UNIT-III
Types of Organic Reactions and Reagents

NUCLEOPHILES vs ELECTROPHILES

"Nucleous loving" species

- typically have a ⊖ charge

or

- non-bonding ē pair available for making a new bond

Examples: $CH_3O^{\ominus}$ or CH_3NH_2

"Electron loving" species

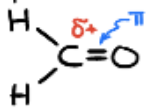
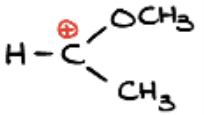
- typically have an atom with a ⊕ charge

or

- have an Electron Withdrawing Group (EWG) that puts a $\delta+$ on an atom

or

- have a polarizable π bond

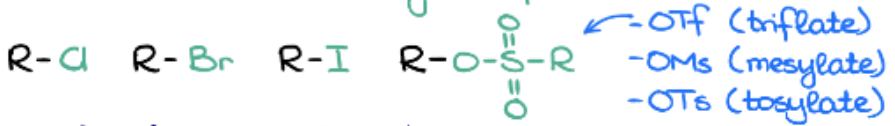
Examples:  or 

Typical Examples of Electrophiles & Nucleophiles

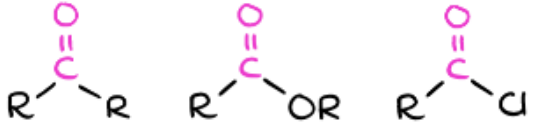
www.OrganicChemistryTutor.com

ELECTROPHILES

1. Molecules with Leaving Groups



2. Molecules with C=O bond



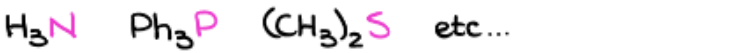
etc...

NUCLEOPHILES

1. Not bulky ⊖-charged ions

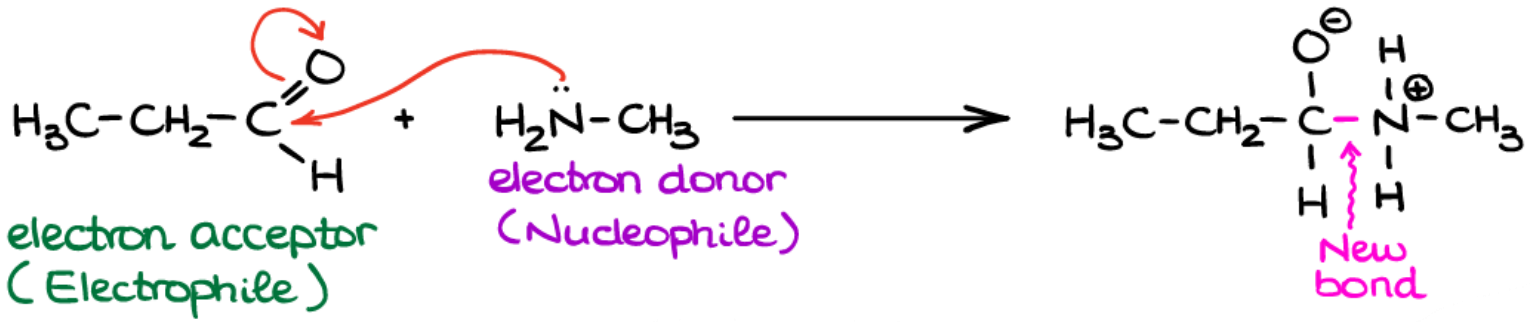
etc...

2. Molecules with neutral N, P, or S

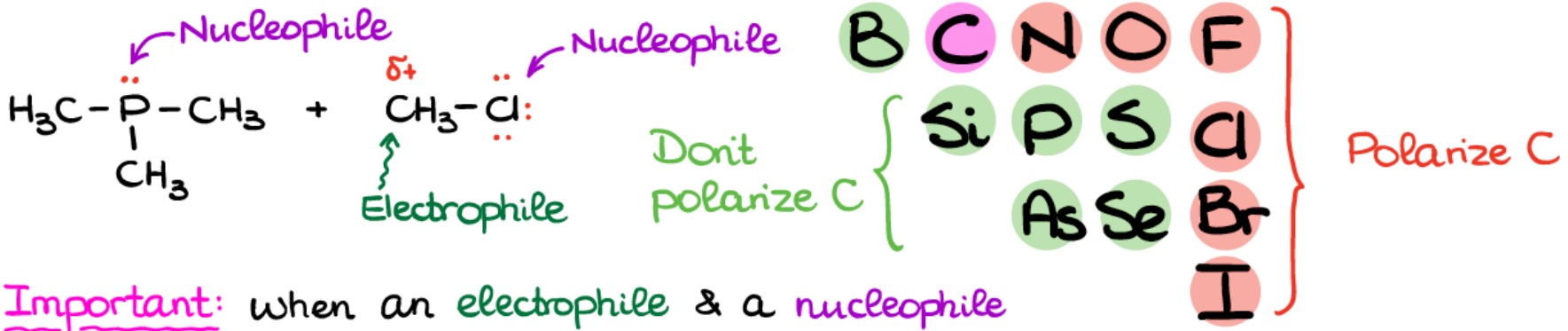


etc...

Senario 1: Both the reaction products & mechanism are given to you



1. Identify all locations with the lack of ē density (δ+) & all locations with extra electrons (δ-)

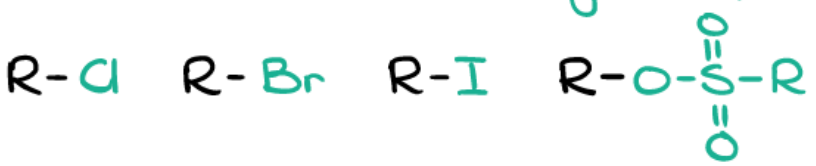


Important: when an electrophile & a nucleophile are adjacent atoms, they cannot react with each other b/c they already have a bond!

Typical Examples of Electrophiles & Nucleophiles

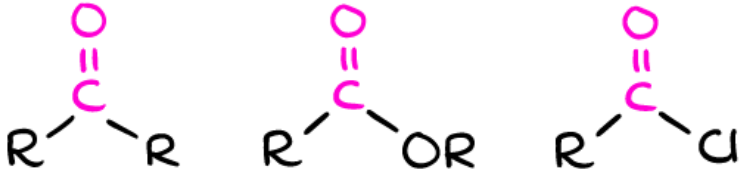
ELECTROPHILES

1. Molecules with Leaving Groups



- -OTf (triflate)
- -OMs (mesylate)
- -OTs (tosylate)

2. Molecules with C=O bond



etc...

NUCLEOPHILES

1. Not bulky ⊖-charged ions

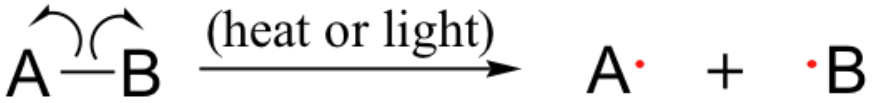
etc...

2. Molecules with neutral N, P, or S

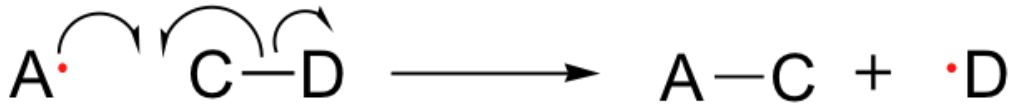
etc...

