

Daily Tutorial Sheet-6	Level-2
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**76.(ACD)** (A): Fehling solution gives red ppt. with all aldehydes (but not with benzaldehyde).

(B): 2, 4 DNP gives orange ppt. with all carbonyl compounds.

(C) : Diethyl amine is a secondary amine,  $C_6H_5CHO$  will not react as it does not have a hydrogen  $CH_3CHO$  will form enamine with diethylamine.

(D): KCN/EtOH gives Benzoin condensation with benzaldehyde only.

**77.(CD)** Tollen's reagent : amm.  $AgNO_3 = [Ag(NH_3)_2OH] = Ag_2O$ 

$$\begin{array}{c} RCHO \xrightarrow{Ag_2O} RCOOH + Ag \downarrow \\ \text{(All aliphatic aldehydes)} & white ppt (silver mirror test) \end{array}$$

(A) Both CH<sub>3</sub>CHO and HCHO  $\longrightarrow$  Ag  $\downarrow$ 

**(B)**  $CH_3CHO \longrightarrow Ag \downarrow$ 

 $C_6H_5CHO \longrightarrow Ag \downarrow$  (Also respond to Tollen's Test)

(C)  $CH_3COOH \xrightarrow{Amm} No reaction$  $HCOOH \longrightarrow Ag \downarrow + CO_2 + H_2O$ 

(Among acids, only formic acid is oxidised by Tollen's reagent)

**(D)** C<sub>6</sub>H<sub>5</sub>CHO responds to Tollen's test, but CH<sub>3</sub>COCH<sub>3</sub> does not.

**78.(BC)**  $\beta$ -hydroxy carbonyl compound is called as an Aldol. Aldehydes and ketones having  $\alpha$ -H forms aldol in alkaline medium. (B) & (C) is correct option as others do not have  $\alpha$ -H.

**79.(A)** MnO<sub>2</sub> oxidises unsaturated alcohols to give  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds.

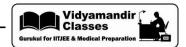
$$\mathsf{CH_3CH_2CH} = \mathsf{CH} - \mathsf{CH_2OH} \xrightarrow{\quad \mathsf{MnO_2} \quad } \mathsf{CH_3CH_2CH} \stackrel{\beta}{=} \overset{\alpha}{\mathsf{CH}} - \mathsf{CH} = \mathsf{O}$$

CrO<sub>3</sub> in CH<sub>3</sub>COOH and H<sub>2</sub>CrO<sub>4</sub> in acetone oxidises 2° alcohols to ketones.

80.(B) 
$$\begin{array}{c} CH_3 - C - CH_3 \xrightarrow{-OH} CH_3 - C = CH - C - CH_3 \xrightarrow{1. \ I_2/NaOH} \\ CH_3 - C - CH_3 \xrightarrow{-OH} CH_3 - C = CH - C - CH_3 \xrightarrow{1. \ I_2/NaOH} \\ CH_3 - C - CH_3 + HO - C - C - OH \xrightarrow{KMnO_4} CH_3 - C = CH - C - OH + CHI_3 \\ Oxidative Cleavage CH_3 \end{array}$$

81.(C) 
$$CHCl_3 \xrightarrow{O_2} COCl_2 \xrightarrow{C_2H_5OH} O = C \xrightarrow{OC_2H_5} \xrightarrow{2CH_3MgBr} O = C \xrightarrow{CH_3} O \xrightarrow{OC_2H_5} O = C \xrightarrow{CH_3} O \xrightarrow{OC_2H_5} O = C \xrightarrow{CH_3} O \xrightarrow{C_2H_5O-C-O-C_2H_5} \xrightarrow{MeMgBr} C_2H_5 - O - C - Me + Mg \xrightarrow{OC_2H_5} O = C \xrightarrow{CH_3} O = C \xrightarrow{CH_3MgBr} O = C \xrightarrow{CH_3} O = C \xrightarrow{CH_3} O = C \xrightarrow{CH_3MgBr} O = C \xrightarrow{CH_3MgBr} O = C \xrightarrow{CH_3} O = C \xrightarrow{CH_3MgBr} O = C \xrightarrow{CH_3} O = C \xrightarrow{CH_3MgBr} O = C \xrightarrow{CH_3} O = C \xrightarrow{CH_3MgBr} O = C \xrightarrow{CH_3$$

**82.(ABC)** Identify aldehydes with no  $\alpha$  -hydrogen atom (a condition for Cannizzaro reaction). (B), (C) and (D) all do not have  $\alpha$  -H. However (D), CCl<sub>3</sub>CHO would prefer to give Chloroform reaction with NaOH.



$$\textbf{83.(CD)} \quad \text{Note}: \quad R - \overset{\beta}{\text{COC}} \overset{\alpha}{\text{H}_2} \text{COOH} \xrightarrow{\quad \Delta \quad} R \, \text{COCH}_3 \quad ; \quad R - \overset{\beta}{\text{CH}_2} \overset{\alpha}{\text{COCOOH}} \xrightarrow{\quad \Delta \quad} R \, \text{CH}_2 \text{COOH} \\ \beta \text{-Keto acid} \qquad \qquad A \, \text{Ketone} \qquad \alpha \text{-Keto acid} \qquad \qquad A \text{n acid}$$

Option (D) is correct : 
$$\begin{array}{c} O \\ \hline \\ COCH_3 \end{array} \xrightarrow{NaOH} \begin{array}{c} H^+ \\ \hline \\ COOH \end{array} \xrightarrow{A} \begin{array}{c} COOH \\ \hline \end{array} \xrightarrow{A} \begin{array}{c} O \\ \hline \\ COOH \end{array}$$

Note :  $\frac{\text{NaOH}}{\text{I}_2}$  (= NaOI) Observe that option (C) is also correct.

**84.(B)** HSO $_3^-$  is a large size nucleophile, hence in the addition product  $C = O \xrightarrow{NaHSO_3} C \xrightarrow{OH} SO_3Na$  there is too much steric crowding.

All aldehydes give this addition reaction however among ketones, only acetone, acetophenone and cyclohexanone give this addition. Hence options (II) and IV are not correct.

A, B, C, are correct options.

**Note:**  $S_E$  (Electrophilic Substitution) are little difficult as 'ortho' position (w. r. t all  $CH_3$  group) is sterically hindered.

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