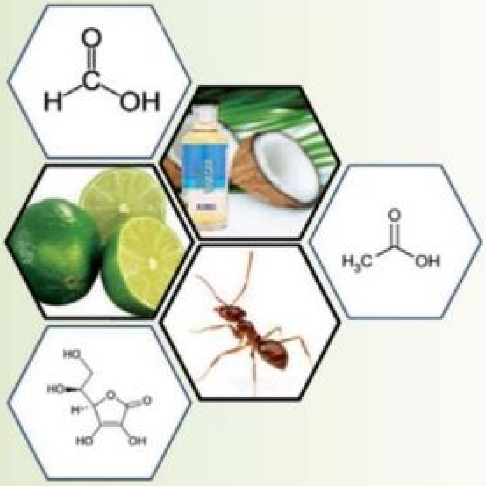


3. Oxygen Containing Organic Compounds

Content

Introduction

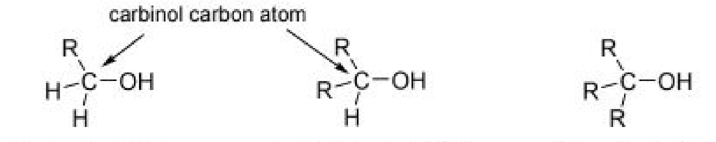
The common oxygen containing organic compounds includes alcohols, phenols, ethers, carbonyl compounds (aldehydes and ketones) and carboxylic acids and carboxylic acid derivatives (esters, amides and acid halides). Alcohols are compounds containing OH group attached to aliphatic carbon atom while phenols are aromatic compounds in which an OH group is attached to a benzene ring. Aldehydes, ketones, carboxylic acids and carboxylic acid derivatives all contain a carbonyl (C=O) group. These classes of compounds differ from each other based on the nature of the two groups attached to the carbonyl carbon.

3.1 Structure, properties and reactions of alcohols

Alcohols are compounds containing an O–H group attached to a *sp*^{3} hybridized carbon atom. Alcohols with one OH group are called monohydric alcohols while those with two, three, four etc. are called dihydric alcohols, trihydric alcohols, tetrahydric alcohols etc. Compounds with many OH groups are commonly called polyhydric alcohols. Our discussion will be mainly confined to monohydric alcohols.

3.1.1 Classification of monohydric alcohols

Similar to the alkyl halides monohydric alcohols are classified into three types depending on the number of H atoms attached to the carbon atom bearing the OH group (carbinol carbon atom) as primary (2 H atoms), secondary (1 H atom) and tertiary (no H atoms attached) as shown below.



Primary alcohol Secondary alcohol Tertiary alcohol

3.1.2 Physical properties

In alcohols the O–H bond is polarized as $R{-}O^{\delta-}{-}H^{\delta+}$. Hence, inter-molecular hydrogen bonds are formed between alcohol molecules **(Figure 3.1)**.

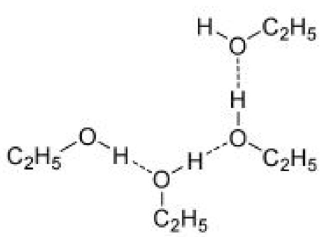


Figure 3.1 Intermolecular H-bonding in ethanol

Because of these relatively strong intermolecular bonds, the boiling points of alcohols have higher values compared to the alkanes and ethers with comparable relative molecular masses **(Table 3.1)**. The boiling point increases in going down the series of alcohols. Similar to alkanes, branching of the alkyl part of the molecule leads to a reduction of boiling point.

Table 3.1 Boiling points of alcohols, ethers and alkanes of comparable relative molecular masses

Compound	Structural formula	Relative molecular mass	Boiling point/ °C
ethanol	CH_3CH_2OH	46	78
dimethyl ether	CH_3OCH_3	46	–25
propane	$CH_3CH_2CH_3$	44	–42
1-propanol	$CH_3CH_2CH_2OH$	60	97
2-propanol	$(CH_3)_2CHOH$	60	83
ethylmethyl ether	$CH_3CH_2OCH_3$	60	11
butane	$CH_3CH_2CH_2CH_3$	58	0
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99
2-methyl-2-propanol	$(CH_3)_3COH$	74	82
diethyl ether	$CH_3CH_2OCH_2CH_3$	74	35
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	88	138
ethyl propyl ether	$CH_3CH_2CH_2OCH_2CH_3$	88	64
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86	68

Alcohols with low relative molecular masses are soluble in water. The solubility of alcohols in water is due to the OH group which can forms H - bonds with water molecules. The non-polar alkyl group in the alcohol molecule is a hindrance to the solubility in water. In going down the homologous series of alcohols the size of the non - polar alkyl group gradually increases relative to the OH group. Accordingly the solubility of alcohols in water gradually decreases **(Table 3.2).**

Table 3.2 Boiling points and solubility (in water) of some long chain alcohols

Alcohol	Structural formula	Boiling point/ °C	Solubility (g/ 100g H_2O)
methanol	CH_3OH	65	∞
ethanol	CH_3CH_2OH	78	∞
1-propanol	$CH_3CH_2CH_2OH$	82	∞
1-butanol	$CH_3(CH_2)_2CH_2OH$	118	7.9
1-penatanol	$CH_3(CH_2)_3CH_2OH$	138	2.3
1-hexanol	$CH_3(CH_2)_4CH_2OH$	158	0.6
1-heptanol	$CH_3(CH_2)_5CH_2OH$	176	0.2
1-octanol	$CH_3(CH_2)_6CH_2OH$	195	0.05

∞ - Miscible in any proportion.

3.1.3 Reactions of alcohols

Alcohols undergo reactions involving cleavage of O–H bond and cleavage of C–O bond.

3.1.3.1 Reactions involving cleavage of O-H bond

(a) *Reaction with sodium (and other alkali metals)*

Alcohols show acidic behaviour because of the polarization of the O–H bond and react with sodium liberating hydrogen and forming sodium alkoxides. The alkoxide ion is a strong nucleophile and also a strong base.

$$RO{-}H + Na \longrightarrow RO^- + H_2$$

However alcohols are not acidic enough to give a substantial reaction with sodium hydroxide to give sodium alkoxide. Thus the equilibrium shown below lies essentially on the side of the alcohol. Hence alcohols are weaker acids than water.

$$ROH + NaOH \rightleftharpoons RO^-Na^+ + H_2O$$

(b) *Reaction with carboxylic acid (Acylation of alcohols to give esters)*

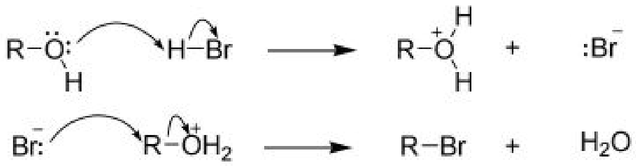
Alcohols react with carboxylic acids to form esters (esterification reaction). Concentrated H_2SO_4 acid acts as a catalyst for this esterification reaction.

$$C_2H_5OH + CH_3COOH \xrightleftharpoons{\text{conc. } H_2SO_4\text{/heat}} CH_3COOC_2H_5 + H_2O$$

3.1.3.2 Nucleophilic substitution reactions involving cleavage of C-O bond

(a) *Reaction with hydrogen halides* (HBr or HI)

Alcohols undergo nucleophilic substitution reaction with HBr or HI to give the corresponding alkyl bromides or alkyl iodides. Protonation of the O atom in the presence of acid (HBr or HI), converts the -OH group into a better leaving group (H_2O).



