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OpenCourseWare (2023)

CHEMISTRY II

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ORGANIC CHEMISTRY: INTRODUCTION

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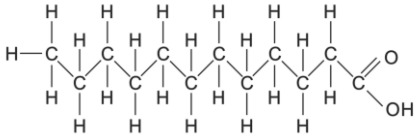
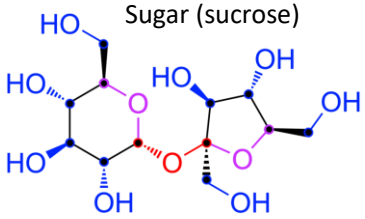
ORGANIC CHEMISTRY is the chemistry of *carbon* and its compounds. *Exception:* Inorganic compounds: CO_2, CO, H_2CO_3

ORGANIC MOLECULES

Lipid



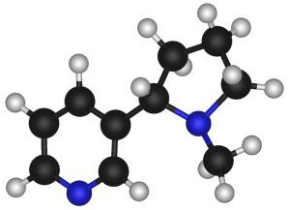
Sugar (sucrose)



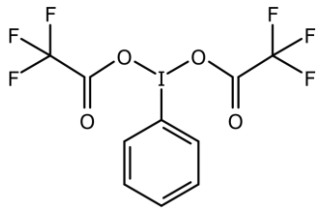
BLOCKS OF LIFE:
- Lipids
- Sugars
- Proteins
- Nucleic acids

- Plastics
- Paintings
- Clothes: cotton, silk..
- Coatings
- Adhesives
- Medicines
- Gasoline…

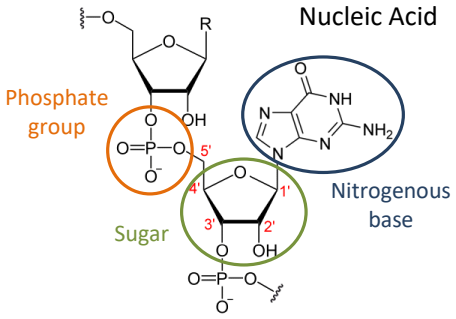
Nicotine



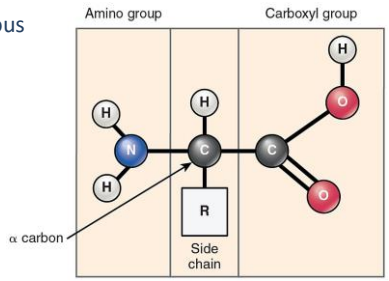
Adhesive



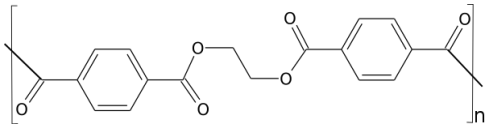
Nucleic Acid



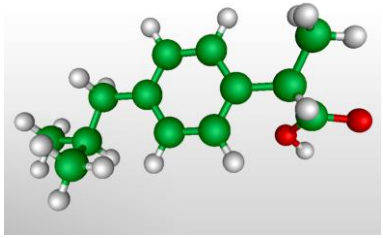
Amino Acid



Polyethylene terephthalate (PET)



Ibuprofen

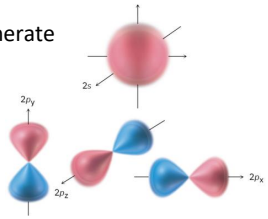


Characteristic Features of Organic Molecules:

- All organic compounds contain carbon and hydrogen atoms.
- Unique atomic structure of Carbon allows it to covalently bond with up to **four** other atoms.
  - Carbon forms single, double, and triple bonds with other atoms (C atoms or not).

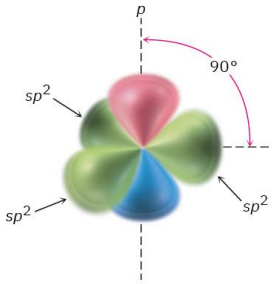
sp^3 hybridization

Overlap to generate 4 sp^3 orbitals

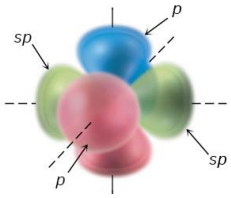


Four tetrahedral sp^3 orbitals

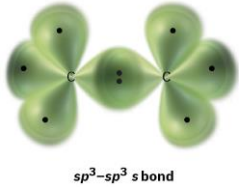
sp^2 hybridization



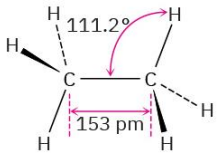
sp hybridization

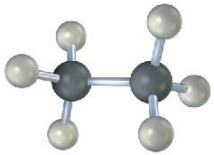


Structure of Ethane

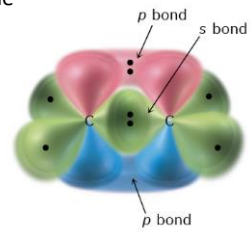


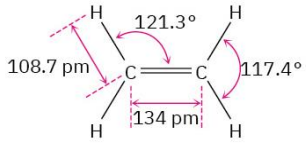
sp^3–sp^3 *s* bond



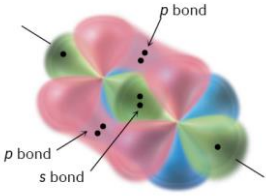


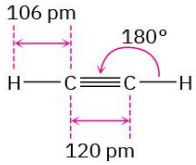
Structure of Ethene





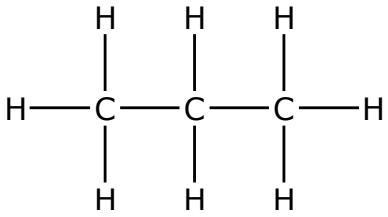
Structure of Ethyne





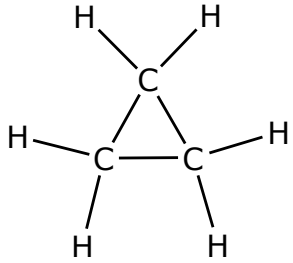
Characteristic Features of Organic Molecules:

- Some compounds have chains of atoms and others have rings.



Propane

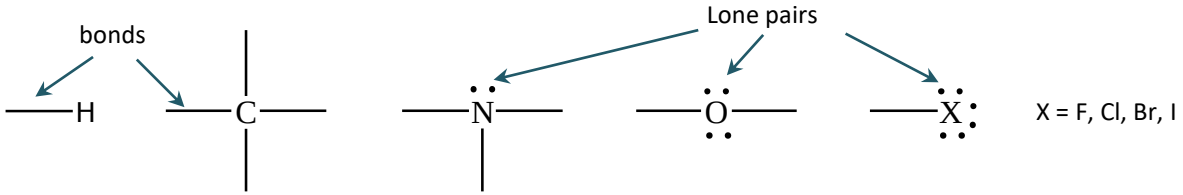
(C_3H_8)



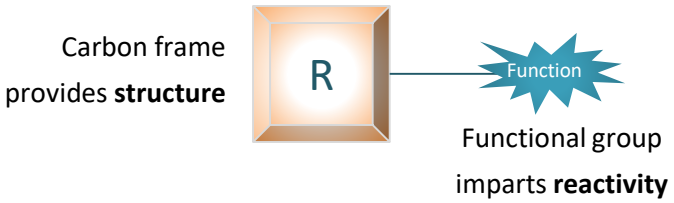
Cyclopropane

(C_3H_6)

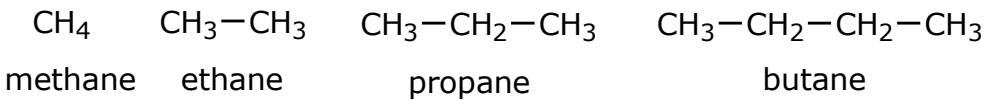
- Organic compounds may also contain elements different than carbon and hydrogen (*heteroatoms*).



