SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

- 1. Carbanion is a :-
 - (A) Base
- (B) Nucleophile
- (C) Both (A) and (B)
- (D) None

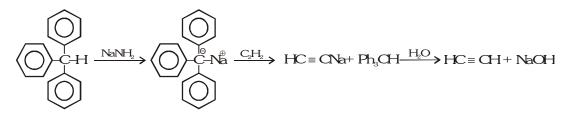
- 2. Electrophile is:
 - (A) H₂O
- (B) NH₂
- (C) AlCl₂
- (D) C₂H₅NH₂

- 3. Which of the following species has a pyramidal shape-
- (B) BF₂
- (C) CH₂-
- (D) CH₂
- 4. Increasing order (least basic first) of basic strength is shown by the set
 - (A) ClNH₂, NH₃, CH₃NH₂

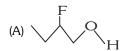
(B) ClNH₂, CH₃NH₂, NH₃

(C) NH₃, ClNH₂, CH₃NH₂

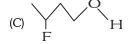
- (D) CH₃NH₂, ClNH₂, NH₃
- 5. The decreasing order of acid strength indicated by the following sequence of reaction is :-

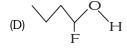


- (A) $NH_{3} > Ph_{3}CH > C_{9}H_{9} > H_{9}O$
- (B) $H_9O > HC \equiv CH > Ph_9CH > NH_9$
- (C) $HC \equiv CH > H_2O > Ph_3CH > NH_3$ (D) $Ph_3CH > HC \equiv CH > H_2O > NH_3$
- 6. In which of the following compounds is hydroxylic proton the most acidic -









- 7. Correct arrangement of the following acids in correct K₂ order is :-
 - (I) H_3N^{\oplus} CH_2 COOH (II) NC CH_2 COOH (III) H_3C CH_2 COOH (IV) $\overset{\Theta}{OOC}$ CH_2 COOH

- (A) I > II > III > IV
- (B) II > I > III > IV
- (C) I > III > II > IV
- (D) IV > III > II > I
- 8. Which of the following orders of acid strength is correct :-
 - (A) RCOOH > ROH > HOH > HC≡CH
- (B) RCOOH > HOH > ROH > HC≡CH
- (C) RCOOH > HOH > HC≡CH > ROH
- (D) RCOOH > HC = CH > HOH > ROH
- 9. Which of them is false for order of - I effect
 - (A) -F > -Cl > -Br > I

(B) $-NR_{a} > -NH_{b} > -NO_{a}$

(C) $-OCH_3 > -OH > -NH_9$

- 10. The order of basicity of halides is :
 - (A) $Cl^{-} < Br^{-} < I^{-} < F^{-}$

(B) $F^{-} < I^{-} < Br^{-} < Cl^{-}$

(C) $I^{-} < Br^{-} < Cl^{-} < F^{-}$

(D) $Cl^{-} < F^{-} < I^{-} < Br^{-}$



(A) $CH_2 = C = CH_2$

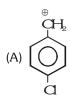
(B) CH₃-CH=CH₂

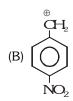
12. In the reaction
$$CH_3CN \xrightarrow{H_3O^+} CH_3COOH$$

the hybridization state of the functional carbon changes from

- (A) sp^3 to sp^2
- (B) sp^2 to sp^3
- (C) sp to sp²
- (D) sp² to sp

Most stable carbocation is :-13.









14. Most stable carbanion is :-

- (A) HC≡C^Θ
- (B) C₆H₅Θ
- (C) (CH₂)₂C-CH₂^Θ
- (D) $(CH_3)_2C = CH^0$

(a)
$$CH_3O \longleftrightarrow CH_2$$

- $\stackrel{\oplus}{\text{-CH}}_2$ (c) $\stackrel{\ominus}{\text{-CH}}_3$ $\stackrel{\oplus}{\text{-CH}}_2$ (d) $\stackrel{\ominus}{\text{-CH}}_3$

The relative stabilities of these carbocations are such that :-

(A) d < b < c < a

(B) b < d < c < a

(C) d < b < a < c

(D) b < d < a < c

16. Among the following, the strongest base is :-

- (A) $C_6H_5NH_2$
- (B) $p-NO_2-C_6H_4NH_2$ (C) $m-NO_2-C_6H_4NH_2$ (D) $C_6H_5CH_2NH_2$

The increasing order of base strength of Cl-, CH2COO-, -OH and F- is : 17.

- (A) $Cl^- < F^- < CH_3COO^- < -OH$
- (B) $Cl^{-} > F^{-} > CH_{3}COO^{-} > {}^{-}OH$
- (C) $CH_3COO^- < Cl^- < F^- < -OH$
- (D) None of these

Formic acid is considered as a hybrid of the four structures 18.

I

II

III

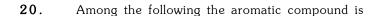
IV

Which of the following order is correct for the stability of the four contributing structures.

- (A) I > II > III > IV
- (B) I > II > IV > III
- (C) I > III > II > IV (D) I > IV > III > II

Which of the following carbonium ion is most stable 19.

- (A) Ph₂C⁺
- (B) $(CH_3)_3 C^+$
- (C) $(CH_3)_2 CH^+$ (D) $CH_2 = CH CH_2^+$











21. Match List- I with List- II and select the correct answer using the codes given below -

List-I (Stability)

List -II (Reason)

(A)
$$H_3C \oplus CH_3$$
 $\rightarrow CH_3$

(1) Inductive effect

(B)
$$H_3C-C$$
 Br CH_3

(2) Resonance

(C)
$$H_3C \xrightarrow{\oplus} CH_3 > H_3C - CH_2^+$$

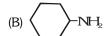
(3) Hyperconjugation and resonance

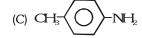
(4) Hyperconjugation and inductive effect

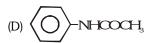
Codes:

22. Which of the following compounds is the strongest base -

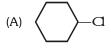
(A)
$$\langle O \rangle$$
-NH₂

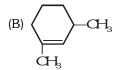


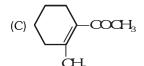




23. In which of the following molecule all the effect namely inductive, mesomeric & hyperconjugation operate:







24. Which of the following reaction is possible :

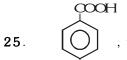
$$(A) \bigcirc OH \bigcirc ONa \longrightarrow NO_2$$

(B)
$$CH_3$$
-C-OH+HCOONa \longrightarrow

$$SO_3Na$$
 $COOH$

$$(C) \longrightarrow + \bigcirc \longrightarrow$$

(D)
$$H-C\equiv C-Na+H_2O \longrightarrow$$



, $\mathsf{pK}_{_{a}}$ value of the compound decreases if X is :-

- (A) -NO₂
- (B) $-NH_2$
- (C) -OH
- (D) -OCH₃
- 26. Which one of the following results most stable carbon free radical :
 - (A) $\dot{C}H_3$

 $(B) \bigcirc \stackrel{\dot{C}H_3}{\longrightarrow}$

(C) $(Ph)_2C = C(Ph)_2 \xrightarrow{\dot{C}H_3}$

- (D) $CH_2 = CH_2 \xrightarrow{\dot{C}H_3}$
- 27. CH_3-C-CH_2 $\xrightarrow{1,2 \text{ shift}} A \text{ (Major)}; \text{ Here A is :}$
 - (A) $CH_3 \overset{\oplus}{C} CH_3$

(B) OH₂

 $(C) CH_3 - \overset{\text{H}}{\underset{\oplus}{\text{C}}} - H_2 C - \overset{\text{C}}{\bigoplus}$

- (D) $CH_3-C=CH_1$ Ph
- **28.** $\langle \rangle$ -CH₂OH; On dehydration with conc. H₂SO₄ forms predominantly:
 - (A) \longrightarrow $=CH_2$
- (B) -CH
- (C) (T)-CH₃
- (D) (T)-CH_s

- 29. Which of the following is incorrect:
 - $(A) \quad \bigcirc \qquad \bigcirc \qquad \bigcirc \qquad + HC$
- $(C) \begin{array}{ccc} & H_1CH_2 & H_3\\ & & H_3-C & H_3-C-CH_2\\ & CH_3 & H & H \end{array}$
- (D) $CH_3CH_2CHO \xrightarrow{HO^-} CH_3 \stackrel{\Theta}{C} HCHO + H_2O$
- 30. The K_a values of alcohols, water and phenol are of order 10^{-17} , 10^{-14} and 10^{-10} respectively. Which of the following reactions is possible :
 - (I) $C_6H_5O^{\Theta} + H_2O \longrightarrow C_6H_5OH + OH^{\Theta}$
- (II) $C_2H_5O^{\Theta} + H_2O \longrightarrow C_6H_5OH + OH^{\Theta}$

- (A) Both I and II
- (B) only II
- (C) only I
- (D) neither of two

(B)
$$CH_2 = CH - \overset{\Theta}{C}H_2$$
 (C)

Stability of: 32.

