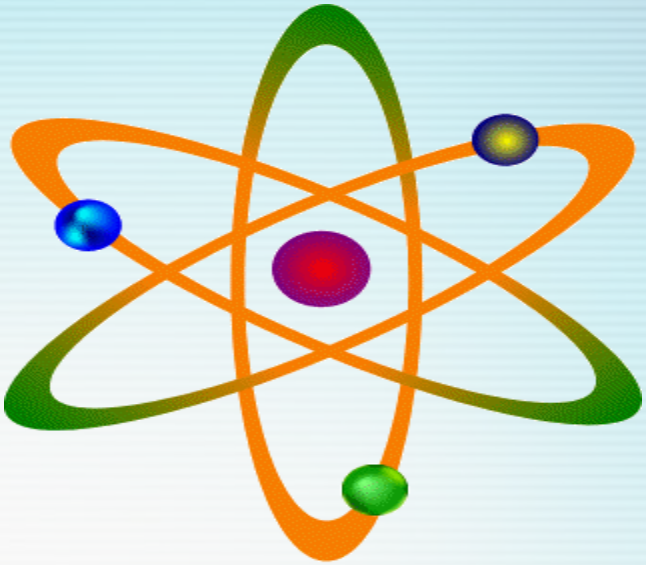
قال صلى الله عليه و سلم: (من سلك طريقا يلتمس به علماً سهل الله له به طريقاً إلى الجنة)

جزيئات ذات أكثر من مركز يدوي

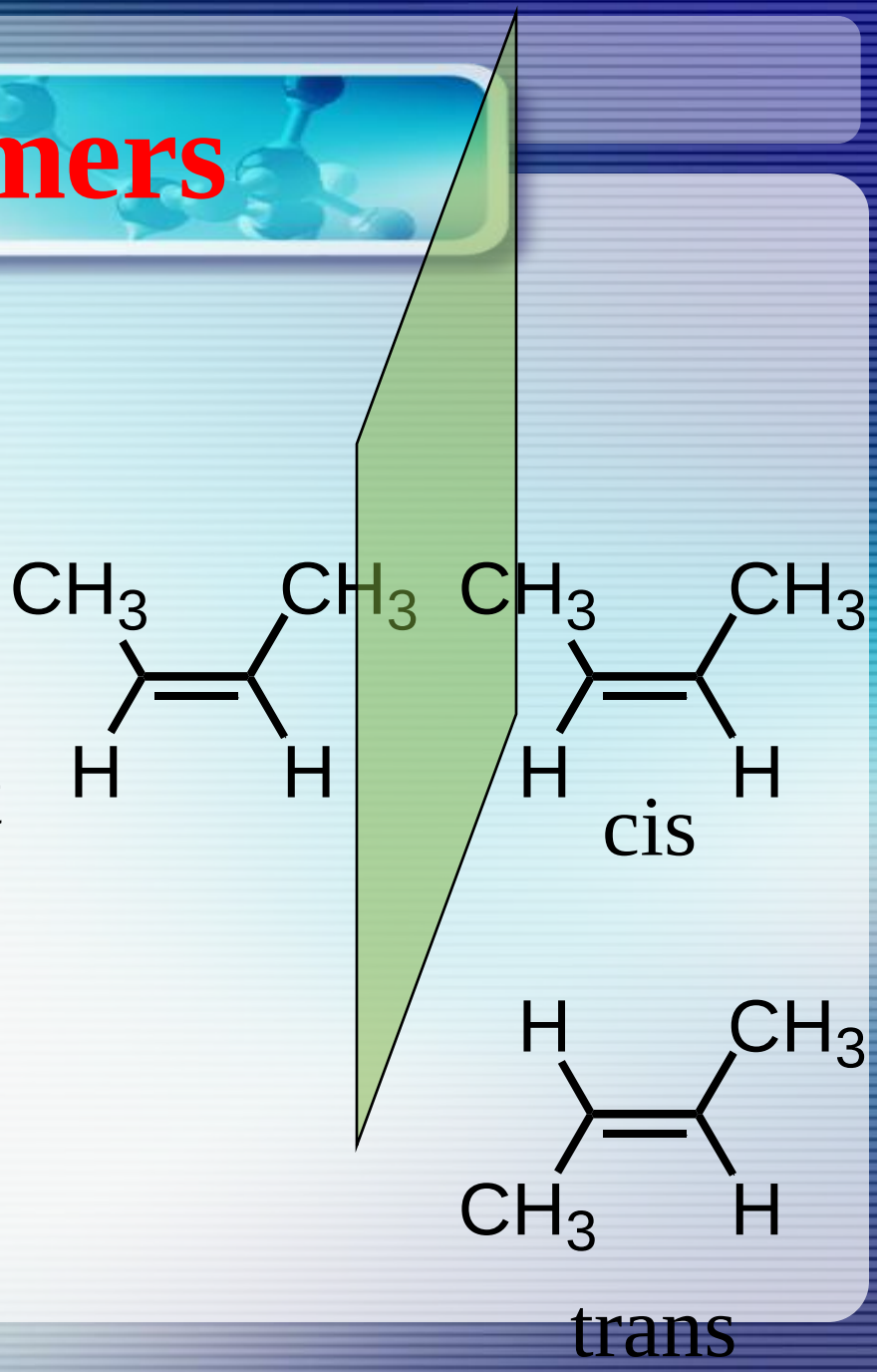


Dr. Asma El-Sharif
Departments of Chemistry
Saturday
20/11/1433 – 07/10/2012

The diastereomers

diasteriomers

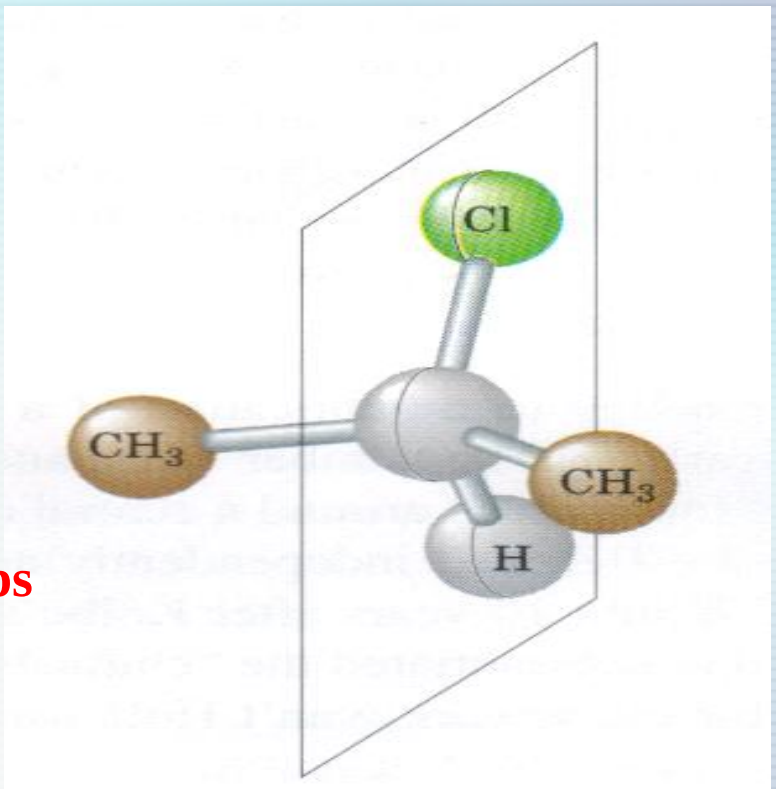
Stereoisomers that are not mirror images are called **diastereomers.**



The diastereomers

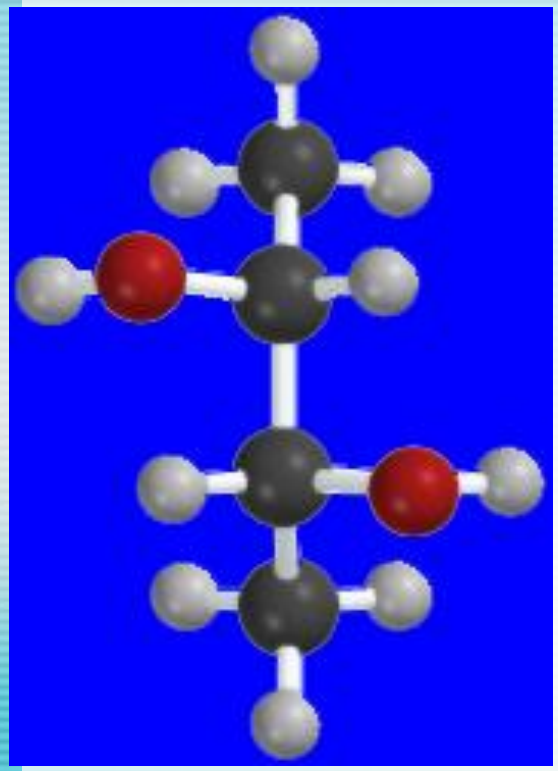
Example: 2-Chloropropane

* Not mirror images. i.e. can superimpose
* Molecule is chiral/not chiral
* One centre of symmetry (stereocentre)



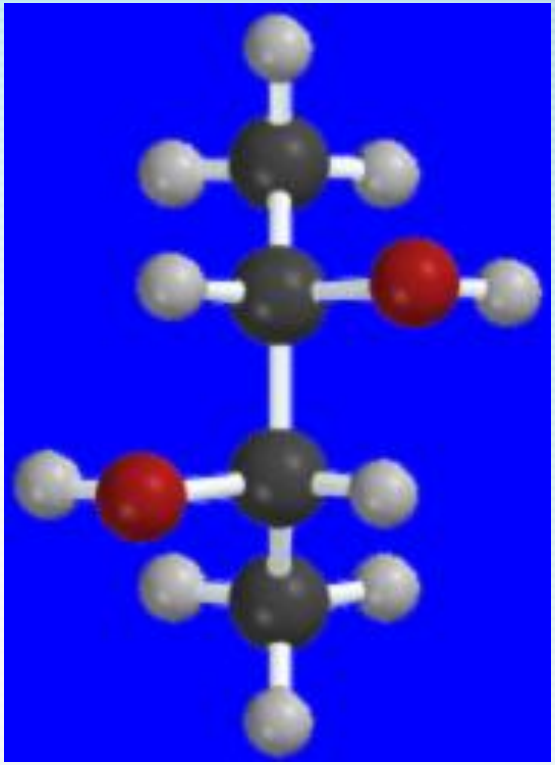
Stereocentre – An atom bearing groups of such nature that an interchange of any two groups will produce a stereoisomer.