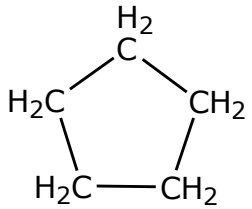
FUNCTIONAL GROUP is a group of atoms that is largely responsible for the chemical behavior of the parent molecule. Different molecules containing the same kind of functional group or groups undergo similar reactions.



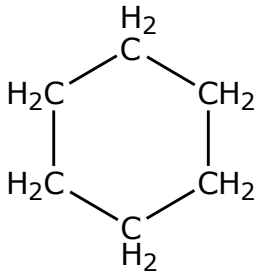
- *Hydrocarbons.* They present the general empirical formula C_xH_y.
  - *Alkanes or Paraffins (C_nH_{2n+2}).* Those containing only SIMPLE BONDS. Carbon atoms have sp^3 hybridization.



  - *Cycloalkanes.* Carbons form a RING.



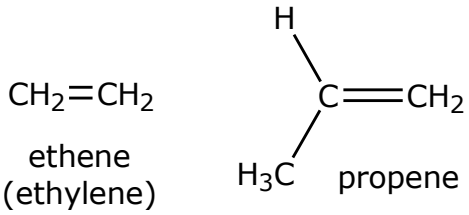
cyclopentane



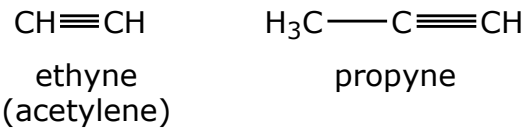
cyclohexane

- *Hydrocarbons. They present the general empirical formula C_xH_y.*

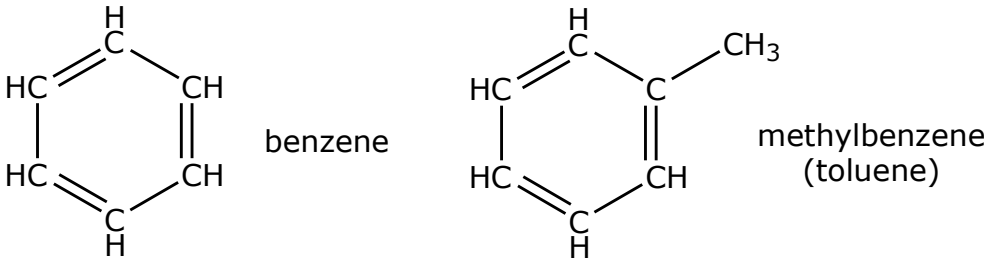
  - *Alkenes or Olefins (C_nH_{2n}).* The functional group is the DOUBLE BOND. Carbon atoms in the double bond are sp^2 hybridized and the double bond is made up of a σ bond and a π bond.



  - *Alkynes (C_nH_{2n-2}).* The functional group is the TRIPLE BOND. Carbon atoms in the triple bond are sp hybridized and the double bond is made up of a σ bond and two π bonds.

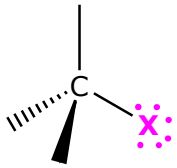


  - *Arenes.* Aromatic compounds, double bonds are incorporated into a six-membered ring.



- *Functional groups with Polar Bonds.* There is a difference in the electronegativity of two atoms bound to each other.
  - *Carbon singly bonded to an electronegative atom.* The bonds are polar, with the carbon atom bearing a partial positive charge (δ^+) and the electronegative atom bearing a partial negative charge (δ^-).

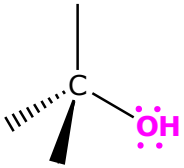
Haloalkanes



CH_3CH_2Cl

chloroethane
(ethylchloride)

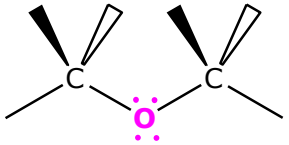
Alcohols



CH_3CH_2OH

ethanol

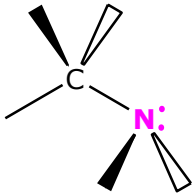
Ethers



$CH_3CH_2OCH_2CH_3$

ethoxyethane
(diethyl ether)

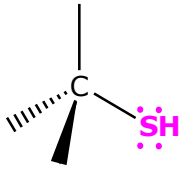
Amines



$(CH_3)_2NH$

N-methylmethanamine
(dimethylamine)

Thiols

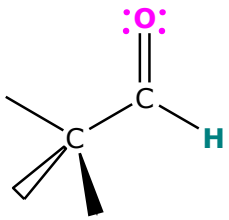


CH_3CH_2SH

ethanethiol

- *Functional groups with Polar Bonds.* There is a difference in the electronegativity of two atoms bound to each other.
  - *Carbon-Oxygen double bond (CARBONYL GROUPS).* These compounds behave similarly but differ depending on the identity of the atoms bonded to the carbonyl-group carbon. The carbonyl carbon atom bears a partial positive charge (δ^+) and the oxygen bears a partial negative charge (δ^-).

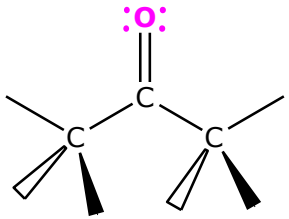
Aldehydes



CH_3CHO

acetaldehyde
(ethanal)

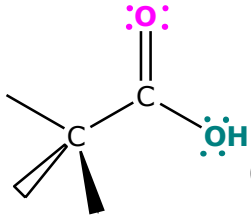
Ketones



$CH_3CH_2COCH_3$

butanone
(methyl ethyl ketone)

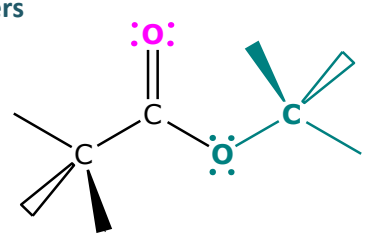
Carboxylic acids



CH_3COOH

acetic acid
(ethanoic acid)

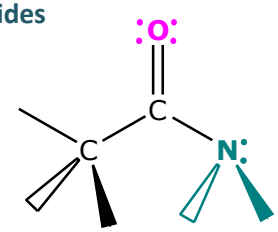
Esters



$CH_3CH_2COOCH_3$

methyl propanoate
(methyl propionate)

Amides



$CH_3CH_2CH_2CONH_2$

butanamide

Naming begins identifying the largest hydrocarbon chain, its branches and functional groups, as well as their *relative priority*.

