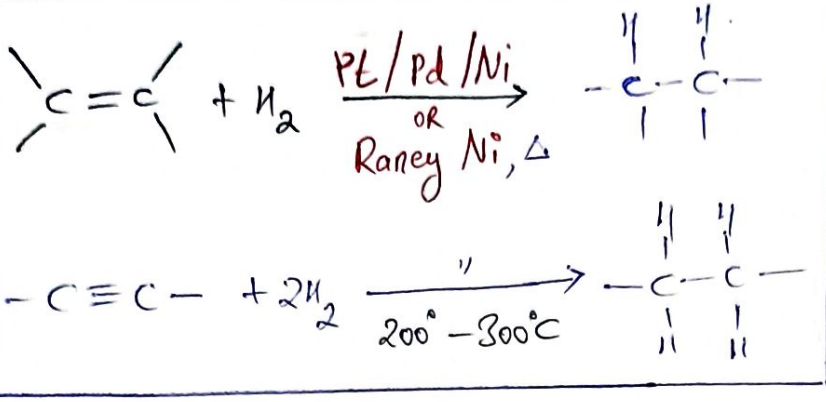
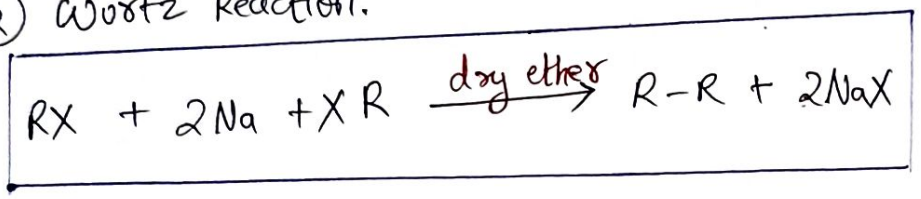
ALKANES

① From Alkenes & Alkynes [Sabatier & Sanderson reaction]



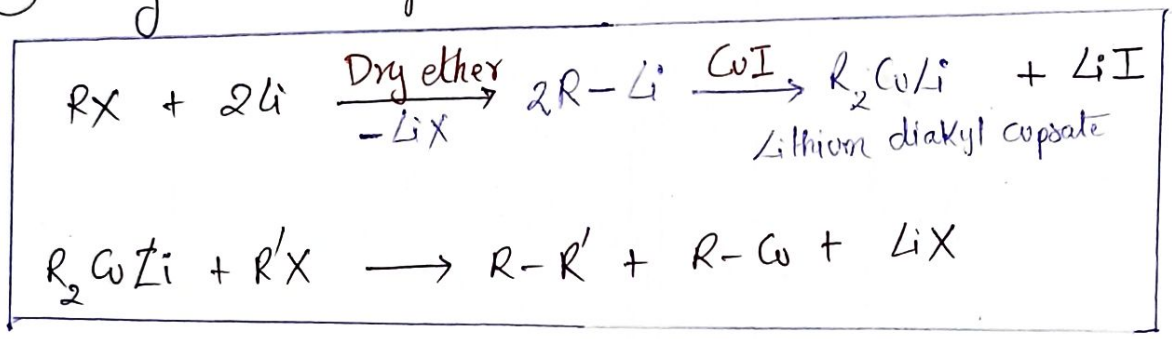
- This method NOT used for prep. of (CH_4), as the starting material must contain atleast two carbon atoms.
- Reactivity : Alkynes > alkene
- Exothermic rxn

② Wurtz Reaction.



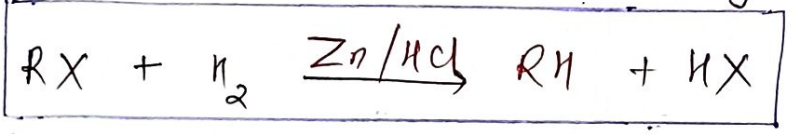
- If different alkyl halide are used, a mixture of product is obtained.

③ Corey House Sysnthesis:

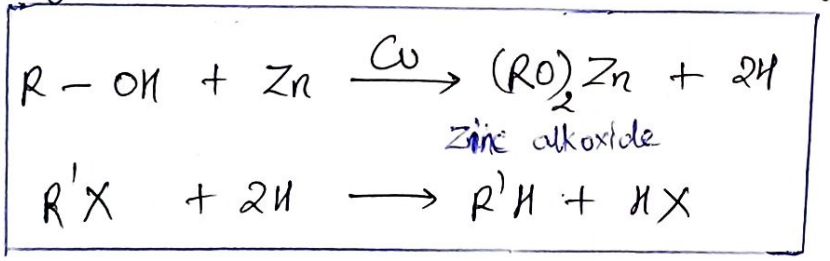


- R & R' may or NOT be same.
- R_2CuLi ↓ [Gilman reagent]

