SENIOR SIX TERM 1

TOPIC 2/2: Organic Chemistry II

Topic competency: The learner analyses reaction mechanisms, evaluates reaction pathways and conditions, and designs multi-step syntheses to achieve target compounds (considering alcohols, phenols, carbonyl compounds).

Alcohols/Alkanols

These are organic compounds that contain at least one hydroxyl group (-OH) attached to saturated carbon atom.

Classification

(a) According to the number of –OH group

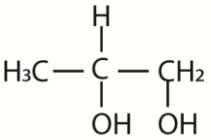
(i) Monohydric alcohols have one hydroxyl (-OH) group

Example CH_3CH_2OH ethanol

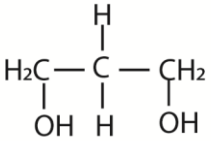
$CH_3\underset{\underset{OH}{|}}{C}HCH_3$ propan-2-ol

(ii) Dihydric alcohols or glycols have two hydroxyl groups

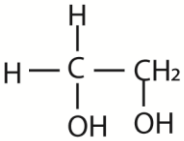
Examples



Propan -1,2 - diol

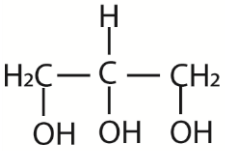


Propan -1,3 - diol



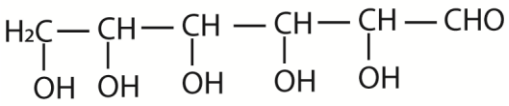
ethane -1,2- diol

(iii) Trihydric alcohols have three hydroxyl groups.



Propan -1,2,3 - triol

(iv) Polyhydric alcohols or polyol contain more than three hydroxyl groups
e.g. sugar



(b) Classification of monohydric alcohols

They are classified according to the number of alkyl groups attached to the carbon atom that bear a hydroxyl (OH) group.

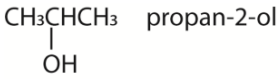
(i) Primary alcohols have one alkyl group bonded to the carbon atom that carry OH group, i.e. ROH.
Example

CH_3CH_2OH Ethanol

$CH_3CH_2CH_2OH$ Propan-1-ol

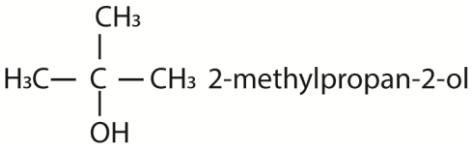
(ii) Secondary alcohols have two alkyl groups bonded to the carbon atom that bear OH group, i.e. R_2CHOH

Example



(iii) Tertiary alcohols: have three alkyl groups bonded to a carbon atom that bear OH group i.e. R_3COH

Example

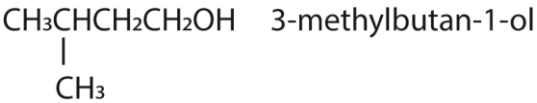


Nomenclature

(a) Are named by replacing the final "e" in the corresponding alkanes with "ol"

(b) The hydroxyl group is taken as a substituent group, and its position is given by numbering the carbon atoms in the chain from from the side nearest to the carbon atom tha t carry OH group.

Examples



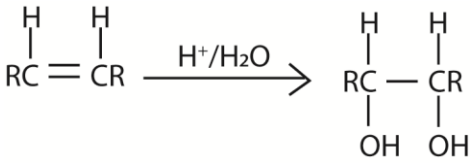
Physical properties

1. Alcohols have high melting and boiling points than corresponding hydrocarbon of similar molecular masses due to intermolecular hydogen bonds, consequently alcohols ate either liquids or solids.
   Example
   Propane (44) Bpt = -42^0C
   Ethanol (46) Bpt = 78^0C
2. Lower members are completely soluble in water due to the formation of hydrogen bonds with water. But solubility of alcohols decrease as alkyl group leghths increase due to increase in "alkane like" character.

Preparation of alcohols

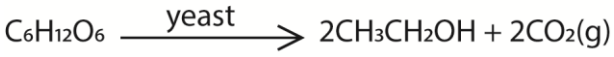
(a) Industrial preparation

(i) From petroleum products, e.g. alkenes

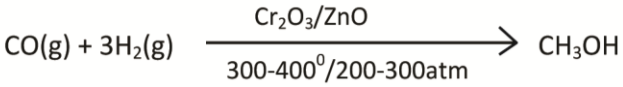


(ii) Fermentation of sugars

Ethanol can be made by fermentation of sugars. Fermentation is usually carried out by adding yeast to a mixutre of sugar and water.

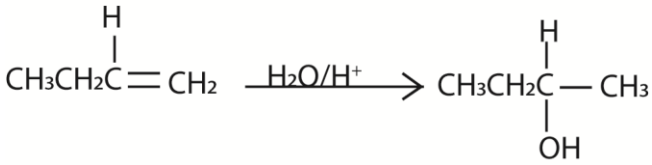


(iii) Methanol is produced by catalytic reduction of carbon monoxide.

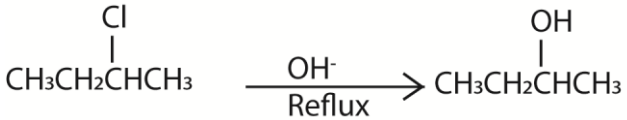


(b) Laboratory preparation

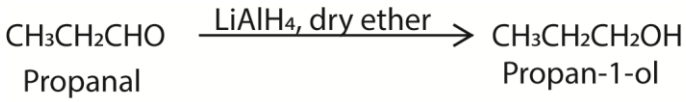
(i) Hydration of alkenes in presence of acid catalyst

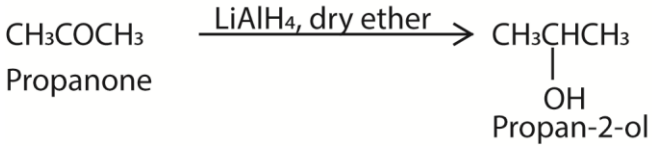


(ii) By hydrolysis of alkyl halides using aqueous alkali

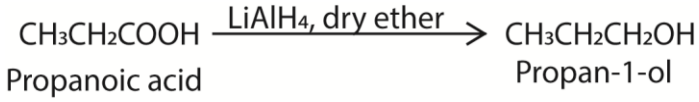


(iii) By reduction of carbonyl compounds (aldehyde and ketones) using lithium aluminium hydride ($LiAlH_4$) in presence of dry ether.





(iv) Reduction of carboxylic acids using $LiAlH_4$ in dry ether



Absolute ethanol

All aqueous solutions of ethanol yield, on fractional distillation a constant boiling mixture (azeotrope) of 96% ethanol and 4% water known as rectified spirit.

(i) In the laboratory rectified spirit is stored over quick lime overnight. Quick lime dehydrates the mixture; then pure ethanol called absolute ethanol is distilled.

$$CaO\ (s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

(ii) In industry, benzene is added to the rectified spirit. Distillation yields three fractions
At 65^0C a constant boiling mixture of ethanol, benzene and water.
At 68^0C a constant boiling mixture of ethanol and water
At 78^0C pure ethanol distills off.

Reactions of monohybrid alcohol

a. Cleavage of O-H bond
b. Cleavage od C-O bond
c. Oxidation
d. Dehydration

(a) Cleavage of O-H bond

(i) Behavior as a weak acid

$$2ROH + 2Na \longrightarrow RO^-Na^+ + H_2(g)$$

Acidity: primary alcohol> secondary alcohol>tertiary alcohol

(ii) Behavior as a base

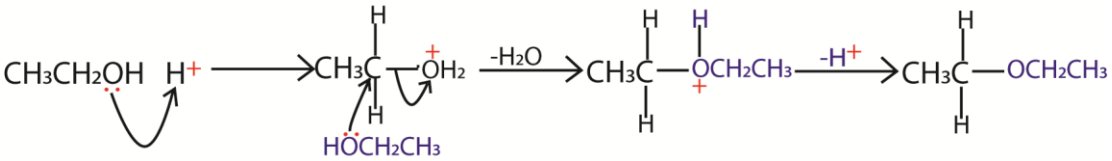
$ROH + H^+ \longrightarrow RO^+H_2$

(iii) Formation of ether

Ethanol reacts presence of concentrated sulphuric acid at 140^0C to form diethyl ether.

$$2CH_3CH_2OH \xrightarrow[140^0C]{\text{Conc. } H_2SO_4} CH_3CH_2OCH_2CH_3$$

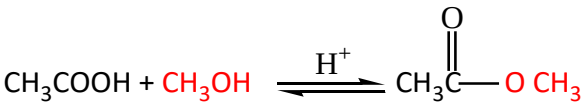
Mechanism



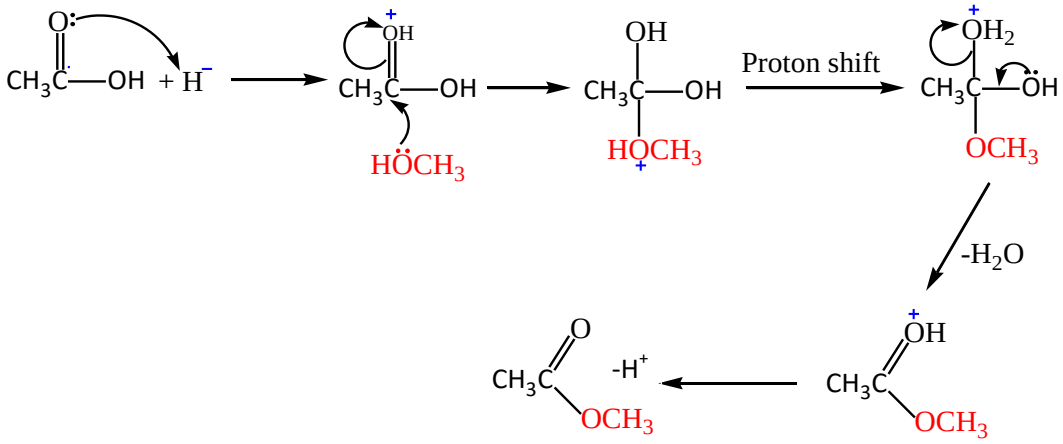
(iv) Formation of esters

(a) Alcohols react with carboxylic acids in the presence of a mineral acid (phosphoric or sulphuric acid) to form esters. However, this is not a good method because the reaction is reversible and does not go to completion.

