

CHIMICA ORGANICA I
con
LABORATORIO

Organizzazione

Docente:

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- Tel.: 040 558 3919

Libri di testo

John McMurry
Chimica Organica
PICCIN-NUOVA LIBRARIA

D'Auria M.V.; Taglialatela Scafati O.;
Zampella A.

Guida ragionata allo svolgimento di
esercizi di chimica organica

LOGHIA

Brown W.H.; Foote, C.S.; Iverson, B.L.
Chimica Organica
EdiSES

Janice Gorzynski Smith
Organic Chemistry
McGraw-Hill

Vollhardt K. Peter; Schore Neil E.
Chimica organica
Zanichelli

Solomons T.W. Graham;
Fryhle Craig B.
Chimica organica
Zanichelli

Seyhan N. Ege
Chimica Organica: Struttura e
reattività
Idelson-Gnocchi

ORGANIC CHEMISTRY = Chemistry of Carbon Compounds



Joseph Proust 1754-1826

The Inorganic World
Non-Living Entities
Rational Laws

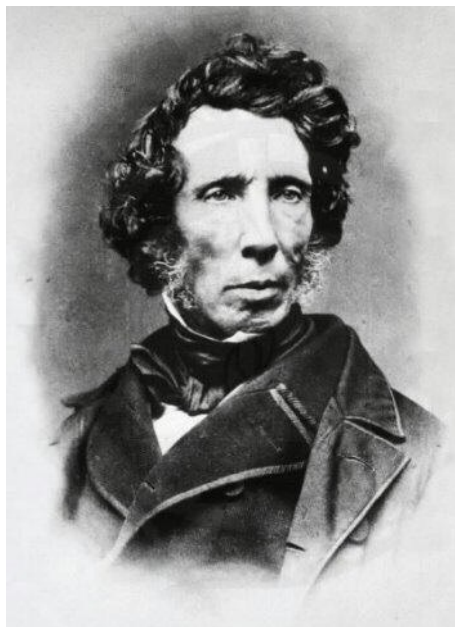
Organic World
Living Entities
Vital Spark

Inorganic Compounds:
Es. NH_3 , H_2O
Definite Proportions

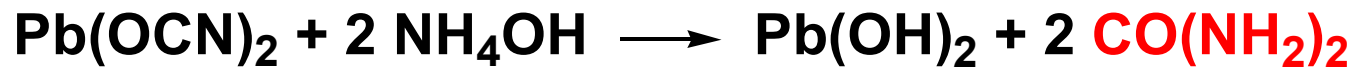
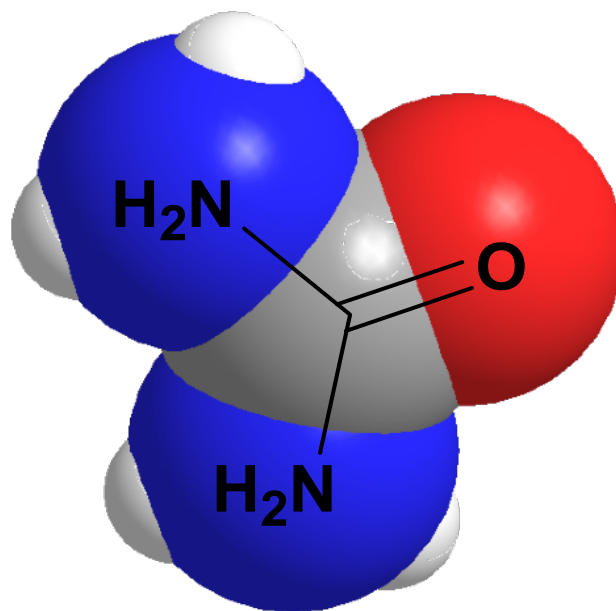
Organic World: Es. CH_4 , C_2H_6 , C_3H_8 ,
 C_2H_4
 C_2H_2

Similar properties but different proportions:
Vitalism!

1828: The End of Vitalism



Friedrich Woehler
1800-1882

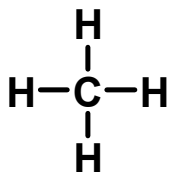


Organic Compounds are Ubiquitous

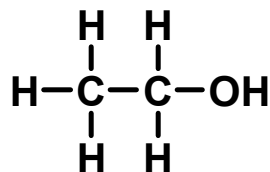
There are approximately 60.000.000 organic molecules.

- Biomolecules: *carbohydrates, lipids, proteins and nucleic acids.*
- Materials: *cotton, paper, wood, leather, silk, wool, benzine, mineral oils.*
- Synthetic molecules and materials: *drugs, plastics, paints, dyes, artificial fibres, fertilizers, aromas, cosmetics, detergents, perfumes, sweeteners, etc.*

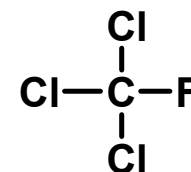
Organic Compounds



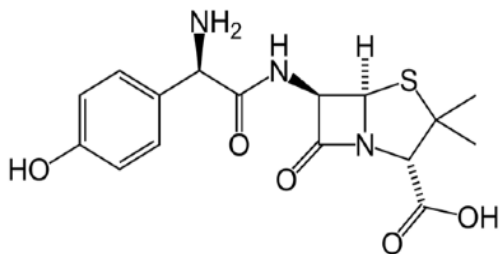
Methane



Ethanol

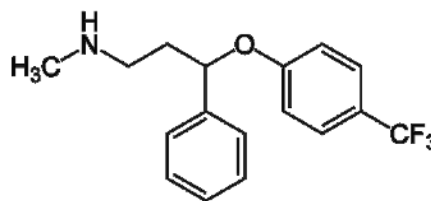


Trichlorofluoromethane



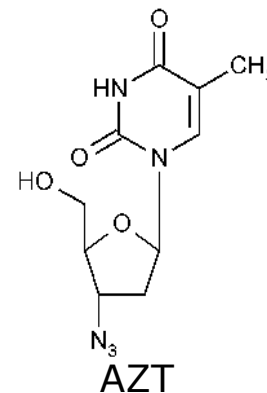
Amoxicillin

(2*S*,5*R*,6*R*)-6-(2-amino-2-(4-hydroxyphenyl)acetamido)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid



Fluoxetin
Prozac

N-methyl-3-phenyl-3-[4-(trifluoromethyl)phenoxy]propan-1-amine



3'-azido-3'-deoxythymidine
AZT

The Carbon Atom

- Atomic Number: 6
- 2 Isotopes
 - ^{12}C (98,9%): 6 protons, 6 neutrons
 - ^{13}C (1,1%): 6 protons, 7 neutrons
- Electron Configuration: $1s^2$
 $2s^2 2p^2$

1. Carbon Forms Covalent Bonds With Many Other Elements

1 H Hydrogen 1.0																	2 He Helium 4.0		
3 Li Lithium 6.9		4 Be Beryllium 9.0												5 B Boron 10.8	6 C Carbon 12.0	7 N Nitrogen 14.0	8 O Oxygen 16.0	9 F Fluorine 19.0	10 Ne Neon 20.2
11 Na Sodium 23.0	12 Mg Magnesium 24.3											13 Al Aluminum 27.0	14 Si Silicon 28.1	15 P Phosphorus 31.0	16 S Sulfur 32.1	17 Cl Chlorine 35.5	18 Ar Argon 40.0		
19 K Potassium 39.1	20 Ca Calcium 40.2	21 Sc Scandium 45.0	22 Ti Titanium 47.9	23 V Vanadium 50.9	24 Cr Chromium 52.0	25 Mn Manganese 54.9	26 Fe Iron 55.9	27 Co Cobalt 58.9	28 Ni Nickel 58.7	29 Cu Copper 63.5	30 Zn Zinc 65.4	31 Ga Gallium 69.7	32 Ge Germanium 72.6	33 As Arsenic 74.9	34 Se Selenium 79.0	35 Br Bromine 79.9	36 Kr Krypton 83.8		
37 Rb Rubidium 85.5	38 Sr Strontium 87.6	39 Y Yttrium 88.9	40 Zr Zirconium 91.2	41 Nb Niobium 92.9	42 Mo Molybdenum 95.9	43 Tc Technetium 99	44 Ru Ruthenium 101.0	45 Rh Rhodium 102.9	46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.8	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.3		
55 Cs Caesium 132.9	56 Ba Barium 137.4	57-71 Lanthanides	72 Hf Hafnium 178.5	73 Ta Tantalum 181.0	74 W Tungsten 183.9	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium 210.0	85 At Astatine 210.0	86 Rn Radon 222.0		
87 Fr Francium 223.0	88 Ra Radium 226.0	89-103 Actinides	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 262	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Uun Ununnilium 272										

57 La Lanthanum 138.9	58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium 147.0	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
89 Ac Actinium 132.9	90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	93 Np Neptunium 237.0	94 Pu Plutonium 242.0	95 Am Americium 243.0	96 Cm Curium 247.0	97 Bk Berkelium 247.0	98 Cf Californium 251.0	99 Es Einsteinium 254.0	100 Fm Fermium 253.0	101 Md Mendelevium 256.0	102 No Nobelium 254.0	103 Lr Lawrencium 257.0

2. Carbon Is Tetravalent

1

2

3 4 3 2 1

1 H Hydrogen 1.0																	2 He Helium 4.0				
3 Li Lithium 6.9	4 Be Beryllium 9.0															5 B Boron 10.8	6 C Carbon 12.0	7 N Nitrogen 14.0	8 O Oxygen 16.0	9 F Fluorine 19.0	10 Ne Neon 20.2
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87 Fr Francium 223.0	88 Ra Radium 226.0	89-103	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 262	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Uun Ununnilium 272												

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89 Ac Actinium 132.9	90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	93 Np Neptunium 237.0	94 Pu Plutonium 242.0	95 Am Americium 243.0	96 Cm Curium 247.0	97 Bk Berkelium 247.0	98 Cf Californium 251.0	99 Es Einsteinium 254.0	100 Fm Fermium 253.0	101 Md Mendelevium 256.0	102 No Nobelium 254.0	103 Lr Lawrencium 257.0

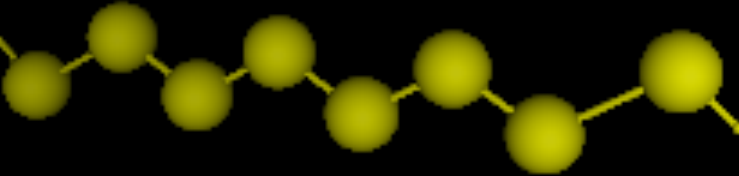
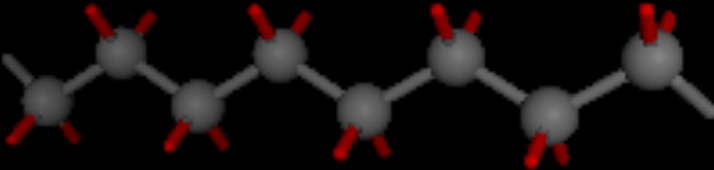
3. Carbon Forms Very Strong Bonds

Bond	Bond Dissociation Energy (kJ/M)
C—C	360
C—H	400-550
C—O	350-400
C—N	360
N—N	250
O—O	180

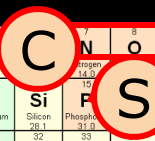
4 Carbon forms chains

Energy (kJ/mol)

C-C 360
 N-N 230-280
 O-O 160-200



																																2										
																																										He
3	4																																									10
Li	Be																																									Ne
Lithium	Beryllium																																									Neon
6.9	9.0																																									18.0
11	12																																									Ar
Na	Mg																																									Ar
Sodium	Magnesium																																									Argon
23.0	24.3																																									36.0
19	20																																									36
K	Ca	21	22	23	24	25	26	27	28	29	30																					36										
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc																					36										
39.1	40.1	45.0	47.9	50.9	52.0	54.9	55.8	58.9	58.7	63.5	65.4																					36										
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																									
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																									
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine	Xenon																									
85.5	87.6	88.9	91.2	92.9	95.9	98.9	101.1	106.4	106.3	107.9	112.4	114.8	118.7	121.8	127.6	126.9	131.3																									
Cs	Ba																															131.3										
Cesium	Barium																															131.3										
132.9	137.4																															131.3										
87	88																															86										
Fr	Ra																															86										
Francium	Radium																															86										
223.0	226.0																															222.0										
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71																												
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																												
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium																												
138.9	140.1	140.9	144.2	147.0	150.4	151.9	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0																												
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103																												
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																												
Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium																												
139.0	232.0	231.0	238.0	237.0	244.0	243.0	247.0	247.0	251.0	254.0	253.0	256.0	254.0	257.0																												



$2s^2 2p^2$

$3s^2 3p^4$

5. Carbon Forms Multiple Bonds

Bond	Bond Dissociation Energy (kJ/M)
C—C	360
C=C	700
C≡C	950
C—O	400
C=O	750
C—N	360
C=N	700
C≡N	950

Organic Chemistry

- Structure
- Reactivity
- *Structure* and *reactivity* are correlated.

