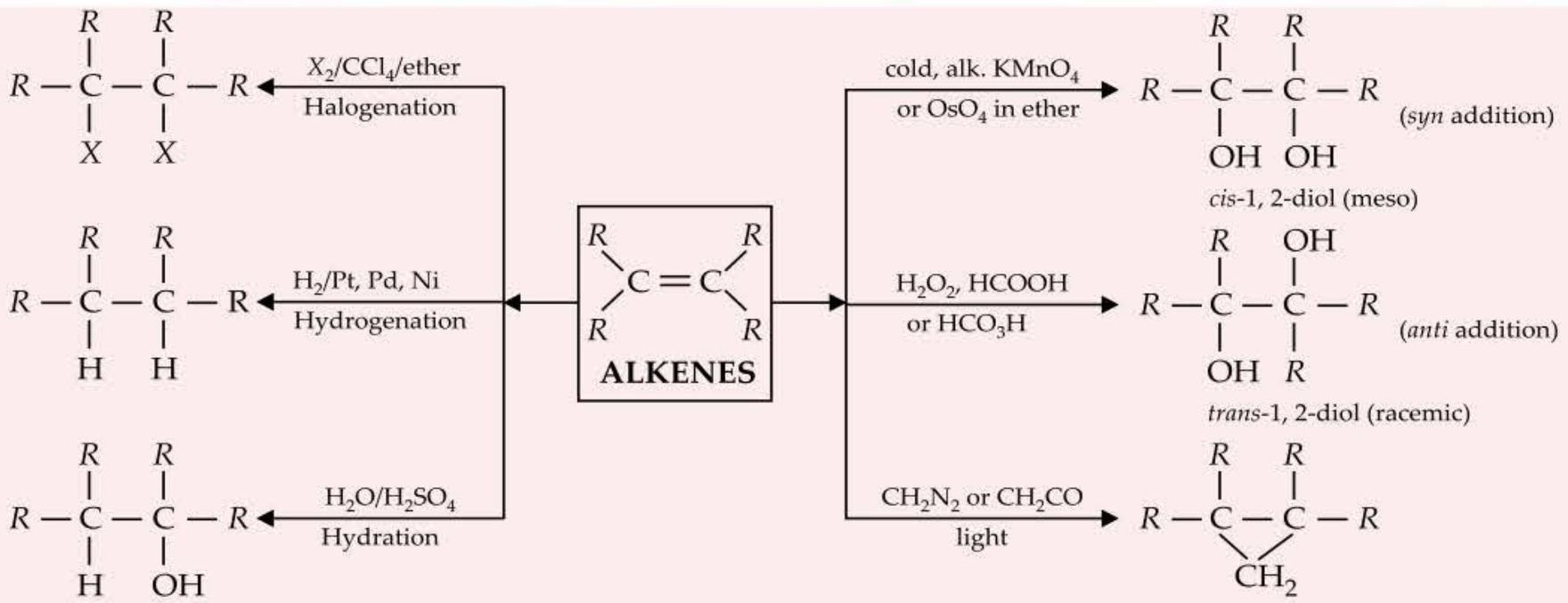
Dienes

Isolated dienes	Conjugated dienes	Cumulated dienes
$-C=C-\underset{\displaystyle|}{C}-C=C-$	$-C=C-C=C-$	$-C=C=C-$

Preparation



Chemical Properties



Alkynes (Acetylenes)