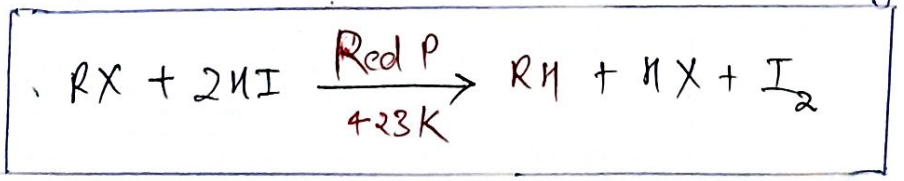
④ Reduction of Alkyl Halide (using Zn/HCl)



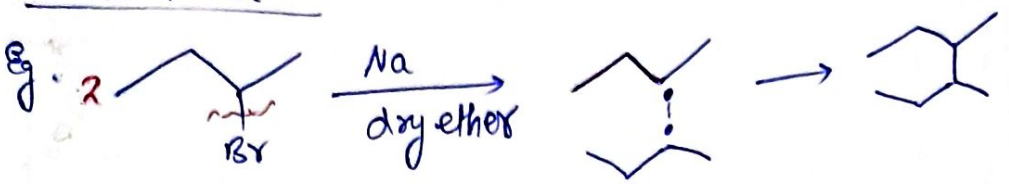
- X can Be = Cl, Br, I except = F
- Order of Reactivity of alkyl halide is R–I > R–Br > R–Cl
- Alkyl Halide can also be reduced by Zinc-Copper couple & –OH

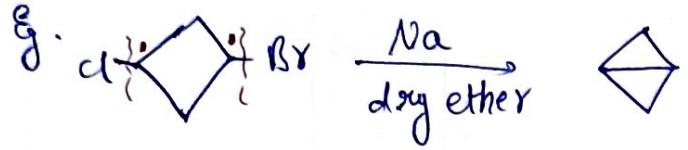


- Alkyl Halide can also be reduced to alkanes by heating with Red-P & HX.



Wurtz Reaction.

Eg. 

Eg. 

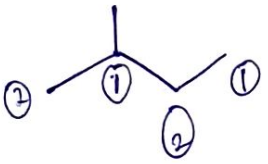
Q How to find total no. of products in Mono halogenation

Eg $CH_4 \xrightarrow[h\nu]{X_2}$ ① Eg.  " → ②

Eg. CH_3-CH_3 " → ①

Eg.  Excluding stereo

① + ② = ③ Including stereo

Eg.  " → ④ Excluding stereo

⑥ ~~Indu~~ Including stereo

Q) How to find Major product in monohalogenation,

Chlorination

More reactive less selective

$\gamma_{pri} : \gamma_{sec} : \gamma_{tert} = 1 : 3.8 : 5$

$$\% 1^\circ = \frac{n_p \gamma_p}{n_p\gamma_p + n_s\gamma_s + n_t\gamma_t} \times 100$$

n_p = no. of $1^\circ H$, n_t = " $3^\circ H$

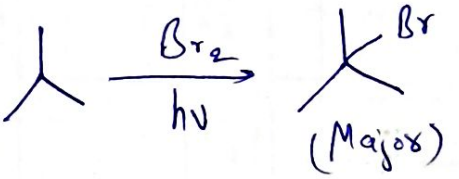
n_s = " $2^\circ H$

Bromination

More selective Less reactive

$\gamma_p : \gamma_s : \gamma_t = 1 : 82 : 1600$

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

Eg 

(Major)

Eg.  $\xrightarrow[h\nu]{Cl_2}$

$n_p = 9 \quad n_s = 0 \quad n_t = 1$

$n_p r_p = 9 \times 1 \quad n_s r_s = 0 \times 3.8 \quad n_t r_t = 1 \times 5$

$= 9 \quad = 0 \quad = 5$ ✓

(Major)

⑤ From carboxylic acid by Decarboxylation Rxn:

$$RCOONa + NaOH \xrightarrow[Heat]{CaO} RH + Na_2CO_3$$

(sodium carbonate)

- NaOH & CaO in the ratio of (3:1) is known as sodalime.

⑥ Kolbe's electrolytic method:

$$RCOOK + RCOOK + 2H_2O \xrightarrow{Electrolysis} R-R + 2CO_2 + H_2 + 2KOH$$

⑦ From Carboxylic acid by Reduction

$$RCOOH + 6HI \xrightarrow[200^\circ C]{Red\ P} RCH_3 + 2H_2O + 3I_2$$

⑧ from $-OH$, $-CHO$, $R-\overset{O}{\overset{\|}{C}}-R$, $R-\overset{O}{\overset{\|}{C}}-Cl$ & amides By reduction Reduction

i) $CH_3OH + 2HI \xrightarrow[150^\circ C]{Red\ P} CH_4 + H_2O + I_2$

ii) $CH_3CHO + 4HI \xrightarrow[150^\circ C]{Red\ P} C_2H_6 + H_2O + 2I_2$

iii) $CH_3COCH_3 + 4HI \xrightarrow[180^\circ C]{Red\ P} CH_3-CH_2-CH_3 + H_2O + 2I_2$

