Alkenes
Organic Chemistry
Methods of Preparations

1. Dehydration of Alcohol
2. Dehydrohalogenation of Alkyl halide
3. From Vicinal & geminal halide

E1 and E2 Reaction

Saytzeff Rules

Carbocation Rearrangement

Alkene and C+ Stability

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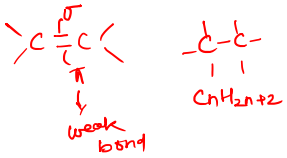
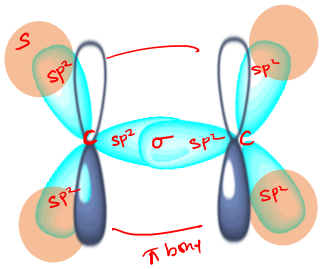
Alkene Organic Chemistry

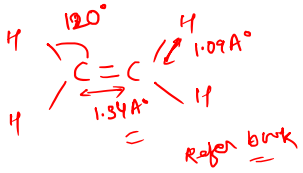
- **Alkenes** are a class of unsaturated hydrocarbons with at least one carbon-to-carbon double bond
- It General formula – C_nH_{2n} n = 2,3,4, - —
- They are also known as olefins (oleum- oil, and fiacre- to make).
- Alkenes are more reactive than alkanes due to the presence of the double bond (σ+π)
- Ethylene (ethene) is the first member of the class



Alkene Organic Chemistry

Structural Information = **SP2 hybridized**





Alkene Organic Chemistry

General Properties

1.Physical state – C2-C4 (Gases), C5-C17 (Liquids) >C17 (Solid at RT)

2.Density – Alkenes are lighter than water.

3.Solubility – Alkenes are insoluble in water and soluble in organic solvents such as benzene etc.

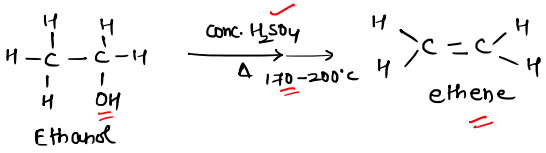
4.Boiling point – The boiling points of alkenes show a **gradual increase** with an increase in the **molecular mass or chain length**, this indicates that the intermolecular attractions become stronger with the increase in the size of the molecule.

Alkene Organic Chemistry

- **Uses of alkenes**
- Manufacture of plastics like polythene for making buckets, bowls, bags etc.
- Manufacture of polystyrene used in making car battery cases and parts of the refrigerator.
- Making ethane-1,2-diol used as anti-freezing for motor car radiators.
- Manufacture of ethanol and synthetic fibre terylene.
- Making an anti-knock for car engines.
- Manufacture of plastic, polypropene for making ropes and packaging material.
- Manufacture of propanol used in making acetone.
- Manufacture of acrylic fibres.

Alkene Preparation Methods

1. Dehydration of alcohol



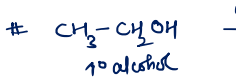
↳ A type of Elimination Reaction

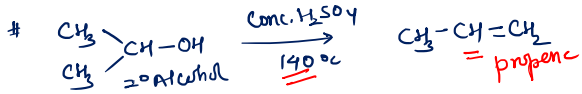
↳ Catalyst = Conc H_2SO_4 at high temp

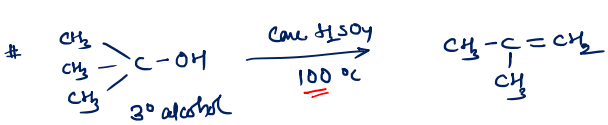
↳ Reaction Mech → E^1 Reaction

↳ Ease of Dehydration in alcohol
= 3° > 2° > 1° alcohol

↳ Other Dehydrating Agents
- P_2O_5] - Vap. phase
- Al_2O_3
- Conc. H_3PO_4
- Dry HCl

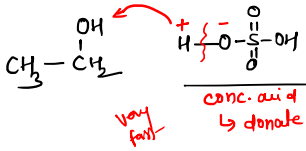






Alkene Preparation Methods

1. Dehydration of alcohol- E¹Reaction Mechanism



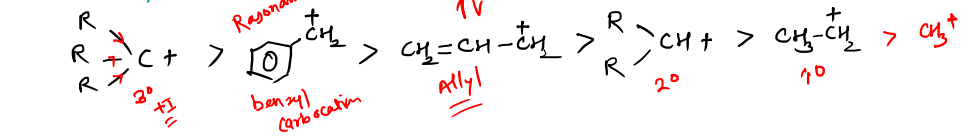
I Ionization → slow step ↳ RDS (I)
II Deprotonation (II)

