

## Chapter 4

organic chemistry  $\Rightarrow$  based on the relationship between molecular structure and properties

$\Downarrow$

three dimensional structure ; stereochemistry

$\Downarrow$

stereoisomer ; different orientation of atoms in space

$\Downarrow$

conformational analysis, enantiomer, diastereomer

the structure of  $\text{CH}_4$  before the direct determination  $\Rightarrow$   $\text{CH}_3\text{Y}$  ; only one compd  $\rightarrow$  (square planar, pyramidal, tetrahedral)

$\text{CH}_2\text{XY}$  ; only one compd  $\rightarrow$  tetrahedral

$\text{CWXYZ}$  ; two compds  $\rightarrow$  tetrahedral

$\Downarrow$

enantiomer

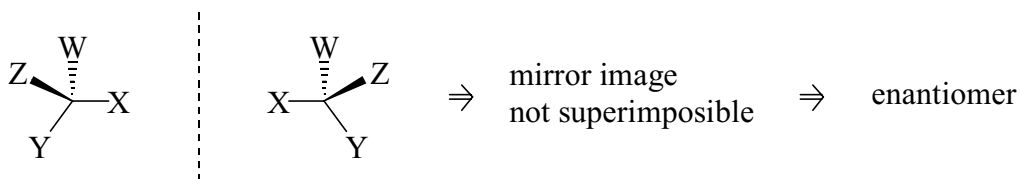
optically active substance  $\Rightarrow$  rotate the plane of polarized light

$\Downarrow$

+  $\leftarrow$  dextrorotatory  $\Leftarrow$  optically inactive  $\Leftarrow$  polarimeter  
 -  $\leftarrow$  levorotatory  $\Leftarrow$  optically active  $\Leftarrow$  Fig 4-2

$\Downarrow$

optical rotation depends on the concn  $\Rightarrow$  specific rotation  $[\alpha] = \frac{\alpha}{l} \times d \rightarrow [\alpha]_D^{20}$   
 $\uparrow \quad \uparrow$   
 (dm) (g/cm<sup>3</sup>)



non superimposable molecules on their mirror images  $\Rightarrow$  chiral  $\Rightarrow$  can exist as enantiomers  
 $\updownarrow$   
 achiral  $\Downarrow$

chiral molecule )  $\Leftarrow$  chiral center (chiral carbon)  $\Leftarrow$  carbon atom to have four different groups  
 achiral molecule )

$\Downarrow$   
 have more than one chiral center

$\Downarrow$   
 molecules without chiral centers can be chiral

enantiomers have identical physical properties except for the direction of rotation of the plane of polarized light  $\Rightarrow$  enantiomers have identical chemical properties except toward optically active reagents

$\Downarrow$   
 $\text{CH}_3\overset{*}{\text{C}}\text{HOHCOOH}$  the same acid strength

with optically active reagents, the results will be different  $\Leftarrow$  from the same products with the same rates  $\Leftarrow$  (alkene  $\xleftarrow{\text{H}_2\text{SO}_4}$  alkyl bromide  $\xleftarrow{\text{HBr}}$  ester  $\xleftarrow{\text{CH}_3\text{COOH}}$   $\text{CH}_3\overset{\text{CH}_3}{\underset{*}{\text{C}}}\text{HCH}_2\text{OH}$ )  
 $\Downarrow$  (transition states are not mirror images)  $\Downarrow$  (transition states are mirror images)

a mixture of equal amounts of enantiomers  $\Rightarrow$  racemic modification  $\Rightarrow$  optically inactive

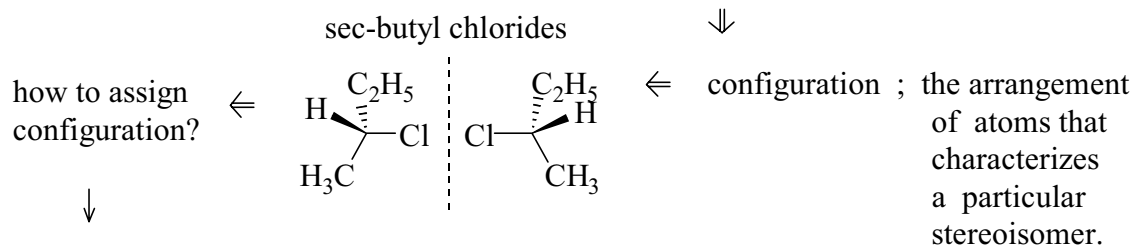
$\Downarrow$   
 (  $\pm$  )

