

# **HINTS & SOLUTIONS**

#### **EXERCISE - 1**

Single Choice

 $C_3H_9N \rightarrow$ 1.

So C is correct option.

**5.**  $C_5H_{10} \rightarrow$  (1)  $CH_3-CH_2-CH_2-CH=CH_3$  (6)



(2)

 $CH_3 - CH = CH - CH_2 - CH_3$ 

(7)



(3)

(8)

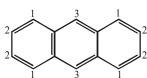
(10)

(4)

(9)

(5)

9. Anthracene



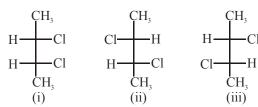
Only three types of hydrogen so only three structural isomers possible.

10.

$$\begin{array}{c} O \\ O \\ Ph-C-CH=CH-CH_3 \\ O \\ OD'(-DOH) \\ Ph-C-CH=CH-\mathring{C}H_3 \end{array} \longrightarrow \begin{array}{c} O^- \\ Ph-C=CH-CH-CH_2 \\ D_2O(-OD') \\ OD \\ Ph-C=CH-CH=CH_2 \\ Tautomerise \\ O \end{array}$$

Product will be

- 11. Ethene  $\rightarrow$  CH<sub>2</sub> = CH<sub>2</sub> Cannot show G.I. Propene  $\rightarrow$  CH<sub>3</sub> - CH = CH<sub>2</sub> Cannot show G.I. Butene  $\rightarrow$  CH<sub>3</sub> - CH = CH - CH<sub>3</sub> Show G.I. and it also show positional isomerism. CH<sub>3</sub> - CH<sub>2</sub> - CH = CH<sub>2</sub> and CH<sub>3</sub> - CH = CH - CH<sub>3</sub>
- OH  $CH_3 C CH_2 CH_3 \text{ exist in isomeric form.}$ H
  - (B)  $CH_3$ —C—H  $\longrightarrow$   $CH_3$  = CH exist in tautomeric form.
  - (C)  $CH_2 = CH Cl$  H no show G.I./or any isomers.
  - (D)  $\begin{array}{ccc} CH_2-CH_2 \\ I & I \\ Cl & Cl \end{array}$  exists in conformational form
- 14. A  $\rightarrow$  CH<sub>3</sub>—C=CH<sub>2</sub> isobutene CH<sub>3</sub>
  - $B \rightarrow \begin{array}{c} CH_3 \\ CH_3 \end{array}$  C=N-OH Acetone oxime
  - $C \rightarrow Ph$  C=N-OH Acetophenone oxime Show G.I.
  - $C \rightarrow Ph$  C=NOHBenzophenone
- 15.  $A \rightarrow \begin{array}{ccc} Cl & Cl \\ I & I \\ CH=CH-CH_2-CH_2-CH_3 & Show G.I. \end{array}$ 
  - $B \rightarrow \begin{array}{c} Cl \\ I \\ CH_2-CH=C-CH_2-CH_3 \text{ Show G.I.} \\ Cl \end{array}$
  - $C \rightarrow Cl$   $C=CH-CH_2-CH_2-CH_3-Not Show G.I.$
  - $D \rightarrow \begin{array}{c} Cl & Cl \\ I & I \\ CH_2-CH=CH-CH-CH_3 \text{ Show GI.} \end{array}$
- 17.  $CH_3$ —CH—CH— $CH_3$ total optical isomers = 3



(II) and (III) are optically active.

$$\begin{array}{c} CH_3-CH_2-CH-CH_3 \xrightarrow{Cl_2/hv} \\ \downarrow \\ CH_3 \end{array}$$

Products are

(I) 
$$CH_3$$
- $CH_2$ - $CH$ - $CH_2$ - $Cl$  (S) (II)  $C$ - $CH_2$ - $C$ - $CH_2$ C $H_3$  (R)  $H$ 

(III) 
$$CH_3$$
— $CH$ — $CH$ — $CH_3$  (S) (IV)  $CH_3$ — $CH$ — $CHCH_3$  (R)  $CH_3$ — $CH_3$  CI  $CH_3$  CI

Only (1) and (3) are optically active.

#### 20. $A \rightarrow$ Planar compound so optically inactive.

 $B \rightarrow$ Non planar and optically active due to absence of POS & COS.

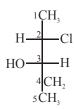
 $C \rightarrow$ Non planer but having POS so, optically inactive.