(III)
$$CH_3-C=CH_2$$

 CH_3

$$\begin{array}{ccc} \text{(IV)} & \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3 \\ & \text{CH}_3 \end{array}$$

in the increasing order is:

(A)
$$I < III < IV < II$$

(D)
$$II < III < IV < I$$

(D) No reaction

34. Spin multiplicity of Triplet nitrene is :

(D) 4

35. The maximum probability of proton loss is in the case of :

(A)
$$CH_3 - \overset{\oplus}{C}H_2$$

(B)
$$CH_3 - CC - CH_3$$
 (C)

36. Select the least stable one:

(A)
$$CH_3-CH_2^{\oplus}$$

(B)
$$CH_2-CH_2-CH_2$$
 (C) CH_2-CH_2 (D) CH_3-CH_2 (D) CH_3-CH_2

37. Which of the following will react fastest with conc. HCl:

(D)
$$\langle O \rangle$$
-CH₂OH

38. Consider the following reaction :

$$OCH_3 + NaNH_2 \longrightarrow Product$$
Br

The product (P) and reaction (R) are :

- (A) NH_2 ; addition-elimination
 - (D) ; cine substitution

; elimination addition

- (C) NH_2 ; elimination addition
- 39. Energy of activation is lower for which reaction :
 - (A) $RCH_2 \overset{\oplus}{O}H_2 \rightarrow R\overset{\oplus}{C}H_2$

(B) $R_2CHOH_2 \rightarrow R_2CH$

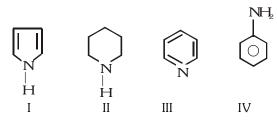
(C) $R_3C\overset{\oplus}{OH}_2 \rightarrow R_3\overset{\oplus}{C}$

(D) all have same $\boldsymbol{E}_{\text{act.}}$

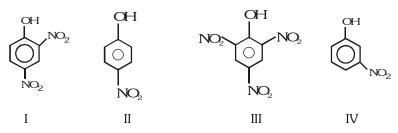
CHEC	K YOU	R GRAS	SP		ANSWER KEY						EXERCISE -1					
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
Ans.	С	С	С	Α	В	D	Α	В	D	С	D	С	С	Α	Α	
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	
Ans.	D	Α	Α	А	Α	В	В	С	D	Α	С	Α	В	С	В	
Que.	31	32	33	34	35	36	37	38	39							
Ans.	D	Α	В	С	С	D	В	С	С							

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

1. The correct order of decreasing basic strength is :



- (A) I > II > III > IV
- (B) II > III > I > IV
- (C) II > IV > I > III
- (D) II > III > IV > I
- 2. The correct order of increasing dissociation constant of the following compound is :-

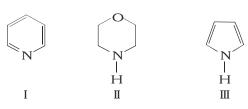


- (A) II < IV < I < III
- (B) IV < III < I < II
- (C) IV < II < I < III
- (D) IV < I < II < III
- 3. In the following arrange the H (numbered) for their ease of displacement during acid base reaction:

- (A) 1 > 2 > 3
- (B) 3 > 2 > 1
- (C) 3 > 1 > 2
- (D) 2 > 3 > 1
- 4. Which one of the following is the strongest base in aqueous medium :-
 - (A) $(C_2H_5)_3N$
- (B) $C_2H_5NH_2$
- (C) NH₃
- (D) $(C_2H_5)_2NH$
- 5. The correct order of acid strength of the following compound is -

- (A) III > II > I
- (B) III > I > II
- (C) II > I > III
- (D) I > II > III
- Which of the following shows the correct order of decreasing basicity in aqueous medium -6.
 - (A) $(CH_3)_3 N > (CH_3)_2 NH > CH_3 NH_2 > NH_3$ (B) $(CH_3)_2 NH > (CH_3)_3 N > CH_3 NH_2 > NH_3$

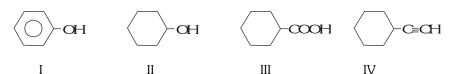
 - (C) $(CH_3)_2 NH > CH_3NH_2 > (CH_3)_3N > NH_3$ (D) $(CH_3)_2 NH > CH_3NH_2 > NH_3 > (CH_3)_3N$
- 7. For the compounds



the order of basicity is -

- (A) III > II > I
- (B) II > III > I
- (C) I > II > III
- (D) II > I > III

- 8. Which of the following shows the correct order of decreasing acidity-
 - (A) $PhCO_2H > PhSO_3H > PhCH_2OH > PhOH$
 - (B) PhSO₃H > PhOH > PhCO₂H > PhCH₂OH
 - (C) PhCO₂H > PhOH > PhCH₂OH > PhSO₃H
 - (D) PhSO₃H > PhCO₂H > PhOH > PhCH₂OH
- 79. Give the correct order of increasing acidity of the following compounds-



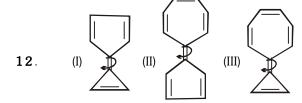
- (A) II < I < III < IV
- (B) IV < II < I < III
- (C) I < II < IV < III
- (D) IV < I < II < III

- 10. Which of the following is the most acidic
 - (A) $CH_2 = CH_2$

(B) $HC \equiv CH$

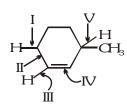
(C) CH₂=CHCH₂CH=CH₂

- (D)
- 11. Which of the following substituents will increase the acidity of phenol -
 - (A) $-NO_2$
- (B) -CN
- (C) -CHO
- (D) CH_3

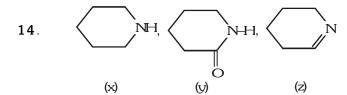


Compare carbon-carbon bond rotation across I, II, III.

- (A) I > II > III
- (B) I > III > II
- (C) II > I > III
- (D) II > III > I
- **13**. Which of the following s-bonds participate in hyperconjugation :

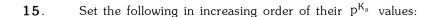


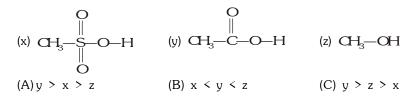
- (A) I and II
- (B) I and V
- (C) I and V
- (D) III and IV



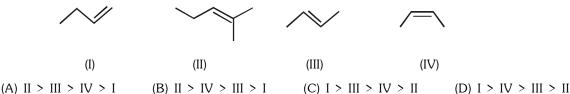
The correct order of decreasing basic strengths of x, y and z is :

- (A) x > y > z
- (B) x > z > y
- (C) y > x > z
- (D) y > z > x





16. Rank the following alkenes in order of decreasing heats of hydrogenation (largest first):



- 17. Which of the following molecules has all the effects : inductive, mesomeric and Baker Nathan effect ?
 - 2 0

(A) C_2H_5Cl

(B)
$$CH_3$$
- CH = CH_2

(C)
$$CH_2$$
= CH - CH = CH_2

(D)
$$CH_3$$
- CH = CH - C - CH_3

(D) x < z < y

18. Which nitorgen in LSD (Lysergic acid diethylamide) is more basic :

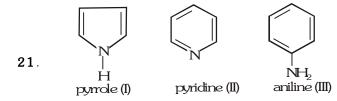
19. Which of the following substituted carboxylic acids has the highest K_a value:

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

 $\textbf{20}. \hspace{1.5cm} \textbf{Which of the following compounds yield most stable carbanion after rupture of (C_1-C_2) bond:}$

(A)
$$CH_3-C-CCI_3$$
 (B) $CH_3-C-CBr_3$ 1 2

(C)
$$CH_3-CH_2-C-CI_3$$
 (D) None of these



Which is/are correct statements?

(A) I is more basic than II

(B) II is more basic than I and III

(C) III is more basic than II

- (D) all are aromatic bases
- 22. Following is true for stability between the two structures :

(B)
$$CH_2$$
= CH - CH = CH - CH_2 : > \dot{CH}_2 - \dot{C} - \dot{CH} - \dot{CH}_3

$$CH_3$$

(C) $CH_2=C-CH_2$ > $CH_3-CH=CH-CH_2$

$$(D) \left\langle \bigcirc \right\rangle - \mathcal{O}' \left\langle \right\rangle -$$

- **23**. Which have acidic hydrogen:
 - (A) CH_3COOH (B)
- (B) (D)—OH
- (C) CH_3-C-CH_2-CN (D) CN_3
- 24. C-C and C=C bond lengths are unequal in :
 - (A) Benzene

(B) 1,3 buta-di-ene

(C) 1, 3 cyclohexa-di-ene

- (D) None
- 25. The acid strength of substituted carboxylic acids is known to be dependent on the nature and position of the substituent. In the following examples, an attempt has been made to arrange the acids in order of acid strength, the strongest first. One of the series is incorrect-which one:
 - (A) $\mathrm{CH_3.CH_2CH(Cl).COOH} > \mathrm{CH_3.CH_2COOH} > \mathrm{CH_3.CH_2.COOH}$
 - (B) NO₂.CH₂.COOH > HOCH₂. COOH > CH₃.COOH
 - (C) Cl₃C.COOH > BrCH₂.COOH > FCH₂.COOH
 - (D) $CH_3.COOH > CH_3.CH_2.COOH > (CH_3)_3C.COOH$
- **26**. Which species is not aromatic :









27. Select the correct option :

- (A) carbonic acid is weaker acid than acetic acid
- (B) the boiling points of acids are higher than corresponding alcohols
- (C) chloroacetic acid is stronger acid than acetic acid
- (D) phenol is more acidic than ethanol
- ${\bf 28}. \qquad \text{Which reacts with $AgNO_3$ to give ppt.}:$