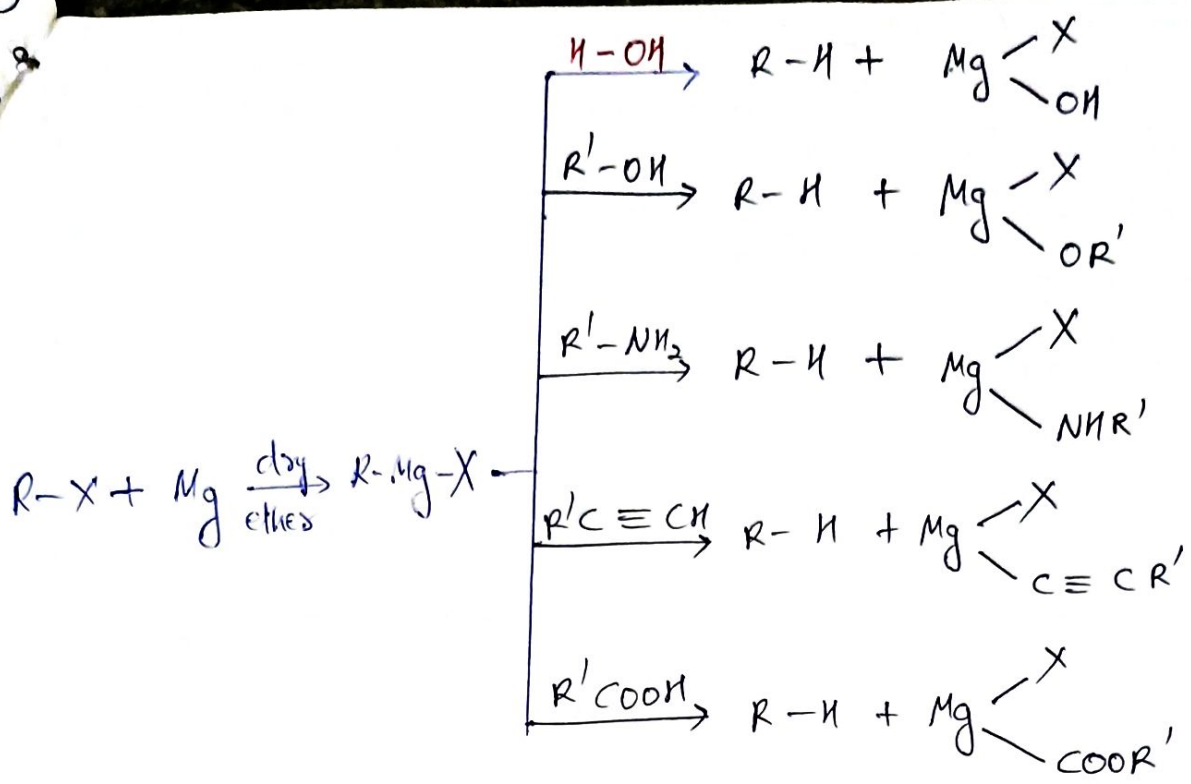
iv) $CH_3-\overset{O}{\overset{\|}{C}}-Cl + 6HI \xrightarrow[200^\circ C]{Red\ P} CH_3-CH_3 + H_2O + HCl + 3I_2$

v) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + 6HI \xrightarrow[200^\circ C]{Red\ P} CH_3-CH_3 + H_2O + NH_3 + 3I_2$

⑨ From Grignard reagent by decomposition reaction:

- with heavy water (D_2O), deuterated alkanes are formed.

$$R-MgX + D-OD \longrightarrow R-D + Mg(OD)X$$



(10) Clemmensen Reduction :

$$R-CHO + 4H \xrightarrow{Zn-Hg/HCl} R-CH_3 + H_2O$$

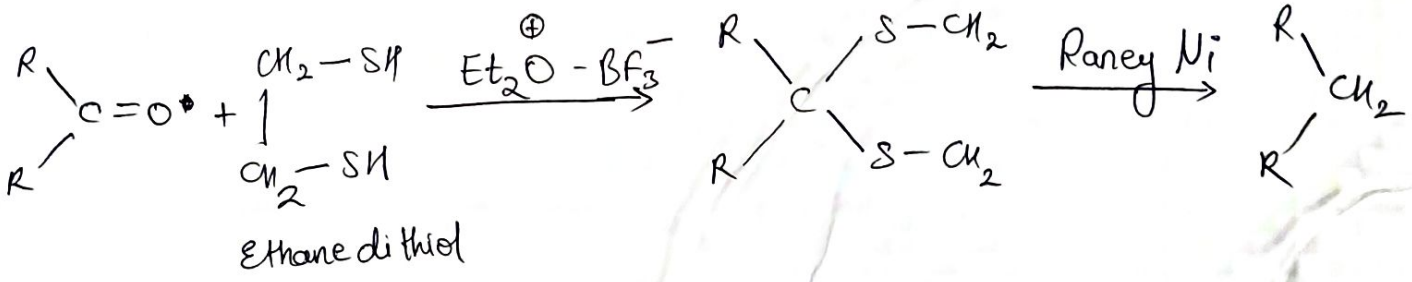
$$R-\overset{O}{\overset{\|}{C}}-R + 4H \xrightarrow{Zn-Hg/HCl} R-CH_2-R + H_2O$$

(11) Wolf-kishner reduction :

$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NH_2-NH_2} R-\overset{CH_3}{\overset{|}{C}}=N-NH_2 \xrightarrow{KOH} R-CH_2-CH_3 + N_2\uparrow$$

Aldehyde/ketone → Alkane

(12) Mozingo Method



Physical properties of alkane.

