



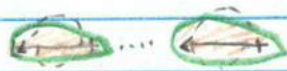
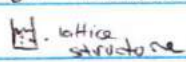


Force	Model	Basis of attraction
Ion-Dipole		Ion charge - dipole charge
H bond	$\delta^- \delta^+ \dots \delta^-$ -A-H ... :B-	Polar bond to H - dipole charge (high EN of N, O, F)
Dipole-Dipole		Dipole charges
Ion induced dipole		Ion charge - polarizable e ⁻ cloud
Dipole induced dipole		Dipole charge - polarizable e ⁻ cloud
Dispersion (London)		Polarizable e ⁻ clouds

Strength: Ionic > Covalent > H bond > Van der Waal forces

Consequences of Intermolecular forces

Determines State of Matter

Surface Tension 

surface molecules only interact w/ liquid molecules below = downward force

[force/unit area] to break through

Capillary Action

narrow tube

Adhesion: molecules \heartsuit container

$A > C$



Cohesion: molecules \heartsuit molecules

$C > A$



Viscosity

resistance to flow

break H-bonds, $\downarrow V$

Vapor Pressure

@ equilibrium, in closed system: pressure exerted by vapor

@ surface bc interacting w/ fewer molecules
determines boiling points

evaporation happens all the time

Solids

Amorphous

looks solid but
isn't organized
glass

Crystals

Ionic

NaCl

Covalent

Sugar, H₂O

Molecular

Metallic

tightly packed, dense
Face-centered cubic
conduct electricity & heat

Simple cubic

Body Centered cubic

Face centered cubic

diagram
p443

Triple Point Temperature

temp @ which all 3 phases can exist

Solution

something dissolved in something else

Solute - thing dissolved

Solvent - dissolver

like dissolves like

polar + polar

nonpolar + nonpolar

1. liquid + liquid

2. solid + liquid

3. gas + gas

4. gas + liquid/solid

5. solid + solid = alloy

✓ mix = miscible

✗ mix = immiscible

Concentration Definitions

Molarity (M)	$\frac{\text{mol solute}}{\text{L solution}}$	any state
Molality (m)	$\frac{\text{mol solute}}{\text{kg solvent}}$	solution only
Parts by mass/volume	$\frac{\text{mass solute}}{\text{mass solution}}$ / $\frac{\text{volume solute}}{\text{volume solution}}$	
mole fraction	$\frac{\text{mol solute}}{\text{mol solute} + \text{mol solvent}}$	

Colligative Properties

Vapour Pressure Lowering

VP of solution is lower than VP of pure solvent

$$\text{Raoult's Law} = \Delta P = X_{\text{solvent}} \cdot P_{\text{solvent}}^{\circ}$$

mole fraction vp solvent

Boiling Point Elevation

@ 1 atm

solution boils @ higher temp than pure solvent

$$\Delta T_b = T_{\text{solution}} - T_{\text{solvent}} \quad \Delta T_b = K_b m$$

bp constant bp constant molality

Freezing Point Depression

solution freezes @ lower temp than pure solvent

$$\Delta T_f = K_f m$$

fp constant molality

Osmotic Pressure

≠ semipermeable membrane

higher concentration ← low concentration Solvent flow



solvent travels to low conc to reach equilibrium

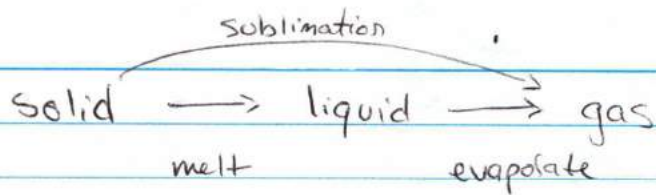
$$\pi = MRT$$

molarity

IF solution is strong electrolyte: consider # particles

$$i = \frac{\text{dissociated ions}}{\text{molecule}}$$

VP lowering: $\Delta P = i (X_{\text{solute}} \cdot P_{\text{solvent}}^{\circ})$ FP depression: $\Delta T_f = i (K_f m)$
 BP elevation: $\Delta T_b = i (K_b m)$ Osmotic Pressure: $\pi = i MRT$



Heat Capacity

heat required to raise temp 1°K

Solid \rightarrow highest IM forces \rightarrow higher HC

liquid \rightarrow weaker IM forces \rightarrow lower HC

$$\text{Sublimation} = \Delta H_g + \Delta H_s$$

when remove heat slowly $g \rightarrow l \rightarrow s$

crystal/organized

when remove heat quickly $g \rightarrow s$

amorphous/disorganized

Suspension

- solute settles out, large particles, hetero

Solution

- homogeneous

Colloid

- hetero, solute is relatively large, but too small to settle

milk/blood

Tyndall effect: scatter light

Acids & Bases

Arrhenius definition

Acid: a substance with H in its formula that dissociates in water to yield H_3O^+

Base: a substance with OH in its formula that dissociates in water to yield OH^-

Brønsted-Lowry definition

Acid: proton donor (H^+ ion)

Base: proton acceptor

Lewis definition

Acid: a species that accepts an electron pair

Base: a species that donates an electron pair

Strong acid - dissociates completely

Weak acid - dissociates slightly, swings in equilibrium

$$\text{Acid-dissociation constant} = K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Autoionization of water:

water dissociates very slightly into ions

ion-product constant:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

$$pH = -\log [H_3O^+]$$

pH scale 0-14

pH < 7 acidic

pH = 7 neutral

pH > 7 basic

$$-\log [10^{-14}] = 14$$

Conjugate Pairs



re: Brønsted Lowry definition

$$\text{Percent HA dissociated} = \frac{[\text{HA}]_{\text{dissoc}}}{[\text{HA}]_{\text{init}}} \cdot 100$$

$$\text{Base-dissociation constant} = K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

$$K_a \cdot K_b = K_w$$

Halogens



↑ electronegativity, ↓ acidity, ↑ pH

Oxoacids

↑ electronegativity, ↑ acidity $\text{H-O-I} > \text{H-O-Br} > \text{H-O-Cl}$

↑ # O, ↑ acidity

electronegativity of O creates δ^- & δ^+ , so e^- goes away from H & leads to dissociation of H⁺

Acid-Base buffers

lessens impact on pH from addition of acid or base

Common-ion effect

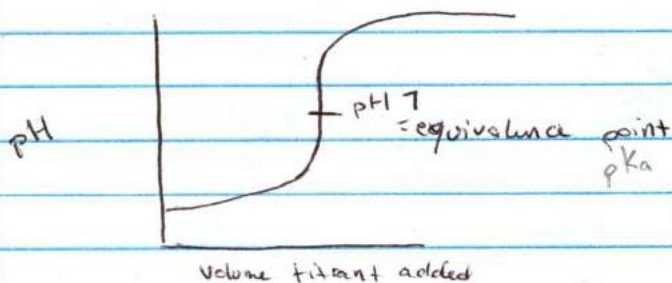
when a given ion is added to an equilibrium mixture that already contains that ion & the position of equilibrium shifts away from forming it

weak acid + salt of conjugate base
weak base + salt of conjugate acid

Henderson-Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

Acid-Base Titration curve



strong acid + strong base \rightleftharpoons salt + water

Solubility Equilibrium

Solubility product constant

$$K_{sp} = [M^{n+}]^p [X^{z-}]^q \quad \text{for } M_p X_q \rightarrow M^{n+} + X^{z-}$$

ion product quotient

$Q_{sp} \approx$ same equation but diff notation to show not at equilibrium

IF

$$Q_{sp} > K_{sp}$$

system still to reach equilibrium

$$Q_{sp} = K_{sp}$$

system @ equilibrium

$$Q_{sp} < K_{sp}$$

has reached equilibrium & rev motion

Metals

Unique Properties

Malleable

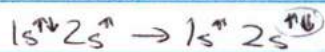
Conduct Heat

Ductile

Conduct Electricity

Conductor of Electricity

Conduction Zone



e^- promotion

Semiconductors

Silicon, Germanium

• Metalloids

N type conductor



P type conductor



Metals exist in an oxidized state

Sources: sea water, earth crust, silver Mountain (Bolivia)

Purification of Metals

must employ reduction approach

Chemical Reduction

Electrolytic Reduction = electrolysis

Alkali Metals

Extremely reactive

(especially to cold water)

Na

sea water, Chile saltpeter

K

Alkaline Metals

less reactive than alkali, most abundant

Mg

Ca

$1s$
 $2s \rightarrow 2p$
 $3s \rightarrow 3p \rightarrow 3d$
 $4s \rightarrow 4p \rightarrow 4d \rightarrow 4f$

Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$
+7					✓				
+6				✓	✓	✓			
+5			✓	✓	✓	✓	✓		
+4		✓	✓	✓	✓	✓	✓	✓	
+3	✓	✓	✓	✓	✓	✓	✓	✓	✓
+2		✓	✓	✓	✓	✓	✓	✓	✓
+1			✓	✓	✓	✓	✓	✓	✓
0	✓	✓	✓	✓	✓	✓	✓	✓	✓

3d shell either accept or donate

lose from 4s first, then 3d b/c 4s is lower energy
 $Mn^{2+} \rightarrow 4s^0 3d^5$

Coordination Compounds

contain at least 1 complex ion (central metal cation bonded to molecules &/or anion called ligands)

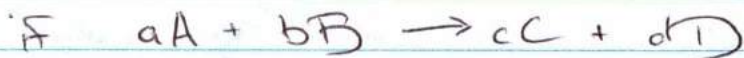
Ligands
 # donor atoms
 "teeth"
 monodentate
 bidentate
 polydentate

Chelate

- a complex ion in which the metal ion is bonded to a bidentate or polydentate ligand

Rate Kinetics

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t}$$



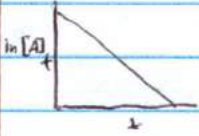
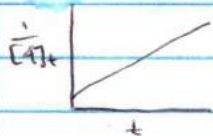
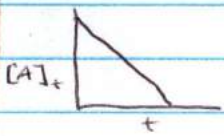
then

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Rate Law:

$$\text{Rate} = k[A]^m[B]^n$$

k = reaction constant
 m/n = reaction orders

	First Order	Second order	Zero Order
Rate Law	$\text{rate} = k[A]$	$\text{rate} = k[A]^2$	$\text{rate} = k$
units for k	$\frac{1}{s}$	$\frac{l}{\text{mol} \cdot s}$	$\frac{\text{mol}}{l} \cdot s$
Half-Life	$\frac{\ln 2}{k}$	$\frac{1}{k[A]_0}$	$\frac{[A]_0}{2k}$
Integrated Rate Law = straight line	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$[A]_t = -kt + [A]_0$
plot for line	$\ln[A]_t$ vs t	$\frac{1}{[A]_t}$ vs t	$[A]_t$ vs t
graph			
slope; y-int	$-k; \ln[A]_0$	$k; \frac{1}{[A]_0}$	$-k; [A]_0$
	If rate doubles when $[A]$ doubles	If rate quadruples when $[A]$ doubles	If rate doesn't change when $[A]$ doubles
		$[A]^2$	$[A]^0$

Arrhenius equation: relationship btwn temp & rate constant

$$k = Ae^{-E_a/RT}$$

k = rate constant

R = gas constant

e = base of nat log

E_a = activation energy

T = absolute temp

A = frequency factor

p7

p651

Activation Energy

the minimum energy with which molecules must collide to react

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{product}$	Unimolecular	Rate = $k[A]$
$2A \rightarrow \text{product}$	Bimolecular	Rate = $k[A]^2$
$A+B \rightarrow \text{product}$	Bimolecular	Rate = $k[A][B]$
$2A+B \rightarrow \text{product}$	Termolecular	Rate = $k[A]^2[B]$