This is a nucleophilic substitution reaction. In this reaction Br^- ion acts as the nucleophile and the leaving group is H_2O.

Alcohols react with HCl only in the presence of Lewis acids or acids.

The Lucas test to distinguish primary, secondary and tertiary alcohols makes use of this fact. In this reaction, ROH is converted to RCl. $ZnCl_2$which is a Lewis acid acts as the catalyst in this reaction. Because alkyl halides are insoluble in water, as the reaction proceeds the reaction mixture becomes cloudy and turbid. The time taken for the turbidity to appear, after the mixing of reagents, can be used to distinguish between primary, secondary and tertiary alcohols. Under the given reaction conditions the above nucleophilic substitution reaction takes place in two steps. Tertiary alcohols form stable intermediate tertiary carbocations and therefore, tertiary alcohols in the presence of the Lucas reagent form turbidity in a very short time. Secondary alcohols take longer time to produce turbidity and primary alcohols react very slowly.

(b) *Reaction with phosphorus trihalides* (PCl_3 or PBr_3)

Alcohols react with PCl_3 and PBr_3 to give alkyl chlorides and alkyl bromides respectively.

$$3\,ROH + PCl_3 \longrightarrow 3\,RCl + H_3PO_3$$
$$3\,ROH + PBr_3 \longrightarrow 3\,RBr + H_3PO_3$$

(c) *Reaction with phosphorus pentachloride* (PCl_5)

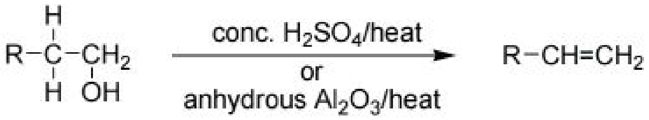
Alcohols react with PCl_5 to give alkyl chlorides.

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

Reactions of alcohols with phosphorous halides described in (b) and (c) above are also nucleophilic substitution reactions where the halide ion acts as the nucleophile.

3.1.3.3 Elimination reaction

Alcohols undergo an elimination reaction when heated with conc. H_2SO_4 or when heated with alumina to a higher temperature. The reaction is the dehydration of alcohols, in which a molecule of water is eliminated from an alcohol. During this reaction an alkene is formed as the product.



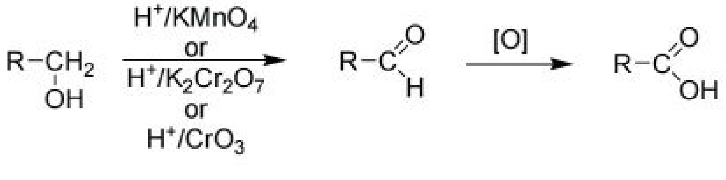
$$R-\underset{H}{\overset{H}{C}}-\underset{OH}{CH_2} \xrightarrow[\text{anhydrous } Al_2O_3\text{/heat}]{\text{conc. } H_2SO_4\text{/heat} \text{ or}} R-CH=CH_2$$

3.1.3.4 Oxidation of alcohols

Alcohols can be oxidized with several oxidizing agents. The product of oxidation depends on whether the alcohol is primary, secondary or tertiary. Oxidation of alcohols can be carried out with $H^+/KMnO_4$ or $H^+/K_2Cr_2O_7$ or H^+/CrO_3.

(a) *Oxidation of primary alcohols*

Primary alcohols are oxidized to carboxylic acids through the corresponding aldehyde with the above oxidizing reagents.

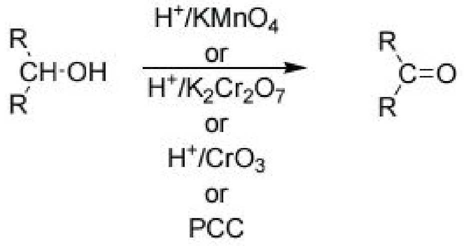


The oxidation reaction will be stopped at the stage where aldehyde is formed when pyridinium chlorochromate $[C_5H_5NH]^+ [CrO_3Cl]^-$ (PCC) is used.

$$R-CH_2-OH \xrightarrow{PCC} R-CHO$$

(b) *Oxidation of secondary alcohols*

Secondary alcohols are oxidized to give ketones with any of the above reagents.



$$R_2CH-OH \xrightarrow[\text{or } H^+/CrO_3 \text{ or } PCC]{H^+/KMnO_4 \text{ or } H^+/K_2Cr_2O_7} R_2C=O$$

(c) *Oxidation of tertiary alcohols*

Generally the tertiary alcohols do not undergo oxidation under conditions that primary and secondary alcohols are oxidized.

3.2 Structure, properties and reactions of phenols

3.2.1 Acidity of phenols

Aromatic compounds, in which an OH group is joined directly to a carbon atom of a benzene ring, are called phenols. Alcohols and phenols dissociate in aqueous solutions as shown below.

$$ROH + H_2O \rightleftharpoons RO^- + H_3O^+$$

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$$

Phenols are more acidic than alcohols. This means that in the above equilibria, the equilibrium point for phenols is more towards the right than alcohols. The reason for this is that the stability of phenoxide ion relative to phenol is greater than the stability of the alkoxide ion relative to the alcohol. This can be understood by considering the resonance structures for phenol and its anion.