MAIN CHAIN

Methane

Number of carbons (*n*)	Name	Formula (C_nH_{2n+2})	Number of carbons (*n*)	Name	Formula (C_nH_{2n+2})
1	Methane	CH_4	9	Nonane	C_9H_{20}
2	Ethane	C_2H_6	10	Decane	$C_{10}H_{22}$
3	Propane	C_3H_8	11	Undecane	$C_{11}H_{24}$
4	Butane	C_4H_{10}	12	Dodecane	$C_{12}H_{26}$
5	Pentane	C_5H_{12}	13	Tridecane	$C_{13}H_{28}$
6	Hexane	C_6H_{14}	20	Icosane	$C_{20}H_{42}$
7	Heptane	C_7H_{16}	30	Triacontane	$C_{30}H_{62}$
8	Octane	C_8H_{18}			

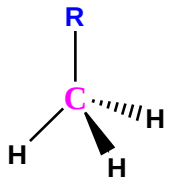
SUBSTITUENT

A methyl group

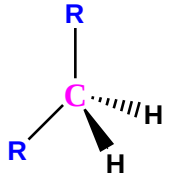
Alkane	Name	Alkyl group	Name (abbreviation)
CH_4	Methane	$-CH_3$	Methyl (Me)
CH_3CH_3	Ethane	$-CH_2CH_3$	Ethyl (Et)
$CH_3CH_2CH_3$	Propane	$-CH_2CH_2CH_3$	Propyl (Pr)
$CH_3CH_2CH_2CH_3$	Butane	$-CH_2CH_2CH_2CH_3$	Butyl (Bu)
$CH_3CH_2CH_2CH_2CH_3$	Pentane	$-CH_2CH_2CH_2CH_2CH_3$	Pentyl, or amyl

Naming begins identifying the largest (or main) hydrocarbon chain, its branches and functional groups, as well as their *relative priority*.

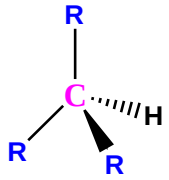
Primary carbon is bonded to one other carbon



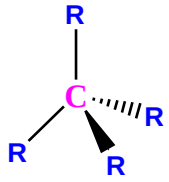
Secondary carbon is bonded to two other carbon



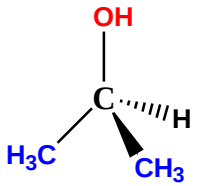
Tertiary carbon is bonded to three other carbon



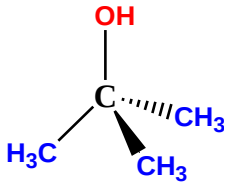
Quaternary carbon is bonded to four other carbon



Examples:

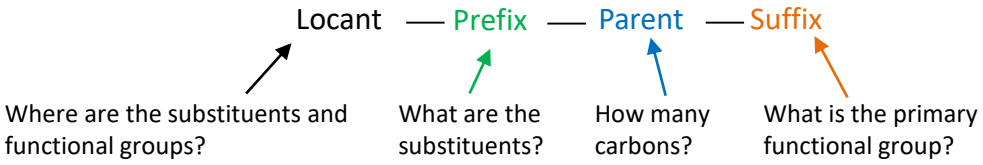


Secondary alcohol, R_2COH



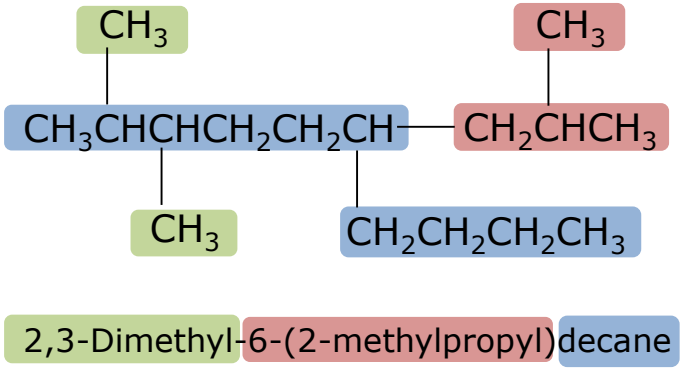
Tertiary alcohol, R_3COH

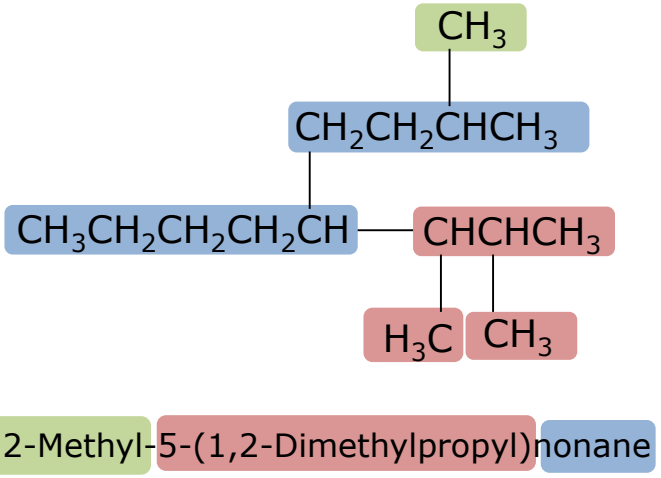
IUPAC Rules for Naming Straight-Chain Alkanes

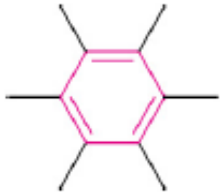
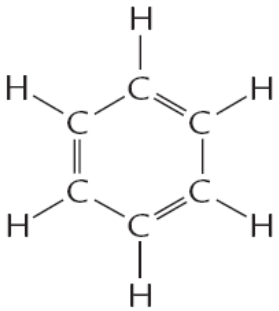
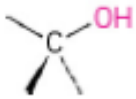
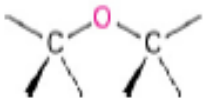


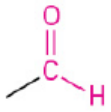
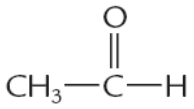
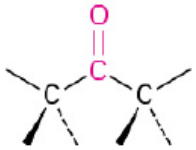
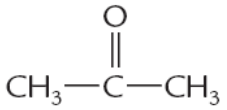
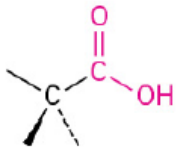
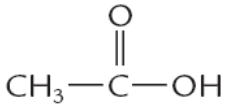
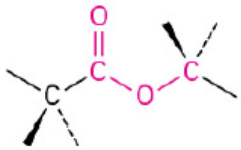
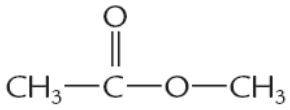
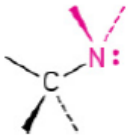
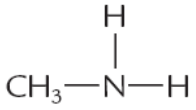
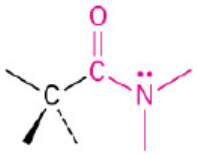
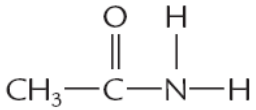
Order of priority of functional groups:

Carboxylic acid > Anhydride > Ester > Alkanoyl halide > Amide > Nitrile > Aldehyde > Ketone > Alcohol > Thiol > Amine



