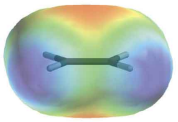
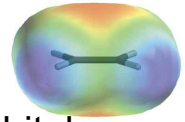


Structure of Alkenes



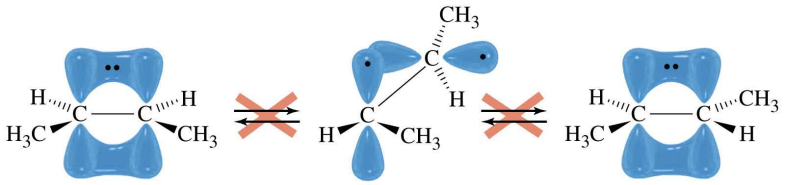
Functional Group

- Pi bond is the functional group.
- More reactive than sigma bond.
- Sigma bonds around C are sp^2 hybridized.
- Angles are approximately 120 degrees.
- Molecule is planar around the double bond.
- Pi bond is formed by the sideways overlap of parallel *p* orbitals perpendicular to the plane of the molecule.

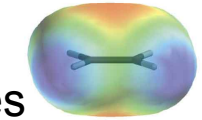


Pi Bond

- Sideways overlap of parallel *p* orbitals.
- No rotation is possible without breaking the pi bond (63 kcal/mole).
- Cis isomer cannot become trans without a chemical reaction occurring.



=>

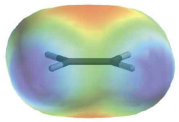


IUPAC Nomenclature Alkenes

- Parent is longest chain containing the double bond.
- -ane changes to -ene. (or -diene, -triene)
- Number the chain so that the double bond has the lowest possible number.
- In a ring, the double bond is assumed to be between carbon 1 and carbon 2.

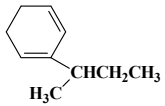
=>

Name These Alkenes

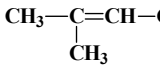


$CH_2{=}CH{-}CH_2{-}CH_3$

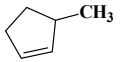
1-butene



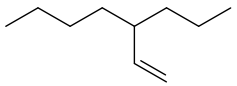
2-*sec*-butyl-1,3-cyclohexadiene



2-methyl-2-butene



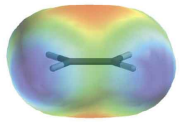
3-methylcyclopentene



3-*n*-propyl-1-heptene

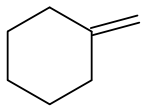
=>

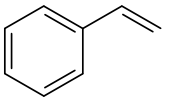
Alkene Substituents



$= CH_2$	$- CH = CH_2$	$- CH_2 - CH = CH_2$
methylene (methylidene)	vinyl (ethenyl)	allyl (2-propenyl)

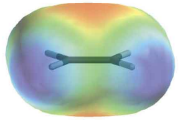
Name:





=>

Common Names



- Usually used for small molecules.
- Examples:

$CH_2{=}CH_2$

ethylene

$CH_2{=}CH{-}CH_3$

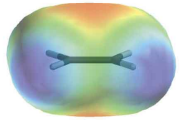
propylene

$CH_2{=}C(CH_3){-}CH_3$

isobutylene

=>

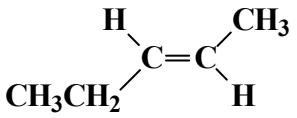
Cis-trans Isomerism



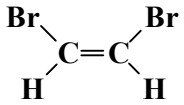
- Similar groups on same side of double bond, alkene is cis.
- Similar groups on opposite sides of double bond, alkene is trans.
- Cycloalkenes are assumed to be cis.
- Trans cycloalkenes are not stable unless the ring has at least 8 carbons.

=>

Name these:



***trans*-2-pentene**



***cis*-1,2-dibromoethene**

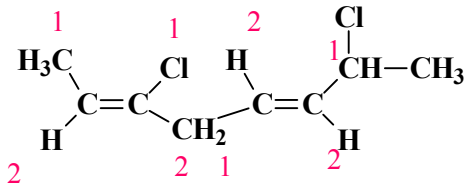
=>

E-Z Nomenclature

- Use the Cahn-Ingold-Prelog rules to assign priorities to groups attached to each carbon in the double bond.
- If high priority groups are on the same side, the name is *Z* (for *zusammen*).
- If high priority groups are on opposite sides, the name is *E* (for *entgegen*).

=>

Example, *E-Z*



2*Z* **5*E***

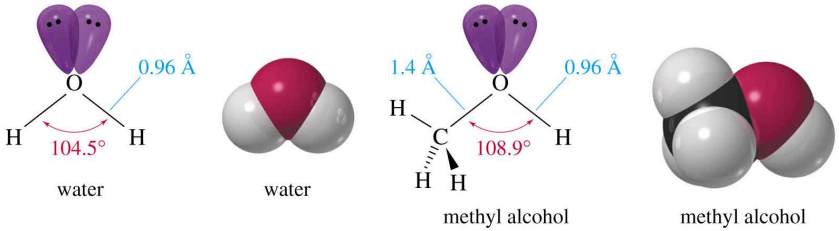
(2*Z*, 5*E*)-3,7-dichloro-2,5-octadiene

=>

Structure of Alcohols

Structure of Alcohols





- Hydroxyl (OH) functional group
- Oxygen is *sp*^{3} hybridized.

