Introduction Of ISOMERISM

The existence of two or more compounds with same molecular formula but different properties (physical, chemical or both) is known as isomerism; and the compounds themselves are called isomers. The term was given by Berzelius. The difference in properties of two isomers is due to the difference in the arrangement of atoms within their molecules. Isomerism may be of two types:

Structural isomerism

When the isomers differ only in the arrangement of atoms or groups within the molecule, without any reference to space, these are known as **structural isomers**
and the phenomenon as
structural isomerism.
Thus the structural isomers have the same molecular formula, but possess different structural formulae. Structural isomerism may again be of several types.

(i) Chain, nuclear or skeleton isomerism
This type of isomerism is
due to the difference in the nature of the carbon chain (i.e. straight or branched)
which forms the nucleus of the molecule, e.g.,

(i) $CH_3CH_2CH_2CH_3$ and $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(ii) $CH_3CH_2CH_2CH_2CH_3$ and $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

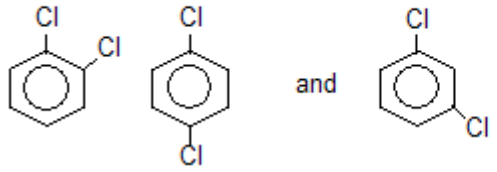
(iii) $CH_3CH_2-C-C\equiv C$ and $H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}}-C\equiv CH_2$

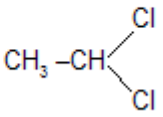
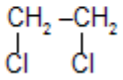
(iv) $CH_3CH_2CH-C\equiv CH$ and $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv CH$

(ii) Position isomerism
It is due to the difference in the position of the substituent atom or group or an unsaturated linkage in the same carbon chain. Examples are

(i) $CH_3CH_2–CH=CH_2$ and $CH_3–CH = CH–CH_3$

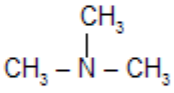
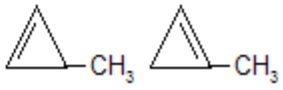
(ii) $CH_3CH_2–C \equiv CH$ and $CH_3 – C\equiv C–CH_3$

(iii)  and

(iv)  and 

(iii) Functional isomerism

This type of isomerism is due to difference in the nature of functional group present in the isomers, e.g.,

C_2H_6O:	$CH_3 – CH_2OH$ Ethyl alcohol (note the alcoholic group)	$CH_3 – O – CH_3$ Dimethyl ether (note the ether group)	
C_3H_6O:	$CH_3.CH_2.CHO$ Propanal	$CH_3.CO.CH_3$ Acetone	$CH_2=CH – CH_2OH$ Allyl alcohol
	(note the different functional groups in 3 isomers)		
$C_3H_6O_2$:	$CH_3.CH_2.COOH$ Propanoic acid (note the acidic group)	CH_3COOCH_3 Methyl acetate (note the ester group)	
C_3H_9N:	$CH_3.CH_2.CH_2.NH_2$ *n*-Propylamine (a *primary* amine)	$CH_3 – NH – C_2H_5$ Methyl ethyl amine (a *sec.* amine)	 Trimethylamine (a *ter.* amine)
C_4H_6	alkyne	alkadiene	cyclo alkene
	$CH_3–CH_2–C\equiv CH$	$C = C = C – C$	
	$CH_3–C\equiv C–CH_3$	$C = C – C = C$	
C_4H_8	alkene	cyclo alkane	