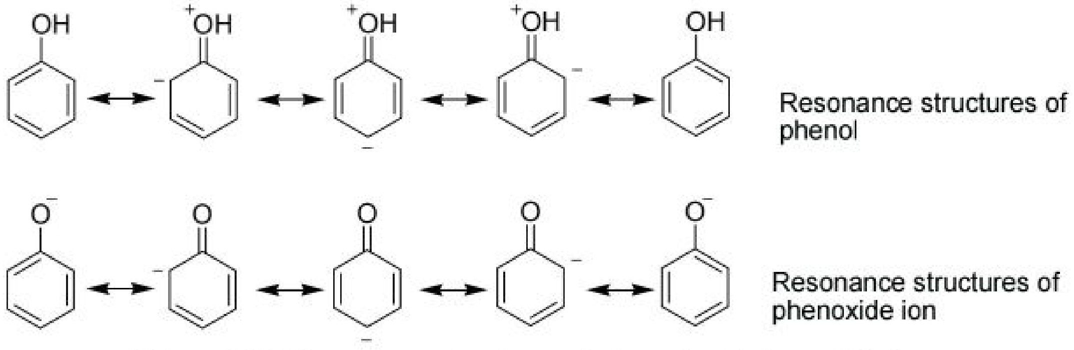


Figure 3.2 Resonance structures of phenol and phenoxide ion

The stabilization of the anion by resonance is greater than the stabilization of the phenol because unlike in the phenol there is no charge separation in the resonance structures of the anion **(Figure 3.2).** There is no corresponding resonance stabilization of alcohol or its anion.

3.2.2 Reactions involving cleavage of the O-H bond

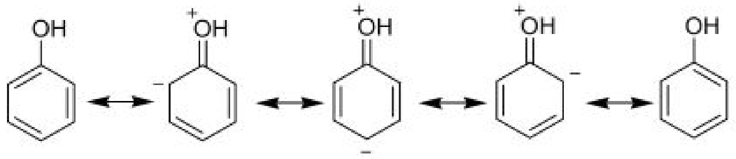
The higher acidity of phenols is confirmed by the following examples. Unlike alcohols, phenols react with NaOH to give sodium phenoxide. However, neither phenols nor alcohols are acidic enough to react with $NaHCO_3$ and evolve CO_2.

$$2\,C_6H_5OH + 2Na \longrightarrow 2\,C_6H_5O^- Na^+ + H_2$$
$$C_6H_5OH + NaOH \longrightarrow C_6H_5O^- Na^+ + H_2O$$

3.2.3 Non-occurrence of nucleophilic substitution reactions by breaking C-O bond

Unlike alcohols phenols do not undergo nucleophilic substitution reactions. Neither the one step nor the two step mechanism takes place because,

(a) The C–O bond is shorter (sp^2 hybridized C atom) and stronger (double bond nature) due to delocalization of lone pair of electrons on the oxygen atom into the benzene ring. This can be shown by resonance.



(b) Phenyl cation is unstable.

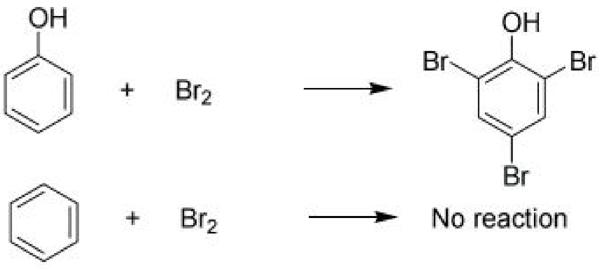
3.3 Reactivity of the benzene ring in phenols

The benzene ring in phenol is electron rich compared to benzene due to the delocalization of a lone pair of electrons on the oxygen atom over the benzene ring in phenol. Therefore the benzene ring in phenol is more reactive towards electrophilic reagents than benzene itself. The O–H group of phenol directs the electrophilic substitution to the *ortho* and *para* positions with respect to the phenolic OH group.

When the electrophilic substitution reactions of phenol are compared with the corresponding reactions of benzene along with the relevant conditions, it is clear that the benzene ring of phenol is more reactive towards electrophiles. Consider the following examples.

3.3.1 Reaction of phenol with Br_2

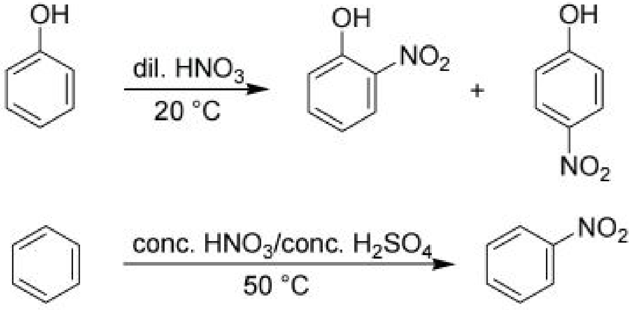
Phenol reacts readily with bromine to form 2,4,6-tribromophenol while benzene does not react with bromine.



When this reaction is carried out with bromine water 2,4,6-tribromophenol is observed as a white precipitate.

3.3.2 Nitration of phenol

Nitration occurs even with dilute HNO_3 at 20 °C while benzene requires conc. HNO_3/conc. H_2SO_4 and higher temperatures for nitration.



It should be noted that Friedel-Crafts alkylation reactions cannot be carried out with phenols because of the complex formation between Friedel-Crafts catalyst and phenols.

3.4 Structure, properties and reactions of aldehydes and ketones

Both aldehydes and ketones contain the carbonyl (C=O) functional group. In aldehydes the carbonyl carbon is attached to an H atom and an alkyl or aryl (aromatic) group. However, the simplest aldehyde, formaldehyde (methanal) has two H atoms attached to the carbonyl carbon. In ketones each of the groups attached to the carbonyl carbon is either an alkyl group or an aryl group. The carbonyl C atom is sp^2 hybridized and the three atoms attached to it lie in one plane (trigonal planar). The carbon oxygen double bond consists of a σ bond and a π bond.

3.4.1 Physical properties

Boiling points of aldehydes and ketones are higher than those of alkanes of comparable relative molecular masses due to the presence of intermolecular dipole-dipole interactions. However their boiling points are lower than alcohols of comparable relative molecular masses as they do not form intermolecular H-bonds **(Table 3.3)**.

Table 3.3 Boiling points and water solubility of aldehydes, ketones, alcohols and alkanes of comparable relative molecular masses

Compound	Structural formula	Relative molecular mass	Boiling point/ °C	Water Solubility (g/100 mL)*
ethanal	CH_3CHO	44	21	∞
ethanol	CH_3CH_2OH	46	78	∞
propane	$CH_3CH_2CH_3$	44	–42	none
propanal	CH_3CH_2CHO	58	49	16
propanone	CH_3COCH_3	58	56	∞
1-propanol	$CH_3CH_2CH_2OH$	60	97	∞
2-propanol	$(CH_3)_2CHOH$	60	83	∞
butane	$CH_3CH_2CH_2CH_3$	58	0	none
butanal	$CH_3CH_2CH_2CHO$	72	76	7
2-butanone	$CH_3COCH_2CH_3$	72	80	26
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118	7.9
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99	29
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36	none
penatanal	$CH_3CH_2CH_2CH_2CHO$	86	103	1
2-pentanone	$CH_3COCH_2CH_2CH_3$	86	102	6
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	88	138	2.3
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86	68	none

∞ - Miscible in any proportion.