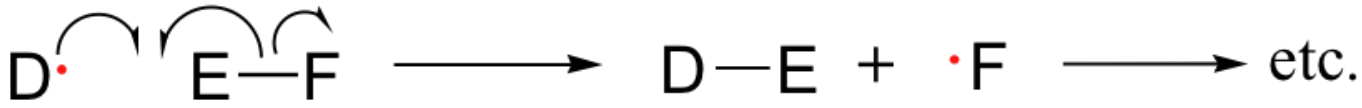
FREE RADICALS

initiation

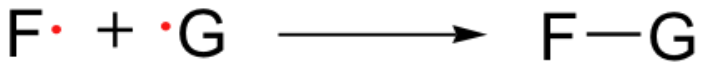


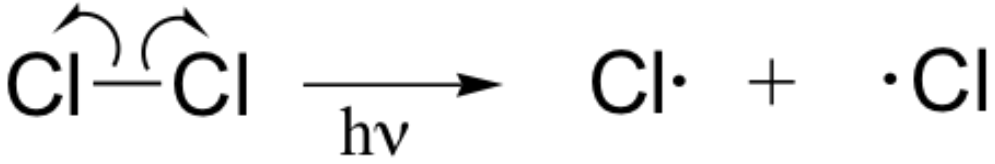
propagation





termination



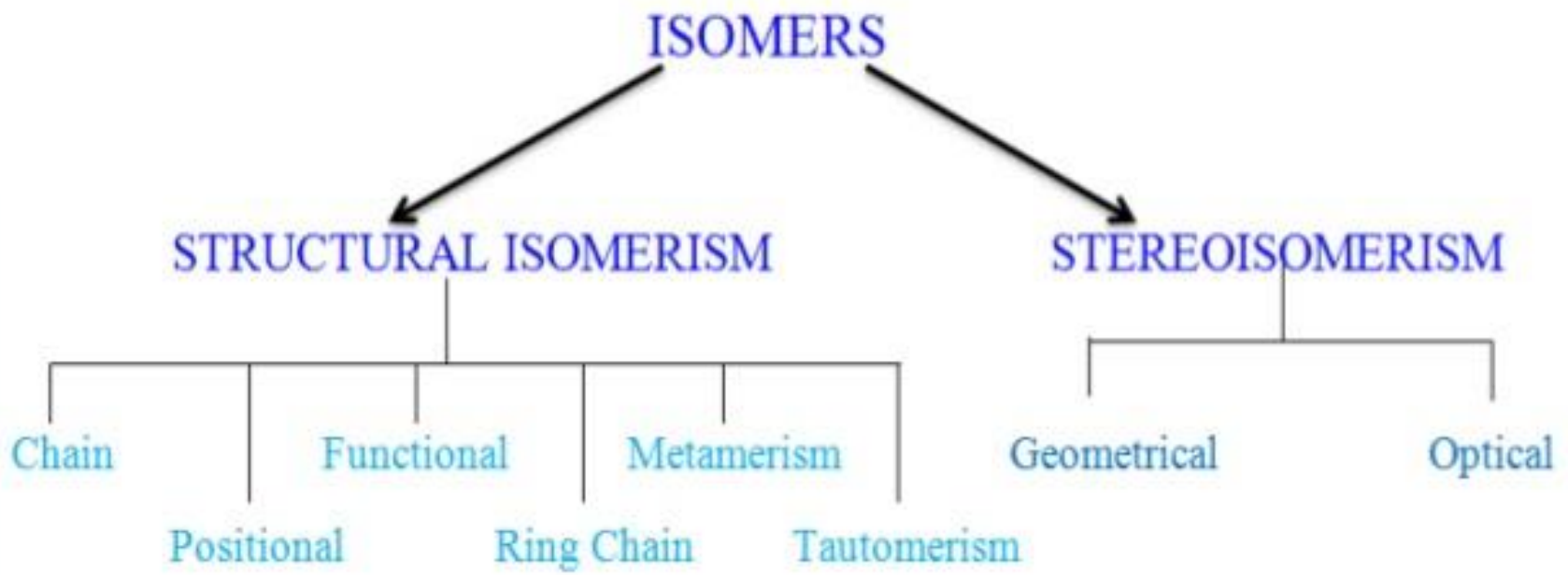


What is Isomerism?

The organic compounds having the same molecular formula but different structures are known as Isomers. This phenomenon is known as Isomerism.

In other words, the organic compounds having the same molecular formula but different arrangements of carbon atoms in them, are known as Isomers.

CLASSIFICATION OF ISOMERISM



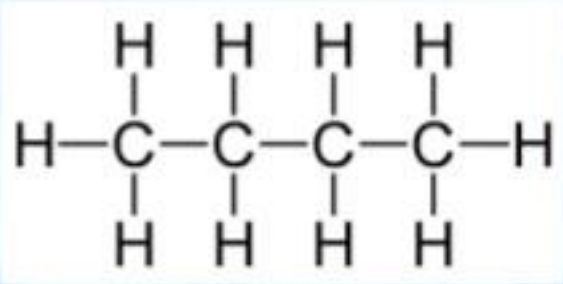
STRUCTURAL ISOMERISM

This type of Isomerism is classified into 6 types-

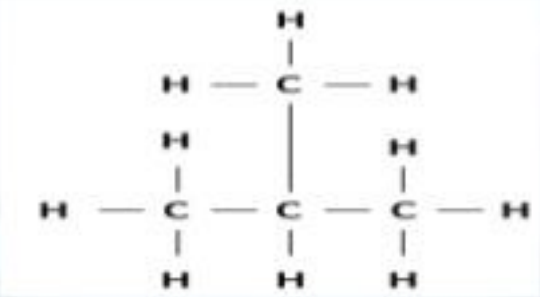
1. Chain Isomerism.
2. Positional Isomerism.
3. Functional Isomerism.
4. Ring Chain Isomerism.
5. Metamerism Isomerism.
6. Tautomerism Isomerism

1. CHAIN ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the nature of carbon chain(straight or branched)
- Example, C_4H_{10} (Butane) has two isomers namely butane and 2-methylpropane.



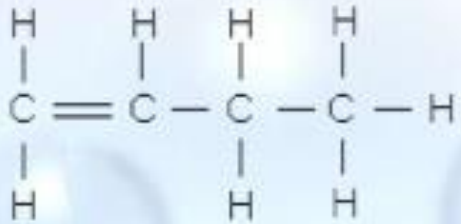
BUTANE



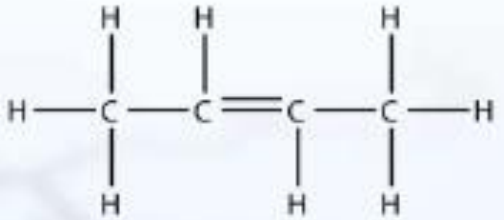
2-METHYLPROPANE

2. POSITIONAL ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the position of the same functional group
- Example, Butene has two isomers namely But-1-ene and But-2-ene.



