

CHAPTER - 09

**ORGANIC CHEMISTRY - SOME BASIC PRINCIPLES
AND TECHNIQUES - PART II**

FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

SYNOPSIS

I. Electronic displacements in a covalent bond

(i) Inductive effect : The permanent displacement of electrons forming a covalent bond towards the more electronegative element or group is called inductive or I-effect or transmission effect. This effect is always transmitted along a chain of carbon atoms. The intensity of the effect decreases as the distance from the source increases.

The phenomenon of inductive effect is very important in organic chemistry as it is helpful in explaining the acidity of carboxylic acids, strength of bases dipole moments of alkyl halides etc.

(ii) Electromeric effect

It is a temporary effect. Organic compounds having a multiple bond show this effect in presence of the attacking reagent only . It is represented by 'E'

(iii) Resonance effect : Resonance effect is defined as the polarity produced in the molecule by the interaction of two π bonds, or between a π bond and lone pair of electrons present on an adjacent atom. The resonance effect (R. effect) may be +R or -R. It is +R when the transference of electron pair is away from the atom and -R, when the transference of electron pair is towards the atom

Some common atoms or groups which cause +R or -R effects are given below +R groups -Cl, -Br, -I, -NH₂, -OH, -OR, -R group -NO₂, -CHO, -C \equiv N

iv) Hyper conjugation : When (C-H) σ electrons are in conjugation to π bond, this conjugation is known as σ - π conjugation or hyperconjugation. Resonating structures due to hyperconjugation may be written involving 'no bond' between alpha carbon and hydrogen, atoms. From this point of view hyperconjugation may be regarded as 'no bond resonance'. Hyper conjugation is of three types

a) σ (C-H) π conjugation in alkenes

b) σ (C-H) positive charge conjugation in alkyl carbocations

c) $\sigma(C-H)$ odd electron conjugation in free radicals. Hyper conjugation is useful in explaining some of the physical and chemical properties of organic molecules. Some of these are

- a) Stability of alkenes
- b) C = C bond length in alkenes
- c) heat of hydrogenation of alkenes
- d) Stability of alkyl carbocations
- e) Stability of alkyl free radicals
- f) Electron releasing power of 'R' in alkyl benzene
- g) dipole moment
- h) directive influence of alkyl groups

II. Reaction intermediates by fission of a covalent bond

Heterolytic and homolytic bond fission results in the formation of short lived fragments called reaction intermediates

i) Carbonium ions (carbocations)

Organic ions which contain a positively charged carbon atom are called carbonium ions. The stability of carbonium ion is influenced by both resonance and inductive effects. For example allyl and benzyl carbonium ions are more stable than propyl carbonium ion by resonance. Electron releasing groups stabilize a carbonium ion, whereas electron withdrawing groups will make a carbonium ion less stable

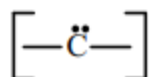
ii) Carban ions

Organic ions which contain a negatively charged carbon atom are called carban ions. They are formed by heterolytic fission. Groups having +I effect decrease the stability while groups having -I effect increase the stability of carban ions

Allyl and benzyl carban ions are stabilized by resonance. Groups like $-NO_2$, $-CN$, (electron attracting) increase the stability of carban ions.

iii) Free radicals : An atom or group of atoms carrying an odd or unpaired electron is called a free radical. They are formed by homolysis of covalent bonds either by heat or light. The order of stability of free radicals is the same as that of carbonium ions i.e. $ter > sec > pr$. This order of stability can be explained on the basis of hyperconjugation effect of alkyl groups. Allyl and benzyl free radicals are more stable than alkyl radicals due to resonance

iv) Carbenes : Carbenes are neutral divalent highly reactive carbon intermediates represented by



carbenes are neutral electrophiles. Substituted carbenes are named as derivatives of carbenes

e.g. dichlorocarbene $\text{Cl}-\ddot{\text{C}}-\text{Cl}$

v) Nitrenes : Nitrenes are defined as the electron deficient species in which nitrogen has a sextet of electrons. They act as strong electrophiles alkyl and acyl nitrenes may be prepared by the photolysis of alkyl azides or acyl azides respectively.

III. Common types of organic reactions

i) Substitution reactions

Reactions which involve the replacement of one atom or group by other atoms or groups are known as substitution reactions. These reactions may be initiated by electrophiles, nucleophiles or free radicals.

