

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 1^0 , 2^0 , 3^0 alcohols have solubility in order : $1^0 > 2^0 > 3^0$.

C1B Method of preparation of Alcohols:

(i) Hydration of Alkenes:

$$CH_3 - CH = CH_2 + H_2O \xrightarrow{\text{dil } H_2SO_4} CH_3 - CH - CH_3$$

$$OH$$

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

(ii) Hydrolysis of Alkyl Halides:

$$R-X+aq$$
. NaOH (or H_2O) $\rightarrow R-OH+NaX$ (or HX)

Reaction can be S_{N^1} or S_{N^2} .

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

(a)
$$RCHO \xrightarrow{LiAlH_4 \text{ or NaBH}_4} RCH_2OH_1^0$$

(b)
$$R$$
 $CO \xrightarrow{\text{LiAlH}_4 \text{ or NaBH}_4} R$ $CHOH$ R $CHOH$

- (c) Acid, acid halide, ester and anhydride are reduced to 10 alcohol.
- (iv) Hydroboration and oxidation:

$$\mathbf{CH_3} - \mathbf{CH} = \mathbf{CH_2} \xrightarrow{\mathbf{BH_3} \text{ in THF}} (\mathbf{CH_3} - \mathbf{CH_2} - \mathbf{CH_2} - \mathbf{)_3} \mathbf{B} \xrightarrow{\mathbf{H_2O_2}, \mathbf{OH}^-} \mathbf{CH_3} \mathbf{CH_2CH_2OH} + \mathbf{B(OH)_3}$$

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

(v) Oxymercuration-Demercuration:

$$CH_{3}-CH=CH_{2} \xrightarrow{Hg(OAc)_{2}} CH_{3}-CH-CH_{2} \xrightarrow{NaBH_{4}} CH_{3}-CH-CH_{3}$$

$$OH$$

$$OH$$

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.

$$R_{1} \longrightarrow C = O + R_{3}MgX \longrightarrow R_{1} - C - OMgX \xrightarrow{H_{3}O^{+}} R_{1} - C - OH + H_{2}O$$

$$R_{2} \longrightarrow R_{3}$$

R, R, can be H, alkyl or aryl but R, is not H.

(b) Grignard reagent with epoxide and after hydrolysis gives 10 alcohol for e.g.,

$$CH_2 - CH_2 + RMgX \rightarrow RCH_2CH_2OMgX \xrightarrow{H_2O} RCH_2CH_2OH$$

$$\downarrow 0$$

Practice Problems:

- 1. 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:
 - (a) alkaline KMnO₄

(b) B_2H_6 and alkaline H_2O_4

(c) O_3/Zn

(d) OsO₄/CH,Cl,

- **(b)**
- 2. Glycol may be obtained:
 - (a) by the oxidation of ethylene with cold, dilute, alkaline permanganate solution
 - (b) by the hydrolysis of ethylene bromide under reflux with aqueous sodium carbonate solution
 - (c) by the hydrolysis of ethylene chlorohydrin on boiling with aqueous sodium bicarbonate
 - (d) by any of the above methods
 - (**d**)
- 3. Which of the following are the starting materials for the Grignard's synthesis of tert. butyl alcohol
 - (a) $CH_3MgI + CH_3COCH_3$
- (b) CH,MgI + CH,CHOHCH,
- (c) CH₃CH₃MgBr + CH₃COCH
- (d) CH,CH,MgBr + CH,CHO

(a)

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

- **C2** Chemical Properties:
 - (i) Dehydration of Alcohol:

$$CH_{3}CH_{2}CHCH_{3} \xrightarrow{conc.H_{2}SO_{4}} CH_{3} - CH_{2} - CH = CH_{2} + CH_{3} - CH = CH - CH_{3}$$

$$(minor) \qquad (major)$$

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

Dehydration of alcohol is in the order $3^{0} > 2^{0} > 1^{0}$ as intermediate is carbocation.

(ii) Reaction with Halogen Acids :

$$R - OH + HX \rightarrow RX + H_2O$$

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:

$$3R - OH + PX_3 \rightarrow 3RX + H_3PO_3$$

(X = Br, I)

$$R - OH + SOCl$$
, $\rightarrow RCl + SO$, $+ HCl$

(iv) Acidic Character of Alcohol:

$$RO - H + Na \rightarrow RO^-Na^+ + \frac{1}{2}H_2$$

alkoxide

The order of acidic character of alcohol with metal is:

$$CH_{2}OH > 1^{0} > 2^{0} > 3^{0}$$
.

The relative acidities is as follows:

$$RCOOH > C_{\alpha}H_{\alpha}OH > H_{\alpha}O > ROH > CH = CH > NH_{\alpha} > RH$$

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

$$CH_3CH_2OH + CH_3 - C - OH \xrightarrow{H^+} CH_3 - C - OC_2H_5 + H_2O$$
ethyl acetate

Thus reactivity of alcohols for given acid is in order:

$$CH_3OH > 1^0 > 2^0 > 3^0$$

and those of acids for given alcohol is in order:

 $HCOOH > CH_1COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$

- (vi) Oxidation of Alcohol:
 - 1. Using Cu

(a)
$$CH_3CH_2OH \xrightarrow{Cu} CH_3CHO + H_2$$

$$\xrightarrow{10} CH_3CHO + H_2$$

(b)
$$CH_{3} \xrightarrow{CHOH} \xrightarrow{Cu} CH_{3} \xrightarrow{CO+H_{2}} CO+H_{2}$$

$$CH_{3} \xrightarrow{CHO_{3}} CH_{3}$$

(c)
$$CH_{3} - C - OH \xrightarrow{Cu} CH_{3} - C = CH_{2} + H_{2}O$$

$$CH_{3} - C + OH \xrightarrow{300^{0}C} CH_{3} - C = CH_{2} + H_{2}O$$

- 2. Oxidation using KMnO₄/K,Cr,O₇
 - (a) $RCH_2OH \xrightarrow{(i)KMnO_4} RCOOH$

(b)
$$RCH_2OH + Cr_2O_7^2 \rightarrow RCOOH + Cr_3^{3+}$$
 green

(c)
$$R - CHOH \xrightarrow{KMnO_4, CrO_3 \text{ in glacial acetic, acid or } K_2Cr_2O_7} \xrightarrow{R} CO$$

- 3. Other reagents used for oxidation :
 - (a) PCC (pyridinium chlorochromate) to oxidise 1⁰ alcohols to aldehydes.
 - (b) MnO₂ selectively oxidises the OH group of allylic and benylic 1⁰ and 2⁰ alcohols to give aldehydes and ketones respectively.
- C3 Test to distinguish 1°, 2° and 3° Acohols:
 - (a) Lucas Reagent (anhydrous ZnCl,/conc. HCl)
 - (b) Oxidation
 - (c) Victor Meyer Test

Practice Problems:

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

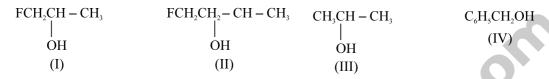
$$\underbrace{Ethanol \xrightarrow{PBr_3}(X) \xrightarrow{Alc.KOH}(Y) - \xrightarrow{H_2SO_4, room \ temp.}}_{H_2O, heat} (Z)$$

- (a) $CH_{2} = CH_{2}$
- (b) CH_3CH_2OH
- $) \qquad CH_{3}CH_{2}OSO_{3}H (d)$
- C,H,OC,H,

2. An organic compound gives hydrogen on reacting with sodium metal. It also gives iodoform test and forms an aldehyde of molecular formula C_2H_4O on oxidation with acidified dichromate. The compound is :

- (a) CH₂OH
- (b) CH,COOH
- (c) CH,CHO
- d) C,H,OH

3. The order of reactivity of the following alcohols,



towards conc. HCl is

(a) I>II>III>IV

(b) I > III > IV

(c) IV > III > II > I

(d) IV > III > I > II

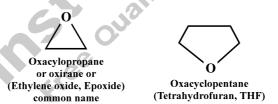
[Answers: (1) b (2) d (3) c]

C4 Ethers

Nomenclature of Ethers:

Cyclic ethers can be named in severay ways:

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



C5 <u>Methods of Preparation of Ether:</u>

(a) Williamson Synthesis:

Example:

(i)
$$(CH_3)_2CH - OH \xrightarrow{Na} (CH_3)_2CHO^-Na^+ + CH_3CH_2CH_2Br$$
 Sodium n-Propylbromide isopropoxide
$$\downarrow S_{N^2}$$

$$CH_3CH_2CH_2OCH(CH_3)_2$$
 Isopropyl n-propyl ether

Discussion: Phenol in Williomson'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] $R - X \rightarrow can be X = -Cl, -Br, I, -OSO, CH, etc.$

(b) Ethers by Intermolecular Dehydration of Alcohols :

Alcohols can dehydrate to form alkenes.

10 Alcohols can also dehydrate to form ethers.

ROH + R - OH
$$\xrightarrow{H^+}$$
 R - O - R

$$\begin{array}{c}
H_2SO_4 \\
180^{\circ}C
\end{array} \Rightarrow CH_2 = CH_2$$

$$\begin{array}{c}
H_2SO_4 \\
H_2SO_4
\end{array} \Rightarrow CH_3CH_2OCH_2CH_3$$

$$\begin{array}{c}
H_2SO_4 \\
140^{\circ}C
\end{array} \Rightarrow CH_3CH_2OCH_2CH_3$$

The formation of ether takes places by S_{N^2} 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° alcohol because they form alkene too easily. This method is not useful for the praparation of unsymmetrical ethers from primary alcohols because the reaction leads to a mixture of products.

$$ROH + R'OH \xrightarrow{\qquad \qquad} R - O - R' + ROR + R'OR' + H_2O$$

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

$$C_{2}H_{5}OH + CH_{2} = C - CH_{3} \xrightarrow{H_{3}SO_{4} \text{ (conc.)}} CH_{3}CH_{2}OC - CH_{3}$$

$$CH_{3} CH_{3}$$

$$CH_{3}$$

$$CH_{3}CH_{2}OC - CH_{3}$$

$$CH_{3}$$

Practice Problems:

1. Which route provides a better synthesis of ether :

C6 Reactions of Ethers:

(a) Ethers are comparitavely 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:

$$R-O-R'+HX \longrightarrow RX+R'OH \xrightarrow{HX} RX+R'X$$

Reactivity of HX: HI > HBr > HCl

Cleavage takes place only under quite vigourous 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 ment of the weakly basic alcohol molecule.

$$R - \ddot{Q} - R' + HX \Longrightarrow R - \dot{Q}^{\dagger} - R' + X^{-}$$

$$R - \overset{H}{\overset{|}{\circ}} - R' + X^{-} \xrightarrow{S_{N}1 \text{ or } S_{N}2} R - X + R'OH$$
weak base
good leaving group

As we might expect primary alkyl group tend to undergo S_{N^2} and $3^{\rm o}$ tend to undergo S_{N^1} .

(b) Acid Hydrolysis:
$$C_2H_5 - O - C_2H_5 + H_3O^+ \rightarrow 2C_2H_5OH$$
.

(c) Acid Hydrolysis of Epoxide :
$$\begin{matrix} & & & CH_2 - OH \\ & & & & \\ & & & CH_2 - OH \\ & & & CH_2 - OH \end{matrix}$$
Ethylene Glycol

(d) Formation of Halohydrin :
$$\begin{array}{c|c} & CH_2 - OH \\ \hline & CH_2 - X \\ \hline & CH_2 - X \\ \hline & Halohydrin \end{array}$$

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, $C_6H_{14}O$, 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

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

Aldehydes & Ketones

C7A Physical Properties:
$$C = 0 \iff C^+ - 0^-$$

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,O hence they are soluble in water to varying extent.

C7B Method of Preparation:

1. Oxidation:

(a)
$$\begin{array}{c} RCH_2OH \xrightarrow{Cu, \Delta} \\ \hline 1^0 \\ \hline \\ C_sH_sNH^{\dagger}CrO_3C\Gamma \\ \hline CH_2Cl_2 \end{array} \begin{array}{c} [C_sH_sNH^{\dagger}CrO_3C\Gamma \rightarrow (PCC) \\ \hline Pyridinium chlorochromate] \end{array}$$

(b)
$$R \longrightarrow CH - OH \xrightarrow{MnO_4^{-}/CrO_3/Cr_2O_7^{2-}} R \longrightarrow R CH = O$$

$$Cu, \Delta \longrightarrow R C = O$$

(c)
$$R \longrightarrow CHOH + [(CH_3)_3CO]_3AI \longrightarrow R \longrightarrow R$$
 CO

This oxidation is called as oppenauer oxidation.

2. Rossenmund Reduction:
$$R - C - Cl + H_2 \xrightarrow{Pd / BaSO_4} R - C - H + HCl$$

3.
$$R-C-Cl \xrightarrow{\text{LiAlH}(OBu-t)_3} RCHO \text{ [LiAlH (O-t-C}_4H_9)_3 or Lithium tri-t-butoxy Aluminium hydride]}$$

4.
$$R - C - CI \xrightarrow{Sn(C_4H_9)_3H} RCHC$$

5. <u>Hydrolysis of Gem-Dihalide</u>

(a)
$$CH_3CH_2-CH$$
 $+$ aq. NaOH \longrightarrow CH_3CH_2CH \xrightarrow{OH} $\xrightarrow{-H_2O}$ CH_3CH_2CHO OH

(b)
$$CH_3-C-CH_3+aq. NaOH \longrightarrow CH_3-C-CH_3 \xrightarrow{-H_2O} CH_3-C-CH_3$$

$$CI \qquad OH \qquad O$$

$$CH_3-C-CH_3+aq. NaOH \longrightarrow CH_3-C-CH_3 \xrightarrow{-H_2O} CH_3-C-CH_3$$