 $D \rightarrow$ Planar compound

meso tartartic acid

d-tartaric acid

They are diasteromers.



**25.** 

24.

R-S configuration of 2nd carbon

$$4 \xrightarrow{3} 1 \longleftrightarrow 2 \xrightarrow{1} S \xrightarrow{3} 3$$

R-S configuration of 3rd carbon.

$$1 \xrightarrow{2} 4 \longleftrightarrow 2 \xrightarrow{1 \text{ S}} 3$$

So option is (A)

#### **27** Mirror imageof D-ribose is known as L-form.

34. Higher Priority groups same side ⇒ Z - form
 Higher Priority groups opposite side ⇒ E - form
 2<sup>nd</sup> and 6<sup>th</sup> carbon is in E-form while 4th carbon is in Z-form.

$$H^{(2)} \xrightarrow{(1)} Z - \text{form}$$

$$(1) E \xrightarrow{(2)} H$$

$$(2) H \xrightarrow{(1)} (1) E - \text{form}$$

$$(1) E \xrightarrow{(2)} H$$

**35.** Alkyl group is different.

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. 
$$H_3C$$
  $E$ -form  $H_3C$   $H$ 

Ring will be Principle carbon chian so we assign numbering for ethylidene group ( $CH_3 - CH = C <$ ) 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 2-same 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

$$CH_3$$
  $H$   $C=C$   $H$   $CH_3$   $H$   $C=C$   $H$   $CH$ 

same compounds

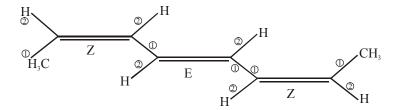
39. Higher Priority groups same side

$$=$$
 Z  $-$  form

Higher Priority groups oppsite side

$$= E - from$$

CH<sub>3</sub> – 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.

$$CH_3 \qquad OH \qquad Ph \qquad OH \qquad Ph \qquad OH$$

$$C = N \qquad C = N \qquad Ph \qquad C = N$$

$$G.I. \boxtimes \qquad H_3C \quad G.I. \boxtimes \qquad Ph \quad G.I. \boxtimes$$

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

H<sub>3</sub>C different group is absent instead of starred carbon.

$$H_3C_{M_3}$$
  $CH_3$   $GI. \boxtimes$ 

42. One chiral carbon Containing Compound always optially active.

$$\begin{array}{c} \operatorname{Br}_{|\bigstar|} \\ \operatorname{CH}_{3} - \operatorname{CH}_{2} - \operatorname{CH} - \operatorname{CH}_{3} \\ \end{array}$$
 (2-forms)

$$C_4H_9-Br$$
  $C-C-C-Br$   $C-C-C-C$   $C-C-C-Br$   $C-C-C$   $C-C$   $C-C-C$   $C-C$   $C-$ 

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

$$C - \stackrel{\bigstar}{C} - \stackrel{\bigstar}{C} - C$$
C1 C1 Active isomer =  $2^{n-1} = 2^{2-1} = 2$ 

Where n = Number of chiral carbon

# EXERCISE - 2

# Part # I : Multiple Choice

5. (A)  $CH_3$ —C—H  $\longrightarrow$   $CH_2$ =C—H No GI.

8. (A) C=N Show GI. (a not equal to b)

(B) Show G.I.

(C) 
$$CH_3$$
  $C=N$   $C=N$   $CH_3$   $C=N$   $CH_3$   $C=N$   $CH_3$   $C=N$   $C=N$   $CH_3$   $C=N$   $C=N$   $CH_3$   $C=N$   $C=N$   $CH_3$   $C=N$   $C=N$   $CH_3$   $C=N$   $C=N$ 

(D) N=N Show GI.

11. (A) H H POS present

12. 
$$A \rightarrow \begin{array}{c} H \\ COOH \end{array}$$
 POS present

$$B \rightarrow H$$
 COOH COS present

$$C \rightarrow H \qquad H \qquad POS \text{ present}$$

$$D \rightarrow \begin{array}{c} H \\ CH_3 \\ CH_3 \end{array}$$
 No POS and COS present

13. (A)  $CH_3 - CH_2 - CH_3$  chiral carbon So optically active.

(B) 
$$H$$
 C=CH -CH<sub>2</sub>-CH=C $H$  optically inactive

(C) H C=C=C=C Does not contain POS or COS so optically active.

(D) Does not contain POS or COS because both benzene rings are 
$$\bot$$
 to each other.

- **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.

