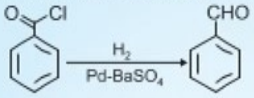
Aldehydes, Ketones and Carboxylic Acids

12 Chapter

ALDEHYDES AND KETONES

1 PREPARATION OF ALDEHYDES

(i) From acyl chlorides (Rosenmund reduction)

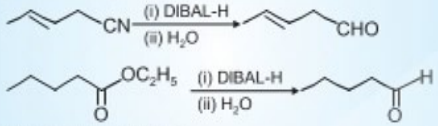


(ii) From Nitriles and Esters

- Stephen reaction

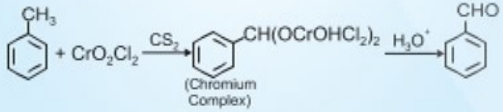
$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$$

(Reduction by DIBAL-H

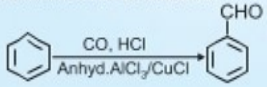


(iii) From Hydrocarbons

- Etard reaction



- Gatterman-Koch reaction



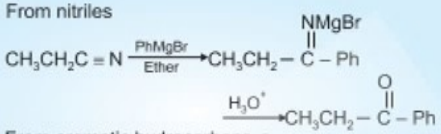
2 PREPARATION OF KETONES

(i) From acyl chlorides

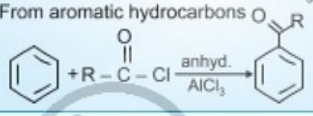
$$2R - Mg - X + CdCl_2 \longrightarrow R_2Cd + 2\,Mg(X)Cl$$

$$2R' - \overset{O}{\overset{\|}{C}} - Cl + R_2Cd \longrightarrow 2R' - \overset{O}{\overset{\|}{C}} - R + CdCl_2$$

(ii) From nitriles



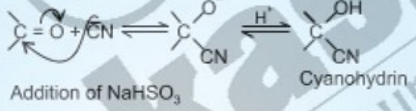
(iii) From aromatic hydrocarbons



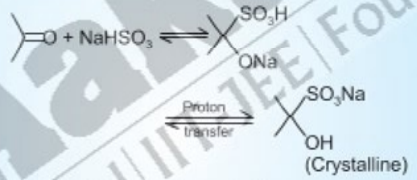
3 CHEMICAL REACTIONS

(i) **Nucleophilic addition reactions**

(a) Addition of hydrogen cyanide (HCN)

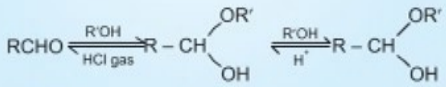


(b) Addition of $NaHSO_3$

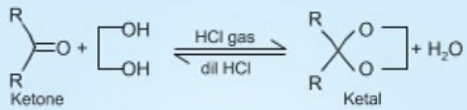


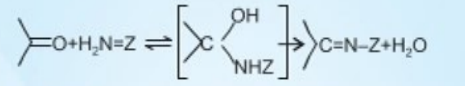
- Bisulphite addition product is crystalline
- It is water soluble and converted back to original carbonyl compound by treating it with acid or alkali
- It is useful for separation and purification of aldehydes.

(c) Addition of alcohols :



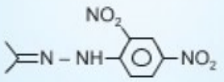
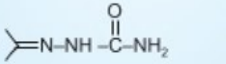
Aldehyde Hemiacetal Acetal





(d) Addition of ammonia and its derivative

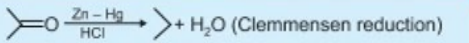
Z = alkyl, aryl, – OH, – NH_2, C_6H_5NH etc

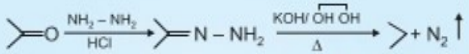
Reagent	Carbonyl derivative	Product name
Ammonia	$=NH$	Imine
Amine	$=NR$	Schiff's base
Hydroxylamine	$=N-OH$	Oxime
Hydrazine	$=N-NH_2$	Hydrazone
2,4-DNP		2, 4- Dinitrophenyl-hydrazone
Semicarbazide		Semicarbazone

(ii) Reduction

(a) Reduction to alcohols : Aldehydes and ketones are reduced to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$

(b) Reduction to hydrocarbons





(Wolff-Kishner reduction)

(iii) Oxidation

- Aldehydes are oxidised to carboxylic acids on treatment with common oxidising agents like HNO_3, $KMnO_4$, $K_2Cr_2O_7$ etc.
- Mild oxidising agents (Tests of aldehydes) **Tollen's test :** Silver mirror is formed on warming aldehyde with freshly prepared ammoniacal $AgNO_3$ solution (*Tollen's reagent*)

$$RCHO + 2[Ag(NH_3)_2]^+ + 3\bar{O}H \rightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$$

Fehling's Test :

- On heating aldehyde with Fehling's reagent, a reddish brown precipitate is obtained.

