Structural Isomerism

Introduction :

Berzelius introduced the term Isomer (Gr. Isos=Same, Mers = parts). Chemical compounds that have identical chemical formulae but differ in properties and t he arrangement of atoms in the molecule are called **isomers**. This phenomenon is known as Isomerism. Isomers exhibit different physical and chemical properties.

Example: n butyl alcohol and diethyl ether, both have the same formula $\mathbf{C_4H_{10}O}$. Only butyl alcohol releases $\mathbf{H_2}$ with Na metal, but not ether. Such compounds are isomers.

There are two main types of Isomerism.

Types of Isomerism

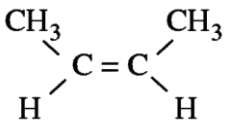
(i) Structural or Constitutional Isomerism; **(ii) Stereo Isomerism or Space Isomerism:**

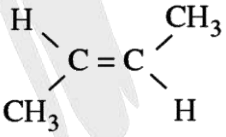
(i) Structural or Constitutional Isomerism; (It is due to difference in the arrangement of atoms within the molecule.)

Example: Ethanol $\mathbf{CH_3CH_2OH}$ and dimethyl ether $\mathbf{CH_3OCH_3}$ have different connectivities inspite of having the same formula $\mathbf{C_2H_6O}$.

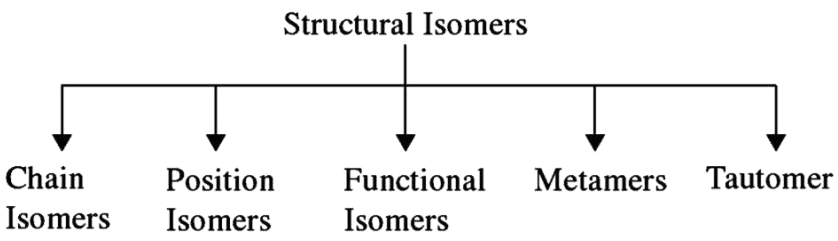
(ii) Stereo Isomerism or Space Isomerism: (It is due to different spatial arrangement of some atoms and groups.)

Example: But-2-ene also exists in two forms, differing in the arrangement of atoms and groups around doubly-bonded carbons.



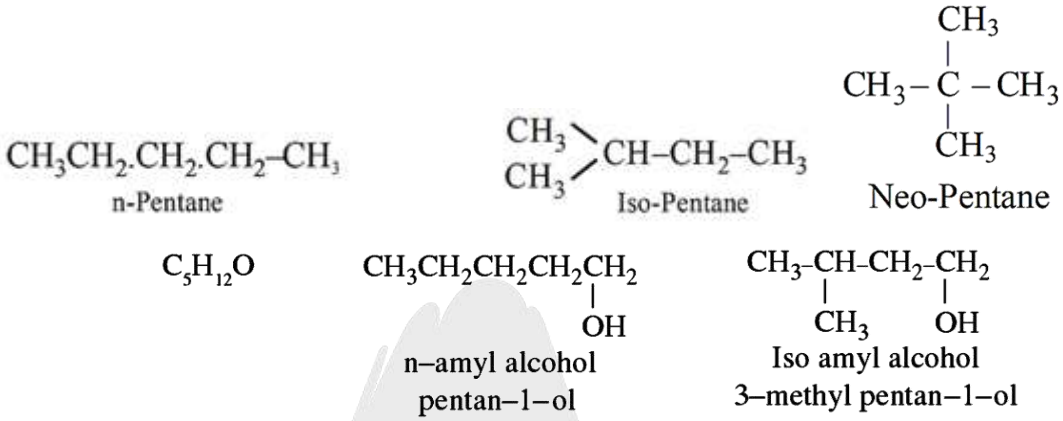


Types of Structural Isomerism :



(i) Chain Isomerism : Chain isomers have different carbon skeletons. Particularly, they have different parent chains. Among chain isomers, possessing a functional group, the functional group present in them is same and the position of it in their parent chains also is same.

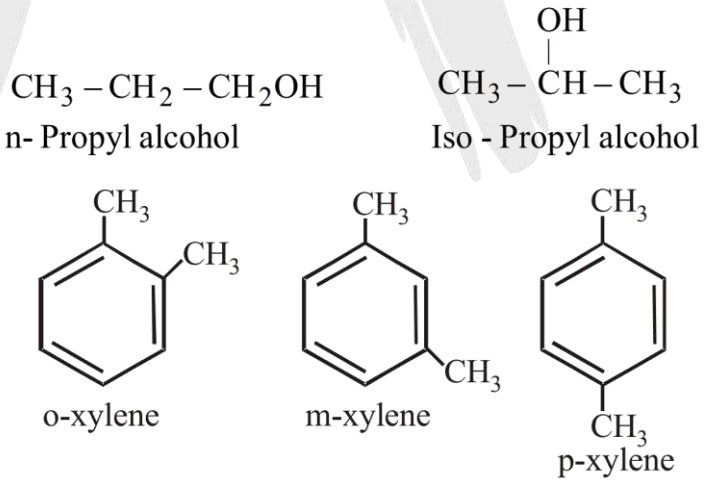
Examples :-



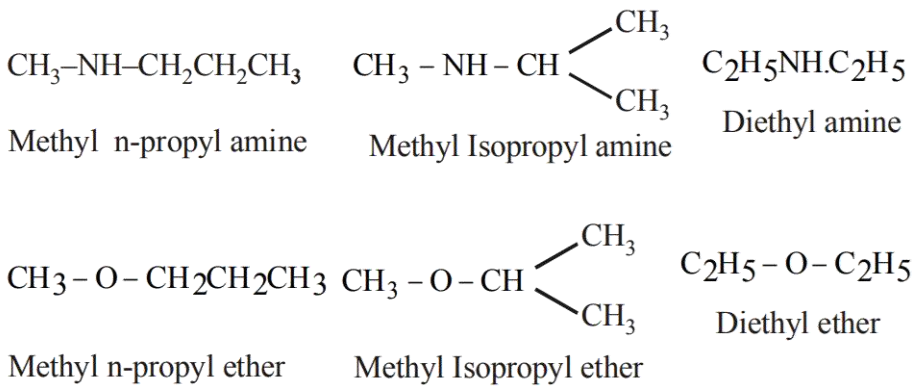
(ii) Functional Isomerism : This is due to difference in the functional groups

C_2H_5OH	**CH_3OCH_3**
ethyl alcohol	dimethyl ether
CH_3COOH	**$HCOOCH_3$**
Acetic acid	Methyl formate
CH_3CH_2CHO	**CH_3COCH_3**
Propionaldehyde	Acetone.