> Physical state:

i. $C_1 - C_4$ Alkanes: odourless, colourless gases

ii. $C_5 - C_{17}$ Alkanes: odourless, colourless liquids

iii. C_{18} & above alkanes: odourless, Colourless solids.

> Boiling Point:

i. Boiling point $\propto$ No. of carbon atoms.

ii. Boiling point $\propto \frac{1}{\text{No. of Branching in compounds}} \propto$ Straight chain compounds

> Melting points:

i. Straight chain alkanes with even number of carbon atoms generally have higher melting points as compared to the immediately lower alkanes with odd number of carbon atoms. This property is commonly called as alternation effect.

> $\boxed{\text{Solubility} \propto \frac{1}{\text{Molecular Mass}}}$

- Benzene, ether, CCl_4 etc ↓ Soluble in non-polar solvents.
- water, methanol, DMSO → insoluble in polar solvents.

> $\boxed{\text{Density} \propto \text{no. of carbon atoms in compound}}$

> All alkanes are lighter than water (H_2O)

(13) Hydroboration of alkenes:

$$R-CH=CH_2 \xrightarrow{B_2H_6} (R-CH_2-CH_2)_3B \xrightarrow{CH_3CO_2H} 3R-CH_2-CH_3$$

(14) Frankland Reaction

$$R-X + Zn + X-R \longrightarrow \underset{\text{Alkane}}{R-R} + ZnX_2$$

(15) By desulfurization:

$$R-S-S-R' + H_2 \xrightarrow{\text{Raney Ni}} R-H + R'-H$$

(16) Birch Reduction

$$R-CH=CH_2 \xrightarrow[\text{ii. } CH_3OH]{\text{i. Na/liq } NH_3} R-CH_2-CH_3$$ } trans

CHEMICAL Properties of Alkanes:

(1) Halogenation.

i. Chlorination: $CH_4 + 4Cl_2 \xrightarrow[573-733K]{h\nu} CCl_4 + 4HCl$

ii. Bromination:

$$C_2H_6 + Br_2 \xrightarrow[\Delta]{AlBr_3} C_2H_5-Br + HBr$$

iii. Iodination:

$$CH_4 + I_2 \underset{\Delta}{\overset{\text{Oxidizing agent}}{\rightleftharpoons}} CH_3I + HI$$

oxidizing agent:
(HIO_3) → iodic acid
(HNO_3) → Nitric acid
(HgO) → Mercuric oxide

iv. fluorination:

$CH_4 + F_2 \longrightarrow X$ due to explosive.

Sulphonation:

$$C_6H_4 + H_2SO_4 \xrightarrow[675K]{SO_3} C_6H_{13}SO_3H + H_2O$$

- Higher alkanes (hexane & above) undergo sulphonation

- The ease of substitution follows the order $3^\circ > 2^\circ > 1^\circ$

(3) Combustion

i) Complete combustion / oxidation

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

ii) Incomplete combustion or oxidation

i. $2CH_{4(g)} + 3O_{2(g)} \xrightarrow{\text{Combustion}} 2CO_{(g)} + 4H_2O_{(g)}$

ii. $CH_{4(g)} + O_{2(g)} \longrightarrow C_{(s)} + 2H_2O_{(l)}$
(limited) Carbon Black

iii) Catalytic / controlled oxidation

a. $2CH_4 + O_2 \xrightarrow{Cu/523K/100\,atm} 2CH_3OH$

b. $CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$

c. $2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$

iv. Chemical oxidation:

$$(CH_3)_3\text{-}CH \xrightarrow[\text{oxidation}]{KMnO_4} (CH_3)_3COH$$ [for alkanes having 3° H atoms]

④ Action of steam:

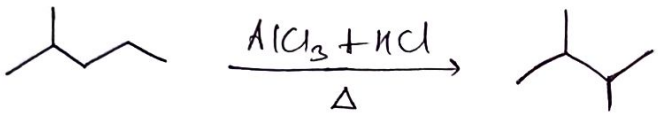
$$CH_4 + \underset{\text{steam}}{H_2O} \xrightarrow[1273K]{Ni} \underbrace{CO + 3H_2}_{\text{Syngas}}$$

- Nickel catalyst (supported over alumina, Al_2O_3)

⑤ Isomerization:

Eg. $CH_3-CH_2-CH_2-CH_3 \xrightarrow[573k,\ 30-35\ atm]{Anhy.\ AlCl_3,\ HCl}$ $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

Isobutane
(Branched chain)

Eg. 

