



# Alkyl Halide

## Organic Chemistry Preparation Methods

- ✓ Halogenation of Alkane
- ✓ Hydrohalogenation of Alkene

B.Pharm. | POC-I | U 3 | L4

### Alkyl Halide Organic Chemistry



#### Classification

1. Mono Haloalkane (Alkyl Halide) → Contains only one halogen atom

↳  $R-\text{CH}_2-X$  1° Alkyl halide

↳  $\begin{matrix} R & \\ & \diagdown \\ R & - C - X \\ & \diagup \\ R & \end{matrix}$  3° Alkyl halide      "C<sub>n</sub>H<sub>2n+1</sub>X"

↳  $\begin{matrix} R & \\ & \diagdown \\ R & - \text{CH} - X \end{matrix}$  2° Alkyl halide

#### 2. Dihaloalkane

↳ Geminal -  $\begin{matrix} & X \\ R & \diagdown \\ & \diagup \\ R & - \text{CH} & - X \end{matrix}$

↳ Vicinal -  $\begin{matrix} & X \\ R & - \text{CH} & - X \\ & | \\ & X \end{matrix}$

#### 3. Trihaloalkane - Haloform

↳ CHCl<sub>3</sub> - Chloroform

↳ CHI<sub>3</sub> - Iodofrom

#### 4. Tetrahaloalkane - CX<sub>4</sub>

↳ CCl<sub>4</sub> - Carbon Tetrachloride

#### 5. Allyl Halide

↳  $\begin{matrix} & X \\ \text{CH}_2 & - \text{CH} - \text{CH}_2 - X \\ & | \\ & \text{CH}_2 \end{matrix}$

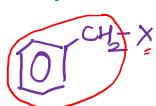


#### 6. Vinyl Halide

↳  $\begin{matrix} & X \\ \text{CH}_2 & = \text{CH} - X \\ & | \\ & \text{CH}_2 \end{matrix}$



#### 7. Benzyl Halide



#### 8. Haloarene



## Preparation of Alkyl Halide



## Methods

1. Halogenation of Alkane  $\rightarrow \text{CH}_4 + \text{X}_2$

2. Hydro-Halogenation of Alkene  $\text{CH}_2=\text{CH}_2 + \text{HX}$

3. From Alcohol –

  - a) Lucas Reagent (Conc. HCl + Anh ZnCl<sub>2</sub>)
  - b) PCl<sub>5</sub>
  - c) PCl<sub>3</sub>
  - d) SOCl<sub>2</sub> (Darzen's Method)

4. Halogen Exchange Methods

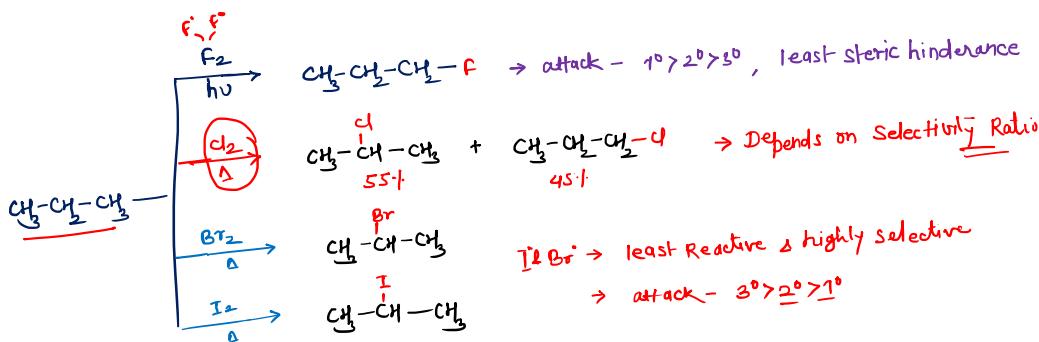
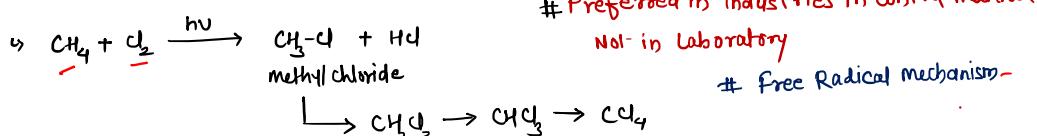
  - a) Finkelstein Reaction
  - b) Swartz Reaction