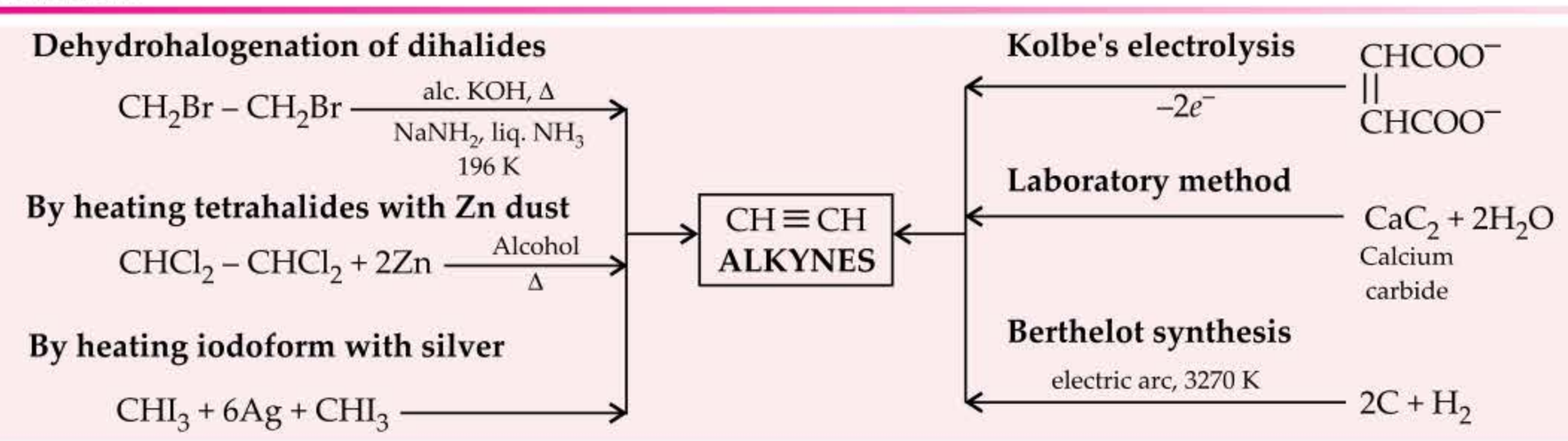
Alkynes contain four hydrogen atoms less than the corresponding alkanes and are characterised by the presence of a triple bond in the molecule. The first and the most important member of this series is acetylene, HC≡CH. Hence, the alkynes (C_nH_{2n-2}) are also called *acetylenes*.

Acidic nature : Acetylene is acidic in nature. As, *s*-character increases, acidic nature increases.

