19. ORGANIC CHEMISTRY

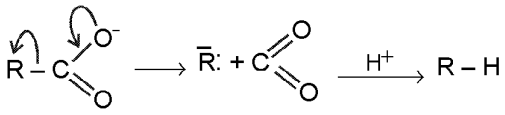
1. Alkane

Wurtz reaction :

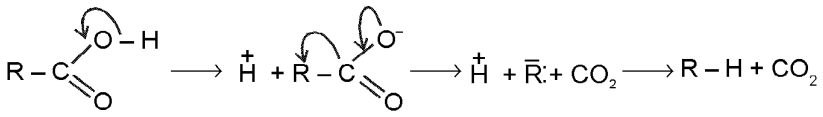
e.g., $R^1X + R^2X + 2Na \longrightarrow R^1 - R^2 + 2NaX$

Decarboxylation :

General reaction $RCOONa \xrightarrow{H^+} R - H + Na_2CO_3$

Mechanism 

The thermal decarboxylation of free acids may be :



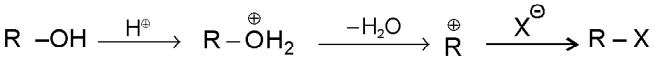
2. Alkyl halide

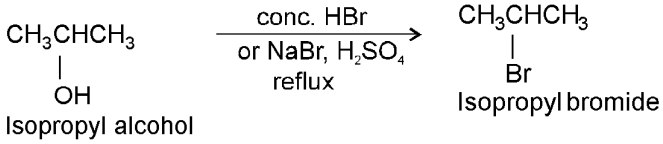
Nucleophilic substitution Reaction (S_N1, S_N2)

S_N1 reaction : $R - OH + HX \longrightarrow R - X + H_2O$ (R may rearrange)

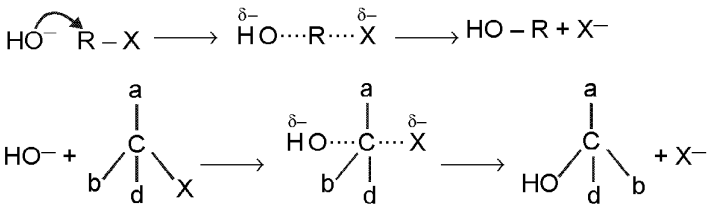
Reactivity of HX : HI > HBr > HCl

Reactivity of ROH : allyl, benzyl > 3° > 2° > 1° (Carboocation)
Carbocation formed

Mechanism 

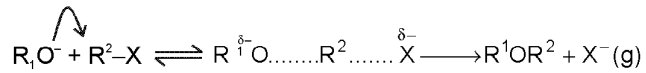
e.g. 

S_N2 reaction : Alkylhalide are hydrolysed to alcohol very solwly by water, but rapidly by silver oxide suspended in boiling water.
$RX + KOH \longrightarrow ROH + KX$

Mechanism 

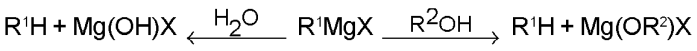
Williamson's synthesis :

It is the reaction in which sodium or potassium alkoxide is heated with an alkyl halide (S_N2).



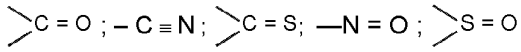
This method is particularly useful for preparing mixed ethers.

3. Grignard Reagents

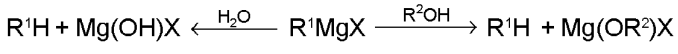


The majority of Grignard reactions fall into two groups

(i) Addition of the Grignard reagent to a compound containing a multiple - bond group e.g.

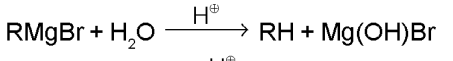


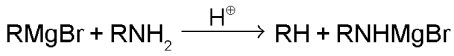
(ii) Double decompsition with compounds containing an active hydrogen atom or a reactive halogen atom.



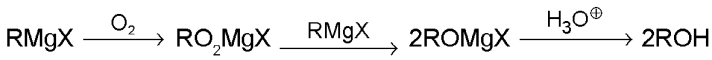
Important chemical synthesis by Grignard reagent

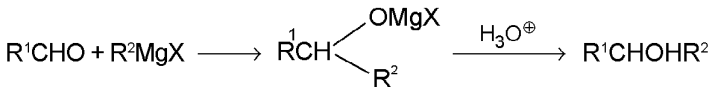
1. **Hydrocarbons :**

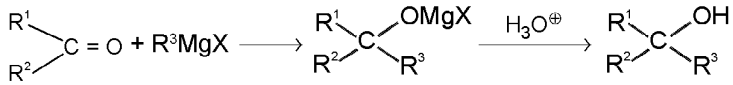




2. **Alcohols :**

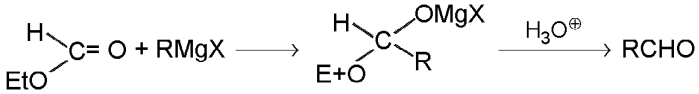
(a) Primary alcohols 

(b) Secondary alcohols 

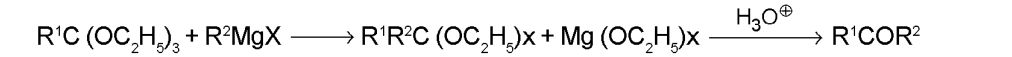
(c) Tertiary alcohols : 