=>

Classification

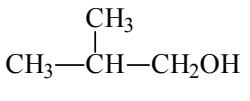


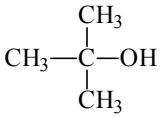
- Primary: carbon with –OH is bonded to one other carbon.
- Secondary: carbon with –OH is bonded to two other carbons.
- Tertiary: carbon with –OH is bonded to three other carbons.
- Aromatic (phenol): -OH is bonded to a benzene ring.

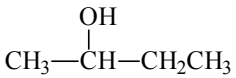
=>

Classify these:



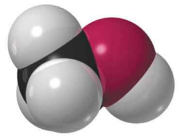






=>

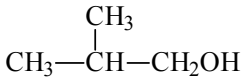
IUPAC Nomenclature



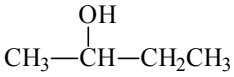
- Find the longest carbon chain containing the carbon with the -OH group.
- Drop the -e from the alkane name, add -ol.
- Number the chain, starting from the end closest to the -OH group.
- Number and name all substituents. =>

Name these:

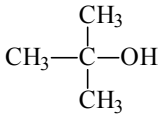




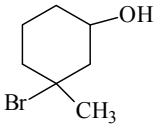
2-methyl-1-propanol



2-butanol



2-methyl-2-propanol



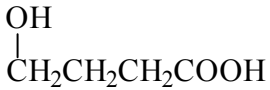
3-bromo-3-methylcyclohexanol

=>

Hydroxy Substituent



- When -OH is part of a higher priority class of compound, it is named as hydroxy.
- Example:



4-hydroxybutanoic acid

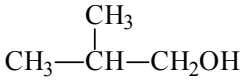
also known as GHB

=>

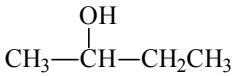
Common Names



- Alcohol can be named as alkyl alcohol.
- Useful only for small alkyl groups.
- Examples:



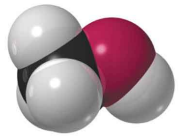
isobutyl alcohol



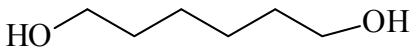
sec-butyl alcohol

=>

Naming Diols



- Two numbers are needed to locate the two -OH groups.
- Use -diol as suffix instead of -ol.



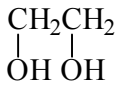
1,6-hexanediol

=>

Glycols

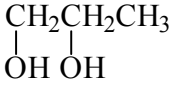


- 1, 2 diols (vicinal diols) are called glycols.
- Common names for glycols use the name of the alkene from which they were made.



1,2-ethanediol

ethylene glycol



1,2-propanediol

propylene glycol

=>

Physical Properties

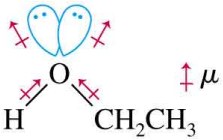


- Unusually high boiling points due to hydrogen bonding between molecules.
- Small alcohols are miscible in water, but solubility decreases as the size of the alkyl group increases.

=>

Boiling Points

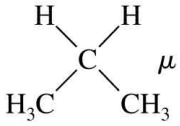




$\mu = 1.69$ D

ethanol, MW 46

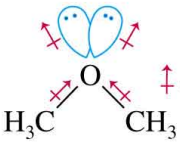
bp 78°C



$\mu = 0.08$ D

propane, MW 44

bp −42°C



$\mu = 1.30$ D

dimethyl ether, MW 46

bp −25°C

=>

Solubility in Water

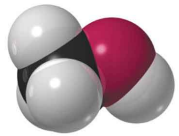
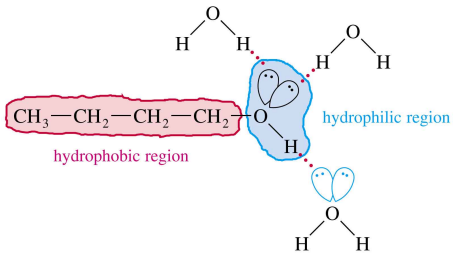


TABLE 10-2 Water Solubility of Alcohols (at 25°C)

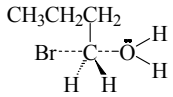
Alcohol	*Solubility in Water*
methyl	miscible
ethyl	miscible
n-propyl	miscible
t-butyl	miscible
isobutyl	10.0%
n-butyl	9.1%
n-pentyl	2.7%
cyclohexyl	3.6%
n-hexyl	0.6%
phenol	9.3%
hexane-1,6-diol	miscible



Solubility decreases as the size of the alkyl group increases.

=>

Biological Oxidation



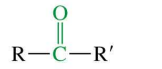
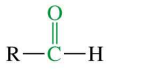
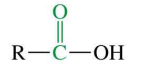
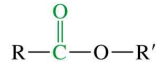
- Catalyzed by ADH, alcohol dehydrogenase.
- Oxidizing agent is NAD^+, nicotinamide adenine dinucleotide.
- Ethanol oxidizes to acetaldehyde, then acetic acid, a normal metabolite.
- Methanol oxidizes to formaldehyde, then formic acid, more toxic than methanol.
- Ethylene glycol oxidizes to oxalic acid, toxic.
- Treatment for poisoning is excess ethanol.

