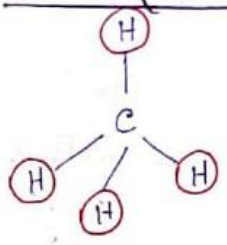
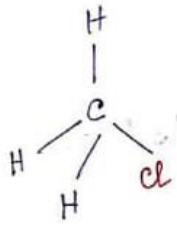
: Haloalkane :



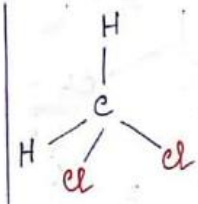
CH_4 → methane.

If, the H atoms are replaced with halogen atoms, then this is called haloalkane.



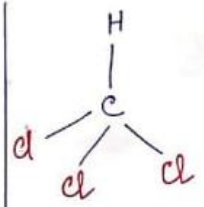
monohaloalkane

chloromethane



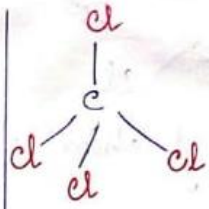
dihaloalkane

dichloro methane (DCM)



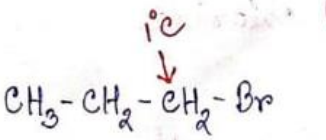
trihaloalkane

trichloro methane



tetrahaloalkane

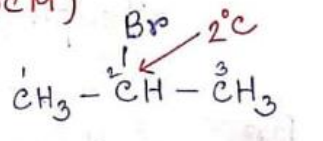
tetrachloro methane



Bromopropane

(1° haloalkane)

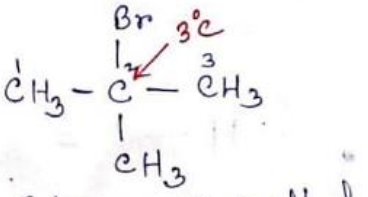
n-propyl bromide



2-bromopropane

(2° haloalkane)

iso propyl bromide



2-bromo-2-methyl propane

(3° haloalkane)

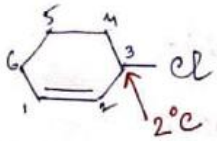
tert butyl bromide

More Examples:

3-chloro prop-1-ene

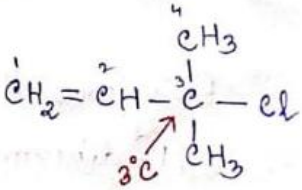
(allyl chloride)

(1°)



3-chlorocyclohexene

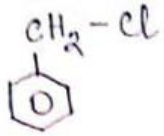
(2° allyl chloride)



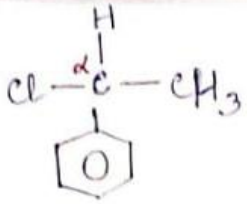
3-chloro-3-methyl butene

(3° allyl chloride)

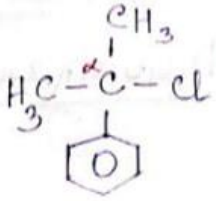
allyl halide

- 

Benzyl chloride
(1°)



α-phenylethyl chloride
(2°)

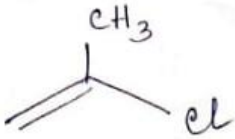


α-methyl-α-phenyl ethyl chloride
(3°)

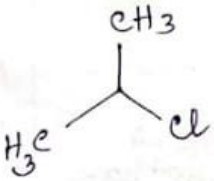
Benzyl halide

- 

Venyl chloride



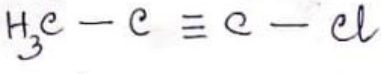
Isopropenyl chloride



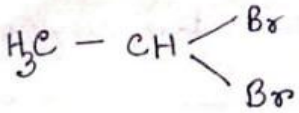
Isopropyl chloride

- 

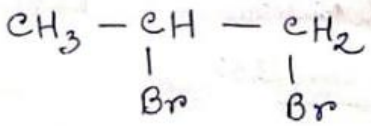
Bromoethyne



Chloropropyne

- 

Ethylene dibromide
(1,1-dibromo ethane)
Zem-dihalide
(Zeminal)



Propylene dibromide
(1,2-dibromo propane)
Vic-dihalide
(Vicinal)

Preparation of Haloalkane :

1. From alcohol :

$$R-OH + HX \longrightarrow R-X + H_2O$$

Reactivity of halogen acid : HI > HBr > HCl

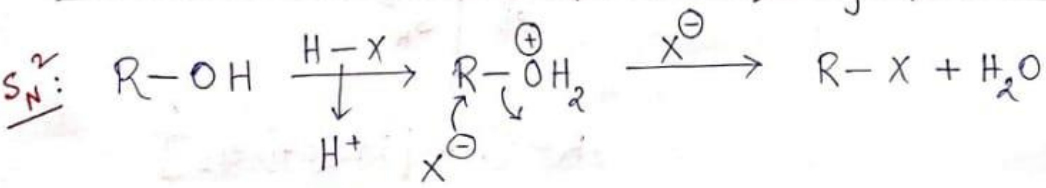
Reactivity of alcohol : 3° alc. > 2° alc. > 1° alc.