5. Hunsdiecker/Borodine-Hunsdiecker Reaction

## Preparation of Alkyl Halide



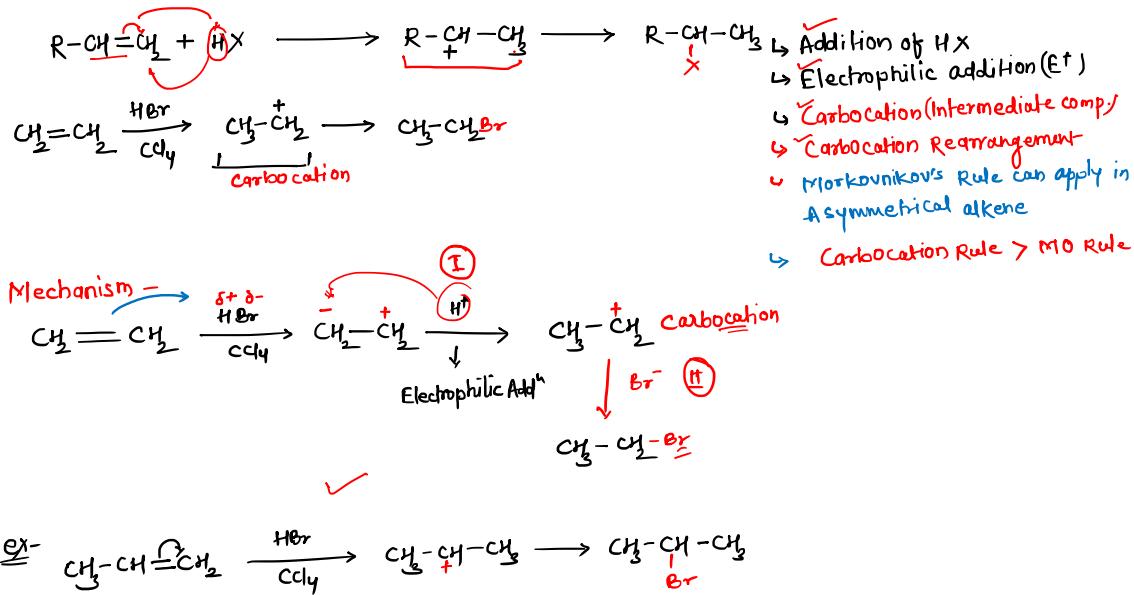
## 1. Halogenation of Alkane



## Preparation of Alkyl Halide



### 2. Hydro-Halogenation of Alkene



# Alkyl Halide

## Organic Chemistry

## Preparation Methods

### From Alcohol

- a) Lucas Reagent (Conc. HCl + Anh ZnCl<sub>2</sub>)
- b) PCl<sub>5</sub>
- c) PCl<sub>3</sub>
- d) SOCl<sub>2</sub> (Darzen's Method)

## Preparation of Alkyl Halide



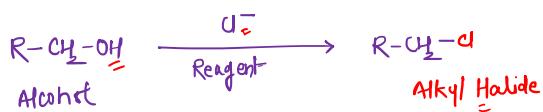
### Methods

1. Halogenation of Alkane
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## Preparation Alkyl Halide



### 2. From Alcohol



**Reaction Mechanism- Nucleophilic Substitution Reaction**

**Reagent Used**

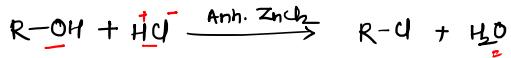
- ✓ a) Luca's Reagent (Conc. HCl + Anh ZnCl<sub>2</sub>)
- ✓ b) PCl<sub>5</sub>
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## Preparation Alkyl Halide

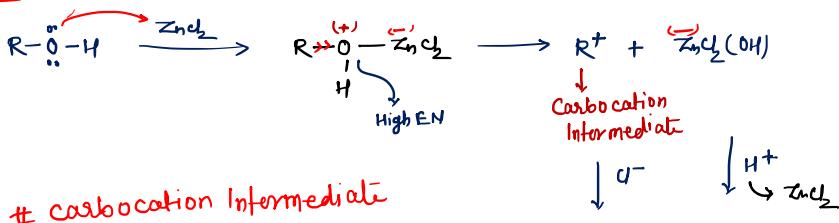


### From Alcohol

#### A. By Conc. HCl + Anhydrous ZnCl<sub>2</sub> - Luca's Reagent



Mechanism -



# carbocation Intermediate

# SN<sup>1</sup> Reaction Mechanism

# Preferred in - 3° alcohol

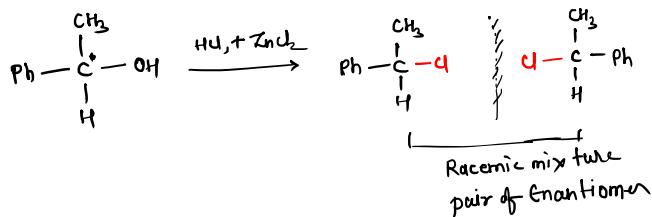
# Retention & Inversion attack

## Preparation Alkyl Halide



### From Alcohol

#### A. By Conc. HCl + Anhydrous ZnCl<sub>2</sub> - Luca's Reagent



# carbocation Intermediate  
# SN<sup>1</sup> Reaction Mechanism  
# Preferred in - 3° alcohol  
# Retention & Inversion attack