29. Which statement is ture :

- (A) $\ddot{N}H_2$ is stronger base than $\ddot{O}H$
- (B) NH_2 -OH is less basic than NH_3
- (C) $\mathrm{CH_3-NH_2}$ is weaker base than $\mathrm{N(CH_3)_3}$ in (aq) medium

$$NH_2$$
 is weaker base than OH_2-NH_2

30. Which is less acidic than phenol:

(A)
$$OH$$
 (B) CH_3-OH (C) OH (D) H_2O

31. The precursor carbocation to the product in the following reaction is:

$$C_{e}H_{\downarrow} \xrightarrow{H^{\oplus}} C_{e}H_{\downarrow} \xrightarrow{H}$$

$$(C) \text{ either of the two} (D) \text{ none of the two}$$

(D) All of three

32. Which of the following ion is formed in the following reaction :



(D) Reaction not possible

34. Predict the nature of A in the following reaction :

$$(A) \bigcirc O \\ CH_2CCC_2H_4$$

35. Which of the following intermediate is most likely to be formed during addition of HBr on crotonic acid:

$$CH_3CH = CHCOOH + HBr(g) \longrightarrow CH_3CH - CH_2COOH : Br$$

(A) $CH_3CH_2 - \overset{\oplus}{C}HCOOH$

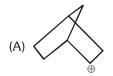
(B) CH₃ CH - CH₂COOH

(c) ch³a+a+c-a+

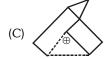
(D) none of these

36. Which will give most stable cation upon strong heating :

(B) (Ph)₃C-Cl



(B)



(D)

38.
$$Q = C - C - F \xrightarrow{F} [X] ; \text{ Here } [X] \text{ is } :$$

(B)
$$Q - C = C - C$$

(A)
$$Q - C = C - F$$
 (B) $Q - C = C - Q$ (C) $Q - C = C - F$ (D) $Cl - C = C - F$

(D)
$$C1 - C = C - F$$

39. H,C
$$CH_3 \xrightarrow{CHG_3} H$$
 the reaction proceeds via :

- (A) carbene
- (B) Carbon free radical
- (C) Carbocation
- (D) Carbanion

40.
$$(A) ; Here A is :$$

$$H$$

$$(D)$$
 (D)

41. Which of the following can give benzyne :

$$(A) \bigcirc H \xrightarrow{NaNH_2}$$

(B)
$$N_2^{\oplus}$$
 Δ

42. Dehydration of the following in increasing order is :

(D)
$$I < IV < II < III$$

43. Increasing tendency for S_N1 and S_N2 reaction is :

(A)
$$S_{N^1}$$
; I < III < II < IV

(B)
$$S_{\mathbb{N}^2}$$
; IV < II < III < I

44. Cyclopentyl ethyl ether can be obtained by :

(D) none is correct

45. Major product in the following reaction is :



- (A) _-OCH_2CH_3
- (B)
- (D)

- **46**. Mechanism of insertion reaction is of :
 - (A) One step for triplet carbene

(B) Two step for singlet carbene

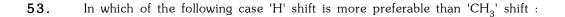
- (C) One step for singlet carbene
- (D) Two step for both
- 47. $\stackrel{6}{\cancel{NH}_{2}} \stackrel{\circ}{\cancel{NH}_{2}} \stackrel{\circ}{\cancel{N$
- (B) 5 0 0 1 1 2 2 3

- 48. $\underbrace{ \bigcap_{5}^{1} \bigcap_{3}^{2} \bigcap_{NH_{2}}^{0} }_{} (A).$ The most probable structure of intermediate A is :
 - (A) $\begin{array}{c}
 CH_3 \\
 11
 \end{array}$
- (B) 5 1 2 3
- (C) 5 0 1 1 2 2 3

- 49. Hybridisation of arrow headed 'C' is
 - (A) $sp^2 sp^3$
- (B) $sp^3 sp^3$
- (C) $sp^2 sp^2$
- (D) $sp^3 sp^3d$

- **50**. Which of the following is most strongest electrophile :
 - (A) singlet $H-\dot{N}$
- (B) triplet H-N
- (C) singlet -C
- (D) triplet -C 1

- **51.** In benzyne two external unshared electronic orbital :
 - (A) do not overlap to form a $\boldsymbol{\pi}$ bond
- (B) can overlap to form a complete π bond
- (C) poorly overlap to form a very weak bond
- (D) contribute in benzene ring
- ${\bf 52}$. Which of the following is aromatic intermediate:
 - (A) carbene
- (B)
- (C) Benzyne
- (D)



$$\begin{array}{c} CH_{3}\\ (A) CH_{3}-C-CH_{2}\\ H\end{array}$$

$$(C) \begin{array}{c} CH_s \\ \downarrow & \oplus \\ -C-CH-CH_s \\ \downarrow \\ Ph \end{array}$$

(D) all

54. Which of the following will not give 1, 2, shift:

$$(A)(CH_3)_3C-\overset{\scriptscriptstyle\oplus}{C}H_2 \qquad (B) (CH_9)_3C \overset{\leftarrow}{C}H-CH_2 \quad (C) \overset{\bigcirc}{\bigcup_{\scriptscriptstyle\oplus}} CH \qquad (D) \text{ all }$$

55. Which of the following reactions is wrong:

(C)
$$HO = C - H + H - C - H \longrightarrow HO - C - H + H - C - H$$
 $H \longrightarrow H$

$$\begin{array}{ccc} CH_3 \\ | & & \\ | & & \\ C & & \\ -C & & \\ -H_3 & & \\ -C & & \\ -H_3 & & \\ -C &$$

56. Methyl benzylic carbonium ion is the most stable one, hence it will react fastest consider the following reaction :

Br
$$CH_s$$
 + CH_s + CH_s (P) ; product (P) will be :

$$\text{(D)} \ \overset{\text{CH}}{\underset{\text{H}}{\bigvee}} \ \overset{\text{CH}}{\underset{\text{H}}{\bigvee}} \ \overset{\text{CH}_{\mathbb{S}}}{\underset{\text{H}}{\bigvee}} \ \overset{\text{CH}_{$$

R - CH = CH₂+ IN
$$_3^{\Theta}$$
 \longrightarrow A , A is :

(A) R-CH-CH₂N₃
$$\stackrel{|}{I}$$

(B)
$$R-CH-CH_{2}I$$
 N_{3}

58.
$$+ CHBr_3 \xrightarrow{1 BuOK}$$
 product; product will be:

$$(D) \bigcup^{CH_3} B_1$$

60.
$$CH_3$$
 OH^0
 A
Product ; major product of the reaction can be :

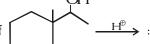
61.
$$CH_{3}COCH_{3} + BrCH_{2}COOEt \xrightarrow{\text{(ii) } Zn} \text{(A) ; the product (A) is :}$$

$$(A) \xrightarrow{CH_s} C \xrightarrow{DCH_s} B_r$$

$$(C) \begin{array}{c} CH_{\bullet} & C \\ CH_{\bullet} & C \end{array}$$

$$(D) \begin{array}{c} CH_{2} \\ CH_{2} \end{array} CBr$$





63. The most probable structure for (P) in the following reaction is :

$$2 \left\langle \begin{array}{c} \\ \\ \end{array} \right\rangle \xrightarrow{\operatorname{conc} H_2 SO_4} (P)$$



 $\bf 64$. Which of the following alcohols is dehydrated most readily with conc. $\rm H_2SO_4$?

$$(B) \bigcirc (B)$$

${\bf 65}$. Dehydration of alcohols by conc. ${\bf H_2SO_4}$ takes palce according to following steps :

$$\frac{0}{1,2-H \text{ shift}} \xrightarrow{\text{CH}_3} CH_3 \xrightarrow{\text{H}_3} CH_2 = C-CH_3$$

$$\frac{1,2-H \text{ shift}}{\text{step-III}} \xrightarrow{\text{CH}_3} CH_2 = C-CH_3$$

the slowest and fastest steps in the above reaction are :

- (A) step I is slowest, while III is fastest
- (B) step II is slowest, while III is fastest
- (C) step II is slowest, while IV is fastest
- (D) all step proceed at equal rate

$$\begin{array}{c|c}
 & + & CHC_3 & \xrightarrow{KOH} & & \\
 & & & H & \\
 & & & (A) & (B)
\end{array}$$

Which of the following intermediate is likely to be formed?



- (A) I and IV
- (B) I and III
- (C) III and IV
- (D) I, III and IV

67.
$$\xrightarrow{\text{conc. H}_2SO_4}$$
 Major product is :

BRAIN	BRAIN TEASERS ANSWI								KEY				E	EXERCIS	SE -2
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	D	С	В	D	Α	С	D	D	В	D	A,B,C	С	В	В	В
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	D	D	В	Α	Α	B,D	A,C	A,B,C	С	С	В	A,B,C,D	B,D	A,D	A,B,D
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	Α	В	С	D	С	С	С	Α	Α	D	D	Α	Α	Α	В
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	С	Α	В	С	В	С	С	Α	В	D	Α	В	С	Α	В
Que.	61	62	63	64	65	66	67								
Ans.	В	С	С	В	С	В	С								

TRUE OR FALSE:

- 1. In benzene, carbon uses all the three p-orbitals for hybridization.
- **2.** All the carbon atoms in bicyclbutane are sp²-hybridized.
- 3. Allene $(CH_2=C=CH_2)$ is a planar molecule.
- **4.** The greater stability of trans-but-2-ene over cis-but-2-ene can be explained on the basis of hyperconjugation effect.
- 5. In a two step reaction, the rate determining step has the lowest energy of activation.