⑥ Aromatization or reforming:

Eg. $CH_3-(CH_2)_4-CH_3 \xrightarrow[Cr_2O_3/V_2O_5/Mo_2O_3\ catalyst]{773k,\ 10-20\ atm}$  $+ 4H_2$

Eg. $CH_3-(CH_2)_5-CH_3 \xrightarrow[Cr_2O_3/V_2O_5/Mo_2O_3\ catalyst]{773k,\ 10-20\ atm}$  $+ 4H_2$

Isomerism

① Butane → 2
② Pentane → 3
③ Hexane → 5
④ Heptane → 9
⑤ Octane → 18
⑥ Nonane → 35
⑦ Decane → 75
⑧ Pentadecane → 4,347

AROMATIC

(MOP)

① Cyclic polymerization of ethyne:

$$3CH\equiv CH \xrightarrow[873K]{\text{red hot Fe-tube}} C_6H_6$$

② Decarboxylation of aromatic acids:

$$C_6H_5-\overset{O}{\overset{\|}{C}}-ONa + NaOH \xrightarrow{CaO,\ \Delta} C_6H_6 + Na_2CO_3$$

③ Reduction of phenol:

$$C_6H_5-OH + \underset{\text{dust}}{Zn} \xrightarrow{\Delta} C_6H_6 + ZnO$$

④ Reduction of chloroBenzene

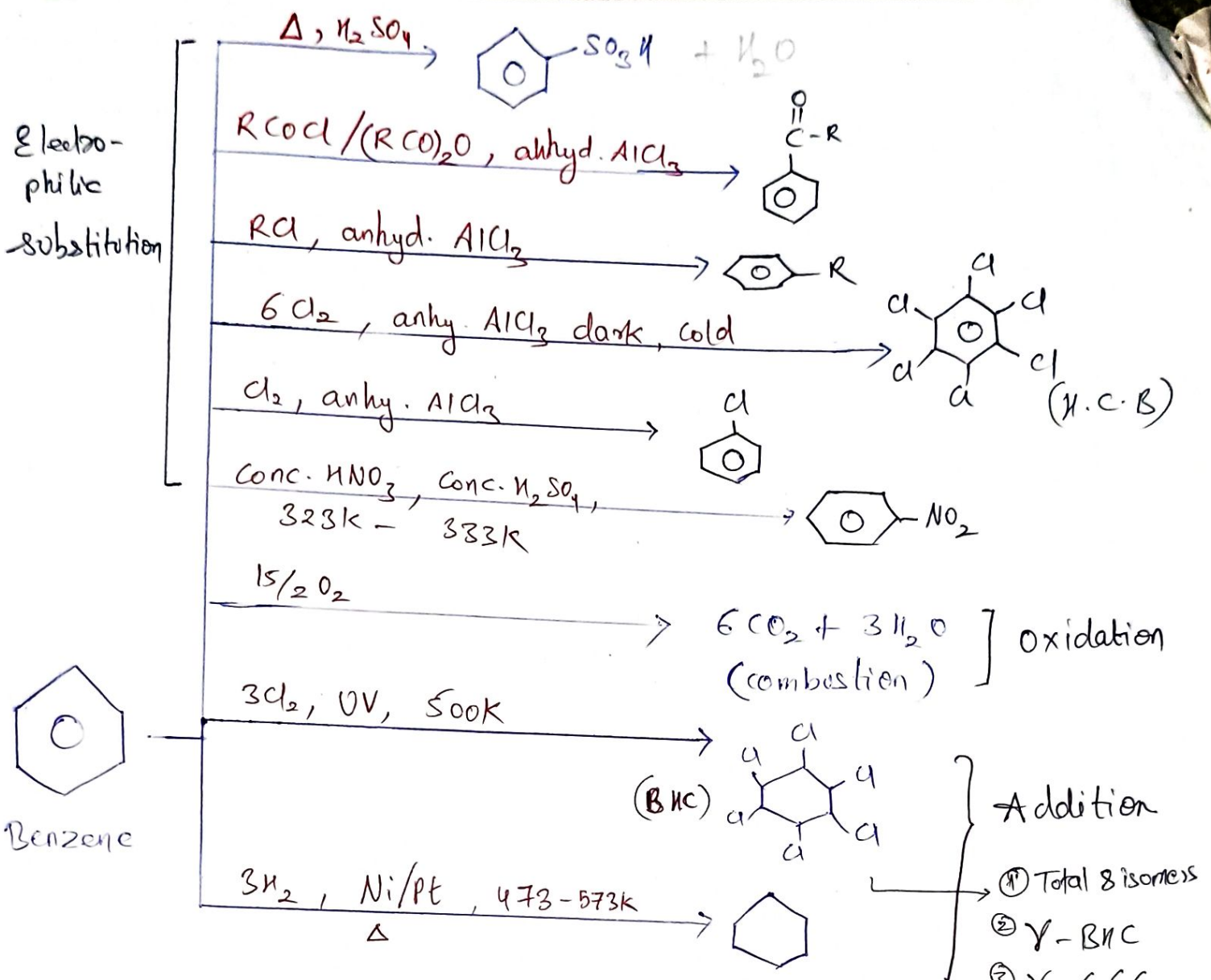
$$C_6H_5-Cl + 2[H] \xrightarrow[NaOH]{Ni-Al\ alloy} C_6H_6 + HCl$$

