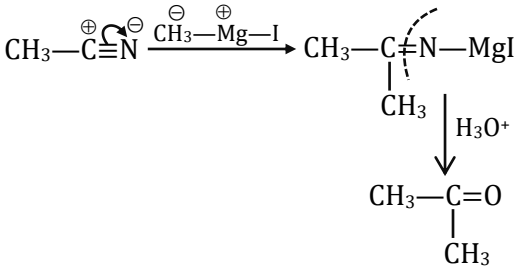
Aldehydes, Ketones and Carboxylic Acids

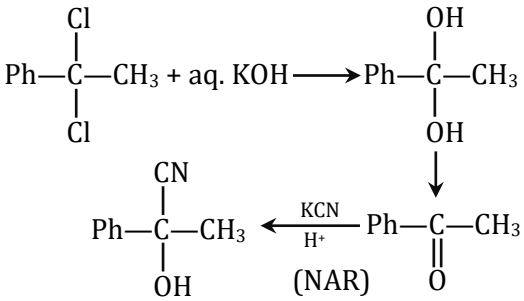
SOLUTIONS

Exercise-I (Conceptual Questions)

1. Ans. (4)

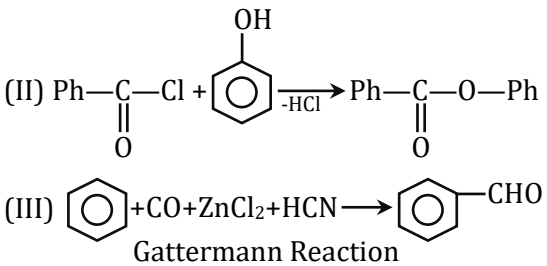


2. Ans. (1)



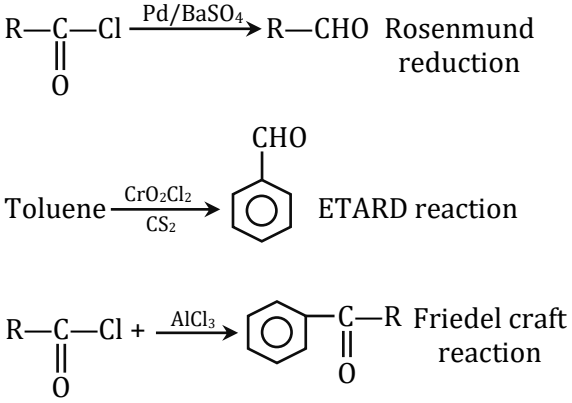
(50%d + 50%ℓ)

3. Ans. (1)

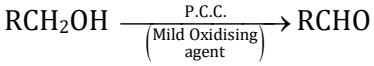


Gattermann Reaction

4. Ans. (4)

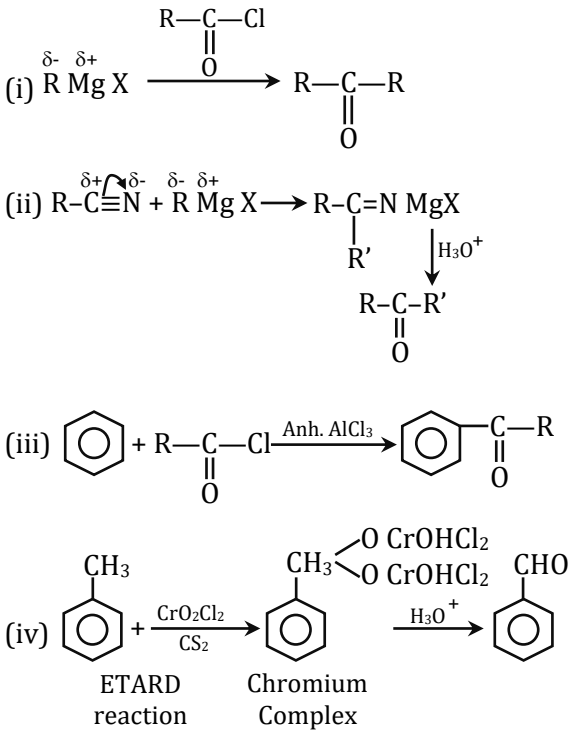


5. Ans. (4)



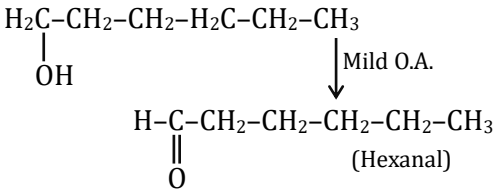
other are strong O.A. → further oxidation possible into acid.

6. Ans. (4)

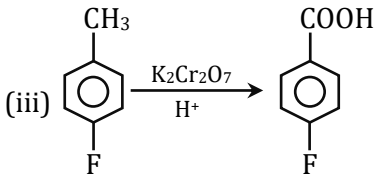


7. Ans. (3)

(i) Hexan-1-ol



(ii) Ethane nitrile $\xrightarrow{DIBAL-H}$ Ethanal



(iv) $CH_3-CH=CH-CH_3 \xrightarrow{O_3, H_2O, Zn} CH_3-\underset{\underset{O}{\|}}{C}-H$

8. Ans. (4)

$CH_3CH_3 \xrightarrow{Cl_2/h\nu} CH_3CH_2Cl \xrightarrow{aq.\ KOH} CH_3CH_2OH$

(A) (B)

(B) $\xrightarrow{PCC}$ $CH_3-\underset{\underset{O}{\|}}{C}-H$ (C)

(C) $\xrightarrow[\Delta]{\overset{\ominus}{O}H}$ $CH_3-CH=CH-CHO$ (D)

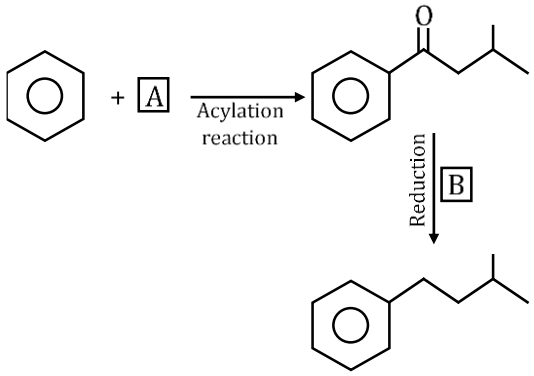
(Aldol Condensation)

9. Ans. (1)

$>C=O \xrightarrow[\text{or}]{\text{Metal + Con. HCl}} >CH_2$

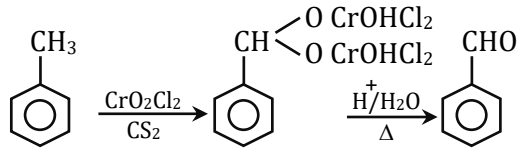
Acidic reduction

10. Ans. (4)



$LiAlH_4$ Reducing agent which reduced polar π Bond into Alcohol/Amine

11. Ans. (2)



ETARD reaction

12. Ans. (3)

$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{\text{Tollen test}} X$

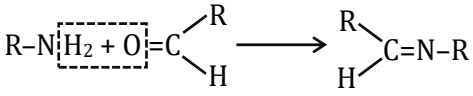
(Acetone)

Tollen test is given by Aldehyde, formic acid α-hydroxy ketone, hemiacetal group.

