CONCEPT MAP

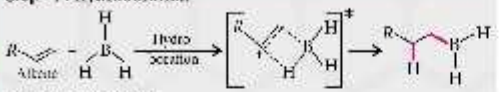
CLASS XI

Mechanistic Approach to Some Name Reactions

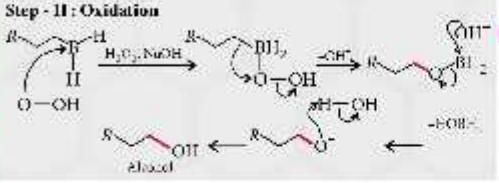
A 'mechanistic' approach to any reaction classifies the reaction according to mechanism rather than by functional group. It explains the stereochemistry involved in a particular reaction, which can either be regioselective, stereoselective or stereospecific.

I Hydroboration – Oxidation Reaction

Step - I : Hydroboration



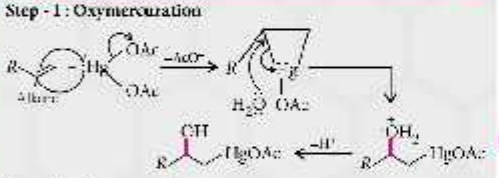
Step - II : Oxidation



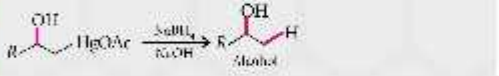
- Rate of formation of the C—B bond > Rate of formation of C—H bond.
- Formation of four-centred transition state.
- Hydroboration is regioselective.
- Hydroboration is a *syn*-addition across the alkene.
- In step-II, boron goes backward and forward between planar neutral structure and anionic tetrahedral structure.
- In step II, cleavage of O—O single bond is the driving force.
- In step I, new C—H bond and in step II new C—O bond are formed.
- The net result of this reaction is addition of water across the double bond.

II Oxymercuration – Demercuration Reaction

Step - I : Oxymercuration



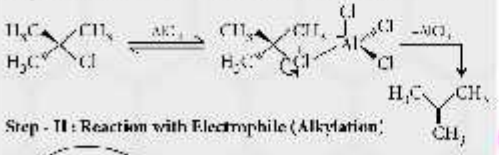
Step - II : Demercuration



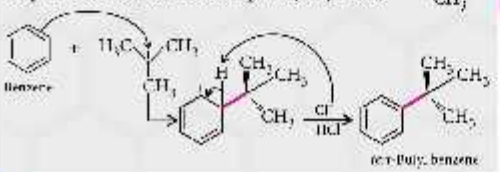
- In step-I, *i.e.*, oxymercuration, —OH and Hg^{2+} are added across the alkene.
- Oxymercuration is regioselective and stereospecific.
- Stereochemically, oxymercuration is an *anti*-addition.
- In step-I, water attacks at the more substituted end of the mercurinium ion (transition state).
- Driving force for demercuration is weak C—Hg bond.
- To replace Hg with H, $NaBH_4$, a reducing agent is used.
- Oxymercuration–reduction is a popular laboratory technique with Markovnikov selectivity while avoiding carbocation intermediate and thus, rearrangement which can lead to complex product mixture.

III Friedel–Crafts Alkylation Reaction

Step - I : Formation of Intermediate (Carbocation)



Step - II : Reaction with Electrophile (Alkylation)



- This reaction follows S_N1 pathway.
- Species having capability to form carbocation are used.
- Carbocation can be generated by
  - protonation to an alkene.
  - the acid-catalysed decomposition of a tertiary alcohol.
  - Lewis acid catalysed decomposition of a tert-alkyl chloride.
- Carbocation rearrangement (to more stable carbocation) takes place whenever possible.
- Friedel—Crafts alkylation with alkyl halides proceeds via a carbocation and chiral alkyl halides are expected to give racemic arene products. The extent of racemisation depends on the Lewis acid and the reaction conditions.

CONCEPT MAP

ACYCLIC HYDROCARBONS

(Open chain structures containing C and H only)

Class XI

Although hydrocarbons are primarily consumed as fuels, non-fuel applications of hydrocarbons are of great importance to society and the economy. Certain hydrocarbons can be found in lubricating oils, greases, solvents, fuels, wax, asphalts, cosmetics and plastics.

Saturated
C—C single bonds present

Alkanes
General formula, C_nH_{2n+2}

Preparation

- **From alkyl halides:**

$2R{-}Br + 2Na \xrightarrow{\text{Dry ether}} R{-}R + 2NaBr$ (Wurtz reaction)

$R{-}X$ can be converted to alkane using Zn + CH_3COOH, Zn + conc. HCl, Zn–Cu + C_2H_5OH, $LiAlH_4$, Zn + NaOH, $NaBH_4$ and Ph_3SnH reducing agents.