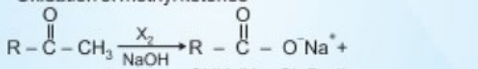
$$R - CHO + 2Cu^{2+} + 5\bar{O}H \rightarrow RCOO^- + Cu_2O\downarrow + 3H_2O$$

(red-brown ppt)

- Aromatic aldehydes do not respond to this test

Haloform reaction :

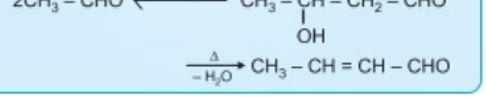
Oxidation of methyl ketones



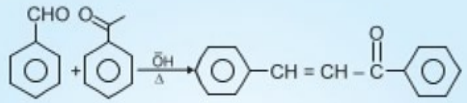
- Iodoform reaction with I_2/NaOH is used for detection of CH_3CO or $CH_3CH(OH)$ groups which produces CH_3CHO group on oxidation.

(iv) Reaction due to α-hydrogen

(i) Aldol condensation reaction :

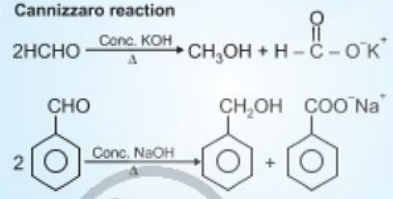


(ii) Cross aldol condenstation

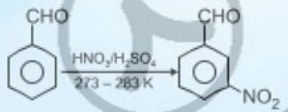


Other reactions

(v) Cannizzaro reaction



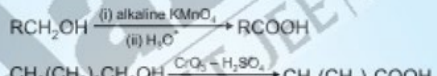
(vi) Electrophilic substitution reaction



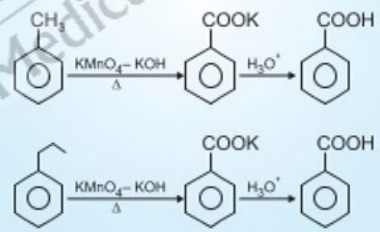
4 CARBOXYLIC ACIDS

- Methods of Preparation

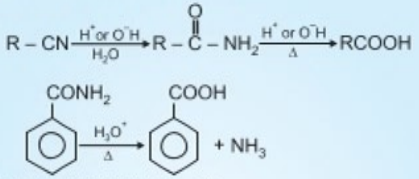
(a) From primary alcohols



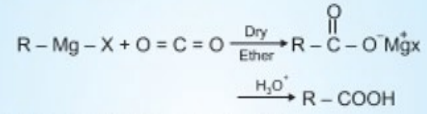
(b) From alkylbenzenes



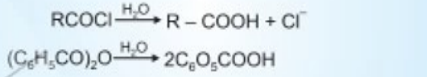
(c) From nitriles and amides



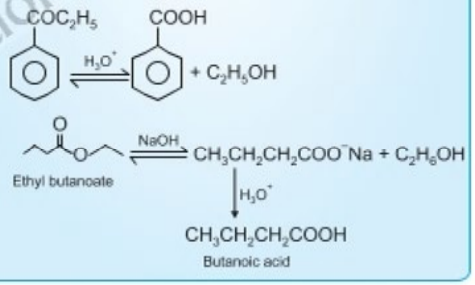
(d) From Grignard reagents



(e) From acyl halides and anhydrides



(f) From esters



5 PHYSICAL PROPERTIES

- Due to extensive association by intermolecular H-bonding carboxylic acids have higher boiling point than aldehydes, ketones and alcohols of comparable molecular mass.
- In vapour phase or in aprotic solvent most carboxylic acids exist as dimer

6 CHEMICAL REACTIONS

(a) Reactions involving cleavage of O – H bond (Acidity)