Reactivity of alcohol in S_N1 reaction mechanism : 3° > 2° > 1°

Reactivity of alcohol in S_N2 reaction mechanism : 1° > 2° > 3°

Mechanism for 1° alcohol (methanol) to prepare haloalkane:

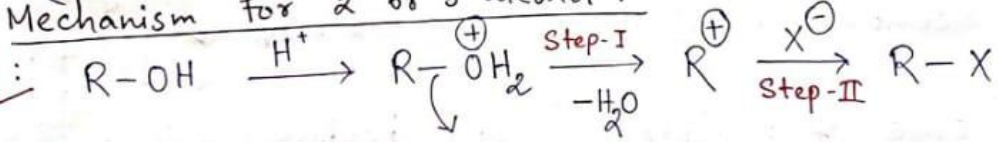
S_N2:



(R = $-CH_3$ ⟹ methanol)

Mechanism for 2° or 3° alcohol :

S_N1:



(R = $H_3C-\underset{\underset{CH_3}{|}}{CH}-$ ⟹ isopropyl alcohol, 2° alcohol)

(R = $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-$ ⟹ tert-butyl alcohol, 3° alcohol)

S_N1:
1. Two step mechanism.
2. Retention and inversion of configuration.
3. Rate = K [Reactant]
   = K [R–OH]
4. 1st order reaction.

S_N2:
1. Single step, concerted pathway.
2. Inversion of configuration.
3. Rate = K [Reactant][Nucleophile]
   = K [R–OH][H–X]
4. Second order reaction.

$CH_3CH_2CH_3 \xrightarrow[\text{room temp.}]{Cl_2/h\nu} CH_3CH_2CH_2Cl + CH_3\underset{\underset{Cl}{|}}{C}HCH_3$

1-chloropropane (45%) minor

2-chloropropane (55%) major

$CH_3CH_2CH_2CH_3 \xrightarrow[127^\circ C]{Br_2/h\nu} CH_3CH_2CH_2CH_2Br + CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$

1-bromobutane (2%) minor

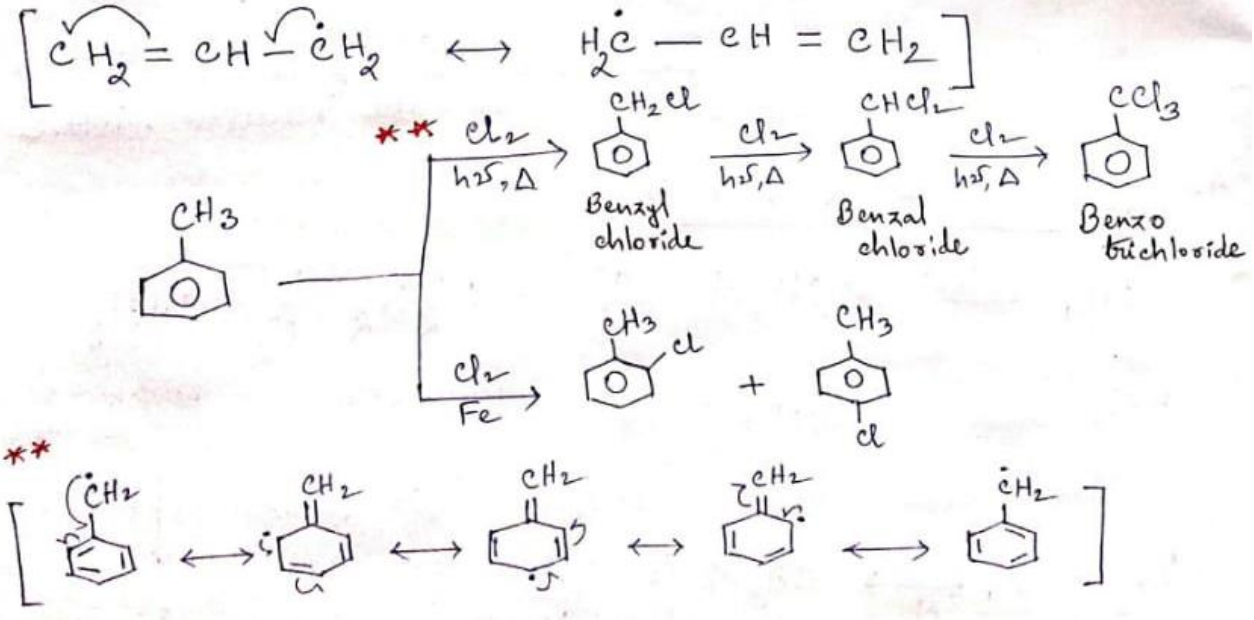
2-bromobutane (98%) major

Reactivity order of Hydrogen : $3^\circ H > 2^\circ H > 1^\circ H$

- Benzylic and allylic radicals are highly reactive because they can form resonating structures. So benzylic and allylic H are highly reactive.

$CH_2=CH-CH_3 \xrightarrow[\text{High temp.}]{Cl_2} CH_2=CH-CH_2Cl + HCl$

3-chloro prop-1-ene



5. Reaction with alkene:

- Symmetrical alkene:

$CH_3CH=CHCH_3 + HBr \longrightarrow CH_3-\underset{H}{CH}-\underset{Br}{CH}-CH_3$

(single product)

2-bromobutane

- Assymetrical alkene:

$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{CH}-CH_3 + CH_3-CH_2-\underset{Br}{CH_2}$

2-bromopropane (major) 90%

1-bromo propane (minor) 10%.

