CHAPTER 23

Organic Reagents

1. **Alcoholic KOH**

   R–X → Alkene; Elimination

2. **Aluminium Ethoxide**

   $R-\underset{\underset{O}{\|}}{C}-H = O \rightarrow R-\underset{\underset{O}{\|}}{C}-O-CH_2R$ (Tischenko Reaction)

   (Aldehyde) (Ester)

3. **Aqueous KOH/NaOH**

   R–X → ROH

   Nucleophilic substitution reaction also used for Cannizzaro reaction with aldehyde.

4. **Baeyer's Reagent** (Alkaline cold dilute $KMnO_4$)

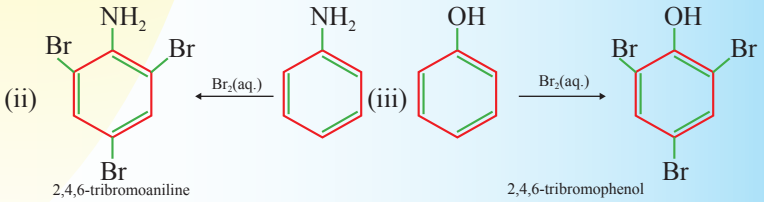
   $RCH = CHR' \rightarrow \underset{\underset{OH}{|}}{RCH}-\underset{\underset{OH}{|}}{CHR'}$ (Syn)

   alkene → 1, 2 diol

   (used to detect unsaturation)

5. **Bromine water**

   (i) Used to detect unsaturation;



6. **Benedict's solution**

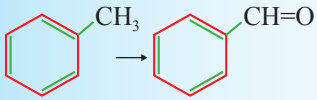
   Used to detect aldehyde group RCHO → RCO_2^- [ketone gives –ve test]

7. **$Cu_2Cl_2 + NH_4OH$**

Used to Detect Terminal Alkyne

Red Precipitate observed

8. **CrO_2Cl_2**



Etard reaction

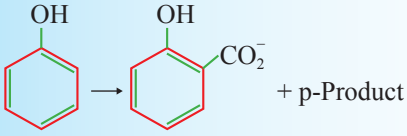
9. **CrO_3**

(i) $RCH_2OH \rightarrow RCHO$,

(ii) $R_2CHOH \rightarrow R_2C{=}O$

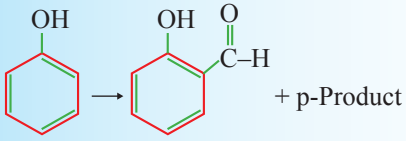
(iii) $R_3COH \rightarrow$ no reaction

10. **$CCl_4 + O^-H^-$** (Reimer Tiemann)



+ p-Product

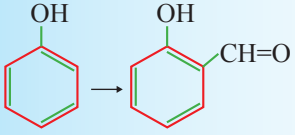
11. **$CO + HCl + AlCl_3$**



+ p-Product

Gatterman koch reaction

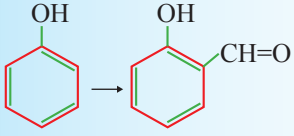
12. **$HCN + HCl + AlCl_3$**



Gatterman Aldehyde Synthesis

13. **$CHCl_3 + KOH$**

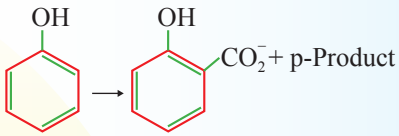
(i)



Reimer Tiemann reaction

(ii) $RNH_2 \rightarrow RNC$ (***Carbyl amine reaction***)
(used to detect 1° amine) (Isocyanide test)

14. $CO_2 + OH^-$ (*high temp. + Pressure*)



Kolbe's reaction

15. Cu/Δ

(i) $RCH_2OH \rightarrow RCHO$,

(ii) $R_2CHOH \rightarrow R_2C{=}O$

(iii) $H_3C{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}OH \longrightarrow H_2C{=}C\begin{matrix}CH_3\\CH_3\end{matrix}$

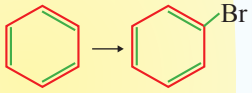
16. 2,4 - D.N.P.

Used to detect carbonyl group (orange ppt. observed)

17. DMSO

Polar aprotic solvent: favour S_N2 mechanism.

18. $Fe + Br_2/FeBr_3$



19. Fehling solution

Used to identify $-\overset{\displaystyle O}{\overset{\|}{C}}-H$ group.