Electrophiles are electron deficient. They may be positive ions or neutral molecules with electron deficient centres. e.g. H^+ , Cl^+ , N^+O_2 , BF_3 , etc.

Nucleophiles are electron rich. They may be negative ions or neutral molecules with free electron pairs

e.g. $\bar{\text{O}}\text{H}^-$, $\bar{\text{C}}\text{N}^-$, Cl^- , $\dot{\text{N}}\text{H}_3$, $\text{R}-\ddot{\text{N}}\text{H}_2$ etc.

a) Electrophilic substitution reactions (SE). When a substitution reaction involves the attack by an electrophile, the reaction is referred to as electrophilic substitution. e.g. nitration of benzene

b) Nucleophilic substitution (SN)

When a substitution reaction involves attack by a nucleophile the reaction is referred to as nucleophilic substitution

e.g. Hydrolysis of alkyl halides by aqueous NaOH

SN reactions are classified as $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$

c) Free radical substitution. These reactions are initiated by free radicals

e.g. Chlorination of methane in presence of light

ii) Addition reactions

Addition reactions are those in which atoms or groups of atoms are added to a double bond or triple bond. These reactions may be initiated by electrophiles nucleophiles or free radicals

a) Electrophilic addition (initial attack is by an electrophile)

e.g. addition of hydrogen halides to alkenes

b) Nucleophilic addition (initial attack is by a nucleophile)

e.g. formation of cyanohydrin from aldehydes and ketones

c) Free radical addition

e.g. addition of HBr to propene in presence of peroxides

iii) Eliminations reactions

Elimination reactions are those which involve the removal of atoms or groups of atoms from two adjacent atoms in the substrate molecule to form a multiple bond. In these reactions a new π bond is formed

a) E^2 reaction (Elimination bimolecular)

In E^2 reaction product formation takes place by formation of transition state

b) E^1 reaction (Elimination unimolecular)

In E^1 reaction product formation takes place by formation of a carbocation as reaction intermediate

iv) Rearrangement reactions

Rearrangement reactions involve the migration of an atom or group of atoms from one site to another within the same molecule

IV. Directive influence of substituents and their effect on reactivity in benzene ring

A substituent which activates the aromatic ring to further substitution is called an activating group

A substituent which deactivates the ring to further substitution is called a deactivating group

All ortho, para directors are ring activating groups. However it has been observed that halogens although ortho, para directors are ring deactivators

All metadirectors are ring deactivating groups

PART-I (JEE MAIN)

SECTION-I- Straight objective type questions

- The C—C bond length in benzene lies between single and double bond due to
1) Resonance 2) Tautomerism 3) Hyperconjugation 4) Inductive effect
- The C—C single bond length in propene is less than 1.54 \AA . This shrinkage is due to
1) Resonance 2) Hyperconjugation 3) Inductive effect 4) Electromeric effect
- Which of the following is not a set of nucleophiles?
1) BF_3 , $\text{CH}_3\text{-I}$, CH_3CHO
2) NH_3 , R_2NH , $\text{C}_2\text{H}_5\text{O}^-$
3) CH_3O^- , I^- , $\text{C}_2\text{H}_5\text{OH}$
4) $\text{CH}_3\text{CH}=\text{CHCH}_3$, $\text{CH}_3\text{C}\equiv\text{C-CH}_3$, C_6H_6

4. Assertion : RNH_2 is a better nucleophile than ROH

Reason : Nitrogen is less electronegative than oxygen.

Choose the correct option:

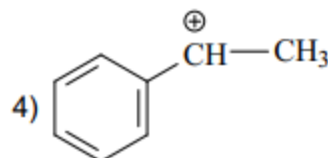
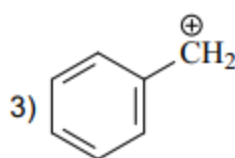
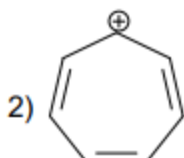
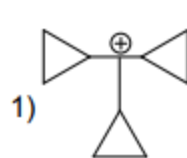
- 1) Both assertion and reason are true and the reason is the correct explanation of the assertion.
- 2) Both assertion and reason are true but reason is not the correct explanation of the assertion.
- 3) Assertion is true but reason is false.
- 4) Assertion is false but reason is true.