Catalyst

Substance that increases rate without being consumed

catalyst \Rightarrow lower $E_a \Rightarrow$ larger $k \Rightarrow$ higher rate

Equilibrium:

Equilibrium: $\text{rate}_{\text{fwd}} = \text{rate}_{\text{rev}}$

Equilibrium Constant

$$K_{\text{eq}} = \frac{[\text{B}]^b}{[\text{A}]^a}$$



Reaction Quotient

$$Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$



at equilibrium $Q = K$

Form of Equation	Form of Q	Form of k
$\text{A} \rightleftharpoons \text{B}$	$Q_r = \frac{[\text{B}]}{[\text{A}]}$	$k_r = \frac{[\text{B}]_{\text{eq}}}{[\text{A}]_{\text{eq}}}$
$\text{B} \rightleftharpoons \text{A}$	$Q_r = \frac{[\text{A}]}{[\text{B}]}$	$k_r = \frac{1}{k_r}$
1) $\text{A} \rightleftharpoons \text{C}$ 2) $\text{C} \rightleftharpoons \text{B}$	$Q_1 = \frac{[\text{C}]}{[\text{A}]}$ $Q_2 = \frac{[\text{B}]}{[\text{C}]}$ overall = $Q_1 \cdot Q_2 = \frac{[\text{B}]}{[\text{A}]}$	overall = $k_1 \cdot k_2 = k_r$
Coefficients multiplied by n	$Q = Q_r^n$	$k = k_r^n$
Reaction with pure solid/liquid component	$Q = Q_r [\text{A}] = [\text{B}]$	$k = k_r [\text{A}] = [\text{B}]$

If

$$Q > K$$

reactants \leftarrow products

$$Q < K$$

reactants \rightarrow products

$$Q = K$$

reactants \rightleftharpoons products

$k_{eq} > 1$	$[product] > [reactants]$
$k_{eq} = 1$	$[product] = [reactants]$
$k_{eq} < 1$	$[product] < [reactants]$

Le Châtelier's Principle

If a system is in equilibrium, is disturbed, it will shift its equilibrium position to compensate & reduce the effect to the disturbance

Disturbance	Effect on Equilibrium	Effect on value k
Concentration		
↑ [reactant]	→	None
↓ [reactant]	←	None
↑ [product]	→	None
↓ [product]	←	None
Pressure		
↑ P	fewer moles of gas	None
↓ P	more moles of gas	None
Temperature		
↑ T	absorption of heat	↑ if $\Delta H_{rxn} > 0$ ↓ if $\Delta H < 0$
↓ T	release of heat	↑ if $\Delta H < 0$ ↓ if $\Delta H > 0$
Catalyst	both rxn affected equally; equilibrium reached sooner	

Vant Hoff Equation

$$\ln \frac{k_2}{k_1} = -\frac{\Delta H_{rxn}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

First Law of Thermodynamics

Energy is conserved; the total energy of the universe is constant

$$\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surrounding}} = 0$$

Second Law of Thermodynamics

processes occur spontaneously in the direction that increases the entropy of the universe

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

Third Law of Thermodynamics

a perfect crystal has zero entropy at absolute zero

Entropy

$$S = k \ln w$$

baaaaaah!

$$k = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

w = # microstates

Microstate

arrangement of particles

$$w = 2^n$$

Entropy of Reaction

$$\Delta S_{\text{rxn}} = \sum m S^{\circ}_{\text{products}} - \sum n S^{\circ}_{\text{reactants}}$$

m, n = coefficients

$$\Delta S_{\text{surr}} = - \frac{\Delta H_{\text{sys}}}{T}$$

Gibbs Free Energy

amount of energy available to do work

$$G = H_{\text{sys}} - TS_{\text{sys}}$$

$$\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

solid < liquid < gas

Entropy shows: spontaneous or not

net energy absorbed or consumed

Direction of equation

ΔH	ΔS	$-T\Delta S$	ΔG	Description
-	+	-	-	spontaneous at all T
+	-	+	+	Nonspontaneous at all T
+	+	-	+ or -	Spont @ higher T Nonspont @ lower T
-	-	+	+ or -	Spont @ lower T Nonspont @ higher T

K	$\ln K$	Q	ΔG	Fwd/Rev/Both
> 1	> 0	$> K$	-	Forward
1	0	$= K$	0	Equilibrium \rightarrow Both
< 1	< 0	$< K$	+	Reverse

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Oxidation Reduction

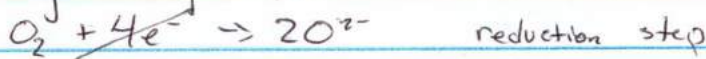
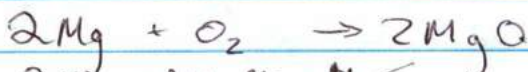
LEO goes GER

Atom $\rightarrow e^- \Rightarrow$ oxidation

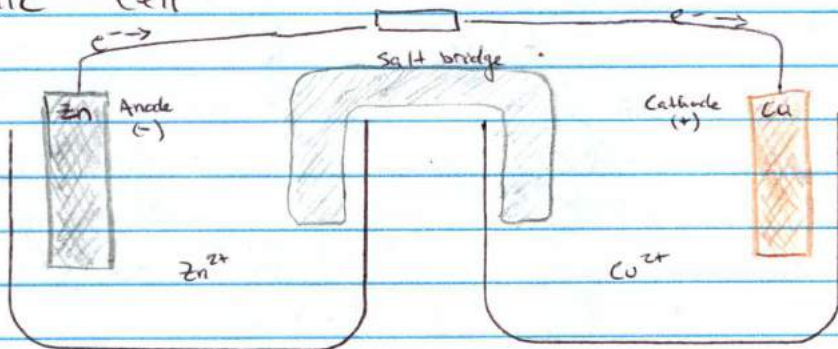
reducing agent

Atom $\leftarrow e^- \Rightarrow$ reduction

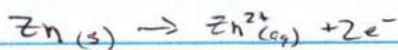
oxidizing agent



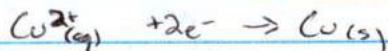
Voltaic Cell



oxidation half reaction



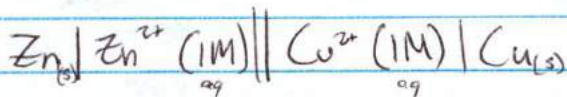
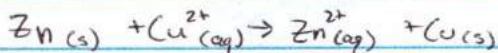
reduction half reaction



AN OX & a RED CAT

anode-oxidation cathode-reduction

overall



Standard Cell Potential

$$\text{Potential} = \frac{\text{Energy}}{\text{Charge}}$$

$$1V = \frac{1J}{C}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

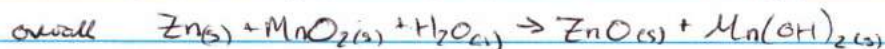
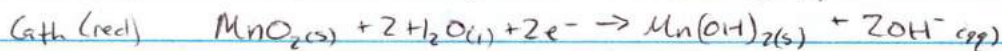
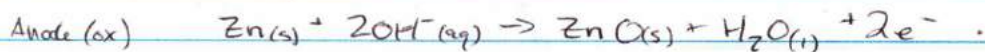
$$\Delta G = -nFE_{\text{cell}}$$

$$F = \text{Faraday's constant} = \frac{9.6 \times 10^4 \text{ C}}{\text{mole } e^-}$$

$$n = \#e^-$$

stage in cell operation	Q	relative [P] to [R]	$\frac{-0.0592 \text{ V}}{n} \log Q$
1 $E > E^\circ$	< 1	[P] < [R]	< 0
2 $E = E^\circ$	= 1	[P] = [R]	= 0
3 $E < E^\circ$	> 1	[P] > [R]	> 0
4 $E = 0$	= K	[P] = [R]	= E°

Alkaline Battery



Lead Acid Battery

Lithium Ion Battery

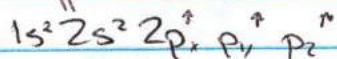
Fuel Cell

Non metals

Nitrogen

atmosphere

trapped as nitrates



gain 3 or lose 5

important b/c DNA

Carbon

mostly biomass in related deposits

graphite - most stable

fullerenes - carbon ball

Hydrogen

water, biomass, fossil fuels

hydrogen bond

hydrides

Phosphorus

very oxidative (up to 6)

D-block

constituent of earth

Sulfur



most stable

Organic Chemistry

Rules For Naming Organic Compounds

1) Naming the longest chain (root)

- Find the longest continuous chain of C atoms
- Select the root that corresponds to the # of C

2) Naming the compound type (suffix)

- For alkanes add -ane to chain root (depends on functional group)
- If chain forms a ring, name preceded by 'cyclo-

3) Naming the branches (prefixes)

- Each branch name consists of a subroot (number of C atoms) & the ending -yl to signify its not part of main chain
- Branch names precede the chain name, 2 or more → alphabetical order
- To specify where the branch occurs along the chain, number the main chain C atoms consecutively. Precede each branch name w/ number of attached main chain C atoms

Roots	# C atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Alkane	Alkenes	Alkynes
Single bonds	at least 1 C=C	at least 1 C≡C
$C_n H_{2n+2}$	$C_n H_{2n}$	$C_n H_{2n-2}$
sp^3 hybridized	sp^2 hybridized (C=C)	sp hybridized
saturated hydrocarbons	unsaturated	
	C=C restricts rotation	

Isomers

Constitutional isomers

same molecular formula, different arrangements

Stereoisomers

same arrangement, different orientation

Optical isomers (enantiomers)

mirror images, cannot be superimposed HANDS

Chirality

optical isomer with a ^{center} C atom bonded to 4 different groups
chiral center

Geometric isomers

cis-trans

have different orientations of groups around a double bond

cis = same side



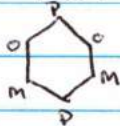
trans = opposite side



Aromatic Hydrocarbons

cyclic molecules with delocalized π electrons

smell nice!



ortho-
meta-
para-

Organic Reactions

R- alkyl group

Addition Reaction

unsaturated becomes saturated

Elimination Reaction

saturated becomes unsaturated

Substitution Reaction

when an atom (or group) from reagent substitutes for one attached to a C

Functional Group	Compound Type	Prefix / Suffix
$\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$	alkene	-ene
$-\text{C}\equiv\text{C}-$	alkyne	-yne
$\begin{array}{c} \\ \text{C}-\ddot{\text{O}}-\text{H} \\ \end{array}$	alcohol	-ol
$\begin{array}{c} \\ \text{C}-\ddot{\text{X}} \\ \end{array} \quad \text{x=halogen}$	haloalkane	halo-
$\begin{array}{c} \\ \text{C}-\ddot{\text{N}}- \\ \end{array}$	amine	-amine
$\begin{array}{c} \text{:O:} \\ \\ \text{C}-\text{H} \end{array}$	aldehyde	-al
$\begin{array}{c} \text{:O:} \quad \text{:O:} \\ \quad \\ \text{C}-\text{C}-\text{C}- \\ \quad \end{array}$	ketone	-one
$\begin{array}{c} \text{:O:} \\ \\ \text{C}-\ddot{\text{O}}-\text{H} \end{array}$	carboxylic acid	-oic acid
$\begin{array}{c} \text{:O:} \\ \\ \text{C}-\ddot{\text{O}}-\text{C}- \\ \end{array}$	ester	-oate
$\begin{array}{c} \text{:O:} \\ \\ \text{C}-\ddot{\text{N}}- \\ \end{array}$	amide	-amide
$-\text{C}\equiv\text{N:}$	nitrile	-nitrile

