

Answers**EXERCISE - 1****PART - I**

- A-1.** (a) I > 2 > 3 ; (b) 1 > 2 > 3 **A-2.** (a) 2 > 1 > 3 > 4 ; (b) 1 > 2 > 3 ; (c) 1 > 2

B-1. Stability order : I < II < III < IV
IV is most stable being 3° and delocalised but III is 2° and delocalised.

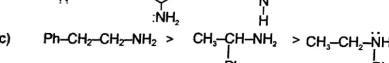
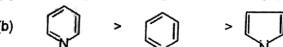
B-2. III > II > I > IV **C-1.** (P) I > III > IV > II ; (Q) IV > III > II > I ; (R) III > II > IV > I

C-2. (II) is more stable carbocation due to extended conjugation



D-1. II > III > IV > I > V

D-2. (a) PhNH₂ > Ph₂NH > PhN

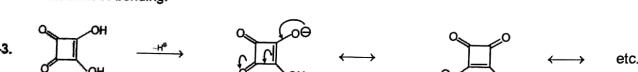


D-3. 2

D-4. I is less basic than II because, in compound (I) the lone pair of electrons is involved in resonance but not in II.

E-1. I - a, II - b, III - c, (acidic strength \propto stability of conjugate base)

E-2. III > I > II (acidic strength \propto stability of conjugate base) In III conjugate base is highly stabilised by intra molecular H-bonding.



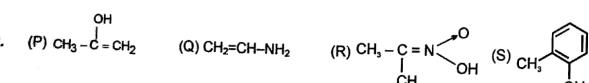
Its conjugate base (anion) is resonance stabilised like RCOO⁻ anion of carboxylic acid.

F-1. (a) Not feasible (b) Feasible (c) Not feasible (d) Not feasible

F-2. (c) Strong base accept H⁺ ions so this reaction is feasible.

F-3. (i, iii, iv, v, vi, vii)

G-1. B, C, E, G, H can show tautomerism.



G-3. In Monocarbonyl Keto form is more stable due to greater strength of the carbon-oxygen double bond as compared to the carbon carbon double bond.

PART - 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) |
1. (A - z) ; (B - x) ; (C - w) ; (D - y)
2. (A - p,q,s) ; (B - p,q,r,s) ; (C - p,q,r,s) ; (D - p,q,r,s)

EXERCISE - 2**PART - 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) | | | |

PART - II

- | | | | |
|--------------------------------|------|---|-----------------------------|
| 1. 7 | 2. 2 | 3. 4 (S ₁ , S ₂ , S ₄ , S ₅) | 4. 5 (ii, iii, iv, vi, vii) |
| 5. 6 (i, ii, iii, vi, vii, ix) | | 6. 5 (i, iv, v, vi, viii) | 7. 5 (i, iv, v, vi, viii) |
| 8. 34 | 9. 3 | 10. 10 | |

PART - III

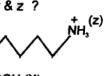
- | | | | | |
|-----------|----------|-----------|----------|----------|
| 1. (ABCD) | 2. (BCD) | 3. (ABCD) | 4. (ACD) | 5. (ACD) |
| 6. (BC) | 7. (BD) | 8. (ABCD) | 9. (ACD) | |

PART - IV

- | | | | | |
|---------|--------|--------|--------|---------|
| 1. (D) | 2. (D) | 3. (A) | 4. (A) | 5. (C) |
| 6. (B) | 7. (C) | 8. (A) | 9. (D) | 10. (D) |
| 11. (C) | | | | |

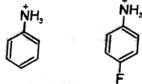
General Organic Chemistry-II

5. What is the acidity order of x , y & z ? [JEE-04(S), 3/84]



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

6. Which one of the following two compounds is the stronger acid? Explain why? [JEE 2004, 4/60]



7. [JEE-05(S), 3/84]

The products will be :

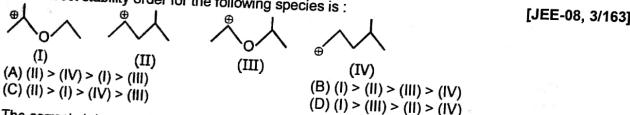
- (A) $H_3C-\text{C}_6\text{H}_4-\text{SO}_3\text{Na} + \text{CH}_3\text{COONa}$ (B) $H_3C-\text{C}_6\text{H}_4-\text{SO}_3\text{Na} + \text{CH}_3\text{COOH}$
 (C) $H_3C-\text{C}_6\text{H}_4-\text{SO}_3\text{H} + \text{CH}_3\text{COOH}$ (D) $H_3C-\text{C}_6\text{H}_4-\text{SO}_3 + \text{SO}_3$

8. [JEE-06, 3/184]

Benzenesulphonic acid and para nitrophenol react with NaHCO_3 separately. The gases produced are respectively.

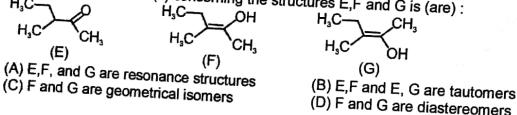
- (A) SO_2, CO_2 (B) SO_2, CO (C) SO_2, NO_2 (D) CO_2, CO_2

9. The correct stability order for the following species is : [JEE-08, 3/163]



- (A) $\text{III} > \text{IV} > \text{I} > \text{III}$
 (B) $\text{I} > \text{II} > \text{III} > \text{IV}$
 (C) $\text{III} > \text{I} > \text{IV} > \text{III}$
 (D) $\text{I} > \text{III} > \text{II} > \text{IV}$

10. The correct statement(s) concerning the structures E, F and G is (are) :

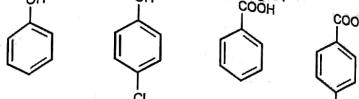


- (A) E, F, and G are resonance structures
 (C) F and G are geometrical isomers
 (B) E, F and E, G are tautomers
 (D) F and G are diastereomers

[IIT-JEE-2008]

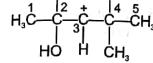
General Organic Chemistry-II

11. The correct acidity order of the following is :



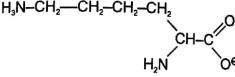
- (A) $\text{III} > \text{IV} > \text{II} > \text{I}$
 (C) $\text{III} > \text{II} > \text{I} > \text{IV}$
 (B) $\text{IV} > \text{III} > \text{I} > \text{II}$
 (D) $\text{II} > \text{III} > \text{IV} > \text{I}$

12. In the following carbocation; H/CH_3 that is most likely to migrate to the positively charged carbon is



- (A) CH_3 at C-4 (B) H at C-4 (C) CH_3 at C-2 (D) H at C-2 [JEE-09, 3/160]

13. The total number of basic groups in the following form of lysine is : [JEE-10, 3/163]



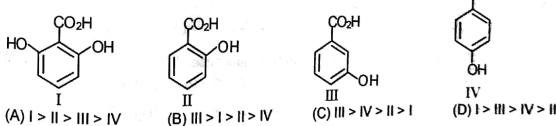
14. Among the following compounds, the most acidic is : [JEE-11, 3/180]
 (A) p-nitrophenol (B) p-hydroxybenzoic acid
 (C) o-hydroxybenzoic acid (D) p-tolualic acid

15. The carboxyl functional group ($-\text{COOH}$) is present in [JEE-12, 3/136]
 (A) picric acid (B) barbituric acid
 (C) ascorbic acid (D) aspirin

16. The compound that does NOT liberate CO_2 on treatment with aqueous sodium bicarbonate solution, is: [JEE(Advanced) 2013, 2/120]

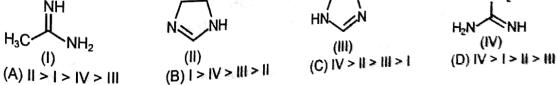
- (A) Benzoic acid (B) Benzenesulphonic acid
 (C) Salicylic acid (D) Carboxylic acid (Phenol)

17. The correct order of acidity for the following compounds is [JEE(Advanced) 2016, 3/124]



- (A) $\text{I} > \text{II} > \text{III} > \text{IV}$ (B) $\text{III} > \text{I} > \text{II} > \text{IV}$ (C) $\text{III} > \text{IV} > \text{II} > \text{I}$ (D) $\text{I} > \text{III} > \text{IV} > \text{II}$ [JEE(Advanced) 2017, 3/122]

18. The order of basicity among the following compounds is

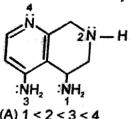


- (A) $\text{II} > \text{I} > \text{IV} > \text{III}$ (B) $\text{I} > \text{IV} > \text{III} > \text{II}$ (C) $\text{IV} > \text{II} > \text{III} > \text{I}$ (D) $\text{IV} > \text{I} > \text{II} > \text{III}$

General Organic Chemistry-II

8. pK_a order of the following compound is :
 (I) NH_2OH (II) NH_2NH_2 (III) NH_3 (IV) H_2O
 (A) IV > I > II > III (B) III > II > I > IV (C) I > IV > II > III (D) III > I > II > IV

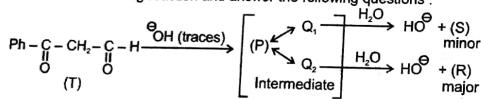
9. The correct basicity order of various atoms is :



