HINTS & SOLUTION TO WORKBOOK

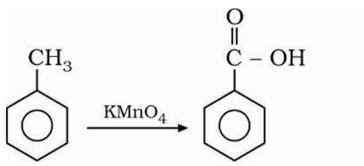
Oxygen Containing Organic Compounds-III

Daily Tutorial Sheet	Level-0

1. Electron withdrawing group increase acidic strength and electron donor group decrease acidic strength.
3,4 dinitrobenzoic acid > 4-nitrobenzoic > Benzoic acid > 4-methoxy benzoic acid.

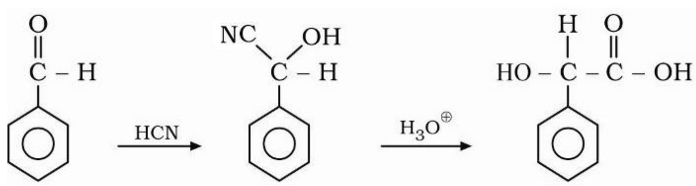
2. → Electron withdrawing group stabilize –ve charge on Carboxylate ion.
→ –I decreases with distance.
Correct order is $CH_3CH_2\,CH(Br)COOH > CH_3\,CH(Br)CH_2-COOH > (CH_3)_2\,CHCOOH$

3. $R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{(A)} R-CHO$
→ Rosenmund Reduction $A = Pd / BaSO_4$

4. 

→ Benzyl group having at least 1 – α hydrogen convert into Benzoic acid on treatment with $KMnO_4$

5. **(i)** Manufacturing of soaps need higher fatty acid.
(ii) In drugs formation such as aspirin, phenacetin etc.

6. 

(α-Hydroxy phenyl acetic acid)

7. **(i)** $\overset{4}{CH_3}-\underset{\underset{OH}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{COOH}$ → hydroxy butanoic acid

(ii) $\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-O-C_2H_5$ → Ethyl butanoate

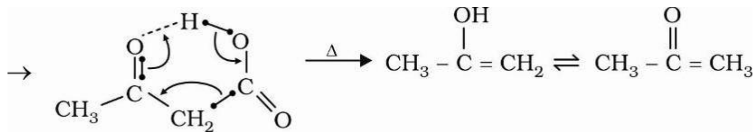
8. **(i)** $NaHCO_3$ reacts only with acids which are stronger than H_2CO_3. Benzoic acid reacts with $NaHCO_3$ giving off CO_2 while ethyl benzoate does not react.
(ii) → Methyl acetate on hydrolysis on acid followed by $I_2/NaOH$ gives no yellow ppt.
→ Ethyl acetate on hydrolysis on acid followed by $I_2/NaOH$ gives yellow ppt.

9. **(i)** HVZ

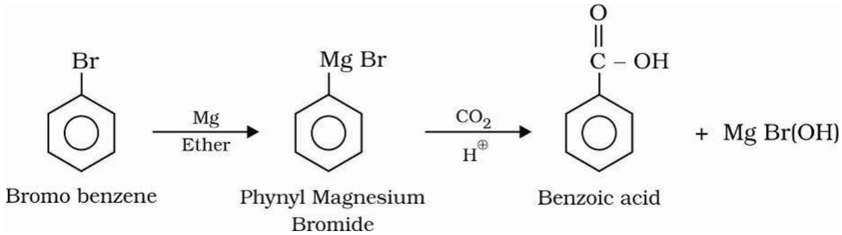
$$R-CH_2-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\text{(Bromination at }\alpha\text{ – position)}]{PBr_3} R-\underset{\underset{Br}{|}}{CH_2}-\overset{\overset{O}{\|}}{C}-OH$$

(ii) Decarboxylation

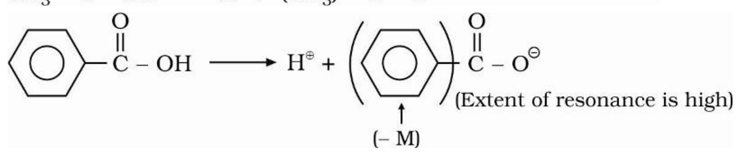
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OH$$



10.



11. **(i)** $CH_3-\overset{\overset{O}{||}}{C}-OH \longrightarrow H^{\oplus} + (CH_3)-\overset{\overset{O}{||}}{C}-O^{\ominus}$ ← (Resonance stabilized)



Electron withdrawing group stabilize –ve charge and make it weak negative charge.

Hence Conjugate acid of this base will be strong acid.