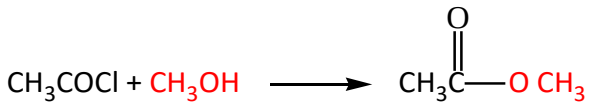
Example



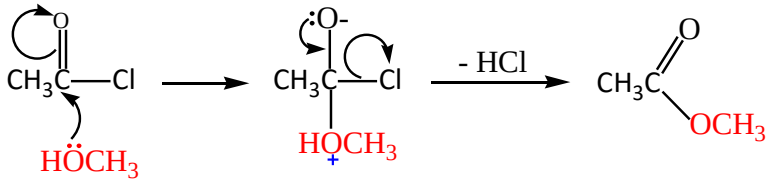
Mechanism



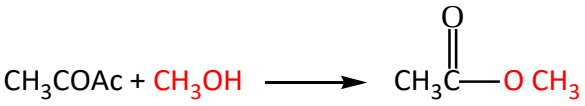
(b) Alcohols react with acid halides to form esters.



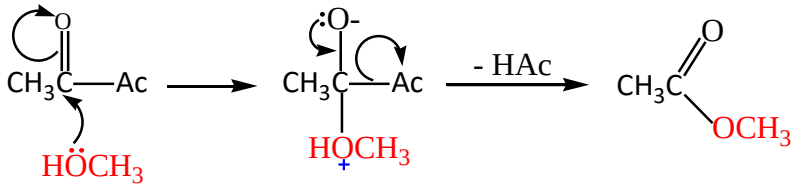
Mechanism



(c) Alcohols react with acid anhydride to form esters.



Mechanism

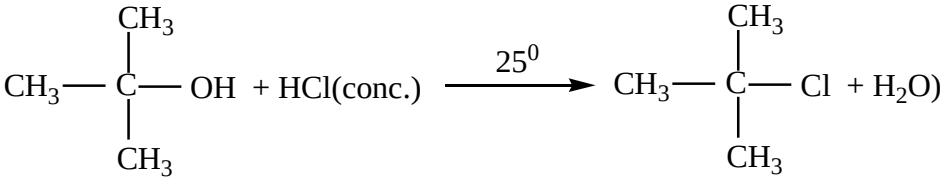


(b) Cleavage of C-O bond

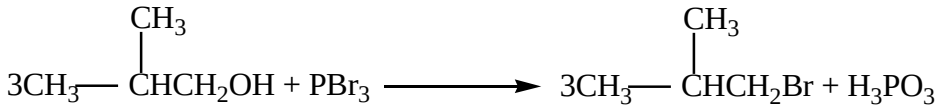
Formation of alkyl halide

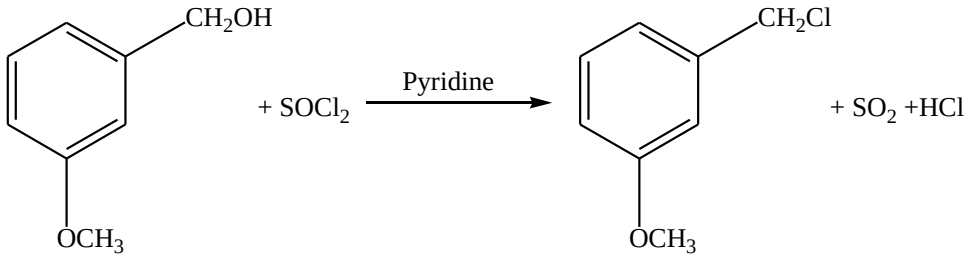
Alcohols react with a variety of reagents to yield alkyl halides. The most commonly used reagents are hydrogen halides (HCl, HBr and HI), phosphorus tribromide (PBr_3) and thionyll chloride.

Examples

(i) 

(ii) $CH_3CH_2CH_2CH_2OH + HBr\ (conc.) \xrightarrow{reflux} CH_3CH_2CH_2CH_2Br$

(iii) 

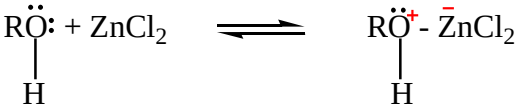
(iv) 

The order of reactivity of hydrogen halides is HI> HBr> HCl whereas the order of reactivity of alcohols is 3^0> 2^0> 1^0. The reaction of HCl with alcohol is catalyzed by anhydrous zinc chloride. The reaction is used to distinguish between primary, secondary and tertiary alcohols.

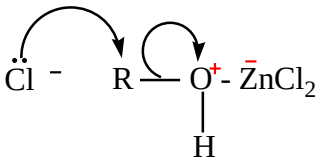
Tertiary alcohol reacts readily with HCl in presence of anhydrous zinc chloride to form an insoluble chloride giving two layers immediately.

Secondary alcohols form two layer in 50 -10minutes

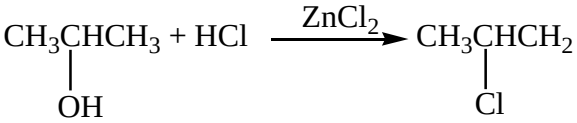
Primary alcohol do not form layers at room temperature.
Mechanism



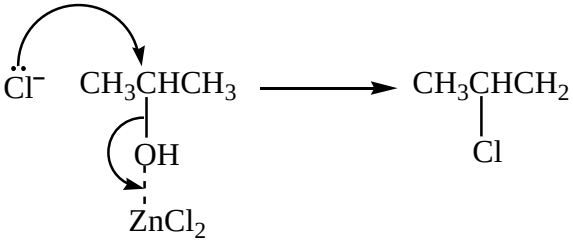
Then,



Example



Mechanism



(c) Oxidation

(i) Alcohols are burnt in oxygen to produce carbon dioxide, water and heat. Due to production of heat on combustion, alcohols are used as fuel.

(ii) Mild oxidizing agents like acidified potassium dichromate oxidize primary alcohols to aldehydes and then, to carboxylic acids. Secondary alcohols are oxidized to ketones.

Tertiary alcohols are not oxidized by potassium dichromate and therefore acidified potassium dichromate is used to distinguish tertiary alcohols from primary or secondary alcohols. When reacted with primary or secondary alcohol, the color of acidified potassium dichromate changes from orange to green.

(d) Dehydration of alcohol

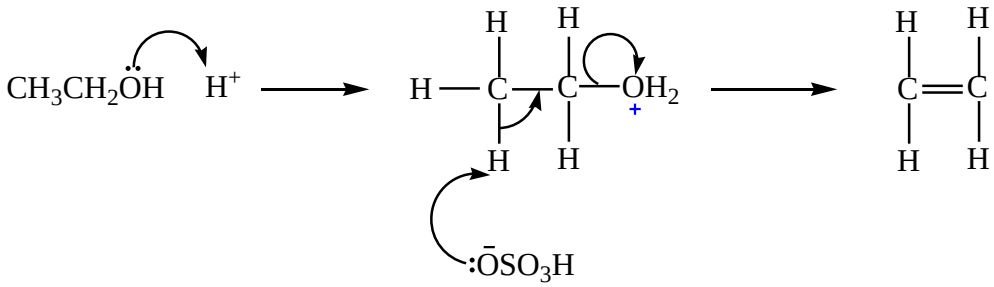
Alcohols are dehydrated by hot concentrated sulphuric or phosphoric acid to form alkenes. The mechanisms depend on the class of alcohols.

(i) Primary alcohol undergo elimination bimolecular; E2.

Example

$$CH_3CH_2OH \xrightarrow[170^0\text{-}180^0]{Conc.H_2SO_4} CH_2{=}CH_2$$

Mechanism

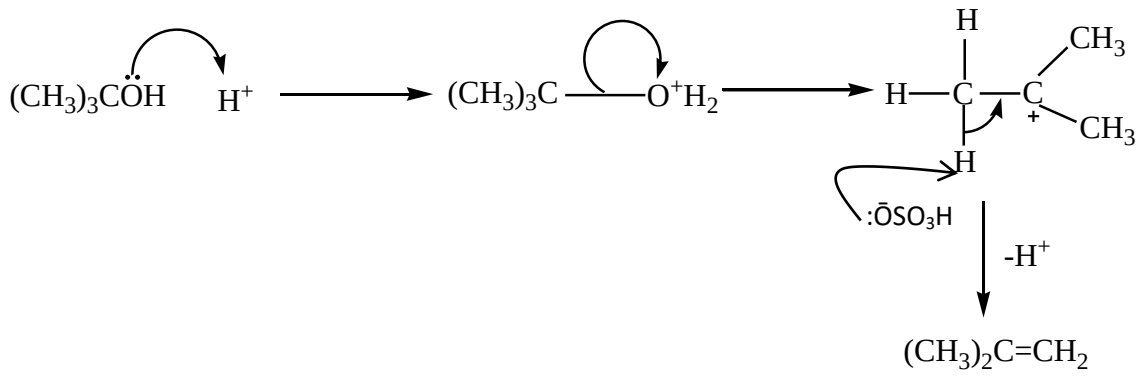


(ii) Tertiary alcohols undergo elimination unimolecular; E1.