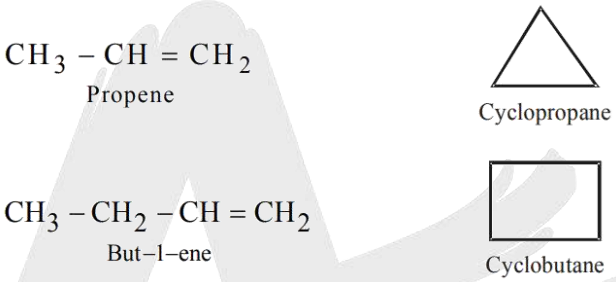
(iii) Position Isomerism : Isomers that have the same parent chain and functional group and which differ in the position of the functional group are called position isomers.



(iv) Metamerism : These are isomers which are having the same functional group and differ in the alkyl or aryl groups present around the functional group.



(v) **Ring Chain Isomerism :** Out of two isomers, if one has open chain structure and the other has ring structure-they are ring chain isomers.



(vi) **Tautomerism (Tauto = Same, Mers = Parts) :** It is due to the presence of a mobile atom in the molecule and the same substance behaves in such a way as if it is a mixture of two or more compounds.

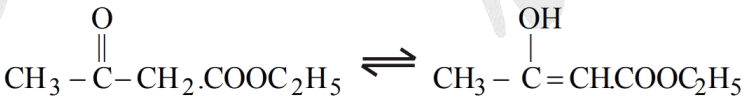
Further we have,

(a) **Dyad System :** When the mobile atom oscillates between two adjacent atoms

e.g. **H – C ≡ N ⇌ H – N ≡ C**

Hydrocyanic acid Iso-hydrocyanic acid

(b) **Triad System :** When the mobile atom oscillates between atoms one position ahead eg.

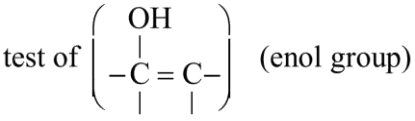


93% Keto form — 7% Enol form

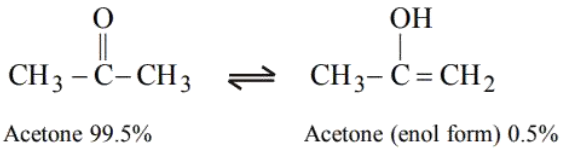
Aceto acetic ester — Aceto acetic ester

Aceto acetic ester reacts with **HCN**, **NH_2OH**, **$C_6H_5NHNH_2$** showing the properties of a ketone and also reacts with **CH_3COCl**, **PCl_5**, Na showing the properties of **OH** group.

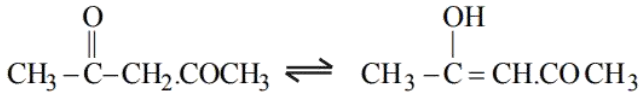
It gives colour change with **1%$FeCl_3$** a characteristic



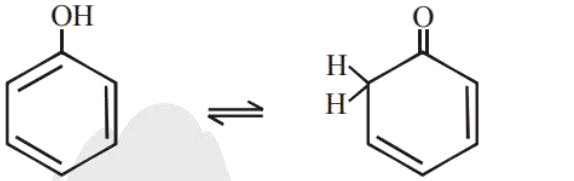
There exists an equilibrium between the two forms which is dynamic in nature.



Acetone 99.5% Acetone (enol form) 0.5%

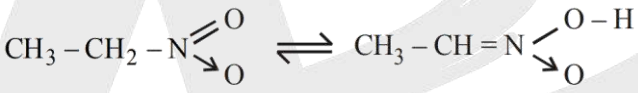


Acetyl acetone (keto form) Acetyl acetone (enol form)



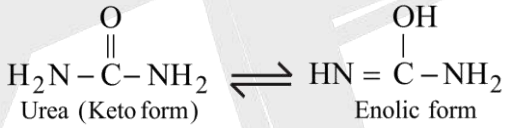
Phenol Keto form of Phenol

Triad system containing nitrogen

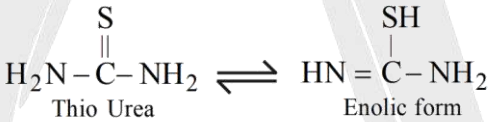


Nitro ethane Aci Nitro ethane

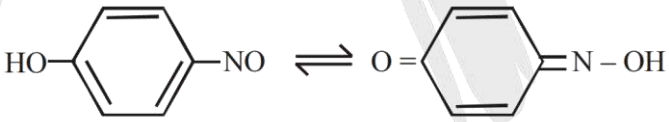
It dissolves in **NaOH** on account of acid form. Tautomeric form which is less stable is called labile form.



Urea (Keto form) Enolic form



Thio Urea Enolic form



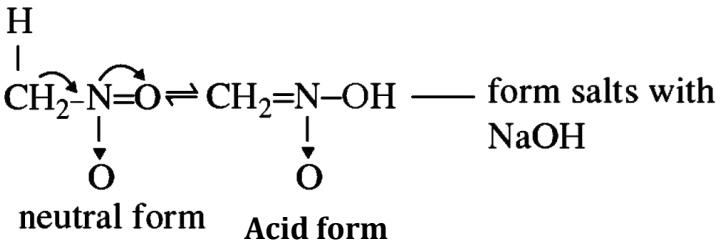
p-Nitrosophenol Keto form

Conditions for Exhibiting Tautomerism

The compound should have strong withdrawing group like $-\overset{\|}{\underset{}{C}}-$, $-\mathbf{NO_2}$ or $\mathbf{C \equiv N}$, with at least one **H** on saturated **α** carbon. Compounds having **H** atom on a saturated carbon which is separated from the withdrawing group by alternate **π** bonds also exhibit tautomerism.

Examples of Compounds Exhibiting Keto-enol Tautomerism

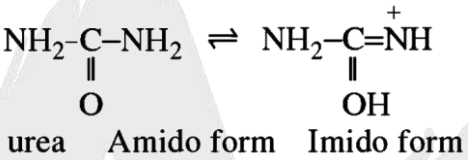
1. Nitro alkanes, with ***α*H** can exhibit tautomerism.



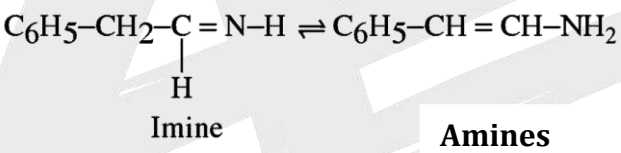
$CH_3–\underset{\underset{CH_3}{|}}{CH}–NO_2$ also exhibits tautomerism but not $CH_3–\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}–NO_2$

Here the **H** migrates to **2nd** atom and called triad system

2. Amides exhibit tautomerism.



3. Amines exhibit tautomerism.



4. Cyanides exhibit tautomerism

$$\mathbf{CH_3 - C \equiv N \rightleftharpoons CH_2 = C = NH}$$

Resonance and Tautomerism

Resonating structures differ only in the position of $\boldsymbol{\pi}$ bonds, not any atom. They cannot be separated as they are hypothetical as real structure is a hybrid of them. Tautomers can be separated and exist in equilibrium.

