Haloalkanes (-X)

General methods of preperation of Haloalkanes.

★ From Alcohols -

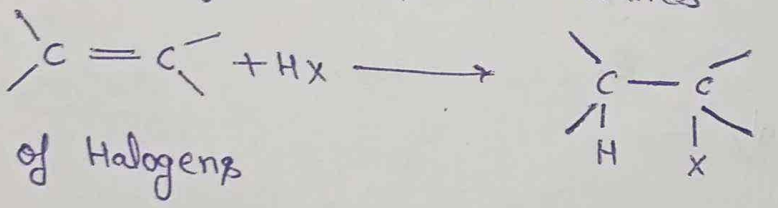
- $R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$ (Groove's process)
- $R-OH + NaBr + H_2SO_4 \longrightarrow R-Br + NaHSO_4 + H_2O$
- $3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$ ($X = Cl, Br$)
- $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$
- $R-OH \xrightarrow{लाल\ P\ /\ X_2} R-X$ ($X_2 = Br_2, I_2$)
- $R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$ (Darzen Process)

★ From Hydrocarbons -

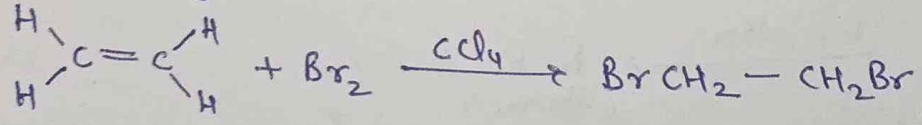
- Free Radical Halogenation of Alkanes

$$CH_3CH_2CH_2CH_3 \xrightarrow[light/heat]{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2\underset{Cl}{CH}CH_3$$

- Addition of Hydrogen Halides on Alkanes



- Addition of Halogens



★ From Halogen Exchange Rxn -

- Finkelstein Reaction

$$R-X + NaI \xrightarrow{dry\ acetone} R-I + NaX \quad (X = Cl, Br)$$

- Swartz Reaction

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr \quad (AgF/Hg_2F_2/COF_2/SbF_3)$$

★ Other ways -

- Hunsdiecker Reaction

$$CH_3COO^-Ag^+ + Br_2 \xrightarrow{CCl_4} CH_3Br + AgBr + CO_2\uparrow$$

Chemical Reactions of Haloalkanes.

★ Nucleophilic Substitution Reactions (S_n Rxns.) –

- $R-X + KOH(aq) \longrightarrow R-OH + KX$
- $R-X + NaOH \longrightarrow R-OH + NaX$
- $R-X + H_2O \longrightarrow R-OH + HX$
- $R-X + NaOR' \xrightarrow{\Delta} R-OR' + NaX$
- $R-X + NaI \longrightarrow R-I + NaX$
- $R-X + NH_3 \longrightarrow R-NH_2 + HX$
- $R-X + R'NH_2 \longrightarrow R-NHR' + HX$
- $R-X + R'R''NH \longrightarrow R-NR'R'' + HX$
- $R-X + KCN \longrightarrow R-CN + KX$
- $R-X + AgCN \longrightarrow R-NC + AgX$
- $R-X + KNO_2 \longrightarrow R-O-N=O + KX$
- $R-X + AgNO_2 \longrightarrow R-NO_2 + AgX$
- $R-X + R'COOAg \xrightarrow{\Delta} R-COOR' + AgX$
- $R-X + Na-C\equiv C-H \xrightarrow{\Delta} R-C\equiv CH + NaX$

★ Reactions with metals –

- Wurtz Reaction

$$Rx + 2Na + XR \xrightarrow{\text{Dry ether}} \underset{\text{(alkane)}}{R-R} + 2NaX$$

- Grignard's Reaction

$$Rx + Mg \xrightarrow{\text{Dry ether}} R-Mg-Br \quad \text{(Grignard's reagent)}$$

★ Dehydro halogenation Reaction –

- β Elimination Reaction

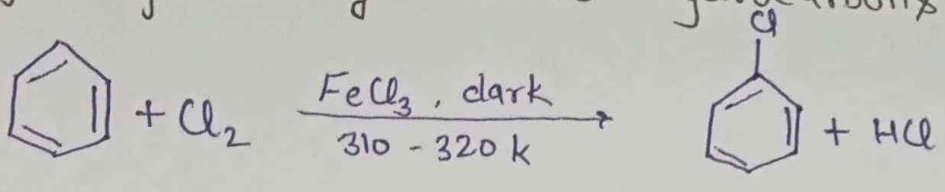
$$C_2H_5Br + KOH(alc.) \xrightarrow{heat} C_2H_4 + KBr + H_2O$$

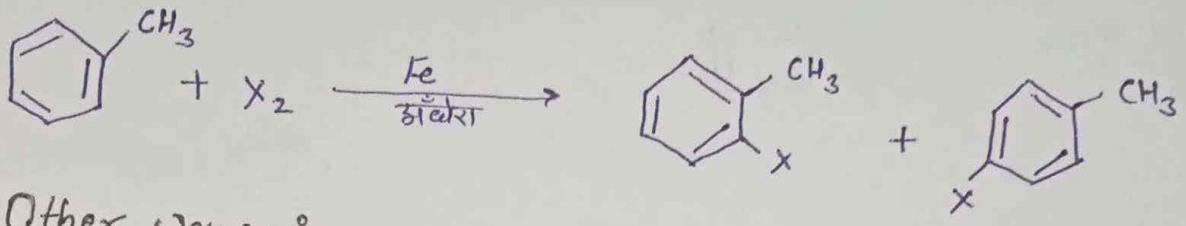
$$CH_3-\underset{}{CH_2}-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow[-KBr,\ -H_2O]{\text{Alc. KOH}} \underset{\text{but-2-ene (major)}}{CH_3-CH=CH-CH_3} + \underset{\text{but-1-ene (minor)}}{CH_3CH_2CH=CH_2}$$

Haloarenes (-X)

General methods of Preparation of Haloarenes.

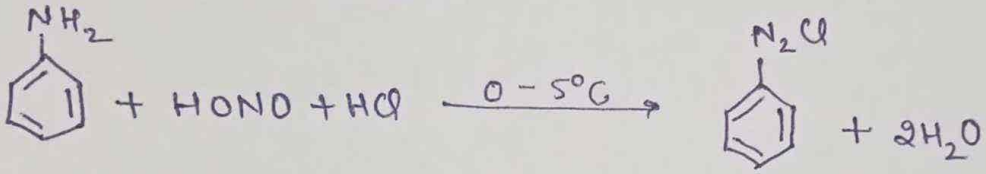
★ By Halogenation of Aromatic Hydrocarbons -

