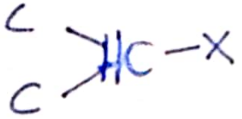
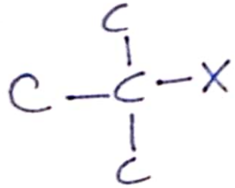
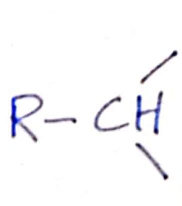
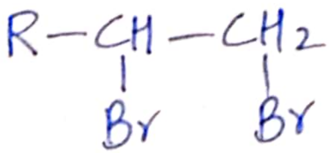
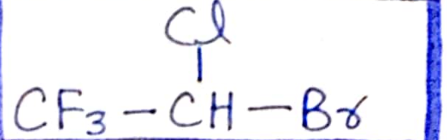
ALKYL HALIDE (R-X)

- Monohalo derivatives of alkane.
- $C_nH_{2n+1}X$ (X = F, Cl, Br, I)
- $C-H_2C-X$ = Primary.
- 
  C_2HC-X = Secondary
- 
  $C-C(C)(C)-X$ = Tertiary
- Organohalogen compounds.

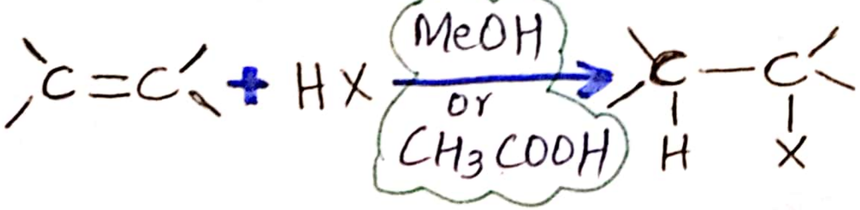
- 
  $R-CHBr_2$ = Geminal Dihalide
- 
  $R-CH(Br)-CH_2(Br)$ = Vicinal Dihalide.


$CF_3-CH(Cl)-Br$

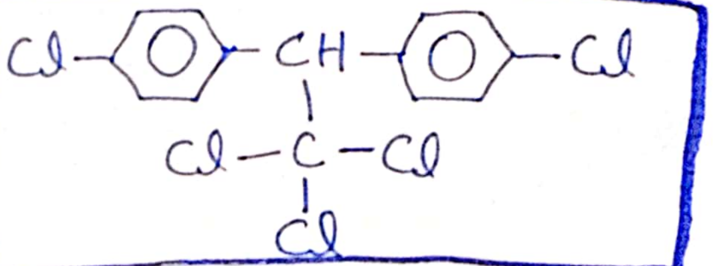
Anesthetic

PREPARATION :-

1. From Alkene (Addition of HX)


$$>C=C< + HX \xrightarrow[\text{or } CH_3COOH]{MeOH} >C(H)-C(X)<$$

- HI > HBr > HCl.



DDT

2. From Alkane :- (Halogenation)

$$R{-}H + \underset{(Cl_2\ or\ Br_2)}{X_2} \xrightarrow[250-400^\circ C]{\Delta\ or\ h\nu} R{-}X + HX$$

- $Cl_2 > Br_2$, difficult to handle gaseous Cl_2 so, $SOCl_2$ used.
- Mix of products formed.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

3. From Alcohol : $\boxed{PX_3\ /\ PX_5\ /\ SOCl_2{-}Py\ /\ HX}$

$$ROH + HX \longrightarrow R{-}X + H_2O$$

- ROH Reactivity order: Benzyl & 3° > 2° > Methyl > 1°
- HX Reactivity order: HI > HBr > HCl

4. From Carboxylic Acid : (Hunsdicker Reaction)

$$\underset{(RCOOH\ +\ Ag_2O)}{RCOO^-Ag} + Br_2 \xrightarrow{CCl_4} RBr + CO_2 + AgBr$$

- R–X formed in order of : Pri > Sec > Ter

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5- Halide Exchange: (For preparation of alkyl iodide)

$$RX + NaI \xrightarrow{\text{Acetone}} RI + NaX$$ (Finkelstein Reaction)

X = Br, Cl

PHYSICAL PROPERTIES

- CH_3Cl , CH_3Br , C_2H_5Cl —— Gases at 25°C
- Soluble in organic solvents.
- M.P° and B.P° higher than corresponding alkane.
- More dense than hydrocarbons.
- B.P° order $\boxed{(1° > 2° > 3°)}$
- Density of iodo, bromo and poly chloro compounds is higher than water.

CHEMICAL REACTIONS

a) Substitution Nucleophilic

b) Elimination.