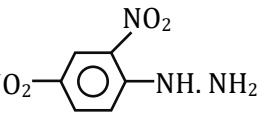
13. Ans. (3)

Carbonyl compound ⟶ NAR

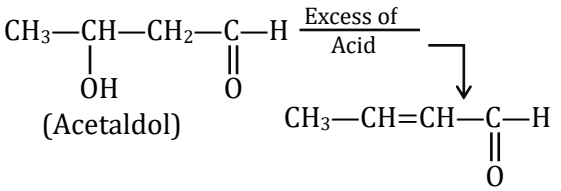
14. Ans. (3)



15. Ans. (3)

Brady's reagent 

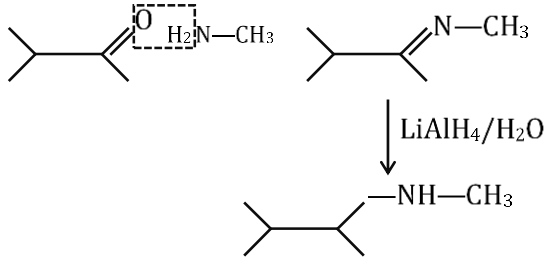
16. Ans. (2)



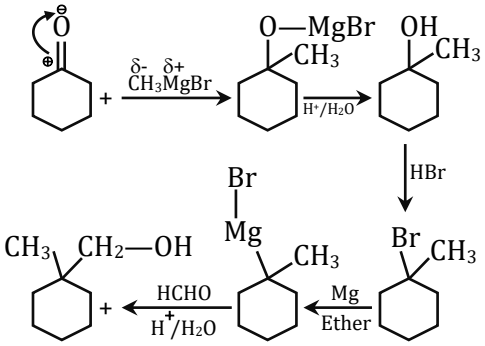
(Acetaldol)

α–β Unsaturated Aldehyde

17. Ans. (2)



18. Ans. (2)



19. Ans. (4)

C = O	C = C
(i) Polar	(i) Non polar [Same EN]
$\mu \neq 0$	$\mu = 0$
(ii) B.L. = 123pm	(ii) 134pm
(iii) $>C=O$	(iii) $>C=C<$
NAR	EAR

20. Ans. (2)

$CH_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Fehling Solution}} CH_3-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{O}\,\overset{\oplus}{Na}$

\+

$Cu_2O\downarrow$

(Cuprous oxide)

Red Brown PPT

21. Ans. (2)

$CH_3—\underset{\underset{O}{\|}}{C}—H$ (Aldehyde) $CH_3—\underset{\underset{O}{\|}}{C}—CH_3$ (Ketone)

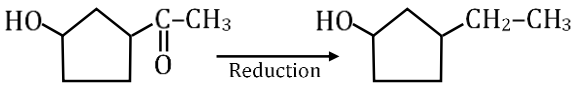
(I) Fehling solution ✓ ×

(II) Both React with RMgX

(III) Schiff regent ✓ ×

(IV) Tollen test ✓ ×

22. Ans. (3)

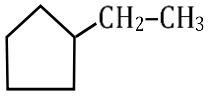


OH group present ∴ Acid sensitive reaction

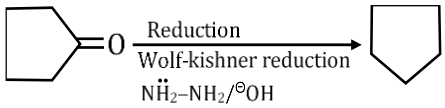
Avoid Zn–Hg/HCl (Clemmenson reduction)

Used $NH_2—NH_2/^{\ominus}OH$ (Wolf- kishner reduction)

Red + HI ⟶ Reduced all given functional group



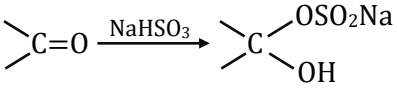
23. Ans. (4)



Clemmenson reduction Zn-Hg/$H^{\oplus}$

Red P + HI

24. Ans. (3)



white crystal (water soluble)

All aldehyde ✓

Only Aliphatic methyl ketones ✓

Aromatic ketones ×

25. Ans. (3)

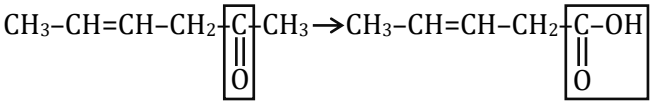
$CH_3—\underset{\underset{O}{\|}}{C}—CH_3$ $CH_3—\underset{\underset{O}{\|}}{C}—H$

(I) I_2 + NaOH ✓ ✓

(II) 2, 4 DNP ✓ ✓

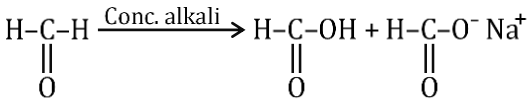
(III) Tollen × ✓

26. Ans. (3)



Halo form reaction is best (Iodo form)

27. Ans. (3)

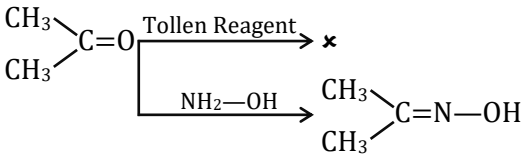


(Cannizzaro reaction) (Acid) (Salt)

28. Ans. (4)

Oxime formation ⇒ (Aldehyde or ketone)

Silver mirror test ×, Ketone ×, Aldehyde ✓



29. Ans. (1)

Fehling solution Aldehyde ✓

Ketone ×

30. Ans. (1)

$CH_3—\underset{\underset{O}{\|}}{C}—H$ + $Ph—\underset{\underset{O}{\|}}{C}—CH_3$

(Acetaldehyde) ↓ (Acetophenone)

$NaHSO_3$ → All Aldehyde + Aliphatic methyl ketones gives positive test

Aromatic ketone ×

31. Ans. (2)

Condition for Iodoform test :- presence of

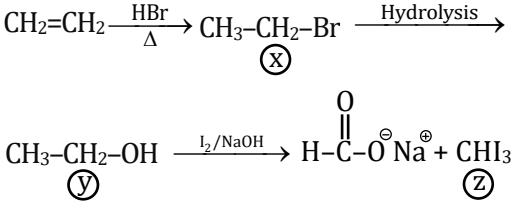
$CH_3–\underset{\underset{O}{\|}}{C}–$ or $CH_3–\underset{\underset{OH}{|}}{CH}–$

have methyl keto group.

But 

do not have methyl keto group.

32. Ans. (3)



∴ Z is CHI_3

33. Ans. (2)

Methyl ketone $\left(CH_3-\overset{\overset{O}{\|}}{C}-\right)$ or $\left(CH_3-\underset{OH}{\underset{|}{CH}}-\right)$

must be present to give haloform test.

