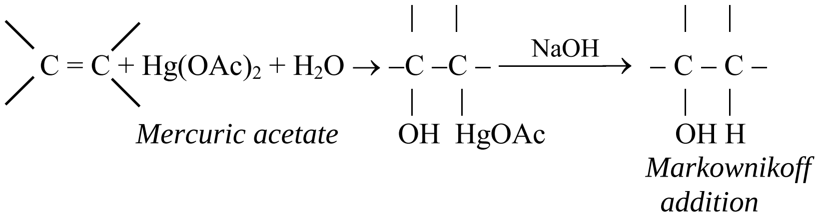
Organic Compounds Containing Oxygen

METHODS OF PREPARATION OF ALCOHOLS

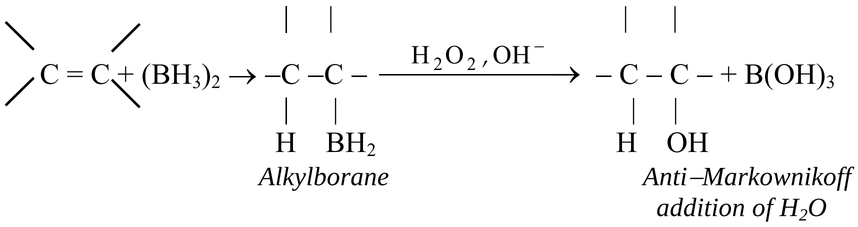
(I) Oxymercuration–Demercuration



$$>C=C< + Hg(OAc)_2 + H_2O \rightarrow -\underset{OH}{\overset{|}{C}}-\underset{HgOAc}{\overset{|}{C}}- \xrightarrow{NaOH} -\underset{OH}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}-$$

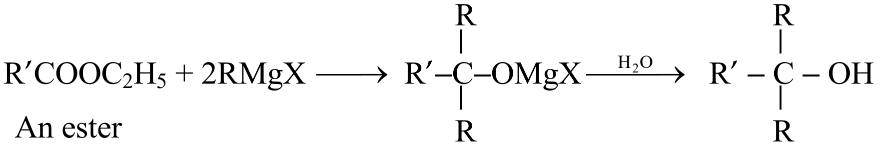
(II) Hydroboration–Oxidation

Alkene reacts with diborane to form trialkyl boranes which upon treatement with alkaline H_2O_2 give alcohols giving anti–markownikoff's addition of water.



$$>C=C< + (BH_3)_2 \rightarrow -\underset{H}{\overset{|}{C}}-\underset{BH_2}{\overset{|}{C}}- \xrightarrow{H_2O_2,\,OH^-} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- + B(OH)_3$$

(IV) By using esters



$$R'COOC_2H_5 + 2RMgX \longrightarrow R'-\underset{R}{\overset{R}{C}}-OMgX \xrightarrow{H_2O} R'-\underset{R}{\overset{R}{C}}-OH$$

(3° alcohol)

(V) Hydrolysis of alkyl halides

$$R–X + OH^{-} \text{ (or } H_2O) \longrightarrow R–OH + X^{-} \text{ (or HX)}$$

PHYSICAL PROPERTIES

The properties of the alcohols are largely determined by OH group.

(a) Boiling point– The lower members like methanol, ethanol, 1–propanol have higher boiling points.

(b) Solubility in water: The lower members of alcohols are highly soluble in water but as the size of the alkyl group increases, the solubility decreases.

CHEMICAL PROPERTIES OF THE ALCOHOLS

(I) Reaction with Hydrogen Halides

When alcohols react with a hydrogen halide, substitution takes place producing an alkyl halide and water.

$$R — OH + HX \rightarrow R — X + H_2O$$

(II) Reaction with PX_3 and PX_5

Alcohols react with PX_3 and PX_5 to yield alkyl halides (PX_3 = PBr_3, PI_3).

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

(1° or 2°)

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

(III) Reaction with $SOCl_2$

$$R - OH + SOCl_2 \longrightarrow R - Cl + SO_2 + HCl$$

(II) Esterification

The third type of replacement of hydroxylic hydrogen by an acyl group is the formation of an ester. An acyl group (RCO–) is derived commonly from acid chloride, acid anhydride or a carboxylic acid. They react with an alcohol to form ester.

(III) Formation of ether

$$R - O - H \xrightarrow[+R]{-H} ROR$$

$$R^1 - OH + R^2 - X \longrightarrow R^1OR^2 + HX$$

(IV) Reaction with RMgX

Alcohol is a weak acid. A Grignard reagent, quite a strong base, is able to abstract hydrogen from (OH) group of an alcohol.

