

NCERT EXERCISES

- 12.1. What is meant by the following terms? Give an example of the reaction in each case.
- (i) Cyanohydrin
- (ii) Acetal
- (iii) Semicarbazone
- (iv) Aldol
- (v) Hemiacetal
- (vi) Oxime
- (vii) Ketal
- (viii) Imine
- (ix) 2,4-DNP derivative
- (x) Schiff's base.

Ans:

(i) Cyanohydrin: gem-Hydroxynitriles, i.e., compounds possessing hydroxyl and cyano groups on the same carbon atom are called cyanohydrins. These are produced by addition of HCN to aldehydes or ketones in a weakly basic medium.

$$>C = O + HCN \xrightarrow{pH=9-10} >C < CN$$

(ii) gem - Dialkoxy compounds in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in presence of dry HCl gas.

monohydric alcohol in presence of dry HCl gas.

$$CH_3 = O + H - OCH_2CH_3 = Dry HCl gas, \Delta + H_2OCH_2CH_3 + H_2OCH_2CH_3$$

When dihydric alcohol is used cyclic acetal is formed

$$CH_3$$
 $C = O + H-O-CH_2$ $PTS, Reflux$ CH_3 $C = O-CH_2$ CH_2 CH_2 CH_2 CH_2 CH_2 CH_2

These are easily hydrolysed by dilute mineral acids to regenerate the original aldehydes. Therefore, these are used for the protection of aldehyde group in organic synthesis.

(iii) Semicarbazones are derivatives of aldehydes and ketones and are produced by action of semicarbazide on them in acidic medium.

$$CH_3$$
 $C = O + H_2NNH - C - NH_2 \xrightarrow{pH 3.5} CH_3$
 CH_3
 $C = NNHCONH_2 + H_2O$

(iv) Aldols are P-hydroxy aldehydes or ketones and are produced by the condensation of two molecules of the same or one molecule each of two different aldehydes or ketones in presence of a dilute aqueous base. For example,

$$CH_{3}CH = O + H - CH_{2}CHO \xrightarrow{\text{Dil NaOH}} CH_{3} - CH - CH_{2} - CHO$$

$$\beta$$
-hydroxy butylaldehyde
(An aldol)

$$C = O + H - CH_2 - C - CH_3 \xrightarrow{Ba(OH)_2} CH_3 - C - CH_2 - C - CH_3$$

$$CH_3 O$$

- (v) gem Alkoxyalcohols are called hemiacetals. These are produced by addition of one molecule of a monohydric alcohol to an aldehyde in presence of dry HCl gas.
- (vi) Oximes are produced when aldehydes or ketones react with hydroxyl amine in weakly acidic medium.

$$CH_3$$
 $C = O + H_2NOH \xrightarrow{pH 3.5} CH_3$
 CH_3
 $C = NOH$

(vii) Ketals are produced when a ketone is heated with dihydric alcohols like ethylene glycol in presence of dry HCl gas or /3-toluene sulphonic acid (PTS).

These are easily hydrolysed by dilute mineral acids to regenerate the original ketones. Therefore, ketals are used for protecting keto groups in organic synthesis.

(viii) Compounds containing -C = N - group are called imines. These are produced when aldehydes and ketones react with ammonia derivatives.

$$>C = O + H_2N - Z \longrightarrow >C = N - Z + H_2O$$

Z = alkyl, aryl, $-NH_2$, $-OH$, $-NHC_6H_5$, $-NHNHCONH_2$, etc.