PhCHO gives –ve test

Observation: red ppt. of Cu_2O formed

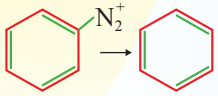
20. Grignard Reagent

Follows (i) Acid base reaction (ii) NAR (iii) NSR

21. H_2(Pd/$CaCO_3$) Quinoline (Lindlar catalyst)

$R - C \equiv C - R \rightarrow R - CH = CH - R$ (cis)

22. H_3PO_2



23. $HN_3 + H_2SO_4$

$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH \longrightarrow RNH_2$

(Schmidt Reaction)

24. H_3PO_4/Δ

$H_3PO_4 \Rightarrow$ Same as H_2SO_4/Δ

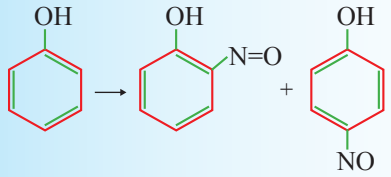
25. H_2SO_4/Δ

$$R\underset{\underset{OH}{|}}{CH}-CH_3 \longrightarrow RCH = CH_2$$

Saytzeff product; C^+ mechanism;
Rearranged alkene can be formed

26. HNO_2 ($NaNO_2$ + HCl)

(i) $RNH_2 \rightarrow R - OH$;
(ii) $PhNH_2 \rightarrow PhN_2^+$ (0 – 5°C)
(iii) $PhNH_2 \rightarrow PhOH$ (high temperature)

(iv) 

27. HIO_4 (Periodic acid)

$$R\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-R \longrightarrow RCH=O + R'CH=O$$

Oxidative cleavage of diol

28. H_2(Ni) can reduce

(i) $R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R_2CHOH$

(ii) $R-\underset{\underset{O}{\|}}{C}-H \longrightarrow RCH_2OH$

(iii) $RCN \rightarrow RCH_2NH_2$; $-C\equiv C- \rightarrow -CH_2-CH_2-$,

$-HC = CH- \rightarrow -CH_2 -CH_2-$

29. $H_2(Pd/BaSO_4)$

Quinoline

$$R-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow RCH=O$$

(Rosenmund reduction)

30. Jones Reagent (CrO_3 + dil. H_2SO_4 + acetone)

(i) $RCH_2OH \rightarrow RCHO$; (ii) $R_2CHOH \rightarrow R_2C = O$

31. $KHSO_4$ Dehydrating Reagent

$$CH_2\underset{\underset{OH}{|}}{-CH}\underset{\underset{OH}{|}}{-CH_2}-OH \longrightarrow CH_2=CH-CH=O$$

32. $K_2Cr_2O_7/H^+$

(i) $RCH_2OH \rightarrow RCO_2H$; (ii) $R_2CHOH \rightarrow R_2C = O$

33. MnO_2

(i) $CH_3–CH = CH–CH_2–OH \rightarrow CH_3–CH = CH–CH = O$

(ii) $PhCH_2OH \rightarrow PhCH = O$

To oxidise allylic/benzylic hydroxyl group into corresponding carbonyl.

34. $NaHCO_3$

$$RCO_2H \xrightarrow{NaH^{14}CO_3} RCO_2^-Na^+ + {}^{14}CO_2\uparrow$$

35. $NaHSO_3$

$$R–\underset{\underset{O}{\|}}{C}–R \longrightarrow RC\begin{matrix}OH\\ \diagup\\ \diagdown\\ SO_3^-Na^+\end{matrix}$$

[White crystals, soluble in water used to separate carbonyl from noncarbonyl compound]

36. $NaOH(aq)$

(i) $R–X \rightarrow R–OH$

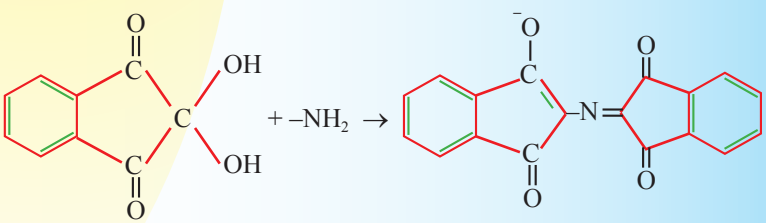
(ii) $$R–\underset{\underset{O}{\|}}{C}–OR' \xrightarrow[(H_2O)]{NaOH} R–\underset{\underset{O}{\|}}{C}–O^- + R'OH$$

(iii) $HCHO \xrightarrow{OH^-} HCO_2^- + CH_3OH$ (cannizaro)

(iv) $$H_3C–CH = O \xrightarrow[\Delta]{OH^-} \underset{\text{(Aldol condensation)}}{H_3C–CH = CH–CH = O}$$

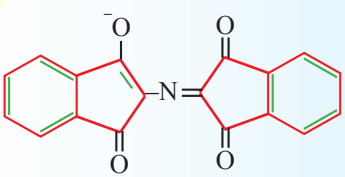
37. **Ninhydrin**

Detection of amino acid



Observation: Purple coloured ion

or



Yellow orange product

38. NaOR

Strong base:

(i) $RCH(X)-CH_2-R \longrightarrow RCH=CH-R$

(Saytzeff Product : E_2 elimination)

(ii) $H_3C-\underset{\underset{O}{\|}}{C}-OEt \longrightarrow H_3C-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OEt$

(claisen condensation) (β keto ester)

39. NaOH + X_2 or NaOX

(i) $RC(=O)-CH_3 \xrightarrow[-CHI_3]{} RCO_2^-$ (Haloform reaction)

(ii) $R-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow RNH_2$ (Hoffman Degradation)

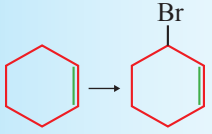
40. NaOH + CaO

$RCO_2H \rightarrow RH$

41. MnO / 300°C

Used for $-CO_2$ & $-H_2O$ in carboxylic acid.