However aldehydes and ketones can participate in intermolecular H-bonding with water **(Figure 3.3).** Therefore aldehydes and ketones with relatively lower molecular masses are soluble in water **(Table 3.3)**.

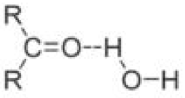


Figure 3.3 Intermolecular H-bonding of aldehydes and ketones with water

3.4.2 Reactions of aldehydes and ketones

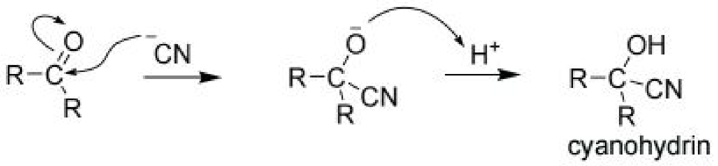
The carbonyl group is a polar group because of the electron negative O atom (${}^{\delta+}C=O^{\delta-}$). Hence the C atom is electron deficient and can react with a nucleophile. The C atom is unsaturated because it is attached only to three atoms. It can therefore form a new bond with a nucleophile. During this process the two π electrons are transferred to the oxygen atom which thereby acquiring a negative charge. This negative charge is neutralized by the attachment of a positively charged species (very often a proton). Therefore the characteristic reactions of aldehydes and ketones are nucleophilic addition reactions.

3.4.3 Nucleophilic addition reactions

3.4.3.1 Addition of HCN to aldehydes and ketones

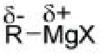
Addition of HCN to aldehydes and ketones is a nucleophilic addition reaction. This is carried out by adding a dilute mineral acid into a mixture of the carbonyl compound and an aqueous solution of sodium cyanide. Here the CN^- ion acts as the nucleophile.

Mechanism of the reaction is as follows.

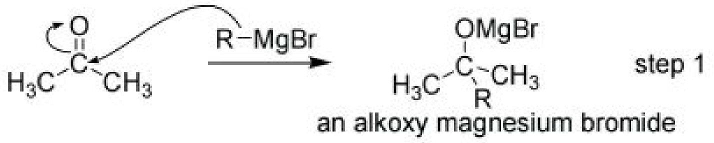


3.4.3.2 Reaction with Grignard reagents

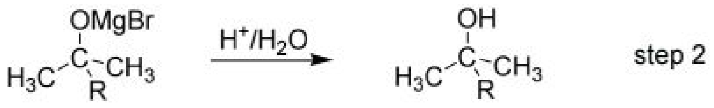
In Grignard reagents the C–Mg bond is polarized as follows.


$$\overset{\delta-}{R}-\overset{\delta+}{MgX}$$

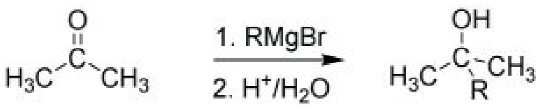
Therefore the R group of the Grignard reagent together with the electron pair of R–Mg bond reacts as a nucleophile with the carbonyl carbon. This leads to the formation of an alkoxy magnesium halide.



Hydrolysis of the alkoxy magnesium halide gives the corresponding alcohol. This is carried out by an aqueous acid.



The overall reaction is as follows:

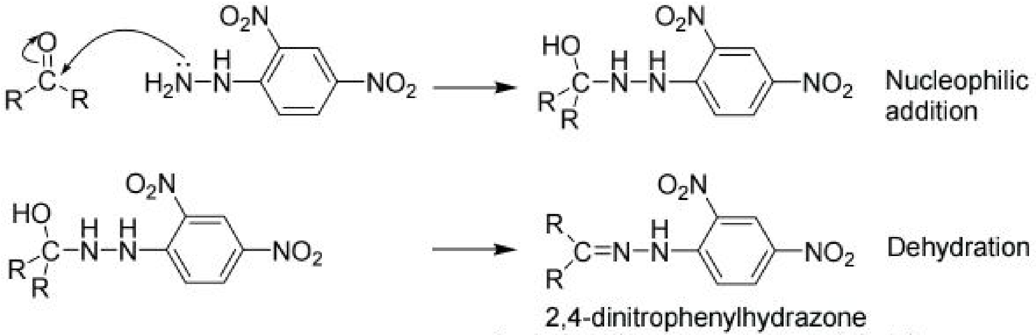


All aldehydes except formaldehyde give secondary alcohols whereas ketones give tertiary alcohols with Grignard reagents. Formaldehyde gives primary alcohols.

Grignard reagents are prepared and reacted with aldehydes and ketones under anhydrous conditions. Hence the formation of the alkoxy magnesium halide and its hydrolysis are two distinct steps.

3.4.3.3 Reaction with 2,4-dinitrophenylhydrazine (2,4-DNP or Brady reagent)

In this reaction, nucleophilic addition of 2,4-dinitrophenylhydrazine to the aldehyde or ketone takes place first. Then a water molecule is eliminated from the intermediate product to form the final product, which is a 2,4-dinitrophenylhydrazone.

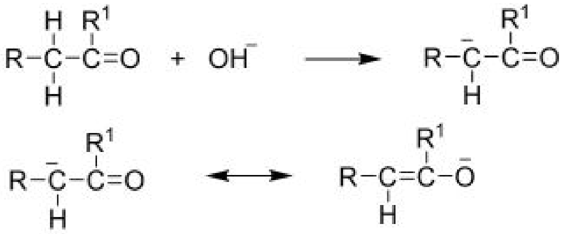


2,4-dinitrophenylhydrazone
(a dark yellow or orange precipitate)

Although this reaction takes place in two steps as shown above, the hydroxy product first obtained by the nucleophilic addition cannot be isolated under the reaction conditions and dehydrates to give the final product. This reaction is used to identify aldehydes and ketones.

3.4.4 Self-condensation reactions of aldehydes and ketones

Due to the strong electron withdrawing nature of the carbonyl group, H atoms attached to the carbon atoms directly bound to the carbonyl carbon (the α-H) become acidic. This α-H can be abstracted as a proton by a base (e.g.: OH^-). The carbanion so formed is stabilized by resonance as shown below.