(c)
$$ArCH_3 \xrightarrow{Cl_2,heat} ArCHCl_2 \xrightarrow{H_2O} ArCHO$$

6. <u>Hydration of Alkynes</u>: Hydration of alkynes gives ketones (except CH = CH which gives CH_3CHO)

(a)
$$CH \equiv CH \xrightarrow{H_2O,H^+} CH_3CHO$$
 (b) $CH_3C \equiv CH \xrightarrow{H_2O,H^+} CH_3COCH_3$

7. Hydroboration Oxidation:

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

$$CH_{3}C = CH \xrightarrow{BH_{3}, THF} (CH_{3} - C = CH) \xrightarrow{BH_{3}} B \xrightarrow{H_{2}O_{2}, OH^{-}} CH_{3} - C = CHOH \xrightarrow{CH_{3} - CH_{2} - CHO} (keto)$$

8. Use of Grignard Reagent:

(a) With HCN aldehyde is formed.

$$\begin{array}{c|c} HCN & \xrightarrow{RMgX} & H - C = NMgX & \xrightarrow{H_2O} & H - C = O \\ & & & & | & & | \\ & & & & R & & R \end{array}$$

(b) With RCN a ketone is formed.

$$R - C \equiv N \xrightarrow{R'MgX} R - C = NMgX \xrightarrow{H_2O} R - C = O$$

$$\downarrow R'$$

$$R'$$

9. With Esters

(a)
$$\begin{array}{ccc}
O & & O \\
\parallel & & & \downarrow \\
H - C - OC_2H_5 + RMgX & \longrightarrow & H - C - OC_2H_5 & \xrightarrow{H^+} & R - C - H + C_2H_5OH \\
R
\end{array}$$

(b)
$$CH_3 - C - OC_2H_5 + RMgX \longrightarrow CH_3 - C - OC_2H_5 \xrightarrow{H^+} CH_3 - C - R + C_2H_5OH_5$$

10. Decarboxylation of calcium salts of carboxylic acids:

$$(R_1COO)_2Ca + (R_2COO)_2Ca \xrightarrow{\Delta} R_1 - C - R_2 + 2CaCO_3$$

11.
$$\underbrace{Oxo Process:}_{-C = C - + CO + H_2} \xrightarrow{100^{\circ}C, Pr.}_{|CoH(CO)_4} \xrightarrow{|COH(CO)_4} - C - C - C + CHO$$

$$2 \text{ CH}_{3}\text{CH} = \text{CH}_{2} + \text{CO} + \text{H}_{2} \xrightarrow{100^{9}\text{C}, \text{Pr.}} \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{0} + \text{CH}_{3} \xrightarrow{\text{CHCHO}}$$

 $[COH(CO)_{A}] \longrightarrow Cobal + Carbonyl hydride$

12. Reduction of acid chloride with organocopper compounds:

$$R' - Li \xrightarrow{CuX} R' - Cu - Li \xrightarrow{RCOCI} R - C - R' \text{ or } Ar - C - R'$$

$$O$$

5.00

13. Friedel-Crafts Acylation:

(a)
$$R-C < O + Ar-H \xrightarrow{AlCl_3} R-C-Ar+HCl$$

Cl Lewis acid O

(b)
$$\bigcirc$$
 COCl + \bigcirc AlCl₃ \longrightarrow CO \bigcirc + HCl Benzophenone

14. From Cadmium and Lithium Salts:

1.
$$2RMgX + CdCl_2 \longrightarrow R - Cd - R + MgCl_2 + MgX_2$$

 $R - Cd - R + R'COCl \longrightarrow RCOR' + RCdCl$

$$R \longrightarrow \text{should be } 1^0 \text{ alkyl or aryl } (-C_6H_5)$$

- 15. Ozonylysis of Alkene (Zn/H^+) \longrightarrow Aldehyde/Ketone
- C8 Chemical Properties:
 - 1. <u>Nucleophilic Addition to the Carbon-Oxygen Double bond</u>:

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

$$\underbrace{\frac{\text{General Reaction}:}{\text{H}}}_{\text{H}} C = O + H - NU \Longrightarrow R - C - OH$$

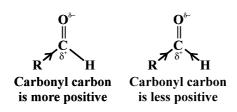
Relative reactivity of Aldehydes versus Ketones:

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

- 1. Steric Factor 2. Electronic factor
- 1. <u>Steric Factor</u>: 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. <u>Electronic Factor:</u> Because alkyl group are electron releasing therefore aldehydes are more reactive on electronic grounds as well. Aldehyde have one electron releasing alkyl group to stablise the partial positive charge on the carbon atom of the carbonyl group. Whereas ketones have two alkyl groups.



(a) Addition of cyanide:

$$\begin{array}{c}
O \\
CH_{3} - C - CH_{3} + NaCN \xrightarrow{H_{3}O^{+}} CH_{3} - C - CN \xrightarrow{H_{2}O/H_{2}SO_{4}} CH_{3} - C - COOH \\
OH OH \\
CH_{3} - C - COOH \\
OH \\
CH_{3} - C - COOH \\
Methylacrylic acid
\end{array}$$

(b) Addition derivatives of ammonia:

(i)
$$C + H_2N - G \xrightarrow{H^+} \begin{bmatrix} -C - NH - G \\ OH \end{bmatrix} \longrightarrow -C = N - G + H_2O$$

(ii) HCHO reacts with NH, differently forming UROTROPINE [hexamethylene tetraamine].

$$H_2N-OH$$
 Hydroxylamine $C=N-OH$ oxime

$$H_2N-NH_2$$
 Hydrazine $C=N-NH_2$ Hydrazone

$$H_2N-NHC_6H_5$$
 Phenylhydrazine $C=N-NHC_6H_5$ Phenylhydrazone

$$H_2N-NHCOCH_2$$
 Semicarbazine $C=NNHCOCH_2$ Semicarbazone

(c) Addition of Alcohols : Acetal Formation

(i)
$$R H H H \\ C + 2ROH \xrightarrow{H^+} R - C - OR + H_2C$$

$$O OR$$

(ii)
$$CH_3 - C = O + 2C_2H_5OH \xrightarrow{HCl} CH_3 - C - OC_2H_5 + H_2O$$

$$OC_2H_5$$
Acetal

$$R' - C - OR + H_2O \xrightarrow{H^+} R' - C = O + 2ROH$$

$$OR \text{ (Acetal)}$$

(d) Addition of Grignard reagents:

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

C9 Other Reactions of Aldehyde and Ketones:

(a) Oxidation:

(i) RCHO or ArCHO
$$\xrightarrow{\text{KMnO}_4}$$
 RCOOH or ArCOOH $Ag(NH_3)_2^+$

Aldehydes (except) benzaldehyde reduce "Fehling's Solution" (Cu^{2+} reduced to Cu^{+}) which is an alkaline solution of Cu^{2+} ion complexed with tetrarate ion.