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ ✓ $\quad C_2H_5-\overset{\overset{O}{\|}}{C}-C_2H_5$ ×

$CH_3-\underset{OH}{\underset{|}{CH}}-C_2H_5$ ✓ $\quad I-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ ✓

34. Ans. (2)

Acetone is mixed with bleaching powder to give chloroform.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

(Bleaching powder)

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 3Cl_2 \longrightarrow CCl_3-\overset{\overset{O}{\|}}{C}-CH_3 + 3HCl$$

$$CCl_3-\overset{\overset{O}{\|}}{C}-CH_3 + CCl_3-\overset{\overset{O}{\|}}{C}-CH_3 + \begin{matrix}HO\\HO\end{matrix}\!\!>\!Ca \longrightarrow \begin{matrix}CH_3-COO\\CH_3-COO\end{matrix}\!\!>\!Ca + CHCl_3$$

35. Ans. (1)

It is Iodoform Test

$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Alkali}]{I_2} \underset{\text{(yellow) ppt}}{CHI_3\uparrow} + CH_3-COOH$$

36. Ans. (3)

Aldol condensation ⟶ Minimum one α H present $H-\overset{\overset{O}{\|}}{C}-H$

NO α H

NO aldol

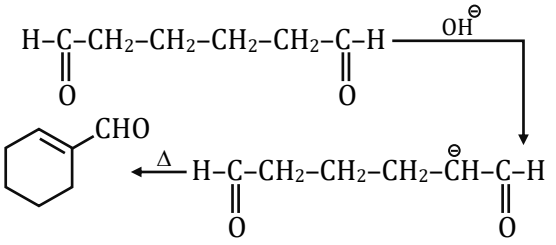
37. Ans. (2)

(Acetaldehyde)

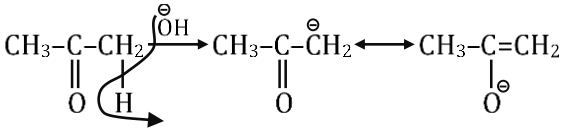
$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{Condensation}]{\text{Aldol}} CH_3-CH=CH-\overset{\overset{O}{\|}}{C}-H$$

Trick $\quad CH_3-CH\!<\!\begin{matrix}O\\ \\ \end{matrix}\!\!\begin{matrix}H\\ \\H\end{matrix}\!>\!CH-\overset{\overset{O}{\|}}{C}-H$

38. Ans. (2)



39. Ans. (4)



(1) Acidic due to strong EWG

(2) Resonance stable of conjugate base

(3) β-Hydroxy ketone with dil. Alkali (Aldol Reaction)

40. Ans. (3)

Cannizzaro reaction is give by – Aldehyde not containing α-hydrogen.

41. Ans. (2)

Methanal, $H-\overset{\overset{O}{\|}}{C}-H$ $\quad$ Ethanal, $CH_3-\overset{\overset{O}{\|}}{C}-H$ $\quad$ Propanone $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Miscible with water because they form hydrogen bond with water.

42. Ans. (1)

NAR reactivity $\propto$ $\underset{\text{on } Sp^2}{\oplus\text{ve charge}} \propto \frac{-M}{+M} \propto \frac{-I}{+I}$

Butanone < Propanone <

$H_3C-\overset{\overset{\delta+}{O}}{\overset{\|}{C}}-H_2C-CH_3$ $\quad$ $H_3C-\overset{\overset{\delta+}{O}}{\overset{\|}{C}}-CH_3$

Propanal < Ethanal

$H_3C-\overset{\overset{\delta+}{O}}{\overset{\|}{H_2C-C}}-H$ $\quad$ $CH_3-\overset{\overset{\delta+}{O}}{\overset{\|}{C}}-H$

43. Ans. (1)

Fehling test given by Aliphatic aldehyde ✓

Aromatic Ald. ×

Fehling reagent = (A) $C_4SO_4.5H_2O$

(B) Na^+ K^+ tartarate (Rochelle salt)

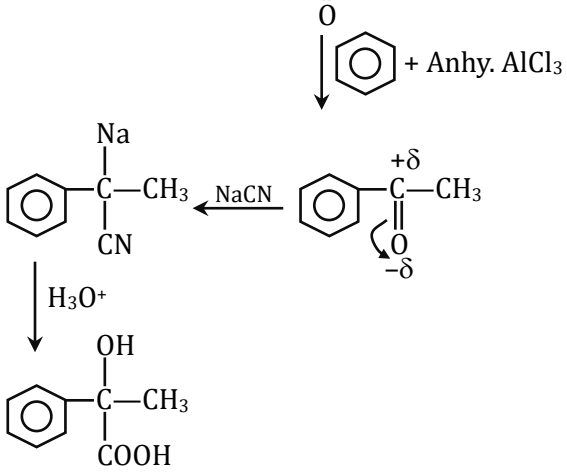
44. Ans. (4)

$CH_3-CH_2-COOH \xrightarrow{NaHCO_3} CH_3CH_2COO^-Na^+$
Propanoic acid
+
H_2CO_3 (Unstable)
↓
$H_2O + CO_2\uparrow$

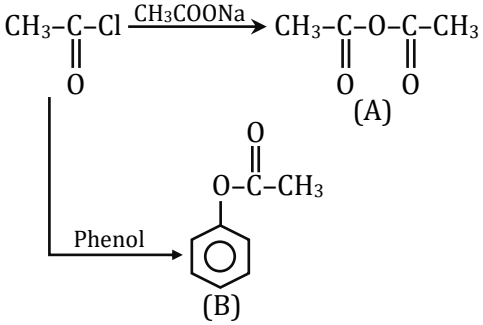
C of CO_2 comes from $NaHCO_3$

45. Ans. (1)

$CH_3COOH \xrightarrow{SOCl_2} CH_3-\underset{\underset{O}{\|}}{C}-Cl$



46. Ans. (2)



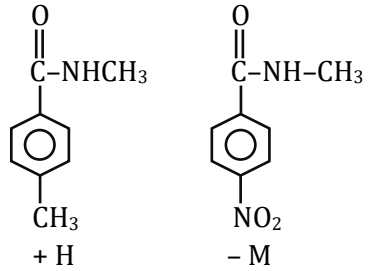
47. Ans. (1)

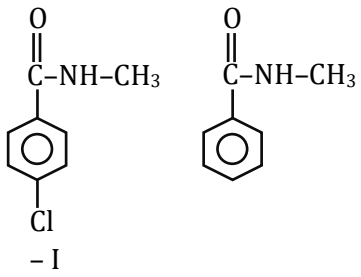
$CH_3-CH_3-COOH \xrightarrow[(HVZ\ Rxn)]{Red\ P+Cl_2} CH_3-\underset{\underset{Cl}{|}}{CH}-COOH$

$CH_2=CH-COOH \xleftarrow{Alc.\ KOH}$

48. Ans. (2)

Reactivity towards Alkaline Hydrolysis $\propto$ Electrophilicity of Carbonyl group $\propto$ –M $\propto$ –I





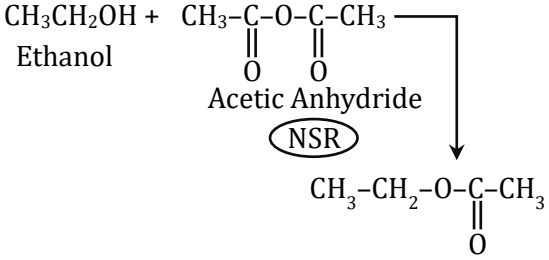
49. Ans. (2)