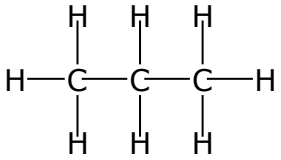
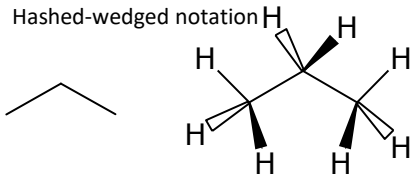
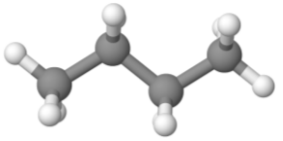
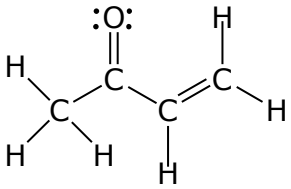
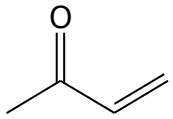
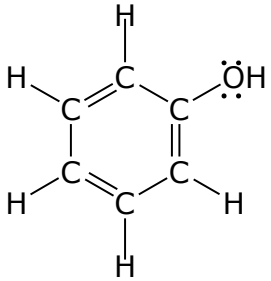
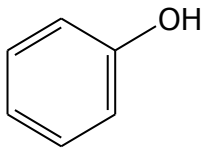
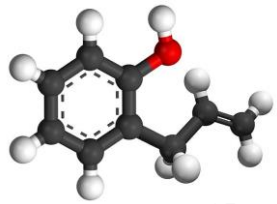


Family	Functional group	Example	Name ending
alkane	C—C and C—H single bonds	$CH_3—CH_3$ Ethane	Eth**ane**
alkene		$CH_2=CH_2$ Ethylene	Eth**ene**
alkyne	–C≡C–	$CH{\equiv}CH$ Acetylene	Eth**yne**
aromatic		 Benzene	**Benzene**
alcohol		$CH_3CH_2—O—H$ Ethyl alcohol	Ethan**ol**
ether		$CH_3—O—CH_3$ Dimethyl ether	Dimethyl **Ether**

Family	Functional group	Example	Name ending
aldehyde		 Acetaldehyde	Ethan**al**
ketone		 Acetone	Propan**one**
carboxylic acid		 Acetic acid	Ethan**oic acid**
ester		 Methyl acetate	Methyl Ethan**oate**
amine		 Methyl amine	Methan**amine**
amide		 Acetamide	Metan**amida**

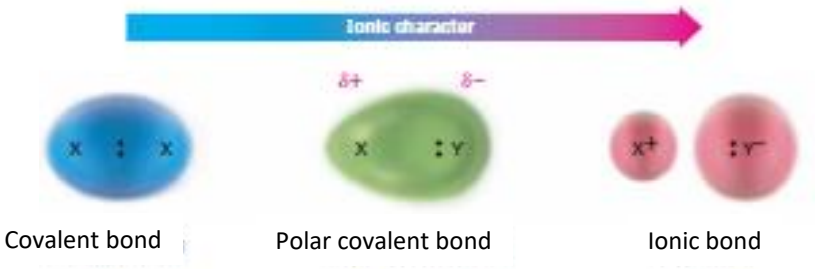
Drawing Chemical Structures

- *Empirical Formula.-* summarizes the kinds and ratios of the elements present.
- *Kekulé (Straight-line Notation).-* straight line notation, with lone pairs (if present) as dots.
- *Condensed Formulas.-* most single bonds and lone pairs are omitted.
- *Bond-Line Formulas or Skeletal Structures.-* carbon frame is represented by zigzag straight lines, omitting all hydrogen atoms.
  - Hashed-wedged/solid-wedged line notation: for tetrahedral carbon.
- *Three-dimensional representation.-* represents the exact position of every atom.

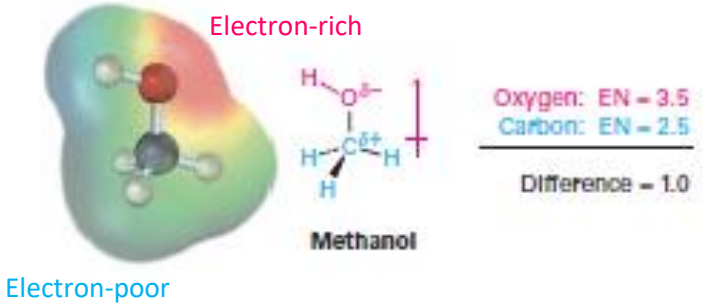
Compound **Empirical Formula**	**Kekulé**	**Condensed**	**Bond-Line Formulas**	**3D representation**
Propane C_3H_8		$CH_3CH_2CH_3$	Hashed-wedged notation 	
3-Buten-2-one C_4H_6O		$CH_3COCH{=}CH_2$		
Phenol C_6H_6O		C_6H_5OH		

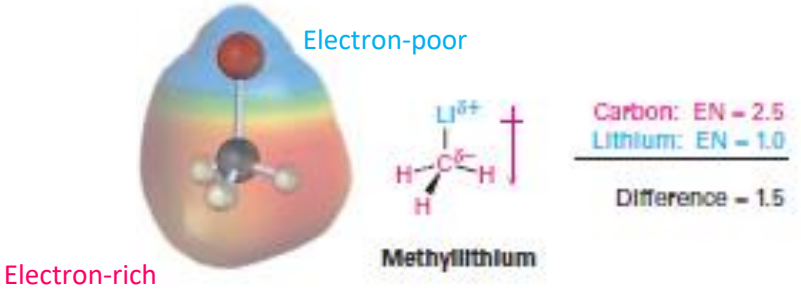
Structure and Reactivity

- *Bond polarity.-* is due to the difference in electronegativity.



Electrostatic Potential Maps





Atom's ability to polarize a bond → *INDUCTIVE EFFECT* → CHEMICAL REACTIVITY

Structure and Reactivity

- *Kinetic and Thermodynamic of Chemical Processes.-* Chemical reactions are governed by two fundamental considerations:
  - *Thermodynamic* controls the extent to which a reaction goes to completion.
  - *Kinetics* describes the speed at which a reaction goes to completion.

What is a *favorable change in energy*?