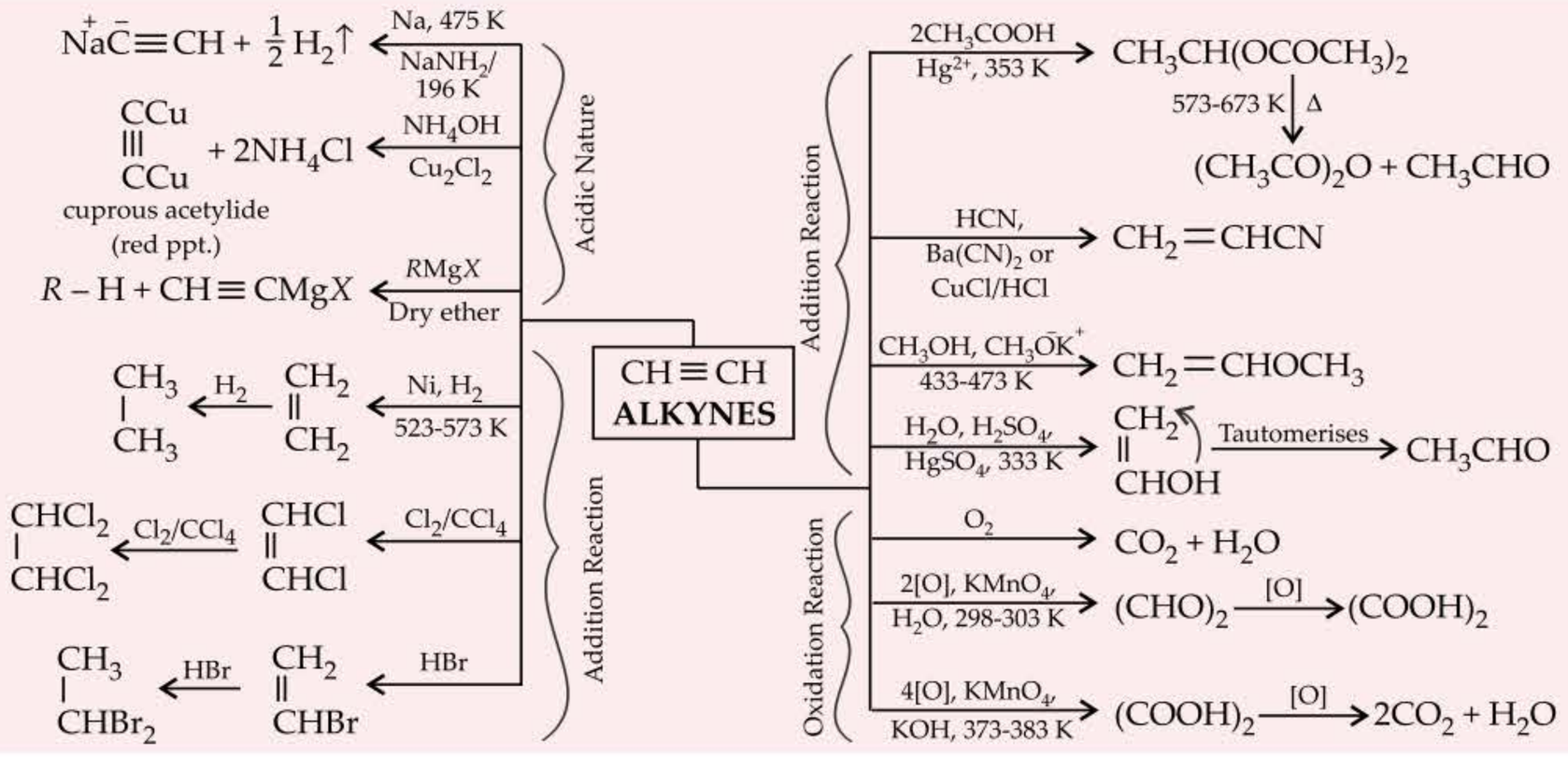
Hybridisation : $sp >$ $sp^2 >$ sp^3 (acidic nature)

s-character : 50% 33.3% 25%

Preparation



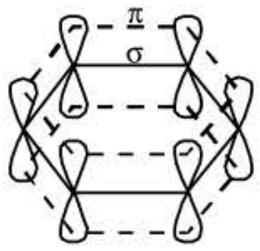
Chemical Properties



AROMATIC HYDROCARBONS (ARENES)

Structure of benzene :

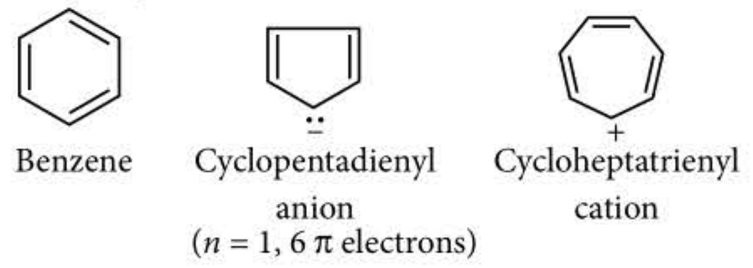
- All six carbon atoms in benzene are sp^2 hybridised.
- The sp^2 hybrid orbitals overlap with each other and with *s*-orbitals of the six hydrogen atoms forming C – C and C – H σ bonds respectively.
- All σ-bonds in benzene lie in one plane and all bond angles are 120°.
- One half of π-molecular orbital lies above and the other half lies below the plane of the σ-bond.



