TOPIC : AROMATIC COMPOUND EXERCISE # 1

Section (A)

- 4. Number of π electron is 6
- **5.** In naphthalene number of π electrons are ten.
- 6. Azulene is exist as dipolar ion

both rings have 6π electron hence aromatic.

8. Those compounds are anti aromatic which are cyclic, planar having $4n \pi$ electrons.



Section (B)

- 1. The characteristic reaction of benzene is electrophilic substitution.
- 2. The characteristic reactions of benzne is electrophilic substitution.
- **4.** –O⁻ is strongest activators and o/p- director.
- **6.** Rate of electrophilic substitution reaction ∞ Stability of arenium ion.
- 7. As the number of CI atom increases deactivation increases.
- **9.** A deactivating group deactivates o-and p-more than m-position because m-position does not have conjugation with the group.

15.
$$(- NH - C - (- NH - C -$$



18. The direct iodination of benzene is not possible because resulting $C_{e}H_{5}I$ is reduced to $C_{e}H_{6}$ by HI



24. Factual



27.
$$CH_3 - CH_2 - CH_2 - CI + AICI_3 \longrightarrow AICI_4^{\oplus} + CH_3 - CH_2 - \overset{\oplus}{C}H_2 \xrightarrow{H^{\oplus}} CH_3 - \overset{\oplus}{C}H - CH_3$$

 $O + CH_3 - \overset{\oplus}{C}H \longrightarrow O + H^{\oplus}$
 $H^{\oplus} + AICI_4^{\oplus} \longrightarrow AICI_3 + HCI$

28.
$$\bigcirc$$
 + CH₂Cl₂ anhydrous AlCl₃ \checkmark CH₂-CH₂
31. \bigcirc + CH₃-C-Cl anhydrous AlCl₃ \bigcirc COCH₃ + HCl

Section (C)

1.
$$Ph-CH_2-CH_3 \xrightarrow{Cl_2/hv} Ph-CH-CH_3$$

Cl

2.
$$(\bigcirc^{CH_3} \xrightarrow{CH_2-CI} \xrightarrow{CH_2-OH} \xrightarrow{CH_2-$$

- 3. Lindane is another name of B.H.C
- 4. Etard Reaction.



5.
$$\frac{Zn + H_2O}{CHO} 3 \stackrel{CHO}{\underset{CHO}{I}}$$

Section (D)

2. Preparation of phenol by hydroperoxide.



- **10.** Salicylic acid undergoes decarboxylation with the formation of 2,4,6-tribromophenol when treated with bromine water. The displacement of carboxyl group occurs only when the reaction is carried out in aqueous solution.
- **11.** It is an example of alkylation of phenol.

Section (E)

2. Nitrobenzene reduced into aniline by metal-acid and electrolytic reduction.





14. Mustard oil reaction given by 1° amines because it has 2 active -H atoms.

Section (F)

2. Diazotisation is given by an aromatic primary amine (–NH₂ attached to nucleus)

10. Phenol prefer coupling in sligtly basic medium.

11. Aniline prefer coupling in slightly acidic medium .

Section (G)

3. Factual.

4. $Ph-NO_2 \longrightarrow Ph-N=N-Ph$

5.
$$Ph-NO_2 \xrightarrow{Zn / alc. NaOH} C_6H_5N=NC_6H_5$$

7.
$$C_{6}H_{6} \xrightarrow{\text{conc. HNO}_{3}} \xrightarrow{\text{PeretrinO}_{3}} \underbrace{(NH_{4})_{2}S}_{NO_{2}} \xrightarrow{(NH_{4})_{2}S} \underbrace{(NH_{4})_{2}S}_{NO_{2}}$$

9. $NH_{4}SH$ is selective reducing agent.
11. $R-CH_{2}-NO_{2} \xrightarrow{HNO_{2}} R-C-NO_{2} \xrightarrow{NaOH} R-C-NO_{2}$
 $N-OH \xrightarrow{N-OH} N-O^{-}Na^{+}$
(nitrolic acid) (Blood red)
(Nitrolic acid) (Blood red)

- **12.** Use of nitro benzene is very wide.
- **13.** Boiling point is more than room temperature.