- (A) 1 < 2 < 3 < 4 (B) 2 < 4 < 3 < 1 (C) 3 < 2 < 1 < 4 (D) 3 < 4 < 1 < 2

Comprehension # 4

Observe the following reaction and answer the following questions :



10. The product 'R' is :

- (A) $\text{Ph}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}=\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{H}$
 (B) $\text{Ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}}{\underset{\text{O}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{H}$
 (C) $\text{Ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}}{\underset{\text{O}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{H}$
 (D) $\text{Ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}}{\underset{\text{O}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{H}$

11. The structure of Q_1 is :

- (A) $\text{Ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}}{\underset{\text{O}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{H}$
 (B) $\text{Ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{H}$
 (C) $\text{Ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}}{\underset{\text{O}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{H}$
 (D) $\text{Ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}}{\underset{\text{O}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{H}$

Comprehension # 5

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

Column-1	Column-2	Column-3
(I)	(i) SbCl_5 or $\text{AlCl}_3(\text{Anhy.})$	(P) Rearrangement
(II)	(ii) Na	(Q) Resonance
(III)	(iii) H^+	(R) Hyperconjugation
(IV)	(iv) NaOH	(S) Carbocation intermediate

General Organic Chemistry-II

12. Which combination will give hydrogen gas ?
 (A) (III) (iii) (P) (B) (II) (ii) (R)
 (C) (IV) (ii) (Q) (D) (I) (iii) (P)
 13. In which product formation is not possible ?
 (A) (I) (ii) (Q) (B) (II) (i) (R)
 (C) (III) (ii) (Q) (D) (IV) (i) (S)
 14. In which among the following aromatic product will not form ?
 (A) (I) (i) (P) (B) (II) (i) (Q)
 (C) (III) (iv) (Q) (D) (IV) (ii) (Q)

Exercise-3

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

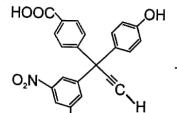
* Marked Questions may have more than one correct option.

1. Which of the following acid has the lowest value of acid dissociation constant : [JEE-02(S), 3/90]
 (A) $\text{CH}_3\text{CHFCOOH}$ (B) $\text{FCH}_2\text{CH}_2\text{COOH}$ (C) $\text{BrCH}_2\text{CH}_2\text{COOH}$ (D) $\text{CH}_3\text{CHBrCOOH}$

2. Match the K_a values :

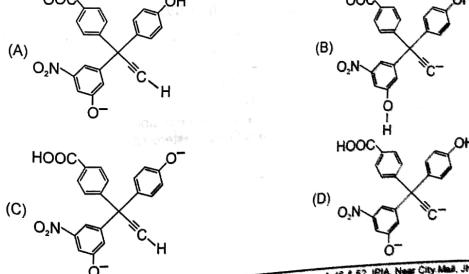
Compounds		K_a
(a) Benzoic acid	(i)	3.3×10^{-5}
(b) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{COOH}$	(ii)	6.3×10^{-5}
(d) $\text{Cl}-\text{C}_6\text{H}_4-\text{COOH}$	(iii)	30.6×10^{-5}
(e) $\text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{COOH}$	(iv)	6.4×10^{-5}
(f) $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$	(v)	4.2×10^{-5}

3. Compound A of molecular formula $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$ exists in keto form and predominantly in enolic form 'B'. On oxidation with KMnO_4 , 'A' gives m-Chlorbenzoic acid. Identify 'A' and 'B'. [JEE(M)-03]



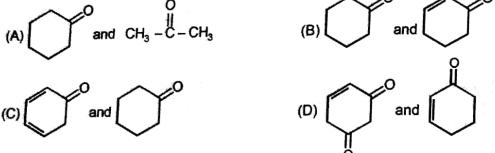
4. $\xrightarrow{2 \text{ moles } \text{NaN}_3}$ A. The product A will be -

[JEE-03(S), 3/84]



General Organic Chemistry-II

3. Among the given pairs, in which pair second compound has less enol content :



PART - IV : COMPREHENSION

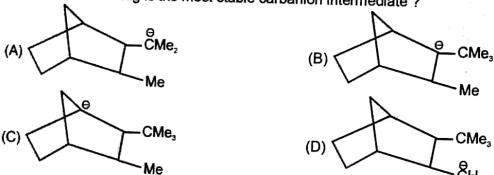
Read the following passage carefully and answer the questions.

Comprehension # 1

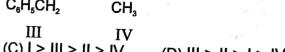
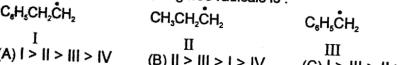
Reaction intermediates : Reaction intermediates are short lived species and are highly reactive. They are formed by heterolytic and homolytic bond fission. There are various types of reaction intermediates in which the most important are carbocation, carbanion and free radical. Carbocation is an organic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

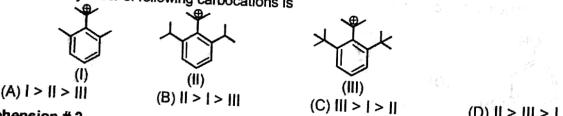
1. Which of the following is the most stable carbanion intermediate ?



2. The stability order of following free radicals is :



3. The stability order of following carbocations is



Comprehension # 2

Ortho effect is a special type of effect that is shown by α -substituents. This ortho-effect operates at the benzoic acids irrespective of the polar type. Nearly all α -substituted benzoic acid are stronger than Benzoic acid. Benzoic acid is a resonance stabilised and so the carboxyl group is coplanar with the ring. An α -substituent tends to prevent this coplanarity.

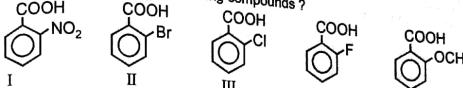
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ADVGOC-II - 36

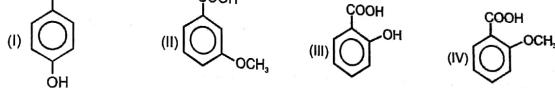
General Organic Chemistry-II

4. What is the order of K_a of following compounds ?



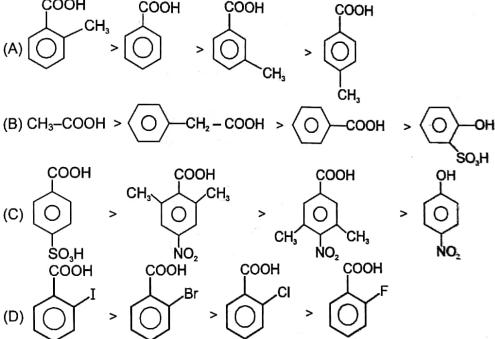
- (A) I > II > III > IV > V (B) II > I > IV > V (C) V > IV > III > I > II (D) III > II > I > V > IV

5. Which among the following will be the strongest acid ?



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

6. Which of the following is/are correct pK_a order ?



Comprehension # 3

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_b . 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 ERG substituent. ERG substituents, such as $-\text{Cl}$, $-\text{NO}_2$ and $-\text{OCH}_3$ increases the basicity and EWG substituents, such as $-\text{Cl}$, $-\text{NO}_2$ and $-\text{CN}$ decreases basicity. While sp^2 -hybridized nitrogen atom in pyridine is less basic than the sp^3 -hybridized nitrogen in an alkylamine.

7. Select the correct order of K_b .

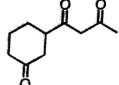
- (A) $\text{CH}_3\text{NH}_2 > \text{NaOH}$
 (B) Pyridine > $\text{CH}_3\text{-NH-CH}_3$
 (C) p-Methyl aniline > p-Chloroaniline > p-Amino acetophenone
 (D) p-Bromoaniline > p-Nitroaniline > p-Amino benzaldehyde

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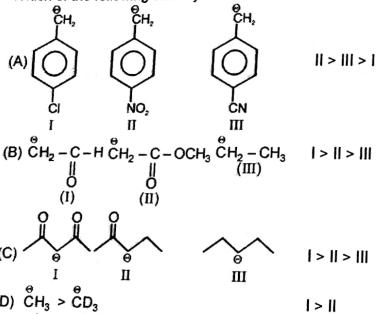
General Organic Chemistry-II

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

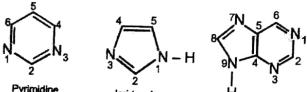
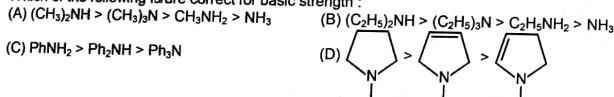


PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

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



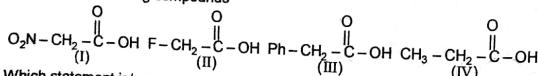
2. a. Which of the following is/are correct for basic strength :



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.

4. a. Consider the following compounds



Which statement is/are correct :

- (A) I > II > III > IV (Acidic strength order)
 (B) I is most acidic because of $-M$ effect of $-\text{NO}_2$ group
 (C) I is most acidic because of $-I$ effect of $-\text{NO}_2$ group
 (D) IV is least acidic because of $+I$ Effect.