Three stereo isomers of 2,3-butanediol



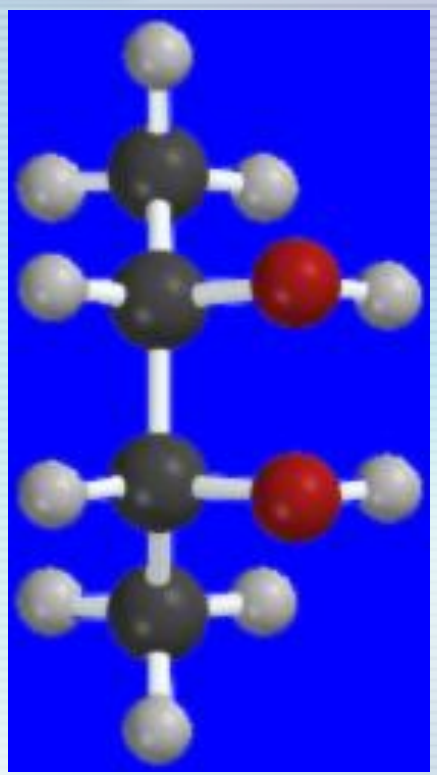
2*R*,3*R*

chiral



2*S*,3*S*

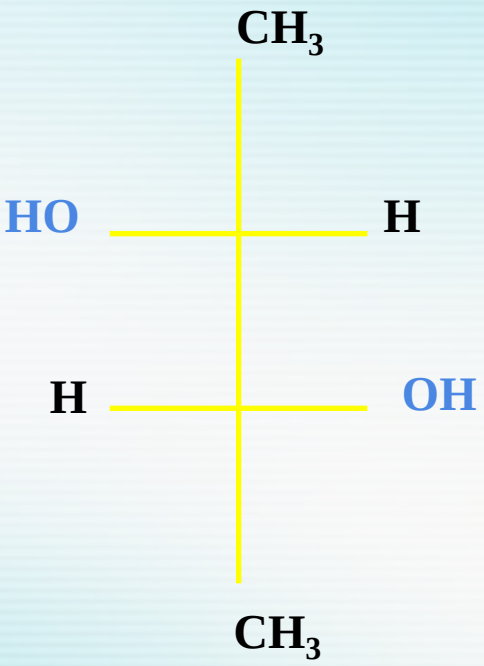
chiral



2*R*,3*S*

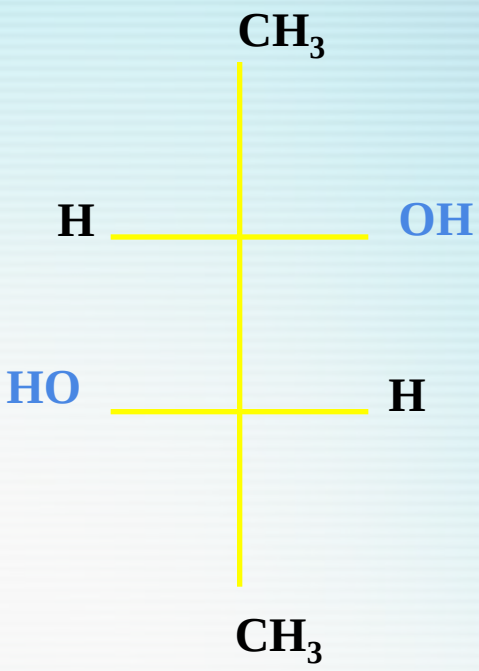
achiral

Three stereo isomers of 2,3-butanediol



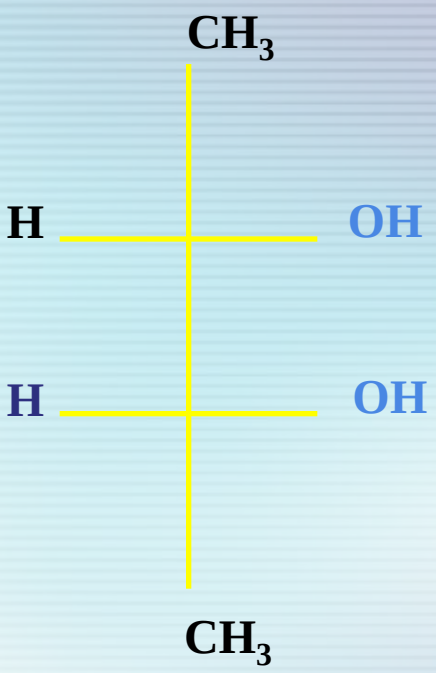
2*R*,3*R*

chiral



2*S*,3*S*

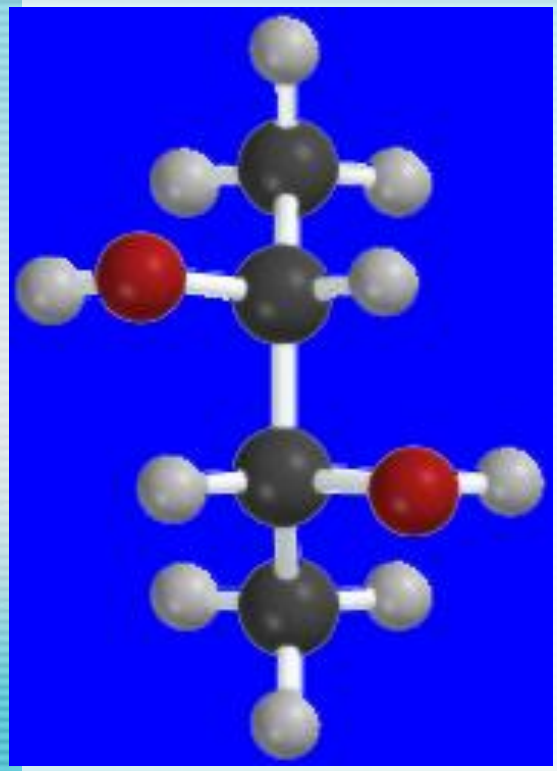
chiral

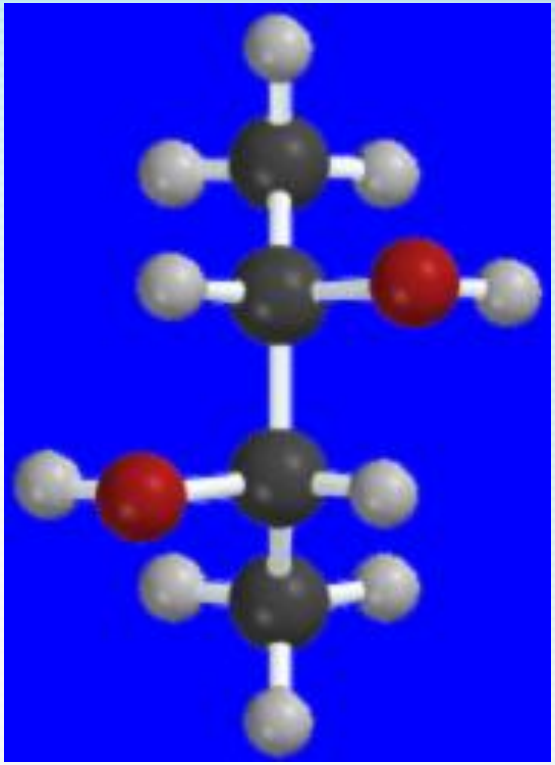


2*R*,3*S*

achiral

Three stereo isomers of 2,3-butanediol





these two are enantiomers

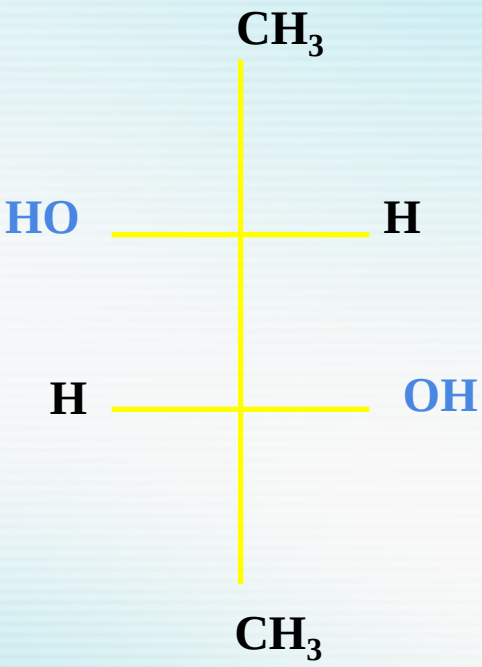
2*R*,3*R*

chiral

2*S*,3*S*

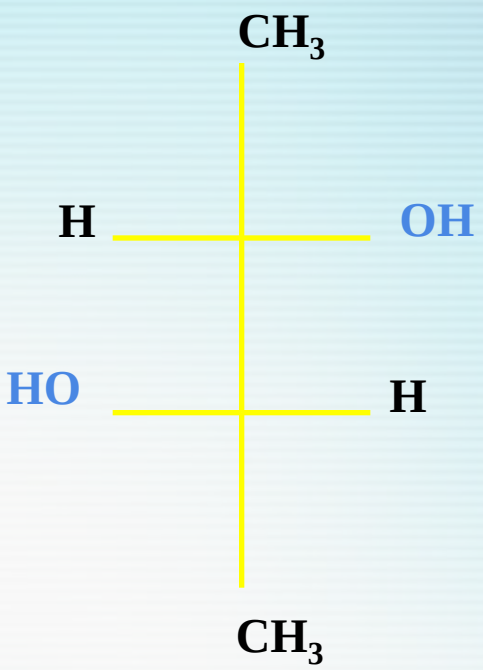
chiral

Three stereo isomers of 2,3-butanediol



2*R*,3*R*

chiral



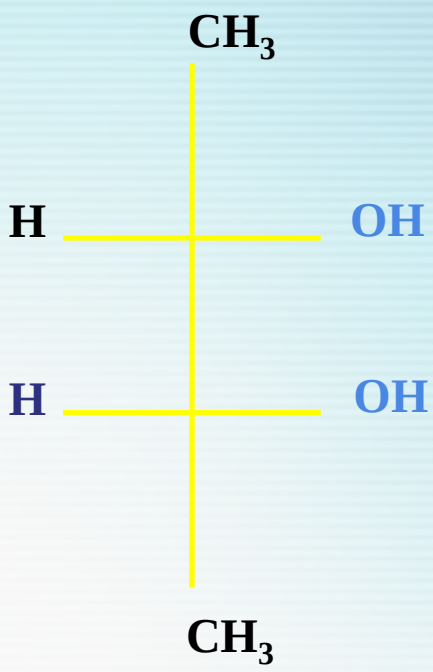
2*S*,3*S*

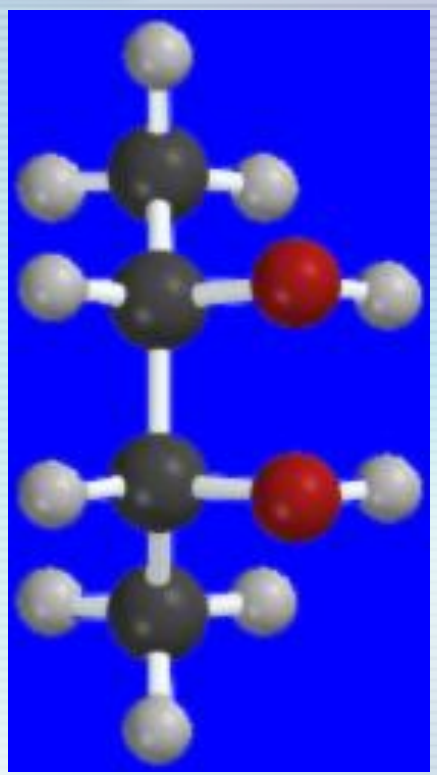
chiral

these two are enantiomers

Mirror Plane
Rotate 180°

Three stereo isomers of 2,3-butanediol



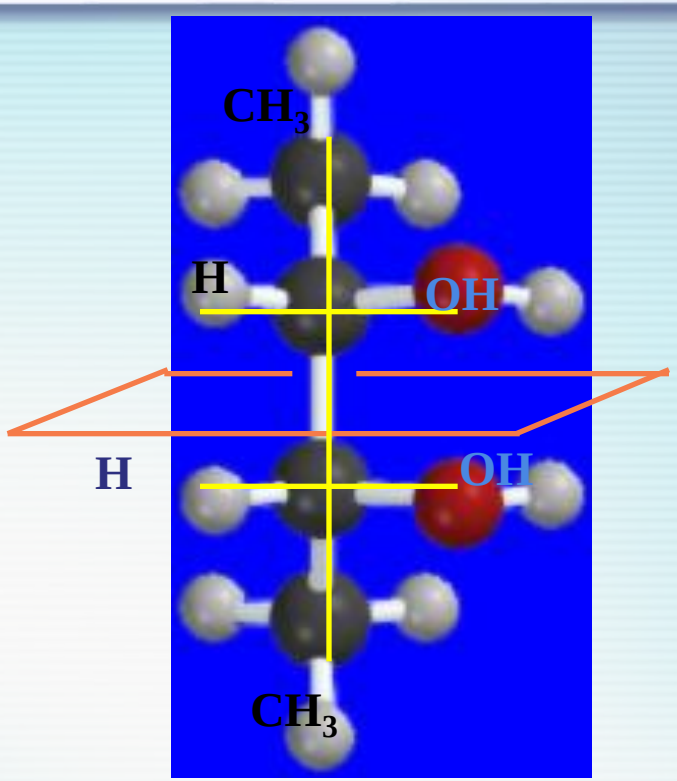


2*R*,3*S*

the third structure is superposable on its mirror image (rotate 180°)

achiral

Three stereo isomers of 2,3-butanediol

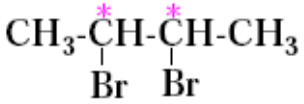


2*R*,3*S*

achiral

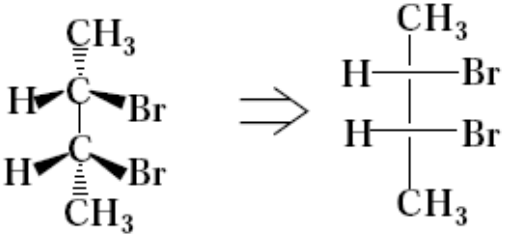
جزيئات ذات أكثر من مركز يدوي

How to Use Fischer Formulas: (S,R)-2,3-Dibromobutane



By convention, Fischer formulas are written with the main chain extending top to bottom.

