New Year's Holiday (Thailand) Holiday (Scotland-U.K.)

GEOMETRICAL ISOMERISM

STUDY MATERIAL

FOR

B. Sc (1st. Semester)

The Gateway to IIT's, NIT's, IISER's, BARC, ONGC and Prominent Engineering/ Science Institutions.

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Wednesday

Geometrical Isomerism or Cis-Trans Isomerism

Geometrical Isomerism is a type of Stereoisomerism which is exhibited by Certain Compounds Containing Double Bonds. Double bonds Consists of a Sigma (σ) and a Pi (π) bond perpendicular to each other. If a molecule is rotated about the double bond, the (π) bond will break and Thus there is no free rotation about a double bond i.e, the Rotation about a double bond is ristricted or Frozen.

Due to hindered Rotation around Carbon-Carbon double bond, the Relative positions of groups attached to doubly bonded Carbon atoms get fixed. As a Result, these Compounds Can exist in two distinct isomeric forms which differ from each other in the relative position of groups in space around double bond. These two isomeric forms are like One another with respect to which atoms are attached but differ from each other in the relative position of atom or groups in Space across double bond.

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4 Thursday

Thus Geometrical isomerism is that type of stereoisomerism in which compounds have same structural formulae but differ in the relative arrangement of atoms or groups in space due to restricted rotation across double bond. Such compounds which exhibit this phenomenon are known as Geometrical Isomers or Cis-trans Isomers.

* Geometrical Isomers can also be regarded as Diastereomers, since they are not mirror images of each other.

* There may be a restricted rotation about a single bond due to steric hindrance. For example, substituted biphenyls. These biphenyls exhibit geometrical isomerism if they are suitably substituted.

* Geometrical isomerism is exhibited by following compounds:

(i) Compounds containing a double bond. For example, C=C, C=N, N=N

(ii) Compounds containing cyclic structure such as Homocyclic, Heterocyclic and fused Ring systems

(iii) Compounds having restricted rotation about a single bond due to steric hindrance. Such as Diguide substituted Biphenyls

"Conditions for Geometrical Isomerism"

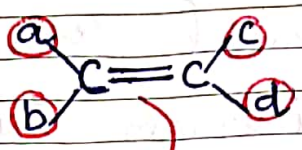
A Compound will show Geometrical Isomerism if it fulfills the following two conditions:

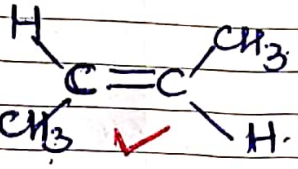
(a) There must be restricted Rotation about a bond in the molecule

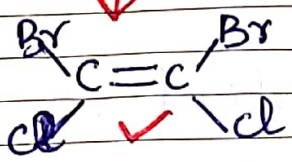
(b) Both substituents on each Carbon about which rotation is restricted should be different

Examples:

Case-I



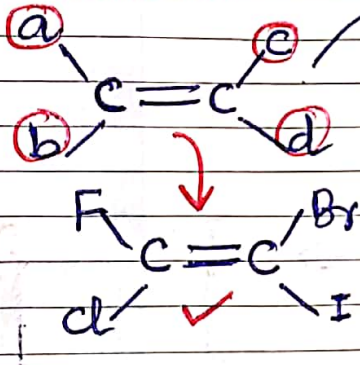




Note:

$a \neq b$	$\Rightarrow$ Show Geometrical Isomerism
$c \neq d$	
$a = c$	
$b = d$	

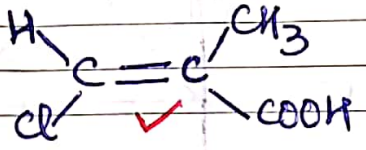
Case-II

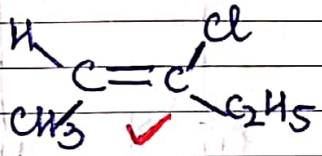


Note:

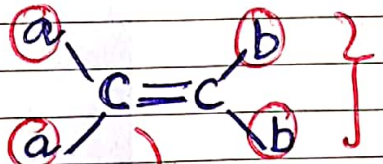
$a \neq b \neq c \neq d$

These compounds will exhibit Geometrical isomerism of E/Z type

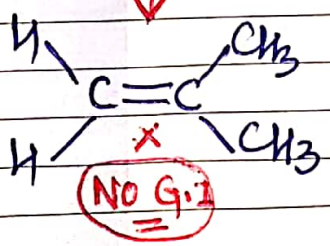


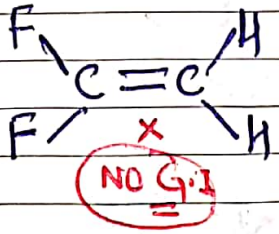


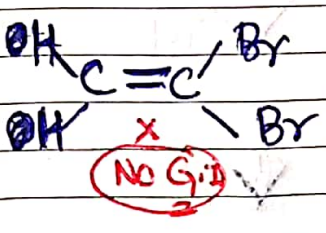
Case-III



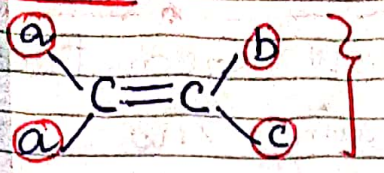
NO Geometrical Isomerism



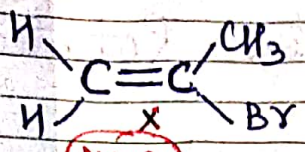




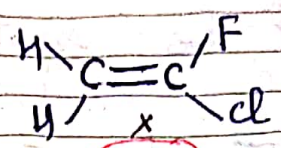
Case-IV



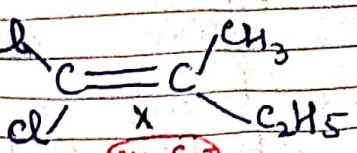
No Geometrical Isomerism



No. G.I



No. G.I



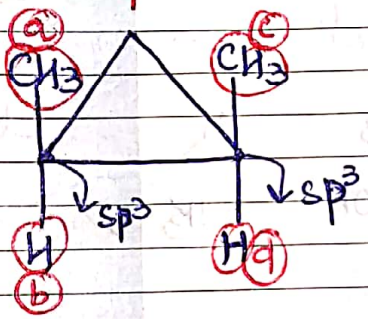
No G.I

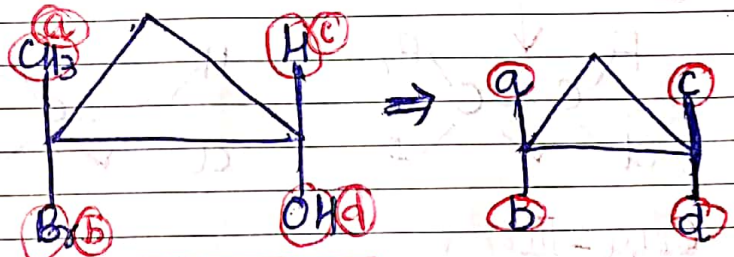
* In cycloalkanes, the essential Conditions for exhibiting Geometrical Isomerism are:

(a) Presence of minimum two sp^3 hybridised atoms

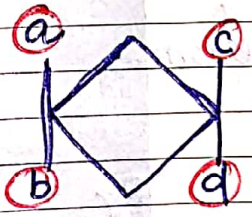
(b) Each sp^3 hybridised atom must possess two different atoms or groups.