- R-Br more reactive than R-Cl (Cheaper)

(used in laboratories) (used in industries)

1. Reduction :- (to alkane)

$R-X + Zn + HX \longrightarrow RH + ZnX_2$

$4R-X + LiAlH_4 \longrightarrow 4RH + AlX_3$

$R-X + H_2 \xrightarrow{Pd-C} RH + HX$

2. Reaction with metals :- (to form organometallic compounds)

$R-Cl + 2Li \xrightarrow[-10^\circ C]{ether} RLi + LiCl$

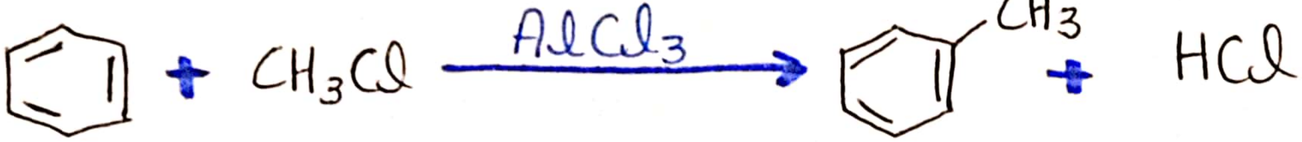
$R-Cl + Mg \xrightarrow{ether} R-MgCl$

3. Wurtz Reaction :-

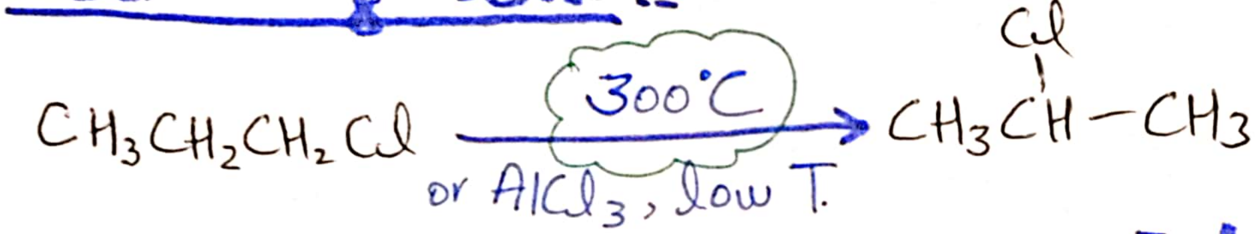
$2CH_3-Cl + 2Na \longrightarrow CH_3-CH_3 + 2NaCl$

- work for Primary alkyl halide, fails with 3°

4. Friedal craft Reaction :-

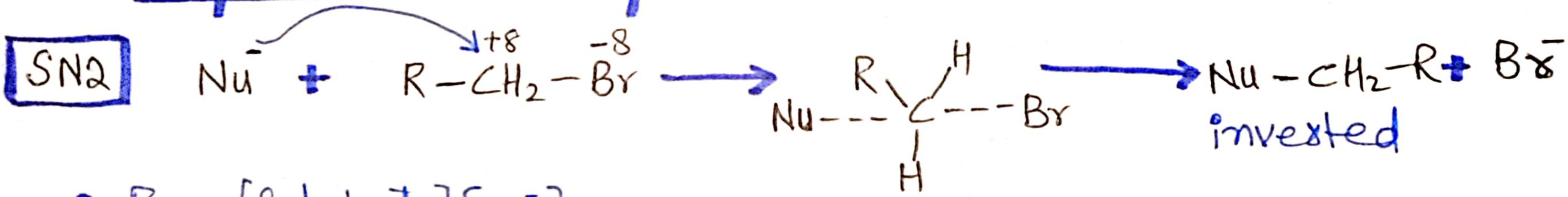


5. Rearrangment :-

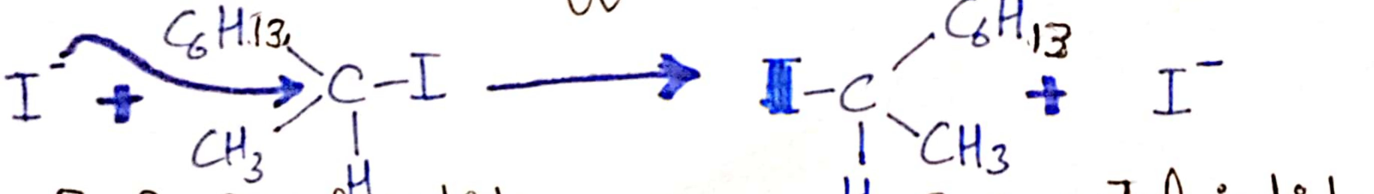


$$CH_3CH_2CH_2Cl \xrightarrow[\text{or } AlCl_3,\ \text{low T.}]{300^\circ C} CH_3\overset{Cl}{C}H-CH_3$$