FILL IN THE BLANKS:

- 1. Out of benzene, ethylene and acetylene, the carbon-carbon bond is longest in
- 2. The cyclopentadienyl cation is while cyclopentadienyl anion is
- 3. The type of delocalization involving sigma bond orbitals with π bond or vacant orbital is called
- 4. Hydroperoxide ion is a stronger but weaker than hydroxide ion.
- **5.** Catalytic hydrogenation of cis-2, 3-diphenyl-2-butene gives......

MATCH THE COLUMN

1. Match the column I with column II.

	Column-I	Column-II	Y	n-II
(A)	$-NO_2$	(p) – m effect	(p)	ect
(B)	-O ⁻	(q) + m effect	(p)	ect
(C)	$-O-CH_3$	(r) + I effect	(r)	ct
(D)	$-C \equiv N$	(s) – I effect	(s)	ct

2. Match the column I with column II.

	Column-I	\bigcap	Column-II
(A)		(p)	Aromatic
(B)		(q)	Non-aromatic
(C)	+	(r)	Anti-aromatic
(D)		(s)	Aliphatic

3. Observe the following compound P and match the column I with column II.

	Column-I	\sum	Column-II
(A)	Strongest acidic group in P	(p)	1
(B)	Weakest acidic group in P	(q)	2
(C)	Number of Intra molecular	(r)	3
	H-Bonding in P		
(D)	Number of mole of hydrogen	(s)	4
	gas that is liberated on reaction		
	of 'P' with excess of sodium metal if		
	one mole of P is used		

ASSERTION & REASON QUESTION:

These questions contains, Statement-I (assertion) and Statement-II (reason).

- (A) Statement-I is True, Statement-II is True; Statement-II is a correct explanation for Statement-I
- (B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I
- (C) Statement-I is True, Statement-II is False.
- (D) Statement-I is False, Statement-II is True.
- 1. Statement-I: Greater the s-character of the hybrid orbital, the smaller is its size.

Because

Statement-II: Bond formed by the overlap of sp³-sp³ hybrid orbital is the longest while the bond formed by the overlap of sp-sp hybrid orbital is shortest.

2. Statement-I: $Me_3\overset{+}{C}$ is more stable than $Me_2\overset{+}{C}H$ and $Me_2\overset{+}{C}H$ is more stable than the $Me\overset{+}{C}H_2$.

Because

Statement-II: Greater the number of hyperconjugative structures, more is the stability of carbocation.

3. Statement-I: Cyclopentadienyl anion is much more stable than allyl anion.

Because

Statement-II: Cyclopentadienyl anion is aromatic in nature.

Statement-I: CH_3OCH_3 and C_2H_5OH have comparable molecular masses but boiling point of C_2H_5OH is higher than dimethyl ether.

Because

Statement-II: C₂H₅OH forms intermolecular H-bonding while CH₃OCH₃ forms intramolecular H-bonding.

5. Statement-I : In the compound, $CH_3 - CH_2 - C \equiv N$, the most electroegative carbon is II.

Because

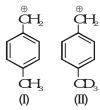
Statement-II: Carbon atom II has more s-character.

 $\textbf{6.} \hspace{15pt} \textbf{Statement-I} : \operatorname{pk}_{\operatorname{al}} \text{ of fumaric acid is more than maleic acid.}$

Because

Statement-II: Conjugate base of fumaric acid is stabilised by intramolecular H-bonding.

7. Statement-I: Carbocation (II) is more stable than carbocation (I)



Because

Statement-II: Carbocation (II) has more positive inductive effect of $-CD_3$ group as compared to $-CH_3$ group.

8. Statement-I: Carbon-oxygen bonds are of equal length in acetate ion.

Because

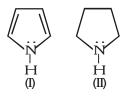
Statement-II: Bond length decreases with the multiplicity of bond between two atoms.

9. Statement-I: The potential energy barrier for rotation about C=C bond in 2-butene is much higher than that in ethylene.

Because

Statement-II: Hyperconjugation effect decreases the double bond character.

10. Statement-I: Pyrrolidine (II) is more basic than pyrrole (I).



Because

Statement-II: Protonated pyrrole has resonance stabilization of positive charge in aromatic ring.

COMPREHENSION BASED QUESTIONS:

Comprehension # 1

The intramolecular delocalisation of π and /non-bonding electrons without any change in the position of atoms is called resonance. Delocalisation may occur in conjugated system involving carbon atom and atom other than the carbon. Delocalisation makes system stable. More is the number of resonating structures, more is the stability of the system. A conjugated structure is least stable when a higher electronegative atom has positive charge and when identical charges are present on adjacent atoms.

1. The decreasing order of stability of the following resonating structures :

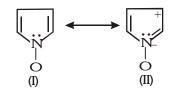
- 2. If A is $PhCH_2$ and B is $CH_2=CH-CH_2$, the greater number of resonating structure is of -
 - (A) A (B) B (C) both A and B (D) None of these

- 3. Which of the following pairs represent resonance?
 - (A) CH₂=CHOH; CH₃CHO

(B)
$$\bar{C}H_2$$
 -CHO; H_2C =CH-OH

4. Examine the structures I and II for nitromethane and choose the statement correctly :

- (A) II is less important because electrons have shifted to oxygen
- (B) II is less important because nitrogen has sextet of electrons
- (C) II is acceptable and important structure
- (D) none of these
- 5. Examine the following two structures for pyrrole and choose the correct statement given below:



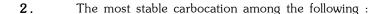
- (A) II is not an acceptable resonating structure because carbonium ions is less stable than nitride ion
- (B) II is not an acceptable resonating structure because there is charge separation
- (C) II is not an acceptable resonating structure because nitrogen has ten valance electrons
- (D) II is an acceptable resonating structure
- 6. Delocalization of electrons increases molecular stability because :
 - (A) Potential energy of the molecule decreases
 - (B) Electron-nuclei attraction decreases
 - (C) Both (A) and (B)
 - (D) Electron-electron repulsion increases

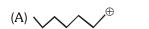
Comprehension # 2

Carbocation is a group of atoms with positively charged carbon atom having six electrons in the valence shell after sharing. Carbocations are formed in the heterolysis of a bond and are planar species. Stability of carbocation is determined by inductive effect, hyperconjugation and resonance effect. Greater the number of contributing structures, more is the stability of a Carbocation. Electron releasing groups (+I effect) increases the stability of a carbocation whereas the electron withdrawing groups (-I effect) have an opposite effect.

- 1. Which of the following is most stable carbocation?
 - (A) CH₂

- (B) $CH_3 \overset{+}{C}H CH_3$ (C) $CH_3 \overset{+}{C}H_2$ (D) $CH_3 \overset{+}{C}-CH_3$







3. In which of the following cases, the carbocation (I) is less stable than the carbocation (II)?

(A)
$$C_6H_5 - \overset{+}{C}H_2$$
 (I), $CH_2 = CH - \overset{+}{C}H_2$ (II)

$$(B) \bigcap^{+} \stackrel{\stackrel{+}{C}H_2}{(I)}, \bigcap^{+} \stackrel{\stackrel{+}{C}H_2}{(II)}$$

(C)
$$CH_2 = \overset{+}{C}H$$
 (I), $CH_3 - \overset{+}{C}H_2$ (II)

(D)
$$H_3C - \stackrel{+}{C}H_2$$
 (I), $CH_2 - \stackrel{\oplus}{C}H_2$ (II)

4. The most stable and the least stable carbocation among (I),
$$CH_2 = CH - \overset{+}{C}H_2$$
 (II), $C_6H_5 - \overset{+}{C}H_2$ (III)

and $CH_3 - \overset{\scriptscriptstyle +}{C}H - CH_3$ (IV) are respectively :

- (A) II, I
- (B) III, IV
- (C) I, II
- (D) I, IV

- **5**. Most stable carbocation is formed by the heterolysis of :
 - (A) $(CH_3)_3CBr$
- (B) $(C_6H_5)_3CBr$
- (C) $(C_6H_5)_2CHBr$
- (D) $C_6H_5CH_9Br$

Comprehension # 3

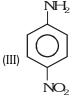
The most important condition for resonance to occur is that the involved atoms in resonating structure must be coplanar or nearly coplanar for maximum delocalisation. If this condition does not fulfil, involved orbitals cannot be parallel to each other and as a consequence delocalisation cannot occcur. Bulky groups present on adjacent atoms inhibit the of orbitats. This phenomenon is known as steric inhibition of resonance. Steric inhibition of resonance has profound effect on

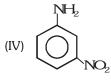
- (1) Physical properties
- (2) Acidity and basicity
- (3) Reactivity of organic compounds

1. Arrange the following in the increasing order of basicity:



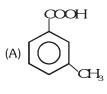


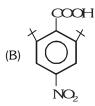


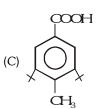


- (A) I > II > III > IV
- (B) IV > III > II > I
- (C) II > I > IV > III
- (D) I > IV > III > II

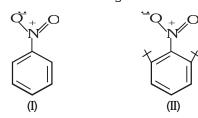
2. Which of the following is most acidic:



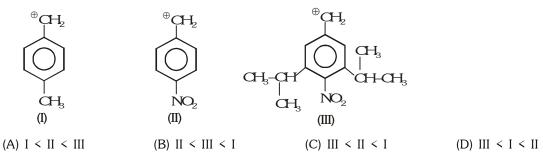




3. Consider the following two structures and choose the correct statements -



- (A) carbon-nitrogen bond length structure I is greater than that in structure II
- (B) carbon-nitrogen bond length in structure I is less than in structure II
- (C) carbon-nitorogen bond length in both structure is same
- (D) It can not be compared
- 4. Arrange the following carbocation in the increasing order of stability:



Comprehension # 4

1-Butene (A) and 1,3-Butadiene (B) differ not only in the number of π bonds, but (B) also has σ and π bonds at alternate positions. This type of the system is called conjugate system. Following are some of the conjugate system.



in such systems, π electron shifting takes place consecutively giving permanent polarity on the chain. This type of π -electron shift in the conjugate systems is called mesomeric effect or resonance.

