

CHEMISTRY

TARGET: JEE Advanced - 2021

CAPS - 22

Nitrogen Containing Compounds

| Answer Key | | | | | | | | | |
|------------|-------|-----|------|-----|-----|-----|-----|-----|-----|
| 1. | (C) | 2. | (D) | 3. | (D) | 4. | (C) | 5. | (B) |
| 6. | (B) | 7. | (C) | 8. | (B) | 9. | (C) | 10. | (C) |
| 11. | (C) | 12. | (C) | 13. | (D) | 14. | (D) | 15. | (A) |
| 16. | (ABC) | 17. | (AB) | 18. | (B) | 19. | (A) | 20. | (C) |
| 21 | (B) | 22 | (B) | | | | | | |

Solution

1. The compound 'X' can be

$$[X] \xrightarrow{OH^{\circ}, CH_2I_2} \xrightarrow{NaNO_2/HCI} \xrightarrow{H_2O \ boil} \xrightarrow{I_2/OH^{\circ}} \xrightarrow{H^+} \xrightarrow{\Delta(-H_2O)} \xrightarrow{O} \bigcirc$$

$$(A) \begin{array}{c} HO \\ \hline \\ OH \\ \end{array} \\ OH \\ \end{array}$$

$$(C) \begin{array}{c} HO \\ \\ HO \\ \end{array} \begin{array}{c} NH_2 \\ \end{array}$$

$$(D) \begin{array}{c} NH_2 \\ NH_2 \\ OH \end{array}$$

Ans. (C)

Sol. HO
$$CH_2-CH_2-CH_2-NH_2$$
 $OH^9+C_2H_2I_2$ $OH^9+C_2H_2$ OH^9+C_2H

2. To get 2, 4, 6- tribromobenzoic acid from aniline the correct sequence of reagents is :

- $(A) \xrightarrow{Br_2} \xrightarrow{H_3O^{\oplus}} \xrightarrow{(i)NaNO_2/HCI,0^{\circ}C} \\ \xrightarrow{(ii)CuCN} \\ (B) \xrightarrow{H_3O^{\oplus}/H_2O} \xrightarrow{Br_2} \xrightarrow{(i)NaNO_2/HCI,0^{\circ}C} \\ \xrightarrow{(ii)CuCN} \\ \xrightarrow{(ii)CuCN}$

Ans. (D)

- 3. Which of the following arylamines will not form a diazonium salt on reaction with sodium nitrite in hydrochloric acid?
 - (A) m-Ethylaniline

(B) p-Aminoacetophenone

(C) 4-Chloro-2-nitroaniline

(D) N-Ethyl-2-methylaniline

Ans. (D)

NH-Et CH_3 Sol.

2°amine will not form diazonium salt

4. The major products obtained from the following sequence of reactions are:

$$(\operatorname{CH_3})\operatorname{CHCH_2N}(\operatorname{CH_2CH_3})_2 \xrightarrow{\operatorname{CH_3I}} \xrightarrow{\operatorname{Ag_2O}} \xrightarrow{\operatorname{heat}} \operatorname{Products}$$

- (A) $(CH_3)_2CHCH_2NH_2 + H_2C = CH_2$ (B) $(CH_3)_2NCH_2CH_3 + H_2C = C(CH_3)_2$

(C) $(CH_3)_2 CHCH_2 - N - CH_2CH_3 + H_2C = CH_2$ (D) $(CH_3)_3 N CH_2CH_3 + H_2C = CH_2$

Ans. (C)

- 5. Deamination (or) diazotization of n-Bu-NH₂/HCl gives.....isomeric butene.
 - (A) 2
- (B) 3
- (C) 4
- (D) 5

Ans. (B)

Sol.
$$NH_2 \xrightarrow{NaNO_2/HCl} M_{\oplus} \longrightarrow M$$

$$\stackrel{\text{H}^{\ominus} \text{ shift}}{/\!\!\!/} \longrightarrow /\!\!\!\!/ + /\!\!\!\!/$$

6. → Product and name of the reaction is:

(D) None of these

Ans. (B)

Sol.
$$\begin{array}{c} CH_3-C \\ \longrightarrow \\ Beckmann rearrangement \end{array}$$

$$\begin{array}{c} OH \\ N=C-CH_3 \\ \longrightarrow \\ \longrightarrow \\ \longrightarrow \\ \end{array}$$

$$\begin{array}{c} OH \\ N=C-CH_3 \\ \longrightarrow \\ \longrightarrow \\ \longrightarrow \\ \longrightarrow \\ \end{array}$$

anti-group will migrate with respect of OH.

