## HINTS \& SOLUTIONS

## EXERCISE - 1

Single Choice

1. $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{~N} \rightarrow$


So C is correct option.
5. $\mathrm{C}_{5} \mathrm{H}_{10} \rightarrow$
(1) $\mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}=\mathrm{CH}_{2}$
(6)

(2) $\mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}_{2}-\mathrm{CH}_{3}$
(7)

(3)

(4)
(5)

(8)
(9)
(10)

9. Anthracene


Only three types of hydrogen so only three structural isomers possible.
10.

)


(a)

(b)


Product will be


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11. Ethene $\rightarrow \mathrm{CH}_{2}=\mathrm{CH}_{2} \quad$ Cannot show G.I.

Propene $\rightarrow \mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}_{2} \quad$ Cannot show G.I.
Butene $\rightarrow \mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}_{3} \quad$ Show G.I. and it also show positional isomerism.
$\mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}=\mathrm{CH}_{2}$ and $\mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}_{3}$
13.
(A)

(B)

(C)

(D)
 exists in conformational form
14. $\mathrm{A} \rightarrow$

isobutene

B $\rightarrow$


Acetone oxime
$\mathrm{C} \rightarrow$


Acetophenone oxime Show G.I.
$\mathrm{C} \rightarrow$


Benzophenone
15.


B $\rightarrow$

$\mathrm{C} \rightarrow$


D $\rightarrow$

17.

total optical isomers $=3$

(i)

(ii)

(iii)
(II) and (III) are optically active.
19.

Isopentene


Products are
(I)

(S)
(II)

(III)

(IV)


Only (1) and (3) are optically active.
20. $\quad \mathrm{A} \rightarrow \quad$ Planar compound so optically inactive.

B $\rightarrow \quad$ Non planar and optically active due to absence of POS \& COS.
$\mathrm{C} \rightarrow \quad$ Non planer but having POS so, optically inactive.
D $\rightarrow \quad$ Planar compound
24.

meso tartartic acid

d-tartaric acid

They are diasteromers.
25.

R-S configuration of 2nd carbon


R-S configuration of 3rd carbon.


So option is (A)

Mirror imageof D-ribose is known as L-form.

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30. 





31.


34. Higher Priority groups same side $\Rightarrow \mathrm{Z}$ - form

Higher Priority groups opposite side $\Rightarrow$ E - form
$2^{\text {nd }}$ and $6^{\text {th }}$ carbon is in E-form while 4th carbon is in Z-form.


35. Alkyl group is different.
$\stackrel{\|}{0}{ }_{-\mathrm{C}-0-}^{0}$ is bivalent group which has different alkyl groups in both compounds.
As we know that according to definitions off matamerism "When alkyl group is different around bivalent. or trivalent atom 1 group compounds termed as metamers.


Although in second compound trans from is present but structurel is also present so it will be metamers not geometrical isomers.
36.


Ring will be Principle carbon chian so we assign numbering for ethylidene group $\left(\mathrm{CH}_{3}-\mathrm{CH}=\mathrm{C}<\right)$ which is E -in configuration.
37. If terminal carbon have same group than it can show geometrical isomerism.


In this compound there is not possibility to show geometrical isomerism because at first double bonded carbon 2same chlorine atom is attached.
38. Both will give $n$-Butane as a product.

Boiling point cis-2-butene $>$ Trans 2-butane
Dipole moment cis-2-butene $>$ Trans 2-butane

Heat of Hydrogenation cis-2-butene $>$ Trans 2-butane
Product same


39. Higher Priority groups same side

$$
=\mathrm{Z}-\text { form }
$$

Higher Priority groups oppsite side

$$
=\mathrm{E}-\text { from }
$$

$\mathrm{CH}_{3}$ - group name more Priority than H - atom

40. Lone pair also counts as a different group.

For G.I. for ground attached to the terminal carbon or Nitrogen must be different.


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41. In cyclo alkane minimum 2 group \& carbon ring required.


 different group is absent instead of starred carbon.

can not show G.I.

G.I. $\boxtimes$
42. One chiral carbon Containing Compound always optially active.

(2-forms)
$\mathrm{C}_{4} \mathrm{H}_{9}-\mathrm{Br}$
$\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{Br}$
(inactive)
 (active)

(inactive)

43. Asymmetric carbon $\equiv$ Chiral carbon.


Telrahedral (Tetravalent carbon) having four different group is known as chiral/Asymmetric carbon.
44. Compound having single chiral carbon always optically active and gives two active compound


Active isomer $=2^{\mathrm{n}-1}=2^{2-1}=2$
Where $\mathrm{n}=$ Number of chiral carbon
(I)

Meso (inactive)
(II)

(active)
(III)

(active)
5.
(A)
 No G.I.
(B)

(C)

 Show G.I. due to ring contain 8-carob.
(D)
 No. G.I.
8.