STRUCTURE



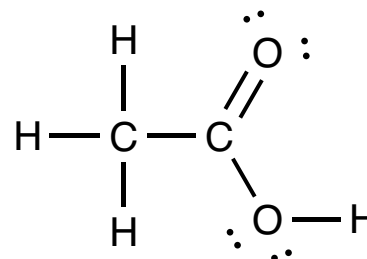
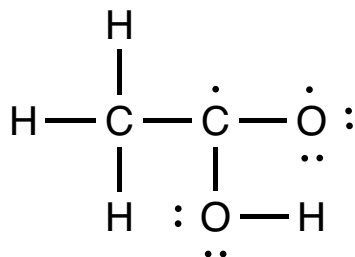
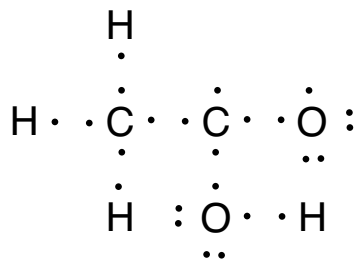
REACTIVITY

Goals

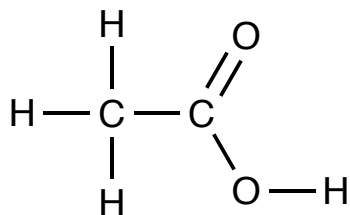
- Assign Structure and Name to Organic Compounds.
- Predict:
 - The tridimensional structure
 - The effects on reactivity (reaction rates and equilibrium constants)
- Design simple synthetic pathways
- Communicate with an appropriate language

Drawing molecules

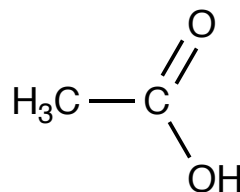
Acetic Acid



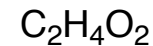
Lewis structures



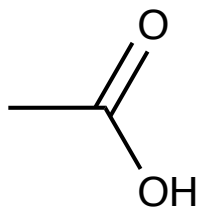
Structural Formula



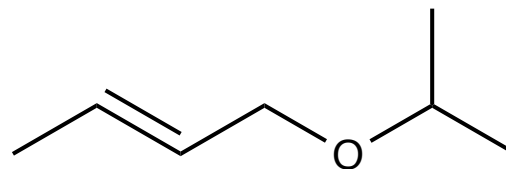
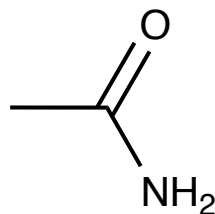
Condensed Formula



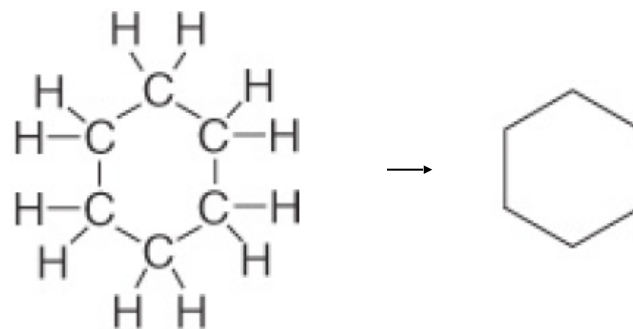
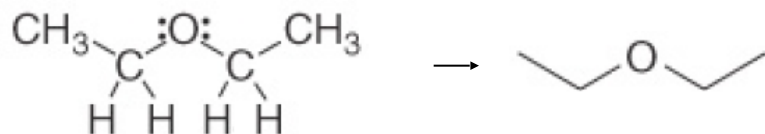
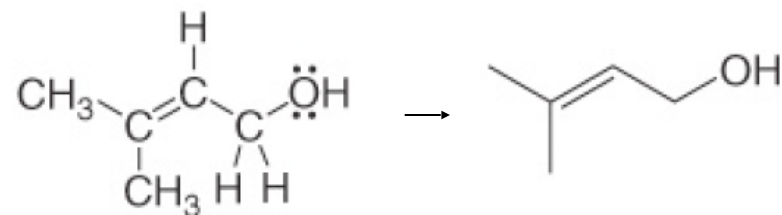
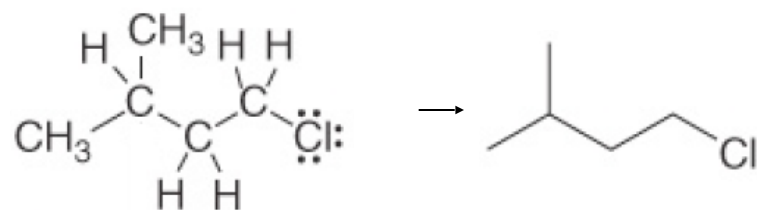
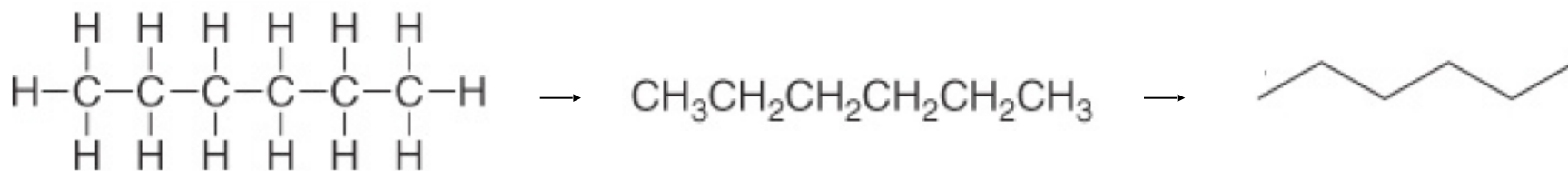
Empirical
Formula



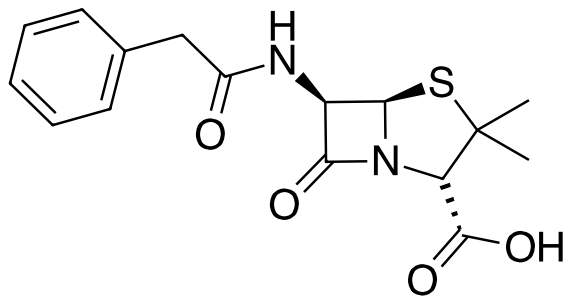
Skeletal Formula



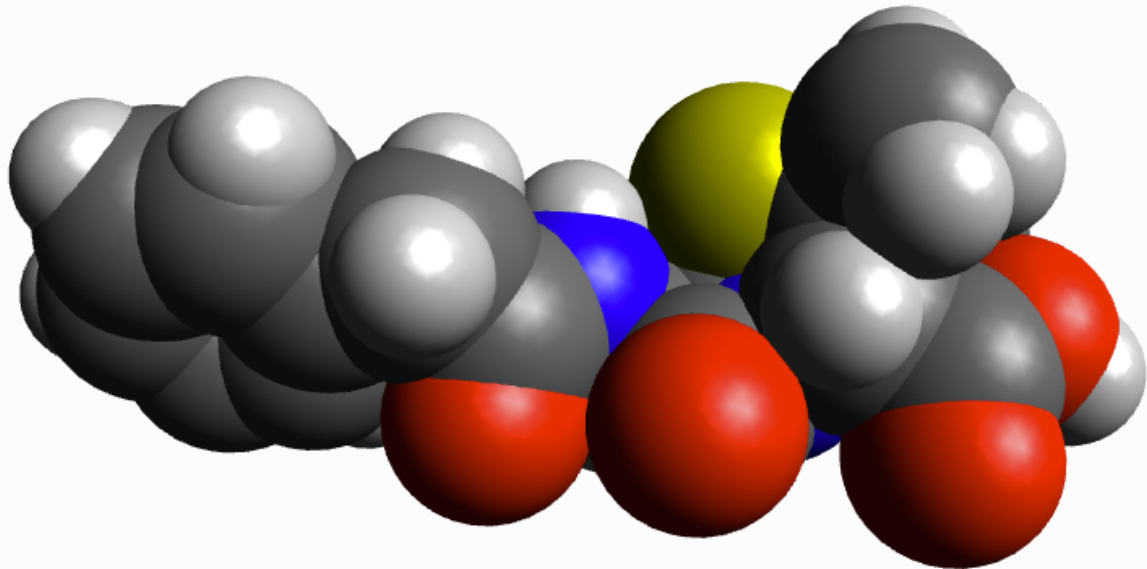
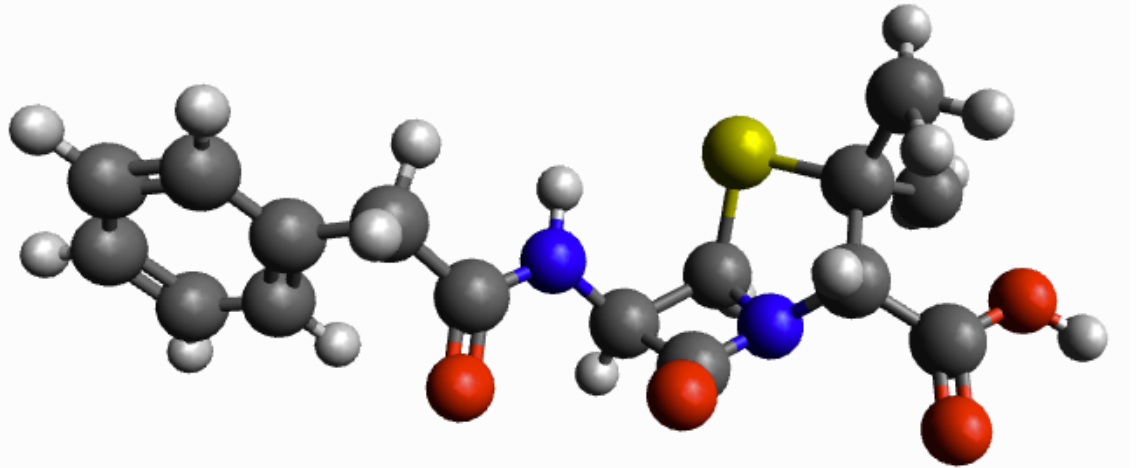
Examples



Molecular Models



Benzylpenicillin
(penicillin G)



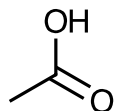
Element Coloring Scheme

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	A*	Rf	Db	Sg	Bh	Hs	Mt									

(L:)	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
(A:)	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

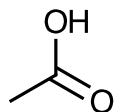
Line Notations

SMILES (**S**implified **M**olecular **I**nput **L**ine **E**ntry **S**ystem)



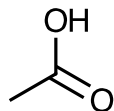
CC(=O)O

InChI (**I**nternational **C**hemical **I**dentifier)

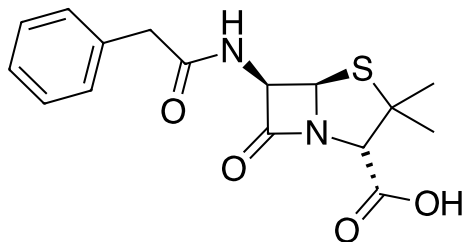


InChI=1S/C2H4O2/c1-2(3)4/h1H3,(H,3,4)

InChIKey (A hashed version of InChI)



QTBSBXVTEAMEQO-UHFFFAOYSA-N



[NIH
molecular
editor](#)

SMILES: CC(=O)[C@@H]3C2C(=O)[C@@H](NC(=O)Cc1ccccc1)[C@H]2SC3(C)C

InChI: InChI=1S/C18H21NO3S/c1-10(20)14-13-16(22)15(17(13)23-18(14,2)3)19-12(21)9-11-7-5-4-6-8-11/h4-8,13-15,17H,9H2,1-3H3,(H,19,21)/t13?,14-,15-,17+/m1/s1

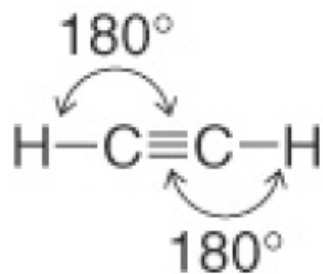
InChIKey: SOQSAIZEYNYAA-LZMBWQIGSA-N

Atomic Structure and Bonding

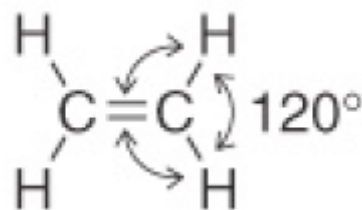
Chapter 1
Organic Chemistry, *8th Edition*
John McMurry

Geometry – VSEPR Theory

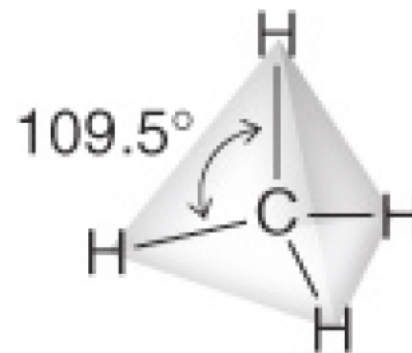
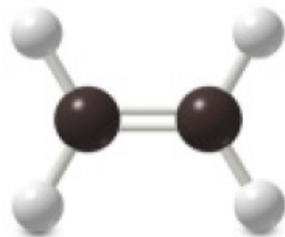
Number of groups	Geometry	Angle
2	linear	180°
3	trigonal planar	120°
4	tetrahedral	109.5°



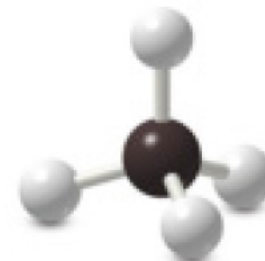
acetylene



ethylene



methane



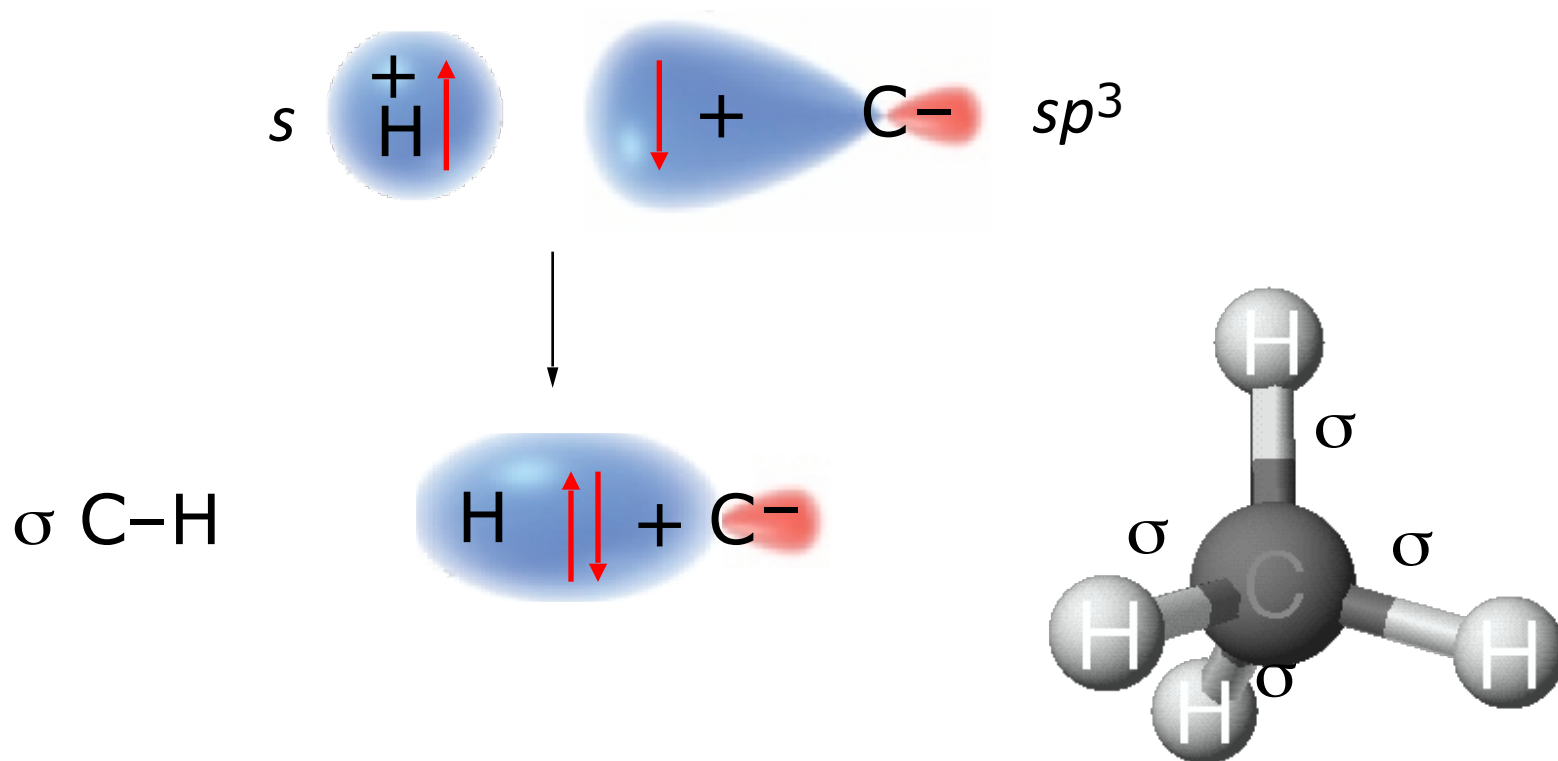
Energies of Multiple Bonds

Bond	Bond Dissociation Energy (kJ/M)
C—C	360
C=C	700
C≡C	950
C—O	400
C=O	750
C—N	360
C=N	700
C≡N	950

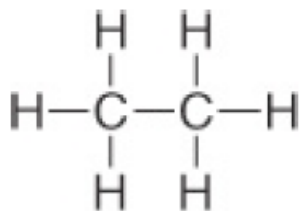
The Lewis model is not adequate!

