**Exercise-1** 

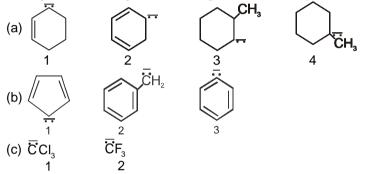
# PART - I : SUBJECTIVE QUESTIONS

## Section (A) : Carbanions

A-1. Arrange the following in decreasing order of stability.

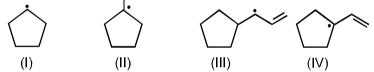
(a)	₽ CH₂−NO₂,	Ө СН₂–СНО	CH ≡ C
	1	2	3
(b)	$CH_{3} - CH_{2} - CH_{2} - CH_{2}$	$O_{CH_3} - O_{CH} - O_2O_3$	$(CH_3)_2C - CH_2CH_3$
	1	2	3

A-2. Arrange the following in decreasing order of stability



# Section (B) : Carbon free radicals

**B-1.** Rank the following free radicals in increasing order of their stability and give appropriate reasons.



B-2. Arrange the following free radicals in decreasing order of stability :

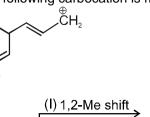
$$\begin{array}{ccc} CH_{3}-\dot{C}H_{2} & \dot{C}H_{2} \\ I \\ I \\ II \\ III \\ IV \\ IV \\ III \\ IV \\$$

## Section (C) : Carbocations

C-1. Arrange the following carbocations in decreasing order of their stability :

	(I)	(II)	(III)	(IV)
(P)	$CH_3$ — $CH_2$ — $\overset{\oplus}{C}H_2$	$CH_3 - CH - CH - CH_2$   F	$CH_3 - CH - \overset{\oplus}{C} H_2$   Br	$CH_3 - CH - \overset{\oplus}{C} H_2$
(Q)	$CH_3 \longrightarrow CH \longrightarrow C_2H_5$	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	$CH_3$   Ph-C_C_C_H_5	Ph   $Ph-C_2H_5$
(R)	CH <sub>3</sub>			ČH <sub>2</sub>

C-2. Which of the following carbocation is more stable and why?



Draw the structures of P and Q.

F-

(V)

⊕ ČH\_

(11)

(P)

(Q)

### Section (D) : Basic strength

C-3.2

**D-1.** Compare the basic strength of the following compounds:  $C_2H_5O^ C_2H_5^ C_2H_5NH^ NH_2^-$ (I) (II) (III) (IV)

(II) 1,2-Bond

shift

D-2. Compare the basic strength of the following compounds :

(a)	PhNH <sub>2</sub>	Ph <sub>2</sub> NH	Ph <sub>3</sub> N
(b)	N	:NH <sub>2</sub>	<b>⊥</b> -ζ
(c)	CH <sub>3</sub> –CH–NH <sub>2</sub>   Ph	CH <sub>3</sub> –CH <sub>2</sub> –NH I Ph	Ph–CH <sub>2</sub> –CH <sub>2</sub> –NH <sub>2</sub>

**D-3.** Which of the following group is most basic in the given compounds :  ${}^{(1)}$   ${}^{\rm NH}_{\rm 2}$ 



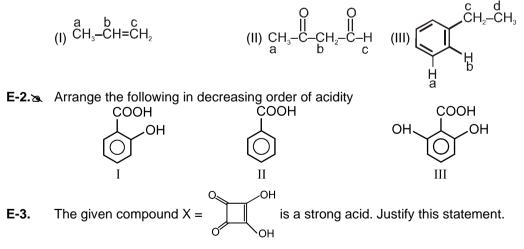
**D-4.** Which of the following is a stronger base ? Give reason to justify your answer.  $CH_2 = CH - \ddot{N}H_2$   $CH_2 = \ddot{N} - CH_3$ 

Π

### Section (E) : Acidic strength

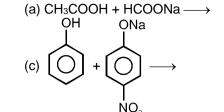
I

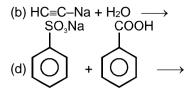
**E-1.** Which 'H' atom is most acidic in the following compounds.



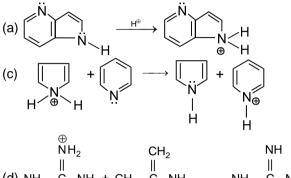
### Section (F) : Feasible reactions of acids and bases

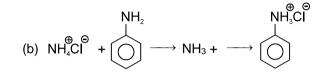
Which of the follwing reactions is/are feasible ? F-1.

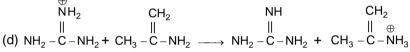




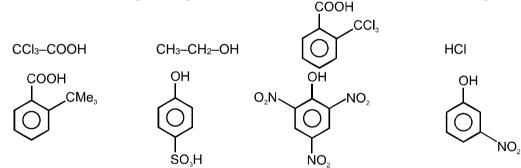
F-2. Which of the following reaction is feasible?





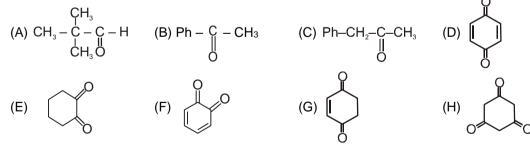


F-3. Which of the following acids (given below) react with NaHCO3 and liberate CO2(g) ?

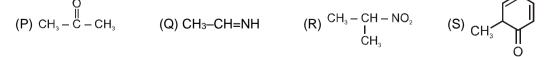


#### Section (G) : Tautomerism

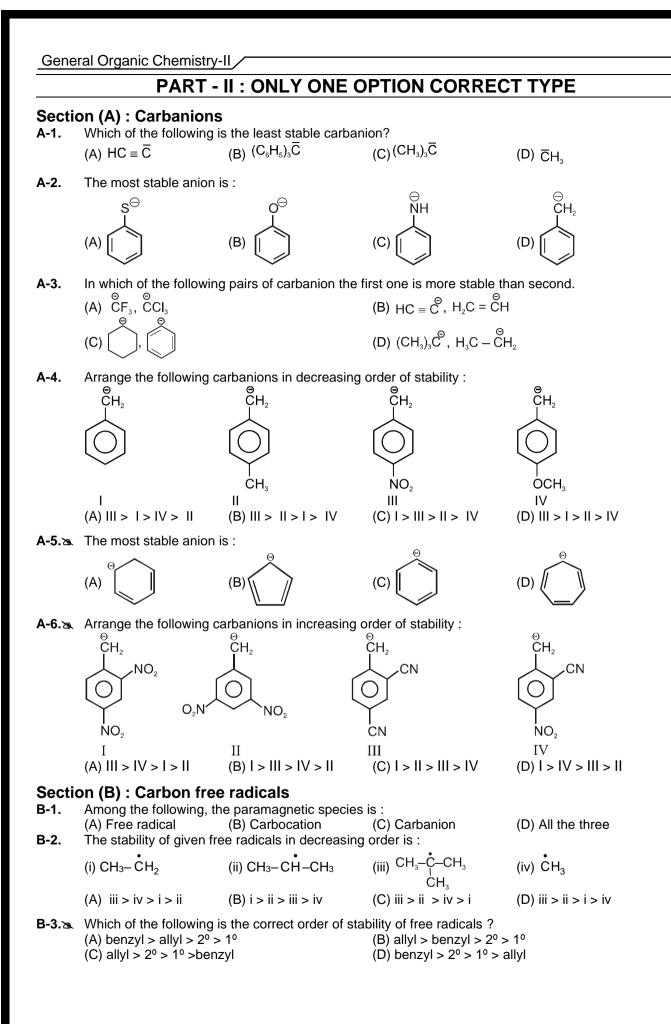
G-1. Which of the following compounds can exhibit tautomerism ?