7.
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Ans. (C)

Sol. Nucleophile attack of the hydroxy group takes place at that carbonyl carbon of amide where electrophilicity is high. –NO₂ group decreases electron density at its -ortho and -para position. So amide at ortho position will convert into carboxylic acid while other will convert in to amine.

Above (C-N) coupling reaction take place at:

(A) low pH (B) Intermediate pH (C) high pH

(D) any pH

Ans. (B)

Sol. Effect of pH on the coupling reaction :

Coupling is best carried out in solutions that are neither too strongly acidic nor alkaline. The reasons for this can be seen if we examine a typical case, the coupling of benzenediazonium chloride with dimethylaniline.

At high pH, the diazonium ion is present in very low concentration, since most of it has been converted to ArN = N – OH and ArN = N – O $^-$. Neither Arn = NOH (the diazohydroxide) nor ArN: N – O $^-$ (the diazotate ion) is e1ectrophilic, and does not couple with the amine. At low pH, the dimethylaniline will be largely protonated to ArN $^+$ Me $_2$ H, and thus the activating effect of the –NMe $_2$ group is destroyed, since the nitrogen atom no longer possesses an unshared pair of electrons:

Product (Y) of this reaction is:

Ans. (C)

Major product (x) in this reaction is:

Ans. (C)

Sol. In the given reaction ICI gives I⁺ and CI⁻

so both -ortho position of the nitro-aniline is occupied by the electrophile I⁺.

$$NH_2$$
 $+ 2ICl \longrightarrow I$
 $+ 2HCl (56-64\%)$
 NO_2
 $+ 2HCl (56-64\%)$

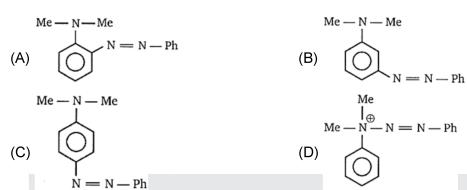
Product (A) is:

(A)
$$Ph - CH_2 - N - CH_2 - Ph$$
 (B) $Ph - CH_2 - N - N = CH_2 - Ph$ (C) $Ph - CH_2 - N$ (D) $Ph - N = CH_2 - Ph$

Ans. (C)

Sol. An interesting example of an internal coupling reaction is provided by the diazotisation of o-diaminobenzene:

12. $Ph-NH_2 \xrightarrow{CH_3-Cl(2mole)} (A) \xrightarrow{Ph-N_2 \overset{\oplus}{Cl}} (B)$ (major) Product of the above reaction is:



Ans. (C)

Sol. $\begin{array}{c} \text{NH-CH}_3 \\ \text{Ph-NH}_2 + \text{CH}_3 \\ \hline \end{array} \begin{array}{c} \text{CH}_3 - \text{Cl} \\$

13.
$$\begin{array}{c} CH_3 \\ \downarrow \\ N \\ \downarrow \\ CH_3 \end{array}$$
 CH₃ Moist Ag₂O Heat

Product, the main product is:

$$(A) \xrightarrow{CH_3} CH_3 \qquad (B) \xrightarrow{CH_3} CH_3 \qquad (C) \xrightarrow{CH_3} CH_3 \qquad (D) \xrightarrow{CH_2} CH_3$$

Ans. (D)

Sol. Hoffmann's elimination.

- **14.** During the Hinsbergs Test, which of the following primary amines is most likely to be detected as a secondary amine?
 - (A) MeNH₂

Ans. (D)

Sol. After formation of N substituted sulphonamide

$$\begin{array}{c} H & O \\ I & II \\ R-N-S \\ I \\ O \end{array} - CH_3$$

With the Hinsbergs peagent, then solubility of the salt

$$\begin{array}{c} O \\ O \\ \parallel \\ N-S \\ \downarrow_{\phi} \parallel \\ K \\ O \end{array} - CH$$

Depends on the length of hydrophobic portion. A very long chain may cause non-dissolutions and the amine may therfore appear as secondary.

