SOLUTIONS

Module - 5 / JEE-2021

In-Chapter Exercises	Chemistry	Oxygen Containing Organic Compounds - III

EXERCISE

1.(C) $CH_3COOAg + Br_2 \xrightarrow{\Delta} CH_3Br$ (Hunsdiecker Reations)

$$CH_3COOH \xrightarrow{P/Br_2} \underset{\underset{Br}{|}}{CH_2} - COOH \xrightarrow[\Delta]{\text{soda lime}} CH_3Br + CO_2$$

2.(ABD) $CH_3COCl + CH_3COONa \longrightarrow CH_3 - \overset{O}{\overset{\|}{C}} - O - \overset{O}{\overset{\|}{C}} - CH_3$; $CH_3COCl + PhOH \longrightarrow CH_3 - COOPh$

3.(B) Decarboxylation occurs in β-ketoacids and β, γ - unsaturated acids.

4.(B) $(CH_3CO)_2O \xrightarrow[\Delta]{\text{ethanol}} \underset{(C)}{CH_3COOEt} + \underset{(B)}{CH_3CH_2OH}$

5.(A) $CH_3 - CH_2 - COOH \xrightarrow[\Delta]{Br_2/P} CH_3 - \underset{\underset{Br}{|}}{CH} - COOH$ (HVZ Reaction)

$$\xrightarrow[\Delta]{NaN_3 + \text{Conc. } H_2SO_4} CH_3CH_2NH_2 \text{ (Schmidt Reaction)}$$

6.(B) The increasing is nucleophilic character is : $\underset{\text{(resonance)}}{CH_3COO^-} < \underset{\text{(elecctronegativety)}}{\bar{O}H} < NH_2^-$

7.(B) **(I)** $CH_3 - \overset{\overset{O}{\|}}{C} - \ddot{O} - CH_3 \longleftrightarrow CH_3 - \overset{\overset{O^-}{|}}{C} = \overset{+}{O} - CH_3$

(II) $CH_3 - \overset{\overset{O}{\|}}{C} - \ddot{O} - \overset{O}{\overset{\|}{C}} - CH_3 \longleftrightarrow CH_3 - \overset{\overset{O^-}{|}}{C} - \overset{+}{O} - \overset{O}{\overset{\|}{C}} - CH_3 \longleftrightarrow CH_3 - \overset{O}{\overset{\|}{C}} - \overset{+}{O} = \overset{O^-}{\overset{|}{C}} - CH_3$

In (II), there are two carbonyl groups, each will get a comparatively lesser chance to get delocalised leading to "a close to double bond" character $\Rightarrow$ lesser bond length $\Rightarrow$ $x > y$.

8.(A) $CH_3CH_2ONa \xrightarrow[2.\ H^+]{1.\ CO,\ \Delta,\ \text{Pressure}} CH_3CH_2COOH(A)$

$$CH_2 = CH_2 + CO + H_2O \xrightarrow[\Delta]{H_3PO_4} CH_3CH_2COOH\ (B)$$

9.(ABC) Sulphonic acids and Carboxylic acids also react with $NaHCO_3$ to give off CO_2.

Picric acid (2, 4, 6-trinitrophenol) is very strong acid due to strong EW nature of three nitro groups. Phenol being weaker acid than H_2O will not reacts with $NaHCO_3$.

10.(A) $C_6H_5CO\overset{\cdot\cdot}{\underset{\cdot\cdot}{:}}OH + CH_3\overset{18}{O}H \xrightarrow{HCl} C_6H_5\overset{O}{\overset{\|}{C}} - \overset{18}{O} - CH_3$

11.(B) $CH_3-\overset{O}{\overset{\|}{C}}-O\,\vdots\,CMe_3 \xrightarrow[H_2O^{18}]{H^+} CH_3-\overset{OH}{\overset{|}{C}}=O+Me_3C-\overset{18}{O}H$

$(CH_3)_3C-OH \xrightarrow[-H_2O]{H^+} \xrightarrow{-H^+} H_2C=C(CH_3)_2$ (If Alcohol part in an ester is 3°, during hydrolysis alkene is formed)

12. (D) $(CH_3)_2C=CHCH_2CHO \xrightarrow{[O]} (CH_3)_2CO + CH_2\langle^{COOH}_{COOH}$

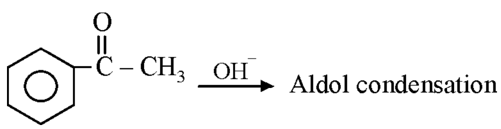
- If we use hot acidic $K_2Cr_2O_7$; then acetone also undergoes degradation to give acetic acid and CO_2.
- Also observe if malonic acid is heated, it too gives acetic acid.

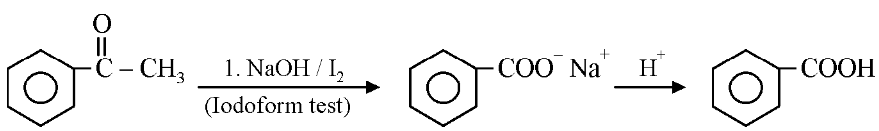
13. (A) $H-\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow{H^+} \underset{(B)}{HCOOH} + \underset{(C)}{CH_3OH} \xrightarrow{[O]} \underset{(B)}{HCOOH}$

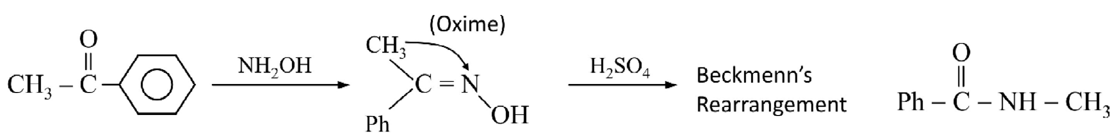
$HCOOH \xrightarrow{\text{Tollen's test}} CO_2 + H_2O + Ag\downarrow$

