Organic Chemistry

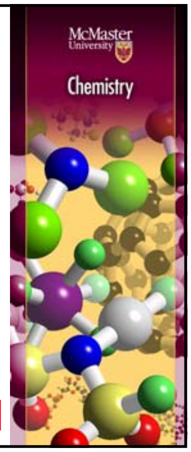
Selected sections Ch 26, 27 + Ch 11

The chemistry of life and living things

↓

The chemistry of carbon compounds

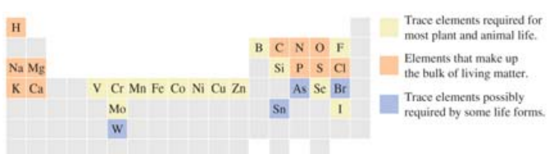
See corrections to slides 22, 137 – in red boxes



The Periodic Table According to Organic Chemists

1 H 1.0079																	2 C 12.011
3 C 12.011	4 C 12.011											5 C 12.011	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 C 12.011
11 C 12.011	12 C 12.011											13 C 12.011	14 C 12.011	15 C 12.011	16 C 12.011	17 Cl 35.453	18 C 12.011
19 C 12.011	20 C 12.011	21 C 12.011	22 C 12.011	23 C 12.011	24 C 12.011	25 C 12.011	26 C 12.011	27 C 12.011	28 C 12.011	29 C 12.011	30 C 12.011	31 C 12.011	32 C 12.011	33 C 12.011	34 C 12.011	35 Br 79.904	36 C 12.011
37 C 12.011	38 C 12.011	39 C 12.011	40 C 12.011	41 C 12.011	42 C 12.011	43 C 12.011	44 C 12.011	45 C 12.011	46 C 12.011	47 C 12.011	48 C 12.011	49 C 12.011	50 C 12.011	51 C 12.011	52 C 12.011	53 I 126.90	54 C 12.011
55 C 12.011	56 C 12.011	71 C 12.011	72 C 12.011	73 C 12.011	74 C 12.011	75 C 12.011	76 C 12.011	77 C 12.011	78 C 12.011	79 C 12.011	80 C 12.011	81 C 12.011	82 C 12.011	83 C 12.011	84 C 12.011	85 C 12.011	86 C 12.011
87 C 12.011	88 C 12.011	103 C 12.011	104 C 12.011	105 C 12.011	106 C 12.011	107 C 12.011	108 C 12.011	109 C 12.011	110 C 12.011								

Evolution of the field

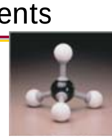


Why is organic chemistry important?

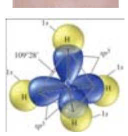
- To understand how we interact with
  - other organisms (food & nutrients, infections),
  - our environment (aromas, pollutants),
  - drugs, and
  - ourselves (metabolism, growth, immunity, cancer)
- To understand how things are made, what they're made of, and how they react with each other

---

Organic Chemistry Components

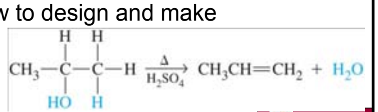


1) Structure: The connectivity and 3-D nature of compounds



2) Theory: Structure and reactivity in terms of atoms and the electrons that bind them together

3) Synthesis: How to design and make new molecules

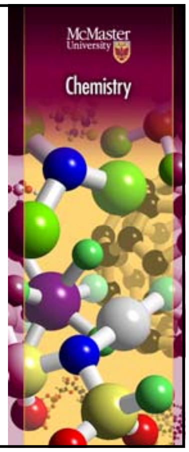


Organic Compounds

- Why give carbon its own field?
  - 98% of all known chemicals are organic
- Inorganic chemistry = the chemistry of everything else
- Nearly all pharmaceuticals are organic

Alkanes

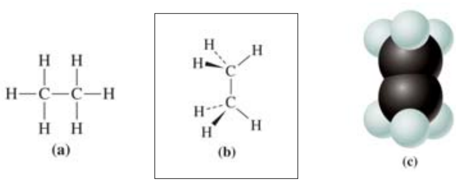
Section 26-1, 26-2



Alkanes

- Hydrocarbons – the simplest organic compounds (C_nH_{2n+2})
- Saturated (all bonding electrons used to make single bonds)
- Methane (various representations):

Ethane (C_2H_6)

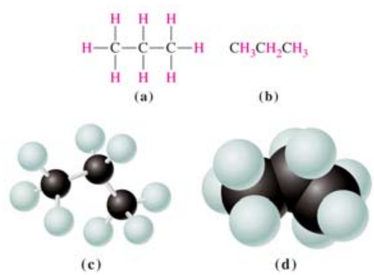


Wedged line: bond is coming forward out of the plane

Dashed line: bond is going backward behind the plane

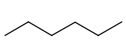
Straight line: bond (and attached group) is in the plane

Propane (C_3H_8)

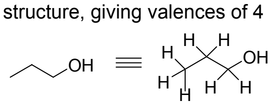


How to Draw Organic Molecules

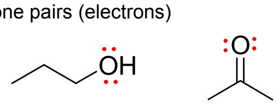
1. Draw molecules in a Zig-Zag shape versus linear structures

 vs $CH_3CH_2CH_2CH_2CH_2CH_3$

2. Assume there are H atoms attached to each carbon in a Zig-Zag structure, giving valences of 4



3. For reactions, draw out the functional groups in detail and include lone pairs (electrons)



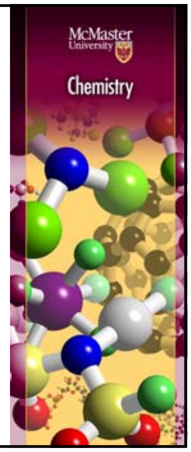
Advice and hints

- Be neat – messy structures lead to mistakes
- Count your carbon atoms!
- Count the substituents on carbon atoms (including implied H atoms)
- In this course, there are never more than four bonds to carbon

Structural Diversity

Isomers, cycloalkanes

Section 26-1, 26-3



Concept Check: Skeletal/Structural Isomerism

Skeletal or structural isomers have:

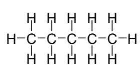
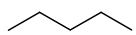
- The same molecular formula but different connectivity.

- Different physical properties.

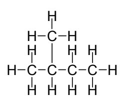
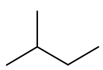
Concept check:

Draw all structural isomers of C_5H_{12}

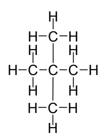
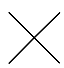
Concept Check: Solution

pentane

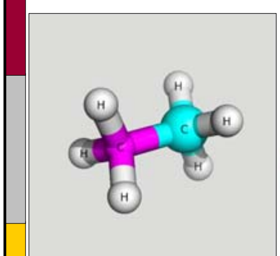



2-methylbutane
or methylbutane

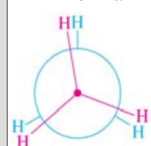



2,2-dimethylpropane or
dimethylpropane

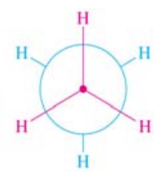
Conformations of alkanes



Newman Projections



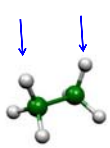
Eclipsed



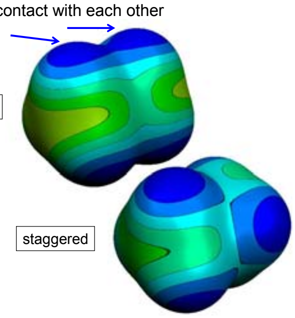
Staggered
Lower E

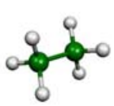
Conformations of alkanes

H atoms in ethane's eclipsed conformation <u>appear</u> to be far apart, but in reality, they are in contact with each other



eclipsed

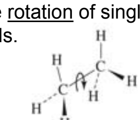




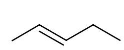
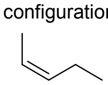
staggered

Conformation versus configuration

- **Conformation**: arrangement of atoms in a molecule that can be changed by simple <u>rotation</u> of single bonds, without breaking any bonds.

