

SLE155 Chemistry for the Professional Sciences

Burwood and Geelong



Class 7

Unsaturated Hydrocarbons

Alkenes

Alkynes

Arenes

Reactions of hydrocarbons

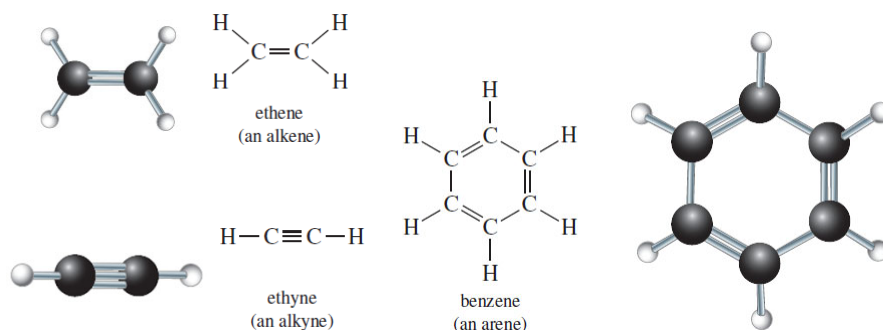
Stereochemistry

References

Blackman A, Bottle S, Schmid G, Mocerino M and Wille U (2019a), *Chemistry*, 4th edn, John Wiley & Sons, Milton, Qld.

Blackman A, Southam D, Lawrie G, Williamson N, Thompson C and Bridgeman A (2019b), *Chemistry: core concepts*, 2nd edn, John Wiley & Sons, Milton, Qld.

Unsaturated hydrocarbons



Source:
Blackman et al.
(2019:817).

Alkenes and Alkynes

Alkenes

1 or more carbon-carbon double bonds
bond angles around each carbon atom of the double bond $\sim 120^\circ$

Alkynes

1 or more carbon-carbon triple bonds
bond angles around each carbon atom in triple bond $\sim 180^\circ$

Alkenes and Alkynes

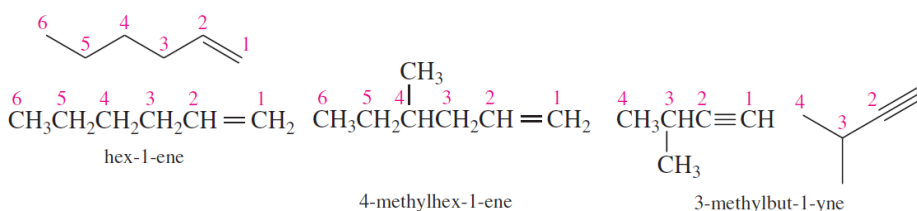
IUPAC nomenclature

alkenes end in *-ene*

alkynes end in *-yne*

Branched alkene or alkyne

number the longest C chain such that the multiple bond has the lowest set of numbers



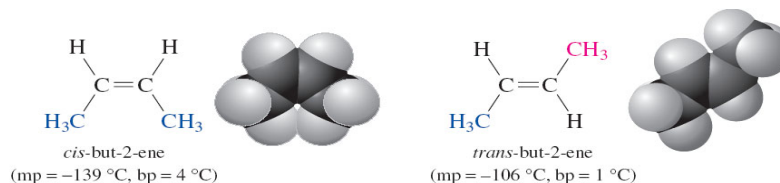
Alkenes and Alkynes

Configurational *cis-trans* isomerism

Restricted rotation about carbon-carbon double bond leads to different compounds with different physical and chemical properties.

cis isomers: 'same side' of the double bond.

trans isomers: 'opposite sides' of the double bond.



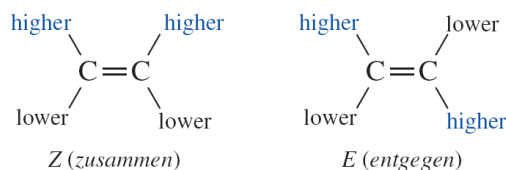
Alkenes and Alkynes

E, Z system

assigns priorities to the substituents on each side of the carbon-carbon double bond

Z configuration if higher priority groups are on the **same** side

E configuration if higher priority groups are on **opposite** sides



Sequence rules for assigning priorities to the four substituents on the carbon-carbon double bond

Assign priorities in **decreasing order of atomic number**.