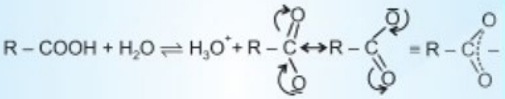
$2RCOOH + 2Na \rightarrow 2RCOO^-Na^+ + H_2$

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

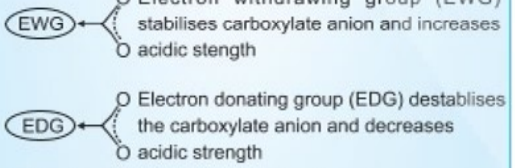
$RCOOH + NaHCO_3 \rightarrow RCOO^-Na^+ + H_2O + CO_2\uparrow$

- Carboxylic acids evolve CO_2 gas on reaction with $NaHCO_3$. This is used to detect the presence of carboxyl group in an organic compound.

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion



- Effect of substituents on the acidity of carboxylic acids :



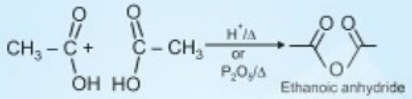
- Acidic strength order of some carboxylic acid

$CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH > ClCH_2CH_2COOH > C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid increases the acidity of corresponding carboxylic acid, Contrary to the decrease expected due to resonance effect.

(b) Reaction involving cleavage of C – OH bond

(i) Formation of anhydrides



(ii) Esterification

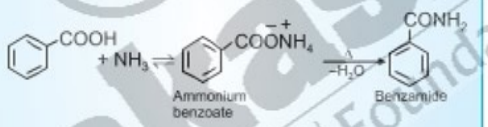
$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$

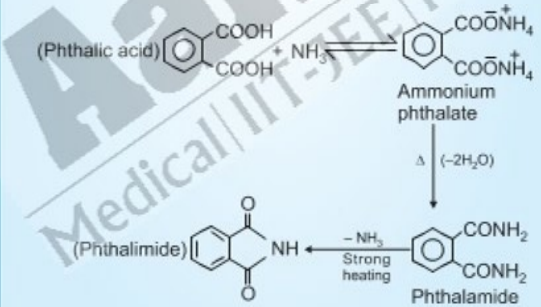
(iii) Reaction with PCl_5 and $SOCl_2$

$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$

$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$

(iv) Reaction with ammonia





(c) Reactions involving – COOH group

(i) Reduction

$RCOOH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4/ether\ or\ B_2H_6} RCH_2OH$

(ii) Decarboxylation

$RCOONa \xrightarrow[\Delta]{NaOH\ \&\ CaO} R - H + Na_2CO_3$

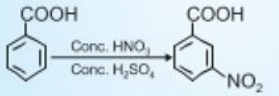
(d) Substitution reactions in the hydrocarbon part

(i) Halogenation (Hell - Volhard-Zelinsky reaction)

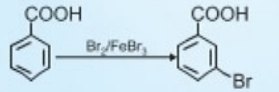
$RCH_2 - COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/Red\ P} R - \underset{X}{CH} - COOH$ (X = Cl, Br)

(ii) Ring substitution

- Aromatic carboxylic acids undergo electrophilic substitution reaction
- They do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating and catalyst aluminum chloride gets bonded to carboxyl group
- Nitration



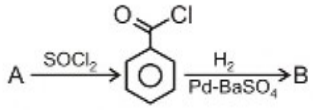
- Bromination



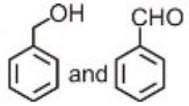
Sharpen Your Understanding

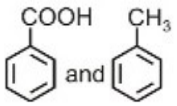
1. Consider the following reaction sequence

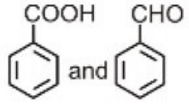
[NCERT Pg. 362]

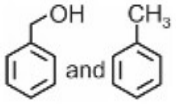


A and B respectively are

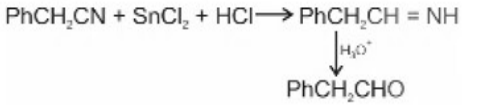
(1) 

(2) 

(3) 

(4) 

2. The given reaction is known as



[NCERT Pg. 362]

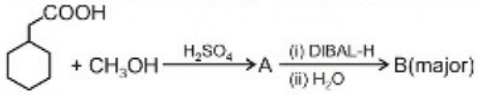
(1) Rosenmund reaction

(2) Stephen reaction

(3) Etard reaction

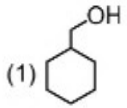
(4) Gatterman-Koch reaction

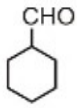
3. Consider the following reaction sequence