Neutral $FeCl_3$
Phenol ⟶ ✓ Violet colour complex
Benzoic acid ⟶ Buff coloured

50. Ans. (2)

Acid and acid chlorides undergo → NSR

51. Ans. (2)



52. Ans. (1)

$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{Reduction} CH_3CH_2NH_2$
Acetamide

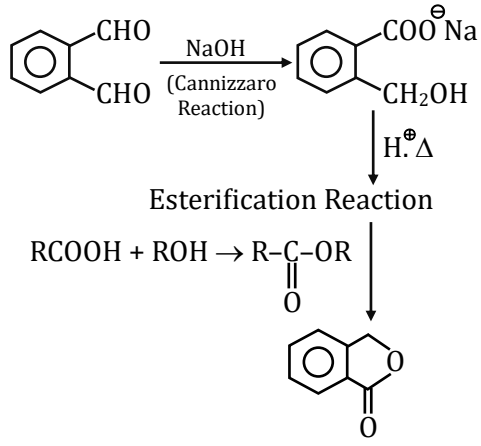
53. Ans. (3)

$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{H_2,\ Pd/BaSO_4} R-\underset{\underset{O}{\|}}{C}-H$
Acid Halide — Aldehyde

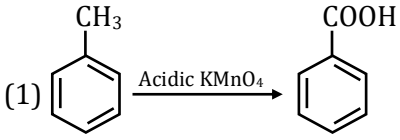
54. Ans. (2)

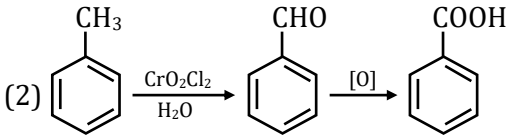
$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{P_2O_5} CH_3-CN$
[Strong dehydrating agent]
$-H_2O$

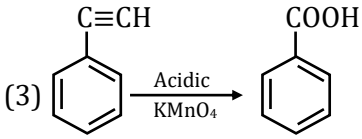
55. Ans. (2)

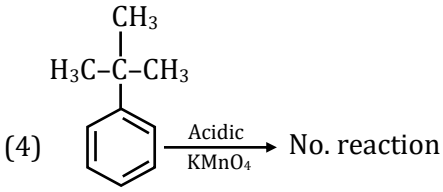


56. Ans. (4)

(1) 

(2) 

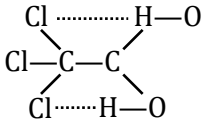
(3) 

(4) 

No. reaction

57. Ans. (3)

Chloral hydrate is stable due to H-bonding

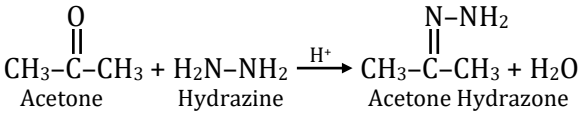


58. Ans. (2)

Carbonyl compounds are best purified by hydrolysis of $NaHSO_3$.

White crystal compound form.

59. Ans. (2)

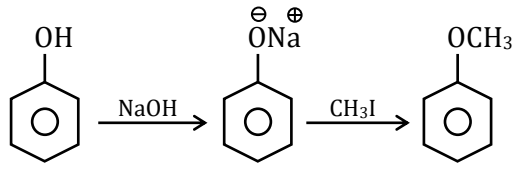


60. Ans. (3)

$NaBH_4$ cannot reduce carboxylic acid to alcohol.

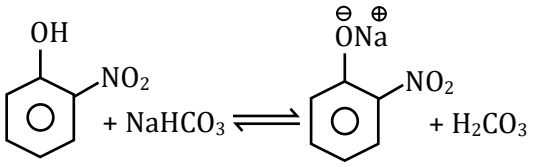
Exercise-II (Previous Year Questions)

1. Ans. (2)



(Anisole)

2. Ans. (3)



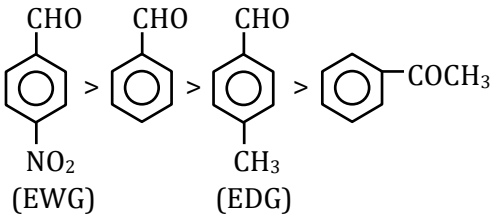
(less acidic) (more acidic)

$\therefore$ reaction is favoured in backward direction.

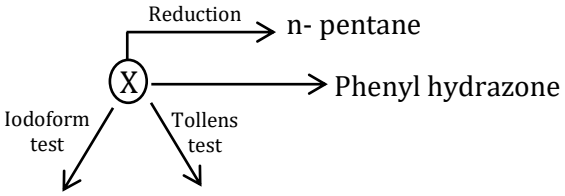
So, It is insoluble in $NaHCO_3$

3. Ans. (4)

NAR $\propto$ electrophilicity of carbonyl group $\propto \frac{1}{\text{Steric hindrance}} \propto \text{EWG} \propto \frac{1}{\text{EDG}}$



4. Ans. (2)

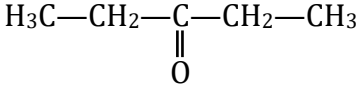


$\therefore C_5H_{10}O$ → Aldehyde / ketone

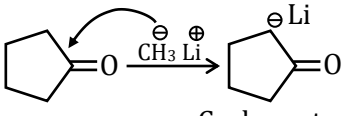
Since, It gives negative response to Tollen's test, It should be ketone and it also gives negative response to the iodoform test so it cannot be methyl ketone.

X on reduction gives n-pentane therefore it must have a straight chain of 5 carbon atoms.

Therefore, X should be 3-pentanone



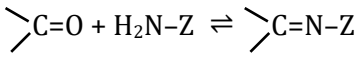
5. Ans. (4)



Cyclopentanoylanion

6. Ans. (4)

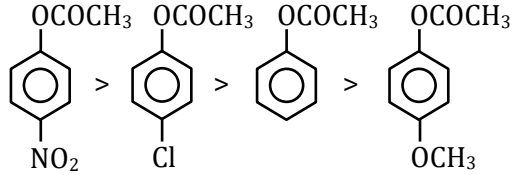
Nucleophilic addition followed by elimination of water



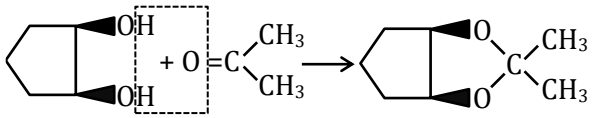
7. Ans. (3)

Esters

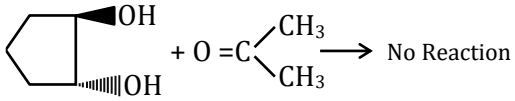
(S_NAE rxn. $\propto$ δ+ charge at $-\overset{\overset{O}{\|}}{C}-$ group $\propto$ EWG)



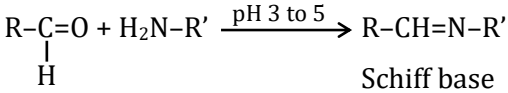
8. Ans. (1)