This type of addition is called Markownikoff addition.

$CH_3-CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3-CH_2-\underset{Br}{CH_2} + CH_3-\underset{Br}{CH}-CH_3$

peroxide → H_2O_2, Na_2O_2

1-bromopropane (major) 90%

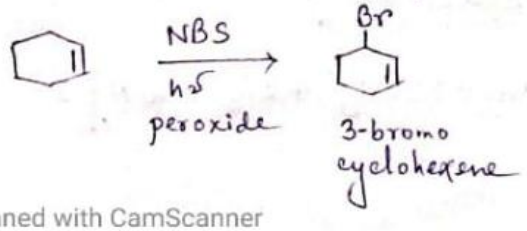
2-bromo propane (minor) 10%

This type of addition is called Anti Markownikoff addition.

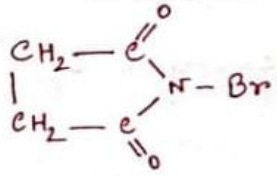
- Allylic Bromination: (Using NBS, N-bromosuccinamide)

$CH_2=CH-CH_3 \xrightarrow[h\nu]{\text{NBS, little peroxide}} CH_2=CH-CH_2-Br$

allyl bromide



3-bromo cyclohexene



NBS

- **Allylic Chlorination** : (Using Sulfuryl chloride, SO_2Cl_2)

$$CH_2=CH-CH_3 + SO_2Cl_2 \xrightarrow{475K} CH_2=CH-CH_2Cl + SO_2 + HCl$$

allyl chloride

6. **By exchange of halogen atom** :

- **Finkelstein Reaction** :

$$CH_3CH_2Cl + NaI \xrightarrow[\Delta]{\text{acetone}} CH_3CH_2I + NaCl$$

chloroethane — iodoethane

- **Swarts Reaction** :

Inorganic fluorides → AsF_3, AgF, SbF_3, Hg_2F_2 have to use in this reaction

$$2\,CH_3CH_2Cl + Hg_2F_2 \longrightarrow 2\,CH_3CH_2F + Hg_2Cl_2$$

fluoroethane

7. **From Carboxylic Acid** :

- **Hunsdicker Reaction** :