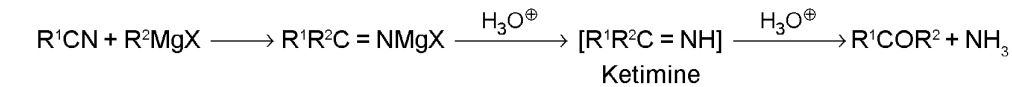
3. **Ethers :**

4. **Aldehydes :**



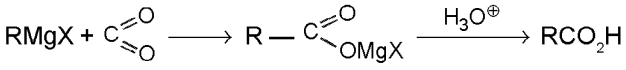
5. **Ketones :**



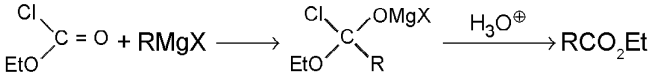


Ketimine

6. **Acids :**



7. **Esters :**



8. Alkyl Cyanides :

$RMgX + (CN)_2 \longrightarrow RCN + Mg(CN)x$

9. Primary amines :

$RMgX + RONH_2 \longrightarrow RNHMgX + RH + Mg(OCH_3)Cl \xrightarrow{H_3O^{\oplus}} RNH_2$ (40-90%)

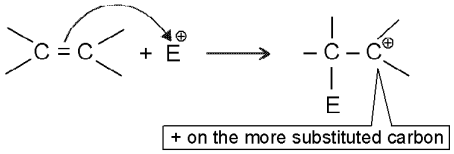
$RMgX + ClNH_2 \longrightarrow RNH_2 + MgxCl$

4. Alkene & Alkyne

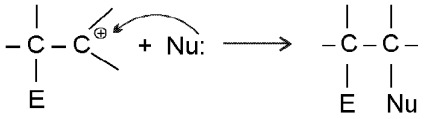
Electrophilic addition reactions :

Mechanism

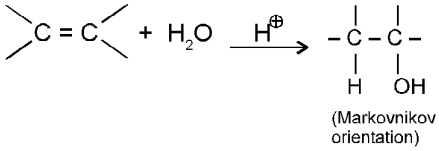
Step 1 : Attack of the electrophile on π bond forms a carbocation.



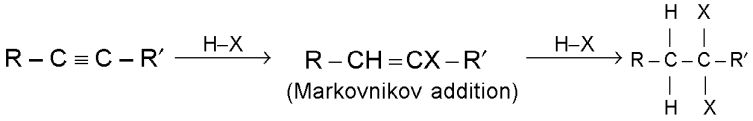
Step 2 : Attack by a nucleophile gives the product of addition.



e.g. (a) Addition of water



(b) Addition of hydrogen halides (where HX = HCl, HBr, HI)

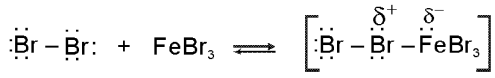


5. Aromatic compounds

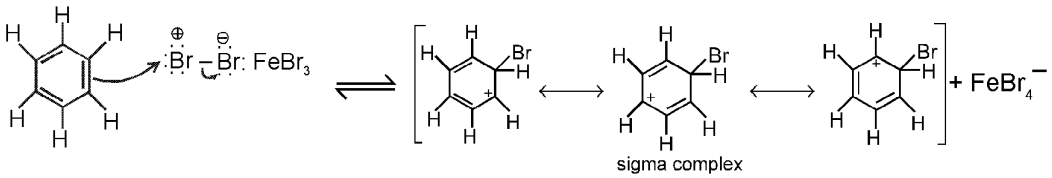
Electrophilic aromatic substitution :

(a) Bromination of Benzene : Bromination follows the general mechanism for electrophilic aromatic substitution. Bromine itself is not sufficiently electrophilic to react with benzene, but a strong Lewis acid such as $FeBr_3$ catalyzes the reaction.

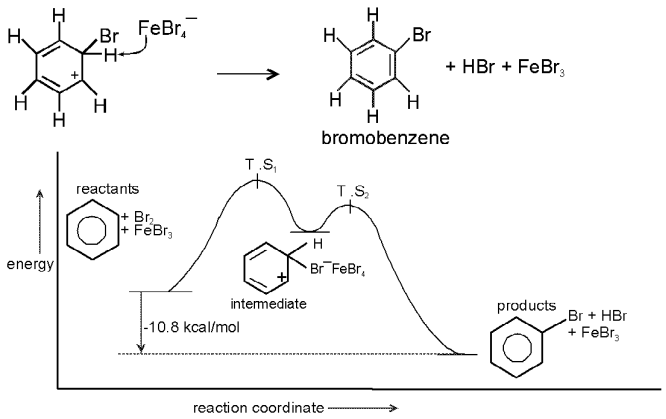
Step 1 : Formation of a stronger electrophile.



