TOPIC : ALDEHYDES, KETONES, CARBOXYLIC ACID & DERIVATIVES EXERCISE # 1



- 6. Electrophilic substitution (Friedel Craft acylation reaction).
- 7. Name reaction

Section (B)

- **1.** Basic Information.
- 2. Nucleophilic attack can be faster at carbon containing more partial (+) charge (more electrophilic centre) and less steric crowding.

Rate of Nucleophilic addition reaction $\propto \delta^+$ at C=O group $\propto \frac{1}{\text{steric hinderance at C = O group}}$

4. Nucleophilic attack can be faster at carbon containing more partial (+) charge (more electrophilic centre) and less steric crowding.

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- 5. $C_6H_5CH=O \xrightarrow{HCN} C_6H_5-CH-OH \xrightarrow{H^+/H_2O} C_6H_5-CH-OH$ Cyanohydrin Mandelic acid
- 6. Those hydrates are stable which can be stabilised by any factor (e.g. Intramolecular H-bonding)

(Chloral hydrate is a stable compound)



Section (C)

- **1.** Aldehydes and ketones having atleast one α -H, give aldol condensation.
- **3.** Basic Information.
- 5. It is aldol condensation reaction
- 8. Name reaction.

Section (D)

1. Disproportionation and redox reaction.

2. Ph-CH=O
$$\xrightarrow{\text{conc. NaOH}}$$
 Ph-CH₂OH + Ph-COONa
Cannizzaro reaction

6. Ph–CHO + HCHO
$$\xrightarrow{\text{KOH}}$$
 Ph–CH₂OH + HCOOK

- 7. Haloform reaction can give by $-C-CH_3$ group. CH₃CHO has this group.
- 8. Compound containing chiral carbon with carbonyl group.
- 9. Compound containing $-C-CH_3$ group give iodoform test.
- 10. Haloform reaction can be given by $-C-CH_3$ and CH_3-CH_- group . OH

11.
$$CH_3-CH=O \xrightarrow{PCI_5} CH_3-CH < CI_1 + POCI_3$$

12. Basic Information.

13.
$$OH \rightarrow CHCl_3 + NaOH \xrightarrow{\text{Reimer Tiemann}} OH \rightarrow CH = O$$

Salicylaldehyde

15. It is fact.

Section (E)

- 1. Lab test.
- 2. Basic Information.
- **3.** Basic Information.
- 4. Aldehydes give silver mirror test but ketones do not.

$$(CH_3)_2CHOH \xrightarrow{[0]} (CH_3)_2C=O \longrightarrow$$
 No silver mirror
Phenyl hydrazine formation is possible.

CHEMISTRY FOR NEET

- 5. Rochelle salt is sodium salt of tartric acid.
- 7. Basic Information.
- **10.** Molecular weight = $2 \times$ vapour density

Section (F)

- 1. $CH_3-C\equiv N \xrightarrow{dil. H^{\oplus}} CH_3COOH$ Acetonitrile
- 2. $C_2H_5Br \xrightarrow{KCN} C_2H_5CN \xrightarrow{Dil. H_2SO_4} C_2H_5COOH$
- 4. $C_2H_5Br CH_2=CH_2$

Section (G)

- 1. HVZ reaction.
- **2.** α -halogenation reaction [α -H must present].

3.
$$CH_{3}I \xrightarrow{Mg} CH_{3}MgI \xrightarrow{(i) Dry ice} CH_{3}COOH \xrightarrow{Cl_{2}} CI-CH_{2}-COOH$$

(*ii*) $H_{3}O^{+}$ (*a*-halogenation)

- 6. Steric hindrance
- 7. Rate of esterification $\propto \frac{1}{\text{Steric}}$ crowding
- 9. $RCOOH + SOCI_2 \longrightarrow RCOCI + SO_2 + HCI$ $RCOOH + PCI_5 \longrightarrow RCOCI + POCI_3$ $RCOOH + PCI_3 \longrightarrow RCOCI + H_3PO_3$

Section (H)