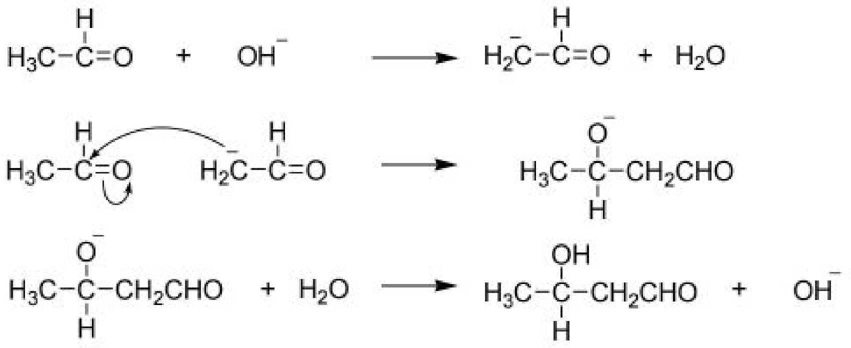
$$R-\underset{H}{\overset{H}{C}}-\overset{R^1}{C}=O + OH^- \longrightarrow R-\underset{H}{\overset{-}{C}}-\overset{R^1}{C}=O$$

$$R-\underset{H}{\overset{-}{C}}-\overset{R^1}{C}=O \longleftrightarrow R-\underset{H}{C}=\overset{R^1}{C}-\overset{-}{O}$$

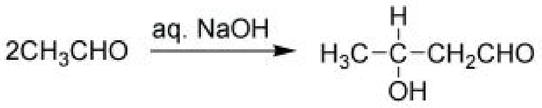
This carbanion reacts as a nucleophile and attacks the carbon atom of the carbonyl group of an un-ionized aldehyde molecule. Hence aldehydes and ketones with α-hydrogens undergo base catalyzed self-condensation reactions.

Let us see some examples.

Reaction of acetaldehyde in the presence of aqueous NaOH

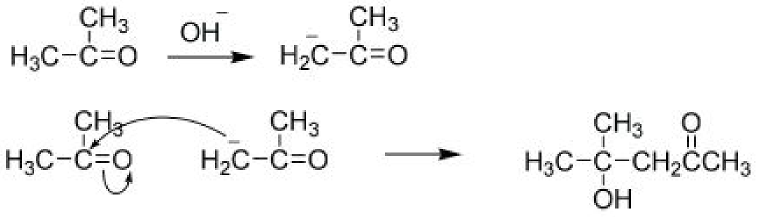


The overall reaction is:

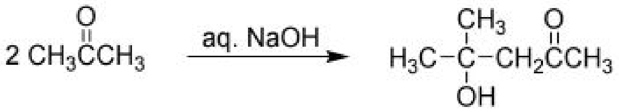


$$2CH_3CHO \xrightarrow{\text{aq. NaOH}} H_3C-CH(OH)-CH_2CHO$$

Condensation of acetone in the presence of aqueous NaOH

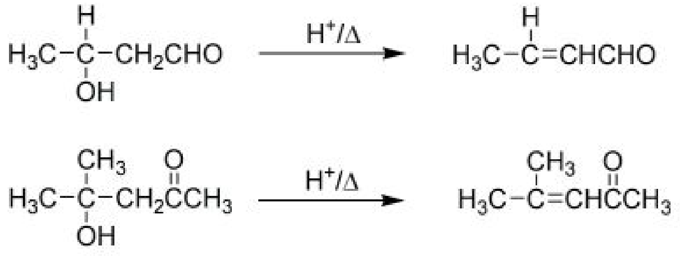


The overall reaction is:



$$2\,CH_3COCH_3 \xrightarrow{\text{aq. NaOH}} H_3C-C(CH_3)(OH)-CH_2COCH_3$$

The addition products obtained above undergo dehydration easily when heated with acids.

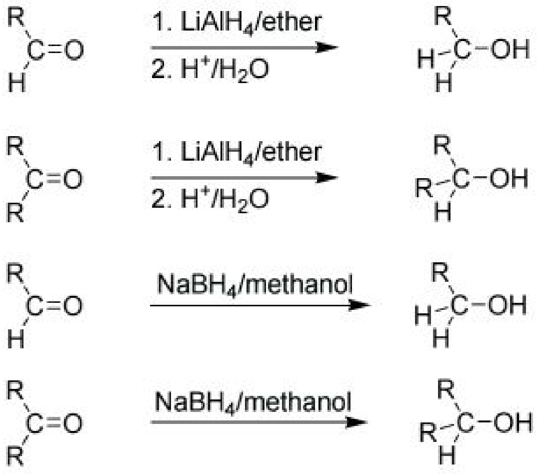


$$H_3C-CH(OH)-CH_2CHO \xrightarrow{H^+/\Delta} H_3C-CH=CHCHO$$

$$H_3C-C(CH_3)(OH)-CH_2COCH_3 \xrightarrow{H^+/\Delta} H_3C-C(CH_3)=CHCOCH_3$$

3.4.5 Reduction of aldehydes and ketones by lithium aluminium hydride ($LiAlH_4$) or sodium borohydride($NaBH_4$)

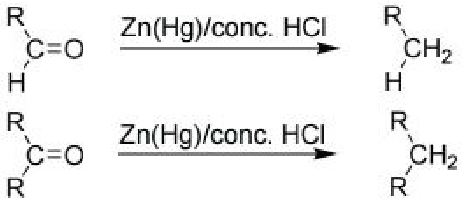
Aldehydes are reduced to primary alcohols with $LiAlH_4$ or $NaBH_4$ while ketones are reduced to give secondary alcohols. In these reductions both $LiAlH_4$ and $NaBH_4$ provide hydride ions (H^-). The hydride ion reacts with the carbonyl C as a nucleophile. Thus these reductions can be considered as nucleophilic addition reactions.



Note that $LiAlH_4$ is too reactive to be used in the presence of water or methanol.

3.4.6 Reduction of aldehydes and ketones by Zn(Hg)/ conc.HCl (Clemmenson reduction)

In this reduction reaction, C=O group is reduced to a methylene (CH_2) group. Thus, both aldehydes and ketones can be converted to hydrocarbons.

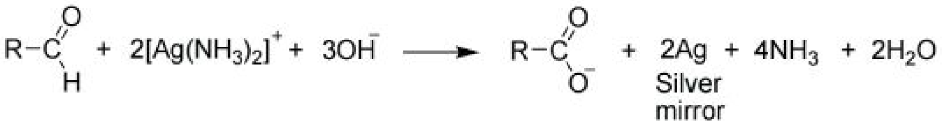


3.4.7 Oxidation of aldehydes

Aldehydes are oxidized to carboxylic acids by oxidizing agents such as acidified potassium dichromate, acidified chromic oxide or acidified potassium permanganate and even by mild oxidizing agents such as Tollen reagent and Fehling solution. In acidic medium aldehydes are oxidized to carboxylic acids while with Tollen and Fehling solution, which are alkaline, the product is a salt of the carboxylic acid. Ketones do not undergo oxidation with these reagents.