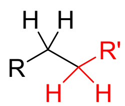


- **Configuration**: the permanent geometry of a molecule resulting from the spatial arrangement of its bonds.
  - Must <u>break</u> bonds to change configuration.

 versus 

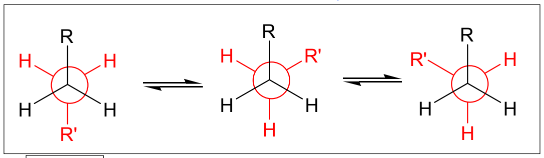
Conformations of 'disubstituted ethane'

Anti conformation



Staggered

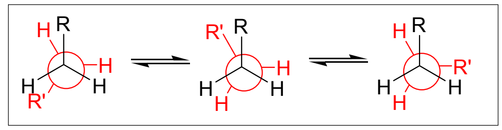
Gauche conformations



Lowest E

Eclipsed Conformations

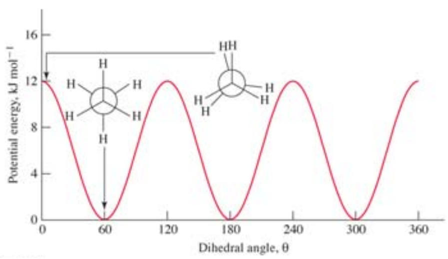
Eclipsed



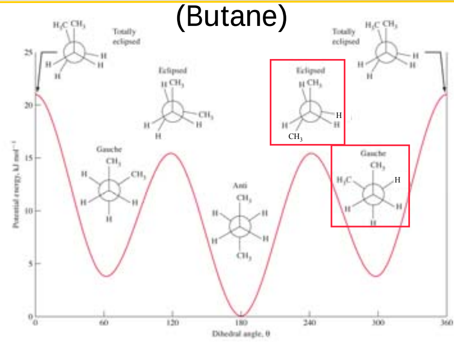
Highest E

- All eclipsed conformations have higher energy than all staggered conformations.

Conformations and Potential Energies (Ethane)

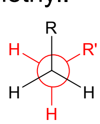


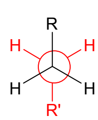
Conformations and Potential Energies (Butane)

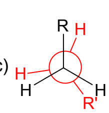


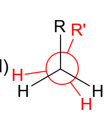
iClicker Question #1

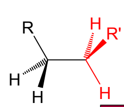
Which conformation has the highest (least favourable) energy? Assume R, R' is methyl.

(a) 

(b) 

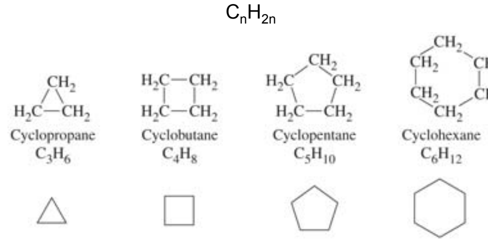
(c) 

(d) 

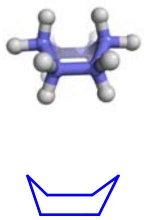
(e) 

Ring Structures: Cycloalkanes

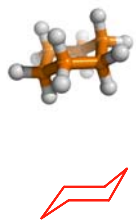
C_nH_{2n}



Molecules are not always flat: Cyclohexane



Boat



Chair

Boat conformation movie

Chair conformation movie

Axial vs. equatorial substituents.

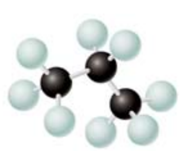
Cyclohexane Conformations

Boat

Chair

Equatorial H atoms are **pink**, axial H atoms are **blue**

Ring Strain in Cycloalkanes



propane

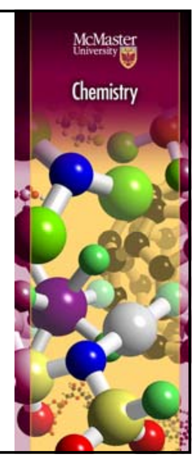
- Bond angles (at C atoms) 109.5º

cyclopropane

- Bond angles (at C atoms) 60º
- H-atoms are eclipsed

Naming

Section 26-1



Naming

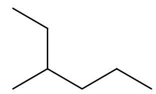
- Chemistry is a visual science: Structures are key to understanding reactivity and physical properties
- Systematic nomenclature: IUPAC rules (assumed knowledge)

IUPAC: International Union of Pure and Applied Chemistry

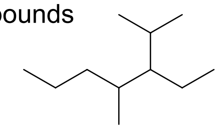
See the supplementary information and podcast about naming in Avenue for more information

Naming Practice

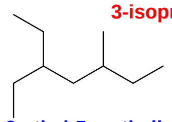
- Name the following compounds



3-methylhexane
not
2-ethylpentane

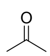


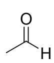
3-ethyl-2,4-dimethylheptane
not
3-isopropyl-4-methylheptane

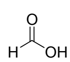


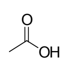
3-ethyl-5-methylheptane
not
5-ethyl-3-methylheptane

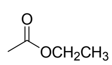
Names of common compounds

Acetone 

Acetaldehyde 

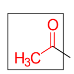
Formic acid 

Acetic acid 

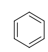
Ethyl acetate 

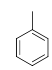
Ether $CH_3CH_2OCH_2CH_3$

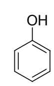
The acetyl group is not a "functional group"; it is a commonly seen structural motif.

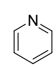
Acetyl group 

Common compounds (continued)

Benzene 

Toluene 

Phenol 

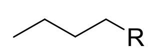
Pyridine 

Some Common Alkyl Substituents (Table 26.1)

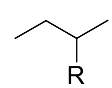
Common Name	IUPAC Name	Structural Formula
Methyl	Methyl	$-CH_3$
Ethyl	Ethyl	$-CH_2CH_3$
Propyl[a]	Propyl	$-CH_2CH_2CH_3$
Isopropyl	1-Methylethyl	$CH_3\underset{\vert}{C}HCH_3$
Butyl[a]	Butyl	$-CH_2CH_2CH_2CH_3$
Isobutyl	2-Methylpropyl	$-CH_2\overset{CH_3}{\overset{\vert}{C}}HCH_3$
sec-Butyl[b]	1-Methylpropyl	$CH_3\underset{\vert}{C}HCH_2CH_3$
tert-Butyl[c]	1,1-Dimethylethyl	$CH_3\overset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}CH_3$

[a]In the past, the prefix *normal* or *n*- was used for a straight-chain alkyl group, such as *n*-propyl or *n*-butyl.
[b]*sec* = secondary
[c]*tert* = tertiary

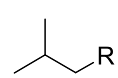
More alkyl names



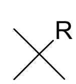
n-butyl



sec-butyl

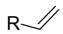


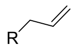
isobutyl

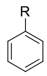


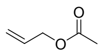
tert-butyl

Substituents

Vinyl groups 

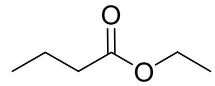
Allyl groups 

Phenyl groups 

Example: Allyl acetate 

Diagnostic iClicker Question

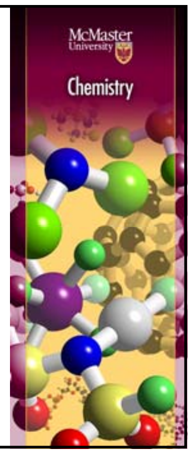
What is the name of this compound?



(a) *sec*-butyl acetate
(b) butyl methyl carboxylic acid
(c) ethyl butanoate
(d) isobutyl acetate
(e) *n*-butyl acetate

Reactions of Alkanes

Section 26-2



Take-Home Practice

$$C_8H_{18}(l) + O_2(g) \longrightarrow ?$$

1) What are the products of the reaction at 298K?
2) Write a balanced chemical equation
3) Predict the signs of ΔH, ΔS and ΔG
4) What type of reaction is shown?