Chapter 4: Alcohols & Alkyl Halides

Functional Group - structural unit in a molecule responsible for characteristic physical properties & behavior under reaction conditions

Nomenclature

Alkyl Halides:

Halo (x) \rightarrow F, Cl, Br, I as substituents

Number C chain from closest to substituent

Halogen, Alkyl group \rightarrow Same priority

Fluoro-, chloro-, bromo-, iodo- -ane

Alcohols:

Longest continuous C chain w/ -OH group

Number from side closest to -OH

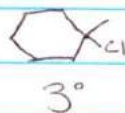
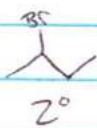
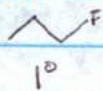
replace -ane with '-ol'

2-Hexanol, Hexan-2-ol

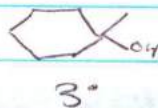
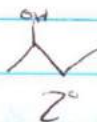
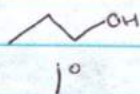
-OH assumed to be on C-1 of cyclic alcohols

Classification

Alkyl Halides:



Alcohols:



Reaction of alcohols w/ hydrogen halides yields alkyl halides
 $R-OH + H-X \rightarrow R-X + H-OH$

Rate: related to classification of alcohol
 $1^\circ-OH < 2^\circ-OH < 3^\circ-OH$

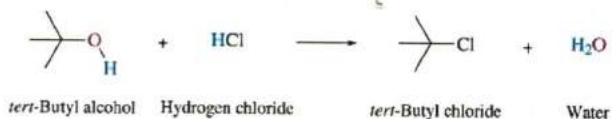
Sol

Mechanism

Mechanism 4.1

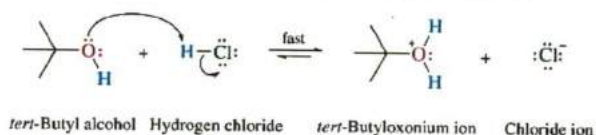
Formation of *tert*-Butyl Chloride from *tert*-Butyl Alcohol and Hydrogen Chloride

THE OVERALL REACTION:

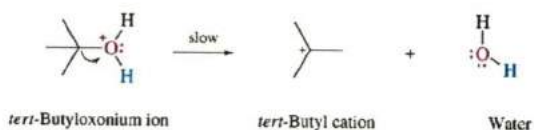


THE MECHANISM:

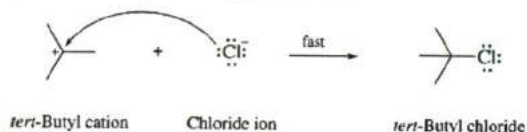
Step 1: Protonation of *tert*-butyl alcohol to give an alkyloxonium ion:



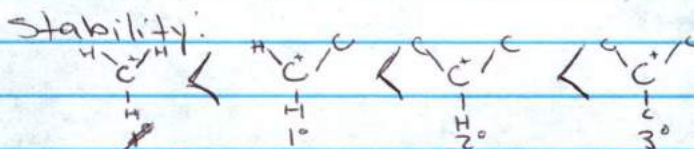
Step 2: Dissociation of *tert*-butyloxonium ion to give a carbocation:



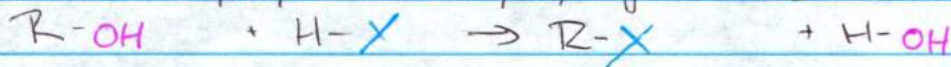
Step 3: Capture of *tert*-butyl cation by chloride ion:



Carbocations - positive charge, sp^2 hybridized, electrophilic, \rightarrow Lewis Acid



Reaction of methyl & 1° alcohols w/ hydrogen halides



S_N2

Mechanism

Mechanism 4.2

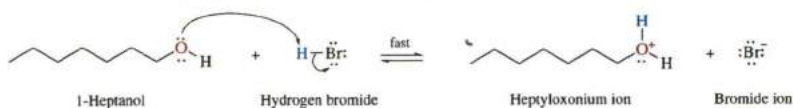
Formation of 1-Bromoheptane from 1-Heptanol and Hydrogen Bromide

THE OVERALL REACTION:

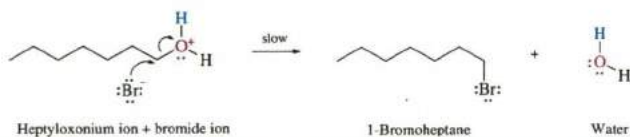


THE MECHANISM:

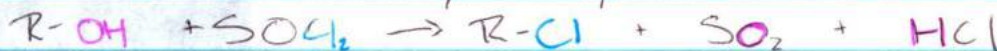
Step 1: Proton transfer from hydrogen bromide to 1-heptanol to give the corresponding alkyloxonium ion:



Step 2: Displacement of water from the alkyloxonium ion by bromide:



Reaction of Alcohols w/ Thionyl Chloride



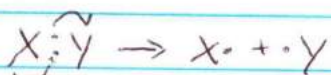
Mechanism

Free Radicals - contain unpaired electrons

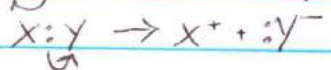
For carbon, more substituted radicals are more stable
- sp^2 hybridized

Bond Cleavage

Homolytic



Heterolytic



more e^- neg

Free Radical Chlorination of Methane



Mechanism

Mechanism 4.3

Free-Radical Chlorination of Methane

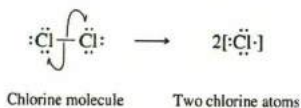
THE OVERALL REACTION:



THE MECHANISM:

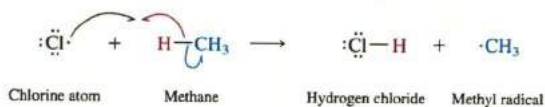
(a) Initiation

Step 1: Dissociation of a chlorine molecule into two chlorine atoms:



(b) Chain propagation

Step 2: Hydrogen atom abstraction from methane by a chlorine atom:



Step 3: Reaction of methyl radical with molecular chlorine:



Steps 2 and 3 then repeat many times.

Selectivity of Halogenation $\rightarrow 1^\circ < 2^\circ < 3^\circ$

Alcohols have hydrogen bonding \rightarrow inter/intra forces

Bond distances $C-F < C-Cl < C-Br < C-I$

Boiling point of **AH** & **Alcohols** increases w/ carbon chain length

Alkyl Halides - insoluble in H_2O

Alcohol - solubility in H_2O related to size of alkyl group attached to $-OH \rightarrow$ hydrogen bonding

Chapter 5: Elimination Reactions

Nomenclature: Alkenes

longest continuous chain w/ double bond

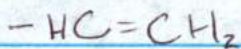
replace -ane with -ene

name chain so first C of alkene has lowest number

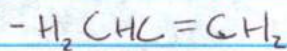
precedence over alkyl & halo substituents

longest continuous chain w/ C=C > longer chain w/o hydroxyl (-OH) > alkenes. -enol

Vinyl



Allyl



Alkene C's \rightarrow sp^2 hybridized

1 σ bond, 1 π bond

C=C stronger & shorter than C-C

σ bond stronger than π bond



cis-



trans-

stereoisomers

Z-configuration

E-configuration

Cahn-Ingold-Prelog system

Priority ranks

highest atomic number

if more than 1 atom, move to next

double bond > single bond

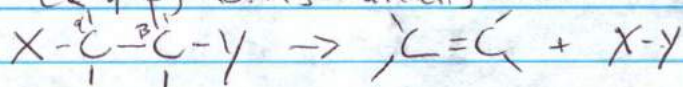
Stability



1. Degree of substitution of $C=C$
 2. Van der Waals strain in cis isomers (steric effect)
 3. Chain branching increasing stability
- More substituted > less substituted
trans > cis

Elimination

elimination of two substituents from adjacent Cs
(α & β) forms alkenes



Dehydration

- removal of H_2O

- high temp

Dehydrogenation

- removal of H_2

(-OH, H) - catalyzed by acid

Regioselectivity

- reactions proceed preferentially to form more of one constitutional isomer

Zaitsev's Rule

- alkene formed in greatest amount corresponds to removal of the hydrogen from the β carbon w/ fewest hydrogens

Stereoselectivity

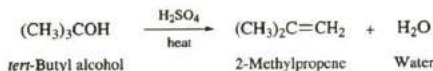
- reactions yield one stereoisomer in preference to another

E1 Mechanism of Dehydration

Mechanism 5.1

The E1 Mechanism for Acid-Catalyzed Dehydration of *tert*-Butyl Alcohol

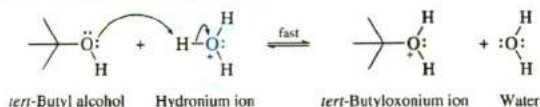
THE OVERALL REACTION:



acid catalyzed

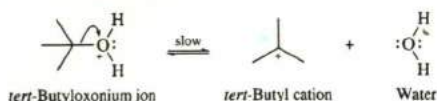
THE MECHANISM:

Step 1: Protonation of *tert*-butyl alcohol:



acid-base reaction \rightarrow -OH protonated by acid

Step 2: Dissociation of *tert*-butyloxonium ion to a carbocation and water:



\leftarrow rate determining step is unimolecular = E1

Step 3: Deprotonation of *tert*-butyl cation:



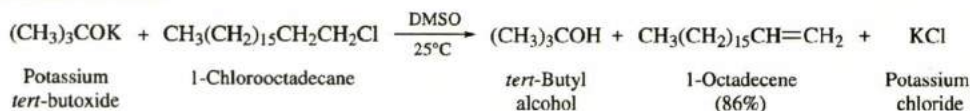
water acts as base, abstracts proton from carbocation

E2 Mechanism of Dehydration

Mechanism 5.4

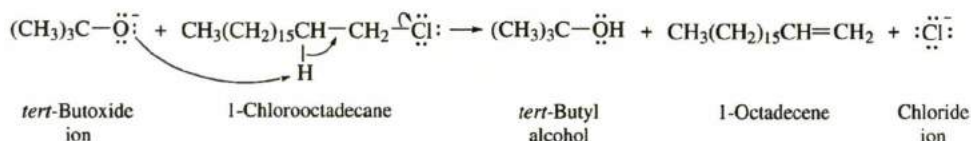
E2 Elimination of 1-Chlorooctadecane

THE OVERALL REACTION:



THE MECHANISM:

The reaction takes place in a single step in which the strong base *tert*-butoxide abstracts a proton from C-2 of the alkyl halide concurrent with loss of chloride from C-1. We can omit writing K^+ in the equation because it appears on both sides of the equation (a "spectator ion").



rate determining bimolecular = E2

1° cations are unstable so 1° alcohols do not react the same

Rearrangement - reaction when connectivity of atoms changes

Carbocation Rearrangement

Mechanism 5.2
Carbocation Rearrangement in Dehydration of 3,3-Dimethyl-2-butanol

THE OVERALL REACTION:

THE MECHANISM:

Steps 1 and 2: These are analogous to the first two steps in the acid-catalyzed dehydration of *tert*-butyl alcohol described in Mechanism 5.1. The alcohol is protonated in aqueous acid to give an oxonium ion that dissociates to a carbocation and water.

Steps 3 and 3': The carbocation formed in step 2 can do two things. It can give an alkene by transferring a proton to a Brønsted base such as water present in the reaction mixture (step 3), or it can rearrange (step 3'). Because alkenes with a rearranged carbon skeleton predominate in the product, we conclude that step 3' is faster than step 3.

Step 3:

← minor pathway

Step 3': Rearrangement by methyl migration is driven by the conversion of a less stable secondary carbocation to a more stable tertiary one.