Rules for resonance forms :

- (i) Individual resonance forms are imaginary, not real
- (ii) Resonance forms differ only in the placement of their π electrons or nonbonding electrons.
- (iii) Different resonance forms of a substance don't have to be equivalent.
- (iv) Resonance forms must be valid Lewis structures and obey normal rules of valencey.
- (v) The resonace hybrid is more stable than any individual resonance.

Rules for stability:

- (i) Structures with more covalent bonds are more stable than other structures.
- (ii) Structures in which all of the atoms have a complete valence shell of electrons (i.e. the noble gas structure) are especially stable and make large contribution to the hybrid.
- (iii) Stability is decreased by an increase in charge separation.
- (iv) Structure that carry negative charge on a more electronegative atom and positive charge on less electronegative atom are comparatively more stable.

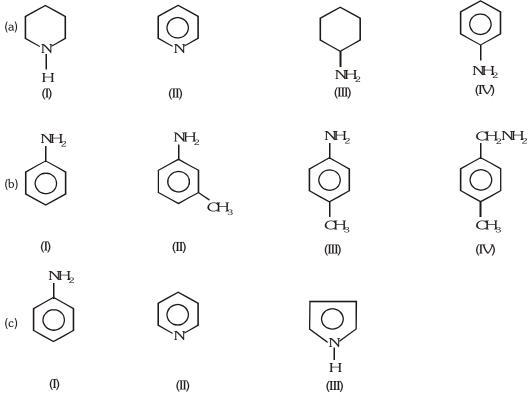
1. In which of the following compound, resonance is not possible :



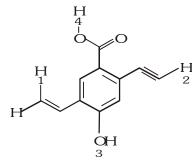
- 2. Which of the following statement is incorrect -
 - (A) In a resonance hybrid all the molecules are the same. A resonance hybrid cannot be expressed by any single structure.
 - (B) The value of the resonance energy of any resonance hybrid is not an absolute value
 - (C) The energy of hybrid structures is always less than that of any resonating structure
 - (D) Only one individual resonating structure explains all characteristics of the molecule
- $\bf 3$. Choose the correct option about stability of resonating structure :

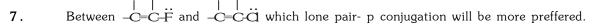
MIS	SCELLANEOUS TYPE	QUESTION	ANS	WER KE	Y		EXERCISE -3
•	<u>True / False</u> 1. F	2. F	3. T	4. F	5 . F		
•	<u>Fill in the Blan</u>	nks					
	 benzene 2,3-diphenylbuta 			3. hype	rconjucation	4. nucle	eophile, base
•	Match the Col		D)	O (A)	(D)	(0)	
	1. (A) \rightarrow p,s; B \rightarrow 3. (A) \rightarrow p; (B) \rightarrow	•		$2.\;(A)\to$	$\cdot q ; (B) \rightarrow p ;$	$(C) \rightarrow p ; (L$)) → r
•	Assertion - Red	ason Questions	<u>s</u>				
	1 . B 6 . C	 A D 	3 . A 8 . B	4. C 9. D			
•	<u>Comprehension</u>	Based Ques	<u>tions</u>				
	Comprehension and Comprehensio	#2 : 1. (D) 2 #3 : 1. (C) 2	2. (C)	3. (B) 3. (C) 3. (B) 3. (C,D)		5. (C) 5. (B)	6. (C)

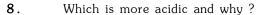
1. Rank the following amines in increasing basic nature :



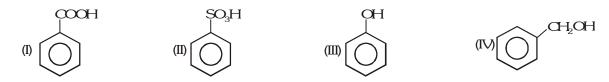
- 2. Rank the following intermediates according to the stability (most stable first).
 - (a) $\mathrm{CH_3CH_2CH_2} \overset{\oplus}{\mathrm{CH_2}}$, $\mathrm{CH_3} \overset{\oplus}{\mathrm{C}} \mathrm{HCH_2CH_3}$, $(\mathrm{CH_3})_2 \overset{\oplus}{\mathrm{C}} \mathrm{CH_2CH_3}$, $(\mathrm{CH_3})_3 \overset{\oplus}{\mathrm{C}}$
 - $(b) \operatorname{CH_3CH_2CH_2} \overset{\cdot}{\operatorname{CH_2}}, \ \operatorname{CH_3} \overset{\cdot}{\operatorname{C}} \operatorname{HCH_2CH_3}, \ (\operatorname{CH_3})_2 \overset{\cdot}{\operatorname{C}} \operatorname{CH_2CH_3}, \ (\operatorname{CH_3})_3 \overset{\cdot}{\operatorname{C}}$
- 3. Rank the following intermediates according to the stability (most stable first).
 - (a) $CH_3CH_2CH_2 \overset{-}{C}H_2$, $CH_3\overset{-}{C}HCH_2CH_3$, $(CH_3)_2\overset{-}{C}CH_2CH_3$, $(CH_3)_3\overset{-}{C}$
 - (b) CH_2 :, CH_3CH :, C_6H_5CH :, $(C_6H_5)_2C$:
- 4. Show why the phenolate ion, $C_6H_5O^-$, has a greater resonance stabilization than phenol, C_6H_5OH .
- 5. Is phenol a stronger acid than acetic acid. Explain your answer with proper reasoning.
- **6.** Arrange all these numbered H in order of their decreasing acidic strength.







9. Arrange the following compound in the correct order of acidity :



11.
$$H \xrightarrow{OH^0} (A)$$
 Product

12.
$$CH_2$$
=CHCHO + $C_2H_5MgBr \xrightarrow{H_3O^+} P$; Here P is :

13. Within each set, select the compound which is more reactive in nucleophilic addition at carbonyl carbon:

(I)
$$\mathrm{CH_3COCH_2CH_2Br}$$
 or $\mathrm{CH_3COCH_2Br}$

14. Rank of the following compounds in increasing order of electrophilicity:

15. Arrange the followings in increasing order of reactivity towards nucleophile:

16. Suggest the product of the reactions :

$$(A) \quad CH_3-CH_2 \xrightarrow{AIC_4/\Delta}$$

(B)
$$CH_3-C=O \xrightarrow{AlCl_3}$$

(C)
$$CH_3 - C - C - C \xrightarrow{KOH/Alc.}$$

$$CH_3 - C - C \xrightarrow{KOH/Alc.}$$

(D)
$$CH_2 = CH - CH = CH_2 \xrightarrow{HBr} A$$

 $= 80 C$

$$(E) \bigcirc \bigcap_{\parallel} O - C - C + G + G$$

$$AlCl_3 \rightarrow E$$

(F)
$$\bigcirc$$
 + \bigcirc + \bigcirc + \bigcirc + \bigcirc + \bigcirc G

(G)
$$CH_3-CH_2-CH-CH_3 \xrightarrow{\Theta} CH$$

$$(H) \bigcirc \stackrel{\bigcirc \\ \stackrel{\square}{\bigcirc} }{\bigcirc} \stackrel{AlCl_3}{\bigcirc} \longrightarrow$$

17. Arrange the following in increasing order of basic character :

(A) Cl^{Θ} , H_2O , Br^{Θ} , H_2S

$$(C) \bigcirc F, \bigcirc F, \bigcirc G, \bigcirc G, \bigcirc G$$

18. Heat of hydrogenation of CH_2 = CH_2 is greater than CH_3 -CH= CH_2 . Why ?

19. In the case of $\begin{bmatrix} \begin{matrix} \begin{matrix} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ \end{matrix} \end{bmatrix}$ OH, less stable 1-Butene is obtained. Why ?

20. When carbene attacks cis 2-butene singlet gives cis product while triplet gives trans product. Why?

- 1. (a) I > III > IV
- (b) IV > III > II > I
- (c) II > I > III
- **2**. (a) $(CH_3)_3 \overset{\oplus}{C} > (CH_3)_2 \overset{\oplus}{C} CH_2 CH_3 > CH_3 \overset{\oplus}{C} HCH_2 CH_3 > CH_3 CH_2 CH_2 \overset{\oplus}{C} H_2$
 - (b) $(CH_3)_3 \stackrel{\cdot}{C} > (CH_3)_2 \stackrel{\cdot}{C} CH_2 CH_3 > CH_3 \stackrel{\cdot}{C} HCH_2 CH_3 > CH_3 CH_2 CH_2 \stackrel{\cdot}{C} H_2$
- 3. (a) $CH_3CH_2CH_2 \overset{-}{C}H_2 > CH_3 \overset{-}{C}HCH_2CH_3 > (CH_3)_2 \overset{-}{C}CH_2CH_3 > (CH_3)_3 \overset{-}{C}$
 - (b) $(C_6H_5)_2C:>C_6H_5CH:>CH_3CH:>CH_2:$
- 4. Free charge has move reactivity than bound charge.
- **5**. No

Anion of acetic acid is more stabilised by resonance than phenoxide ion.