(ii) → Stability of –ve charge ∝ No. of Electron withdrawing Group.

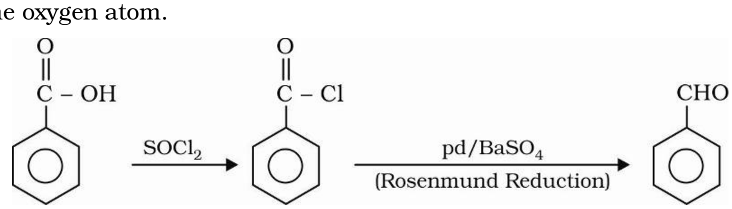
Stable –ve charge = weak negative charge = Conjugate of strong acid.

12. **(i)** Cl being an electron withdrawing group increases electrophilic character of Carbonyl carbon and make substrate more suceptible to nucleophilic attack.

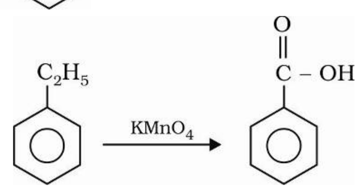
(ii) COOH group being a E.W.G., deactave benzene ring (↓es charge density) towards electrophilic substitution.

13. In acetate ion, the –ve charge is delocalized on two oxygen atom centers, while in phenoxide ion, the charge is delocalized on one oxygen and 3 – Carbon centers. Because oxygen is much more electronegative than carbon, the delocalization of –ve charge over two oxygen is better than delocalization over one oxygen atom.

14. **(i)**

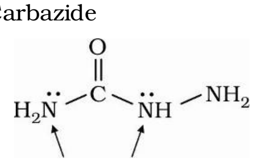


(ii) $CH_3-C\equiv N \xrightarrow{H_2O/H^{\oplus}} CH_3-\overset{\overset{O}{||}}{C}-OH + NH_3$ **(iii)**



15. **(i)** In case of cyclohexanone $CN^{\ominus}$ can easily attack without any steric hindrance. However in case of 2, 2, 6 trimethyl cyclohexanone, methyl group at α–position offer steric hindrance as a result $CN^{\ominus}$ can not attack effectively.

(ii) Semi Carbazide



Lone pair of *N*-atoms are in resonance with Carbonyl group and are not available to attack on other nucleophilc. While one NH_2 group is not involved in resonance and can act as a nucliophile.

(iii) In acidic medium the reactions is reversible. If either water or ester is not removed it reacts to give back the reactant.

16.

ATOM	%	No. of atoms
C	69.77	$\frac{69.77}{12}$
H	11.63	$\frac{11.63}{1}$
O	18.6	$\frac{18.6}{16}$

→ Ratio of C : H : O atom

$\Rightarrow$ 5.81 : 11.63 : 1.16 $\Rightarrow$ 5 : 10 : 1

→ Empirical formula : $C_5H_{10}O_1$

→ Empirical formula mass $= 5 \times 12 + 1 \times 10 + 16 \times 1 = 86$

Molecular mass = 86

Molecular formula $= C_5H_{10}O$

→ Compound does not reduce tollen's Reagent. It is not an aldehyde.

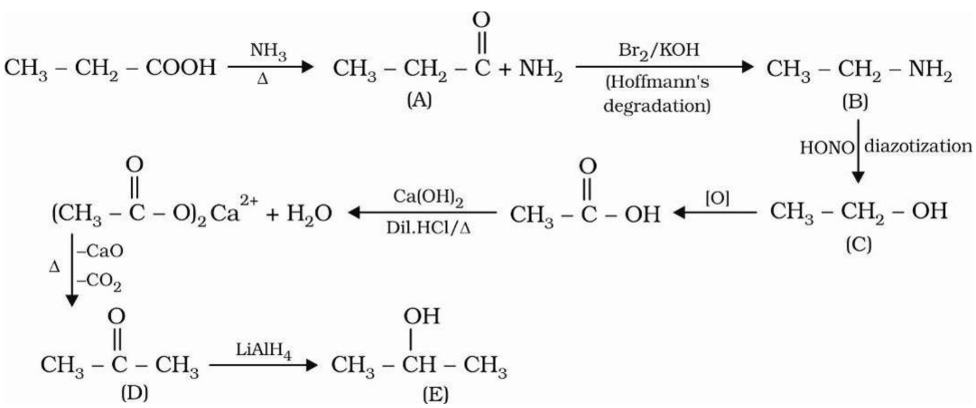
→ Compound form sodium hydrogen sulphate addition product and gives a positive iodoform test.

→ It must be a methyl keton.

