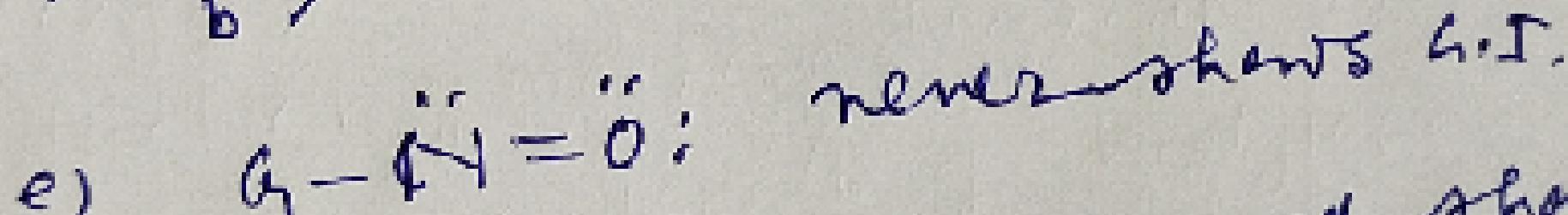
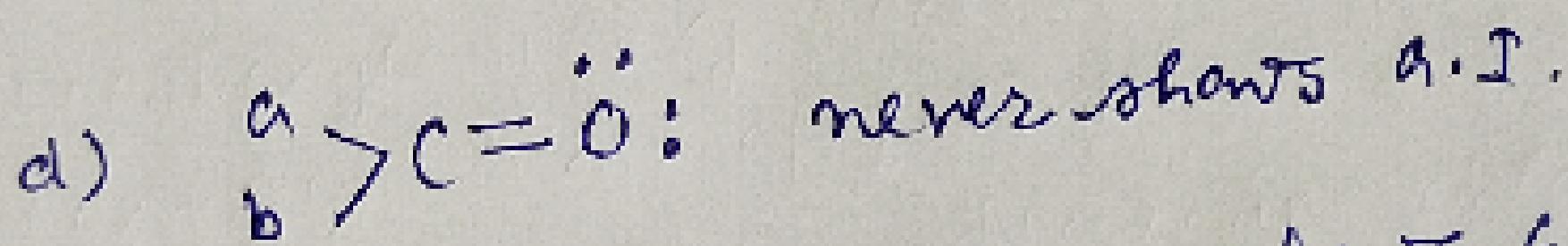
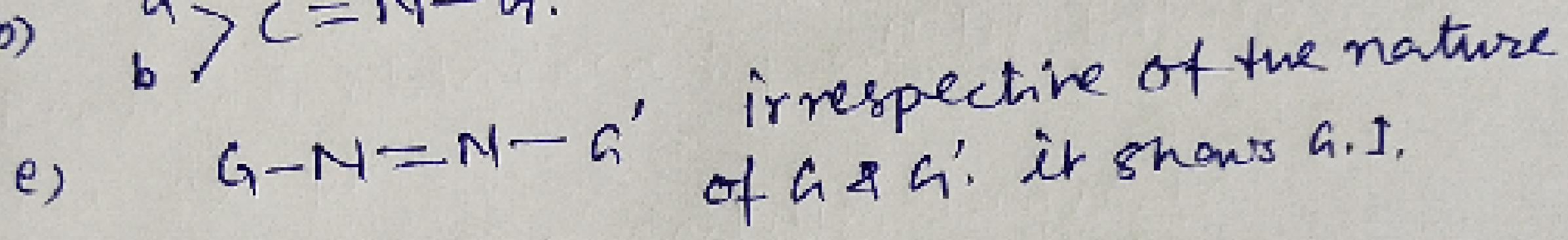
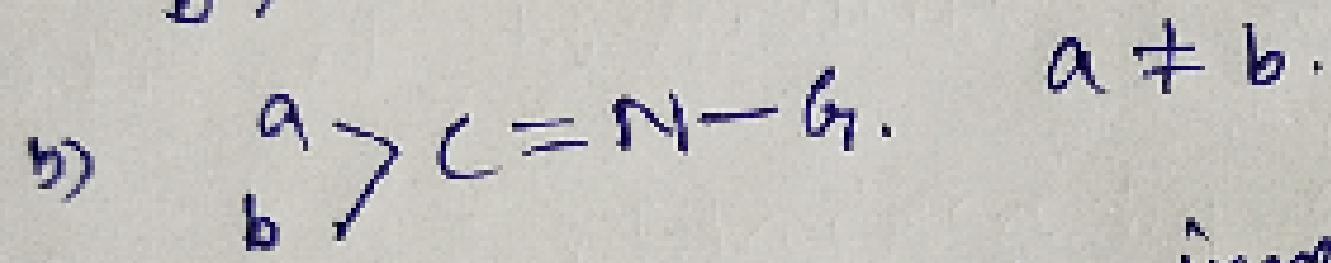
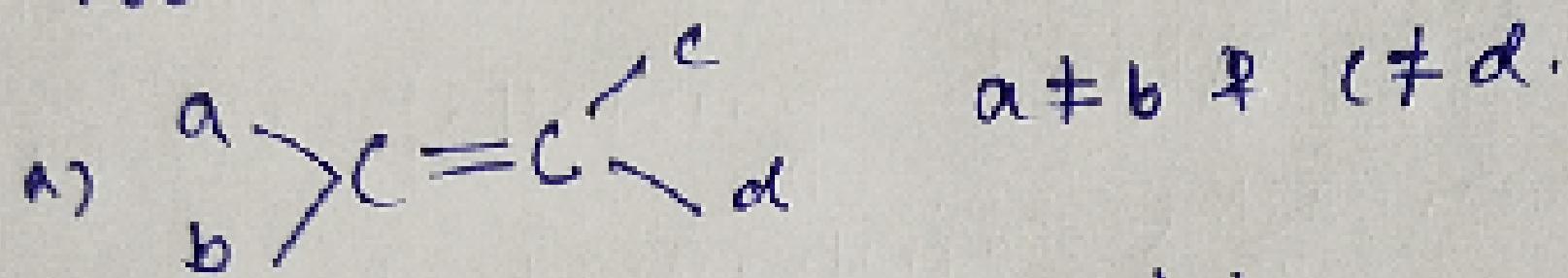


Geometrical Isomerism:

1

It is applicable for those systems where different spatial arrangements of groups or atoms in a molecule around the rigid double bond or a cyclic structure. It is also denoted cis-trans isomerism or E-Z isomerism.

The following systems can show geometrical isomerism under condition.



Which of the following compound shows G.I?

a) But 2ene : yes

b) 1-Phenyl but 1ene. : yes.

c) Azobenzene ($\text{Ph-N}=\text{N-Ph}$)

d) Hypo Nitro acid (dimer) : Yes.

e) Nitro acid having molecular formula: $\text{H}_2\text{N}_2\text{O}_2$: No.

f) Styrene (Ph-CH=CH_2) :

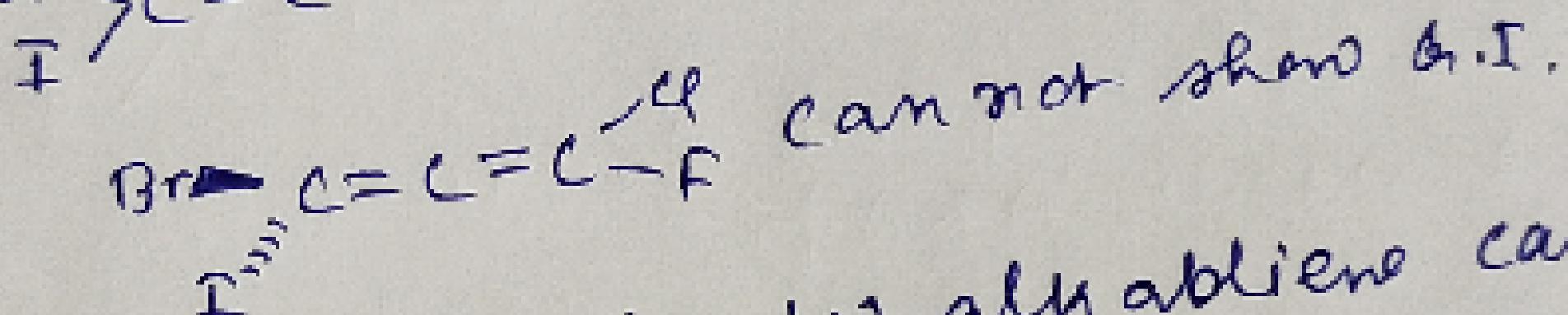
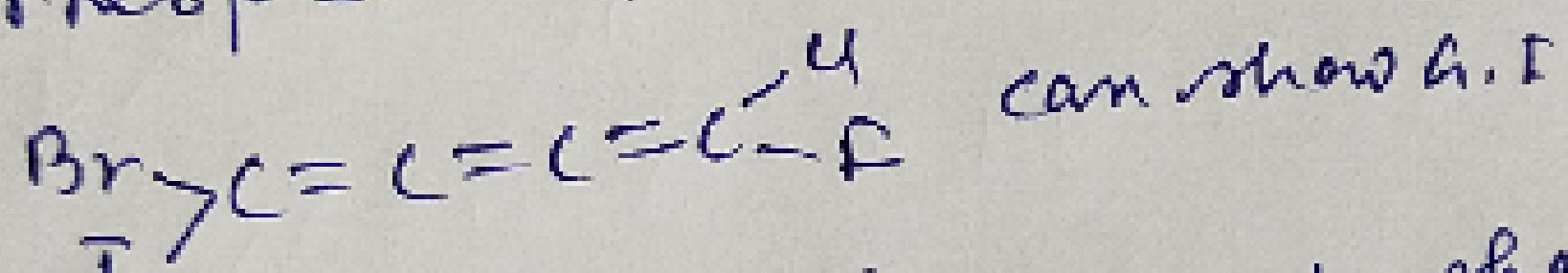
g) Stilbene (Ph-CH=CH-Ph) : Yes.

h) Oxime of acetaldehyde : Yes.

2

b) Condition for G.I. in alkene system.

- ⇒ With odd number of double bond
Alkene system can show G.I. provided terminal groups of every terminal carbon atom are different.
- ⇒ With even number of double bond, as terminal groups are not in the same plane then they can not show geometrical isomerism. irrespective of its nature.

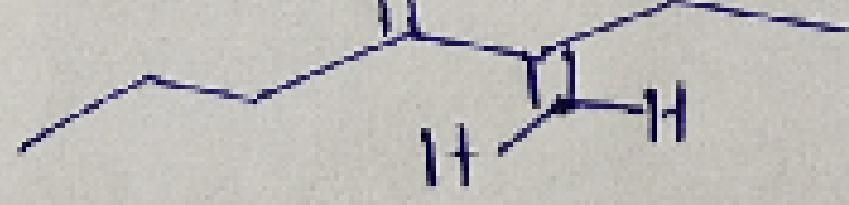


⇒ Isolated & conjugated alkadiene can not show geometrical isomerism.

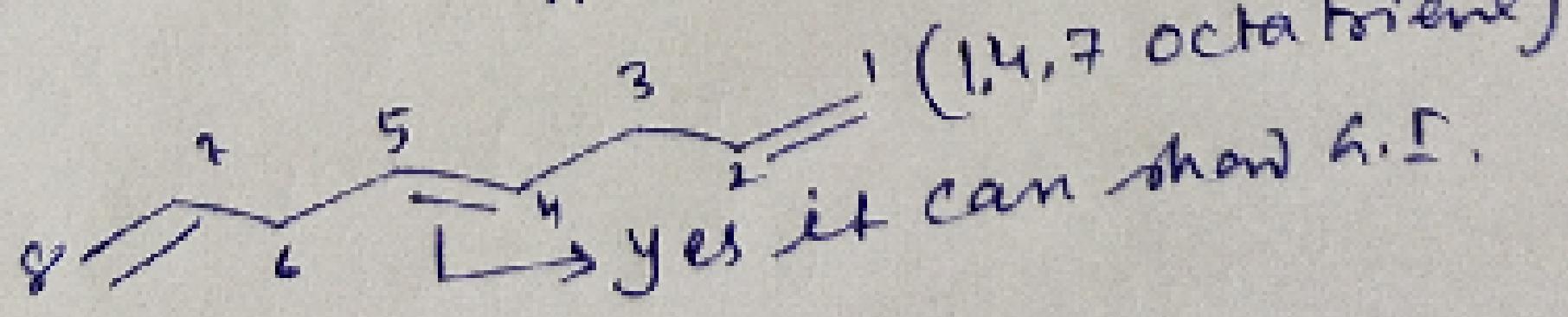


a) $\text{H} > \text{C}=\text{CH}-\text{(CH}_2)_3-\text{CH}=\text{CH}_2$ yes. $\text{H} \rightarrow \text{CH}_2$ → yes it can show G.I.

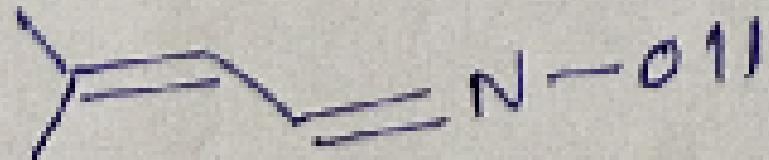
b)



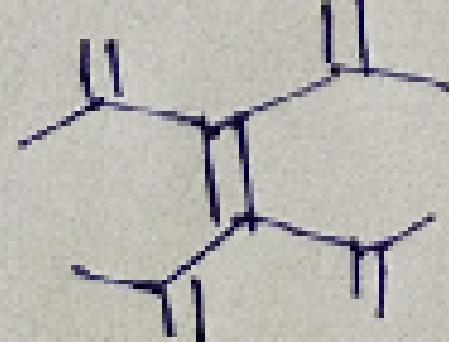
c)



d)

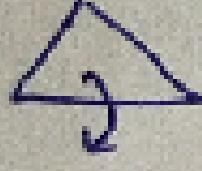


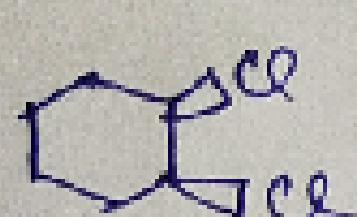
e)



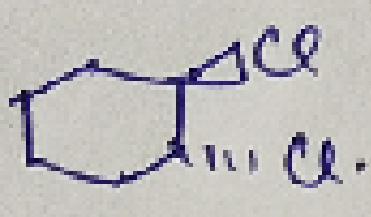
no double bond can show G.I.

Condition for Geometrical Isomerism in Cycloalkane. 3

\Rightarrow  Cycloalkane because of single bond free rotation, it can show G.I provided any (at least) two carbon atom has different groups/atoms attached with individual ring atom.