3° > 2° > 1°

# Luca's test for Alcohol -  $\text{R-OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{R-Cl} + \text{H}_2\text{O}$  (ppt white)

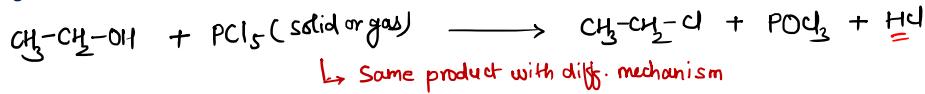
- ① 3° Alcohol  $\longrightarrow$  R-Cl ↓ - Immediately
- ② 2° Alcohol  $\longrightarrow$  R-Cl ↓ - After 5 - 10 min
- ③ 1° Alcohol  $\longrightarrow$  No React at Room temp

## Preparation Alkyl Halide

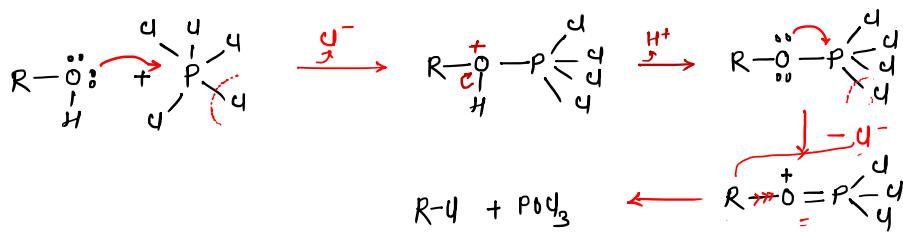


### From Alcohol

#### B. By $\text{PCl}_5$



Mechanism —  $\text{PCl}_5$  (gas)  $\rightarrow \text{S}^{\text{N}}\text{i}$  - Intramolecular React<sup>+</sup> — NO c+ intermediate

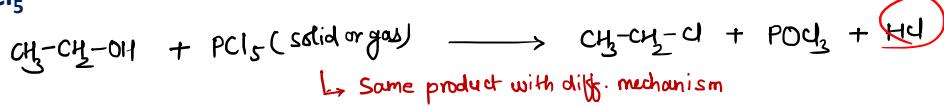


## Preparation Alkyl Halide

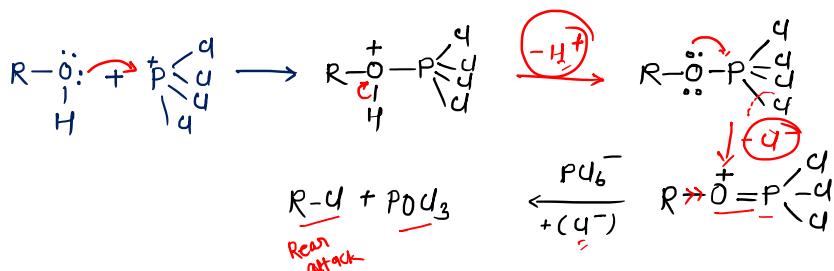
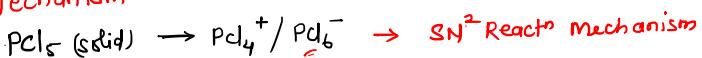


### From Alcohol

#### B. By $\text{PCl}_5$



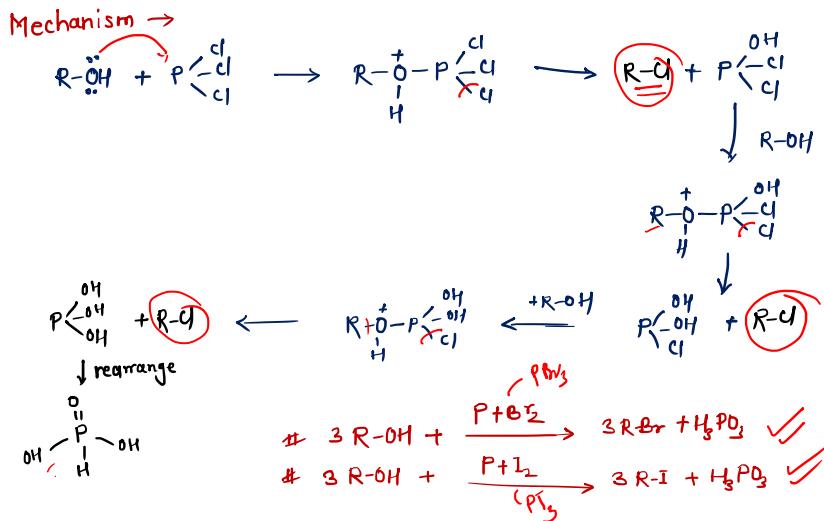
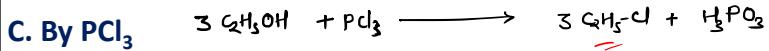
Mechanism —