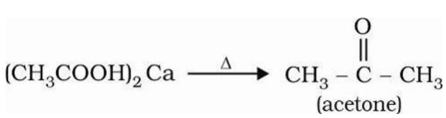
→ The compound also gives a mixture of ethanoic acid and propanoic acid on oxidation.

→ Hence the given Compound is pentan-2-on.

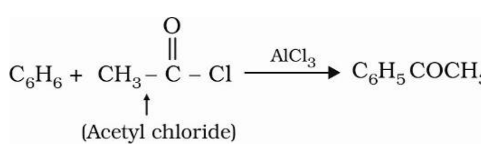
17.



18. **(i)**



(ii)



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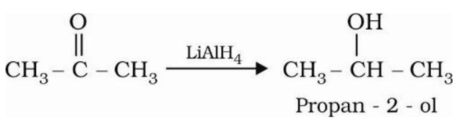


19. α – hydrogen in Carbonyl compound is the hydrogen attached to the Carbon next to Carbonyl carbon. This hydrogen is acidic in nature.

(i) NaOH reacts with CH_3COH, because it has α – hydrogen.

NaOH does not react with C_6H_5CHO, because it has no α – hydrogen.

(ii) Tollen's reagent reacts with aromatic and aliphatic aldehyde both.

20. $(C) \xrightarrow[-H_2O]{H^{\oplus}/\Delta} CH_2 = CH - CH_2 - CH_3$

C May be

$\underset{\displaystyle OH}{\underset{|}{CH_2}} - CH_2 - CH_2 - CH_3\ (x)$ Or $CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3\ (y)$

$[C] \xrightarrow{[O]} \text{Acid}$

On oxidation of y, it does not give acid.

→ C must be Butan-1-ol

→ B must be Butanoic acid

→ $A \equiv CH_3 - CH_2 - CH_2 - \overset{\displaystyle O}{\overset{||}{C}} - O - C_4H_9$

21. $X \xrightarrow{H^{\oplus}/H_2O} \underset{(acid)}{Y} + \underset{(alcohal)}{Z}$

$\underset{(Y)}{R - COOH} + Na_2CO_3 \longrightarrow R - \overset{\displaystyle O}{\overset{||}{C}} - O^-Na^{\oplus} + H_2O \xrightarrow[(-CO_2)]{\text{soda lime}} B\ (CH_4)$

$\Rightarrow \underset{(A)}{CH_3 - \overset{\displaystyle O}{\overset{||}{C}} - O^-Na^{\oplus}} \xrightarrow[\Delta,\ -CO_2]{\text{soda lime}} \underset{(B)}{(CH_4)}$

$Y \equiv CH_3COOH$

$CH_3COOH \xrightarrow{LiAlH_4} \underset{(Z)}{CH_3 - CH_2 - OH}$

22. $\underset{(alcohal)}{A} + CH_3COOH \xrightarrow{\text{Con. } H_2SO_4} (B)$

$A \xrightarrow[\text{Mild oxidation}]{[O]} \underset{\text{(aldehyde or Ketone)}}{C}$

$C \xrightarrow[\text{Strong Basic Condition (Favour Cannizaro reaciton)}]{(1)\ 50\%\ KOH} A + D$

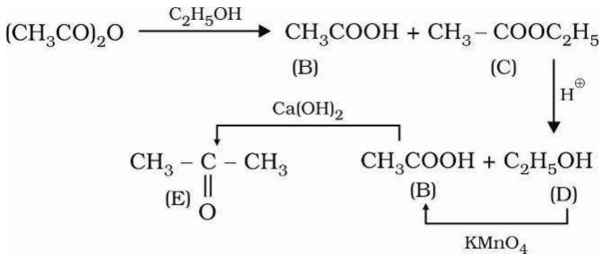
C is Carbonyl compound having no α – Hydrogen.