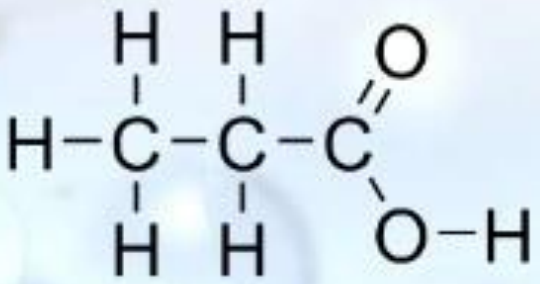
BUT-1-ENE



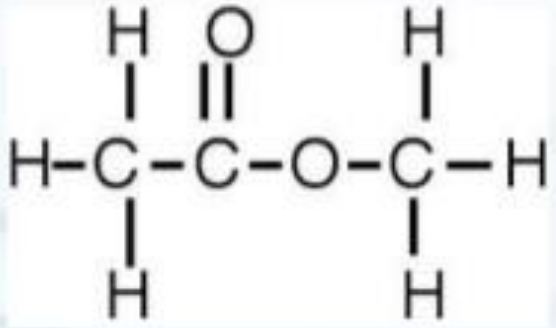
BUT-2-ENE

3. FUNCTIONAL ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the nature of the functional group.
- Example, $C_3H_6O_2$ has two isomers namely Propanoic acid and Methyl ethanoate.



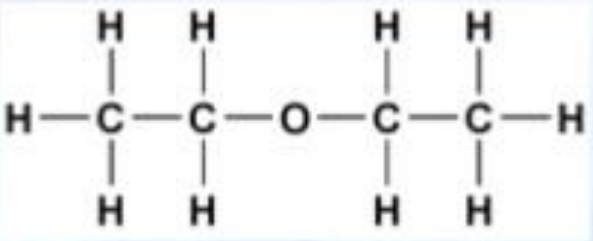
PROPANOIC ACD



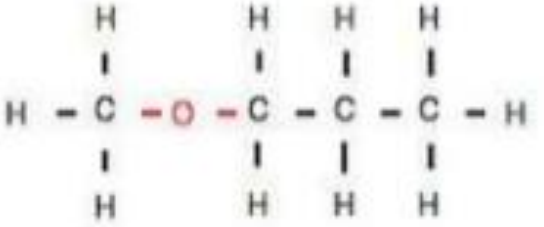
METHYL ETHANOATE

4. METAMERISM ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the nature of the alkyl groups attached to the same functional group.
- Example, Diethyl ether and Methyl propyl ether are metamerical isomers.



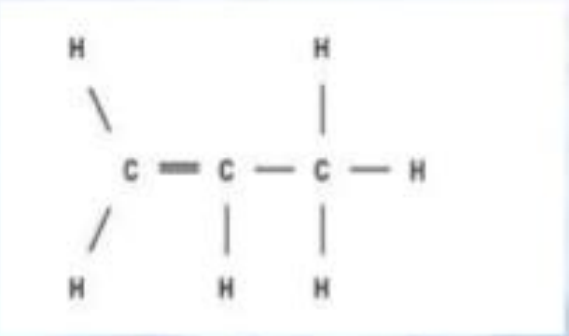
DIETHYL ETHER



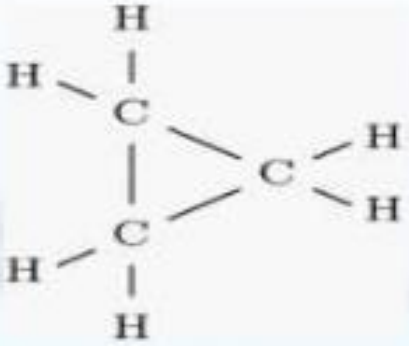
METHYL PROPYL ETHER

5. RING CHAIN ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the mode of linkage of carbon atoms.
- The isomers have either open chain or closed chain.
- Example, Propene and cyclopropane are ring chain isomers.



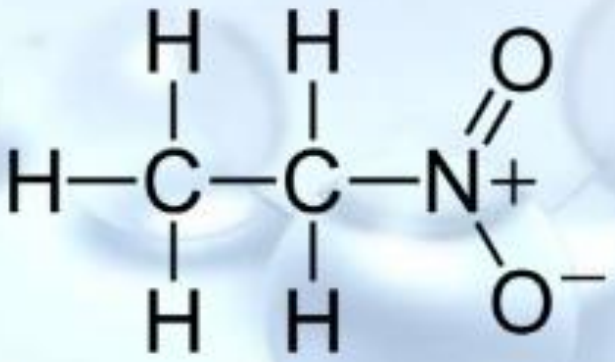
PROPENE



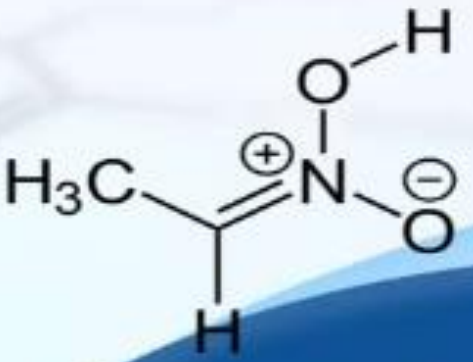
CYCLOPROPANE

6. TAUTOMERISM ISOMERISM

- The same molecular formula represents two or more compounds.
- It exists in dynamic equilibrium with each other. It can be present in many form such as Nitroform and Aci form, Ketoform and Enolic forms etc.
- Example, Nitro- ethane and Isonitroethane are Tautomerical isomers.



NITRO-ETHANE(nitro form)



ISONITROETHANE(aciform)

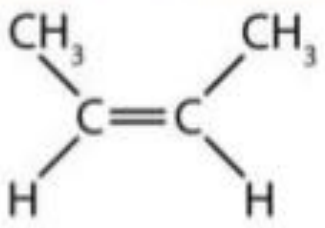
STEREOISOMERISM

This type of Isomerism differs in the spatial arrangement of atoms or groups. It is of two types –

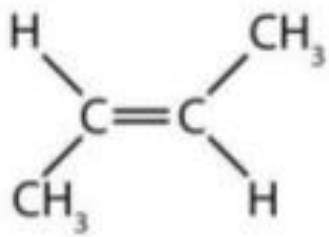
1. Geometrical Isomerism.
2. Optical Isomerism.

6. GEOMETRICAL ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the spatial arrangement of atoms or groups around carbon-carbon double bond.
- It is of two types-If same group are on same side then, it is called 'cis' isomers and if it is on opposite sides, then it is called 'trans' isomers.
- Example, cis-2-butene and trans-2-butene are 'cis' and 'trans' isomers.