Example

$$(CH_3)_3COH \xrightarrow[\text{heat}]{\text{Conc. } H_2SO_4} (CH_3)_2C{=}CH_2$$

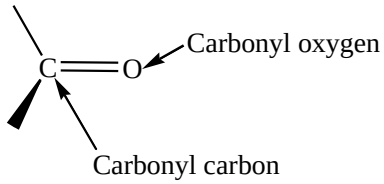
Mechanism



(iii) Secondary alcohol undergo either E2 or E1 mechanism

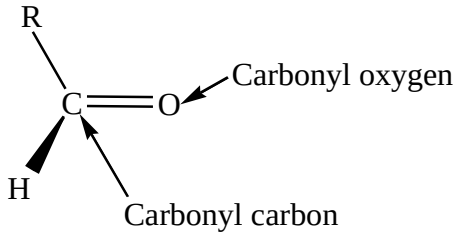
Carbonyl compounds

These are compounds that contain carbonyl group



Aldehydes

Thes are carbonyl compounds with the following structure.



R = alkyl group

Nomenclature of aldehydes

1. Aldehydeare named by replacing the final “e” of the names of corresponding alkanes with “al.”
2. Since the aldehyde group must be at the end of the chain its position in not indicated.
3. When other sustituents are present, the carbonyl carbon is assumed to occupy position one.

Examples

HCHO	Methanal (40% solution is called formalin) or formaldehyde
CH_3CHO	Ethanal or Acetaldehyde
CH_3CH_2CHO	Propanal or propionaldehyde

$CH_3CH_2CH_2CHO$ Butanal or butyraldenhyde

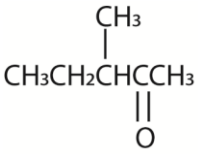
$CH_3CH_2CH_2CH_2CHO$ Pentanal or veraldehyde

Nomenclature of ketones

1. Their names end in suffix "one"
2. The position of the ketone group (-CO-) is given the lowest number.

CH_3COCH_3 Propanone

$CH_3CH_2COCH_3$ Butanone

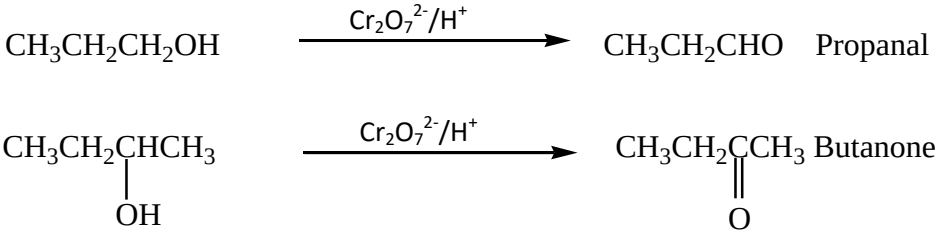


3-methylpentanone

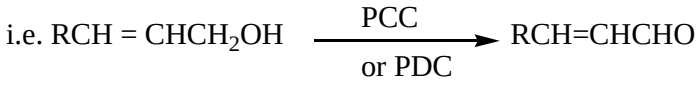
Preparation of carbonyl compounds

a. Oxidation of alcohol with acidified potassium dichromate, sodium dichromate or potassium permanganate. Primary alcohols give aldehydes whereas secondary alcohols give ketones.

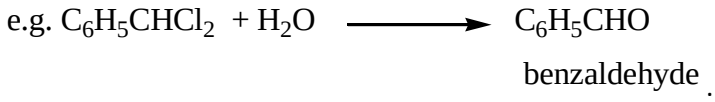
Example



b. Oxidation of alcohols using pyridiumchlorochromate [PCC, $\{C_5H_5NH^+\}Cl.CrO_3$] and pyridinium dichromate [PDC, $\{C_5H_5NH^+\}_2Cl.Cr_2O_7^{2-}$] are currently the reagents of choice, particularly for oxidation of α,β- unsaturated primary and secondary alcohols to give aldehydes and ketones respectively.

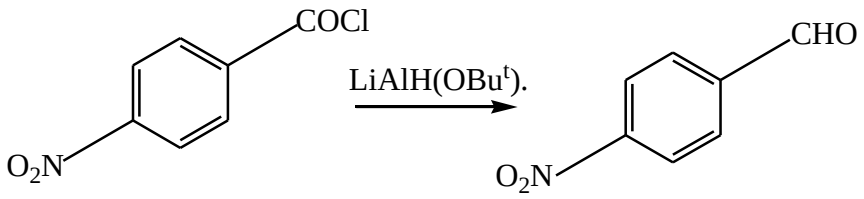


3. Hydrolysis of gem dihalide, ($RCHCl_2$, R_2CCl_2)

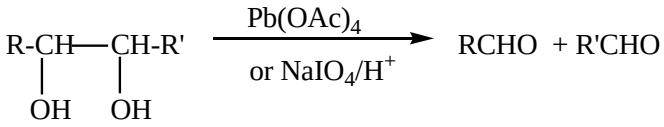


4. Reduction of acid chloride by hydrogen on palladium which is supported on barium sulphate or by using $LiAlH(OBu^t)$.

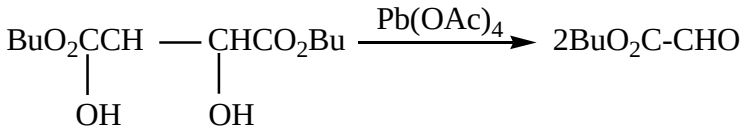
$$CH_3CH_2COCl \xrightarrow{H_2/Pd} CH_3CH_2CHO$$



5. Cleavage of 1,2-diol using either lead tetraacetate or sodium metaperiodate



Example



6. Preparation of ethanal
   (i) By oxidation of ethene with palladium chloride in water

   $CH_2=CH_2 + H_2O + PdCl_2 \longrightarrow CH_3CHO$

   (ii) Passing ethyne through dil. sulphuric acid in presence of mercury sulphate as a catalyst.

   $$HC\equiv CH \xrightarrow{H^+/HgSO_4} CH_3CHO$$

   (iii) Oxidation ethanol

   $$2CH_3CH_2OH + O_2 \xrightarrow{Ag,\ 500^0} 2CH_3CHO + 2H_2O$$

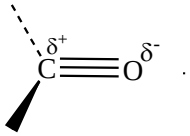
   $$CH_3CH_2OH \xrightarrow{Cu,\ 500^0} CH_3CHO + H_2$$

Physical properties

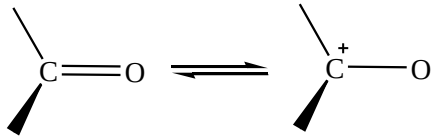
(a) The polar carbonyl group makes carbonyl compounds polar and therefore, the have melting and boiling points than non-polar compounds with similar molecular mass.
(b) Lower members are soluble in water but the solubility decreases with the increase in chain length.

Chemical properties

The structure of carbonyl compound is sp^2 hybridized

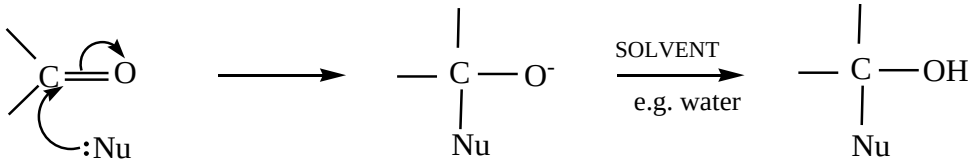


Possible structure

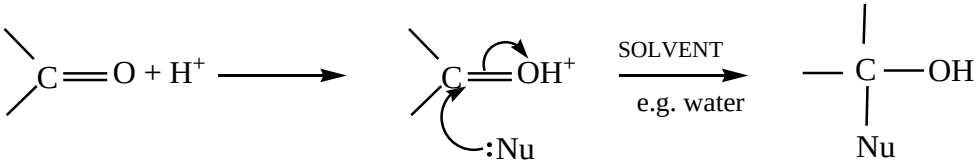


As a result of the partial positive charge, the carbonyl carbon is subjected to nucleophilic attack by a large number of nucleophiles. This results in nucleophilic addition reaction a cross the carbon-oxygen double bond. The nucleophilic addition to the carbon-oxygen double bond, can be regarded to occur in two possible ways generally.

(i) In presence of a strong nucleophile.



(ii) Weak nucleophile, the carbon oxygen bond has to be protonated first.