$$CH_3COOAg + Br_2 \xrightarrow[\text{reflux}]{CCl_4} CH_3Br + CO_2 + AgBr$$

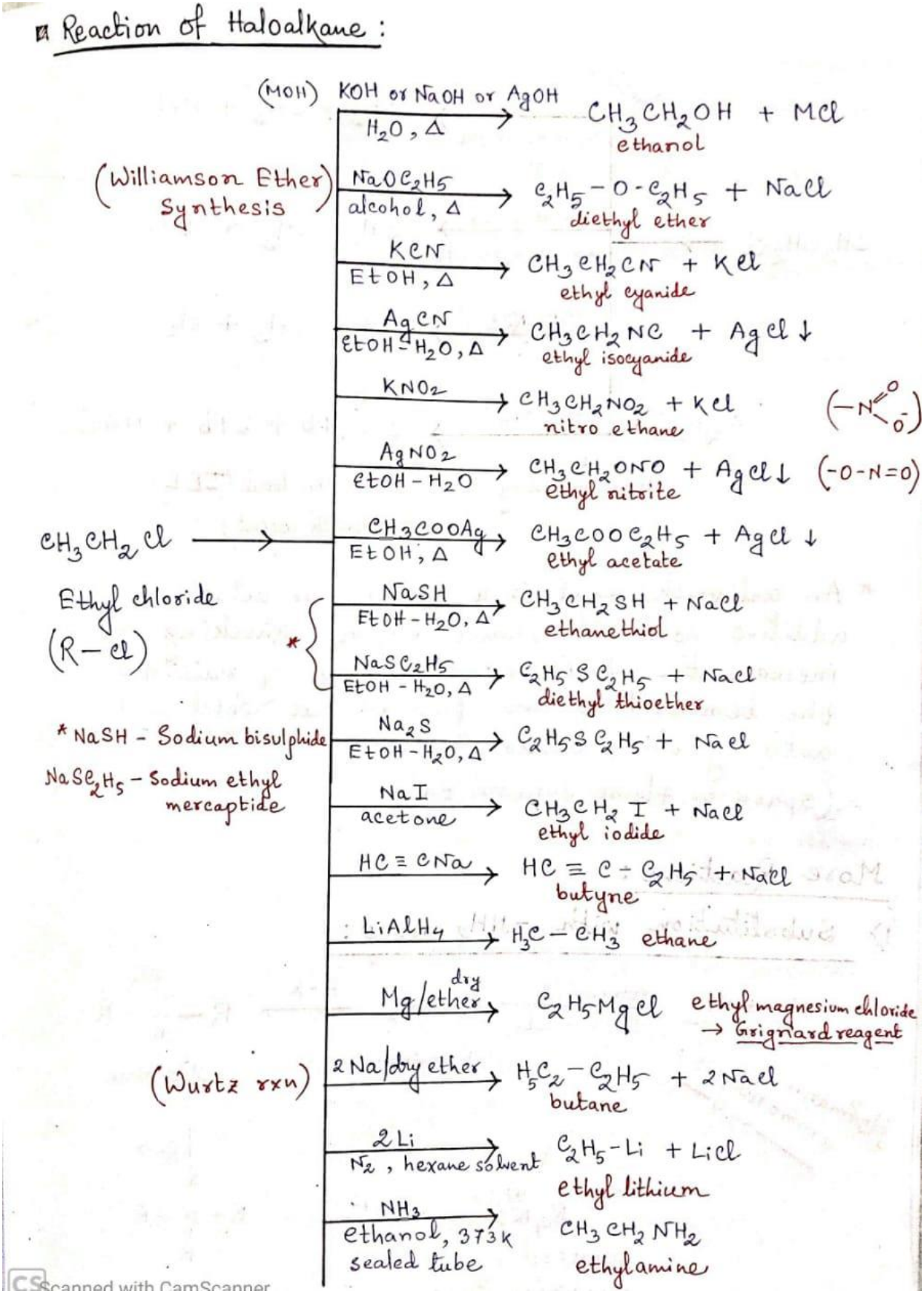
Silver acetate — methyl bromide

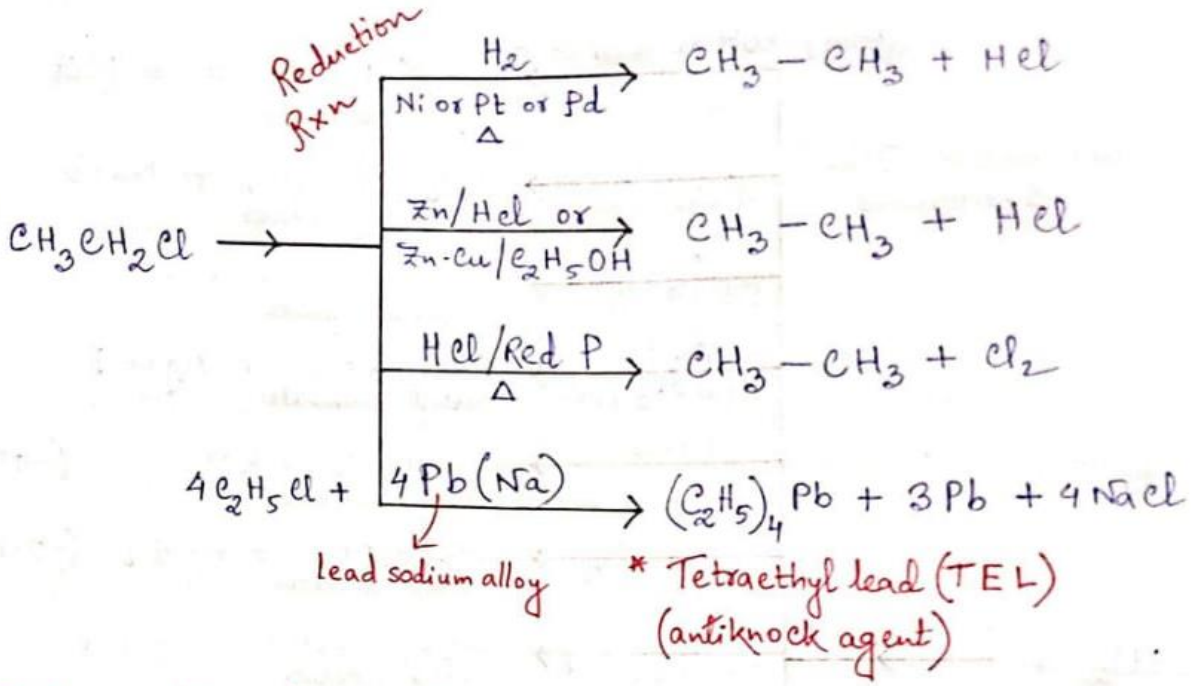
Using the above procedure, we can not prepare alkyl iodide. In this case, ester will be formed.

Birnbaum - Simonini Reaction :

$$2\,CH_3COOAg + I_2 \xrightarrow[\text{reflux}]{CCl_4} CH_3COOCH_3 + CO_2 + 2\,AgI$$

Reaction of Haloalkane :





* An antiknock agent is a gasoline or petrolium additive used to reduce engine knocking and increase the fuel's octane rating by raising the temperature and pressure at which auto-ignition occurs.
(spark or flame generation)

More Reactions:

1) Substitution with $-NH_2$ group:

Hofmann ammonolysis:

$R-X + NH_3 \xrightarrow[\text{Sealed tube}]{\text{ethanol}/\Delta} R-NH_2$ (1° amine) $\xrightarrow{R-X}$ $R-\underset{H}{N}-R$ (2° amine) $\xrightarrow{R-X}$ $R-\underset{R}{\overset{R}{N}}-R$ (3° amine) $\xrightarrow{R-X}$ $R_4\overset{\oplus}{N}X^{\ominus}$ quaternary ammonium salt.