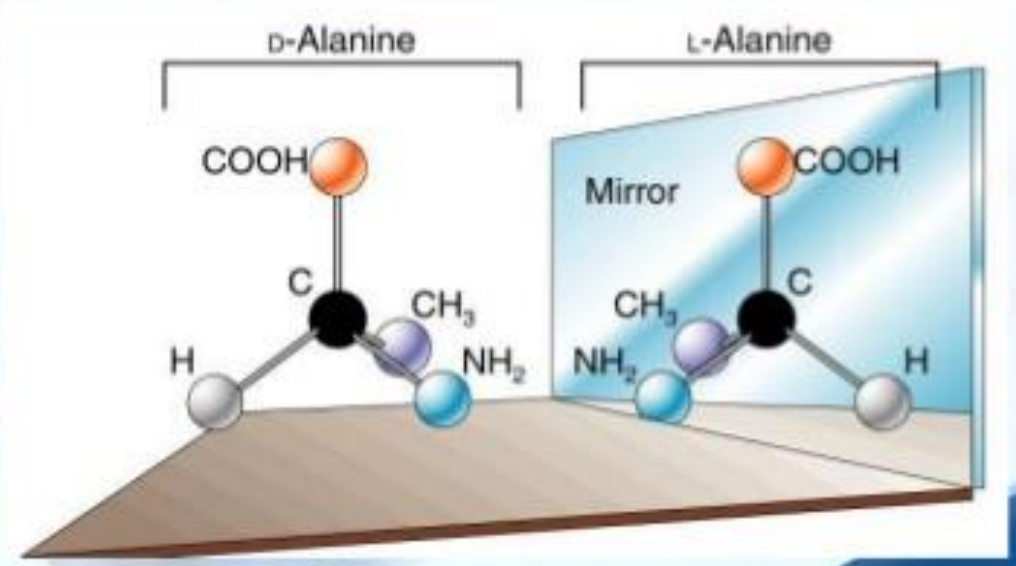
cis-2-butene



trans-2-butene

6. OPTICAL ISOMERISM

- Optical Isomers are named like this because of their effect on plane polarized light.
- Optical Isomers, which are non-superimposable mirror images of each other, are called Enantiomers.
- Example, d-Alanine and l-Alanine, lactic acid etc.



OPTICAL ISOMERISM

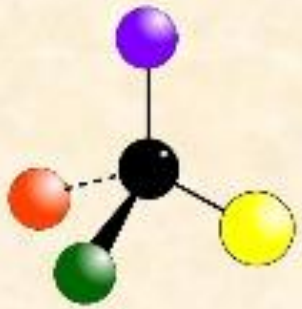
Occurrence

another form of stereoisomerism
occurs when compounds have non-superimposable mirror images

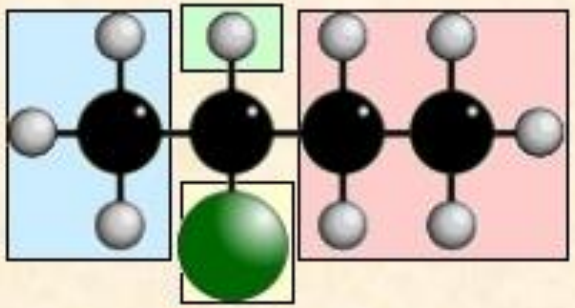
Isomers

the two different forms are known as optical isomers or enantiomers
they occur when molecules have a chiral centre
a chiral centre contains an asymmetric carbon atom
an asymmetric carbon has four different atoms (or groups)
arranged tetrahedrally around it.

CHIRAL CENTRES



There are four different colours arranged tetrahedrally about the carbon atom

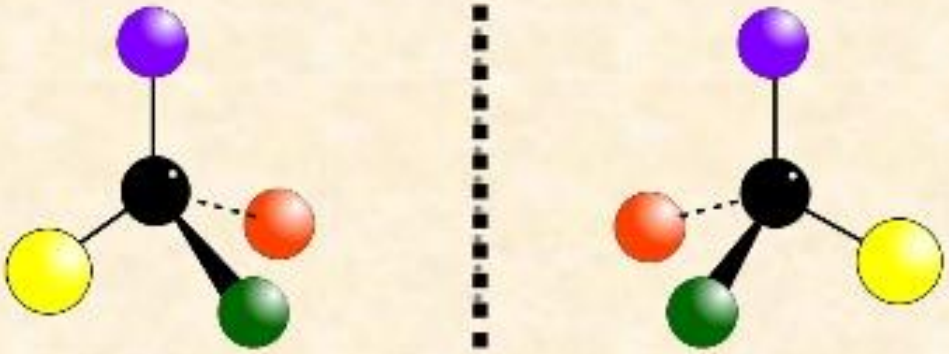


2-chlorobutane exhibits optical isomerism because the second carbon atom has four different atoms/groups attached

OPTICAL ISOMERISM

Spatial differences between isomers

- two forms exist which are NON-SUPERIMPOSABLE MIRROR IMAGES of each other
- non-superimposable means you you can't stack one form exactly on top of the other



OPTICAL ISOMERS - DIFFERENCE

- isomers differ in their reaction to plane-polarised light
- plane polarised light vibrates in one direction only
- one isomer rotates light to the right, the other to the left
- rotation of light is measured using a polarimeter
- rotation is measured by observing the polarised light coming out towards the observer

OPTICAL ISOMERS - DIFFERENCE

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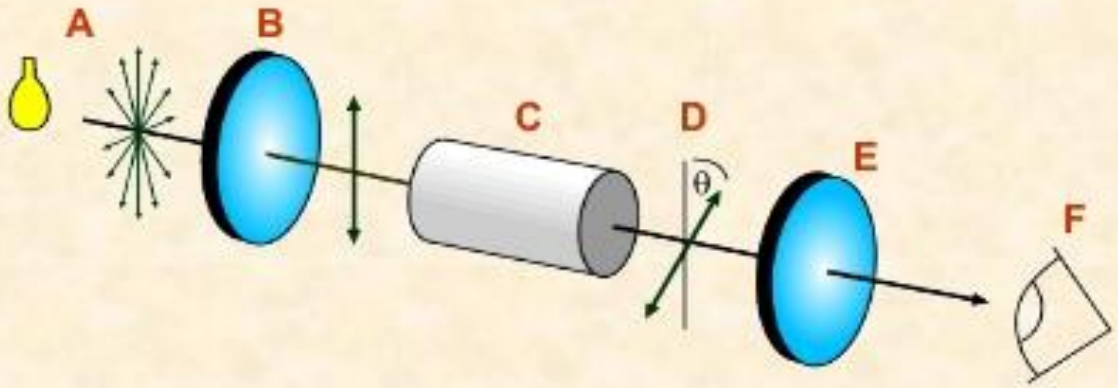
- rotation is measured by observing the polarised light coming out towards the observer

• If the light appears to have	turned to the right	turned to the left
	DEXTROROTATORY	LAEVOROTATORY
	d or + form	l or - form

