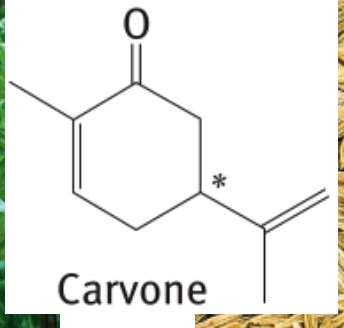
Chapter 5: Stereoisomerism

Stereoisomers are compounds that have the same structural formula in terms of order of attachment, but differ in arrangements of the atoms in space.

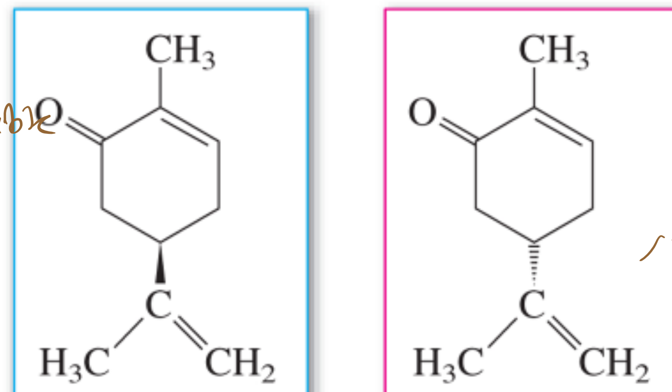


The difference in odor between caraway seeds and mint leaves arises from two stereoisomers of carvone due to different arrangement of atoms at the carbon (*)

Spearmint leaves

Caraway seeds

meror image
not superimposable
enantiomers



d

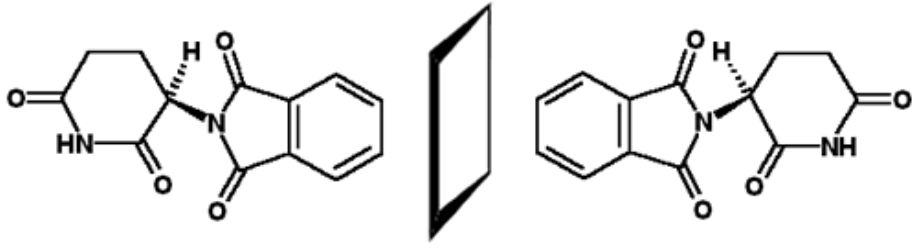
(R)-(−)-Carvone
(from spearmint oil)

l

(S)-(+)-Carvone
(from caraway seed oil)

rotation
meror images
not superimposable

enantomers



R-Thalidomide
(sleep-inducing)

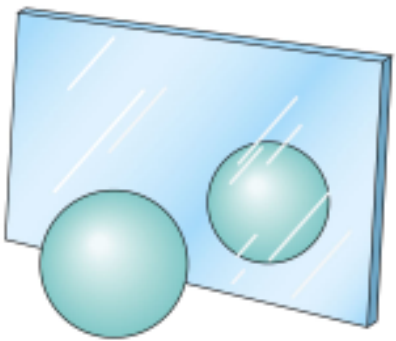
S-Thalidomide
(teratogenic)

Mirror-image relationship of chiral and achiral objects

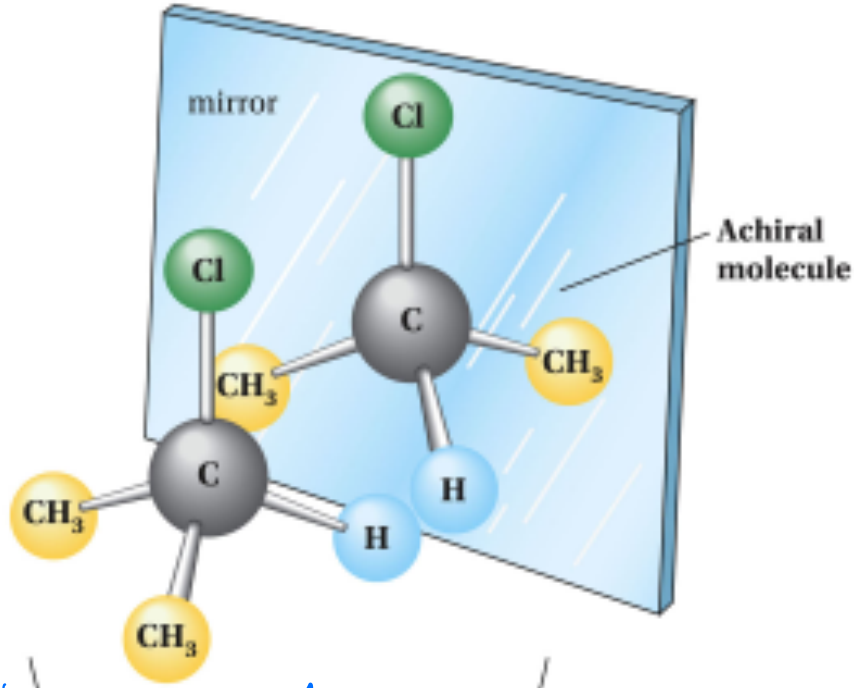
The mirror image of a left hand is not a left hand, but a right hand.

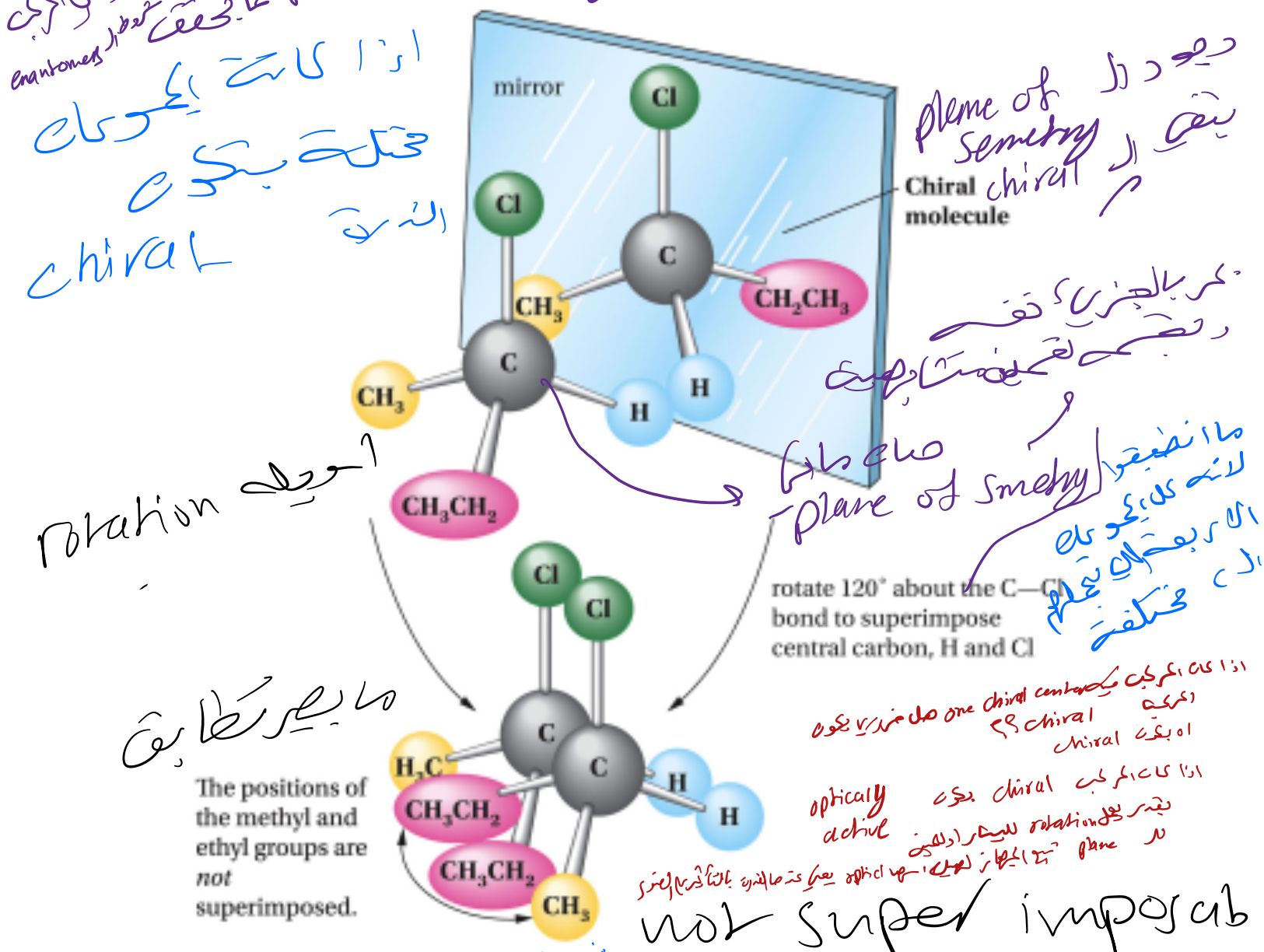
Chiral object

The mirror image of a ball is identical with the object itself.

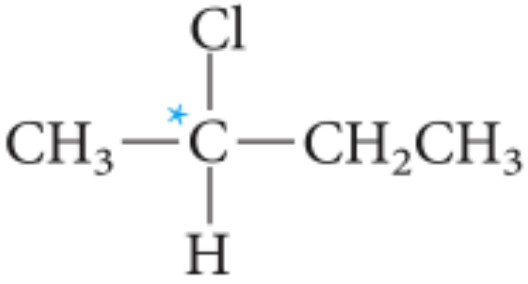


Achiral object

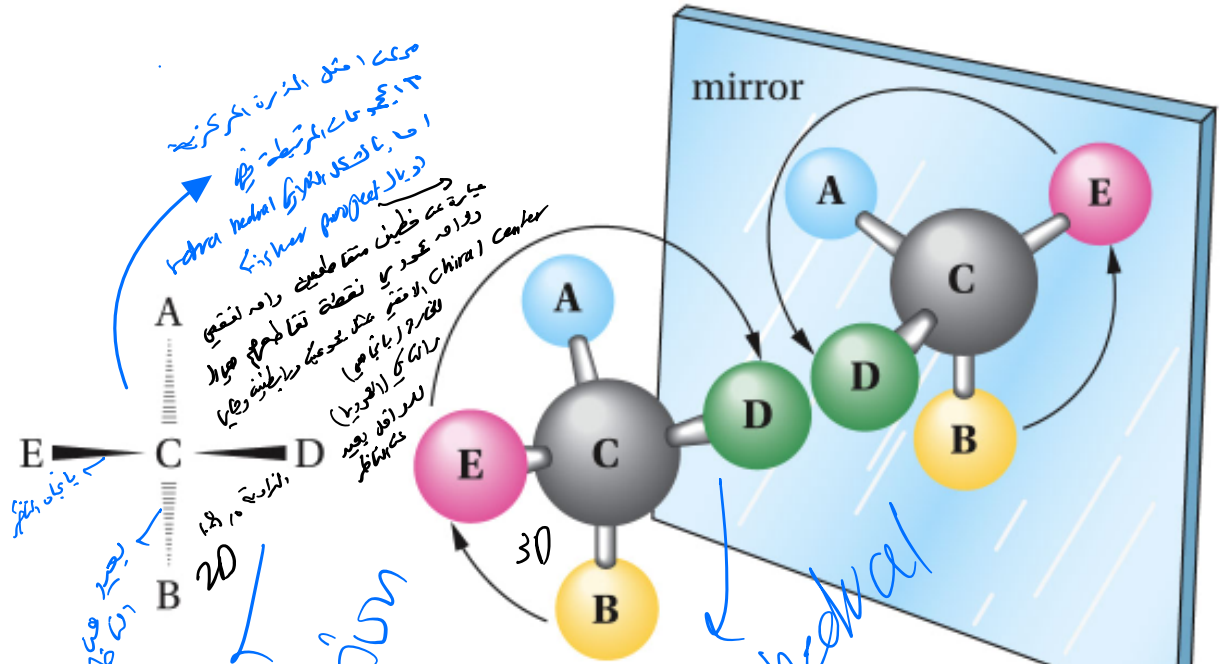

mirror
Cl
Cl
C
CH3
CH3
C
CH3
H
H
CH3
Achiral molecule
rotate 120° about the C—Cl bond
Cl
Cl
C
C
CH3
CH3
H
H
CH3
CH3