Methane

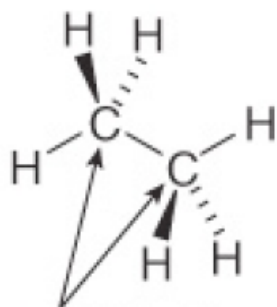
The overlap of a half-full $1s$ orbital of hydrogen with a half-full sp^3 orbital of carbon bond gives a σ orbital.



Ethane

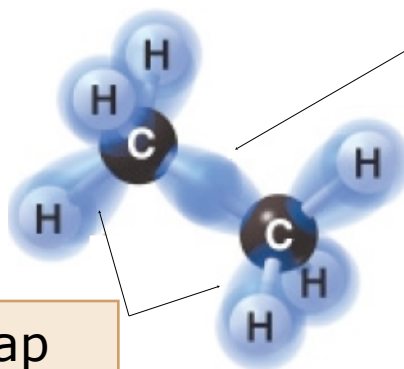
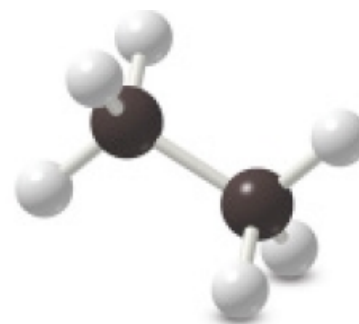


ethane



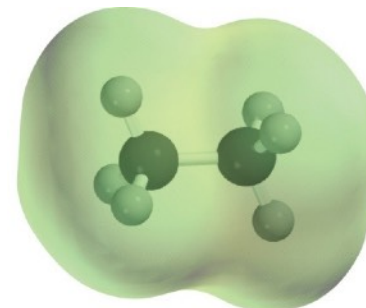
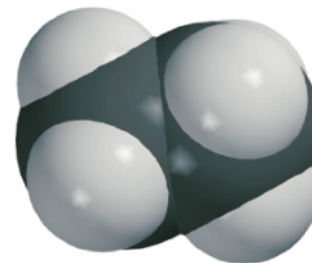
tetrahedral sp^3 C

=

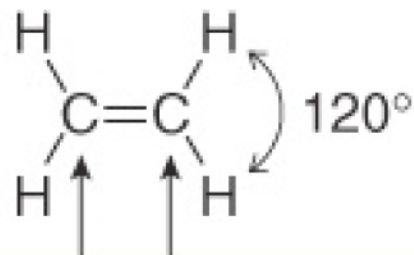


sp^3 hybrids on C overlap with $1s$ orbitals on H giving the C-H σ bonds.

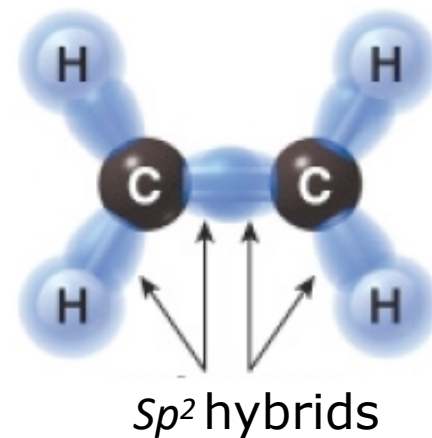
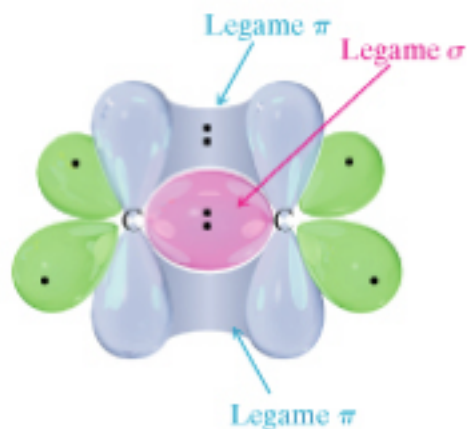
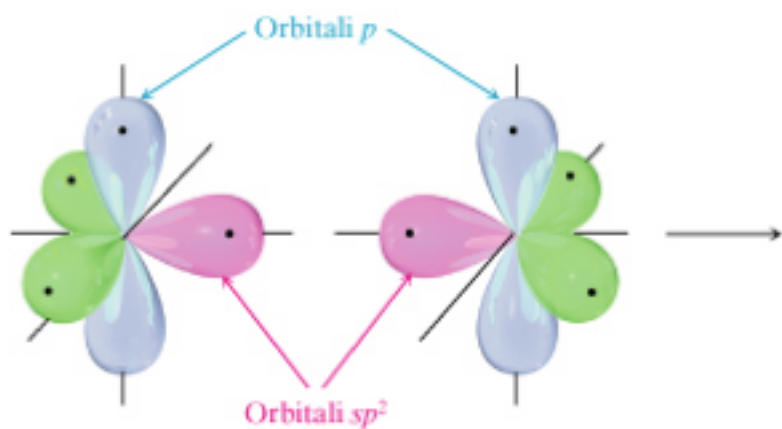
Two sp^3 hybrids overlap giving the C-C σ bond



Ethylene C₂H₄

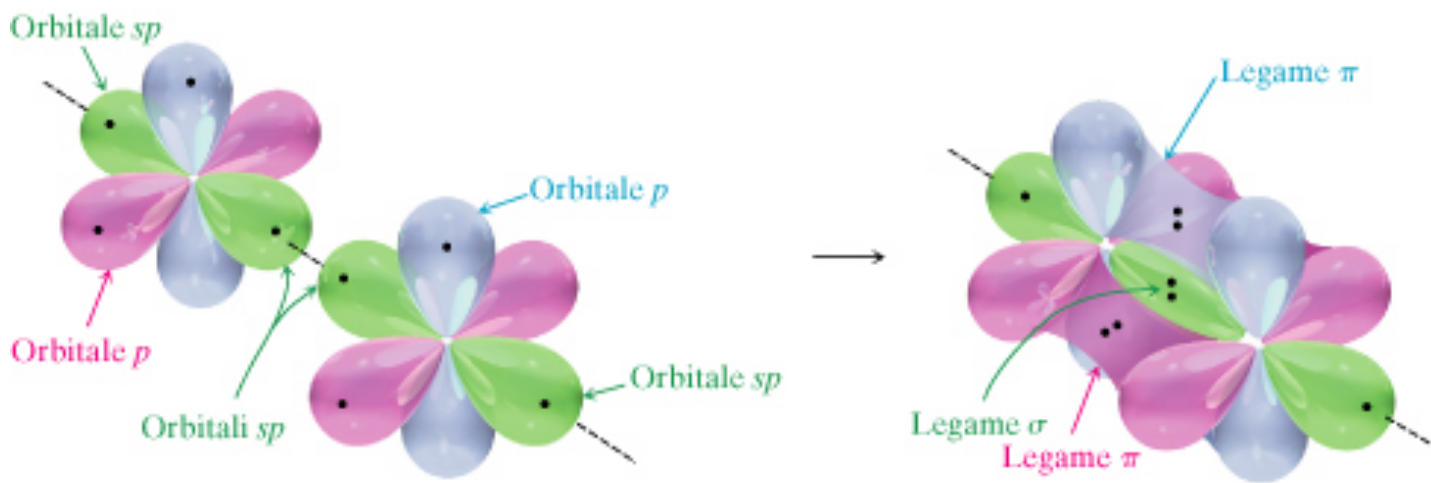


3 groups around C
C atoms are sp^2

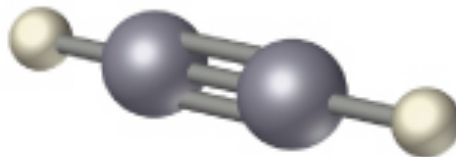
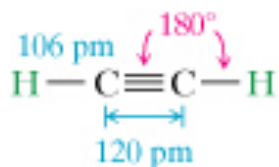


C-C double bond

Acetylene C₂H₂



C-C triple bond



Polar Bonds

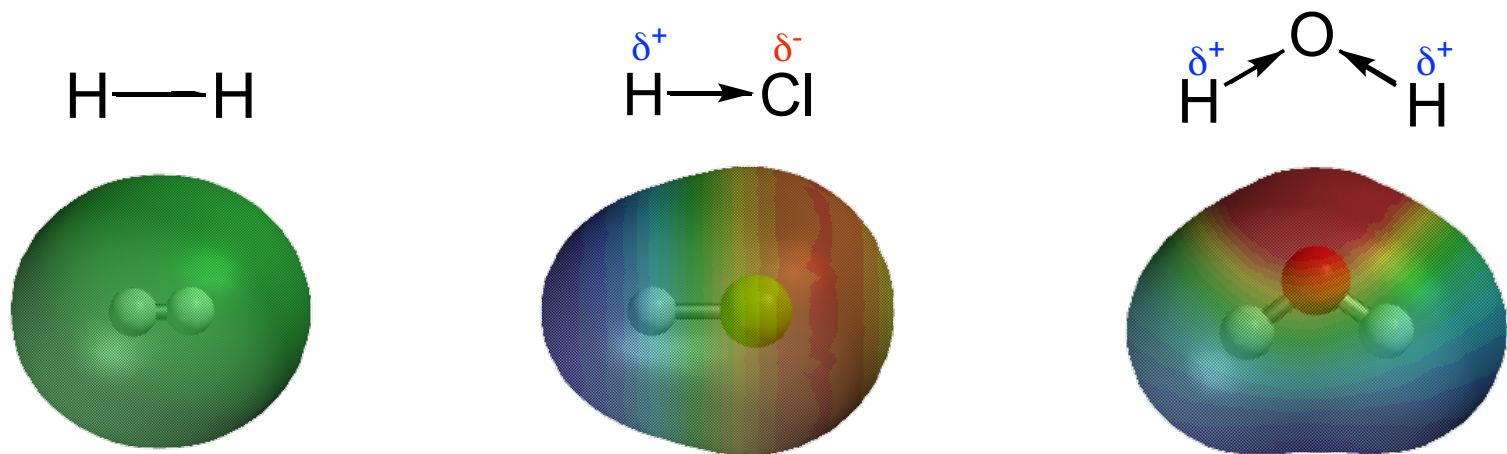
Intermolecular Interactions

Delocalised Bonds

Chapter 2
Organic Chemistry, *8th Edition*
John E. McMurry

Polar Covalent Bonds

- In polar bonds, bonding electrons are attracted towards the more electronegative atom.



- The higher the electronegativity difference, the higher the polar character of a covalent bond.
 - $\Delta X > 1.9 \Rightarrow$ ionic bond
 - $\Delta X < 0.5 \Rightarrow$ covalent bond
 - $\Delta X = 0.5 - 1.9 \Rightarrow$ polar covalent bond

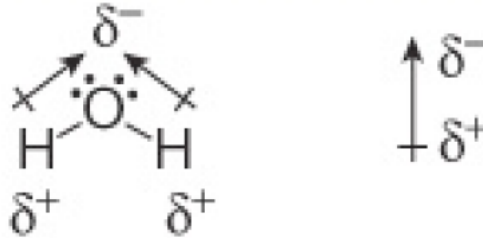
Pauling's Electronegativities

Element	Electronegativity
H	2,1
Li	1,0
Be	1,6
Na	0,9
Mg	1,2
K	0,8
Ca	1,0
Rb	0,8
Sr	1,0
Cs	0,7
Ba	0,9
Sc	1,3
Y	1,2
La	1,0
Ti	1,5
Zr	1,4
Hf	1,3
V	1,6
Nb	1,6
Ta	1,5
Cr	1,6
Mo	1,8
W	1,7
Mn	1,5
Tc	1,9
Re	1,9
Fe	1,8
Ru	2,2
Os	2,2
Co	1,9
Rh	2,2
Ir	2,2
Ni	1,9
Pd	2,2
Pt	2,2
Cu	1,9
Ag	1,9
Au	2,4
Zn	1,6
Cd	1,7
Hg	1,9
Al	1,5
Ga	1,6
In	1,7
Tl	1,8
B	2,0
Zn	1,6
Hg	1,9
Si	1,8
Ge	1,8
Sn	1,8
Pb	1,9
C	2,5
Si	1,8
Ge	1,8
Sn	1,8
Pb	1,9
N	3,0
P	2,1
As	2,0
Sb	1,9
Bi	1,9
O	3,5
S	2,5
Se	2,4
Te	2,1
Po	2,0
F	4,0
Cl	3,0
Br	2,8
I	2,5
At	2,1

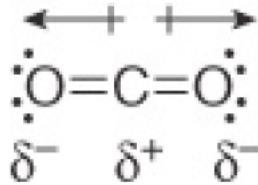
Dipole Moments

- Polar molecules have one or more polar bonds.