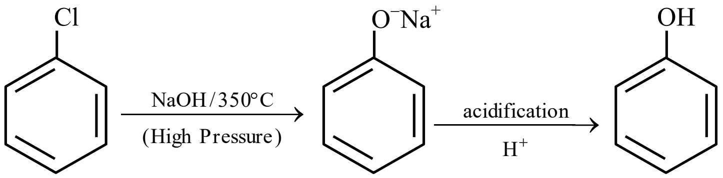
$$CH_3 - O - H + CH_3MgI \longrightarrow CH_3 - OMgI + CH_4\uparrow$$

PHENOLS

METHODS OF PREPARATION OF PHENOLS

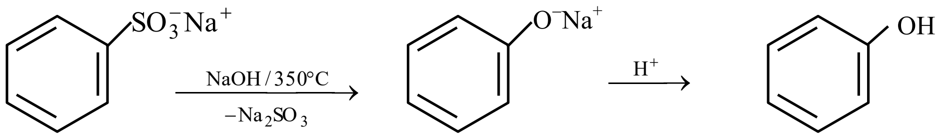
(I) Hydrolysis of chlorobenzene

In this process chlorobenzene is heated at 350°C under high pressure with aqueous NaOH. The reaction produces $C_6H_5O^-Na^+$ (sodium phenoxide) which on acidification yields phenol. This reaction is called as *Dow's process*.



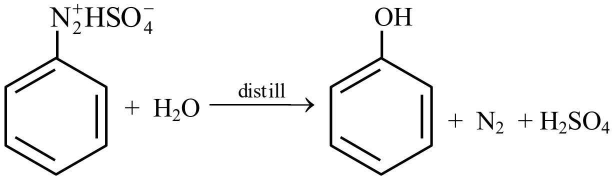
(II) Alkali fusion of Sodium Benzene Sulphonate

In this method sodium benzene sulphonate is melted (fused) with sodium hydroxide to produce sodium phenoxide which after acidification gives phenol.



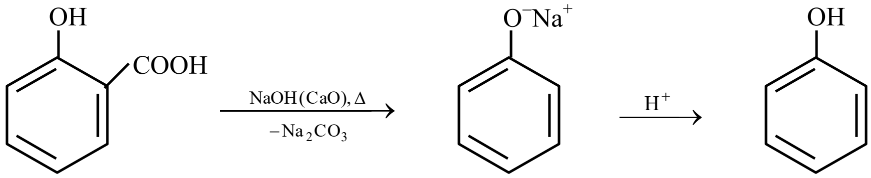
(III) Hydrolysis of Diazonium Salts

When a diazonium sulphate solution is steam–distilled, phenol is produced.



(V) By Distillation of Phenolic Acid

When phenolic acids are heated with soda lime, decarboxylation takes place producing phenols.



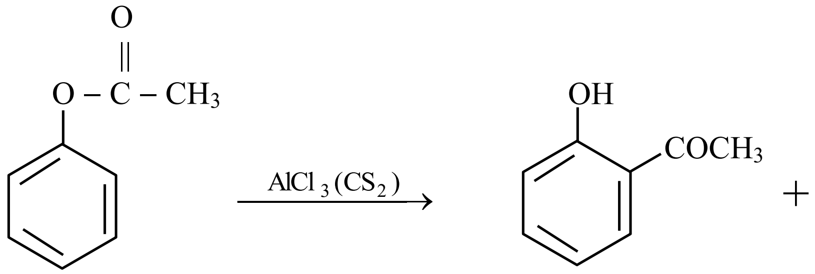
PHYSICAL PROPERTIES OF THE PHENOLS

Phenol is a colourless solid m.p. 41°C and b.p. 182°C. It becomes coloured on exposure to air. It is fairly soluble in water.

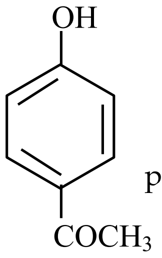
CHEMICAL PROPERTIES OF THE PHENOLS

(I) Fries rearrangement

Phenyl acetate undergoes the *Fries rearrangement* with $AlCl_3$ to form ortho and para hydroxy acetophenone. The ortho isomer is seprated from the mixture by the steam–distillation.



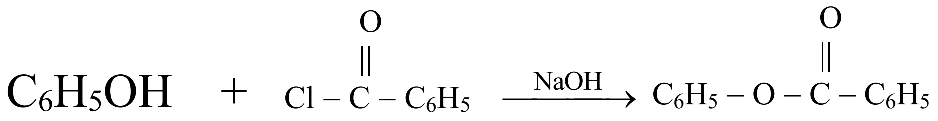
o–Hydroxy acetophenone



p–Hydroxy acetophenone

(II) Schotten – Baumann Reaction

When alkaline solution of phenol is shaken vigorously with benzoyl chloride, it forms phenyl benzoate. This is known as *Schotten – Baumann reaction.*



$$C_6H_5OH + Cl-\overset{\overset{O}{||}}{C}-C_6H_5 \xrightarrow{NaOH} C_6H_5-O-\overset{\overset{O}{||}}{C}-C_6H_5$$

Phenol Benzoyl chloride

Phenyl benzoate

(III)Reaction with PCl_5

When phenol is treated with PCl_5, it forms aryl chloride (poor yield). In this reaction triphenyl phosphate is the major product.

$$C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$$

$$3C_6H_5OH + POCl_3 \longrightarrow O = P(OC_6H_5)_3 + 3HCl$$

(Triphenyl phosphate)

$$3C_6H_5OH + PCl_3 \longrightarrow 3C_6H_5Cl + H_3PO_3$$

(IV) Reaction with NH_3

When phenol is treated with ammonia in the presence of anhydrous $AlCl_3$ or $ZnCl_2$ or $CaCl_2$ at 573 K under high pressure, phenol forms aniline.