(S,R)-2,3-Dibromobutane (meso)



3-dimensional representation

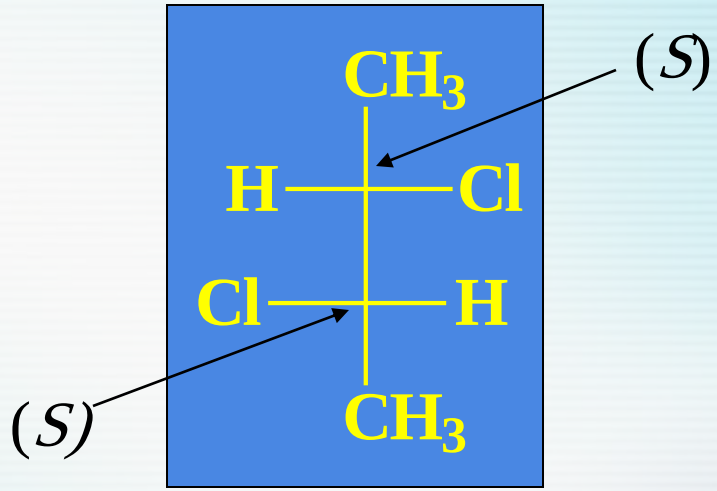
Fischer Formula

Note: A plane of symmetry identifies this stereoisomer as achiral in both representations.

The superimposability test may be used with Fischer formulas to determine whether structures are identical or different.

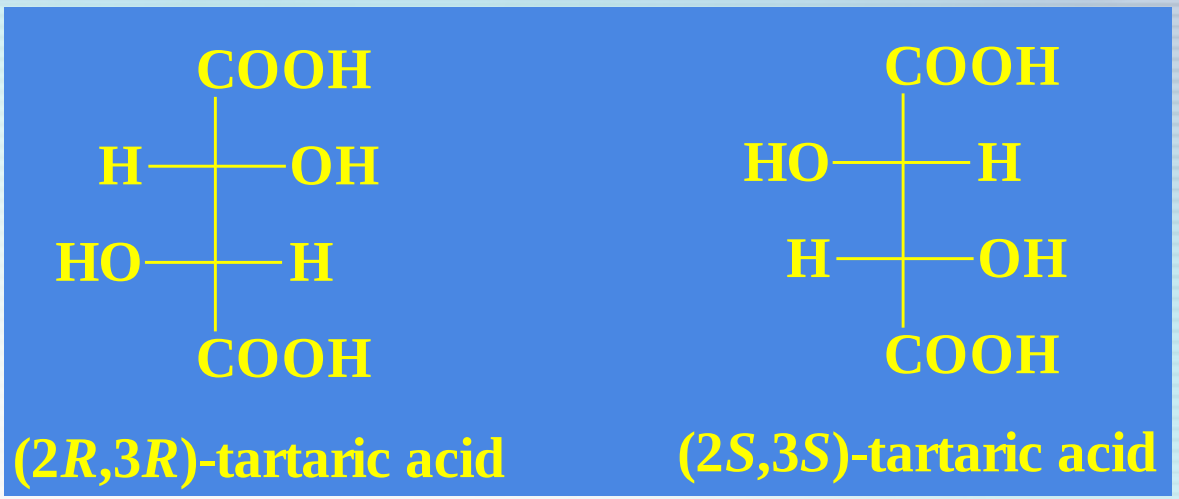
Fischer (*R*) and (*S*)

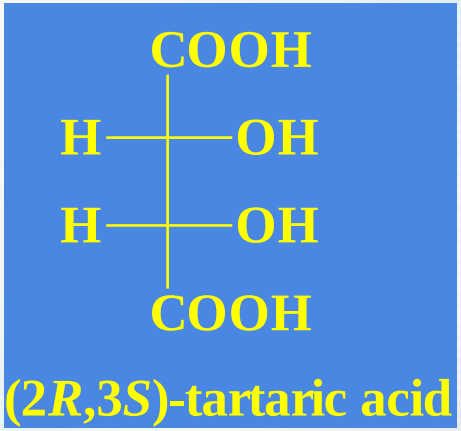
- Lowest priority (usually H) comes forward, so assignment rules are backwards!
- Clockwise 1-2-3 is (*S*) and counterclockwise 1-2-3 is (*R*).
- Example:



جزيئات ذات أكثر من مركز يدوي

Examples





جزيئات ذات أكثر من مركز يدوي

Molecules with More than One Stereocenter

A compound with one stereocenter can exist in two stereoisomeric forms (enantiomers) called (R) and (S). If there are two stereocenters, each center may be (R) or (S). The various stereocenter combinations are shown in the table.

Stereocenters	Possible Combinations	Stereoisomers
1	R S	2
2	R R S S R S S R	4

The maximum number of stereoisomers is 2^n, where n is the number of stereocenters.

جزيئات ذات أكثر من مركز يدوي

The Stereoisomers of 2,3--Dibromopentane

$CH_3\overset{*}{C}HBr\,\overset{*}{C}HBrCH_2CH_3$

two stereocenters

$2^n = 4$ *stereoisomers*

What are the four stereoisomers and how are they related to each other?