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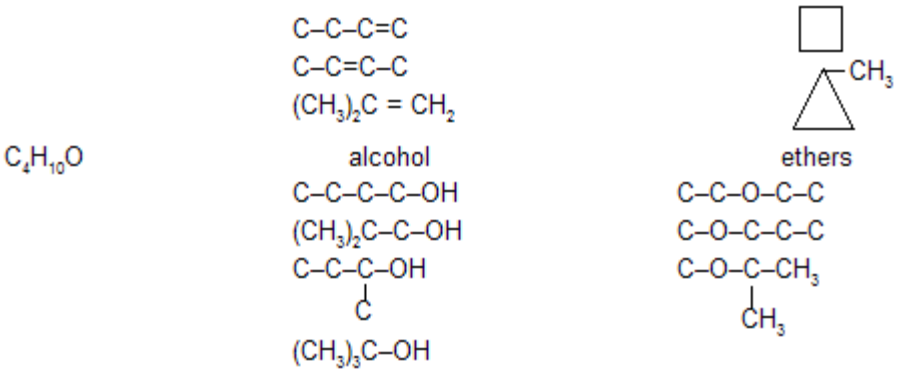
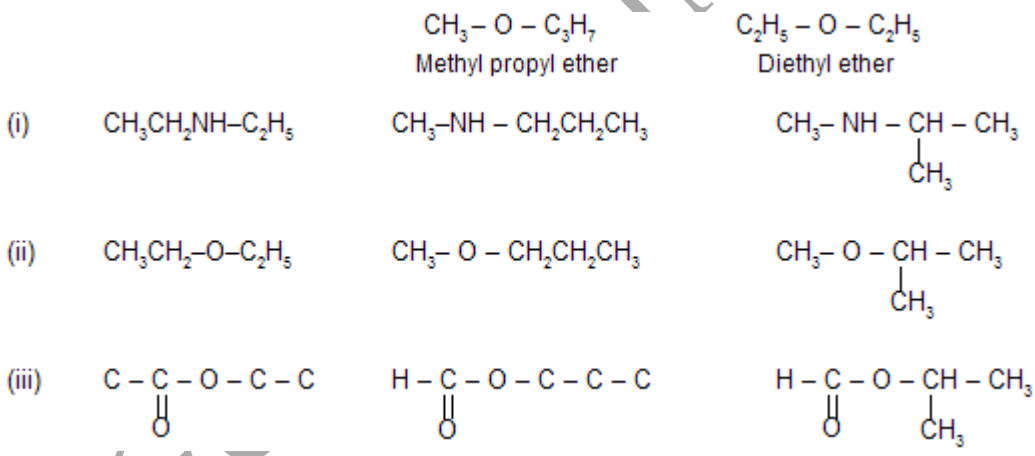


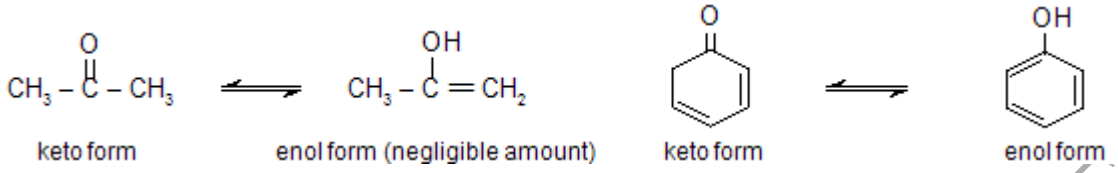
(iv) Metamerism

It is due to the difference in nature of alkyl groups attached to the same functional group. This type of isomerism is shown by compounds of the same homologous series. For example,



(v) Tautomerism

Tautomerism may be defined as the phenomenon in which a single compound exists in two readily interconvertible structures that differ markedly in the relative position of at least one atomic nucleus, generally hydrogen. The two different structures are known as tautomers of each other.
Sometimes the term tautomerism is also called as **desmotropism** (Greek *desmos*-bond; *tropos*-turn), since the interconversion of the two forms involves a change of bonds or **dynamic isomerism** as the two forms are in dynamic equilibrium with each other. Other names for tautomerism are kryptomerism, allelotropism or merotropy; however, tautomerism is the most widely accepted term.
There are several types of tautomerism of which *keto-enol tautomerism* is the most important. In this type, one form (tautomer) exists as a ketone while the other exists as an enol. The two simplest examples are of acetone and phenol.



keto form | enol form (negligible amount) | keto form | enol form

However, the most widely studied example of keto-enol tautomerism is that of acetoacetic ester (ethyl acetoacetate)

keto form (92.3 %) | enol form (7.7 %)

The two forms are readily interconvertible by acid or base catalysts, and under ordinary conditions surface of the glass is sufficient to catalyse the interconversion. The exact composition of the equilibrium depends upon the nature of the compound, solvent, temperature, etc. *The conversion of a keto form into enol from is known as* **enolisation.** The two forms of acetoacetic ester have been isolated under suitable conditions.