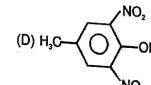
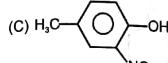
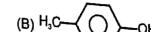
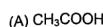
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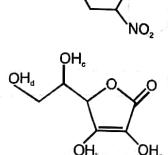
ADVGOC-II - 34

General Organic Chemistry-II

Carboxylic acid is less acidic than :



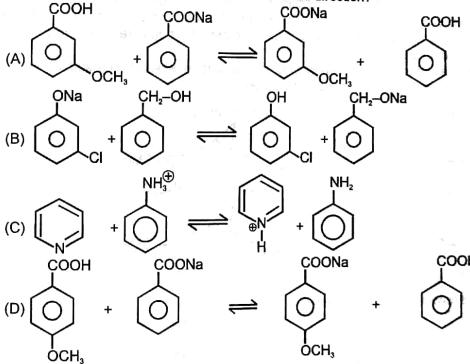
6.



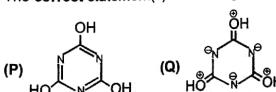
Observe the compound and choose correct statement :

- (A) It has carboxylic acid group (B) It is Ascorbic acid
 (C) H_3 is most acidic Hydrogen atom (D) H_4 is least acidic Hydrogen atom

7. a. Which of the following reactions favour backward direction?



8. The correct statement(s) concerning the structures P, Q, R & S is/are



- (A) Q & S are not resonating structures (B) R & S are resonating structures
 (C) P & R are tautomers (D) P & Q are resonating structures

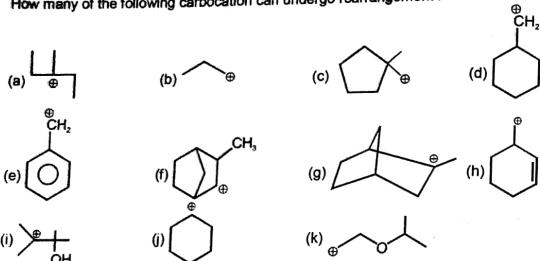
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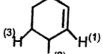
General Organic Chemistry-II

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

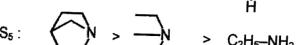
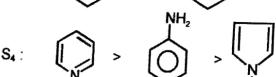
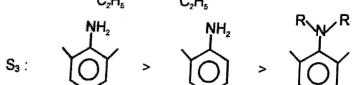
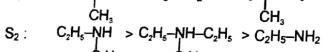
1. a. How many of the following carbocation can undergo rearrangement :



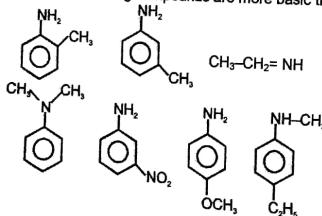
2. Consider following compound, which H-atom deprotonated first ?



3. a. How many of the following are correct orders for Basic Strength :

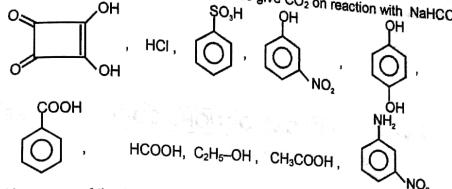


4. How many following compounds are more basic than aniline.

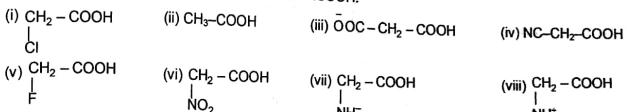


General Organic Chemistry-II

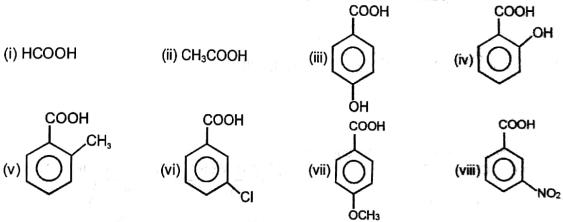
5. How many of the following compounds give CO₂ on reaction with NaHCO₃.



6. How many of the following are more acidic than HCOOH.

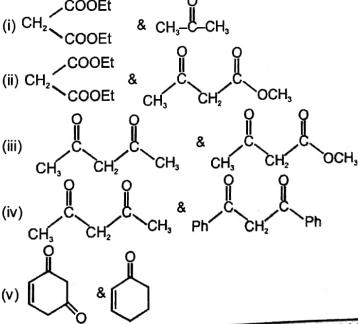


7. a. How many of the following compound have less pKa than benzoic acid :



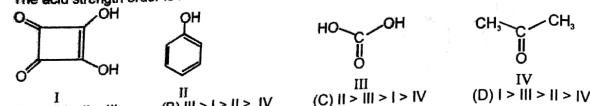
8. 90 g of acetic acid react with excess of NaHCO₃ then what volume of CO₂ will produce at S.T.P. Write your answer in terms of nearest integer.

9. In how many of the following pairs first will have higher enol content than second.

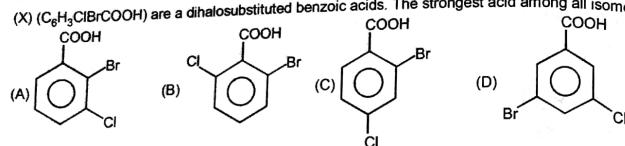


General Organic Chemistry-II

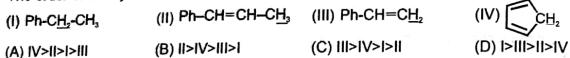
14. The acid strength order is :



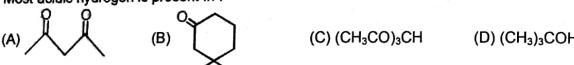
15. $(X) C_6H_3ClBrCOOH$ are a dihalosubstituted benzoic acids. The strongest acid among all isomers is -



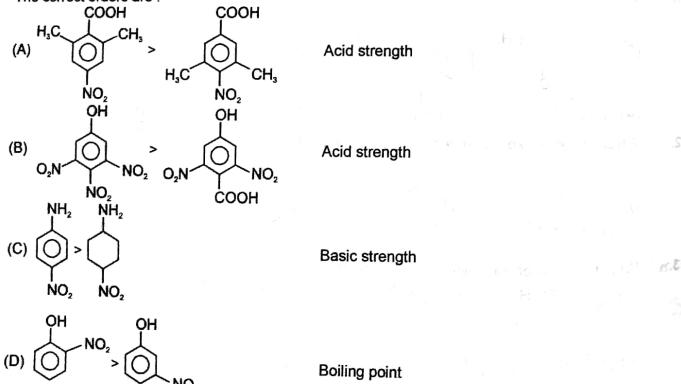
16. The order of acidity of the H-atoms underlined in the following compounds is in the order :



17. Most acidic hydrogen is present in :

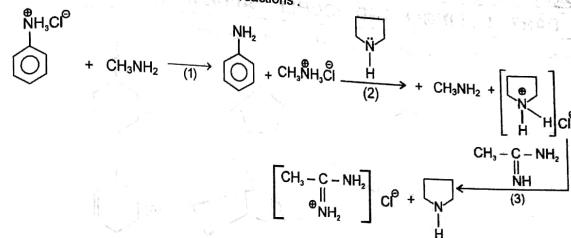


18. The correct orders are :

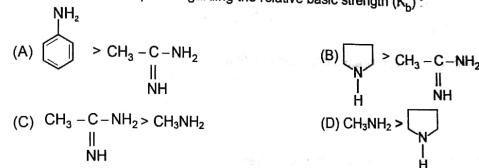


General Organic Chemistry-II

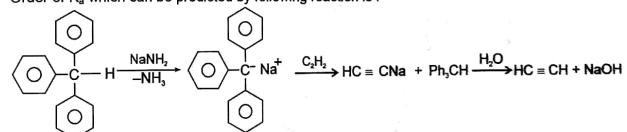
19. Observe the following sequence of reactions :



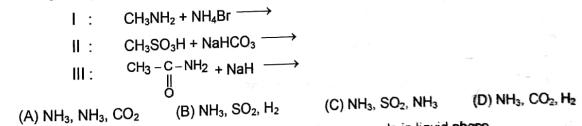
Select the correct option regarding the relative basic strength (K_b) :



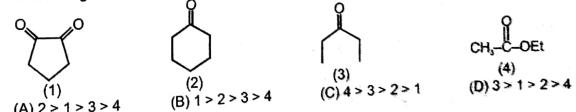
20. Order of K_a which can be predicted by following reaction is :