Generally, aldehydes undergo nucleophilic addition reaction more readily than ketones

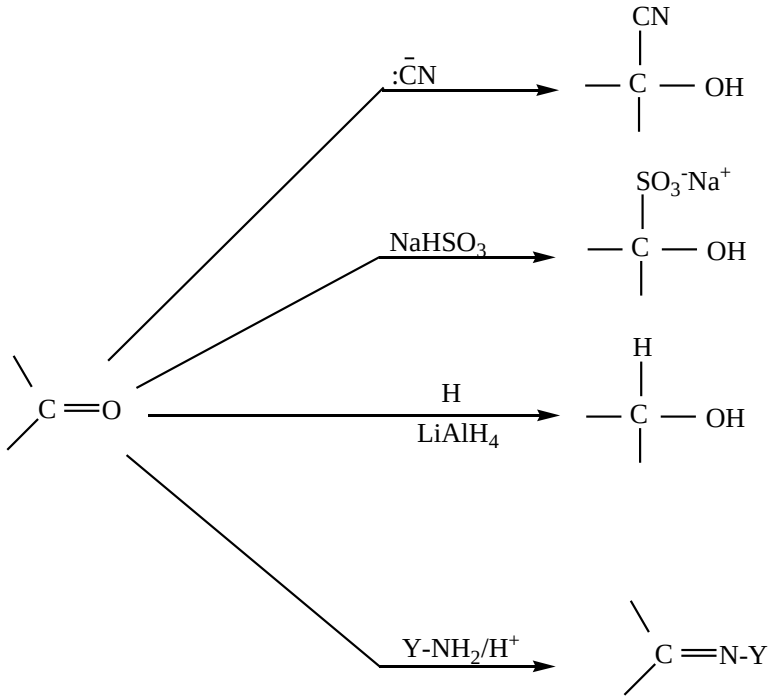
Reasons

(i) **Steric effect**: the bulkiness of the alkyl groups attached to the carbonyl carbon hinders the approach of nucleophile.

(ii) **Inductive effect:** the positive inductive effect of the alkyl groups attached to the carbonyl carbon in ketones, reduce the positivity of the carbonyl carbon thus rendering it less reactive towards nucleophiles.

NB. Presence of an electron withdrawing group on the alkyl carbon make the carbonyl carbon more reactive towards nucleophilic addition reaction. For example, CCl_3CHO is more reactive than CH_3CHO.

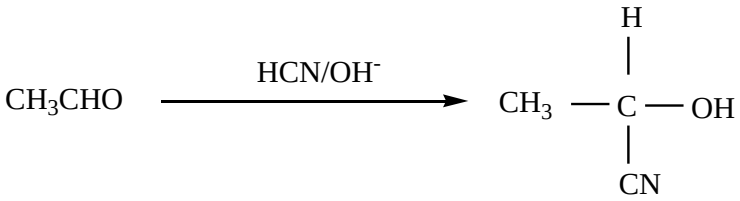
General scheme of nucleophilic reaction to carbonyl compounds



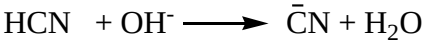
Reaction of carbonyl compounds with HCN or KCN

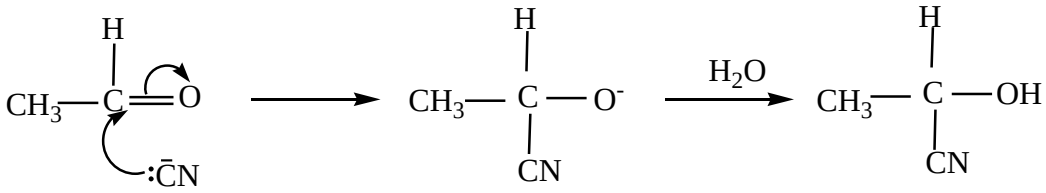
The reaction for addition of HCN is catalyzed by NaOH or KOH

Example



Mechanism





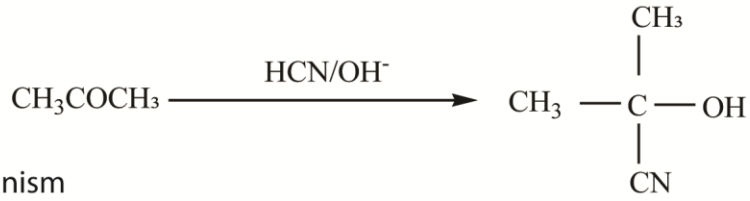
This reaction can be used to increase the carbon chain by one carbon atom

Trial 1

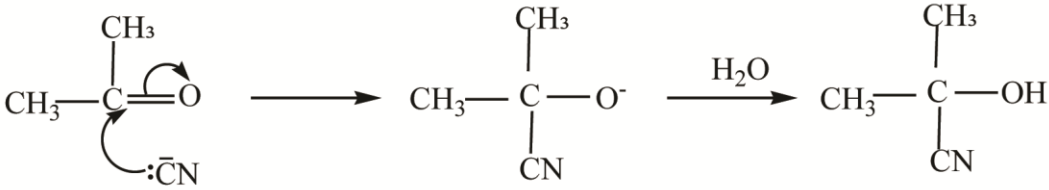
Complete and write a mechanism

$CH_3COCH_3 + KCN \longrightarrow$

Solution

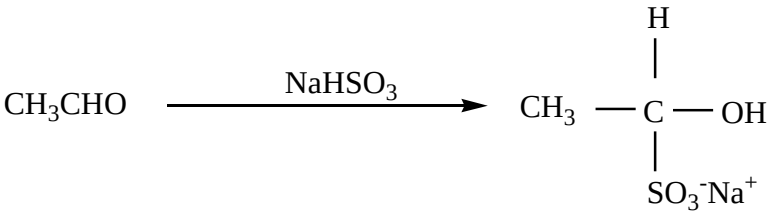


Mechanism

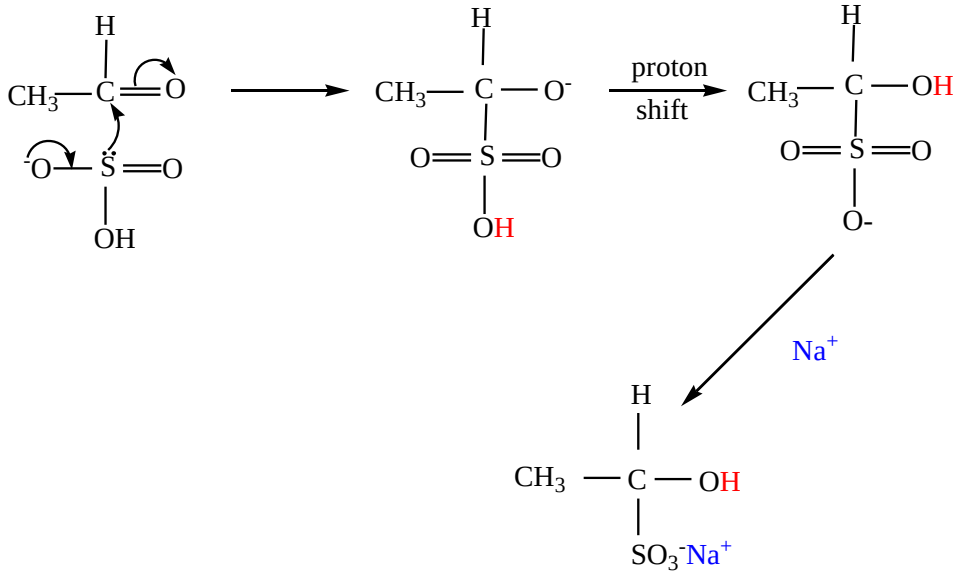


Reaction of carbonyl compounds with sodium hydrogensulphite, NaHSO3.

Example



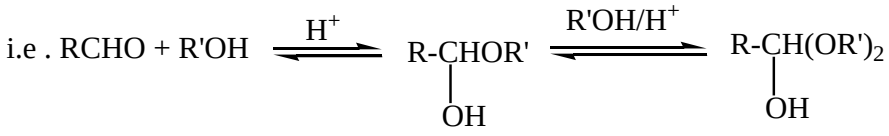
Mechanism



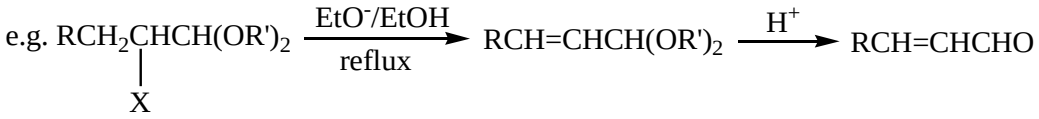
The reaction can be used to purify carbonyl compound since the products formed are solid. After crystallization, the can be redissolved.

Reaction of carbonyl compounds with alcohols

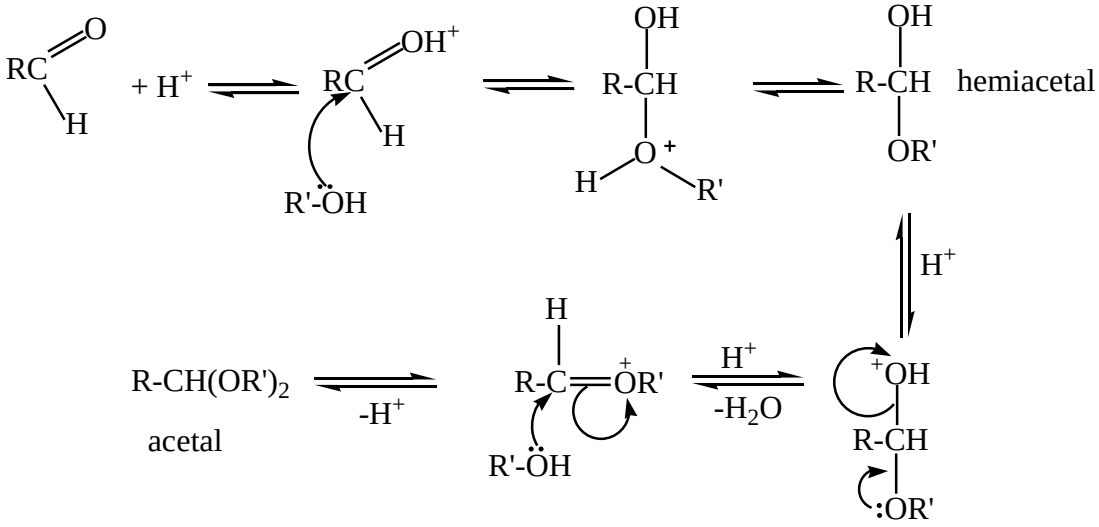
- 1mole of aldehyde + 1mole of alcohol in presence of an acid the product is hemiacetal
- 1mole of aldehyde + 2moles of alcohol in presence of an acid is acetal.