42. NBS

(i) 

(ii) $PhCH_3 \rightarrow PhCH_2-Br$

43. $NaNO_2$ + HCl

$RNH_2 \rightarrow R-OH$

44. $NaNH_2$ in paraffin

Non-terminal Alkyne → Terminal Alkyne

(2-Butyne → 1-Butyne)

45. Na/EtOH

Reduce all except c/c double & triple bond

46. Zn(Hg) + HCl [Clemmensen's reduction]

$R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-CH_2-R$

47. **NH_2 –NH_2/OH^-** [Wolf Kishner reduction]

$$R-\overset{\overset{O}{\|}}{C}-R \rightarrow R-CH_2-R$$

48. **Na in Liq. NH_3** [Birch reduction]

$$R-C\equiv CR \longrightarrow \underset{H}{\overset{R}{\diagdown}}C=C\underset{R}{\overset{H}{\diagup}}$$

(trans alkene)

49. **$OsO_4 + H_2O$**

$$RCH=CHR \longrightarrow RCH(OH)-CH(OH)-R$$

(syn addition)

50. **O_3:** $R-CH=CH-R \xrightarrow[H_2O\backslash Zn]{O_3} R-CHO+R-CHO$

(Ozonolysis process)

51. **Oxirane followed by H^+**

$RMgX \rightarrow RCH_2-CH_2-OH$

52. **PCC**

(i) $RCH_2OH \rightarrow RCHO$,

(ii) $R_2CHOH \rightarrow R_2C=O$

(iii) $R_3COH \rightarrow$ no reaction

(Mild oxidizing reagent)

53. **P(red) + Br_2**

(i) $CH_3CO_2H \longrightarrow H_2C(Br)-CO_2H$ (HVZ reaction)

(ii) $ROH \rightarrow R-Br$

54. **P (red) + HI**

$CH_3CO_2H \rightarrow CH_3-CH_3$

$CH_3CH=O \rightarrow CH_3-CH_3$

$CH_3CH_2OH \rightarrow CH_3-CH_3$

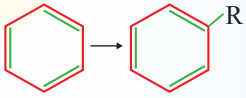
(strong reducing agent can reduce any oxygen or halogen containing compound to alkane)

55. **Perbenzoic acid** [Baeyer Villiger Oxidation]

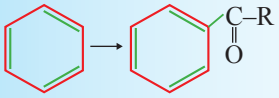
$$R-\overset{\overset{O}{\|}}{C}-R' \longrightarrow R-\overset{\overset{O}{\|}}{C}-OR'$$

R' having more migrating tendency than R

56. **RCl + $AlCl_3$** [Friedel craft alkylation]



57. $RCOCl + AlCl_3$ [Friedel craft acylation]

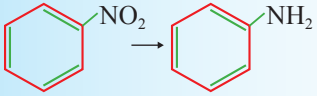


58. $ROH + R{-}\underset{\underset{O}{\|}}{C}{-}OH \xrightarrow[H_2SO_4]{Conc.} R{-}\underset{\underset{O}{\|}}{C}{-}OR$

Ester formed (Esterification reaction)

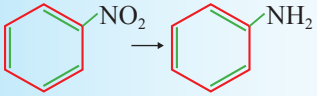
59. $SnCl_2 + HCl$

(i) $R{-}N{=}N{-}R' \rightarrow RNH_2 + R'NH_2$

(ii) 

(iii) $RCN \rightarrow R{-}CH_2NH_2$

60. Sn + HCl

(i) 

(ii) $RCN \rightarrow R{-}CH_2NH_2$

61. Silver salt RCOOAg (Hunsdiecker reaction)

$Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

62. AgOH/moist Ag_2O; $R_4\overset{+}{N}\overset{-}{X} \rightarrow R_4\overset{+}{N}\overset{-}{O}H$

$Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

63. $SOCl_2$

$R{-}\underset{\underset{O}{\|}}{C}{-}OH/R{-}OH \rightarrow R{-}\underset{\underset{O}{\|}}{C}{-}Cl/R{-}Cl$

64. Tollens Reagent Test

(i) Terminal alkyne gives
(ii) Aldehyde Group gives
(iii) Ketone gives –ve test
(iv) α-hydroxy ketone gives
(v) HCOOH gives
(vi) Hemi acetal gives
(vii) PhNH–OH gives

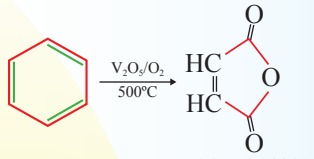
65. Benzene sulphonyl chloride

It is used to distinguish and separate (Hinsberg reagent) 1°, 2° and 3° amines.

66. Tetra ethyl lead (TEL)

Used as antiknock compound

67. V_2O_5

(i) 

(Maleic anhydride)

(ii)