6. Aliphatic Nucleophilic substitution :-

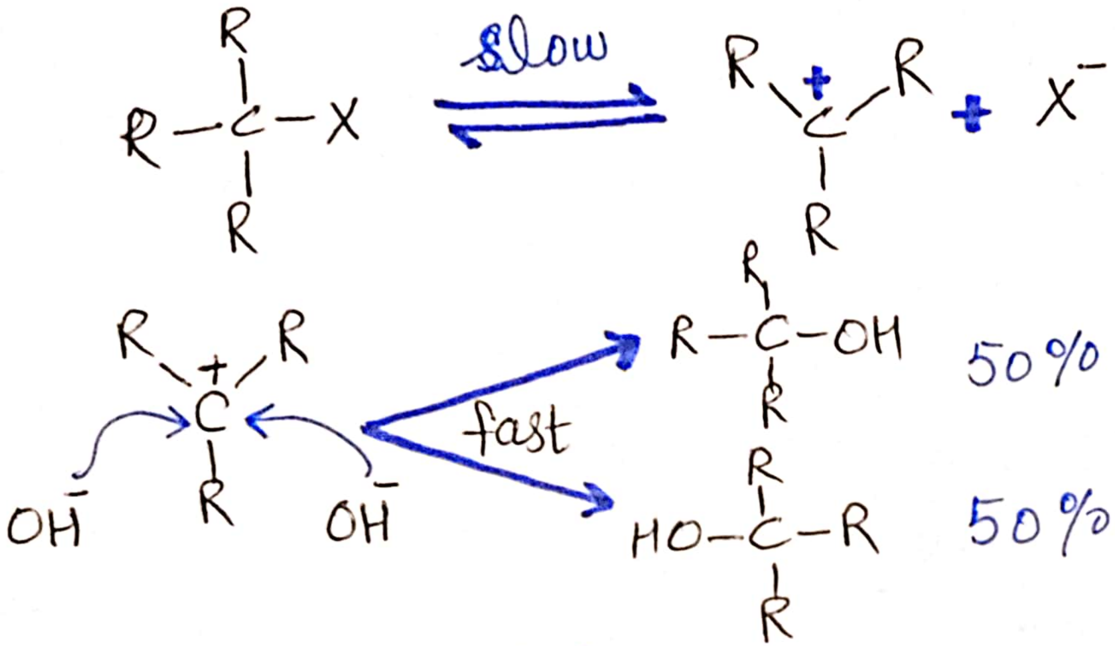


- $R \propto [\text{Substrate}][Nu^-]$
- Order of reaction = 2
- Stereochemical effect: Walden Inversion.



R- 2- Octyl iodide

S-2-octyl iodide



- $R \propto [\text{Substrate}]$
- Order of Reaction = 1.

Factors affecting SN Reactions:-

I. Effect of Substrate

SN2: $CH_3 > 1^\circ > 2^\circ > 3^\circ$

SN1: $3^\circ > 2^\circ > 1^\circ > CH_3$

R group	SN2	SN1
$-CH_3$	30	1
$-C_2H_5$	1	1
—isopropyl	0.02	12
t-butyl	0	1200000

II. Effect of Nu^-:

- **SN2:** -ve charge of Nu must be stronger than its conjugated acid $\boxed{OH^- > H_2O}$

- $NH_2^- > RO^- > \overset{-}{O}H > R_2NH > NH_3 > F^- > H_2O > ClO_4^-$

- Order of Nucleophilicity of X $\boxed{I^- > Br^- > Cl^- > F^-}$

- Large ions are more polarizable. $\boxed{RS^- > RO^-}$

- **SN1:** No effect

III. Effect of Solvent:

- **SN1:** polar solvent stabilizes C^+
  - Rate of hydrolysis increases 100 times when solvent changes from R-OH to H_2O
- favors by polar solvent.
- **SN2:** less polar solvent
- favors by non-polar solvent

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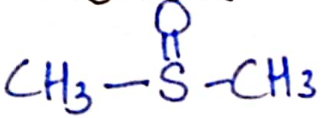
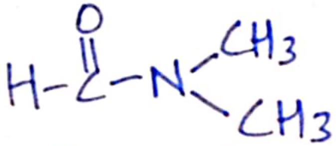
- Aprotic polar solvent favors SN2.