- **2.** Ph–COCI $\xrightarrow{\text{NH}_3}$ Ph–CONH₂ + HCI
- **3.** $CH_3COONa + CH_3COCI \longrightarrow CH_3-COO-COCH_3$
- 4. $R-CH_2OH + RCOCI \longrightarrow R-CH_2-O-CO-R$

Section (I)

- **1.** Reactivity \propto Partial positive charge on C=O carbon.
- 2. $CH_3CH_2CH_2CONH_2 \xrightarrow{NaOH} CH_3CH_2CH_2COO^- \xrightarrow{HCI} CH_3CH_2CH_2COOH + NH_4CI$



EXERCISE # 2



2.
$$CH_{3} - C - CH_{3} \xrightarrow{OH^{-}/H_{2}O} CH_{3} - C - CH_{3} \xrightarrow{H_{2}O} CH_{3} - C - CH_{3} \xrightarrow{H_{2}O} CH_{3} - C - CH_{3}$$

3. Electrophilic substitution reaction.

$$\bigcirc + CH_{3}-C-CI \xrightarrow{AICI_{3}} \bigcirc C-CH_{3}$$
(Acetophenone)

- **4.** As steric hinderance increases around carbonyl group, the rate of nucleophilic addition reaction decreases.
- **5.** As steric hinderance increases around carbonyl group, the rate of nucleophilic addition reaction decreases.

6.
$$CH_{3}-C-H+HCN \longrightarrow CH_{3}-C-H \xrightarrow{H_{2}O} CH_{3}-CH-COOH$$

 U
 O
 OH
 OH
 OH

7.
$$CH_{3}-C-H+HCN \longrightarrow CH_{3}-C-H \xrightarrow{H_{2}O} CH_{3}-\overset{*}{C}H-COOH \xrightarrow{I} H_{2}O \xrightarrow{$$

8. Ph-C=CH
$$\xrightarrow{HgSO_4}$$
 Ph-C=CH $\xrightarrow{H_2\ddot{O}}$ Ph-C-CH₃ $\xrightarrow{NH_2OH}$ \xrightarrow{Ph} C $\xrightarrow{CH_3}$ \xrightarrow{Ph} C $\xrightarrow{CH_3}$ C \xrightarrow{Ph} C $\xrightarrow{CH_3}$ C \xrightarrow{Ph} C $\xrightarrow{CH_3}$ C \xrightarrow{Ph} C \xrightarrow

9.
$$CH_3 - CH_2 - C - H \xrightarrow{KCN / H_2SO_4} CH_3 - CH_2 - CH - CN \xrightarrow{LiAlH_4} CH_3 - CH_2 - CH - CH_2 - \dot{N}H_2$$

10.
$$C_{6}H_{5} - \overset{\frown}{C} - H + \overset{\ominus}{C}_{12} - NO_{2} \xrightarrow{H^{+}} C_{6}H_{5} - CH - CH_{2} - NO_{2} \xrightarrow{\Delta} C_{6}H_{5} - CH = CH - NO_{2}$$

- 11. Perkin reaction $Ph - CH = CH - COOH \xrightarrow{HBr} Ph - CH - CH_2 - COOH$ |Br
- **12.** $CH_3 CHO (\alpha Hydrogen is present).$

13.



14. The compound which contains $CH_3 - C -$ or $CH_3 - CH -$ group gives iodoform test.

- 16. Tollen's reagent.
- 18. Iodoform test.
- 20. Basic Information.