## Preparation Alkyl Halide



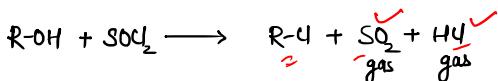
### From Alcohol



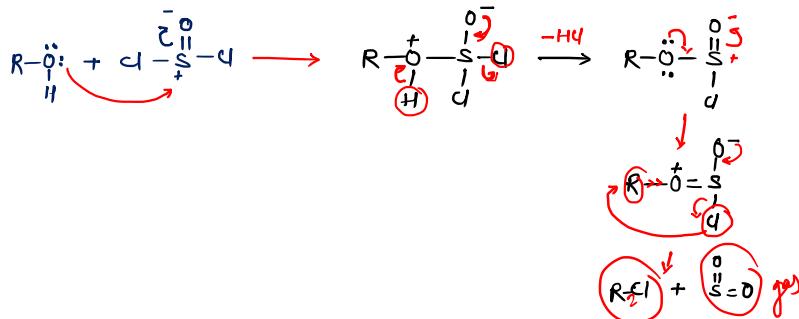
## Preparation Alkyl Halide



### From Alcohol



Mechanism →  $\text{S}^{\text{N}}\text{i}$  Reaction mechanism





# Alkyl Halide

## Organic Chemistry Preparation Methods

Halogen Exchange Methods

- a) Finkelstein Reaction
- b) Swartz Reaction

Hunsdiecker/Borodine-Hunsdiecker  
Reaction

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### Preparation of Alkyl Halide



#### Methods

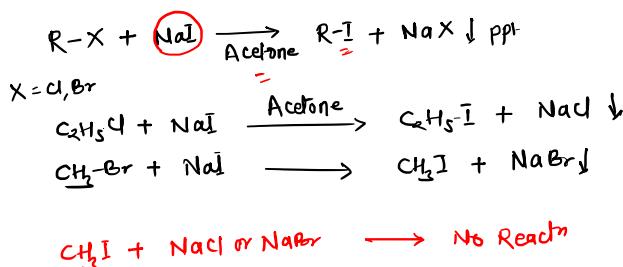
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## Preparation Alkyl Halide



### 4. Halogen Exchange Method

#### a) Finkelstein Reaction- exclusively for preparation of alkyl iodide (RI)



# Acetone - Co-valent solvent

# Fajan's Rule -  $\frac{+}{\ominus}$   $\frac{-}{\oplus}$   $\rightarrow \uparrow$  covalent character  
in ionic bond

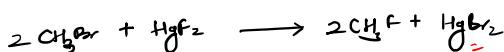
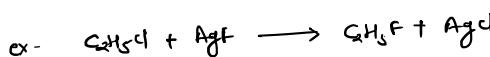
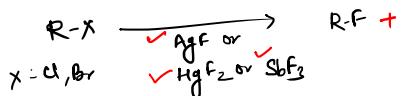
$\hookrightarrow$   $NaI \rightarrow$  have good covalent character  
and soluble in acetone

## Preparation Alkyl Halide



### 4. Halogen Exchange Method

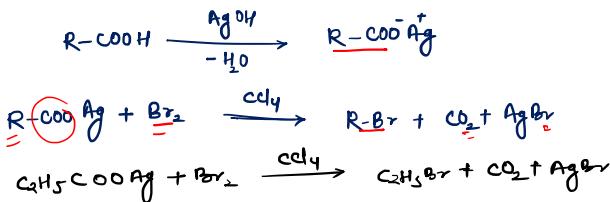
#### a) Swartz Reaction- exclusively for preparation of alkyl fluoride (RF)



## Preparation Alkyl Halide



### 5. Hunsdiecker/Borodine-Hunsdiecker Reaction

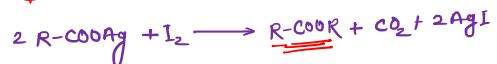


\* For prep. of alkyl Bromide

\* Descent of chain

\* silver salt of carboxylic acid is used

\* Bimbaum Simonini Reactn



Mechanism — Free Radical mechanism