OPTICAL ISOMERISM

The polarimeter

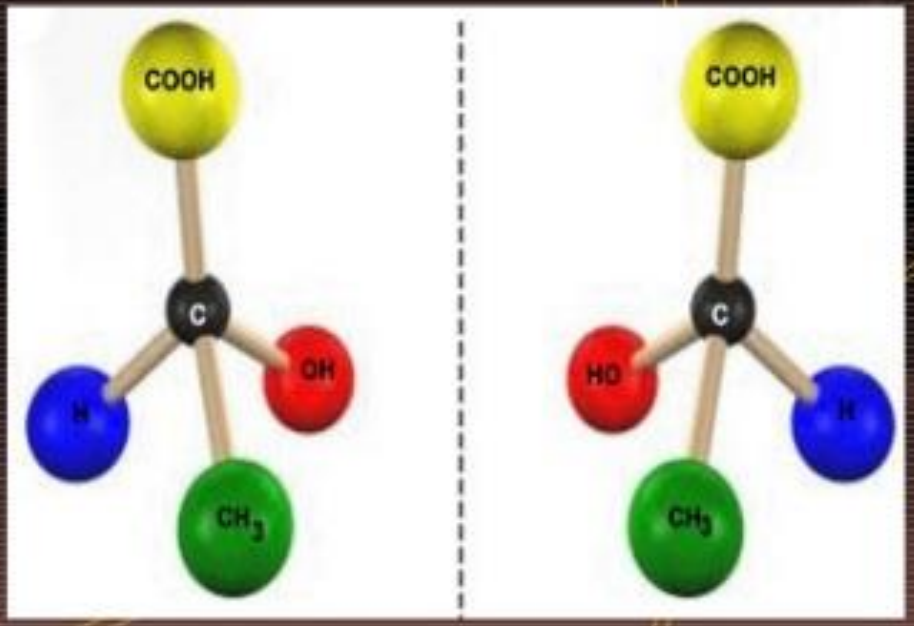


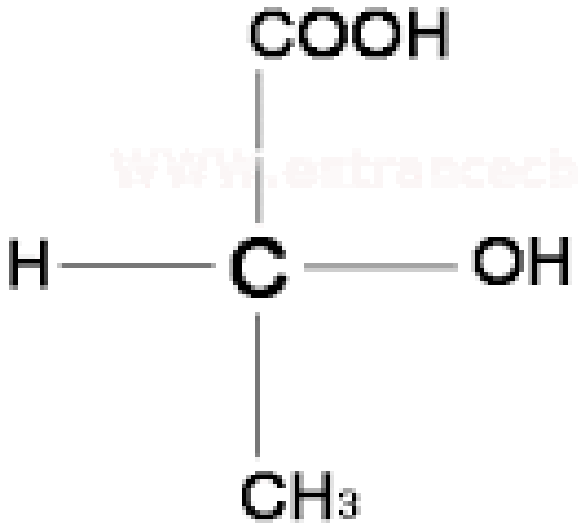
- **A** Light source produces light vibrating in all directions
- **B** Polarising filter only allows through light vibrating in one direction
- **C** Plane polarised light passes through sample
- **D** If substance is optically active it rotates the plane polarised light
- **E** Analysing filter is turned so that light reaches a maximum
- **F** Direction of rotation is measured coming towards the observer

If the light appears to have	turned to the right	turned to the left
	DEXTROROTATORY	LAEVOROTATORY

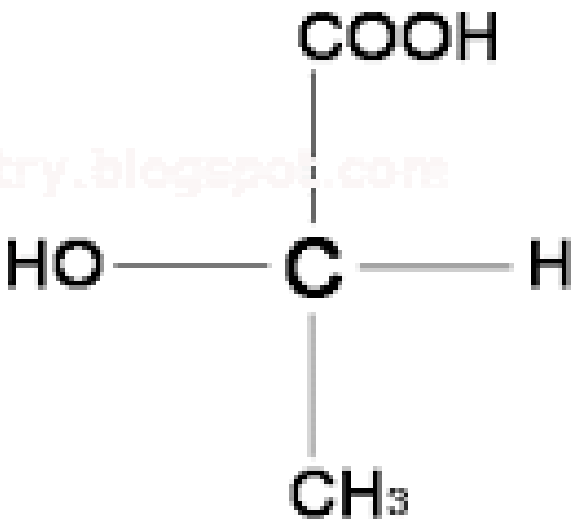
Lactic Acid :

Lactic acid is an optical isomer and it contains one asymmetric carbon atom .Three forms of lactic acid are known . Two are optically active and third is optically inactive .





d- lactic acid



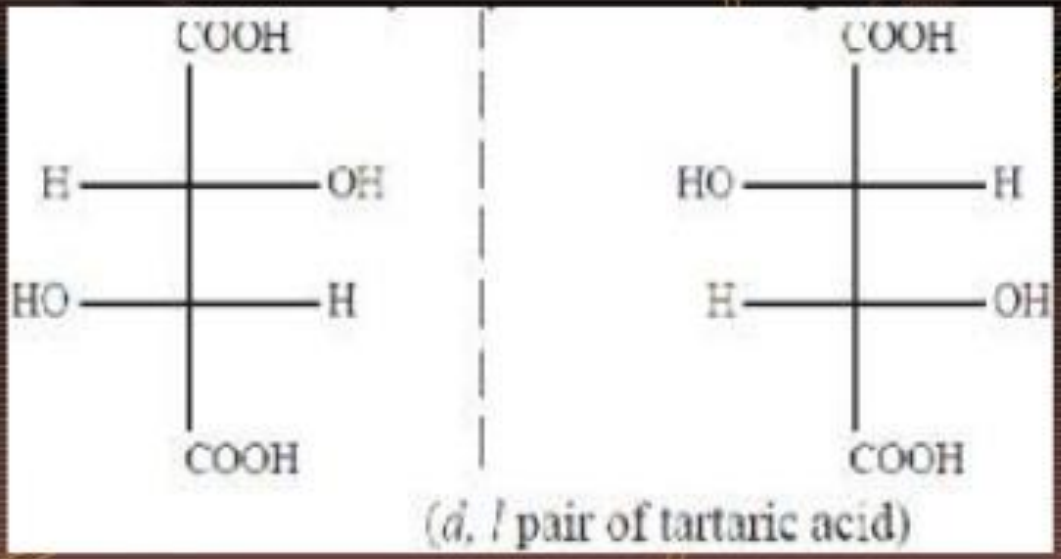
l- lactic acid

In lactic acid CH_3 - CHOH - COOH, second carbon is chiral.