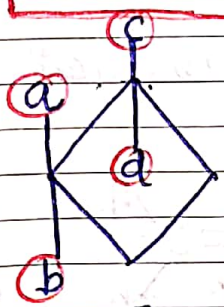
Examples:-

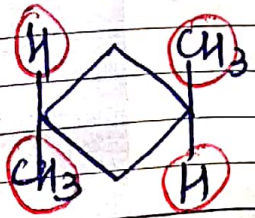


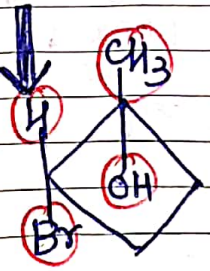


$a \neq b$ and $c \neq d$









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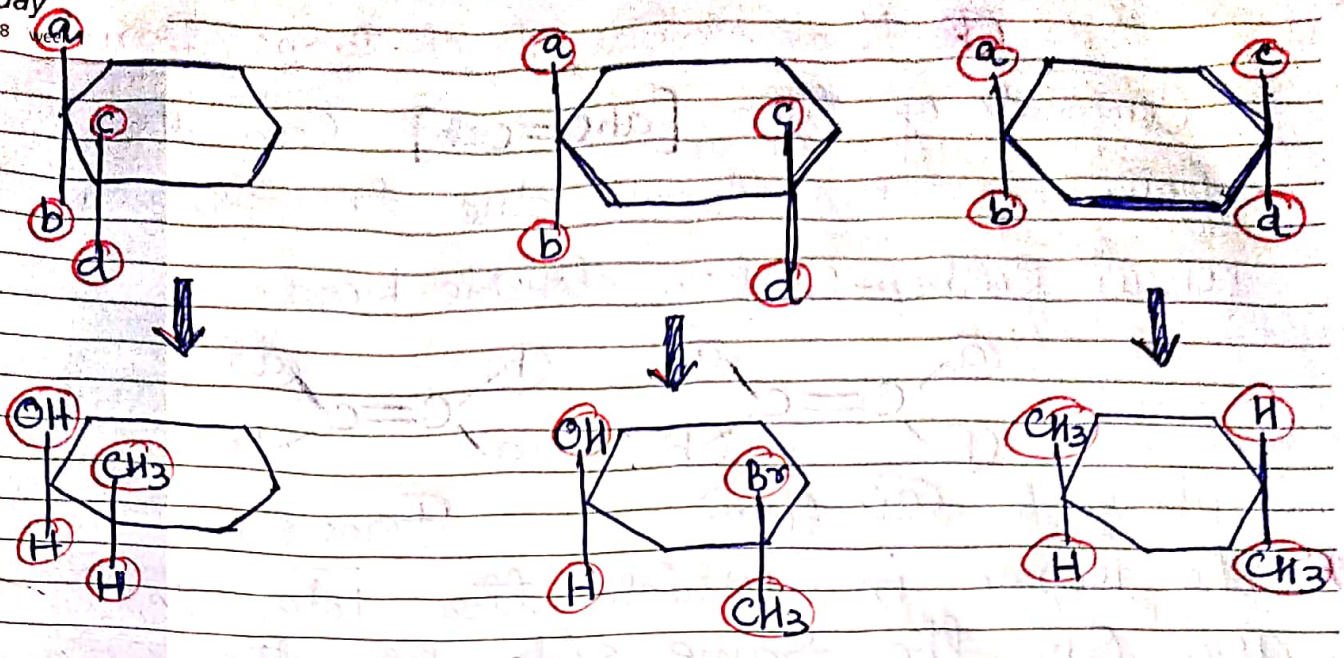
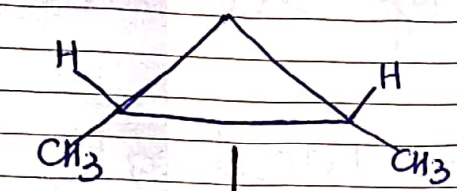
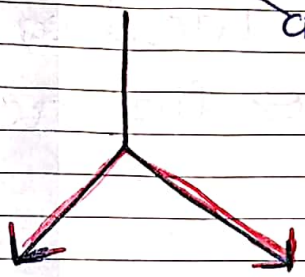
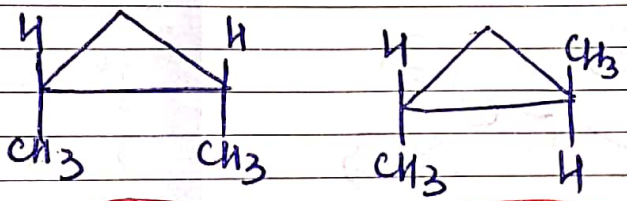


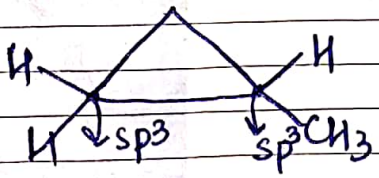


⇒ Show Geometrical isomerism



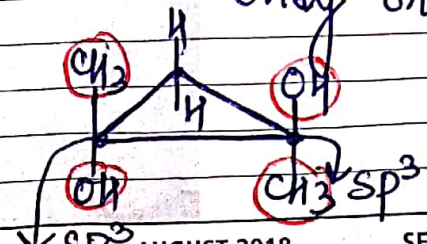


cis-form trans-form



⇒ No. Geometrical Isomerism

* Two sp^3 hyb. atoms
* Only one sp^3 hyb. atom posses different groups.