If the higher priority groups are on the same side of the double bond, the alkene is **Z** (*zusammen*).

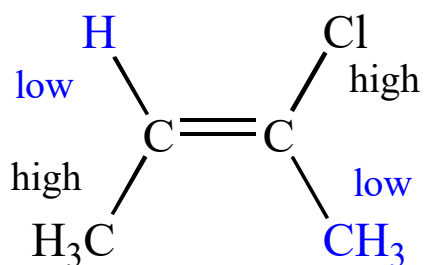
Sequence rules for assigning priorities to the four substituents on the carbon-carbon double bond

Assign priorities in **decreasing order of atomic number**.

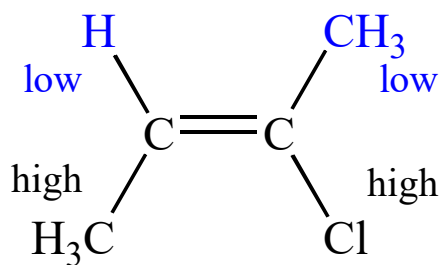
If the higher priority groups are on the opposite side of the double bond, the alkene is **E** (*entgegen*).

Stereochemistry

E, Z designation

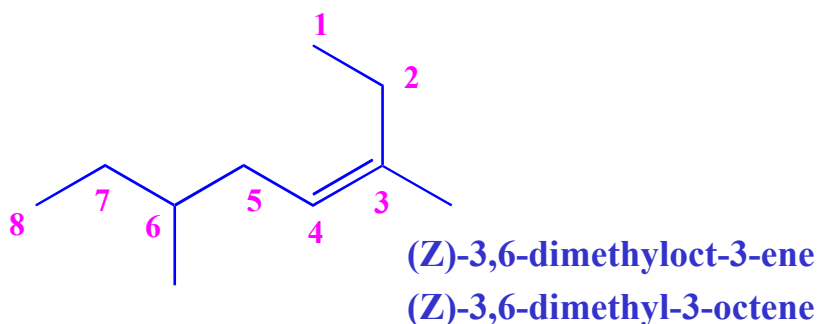


(E)-2-chlorobut-2-ene



(Z)-2-chlorobut-2-ene

Name the following compound



The ethyl group at C3 is higher priority than the methyl group at C3

The alkyl group at C4 is higher priority than the H atom at C4

Configuration is **Z**

Alkenes and Alkynes

Dienes, trienes and polyenes

alkadienes have 2 C=C double bonds

alkatrienes have 3 C=C double bonds

polyenes have multiple C=C double bonds

n carbon-carbon double bonds:

maximum 2^n *cis-trans* isomers possible

Physical properties of alkenes/alkynes

non-polar compounds

dispersion forces (only attractive forces)

physical properties similar to alkanes

Reactions of alkanes

Alkanes undergo **combustion** by reacting with oxygen to produce carbon dioxide, water, and energy.

Alkanes are not very reactive due to strong C-C single bonds.



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Reactions of alkanes

Halogenation – a substitution reaction

When alkanes react with halogens,

- The reaction is called **substitution**, one or more H atoms are replaced with a halogen usually Cl or Br.
- Light or heat is required.
- A mixture of halogenated products results, but we write the equation with the monosubstituted product.

Example: ethane and chlorine

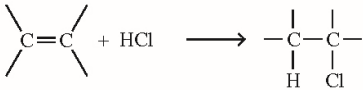
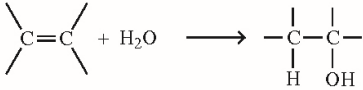
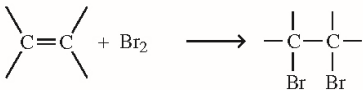
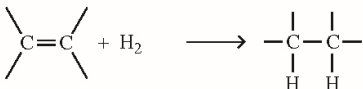


Organic Chemistry

Types of Reagents

- **Nucleophile** - an electron rich reagent that can donate an electron pair to another species in a reaction.
- **Electrophile** - an electron poor reagent that can accept an electron pair from another species in a reaction.
- **Radical** - a species that contains an odd number of electrons.