21. The gases produced in the following reactions are respectively



22. Decreasing order of enol content of the following compounds in liquid phase



General Organic Chemistry-II

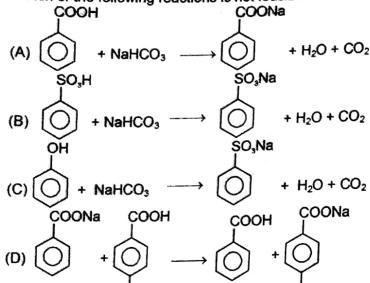
2. **Correct decreasing stability order of following carbanions :**
- $$\text{CH}_3-\text{CHO} \quad \text{CH}_3-\overset{\oplus}{\text{C}}(\text{O})-\text{CH}-\text{CH}_3 \quad \text{H}-\overset{\oplus}{\text{C}}(\text{O})-\text{CH}-\text{C}(=\text{O})-\text{H}$$
- I II III
- (A) III > IV > II > I (B) IV > II > III > I (C) IV > III > II > I (D) III > II > I > IV
3. **Select the most stable intermediates :**
- (A) (B) (C) (D)
4. **Which of the following is most stable carbocation?**
- (A) CH_3CH_2^+ (B) $\text{CH}_3\text{C}=\text{O}^+$ (C) $\text{CH}_3-\overset{\oplus}{\text{C}}=\text{NH}^+$ (D) $\text{CH}_2=\overset{\oplus}{\text{CH}}^+$
5. **The most stable carbocation is :**
- (A) (B) (C) (D)
6. **The following carbocation rearranges to**
- $\text{CH}_2=\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}-\text{CH}-\text{CH}_3$
- (A) $\text{CH}_2=\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}-\text{CH}-\text{CH}-\text{CH}_3$ (B) $\text{CH}_2=\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}-\text{CH}_2-\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}_3$
- (C) $\text{CH}_2=\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}-\text{CH}-\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}_3$ (D) $\text{CH}_2=\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}-\text{CH}-\text{CH}_3$
7. **Correct basic strength order is :**
- (A) p (B) q (C) r (D) s

General Organic Chemistry-II

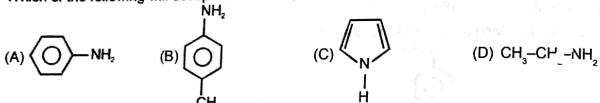
8. **The order of basic strength of the given basic nitrogen atoms is :**
-
- (A) III > II > I > IV (B) III > I > II > IV (C) I > III > II > IV (D) II > III > I > IV
9. **In the labelled N-atoms which is correct basic strength order :**
-
- (A) 2 > 1 > 3 (B) 3 > 1 > 2 (C) 2 > 3 > 1 (D) All are equally basic
10. **Choose the strongest base among the following :**
- (A) (B) (C) (D)
11. **Select the basic strength order of following molecules ?**
- I II III IV
- (A) III > II > I (B) II > III > I (C) I > III > II (D) III > I > II
12. **Which is the weakest base among the followings ?**
- (A) (B) (C) (D)
13. **Write the order of K_{a_1} values of following acids :**
- (I) (II) (III)
- (A) II > III > I (B) I > III > II (C) III > II > I (D) II > I > III

General Organic Chemistry-II

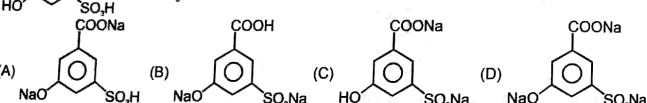
F-2. Which of the following reactions is not feasible?



F-3. Which of the following will accept H^+ from NH_4^+ ion.

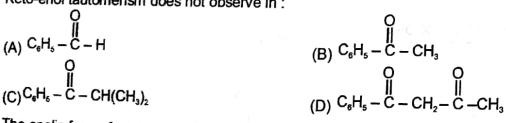


F-4. 



Section (G) : Tautomerism

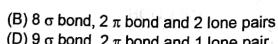
G-1. Keto-enol tautomerism does not observe in :

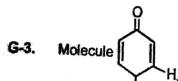


G-2. The enolic form of acetone contains :

(A) 9 σ bonds, 1 π bond and 2 lone pairs

(C) 10 σ bonds, 1 π bond and 1 lone pair



G-3. Molecule  can be enolised by which hydrogen?

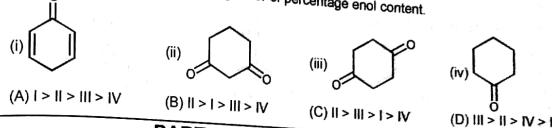
- (A) y-H (B) z-H (C) both (D) None of these

General Organic Chemistry-II

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



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

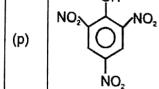
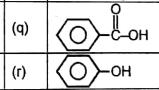
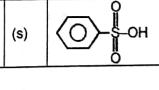
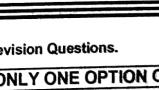


PART - III : MATCH THE COLUMN

1. Match the column :

Column-I (Keto)	Column-II (% enol)
(A) $CH_3-C=O$	(x) 95 %
(B) $Ph-C(=O)-CH_2-C(=O)-Ph$	(y) 76 %
(C) $CH_3-C(=O)-CH_2-C(=O)-OEt$	(z) 0.0001 %
(D) $CH_3-C(=O)-CH_2-C(=O)-CH_3$	(w) 7.2 %

2. Match the column :

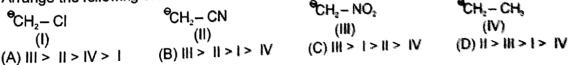
Column-I	Column-II
(A) $NaHCO_3$ will react with	(p) 
(B) Na will react with	(q) 
(C) NaOH will react with	(r) 
(D) $NaNH_2$ will react with	(s) 

Exercise-2

Marked Questions may have for Revision Questions.

PART - I : ONLY ONE OPTION CORRECT TYPE

1. Arrange the following carbanions in decreasing order of stability :



General Organic Chemistry-II

D-5. Select the basic strength order of following molecules?



- (I) Pipidine
(A) (IV) > (I) > (III) > (IV)
(C) (II) > (I) > (III) > (IV)



- (II) Pyridine
(A) (IV) > (I) > (III) > (IV)



- (III) Morpholine
(B) (III) > (I) > (IV) > (II)
(D) (I) > (III) > (II) > (IV)



- (IV) Pyrrole

D-6. Arrange the following in increasing order of pK_a value?



- (I) NH₂
(A) II < I < III



- (II) NH₂-CH₃
(B) III < I < II



- (III) NH₂-CH₂-CH₃
(C) III < II < I
(D) II < III < I

D-7. Select the decreasing order of relative basic strengths of following species:



- (I) NH₂-C₆H₄-NH₂
(A) II > IV > I > III



- (II) NH₂-C₆H₄-NH₂
(B) III > I > IV > II



- (III) NH₂-C₆H₄-NO₂
(C) III > IV > I > II



- (IV) NH₂-C₆H₄-Cl
(D) II > I > IV > III

D-8. Select the basic strength order of following molecule:



- (I) NH₂
(A) II > III > IV > I



- (II) NH₂-CH₃
(B) II > IV > III > I



- (III) NH₂-CH₂-CH₃
(C) IV > II > III > I



- (IV) NH₂-CH₂-CH₃
(D) IV > III > I > II

Section (E) : Acidic strength

E-1. Among the following compounds, the strongest acid is :

- (A) HC ≡ CH (B) C₆H₆ (C) C₂H₆ (D) CH₃OH

E-2. Which of the following is not correct decreasing K_a order.

- (A) CH₄ > NH₃ > H₂O > HF
(B) CH₃-OH > CH₃-NH₂ > CH₃-F > CH₃-CH₃
(C) HI > HBr > HCl > HF
(D) PhOH > H₂O > C₂H₅OH > CH₃-C≡CH

E-3. Which of the following acid has the smallest dissociation constant ?

- (A) CH₃-CH-COOH
|
NO₂
(B) O₂N-CH₂-CH₂-COOH
(C) Cl-CH₂-CH₂-COOH
(D) NC-CH₂-CH₂-COOH

E-4. Find the strongest acid among the following compounds is :

- (A) HOOC-(CH₂)₂-COOH
(B) H₃N⁺-(CH₂)₂-COOH
(C) F-(CH₂)₂-COOH
(D) CH₃-(CH₂)₂-COOH

E-5. Which of the following option shows the correct order of decreasing acidity :

- (A) PhCO₂H > PhSO₃H > PhCH₂OH > PhOH
(B) PhSO₃H > PhOH > PhCH₂OH > PhCO₂H
(C) PhCO₂H > PhOH > PhCH₂OH > PhSO₃H
(D) PhSO₃H > PhCO₂H > PhOH > PhCH₂OH

General Organic Chemistry-II

E-6. Arrange increasing order of acidic strength of following dibasic acids :

- (I) oxalic acid,
(A) III < II < I < IV

- (II) succinic acid,
(B) II < III > I > IV

- (III) malonic acid,
(C) I > III > II > IV

- (IV) adipic acid
(D) II > I > III < IV

- (IV) adipic acid
(D) II > I > III < IV

- (IV) adipic acid
(D) II > I > III < IV

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- (IV) adipic acid
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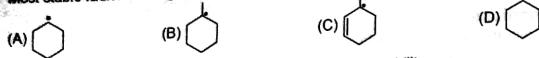
- (IV) adipic acid
(D) II > I > III < IV

- (IV) adipic acid
(D) II > I > III < IV

- (IV) adipic acid
(D) II > I > III < IV

General Organic Chemistry-II

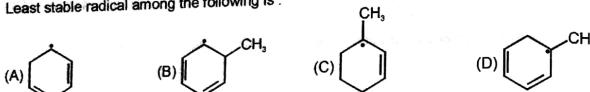
B-4. Most stable radical among the following is :



B-5. Arrange the following radicals in decreasing order of their stability.