⑤ Benzene diazonium chloride

$$C_6H_5-N_2^+Cl^- + 2[H] \xrightarrow[Cu^+]{H_3PO_2} C_6H_6 + N_2\uparrow + HCl$$

⑥ By Hydrolysis of benzene sulphonic acid.

$$C_6H_5-SO_3H + H_2O \xrightarrow[HCl,\ \text{pressure}]{\text{(steam)}\ 423-473K} C_6H_6 + H_2SO_4$$



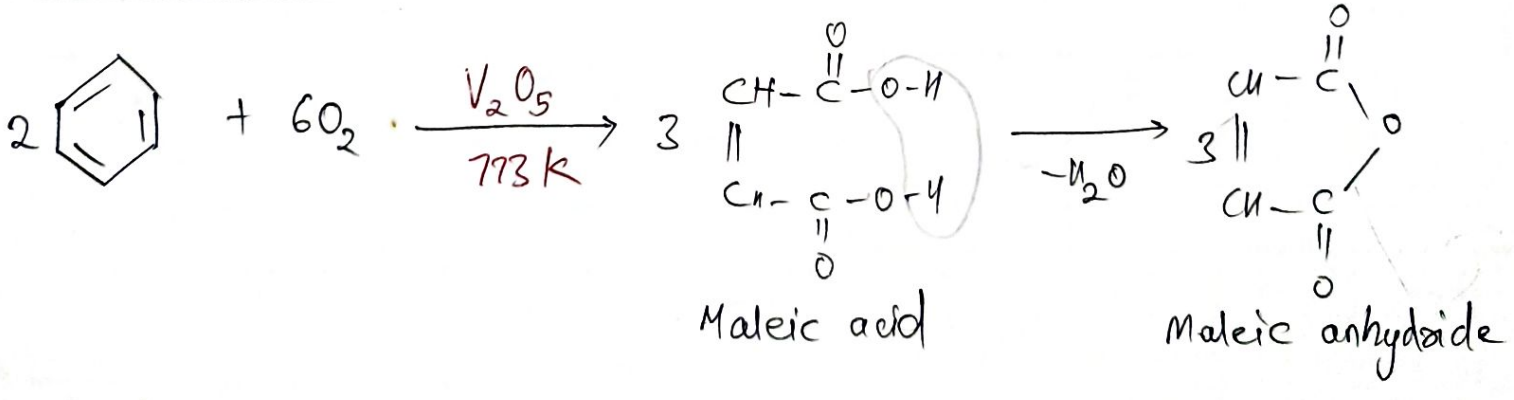
Ortho- & para directing / activiting groups:

$-CH_3$, $-C_2H_5$, $-OCH_3$, $-NH_2$, $-NHR$, $-NHCOCH_3$, etc.

Meta directing / deactiviting groups.

$-NO_2 > SO_3H > CN > COOH$, CHO, COR, COOR, $-CF_3$

Controlled oxidation



Maleic acid

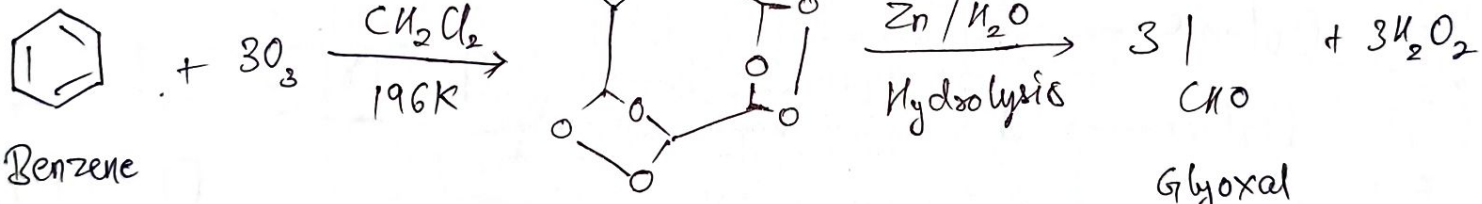
Maleic anhydride

Degree of unsaturation:- It gives the idea of total no. of multiple Bonds (π Bonds) and/or rings present in the molecule is called degree of unsaturation.

$$\text{The no. of D.O.U.S.} = \frac{2(\text{no. of carbon atoms}) - (\text{no. of H atom}) + 2}{2}$$

Eg. A compound with 2 degree of unsaturation has :- (1) Two Double Bonds OR (2) Two rings OR (3) One ring & one Double Bond OR (4) One Triple Bond.