Possible Combinations of the Stereocenters

1 2 3 4 5

CH_3-CHBr-CHBr-CH_2CH_3

(2R) (3R)

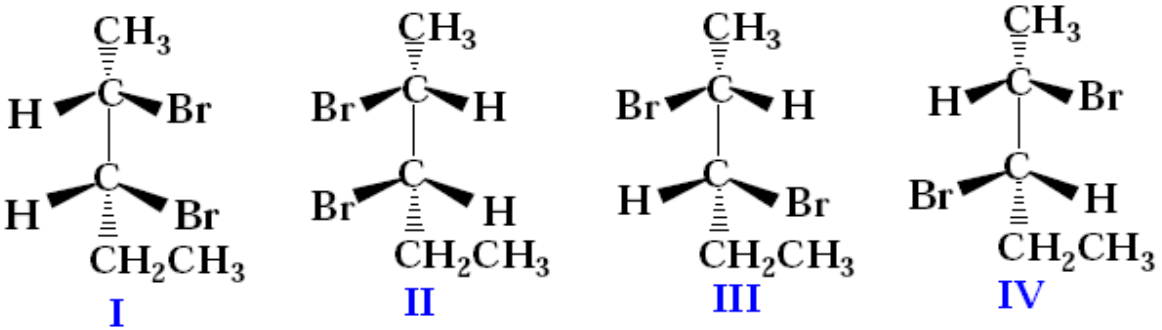
(2R) (3S)

(2S) (3R)

(2S) (3S)

جزيئات ذات أكثر من مركز يدوي

The Four Stereoisomers of 2,3--Dibromopentane



(1) *Use eclipsed conformations for easier assignment of (R) or (S).*

(2) *Add the groups around the stereocenters in one stereoisomer and assign labels to the stereocenters.*

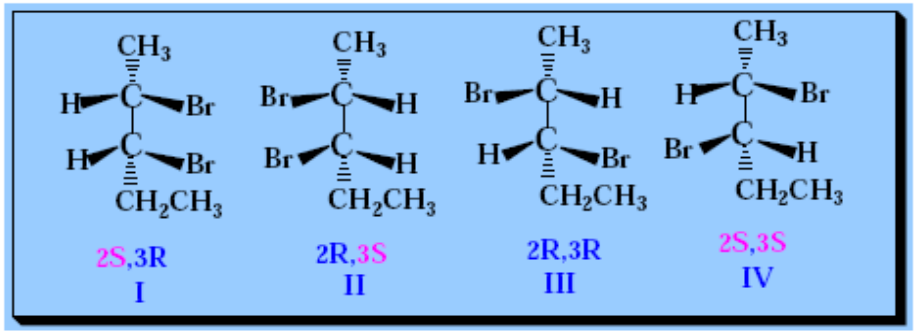
(3) *Draw the mirror image of I. That gives II. Each stereocenter changes configuration.*

(4) *Change the configuration only at C-2 in I from S to R. That gives III.*

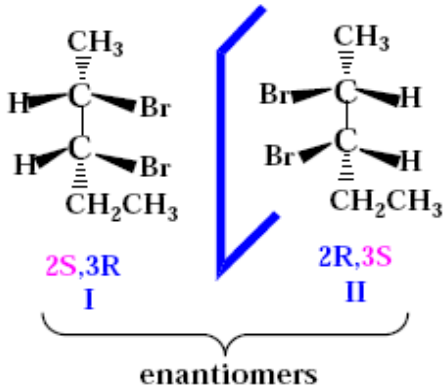
(5) *Draw the mirror image of III. That gives IV.*

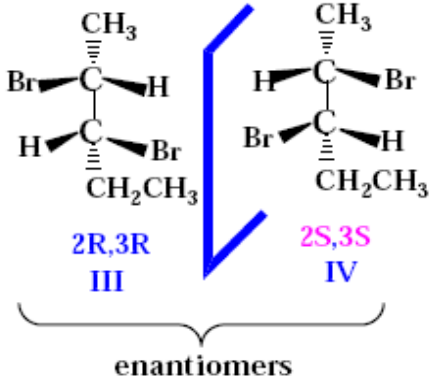
جزيئات ذات أكثر من مركز يدوي

The Relationships Among the Four Stereoisomers of 2,3-Dibromobutane



Stereoisomer pairs I/II and III/IV are mirror image related. They are enantiomers. Note that all stereocenters change in going from one enantiomer to the other.

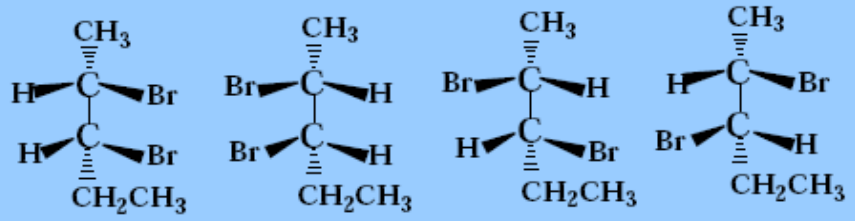




جزيئات ذات أكثر من مركز يدوي

Stereoisomers that are not Enantiomers are Diastereomers of Each Other

Among the following four stereoisomers,



the diastereomeric pairs are: I/III, I/IV, II/III, II/IV.

Note: In diastereomers, all the stereocenters are not mirror image related as in enantiomers.

Unlike the mirror-image related enantiomers, diastereomers have different physical and chemical properties. The diastereomeric relationship between structures is an important and fundamental principle in simple organic and biological systems.

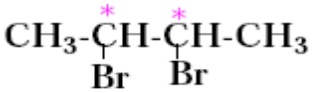
جزيئات ذات أكثر من مركز يدوي

Meso Compounds: A Special Stereochemical Situation

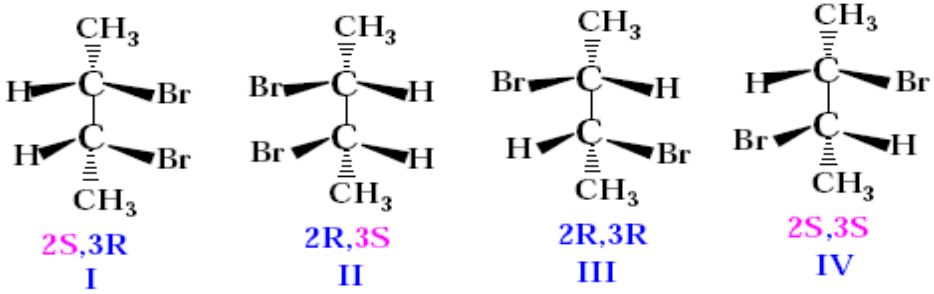
The maximum number of stereoisomers when there are two stereocenters is $2^2 = 4$. But structural symmetry influences this analysis.

Example: 2,3-dibromobutane

There are two stereocenters in this compound.



The four possible stereoisomers of 2,3-dibromobutane are:

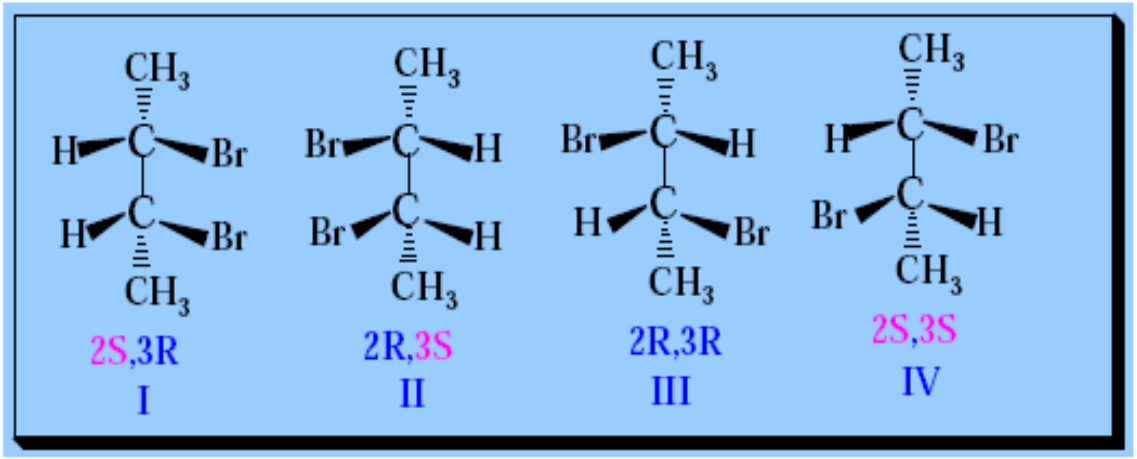


At first view, it may appear that this compound exists in four unique stereoisomeric forms as found in 2,3-dibromopentane, but.....

جزيئات ذات أكثر من مركز يدوي

Structural Symmetry: The Meso Diastereomer

symmetry reduces the number of stereoisomers from four to three.



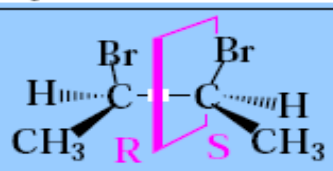
A more careful inspection of the four possible stereoisomers reveals that I and II are not different because one structure may be superimposed on the other. They are the same stereoisomer.

Thus, 2,3-dibromobutane exists in only three unique stereoisomeric forms: I=II, and the enantiomeric pair III and IV.

جزيئات ذات أكثر من مركز يدوي

The Diastereomers of 2,3-Dibromobutane

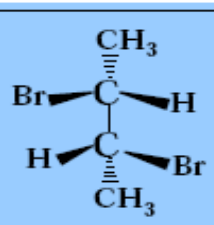
Stereoisomer I=II is achiral and is called a meso diastereomer. The meso diastereomer has an internal plane of symmetry that necessarily makes it achiral.



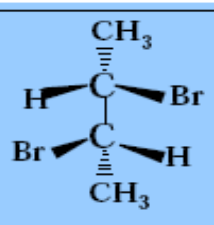
The meso diastereomer of 2,3-dibromobutane is achiral and does not exist in enantiomeric forms.

The Chiral Diastereomer of 2,3-Dibromobutane

Stereoisomers III and IV are the two enantiomers of the chiral diastereomer of 2,3-dibromobutane.