5. Statement-I : Tert-butyl cation and tert-butyl free radical, respectively, are more stable than isopropyl cation and isopropyl free radical.

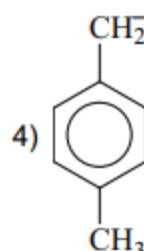
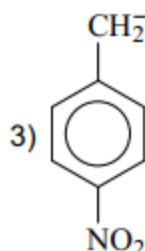
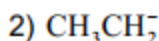
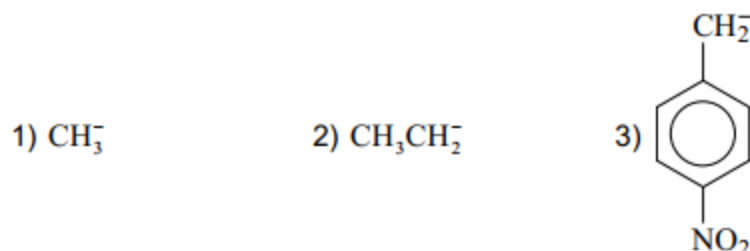
Statement-II : The anion $(\text{CH}_3)_3\text{C}^-$ is more stable than the anion $(\text{CH}_3)_2\text{CH}^-$

Choose the correct option:

- 1) Both statement-I and statement-II are true
 - 2) Both statement-I and statement-II are false
 - 3) Statement-I is true but statement-II is false
 - 4) Statement-I is false but statement-II is true
6. Which among the following is the least stable carbocation?



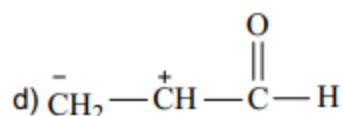
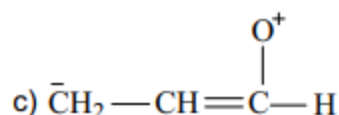
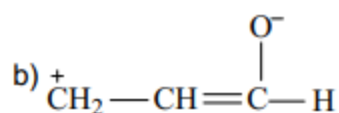
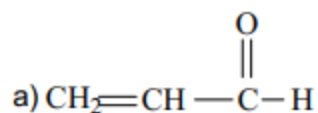
7. The most stable carbanion among the following is



8. The correct order of acid strength of the following compounds is

- 1) $\text{CH}_3 - \text{COOH} > \text{C}_6\text{H}_5\text{OH} > \text{CH}_3\text{CH}_2\text{OH} > \text{H}_2\text{O} > \text{CH}_3\text{C} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$
- 2) $\text{C}_6\text{H}_5\text{OH} > \text{CH}_3 - \text{COOH} > \text{CH}_3\text{CH}_2\text{OH} > \text{H}_2\text{O} > \text{CH}_3\text{C} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$
- 3) $\text{C}_6\text{H}_5\text{OH} > \text{CH}_3 - \text{COOH} > \text{H}_2\text{O} > \text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3 - \text{CH}_3 > \text{CH}_2 = \text{CH}_2 > \text{CH}_3\text{C} \equiv \text{CH}$
- 4) $\text{CH}_3 - \text{COOH} > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{C} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$

9. Arrange the following resonance structures in the correct order of stability



1) $a > b > d > c$

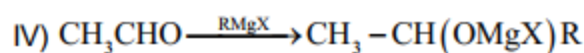
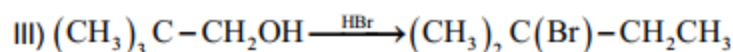
2) $a > b > c > d$

3) $b > a > d > c$

4) $b > a > c > d$

10. Match List-I with List-II

List-I (Reaction)



A) I \rightarrow Q; II \rightarrow R; III \rightarrow S; IV \rightarrow P

B) I \rightarrow S; II \rightarrow R; III \rightarrow S; IV \rightarrow R

C) I \rightarrow Q; II \rightarrow R; III \rightarrow RS; IV \rightarrow P

D) I \rightarrow S; II \rightarrow P; III \rightarrow S; IV \rightarrow R

List-II (Type)