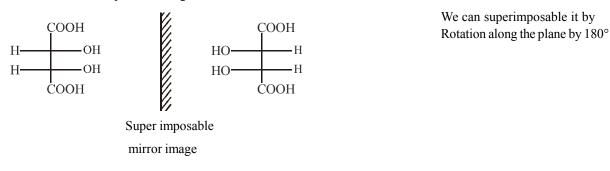
20. Single chiral carbon have two form dextrorotaory and laevorotatory.

Chiral carbon or Asymmetric carbon is always stereo centre.

Ether and alcohol are functional isomers.

21. POS or COS both present.

Meso is achiral compound having minimum two chiral carbon.



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.

#### 23. Check conformers of the compounds

$$(A) \\ H_{3}C \\ OH \\ OH \\ OH \\ CH_{3} \\ CH_{3}$$

(D) 
$$H_3C$$
 OH OH rotation of from carbon by 120° anticlock wise  $H_3C$  HO H (same compound)

## 24. Check R/S configuration

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

$$\begin{array}{c|ccccc} CH_3 & CH_3 & CH_3 \\ H & OH & H & OH \\ H & OH & OH & H & OH \\ \hline \\ C_2H_5 & C_2H_5 & C_2H_5 & C_2H_5 \end{array}$$

**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)

Non - Planer POS x COS x (Resolvable)

**26.** Two different group – H and –CH<sub>3</sub> is present.

When two groups (Bulky) are at 60° Dihedral angle is known as sancle form

Part # II : Assertion & Reason

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

$$C = \frac{169 \,\mathrm{gm}}{845 \,\mathrm{gm}} \quad l = 2 \,\mathrm{dm}$$

$$[\theta^{\circ}] = \frac{\theta}{Cl} = \frac{9.6}{169/845 \times 2} = -24^{\circ}$$

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

RM = 100 - optical of purity= 100 - 83.33 = 16.66%

(-) MSG total in mixture 
$$\Rightarrow$$
 83.33%  
 $+8.33\%$   
 $91.66\%$ 

3. 
$$[(+) MSG \Rightarrow 33.8 \text{ gm in } 338 \text{ ml}]$$

(-) MSG  $\Rightarrow$  16.9 gm in 169 ml

Optical purity in mixture (+) MSG = 16.9 gm in 507 ml solution

$$C = \frac{16.9}{507} \text{ gm/ml}$$

$$l=4 \, \mathrm{dm}$$

$$\theta_{Observed} = [\theta^{\circ}] \times C.l.$$

$$=24 \times \frac{16.9}{507} \times 4 = +3.2\%$$

#### Comprehension #5:

1. 
$$[(A) CD_2 = C - P]$$

2. (A) 
$$CH_2 = C$$
 $H$ 

Repulsion can be minimized by rotation pairs

Antiaromatic

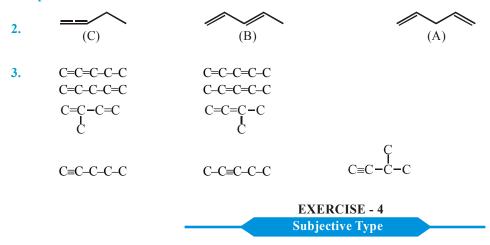
When tautomerize enol is antiaromatic while

Keto form is unstable due to repulsion between lone

#### Aromatic

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

#### Comprehension #6:



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.

$$\begin{array}{c|c} Cl & Cl & Cl \\ \hline \end{array}$$

- 3. There are 7. 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, diethyl ether, methyl propyl ether, and methylisopropyl ether.
- 4. 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 +ve charge are parallel. So the electrons may be delocalized. The +ve charge is effectively spread out over two carbons; delocalized.

$$\begin{array}{c} H & \nearrow \pi \text{-orbital} \\ H & \nearrow C & \nearrow \text{empty orbital} \\ H & \nearrow H & \nearrow H \end{array}$$

$$CH_{,=} CH - \overset{\scriptscriptstyle +}{C}H_{,-} \longleftrightarrow \overset{\scriptscriptstyle +}{C}H_{,-} - CH = CH$$

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.