- 

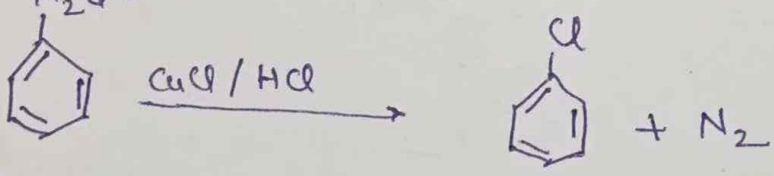
- 

★ Other ways -

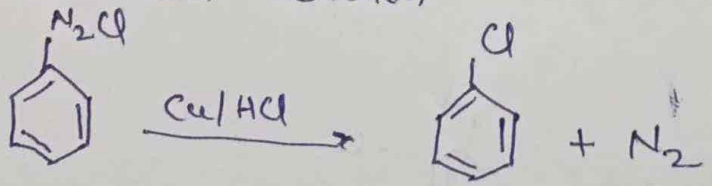
- Diazotisation Reaction



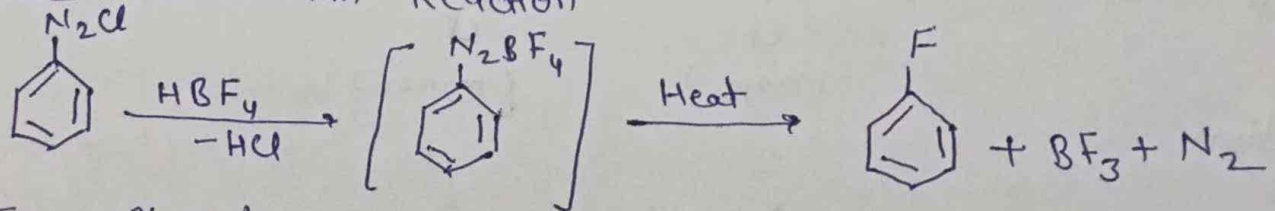
- Sandmeyer's Reaction



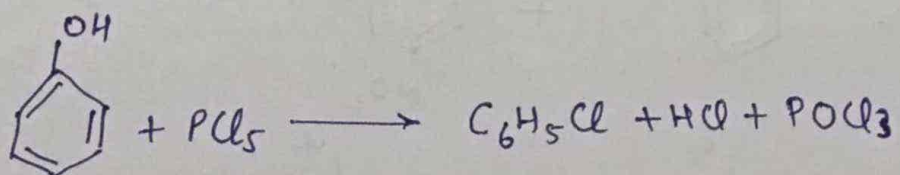
- Gattermann Reaction

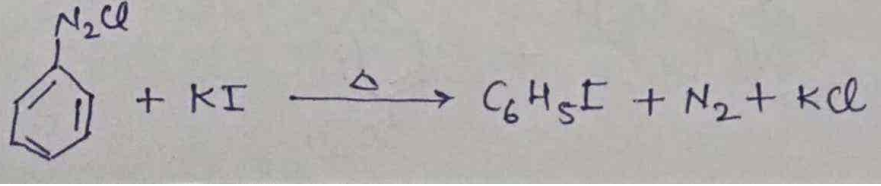


- Balz Schiemann Reaction



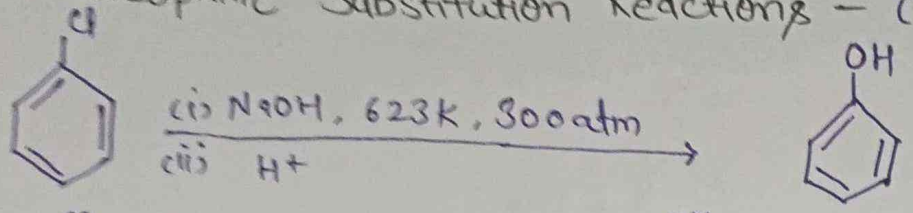
- From Phenol

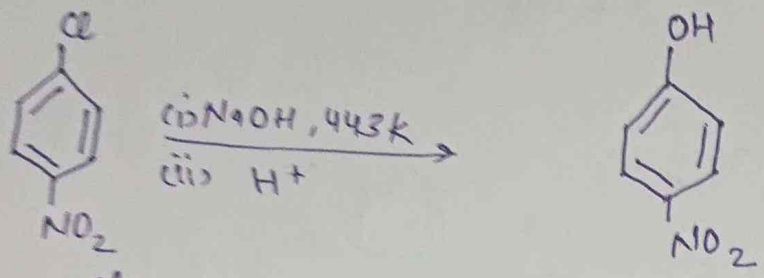


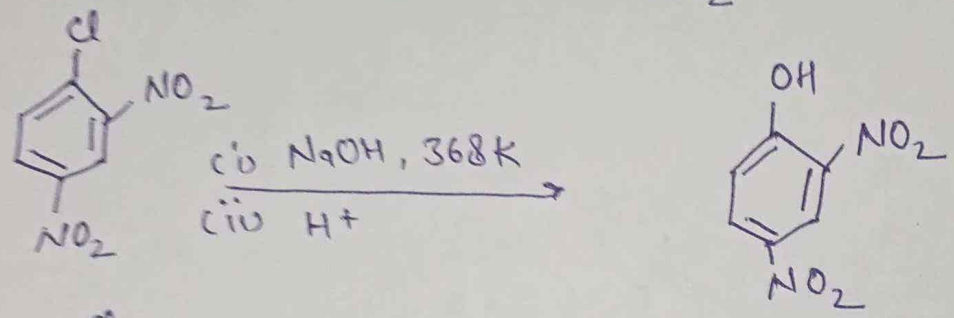
- 

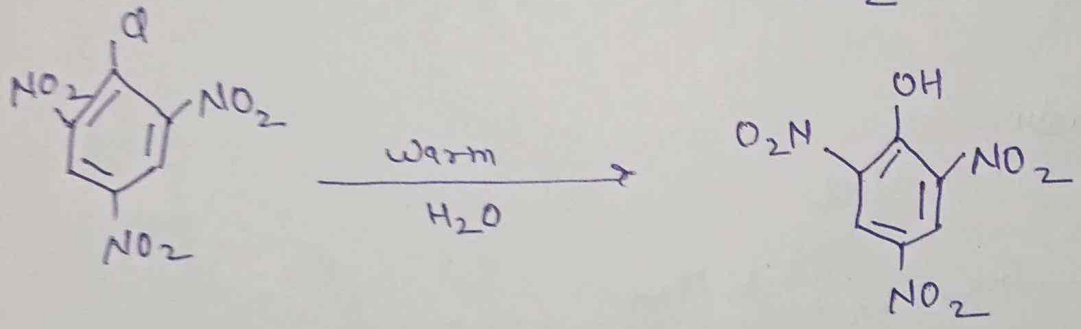
Chemical Reactions of Haloarenes.

★ Nucleophilic Substitution Reactions – (Replacement by Hydroxil group)

- 

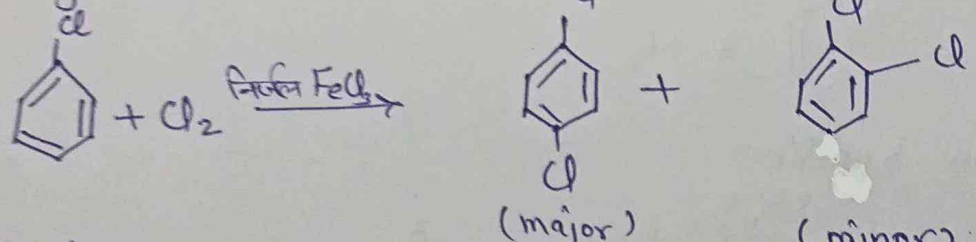
- 

- 

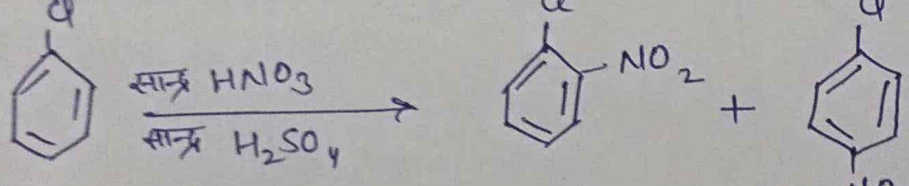
- 

★ Electrophillic Substitution Reactions –

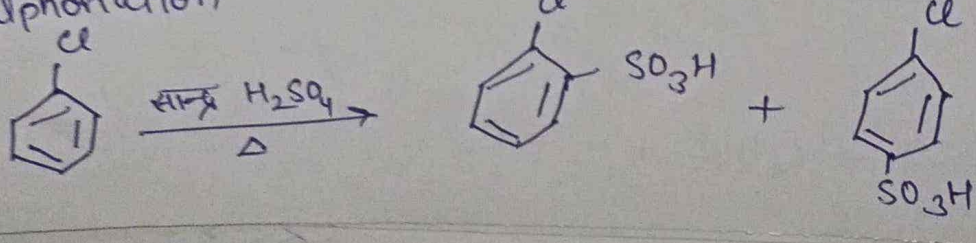
- Halogenation



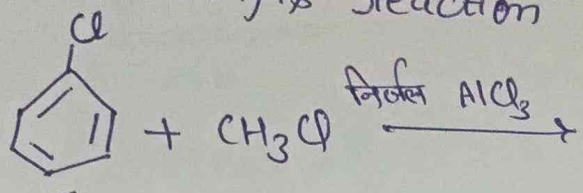
- Nitration

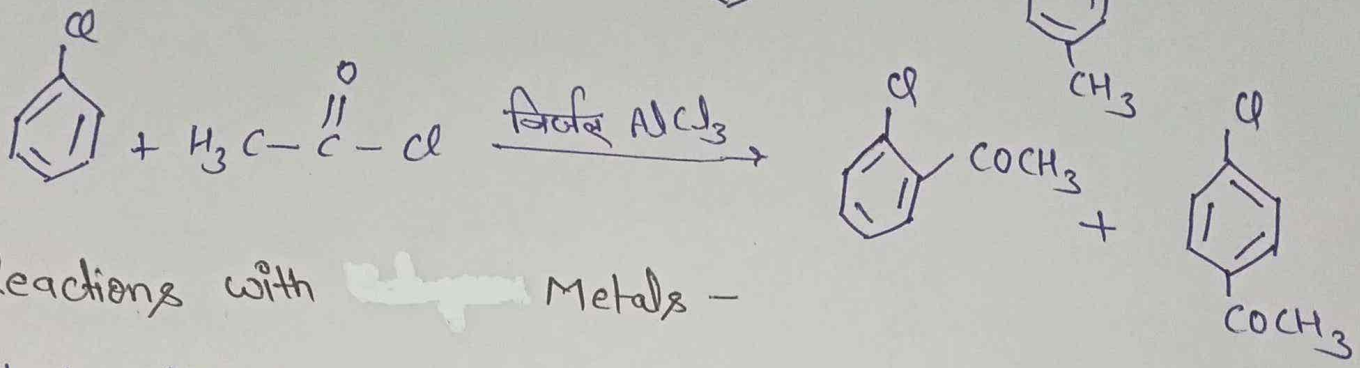


- Sulphonation



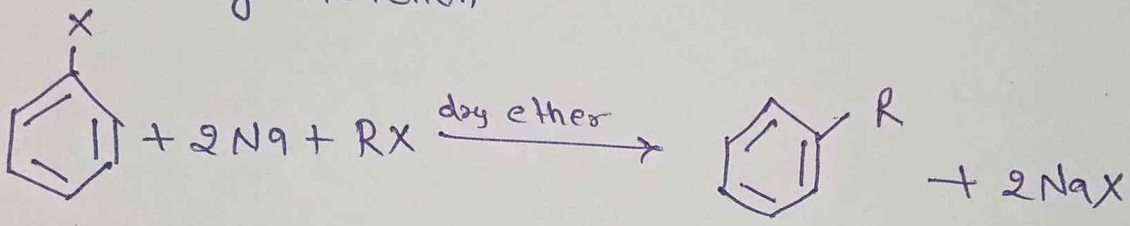
- Friedel - Crafts reaction



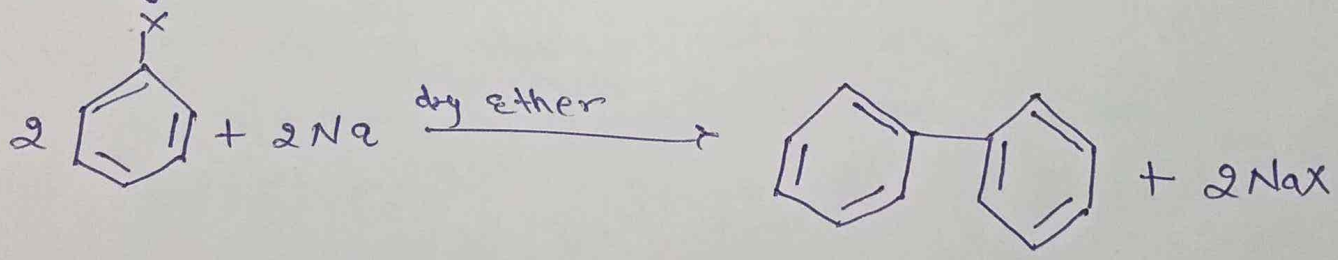


★ Reactions with Metals –

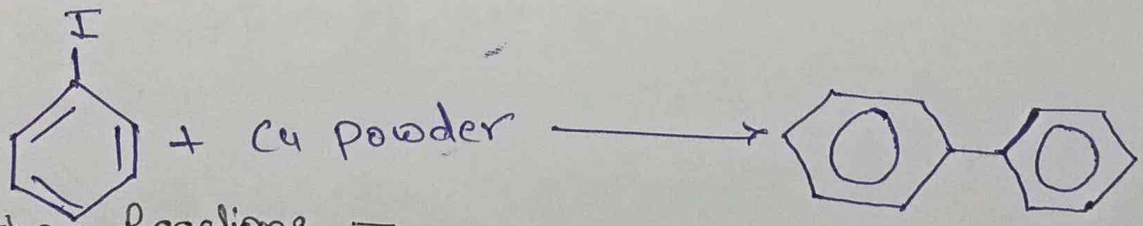
- Wurtz fitting reaction



- Fitting reaction

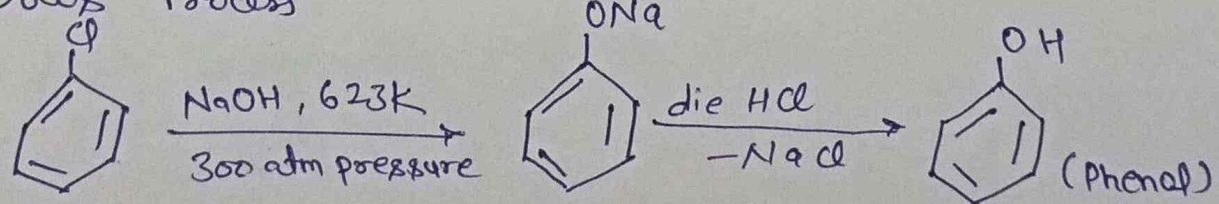


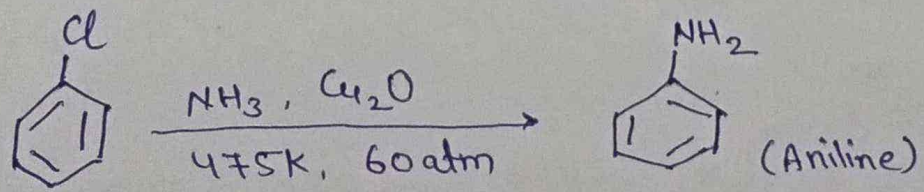
- Ullmann reaction



★ Other Reactions –

- Dows Process



- 

Alcohol (-OH)

General methods of preparation of Alcohol.