← major pathway, METHYL SHIFT more stable 3° C+

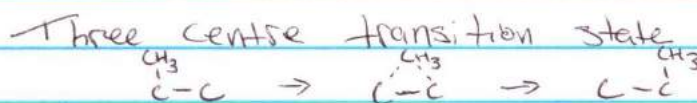
Steps 4 and 4': The tertiary carbocation formed in step 3' can be deprotonated in two different directions. The major pathway (step 4') gives a tetrasubstituted double bond and predominates over step 4, which gives a disubstituted double bond.

Step 4:

Step 4':

carbocations 1° < 2° < 3°

H can be abstracted from either of the alkene C's → two isomers



Hydride Shift

Mechanism 5.3

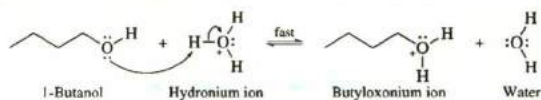
Hydride Shift in Dehydration of 1-Butanol

THE OVERALL REACTION:

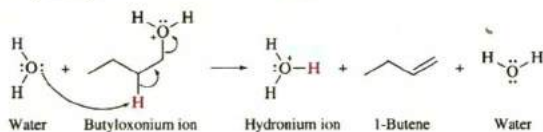


THE MECHANISM:

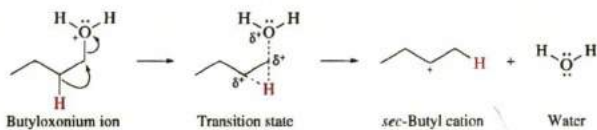
Step 1: Protonation of the alcohol gives the corresponding alkyloxonium ion.



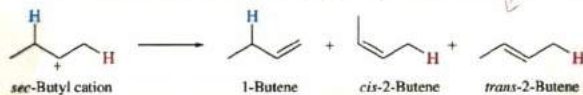
Step 2: One reaction available to butyloxonium ion leads to 1-butene by an E2 pathway.



Step 2': Alternatively, butyloxonium ion can form a secondary carbocation by loss of water accompanied by a hydride shift.



Step 3: The secondary carbocation formed in step 2 can give 1-butene or a mixture of *cis*-2-butene and *trans*-2-butene, depending on which proton is removed.

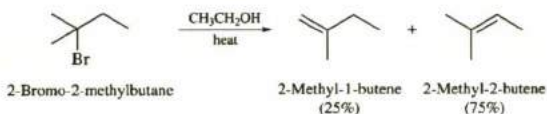


E1 Dehydrohalogenation

Mechanism 5.5

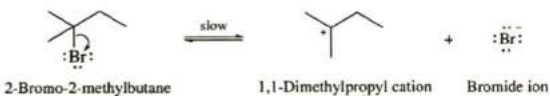
The E1 Mechanism for Dehydrohalogenation of 2-Bromo-2-methylbutane

THE OVERALL REACTION:

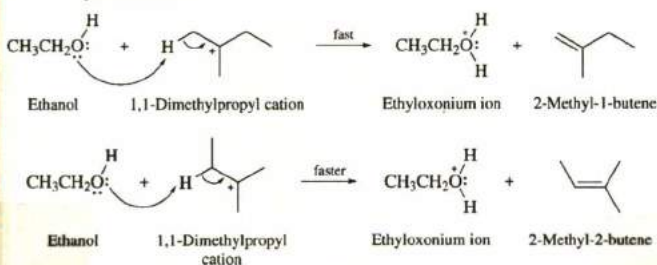


THE MECHANISM:

Step 1: Ionization The alkyl halide dissociates by heterolytic cleavage of the carbon-halogen bond. The products are a carbocation and a halide ion. This is the rate-determining step.



Step 2: Deprotonation Ethanol acts as a Brønsted base to remove a proton from the carbocation to give the two alkene products. Zaitsev's rule is followed, and the regioisomer with the more highly substituted double bond predominates.



rate dependent on concentration of base

loss of H & halogen from alkyl halide

Selectivity: Zaitsev Rule

more substituted alkene preferred
prefers trans stereoisomer

Leaving Group - Halide ion that leaves alkyl halide
 $\text{RF} < \text{RCI} < \text{RBr} < \text{RI}$

E1 - concerted reaction

E2 - step by step mechanism

↕
oops

Rate = k [alkyl halide]

1° < 2° < 3°

Chapter 6: Addition Reactions of Alkenes

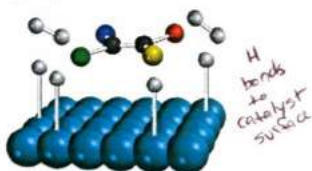


Hydrogenation of Alkenes

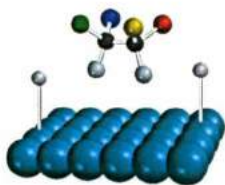
Mechanism 6.1

Hydrogenation of Alkenes

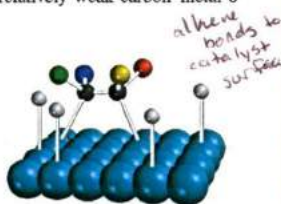
Step 1: Hydrogen molecules react with metal atoms at the catalyst surface. The relatively strong hydrogen-hydrogen σ bond is broken and replaced by two weak metal-hydrogen bonds.



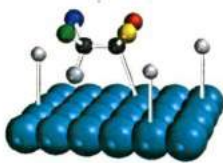
Step 3: A hydrogen atom is transferred from the catalyst surface to one of the carbons of the double bond.



Step 2: The alkene reacts with the metal catalyst. The π component of the double bond between the two carbons is replaced by two relatively weak carbon-metal σ bonds.



Step 4: The second hydrogen atom is transferred, forming the alkane. The sites on the catalyst surface at which the reaction occurred are free to accept additional hydrogen and alkene molecules.



Syn

- addition on same side of alkene $C=C$

Anti

- addition on opposite sides of $C=C$

$1^\circ < 2^\circ < 3^\circ < 4^\circ$

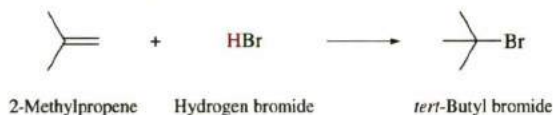
stability

Addition of Hydrogen Halides to Alkenes

Mechanism 6.2

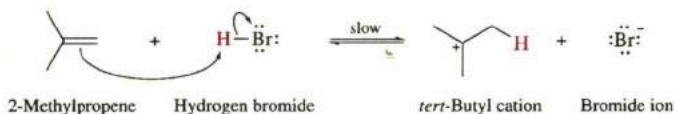
Electrophilic Addition of Hydrogen Bromide to 2-Methylpropene

THE OVERALL REACTION:

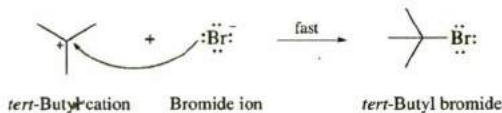


THE MECHANISM:

Step 1: This is the rate-determining step and is bimolecular. Protonation of the double bond occurs in the direction that gives the more stable of two possible carbocations. In this case the carbocation is tertiary. Protonation of C-2 would have given a less stable secondary carbocation.



Step 2: This step is the combination of a cation (Lewis acid, electrophile) with an anion (Lewis base, nucleophile) and occurs rapidly.



Alkene + hydrogen halide \rightarrow alkyl halide

$F << Cl < Br < I$

$1^\circ < 2^\circ < 3^\circ$

highly selective

\hookrightarrow Markovnikov

Rate Determining \rightarrow
produces most stable cation

Markovnikov's Rule - when an unsymmetrically substituted alkene reacts w/ hydrogen halide, the hydrogen adds to the carbon that has more hydrogens, the halogen adds to the carbon w/ fewer hydrogens.
H \heartsuit H

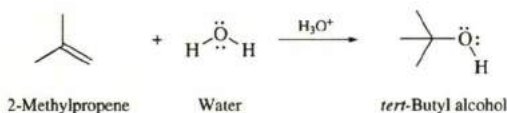
\rightarrow Carbocation Rearrangement \rightarrow Hydride shift

Addition of Water to Alkenes

Mechanism 6.3

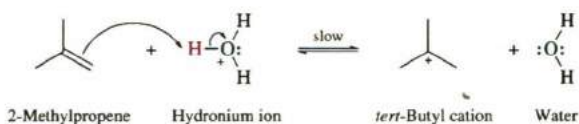
Acid-Catalyzed Hydration of 2-Methylpropene

THE OVERALL REACTION:



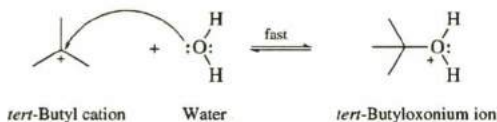
THE MECHANISM:

Step 1: Protonation of the carbon-carbon double bond in the direction that leads to the more stable carbocation:



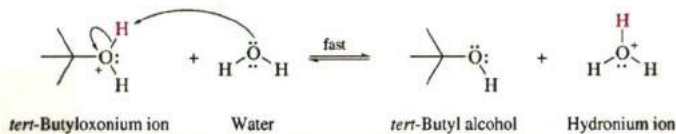
→ rate determining

Step 2: Water acts as a nucleophile to capture *tert*-butyl cation:



selective → Markovnikov

Step 3: Deprotonation of *tert*-butyloxonium ion. Water acts as a Brønsted base:



1° < 2° < 3°

carbocation intermediates

Hydration \rightleftharpoons Dehydration

Le Chatelier's Principle - a system at equilibrium adjusts to minimize any stress applied to it
 H_2O is key stress

Anti-Markovnikov Addition of Water

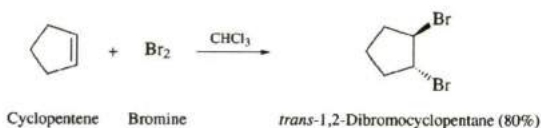
indirect method - involves sequential hydroboration & oxidation

Addition of Halogens to Alkenes

Mechanism 6.6

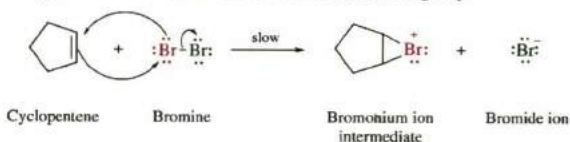
Bromine Addition to Cyclopentene

THE OVERALL REACTION:

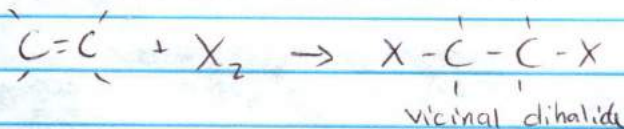
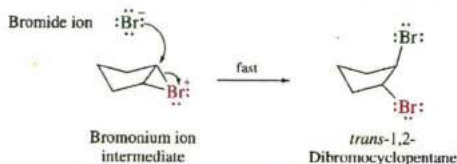


THE MECHANISM:

Step 1: Bromine acts as an electrophile and reacts with cyclopentene to form a cyclic bromonium ion. This is the rate-determining step.



Step 2: Bromide ion acts as a nucleophile, forming a bond to one of the carbons of the bromonium ion and displacing the positively charged bromine from that carbon. Because substitutions of this type normally occur with the nucleophile approaching carbon from the side opposite the bond that is broken, the two bromine atoms are *trans* to one another in the product.



trans-dihalides exclusively formed by anti addition

Chapter 7: Chirality

Chiral molecule: mirror image forms are NOT superimposable
most often found when C is attached to 4 diff groups.