(ii) Example: Tollen's Test:

CH₃CHO + 2Ag(NH₃)₂⁺ + 3OH⁻
$$\longrightarrow$$
 CH₃COO⁻ + 2Ag + 4NH₃ + 2H₂O

Colourless Solution

Silver mirror

Fehling Solution CH₃CHO + 2Cu²⁺ + 3OH[−]
$$\longrightarrow$$
 CH₃COO[−] + 2Cu⁺ \downarrow +2H₂O

Tollen's test is cheifly given by aldehydes. Tollen's reagent does not attack carbon-carbon double bond. Aldehyde also reduce benedict's solution (Cu^{2+} 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.

$$\begin{array}{c|c} RCH_2 \stackrel{a}{=} C \stackrel{b}{=} CH_2R' & \xrightarrow{Oxidant} & RCH_2COOH + R'COOH \\ & & & & \\ O & & & \\ \end{array}$$

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 (H_2SO_5) or peroxybenzoic acid $(C_6H_5CO_3H)$ to esters. $RCOR' \xrightarrow{H_2SO_5} RCOOR'$ [Bayer's Villiger Oxidation]
- (c) Haloform Test:

(i) Methylketones:

(ii) <u>Hypohalite</u> NaOX ($NaOH + X_2$) cannot only halogenate can also oxidise alcohols

$$\begin{array}{ccc}
H & O \\
| & | \\
R - C - CH_3 + NaOI \longrightarrow R - C - CH_3 + NaI + H_2O \\
OH & OH
\end{array}$$

(d) Reduction:

(a) Reduction to alcohol
$$>$$
 $C = O \xrightarrow[\text{then H}]{H_{4}/Ni, Pt \text{ or Pd}} - C - OH$

- (f) Reductive Amination (Discussed under Amines)
- (g) <u>Cannizzaro reaction</u>: 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.

(i)
$$\begin{array}{c} H \\ 2H - C = O \\ \hline \\ An \text{ aldehyde with} \\ no \alpha - hydrogens \\ \end{array}$$
 HCOO⁻ + CH₃OH Acid Salt Alcohol

(ii) 2
$$CHO$$
 $COOK$ CH_2OH $COOK$ CH_2OH

m-chlorobenzoldehyde

m-chloropotassium benzoate m-chlorobenzylalcohol

(h) Crossed Cannizzaro reaction :

CHO
$$\begin{array}{ccccc}
CH_2OH \\
& & & & & \\
CH_2OH \\
& & & & & \\
& & & & & \\
& & & & & \\
OCH_3 & & & & & \\
& & & & & & \\
OCH_3 & & & & & \\
\end{array}$$
+ HCOO-
$$\begin{array}{cccccc}
OCH_3 & & & & & \\
OCH_3 & & & & & \\
\end{array}$$

Veratraldehyde (3, 4-Dimethoxy benzaldehyde)

(3, 4- Dimethoxybenzyl alcohol)

(i) <u>Tischenko Reaction</u>:

All aldehyde in presence of aluminium ethoxide, $Al(OC_2H5)_3$ 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) <u>Distinction</u>

Aldehyde and Ketones

<u>S.No.</u>	<u>Test</u>	<u>RCHO</u>	RCOR
1.	Schiffs 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 C ₆ H ₅ CHO)	is not reduced α-hydroxy, ketones reudce Tollen's re agent and Fehling's solution - CH - CO -

Practice Problems:

			IID.	IIdl	NaOH
1.	Identify (Z) in the reaction series,	$CH_2 = CH_2 -$	$\xrightarrow{\text{HBr}}$ (X) $-$	$\xrightarrow{\text{Hydrolysis}} (\mathbf{Y})$	$\xrightarrow{I_2(\text{excess})} (\mathbf{Z})$

- (a) C_2H_5I
- b) C,H,OH
- (c) CHI₃
- (d) CH₃CHO
- 2. A compound (X) of the formula C₃H₈O yields a compound C₃H₆O on oxidation. To which of the following class of compounds could (X) belong
 - (a) aldehyde

(b) secondard alcohol

(c) alkene

- (d) tert. alcohol
- 3. Which statement is incorrect in the case of acetaldehyde and acetone
 - (a) both react with hydroxylamine
 - (b) both react with NaHSO,
 - (c) both react with hydrazine
 - (d) both reduce ammonical silver nitrate
- 4. Which of the following undergoes Cannizzaro's reaction
 - (a) CH₃CHO
- (b) CH₃CH₂CHO
- $(CH_3)_2$ CHCHO (d)
- НСНО

- 5. Urotropine is formed by the action of ammonia on
 - (a) acetaldehyde
- (b) formaldehyde (c)
- acetone
- (d) phenol
- 6. Hydrocarbons are formed when aldehydes and ketones are reacted with amalgamated zinc and conc. HCl. The reaction is called
 - (a) Cannizzaro's reaction
- (b) Clemmensen's reduction
- (c) Rosenmund's reaction
- (d) Tischenko reaction