EXERCISE - I

Q.1 The compounds $C_2H_5OC_2H_5$ and $CH_3OCH_2CH_2CH_3$ are

(A) Chain isomers (B) Position isomers

(C) Metamers (D) Conformational isomers

Q2. The number of primary, secondary and tertiary amines possible with the molecular formula C_3H_9N respectively.

(A) **1, 2, 2** (B) 1, 2, 1 (C) 2, 1, 1 (D) **3, 0, 1**

Q3. How many benzenoid aromatic isomers shown by C_7H_7Cl?

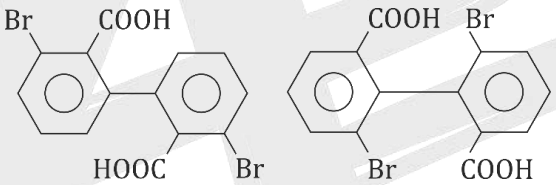
(A) 4 (B) 3 (C) 5 (D) 6

Q4. Molecular formula $C_3H_6Br_2$ can have:

(A) Two gem dibromide (B) Three vic dibromide

(C) Two tert. -dibromo alkane (D) Two sec.-dibromo alkane

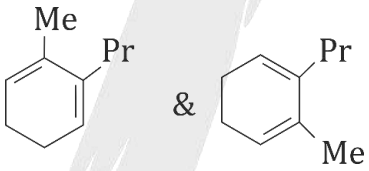
Q5. Following compounds are:



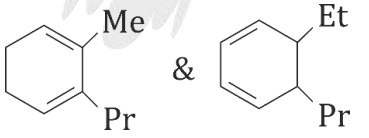
(A) Position isomer (B) Chain isomer

(C) Metamers (D) Functional isomer

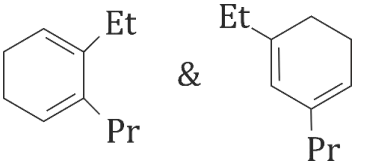
Q6. Which of the following is incorrect relation:

(A) 

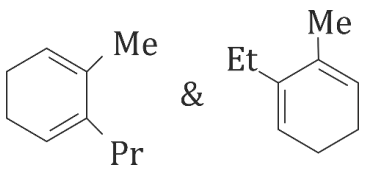
identical

(B) 

positional isomers

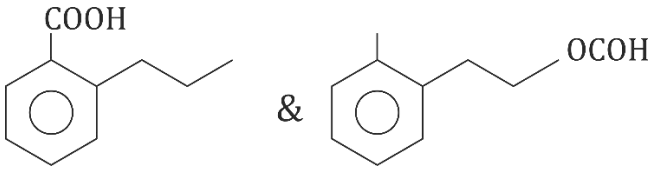
(C) 

positional isomers

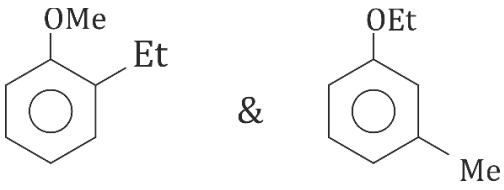
(D) 

homologues

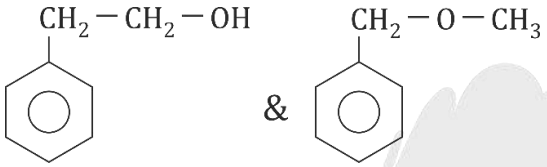
Q7. Select whether given realationship is true or false?



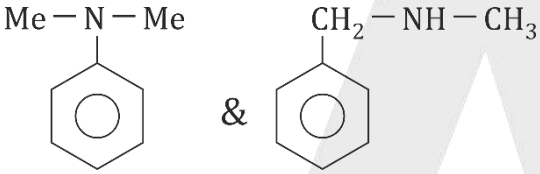
functional isomer



metamers



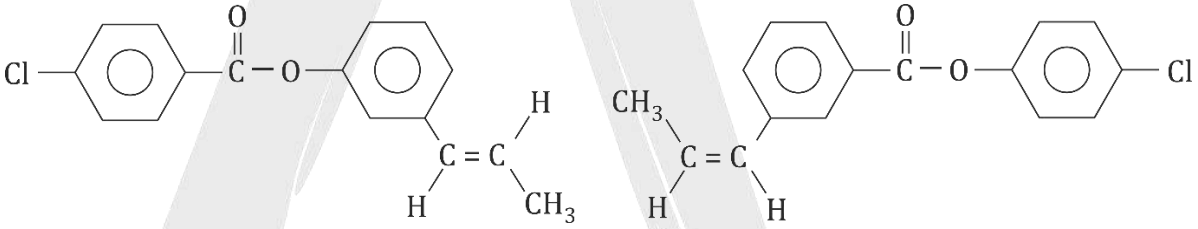
metamers



functional isomers

(A) TFTF (B) FTTF (C) TTFT (D) TFFT

Q8. Following compounds are:



(A) Functional isomer (B) Chain isomer

(C) Metamer (D) Position isomer

Q9. The type of isomerism observed in urea molecule is

(A) Chain (B) Position (C) Metamers (D) Functional

Q10. How many minimum no. of **C**-atoms are required for position isomer in alkene?

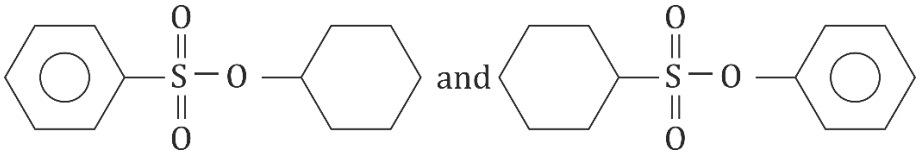
(A) 6 (B) 4 (C) 3 (D) 5

Q.11 Which of the following cannot be written in an isomeric form?

(A) $\mathbf{CH_3 - CH(OH) - CH_2 - CH_3}$ (B) $\mathbf{CH_3 - CHO}$

(C) $\mathbf{CH_2 = CH - Cl}$ (D) $\mathbf{Cl - CH_2CH_2 - Cl}$

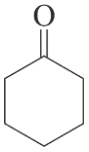
Q12. Given compound shows which type of isomerism



(A) Chain isomerism (B) Positional isomerism

(C) Metamerism (D) Functional group isomerism

Q.13 Which of the following involves Diad system for prototropy:

(A) $\mathbf{CH_3COCH_3}$ (B) $\mathbf{CH_3CH_2NO_2}$ (C)  (D) HCN

Q.14 How many structural isomers of $\mathbf{C_5H_{10}}$ are possible.

(A) 10 (B) 11 (C) 12 (D) 13

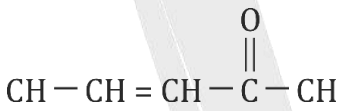
Q.15 The number of isomers of dibromoderivative of an alkene (molar mass $\mathbf{186\ g\ mol^{-1}}$) is

(A) 2 (B) 3 (C) 4 (D) 6

Q.16 How many structural isomeric primary amines are possible for the formula $\mathbf{C_4H_{11}\ N}$?