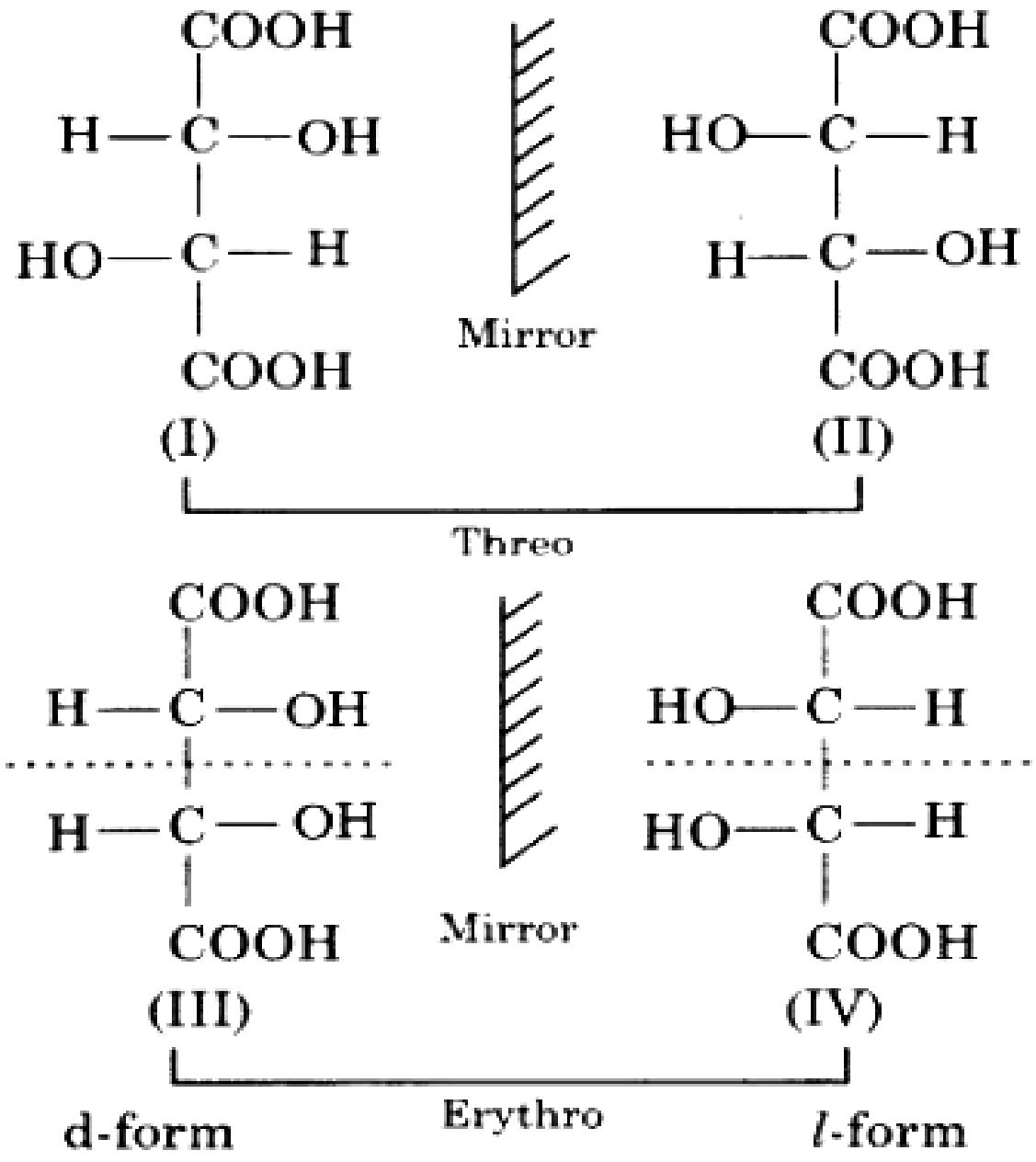
There are two optically active isomers of Lactic acid: d-lactic acid and l-lactic acid. In addition to these optically active varieties there is an optically inactive form which results when dextro and laevo (levo) varieties are present in equal quantities. It is called racemic mixture or (+-) lactic acid.

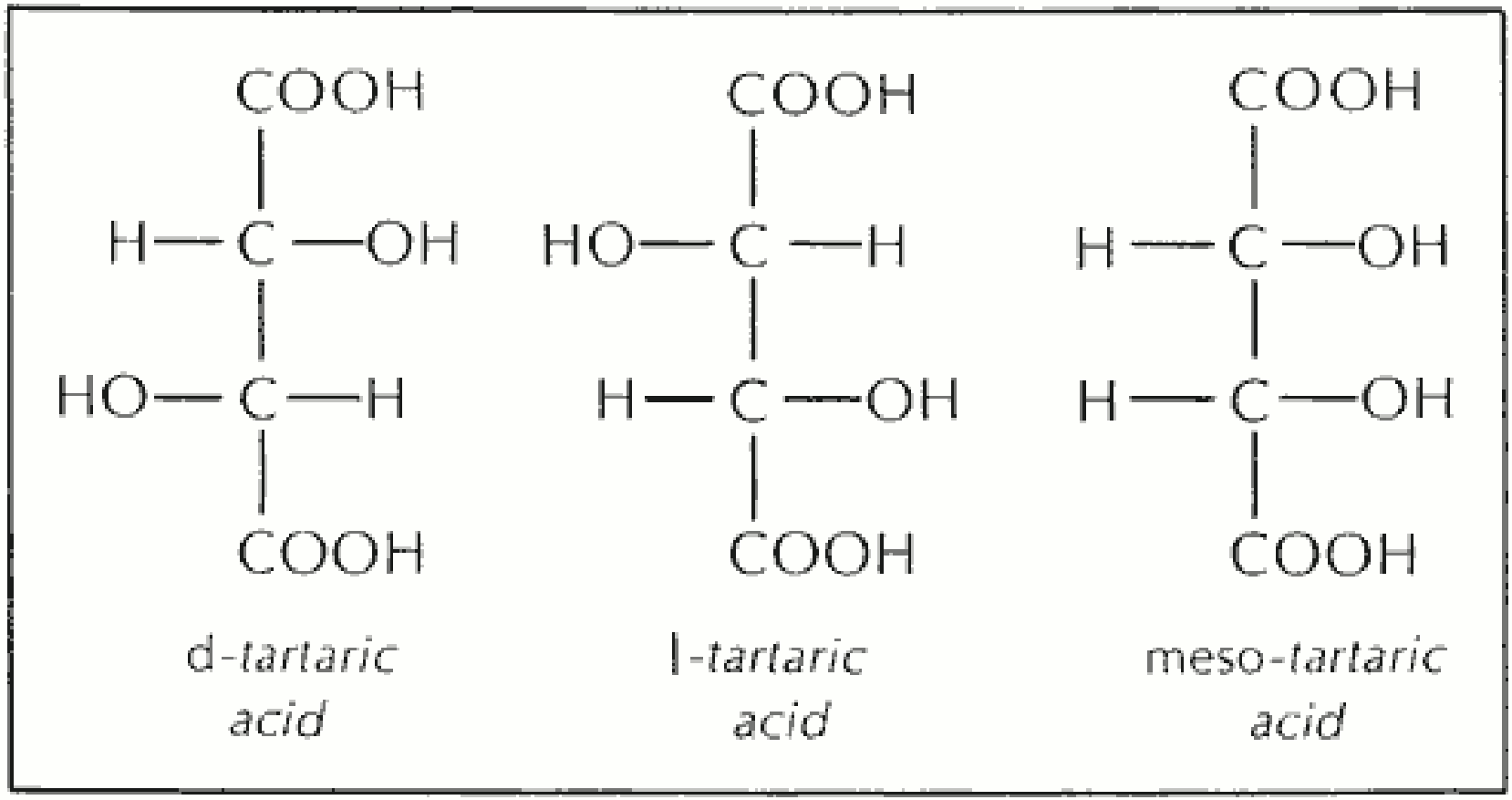
Tartaric Acid :

Tartaric acid show optical isomerism. It contains Two asymmetric carbon atom. Four forms of tartaric acid are known .Two of them optically active and two are optically inactive.