Aromaticity (Huckel Rule) : Huckel rule of aromaticity is applied to all the ring systems whether they have benzene ring or not and possess the following characteristics :

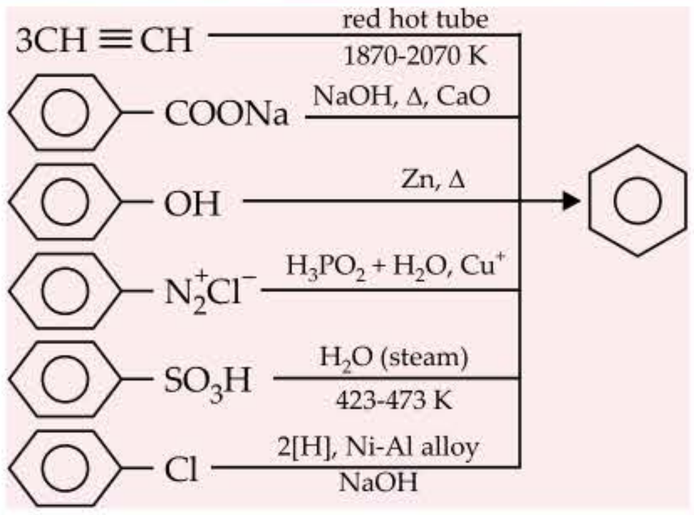
- Planarity
- Complete delocalisation of π-electrons in the ring.
- Presence of $(4n + 2)\pi$-electrons in the ring where $n = 0, 1, 2, 3, \ldots$.