$$C_6H_5OH + NH_3 \xrightarrow[573\,K]{ZnCl_2} C_6H_5NH_2 + H_2O$$

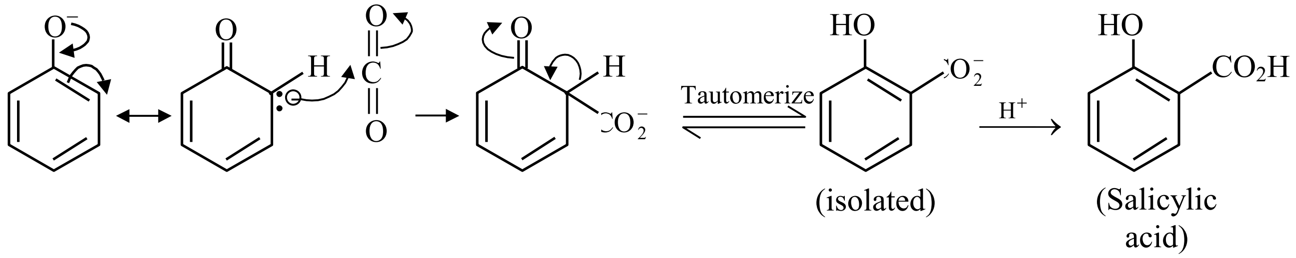
(VI) Reaction with Zn dust

When phenols are heated with Zn dust, these are reduced to aromatic hydrocarbons.

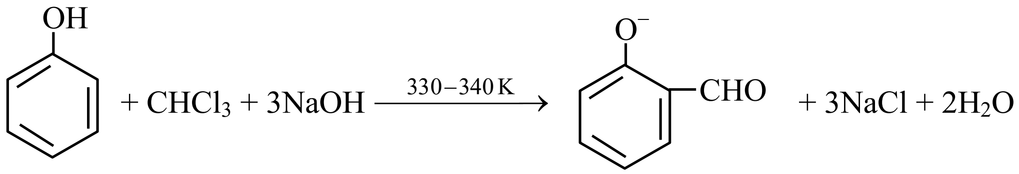
$$C_6H_5OH \xrightarrow[\text{or } H_2/MnO_2 \text{ at 1 atm}]{Zn/\Delta} C_6H_6 + Zn$$

(VI) Kolbe's–Schmidt Reaction

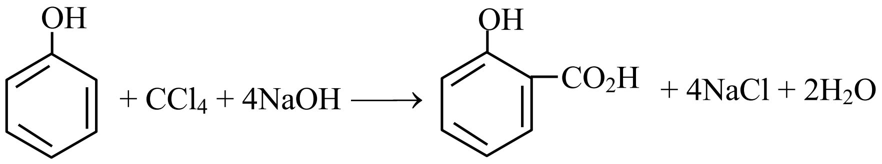
When carbon dioxide gas is passed through sodium phenoxide at 400 K under 6–7 atomospheric pressure, it forms sodium salicylate which on acidification forms salicylic acid, although some para isomer is also formed.



(VI) Reimer–Tiemann reaction



When phenol is reacted with CCl_4 in the presence of NaOH, salicylic acid is obtained.



ETHERS

METHODS OF PREPARATION OF ETHERS

(I) Williamson's Continuous Etherification Process

This method was developed by Williamson and it involves the interaction of sodium alkoxide with alkyl halide. Sodium alkoxide is produced by the action of Na on alcohol.

$$2\,R-O-H + 2\,Na \longrightarrow 2R-O^{-}Na^{+} + H_2\uparrow$$

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

(II) Intermolecular Dehydration of Alcohols

$$R—O—H + H—O—R \xrightarrow[140°C]{\Delta} R—O—R + H_2O$$

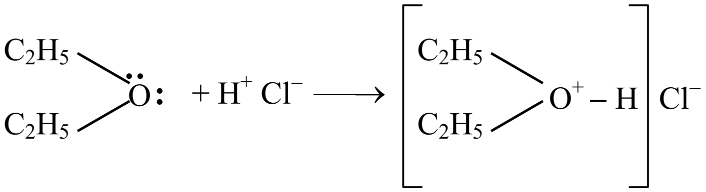
PHYSICAL PROPERTIES OF THE ETHERS

Ethers boil at a temperature much lower than the alcohols from which they are derived or than alcohols of similar molecular weight, but boiling points correspond closely to those of comparably substituted alkanes of similar molecular complexity.

CHEMICAL PROPERTIES OF THE ETHERS

(I) Salt formation

Though ethers are neutral compound but these form oxonium salts with inorganic acids.



Diethylether hydrochloride

This reaction is due to lone pair of electron on oxygen of ether functional group.