Keto-enol tautomerism in acetoacetic ester is proved by the fact that under ordinary conditions the compound gives the properties of the ketonic group as well as that of the enolic group.

ketonic form | enolic form

(note the presence of a ketonic group) | (note the presence of a double bond and acidic –OH group)

Note that in *all the examples of keto-enol tautomerism the two isomeric forms are interconvertible by the migration of a proton from one atom (carbon) to the other with the simultaneous shifting of bonds.*

Remember that *keto-enol tautomerism is possible only in those* **aldehydes and ketones which have at least one a -hydrogen atom** which can convert the ketonic group to the enolic group. Examine the following compounds.

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(i) $CH_3 - \overset{O}{\overset{\|}{C}} - CH_2 - \overset{O}{\overset{\|}{C}} - CH_3 \rightleftharpoons CH_3 - \overset{OH}{\overset{|}{C}} = CH - \overset{O}{\overset{\|}{C}} - CH_3$

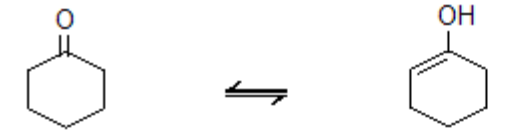
ketonic form — Acetylacetone — enolic form

(ii) $C_6H_5 - \overset{O}{\overset{\|}{C}} - CH_3 \rightleftharpoons C_6H_5 - \overset{OH}{\overset{|}{C}} = CH_2$

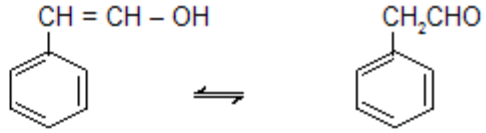
ketonic form — Acetophenone — enolic form

(iii) $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - H \rightleftharpoons CH_3 - CH = \overset{OH}{\overset{|}{C}} - H$

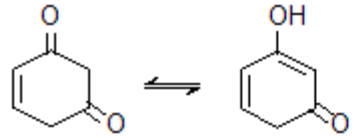
ketonic form — Propionaldehyde — enolic form

(iv) 

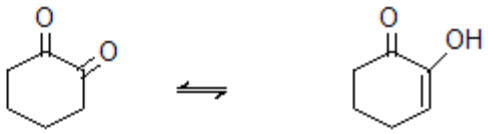
ketonic form — Cyclohexanone — enolic form

(v) 

(Tautomerism possible)

(vi) 

(Tautomerism possible)

(vii) 

(Tautomerism possible)

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(viii) $C_6H_5 - \overset{O}{\overset{\|}{C}} - H$, No α-Hydrogen

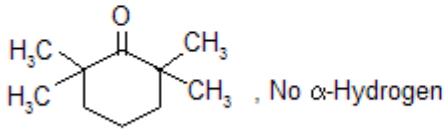
Benzaldehyde

(tautomerism not possible)

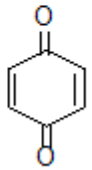
(ix) $C_6H_5 - \overset{O}{\overset{\|}{C}} - C_6H_5$, No α-Hydrogen

Benzophenone

(tautomerism not possible)

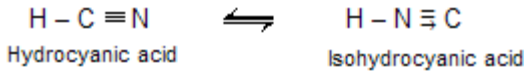
(x)  , No α-Hydrogen

(tautomerism not possible)

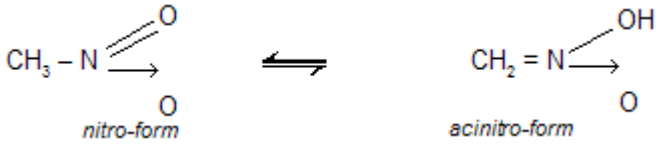
(xi)  , No α-Hydrogen

(tautomerism not possible)

Alkyl cyanides (RCN) and alkyl isocyanides (RNC) are also examples of tautomerism.



Similarly, nitro compounds also show tautomerism.



Distinction of tautomerism from resonance :

The tautomeric forms are quite chemically distinct entities and can be separated (in suitable cases e.g. acetoacetic ester) and characterised. On the other hand, resonating forms differ only in the distribution of electrons and can never be separated from one another since neither of them has any real existence. The important differences between resonance and tautomerism can be summarised as below.