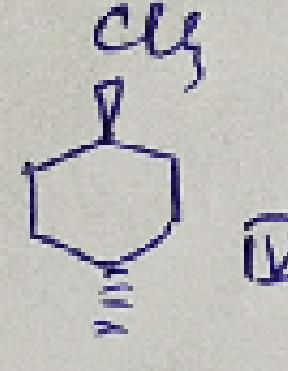
Cis isomer
(I)



Trans isomer
(II)



Cis isomer



Trans isomer

I, II & III, IV are related as Geometrical isomers

Points to be noted

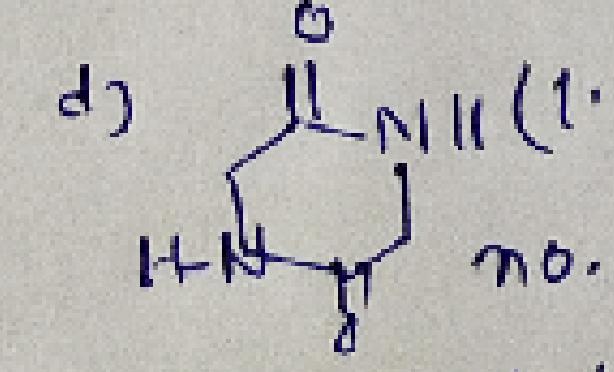
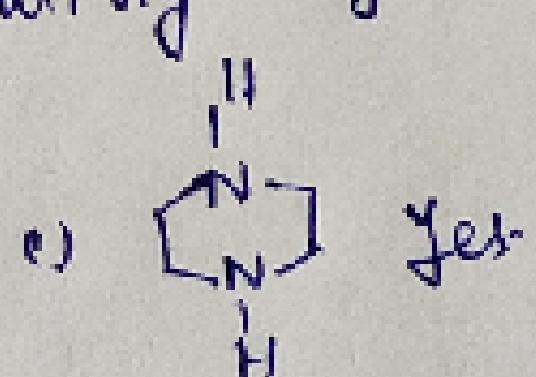
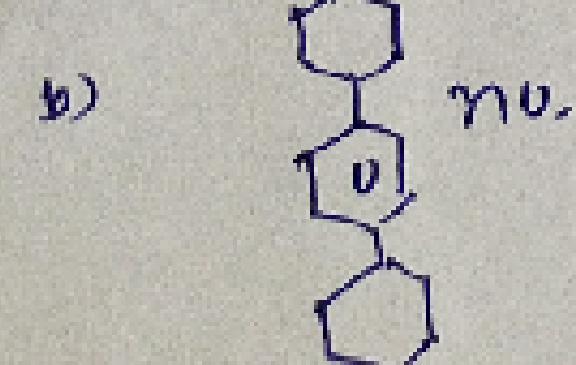
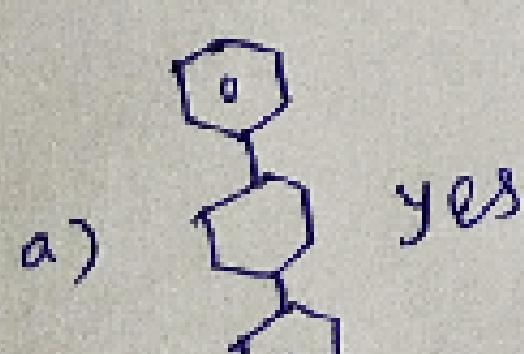
\Rightarrow Monosubstituted cycloalkane can not show G.I.

\Rightarrow 1,1 disubstituted cycloalkane can not show G.I.

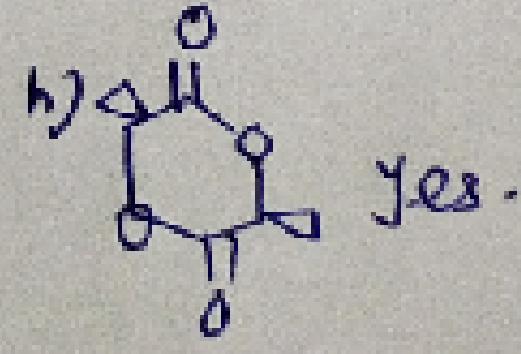
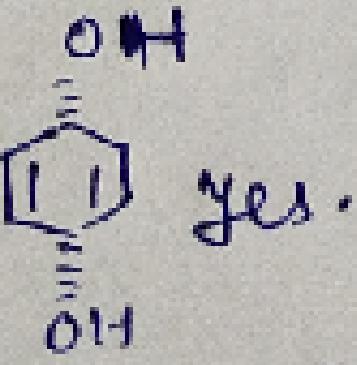
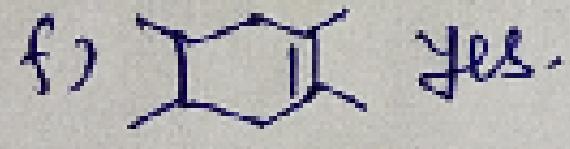
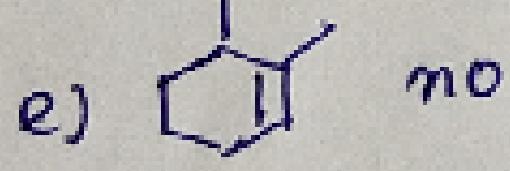
\Rightarrow 1,1,1 disubstituted cycloalkane

\Rightarrow 1,2; 1,3; 1,4 disubstituted cycloalkane always shows G.I.

\Rightarrow Whiching the following system shows Geometrical Isomerism?



lone pair delo
(elisa; sp^2 hybridized)
G.I not possible



i) G.I of spiro/ring with = bond system

4



I Even no. of rings in spiro

system can not show G.I when the terminal groups are not in the same plane.

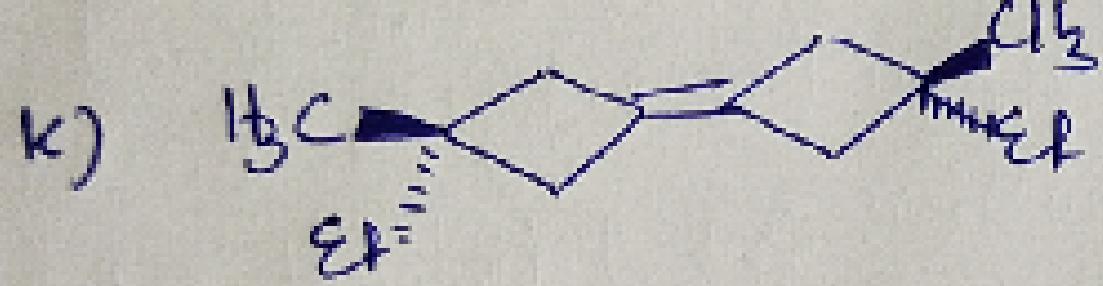
j)



Odd no. of rings in

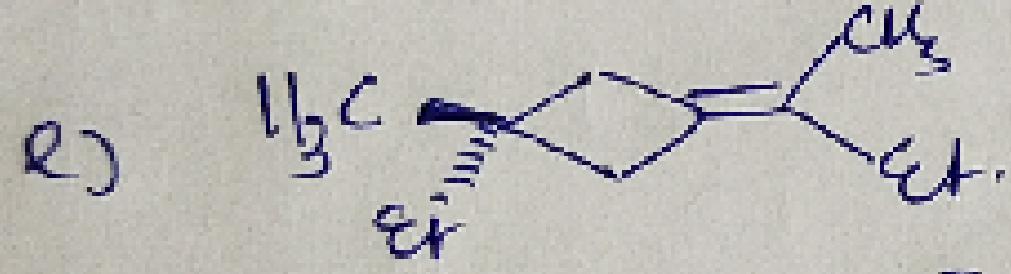
spiro system can show G.I when the terminal groups are in the same plane & fermi-carbon having different groups/atoms.

k)



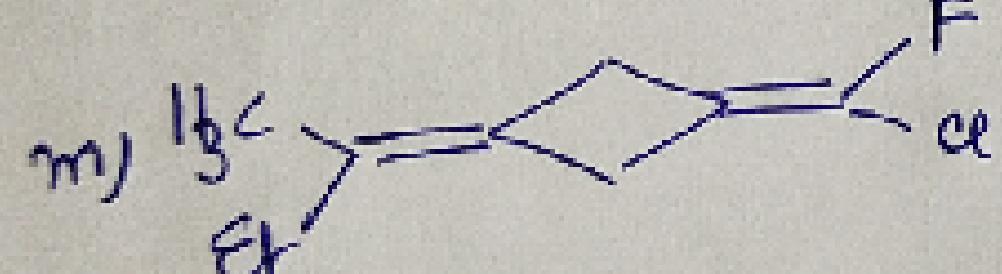
G.I possible

l)



G.I not possible.

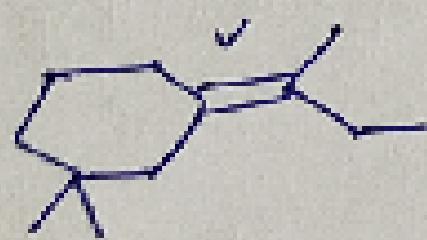
m)



G.I possible.

yes G.I possible about
the indicated(+) double bond.

n)



no G.I not possible.

o)



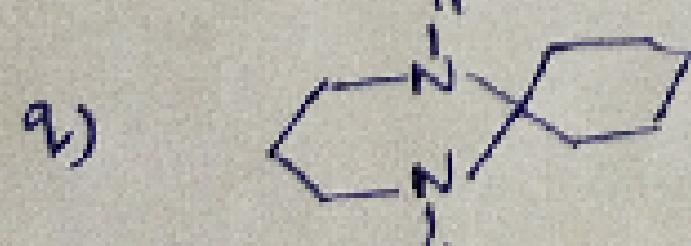
no G.I not possible.

p)



G.I possible.

q)

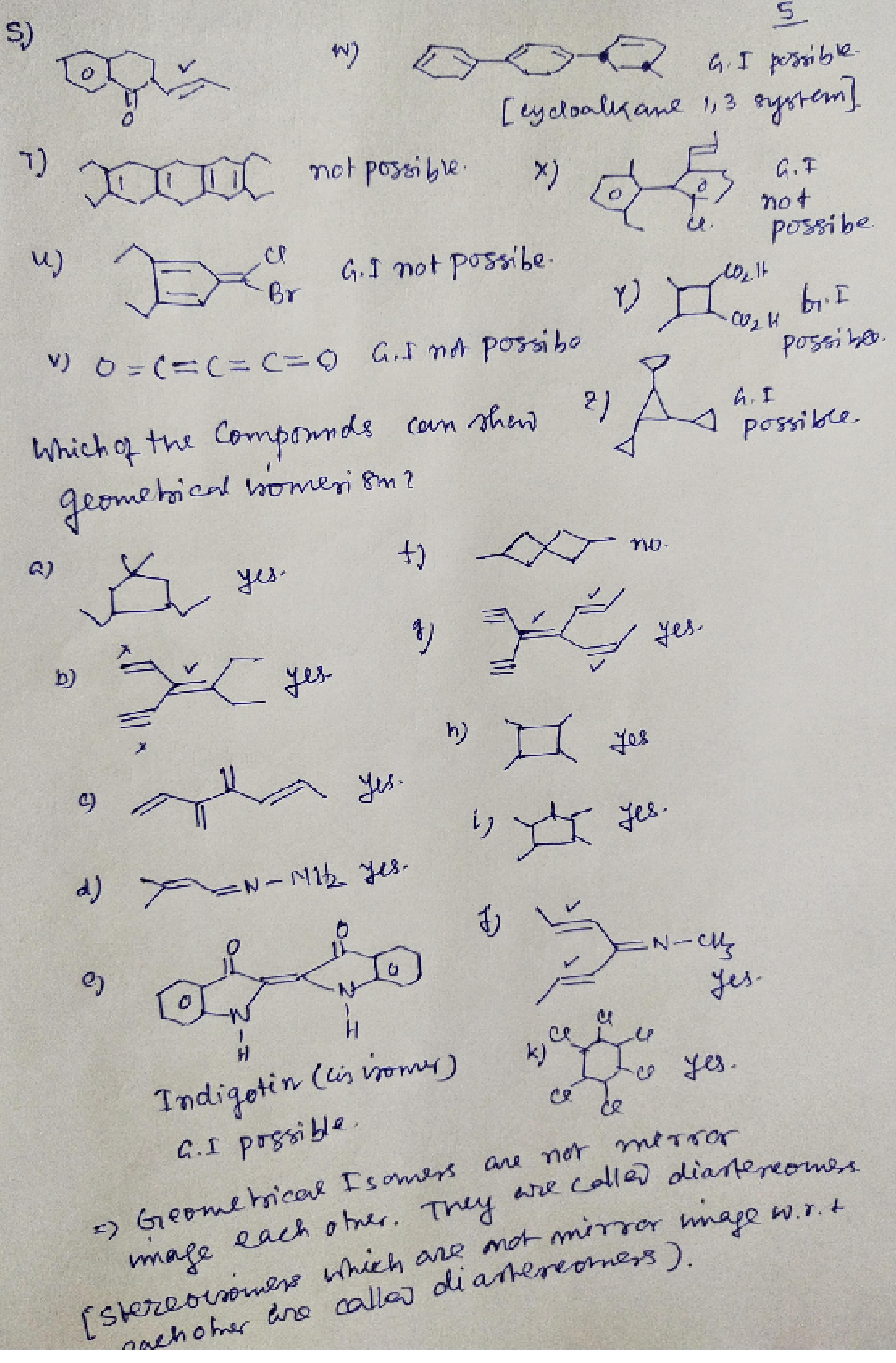


G.I possible.

r)



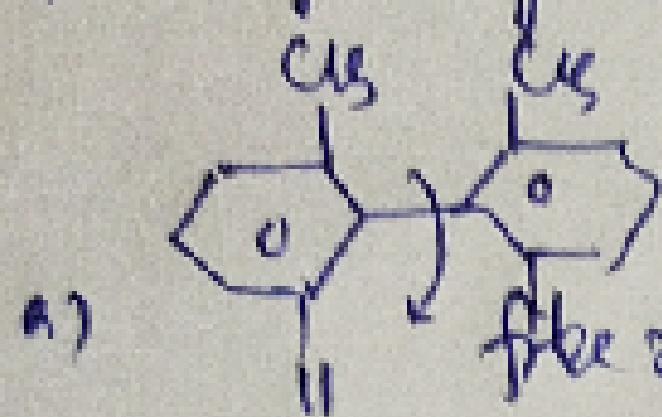
G.I possible.



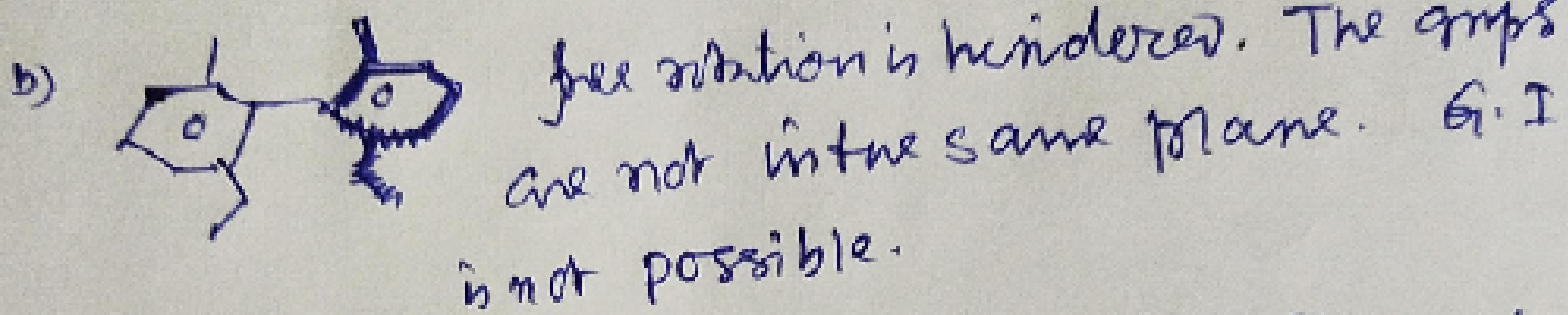
G.I in Biphenyl & Triphenyl System.