- **6**. 4 > 3 > 2 > 1
- 7. In -C=C-F, lone pair p conjugation will be more due to more overlaping of orbitals involved in conjugation.
- **8.** Phenol is more acidic as after loss of H+, phenoxide ion is Resonance stabilised. No such resonance is seen in conjugate base of cyclohexanol.
- 9. || > | > || > |V
- 10. Due to the non-planar structure.

12.

- Rank the following sets of intermediates in increasing order of their stability giving appropriate reasons for your choice.
 - (a) : CH₂, : C(C₆H₂)₂, CH₃CH:, C₆H₅CH:, O₂NCH₂CH:

(b)
$$\bigcirc$$
 + \bigcirc + \bigcirc + \bigcirc + \bigcirc + \bigcirc

2. For the following compounds, arrange the labelled proton in increasing order of their ease of deprotonation :

$$C = C - H^{3}$$

$$(i) C + \frac{1}{2}$$

$$H^{2}$$

$$H^{3}$$

$$H^{2}$$

$$H^{2}$$

$$H^{2}$$

$$H^{3}$$

$$H^{2}$$

$$H^{2}$$

- 3. Benzene sulphonic acid is a stronger acid than benzoic acid, explain.
- 4. Which is a stronger acid, A or B and why?

$$(I) \begin{array}{c} COOH \\ \\ \\ NO_2 \\ (A) \end{array} \begin{array}{c} COOH \\ \\ \\ NO_2 \\ (B) \end{array}$$

- **5.** Descuss the following observations :
 - (a) C-Cl bond in vinyl chloride is stronger than in chloroethane.
 - (b) Carbon-carbon bond length in ethene is shorter than in CH_2 = $CHOCH_3$.
 - (c) CH₃SH is stronger acid than CH₃OH.
 - (d) $CH_3CH_2NH_2$ is stronger base than CH_2 = $CHNH_2$.

6. Discuss the basic strength of two nitrogens in benzimidazole.

Benzimidazole

7. In each of the following pair of compounds, which is more basic in aqueous solution? Give an explaination for your choice:

(i)
$$CH_3NH_2$$
 or CF_3NH_2 (ii) CH_3CONH_2 or H_2N (iii) $PhNH_2$ or CH_3CN

- 8. Answer the following questions:
 - (i) Which of the indicated H is abstracted rapidly by bromine radical and why?

(ii) One of the indicated proton H_a or H_b , is approximately 10^{30} times more acidic than other, which is more acidic and why ?

- **9.** Explain the following
 - (i) $NC-CH_2-CN$ is a stronger acid than $CH_3-CO-C_2H_5$.
 - (ii) $CH_3-CO-C_2H_5$ is more acidic than $CH_3-CH=CH_2$.
 - (iii) $CH_3-CH=CH-OH$ is more acidic than $CH_2=CH-CH_2-OH$.
- 10. Compare the bond dissociation energies of C-H bonds in the following

(i)
$$H-CH_2-CH_2-CH_3$$
 (ii) H_3C CH_3 (iii) H_3C-H_3 (iii) H_3C-H_3

11. The most stable intermediatry carbocation and major product in following reactions:

(i)
$$H^{\oplus}$$
 $[C^{\oplus}]$ Product

(ii)
$$H^{\oplus}$$
 [C $^{\oplus}$] Product

(iii)
$$OH$$

$$C \xrightarrow{HBr} [C^{\oplus}] \longrightarrow Product$$

(a)
$$(II)$$
 (b) (II) (II)

13. Find the product in following reaction :

$$(a) \qquad \xrightarrow{Ag^{\oplus}} A \qquad \qquad (b) \qquad + CH_2Cl_2 \xrightarrow{\stackrel{\oplus}{\text{Bu}} \stackrel{\ominus}{\text{O}} \stackrel{\oplus}{\text{N}}}$$

(c)
$$\stackrel{\stackrel{\cdot}{\downarrow}}{\downarrow}$$
 + CHC₃ $\stackrel{\cdot}{\longleftrightarrow}$ C+D (d) $\stackrel{\stackrel{\cdot}{\downarrow}}{\biguplus}$ E

(e)
$$\xrightarrow{\text{NaOH}} \text{[Intermediate]} \xrightarrow{\text{(i) CO}_2} F$$

14. Write the mechanism of following reaction :

(a)
$$\xrightarrow{OH}$$
 $\xrightarrow{dil H^{\oplus}}$ [A]

(b)
$$\longrightarrow$$
 O-O-H $\xrightarrow{H^{\oplus}}$ [B] (c) \xrightarrow{Me} $\xrightarrow{H-C}$ [A] \xrightarrow{Me} \xrightarrow{Me}

(d)
$$OTs \xrightarrow{KI} A + F$$

15. Find the major product in the reaction the following :

(i)
$$HO$$
 NH_2
 HO

16. Decreasing order of E.S.R.

17. Complete the following equations:

$$(A) \qquad H^{+} \xrightarrow{O} \xrightarrow{NaOH} \xrightarrow{H_{3}O}$$

(B)
$$\stackrel{+}{\bigvee}$$
 $\stackrel{O}{\longrightarrow}$ $\stackrel{\text{NaOH}}{\longrightarrow}$ $\stackrel{\oplus}{\longrightarrow}$

2-equivalent 1-equivalent

18. Suggest the mechanism of the following reaction :

$$(i) CH_3-CH_2-CH-CH_3 \xrightarrow{H_2SO_4} CH_3 \xrightarrow{CH_3} C \xrightarrow{trans} CH_3$$

$$(ii) \begin{array}{ccc} CH_3 & CH_2 \\ | & | & | \\ | & | \\ C-Br & \underline{\text{NaOH}} & CH_3-C \\ | & | & | \\ CH_3 & CH_3 \end{array}$$

$$\begin{array}{ccc} & & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & \\ & & \\ & \\ & & \\ &$$

$$(iv) \bigcirc \stackrel{\text{Br}}{\longleftarrow} \stackrel{H}{\stackrel{|}{\longleftarrow}} \stackrel{\text{NaOH}}{\stackrel{\text{alc.}}{\longleftarrow}} \bigcirc \stackrel{\text{CH=CH}_2}{\longrightarrow}$$

- $Y \xleftarrow{CH_3OH} CH_3OH \xrightarrow{CH_3OH} X \; ; \; \text{Here} \; \; X \; \text{ and} \; \; Y \; \text{respectively are}.$
- $COOC_2H_s \xrightarrow{C_2H_sON_0} Z$; the product Z is. 20. COOC,H₅
- CH_3 CH_2 CH_2 CH_2 CH_3 CH_2 CH_3 CH_3 21.
- $\stackrel{H^{\oplus}}{\longrightarrow} [X] \ ; \ most \ likely \ the \ compound \ [X] \ is.$
- H ; the above intermediatory involves. 23.
- 24. Suggest the product of the reactions:

(A)
$$CH_3$$
- CH = CH_2 O / H

$$(B) \bigcirc \stackrel{H}{\longrightarrow} \stackrel{CHC_3}{\longrightarrow} \bigcirc \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{N} = \stackrel{\circ}{C}$$

$$(C) CH_3-C-O-C-CH_3+O-AICI_3 (B) (D) C-H$$

$$(D) CH_3-C-O-C-CH_3+O-AICI_3 (D) C-H$$

(D)
$$+H-CO_3 \xrightarrow{NaOH} C$$

$$(E) \bigcirc \stackrel{O}{\longrightarrow} C-H \xrightarrow{NaOH} D$$

$$(G) \xrightarrow{OH} \xrightarrow{H^{\oplus}} P$$

(H)
$$O_2N$$
 $C - CH_3$
 N_3OH
 Δ
 OH

1. (a) O₂NOH,CH: < CH₂: < CH₂CH: < C₂H₂CH: < (C₂H₂)₂C:

(b)
$$\bigcirc$$
 $^+$ $^{<}$ \bigcirc $^+$ $^{<}$ \bigcirc $^+$

- **2.** (i) 2 < 1 < 3 (ii) 3 < 1 < 2
- 3. Conjugate base of benzene sulphonic acid has greater resonance stabilization than benzoate ion, hence benzene sulphonic acid is stronger acid than benzoic acid. PhSO₃⁻ has three equivalent resonance structure, so more stable.but PhCOO⁻ has only two equivalent resonance structure, so less stable.
- **4.** B is stronger base than A. Here basic strength is controlled by -R effect of $-NO_2$. In B, due to steric inhibition to resonance of $-NO_2$ by two bulky tertiary butyl group, it is not decreasing basic strength by -R effect, hence B is stronger base than Al.
- **5.** (a) Due to resonance in vinyl chloride, C—Cl bond acquire some double bond character while in chloroethane, C—Cl bond is pure, single sigma covalent bond.
 - (b) Due to resonance in methyl vinyl ether, bond order of C-C is slightly reduced from two while in ethene C-C bond order is exactly 2.
 - (c) Larger size of sulphur compared to oxygen gives greater acidity to $\mathrm{CH_{3}SH}$.
 - (d) Lone-pair of electron in vinyl amine is involved partly in resonance delocalization and less available for donation to a lewis acid, hence a weaker Lewis base.
- 6. Lone pair of the basic nitorgen is fully available with nitrogen, i.e. not involved in delocalization while lone pair of non-basic nitrogen is part of aromatic delocalization.