⇒ Show Geometrical Isomerism

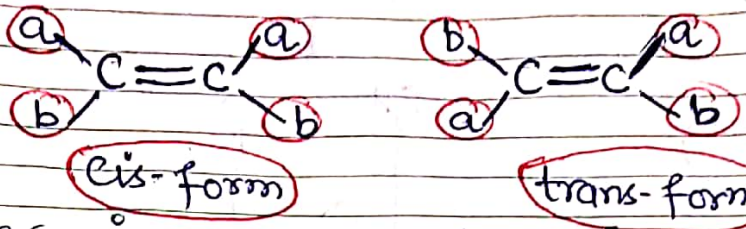
JULY 2018 AUGUST 2018 SEPTEMBER 2018 OCTOBER 2018 NOVEMBER 2018 DECEMBER 2018

Scanned by CamScanner

Coming-of-Age Day (Japan)

Nomenclature of cis-trans Isomerism

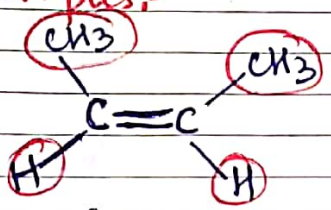
Compounds of type [abC=Cab] can exist in the following two forms due to frozen rotation about Carbon-Carbon double bond.



The isomer in which the identical groups are on the same side of the double bond is called cis-Isomer.

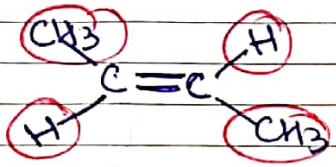
The isomer in which the identical groups are on the opposite side of the double bond is called trans-Isomer.

Examples:-



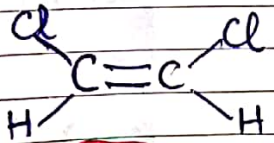
cis-But-2-ene

(Similar groups on same side of double Bond)

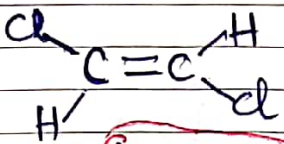


trans-But-2-ene

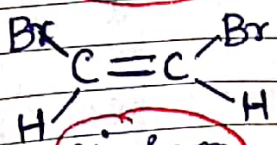
(similar groups on opposite side of double Bond)



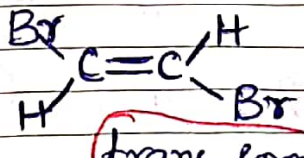
cis-form



trans-form



cis-form



trans-form

JANUARY 2018

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FEBRUARY 2018

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26	27	28				

MARCH 2018

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APRIL 2018

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30						

MAY 2018

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JUNE 2018

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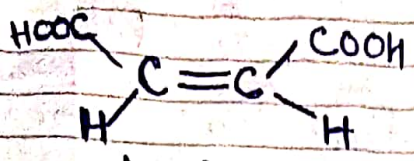
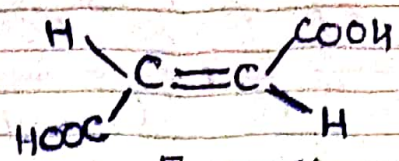
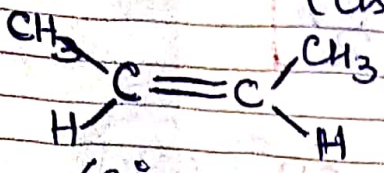


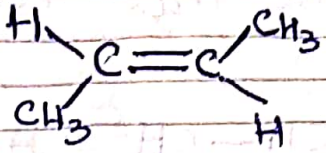
Maleic acid
(cis-form)



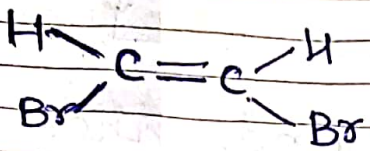
Fumaric acid
(trans-form)



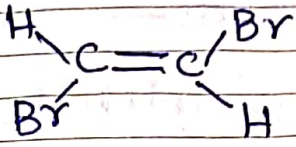
(cis-form)



(trans-form)

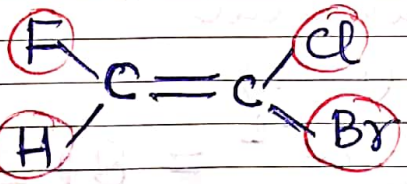


(cis-form)



(trans-form)

Cis-trans nomenclature can be used only in those compounds in which only two or three types of groups (ligands) are attached to both the double bonded carbons. When all the four groups attached to doubly bonded carbon atoms are different, this nomenclature cannot be used. For example,



All the four groups are different, for these compounds cis-trans nomenclature is not applicable.