(II) Cleavage by acids

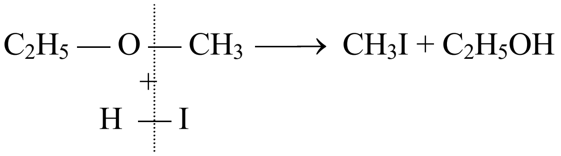
$$R{-}O{-}R' + HX \longrightarrow R{-}X + R'{-}OH \; R'{-}X + H_2O$$

Reactivity of HX : HI > HBr > HCl

Cleavage takes place only under vigorous conditions i.e. concentrated acids (usually HI or HBr) and at high temperatures.

Action of HI

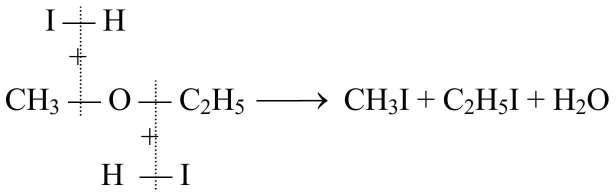
(a) At room temperature



$$C_2H_5 - O - CH_3 + H - I \longrightarrow CH_3I + C_2H_5OH$$

$$CH_3 - O - C(CH_3)_3 + HI \longrightarrow CH_3OH + (CH_3)_3C - I$$

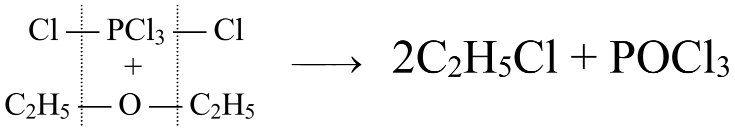
(b) At 100° C (excess of HI)



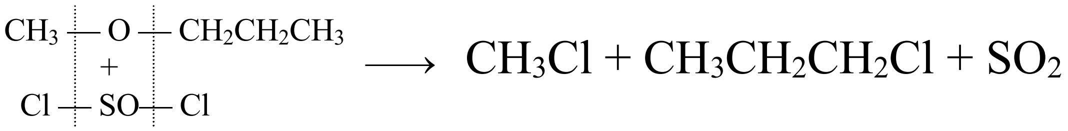
$$CH_3 - O - C_2H_5 + 2HI \longrightarrow CH_3I + C_2H_5I + H_2O$$

Thus the metameric ethers can be easily identified by the cleavage with HI.

(III) Action of PCl_5 or $SOCl_2$



$$C_2H_5 - O - C_2H_5 + Cl - PCl_3 - Cl \longrightarrow 2C_2H_5Cl + POCl_3$$



$$CH_3 - O - CH_2CH_2CH_3 + Cl - SO - Cl \longrightarrow CH_3Cl + CH_3CH_2CH_2Cl + SO_2$$

Thus the reaction of PCl_5 or $SOCl_2$ can be used to identify the metameric ethers.

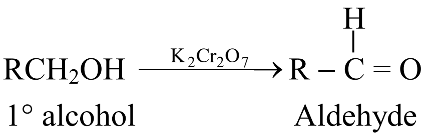
ALDEHYDES & KETONES

Aldehydes and ***ketones*** belong to a class of compounds having general formula $C_nH_{2n}O$ and are represented as RCHO and RR'CO respectively.

METHODS OF PREPARATION OF ALDEHYDES

(I) Oxidation of primary alcohols

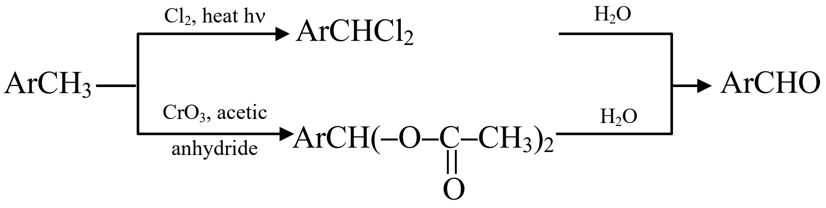
Oxidation can be affected with acidic $K_2Cr_2O_7$ or with PCC (Pyridine Chlorochromate, mild oxidising agent) in CH_2Cl_2.



$$\underset{1^\circ \text{ alcohol}}{RCH_2OH} \xrightarrow{K_2Cr_2O_7} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O}$$

(By special distillation method)

(II) Oxidation of Methylbenzenes



A gem–diacetate
(Non oxidizable but
isolable)

(III) By heating a mixture of the calcium salts of formic acid and any one of its homologues

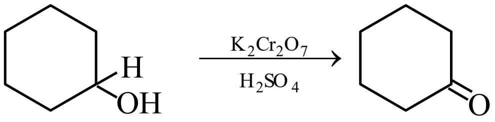
$$(RCO_2)_2Ca + (HCO_2)_2Ca \xrightarrow[\text{distillati on}]{\text{Dry}} 2RCHO + CaCO_3$$

$$(HCO_2)_2Ca \xrightarrow[\text{distillati on}]{\text{Dry}} HCHO + CaCO_3$$

METHODS OF PREPARATION OF KETONES

(I) Oxidation of secondary alcohols

$$RCH(OH)R' \xrightarrow[K_2Cr_2O_7,\, H_2SO_4]{CrO_3 \text{ or}} RCOR'$$



(II) By heating the calcium salt of any monocarboxylic acid other than formic acid