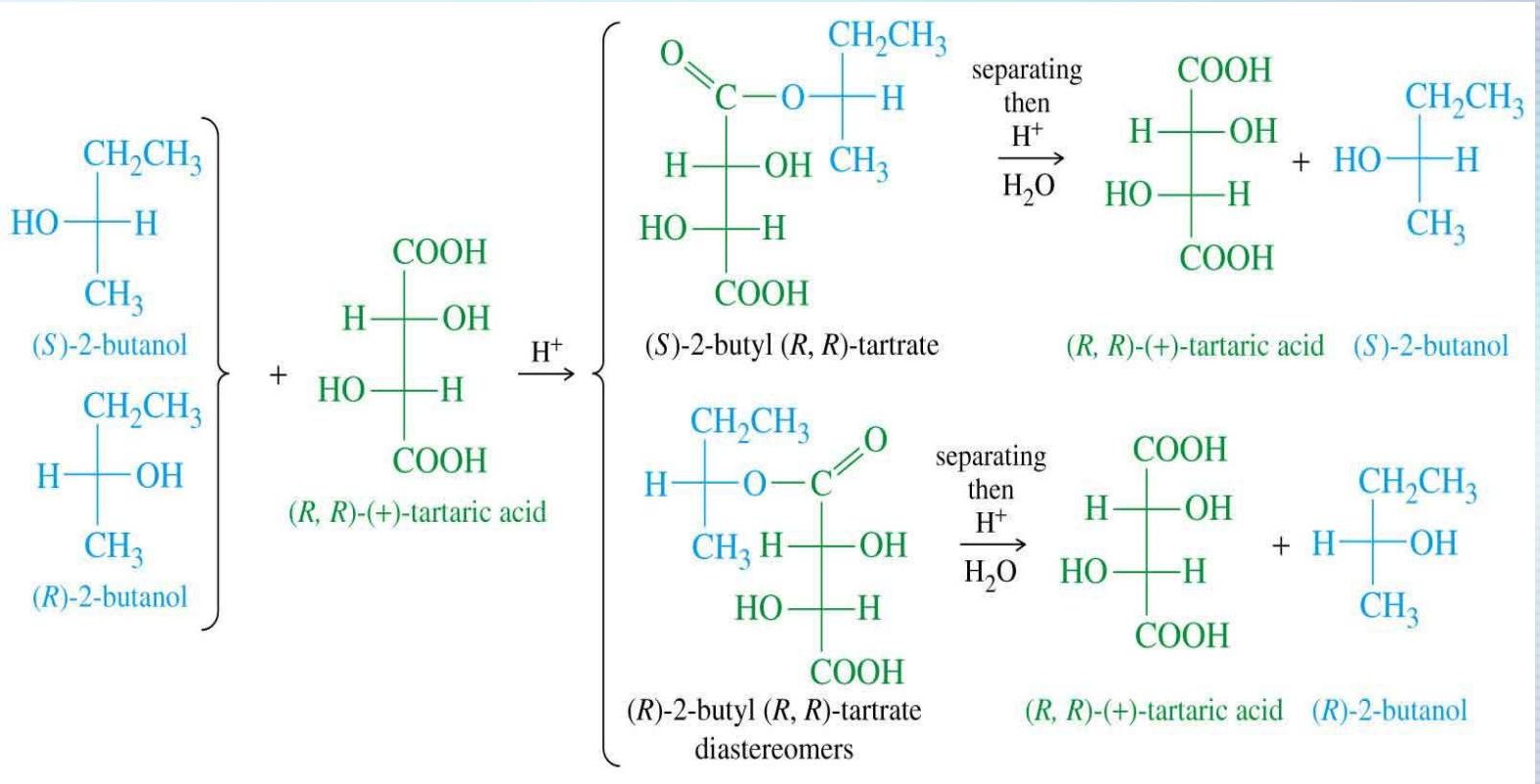
2R,3R
III



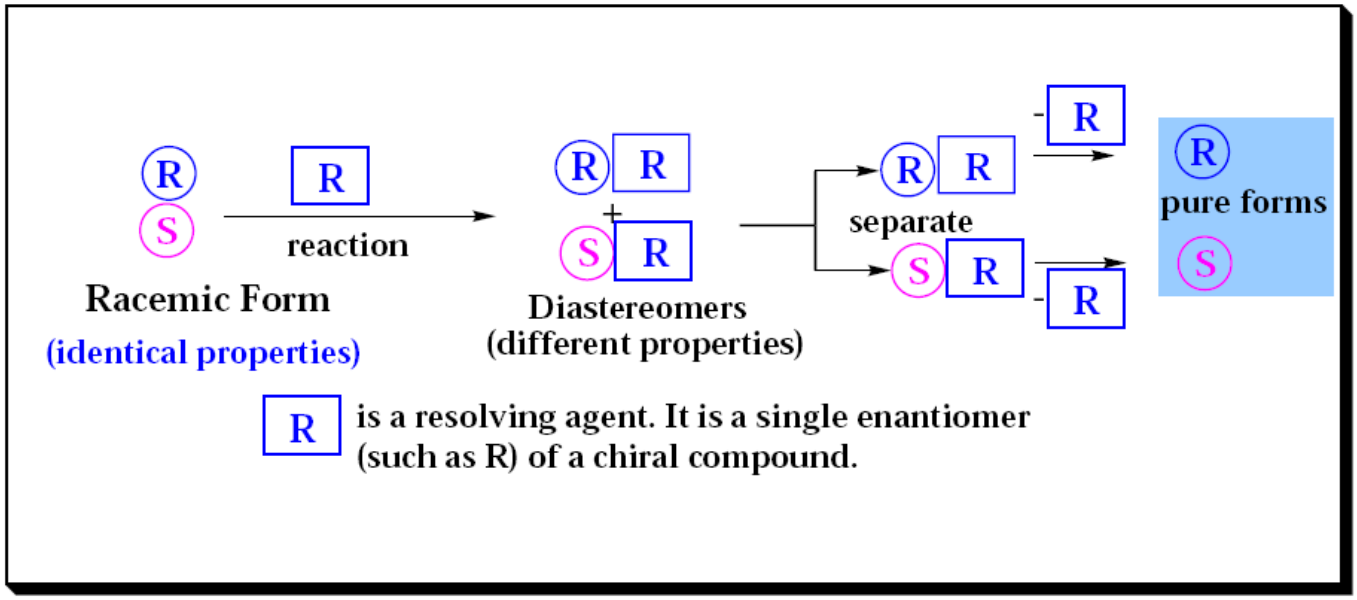
2S,3S
IV

This diastereomer is sometimes called the (±) or (d,l) diastereomer, meaning it exists in enantiomeric forms, to distinguish it from the meso-diastereomer.