For example,

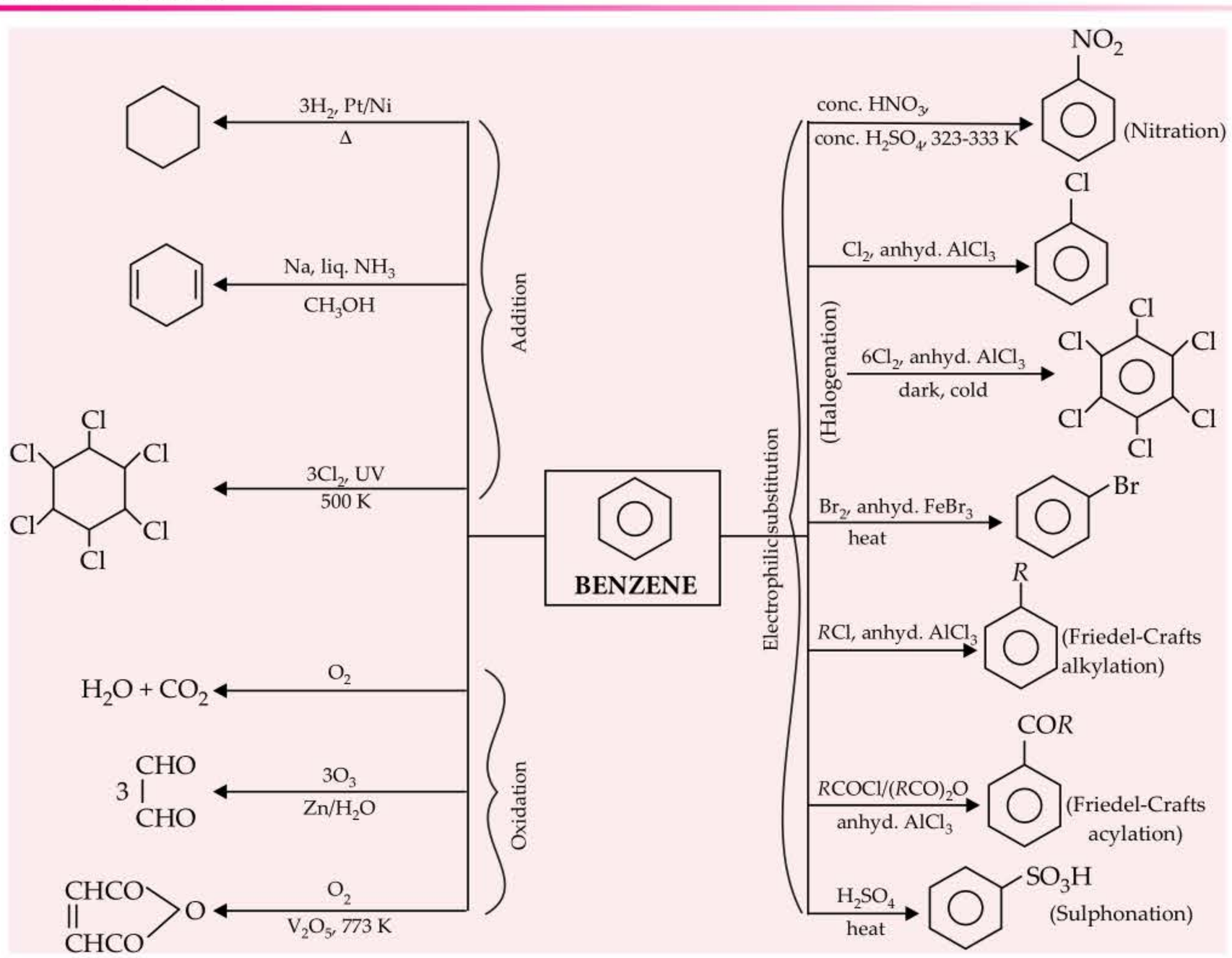


Benzene | Cyclopentadienyl anion ($n = 1$, 6 π electrons) | Cycloheptatrienyl cation

PREPARATION



CHEMICAL PROPERTIES

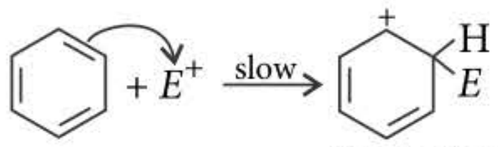


- **Mechanism of electrophilic substitution reactions :** Benzene undergoes substitution because it is an electron rich system due to delocalised π-electrons.

Step 1 : Formation of an electrophile

$$E \overset{\curvearrowright}{-} Nu \longrightarrow E^+ + :Nu^-$$

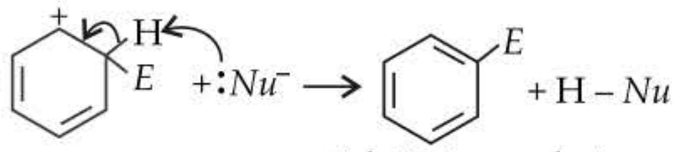
Step 2 : Electrophile attacks on aromatic ring to form σ-complex.



(σ-complex)

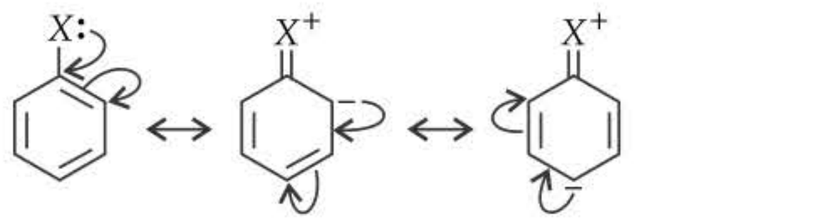
stabilises due to resonance

Step 3 :



Substitution product

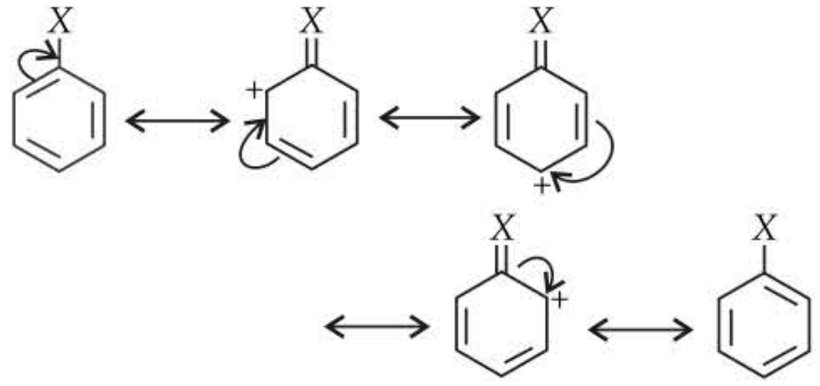
- **Directive influence :**
  - Groups with positive mesomeric effect (+*M*) increases electron density at *o*- and *p*-positions due to delocalisation.



