

ORGANIC COMPOUND
CONTAINING OXYGEN

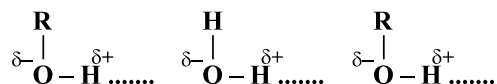
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CONCEPTS (Monohydric Alcohols & Ether)

Alcohols :

C1A Physical Properties :

The lower alcohols are completely soluble in water but as the number of carbon atoms increases, solubility decreases. This solubility in water is due to intermolecular H-bonding between water and alcohols molecules due to their polar character.

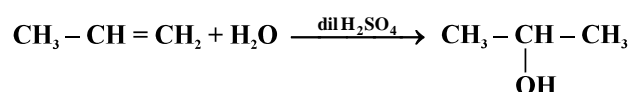


Increase in C-chain increases organic part hence solubility in water decreases.

Isomeric 1°, 2°, 3° alcohols have solubility in order : 1° > 2° > 3°.

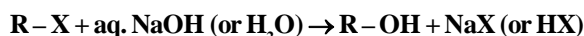
C1B Method of preparation of Alcohols :

(i) Hydration of Alkenes :



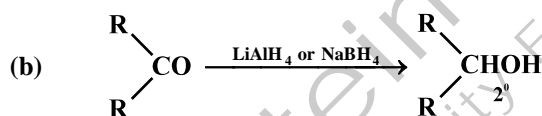
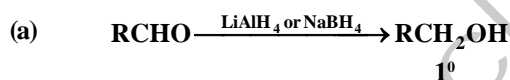
Intermediate is carbonium ion that can change to more stable carbanion ion by hydride shift, alkyl or phenyl shift.

(ii) Hydrolysis of Alkyl Halides :



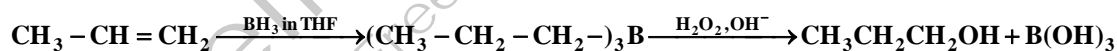
Reaction can be S_N¹ or S_N².

(iii) Reduction of Carbonyl Compounds (including acid derivative) :



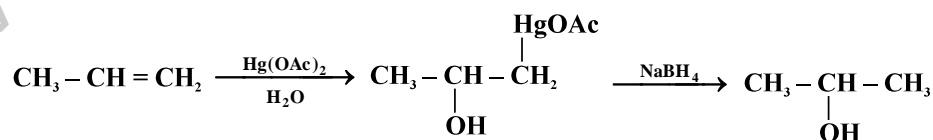
(c) Acid, acid halide, ester and anhydride are reduced to 1° alcohol.

(iv) Hydroboration and oxidation :



The hydroboration-oxidation (HBO) process gives product corresponding to anti-Markownikoff addition of H₂O to the carbon-carbon double bond.

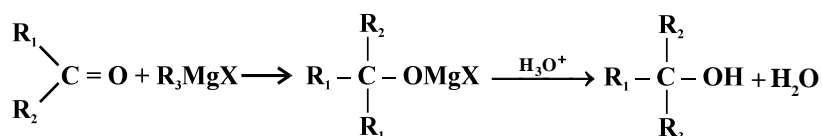
(v) Oxymercuration-Demercuration :



The alcohol obtained corresponds to Markownikov's addition of water to an Alkene.

(vi) (a) Through Grignard Reagent :

Addition of Grignard Reagent on carbonyl compounds followed by hydrolysis yields alcohols nature of which depends upon types of carbonyl compounds used.



R_1, R_2 can be H, alkyl or aryl but R_3 is not H.

- (b) Grignard reagent with epoxide and after hydrolysis gives 1° alcohol for e.g.,



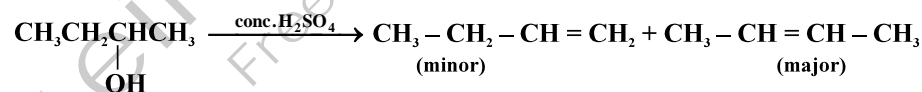
Practice Problems :

- Propene, $CH_3 - CH = CH_2$ can be converted into 1-propanol, Which of the reagent among the following is ideal to affect the conversion :
 - alkaline $KMnO_4$
 - B_2H_6 and alkaline H_2O_2
 - O_3/Zn
 - OsO_4/CH_2Cl_2
- Glycol may be obtained :
 - by the oxidation of ethylene with cold, dilute, alkaline permanganate solution
 - by the hydrolysis of ethylene bromide under reflux with aqueous sodium carbonate solution
 - by the hydrolysis of ethylene chlorohydrin on boiling with aqueous sodium bicarbonate
 - by any of the above methods
- Which of the following are the starting materials for the Grignard's synthesis of tert. butyl alcohol
 - $CH_3MgI + CH_3COCH_3$
 - $CH_3MgI + CH_3CHOHCH_3$
 - $CH_3CH_2MgBr + CH_3COCH_3$
 - $CH_3CH_2MgBr + CH_3CHO$

[Answers : (1) b (2) d (3) a]

C2 Chemical Properties :

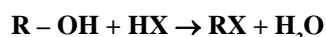
- (i) Dehydration of Alcohol :



Alcohols leading to conjugated alkenes are more easily dehydrated than those of alcohols leading to non-conjugated alkenes.

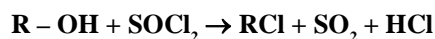
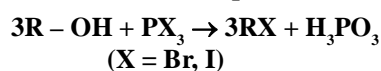
Dehydration of alcohol is in the order $3^\circ > 2^\circ > 1^\circ$ as intermediate is carbocation.

- (ii) Reaction with Halogen Acids :

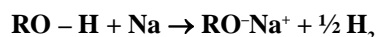


Intermediate is carbonium ion. The order of reactivity of HX : $HI > HBr > HCl$ for a given alcohol.

- (iii) Reaction with Phosphorous Halides and Thionyl Chloride :

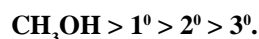


- (iv) Acidic Character of Alcohol :

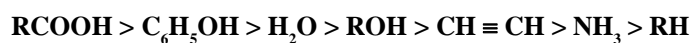


alkoxide

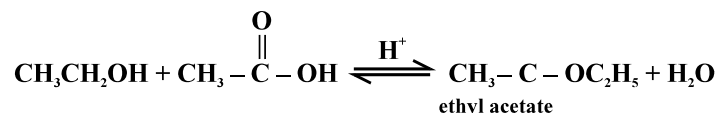
The order of acidic character of alcohol with metal is :



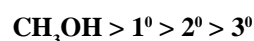
The relative acidities is as follows :



(v) Ester Formation (alcohol can act as a nucleophile also).



Thus reactivity of alcohols for given acid is in order :

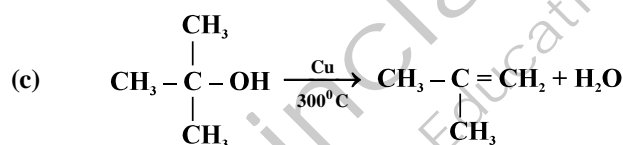
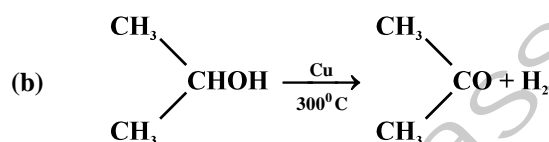
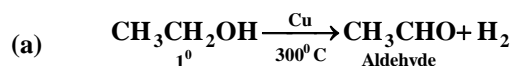
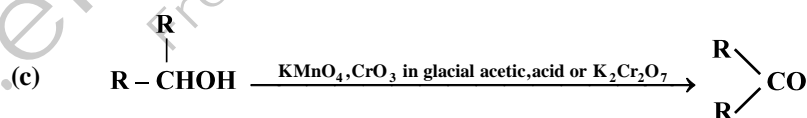
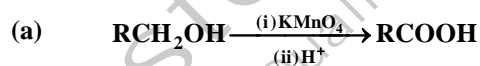


and those of acids for given alcohol is in order :



(vi) Oxidation of Alcohol :

1. Using Cu

2. Oxidation using $\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$ 

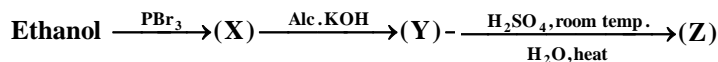
3. Other reagents used for oxidation :

(a) PCC (pyridinium chlorochromate) to oxidise 1° alcohols to aldehydes.(b) MnO_2 selectively oxidises the OH group of allylic and benzylic 1° and 2° alcohols to give aldehydes and ketones respectively.C3 Test to distinguish 1° , 2° and 3° Alcohols :

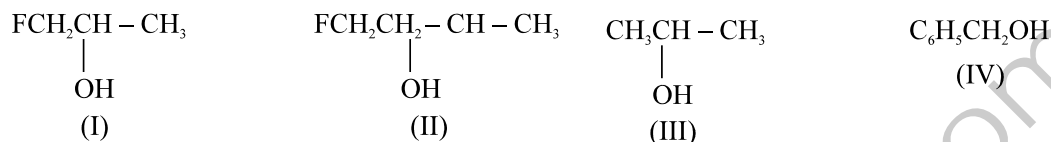
- (a) Lucas Reagent (anhydrous $\text{ZnCl}_2/\text{conc. HCl}$)
- (b) Oxidation
- (c) Victor Meyer Test

Practice Problems :

1. Identify (Z) in the following reactions series :



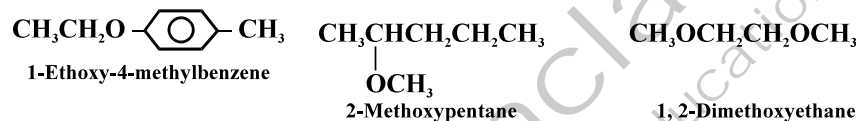
- (a) $\text{CH}_2 = \text{CH}_2$ (b) $\text{CH}_3\text{CH}_2\text{OH}$ (c) $\text{CH}_3\text{CH}_2\text{OSO}_3\text{H}$ (d) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
2. An organic compound gives hydrogen on reacting with sodium metal. It also gives iodoform test and forms an aldehyde of molecular formula $\text{C}_2\text{H}_4\text{O}$ on oxidation with acidified dichromate. The compound is :
- (a) CH_3OH (b) CH_3COOH (c) CH_3CHO (d) $\text{C}_2\text{H}_5\text{OH}$
3. The order of reactivity of the following alcohols,



towards conc. HCl is

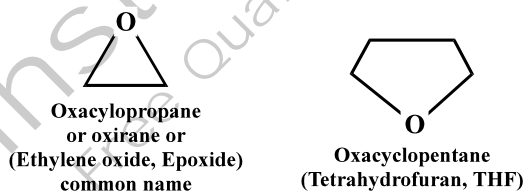
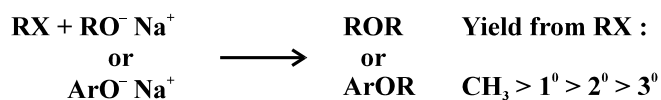
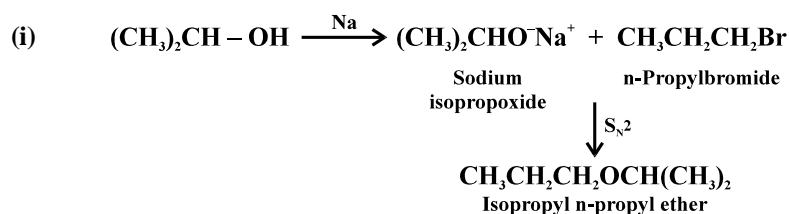
- (a) $\text{I} > \text{II} > \text{III} > \text{IV}$ (b) $\text{I} > \text{III} > \text{II} > \text{IV}$
 (c) $\text{IV} > \text{III} > \text{II} > \text{I}$ (d) $\text{IV} > \text{III} > \text{I} > \text{II}$

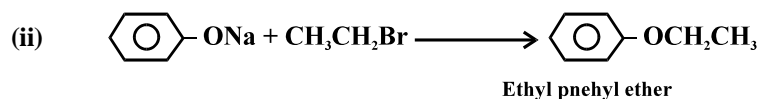
[Answers : (1) b (2) d (3) c]

C4 Ethers**Nomenclature of Ethers :**

Cyclic ethers can be named in several ways :

In another system, a cyclic three membered ether is named as oxirane and a four membered ether is called oxetane.