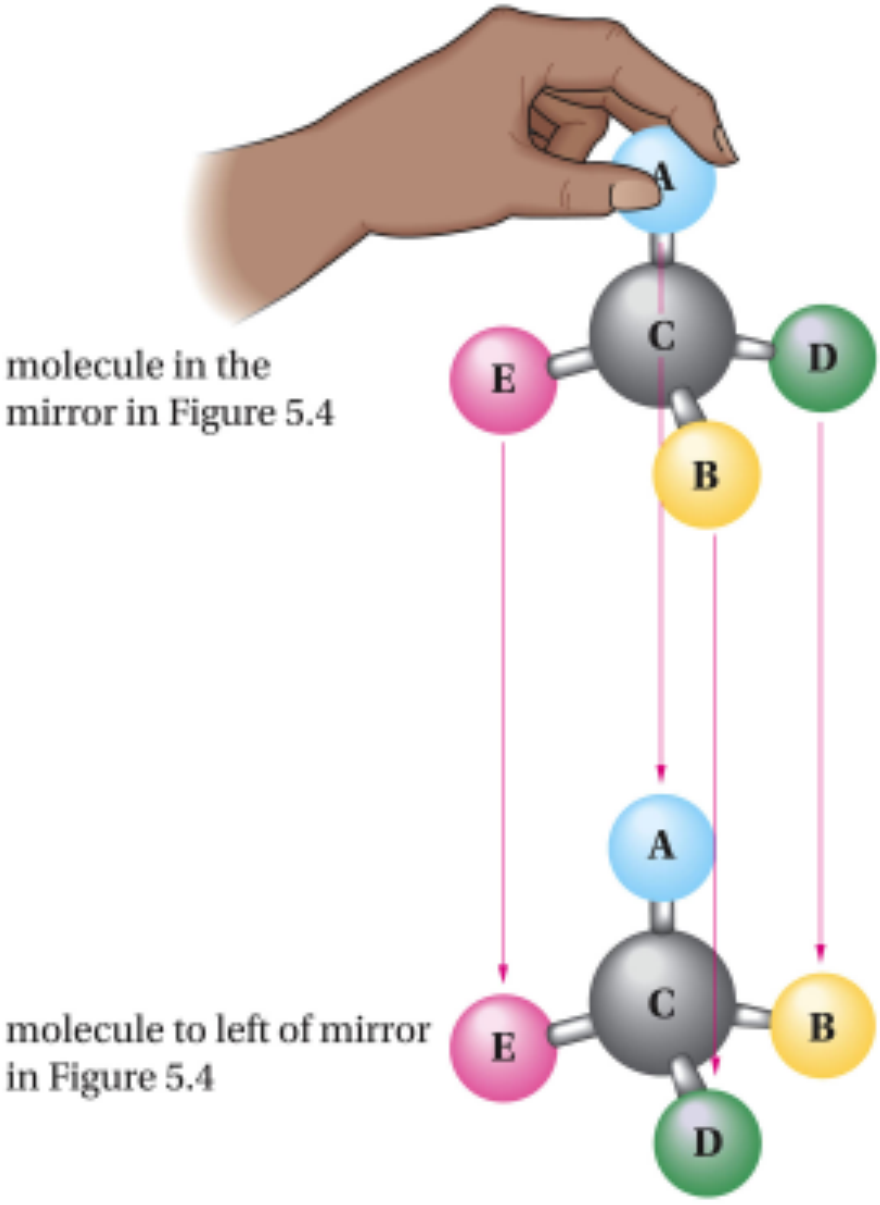

mirror
Cl
Cl
C
CH_2CH_3
CH_3
C
CH_3
H
H
CH_3CH_2
Chiral molecule
rotate 120° about the C—Cl bond to superimpose central carbon, H and Cl
Cl
Cl
C
C
H_3C
H
H
CH_3CH_2
CH_3CH_2
CH_3
The positions of the methyl and ethyl groups are *not* superimposed.

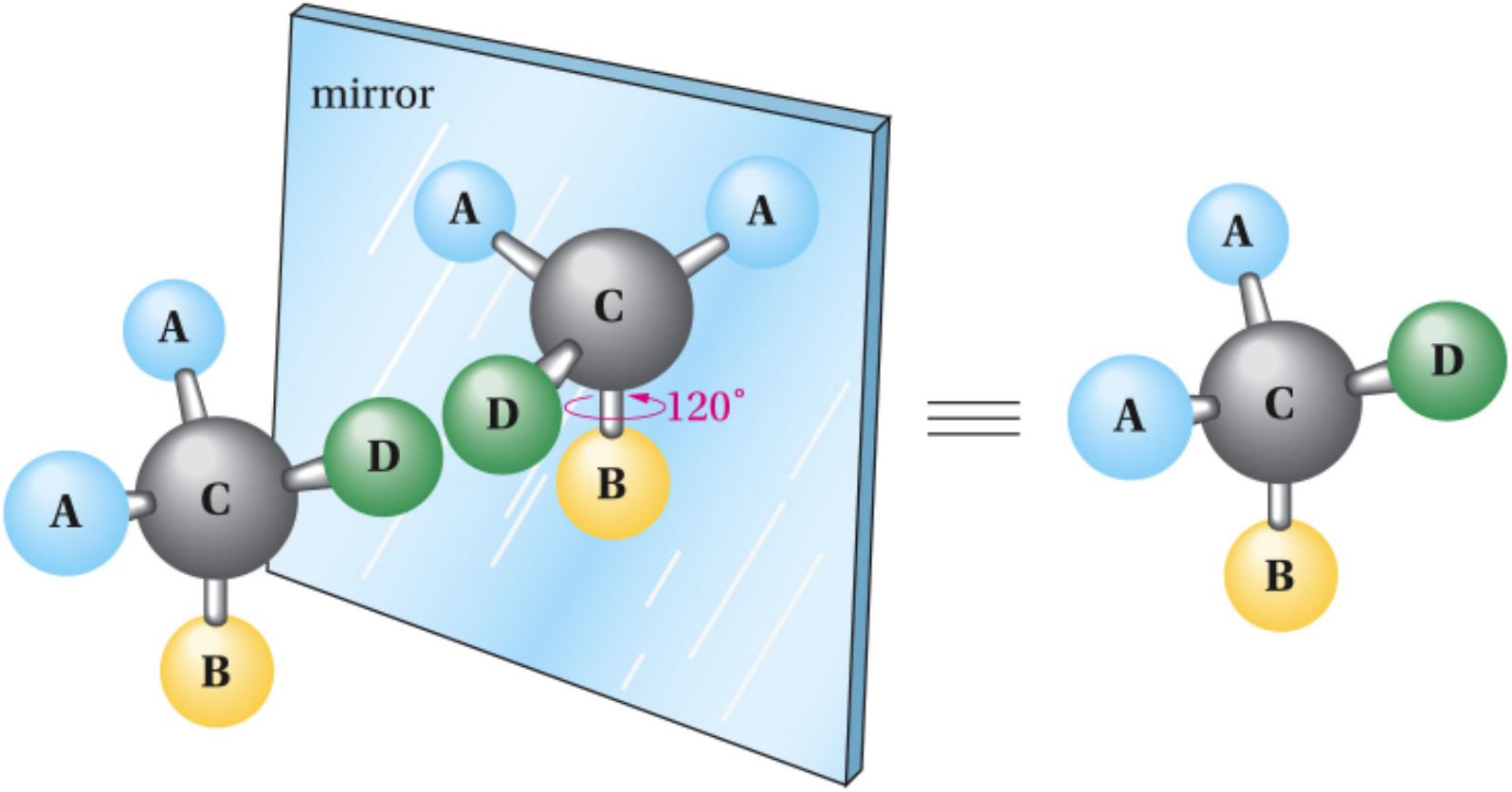
Stereogenic Centers: the Stereogenic Carbon Atom

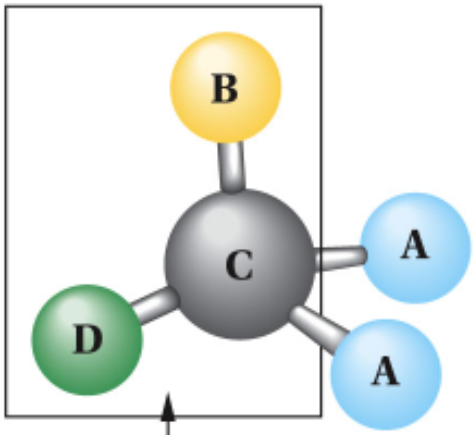


Carbon atoms with four different groups attached to them are called stereogenic carbon atoms (also called chiral carbon)

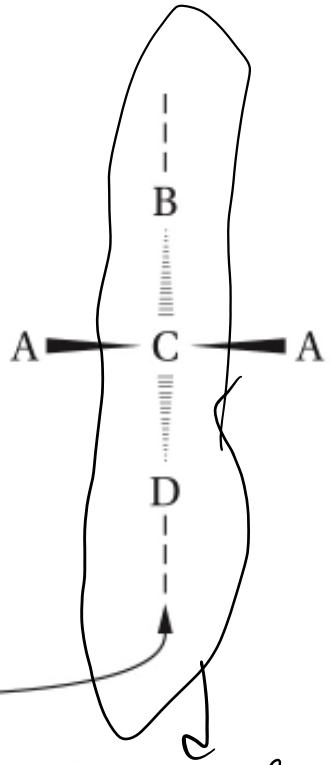

mirror
A
E
C
D
B
A
E
C
D
B


molecule in the
mirror in Figure 5.4
A
C
E
D
B
molecule to left of mirror
in Figure 5.4
A
C
E
B
D

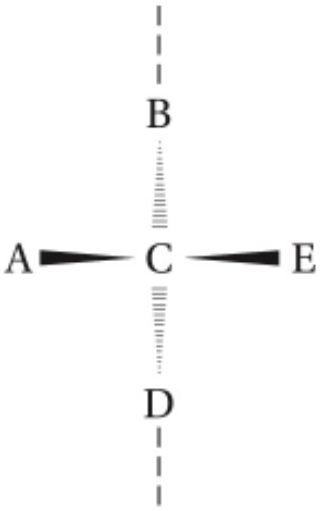

mirror
A
A
C
D
120°
B
A
A
C
D
B
A
C
D
B



≡



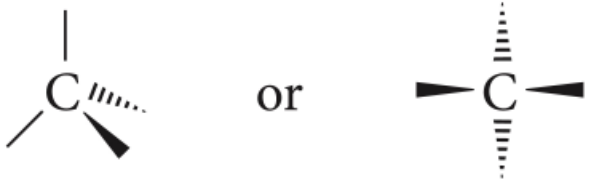
plane of symmetry (achiral)
[molecule $C(A_2BD)$ from Fig. 5.6]



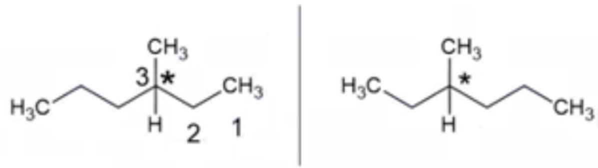
not a plane of symmetry ~~(chiral)~~
[molecule C(ABDE) from Fig. 5.4]

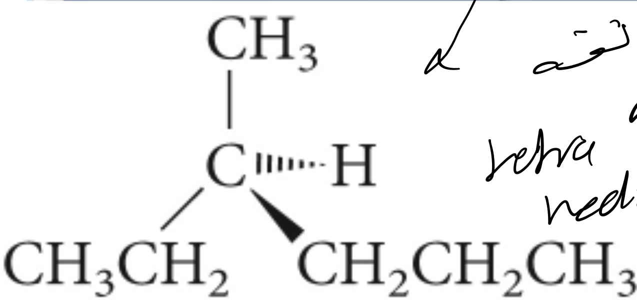
optically inactive
optically active

Locate the stereogenic center in 3-methylhexane and draw the two enantiomers of 3-methylhexane.



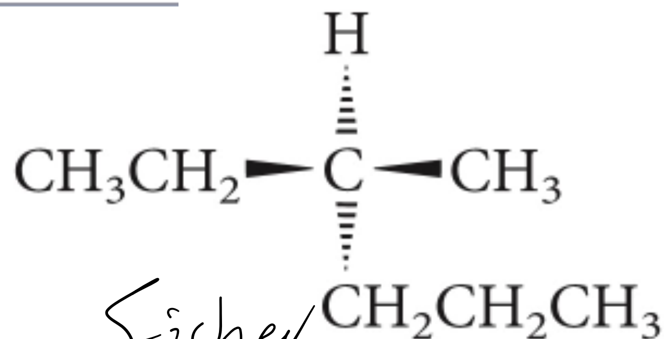
enantumeric isomers





tetra hedral

or

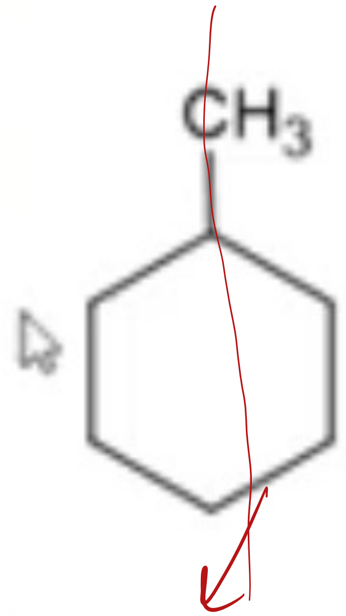


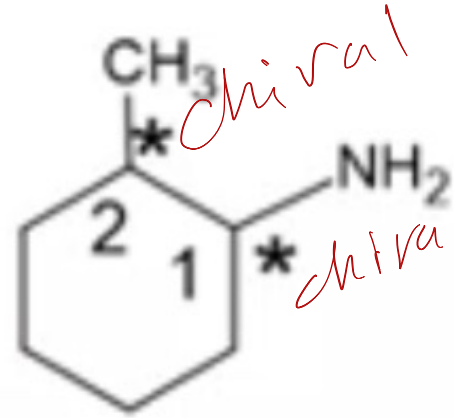
Fisher

معكوسة لأنه تركيب يحتوي ع

لأن الكربون chirell center

كاربون لا





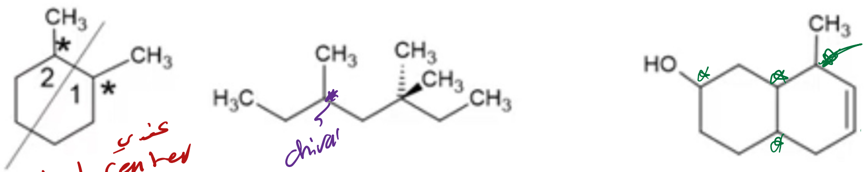
chiral center

plane of symmetry

not chiral

chiral

plane



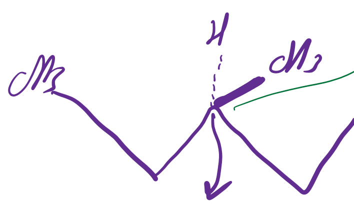
الرابطة الثنائية والثلاثية ما بتعمل Chiral كاربون

عندي 2chiral center بس المركب كامل مش chiral لانه عندي plane of cemetry

فش شرط انه اذا كان عندي اكثر من chiral center انه المركب كله يكون chiral

ممكن يكون وممكن لا وعشان نحدد اذا يكون او لا حسب ال plan..