1. Tautomerism involves a change in the position of atom (generally hydrogen), while resonance involves a change in the position of the unshared or
π electron
only.

2. Tautomers are definite compounds and may be separated and isolated. Resonating structures are only imaginary and can't be isolated.

3. The two tautomeric forms have different structures (i.e. functional groups). The various resonating structures have the same functional group.

4. Tautomers are in dynamic equilibrium with each other, resonating structures are not in dynamic equilibrium.

5. Tautomerism has no effect on bond length, while resonance affects the bond length (single bond is shortened while the double bond becomes longer).

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6. Tautomerism does not lower the energy of the molecule and hence does not play any role in stabilising the molecule, while resonance decreases the energy and hence increases the stability of the molecule.

7. Tautomerism is indicated by ' $\rightleftharpoons$ ' while resonance by '$\longleftrightarrow$'.

8. Tautomerism can occur in planar as well as non-planar molecules, while resonance occurs only in planar molecules.

Distinction of tautomerism from isomerism. In fact there is no sharp line of distinction between isomers and tautomers since some substances which are isomers under normal conditions can be converted into tautomeric forms under more drastic conditions. For example, propyl and iso-propyl bromides are isomeric compounds under normal conditions but form an equilibrium mixture on heating at 250°C in a sealed tube.

And hence *dynamic isomerism* is a better term for this phenomenon than *tautomerism.*

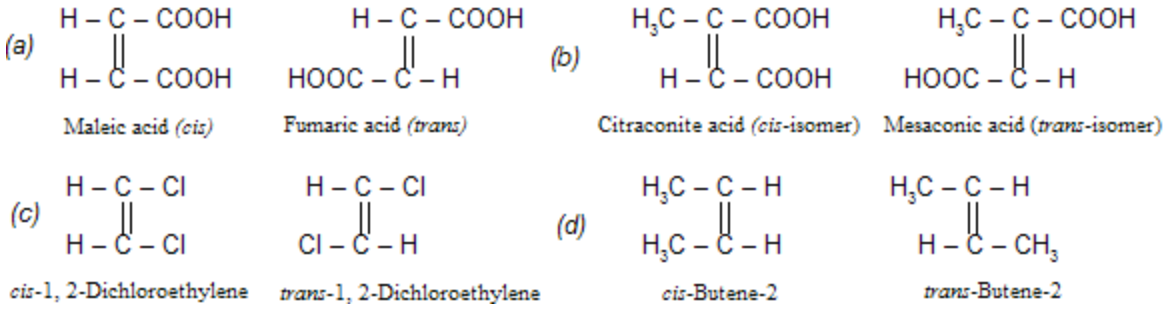
Distinction of tautomerism from molecular rearrangement. Although there is no sharp difference between tautomerism and molecular rearrangement, yet the two can be distinguished by the fact that the former is a rapid and reversible phenomenon whereas the latter is neither reversible nor rapid.

Stereo isomerism

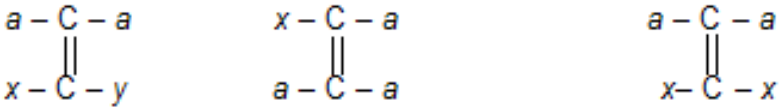
When isomers have the same structural formula but differ in relative arrangement of atoms or groups in space within the molecule, these are known as stereoisomers and the phenomenon as stereoisomerism. The spatial arrangement of atoms or groups is also referred to as configuration of the molecule and thus we can say that the stereoisomers have the same structural formula but different configuration. Stereoisomerism is of two types.

(i) Geometrical isomerism

*The isomers which possess the same structural formula but differ in the spatial arrangement of the groups***around the double bond** *are known as geometrical isomers* and the phenomenon is known as*geometrical isomerism*. This isomerism is shown by alkenes or their derivatives. When similar groups lie on the same side, it is the *cis*-isomer; while when the similar groups lie on opposite sides, the isomer is*trans.* For example,

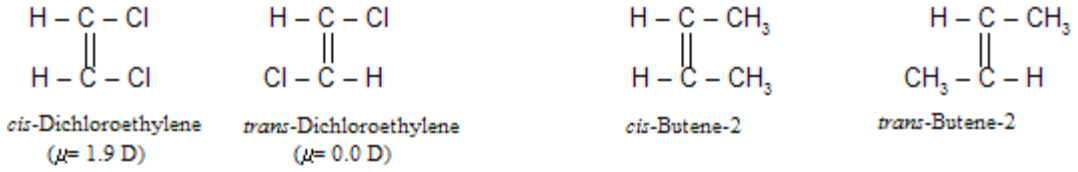


Remember that geometrical isomerism is possible only when each of the doubly bonded carbon atom has two different groups (see examples above). Thus compounds of the following type will not show geometrical isomerism.