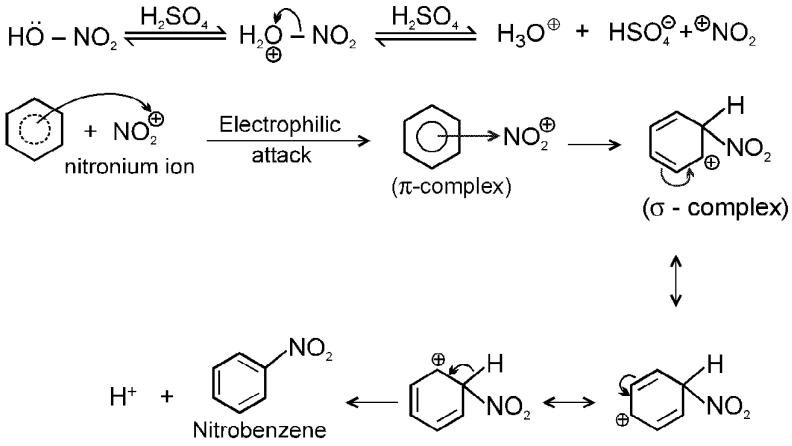
Step 2 : Electrophilic attack and formation of the sigma complex.



Step :2 Loss of a proton gives the products.

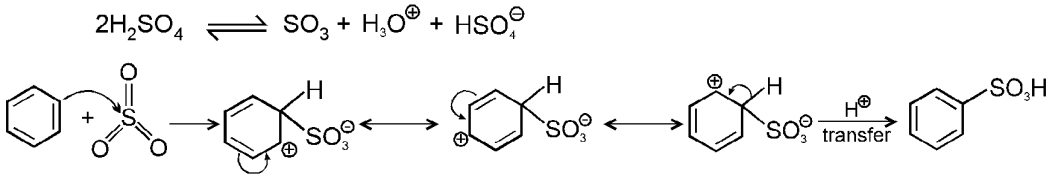


(b) Nitration



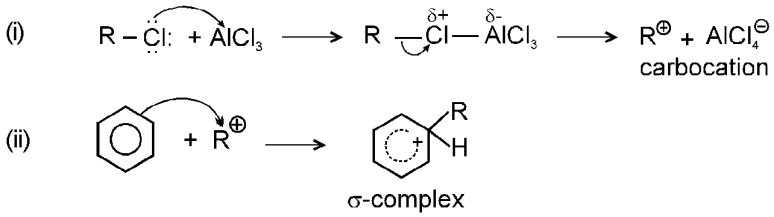
(c) Sulphonation :

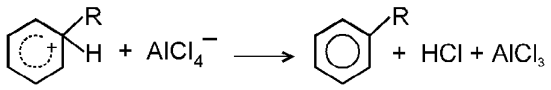
The electrophilic reagent, SO_3, attacks the benzene ring to form the intermediate carbocation.



(d) Friedel Craft reaction :

Alkylation mechanism

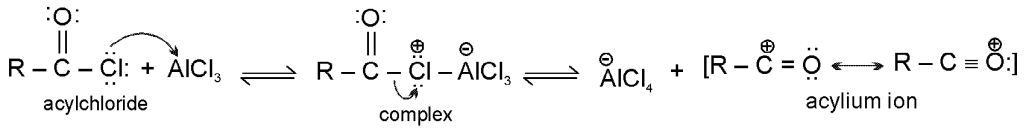


(iii) 

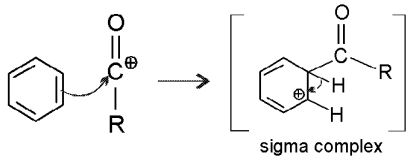
Acylation mechanism

Acylation of benzene may be brought about with acid chlorides or anhydrides in presence of Lewis acids.

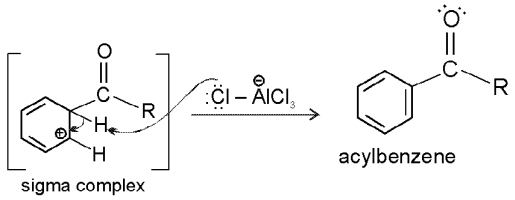
Step 1 : Formation of an acylium ion.

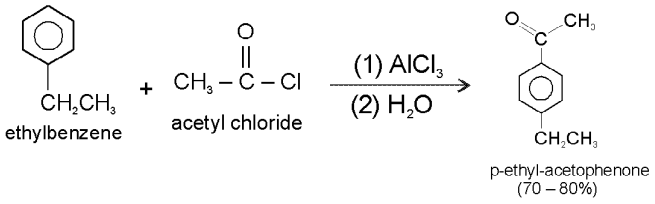


Step 2 : electrophilic attack.

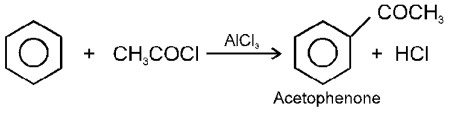


Step 3 : Loss of a proton. Complexation of the product.