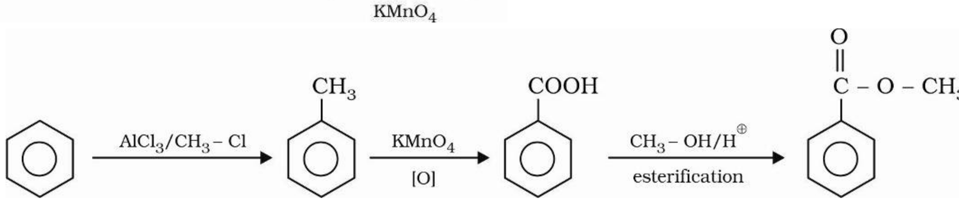
$A \equiv CH_3 - OH$

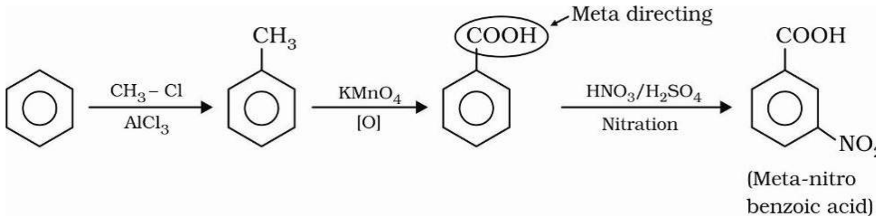
$C \equiv H - \overset{\displaystyle O}{\overset{||}{C}} - H$ (no α – Hydrogen)

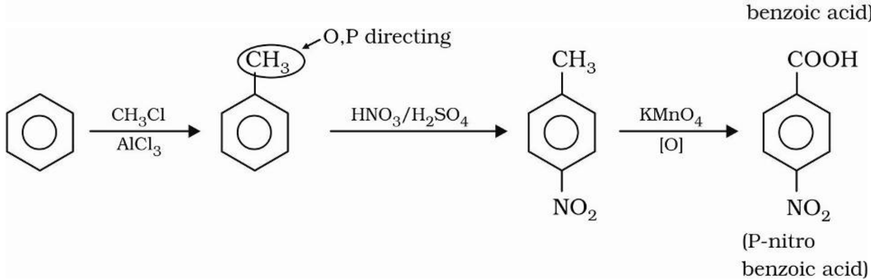
$H - \overset{\displaystyle O}{\overset{||}{C}} - OH \xrightarrow{PCl_5} H - \overset{\displaystyle O}{\overset{||}{C}} - Cl \xrightarrow{NH_3} H - \overset{\displaystyle O}{\overset{||}{C}} - NH_2\ (E) \xrightarrow[(P_2O_5)]{\Delta} HCN + H_2O$

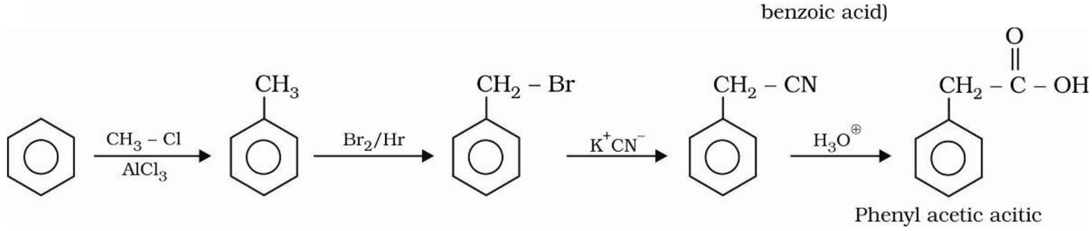
$B = CH_3 - \overset{\displaystyle O}{\overset{||}{C}} - O - CH_3$

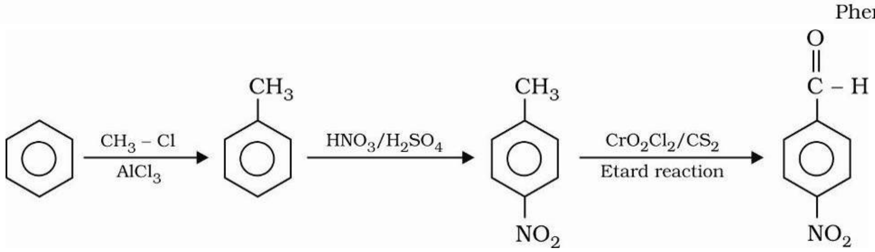
23. 

24. **(i)** 

(ii) 

(iii) 

(iv) 

(v) 

25. **(i)** $CO + NaOH \xrightarrow{H_2O} \underset{\text{sodium formate}}{HCOONa} \xrightarrow{H_2SO_4} \underset{\text{(formic acid)}}{HCOOH}$

(ii) used as preservative and antibacterial

(iii) $CH_3 - OH \xrightarrow{PCl_5} CH_3 - Cl \xrightarrow[NaCN]{\text{Ethanolic}} CH_3 - CN \xrightarrow{H^{\oplus}/H} CH_3COOH$

(iv) Ethanoic acid is a main component of vinegar and gives vinegar its characteristic smell.
$\rightarrow$ In the manufacture of plastic items

(v) Sodium benzoate is used as food preservative.