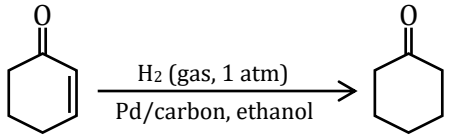
Reaction feasible



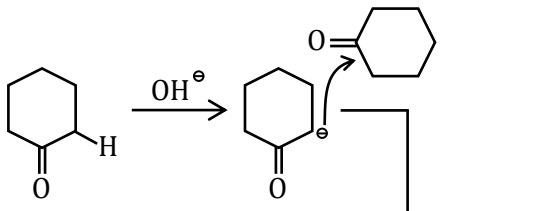
9. Ans. (1)



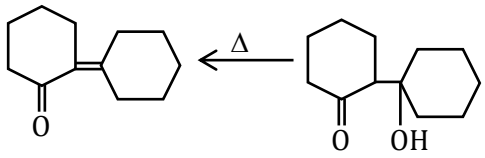
10. Ans. (4)



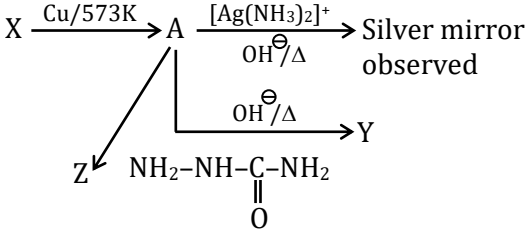
11. Ans. (1)



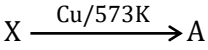
(Aldol condensation)



12. Ans. (2)



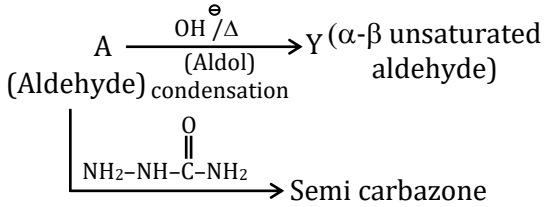
⇒ Since (A) gives silver mirror test, It should be aldehyde



⇒ (Alcohol) (Aldehyde)

(X) should be alcohol

⇒



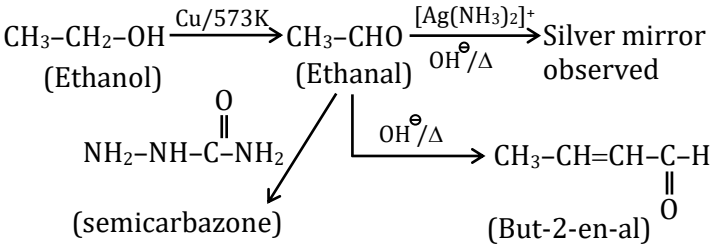
Therefore, we can clearly see from options

(A) → Ethanal

(X) → Ethanol

(Y) → But-2-en-al

(Z) → semicarbazone



13. Ans. (4)

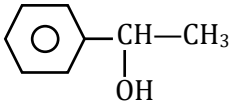
Carboxylic acids have higher boiling points than aldehydes, ketones and alcohols of comparable molecular mass due to a dimer formation by intermolecular H-bonding.

14. Ans. (3)

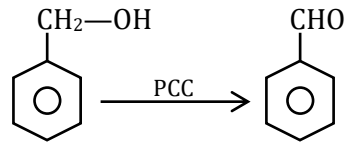
(A) $C_8H_{10}O \xrightarrow{NaOI}$ Yellow ppt

(Haloform reaction)

∴ (A) must have $CH_3-\underset{\underset{OH}{|}}{CH}-$ group or $CH_3-\overset{\overset{O}{\|}}{C}-$ group.

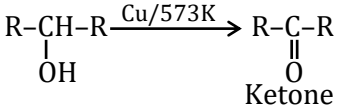
Thus (A) will be 

15. Ans. (3)

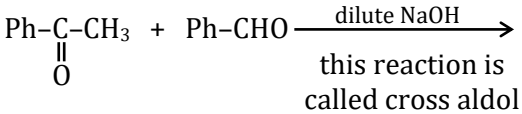


PCC is a mild oxidising agent.

16. Ans. (3)

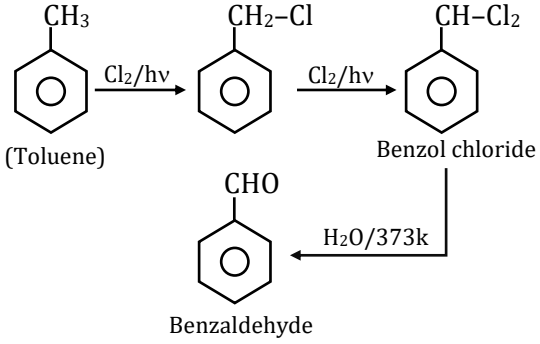


17. Ans. (1)

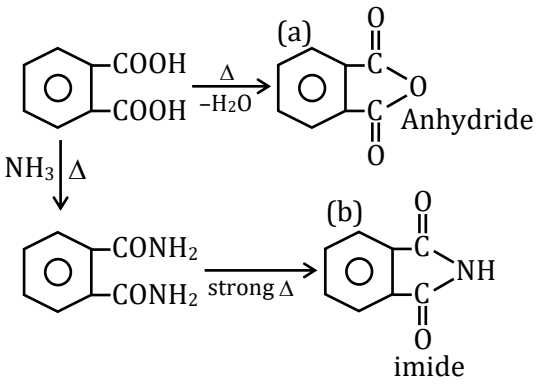


this reaction is called cross aldol condensation.

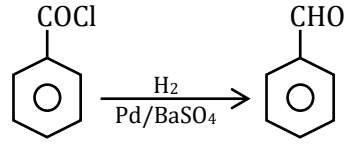
18. Ans. (4)



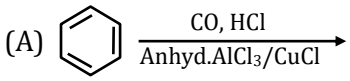
19. Ans. (1)



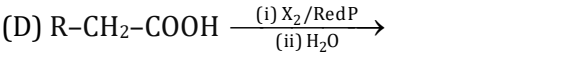
20. Ans. (1)



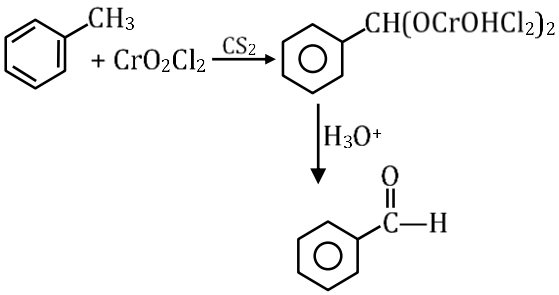
21. Ans. (4)