Example:

$CH_3CH_2Br + NH_3 \xrightarrow[\text{sealed tube}]{EtOH, \Delta} CH_3CH_2NH_2 + HBr$

$CH_3CH_2NH_2$: 1° amine, ethyl amine

CH_3CH_2Br, EtOH, Δ, sealed tube

$(CH_3CH_2)_2NH + HBr \xleftarrow[EtOH, \Delta]{CH_3CH_2Br} (CH_3CH_2)_3N + HBr$

$(CH_3CH_2)_2NH$: 2° amine, N,N-diethyl amine

$(CH_3CH_2)_3N$: 3° amine, N,N,N-triethyl amine

CH_3CH_2Br, EtOH, Δ, sealed tube

$(CH_3CH_2)_4N^{\oplus}Br^{\ominus}$

Tetraethyl ammonium bromide (quaternary ammonium salt)

2) Rearrangement of haloalkane:

Example: 1 $CH_3CH_2CH_2Cl \xrightarrow[573K]{AlCl_3} CH_3CHClCH_3$

1-chloropropane → 2-chloropropane

Anhydrous $AlCl_3$ → acts as Lewis acid

Mechanism:

$CH_3CH_2CH_2-\ddot{Cl}: \xrightarrow{AlCl_3} CH_3-\overset{H}{\overset{\curvearrowleft}{CH}}-CH_2-\overset{\oplus}{Cl}-AlCl_3^{\ominus}$

$\xrightarrow{H^{\ominus}\ shift}$

$AlCl_3-Cl^{\ominus} + CH_3-\overset{\oplus}{CH}-CH_3$

$H_3C-\underset{Cl}{CH}-CH_3 + AlCl_3$

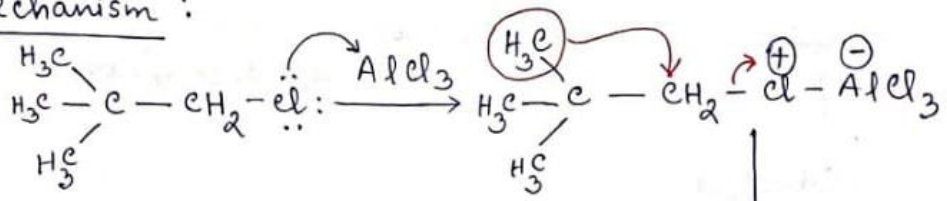
Example - 2 :

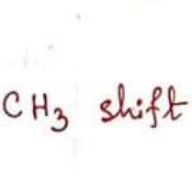
$(CH_3)_3C\,CH_2Cl \xrightarrow[573K]{anhy.\ AlCl_3} (H_3C)_2C(Cl)CH_2CH_3$

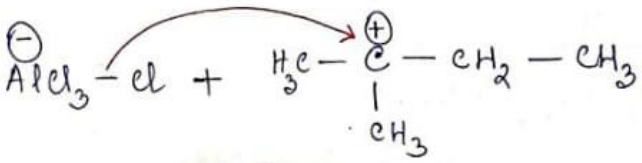
1-chloro-2,2-dimethyl propane (neopentyl chloride)

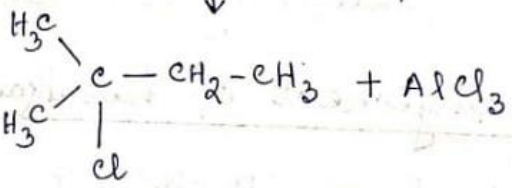
2-chloro-2-methylbutane

Mechanism :





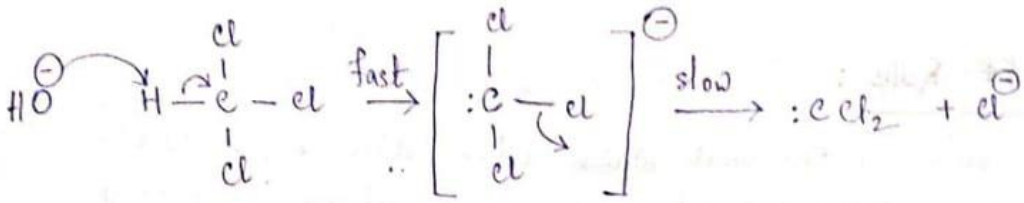




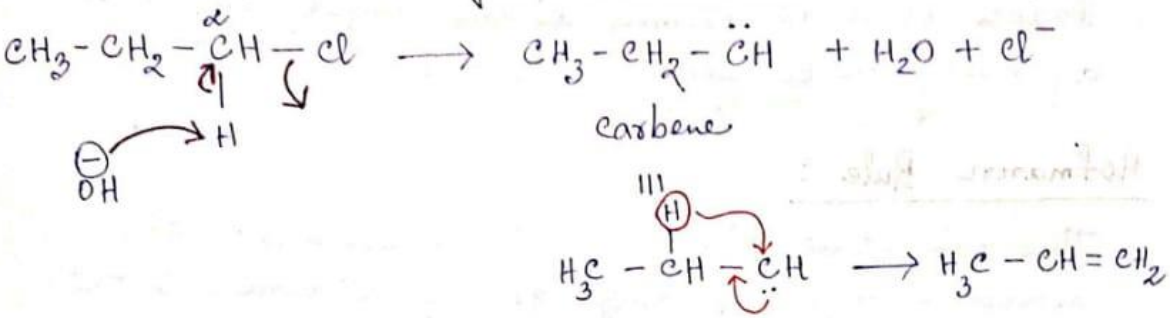
3) Elimination Reaction (Dehydrohalogenation Rxn):

(i) α - Elimination or (1,1) - Elimination :

Elimination reaction involving loss of two atoms or groups from the same atom in a molecule, leading to the formation of hypovalent neutral species like carbene, is called α - elimination or (1,1)-elimination.