**C5 Methods of Preparation of Ether :**(a) **Williamson Synthesis :****Example :**

**Discussion : Phenol in Williamson's synthesis :**

Because phenols are stronger acids than alcohols they can react with NaOH to change into sodium phenoxide ion. But alcohols can be converted into sodium alkoxide ion by reaction with sodium metal only.

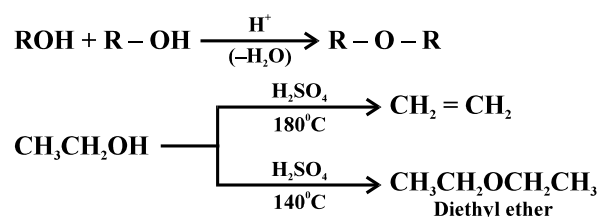
[Alkyl halide used here can not be aryl halide as it does not undergo nucleophilic substitution easily]

R – X → can be X = –Cl, –Br, I, –OSO₃CH₃ etc.

(b) Ethers by Intermolecular Dehydration of Alcohols :

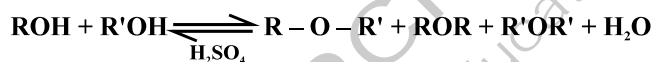
Alcohols can dehydrate to form alkenes.

1^o Alcohols can also dehydrate to form ethers.

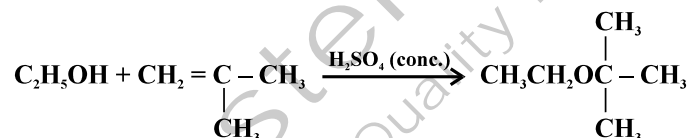


The formation of ether takes places by S_N2 mechanism mainly, with one molecule acting as the nucleophile and with another protonated molecules of the alcohol acting as the substrate.

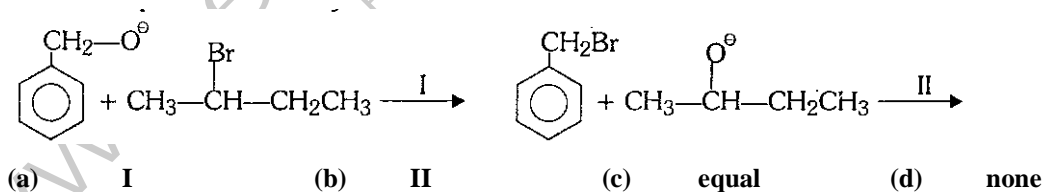
Finally this method is not useful for the preparation of ether with 3^o alcohol because they form alkene too easily. This method is not useful for the preparation of unsymmetrical ethers from primary alcohols because the reaction leads to a mixture of products.



(c) Ethers may be prepared by the addition of alcohols to alkenes in the presence of acid e.g.

**Practice Problems :**

1. Which route provides a better synthesis of ether :



[Answers : (1) b]

C6 Reactions of Ethers :

(a) Ethers are comparatively unreactive compounds. The ether linkage are quite stable towards bases, oxidizing agent, reducing agents. Ether can undergo just one kind of reaction, cleavage by acids :

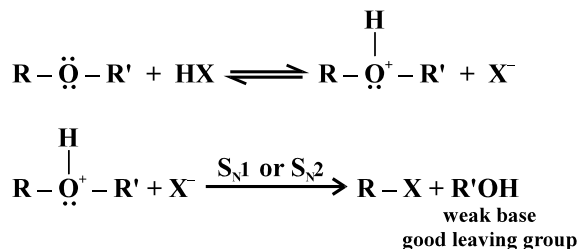


Reactivity of HX : HI > HBr > HCl

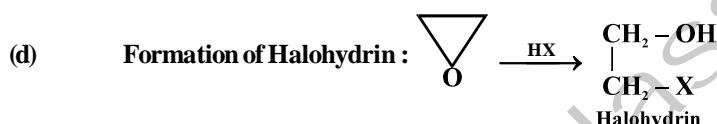
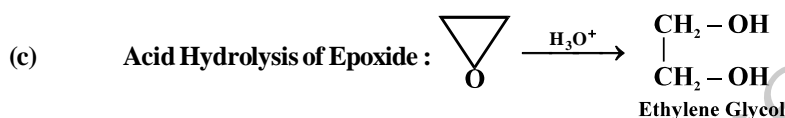
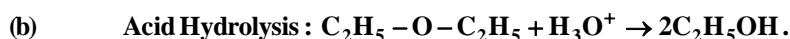
Cleavage takes place only under quite vigorous conditions : concentrated acids (usually HI or HBr) and high temperature.

Oxygen of the ether is basic, like the oxygen of alcohol. The initial reaction between an ether and an acid is undoubtedly formation of the protonated ether.

Cleavage then involves the nucleophilic attack by halide ion on this protonated ether, with displacement of the weakly basic alcohol molecule.



As we might expect primary alkyl group tend to undergo $\text{S}_{\text{N}}2$ and 3° tend to undergo $\text{S}_{\text{N}}1$.



Practice Problems :

1. Ethoxy ethane does not react with

- (a) HI (b) conc. H_2SO_4 (c) PCl_5 (d) Na

2. An ether, (A) having molecular formula, $\text{C}_6\text{H}_{14}\text{O}$, when treated with excess of HI produced two alkyl iodides which on hydrolysis yield compounds (B) and (C). Oxidation of (B) gives an acid (D), whereas oxidation of (C) results in the formation of a mixed ketone, (E). Thus structures of (A) is

- (a) $\text{H}_3\text{C}-\overset{\text{H}_3\text{C}}{\underset{|}{\text{CH}}}-\text{CH}_2\text{OCH}_2-\text{CH}_3$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$
- (c) $\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\underset{|}{\text{CHO}}}\text{CH}_2\text{CH}_3$ (d) $\text{CH}_3\overset{\text{CH}_3}{\underset{|}{\text{CHO}}}\text{CH}_2\text{CH}_2\text{CH}_3$

[Answers : (1) d (2) c]

Aldehydes & Ketones

C7A Physical Properties : $\text{>C}=\overset{\curvearrowright}{\text{O}} \longleftrightarrow \text{>C}^+-\text{O}^-$

It has high dipole moment

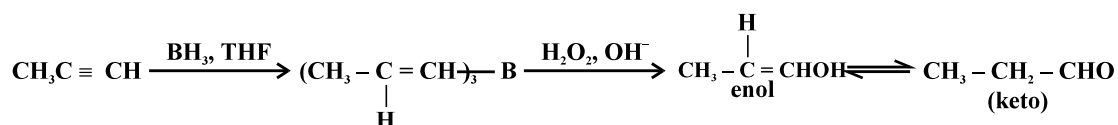
Boiling point are lower than alcohols due to their inability to form intermolecular H-bonding.

B.Pt. are higher than corresponding alkanes due to dipole-dipole interaction.

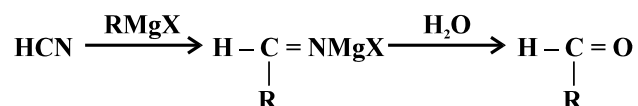
Carbonyl group can form H-bond with H_2O hence they are soluble in water to varying extent.

7. Hydroboration Oxidation :

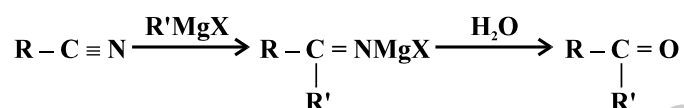
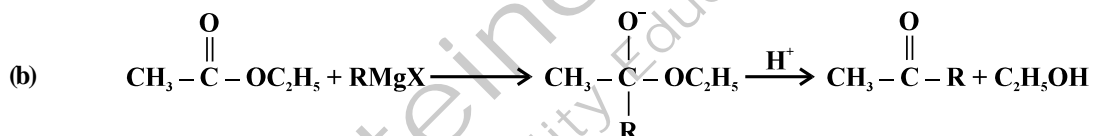
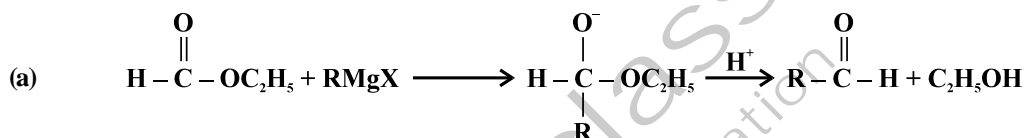
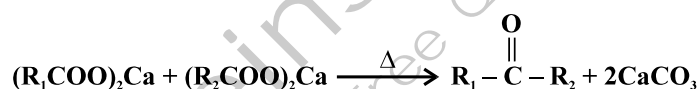
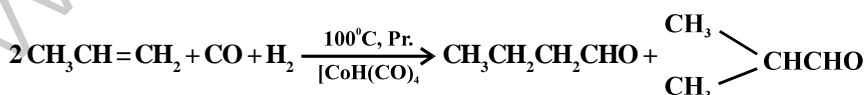
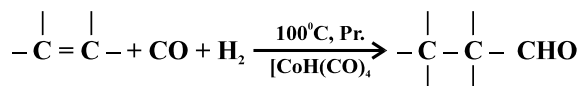
Hydroboration of a non-terminal alkyne followed by oxidation of the intermediate yields a ketone but terminal alkyne yield aldehyde.

8. Use of Grignard Reagent :

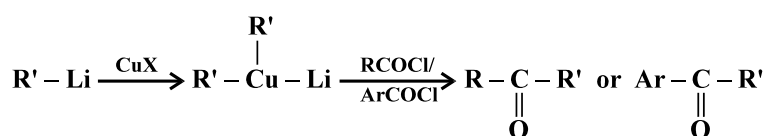
(a) With HCN aldehyde is formed.

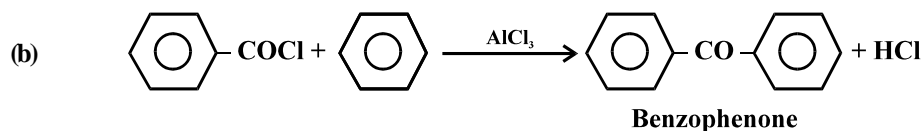
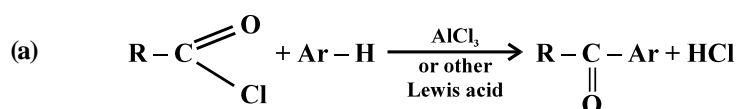
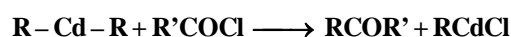
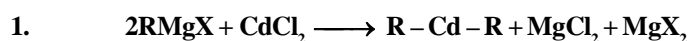


(b) With RCN a ketone is formed.

9. With Esters10. Decarboxylation of calcium salts of carboxylic acids :11. Oxo Process :

$[\text{COH(CO)}_4]$ \longrightarrow Cobal + Carbonyl hydride

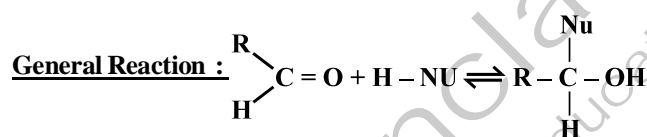
12. Reduction of acid chloride with organocopper compounds :

13. Friedel-Crafts Acylation :14. From Cadmium and Lithium Salts :

$\text{R} \longrightarrow$ should be 1° alkyl or aryl ($-\text{C}_6\text{H}_5$)

15. Ozonolysis of Alkene (Zn/H^+) \longrightarrow Aldehyde/KetoneC8 Chemical Properties :1. Nucleophilic Addition to the Carbon-Oxygen Double bond :

The most characteristic reaction of aldehyde and ketone is nucleophilic addition to the carbon-oxygen double bond.