Show G.I. (a not equal to $b$ )
(B)

Show G.I.
(C)

$\mathrm{a}=\mathrm{b}$ so not show G.I.
(D)


Show G.I.
11.
(A)
 POS present
(B)


No POS \& COS present
(C)


POS present
(D)


No POS and COS.

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12. 

$\mathrm{A} \rightarrow$


POS present
$B \rightarrow$
 COS present
$\mathrm{C} \rightarrow$


D $\rightarrow$


POS present

No POS and COS present
13.
(A)

(B)
 optically inactive
(C)
 Does not contain POS or COS so optically active.
(D)
 Does not contain POS or COS because both benzene rings are $\perp$ to
each other.
14.
(A)


(B)

(C)

(D)

POS present
16. Same group same side Erythro and same group opposite side then.
18. In structural isomerism Connectivity of atoms remains same.

In tautomerism atom must ossilate in the compound.
Geometrical isomerism shown by many compounds like, alkene, cycloalkanes, oximes, etc.
19. Groups around the area which rotation has been restricted should be different.

Lone pair and isotopes also counts as a different groups.

restricted Rotation and different groups

cis


groups of carbon is same G.I. absent

Syn

20. Single chiral carbon have two form dextrorotaory and laevorotatory.

Chiral carbon or Asymmetric carbon is always stereo centre.
$\mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{OH}$
alochol
and
$\mathrm{CH}_{3}-\mathrm{O}-\mathrm{CH}_{3}$ ether

Ether and alcohol are functional isomers.
21. POS or COS both present.

Meso is achiral compound having minimum two chiral carbon.



We can superimposable it by
Rotation along the plane by $180^{\circ}$
22. POS or COS may be present.

Meso are the compounds with was minimum 2-chiral carbon or more and having POS or COS or both.
Fro optical activity two necessary condition us compound must be asymmetric. It POS or COS present then it will super impose on its mirror image.

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23. Check conformers of the compounds



24. Check $\mathrm{R} / \mathrm{S}$ configuration

Fischer is in eclipse form so first we have to convert above compound into total eclipsed form.





25．Optially active compound will be resolvable．
Resolution is a process by we separate entiomers and we know that entiomers are individually active so check POS and COS．



Planer molecular Molecular POS （Inactive）


POS x COS x（Resolvable）

26．Two different group -H and $-\mathrm{CH}_{3}$ is present．
When two groups（Bulky）are at $60^{\circ}$ Dihedral angle is known as sancle form

POS 区
COS 区
Active $\square$

POS
$\operatorname{COS} \boxtimes$
Active $\boxtimes$

POS 区
COS 区
Active $\square$

POS
COS
Active $\boxtimes$

## Part \＃II ：Assertion \＆Reason

3． $\mathrm{Me}-\mathrm{C} \equiv \mathrm{N}$ and $\mathrm{Me}-\mathrm{N} \overrightarrow{=} \mathrm{C}$ are functional isomers but $\mathrm{H}-\mathrm{C} \equiv \mathrm{N}$ and $\mathrm{H}-\overrightarrow{\mathrm{N}}$ are Tautomer

4．The enol form of 5，5－dimethyl－1，3－cyclohexanedione is stable due to chelation，but same is not true in 2，2－dimethyl 1,3 －cyclohexanedione dur to absence of $\alpha$－hydrogen because it is not having more acidic hydrogen．

EXERCISE－ 3

## Part \＃II ：Comprehension

## Comprehension \＃ 4 ：

1．［Specific rotation of $(-)$ MSG］

$$
\begin{aligned}
\mathrm{C} & =\frac{169 \mathrm{gm}}{845 \mathrm{gm}} \quad l=2 \mathrm{dm} \\
{\left[\theta^{\circ}\right]=\frac{\theta}{\mathrm{Cl}} } & =\frac{9.6}{169 / 845 \times 2}=-24^{\circ}
\end{aligned}
$$

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2. Optical of purity ( - ) $\mathrm{MSG}=\frac{\theta_{\text {Observed }}}{\theta_{\text {Standard }}} \times 100=83.33 \%$