$\Downarrow$   
 resolution  $\Leftarrow$  inseparable by usual methods

the material containing an excess of one enantiomer  $\Rightarrow$  shows optical activity if there is no rapid interconversion  $\Rightarrow$  configurational enantiomers

conformational enantiomers  $\downarrow$  easy interconversion

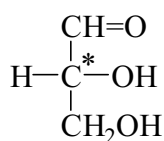
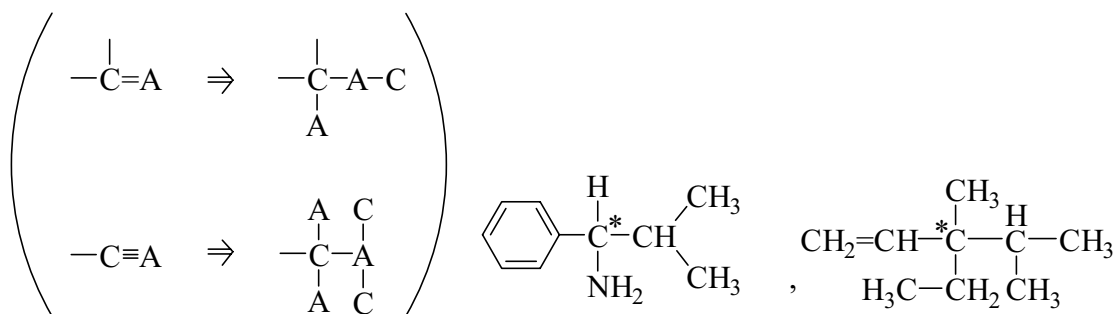
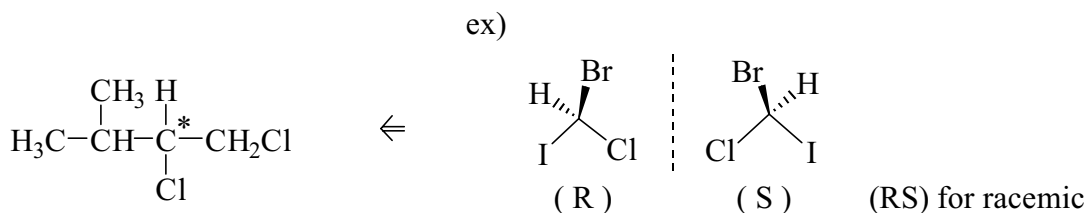
no interconversion



( X-ray analysis )  $\Rightarrow$  how to specify configuration

( derivatization )  $\Rightarrow$

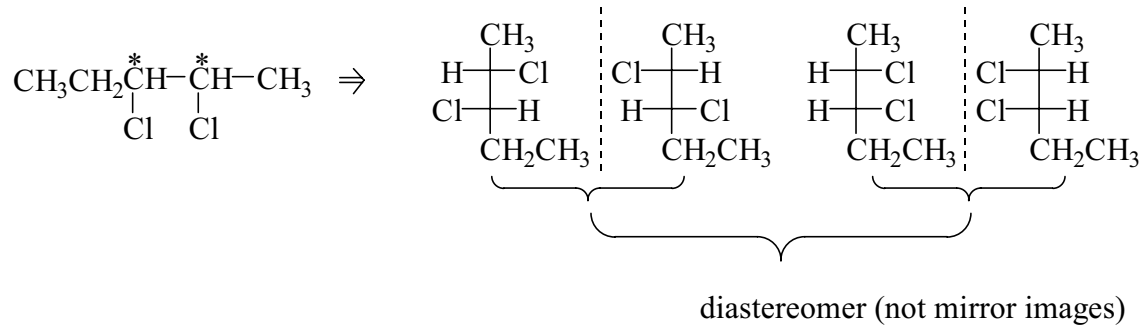
- $\Downarrow$
- 1) assign a sequence of priority
  - 2) R ; clockwise
  - S ; counterclockwise



compounds containing more than one chiral center

(not superimposable) enantiomers

(not superimposable) enantiomers



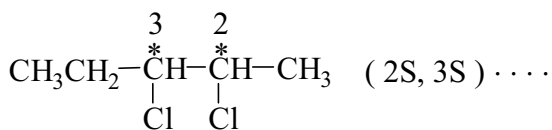
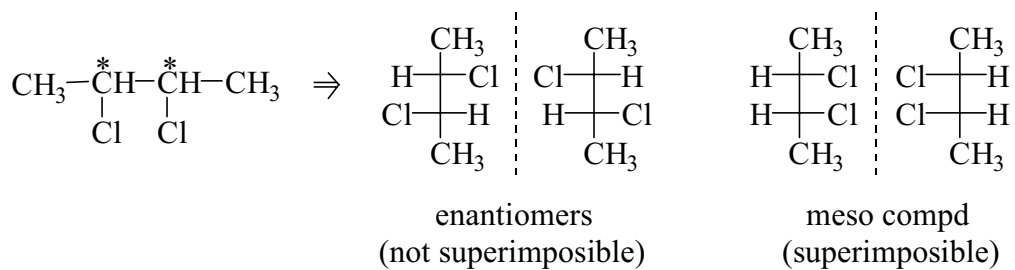
diastereomers ; different chemical & physical properties