P) Addition reaction

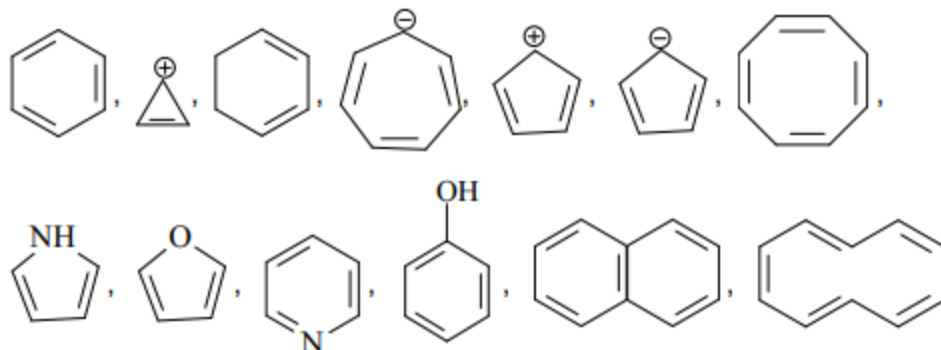
Q) Elimination reaction

R) Substitution reaction

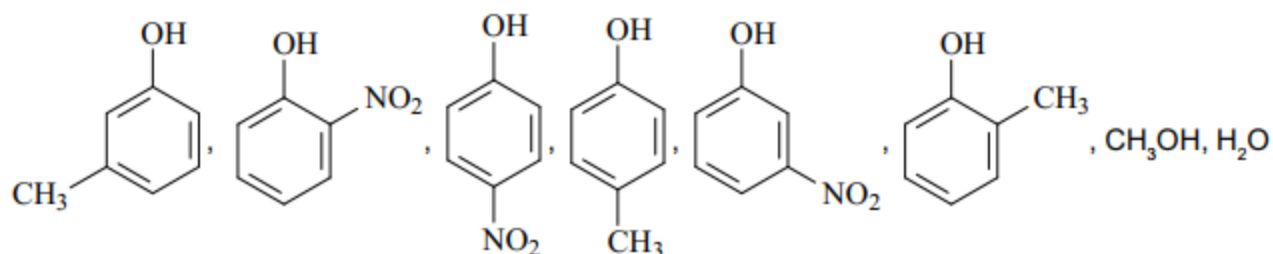
S) Rearrangement reaction

SECTION-II - Numerical Type Questions

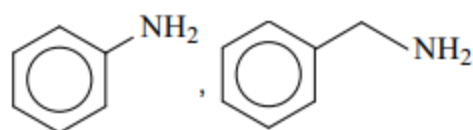
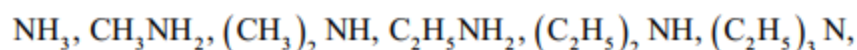
11. The total number of aromatic species among the following is



12. How many of the following compounds is/are more acidic than phenol?



13. How many of the following is/are less basic than trimethylamine?



14. How many of the following statements is/are correct?

1) Amides (RCONH_2) are less nucleophilic than amines (RNH_2)

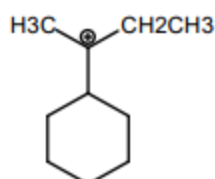
2) Aldehydes are more electrophilic than ketones

3) The order of leaving group ability is $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

4) The order of $-\text{I}$ effect is $-\text{I} < -\text{Br} < -\text{Cl} < -\text{F}$

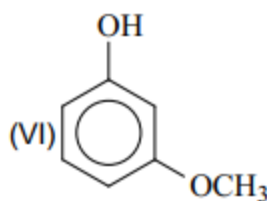
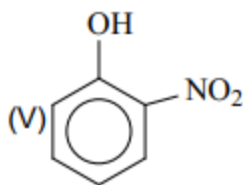
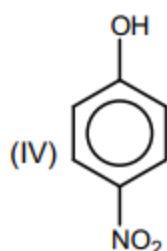
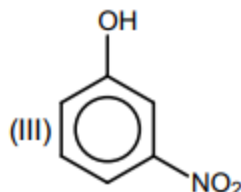
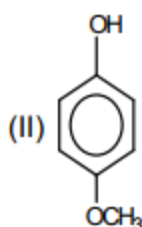
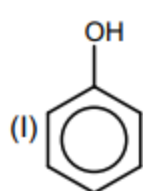
5) Both allyl carbocation and phenyl cation are resonance stabilised

15. The total number of contributing structures showing hyperconjugation (involving $\text{C}-\text{H}$ bonds) for the following carbocation is