The reaction is used to protect the aldehyde group in chemical synthesis.



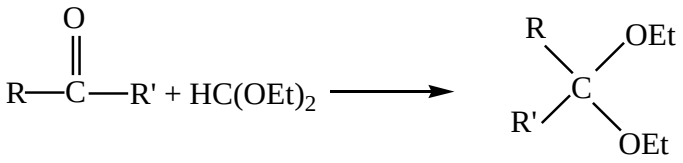
Mechanism



NB (i) Formation of acetals is sensitive to steric hindrances, i.e. depends on the size of groups attached to carbonyl carbon and the size of alcohol. Simple compounds give up to 80% yield, but the yield decrease with the increase in the size of the groups.

(ii) Reaction is reversible; therefore, it's necessary to reduce the concentration of the acid to minimize the reversibility of the reaction.

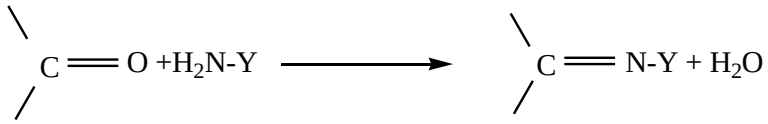
(iii) Ketals are not prepared by direct reaction between ketones and alcohol. This is because the equilibrium of the reaction lies mainly to the left. In this case **orthoformate** is used.

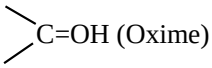
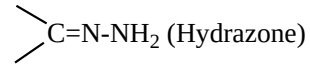
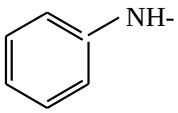
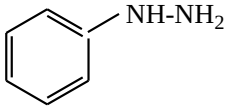
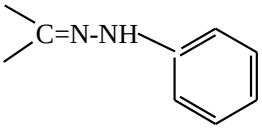
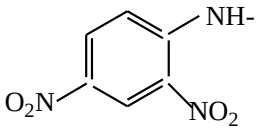
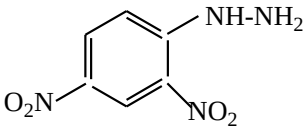
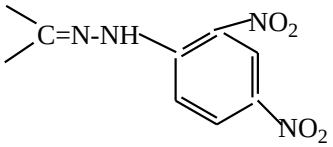
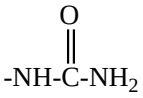
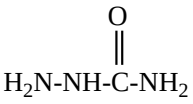
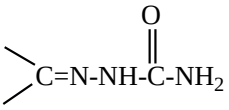


Reaction of carbonyl compounds with ammonia derivatives

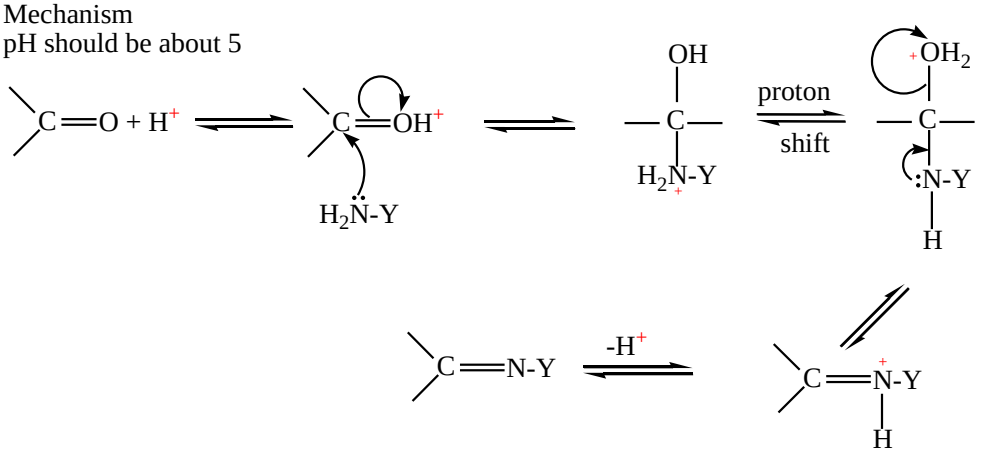
Carbonyl compounds react with compounds of the general formula H_2N-Y with elimination of water. The reaction is catalyzed by acids. A reaction in which two molecules combine with elimination of small molecules e.g. water is called **condensation reaction**.

General equation



Y	REAGENTS	PRODUCTS
-OH	H_2N-OH	
$-NH_2$	H_2N-NH_2	
		 Phenylhydrazone
		 2,4-dinitrohenylhydrazone
		 Semicarbazone

Mechanism
pH should be about 5



The products of these condensation reactions, i.e. oxime and hydrazones are orange crystalline solids with sharp melting points. Thus, they can be used to characterize carbonyl compounds. The most commonly used ammonia derivatives to characterize carbonyl compounds is 2,4-dinitrophenyl hydrazine (Brady's reagent). Reaction of carbonyl compounds with this reagent produces orange colored crystalline solids.

Example

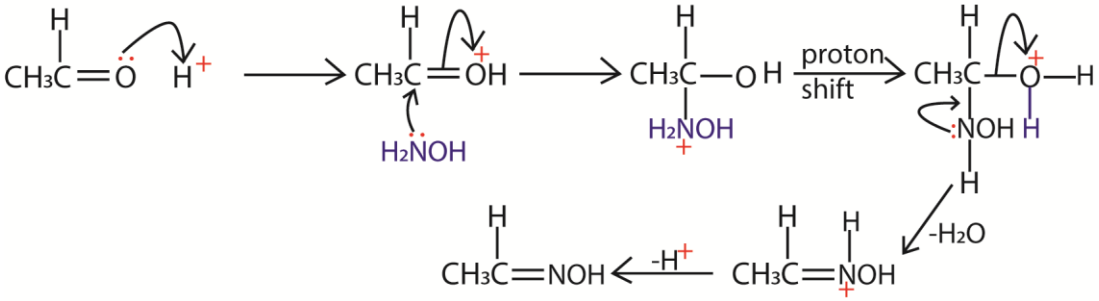
Complete and write mechanism

(i) $CH_3CHO + H_2NOH \xrightarrow{H^+}$

Solution

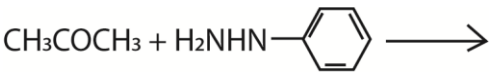
$CH_3CHO + H_2NOH \longrightarrow CH_3CH=NOH$

Mechanism

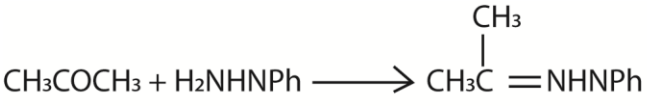


Trial 2

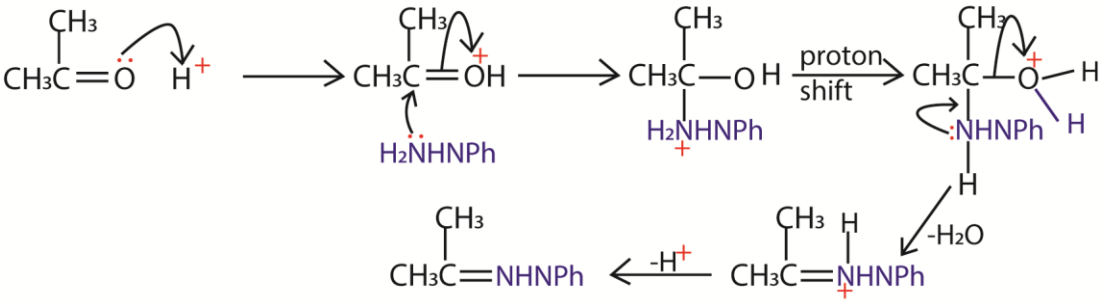
Complete and write a mechanism



Solution



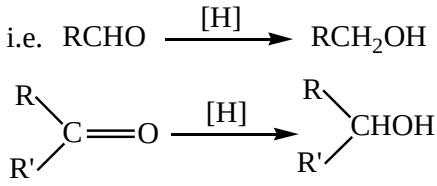
Mechanism



Reduction of carbonyl compounds

(i) Reduction of carbonyl compounds to alcohols

Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols

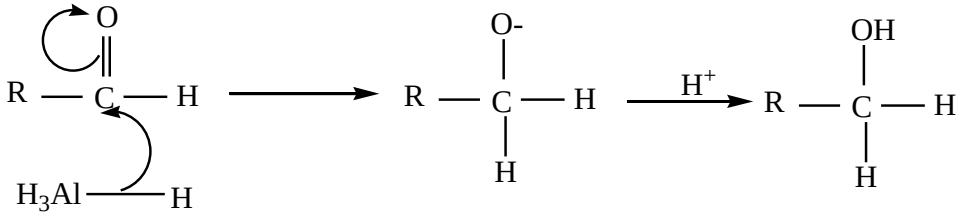


Reducing agents include

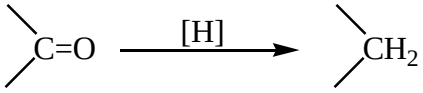
(a) H_2/catalyst (Ni, Pt, Pd): the disadvantage with this reagent is that it reduces double bonds when present.