Reactions of alkenes

Reaction	Descriptive name(s)
	hydrochlorination (an example of hydrohalogenation)
	hydration
	bromination (an example of halogenation)
	hydrogenation (reduction)

Source: Blackman et al.
(2019:847).

Reactions of alkenes

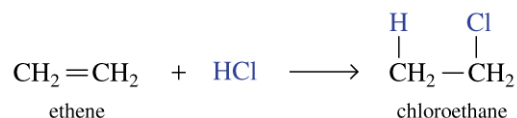
Electrophilic addition reactions

hydrohalogenation

addition of HCl, HBr or HI to alkene

addition obeys Markovnikov's rule

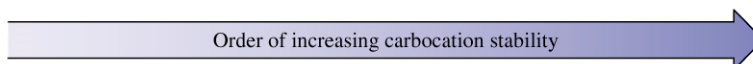
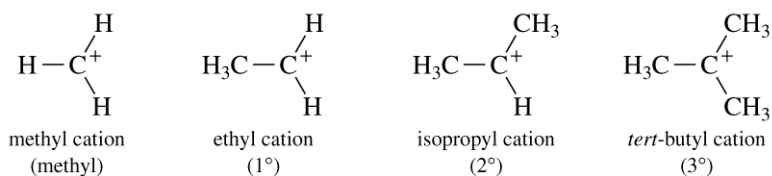
hydrogen adds to carbon with most hydrogens so that reaction proceeds via the most stable carbocation intermediate



Reactions of alkenes

Electrophilic addition reactions

Stability of carbocations



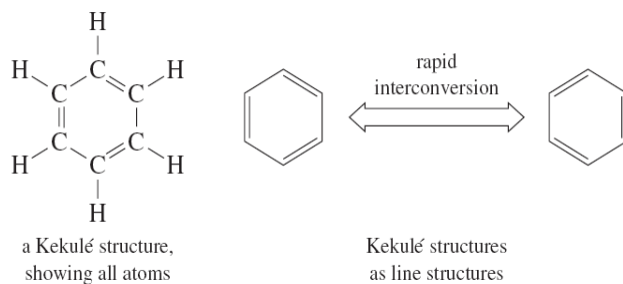
Source: Blackman
et al. (2019:854).

Aromatic compounds

Benzene

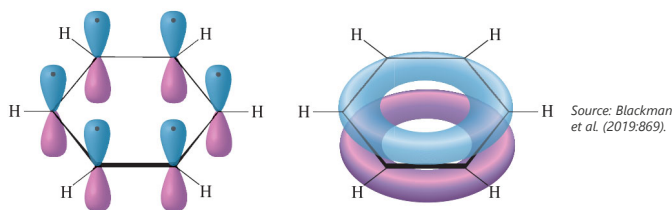
aromatic, parent **arene**, highly unsaturated
does not undergo addition, oxidation or reduction,
reacts by substitution

Kekulé's model of benzene

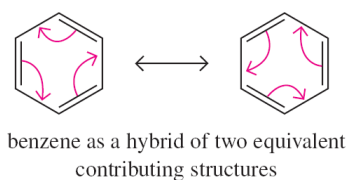


Aromatic compounds

Orbital overlap model

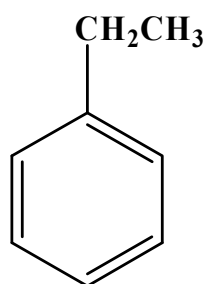


Resonance

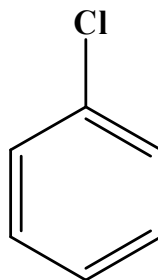


Naming aromatic compounds

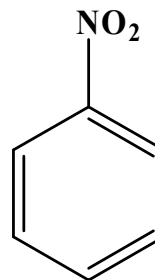
'substituent name' followed by 'benzene'