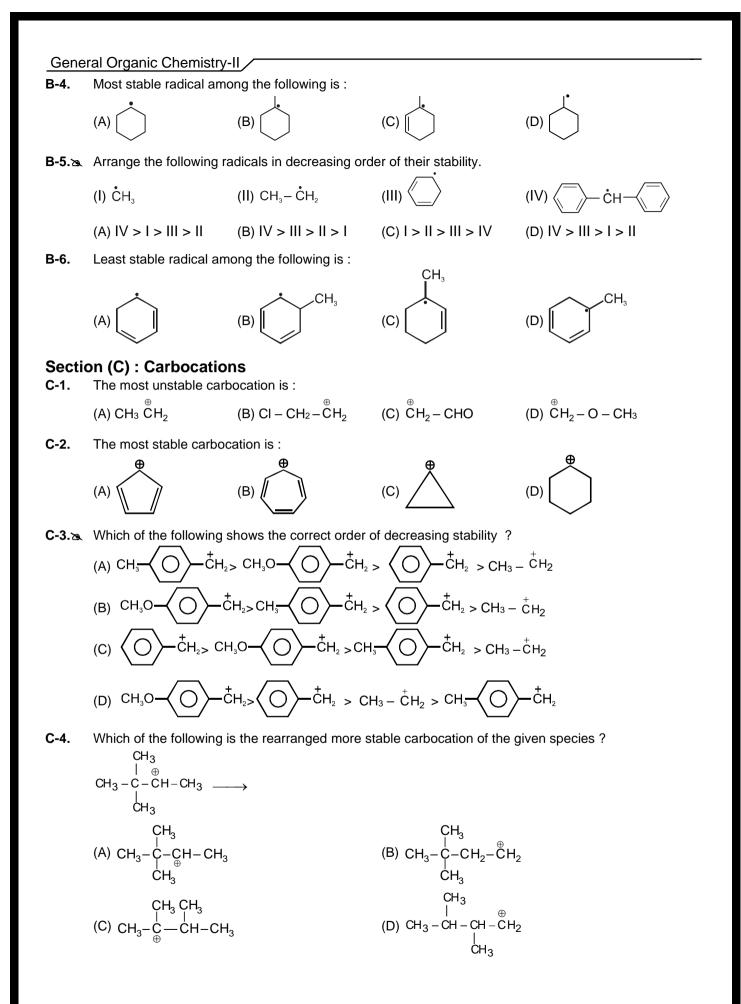


G-2. Write the tautomers of the following compounds :

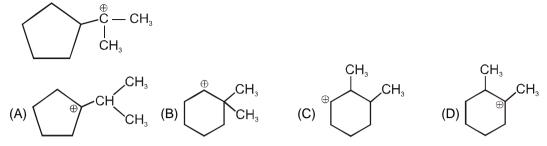


G-3. Monocarbonyl compounds have very small percentage enol form at equilibrium. Explain.

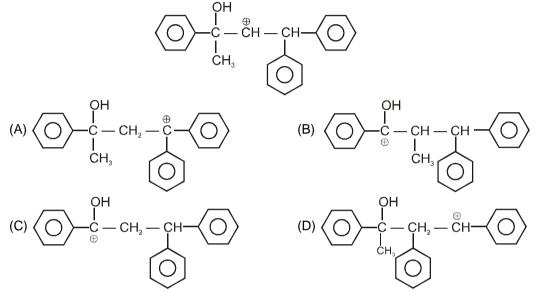




C-5. Most stable rearranged form of given carbocations is :



C-6.> Which of the following in the rearranged more stable carbocation of the given species?

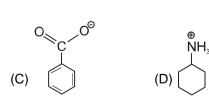


### Section (D) : Basic strength

D-1. The correct basic strength order of following anions is :

- (A)  $CH_3 \overset{\ominus}{C}H_2 > \overset{\ominus}{N}H_2 > CH_2 = \overset{\ominus}{C}H > CH = \overset{\ominus}{C} > H\overset{\ominus}{O} > \overset{\ominus}{F}$ (B)  $\overset{\ominus}{N}H_2 > CH_3 - \overset{\ominus}{C}H_2 > CH_2 = \overset{\ominus}{C}H > CH = \overset{\ominus}{C} > \overset{\ominus}{F} > H\overset{\ominus}{O}$ (C)  $CH_3 - \overset{\ominus}{C}H_2 > CH_2 = \overset{\ominus}{C}H > \overset{\ominus}{N}H_2 > CH = \overset{\ominus}{C} > H\overset{\ominus}{O} > \overset{\ominus}{F}$ (D)  $\overset{\ominus}{F} > H\overset{\ominus}{O} > CH = \overset{\ominus}{C} > CH_2 = \overset{\ominus}{C}H > \overset{\ominus}{N}H_2 > CH_3 - \overset{\ominus}{C}H_2$
- **D-3.** Find the order of basic strength. (If R = Me)? (I)  $R_4 N^+OH^-$  (II)  $R_3N$ (A) I > III > IV > II (B) IV > III > I > II
- **D-4.** Which of the following cannot be a base?