يعني لما يكون عندي 2 chiral center او اكثر المركب ممكن يكون chiral او لا حسب ال plane



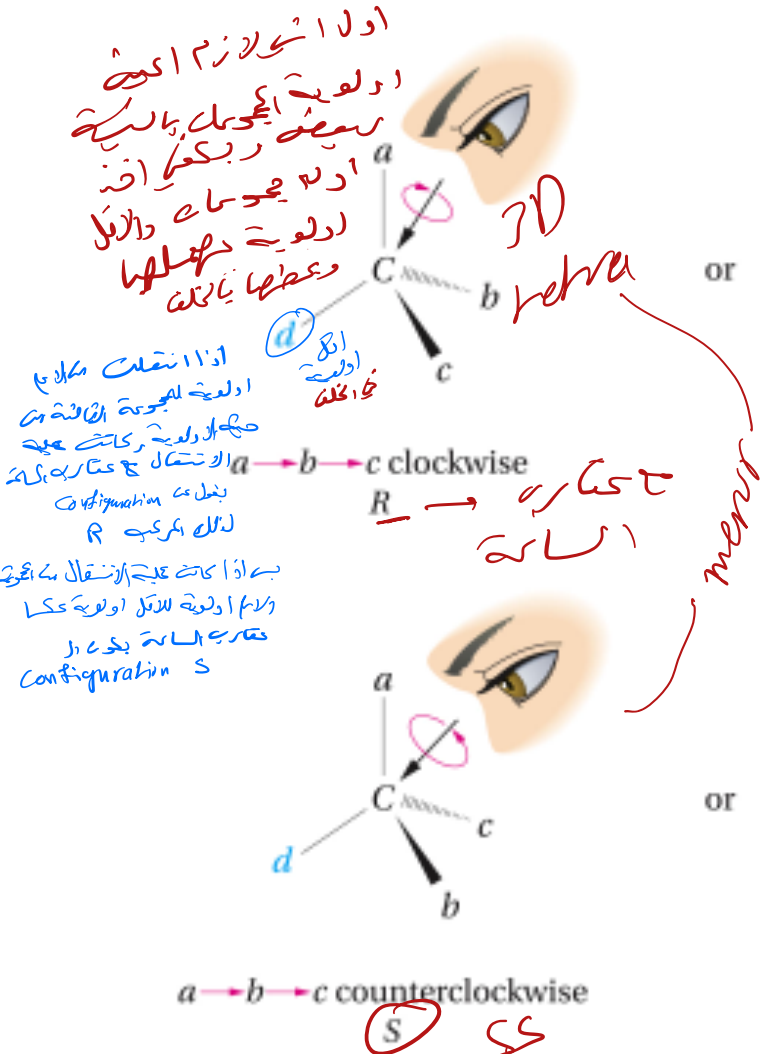
هيك بتصير chiral لو ضفنا بدل CH3 CH3

Achiral

لانه من اليسار ومن اليمين المجموعتين متشابهين

اما اذا كان عندي one chiral center فبدون تفكير بكون المركب chiral لانه ما بكون فيه plan..

Configuration and the R–S Convention



Rule 1

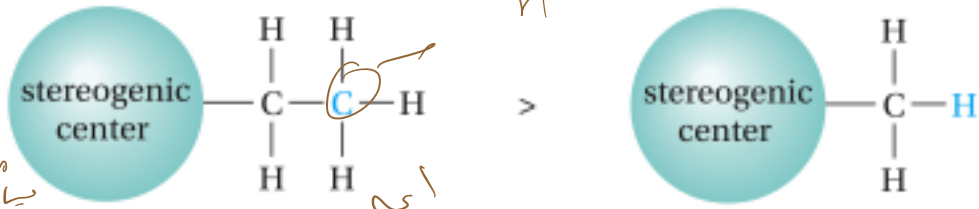
The atoms directly attached to the stereogenic center are ranked according to atomic number. The higher the atomic number, the higher the priority

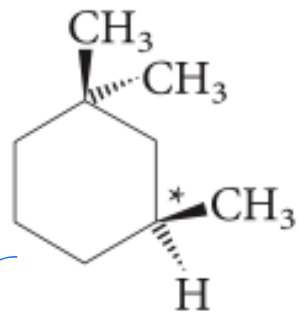
$$Cl > O > C > H$$

high priority — low priority

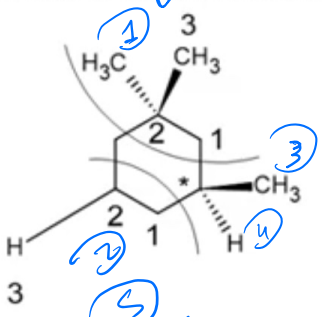
Rule 2

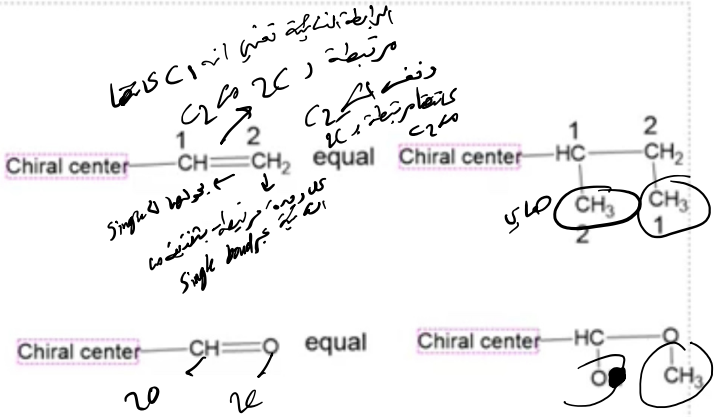
If a decision cannot be reached with rule 1, work outward from the stereogenic center until a decision is made. Example of ethyl and methyl below.

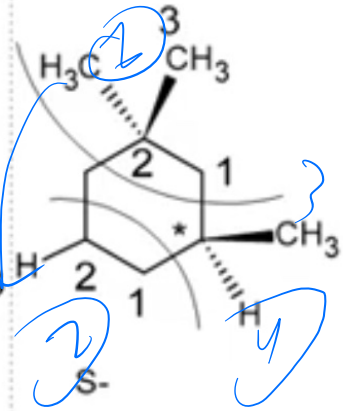


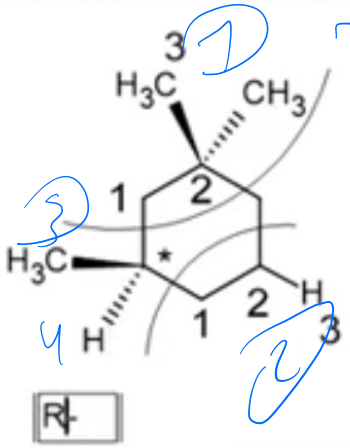


1,1,3-trimethylcyclohexane



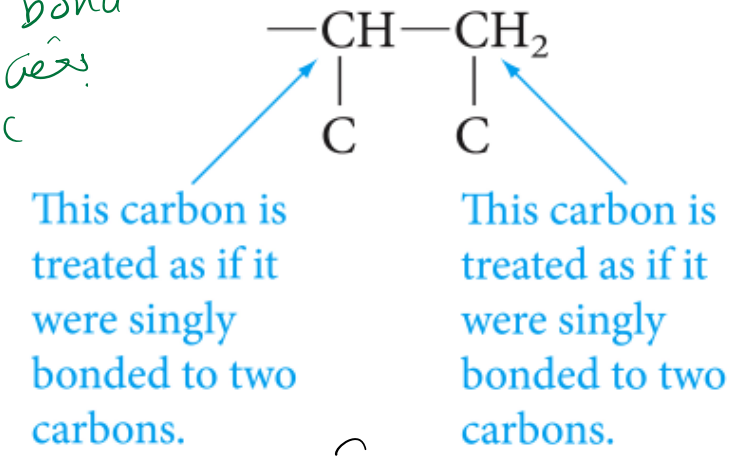

Chiral center
equal
Chiral center
Chiral center
equal
Chiral center
Chiral center
equal
Chiral center

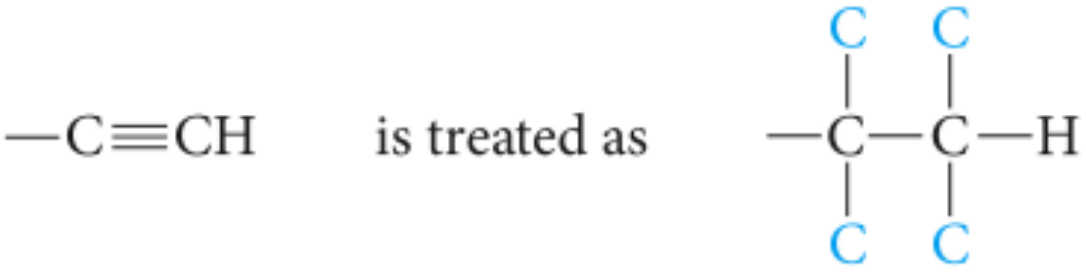


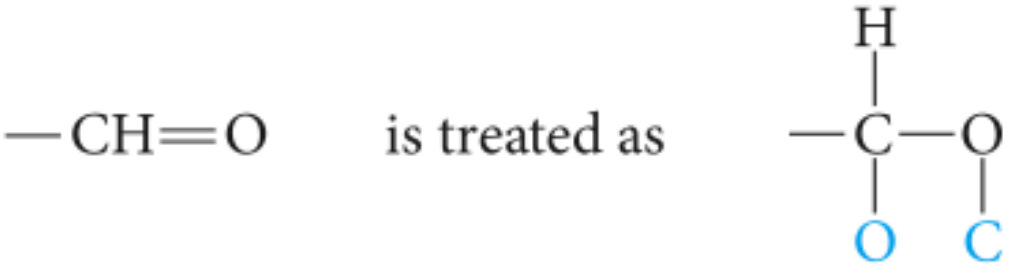

R
Chiral cen

Rule 3

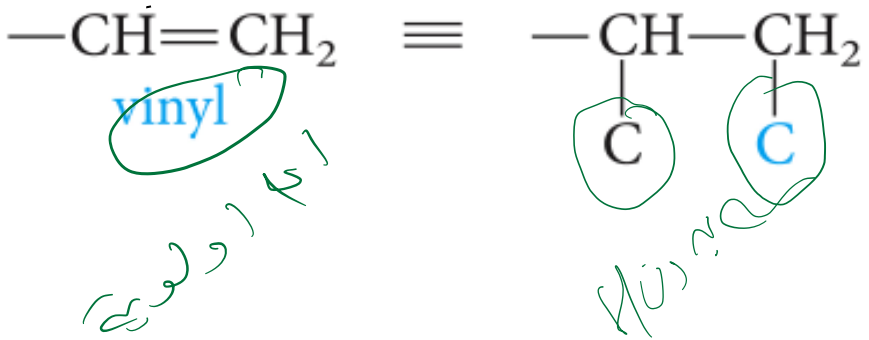
Multiple bonds are treated as if they were an equal number of single bonds.