Section (H)

1. $R-C \equiv N+H_2O \xrightarrow{H^+} R-COOH+NH_3$ (Hydrolysis reaction).

2.
$$\begin{array}{c} CH_{3} \\ CH_{3} \end{array} C = N - OH \xrightarrow{Na/C_{2}H_{5}OH} CH_{3} \\ CH_{3} \end{array} CH - NH_{2} \end{array}$$

- 5. Hoffmann mustard oil reaction.
- 7. 3^o amine does not contain active hydrogen so reaction is not possible with Hinseberg's reagent.

11.
$$C_2H_5I + AgCN \xrightarrow{alcohol} C_2H_5 \longrightarrow N \cong C$$

12.
$$CH_3CH_2CH_2 - CI + KCN \longrightarrow CH_3CH_2CH_2CN + KCI$$

13.
$$\begin{array}{c} O \\ \parallel \\ R - C - NH_2 \xrightarrow{P_2O_5} \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \right) R - C \equiv N$$

- 16. Iso cyanides on hydrolysis forms primary amines not ammonia.
- **17.** $CH_3N \Longrightarrow C \xrightarrow{H_2O/H^+} CH_3NH_2 + HCOOH$
- 20. CH₃–N=C=O Methyl isocyanate

EXERCISE # 2 PART - I

- 1. In compound (4) both ring obey huckel rule hence it is aromatic.
- 2. If compound have acidic hydrogen & conjugased base of compound is aromatic in nature, then compound librate H₂ gas with K metal.

$$- K \rightarrow \bigvee_{\Theta} + H_2 \uparrow$$

(Anti aromatic)

So reaction is not feasible.

- **3.** According to energy profile diagram.
- **4.** Rate of electrophilic substitution ∞ Stability of arenium ion.
- 5. Due to +M effect of –SH group.
- 6. Cinnanyl system is ortho-para directing group.

7.
$$O \xrightarrow{\text{Conc. HNO}_3} O \xrightarrow{\text{Cl}_2/\text{FeCl}_3} O \xrightarrow{\text{NO}_2} O \xrightarrow{\text{Cl}_2/\text{FeCl}_3} O \xrightarrow{\text{C$$

stability of intermediate I > II

9. Electrophile attacks on that ring which has more +M effect.



- **10.** Rate of nitration at benzene does not affect by H or D because H or D leave in the fast step.
- **11.** Electrophile attacks on that ring which has more +M effect.





- **13.** According to hyperconjugation effect.
- **14.** Electrophile attacks on that ring which has more +M effect.
- 15. It is Friedal-Crafts reaction and is used for the preparation of diphenylmethane.
- **16.** In the presence of a Lewis acid like anhydrous AICl₃, an neopentyl cation rearranges to a more stable tertiary cation (I)



Now intermedite attacks the benzene ring to give



17. It is Friedel-Crafts alkylation reaction. Alkyl carbocation is formed alcohol as follow.

$$R-OH + BH_{3} = \begin{bmatrix} H \\ I \\ R-O \\ -BF_{3} \end{bmatrix} = R^{+} + HO - BF_{3}^{-}$$

- **18.** In vinyl chloride, lone pair of chlorine atom take part in resonance so partial double bond character introduce in C–Cl bond.
- **19.** Aniline form salt with lewis acid and deactivates the benzene ring so Friedel Craft reaction doesnot take place.