(A) 2 (B) 3 (C) 4 (D) 5

Q.17 For the given compound, choose the incorrect option?



(A) On treatment with $\mathbf{NaOD/D_2O}$ for long time, it has 7 deuterium in its enol form

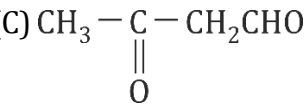
(B) It has all types of permanent electronic displacement effect present.

(C) It has IUPAC name "Pent-2-en-4-one."

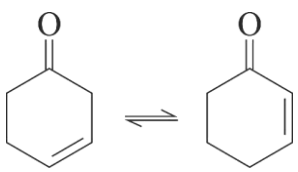
(D)None of the above.

Q.18 Among the following the compounds having the highest enol content:

(A) $\mathbf{CH_3CHO}$ (B) $\mathbf{CH_3COCH_3}$

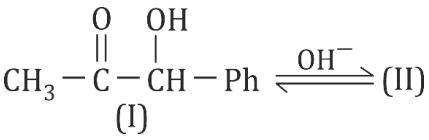
(C)  (D) $\mathbf{CH_3 - CO - CH_2 - CO_2CH_3}$

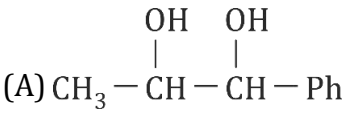
Q.19 Given interconversion takes place in

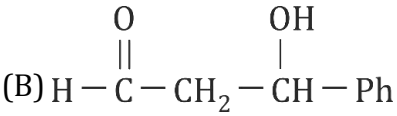


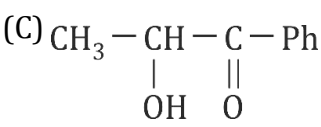
(A) Acidic medium (B) Basic medium (C) Both (D) None

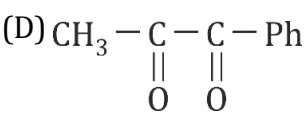
Q.20 (I) isomerizes to (II) on addition on small amount of base then structure of (II) is



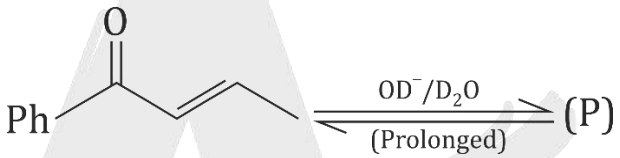
(A) 

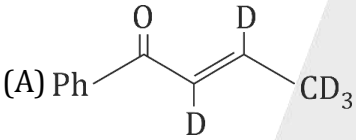
(B) 

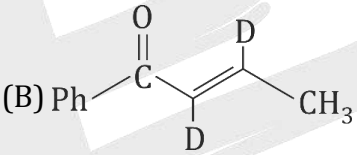
(C) 

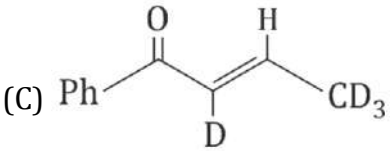
(D) 

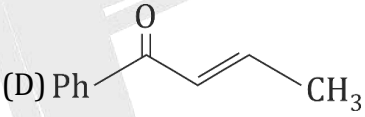
Q.21 Major product (**P**) obtained is:



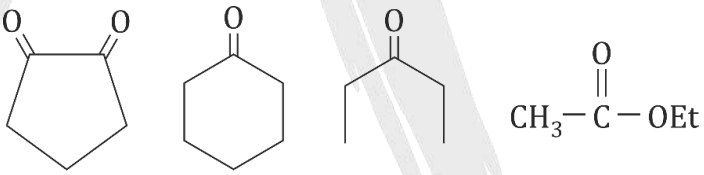
(A) 

(B) 

(C) 

(D) 

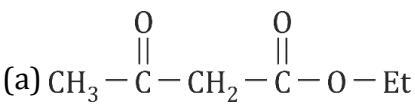
Q.22 Decreasing order of enol content of the following compounds in liquid phase is:

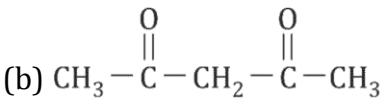


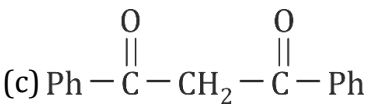
(1) (2) (3) (4)

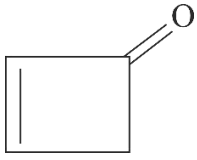
(A) **2 > 1 > 3 > 4** (B) **1 > 2 > 3 > 4** (C) **4 > 3 > 2 > 1** (D) **3 > 1 > 2 > 4**

Q.23 Decreasing order of enol content of the following compound in liquid phase

(a) 

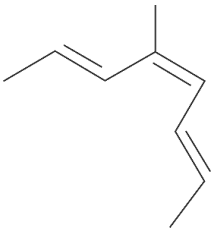
(b) 

(c) 

(d) 

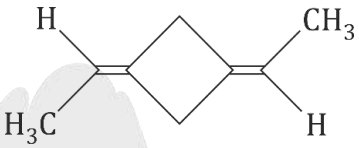
(A) a > b > c > d (B) c > b > a > d (C) c > b > d > a (D) b > c > a > d

Q.24 What is the correct IUPAC name of the following compound



(A) 2E, 4E, 6Z 4-methyl octa-2, 4, 6 triene
(B) 2E, 4Z, 6Z 5-methyl octa-2, 4, 6 triene
(C) 2Z, 4Z, 6Z 5-methyl octa-2, 4, 6 triene
(D) **2E**, **4Z**, **6E** 4-methyl octa-2, 4, 6 triene

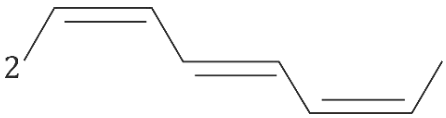
Q.25 The IUPAC name of the given compound is



(A) 2, 4-di[(E)-ethylidene] cyclobutene
(B) 1,3-di-[(E)-ethylidene] cyclobutane
(C) 1, 4-di-E-ethyldenecyclobutane
(D) (E)-1, 4-diethylidenecyclobutane

EXERCISE - II

Q1. The IUPAC name of the compound is:



(A) (2E, 4E, 6Z)-octa-2,4,6-triene (B) (2E, 4E, 6E)-octa-2,4,6-triene

(C) (**2Z**, **4E**, **6Z**)-octa-2,4,6-triene (D) (2Z, 4Z, 6Z)-octa-2,4,6-triene

Q2. Which of the following statements is (are) not correct?