The *Gibbs free energy change* is related to changes in bond strengths and the degree of energy dispersal in the system

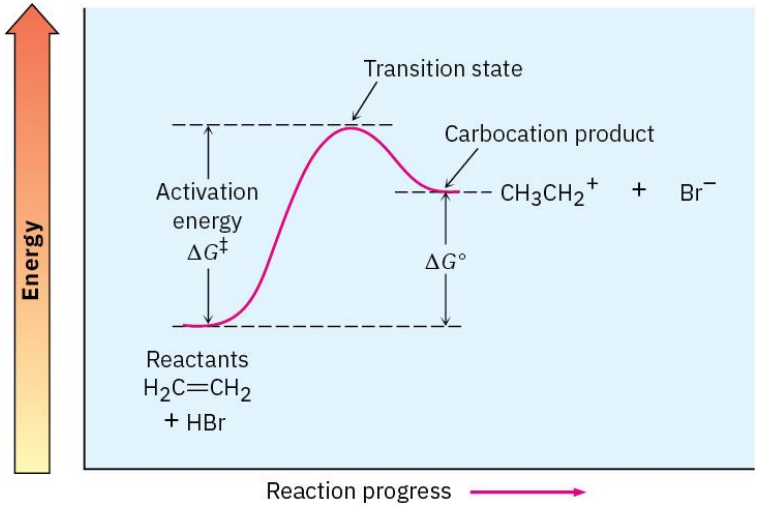
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \Delta G^0 + RTLnQ \qquad \Delta G = \Delta G^0 + RTLn\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

At Equilibrium: $\Delta G = 0$ and Q = K

$$\Delta G^0 = -RTLnK$$

POTENTIAL ENERGY DIAGRAM



The *rate* of a chemical reaction depends on the activation energy

Temperature affects reaction rate

$$K = Ae^{-\frac{E_a}{RT}}$$

Structure and Reactivity

➢ *Acids and Bases.-* many processes in organic chemistry exhibit characteristics of acid-base reactions.

Estimation of relative acid and base strengths from a molecule's structure:

Assessing Acidity of HA:

- Factor 1: Electronegativity of A

Increasing electronegativity of **A**

H_4C H_3N H_2O HF

Increasing **acidity**

- Factor 2: Hybridization of C

Increasing **s** character of **C**

$H_3C–CH_3$ $H_2C=CH_2$ HC≡CH

Increasing **acidity**

- Factor 3: Inductive effect

Increasing electron-attracting **inductive** effect

$H_3C–CH_2OH$ $FH_2C–CH_2OH$ $F_2HC–CH_2OH$ $F_3C–CH_2OH$

Increasing **acidity**

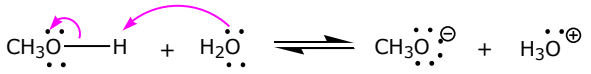
- Factor 4: Size of A

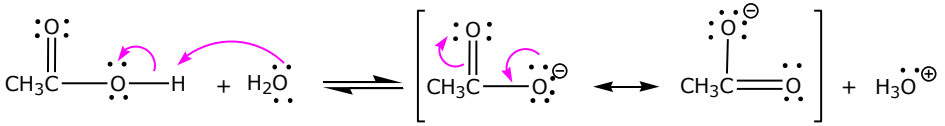
Increasing size of **A**

HF HCl HBr HI

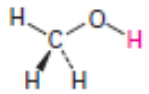
Increasing **acidity**

- Factor 5: Resonance in A^-

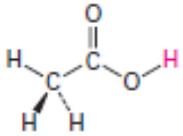




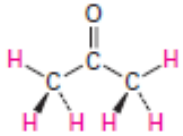
- *Acids and Bases.*
  - Organic Acids. Presence of positively polarized hydrogen atom



Methanol
(pK_a = 15.54)

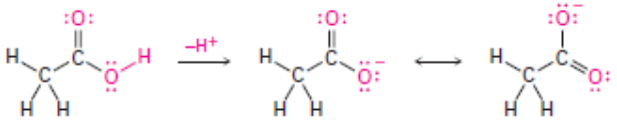


Acetic acid
(pK_a = 4.76)

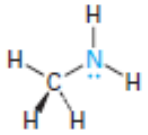


Acetone
(pK_a = 19.3)

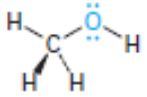
Anion is stabilized both by having negative charge on a highly electronegative atom and by resonance



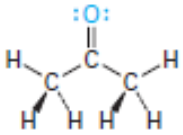
  - Organic Bases. Presence of an atom with a lone pair of electrons that can bond to H^+.



Methylamine



Methanol

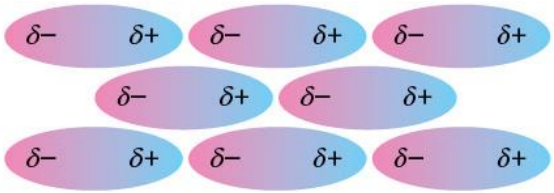


Acetone

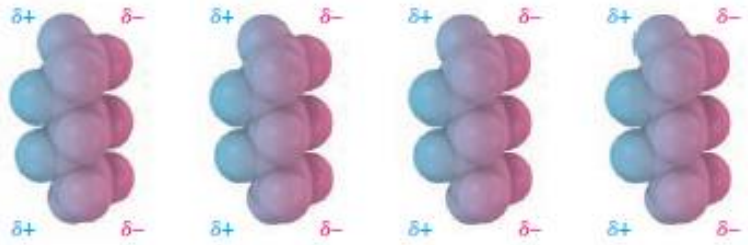
Structure and Reactivity

- *Intermolecular Forces.-* affect chemical reactivity.