7.	When ace	etaldehyde is tre	ated with	aluminium etho	xide, it for	ms		
	(a)	ethyl acetate			(b)	ethyl alcohol		
	(c)	acetic acid			(d)	methyl propion:	ate	
8.	Chloreton	ne is formed whe	n chlorofe	orm reacts with				
	(a)	formaldehyde	(b)	acetaldehyde	(c)	acetone (d)	benzaldeh	yde
9.	Which of	the following rea	gent reac	ts differently wi	th HCHO,	CH ₃ CHO and CH	COCH,	
	(a)	HCN	(b)	NH ₂ OH	(c)	$C_6H_5NHNH_2$	(d) N	NH ₃
10.	In the foll	lowing sequence	of reactio	ns, the end pro	duct is			
	CaC ₂ –	$H_2O \rightarrow (A)$	g^{2+}/H_2SO_4	\rightarrow (B) $\stackrel{[O]}{\longrightarrow}$	(C)—Ca(C	$\stackrel{\text{OH})_2}{\longrightarrow} (D) \stackrel{\text{heat}}{\longrightarrow}$	→(E)	
	(a)	acetaldehyde	(b)	formaldehyde	(c)	acetic acid	(d) a	cetone
11.	In the foll	lowing sequence	of reactio	ns, the end pro	duct is			
	$HC \equiv C$	$H = \frac{Hg^{2+}/H_2SO_4}{H}$	→(A)—	$\xrightarrow{\text{CH}_3\text{MgX}} \rightarrow (B)$	(C	C)		
	(a)	acetaldehyde		[1120]	(b)		ol	
	(a) (c)	acetandenyde			(d)	ethyl alcohol	or Control	
					` '		ш.о.	
12.			of reactio	ons, the end pro		H_3 CHO $\xrightarrow{\text{HCN}}$		→(B)
	(a)	CH ₃ COOH				CH ₃ CHOHCOC)H	
	(c)	CH ₃ CH ₂ NH ₂	_		(d)	3 2		
13.		ınd, C ₅ H ₁₀ O, for reduction gives 1				gative Tollen's and	iodoform te	sts. The com-
	(a)	pentanal (b)	pentan	_		none-3 (d)	amyl alcol	hol
14.	The prod	uct Z in the seri	es is	one 2 (c)	penun	ione of the	uniyiuico	1101
	The prod		C S S S	No. 6				
	$CH_2 = 0$	Solution (a) for the serion (b) for the serion (c)	Hydroly —	$\xrightarrow{\text{sis}} Y \xrightarrow{\text{I}_2(\text{exc})}$	$\xrightarrow{\cos_3} Z$			
	(a)	C_2H_5I	(b)	C ₂ H ₅ OH (c)	CHI,	(d)	СН,СНО	
15.	If formal	dehyde and KOF	I are treat	ed together, we g	get			
	(a)	methane (b)	methar	nol (c)	ethyl a	cetate (d)	acetylene	
16.	The corre	ect order of react	ivity in nu	cleophilic additi	on reaction	CH ₃ CHO, CH ₃ C	OC ₂ H ₅ and C	CH ₃ COCH ₃ is
	(a)	CH ₃ CHO > CH	"COCH ₃ >	· CH ₃ COC ₂ H ₅				
	(b)	C ₂ H ₅ COCH ₃ >						
	(c)	CH ₃ COCH ₃ >C	-					
	(d)	CH ₃ COCH ₃ >C	2 3	3 3				
17.		•	pentanone	-		eagent can be used	l	
	(a)	NaOH/I ₂		(b)		's reagent		
	(c)	$K_2Cr_2O_7/H^+$			(d)	Zn-Hg, HCl		
18.				$H_3 - CH = CHC$		g oxidising agent a		
	(a)	alkaline KMnO	7		(b)	K ₂ Cr ₂ O ₇ /conc.	H ₂ SO ₄	
	(c)	ammonical AgN			(d)	dilute HNO ₃		
19.		•				emperature 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							

none

- 20. The reagent which can be used to distinguish acetophenone from benzophenone is:
 - (a) 2, 4-dinitrophenyl hydrazine
- (b) benedict reagent

(c) I, and Na, CO,

- (d) aqueous solution of NaHSO,
- 21. Best starting material to synthesize 2-methyl-2-butenoic acid is

(a)
$$CH_3 - C - CH_3$$

$$CH_3 - C - CH_3$$

$$OH$$

(b) CH₃CH₂CH₂CHO

(d)
$$CH_3CH_2 - C - CH$$

22. 1-pentyne — \longrightarrow BH₃. THF/H₂O₂, OH⁻

- \boldsymbol{X} and \boldsymbol{Y} can be distinguished by :
- (a) silver-mirror test(b) iodoform test Which of the following will give haloform test
- (a) $CH_3 C CCl_3$

(b) $CH_3 - C - CH_2I$

(c) $CH_3 - C - CH_2C$

(d) all

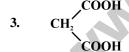
(c)

[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 a (17) a (18) a (19) d (20) c (21) c (22) c (23) d] (16)

Carboxylic Acids and Derivatives

- C10 Common name of carboxylic acids:
- 1. CH₂CH₂CH₂COOH valeric acid

2. COOH oxalic acid



23.

Malonic acid; CH₃ – CH – COOH

4. CH₂ – COOH Succinic acid CH₂ – COOH

СНСООН 5. || СНСООН

- maliec acid
- Methyl malonic acid
 CH COOH
 ||
 HOOC CH
- Fumaric acid

- CH₂ CH₂ COOH
 - $CH_2 CH_2 COOH$
- adipic acid

COOH

- 8. HOOCCH,CH,CH,COOH
- 9. $CH_2 = CH COOH$ (acrylic acid)

Glutoric acid
Carboxylic acids (derivative of benzene)

- 10. COOH

 CH₃ O-Toluic acid
- COOH

 COOH

 Phathalic acid

Terphthalic acid

- COOH

 Isophthalic acid

 13.
- COOH

 14. Salicylic acid

 15. COOH

 NH₂ Anthranilic acid
- 16. $\begin{array}{c} \text{COOH} \\ \text{H}_3\text{C} \\ \text{CH}_3 \\ \end{array}$ $\begin{array}{c} \gamma \\ \beta \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ \\ \gamma \text{ phenyl butylic acid} \\ \end{array}$

Mesitoic acid (2, 4, 6-Trimethyl benzoic acid)

- 18. CH₃ CH COOH (Lactic acid)
 OH
- 19. $CH_3 CH = CH COOH$ (crotonic acid)
- 20. CH₃ C COOH (Pyruvic acid)
- C11 Methods of preparation of carboxylic acid :
 - (a) By acid hydrolysis of cyanidies $R CN \xrightarrow{H^{\dagger}/H,O} R C OH + NH_4$
 - (b) By the use of Grigrand Reagent
 - $O = C = O \xrightarrow{RMgX} R C OMgX \xrightarrow{H_3O^+} R C OH$

- (c) By oxidation method
 - (i) Oxidation of alcohols (10) RCH₂OH $\xrightarrow{K_2Cr_2O_7/H^* \text{ or alk. KMnO}_4}$ RCOOH
 - (ii) Oxidation of aldehyde $CH_3C H \xrightarrow{Tollen's reagent} CH_3COOH$

$$\begin{array}{c}
O \\
\parallel \\
CH_{3}C - H \xrightarrow{K_{2}Cr_{2}O_{7}/H^{+} \text{ or alk. } KMnO_{4}}
\end{array}$$

$$CH_{3}COOH$$

(iii) Oxidation of ketones

Iodoform Test:

(d) Oxidation of alkenes and alkynes $R - CH = CH - R \xrightarrow{(i)Alkaline \ KMnO_4} 2RCOOH$

$$R - CH = CH - R \xrightarrow{(i)O_3} 2RCOOH$$

Practice Problems:

- 1. Cyanohydrin of which of the following gives lactic acid on hydrolysis
 - (a) acetone (b) acetaldehyde (c)
 - (c) propanal (d)
- НСНО

[Answers: (1) b]

C12 Chemical Properties of Carboxylic Acids:

- (a) Carboxylic acid undergo nucleophilic substitution reaction
 - (i) Formation of a mide from carboxylic acid RCOOH $\xrightarrow{\mathrm{NH}_3,\,\Delta}$ RCONH₂
 - (ii) Formation of Acyl chloride RCOOH $\xrightarrow{PCl_s \text{ or } PCl_s \text{ or } SOCl_2}$ \Rightarrow RCOCl
 - (iii) Formation of esters RCOOH $\xrightarrow{R'OH/H^+}$ RCOOR'
- (b) Formation of anhydride: $2RCOOH \xrightarrow{P_2O_5} (RCO)_2O$
- (c) Schmidt reaction: RCOOH $\xrightarrow{N_3H, \Delta}$ RNH₂
- (d) HVZ reaction : $CH_3COOH \xrightarrow{red P/Br_2} BrCH_2COOH$
- (e) Reduction of caboxylic acid : $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH$
- (f) Formatin of alkane : $CH_3COOH \xrightarrow{NaOH+CaO} CH_4$
- (g) Formatin of Salts: $CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$ effect of heating on salts: $(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3COCH_3$
- (h) Kolbe electrolysis : $CH_3COOH \xrightarrow{(i)KOH} CH_3CH_3$
- (i) Acidic character: $CH_3COOH \xrightarrow{NaHCO_3} CH_3COONa + CO_2 + H_2O$

Practice Problems:

- 1. Which of the following will not undergo HVZ reaction
 - (a) 2, 2-dimethyl propanoic acid
- (b) propanoic acid

(c) acetic acid

- (d) 2-methyl propanoic acid
- 2. Amongst the acids (a) CH = CCOOH (b) $CH_2 = CHCOOH$ and (c) CH_3CH_2COOH , the acid strength follows the sequence
 - (a)
- (a) > (b) > (c)
- **(b)**
- (a) < (b) < (c)
- (a) = (b) = (c)
- (d) (a) = (b) < (c)
- 3. $CH_3CH_2COOH \xrightarrow{Cl_2} (A) \xrightarrow{Alc.KOH} (B)$ The compound (B) is
 - (a) CH,CH,OH

(b) CH,CH,CN

(c) $CH_2 = CHCOOH$

(d) CH₃CHClCOOH

- 4. Formic acid
 - (a) is immiscible with water
 - (b) reduces ammonical silver nitrate
 - (c) is a weak acid nearly three and a half times weaker than acetic acid
 - (d) is prepared by heating potassium formate
- 5. Strongest acid out of CH₃CO₂H, CH₂ = CHCO₂H,
 - (a) CH,CO,H

(b) $CH_2 = CHCO_2H$

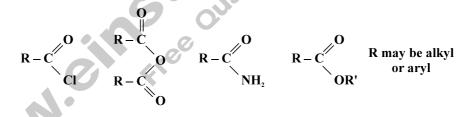
(c) $\langle \bigcirc \rangle$ $-CO_2H$

(d) equal Ka

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

CARBOXYLIC ACID DERIVATIVES

C13A <u>Structures</u>: Closely related to the cabroxylic 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, -NH, or -OR'



They all contain acyl group R - C -

C13B Physical properties: The presence of – 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 molcular 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 chracteristic odours; they are often used in the praparation 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, -C

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

- (a) It provides a site for nucleophilic attack
- (b) It increases the acidity of hydrogents attached to the alpha carbon.

Acyl compounds i.e. Carboxylic acids and their derivatives, typically undergo nucleophilic substitution in which - OH, - Cl, - OOCR, or - 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 - NH, by - OH.

$$R-C \bigvee_{W}^{O} + : Z^{-} \longrightarrow R-C \bigvee_{Z}^{O} + : W$$

$$-W = -OH, -CI, -OOCR, -NH_2, -OR'$$

Let us discuss now properties of acyl compounds.

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

- (a) The tendency of oxygen to acquire the negative charge.
- (b) The relatively unhindered transition state leading from the trigonal reactant to the tetrahedral intermediate. These factors make acyl compounds, too suceptible 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 :W group, returning to a trigonal compound and thus result in substitution.

$$R - C \xrightarrow{O} + : Z \longrightarrow R - C - Z \xrightarrow{H^{+}} R - C - Z$$

$$R' \xrightarrow{R'} R'$$
(Aldehyde or Ketone)
$$Addition reaction$$

- C15A <u>Acid Chlorides</u>: Acid chlorides are prepared from the corresponding acids by reaction with $SOCl_2$, PCl_3 or PCl_4 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.

(a) Conversion into acids, hydrolysis:
$$R - C$$
 $+ H_2O \xrightarrow{H^{\dagger}/OH^{-}} R - COOH + HCI$

(b) Conversion into amides:
$$R - C$$
 $+ 2NH_3 \longrightarrow R - C$ $+ NH_4Cl$ NH_2

(c) Conversion into Esters:
$$R - C$$
 + R'OH \longrightarrow $R - C$ + HCl OR'

An ester

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 neutrilize the HCl evolved but also to catalyze the reaction.

2. Formation of Ketones. Friedel - Craft's acylation:
$$R - C$$
 Cl
 $+ Ar - H \xrightarrow{AlCl_3 \text{ or other lewis acid}} R - C - Ar + HCl$

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

- 4. Formation of aldehydes by reduction: RCOCl or ArCOCl $\xrightarrow{\text{LiAlH}(OBU-t)_3}$ RCHO or ArCHO
- 1. Sodium acetate + acetyl chloride gives
 - (a) CH₃COOH

(b) sodium formate

(c) acetic anhydride

(d) acetone

(c)

C16A Acid Anhydrides

Preparation:

(i) Acetic anhydride is prepared by the reaction of acetic acid with ketene $CH_2 = C = O$, which itself is prepared by high teperature dehydration of acetic acid.

$$CH_3COOH \xrightarrow{AlPO_4} H_2O + CH_2 = C = O \xrightarrow{CH_3COOH} (CH_3CO)_2O$$

(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.

(b)
$$COOH \xrightarrow{200^{\circ}C} COOH \xrightarrow{C} O + H_2O$$

Phthalic anhydride

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):

$$\begin{array}{c|c}
\hline
COOH & Ba(OH)_2 \\
\hline
COOH & 285 - 295^{\circ}C
\end{array}$$

$$\begin{array}{c|c}
\hline
C + CO_2 + H_2O$$

Cyclopentanone

C16B Reactions of Acid Anhydrides:

(i) Conversion into acids. Hydrolysis:

Example: $(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$

Acetic anhydride Acetic anhydride

(ii) Conversion into amides. Ammonolysis:

Example:
$$(CH_3CO)_2O + 2NH_3 \rightarrow CH_3CONH_2 + CH_3COONH_4$$

Acetic anhydride Acetamide Ammonium

$$O + 2NH_3 \rightarrow CH_2COO^-NH_4^+ \xrightarrow{H^+} CH_2COOH$$

$$CH_2CONH_2 \rightarrow CH_2CONH_2$$
Succinic anhydride
$$O + 2NH_3 \rightarrow CH_2COOH_4^+ \xrightarrow{H^+} CH_2COOH_2^+$$

$$CH_2CONH_2 \rightarrow CH_2CONH_2^+$$
Succinamic succinamic acid

(iii) Conversion into esters: $(CH_3CO)_2O + CH_3OH \longrightarrow CH_3COOCH_3 + CH_3COOH_3$

$$\begin{array}{c}
O \\
C \\
C \\
O
\end{array}
+ CH_3CH_2OH \longrightarrow
\begin{array}{c}
O \\
C \\
C \\
OOOH
\end{array}$$