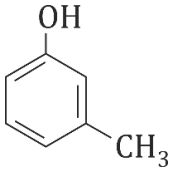
(A) Metamerism belongs to the category of structural isomerism

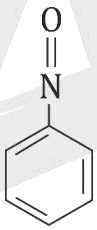
(B) Tautomeric structures are the resonating structures of a molecule

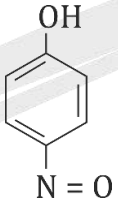
(C) Keto form is always more stable than the enol form

(D) Both B and C

Q3. Which compound can show tautomerism:

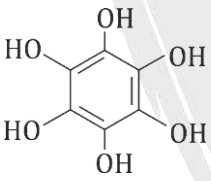
(A) 

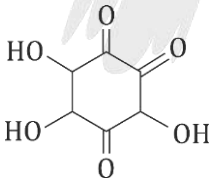
(B) 

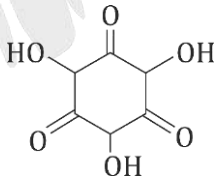
(C) 

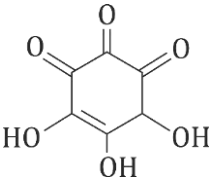
(D) Acetyl acetone

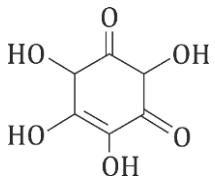
Q4. Tautomerism form of this compound is(are):



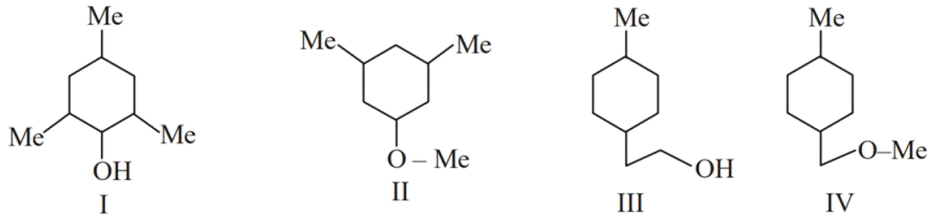
(A) 

(B) 

(C) 

(D) 

Q5. Which of the following is not the correct relationship



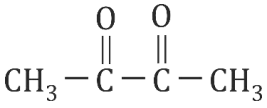
(A) II & IV are metamer

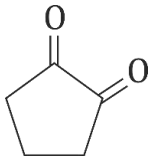
(B) I & II are functional isomer

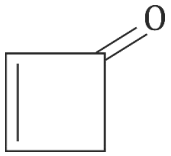
(C) I & III are chain isomer

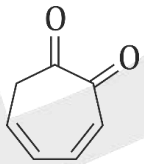
(D) I and IV are positional isomer

Q6. Which of the following compounds have higher enolic content than Keto content:

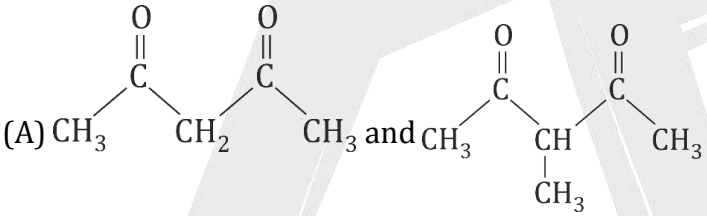
(A) 

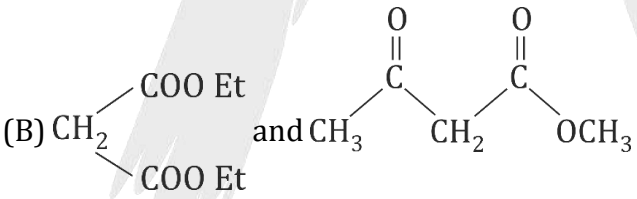
(B) 

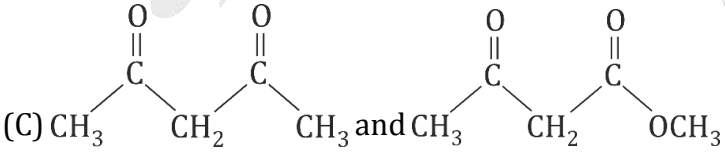
(C) 

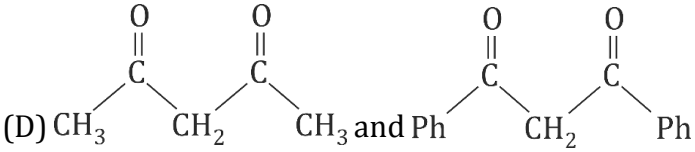
(D) 

Q7. In which of the following pairs first will have higher enol content than second:

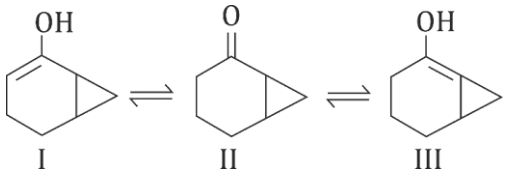
(A) 

(B) 

(C) 

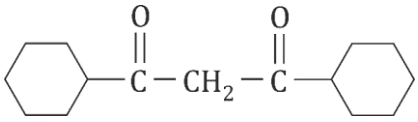
(D) 

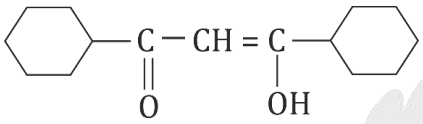
Q8. Among these tautomers, correct stability order is:

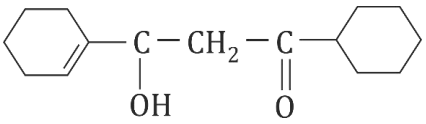


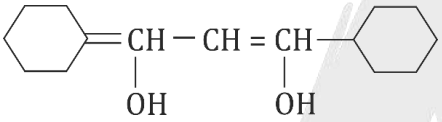
(A) I > II > III (B) III > II > I (C) II > I > III (D) II > III > I

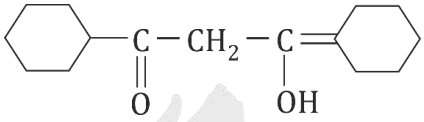
Q9. Most stable tautomer of following compound is:



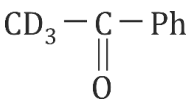
(A) 

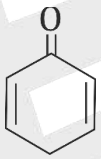
(B) 

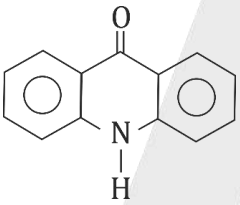
(C) 

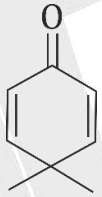
(D) 

Q10. Which of the following can show tautomerise.

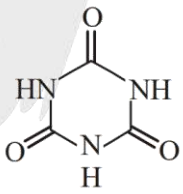
(A) 

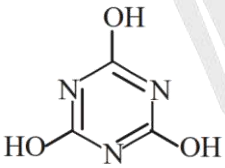
(B) 

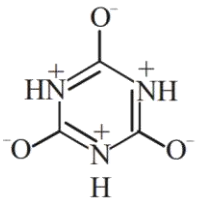
(C) 

(D) 

Q11. What is relation between (I), (II) and (III)?