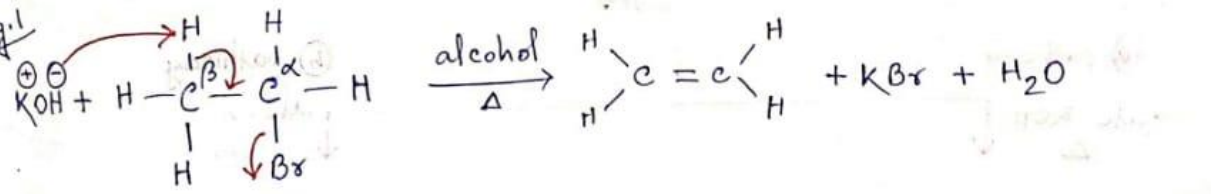
1,1 - elimination leading to formation of alkene :



(ii) β - elimination or (1,2) - elimination :

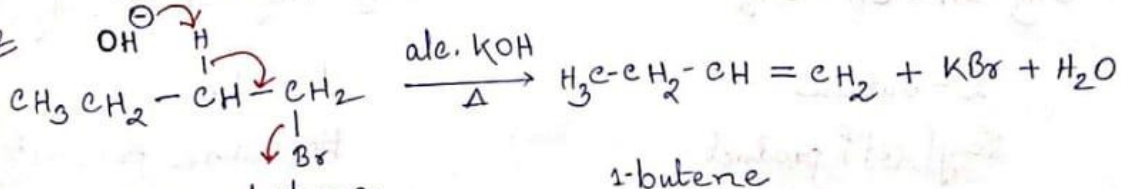
When two substituents in a substrate molecule are lost from a pair of adjacent centres in a chain or ring, that reaction is called β-elimination or (1,2) - elimination.

Eg.1



bromoethane

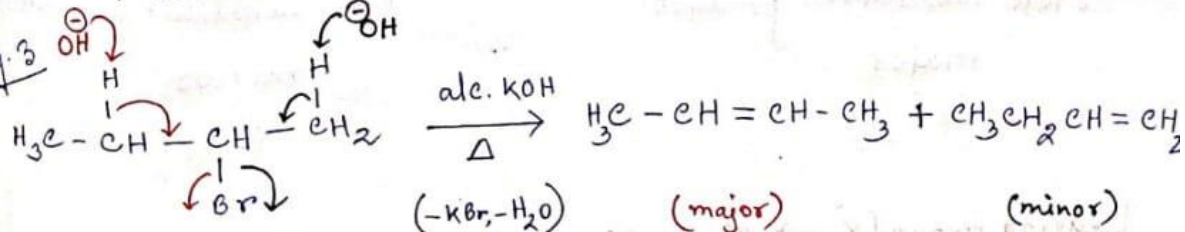
Eg.2



1-bromo butane

1-butene

Eg.3



2-bromobutane

(major) 2-butene

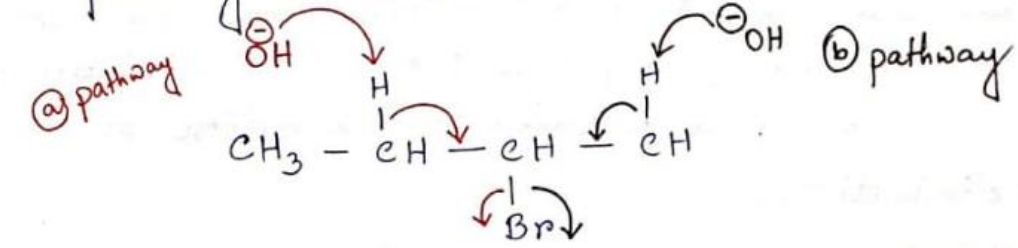
(minor) 1-butene

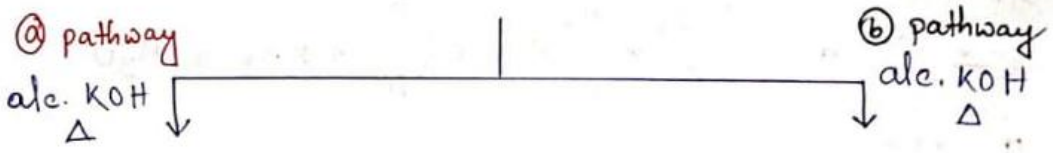
Saytzeff Rule :

This rule states that when alternative regioselective isomeric alkenes are possible, the alkene bearing highest number of alkyl groups attached to the double bond is formed as the major compound depending on certain conditions.

Hofmann Rule :

This rule states that the alkene which has the lowest number of alkyl groups attached to the double bond is also possible (minor product) depending on certain conditions.