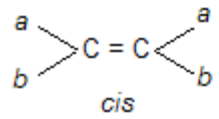
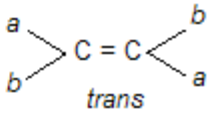
Note the similar atoms (groups) on one or both of the carbon atoms.

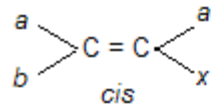
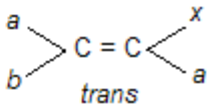
Distinction between *cis* **-and** *trans*- **isomers**. (a) Generally, the *cis*-isomer (e.g. maleic acid) cyclises on heating to form the corresponding anhydride while the *trans*-isomer does not form its anhydride at all.
(b) The *cis*-isomer of a symmetrical alkene (alkenes in which both the carbon atoms have similar groups) has a definite dipole moment, while the trans-isomer has zero dipole moment. For example, 1, 2-dichloroethylene and butene-2.

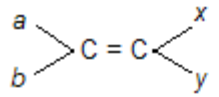
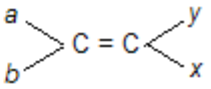


In *trans*-isomer of the symmetrical alkenes, the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.
In case of unsymmetrical alkenes, the *cis*-isomer has higher dipole moment than the corresponding*trans*-isomer. For example,

The E and Z Nomenclature of Geometrical Isomers. As discussed earlier, the geometrical isomerism is possible in structures of the following three types.

I.  and 

II.  and 

III.  and 

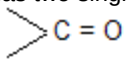
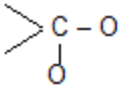
In the first two types, the geometrical isomers are labelled as cis and trans on the basis of the fact that the common groups are on the same or opposite sides of the double bond. But in type 3 where all the four substituents are different, cis-trans type of isomerism cannot be applied. Moreover, the cis-trans system (also syn-anti system in oximes) is often ambiguous because the cofigurational descriptions have not been defined according to any general and clear set of rules. So an unambiguous system of configurational assignments for all types of structures showing geometrical isomerism was developed in 1968. This system is known as E-Z system of nomenclature and is based upon the sequence rules of Cahn, Ingold and Prelog originally developed for naming optical isomers on the R-S system. The following procedure is followed in specifying the configuration of such compounds.

i) Assign the priority order to the two groups attached to each of the doubly bonded carbon atoms in accordance with the sequence rules. Sequence rules are for determining the priority order to atoms or groups attached to doubly bonded carbon atoms.

(a) Higher priority is assigned to atoms (directly attached to the carbon atom) of higher atomic number.

(b) If isotopes of the same element are attached, the isotope with higher mass number will have a higher priority. If the priority cannot be decided by this rule, it is then determined by comparing the next atom in the group and so on.

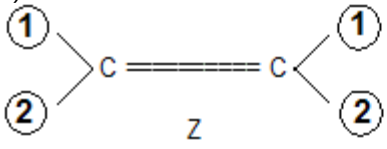
(c) A doubly or triply bonded atom is considered equivalent to two or three such atoms. Thus a carbonyl group is considered as if carbon has two single bonds with oxygen, i.e.,

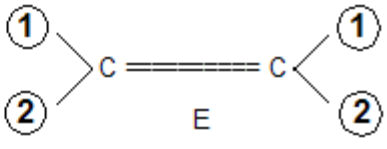
 equal to 

By the application of these rules some common substituents have been given the following priority sequence:-

I, Br, Cl, F, O, N, C, H $-C(CH_3)_3$, $-CH(CH_3)_2$, $-CH_2CH_3$, $-CH_3$

(ii) Select the atom/group with higher priority on each doubly bonded carbon. If the atoms/groups of higher priority (denoted by 1) on each carbon are on the same side of the double bond, the isomer is assigned the configuration Z (from the German word, zusammen meaning together). On the other hand, if the atoms/groups of higher priority on each carbon are on the opposite sides of the double bond, the isomer is assigned the configuration E (from the German word entgegen meaning against).