6. Only CHBr = CHCl can exist as geometric Isomers:

$$\frac{Br}{H}C = C \underbrace{Cl}_{H} \text{ and } \frac{Br}{H}C = C \underbrace{Cl}_{Cl}$$

In  $CH_2CI - CH_2CI$  and  $CH_2CI - CH_2Br$ , 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. In  $CH_2CI_2$ , 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  $p\pi$  conjugation between fluorine and carbon will be more effective than between chlorine and carbon.
- 9. III > IV > I > II
- 11. (A) -Br > -CH, CH, OH > -CH, CH, > -H,
  - (B) -OH > -COOCH<sub>3</sub> > -COOH > -CH<sub>2</sub>OH
  - (C) -NH<sub>2</sub>>-CN>-CH<sub>2</sub>NHCH<sub>3</sub>>-CH<sub>2</sub>NH<sub>2</sub>
  - (D) -Br>-Cl>-CH<sub>2</sub>Br>-CH<sub>2</sub>Cl
- 12. Tertiary amines have pyramideal geometry with sp<sup>3</sup> 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 kJ mol<sup>-1</sup>). Hence, reapid nitrogen or amine inversin takes palce.

$$R_1$$
 $R_2$ 
 $R_3$ 
 $R_2$ 
 $R_3$ 
 $R_3$ 
 $R_4$ 
 $R_4$ 
 $R_5$ 
 $R_7$ 
 $R_8$ 
 $R_8$ 
 $R_8$ 
 $R_8$ 
 $R_8$ 
 $R_9$ 
 $R_9$ 

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

13. 
$$\overrightarrow{CH_2} = \overrightarrow{CH} - \overrightarrow{N}H - \overrightarrow{CH_3}$$

$$\overrightarrow{CH_2} - \overrightarrow{CH} = \overrightarrow{N}H - \overrightarrow{CH_3} \text{ (this shows Geometrical isomerism)}$$

- 15. a & b are tautomers and a & c are resonating structures.
- 16. Le x is the % of (+) 2-butanol.

$$13.9 \times -13.9 (100 - x) = -300.$$

x = 39.2, % of d form = 39.2, % of 1 form = 60.8.

17. (i) Hydroxyl bearing carbon is stereogenic centre,

(ii) 
$$^{5=2}$$
  $^{3=4}$   $^{2=5}$  It has no stereogenic cetre.

- Br | CH<sub>3</sub>-CH<sub>2</sub>-CH CH<sub>2</sub>-CH<sub>3</sub> It has no stereogenic centre.
- **18.** (i) 2R, 3R (ii) 2S, 3R

- 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. 
$$O$$
 >  $O$  >  $O$  >  $O$  O  $O$  O

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

25. Stable are : (A) diequatorial, (B) 
$$H_3C_2$$
  $H_3C_2$   $H_3C_3$   $H_3C_4$   $H_3C_5$   $H_3C_5$   $H_3C_5$   $H_3C_5$   $H_3C_5$ 

(E) 
$$CHMe_2$$
  $C_2H_5$  (F)  $C_2H_5$ 

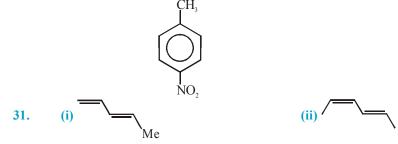
- **28.** (A) cis (B) cis (C) cis (D) trans (E) trans (F) trans
- 29. Ph-C = CH Ph-C-CH<sub>2</sub>
  OH OH O OH
  (B) (C)

(Mechanism)



$$\begin{array}{c|cccc} Ph-C-CH_2 & \xrightarrow{(-OH^{\bullet})} & Ph-C-\overset{\bullet}{C}H \\ \hline & & & & & & & & & & \\ O & OH & & & & & O & OH \\ \hline & & & & & & & & \\ & & & & & & & & \\ \end{array}$$

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



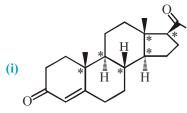
(iii) 
$$C_2H_5$$

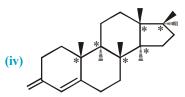
$$\begin{array}{c|c} & Pr & \\ \hline & & \\ & & \\ CH_3 & \end{array}$$

(v) Br 
$$C_3H_7$$
  $C_2H_5$ 

$$\begin{array}{c|c} CH_3 \\ \text{(vi)} & H & Br \\ \hline & H & Br \\ \hline & CH_3 \end{array}$$

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

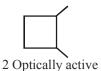




- $\textbf{(A)} 4, 1, 2, 3, \textbf{(B)}, 4, 1, 2, 3, \textbf{(C)} 1, 3, 2, 4, \textbf{(D)} 4, 3, 2, 1, \textbf{(E)} 2, 4, 3, 1, \textbf{(F)} 4, 2, 3, 1 \textbf{(G)} 3, 1, 4, 2 \textbf{(H)} 2, 4, 1, 3 \textbf{(I)} 3, 2, 1, 4 \textbf{(J)} 2, 1, 4, 3 \textbf{(I)} 3, 2, 1, 4 \textbf{(J)} 2, 1, 4, 3 \textbf{(I)} 3, 2, 1, 4 \textbf{(I$ 33.
- 34.