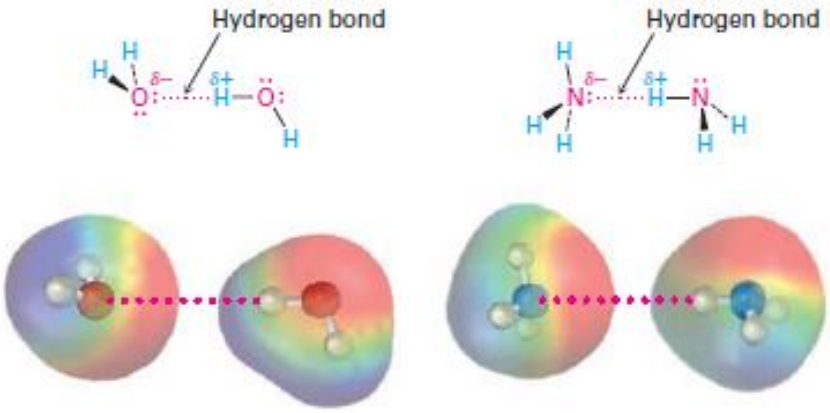
Dipole-Dipole Forces

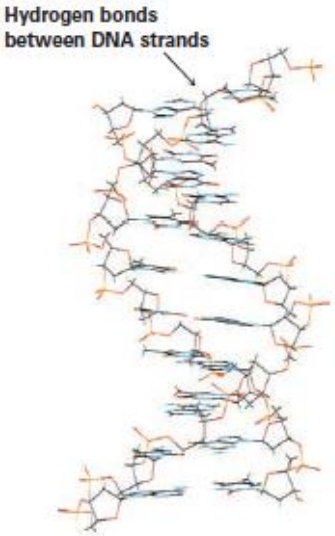


Dispersion Forces



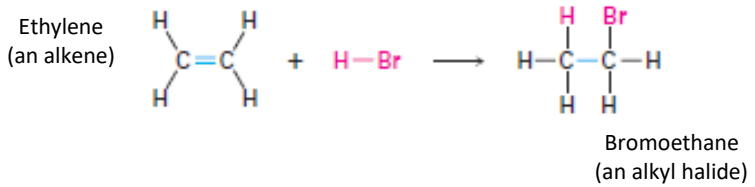
Hydrogen Bonds



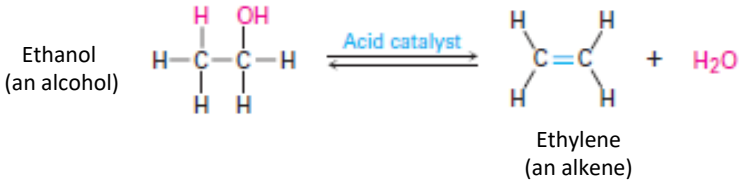


Kinds of Organic Reactions

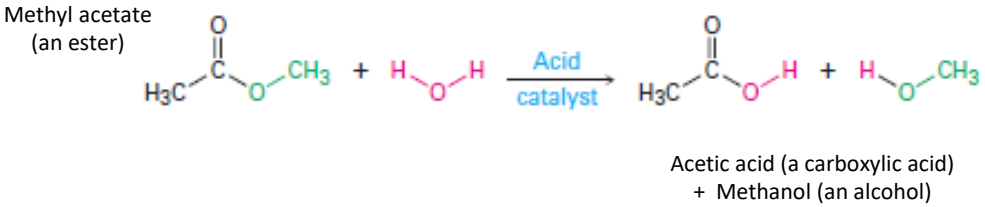
- *Addition.-* two reactants add together to form a single product.



- *Elimination.-* a single reactant splits into two products, often with formation of a small molecule.

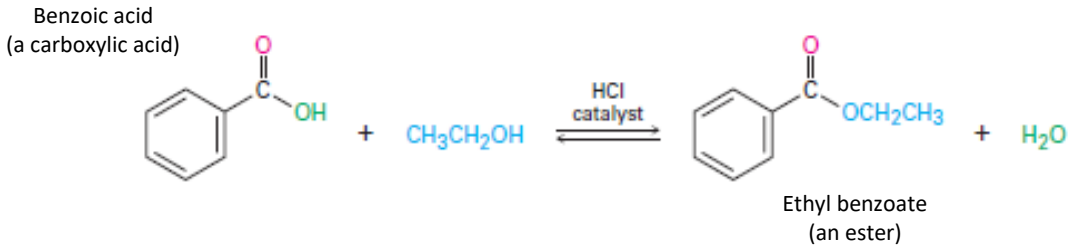


- *Substitution.-* two reactants exchange parts to give two new products.

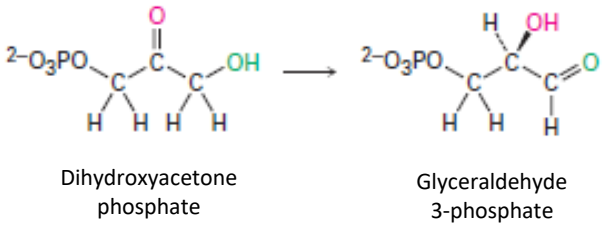


Kinds of Organic Reactions

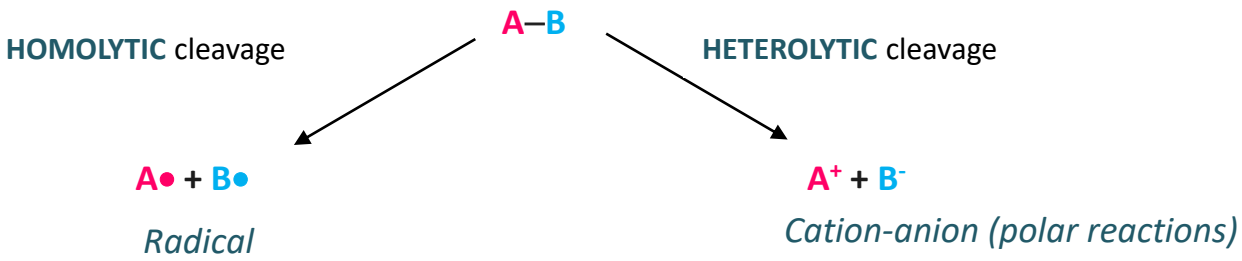
- *Condensation.-* two functional groups are combined to eliminate a small molecule.



- *Rearrangement*.- a single reactant undergoes a reorganization of bonds and atoms.



Mechanisms of Organic Reactions



Radicals and ions are *reaction intermediates* that are formed by the action of reactants

❖ Symmetrical bond-breaking and bond-forming:

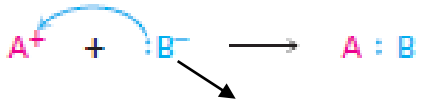
One bonding electron stays with each product

One bonding electron is donating by each product

❖ Unsymmetrical bond-breaking and bond-forming:

Two bonding electron stay with one product

Two bonding electrons are donated by one reactant



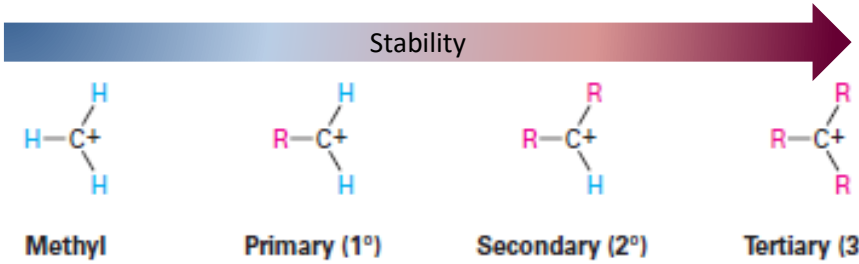
- It likes negative charges
- Able to accept electrons
- Attack through the δ^+ end of the polar bond

- It likes positive charges
- Able to donate electrons
- Attack through the δ^- end of the polar bond

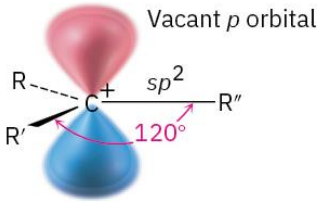
HETEROLYTIC cleavage

Intermediates: CARBOCATION STABILITY

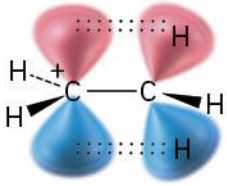
Carbocation is an *Electrophile* reactant

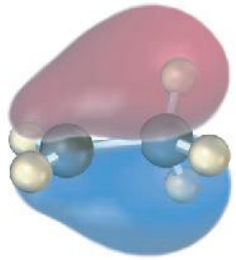


Trigonal planar

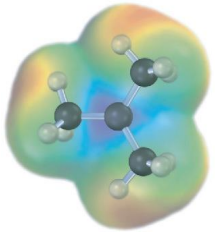


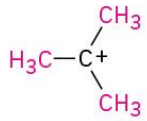
• **Hyperconjugation.-** Electron interaction between a σ bond and a p orbital





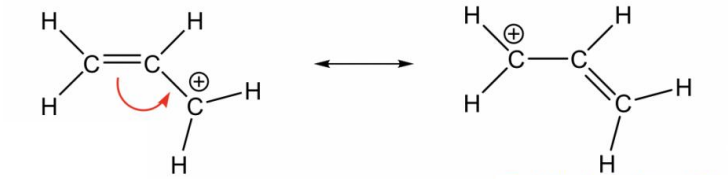
• **Inductive effect.-** Transmision of the effect of an electron-withdrawing or electron-donating group through σ bonds.