↓

can be separated by usual methods

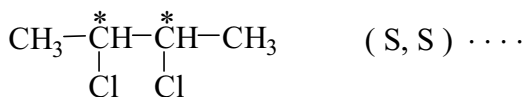
↓

4 possible stereoisomers  $\Rightarrow$  for n chiral centers  $\rightarrow 2^n$  possible isomers



↓

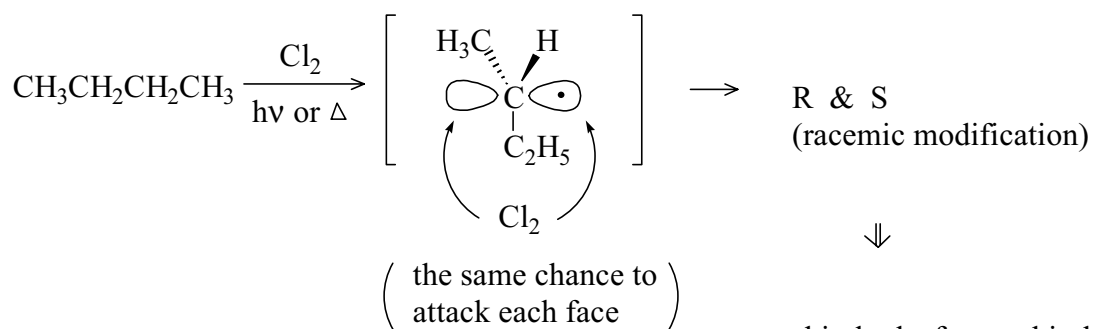
optically inactive



↓

have a plane of symmetry

$\left\{ \begin{array}{l} \text{conformational isomer (conformer)} \\ \text{configurational isomer (inversional isomer)} \end{array} \right. \Rightarrow$ 
 examine superimposability & interconvertibility



⇓

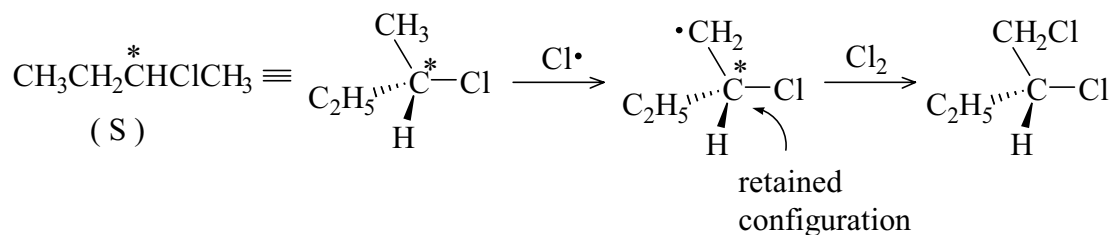
chiral pdts from achiral reactants are racemic modification

⇓

inseparable by usual methods

⇐

optically inactive reactants give optically inactive products



X-ray diffraction can determine the configuration of a particular enantiomer

⇒

time-consuming  
applied only to certain compds

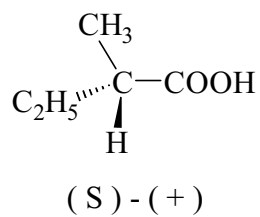
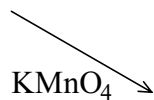
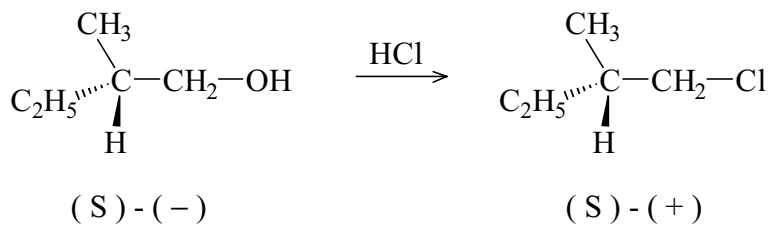
⇓

the chemical conversion should not involve the chiral center.