Z

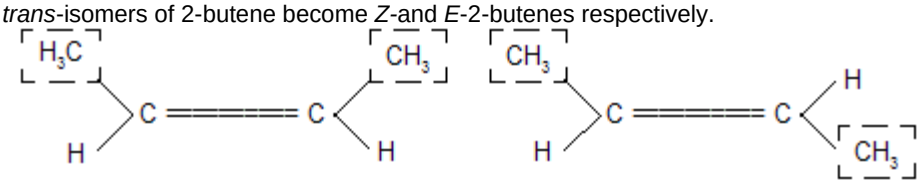

E

Where 1 and 2 represent the atoms (groups) of higher and lower priority respectively.

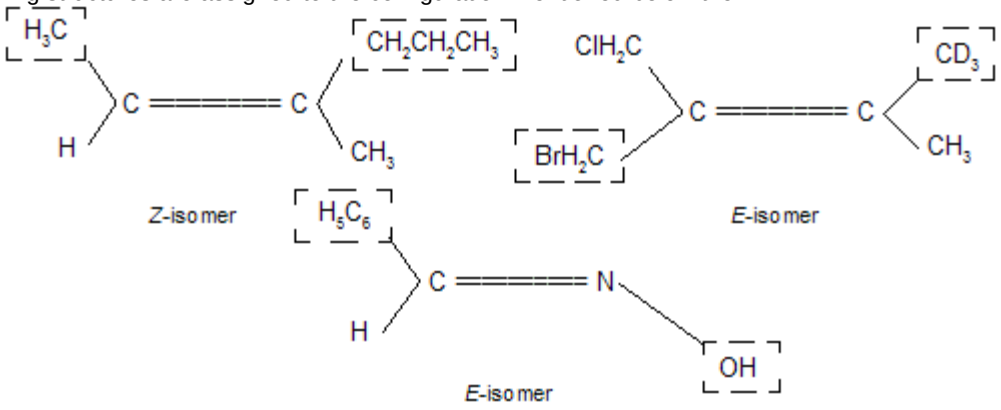
Now let us consider the example of an alkene in which one of the doubly bonded carbon atoms has Br and I and the other has F and Cl. Now since I has a higher atomic number than Br, it is assigned higher priority (1); similarly Cl is of higher priority than F on the second olefinic carbon atom. Thus the *E* and *Z* configuration of the two isomers of 1-bromc-2-chloro-2-fluoro-1-iodoethene are assigned as below.

Note : The bracketed groups indicate groups of higher priority on the respective olefinic carbon atom.

Thus the *cis*- and *trans*-isomers of 2-butene become *Z*-and *E*-2-butenes respectively.



Similarly, following structures are assigned to the configuration mentioned below them.

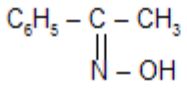


Geometrical Isomerism in Oximes (Compounds containing $>$C=NOH group).

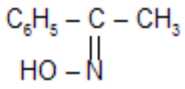
Aromatic aldoximes and aromatic ketoximes also show geometrical isomerism. In aldoximes, when H and OH groups are on the same side, the isomer is known as syn (analogous to cis) and when these groups are on the opposite sides, the isomer is known as *anti* (analogous to *trans).*

In ketoximes the prefixes syn and anti indicate which group of ketoxime is syn (on the same side) or anti (on the opposite sides) to the OH group. For example,

(i)