ethylbenzene



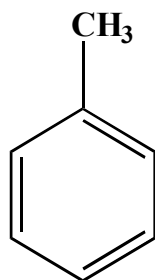
chlorobenzene



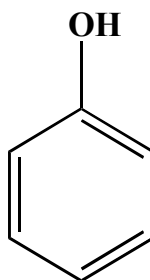
nitrobenzene

Naming aromatic compounds

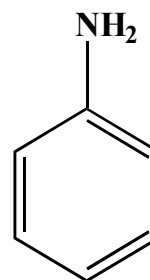
Some aromatic compounds have non-systematic names allowed by IUPAC. **You must use them!**



methylbenzene
(toluene)



hydroxybenzene
(phenol)

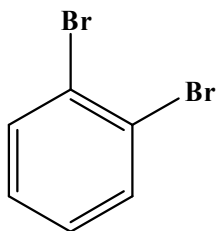


aminobenzene
(aniline)

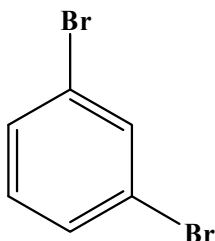
Naming aromatic compounds

when there is >1 substituent, numbers are used to specify their relative position

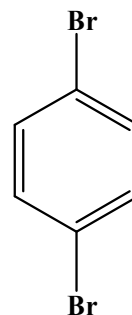
ortho-, *meta-* and *para-* may be used in place of numbers for disubstituted benzenes



1,2-dibromobenzene
ortho-dibromobenzene



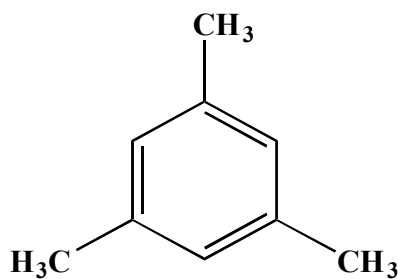
1,3-dibromobenzene
meta-dibromobenzene



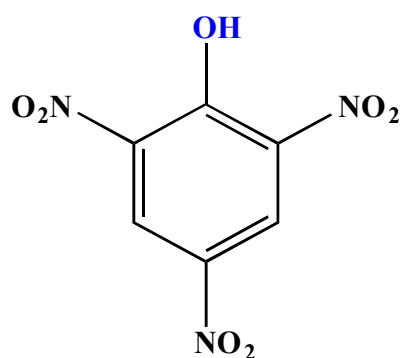
1,4-dibromobenzene
para-dibromobenzene

Naming aromatic compounds

when there are >2 substituents, numbers must be used to specify their relative positions



1,3,5-trimethylbenzene



2,4,6-trinitrophenol

Reactions of aromatic compounds

In a **substitution** reaction, a hydrogen atom on a benzene ring is replaced by an atom or group of atoms.

Type of substitution **H on benzene replaced by**

Halogenation

chlorine or bromine atom

Nitration

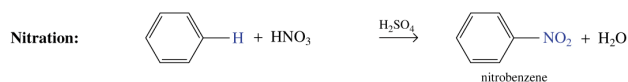
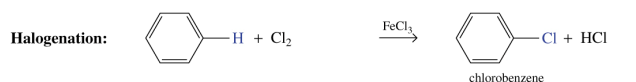
nitro group ($-\text{NO}_2$)

Sulfonation

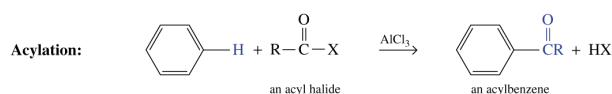
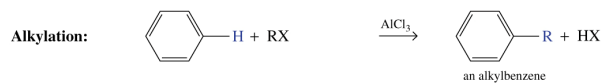
$-\text{SO}_3\text{H}$ group



Reactions of aromatic compounds



Source:
Blackman et al.
(2019a:1013).