Addition of ozone:



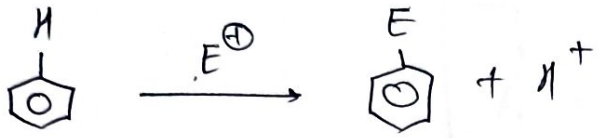
Benzene

Benzene triozonide (unstable)

Glyoxal

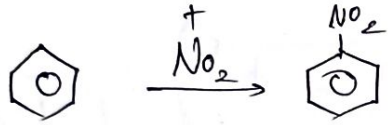
Chemical Properties

I] Electrophilic Aromatic substitution Rxn:



Types of E.A.S Rxns:

① Nitration : Reagent → ① Conc. HNO_3 + conc. H_2SO_4
② $NO_2^+ BF_4^-$
③ $N_2O_5 \rightarrow NO_2^+ NO_3^-$

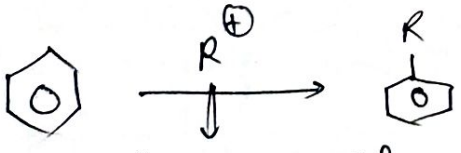


② Halogenation Rxn : Reagent → ① X_2 + Anhy $AlCl_3$
② X_2 + Anhy $FeCl_3$

③ Sulphonation : Reagent → 1) fuming H_2SO_4
2) $H_2S_2O_7$
3) SO_3 / H_2SO_4

④ Friedal Crafts Rxn

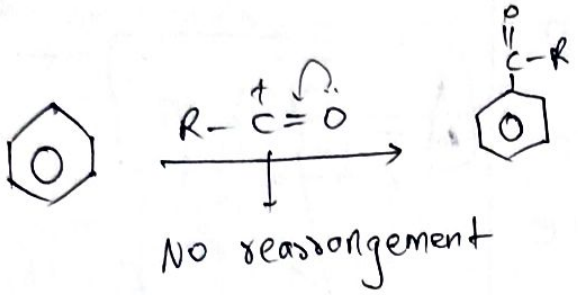
a) Alkylation : Reagent → 1) R-X + Anhy $AlCl_3$
2) ROH + H^+
3) Alkene + H^+



Rearrange if possible

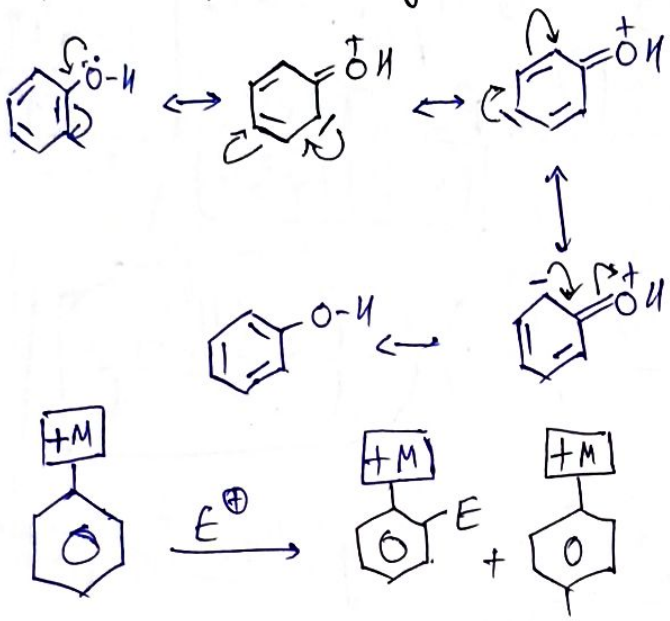
b) Acylation :→ Reagent → ① $R-\overset{O}{\overset{\|}{C}}-Cl$ + Anhy $AlCl_3$

② $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ + Anhy $AlCl_3$

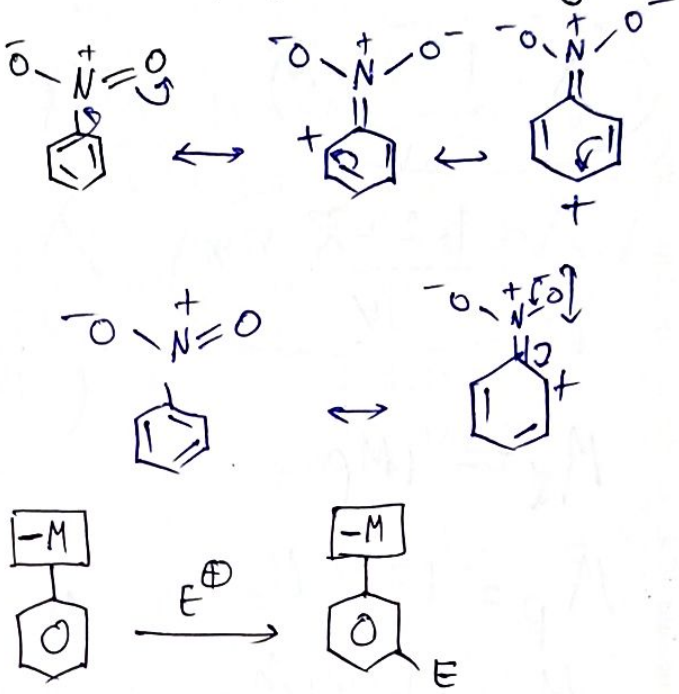


No rearrangement

+M (o,p directing)



-M (Meta directing)