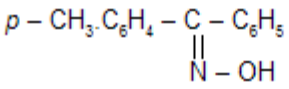


syn-Methylphenyl ketoxime
(anti-Phenylmethyl ketoxime*)*

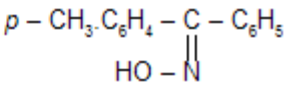


syn-Phenylmethyl ketoxime
(anti-Methylhenyl ketoxime*)*

(ii)



syn-Phenyl-*p*-toluyl ketoxime
(anti-p-Toluyl-phenyl ketoxime*)*



syn-p-Toluyl-phenyl ketoxime
(anti-Phenyl-*p*-toluyl ketoxime*)*

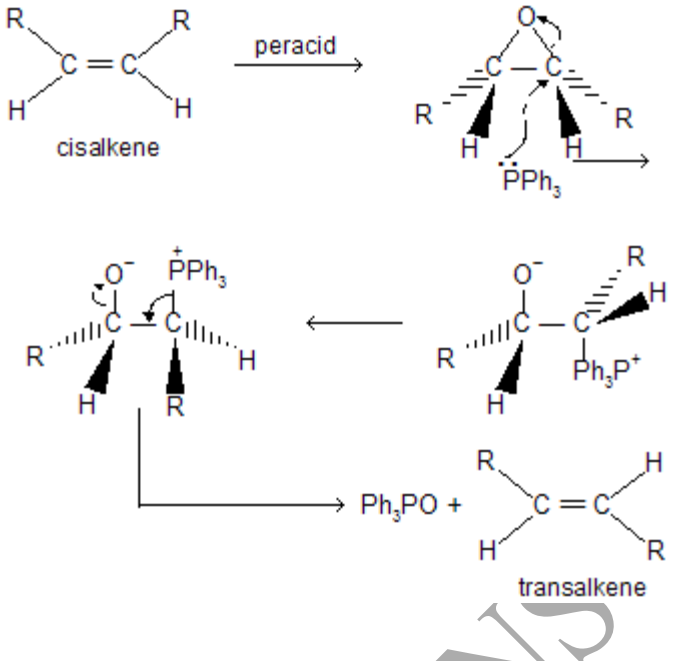
However, remember that all aromatic ketoximes do not show geometrical isomerism e.g., $(C_6H_5)_2C = NOH$, (benzophenone oxime) having two similar aryl groups does not show geometrical isomerism.

Interconversion of Cis- Trans isomers

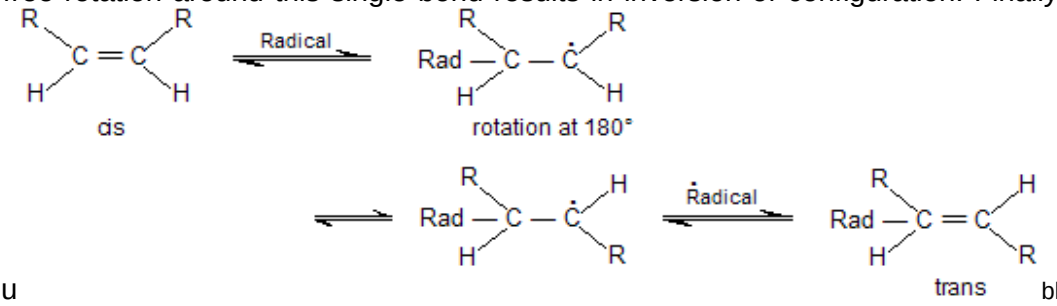
The cis and trans isomers of alkenes do not interconvert under ordinary conditions because of π-bond, bond strength of 68 kcal/mole. This amount of energy is available only at high temprature or with ultraviolet light, so these two isomers exist as stable compounds at room temprature.

The geometrical isomers can be interconverted if energy of more than 68 kcal/mole (the π-bond energy), is applied by heat or uv light; then the π-bond is broken and allows free rotation to occur about the carbon carbon σ bond.

Interconversion of double bond diastereomers can also be brought Via epoxidation deoxygenation sequence. The nucleophile attack by phosphours regents example, triphenyl phosphine at the oxirane carbon leads to inversion of configuration and yields a charge separated intermediate (a betaine). This undergoes elimination Via a four center cyclic transition state which requires a 180° rotation around the C — C bond to establish the appropriate geometry. Therefore, if these are cis in the oxirane they become trans in the alkene.



Conversion of cis into trans or vice versa by heat or uv medium or by free radical initiator is known as stereomutation. In the presence of free radical double bond first gets converted into single bond then free rotation around this single bond results in inversion of configuration. Finally, regeneration



of double bond occurs.

Geometrical isomerism also occurs in some saturated cyclic diols, di halide and di carboxylic acids.

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