=>

Ketones and Aldehydes

Carbonyl Compounds

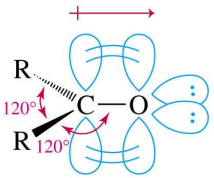
TABLE 18-1 Some Common Classes of Carbonyl Compounds

Class	General Formula	Class	General Formula
ketones		aldehydes	
carboxylic acids		acid chlorides	
esters		amides	

=>

Carbonyl Structure

- Carbon is sp^2 hybridized.
- C=O bond is shorter, stronger, and more polar than C=C bond in alkenes.



	length	*energy*
ketone C═O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
alkene C═C bond	1.34 Å	146 kcal/mol (611 kJ/mol)

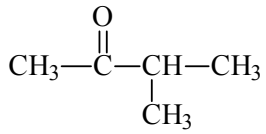
=>

IUPAC Names for Ketones

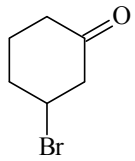
- Replace -*e* with -*one*. Indicate the position of the carbonyl with a number.
- Number the chain so that carbonyl carbon has the lowest number.
- For cyclic ketones the carbonyl carbon is assigned the number 1.

=>

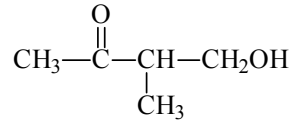
Examples



3-methyl-2-butanone



3-bromocyclohexanone



4-hydroxy-3-methyl-2-butanone

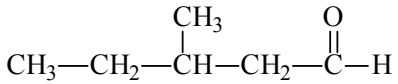
=>

Naming Aldehydes

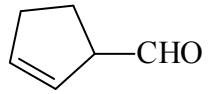
- IUPAC: Replace -*e* with -*al*.
- The aldehyde carbon is number 1.
- If -CHO is attached to a ring, use the suffix -*carbaldehyde*.

=>

Examples



3-methylpentanal

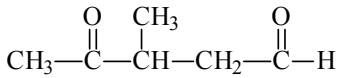


2-cyclopentenecarbaldehyde

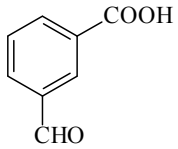
=>

Name as Substituent

- On a molecule with a higher priority functional group, C=O is *oxo*- and -CHO is *formyl.*
- Aldehyde priority is higher than ketone.



3-methyl-4-oxopentanal

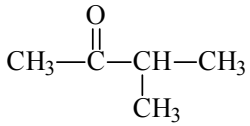


3-formylbenzoic acid

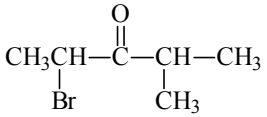
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Common Names for Ketones

- Named as alkyl attachments to -C=O.
- Use Greek letters instead of numbers.



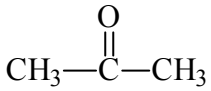
methyl isopropyl ketone



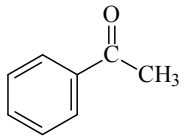
α–bromoethyl isopropyl ketone

=>

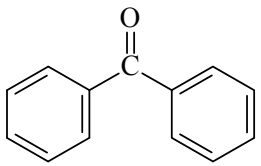
Historical Common Names



acetone



acetophenone



benzophenone

=>

Aldehyde Common Names

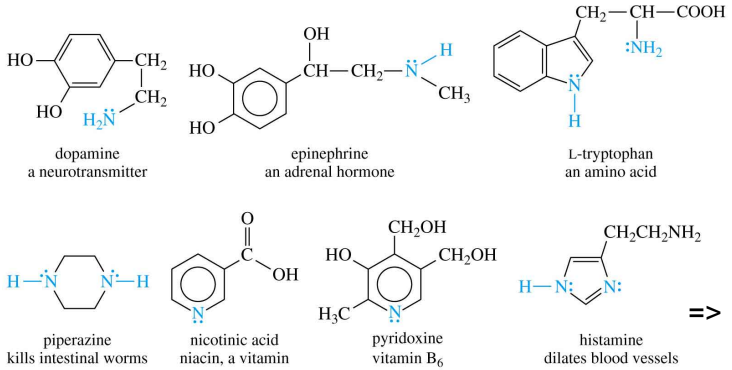
- Use the common name of the acid.
- Drop *-ic acid* and add *-aldehyde*.
  - 1 C: formic acid, formaldehyde
  - 2 C's: acetic acid, acetaldehyde
  - 3 C's: propionic acid, propionaldehyde
  - 4 C's: butyric acid, butyraldehyde.

=>

Amines

Introduction

- Organic derivatives of ammonia
- Many are biologically active.



=>

Biological Activity

- Neurotransmitters: dopamine
- Bioregulators: epinephrine
- Vitamins: niacin, B_6
- Alkaloids: nicotine, morphine, cocaine
- Amino acids

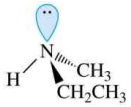
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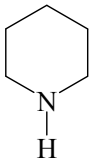
Classes of Amines

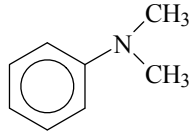
- Primary (1°): one C-N bond, 2 N-H bonds.
- Secondary (2°): two C-N bonds, 1 N-H bond.
- Tertiary (3°): three C-N bonds, no N-H bond.
- Quaternary (4°): four C-N bonds, nitrogen has a + formal charge.