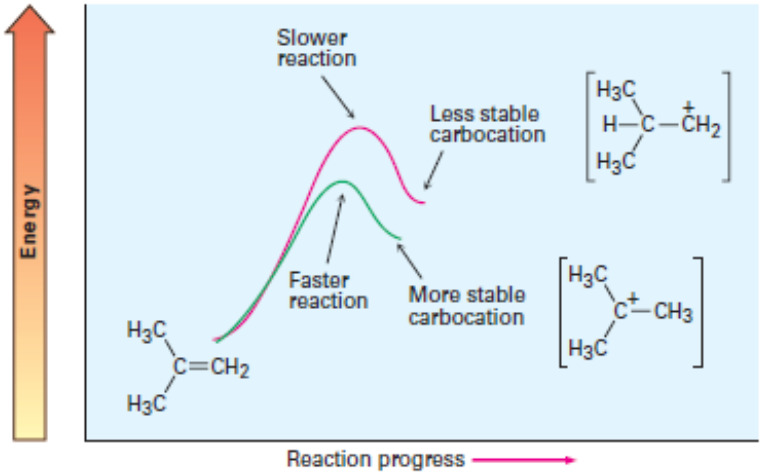
Tertiary:
Three alkyl groups donating electrons

• **Resonance.-** Movement of electrons. Delocalization of π electrons.



HETEROLYTIC cleavage

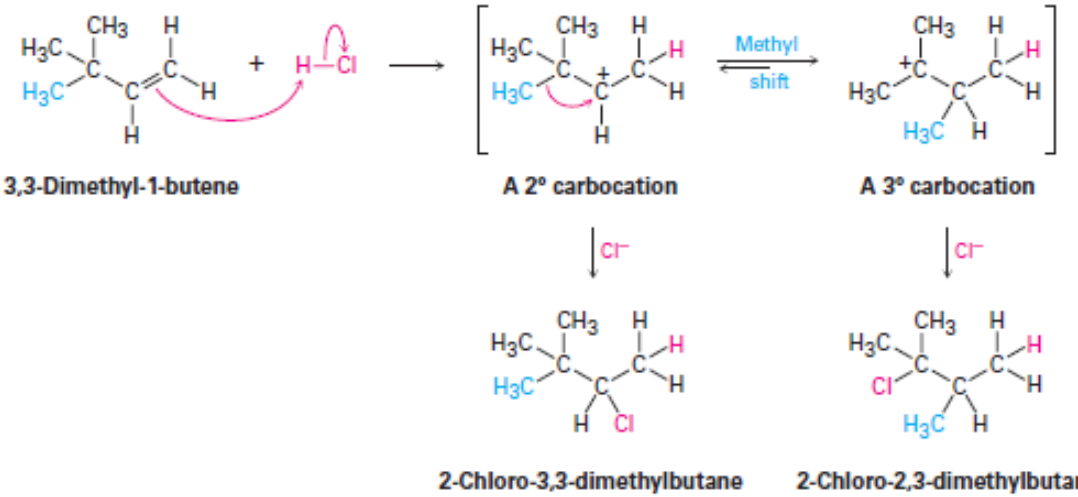
Intermediates: CARBOCATION STABILITY



Higher alkyl substitution
⇓
Carbocations more stable
⇓
It stabilizes Transition states
⇓
Faster reaction

TRANSPOSITION.- spontaneous rearrangement of atoms looking for the highest stability.

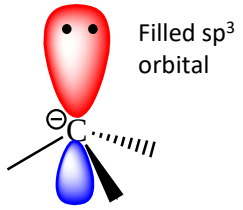
Example:

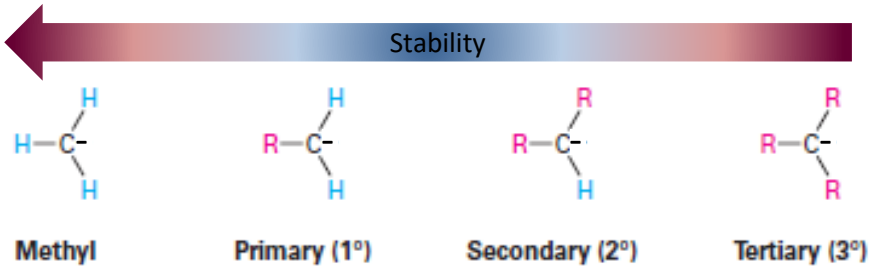


HETEROLYTIC cleavage

Intermediates: CARBANION STABILITY

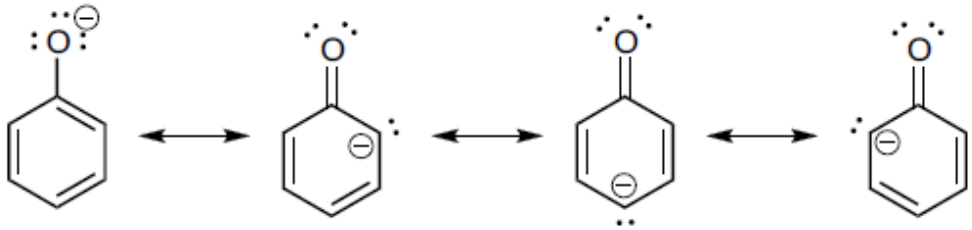
Carbanion is a *Nucleophile* reactant





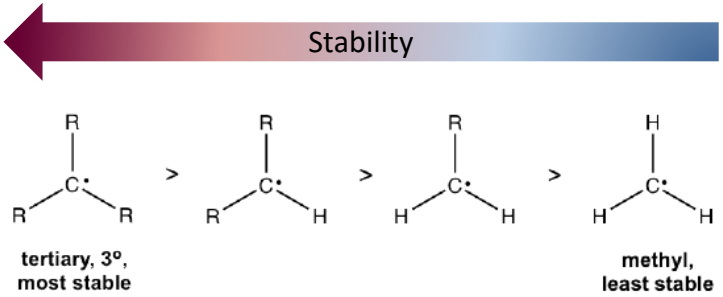
- **Inductive effect.-** Transmision of the effect of an electron-withdrawing or electron-donating group through σ bonds.