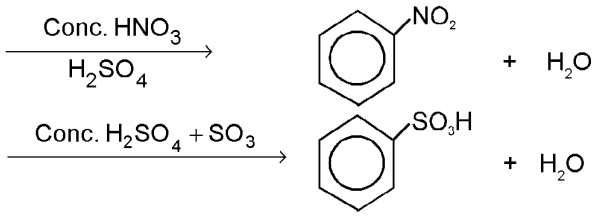


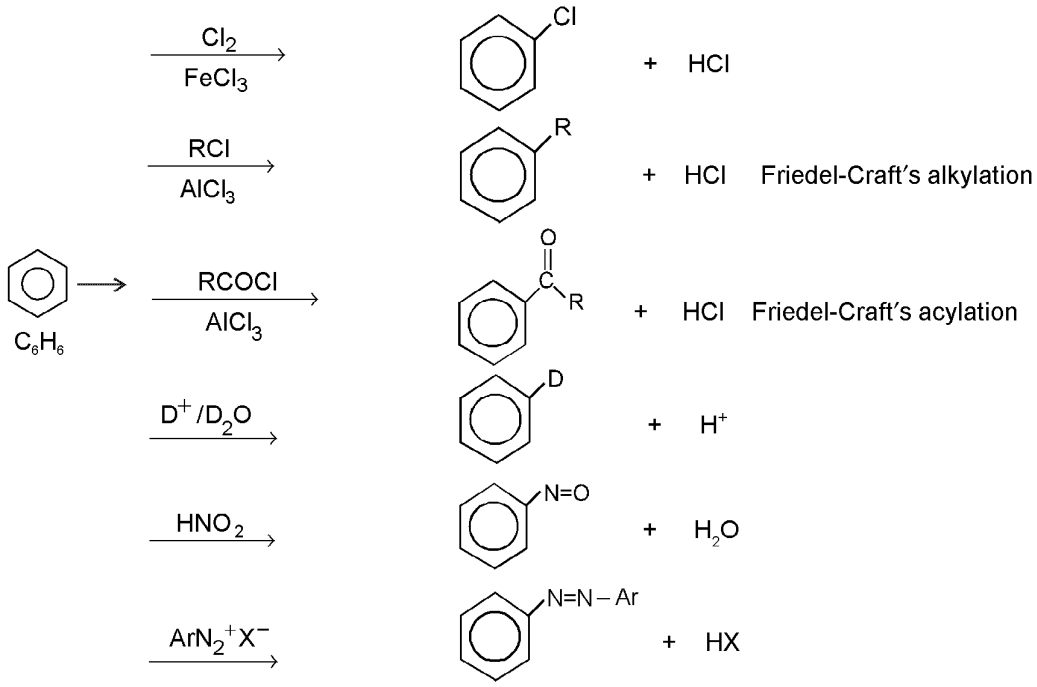
e.g. 

Note : Friedal - Crafts acylations are generally free from rearrangements and multiple substitution. They do not go on strongly deactivated rings.

e.g. 

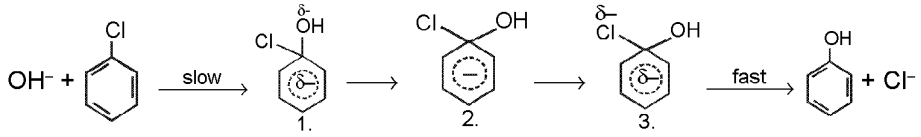
Chemical Reactions of Benzene :