(b) LiAlH4, NaBH4 – do not reduce double bonds

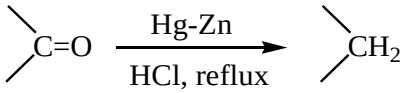
Mechanism



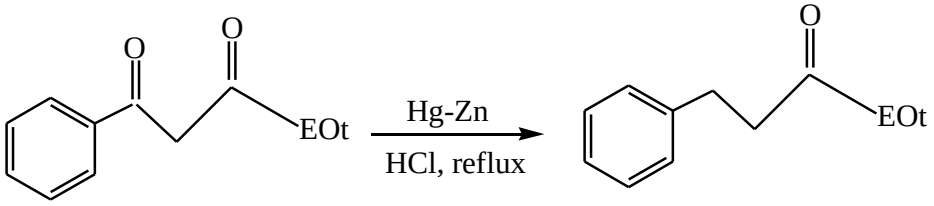
(ii) Reduction of carbonyl compounds to methylene. i.e.



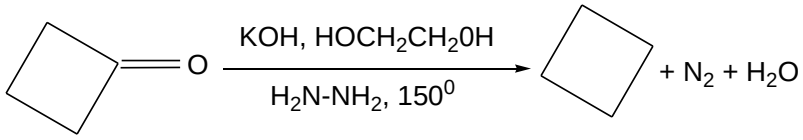
(a) Clemmensen's reduction: it is useful for compounds that are stable under acidic conditions
It is carried out by refluxing a ketone with hydrochloric acid containing amalgamated zinc. Zinc and hydrochloric acid also reduces nitro groups to amines.



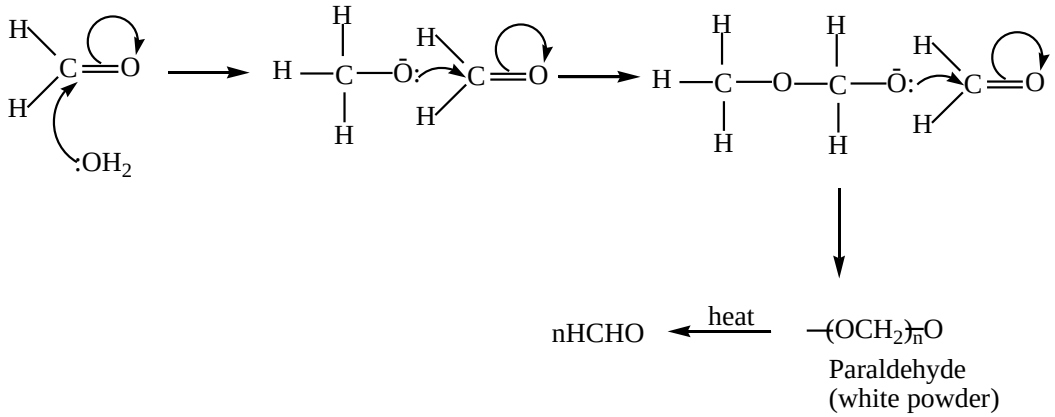
Example



(b) Hong-Mislon modification of Walf-Kishner reaction: a carbonyl compound is heated in presence of high boiling polar solvent, e.g. ethane-1,2-diol with hydrazide + KOH



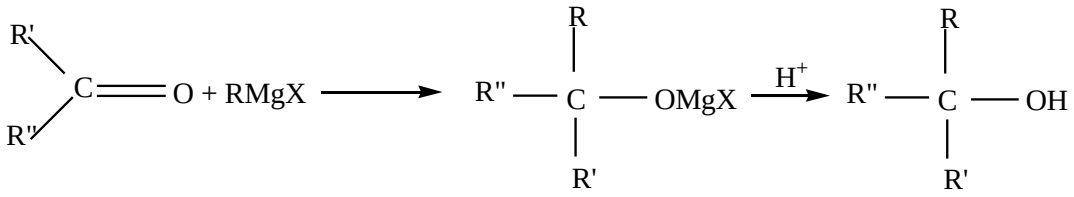
3. Polymerization of aldehyde
Aldehyde(methanal) polymerizes, mainly under basic conditions.



Paraformaldehyde is a useful form for transportation of methanal

Reaction of Grignard's reagents with carbonyl compounds

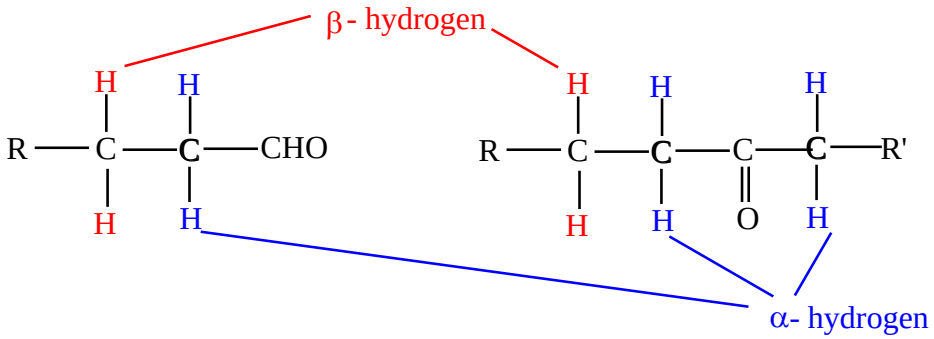
Reaction of carbonyl compounds with Grignard's reagents produces all the three types of alcohols. Thus this is an important reaction for the preparation of alcohols.



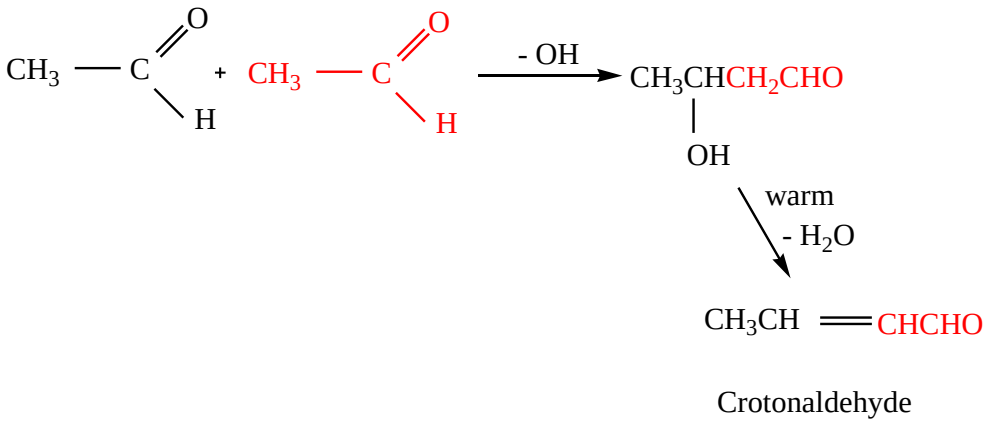
Alcohol

Aldol condensations

Carbonyl compounds which contain at least one alpha hydrogen, react in presence of alkali to form hydroxyl carbonyl compounds called Aldol



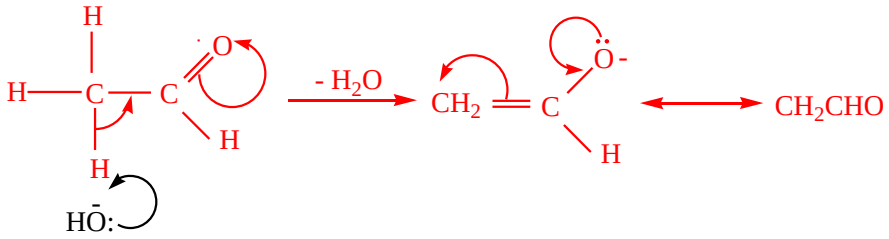
(i) Two molecules of ethanal combine to form 3-hydroxybutanal



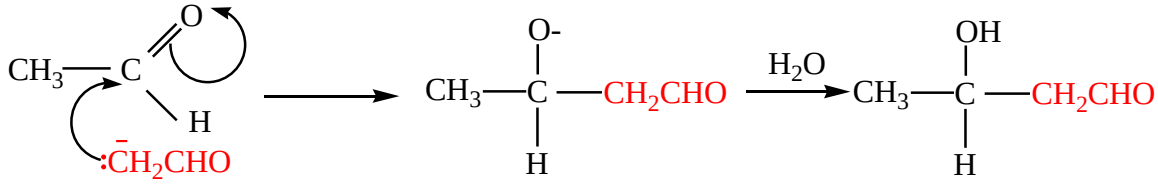
Crotonaldehyde

Crotonaldehyde is used to calibrate spectrometer because it's absorbance is known