15. Statement-1: $R - CO - NH_2$ and $R - CO - ND_2$ on treating with KOBr produce the same product $R - NH_2$

Statement-2: In both the reactions the intermediate is R - N = C = O

- (A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1
- (B) Statement 1 is True, Statement 2 is Tue; Statement 2 is NOT a correct explanation for Statement 1.
- (C) Statement 1 is True, Statement 2 is False
- (D) Statement 1 is False, statement 2 is True.

Ans. (A)

Sol.

MCQ

16.

Zn dust
$$\begin{array}{c|c}
 & CHCI_{2}/KOH \\
\hline
 & Zn dust
\end{array}$$

$$\begin{array}{c|c}
 & CHCI_{2}/KOH \\
\hline
 & Zn dust
\end{array}$$

$$\begin{array}{c|c}
 & CHCI_{2}/KOH \\
\hline
 & Zn dust
\end{array}$$

$$\begin{array}{c|c}
 & Oxidation \\
\hline
 & Oxidation
\end{array}$$

$$\begin{array}{c|c}
 & Oxidation \\
\hline
 & Oxidation
\end{array}$$

Ans. (ABC)

Sol. OH OH CHO

$$(P)$$

$$Zn dust$$

$$(R)$$

$$Zn dust$$

$$(R)$$

$$Zn dust$$

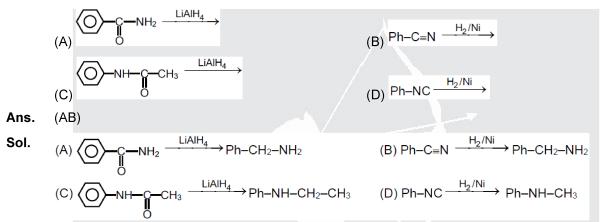
$$Zn dust$$

$$(R)$$

$$Zn dust$$

$$Zn d$$

17. Find out the reaction in which obtained product will give positive isocyanide test:



Comprehension

18. Given is mechanism of Beckmann rearrangement.

$$CH_{3} = N \xrightarrow{H^{+}} CH_{3} \xrightarrow{C} C = N \xrightarrow{(II)} CH_{3} \xrightarrow{C} C = N \xrightarrow{(IV)} CH_{3} \xrightarrow{C} C = N \xrightarrow{C} CH_{3} \xrightarrow{C} C CH_{3} CH_{4} \xrightarrow{C} C CH_{4} CH_{4} CH_{4} \xrightarrow{C} C CH_{4} CH$$

Rate determining step in Beckmann rearrangement:

(D) IV

Ans. (B)

Sol. Alkyl group anti migration is RDS

19. Given is mechanism of Beckmann rearrangement.

$$CH_{3} = N \xrightarrow{H^{+}} C = N \xrightarrow{(I)} CH_{3} = N \xrightarrow{(I)} CH_{3} - C = N \xrightarrow{(IV)} CH_{3} - C = N$$

On treatment H2SO4 followed by hydrolysis in acidic medium above compound gives.

(A)
$$CH_3 - CO_2H$$
, $Ph - NH_2$

(B)
$$CH_3 - NH_2$$
, $Ph - CO_2H$

(C)
$$Ph - CH_2 - NH_2 + Ph - CO_2H$$

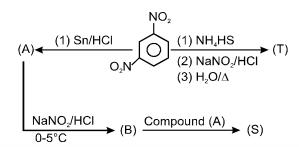
(D)
$$Ph - CO_2H + CH_3 - CO_2H$$

Ans. (A)

Paragraph for Question Nos. 20 to 22

Observe the following reactions and answer the following questions.