- 21. Benzene least likely to give reaction with chlorine free radical.
- **22.** Reactions (3) is free radical substitution reaction.

$$\mathbf{23.} \qquad \bigcirc^{\mathsf{CH}_2-\mathsf{CI}}_{\mathsf{O}} + \bigcirc^{\mathsf{CH}_3}_{\mathsf{O}} + \bigcirc^{\mathsf{CH}_3}_{\mathsf{CI}} + \bigcirc^{\mathsf{CH}_3}_{\mathsf{CI}} + \bigcirc^{\mathsf{CH}_3}_{\mathsf{CI}}$$



25. It is aromatic bimolecular nucleophilic substitution reaction. It is also called addition-elimination mechanism.

$$26. O_2 N - O_2 N -$$

27.
$$H_{3}C \longrightarrow OH + CH_{2} = CH-CH_{2}-CI \xrightarrow{\text{NaOH}} H_{3}C \longrightarrow O-CH_{2}-CH=CH_{2} \longrightarrow H_{3}C \longrightarrow OH + CH_{2}-CH=CH_{2}$$





- **30.** o-nitrophenol is steam volatile due to intramolecular hydrogen bonding.
- 31. The phenyl acetate formed undergoes Fries rearrangement to give the final product



Phenoxide ions are so strongly activated that they undergo electrophilic aromatic substitution with CO₂, a weak electrophile.

33.
$$(B)$$
 $OCOCH_3 \leftarrow NaOH \\ CH_3COCI \qquad OH \quad Zn \\ Distillation \qquad (A)$

34.
$$(\bigcirc)$$
 $-SO_3Na \xrightarrow{NaOH} (\bigcirc)$ $-ONa \xrightarrow{CH_3I} (\bigcirc)$ $-OCH_3 \xrightarrow{HI} C_6H_5OH + CH_3I$

→ hydrazobenzene 35. Zinc Conc.HNO₃ Phenol → Benzene -→ Nitrobenzene – Conc.H₂SO₄ at 60°C (electrophilic substitution) distillation NaOH (Reduction) OH C OH NO₂ NH₂ NaOH/ Δ Sn/HCI 36. ŇΟ, NO₂ ŃΗ,

- 37. It is fact.
- **38.** $Ph-NH_2+CH_3COCI \xrightarrow{Pyridine}{} Ph-NH-COCH_3$ (acetanilide)





52.
$$CH_3-CH_2-N \rightarrow O \xrightarrow{\text{Reduction}} CH_3-CH_2-NH_2$$

53.
$$C_2H_5Br \xrightarrow{AgCN} C_2H_5NC \xrightarrow{H_3O^+} HCOOH + C_2H_5NH_2$$

 $C_2H_5NH_2 \xrightarrow{CHCI_3} CH_3NC \xrightarrow{Reduction} CH_3NHCH_3$



12. In phenols, the presence of electron releasing groups decreases the acidity, whereas presence of electron withdrawing groups increase the acidity, compared to phenol. Among the meta and paranitrophenols, the latter is more acidic as the present of $-NO_2$ group at para position stabilises the phenoxide ion to a greater extent than when it is present at meta position. Thus, correct order of acidity is :

Para-nitrophenol > meta-nitrophenol > phenol > methyl phenol (iv) (ii) (i) (ii)

13. Electrophiles are electron deficient species. Among the given, H_3O^{\oplus} has lone pair of electrons for donation, thus it is not electron deficient and hence, does not behave like an electrophile.





15. Due to + M effect of – OH group and hyperconjugation of – CH_3 group









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- **19.** CH_2-NH_2 compound is most basic due to localized lone pair of electron on nitorgen atom while other compounds have delocalized lone pair of electron.
- **20.** Electrophilic rate order



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Toluene Toluene is most reactive.



Benzoic acid

Nitrobenzene

21. $CH_{3}-CH-NH_{2} \xrightarrow{HNO_{2}} CH_{3}-CH-OH + N_{2}^{\uparrow}$ $CH_{3} \xrightarrow{CH_{3}-CH-OH} CH_{3}$ $CH_{3}-CH-N \cong C \xrightarrow{reduction} CH_{3}-CH-NH-CH_{3}$ $CH_{3} \xrightarrow{CH_{3}-CH-NH-CH_{3}} CH_{3}$

Isopropyl methyl amine

- **22.** $-NO_2$ group is most deactivating group due to strong -I and -M effect.
- 23. Nitrobenzene is strongly deactivated, hence will not undergo Friedal-craft's reaction.
- 24. In (3) option the given reaction will not yield benzaldehyde.
- 25. The question is conceptually wrong, However among the given option, the closest option is "2"

26. H_3PO_2 and H_2O reduces the $-N_2CI$ to -H





It is an electrophilic substitution reaction. Coupling reaction of aniline takes place at the para-position to NH_2 group in benzene nucleus gives azodye.