- (I) $\dot{\text{C}}\text{H}_3$ (II) $\text{CH}_2-\dot{\text{C}}\text{H}_2$ (III)  (IV) 
 (A) IV > I > III > II (B) IV > III > II > I
 (C) I > II > III > IV (D) IV > III > I > II

B-6. Least stable radical among the following is :



Section (C) : Carbocations

C-1. The most unstable carbocation is :

- (A) $\text{CH}_3\overset{\oplus}{\text{C}}\text{H}_2$ (B) $\text{Cl}-\text{CH}_2-\overset{\oplus}{\text{C}}\text{H}_2$ (C) $\overset{\oplus}{\text{CH}}_2-\text{CHO}$ (D) $\overset{\oplus}{\text{CH}}_2-\text{O}-\text{CH}_3$

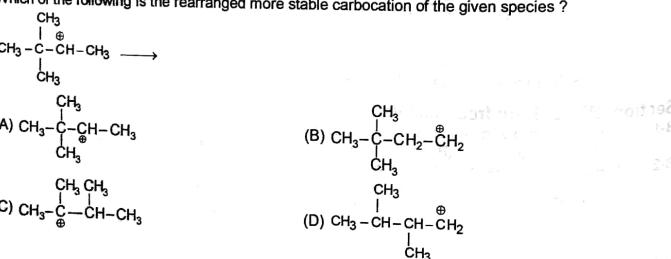
C-2. The most stable carbocation is :



C-3. Which of the following shows the correct order of decreasing stability ?

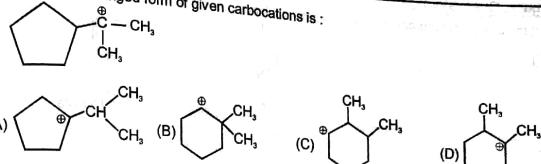
- (A) $\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3\text{O}-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$
 (B) $\text{CH}_3\text{O}-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$
 (C) $\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3\text{O}-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$
 (D) $\text{CH}_3\text{O}-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$

C-4. Which of the following is the rearranged more stable carbocation of the given species ?

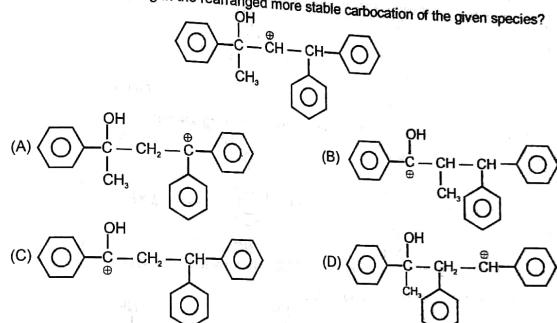


General Organic Chemistry-II

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



C-6. Which of the following is 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) $\text{CH}_3-\overset{\ominus}{\text{C}}\text{H}_2 > \overset{\ominus}{\text{N}}\text{H}_2 > \text{CH}_2=\overset{\ominus}{\text{C}}\text{H} > \text{CH}=\overset{\ominus}{\text{C}}\text{H} > \text{HO} > \text{F}$
 (B) $\overset{\ominus}{\text{N}}\text{H}_2 > \text{CH}_3-\overset{\ominus}{\text{C}}\text{H}_2 > \text{CH}_2=\overset{\ominus}{\text{C}}\text{H} > \text{CH}=\overset{\ominus}{\text{C}}\text{H} > \text{HO} > \text{F}$
 (C) $\text{CH}_3-\overset{\ominus}{\text{C}}\text{H}_2 > \text{CH}_2=\overset{\ominus}{\text{C}}\text{H} > \overset{\ominus}{\text{N}}\text{H}_2 > \text{CH}=\overset{\ominus}{\text{C}}\text{H} > \text{HO} > \text{F}$
 (D) $\text{F} > \text{HO} > \text{CH}=\overset{\ominus}{\text{C}}\text{H} > \text{CH}_2=\overset{\ominus}{\text{C}}\text{H} > \overset{\ominus}{\text{N}}\text{H}_2 > \text{CH}_3-\overset{\ominus}{\text{C}}\text{H}_2$

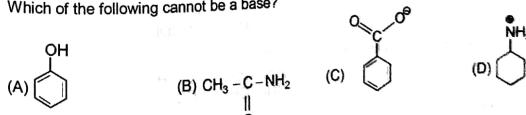
D-2. Which of the following shows the correct order of decreasing basicity in gas phase ?

- (A) $(\text{CH}_3)_2\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$ (B) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3 > (\text{CH}_3)_2\text{N}$
 (C) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{N} > \text{NH}_3$ (D) $(\text{CH}_3)_2\text{N} > \text{CH}_3\text{NH}_2 > \text{NH}_3 > (\text{CH}_3)_2\text{N}$

D-3. Find the order of basic strength. (If R = Me) ?

- (I) $\text{R}_4\text{N}^+\text{OH}^-$ (II) R_3N^- (III) R_2NH (IV) RNH_2
 (A) I > III > IV > II (B) IV > III > I > II (C) II > IV > III > I (D) II > IV > I > III

D-4. Which of the following cannot be a base?



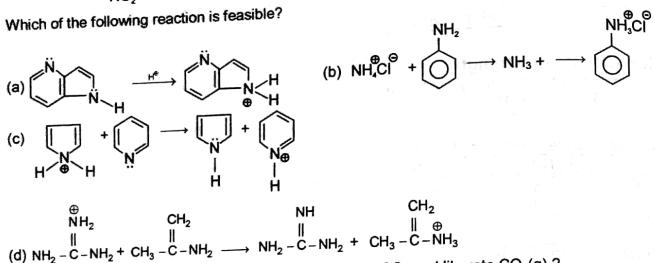
General Organic Chemistry-II

Section (F) : Feasible reactions of acids and bases

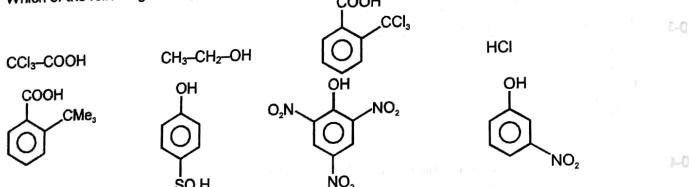
F-1. Which of the following reactions is/are feasible?



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

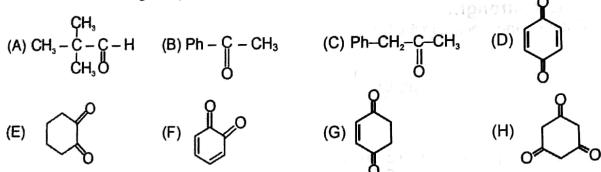


F-3. Which of the following acids (given below) react with NaHCO_3 and liberate CO_2 (g) ?

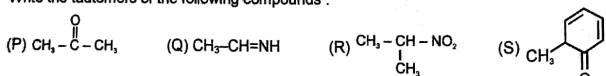


Section (G) : Tautomerism

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.

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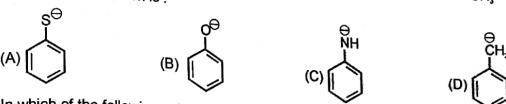
PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Carbanions

A-1. Which of the following is the least stable carbanion?

- (A) $\text{HC}\equiv\text{C}^-$ (B) $(\text{C}_2\text{H}_5)_2\text{C}^-$ (C) $(\text{CH}_3)_2\text{C}^-$ (D) CH_3^-

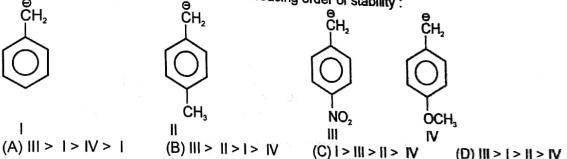
A-2. The most stable anion is :



A-3. In which of the following pairs of carbanion the first one is more stable than second?

- (A) CF_3^- , CCl_3^- (B) $\text{HC}\equiv\text{C}^-$, $\text{H}_2\text{C}=\text{CH}^-$
 (C) $\text{C}_6\text{H}_5\text{CH}_2^-$, $\text{C}_6\text{H}_5\text{N}^-$ (D) $(\text{CH}_3)_2\text{C}^-$, $\text{H}_2\text{C}=\text{CH}^-$

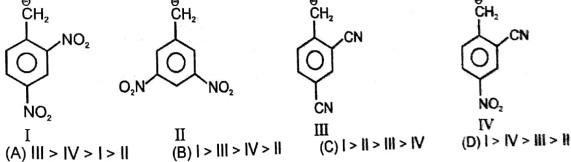
A-4. Arrange the following carbanions in decreasing order of stability :



A-5. The most stable anion is :



A-6. Arrange the following carbanions in increasing order of stability :



Section (B) : Carbon free radicals

B-1. Among the following, the paramagnetic species is :

- (A) Free radical (B) Carbocation (C) Carbanion (D) All the three

B-2. The stability of given free radicals in decreasing order is :

- (i) $\text{CH}_3 - \cdot \text{CH}_2$ (ii) $\text{CH}_3 - \cdot \text{CH} - \text{CH}_3$ (iii) $\text{CH}_3 - \overset{\cdot}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_3$ (iv) $\text{CH}_3 - \cdot$
 (A) iii > iv > i > ii (B) i > ii > iii > iv (C) iii > ii > iv > i (D) iii > ii > i > iv

B-3. Which of the following is the correct order of stability of free radicals?