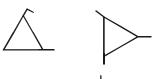
4 Optically active isomers





2+2+4=8

**35.** 12



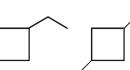




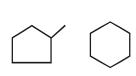












**36.**  $CH_3 - CH_2 - CH_2 - CH = CH - CH_3 \Rightarrow cis and trans$  $CH_3$ - $CH_2$ -C=CH- $CH_3$   $\Rightarrow$  cis and trans  $CH_3$ -CH-CH=CH- $CH_3$   $\Rightarrow$  cis and trans  $CH_3$ 

37. [4]
$$CH_{3}-CH_{2}-CH_{2}-CH=CH-CH_{3} \Rightarrow cis \text{ and trans}$$

$$CH_{3}-CH_{2}-C=CH-CH_{3} \Rightarrow cis \text{ and trans}$$

$$CH_{3}$$

$$CH_{3}-CH-CH=CH-CH_{3}$$

$$CH_{3}$$

**38.** [5]

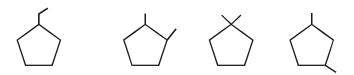
$$\begin{array}{c} OH \\ \hline \\ OH \\ \hline \\ CH_3 \end{array}, \begin{array}{c} OH \\ \hline \\ CH_3 \end{array}, \begin{array}{c} O-CH_3 \\ \hline \\ CH_3 \end{array}, \begin{array}{c} CH_2-OH \\ \hline \\ CH_3 \end{array}$$

**40.** [10]

$$Cl$$
 $Br$ 
 $Cl$ 
 $Br$ 
 $Cl$ 
 $Br$ 
 $Cl$ 
 $Br$ 

- **41.** (A) 1; (B) 1; (C) 1; (D) 1; (E) 1
- **42.** [7]

**43.** [4]



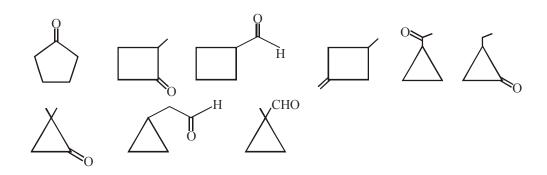
44. [8]

- **45. (A)** [4>1>3>2], **(B)** [3>1>4>2]
- **46.** [(**A**) 2; (**B**) 2; (**C**) 1; (**D**) 2; (**E**) 1]
- 47. [(A) 3>1>2; (B) 4>2>1>3]
- 48. [3>2>4>1]

- **49.** [3>1>2]
- **50.** [9]

Explanation:

Those isomers which can't show GI.



Those isomers which can show G.I.





Explanation:

Those isomer which can't show G.I.

Those isomers which can show G.I.



$$C=C-C-C-C$$

**52.** [4]



$$\begin{array}{c|c}
CH_3 & H \\
Cl & H \\
CH_3 & H
\end{array}$$

$$\begin{array}{c|c}
CH_3 & H \\
CH_3 & H
\end{array}$$

$$\begin{array}{c|c}
CH_3 & H \\
CH_3 & H
\end{array}$$

**53.** [3, 1]

**54.** [8

R
S
[8]
$$CH_3$$

$$Cl_2$$

$$hv \downarrow Cl_2$$

$$CH_3$$

$$+ \text{ enantiomer}$$

$$hv \downarrow Cl_2$$

$$CH_3$$

$$Cl_2$$

$$CH_3$$

**55.** [3]

#### EXERCISE - 5

# Part # I : AIEEE/JEE-MAIN

17.  $H_3C-HC=CH-CH_2-Ph$ Both double bonded carbon are differently disubstituted.

# Part # II : IIT-JEE ADVANCED

**18.** Molecule is unsymmetrical

$$n = 2$$

Total stereoisomers =  $2^n = 2^2 = 4$ 

Only three stereocentre are present.

$$\therefore$$
 Total isomer =  $2^3 = 8$ 

But one is optically inactive. (Meso compound)

So optically active = 8 - 1 = 7