Take-Home Practice: Solution

$$C_8H_{18}(l) + \frac{25}{2}\, O_2(g) \rightarrow 8\, CO_2(g) + 9\, H_2O(l)$$

$\Delta H° = -5.48 \times 10^3$ kJ mol^{-1} (exothermic!)

ΔS° is negative (note H_2O is in liquid form at 298K)

ΔG° = ΔH°-TΔS°, ΔG° should be negative (ΔH° is large)

Reaction type: Combustion, redox

Halogenation

$$CH_4 \xrightarrow[\text{Light or heat}]{X_2} CH_3X + HX + CH_3\text{-}CH_3$$

Halogenation

Initiation: $Cl\text{-}Cl \xrightarrow{\Delta \text{ or } h\nu} 2\ Cl\cdot$

Propagation: $H_3C\text{-}H + Cl\cdot \rightarrow H_3C\cdot + HCl$

$H_3C\cdot + Cl_2 \rightarrow H_3C\text{-}Cl + \boxed{Cl\cdot}$

Termination: $Cl\cdot + Cl\cdot \rightarrow Cl\text{-}Cl$

$H_3C\cdot + Cl\cdot \rightarrow H_3C\text{-}Cl$

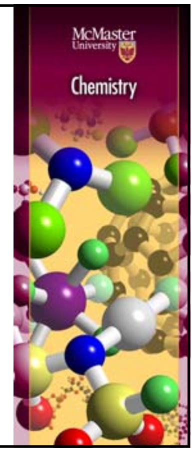
$H_3C\cdot + H_3C\cdot \rightarrow H_3C\text{-}CH_3$

Applicable also for F_2 (often explosive), Br_2 (slow), but not I_2 (no reaction)

Bonding in alkanes

Hybridization

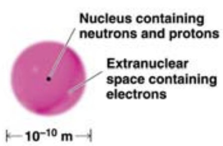
Section 11-3



Review: Electronic Structure and Bonding

The following section, up to "Review: p-orbitals", is assumed knowledge and will not be discussed in class.

The Atom: A dense nucleus surrounded by a much larger extranuclear space



Review: Principal Energy Levels

- Electrons are confined to shells defined by the principal quantum number (n)
- n = 1, 2, 3 …
- Each shell can contain $2n^2$ electrons
- The lower the value of n, the lower the energy of the shell (nearest to the nucleus)

Review: Orbitals

- Shells are divided into sub-shells s, p, d, f
- p, d, and f orbitals are further divided up based on their spatial orientation

Shell	Orbitals in that shell
n = 1	1*s*
n = 2	2*s*, $2p_x$, $2p_y$, $2p_z$
n = 3	3*s*, $3p_x$, $3p_y$, $3p_z$, + 5 3*d*

Review: Electron Configuration

Three principles/rules are used to determine the electron configuration:

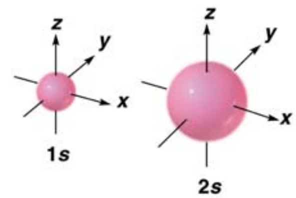
Aufbau Principle
Pauli Exclusion Principle
Hund's rule

Review: Orbitals (subshells)

- Each type of orbital (s, p, d, f) has a distinct shape
- The shape represents the probability of finding an electron (quantum mechanics)
- Organic chemists are interested in shells 1, 2, and sometimes 3

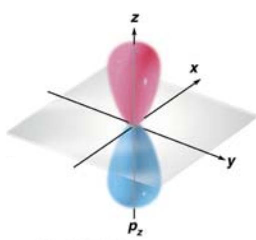
Review: s-orbitals

Spherical:



Review: p-orbitals

3 of them: p_x, p_y, p_z



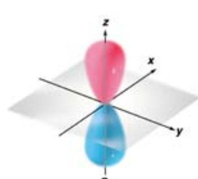
Example: Carbon

$1s^2 2s^2 2p^2$

The outer most electrons of atoms (valence electrons) govern the chemical and physical properties

p-Orbital Shapes

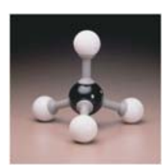
- The p-orbitals in carbon are at 90° to each other



- Atoms bonding to a carbon atom should therefore be situated at 90° to each other…?

Methane - CH_4

- Problem: the shape of methane is tetrahedral (AX_4)
- Bond angles are 109.5° not 90°



Hybridization

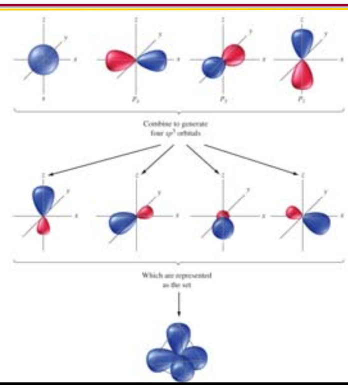
- Comes from the word hybrid which means something is of mixed origin or composition
- Hybrid orbitals arise by combination of atomic orbitals within an atom

sp^3 Hybridization (section 11-3)

$1s^2 2s^2 2p^2$
Ground state
4 atomic orbitals

4 sp^3 hybrid orbitals

sp^3 Hybridization



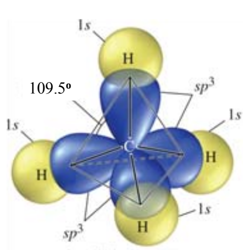
sp^3 Hybridization

The number of hybrid orbitals is equal to the number of combining atomic orbitals

Combine one 2s orbital and three 2p orbitals → four *sp*^{3} orbitals

Bonding-methane

Overlap of sp^3 orbitals from carbon and 1s-orbitals from hydrogen

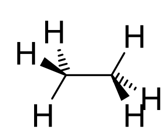


End-on (or end-to-end) overlap produces sigma (σ) bonds.

End-on overlap of sp^3-orbitals also produces σ-bonds.

iClicker Question #2

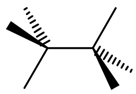
How many σ-bonds are there in this molecule?



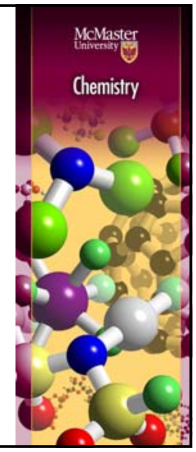
(a) 1
(b) 2
(c) 7
(d) 14

Take-Home Practice Question

How many sp^3-sp^3 σ-bonds are there in this molecule?

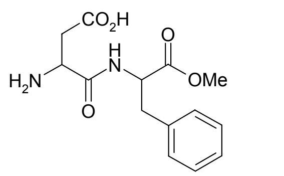


(a) 1
(b) 2
(c) 7
(d) 14



Moving beyond alkanes: Functional Groups

Sample Problem



What functional groups do you see?