3.4.7.1 Oxidation by Tollens reagent

Tollens reagent, is a solution containing Ag^+ in the form $[Ag(NH_3)_2]^+$. During the oxidation of aldehydes to carboxylic acids, Ag^+ ions are reduced to metallic silver giving a silver mirror in the test tube.

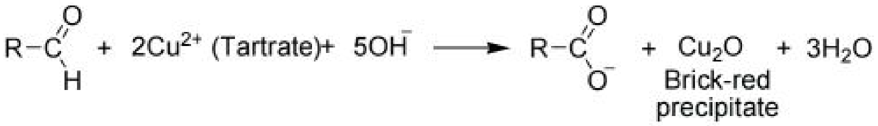


$$R\text{-}CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow R\text{-}COO^- + \underset{\text{Silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

Oxidation of aldehydes by Tollens reagent or the silver mirror test is used to distinguish between aldehydes and ketones.

3.4.7.2 Oxidation by Fehling solution

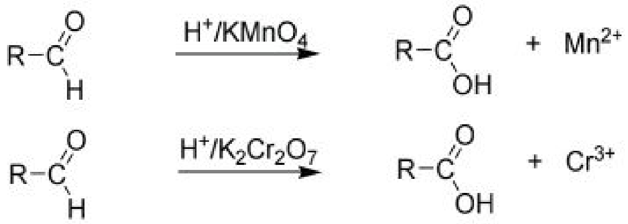
A solution of Copper (II) tartrate in aqueous NaOH is known as Fehling solution. This is a dark blue solution. When a few drops of an aldehyde are added to this reagent and heated, the blue colour of the solution gradually disappears and a brick red precipitate of cuprous oxide is formed.



Aldehydes and ketones can be distinguished from each other by reacting with Fehling solution.

3.4.7.3 Oxidation by acidified potassium dichromate or acidified chromic oxide or acidified potassium permanganate

Aldehydes get oxidized to carboxylic acids by reacting with oxidizing agents such as acidified potassium dichromate or acidified chromic oxide or acidified potassium permanganate.



The pink colour of $H^+/KMnO_4$ solution becomes colourless in the presence of an aldehyde while the orange colour of $H^+/ Cr_2O_7^{2-}$ solution turns green. By using these reagents aldehydes and ketones can be distinguished from each other.

Since ketones do not contain an H atom attached to the C=O group, they do not undergo oxidation with these oxidizing reagents.

However strong oxidizing agents like potassium permanganate can oxidize ketones when heated. During this oxidation carbon-carbon bonds are broken resulting in the decomposition of the ketone.

3.5 Structure, properties and reactions of carboxylic acids

Carboxylic acids are compounds containing carboxyl (COOH) group which consists of a C=O and OH groups **(Figure 3.4)**. Carboxylic acids are generally more acidic than other organic compounds containing OH groups but weaker than the common mineral acids.

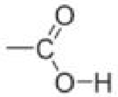


Figure 3.4 Structure of the carboxyl group

3.5.1 Physical properties

Carboxyl group is a polar functional group. Due to the polarity of C–O and O–H groups it forms intermolecular hydrogen bonds. Carboxylic acids are capable of forming dimeric structures in which carboxylic acid molecules are attached by hydrogen bonds as pairs **(Figure 3.5)**.

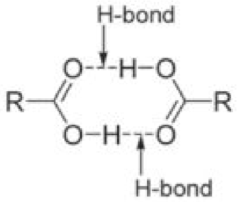


Figure 3.5 Dimeric structure of carboxylic acids due to H-bonding

Due to these reasons carboxylic acids show higher boiling points than the alcohols, aldehydes and ketones with comparable relative molecular masses **(Table 3.4)**.

Table 3.4 Boiling points of some carboxylic acids, alcohols, aldehydes and ketones of comparable relative molecular masses

Compound	Structural formula	Relative molecular mass	Boiling point/ °C
methanoic acid	HCO_2H	46	100
ethanol	CH_3CH_2OH	46	78
ethanal	CH_3CHO	44	20
ethanoic acid	CH_3CO_2H	60	118
1-propanol	$CH_3CH_2CH_2OH$	60	97
2-propanol	$(CH_3)_2CHOH$	60	83
propanal	CH_3CH_2CHO	58	49
propanone	$(CH_3)_2C{=}O$	58	56
propanoic acid	$CH_3CH_2CO_2H$	74	141
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99
butanal	$CH_3CH_2CH_2CHO$	72	75
butanone	$CH_3COCH_2CH_3$	72	80

Carboxyl group can form H-bonds with water. Therefore carboxylic acids of C_1 to C_4 dissolve well in water. When the number of carbon atoms increases solubility decreases. Aromatic carboxylic acids are water insoluble and exist as solid crystalline substances. Almost all the carboxylic acids are soluble in organic solvents.

3.5.2 Comparison of the reactivity pattern of -COOH group with >C=O group in aldehydes and ketones and -OH group in alcohols and phenols

Similar to alcohols, the O–H group of carboxylic acids also undergoes reactions involving cleavage of both C–O bond and O–H bond.

3.5.2.1 Reactions involving cleavage of the O–H bond

Carboxylic acids are acidic. They react with alkali metals such as sodium and potassium, alkali such as NaOH and KOH and bases such as Na_2CO_3 and $NaHCO_3$.

$$2\,RCOOH + 2\,Na \longrightarrow 2\,RCOO^-Na^+ + H_2$$

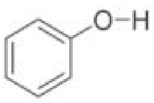
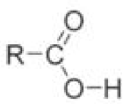
$$RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$$

$$2\,RCOOH + Na_2CO_3 \longrightarrow 2\,RCOO^-Na^+ + CO_2 + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + CO_2 + H_2O$$

A comparison of the reactions of alcohols, phenols and carboxylic acids with sodium, sodium hydroxide and sodium bicarbonate is given in the **Table 3.5.**

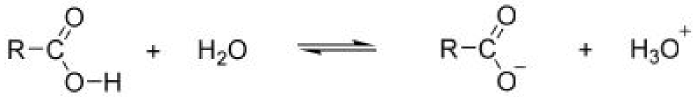
Table 3.5 Reactions of alcohols, phenols and carboxylic acids with sodium, sodium hydroxide, sodium carbonate and sodium bicarbonate

Compound	**Reaction with**		
	Metallic Na	**aq. NaOH**	**aq. Na_2CO_3 or $NaHCO_3$**
	Liberates H_2 gas forming RO^-Na^+	No reaction	No reaction
	Liberates H_2 gas forming $C_6H_5ONa^+$	Dissolves in aq. NaOH forming a solution of $C_6H_5O^-Na^+$	No reaction
	Liberates H_2 gas forming $RCOONa^+$	Dissolves in aq. NaOH forming a solution of $RCOONa^+$	Dissolves in aq. Na_2CO_3 or aq. $NaHCO_3$ forming a solution of $RCOONa^+$and liberating CO_2 gas

Thus the acidic strengths of alcohols, phenols and carboxylic acids vary as follows.