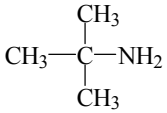
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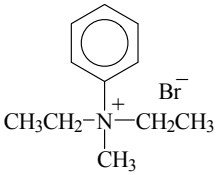
Classify:





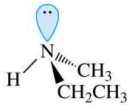




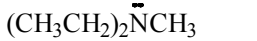


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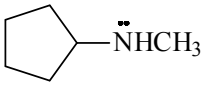
Common Names



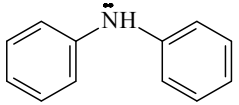
Name the alkyl or aryl groups bonded to nitrogen, then add suffix -*amine*.



diethylmethylamine



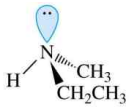
cyclopentylmethylamine



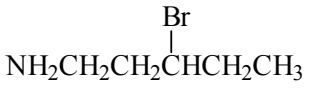
Diphenylamine

=>

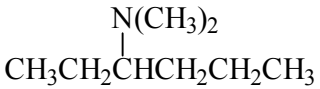
IUPAC Names



- Name is based on longest carbon chain.
- -*e* of alkane is replaced with -*amine*.
- Substituents on nitrogen have *N*- prefix.



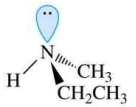
3-bromo-1-pentanamine



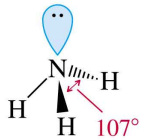
N,*N*-dimethyl-3-hexanamine

=>

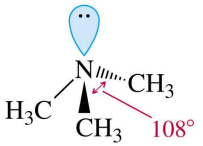
Structure of Amines



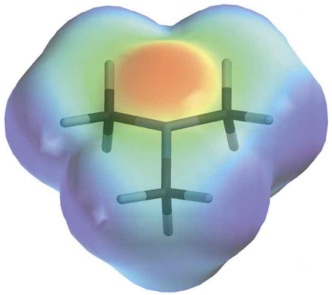
Nitrogen is sp^3 hybridized with a lone pair of electrons in an sp^3 orbital.



ammonia



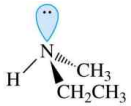
trimethylamine



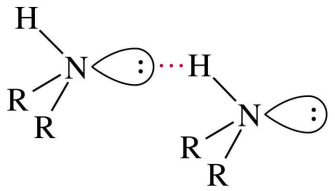
electrostatic potential map of trimethylamine

=>

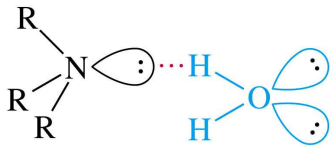
Boiling Points



- N-H less polar than O-H.
- Weaker hydrogen bonding.
- Tertiary amines cannot hydrogen bond.



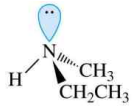
1° or 2° amine: hydrogen bond donor and acceptor



3° amine: hydrogen bond acceptor only

=>

Solubility and Odor



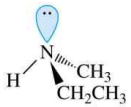
- Small amines (<6 C) soluble in water.
- All amines accept hydrogen bonds from water and alcohol.
- Branching increases solubility.
- Most amines smell like rotting fish.

$NH_2CH_2CH_2CH_2CH_2CH_2NH_2$

1,5-pentanediamine or cadaverine

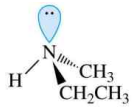
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Basicity of Amines

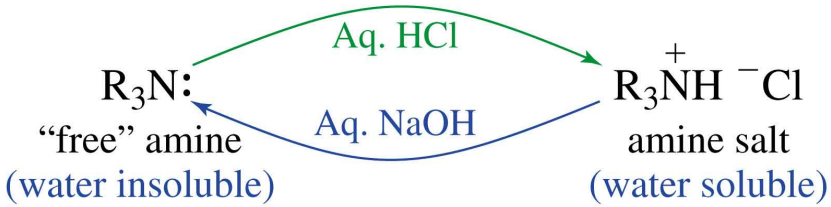


- Lone pair of electrons on nitrogen can accept a proton from an acid
- Aqueous solutions are basic to litmus.
- Ammonia pK_b = 4.74
- Alkyl amines are usually stronger bases than ammonia. Increasing the number of alkyl groups decreases solvation of ion, so 2° and 3° amines are similar to 1° amines in basicity. =>

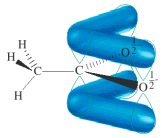
Amine Salts



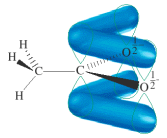
- Ionic solids with high melting points
- Soluble in water
- No fishy odor



=>



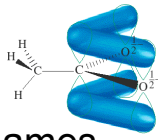
Carboxylic Acids



Introduction

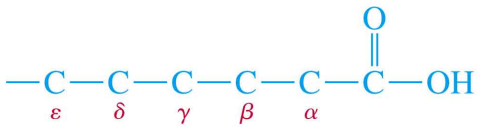
- The functional group of carboxylic acids consists of a C=O with -OH bonded to the same carbon.
- Carboxyl group is usually written -COOH.
- Aliphatic acids have an alkyl group bonded to -COOH.
- Fatty acids are long-chain aliphatic acids.