21. + CH₃CHO

$$\begin{array}{c} CH_2 - OH \\ | \\ CH_2 - OH \end{array} + CH_3CHO \xrightarrow{dry HCl} CH_3 - CH \swarrow \begin{array}{c} O - CH_2 \\ | \\ O - CH_2 \end{array}$$

- 24. $CH_3-C-CH_3 \xrightarrow{Zn-Hg/HCl} CH_3-CH_2-CH_3$ $\downarrow O$
- **25.** Addition of HCN on carbonyl compound is nucelophilic addition reaction Rate of nucleophilic addition ∞ electropositive character of 'C' of carbonyl group

26. Since all compounds do not contain ' α ' H atom thus, all can show Cannizaro reaction

27. PhCH₂CHO
$$\xrightarrow{\overset{\circ}{O}H, \text{ heat}}$$
 Ph—C=CHCH₂Ph $\xrightarrow{\text{LiAlH}_4}$ Ph—CH—CH₂CH₂Ph
I CHO CH₂OH
(P) (Q)

Here it should be noted that double bond in conjugation with phenyl group can be reduced by LiAlH_4 . Since (Q) does not contain C = C bond hence it cannot decolourise Baeyer reagent.

28.
$$CH_3 - C - CH_3 + CN^- \xrightarrow{H^+} CH_3 \xrightarrow{H_2O} CH_3 \xrightarrow$$

29. $C_6H_5CH(OCH_3)_2 \xrightarrow{H^+}{H_2O} PhCHO + CH_3OH$

30.
$$CH_3-CH_2-CH_2-CH_2-CH_3 \xrightarrow{H_2CrO_4} CH_3-C_2-CH_2-CH_2-CH_2-CH_3$$

OH O

31. It is decarboxylation of β -keto acid.

32.
$$CH_{3}-CH-CH_{3} \xrightarrow[]{K_{2}Cr_{2}O_{7}/H_{2}SO_{4}} CH_{3}-C-CH_{3} \xrightarrow[]{I_{2}/NaOH} CHI_{3} + CH_{3}COONa$$

OH

33.
$$CH_3 - CH_2 - C - CH_2 - CH_3 \xrightarrow{\text{Reduction}} CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

Among Carbonyl Compounds, reactivity decrease with increase in alkyl groups as alkyl groups (+/ effect) decrease positive character on C-atom. Thus, the correct order of reactivity is
 HCHO > CH₃CHO > C₆H₅CHO

38.
$$CH_3COCI \xrightarrow{2H}_{Pd/BaSO_4} CH_3CHO + HCI$$

41.
$$CH_{3} - CH - CH_{2} - CH_{3} \xrightarrow{KMnO_{4}} CH_{3} - CH_{2} - CH_{2}CH_{3}$$

$$OH_{2} - Butanol$$

44. (1)
$$C_9H_{18} + O_3 \rightarrow H_3C - C - CHO + CH_3CH_2COCH_3$$

 $\downarrow CH_3$
 $2,2 \text{ dimethyl propanal}$

On the basis of product formation, it would be alkene

$$CH_{3} CH_{3} CH_{3}$$

$$CH_{3} - C - HC = C - CH_{2}CH_{3}$$

$$CH_{3} - C - HC = C - CH_{2}CH_{3}$$

$$CH_{3} - CH_{3}$$

$$CH_$$



56. In fumaric acid both COOH groups are present at opposite side so it is unaffected on heating.



- **58.** $CH_3 CH_2 CH_2 Br \xrightarrow{NaCN} CH_3 CH_2 CH_2 CN \xrightarrow{H_3O^{\oplus}} CH_3 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_3$
- **59.** Citric acid makes a lemon sour.
- 60. Vinegar contains 7–8% acetic acid
- **61.** $CO_2 + NaOH \longrightarrow HCOONa \longrightarrow HCOOH$
- 62. It is Hell Volhard Zelinsky reaction.
- **63.** NaBH₄ does not reduce ester functional group.
- **64.** Rate of hydrolysis ∞ partial positive charge on >C= O groups.
- 65. When an ester converts into another ester, it is called trans esterification.
- **66.** CH_3 -COOH + $C_2H_5OH \xrightarrow{H^{\oplus}} CH_3COOC_2H_5$ (ester)
- **67.** β-Keto acid decarboxylates faster through 6 member cyclic transition state.