6

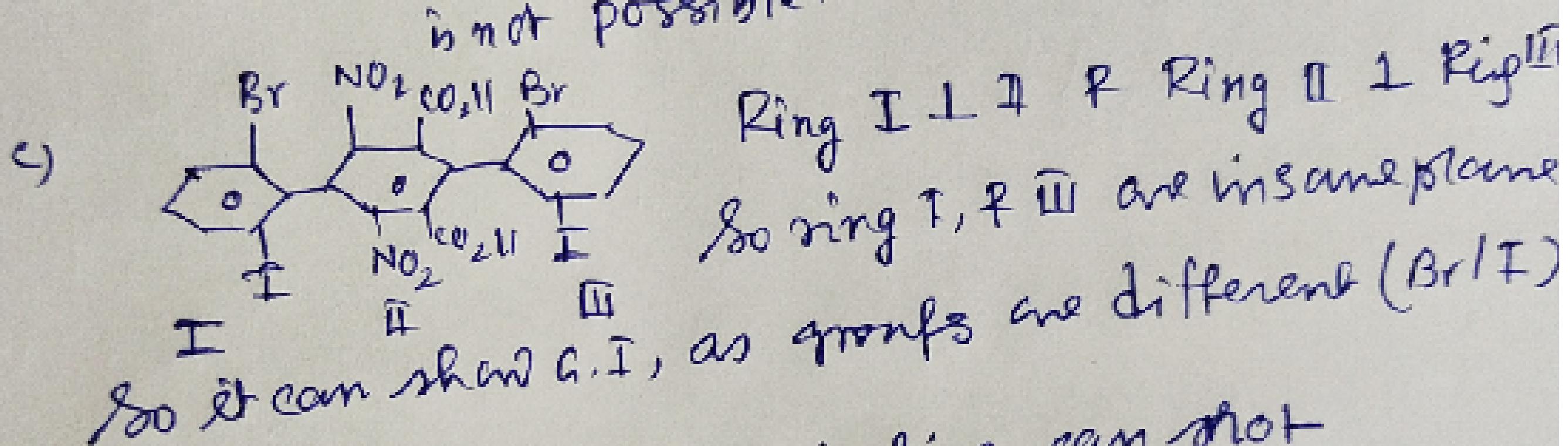
Biphenyl system does not show G.I.



a) free rotation can take place. Qo. no. G.I.



free rotation is hindered. The groups are not in the same plane. G.I. is not possible.



Ring I \perp Ring II & Ring II \perp Ring III
So ring I, & III are in same plane
So ring I, & III are different (Br/I)

So it can show G.I., as groups are different (Br/I)

b) Benzene & its derivative can not show geometrical isomerism.



c)
It shows G.I.; not because of benzene ring but because of (=CH system).

f) $\text{CH}_2-\text{CH}=\text{CH}_2-\text{CH}_2-\text{CH}_3$ yes. [all 5 double bond shows G.I.]

g)

no, it can not show G.I.

PhCH=CH-CO₂H

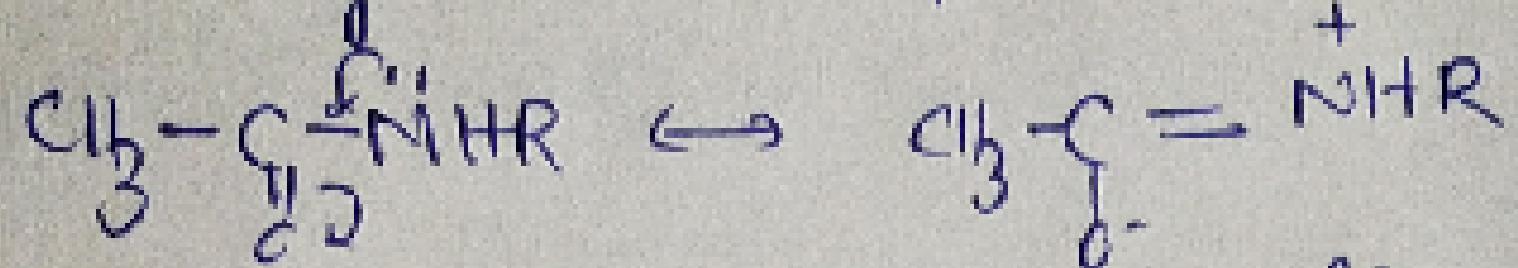
i) Cinnamic Acid: yes. PhCH=CH-CO₂H

j) Cinnamaldehyde: yes. PhCH=CH-CO₂H

k) Acrolein: no. CH₂=CH-CO₂H

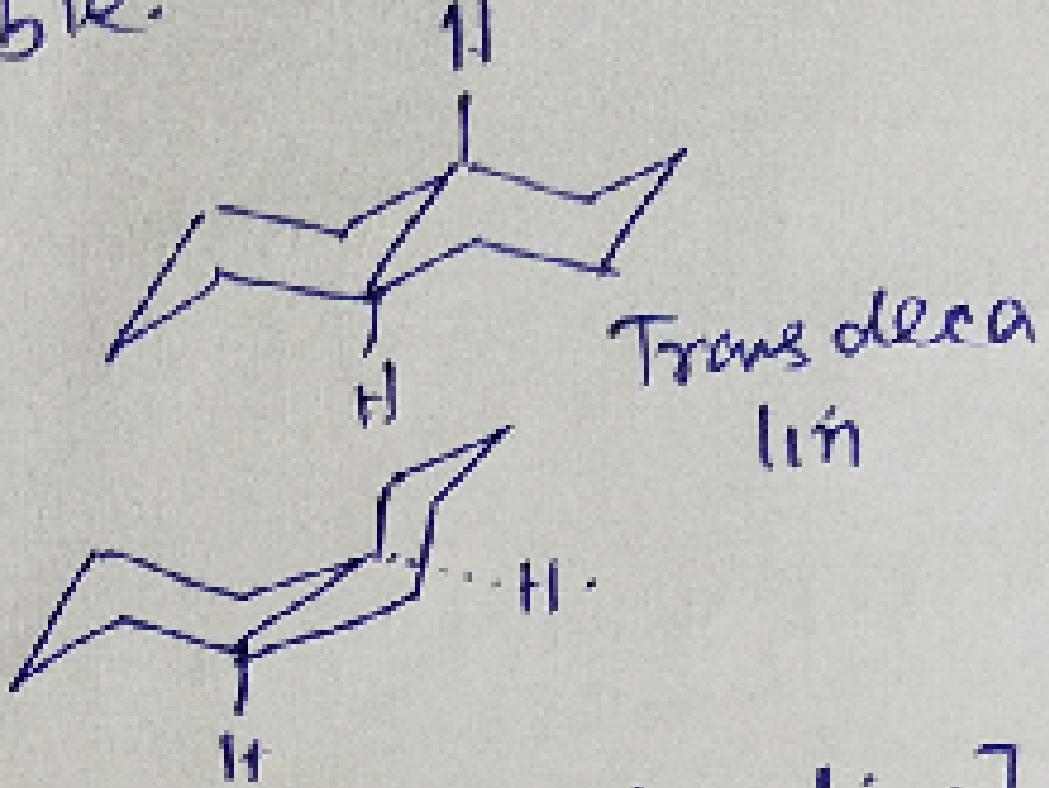
l) Crotonaldehyde: yes. CH₂-CH=CH-CO₂H

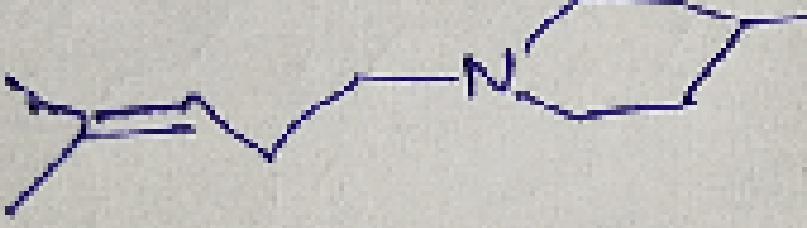
⇒ Resonating structures of amide can ~~not~~ show G.I. 7



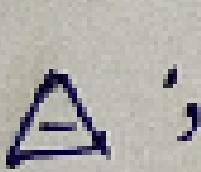
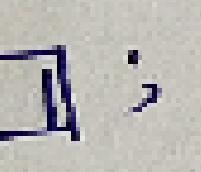
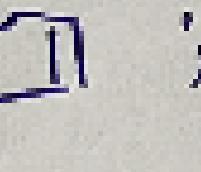
due to double bond character it undergoes restricted rotation. So G.I. is possible.

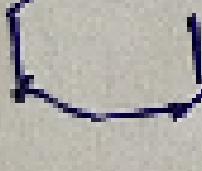
⇒  decalin can show G.I.



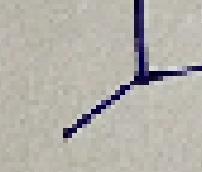
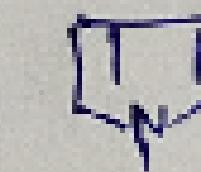
⇒  yes. [due to cyclic structure].

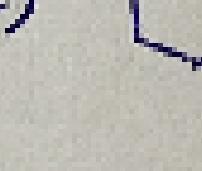
⇒ Cycloalkene can show G.I. when $n > 7$.

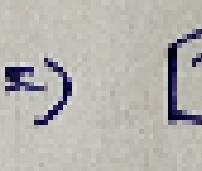
⇒  ;  ;  ;  can not show geometrical isomerism.

⇒  always shows G.I.

⇒  yes. ⇒  yes ⇒  no.

⇒  yes. ⇒  yes ⇒  no

⇒  no. ⇒  yes

⇒  yes. ⇒  yes. ⇒  no. (THF)

⇒ Benzophenone oxime can not show G.I.

⇒ Minimum carbon shown required to

show Geometrical isomerism = 0.

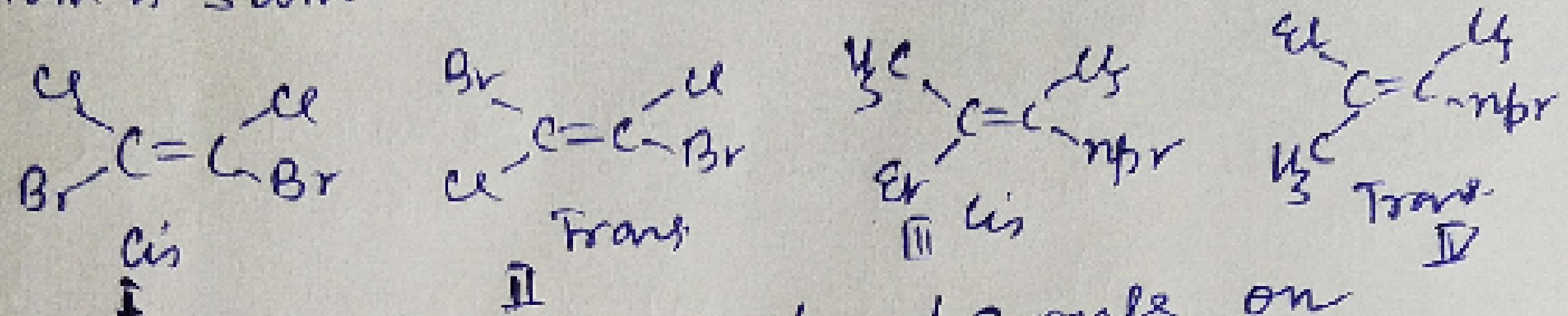
are related as
Geometrical Isomers.

⇒  vs 

Nomenclature of Geometrical Isomerism:

i) cis Trans isomerism

It is applicable for $C=C$ system where at least one pair of groups/atom on adjacent carbon atom is same.



In I & II, the both pair of atoms/ groups on adjacent carbon atom is identical. In III & IV one pair of atom/ groups on adjacent carbon atom is identical. In (i) & (ii) system, cis trans isomericism is applicable. or $G'''=G$. or $G''=G'$.