Resolution of Enantiomers

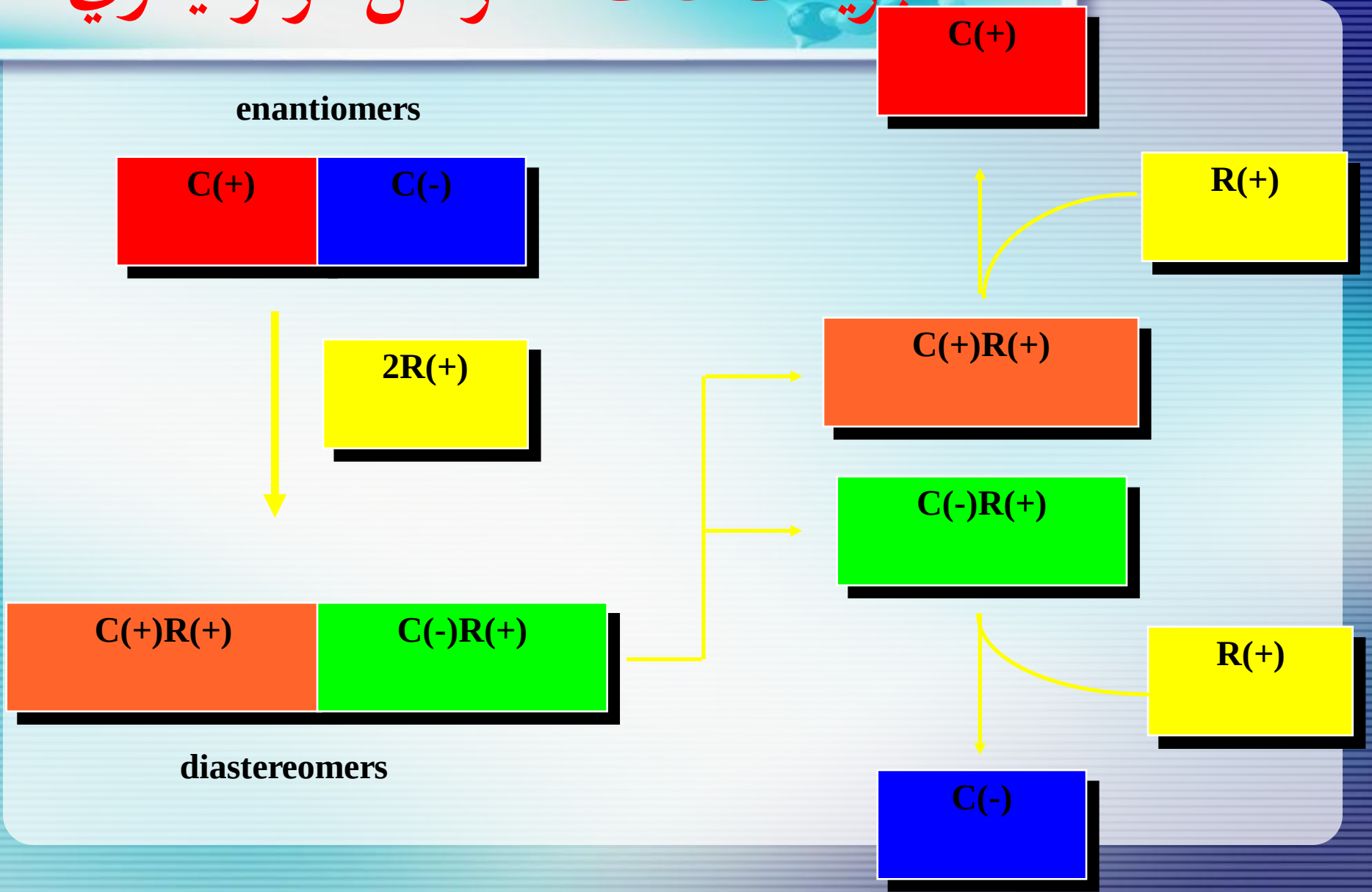


جزيئات ذات أكثر من مركز يدوي

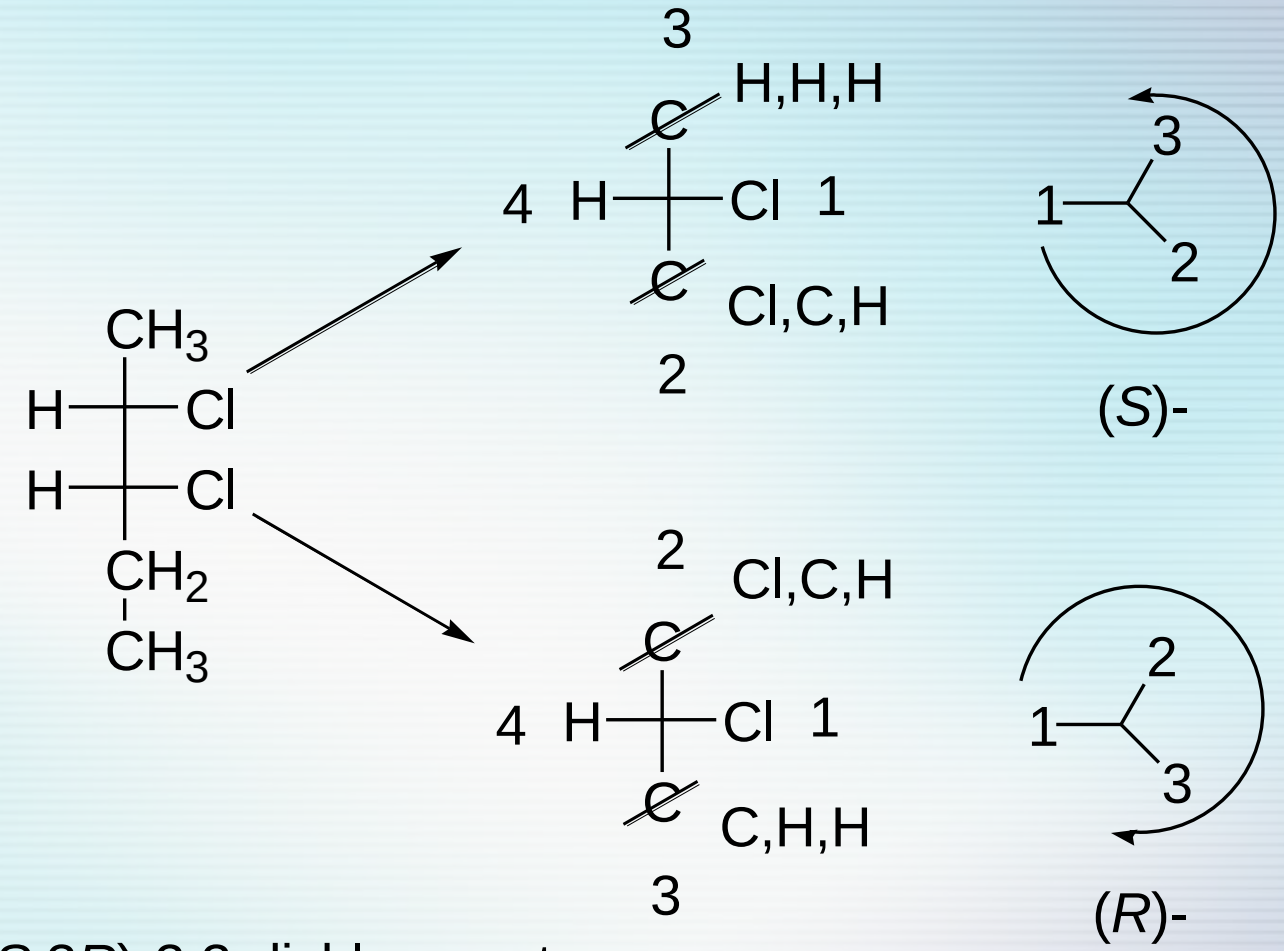


The racemic form (R,S) is reacted with a single enantiomer (R) of a resolving agent to produce diastereomers (R,R and S,R) that are separable by physical means. The resolving agent is then removed producing the pure enantiomers R and S.

جزيئات ذات أكثر من مركز يدوي

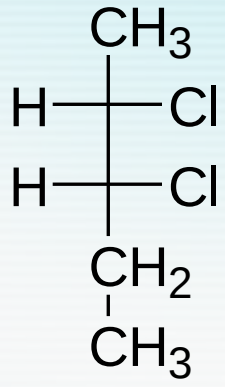


جزيئات ذات أكثر من مركز يدوي

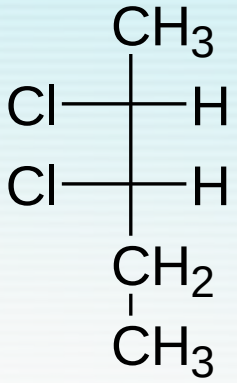


(2*S*,3*R*)-2,3-dichloropentane

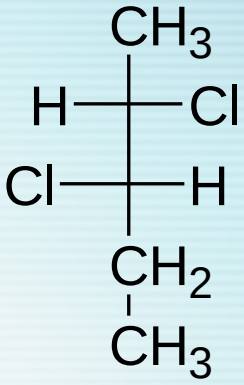
جزيئات ذات أكثر من مركز يدوي



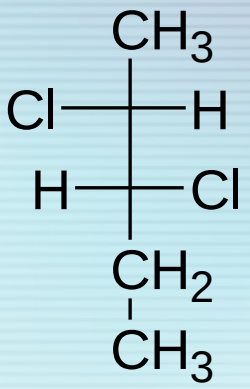
(2S,3R) -



(2R,3S)-



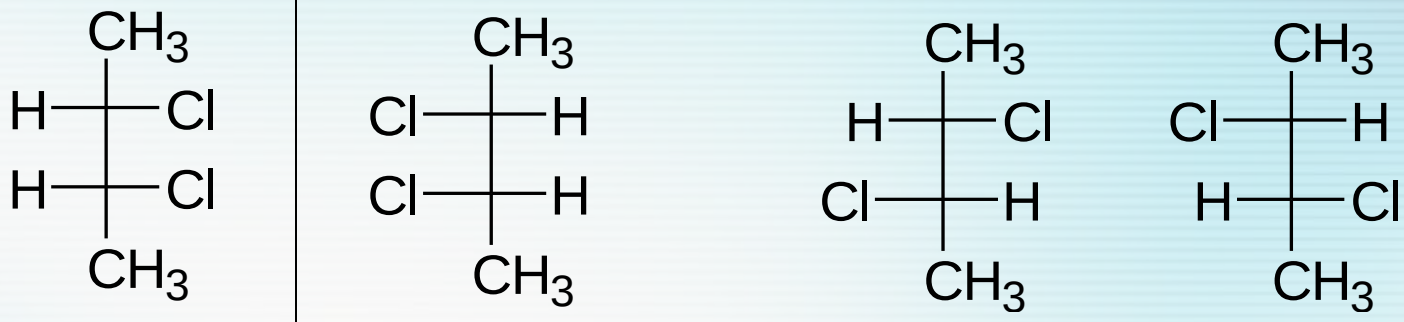
(S,S)-



(R,R)-

جزيئات ذات أكثر من مركز يدوي

2,3-dichlorobutane **$CH_3CHCHCH_3$**
Cl Cl

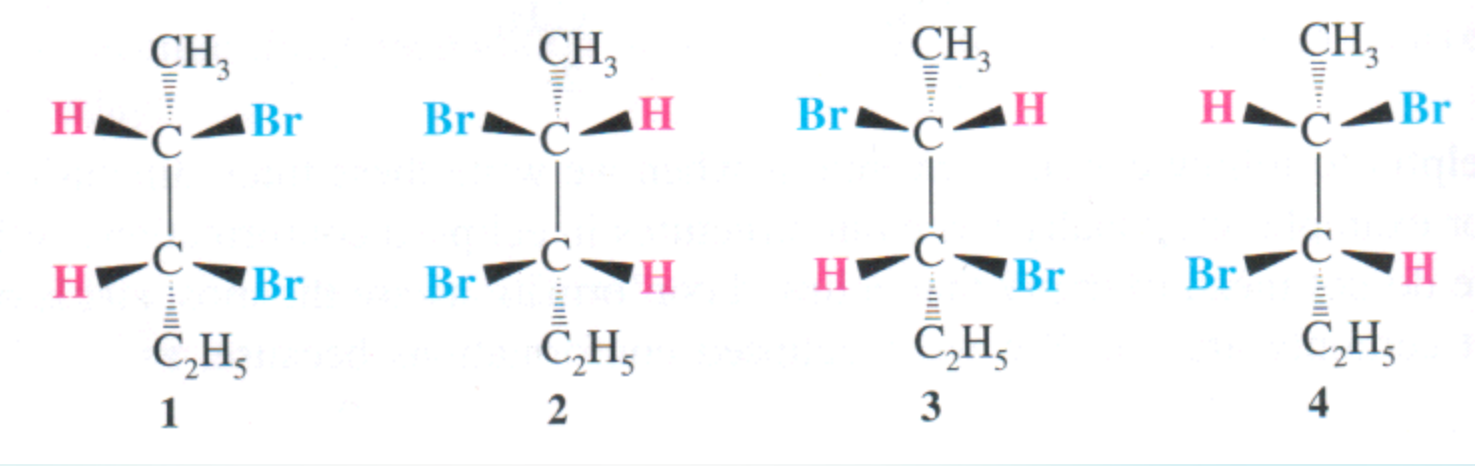


meso-compound – a compound that has chiral centers but is not chiral (optically inactive).