(A) 
$$(B) CH_3 - C - NH_2$$

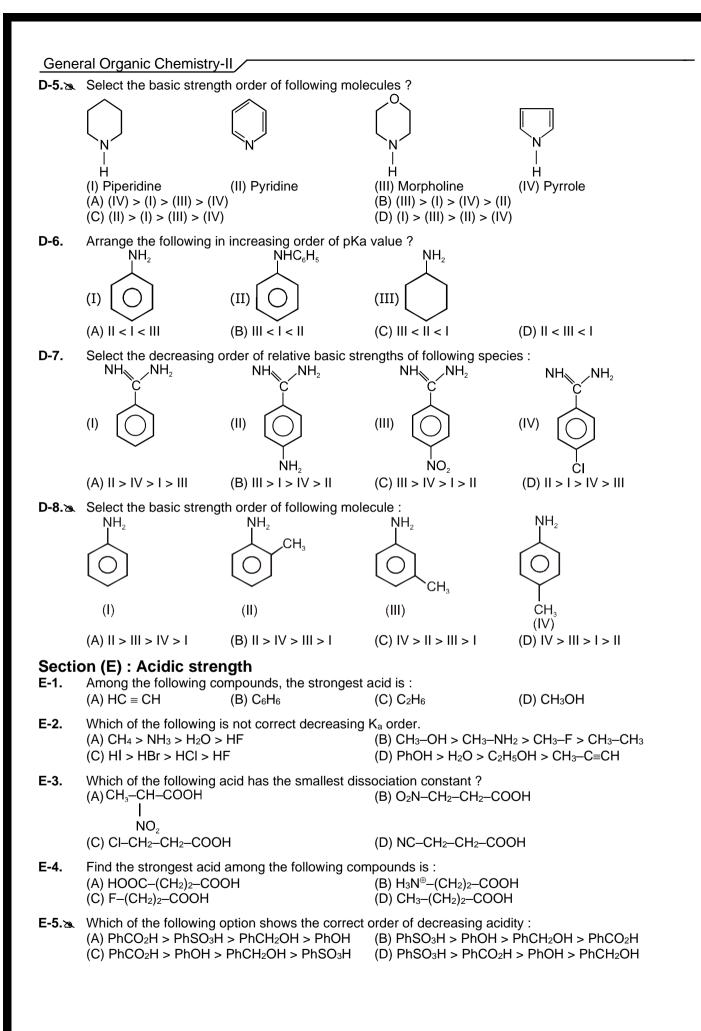


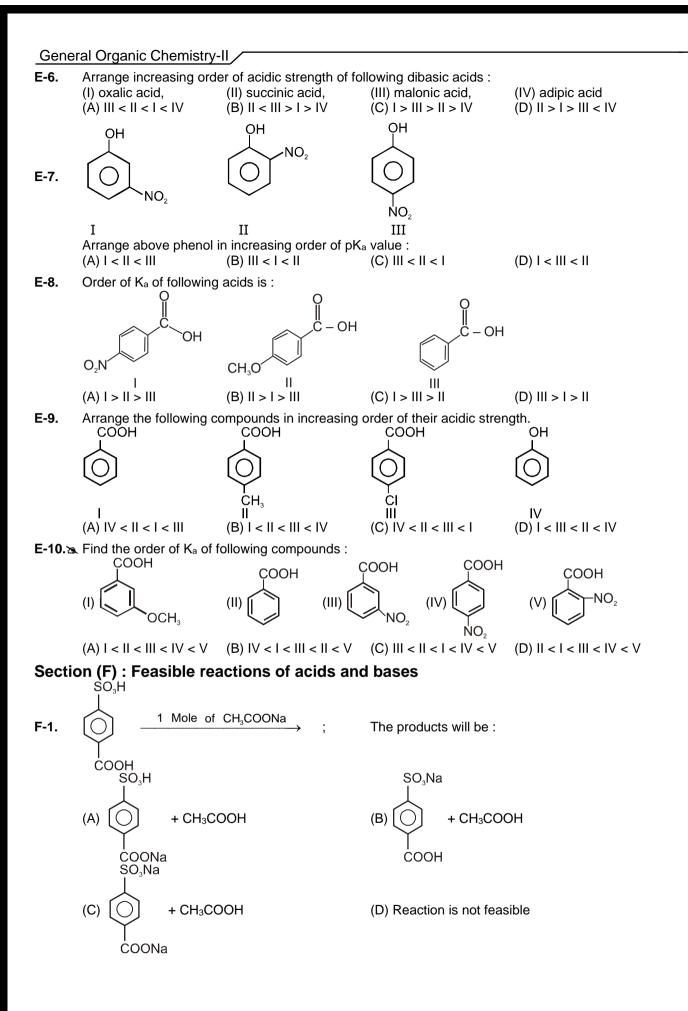
(III) R<sub>2</sub>NH

(C) || > |V > ||| > |

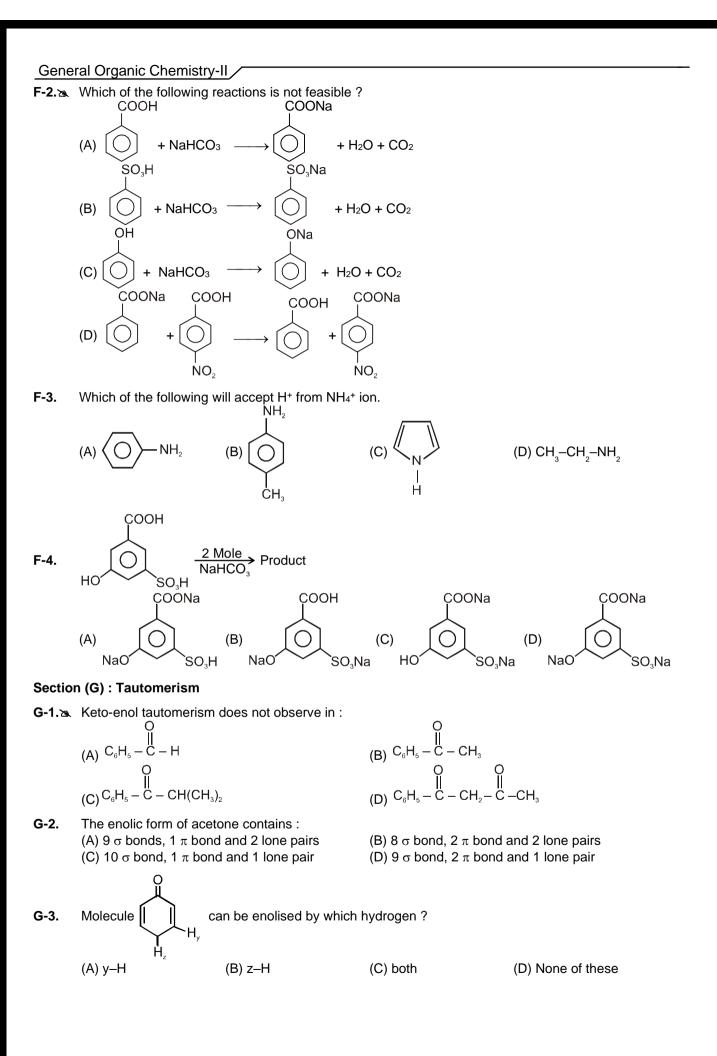
(IV) RNH<sub>2</sub>

(D) || > |V > | > |||





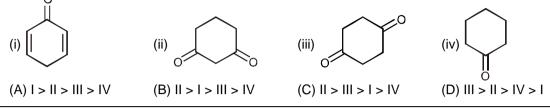
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G-4. Which among the following compound will give maximum enol content in solution :

(A)  $C_{5}H_{5} - C - CH_{2} - C - CH_{3}$ (B)  $CH_{3} - C - CH_{2} - C - CH_{3}$ (C)  $CH_{3} - C - CH_{2} - CH_{2} - CH_{3}$ (D)  $CH_{3} - C - CH_{2} - CH_{2} - CH_{3}$ 

G-5. Arrange the following in decreasing order of percentage enol content.



# PART - III : MATCH THE COLUMN

1. Match the column %

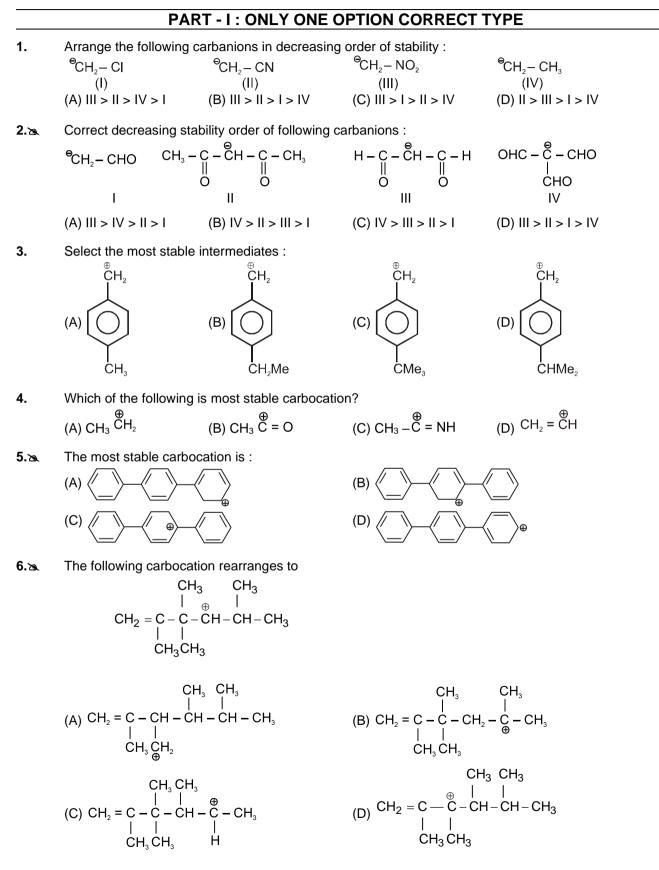
	Column-I (Keto)		Column-II (% enol)
(A)	$CH_3 - CH = O$	(x)	95 %
(B)	$Ph - C - CH_2 - C - Ph$ $\parallel$ $\parallel$ $0$ $O$	(y)	76 %
(C)	$CH_3 - C - CH_2 - C - OEt$	(z)	0.0001 %
(D)	$\begin{array}{c} CH_3 - C - CH_2 - C - CH_3 \\ \\ H \\ O \\ O \end{array} $	(w)	7.2 %

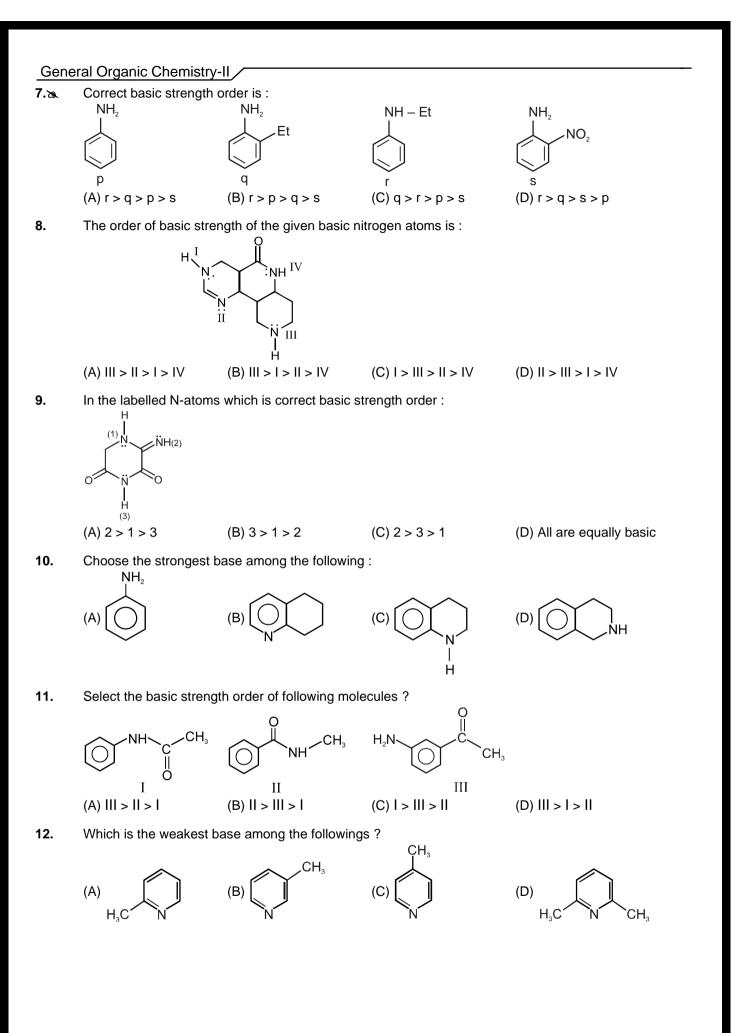
# 2. Match the column :