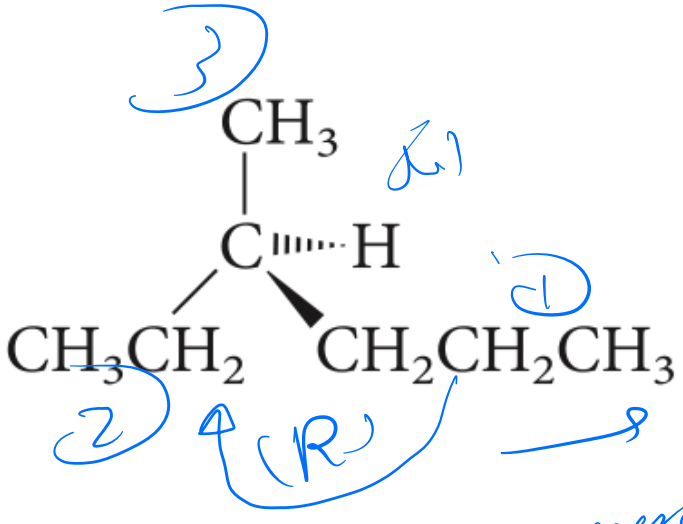

—C≡CH
is treated as
C
C
C
C
H
C
C

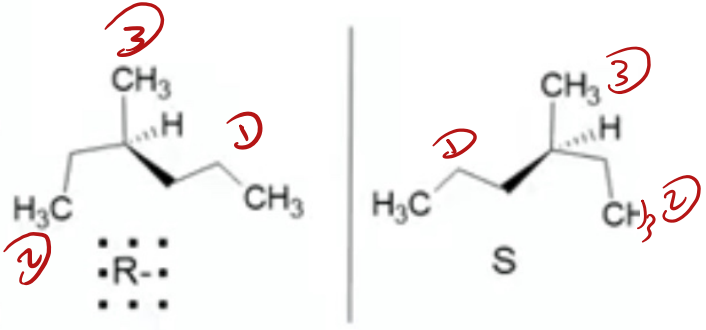

—CH=O
is treated as
H
C
O
O
C

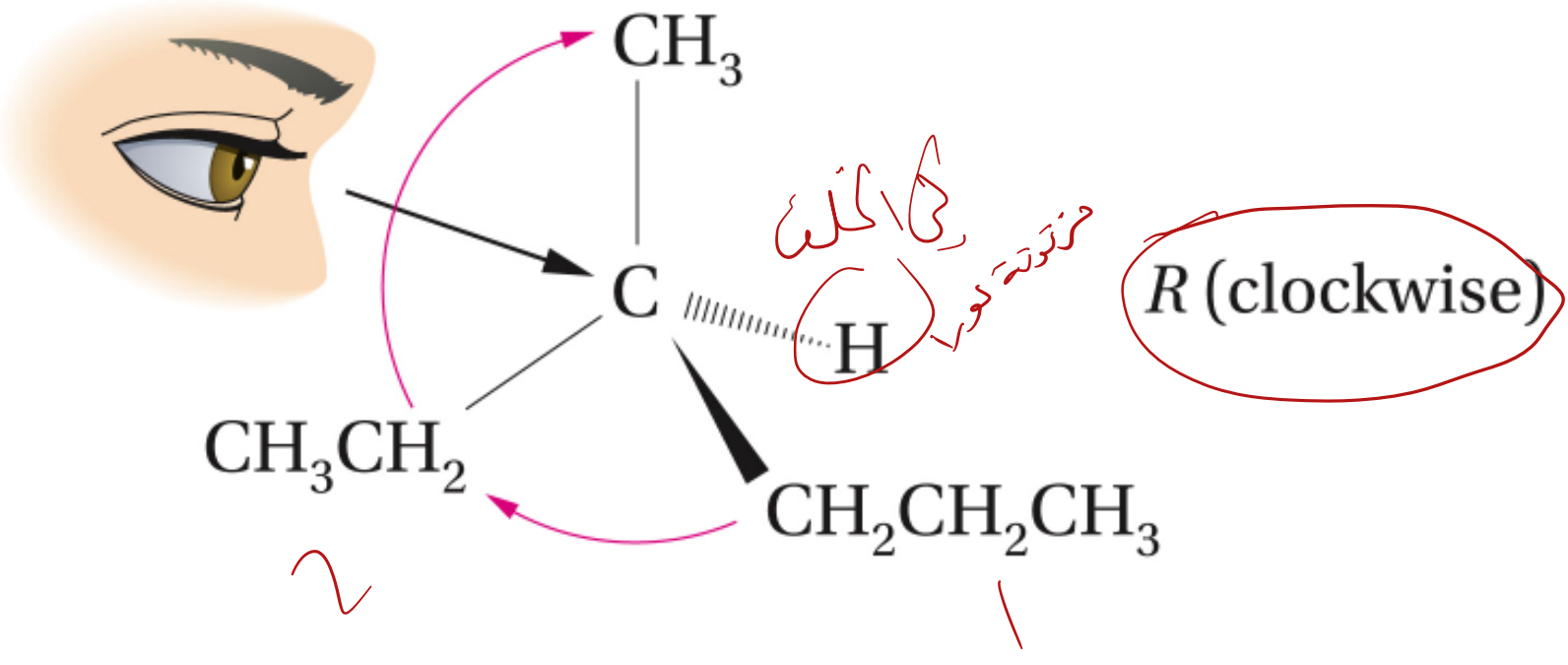
Which group has the higher priority, isopropyl or vinyl?

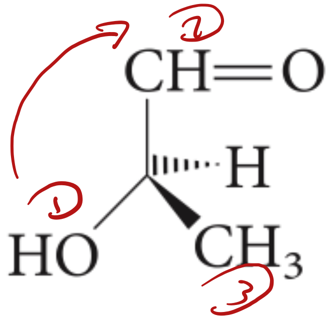


Assign the configuration (R or S) to the following enantiomer of 3-methyl-hexane

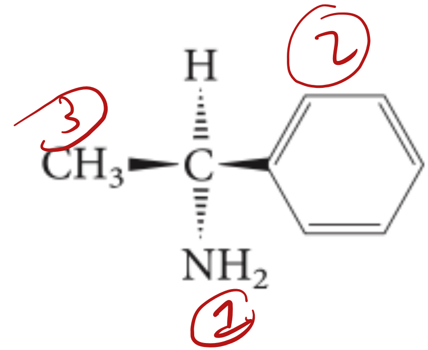





CH3
C
H
CH3CH2
CH2CH2CH3
R (clockwise)

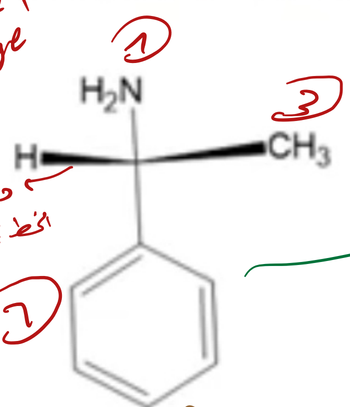


(R)



(S)

mirrore image



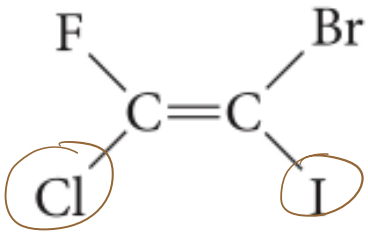
(R)

S

واقعة باتجاهي الخط اذا تغير (بس الجروب اللي ما له اولوية بعكسها للخلف) نعكس الـconfiguration فظاهرة صحيح (S) بس حقيقة (R)

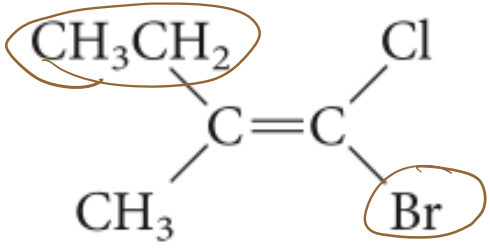
يعني اذا اعطاني Fisher او 3D وكانت H باتجاهي بعطيه configuration الـR او S بعدين بعكسه . لاني بدي اياها H للخلف والاعلى H للخلف بعكس الـconfiguration اللي اوجدته اذا كان R بطلعه (S) اذا كان S بطلعه (R)

The *E*–*Z* convention for *Cis*–*Trans* Isomers



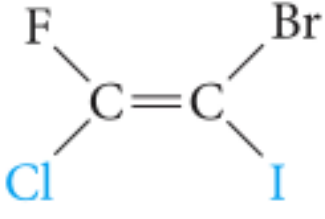
cis or *trans*?

cis / Z

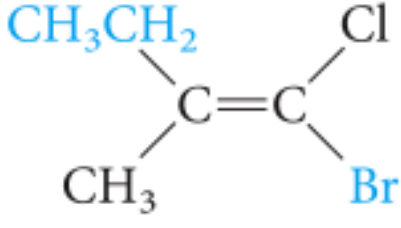


cis or *trans*?

trans / E

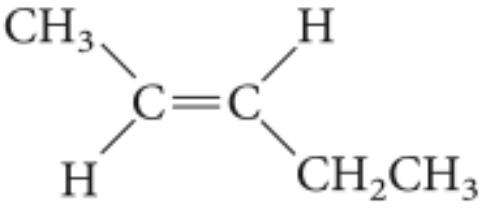


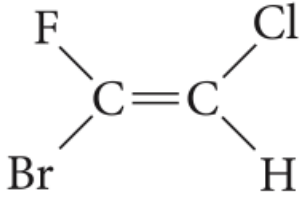
(*Z*)-1-bromo-2-chloro-2-fluoro-1-iodoethene