Sample Problem: Solution

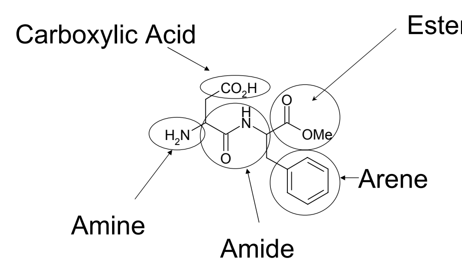


Table 26.2

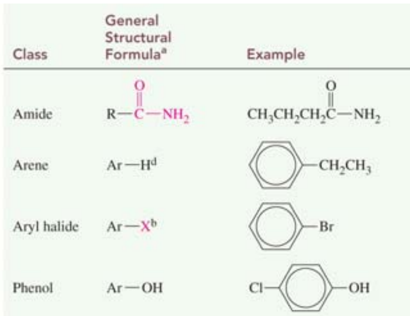
Class	General Structural Formula[a]	Example
Alkane *	R—H	$CH_3CH_2CH_2CH_2CH_2CH_3$
Alkene	C=C	$CH_2{=}CHCH_2CH_2CH_3$
Alkyne	—C≡C—	$CH_3C{\equiv}CCH_2CH_2CH_2CH_2CH_3$
Alcohol	R—OH	$CH_3CH_2CH_2CH_2OH$
Alkyl halide	R—X[b]	$CH_3CH_2CH_2CH_2CH_2CH_2Br$
Ether	R—O—R	CH_3—O—$CH_2CH_2CH_3$
Amine	R—NH_2	$CH_3CH_2CH_2$—NH_2

p. 1154 * Not a functional group

Table 26.2

Class	General Structural Formula[a]	Example
Aldehyde	R—C(=O)—H	$CH_3CH_2CH_2C(=O)$—H
Ketone	R—C(=O)—R	$CH_3CH_2C(=O)CH_2CH_2CH_3$
Carboxylic acid	R—C(=O)—OH	$CH_3CH_2CH_2C(=O)$—OH
Ester	R—C(=O)—OR	$CH_3CH_2CH_2C(=O)$—OCH_3
carboxylic acid anhydride	R—C(=O)—O—C(=O)—R	H_3C—C(=O)—O—C(=O)—CH_3

Table 26.2

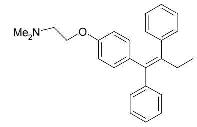


Class	General Structural Formula[a]	Example
Amide	R—C(=O)—NH_2	$CH_3CH_2CH_2C(=O)—NH_2$
Arene	Ar—H[d]	—CH_2CH_3
Aryl halide	Ar—X[b]	—Br
Phenol	Ar—OH	Cl— —OH

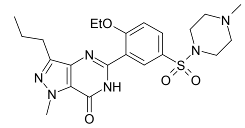
Arene = any hydrocarbon containing an aromatic group (e.g. a benzene-like ring)

You must be able to recognize these functional groups

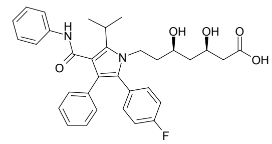
Organic Compounds: Medicines



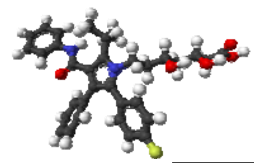
Tamoxifen



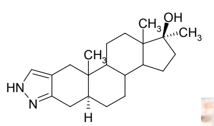
Viagra



Lipitor

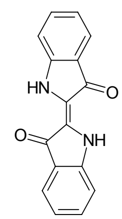


Organic Compounds: Drugs

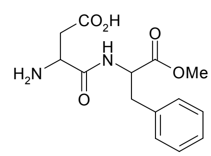


Stanozolol

Organic Compounds: Industrial Chemicals

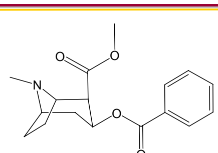


Indigo dye
(blue jeans)

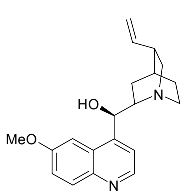


Aspartame

Organic Compounds: Natural Products



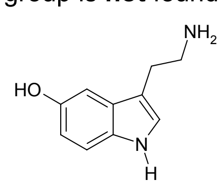
Cocaine



Quinine

Diagnostic iClicker Question

Which functional group is **not** found in this molecule?



(a) alkene
(b) amine
(c) amide
(d) phenol

Alkenes

Section 26-5

Alkenes (C_nH_{2n})

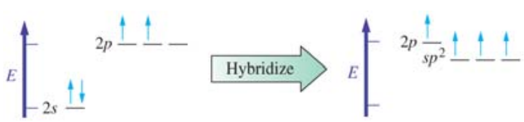
$CH_2{=}CH_2$ Ethene (ethylene)

$CH_3CH_2CH{=}CH_2$ 1-Butene

$CH_3CH_2CH_2C(CH_2CH_3){=}CH_2$ 2-Ethyl-1-pentene

Multiple Covalent Bonds

- Ethylene has a *double* bond in its Lewis structure
- VSEPR says trigonal planar shape at C



sp^2 hybridization

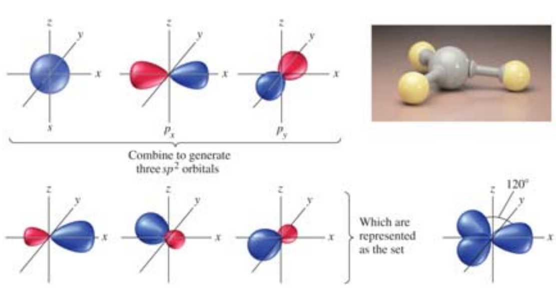
p. 461

sp^2 Hybrid Orbitals (section 11-4)

Combine one 2s orbital + two 2p orbitals → three *sp²* orbitals (+ one 2p orbital left over)

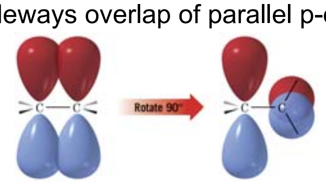
Hybrid orbital lobes pointing in the direction of an equilateral triangle: bond angles =120°

sp^2 Hybrid Orbitals



sp^2 Hybrid Orbitals

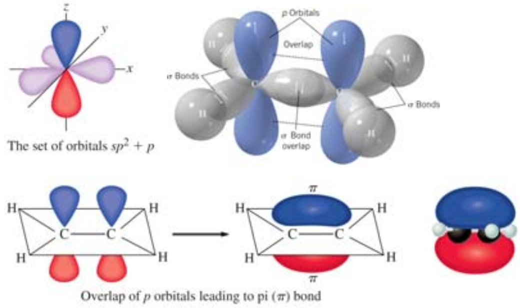
- The extra p-orbital can be used to form a π-bond
- π-bonds are covalent bonds that form by the sideways overlap of parallel p-orbitals



eclipsed p-orbitals
π-bond

staggered p-orbitals
no π-bond

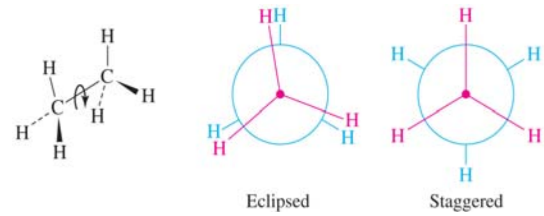
Ethene



Section 11-4

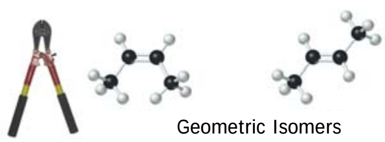
Overlap above and below plane of atoms gives one π bond (in total).

Recall: Conformations of alkanes



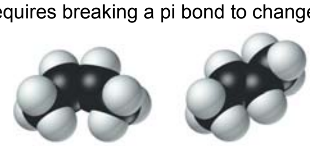
Rotation around C-C single bonds leads to different *conformations.*

Alkenes have restricted rotation



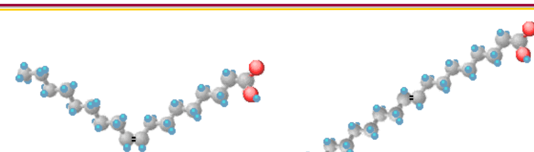
Geometric Isomers

<u>Restricted</u> rotation leads to different *configurations.*
Rotation requires breaking a pi bond to change configuration.



p. 1176 *cis* *trans*

cis versus *trans* fatty acids: impact of geometry

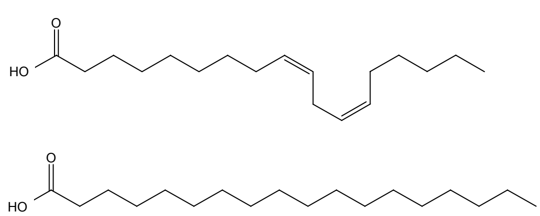


cis-9-octadecenoic acid (Oleic acid)

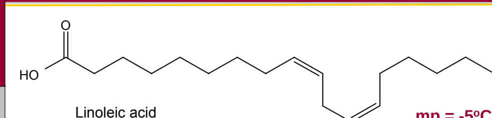
trans-9-octadecenoic acid (Elaidic acid)

Take-Home Practice

Which of these two fatty acids has the higher melting point and why?