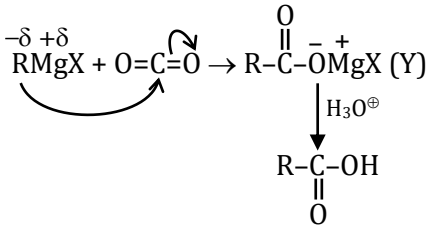
Gattermann-Koch Reaction



22. Ans. (1)



23. Ans. (4)

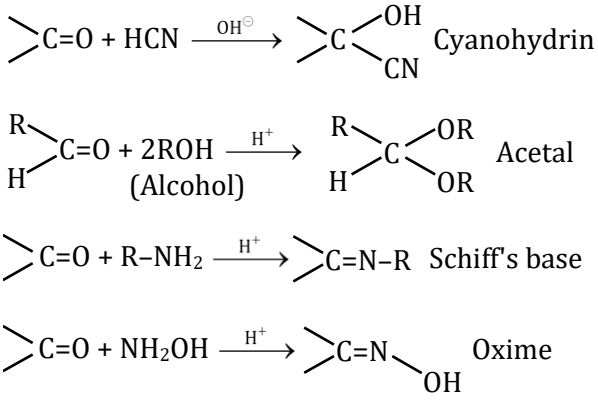


24. Ans. (4)

Boiling point of comparable molecular mass molecules

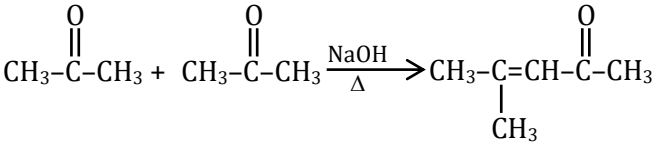
R – OH > Aldehyde – Ketone > Alkane
(H-bonding) (Dipole-dipole) (Non-polar)

25. Ans. (3)

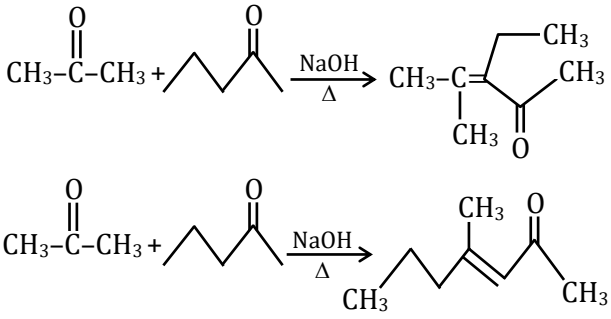


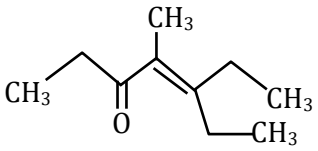
26. Ans. (1)

Self aldol



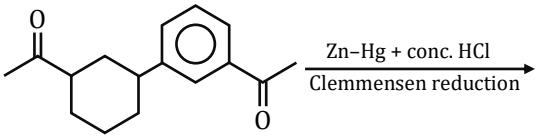
Cross Aldol

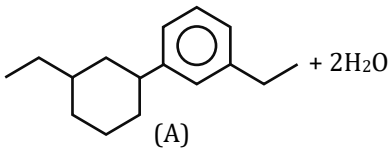




will not form

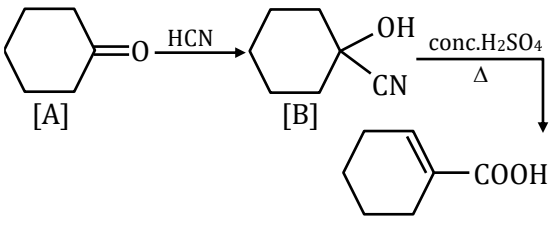
27. Ans. (4)





(A)

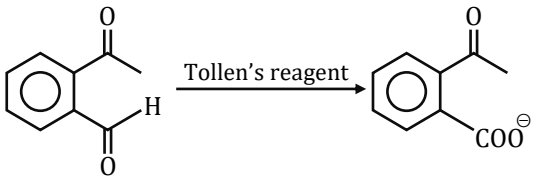
28. Ans. (3)



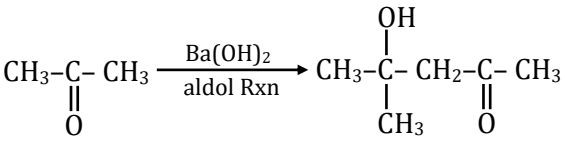
[A] [B] [C]

(Hydrolysis of Cyanide)
& (dehydration of alcohol)

29. Ans. (2)



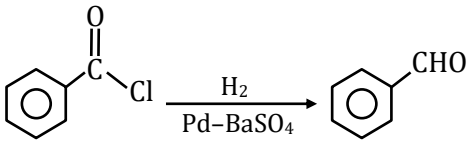
30. Ans. (4)



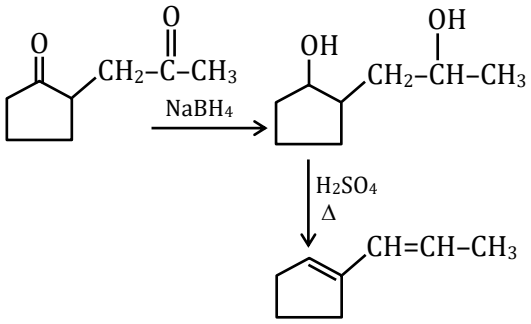
Functional groups present in product are alcohol and ketone.

31. Ans. (4)

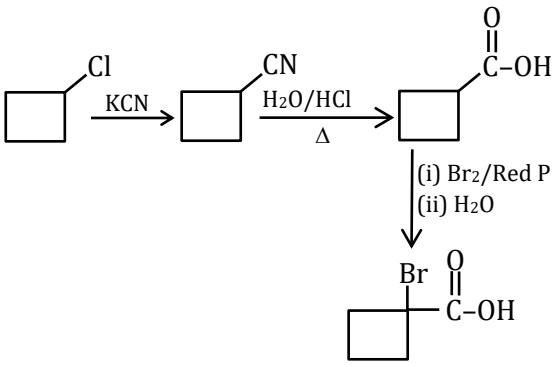
Rosenmund reaction



32. Ans. (1)



33. Ans. (2)



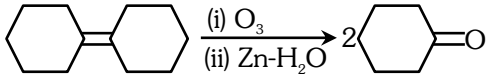
34. Ans. (1)

Fehling reagent comprises of two solution

Fehling A $\rightarrow$ aq. solution of $CuSO_4$

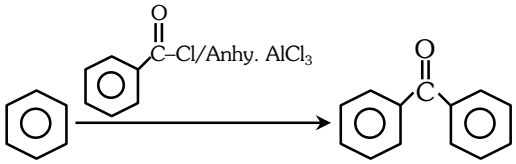
Fehling B $\rightarrow$ alkaline sodium potassium tartrate (Rochelle salt)

35. Ans. (3)

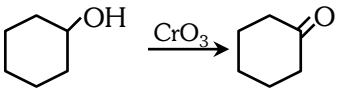
A-IV 

Reductive Ozonolysis

B-I

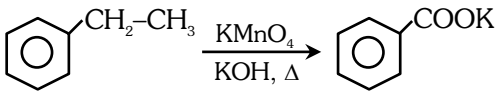


Friedal craft Acylation

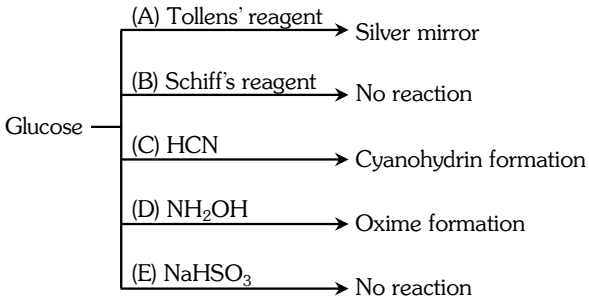
C-II 

Mild oxidising agent

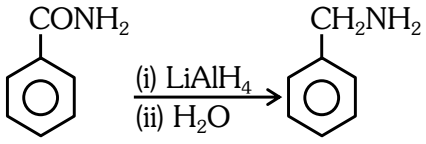
D-III



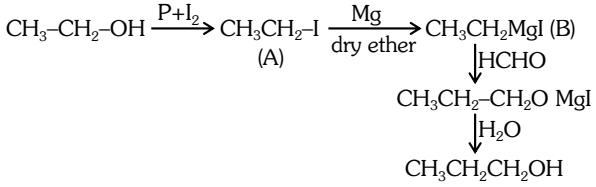
36. Ans. (3)