★ From Alkenes —

• By acid catalysed hydration

$$>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >C(H)-C(OH)<$$

(Markownikoff's rule)

• By hydroboration oxidation

$$CH_3-CH=CH_2 + (H-BH_2)_2 \longrightarrow CH_3-CH(H)-CH_2(BH_2)$$

Prop-1-ene

$$(CH_3-CH_2-CH_2)_3B \xleftarrow{CH_3-CH=CH_2} (CH_3-CH_2CH_2)_2BH$$

$$(CH_3-CH_2-CH_2)_3B \xrightarrow[H_2O]{3H_2O_2,\ \bar{O}H,} 3CH_3-CH_2-CH_2-OH + B(OH)_3$$

Propane-1-ol

★ From Carbonyl Compound —

• By reduction of aldehydes and ketones

$$R-CHO + H_2 \xrightarrow{Ni/Pd/Pt} RCH_2-OH$$ 1° Alcohol

$$RCOR' \xrightarrow{NaBH_4} R-CH(OH)-R'$$ 2° Alcohol

• By reduction of carboxylic acids and ester.

$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$$

$$RCOOR' \xrightarrow[catalyst]{H_2} RCH_2OH + R'OH$$

★ from Grignard's reagents.

$$>C=O + R-Mg-X \longrightarrow \left[>C(R)-\bar{O}\overset{+}{M}gX\right] \xrightarrow{H_2O} >C(R)-OH + Mg(OH)X$$

$$HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(X)(OH)$$

1° Alcohol

$$RCHO + R'MgX \xrightarrow{H_2O} R-CH(R')-OMgX \xrightarrow[-Mg(OH)X]{H_2O} R-CH(R')-OH$$

2° Alcohol

$$RCOR + R'MgX \longrightarrow R-\underset{\underset{R}{|}}{\overset{\overset{R'}{|}}{C}}-OMgX \xrightarrow[-Mg(OH)X]{H_2O} R-\underset{\underset{R}{|}}{\overset{\overset{R'}{|}}{C}}-OH$$

3° Alcohol.

★ Other ways —

- Hydrolysis of alkyl halides

$$R-X + KOH\,(aq) \longrightarrow ROH + KX$$

- Hydrolysis of ethers

$$R-\ddot{O}-R + H_2O \xrightarrow{H_2SO_4} 2ROH$$

- From Primary amines

$$RNH_2 + HONO \xrightarrow{(NaNO_2 + HCl)} ROH + N_2\uparrow + H_2O$$

- By alcoholic fermentation

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose and fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2(g)$$

ethyl alcohol

- From haloalkanes

$$R-X + KOH\,(aq) \longrightarrow R-OH + KX$$

Chemical Reactions Of Alcohol.

★ Reactions involving cleavage of O-H Bond —

- Acidity of Alcohols

$$2R-OH + 2Na \longrightarrow 2R-O-Na + H_2$$

1° > 2° >> 3°

- Esterification

$$R-OH + R'COOH \underset{}{\overset{H^+}{\rightleftharpoons}} R-OCOR' + H_2O$$

$$R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} R-OCOR' + R'COOH$$

$$R-OH + R'COCl \xrightarrow{\text{Pyridine}} R-OCOR' + HCl$$

★ Reactions involving cleavage of C-O Bond —

- Reaction with halogen acids -

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

I > Br > Cl

1° < 2° < 3°

- Reaction with phosphorus halides

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

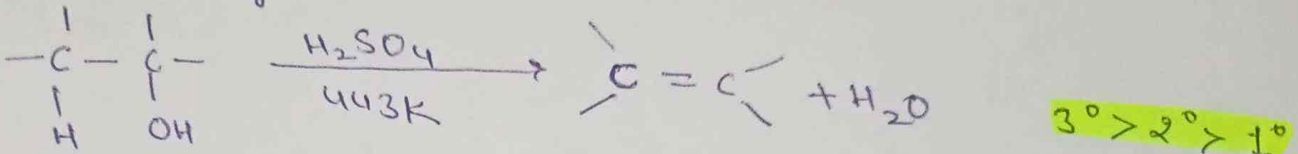
$$3ROH + PBr_3 \longrightarrow 3RBr + H_3PO_3$$

$$3ROH + PI_3 \longrightarrow 3RI + H_3PO_3$$

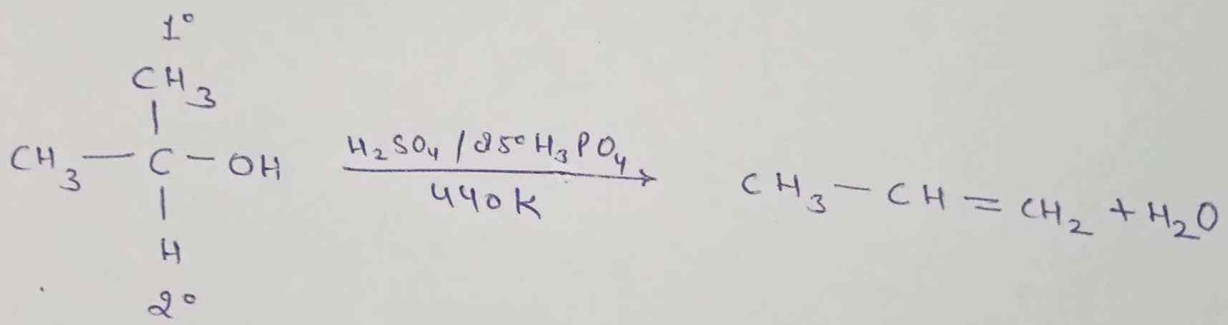
- Reaction with thionyl chloride.

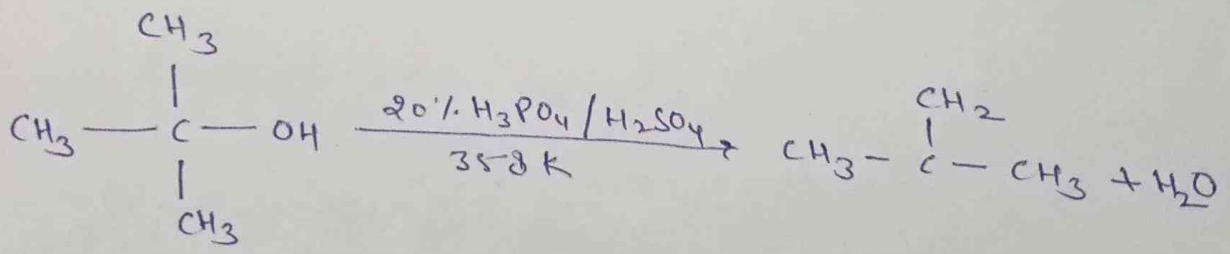
$$ROH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

- Dehydration of Alcohols -



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





- Oxidation Reactions -

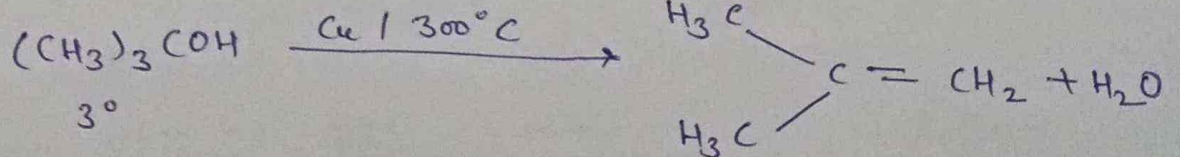
- Dehydrogenation -

$$RCH_2OH \xrightarrow{Cu/300^\circ C} RCHO + H_2\uparrow$$

(1°)

$$RCHOH-R' \xrightarrow{Cu/300^\circ C} R-CO-R' + H_2\uparrow$$

(2°)



(3°)

★ Other Reactions —

- Reaction with active Metals -

$$2R-OH + 2Na \longrightarrow 2RONa + H_2\uparrow$$

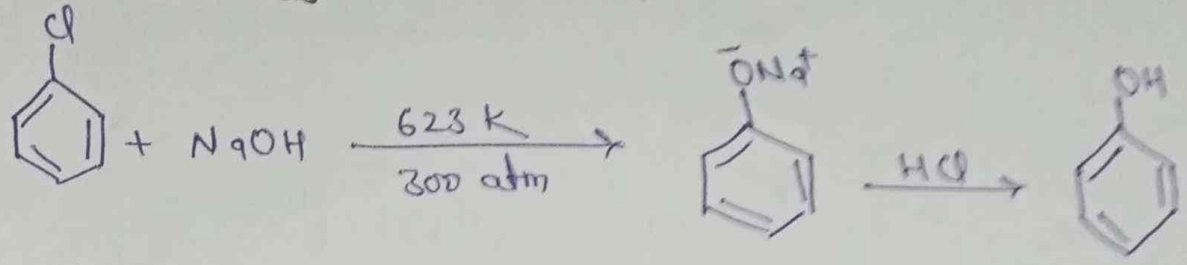
- Reaction with Grignard Reagent -

$$ROH + R-MgBr \longrightarrow R-H + Mg\begin{matrix}OR'\\Br\end{matrix}$$

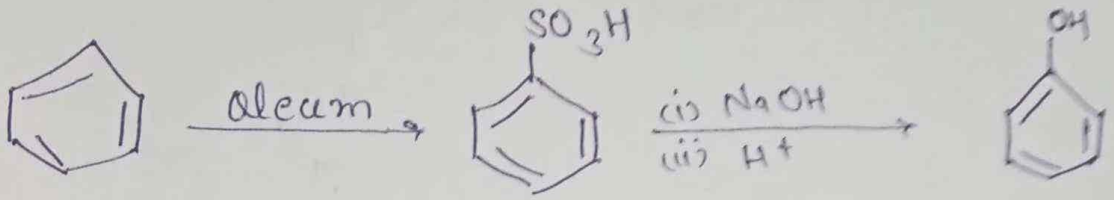
Phenols (-OH)