- (A) benzyl > allyl > 2° > 1° (B) allyl > benzyl > 2° > 1°
 (C) allyl > 2° > 1° > benzyl (D) benzyl > 2° > 1° > allyl

Exercise-1

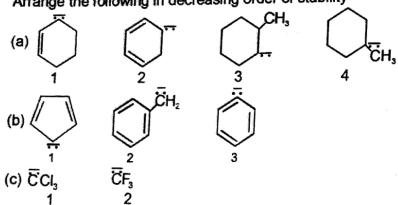
Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS**Section (A) : Carbanions**

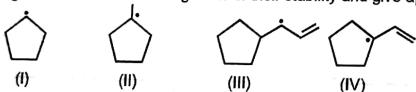
A-1. Arrange the following in decreasing order of stability.

(a)	$\text{CH}_2-\overset{\oplus}{\text{NO}_2}$ 1	$\text{CH}_2-\overset{\oplus}{\text{CHO}}$ 2	$\text{CH} \equiv \overset{\ominus}{\text{C}}$ 3
(b)	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\oplus}{\text{CH}_2}$ 1	$\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{CH}_2\text{CH}_3$ 2	$(\text{CH}_3)_2\overset{\oplus}{\text{C}}-\text{CH}_2\text{CH}_3$ 3

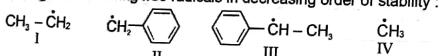
A-2. Arrange the following in decreasing order of stability

**Section (B) : Carbon free radicals**

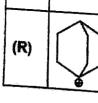
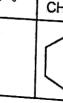
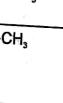
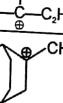
B-1. Rank the following free radicals in increasing order of their stability and give appropriate reasons.



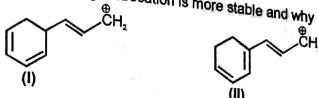
B-2. Arrange the following free radicals in decreasing order of stability :

**Section (C) : Carbocations**

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

	(I)	(II)	(III)	(IV)
(P)	$\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{C}}\text{H}_2$	$\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{CH}_2$ F	$\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{CH}_2$ Br	$\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{CH}_2$ Cl
(Q)	$\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{C}_2\text{H}_5$	$\text{CH}_3-\overset{\oplus}{\text{C}}(\text{CH}_3)_2-\text{CH}_3$	$\text{Ph}-\overset{\oplus}{\text{C}}(\text{CH}_3)_2-\text{C}_2\text{H}_5$	$\text{Ph}-\overset{\oplus}{\text{C}}(\text{CH}_3)_2-\text{C}_2\text{H}_5$
(R)				

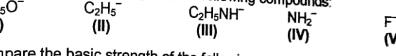
C-2. Which of the following carbocation is more stable and why ?

C-3. 
(I) 1,2-Me shift → (P)
(II) 1,2-Bond shift → (Q)

Draw the structures of P and Q.

Section (D) : Basic strength

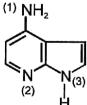
D-1. Compare the basic strength of the following compounds:



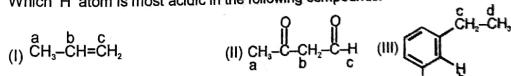
D-2. Compare the basic strength of the following compounds :

(a)	PhNH ₂	Ph ₂ NH	Ph ₃ N
(b)			
(c)	CH ₃ -CH-NH ₂ Ph	CH ₃ -CH ₂ -NH ₂ Ph	Ph-CH ₂ -CH ₂ -NH ₂

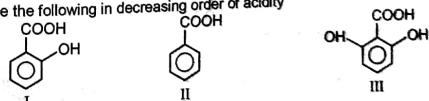
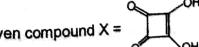
D-3. Which of the following group is most basic in the given compounds :

D-4. Which of the following is a stronger base ? Give reason to justify your answer.
CH₂=CH-NH₂ CH₂=N-CH₃
I II**Section (E) : Acidic strength**

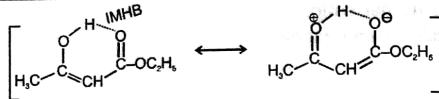
E-1. Which 'H' atom is most acidic in the following compounds.



E-2. Arrange the following in decreasing order of acidity

E-3. The given compound X =  is a strong acid. Justify this statement.

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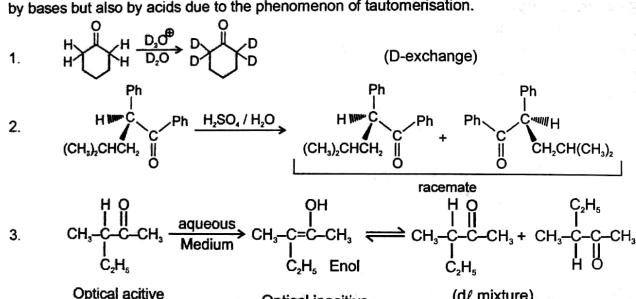
(d) If active methylene group is more acidic then enol content will be more.

For example in acetyl acetone ($\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{CH}_3$) enolic content is 75–76% while it is 7–8% in acetoacetic ester because ester group shows less electron withdrawing nature than keto group.

(b) Percentage of enol content is more in non-polar media while % of keto form is more in polar media.

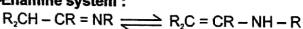
(e) Percentage of enol content is more in hibiscus.

Racemisation and D-exchange : Exchange of α -hydrogen from deuterium as well as racemization at the α -carbon are catalyzed not only by acids but also by bases.



Th12. Other examples of tautomers (not to be done in class only for the reference of students)

(a) Imine-Enamine system :

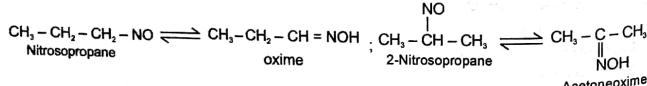


Imine Enamine

Among these two tautomers, enamines are stable only when there is no hydrogen on the nitrogen, otherwise the imine form predominates.

(b) Nitroso-oxime system:

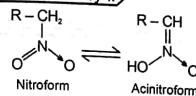
Like primary and secondary nitro compounds, primary and secondary nitroso compounds also exhibit tautomerism with their more stable isonitroso or oxime form.



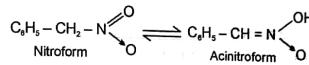
(c) Nitro-Acinitro system:

The acidic nature of the nitro compounds gives rise to the belief that the nitro compounds exist in two forms, a more stable or normal nitro form and the less stable acinotro form.

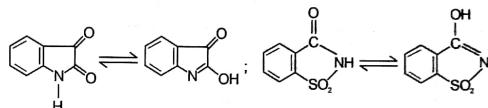
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The stability of the nitro form is more as compared to the acinitro form because it is stabilised by resonance.

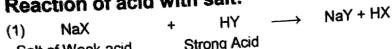


(d) Lactam-Lactim system :



CHECK LIST

Definitions (D)		Theories (Th)	
D1:	Carbanion	<input type="checkbox"/>	
D2:	Free radicals	<input type="checkbox"/>	
D3:	Carbocation	<input type="checkbox"/>	
D4:	Carbenes (Divalent carbon intermediates)	<input type="checkbox"/>	
D5:	Nitrenes	<input type="checkbox"/>	
D6:	Benzyn	<input type="checkbox"/>	
D7:	Arrhenius base	<input type="checkbox"/>	
D8:	Bronsted base	<input type="checkbox"/>	
D9:	Lewis definition of acids and bases	<input type="checkbox"/>	
D10:	Arrhenius acid	<input type="checkbox"/>	
D11:	Bronsted acid	<input type="checkbox"/>	
D12:	Lewis definition of acids and bases	<input type="checkbox"/>	
D13:	Ortho effect	<input type="checkbox"/>	
D14:	Tautomerism	<input type="checkbox"/>	
Th1:	Reaction intermediates		
Th2:	Bases		
Th3:	Basic strength of aromatic amines and substituted anilines		
Th4:	Solvent effect in bases		
Th5:	Reactions of bases		
Th6:	Acids		
Th7:	Ortho effect		
Th8:	Reactions of acids with salts		
Th9:	Tautomerism		
Th10:	Keto-enol tautomerisation		
Th11:	Racemisation and D-exchange		
Th12:	Other examples of tautomers		

Section (F) : Feasible reactions of acids and bases**Th8. Reaction of acid with salt:**

Remark: A stronger acid displaces the weaker acid from weak acid metal salt. The weaker acid is released out as a gas or liquid or precipitates out as a solid. The weaker acid cannot displace the stronger acid from the salt.

1. $2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ No reaction
2. $\text{Na}_2\text{SO}_4 + 2\text{HCl} \rightarrow$ CH₃COONa + CH₃SO₃H → CH₃COOH + CH₃SO₃Na (feasible)
3. $\text{CH}_3\text{COONa} + \text{CH}_3\text{SO}_3\text{H} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{SO}_3\text{Na}$ (not feasible)
4. $\text{CH}_3\text{COONa} + \text{PhOH} \rightarrow \text{PhONa} + \text{CH}_3\text{COOH}$ (not feasible)

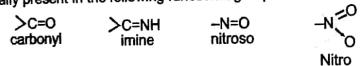
Section (G) : Tautomerism**Th9. Tautomerism****D14: Definition :**

Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen.