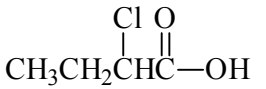
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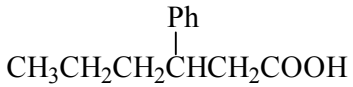
Common Names

- Many aliphatic acids have historical names.
- Positions of substituents on the chain are labeled with Greek letters.



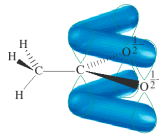


α-chlorobutyric acid



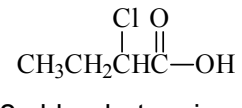
β-phenylcaproic acid

=>

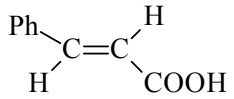


IUPAC Names

- Remove -*e* from alkane (or alkene) name, add -*oic acid*.
- The carbon of the carboxyl group is #1.



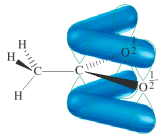
2-chlorobutanoic acid



trans-3-phenyl-2-propenoic acid (cinnamic acid)

=>

Dicarboxylic Acids



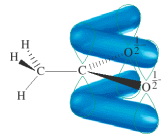
- Aliphatic diacids are usually called by their common names (to be memorized).
- For IUPAC name, number the chain from the end closest to a substituent.
- Two carboxyl groups on a benzene ring indicate a phthalic acid.



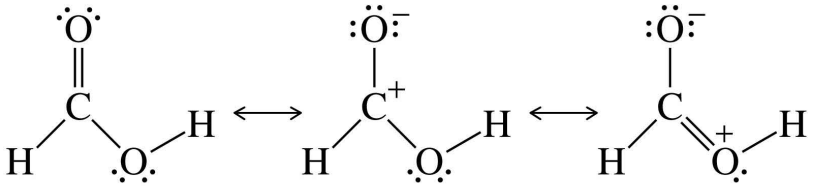
3-bromohexanedioic acid
β-bromoadipic acid

=>

Structure of Carboxyl

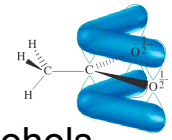


- Carbon is sp^2 hybridized.
- Bond angles are close to 120°.
- O-H eclipsed with C=O, to get overlap of π orbital with orbital of lone pair on oxygen.

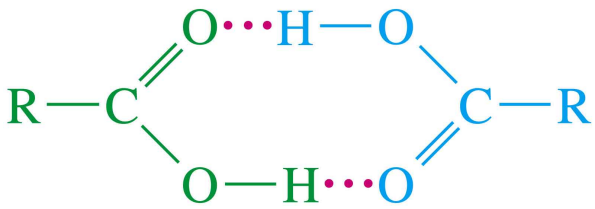


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Boiling Points



Higher boiling points than similar alcohols, due to dimer formation.

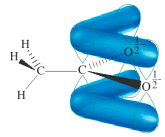


hydrogen-bonded acid dimer

Acetic acid, b.p. 118°C

=>

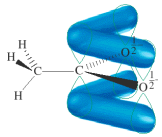
Solubility



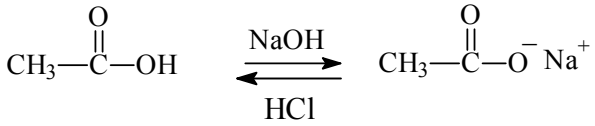
- Water solubility decreases with the length of the carbon chain.
- Up to 4 carbons, acid is miscible in water.
- More soluble in alcohol.
- Also soluble in relatively nonpolar solvents like chloroform because it dissolves as a dimer.

=>

Salts of Carboxylic Acids

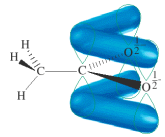


- Sodium hydroxide removes a proton to form the salt.
- Adding a strong acid, like HCl, regenerates the carboxylic acid.

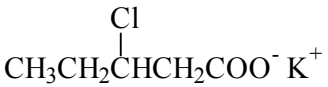


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Naming Acid Salts



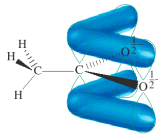
- Name the cation.
- Then name the anion by replacing the -ic acid with -ate.



potassium β-chlorovalerate
potassium 3-chloropentanoate

=>

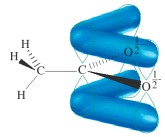
Properties of Acid Salts



- Usually solids with no odor.
- Carboxylate salts of Na^+, K^+, Li^+, and NH_4^+ are soluble in water.
- Soap is the soluble sodium salt of a long chain fatty acid.
- Salts can be formed by the reaction of an acid with $NaHCO_3$, releasing CO_2.

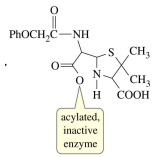
=>

Some Important Acids

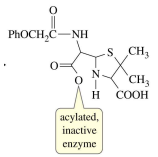


- Acetic acid is in vinegar and other foods, used industrially as solvent, catalyst, and reagent for synthesis.
- Fatty acids from fats and oils.
- Benzoic acid in drugs, preservatives.
- Adipic acid used to make nylon 66.
- Phthalic acid used to make polyesters.