$$G/G' \equiv G''/G''' \text{ or at least } G=G'' \text{ or } G=G'$$

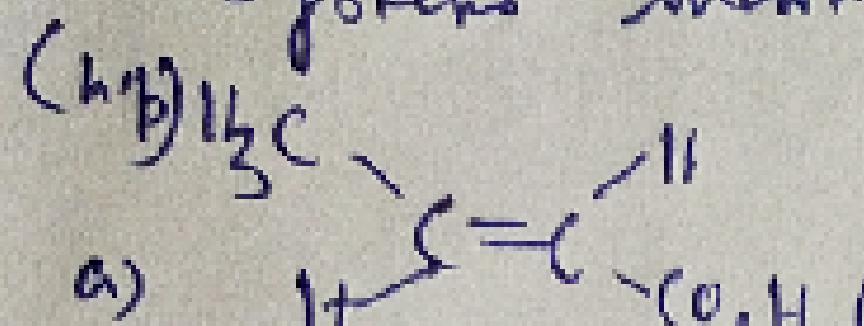
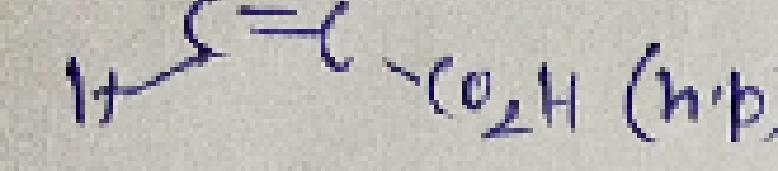
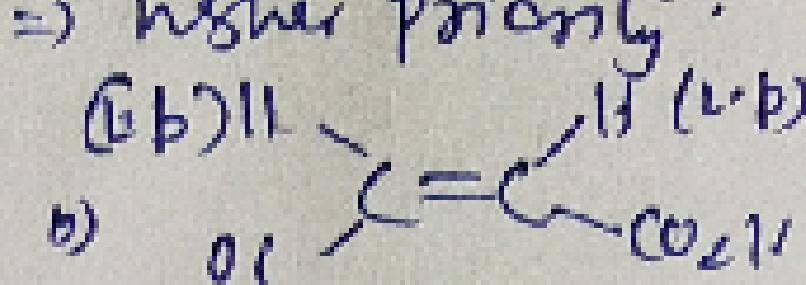
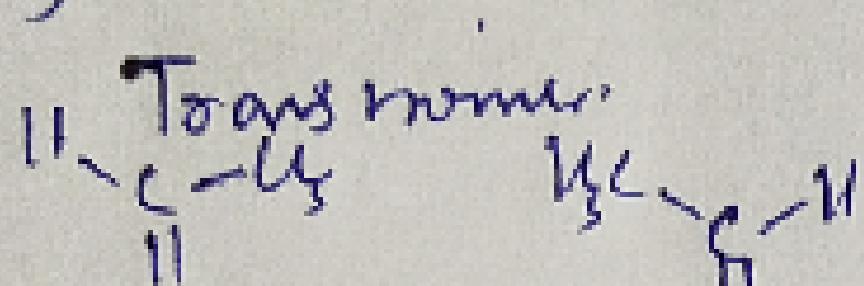
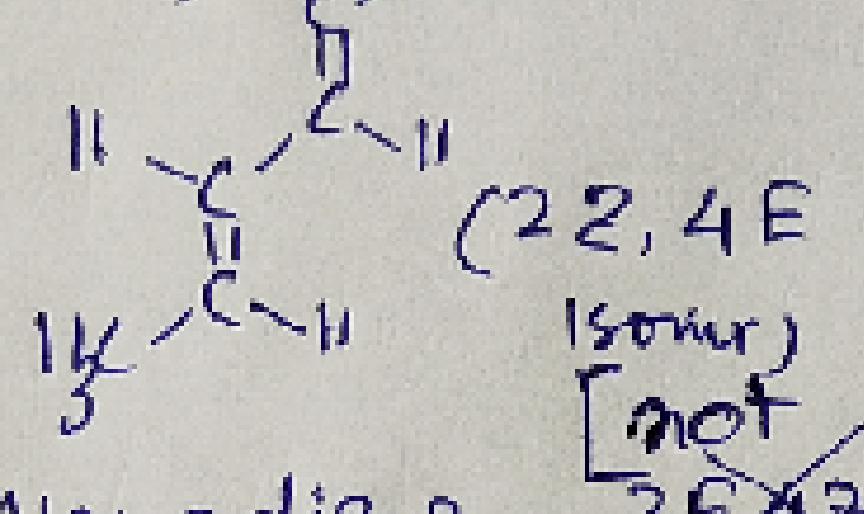
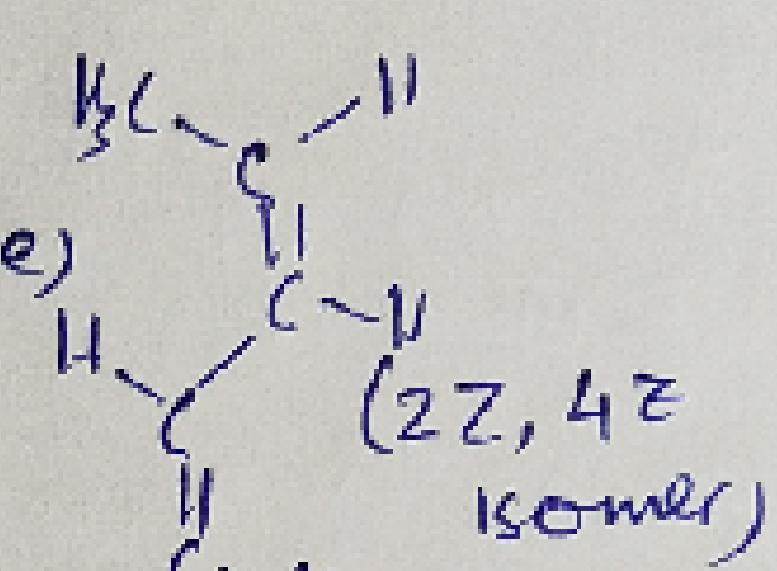
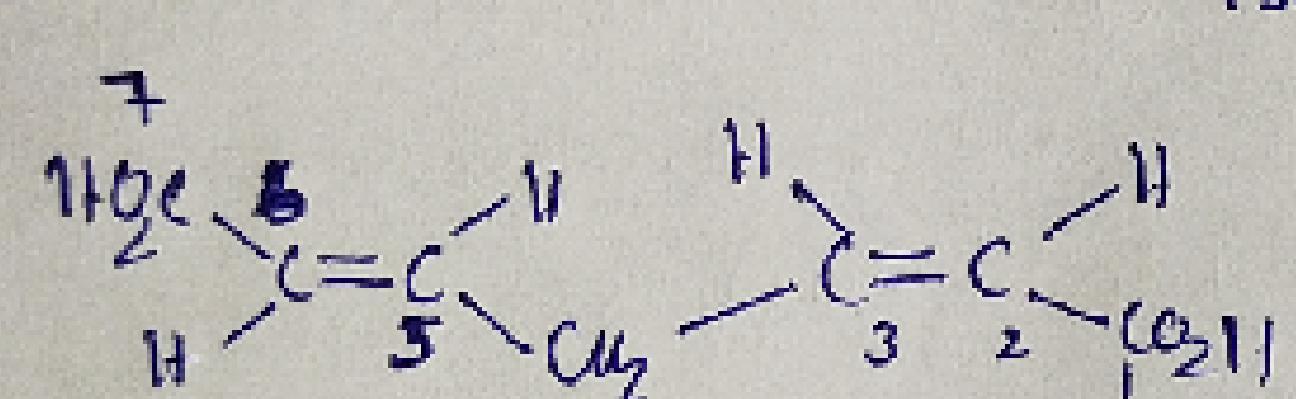
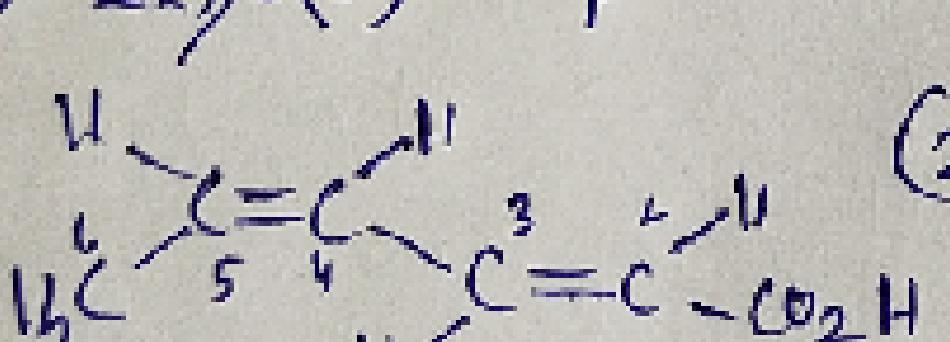
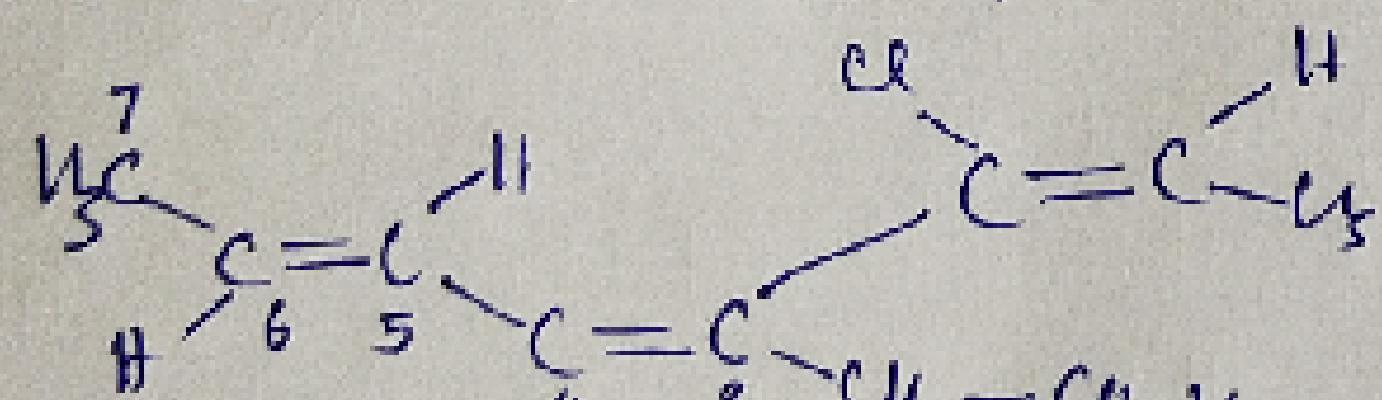
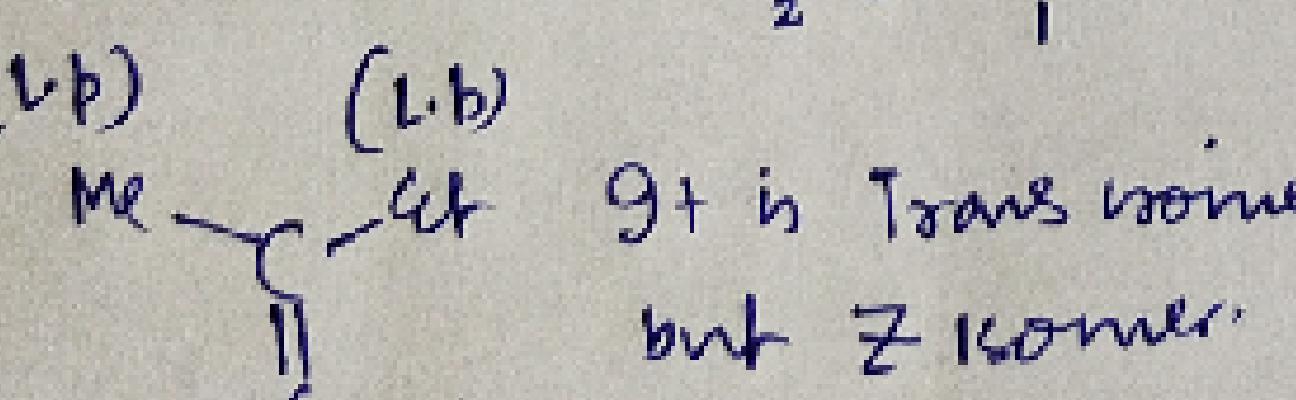
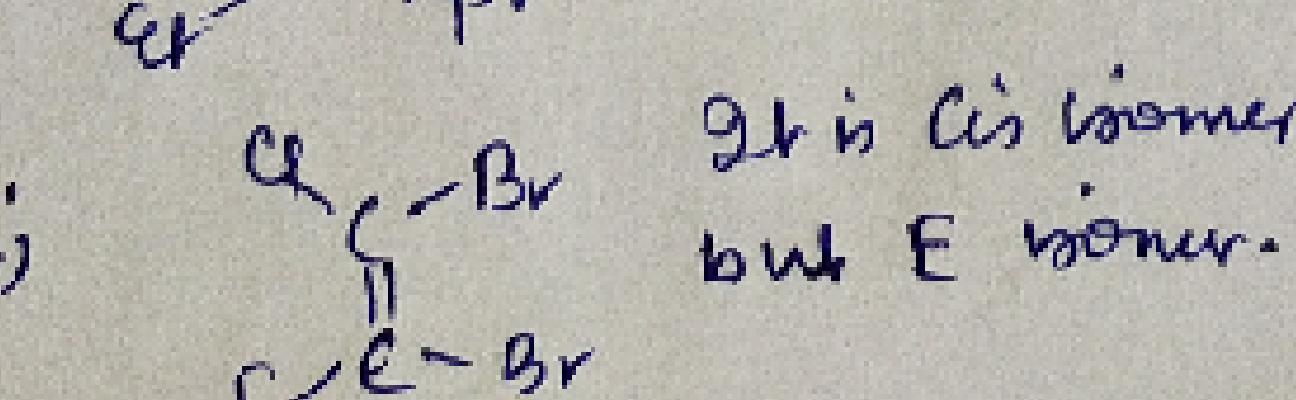
When system like $\begin{array}{c} F \\ | \\ H-C=C-Br \end{array}$ where all atoms attached with $C=C$ system are different, then we can not apply cis-trans isomericism. Then E-Z nomenclature is applicable.

E-Z nomenclature
if higher priority groups are in the opposite side then it is called E-isomer.

$E \Rightarrow Entgegen$ (german word meaning opposite)
(Priority is decided based on atomic no. of groups).

(L.P.) II $> C=C-Cl$ (L.P.) If some priority groups are in (R.P.) II $> C=C-Br$ (R.P.) the same side then it is called Z-isomer. $Z \Rightarrow$ (Zusammen meeting together)

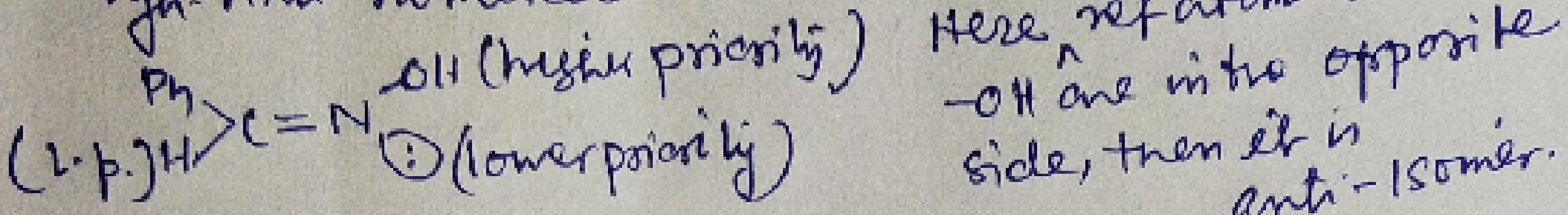
Actually E-Z nomenclature is application for all systems showing geometrical isomerism. 9

- (h.p) 
- a)  (E)-But-2-enoic acid.
- b)  (Z)-But-2-enoic acid
cis isomer.
- c)  Trans isomer.
- d)  (2Z,4E)-hexa-2,4-dienoic acid.
(2E,4E)-2,4-hexadiene.
- e)  (2Z,4E)-hexa-2,4-dienoic acid.
not 2E/4Z isomer.
- f)  (2Z,5E)-hepta-2,5-dienoic acid.
- g)  (2E,4Z)-hexa-2,4-dienoic acid.
- h)  3[E-1-chloropropenyl]
- i)  (2E,4Z)-hepta-2,4-dienoic acid.
but Z isomer.
- j)  (2E,4Z)-hepta-2,4-dienoic acid.
but E isomer.
- Z can be Trans &
E can be cis when
Middle priority groups
are attached with
both carbon (double
bonded).

Oximes ($\text{C}=\text{N}-\text{OH}$) ; Hydrazones ($\text{C}=\text{N}-\text{NH}_2$) ;
 Azo system ($-\text{N}=\text{N}-$). Can show cis Trans isomerism
 & E - Z nomenclature. They also can show

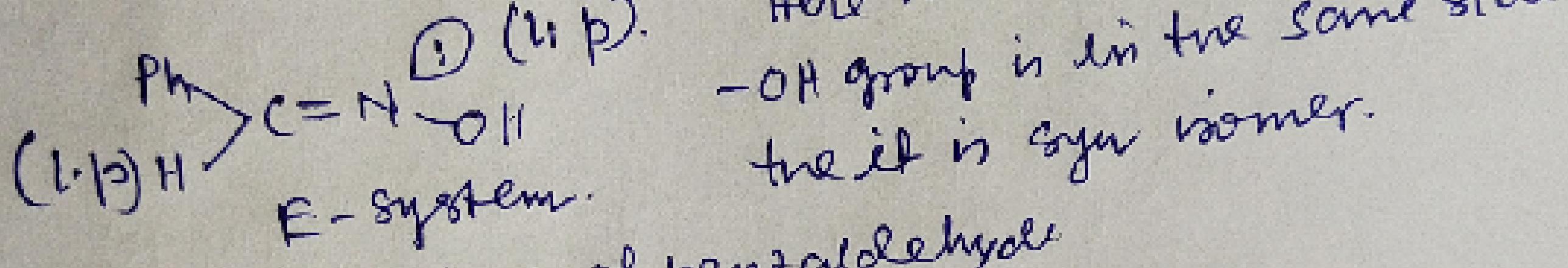
w.r.t

Syn-Anti nomenclature.



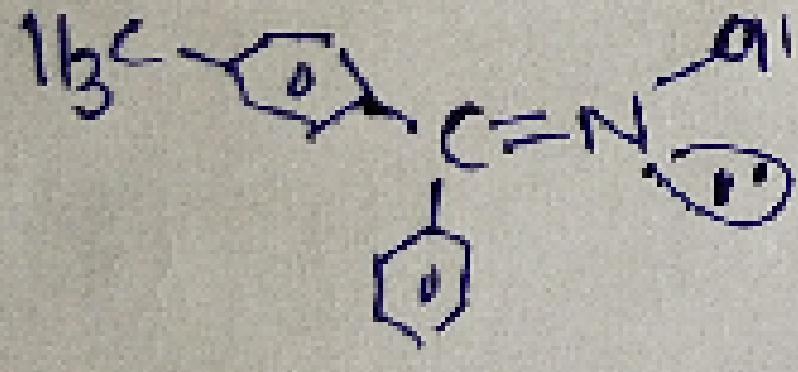
Z-system.

but anti-oxime of benzaldehyde.