Relative reactivity of Aldehydes versus Ketones :

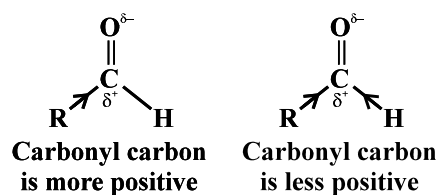
Aldehydes are more reactive than Ketones. There are two reasons for this, they are as follows :

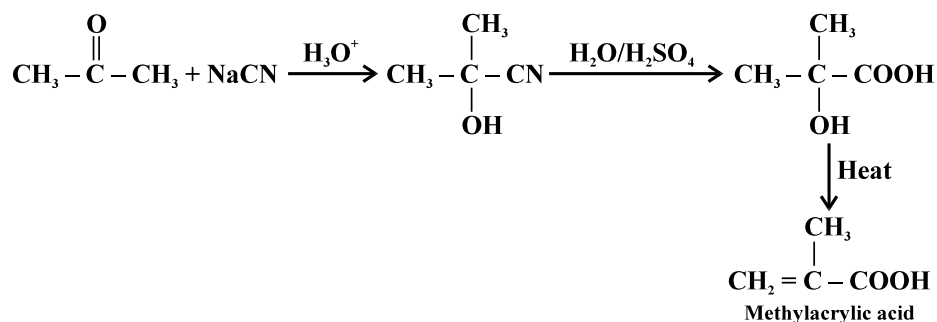
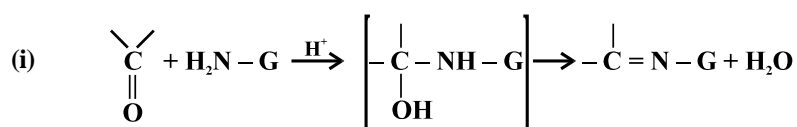
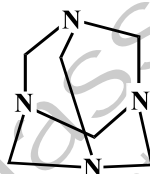
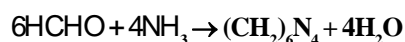
1. Steric Factor 2. Electronic factor

1. Steric Factor : With one group being the small hydrogen atom, the central carbon of the tetrahedral product formed from the aldehyde is less crowded and the product is more stable.

With ketones two alkyl groups at the carbonyl carbon causes greater steric crowding in the tetrahedral product and make it less stable. Therefore small concentration is present at equilibrium.

2. Electronic Factor : Because alkyl group are electron releasing therefore aldehydes are more reactive on electronic grounds as well. Aldehyde have one electron releasing alkyl group to stabilise the partial positive charge on the carbon atom of the carbonyl group. Whereas ketones have two alkyl groups.

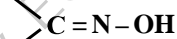


(a) Addition of cyanide :(b) Addition derivatives of ammonia :(ii) HCHO reacts with NH₃ differently forming UROTROPINE [hexamethylene tetraamine].H₂N-G

Product

H₂N-OH

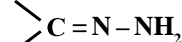
Hydroxylamine



oxime

H₂N-NH₂

Hydrazine



Hydrazone

H₂N-NHC₆H₅

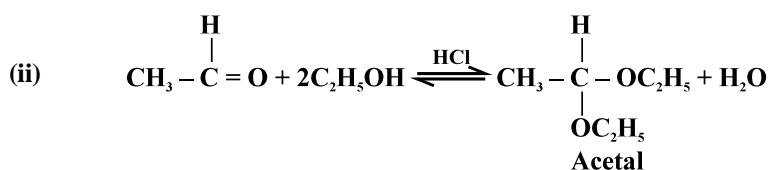
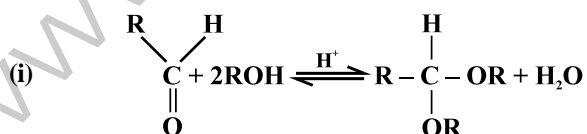
Phenylhydrazine

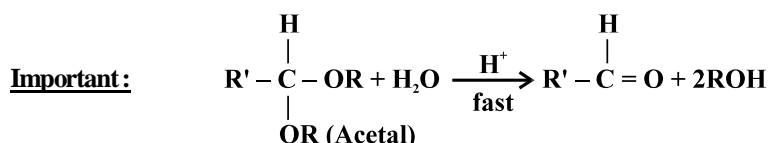
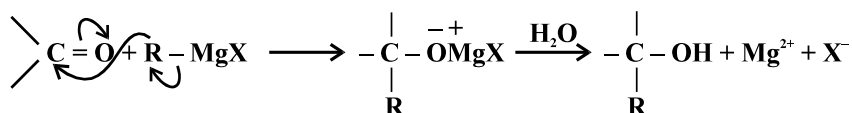


Phenylhydrazone

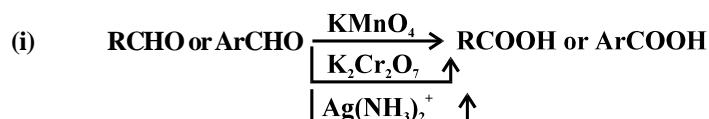
H₂N-NHCOCH₂ Semicarbazine

Semicarbazone

(c) Addition of Alcohols : Acetal Formation

(d) Addition of Grignard reagents:

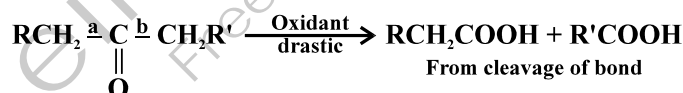
Formaldehyde with Grignard Reagent gives 1^o alcohol, all higher aldehydes with grignard reagent give 2^o alcohol and ketones with grignard reagent gives the 3^o alcohol.

C9 Other Reactions of Aldehyde and Ketones:(a) Oxidation:

Aldehydes (except) benzaldehyde reduce “Fehling’s Solution” (Cu²⁺ reduced to Cu⁺) which is an alkaline solution of Cu²⁺ ion complexed with tetrarate ion.

(ii) Example: Tollen’s Test:

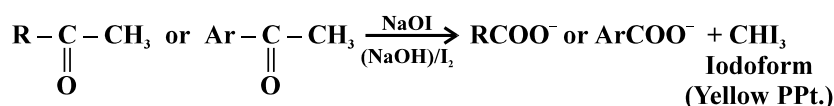
Tollen’s test is chiefly given by aldehydes. Tollen’s reagent does not attack carbon-carbon double bond. Aldehyde also reduce benedict’s solution (Cu²⁺ complexed with citrate ion) to Cu⁺

(b) (i) Ketones with strong oxidants and at high temperature undergo cleavage of C-C bond on either side of carbonyl group.

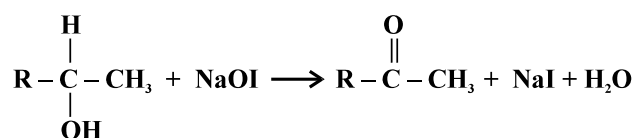
Carbonyl Group after bond cleavage goes with that alkyl group which is of smaller size.

(ii) Ketones are also oxidised from cleavage of bond by caro’s acid (H₂SO₅) or peroxybenzoic acid (C₆H₅CO₃H) to esters. RCOR' $\xrightarrow[\text{[O]}]{\text{H}_2\text{SO}_5}$ RCOOR' [Bayer’s

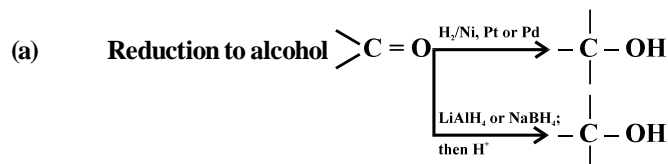
Villiger Oxidation]

(c) Haloform Test:(i) Methylketones:

- (ii) Hypohalite NaOX (NaOH + X₂) cannot only halogenate can also oxidise alcohols



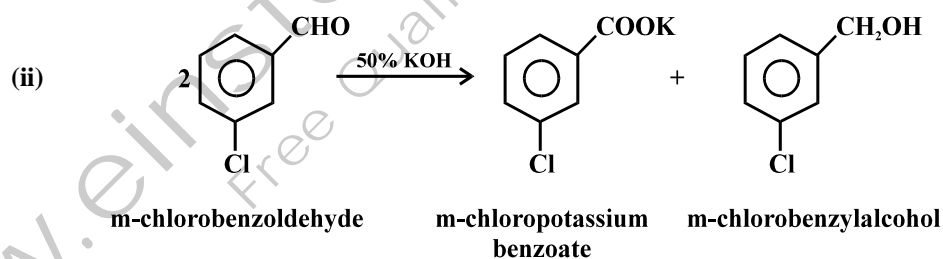
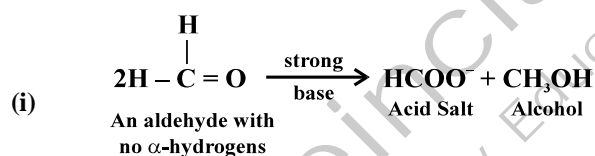
- (d) Reduction :



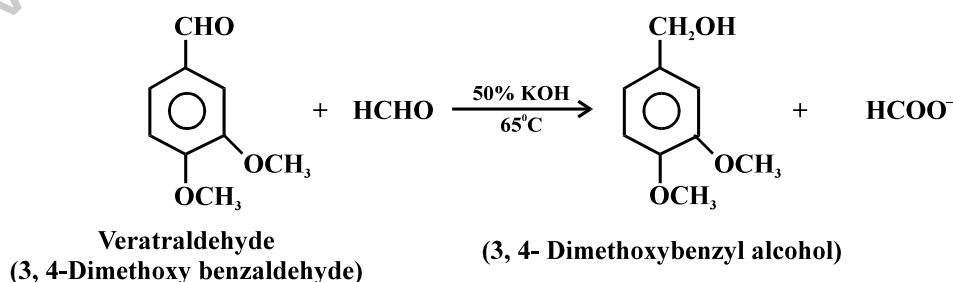
- (e) Reduction to hydrocarbons : $\begin{array}{c} > \text{C} = \text{O} \\ | \\ \text{O} \end{array} \xrightarrow[\text{HCl}]{\text{Zn(Hg)/conc.}} \begin{array}{c} | \\ -\text{C}-\text{H} \\ | \\ \text{H} \end{array}$ (Clemmenson's reduction)
- $\xrightarrow[\text{base}]{\text{NH}_2\text{NH}_2} \begin{array}{c} | \\ -\text{C}-\text{H} \\ | \\ \text{H} \end{array}$ (Wolff-kishner reduction)

- (f) Reductive Amination (Discussed under Amines)

- (g) Cannizzaro reaction : In the presence of an concentrated base i.e. alkali, aldehydes containing no α -hydrogens undergo self oxidation and reduction to yield a mixture of an alcohol.

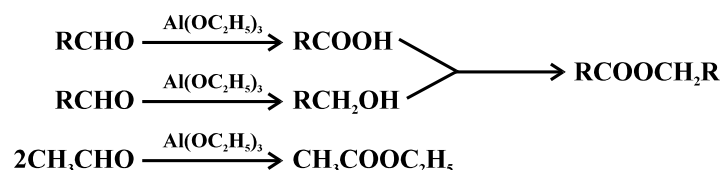


- (h) Crossed Cannizzaro reaction :



(i) Tischenko Reaction :

All aldehyde in presence of aluminium ethoxide, $\text{Al}(\text{OC}_2\text{H}_5)_3$ can be simultaneously oxidised (to acid) and reduced (to alcohols) to form ester. This is called Tischenko reaction and is thus like cannizaro reaction.