=>

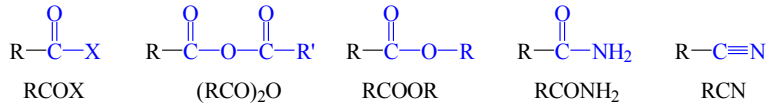


Carboxylic Acid Derivatives

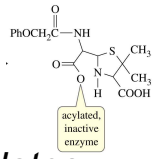


Acid Derivatives

- All can be converted to the carboxylic acid by acidic or basic hydrolysis.
- Esters and amides common in nature.

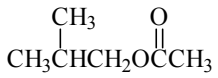


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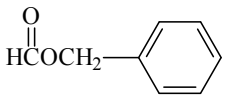


Naming Esters

- Esters are named as *alkyl carboxylates.*
- *Alkyl* from the alcohol, *carboxylate* from the carboxylic acid precursor.

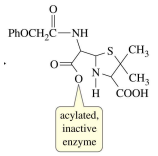


isobutyl acetate
2-methylpropyl ethanoate



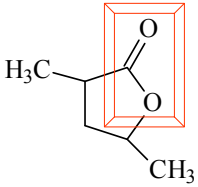
benzyl formate
benzyl methanoate

=>



Cyclic Esters

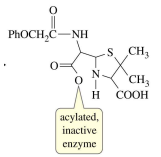
- Reaction of -OH and -COOH on same molecule produces a cyclic ester, lactone.
- To name, add word *lactone* to the IUPAC acid name or replace the *-ic acid* of common name with *-olactone*.



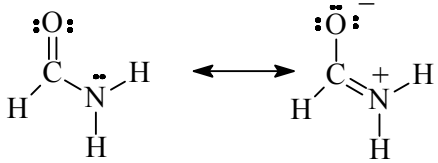
4-hydroxy-2-methylpentanoic acid lactone
α-methyl-γ-valerolactone

=>

Amides



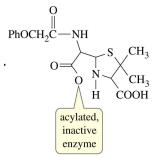
- Product of the reaction of a carboxylic acid and ammonia or an amine.
- Not basic because the lone pair on nitrogen is delocalized by resonance.



Bond angles around N are close to 120°.

=>

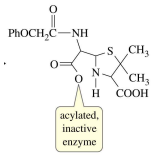
Classes of Amides



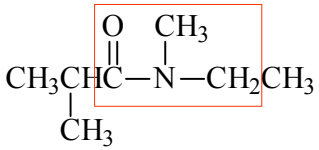
- 1° amide has one C-N bond (two N-H).
- 2° amide or *N*-substituted amide has two C-N bonds (one N-H).
- 3° amide or *N,N*-disubstituted amide has three C-N bonds (no N-H).

=>

Naming Amides



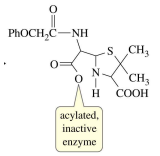
- For 1° amide, drop *-ic* or *-oic acid* from the carboxylic acid name, add *-amide*.
- For 2° and 3° amides, the alkyl groups bonded to nitrogen are named with *N-* to indicate their position.



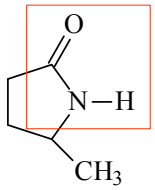
N-ethyl-*N*,2-dimethylpropanamide
N-ethyl-*N*-methylisobutyramide

=>

Cyclic Amides



- Reaction of -NH_2 and -COOH on same molecule produces a cyclic amide, lactam.
- To name, add word *lactam* to the IUPAC acid name or replace the *-ic acid* of common name with *-olactam*.



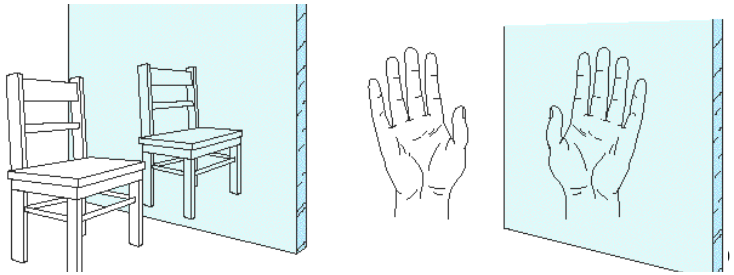
4-aminopentanoic acid lactam
γ-valerolactam

=>

Stereochemistry

Chirality

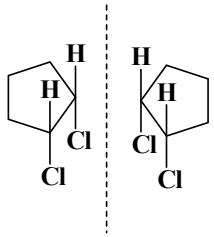
- "Handedness": right glove doesn't fit the left hand.
- Mirror-image object is different from the original object. =>



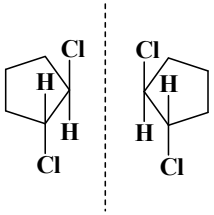
Stereoisomers

- Geometric isomers: cis-trans isomers.
- Enantiomers: nonsuperimposable mirror images, <u>different</u> molecules.