No. of Geometrical Isomers in Polyenes

(a) When a compound has 'n' no. of double bonds and ends of a polyene are different,

No. of geometrical isomers = 2^n

Example:

$CH_3-CH\overset{①}{=}CH-CH\overset{②}{=}CH-CH\overset{③}{=}CH-CH\overset{④}{=}CHCl$

↓ Different ends ←→ ↓

There are four double bonds and the ends are different, No. of G.I = $2^4 = 16$

(b) When the ends of a polyene are identical:

(i) If the no. of double bonds (n) is even

then no. of G.I = $2^{n-1} + 2^{n/2-1}$

Example:

$ClCH\overset{①}{=}CH-CH\overset{②}{=}CH-CH\overset{③}{=}CH-CH\overset{④}{=}CHCl$

Ends = Identical

n = 4 (even)

No. of G.I = $2^{4-1} + 2^{4/2-1} = 8 + 2 = 10$

(ii) If the no. of double bonds (n) is odd

No. of G.I = $2^{n-1} + 2^{(n+1)/2-1}$

Example: $PhCH\overset{①}{=}CH-CH\overset{②}{=}CH-CH\overset{③}{=}CHPh$

Ends = Identical

n = 3 (odd)

No. of G.I = $2^2 + 2 = 6$

E-Z Nomenclature

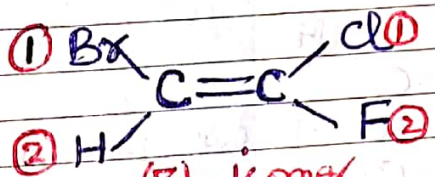
This nomenclature of Geometrical Isomers is more general and can be applied to all compounds. E-Z nomenclature is based on the Cahn-Ingold-Prelog (CIP) system.

In E/Z System, the group of highest priority on each carbon atom is identified by using Sequence Rules. The group having highest atomic number is given highest priority.

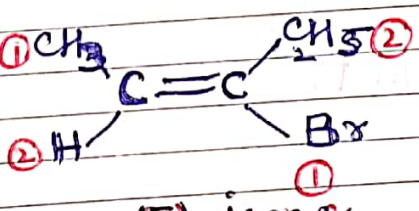
If the highest priority groups are on the same side of double bond, the configuration is Z (Zusammen)

If the highest priority groups are on the opposite side of double bond, the configuration is E (entgegen)