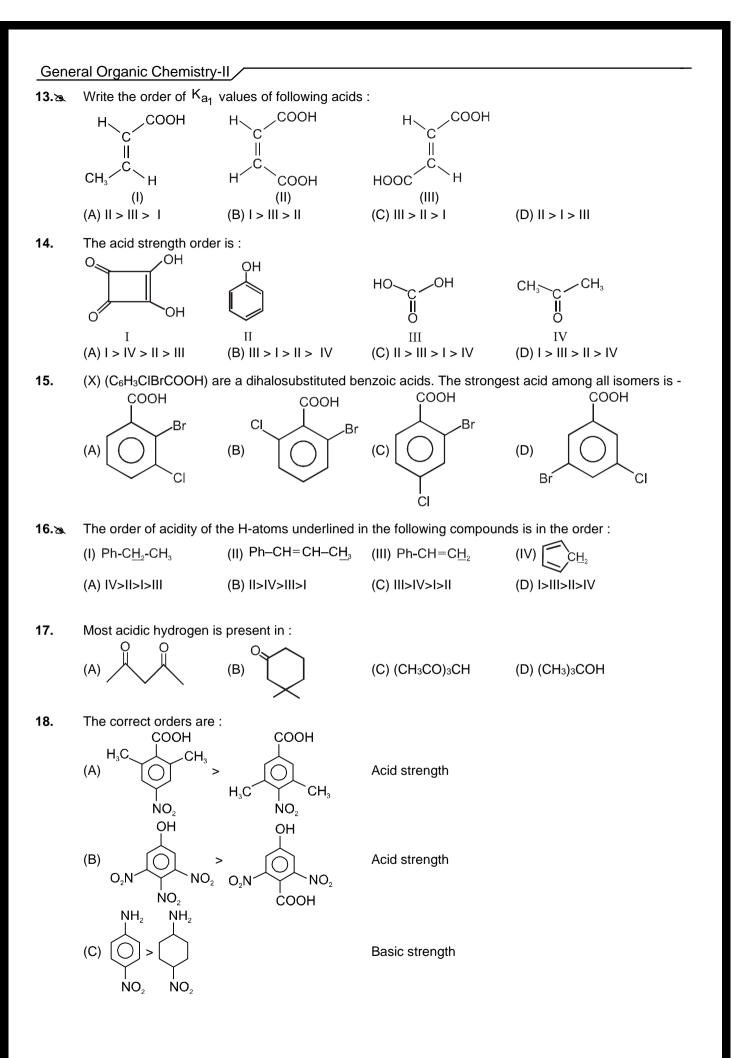
	Column-I		Column-II
(A)	NaHCO $_3$ will react with	(p)	
(B)	Na will react with	(q)	О С−ОН
(C)	NaOH will react with	(r)	О-он
(D)	$NaNH_2$ will react with	(s)	

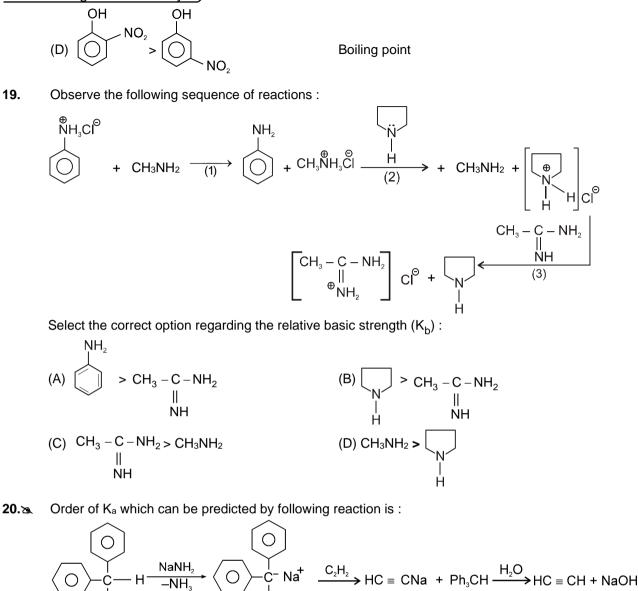
**Exercise-2** 

> Marked questions are recommended for Revision.









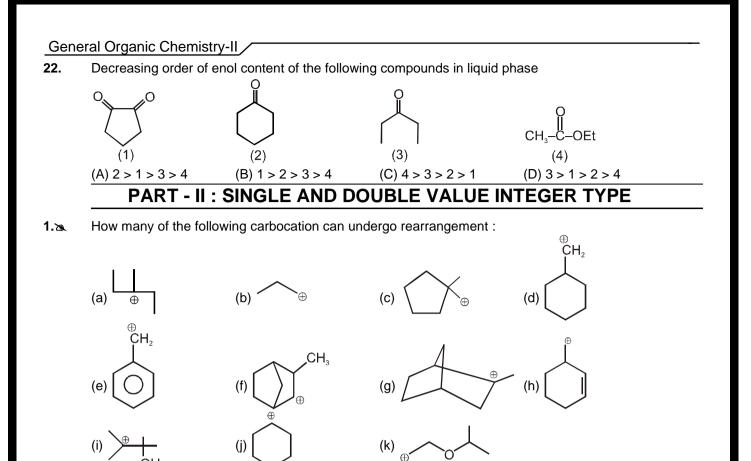
(A)  $NH_3 > Ph_3CH > C_2H_2 > H_2O$  (B)  $H_2O$ (C)  $HC \equiv CH > H_2O > Ph_3CH > NH_3$  (D)  $Ph_3C$ 

(B)  $H_2O > HC \equiv CH > Ph_3CH > NH_3$ (D)  $Ph_3CH > HC \equiv CH > H_2O > NH_3$ 

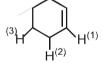
21. The gases produced in the following reactions are respectively

Ο

 $I : CH_{3}NH_{2} + NH_{4}Br \longrightarrow$   $II : CH_{3}SO_{3}H + NaHCO_{3} \longrightarrow$   $III : CH_{3} - C - NH_{2} + NaH \longrightarrow$   $III : \bigcup_{O} (A) NH_{3}, NH_{3}, CO_{2} (B) NH_{3}, SO_{2}, H_{2} (C) NH_{3}, SO_{2}, NH_{3} (D) NH_{3}, CO_{2}, H_{2}$ 



2. Consider following compound, which H-atom deprotonated first ?

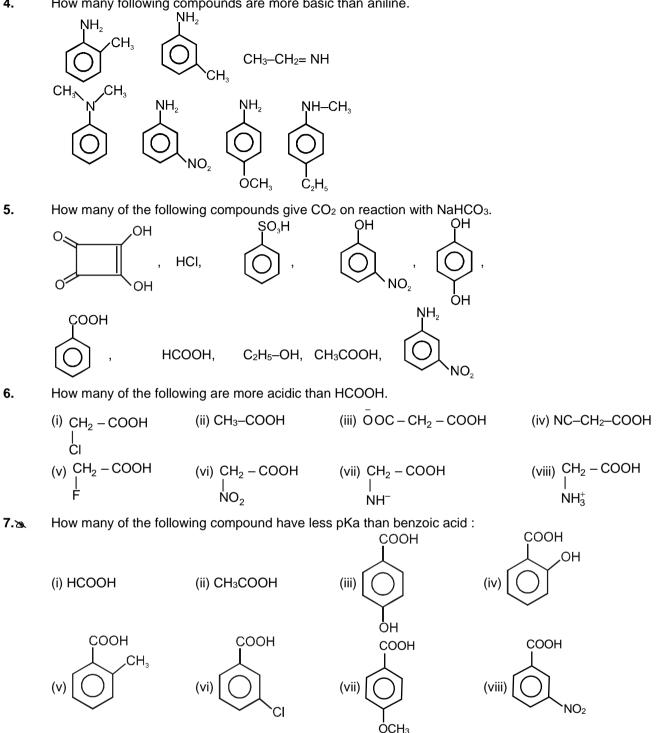


**3.** How many of the following are correct orders for Basic Strength :  $S_1: CH_3-NH > CH_3-NH_2 > CH_3-N-CH_3$ CH. CH.