#1 - Rate of Reactⁿ ∝ conc. of [CH3CH2OH]¹ · 1st order kinetic
Unimolecular
E¹ → Unimolecular Elimination Reaction

#2 - Intermediate → Carbocation C+
↳ Stable C+ Faster Reactⁿ - 3° > 2° > 1°

#3 - Rearrangement of Carbocation
1° → 2° → 3° [Hydride shift, methyl shift, phenyl shift]

Stability order of C+

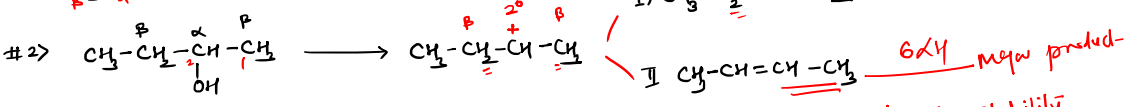


Alkene Preparation Methods

1. Dehydration of alcohol

#1> $CH_3-CH_2-OH \longrightarrow CH_2=CH_2$

#2>



I) $CH_3-CH_2-CH=CH_2$ — 2αH
II) $CH_3-CH=CH-CH_3$ — 6αH — more product

Saytzeff Rule → Form stable alkene, no of αH - stability
→ H eliminated from C-atm with fewer H-atm

#3> $CH_3-CH_2-CH_2-CH_2-OH \longrightarrow CH_3-CH_2-CH_2-CH_2^+$ (1°) → Rearrangement

↓ Hydride shift (H⁻)

$CH_3-CH_2-CH^+-CH_3$ = 2° Carbocation

$\xrightarrow{HSO_4^-}$ $CH_3-CH=CH-CH_3$
But-2-ene

Alkene Preparation Methods

1. Dehydration of alcohol

#4) $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-OH \xrightarrow{Conc.\ H_2SO_4}$

$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^+}}}}-CH_2 \xrightarrow{CH_3^- \text{ shift}} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^+}}}}-CH_2-CH_3$ (3°)

$\downarrow$

$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$

2-methyl but-2-ene

Alkene Preparation Methods

2. Dehydrohalogenation of alkyl halide-

↳ E^2 Elimination Reaction

↳ α-β elimination

↳ In presence of strong base as Reactant

- ↳ alcoholic KOH
- ↳ Alc. NaOH
- ↳ NH_2-NH_2/C_2H_5ONa

$H_3C-\underset{Cl}{\underset{|}{C}}H-\underset{H}{\underset{|}{C}}H_2 \xrightarrow[\text{strong base}]{\text{alcoholic KOH}}_{\Delta} H_2C=CH_2$

Ethyl chloride → ethene

↳ $CH_3-\underset{Br}{\underset{|}{\overset{\beta}{C}}}H-\overset{\beta}{C}H_3 + KOH \xrightarrow[\Delta]{\text{Alcohol}} CH_3-CH=CH_2$

↳ $CH_3-\underset{Br}{\underset{|}{\overset{\beta}{C}}}H-\overset{\alpha}{C}H_2-CH_3 + KOH \xrightarrow[\Delta]{\text{Alcohol}}$