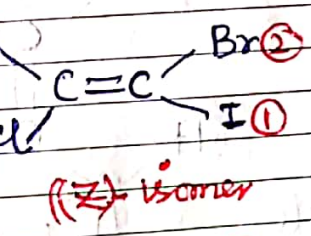
Examples:-



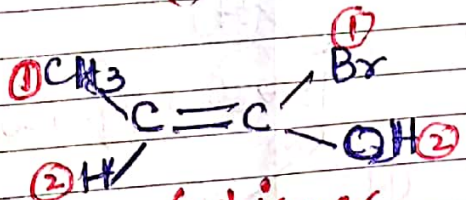
(Z) - isomer



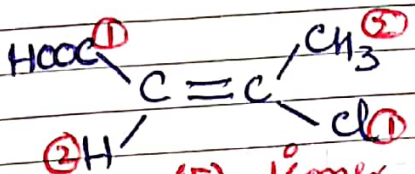
(E) - isomer



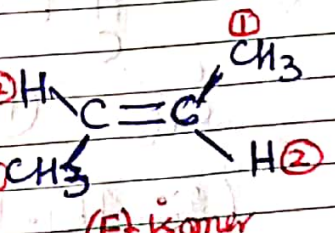
(Z) - isomer



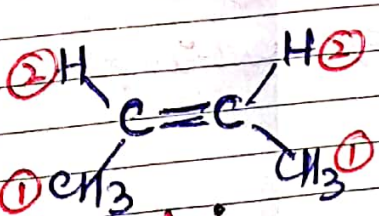
(Z) - isomer



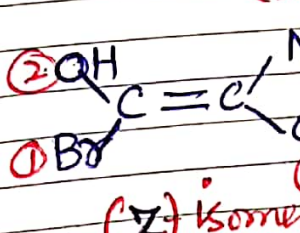
(E) - isomer



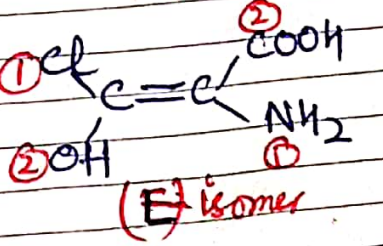
(E) - isomer



(Z) - isomer



(Z) - isomer

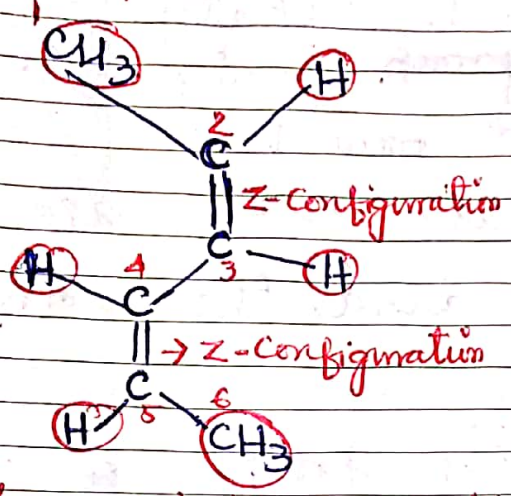


(E) - isomer

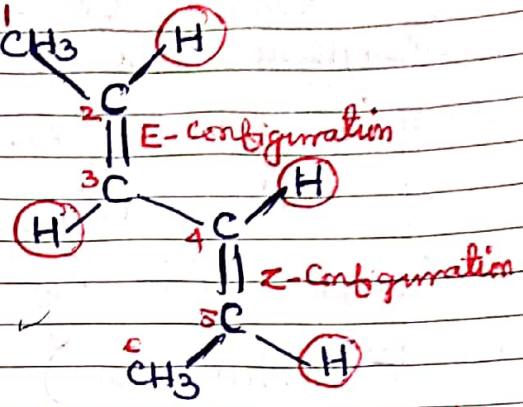
Nomenclature of Compounds Containing more than one Double Bonds

If a compound contains two or more double bonds around which geometrical Isomerism is possible, then (E) and (Z) designations are given to each double bond.

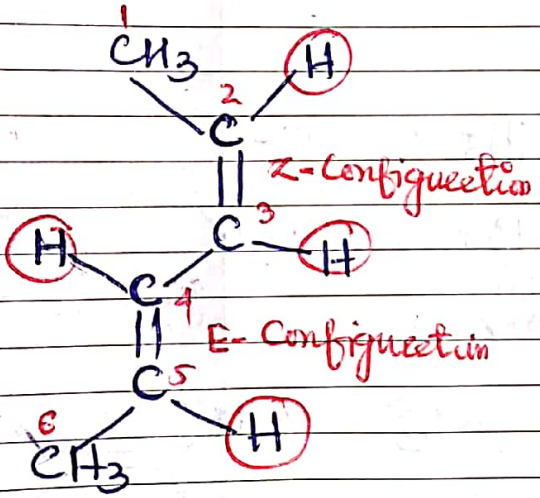
Examples:-



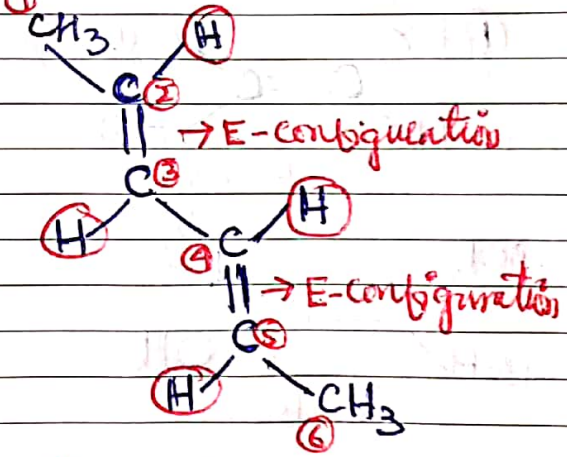
(2Z, 4Z)-Hexa-2,4-diene.



(2E, 4Z)-Hexa-2,4-diene



(2Z, 4E)-Hexa-2,4-diene



(2E, 4E)-Hexa-2,4-diene