PART-II (JEE ADVANCED)**Section-III - Only one option correct type**

16. The correct order of acidity of the following compounds is



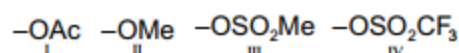
A) IV > V > III > I > VI > II

B) V > IV > III > I > VI > II

C) V > IV > III > VI > I > II

D) IV > V > III > VI > I > II

17. In the following groups:



the order of leaving group ability is

A) I > II > III > IV

B) IV > III > I > II

C) III > II > I > IV

D) II > III > IV > I

18. Which of the following has the most acidic hydrogen?

A) 3-Hexanone

B) Hexane-2,4-dione

C) Hexane-2,5-dione

D) Hexane-2,3-dione

19. Which of the following acids has the smallest dissociation constant?

A) $\text{CH}_3\text{CHF}\text{COOH}$

B) $\text{FCH}_2\text{CH}_2\text{COOH}$

C) $\text{BrCH}_2\text{CH}_2\text{COOH}$

D) $\text{CH}_3\text{CHBr}\text{COOH}$

20. What is the decreasing order of strength of the bases OH^- , NH_2^- , $\text{HC} \equiv \text{C}^-$ and CH_3CH_2^- ?

A) $\text{CH}_3 - \text{CH}_2^- > \text{NH}_2^- > \text{H} - \text{C} \equiv \text{C}^- > \text{OH}^-$

B) $\text{CH}_3 - \text{CH}_2^- > \text{H} - \text{C} \equiv \text{C}^- > \text{NH}_2^- > \text{OH}^-$

C) $\text{OH}^- > \text{NH}_2^- > \text{H} - \text{C} \equiv \text{C}^- > \text{CH}_3 - \text{CH}_2^-$

D) $\text{CH}_3 - \text{CH}_2^- > \text{NH}_2^- > \text{OH}^- > \text{H} - \text{C} \equiv \text{C}^-$

21. The bond length between $C_2 - C_3$ carbons in buta-1,3-diene is

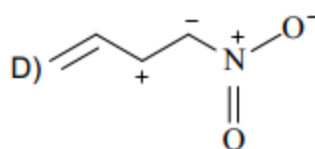
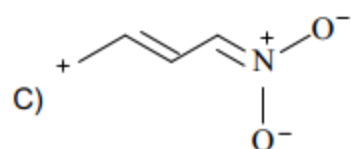
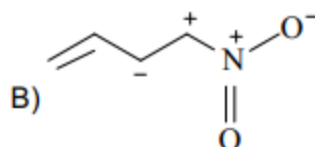
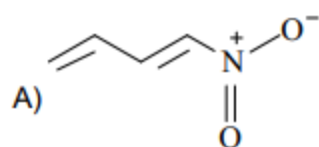
A) between 1.20 \AA and 1.34 \AA

B) less than 1.34 \AA

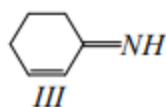
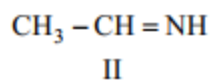
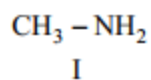
C) greater than 1.54 \AA

D) between 1.34 \AA and 1.54 \AA

22. Which of the following is an incorrect resonance structure?



23. Increasing order of bond length between carbon and nitrogen is



A) $\text{II} < \text{III} < \text{I}$

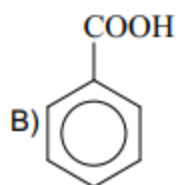
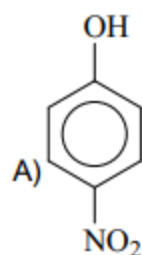
B) $\text{I} < \text{II} < \text{III}$

C) $\text{III} < \text{II} < \text{I}$

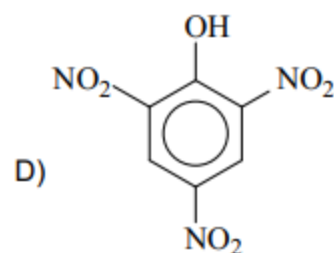
D) $\text{II} < \text{I} < \text{III}$

Section IV - One or more option correct type

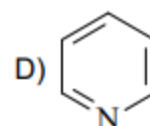
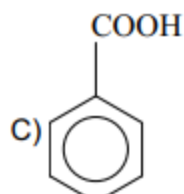
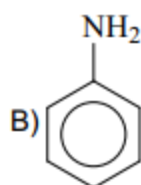
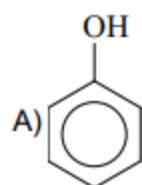
24. The compound(s) that can liberate CO_2 in the reaction with NaHCO_3 is/are