- **19.** $R-CH = O + H_2N NH_2 \longrightarrow R-CH = N NH_2$ It is a Nucleophilic addition-elimination reaction.
- **20.** Electron withdrawing (–I, –M) groups increases reactivity towards nucleophilic addition reaction. CHO

In \bigcirc NO₂ (-I, -M) group increases the reactivity towards nucleophilic addition reaction at CHO



- 22. In basic medium rate of hydrolysis increases with electron withdrawing group (-M effect predominates)
- **23.** With Ammonia derivation carbonyl compounds give addition followed by elimination reaction. Sligtly acidic medium will generate a nucleophilic centre for weak base like ammonia derivatives.

Schiff's Base

$$>C=O + H_2N-R \longrightarrow >C=N-R$$

Aldehyde/ketone



26. It is known that basic need for the existance of Keto-enol tautomers is the presence of at least one hydrogen atom at adjacent sp³ carbon of carbonyl carbon.

$$C_{2}H_{6}O(CH_{3}CH_{2}OH) \xrightarrow{Cu, 573K} C_{2}H_{4}O(CH_{3}CHO) \xrightarrow{[Ag(NH_{3})_{2}]^{+}} Ag \text{ Silver mirror}$$
Ethanol (X)
$$C_{2}H_{6}O(CH_{3}CH_{2}OH) \xrightarrow{Cu, 573K} C_{2}H_{4}O(CH_{3}CHO) \xrightarrow{[-OH, \Delta]{-OH, \Delta}} Ag \text{ Silver mirror}$$

$$C_{1}H_{2}-H_{2}H_{2} \xrightarrow{O}H_{2}-H_{2} \xrightarrow{O}H_{2} \xrightarrow{O}H_{2$$

28. Carboxylic acid have higher boiling point and than aldehyde, ketones, alcohol due to formation of Inter molecular H–bonding



PART - II

- 1. $CH_3COOC_2H_5 \xrightarrow{NaOH} CH_3-COO^{\circ} + C_2H_5OH$ [Ethanol can give iodoform test]
- 4. Iodoform test is carried out in hot alkaline medium. Under these conditions the esters will hydrolyse to give corresponding alcohols. Now ethyl alcohol will repond to iodoform test to give yellow ppt. of iodoform while methanol will not give iodoform.
- **5.** Aldehydes having α -H atoms undergo aldol condensation in the presence of dil. NaOH and yield β -hydroxy aldehydes.

$$CH_{3}CHO + CH_{3}CHO \xrightarrow{\text{NaOH}} CH_{3} \xrightarrow{-CH-CH_{2}CHO} 3-hydroxy butanal$$

- 6. $C_{2}H_{5}OH + [O] \xrightarrow[\text{in } CH_{2}Cl_{2}]{} CH_{3}CHO$ $CH_{3}CHO + 4NaOH + 3l_{2} \longrightarrow CHl_{3} + HCOONa + 3H_{2}O + 3Nal$ (triiodomethane)
- **7.** If D₂O (heavy water) is taken instead of H₂O, as solvent, the reaction takes place in the following manner :

$$R - C = O \xrightarrow[H]{OD^{-}} R - C \xrightarrow[H]{OD^{-}} R - C \xrightarrow[H]{OD^{-}} R - C = O + R - C = O + R - C \xrightarrow[H]{OD^{-}} RCOO^{-} + RCH_2OD$$

8.
$$(CH_{3})C = O \xrightarrow{H^{+},HCN} CH_{3} \xrightarrow{O} CH_{2} = C - COOH$$
$$\xrightarrow{H_{2}SO_{4}} CH_{2} \xrightarrow{O} CH_{2} = C - COOH$$
$$\xrightarrow{I} CH_{3} \xrightarrow{O} CH_{3} \xrightarrow{O}$$

CH₃

- 16. Benzaldehyde is more reactive than ethanol towards nucleophillic attack because of -I and + R effect of phenyl group which decreases the electron density on carbon atom of >C=O group.
- 17. Hydration minimises strain in (2) to maximum extent and then in (1)



CH₃

α-Halogenation of carbonyl compound by Br2 in presence of alkali medium

CH₃



PART - III

- 1. $H_3C-C=CH-CH_2-CHO \xrightarrow{[O]} H_3C-C-CH_3+CH_2-COOH$ $I \qquad II \qquad II \qquad I \qquad O \qquad COOH$
- 2. Benzaldehyde undergoes disproportionation with 50% NaOH to give benzyl alcohol and sodium benzoate

 $C_6H_5CHO \xrightarrow{50\% \text{ NaOH}} C_6H_5CH_2OH + C_6H_5COONa$ (Cannizzaro's reaction.)