37. Ans. (2)

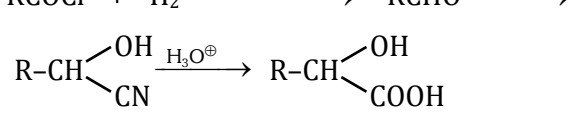


38. Ans. (1)

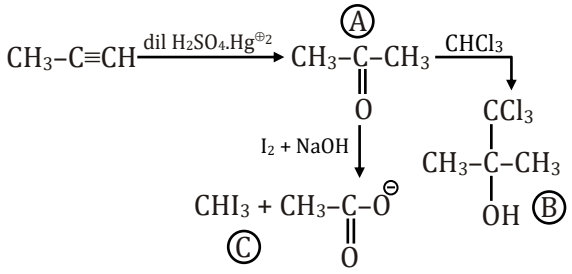


Exercise-III (Analytical Questions)

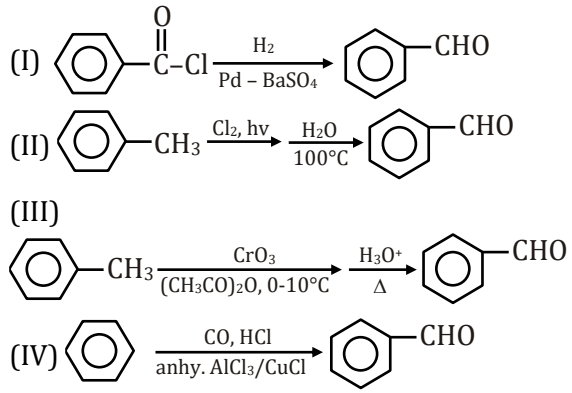
1. Ans. (2)



2. Ans. (3)



3. Ans. (4)

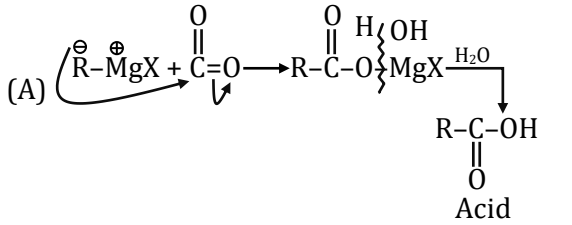


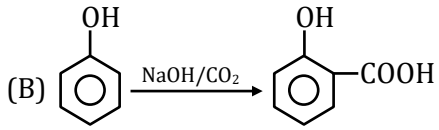
4. Ans. (2)

CH_3–$(CH_2)_4$–CN $\xrightarrow{\text{DIBAL–H}}$ CH_3–$(CH_2)_4$–CHO

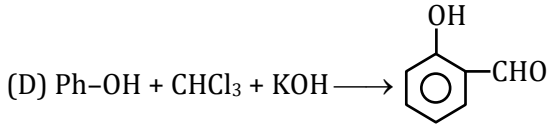
CH_3–$(CH_2)_4$–$COOC_2H_5$ $\xrightarrow{\text{DIBAL–H}}$ $CH_3(CH_2)_4CHO$.

5. Ans. (1)





(C) Ph–CN $\xrightarrow{H_3O^+}$ Ph–COOH



6. Ans. (4)

Aldehyde ✓

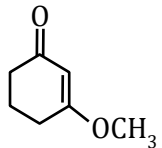
Only methyl aliphatic ketone ✓

Aromatic ketone ✗

7. Ans. (3)

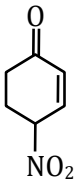
NAR $\propto$ electrophilicity of carbonyl carbon $\propto$

$$\text{EWG} \propto \frac{1}{\text{EDG}} \propto \frac{1}{\text{Steric hindrance}}$$



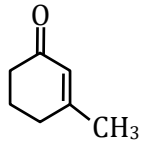
EDG

+M



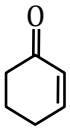
EWG

–I



EDG

+H/+I



Reactivity = b > d > c > a

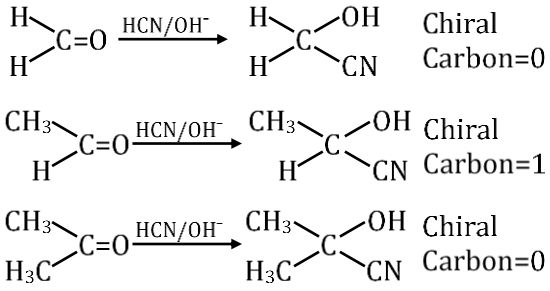
8. Ans. (2)

NAR $\Rightarrow$ Aldehydes > ketone.

reactivity due to less steric hindrance.

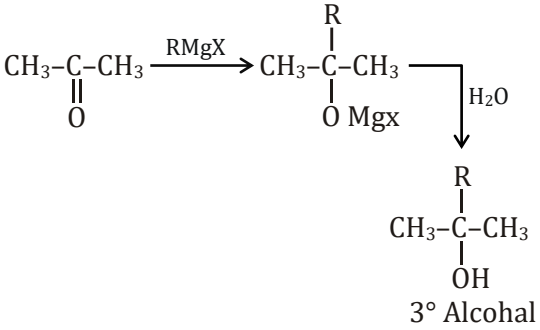
HCHO $\Rightarrow$ most reactive due to less steric hindrance.

9. Ans. (2)



Unsym. aldehyde/ketone $\xrightarrow{HCN/OH^-}$ Show OI.

10. Ans. (3)



11. Ans. (3)

Iodo form test is given by those compounds which have $CH_3-\overset{\overset{O}{\|}}{C}-$ and $CH_3-\underset{\underset{OH}{|}}{CH}-$ group.

12. Ans. (3)

	Iodoform test positive		Tollens or Fehling test
1.	CH_3CHO	+ve	+ve
2.	CH_3CH_2CHO	–ve	+ve
3.	$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	+ve	–ve
4.	$CH_3-CH=CH-CHO$	–ve	+ve

13. Ans. (3)

Iodoform test is given by those compounds which have $CH_3-\overset{\overset{O}{\|}}{C}-$ and $CH_3-\underset{\underset{OH}{|}}{CH}-$ group.