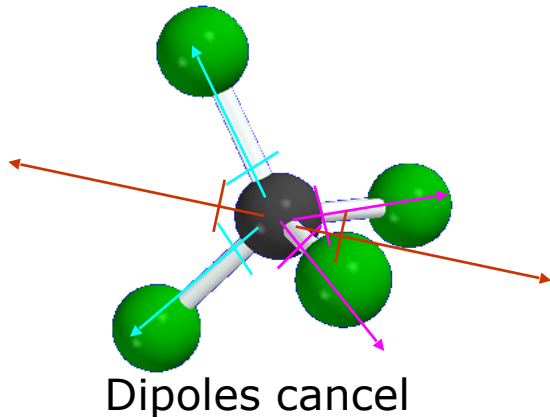
Es. H₂O



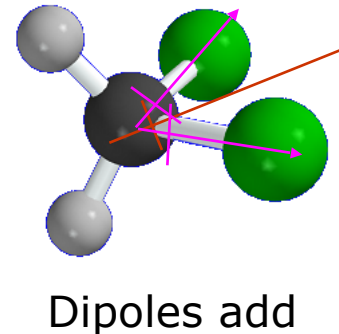
- Apolar molecules either do not have polar bonds or have polar bonds whose dipoles cancel each other. E.g. CO₂



CCl₄ $\mu = 0$ D



CH₂Cl₂ $\mu = 1.62$ D



Intermolecular interactions

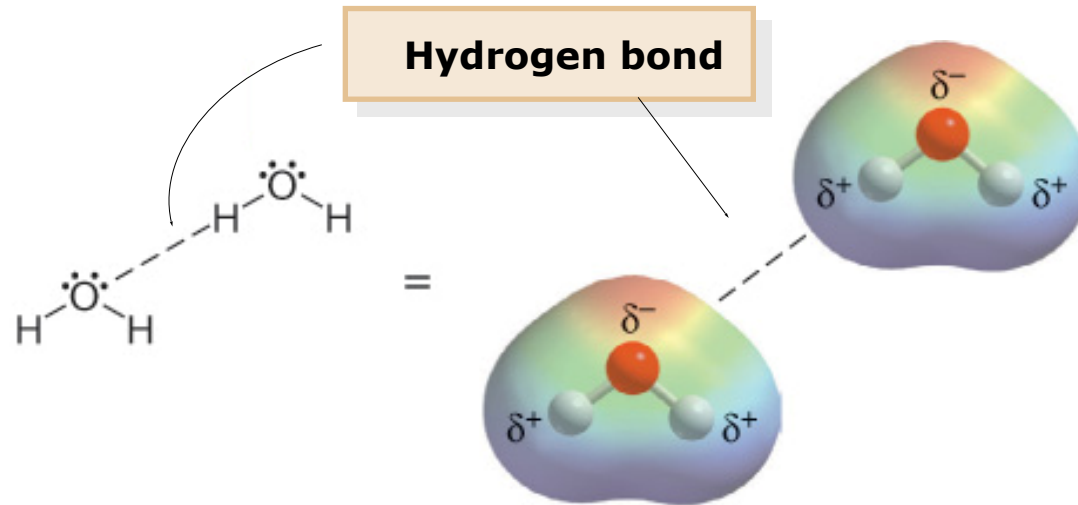
- ❑ Intermolecular interactions are also called non-covalent or non-bonded interactions.
- ❑ Intermolecular interactions depend on the type and number of functional groups.
- ❑ In neutral molecules there are three main types of intermolecular interactions.
 - Vand der Waals interactions (London dispersion forces) – VDW
 - Dipole-dipole interactions – DD
 - Hydrogen bonds– HB



strength

The Hydrogen Bond

- The hydrogen bond is an electrostatic interaction between a O-H or N-H group and a lone pair on O or N.

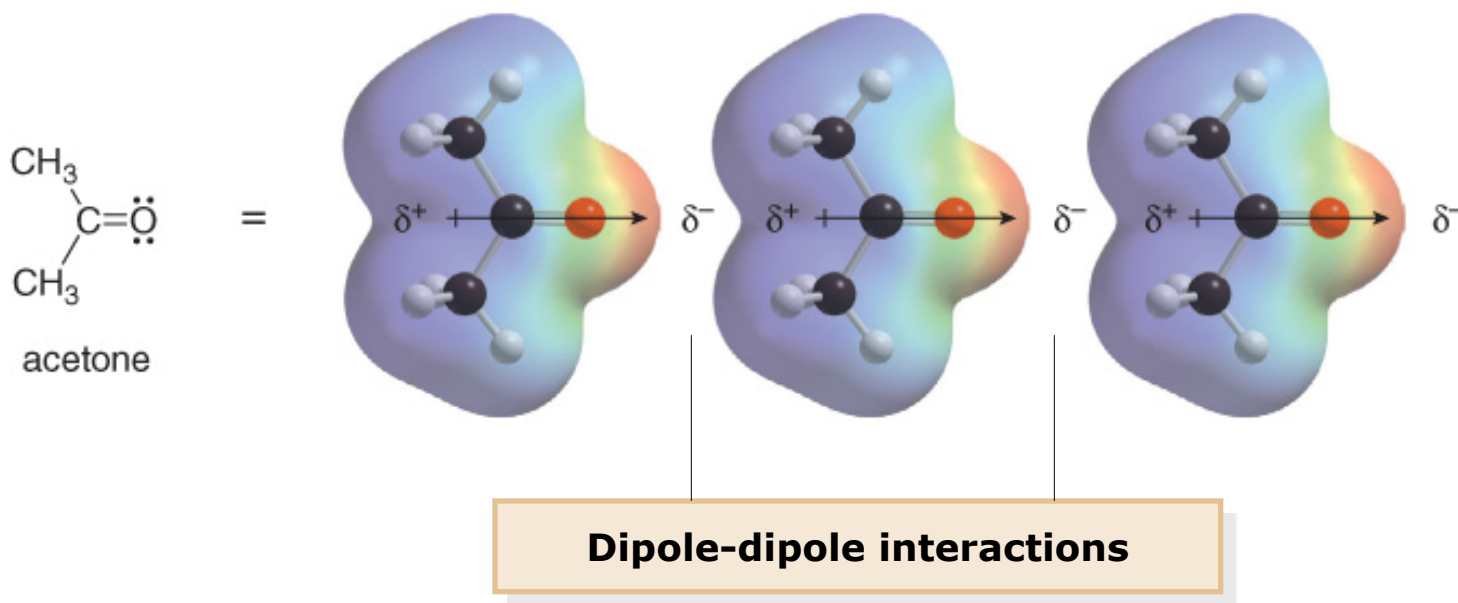


The Hydrogen Bond

	<i>MW</i>	<i>b.p. (°C)</i>	<i>H-bond</i>
$\text{H}_3\text{C}-\text{CH}_3$	30	-89	<i>none</i>
$\text{H}_3\text{C}-\text{NH}_2$	31	-6	<i>weak</i>
$\text{H}_3\text{C}-\text{OH}$	32	65	<i>strong</i>

Dipole-Dipole Interactions

- Dipole-dipole interactions are attraction forces between the permanent dipoles of two molecules.

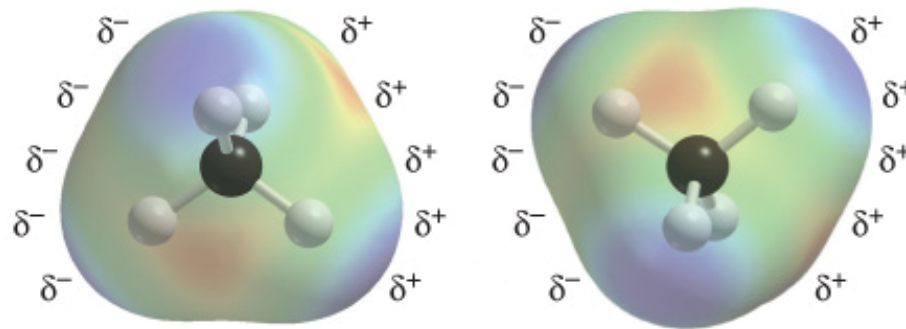


	<i>MW</i>	<i>b.p. (°C)</i>
<chem>CC=C</chem>	56	-5
<chem>CC(=O)C</chem>	58	56

Van der Waals (London) Forces

- ❑ VdW forces are weak interactions originating from temporary variations of the molecule's electron density distribution.
- ❑ They are the only attractive forces in apolar molecules.

Van der Waals interactions between two CH₄ molecules

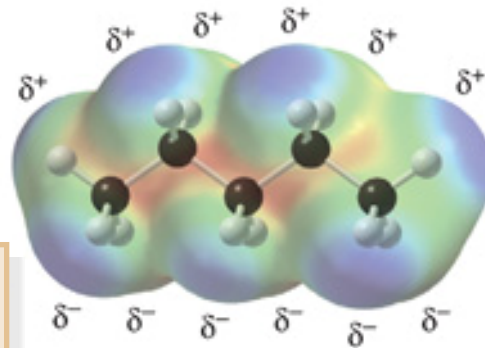


Dipoles generated by a temporary asymmetry in the electron density

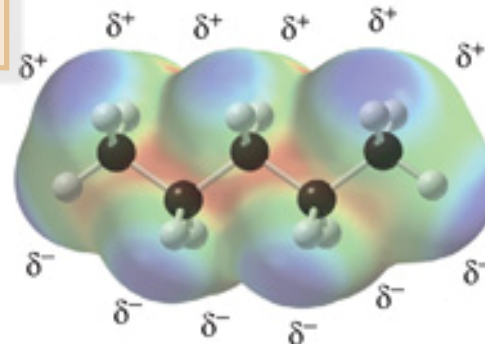
Van der Waals (London) Forces

- Van der Waals interactions are present in all molecules.
- The larger the surface area, the larger the attractive force between two molecules, and the stronger the intermolecular forces.

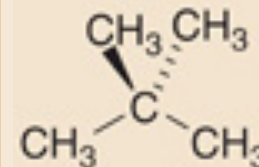
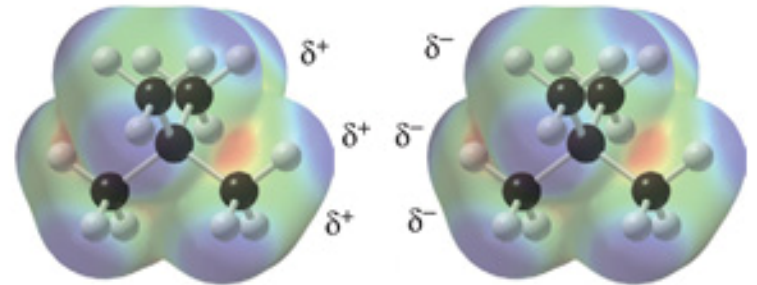
**Long, cylindrical molecules:
stronger interactions**



$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
n-pentane
***b.p.* 36 °C**



**Compact, spherical molecules:
weaker interactions**



neopentane
***b.p.* 10 °C**

Van der Waals (London) Forces

- ❑ VdW forces depend on polarizability.
- ❑ Larger atoms, like iodine, which have more loosely held valence electrons, are more polarizable than smaller atoms like fluorine, which have more tightly held electrons

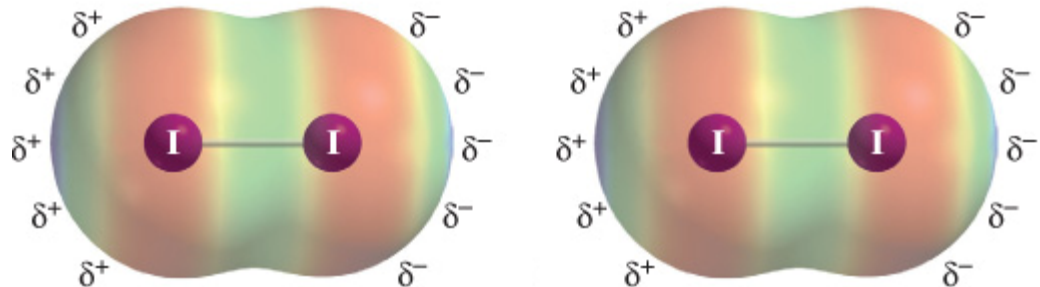
Weak interaction

Small atoms: lower polarizability



Large atoms: higher polarizability

Stronger interaction



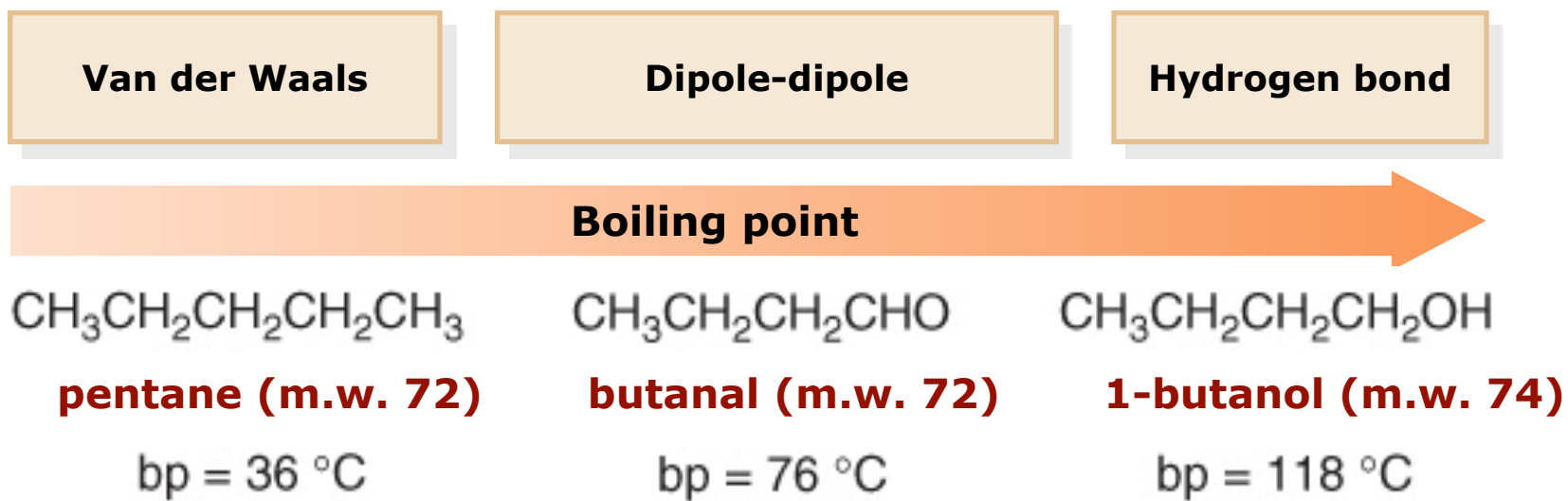
Summary

Interaction	Relative strength	Present in	Examples
Van der Waals VDW	Very weak	All molecules	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
Dipole-dipole DD	weak	Permanent dipoles	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
Hydrogen bond HB	strong	Molecules with OH, NH, funct. groups	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
ionic	Very strong	Ionic compounds	NaCl, LiF

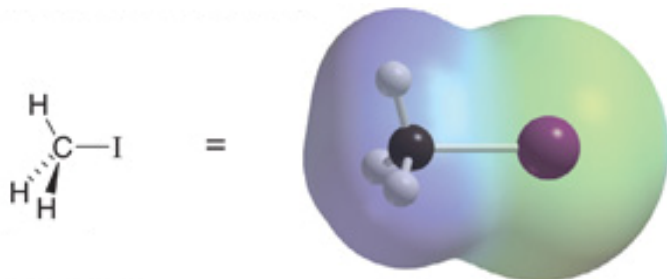
Polar molecules interact strongly than apolar ones.