⇐

use chemical conversion of a compd with the known configuration to the compd to be examined.

ex)



specific rotation

pure (S) - (-)-2-methyl-1-butanol

-5.90

↓

(S) -1-chloro-2-methylbutane

+1.67

→

dextrorotatory  
optically pure

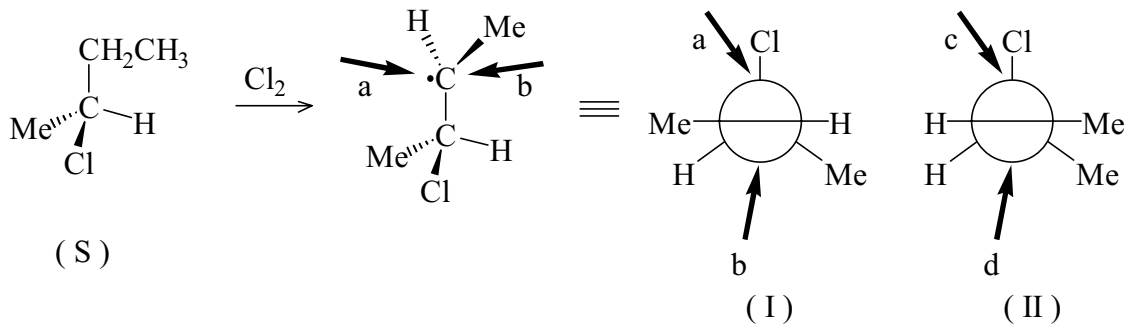
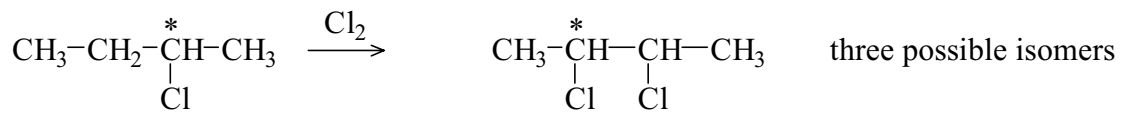
↓

+0.835 : have 50% optical purity

↓

75% (S) - (+)

25% (R) - (-)



1) the configuration of the original chiral center is retained.

2) attack from a, d  $\rightarrow$  (S, S)  
 attack from b, c  $\rightarrow$  (R, S or meso)

3) attacking chances are different

conformation (I)  $\rightarrow$  b is favored  
 conformation (II)  $\rightarrow$  d is favored

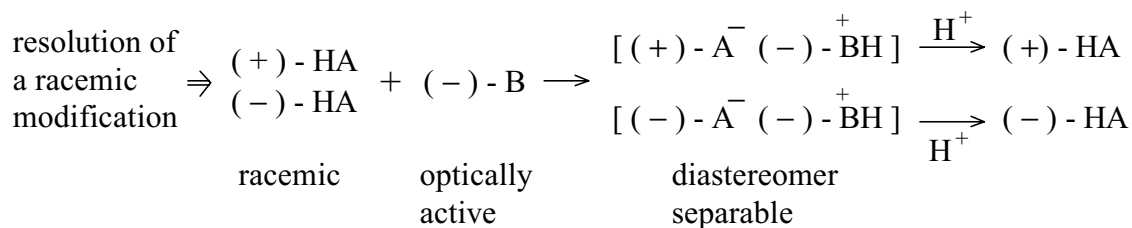
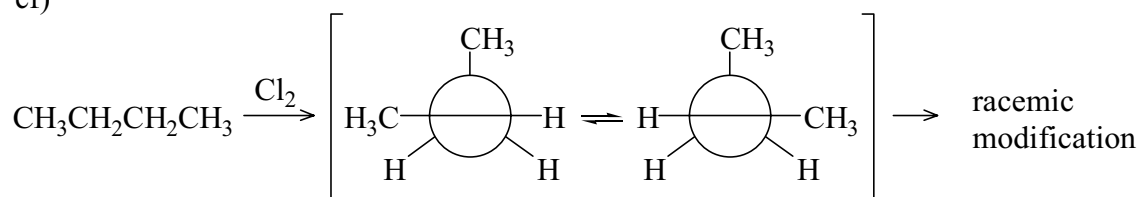
4) conformation (I) is favored over (II)

5) (S, S) / (R, S) = 29 / 71

6) from (R)-isomer of sec-butyl chloride (R, R) / (R, S) = 29/71

7) racemic sec-butyl chloride  $\Rightarrow$  optically inactive pds

cf)



What is the stereochemistry of rxns in which the bonds to the chiral center are broken?  $\Rightarrow$  depends on the mechanism

ex) for halogenation, two possible mechanisms

racemization is not likely with optically active RH