3.
$$(H_3 \longrightarrow H^{\oplus}) (H_3 \oplus H^{\oplus$$

4. As steric hinderance around carbonyl group increases, the rate of nucleophilic addition reaction decreases.

6.
$$CH_3$$
-CH=CH-CH $_3 \xrightarrow{O_3/Zn} CH_3$ -CHO

7.
$$Ph-C-H+OH \xrightarrow{fast} Ph-C-H \xrightarrow{O} Ph-C-OH + Ph-CH_2 - O \xrightarrow{H^{\circ}} Ph-C-O + Ph-CH_2 - O \xrightarrow{H^{\circ}} Ph-C-O + Ph-CH_2 - OH$$

8. The cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.

$$CI \xrightarrow[]{CI} CI \xrightarrow[]{CI} CI \xrightarrow[]{CI} CI OH$$

$$CI \xrightarrow[]{C} C \xrightarrow[]{C} C \xrightarrow[]{CI} CI \xrightarrow[]{CI} CI \xrightarrow[]{CI} OH$$

$$CI \xrightarrow[]{CI} OH$$

$$CI$$

But this reaction is manily proceed as below.

$$CI \xrightarrow[]{CI} CI \xrightarrow[]{CI} C \xrightarrow[]{NaOH} CHCI_3 + HCOONa$$

9.
$$CH_3 - C \overset{e}{\searrow} \overset{O}{\longrightarrow} H \xrightarrow{[Ag(NH_3)_2]^+} CH_3 - C \overset{e}{\searrow} \overset{O}{\longrightarrow} + Ag \downarrow$$

$$H = \stackrel{O}{\overset{H}{=}} H = \stackrel{[Ag(NH_3)_2]^*}{\longrightarrow} H = C \stackrel{O}{\overset{O}{\searrow}} + Ag \downarrow$$

10. $CH_3 - CH - CH_2 - OH$ isobutyl alcohol does'nt give positive iodoform test. I_{CH_3}

CHEMISTRY FOR NEET



-OH group and alkene are acid-sensitive groups so clemmensen reduction can not be used.

13.
$$CH_3CH_2COOH \xrightarrow{Cl_2} CH_3CH - COOH \xrightarrow{KOH(alc.)} CH_2 = CHCOOH$$

- CI 14. Among the given option CI[−] is the best leaving group hence the rate of reaction will be fastest in case of RCOCI.
- **15.** The correct order of increasing acid strength is



- **16.** No reaction occurs on mixing NaCl and ethyl acetate.
- **17.** When two electron releasing groups are present the incoming group will occupy para or ortho position to the group which has more + R effect.
- **18.** The empirical formula from given percentage data is N_2H_4CO . Urea on heating gives biurate & ammonia. Biurate gives violet colour with CuSO₄ solution.

$$2NH_2$$
-CO-NH₂ $\xrightarrow{\Lambda}$ $150^{\circ}C$ NH_2 -CO-NH-CONH₂ + NH₃

Biurate

19.
$$CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

Ester (Fruity smell)

20.
$$CH_3 - C \subset C_1 \xrightarrow{O} C_2H_5O^- CH_3 - C \subset O_2H_5^+ CI^-$$

Ethylethanoate

21. By reaction with one mole of CH_3 –C–CI with one – NH_2 group the molecular mass increases with 42 unit. Since the mass increases by (390 – 180) = 210 hence the number of – NH_2 groups is 5.

$$R - NH_2 + CH_3 - C - CI \xrightarrow[(-HCI)]{} R - NH - C - CH_3$$



(Phthalic anhydride)



Intramolecular aldol condensation