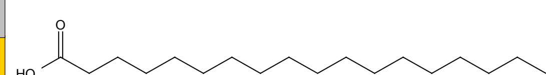


Take-Home Practice: Solution



Linoleic acid **mp = -5ºC**

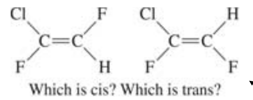
Less efficient packing because of kink in chain geometry, therefore weaker intermolecular forces and lower melting point.



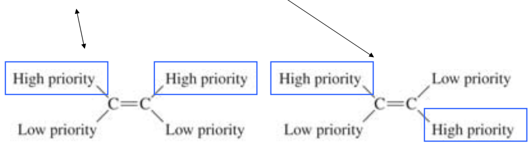
Stearic acid **mp = 70ºC**

Straight chain allows more efficient packing, therefore stronger intermolecular forces and higher melting point.

The *E,Z* System of Nomenclature



- Need a new system:
  Higher priority → higher atomic number



Z isomer

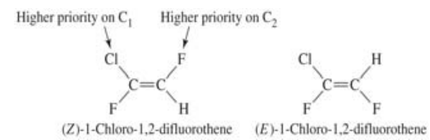
High priority groups on same side

E isomer

High priority groups on opposite sides

p. 1178

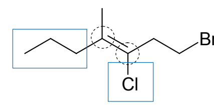
Assigning *E* and *Z*



Look first at atoms directly bonded to double bond.

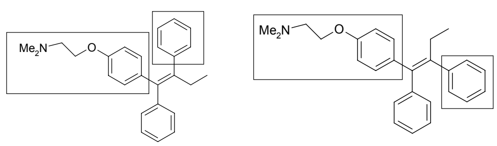
Look at next set of atoms until a difference in priority is found.

Assign the molecule as *E* or *Z*.



E/*Z* Take-Home Practice:

Label these tamoxifen isomers as *E* or *Z*:



Z *E*

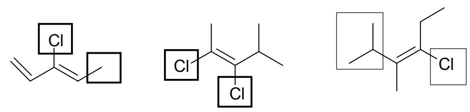
Why is this important?

Tamoxifen (*Z*-isomer, left) is used to treat hormone dependent breast cancer.

The *E*-isomer (right) can promote cancer growth.

iClicker Question #3

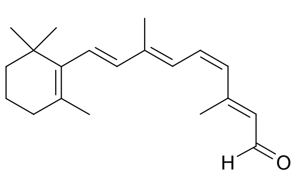
Which of these molecules has/have a *Z* configuration?



(i) (ii) (iii)

(A) i
(B) ii
(C) iii
(D) i, ii
(E) none

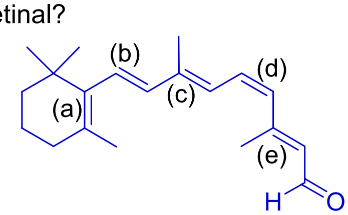
Organic Compounds: Biological



11-*cis*-retinal

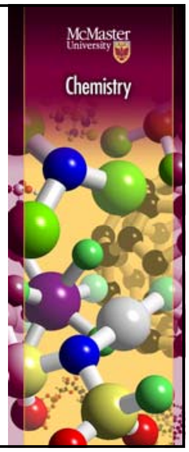
Take-Home Practice

Which is the *cis (or Z)* double bond in 11-*cis*-retinal?



(d) is the *cis* (or *Z*) double bond. We can use the term *cis* here because there is only one non-H substituent on each carbon atom of that double bond.

Reactions involving alkenes



Section 27-5

Chemical Reactions

- Charge attraction draws molecules together
- In organic chemistry, there is often not a full cation reacting with an anion
- It is more common to have a charged reagent be attracted to an organic compound that has a dipole
- The reagent does not necessarily need to be charged: Lone electron pairs would also be attracted to a dipole

p. 1209

Chemical Reactions

- The majority of reactions in organic chemistry involve the flow of electrons from one molecule to another
- nucleophile (nucleus loving) = electron donor = Lewis base
- electrophile (electron loving) = electron acceptor = Lewis acid

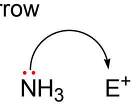
p. 1211

Chemical Reactions

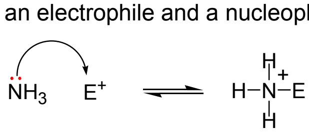
- In most organic reactions the orbitals of the nucleophile and electrophile are directional → therefore the two orbitals must be correctly aligned for a reaction to occur

Mechanism

- The flow of electrons between a nucleophile and electrophile can be represented by a double-barbed curly arrow

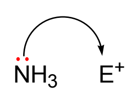


- The result of the movement is to form a bond between an electrophile and a nucleophile

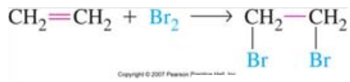


Mechanism (continued)

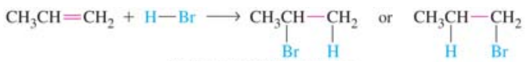
- The arrow tail starts at the source of the moving electrons and the arrow head indicates its final destination



Addition Reactions



ANTI addition (Br atoms add to opposite faces of alkene)

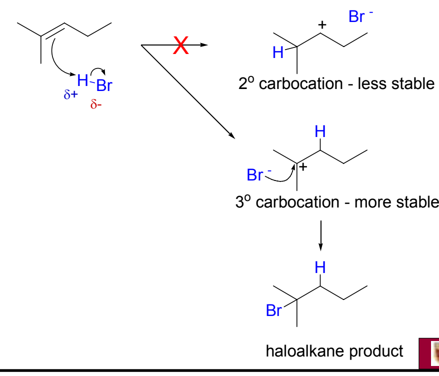


Not observed

Markovnikov's rule: the H atom ends up attached to that carbon atom of the double bond that has the most hydrogen atoms to start with.

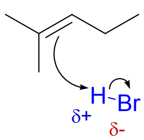
p. 1240-1241

Explanation of Markovnikov's rule



Curly arrows

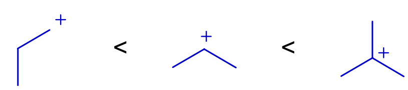
- One curly arrow represents electrons moving from the alkene π-bond to the proton of HBr, forming a C-H bond.



- The next arrow shows that the bond between H and Br breaks, with the electron pair going to Br (Br^- is formed).

Carbocation stability

Stability:

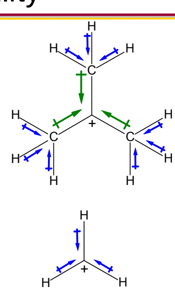
H_3C^+ < 

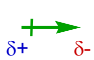
methyl < 1° < 2° < 3°

Carbocation stability

Electronic:

- Alkyl substituents are electron donating compared with H.
- Donating electrons to an electron deficient (positively charged) centre stabilizes it.

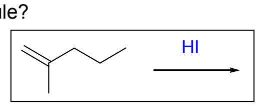


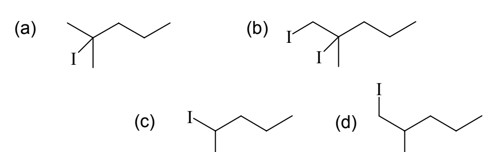


= a permanent electric dipole

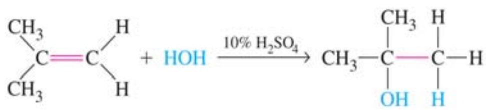
iClicker Question #4

What is the expected product, according to Markovnikov's rule?