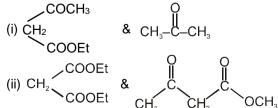
$$S_2: C_2H_5 - NH > C_2H_5 - NH - C_2H_5 > C_2H_5 - NH_2$$
  
 $C_2H_5 - C_2H_5 - C_2H_5 - NH_2$ 

$$S_{3}: \qquad \bigvee_{NH_{2}} \qquad \bigvee_{NH_{2}} \qquad R_{NH_{2}} \qquad S_{NH_{2}} \qquad F_{NH_{2}} \qquad F_{NH_{$$

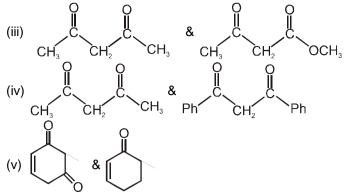
4. How many following compounds are more basic than aniline.



- 90 g of acetic acid react with excess of NaHCO3 then what volume of CO2 will produce at S.T.P. Write 8.2 your answer in terms of nearest integer.
- In how many of the following pairs first will have higher enol content than second. 9.2



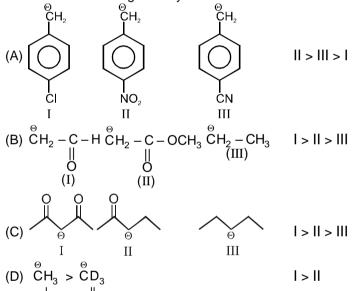




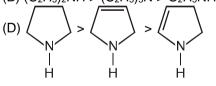
10. Consider the following compound and write number of enolizable H-atom

# **PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE**

1.a. Which of the following stability order of anions is/are correct :

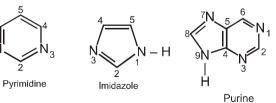


- Which of the following is/are correct for basic strength : (A)  $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$  (B)  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ 
  - (C)  $PhNH_2 > Ph_2NH > Ph_3N$



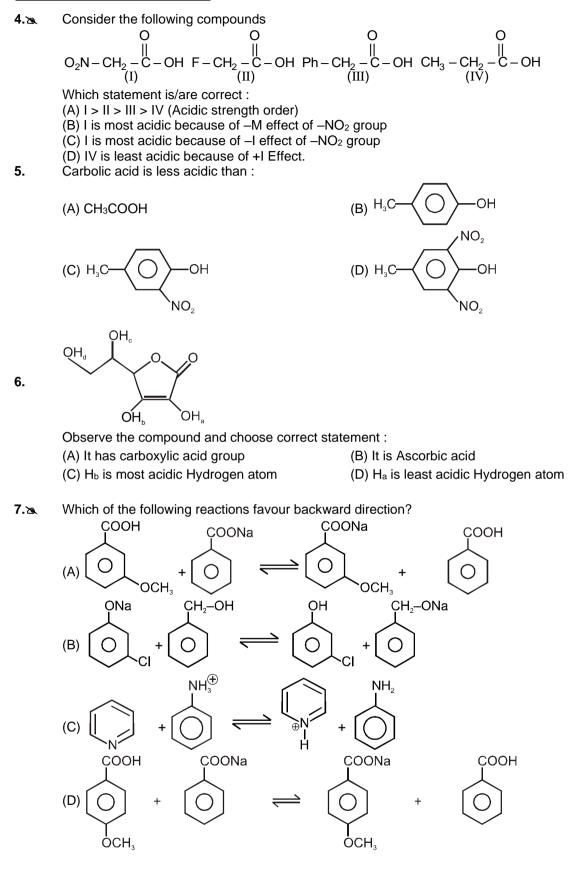


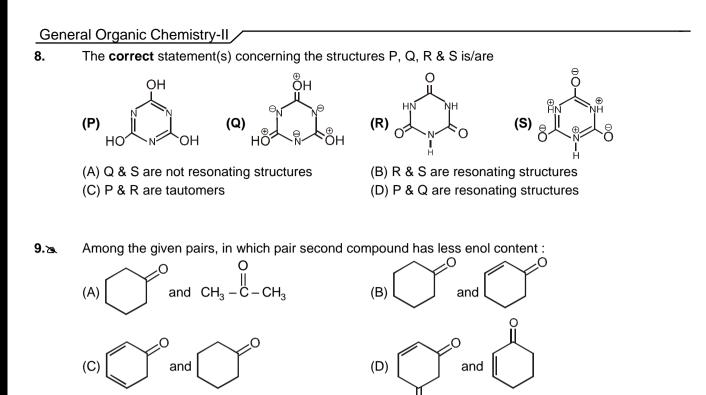
2.2



Among the following which statement(s) is/are correct :

- (A) Both N of pyrimidine are same basic strength
- (B) In imidazole protonation take places on N-3.
- (C) In purine only one lone pair of N is delocalised.
- (D) Pyrimidine, imidazole and purine all are aromatic.





# **PART - IV : COMPREHENSION**

#### Read the following passage carefully and answer the questions.

#### Comprehension #1

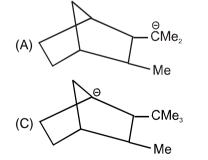
**Reaction intermediates:** Reaction intermediates are short lived species and are highly reactive. They are formed by heterolytic and homolytic bond fission. There are various types of reaction intermediates in which the most important are carbocation, carbanion and free radical.

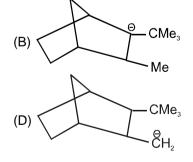
Carbocation is an organic species in which carbon have positive charge and six electrons in its outermost shell. The stability of carbocation can be increased by positive inductive effect, hyperconjugation and delocalisation. If  $\alpha$ -atom with respect to carbocation has one or more lone pair of electrons then lone pair of electron strongly stabilises the carbocation due to octet completion.

Species in which carbon have negative charge is called carbanion. Carbanion carries three bond pairs and one lone pair. The stability of carbanion can be increased by negative inductive effect, negative mesomeric effect and delocalisation.

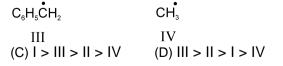
Free radical is a species which have seven electrons in its outermost shell. The stability of free radical can be increased by hyperconjugation and delocalisation.

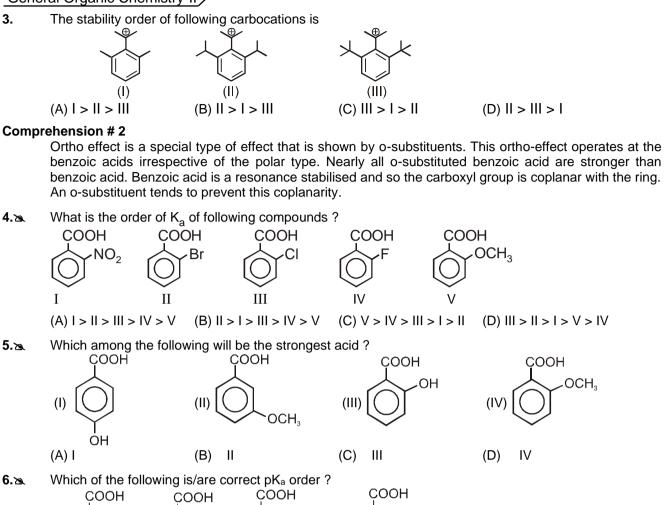
1. Which of the following is the most stable carbanion intermediate ?

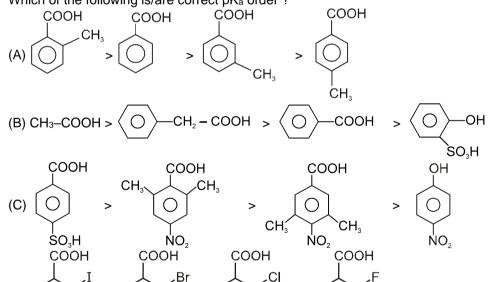




- **2.** The stability order of following free radicals is :  $C_{a}H_{a}CH_{2}\dot{C}H_{2}$   $CH_{3}CH_{2}\dot{C}H_{2}$ 
  - $\begin{matrix} I \\ (A) \ I > II > III > IV \end{matrix} \qquad (B) \ II > III > I > IV$







#### Comprehension # 3

(D)

The lone pair of amines makes them basic. They react with acids to form acid-base salts. Amines are more basic than alcohols, ethers and water. When an amine is dissolved in water, an equilibrium is established, where water acts as an acid and transfer a proton to the amine. The basic strength of an amine can be measured by basicity constant K<sub>b</sub>.

OCH<sub>3</sub>

Arylamines are less basic than alkylamines because the lone pair of nitrogen is delocalised with the aromatic ring and are less available for donation.

Substituted arylamines can be either more basic or less basic than aniline, depending on the substitutent. ERG substituents, such as  $-CH_3$ ,  $-NH_2$  and  $-OCH_3$  increases the basicity and EWG substituents, such as -CI,  $-NO_2$  and -CN decreases basicity. While sp<sup>2</sup>-hybridized nitrogen atom in pyridine is less basic than the sp<sup>3</sup>-hybridized nitrogen in an alkylamine.