(*E*)-1-bromo-1-chloro-2-methyl-1-butene

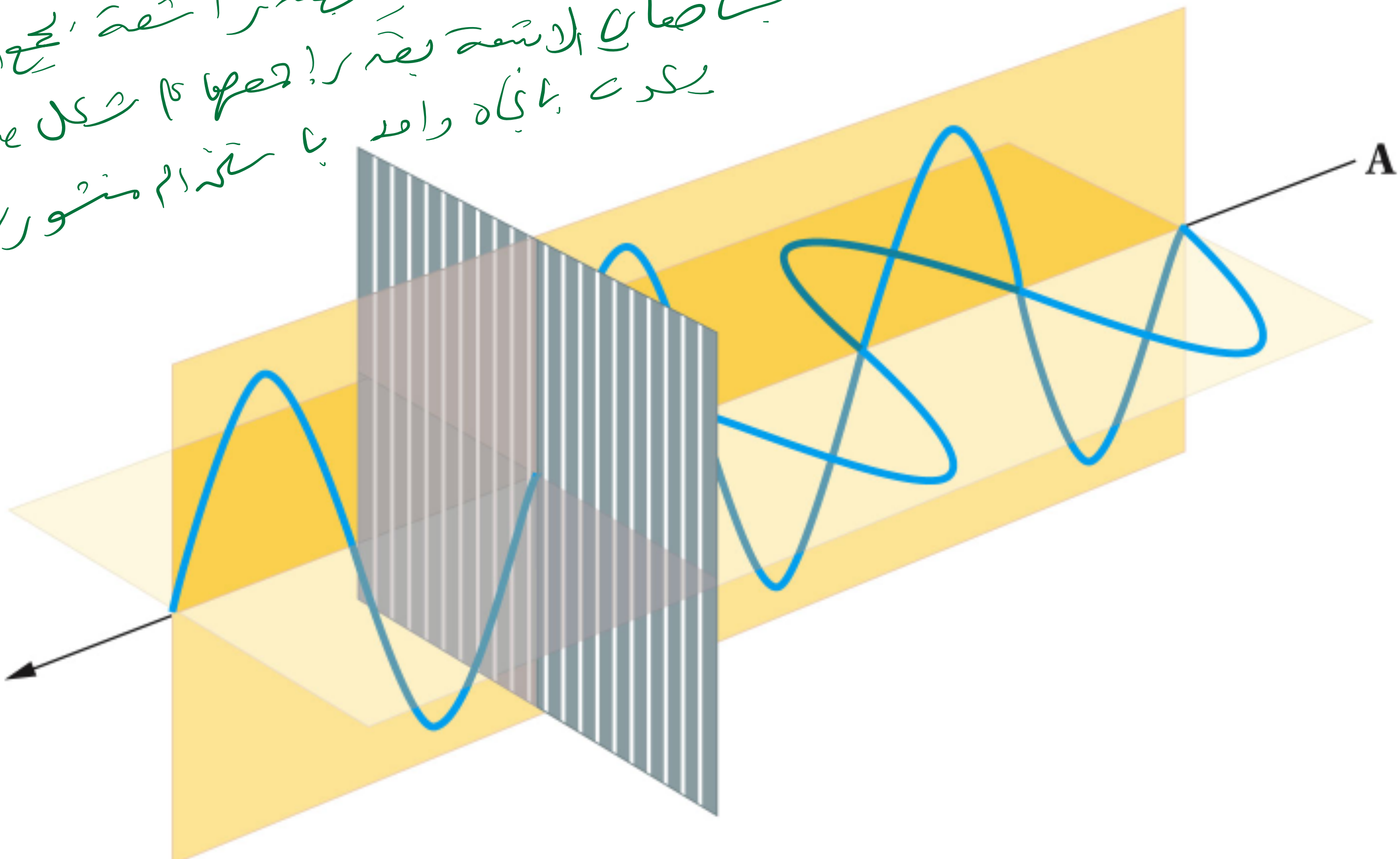
Name each compound by the E–Z system

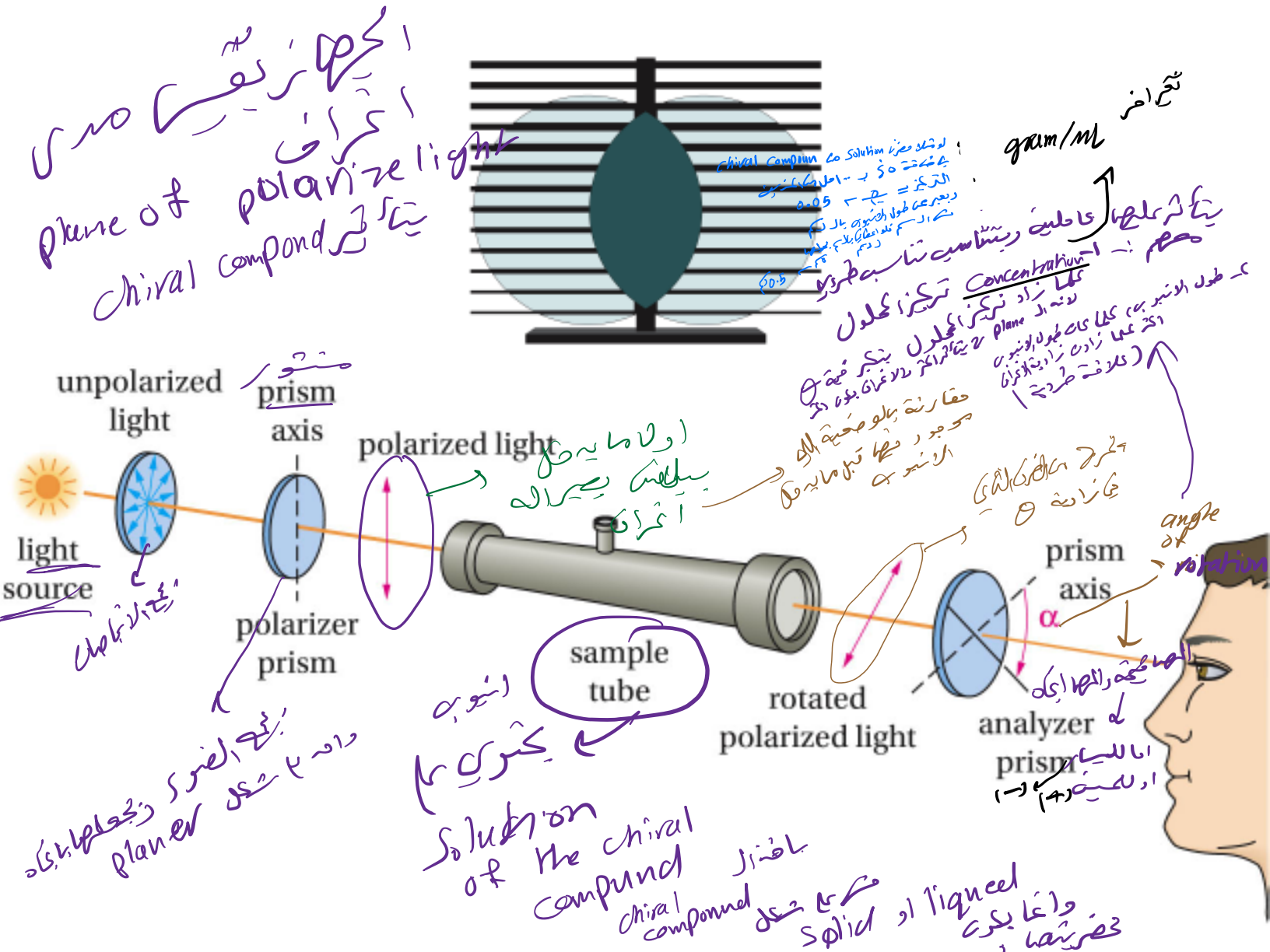


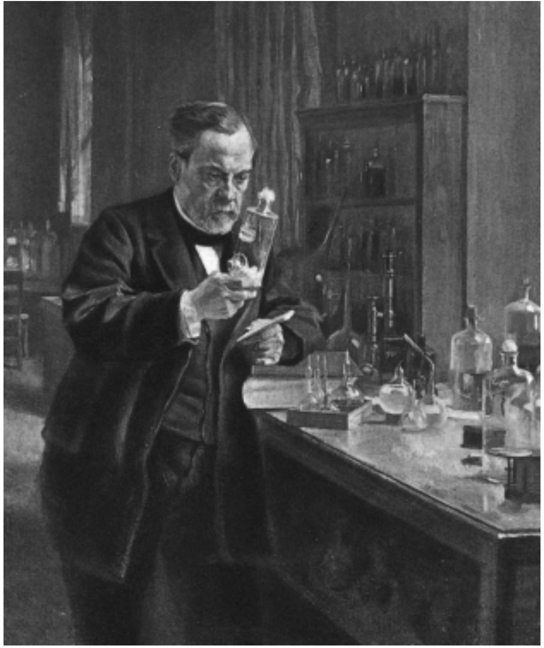


Polarized Light and Optical Activity

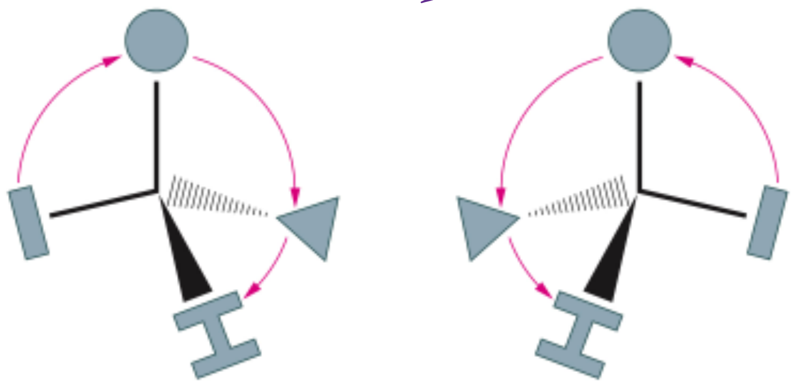
اي مصدر ضوء عادي يصدر اشعة بجميع الاتجاهات
بس هاي الاشعة بقدر احصرها بشكل plane
يكون باتجاه واحد باستخدام منشور زجاجي




unpolarized light
prism axis
polarized light
light source
polarizer prism
sample tube
rotated polarized light
prism axis
analyzer prism



solution تركيز معين



$$\text{Specific rotation} = [\alpha]^{t}_{\lambda} = \frac{\alpha}{l \times c} (\text{solvent})$$

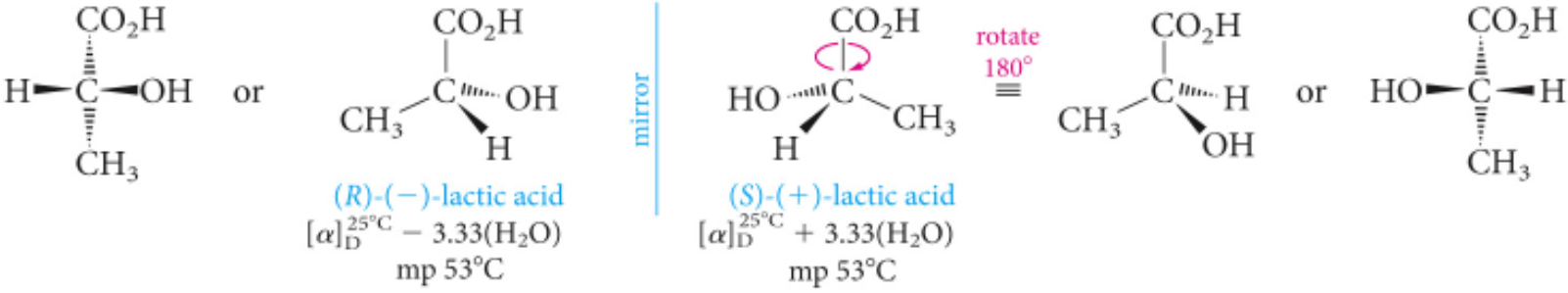
α → rotation نقيسها باستخدام الجهاز

l → طول الانبوب (dm)

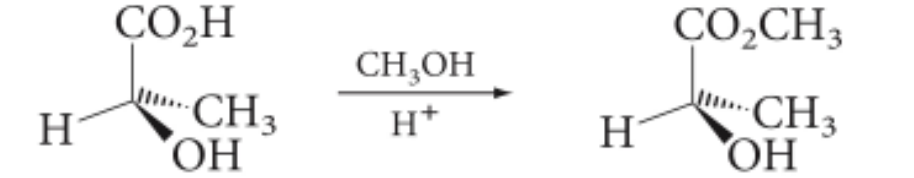
c → gr/mL

(solvent) → الشيء الثابت لانه كلما زاد l و c تزداد α

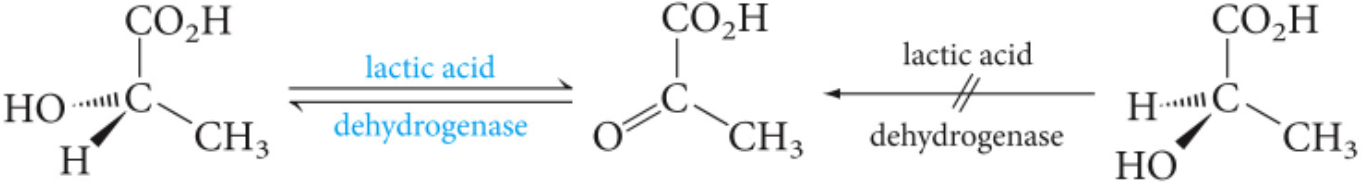
كيف بدي احل الزاوية ثابتة
تصبح صفة الحركية مثل اي صفة
فيزيائية اخرى بعبر عنها بجهاز لقيم


CO2H
H
C
OH
CH3
or
CO2H
CH3
C
OH
H
(R)-(−)-lactic acid
[α]D25°C − 3.33(H2O)
mp 53°C
mirror
CO2H
HO
C
CH3
H
(S)-(+)-lactic acid
[α]D25°C + 3.33(H2O)
mp 53°C
rotate
180°
≡
CO2H
CH3
C
H
OH
or
CO2H
HO
C
H
CH3

Properties of Enantiomers

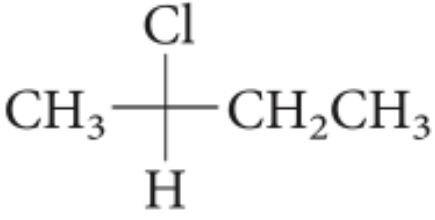


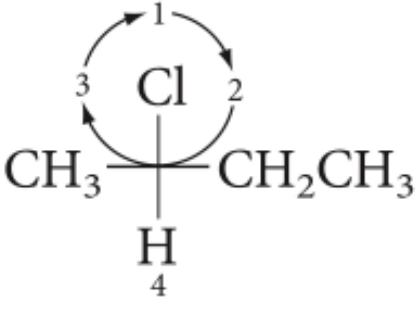
(*R*)-(−)-lactic acid (*R*)-(+)-methyl lactate



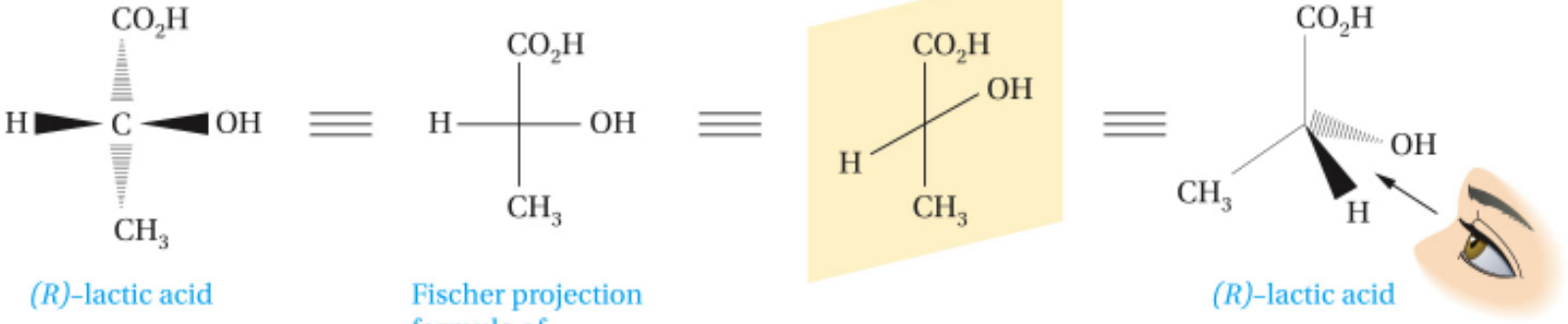
(+)-lactic acid pyruvic acid (−)-lactic acid