$CH_3-CH=CH-CH_3$

2-butene

Saytzeff product

More substituted product

major

(80%)

$CH_3-CH_2-CH=CH_2$

1-butene

Hofmann product

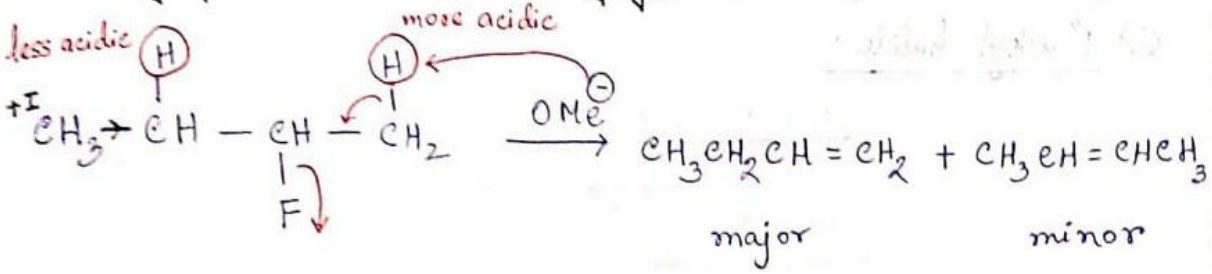
Less substituted product

minor

(20%)

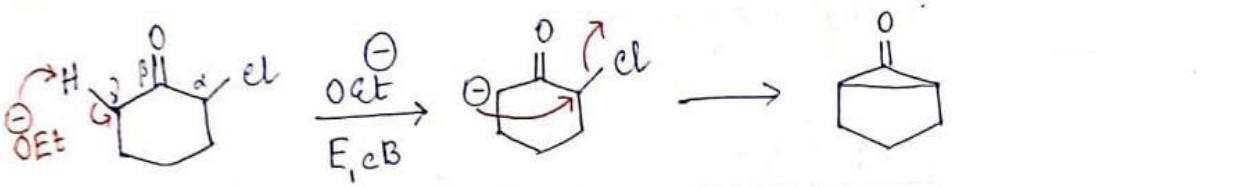
Leaving group (X) → Cl, Br, I ⇒ Saytzeff pdt major

Leaving gr. → F (bad leaving gr.) ⇒ Hofmann pdt major



(iii) γ-elimination or (1,3)-elimination :

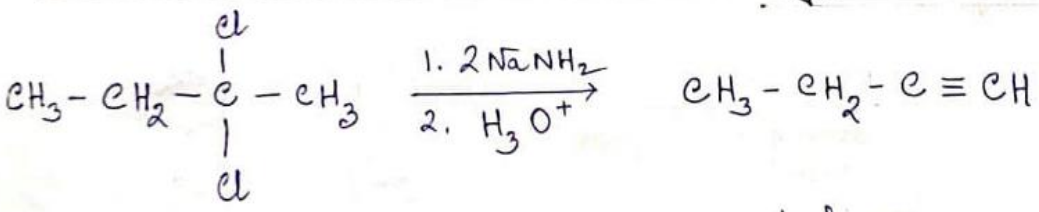
Elimination reaction in which two leaving groups are separated by another atom is called γ-elimination or (1,3)-elimination.



2-chlorocyclohexanone

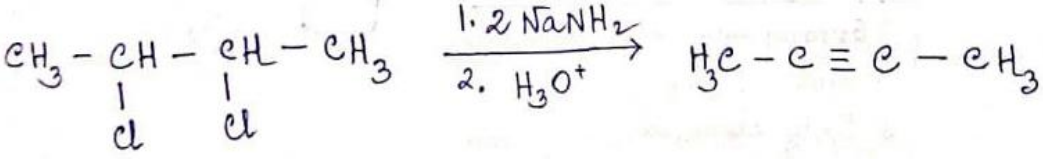
Bicyclo-[3.1.0]-hexan-6-one

4) Formation of C≡C Triple bond by Elimination Reaction:



2,2-dichlorobutane

butyne



2,3-dichlorobutane

2-butyne

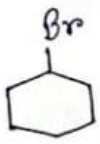
5) Elimination vs. Substitution of haloalkane :

(i) 1° alkyl halide :

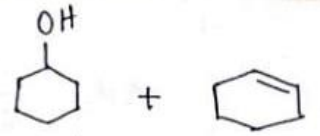
CH_3CH_2Br

- $KOH, H_2O, 100^\circ C$ → CH_3CH_2OH (S_N^2)
  1. Strong nucleophile and base
  2. polar solvent
- KOH, alcohol, $200^\circ - 280^\circ C$ → $H_2C=CH_2$ (E_2)
  1. Strong nucleophile and base
  2. Less polar solvent
  3. High temperature
- $K^{\oplus}O^{\ominus}C(CH_3)_3$ → $H_2C=CH_2$ (E_2)
  1. Strong and large size base
  2. Not act as nucleophile
  3. Only elimination possible