- 7. Select the correct order of K<sub>b</sub>.
  - (A)  $CH_3NH_2 > NaOH$
  - (B) Pyridine >  $CH_3$ – $\ddot{N}H$ – $CH_3$
  - (C) p-Methyl aniline > p-Chloroaniline > p-Amino acetophenone
  - (D) p-Bromoaniline > p-Nitroaniline > p-Amino benzaldehyde
- **9.** The most basic carbanion is :

(C) Ph - C - CH = C - H



(III) NH<sub>3</sub>

(C) | > |V > || > |||



 $(IV) H_2O$ 

(D) III > I > II > IV

#### Comprehension # 4

Observe the following reaction and answer the following questions :

⊖ CH≡C

10.The product 'R' is :  
(A) 
$$Ph - C = C = C - H$$
  
 $OH$ (B)  $Ph - C - CH = C - OH$   
 $OH$ (C)  $Ph - C - CH = C - H$   
 $OH$ (D)  $Ph - C = CH - C - H$   
 $OH$ (C)  $Ph - C - CH = C - H$   
 $OH$ (D)  $Ph - C = CH - C - H$   
 $OH$ 11.The structure of Q1 is :  
 $A$   
 $OH$ (A)  $Ph - C = CH - C - H$   
 $OH$ (B)  $Ph - C = C = C - H$   
 $OH$ 

$$(B) PH = C = C = C = C = H$$
$$O = O = O = O = H$$
$$O = O = C = H$$

### Comprehension # 5

Answer 12, 13 and 14 by appropriately matching the information given in the three columns of the following table.

Colum	nn-1, 2 & 3 containin	g starting		ion & eleo	ctronic effect / intermediate respectively.
	Column-1 Column-2 Column-3				Column-3
(I)	CI	(i)	SbCl5 or AICl3(Anhy.)	(P)	Rearrangement
(11)	CI (ii) Na		Na	(Q)	Resonance
(111)	⊕ N H	(iii)	H+	(R)	Hyperconjugation
(IV)	CI	(iv)	NaOH	(S)	Carbocation intermediate

12.	Which combination wil (A) (III) (iii) (P)	l give hydrogen gas ? (B) (II) (ii) (R)	(C) (IV) (ii) (Q)	(D) (I) (iii) (P)
13.	In which product forma (A) (I) (ii) (Q)	ation is not possible ? (B) (II) (i) (R)	(C) (III) (ii) (Q)	(D) (IV) (i) (S)
14.	In which amongs the fo (A) (I) (i) (P)	ollowing aromatic produc (B) (II) (i) (Q)	t will not form ? (C) (III) (iv) (Q)	(D) (IV) (ii) (Q)

# Exercise-3

\* Marked Questions may have more than one correct option.

# PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Which of the following acid has the lowest value of acid dissociation constant : [JEE-02(S), 3/90] (A) CH<sub>3</sub>CHFCOOH (B) FCH<sub>2</sub>CH<sub>2</sub>COOH (C) BrCH<sub>2</sub>CH<sub>2</sub>COOH (D) CH<sub>3</sub>CHBrCOOH

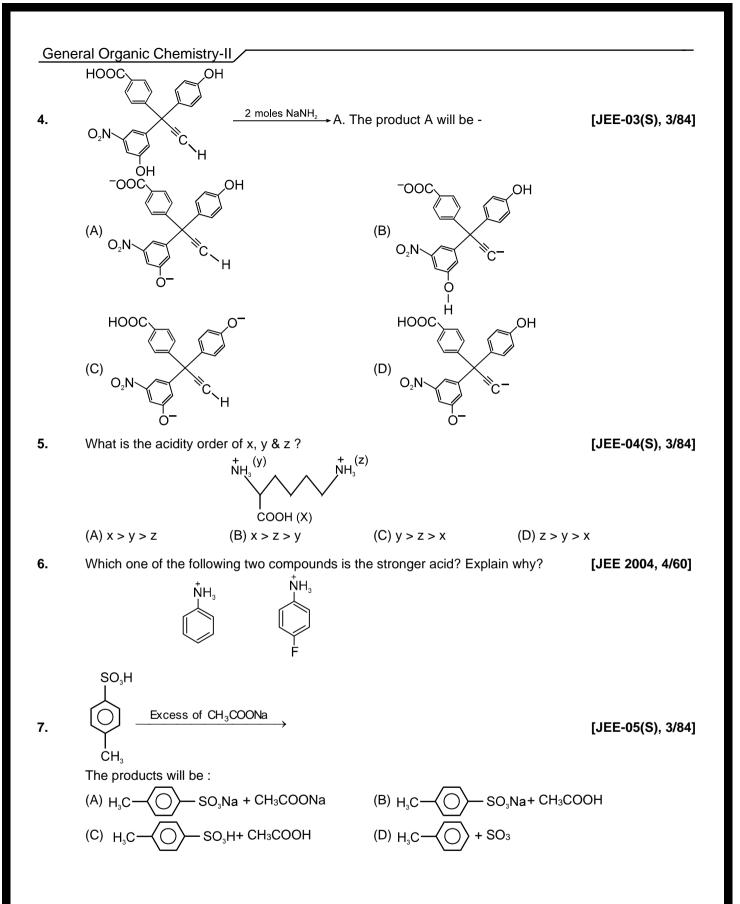
2. Match the Ka values :

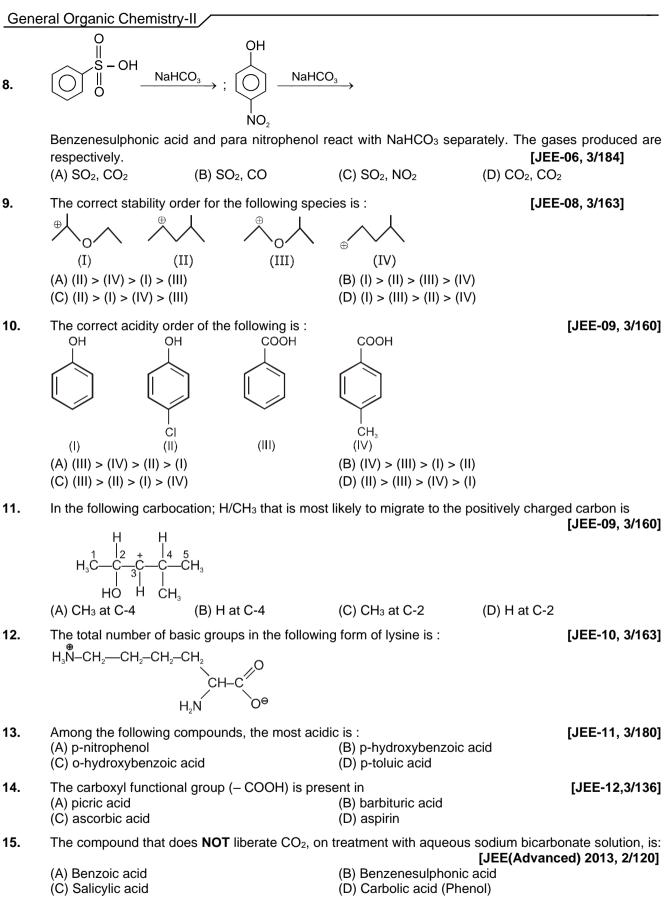
	Compounds		Ka	
(a)	Benzoic acid	(i)	3.3 × 10 <sup>–₅</sup>	
(b)	O₂N → COOH	(ii)	6.3 × 10⁻⁵	
(d)	сі———соон	(iii)	30.6 × 10 <sup>–5</sup>	
(e)	Н₃СО→СООН	(iv)	6.4 × 10 <sup>−5</sup>	
(f)	н,сСоон	(v)	4.2 × 10 <sup>-5</sup>	