Fischer Projection Formulas





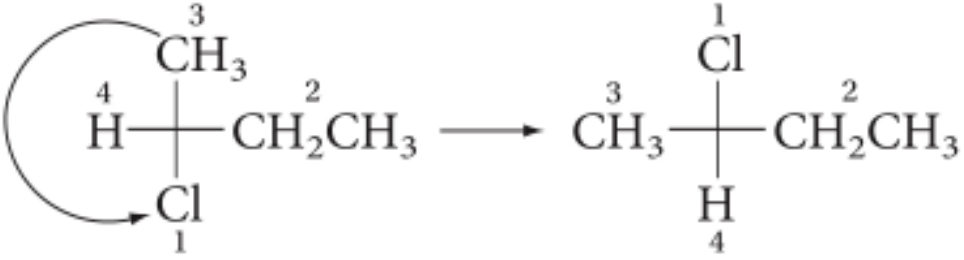
clockwise = *R*



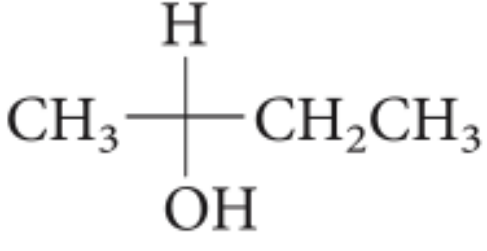
(R)–lactic acid

Fischer projection formula of *(R)*–lactic acid

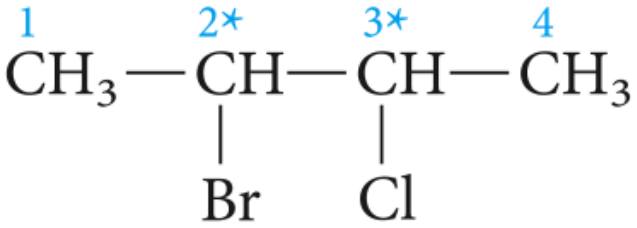
(R)–lactic acid



Determine the absolute configuration of of the following enantiomer of 2-butanol from its Fischer projection



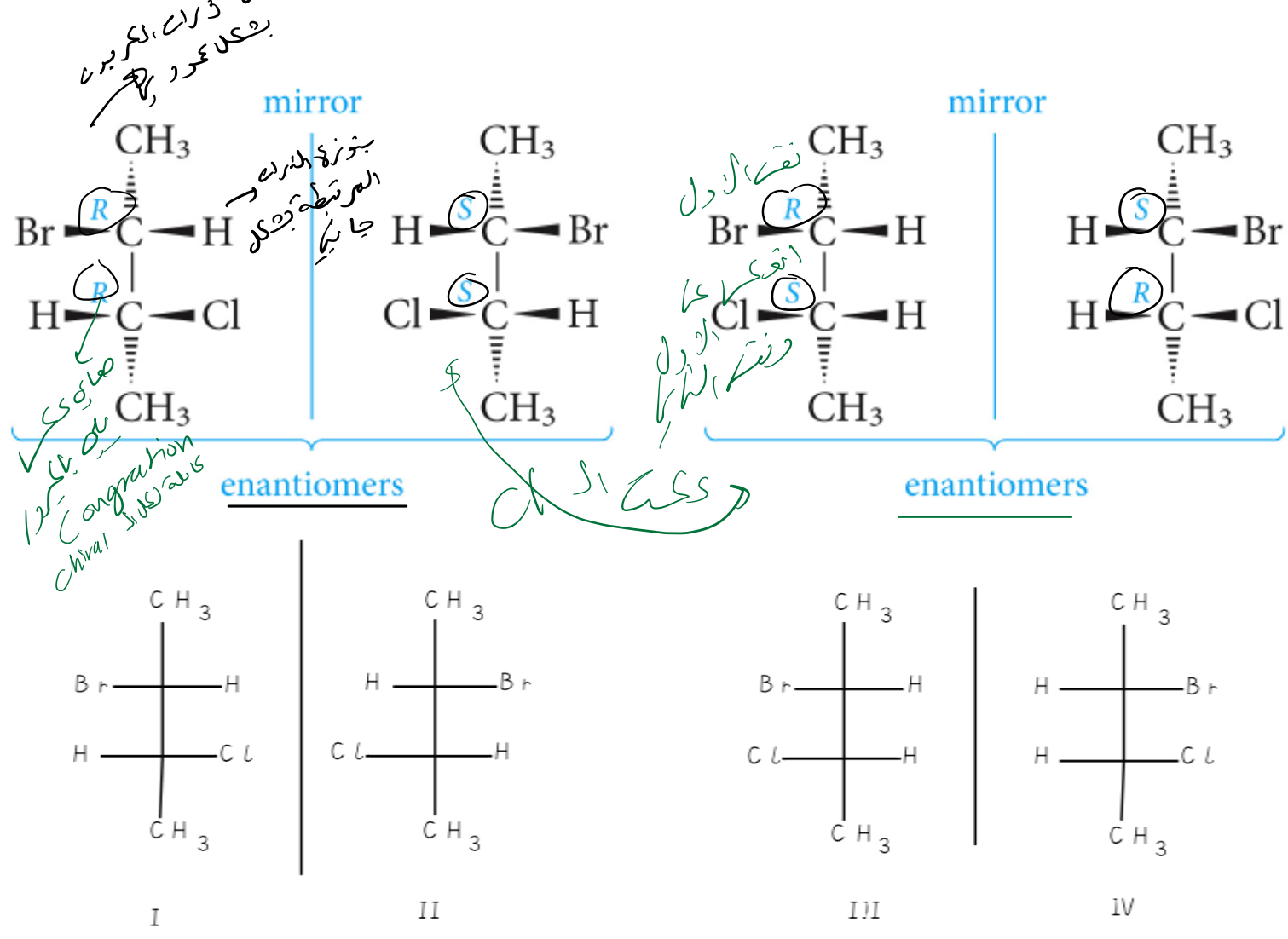
Compounds with More Than One Stereogenic Center; Diastereomers

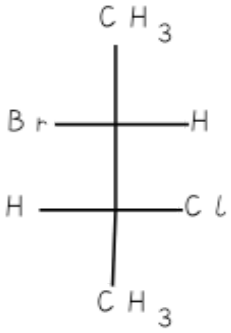


2-bromo-3-chlorobutane

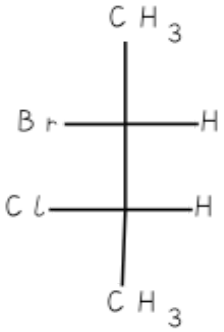
Number of stereoisomers = 2^n (n = عدد الـ chiral)

n = # of chiral centers

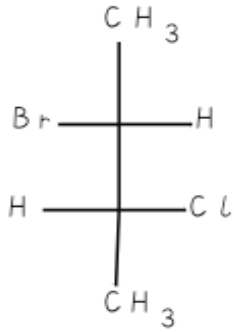

mirror
mirror
enantiomers
enantiomers
I
II
III
IV



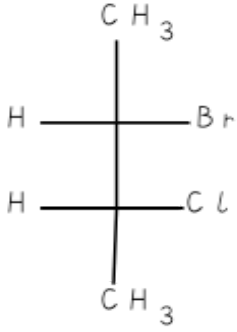
I



III

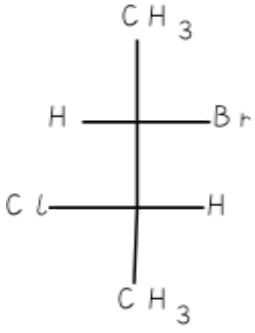


I

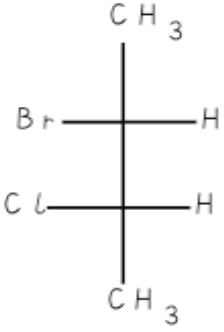


IV

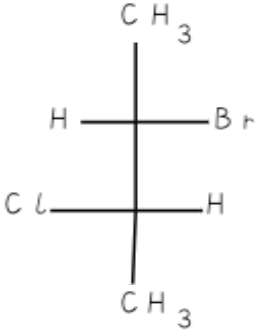
diastereo isomers



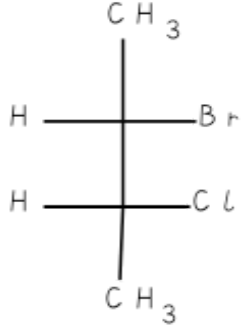
II



III



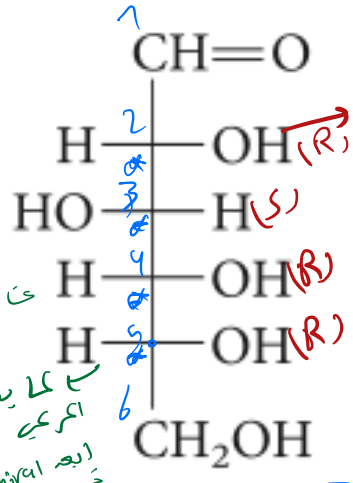
II



IV

ایزومر diastreoc

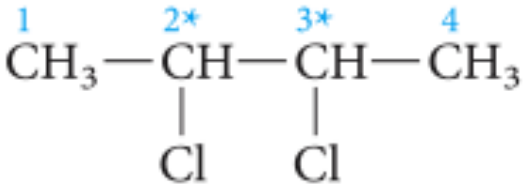
ایزومر enantiomeric



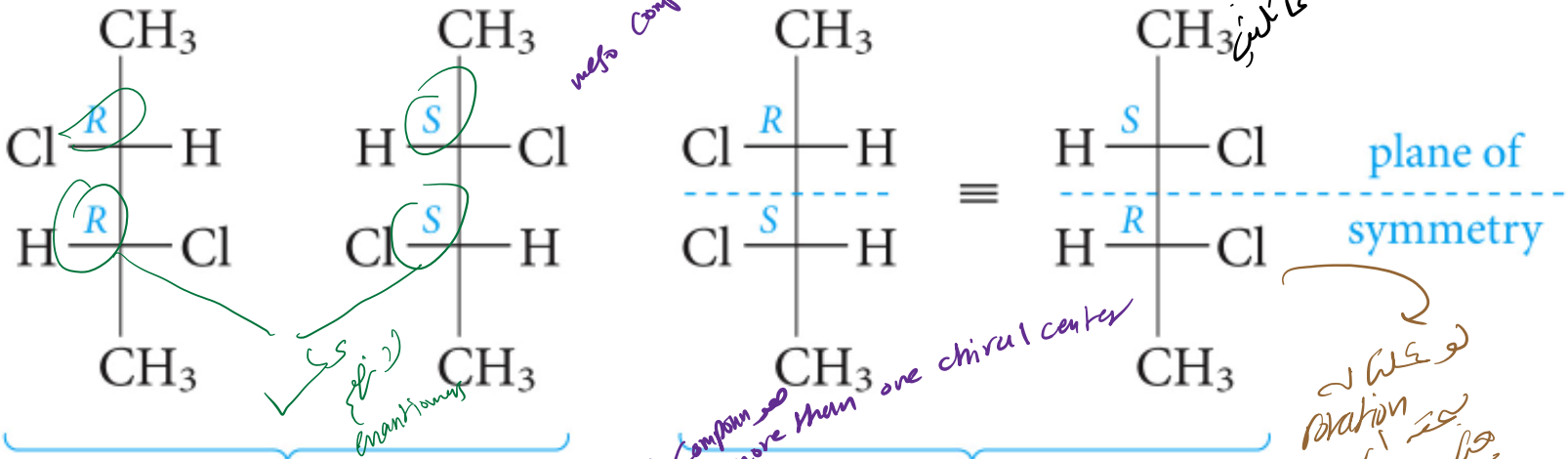
4 chiral

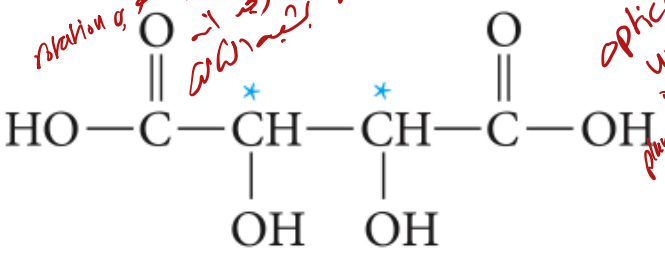
Given is the Fischer projection of glucose (blood sugar), how may stereoisomers of this sugar are possible?