(ix) 2, 4-Dinitrophenyl hydrazone (i.e., 2,4-DNP derivatives) are produced when aldehydes or ketones react with 2,4-dinitrophenyl hydrazine in weakly acidic medium.

$$CH_3$$

$$C = O + H_2NNH$$

$$NO_2 \xrightarrow{pH 3 5} CH_3$$

$$CH_3$$

$$C = NNH$$

$$CH_3$$

- 2, 4-DNP derivatives are used for identification and characterisation of aldehydes and ketones.
- (x) Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines or SchifFs bases.

$$R - CH = O + H_2 N - R' \xrightarrow{\text{Trace of } H^+} R - CH = N - R' + H_2O$$
Schiff's Base

e.g.,
$$CH_3CH = O + H_2NCH_2CH_3 \xrightarrow{Trace \text{ of } H^+} CH_3CH = NCH_2CH_3 + H_2O$$

- 12.2 Name the following compounds according to IUPAC system of nomenclature:
- (i) CH₃CH (CH₃)-CH₂ CH₂-CHO
- (ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2CI$
- (iii) CH3CH=CHCHO
- (iv) CH₃COCH₂COCH₃
- (v) CH₃CH(CH₃)CH₂C(CH3)2COCH₃
- (vi) (CH₃)₃CCH₂COOH.
- (vii) OHCC₆H₄CHO-p

Ans:

- (i) 4-Methyl pentanal
- (ii) 6-Chloro-4-ethylhexan-3-one
- (iii) But-2-en-l-al

- (iv) Pentane-2,4-dione
- (v) 3,3,5-Trimethyl-hexan-2-one
- (vi) 3,3-Dimethyl butanoic acid
- (vii) Benzene-1,4-dicarbaldehyde
- 12.3. Draw the structures of the following compounds:
- (i) 3-Methylbutanal
- (ii) p-Nitropropiophenone
- (iii) p-Methylbenzaldehyde
- (iv) 4-Methylpent-3-en-2-one
- (v) 4-Chloropentan-2-one
- (vi) 3-Bromo-4-phenylpentanoic acid
- (vii) pp-Dihydroxybenzophenone
- (viii) Hex-2-en-4-ynoic acid

Ans:

(iv)
$$CH_3 - C - CH = C - CH_3$$

 $CH_3 - CH_3$

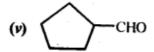
(viii)
$$CH_3 - C = C - CH = CH - COOH$$

12.4. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

- (i) $CH_3CO(CH_2)_4CH_3$
- (ii) CH_3CH_2CH $BrCH_2CH(CH_3)CHO$

(iii) CH₃(CH₂)₅CHO

(iv) Ph-CH=CH-CHO



(vi) Ph COPh

Ans:

IUPAC name

- (i) Heptan-2-one
- (ii) 4-Bromo-2-methylhexanal
- (iii) Heptanal
- (iv) 3-Phenylpropan-2en-1-al
- (v) cyclopentane carbaldehyde
- (vi) Diphenylmethanone

Common name

γ-Bromo-α-methyl caproaldehyde

β-Phenyl acrolein

Benzophenone

12.5. Draw structures of the following derivatives:

- (i) The 2,4-dinitrophenylhydrazone of benzaldehyde
- (ii) Cydopropanone oxime
- (iii) Acetaldehydedimethylacetal
- (iv) The semicarbazone of cyclobutanone
- (v) The ethylene ketal of hexan-3-one
- (vi) The methyl hemiacetal of formaldehyde Ans:

- 12.6. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents. .
- (i) PhMgBr and then H₃O⁺
- (ii) Tollen reagent
- (iii) Semicarbazide and weak acid
- (iv) Excess ethanol and acid
- (v) Zinc amalgam and dilute hydrochloric acid Ans:

$$(i) \qquad \begin{array}{c} OMgBr \\ CH = O \\ \hline CPh - MgBr \\ \hline Dry \, ether \end{array} \qquad \begin{array}{c} OH \\ C - H \\ \hline Ph \end{array} \qquad \begin{array}{c} CH - H \\ \hline Ph \end{array} \qquad \begin{array}{c} OH \\ C - H \\ \hline Ph \end{array} \qquad \begin{array}{c} OH \\ C - H \\ \hline Ph \end{array} \qquad \begin{array}{c} OH \\ \hline Ph \end{array}$$

12.7. Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation

and Cannizzaro reaction.