Enantiomers: stereoisomers that are mirror images that are non-superimposable

To check whether molecules are superimposable rotate mirror images so one group points in same direction & check if line up

Chirality Center $\begin{array}{c} x \\ | \\ w - C - y \\ | \\ z \end{array}$ wxyz are different

Achiral molecule: mirror images are superimposable

Plane of Symmetry: bisects a molecule so one half is mirror image of the other half $\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array}$

Center of Symmetry: for any atom in a molecule, an identical atom exists diametrically opposite center an equal distance from center 

Optical Activity

if it rotates plane of polarized light
to be optically active, sample must contain chiral substance
w/ one enantiomer in excess of the other

α = observed rotation = magnitude (+), (-) = direction

Enantiomers have $[\alpha]$ of equal magnitude but opposite sign

Enantiomeric excess = (% major enantiomer) - (% minor enantiomer)

if ee = 100% it is **enantiopure**

Racemic Mixture: 1:1 mixture of enantiomers, optically inactive

Absolute Configuration: 3D spatial arrangement of substituents at chirality center

Relative Configuration:

Cahn-Ingold-Prelog Rules

- ① Rank substituents at chirality center according to $Z-Z$ notation
highest = $\text{OH} > \text{CH}_2\text{CH}_3 > \text{CH}_3 > \text{H}$ = lowest
- ② Orient molecule so lowest ranked substituent points away from you
- ③ If decreasing precedence is clockwise \curvearrowright = **R configuration**
If decreasing precedence is counterclockwise \curvearrowleft = **S configuration**

Names of Enantiomers differ only in R/S assignment
(S)-2-butanol vs (R)-2-butanol

Chirality Center in a Ring

high priority path vs lower priority path
C=C counts as 2 bonds to C

Fischer Projections: Planar representation of chiral centers

vertical lines - away

horiz lines - towards

carbon chain is vertical

lowest numbered C @ top of chain



- ① Draw structure so lowest # carbon is on top
- ② Arrange horizontal bonds facing towards you
- ③ Flatten molecule & Draw

Reactions that Create Chiral Centers

Alkene is planar so it is attacked from top/bottom equally

Racemic mixture of enantiomers are formed

Addition of HBr to Alkene

Chlorination of Alkanes

Molecules w/ Two Chirality Centers

Each stereocenter can be R or S

4 possible stereoisomers 2R, 3R 2S, 3S 2R, 3S 2S, 3R

• ← enantiomers → •

• ← enantiomers → •

Diastereomers: stereoisomers that are not enantiomers

• ← diastereomers → •, •

• ← diastereomers → •, •

Erythro isomers: have like substituents on same side of Fischer projection

Threo isomers: have like substituents on opposite sides of Fischer

Physical Properties

Enantiomers: identical except for rotation of polarized light

Diastereomers: may differ in any physical property

Alkenes



Molecules w/ n stereocenters can have 2^n stereoisomers

How to separate enantiomers:

- ① Transform mix of enantiomers into mix of diastereomers
- ② Separate diastereomers based on differing physical properties
- ③ Reform separated enantiomers

Chirality Centers other than Carbon

Silicon \rightarrow tetrahedral arrangement

Trigonal pyramidal amines are chiral but undergo rapid inversion at nitrogen

Phosphines undergo much slower inversion

Methods of Describing Molecules

Composition

Number & kinds of atoms that make up a molecule

Constitution

Bonding pattern of the atoms of a molecule

i.e. which atoms are connected to each other & the type of bonds

Configuration

Permanent spatial relationship of atoms in a molecule
→ cis & trans, R & S

Conformation

Variable spatial relationship of atoms in a molecule
→ gauche & anti

Constitutional Isomers (Different Bonding Patterns) { Stable Structural Isomers
Tautomers (Rapidly Interconverted)

Stereoisomers (Different orientations of atoms in space) { Configurational Isomers
Conformational Isomers (Interconverted by Twisting about bonds)

Stereoisomers { Enantiomers - Chiral (Non identical, mirror images)
Diastereomers - [Chiral
Achiral (meso)

Chapter 8: Nucleophilic Substitution

Nucleophilic Substitution

Lewis base acts as nucleophile & substitutes for leaving group on Carbon

Polar Carbon-Halogen bond is broken & C-nucleophile is made

Charged nucleophile has metal cation as counterion

Nucleophilic Reagents

MOR	metal alkoxide	RO^-
MOCOR	metal carboxylate	RCO_2^-
MSH	metal hydrogen sulfide	HS^-
M CN	metal cyanide	$^-\text{C}\equiv\text{N}$
MN_3	metal azide	$^-\text{N}=\text{N}=\text{N}^-$

Functional Group Transformation

From alkyl halide to new functional group dependent on nucleophile

Alkoxide ion	oxygen atom of metal alkoxide replaces halogen of alkyl halide. Product = ether	$\text{RO}^- + \text{R}'\text{X} \rightarrow \text{ROR}' + \text{X}^-$
Carboxylate ion	oxygen of carboxylate replaces halogen. Product = Ester	$\text{RCO}_2^- + \text{R}'\text{X} \rightarrow \text{RCO}_2\text{R}' + \text{X}^-$
Hydrogen sulfide ion	HS^- as nucleophile permits thiols	$\text{HS}^- + \text{R}'\text{X} \rightarrow \text{HSR}' + \text{X}^-$
Cyanide ion	negatively charged carbon of cyanide is nucleophilic site. Extends carbon chain. Products: Alkyl cyanide, nitrile	$\text{N}\equiv\text{C}^-$

sp^3 Carbon reactive
 sp^2 carbon Not reactive

Alkyl iodides most reactive because C-I bond is weakest + I is weakest base
 $I > Br > Cl >> F$

S_N2 Rate

Rate determining step involves breaking C-X bond AND nucleophile

Rate = $k [RX] [Nuc]$ one step! inversion

Nucleophile attacks from side opposite bond to leaving group

Chirality center inversion

Nucleophile attacks lowest unoccupied molecular orbital (LUMO) - σ^* , antibonding

Rate decreases with increasing steric hindrance

methyl $> 1^\circ > 2^\circ > 3^\circ$

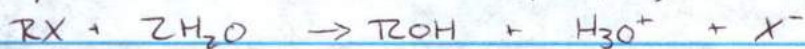
β -Substitution \rightarrow \uparrow steric hindrance, \downarrow rate

methyl $> 1^\circ > 2^\circ > 3^\circ$

Neutral Nucleophiles

Amines (RN_2) Sulfides (RS_2) Phosphines (RP_3)

Solvolysis reactions w/ water (hydrolysis) & alcohols



Nucleophilicity: nucleophile strength. Measure of how fast

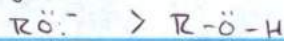
Lewis base displaces halogen in substitution

stronger base = stronger nucleophile

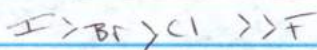
(stronger base is conjugate base of weaker acid)

holds true when comparing Nuc in same row on periodic table

charged Nuc $>$ non charged when comparing same atoms



Period on periodic table \rightarrow solvation of nucleophile

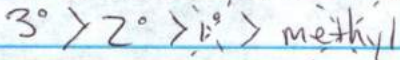


Sulfonates are good leaving groups
alcohol \rightarrow sulfate \rightarrow leave
can form alkyl halides via sub

S_N1

$$\text{Rate} = k[\text{RX}]$$

Carbocation intermediate (planar)



Although NUC can attack from either side of plane, the leaving group shields front side of carbocation; NUC attacks faster from back \rightarrow inversion \rightarrow retention

Rearrangements \rightarrow hydride shift / methyl shift

Effect of Solvent on Substitution

Affects rate, not products formed

Protic solvents: capable of hydrogen bonding (-OH, N-H group)

Aprotic solvents: no hydrogen bonding

Polarity: related to dielectric constant (ϵ)

Solvents & S_N2

Polar Protic \rightarrow H-bond to \ominus , suppress nucleophile, \downarrow rate

$\checkmark\checkmark$ Polar Aprotic \rightarrow provide dipoles, but don't H-bond, \uparrow rate

Solvents & S_N1

$\checkmark\checkmark$ Polar Protic \rightarrow reduce energy in transition carbocation \uparrow rate

Substitution vs E Elimination

1) Base strength of Nucleophile

Weak \rightarrow substitution \uparrow

Strong \rightarrow elimination \uparrow

2) Steric Hindrance @ Reacting Carbon

Sterically unhindered - with 1°

sterically hindered; $1^\circ, 2^\circ, 3^\circ$

Substitution \uparrow

elimination \uparrow

3) Steric Hindrance of Strongly Basic Nucleophile

Sterically unhindered

sterically hindered

substitution maybe

elimination favored

Alkyl Halide	Prot Nuc EtOH	weak Base CH ₃ OH	Strong, Unhindered Base CH ₃ OH	Strong, hindered Base (CH ₃) ₃ COH
methyl 1°	No reaction	S _N 2	S _N 2	S _N 2
unhindered	No reaction	S _N 2	S _N 2	E2
branched	No reaction	S _N 2	E2	E2
2°	slow S _N 1, E1	S _N 2	S _N 2, E2	E2
3°	S _N 1, E1	S _N 1, E1	E2	E2

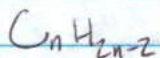
Properties

Mechanism	Stereochemistry	Rate	Rearrangement
S _N 2	Inversion	k[sub][Nuc]	Never
S _N 1	Racemic - inversion pref	k[sub]	often, if possible
E2	Anti-coplanar Zaitsev	k[sub][base]	Never
E1	Zaitsev	k[sub]	often, if possible

Chapter 9: Alkynes

Alkynes

Carbon-carbon triple bond



Acetylene $H\equiv C-H$ is simplest alkyne

Terminal alkyne: alkyne @ end of carbon chain $R\equiv C-H$

Naming Alkynes

-yne

number so first multiple bond lowest number

Properties & Structures of Alkynes

resemble alkanes & alkenes in physical properties

Low density & low water solubility

Boiling points similar to corresponding alkane

Acetylene is linear 180°

Smallest stable cycloalkyne = cyclononyne

sp hybridized $1\sigma, 2\pi$

Acidity

Terminal alkynes similar to acetylene in acidity $pK_a = 25.5$

After deprotonation, acetylide electron pair is in sp orbital

Acid-Base Reactions

Need strong anionic base

Hydroxide \rightarrow weak eq lies to left

Amide (NH_2^-) \rightarrow strong eq lies to right

Acetylide Anions as Nucleophiles

React w/ methyl & 1° alkyl halides via S_N2 reaction



Elimination Reactions w/ Acetylide Anions

Acetylide = very basic

Elimination from 2° or 3° alkyl halides

Preparation of Alkynes by Elimination

via double dehydrohalogenation of geminal or vicinal dihalides

Geminal dihalide: Xs attached to same Cs



Vicinal dihalide: Xs attached to adjacent Cs



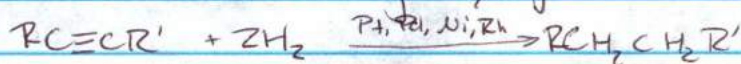
Vicinal dibromides formed on bromination of alkenes

Protonation of acetylide anion

3x base are required if alkyne is terminal

Hydrogenation of Alkynes

reduced to alkanes using hydrogen + transition metal catalyst



Stability of Alkynes

Hydrogenation with Lindlar Catalyst

alkynes \rightarrow alkenes

yield cis-alkenes via syn addition

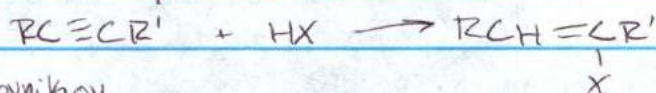
Metal Ammonia Reduction of Alkynes

Group 1 metals in liquid ammonia \rightarrow trans alkenes

key intermediate = vinyl radical (prefers trans conformation)