General methods of preparation of Phenols -

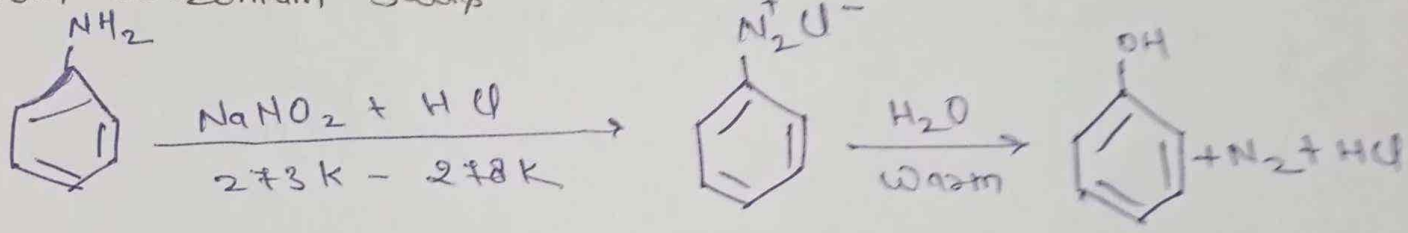
★ From haloarenes



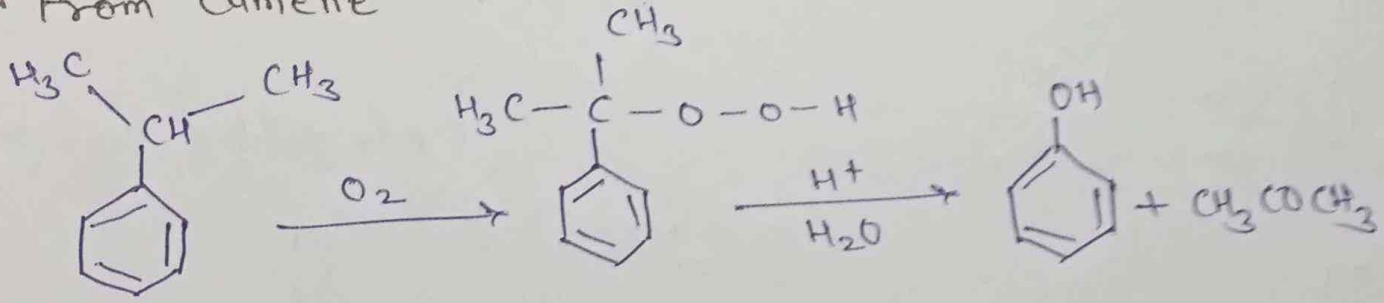
★ From benzene Sulphonic acid



★ From diazonium Salts



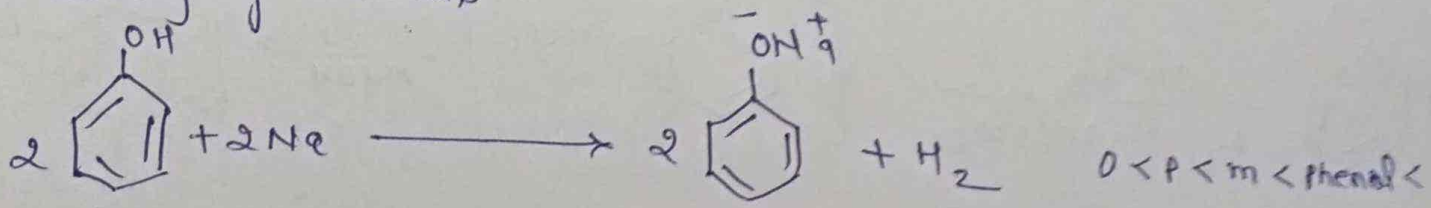
★ From Cumene



CHemical Reactions of Phenol -

★ Reactions involving cleavage of O-H Bond.

- Acidity of Phenols.



$O < P < m <$ Phenol $<$

- Esterification

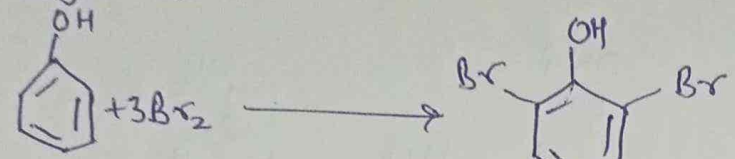
$$Ar-OH + R'COOH \underset{}{\overset{H^+}{\rightleftharpoons}} Ar-OCOR' + H_2O$$

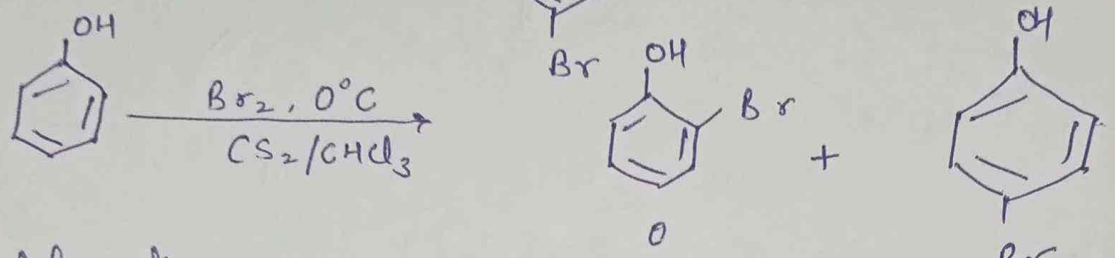
$Ar-OH + (R'CO)_2O \xrightleftharpoons{H^+} Ar-OCOR' + R'COOH$

$Ar-OH + R'COCl \xrightarrow{Pyridine} Ar-OCOR' + HCl$

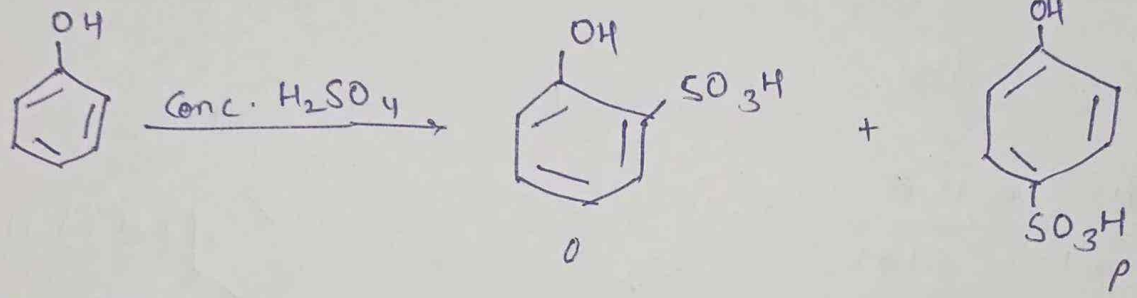
★ Electrophilic Substitution Reactions :-