(ii) 2° alkyl halide :-

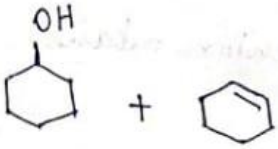


- KOH, alcohol
  1. Strong nucleophile and base

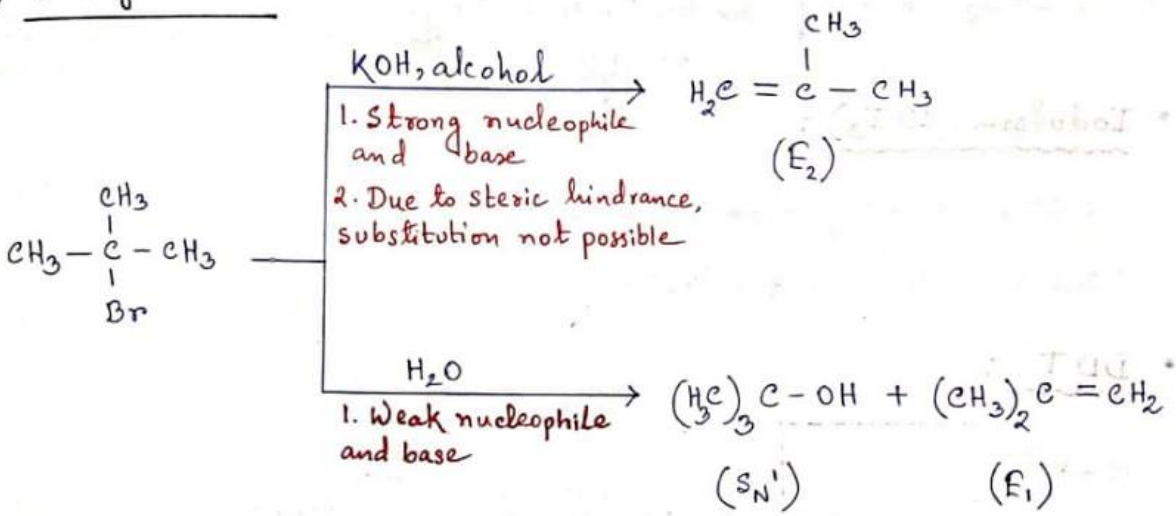
  (S_N^2) + (E_2)
- $K^{\oplus}O^{\ominus}C(CH_3)_3$
  1. Strong and large size base
  2. Not act as nucleophile
  3. Only elimination possible

   (E_2)
- H_2O
  1. Weak nucleophile and base

  (S_N^1) + (E_1)

(iii) 3° alkyl halide :



Polyhalogen Compounds :

Compounds having more than one halogen atom.

E.g. - Dichloro methane (DCM) - CH_2Cl_2

Trichloro methane (chloroform) - $CHCl_3$

Triiodo methane (Iodoform) - CHI_3

Tetrachloro methane (carbon tetrachloride) - CCl_4

Chloro fluoro carbon (CFC) or Freon

Dichloro diphenyl trichloroethane (DDT)

• Chloroform ($CHCl_3$) :

i) $$2CHCl_3 + O_3 \xrightarrow{h\nu} 2COCl_2 + 2HCl$$

phosgene (carbonyl chloride) ⇒ harmful poisonous gas

To restrict this oxidation of chloroform 0.6 – 1% pure ethanol is added to it and kept it in airtight brown or black bottle in a dark place. Here ethanol acts as antioxidant.

If a little amount phosgene is formed, then it reacts with ethanol and produce less toxic diethyl carbonate.

$$O=C(Cl)(Cl) + 2\,C_2H_5OH \longrightarrow O=C(OC_2H_5)(OC_2H_5) + 2HCl$$

diethyl carbonate

ii) $2\,CHCl_3 + 6\,Ag \xrightarrow{\Delta} HC \equiv CH + 6\,AgCl$

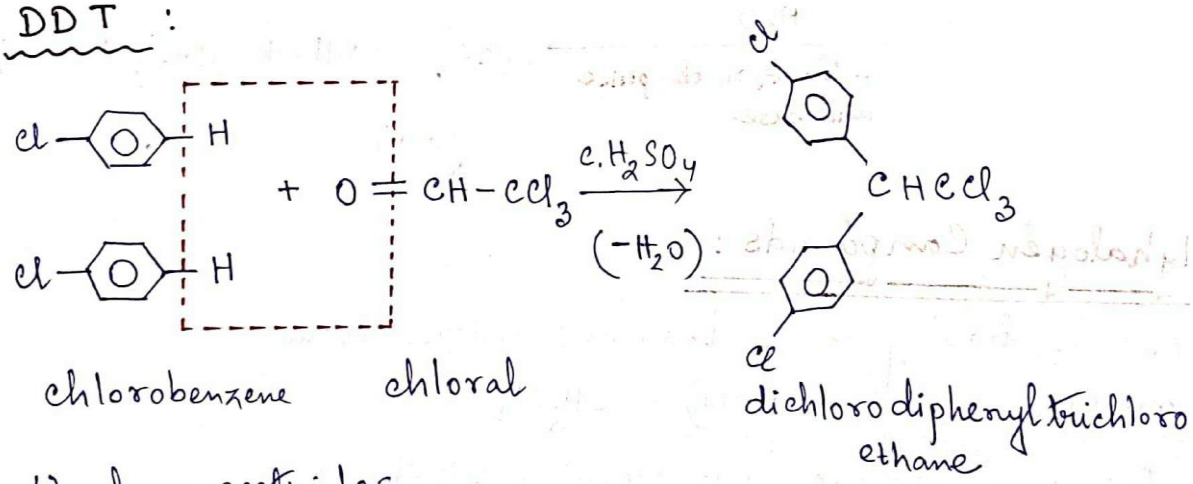
acetylene

- **Iodoform (CHI_3):**

$$2\,CHI_3 + 6\,Ag \xrightarrow{\Delta} HC \equiv CH + 6\,AgI$$

Used as antiseptic for dressing.

- **DDT :**



chlorobenzene chloral

dichloro diphenyl trichloro ethane

Used as pesticides.

- **Carbon tetrachloride (CCl_4):**

CCl_4 is also referred as pyrene and it can be used as a fire extinguisher.