(here *X* may be – OH, – F, – Cl, – Br, – I)

Thus, electrophile attacks on *o*- and *p*-positions because these are electron rich positions while nucleophile will attack on *m*-position because *m*-position is less electron rich.

  - Groups with negative mesomeric effect (–*M*) decreases electron density on *o*- and *p*-positions, so electrophile will attack on *m*-position and nucleophile will attack on *o*- and *p*-positions.



(here, *X* may be – NO_2, – SO_3H, – CN.)

Physical Properties

- Aromatic hydrocarbons are non-planar molecules.
- These are colourless liquids or solids with characteristic aroma.
- These are immiscible with water but miscible in organic solvents and burn with sooty flame.
- Boiling point of arenes increases with increase in the molecular size due to increase in van der Waals' forces of attraction.
- Melting point depends on molecular size and symmetry. Among *o*-, *m*- and *p*-xylenes, *p*-isomer has highest melting point.

Environmental Chemistry

Introduction

- Environmental chemistry is the branch of chemistry that deals with the study of various chemical processes taking place in the various segments of the environment. It is the study of sources, transportation, reactions, effects and fates of the chemical species occurring in one or more segments of the environment.

Components of Environment

- **Atmosphere :** Cover of gases upto the height of 1600 km from the surface of earth.

Regions of atmosphere

Region	Altitude from earth's surface	Temperature range	Gases/Species present
Tropo-sphere	0-11 km	Decreases from 15 to –56°C	N_2, O_2, CO_2, H_2O vapours
Strato-sphere or (ozono-sphere)	11-50 km	Increases from –56 to –2°C	N_2, O_2, O_3 O-atoms

Meso-sphere	50-85 km	Decreases from –2 to –92°C	N_2, O_2, O_2^+, NO^+
Thermo-sphere	85-500 km	Increases from – 92 to 1200°C	O_2^+, O^+, NO^+, e^-.

- **Hydrosphere :** Water bodies (sea, oceans, rivers, lakes, etc.) covers about 75% of earth's surface.
- **Lithosphere :** Solid part consisting of soil, rocks, mountains, etc.
- **Biosphere :** Part where living organisms interact with lithosphere, hydrosphere and atmosphere.
- **Abiotic components (non-living) :** Lithosphere, hydrosphere, atmosphere.
- **Biotic components (living) :** plants, animals and human beings.

Types of Pollutants

- A substance present in the environment in greater proportion than its natural abundance, resulting into harmful effects is called a pollutant.
- *Primary pollutants* are those which after their formation enter the environment and remains as such. For example, NO.
- *Secondary pollutants* are those harmful materials which are formed by chemical reactions between the primary pollutants in the atmosphere or hydrosphere. For example - PAN.
- *Biodegradable pollutants* are materials which are easily decomposed by microorganisms either by nature itself or by suitable treatment and thus are not harmful but if these are present in excess in the environment, they become pollutants. For example, cow-dung.
- *Non-biodegradable pollutants* are materials which do not degrade or degrade very slowly but their presence even in very small amounts in the environment is harmful. For example, Hg, Al.

Air Pollution

- **Air Pollution :** It is the addition of undesirable materials into the atmosphere either due to natural phenomena or due to human activity on the earth which adversely affect the quality of the air and hence affects the life on the earth.