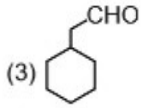


Major product B is

[NCERT Pg. 362, 381]

(1) 

(2) 

(3) 

(4) 

4. Methyl cyanide on reaction with phenyl magnesium bromide followed by hydrolysis yields [NCERT Pg. 364]

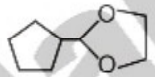
(1) Benzophenone

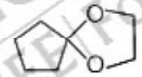
(2) Acetophenone

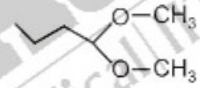
(3) Phenylacetaldehyde

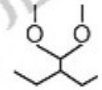
(4) Phenylacetic acid

5. Which among the following is a ketal? [NCERT Pg. 367]

(1) 

(2) 

(3) 

(4) 

6. The pair of compounds which can be distinguished by Tollen's reagent is [NCERT Pg. 369]

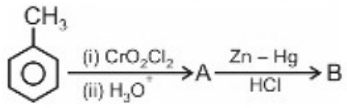
(1) Acetone and Acetaldehyde

(2) Formic acid and Benzaldehyde

(3) Acetic acid and Acetone

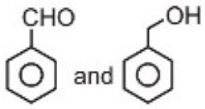
(4) Formaldehyde and Benzaldehyde

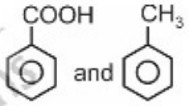
7. Consider the following reaction sequence

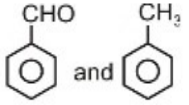


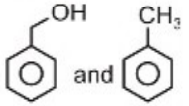
[NCERT Pg. 362, 368]

A and B respectively are

(1) 

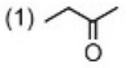
(2) 

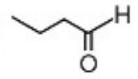
(3) 

(4) 

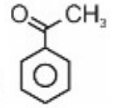
8. The compound which will not give iodoform when reacted with I_2/NaOH(aq) is

[NCERT Pg. 370]

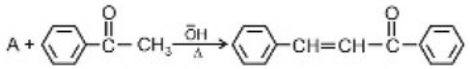
(1) 

(2) 

(3) 

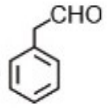
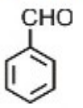
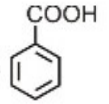
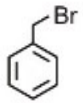
(4) 

9. Consider the following reaction



Compound A is

[NCERT Pg. 372]

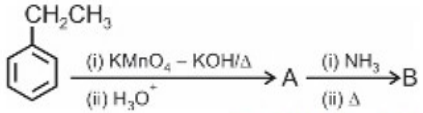
(1) 
(2) 
(3) 
(4) 

10. Strongest acid among the following is

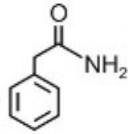
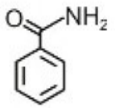
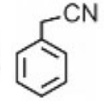
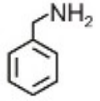
[NCERT Pg. 381]

(1) NO_2CH_2COOH
(2) $HCOOH$
(3) FCH_2COOH
(4) C_6H_5COOH

11. In the given reaction sequence product B is

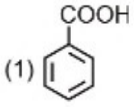
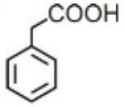
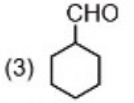


[NCERT Pg. 376, 382]

(1) 
(2) 
(3) 
(4) 

12. The compound which will give HVZ reaction is

[NCERT Pg. 383]

(1) 
(2) 
(3) 
(4) 

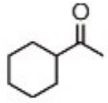
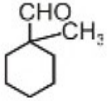
13. When a mixture of acetaldehyde and propionaldehyde is heated in presence of dilute alkali then which of the given compounds is not formed as a product

[NCERT Pg. 372]

(1) $CH_3CH = CH - CHO$
(2) $CH_3CH_2CH = CHCHO$
(3) $CH_3 - CH = C(CH_3) - CHO$
(4) $CH_3 - C(CH_3) = CH - CHO$

14. The compound which will not undergo aldol condensation reaction is

[NCERT Pg. 371]