RM $=100-$ optical of purity
$=100-83.33=16.66 \%$
$(-)$ MSG total in mixture $\quad \Rightarrow \quad 83.33 \%$

$$
\begin{aligned}
& +8.33 \% \\
& 91.66 \%
\end{aligned}
$$

3. $[(+) \mathrm{MSG} \Rightarrow 33.8 \mathrm{gm}$ in 338 ml$]$
$(-) \mathrm{MSG} \Rightarrow 16.9 \mathrm{gm}$ in 169 ml
Optical purity in mixture ( + ) $\mathrm{MSG}=16.9 \mathrm{gm}$ in 507 ml solution

$$
\begin{array}{ll}
\mathrm{C}=\frac{16.9}{507} \mathrm{gm} / \mathrm{ml} & l=4 \mathrm{dm} \\
\theta_{\text {Observed }}=\left[\theta^{\circ}\right] \times \mathrm{C} . l . & =24 \times \frac{16.9}{507} \times 4=+3.2 \%
\end{array}
$$

Comprehension \# 5 :
1.

(B)

(C)

2.
(A)

(B)

(C)

(D)

3.
(I)


Repulsion can be minimized by rotation pairs


When tautomerize enol is antiaromatic while
(II)


Keto form is unstable due to repulsion between lone


When tautomerize enol is aromatic so IV preferes to be in enol form

## Comprehension \# 6 :

2. 


(C)

(B)

(A)
3.

$\mathrm{C} \equiv \mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{C}$
$\mathrm{C}-\mathrm{C} \equiv \mathrm{C}-\mathrm{C}-\mathrm{C}$


EXERCISE - 4
Subjective Type

1. If the bonds were localized, there would be 4 isomers ; actually there are only 3 of the following the first two are identical, because the bods are not localized.




2. There are 7. 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, diethyl ether, methyl propyl ether, and methylisopropyl ether.
3. 



This is cis form. Two H atoms on the same side. To get trans, ring must be twisted.

Double bond becomes severely twisted-destablized. Effective overlap of P orbitals is missing, so does not exist.
5. The $P_{z}$ orbitals forming $\pi$-bonds and the empty $P_{z}$ orbital of the carbon with $+v e$ charge are parallel. So the electrons may be delocalized. The +ve charge is effectively spread out over two carbons; delocalized.

$\mathrm{CH}_{2}=\mathrm{CH}-\stackrel{+}{\mathrm{C}} \mathrm{H}_{2} \longleftrightarrow \stackrel{+}{\mathrm{C}} \mathrm{H}_{2}-\mathrm{CH}=\mathrm{CH}$
In n-propyl cation, + I effect of R increases the stability.
In alyl +M effect increases the stability. But +M effect in allyl cation is more effective. So allyl $>$ propyl.
A group with +M effect stabilized cation; destabilizes anion.

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6. Only $\mathrm{CHBr}=\mathrm{CHCl}$ can exist as geometric Isomers :


In $\mathrm{CH}_{2} \mathrm{Cl}-\mathrm{CH}_{2} \mathrm{Cl}$ and $\mathrm{CH}_{2} \mathrm{Cl}-\mathrm{CH}_{2} \mathrm{Br}$, the carbon atoms are connected by a single bond about which the groups can rotate relatively freely. Thus any conformation of the halogen atoms may be converted into any other simply by rotation about the single bond. $\mathrm{In}_{\mathrm{CH}_{2} \mathrm{Cl}_{2}}$, the configuration of the molecule is tetrahedral and all interchanges of atoms yield exactly equivalent configurations.
7. Maleic acid forms an anhydride where as fumaric acid does not.

8. Lone pair - $\mathrm{p} \pi$ conjugation between fluorine and carbon will be more effective than between chlorine and carbon.
9. $I$ III $>$ IV $>$ I $>$ II
11. (A) $-\mathrm{Br}>-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}>-\mathrm{CH}_{2} \mathrm{CH}_{3}>-\mathrm{H}$,
(B) $-\mathrm{OH}>-\mathrm{COOCH}_{3}>-\mathrm{COOH}>-\mathrm{CH}_{2} \mathrm{OH}$
(C) $-\mathrm{NH}_{2}>-\mathrm{CN}>-\mathrm{CH}_{2} \mathrm{NHCH}_{3}>-\mathrm{CH}_{2} \mathrm{NH}_{2}$
(D) $-\mathrm{Br}>-\mathrm{Cl}>-\mathrm{CH}_{2} \mathrm{Br}>-\mathrm{CH}_{2} \mathrm{Cl}$
12. Tertiary amines have pyramideal geometry with $\mathrm{sp}^{3}$ hybridization at nitrogen.