Boiling Point

- ❑ The boiling point is the temperature at which the vapor pressure of a liquid is equal to the external pressure.
- ❑ Energy is required to break intermolecular interactions.
- ❑ The higher the intermolecular interactions, the higher the b.p..
- ❑ Compounds with similar M.W.:

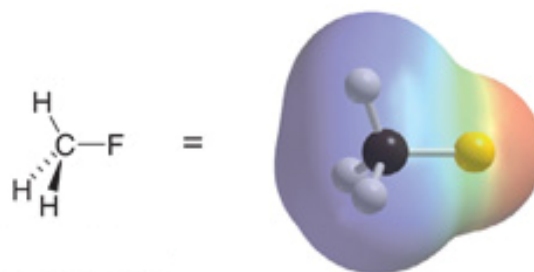


Boiling Point



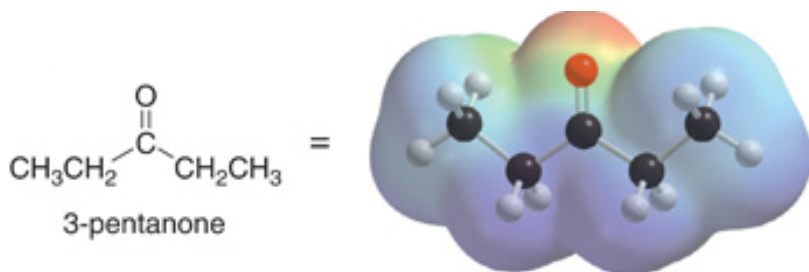
b.p. = 42 °C

I is more polarizable



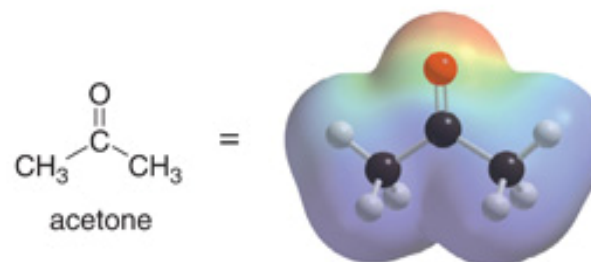
b.p. = -78 °C

Smaller F has a low polarizability



b.p. = 102 °C

Larger surface area



b.p. = 56 °C

Smaller surface area

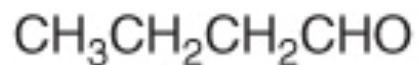
Melting Point

- M.p. and b.p. follow the same trend.



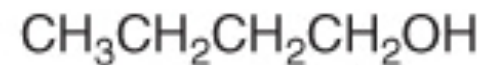
pentane

mp = $-130\text{ }^\circ\text{C}$



butanal

mp = $-96\text{ }^\circ\text{C}$



1-butanol

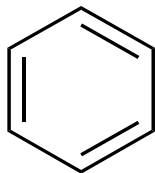
mp = $-90\text{ }^\circ\text{C}$

Melting point

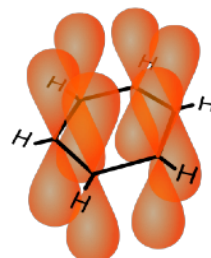


Resonance - Delocalized Bonds

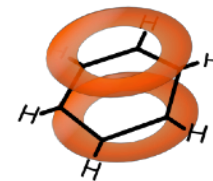
Benzene (C_6H_6)



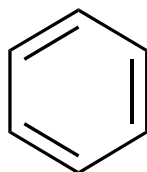
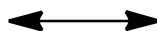
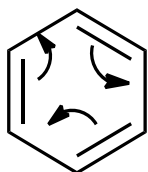
Very stable
6 identical C-C bonds



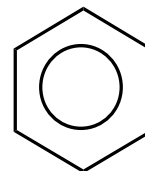
6 p-orbitals



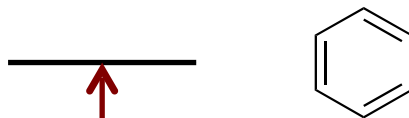
delocalized



Resonance structures

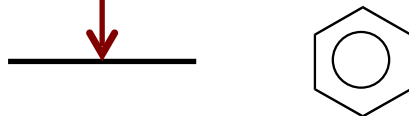


Resonance hybrid



6 localized
 π electrons

$E_r = 150.7 \text{ kJ/mol}$
(36 kcal/mol)



6 delocalized
 π electrons

Resonance

1. Resonance structures **are not real**. No single resonance structure can adequately represent the real structure of a species with delocalized electrons.
2. Resonance structures **are not isomers**. They only differ in the distribution of electrons not in the disposition of the nuclei.
3. Resonance structures **are not in equilibrium**.

Acids and Bases

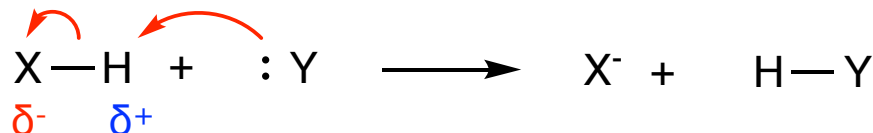
Electrophiles and Nucleophiles

Organic Reaction Mechanisms

Chapters 2 & 6
Organic Chemistry, *8th Edition*
John McMurry

Brønsted-Lowry Acids and Bases

- An acid-base reaction is a proton transfer reaction



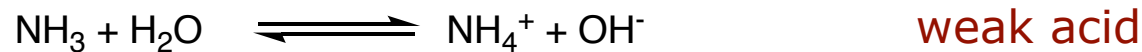
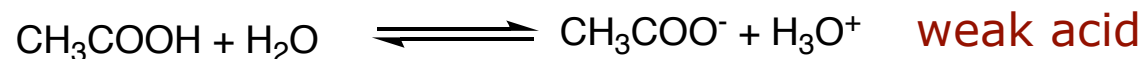
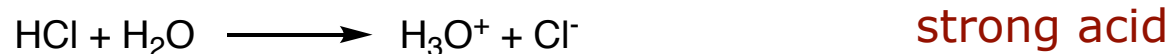
- Acids donate protons to an acceptor

All Brønsted-Lowry acids contain a polar X-H bond.

(X=O, Halogens)

- Bases accept protons from a donor

All Brønsted-Lowry bases contain a lone pair.



Organic Acids

Element	Electronegativity	Bond	Acidity
H	2.1		
C	2.5	C-H	NO
N	3.0	N-H	NO
O	3.5	O-H	YES

Formula	Name	K_a	pK_a	acidity
R-OH	alcohols	$< 10^{-15}$	> 15	less than H ₂ O
Ar-OH	phenols	10^{-9}	9	slightly dissociated
R-COOH	carboxylic acids	$> 10^{-5}$	> 5	more dissociated

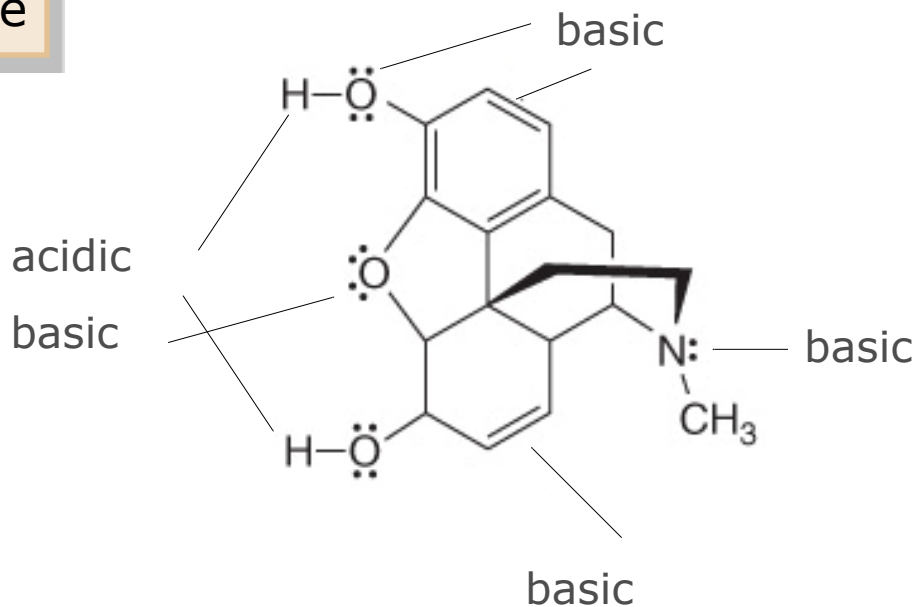
Organic Bases

Group	electron pairs	electronegativity	Basicity
$\begin{array}{c} \\ -\text{C}- \\ \end{array}$	NO	-	NO
$\begin{array}{c} \\ -\text{N}: \\ \end{array}$	1	3.0	YES
$\begin{array}{c} \cdot\cdot \\ \\ -\text{O}- \\ \\ \cdot\cdot \end{array}$	2	3.5	WEAK
$\begin{array}{c} \cdot\cdot \\ \\ \text{X}^- \\ \\ \cdot\cdot \end{array}$	at least 1		STRONG

Brønsted-Lowry Acids and Bases

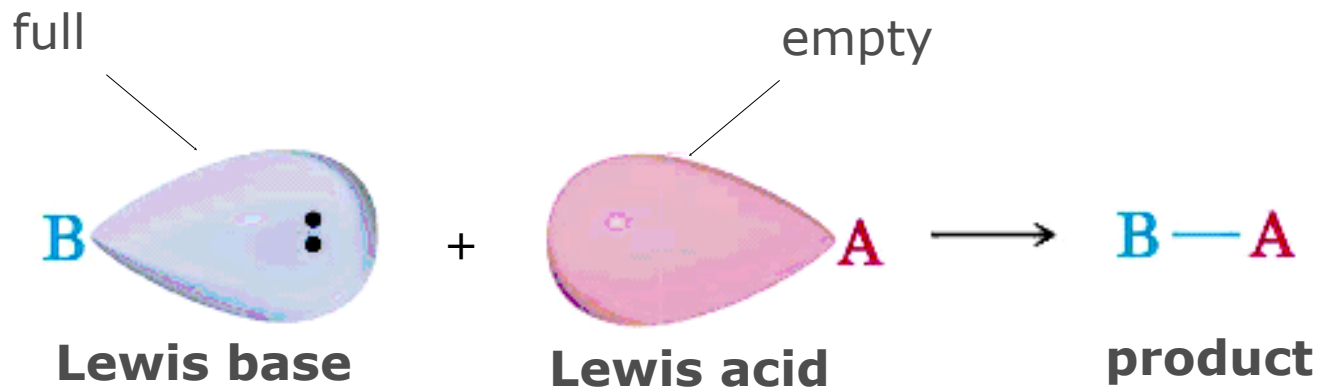
- Certain molecules can behave both as acids and bases.

Morphine



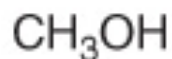
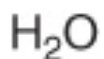
Lewis Acids and Bases

- A Lewis acid accepts an electron pair from a donor. Lewis acids have a low energy empty orbital.
- A Lewis base donates an electron pair to an acceptor. Lewis bases have a high energy full orbital (lone pair or π bonds).



Lewis Acids and Bases

- All Brønsted-Lowry acids are Lewis acids. Not all Lewis acids are Brønsted-Lowry acids.
- Only species with ionizable protons are Brønsted-Lowry acids. Any electron acceptor is a L.A.

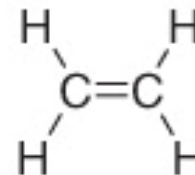
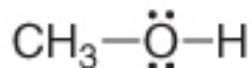
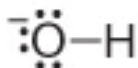


Brønsted-Lowry and
Lewis acids



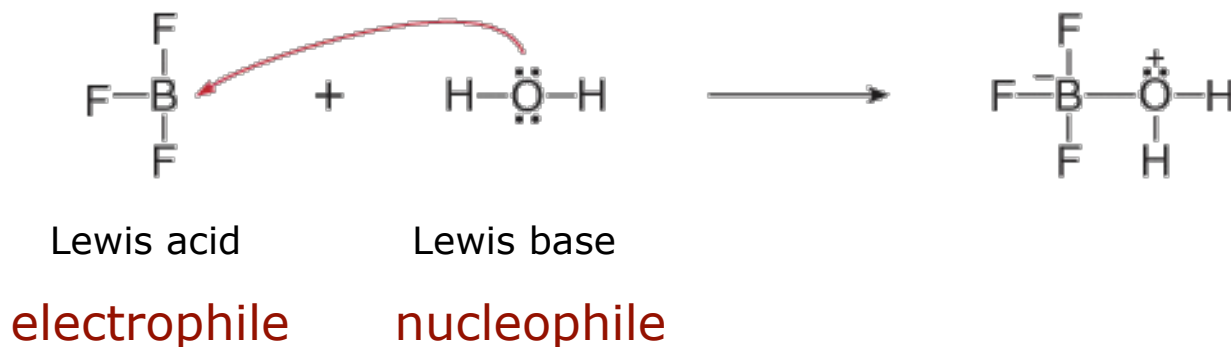
Lewis acids

- All Brønsted-Lowry bases are also Lewis bases. They must have either a lone pair or a π bond.