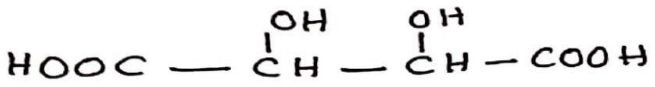


(*d, l* pair of tartaric acid)

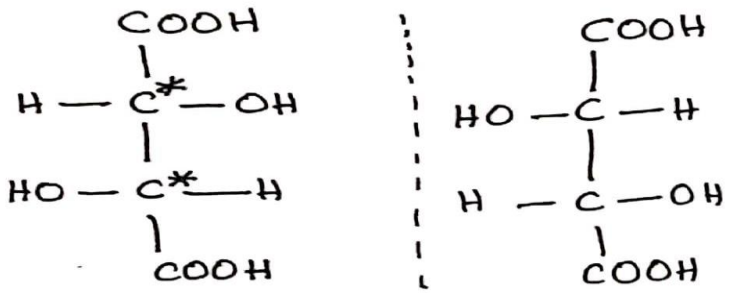

COOH
H—C—OH
HO—C—H
COOH
(I)
Mirror
COOH
HO—C—H
H—C—OH
COOH
(II)
Threo
COOH
H—C—OH
H—C—OH
COOH
(III)
Mirror
COOH
HO—C—H
HO—C—H
COOH
(IV)
d-form
Erythro
l-form


COOH
H—C—OH
HO—C—H
COOH
d-tartaric acid
COOH
HO—C—H
H—C—OH
COOH
l-tartaric acid
COOH
H—C—OH
H—C—OH
COOH
meso-tartaric acid

Tartaric acid

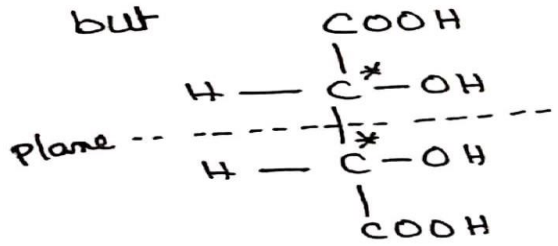


3 Isomers Two optically active one is optically inactive



non superimposable mirror images of each other is called enantiomers in this pair one 'd' (+) and another 'l' (−) optically active

but



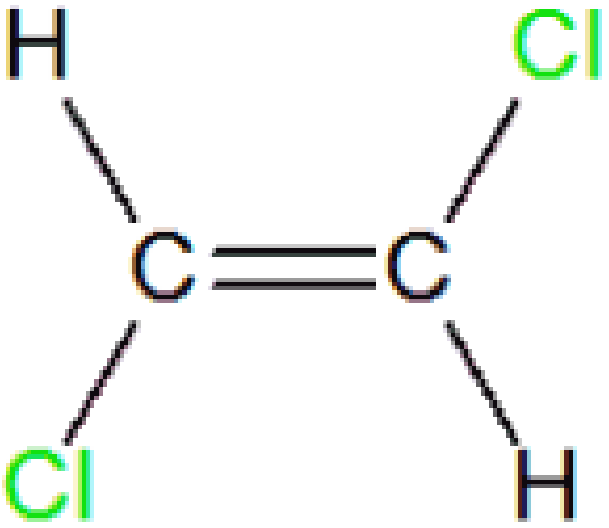
Meso optically inactive

in this case also we have Two chairal centres but this is Meso compound that means it obeys plane of symmetry due to presence of identical chiral centre so it's called Meso compound

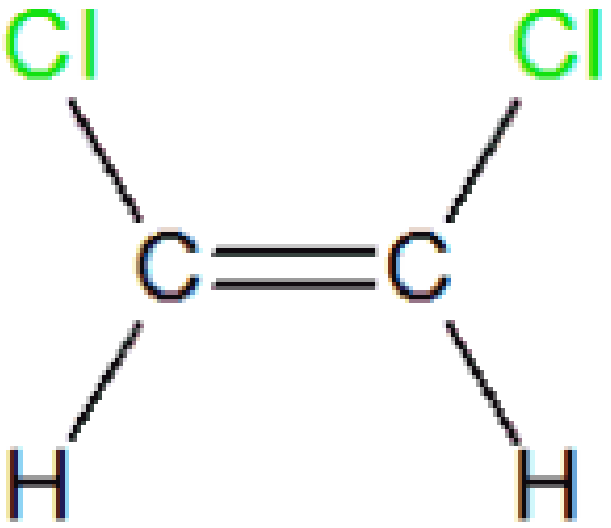
Racemic mixture : 50% of d(+) and 50% of l(−)

(or) equal amounts of d and l gives Racemic mixture it is optically inactive

1,2 - dichloroethene shows cis-trans or geometrical isomerism.