1. $CH_3-\overset{\overset{O}{\|}}{C}-R$ +ve Iodoform test

2. CH_3CHO +ve Iodoform test

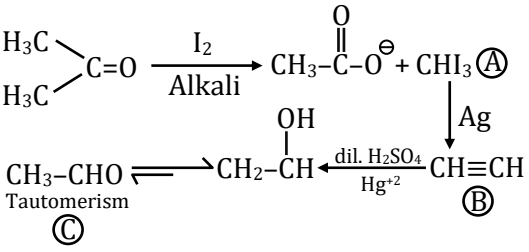
3. $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$

$\downarrow$

$2°OH \rightarrow$ (–ve iodoform test)

4. $R-CH_2OH \xrightarrow{(o)} R-\overset{\overset{O}{\|}}{C}-$ the iodoform test

14. Ans. (2)



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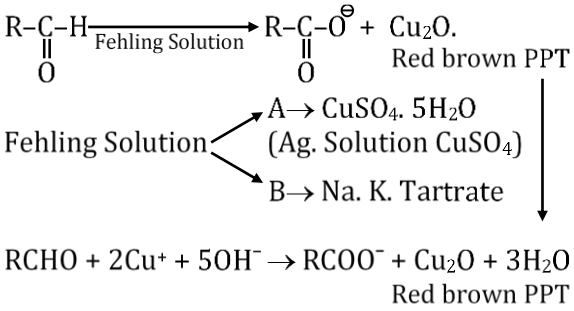
15. Ans. (2)

	CH_3-CHO		$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
1.	Fehling Solution	+ve	–ve
2.	Grignard reagent	+ve	+ve
3.	Schiff reagent	+ve	–ve
4.	Tollen's reagent	+ve	–ve

16. Ans. (3)

Fehling test → Only aliphatic aldehyde.



$RCHO + 2Cu^{+} + 5OH^{-} \rightarrow RCOO^{-} + Cu_2O + 3H_2O$

Red brown PPT

17. Ans. (4)

R—CHO $\xrightarrow{\text{Oxidation}}$ R—COOH.

18. Ans. (3)

→ Aldehydes easily oxidised to form carboxylic acid

→ Ketone difficult to oxidised to formed less number of carbon acid (carboxylic acid)

19. Ans. (3)

(A) Acetone $\xrightarrow[\text{Reagent}]{\text{Schiff}}$ No reaction

(B) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CHCl_3 \longrightarrow CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CCl_3}{|}}{C}}-CH_3$

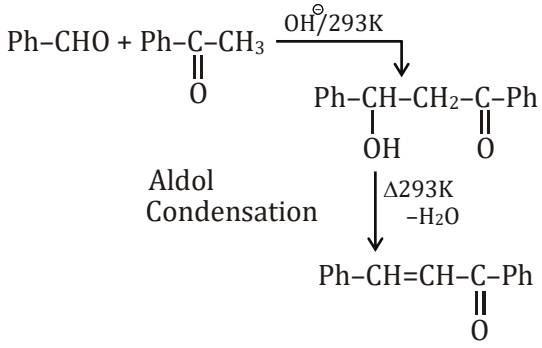
Chloritone (Hypnotic in nature)

(C) $H_3C-\underset{\underset{O}{\|}}{C}-CH_3$

Ketone difficult to oxidised to acid

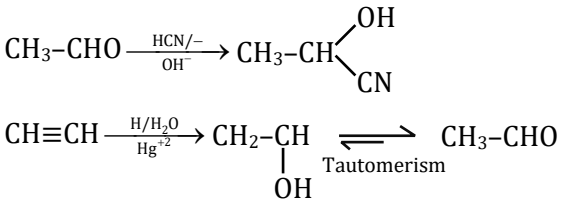
(D) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[H_2O]{Mg-Hg} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

20. Ans. (4)



21. Ans. (3)

CH_3CHO → easily oxidised to acid



$CH_3-CHO \xrightarrow{OH^-/\Delta}$ aldol condensation.

$3\alpha H$

22. Ans. (3)

Cannizzaro reaction → Aldehyde which don't have an α–Hydrogen atom undergo self oxidation & reduction an heating with conc. Alkali

23. Ans. (4)

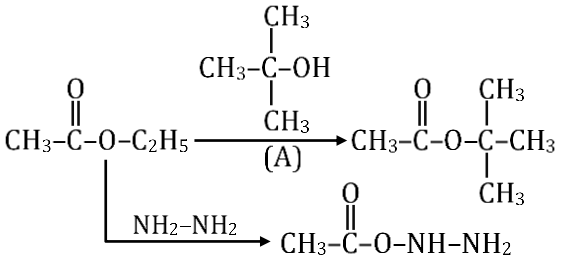
$Ph-CHO + HCHO \xrightarrow{OH^-/\Delta} Ph-CH_2OH + H-\overset{\overset{O}{\|}}{C}-O^{\ominus}$

Cannizzaro reaction

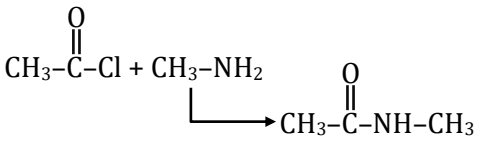
HCHO → Oxidised to salt of carboxylic acid (more reactive)

Ph CHO → reduced to Alcohol (less reactive)

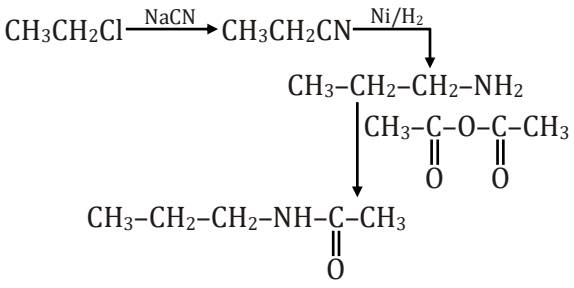
24. Ans. (3)



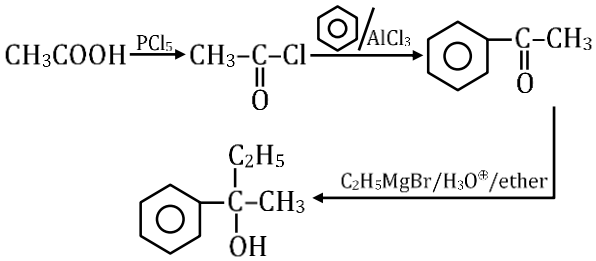
25. Ans. (3)



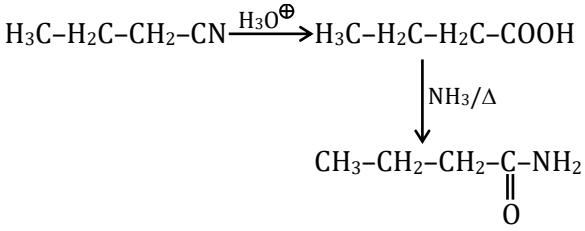
26. Ans. (1)



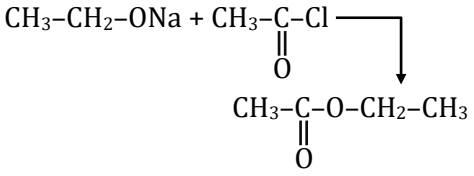
27. Ans. (4)



28. Ans. (4)



29. Ans. (2)



30. Ans. (1)

Hell-volhard-Zelinsky reaction

α–Hydrogen of carboxylic acid substitute by halogen