→ DMSO



$CH_3-\overset{O}{\overset{\|}{S}}-CH_3$

→ DMF



$H-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$

IV. Effect of leaving group:

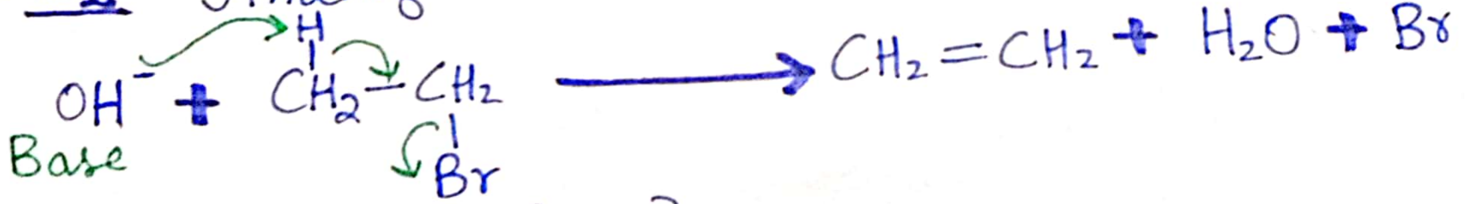
Best leaving group —— one that is stable after apart

- Good leaving groups: Cl^-, Br^-, I^-, HSO_4^-
- Poor leaving groups: OH^-, OR^-, NH_2^-

7- Elimination Reactions:

β-H , Alcoholic KOH

- **E₂** Analogue to SN2



$OH^- + \overset{H}{\overset{|}{C}H_2}-\underset{Br}{\underset{|}{C}H_2} \longrightarrow CH_2=CH_2 + H_2O + Br^-$

- $R \propto [Substrate][Base]$
- Order of Reaction = 2.

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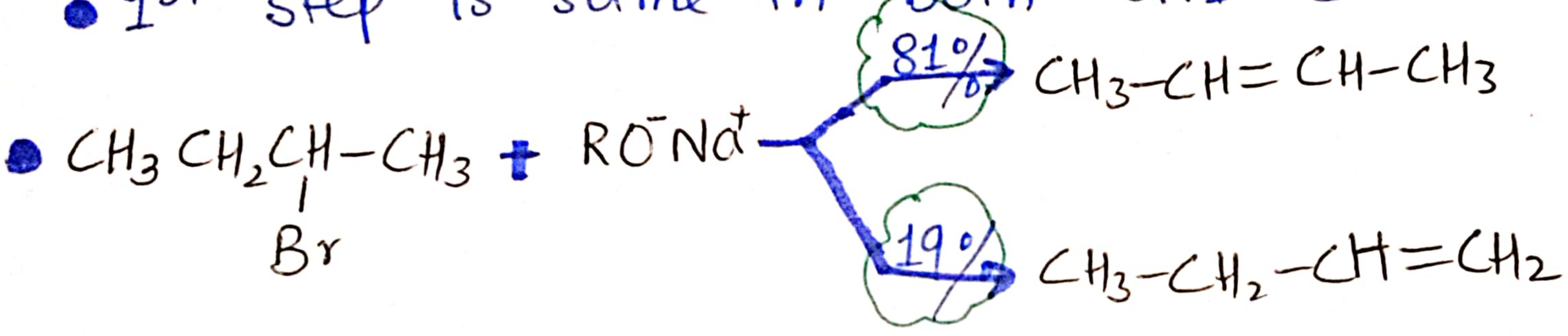
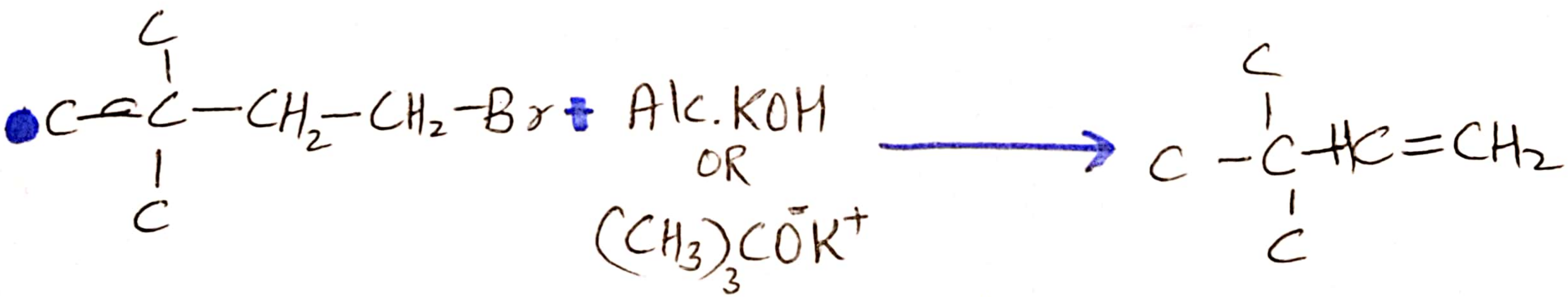
- **E1**: Analogue to SN1.
- Order of Reaction = 1.
- 1st step is same in both SN1 & E1.