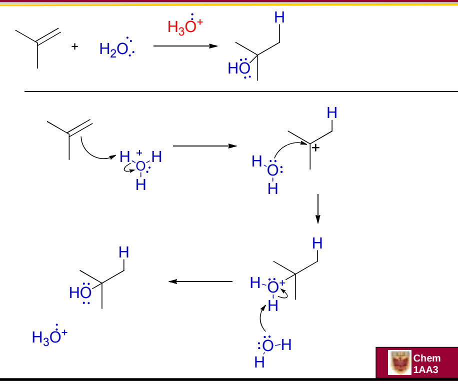
Hydration Reaction



- Addition (forward reaction) is favoured in dilute acid
- Elimination (reverse reaction) is favoured in concentrated acid (conc. H_2SO_4), heat

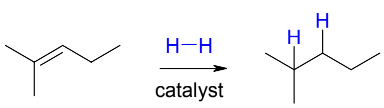
p. 1242

Hydration also follows Markovnikov's rule



Reduction of Alkenes

Hydrogenation



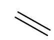
Catalyst: typically a group 10 metal (Pd, Pt or Ni)

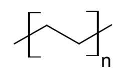
SYN addition (H atoms add to same face of alkene)

p. 1240

Polymerization of Alkenes

- Monomer Polymer





C_2H_4, ethylene polyethylene

- Production of polymer chain follows chain reaction mechanisms
- Initiation often starts with an organic peroxide (R-O-O-R) which dissociates by heat into 2 R-O• radicals. These react with a monomer to complete the initiation.

p. 1250-1252

Chain Mechanism

- Initiation:

$$\text{R-O-O-R} \rightarrow \text{R-O}\cdot + \cdot\text{O-R}$$

$$\text{R-O}\cdot + CH_2{=}CH_2 \rightarrow \text{R-O-}CH_2CH_2\cdot$$

- Propagation:

$$\text{R-O-}CH_2CH_2\cdot + CH_2{=}CH_2 \rightarrow \text{R-O-}[CH_2CH_2]_2\cdot$$

$$\text{R-O-}[CH_2CH_2]_n\cdot + CH_2{=}CH_2 \rightarrow \text{R-O-}[CH_2CH_2]_{n+1}\cdot$$

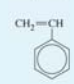
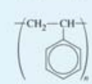
etc. (chain continues to grow in 2C units)

- Termination:

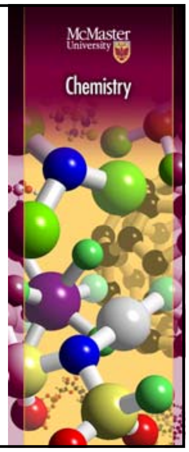
$$\text{R-O-}[CH_2CH_2]_m\cdot + \text{R-O-}[CH_2CH_2]_n\cdot \rightarrow \text{R-O-}[CH_2CH_2]_{m+n}\text{OR}$$

Examples of Polymers

TABLE 27.5 Some Polymers Produced by Chain-Reaction Polymerization

Name	Monomer	Polymer	Uses
Polyethylene	$CH_2{=}CH_2$	$\text{-}(CH_2-CH_2)_n\text{-}$	Bags, bottles, tubing, packaging film
Polypropylene	$CH_2{=}CHCH_3$	$\left(CH_2-\underset{CH_3}{CH}\right)_n$	Laboratory and household ware, artificial turf, surgical casts, toys
Poly(vinyl chloride) PVC	$CH_2{=}CHCl$	$\left(CH_2-\underset{Cl}{CH}\right)_n$	Bottles, floor tile, food wrap, piping, hoses
Poly(tetrafluoroethylene), Teflon	$CF_2{=}CF_2$	$\text{-}(CF_2-CF_2)_n\text{-}$	Bearings, insulation, nonstick surfaces, gaskets, industrial ware
Polystyrene			Packaging, refrigerator doors, cups, ice buckets, and coolers (as foam)

Alkynes



Section 26-5

Alkynes

$HC{\equiv}CH$	$CH_3CH_2C{\equiv}CH$	$CH_3CH(CH_3)C{\equiv}CCH_3$
Ethyne (acetylene)	1-Butyne (ethylacetylene)	4-Methyl-2-pentyne (isopropylmethylacetylene)

According to VSEPR, alkynes are linear

p. 1175

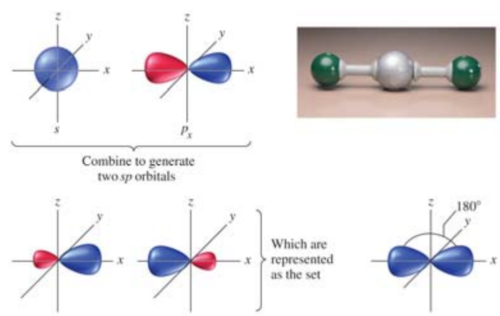
sp Hybrid Orbitals

- Combine one 2s orbital + one 2p orbital → two sp orbitals (+ two 2p orbitals left over)

sp hybridization

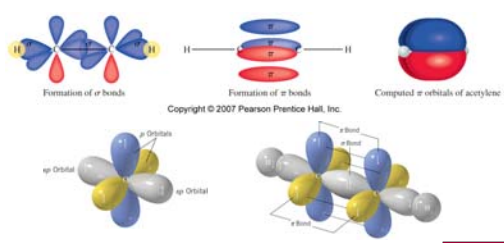
Section 11-4, p. 462

sp Hybrid Orbitals

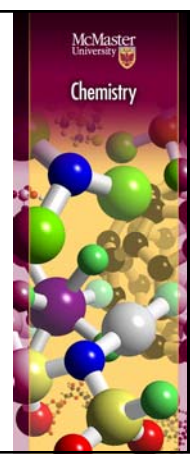


Acetylene: Orbitals

- Acetylene, C_2H_2, has a *triple* bond.
- Linear at carbon

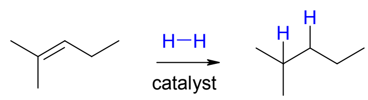


Reactions of Alkynes



Reduction of Alkenes and Alkynes

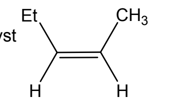
Recall:



Similarly:

$CH_3CH_2C{\equiv}CCH_3 + 2H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2CH_2CH_3$

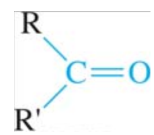
$CH_3CH_2C{\equiv}CCH_3 + \underset{\text{excess}}{H_2} \xrightarrow{\text{Lindlar's catalyst}}$



Cis (Z) isomer only!

p. 1240

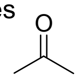
The Carbonyl Group: ketones and aldehydes



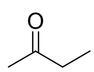
Section 26-7

Examples

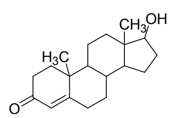
Ketones



Acetone

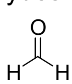


Methyl ethyl ketone (MEK)

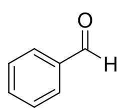


Testosterone

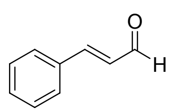
Aldehydes



Formaldehyde



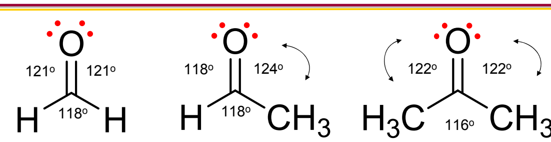
Benzaldehyde



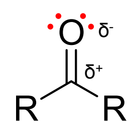
Cinnamaldehyde

p. 1184

Structure and Polarity



AX_3 trigonal planar geometry (sp^2-hybridized at C)