It should be a chiral molecule (assuming lone pair to be a substituent).
Thus, tertiary amines exist as racemic mixture but they cannot be resolved.


This is due to the reason that the energy difference between the isomer is very small ( $25 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). Hence, reapid nitrogen or amine inversin takes palce.


Enantiomers
Tertiary amine N -oxide has four group hence nitrogen inversion is not possible, thus tertiary amine -N -oxide can be resolved.
13.

15. $\mathrm{a} \& \mathrm{~b}$ are tautomers and a \& c are resonating structures.
16. Le $x$ is the $\%$ of $(+)$ 2-butanol.
$13.9 x-13.9(100-x)=-300$.
$\mathrm{x}=39.2, \%$ of d form $=39.2, \%$ of 1 form $=60.8$.
17.
(i)
 Hydroxyl bearing carbon is stereogenic centre,
(ii)

(iii)

(iv)
 It has no stereogenic centre.
18.
(i) $2 \mathrm{R}, 3 \mathrm{R}$
(ii) $2 \mathrm{~S}, 3 \mathrm{R}$
19.

21. (A) Positional
(B) Functional
(C) Metamerism
(D) Positional
(E) Functional
(F) Tautomerism
22.

Z-I, II, III, VI, VII; E-IV, V, VIII, IX, X, XI, XII
23.
(A) 2 ;
(B) 2
24.

(A) Tightly on stable keto dur to repulsion between $\alpha-\mathrm{CO}$ 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 $\mathrm{e}^{-}$donator group which causes repulsion in enolic form.
(D) Due to ester group acidic structure of active H decreases $\& \mathrm{C}=\mathrm{C}$ of enol undergoes cross resonance $>$
(E) Lowest enolic content because $<\mathrm{C}=\mathrm{O}$ is more stable than $<\mathrm{C}=\mathrm{C}<$ bond $]$

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25. 

Stable are : (A) diequatorial, (B)

, (C)

, (D)

(E)

(F)

26.
(A)

(B)

27.

(A) cis
(B) cis
(C) cis
(D) trans
(E) trans
(F) trans
29.

(B)
(C)
(Mechanism)

$\downarrow$

30. Position isomers, Functional isomers, Tautomers isomers, Geometrical isomers

31.
(i)

(ii)

(iii)

(iv)

(v)

(vi)

32. (i) 6 , (ii) 8 , (iii) 6 , (iv) 6
(i)

(ii)

(iv)

(ii)

33. (A) $4,1,2,3$, (B) $, 4,1,2,3$, (C) $1,3,2,4$, (D) $4,3,2,1$, (E) $2,4,3,1$, (F) $4,2,3,1$ (G) $3,1,4,2$ (H) $2,4,1,3$ (I) $3,2,1,4$ (J) $2,1,4,3$
34. 8

4 Optically active isomers

2 Optically active

2 Optically active
$2+2+4=8$
35. 12










36. [4]


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37. [4]

38. [5]

39. [7]
40. [10]

41. (A) $1 ;(\mathrm{B}) 1 ;(\mathrm{C}) 1 ;(\mathrm{D}) 1 ;(\mathbb{E}) 1$
42. [7]

43. [4]




44. [8]

(1)

(1)

(3)

(3)
45. 
46. $\quad[(\mathrm{A}) 3>1>2$; (B) $4>2>1>3]$
[ $3>1>2$ ]
47. [9]

Explanation:
Those isomers which can't show GI.


Those isomers which can show G.I.


51. [8]

Explanation:
Those isomer which can't show G.I.
Those isomers which can show G.I.







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52. [4]

(1)

(2)

(3)

(4)
53. $[3,1]$

54. [8]

$\mathrm{hv} \downarrow \mathrm{Cl}_{2}$

$\mathrm{hv} \downarrow \mathrm{Cl}_{2}$

55. [3]

## EXERCISE-5

## Part \# I : AIEEE/JEE-MAIN

17. $\mathrm{H}_{3} \mathrm{C}-\mathrm{HC}=\mathrm{CH}-\mathrm{CH}_{2}-\mathrm{Ph}$

Both double bonded carbon are differently disubstituted.

## Part \# II : IIT-JEE ADVANCED

18. Molecule is unsymmetrical
$\mathrm{n}=2$


Total stereoisomers $=2^{n}=2^{2}=4$
19.


Only three stereocentre are present.
$\therefore$ Total isomer $=2^{3}=8$
But one is optically inactive. (Meso compound)


So optically active $=8-1=7$