- HCOOH being easily oxidizable, gives Tollen's test

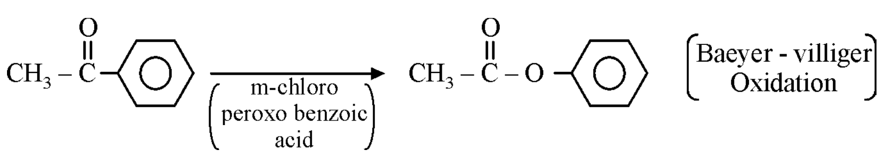
14. (D) $\underset{(X)}{CH_3\overset{O}{\overset{\|}{C}}-OH + HN_3} \xrightarrow{H_2SO_4} \underset{(Y)}{CH_3NH_2} + CO_2 + N_2$ [Schmidt Reaction)

15. (B) (A) 

(B) 

(C) 

- Also visualise the other geometric isomer of oxime and another amide after rearrangement.

(D) 

16. (B) $BaCO_3 + H_2SO_4 \longrightarrow CO_2(g)$

$CH_2=CHBr \xrightarrow{Mg/THF/\Delta} CH_2=CH-MgBr \xrightarrow[H_3O^+]{CO_2} CH_2=CH-COOH$ (Acrylic acid)

17. (C) $CH_3CH=CHCHO \xrightarrow{1.\ NaBH_4} CH_3CH=CH-CH_2OH \xrightarrow[ZnCl_2]{HCl}$ Lucas Test (Positive Result)

(allylic alcohol also give Lucas test)

$CH_3CH=CH-CH_2OH \xrightarrow{HCN/ZnCl_2} CH_3CH=CHCH_2Cl \xrightarrow[H_3O^+]{KCN} CH_3CH=CH-CH_2COOH$

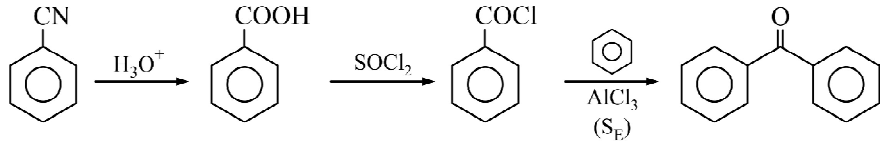
18. (B) $CH_3CH(OH)-CH_2COOH \xrightarrow{CrO_3} CH_3-\underset{\underset{O}{\|}}{C}-CH_2COOH \xrightarrow{\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CO_2$

(β – keto acid)

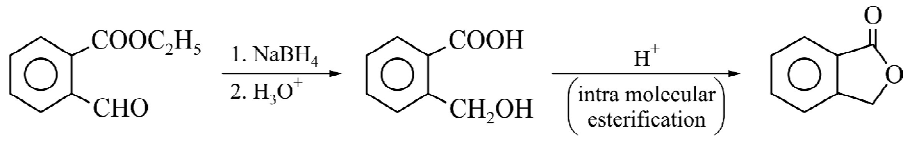
19. (B) Refer to text (Weaker base is a good leaving group).

20. (B) $C_6H_5CH_2OH \xrightarrow{1.\ PBr_3} C_6H_5CH_2Br \xrightarrow{2.\ KCN} C_6H_5CH_2CN \xrightarrow[NaOH/H_2O]{H_2O_2} C_6H_5CH_2\overset{\overset{O}{\|}}{C}-NH_2$

(Δ)

21. (A) 

22. (D) $C_2H_5-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow[2.\ H_2SO_4\,(Cold)]{1.\ MeMg(Br\,(excess)\ ether} C_2H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$

23. (D) 

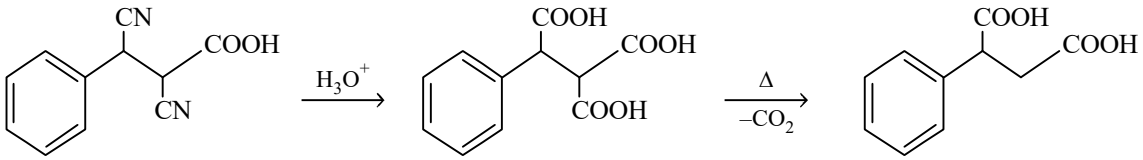
24.(B) $CH_3CH_2COOC_2H_5 \xrightarrow{C_2H_5\overset{-}{O}\overset{+}{Na}} CH_3CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OC_2H_5 + C_2H_5OH$ [Claisen Condensation]

(A)

$\xrightarrow{H^+(aq)}$

$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-COOH \xrightarrow{\Delta} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

(β-keto acid)

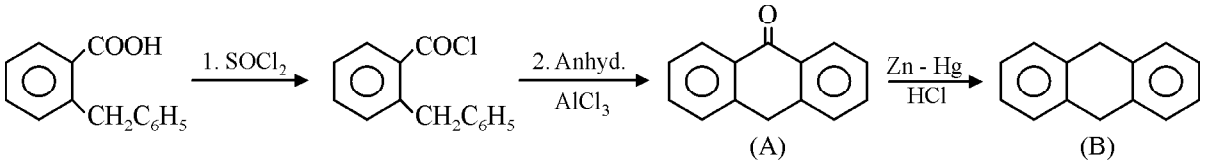
25.(C) 

26. (C) $PCl_5 + SO_2 \longrightarrow \underset{(A)}{SOCl_2} + POCl_3$

$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$

$2CH_3COCl + (CH_3)_2Cd \longrightarrow 2CH_3COCH_3 + CdCl_2$

27. (B)



28.(B)