Pollutants	Major Sources	Effects
CO	Incomplete combustion of carbonaceous matter in automobile engines and defective furnaces, incomplete combustion of agricultural and slash matter, volcanic eruptions, forest fires.	Carbon monoxide is toxic. It binds with haemoglobin in red blood cells and prevents them from combining with oxygen. Low levels of CO cause headaches and dizziness. Concentrations of ~1% causes death in minutes.
NO_x	Combustion of fuel, natural-forest fires, anthro-stationary combustion sources (factories and power plants), transportation.	Toxic to living tissues, harmful to paints, textiles and metals.
SO_x	Anthro-stationary combustion sources, industries, volcanic eruptions and also found in metal ores, coal and decay products.	They are respiratory tract irritants, low concentration causes throat and eye-irritation, causes breathlessness, affect larynx.
CFC's	CFC's were used primarily as refrigerants, in aerosol sprays and in the plastics industry. Freons are stable (lasts for over 80 years), inflammable and inert (in the lower atmosphere).	React with stratospheric ozone. When CFC's are broken down, chlorine free radicals are produced which can react with more than 100,00 molecules of ozone thus, depleting the ozone layer.
Particulates	Volcanic eruptions, fly ash, smelting and mining operations, smoke from incomplete combustion, dust from crushers and grinders.	Inhalation of metallic particles leads to respiratory disorders like asthma, bronchitis, lung cancer, etc.

INFO SHOTS

A new approach to recycle greenhouse gas!

Professor of molecular biology & biochemistry at the Ayala School of Biological Sciences, the researchers found that they could successfully express the reductase component of the nitrogenase enzyme alone in the bacterium Azotobacter vinelandii and directly use this bacterium to convert CO_2 to CO. The intracellular environment of the bacterium was shown to favor the conversion of CO_2 in a way that would be more applicable to the future development of strategies for large-scale production of CO. The findings were surprising to the group, as nitrogenase was only previously believed to convert nitrogen (N_2) to ammonia (NH_3) within the bacterium under similar conditions. The intracellular environment of the bacterium Azotobacter vinelandii favors other reduction reactions, due in part to its well-known oxygen protection mechanisms and presence of physiological electron donors. The bacterium could reduce CO_2 and release CO as a product, which makes it an attractive whole-cell system that could be explored further for new ways of recycling atmospheric CO_2 into biofuels and other commercial chemical products. These findings of Hu's group establish the nitrogenase enzyme as a fascinating template for developing approaches to energy-efficient and environmentally-friendly fuel production. Researcher's observation that a bacterium can convert CO_2 to CO opens up new avenues for biotechnological adaptation of this reaction into a process that effectively recycles the greenhouse gas into the starting material for biofuel synthesis that will help us simultaneously combat two major challenges we face nowadays: global warming and energy shortages.

Greenhouse Effect and Global Warming

- The retention of heat by the earth and atmosphere from the sun and its prevention to escape into the outer space is known as *greenhouse effect*.
  - Greenhouse gases such as CO_2, ozone, methane, chlorofluorocarbon compounds and water vapour form a thick cover around the earth which prevents the IR rays emitted by the earth to escape.
  - It gradually leads to increase in temperature of atmosphere.
- **Consequences of Greenhouse Effect**
  - Global warming would result in rise in sea level due to increased rate of melting of glaciers and floods.
  - Spread of some tropical diseases.
  - New weather patterns.
- **Control and prevention**
  - *Catalytic converters* : Devices attached to a vehicle's exhaust system to convert CO and hydrocarbons into water and carbon dioxide.
  - *Scrubbers* : Pollutant-laden air is passed through a mixture of water and lime which traps particulates and sulphur oxide gases.
  - HCFC's and HFC's are used in place of CFC's because they are largely destroyed in the lower region of the atmosphere.

Acid Rain

- The oxides of C, N and S present in the atmosphere, dissolve in water and produce acids and lower the pH of water to below 5.6.

$$H_2O + CO_2 \longrightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$2H_2O + 2SO_2 + O_2 \longrightarrow 2H_2SO_4 \rightleftharpoons 4H^+ + SO_4^{2-}$$

$$2H_2O + 4NO_2 + O_2 \longrightarrow 4HNO_3 \rightleftharpoons 4H^+ + 4NO_3^-$$

The acids are toxic to vegetation, react with marble and damage buildings.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

Smog

- The word *smog* is derived from smoke and fog. It is the major air pollutant.

Smoke + Fog $\longrightarrow$ Smog
(containing harmful gases)

Classical smog	Photochemical smog
Also called as *London smog.*	Also called as *Los Angeles smog.*
Formed due to oxides of sulphur.	Formed due to oxides of nitrogen.
Contains primary pollutants.	Contains secondary pollutants.
Causes bronchitis and problems in lungs.	Causes irritation in eyes.
It is reducing in nature.	It is oxidising in nature.