7. (i)
$$CH_3NH_2$$
, (ii) $H_2N-C-NH_2$ (iii) $PhNH_2$ NH

- 8. (i) $H_c > H_a > H_b$ (ii) H_a : Conjugate base is aromatic
- **9.** Acidic strength ∞ stability of anion formed after removal of $H^+ \infty$ number of e^- withdrawing groups.
- **10**. | | | > | | > |

B.D.E.
$$\propto \frac{1}{\text{stability of intermediate formed}}$$

19.
$$X : HOCH_2-CHCH_3$$
 and $Y : CH_2-CHCH_3$

$$CCH_3 \qquad CCH_4 OH$$

EXERCISE-05(A)

PREVIOUS YEARS QUESTIONS

1. In the following benzyl/allyl system

 $R-CH=CH_2$ or R

[AIEEE 2002]

(R is alkyl group)

decreasing order of inductive effect is-

- $(1) (CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2-$
- (2) $CH_3 CH_2 > (CH_3)_2 CH > (CH_3)_3 C -$
- (3) $(CH_3)_9CH- > CH_3CH_9- > (CH_3)_3CH-$
- (4) None of these
- 2. In the anion HCOO⁻ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it-
 - (1) Electronic orbits of carbon atoms are hybridised
 - (2) The C=O bond is weaker than the C-O bond
 - (3) The anion HCOO- has two resonating structure
 - (4) The anion is obtained by removal of a proton form the acid molecule
- 3. The correct order of increasing basic nature for the bases NH_3 , CH_3NH_2 and $(CH_3)_2NH$ is-[AIEEE 2003]
 - (1) $CH_3NH_2 \le NH_3 \le (CH_3)_2NH$
 - (2) $(CH_3)_2NH < NH_3 < CH_3NH_2$
 - (3) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
 - (4) $CH_3NH_9 < (CH_3)_9NH < NH$
- 4. Consider the acidity of the carboxylic acids-

[AIEEE 2004]

(i) PhCOOH

(ii) o-NO₂C₆H₄COOH

(iii) p-NO₂C₆H₄COOH

(iv) $m-NO_{2}C_{6}H_{4}COOH$

which of the following order is correct for acidic strength-

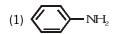
(1) i > ii > iii > iv

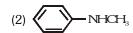
(2) ii > iv > iii > i

(3) ii > iv > i > iii

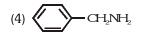
- (4) ii > iii > iv > i
- 5. Which of the following is the strongest base-

[AIEEE 2004]









- 6. Rate of the reaction $R C \neq Z + Nu R C \neq Z + Z$ is fastest when Z is [AIEEE 2004]
 - (1) OCOCH₃

(2) NH_{2}

(3) $OC_{2}H_{5}$

- (4) Cl
- 7. Which one of the following does not have sp^2 hybridised carbon

[AIEEE 2004]

(1) Acetamide

(2) Acetic acid

(3) Acetonitrile

- (4) Acetone
- 8. Due to the presence of an unpaired electron, free radicals are

[AIEEE-2005]

(1) Chemically inactive

(2) Chemically reactive

(3) Cations

(4) Anions

(b) CH₃O

(c) CN-

(d)
$$H_3C$$
 \longrightarrow $\begin{bmatrix} O \\ II \\ S \\ O \end{bmatrix}$ is

(1) (d), (c), (b), (a)

(2) (a), (b), (c), (d)

(3) (c), (b), (a), (d)

(4) (b), (c), (a), (d)

10. Tertiary alkyl halides are practically inert to substitution by SN^2 mechanism because of [AIEEE-2005]

(1) unstability

(2) insolubility

(3) steric hinderance

(4) inductive effect

11. Among the following acids which has the lowest pk_a value-

[AIEEE-2005]

(1) CH₃CH₂COOH

(2) (CH₃)₂CHCOOH

(3) HCOOH

(4) CH₂COOH

12. Amongest the following the most basic compound is-

[AIEEE-2005]

(1) p-nitro aniline

(2) Acetanilide

(3) Aniline

(4) Benzylamine

 ${f 13.}$ The increasing order of the rate of HCN addition to compounds A-D is

[AIEEE-2006]

(A) HCHO

(B) CH₃COCH₃

(C) PhCOCH₃

(D) PhCOPh

(1) D < B < C < A

(2) D < C < B < A

(3) C < D < B < A

(4) A < B < C < D

14. The increasing order of stability of the following free radicals is

[AIEEE-2006]

$$(1) (C_6H_5)_3 C < (C_6H_5)_2 CH < (CH_3)_3 C < (CH_3)_2 CH$$

$$(2) (C_6H_5)_2 CH < (C_6H_5)_3 C < (CH_3)_3 C < (CH_3)_2 CH$$

(3)
$$(CH_3)_2 CH < (CH_3)_3 C < (C_6H_5)_3 C < (C_6H_5)_2 CH$$

$$(4) (CH_3)_2 CH < (CH_3)_3 C < (C_6H_5)_2 CH < (C_6H_5)_3 C$$

15. $CH_3Br + Nu^- \longrightarrow CH_3 - Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu⁻) A to D is [AIEEE-2006]

 $[Nu^{-} = (A) PhO^{-},$

(B) AcO^{-} , (C) HO^{-} ,

(D) CH₂O⁻]

(1) D > C > B > A

(2) A > B > C > D

(3) B > D > C > A

(4) D > C > A > B

16. The correct order of increasing acid strength of the compounds is

[AIEEE-2006]

(a) CH₃CO₂H

(b) MeOCH2CO2H

(c) CF_3CO_2H

(d) Me O_2H

(1) d < a < c < b

(2) d < a < b < c

(3) a < d < c < b

(4) b < d < a < c

17.
$$\bigcirc$$
 + CHCl₃ + NaOH \longrightarrow \bigcirc CHO

The electrophile involved in the above reaction is

[AIEEE-2006]

- (1) dichlorocarbene (:CCl₂)
- (2) trichloromethyl anion (CCl_3)
- (3) formyl cation (CHO)
- (4) dichloromethyl cation $(CHCl_2)$
- 18. Which one of the following is the strongest base in aqueous solution?

[AIEEE-2007]

(1) Trimethylamine

(2) Aniline

(3) Dimethylamine

- (4) Methylamine
- 19. The electrophile, E^{\oplus} attacks the benzene ring to generate the intermediate σ -complex. Of the following, which σ -complex is of lowest energy? [AIEEE-2008]









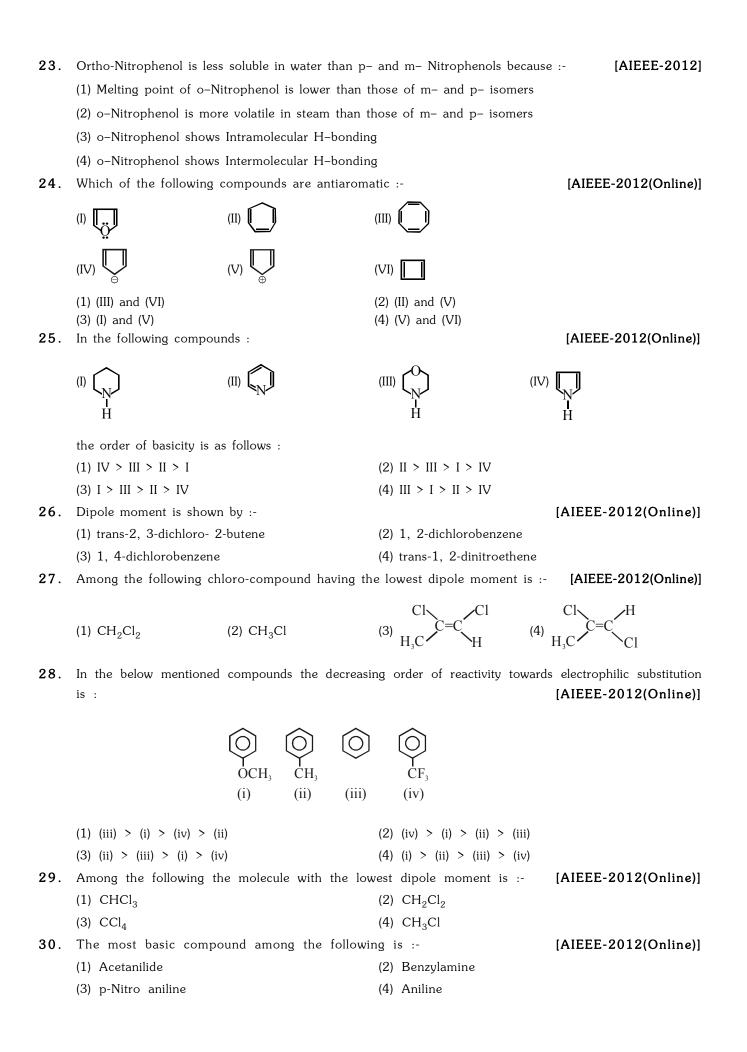
- $\textbf{20.} \quad \text{Arrange the carbanions, } (CH_3)_3 \, \overline{C} \; , \; \; \overline{C}Cl_3 \; , \; (CH_3)_2 \, \overline{C}H \; , \; C_6H_5 \, \overline{C}H_2 \; , \; \text{in order of their decreasing stability :-}$
 - (1) $\overline{CCl}_3 > C_6H_5\overline{CH}_2 > (CH_3)_2\overline{CH} > (CH_3)_3\overline{C}$