29. Benzene diazonium chloride is most stable due to conjugation



- 35. Chlorine of chlorobenzene is inert towards nucleophile, which is phthalimide ion.
- 36. If large amount of KHSO₄ is added, Concentration of NO₂⁺ will decrease and hence the rate of nitration will be slower.



CH_=CH-CI, 38.

Not suitable for friedal-craft Reaction in Benzene. Isopropyl chlrodie is suitable.



Electron density is maximum on-2,5th carbon.







Aniline is basic in nature and in strong acidic medium after acid-base reaction aniline convert into anilium ion which deactivate ring and known as meta director





Cumene React with oxygen produce cumene peroxide product (A)

PART - II



9. 2° amine gives oilynitroso amine with nitrous acid.

10.
$$\underbrace{\operatorname{Conc. HNO_3}}_{\operatorname{Conc. H2SO_4}} \qquad \underbrace{\operatorname{LiAlH_4}}_{\operatorname{LiAlH_4}} \land \bigcirc \mathsf{N} = \mathsf{N} - \bigcirc \diamond$$

11.
$$Ph - NH_2 \xrightarrow{HNO_2} Ph - \stackrel{\oplus}{N} \equiv N \xrightarrow{HF}_{BF_3} Ph - N^+ \equiv NBF_4 \xrightarrow{\Delta} Ph - F + N_2 + BF_3$$

- 12. Greater is the electron density on aromatic ring, greater will be the reactivity towards electrophilic aromatic substitution.
- $ArN_{2}^{+} + KI \longrightarrow Ar I + N_{2}^{\uparrow}$ 13.

 Nitration of salicylic acid gives picric acid by elimination of –COOH group. This happens because –OH group is strongly activating group. Hence, S_E reaction occurs at o- and p- positions.



-OH group is more activating so attack of Br⁺ (electrophile) occurs at ortho position of -OH group during ESR



This is electrophilic substitution reaction known as Friedal Craft acylation





NO₂

Br₂/FeBr₃

This is electrophilic substitution in Aromatic Compound and Position of Br⁺ decided by directing effect of oxygen.

This is a Reimer-Tieman Reaction of phenol.



PART - III

- **1.** It is 2, 4, 6-trinitrophenol.
- **2.** $C_2H_5NH_2 + CHCI_3 + 3KOH \rightarrow C_2H_5N \cong C + 3KCI + 3HCI$

Ethyl isocyanide

3. Alkyl isocyanides are hydrolysed by dilute mineral acids to form primary amines.

 C_2H_5N ⇒ $C + 2H_2O$ $\xrightarrow{H^+}$ $C_2H_5NH_2$ + HCOOH ethylisocyanide ethylamine methanoic acid

- 4. $(\bigcirc_{CH_3}^{NH_2} + CHCl_3 + 3KOH \longrightarrow (\bigcirc_{CH_3}^{N \Rightarrow C} + 3KCl + 3H_2O)$
- 5. In Wurtz reaction alkyl halide reacts with sodium metal in the presence of dry ether to give alkane.



- 8. $CH_3CH_2 NH_2 + CHCI_3 + 3KOH \longrightarrow C_2H_5 N \equiv C + 3KCI + 3H_2O$ Carbylamine reaction.
- **9.** -NO₂ group in benzene ring shows I and M effect, which deactivates the ring towards electrophilic substitution but activates towards nucleophilic substitution.



(pain Killer)

-CH₃



NO₂ % para = 51 % meta = 47 % ortho = 2

Reason : Aniline in acidic medium converts into anilinium ion and it is meta directing so significant amount of meta product is obtained.