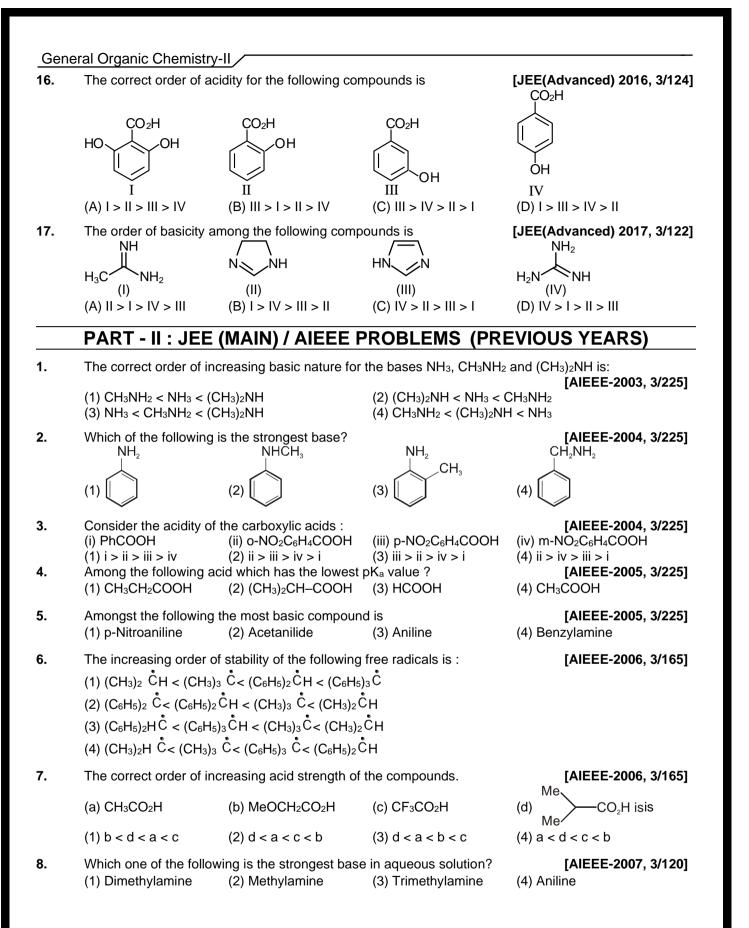
3.

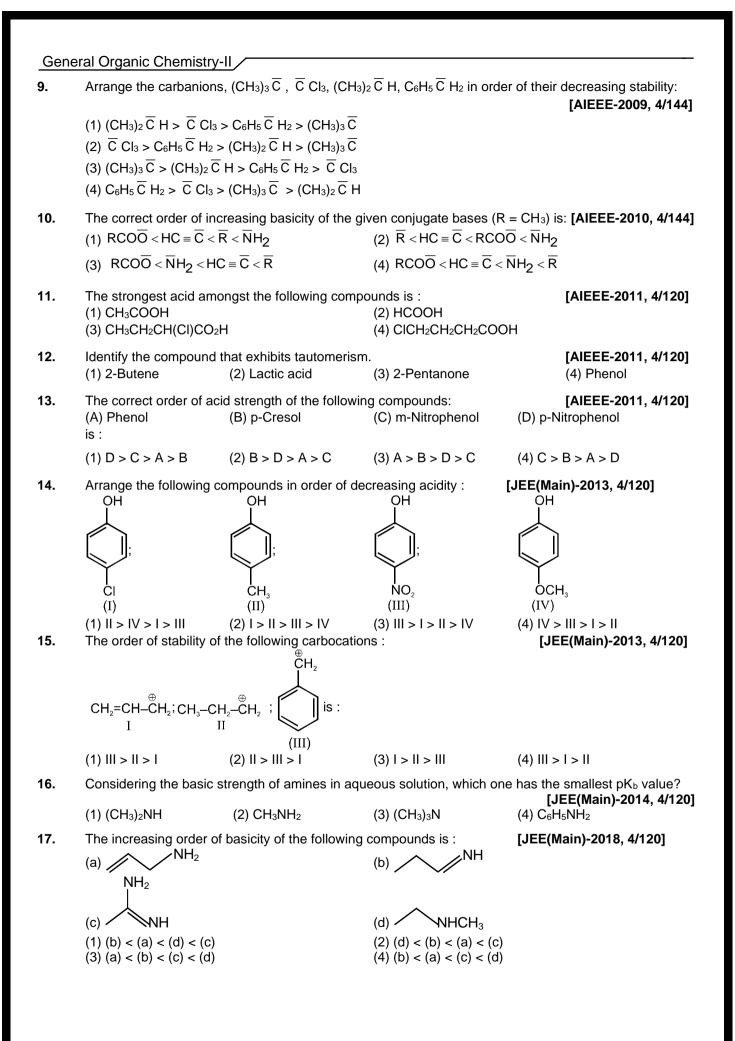
Compound A of molecular formula  $C_9H_7O_2CI$  exists in keto form and predominantly in enolic form 'B'. On oxidation with KMnO<sub>4</sub>'A' gives m-Chlorobenzoic acid. Identify 'A' and 'B'. **[JEE(M)-03]** 

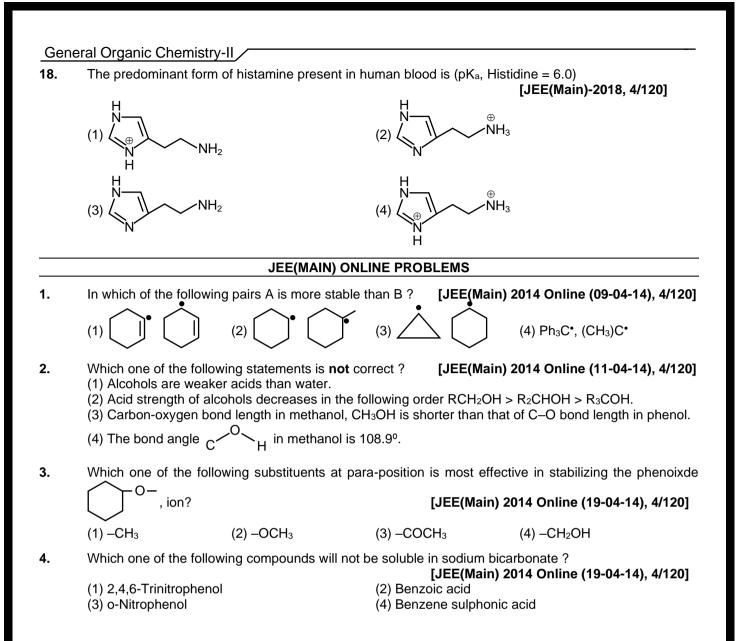
[JEE-03(M), 2/60]











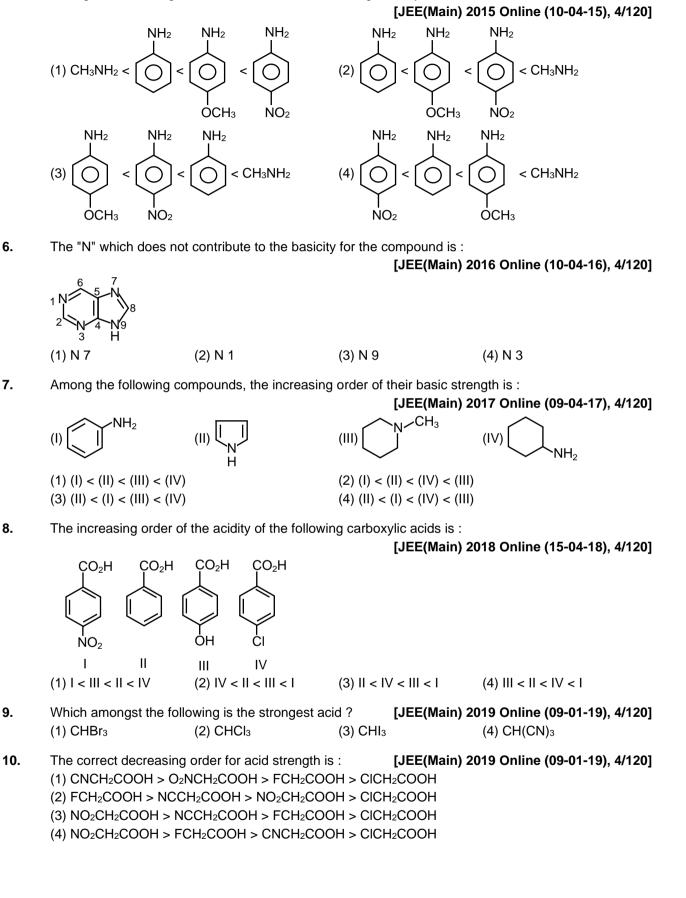
6.