(j) DistinctionAldehyde and Ketones

<u>S.No.</u>	<u>Test</u>	<u>RCHO</u>	<u>RCOR</u>
1.	Schiff's reagent	magenta colour restored by RCHO	no. reaction
2.	Tollen's reagent	is reduced by RCHO	is not reduced
3.	Fehling's solution	is reduced by RCHO (except $\text{C}_6\text{H}_5\text{CHO}$)	is not reduced α -hydroxy, ketones reduce Tollen's reagent and Fehling's solution $\begin{array}{c} -\text{CH}-\text{CO}- \\ \\ \text{OH} \end{array}$

Practice Problems :

- Identify (Z) in the reaction series, $\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{HBr}} (\text{X}) \xrightarrow{\text{Hydrolysis}} (\text{Y}) \xrightarrow[\text{I}_2 (\text{excess})]{\text{NaOH}} (\text{Z})$
 - $\text{C}_2\text{H}_5\text{I}$
 - $\text{C}_2\text{H}_5\text{OH}$
 - CHI_3
 - CH_3CHO
- A compound (X) of the formula $\text{C}_3\text{H}_8\text{O}$ yields a compound $\text{C}_3\text{H}_6\text{O}$ on oxidation. To which of the following class of compounds could (X) belong
 - aldehyde
 - secondary alcohol
 - alkene
 - tert. alcohol
- Which statement is incorrect in the case of acetaldehyde and acetone
 - both react with hydroxylamine
 - both react with NaHSO_3
 - both react with hydrazine
 - both reduce ammoniacal silver nitrate
- Which of the following undergoes Cannizzaro's reaction
 - CH_3CHO
 - $\text{CH}_3\text{CH}_2\text{CHO}$
 - $(\text{CH}_3)_2\text{CHCHO}$
 - HCHO
- Urotropine is formed by the action of ammonia on
 - acetaldehyde
 - formaldehyde
 - acetone
 - phenol
- Hydrocarbons are formed when aldehydes and ketones are reacted with amalgamated zinc and conc. HCl. The reaction is called
 - Cannizzaro's reaction
 - Clemmensen's reduction
 - Rosenmund's reaction
 - Tischenko reaction

7. When acetaldehyde is treated with aluminium ethoxide, it forms
- (a) ethyl acetate (b) ethyl alcohol
(c) acetic acid (d) methyl propionate
8. Chloroform is formed when chloroform reacts with
- (a) formaldehyde (b) acetaldehyde (c) acetone (d) benzaldehyde
9. Which of the following reagent reacts differently with HCHO, CH₃CHO and CH₃COCH₃
- (a) HCN (b) NH₂OH (c) C₆H₅NHNH₂ (d) NH₃
10. In the following sequence of reactions, the end product is
- $$\text{CaC}_2 \xrightarrow{\text{H}_2\text{O}} (\text{A}) \xrightarrow{\text{Hg}^{2+}/\text{H}_2\text{SO}_4} (\text{B}) \xrightarrow{[\text{O}]} (\text{C}) \xrightarrow{\text{Ca}(\text{OH})_2} (\text{D}) \xrightarrow{\text{heat}} (\text{E})$$
- (a) acetaldehyde (b) formaldehyde (c) acetic acid (d) acetone
11. In the following sequence of reactions, the end product is
- $$\text{HC} \equiv \text{CH} \xrightarrow{\text{Hg}^{2+}/\text{H}_2\text{SO}_4} (\text{A}) \xrightarrow[\text{[H}_2\text{O]}]{\text{CH}_3\text{MgX}} (\text{B}) \xrightarrow{[\text{O}]} (\text{C})$$
- (a) acetaldehyde (b) isopropyl alcohol
(c) acetone (d) ethyl alcohol
12. In the following sequence of reactions, the end product is CH₃CHO $\xrightarrow{\text{HCN}}$ (A) $\xrightarrow{\text{H}_2\text{O}}$ (B)
- (a) CH₃COOH (b) CH₃CHOHCOOH
(c) CH₃CH₂NH₂ (d) CH₃CONH₂
13. A compound, C₅H₁₀O, forms a phenyl hydrazone and gives negative Tollen's and iodoform tests. The compound on reduction gives n-pentane. The compound A is
- (a) pentanal (b) pentanone-2 (c) pentanone-3 (d) amyl alcohol
14. The product Z in the series is
- $$\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{HBr}} \text{X} \xrightarrow{\text{Hydrolysis}} \text{Y} \xrightarrow[\text{I}_2(\text{excess})]{\text{Na}_2\text{CO}_3} \text{Z}$$
- (a) C₂H₅I (b) C₂H₅OH (c) CHI₃ (d) CH₃CHO
15. If formaldehyde and KOH are treated together, we get
- (a) methane (b) methanol (c) ethyl acetate (d) acetylene
16. The correct order of reactivity in nucleophilic addition reaction CH₃CHO, CH₃COC₂H₅ and CH₃COCH₃ is
- (a) CH₃CHO > CH₃COCH₃ > CH₃COC₂H₅
(b) C₂H₅COCH₃ > CH₃COCH₃ > CH₃CHO
(c) CH₃COCH₃ > CH₃CHO > C₂H₅COCH₃
(d) CH₃COCH₃ > C₂H₅COCH₃ > CH₃CHO
17. To distinguish between 2-pentanone and 3-pentanone which reagent can be used
- (a) NaOH/I₂ (b) Tollen's reagent
(c) K₂Cr₂O₇/H⁺ (d) Zn-Hg, HCl
18. CH₃CH = CHCHO is oxidised to CH₃-CH = CHCOOH, using oxidising agent as
- (a) alkaline KMnO₄ (b) K₂Cr₂O₇/conc. H₂SO₄
(c) ammonical AgNO₃ (d) dilute HNO₃
19. m-chloro benzaldehyde on reaction with conc. KOH at room temperature gives
- (a) potassium m-chloro benzoate and m-hydroxy benzaldehyde
(b) m-chloro benzyl alcohol and m-hydroxy benzaldehyde
(c) m-chloro benzyl alcohol and m-hydroxy benzyl alcohol
(d) m-chloro benzyl alcohol and potassium m-chloro benzoate

20. The reagent which can be used to distinguish acetophenone from benzophenone is :

- (a) 2, 4-dinitrophenyl hydrazine (b) benedict reagent
 (c) I_2 and Na_2CO_3 (d) aqueous solution of $NaHSO_3$

21. Best starting material to synthesize 2-methyl-2-butenic acid is

- (a) $\begin{array}{c} CH_3 \\ | \\ CH_3 - C - CH_3 \\ | \\ OH \end{array}$ (b) $CH_3CH_2CH_2CHO$
 (c) $\begin{array}{c} CH_3 \\ | \\ CH_3 - CH - CHO \\ | \\ CH_3 \end{array}$ (d) $CH_3CH_2 - \overset{O}{\parallel} C - CH_3$

22. 1-pentyne $\xrightarrow{HgSO_4/H_2SO_4}$ X
 $\xrightarrow{BH_3 \cdot THF/H_2O_2, OH^-}$ Y
 X and Y can be distinguished by :

(a) silver-mirror test (b) iodoform test (c) both (d) none

23. Which of the following will give haloform test

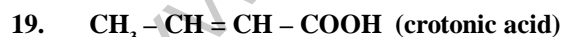
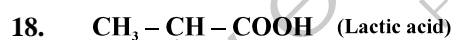
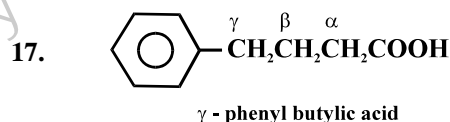
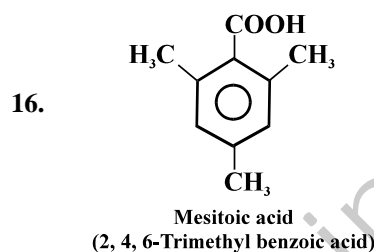
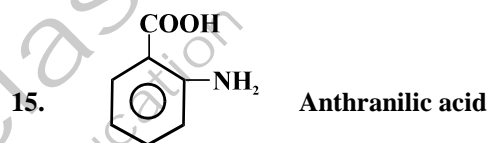
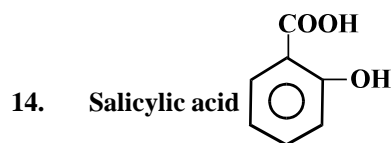
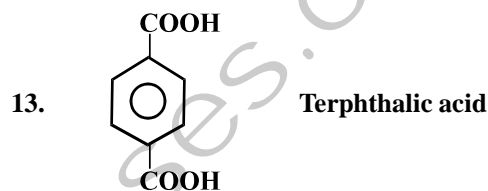
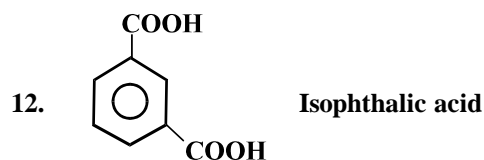
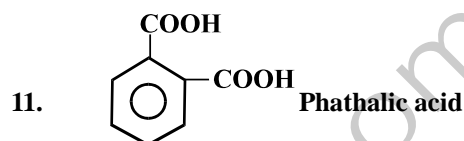
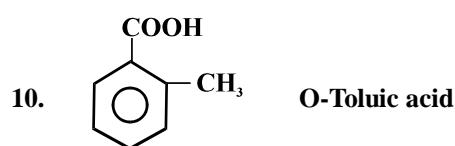
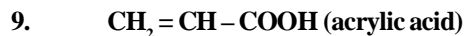
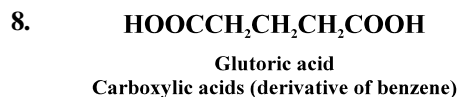
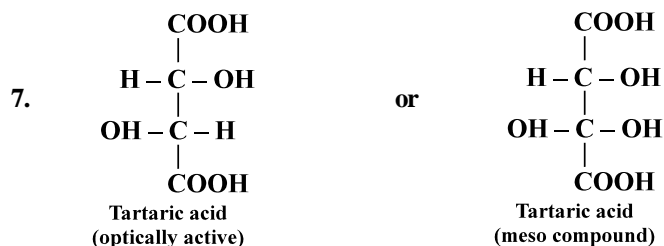
- (a) $CH_3 - \overset{O}{\parallel} C - CCl_3$ (b) $CH_3 - \overset{OH}{\underset{|}{C}} - CH_2I$
 (c) $CH_3 - \overset{O}{\parallel} C - CH_2Cl$ (d) all

[Answers : (1) c (2) b (3) d (4) d (5) b (6) b (7) a (8) c (9) d (10) d (11) c (12) b (13) c (14) c (15) b (16) a (17) a (18) a (19) d (20) c (21) c (22) c (23) d]

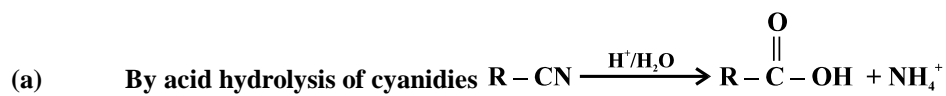
Carboxylic Acids and Derivatives

C10 Common name of carboxylic acids :

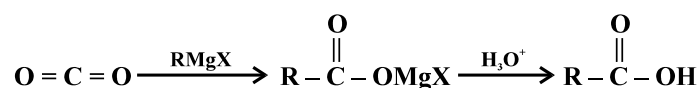
1. $CH_3CH_2CH_2CH_2COOH$ valeric acid
2. $\begin{array}{c} COOH \\ | \\ COOH \end{array}$ oxalic acid
3. $\begin{array}{c} COOH \\ / \\ CH_2 \\ \backslash \\ COOH \end{array}$ Malonic acid; $\begin{array}{c} CH_3 - CH - COOH \\ | \\ COOH \end{array}$ Methyl malonic acid
4. $\begin{array}{c} CH_2 - COOH \\ | \\ CH_2 - COOH \end{array}$ Succinic acid
5. $\begin{array}{c} CHCOOH \\ || \\ CHCOOH \end{array}$ malic acid ; $\begin{array}{c} CH - COOH \\ || \\ HOOC - CH \end{array}$ Fumaric acid
6. $\begin{array}{c} CH_2 - CH_2 - COOH \\ | \\ CH_2 - CH_2 - COOH \end{array}$ adipic acid



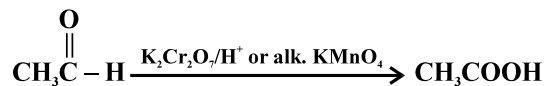
C11 Methods of preparation of carboxylic acid :



(b) By the use of Grignard Reagent

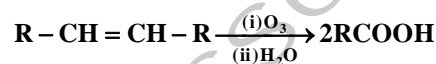
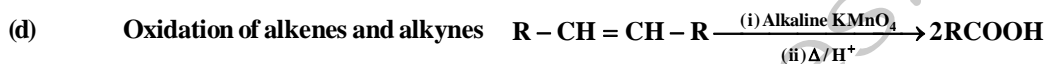
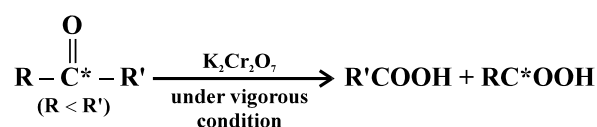
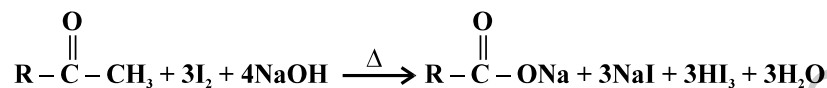