(iv) Formation of Ketone: Friedel craft acylation

$$(CH_3CO)_2O + ArH \xrightarrow{AlCl_3} R - C - Ar + RCOOH$$

$$0$$

Phthalic anhydride

Amides

C17A <u>Preparation</u>: 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:

1.
$$\underbrace{\text{Hydrolysis}:}_{\text{NH}_{2}} \text{R-COOH} + \text{NH}_{4}^{+}$$

$$\underbrace{\text{OH}^{+} \text{RCOO}^{+} + \text{NH}_{3}}_{\text{OH}} + \text{RCOO}^{+} + \text{NH}_{3}$$

$$\underbrace{\text{OH}^{-} \text{COOH}}_{\text{OH}_{2}} + \text{H}_{2}\text{SO}_{4} + \text{H}_{2}\text{O} \rightarrow \underbrace{\text{COOH}}_{\text{OH}_{2}} + \text{COOH}$$

2. Conversion into nitrile:
$$R - C - NH_2 \xrightarrow{P_2O_5} RCN + H_2O$$

3. Conversion into imides :

Example:

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C & O \\
C & O
\end{array}$$

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4. <u>Hoffmann degradation of amides :</u>

RCONH₂ or ArCONH₂
$$\xrightarrow{\text{NaOH/Br}_2}$$
 $R - \text{NH}_2$ or ArNH₂ + Na₂CO₃
(Discussed in amine) 1° Amine

Practice Problems:

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

$$CH_3COOH \xrightarrow{NH_3} (A) \xrightarrow{heat} (B) \xrightarrow{P_2O_5} (C)$$

(a) CH₄

(b) CH₂OH

(c) acetonitrile

- (d) ammonium acetate
- 2. In a reaction, (A) $\xrightarrow{NH_3}$ (B) \xrightarrow{heat} (C) $\xrightarrow{P_2O_5}$ C_2H_5CN (A), (B) and (C) are:
 - (a) CH,COOH, CH,COONH, and CH,CONH,
 - (b) CH,COCl, CH,CONH, and CH,COONH,
 - (c) C₂H₅COOH, C₂H₅COONH₄ and C₂H₅CONH₂
 - (d) C,H,COONH, C,H,CONH, and C,H,COOH

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

Esters:

C18A Preparation of Esters:

1. From acids:
$$R-C-OH + R'OH \xrightarrow{H^+} R-C-OR' + H_2O$$
(R may be alkyl or aryl)

Reactivity of R'OH is $1^{\circ} > 2^{\circ} > 3^{\circ}$

$$\begin{array}{ccc} O & O \\ \parallel & \parallel \\ (R-C-OH) \text{ similarly } HC-OH > 1^{0} > 2^{0} > 3^{0} \end{array}$$

2. From Acid Chloride or anhydride:

$$\begin{array}{ccc}
O & O & O \\
R - C & + R'OH (or ArOH) & \longrightarrow R - C & (or R - C - OAr) + HCl \\
Cl & OR'
\end{array}$$

$$(RCO)_{,O} + R'OH \longrightarrow R - COOR' (or RCOOAr) + RCOOH$$

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 looses water spontaneously by yield of cyclic ester known as lactone. Treatment with base (OH⁻) rapidly opens the lactone ring.

$$\begin{array}{c|c} R-CHCH_2CH_2COO^+Na & \xrightarrow{H^+} & \begin{array}{c} H_2C-C \\ | & OO\\ \hline OH \end{array} \\ \begin{array}{c} OH^- \\ \hline \end{array} \\ \begin{array}{c} OH_2-CHR \\ \hline \gamma-lactone \\ cyclic ester: five membered ring \end{array}$$

C18B Reactions of Esters:

1 Conversion into acids and acid derivatives
$$R - C$$
 $+ H_2O$ $\xrightarrow{H^+} R - C - OH + R'OH$
 OR' $\rightarrow R - COO^- + R'OH$

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2. Conversion into amides

$$CH_1COOC_1H_2 + NH_3 \rightarrow CH_1CONH_1 + C_1H_2OH_1$$

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, —OR' is replaced by –NH,.

3. Conversion into esters: Transesterfication:
$$R - C$$
 $+ R'' - OH$ $R - C$ $+ R'OH$ OR''

Acid is \rightarrow H₂SO₄ or dry HCl

Base \rightarrow alkoxide ion generally used.

4. Reactions with Grignard Reagent:
$$R-C-O'R+2R''-MgX \longrightarrow R-C-R''$$
OH
Tertiary alcohol

5. Reduction to alcohols:

(a) <u>Catalytic hydrogenation : Hydrogenolysis</u>

$$RCOOR' + 2H_2 \xrightarrow{CuO, CuCr_2O_4} RCH_2OH + R'OH_2OH +$$

(b) Chemical Reduction:
$$R - COOR' + LiAlH_4 \xrightarrow{Anhyd.ether} RCH_2OH + R'OH$$

6. Reaction with carbanions: Clasien Condensation:

$$R-C \xrightarrow{H} C -C \xrightarrow{O} C \xrightarrow{OC_2H_s} R-C -CH_2 -C \xrightarrow{O} OR'$$

Example:

2CH₃COOC₂H₅ + Na⁺⁻OC₂H₅
$$\xrightarrow{C_2H_5OH}$$
 CH₃ - C - CH - C - OC₂H₅ +Na + 2C₂H₅OH
$$\downarrow H^+$$
O
CH₃ - C - CH₂COOC₂H₅
Ethylacetoacetate
$$\beta$$
-keto ester

7. Crossed Clasien Condensation :

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

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PHENOLS

(Catechol)

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 napthols and phenanthrols, e.g.

C19B <u>Physical Properties of Phenols</u>: 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.

(Resorcinol)

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

(Hydroquinone)

C20A Synthesis of Phenols:

<u>Laboratory Synthesis</u>: 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.

1. General Reaction:
$$Ar - NH_2 \xrightarrow{HONO} Ar - N_2^+ \xrightarrow{Cu,O} Ar - OH$$

$$\underbrace{\begin{array}{c} \text{NH}_2 \\ \text{Specific Example :} \\ \hline \\ \text{CH}_3 \end{array} \xrightarrow{\begin{array}{c} \text{OI NaNO}_2, \text{ H}^+, 0\text{-}5^{\circ}\text{C} \\ \hline \\ \text{(2) Cu}_2\text{O}, \text{Cu}^{2^+}, \text{H}_2\text{O} \end{array}} \xrightarrow{\begin{array}{c} \text{OH} \\ \text{Br} \\ \text{CH}_3 \end{array}} \text{Br}$$

2-Bromo-4-Methylphenol

Industrial Synthesis:

2. <u>Hydrolysis of Cholorobenzene (Dow Process)</u>:

$$\begin{array}{c}
Cl \\
+ 2NaOH \xrightarrow{350^{\circ}C} & ONa \\
+ NaCl + H_2O
\end{array}$$

$$\begin{array}{c}
ONa \\
+ NaCl + H_2O
\end{array}$$

$$\begin{array}{c}
OH \\
+ NaCl
\end{array}$$

(The mechanism for the reaction probably involves benzyne intermediate)

3. <u>Alkali Fusion of Sodium benzene sulfonate</u>: Sodium benzene sulfonate is melted (fused) with sodium hydroxide at 350°C to produce sodium phenoxide acidification then yields phenol.