- (i) Methanal
- (ii) 2-Methylpentanal
- (iii) Benzaldehyde
- (iv) Benzophenone
- (v) Cyclohexanone
- (vi) 1-Phenylpropanone
- (vii) Phenylacetaldehyde
- (viii) Butan-1-ol 1
- (ix) 2,2-Dimethylbutanal

Ans:

2-Methylpertfanal, cyclohexanone, 1-phenylpropanone and phenylacetaldehyde contain one or more a-hydrogen and hence undergo aldol condensation. The reactions and the structures of the expected products are given below:

$$(ii) \ \ 2\text{CH}_3\text{CH}_2\text{CH}_2 - \text{CH} - \text{CHO} \xrightarrow{\text{Dil NaOH}} \ \ \text{CH}_3\text{CH}_2\text{CH}_2 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_2\text{CH}_2\text{CH}_3$$

$$\text{CH}_3 \qquad \qquad \text{CH}_3 \qquad \qquad \text{CH}_3 \quad \text{CH}_2\text{CH}_2\text{CH}_2$$

$$\text{CH}_3 \qquad \qquad \text{CH}_3 \quad \text{OH} \quad \text{CHO}$$

$$\text{2-Methylpentanal} \qquad \qquad \text{3-Hydrox-2-4-dimethyl}$$

$$\text{2-propylheptanal} \qquad \qquad \text{3-Pydrox-2-4-dimethyl}$$

$$(v) \ 2 \longrightarrow O \xrightarrow{\text{Dil NaOH}} O \xrightarrow{\text{OH}} OH$$

2-(1-Hydroxy-1-cyclohexyl) cyclohexan-1-one

(vi)
$$2 \longrightarrow COCH_2CH_3 \longrightarrow COCH_2CH_2 \longrightarrow COCH_2CH_2 \longrightarrow COCH_2CH_2 \longrightarrow COCH_2CH_2CH_2 \longrightarrow COCH_2CH_2 \longrightarrow COCH_2CH_2 \longrightarrow COCH_2CH_2 \longrightarrow COCH_2 \longrightarrow COCH$$

3-Hydroxy-2-methyl-1,3-dipheylpentan-1-one

Methanal, benzaldehyde and 2,2-dimethylbutanal do not contain α -hydrogen and hence undergo Cannizzaro reaction. The reactions and the structures of the expected products are given below:

$$(ix) \quad \begin{array}{c} \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 \text{CH}_2 - \overset{}{\text{C}} - \text{CHO} \xrightarrow{\text{Conc. NsOH}} \text{CH}_3 \text{CH}_2 - \overset{}{\text{C}} - \text{CH}_2 \text{OH} + \text{CH}_3 \text{CH}_2 - \overset{}{\text{C}} - \text{COONa} \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \end{array}$$

Benzophenone (iv) is a ketone having no α -hydrogen while butan-l-ol (viii) is an alcohol. Both of these neither undergo aldol condensation nor cannizzaro reaction.

- 12.8. How will you convert ethanal into the following compounds?
- (i) Butane-1,3-diol
- (ii) But-2-enal
- (iii) But-2-enoic acid

Ans:

(ii)
$$2 \text{CH}_3 \text{CHO} \xrightarrow{\text{Dil NaOH}} \text{CH}_3 \text{CH}(\text{OH}) \text{CH}_2 \text{CHO} \xrightarrow{\text{H}_3 \text{O}^+} \text{CH}_3 \xrightarrow{\text{CH} = \text{CH}} \text{-CHO}$$

(iii)
$$CH_3CHO \xrightarrow{(i)Dil NaOH} CH_3CH = CHCHO \xrightarrow{[Ag(NH_3)_2]^+OH^-} CH_3CH = CHCO_2H_3CH = CHCO_2H_3$$

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