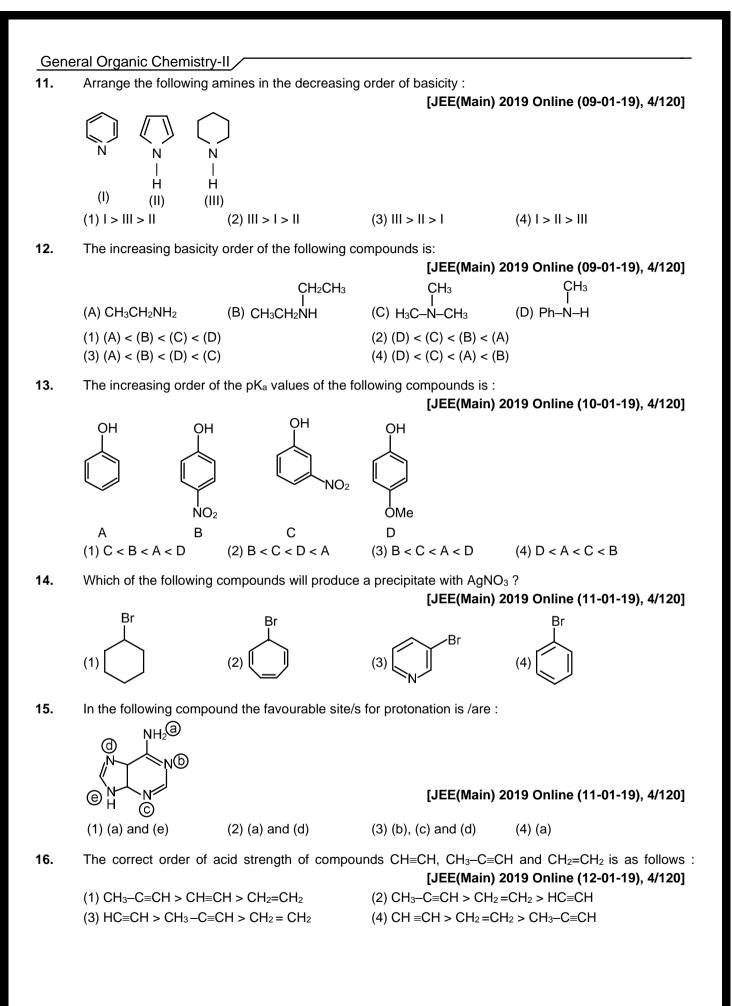
7.

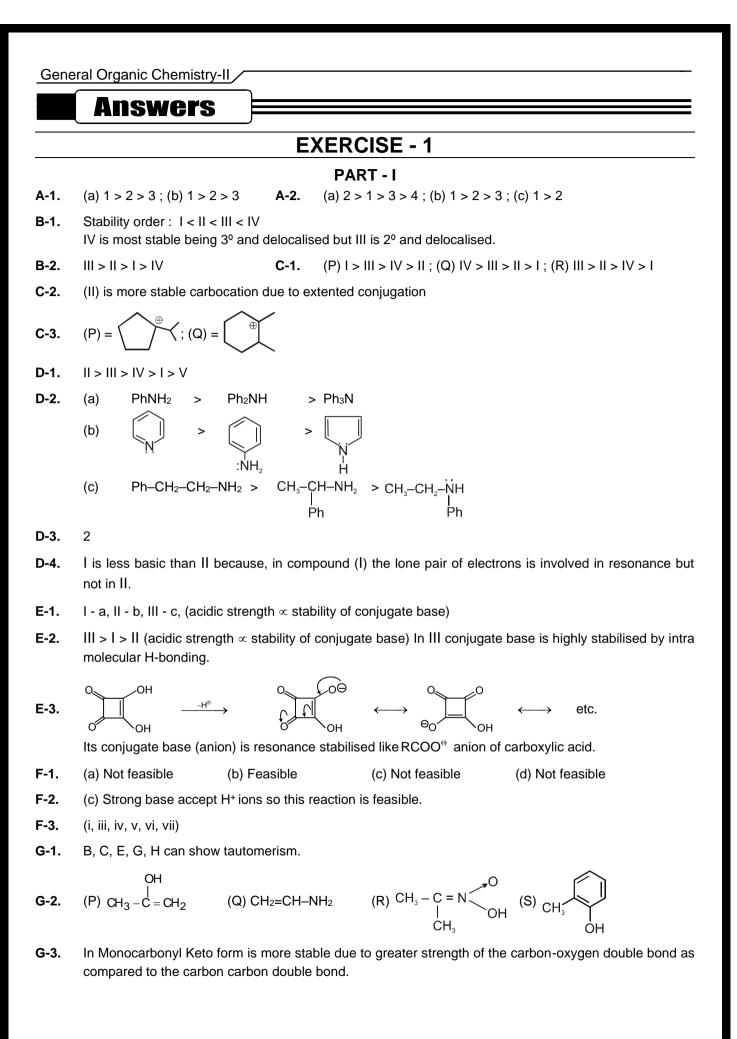
8.

9.

5. Arrange the following amines in the order of increasing basicity :







Gene	eral Organic C	hemistry	/-   /						
	0			PAF	<b>२</b> Т - II				
A-1.	(C)	A-2.	(A)	A-3.	(B)	A-4.	(D)	A-5.	(B)
A-6.	(D)	B-1.	(A)	B-2.	(D)	B-3.	(A)	B-4.	(C)
B-5.	(B)	B-6.	(C)	C-1.	(C)	C-2.	(B)	C-3.	(B)
C-4.	(C)	C-5.	(D)	C-6.	(B)	D-1.	(C)	D-2.	(A)
D-3.	(A)	D-4.	(D)	D-5.	(D)	D-6.	(A)	D-7.	(D)
D-8.	(D)	E-1.	(D)	E-2.	(A)	E-3.	(C)	E-4.	(B)
E-5.	(D)	E-6.	(C)	E-7.	(C)	E-8.	(C)	E-9.	(A)
E-10.	(D)	F-1.	(B)	F-2.	(C)	F-3.	(D)	F-4.	(C)
G-1.	(A)	G-2.	(A)	G-3.	(B)	G-4.	(A)	G-5.	(A)
				PAF	RT - III				
1.	(A - z) ; (B - x) ; (C - w) ; (D - y)			2.	(A - p,q,s) ;	(B - p,q,r,s	s) ; (C - p	,q,r,s) ; (D - p,o	q,r,s)
				EXER	CISE - 2				
				PA	RT - I				
1.	(B)	2.	(C)	3.	(A)	4.	(C)	5.	(A)
6.	(D)	7.	(B)	8.	(D)	9.	(A)	10.	(D)
11.	(A)	12.	(D)	13.	(A)	14.	(D)	15.	(B)
16.	(A)	17.	(C)	18.	(A)	19.	(C)	20.	(B)
21.	(D)	22.	(B)						
				PAF	RT - II				
1.	7	2.	2	3.	4 (S <sub>1</sub> , S <sub>2</sub> , S <sub>4</sub>	4, <b>S</b> 5)	4.	5 (ii, iii, iv, vi,	vii)
5.	6 (i, ii, iii, vi, v	′ii, ix)		6.	5 (i, iv, v, vi	, viii)	7.	5 (i, iv, v, vi, v	⁄iii)
8.	34	9.	3	10.	10				
				PAF	RT - III				
1.	(ABCD)	2.	(BCD)	3.	(ABCD)	4.	(ACD)	5.	(ACD)
6.	(BC)	7.	(BD)	8.	(ABCD)	9.	(ACD)		
				PAF	RT - IV				
1.	(D)	2.	(D)	3.	(A)	4.	(A)	5.	(C)
6.	(B)	7.	(C)	8.	(A)	9.	(D)	10.	(D)
11.	(C)	12.	(C)	13.	(D)	14.	(A)		

# **EXERCISE - 3**

# PART - I

1.	(C)	2.	(a) – (ii) ; (b) –	- (iii) ; (c)	) – (iv) ; (d) – (i) ;	(e) – (v	)		+
3.	A. CI	; B. +	СНО	4.	(A)	5.	(A)	6.	*H <sub>3</sub>
7.	(B)	8.	(D)	9.	(D)	10.	(A)	11.	(D)
12.	2	13.	(C)	14.	(D)	15.	(D)	16.	(A)
17.	(D)								

# PART - II

			JEE	E(MAIN) OFF	LINE PRO	BLEMS			
1.	(3)	2.	(4)	3.	(2)	4.	(3)	5.	(4)
6.	(1)	7.	(3)	8.	(1)	9.	(2)	10.	(4)
11.	(3)	12.	(3)	13.	(1)	14.	(3)	15.	(4)
16.	(1)	17.	(1)	18.	(2)				
			JE	E(MAIN) ON	LINE PROE	BLEMS			
1.	(4)	2.	(3)	3.	(3)	4.	(3)	5.	(4)
6.	(3)	7.	(4)	8.	(4)	9.	(4)	10.	(3)
11.	(2)	12.	(4)	13.	(3)	14.	(2)	15.	(3)
40	( <b>0</b> )								

**16.** (3)