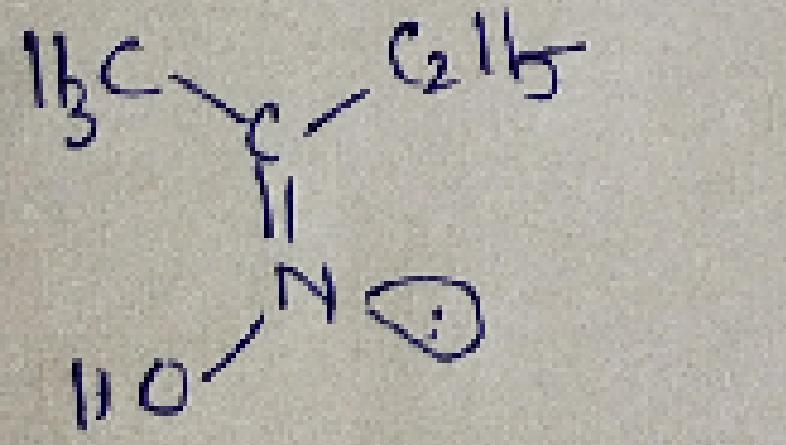


but syn-oxime of benzaldehyde

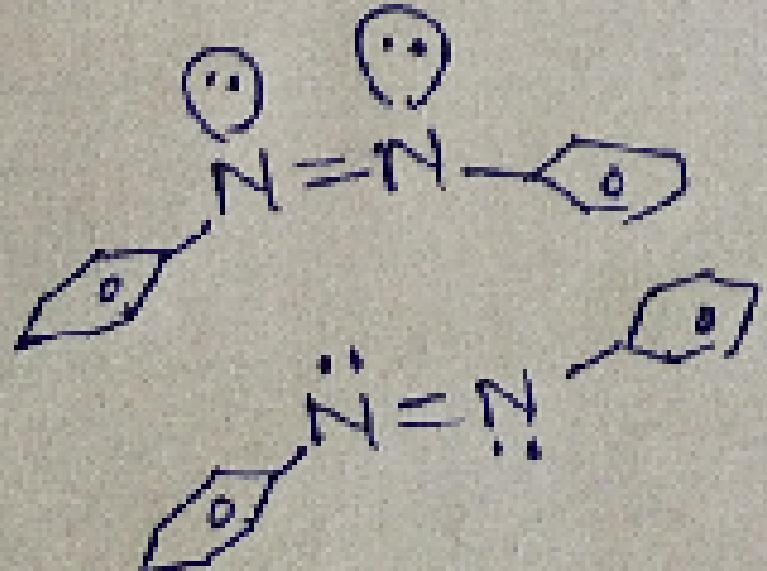
In case of keto oximes, the prefix syn or anti indicates the configurational relationship between the first group & the hydroxyl group.



anti-phenyl- β -tolyl ketoxime
 or
 syn β -tolyl phenyl ketoxime
 (2) phenyl β -tolyl ketoxime.



syn-methyl ethyl ketoxime
 Anti ethyl or methyl ketoxime
 (E)-butanone Oxime.



Z-Azobenzene * Syn-Azobenzene.

E-Azobenzene * Anti-Azobenzene

Priority order (CIP rule)

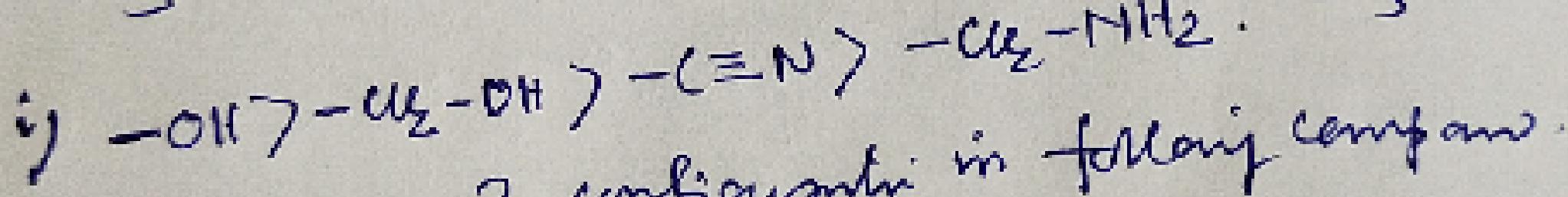
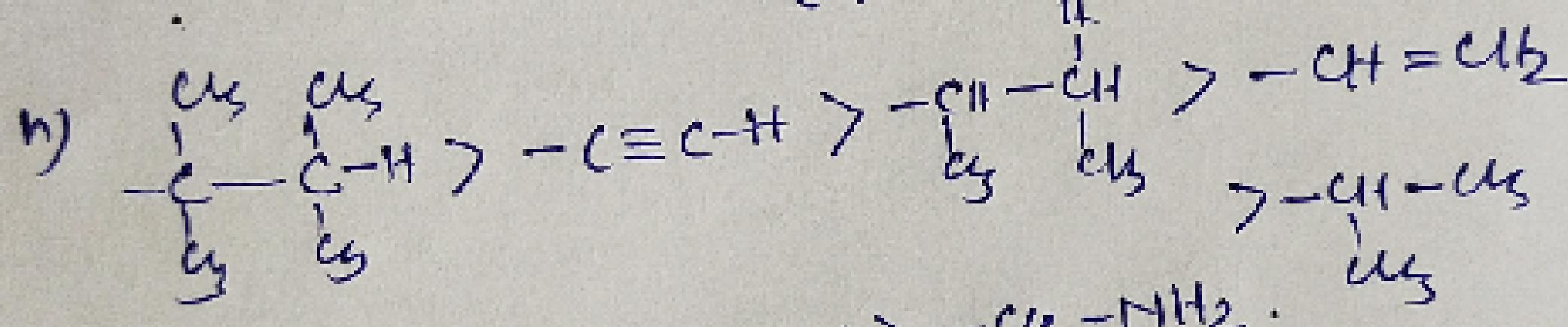
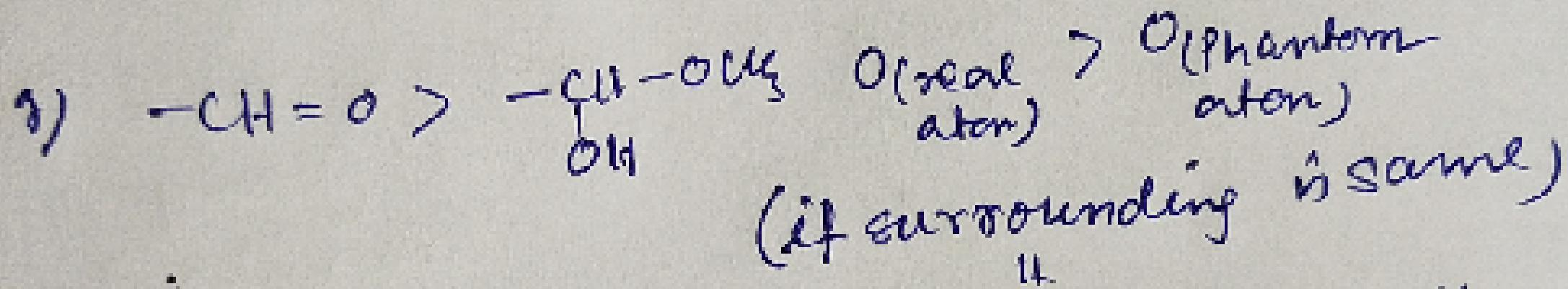
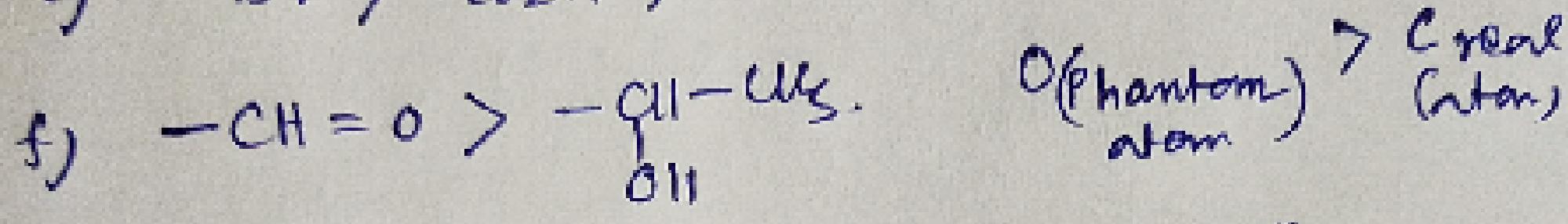
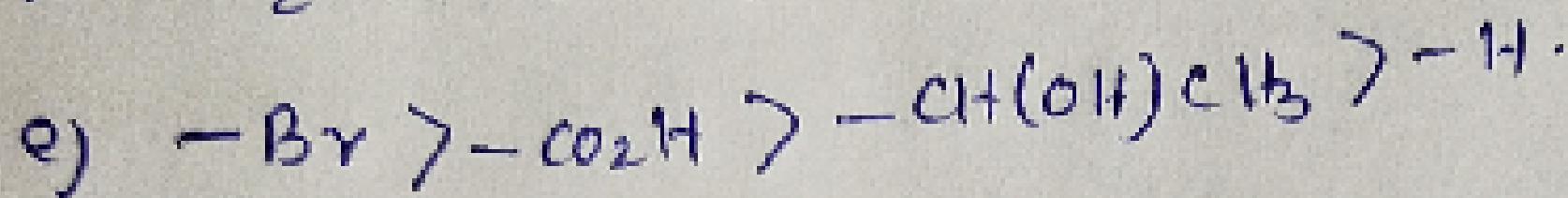
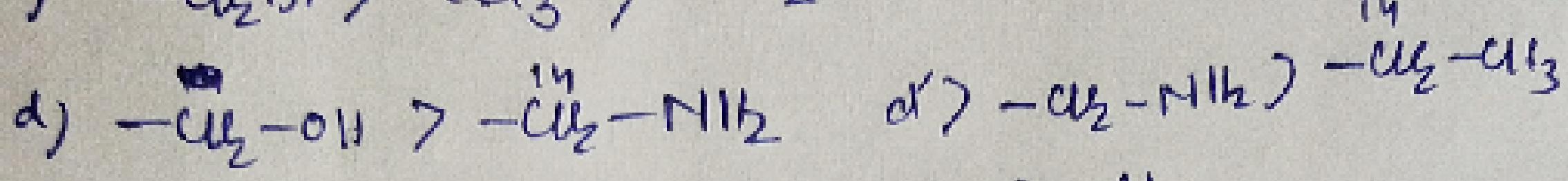
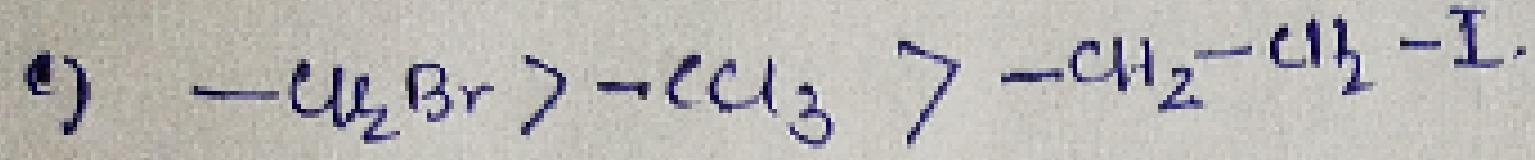
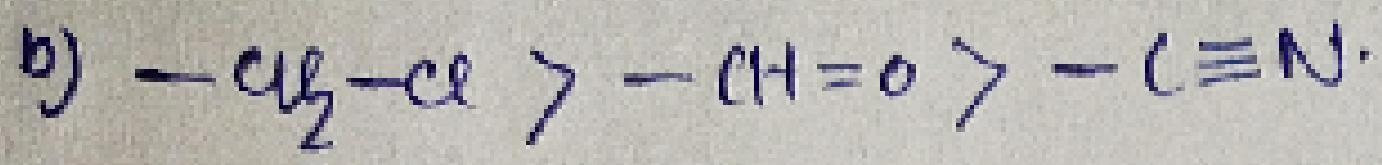
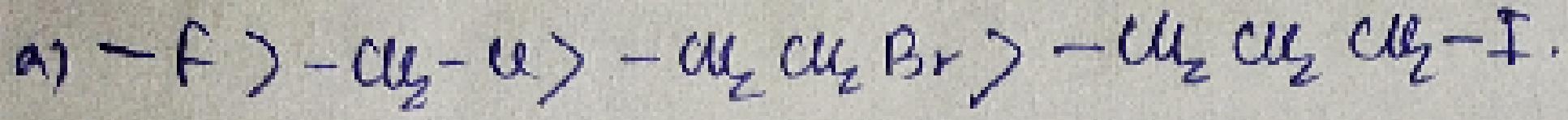
- ⇒ Higher atomic number precedes lower.
- ⇒ When atomic number of all set of atoms are same then higher atomic mass number precedes lower.
- ⇒ Multiple bond has more priority than single bond more is the multiple bond character, more is the priority provided multiple bonded atoms must be same.
 $\text{C}\equiv\text{C} > \text{C}=\text{C} > \text{C}-\text{C}$; $-\text{C}\equiv\text{N} > -\text{CH}=\text{NH} > -\text{CH}_2-\text{NH}_2$
- ⇒ Cs gets more priority than trans.
 Z precedes E ; (R) configuration gets more priority than (S) configuration

Priority order.

