CONCEPT MAP

HYDROCARBONS

Compounds composed entirely of carbon and hydrogen atoms bonded to each other by covalent bonds.

Acyclic/Open chain/Aliphatic

[Source: Petroleum]

Saturated

Alkanes/paraffins [C_nH_{2n+2}] :

- Isomerism - Chain, Conformational.
- Hybridisation - sp^3
- Preparation -

$2CH_3COONa + 2H_2O$ (Kolbe's electrolysis) $\rightarrow CH_3-CH_3$

$CH_2=CH_2 + H_2 \xrightarrow{Ni, 200°C} CH_3-CH_3$ (Sabatier & Senderen's)

$CH_3CHO + 4[H] \xrightarrow{Zn-Hg/HCl} CH_3-CH_3$ (Clemmensen reduction)

$CH_3Br + 2Na + CH_3Br \xrightarrow{\Delta, \text{ Dry ether}} CH_3-CH_3$ (Wurtz reaction)

$CH_3I + Zn + ICH_3 \rightarrow CH_3-CH_3$ (Frankland reaction)

- Special method for CH_4

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4\uparrow$

Aluminium carbide

Properties

Alkanes

Physical

- **Boiling point** : For straight chain alkanes, b.pt ∝ molecular size.
  In isomeric alkanes, b.pt ∝ 1/branching.
- **Melting point** : Even no. of C-atoms → Higher m.pt.; Odd no. of C-atoms → Lower m.pt.
- Density ∝ molecular mass.

Chemical

- Least reactive because of strong C—C and C—H σ bonds.
- Undergo only substitution reactions.
- Sulphonation and halogenation occur by free radical mechanism.

Unsaturated

Alkenes/olefins [C_nH_{2n}] :

- Isomerism - Chain, Position, Geometrical, Ring-chain.
- Hybridisation - sp^2
- Preparation -

$C_2H_5OH \xrightarrow[170°C]{\text{Conc. } H_2SO_4} CH_2=CH_2$

$CH\equiv CH \xrightarrow[\text{quinoline}]{H_2, Pd/CaCO_3 + S} CH_2=CH_2$

$(CH_2COONa)_2 \rightarrow CH_2=CH_2$ (Kolbe's electrolysis)

$(CH_2Br)_2 + Zn \rightarrow CH_2=CH_2$

Properties

Alkenes

Physical

- B. pt, m. pt. and specific gravity ∝ molecular mass.
- Less volatile than alkanes *i.e.* b. pt. and m. pt. are higher than alkanes.

Chemical

- Undergo electrophilic addition reactions.
- Test for unsaturation-Gives bromine water and Baeyer's tests.
- Addition of unsymmetrical reagents (HX, H_2O, HOX, etc.) → Markovnikov's rule.
- In presence of peroxides, addition is anti-Markovnikov's or Peroxide or Kharasch effect.

Alkynes [C_nH_{2n-2}] :

- Isomerism - Chain, Position, Functional, Ring-chain.
- Hybridisation - sp
- Preparation -

$CaC_2 + 2H_2O \rightarrow CH\equiv CH$

$(CH_2Br)_2 \xrightarrow{\text{alc. KOH}} CH\equiv CH$

$2CHI_3 + 6Ag \rightarrow CH\equiv CH$

$2C + H_2 \rightarrow CH\equiv CH$ (Berthelot reaction)

$(CHCOOK)_2 \rightarrow CH\equiv CH$ (Kolbe's electrolysis)

Properties

Alkynes

Physical

- **Melting and boiling points** : Alkynes > alkanes and alkenes.
- **Solubility** : Insoluble in water but soluble in organic solvents.

Chemical

- **Acidity** : Alkynes > alkenes > alkanes (% s-character ∝ acidity).
- Test for unsaturation-Gives bromine water and Baeyer's test.
- Undergo electrophilic and nucleophilic addition reactions.
- Degree of unsaturation or index of hydrogen deficiency = $(2n_1 + 2 - n_2)/2$, where n_1 = number of carbon atoms, n_2 = number of hydrogen atoms.

Cyclic/Closed chain

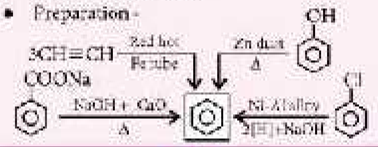
Aromatic

[Source: Coal]

Benzenoids/arenes [C_nH_{2n-6m}]:

(where, n = no. of C-atoms, m = no. of rings.)

- Isomerism - Position.
- Preparation -



Properties

Benzenoids

Physical

- Melting and Boiling points ∝ molecular size.
- **Solubility** : Insoluble in water but soluble in organic solvents.

Chemical

- **Reactivity** : Alkenes > alkynes > arenes > alkanes.
- Undergo electrophilic substitution reactions.
- Do not give Baeyer's test.

Non-benzenoids :

- Do not contain benzene ring.
  e.g., Azulene, tropolone, pyrrole, etc.

Alicyclic

- Contain a ring of three or more C-atoms.
  e.g., Cyclopropane, cyclobutene etc.

Aromaticity-Hückel's Rule

- An aromatic molecule -
  - Planar, cyclic and completely conjugated.
  - Contains $(4n+2)$ π-electrons, (where n = an integer).
  - If, on ring closure, the π electron energy of an open chain polyene *decreases*.
    e.g., [6] annulene (Benzene)
- An anti-aromatic molecule -
  - Planar, cyclic and completely conjugated.
  - Contains $4n$ π-electrons, (where n = an integer).
  - If, on ring closure, the π-electron energy *increases*.
    e.g., [4] annulene (Cyclobutadiene)
- A non-aromatic molecule -
  - Non planar, non cyclic and not completely conjugated.
  - If, on ring closure, the π-electron energy *remains the same*.
    e.g., Alkanes, alkenes and 1, 3, 5-cycloheptatriene.

Have A Look!

- The first three members of alkanes do not exhibit isomerism.
- Alkanes containing odd no. of C atoms cannot be prepared by Kolbes electrolysis.
- Methane cannot be prepared by Sabatier and Senderen's reaction.
- Method -
  - to ascend the C-chain - Wurtz reaction.
  - to descend the C-chain - Decarboxylation.
- Benzene + X_2 $\xrightarrow{\text{Lewis acid}}$ Substitution reaction.
  Benzene + X_2 $\xrightarrow{h\nu}$ Addition reaction.
- Octane no.-Knocking quality of an automobile fuel

Iso-octane
Octane no. = 100
[Free from knocking]

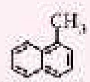
Heptane
Octane no. = 0
[Knocks badly]

- Gasolines
  - Octane no. = 74 → Regular gasoline
  - Octane no. < 74 → Third grade gasoline
  - Octane no. > 74 → Premium gasoline

- Tetraethyl lead (an antiknock compound) is used as a mixture of TEL (63%), ethylene bromide (26%), ethylene chloride (9%) and methylene blue (2%).
- Cetane no. - Scale to decide quality of diesel fuel.

$CH_3(CH_2)_{14}CH_3$

Hexadecane
Cetane no. = 100
[Ignites rapidly]



1-Methyl naphthalene
Cetane no. = 0
[Ignites badly]

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