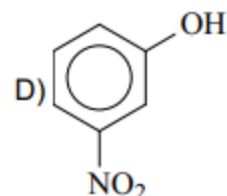
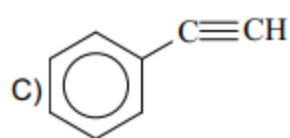
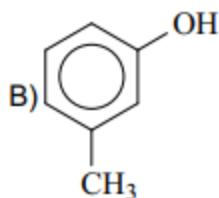
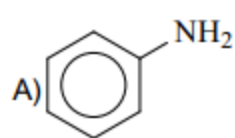
C) $\text{CH}_3 - \text{COOH}$



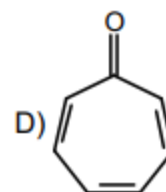
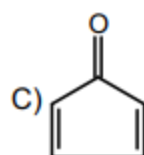
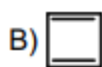
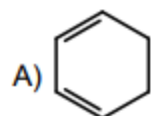
25. The compound(s) that dissolve in dilute HCl is/are

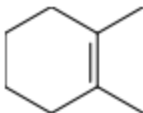


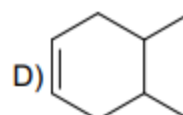
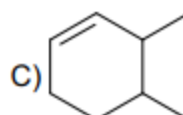
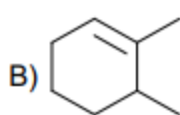
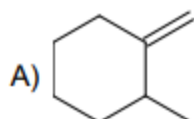
26. The compound(s) that can be deprotonated with NaOH is/are



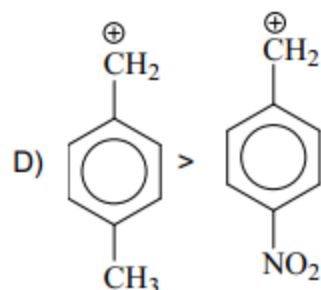
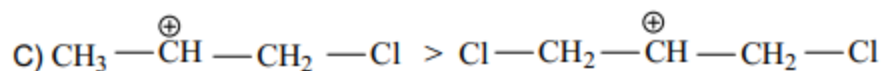
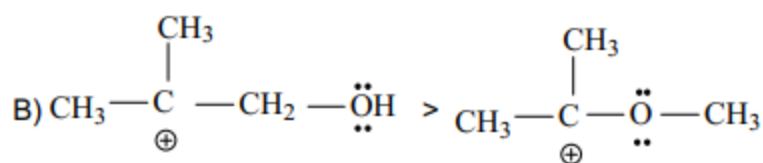
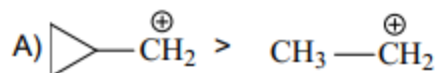
27. Which of the following molecules, in pure form, is (are) unstable at room temperature?



28. Heat of hydrogenation of  is less than that of

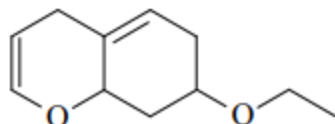


29. Which of the following stability order of carbocations is/are correct?



Section V - Numerical type questions

30. On treatment of the following compound with a strong acid, the total number of carbon-oxygen bond(s) that can give rise to allylic carbocation after bond cleavage is (Do not consider rearrangement)



31. The total number of polar compound(s) among the following is



32. The total number of atoms present in one plane in the cyclopentadienyl anion is
 33. The total number of carbon atoms arranged linearly in pent-2-yne is
 34. The difference between the number of resonance structures of aniline and anilinium ion is

Section-VI - Matrix match type

35. **Column-I (compounds)**

- I) Naphthalene
 II) Furan
 III) Cyclopropenyl cation
 IV) Cyclooctatetraene

Column-II (no of π electrons)

- P) 10
 Q) 6
 R) 4
 S) 2
 T) 8

A) I \rightarrow P, II \rightarrow Q; III \rightarrow S; IV \rightarrow T

B) I \rightarrow Q, II \rightarrow R; III \rightarrow R; IV \rightarrow T

C) I \rightarrow P, II \rightarrow T; III \rightarrow S; IV \rightarrow P

D) I \rightarrow Q, II \rightarrow R; III \rightarrow S; IV \rightarrow T