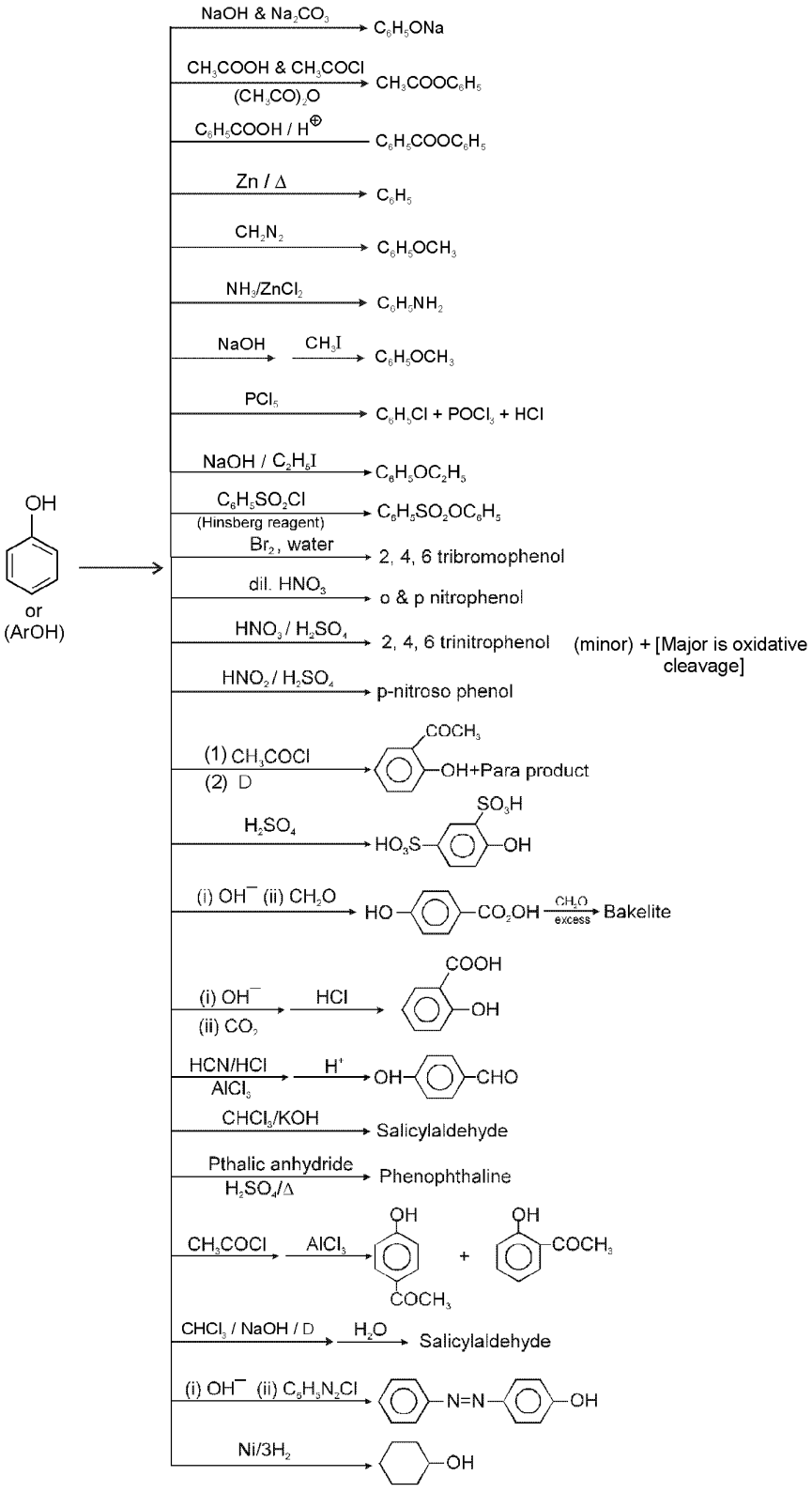


Nucleophilic Aromatic Substitution :

The reaction is second-order in which nucleophilic sbustitution occurs on benzene ring. It is generally accepted that the reaction proceeds via an intermediate σ-complex, the benzenonium carbanion (or the pentadienyl anion), e.g.,

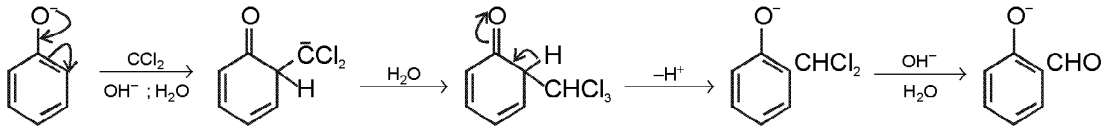


6. Chemical Reactions of Phenol



Reimer-Tiemann reaction :

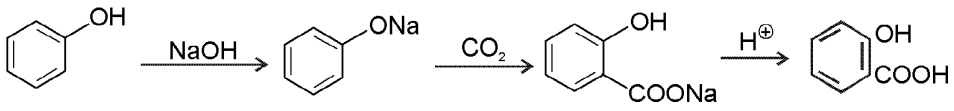
The reaction is conversion of phenol to salicylaldehyde. The mechanism of the Reimer-Tiemann reaction is believed to involve the formation of dichloromethylene.



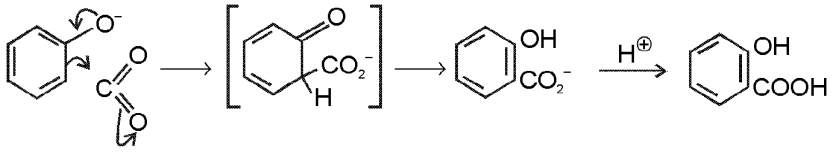
Kolbe Reaction :

It is the industrial method of preparation of salicylic acid from phenol.

General reaction :



Mechanism

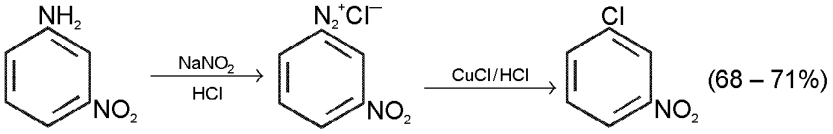


7. Chemical reactions of aniline

Sandmyer's Reaction :

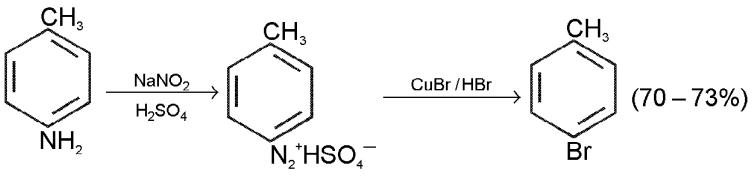
When a diazonium salt solution is run into a solution of cuprous halide dissolved in the corresponding halogen acid, the diazo-group is replaced by a halogen atom.