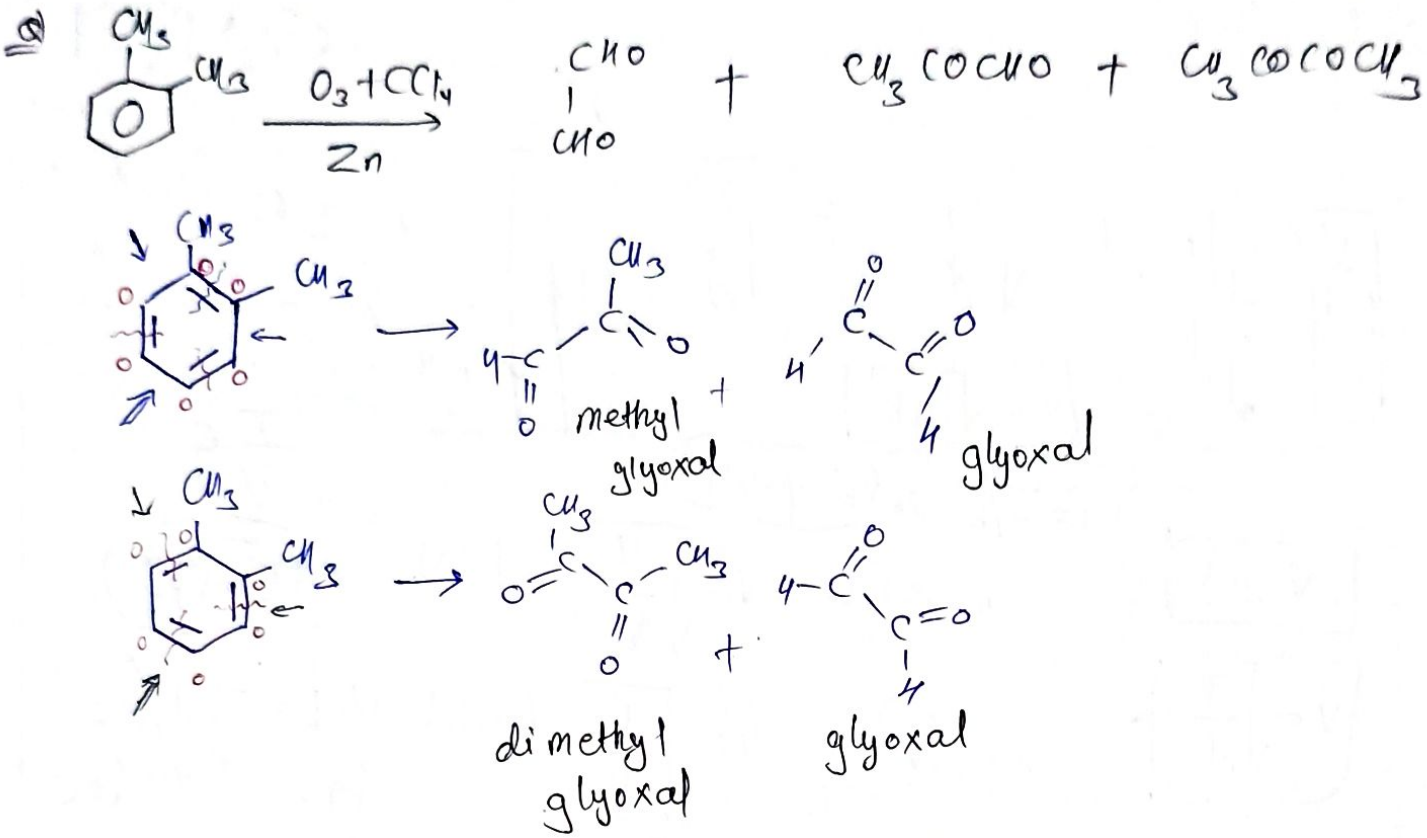


Q) (CH_3) +M → Conc. HNO_3 / conc. H_2SO_4 → CH_3, NO_2 + CH_3, NO_2

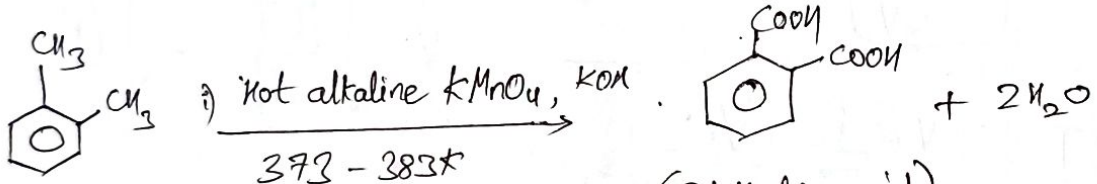
Q) NO_2 -M → Conc. HNO_3 / Conc. H_2SO_4 → NO_2, NO_2

Conc. HNO_3 / Conc. H_2SO_4 (2 mol)

Q) CHO -M → Br_2 / Anhy $FeBr_3$ → CHO, Br



Oxidation with Potassium permanganate :



o-Xylene

(Phthalic acid)

Similarly, m-Xylene gives iso-phthalic acid & p-xylene gives Terephthalic acid