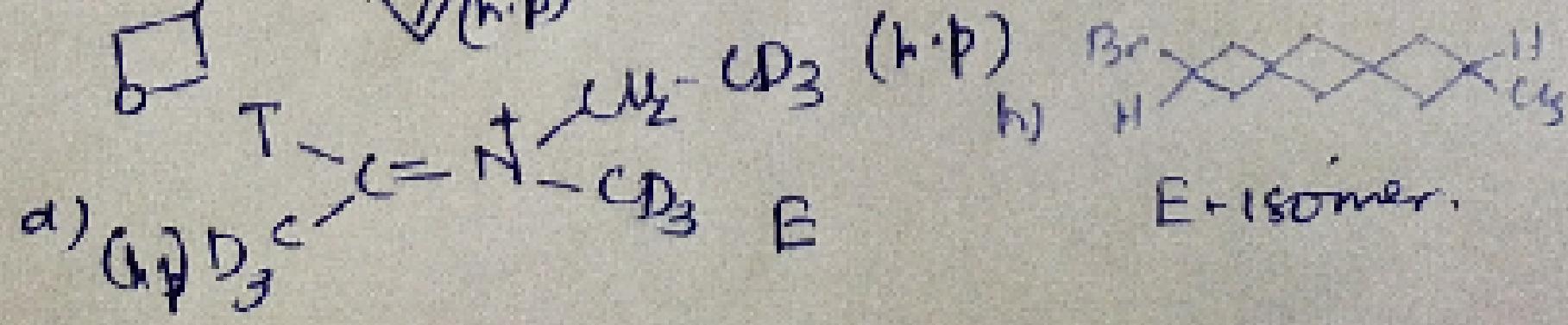
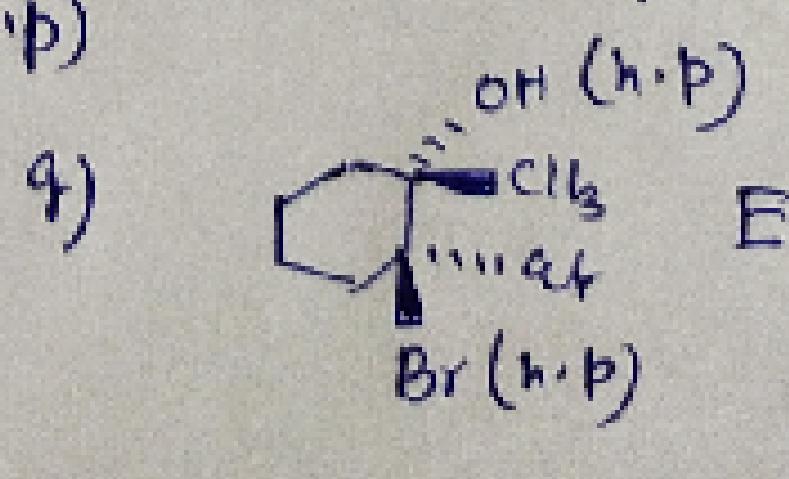
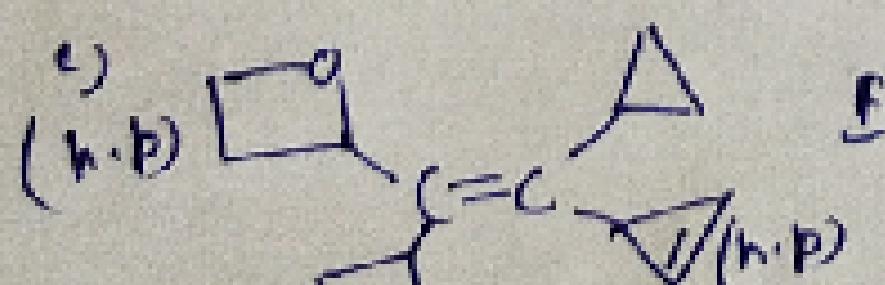
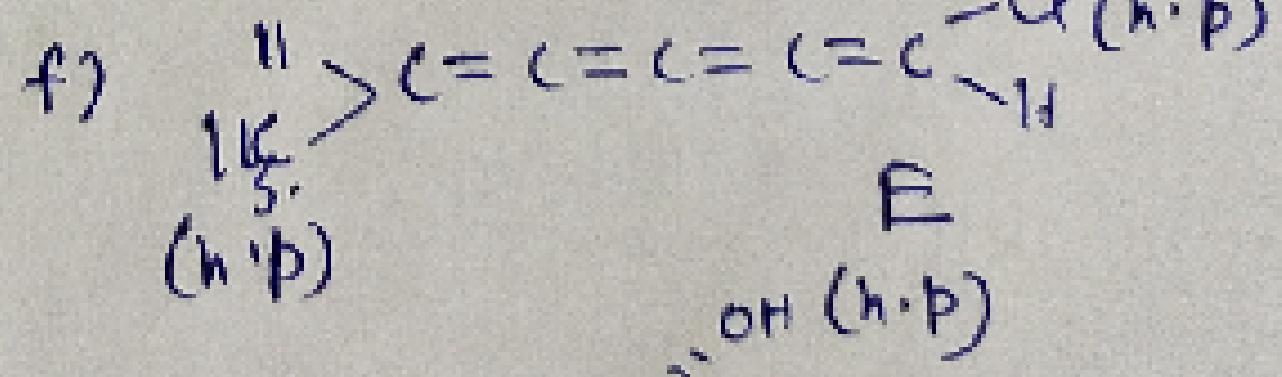
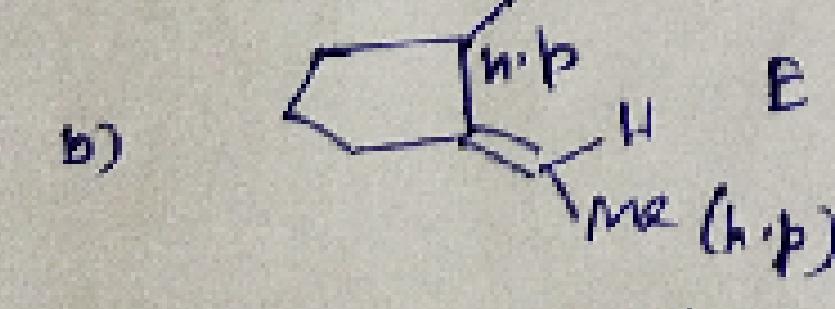
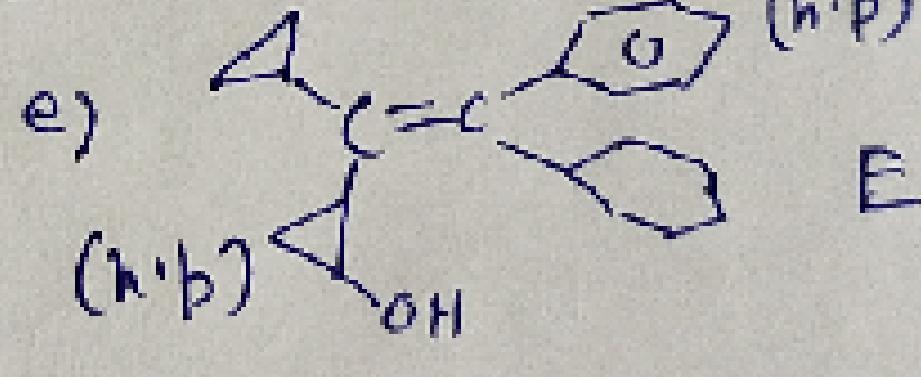
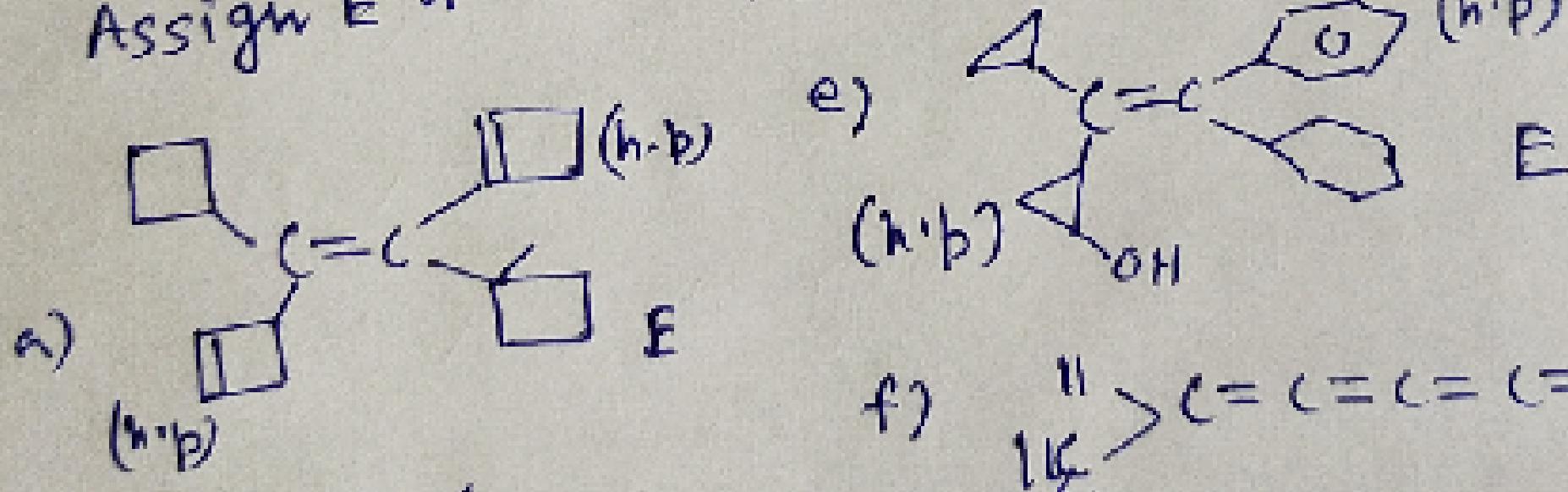
- a) $-\text{I} > -\text{Br} > -\text{Cl}$.
- b) $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{OR}) > -\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{OH}) > -\text{S-Cs} > -\text{SH}$.
- c) $-\text{F} > -\text{O}-\overset{\text{Cs}}{\underset{\text{H}}{\text{C}}}\text{Cs} > -\text{O}-\text{CH}_3 > -\text{OH}$.
- d) $-\text{NO}_2 > -\text{NO} > -\overset{\text{Cs}}{\underset{\text{H}}{\text{N}}}\text{Cs} > -\text{NH}-\text{Cs} > -\text{NH}_2$
- e) $-\text{CT}_3 > -\text{CBrt}_3 > -\text{CCl}_3$
- f) $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{U}) > -\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{O}-\text{R}) > -\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{OR}) > -\text{OH}$.
- g) $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{NH}_2) > -\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{Cs}) > -\text{CH}=\text{O} > -\text{CR}_2-\text{OH} > \text{CH}-\text{R} > -\text{CH}_2-\text{OH}$
- h) $-\text{CH}_2-\text{NH}_2 > -\text{C}\equiv\text{C}-\text{Cs} > -\text{C}\equiv\text{C} > -\text{C}\equiv\text{CH}$.
- i) $-\text{CH}=\text{Cs} > -\overset{\text{Cs}}{\underset{\text{H}}{\text{C}}}\text{Cs} > -\overset{\text{Cs}}{\underset{\text{H}}{\text{CH}}}\text{Cs} > -\text{CH}_2-\text{Cs}$
- j) $-\text{CH}_3 > -\text{T} > -\text{D} > -\text{H} >$ O lone pair has lowest priority.

Some more examples of priority order.

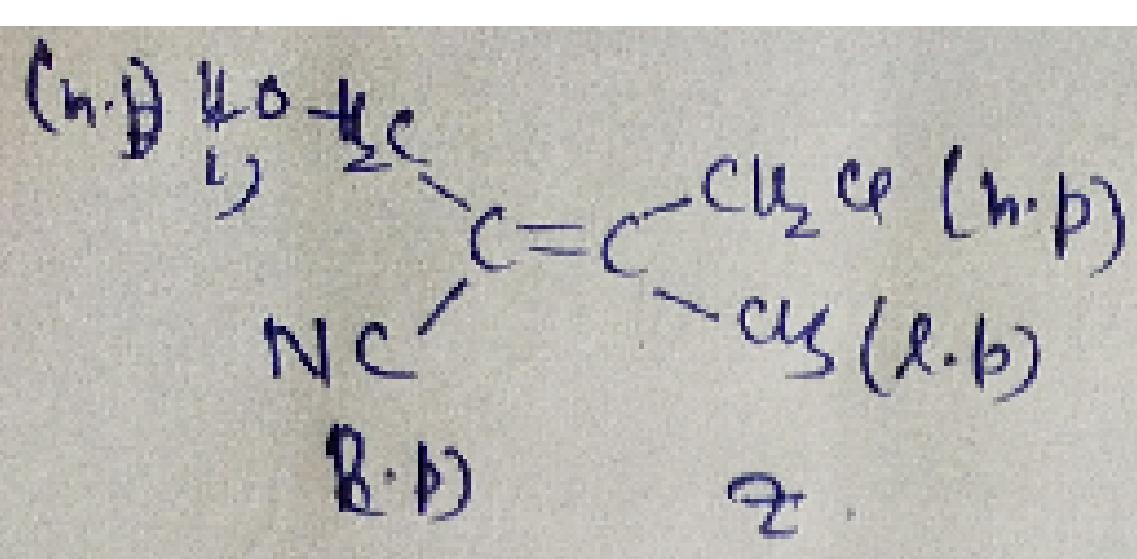
12



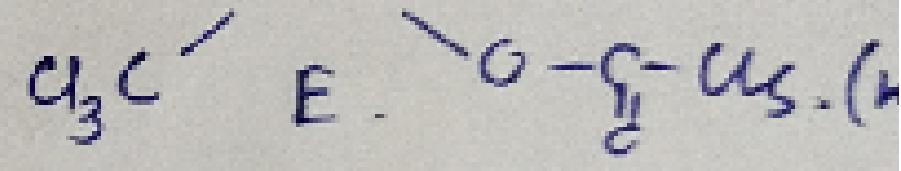
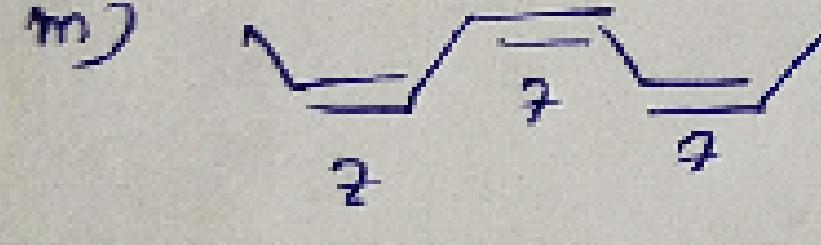
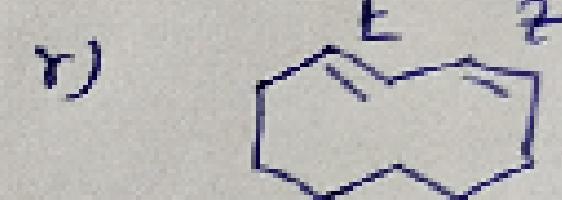
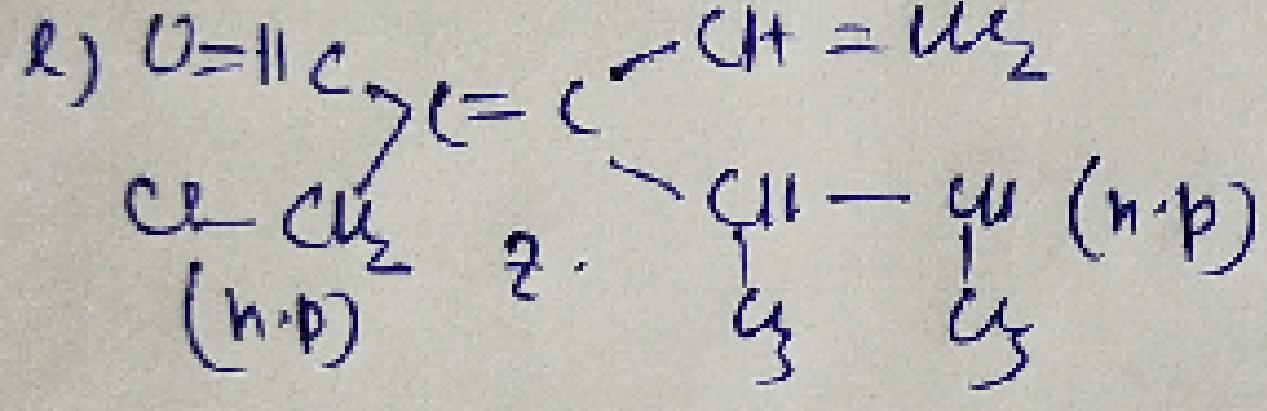
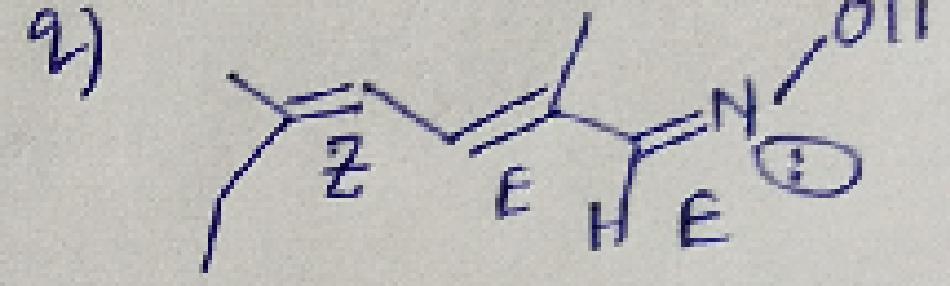
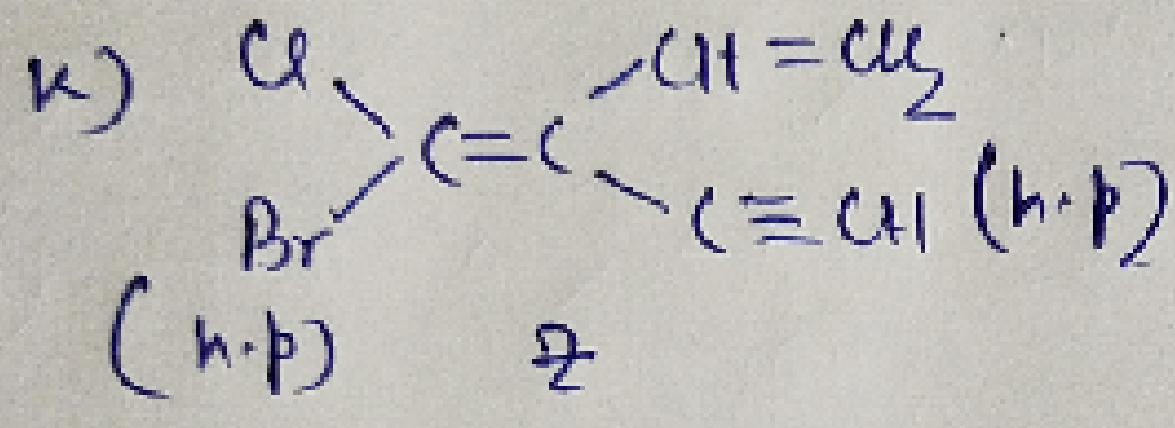
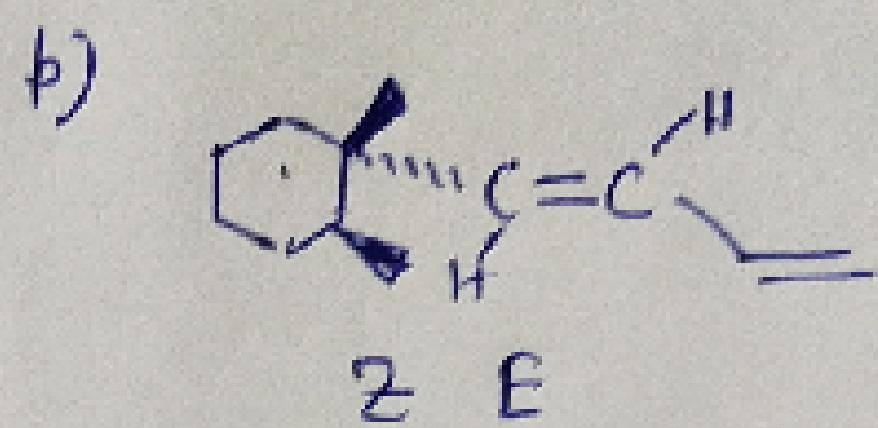
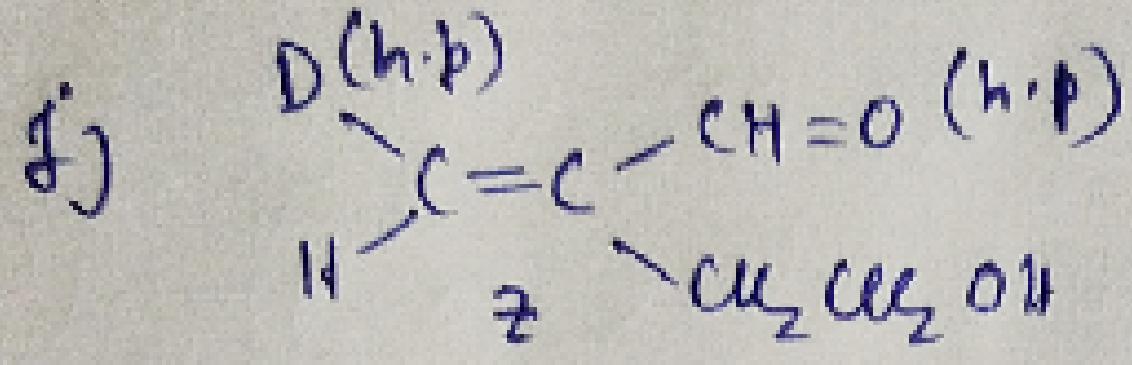
Assign E or Z configuration in following compound.