m – Chloronitrobenzene



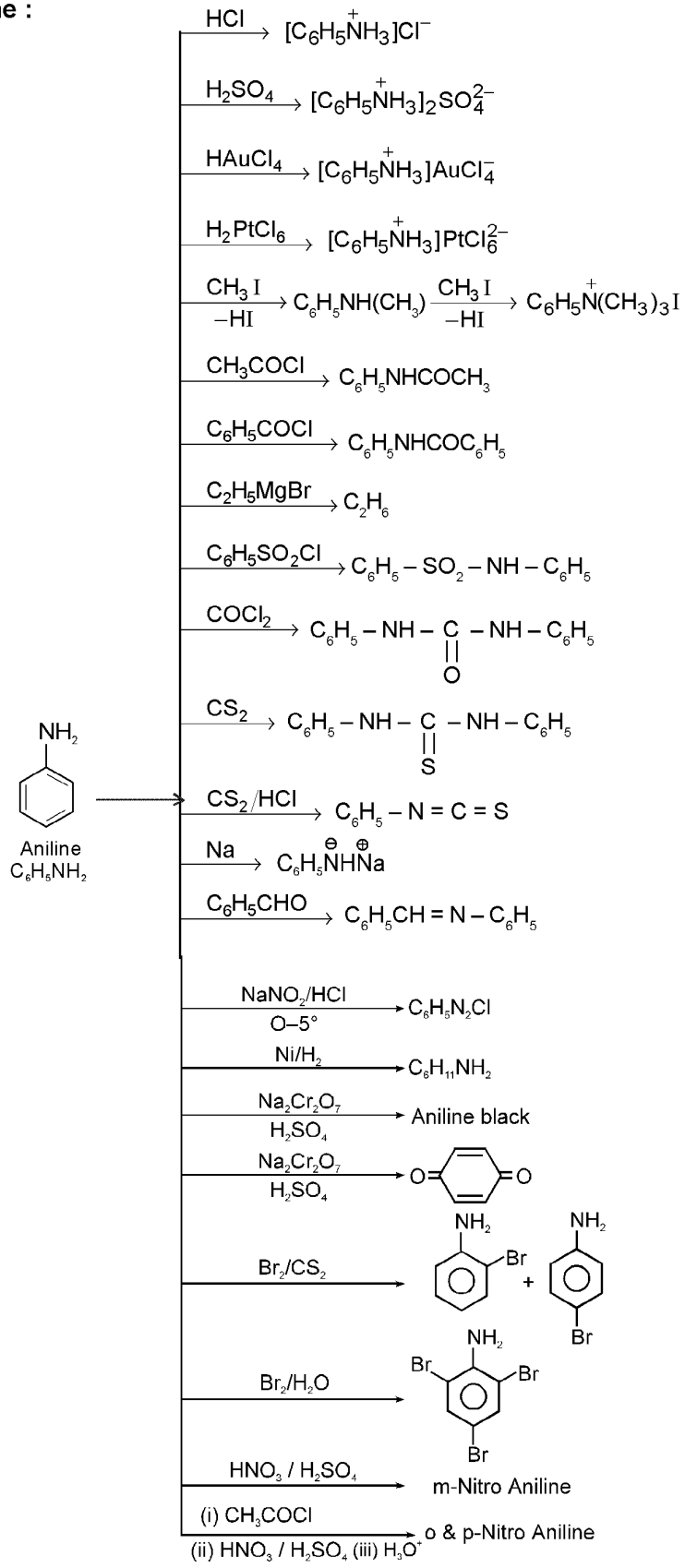
(68 – 71%)

p – Bromotoluene



(70 – 73%)

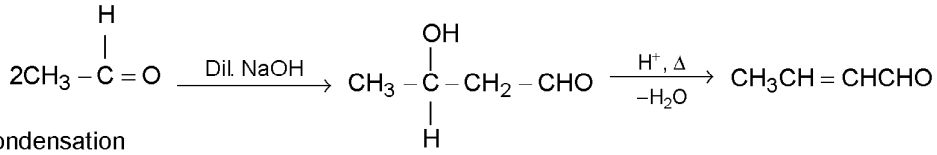
Chemical Reactions of Aniline :



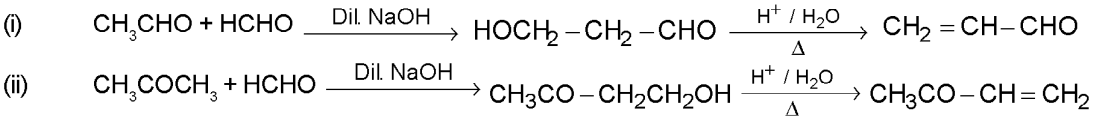
8. Aldehyde & ketone

Aldol condensation :

Carbonyl compounds having acidic α - H shows this reaction in presence of dil. NaOH or dil. acid.