[AIEEE-2009]

- (2) $(CH_3)_3\overline{C} > (CH_3)_2\overline{C}H > C_6H_5\overline{C}H_2 > \overline{C}Cl_3$
- (3) $C_6H_5\overline{C}H_2 > \overline{C}Cl_3 > (CH_3)_2\overline{C} > (CH_3)_2\overline{C}H$
- (4) $(CH_3)_2 \overline{CH} > \overline{CCl}_3 > C_6H_5 \overline{CH}_2 > (CH_3)_3 \overline{C}$
- 21. The correct order of increasing basicity of the given conjugate base (R=CH₃) is :- [AIEEE-2010]
 - (1) $RCO\overline{O} \le HC \equiv \overline{C} \le \overline{N}H_2 \le \overline{R}$
 - (2) $RCO\overline{O} \le HC \equiv \overline{C} \le \overline{R} \le \overline{N}H_2$
 - (3) $\overline{R} < HC \equiv \overline{C} < RCO\overline{O} < \overline{N}H$,
 - (4) $RCO\overline{O} < \overline{N}H_2 < HC \equiv \overline{C} < \overline{R}$
- 22. The strongest acid amongst the following compounds is ?

[AIEEE-2011]

- (1) CH₃CH₂CH(Cl)CO₂H
- (2) CICH₂CH₂CH₂COOH
- (3) CH₃COOH
- (4) HCOOH



- 31. Among the following the order of reactivity toward nucleophilic addition is :-[AIEEE-2012(Online)]
 - (1) HCHO > CH₃CHO > CH₃COCH₃
 - (2) CH₃CHO > HCHO > CH₃COCH₃
 - (3) CH₃CHO > CH₃COCH₃ > HCHO
 - (4) CH₃COCH₃ > CH₃CHO > HCHO
- **32.** The order of stability of the following carbocations:

$$CH_{2}=CH-\overset{\oplus}{C}H_{2}\;;\;CH_{3}-CH_{2}-\overset{\oplus}{C}H_{2}\;;\; \qquad \qquad \text{[JEE(MAIN)-2013]}$$

- (1) III > II > I
- (2) II > III > I
- (3) I > II > III
- (4) III > I > II
- 33. Arrange the following compounds in order of decreasing acidity :

[JEE(MAIN)-2013]

$$\begin{array}{c|c} OH & OH & OH \\ \hline \bigcirc \\ CI & CH_3 & NO_2 & OCH_3 \\ (I) & (II) & (III) & (IV) \\ \end{array}$$

(1) II > IV > I > III

(2) I > II > III > IV

(3) III > I > II > IV

(4) IV > III > I > II

PREVIOUS YEAR QUESTIONS ANSWER KEY											EXE	RCI	SE-O	5(A)	
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans	1	3	3	4	4	4	3	2	4	3	3	4	2	4	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans	2	1	3	2	1	1	1	3	4	3	2	1	4	3	2
Que.	31	32	33				· · · · ·		· · · · · ·			-	<u> </u>	- · · · · ·	
Ans	1	4	3												

EXERCISE-05(B)

PREVIOUS YEARS QUESTIONS

1. Which one of the following has the smallest heat of hydrogenation per mole? [IIT-93]

(A) 1-Butene

(B) trans-2-Butene

(C) cis-2-Butene

(D) 1, 3-Butadiene

2. What is the decreasing order of strength of bases $\overset{\ominus}{OH}$, $\overset{\ominus}{NH}_2$, $\overset{\ominus}{HC}=C$, $\overset{\ominus}{CH}_3-\overset{\ominus}{CH}_2$ [IIT-93]

 $(A) \quad CH_3-CH_2> \ NH_2> \ HC\equiv C> \ CH$

(B) $HC = C > CH_1 - CH_2 > NH_3 > OH$

 \ominus \ominus \ominus \ominus \ominus \ominus \ominus \ominus (C) $OH > NH₂ > HC<math>\equiv$ C > CH_2 - CH_3

3. In the following compounds

The order of acidity is -

(A) III > IV > I > II

(B) I > IV > III > II

(C) II > I > III > IV

(D) IV > III > I > II

4. The formation of cyanohydrin from a ketone is an examples of -

[IIT-98]

[IIT-96]

(A) Electrophilic addition

(B) Nucleophilic addition

(C) Nucleophilic substitution

(D) Electrophilic substitution

5. The most unlikely representation of resonance structure of p-nitrophenoxide ion is - [IIT-99]

6. An aromatic molecule will not [IIT-99]

(A) have $4n \pi$ electrons

(B) have $(4n + 2)\pi$ electrons

(C) be planar

(D) be cyclic

7. Amongst the following, the most basic compound is -

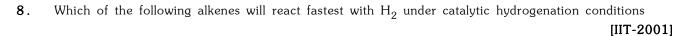
[IIT-2000]

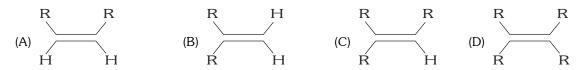
(A) $C_6H_5NH_2$

(B) $p-NO_2-C_6H_4NH_2$

(C) $m-NO_2-C_6H_4NH_2$

(D) $C_6H_5CH_2NH_2$





9. The correct order of basicities of the following compounds is:

[IIT-2001]

10. Which of the following is least stable:

[IIT-2005]

11. Among the following, the least stable resonance structure is -

[IIT-2007]

$$(A) \qquad \stackrel{\oplus}{\ominus} \qquad \stackrel{\bigcirc}{N} \qquad O$$

$$(D) \oplus \overset{\oplus}{N} \overset{\ominus}{N}$$

12. The major product of the following reaction is :

[IIT-2008]

$$(A) \qquad \begin{array}{c} Me & SPh \\ \hline \\ NO_2 \end{array} \qquad \begin{array}{c} Me$$

- (A) II > IV > I > III
- (B) I > II > III > IV
- (C) II > I > IV > III
- (D) I > III > II > IV
- 14. Statement-I: p-Hydroxybenzoic acid has a lower boiling point that o-hydroxybenzoic acid.

Because

Statement-II: o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

[IIT 2003]

- (A) Statement-I is True, Statement-II is True; Statement-II is a correct explanation for Statement-I
- (B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I
- (C) Statement-I is True, Statement-II is False.
- (D) Statement-I is False, Statement-II is True.
- 15. Statement-I : Bromobenzene upon reaction with $\mathrm{Br_2}/\mathrm{Fe}$ gives 1, 4-dibromobenzene as the major product. Because

Statement-II: In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. [IIT 2008]

- (A) Statement-I is True, Statement-II is True; Statement-II is a correct explanation for Statement-I
- (B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I
- (C) Statement-I is True, Statement-II is False.
- (D) Statement-I is False, Statement-II is True.
- 16. Out of anhydrous AlCl₃ and hydrous AlCl₃ which is more suluble in diethyl ether? Explain with reason.

[IIT 2003]

17. Match K_a values with suitable acid :

[IIT 2003]

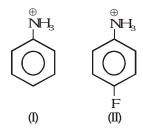
(B)
$$4.2 10^{-5}$$
 (q) Me— (COOH)

(D)
$$6.4 10^{-5}$$
 (s) MeO—(COOH

(E)
$$30.6 10^{-5}$$
 (t) $O_2N - OOH$

19. Which of the following is more acidic and why?

[IIT 2004]



- 20. The compound that does NOT liberate ${\rm CO_2}$, on treatment with aqueous sodium bicarbonate solution, is [JEE ADVANCED 2013]
 - (A) Benzoic acid

(B) Benzenesulphonic acid

(C) Salicylic acid

- (D) Carbolic acid (phenol)
- 21. The hyperconjugative stbilities of tert-butyl cation and 2-butene, respectively, are due to
 - (A) $\sigma{\longrightarrow} p$ (empty) and $\sigma{\longrightarrow} \pi^*$ electron delocalisations

[JEE ADVANCED 2013]

- (B) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations
- (C) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations
- (D) p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations
- 22. The total number of lone-pairs of electrons in melamine is

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PREVIOUS	YEARS QUE	STIONS		ANSWER	KEY		EXERCISE -	5(B)
1 . (D)	2. (A)	3. (D)	4. (B)	5 . (C)	6 . (A)	7. (D)	8. (A)	
9 . (B)	10 . (D)	11 . (A)	12 . (A)	13 . (D)	14 . (D)	15 . (C)		
16. Anhyo	lrous AlCl ₃ is 1	more soluble.						
17 . A-(s) ;	B-(q); C-(p)	; D-(r) ; E-(t)	;					
19 . II is	more acidic.	2	0 . (D)	21 . (A)	2	22 . (6)		