Organic Chemistry

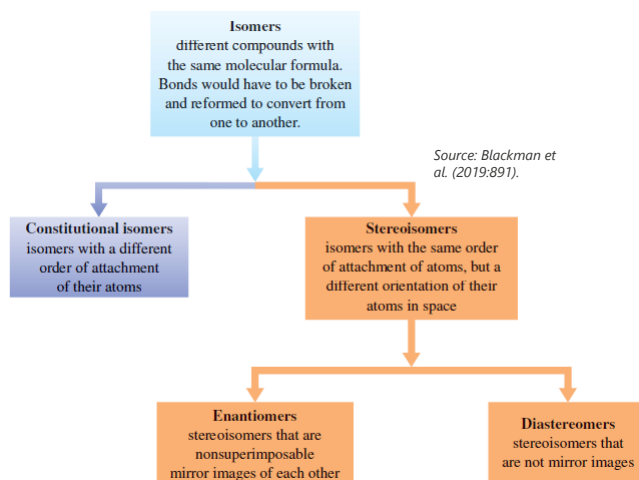
Stereochemistry

Isomers

- **Isomers are molecules with the same formula but different structures.**

ISOMERS

Same molecular formula, different structures or configuration



Organic Chemistry

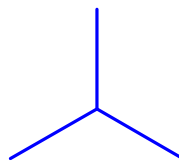
Stereochemistry

Isomers

- **Constitutional** isomers differ in the order in which their atoms are bonded.



$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
butane



$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$
2-methylpropane

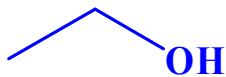
Same family, they are both alkanes

Organic Chemistry

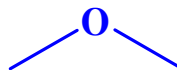
Stereochemistry

Isomers

- **Constitutional** isomers differ in the order in which their atoms are bonded.



$\text{CH}_3\text{CH}_2\text{OH}$ ethanol
(an alcohol)



CH_3OCH_3 methoxymethane
(an ether)

Different families

Organic Chemistry

Stereochemistry

Isomers

- **Constitutional** isomers differ in the order in which their atoms are bonded, and
- have different physical properties.
- Their chemical properties will be different if they are from different families.

Organic Chemistry

Stereochemistry

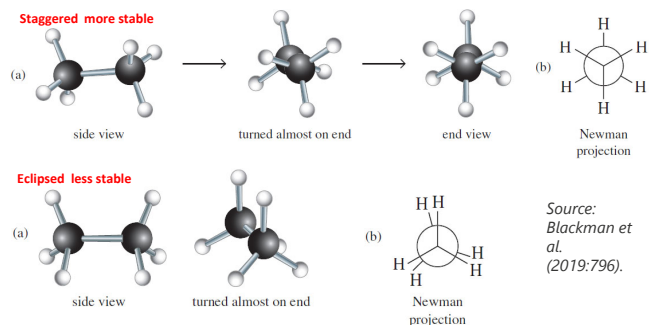
Conformers

- Change from one **conformation** to another involves rotations about a single bond.

Organic Chemistry

Stereochemistry

Conformers



Organic Chemistry

Stereochemistry

Isomers

- Change from one **conformation** to another involves rotations about a single bond.
- Change from one **configuration** to another involves breaking and making of bonds.
- **Stereoisomers** have the same structure but different arrangement in space of atoms (different configurations).

Organic Chemistry

Stereochemistry

Isomers

- **Stereoisomers** have the same structure but different arrangement in space of atoms (different configurations).

Organic Chemistry

Stereochemistry

Isomers

- Two types of stereoisomers are **optical** and **geometrical**.

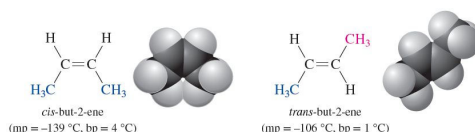
Organic Chemistry

Stereochemistry

Geometrical Isomers

cis-trans isomerism

Restricted rotation about C to C double bond leads to different compounds with different properties.



cis isomers: 'same side' of the double bond.

trans isomers: 'opposite sides' of the double bond.