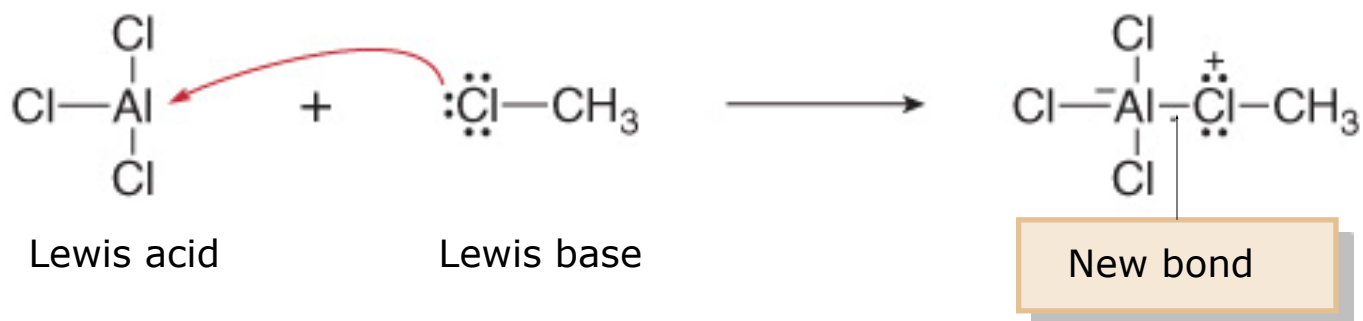
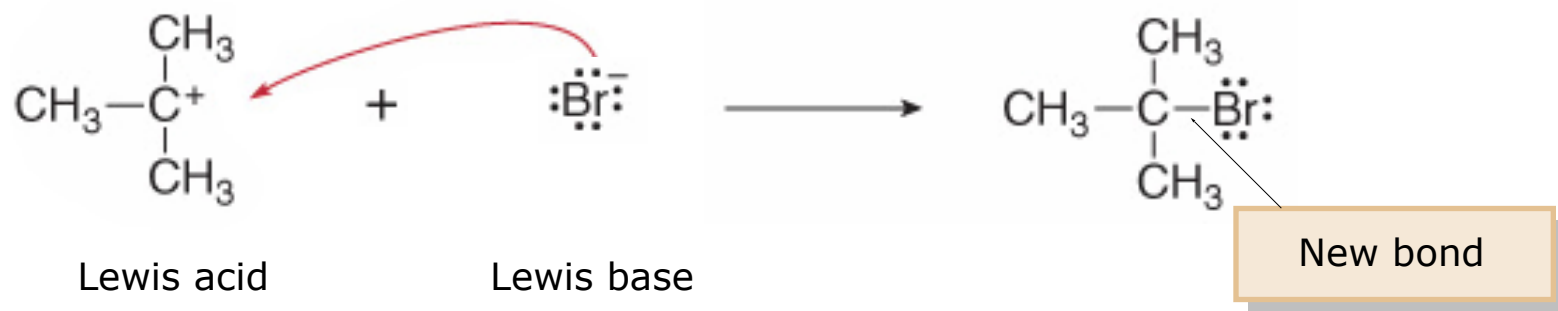
Reactions Between Lewis Acids and Bases

- Organic reactions can in most cases be described as reactions between electron poor species (Lewis acids) and electron rich species (Lewis bases).
- The electron poor species (Lewis acid) is called **electrophile**.
- The electron rich species (Lewis base) is called **nucleophile**.
- The movement of electrons is indicated with curved arrows.



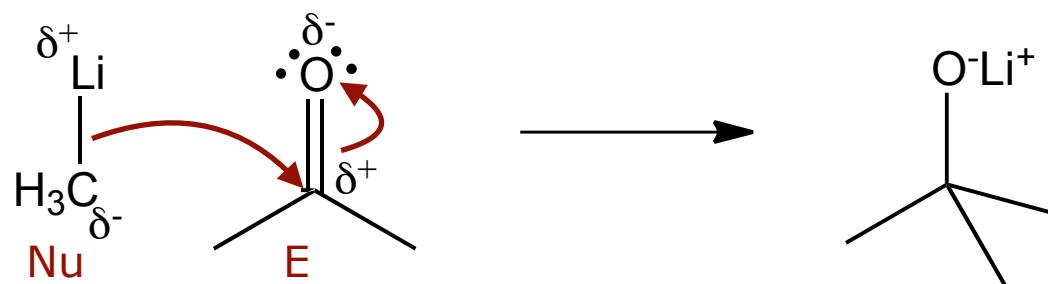
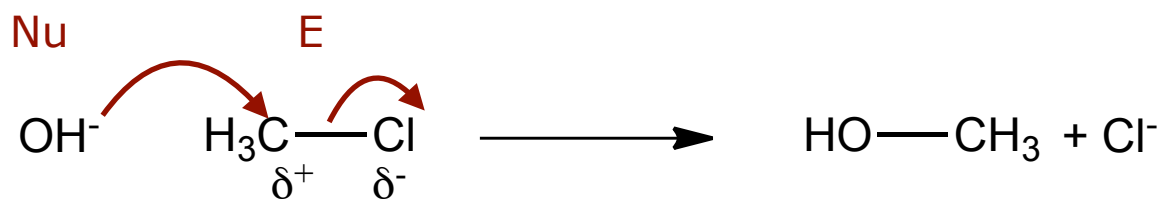
Electrophiles and Nucleophiles

electrophile nucleophile



Electrophiles and Nucleophiles

- Nucleophiles and electrophiles may also contain polar bonds

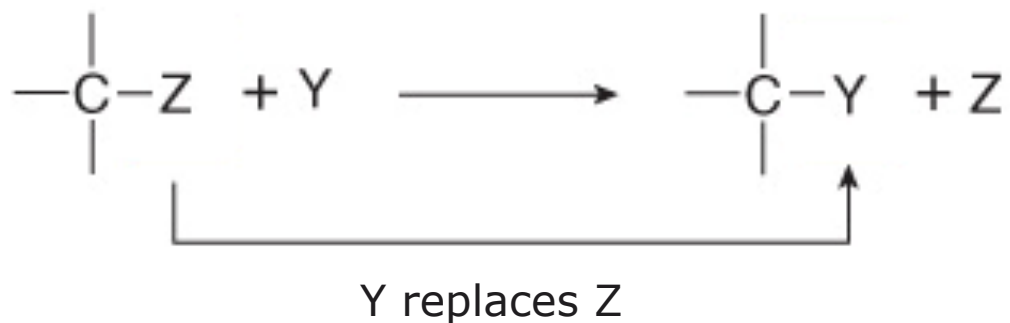


Organic Reactions

- Type of reaction (bond breaking/bond formation):
 - substitution
 - addition
 - elimination
 - rearrangement/transposition
- Mechanism = movement of electrons:
 - ionic (polar)
 - radicalic
 - pericyclic

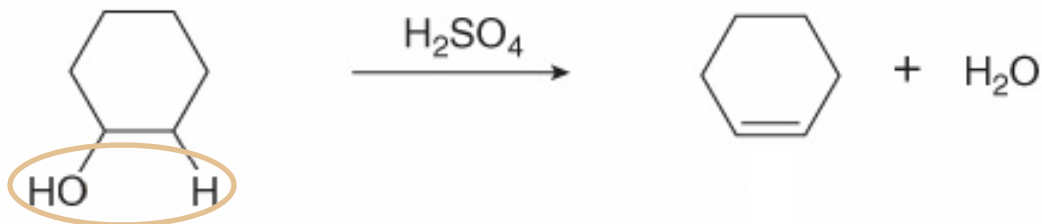
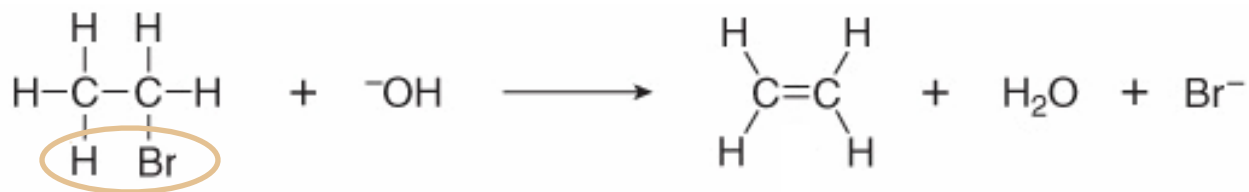
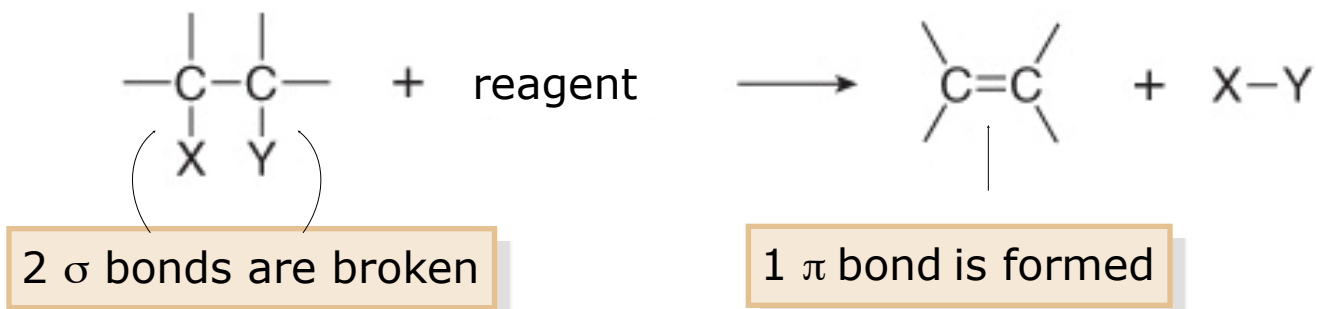
Substitutions

- ❑ In a general substitution reaction, an atom or group Y replaces an atom or group Z at carbon.
- ❑ Substitutions involve breaking and forming σ bonds.



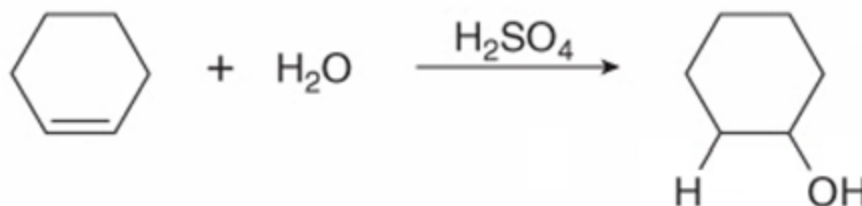
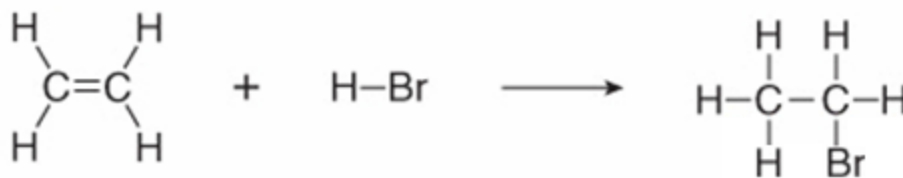
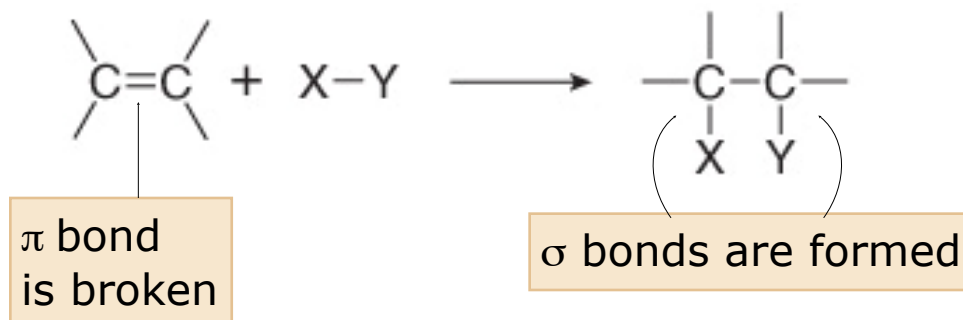
Eliminations

- In an **elimination** reaction two σ bonds are broken and one π bond is formed.



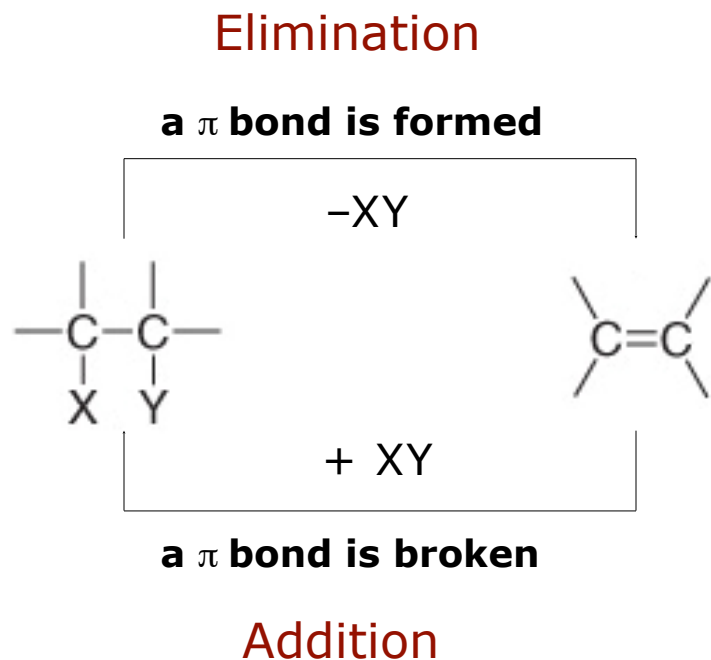
Additions

- In an **addition** reaction a π bond is broken and two new σ bond are formed.



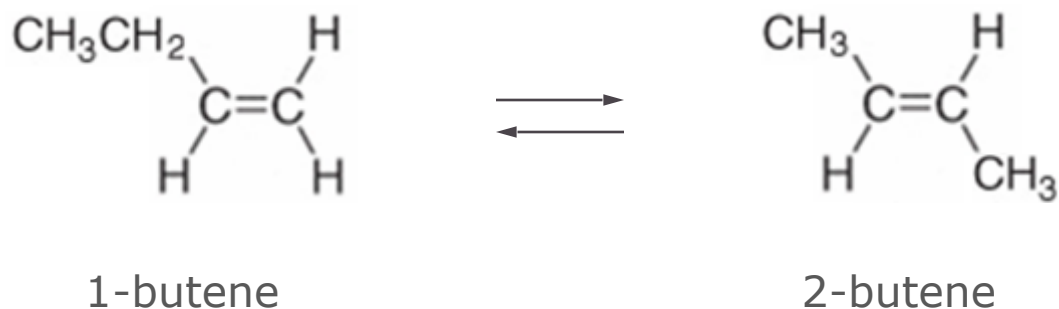
Additions and Eliminations

- Eliminations are the inverse of additions. A π bond is formed in eliminations and a π bond is broken in additions.

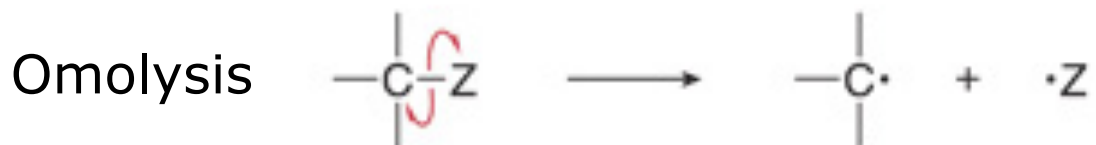


Rearrangements or Transpositions

- In a rearrangement or transposition the bonding pattern of a single reagent changes giving a constitutional isomer.



Bond Breaking



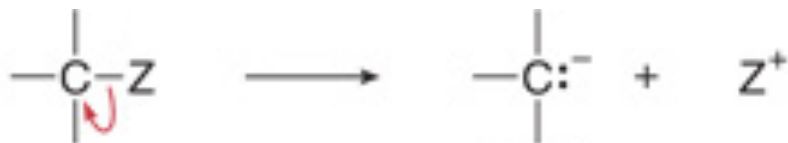
radicals are formed in *radical (homolytic) reactions*

Radical



ions are formed or react in *polar (ionic) reactions*

Carbocation

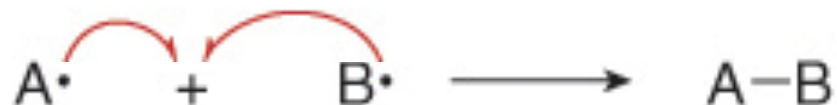


Carbanion

Bond Formation

□ A new bond can be formed in two ways:

- From two **radicals** each contributing a single electron.