- Halogenation

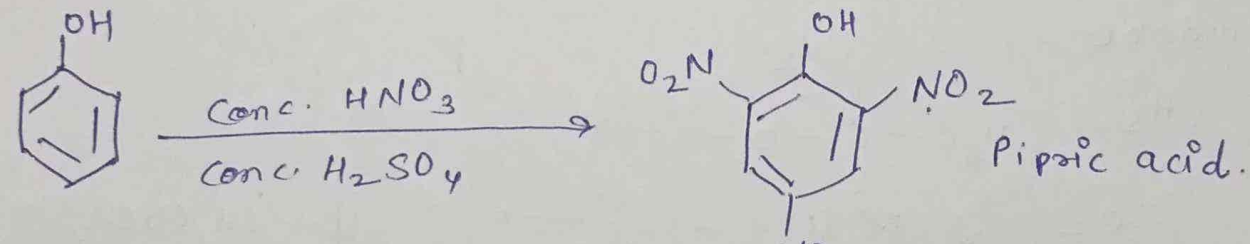


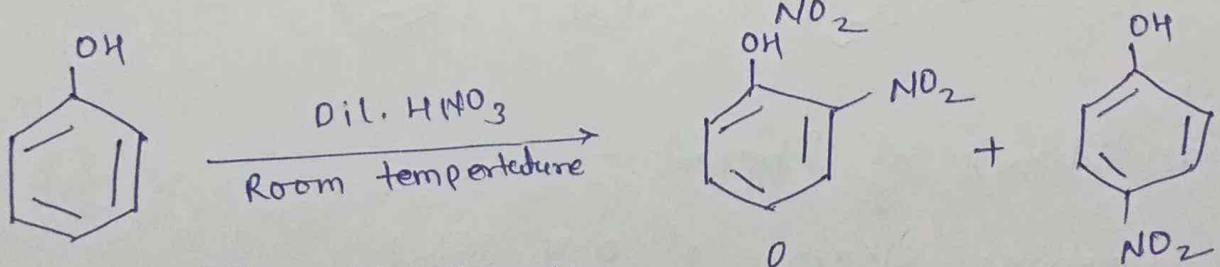


- Sulphonation

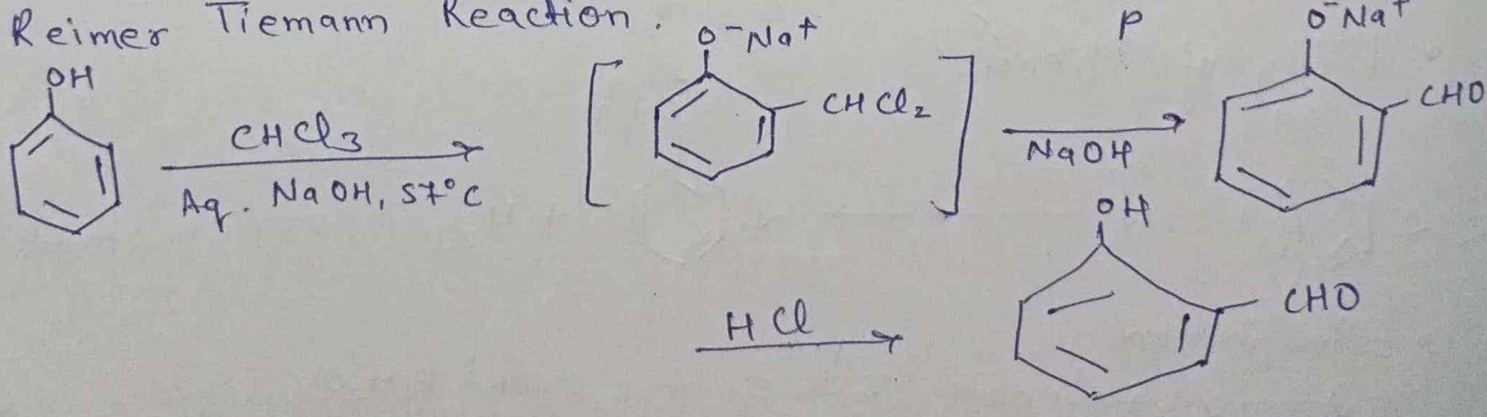


- Nitration



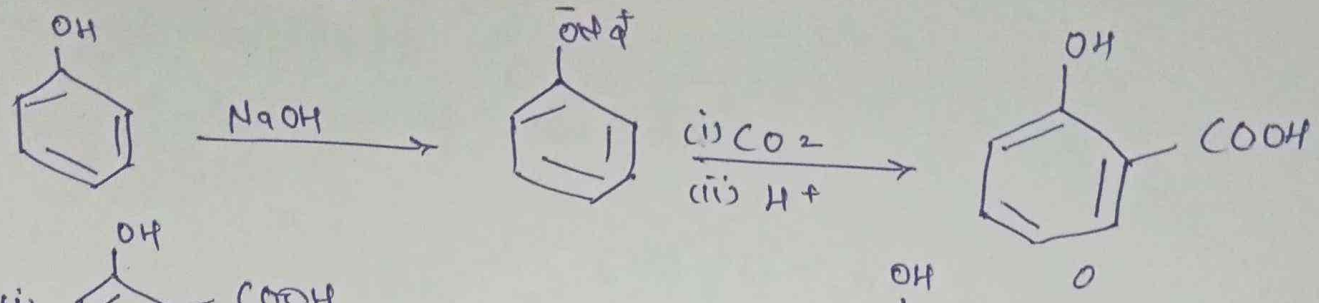


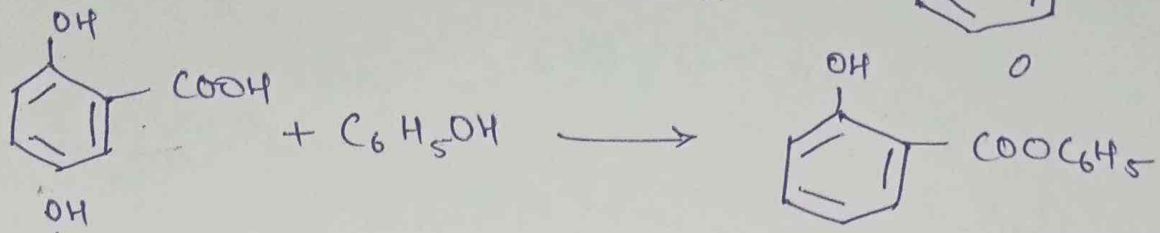
- Reimer Tiemann Reaction.

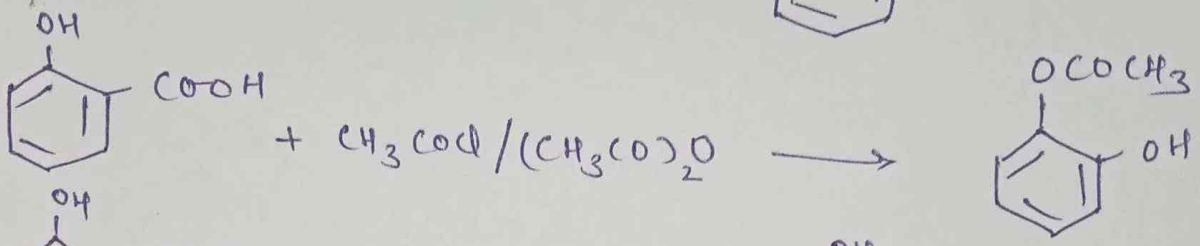


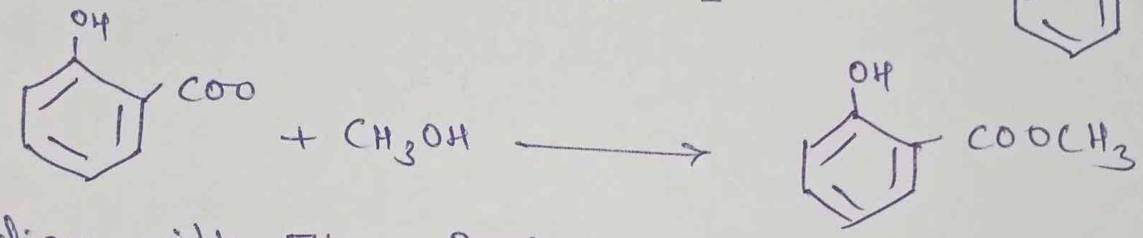
★ Other Reactions —:

- Kolbe's reaction

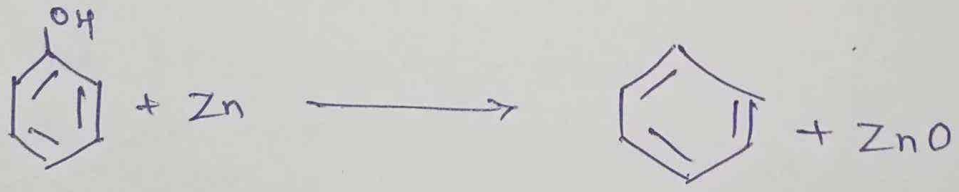


(i) 

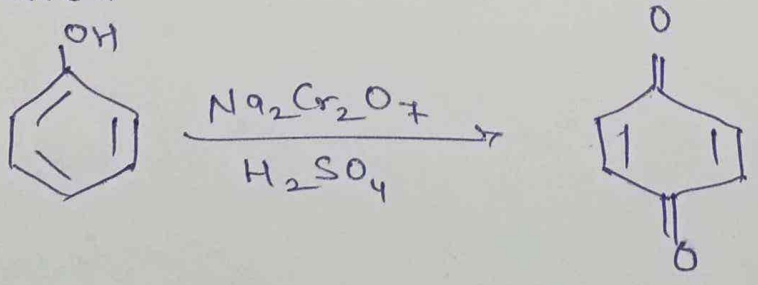
(ii) 

(iii) 

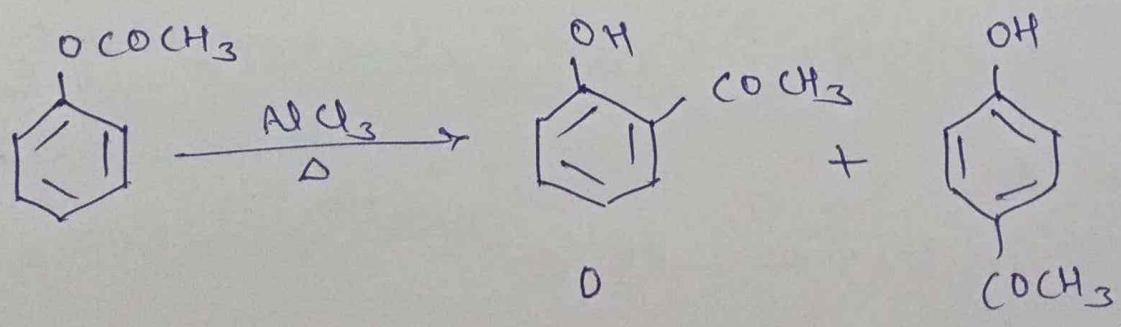
- Reaction with Zinc Dust.



- Oxidation



- Fries rearrangement



Ether (–O–)

General methods of Preparation –

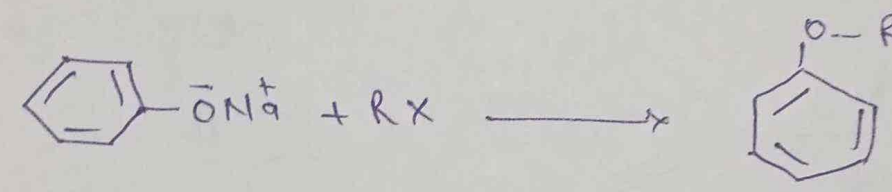
★ By dehydration of alcohols –

$$2\,CH_3CH_2OH \xrightarrow[413K]{Conc.\,H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

$$CH_3CH_2OH \xrightarrow[443K]{Conc.\,H_2SO_4} CH_2=CH_2 + H_2O$$

★ Williamson's synthesis –

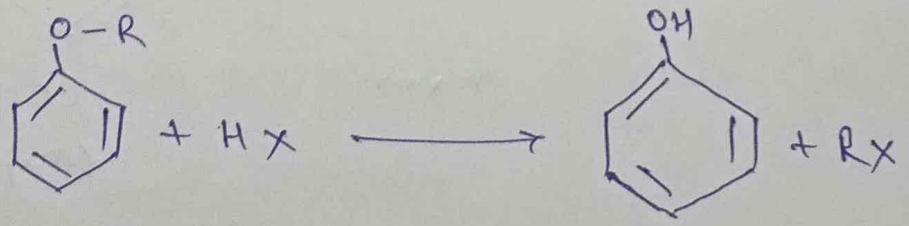
$$R-X + R'\bar{O}-Na^+ \longrightarrow R-O-R' + NaX$$



Chemical Reactions of Ether.