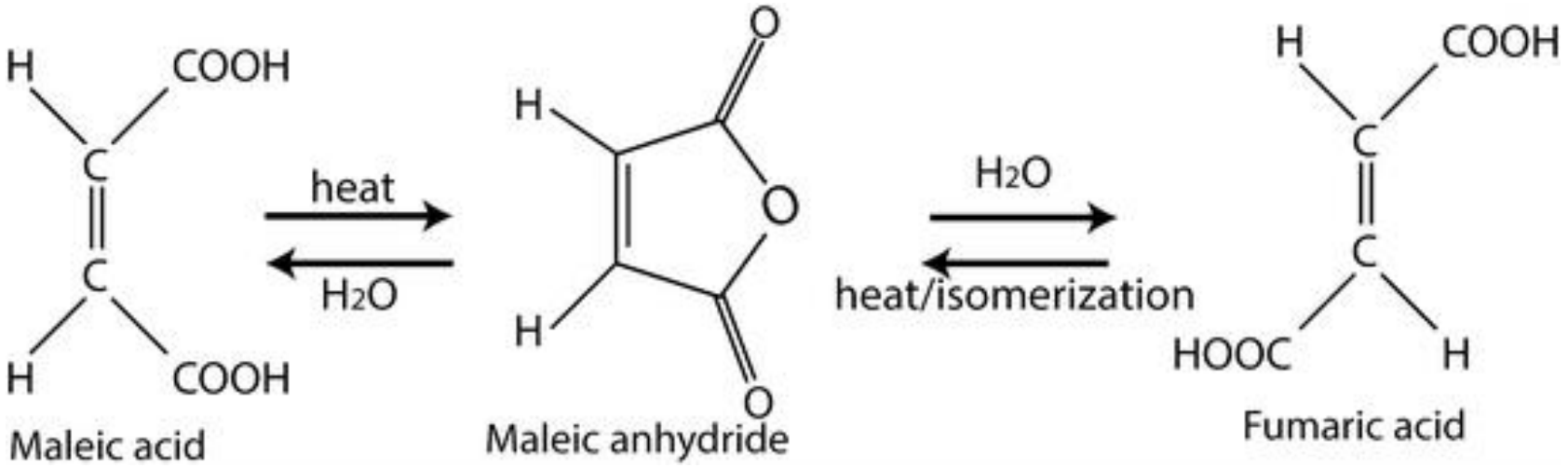
trans-1,2-dichloroethene

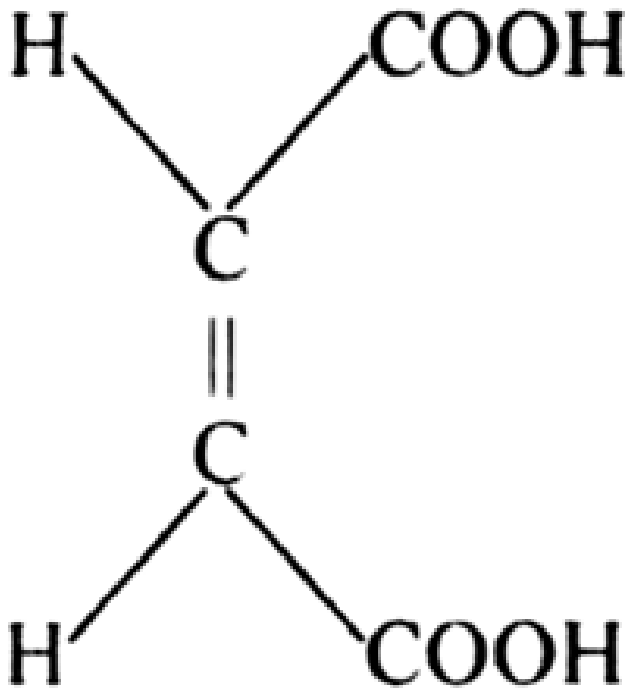


cis-1,2-dichloroethene

GEOMETRICAL ISOMERISM IN MALEIC AND FUMARIC ACID

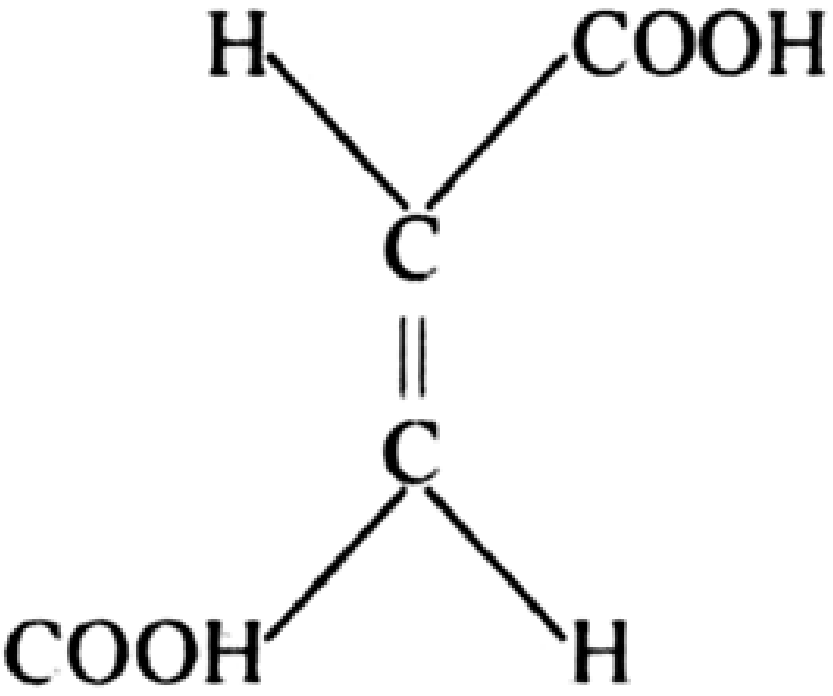
Chemical structures of maleic acid, fumaric acid and maleic anhydride





cis

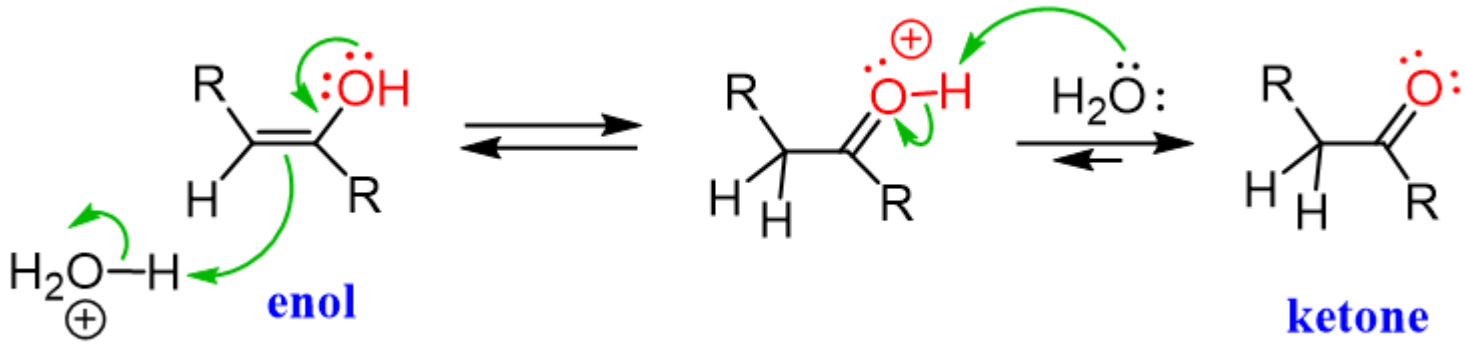
(Maleic acid)

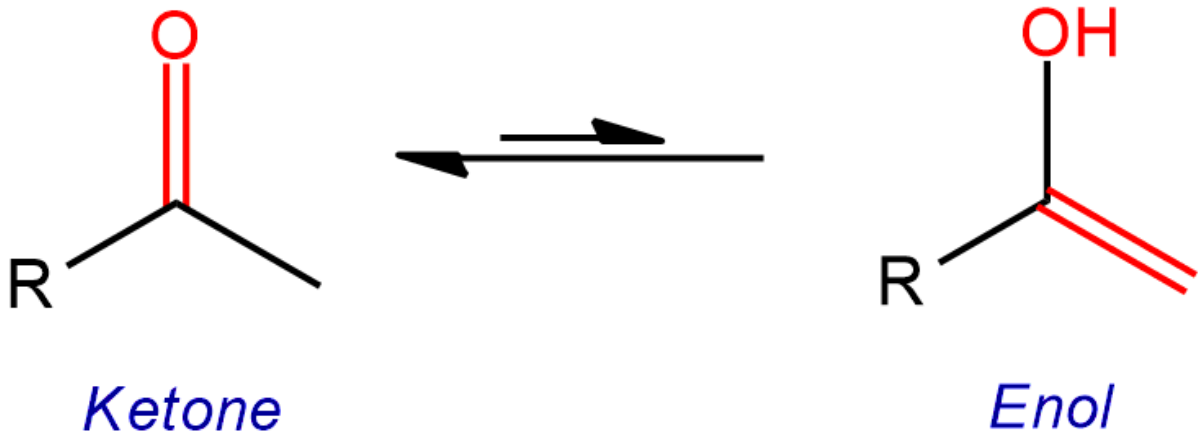


trans

(Fumaric acid)

Keto – Enol Tautomerism



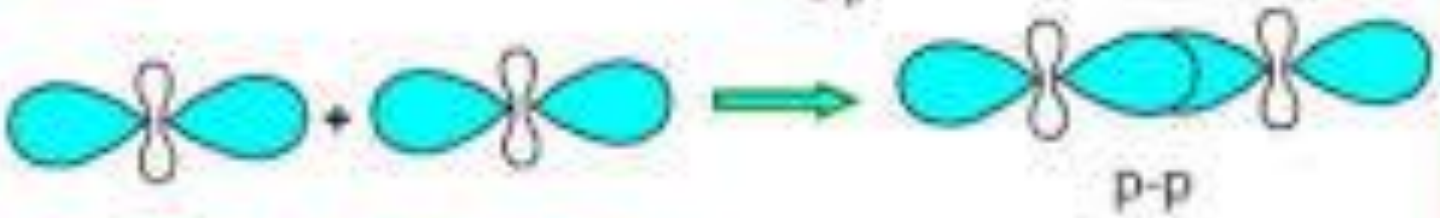


Ketones and other carbonyl compounds containing a hydrogen adjacent to the carbonyl are in the equilibrium with a constitutional isomer called enol.

Orbital Overlap Concept

s-s

s-p



p-p

Strength of these sigma bonds is in the order:

p-p > s-p >s-s