Alcohols < Phenols < Carboxylic acids

In aqueous medium carboxylic acids exist in the following equilibrium.



The equilibrium point of the above equilibrium is more shifted towards the right side relative to the corresponding equilibrium attained by the phenols. The reason for this is that the stabilization of the carboxylate ion relative to the carboxylic acid is greater than the stabilization of the phenoxide ion relative to phenol. Both the carboxylate ion and carboxylic acid are stabilized by resonance **(Figure 3.6)** as in the case of phenoxide ion and phenols **(Figure 3.2)**.

Resonance structures of a carboxylic acid

Resonance structures of a carboxylate anion

Figure 3.6 Resonance structures of a carboxylic acid and a carboxylate anion

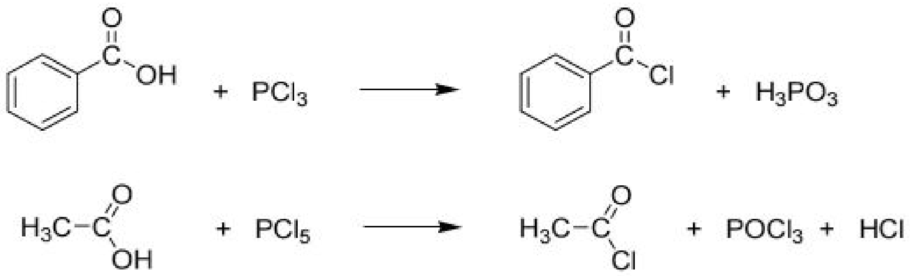
The stabilization of the carboxylate anion by resonance is greater than the stabilization of the acid because unlike in the acid there is no charge separation in the resonance structures of the anion **(Figure 3.6)**.

The higher acidity of the carboxylic acids can be explained by the fact that the carboxylate ion is stabilized by the delocalization of the negative charge between two equivalent electronegative oxygen atoms in contrast to the delocalization of the negative charge on oxygen and carbon atoms in phenoxide anion.

3.5.2.2 Reactions involving cleavage of the C–O bond

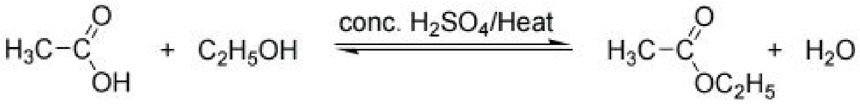
(a) *Reaction with PCl_3 or PCl_5*

Carboxylic acids react with PCl_3 or PCl_5 giving carboxylic acid chlorides.

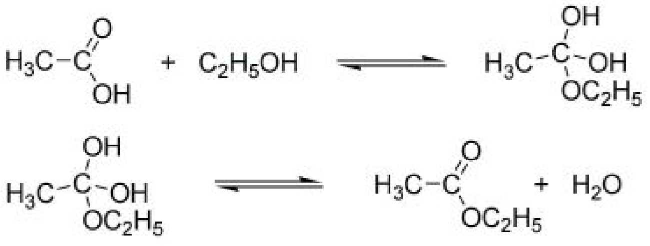


(b) *Reaction with alcohols*

Carboxylic acids react with alcohols in the presence of acid catalyst to give esters.



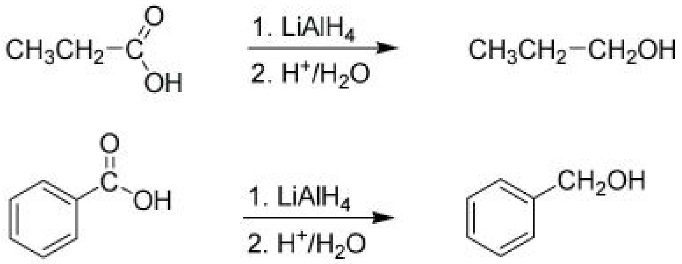
Although the above reaction appears to be a simple nucleophilic substitution reaction (OH being replaced by OC_2H_5) it actually involves first the nucleophilic addition of the C_2H_5OH molecule across the C=O to give a tetrahedral intermediate. Under acidic condition of the reaction this intermediate loses a molecule of water to give the ester.



Note: *Please also see the discussion in the* ***Section 3.6.***

3.5.2.3 Reduction of carboxylic acids with $LiAlH_4$

Carboxylic acids react with $LiAlH_4$ which is a powerful reducing agent to give alcohols. Note that carboxylic acids and their derivatives are not reduced by $NaBH_4$ which is a less powerful reducing agent than $LiAlH_4$.



3.6 Reactions of carboxylic acid derivatives

It is instructive to compare the reactions of carboxylic acid derivatives and carboxylic acids with those of aldehydes and ketones **(Figure 3.7)**.

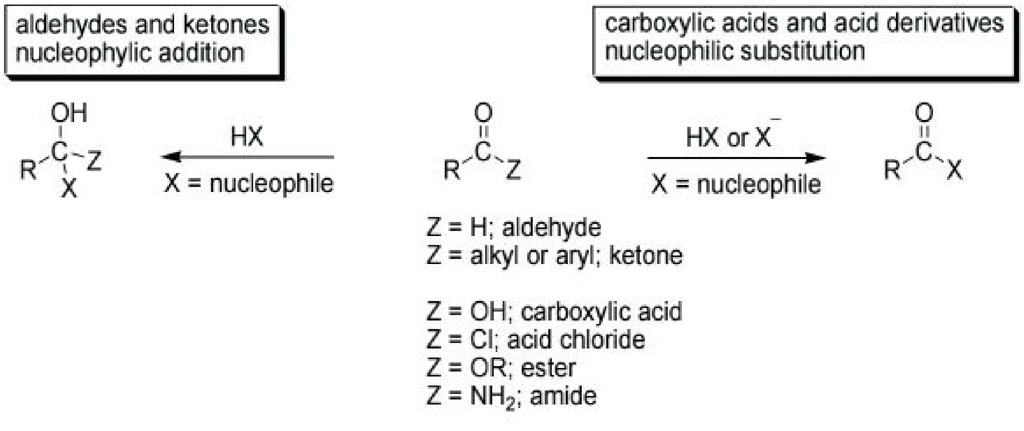


Figure 3.7 Comparison of characteristic reactions of aldehydes/ ketones with those of carboxylic acids and their derivatives

The essential difference is that in contrast to aldehydes and ketones, the Z group in carboxylic acid derivatives and carboxylic acids is capable of behaving as a leaving group. That is in reactions involving heterolytic cleavage of C–Z bond, Z leaves with the electron pair of the bond.