(c) By oxidation method



(iii) Oxidation of ketones

Iodoform Test :

**Practice Problems :**

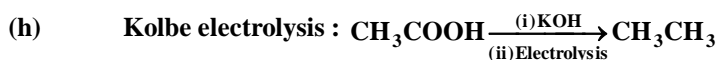
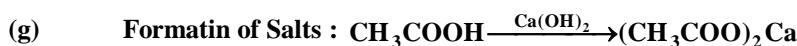
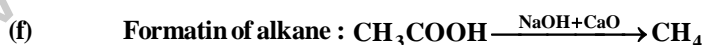
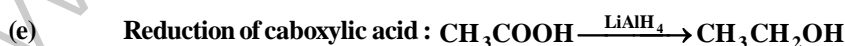
1. Cyanohydrin of which of the following gives lactic acid on hydrolysis

- (a) acetone (b) acetaldehyde (c) propanal (d) HCHO

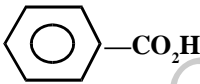
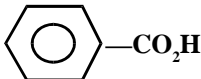
[Answers : (1) b]

C12 Chemical Properties of Carboxylic Acids :

(a) Carboxylic acid undergo nucleophilic substitution reaction



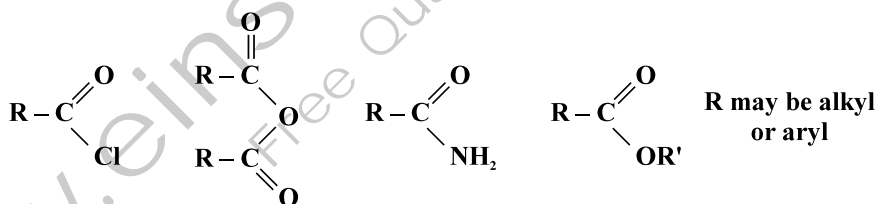
Practice Problems :

- Which of the following will not undergo HVZ reaction
 - 2, 2-dimethyl propanoic acid
 - propanoic acid
 - acetic acid
 - 2-methyl propanoic acid
- Amongst the acids (a) $\text{CH}\equiv\text{CCOOH}$ (b) $\text{CH}_2=\text{CHCOOH}$ and (c) $\text{CH}_3\text{CH}_2\text{COOH}$, the acid strength follows the sequence
 - (a) > (b) > (c)
 - (a) < (b) < (c)
 - (a) = (b) = (c)
 - (a) = (b) < (c)
- $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{P}]{\text{Cl}_2} (\text{A}) \xrightarrow{\text{Alc.KOH}} (\text{B})$ The compound (B) is
 - $\text{CH}_3\text{CH}_2\text{OH}$
 - $\text{CH}_3\text{CH}_2\text{CN}$
 - $\text{CH}_2=\text{CHCOOH}$
 - $\text{CH}_3\text{CHClCOOH}$
- Formic acid
 - is immiscible with water
 - reduces ammonical silver nitrate
 - is a weak acid nearly three and a half times weaker than acetic acid
 - is prepared by heating potassium formate
- Strongest acid out of $\text{CH}_3\text{CO}_2\text{H}$, $\text{CH}_2=\text{CHCO}_2\text{H}$, -CO₂H
 - $\text{CH}_3\text{CO}_2\text{H}$
 - $\text{CH}_2=\text{CHCO}_2\text{H}$
 - -CO₂H
 - equal K_a

[Answers : (1) a (2) a (3) c (4) b (5) c]

CARBOXYLIC ACID DERIVATIVES

- C13A Structures :** Closely related to the carboxylic acids and to each other are a number of chemical families known as functional derivative of carboxylic acids : Acid chlorides, anhydrides, amides and esters. Acid chlorides, anhydrides, amides and esters. These derivatives are compounds in which the -OH of a carboxylic group has been replaced by -Cl, -OOCR, -NH₂ or -OR'

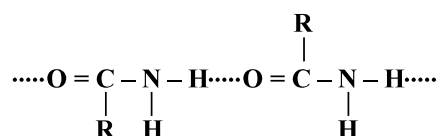


They all contain acyl group $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-$

- C13B Physical properties :** The presence of $-\overset{\text{O}}{\parallel}{\text{C}}-$ group makes the acid derivatives polar compounds.

Acid chlorides and anhydrides and esters have boiling point is same as of aldehydes and ketones of corresponding molecular weight.

Amides have quite high boiling points because they are capable of strong intermolecular hydrogen bonding.



The borderline for solubility in water ranges from three to five carbons for the esters to five to six carbons for the amides. The acid derivatives are soluble in usual organic solvents.

Volatile esters have pleasant, rather characteristic odours; they are often used in the preparation of perfumes and artificial flavoring.

Acid chlorides have sharp, irritating odours, at least partly due to their ready hydrolysis to HCl and carboxylic acids

C14A Nucleophilic acyl substitution :

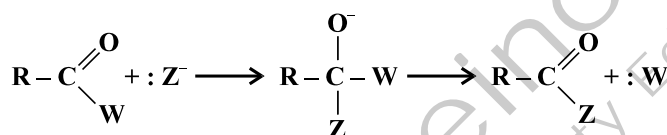
Each derivative is nearly always prepared - directly or indirectly from carboxylic acids, and can be readily converted into the carboxylic acid by simple hydrolysis.

The derivatives of carboxylic acids, like the acids themselves, contain the carbonyl group, $\overset{\text{O}}{\parallel} \text{C} -$.

Here, too, as in aldehydes and ketones, the carbonyl group performs two functions :

- It provides a site for nucleophilic attack
- It increases the acidity of hydrogens attached to the alpha carbon.

Acyl compounds i.e. Carboxylic acids and their derivatives, typically undergo nucleophilic substitution in which $-\text{OH}$, $-\text{Cl}$, $-\text{OOCR}$, or $-\text{OR}$ is replaced by some other basic group. Substitution takes place much more readily than at a saturated carbon atom; many of these substitution do not take at all in the absence of carbonyl group e.g. replacement of $-\text{NH}_2$ by $-\text{OH}$.



$-\text{W} = -\text{OH}, -\text{Cl}, -\text{OOCR}, -\text{NH}_2, -\text{OR}'$

Let us discuss now properties of acyl compounds.

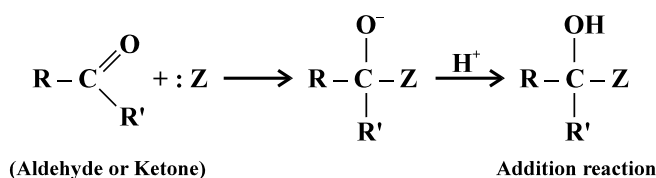
Both electronic and steric factors make the carbonyl carbon susceptible to nucleophilic attack.

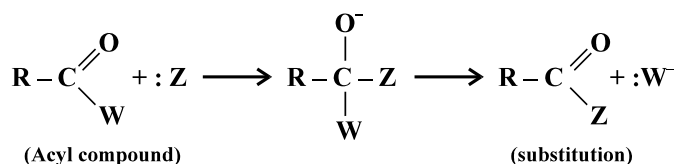
- The tendency of oxygen to acquire the negative charge.
- The relatively unhindered transition state leading from the trigonal reactant to the tetrahedral intermediate. These factors make acyl compounds, too susceptible to nucleophilic attack.

It is the second step of reaction that acyl compounds differ from aldehydes and ketones.

The tetrahedral intermediate from an aldehyde/ketone compound gains a proton and the result is addition.

The tetrahedral intermediate from an acyl compound ejects the $:\text{W}$ group, returning to a trigonal compound and thus result in substitution.

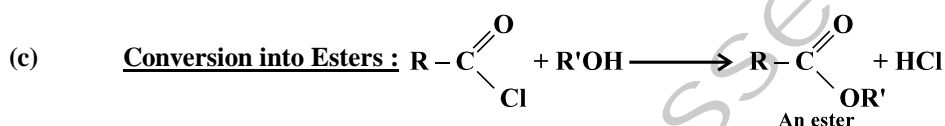
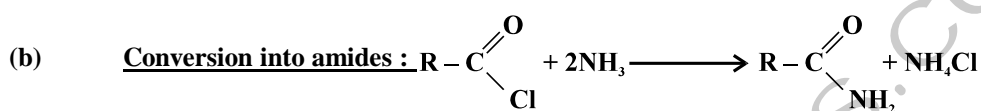
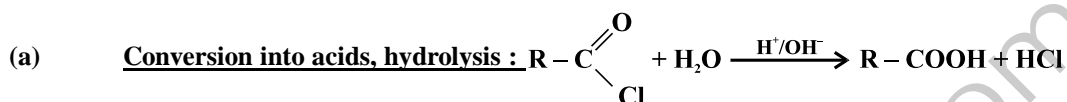




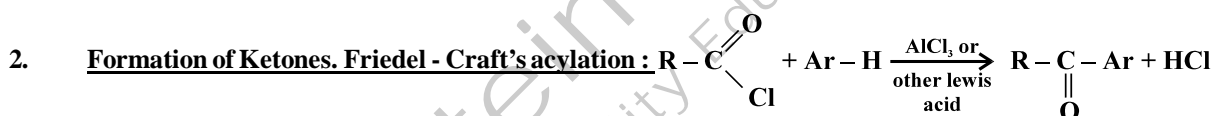
C15A Acid Chlorides : Acid chlorides are prepared from the corresponding acids by reaction with SOCl_2 , PCl_5 or PCl_3 as already discussed.

C15B Reactions : Acid chlorides are the most reactive of the derivatives of carboxylic acids.

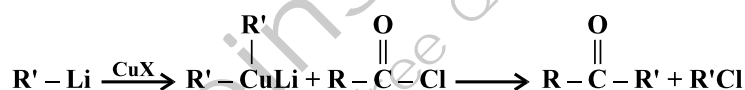
1. Like other derivatives it also undergo nucleophilic substitution reaction. Chlorine is expelled as chloride and its place is taken by some other basic group.



Acid chloride is added in portions to a mixture of the hydroxy compound and a base usually aq. NaOH or pyridine. Base serves not only to neutralize the HCl evolved but also to catalyze the reaction.



3. Formation of ketones, Reaction with organo copper compounds :



4. Formation of aldehydes by reduction : RCOCl or $\text{ArCOCl} \xrightarrow{\text{LiAlH}(\text{OBU}-\text{t})_3} \text{RCHO}$ or ArCHO

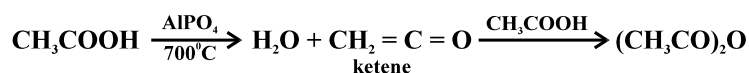
1. Sodium acetate + acetyl chloride gives

- | | |
|------------------------------|--------------------|
| (a) CH_3COOH | (b) sodium formate |
| (c) acetic anhydride | (d) acetone |

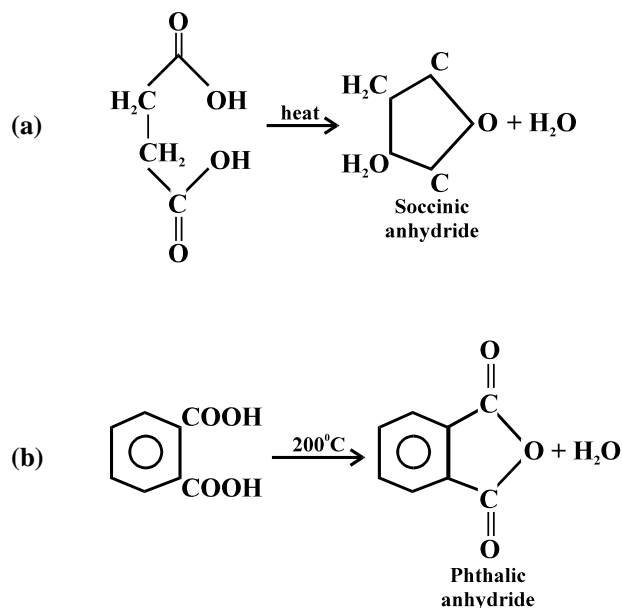
C16A Acid Anhydrides

Preparation :

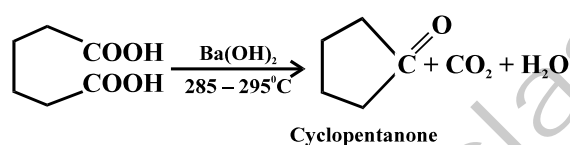
(i) Acetic anhydride is prepared by the reaction of acetic acid with ketene $\text{CH}_2 = \text{C} = \text{O}$, which itself is prepared by high temperature dehydration of acetic acid.