Meso Compounds; the Stereoisomers of Tartaric Acid



2,3-dichlorobutane

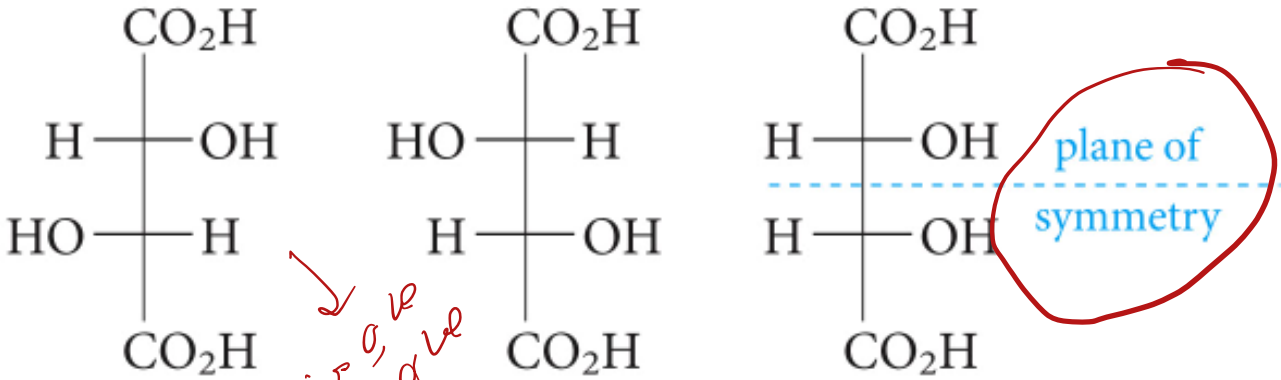




tartaric acid

optically unactive

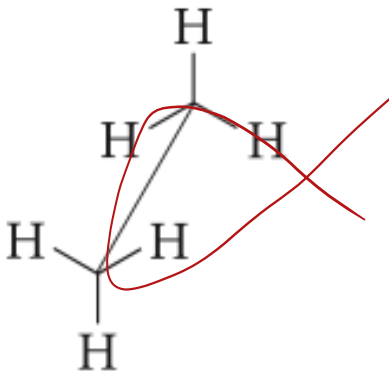
enantomers isomer of 3 they are identical



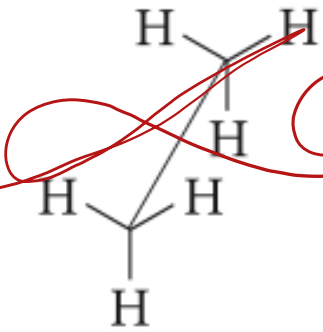
Configuration	(*R*,*R*)	(*S*,*S*)	*meso* (*R*,*S*)
$[\alpha]_D^{20°}$ (H_2O)	+12	−12	0
Melting point, °C	170	170	140

Stereochemistry A Recap of Definitions

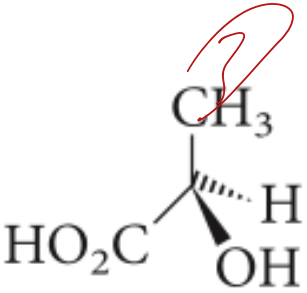
Cis-trans 2-butene (Z and E notation)



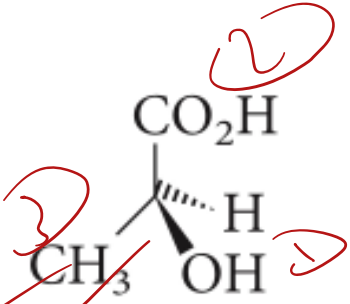
and



Staggered and eclipsed

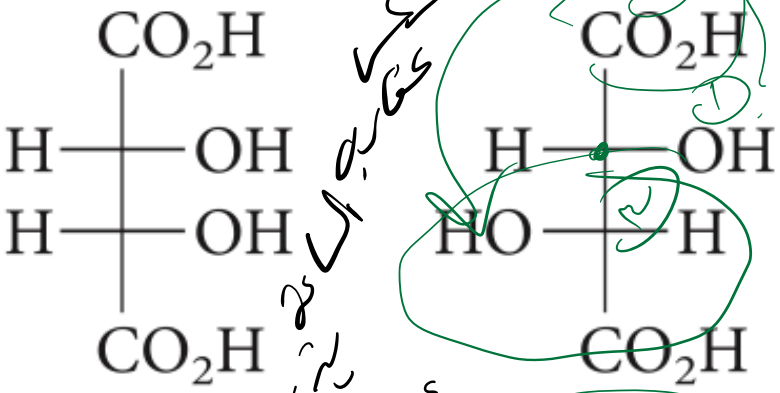


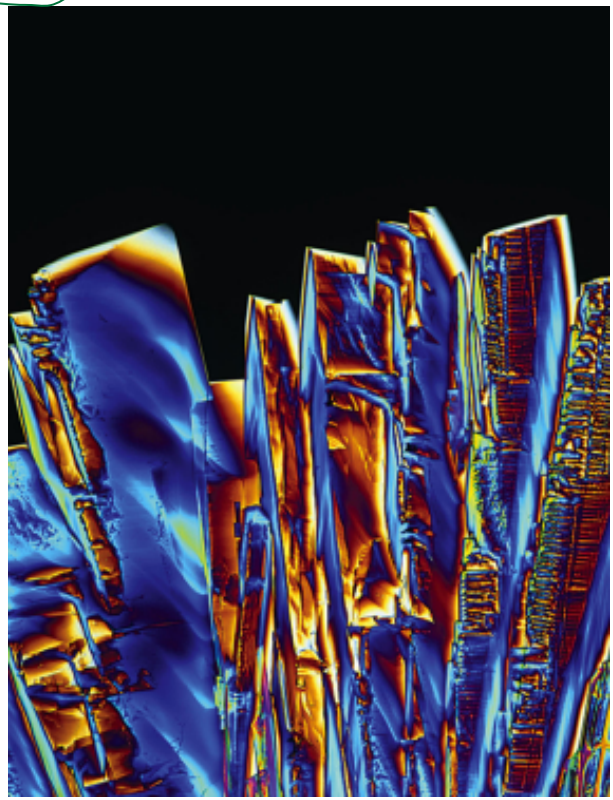
and



(R)- and (S)-lactic acids

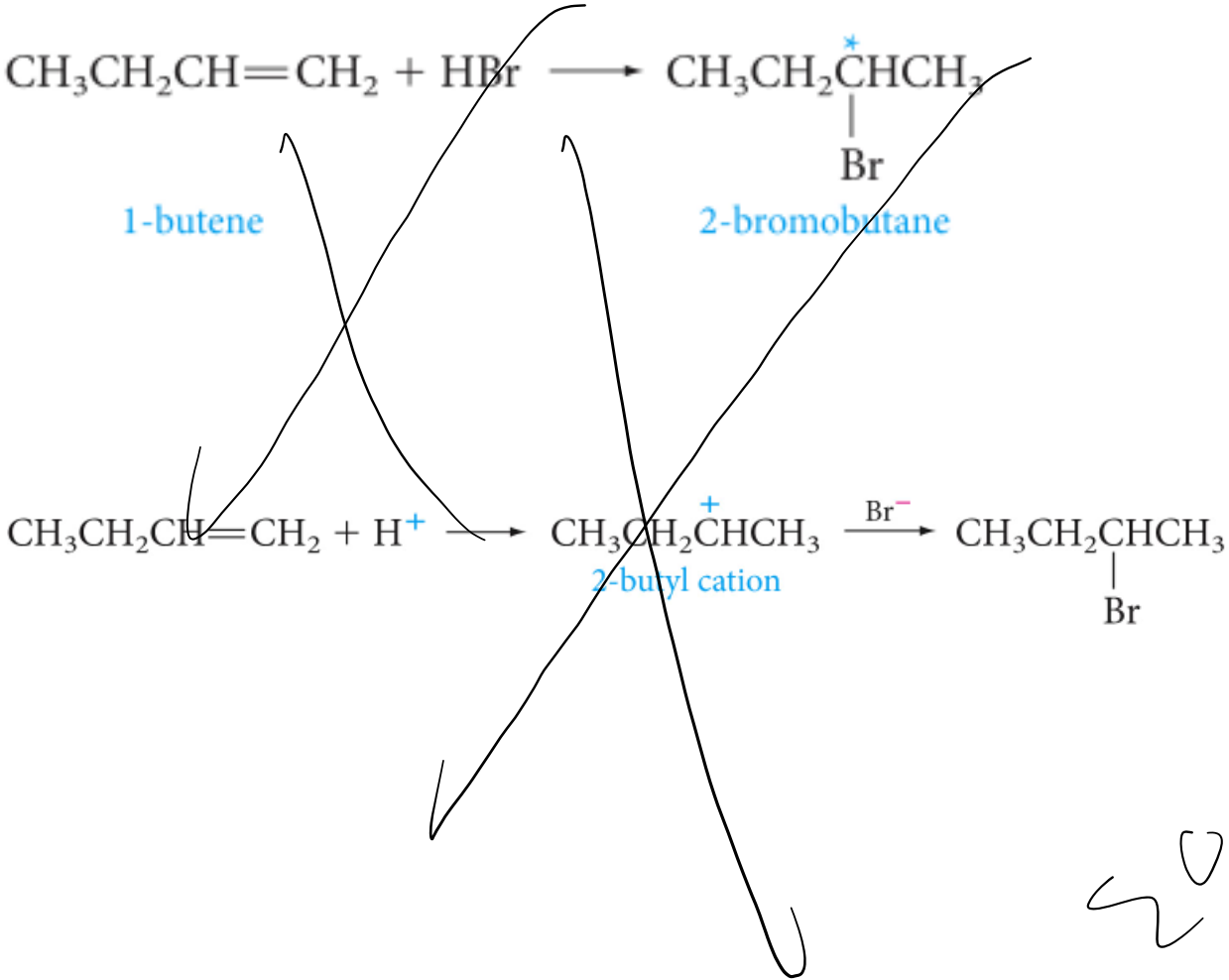
Meso- and (RR)-tartaric acids

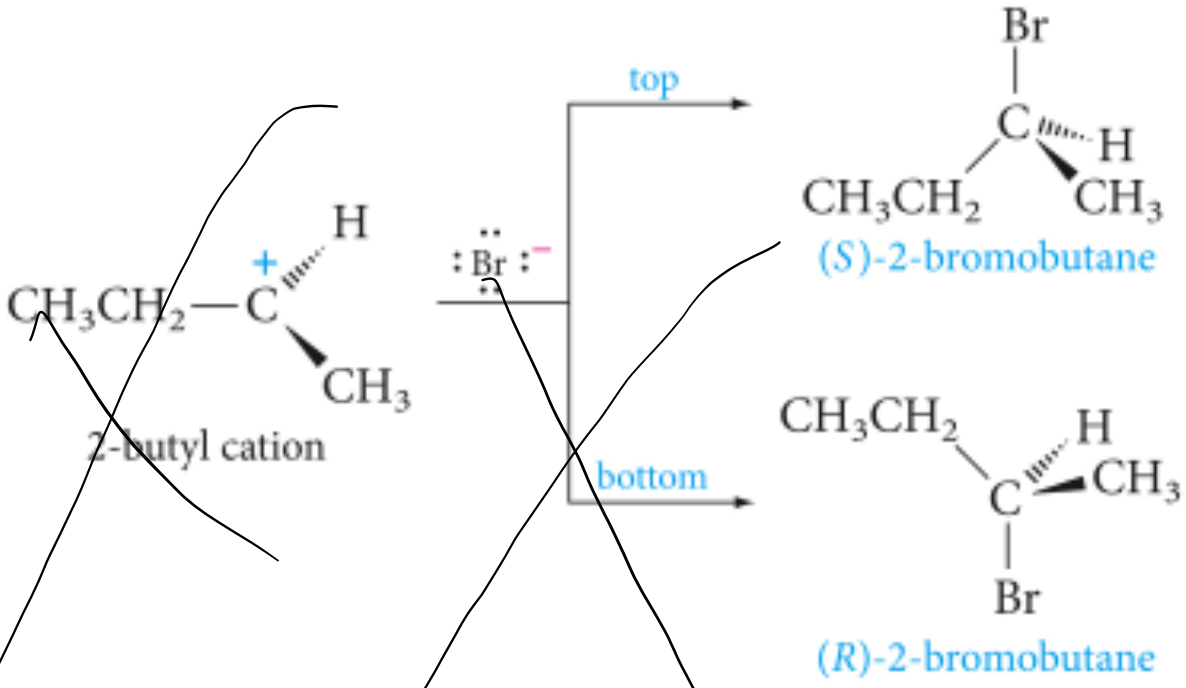




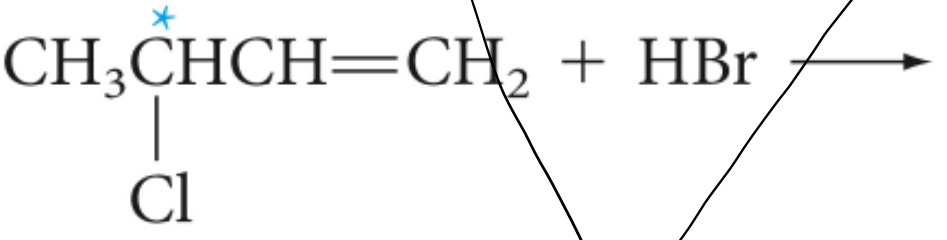
Tartaric acid crystals under polarized light

Stereochemistry and Chemical Reactions

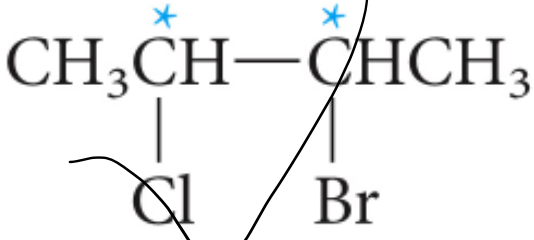




When chiral products are obtained from achiral reactants, both enantiomers are formed at the same rates, in equal amounts.