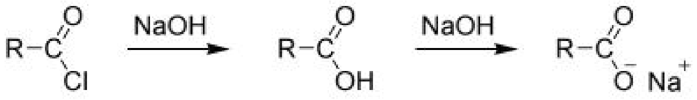
As in the case of aldehydes and ketones the first step of the reaction is the attack of a nucleophile on the carbonyl carbon of acids and acid derivatives with the opening of the carbon oxygen double bond to give a tetrahedral intermediate. This is followed by re-formation of the carbon oxygen double bond with the loss of Z as Z^- under basic or neutral conditions or as ZH under acidic conditions.

Thus the carbon atom regains its trigonal geometry and the overall reaction is the substitution of Z with a nucleophile. This reaction pathway is not available in aldehydes and ketones as H, alkyl and aryl do not behave as leaving group.

3.6.1 Reactions of acid chlorides

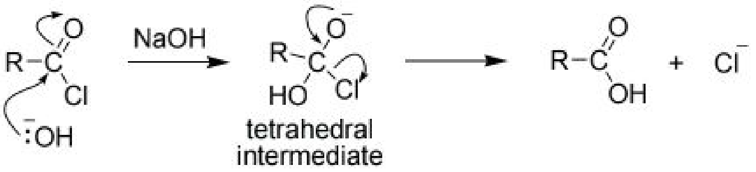
3.6.1.1 Reaction with aqueous sodium hydroxide

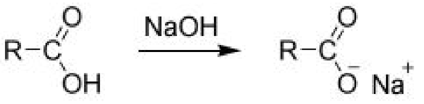
Acid chlorides react with aqueous NaOH to form the corresponding carboxylic acid which reacts with excess NaOH to form its sodium salt.



$$\mathrm{R{-}COCl} \xrightarrow{NaOH} \mathrm{R{-}COOH} \xrightarrow{NaOH} \mathrm{R{-}COO^-\,Na^+}$$

The mechanism of the reaction is as follows.



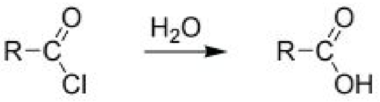


$$\mathrm{R{-}COOH} \xrightarrow{NaOH} \mathrm{R{-}COO^-\,Na^+}$$

In the above reaction the OH^- is the nucleophile and Cl^- is the leaving group.

3.6.1.2 Reaction with water

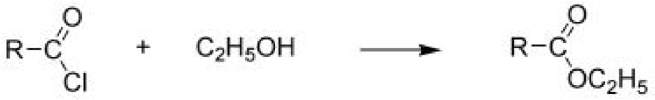
Acid chlorides react with water by a similar mechanism to form the corresponding carboxylic acid.

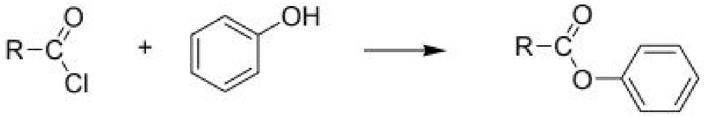


$$\mathrm{R{-}COCl} \xrightarrow{H_2O} \mathrm{R{-}COOH}$$

3.6.1.3 Reaction with alcohols and phenols

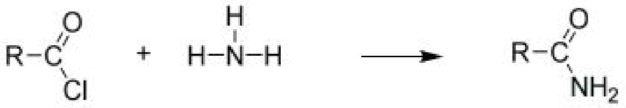
Acid chlorides react with alcohols and phenols to form alkyl esters and phenyl esters respectively.



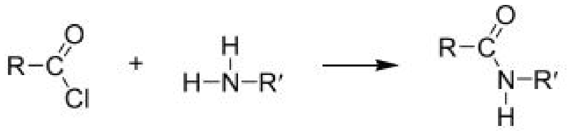


3.6.1.4 Reaction with ammonia and primary amines

Acid chlorides react with ammonia to form primary amides.



Acid chlorides react with primary amines to form secondary amides.

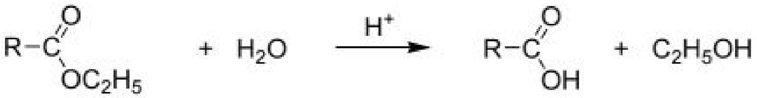


Note: *Amides are classified as primary amides when two H atoms are attached to the N atom. If one H atom is replaced by an alkyl group, it is classified as a secondary amide and if both H atoms are replaced by two alkyl groups the amide is classified as tertiary amide.*

3.6.2 Reactions of esters

3.6.2.1 Reaction with dilute mineral acids

Esters react with dilute acids and give corresponding carboxylic acid and the alcohol as the products. In this reaction water acts as the nucleophile and the ester undergoes hydrolysis. This reaction also goes through the same tetrahedral intermediate involved in the formation of esters as given in **Section 3.5.2.2** (b).



3.6.2.2 Reaction with aqueous sodium hydroxide

Esters when reacted with aqueous NaOH form the sodium salt of corresponding carboxylic acid and the alcohol. The mechanism of this reaction is similar to the mechanism of the reaction of acid chlorides with NaOH **(Section 3.6.1.1)**.

3.6.2.3 Reaction with Grignard reagent

Esters react with Grignard reagents to give tertiary alcohols. In this reaction, the ester is first converted to a ketone which reacts rapidly with the Grignard reagent again to give the tertiary alcohol as the product.

Note that as ketones react faster than esters with Grignard reagents it is not possible to stop the reaction at the ketone stage.

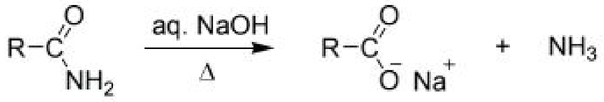
3.6.2.4 Reduction by $LiAlH_4$

Esters react with $LiAlH_4$ and reduce to give alcohols.

3.6.3 Reactions of amides

3.6.3.1 Reaction with aqueous sodium hydroxide

When amides are warmed with an aqueous solution of NaOH, the sodium salt of the corresponding carboxylic acid is formed with liberation of gaseous NH_3.



3.6.3.2 Reduction with $LiAlH_4$

Amides are reduced to the corresponding primary amine with $LiAlH_4$.