(ii) In contrast to monocarboxylic acids, certain dicarboxylic acids yield anhydrides on simple heating. In those cases where five or six membered ring is produced.

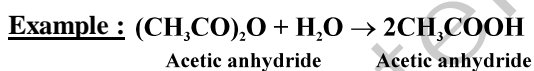


Ring size is crucial : with adipic acid, e.g. anhydride formation would produce seven-membered ring and does not take place. Instead carbon dioxide is lost and cyclopentanone is produced (a five membered ring is formed) :

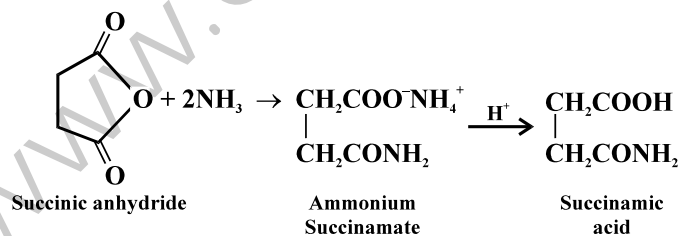
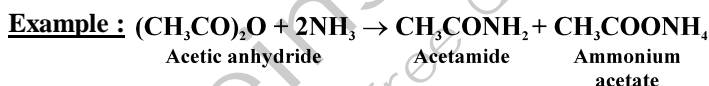


C16B Reactions of Acid Anhydrides :

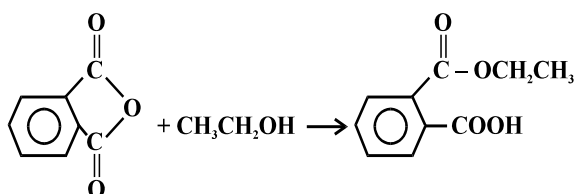
(i) Conversion into acids. Hydrolysis :

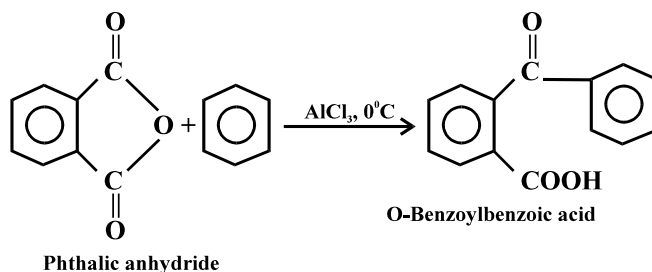
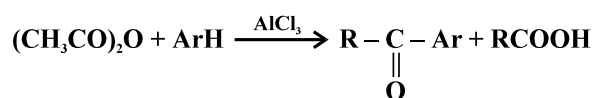


(ii) Conversion into amides. Ammonolysis :



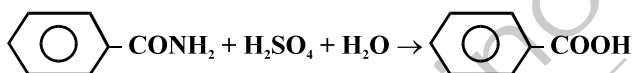
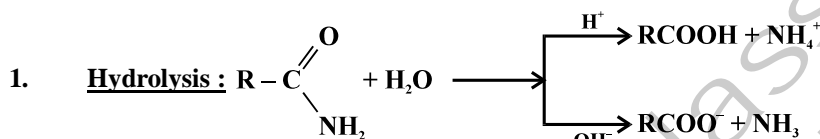
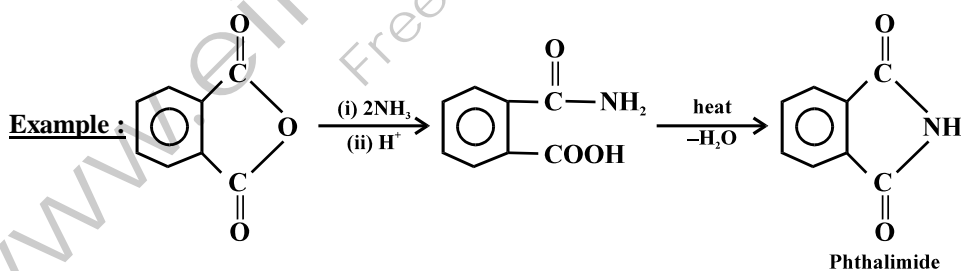
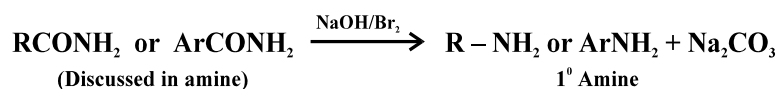
(iii) Conversion into esters : $(\text{CH}_3\text{CO})_2\text{O} + \text{CH}_3\text{OH} \longrightarrow \text{CH}_3\text{COOCH}_3 + \text{CH}_3\text{COOH}$



(iv) Formation of Ketone : Friedel craft acylationAmides

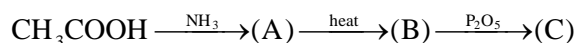
C17A Preparation : In the laboratory method of preparation of amide includes its preparation from acid chloride with ammonia, acid anhydride with ammonia.

In industry they are prepared by heating ammonium salts of carboxylic acids.

C17B Reaction of Amides :3. Conversion into imides :4. Hoffmann degradation of amides :

Practice Problems :

1. The end product in the following series of reaction is

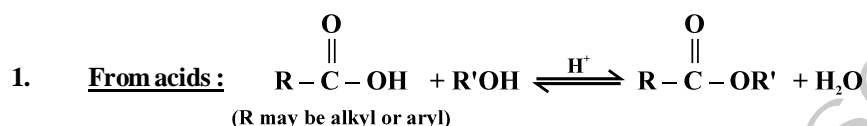
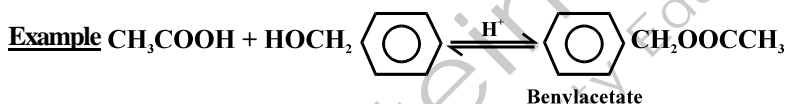


- (a) CH_4 (b) CH_3OH
 (c) acetonitrile (d) ammonium acetate

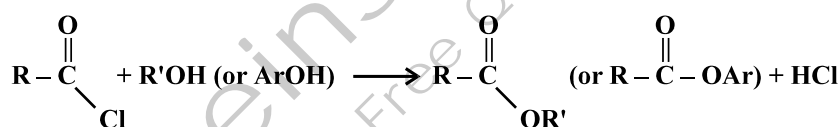
2. In a reaction,
- $(\text{A}) \xrightarrow{\text{NH}_3} (\text{B}) \xrightarrow{\text{heat}} (\text{C}) \xrightarrow{\text{P}_2\text{O}_5} \text{C}_2\text{H}_5\text{CN}$
- (A), (B) and (C) are :

- (a) CH_3COOH , $\text{CH}_3\text{COONH}_4$ and CH_3CONH_2
 (b) CH_3COCl , CH_3CONH_2 and $\text{CH}_3\text{COONH}_4$
 (c) $\text{C}_2\text{H}_5\text{COOH}$, $\text{C}_2\text{H}_5\text{COONH}_4$ and $\text{C}_2\text{H}_5\text{CONH}_2$
 (d) $\text{C}_2\text{H}_5\text{COONH}_4$, $\text{C}_2\text{H}_5\text{CONH}_2$ and $\text{C}_2\text{H}_5\text{COOH}$

[Answers : (1) c (2) c]

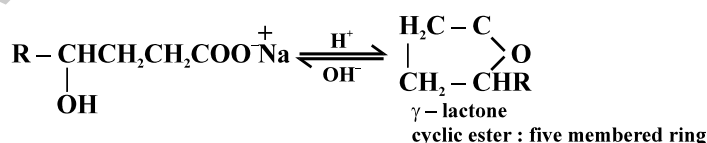
Esters :**C18A Preparation of Esters :**Reactivity of $\text{R}'\text{OH}$ is $1^\circ > 2^\circ > 3^\circ$ 

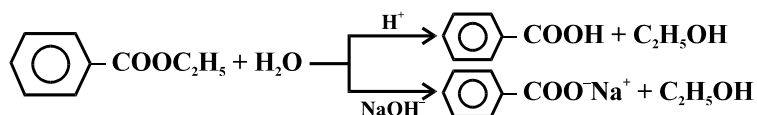
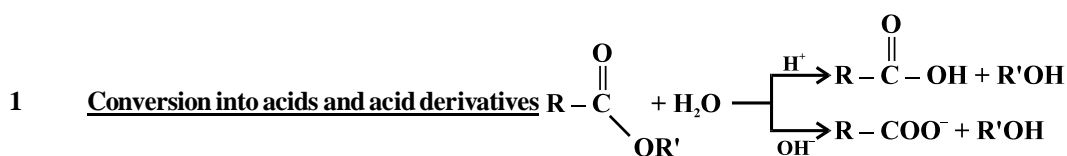
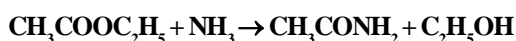
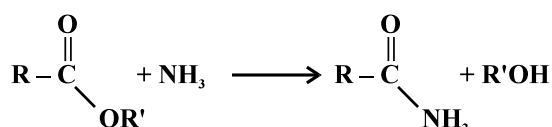
- 2.
- From Acid Chloride or anhydride :**



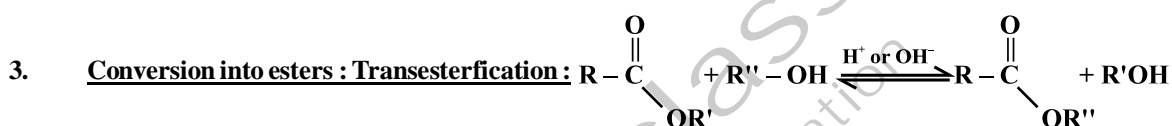
- 3.
- Formation of cyclic esters (Lactone)**

A hydroxy acid is both alcohol and acid. In those cases where five or six membered ring can form intermolecular esterification occurs. Thus γ or δ hydroxy acid loses water spontaneously by yield of cyclic ester known as lactone. Treatment with base (OH^-) rapidly opens the lactone ring.



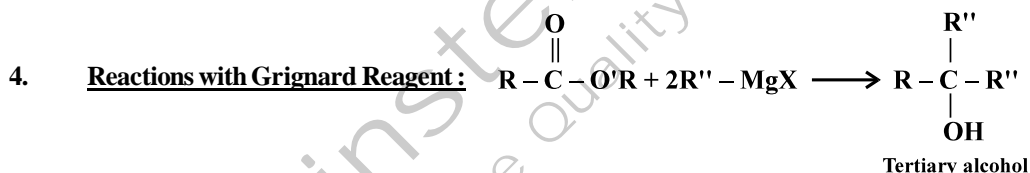
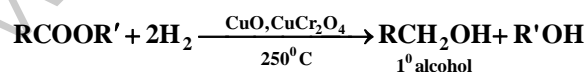
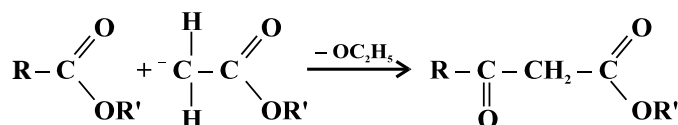
C18B Reactions of Esters :2. Conversion into amides

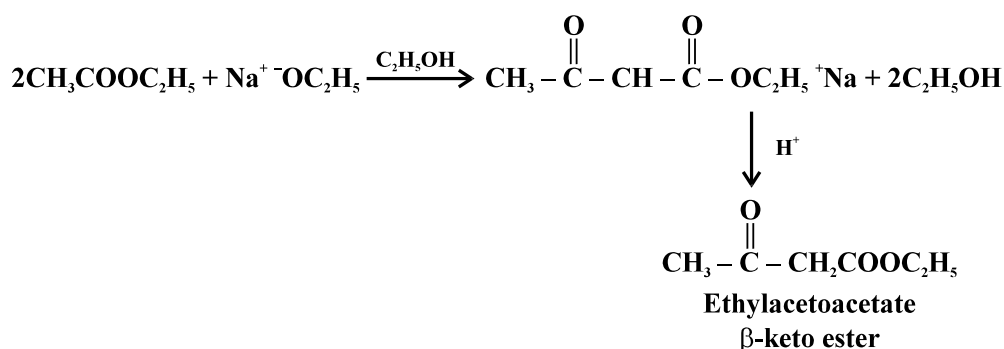
Treatment of an ester with ammonia, generally in ethylalcohol solution yield the amides. This reaction involved the nucleophilic attack by a base, ammonia, on the electron-deficient carbon; the alkoxy group, $-\text{OR}'$ is replaced by $-\text{NH}_2$.