★ Reaction with HX –

$$R-O-R + HX \longrightarrow RX + R-OH$$



I > Br > Cl

★ Halogenation –

$$CH_3CH_2OCH_2CH_3 \xrightarrow[Dark]{Cl_2} CH_3CHClOCH_2CH_3$$

$$C_2H_5OC_2H_5 + 10Cl_2 \xrightarrow[light]{h\nu} C_2Cl_5OC_2Cl_5 + 10HCl$$

★ Reaction with PCl_5

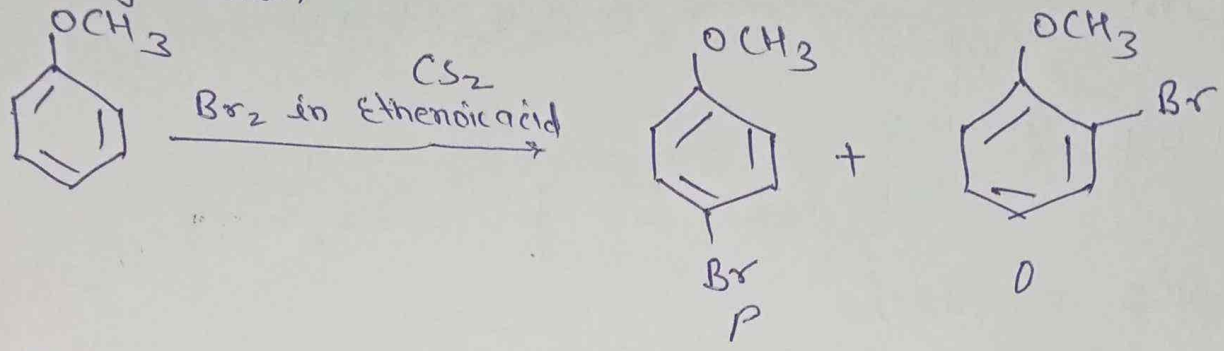
$$R-O-R + PCl_5 \xrightarrow{\Delta} 2RCl + POCl_3$$

★ Reaction with CO

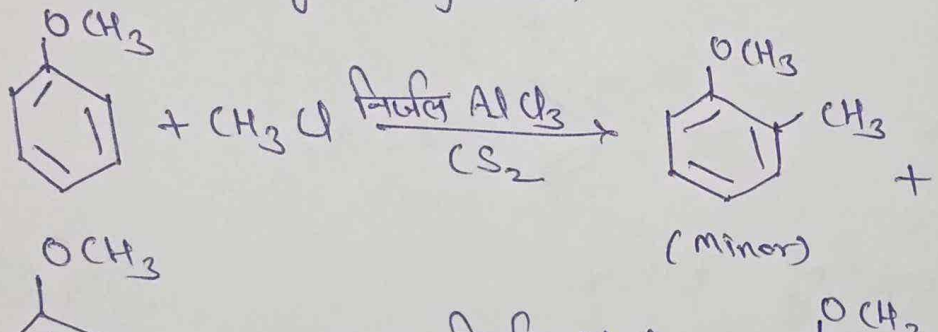
$$ROR + CO \xrightarrow[500\ atm]{BF_3 / 150^\circ C} RCOOR$$

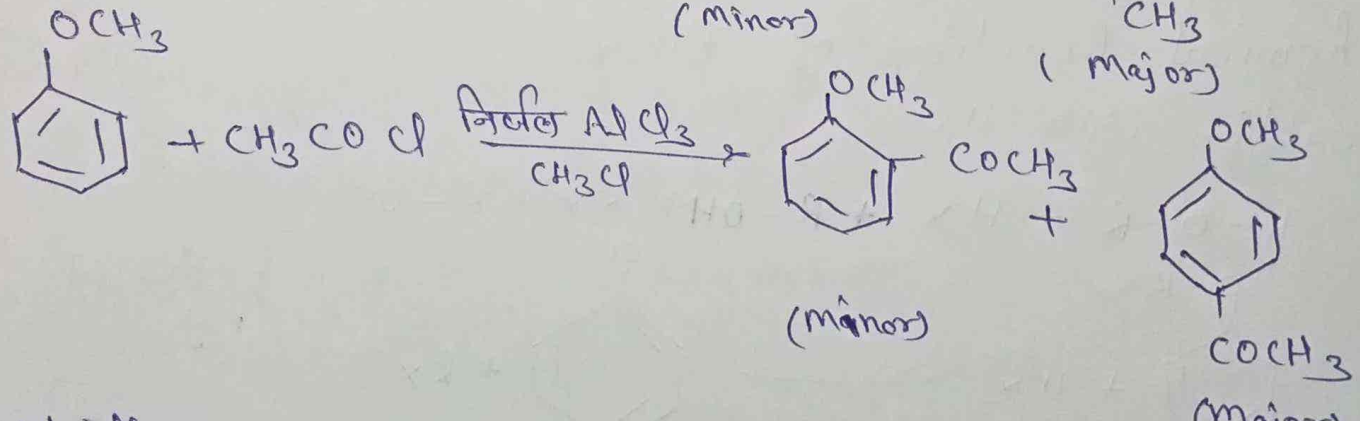
★ Electrophilic Substitution Reactions –

- Halogenation

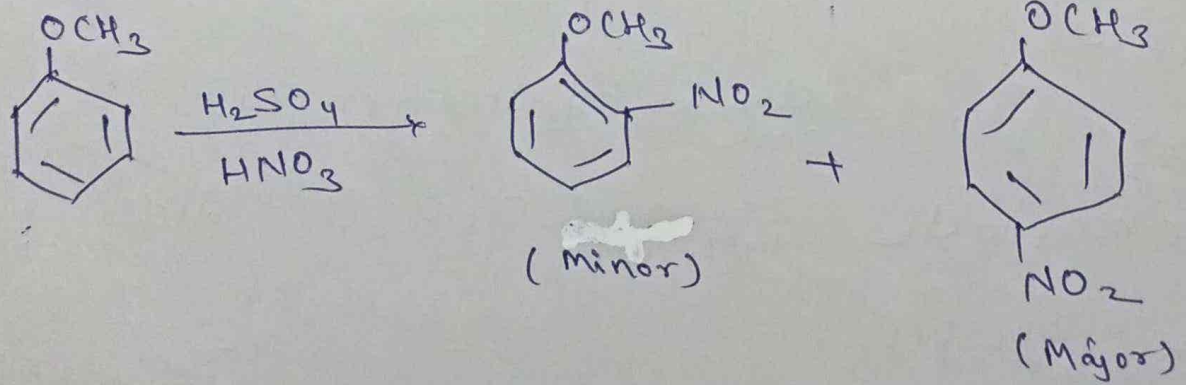


- Friedel Craft acylation





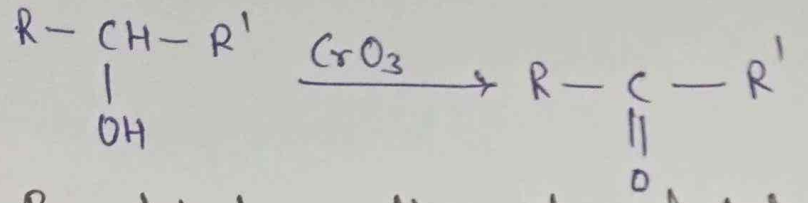
- Nitration –



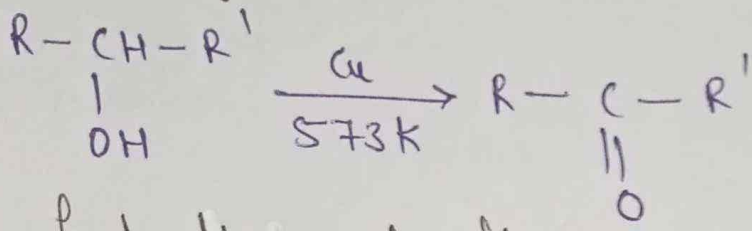
Ketones (-CO-) group

General methods of preparation of ketones.

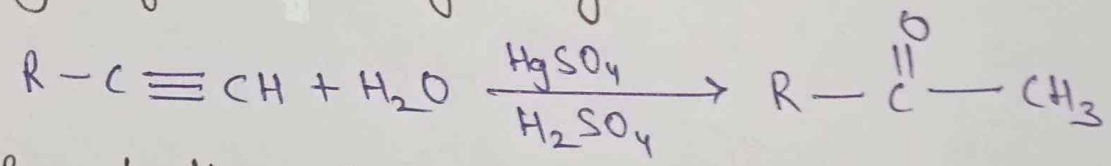
* By oxidation of alcohols.



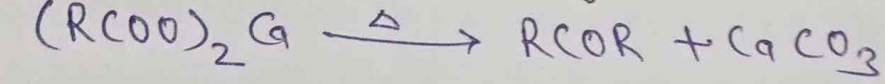
* By dehydrogenation of alcohols.



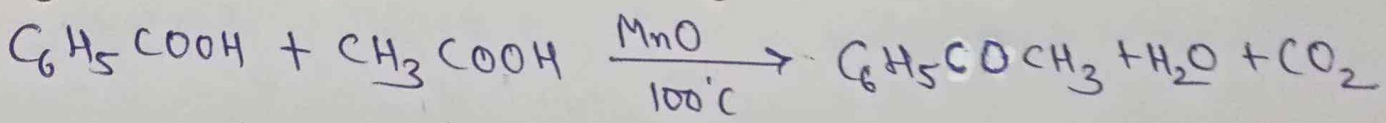
* By hydration of alkynes.



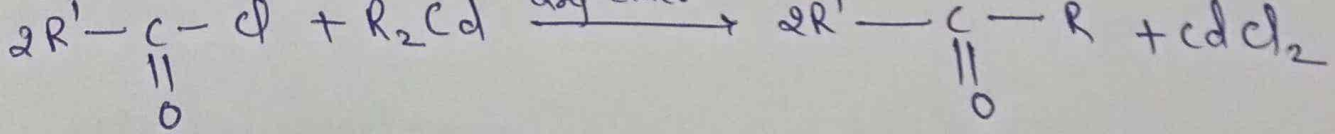
* By heating Ca Salt of acid



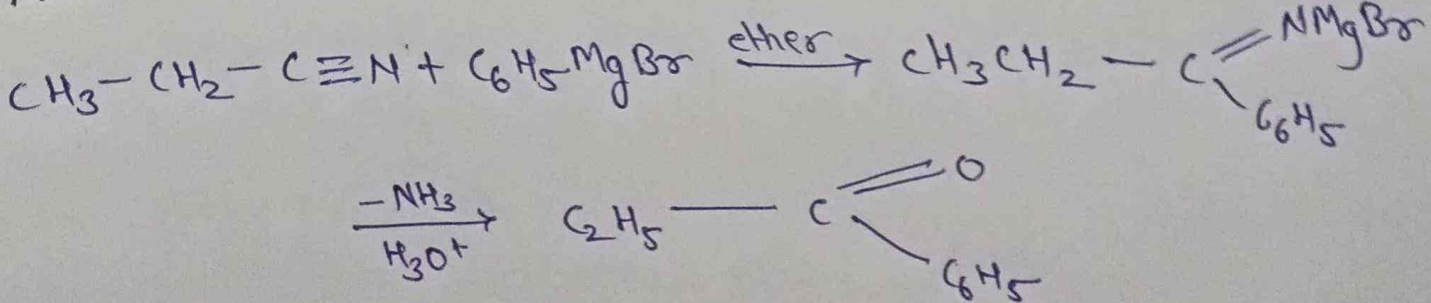
* By decarboxylation and dehydration of aromatic acids.