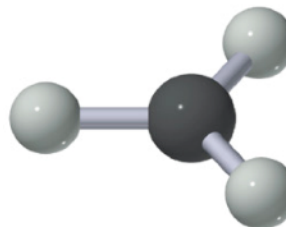
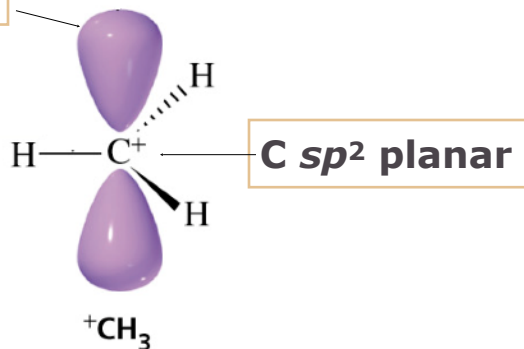
- From a **nucleophile** contributing an electron pair and an **electrophile** accepting the electron pair. Nu and E may be ions or neutral molecules



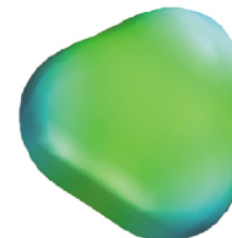
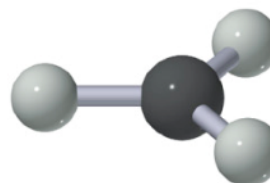
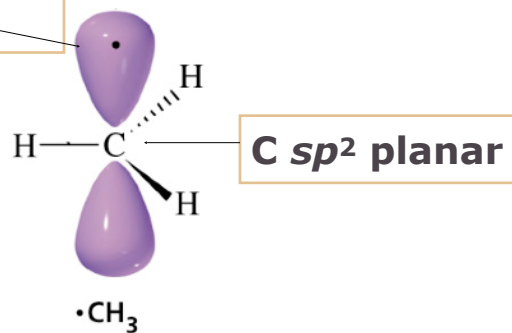
Energy is released in the formation of a bond

Carbocations, Carbanions, Radicals

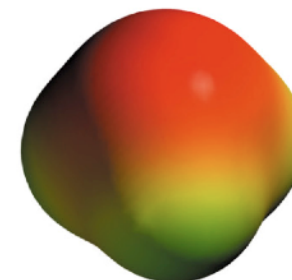
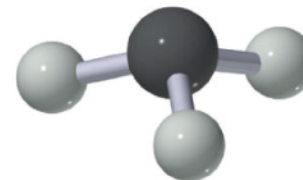
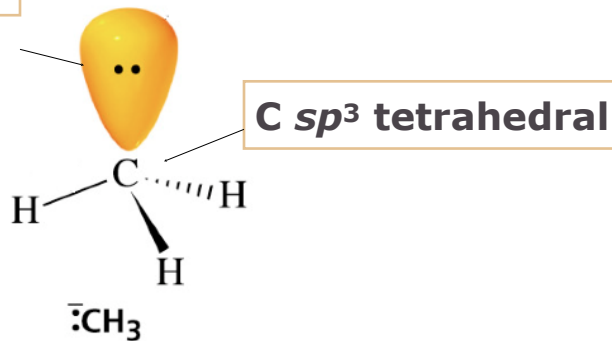
empty p orbital



Singly occupied p orbital

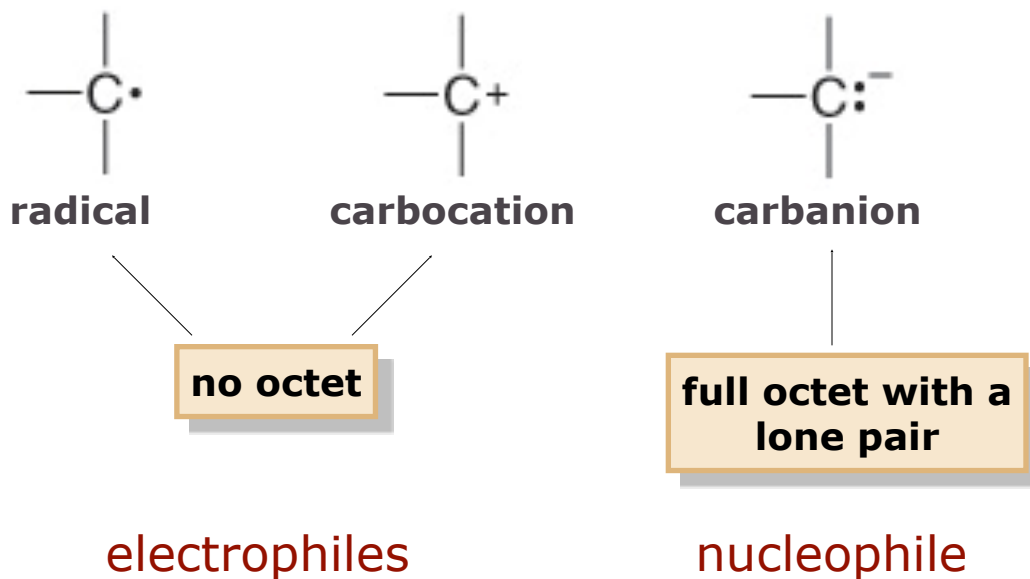


lone pair sp^3



Carbocations, Carbanions, Radicals

- Radicals and carbocations are **electrophiles** because the carbon atom does not have a full octet.
- Carbanions are **nucleophiles** because the carbon atom has a lone pair.



A Reaction Mechanism.....

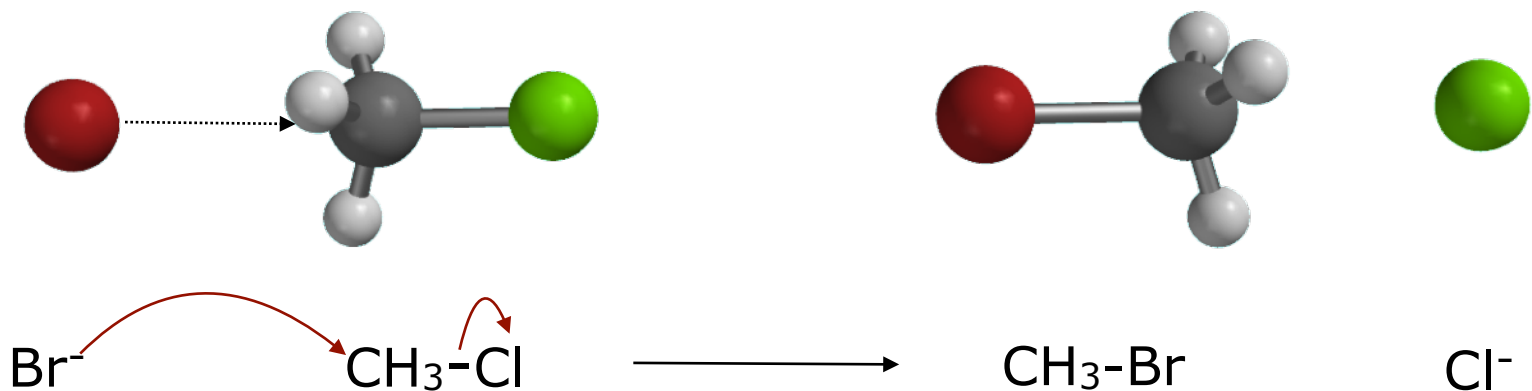
- Accounts for all reagents and products and their ratios.
- Describes in which order bonds are broken and formed and the rates of individual steps.
- In a *concerted reaction* reagents are directly converted into products in a single step.



- A multistep reaction involves the formation of one or more reactive intermediates.

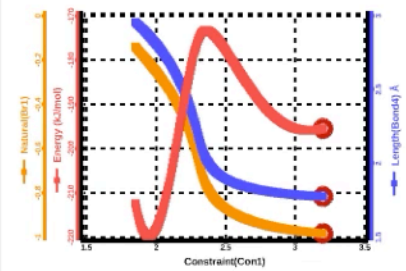
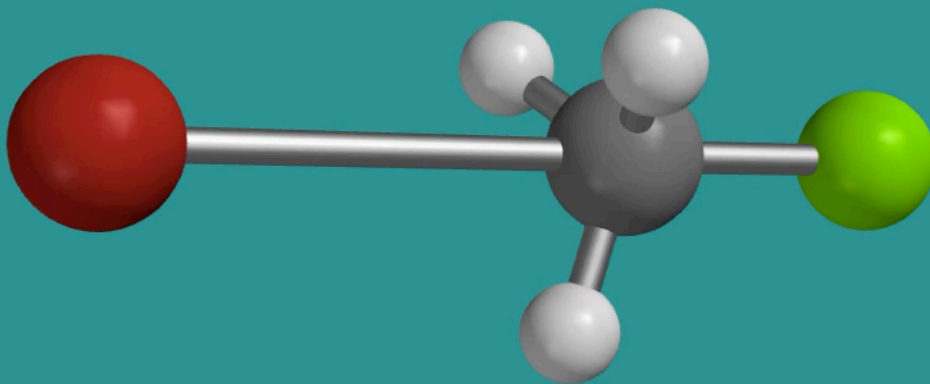


Transition State Theory and Collisional Theory



- ❑ Collisional theory: rigid collision between reacting species.
- ❑ Transition state theory: continuous deformation of reagent structure into product structure

Transition State Theory



Transition State Theory - Energy Diagrams

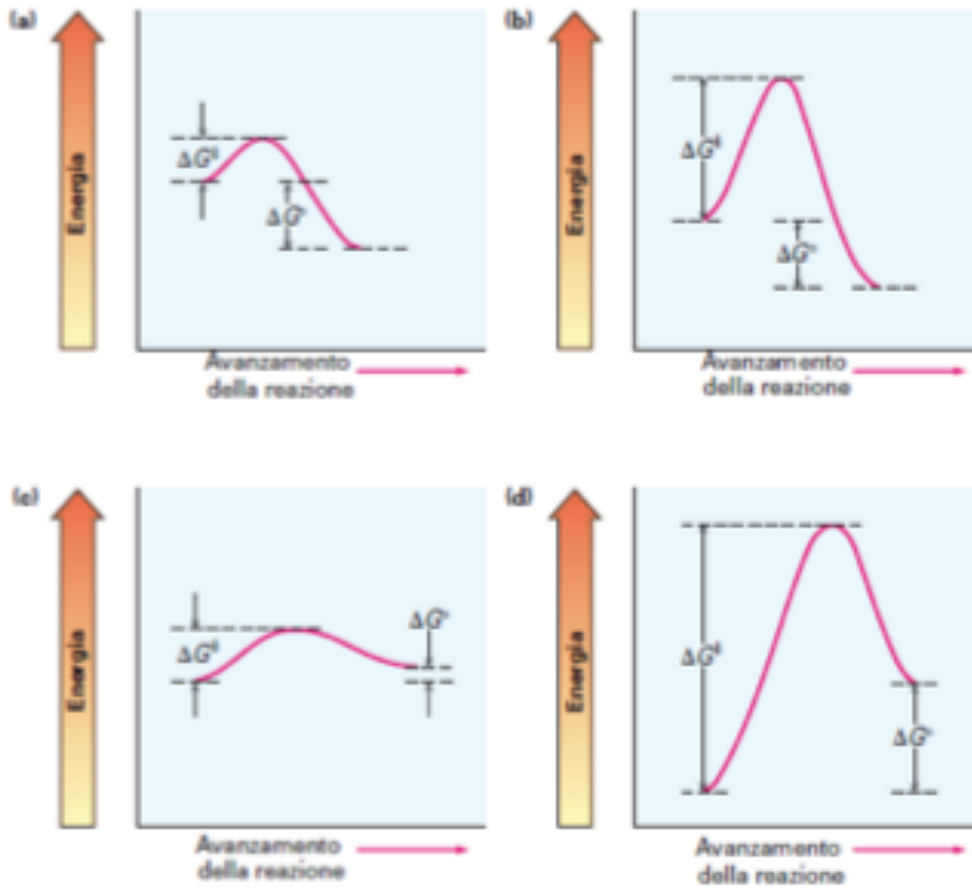
- The activation energy ΔG^\ddagger is the energy required for a reaction to take place.
- $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$
- ΔG^\ddagger is correlated with the reaction's rate constant.

Eyring equation:

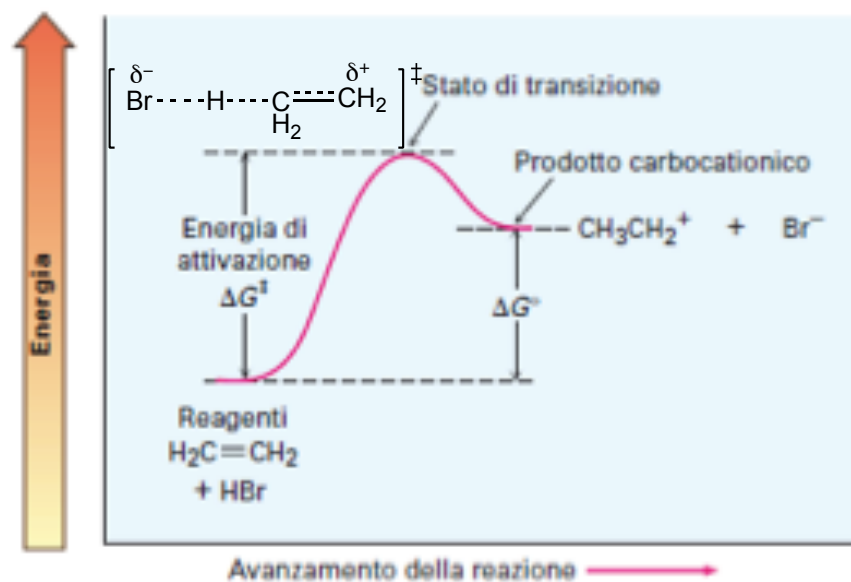
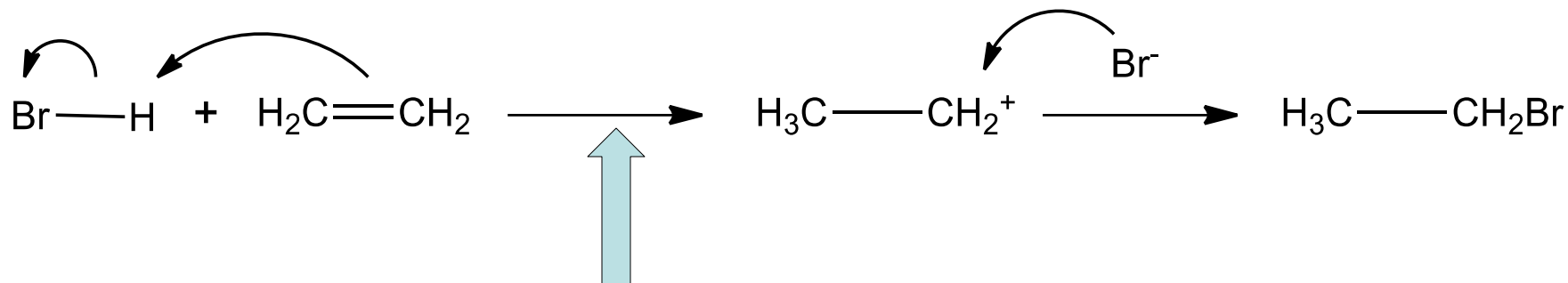
$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

- The transition state structure is intermediate between the structures of reagents and products. In the transition state there are partial bonds and partial charges (if the mechanism is ionic).
- Transition states are represented in brackets with the \ddagger symbol.