(II) 

(III) 

(A) I and II are tautomers

(B) III is conjugate base of II

(C) III is resonance structure of I

(D) no relation exists

Q12. The isomerism observed in cyclo alkanes is(are):

(A) metamerism (B) chain isomerism

(C) position isomerism (D) Both B and C

Q13. Only two isomeric monochloro derivatives structure are possible for:

(A) n-butane (B) 2, 4-dimethyl pentane

(C) benzene (D) 2-methyl propane

Q14. An organic compound with molecular formula $\mathbf{C_2H_5NO}$ contains doubly linked atoms. It can shows:

(A) chain isomerism (B) Functional Isomerism

(C) tautomerism (D) positional isomerism

Q15. Which of the following can exist in 'syn' and 'anti' form?

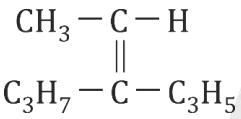
(A) $\mathbf{CH_3 - N = N - OH}$

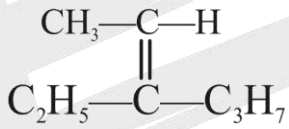
(B) $\mathbf{CH_3 - N = N - CH_3}$

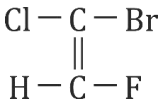
(C) $\mathbf{CH_3 - CH = N - OH}$

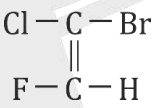
(D) $\mathbf{(CH_3)C = N - OH}$

Q16. The Z-isomer among the following are:

(A) 

(B) 

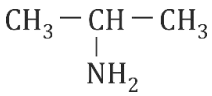
(C) 

(D) 

Q17. Which of the following is/are correct matchings?

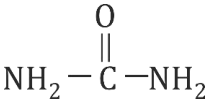
(A)  – Metamers

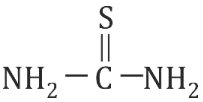
(B) $\mathbf{CH_3 - CH_2 - C \equiv CH}$ and $\mathbf{CH_3 - C \equiv C - CH_3}$ – Position iso

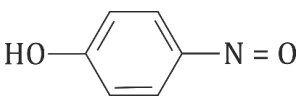
(C) $\mathbf{CH_3CH_2CH_2NH_2}$ and  – Tautomers

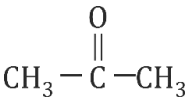
(D) $\mathbf{CH_3CH_2OH}$ and $\mathbf{(CH_3)_2O}$ – Functional isomer

Q18. Which of the following compounds can show tautomerism?

(A) 

(B) 

(C) 

(D) 

Q19. Which of the following has (have) more number of stable conformations than ethyl chloride?

(A) Butane (B) Isopropanol

(C) n-pentane (D) Neohexane

Q20. **Statement-1 :** E-cyclodecene is having more ΔH_C (Heat of combustion) than **Z** isomer.

Statement-2 : E-cyclodecene is more stable than **Z** isomer.

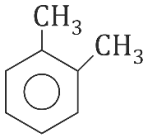
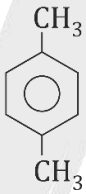
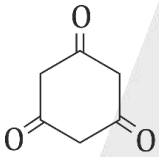
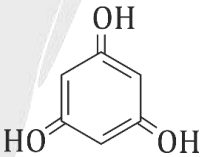
(A) Statement- 1 is true, statement- 2 is true and statement- 2 is correct explanation for statement- 1 .

(B) Statement- 1 is true, statement- 2 is true and statement- 2 is NOT the correct explanation for statement-1.

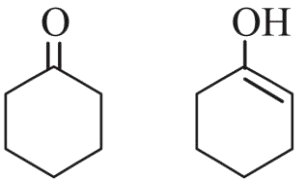
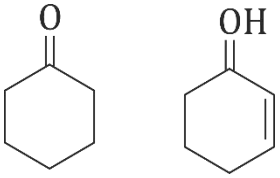
(C) Statement- 1 is true, statement- 2 is false.

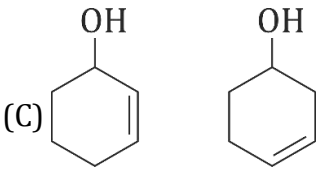
(D) Statement- 1 is false, statement- 2 is true.

Q21. Match the Column I with Column II:

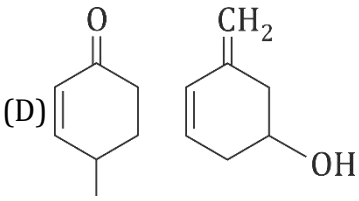
Column I (Pair)	**Column II (Relation)**
(A) $CH_3-\overset{\overset{O}{\|}}{C}-O-C_3H_7$ & $Et-\overset{\overset{O}{\|}}{C}-O-Et$	(P) Chain isomer
(B)  & 	(Q) Positional isomer
(C)  & 	(R) Metamers
(D) $CH_3-\underset{\underset{CH}{\|}}{CH}-O-CH_3$ & $CH_3-CH_2-CH_2-O-CH_3$	(S) Tautomers

Q22. Match the column :

Column I	**Column II**
(A) 	(P) Tautomers
(B) 	(Q) Structural isomers

(C) 

(R) Position isomers

(D) 

(S) Atleast one of the two structures is enol

EXERCISE - III

Q1. How many benzenoid isomer are possible for molecular formula of cresol?

Q2. Find out the total number of cyclic structural isomers of C_6H_{12}.

Q3. Calculate the number of Benzenoid isomers possible for C_6H_3ClBrI.

Q4. Calculate the total number of structural isomers of **3**°-amines for the molecular formula $C_6H_{15}N$ are?

Q5. How many cyclopentane structural isomers are possible for C_7H_{14}.

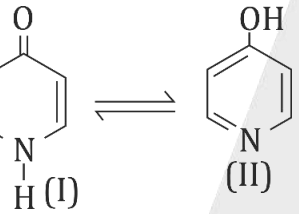
Q6. Mention the specific type of isomerism exhibited by each of the following pairs:

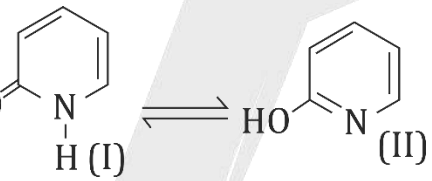
(a) 1,2-dichloro ethane and 1,1-dichloro ethane (b) Propanoic acid and methyl acetate

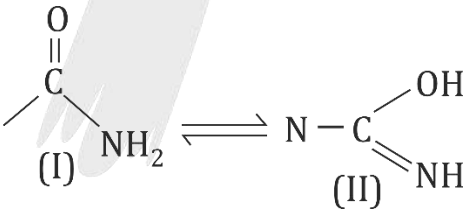
(c) Methyl acetate and ethyl formate (d) o-Nitrophenol and P-nitrophenol