* from acyl chlorides



* from nitriles



* Oppenauer oxidation

$$R_2CHOH + (CH_3)_2C=O \xrightarrow{[(CH_3)_3CO]_3Al} R_2C=O + (CH_3)_2CHOH$$

Aldehyde (-CHO)

General methods of Preparation of Aldehydes.

★ By oxidation of alcohols -

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

★ By dehydrogenation of alcohols -

$$R\text{-}CH_2\text{-}OH \xrightarrow[573K]{Cu} RCHO$$

★ By ozonolysis of alkenes -

$$R\text{-}CH=CH\text{-}R \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} 2RCHO$$

★ By hydration of alkynes -

$$CH \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}H$$

★ By heating Ca Salt of acid -

$$(RCOO)_2Ca + (RCOO)_2Ca \xrightarrow{\Delta} 2RCHO + 2CaCO_3$$

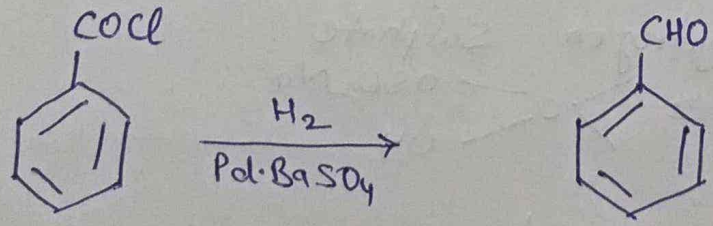
★ By decarboxylation and dehydration of aromatic acids. -

$$C_6H_5COOH + HCOOH \xrightarrow[300°C]{MnO} C_6H_5CHO + H_2O + CO_2$$

★ From gem dihalides -

$$CH_3CH\begin{matrix}Cl\\Cl\end{matrix} + 2KOH\,(aq) \xrightarrow{-2KCl} CH_3CH(OH)_2 \xrightarrow{-H_2O} CH_3CHO$$

★ Rosenmund reduction



★ From nitriles and esters -:

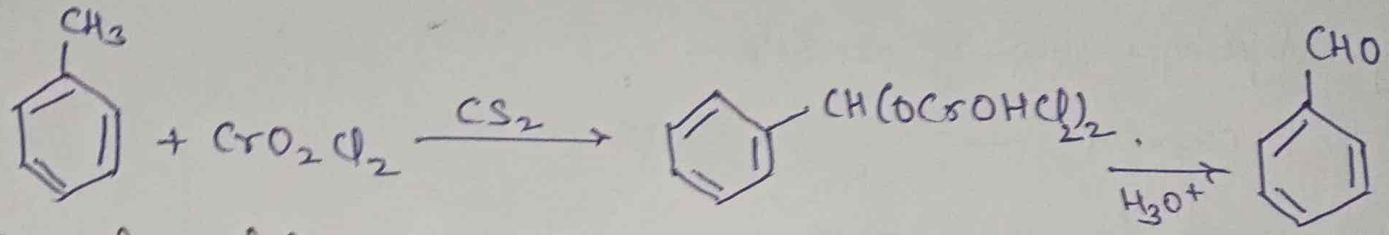
Stephen Reaction

$$RCN + SnCl_2 + HCl \xrightarrow{dry\ ether} RCH=NH \xrightarrow{H_3O^+} RCHO$$

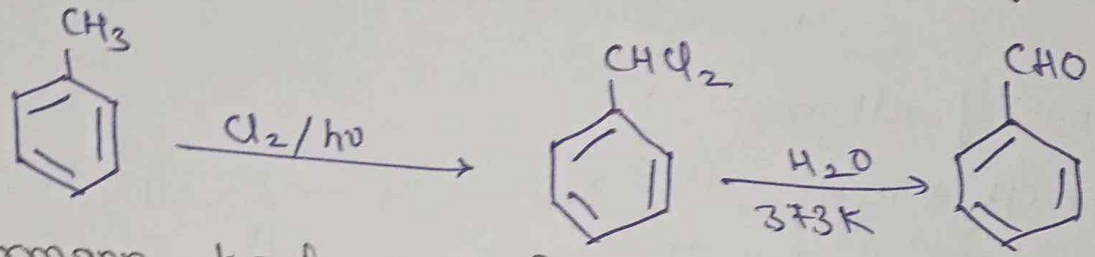
$$RCN \xrightarrow[(ii)\ H_2O]{(i)\ AlH(iBu)_2} RCHO$$

$$CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[(ii)\ H_2O]{(i)\ DiBAL-H} CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-H$$

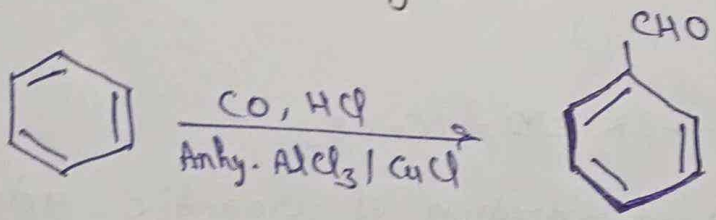
★ Etard reaction



★ Side chain halogenation followed by hydrolysis of toluene —



★ Gattermann - koch synthesis.



Chemical Reactions of Aldehydes and Ketones —:

★ Nucleophilic addition reactions —

• Addition of hydrogen cyanide (HCN)

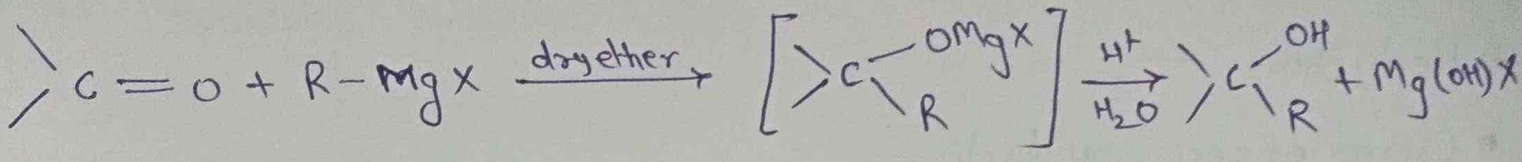
$$H-CN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$

$$>C=O + \bar{C}N \longrightarrow \left[>C(-O^-)-CN\right] \xrightarrow{H^+} >C(-OH)-CN$$

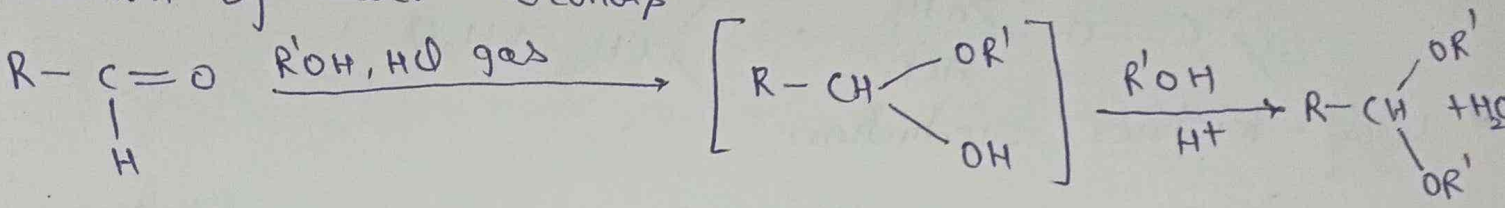
• Addition of sodium hydrogen sulphate

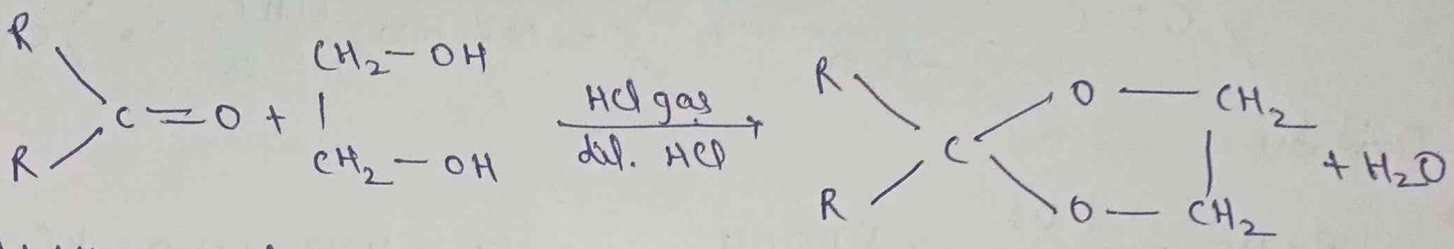
$$>C=O + NaHSO_3 \rightleftharpoons >C(-OSO_2Na)-OH$$