Organic Chemistry

Stereochemistry

Isomers

- An object that is not superimposable on its mirror image is said to be **chiral**.
- **Chirality** in organic molecules is caused by the presence of a **tetrahedral** carbon atom that is bonded to four different groups.



Organic Chemistry

Stereochemistry

Isomers

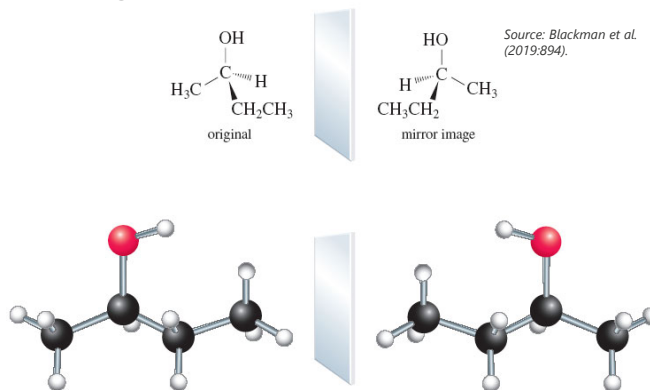
- **Chirality** in organic molecules is usually caused by the presence of a **tetrahedral** carbon atom that is bonded to four different groups.
- Such a carbon atom is described as a **chiral carbon** or **stereocentre**.

Organic Chemistry

Stereochemistry

Enantiomers

Stereoisomers that are non-superimposable mirror images.



Organic Chemistry

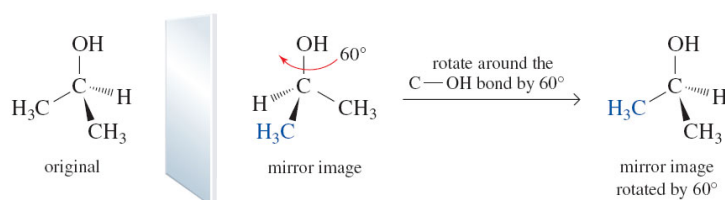
Stereochemistry

Achiral molecules

Central carbon bears 2 or more groups which are the same, e.g., 2-propanol.

Mirror image is superimposable on the original.

The molecule and its mirror image are identical, **achiral** (without chirality).



Organic Chemistry

Stereochemistry

Stereocentres or stereogenic centres

A carbon atom with 4 different groups bonded to it is the most common cause of enantiomerism in organic molecules.

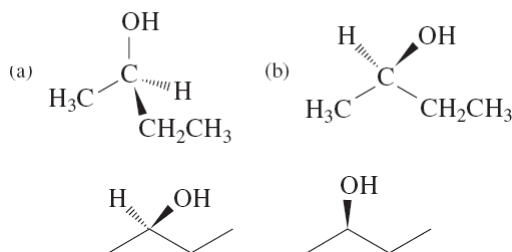
Organic Chemistry

Stereochemistry

Representing enantiomers

Keep carbon framework in the plane of the paper.

One atom coming out of the plane and the other atom behind the plane, e. g., one enantiomer of **2-butanol**.



Organic Chemistry

Stereochemistry

Isomers

- The **absolute configuration** of a stereogenic centre refers to the exact three-dimensional arrangement of the groups.
- The method for naming enantiomers is called the **Cahn-Ingold-Prelog** convention.

Organic Chemistry

Stereochemistry

Isomers

- **This is based on describing the relative positions of the substituents attached to the stereogenic centre.**

Organic Chemistry

Stereochemistry

Isomers

- **A set of rules is used to establish the stereochemical configuration of stereogenic carbon centres:**

Sequence rules for assigning priorities to the four substituents on the chiral carbon

①

Look at the four atoms directly attached to the stereogenic centre.