E-isomer.



13

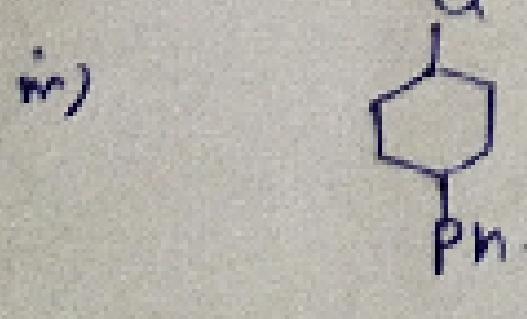


Calculating the total number of Geometrical Isomers:-

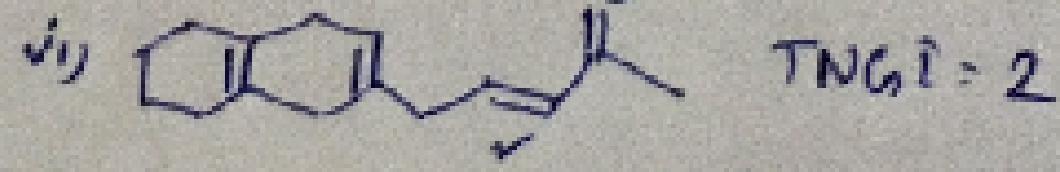
I. If cpd has one double bond & it shows G.I.

If cpd has one double bond & it shows G.I.
 then no. of geometrical isomers = 2.

$$TNGI = 2$$



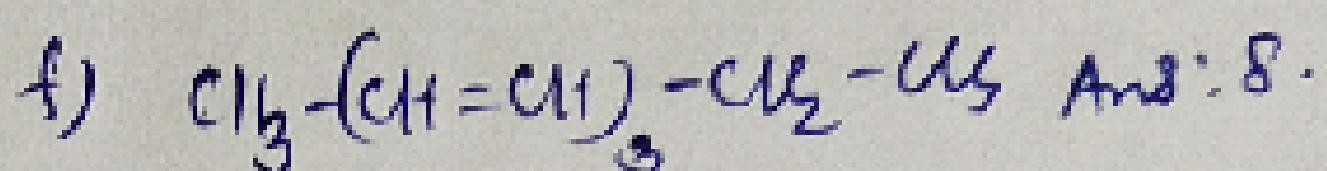
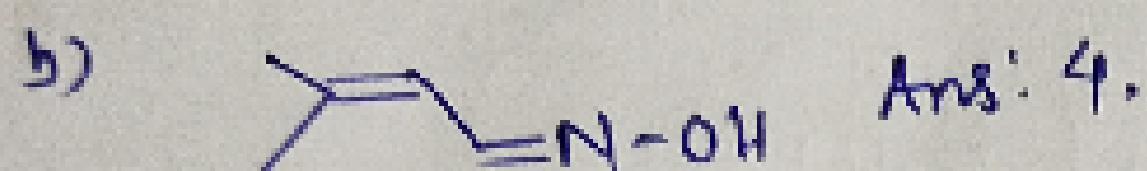
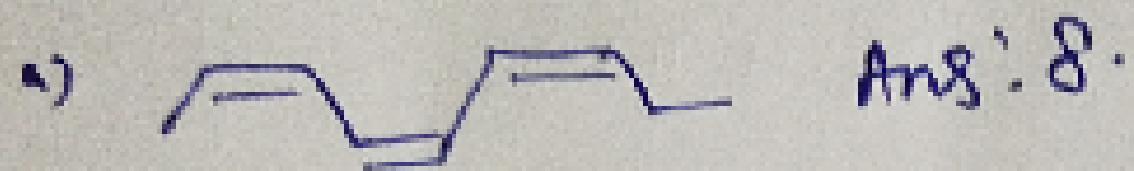
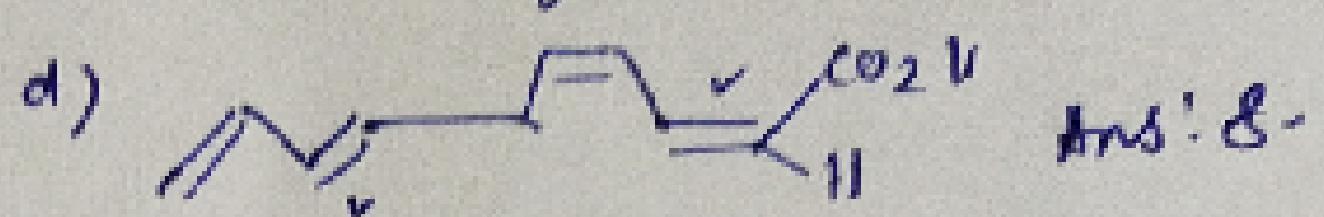
$$TNGI = 2.$$



Calculation of TN_nI (compounds with n. no. of double bonds n > 1, & all show geometrical isomerism)

I. If n > 1 & cpd is non-symmetrical then

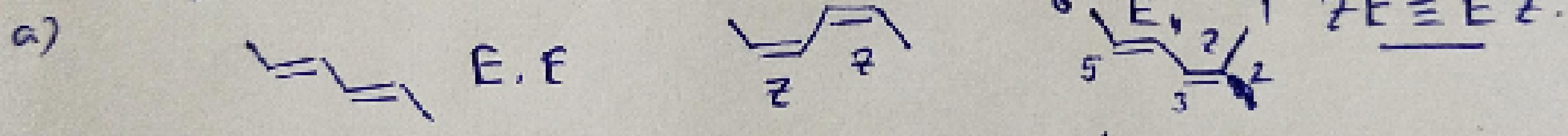
$$TN_nI = 2^n.$$



II. If n > 1, & cpd is symmetrical.

$$\text{the for even no. of } n, \quad TN_nI = 2^{\frac{n-1}{2}} + 2^{\frac{n-1}{2}-1}$$

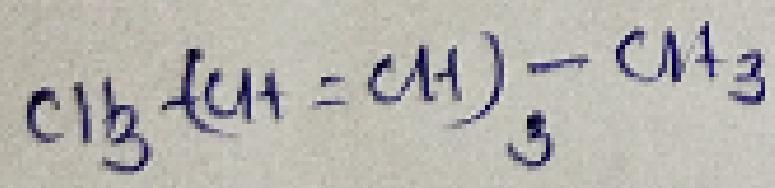
$$CH_3-CH=CH-CH_3 = CH-CH_3 \quad TN_nI = 2^{2-1} + 2^{\frac{2-1}{2}-1} = 3.$$



$$b) CH_3-(CH=CH)_2-CH_3. \quad TN_nI = 2^{\frac{4-1}{2}} + 2^{\frac{4-1}{2}-1} = 2^3 + 2^1 = 10.$$

III. If n > 1, & cpd is symmetrical.

$$\text{then for odd no. of } n, \quad TN_nI = 2^{\frac{n-1}{2}} + 2^{\frac{n+1}{2}-1}$$



I CCC

II CCT

III CTC

\overline{IV} TCC (same as II)

V TCT

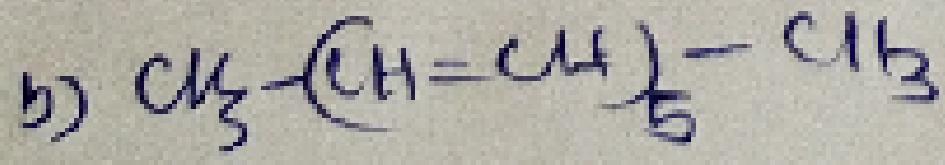
VI CTT

\overline{VII} TTC (same as VI)

\overline{VIII} TTT.

Ans: TN₃I = 6.

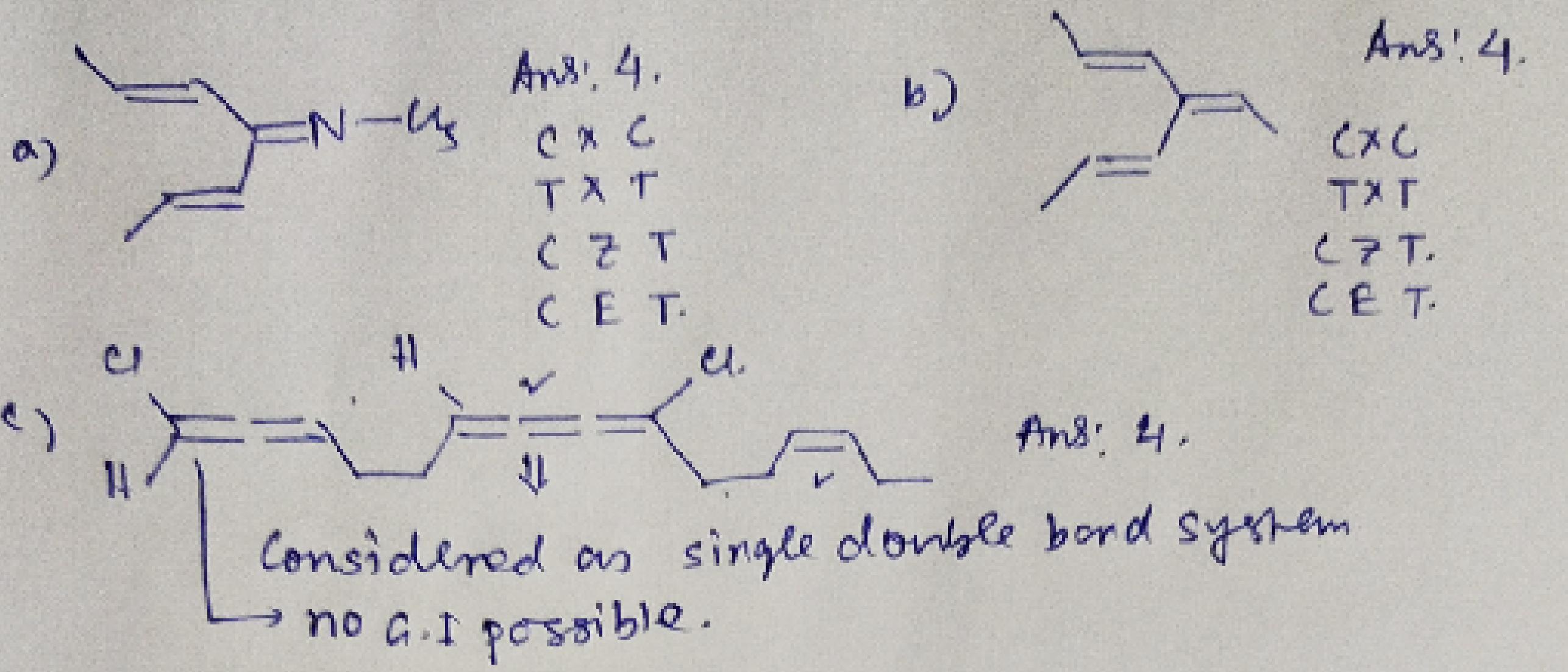
$\overline{IV} = \overline{VII}$; $\overline{II} = \overline{IV}$.



$$\text{Ans: } TN_nI = 2^{\frac{5-1}{2}} + 2^{\frac{5+1}{2}-1} = 2^4 + 2^2 = 20.$$