Energy Diagrams

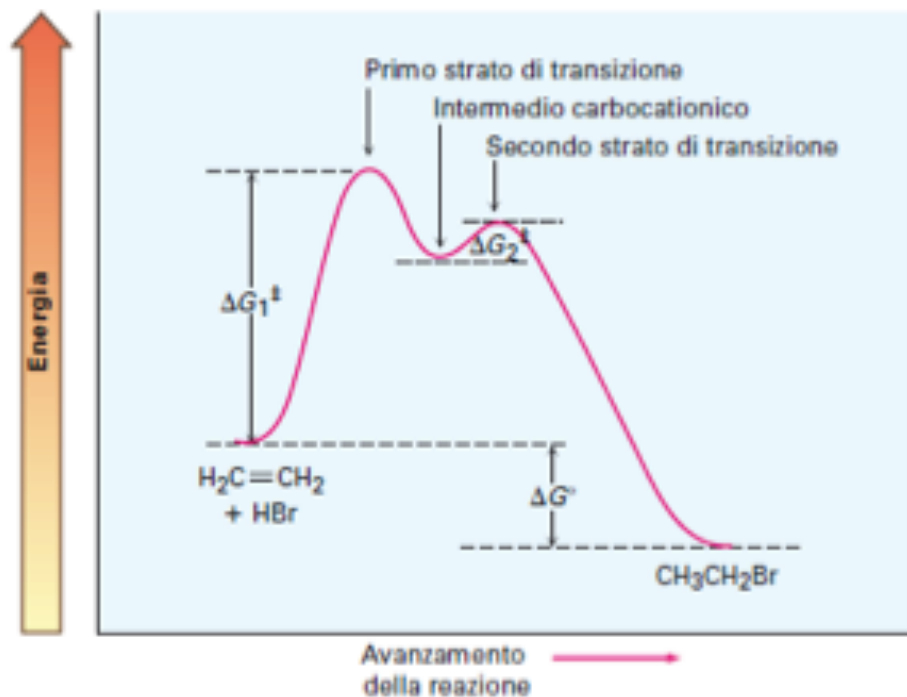
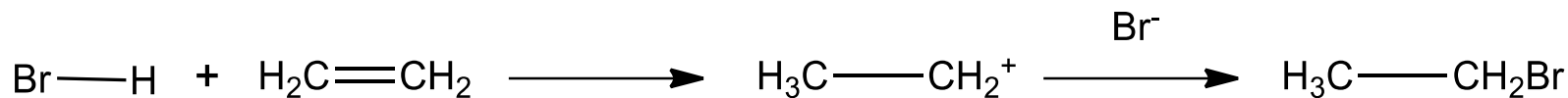


Energy Diagrams



Energy Diagrams

Complete energy diagram for the two-step reaction:



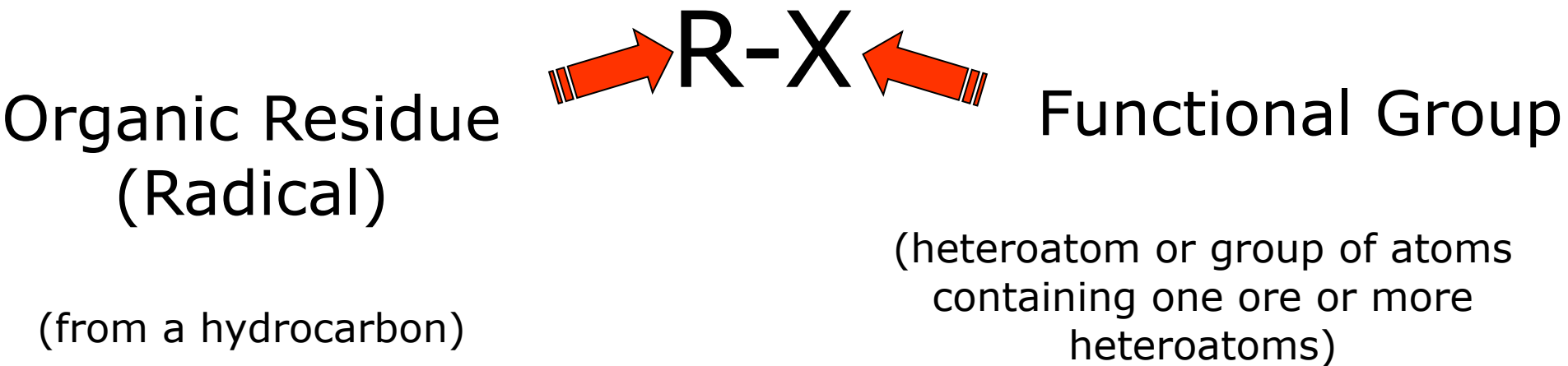
Functional Groups

Chapter 3.1

Organic Chemistry, *8th Edition*

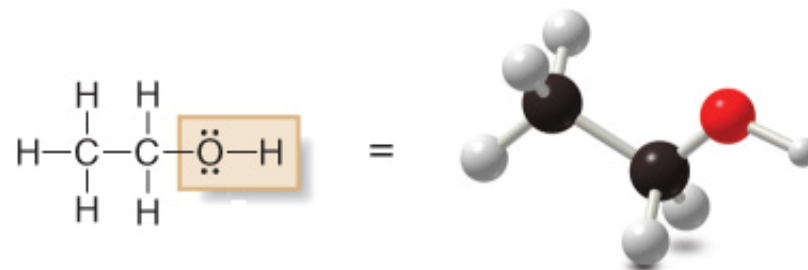
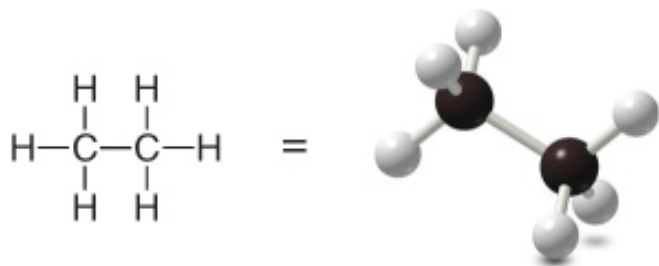
J. McMurry

Functional Groups



A functional group is an atom or a group of atoms all or in part \neq than C with specific and well defined physico-chemical properties.

Functional Groups



- Only C—C and C—H bonds
- No functional groups
- Does not possess polar bond or π bonds: very unreactive.
- Gas at NTP
- Insoluble in water

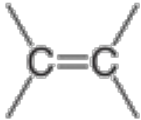
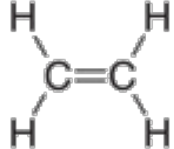


- OH functional groups
- Polar C-O and O-H bonds
- Lone pair on O
- Reacts with electrophiles
- Reacts with strong bases
- Liquid at NTP
- Soluble in water

Functional Groups

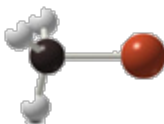
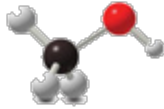

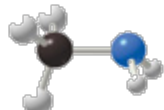

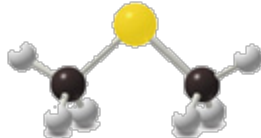
1. Define a class of compounds
 - Compounds belonging to the same class have **similar properties and reactivity**.
2. Are frequently the **reaction site**
 - Define the **reactivity** of a molecule
3. Determine the name
 - For example all ketones have the suffix **-one**:
 - » acet**one**
 - » cyclopropan**one**
 - » cortis**one**

Hydrocarbons

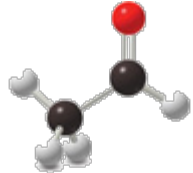
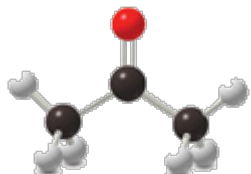
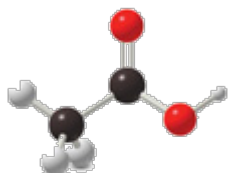
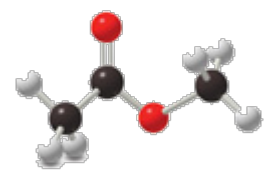
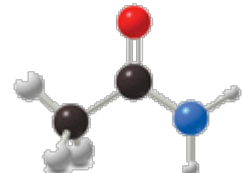
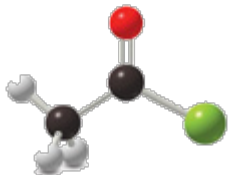
- Hydrocarbons possess only C–C e C–H bonds.
 - aliphatic** (alkanes, alkenes, alkynes) and **aromatic**.

Hydrocarbon	General	Example	Functional
Alkanes	R–H	CH ₃ CH ₃	-----
Alkenes			Double bond
Alkynes	—C≡C—	H–C≡C–H	Triple bond
Aromatics			Aromatic ring

Functional Groups Containing C–Y σ bonds

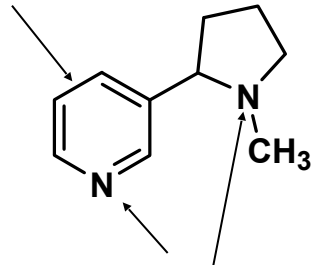
Class Name	Structure	Example	3D Structure	Functional Group
Alkyl Halide	$\text{R}-\ddot{\text{X}}:$ (X=F, Cl, Br, I)	$\text{CH}_3-\ddot{\text{Br}}:$		-X halo
Alcohol	$\text{R}-\ddot{\text{O}}\text{H}$	$\text{CH}_3-\ddot{\text{O}}\text{H}$		-OH hydroxy
Ether	$\text{R}-\ddot{\text{O}}-\text{R}$	$\text{CH}_3-\ddot{\text{O}}-\text{CH}_3$		-OR alcoxy
Amine	$\text{R}-\ddot{\text{N}}\text{H}_2 \text{ or } \text{R}_2\ddot{\text{N}}\text{H} \text{ or } \text{R}_3\ddot{\text{N}}$	$\text{CH}_3-\ddot{\text{N}}\text{H}_2$		-NH ₂ amino
Thiol	$\text{R}-\ddot{\text{S}}\text{H}$	$\text{CH}_3-\ddot{\text{S}}\text{H}$		-SH mercapto
Sulfide	$\text{R}-\ddot{\text{S}}-\text{R}$	$\text{CH}_3-\ddot{\text{S}}-\text{CH}_3$		-SR alkylthio

Functional Groups Containing The C=O Bond

Class Name	Structure	Example	3D Structure	Functional Group
Aldehyde	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\text{H} \end{array}$		H-C=O formyl
Ketone	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CH}_3 \end{array}$		C=O carbonyl
Carboxylic Acid	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}\text{H} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{O}}\text{H} \end{array}$		-COOH carboxylate
Ester	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}\text{R} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{O}}\text{CH}_3 \end{array}$		-COOR
Amide	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{N}}\text{H} \text{ (o R)} \\ \\ \text{H} \text{ (o R)} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{N}}\text{H}_2 \end{array}$		-CONH ₂ -CONHR -CONR ₂
Acid Chloride	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{Cl}}\text{:} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{Cl}}\text{:} \end{array}$		-COCl

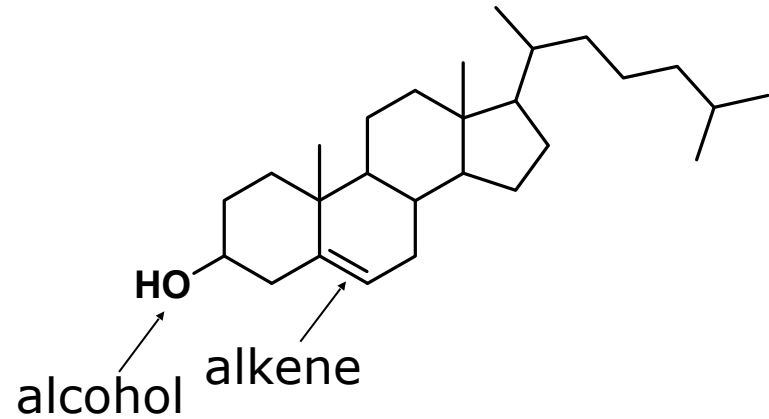
Polyfunctional Molecules

aromatic



amino groups

nicotine

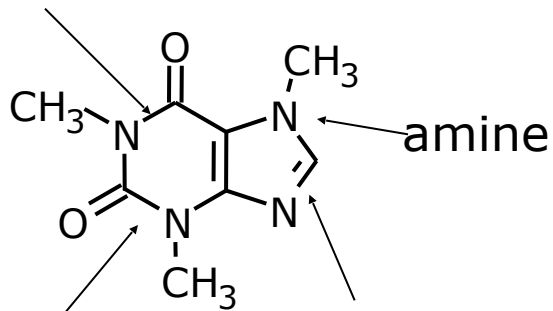


alcohol

alkene

cholesterol

amide

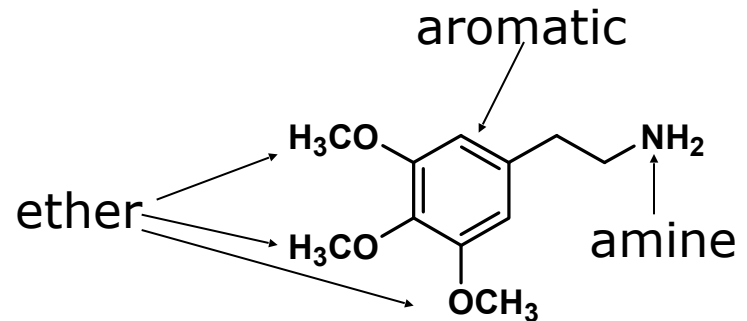


amine

amide

imine

caffeine



ether

aromatic

amine

mescaline