Assign priorities in **decreasing order of atomic number** (number of protons).

Designate these groups **high, medium, low and lowest**.

Sequence rules for assigning priorities to the four substituents on the chiral carbon

②

If the priorities cannot be determined by rule 1:

Compare the atomic numbers of the **second** atoms away from the stereogenic centre.

Continue if necessary to the third and fourth atoms until some difference is noted.

Sequence rules for assigning priorities to the four substituents on the chiral carbon

3

Multiply bonded atoms are considered to be an equivalent number of singly bonded atoms.

Sequence rules for assigning priorities to the four substituents on the chiral carbon

Mentally orientate the molecule so that the lowest priority group is pointing away from you.

If a curved arrow drawn from high to medium to low is **clockwise**, the configuration at the stereogenic centre is **R** (*rectus*, right).

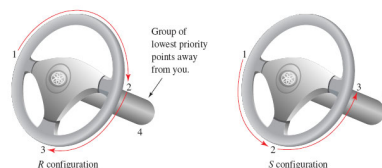
If it is **anticlockwise**, the configuration is **S** (*sinister*, left).

Organic Chemistry

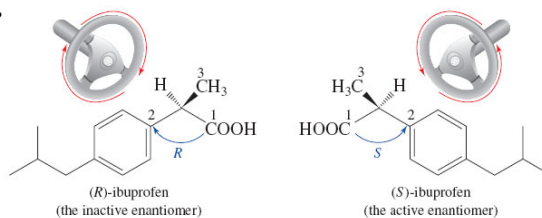
Stereochemistry

R configuration: groups are in a clockwise direction.

Source: Blackman et al.
(2019a:1053).



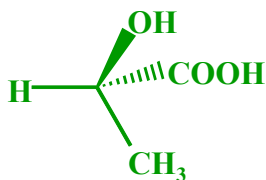
S configuration: groups are in an anti-clockwise direction.



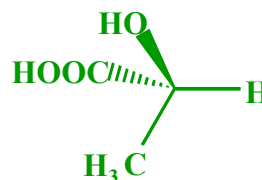
Organic Chemistry

Stereochemistry

Isomers



(-) lactic acid
found in sour milk



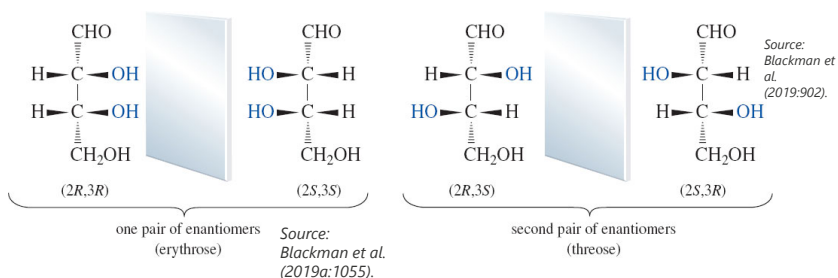
(+) lactic acid
produced by muscle
tissue in humans

Organic Chemistry

Stereochemistry

For a molecule with n stereocentres, maximum number of stereoisomers is 2^n .

e.g. 2,3,4-trihydroxybutanal has 4 stereoisomers.

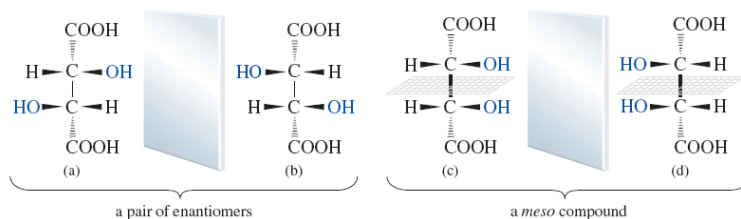


(a) and (c) are called **diastereomers** which are stereoisomers that are NOT mirror images.

Organic Chemistry

Stereochemistry

Meso compound: an achiral compound with 2 or more stereocentres, e.g. tartaric acid.



(a) and (b) are enantiomers.