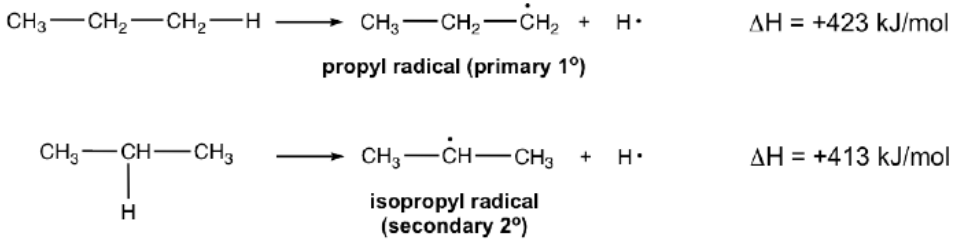
- **Resonance.-** Delocalization of π electrons



HOMOLYTIC cleavage

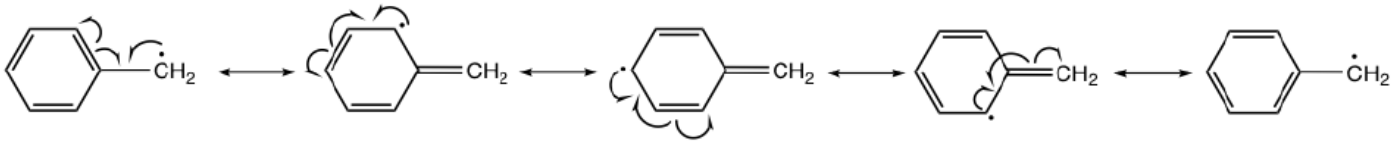
Intermediates: RADICAL STABILITY





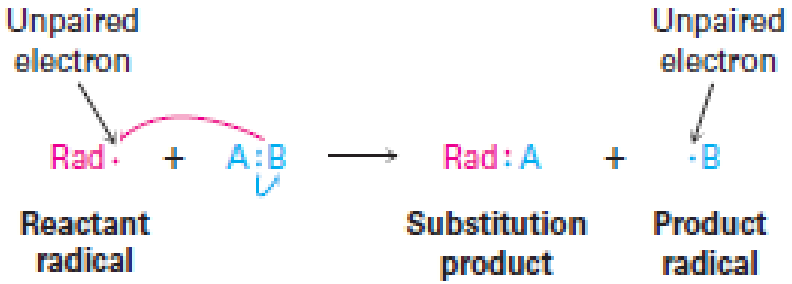
- **Hyperconjugation.-** Electron interaction between a σ bond and a p orbital

- **Resonance.-** Movement of electrons. Delocalization of π electrons.

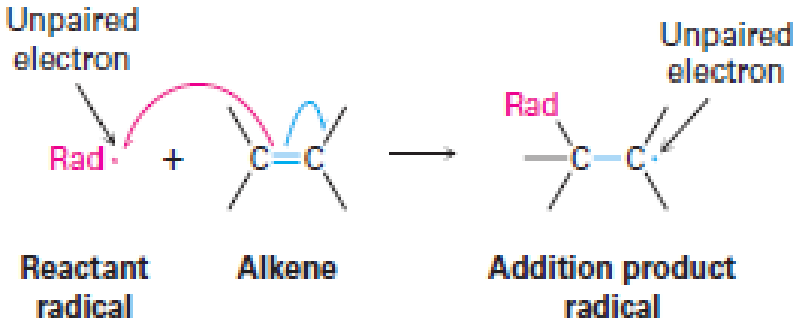


Radical Reactions

Radical substitution reaction



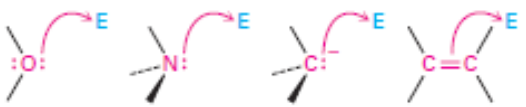
Radical addition reaction



The octet rule must be followed

Polar Reactions

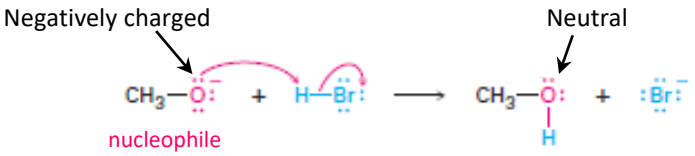
- ✓ Electrons move from a nucleophilic source to an electrophilic sink.

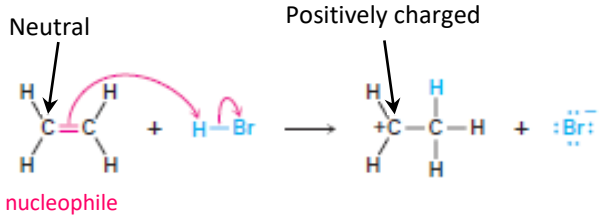


Electrons flow *from* the nucleophile

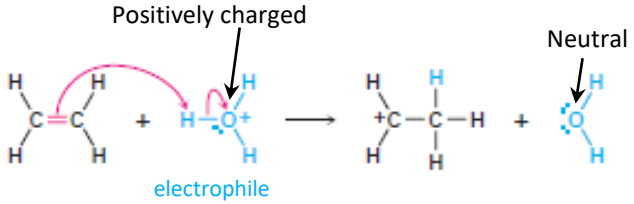
Electrons flow *to* the electrophile

- ✓ The nucleophile can be either negatively charged or neutral.





- ✓ The electrophile can be either positively charged or neutral.



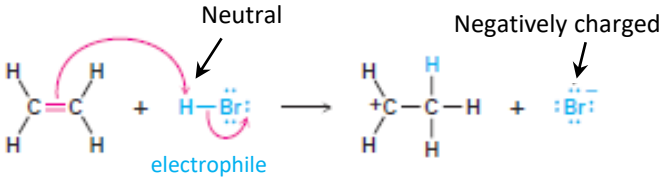


Image Credits

Slide 3:

- Fatty Acid: "Medical gallery of Blausen Medical 2014". WikiJournal of Medicine 1 (2). DOI:10.15347/wjm/2014.010. ISSN 2002-4436., CC BY 3.0, https://commons.wikimedia.org/wiki/File:Blausen_0396_FattyAcid.png.
- Sugar (sucrose): Riccardo Rovinetti, CC BY-SA 4.0, https://commons.wikimedia.org/wiki/File:Sucrose2col.png.
- Nucleic Acid: en: Narayanese, CC BY-SA 3.0, https://commons.wikimedia.org/wiki/File:RNA_chemical_structure_hy.png.
- Amino Acid: OpenStax College, CC BY 3.0, https://commons.wikimedia.org/wiki/File:223_Structure_of_an_Amino_Acid-01.jpg.
- Nicotine: Michael Ströck, CC BY 3.0, https://commons.wikimedia.org/wiki/File:Nicotine_3D_Model.png.
- Adhesive: Mrgreen71, CC BY-SA 3.0, https://commons.wikimedia.org/wiki/File:(bis(trifluoroacetoxy)iodo)benzene.svg.
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- Ibuprofen: Michael Ströck, CC BY-SA 3.0, https://commons.wikimedia.org/wiki/File:Ibuprofen_3D_Model.png.

Slides 4, 10, 13, 14, 16, 17, 19-22, 24-26, 28, 29:

- Organic Chemistry. A tenth Edition. John McMurry, Cornell University (Emeritus), CC BY-SA 4.0, https://openstax.org/details/books/organic-chemistry.

Slides 5-9, 11, 12, 15, 18, 26 (carbanion):

- Images made by the authors.

Slide 15:

- Propane (3D structure): Johannes Botne, CC BY-SA 3.0, https://snl.no/alkaner.
- Phenol (3D structure): Claudio Pistilli, CC BY 3.0, https://eo.wikipedia.org/wiki/Dosiero:2-Allyl-phenol_3D.jpeg.

Slides 24 (resonance image), 27:

- Organic Chemistry I. Xin Liu. Kwantlen Polytechnic University, Surrey BC, CC BY-SA 4.0, https://open.umn.edu/opentextbooks/textbooks/1119.

Slides 26 (resonance image):

- Chemistry II. David Karlin. Williams School. CC BY-NC-SA 4.0, https://chem.libretexts.org/Courses/Williams_School/Chemistry_II.