=>



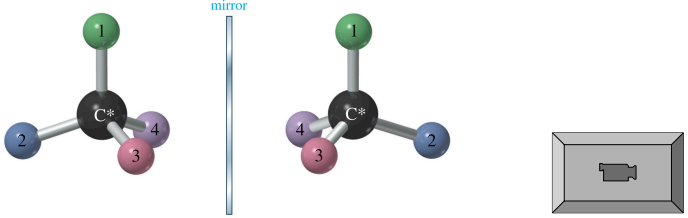
cis-1,2-dichlorocyclopentane



trans -1,2-dichlorocyclopentane

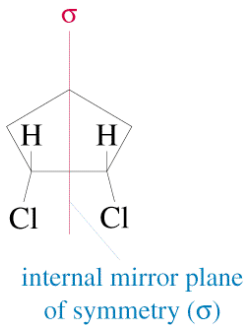
Chiral Carbons

- Tetrahedral carbons with 4 <u>different</u> attached groups are chiral.
- Its mirror image will be a different compound (enantiomer). =>

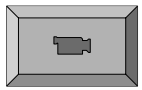


Mirror Planes of Symmetry

- **If two groups are the same, carbon is achiral. (animation)**
- **A molecule with an internal mirror plane <u>cannot</u> be chiral.***

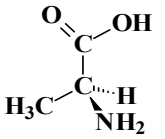


Caution! If there is no plane of symmetry, molecule may be chiral or achiral. See if mirror image can be superimposed. =>



(*R*), (*S*) Nomenclature

- Different molecules (enantiomers) must have different names.
- Usually only one enantiomer will be biologically active.
- Configuration around the chiral carbon is specified with (*R*) and (*S*).



natural alanin

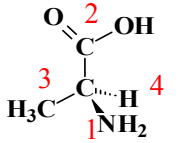
=>

Cahn-Ingold-Prelog Rules

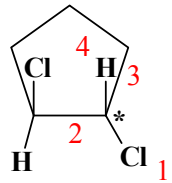
- Assign a priority number to each group attached to the chiral carbon.
- Atom with highest atomic number assigned the highest priority #1.
- In case of ties, look at the next atoms along the chain.
- Double and triple bonds are treated like bonds to duplicate atoms.

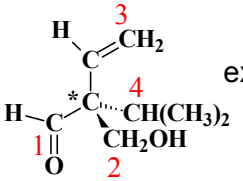
=>

Assign Priorities

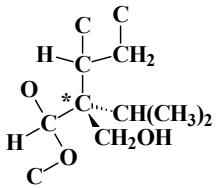


natural alanin



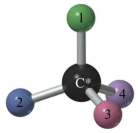


expands to



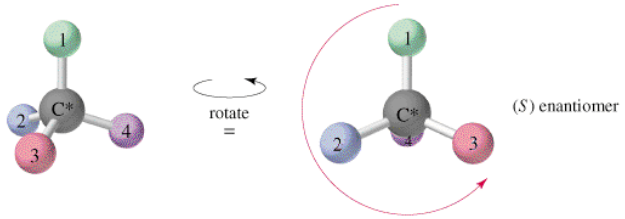
=>

Assign (*R*) or (*S*)

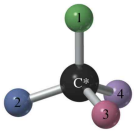


- Working in 3D, rotate molecule so that lowest priority group is in back.
- Draw an arrow from highest to lowest priority group.
- Clockwise = (*R*), Counterclockwise = (*S*)

=>



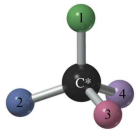
Properties of Enantiomers



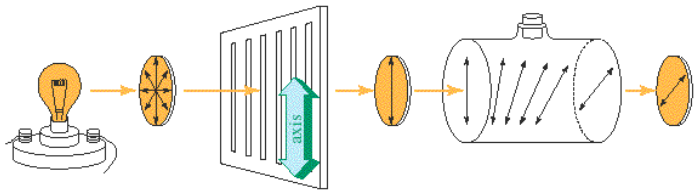
- Same boiling point, melting point, density
- Same refractive index
- Different direction of rotation in polarimeter
- Different interaction with other chiral molecules
  - Enzymes
  - Taste buds, scent

=>

Optical Activity

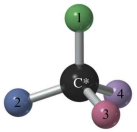


- Rotation of plane-polarized light
- Enantiomers rotate light in opposite directions, but same number of degrees.

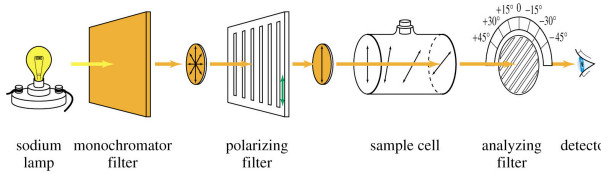


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Polarimetry

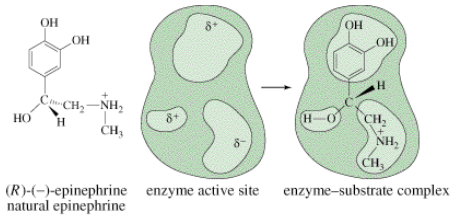


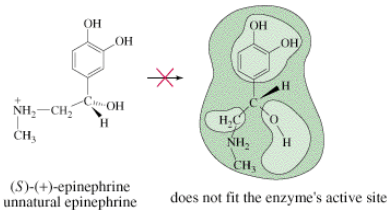
- Use monochromatic light, usually sodium D
- Movable polarizing filter to measure angle
- Clockwise = dextrorotatory = *d* or (+)
- Counterclockwise = levorotatory = *l* or (-)
- <u>Not</u> related to (*R*) and (*S*)



=>

Biological Discrimination





=>

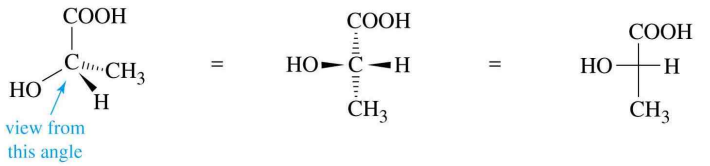
Racemic Mixtures

- Equal quantities of *d*- and *l*- enantiomers.
- Notation: (*d,l*) or (±)
- No optical activity.
- The mixture may have different b.p. and m.p. from the enantiomers!