(A) $CH_3-CH=CH-CH_3$ — Major ✓

(B) $CH_2=CH-CH_2-CH_3$ ✗

Saytzeff Product - Stable alkene

↳ Ease of Dehydrohalogenation

$3^\circ > 2^\circ > 1^\circ$ alkyl halide

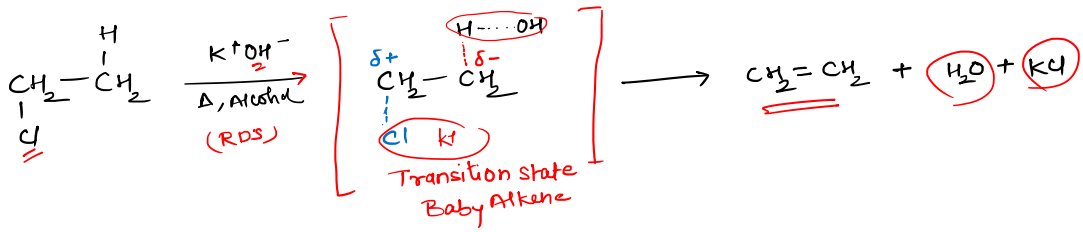
$RI > RBr > RCl > RF$

$I^- > Br^- > Cl^- > F^-$

leaving tendency

Alkene Preparation Methods

2. Dehydrohalogenation of alkyl halide- E^2 Reaction Mechanism



E^2 Reaction – Bimolecular Elimination Reaction
Rate of Elimination ∝ conc of [RX] [KOH] # 2nd order kinetics
Single step Reaction
Intermediated comp – Baby alkene,
stability of alkene – $CH_2=\overset{3^\circ}{C}(R)-R > R-\overset{2^\circ}{CH}=CH_2 > \overset{1^\circ}{CH_2}=CH_2$
NO Carbocation, # NO Rearrangement

Alkene Preparation Methods

2. Dehydrohalogenation of alkyl halide-

1) $CH_3-CH_2-Br \xrightarrow[\Delta]{\text{alc NaOH}} CH_2=CH_2$

2) $CH_3-CH_2-\underset{Br}{CH}-CH_3 \longrightarrow CH_3-CH=CH-CH_3$

Saytzeff Rule

3) $CH_3-CH_2-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-Br \longrightarrow CH_3-CH_2-CH=CH_2$ but-1-ene

4) $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{\beta}{C}}}-\overset{\alpha}{CH_2}-Br \longrightarrow$ No Reaction

No Hydrogen at β-C

Alkene Preparation Methods

2. Dehydrohalogenation of alkyl halide-

In E^2 Reactn — Hoffmann Product can also produced
↳ less stable product

Saytzeff product - stable product

↳ If used Bulky base (R)(R)(R)C-ONa ter butoxide, $(C_2H_5)_3N$ triethylamine

↳ Due to bulky group (steric hinderance), they can not find appropriate β-hydrogen, so they select easily targetable β-Hydrogen

$CH_3-CH_2-\underset{Br}{CH}-CH_3 \xrightarrow[\Delta]{(R)(R)(R)C-ONa} CH_3-CH_2-CH=CH_2$ but-1-ene

bulky strong base

simple strong base | Saytzeff | $CH_3-CH=CH-CH_3$

$R-X + KOH \rightarrow R-OH$ Substitution Reactn

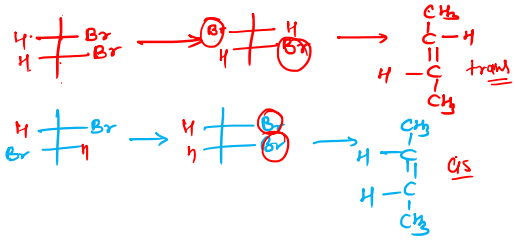
Alkene Preparation Methods

3. From Vicinal and Geminal Halides

Vicinal — $\overset{}{C}-\overset{}{C}$ (Cl, H) # Geminal — C(Cl)(Cl)H

From Vicinal Halide :- E^2 Reactn, Anti Elimination

1) $CH_3-\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow[NaI/Acetone]{Zn\ dust-\Delta} CH_3-CH=CH_2$

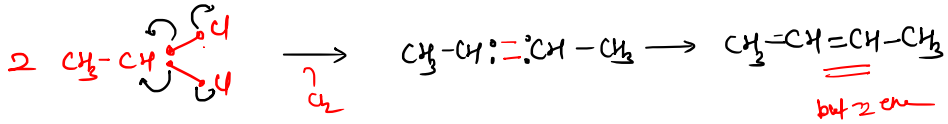


2) $CH_3-\underset{Br}{CH}-\underset{Br}{CH}-CH_3 \longrightarrow CH_3-CH=CH-CH_3$