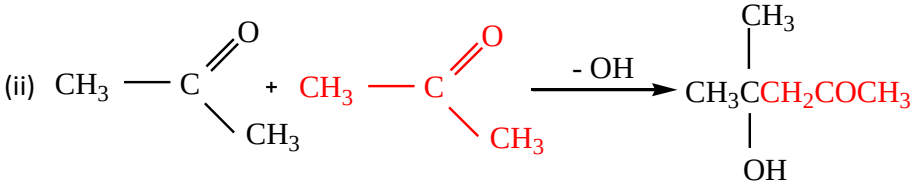
Mechanism

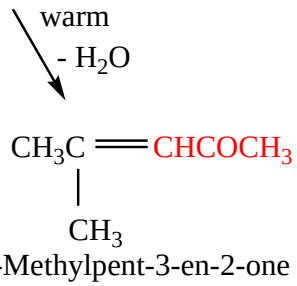


Then,



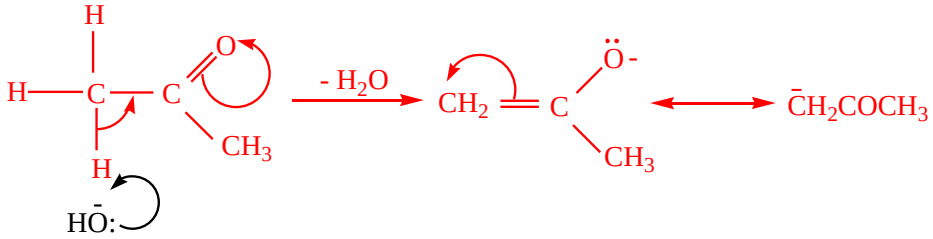
(ii)



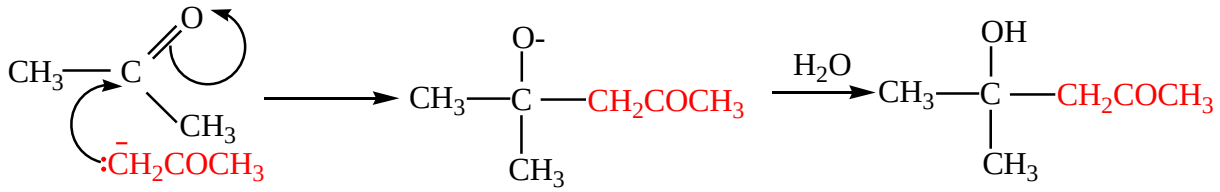


4-Methylpent-3-en-2-one

Mechanism



Then



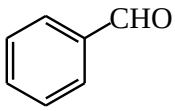
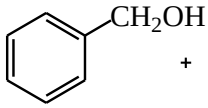
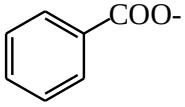
Cannizzaro reaction

This is a reaction between sodium hydroxide solution and aldehydes with no α-hydrogen

It's a self-oxidation – reduction reaction

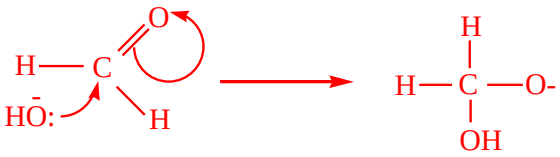
Examples

(i) $2HCHO \xrightarrow[150^0]{^-OH(aq)} HCH_2OH + HCOO^-$

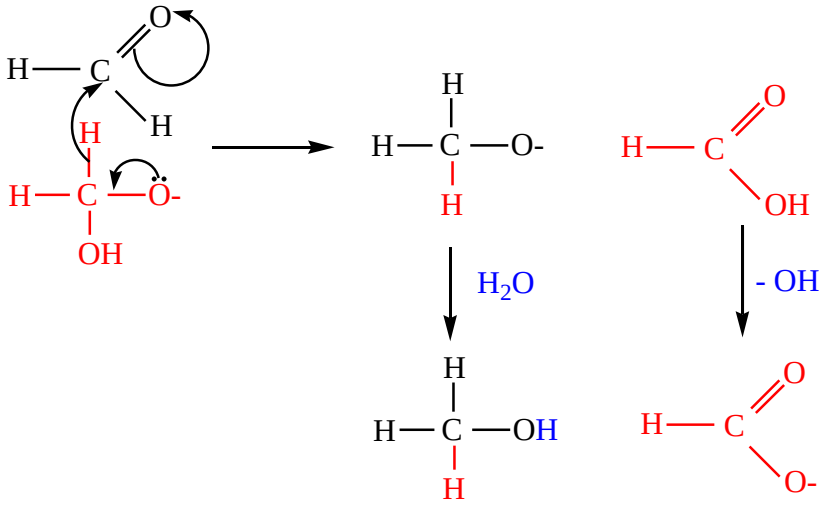
(ii) 2  $\xrightarrow[150^0]{^-OH(aq)}$  + 

Benzaldehyde Benzylalcohol Benzoate

Mechanism

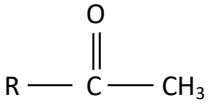


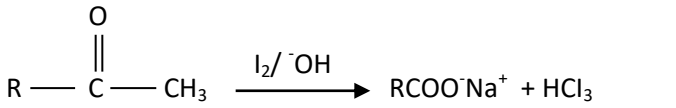
Then,

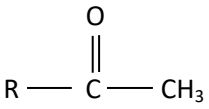


Iodoform reactions

Iodine in presence of sodium hydroxide solution react with carbonyl compounds with structure

 to form a yellow ppt.

i.e. 

NB (i) the reaction is useful when identifying compound with the group 

(ii) Ethanal is the only aldehyde that gives a positive iodoform test
(iii) All ketone with the structure $RCOCH_3$ give positive iodoform test
(iv) Secondary alcohols of the group $RCHOHCH_3$ give positive iodoform test
(v) Ethanol is the only primary alcohol that gives a positive iodoform test.

Trial 3

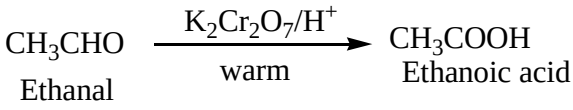
Give one reagent that can be used to distinguish between the following pairs of substances. In each case state what would be observed the reagent is treated separately with the reagent you have mentioned.

(i) CH_3OH and CH_3CH_2OH
(ii) HCHO and CH_3CHO
(iii) $CH_3COCH_2CH_2CH_3$ and $CH_3CH_2COCH_2CH_3$

Oxidation of carbonyl compounds

Aldehydes are easily oxidized to carboxylic acid. The oxidizing agent, normally used are $K_2Cr_2O_7/H^+$, $Na_2Cr_2O_7/H^+$, $KMnO_4/H^+$.

Example



Ketones are not oxidized under mild condition

Distinguishing between aldehydes and ketone

Reagent	Observation	
	Aldehydes	Ketones
Fehling's solution	Brown ppt	No observable change
Tollen's reagent or ammoniacal silver nitrate	Black ppt or silver mirror	No observable change
Acidified potassium dichromate	Orange solution turns green	No observable change

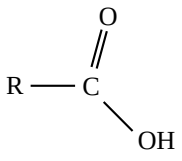
Trial 4

Give one reagent that can be used to distinguish between the following pairs of substances. In each case state what would be observed the reagent is treated separately with the reagent you have mentioned.

(i) CH_3CH_2CHO and CH_3COCH_3

Carboxylic acid or alkanoic acids

These are cmpounds with the formula



where R is a hydrogen or an alkyl group.

The carboxylic group is a combination of carbonyl group and an hydroxyl group(OH): the name carboxylic group.

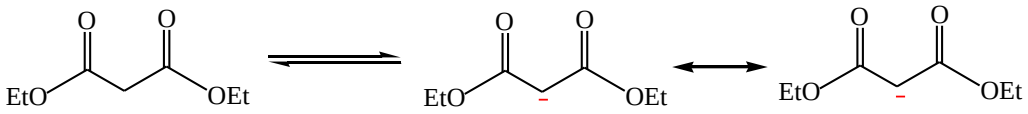
Nomenclature

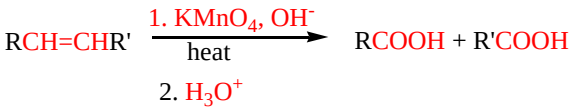
1. Their names end with suffic “oic” followed by the word acid.
2. The carboxylic group must always be at the end of the chain and therefore it’s position need not to be specified. Take longest chain that contain the carboxylic group and start numbering from the carboxylic carbon

Examples	Systematic name	Common name
HCOOH	Mechanoic acid	Formic acid
CH_3COOH	Ethanoic	Acetic acid
CH_3CH_2COOH	Propanoic acid	Propionic acid
$CH_2CH_2CH_2COOH$	Butanoic acid	Butyric acid
$CH_3CH(CH_3)COOH$	2-methylpropanoic acid	Isobutyric acid

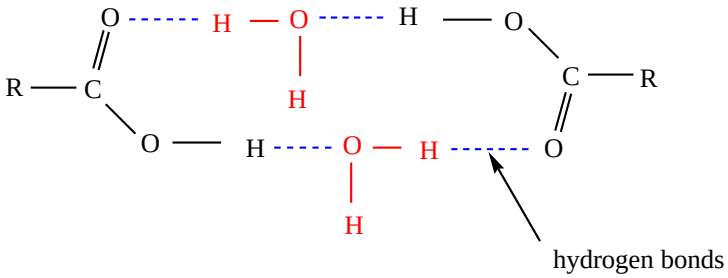
Physical properties

1. Lower member are liquids and higher members are waxy solids. With boiling points which are higher than expected, this because, their molecules are associated by hydrogen bonds.