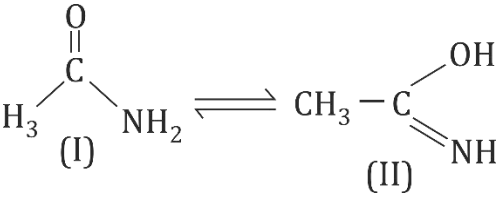
(e) Anisole and o-cresol (f) Phenol and Cyclohexa-2,4-dien-1-one

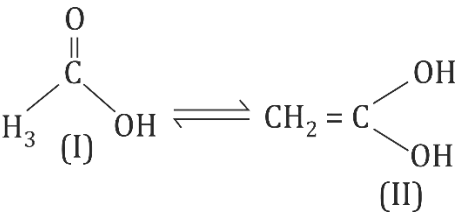
Q7. In each of the following pairs which is more stable:

(A) 

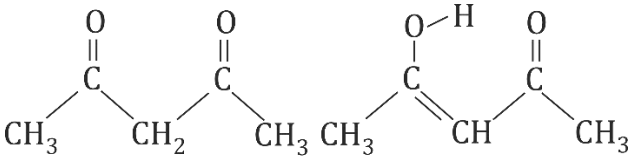
(B) 

(C) 

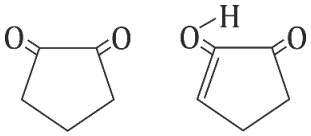
(D) 

(E) 

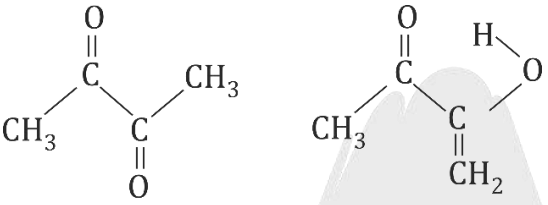
Q8. In each of the following pairs which is more stable:

(A) 

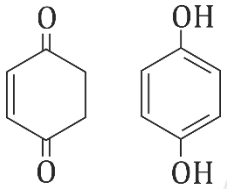
(I) (II)

(B) 

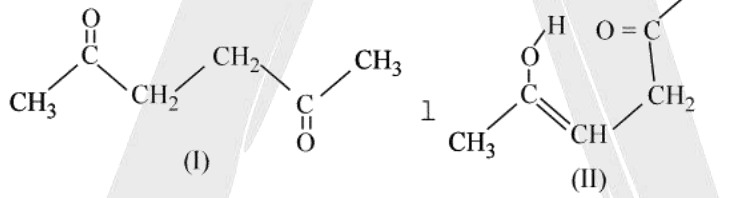
(I) (II)

(C) 

(I) (II)

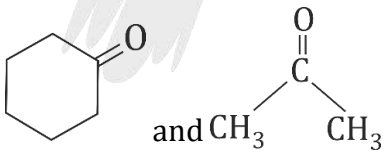
(D) 

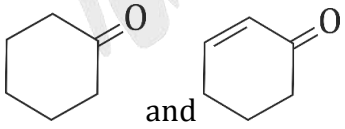
(I) (II) s

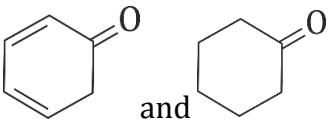
(E) 

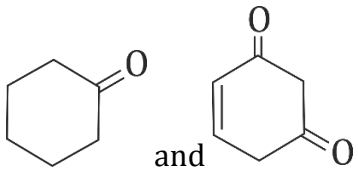
(I) (II)

Q9. In each of the following pairs which will have less enol content:

(A) 

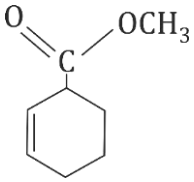
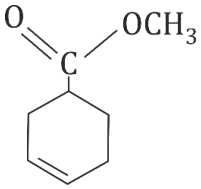
(B) 

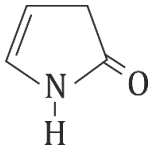
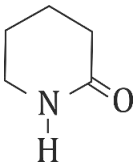
(C) 

(D) 

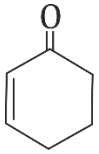
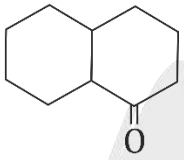
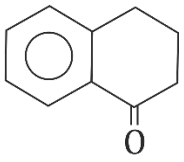
(E) CH_2-CHO and CH_3-CHO
|
Cl

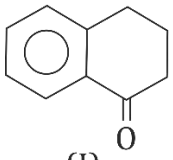
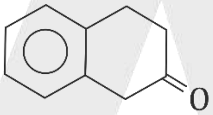
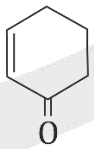
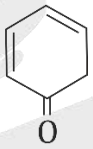
Q10. In each of the following pairs which will have less enol content:

(A)  and 

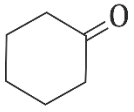
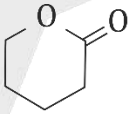
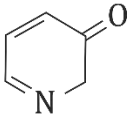
(B)  and 

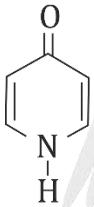
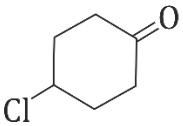
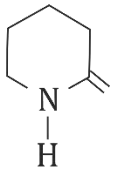
Q11. In each of the following sets of compounds write the decreasing order of % enol content.

(A)  (I)  (II)  (III)

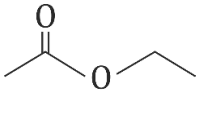
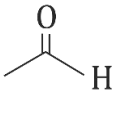
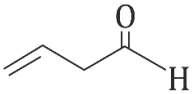
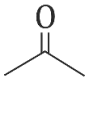
(B)  (I)  (II)  (III)  (IV)

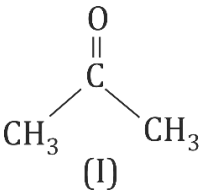
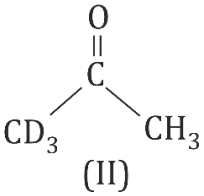
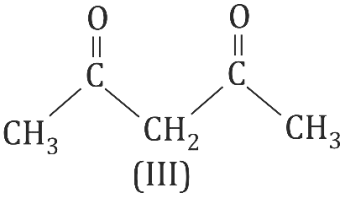
Q12. In each of the following sets of compounds write the decreasing order of % enol content.

(A)  (I)  (II)  (III)  (IV)

(B)  (I)  (II)  (III)  (IV)

Q13. In each of the following sets of compounds write the decreasing order of % enol content.

 (I)  (II)  (III)  (IV)

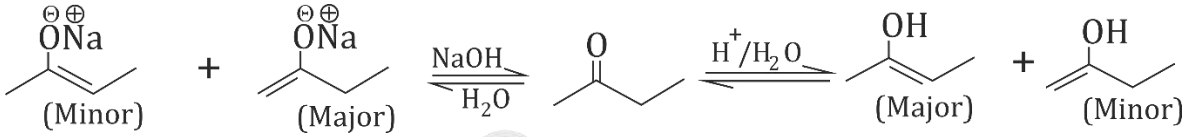
Q14.  (I)  (II)  (III)

Among these give ease of enolization.