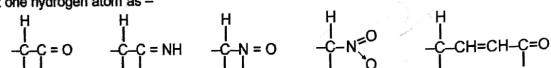
These two isomers remain in dynamic equilibrium and can be isolated also give different lab test.

Conditions :

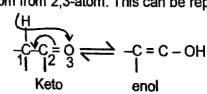
1. Usually present in the following functional groups



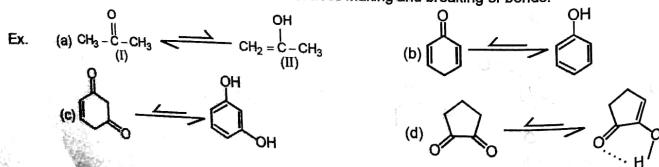
2. Basic need for its existence is attachment of these groups with the sp³ hybridised C-atom having atleast one hydrogen atom as –



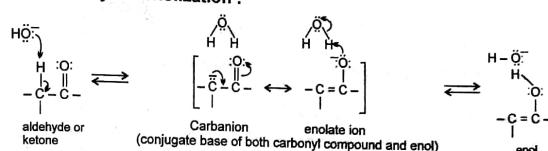
To get tautomer of above structures α-hydrogen atom is shifting to more electronegative atom attached to double bond (i.e. hydrogen atom from 1st atom to 3rd atom) and double bond is developed between 1,2-atom from 2,3-atom. This can be represented as:



These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds.



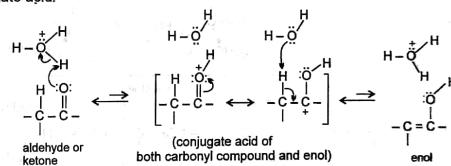
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Th10. Keto-enol tautomerisation :**10.1 (A) Base-catalyzed enolization :**

Protonation of the carbanion by water on the α-carbon gives back the carbonyl compound. Protonation on oxygen gives the enol. Notice that the enolate ion is the conjugate base of both the carbonyl compound and the enol.

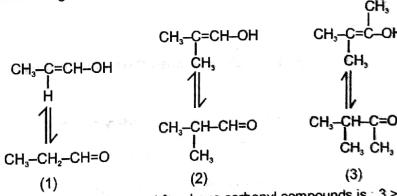
(B) Acid-catalyzed enolization :

Involves the conjugate acid of the carbonyl compound. Recall that this ion has carbocation characteristics. Loss of the proton from oxygen gives back the starting carbonyl compound; loss of the proton from the α-carbon gives the enol. Notice that an enol and its carbonyl isomer have the same conjugate acid.

**10.2 % Enol content in the carbonyl compounds :**

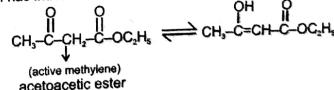
(a) For monocarbonyl % Enol is very less

(b) Enol content increases with increase in the stability of enol by resonance, hyperconjugation, hydrogen bonding etc.



Decreasing order of enol content for above carbonyl compounds is : 3 > 2 > 1.

(c) For a carbonyl compound having active methylene group percentage of enol content will be more because enolic form has intramolecular H-bonding and also it will be stabilised by resonance.



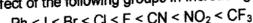
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- Ex.
- $\text{F}-\text{CH}_2-\text{COOH} > \text{Cl}-\text{CH}_2-\text{COOH} > \text{Br}-\text{CH}_2-\text{COOH} > \text{I}-\text{CH}_2-\text{COOH}$
 - $\text{Cl}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}-\text{COOH} > \text{Cl}-\overset{\text{Cl}}{\underset{\text{H}}{\text{CH}}}-\text{COOH} > \text{Cl}-\text{CH}_2-\text{COOH} > \text{CH}_3-\text{COOH}$
 - $\text{HOOC} > \text{CH}_3\text{COOH} > \text{CH}_3-\text{CH}_2-\text{COOH}$
 - $\text{COOH} > \overset{\text{COOH}}{\underset{\text{COOH}}{\text{CH}_2}} > \overset{\text{COOH}}{\underset{\text{COOH}}{\text{CH}_2}}-\text{COOH} > \text{CH}_2-\text{COOH}$

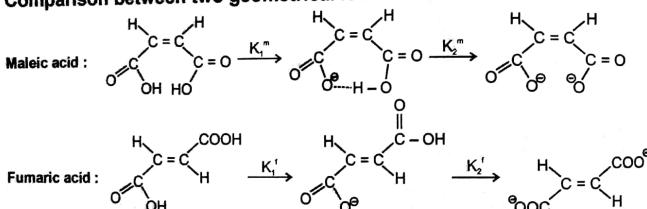
The effect of the following groups in increasing acidity order is

[Ref. NCERT]



Thus, the following acids are arranged in order of decreasing acidity (based on K_a values) :
 $\text{CF}_3\text{COOH} > \text{CCl}_2\text{COOH} > \text{CHCl}_2\text{COOH} > \text{NO}_2\text{CH}_2\text{COOH} > \text{NC}-\text{CH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CICH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{HCOOH} > \text{ClCH}_2\text{CH}_2\text{COOH} > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{CH}_2\text{CH}_2\text{COOH}$

6.4 Comparison between two geometrical isomers :



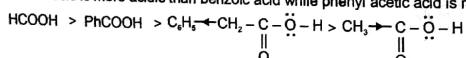
Now $K_m^m > K_f^f$

Since the conjugate base is stabilised by intramolecular H bonding.

But $K_f^f > K_m^m$ Since in maleate ion, after donation of H^\oplus two $-\text{COO}^\ominus$ groups faces each other and makes system unstable. In fumarate ion this repulsion is minimised.

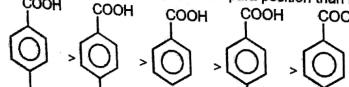
6.5 Acidic strength of substituted benzoic acids :

Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

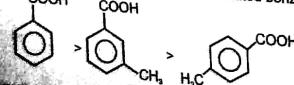


Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

If electron donating group present at para position than it is always less acidic than benzoic acid.



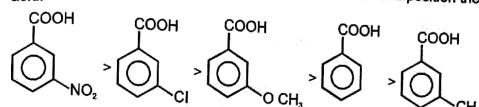
Also it is less acidic than meta substituted benzoic acid.



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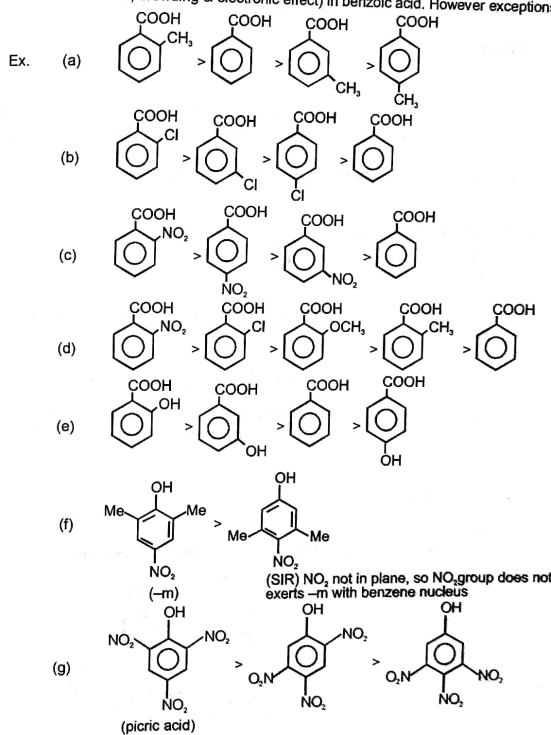
General Organic Chemistry-II

On the other hand if e^- withdrawing group is present at meta position then it is more acidic than benzoic acid.



Th7. Ortho effect :

D13. It is common observation that generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acids itself. This is called ortho effect (which is combined effect of steric hindrance, crowding & electronic effect) in benzoic acid. However exceptions are seen.



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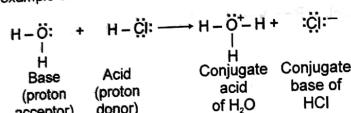
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Section (E) : Acidic strength

Th6. Acids

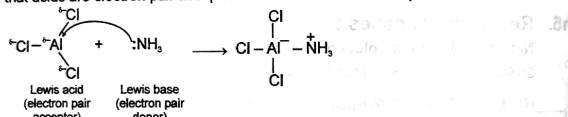
- D10: (a) Arrhenius acid: An acid is a substance that can donate (or loose) a proton in H_2O .
 D11: (b) The Brønsted Lowry definition of acids and bases:
 An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.
 Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :



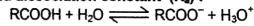
Hydrogen chloride, a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are a hydronium ion (H_3O^+) and a chloride ion (Cl^-). The molecule or ion that forms when an acid loses its proton is called the conjugate base of that acid. (The chloride ion is the conjugate base of HCl). The molecule or ion that is formed when a base accepts a proton is called the conjugate acid of that base.

- D12: (c) The Lewis definition of acids and bases

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.