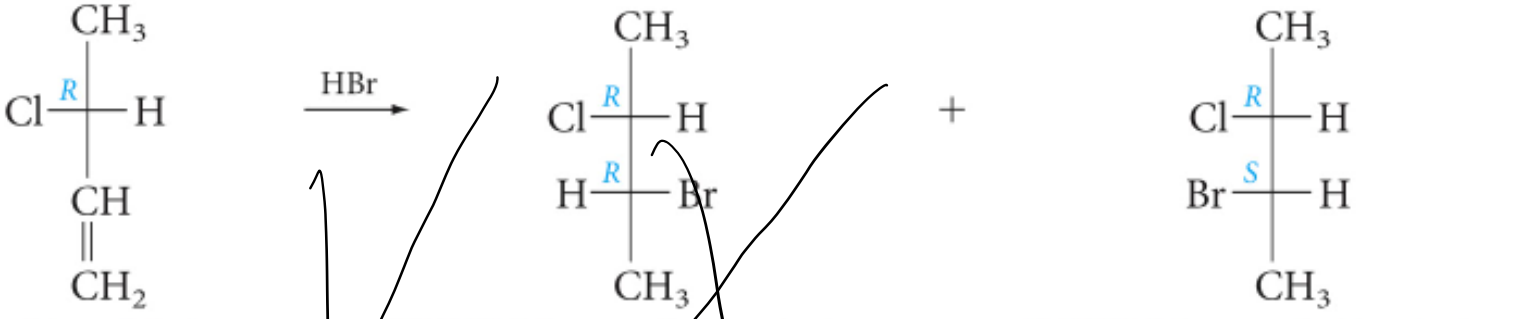


3-chloro-1-butene



2-bromo-3-chlorobutane

Reaction of a chiral regent with an achiral reagent when it creates a new stereogenic center, leads to diastereomeric products at different rates and in unequal amounts.

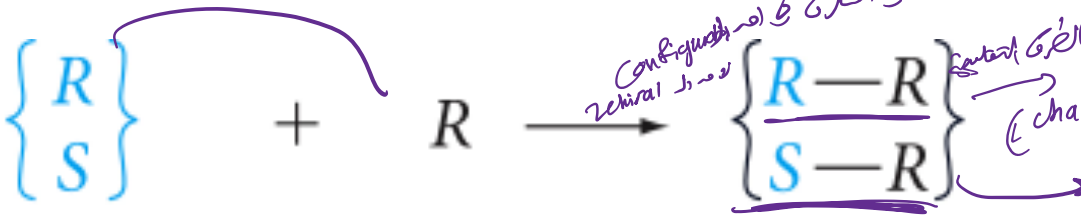


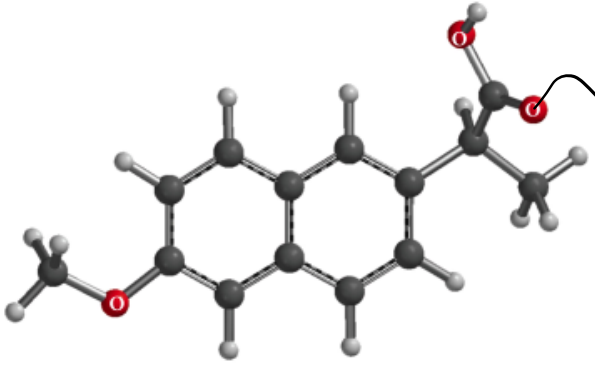
(*R*)-3-chloro-1-butene (2*R*,3*R*)-2-bromo-3-chlorobutane (2*S*,3*R*)-2-bromo-3-chlorobutane

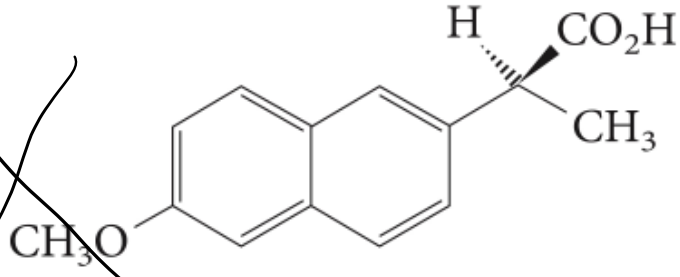
Reaction of a chiral reagent with an achiral reagent, when it creates a new stereogenic center, leads to diastereomeric products at different rates and in unequal amounts.

Resolution of a Racemic Mixture

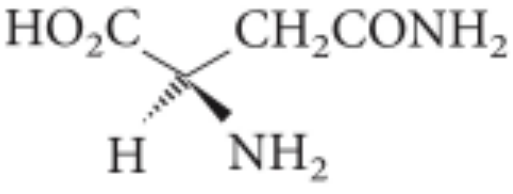
To separate a racemic mixture, we first react with a chiral reagent. The product will be a pair of diastereomers. These, differ in all types of physical properties and can therefore be separated by ordinary methods.



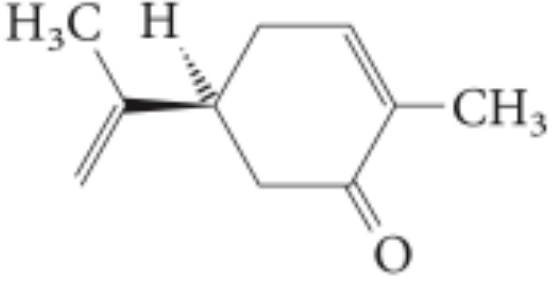




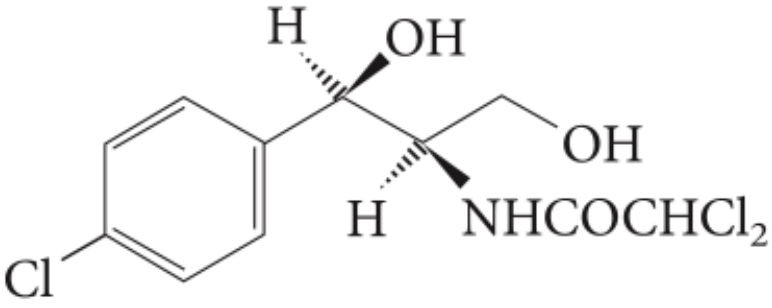
(*S*)-naproxen



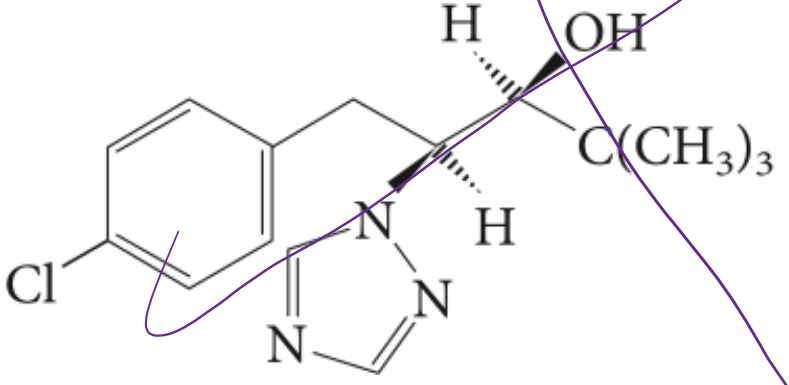
(*R*)-asparagine



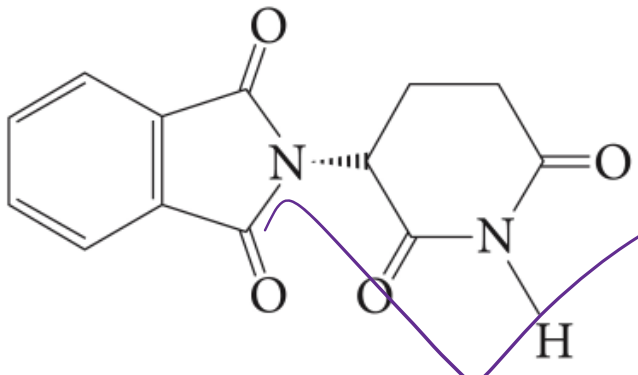
(*S*)-carvone



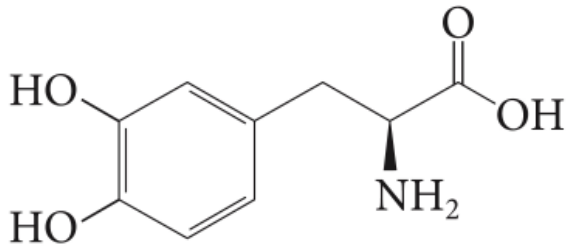
(*R*,*R*)-chloramphenicol



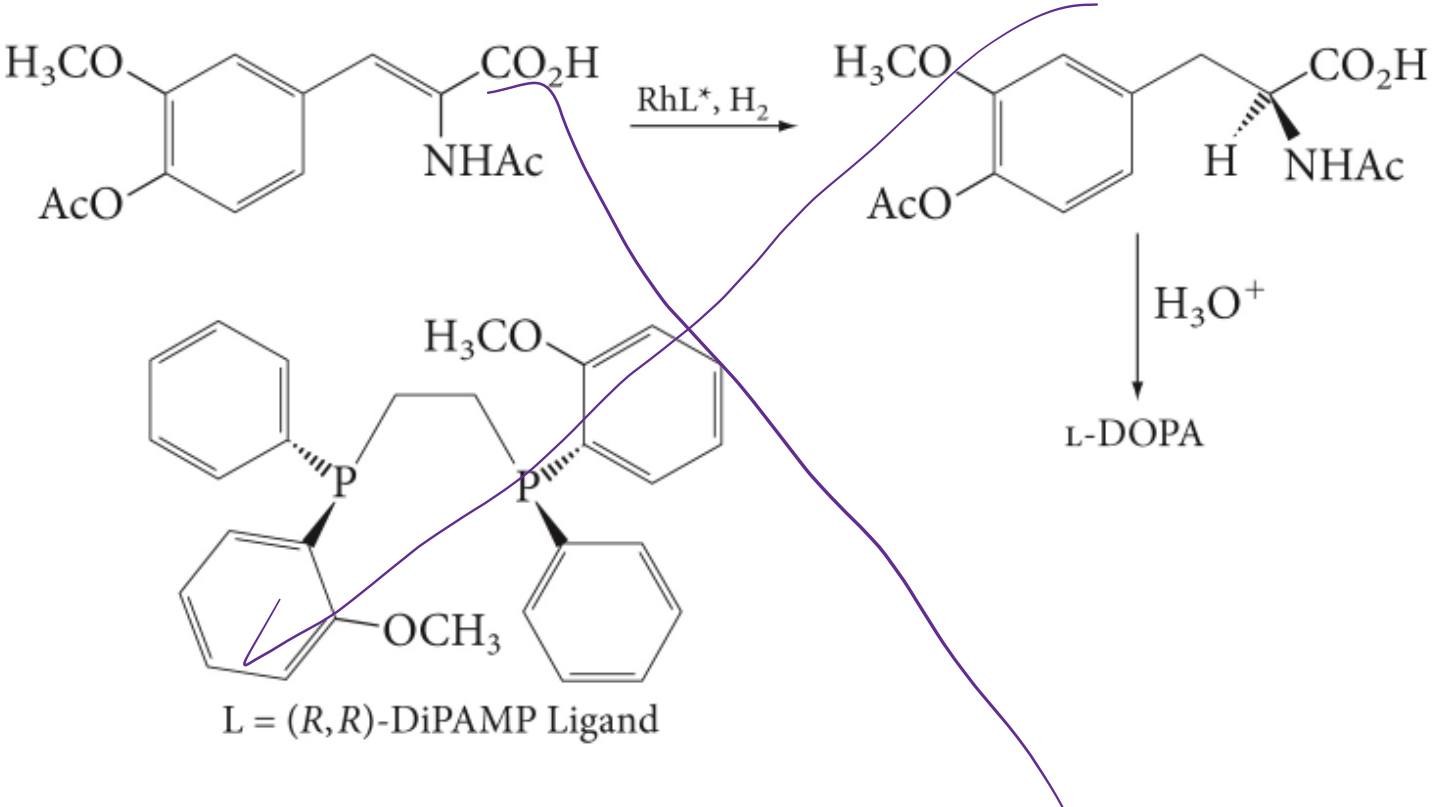
(*S*,*S*)-paclobutrazol



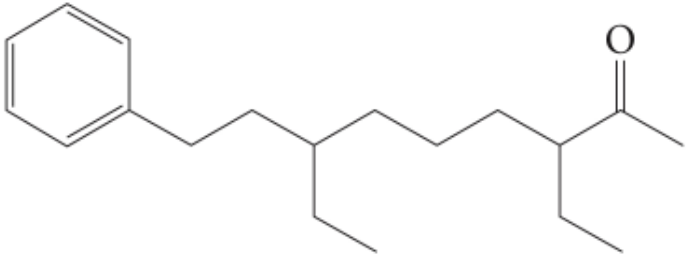
(*R*)-thalidomide



L–DOPA



L = (*R*,*R*)-DiPAMP Ligand



Mature crocodiles secrete from their skin glands the compound with the following structure. The compound is thought to be a communication pheromone for nesting and mating.

How many stereogenic centers are in the compound? Mark then with an asterisk.

How many stereoisomers of this compound are possible.