Q15. % enol content of acetylacetone in following solvents is found as:

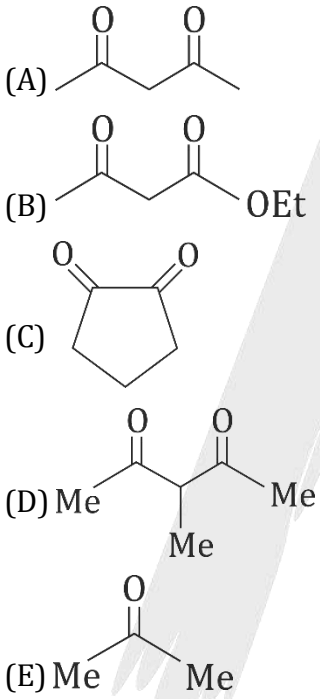
Solvent	**% enol content**
H_2O	**15**
Liquid state	**76**
hexane	**92**
gas phase	**92**

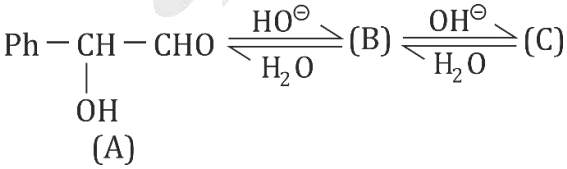
Explain the observation.

Q16. 

Explain the observation.

Q17. Decreasing order of enol content of the following. (along with proper explanation).



Q18. 

(A), (B) and (C) are structural isomers and isomerization is effectively carried out by trace of base. Give structure of (B) and (C) and also write base catalysed mechanism for this interconversion.

Q19. Calculate the total number of open chain isomeric carbonyl compounds of molecular formula **C_5H_8O** .

ANSWER KEY

EXERCISE – I

1.	(C)	**2.**	(C)	**3.**	(A)	**4.**	(A)	**5.**	(A)	**6.**	(B)	**7.**	(C)
8.	(C)	**9.**	(D)	**10.**	(B)	**11.**	(C)	**12.**	(C)	**13.**	(D)	**14.**	(A)
15.	(B)	**16.**	(C)	**17.**	(C)	**18.**	(C)	**19.**	(C)	**20.**	(C)	**21.**	(C)
22.	(B)	**23.**	(B)	**24.**	(D)	**25.**	(B)						

EXERCISE – II

1.	(C)	**2.**	(D)	**3.**	(A, C, D)	**4.**	(A, B, D)	**5.**	(A, D)
6.	(B, D)	**7.**	(A, C)	**8.**	(C)	**9.**	(A)	**10.**	(A, B, C)
11.	(A)	**12.**	(D)	**13.**	(A, D)	**14.**	(C)	**15.**	(C)
16.	(A, C)	**17.**	(B, D)	**18.**	(A, B, C, D)	**19.**	(A, B, C)	**20.**	(C)

21. (A) R, (B) Q, (C) S, (D) Q

22. (A) P, Q, S (B) Q, S (C) Q, R, S, (D) Q, S

EXERCISE – III

1.	(5)	**2.**	(12)	**3.**	(10)	**4.**	(7)	**5.**	(4)

6. (a) Positional (b) Functional (c) Metamerism (d) Positional (e) Functional (f) Tautomerim

7. (a) 2; (b) 2; (c) 1; (d) 1; (e) 1

8. (a) 2; (b) 2; (c) 1; (d) 2; (e) 1

9. (a) 2; (b) 1; (c) 2; (d) 1; (e) 2

10. (a) 2; (b) 2

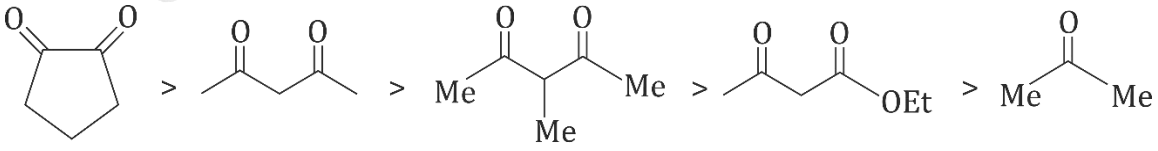
11. (a) 3>1>2; (b) 4>2>1>3;

12. (i) 4 > 1 > 3 > 2; (ii) 3 > 1 > 4 > 2

13. 3 > 4 > 2 > 1

14. 3>1>2

17.



(a) (b) (c) (d) (e)

(a) Tightly on stableketo due to repulsion between **α − CO** groups has **100**% enol.

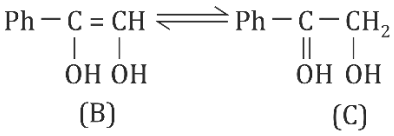
(b) Active ' **H** ' atom / Acidic 'H' atom so has more enolic content (enol stabilise by resonance & Intra molecular **H**-bonding)

(c) Enolic contents decreases with introduction of $\mathbf{e^-}$donator group which causes repulsion in enolic form.

(d) Due to ester group acidic structure of active **H** decreases &**C** = **C** of enol undergoese cross resonance.

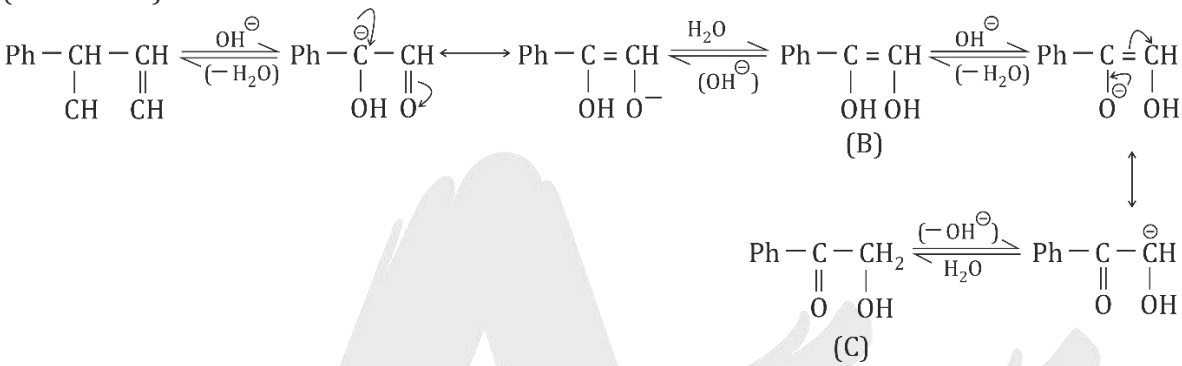
(e) Lowest enolic content because $\rangle C = O$ is more stable than $\rangle C = O\langle$ Bond

18.



(B) (C)

(Mechanism)



19. (8)