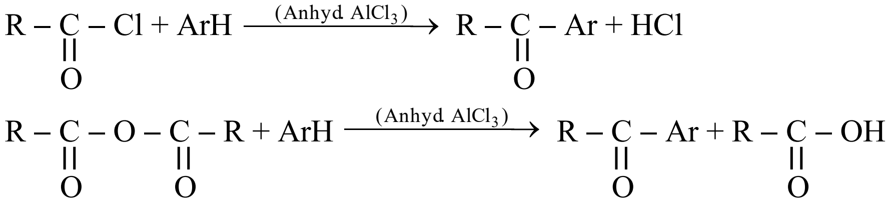
$$(RCO_2)_2Ca \xrightarrow[\text{distillati on}]{\text{Dry}} R_2CO + CaCO_3$$

For example,

$$(C_2H_5COO)_2Ca \xrightarrow[\text{distillati on}]{\text{Dry}} C_2H_5COC_2H_5 + CaCO_3$$

(III) Friedel – Craft's acylation

Used for the preparation of aliphatic–aromatic ketones or aromatic ketones.



$$R-\underset{\underset{O}{\|}}{C}-Cl + ArH \xrightarrow{(\text{Anhyd } AlCl_3)} R-\underset{\underset{O}{\|}}{C}-Ar + HCl$$

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R + ArH \xrightarrow{(\text{Anhyd } AlCl_3)} R-\underset{\underset{O}{\|}}{C}-Ar + R-\underset{\underset{O}{\|}}{C}-OH$$

PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

The polar carbonyl group makes aldehydes and ketones polar compounds and hence they have higher boiling points than non-polar compounds of comparable molecular weights.

CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

1. Oxidation

(a) $RCH{=}O \xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7\text{ , }H^+} RCO_2H$

or or

$ArCH{=}O$ $ArCO_2H$

(b) Tollen's Reagent

A specific oxidant for RCHO is $Ag(NH_3)_2^+$ $RCH = O + 2Ag(NH_3)_2^+ + 3OH^- \longrightarrow RCOO^- + 2H_2O + 4NH_3 + 2Ag$

(Silver mirror)

Tollen's test is chiefly used for the detection of aldehydes.

(c) Strong Oxidants

Ketones resist mild oxidation, but with strong oxidants at high temperature they undergo cleavage of C – C bond on either sides of the carbonyl group.

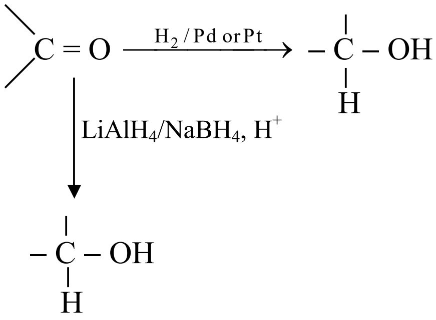
$\mathrm{RCH_2\overset{a}{-}CO\overset{b}{-}CH_2R'} \xrightarrow[\text{(drastic)}]{\text{oxidation}}$ $\mathrm{RCO_2H}$ + $\mathrm{R'CH_2CO_2H}$ + $\mathrm{RCHCO_2H}$ + $\mathrm{R'CO_2H}$

(d) Haloform Reaction is shown by methyl ketones.

CH_3COR are readily oxidsed by NaOI (NaOH + I_2) to iodoform, CHI_3, and RCO_2Na.

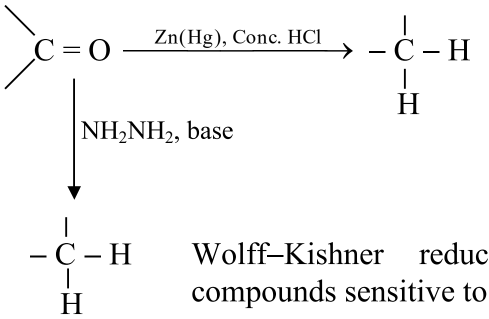
2. Reduction

(a) Reduction to alcohols: Reduction to alcohols can be achieved either by hydrogenation in the presence of Pt or Pd or by $LiAlH_4/NaBH_4$.



Aldehydes ⟶ 1° alcohols, ketones ⟶ 2° alcohols

(b) Reduction to Hydrocarbons

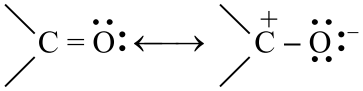


Clemmensen reduction for compounds sensitive to base

Wolff–Kishner reduction for compounds sensitive to acids

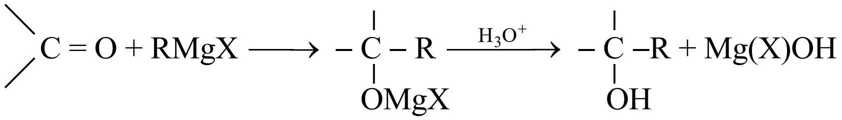
3. Addition Reactions of Nucleophiles

The carbon of the carbonyl group is electrophilic



and thus initially attacked by a nucleophile.