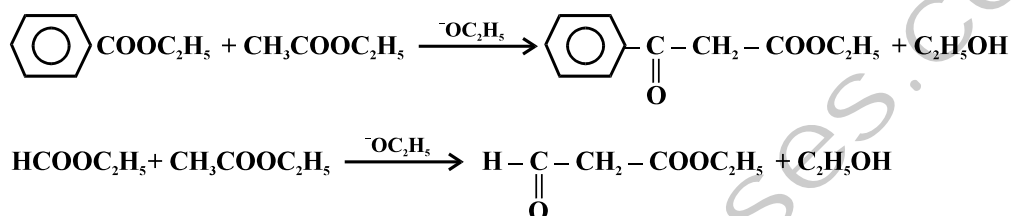
Acid is $\rightarrow \text{H}_2\text{SO}_4$ or dry HCl

Base \rightarrow alkoxide ion generally used.

5. Reduction to alcohols :(a) Catalytic hydrogenation : Hydrogenolysis(b) Chemical Reduction : $\text{R}-\text{COOR}' + \text{LiAlH}_4 \xrightarrow{\text{Anhyd. ether}} \text{RCH}_2\text{OH} + \text{R}'\text{OH}$ 6. Reaction with carbanions : Clasién Condensation :

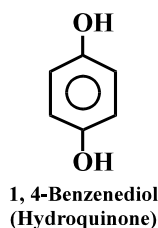
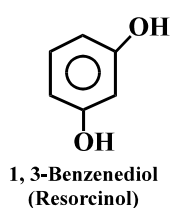
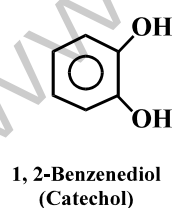
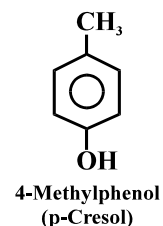
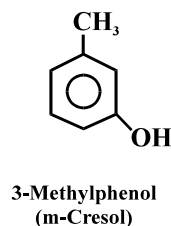
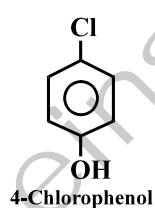
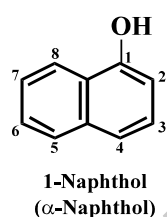
Example :**7. Crossed Claisen Condensation :**

Like a crossed aldol condensation, a crossed claisen condensation is also possible only when one of the reactants has no α-hydrogens and thus is incapable of undergoing self condensation.

**PHENOLS****C19A Structure and Nomenclature of Phenols :**

Compounds that have a hydroxyl group directly attached to benzene ring are called phenols. Thus phenol is specific name of hydroxy benzene

Compounds that have a hydroxyl group attached to a polycyclic benenoid ring are chemically similar to phenols, but they are called naphthols and phenanthrols, e.g.

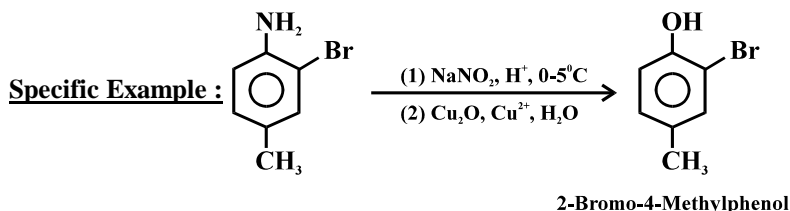
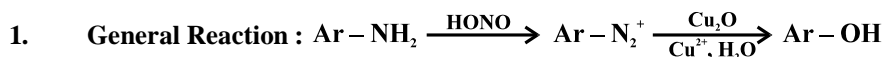
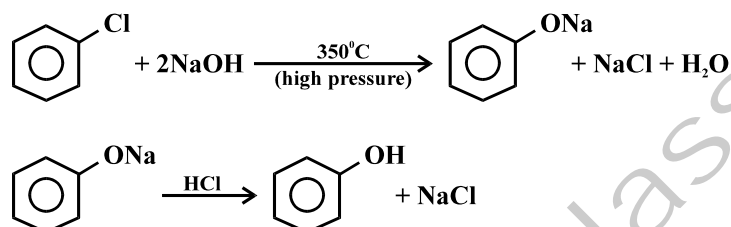
**C19B Physical Properties of Phenols :** The presence of hydroxy groups in the molecules of phenols means that phenols are like alcohols in being able to form strong intermolecular hydrogen bonds.

This hydrogen bonding causes phenols to be associated and therefore to have higher boiling points than hydrocarbons of the same molecular weight.

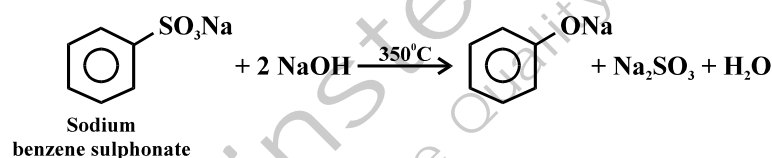
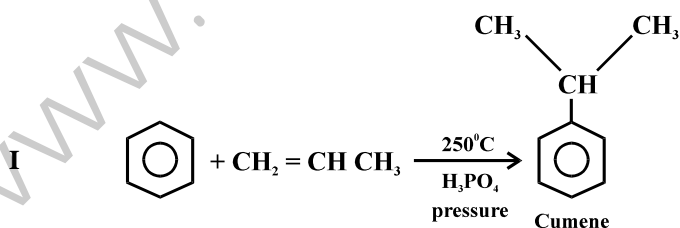
C20A Synthesis of Phenols :

Laboratory Synthesis : The most important laboratory synthesis of phenols is by hydrolysis of arenediazonium salts.

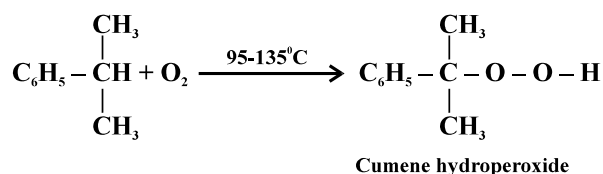
This method is highly versatile and the conditions required for the diazotisation step and the hydrolysis step are mild.

**Industrial Synthesis :**2. **Hydrolysis of Chlorobenzene (Dow Process) :**

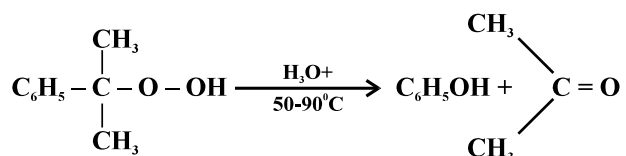
(The mechanism for the reaction probably involves benzyne intermediate)

3. **Alkali Fusion of Sodium benzene sulfonate :** Sodium benzene sulfonate is melted (fused) with sodium hydroxide at 350°C to produce sodium phenoxide acidification then yields phenol.4. **From Cumene Hydroperoxide :**

II This cumene is oxidized to cumene hydroperoxide



Finally, when treated with 10% sulfuric acid, cumene hydroperoxide undergoes a hydrolytic rearrangement that yields phenol and acetone.

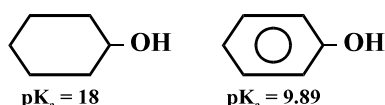


C20B Chemical Properties of Phenol :

1. Reaction of Phenol as Acid : Strength of phenols as acids :

Although phenols are structurally similar to alcohols, they are much stronger acids. The pK_a values of most alcohols are of the order of 18. However the pK_a values of phenols are smaller than 11.

Let us compare two superficially similar compounds cyclohexanol and phenol.



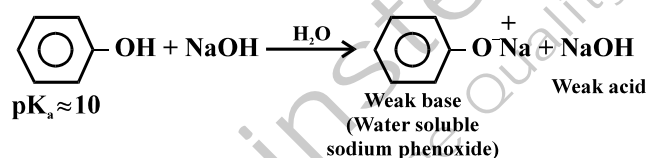
Although phenol is weak acid when compared with carboxylic acid such as acetic acid (pK_a = 4.75) phenol is much stronger than cyclohexanol by a factor of 8.

Phenols are more acidic than cyclohexanol because of following reasons :

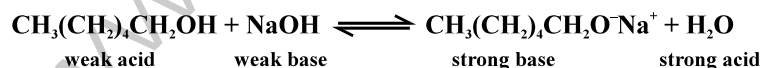
Phenoxide ion is more resonance stabilized than phenol. Resonance structures of phenoxide ion do not involve charge separation. No resonance structure can be written for cyclohexanol and its anion of course. The benzene ring of phenol acts as if it were as electron withdrawing group when we compare it with cyclohexanol. That causes -OH oxygen to be more positive.

Reason : Carbon atom that bears hydroxyl group in phenol is sp² hybridized, whereas in cyclohexanol sp³ hybridised. Greater the s-character more electronegative the carbon. Thus carbon of benzene is more electronegative than cyclohexanol.

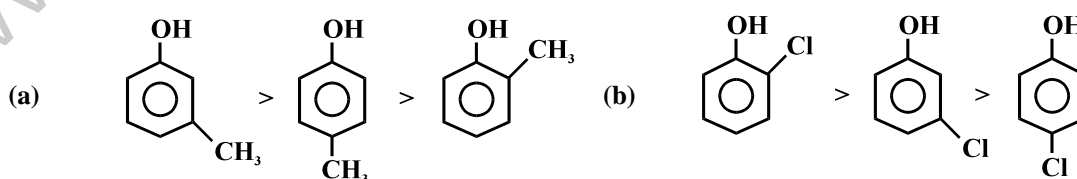
Because phenols are more acidic than water, the following reaction goes almost completion.

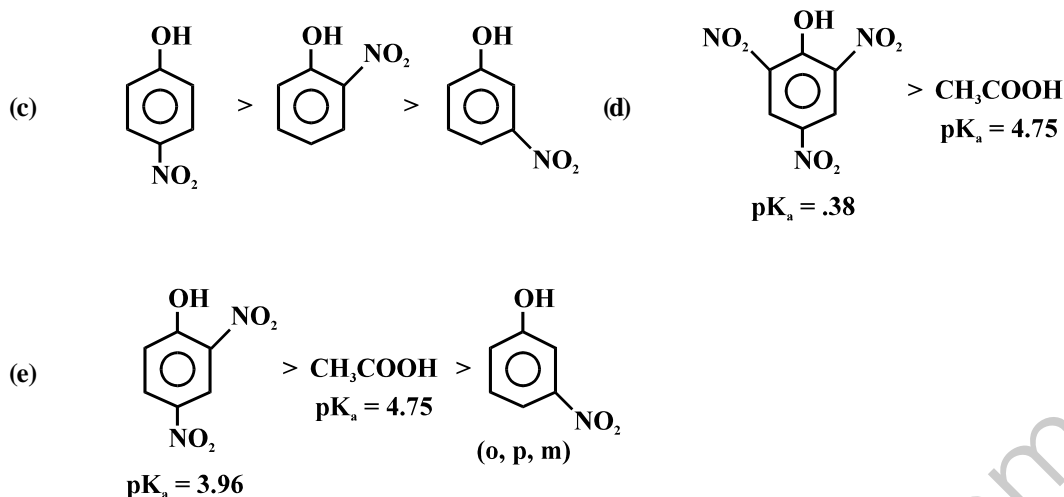


The reaction between cyclohexanol and NaOH does not occur to significant extent as H₂O is stronger acid than 1-cyclohexanol.