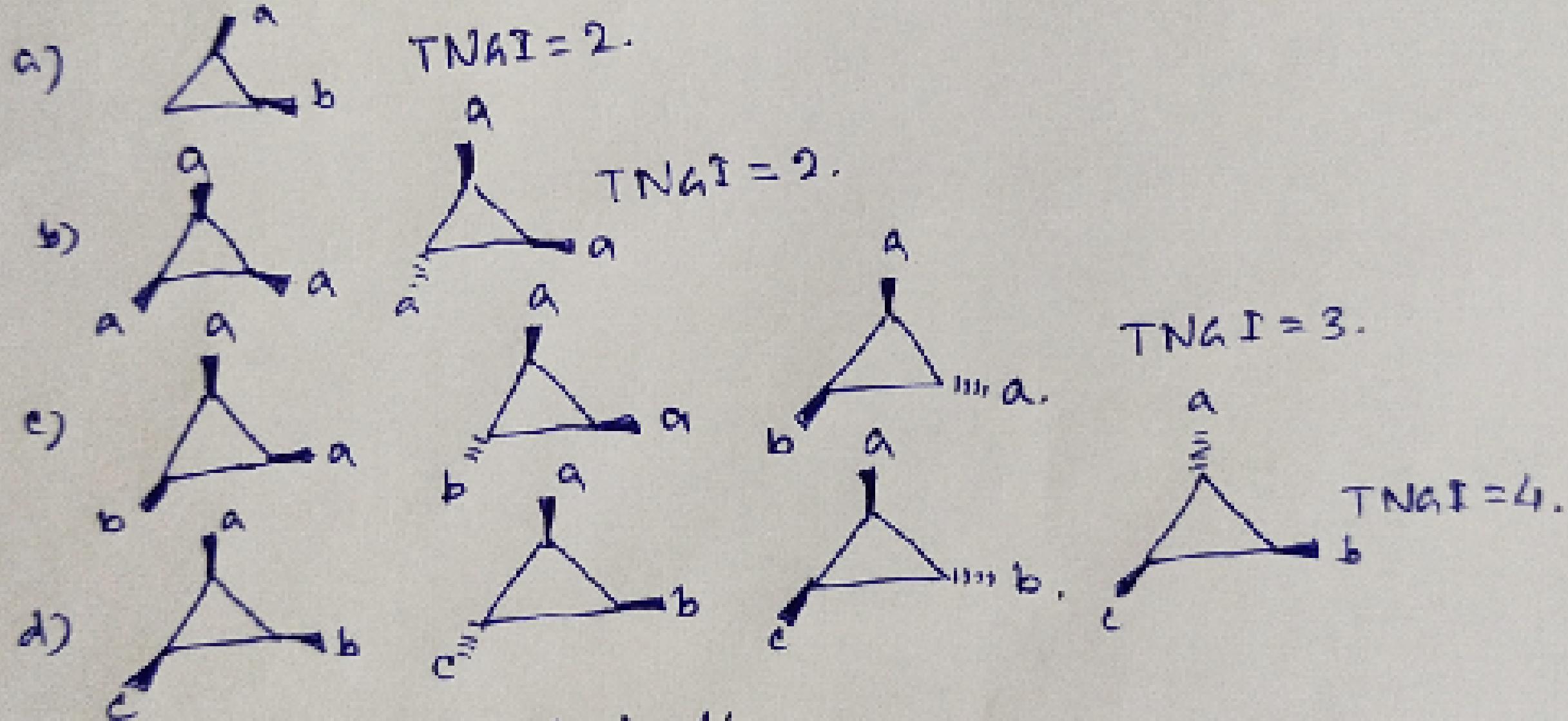
'Some other system':

15

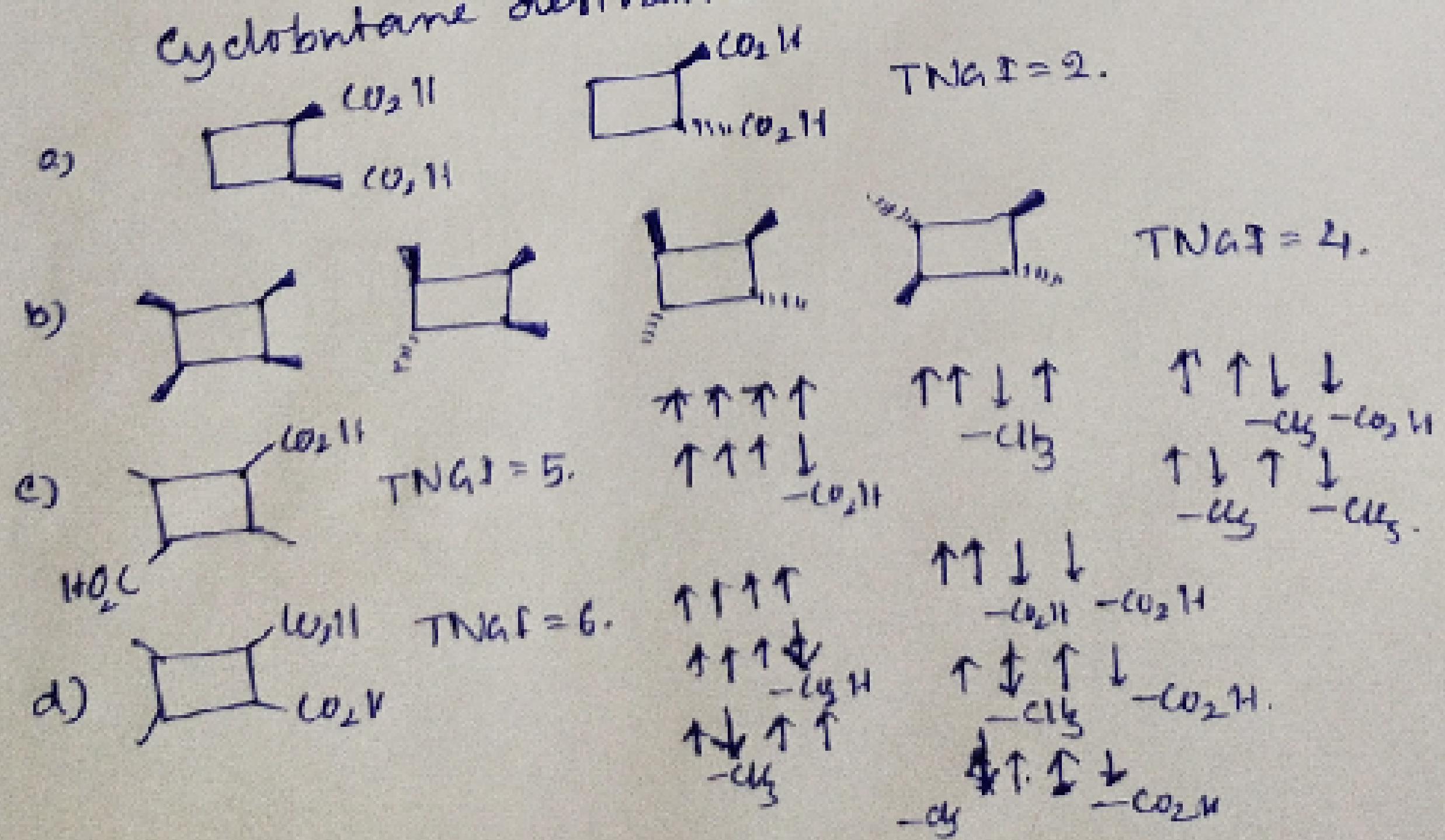


'G.I. for cyclic system':

Cyclopropane derivative

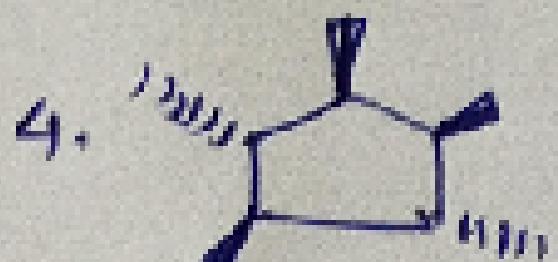
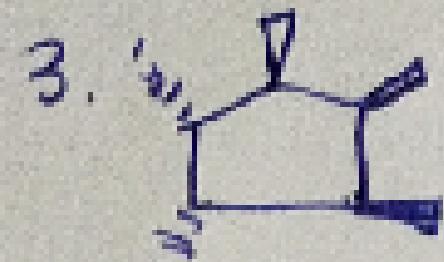
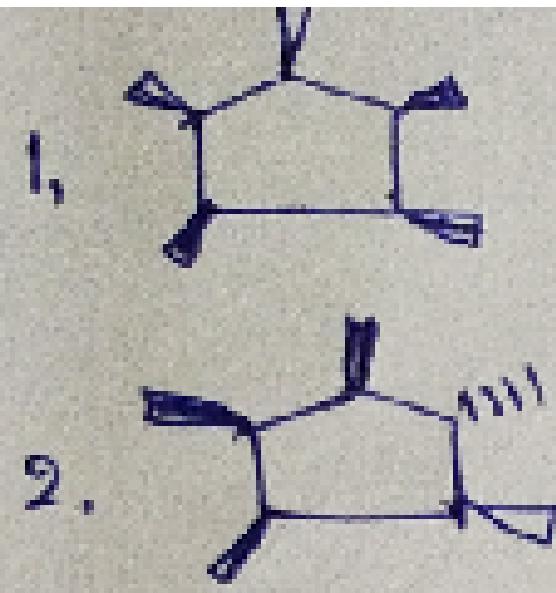


Cyclobutane derivative



cyclopentane system

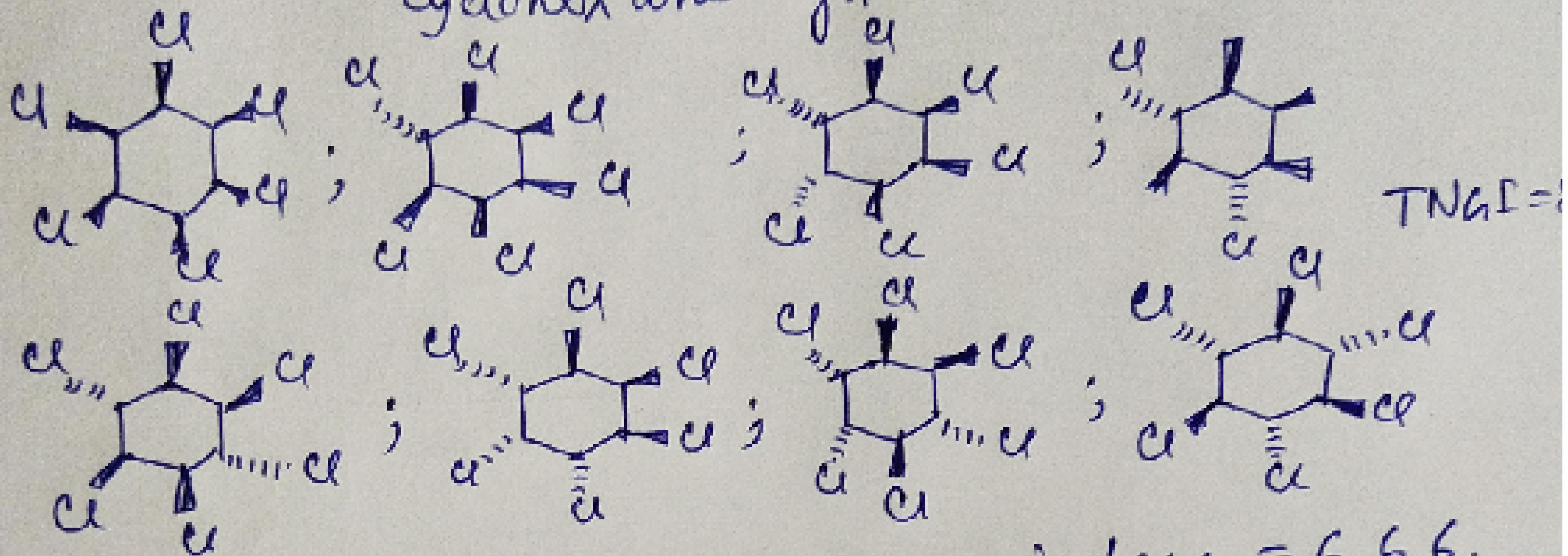
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TNAI = 4.

[Pentamethyl cyclopentane].

Cyclohexane System

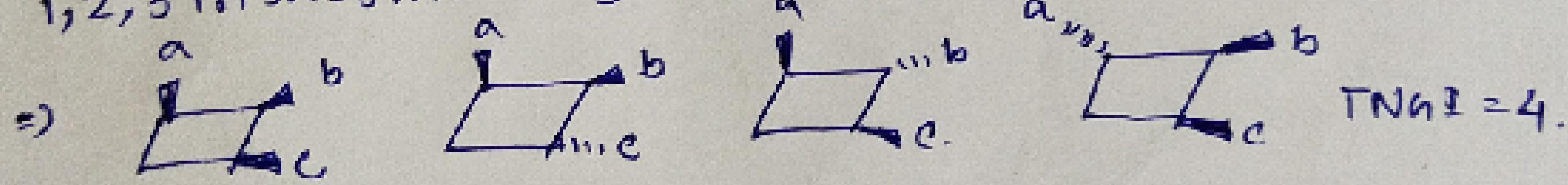


TNAI = 8.

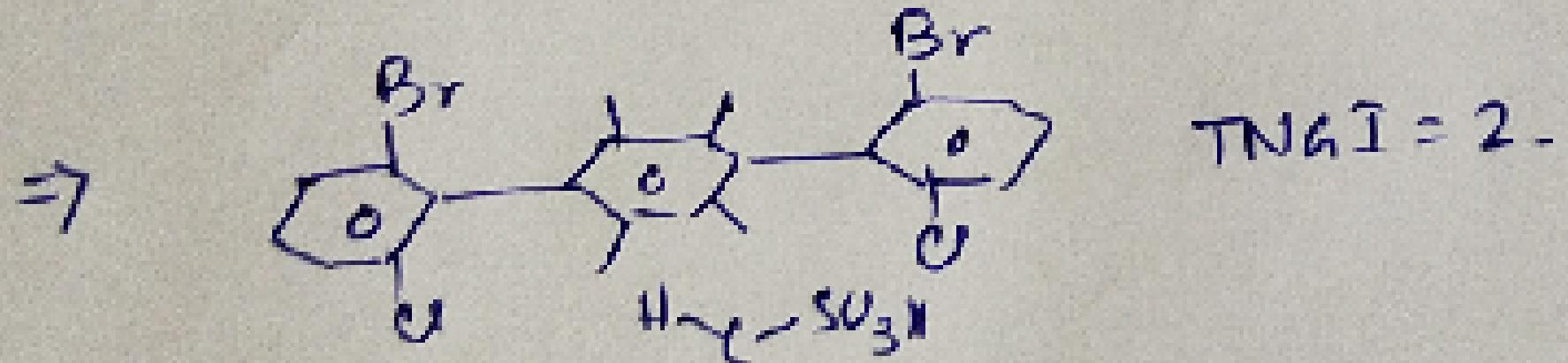
Hexachlorobenzene \equiv BHC \equiv Lindane \equiv 6, 6, 6.
 $(C_6H_5Cl_6) \Rightarrow \equiv$ Grammaxene

Other examples:

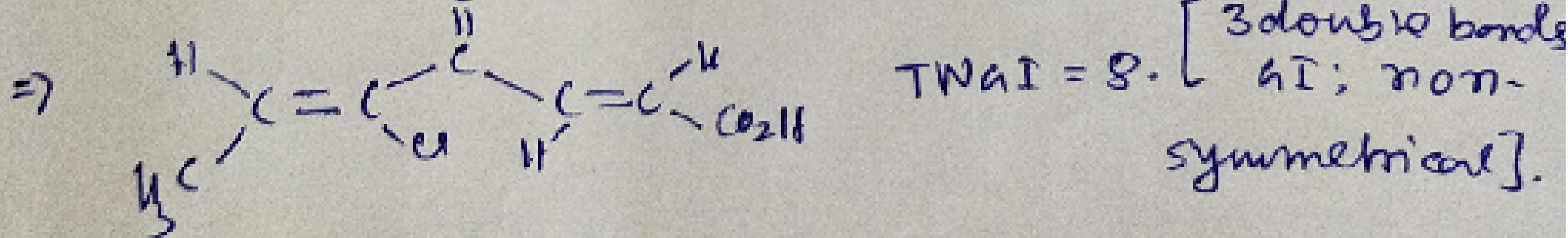
1, 2, 3 trisubstituted cyclobutane [$a \neq b \neq c$].



TNAI = 4.



TNAI = 2.



TNAI = 8. [3 double bonds; GI; non-symmetrical].



TNAI = 6.

[3 double bonds; GI; symmetrical].



GI is not possible.