Synthesis and reactions of aldehydes and ketones

Section 26-7

Primary, Secondary & Tertiary Alcohols

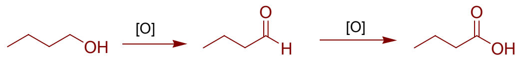
R–CH₂·OH — Primary (1°)

R–CH(R')–OH — Secondary (2°)

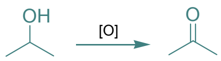
R–C(R'')(R')–OH — Tertiary (3°)

Oxidation of ROH yields Carbonyls

- Primary alcohol → aldehyde → carboxylic acid



- Secondary alcohol → ketone



[O] = Oxidizing agent

- Tertiary alcohol → no reaction
  - a C-C bond would have to break in order for oxidation to occur

p. 1185

Oxidizing Agents

- Oxidation: Addition of an O **or** removal of (a molecule of) hydrogen
- Agents: commonly metals in high oxidation states (transfer of 2 to 4 electrons)

  e.g., MnO_4^-, $Cr_2O_7^{2-}$ ($KMnO_4$, $K_2Cr_2O_7$)
- Usually done in acid or base to facilitate electron transfer
- Pyridinium chlorochromate (PCC in CH_2Cl_2)
  - Specific for oxidizing 1º alcohols to aldehydes

  Will also oxidize secondary alcohol to ketone (does one oxidation step only)

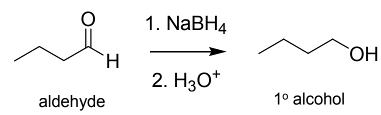
iClicker Question #5

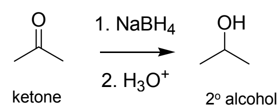
What is the expected product of oxidation of 2-pentanol?

(a) dimethyl ketone
(b) 2-pentanone
(c) pentanoic acid
(d) none of the above

Addition Reactions to the Carbonyl Group

Reduction: $NaBH_4$ is a source of H^- (hydride)

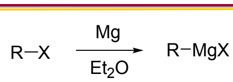




p. 1185

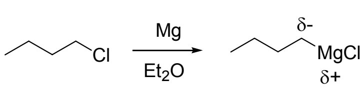
Grignard Reagent

Formation of a Grignard reagent:



X = Cl, Br or I

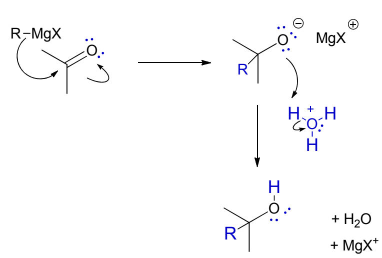
Example:



Magnesium is very electropositive:
→Carbon in Grignard reagent gains partial negative charge
→This carbon now acts as nucleophile

(p. 1264, Q78)

Mechanism of Grignard Addition



Mechanism of Grignard Addition

The carbanion of Grignard reagent is a Lewis base (in the extreme view it has a C with a lone pair of electrons and a negative charge).

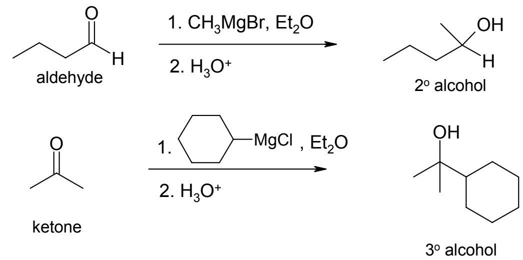
This carbanion donates an electron pair to the slightly positive (δ+) carbon atom of a carbonyl group (such as those in aldehydes, ketones, or carbon dioxide). This C atom is a Lewis acid (electron deficient).

This forces the π bond between carbon and oxygen to break; the π bond electrons end up as a lone pair on O.

This results in the formation of a C-C bond, and a negatively charged O atom.

Addition of acid produces a neutral functional group (alcohol, or carboxylic acid if you started from CO_2).

C-C bond formation: Addition of a Grignard



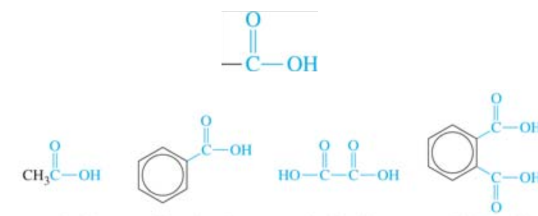
Synthesis and Reactions of Carboxylic Acids and Derivatives

Section 26-7

McMaster University

Chemistry

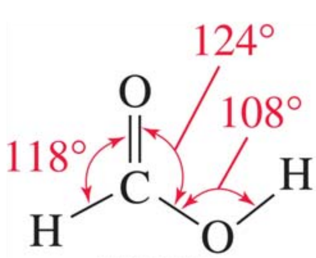
Examples



Acetic acid (an aliphatic acid) | Benzoic acid (an aromatic acid) | Oxalic acid (an aliphatic dicarboxylic acid) | *o*-Phthalic acid (an aromatic dicarboxylic acid)

p. 1187

Carboxylic Acid: Structure



Carboxylic Acid Reactivity and Synthesis

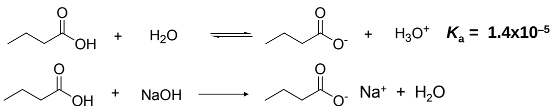
Section 26-7

McMaster University

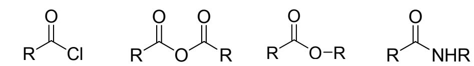
Chemistry

Carboxylic acids

Weak acids:

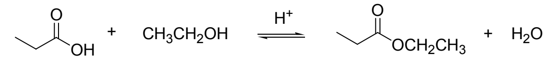


Derivatives:



Acid chloride   Anhydride   Ester   Amide

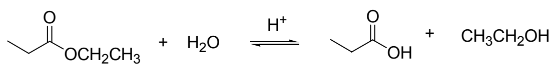
Preparation of Esters



- Fischer Esterification
- Acid catalyst
- Condensation reaction

p. 1188

Hydrolysis of Esters



- Reverse of previous reaction
- Also requires acid catalyst
- Use excess water, heat

Synthesis of RCOOH

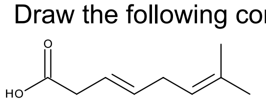
- Oxidation of 1° alcohol or aldehyde – seen
- Addition of Grignard to CO_2, with acid work-up

$$R{-}MgX \xrightarrow[2.\ H_3O^+]{1.\ CO_2} R{-}CO_2H$$

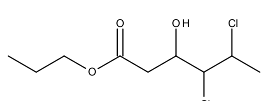
O=C=O

Challenging Naming Practice

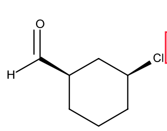
- Draw the following compounds



***E*-7-methylocta-3,6-dienoic acid**

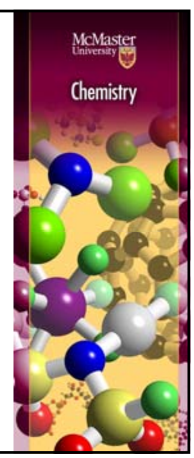


propyl 4,5-dichloro-3-hydroxyhexanoate



***cis*-3-chlorocyclohexanal**

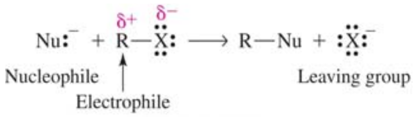
Substitution Reactions and Mechanisms



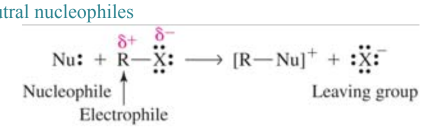
Section 27-2

Substitution Reactions at sp^3 Hybridized Carbon

Charged nucleophiles



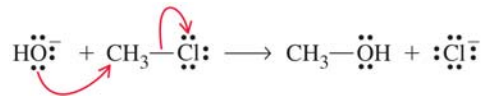
Neutral nucleophiles



p. 1212

S_N2 Mechanism

S = substitution; N = nucleophilic, 2 = bimolecular



Rate = $k[OH^-][CH_3Cl]$

p. 1213

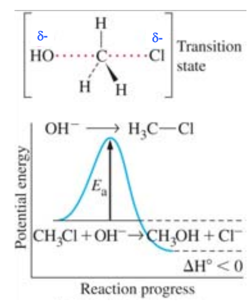
iClicker Question #6

What are the nucleophile and the electrophile in this reaction?