(a) Addition of Grignard Reagent

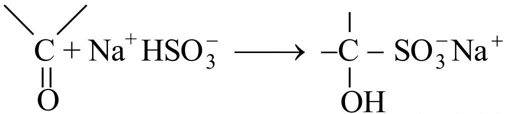


(b) Addition of hydrogen cyanide

$$R_2C = O + HCN \xrightarrow{OH^-} R-\overset{\displaystyle R}{\underset{\displaystyle OH}{C}}-CN$$

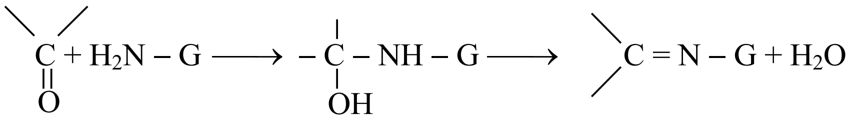
(c) Addition of sodium bisulfite

Bisulphite compound formation is confined to aldehydes, methyl ketones and some cyclic ketones.



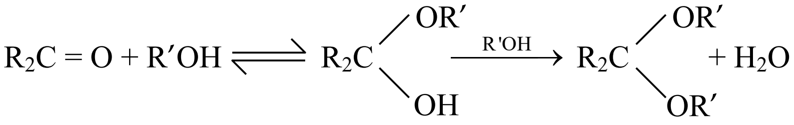
Bisulphite addition product
(Used in purification)

(d) Nucleophilic addition of derivatives of ammonia



4. Addition of Alcohols

The carbonyl compounds react with alcohols, R'OH, to yield hemi–acetals.



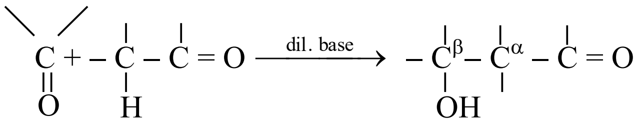
Acetal (gem–diether)

5. Cannizzaro Reaction

$$2\ -CHO \xrightarrow[\text{base}]{\text{Strong}} -CO_2^- \quad + \quad -CH_2OH$$

(no α – H) Acid salt Alcohol

6. Aldol Condensation



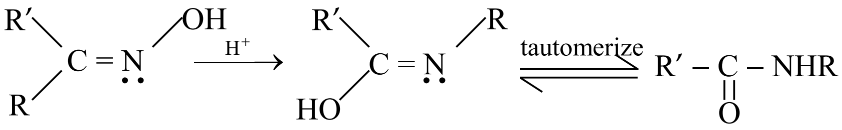
An aldol
(A β–hydroxycarbonyl compound)

7. Perkin Condensation

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH = CHCOOH$$

8. Beckmann Rearrangement

The acid catalyzed conversion of ketoximes to N–substituted amides is known as Beckmann rearrangement.



CARBOXYLIC ACIDS & DERIVATIVES

Methods of Preparation of Carboxylic Acids

(I) By oxidation of Primary alcohol

$$(CH_3)_2CHCH_2CH_2OH \xrightarrow[\Delta]{K_2Cr_2O_7,H^+} (CH_3)_2CHCH_2COOH$$

(II) By hydrolysis of cyanides

$$R-C\equiv N \xrightarrow{H^+/HOH} R-COOH$$

$$C_6H_5CH_2CN \xrightarrow[\Delta]{aq.\ H_2SO_4} C_6H_5CH_2COOH$$

General Physical Properties of the Carboxylic Acids

The molecules of carboxylic acids are polar and exhibit ***hydrogen bonding***. The first four members are miscible with water. The higher acids are virtually insoluble. The simplest aromatic acid, benzoic acid contains too many carbon atoms to show appreciable solubility in water.

General Chemical Properties of the Carboxylic Acids

(I) Acidic Property

The carboxylic acids react with metal to liberate hydrogen and are soluble in NaOH and $NaHCO_3$ solutions.

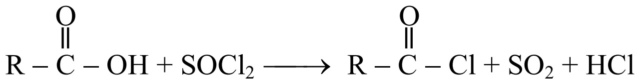
For example,

$$2CH_3COOH + 2Na \longrightarrow 2CH_3COO^-Na^+ + H_2$$

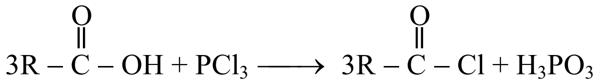
$$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2$$

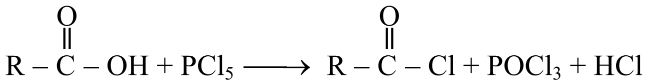
(II) Formation of acid halide



$$R-\overset{\overset{O}{\parallel}}{C}-OH + SOCl_2 \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-Cl + SO_2 + HCl$$



$$3R-\overset{\overset{O}{\parallel}}{C}-OH + PCl_3 \longrightarrow 3R-\overset{\overset{O}{\parallel}}{C}-Cl + H_3PO_3$$



$$R-\overset{\overset{O}{\parallel}}{C}-OH + PCl_5 \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-Cl + POCl_3 + HCl$$

(III) Reduction to Alcohols

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

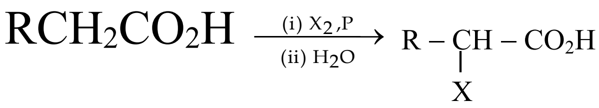
$LiAlH_4$ is the only reducing agent employed to reduce acid to 1°–alcohols as it is a strong reducing agent with respect to $NaBH_4$.