$$CH_3CH_2\underset{|\atop Br}{CH}-CH_3 + RO^-Na^+ \begin{cases} \xrightarrow{81\%} CH_3-CH=CH-CH_3 \\ \xrightarrow{19\%} CH_3-CH_2-CH=CH_2 \end{cases}$$

Sytzeff's Rule



$$C-\overset{C}{\underset{C}{C}}-CH_2-CH_2-Br + \text{Alc. KOH} \text{ OR } (CH_3)_3CO^-K^+ \longrightarrow C-\overset{C}{\underset{C}{C}}-HC=CH_2$$

Hoffman Rule.

- Substitution competes with Elimination.

I. Effect of Substrate :-

- Crowding / Steric hindrance favours elimination.

II. Effect of Temperature :-

- Activation energy (Elimination > Substitution)
- High Temp. favours substitution.

III. Effect of Solvent:

- Elimination reaction is favoured by decreasing polarity

H_2O — Sub
R–OH — Eli

IV. Effect of Base:

- Strong base — E2 favoured. over SN1.
- Low conc. base — SN1 favoured over E1

GRIGNARD REAGENT

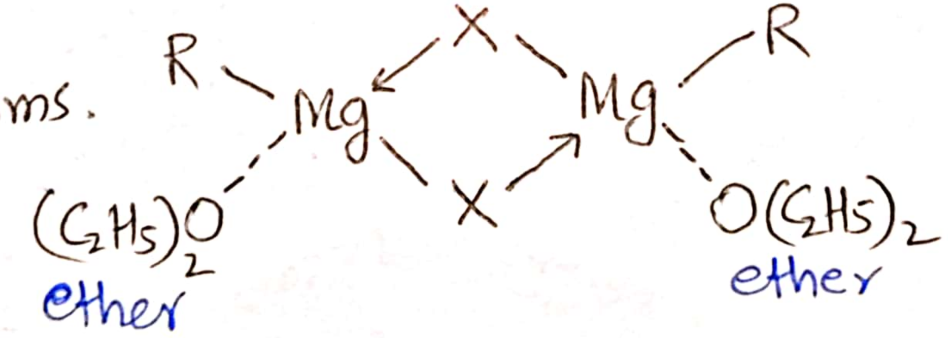
$$R{-}X + Mg \xrightarrow[\text{6-8 hours heating.}]{\text{dry ether}} R{-}Mg{-}X$$

R: 3° > 2° > 1°

X: I > Br > Cl

THF can also be used.

- Dimeric forms.



- Order of reactivity of R–X   R = $CH_3 > C_2H_5 > C_3H_7$

- **Reactivity** :- $-\overset{\delta-}{\underset{|}{\overset{|}{C}}}-\overset{+\delta}{Mg}-X$
  - Nucleophilic C
  - Most reactions — Exothermic
- **Reactions** :

	Reagent	**Product on Hydrolysis**
RMgX	Formaldehyde $H-\overset{O}{\overset{\|}{C}}-H$	$1^\circ-OH$
	Acetaldehyde $CH_3-\overset{O}{\overset{\|}{C}}-H$	$2^\circ-OH$
	Ketone $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	$3^\circ-OH$
	Epoxide 	$1^\circ-OH$ with higher no. of Cs.
	CO_2	Carboxylic acid with 1 more C
	Ester. $R-\overset{O}{\overset{\|}{C}}-O-R$	Ketone, finally $3^\circ-OH$
	Acetyl chloride $R-\overset{O}{\overset{\|}{C}}-Cl$	〃 〃
	Nitrile $R-C\equiv N$	amine
	O_2	Alcohol

RMgX	S	R–SH (Thiol)
	$ZnCl_2$	R_2Zn.
	$R-OH, R-NH_2, H_2O$	Alkane.
	$\overset{+\delta}{CN}-\overset{-\delta}{Cl}$	R–CN Nitrile.
	Carbonate ($EtO\overset{O}{\overset{\|}{C}}OEt$)	3°–OH.
	orthoformate $HC(OEt)_3$	Aldehyde.
	orthoester other than formate $R'C(OEt)_3$	Ketone.

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