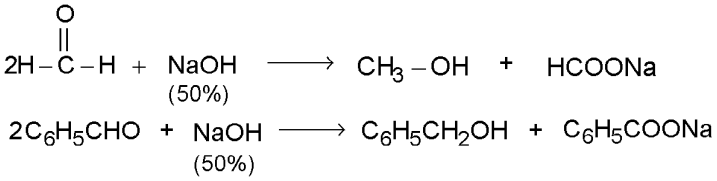


Crossed aldol condensation

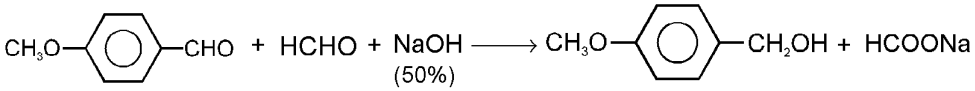


Cannizzaro reaction :

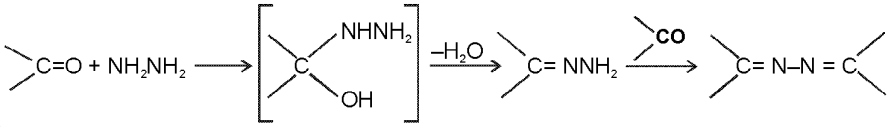
Carbonyl compounds not having α-H shows following disproportion reaction



Crossed Cannizzaro reaction :



Formation of hydrzones and azines



Amides formation :

$RCO_2H + CO(NH_2)_2 \longrightarrow RCONH_2 + CO_2 + NH_3$ (g. –v.g.)

$RCOCl + 2NH_3 \longrightarrow RCONH_2 + NH_4Cl$ (v.g.)

$(RCO)_2O + 2NH_3 \longrightarrow RCONH_2 + RCO_2NH_4$ (v.g.)

$R^1COOR^2 + NH_3 \longrightarrow R^1CONH_2 + R^2OH$ (g.)

Carbyl amine reaction

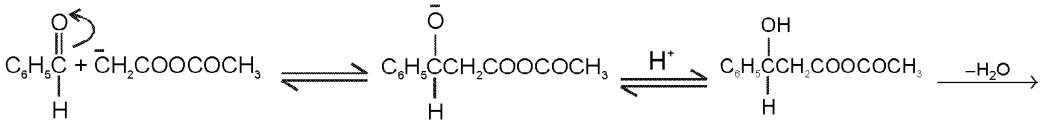
$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

Perkin reaction :

When benzaldehyde (or any other aromatic aldehyde) is heated with the anhydride of an aliphatic acid (containing two α-hydrogen atoms) in the presence of its sodium salt, condensation takes place to form a β-arylacrylic acid ; e.g., with acetic anhydride and sodium acetate, cinnamic acid is formed.

$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2Na} C_6H_5CH = CHCO_2H$

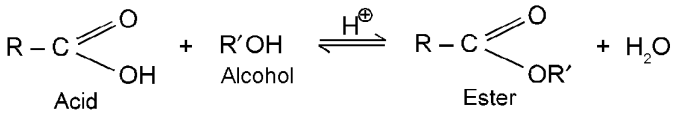
$CH_3COOCOCH_3 + CH_3CO_2^- \rightleftharpoons \bar{C}H_2COOCOCH_3 + CH_3CO_2H$



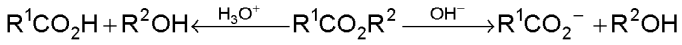
$C_6H_5CH = CHCOOCOCH_3 \xrightarrow{H_2O} C_6H_5CH = CHCO_2H + CH_3CO_2H$