Alkene Preparation Methods

3. From Vicinal and Geminal Halides

From Geminal Halide



Alkenes
Organic Chemistry
Methods of Preparations

Birch Reduction

Lindlar's Reduction

Kolbe's Electrolysis

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Alkene Preparation Methods

4. hydrogenation of Alkyne

$R-C\equiv CH \xrightarrow[H_2]{\text{Reduction}} R-CH=CH_2$
Alkyne → Alkene

\# Required Appropriate Reducing agent

$R-C\equiv CH \xrightarrow[Pd/H_2]{Ni/H_2 \text{ or}} R-CH=CH_2 \longrightarrow R-CH_2-CH_3$
Alkene → Alkane
Complete hydrogenation Reaction

$R-C\equiv CH \xrightarrow[\text{Partial Reduction}]{1\ eq.\ H_2} R-CH=CH_2$
Alkyne → Alkene

Alkene Preparation Methods

A) Birch Reduction

\# Catalyst - Na/ liquid NH_3 or Li/liq NH_3
\# Form Trans Alkene
\## Not in terminal alkyne – $R-C\equiv CH$ (CH≡CH) NO Birch Reduction
$R-CH_2-C\equiv C-CH_2-R$
$R-CH_2-C\equiv C-R$

$CH_3-C\equiv C-CH_3 \xrightarrow{Li/liq\ NH_3}$ but-2-yne → Trans But-2-ene

Mechanism → 2 Li → $2e^-$ ↑ + $2Li^+$

Electronic Repulsion

NH_3-H (donate H^+)

NH_3 (H^+)

e^-

Trans But-2-ene

Alkene Preparation Methods

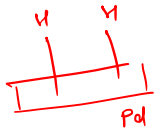
B) Lindlar's Catalyst Reduction

$CH_3-C\equiv C-CH_3 \xrightarrow[\text{quinoline}]{Pd/BaSO_4} CH_3-C(H)=C(H)-CH_3$

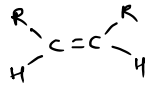
Catalyst - $Pd/BaSO_4$ or $Pd/CaCO_3$ in presence of quinoline or sulphur
↳ poison for catalyst

For cis Alkene

Not in terminal Alkyne $R-C\equiv CH$ ✗



Other Catalyst act similar as Lindlars → P2 catalyst - Ni/B or NiB_2

$R-C\equiv C-R \longrightarrow$  cis

Alkene Preparation Methods

5. Kolbe's Electrolysis- electrolysis on sodium/potassium salt of dicarboxylic acid

Succinic acid $\xrightarrow{K}$ dipotassium Succinate $\xrightarrow[\text{Electrolysis}]{+2H_2O}$ $CH_2=CH_2 + 2CO_2$ — Anode (decarboxylation)
$H_2 + 2KOH$ — cathod

Mechanism :→ $CH_2-COOK \longrightarrow CH_2-COO^- + 2K^+$
$CH_2-COOK \longrightarrow CH_2-COO^-$

$2H_2O \longrightarrow 2H^+ + 2OH^-$

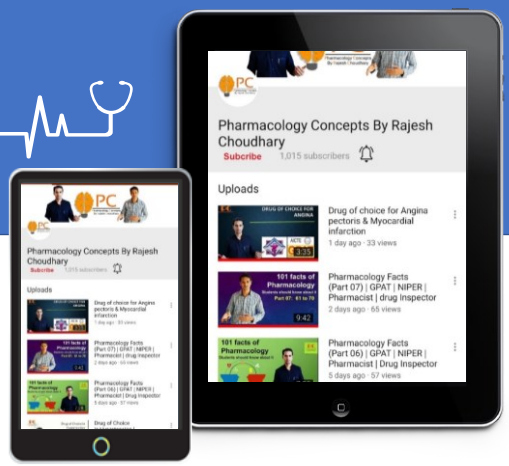
Anode ↓ loss of e^- : $CH_2-COO^- \longrightarrow 2e^- + CH_2-COO^\cdot$
CH_2-COO^- $\quad CH_2-COO^\cdot$

$CH_2-COO^\cdot \xrightarrow{\text{decarboxylation}} CH_2^\cdot + 2CO_2$
$CH_2^\cdot$

$CH_2^\cdot + CH_2^\cdot \longrightarrow$ Cyclobutane + Ethene major

Cathode ↓ gain of e^- : $2H^+ + 2e^- \rightarrow H_2$ ($H^\cdot + H^\cdot \rightarrow H-H$ (H_2))
$2K^+ + 2OH^- \rightarrow 2KOH$

Thanks for Watching



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