(IV) Decarboxylation of Carboxylic acids

$$RCOOH \xrightarrow{\text{decarboxylation}} RH + CO_2$$

(V) Halogenation of Aliphatic acids:
(HELL–VOLHARD–ZELINSKY REACTION)

Aliphatic carboxylic acids react with Br_2 or Cl_2 in presence of phosphorus (or phosphorous halides) to give α–haloacids.



$$RCH_2CO_2H \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2, P} R-\underset{\displaystyle X}{\underset{|}{C}H}-CO_2H$$

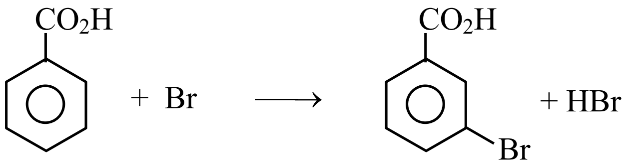
(VIII) Schmidt Reaction

Carboxylic acids react with hydrazoic acid in presence of concentrated H_2SO_4 to give amine.

$$RCOOH + HN_3 \xrightarrow[\Delta]{H_2SO_4} R-NH_2 + CO_2 + N$$

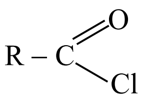
(IX) Some Specific Reactions of Benzoic acids and substituted benzoic acid

(a) Benzoic acid is attacked by the usual electrophilic reagents Chlorine, Bromine, Nitric and sulphuric acids to give m–derivatives.

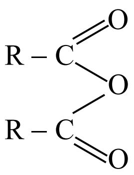


Derivatives of Carboxylic Acids

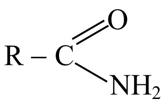
Acid derivatives are the compounds in which –OH group of carboxyl group has been replaced by –Cl, –COR, $-NH_2$ or –OR'



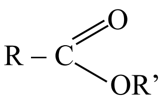
Acid chloride



Anhydride



Amide



Ester

Acyl Chlorides

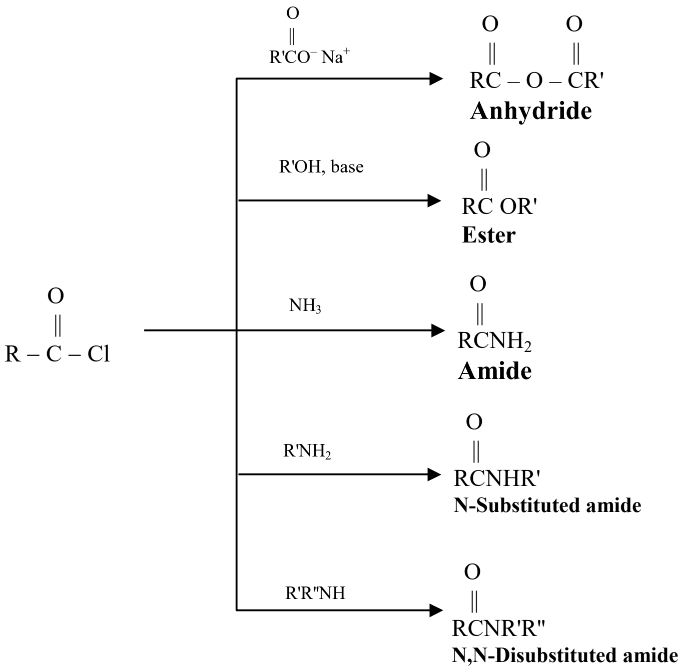
Preparation of Acyl Chlorides

By reaction with $SOCl_2$, PCl_5 and PCl_3

(Already discussed in chemical reactions of carboxylic acid)

Reactions of Acyl Chloride

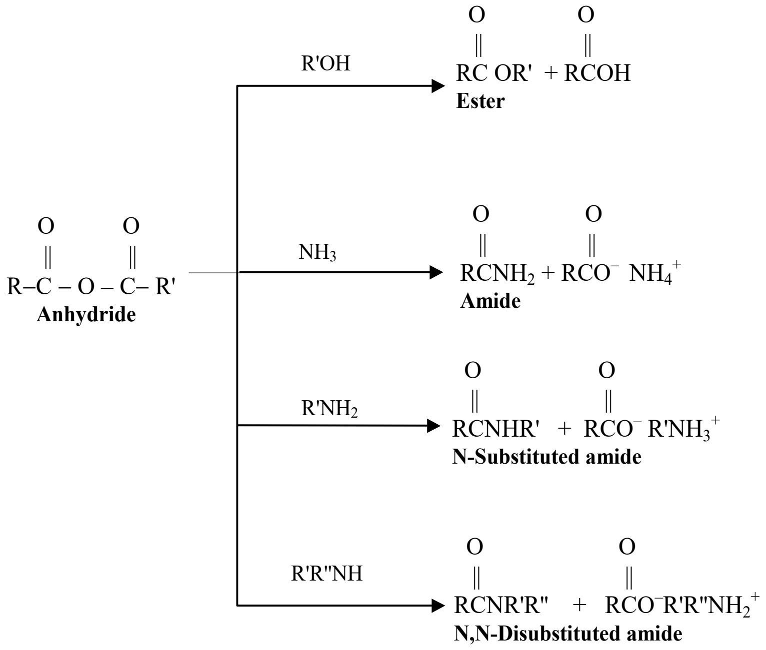
(I) Nucleophilic Substitution Reactions



Acyl chlorides also react with water and (even more rapidly) with aqueous base to undergo hydrolysis to carboxylic acids.