- **From carboxylic acids:**

$RCOOH \xrightarrow{\text{Red. P/HI}} RCH_3 + H_2O + I_2$

$2RCOONa + NaOH \xrightarrow{\Delta} Na_2CO_3 + RH$

$2RCOOK + 2H_2O \xrightarrow{\text{Electrolysis}} R{-}R + 2CO_2 + H_2 + 2KOH$ (Kolbe's electrolysis method)

- **From carbonyl compounds:**

$RCOCH_3 \xrightarrow[C_2H_5ONa]{NH_2NH_2} R{-}CH_2{-}CH_3$ (Wolff–Kishner reduction)

$RCOCH_3 \xrightarrow[\text{conc. HCl}]{Zn{-}Hg} RCH_2CH_3 + H_2O$ (Clemmensen reduction)

Properties

- **Substitution reaction:**

$CH_3CH_2CH_3 \xrightarrow{Cl_2} {-}CH_2CH_2CH_2Cl$ / $-CH_2{-}\underset{Cl}{CH}{-}CH_3$

Order of reactivity:

Alkanes $3^\circ > 2^\circ > 1^\circ > CH_4$

Halogens $F_2 > Cl_2 > Br_2 > I_2$

- **Oxidation:**

(a) Combustion or complete oxidation:

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

(b) Catalytic oxidation:

$2CH_4 + O_2 \xrightarrow[120 \text{ atm}/475K]{\text{Cu-tube}} 2CH_3OH$

(S) (L)

Alkenes ($>C{=}C<$)
General formula, C_nH_{2n}

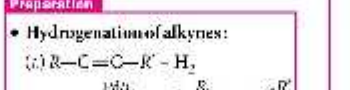
Preparation

- **Hydrogenation of alkynes:**

(a) $R{-}C{\equiv}C{-}R' + H_2 \xrightarrow[\text{(Lindlar's catalyst)}]{Pd/C}$ $\underset{\text{(cis alkene)}}{\overset{R}{\overset{|}{C}}{=}\overset{R'}{\overset{|}{C}}}$ (H's on same side)

(b) $R{-}C{\equiv}C{-}R' + H_2 \xrightarrow[\text{or } LiBH_4]{Na/liq.\ NH_3}$ $\underset{\text{(trans-alkene)}}{\overset{R}{\overset{|}{C}}{=}\overset{R'}{\overset{|}{C}}}$ (H's on opposite sides)

- **Dehydrohalogenation:**



- **Dehalogenation:**

$\underset{\text{(Vic. dihalide)}}{X{-}CH_2{-}CH_2{-}X} + Zn \xrightarrow[\Delta]{\text{Methanol}} CH_2{=}CH_2 + ZnX_2$

- **Dehydration of alcohols:**

$CH_3CH_2{-}OH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_2{=}CH_2$

Properties

- **Addition of halogen:**

$CH_2{-}CH_2 + Br_2 \xrightarrow{CCl_4} \underset{\text{(Loses colour)}}{CH_2{-}Br \atop CH_2{-}Br}$ (Colourless)

- **Addition of halogen acid:**

$CH_3{-}CH{=}CH_2 + HBr \xrightarrow[\text{rule}]{\text{Markownikoff's}} CH_3{-}\underset{Br}{CH}{-}CH_3$

HBr addition in presence of peroxide follows *anti-Markownikoff's rule*, known as *Kharasch effect or peroxide effect*.

- **Oxidation:**

$CH_2{=}CH_2 + H_2O + O_2 \xrightarrow[295\text{–}303\ K]{\text{alk. } KMnO_4} HO{-}CH_2{-}CH_2{-}OH$

Alkynes ($-C{\equiv}C-$)
General formula, C_nH_{2n-2}

Preparation

- **From calcium carbide:**

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

- **Dehalogenation:**

$\underset{Br}{\overset{Br}{CH_2{-}CH_2}} \xrightarrow{KOH} CH_2{=}CHBr \xrightarrow{NaNH_2} CH{\equiv}CH$

Properties

- **Acidic nature:**

$CH{\equiv}CH + Na \xrightarrow{\text{liq. } NH_3} CH{\equiv}CNa + \frac{1}{2}H_2$

- **Addition reactions:**

$CH{\equiv}CH \xrightarrow[\text{Lindlar's}]{\text{Pd/BaSO}_4} CH_2{=}CH_2$

$CH_3{-}C{\equiv}CH \xrightarrow[CCl_4]{Br_2} CH_3{-}CBr_2{-}CHBr_2$

$CH_3{-}C{\equiv}CH \xrightarrow{H_2O} CH_3{-}\underset{OH}{C}{=}CH_2 \xrightarrow{\text{Isomerisation}} CH_3{-}\underset{O}{\overset{\|}{C}}{-}CH_3$

Commercial Uses

- **Alkanes :** Ethane is used for making tetrachloroethane which is an *artificial camphor*. Higher alkanes in the form of gasoline, kerosene oil, diesel, lubricating oils and paraffin wax are widely used.
- **Alkenes :** Ethene is used as a general anaesthetic. It is a starting material for a large number of compounds such as glycol, ethyl halides, ethyl alcohol, ethylene oxide, etc.
- **Alkynes :** Acetylene is used as a general anaesthetic under the name *narcylene*. Acetylene is used as an illuminant.

MASTERJEE CLASSES