(d) Acid dissociation constant (K_a):



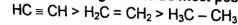
$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]}$$

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

$$pK_a = -\log K_a$$

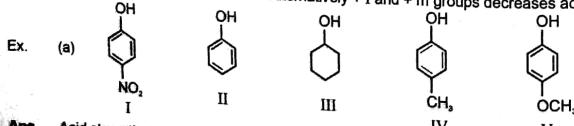
6.1 Relative acidity of hydrocarbons :

Being most electronegative the sp hybridised carbon atom of ethyne polarizes its C-H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hydrocarbon.



6.2 Acidity of phenols :

The phenoxide ion is more stabilised by resonance than the unionised phenol. Groups which are $-I$, $-m$ increases acidic character of phenol because effectively dispersing the negative charge of phenoxide ion. Alternatively $+I$ and $+m$ groups decreases acid strength.



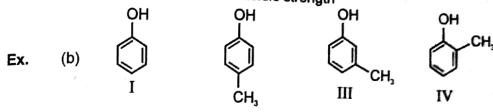
Ans. Acid strength order : I > II > IV > V > III

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ADVOCATE

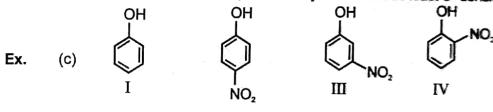
General Organic Chemistry-II

- Sol. Step-1. III will be least acidic as it has no dispersion of negative charge (No delocalisation of negative charge).
 Step-2. Since $-I$, $-m$ group will increase acid strength, Nitrophenol will be most acidic followed by Step-3. Amongst cresol and methoxyphenol, methoxyphenol has $+M$ effect of $-OCH_3$ which increases e^- density hence decrease acidic strength



Ans. Acid strength order: I > III > II > IV

- Sol. Step-1: Notice that CH_3 have $+I$ effect so all methylphenols (cresols) are less acidic than phenol (I). Step-2: Now amongst cresols p - and o - CH_3 are increasing the e^- density due to their hyper conjugation but ortho isomer has viable $+I$ effect also, which will help in destabilising phenoxide ion therefore o - is least acidic. Since at meta position only $+I$ works it as least e^- density amongst the cresol.



Ans. Acid strength order: II > IV > III > I

- Sol. Step-1 : In nitrophenols $-I$ effect of NO_2 will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols
 Step-2 : Only $-I$ effect is applicable in meta nitrophenol it will be number three. Now $-o$, $-p$ have both $-I$ and $-m$ effect of NO_2 group over OH and in this particular case para isomer is more acidic than ortho since

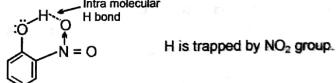


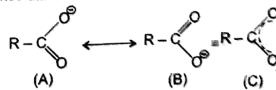
Table : pK_a values of some phenols and Ethanol. (Ref. NCERT)

Compound	Formula	pK_a	Compound	Formula	pK_a
o-Nitrophenol	$o-O_2N-C_6H_4-OH$	7.2	o-Cresol	$o-CH_3-C_6H_4-OH$	10.2
m-Nitrophenol	$m-O_2N-C_6H_4-OH$	8.3	m-Cresol	$m-CH_3-C_6H_4-OH$	10.1
p-Nitrophenol	$p-O_2N-C_6H_4-OH$	7.1	p-Cresol	$p-CH_3-C_6H_4-OH$	10.2
Phenol	C_6H_5-OH	10	Ethanol	C_2H_5OH	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

6.3 Acidity of carboxylic acids :

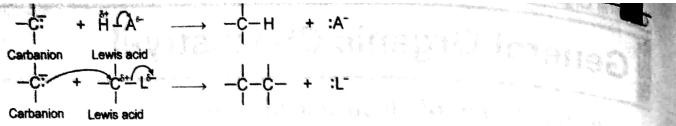
Conjugate base of carboxylic acid exists as two equivalent canonical structures (A) and (B). This ion is resonance stabilised and resonance hybrid structure is (C).



Electron withdrawing group ($-M$, $-I$ effect) increases acidic nature.

Electron releasing group ($+M$, $+I$ effect) decreases acidic nature.

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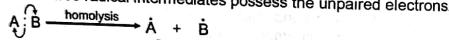
Examples of stability order:

- x. (a) CH_3 , $\text{CH}_3\text{-CH}_2$, $\text{CH}_3\text{-CH}_2\text{-CH}_3$, $\text{CH}_3\text{-}\overset{\ominus}{\text{C}}\text{-CH}_3$ (Stability order: 1>2>3>4)
- (b) $\text{CH}=\text{C}^{\ddagger}$, $\text{CH}_2=\overset{\ddagger}{\text{CH}}$, $\text{CH}_3=\overset{\ddagger}{\text{CH}}_2$ (Stability order: 1>2>3)
- (c) 1, 2, 3 (Stability order: 1>2>3)
- (d) $\text{CH}_2=\text{CH}-\overset{\ominus}{\text{CH}}_2$, $\text{C}_6\text{H}_5-\overset{\ominus}{\text{CH}}_2$, $(\text{C}_6\text{H}_5)_3\overset{\ominus}{\text{C}}$ (Stability order: 1<2<3)

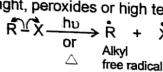
Rearrangement: Generally carbanions do not undergo rearrangement.

Section (B) : Carbon free radicals

Q2: **Free radical:** An uncharged intermediate which has three bond pair and an unpaired electron on carbon.
Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.



It is generated in presence of sun light, peroxides or high temperature



Note: (i) It is neutral species with odd e^- .
(ii) It is paramagnetic in nature due to odd e^- .
(iii) Rearrangement is not observed generally.
(iv) Carbon atom having odd electron is in sp^3 hybridised state.
(v) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

Stability of free radical: It is stabilised by resonance, hyperconjugation and +I groups.

- (a) $(\text{H}_3\text{C})_3\overset{\cdot}{\text{C}} > \text{H}_3\text{C}-\overset{\cdot}{\text{CH}}-\text{CH}_3 > \text{H}_3\text{C}-\overset{\cdot}{\text{CH}}_2 > \overset{\cdot}{\text{CH}}_3$ (Stability order)
(b) $\overset{\cdot}{\text{CH}}_3 < \text{CH}_3-\overset{\cdot}{\text{CH}}_2 < \text{CH}_3-\overset{\cdot}{\text{CH}}-\text{CH}_3 < \text{CH}_3-\overset{\cdot}{\text{C}}-\text{CH}_3$ (Stability order)
(c) $\text{CH}_3-\overset{\cdot}{\text{CH}}_2 > \text{CH}_3-\text{CH}_2-\overset{\cdot}{\text{CH}}_2 > \begin{matrix} \text{CH}_3 \\ | \\ \text{CH}_3-\text{CH}-\overset{\cdot}{\text{CH}}_2 \end{matrix} > \begin{matrix} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\overset{\cdot}{\text{CH}}_2 \end{matrix}$ (Stability order)
(Due to resultant of inductive effect and hyperconjugation, both operates in same direction)
(d) $(\text{C}_6\text{H}_5)_3\overset{\cdot}{\text{C}} > (\text{C}_6\text{H}_5)_2\overset{\cdot}{\text{CH}} > \text{C}_6\text{H}_5-\overset{\cdot}{\text{CH}}_2 > \text{CH}_2=\text{CH}-\overset{\cdot}{\text{C}}-\text{CH}_3$ (Stability order)

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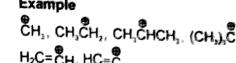
Section (C) : Carbocations

D3: A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation.
Hybridisation: Carbocation may be sp^2 or sp hybridized.

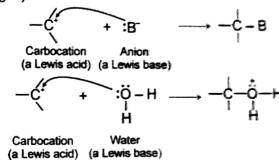
Hybridisation

sp^2
 sp

Example



Carbocations are electron deficient. They have only six electrons in their valence shell, and because of this, carbocations act as Lewis acids. Most of the carbocations are short-lived and highly reactive, they occur as intermediates in some organic reactions. Carbocations react with Lewis bases or ions that can donate the electron pair that they need to achieve a stable octet of electrons (i.e., the electronic configuration of a noble gas):

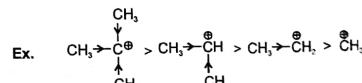
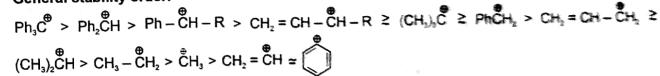


Because carbocations are electron seeking reagents, chemists call them electrophiles. All Lewis acids, including protons, are electrophiles. By accepting an electron pair, a proton achieves the valence shell configuration of helium; carbocations achieve the valence shell configuration of Neon.

Stability: Carbocations are stabilised by

- (i) +M effect (ii) Delocalisation of charge (iii) Hyperconjugation (iv) +I effect

General stability order:



t-Butyl carbocation has +I effect of three Me-groups and also Hyperconjugation effect which makes it most stable.



In Benzyl cation, extensive resonance is seen which stabilises C^+ .

In Ethyl carbocation +I and hyperconjugation of Me-group stabilizes carbocation.
In vinyl carbocation stability decreases rapidly since carbon of $(\text{CH}_2)=\overset{\oplus}{\text{CH}}$ is sp^2 hybridized which is slightly more electronegative hence acts as -I group which increases (+) charge density.