2. Lower members are soluble in water but the solubility decreases with the increasing molecular mass of carboxylic acid. This is because carboxylic acids are capable of formation of hydrogen bonds with water



3. Melting points

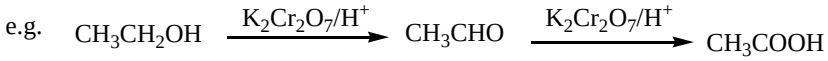
Compounds	Mpt (^{0}C)	Bpt (^{0}C)	Ka
HCOOH	8	100.5	1.7×10^{-4}
CH_3COOH	16.6	118	1.77×10^{-5}
CH_3CH_2COOH	21	141	1.34×10^{-5}
$CH_3(CH_2)_2COOH$	-6	164	1.54×10^{-5}
$CH_3(CH_2)_3COOH$	-34	187	1.52×10^{-5}
$CH_3(CH_2)_4COOH$	-3	205	
$CH_3(CH_2)_5COOH$	16	259	

Generally the melting point increase with the molecular mass. However, the melting points of lower carboxylic acids are relatively higher than those of higher carboxylic acids because they form stronger hydrogen bonds.

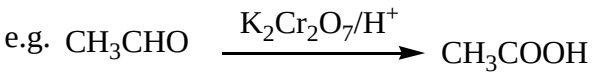
4. The acidity of carboxylic acids decrease with the increase in molecular mass due to positive inductive effect of alkyl group. Electron with drawing groups make carboxylic acid more acidic. For example CCl_3COOH is more acidic than CH_3COOH.

Methods of preparation

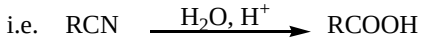
1. By oxidation of primary alcohols using $K_2Cr_2O_7/H^+$, $Na_2Cr_2O_7/H^+$, or $KMnO_4/H^+$

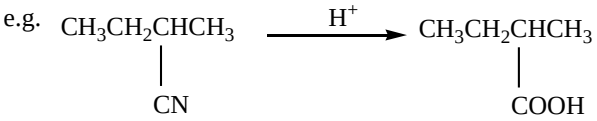


2. Oxidation of aldehyde using $K_2Cr_2O_7/H^+$, $Na_2Cr_2O_7/H^+$, or $KMnO_4/H^+$

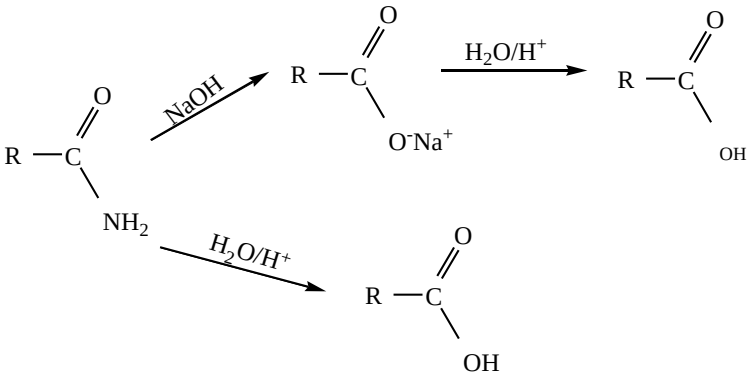


3. Hydrolysis of nitrile in presence of a mineral acid.



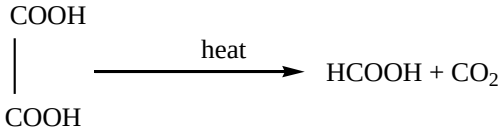


4. Hydrolysis of acid amide with a mineral acid or alkali

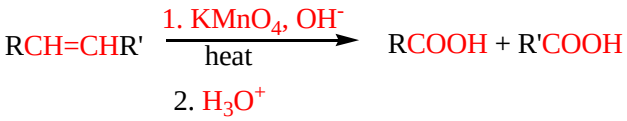


5. Reaction of carbon dioxide with a grignard reagent followed with hydrolysis.

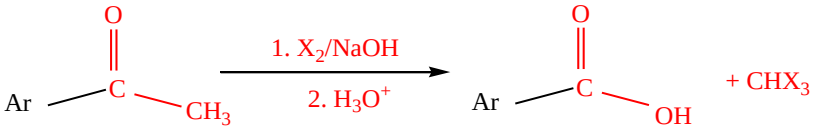
6. Preparation of methanoic acid
   By heating a solution of ethane dioic acid in propane-1,2,3-triol



7. Oxidation of alkenes using hot alkaline $KMnO_4$.

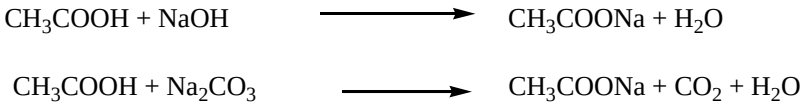


8. Oxidation of methyl ketone

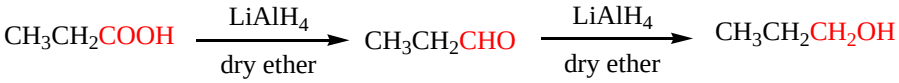


Chemical properties

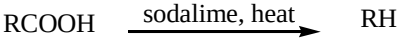
1. Carboxylic acid react with base to form salts and even liberate caarbon dioxide from carbonates.
   Examples

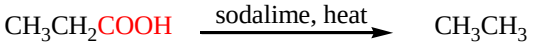


2. Reduction of carboxylic acid
   Carboxylic acids are resistant to reduction by mild reducing agents. However, they can be reduced through aldehydes to primary alcohols by LiAlH4 in presence of dry ether.
   Example



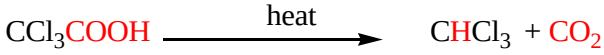
3. Decarboxylation
   This is a reaction in which a molecule of CO_2 is removed from carboxylic acids.
   (i) Simple carboxylic acids are not easily decarboxylated but their salts are easily decarboxylated in presence of soda lime.



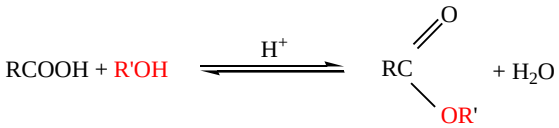
   (ii) 

   (iii) Acids with electron withdrawing groups on α-carbon are easily decarboxylated on heating.

   Example



   (iv) Esterification: Carboxylic acids react with alcohol in presence of mineral acids to form ester

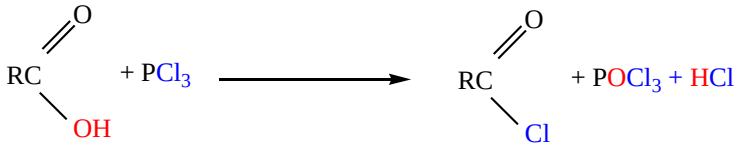


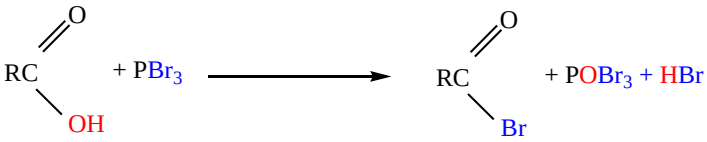
   Easter have got sweet smell; this is why this reaction is used in identification of carboxylic acids

Reactivity of alcohols is in order $1^0 > 2^0 > 3^0$, and the reactivity of carboxylic acids is in order HCOOH› CH_3COOH › RCH_2COOH › $R_2CHCOOH$ › R_3CCOOH, due to steric hindrance. i.e. the presence of bulky groups near the site of reaction, whether in the alcohol or in acid slows esterification.

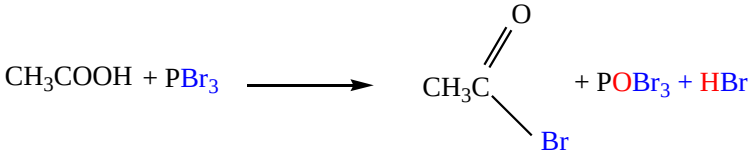
4. Formation of acid halides

Carboxylic acids (except methanoic acid) react with phosphorus halides to form acid halides



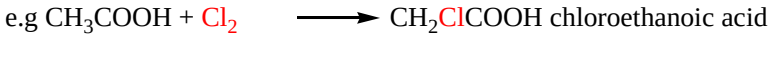


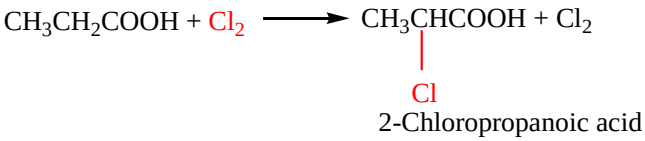
Example



5. Halogenation of aliphatic acids

(a) Carboxylic acids (except methanoic acid) react with chlorine in presence of sunlight or u.v light, thereby a chlorine atom replacing an α-hydrogen.





(b) Bromine replaces an α-hydrogen in presence of red phosphorous (hell-vohlard zelensky reaction)

Thank you
Dr. Bbosa Science