I **II** **III**

جزيئات ذات أكثر من مركز يدوي

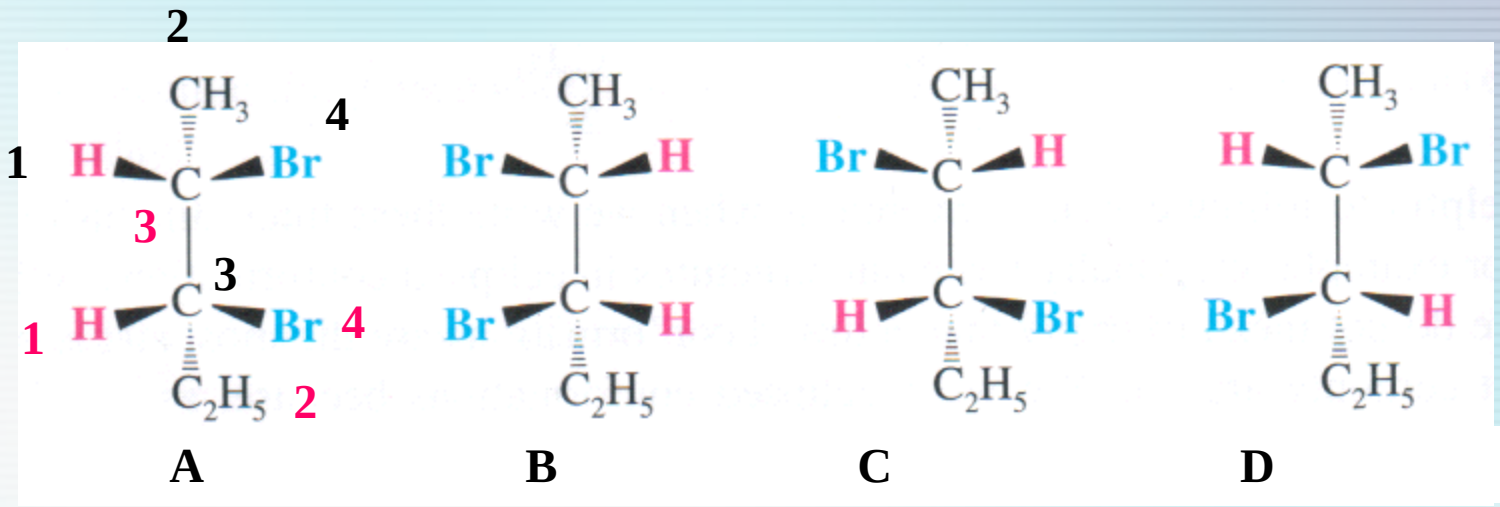
Example: 2,3-Dibromopentane



A	B	C	D

How many stereocenters are there?
How many enantiomers and which are them?
How many diastereomers and which are them?

جزيئات ذات أكثر من مركز يدوي

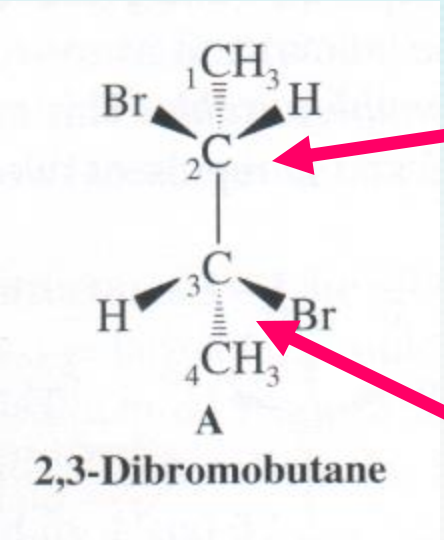


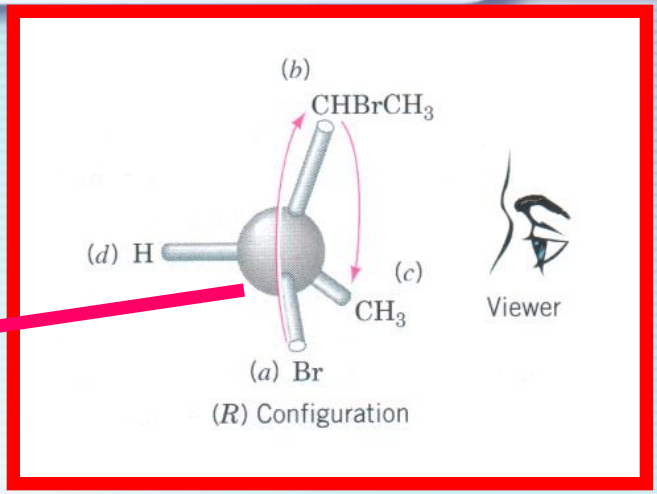
2 stereocenters (4 stereoisomer, $2^2 = 4$)

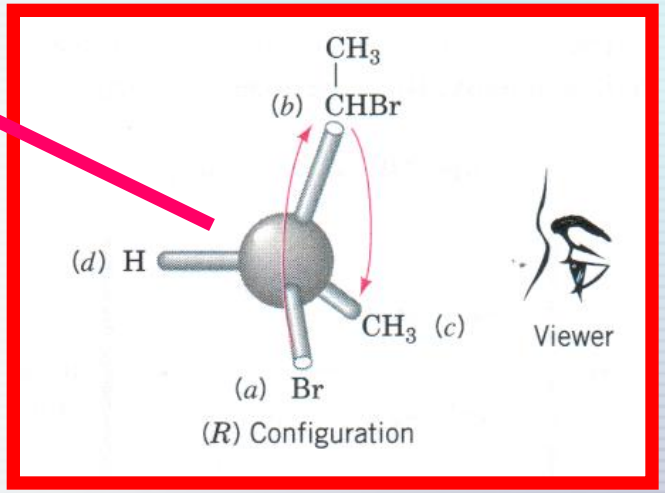
2 pairs of enantiomers: A and B; C and D.