Acidity order of Phenols :





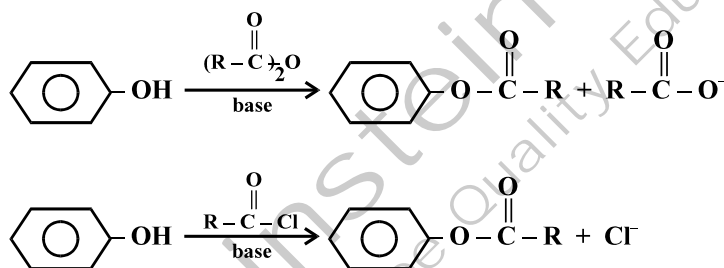
Distinguishing and separating phenols from alcohols and carboxylic acids :

1. Phenols dissolve in aqueous sodium hydroxide whereas most alcohols with six carbon atoms or more do not. Thus we can distinguish them.
2. Alcohols with five carbon atoms are more or less soluble in NaOH but do not form appreciable amount of sodium alkoxide.
3. Most phenols are not soluble in aqueous sodium bicarbonate, but carboxylic acids are soluble.

C21 Other reactions of the O – H Group of Phenols :

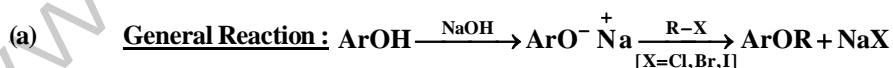
1. Phenols react with carboxylic acid anhydrides and acid chlorides to form esters.

These reactions are similar to alcoholic as we have already discussed in alcohols.

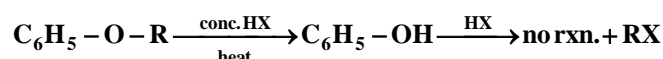


2. **Phenols in the Williamson Synthesis :**

Because phenols are more acidic than alcohols they can be converted to sodium phenoxide through the use of sodium hydroxide (rather than use of sodium metal, the reagent that convert alcohols to alkoxide ion).

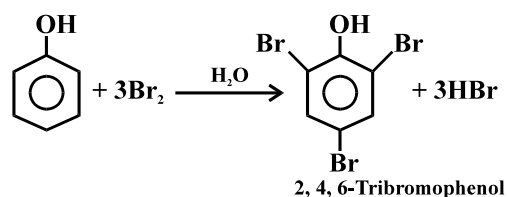


- (b) **Cleavage of Alkyl-Aryl Ether :**

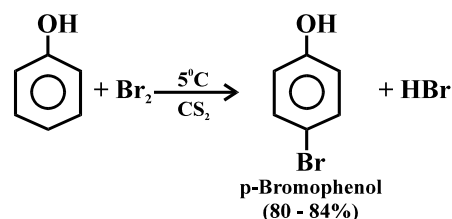


3. **Reactions of the Benzene ring of Phenol :**

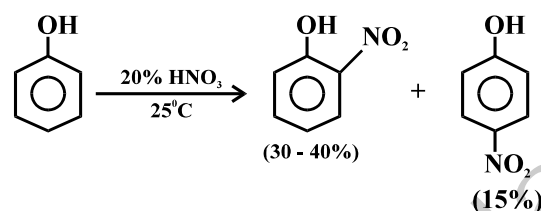
- (a) **Bromination :** The hydroxyl group is a powerful activating group and an ortho-para director in electrophilic substitution. Phenol itself react with Br_2 in aqueous solution to yield 2, 4, 6-tribromophenol. Note that a Lewis acid is not required for the bromination of this highly activated ring.



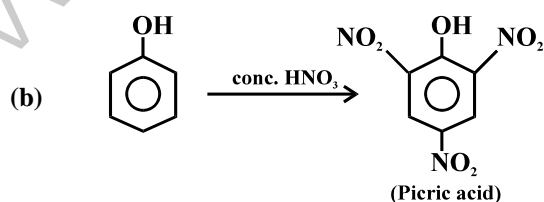
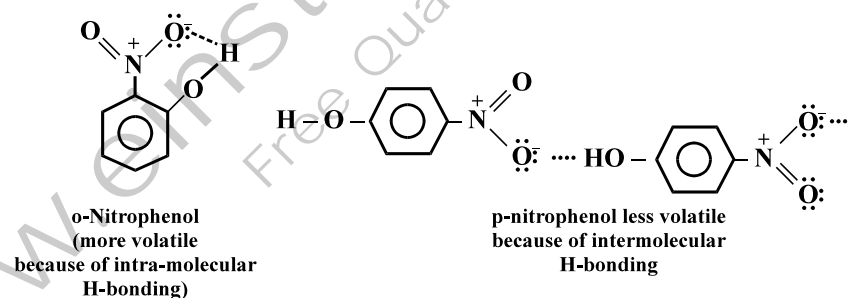
- (b) Monobromination of phenol can be achieved by carrying out the reaction in carbon disulfide (CS_2) at low temperature. Conditions that reduce the electrophilic activity of bromine. The major product is the para isomer.



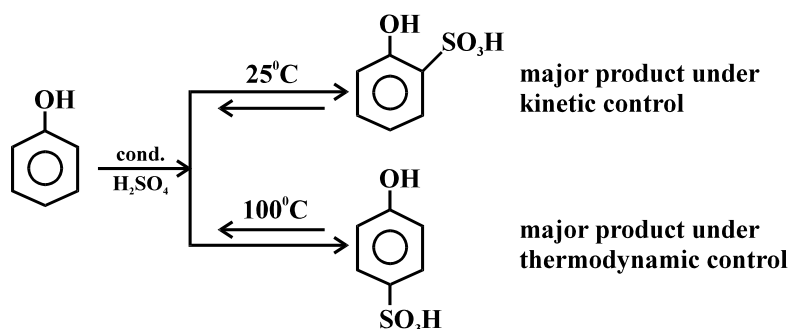
4. (a) **Nitration** : Phenol react with dilute nitric acid to yield a mixture o- and p-nitrophenol



Although the yield is relatively low (because of oxidation of ring). The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is more volatile isomer because its intramolecular hydrogen bonding. p-Nitrophenol is less volatile because intermolecular H-bonding causing association among molecules. Thus o-nitrophenol passes over steam and p-Nitrophenol remain in the distillation flask.



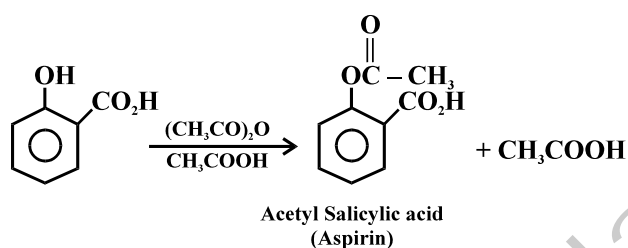
5. **Sulfonation** : Phenol reacts with concentrated sulfuric acid to yield mainly o-sulphonated product if the reaction is carried out at 25°C and mainly the para substituted product if the reaction is at 100°C .



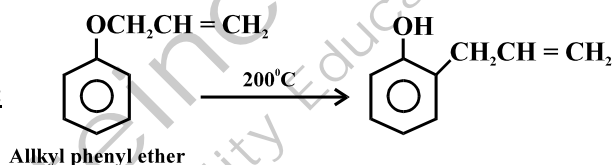
6. **Kolbe's Reaction** : The phenoxide ion is even more susceptible to electrophilic aromatic substitution, than phenol itself.

High reactivity of phenoxide ion is used in a reaction called as kolbe reaction. In kolbe reaction carbon dioxide act as the electrophile.

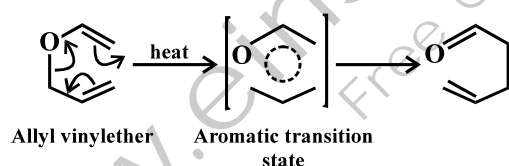
Reaction of salicylic acid with acetic anhydride yields widely used pain reliver aspirin.



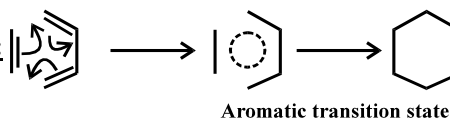
7. **The Claisen rearrangement** :



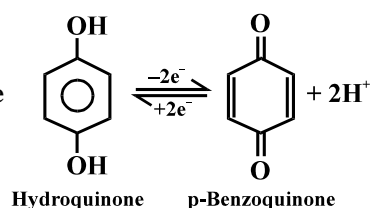
Claisen rearrangement can also take place when allyl vinyl ether are present



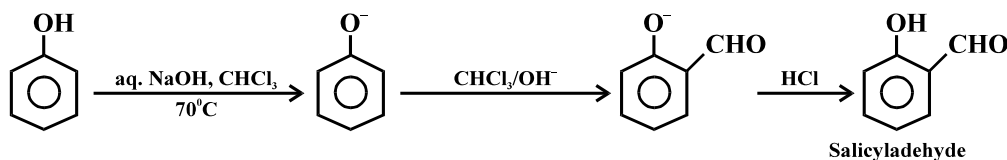
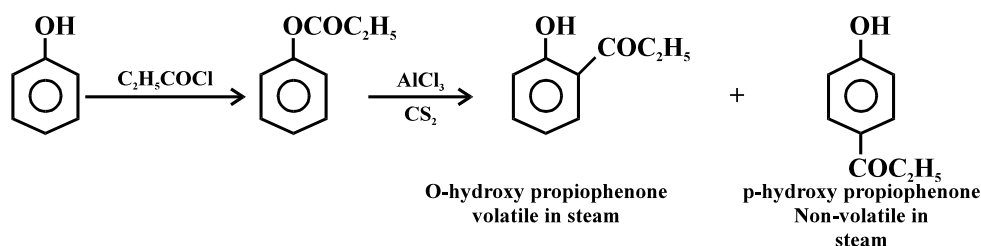
8. **Diel Alder reaction is also pericyclic reaction** :



9. **Quinones** : Oxidation of hydroquinone gives quinone



10. **Reimer-Tiemann Reaction** :

11. Fries rearrangement :

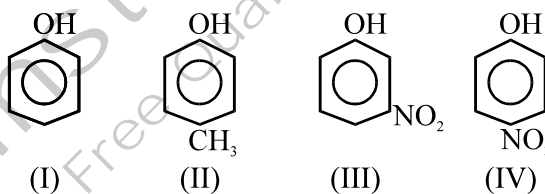
Rearrangement involves RCO^+ , which then attacks the ring.

Practice Problems :

- When phenol is distilled with zinc dust, the main product is
 - biphenyl
 - benzene
 - benzaldehyde
 - phenolphthalein
- When sodium benzene sulphonate is fused with sodium hydroxide (solid), the product formed is
 - benzene
 - phenol
 - benzene triphenol
 - none of these
- Which of the following acids is strongest
 - $\text{C}_6\text{H}_5\text{SO}_3\text{H}$
 - CH_3COOH
 - $\text{C}_6\text{H}_5\text{COOH}$
 - $(\text{COOH})_2$
- Phenol is less acidic than
 - p-nitrophenol
 - ethanol
 - cresol
 - benzyl alcohol
- Cumene $\xrightarrow[\text{(ii) H}_2\text{O, H}^+]{\text{(i) O}_2}$ (X) and (Y)

(X) and (Y) respectively are

 - toluene, propene
 - toluene, propylchloride
 - phenol, acetone
 - phenol, acetaldehyde
- In the following compounds



the order of acidity is

- $\text{III} > \text{IV} > \text{I} > \text{II}$
 - $\text{I} > \text{IV} > \text{III} > \text{II}$
 - $\text{II} > \text{I} > \text{III} > \text{IV}$
 - $\text{IV} > \text{III} > \text{I} > \text{II}$
- When phenol reacts with benzene diazonium chloride, the product obtained as
 - phenyl hydrazine
 - p-amino azobenzene
 - phenol hydroxylamine
 - p-hydroxy azobenzene
 - Phenol $\xrightarrow[\text{distillation}]{\text{Zinc}}$ (A) $\xrightarrow[\text{at } 60^\circ]{\text{Conc. H}_2\text{SO}_4}$ (B) $\xrightarrow[\text{NaOH}]{\text{Zn}}$ (C). In the above reaction, compounds (A),

(B) and (C) are

- benzene, nitrobenzene and aniline
- benzene, dinitrobenzene and m-nitroaniline
- toluene, nitrobenzene and m-toluidine
- benzene, nitrobenzene and hydrazobenzene

[Answers : (1) b (2) b (3) a (4) a (5) c (6) d (7) d (8) d]