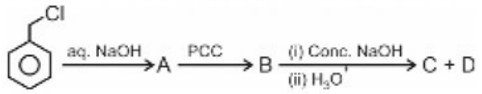
(1) 
(2) 
(3) 
(4) 

15. The compound which will not give positive Fehling test is

[NCERT Pg. 369]

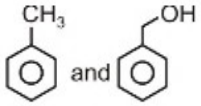
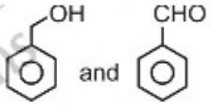
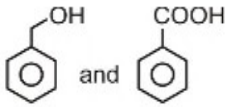
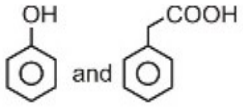
(1) Acetaldehyde (2) Benzaldehyde
(3) Formic acid (4) Formaldehyde

16. Consider the following reaction sequence



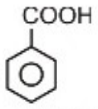
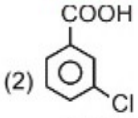
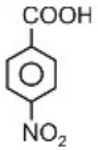
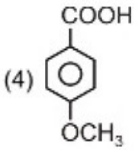
Products C and D are

[NCERT Pg. 372]

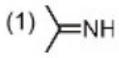
(1) 
(2) 
(3) 
(4) 

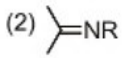
17. Strongest acid among the following is

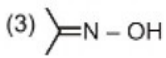
[NCERT Pg. 381]

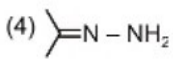
(1) 
(2) 
(3) 
(4) 

18. Which among the following is an oxime? [NCERT Pg. 368]

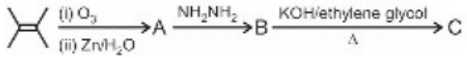
(1) 

(2) 

(3) 

(4) 

19. Consider the following reaction sequence



Product C is [NCERT Pg. 369]

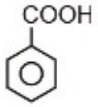
(1) 

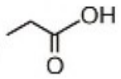
(2) 

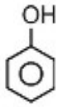
(3) 

(4) 

20. The compound which does not treact with $NaHCO_3$ is [NCERT Pg. 379]

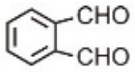
(1) 

(2) 

(3) 

(4) HCOOH

Thinking in Context

1. IUPAC name of  compound is _____. [NCERT Pg. 359]

2. Reagent used in Etard reaction is _____. [NCERT Pg. 362]

3. Treating an alkyl nitrile with Grignard reagent followed by hydrolysis yields _____. [NCERT Pg. 364]

4. Aldehydes react with one equivalent of monohydric alcohol in the pressure of dry HCl to yield alkoxyalcohol intermediate, known as_____. [NCERT Pg. 367]

5. In Wolff-Kishner reduction solvent used is_____. [NCERT Pg. 369]

6. Fehling solution A is _____ and Fehling solution B is_____. [NCERT Pg. 369]

7. When benzaldehyde is heated with acetophenone in presence of dilute NaOH then_____ is obtained as major product [NCERT Pg. 372]

8. In Cannizzaro reaction, one molecule of aldehyde is reduced to_____ while another is oxidized to_____. [NCERT Pg. 372]

9. _____ is called Jones reagent. [NCERT Pg. 372]

10. Butanal when treated with ammoniacal $AgNO_3$ solution then organic product obtained is _____. [NCERT Pg. 369]

11. _____ react with dry ice to form salts of carboxylic acids [NCERT Pg. 376]

12. Benzamide on acidic hydrolysis forms_____. [NCERT Pg. 376]

13. _____ lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda lime [NCERT Pg. 383]

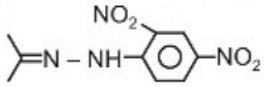
14. Ethanoic acid on heating with P_2O_5 gives_____. [NCERT Pg. 381]

15. Phthalamide on strong heating forms_____. [NCERT Pg. 383]

16. Carboxylic acids are reduced to _____ with $LiAlH_4$. [NCERT Pg. 385]

17. Iodoform reaction with sodium hypoiodite is used for detection of _____ or _____ groups. [NCERT Pg. 370]

18. Addition of ammonia derivative to carbonyl compounds is catalyzed by_____. [NCERT Pg. 368]

19. Compound  is formed when _____ reacts with 2, 4–DNP. [NCERT Pg. 368]

20. Addition of HCN to aldehydes and ketones is catalyzed by_____. [NCERT Pg. 367]

❑ ❑ ❑