Addition of Hydrogen Halides

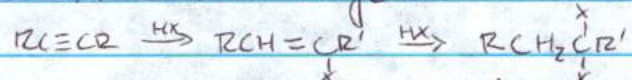
yield alkene halides



Markovnikov

two equivalents of HX

Excess HX leads to geminal dihalides

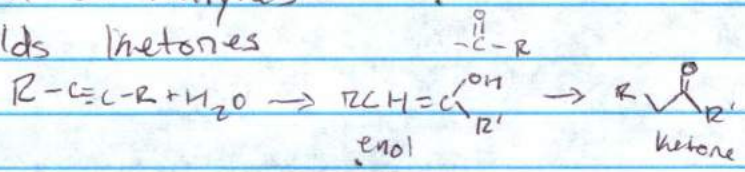


since each addition follows Markovnikov \rightarrow same carbon

Anti-Markovnikov addition of HBr is performed w/ peroxide

Hydration of Alkynes

yields ketones



Enol rapidly isomerizes to keto via keto-enol tautomerism

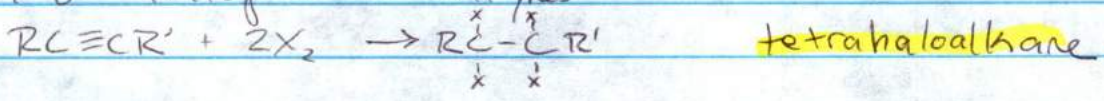
Tautomerism: constitutional isomers that equilibrate

by migration of an atom or group

Markovnikov

terminal alkynes yield methyl ketones (not aldehydes)

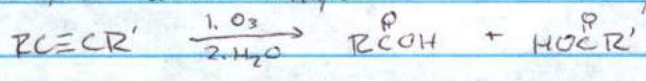
Addition of Halogens to Alkynes



(an anti dihaloalkene can be isolated if exactly one equivalent of hydrogen is used)

Ozonolysis of Alkynes

Ozonolysis cleaves alkynes to form carboxylic acids



Chapter 10

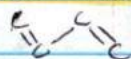
Conjugation in Alkadienes & Allylic Systems

A double bond can act like a substituent & give other groups special properties & reactivity

Carbocations, radicals & anions connected to alkenes are called **allylic**

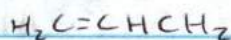


Alkenes connected by a single bond \rightarrow **Conjugated dienes**

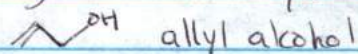


The Allylic Group

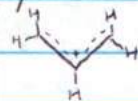
Allyl is common name & IUPAC name



sp^3 hybridized carbon = allylic carbon



Allyl groups are resonance stabilized when charge/radical are shared between the two end carbons



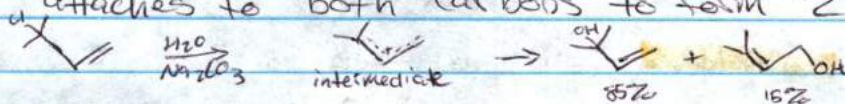
Allylic radicals & ions are more stable

Allylic Halides in $\text{S}_{\text{N}}1$ Reactions

React faster than 3° alkyl halides

Resonance stabilized allyl carbocations is more stable

Because + charge is shared between 2 carbons, substituents attaches to both carbons to form 2 products



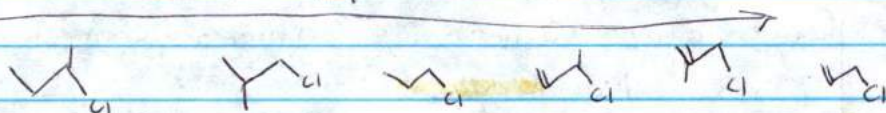
major product corresponds to more stable resonance structure

Hydrolysis of Allylic Halides

Allylic Chlorides & S_N2 Reactions

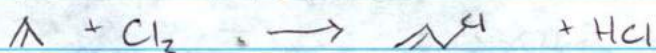
occur between allylic chlorides & good nucleophile (NaOCH₂CH₃)

Allyl Halides > alkyl halides in S_N2



Allylic Halogenation

Free radical reaction



Allylic Bromination usually carried out w/ NBS



N-bromo-succinimide

~~Allylic~~ If allylic forms are not equivalent, mixture of isomeric products is formed

Allylic Anions

planar, stabilized by electron delocalization

Classes of Dienes

Conjugated with two alkenes joined by C-C single bond



Isolated with at least one sp³ C between alkenes



Cumulated with two alkenes sharing a carbon



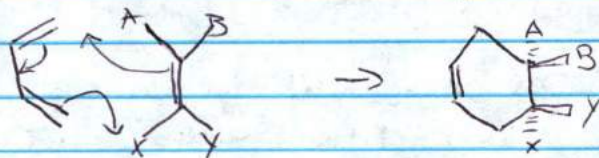
Naming

Replace -ane with -adiene

Conjugated more stable than isolated

Diels-Alder Reaction

diene + dienophile = cyclohexene




Electron withdrawing groups on alkene increase rate
Product will always contain 1 more ring than starting

Diene must be cis to react
steric effects slow reaction

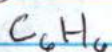
Stereospecific reactions go from stereoisomeric reactants to stereoisomeric products
cis yields cis, trans yields trans

Stereoselective reactions preferentially form one stereoisomer
two cis products: Endo $\frac{1}{2}$, exo (endo favored)

Chapter 11: Arenes & Aromaticity

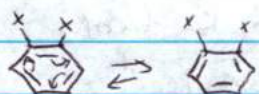
Arenes are hydrocarbons based on benzene unit 

Benzene



All hydrogens of benzene are equivalent

4 bonds to each carbon



rapidly interconvert

Kekulé Structure

planar, all Cs are sp^2 hybridized
6 delocalized π electrons
resonance energy

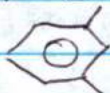
Compounds that contain benzene are aromatic

Disubstituted Benzenes

1,2
ortho



1,3
meta



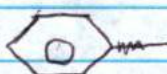
1,4
para



Trisubstituted Benzenes

substituents numerically 1, alphabetically

Benzene AS a Substituent



C_6H_5-
phenyl



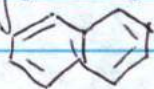
$C_6H_5CH_2-$
benzyl

Biphenyls

one ring named with numbers, the other with primed numbers (3')

Polycyclic Aromatic Hydrocarbons

benzene rings fused together



← most stable resonance structure

larger polycyclic aromatics \rightarrow higher melting pts

Benzylic Cations, Anions & Radicals

Stabilized by Resonance!



major contributors

S_N1 Reactions of Benzylic Halides

benzylic react faster than 3° halide

benzylic cation is more stable

Despite charge delocalization, the nucleophile is only attached to the benzylic carbon



Relative Rates of S_N2 Reactions

Benzylic halides react faster than primary & allylic halides

$1^\circ \rightarrow$ substitution

$2^\circ, 3^\circ \rightarrow$ substitution, elimination

Benzylic Bromination

benzylic halide formed w/ NBS, Δ , CCl_4

Oxidation of Alkylbenzenes

inorganic oxidants
alkyl benzene + inorganic oxidant \longrightarrow carboxylic acid

Synthesis of Alkylbenzenes

Dehydration, dehydrogenation, dehydrohalogenation

Reactions of Alkenylbenzenes \rightarrow act like alkenes

if there is a carbocation intermediate will selectively form the benzyl cation

Reduction of Benzene (Birch Reduction)

A Group 1 metal in liquid ammonia in ethanol = ^{good} reducing agent

Hückel's Rule

in order for a molecule to be aromatic

planar

monocyclic

fully conjugated

$(4n+2)$ π electrons

Anti aromatic

$4n$ π electrons

Frost's Circle

1) Draw circle

2) Draw regular polygon (w/ corner @ bottom)

3) Every point where corner intersects the circle to a p electron energy level

4) Middle of circle defines nonbonding orbital
bonding orbitals below, antibonding above



Benzene has 3 filled bonding orbitals

Chapter 14

Organometallic Compounds - compounds w/ carbon-metal bond
 used as reagents in organic synthesis
 Catalysts

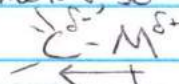
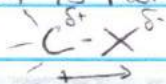
Nomenclature

Metal is the parent, attached alkyl groups identified by prefix
 $\text{CH}_3\text{CH}_2\text{MgBr}$ = ethyl magnesium bromide

Carbon-Metal Bonds

Polarity

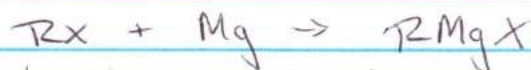
Carbon is more polar than the metal, so C-M bond is polar



carbanionic characteristic = useful as nucleophilic carbon

Prep of Organolithium & Organomagnesium Compounds

Reaction of organic halides & the metal in anhydrous aprotic solvent



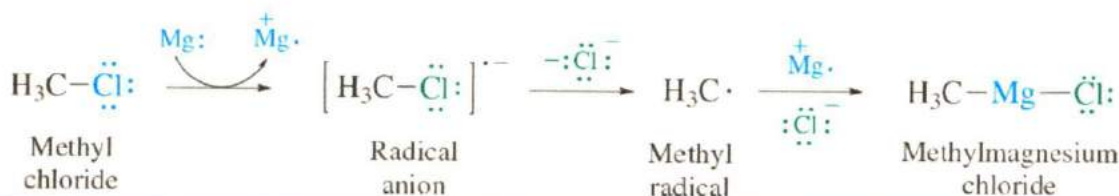
<- ionic!

diethyl ether = good solvent

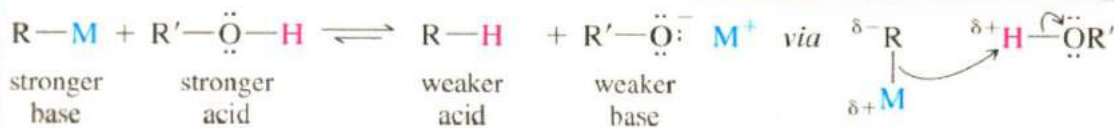
Organomagnesium compounds = Grignard Reagent

Halide Reactivity $\text{I} > \text{Br} > \text{Cl} > \text{F}$

Alkyl halides > Aryl, Vinyl Halides

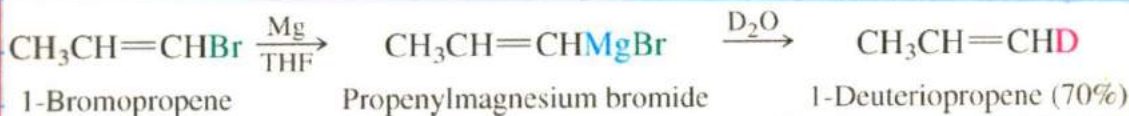


Organolithium & Organomagnesium as Brønsted Bases
 Strong Bases \rightarrow react w/ $-OH, -NH, -SH$ groups



Conjugate bases of weak acids are strong bases

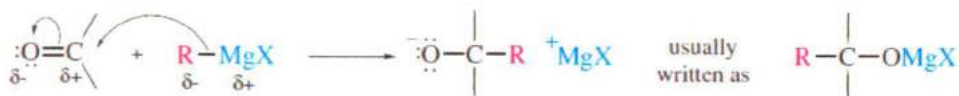
Basicity of organometallics used to prepare isotopically enriched compounds