(Aromatic, T)



- **20.** The Product S can be:
 - (A) White compound

(B) Blue compound

(C) Red Brown compound

(D) Colourless liquid

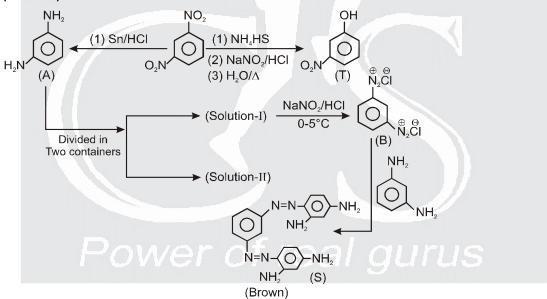
- Ans. (C)
- **21.** For Product (T), The correct statement is :
 - (A) Turns Red litmus blue

- (B) Turns FeCl₃ (Neutral) into coloured solution
- (C) Gives Friedel-Craft-Alkylations reaction
- (D) Contains two 'N' atoms

- Ans. (B)
- **22.** The product B on heating with H₂O produces :
 - (A) m-cresol
- (B) Resorcinol
- (C) Salicylic acid
- (D) Salicylaldehyde

Ans. (B)

Sol. (20 to 22)



Subjective

23. Observe the following synthesis

$$\begin{array}{c}
NH_{2} \\
\hline
NO_{2} \\
\hline
\end{array}
\xrightarrow{(1)}
\begin{array}{c}
NaNO_{2} / HCI \\
\hline
0^{\circ}C \\
\end{array}
\xrightarrow{(2)}
\begin{array}{c}
CuBr \\
\hline
(3)
\end{array}
\xrightarrow{(3)}
\begin{array}{c}
Sn / HCI \\
\hline
(4)
\end{array}
\xrightarrow{(4)}
\begin{array}{c}
NaNO_{2} / HCI \\
\hline
(5)
\end{array}
\xrightarrow{(6)}
\begin{array}{c}
H_{3}PO_{2} \\
\hline
(6)
\end{array}
\xrightarrow{(6)}$$

Sol.
$$\begin{array}{c} NH_2 \\ NO_2 \end{array} \xrightarrow{Br_2/Fe \text{ (excess)}} \xrightarrow{Br} \xrightarrow{NANO_2/HCl} \xrightarrow{Br} \xrightarrow{NaNO_2/HCl} \xrightarrow{Br} \xrightarrow{Sn/HC} \xrightarrow{Br} \xrightarrow{NaNO_2/HCl} \xrightarrow{NANO$$

24. Compound (A) having M.F. C₈H₈O on treatment with NH₂OH.HCl gives (B) and (C). (B) and (C) rearrange to give (D) and (E), respectively on treatment with acid. Compounds (B), (C), (D) and (E) are all isomers of molecular formula C₈H₉NO. When (D) is boiled with alcoholic KOH, an oil (F) C₆H₇N separated out. (F) reacts rapidly with CH₃COCl to give back (D). On the other hand, (E) on boiling with alkali followed by acidification gives a white solid (G), C₇H₆O₂. Identify the compounds (A) to (G).

Sol.
$$C_6H_5$$
 H_3C OH H_3C $C=N$ $C=N$ $C=N$ $C=N$ C_6H_5 OH

(A) (B) (C)

Acetophenone Acetophenone oxime Z -Acetophenone oxime

- 25. Two isomeric compounds (A) and (B) have C₄H₁₁N as molecular formula. Both on separately treating with HNO₂ lose their N₂ producing two isomeric alcohols (C) and (D) respectively of molecular formula C₄H₁₀O. (C) reacts with Lucas reagent immediately and units oxidation. (D) does not reacts with Lucas reagent in cold but can be easily oxidized. Complete methylation of either (A) or (B) is made which on decomposition does not produce 1-butene. Identify A to D.
- **Sol.** $A = (CH_3)_3C NH_2$, $B = (CH_3)_2CH CH_2 NH_2$ $C = (CH_3)_3C - OH$, $D = (CH_3)_2CHCH_2OH$
- **26.** Aniline in a set of reaction yield a product D. The structure of products A, B, C, D would be:

Sol. A: $C_6H_5N_2^+CI^-$ B: C_6H_5CN C: $C_6H_5CH_2NH_2$ D: $C_6H_5CH_2OH$