• Addition of Grignard reagent

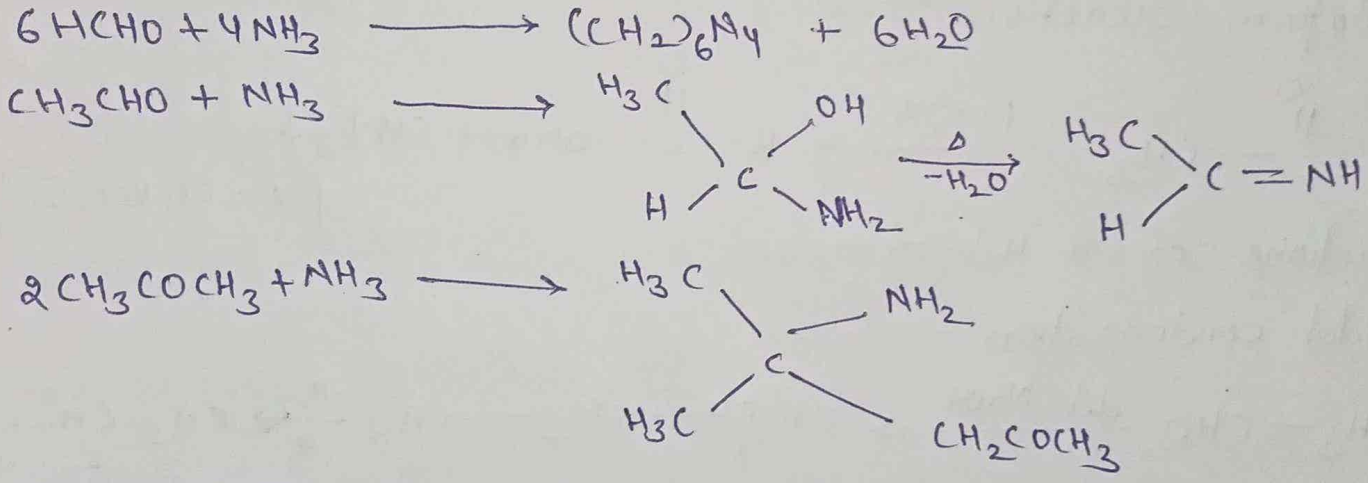


- Addition of lower alcohols

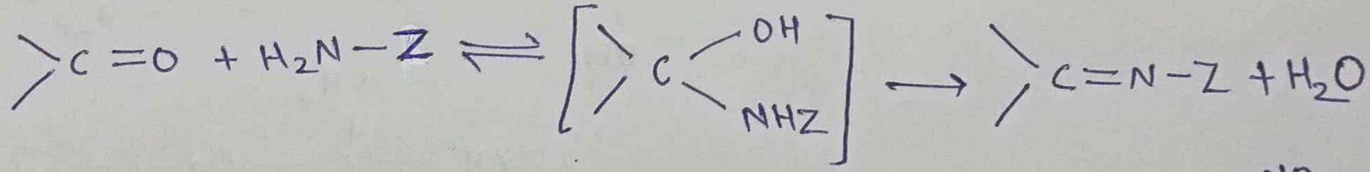


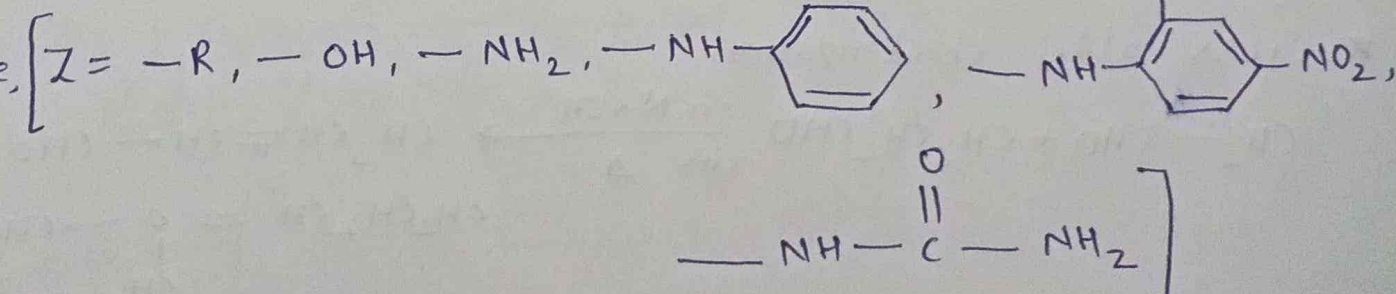


- Addition of ammonia and its derivatives



★ Nucleophillic Addition Elimination Reactions

- 

there, [Z = ]

★ Reduction —

• Clemmensen reduction

$$>C=O \xrightarrow[HCl]{Zn\cdot Hg} >CH_2 + H_2O$$

• Wolf-Kishner reduction

$$>C=O \xrightarrow[-H_2O]{H_2N\ NH_2} >C=N-NH_2 \xrightarrow[\Delta]{KOH/\ ethylene\ glycol} >CH_2 + N$$

★ Oxidation —

$$RCHO \xrightarrow{[O]} RCOOH \qquad [[O] = HNO_3, KMnO_4, k_2Cr_2O_7,$$

★ Haloform reaction —

$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{O}{\|}}{C}-ONa + CHX_3\downarrow$$

$[X = Cl, Br, I]$

★ Reactions of α-Halogen —

★ Aldol condensation -

$$2CH_3-CHO \xrightarrow{dil.\ NaOH} CH_3\underset{\underset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[\Delta]{-H_2O} CH_3-CH=CHCH$$

$$2CH_3COCH_3 \xrightarrow{dil\ Ba(OH)_2} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2COCH_3 \xrightarrow[-H_2O]{\Delta}$$

$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-COCH_3$$

★ Cross aldol condensation -

$$CH_3-CHO + CH_3CH_2CHO \xrightarrow[(ii)\ \Delta]{(i)\ NaOH} CH_3CH=CH-CHO +$$

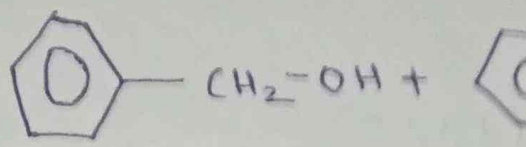
$$CH_3CH_2CH=\underset{\underset{CH_3}{|}}{C}-CHO +$$

$$CH_3-CH_2-CH=CH-CHO + CH_3-CH=\underset{\underset{CH_3}{|}}{C}CHO$$

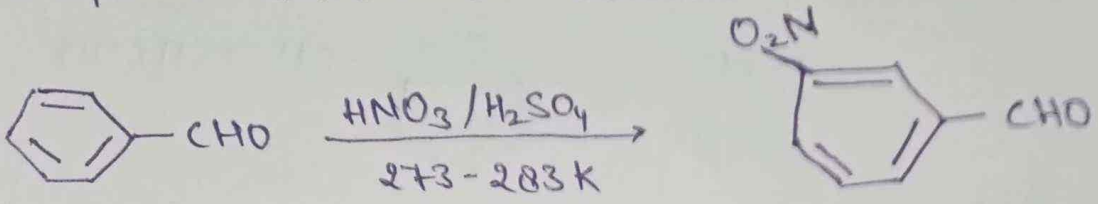
★ Other Important Reactions -

★ Cannizzaro reaction

$$2HCHO \xrightarrow{KOH\ (conc.)} CH_3OH + H-\overset{\overset{O}{\|}}{C}-OK$$

$$C_6H_5CHO \xrightarrow{NaOH\ (conc.)} \text{  }$$

★ Electrophilic substitution reaction



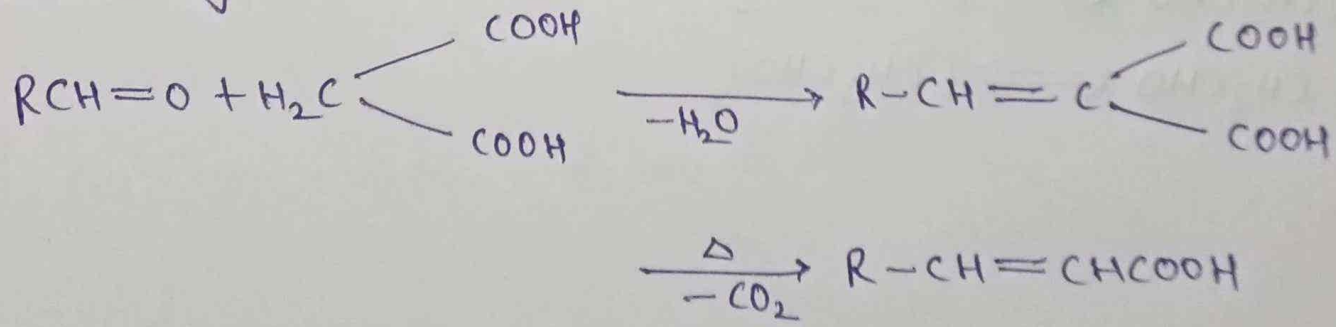
★ Baeyer Villiger oxidation

$$R_2CO + R'CO_3H \longrightarrow RCOOR + R'COOH$$

★ Tischenko's reaction

$$2CH_3CHO \xrightarrow{(C_2H_5O)_3Al} CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5$$

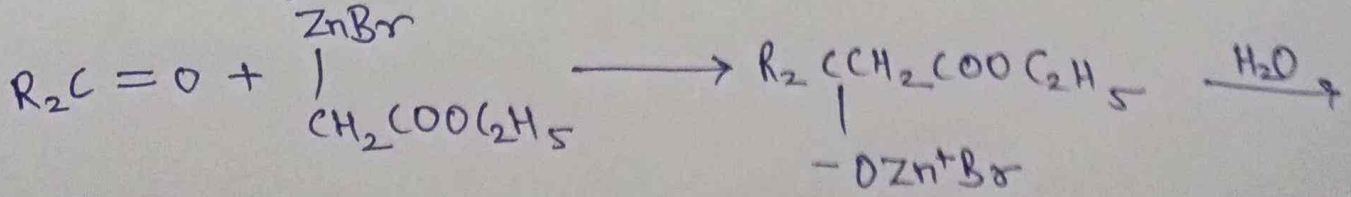
★ knoevenagel's reaction



★ Schmidt reaction

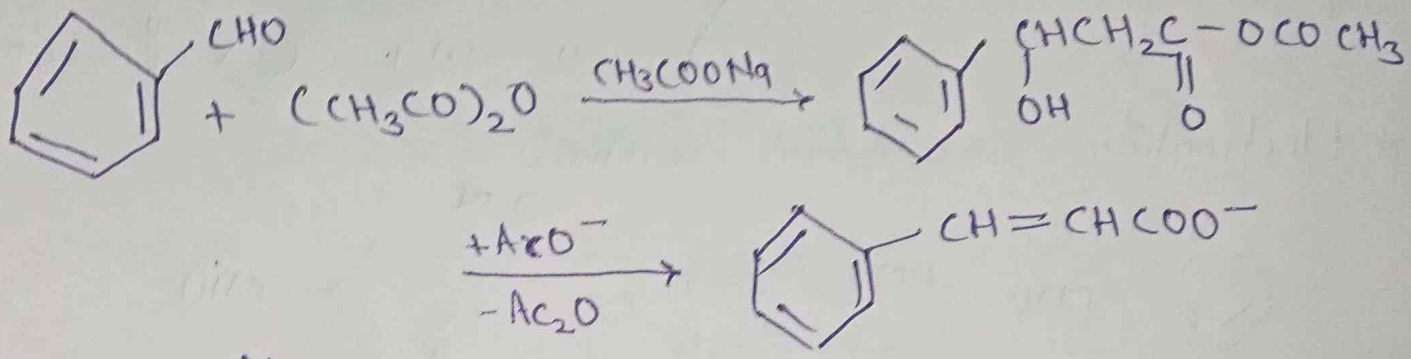
$$RCHO + N_3H \xrightarrow[\Delta]{Conc.\ H_2SO_4} HCONHR + N_2$$

★ Reformatsky reaction



$$R_2C(OH)-CH_2COOC_2H_5 \xrightarrow[\Delta]{\text{conc. } H_2SO_4} R_2C=CHCOOC_2H_5$$

★ Perkin's reaction



★ Wittig reaction

$$>C=O + PPh_3=CH_2 \longrightarrow >C=CH_2 + Ph_3P=O$$

★ Polymerisation

$$nHCHO \rightleftharpoons (CH_2O)_n$$

$$3HCHO \rightleftharpoons (HCHO)_3$$

$$3CH_3CHO \rightleftharpoons (CH_3CHO)_3$$

$$4CH_3CHO \rightleftharpoons (CH_3CHO)_4$$