Carboxylic Acid Anhydride

Reactions of Carboxylic Acid Anhydrides

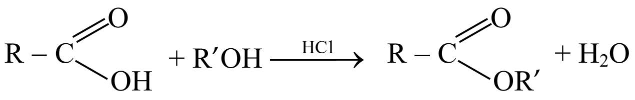


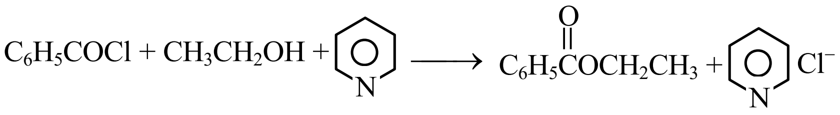
Esters

Preparation of Esters

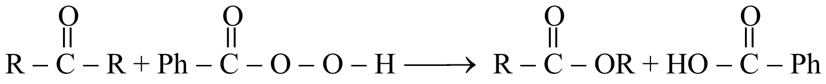
(I) Esterification: Already discussed in chemical properties of carboxylic acids.

(II) Esters from Acyl chlorides:





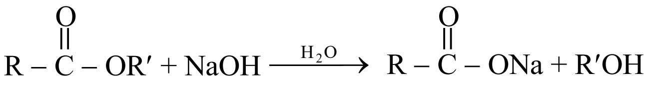
III. From ketones (Baeyer–Villiger Oxidation)



$$R-\overset{\overset{\large O}{\|}}{C}-R+Ph-\overset{\overset{\large O}{\|}}{C}-O-O-H\longrightarrow R-\overset{\overset{\large O}{\|}}{C}-OR+HO-\overset{\overset{\large O}{\|}}{C}-Ph$$

Reactions of Esters

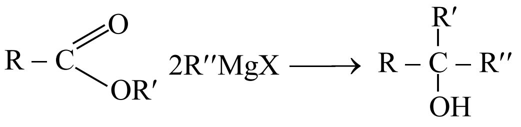
(I) Base–promoted hydrolysis of esters: Saponification



$$R-\overset{\overset{\large O}{\|}}{C}-OR'+NaOH\xrightarrow{H_2O}R-\overset{\overset{\large O}{\|}}{C}-ONa+R'OH$$

The carboxylate ion is very unreactive towards nucleophilic substitution because it is negatively charged, hence the reaction is essentially irreversible.

(II) Reaction with Grignard reagent



Acid Amides

Preparation of Acid Amides

(I) Nucleophilic Substitution

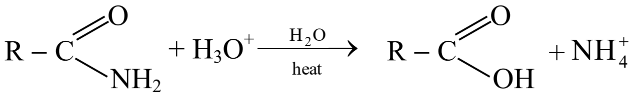
Amides can be synthesized by nucleophilic substitution of NH_3 in acyl chloride, acids anhydride or esters.

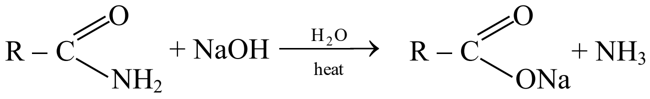
(II) By Heating Ammonium Carboxylate

$$RCOONH_4 \xrightarrow{\text{heat}} RCONH_2 + H_2O$$

Reactions of Acid Amides

(I) Hydrolysis

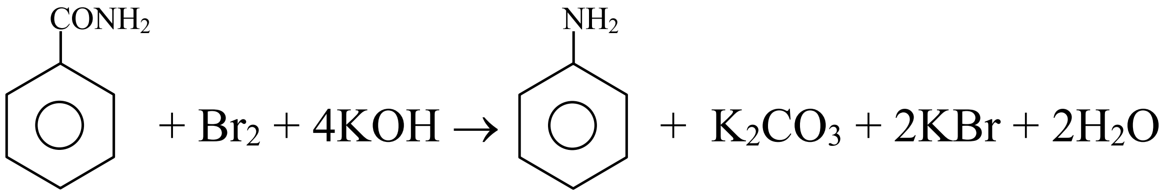




(II) Hoffmann's Bromamide Reaction

Amides (having primary nitrogen atom) react with bromine in the presence of alkali to form a primary amine having one carbon atom less than the parent amide:

$$R - CO - NH_2 + Br_2 + 4KOH \rightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$


CONH$_2$
+ Br$_2$ + 4KOH →
NH$_2$
+ K$_2$CO$_3$ + 2KBr + 2H$_2$O