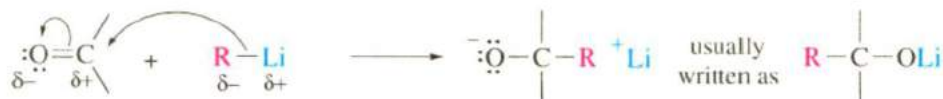
Synthesis of Alcohols Using Grignard & Organolithium Reagents
 produces alcohols

Nucleophilic attack:

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Protonation:

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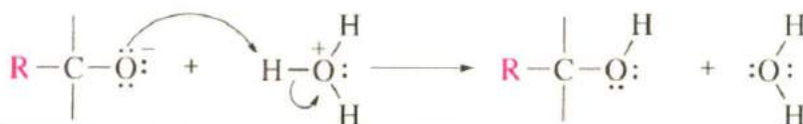


TABLE 14.1 Reactions of Grignard Reagents with Aldehydes and Ketones

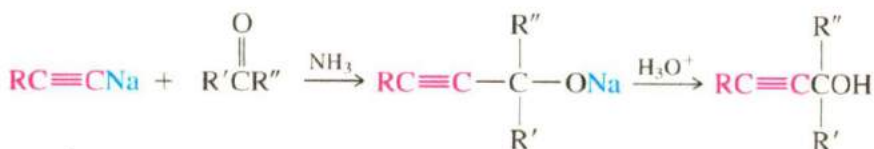
Reaction	General equation and specific example
<p>Reaction with formaldehyde Grignard reagents react with formaldehyde ($\text{H}_2\text{C}=\text{O}$) to give <i>primary</i> alcohols having one more carbon than the Grignard reagent.</p>	$\text{RMgX} + \begin{array}{c} \text{O} \\ \parallel \\ \text{HCH} \end{array} \xrightarrow{\text{diethyl ether}} \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OMgX} \\ \\ \text{H} \end{array} \xrightarrow{\text{H}_3\text{O}^+} \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$ <p>Grignard reagent Formaldehyde Primary alkoxymagnesium halide Primary alcohol</p> $\text{Cyclohexyl-MgCl} + \begin{array}{c} \text{O} \\ \parallel \\ \text{HCH} \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \text{Cyclohexyl-CH}_2\text{OH}$ <p>Cyclohexylmagnesium chloride Formaldehyde Cyclohexylmethanol (64–69%)</p>
<p>Reaction with aldehydes Grignard reagents react with aldehydes ($\text{R}'\text{CH}=\text{O}$) to give <i>secondary</i> alcohols.</p>	$\text{RMgX} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}'\text{CH} \end{array} \xrightarrow{\text{diethyl ether}} \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OMgX} \\ \\ \text{R}' \end{array} \xrightarrow{\text{H}_3\text{O}^+} \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R}' \end{array}$ <p>Grignard reagent Aldehyde Secondary alkoxymagnesium halide Secondary alcohol</p> $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{MgBr} + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH} \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ <p>Hexylmagnesium bromide Ethanol (acetaldehyde) 2-Octanol (84%)</p>
<p>Reaction with ketones Grignard reagents react with ketones ($\text{R}'\text{CR}''=\text{O}$) to give <i>tertiary</i> alcohols.</p>	$\text{RMgX} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}'\text{CR}'' \end{array} \xrightarrow{\text{diethyl ether}} \begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{C}-\text{OMgX} \\ \\ \text{R}' \end{array} \xrightarrow{\text{H}_3\text{O}^+} \begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R}' \end{array}$ <p>Grignard reagent Ketone Tertiary alkoxymagnesium halide Tertiary alcohol</p> $\text{CH}_3\text{MgCl} + \begin{array}{c} \text{O} \\ \parallel \\ \text{Cyclopentane ring} \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \text{1-Methylcyclopentanol}$ <p>Methylmagnesium chloride Cyclopentanone 1-Methylcyclopentanol (62%)</p>

Synthesis of Acetylenic Alcohols

Acetylide anions react as nucleophiles with carbonyls

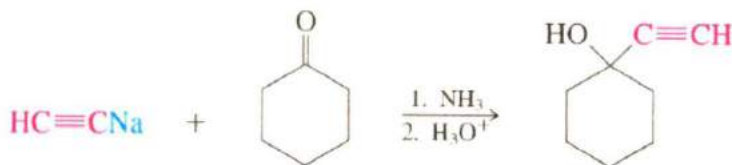
General reaction:

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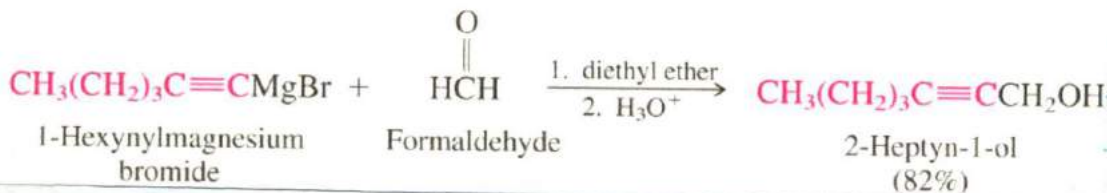
Example:

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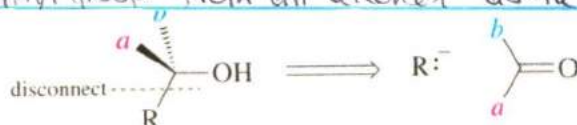
Use of Grignards:

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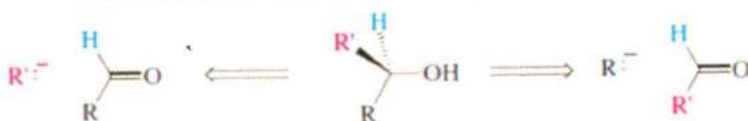
Retrosynthetic Analysis & Grignard & Organolithium Reagents

Disconnect one alkyl group from an alcohol as the organometallic



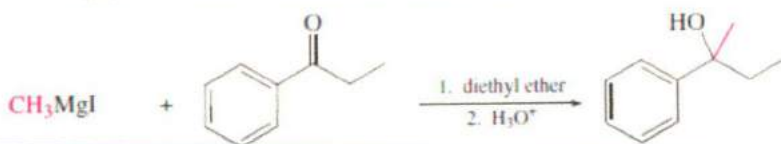
Two synthetic options:

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Synthesis:

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Organozinc Reagent for cyclopropane synthesis

Zinc reacts with alkyl halides in diethyl ether

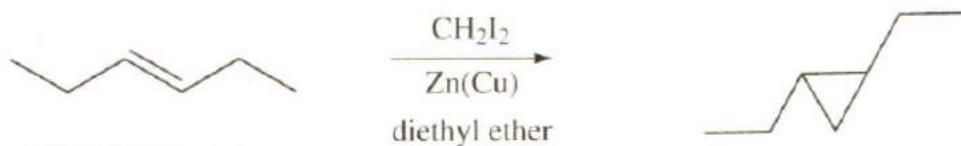
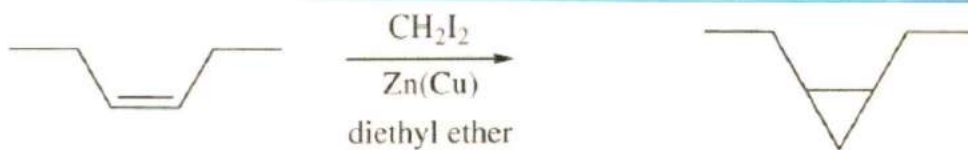


Carbon-zinc bond is less polar than C-Mg or C-Li

Simmons-Smith Reaction: Cyclopropane formation

The reagent is a carbenoid & reacts like carbene $:\text{CH}_2$

Stereospecific



Transition-Metal Organometallic Compounds

Transition metals: groups 3-11 on Periodic Table

partially filled d-orbitals

d-block elements include group 12

Group number gives number of valence electrons

Structural elements attached to the metal = ligands

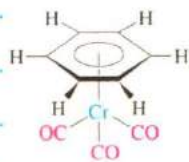
ligands attached to transition metal \rightarrow e^- of bonds + M's valence = 18

Ligands \rightarrow electron pair donors (Lewis base)

$:H^-$ $:R^-$ $:NH_3$ $:P(C_6H_5)_3$ $:CN^-$

Special: Benzene as $6e^-$ donor ligand

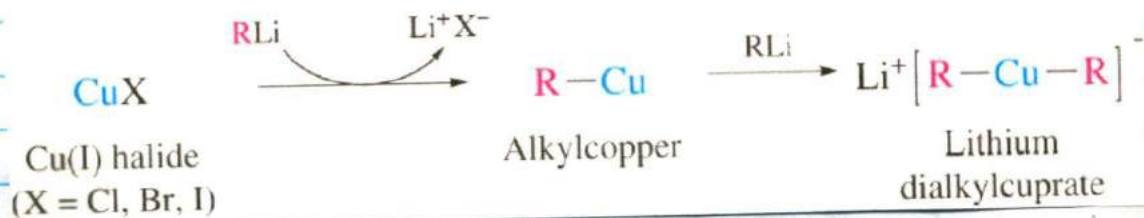
Cyclopentadienyl anion as $6e^-$ donor ligand (Ferrocene)



Organocopper Reagents

Prepared from organolithium reagents

Lithium diorganocuprates = Gilman reagents



Reactions of Organocuprates

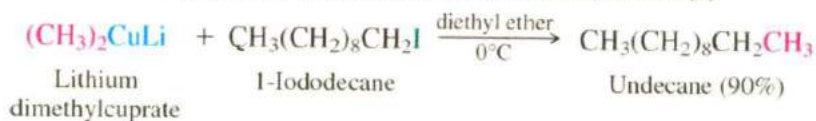
Cross-coupling Reactions

↳ connection of two different groups



Example:

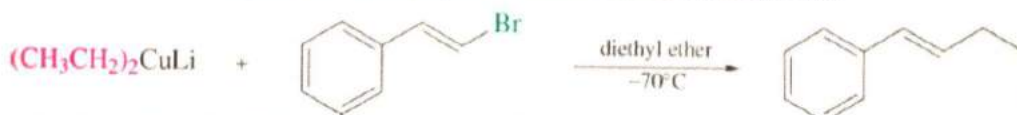
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Relative Reactivity: $\text{KI} > \text{RBr} > \text{RCl} > \text{Rf}$
 $\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$

Substitution/Elimination:

mainly substitutions w/ 1° alkyl halides

Elimination w/ 2° or 3° alkyl halides

Stereochemistry:

Inversion of configuration at sp^3 -hybridized carbon

Mechanism:

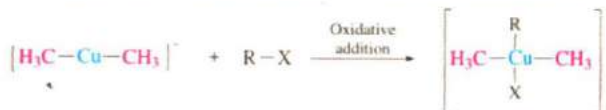
Nature of the organocuprate:

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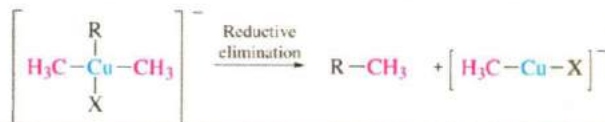
Oxidative addition of RX:

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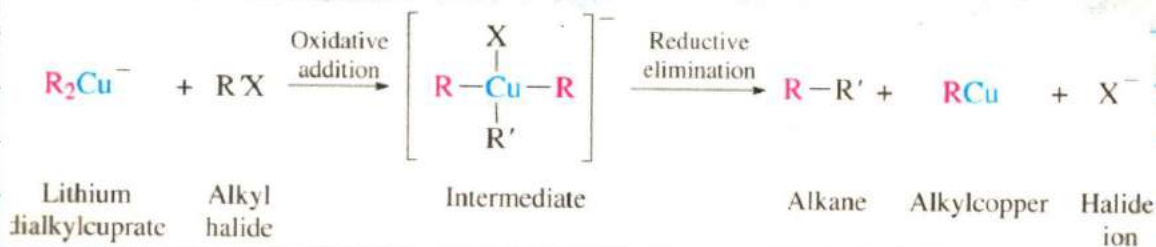


Reductive elimination of RCH₃:

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Oxidative Addition - Reductive Elimination



Palladium-Catalyzed Cross-Coupling

Organotin reagents (Stille)

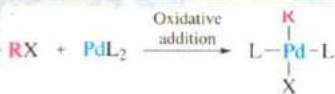
Organozinc reagents (Negishi)

Organoboron reagents (Suzuki)

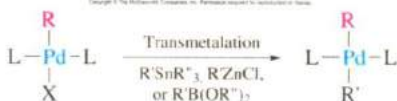
Alkene (Heck)

---> π-complex intermediate

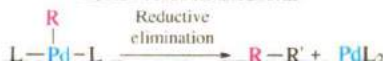
Mechanism: oxidative addition - transmetalation - reductive elimination



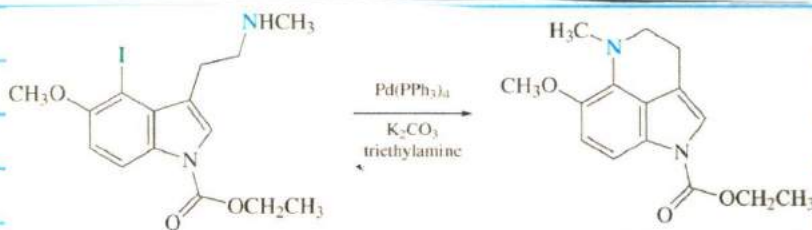
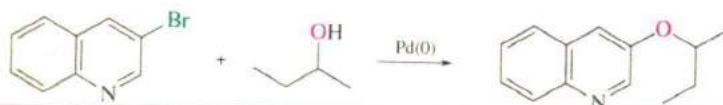
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C-O & C-N Bond Formation



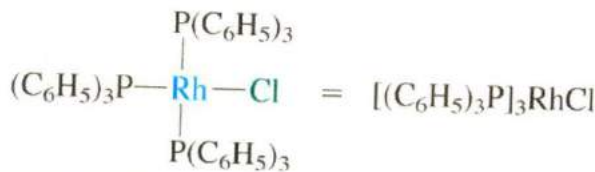
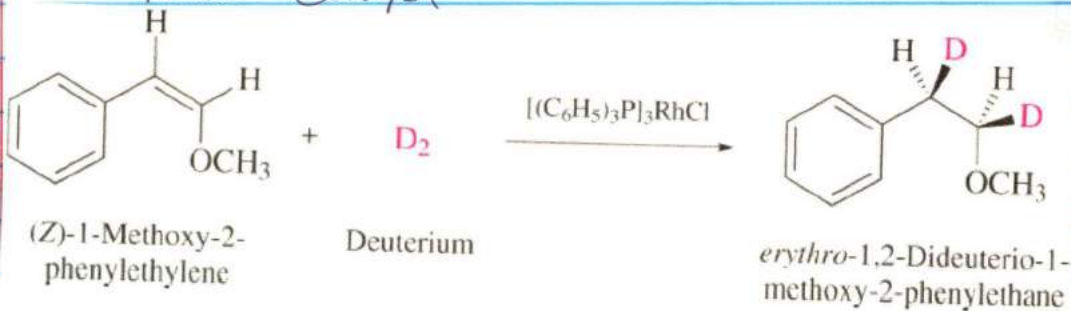
Homogeneous Catalytic Hydrogenation

Wilkinson's catalyst soluble in many organic solvents

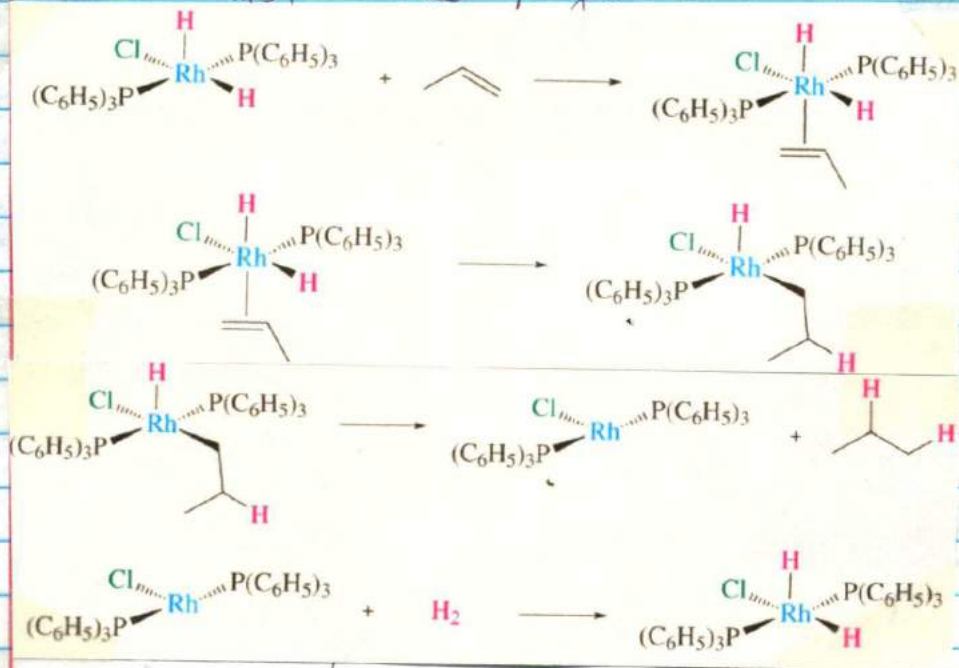
Selective for: less substituted alkenes
alkenes over carbonyls

Syn Addition

Active Catalyst



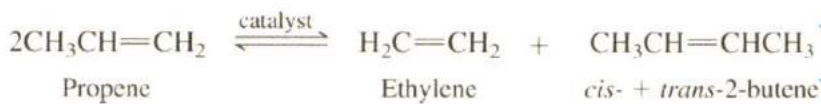
Mechanism of the Hydrogenation



Olefin Metathesis

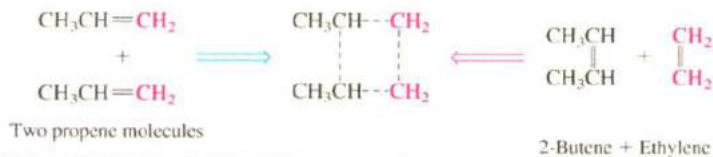
First observation:

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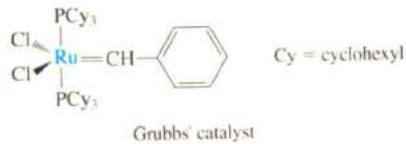
Cross metathesis:

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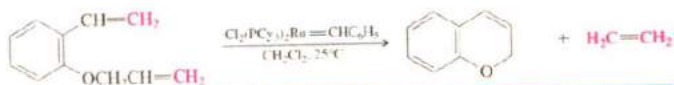
Active Catalysts Grubbs' catalyst:

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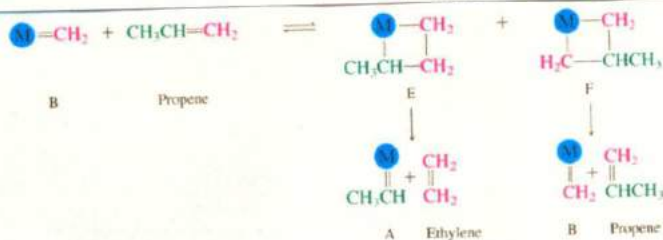
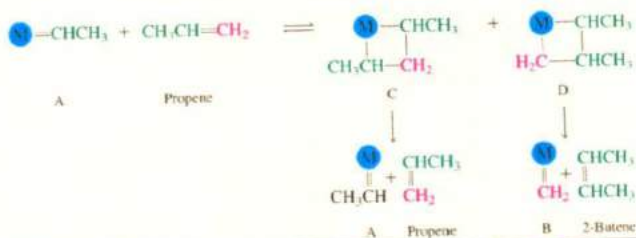
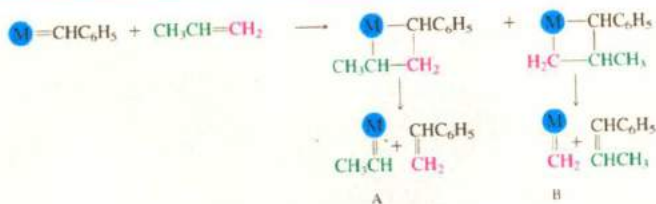


Ring closing example:

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Mechanism of Metathesis



Stage 1
Formation of
2 new complexes

Stage 2. Complex A

Addition of propene
to formation of 2-butene

Stage 2. Complex B

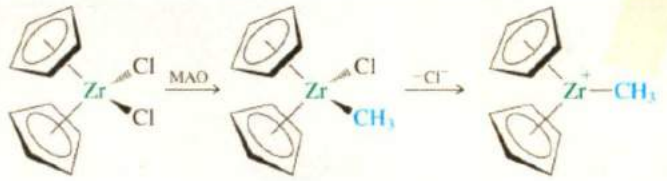
Addition of propene
to formation of ethylene

Stage 3. Repetition of Stage 2 with
the complexes formed in stage 2

Ziegler-Natta Catalysis of Alkene Polymerization

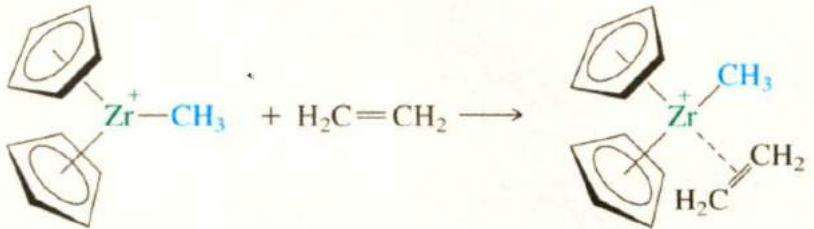
Step 1

Formation of the active catalyst



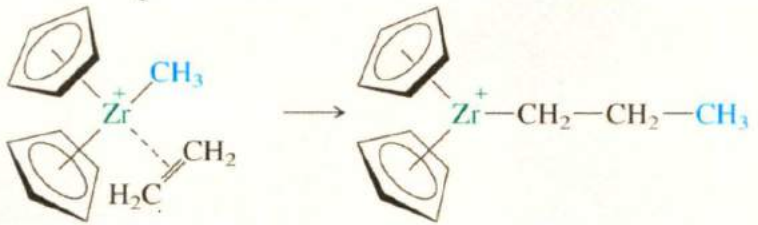
Step 2

π -Addition



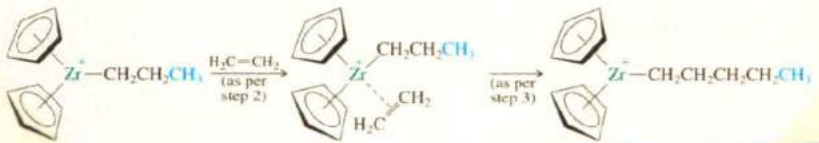
Step 3

Methyl migration



Step 4

π -Addition then alkyl migration



After thousands of repetitions polyethylene is formed