4. From Cumene Hydroperoxide:

$$CH_{3}$$

$$C$$

II This cumene is oxidized to cumene hydrolperoxide

$$C_{6}H_{5} - CH + O_{2} \xrightarrow{95-135^{0}C} C_{6}H_{5} - C - O - O - H$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CUmene hydroperoxide$$

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

$$C_{6}H_{5} - C - O - OH \xrightarrow{H_{3}O+ \\ CH_{3}} C_{6}H_{5}OH + C = O$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

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 pKa values of most alcohols are of the order of 18. However the pKa values of phenols are smaller than 11.

Let us compare two superficially similar compounds cyclohexanol ane phenol.

$$OH \qquad OH \qquad PK_a = 18 \qquad pK_a = 9.89$$

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 phenoxid 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 sp^2 hybridized, whereas in cyclohexanol sp^3 bybridised. Greater the S- characted 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 ${\rm H_2O}$ is stronger acid than 1-wexanol.

Acidity order of Phenols:

(a)
$$OH OH OH CH_3$$
 (b) $OH OH OH CH_3$ $CH_3 CH_3 CH_3$ (c) $OH OH OH CH_3$ $CH_3 CH_3$ (d) $OH CH_3$ O

(c) OH OH NO₂ OH NO₂ OH NO₂
$$\rightarrow$$
 CH₃COOH \rightarrow NO₂ \rightarrow NO₂ \rightarrow CH₃COOH \rightarrow NO₂ \rightarrow NO₂ \rightarrow NO₂ \rightarrow NO₂ \rightarrow NO₂ \rightarrow NO₃ \rightarrow NO₄ \rightarrow NO₅ \rightarrow NO₅ \rightarrow NO₆ \rightarrow NO₇ \rightarrow NO₇ \rightarrow NO₈ \rightarrow NO₈ \rightarrow NO₈ \rightarrow NO₈ \rightarrow NO₈ \rightarrow NO₉ \rightarrow

Distinguishing and separating phenols from alcohols and carboxylic acids:

- 1. Phenols dissolve in aqueous sodium hyroxide 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 solible 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.

Thest 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).

(a) General Reaction:
$$ArOH \xrightarrow{NaOH} ArO^{-} \stackrel{+}{N} a \xrightarrow{R-X} ArOR + NaX$$

(b) <u>Cleavage of Alkyl-Aryl Ether:</u>

$$C_6H_5 - O - R \xrightarrow{conc.HX} C_6H_5 - OH \xrightarrow{HX} no rxn. + RX$$

- 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.

OH
$$+ 3Br_{2} \xrightarrow{H_{2}O} \xrightarrow{Br} + 3HBr$$

$$Br$$

$$2, 4, 6-Tribromophenol$$

(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.

OH
$$+ Br_{2} \xrightarrow{5^{\circ}C} \rightarrow \qquad + HBr$$

$$\xrightarrow{Br}$$
p-Bromophenol
$$(80 - 84\%)$$

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

$$\begin{array}{c|c}
OH & OH \\
\hline
 & 20\% \text{ HNO}_3
\end{array}$$

$$\begin{array}{c}
OH \\
+ OH \\
\hline
 & NO_2
\end{array}$$

$$\begin{array}{c}
OH \\
+ OH \\
\hline
 & NO_2
\end{array}$$

$$\begin{array}{c}
OH \\
+ OH \\
\hline
 & NO_2
\end{array}$$

$$\begin{array}{c}
(15\%)
\end{array}$$

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.

(b)
$$OH \longrightarrow NO_2 \longrightarrow OH \longrightarrow NO_2$$

$$OH \longrightarrow NO_2 \longrightarrow NO_2$$

$$OH \longrightarrow NO_2 \longrightarrow OH \longrightarrow NO_2$$

$$OH \longrightarrow OH \longrightarrow OH$$

$$OH \longrightarrow OH \longrightarrow OH$$

$$OH \longrightarrow OH$$

$$OH$$

5. <u>Sulfonation</u>: 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. <u>Kolbe's Reaction:</u> The phenoxide ion is even more suceptible to electrophilic aromatic substitution, then 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 anyhydride yields widely used pain reliver aspirin.

OH OC - CH₃

$$CO_2H$$
 CO_2H
 CO_2H
 CO_3COOH

Acetyl Salicylic acid
(Aspirin)

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

10. Reimer-Tiemann Reaction:

11. Fries rearrangement:

Rearrangement involves RCO+, which then attacks the ring. <u>Practice Problems :</u>

1. When phenol is distilled with zinc dust, the main product is

(b)

(a) biphenyl

(b) benzene

(c) benzaldehyde

- (d) phenolphtalein
- 2. When sodium benzene sulphonate is fused with sodium hydroxide (solid), the product formed is
 - (a) benzene

(b) phenol

(c) benzene triphenol

- (d) none of these
- 3. Which of the following acids is strongest
 - (a) $C_6H_5SO_3H$
- CH₃COOH
- C₆H₅COOH
- (d) $(COOH)_2$

- 4. Phenol is less acidic then
 - (a) p-nitrophenol

(b) ethanol

(c)

(c) cresol

(d) benzyl alcohol

5. Cumene
$$\xrightarrow{(1)O_2}$$
 (X) and (Y)

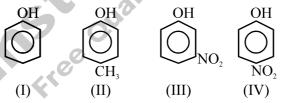
- (X) and (Y) respectively are
- (a) toluene, propene

(b) toluene, propylchloride

(c) phenol, acetone

(d) phenol, acetaldehyde

6. In the following compounds



the order of acidity is

- (a) (c)
- III > IV > I > II II > I > III > IV

- (b) I > IV > III > II
- (d) IV > III > I > II
- 7. When phenol reacts with benzene diazonium chloride, the product obtained as
 - (a) phenyl hydrazine

- (b) p-amino azobenzene
- (c) phenol hydroxylamine
- (d) p-hydroxy azobenzene

8. Phenol
$$\xrightarrow{\text{Zinc}}$$
 (A) $\xrightarrow{\text{Conc.H}_2\text{SO}_4}$ (B) $\xrightarrow{\text{NaOH}}$ (C) . In the above reaction, compounds (A), at 60°

- (B) and (C) are
- (a) benzene, nitrobenzene and aniline
- (b) benzene, dinitrobenzene and m-nitroaniline
- (c) toluene, nitrobenzene and m-toluidine
- (d) benzene, nitrobenzene and hydrazobenzene

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