(c) and (d) are superimposable mirror images and therefore achiral (as same molecule).

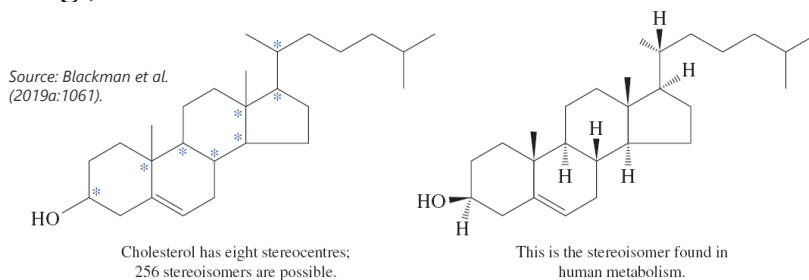
Stereoisomer represented by (c) or (d) is called a **meso compound**.

Organic Chemistry

Stereochemistry

Molecules with 3 or more stereocentres

e.g., cholesterol has 8 stereocentres.

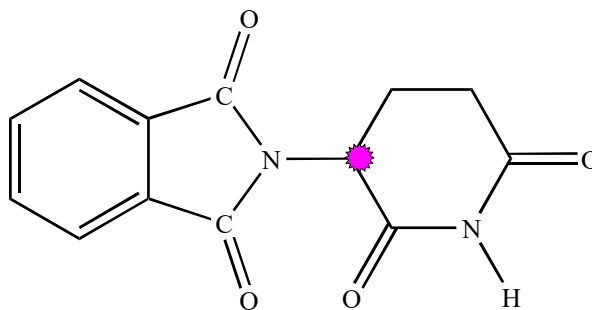


$2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 = 2^8$ stereoisomers are possible.

Organic Chemistry

Stereochemistry

Isomers



thalidomide has a chiral carbon

Organic Chemistry

Stereochemistry

Isomers

- Thalidomide has a chiral carbon.
- The (-) enantiomer has **teratogenic** properties.
- The (+) isomer has a **hypnotic** action.

Organic Chemistry

Stereochemistry

Almost all molecules in living systems (both plant and animal) are chiral.

Although chiral molecules can exist as a number of stereoisomers, almost invariably, only **one** stereoisomer is found in nature.

The enzyme **chymotrypsin** has 251 stereocentres but only 1 of its stereoisomers is produced and used by any given organism.

Organic Chemistry

Stereochemistry

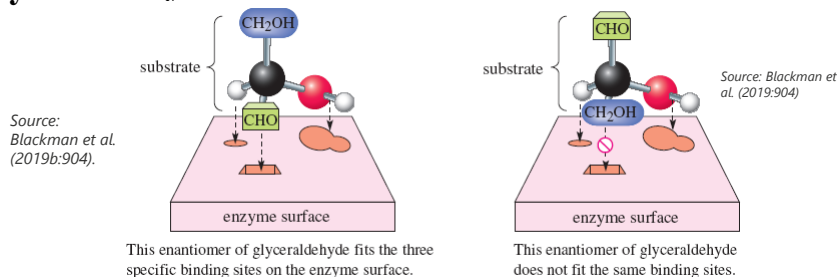
Enzymes are chiral substances which only produce or react with substances that match their stereochemical requirements.

For an enzyme to catalyse a biological reaction, the molecule involved must fit into enzyme's chiral binding site.

Organic Chemistry

Stereochemistry

e. g., enzyme that catalyses reaction by glyceraldehyde.



Enzyme can distinguish between different enantiomers of glyceraldehyde!

Summary

Carbon – hydrogen frameworks

alkanes, cycloalkanes, alkenes, alkynes, arenes

Nonpolar compounds with dispersion forces

Isomers have different properties

Stereoisomers differ in 3-D orientation of their atoms in spaces and are particularly important in the biological world and synthesising drugs

Chiral objects are nonsuperimposable on their mirror images

Enantiomers differ in their optical activity

Stereocentres are named using the *R,S* system