4 pairs of diastereomers: A and D; A and C, B and C; B and D

جزيئات ذات أكثر من مركز يدوي

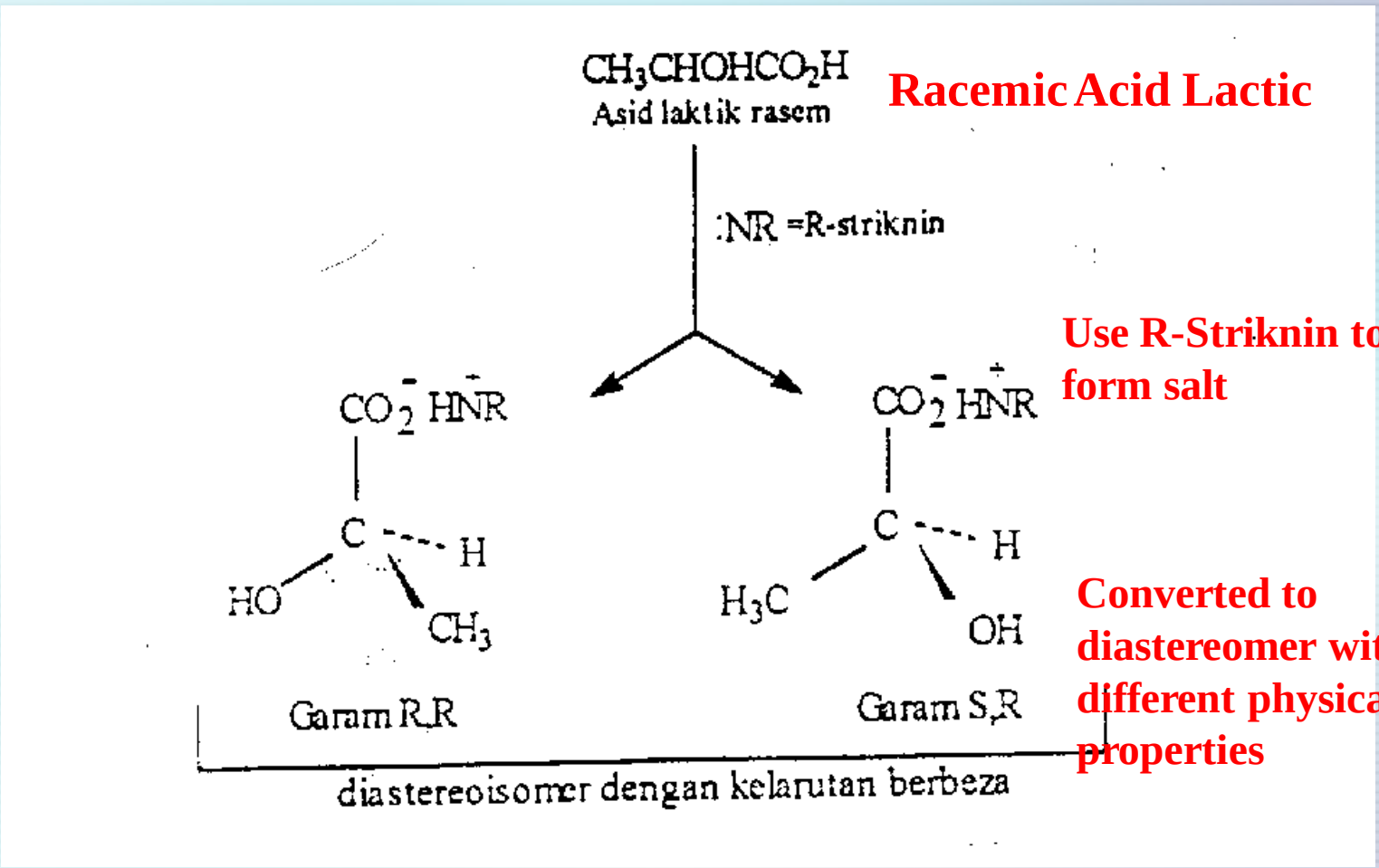




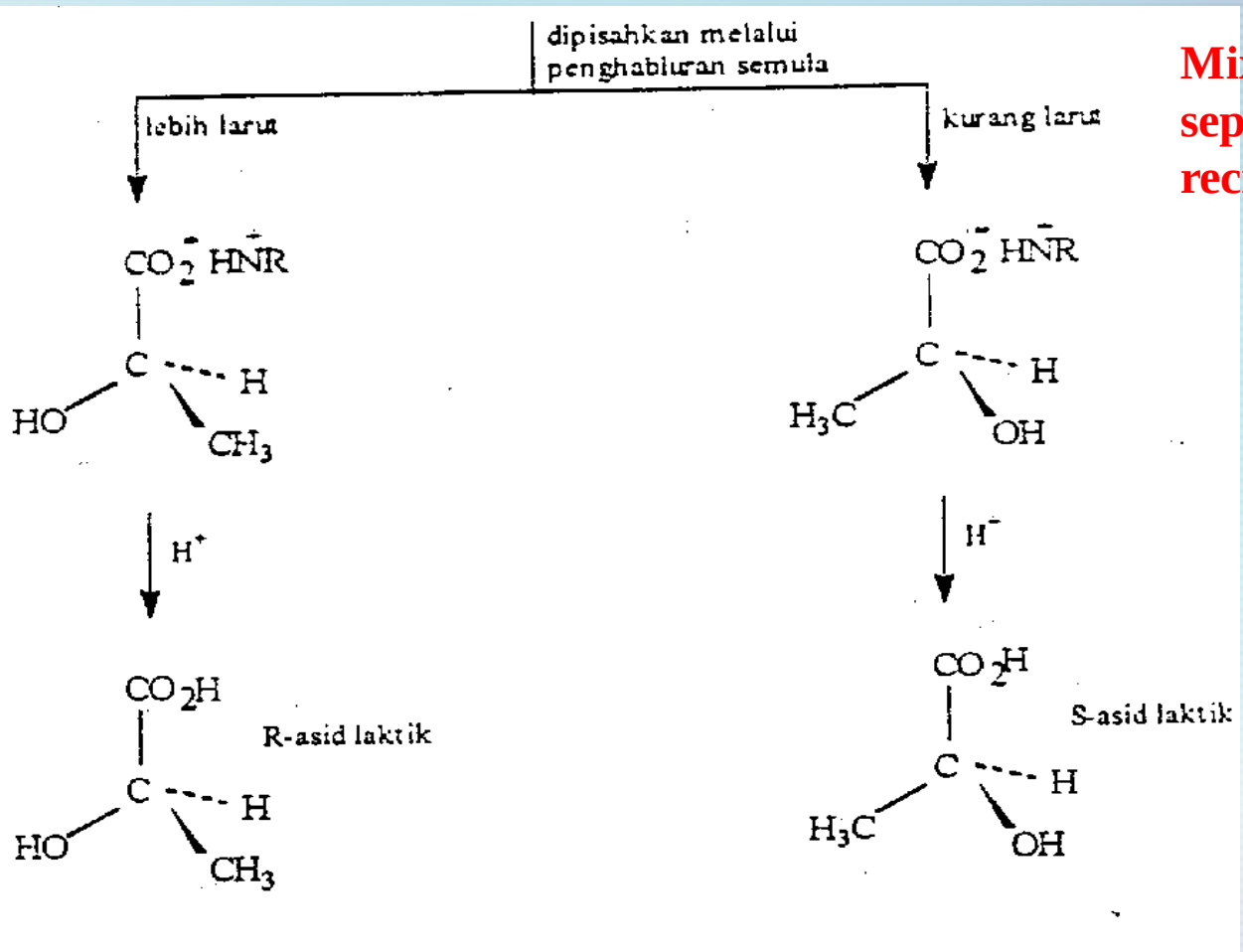


(2R, 3R)-2,3-Dibromobutane

جزيئات ذات أكثر من مركز يدوي



جزيئات ذات أكثر من مركز يدوي



Mixture of salts separated by recrystallization

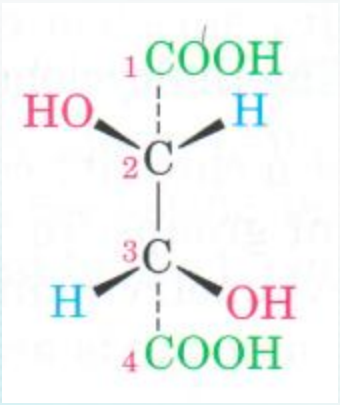
The salt is hydrolyzed to produce the two different enantiomeric forms.

Exercise III

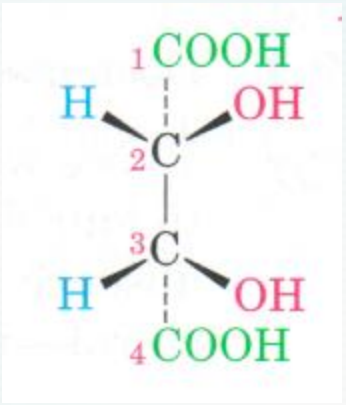
For the tartaric acid compounds shown below:

1. Determine whether the configuration is R or S for each stereocentre.

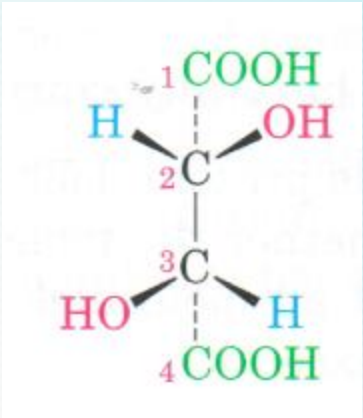
2. Which are the enantiomers and meso compounds?



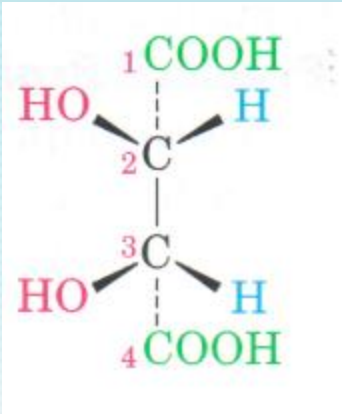
A



B

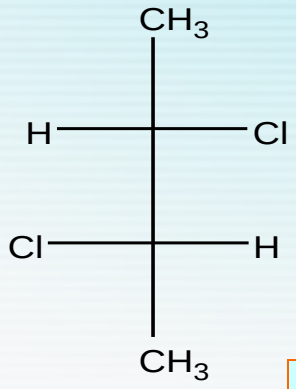


C



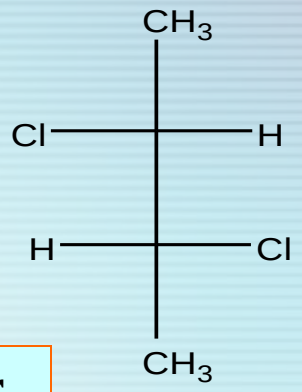
D

جزيئات ذات أكثر من مركز يدوي



S

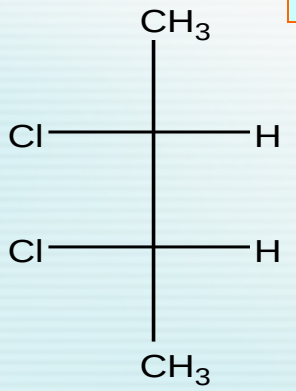
S



R

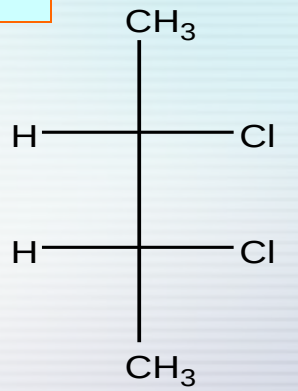
R

As we had before here are the four structures produced by systematically varying the configuration at each chiral carbon.



R

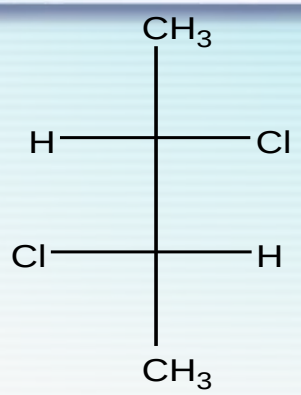
S



S

R

جزيئات ذات أكثر من مركز يدوي

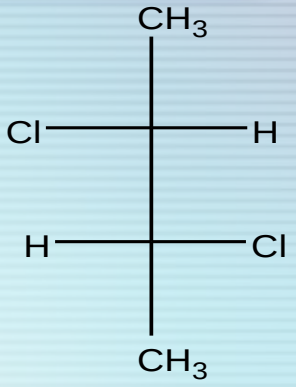


S

S

Enantiomers

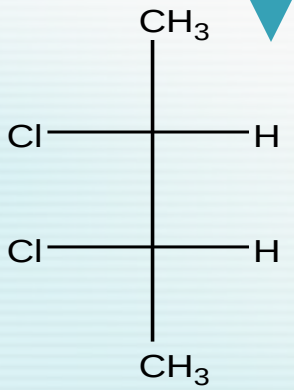
Mirror images, not superimposable.



R

R

Diastereomers.

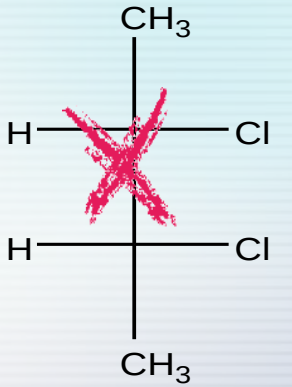


R

S

Meso

Mirror images! But superimposable via a 180 degree rotation. Same compound.



S

R

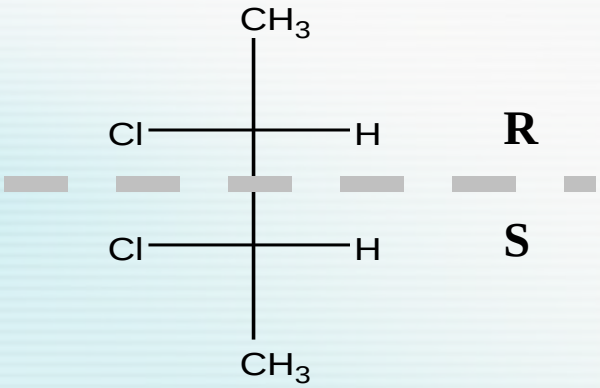
جزيئات ذات أكثر من مركز يدوي

Has at least two chiral carbons. Corresponding carbons are of opposite configuration.

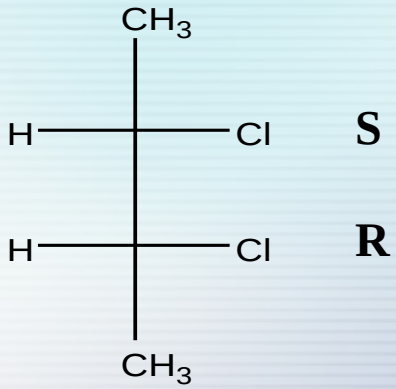
Can be superimposed on mirror object, optically inactive.

Can demonstrate mirror plane of symmetry

Molecule is achiral. Optically inactive. Specific rotation is zero.



Meso



Can be superimposed by 180 deg rotation.

The End