9. Ester formation

General reaction

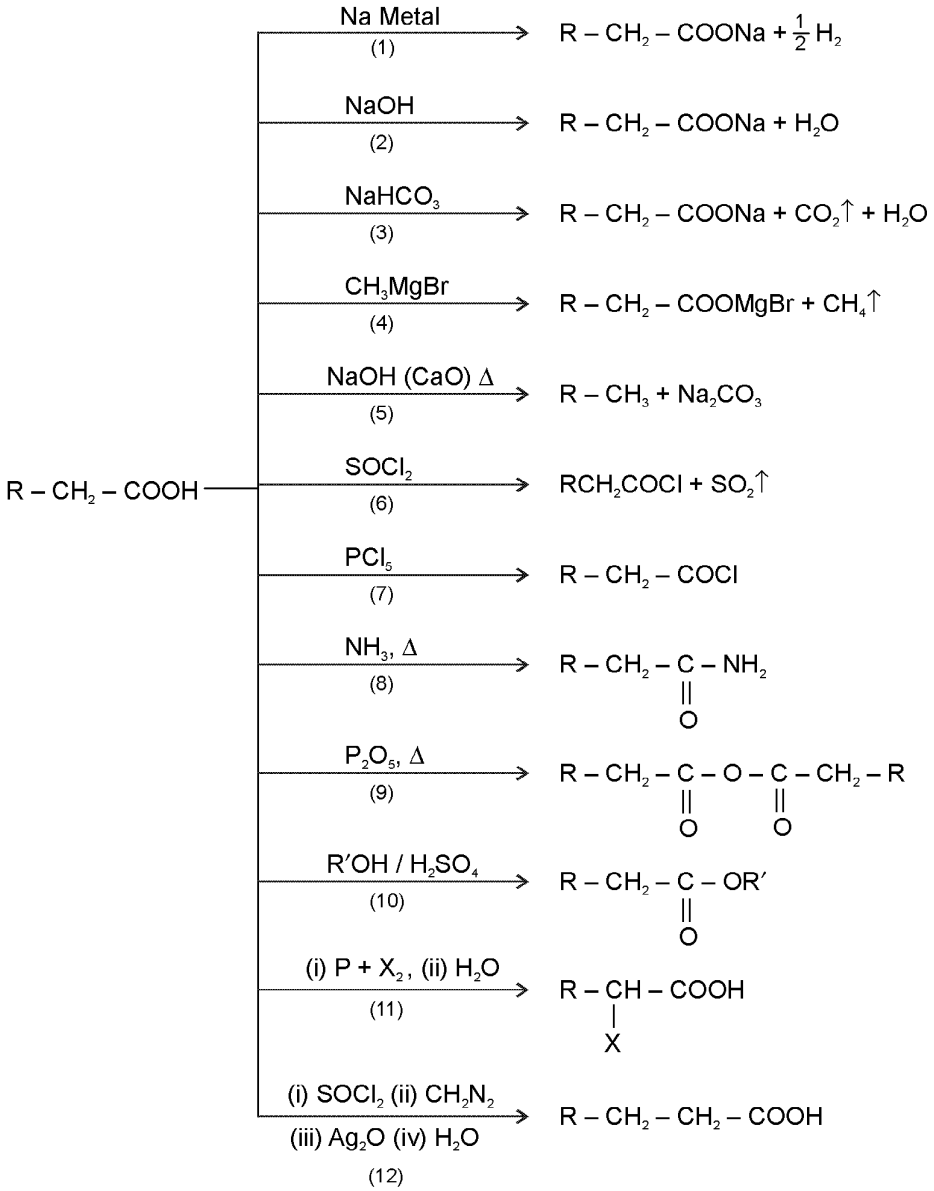


Hydrolysis of ester



10. Carboxylic Acids

Chemical Reactions of acids



Identification of Functional Groups by Laboratory Tests (POC)

Table :

Functional Groups	Reagent	Observation	Reaction	Remarks
C = C / C ≡ C	[Bayer's reagent] alk. dil. cold $KMNO_4$	Pink colour Disappears	$CH_2 = CH_2 + H_2O + O \xrightarrow{\text{alk. } KMnO_4} \underset{OH}{CH_2}-\underset{OH}{CH_2}$	Hydroxylation
	Br_2 / H_2O	Red colour decolourises	$Br_2 + CH_2 = CH_2 \longrightarrow$ white ppt	Bromination
R – C ≡ CH	(a) Cuprous chloride + NH_4OH	Red ppt.	$R - C \equiv CH + CuCl \xrightarrow{NH_4OH} R - C \equiv C\,Cu \downarrow$ (red)	
	(b) $AgNO_3 + NH_4OH$	White ppt.	$R - C \equiv CH + Ag^+ \longrightarrow R - C \equiv C\,Ag \downarrow$ (white)	
ROH 3° 2° 1°	Lucas Reagent [Conc. HCl + anhyd. $ZnCl_2$]	(3)° Cloudiness appears immidiately (2°) Cloudiness appears within 5 min. (1°) Cloudiness appear after 30 min.	$R - OH + HCl \xrightarrow{\text{anhydrous } ZnCl_2} \underbrace{R - Cl}_{\text{cloudiness}} + H_2O$	Lucas Test I. ter. alcohol II. sec. alcohol III. pri. alcohol

Functional Groups	Reagent	Observation	Reaction	Remarks
Ar – OH Enols	$FeCl_3$ (Neutral)	Coloured ppt. (violet, blue, green buff)	$6\,C_6H_5OH + FeCl_3 \longrightarrow [Fe(PhO)_6]^{-3}$	Test of enols / phenols
$>C=O$	2, 4-Dinitrophenyl hydrazine (2, 4-DNP) solution	Yellow orange ppt.	$>C=O + H_2N{\cdot}NH-C_6H_3(NO_2)_2 \longrightarrow >C=N{\cdot}NH-C_6H_3(NO_2)_2$ (yellow orange ppt.)	DNP-test
R – CHO	Fehling solution A & B	Red ppt.	$RCHO + Cu^{+2} \xrightarrow[\text{Fehling sol}^n.]{} RCOOH + Cu_2O \downarrow (\text{Red}) + 2H_2O$	Fehling's test
	Tollen's reagent	Black ppt. or silver mirror	$RCHO + Ag^{+} \downarrow \longrightarrow RCOOH + 2Ag$ (Silver mirror)	Tollen's test
	Schift's Reagent *	Pink colour resume		
$R-COCH_3$ or $ArCOCH_3$ or CH_3CHO	I_2 / NaOH	Yellow ppt of CHI_3 (iodoform)	$R-C(=O)-CH_3 \xrightarrow{I_2;\ NaOH} R-C(=O)-ONa + CHI_3$ (Iodoform)	Iodoform reaction
$R-C(=O)-OH$	Blue litmus	Litmus change to red.		Litmus test.
	Conc. $NaHCO_3$ solution	Effervescence evolve.	$R-COOH + NaHCO_3 \longrightarrow R\,COO\,Na + H_2O + CO_2 \uparrow$	Sodium bicarbonate test

★ Schift's reagent : p-Rosiniline hydrochloride saturated with SO_2 so it is colourless. The pink colour is resumed by RCHO.