$Na^+OCH_3^- + CH_3Br \longrightarrow CH_3OCH_3 + NaBr$

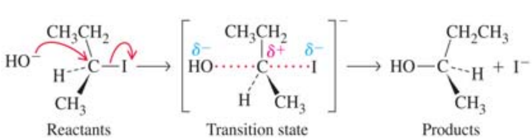
	Nucleophile	Electrophile
(a)	$^-OCH_3$	Br^-
(b)	$^-OCH_3$	CH_3Br
(c)	CH_3Br	$^-OCH_3$
(d)	Na^+	CH_3Br

S_N2 Mechanism



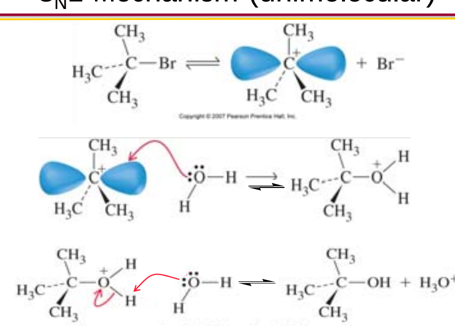
p. 1216

S_N2: Inversion of Configuration



S_N2 shows only inversion

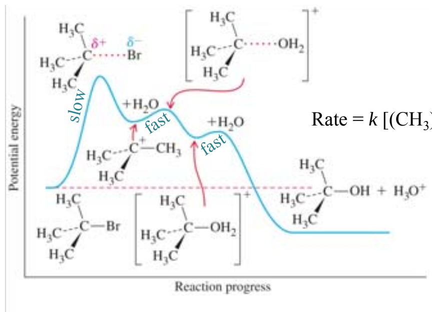
S_N1 Mechanism (unimolecular)



S_N1 can show mixture of inversion and retention of stereochemistry because of carbocation in Step 1

p. 1216

S_N1 Mechanism

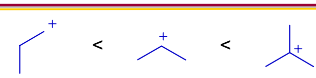


Rate = k [$(CH_3)_3CBr$]

S_N1 versus S_N2

- The mechanism depends on many factors, but as a general rule:
- 1° electrophile = S_N2
  - less stable carbocation intermediate, less steric hindrance to nucleophilic attack
- 2° electrophile = ?
  - hard to predict (you will see this next year)
- 3° electrophile = S_N1
  - more stable carbocation intermediate, more steric hindrance to nucleophilic attack

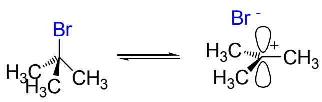
Carbocation stability

Stability: H_3C^+ < 

methyl < 1° < 2° < 3°

Two ways for alkyl substituents to increase cation stability:

1. Steric:

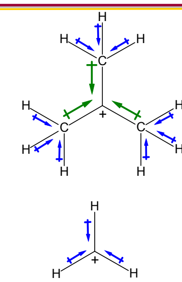


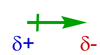
The cationic carbon atom rehybridizes from sp³ to sp², relieving the steric clash between substituents

Carbocation stability

2. Electronic:

- Alkyl substituents are electron donating compared with H.
- Donating electrons to an electron deficient (positively charged) centre stabilizes it.

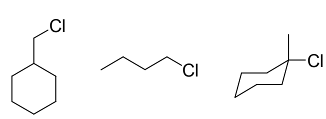




= a permanent electric dipole

iClicker Question #7

Rank the likelihood of the following compounds to undergo S_N2 nucleophilic substitutions:

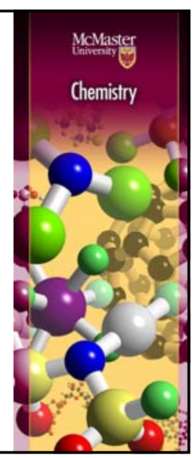


i *ii* *iii*

(a) i ≈ iii < ii
(b) i ≈ ii < iii
(c) i < ii > iii
(d) ii ≈ i > iii

Synthesis

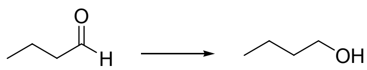
Section 27-9: Refer to the Chem 1AA3 synthesis chart, posted in Avenue



Synthesis

1) Functional group interconversion

– e.g., Converting an aldehyde to an alcohol



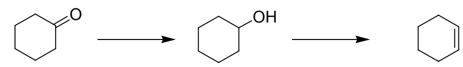
2) Carbon-carbon bond forming reactions

– e.g., Grignard reaction

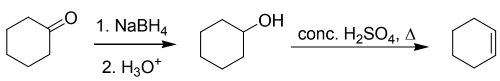
$$R{-}MgX \xrightarrow[2.\ H_3O^+]{1.\ CO_2} R{-}CO_2H$$

Practice Question : Synthesis

Fill in the missing reagents:

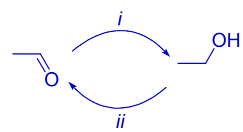


Practice Question: Solution



Take-Home Practice #1

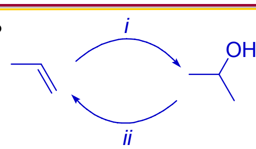
What are conditions *i* and *ii*?



	i	*ii*
(a)	H_2 / Pt	$KMnO_4$
(b)	PCC	10% H_2SO_4
(c)	(1) $NaBH_4$, (2) H_3O^+	$KMnO_4$
(d)	(1) $NaBH_4$, (2) H_3O^+	PCC

Take-Home Practice #2

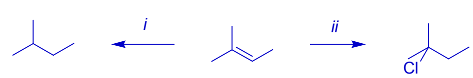
What are conditions *i* and *ii*?



	i	*ii*
(a)	10% H_2SO_4	conc. H_2SO_4
(b)	PCC	10% H_2SO_4
(c)	10% H_2SO_4	H_2/Pd-C
(d)	conc. H_2SO_4	10% H_2SO_4

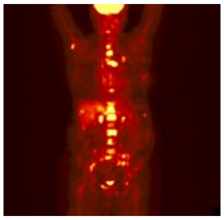
Take-Home Practice #3

What are conditions *i* and *ii*?

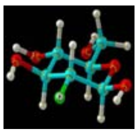


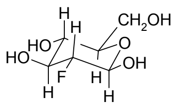
	i	*ii*
(a)	PCC	Cl_2
(b)	H_2/Pd-C	HCl
(c)	H_2/Pd-C	Cl_2
(d)	conc. H_2SO_4	HCl

Medical Application: Molecular Imaging



PET scans

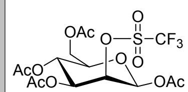




^{18}F-fluorodeoxyglucose

Synthesis of ^{18}F-FDG

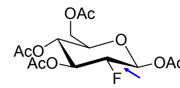
- The half-life of ^{18}F is 109.8 minutes
  - it must be produced in a cyclotron and immediately used
  - the synthesis of ^{18}F-FDG must be fast and reliable.



Mannose triflate tetraacetate

$\xrightarrow[\text{2,2,2-Krypt}]{^{18}F^-,\ CH_3CN}$

S_N2 reaction



Note the inversion!

F is equatorial, but triflate group was axial, therefore inversion has occurred.

$\xrightarrow[H_2O]{HCl}$

Ester Hydrolysis