=>

Fischer Projections

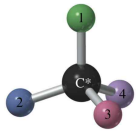
- Flat drawing that represents a 3D molecule
- A chiral carbon is at the intersection of horizontal and vertical lines.
- Horizontal lines are forward, out-of-plane.
- Vertical lines are behind the plane.



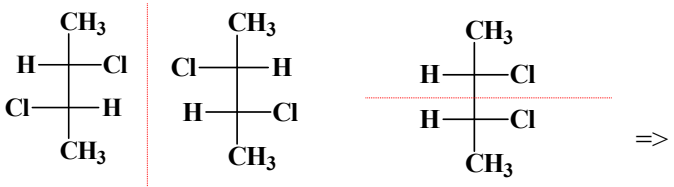
Fischer Rules

- Carbon chain is on the vertical line.
- Highest oxidized carbon at top.
- Rotation of 180° in plane doesn't change molecule.
- Do not rotate 90°!
- Do not turn over out of plane! =>

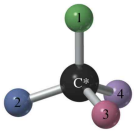
Fischer Mirror Images



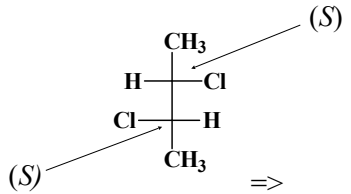
- Easy to draw, easy to find enantiomers, easy to find internal mirror planes.
- Examples:



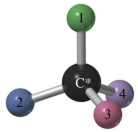
Fischer (*R*) and (*S*)



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



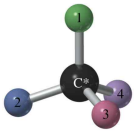
Diastereomers



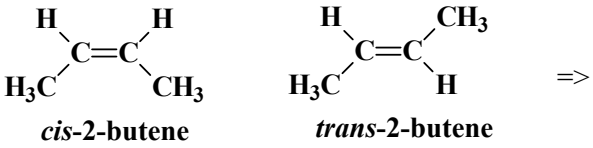
- Stereoisomers that are <u>not</u> mirror images.
- Geometric isomers (cis-trans)
- Molecules with 2 or more chiral carbons.

=>

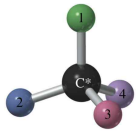
Alkenes



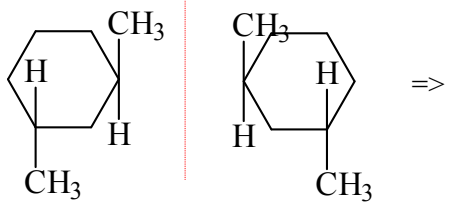
Cis-trans isomers are not mirror images, so these are diastereomers.



Ring Compounds

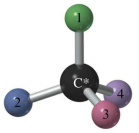


- Cis-trans isomers possible.
- May also have enantiomers.
- Example: *trans*-1,3-dimethylcylohexane



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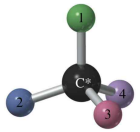
Two or More Chiral Carbons

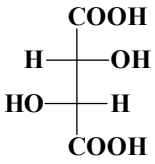


- Enantiomer? Diastereomer? Meso? Assign (*R*) or (*S*) to each chiral carbon.
- Enantiomers have opposite configurations at each corresponding chiral carbon.
- Diastereomers have some matching, some opposite configurations.
- Meso compounds have internal mirror plane.
- Maximum number is 2^n, where n = the number of chiral carbons.

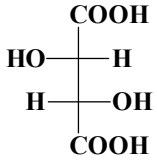
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Examples

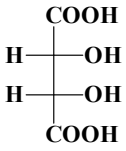




(2*R*,3*R*)-tartaric acid



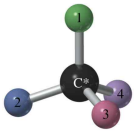
(2*S*,3*S*)-tartaric acid

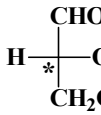


(2*R*,3*S*)-tartaric acid

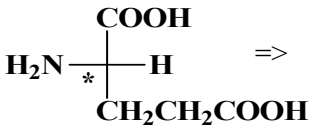
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D and L Assignments



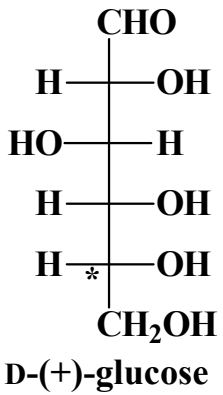


D-(+)-glyceraldehyde



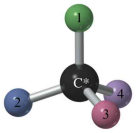
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L-(+)-glutamic acid



D-(+)-glucose

Properties of Diastereomers



- Diastereomers have different physical properties: m.p., b.p.
- They can be separated easily.
- Enantiomers differ only in reaction with other chiral molecules and the direction in which polarized light is rotated.
- Enantiomers are difficult to separate.

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