Stratospheric Pollution

- **Ozone depletion :**
  - The ozone layer, existing between 20 to 35 km above the earth's surface, shield the earth from the harmful UV radiations from the sun. The UV radiations cause skin cancer, cataract of eye, and harmful to vegetation.
  - Depletion of ozone is caused by oxides of nitrogen.

$$N_2O + h\upsilon \longrightarrow \underset{\text{(Reactive)}}{NO} + N$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$O_3 + h\upsilon \longrightarrow O_2 + O$$
$$NO_2 + O \longrightarrow NO + O_2$$
$$2O_3 + h\upsilon \longrightarrow 3O_2 \text{ (Net reaction)}$$

  - The presence of oxides of nitrogen increase the decomposition of O_3. Depletion of ozone by chlorofluoro-carbons.

$$CF_2Cl_2 + h\upsilon \longrightarrow CF_2Cl^{\bullet} + Cl^{\bullet}$$
$$CFCl_3 + h\upsilon \longrightarrow \underset{\text{(Reactive)}}{CFCl_2^{\bullet}} + Cl^{\bullet}$$
$$\dot{Cl} + O_3 \longrightarrow Cl\dot{O} + O_2$$
$$Cl\dot{O} + O \longrightarrow \dot{Cl} + O_2$$
$$O_3 + O \longrightarrow 2O_2 \text{ (Net reaction)}$$

Water Pollution

- Water pollution is defined as, the contamination of water by foreign substances which makes it harmful for health of animals, plants or aquatic life and makes it unfit for domestic, industrial and agricultural use.
- **Effects of water pollution :**
  - High concentrations of fluoride (over 10 ppm) are poisonous and harmful to bones and teeth.
  - Excess nitrate in drinking water can lead to '*blue baby*' *syndrome*.
  - Excess sulphate (> 500 ppm) causes laxative effect.
- **Remedial measures :**
  - Degradation of organic content of waste water by microbial oxidation.
  - Removal of phosphates, coagulation, filtration and disinfection using chlorine for improving the quality of waste water.
  - Sewage treatment should be improved.
  - Settlement of the filtered waste water to remove suspended solids, oily and greasy material which floats on the surface can be skimmed off.
- **Biochemical Oxygen Demand (BOD) :** It is defined as, the amount of free oxygen required for biological oxidation of the organic matter by aerobic conditions at 20°C for a period of five days. Its unit is mg/L or ppm. An average sewage has BOD value of 100 to 150 mg/L.
- **Chemical Oxygen Demand (COD) :** It is a measure of all types of oxidisable impurities (biologically oxidisable and biologically inert organic matter such as cellulose) present in the sewage. COD values are higher than BOD values.

Soil Pollution

- The addition of substances in an indefinite proportion which changes the productivity of the soil is known as *soil pollution*.
- **Sources of soil pollution :**
  - Agricultural pollutants : Chemicals like pesticides, fertilizers, fumigants, insecticides, herbicides, fungicides.
  - Domestic refuge and industrial wastes.
  - Radioactive wastes from research centres and hospitals.
  - Soil conditioners containing toxic metals like Hg, Pb, As, Cd etc.
  - Pollutants present in air from chemical works.
- **Effects of soil pollution :**
  - Pollution runs-off into rivers and kills the fishes, plants and other aquatic life.
  - Crops and fodder grown on polluted soil may pass on the pollutants to the consumers.
  - Soil structure is damaged (clay ionic structure impaired).
- **Control of soil pollution :**
  - Reuse and recycle unwanted items. The less rubbish we create, the less chance the waste will end up in our soil.
  - Make use of organic fertilizers and organic pesticides, because they are usually made of natural substances so are biodegradable.
  - Insist on buying natural and organic food, because chemical pesticides and fertilizers are not used in their growing process.
  - Cut down the usage of paper or use recycled paper.